Novel Multidimensional Fractionation Techniques for the Compositional Analysis of Impact Polypropylene Copolymers

by

Sadiqali Cheruthazhekatt

Dissertation presented in partial fulfilment of the requirements for the degree of
Doctor of Philosophy (PhD) in Polymer Science

at the

University of Stellenbosch

Promoter: Prof. Harald Pasch   March 2013

Declaration

I, the undersigned, hereby declare that the work presented in this dissertation is my own original work and has not previously been submitted in its entirety or in part at any university for a degree.

……………………………

Sadiqali Cheruthazhekatt   March 2013

Abstract

Impact Polypropylene Copolymers (IPCs) are extremely complex materials, consisting of a mixture of polypropylene homopolymer and copolymers having different comonomer (ethylene) contents and chemical composition distributions. IPC can only be effectively analysed by multidimensional analytical approaches. For this, initially, the individual components have to be separated according to any of their molecular characteristics, either by chemical composition distribution (CCD) or molar mass distribution (MMD), followed by further analysis of these separated fractions with conventional analytical techniques. The combination of preparative temperature rising elution fractionation (TREF) with several other analytical techniques have been reported for the thorough characterization of this material. However, even the combinations of these methods were of limited value due to the complex nature of this polymer. Therefore, novel analytical approaches are needed for a more detailed compositional analysis of IPCs.

This work describes a number of multidimensional analytical techniques that are based on the combination of fractionation and hyphenated techniques. Firstly, preparative TREF was combined with high temperature size exclusion chromatography-FTIR (HT SEC-FTIR), HT SEC-HPer DSC (High Performance Differential Scanning Calorimetry) and high temperature two-dimensional liquid chromatography (HT 2D-LC) for the comprehensive analysis of a typical impact polypropylene copolymer and one of its midelution temperature TREF fractions. HT SEC-FTIR analysis provided information regarding the chemical composition and crystallinity as a function of molar mass. Thermal analysis of selected SEC fractions using a novel DSC method - High Speed or High Performance Differential Scanning Calorimetry (HPer DSC) - that allows measuring of minute amounts of material down to micrograms, yielded the melting and crystallization behaviour of these fractions which is related to the chemical heterogeneity of this complex copolymer. High temperature 2D-LC analysis provided the complete separation of this TREF fraction according to the chemical composition of each component along with its molar mass distribution. In a second step, the compositional characterization by advanced thermal analysis (HPer DSC, Flash DSC 1, and solution DSC) of the TREF-SEC fractions was extended to all semi-crystalline and higher temperature TREF fractions. By applying HPer DSC at scan rates of 5−200 °C/min and Flash DSC 1 at scan rates of 10−1000 °C/s, the metastability of one of the fractions was studied in detail. DSC measurements of TREF-SEC cross-fractions at high scan rates in p-xylene successfully connected reversely to the slow scan rate in TREF elution, if corrected for recrystallization. Finally, the exact chemical structure of all HT HPLC separated components was determined by coupling of HT HPLC with FTIR spectroscopy via an LC-Transform interface. This novel approach revealed the capability of this hyphenated technique to determine the exact chemical composition of the individual components in the complex TREF fractions of IPCs. The HT HPLC–FTIR results confirmed the separation mechanism in HPLC using a solvent gradient of 1-decanol/TCB and a graphitic stationary phase at 160 °C. FTIR analysis provided information on the ethylene and propylene contents of the fractions as well as on the ethylene and propylene crystallinities.

Opsomming

Impak Polipropileen Kopolimere (IPKe) is uiters komplekse materiale, bestaande uit 'n mengsel van polipropileen homopolimeer en kopolimere met verskillende komonomeer (etileen) inhoud en chemiese samestelling verspreiding. IPKe kan slegs doeltreffend ontleed word deur multi-dimensionele analitiese benaderings te volg. Hiervoor moet die individuele komponente aanvanklik eers geskei word volgens enige van hul molekulêre eienskappe, hetsy deur die chemiese samestelling verspreiding (CSV) of molêre massa verspreiding (MMV), gevolg deur 'n verdere ontleding van hierdie geskeide fraksies met konvensionele analitiese tegnieke. Die kombinasie van voorbereidings temperatuur-verhogings eluasie fraksionering (TVEF) met verskeie ander analitiese tegnieke is gerapporteer vir die deeglike karakterisering van hierdie materiaal. Maar selfs die kombinasies van hierdie metodes was van beperkte waarde as gevolg van die komplekse aard van hierdie polimeer. Daarom word nuwe analitiese benaderings benodig vir 'n meer gedetailleerde komposisionele ontleding van IPKe.

Hierdie studie beskryf 'n aantal multidimensionele analitiese tegnieke wat gebaseer is op die kombinasie van fraksionering en gekoppelde tegnieke. Eerstens is voorbereidings TVEF gekombineer met hoë temperatuur grootte-uitsluitingschromatografie-FTIR (HT GUC-FTIR), HT GUC-HPer DSK en hoë temperatuur twee-dimensionele vloeistof chromatografie (HT 2D-VC) vir die omvattende ontleding van 'n tipiese impak polipropileen kopolimeer en een van sy mid-eluasie temperatuur TVEF fraksies. HT GUC-FTIR analiese het inligting verskaf met betrekking tot die chemiese samestelling en kristalliniteit as 'n funksie van molêre massa. Termiese analiese van geselekteerde GUC fraksies deur gebruik te maak van 'n nuwe-DSK metode - Hoë Spoed of Hoë Prestasie Differensïele skandeer kalorimetrie (HPer DSK) - wat die meting van klein hoeveelhede materiaal tot by mikrogram hoeveelhede toelaat, het die smelt en kristallisasie gedrag van hierdie fraksies bepaal wat verwant is aan die chemiese heterogeniteit van hierdie komplekse kopolimeer. Hoë temperatuur 2D-LC analiese het die volledige skeiding van hierdie TVEF fraksie volgens die chemiese samestelling van elke komponent saam met die molêre massa verspreiding moontlik gemaak. In 'n tweede stap, is die komposisionele karakterisering deur gevorderde termiese analiese (HPer DSK, Flash DSK 1 en oplossing DSK) van die TVEF-GUC fraksies uitgebrei na alle semi-kristallyne en hoër temperatuur TVEF fraksies. Deur die gebruik van HPer DSK, teen 'n skandeerspoed van 5-200 °C / min, en Flash DSK 1, teen 'n skandeerspoed van 10-1000 ° C / s, is die meta-stabiliteit van een van die fraksies in detail bestudeer. DSK metings van TVEF-GUC kruis-fraksies by 'n hoë skandeeerspoed in p-xyleen het suksesvol omgekeerd verbind aan die stadige skandeerspoed in TVEF eluasie, wanneer gekorrigeer vir dekristallisasie. Ten slotte is die presiese chemiese struktuur van al die HT HPVC geskeide komponente bepaal deur die koppeling van HT HPVC met FTIR spektroskopie deur middel van 'n LC-transform-koppelvlak. Hierdie nuwe benadering het die vermoë van die gekoppelde tegniek om die presiese chemiese samestelling van die individuele komponente in die komplekse TVEF fraksies of IPKe te bepaal aan die lig gebring. Die HT HPVC-FTIR resultate het die skeidingsmeganisme in HPVC bevestig deur die gebruik van 'n oplosmiddelgradiënt van 1-

dekanol/TCB en 'n graphitiese stasionêre fase by 160 °C. FTIR analiese verskaf inligting in verband met die etileen en propileen inhoud van die fraksies sowel as die etileen en propileen krystalliniteit.

Dedicated to

To my parents and family members

Acknowledgements

I would like to thank the ***God, the Most Gracious and the Most Merciful*** for carrying me throughout my research work and his blessing in completing this thesis.

I wish to express my sincerest gratitude to the following people and institutions for their contribution towards this study:

First of all, I would like to express my deepest sense of gratitude to my supervisor **Prof. Harald Pasch**, for his support. Constant encouragement and valuable suggestions throughout the experimental and thesis works have contributed to the success of this research.

Dr. Gareth Harding for giving training on many instruments which I used for this study and his endless guidance and support that helped me to complete my study within short time.

Prof. Vincent B.F. Mathot for the FSC analysis of samples, and his contribution to my publications.

Thijs F.J. Pijpers for the great effort that he put in the careful FSC measurements.

Prof. Albert J. van Reenen for giving me absolute access to the olefins research lab and and making the facilities available.

Sasol Polymers for providing samples. Special thanks to Elias, Christopher, Nyambeni and Robert for their assistance with HPer DSC measurements.

Prof. P.E. Mallon and **Prof. K.R. Koch** for their support and encouragement whenever I was in need.

Madeleine, Divann, Tiaan, and all other olefin research members for their kind support and help, for making by work enjoyable.

All the staff at the Department of Chemistry and Polymer Science, **Dr Margie Hurndall, Dr Lizl Cronje, Mrs Erinda Cooper, Mrs Aneli Fourie, Mr Deon Koen, Mr Jim Motshweni**

Finally, I thank all those who have helped me directly or indirectly in the successful completion of this study. Anyone missed in this acknowledgement is also thanked.

Contents

x

Chapter 1

General Introduction and Objectives

This chapter provide a general introduction to impact polypropylene copolymers and various analytical techniques used for their characterization. The main objectives for this study and the layout of the dissertation are explained.

1.1 Introduction

Polyolefins are the world's most widely manufactured synthetic polymers used in various applications ranging from low molar mass hydrocarbon waxes to ultra-high molar mass rigid plastics. Polyolefins include mainly polyethylene (PE), polypropylene (PP), poly-1-butene, ethylene-1-alkene copolymers (also known as linear low density PE) and propene-alkene copolymers. [1-6] Compared to other plastics, polyolefins take great advantage of their low cost, ease of processing into desired products, and simple chemical nature (being composed of carbon and hydrogen only), and therefore they are non-toxic and non-contaminating. Most of the polyolefins are prepared by Ziegler-Natta catalysis that involves rapid polymerization of olefins under mild conditions in the presence of transition metal compounds as catalysts. Metallocenes and late transition metal complexes are found to be effective catalysts for the homogeneous polymerization of olefins, enabling the production of polyolefins with a tunable microstructure and molar mass distribution (MMD). Since the discovery in the early 1950s (Ziegler-Natta catalyst), research in the field of polyolefin catalysis opened the way for generations of catalyst systems by the introduction of different catalytic components such as support materials (inorganic and organic) and co-catalysts. Developments in catalysis combined with advances in process technology allow improved control of the molecular architecture of polyolefins for designing resins for targeted applications. The combination of different polyolefins, so-called polyolefin blends, made from different homo- and copolymers in one material, is widely used. These multicomponent polymeric systems are an important part of commercial polyolefin materials. An advantage of these materials is the useful combination of the properties of the components without creating chemically new polymers. This approach in many cases is more feasible than developing new tailor-made polymer structures. [4,7-14]

Polyolefins exhibit multiple distributions in various molecular characteristics such as molar mass, chain architecture, functionality, composition, etc. The most important is the molar mass distribution, sometimes called molar mass dispersity (Đ). [5] Another type of heterogeneity involves distributions in chemical composition and monomer sequence, that are typical for statistical, alternating, block, and graft copolymers. Even though molar mass is also of importance, the comonomer content in the copolymer and the chemical composition distribution (CCD) are dominant parameters to determine the final physical and mechanical properties of ethylene/propylene-α-olefin copolymers. [15-17] Several factors may contribute to CCD: the statistical nature of polymerization, multiple-site catalysts, spatial variations in the monomer concentration and temperature during polymerization. The determination of the CCD in polyolefins is of key importance [18] and crucial for an in-depth understanding of structure-property relationships, polymerization kinetics and mechanisms, and polymer reaction engineering. [19,20] In the case of olefin copolymers with polar comonomers, the functionality generates another type of heterogeneity. Molecular architecture provides yet another type of heterogeneity, dictated by the topology of the macromolecules, e.g. branched vs. linear polymer chains. The analytical scientist must take all these types of heterogeneity into account even when 'just' measuring the molar mass by relative methods. [5]

Among the commercial polymers, isotactic polypropylene (PP) is one of the most widely used commodity plastics in various formulations, because of its relatively low cost, chemical resistance, high melting point, and good dimensional stability. PP offers the best stress-crack resistance of all polyolefins; due to the thermal stability of this polymer, articles made from PP can be sterilized. PP is typically used at temperatures between the T_g (up to 5 °C) and the melting temperature (160 °C). Under these conditions the strength and stiffness from the crystalline regions are combined with toughness of the amorphous tie points. Products made of PP are brittle at 0 °C and may crack or break if dropped from bench top height, so that the impact resistance becomes negligible and limits its applications as an engineering plastic, especially for low temperature use.[21-29]

The impact properties of PP homopolymer can be improved by addition of an ethylene-propylene rubber, copolymers, polyethylene homopolymer, or plastomers.[30-33] Recently, with the development in catalyst systems and polymerization technology, a new polymeric material called Impact Polypropylene Copolymer (IPC) has been introduced in to the PPfamily. The IPCs are a commercial grade of PP which features improved low temperature impact resistance. This class of polymers has seen growing demand in the thermoplastic market in recent times. The modified impact resistance of such heterophasic PP, together with the excellent properties of the polypropylene homopolymer such as rigidity, light weight, ease of processing, thermal and chemical resistance, makes the material highly useful in automotive and other applications. Among the several ways reported for its production, the two-stage copolymerisation process of propylene with ethylene is found to be the most effective method and the commercially adopted one. The sequential multistage polymerisation leads to the formation of highly complex materials consisting of many products, including amorphous, random and segmented ethylene-propylene copolymers with different monomer sequence length distributions and molar mass distributions, as well as highly isotactic polypropylene and polyethylene homopolymers.[34-44]

Thus, impact polypropylene copolymers are attractive and increasingly common in many applications and they are a major subject of research. The properties of IPCs strongly depend on their microstructure, e.g., the distribution of ethylene monomer and tacticity as well as ethylene and propylene sequence distributions and average sequence lengths. Therefore, characterisation of IPC remains a subject of great interest for researchers in the polyolefin field. FTIR and ^{13}C NMR are the two spectroscopic methods used for determining comonomer contents, isotacticity and the distribution of the two monomers in such complex materials. DSC is the thermal analysis method most often used to study the thermal behaviour (the melting and crystallisation temperatures). Temperature rising elution fractionation (TREF) and crystallization analysis fractionation (CRYSTAF) are non-chromatographic separation techniques which are used to determine the CCD in such copolymer systems. Preparative fractionation and subsequent analysis of the individual fractions is found to be an effective method for the complete characterisation of IPCs. The combination of Prep TREF and techniques such as HT SEC, HT ^{13}C NMR, DSC, FTIR, and CRYSTAF are most often used for the structural analysis of IPCs. Offline coupling of SEC with FTIR is an established technique which has

3

been used to characterise the chemical composition distribution across the molar mass distribution.[45-52]

1.3 Objectives and methodology

The main objective of this study was to develop novel multidimensional analytical techniques to study the complex composition of impact polypropylene copolymers. A combination of various fractionation methods (both in preparative and analytical scale) have to be used to perform such analyses.

In a first approach, combinations of preparative TREF with various hyphenated techniques, SEC-FTIR, SEC-HPer DSC, and high temperature two dimensional liquid chromatography have to be used for the compositional analysis of an important mid-elution temperature TREF fraction of a commercial IPC sample. TREF-SEC followed by FTIR provides information regarding the chemical composition and crystallinity as a function of molar mass. Thermal analysis of the SEC fractions by HPer DSC provides information on the thermal properties of the different molar mass fractions, and, thereby, the compositional heterogeneity of the components. A complete characterization according to chemical and molar mass distribution for this specific fraction shall be achieved by high temperature two-dimensional liquid chromatography (HT 2D-LC).

The second objective was to study the complex composition of this polymer by advanced thermal analysis, using the combination of Fast Scanning Calorimetry (HPer DSC, Flash DSC 1 and solution DSC) with SEC fractionation subsequent to TREF fractionation. FSC allows measuring of minute amounts of material down to micrograms, and helps to investigate the relationships between the molecular structure of the polymer chains and their thermal properties (melting and crystallization behaviour). This study was mainly focussed on the influence of the molar mass on the thermal properties of the materials.

The multidimensional approaches discussed above were expected to be effective methods for the molecular characterization and thermal analysis of the TREF-SEC cross-fractions that can provide sufficient information regarding the complex composition of this material. Therefore, this study was extended to all TREF fractions. The final objective for this study was to develop a new analytical technique in order to provide a more detailed picture about the exact chemical structure of the individual components in the complex TREF fractions of IPC. For this type of analysis, Prep TREF was coupled with HT HPLC, achieving a complete separation according to the chemical structure of the polymer chains, with the separated fractions being subsequently collected via the LC Transform system for further identification of the exact chemical nature of the separated species by FTIR. This hyphenated technique combines the fast and efficient separation capability of HT HPLC according to the microstructure of the polymer chains, with the power of FTIR to detect such minute amounts of the HPLC-separated fractions.

1.4 Layout of this dissertation

This dissertation is divided into the following four chapters:

Chapter 1

A general introduction about polyolefins and various analytical techniques for their characterization has been presented in the first section of this chapter and the objectives for this study have been formulated.

Chapter 2

The historical section of this chapter summarises the different analytical techniques reported in the literature up to now for the molecular characterization of complex polyolefins. This is followed by a short discussion of the theoretical background of the work.

Chapter 3

The results of this study, according to the three main objectives of this work are presented here in the form of published articles. The first section contains the results obtained by multidimensional analysis through the combination of preparative TREF with hyphenated techniques such as SEC-FTIR, SEC-HPer DSC, and high temperature 2D-LC. The second section contains the results obtained by advanced thermal analysis using the combination of fast scanning DSC (HPer DSC, Flash DSC 1 and solution DSC) with SEC fractionation subsequent to TREF fractionation. The third section explains a novel analytical approach, Prep TREF - HT HPLC - FTIR; in which the exact chemical composition of all species is determined by coupling FTIR spectroscopy to HT HPLC via an LC-Transform interface.

Chapter 4

The conclusions of all three sections of this study are summarised and recommendations are proposed for future studies within this field of research.

1.5 References

1. P.Galli. *Prog.Polym.Sci.* 1994, 19, p 959.

2. Fred W.Billmeyer, JR, Third Edition, Textbook of Polymer Science, Wiley-Interscience, 1984.

3. Fawcett, EW.; Gibson, RO.; Perrin, MW.; Patton, JG.; Williams, EG. B Patent 471,590, September 6, 1937.

4. Kaminsky, W. *Macromol. Chem. Phys.* 2008, 209, p 459.

5. Sperling, L. H. (Leslie Howard), 1932–Introduction to physical polymer science. 4th ed.

6. Whiteley, K. S.; Heggs, T. G.; Koch, H.; Mawer, R. L.; Immel, W. Ullmann's Encyclopedia of Industrial Chemistry, 6th ed.; Wiley-VCH: Weinheim, 2003, 28, p 393.

7. Ziegler K. Ger Patent. 1953, 878, p 560.

8. Qiao, J.; Guo, M.; Wang, L.; Liu, D.; Zhang, X.; Yu, L.; Song, W.; Liu, Y. *Polym. Chem*. 2011, 2, p 1611.

9. Boor J. Ziegler-Natta catalysts and polymerizations. New York: Academic Press, 1979.

10. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. Vol. 26, p 502.

11. Mikenas, T. B.; Zakharov, V. A.; Nikitin, V. E.; Echevskaya, L. G.; Matsko, M. A.. *Russ. J. Applied Ch.* 2010, 83, p 2210.

12. Galli, P.; Vecellio, G. *Prog. Polym.Sci.* 2001, 56, p 1287.

13. Chum, S.P.; Swogger, K.W. *Prog. Polym. Sci.* 2008, 33, p 797.

14. Choi, Y.; Soares, J.B.P. *Polymer* 2010, 51, p 4713.

15. Soo Ko, Y.; Jeon, J.Ki.; Yim, J.H.; Park, Y.K. *Macromol. Res.* 2009, 17, p 296.

16. Chung C. Tso, Paul J. DesLauriers. *Polymer* 2004, 45, p 2657.

17. Wild, L.; Ryle, T. R.; Knobeloch, D. C.; Peat, I. R. *J. Polym. Sci., Part B: Polym. Phys.* 1982, 20, p 441

18. Wallace, W. Yau.; Gillespie, D. *Polymer* 2001, 42, p 8947.

19. Soares, J. B. P.; Anatawarskul, S. *J. Polym. Sci., Part B: Polym. Phys.* 2005, 43, p 1557.

20. Albrecht, A.; Brüll, R.; Macko, T.; Sinha, P.; Pasch, H. *Macromol. Chem. Phys.* 2008, 209, p 1909.

21. Kojima, M. J*. Macromol. Sci., Phys. Edn.* 1981, B19, p 523.

22. Takahashi, T.; Mizuno, H.; Thomas, E. L. *J. Macromol. Sci-Phys.*1983, 2, p 425.

23. Busico, V.; Cipullo, R. *Prog.Polym.Sci.* 2001, 26, p 443.

24. Karger-Kocsis, J.; Kallo, A.; Szafner A.; Bodor, G.; Senyei, Z. *Polymer* 1979, 20, p 37.

25. Sano, H.; Usami, T.; Nakagawa, H.; *Polymer* 1986, 27, p 1497.

26. D'Orazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G.; *Polymer* 1993, 34, p 3671.

27. Dezhu, M. A.; Xiqiang, L. I.; Ruiyun, Z.; Kunlun, H.; Xiaolie, L.; Chin. *J. Polym. Sci.* 1994, 12, p 164.

28. Liang, J.Z.; Li, R.K.Y. *J. Appl. Polym. Sci.* 2000, 77, p 409.

29. Ozzeti, RA.; De Oliveira Filho, AP.; Schuchardt, U.; Mandelli, D. *J. Appl. Polym. Sci.* 2002, 85, p 734.

30. Wu, S. *Polym. Eng. Sci.* 1990, 30, p 753.

31. Van der Wal, A.; Mulder, J. J.; Oderkerk, J.; Gaymans, R. J. *Polymer* 1998, 39, p 6781.

32. Cecchin, G.; Morini, G.; Pelliconi, A. *Macromol. Symp.* 2001, 173, p 195.

33. Jang, B. Z.; Uhlman, D. R.; Vander Sande, J. B. *Polym. Eng. Sci.* 1985, 25, p 643.

34. Pires, M.; Mauler, R.S. ; Liberman, S.A. *J. Appl. Polym. Sci.* 2004, 92, p 2155.

35. Song, S. ; Feng, J. ; Wu, P. ; Yang, Y. *Macromolecules* 2009, 42, p 7067.

36. Liu, N. C.; Baker, W. E. *Polymer* 1994, 35, p 988.

37. Zhang, Y. Q.; Fan, Z. Q.; Feng, L. X. *J. Appl. Polym. Sci.* 2002, 84, p 445.

38. Fan, Z. Q.; Zhang, Y. Q.; Xu, J. T.; Wang, H. T.; Feng, L. X. *Polymer* 2001, 42, p 5559.

39. Galli P, Haylock JC. *Prog. Polym. Sci.* 1991, 16, p 443.

40. Simonazzi, T.; Cecchin, G.; Mazzullo, S. *Prog. Polym. Sci.*1991, 16, p 303.

41. Urdampilleta, I.; Gonzalez, A.; Iruin, J.J.; de la Cal, J.C.; Asua, J.M. *Macromolecules*

2005, 38, p 2795.

42. Mirabella, F. M. *Polymer* 1993, 34, p 1729.

43. E. Moore, Jr., Polypropylene Handbook. 92, Hanser Publishers, Munich, 1996.

44. Usami, T.; Gotoh, Y.; Umemoto, H.; Takayama, S. *J. Appl. Polym. Sci., Appl. Polym. Symp.*

1993, 52, p 145.

45. Hongjun, C.; Xiaolie, L.; Dezhu, M.; Jianmin, W.; Hongsheng, T. *J. Appl. Polym. Sci.* 1999, 71, p 93.

46. Xue, Y.; Fan, Y.; Shuqin, Bo.; Xiangling, Ji. *Eur. Polym. J.* 2011, 47, p 1646.

47. Zacur, R.; Goizueta, G.; Capiati, N. *Polym. Eng. Sci.* 1999, 39, p 921.

48. Rafael, A.; García, B. C.; María-Teresa, E.; Inmaculada, S.; Almudena, F.; Susana, Caveda. *Macromol. Res.* 2011, 19, p 778.

49. de Goede, E.; Mallon, P.; Pasch, H. *Macromol. Mater. Eng.* 2010, 295, p 366.

50. Zhisheng, F.; Junting, X.; Yanzhong, Z.; Zhiqiang F. *J. Appl. Polym. Sci.* 2005, 97, p 640.

51. Hongjun, L. C.; Xiaolie, M. D.; Jianmin, W.; Hongsheng, T. *J. Appl. Polym. Sci.* 1999, 71, p 103.

52. Mncwabe, S.; Luruli, N.; Marantos, E.; Nhlapo, P.; Botha, L. *Macromol. Symp.* 2012, 313, p 33.

Chapter 2

Historical Overview and Theoretical Background

This chapter gives a general overview on the different analytical techniques reported in the literature up to now to study the molecular characteristics of complex polyolefins and the motivation for this present work. The theoretical background of the work is briefly discussed.

2.1 Introduction

Commercial impact polypropylene copolymers are produced by multistage continuous polymerization processes in which homopolymerization of propylene takes place in the first reactor, followed by the copolymerization of propylene and ethylene in the second reactor. This method of production can provide better impact properties and lower production costs than previously used techniques such as mechanical blending of the iPP with PE homopolymer, ethylene-propylene copolymers and other thermoplastic elastomers. The sequential two-stage polymerization process produces a complex mixture consisting of mainly highly crystalline polypropylene homopolymer blended with elastomeric ethylene-propylene random copolymer containing small amounts of polyethylene homopolymer and semi-crystalline ethylene-propylene copolymers (EPCs) of different ethylene contents and sequence lengths. In this multiphase system, the rubbery phase consisting of ethylene-propylene random copolymer (EPR) is dispersed in the iPP homopolymer matrix and the copolymer phase (EPC segmented or block copolymers) acts a compatibilizer, which facilitates the interfacial interaction between these two phases, enhancing the total impact strength of the product. However, the EPC components are expected to consist of a series of components of different structures such as ethylene-propylene random copolymer, ethylene-propylene blocky and segmented copolymers with different monomer sequence lengths and distributions. Even for the same type of component, the differences in composition and molar mass may affect the total performance of this complex material.[1-15] Consequently, the impact properties of these materials can be expected to depend strongly on the amount of the different components (EPR and EPCs), their molecular structure, and synergistic interactions between the different components present. The microstructure of this material determines the properties and end-use applications. Therefore, a very detailed structural analysis must be done to understand the copolymer composition and the role of particular components in such complex multicomponent systems. Several studies on composition, microstructure, morphology, and thermal properties (crystallization and melting behaviour) of IPC have been reported in the literature.[16-31] However, the complete molecular structure analysis of such complex polymers is a difficult task using the variety of the analytical techniques reported till now.

2.2 Molecular characterization of complex polyolefins –An overview

Due to the heterogeneous nature of the polyolefins, two kinds of molecular parameters are the most important: MMD and CCD. High temperature SEC is a relatively rapid method for the determination of molar mass and MMD. The detectors most commonly used are the refractive index (RI) and viscosity detectors which help obtain the information regarding the MMD. Combining a light scattering (LS) detector with the HT SEC helps to determine the chain dimensions and branching in terms of the mean square radius of gyration. When SEC is combined with IR detection, it offers the additional advantage of determining the chain branching across the MMD. Principally, SEC separates polymers according to the hydrodynamic size of the molecules[32-34] and the extent to which they are excluded from the pores of a stationary phase. However, the size of the polymer molecules in solution is

9

influenced not only by the number of repeat units in the polymer chains, but also by their molecular architecture, especially short chain branching for lower α-olefin copolymers. Due to the small differences in side chains, polymer molecules with identical hydrodynamic volumes, but different chemical compositions, may co-elute at the same elution volume in SEC. So the knowledge of MMD available from SEC analysis is no longer sufficient to define the compositional heterogeneity of olefin copolymers and/or blends.[35,36]

Two methods used to analyse the compositional heterogeneity of polyolefins, TREF, developed in the late 1970s by Wild, and CRYSTAF, developed by Monrabal in the early 1990s, have been introduced. Both fractionate the sample on the basis of crystallisability, which is a function of CCD. Both techniques have since then been used to fractionate semi-crystalline polyolefin copolymers and blends, and are based on the crystallisation of the macromolecules from a hot solution.[37-41] The disadvantage of TREF is that it is labour-intensive and it takes a long time to analyse one sample. Although CRYSTAF is fast compared to TREF, the fractions cannot be analysed separately. More recently, Monrabal has reported the use of Crystallization Elution Fractionation (CEF), a refinement of the basic TREF technique, which affords rapid analysis (compared to conventional analytical TREF and CRYSTAF) and good separation.[44] Recently, a new technique based on the ''turbidity fractionation analysis'' developed by Shan et al., named as solution crystallization analysis by laser light scattering (SCALLS), has been reported to determine the CCD of polyolefins.[43] This technique yields similar results to CRYSTAF but in a shorter time, uses a comparatively minimal amount of solvent, and with apparently greater sensitivity in some cases. However, all these techniques are limited to well-crystallisable samples.

DSC is a thermal analysis method to study the melting and crystallization behaviour, which is related to the chemical structure of the polymer chain (chemical composition). Therefore, DSC has been used as an alternative tool for the qualitative analysis of the CCD. ^{13}C NMR spectroscopy is the method of choice for the microstructural analysis, mainly based on the final copolymer composition and comonomer sequences, or chemical heterogeneity at various compositions and configuration levels. The applicability of this technique for the compositional analysis of complex materials is quite difficult, since it can provide only the average chemical composition values. Inaddition to this, it is difficult to determine the exact CCD, due to the relatively low concentration of the individual components in this complex system, requiring a previous preparative fractionation.

The combination of MMD and short chain branch content per molar mass slice gives characteristic profiles for understanding material properties. Several methods are available to perform this type of analysis. Fourier transform infrared (FT-IR) spectroscopy, in addition to providing information regarding comonomer composition, also provides measurements of polymer chain configuration, branching, and crystallinity. A combined method of chromatography and infrared spectroscopy is employed to map the distribution of monomers in copolymer samples.[44] When HT SEC is coupled to multiple detectors; it allows obtaining a fully detailed and fast characterization since the several techniques involved yield a lot of structural data that are obtained simultaneously with the standard

SEC analysis. Combinations of a variety of techniques have been applied to determine the copolymer composition and comonomer distribution along the MMD. TREF combined with SEC and FTIR, SEC with TREF and CRYSTAF, and SEC with triple detectors (GPC-3D) have been reported to perform this type of analysis.[45-49]

It is well known that fractionation and subsequent analysis of the separated fractions is an essential approach to study the heterogeneity in multicomponent systems. Preparative fractionation followed by subsequent analysis of the fractions by SEC and NMR or SEC-FTIR can provides a clearer picture of the chemical composition along the MMD.[50,] The method of choice does not only depend on the factors such as accuracy, labour and time demands, but also the versatility and practicability. Preparative TREF fractionation followed by SEC-FTIR is capable of measuring even heterogeneous low branched samples in a rapid and satisfactory matter. [51-53] However, even this approach provides only an average chemical composition per molar mass fraction, and the CCD cannot be obtained since each molar mass fraction can be heterogeneous with respect to chemical composition. The main drawback of this method is that preparative TREF involves the time consuming operations of separation, filtration and drying of the fractions.

The CCD (the chain structure, polymer type, and chain branching) and MMD primarily influence the thermal properties (melting and crystallization behaviour) of semicrystalline polymers. For a complex copolymer consisting of different chain structures, it is highly important to study the relationship between the thermal behaviour and the chemical structure of individual components to optimize the processing conditions and to reduce the production cycle time. For such polymers, crystallization is an important factor, as this determines the final mechanical properties of the material, and much attention has to be paid to it. Various analytical approaches have been reported to correlate the molecular characteristics of polyolefins with their thermal and mechanical properties. The combination of Prep TREF with standard DSC has been reported in the literature to relate the CCD to the thermal properties of olefin copolymers.[51] Even by this method it is very difficult to gain a complete understanding of the relationship between the complicated chain structure and the crystallization behaviour of such complex components. It has been reported that it is possible to couple SEC fractionation with standard DSC[54], but even better with HPer DSC (High Performance DSC) in order to study the short chain branching distribution along the MMD.[55] This is important due to the effect of molecular structure on the crystallisation behaviour, and thereby the final properties of the materials.[56] SEC-DSC can be used as a complimentary method to SEC-FTIR to explain the compositional distribution across the MMD in terms of thermal properties. HPer DSC has the ability to measure very small sample masses, while scanning at higher heating rates (up to 500 °C/min) than traditional standard DSC. Fast scanning rates help to separate or reduce reorganizational thermal processes, such as cold crystallization, recrystallization and decomposition which may occur during heating. The improvement in fast scanning DSC technology also offers the opportunity to detect weak transitions, including weak glass transitions which could not be determined by standard DSC. This approach (SEC-HPer DSC) will be highly useful for the investigation of the relationships between the molecular

structure of the polymer chains and their thermal properties (the influence of the molar mass on the thermal properties of the materials).

Liquid chromatography (LC) is found to be an efficient analytical technique for the fast separation of the polymer chains according to their chemical compositions.[57] However, the corresponding high temperature LC methods were only developed during last couple of years by Pasch et al. They are mainly based on a selective precipitation or adsorption mechanism on the different stationary phases. The separated fractions were eluted by using a suitable solvent gradient, which results in the dissolution or desorption of the polymer chains from the stationary phase.[58-60] Recently, Pasch et. al reported the use of the graphite stationary phase (Hypercarb) for the separation of the polypropylene according to tacticity, in addition to the chemical composition separation of polyethylene from polypropylene, by using a solvent gradient from 1-decanol to TCB (1,2,4-Trichlorobenzene).[61] To this date this is the only method for the fast and efficient separation of polyolefins and olefin copolymers according to their chemical compositions, within a short period of time.[62-68] A new technique, high temperature thermal gradient interaction chromatography (HT TGIC), has been reported for the separation of the ethylene-1-octene copolymers with a wide range of comonomer contents, based on the interaction of the polymer chains with the Hypercarb stationary phase upon a temperature change in an isocratic solvent.[69] Among the several analytical techniques reported for the characterization of polyolefins, HT HPLC is found to be a suitable method for the fast and complete separation of the polymer chains according to CCD. Most recently, high temperature two dimensional liquid chromatography (HT 2D-LC) has also been reported for the two dimensional mapping of the heterogeneity in polyolefins. In 2D-LC the chromatographic separation by HT HPLC is hyphenated to HT SEC to get a complete separation in terms of both CCD and MMD. This technique enables the generation of two dimensional characterization data for all polyolefins over a wider composition range, regardless of their crystallinity.[70-73]

2.3 Characterization of impact polypropylene copolymers

Due to the structural complexity, fractionation is a well-known procedure so far used for the separation of the various species in IPCs. Fractionation techniques such as Soxhlet extraction,[74] successive solvent extraction,[17,18,75] temperature gradient extraction fractionation (TGEF)[76,7] and TREF have been reported in the literature as a preliminary step for the detailed analysis of IPCs. Mirabella reported the use of prep TREF as a powerful tool to separate the complex components (having dissimilar physical or chemical nature).[4,77] Ever since, prep TREF or analytical TREF have been employed as an initial step for the detailed structural characterization of IPCs.[8,10,78-83,] Later, Usami et al used a TREF-SEC procedure for the compositional analysis of IPCs.[5] Two spectroscopic techniques, FTIR and ^{13}C NMR have been reported by several authors for the structural study (chain structure and microstructure) of both unfractionated and fractionated IPC samples.[7,10,17,24,83] DSC is the simple thermal analysis method used to determine the compositional heterogeneity in IPCs, on the basis of their thermal behaviour (melting and crystallization).[8,38,74,76] Several authors have used

the combination of prep TREF and other conventional analytical techniques such as SEC, DSC, CRYSTAF, FTIR and ^{13}C NMR for the microstructure characterization of IPCs.[6,18,20,24,26-28,31] Recently, de Goede et al. demonstrated that the combination of TREF and a hyphenated technique SEC-FTIR can provide more detailed information regarding the chemical nature of the different species present in various TREF fractions, as a function of molar mass.[51]

There are many studies reported by several authors for the structural and morphological studies of IPCs to investigate the relationship between the chain structure and phase morphology, which has an important role in determining the impact performance of such materials. Morphological aspects, such as mainly the architecture of the iPP particles; size, localization and dispersion of the EPR in the iPP matrix, were studied by scanning electron microscopy (SEM),[84-86,17] transmission electron microscopy (TEM)[67,87-89] and atomic force microscopy (AFM).[90] More recently a multi-layered core-shell structure of the dispersed phase of IPC was reported by Chen et al. The function of the crystallisable ethylene-propylene copolymers in the formation of such core-shell structures was well explained.[91]

2.4 Motivation

Advanced progress in catalyst tailoring and optimization of the polymerization processes made rapid growth in the production and use of impact modified polypropylene in recent years possible. Researchers in these fields are still trying to produce polyolefins with exciting new properties and applications. It is possible to control the chemical composition of the IPCs and, thereby, their final mechanical properties and impact performance. For this multiphase system, the nature of the reactor conditions and the amount of the comonomer incorporation play an important role. With the realization of the complex nature of IPC, the total characterization of such materials is a growing challenge in analytical chemistry, both as an important step in confirming the molecular structure of the materials and also as a tool to give insight into the mechanism of the polymerization reaction. In order to take full advantage of these new developments in polyolefin synthesis, it is essential to have modern analytical tools for rapid molecular structural characterization of such complex polyolefins to correlate the structure/property relationships for a given application. Knowledge of the MMD and CCD of polyolefins is important in understanding their properties during processing and application. The MMD is directly related to physical properties such as toughness, melt viscosity and crystallinity. It is also useful in tailoring or modifying catalyst structures or polymerization conditions during synthesis, to influence the final properties of the polymers. It is noticeable from the literature reviewed here (methods used and the results obtained for the molecular characterization of IPCs up to now), that the precise analysis of such polymers with multivariate distributions is a difficult task and a single separation method is often not able to provide complete information. A more reasonable approach to characterize such complex samples is to find out by using the combination of different analytical techniques, which ones separate exclusively or at least predominantly according to a single molecular characteristic and to combine them to carry out a multidimensional mapping of the multivariate distribution. It will be the main aim of this study to develop novel multidimensional analytical

approaches, which can be used for the complete molecular characterization of IPCs and other complex polyolefins.

2.5 References

1. Galli, P.; Haylock, J. C. *Prog. Polym. Sci.* 1991, 16, p 443.

2. Debling, J. A.; Ray, W. H. *J. Appl. Polym. Sci.* 2001, 81, p 3085.

3. Kittilsen, P.; Mckenna, T. F. *J. Appl. Polym. Sci.* 2001, 81, p 1047.

4. Mirabella, F. M. *Polymer* 1993, 34, p 1729.

5. Usami, T.; Gotoh, Y.; Umemoto, H.; Takayama, S. *J. Appl. Polym. Sc. Appl. Polym. Symp.*

1993, 52, p 145.

6. Cai, H.; Luo, X.; Ma, D.; Wang, J.; Tan, H. *J. Appl. Polym. Sci.* 1999, 71, p 93.

7. Fan, Z.; Zhang, Y.; Xu, J.; Wang, H.; Feng, L. *Polymer* 2001, 42, p 5559.

8. Xu, J.; Feng, L.; Yang, S.; Wu, Y.; Yang, Y.; Kong, X. *Polymer* 1997, 38, p 4381.

9. Urdampilleta, I.; Gonza´lez, A.; Iruin, J. J.; de la Cal, J. C.; Asua, J. M. *Macromolecules* 2005, 38, p 2795.

10. Feng, Y.; Hay, J. N. *Polymer* 1998, 39, p 6723.

11. Song, S. P.; Feng, Wu, J.; Ye, M.; Yang, Y. *Polymer* 2009, 50, p 286.

12. E. O. Moore, Jr., PolypropyleneHandbook. 92, Hanser Publishers, Munich (1996).

13. Sano, H.; Usami, T.; Nakagawa, H. *Polymer* 1986, 27, p 1497.

14. Takahashi, T.; Mizuno, H.; Thomas, E. L. *J. Macromol. Sci-Phys.*1983, 2, p 425.

15. Kojima, M. J. *Macromol. Sci., Phys. Edn.* 1981, B19, p 523.

16. Karger-Kocsis, J.; Kallo, A.; Szafner A.; Bodor, G.; Senyei, Z. *Polymer* 1979, 20, p 37.

17. Hongjun, C.; Xiaolie, L.; Dezhu, M.; Jianmin, W.; Hongsheng, T. *J. Appl. Poly. Sci.* 1999, 71, p 93.

18. Hongjun, C.; Xiaolie, L.; Xiangxu, C.;Dezhu, M.; Jianmin, W.; Hongsheng, T. *J. Appl. Poly. Sci.* 1999, 71, 103

19. Zacur, R.; Goizueta, G.; Capiati, N. *Polym. Eng. Sci.* 1999, 39, P 5.

20. Zhang, Yu-Dong.; Chang-Jiang, W. U.; Zhu, S.N. *Polym. J.* 2002, 34, p 700.

21. Tan, H.; Li, L.; Chen, Z.; Song, Y.; Zheng, Q. *Polymer* 2005, 46, p 3522.

22. Fu, Z.; Xu, J.; Zhang, Y.; Fan, Z. *J. Appl. Poly. Sci.* 2005, 97, p 640.

23. Xu, J. T.; Jin, W.; Fu, Z. s.; Fan, Z.Q. *J. Appl. Poly. Sci.* 2005, 98, p 243.

24. Mahdavi, H.; Nook, M. E. Polym. Int. 2010, 59, p 1701.

25. Zhang, C.; Shangguan, Y.; Chen, R.; Wu, Y.; Chen, F.; Zheng, Q.; Hu, G. *Polymer* 2010, 51, p 4969.

26. Zhang, C.; Shangguan, Y.; Chen, R.; Zheng, Q. *J. Appl. Poly. Sci.* 2011, 119, p 1560.

27. García, R. A.; Coto, B.; Expósito, M. T.; Suarez, I.; Fernández, A.; Caveda, S. *Macromol. Res.* 2011, 19, p 778.

28. Xue, Y.; Fan, Y.; Bo, S.; Ji, X. *Eur. Polym. J.* 2011, 47, p 1646.

29. Mahdavi, H.; Nook, M. E. *J. Appl. Poly. Sci.* 2012, 125, p 1606.

30. Van Reenen, A. J.; Basson, N. C.. *eXPRESS Polymer Letters* 2012, 6, p 427.

31. Mncwabe, S.; Luruli, N.; Marantos, E.; Nhlapo, P.; Botha, L. *Macromol. Symp.* 2012, 313, p 33.

32. Mori, S.; Barth, H.G. Size Exclusion Chromatography, Springer, Berlin (1999).

33. Yau, W.W.; Kirkland. J.J.; Bly, D.D. Modern Size Exclusion Chromatography, Wiley, New York (1979).

34. Tribe, K.; Saunders, G.; Meißner, R. *Macromol. Symp. Special Issue: Olefin Polymerization* 2006, 236, p 228.

35. Piel, C.; Jannesson, E.; Qvist, A. *Macromol. Symp. Special Issue: Polyolefin Characterization - ICPC 2008.* 2009, 282, p 41.

36. Liu, M. X.; Dwyer, J. L. *Appl. Spectrosc.* 1996, 50, p 349.

37. Harding, G.H.; Van Reenen, A. J. *Macromol. Chem. Phys.* 2006, 207, p 1680.

38. Soares, J. B. P.; Hamielec, A. E. *Polymer* 1995, 36, p 1639.

39. Soares, J. B. P.; Anatawarskul, S.; Adams, P. M. W. *Adv. Polym. Sci.* 2005, 182, p 1.

40. Kissin, Y. V.; Fruitwala, H. A. *J. Appl. Poly. Sci.* 2007, 106, p 3872.

41. Pasch, H.; Brüll, R.; Wahner, U.; Monrabal, B. *Macromol. Mater. Eng.* 2000, 279, p 46.

42. Monrabal, B.; Sancho-Tello, J.; Mayo, N.; Romero, L. *Macromol. Symp.* 2007, 257, p 71.

43. Van Reenen, A. J.; Brand, M.; Rohwer, E.; Walters. P. *Macromol. Symp.* 2009, 282, p 25.

44. Luruli, N.; Pijpers, T.; Brüll, R.; Grumel, V.; Pasch, H.; Mathot, V. *J. Polym. Sci., Part B: Polym. Phys.* 2007, 45, p 2956.

45. Alghyamah, A. A.; Soares, J.B.P. *Macromol Symp.* 2009, 285, p 8.

46. Wang, W.; Kharchenko, S.; Migler, K.; Zhu, S. *Polymer* 2004, 45, p 6495.

47. Yau, W. W.; Gillespie, D. *Polymer* 2001, 42, p 8947.

48. Gabriel, C.; Lilge, D. *Polymer* 2001, 42, p 297.

49. Starck, P.; Lehmus, P.; Seppälä, J. V. *Polym. Eng. Sci.* 1999, 39, p 1444.

50. Hiller, W.; Pasch, H.; Macko, T.; Hofmann, M.; Ganz, J.; Spraul, M.; Braumann, U.; Streck, R.; Mason, J.; Van Damme, F. *J. Magn. Reson.* 2006, 183, p 290.

51. de Goede, E.; Mallon, P.; Pasch, H. *Macromol. Mater. Eng.* 2010, 295, p 366.

52. Albrecht, A.; Heinz, L.C.; Dieter, L.; Pasch, H. *Macromol. Symp.* 2007, 257, p 46.

53. Macko, T.; Brüll, R.; Zhu, Y.; Wang, Y. *J. Sep. Sci. Special Issue: Polymer Analysis.* 2010, 33, p 3446.

54. V.B.F. Mathot: The crystallization and melting region, in: V.B.F. Mathot (Ed.), Calorimetry and Thermal Analysis of Polymers, Hanser Publishers, Munich/Vienna/New York, 1994, chapter 9, pp. 231–299.

55. Krumme, A.; Basiura, M.; Pijpers, T.; Poel, G.V.; Heinz, L.C.; Brüll, R.; Mathot, V.B.F. *Mater. Sci.* 2011, 17, p 260.

56. Poel, G.V.; Mathot, V.B.F. *Thermochim. Acta.* 2007, 461, p 107.

57. Pasch, H.; Trathnigg, B. HPLC of Polymers, 1st ed.; Springer: Berlin, 1998.

58. Heinz, L.C.; Pasch, H. *Polymer* 2005, 46, p 12040.

59. Macko, T.; Pasch, H.; Brüll, R. *J. Chromatogr. A.* 2006, 111, p 81.

60. Macko, T.; Denayer, J.F.; Pasch, H.; Baron, G.V. *J. Sep. Sci.* 2003, 26, p 1569.

61. Macko, T.; Pasch, H. *Macromolecules* 2009, 42, p 6063.

62. Pereira, L. *J. Liq. Chromatogr. Related. Tech.* 2008, 31, p 1687.

63. Albrecht, A.; Heinz, L.C.; Dieter, L.; Pasch, H. *Macromol. Symp.* 2007, 257, p 46.

64. Macko, T.; Brüll, R.; Alamo, G.; Thomann, Y.; Grumel, V. *Polymer* 2009, 50, p 5443.

65. Macko, T.; Cutillo, F.; Busico, V.; Brüll, R. *Macromol. Symp.* 2010, 298, p 182.

66. Dolle, V.; Albrecht, A.; Brüll, R.; Macko, T. *Macromol. Chem. Phys.* 2011, 212, p 959.

67. Chitta, R.; Macko, T.; Brüll, R.; Doremaele, G.V.; Heinz, L.C. *J. Polym. Sci., Part A: Polym. Chem.* 2011, 49, p 1840.

68. Macko, T.; R. Brüll, R.; Alamo, R.G.; Stadler, F.J.; Losio, S. *Anal. Bioanal. Chem.* 2011, 399, p 1547.

69. Cong, R.; deGroot, W.; Parrott, Al.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* 2011, 44, p 3062.

70. Ginzburg A, Macko T, Dolle V, Brüll R. *J. Chromatog. A.* 2010, 1217, p 6867.

71. Roy A, Miller MD, Meunier DM, de Groot AW, Winniford WL, van Damme FA, Pell, R. J.; Lyons, J.W. *Macromolecules* 2010, 43, p 3710.

72. Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *Eur. Polym. J.* 2011, 47, p 319.

73. R. Chitta, A. Ginzburg, G. Doremaele, T. Macko, R. Brüll. *Polymer* 2011, 52, p 5953.

74. Sun, Z.;Yu, F.; Qi,Y. *Polymer* 1991, 32, p 1059.

75. Besomles, M.; Menguel, J.-F.; Delmas, G. J. *J. Polym. Sci., Part B; Polym. Phys.* 1988, 26, p 1881.

76. Tan, H.; Li, L.; Chen, Z.; Song, Y.; Zheng, Q. *polymer* 2005, 46, p 3522.

77. Mirabella, F. J. *J. Appl. Pol. Sci., Appl. Polym. Symp.* 1992, 51, p 117.

78. Pires, M.; Mauler, R. S.; Liberman, S. A. *J. Appl. Polym. Sci.* 2004, 92, p 2155.

79. Xu, J.; Fu, Z.; Fan, Z.; Feng, L. *Eur. Polym. J.* 2002, 38, p 1739.

80. Feng, Y.; Jin, X.; Hay, J. N. *J. Appl. Polym. Sci.* 1998, 68, p 381.

81. Xu, J.; Feng, L. *Eur. Polym. J.* 2000, 36, p 867.

82. Xu, J.; Feng, L.; Yang, S.; Yang, Y.; Kong, X. *Eur. Polym. J.* 1998, 34, p 431.

83. Baker, B. B.; Bonesteel, J. K.; Keating, M. Y. *Thermochim. Acta.* 1990, 166, p 53.

84. Zacur, R.; Goizueta, G.; Capiati, N. *Polym. Eng. Sci.* 2000, 40, p 1921.

85. Urdampiletta, I.; González, A.; Iruin, J. J.; de la Cal, J. C.; Asua, J. M. *Macromolecules* 2005,

38, p 2795.

86. Sun, Z.; Yu, F.; Qi, Y. *Polymer* 1991, 32, p 1059.

87. Fu, Z.-S.; Fan, Z.-Q.; Zhang, Y.-Q.; Feng, L.-X. *Eur. Polym. J.* 2003, 39, p 795.

88. Karger-Kocsis, J.; Kallo, A.; Kuleznev, V. N. *Polymer* 1984, 25, p 279.

89. Chen, Y.; Chen, Y.; Chen, W.; Yang, D. *Polymer* 2006, 47, p 6808.

90. Tanem, B. S.; Kamfjord, T.; Augestad, M.; Løvgren, T. B.; Lundquist, M. *Polymer* 2003, 44,

p 4283.

91. Tong, C.; Lan, Y.; Chen,Ye.; Chen, Yong.; Yang, D.; Yang, X. *J. Appl. Poly. Sci.* 2012, 123, p 1302.

Chapter 3

Results and Discussion

A brief summary of the overall results obtained from various analytical approaches for the analysis of impact polypropylene copolymers are discussed in this chapter. More detailed information is given in the three published articles that are presented here.

3.1 Summary of the results

The first part of this study describes the combination of fractionation and various analytical techniques, including highly sensitive advanced thermal analysis to investigate the correlation between molecular properties and thermal behaviour of bulk IPC sample and one of its midelution temperature TREF fractionations. Two nonstabilized commercial IPC samples, designated as 3V and 3VA (obtained from Sasol Polymers, Secunda, South Africa) were used for this study.

***Publication 1: Multidimensional Analysis of the Complex Composition of Impact Polypropylene Copolymers: Combination of TREF, SEC-FTIR-HPer DSC, and High Temperature 2D-LC** (S. Cheruthazhekatt, T.F.J. Pijpers, G.W. Harding, V.B.F. Mathot, H. Pasch. Macromolecules 45 (2012) 2025−2034).*

In this publication a typical IPC with an ethylene content of 10.5 mol% was analysed. In the first step of the investigation, the bulk sample was analysed by SEC, DSC and the more advanced hyphenated SEC-FTIR to determine the ethylene/ propylene content and the crystallinity distribution across the molar mass distribution. A relatively high value for propylene content and PP crystallinity was observed across MMD with little or no crystallisable ethylene sequences (see Figure 3). This indicated that the analysis of the bulk sample, having a small amount of comonomer (ethylene content. 10.5 mol%), by this technique is limited in terms of differentiating the crystallisable ethylene sequences from the major component of the material which is isotactic polypropylene. A single distinct melting peak at 159 °C (see Figure 4a), similar to the iPP homopolymer was noticed for this bulk IPC by DSC analysis. Melting or crystallization events related to the ethylene propylene copolymer components were not observed.

The thermal behaviour of different SEC fractions was studied by using a novel DSC method - HPer DSC - in order to obtain first information on the chemical composition of various SEC fractions from their melting and crystallization behaviour. These SEC fractions were collected on an aluminium foil, and the deposits were divided into different molar mass fractions by cutting the aluminium foil at predetermined SEC retention times. An increase in the melting and crystallization temperature with molar mass was observed for all SEC fractions (see Figures 6 and 7). The presence of highly crystalline iPP homopolymer and a molar mass dependence on the T_m and T_c values were confirmed. Comparatively broad melting and crystallization peaks were observed for the medium molar mass fractions, which may indicate the compositional heterogeneity in addition to the well-known stronger dependence of the crystallisation and melting temperatures on molar mass in the lower molar mass range. However, SEC fractions that are characteristic for the copolymer content could not be isolated. This indicates that a simple SEC separation is not adequate for such complex multicomponent materials, in particular when the comonomer content is low.

In order to obtain a complete separation according to chemical composition, the bulk IPC was further analysed by HT HPLC using a solvent gradient from 1-decanol to TCB on a Hypercarb stationary

phase (see Figure 5). Two peaks were observed in isocratic and gradient elution. Similar elution profiles were observed for iPP standards with different molar masses (except for very low molar mass standards). The low molar mass component of the iPP eluted isocratically in 100% 1-decanol and the higher molar mass chains were partially retained on the Hypercarb column using 1-decanol, being desorbed in the gradient from 1-decanol to TCB. No peaks corresponding to EP rubber, EP segmented copolymers, or PE homopolymer were observed due to the very low concentration of these components.

From the above results, it was concluded that the traditional bulk sample analysis by using advanced thermal analysis or even with the highly sophisticated HT HPLC method is not a proper choice for the thorough characterization of such complex copolymers. Thus, for a detailed analysis the bulk sample was fractionated into amorphous rubber, semicrystalline ethylene-propylene copolymers, and highly crystalline iPP or PE homopolymer by preparative TREF (see Figure 8) to obtain more homogeneous fractions. This allows the further analysis of these separated fractions to obtain more detailed information, since the various components obtained by TREF can be analysed separately with much higher sensitivity.

With the focus on method development, an in-depth analysis of one of the midelution temperature TREF fractions (80 °C) was done by the above described techniques. HT SEC analysis of this fraction showed a bimodal molar mass distribution (see Figure 9) which indicates the presence of chemically different components, which may result from co-crystallization during TREF separation. In order to further identify the chemical nature of the different components, this 80 °C TREF fraction was analysed by SEC-FTIR. The results showed that the higher and medium molar mass fractions are mixtures of ethylene-propylene copolymers having different amounts of ethylene or propylene, and the low molar mass fraction was iPP homopolymer (see Figure 4). Two melt endotherms were observed for this fraction by DSC analysis (see Figure 10), which indicates the presence of two crystallisable components melting at different temperatures due to their differences in molecular structure. However, it was difficult to assign these peaks to a particular chain type due to the overlapping effects of ethylene comonomer distribution and propylene tacticity distribution in these fractions. These results indicate that a more in-depth analysis is needed in order to assign the crystallisation and melting transitions to particular chain types. Therefore, the TREF fraction was further fractionated by SEC and the resulting fractions analysed by HPer DSC (see Figure 12 and 13). Broad or multiple melting and crystallization peaks were observed for the high and medium molar mass SEC fractions, indicating that these fractions contain a complex mixture of ethylene-propylene copolymers, ethylene-rich copolymers and/or segmented EP copolymers, possibly branched to almost linear, semi-crystalline polyethylene, and finally, possibly low tacticity polypropylene homopolymer. A good agreement with the SEC-FTIR results was noticed, the copolymers which are richest in ethylene eluted at low retention times (higher molar mass part) and those which are richest in propylene were found to be eluted later (lower molar mass part). It was concluded that the crystalline iPP

homopolymer was found in the low molar mass part, while crystalline polyethylene or PE segments of segmented EP copolymers were found in the higher molar mass fractions.

A co-elution of EPC with iPP due to the tacticity distribution was observed for this mid-elution temperature fraction based on the FTIR and HPer DSC analysis. This again points to the fact that a complete separation according to CCD was not achieved by prep TREF due to the co-crystallization effects. Therefore, the same TREF fraction was analysed by high temperature HPLC, and a clear separation according to chemical composition was obtained within a very short analysis time (see Figure 14). The HPLC peaks correspond to low and high molar mass iPP, ethylene and propylene rich EPC and PE homopolymer. The combination of prep TREF and HT HPLC was found to be a suitable method for the separation and identification of the chemically different components in this system. Finally, a complete separation according to chemical composition and molar mass was achieved by HT 2D-LC. All components of this fraction were well separated from each other by both CCD and MMD (see Figure 15). It was noticed that the iPP had a lower molar mass component which elutes in pure 1-decanol and a second slightly higher molar mass component eluting in the gradient. EPC with different ethylene and propylene sequences as well as PE homopolymer having similar molar masses eluted according to their interaction with the Hypercarb column. There was a clear separation between the iPP and EPC copolymers. EPC dominated by longer propylene sequences elute closer to iPP while those dominated by longer ethylene sequences elute together with PE homopolymer. As a result the HT 2D-LC represents a complete characterisation of this TREF fraction in terms of both molar mass and chemical composition, accomplished within a relatively short analysis time.

To summarize, the combination of prep TREF and two hyphenated techniques, SEC-FTIR and SEC-HPer DSC, was found to be an excellent analytical tool for the compositional and thermal analysis of the complex TREF fractions of an IPC. Therefore, as the second part of this study, we decided to extend this type of analysis to all semicrystalline and some highly crystalline TREF fractions (since they are expected to be highly crystalline iPP homopolymer) to investigate the influence of molar mass on the thermal properties of chemically different components present in each TREF fraction. In addition, some of the selected TREF-SEC dual fractions were analysed by advanced thermal analysis using fast scanning calorimetry (Flash DSC 1) and solution DSC.

Publication 2: Compositional Analysis of an Impact Polypropylene Copolymer by Fast Scanning DSC and FTIR of TREF-SEC Cross-Fractions (S. Cheruthazhekatt, T.F.J. Pijpers, G.W. Harding, V.B.F. Mathot, H. Pasch, Macromolecules 45 (2012) 5866-5880).

As has been shown in the first publication, prep TREF does not yield fractions that are homogeneous regarding chemical composition or molar mass. Co-elution/co-crystallization effects play a significant role. In the present investigation, SEC analysis of the all semicrystalline TREF fractions revealed bimodal or multimodal elution curves (see Figure 2), indicating that polymer chains which differ in molar mass (and/or chemical composition) were crystallised and dissolved at the same temperature

21

range during the TREF crystallization and elution step, respectively. Two melt endotherms were observed for all these fractions by standard DSC analysis, indicating the presence of chemically different components other than the molar mass dependence on the T_c and T_m. Therefore, a more detailed analysis of the TREF-SEC dual fractions by FTIR analysis was performed to obtain a better understanding of the molecular structure of the various molar mass fractions. The results were then complimented by the thermal analysis of these fractions using HPer DSC.

The samples for HPer DSC measurements were taken in such a way that information about the underlying molecular structure could be obtained. For the 60 °C TREF fraction, two SEC fractions corresponding to the high and low molar mass parts of the bimodal MMD were selected (see Figure 3). The DSC curve of the high molar mass part of the MMD shows a broad melting curve with a peak maximum temperature of approximately 80 °C and an end melting temperature of 95 °C, which represents an EP copolymer. The DSC curve of the low molar mass part of the MMD is found to be originating from low-isotacticity PP. The presence of higher amounts of polypropylene in the lower molar mass region was completely confirmed by the FTIR information on this SEC fraction with no crystallisable ethylene sequences. A detailed explanation of the analysis of the 80 °C TREF fraction was given in publication 1. Besides the 60 and 80 °C TREF fractions, which show bimodal SEC curves, a multimodal SEC curve was obtained for the 90 °C TREF fraction. Thermal analysis of the higher and medium molar mass parts shows the presence of a copolymer fraction, more specifically low propylene content EPC. The crystallization curve indicates the presence of more than one species crystallizing, though these do not show up separately in the melting curve. The low molar mass SEC fraction shows PP crystallinity, but at lower temperatures than the middle part of the MMD (see Figure 8). This could be explained by the decreasing effect that lower molar masses have on the crystallization and melting. For the higher temperature TREF fractions (110 and 120 °C) only one melt endotherm was observed by standard DSC analysis, and a uniform distribution of propylene content and crystallinity was obtained by SEC-FTIR. For both fractions the DSC curve of the middle part of the MMD clearly shows high-isotacticity PP with melting peak maximum temperatures in the range of 153 to 160 °C. For the very low molar mass fraction the melting peak maxima decrease, most probably due to the decreasing effect of the low molar mass (see Figure 10 and 11).

For all semicrystalline fractions, propylene type crystallization was observed in the lower molar mass part. In the intermediate and high molar mass parts, both ethylene and propylene crystallinities were found as related to copolymers varying in propylene content and to polypropylene varying in isotacticity, respectively. With increasing TREF elution temperature the isotacticity of the polypropylene increases appreciably, leading to longer sequences of isotactic polypropylenes and concomitant increasing melting temperatures. At the same time cross-fractions showing ethylene-crystallinity are seen to be ethylene-propylene copolymers (EPC) with various ethylene and propylene sequence length distributions. With increasing TREF elution temperature their ethylene sequence lengths increase because of the decreasing amount of propylene incorporated in the chains.

In order to study the (meta)stability of the crystallites and the occurrence of possible reorganization phenomena, a more extensive evaluation was performed by applying a variety of combinations of scan rates of 5, 50, 100 and 200 °C/min using HPer DSC. Thereby, the effect of different heating and cooling rates on the metastable structures and their thermal properties can be obtained. In addition, the range of scan rates applied was extended appreciably by using the Flash DSC 1. Reasonable melting and crystallization peaks were obtained for very small SEC fractions by using a higher scanning rate, 100 °C/s (see Figure 5 and 7a). This preliminary result promises that the Flash DSC 1 can be used to study the thermal properties of minute amounts of material that can be obtained from submicro scale synthesis, cross fractions, multilayers and coatings.

From the HPer DSC and Flash DSC 1 measurements on selected SEC fractions, a decrease in T_m and T_c with increasing cooling rate was observed. Additionally, continuity of the HPer DSc and Flash DSC 1 data was also noticed (see Figure 7b). This indicates that the Flash DSC 1 can operate from low scanning rates which partly overlap with other commercial DSC equipment to much higher heating and cooling rates, thereby extending the scan rate operating window to more than 4 orders of magnitude compared to commercial DSCs. These findings confirm that the Flash DSC 1 can be used as an excellent analytical tool for the thermal analysis of materials under conditions that occur in actual processing conditions of these commodity plastics.

In order to get an idea about the release (co-elution) of polymer chains with different molecular structures at the same temperature range in the TREF elution step, a dissolution experiment by DSC of 3V 90 in p-xylene was performed. The solution DSC results for a medium molar mass fraction show that all chains of these fractions were dissolved completely at the final TREF elution temperature range (90 °C) of this fraction (see Figure 13b). However, here the dissolution process starts 25 degrees before 80 °C, which is caused by the partial dissolution of polymer chains giving a heat flow in the DSC at the cost of the heat of fusion measured. But these chains cannot yet elute in TREF due to the presence of more stable segments in the same chain and they may be still connected to other molecules within the same and/or other crystallites. That means a chain will elute when the most stable segment of that chain dissolves.

Even though HPer DSC measurements were performed at higher heating and cooling rates compared to TREF, the results were found to be reasonable. These preliminary results highlight the possibilities of using solution DSC to study the crystallization and melting behaviour of complex polyolefins in solvents like p-xylene, and HPer DSC as an extremely fast technique to optimize the TREF elution temperature scheme, or CRYSTAF crystallization temperature profile, with very small amounts of sample and solvents.

To summarize, the complex composition of an IPC has been revealed by advanced thermal analysis, using the combination of fast scanning DSC (HPer DSC, Flash DSC 1, and solution DSC) with SEC fractionation subsequent to TREF fractionation. The findings were confirmed by structural information that was obtained using FTIR measurements of these TREF-SEC dual fractions. The metastability of

23

one of the fractions was studied by applying HPer DSC at 5 to 200 °C/min and Flash DSC at 10 to 1000 °C/sec. Releasing of the polymer chains in TREF elution step was well explained in terms of the thermal behaviour observed from solution DSC measurements of TREF-SEC cross-fractions in p-xylene.

Publication 3: Comprehensive High Temperature 2D-LC Combined with High Temperature Gradient HPLC-FTIR for the Analysis of Impact Polypropylene Copolymers (S. Cheruthazhekatt, G.W. Harding, H. Pasch. J. Chromatog. A. (2013) http://dx.doi.org/10.1016/j.chroma.2013.02.052.

As reported in the first publication, the combination of prep TREF and HT 2D-LC were found to be a suitable method for the complete separation of the individual components in a complex TREF fraction in terms of CCD and MMD. In this section, a comparative study of the complete set of TREF fractions of two commercial IPCs was conducted, to prove the applicability of this presented method for the detailed microstructural analysis of IPCs. As a final part of this study, a novel multidimensional approach using the combination of prep TREF and a hyphenated technique, HT HPLC-FTIR, was used to determine the exact chemical composition distributions present in all the HPLC separated fractions.

Two IPC samples designated as 3V and 3V A, were fractioned into eight fractions by preparative TREF (see Figure 2). The shapes of the MMD curves obtained for all TREF fractions of both samples were found to be similar and two melt endotherms were observed for the all semicrystalline (midelution temperature) TREF fractions by DSC analysis as well (see Figures 1 and 2 in supporting information, Appendix A). It is clear that conventional SEC and DSC analysis cannot provide much information regarding the microstructure of these materials, either in bulk or based on the TREF fractions. Therefore, the comonomer content, monomer sequence distributions, tacticity and number average ethylene and propylene sequence lengths of the two IPC samples were calculated from ^{13}C NMR analysis (see supporting information Table 1 and 2). Sample 3V A showed relatively higher ethylene content (11.78 mol%) and lower tacticity (87.53 %) compared to 3V. Differences in the microstructure distributions (EP junctions, segment lengths and average sequence lengths) were observed for these two IPC samples. However, the NMR analysis can provide only the average chemical composition, and exact CCD cannot be determined in this way. Therefore, all the TREF fractions were analysed by using HT HPLC and HT 2D-LC to obtain a complete separation.

Ethylene-propylene random copolymers with a small amount of low molar mass iPP were found in the 30 °C amorphous fraction of both IPC samples (see Figure 10a and 10b). Additionally, the presence of highly branched components, which eluted in SEC mode, was observed in the sample 3V – 30. EPC with different ethylene and propylene sequence lengths and PE homopolymer having similar molar masses were observed in all mid-elution temperature fractions (60, 80, and 90 °C) of both samples (see Figure 10). From the HT HPLC and 2D-LC analysis results, it was concluded that the amount and chemical structure of the components were different in the equivalent TREF fractions of

both samples (see Figure 3 and 10). Low and high molar mass iPP was found to be the major constituents in the higher temperature (above 100 °C) TREF fractions (see Figure 4).

As a final step, the chemical composition distributions and the crystallinity distributions of the HPLC separated components in the most important TREF fractions of IPC 3V A were determined by offline coupling of HT HPLC with FTIR (see Figure 7 and 8). The exact chemical nature of the HPLC-separated components was determined by analysing the individual FTIR spectra at the peak maximum (see Figure 9). The first component and the one eluting immediately after the start of gradient was identified as being iPP homopolymer. For the later eluting fractions, a clear difference in chemical structure from propylene-rich EPC to ethylene-rich EPC or PE homopolymer was confirmed from the corresponding IR spectra. The presence of highly crystalline PE homopolymer in the 130 °C TREF fraction of sample 3V A was also confirmed (see Figure 12 and 13). By this way a complete compositional analysis of a complex polyolefin such as IPC was achieved.

To summarize, for the first time, a complete microstructural analysis of IPC was done by using a multidimensional analytical approach (developed by the combination of prep TREF and HT 2D-LC). The results showed that this is the method of choice for differentiating the complex polyolefins in terms of their CCD, which is not possible with conventional analytical techniques such as SEC and DSC, which show similar results. The exact CCD and the crystallinity distributions of the HPLC separated components in the complex TREF fractions were successfully determined by using a novel hyphenated technique, HT HPLC-FTIR.

Chapter 4

Conclusions and Recommendations

In this chapter the overall results of this study are concluded and some recommendations for future research work in the same field are proposed.

4.1 Conclusions

In this study it was demonstrated that various multidimensional analytical techniques based on the combination of Prep TREF, HT 2D LC, and advanced thermal analysis, such as fast scanning calorimetry, are highly useful for the compositional analysis of complex polyolefins such as IPCs.

By using these novel analytical approaches, the following conclusions were obtained for the analysis of impact polypropylene copolymers.

(1) In the first part of this study, a hyphenated technique, SEC-HPer DSC, was used to study the influence of the molar mass on the thermal properties of impact polypropylene. From this, the applicability of the HPer DSC measurements on SEC fractions (in milligram down to microgram levels) of a bulk IPC sample was confirmed. The results showed reasonable melting and crystallization curves for the different molar mass fractions, and preliminary information regarding the compositional heterogeneity in this bulk copolymer sample was obtained. In-depth information regarding the chemical composition and thermal behaviour of the various components in this polymer was obtained by the thermal analysis of TREF-SEC fractions by using HPer DSC. These results were in agreement with information obtained from SEC-FTIR analysis of these fractions and the technique was therefore found to be a complimentary method for the compositional analysis of such materials in terms of their thermal behaviour. It was concluded from this part that the ability to measure the thermal behaviour of very small sample masses (SEC fractions) with HPer DSC enables the investigation of the thermal properties across the MMD of these complex fractions.

(2) In the second part, this work was extended to advanced thermal analysis of TREF-SEC dual fractions by using HPer DSC and Flash DSC 1 with higher scan rates for both heating and cooling to study the metastablity of the different species. A first and important conclusion from these measurements is that continuity of the T_c and T_m data was found for the HPer DSC and the Flash DSC 1. In this scan rate range spanning over four decades – from approximately 0.1 till 1000 °C/s – T_c dropped linearly in this restricted area, while the decrease of T_m levelled off at high scan rates, signifying that the melting process is dominated by fast reorganization processes - too fast for the present instrumentation to be influenced significantly. An impression about the release of molecules during TREF elution was obtained from the solution DSC measurements on a selected SEC fraction in p-xylene. This opened the possibilities to use HPer DSC with minute amounts of sample and lower volumes of solvent to measure the crystallization and dissolution behaviour of polymer chains in solvents like p-xylene, that can be used to design the TREF and CRYSTAF temperature profile for complex copolymers.

(3) In the next step the molecular characterization of IPC copolymers was accomplished by using a combination of prep TREF with HT 2D LC. For the first time, a complete separation according to chemical composition and molar mass distributions was obtained for each component in the TREF fractions. The presence of low molar mass polypropylene was observed in all semicrystalline

27

fractions, which was not expected according to the TREF separation mechanism. Additionally, the presence of significant amounts of PE homopolymer in the mid-elution temperature TREF fractions was confirmed, which was not obtainable with other analytical techniques reported in the literature till now. A comparative study on two commercial IPC samples with similar ethylene contents was made by using this approach, a clear difference in their microstructure (distribution of the comonomer) being detected. From the results, it was concluded that this is the method of choice for the thorough characterization of such complex materials, which shows similar results when analysed by conventional techniques such as HT SEC, DSC, etc.

(4) Finally a complete microstructural analysis of the HPLC-separated fractions was achieved by coupling the HT HPLC with FTIR. In this way the exact chemical structures of the individual components were identified. The results obtained are in agreement with the separation mechanism on the Hypercarb stationary phase. EPC copolymers with varying propylene-ethylene compositions and slightly branched PE homopolymer were identified from the FTIR spectra of the deposited HPLC fractions. Additionally, this method can provide the ethylene/propylene crystallinity distribution. To date this is the only method to identify the actual chemical composition present in such complex copolymer systems.

The overall results demonstrate that these multidimensional techniques are excellent analytical tools, necessary for a proper understanding of the molecular characteristics and thermal behaviour of IPCs and other complex polyolefins.

4.2 Recommendations

For a complex copolymer such as IPC, its macromolecular chain structure is an important factor, which affects the crystallization behaviour, melting temperature, morphologies and rheological properties. Therefore, it is suggested to develop a new analytical technique in order to provide a more detailed picture to explain how the various chain microstructures affect the thermal properties of this complex copolymer. In IPC, the propylene tacticity and ethylene comonomer distribution can complicate the macromolecular chain structure, which may lead to the complex crystallization and melting behaviour that was observed from the HPer DSC analysis of selected molar mass fractions (TREF-SEC dual fractions). Therefore, a thorough characterization is necessary to investigate how microstructure can affect the thermal properties of this material. It is clearly observed from the first section of this study that a complete separation of the individual components is not possible with TREF due to co-crystallization effects. For future work the HT-HPLC system must be used to separate the individual components and to collect more homogenous fractions. The separated fractions can be collected on the sample target (Germanium disc covered with aluminium foil) in the LC transform interface. These deposited fractions should be further subjected to thermal analysis methods such as HPer DSC and Flash DSC 1. This hyphenated technique can combine the fast and efficient

separation capability of HT-HPLC according to the microstructure of the polymer chains with the power of HPer DSC to measure small sample masses while scanning at higher rates, which helps to separate or reduce reorganizational thermal behaviour such as cold crystallization, recrystallization, and decomposition which may occur during heating.

Additionally, Prep TREF is a time consuming technique - the information that can be obtained from the analysis of individual fractions is exciting and extremely relevant. Based on the results that were observed from this study, the possibility of combining Prep TREF with other techniques for the characterization of polyolefins should be further explored. Therefore it is proposed to combine prep TREF with high-resolution solid-state nuclear magnetic resonance spectroscopy for the identification of the components. Additionally the morphology, chain dynamics, miscibility and micro-phase structure can be obtained with this NMR technique.

Research Output

(Publications)

Multidimensional Analysis of the Complex Composition of Impact Polypropylene Copolymers: Combination of TREF, SEC-FTIR-HPer DSC, and High Temperature 2D-LC

Sadiqali Cheruthazhekatt,[†] Thijs F. J. Pijpers,[‡,§] Gareth W. Harding,[†] Vincent B. F. Mathot,[‡,§] and Harald Pasch*,[†]

[†]Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa
[‡]SciTe, Ridder Vosstraat 6, 6162 AX Geleen, The Netherlands
[§]Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

ABSTRACT: A new multidimensional fractionation technique, temperature rising elution fractionation (TREF) combined with high temperature size exclusion chromatography FTIR (HT-SEC-FTIR), HT-SEC-DSC and high temperature two-dimensional liquid chromatography (HT-2D-LC) is used for the comprehensive analysis of a commercial impact polypropylene copolymer. HT-SEC-FTIR provides information regarding the chemical composition and crystallinity as a function of molar mass. Thermal analysis of selected SEC fractions yields the melting and crystallization behavior of these fractions which is related to the chemical heterogeneity of this complex copolymer. The thermal analysis of the fractions is conducted using a novel DSC method — high speed or high performance differential scanning calorimetry (HPer DSC) - that allows measuring of minute amounts of material down to micrograms. The most interesting and complex "midelution temperature" TREF fraction (80 °C) of this copolymer is a complex mixture of ethylene-propylene copolymers (EPC's) with varying ethylene and propylene contents and sequence length distributions, as well as iPP. High temperature solvent gradient HPLC has been used to show that there is a significant amount of PE homopolymer and EPC's containing long ethylene sequences in this TREF fraction. High temperature 2D-LC analysis reveals the complete separation of this TREF fraction according to the chemical composition of each component along with their molar mass distributions.
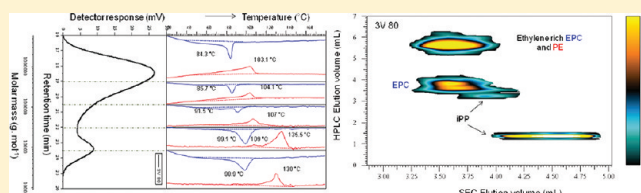
INTRODUCTION

Impact polypropylene copolymers (IPC) are a commercial grade of polypropylene (PP) which feature improved low temperature impact resistance. This class of polymers has seen growing demand in the thermoplastic market in recent times. The modified impact resistance of such heterophasic PP, together with the excellent properties of the polypropylene homopolymer such as rigidity and thermal and chemical resistance, makes the material highly useful in automotive and other applications.[1,2] Among the several methods reported for its production, the two-stage copolymerization process of propylene with ethylene is found to be the most effective and commercially adopted. The sequential multistage polymerization leads to the formation of highly complex materials consisting of many products, including amorphous, random, and segmented ethylene-propylene copolymers with different monomer sequence length distributions and molar mass distributions (MMD), as well as highly isotactic polypropylene and polyethylene homopolymers.[3-6] Preparative fractionation and subsequent analysis of the individual fractions is found to be an effective method for the complete characterization of such complex polymeric materials.[7-10] Offline coupling of SEC with FTIR is an established technique which has been used to

characterize the chemical composition distribution (CCD) across the molar mass distribution.[11]

Despite the fact that SEC-FTIR can indicate the level of ethylene and propylene crystallinity across these bimodal molar mass distributions, it is necessary to study the thermal behavior and crystallinity of these fractions thoroughly.[12-15] It has been reported that it is possible to couple SEC fractionation with standard DSC,[16] and even better with HPer DSC in order to study the short chain branching distribution along the MMD.[17] This is important due to the effect of molecular structure on the crystallization behavior, and thereby the final properties of the materials.[18] HPer DSC has the ability to measure very small sample masses while scanning at higher heating rates (up to 500 °C/min) than traditional, standard DSC. Fast scanning rates help to separate or reduce reorganizational thermal behavior, such as cold crystallization, recrystallization and decomposition which may occur during heating. The improvement in fast scanning DSC technology also offers the opportunity to detect weak transitions, including glass transitions which could not be determined by standard DSC.[18]
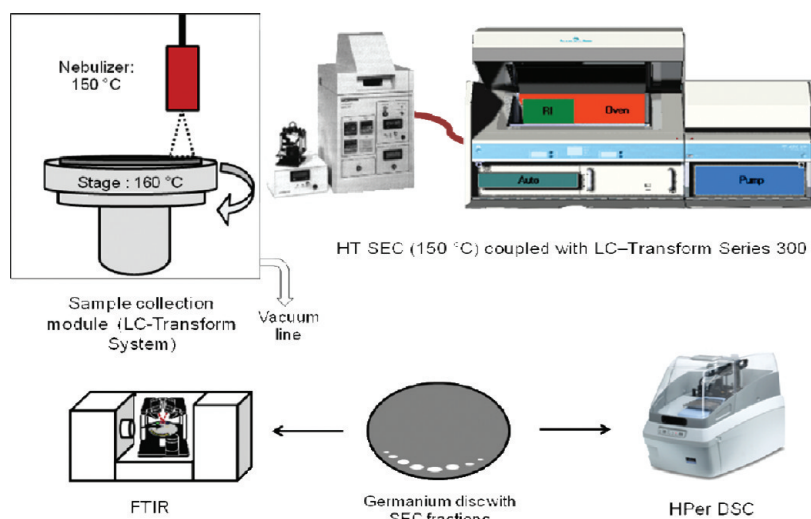
Figure 1. Polymer cross-fractionation techniques (SEC-FTIR and SEC-HPer DSC).

For many polymers, it has been proven that liquid chromatography is an efficient analytical technique for the fast separation of the polymer chains according to their chemical compositions.[19] However, the separation of polyolefins by high temperature liquid chromatography was only developed during the last couple of years by Pasch et al.[20] Initial work utilizing zeolites enabled the separation of polyolefins according to their chemical composition, however, the components could not be easily desorbed from the column packing.[21,22] Further development led to the separation of a blend of polypropylene and polyethylene based on the precipitation-redissolution mechanism on a modified silica gel column, using a solvent gradient of ethylene glycol monobutyl ether (EGMBE) (which is a good solvent for PP and not for PE) to 1,2,4-trichlorobenzene (TCB).[20,21] Most recently, research led to an HT-HPLC method capable of separating polypropylene according to tacticity in addition to the chemical composition separation of polyethylene from polypropylene.[23] This method is based on the adsorption–desorption mechanism and utilized the unique properties of the Hypercarb column.[24] To this date this is the only method for the swift and efficient separation of polyolefins and olefin copolymers according to their chemical compositions, where all components can be recovered from the column. The HPLC method separates polyolefin materials according to their chemical composition, although a slight molar mass influence on the retention volume has been observed for low molar masses. Despite this fact, the separation is governed mainly by the chemical composition or tacticity of samples; i.e., nearly baseline-separated peaks are obtained for all components. Several articles have been published based on the same separation methods for the analysis of polyolefins.[25−30] A new technique, high temperature thermal gradient interaction chromatography (HT-TGIC), has also been reported for the separation of olefin copolymers according to their comonomer content.[31] HT-HPLC allows one to estimate the chemical composition distribution (CCD) in such complex materials within a short period of time, which is a significant step forward for the characterization of these materials.

This study focuses on the molecular complexity of IPC and the analysis of different IPC components as separated by TREF and SEC using offline coupling with FTIR and HPer DSC, with emphasis on those TREF fractions exhibiting multimodal molar mass distributions. A single SEC separation and deposition is found to be sufficient for HPer DSC analysis. Melting and crystallization of an IPC sample and its 80 °C TREF fraction were studied. These investigations were complemented by fractionation and analysis using HT-HPLC and HT-2D-LC.

■ EXPERIMENTAL SECTION

A nonstabilized commercial IPC (designated as 3 V) was obtained from SASOL Polymers (Secunda, South Africa). The IPC sample has a comonomer (ethylene) content of 10.48 mol %, with a weight-average molar mass (M_w) and dispersity (D) of 228 kg·mol^{-1} and 3.5, respectively.

Size Exclusion Chromatography (SEC). Molar mass measurements for all samples were performed at 150 °C using a PL GPC 220 high temperature chromatograph (Polymer Laboratories, Church Stretton, U.K.) equipped with a differential refractive index (RI) detector. The column set used consisted of three 300 × 7.5 mm PLgel Olexis columns together with a 50 × 7.5 mm PLgel Olexis guard column (Polymer Laboratories, Church Stretton, UK). The eluent used was TCB at a flow rate of 1.0 mL/min with 0.0125% 2,6-ditert-butyl-4-methylphenol (BHT) added as a stabilizer. Samples were dissolved at 160 °C in TCB at a concentration of 1 mg/mL for 1- 2 h (depending on the sample type) and 200 µL of each sample was injected. Narrowly distributed polystyrene standards (Polymer Laboratories, Church Stretton, U.K.) were used for calibration.

Temperature Rising Elution Fractionation (TREF). Preparative TREF was carried out using an instrument developed and built in-house. Approximately 3.0 g of polymer and 2.0 w/w % Irganox 1010 (Ciba Specialty Chemicals, Switzerland) were dissolved in 300 mL of xylene at 130 °C in a glass reactor. The reactor was then transferred to a temperature-controlled oil bath and filled with sand (white quartz, Sigma-Aldrich, South Africa), used as a crystallization support. The oil bath and support were both preheated to 130 °C. The oil bath was then cooled at a controlled rate of 1 °C/h in order to facilitate the controlled crystallization of the polymer. The crystallized mixture was then packed into a stainless steel column which was inserted into a modified gas chromatography oven for the elution step. Xylene (preheated) was used as eluent in order to collect the fractions at predetermined intervals as the temperature of the oven was raised. The fractions were isolated by precipitation in acetone, followed by drying to a constant weight.

Deposition of SEC Fractions by the LC Transform Interface. An LC-Transform series model 300 (Lab Connections) was coupled to a PL GPC 220 (Polymer Laboratories, Church Stretton, England) in order to collect the SEC eluate. Samples were dissolved at 160 °C in TCB at a concentration of 2 mg/mL, with 200 µL of each sample being injected. The SEC column outlet was connected to the LC transform interface (see Figure 1) through a heated transfer line set at 150 °C.

Macromolecules

The fractions were deposited by rotating a germanium disk (sample target in the LC-transform) at a speed of 20°/min. The disk stage and nozzle temperatures of the LC-transform were set to 160 and 150 °C, respectively. For HPer DSC sample preparation an aluminum foil was wrapped around the germanium disk in such a way as to ensure good contact with the disk, with the opaque side of the foil being used for collection of the polymer deposits. The surface roughness of the opaque side of the foil enables comparatively higher adhesion as compared to the glossy side of the Al foil.[32] The bulk sample was collected by deposition of the entire sample at a single point on the germanium disk (no rotation). All the samples for SEC-FTIR and SEC-HPer DSC were prepared under the same deposition and cooling conditions in order to ensure comparable sample and thermal histories.

FTIR Analyses of the Deposited Fractions. FTIR analyses of the deposited SEC fractions were performed on a Thermo Nicolet iS10 Spectrometer (Thermo Scientific, Waltham, MA), equipped with the LC-transform FTIR interface connected to a standard transmission baseplate. Spectra were recorded at a resolution of 8 cm^{-1} with 16 scans being recorded for each spectrum. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

Differential Scanning Calorimetry (DSC). Melting and crystallization behavior of the bulk material and 80 °C TREF fraction were measured on a TA Instruments Q100 DSC system, calibrated with indium metal according to standard procedures. A heating rate of 10 °C/min was applied across the temperature range of 0−180 °C. Data obtained during the second heating cycle were used for all thermal analysis calculations. Measurements were conducted in a nitrogen atmosphere at a purge gas flow rate of 50 mL/min.

High Performance Differential Scanning Calorimetry (HPer DSC). Thermal properties of the SEC LC-Transform deposits were investigated using a Perkin-Elmer DSC 8500 (situated at SciTe's laboratory, Katholieke Universiteit Leuven, Belgium). A single deposition on the aluminum foil delivers enough material (not weighed as yet) for measurement at 50 °C/min, in both cooling and heating regimes. The foil is cut between various rotation angles for sample analysis (see Figure 2). The sample on the foil is folded into a
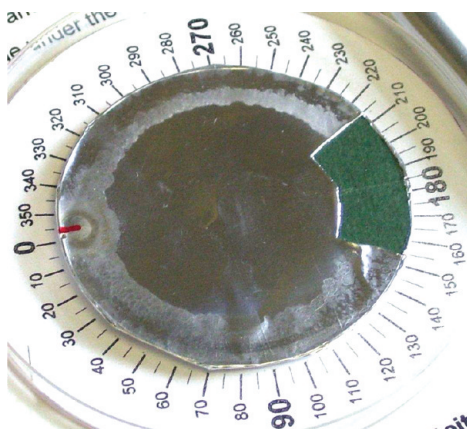

Figure 2. Example of an aluminum-covered disk after cutting out a sample for HPer DSC measurement. The portion of the aluminum foil removed is between 155° and 215°. This equates to the removal of the portion of the SEC eluate deposited between retention volumes of 20.75 to 24.75 mL.

flat package for analysis. For each sample, the first heating, first cooling, and second heating curves have been measured and plotted (endo up, exo down). All transitions observed turn out to be either crystallization (during cooling) or melting (during heating), and possibly recrystallization.

Chromatographic System. All chromatographic experiments were performed using a new chromatographic system for high-temperature two-dimensional liquid chromatography constructed by

Polymer Char (Valencia, Spain), comprising of an autosampler, two separate ovens, 2D switching valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). One oven was used for the HPLC column, while the second oven, where the injector and a switching valve were located, was used for the SEC column. The autosampler is a separate unit connected to the injector through a heated transfer line. A high-pressure binary gradient pump was used for HPLC in the first dimension and an isocratic pump was used for SEC in the second dimension. An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: A gas flow rate of 1.5 L/min, a nebulizer temperature of 160 °C, and an evaporator temperature of 270 °C.

High Temperature HPLC. HT-HPLC was carried out using a Hypercarb column (Hypercarb, Thermo Scientific, Dreieich, Germany) with the following parameters: 100 × 4.6 mm i.d., packed with porous graphite particles with a particle diameter of 5 μm, a surface area of 120 m^2/g, and a pore size of 250 Å. The flow rate of the mobile phase was 0.5 mL/min. The column was placed in the column oven maintained at 160 °C. The HPLC separations were accomplished by applying a linear gradient from 1-decanol to TCB. The volume fraction of TCB was linearly increased to 100% within 10 min after the sample injection and then held constant for 20 min. Finally, the initial chromatographic conditions were re-established with 100% 1-decanol. Samples were injected at a concentration of 1−1.2 mg/mL, with 20 μL of each sample being injected.

High Temperature Two-Dimensional Liquid Chromatography (HT-2D-LC). The coupling of HT-HPLC and HT-SEC was achieved by using an electronically controlled eight-port valve system (VICI Valco instruments, Houston, TX) equipped with two 100 μL sample loops. A 110 μL sample loop was used for injection into the first dimension. The flow rate for the first dimension was 0.05 mL/min, using the same gradient as for one-dimensional analysis, adjusted for the longer analysis time. TCB was used as the mobile phase for the second dimension at a flow rate of 2.75 mL/min. The second dimension column used was a PL Rapide H (Polymer Laboratories, Church Stretton, U.K.) 100 × 10 mm i.d. column with a 6 μm particle diameter. The column was placed in the top heated oven, maintained at 160 °C. Detection was performed with an ELSD using the same settings as for the one-dimensional (HPLC) separation.

■ RESULTS AND DISCUSSION

This study explores the combination of selective fractionation with highly sensitive thermal analysis to investigate the correlation between molecular properties (chemical composition and molar mass) and thermal behavior. In a first step the bulk IPC sample has been investigated followed by TREF fractionation and the analysis of the most complex part of the sample, the midtemperature (80 °C) TREF fraction (3 V 80). Up to now the investigation of such complex polyolefins by SEC-HPer DSC cross-fractionation is at a preliminary stage.

Analysis of the Bulk Sample. When HT-SEC is coupled to FTIR, information about the chemical composition as a function of molar mass can be obtained. Using the LC-transform approach, a polymer concentration profile similar to the response from the conventional RI detector of the SEC instrument is obtained by integrating the spectral peak area over the 2800−3200 cm^{-1} range of the FTIR spectrum.[33,34] This time-based representation of the total IR absorbance over this range during elution as a function of the total amount of the polymer sample is termed the Gram-Schmidt (GS) plot. The composition distribution can be determined from the deposition on the disk by analyzing the characteristic fingerprint region for particular functional groups. The propylene content was quantified by the ratio of the areas of the CH$_3$ and CH$_2$ bending bands at 1376 and 1462 cm^{-1}, respectively. The ethylene content was quantified by the area ratio of the bands
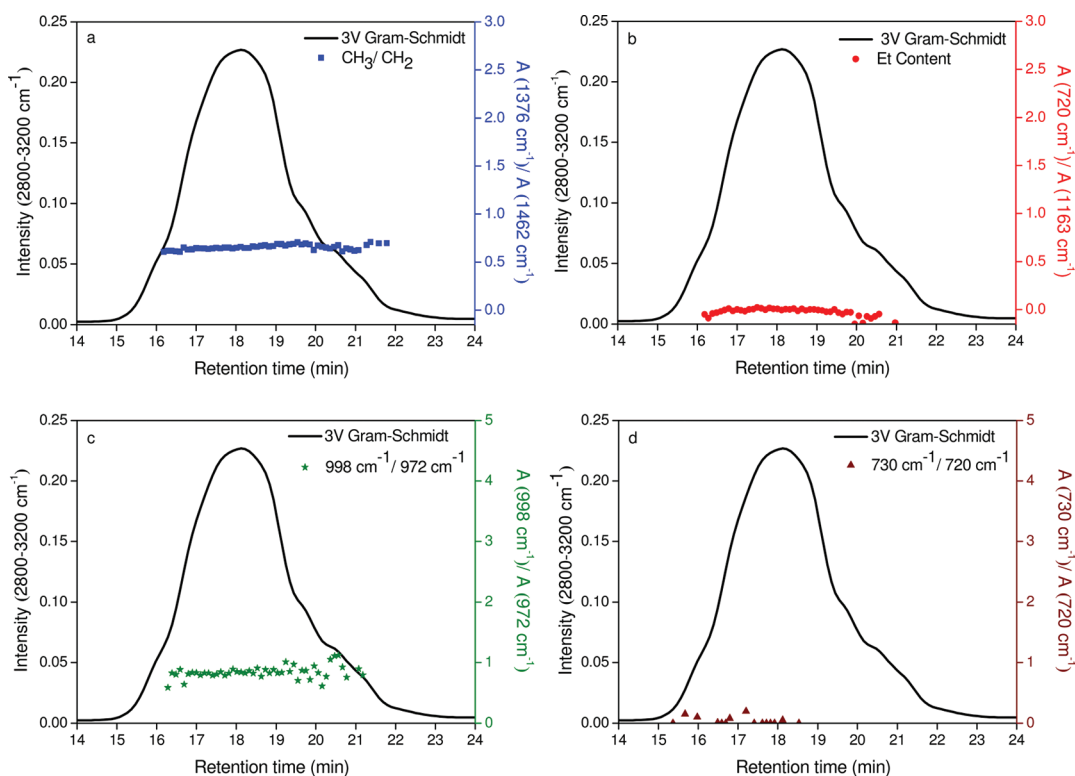
Figure 3. SEC-FTIR analysis of the bulk sample (3 V) illustrating (a) the propylene (CH_3/CH_2) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c and d), respectively.

at 720 and 1163 cm^{-1}, which is used to determine the comonomer composition within EP block copolymers.[11,35,36]

Figure 3 illustrates the SEC-FTIR results for the bulk sample (3 V). A uniform propylene concentration and its crystallinity distribution (Figure 3a and 3c) were observed across the GS curve for the bulk sample. The ethylene content and its crystallinity distribution (Figure 3b and 3d) have a lower value across the GS plot. This means that either the methylene (CH_2) sequence lengths are short or that the number of methylene chain units is few, due to the relatively low ethylene content in the bulk copolymer sample.

It is possible to construct a crystalline distribution of ethylene and propylene (crystalline parts of PE and PP) across the GS. The two absorptions at 998 and 730 cm^{-1} are the result of molecular vibrations from crystalline PP and PE regions, respectively. The absorption bands at 998 and 841 cm^{-1} are known to originate from long repeating monomer units in the crystalline 3-fold helical structure of iPP. The band at 972 cm^{-1} is associated with short helix segments from the amorphous region of PP. The relative intensity of the two bands at 998 and 972 cm^{-1} can be used to estimate the level of PP crystallinity in the sample.[37–41] Similar to the propylene content distribution, a uniform propylene crystallinity distribution is observed across the GS plot. Because of the presence of crystalline ethylene sequences, the peak at 720 cm^{-1} splits and an additional peak appears at 730 cm^{-1}.[33,42] The relative ethylene crystallinity can be determined from the ratio of the absorbance at 730 cm^{-1} to 720 cm^{-1}. In the present sample the value of 730 cm^{-1}/720 cm^{-1} ratios across the GS curve was found to be zero, which indicates that either the sample does not contain any long crystallizable ethylene sequences or that the relative amount of long ethylene sequences in the sample is too low to be detected by SEC-FTIR of the bulk material.

The coupling of SEC with FTIR provides information on the propylene distribution and its crystallinity distribution across the molar mass distribution for this copolymer sample. On the other hand, it is difficult to determine the ethylene distribution and its crystallinity distribution for the bulk sample by using this technique. Since the amount of ethylene within this copolymer is small (10.5 mol %), it is difficult to differentiate it from the major component of the material which is isotactic polypropylene.

The DSC result for the bulk sample is displayed in Figure 4a showing a single distinct peak maximum for melting at 159 °C. This can be related to the melting process of the iPP matrix, since this melting endotherm is also observed in a pure iPP homopolymer sample and shows a similar melting temperature.[43,44] DSC on the bulk sample does not reveal any melting or crystallization events corresponding to the IPC components such as EPR, EPC, or PE homopolymers.

HPer DSC analysis of the bulk sample revealed that at 50 °C/min cooling and heating the peak maximum temperatures for crystallization and melting are approximately 100 and 159 °C, respectively, see Figure 4b. Compared to the standard DSC scan rate of 10 °C/min the crystallization temperature has shifted by 10 °C toward the lower temperature side with increasing the cooling rate from 10 °C/min to 50 °C/min. However, the peak maximum temperature of melting does not change, probably reflecting reorganization during heating, not nullified by heating at 50 °C/min because it would ask for a much higher heating rate. As is seen from Figure 4b, the cooling curve is broadened at 50 °C/min compared to the cooling curve at 10 °C/min, Figure 4a, the reason being that—when the sample mass is kept constant like in Figure 4 because the same sample packed in aluminum was used in both cases—the lowest scan rates induce the narrowest DSC peaks, while increasing the
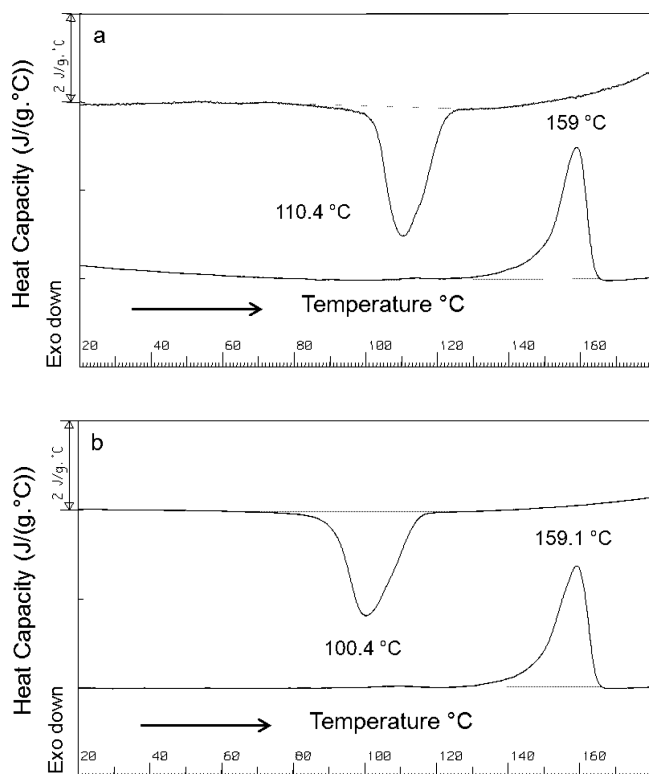
Figure 4. HPer DSC results for the bulk sample, (a) DSC 1st cooling and 2nd heating curves at 10 and 50 °C/min, respectively, and (b) 1st cooling and 2nd heating curves, both obtained at a scan rate of 50 °C/min.

scan rate will broaden these peaks,[18] as is the case here for the cooling curves.

A chemical composition separation of the sample can be achieved by HT-HPLC where elution takes place regarding the E/P content. Figure 5 indicates that the bulk sample elutes in
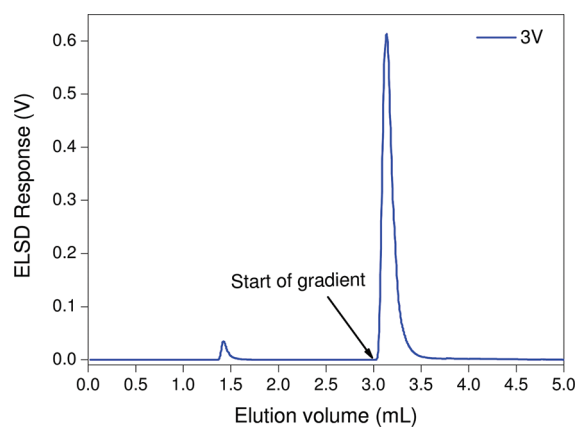

Figure 5. HT-HPLC chromatogram obtained after isocratic and gradient elution for the bulk IPC copolymer sample (3 V).

two regions, the first elutes in 1-decanol while the second elutes after the start of the gradient elution. All iPP standards, with the exception of the very low molar mass standards, elute in these two zones meaning that the PP chains are partially retained on the Hypercarb column from 1-decanol, being desorbed in the gradient from 1-decanol to TCB.[45] No peaks corresponding to EPR, EPC, or PE homopolymer were observed in the

chromatogram for the bulk sample due to the low concentration of these components.

A first information on the thermal properties as a function of molar mass can be obtained by combining HT-SEC and HPer DSC. As is shown in the Experimental Section, different molar mass fractions are collected using the LC Transform system. The SEC depositions (approximately 0.4 mg of total weight), forming a continuous film on the aluminum foil, were divided into five separate SEC fractions. These fractions are subsequently subjected to HPer DSC measurements providing well resolved melting and crystallization curves.

The capability of measuring minute amounts of material from fractionations stems from the fact that by increasing the scan rate the sensitivity of the DSC is increased. However, the thermal lag also increases and, thus, smaller samples are to be taken in order to keep the thermal lag acceptable, meaning at the same level as is accepted for standard DSC. In practice, for HPer DSC, milligrams down to micrograms of material are being used, and the present, limited amounts available from the fractionations pose no problem for the HPer DSC.

Figure 6 combines the results from the first cooling and second heating HPer DSC curves for the SEC fractions of 3 V. The HPer DSC curves for each SEC fraction range are compared to the overall SEC chromatogram in terms of retention time as well as its calibrated molar mass distribution.

Figure 7 illustrates the molar mass dependence on the melting peak temperatures. The peak melting temperatures increase within the temperature range 145−165 °C, indicating the presence of crystalline iPP. The fractions eluting from 20.5 min onward show some broadening. This could indicate compositional heterogeneity in addition to the well-known stronger dependence of the crystallization and melting temperatures on molar mass in the lower mass range. A simple SEC separation is not able to reveal such subtleties, especially not for a bulk sample with relatively low comonomer content. SEC fractionation followed by HPer DSC analysis is a promising combination to provide important information regarding the chemical composition of the bulk sample.

As has been shown in these first and preliminary experiments, traditional bulk sample analysis even using the highly sophisticated HT-HPLC method cannot provide sufficient information regarding the different components in these complex copolymers. New analytical approaches are needed to obtain more detailed information about the different components, in particular when they are present in small concentrations. It is clear that for thorough characterization of such materials, the components with vastly differing chemical composition must be separated so that these components can be analyzed separately in higher concentrations. In principle, preparative TREF can be considered as a suitable method for the separation, isolation, and complete analysis of the individual components in the copolymer system, as one expects these would show different fractionation behavior based on the components' different crystallizabilities from solution.[7,10,11]

As has been shown previously by us and others, IPC can be separated into three major fractions, namely the highly crystalline iPP, the amorphous EP rubber and a "midtemperature" fraction that is speculated to contain segmented EP copolymers. This fraction elutes in the temperature range of 60−80 °C and amounts only to about 5 wt % of the total sample. It is assumed to be the most complex fraction, at the same time being very important for the phase formation in these multiphase copolymers. In the following section, this
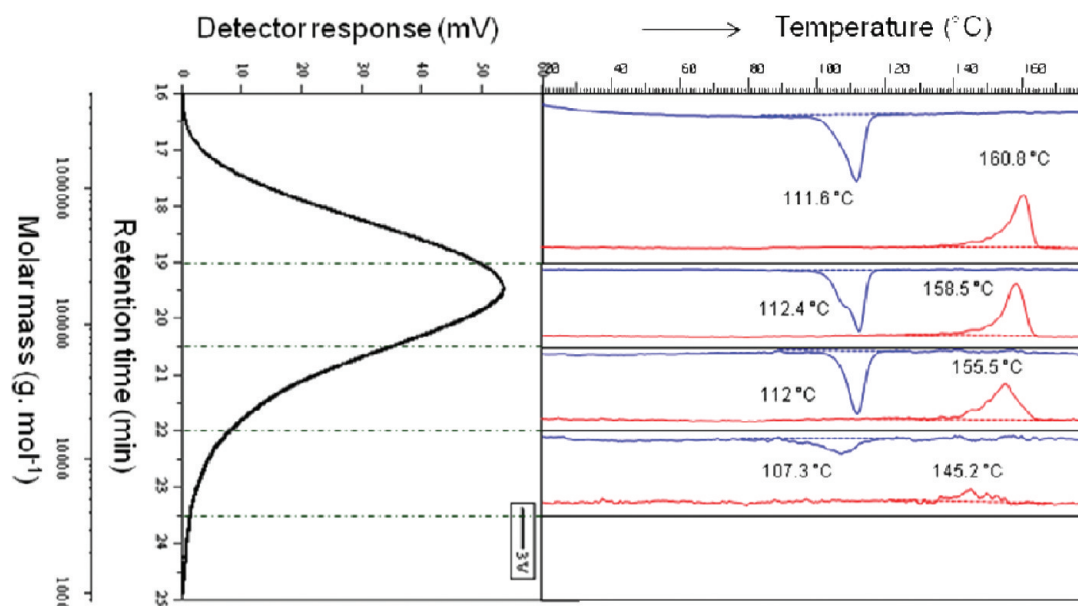
Figure 6. HPer DSC 1st cooling and 2nd heating curves for the SEC fractions of the bulk sample (3 V) at scan rates of 50 °C/min, along with the overall SEC elution profile. The left half of the figure depicts the molar mass distribution as recorded by the RI detector, while the right half of the figure depicts the individual HPer DSC results from each fraction as cut out from the aluminum foil at the specific retention time windows.
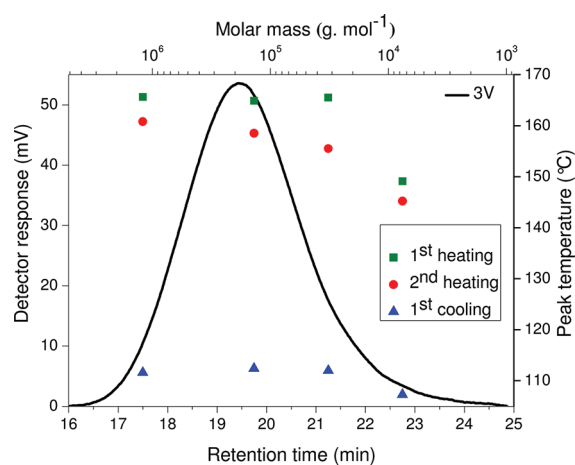

Figure 7. SEC curve of the bulk product 3 V showing the retention time axis and molar mass axis, indicating the peak maximum temperatures of the HPer DSC cooling and heating curves of the SEC fractions at 50 °C/min.

Figure 8. Mass distribution and mass fraction per temperature increment for the TREF fractions of copolymer 3 V.[11]

Figure 9. SEC curves for the bulk sample (3 V) and its 80 °C TREF fraction (3 V 80).

fraction shall be studied in detail to reveal its compositional complexity.

Analysis of the 80 °C TREF Fraction (3 V 80). The TREF fractionation of the bulk sample is presented in Figure 8. As has been discussed previously, the 30 °C TREF fraction contains mainly the EP rubber while the 100−130 °C TREF fractions contain mainly iPP.[11]

The molar mass distributions for the bulk sample 3 V and its 80 °C TREF fraction are compared in Figure 9. The 80 °C fraction shows a clear bimodality in MMD, which indicates compositional heterogeneity due to the coelution (from TREF) of nonidentical components. Multimodal distributions are often observed for these midelution temperature TREF fractions due to the coelution of semicrystalline EPCs and PP homopolymers, due to the tacticity distribution of PP.[11] The PP homopolymer does not elute entirely at temperatures >100 °C
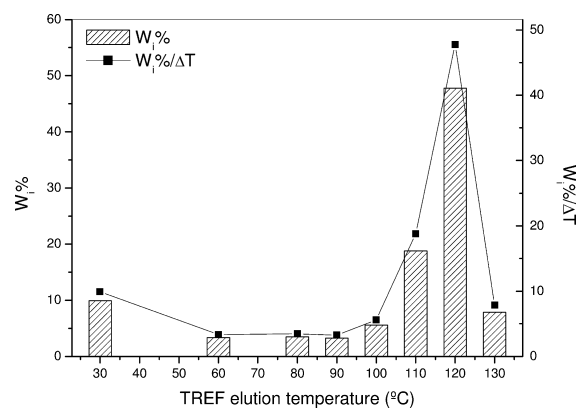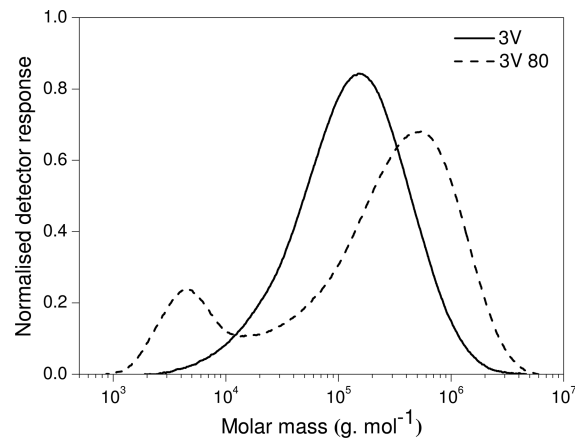
due to the fact that chains of lower tacticity become soluble at the same lower temperatures as the EPC phase of similar solubility.

TREF-SEC does not supply information on the chemical composition of these TREF fraction. It is clear that even the knowledge of MMD available from SEC analysis for the 80 °C TREF fraction is not sufficient to define the compositional heterogeneity, since SEC separates polymers according to the hydrodynamic volume of the molecules. It is important to understand the exact nature of the molecular species in this important fraction since they affect thermal, mechanical, and optical properties by the way they constitute the various phases present after cooling, like crystalline, amorphous, and possible rigid amorphous phases etc. In addition, on the molecular level, with respect to mechanical properties, the crystallites and their connections play an important role; such organization strongly depends on the way of crystallization as determined by the molecular architecture and the cooling conditions.

Two melt endotherms were observed for the 80 °C TREF fraction by standard DSC analysis, see Figure 10, which
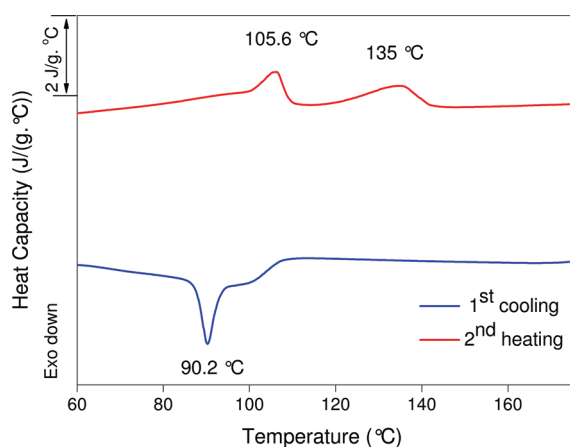

Figure 10. Two DSC melt endotherms present in the 80 °C TREF fraction (3 V 80). Heating and cooling rates were 10 °C/min.

indicates the compositional heterogeneity in the midtemperature eluting fraction. It is impossible to assign the melting endotherms from the standard DSC technique, for this specific complex TREF fraction, to a chain structure, since a single peak could result from one component overruling others, as is seen in the case of the bulk material. Possibly, one of the melting endotherms is due to the propylene rich segments of the EPC, while the other is due to the melting of the ethylene rich segments, crystallized in their respective crystal structures. However, due to variations in the tacticity of polypropylene, as well as comonomer content for the copolymers, it is possible that either monomer type could melt at both the observed temperatures. A more in-depth analysis is needed in order to assign the crystallization and melting transitions to particular chain types.

SEC-FTIR (Figure 11), has been used for the determination of the chemical composition and crystallinity distributions across the molar mass distribution for fraction 3 V 80. The fraction exhibits a gradual increase in the CH_3/CH_2 ratio (Figure 11a) across the bimodal molar mass distribution, indicating higher propylene content within the low molar mass component. The 720 cm^{-1}/1162 cm^{-1} area ratio (Figure 11b) of this fraction indicates the presence of ethylene within the higher molar mass component only. The 998 cm^{-1}/972 cm^{-1} ratio (Figure 11c) is essentially zero for low retention volumes and increases only at higher retention volumes where the low

molar mass component of the fraction elutes which is revealed to be mostly polypropylene. Ethylene crystallinity (Figure 11d) is only observed at low elution volumes. It is concluded that the lower molar mass component of the bimodal distributions consists principally of propylene homopolymer only; whereas EPC's with different monomer distributions and longer crystallizable ethylene sequences are present within the higher molar mass component.

TREF-(SEC-HPer DSC) turns out to be an excellent tool for probing the crystallization and melting effects observed for complex polymer mixtures. What is difficult to realize with standard DSC is relatively easily revealed by the HPer DSC analysis of the TREF-SEC fractions as seen in Figure 12. All of the first three (high molar mass) SEC fractions have broad melting endotherms, indicating that these fractions probably contain a complex mixture of ethylene-propylene copolymers, possibly ethylene-rich copolymers and/or segmented EP copolymers; possible branched to almost linear, semicrystalline polyethylene, and finally, possibly low tacticity polypropylene homopolymer. This is in agreement with the SEC-FTIR results (Figure 11), which show that the copolymers which are richest in ethylene elute at low retention times (higher molar mass) and that there is a gradual increase in the propylene concentration with increasing retention time (decreasing molar mass). Crystalline polypropylene is found within the low molar mass fraction while crystalline polyethylene or PE segments of segmented EP copolymers are found in the higher molar mass fraction.

SEC fractions (Figures 12 and 13) at retention times of 16 to 22 min show a melting peak in the range of 103 to 107 °C (lower than T_m of HDPE and T_m of iPP). This suggests that there are insufficiently long iPP or PE segments to form highly stable crystallites of appreciable dimensions and perfection dissolving at 80 °C during TREF and eluting in this specific molar mass region of the TREF fraction.[46] SEC-FTIR results indicate that this fraction contains ethylene−propylene copolymers to a significant extent, with mainly longer ethylene sequences. Increasing melting temperature with retention time is observed even for late eluting fractions. SEC fractions eluting between 22 and 26.5 min show melting endotherms at 135 and 130 °C, respectively. The SEC-FTIR data (Figure 11) indicate the presence of high amounts of propylene in these fractions, with little or no ethylene present. These SEC fractions contain mostly propylene-rich copolymers or polypropylene homopolymers with lower tacticity and molar mass, which probably results in the formation of crystallites with reduced lamellar thickness and lower perfection as compared to highly crystalline iPP.[47−49] The lower tacticity and by that lower crystallizability is quite obvious if one compares the maximum peak temperatures of melting in this range of e.g. a molar mass fraction of 10000 g/mol (approximately 135 °C for the present case) with the one for the bulk sample 3 V 0 h (approximately 150 °C).

Finally, it has to be pointed out that the data as obtained by SEC-FTIR in principle have to be compared with the results obtained from the first heating experiment of the DSC, because then the thermal and sample histories by deposition on the disk are the same. For the present qualitative discussion, however, using the results from the second heating curves is acceptable because these are qualitatively analogous to the first heating curves; see Figures 7 and 13.

It is evident from the TREF-(SEC-FTIR) and TREF-(SEC-HPer DSC) results that there is an overlapping of EPC with
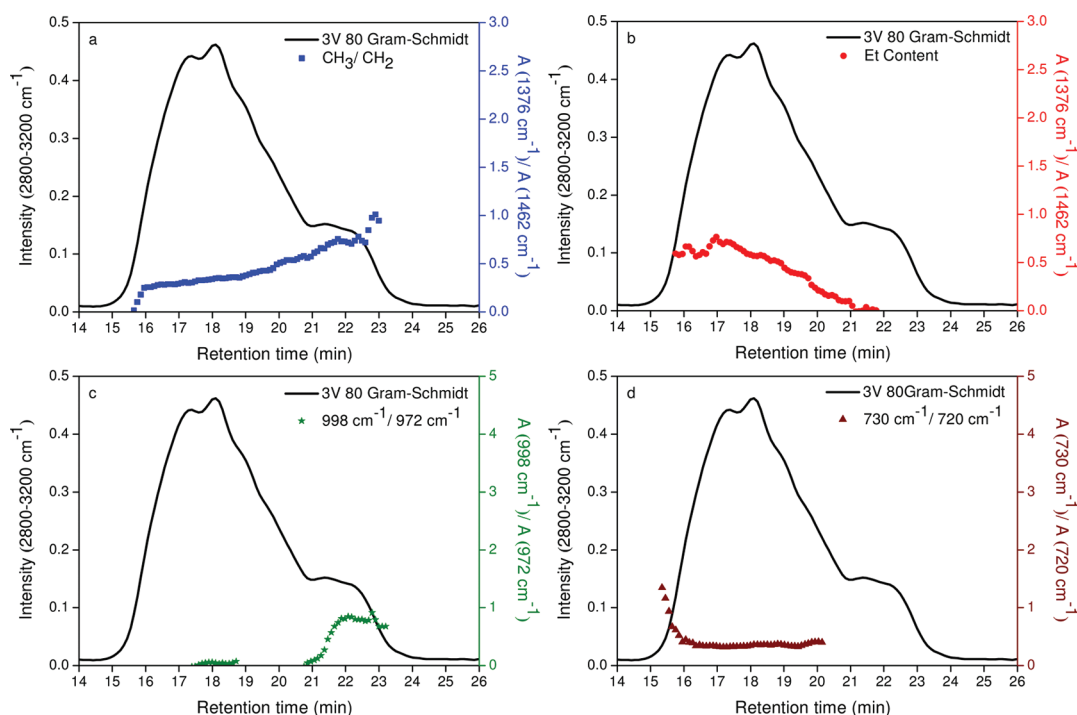
Figure 11. SEC-FTIR analysis of fraction 3 V 80, illustrating (a) the propylene (CH_3/CH_2) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c and d), respectively.
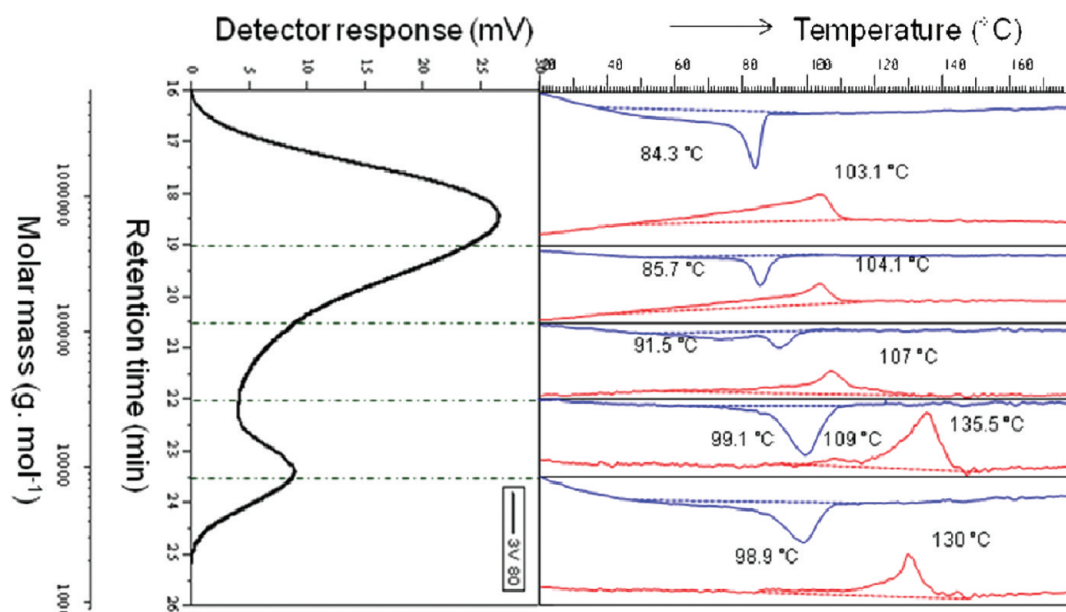

Figure 12. SEC curve of fraction 3 V 80 showing the retention time axis and molar mass axis, as well as the HPer DSC cooling and heating curves for the SEC fractions as "retention time boxes". HPer DSC scan rates were 50 °C/min.

iPP due to the tacticity distribution for this midelution temperature fraction (3 V 80). A complete separation of these components according to the chemical composition by using TREF is not possible, undoubtedly also due to cocrystallization of the components at the same temperature. Separation of blends of polyolefins containing iPP, sPP, aPP, and PE on a Hypercarb stationary phase with a gradient from 1-decanol to TCB has been previously reported.[23,50] In order to further investigate the 80 °C TREF fraction and confirm the results obtained from HPer DSC we separated the components in this fraction of an IPC sample using the same method

reported for the blend. The results of this separation are given in Figure 14.

The low molar mass isotactic PP elutes in 100% 1-decanol at approximately 1.5 mL, followed by the retained iPP components that are desorbed by the gradient. Although the chemical composition is the primary parameter and governs the separation, the molar mass of the components also plays a role, especially for low molar masses. The EPC and linear PE are also fully retained due to their selective adsorption on the column packing, being only eluted in the gradient. It can be seen that the Hypercarb column is very selective with respect to
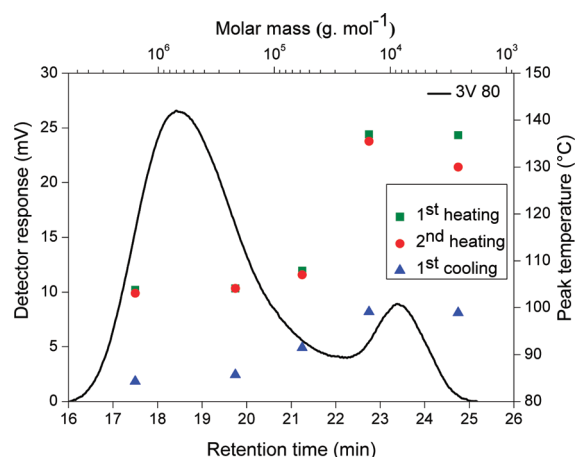
Figure 13. SEC curve of fraction 3 V 80 showing the retention time axis and molar mass axis, indicating the peak maximum temperatures of the HPer DSC cooling and heating curves for the SEC fractions at 50 °C/min.
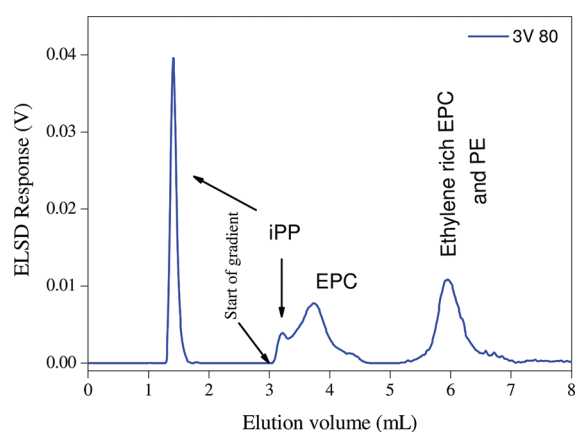

Figure 14. Chromatogram obtained after isocratic and gradient elution for fraction 3 V 80.

the chemical composition of the polymers, differentiating even with respect to their microstructure.

In order to study the influence of the molar mass of the components on the elution volume in HPLC, the fraction 3 V 80 was analyzed by HT-2D-LC. The corresponding contour plot is presented in Figure 15.

All components of fraction 3 V 80 are well separated from each other by both chemical composition and molar mass. It can be seen that the iPP has a lower molar mass component which elutes in pure 1-decanol and a second slightly higher molar mass component eluting in the gradient.[44] While EPC with different ethylene and propylene sequences as well as PE homopolymer having similar molar masses eluted according to their interaction on the Hypercarb column. There is a clear separation between the iPP and EPC copolymers. EPC dominated by longer propylene sequences elute closer to iPP while those dominated by longer ethylene sequences elute together with PE homopolymer (eluting at approximately 6.0 mL). As a result the HT-2D-LC represents a complete characterization of this TREF fraction in terms of both molar mass and chemical composition, accomplished within a relatively short analysis time.

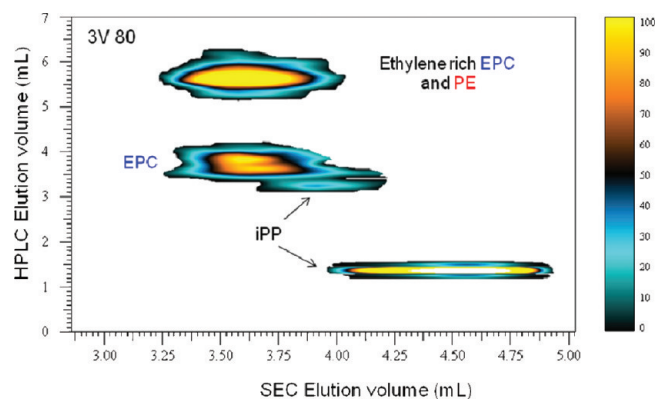The ethylene−propylene random/segmented copolymers (which constitute the bulk of the midelution TREF fractions)

Figure 15. HT-2D-LC contour plot for the fraction 3 V 80.

improve the adhesion between the EPR phase and the iPP matrix by acting as a compatibiliser between the phases. Therefore, the role of such fractions is very important for the overall properties of impact copolymers. From an analytical point of view, SEC-HPer DSC yields further insight into the thermal and mechanical properties of such complex materials, while HT-HPLC can completely separate the components in the midelution temperature fractions according to their chemical composition. Thus, these techniques are found to be very important for the industrial, as well as academic fields.

■ CONCLUSIONS

The molecular characteristics (molar mass, chemical composition, and tacticity distributions) and thermal behavior (melting and crystallization) of a commercial impact polypropylene and its midelution temperature TREF fraction were investigated using various multidimensional analytical techniques such as SEC-FTIR, SEC-HPer DSC, and high temperature two-dimensional liquid chromatography. Analysis of the bulk sample by the above-mentioned techniques does not provide any in-depth information regarding the chemical composition and thermal behavior of the various components in this complex polymer system. For this reason, fractionation of the bulk sample and a more detailed study on one of the midelution temperature TREF fractions has been carried out in order to identify the complex components in the total polymer system and evaluate their effect on the thermal properties.

SEC-FTIR results indicate the presence of EPC copolymer and iPP homopolymer as the main constituents of the 80 °C TREF fraction. The crystallinity distribution of ethylene and propylene across the MMD by this technique indicates the presence of crystallizable ethylene sequences in the high molar mass component, with highly crystalline PP being found in the low molar mass component. Thermal analysis of the SEC fractions by HPer DSC provides information on the thermal properties of the different molar mass fractions, and, thereby, the compositional heterogeneity of the components. SEC-HPer DSC results also confirm the presence of EPC copolymers with crystalline sequences of ethylene and propylene with varying sequence lengths as well as ethylene homopolymers in the high molar mass SEC fractions, while crystalline PP homopolymer is found in the low molar mass SEC fractions. The ability to measure the thermal behavior of very small sample masses (SEC fractions) with HPer DSC enables the investigation of the thermal properties across the MMD of this complex midelution temperature TREF fraction. The combination of the two cross-fractionation techniques is found to be highly useful

Macromolecules

for the mapping of the CCD across the molar mass slices for these complex TREF fractions.

The presence of PE homopolymer and EPCs containing long ethylene sequences in the 80 °C TREF fraction was proven by HT-HPLC. This is the first time that individual components in the midelution temperature TREF fraction of an IPC were separated according to their chemical composition using high temperature solvent gradient HPLC, which is based on the selective adsorption and desorption of the polymer molecules on a Hypercarb stationary phase at 160 °C. Finally, a complete separation of each component according to their chemical composition and molar mass was achieved through HT-2D-LC. The overall results demonstrate that these multidimensional techniques are found to be excellent analytical tools, necessary for a proper understanding of the molecular characteristics and thermal behavior of complex polymer fractions.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: hpasch@sun.ac.za.
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Maier, C.; Calafut, T. Polypropylene, The Definitive User's Guide and Databook. In *Polypropylene*; Plastics Design Library; Elsevier Inc.: Amsterdam, 1998; pp 11−25.
(2) Galli, P.; Haylock, J. C.; Simonazzi, T. Manufacturing and Properties of Polypropylene Copolymers. In *Polypropylene: Structure Blends and Composites*, Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; Vol. 2, p 1.
(3) Tortorella, N.; Beatty, C. L. *Polym. Eng. Sci.* **2008**, *48*, 1476−148.
(4) Fan, Z. Q.; Zhang, Y. Q.; Xu, J. T.; Wang, H. T.; Feng, L. X. *Polymer* **2001**, *42*, 5559−5566.
(5) Tan, H.; Li, L.; Chen, Z.; Song, Y.; Zheng, Q. *Polymer* **2005**, *46*, 3522−3527.
(6) Hongjun, C.; Xiaolie, L.; Dezhu, M.; Jianmin, W.; Hongsheng, T. *J. Appl. Polym. Sci.* **1999**, *71*, 93−101.
(7) Francis, M.; Mirabella Jr. *Polymer* **1993**, *34*, 1729−1735.
(8) Xue, Y.; Fan, Y.; Shuqin, B.; Xiangling, J. *Eur. Polym. J.* **2011**, *47*, 1646−1653.
(9) Zacur, R.; Goizueta, G.; Capiati, N. *Polym. Eng. Sci.* **1999**, *39*, 921−929.
(10) Rafael, A.; García, B. C.; María-Teresa, E.; Inmaculada, S.; Almudena, F.; Caveda, S. *Macromol. Res.* **2011**, *19*, 778−788.
(11) de Goede, E.; Mallon, P.; Pasch, H. *Macromol. Mater. Eng.* **2010**, *295*, 366−373.
(12) Karger, K. J.; Kallo, A.; Szafner, A.; Bodor, G. *Polymer* **1979**, *20*, 37−43.
(13) Zhisheng, F.; Junting, X.; Yanzhong, Z.; Zhiqiang, F. *J. Appl. Polym. Sci.* **2005**, *97*, 640−647.
(14) Hongjun, L. C.; Xiaolie, M. D.; Jianmin, W.; Hongsheng, T. *J. Appl. Polym. Sci.* **1999**, *71*, 103−113.
(15) Luruli, N.; Pijpers, T.; Brüll, R.; Grumel, V.; Pasch, H.; Mathot, V. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 2956−2965.
(16) Mathot, V. B. F.: The Crystallization and Melting Region. In *Calorimetry and Thermal Analysis of Polymers*: Mathot, V. B. F., Ed.; Hanser Publishers: Munich/Vienna/New York, 1994; Chapter 9, pp 231−299.
(17) Krumme, A.; Basiura, M.; Pijpers, T.; Poel, G. V.; Heinz, L. C.; Brüll, R.; Mathot, V. B. F. *Mater. Sci.* **2011**, *17* (3), 260−265.
(18) Poel, G. V.; Mathot, V. B. F. *Thermochim. Acta* **2007**, *461*, 107−121.
(19) Pasch, H.; Trathnigg, B. *HPLC of Polymers*, 1st ed.; Springer: Berlin, 1998.
(20) Heinz, L. C.; Pasch, H. *Polymer* **2005**, *46*, 12040−12045.
(21) Macko, T.; Pasch, H.; Brüll, R. *J. Chromatogr. A* **2006**, *111*, 81−87.
(22) Macko, T.; Denayer, J. F.; Pasch, H.; Baron, G. V. *J. Sep. Sci.* **2003**, *26*, 1569−1574.
(23) Macko, T.; Pasch, H. *Macromolecules* **2009**, *42*, 6063−6067.
(24) Pereira, L. *J. Liq. Chromatogr. Related Technol.* **2008**, *31*, 1687−1731.
(25) Albrecht, A.; Heinz, L. C.; Dieter, L.; Pasch, H. *Macromol. Symp.* **2007**, *257*, 46−55.
(26) Macko, T.; Brüll, R.; Alamo, G.; Thomann, Y.; Grumel, V. *Polymer* **2009**, *50*, 5443−5448.
(27) Macko, T.; Cutillo, F.; Busico, V.; Brüll, R. *Macromol. Symp.* **2010**, *298*, 182−190.
(28) Dolle, V.; Albrecht, A.; Brüll, R.; Macko, T. *Macromol. Chem. Phys.* **2011**, *212*, 959−970.
(29) Chitta, R.; Macko, T.; Brüll, R.; Doremaele, G. V.; Heinz, L. C. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1840−1846.
(30) Macko, T.; R. Brüll, R.; Alamo, R. G.; Stadler, F. J.; Losio, S. *Anal. Bioanal. Chem.* **2011**, *399*, 1547−1556.
(31) Cong, R.; deGroot, W.; Parrott, Al.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062−3072.
(32) Zhu, W. W.; Allaway, J. R. *J. Chromatogr. A* **2004**, *1055*, 191−196.
(33) Noel, L. V.; Baldo, L.; Bremmers, S. *Polymer* **2001**, *42*, 5523−5529.
(34) Liu, M. X.; Dwyer, J. L. *Appl. Spectrosc.* **1996**, *50*, 349−356.
(35) DesLauriers, P. J.; Rohlfing, D. C.; Hsieh, E. T. *Polymer* **2002**, *43*, 159−170.
(36) Tso, C. C.; DesLauriers, P. J. *Polymer* **2004**, *45*, 2657−2663.
(37) Liang, C. Y.; Pearson, F. G. *J. Mol. Spectrosc.* **1960**, *6*, 290−306.
(38) Luongo, J. P. *J. Appl. Polym. Sci.* **1960**, *3*, 302.
(39) Andreassen, E. Infrared and Raman Spectroscopy of Polypropylene. In *Polypropylene: An A-Z reference*; Karger- Kocsis, J., Ed.; Kluwer Publishers: Dordrecht, The Netherlands, 1999; p 320.
(40) Painter, P. C.; Watzek, M.; Koenig, J. L. *Polymer* **1977**, *18*, 1169.
(41) Monasse, B.; Haudin, J. M. Molecular Structure of Polypropylene Homo- and Copolymers. In *Polypropylene: Structure, Blends and Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; p 3.
(42) Cossar, M.; Teh, J.; Kivisto, A.; Mackenzie, J. *Appl. Spectrosc.* **2005**, *59*, 300−304.
(43) Schick, C. *Anal. Bioanal. Chem.* **2009**, *395*, 1589−1611.
(44) Burfield, D. R. *Macromolecules* **1983**, *16*, 702−704.
(45) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *Eur. Polym. J.* **2011**, *47*, 319−329.
(46) Zhang, C.; Shangguan, Y.; Chen, R.; Zheng, Q. *J. Appl. Polym. Sci.* **2011**, *119*, 1560−1566.
(47) Mahdavi, H.; Nook, M. E. *Polym. Int.* **2010**, *59*, 1701−1708.
(48) Zhang, C.; Shangguan, Y.; Chen, R.; Wu, Y.; Chen, F.; Zheng, Q.; Hu, G. *Polymer* **2010**, *51*, 4969−4977.
(49) Tan, H.; Li, L.; Chen, Z.; Songa, Y.; Zheng, Q. *Polymer* **2005**, *46*, 3522−3527.
(50) Macko, T.; Brüll, R.; Zhu, Y.; Wang, Y. *J. Sep. Sci.* **2010**, *33*, 3446−3454.

Compositional Analysis of an Impact Polypropylene Copolymer by Fast Scanning DSC and FTIR of TREF-SEC Cross-Fractions

Sadiqali Cheruthazhekatt,[†] Thijs F. J. Pijpers,[‡,§] Gareth W. Harding,[†] Vincent B. F. Mathot,[‡,§] and Harald Pasch*,[†]

[†]Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa

[‡]SciTe, Ridder Vosstraat 6, 6162 AX Geleen, The Netherlands

[§]Polymer Chemistry and Materials, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

ABSTRACT: For the first time, the complex composition of a two-reactor-produced impact polypropylene copolymer (IPC) has been fully revealed by advanced thermal analysis, using the combination of fast scanning DSC (HPer DSC, flash DSC, and solution DSC) with SEC fractionation subsequent to TREF fractionation. The dual TREF-SEC separation provided fractions of a few micro- or nanograms that were used to correlate the molecular structure of the polymer chains and their thermal properties (melting and crystallization behavior of the different macromolecules under a variety of different conditions). The SEC fractions were collected using the LC transform interface and subjected to FTIR and fast scanning DSC analysis. The SEC curves showed mono-, bi-, and multimodal molar mass distributions. The SEC fractions collected were analyzed by HPer DSC at 50 °C/min by which the thermal properties of the fractions could be established

and salient details revealed. The findings were confirmed by structural information that was obtained using FTIR measurements. These results confirmed that even after TREF fractions were obtained they were complex regarding molar mass and chemical composition. By applying HPer DSC at scan rates of 5−200 °C/min and flash DSC at scan rates of 10−1000 °C/s, the metastability of one of the fractions was studied in detail. The high molar mass part of the material appeared to be constituted of both highly isotactic PP and low to medium propylene content ethylene copolymers (EPC). The medium molar mass part consisted of high to medium isotactic PP and of low propylene content EPC. The low molar mass part did not show ethylene crystallinity; only propylene crystallinity of medium to low isotacticity was found. DSC measurements of TREF-SEC cross-fractions at high scan rates in *p*-xylene successfully connected reversely to the slow scan rate in TREF elution, if corrected for recrystallization. All EPC's show only ethylene-type crystallization. The wealth of information obtainable from these method combinations promises to be extremely useful for a better understanding of the melting and crystallization processes of such complex materials. The ability to run DSC experiments at very high scan rates is an important prerequisite to understanding the melting and crystallization behavior under conditions that are very close to melt processing of these key commodity polymers.
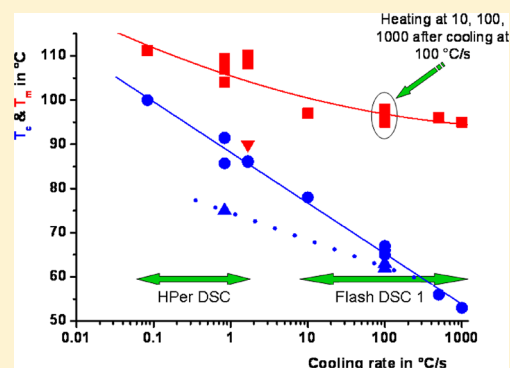
1. INTRODUCTION

Although polyolefins have existed for a long time, some of the various types of polyethylenes and polypropylenes still pose quite a challenge to reveal their detailed molecular structure in order to understand its relations with the catalyst and polymerization conditions applied on one hand and with the properties as modulated by processing on the other.[1] For some types the link between the two is pretty straightforward, meaning that mainly the chain structure defines the properties. This is the case for ethylene-based rubbers where the sequence length distribution of the crystallizable ethylene units is the main variable. However, this is an exception. Normally, appreciable variations are possible if one can change the topology of the chains and the way of crystallization considerably. Examples are the applications of UHMWPE for producing both strong fibers by way of extending most of the chains, and fixation of that topology by crystallization, as well as

its use for linears of skis, by way of forming a low-crystalline coating leading to decreasing resistivity. Crystallization also culminates in a final morphology with consequences for optical behavior, permeability, etc. The crystallization capability strongly depends on the molecular structure or chain architecture on one hand and the way of handling/processing on the other.

Therefore, it is crucial to investigate these phenomena and to explore their possible interactions by performing a detailed analysis of the molecular structure and linking it to the crystallization behavior under the (process) conditions of interest. Recently, some very interesting, new characterization tools became available, which are discussed in this report. First

of interest for determining the detailed molecular structure, high-temperature HPLC with cross-fractionation by SEC (HT-2D-LC) has become available for the analysis of IPC's.[2] Second, for exploration of the capabilities of a specific polyolefin to crystallize, the recently introduced fast scanning calorimeters (FSC[3−5]), high performance DSC (HPer DSC[6]), and flash DSC 1[7] are great tools.

To investigate to what extent these tools can be of use, ongoing research on IPC is taking place.[2,8] It is known for a long time that IPC is a complex polymer system, being a blend of various types of polyolefins: ethylene−propylene rubber (EPR), various propylene-copolymerized polyethylenes (ethylene−propylene copolymers, EPC), and polypropylene (PP) chains having a variety of tacticities. The majority of the chains are isotactic in nature, which in practice means that other, minor components can be partly overshadowed or even overruled when these IPC's are characterized in bulk, even though from a properties' point of view these minor components can be crucial. The cause of this complex molecular structure is found in the choices made in combining a heterogeneous Ziegler−Natta catalyst and the method of polymerization. The present PP studied has been polymerized in a two-reactor setup.

From the very early days of polyolefins onward, many research groups have aimed at solving the problem of determination of the complex structure of impact PP by trying to separate its constituents physically.[9,10] A number of (cross) fractionation methods have been applied with variable success. A popular method of fractionation is temperature rising elution fractionation (TREF) (see ref 11 for early references). The technique makes use of the differences in crystallizability of the various components, especially as a function of temperature. The cooling rate is set very low, typically 1 °C/h, decreasing from a high temperature (e.g., 130 °C) in a solvent (e.g., xylene) and at a concentration of ~1 wt %. By using such a slow rate, it is expected to separate the components present as completely as possible by selective crystallization and to avoid reorganization effects during dissolution by heating in the next step. Co-crystallization should also be minimized, as the (segments of) chains are expected to have ample time to crystallize by searching for equals or on their own. During the stepwise, faster heating (typically at 0.5 °C/min) of the elution step, it is assumed that chains dissolve without too much reorganization and that they are removed from the solution at increasing temperatures. The amount of removed polymer material is subsequently determined, and the fractions are possibly studied further with regards to composition and molar mass.

A few remarks can be made regarding TREF fractionation. First, at a concentration of 1 wt % the macromolecules experience a situation between a dilute solution and a melt according to Mandelkern;[12] therefore, molar mass comes into play because the chains are still entangled causing crystallization to be hindered.[11] Second, even during such slow cooling and subsequent heating, reorganization can take place.[13] It is of importance to realize that the chains dissolve only when the most stable segment of the chain dissolves, which is usually related to the longest sequence of a crystallizable unit in the case of a branched polymer or copolymer. Thus, the earlier dissolution of less stable sequences goes unnoticed. The so-called "amorphous" fraction, which relates to amorphous behavior at room temperature, could have crystallizability at subambient temperatures down to the glass transition,

significantly altering mechanical properties at subambient temperatures.

A major problem is that two apparently different components can still elute at the same TREF temperature. This possibility arises because—from the temperature point of view—such components could be different with respect to their temperature ranges of crystallization and melting in case one works without solvent, directly from the melt. Using a solvent in TREF or in crystallization analysis fractionation (CRYSTAF[14]), fractionations can nevertheless bring such ranges closer to each other or move them farther from each other, depending on constitution and interaction.

Actually, bringing the crystallization ranges closer to each other can be the case for PP blends containing ethylene-based components. Although these components could have dissimilar crystallizing and melting temperature ranges from polypropylene in the melt, in solution they can end up in similar temperature ranges because the depressions of these ranges by the solvent can be different for the respective components; e.g., they can be substantially larger for PP than for ethylene-based components. Of course, in such a case the separation of the components is difficult to realize. Still, the possibility remains to perform a second (cross) fractionation with another technique, e.g., SEC. Indeed, TREF-SEC has been applied for ethylene−1-pentene copolymers[15] and bimodal HDPE,[16] and the use of this method will also be the subject of this paper.

It should be pointed out that fractionation and evaluation of the results would be more straightforward if the cross-fractionation was done in the reverse order, e.g., SEC or direct extraction (DE)[17,18] followed by TREF,[11,19] because SEC is only slightly influenced by comonomer content or short chain branching; therefore, the first fractionation step according to molar mass would be almost unequivocal, while the second step, TREF, acts on chain composition by way of crystallization of the molar mass fractions obtained by SEC.

New, exciting possibilities lie ahead, especially by application of HT-2D-LC. HT-2D-LC separates according to chemical composition, but not via a crystallization route as in TREF and CRYSTAF.[20−23] SEC can then be applied as the second step in this cross-fractionation. The first results have been published[2] and show a crystallization-independent fractionation with good resolution toward the various components present.

In all cases, be it combinations of TREF, HT-SEC, or HT-HPLC, it is necessary to add other characterization techniques for complete unraveling of the molecular structure. Among the techniques capable to work on the (often) minute amounts of (cross) fractions, FTIR and DSC turn out to be very useful. Besides providing additional information regarding the chemical constitution, FTIR also detects molecules that are in the (semi)crystalline state. DSC measures the thermal properties and information about crystallizability is obtained. The combination of these techniques provides a powerful set of tools for in-depth characterization of crystallizable polymers, as is shown in this paper for the combinations of TREF-SEC-LC transform with FTIR and FSC. In this setup, the LC transform interface instrument is used to collect the polymer fractions from the SEC elution on a disk by removing the solvent at high temperature and at the same time cooling and depositing the sample onto the disk. The collected fractions are then directly measured by off-line FTIR and FSC.

2. EXPERIMENTAL SECTION

A nonstabilized IPC, designated as 3V, was obtained from SASOL Polymers (Secunda, South Africa). The IPC sample has a comonomer (ethylene) content of 10.5 mol %, with a weight-average molar mass (M_w) and dispersity (D) of 228 kg mol^{-1} and 3.5, respectively.

Size Exclusion Chromatography (SEC). Molar mass measurements for all samples were performed at 150 °C using a PL GPC 220 high temperature chromatograph (Polymer Laboratories, Church Stretton, U.K.) equipped with a differential refractive index (RI) detector. The column set used consisted of three 300 × 7.5 mm PLgel Olexis columns together with a 50 × 7.5 mm PLgel Olexis guard column (Polymer Laboratories, Church Stretton, U.K.). The eluent used was TCB at a flow rate of 1.0 mL/min with 0.0125% 2,6-di-*tert*-butyl-4-methylphenol (BHT) added as a stabilizer. Samples were dissolved at 160 °C in TCB at a concentration of 1 mg/mL for 1−2 h (depending on the sample type), and 200 μL of each sample was injected. Narrowly distributed polystyrene standards (Polymer Laboratories, Church Stretton, U.K.) were used for calibration.

Temperature Rising Elution Fractionation (TREF). Preparative TREF was carried out using an instrument developed and built in-house. Approximately 3.0 g of polymer (concentration of ∼1 wt %) and 2.0% w/w Irganox 1010 (Ciba Specialty Chemicals, Switzerland) were dissolved in 300 mL of xylene at 130 °C in a glass reactor. The reactor was then transferred to a temperature-controlled oil bath and filled with sand (white quartz, Sigma-Aldrich, South Africa), used as a crystallization support. The oil bath and support were both preheated to 130 °C. The oil bath was subsequently cooled to room temperature at a controlled rate of 1 °C/h in order to facilitate the controlled crystallization of the polymer. Next, the crystallized mixture was packed into a stainless steel column which was inserted into a modified gas chromatography oven for the elution step. Preheated xylene was used as eluent in order to collect the fractions in heating at predetermined temperatures ranging from 30 to 130 °C with isothermal stays of 20 min. The fractions were isolated by precipitation in acetone, followed by drying to a constant mass.

Deposition of SEC Fractions by the LC Transform Interface. An LC transform series model 303 (Lab Connections) was coupled to the PL GPC 220 in order to collect the SEC eluate. Samples were dissolved at 160 °C in TCB at a concentration of 2 mg/mL with 200 μL (in total 0.4 mg) of each sample being injected. The SEC column outlet was connected to the LC transform interface through a heated transfer line set at 150 °C. The fractions are usually deposited on a germanium disk (sample target in the LC transform) rotating at a speed of 20°/min. The disk stage and nozzle temperatures of the LC transform were set to 160 and 150 °C, respectively. For HPer DSC sample preparation an aluminum foil was wrapped around the germanium disk in such a way as to ensure good contact with the disk, with the opaque side of the foil being used for collection of the polymer deposits. The surface roughness of the opaque side of the foil enables comparatively higher adhesion as compared to the glossy side of the Al foil. The bulk sample was collected by deposition of the entire sample at a single point on the germanium disk (no rotation) in order to give it the same SEC history as the fractions thereof. All samples for SEC-FTIR and SEC-HPer DSC, including the bulk polymer 3V, were prepared under the same deposition and cooling conditions in order to ensure comparable sample and thermal histories. Therefore, the FTIR results—especially the crystallinity results—are based on these cooling conditions and by that, strictly spoken, comparable with results obtained from the first heating curve of the DSC used. Mostly, the first and second heating curves reported here are not very different, though sometimes the area and/or the position of the melting peak maximum is different (see e.g. Figure 10a).

FTIR Analyses of the Deposited Fractions. FTIR analyses of the deposited SEC fractions were performed on a Thermo Nicolet iS10 spectrometer (Thermo Scientific, Waltham, MA), equipped with the LC transform FTIR interface connected to a standard transmission base plate. Spectra were recorded at a resolution of 8 cm^{-1} with 16 scans being recorded for each spectrum. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

Fast Scanning Calorimetry by HPer DSC and Flash DSC 1. Thermal properties of the TREF-SEC-LC transform interface deposits were investigated using two types of power-compensating, twin-type FSC's: a Perkin-Elmer DSC 8500 with an intracooler at −120 °C and a MEMS-technology, chip-based calorimeter flash DSC 1 of Mettler-Toledo,[6] both situated at SciTe's laboratory, Katholieke Universiteit Leuven, Belgium.

A single deposition on the aluminum foil delivers enough material (not weighed as yet) for measurement in both cooling and heating by the DSC 8500 at a standard rate of 50 °C/min between 0 and 200 °C, but usually plotted from 0 or 20 to 180 °C. Because the sample mass was not known, in the calculations and figures a sample mass of 1 mg has been taken. Isothermal stays at the start and end temperatures were 3 min. For measurement, the aluminum foil with the sample deposited is cut between various rotation angles. The sample on the foil is then folded into a flat package for analysis at the sample spot of the DSC 8500. At the reference spot an (empty) aluminum foil is placed. Nitrogen is used as a purge gas. Most curves are corrected by subtracting an empty-cell curve. In addition, all curves have been corrected for thermal lag for the various cooling and heating rates applied. For the measurements in xylene (consisting of 98% *p*-xylene) in between room temperature and 130 °C with an isothermal stay of 15 min at 130 °C, the aluminum foil with the sample was placed in a large volume capsule (LVC) pan with 20 μL of xylene. As the SEC-LC transform interface is loaded with 200 μL containing 0.4 mg, ∼0.04−0.2 mg of sample will be in solution (supposing the sample mass is about 10−50 wt % of the total TREF fraction mass respectively), leading to a concentration of ∼0.2−1 wt %. This is to be compared with the typical TREF concentration of ∼1 wt %.

In the case of the flash DSC 1, part of the sample deposited on the aluminum foil is scraped and put on the sample hotspot of the sensor and measured at a standard rate of 100 °C/s between room temperature and 200 °C but plotted until 160 °C. For both DSCs also other scan rates have been applied: 5, 10, (50), 100, and 200 °C/min for the DSC 8500 and 10, (100), 500, and 1000 °C/s in cooling and heating for the flash DSC 1. First heating, first cooling, and second heating curves have been measured and plotted (endo up, exo down). All transitions observed turned out to be either crystallization (during cooling, curves in blue) or melting (during heating, curves in red) and possibly recrystallization (meaning the sample follows the sequence melting−recrystallization−remelting during heating).

3. RESULTS AND DISCUSSION

The elucidation of the molecular structure of the IPC 3V is accomplished by studying thermal properties using DSC, with additional information from FTIR. For detailed information on the IPC and on the fractionation techniques used, the reader is referred to a recent paper.[2] In short, the bulk IPC 3V sample was fractionated by TREF. In total, eight fractions were obtained at 30, 60, 80, 90, 100, 110, 120, and 130 °C elution temperatures, which are coded as 3V *x.y*, with *x* denoting the TREF elution temperature. The number of depositions (on the LC transform disk) prepared is denoted by *y* = 1, 2, and 3, leading to codes such as 3V 80.2. One deposition delivers enough material for the DSC 8500 to result in DSC curves with reasonable to good heat flow rates. All samples deposited are reported in this report, except for TREF fractions 30, 100, and 120 °C. Because of the fact that the 30 °C TREF fraction is such an important fraction, and also a major constituent of most IPC's, it was decided to investigate the (sub)ambient crystallization in more detail in a subsequent study. A thorough evaluation of the complex composition of the 30 °C TREF fraction is very important, especially with regard to its influence on the low-temperature mechanical properties of the IPC. The two higher temperature fractions (100 and 120 °C) are known

to be mainly isotactic PP, and so there is not much new information that could be expected from these fractions.

Figure 1 shows the resulting mass distribution constituted by the TREF fractions obtained per temperature increment. As can
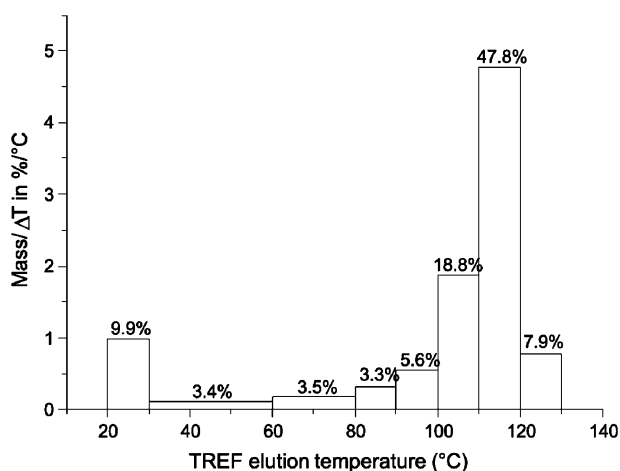

Figure 1. Mass distribution in percent per temperature increment as a function of the elution temperature for the TREF fractions obtained.

be seen, an appreciable amount of material elutes already at 30 °C. This amorphous fraction also contains components which are crystallizable at (sub)ambient temperatures. For these components, the often-used wording "amorphous fraction" just describes the situation at 30 °C. It also reflects the fact that it is difficult to perform TREF at (sub)ambient temperatures because solvents such as *p*-xylene will crystallize, and one may face technical problems of operating and handling at lowered temperatures.

In ref 8 the corresponding DSC second heating curves of the TREF fractions of 30−120 °C were reported, as measured from 25 to 200 at 10 °C/min. The authors concluded that no melting endotherm is present in the 30 °C fraction as was expected for a random ethylene−propylene copolymer (EP rubber). All fractions eluting from 60 to 100 °C exhibit two melting endotherms, namely at 89 and 112 °C (fraction 60 °C),

103 and 130 °C (fraction 80 °C), 118 and 146 °C (fraction 90 °C), 118 and 150 °C (fraction 100 °C). Clearly, in melting subsequent to crystallization from the melt, these polymer fractions show such distinct melting temperatures, and the presence of (at least) two crystallizable components melting at different temperatures must be assumed that are caused by appreciable differences in molecular structures.

The 110 and 120 °C fractions show single, distinct melting peaks at 159 and 161 °C, respectively, which are ascribed to highly isotactic PP. With increasing TREF elution temperatures, the peak areas increase indicating increasing crystallinities. Data on the 130 °C fraction were not available: they are expected to be similar to the 100 and 110 °C fractions.

Elution at one and the same TREF temperature, and bimodality of the melting point distribution, as seen for some of the DSC curves, can have various causes. First, crystallization in a solvent under TREF conditions is different from crystallization from the melt for various reasons. The molar mass influence on crystallization is appreciable for the pure polymer, while in solution the influence is dependent on the quality of the solvent and the concentration. Second, for the present case, molecules that dissolve at one and the same TREF elution temperature can also do so because the melting point depression caused by the solvent ($T_m^{melt} - T_m^{solution}$) is larger for a polymer with propylene crystallinity than in the case of ethylene crystallinity. In this way, differences in e.g. maximum or end melting points in the case of melt crystallization between molecules having ethylene-based (PE: various amounts of propylene incorporated in the chains) and propylene-based (PP: various isotacticities) crystallization can be (partly) canceled by having crystallization done in a solvent; see further on at the analysis of the 80 °C (Figure 6b) and 90 °C (Figure 8b) TREF fractions.

In order to determine possible differences in melting behavior across the MMD, each of the TREF fractions was fractionated according to molar mass by HT-SEC; see Figure 2, showing all SEC curves obtained on the (bulk) 3V, and on 3V *x.y* samples.

The SEC curves are plotted in their respective temperature ranges of elution. For example: fraction 3V 100 is plotted in
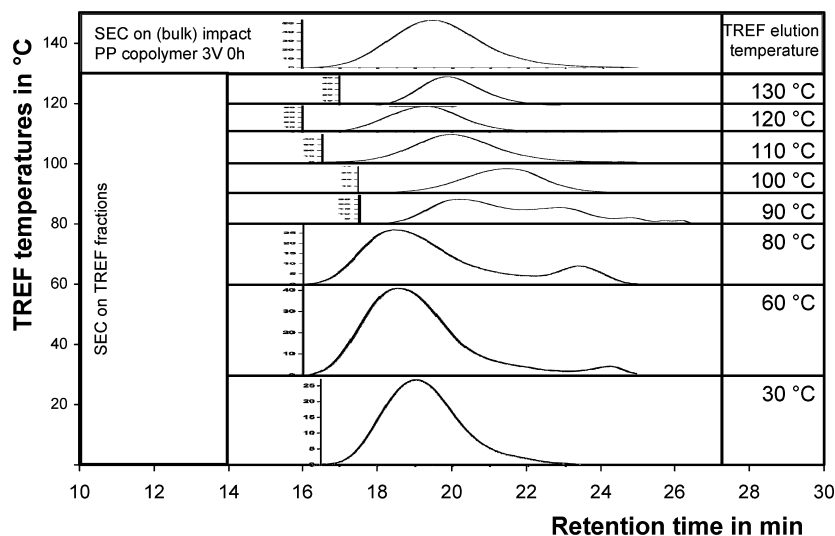

Figure 2. High-temperature SEC curves obtained on the (bulk) 3V (top) and on 3V TREF fractions thereof as obtained at various TREF elution temperatures: 30, 60, 80, 90, 100, 110, 120, and 130 °C. See text for explanation.
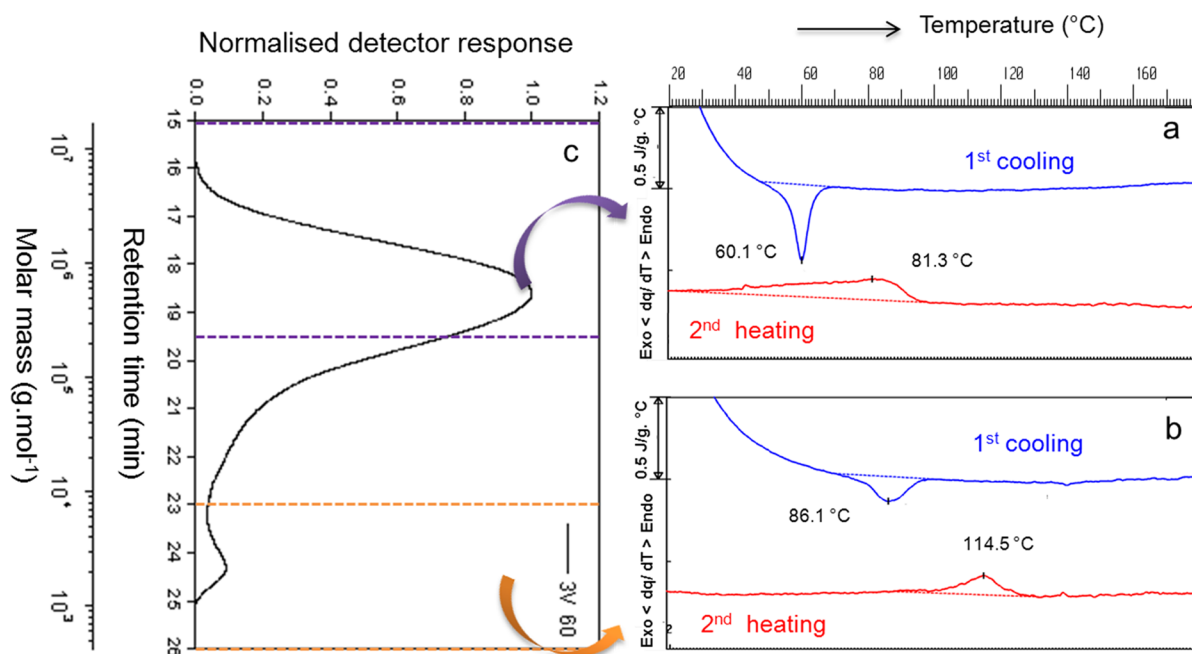
Figure 3. SEC-DSC analysis of sample TREF 3V 60. DSC curves of first cooling and second heating of two SEC fractions of TREF fraction 3V 60.

between the temperatures 90 and 100 °C, since it has been obtained by elution in that temperature range; the preceding fraction 3V 90 covered the temperature range from 80 until 90 °C, and the next fraction 3V 110 is plotted in the range from 100 to 110 °C, and so forth.

From this plot it is clear that some fractions are bimodal, meaning that part of the low molar mass polymer chains are dissolved at the same temperature as a part of the high molar mass polymer chains. One may wonder whether the bimodality of the SEC curves, seen for the 60, 80, and 90 °C TREF fractions, is connected with the bimodality of the 60, 80, 90, and 100 °C TREF fractions seen in the DSC curves[8] (see earlier remark). The next part of this topic is addressed on the basis of TREF-SEC cross-fractions, using DSC and FTIR analyses after deposition on a disk by the LC transform interface. Details of the experimental method using the LC transform interface can be found in the Experimental Section and in ref 2.

Analysis of the Bulk Sample. In the preceding paper,[2] results on the bulk sample 3V have been discussed in detail. The crystallization and melting behavior by HPer DSC at 10 and 50 °C/min was seen to be dominated by the high-isotacticity PP molecules present, overshadowing the other components in the PP system. The FTIR information regarding the PP and PE content and the PP and PE crystallinities confirm this conclusion: the propylene content across the MMD is constant, and the ethylene content of 10.5 mol % is essentially zero, as the level is too low to be detected (in the bulk sample), across the MMD. Similarly, the propylene crystallinity showed to be constant. However, no ethylene crystallinity is noticed; most probably its contribution is too low to be detected, as it is overshadowed by the PP. The crystallization behavior is sensitive to the cooling rate: changing from 10 to 50 °C/min lowers the crystallization peak maximum temperature by 10 °C. However, in both cases the subsequent heating at 50 °C/min leads to a melting peak maximum temperature of 159 °C. Therefore, it is quite obvious that

reorganization takes place during heating and is not hindered by the heating rate of 50 °C/min.

Analysis of TREF Fraction 3V 60 (3.4 wt % of Total). This is the first TREF fraction with a bimodal MMD (see Figure 3c) and with two melting peaks in the DSC curve (see ref 8) similar to all DSC curves of TREF fractions up to 100 °C. Two SEC fractions with an extreme difference in molar mass were chosen see Figure 3c): one centered around a molar mass of 1 000 000 g/mol (top box) and the other around 2000 g/mol (bottom box).

These fractions represent the two peaks in the SEC curve; the corresponding DSC curves reflect the crystallization and melting behavior. The first heating curves resemble those of the second heating and are not plotted here. The DSC curve of the high molar mass part of the MMD suggests to represent an EP copolymer crystallizing around 60 °C and showing a characteristic,[19] broad melting curve with a peak maximum temperature of ~80 °C and an end melting temperature of 95 °C. The curves resemble EP copolymers such as those in ref 24; see e.g. the EP copolymer EJ 207 as a very typical example. This copolymer is slightly random[25−27] and has 10.6 mol % of propylene and M_n, M_w, M_z of 39 000, 120 000, 220 000 g/mol, respectively. The chain statistics of this EP copolymer is between alternating and random, with a product of copolymer reactivity ratios, $r_E \cdot r_P$ (E: ethylene; P: propylene) of about 0.50. As the statistics of the present TREF fraction is unknown, it is too speculative to make any further conclusions, the more so because the literature example has been polymerized in a very much designed and ideal way, using a single site, vanadium-type catalyst, leading to a homogeneous type of copolymer.[26] For such a copolymer, the melting curve is expected to resemble the broad ethylene sequence length distribution (ESLD), resulting from the copolymerization statistics.[25] The amount of propylene of the whole fraction 3V 60 is much higher—45 mol %[7]—by which most of the propylene units must be located in molecules of the rest of the distribution, and thus is to be found as a propylene-rich part of the MMD in the medium and lower molar mass regions.
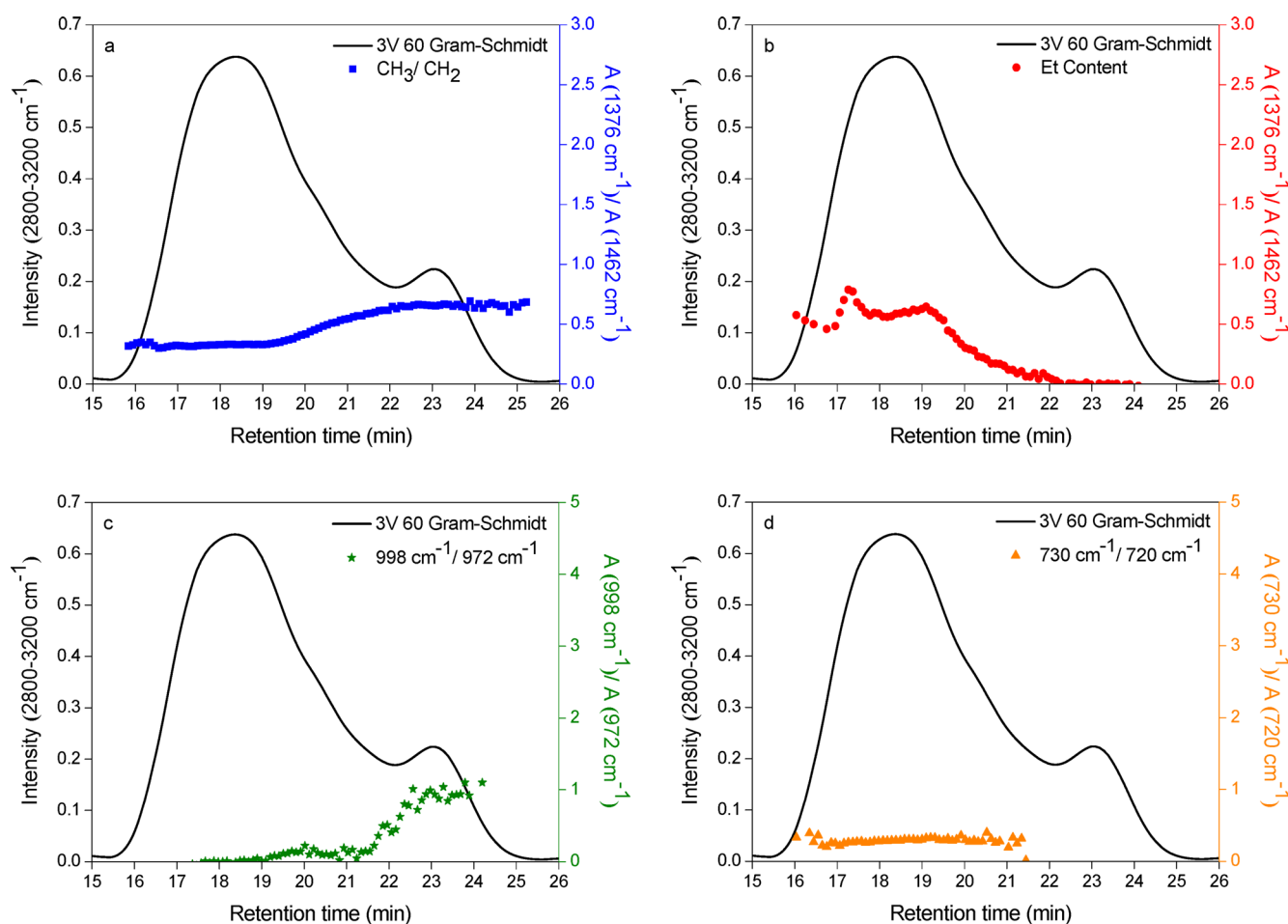
Figure 4. SEC-FTIR analysis of the 60 °C TREF fraction (3V 60) illustrating (a) the propylene (CH_3/CH_2) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c) and (d), respectively.

The DSC curve of the low molar mass part of the MMD suggests to be originating from low-isotacticity PP because the difference, ΔT, between the melting peak maximum temperature of approximately $T_m = 115$ °C and the crystallization peak maximum temperature of approximately $T_c = 86$ °C seems to be somewhat too large ($\Delta T = T_m - T_c = 30$ °C) to be caused by a polyethylene type of crystallization. The occurrence of polypropylene in the lower molar mass region would also account for the rest of the propylene content as mentioned before. The reasoning given is completely confirmed by the FTIR information on the fraction studied (see Figure 4). The composition (propylene and ethylene content) and their crystallinity distributions across MMD are determined as explained in our previous publications.[2,8]

In Figure 4, it is seen that propylene (Figure 4a) is present at all molar masses, and its content increases toward low molar masses. The high molar mass region shows almost exclusively ethylene crystallinity (Figure 4d), while the propylene present is slightly or not crystalline (Figure 4c). In the low molar mass region ethylene is absent (top right) which is why no ethylene crystallinity is noticed (Figure 4d), but only propylene crystallinity (Figure 4c). Both DSC and FTIR results point to a simple explanation of the double melting behavior of the whole TREF fraction 3V 60, as seen in ref 8 and discussed earlier with crystallization/melting peak maximum temperatures of 63 °C/89 °C and 112 °C (at 10 °C/min), namely to connect these to the melting of crystalline structures constituted by ethylene units and propylene units, respectively.

Analysis of TREF Fraction 3V 80 (3.5 wt % of Total). In our preceding paper[2] results on TREF fraction 80 °C and SEC fractions thereof have been discussed. Now, extended measurements show additional, interesting information on this sample.

In Figure 5, the MMD of sample TREF 3V 80 is shown as well as crystallization and melting peak maximum temperatures (from second heating) for SEC fractions obtained by DSC. In this figure, three different melting behaviors are seen, and Figure 6 shows characteristic DSC curves, representative for the three groups of samples, distinguishable by their melting behavior:

Group 1. Fractions of the middle molar mass part of the MMD, having low melting peak maximum temperatures between 103 and 111 at 50 °C/min cooling/heating rate. In ref 8, 103 °C has been found for the corresponding melting peak at 10 °C/min cooling/heating rate, which makes sense. As an example, in Figure 6a DSC curves are shown of the characteristic sample at 150°−180° (angle on the Ge disk corresponding to a retention time of 20.5−22 min), covering the molar masses as indicated by the red box in Figure 5 (roughly 10−80 kg/mol).

Varying the scan rates from 5, 50, to 100 °C/min, the DSC curves of this sample do not vary much, and values of approximately $T_c \sim 91$ °C and $T_m \sim 110$ °C are found.
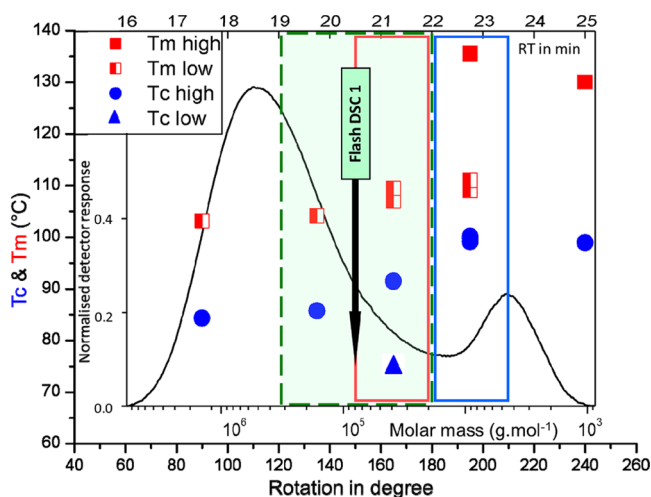
Figure 5. SEC separation of sample TREF 3V 80. SEC curve with boxes indicating the molar mass ranges covered by the HPer and Flash DSC measurements shown in Figures 6 and 7 (see text). Red box: middle molar mass part; blue box: low molar mass part; black arrow: molar mass of sample measured by flash DSC 1; green box: molar mass range measured by HPer DSC and combined with flash DSC 1 results (see Figure 7).

Group 2. Fractions of the low-M part of the MMD have high melting peak maximum temperatures, between 130 and 136 °C, at 50 °C/min cooling/heating rate. For comparison, in ref 8 130 °C has been found for the corresponding melting peak at 10 °C/min cooling/heating rate, which again makes sense. As an example, in Figure 6c, DSC curves are shown of the characteristic sample from 210° to 270° (retention time 23.5−26.5 min), covering the molar masses less than 4000 g/mol.

Group 3. As indicated by the blue box in Figure 5, the SEC fraction at 180°−210° (retention time 22−23.5 min) combines the characteristics of groups 1 and 2 by showing both low and

high melting temperatures in one and the same curve. Varying the scan rates from 5, 50, 100 to 200 °C/min for this sample results in DSC figures with approximately $T_c \sim 100$ °C and $T_m \sim 136$ °C. In addition, 5 out of 9 measurements done show an additional low-melting peak at ∼111 °C in the second heating curve (see the peak at 109 °C in Figure 6b). This suggests that an additional component—and probably a low propylene content EPC—is present of which the melting (peak maximum at 109 °C) is separated from the main medium-isotacticity PP peak (with a maximum at 135.5 °C), while their crystallization peaks coincide at 99.1 °C. It is possible that the nucleation of one of these is triggered by the other.

At least two explanations of this split into three different groups are possible:

First, for PE it has been reported[11] that the melting peak maximum temperature increases when the molar mass is increased from paraffins to high molar mass linear polyethylenes (LPE) in excess of 1 000 000 g/mol. At the same time, the crystallization peak maximum temperature, T_c, after an initial increase with increasing M to ∼20 000 g/mol, shows a slight decrease up to 60 000 g/mol, after which T_c stays constant until the highest M. The explanation is that initially the chain topology in the crystallites changes from extended into folded and that subsequently entanglements set in which hinder crystallization. At >60 000 g/mol M does not affect the crystallization behavior anymore because segments of the long or very long chains crystallize themselves and increasingly independently from the others. Thus, if a chain does not re-enter the same crystallite, either it will stay in the amorphous part or it will crystallize in another crystallite, thereby bridging two crystallites and becoming a tie molecule. The melting behavior does not mimic this behavior because of the occurrence of extensive reorganization by sliding diffusion of chains during cooling after crystallization and subsequent heating toward melting. This specific crystallization behavior is
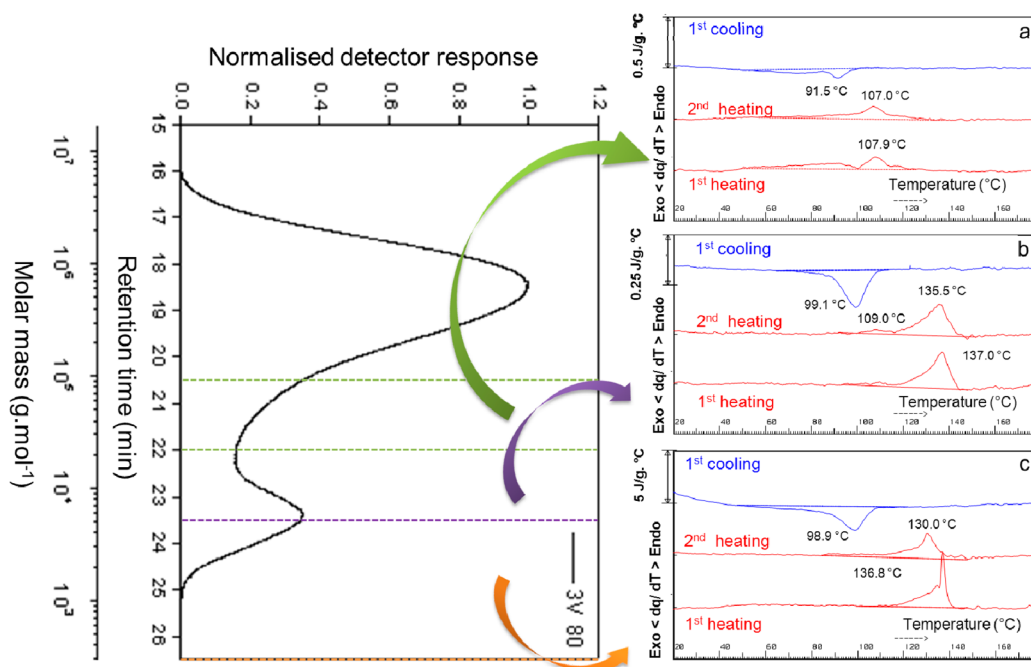

Figure 6. DSC analysis of different molar mass fractions of sample TREF 3V 80: (a) a middle-M part, see red box in Figure 5; (b) a low-M part, see blue box in Figure 5; (c) the lowest-part M of less than 4000 g/mol.

strongly dependent on the cooling rate: at lower scan rates the decrease in T_c with increasing M is less; at higher rates T_c decreases appreciably with increasing M. For branched polyethylenes, be it either copolymers or branched material like LDPE, the effects have been seen to be stronger, and even the melting behavior becomes affected. For instance LDPE, at constant branching, shows a 12 °C lowering of T_c and 7 °C for T_m, occurring at the same apparent molar mass as for LPE. Obviously, reorganization is not possible anymore because the short side chain branching hinders sliding diffusion and by that the process of reorganization is slowed down drastically. One may speculate that PP is affected in the same way, noticing that the abrupt change in T_m by 25−30 °C in Figure 5 also occurs at ~20 000 g/mol. However, T_c also shows a decrease with increasing M but—in sharp contrast with the PE case—to a lesser extent of about 15 °C and not in an abrupt way.

Second, as before for 3V 60, the differences in T_m and T_c could reflect different molecular structures. The highest molar mass SEC fractions have reasonably narrow crystallization peaks with a long low-temperature tail and broad melting endotherms (see Figure 11 in ref 2), characteristic of polymers with crystallizable ethylene sequence lengths found e.g. in ethylene−propylene copolymers. The low molar mass fractions show much higher melting temperatures, and from the difference between the peak maximum temperatures for melting (T_m) and crystallization (T_c), $\Delta T = T_m - T_c$, it is supposed that these temperatures point to medium-isotacticity PP.

Evaluating the results obtained with FTIR leads to the conclusion that these confirm the second possibility. This does not necessarily rule out the first one: possibly the melting and crystallization temperature distributions are also lowered partly because of increasing molar mass. It is clear that the bimodal melting behavior reported earlier[8] is explained by the occurrence of the 2 groups of molecules differing in melting behavior, while "intermediate" molecules indicated as group 3 can also show up in the same molar mass range of limited width. It has to be realized that though the melting behavior after crystallization from the melt is very different, all three groups match by eluting in the same TREF temperature range. Interestingly group 3 consists of molecules having the same M, meaning that the matching toward the same elution temperature is mainly governed by the ethylene sequences in the ESLD of the low propylene content EPC and governed by the isotactic sequences for the medium-isotacticity PP.

To probe the (meta)stability[28,29] of the crystallites and the occurrence of possible reorganization phenomena, a more extensive evaluation has been performed by applying a variety of combinations of scan rates of 5, 50, 100, and 200 °C/min using HPer DSC. Increasing the cooling rate from the standard rate of 50 to 100 °C/min results in the lowering of the crystallization peak maximum temperature by a maximum of 5 °C. In the case of decreasing the cooling rate to 5 °C/min, crystallization occurs 10 °C higher than at a cooling rate of 50 °C/min. The spread in melting peak maximum temperatures for these cooling conditions is 4 °C at most, which is a rather low value.

Therefore, in addition, the range of scan rates applied was extended appreciably by using the flash DSC 1. For flash DSC, a sample representative of the high molar mass samples was taken at a retention time of 20.5 min by scraping it off the disk. This retention time corresponds to a rotation angle of 150° and an approximate molar mass of 80 000 g/mol, as is seen in

Figure 5, black arrow. For linking the data of flash DSC 1 and HPer DSC, samples around this retention time were involved by including measurements by HPer DSC on retention times of 19−20.5 and 20.5−22 min, represented in Figure 5 by the green box.

Figure 7a shows the flash DSC 1 first cooling and second heating curves for the sample at 20.5 min. In Figure 7b, the
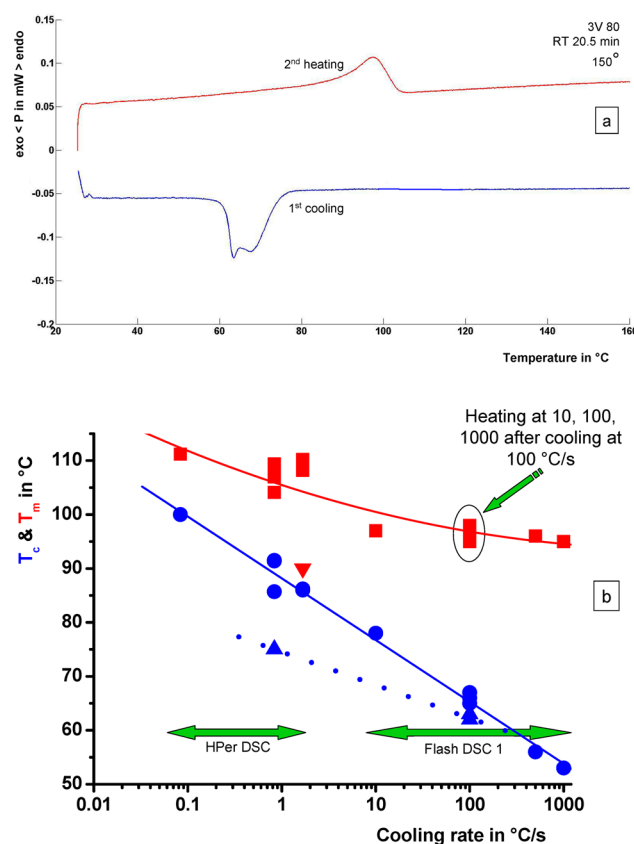

Figure 7. DSC measurements of sample TREF 3V 80. (a) An example of a flash DSC 1 measurement at 100 °C/s in both cooling and heating. (b) HPer DSC and flash DSC 1 results combined for the fractions in the molar mass range indicated in Figure 5 by the green box and by the black arrow, respectively. Peak maxima of T_c and T_m main and small peaks are represented by ●, ▲ and ■, ▼, respectively. The lines are guides to the eye.

results obtained by HPer DSC and by the flash DSC 1 are combined. The cooling data show a continuous decrease of T_c with increasing cooling rate. The T_m from the subsequent second heating measurements also shows a decrease. Both show continuity of the HPer DSC and flash DSC 1 data without any adjustment which is not trivial.[3,5] The small peak seen in Figure 6a, indicated by the blue triangle in Figure 5, has not been evaluated.

With respect to the behavior of T_c as a function of cooling rate, analogous data are not found in literature up until now, and even so, sample results will differ with respect to branching content and distribution, molar mass, etc. A (very) limited comparison can be made with results on UHMWPE[5] for the onset temperature of crystallization as a function of cooling rate, varying from 10^{-3} to 10^4 °C/s. For this tremendous variation over 7 decades, three different calorimeters (a Mettler-Toledo DSC 822, a PerkinElmer Pyris1 DSC, and a fast scanning calorimeter based on thin film chip sensors) have
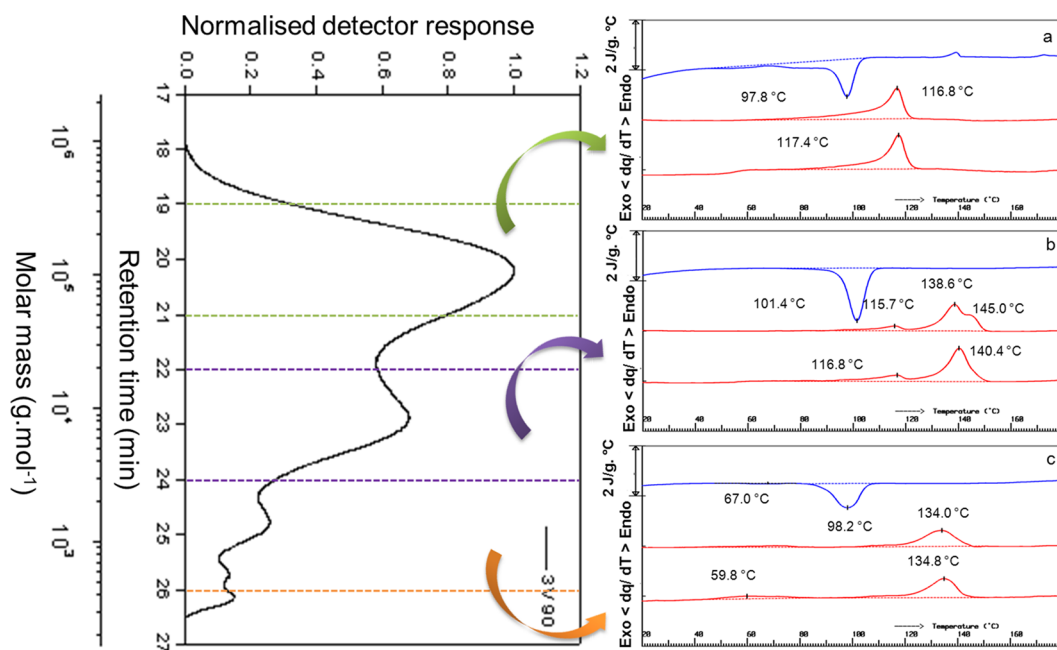
Figure 8. SEC-DSC analysis of sample TREF 3V 90. DSC curves for three representative samples of 3V 90.3, reflecting the coverage of the peaks in the SEC curve, see colored boxes; the high-*M* peak (sample 3V 90.3, 120°−160°); middle-*M* peak (3V 90.3, 180°−220°); and the two low-*M* peaks for sample 3V 90.3, 220°−260°).

Figure 9. SEC-FTIR analysis of the 90 °C TREF fraction (3V 90) illustrating (a) the propylene (CH_3/CH_2) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c) and (d), respectively.

Figure 10. SEC-DSC analysis of sample TREF 3V 110. Measurements by HPer DSC on two SEC fractions, taken from the middle and very low-*M* part of the MMD as indicated in the graph on the left.
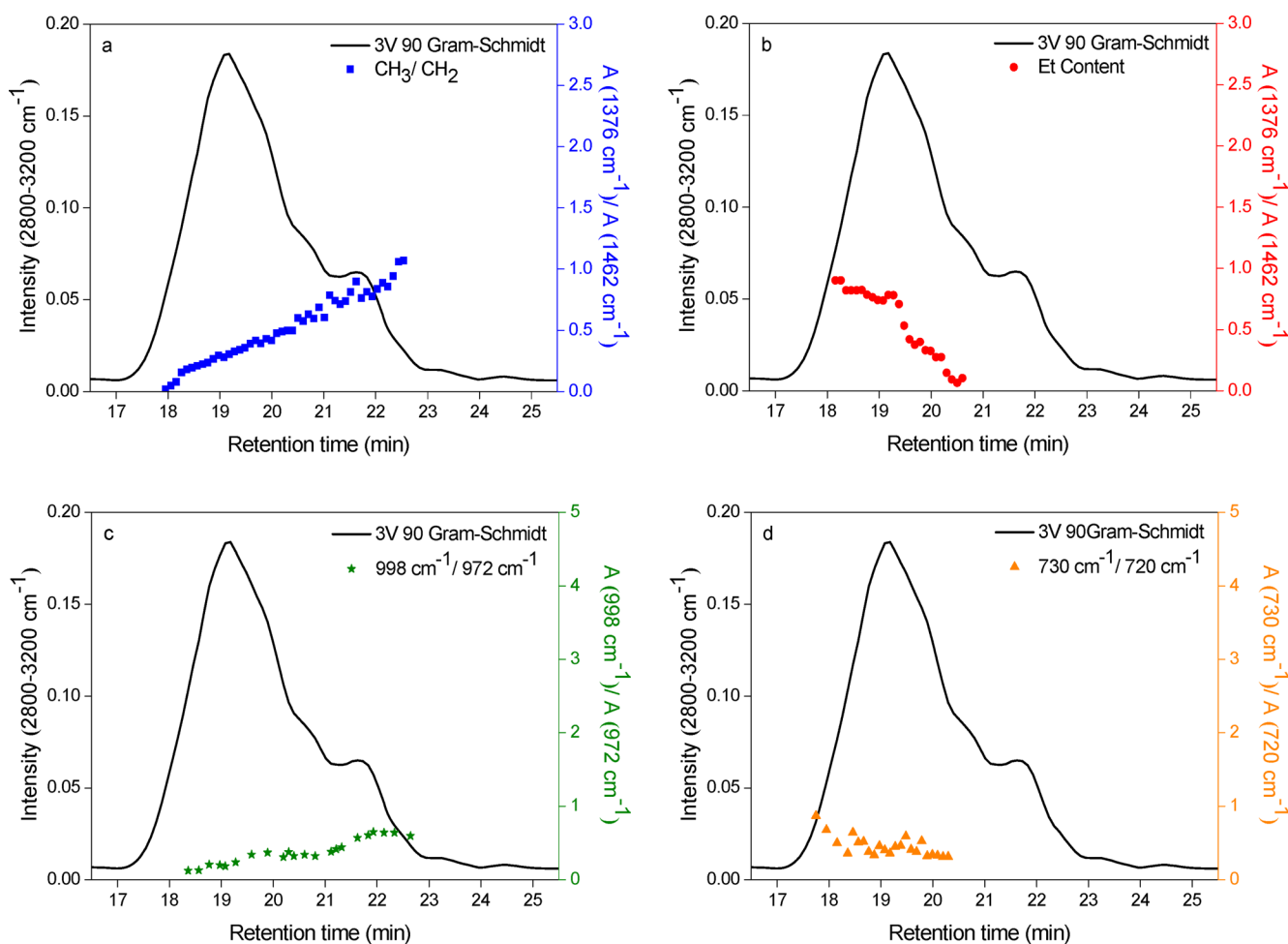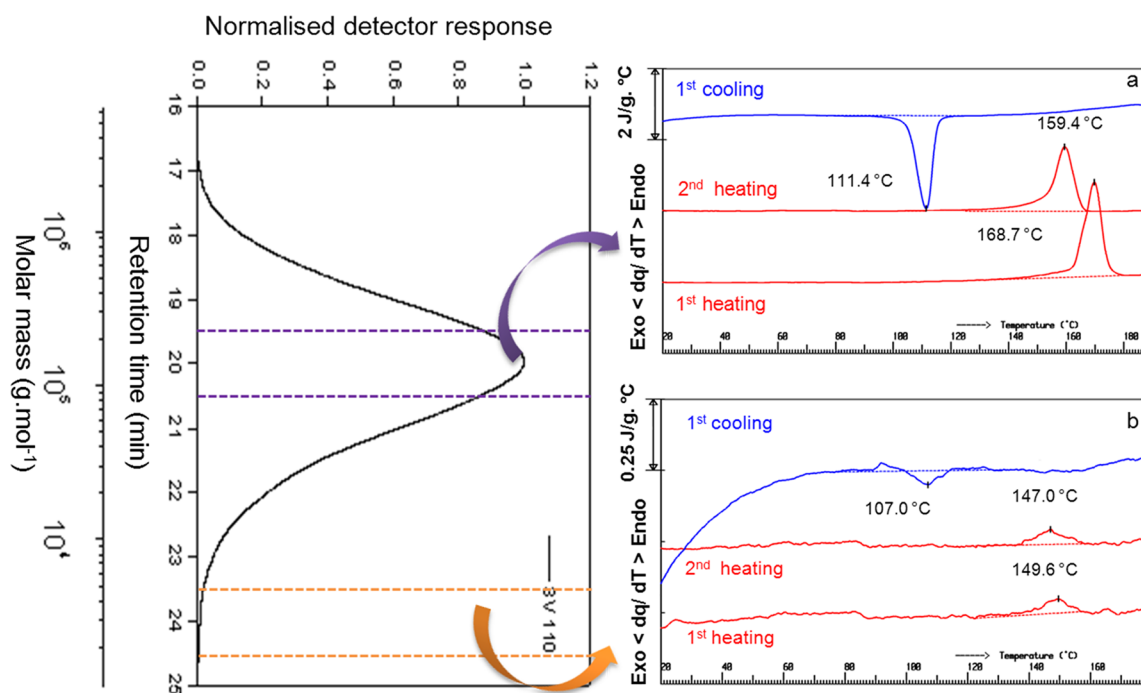
been used. Of interest is that these data show the same lowering of the crystallization peak maximum temperatures (T_c) with cooling rate (β)—the slope of $T_c(\beta)$—as found here, though at a 30 °C higher level.

The behavior of T_m is interesting because it is seen to start to level off with increasing, preceding cooling rate. This occurs irrespective of the heating rate applied; see the T_m data −98, 97, and 96 °C for heating at 10, 100, and 1000 °C/s, respectively, subsequent to cooling at 100 °C/s. In addition to the leveling off, a small variation of T_m is typical for polymers which are able to reorganize very fast during heating, which is why one needs extremely high scan rates to hinder reorganization,[3,5,30] much higher than even the flash DSC 1 is capable of.

Analysis of TREF Fraction 3V 90 (3.3 wt % of Total). Besides the TREF fractions showing a bimodal-shaped SEC curve, one TREF fraction shows a multimodal SEC curve (see Figure 2). As can be seen in Figure 8, the MMD of 3V 90 comprises at least four well-distinguishable peaks. To find out what kind of polyolefins constitute these peaks, the DSC curves of three depositions have been measured, covering most of the MMD; see the three boxes indicating the parts of the MMD covered.

Following the same reasoning as for the other samples discussed, Figure 8a represents (see discussion at 3V 80) group 1 melting behavior: it shows the presence of a copolymerized polyethylene, more specifically low propylene content EPC, in the high-*M* part of the MMD for sample 3V 90, 120°−160°. The crystallization curve indicates the presence of more than one species crystallizing, though these do not show up separately in the melting curve.

The curves in Figure 8b (sample 3V 90, 180°−220°) representing the middle part of the MMD show group 3 behavior. The presence is seen of both PP having a lowered isotacticity or a "medium isotacticity" PP (a melting peak maximum of 138.6 °C) and in addition most probably a propylene-copolymerized PE, a low-propylene content EPC (a

melting peak maximum at 115.7 °C). Again, it is seen that the crystallization temperatures of both the polymers present coincide, giving rise to a single crystallization peak with a maximum at 100.4 °C. The main melting peak at the highest temperatures shows two peaks at 138.6 and 145 °C, most probably caused by recrystallization. It illustrates that through a thermal history melting temperatures of 140 °C and higher can be realized; see also the first heating curve.

The third SEC fraction (sample 3V 90, 220°−260°) related to the low molar mass part of the MMD (see Figure 8c) represents group 2 melting behavior. Surprisingly, it again shows PP crystallinity, but at lower temperatures than the middle part of the MMD. This could be explained by the decreasing effect lower molar masses have on the crystallization and melting. Seeing the change in molecular structure with decreasing molar mass from the one extreme—high molar mass and low propylene content PE—to the other extreme—low molar mass and medium-isotacticity PP—it is evident that the middle molar mass fraction can be seen as an intermediate between the two extremes, showing the presence of both low propylene content EPC and medium-isotacticity PP.

According to FTIR (see Figure 9), in the highest-*M* part of the MMD—not covered by the boxes shown in Figure 8— propylene is present but not crystallized; thus only ethylene crystallinity will be present. In the high-*M* part of the MMD some PP crystallinity would be present, which is not confirmed by DSC. The middle-*M* part of the MMD indeed shows both ethylene and propylene crystallinity, while the low-*M* part of the MMD is characteristic of propylene crystallinity, ethylene crystallinity being absent.

Analysis of TREF Fraction 3V 110 (18.8 wt % of Total). According to Figure 1, this TREF fraction is the second largest fraction. The TREF fraction is the first one, which—with increasing TREF temperature—did show one melting endotherm on heating by DSC, while all TREF fractions eluting from 60 to 100 °C exhibited two melting endotherms.[8]
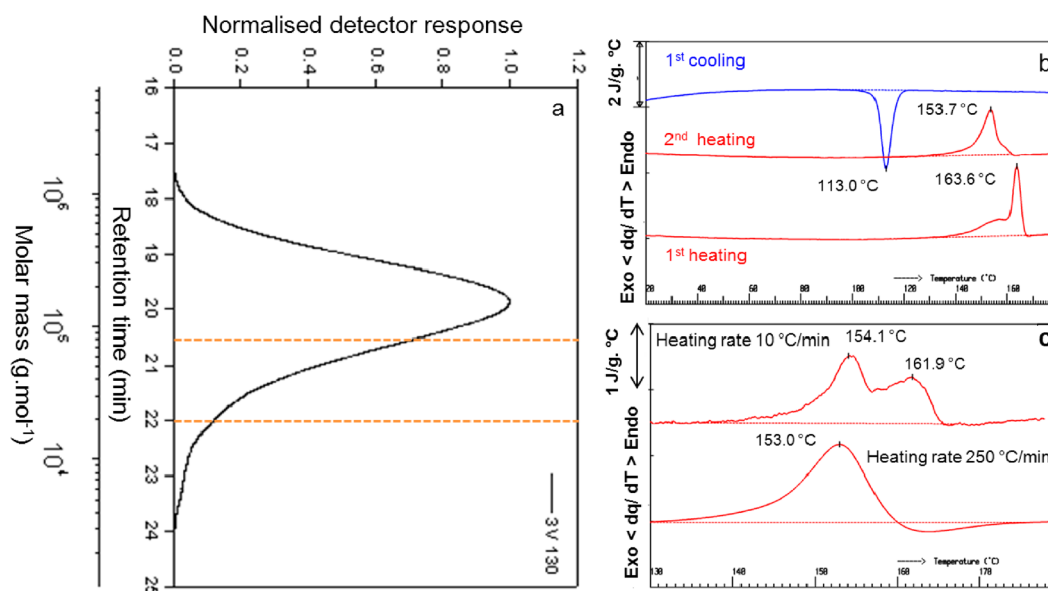
Figure 11. SEC-DSC analysis of sample TREF 3V 130. Crystallization and melting at 50 °C/min by HPer DSC of a low-M part of the SEC fraction of TREF fraction 3V 130; see box drawn on SEC curve on (a). Recrystallization is screened through variation of heating rate—10 and 250 °C/min in addition to 50 °C/min—subsequent to cooling at 50 °C/min.

Also, its SEC curve is unimodal (see Figure 10). For this fraction the DSC curve on the middle part of the MMD (see Figure 10a) clearly shows high-isotacticity PP with melting peak maximum temperatures of 158 (second heating curve) up to 168 °C (first heating). Crystallization still takes place around a low temperature, 111.4 °C, showing the high ΔT between the peak maximum temperatures of melting and crystallization, typical for PP. A very low molar mass fraction (see Figure 10b) still resembles a high-isotacticity PP (see the high crystallization temperature of 107 °C), though the melting peak maxima are lowered to 148 °C, probably mostly due to the decreasing effect of the low molar mass.

The DSC results are confirmed by the FTIR results, showing that the amount of propylene content is constant across the MMD as is the propylene crystallinity. No ethylene content is measurable, and no ethylene crystallinity is present. The DSC data also do not show the presence of polyethylene.

Analysis of TREF Fraction 3V 130 (7.9 wt % of Total). One fraction out of the total distribution is discussed, namely the SEC curve for the molar mass range covered by the orange box in Figure 11a. As seen in Figure 11b, this TREF fraction with the highest elution temperature of 130 °C shows crystallization (around the peak maximum of 113 °C) and melting of a high-isotacticity PP, with a melting main peak maximum at 153.7 °C and a shoulder at 160 °C for the second heating curve and 157 °C (shoulder) and 163.6 °C (main peak maximum) for the first heating curve.

The DSC data do not show the presence of polyethylene. Of interest is that—analogous to TREF fraction 3V 90—the shoulders and main peaks are most probably related to each other via recrystallization. To prove this, a variation of the heating rate subsequent to crystallization during cooling at 50 °C/min has been applied: besides heating at the same rate of 50 °C/min subsequent to cooling, heating at 10 and 250 °C/min have also been realized, presented in Figure 11c. Heating at 250 °C/min eliminates the highest melting peak maximum, by which the new maximum is situated at a slightly lowered value of 153 °C. Heating at 10 °C/min strengthens recrystallization,

giving rise to two pronounced maxima. Clearly, the peak without recrystallization is marked by a maximum at ~154 °C while (if melting−recrystallization−remelting occurs) a second, high-temperature peak arises at ~162 °C at the expense of the low-temperature peak. Heating at 250 °C/min from 160 °C on results in an "overshoot": the experimental curve lies under the line extrapolated for the melt. However, this phenomenon does not influence the conclusions with respect to recrystallization.

DSC Results on Melting of TREF-SEC Cross-Fractions: An Overview. Hitherto, salient DSC curves of specific TREF-SEC cross-fractions have been presented. Figure 12 gives an overview by displaying melting peak maximum temperatures, measured at 50 °C/min, on SEC fractions for all TREF fractions studied. The cross-fractions have been divided into two groups on the basis of high or low ΔT, meaning as before the difference between the peak maximum temperatures for melting, T_m, and crystallization, T_c (not shown here), $\Delta T = T_m - T_c$. Propylene crystallinity relates to crystallization and melting behavior with a higher ΔT and (usually) a higher T_m compared to ethylene-based polymers. From Figure 12b, a good correlation between T_m and $T_{elution}^{TREF}$ is seen for both groups of cross fractions having propylene and ethylene crystallinities. The group with propylene crystallinity shows an increase of T_m and $T_{elution}^{TREF}$ because of increasing isotacticity resulting in longer isotactic propylene sequences. The group with ethylene crystallinity shows an increase of T_m and $T_{elution}^{TREF}$ because of decreasing propylene content, resulting in longer ethylene sequences within the chains of these ethylene−propylene copolymers (EPC). The lowest T_m values are expected for ethylene−propylene rubbers (EPR) having short ethylene sequences. However, EPR, which is supposed to crystallize at (sub)ambient temperatures, and therefore it shows up in the TREF fraction 30 °C, will be reported separately. Overlap between the two groups of the melting temperatures is seen at the mid-elution temperatures. In the low-M range of the molar mass distribution no ethylene crystallinity is present; however, for higher molar masses both ethylene and propylene crystallinities are seen.
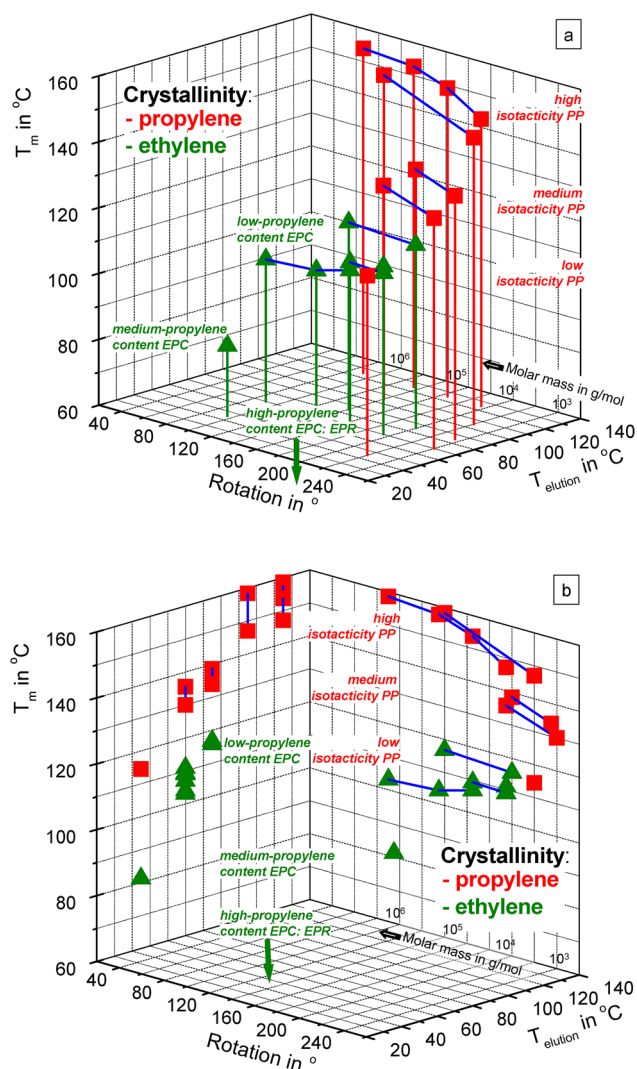
Figure 12. Correlation of melting temperature from DSC, molar mass (from SEC) and TREF fractionation for various samples TREF 3 V x. Melting related to ethylene and propylene crystallinities is represented by (▲) and (■), respectively. (a) 3D T_m^{max} of SEC fractions—denoted by the average angle of rotation of the disk, see also the M-axis—of TREF fractions eluted at the average $T_{elution}$. (b) Two 2D projections of the data shown in (a) with the same axes.

Linking Elution from TREF to Dissolution in DSC. As was concluded at Figure 8 for 3V 90.3, the high molar mass fraction (rotation angle 120°−160°), see also Figure 13a, represents low-propylene content EPC. The medium molar mass fraction (rotation angle 180°−220°), see Figure 13b, was judged to be an intermediate between the extremes of PP and propylene copolymerized polyethylene(s) because it contains both components, though the PP content is much higher. The constituents of this intermediate fraction differ considerably with respect to their melting temperatures—116 °C for the PE component and 139 °C/145 °C for the PP component—while their crystallization maximum temperatures probably coincide at 100 °C (see Figure 8). Compared to PE types, PP can show an appreciable ΔT. Despite these differences in the TREF dissolution procedure they both elute in between 80 and 90 °C, clearly pointing to the fact that ΔT is polymer- and solvent-dependent and different for crystallization and melting of the pure polymer (from and into the melt) and in solution. Thus,

in the present case two different polymers, with different thermal behavior when measured from their melt state, elute in the same temperature range, masking these differences. Such occurrence of coeluting polymers with quite different molecular structures in the same temperature range leads to the complexity of interpreting the data and of elucidating the molecular structure.

To get an impression of the release of molecules during elution in a TREF setup, a dissolution experiment by DSC of 3V 90, in *p*-xylene, was performed. The concentrations are reasonably comparable: TREF 1 wt % and HPer DSC around 2 wt %. However, the cooling and heating rates are very different: very slow in case of TREF and 10−50 °C/min for DSC. Despite this, the result is clarifying (see Figure 13b): the final dissolution temperature by DSC of fraction 3V 90 coincides with the end temperature of the TREF range for the fraction used, 90 °C. Notice that the dissolution by DSC starts 25 °C before 80 °C which is caused by chains that partly dissolve, giving rise to a heat flow rate in the DSC and at the cost of a heat of fusion measured, but which cannot yet elute in TREF due to the presence of segments in the same chain that are more stable than the dissolved ones and by that still stay connected to other molecules within the same and/or other crystallites. In general, a chain will elute when the most stable segment of that chain dissolves. Because incorporation of ethylene and propylene units will always end up with ethylene and propylene distributions along the chains, various kinds of sequence lengths will be available.

Especially, for a given sequence of dissolved ethylene units or of isotactic propylene units, longer sequences and/or more perfect ones will in principle be still stable at the temperature of dissolution, and will dissolve and elute at higher temperatures and so on until the most stable sequence dissolves and the chain can elute. In contrast, the DSC will measure dissolution at the temperature/time of transition, whether they elute or not (yet).

From Figure 13a, one could conclude that in this case the dissolution range in TREF is beyond the 80−90 °C range. However, this "overshoot" is caused by recrystallization during heating of the solution in the DSC, giving a bimodal DSC heating curve with dissolution peak maxima at 83 and 95 °C. The fact that this sample has been eluted between 80 and 90 °C in TREF means that all material has been eluted for which the whole chain is dissolved before or at 90 °C and which chain is not capable anymore of recrystallization in xylene at 90 °C. If it would recrystallize just before and at 90 °C, then it would elute at temperatures higher than 90 °C, in the next elution temperature range of 90−100 °C.

To prove the occurrence of recrystallization, one usually increases the heating rate, by which less time is available for recrystallization and remelting. However, heating at 50 °C/min is a suitable but already a high heating rate for a polymer in solution in LVC pans. Therefore, the choice was made to decrease the cooling rate instead. Thus, the fact that recrystallization occurs for the SEC fraction 120°−160° of TREF fraction 3V 90.3 now follows from the experiment done (see Figure 13a) at 10 °C/min cooling and heating. At this slower rate the crystallization is better in terms of stability of the crystallites formed, by which the possibility of the occurrence of recrystallization is less. Indeed, the first, low-temperature melting peak is larger and the second, high-temperature remelting peak smaller. Decreasing the cooling rate further would remove the second high-temperature peak
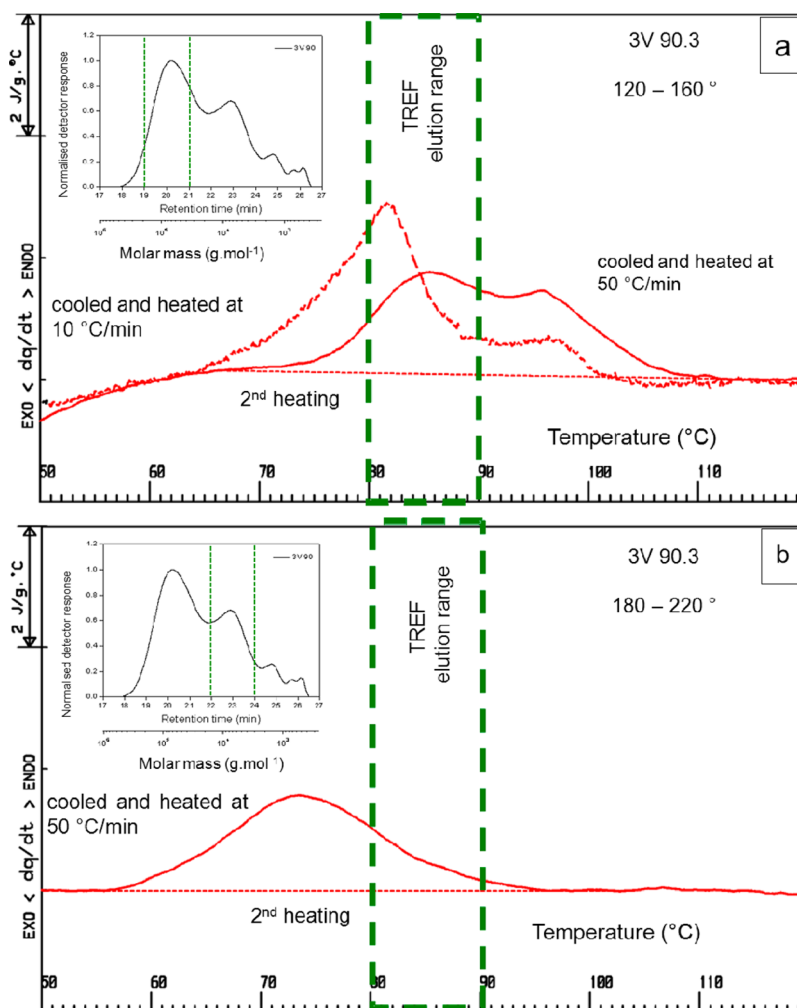
Figure 13. SEC-solution DSC analysis of sample TREF 3V 90. (a) Dissolution curves of 0.495 mg in approximately 20 mg of *p*-xylene at 10 and 50 °C/min subsequent to cooling at 10 (⋯) and 50 °C/min (—), respectively, of SEC fraction 120°−160° of TREF fraction 3V 90.3. (b) Dissolution curves of 0.345 mg in ~20 mg of *p*-xylene at 50 °C/min subsequent to cooling at 50 °C/min (—) of SEC fraction 180°−220° of TREF fraction 3V 90.3. Both samples were measured between 10 and 130 °C with an isothermal stay of 15 min at 130 °C. The TREF elution temperature range of 80−90 °C is indicated by a green box. Insets: the parts of the MMD by SEC as covered by the samples are indicated by boxes as before.

fully leaving the low-temperature melting peak ending around 90 °C as expected from the TREF temperature range of 80−90 °C. Again, the dissolution starts earlier, ~15 °C before 80 °C.

Having this in mind, the results found by HPer DSC are reasonable—even though it is operated at much higher scan rates compared to TREF experiments. Thus, from these preliminary experiments it is clear that measuring of crystallization and dissolution in liquids like *p*-xylene looks to be very rewarding: it opens possibilities to use HPer DSC as an extremely fast technique enabling designing of an optimal TREF elution temperatures scheme and the same for determination of optimal temperatures of crystallization in a liquid using CRYSTAF. Finally, to arrive at a useful method, it would be of interest to systematically study the occurrence of recrystallization as a function of molar mass and composition.

4. CONCLUSIONS

For the analysis of the complex molecular structure of impact PP various sophisticated techniques and methods have been combined. Starting with preparative TREF of the bulk IPC dissolved in xylene, various fractions were obtained at temperatures between 30 and 130 °C. Each fraction was subsequently fractionated by SEC and continuously deposited on a rotating disk wrapped with aluminum foil, under evaporation of the TCB using the LC transform interface. Fractions deposited in this way were measured by HPer DSC and compared with FTIR data. FTIR provided the ethylene and propylene content as a function of the rotating angle of the disk, which is related to the MMD. In addition, FTIR shows whether ethylene and/or propylene crystallinity had been developed, which was also presented as a function of MMD. For HPer DSC, samples of the TREF-SEC cross-fractions obtained were cut from the aluminum disk, resulting in 7 parts that vary in molar mass. Increasing the scan rates to 50 °C/min gave reasonable to good DSC curves, and in all cases the thermal behavior could be recorded very well. In the case that crystallization and melting occurred, it could be decided in most cases—e.g. on the basis of the difference between the peak maximum temperatures for melting (T_m) and crystallization (T_c)—what kind of polymer(s) caused the corresponding DSC peaks. Combining the findings with results from FTIR showed these to be complementary and unanimous and to be very useful in order to arrive at the complete picture of molecular structure.

The first fraction was eluted by TREF at 30 °C; however, this TREF fraction will be discussed in more detail in a separate study. The following TREF fractions, with eluting temperatures of 60 °C (3.4 wt %) and 80 °C (3.5 wt %), displayed bimodal SEC curves while the MMD of TREF fraction 90 °C (3.3 wt %) comprised at least four well-distinguishable SEC peaks. The higher TREF temperature fractions analyzed—110 °C (18.8 wt %, second largest) and 130 °C (7.9 wt %)—were unimodal. Together with TREF fraction 120 °C (47.8 wt %, largest), by their high weight percentage (in total almost 75 wt %), these fractions dominate in the characterization results and these often just seem to resemble bulk PP. Nevertheless, the smaller fractions can have a significant influence on properties, e.g., impact properties, far beyond from what one would expect on the basis of their weight percentage.

The samples for DSC were taken in such a way that information about the underlying molecular structure could be obtained. It turned out that in the lower M part of the MMD only propylene crystallinity was present. At intermediate and high M, both ethylene and propylene crystallinities were found to be related to polyethylene varying in propylene content and to polypropylene varying in isotacticity, respectively. With increasing TREF elution temperature the isotacticity of the polypropylene increased appreciably, leading to longer sequences of isotactic polypropylene and concomitant increasing melting temperatures. At the same time cross-fractions showing ethylene crystallinity were seen to be ethylene–propylene copolymers (EPC) with various ethylene and propylene sequence length distributions. With increasing TREF elution temperature their ethylene sequence lengths increased because of the decreasing amount of propylene incorporated in the chains.

As can be expected for the present components constituting the impact PP copolymer studied here, the DSC curves resemble metastable states with associated reorganization phenomena including recrystallization. Therefore, though the PerkinElmer DSC 8500 is quite capable to measure at 50 °C/min samples having such minute amounts of material as in the present case, to find out to what extent the scan rate is of importance it was varied by taking rates of 5, 50, 100, and 200 °C/min. For the same reason, measurements at 10, 100, and 1000 °C/s with the Mettler-Toledo flash DSC 1 have also been added. A first and important conclusion from these measurements is that continuity of the T_c and T_m data was found for the HPer DSC and the flash DSC 1. In this scan rate range spanning over 4 decades—from ~0.1 to 1000 °C/s—T_c dropped linearly in this restricted area, while the decrease of T_m leveled off at the high scan rates, signifying that the melting process is dominated by fast reorganization processes: too fast for the present instrumentation to be influenced significantly.

Crystallization and dissolution measurements with the DSC 8500 on fractions in p-xylene gave useful information—after correction for recrystallization—on the lowering of T_c and T_m compared to crystallization and melting without liquid, from and into the melt state, even though the cooling and heating rates were much higher. This method is thought to be of interest for designing experiments using a solvent, like TREF and CRYSTAF, and in general fractionation by way of crystallization and dissolution in a solvent.

Finally, though the samples measured by HPer DSC were of the order of a few tens of micrograms, the limit has not been reached yet: it should be possible to work on sample masses down to the low microgram or high nanogram level. For even lower sample masses one can rely on the flash DSC 1.

The fact that the molecular properties can be correlated with thermal properties at very high heating and cooling rates promises to be the breakthrough for a better understanding of melting and crystallization under the conditions of materials processing, e.g., extrusion. This, in our opinion, is a significant advance in the present field of research.

■ AUTHOR INFORMATION

Notes

■ REFERENCES

(1) Kaminsky, W. *Macromol. Chem. Phys.* **2008**, *209*, 459−466.
(2) Cheruthazhekatt, S.; Pijpers, T. F. J.; Harding, G. W.; Mathot, V. B. F.; Pasch, H. *Macromolecules* **2012**, *45*, 2025−2034.
(3) Schick, C. *Anal. Bioanal. Chem.* **2009**, *395*, 1589−1611.
(4) Zhuravlev, E.; Schick, C. *Thermochim. Acta* **2010**, *505*, 1−13.
(5) Zhuravlev, E.; Schick, C. *Thermochim. Acta* **2010**, *505*, 14−21.
(6) Pijpers, T. F. J.; Mathot, V. B. F.; Goderis, B.; Scherrenberg, R. L.; van der Vegte, E. W. *Macromolecules* **2002**, *35*, 3601−3613.
(7) Mathot, V. B. F.; Pyda, M.; Pijpers, T. F. J.; V Poel, G. V.; van de Kerkhof, E.; van Herwaarden, S.; van Herwaarden, F.; Leenaers, A. *Thermochim. Acta* **2011**, *522*, 36−45. See www.mt.com/TA-FlashDSC and www.scite.nl.
(8) de Goede, E.; Mallon, P.; Pasch, H. *Macromol. Mater. Eng.* **2010**, *295*, 366−373.
(9) Mirabella, F. M. *Polymer* **1993**, *34*, 1729−1735.
(10) Zhang, C.; Shangguan, Y.; Chen, R.; Wu, Y.; Chen, F.; Zheng, Q.; Hu, G. *Polymer* **2010**, *51*, 4969−4977.
(11) Mathot, V. B. F. The Crystallization and Melting Region. In *Calorimetry and Thermal Analysis of Polymers*; Hanser Publishers: Munich, 1994; Chapter 9, pp 231−299.
(12) Mandelkern, L. *Crystallization of Polymers*; Cambridge University Press: Cambridge, 2004; Vol. 2.
(13) Phuong-Nguyen, H.; Delmas, G. *Thermochim. Acta* **1994**, *238*, 257−275.
(14) Monrabal, B. *J. Appl. Polym. Sci.* **1994**, *52*, 491−499.
(15) Luruli, N.; Pijpers, T.; Brüll, R.; Grumel, V.; Pasch, H.; Mathot, V. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 2956−2965.
(16) Krumme, A.; Basiura, M.; Pijpers, T.; Poel, G. V.; Heinz, L. C.; Brüll, R.; Mathot, V. B. F. *Mater. Sci.* **2011**, *17*, 260−265.
(17) Holtrup, W. *Macromol. Chem.* **1977**, *178*, 2335.
(18) Mathot, V. Polycon "84 LLDPE" The Plastics and Rubber Institute London; proceedings 1 (1984).
(19) Mathot, V. B. F.; Pijpers, M. F. J. *Polym. Bull.* **1984**, *4*, 297−304.
(20) Macko, T.; Brüll, R.; Zhu, Y.; Wang, Y. *J. Sep. Sci.* **2010**, *33*, 3446−3454.
(21) Cong, R.; deGroot, W.; Parrott, Al.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062−3072.
(22) Ginzburg, A.; Macko, T.; Dolle, V.; Brüll, R. *Eur. Polym. J.* **2011**, *47*, 319−329.
(23) Shan, C. L. P.; Miller, M.; Lee, D.; Zhou, Z. *Macromol. Symp.* **2012**, *312*, 1−19.
(24) Eynde, S. V.; Mathot, V.; Koch, M. H. J.; Reynaers, H. *Polymer* **2000**, *41*, 3437−3453.
(25) Mathot, V. B. F.; Fabrie, C. C. M. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 2487−2507.
(26) Mathot, V. B. F.; Fabrie, C. C. M.; Tiemersma-Thoone, G. P. J. M.; Van Der Velden, G. P. M. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 2509−2526.
(27) Karssenberg, F. G.; Mathot, V. B. F.; Zwartkruis, T. J. G. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 722−737.
(28) Mathot, V. B. F.; Scherrenberg, R. L.; Pijpers, T. F. J. *Polymer* **1998**, *39*, 4541−4559.

(29) Poel, G. V.; Mathot, V. B. F. *Thermochim. Acta* **2007**, *461*, 107–121.

(30) Minakov, A. A.; van Herwaarden, A. W.; Wien, W.; Wurm, A.; Schick, C. *Thermochim. Acta* **2007**, *461*, 96–106.

ARTICLE IN PRESS

Comprehensive high temperature two-dimensional liquid chromatography combined with high temperature gradient chromatography-infrared spectroscopy for the analysis of impact polypropylene copolymers

Sadiqali Cheruthazhekatt[a], Gareth W. Harding[b], Harald Pasch[a,*]

[a] *Department of Chemistry and Polymer Science, University of Stellenbosch, 7602 Matieland, South Africa*
[b] *Sasol Polymers, Midland Factory, Bergius Street, Sasolburg 321, South Africa*

A B S T R A C T

Impact polypropylene copolymers (IPC) are extremely complex materials that can only be effectively analysed by multidimensional analytical approaches. IPC consists of isotactic polypropylene (iPP) as the major phase, ethylene–propylene (EP) copolymers of various compositions and small amounts of polyethylene. The molecular heterogeneity of two IPC samples having different ethylene contents was studied by using a novel cross-fractionation technique, developed from a combination of various analytical separation methods into an effective characterisation tool for complex polyolefins. The initial step involves the fractionation of the sample into EP rubber, EP segmented copolymer, and iPP, by preparative temperature rising elution fractionation (TREF). The resulting fractions are still distributed with regards to chemical composition and molar mass. The separation with respect to these parameters is conducted by comprehensive HT 2D-LC. This is the first time that the individual components in all TREF fractions of an IPC are separated and analysed mutidimensionally, by both SEC-FTIR, high-temperature (HT) HPLC-FTIR, and HT 2D-LC. Molar mass analysis of the chemically homogeneous fractions from HT HPLC is accomplished by HT SEC in the second dimension of HT 2D-LC. The chemical composition of all species is determined by coupling FTIR spectroscopy to HT HPLC via an LC-transform interface. This novel approach reveals the capability of this hyphenated technique to determine the exact chemical composition of the individual components in the complex TREF fractions of IPCs. The HT HPLC-FTIR results confirm the separation mechanism in the given chromatographic system using a 1-decanol to TCB solvent gradient and a Hypercarb stationary phase. The components of differing chemical composition are separated according to the nature and length of the propylene/ethylene segments, with their arrangement in the chains strongly affecting their adsorption/desorption on the stationary phase. FTIR analysis provides information on the ethylene and propylene contents of the fractions as well as on the ethylene and propylene crystallinities.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The ability to synthesise materials, such as impact polypropylene copolymers (IPC), having improved low temperature impact properties, has significantly widened the application range of isotactic polypropylene. Using a two-stage, two-reactor polymerization process, involving the homopolymerisation of propylene followed by the copolymerization of propylene and ethylene, results in a highly complex mixture of polymer chains, consisting of iPP homopolymers, ethylene–propylene copolymers, including random and segmented structures with different monomer sequence length distributions and molar mass distributions (MMD), as well as polyethylene homopolymers [1–4].

Information regarding the MMD and chemical composition distribution (CCD) of such complex polyolefins is important in order to fully understand their properties during processing and final application. The MMD is directly related to physical properties such as toughness, melt viscosity, and crystallinity. Accurate knowledge of the MMD is also useful for tailoring, or modifying catalyst structures or polymerization conditions during synthesis, in order to influence the final properties of the polymers. Even though molar mass is an important factor, CCD is a dominant parameter in determining the final physical and mechanical properties of such complex copolymers [5]. A number of non-chromatographic separation techniques

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

2   S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

have been used to analyse the CCD in olefin copolymers, including temperature rising elution fractionation (TREF), crystallization analysis fractionation (CRYSTAF), and crystallization elution fractionation (CEF), which fractionate the sample according to the differences in crystallisability of the polymer chains. Accordingly, these techniques have limitations both in terms of analysis time and their applicability to well-crystallisable vs. non-crystallizable components [6–14].

The precise analysis of such materials with multivariate distributions is a difficult task and (as has been demonstrated by ourselves and others) requires a multidimensional approach. Multiple fractionations will be an essential analytical tool for the full characterization of such complex multi-component systems [6,7,15]. In principle, preparative TREF can be considered to be a suitable method for the separation of the individual components as one expects that the fractionation behaviour is based on the components' different crystallisabilities (and hence chemical compositions) from solution [3]. Indeed, preparative fractionation and subsequent analysis of the individual fractions by SEC-FTIR has been found to be an effective method for the determination of the chemical composition per molar mass slice [16]. This approach provides an average chemical composition per molar mass fraction, however, the CCD cannot be obtained since each molar mass fraction can be heterogeneous with respect to chemical composition.

High temperature HPLC is a very recent fractionation method that enables the fast and complete separation of polyolefins, according to their chemical composition. To this date, this is the only method for the swift and efficient separation of polyolefins and olefin copolymers according to chemical composition, which is not based on the components' crystallisability [17–21]. However, as the distributions present in a polymer sample are interrelated, fractionation with regard to all parameters of interest, i.e. the chemical composition and the molar mass, is required. Therefore, a two-dimensional mapping of the multivariate distribution (separation according to chemical composition and molar mass) is required and can be achieved by the recently developed HT 2D-LC [22–27]. In a previous study, we separated and analysed the individual components in a mid-elution temperature TREF fraction of an IPC by the combination of Prep TREF with HT HPLC and HT 2D-LC [28]. During subsequent work, the TREF fractions were analysed by HT SEC coupled to advanced thermal analysis [29]. Using HPer DSC and Flash DSC 1, it was found that fractions from dual TREF-SEC fractionation exhibited multiple melting and crystallization peaks that indicate the complex structure and thermal behaviour of these fractions.

These findings prompted us to conduct a study on the multidimensional and comprehensive characterization of all TREF fractions (amorphous, semi-crystalline and highly crystalline) of IPC by HT HPLC-FTIR and HT 2D-LC. It will be demonstrated that this approach is the only way for a complete separation of all individual components and their comprehensive analysis regarding CCD and MMD.

2. Experimental

2.1. Materials

Two non-stabilised IPCs (designated as 3V and 3V A) were obtained from SASOL Polymers (Secunda, South Africa). The samples were commercial products that were synthesized in a dual reactor polymerization setup. Molar mass, dispersity and comonomer content of the samples are given in Table 1. 1-Decanol and 1,2,4-trichlorobenzene (TCB) (Sigma–Aldrich, South Africa) were used as the mobile phase, as received.

Table 1
Important molecular properties of the two IPC samples, 3V and 3V A.

Sample	Ethylene content (mol.%)	Isotacticity(%mmmm)	M_w [a] (kg mol^{-1})	Dispersity
3V	10.5	88.82	228	3.5
3V A	11.78	87.53	361	6

[a] Molar masses are polystyrene equivalents.

2.2. Size exclusion chromatography (SEC)

Molar mass measurements for all samples were performed at 150 °C using a PL GPC 220 high temperature chromatograph (Polymer Laboratories, Church Stretton, UK) equipped with a differential refractive index (RI) detector. The column set used consisted of three 300 × 7.5 mm PLgel Olexis columns together with a 50 × 7.5 mm PLgel Olexis guard column (Polymer Laboratories, Church Stretton, UK). The eluent used was 1,2,4-trichlorobenzene (TCB) at a flow rate of 1.0 mL/min with 0.0125% 2,6-di-tert-butyl-4-methylphenol (BHT) added as a stabiliser. Samples were dissolved at 160 °C in TCB at a concentration of 1 mg/mL for 1–2 h (depending on the sample type) and 200 μL of each sample was injected. Narrowly distributed polystyrene standards (Polymer Laboratories, Church Stretton, UK) were used for calibration.

2.3. Temperature rising elution fractionation (TREF)

Preparative TREF was carried out using an instrument developed and built in-house. Approximately 3.0 g of polymer and 2.0 w/w% Irganox 1010 (Ciba Speciality Chemicals, Switzerland) were dissolved in 300 mL of xylene at 130 °C in a glass reactor. The reactor was then transferred to a temperature-controlled oil bath and filled with sand (white quartz, Sigma–Aldrich, South Africa), used as a crystallisation support. The oil bath and support were both preheated to 130 °C. The oil bath was then cooled at a controlled rate of 1 °C/h in order to facilitate the controlled crystallisation of the polymer. The crystallised mixture was then packed into a stainless steel column which was inserted into a modified gas chromatography oven for the elution step. Xylene (pre-heated) was used as eluent in order to collect the fractions at pre-determined intervals as the temperature of the oven was raised. The fractions were isolated by precipitation in acetone, followed by drying to a constant weight.

2.4. ^{13}C NMR spectroscopy

^{13}C NMR spectra were measured on a 600 MHz Varian Unity Inova NMR spectrometer, at a resonance frequency of 150 MHz for carbon. Deuterated 1,1,2,2-tetrachloroethane-d2 (95.5 +atom %D, Sigma–Aldrich) at δ 74.3 ppm as internal reference, was used as solvent for the sample preparation (at a concentration of 6 wt.%). Analyses were carried out at 120 °C in nitrogen atmosphere, with an acquisition time of 0.79 s, and pre-acquisition delay time of 15 s. This lead to total analysis times of 3–10 h per sample.

2.5. Chromatographic system

All chromatographic experiments were performed using a new chromatographic system for high temperature two-dimensional liquid chromatography constructed by Polymer Char (Valencia, Spain), comprising of an autosampler, two separate ovens, 2D switching valves and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). One oven was used for the HPLC column, while the second oven, where the injector and a switching valve were located, was used for the SEC column. The autosampler is a separate unit connected to the injector through a heated

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

3

transfer line. A high-pressure binary gradient pump was used for HPLC in the first dimension and an isocratic pump was used for SEC in the second dimension. An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: a gas flow rate of 1.5 L/min, a nebuliser temperature of 160 °C, and an evaporator temperature of 270 °C. For the analysis of 3V and 3V A two different ELS detectors were used. They had different total sensitivities and, thus, their total detector responses were different.

2.5.1. High temperature HPLC

HT HPLC was carried out using a Hypercarb column (Hypercarb®, Thermo Scientific, Dreieich, Germany) with the following parameters: 100×4.6 mm i.d., packed with porous graphite particles with a particle diameter of 5 μm, a surface area of $120 \, m^2/g$, and a pore size of 250 Å. The flow rate of the mobile phase was 0.5 mL/min. The column was placed in the column oven maintained at 160 °C. The HPLC separations were accomplished by applying a linear gradient from 1-decanol to TCB. The volume fraction of TCB was linearly increased to 100% within 10 min after the sample injection and then held constant for 20 min. The dwell volume (1.7 mL) and void volume (1.1 mL) were measured according to the method described by Ginzburg et al. [23]. That means there is an isocratic elution of 1-decanol (1.7 mL) before the start of the linear solvent gradient hits the column. Finally, the initial chromatographic conditions were re-established with 100% 1-decanol. Samples were injected at a concentration of 1–1.2 mg/mL, with 20 μL of each sample being injected.

2.5.2. Collection of HPLC fractions by the LC transform interface

An LC-Transform series model 303 (Lab Connections) was coupled to a high temperature solvent gradient interaction chromatograph (SGIC) constructed by Polymer Char (Valencia, Spain), in order to collect the HPLC eluate (see Fig. 1). Samples were dissolved at 160 °C in 1-decanol at a concentration of 1–1.2 mg/mL, with 110 μL of each sample being injected. The HPLC column outlet was connected to the LC transform interface (see Fig. 1) through a heated transfer line set at 160 °C. The fractions were deposited by rotating a germanium disc (sample target in the LC-Transform) at a speed of rotation of 10°/min. The disc stage and nozzle temperatures of the LC-Transform were set to 160 °C.

2.5.3. FTIR analyses of the deposited fractions

FTIR analyses of the deposited HPLC fractions were performed on a Thermo Nicolet iS10 Spectrometer (Thermo Scientific, Waltham, MA), equipped with the LC-Transform FTIR interface connected to a standard transmission baseplate. Spectra were recorded at a resolution of 8 cm^{-1} with 16 scans being recorded for each spectrum. Thermo Scientific OMNIC software (version 8.1) was used for data collection and processing.

2.5.4. High temperature two-dimensional liquid chromatography (HT 2D-LC)

The coupling of HT HPLC and HT SEC was achieved by using an electronically controlled eight-port valve system (VICI Valco instruments, Houston, TX, USA) equipped with two 100 μL sample loops. A 110 μL sample loop was used for injection into the first dimension. Samples were prepared at a concentration of 2.5 mg/mL in 1-decanol. The flow rate for the first dimension was 0.05 mL/min, using the same gradient as for one-dimensional analysis, adjusted for the longer analysis time. TCB was used as the mobile phase for the second dimension at a flow rate of 2.75 mL/min. The second dimension column used was a PL Rapide H (Polymer Laboratories, Church Stretton, UK) 100×10 mm i.d. column with a 6 μm particle diameter. The column was placed in the top heated oven, maintained at 160 °C. Detection was performed with an ELSD using the same settings as for the one-dimensional (HPLC) separation.

3. Results and discussion

Two IPC samples designated as 3V and 3V A, were fractioned into eight fractions by preparative TREF. As shown from the TREF data in Fig. 2, the 30 °C fraction, together with those eluting from 110 to 120 °C, constitute the largest weight percentage of both samples.

Since TREF fractionates according to crystallisability, the 30 °C fraction is expected to be amorphous, while the fractions eluting at the highest temperature (around 120 °C) should be highly crystalline, with those eluting in between being semi-crystalline. A comparison of the TREF data (weight percentage of each fraction) for both samples, reveals that the weight percentages for the 30 and 110 °C fractions of sample 3V A are relatively higher, while the other fractions (60, 80, 90, 100, 120 and 130) are relatively lower than for sample 3V. In-depth analysis of all the TREF fractions of
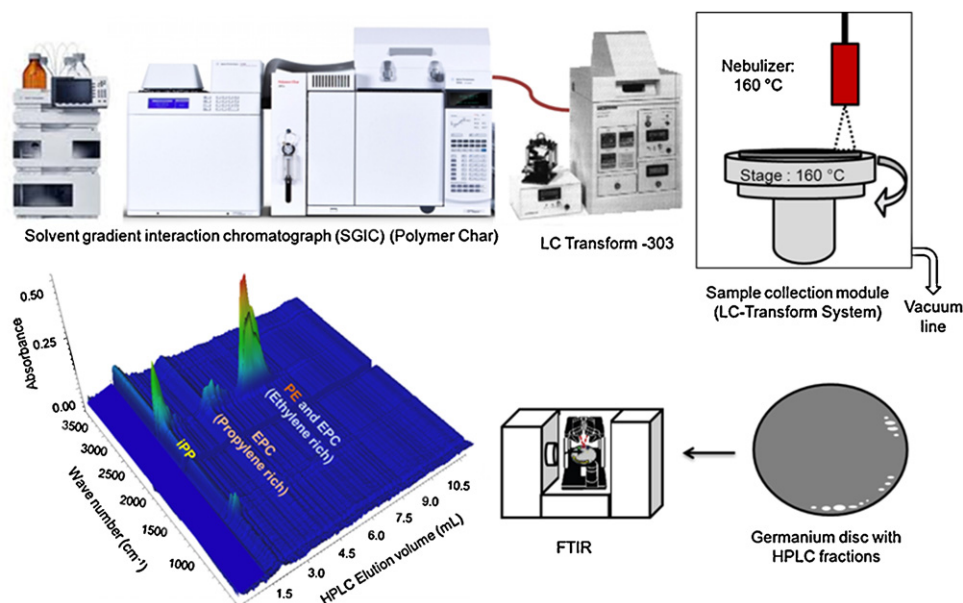

Fig. 1. Schematic representation of HT HPLC-FTIR analysis.

Stellenbosch University http://scholar.sun.ac.za

G Model
CHROMA-354116;   No. of Pages 14

ARTICLE IN PRESS

4   S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx
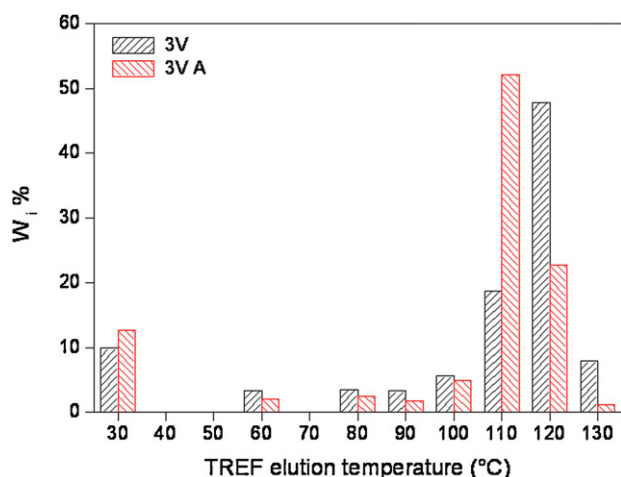
Fig. 2. Prep-TREF profile for sample 3V and 3V A, indicating the overall weight percentage of each fraction as a function of elution temperature.

sample 3V by HT SEC, DSC and HT ^{13}C NMR, and the most important fractions (60, 80, 90, 100 °C) by using SEC-FTIR was reported in our previous publication (see Ref. [16]).

The shapes of the MMD curves obtained for the sample 3V A and all TREF fractions (see supporting information Fig. 1) agree well with those observed for the 3V (see Fig. 2 in Ref. [16]). All molar masses are polystyrene equivalents. DSC analysis of these TREF fractions also follows the same trend that has been found for the TREF fractions of sample 3V, except for the 130 °C fraction of 3V A (see supporting information Fig. 2).

Comonomer content, monomer sequence distributions, tacticity and number average ethylene and propylene sequence lengths were calculated [30–32] from ^{13}C NMR analysis of two IPC samples, 3V and 3V A (see supporting information Table 1 and 2). Sample 3V A shows relatively higher ethylene content (11.78 mol.%) and lower tacticity (87.53%) compared to 3V. The difference in the microstructure distributions (EP junctions, segment lengths and average sequence lengths) were observed for these two IPC samples.

It is obvious that the information available for each TREF fraction from HT SEC, DSC and ^{13}C NMR analysis is not sufficient to determine their compositional heterogeneity. It will be challenging to differentiate between both samples by even the combination of Prep TREF with SEC-FTIR as well, since only average values can be determined. In order to obtain a fast and complete separation of such a complex polymeric system according to chemical composition, prep TREF should be combined with high temperature HPLC, which separates the polymer chains according to their microstructure. The current study made use of the combination of Prep TREF and HT HPLC, which we reported on previously for the separation of the individual components in one of the midelution temperature TREF fractions of an ICP (3V) [28] although this study additionally makes use of FTIR as a compositional detection method, after HT HPLC.

The HT HPLC chromatograms, obtained after gradient elution for all the TREF fractions of the two IPC samples are given in Figs. 3 and 4. A complete separation according to the chemical composition was obtained for all fractions. As reported by Pasch and Macko [17] linear ethylene sequences show a strong retention on the Hypercarb stationary phase and elute later, while linear propylene sequences are not retained to the same extent. Although the chemical composition is the primary parameter and governs the separation, the molar mass of the components also plays a role, especially for low molar masses. For all the TREF fractions, a fraction of iPP homopolymer having a low molar mass is not absorbed on

the column but elutes in 100% 1-decanol before the start of the gradient. The concentration of this component increases as the TREF fractionation temperature increases. It is expected (from the TREF fractionation) that the 30 °C fraction consists of mainly ethylene propylene random copolymers, with some atactic PP or branched polyethylene homopolymers also present.

It is clear that the concentration and length of the propylene/ethylene sequences in the chain influence their retention on the stationary phase [18]. The chromatogram obtained for the 30 °C fraction of 3V is given Fig. 3a, the major component of this fraction eluted between approximately 3.5–5.5 mL together with two small iPP components at approximately 1.2 and 1.5 mL, respectively, which eluted in SEC mode. The chromatogram obtained for 3V A-30 (see Fig. 3b) shows a bimodal HPLC elution profile (between 3.2 and 5 mL), indicating the retention behaviour of two chemically different components in the same 30 °C fraction. It is most likely that the first component (eluted between 3.2 and 4.2 mL) consists of chains with atactic propylene units or E/P segments in random sequences, in which the short ethylene segments may enable the retention to a lesser extent. The second component will either be random EP polymer with chains having higher amounts of ethylene units, or PE homopolymers with appreciable amounts of branching – possibly long chain branches, rendering this component amorphous, which results in retention on the column and later elution (approximately between 4.2 and 5.2 mL).

Two nearly baseline-separated peaks in addition to the first iPP component are observed for the 60 °C fraction of 3V (see Fig. 3c). A small fraction of slightly higher molar mass iPP eluted after the start of the gradient, at approximately 3 mL, followed by the propylene rich EPC (eluted approximately between 3.25 and 4.8 mL), and EPC copolymer with chains, comprised of long ethylene sequences, eluted together with PE homopolymers (approximately between 5 and 6.25 mL). Three chemically different components were found in the 3V A-60 fraction in addition to the low and high molar mass iPP components. High molar mass iPP and propylene rich EPC were eluted approximately between the elution volumes of 3–3.5 mL. Two relatively intense peaks, one corresponding to the ethylene rich EPC and the other to PE homopolymer, were observed at peak maximum elution volumes of 4.85 and 5.5 mL, respectively. These results indicate that only HT HPLC allows the fast and precise separation of individual components in this semi-crystalline TREF fraction of two IPC samples, which show similar bimodal SEC profiles and two melt endotherms by DSC (see Figs. 2 and 3 in Ref. [16]). The relative intensity of the late eluting components is higher for the 3V A-60 fraction, which indicates the presence of a high amount of ethylene units (ethylene content) in this fraction. From these overall results for the 60 °C fraction of the two IPC samples, it is clear that the amount (concentration) and chemical composition of such components have great importance in bridging the dispersed EPR phase with iPP matrix, in order to enhance the interfacial interaction between these two phases, which strongly affect the total impact performance of such complex materials [33,34].

The HPLC results for the 3V 80 °C fraction have been discussed in our recent publication (see Ref. [28]) while here we compare the results obtained for the 3V A-80 fraction with 3V 80 (Fig. 3e and f). The chromatogram obtained for 3V A-80 shows mainly two intense peaks, the first corresponding to the iPP component, which eluted in SEC mode, and the second to EPC (ethylene rich) or PE homopolymers eluted at approximately 5.6 mL. A small amount of relatively high molar mass iPP (eluted from 3 to 3.5 mL) is also observed for this fraction. A comparison of the intensities of the peaks obtained for 3V 80 to that of 3V A-80, reveals that the amount of ethylene rich EPC or PE homopolymers is greater in the 80 °C fraction of 3V A. These results again confirm the capability of HT HPLC as the only suitable method to distinguish the CCD present in such complex TREF fractions, which are indistinguishable by SEC (MMD) and DSC
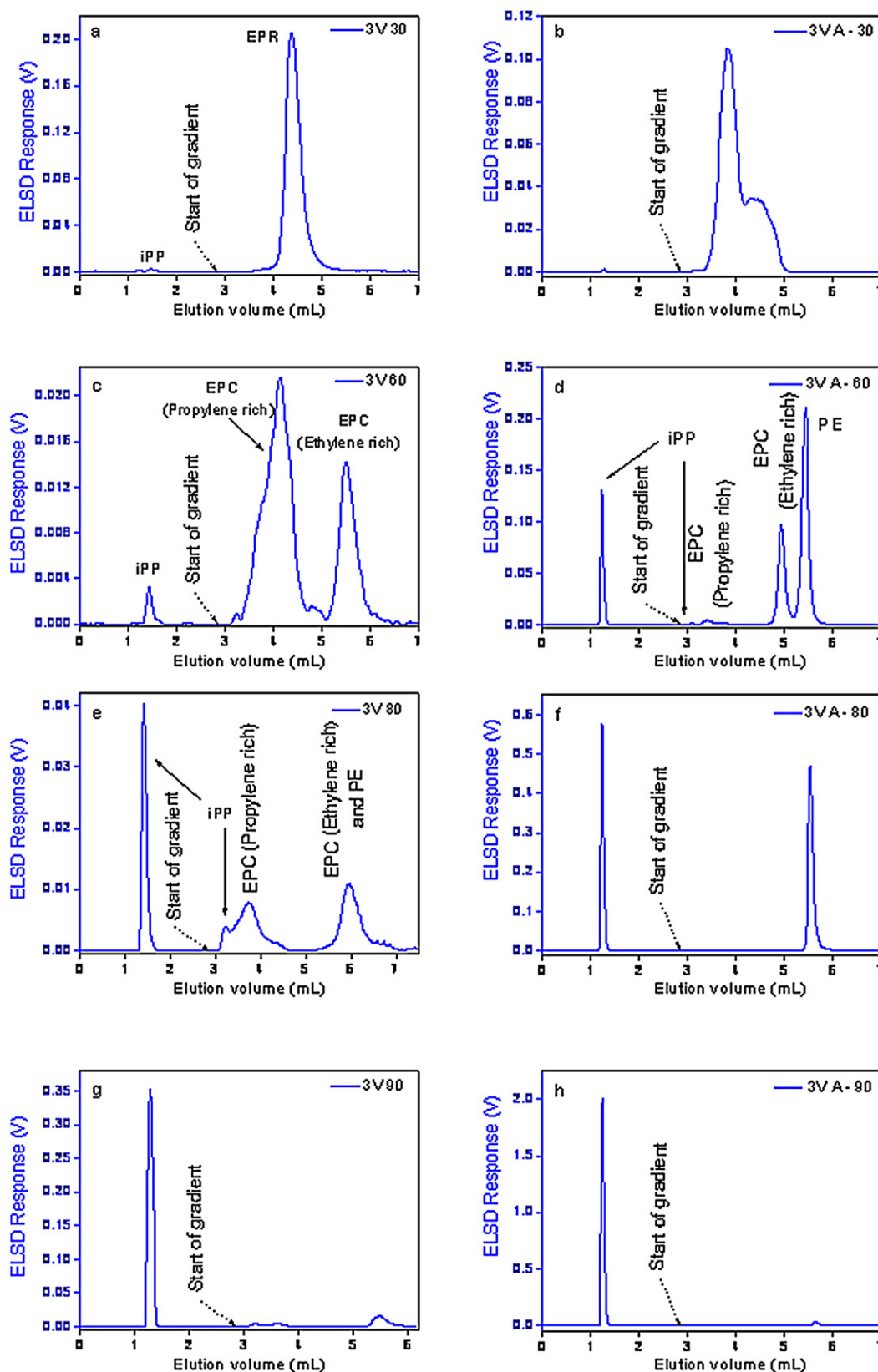
G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

5

Fig. 3. Chromatograms obtained after isocratic and gradient elution for the TREF fractions (30, 60, 80 and 90 °C) of 3V and 3V A.

(melting behaviour). The chromatogram obtained for 3V 90 is given in Fig. 3g, the main component is found to be low molar mass iPP, together with a relatively lower amount of high molar mass iPP, as well as propylene and ethylene rich EPC. The low molar mass iPP elutes in 100% 1-decanol at approximately 1.25 mL, followed by the retained iPP components and propylene rich EPC that are desorbed by the gradient. The EPC (ethylene rich) and linear PE are also fully retained due to their selective adsorption on the column packing,
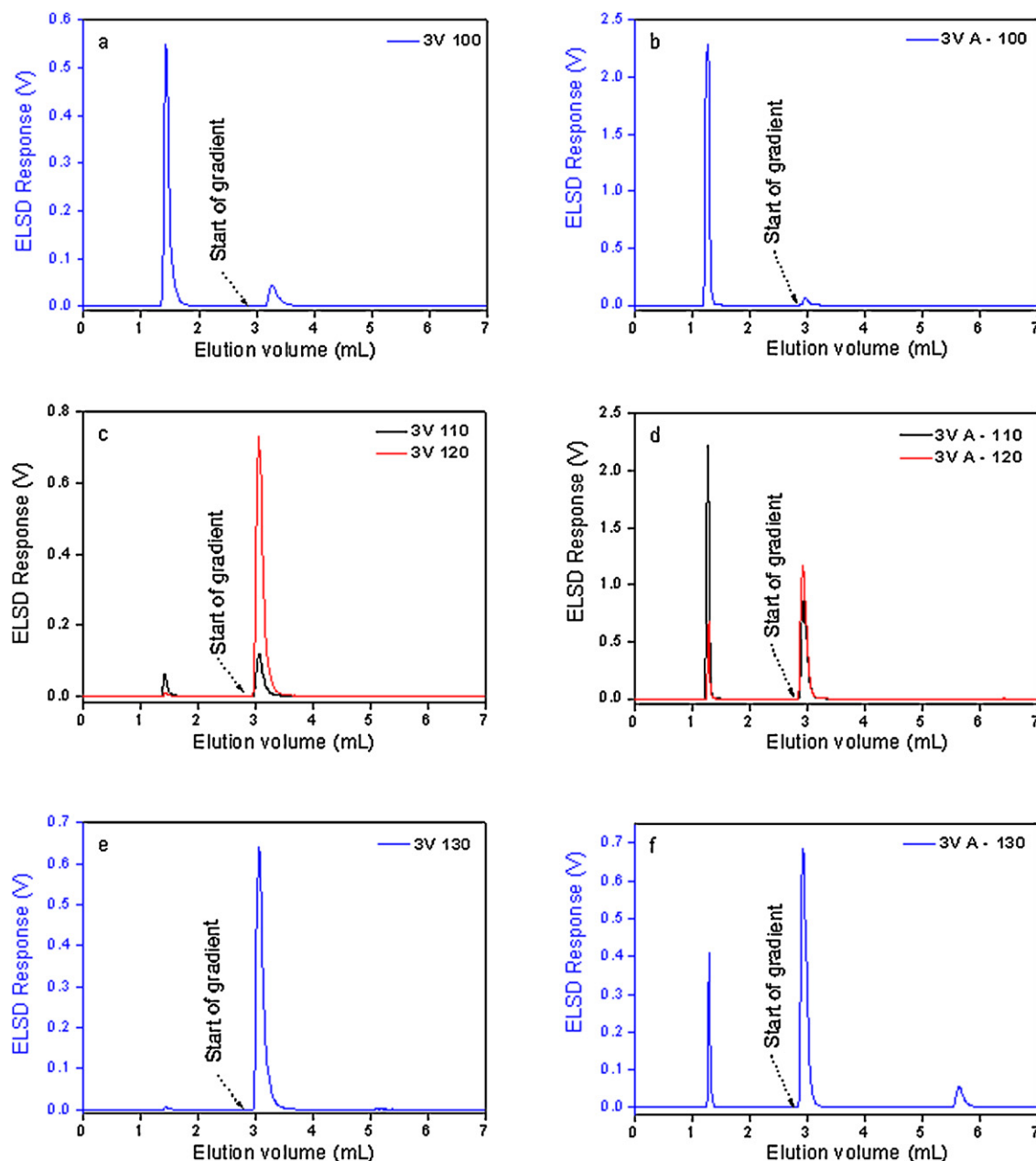
Stellenbosch University http://scholar.sun.ac.za

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

6   S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

Fig. 4. Chromatograms obtained after isocratic and gradient elution for the TREF fractions (100, 110, 120 and 130 °C) of 3V and 3VA.

being only eluted in the gradient. A similar chromatographic elution profile is obtained for 3V A-90, with the exception that the propylene rich EPC is absent for this fraction. Differences in the intensity (or concentration) of the peaks were observed for both fractions of the two IPC samples. The EPC and PE homopolymers eluted later (approximately at 5.8 mL) for the 3V A-90 sample, as compared to 3V 90 (eluted approximately at 5.5 mL), which indicates the higher ethylene content, and longer ethylene sequence lengths of this component in the 3V A-90 fraction compared to that of 3V 90.

The 100–130 °C TREF fractions of both samples are expected to consist of mainly highly crystalline iPP homopolymers. For all these TREF fractions, a low molar mass iPP component is eluted in 100% 1-decanol in SEC mode. A high molar mass iPP component elutes immediately after the start of the gradient (approximately 3.0 mL), for each of these TREF fractions, with the exception for the 100 °C fraction of 3V. From Fig. 4a, it is clear that the second component,

eluting at approximately 3.25 mL, shows a slight retention towards the stationary phase, possibly as a result of a more random distribution of the propylene sequences in terms of their stereochemistry, as well as the presence of ethylene sequences, which has already been proven from the SEC-FTIR results for this fraction [16] This indicates that EPC copolymers containing long ethylene sequences were adsorbed selectively and eluted only after the gradient at 3.25 mL. The peak intensity of the first iPP component (eluted in 100% 1-decanol, SEC mode) decreases, while the peak intensity increases for the second iPP component (eluted after the start of gradient) going from the 100 to the 130 °C fraction, which follows the TREF separation mechanism; iPP chains having the highest crystallinity and molar mass will crystallize out at higher temperature during the slow TREF crystallization step and are eluted in between the temperature range of 100–130 °C.

DSC analysis reveals that the 130 °C fraction of 3V A-130 exhibits two melt endotherms, and we assumed the presence of highly
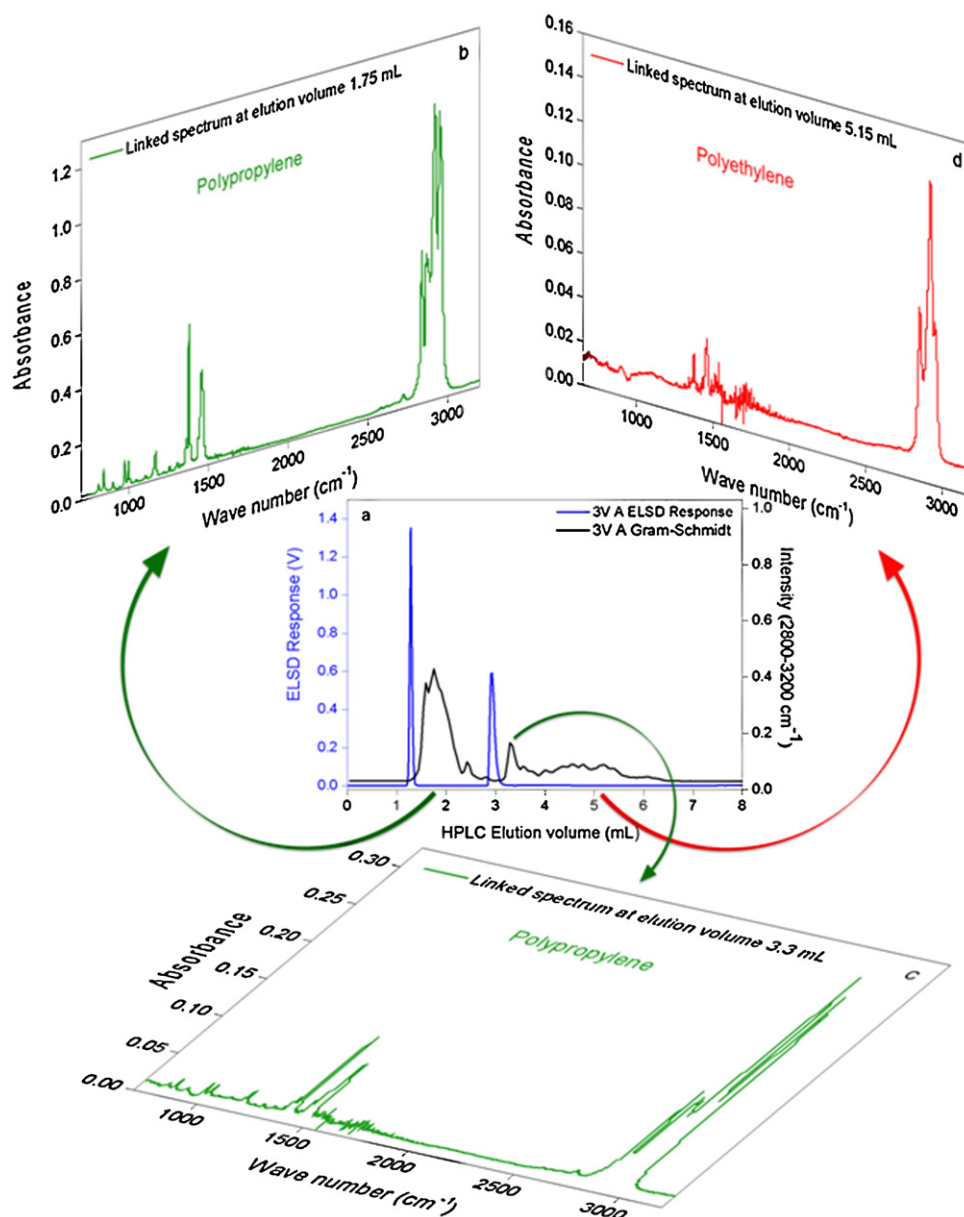
Stellenbosch University http://scholar.sun.ac.za

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

7

Fig. 5. HT HPLC-FTIR analysis for the bulk 3V A sample, (a) overlay of the ELSD response and Gram-Schmidt. (b), (c) and (d) Shows the individual linked spectra extracted from the Gram-Schmidt at elution volumes of 1.75, 3.3 and 5.15 mL, respectively.

crystalline PE homopolymer. These results were further confirmed by HT HPLC analysis of this fraction and the chromatogram obtained is given in Fig. 4f. Three clearly baseline-separated peaks were obtained for this fraction; the first two peaks are similar to what was observed for the other higher temperature fractions in both samples. In addition to these peaks, a component at 5.8 mL (not observed in 3V 130) was also observed, which corresponds to linear PE.

As described above, for the HT HPLC separation of all TREF fractions of both IPC samples 3V and 3V A, it is notable that the sample components were separated with regard to their chemical composition or ethylene/propylene content and tacticity distributions. A typical concentration detector, such as an ELSD (the principal choice for high temperature solvent gradient interaction chromatography), does not provide information about the exact compositional distribution within the individual components of the HPLC separated fractions. Therefore, the hyphenation of HT HPLC with FTIR is found to be an important technique for the analysis of

the exact chemical structure of these separated fractions [35–38]. A solvent elimination approach, utilising the LC transform interface (as explained in Section 2), was used to collect the separated fractions by depositing them onto a germanium disc, followed by subsequent analysis by offline coupling with FTIR to determine the compositional distribution present in each component. Quantitative analysis of the FTIR spectra for the identification of the exact chemical structure of individual components and their crystallinity distributions was accomplished as explained in our previous publications regarding offline coupling of SEC with FTIR [16,28].

HPLC-FTIR analysis results for the bulk 3V A sample are shown in Fig. 5. A comparison of the polymer concentration profile obtained from the ELSD with the FTIR scan (total polymer concentration by IR absorption, Gram-Schmidt (GS)) is shown in Fig. 5a. The overall shape and overlapping of both curves are comparable; a small shift in the HPLC elution volume axis for the GS was observed. This is caused by the difference in the length (volume of the capillary) of the transfer line used to connect the LC transform interface. In

Stellenbosch University http://scholar.sun.ac.za

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

8   S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

both cases two main peaks, one corresponding to low molar mass iPP (isocratic elution in 100% 1-decanol), and the other to relatively high molar mass iPP (eluted only after the start of gradient), are observed as reported for the bulk IPC sample 3V in our previous study [28]. In addition to this, the GS curve shows the polymer concentration profile up to an elution volume of 6 mL. In order to confirm the presence and prove the chemical identity of such very small amounts of the sample fractions that had adsorbed on the column and eluted later in TCB, we further analysed the individual spectra at peak maximum for each component by exporting the linked individual IR spectrum at the particular HPLC elution volume window. The results are shown in Fig. 5b, c and d. It is surprising that we are able to identify such late eluting minute fractions, using the power of infrared spectroscopy, which is not possible with a typical concentration detector such as an ELSD. The fractions eluting between the elution volumes 1.75 and 3.3 mL are found to be isotactic PP homopolymers, and the fraction at 5.15 mL consists of PE homopolymers with a certain extent of branching, which confirms the selective adsorption/desorption mechanism of this component on the Hypercarb column by using a solvent gradient from 1-decanol to TCB. These preliminary results show promise, and indicate that this hyphenated technique can provide a wealth of information regarding the microstructure of chemically different components in such complex polyolefins and olefin copolymers, especially if they are present in very low concentrations which would otherwise be undetectable by other detection systems.

The information on the chemical composition (propylene content and ethylene content) and their crystallinity distributions obtained by HT HPLC-FTIR for the 3V A bulk sample is given in Fig. 6. A decrease in the peak area ratio value of CH_3/CH_2 (Fig. 6a), and an increase in the ethylene content value (Fig. 6b) with increasing elution volume were observed, which is in agreement with the separation mechanism: linear propylene sequences were not well-absorbed on the column, while linear ethylene sequences are strongly retained. Relatively linear polyethylene homopolymers with less branching (lower CH_3/CH_2 value for late eluting fractions) eluted at approximately 6 mL. Highly crystalline propylene was found in the early eluting fractions (Fig. 6c) with no crystalline ethylene sequences (Fig. 6d), while crystalline polyethylene was found in the late eluting fraction, as expected. This again confirms the proposed adsorption/desorption mechanism on the Hypercarb stationary phase according to the E/P content and sequence lengths in the sample.

The bulk sample separation, deposition and FTIR analysis, still do not reveal the complete picture regarding the individual components and their distributions. Due to the relatively low ethylene content of this copolymer the results are overshadowed by iPP as the major component in this complex material. Therefore, the combination of Prep TREF and HT HPLC-FTIR analysis will be an excellent tool for the comprehensive analysis of chemically different components, as they are present in relatively higher concentrations in each TREF fraction; the results obtained for the most important, amorphous (30 °C) and all semi-crystalline (60, 80 and 90 °C) fractions of sample 3V A, are shown in Figs. 7 and 8. The higher temperature fractions are expected to be highly crystalline iPP according to the TREF separation mechanism, and are not discussed here.

A gradual decrease in the propylene content value (peak area ratio of CH_3/CH_2) across the GS with increase in elution volume is observed (see Fig. 7a) for the 30 °C fraction. The ethylene content value is zero (Fig. 7e) for the first eluting component (approximately at elution volume of 1.8 mL), and increases towards the late eluting fractions, showing much higher ethylene content values for the component eluting at approximately 6 mL. The first component of this fraction does not show either propylene or ethylene crystallinity values (see Fig. 8a and e) across the GS. These results indicate that the first eluting component (in 100% 1-decanol) is iPP, and the components eluting after the start of the gradient are
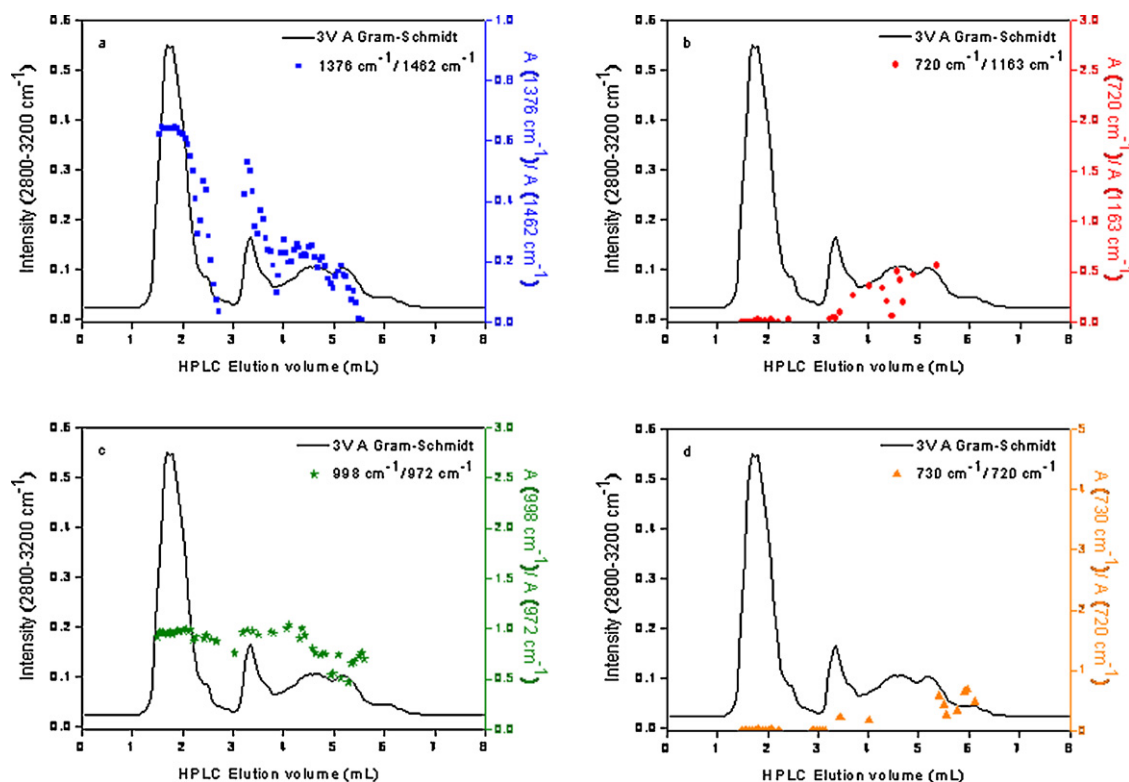

Fig. 6. HT HPLC-FTIR analysis for the bulk sample, 3V A, illustrating (a) the propylene (CH_3/CH_2) and (b) the ethylene (Et content) distributions as well as their crystallinity distributions (c) and (d) across Gram-Schmidt.
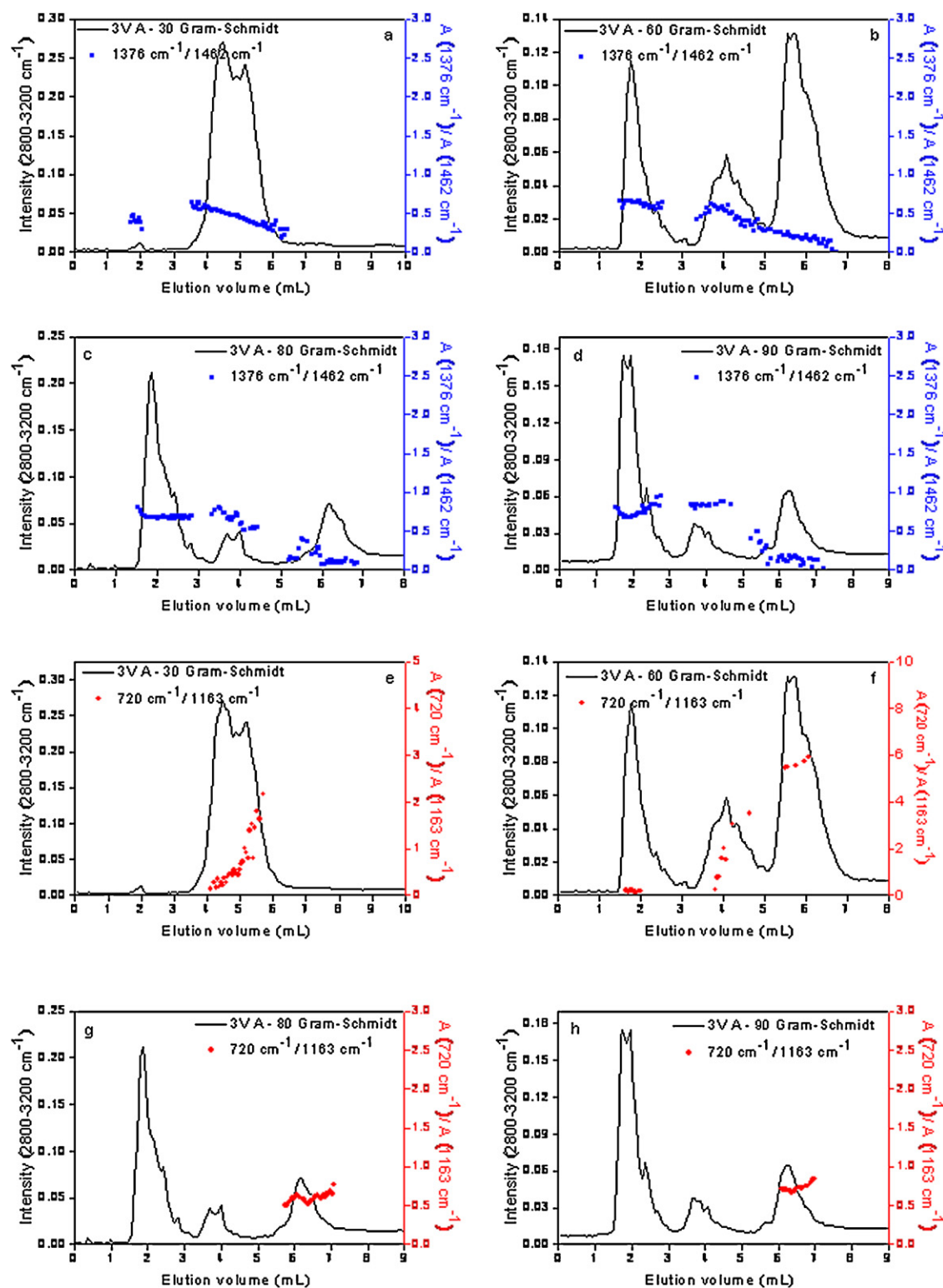
G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

9

Fig. 7. HT HPLC-FTIR analysis for the TREF fractions 30, 60, 80 and 90 of 3V A, illustrating propylene (CH_3/CH_2), and ethylene (Et content) distributions.

ethylene propylene copolymers. As observed from the HT HPLC results, the EPR, which is richest in propylene or having significant amounts of branches (shows higher value of CH_3/CH_2), elutes between 3.2 and 4.5 mL, while the EPR richest in ethylene is retained on the column and elutes in between 5 and 6.2 mL.

In order to further confirm these results, and to verify the exact chemical structure of these separated components, we analysed the individual IR spectra at peak maximum for each component,

the results of which are shown in Fig. 9a. It is clear that the component eluting at 2.0 mL shows the IR spectrum of iPP homopolymer, and the component eluting at 4.2 mL that of an ethylene propylene copolymer, or a propylene rich or branched copolymer, since the absorbances due to methylene deformation (at $1464\,cm^{-1}$) and methyl stretches (at $1377\,cm^{-1}$) show nearly equal peak intensities. The individual spectrum for the component eluting at 5.5 mL is that of PE homopolymer, with an additional shoulder
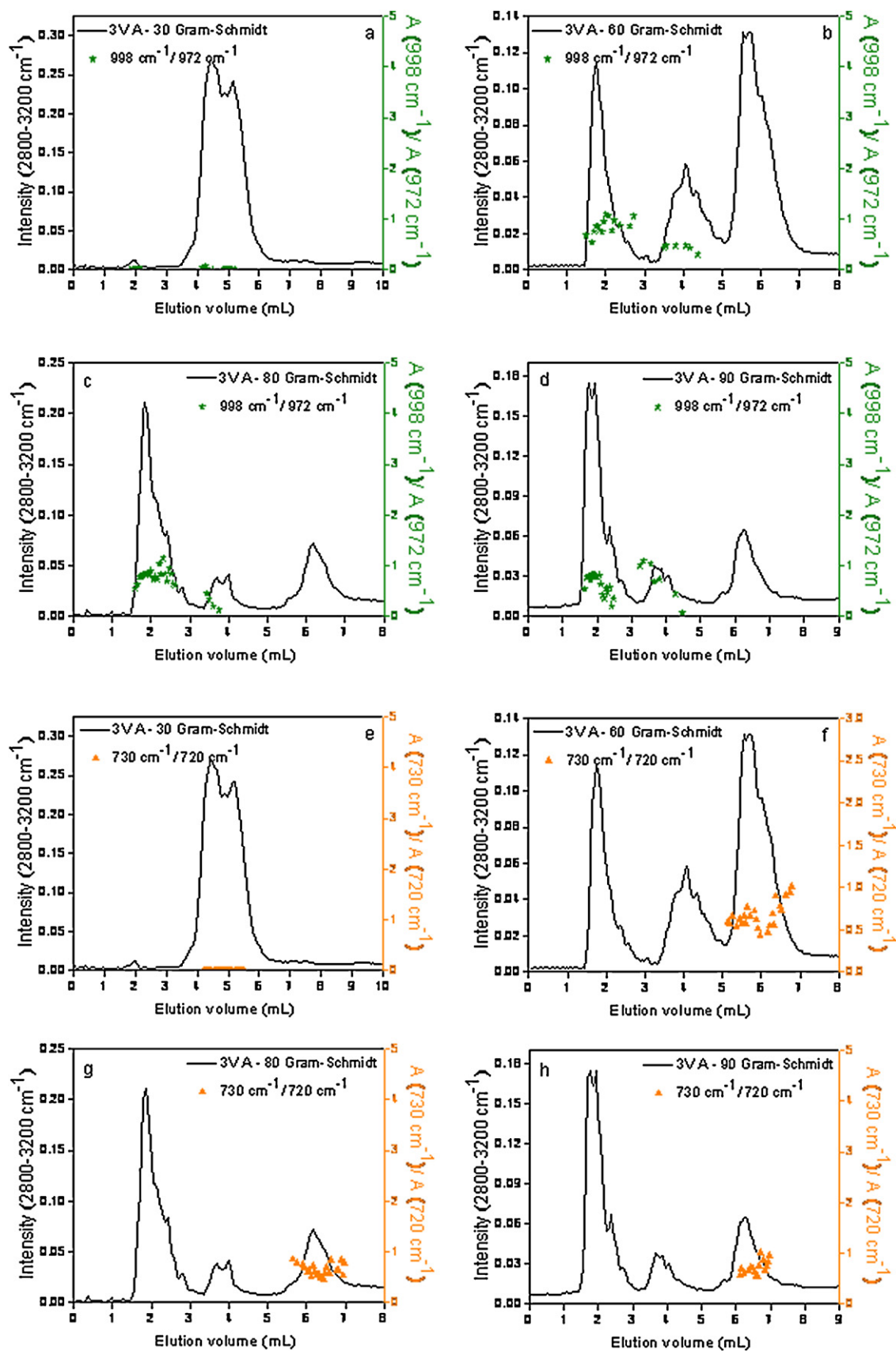
Stellenbosch University http://scholar.sun.ac.za

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

10 S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

Fig. 8. HT HPLC-FTIR analysis for the TREF fractions 30, 60, 80 and 90 of 3V A, illustrating propylene (a–d) and ethylene (e–h) crystallinity distributions.
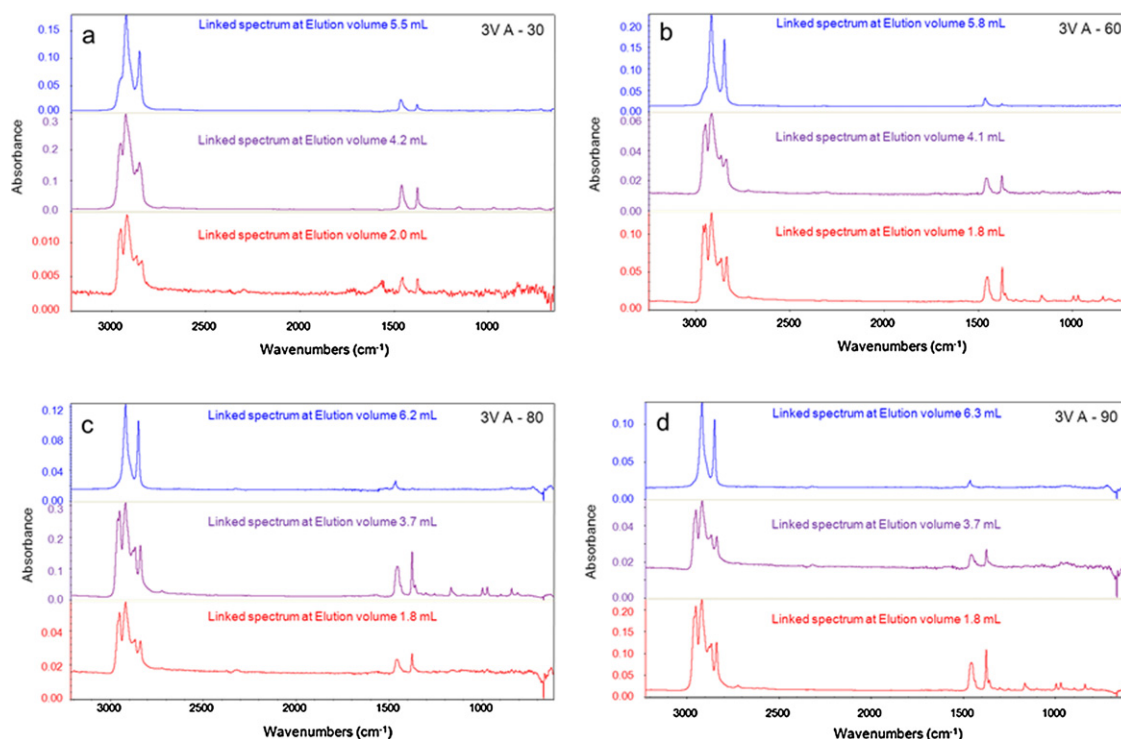
Stellenbosch University http://scholar.sun.ac.za

G Model
CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx
11

Fig. 9. Individual spectra exported from the Gram-Schmidt at peak maximum of all HPLC separated components in the TREF fractions 30, 60, 80 and 90 of 3V A.

at 2962 cm^{-1} due to methyl stretch. This plus the relatively low peak intensity of the band at 1377 cm^{-1} compared to the band at 1464 cm^{-1} indicates that this component is either an ethylene rich copolymer or less branched PE homopolymer, which was retained strongly on the column due to the appreciable amount of ethylene sequences.

The propylene contents for the 60, 80 and 90 °C TREF fractions show much higher values for the first two eluting peaks (with low or no ethylene content), and higher ethylene content values for the late eluting fractions (see Fig. 7). Fig. 10 indicates a similar trend in the propylene and ethylene crystallinity values. The individual spectra at peak maximum for each component are given in Fig. 9b–d. For the 60 °C fraction, the first eluting component shows the spectrum of iPP homopolymer, while the component eluting at 4.1 mL that of an ethylene propylene copolymer. The component eluting at 5.8 mL is found to be ethylene rich copolymer or less branched PE homopolymer. However, the intensity of the band at 2962 cm^{-1} (due to the methyl stretches) decreased compared to the component eluting at 5.5 mL in the 30 °C fractions, indicating lower propylene content, less branching, or low molar mass polymer (chain ends) in this component (see Fig. 7b and f), therefore retained longer and eluted at 5.8 mL.

Uniform propylene contents (Fig. 7c and d) and crystallinity distributions (Fig. 8c and d) are observed for the first two peaks in the 80 and 90 °C fractions, with no crystallisable ethylene content (Figs. 7g,h and 8g,h) across the GS, which indicates the lower and higher molar mass iPP components, respectively. This is again confirmed by analysing the linked spectrum at peak maximum (Fig. 9c and d) for the first two components which show the IR spectrum of iPP homopolymers with crystallisable propylene sequences (absorbance at 998 and 841 cm^{-1}). This can be compared to the components eluting at same elution volume for 30 and 60 °C fractions. The component eluting at 6.2 and 6.3 mL for the 80 and 90 °C fraction, respectively shows the IR spectrum (Fig. 9c and d) of HDPE. The methylene deformation band (at 1464 cm^{-1}) splits and an additional absorbance at 1473 cm^{-1} is observed due to the crystallinity

of polyethylene. The absorbance originating from methyl stretches (at 1377 cm^{-1}) is absent or its intensity is very low, indicating that there is no appreciable amount of propylene or branching for this component. These results are in accordance with the ethylene content and the crystallinity distribution illustrated in Fig. 8g and h; only crystalline ethylene sequences are present in the late eluting fractions.

From the overall HT HPLC-FTIR results, it is observed that the elution volume of the first component in each fraction is nearly the same. The elution volume of the second component in the 80 and 90 °C fractions decreased compared to the similar component in the 30 and 60 °C fraction, and the elution volume of the late eluting fraction increased from the 30 to the 90 °C fraction. The first component for all the fractions is iPP homopolymer which co-crystallized with other components during the TREF crystallization step, either due to differences in their tacticity or molar mass distribution compared to other PP chains. The lower elution volume for the second component of the 80 and 90 °C fractions (3.7 mL) as compared to the same component for the 30 and 60 °C fractions (4.2 mL), indicates the longer ethylene sequences present in these fractions (30 and 60 °C). For the late eluting component the elution volume increases from 5.5 to 6.3 mL for all fractions (30–90 °C), accordingly, this indicates the difference in the chemical structure or distribution of the chemical composition in each component, which changes from ethylene rich EPC to linear or slightly branched crystalline PE homopolymers as the TREF fractionation temperature increases.

Finally, a complete separation according to CCD and MMD for these fractions was achieved by HT 2D LC analysis, where the HT HPLC separation is hyphenated to HT SEC. The 2D contour plots for the 30 °C and all mid-elution temperature TREF fractions of the two IPC samples are given in Fig. 10. Separation of low molar mass iPP and high molar mass EPR is realised for the 30 °C fraction of 3V (Fig. 10a). It is interesting to note that for this fraction there are two low molar mass components which are eluted in SEC mode with a slight difference in their molar mass. It is assumed that the first component (early eluting, approximately between 4.125 and
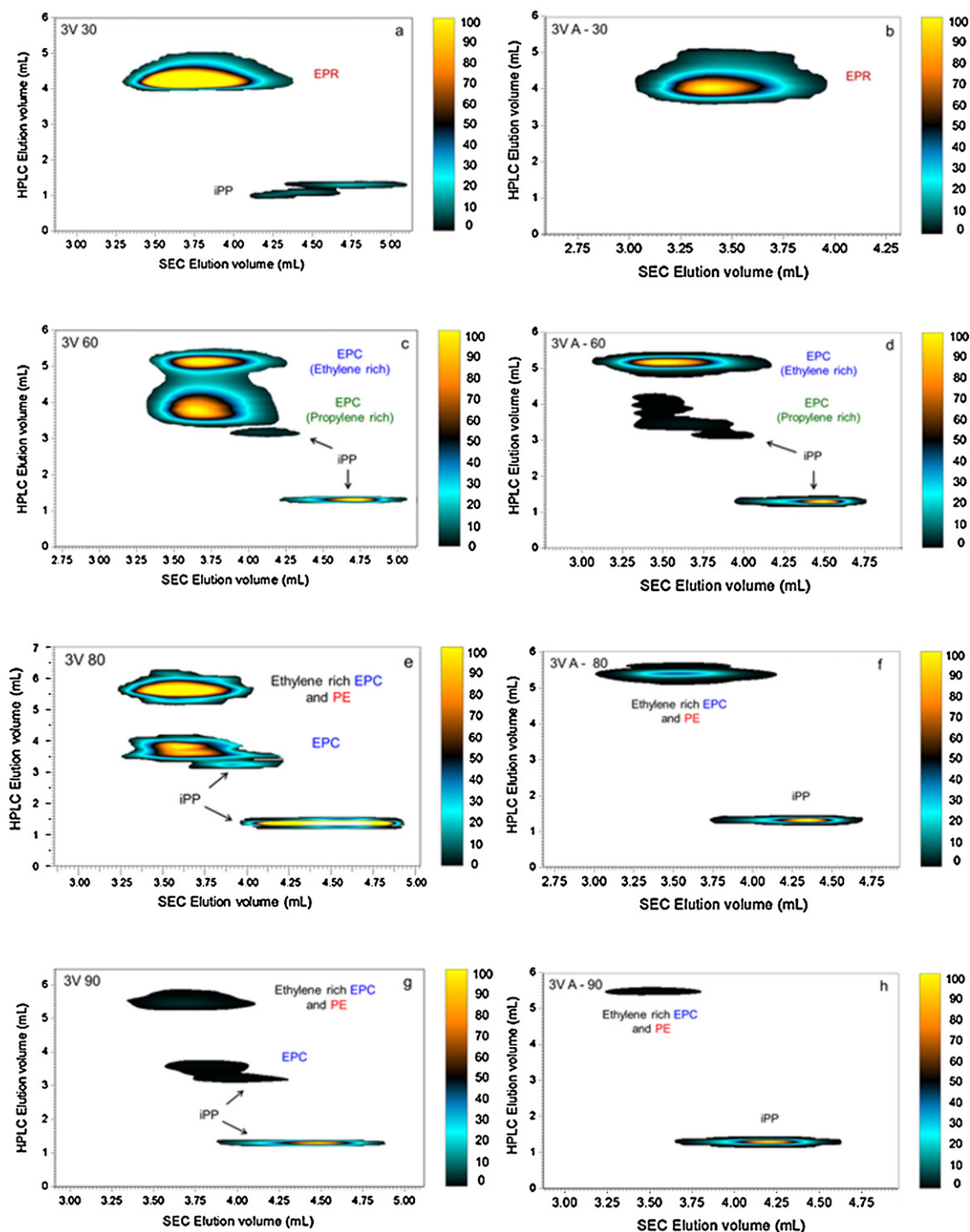
Fig. 10. HT 2D-LC contour plots for the fractions 30, 60, 80 and 90 of 3V (left side) and 3V A (right side).

4.75 mL, SEC axis) is comprised of highly branched chains, which no longer show adsorption towards the stationary phase due to the interruption of the long continuous methylene sequences by the branch points, or even random ethylene–propylene sequences in the backbone chain. These chains are not able to access the pores of the SEC column due to their large hydrodynamic volume and are eluted earlier than the low molar mass iPP that is usually observed. EPR components of 3V A-30, show quite high molar masses as compared to the 3V 30, and no low molar mass iPP component is observed in this fraction (see Fig. 10b).

The separation of EPC of similar molar masses, with differing ethylene and propylene sequence lengths, and a clear molar mass separation for the low and high molar mass iPP components, was obtained for the 60 °C fraction of both samples (Fig. 10c and d). For the 80 and 90 °C fractions of sample 3V (Fig. 10e and g), the lower molar mass iPP component eluted in pure 1-decanol, and a second slightly higher molar mass component eluted after the start of the gradient. EPC with different ethylene and propylene sequences, as well as PE homopolymers of similar molar masses, eluted according to their interaction with the Hypercarb column. There is a
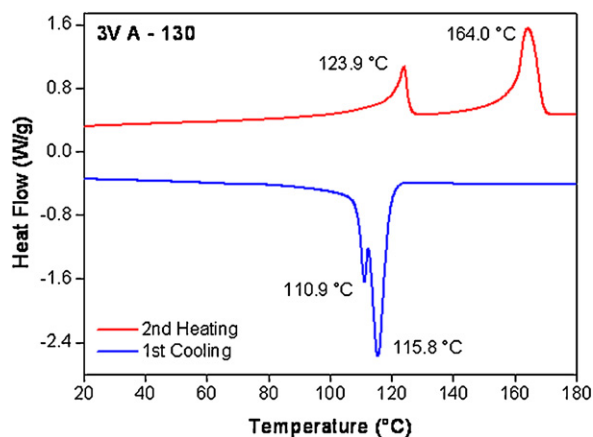
Fig. 11. DSC curve shows two melt endotherms for the 3V A-130. Heating and cooling rates were 10 °C/min.

Fig. 13. Individual spectra exported from the Gram-Schmidt at peak maximum of all HPLC separated components in the TREF fraction 130 of 3V A.

clear separation between the iPP and EPC copolymers, EPC dominated by longer propylene sequences elute closer to iPP while those dominated by longer ethylene sequences elute together with PE homopolymers (eluting at approximately 6.0 mL). The same fractions for 3V A show only low molar mass iPP and high molar mass EPC (ethylene rich). For 3V A-80, EPC (ethylene rich) eluted with PE homopolymers having similar molar mass, at approximately 5.5 mL.

In order to confirm the results obtained for the 130 °C TREF fraction by DSC (which shows two melt endotherms, see Fig. 11) and HT HPLC, and to identify the individual components in this higher temperature fraction, HT HPLC-FTIR analyses were performed and the results are shown in Figs. 12 and 13. The first two peaks show uniform propylene contents, and their crystallinity distribution across GS indicates the presence of highly crystalline iPP
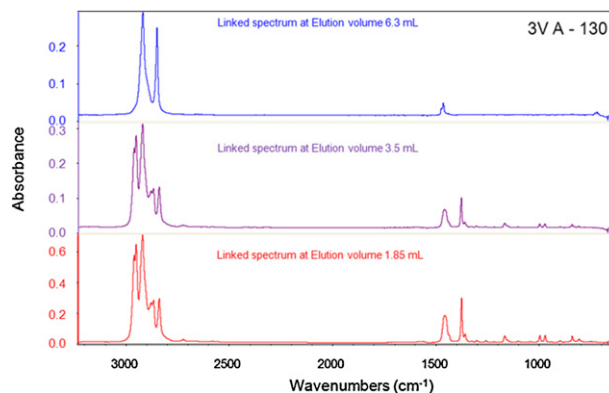
homopolymers. The late eluting component shows higher ethylene content and ethylene crystallinity, and is essentially highly crystalline PE homopolymer. These results are confirmed by the analysis of the individual spectra exported at the peak maximum for each component from the GS plot (see Fig. 13). The FTIR spectra of iPP homopolymers are observed for the first two components. The component eluting at 6.3 mL shows the characteristic absorption bands of highly crystalline PE homopolymer, identified as HDPE.

Finally, a complete separation for this fraction is obtained by HT 2D-LC analysis; the 2D contour plot is given in Fig. 14 with the chemical composition information obtained for each component by HT HPLC-FTIR analysis. A clear separation of three components in this fraction according to CCD and MMD is obtained. The iPP component with a low molar mass eluted in 100% decanol followed by the slightly higher molar mass iPP, and relatively medium molar mass PE homopolymer, which eluted approximately at 5.6 mL. As
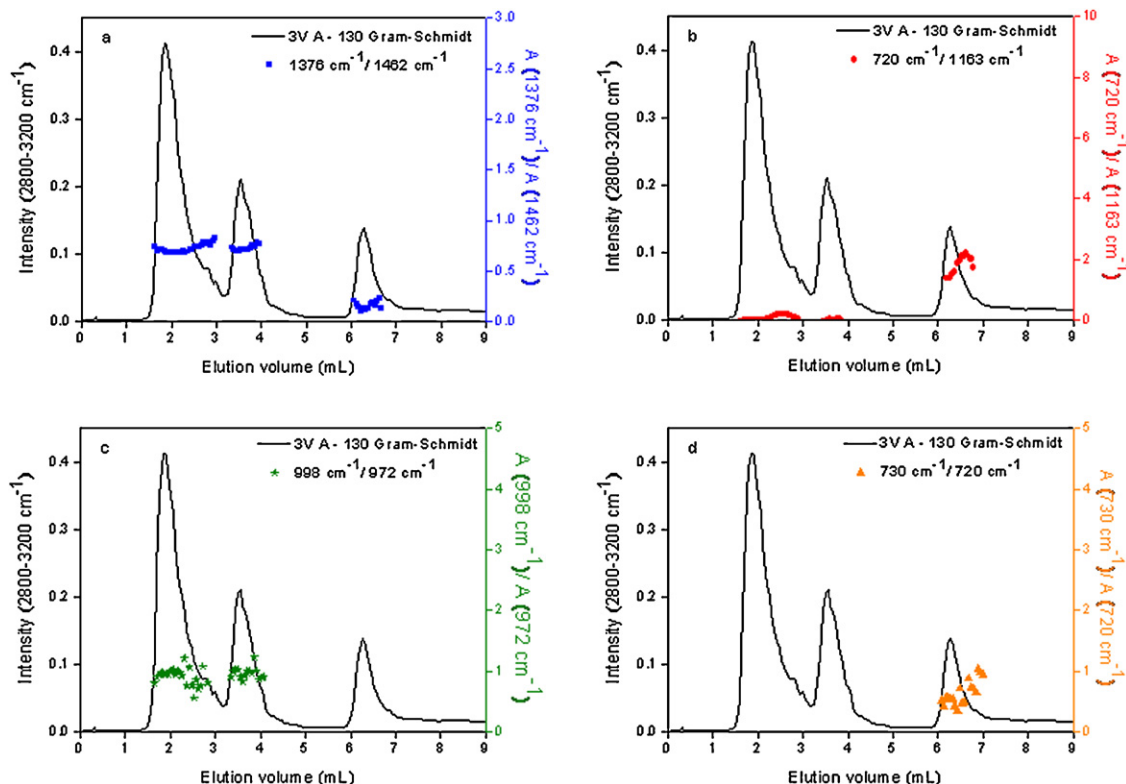

Fig. 12. HT HPLC-FTIR analysis for the TREF fraction 130 of sample 3V A, illustrating propylene and ethylene content and their crystallinity distributions.
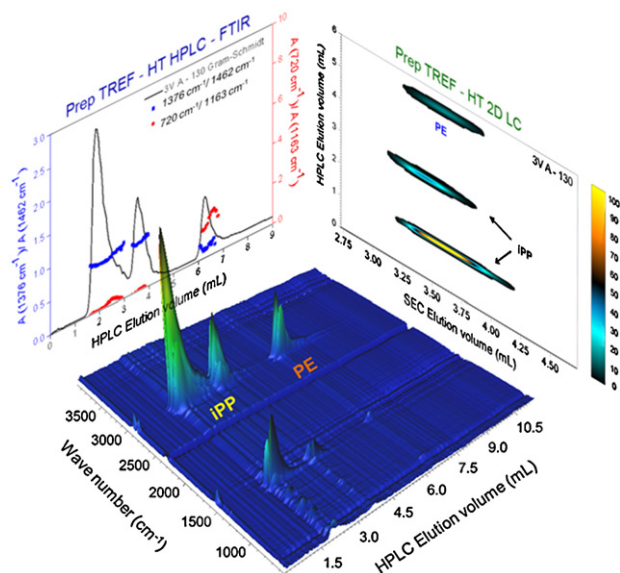
Stellenbosch University http://scholar.sun.ac.za

G Model

CHROMA-354116; No. of Pages 14

ARTICLE IN PRESS

14   S. Cheruthazhekatt et al. / J. Chromatogr. A xxx (2013) xxx–xxx

Fig. 14. HT HPLC and HT 2D-LC analysis for the 130 °C TREF fraction of sample 3V A.

the results demonstrate, the combination of Prep TREF and HT 2D-LC represents a complete characterisation of all TREF fractions in terms of both molar mass and chemical composition distribution, accomplished within a relatively short analysis time.

4. Conclusions

Preparative fractionation and subsequent analysis of the individual fractions by high temperature solvent gradient interaction chromatography and 2D LC is found to be an effective method for the complete characterisation of complex polymeric materials such as IPC's. A solvent gradient from 1-decanol to TCB with Hypercarb as the stationary phase at 160 °C was used for the chromatographic separation of the individual components in the complex TREF fractions of two IPC samples. Ethylene propylene random copolymer with a small amount of iPP was found in the 30 °C amorphous fraction of sample 3V. The presence of highly branched components, which eluted in SEC mode, is also observed for this fraction. A relatively higher molar mass EPR was observed in the similar TREF fraction of 3V A. EPC with different ethylene and propylene sequence lengths and PE homopolymers were observed in all mid-elution temperature fractions (60, 80, and 90 °C) of both samples. From the HT HPLC analysis results, it is concluded that the chemical structure of the components are different in the equivalent TREF fractions of both samples. Low and high molar mass iPP was found to be the major constituent in the higher temperature TREF fractions (above 100 °C). These overall results illustrate the bright future for the use of HT HPLC as an efficient separation technique, and furthermore, as the primary tool of choice to determine the compositional heterogeneity in complex TREF fractions. Other techniques, such as HT SEC and DSC, are not able to differentiate between these samples, which show similar MMD profiles and melting behaviour for these fractions – according to their microstructure. The chemical composition distributions and the crystallinity distributions of the HPLC separated components in the most important TREF fractions of IPC 3V A, were determined by offline coupling of HT HPLC with FTIR. The presence of highly

crystalline PE homopolymers in the 130 °C TREF fraction of sample 3V A was also confirmed. To this date, this is the only method to identify the actual chemical composition present in such complex polyolefins. For the first time, a complete microstructural analysis of all fractions of IPC's, in terms of CCD and MMD, is reported by the combination of a number of cross fractionation methods.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2013.02.052.

References

[1] Z.Q. Fan, Y.Q. Zhang, J.T. Xu, H.T. Wang, L.X. Feng, Polymer 42 (2001) 5559.
[2] H.N. Cheng, G.H. Lee, Macromolecules 20 (1987) 436.
[3] M. Francis, Mirabella Jr., Polymer 34 (1993) 1729.
[4] Z. Sun, F. Yu, Y. Qi, Polymer 32 (1991) 1059.
[5] L.H. Sperling, Introduction to Physical Polymer Science, 4th ed., John Wiley & Sons, 2006.
[6] L. Wild, T. Ryle, D. Knobeloch, I.R. Peat, J. Polym. Sci., Polym. Phys. Ed. 20 (1982) 441.
[7] L. Wild, Adv. Polym. Sci. 98 (1991) 147.
[8] B. Monrabal, J. Appl. Polym. Sci. 52 (1994) 491.
[9] B. Monrabal, Macromol. Symp. 110 (1996) 81.
[10] B. Monrabal, J. Blanco, J. Nieto, J.B.P. Soares, J. Polym. Sci., Part A: Polym. Chem. 37 (1999) 89.
[11] B. Monrabal, J. Sancho-Tello, N. Mayo, L. Romero, Macromol. Symp. 257 (2007) 71.
[12] S. Anantawaraskul, J.B.P. Soares, M. Paula, W. Adams, Adv. Polym. Sci. 182 (2005) 1.
[13] H. Pasch, R. Brüll, W. Udo, B. Monrabal, Macromol. Mater. Eng. 279 (2000) 46.
[14] H. Pasch, M.I. Malik, T. Macko, Adv. Polym. Sci. 251 (2013) 77.
[15] W. Holtrup, Makromol. Chem. 178 (1977) 2335.
[16] E. de Goede, P. Mallon, H. Pasch, Macromol. Chem. Phys. 295 (2010) 366.
[17] T. Macko, H. Pasch, Macromolecules 42 (2009) 6063.
[18] T. Macko, F. Cutillo, V. Busico, R. Brüll, Macromol. Symp. 298 (2010) 182.
[19] T. Macko, R. Brüll, G. Alamo, Y. Thomann, V. Grumel, Polymer 50 (2009) 5443.
[20] T. Macko, R. Brüll, Y. Zhu, Y. Wang, J. Sep. Sci. 33 (2010) 3446.
[21] T. Macko, R. Brüll, R.G. Alamo, F.J. Stadler, S. Losio, Anal. Bioanal. Chem. 399 (2011) 1547.
[22] R. Roy, M.D. Miller, D.M. Meunier, A.W. deGroot, W.L. Winniford, F.A. Van Damme, R.J. Pell, J.W. Lyons, Macromolecules 43 (2010) 3710.
[23] A. Ginzburg, T. Macko, V. Dolle, R. Brüll, J. Chromatogr. 1217 (2010) 6867.
[24] D. Lee, M.D. Miller, D.M. Meunier, J.W. Lyons, J.M. Bonner, R.J. Pell, C.Li.Pi. Shan, T. Huang, J. Chromatogr. 1218 (2011) 7173.
[25] A. Ginzburg, T. Macko, V. Dolle, R. Brüll, Eur. Polym. J. 47 (2011) 319.
[26] R. Chitta, A. Ginzburg, G. Doremaele, T. Macko, R. Brüll, Polymer 52 (2011) 5953.
[27] T. Macko, A. Ginzburg, K. Remerie, R. Brüll, Macromol. Chem. Phys. 213 (2012) 937.
[28] S. Cheruthazhekatt, T.F.J. Pijpers, G.W. Harding, V.B.F. Mathot, H. Pasch, Macromolecules 45 (2012) 2025.
[29] S. Cheruthazhekatt, T.F.J. Pijpers, G.W. Harding, V.B.F. Mathot, H. Pasch, Macromolecules 45 (2012) 5866.
[30] G.J.P. Ray, E. Johnson, J.R. Knox, Macromolecules 10 (1977) 773.
[31] J.C. Randall, Macromolecules 11 (1978) 33.
[32] T. Kanezaki, K. Kume, K. Sato, T. Asakura, Polymer 34 (1993) 3129.
[33] H. Tan, L. Li, Z. Chen, Y. Song, Q. Zheng, Polymer 46 (2005) 3522.
[34] C. Zhang, Y. Shangguan, R. Chen, Y. Wu, F. Chen, Q. Zheng, G. Hu, Polymer 51 (2010) 4969.
[35] A. Albrecht, L.C. Heinz, D. Lilge, H. Pasch, Macromol. Symp. 257 (2007) 46.
[36] H. Pasch, A. Albrecht, R. Brüll, T. Macko, W. Hiller, Macromol. Symp. 282 (2009) 71.
[37] A. Albrecht, R. Brüll, T. Macko, P. Sinha, H. Pasch, Macromol. Chem. Phys. 209 (2008) 1909.
[38] V. Dolle, A. Albrecht, R. Brüll, T. Macko, Macromol. Chem. Phys. 212 (2011) 959.