 DOI: 10.1002/masy.200751409

Propylene Copolymers with Odd Carbon Number Olefins

Ioan Tincul,[*1] *Dawie Joubert,*[2] *Ron Sanderson*[1]

Summary: Preliminary investigation on propylene copolymers with odd carbon number olefin are reviewed. Additional experimental data presents propylene copolymers with 1-heptene and 1-nonene having higher impact strength and lower tensile strength values than copolymers of propylene and 1-pentene.Thermoanalysis shows that the melting temperatures of the different copolymers decreases with increasing comonomer content. Slight changes were observed between the different propylene/1-heptene copolymer melting and propylene/1-pentene while the 1-nonene copolymers show broadening of the melting curves as the comonomer content increases. It was highlighted that the source of novelty for these polymers is the comonomer type and content.

Keywords: co-polymers; Fischer-Tropsch; olefins; polymerization; propylene

Introduction

Ethylene, 1-butene and 1-hexene have traditionally been the commoners of choice for the copolymerization of propylene while the application off odd carbon number olefin has until recently been neglected. Even carbon number olefins are obtained mainly by oligomerization while the main source of odd carbon number olefin is the Fischer-Tropsch process. The Fischer-Tropsch process, an olefin source alternative to oil is becoming more market friendlier as the energy demand increases and oil is becoming less affordable. The route to olefins is shorter and a complex mixture of hydrocarbon rich in olefin is obtained. Therefore the Fischer-Tropsch process is viewed as a sound solution for the oil crisis and a resource for comonomers with potential application.

Since 1996 when the first paper on propylene/1-pentene copolymers[1] was published Sasol Technology was pioneering the field with other contribution from the University of Stellenbosch and University of Budapest. A couple of patents[2–4] present methods of preparation and margins of application. A large experimental work and scientific interpretation is captured in less known graduation thesis[5–7] while most of the additional published literature refers to particular aspects. The introductory papers on propylene copolymers with higher alpha olefins[8,9] were followed as well by some systematic particular studies. The aim of this paper is to review the main publications that refer to propylene copolymerization with odd carbon olefin over Ziegler Natta catalyst under, to update some experimental results and discuss some particularities of these polymers insufficiently yet known.

Experimental Part

A 10-litre stainless steel automated autoclave was thoroughly flushed with nitrogen and 3 000 g of purified heptane added. The temperature was increased to 70 °C and the catalyst system comprising 50 ml of a 10%

[1] The IUPAC/UNESCO Centre for Macromolecules and Material Science- University of Stellenbosch, South Africa
E-mail: ioan.tincul@metroweb.co.za
[2] Sasol Technology R&D, PO Box 1, Sasolburg, South Africa

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

solution of tri-ethyl aluminium (TEA) in heptane, 2 ml diphenyl dimethoxy silane and 1 g of a supported titanium chloride catalyst prepared as previously described[4] was added and stirred for 5 minutes. After this "ageing" period, propylene and the comonomer were continuously introduced over a period of 25 minutes at a fixed ratio after which the monomer feeds were stopped and the reaction continued for a further 95 minutes. Molecular weight was regulated with hydrogen and the comonomer content by the propylene/comonomer ratio. The catalyst in the copolymer slurry was deactivated with iso-propanol, filtered, washed and dried.

The 1-pentene content of the copolymers was determined on a Perkin Elmer FT-IR 1720X instrument on compression moulded film samples. A calibration curve was obtained from standard melt-blended samples of polypropylene with known poly(1-pentene) content. The moderately strong peak at 969 cm^{-1} in the spectrum of polypropylene (PP) arises from coupling vibrations, while the rocking of the CH_3 group at 734 cm^{-1} was used to quantify the concentration of the propyl branch.

The molecular weights of the copolymers were determined on a Waters 150 CV GPC with a refractive index detector in 1,2,4-trichlorobenzene solution at 150 °C. Melt flow index (MFI) was determined according to ASTM D 1238, mechanical properties according to ASTM D 638 M and notched Izod impact strength according to ASTM 256. Melting behavior was determined on a Perkin Elmer DSC-7 fitted with a TAC 7/PC instrument controller. The samples were heated from 50 to 200 °C at 20 °C/min, held at 200 °C for 1 minute, cooled to 50 °C at a rate of 20 °C/min during which time the crystallization curve was recorded. At 50 °C, the temperature was kept constant for 1 min and the melting curve was recorded between 50 and 200 °C at a heating rate of 10 °C/min.

Results and Discussion

Propylene/1-Pentene Random Copolymers

Different aspects are presented in the literature: polymerization on Ziegler Natta catalyst;[1–5,10,12,14] characterization[1–6,10,11,13] structure, morphology, thermo-analysis[5–7] application properties and processing.[1–6,10,15] The influence of randomly dispersed 1-pentene units on the

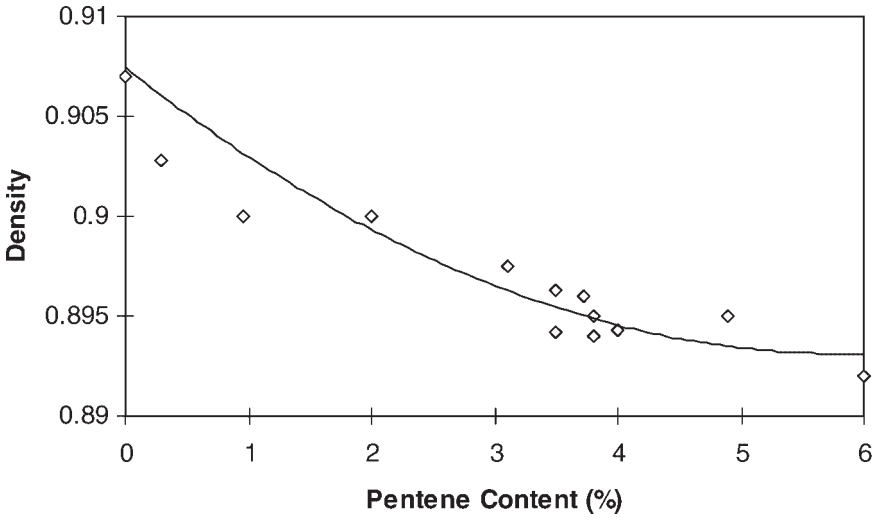

Figure 1.
Density (g/cm^3) of propylene/1-pentene random copolymers.[6]

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

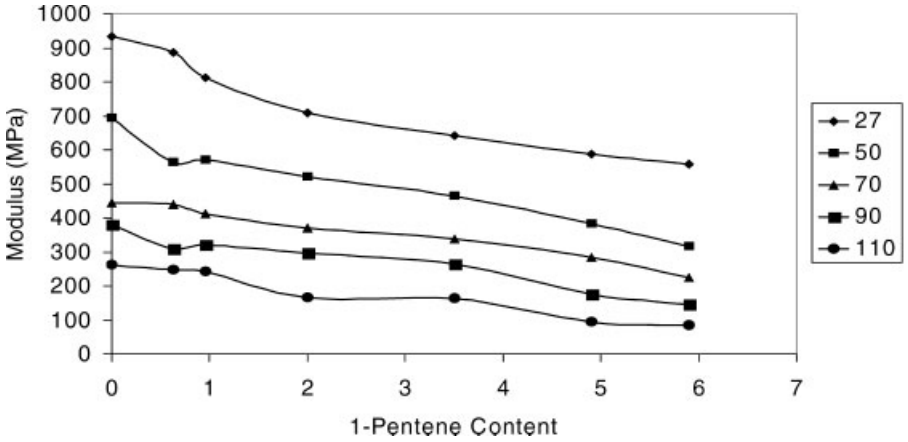

Figure 2.
Modulus of random copolymers as a function of 1-pentene content at different temperatures (27,50, 70, 90, and 110 °C).[6]

crystal structure and properties is reflected in some particularities that can be summarised as follows:[6,7]

1 Together with the usual alpha polymorph, the unique gamma crystalline form appears
2 An increase in the 1-pentene content results in a decrease in crystallinity
3 The increase in comonomer content results in a decrease in melting temperature, equilibrium melting temperature and melting enthalpy.
4 The increase of 1-pentene increases impact strength improves optical properties.

The inverse relationship between density and comonomer content is known from early literature. Measurements[6] showed that the density (ρ) is directly related to 1-pentene content (P) as shown in Figure 1. For these random copolymers it was found to approximately comply with the equation $\rho = 0.0001\mathrm{P}^2 - 0.005\mathrm{P} + 0.908$.[10]

The influence of the crystallinity on short term deformation properties is also known. Experimental data confirm the

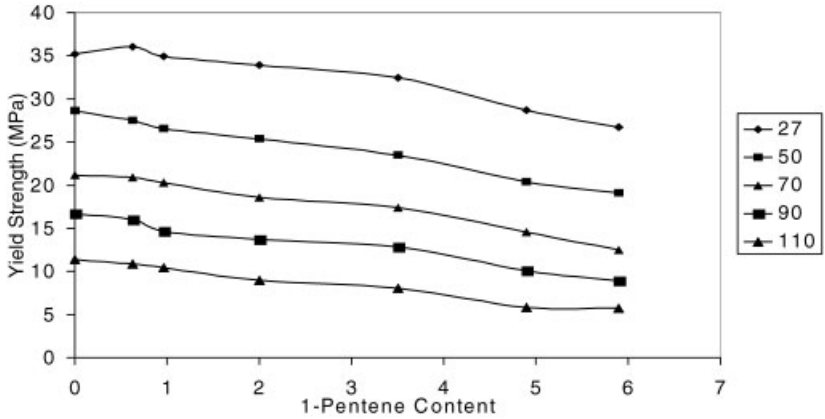

Figure 3.
Tensile yield strengths of propylene random copolymers with 1-pentene as comonomer.[6]

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

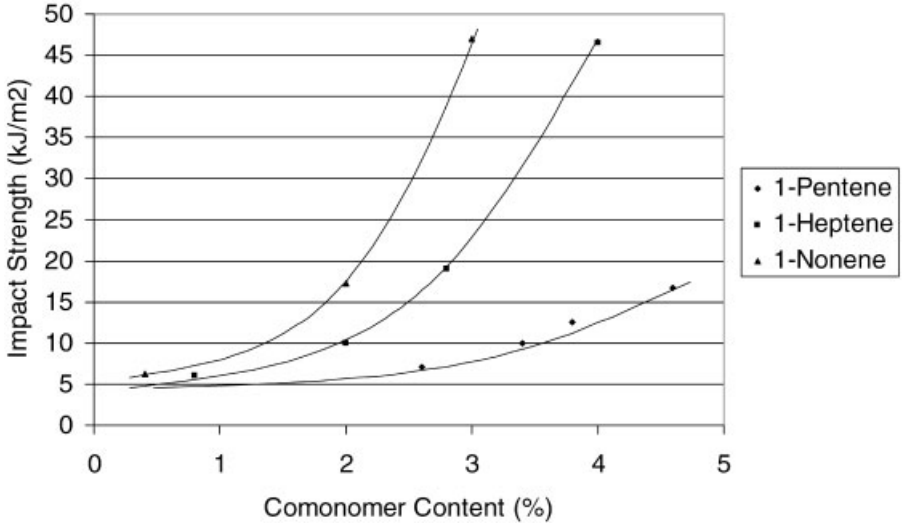

Figure 4.
Dependence of Impact Strength on Comonomer Type and Content.

decrease in modulus and tensile strength at yield with an increase in 1-pentene content and therefore decreased crystallinity as shown in Figure 2 and 3 below.[6]

Rheological measurements show a normal processing behavior of propylene/1-pentene random copolymer and processing was be done successfully on similar equipment as for the commercial propylene/ethylene random copolymer.[6,14,15]

Propylene/1-Heptene and Propylene/1-Nonene Random Copolymers

Propylene copolymers with higher alpha olefin Fischer-Tropsch derived have been also been previously described.[4,8,9] As for propylene-1-pentene, also for the propylene-1-heptene and propylene/1-nonene polymers the mechanical properties such as modulus, hardness, tensile strength at yield, impact strength and as well the crystalline

Table 1.
Thermal Properties of Propylene/α-Olefin Copolymers.

	MFI (dg/min)	Melting Temp °C)	Fusion Enthalpy (J/g)*	Crystallinity (%)
1-Pentene (%)				
0	7.4	166	101	48.3
2.6	3.5	146	55.5	26.5
3.4	7	145	53.5	25.6
3.8	5	145	54	25.8
4.6	6.5	142	32.5	15.5
1-Heptene (%)				
0.8	11	150	61	29.2
2.0	13	150	53	25.3
2.8	10	149	51	24.4
4.0	5	149	48	22.9
1-Nonene (%)				
0.4	2.4	152	63	30.1
1.8	2.3	151	60	28.7
2.1	3.3	150	60	28.7
3.0	2.2	149	57.5	27.5

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

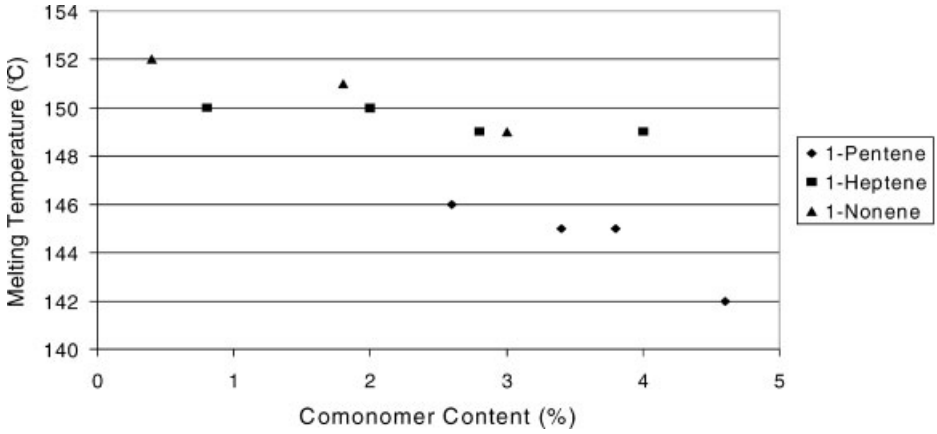

Figure 5.
Melting Temperatures of Different Propylene/α-Olefin Copolymers.

melting temperature depend on crystallinity.[4]

In Figure 4 the impact strength of the different copolymers are observed to be related to comonomer content. For the propylene copolymers, the impact strength does not start increasing immediately as was observed for the ethylene copolymers. Here the increase in impact strength is more gradual and follow an exponential increase with comonomer content in the range studied.

In Table 1 the thermal properties of some propylene copolymers prepared with 1-pentene, 1-heptene and 1-nonene are compared. Crystallinity was calculated from fusion enthalpy based on a value of 209 J/g for 100% crystalline material.[5]

The melting temperatures of the different copolymers show a general decrease with increasing comonomer content as seen in Figure 5.

In Figure 6–8 the DSC melting and crystallization curves are presented for the

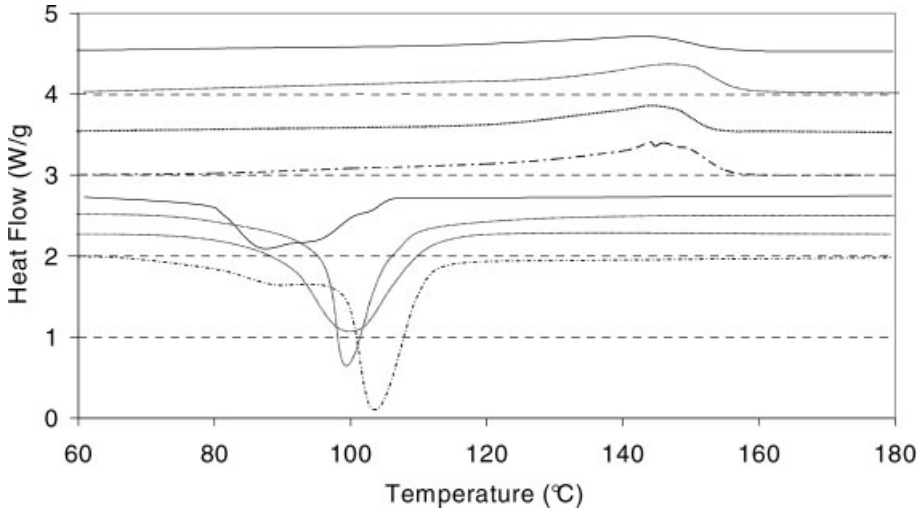

Figure 6.
Melting and Crystallization Curves for Propylene/1-Pentene Copolymers. ----------2.6%, ———3.4%, ·····3.8%, ————4.6%.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

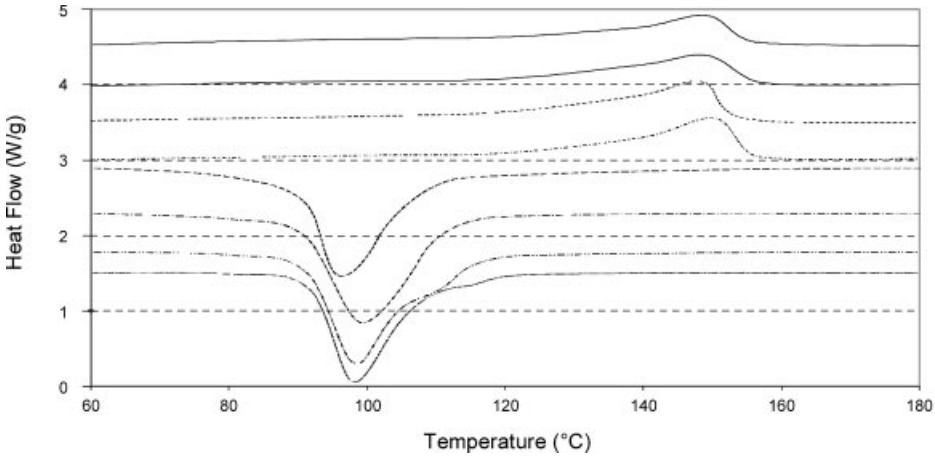

Figure 7.
Melting and Crystallization Curves for Propylene/1-Heptene Copolymers. 0.8%, 1.0%, 2.8%, 4.0%.

propylene/1-pentene, prtopylene/1-heptene and propylene 1-nonene polymers.

For the propylene/1-pentene copolymers shown in Figure 6 double melting peaks start to be visible for the copolymer.

As seen in Figure 7 only very slight changes were observed between the different propylene/1-heptene copolymer melting curves. Increasing the 1-heptene content from 0.8 to 4% decreased the melting temperature by only 1 °C, which indicates that this difference in comonomer content did not have a substantial influence on lamellar thickness. For the 1-nonene

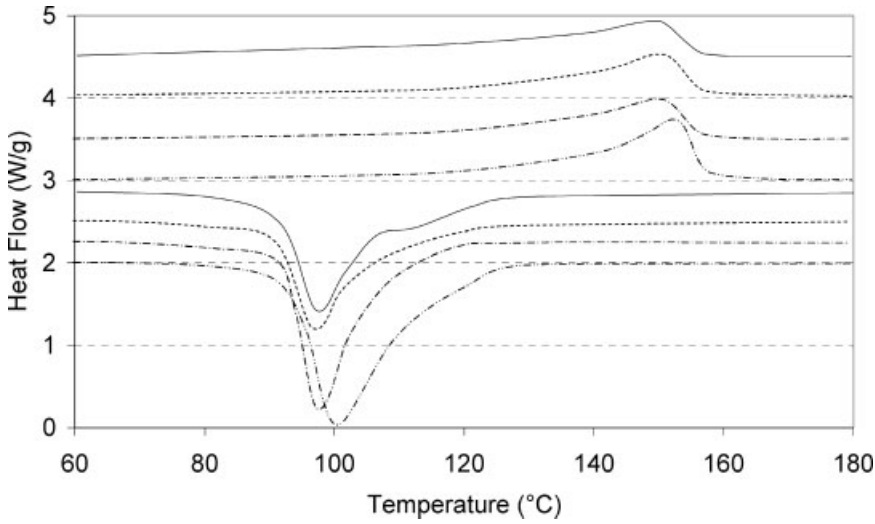

Figure 8.
Melting and Crystallization Curves for Propylene/1-Nonene Copolymers. 0.4%, 1.8%, 2.0%, 3.0%.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

copolymers shown in Figure 8 a substantial broadening of the melting curves can be seen as the comonomer content increases.

Conclusion

Propylene copolymersation with odd carbon number olefin is a technical tool for new classes of propylene polymers. The first one investigated, the random copolymers of propylene with 1-pentene have very good impact and optical properties and good processability due to particular microstructure and morphology. Propylene copolymers with 1-heptene and 1-nonene less investigated up to now are equally interesting for the polymer scientist and having particular thermal behavior are applicable new polymers with even higher impact strength values. The source of novelty in application and added value is coming from the most neglected source in polyolefin development, the olefin comonomer itself. Finally the source of all these new possibilities is the Fischer-Tropsch process an affordable source for hydrocarbons that is gaining momentum in this century.

Acknowledgements: We thank Sasol Technology for the support in presenting this paper. Also Drs.Potgieter A and Juhasz P for the experimental work and interpretation depicted in their PhD Thesis.

[1] I. Tincul, I. H. Potgieter, *MBS PE 96 World Congress*, **1996**, Zurich, I, 3, 1–17.
[2] D. Joubert, I. H. Potgieter, A. H. Potgieter, I. Tincul, *WO 96/24623*.
[3] I. Tincul, D. Joubert, A. H. Potgieter, I. H. Potgieter, *WO 99/01485*.
[4] I. Tincul, D. Joubert, D. Young, *WO 00/32657*.
[5] D. Joubert, *PhD Thesis*, U Stellenbosch, **2000**.
[6] A. H. Potgieter, *PhD Thesis*, U Stellenbosch, **2001**.
[7] P. Iuhasz, *PhD Thesis*, Budapest University, **2001**.
[8] I. Tincul, & all. *MBS PP 99 World Conference*, **1999**, Zurich, IX, 3, 1–13.
[9] I. Tincul, & all. *Polymeric Materials. Science and Engineering* **2001**, 84.
[10] I. Tincul, D. Joubert, *Polymer 98 Proceedings*, **1998**, Brighton, UK.
[11] I. Tincul, & all. *PDDG symposium Proceedings*, **1996**, Warwick.
[12] I. Tincul, & all. *ACS, Fall Meeting Proceedings*, **1998**, Boston.
[13] A. H. Potgieter, I. Tincul, *SPO Proceedings* **1999**, Houston, TX.
[14] I. Tincul, D. Joubert, *ACS Advances in Polyolefin III*, **2001**, Sonoma, CA.
[15] I. Tincul, D. Joubert, *PPS, Taiwan Proceedings*, **2002**, Taipei, G12/052.

Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim