

Ph.D. Thesis

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Crystallisation kinetics and morphology of propylene/ α -olefin
random copolymers

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Introduction

Isotactic polypropylene belongs today to the most important commodity polymers. Due to its good mechanical properties and its low price, its production and application are in constant development. Random copolymers of propylene and α -olefins are also important commercial products. Indeed, polypropylene homopolymer itself has good physical properties, like high tensile strength and stiffness. However, its impact strength and transparency is rather poor, and its brittleness at low temperatures set a limit to its application. Since comonomers in the polymer chain decreases both the degree of crystallinity and the glass transition temperature, in applications requiring good clarity, flexibility and impact strength, such as films, usually propylene/ α -olefin copolymers are used.

At the same time, isotactic polypropylene (iPP) and its random copolymers have always been in the centre of interest in the field of scientific polymer research. Despite of the chemical simplicity of the polymer chain, isotactic polypropylene is known to crystallise in at least four different crystal forms, which differ in the geometry of chain packing in the unit cell. The most commonly observed crystal form is the monoclinic α form, being found in melt-crystallised iPP samples. The trigonal β modification is formed either in samples crystallised from sheared melt, in samples prepared with the temperature gradient method, or in samples nucleated with selective β -nucleating agents. The orthorombic γ form was observed either in very low molecular weight polypropylenes, in random copolymers, or in homopolymers crystallised at elevated pressure. The fourth crystal form, usually referred to as smectic, is found in quenched samples of iPP.

The aim of this thesis is to analyse the factors that are responsible for the formation of different crystal forms in polypropylene random copolymers. The effect of comonomer content, crystallisation conditions, and different types of nucleating agents on the formation of the β and γ modifications are discussed in detail. Since each crystal form has different mechanical properties, the knowledge of polymorphic composition and its influential factors is essential for understanding the macroscopic behaviour of random copolymers.

This far, structural investigations of propylene/ α -olefin random copolymers were confined to copolymers with ethylene, 1-butene and 1-hexene. This thesis deals mostly with propylene/1-pentene random copolymers, which were developed only recently. These studies contribute not only to the elucidation of the crystallisation habits of copolymers, but also provide new literature data on these materials.

Methodology

- The formation of the γ modification in random copolymers was studied as a function of comonomer content and crystallisation temperature. The studies were carried out on propylene/1-pentene random copolymers with pentene content between 0.38 and 3.63 mol%.
- The effect of nucleating agents on the crystal structure was studied with nucleated propylene/ethylene random copolymers crystallised under isothermal and non-isothermal conditions.
- The effect of comonomer content on the formation of the β modification was studied with β -nucleated propylene/1-pentene copolymers. Calcium salt of suberic acid was used for the selective nucleation of the β form.
- Identification and quantitative analysis of the different crystal forms, as well as the determination of the degree of crystallinity were carried out with wide-angle X-ray scattering.
- Crystallisation and melting characteristics of the copolymers were studied with differential scanning calorimetry. The equilibrium melting point of the copolymers was determined with the Hoffman-Weeks method. The Avrami equation was used to describe the crystallisation kinetics of the copolymers.
- The supermolecular structures formed during isothermal crystallisation of β -nucleated copolymers were studied with polarised light microscopy. The technique was also used to determine the temperature limits of formation of the β form.
- The different approaches, which are used for the determination of the equilibrium melting point, were reviewed. A linear and a non-linear extrapolation method, based on the temperature dependence of the melting point, were used to calculate the equilibrium melting point of the β form of isotactic polypropylene.

New scientific results

- I studied the crystallisation and melting behaviour of novel propylene/1-pentene random copolymers. I found that the presence of pentene comonomer induces the formation of the unique γ crystal form. I showed that both an increase in crystallisation temperature and in pentene content enhances the formation of the γ phase. In the case of

pentene comonomer, the relative γ content increases at a much higher rate with increasing comonomer content, than in the case of other α -olefin comonomers. From these observations I conclude that the size of the side group of the comonomer has a great influence on the formation of the γ phase.

- I proved that the thermodynamic heat of fusion of the γ form differs from that of the α form, and its value depends on the comonomer content as well. This dependence can only be attributed to the decrease of cohesion between the polymer chains, caused by the inclusion of pentene comonomer in the crystal lattice. Comparison of our results to literature data let me come to the conclusion that the propyl group is the longest side group that can be included in the crystals.
- I determined the equilibrium melting temperature of the α form in propylene/1-pentene copolymers by using the Hoffman-Weeks method. These values show a non-linear dependence on comonomer content, and are much lower than the ones calculated by the Flory equation. With analysis of the crystallisation kinetics I proved that the decrease of the crystallisation rate with increasing comonomer content is caused mainly by the decrease in the equilibrium melting point. I also showed, that the Avrami equation adequately describes the crystallisation process of propylene/1-pentene copolymers in a wide temperature range and even in the final stage of crystallisation. The nucleation-controlled, three-dimensional mechanism of crystal growth is not altered significantly with increasing pentene content.
- I studied the effect of different commercial nucleating agents on the crystal structure of polypropylene homopolymer and propylene/ethylene random copolymer. I observed that certain nucleating agents highly promoted the formation of the γ phase in nucleated random copolymers. I proved with the help of simple non-isothermal methods that the increase in the relative γ content was solely the consequence of high crystallisation temperatures, and not of a selective γ -nucleating ability of the nucleating agents. Results of isothermal measurements also justified the validity of this thesis. Comparison of the characteristic temperatures of non-isothermal crystallisations to the subsequent melting endotherms revealed that the formation of the γ form is favoured thermodynamically only above a certain temperature, which can be achieved either with nucleating agents of high efficiency or by very slow cooling rate. During the study of nucleated polymers I also observed that certain nucleating agents, especially talc, induce the formation of oriented crystal structures.

Moreover, I found that the efficiency of nucleating agents could be influenced by the presence of comonomer.

- I investigated the crystallisation, recrystallisation and melting behaviour of β -nucleated propylene/pentene random copolymers as a function of comonomer content. With the proper choice of crystallisation conditions and with proper amount of β -nucleating agent I produced samples that contained both the α , β and γ crystal modifications.
- I found that β -nucleated copolymers show similar tendency to $\beta\alpha$ - and $\beta\beta'$ -recrystallisation as observed in β -nucleated homopolymers, but the rate of crystallisation and the melting temperatures decrease with increasing comonomer content. The crystallisation at low temperatures leads to the formation of crystal structures with high instability, which provides the possibility to study the $\beta\beta'$ -recrystallisation process in more detail.
- In the same materials I also found that the critical crossover temperature decreases significantly with increasing comonomer content. However, I found no remarkable difference in the critical recooling temperature of the β form between homopolymer and copolymers.
- By studying β -nucleated random copolymers I found that the Hoffman-Weeks method is not suitable for determination of the equilibrium melting point of the β form. Therefore, I investigated the factors that have an influence on the determination method. I measured the melting point of the β -form of isotactic polypropylene as a function of crystallisation time and temperature. I observed that the melting point of β -iPP increases linearly with the logarithm of crystallisation time. To avoid the time dependence of the lamellar thickening process, I estimated by extrapolation the melting points of original (non-thickened) crystals. I used a new extrapolation procedure for that purpose, which is based on the use of the apparent induction time of crystallisation. Using the non-linear Hoffman-Weeks method, the equilibrium melting point of β -iPP was found to be $T_m^0 = 209.2^\circ\text{C}$, which is about 32°C higher than the value obtained using the linear Hoffman-Weeks extrapolation ($T_m^0 = 177.3^\circ\text{C}$). These results obtained exemplify the importance of accounting for both the isothermal lamellar thickening effects and the non-linearity in the T_m - T_c correlation, when the determination of an equilibrium melting point is carried out using a procedure based on the predictions of the Lauritzen-Hoffman secondary nucleation theory.

Publications

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4. Belina, K.; Juhász, P.; Csongor, D.; Schott, Nick R.: Interaction in PC/ABS blends prepared in a dynamic melt mixer, *ANTEC 2001 Technical Papers* Vol. XLVII, 2240-2242
5. Klébert, Sz.; Juhász, P.; Szulmanné Binet, M.; Belina, K.: PET hulladék módosítási lehetőségeinek tanulmányozása, *Műanyag és Gumi* 2001, **38(5)**, 182-185
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10. Juhász, P.; Varga, J.; Belina, K.; Marand, H.: Determination of the equilibrium melting point of the β -form of polypropylene, accepted in *Journal of Thermal Analysis and Calorimetry*

Presentations

1. Juhász, P.; Belina, K.; Lengyel, Z.; Oláh, A.; Domenik, I.; Tóth, A.: Kölcsönhatás PE-CPE keverékekben, *MTA Műanyagkémiai Munkabizottság Ülése*, Tiszaújváros, Hungary, April 8, 1998
2. Juhász, P.; Belina, K.; Vorster, O.; Halász, L.; Potgieter, A.H.; Tincul, I.: Crystallisation kinetics of propene/pentene copolymers, *ESTAC 7*, Balatonfüred, Hungary, August 30 - September 4, 1998
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12. Juhász, P.; Varga, J.; Belina, K.; Belina, G.: Efficiency of β nucleating agents in propylene/ α -olefin copolymers, *EPS 2001 Conference on Morphology and Properties of Crystalline Polymers*, Eger, Hungary, September 2-5, 2001
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Personal data

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Date of birth 11th November 1974
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Education

2001-2002 Founded researcher of the Varga József Foundation
1998-2001 Ph.D. studies at the Department of Plastics and Rubber Technology, BUTE
1998 M.Sc. degree in chemical engineering
1993-1998 Budapest University of Technology and Economics
Faculty of Chemistry
Special studies in rubber and plastics engineering
1989-1993 Petrik Lajos Technical Highschool of Chemistry

Teaching activities

Laboratory practices:

- Thermal Analysis of Polymers (DSC, POM, TGA, OIT)
- Termorelaxation, Optical Stress Analysis of Glassy Polymers
- Standard Testing Methods in the Rubber Industry

Language skills

- Intermediate level state examination of English Language (1995)
- Intermediate level state examination of German Language (1992)

Awards

Best Poster Award, First Prize, EPS 2001 Conference on Morphology and Properties of Crystalline Polymers, 2-5 September 2001, Eger, Hungary