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Crystallization of syndiotactic polypropylene (sPP) from oriented melts

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Summary

The influence of the syndiotacticity on the crystallization behaviour of syndiotactic polypropylene (sPP) has been investigated. The syndiotacticity has been measured by ^{13}C-NMR spectroscopy and the phase formation has been observed by electron diffraction of oriented samples. It is shown that the crystal phase formation depends strongly on the perfection of the tacticity of the macromolecules.

Introduction

The existence of both the twofold helical $(ttgg)_2$ and the planar all-trans (tttt) chain conformation in the crystalline state of syndiotactic polypropylene (sPP) was postulated on conformational analysis (1, 2) and was later confirmed by the determination of the crystal structures. Three different crystal phases based on the $(ttgg)_2$ chain conformation have been observed, one with isochiral chains packed in a c-centred orthorhombic unit cell (cell I) (3, 4), one with antichiral chains packed along the a-axis of the unit cell (cell II) and the third with antichiral chains packed along the a- and b-axes of the unit cell (cell III) (5-8). A crystal structure based on the all-trans chain conformation, called all-trans-phase in this paper, is found only in samples, which are cold drawn below the glass transition temperature of ~0°C (9-11).

The influence of tacticity defects of macromolecules on the formation of the different crystal phases and of the physical properties of sPP is still under investigation (12-14). It is the purpose of this paper to report the crystallization behaviour of sPP under elongational deformation depending on the amount of tacticity defects.

Experimental

Two different samples of sPP (**A** and **B**) polymerized in our laboratory were investigated. All polymerization procedures were carried out under argon atmosphere employing standard Schlenk techniques (15-17). Toluene (Merck KG aA) was refluxed over sodium/potassium for several days and distilled prior to use. Propylene was purchased from Gerling, Holz & Co. and purified by passage through columns with Cu catalyst (BASF R3-11) and molecular sieve of 1 nm. $[Me_2C(Cp)(Fluo)]ZrCl_2$ was synthesized according to literature (18). Methylaluminoxane (MAO, 10% in toluene) was purchased from Witco. Polymerizations were performed in a 1 l Büchi type I autoclave, which had been evacuated at 95°C for 2 hours. The reactor was charged with

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200 ml toluene and 250 mg MAO (600 mg for sample **B**) and cooled to 30°C (-10°C for sample **B**). The toluene was saturated with propylene at $2x10^5$ Pa and polymerization initiated by injection of 1.25 µmol zirconocene (20 µmol for sample **B**) which had been allowed to prereact with 50 mg MAO (400 mg for sample **B**) for 15 minutes. The polymerization was terminated after 1 hour (3 h for sample **B**) by addition of 5 ml ethanol and by propylene release. Workup consisted of stirring the polymer suspension overnight with acidic ethanol followed by filtration, neutralization with $NaHCO_3$ washing with water and drying in vacuum at 70°C.

Polymer ^{13}C-NMR measurements were made in a Bruker MSL 300 spectrometer operating at 75.47 MHz and 100°C using perchlorobutadiene/tetrachloroethane-d_2 as solvent. Syndiotactic block lengths n_{syn} were calculated from the investigations of the methyl signals in accordance with methods in literature (19, 20).

The solution viscosities were measured with an Ubbelohde capillary 0a (k=0.005) in decahydronaphthalene at 135°C and the molecular weights M_η were calculated using Mark-Houwink constants $[\eta]=2.38*10^{-4}*M^{0.725}$ (21). Molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C instrument at 135°C using trichlorobenzene as solvent.

The melting temperatures of the samples were determined with a TA/DuPont DSC 2910 system at a heating rate of 10°/min..

Highly uniaxially oriented films of sPP suitable for transmission electron microscopy (TEM) investigations were prepared by a special melt drawing technique reported by Petermann and Gohil (22). A small amount of 0.5 wt% solution of the polymer in xylene was poured and spread on a preheated glass slide (90°C to 120°C). After evaporating the solvent, the remaining polymer film was picked up with a drawing speed of 20 cms^{-1}. The resulting films were ~50 nm thick and were directly used for TEM investigations on a Philips CM200 electron microscope operated at 200 kV.

Results and discussion

Table 1 shows the amount of different configuration defects, the calculated pentad syndiotacticities and syndiotactic block lengths, the molecular weights and distributions of the samples **A** and **B** and the melting points of the samples, which were crystallized under the same conditions. In order to produce a highly syndiotactic polypropylene, the polymerization temperature has been lowered and a high monomer concentration has been chosen. The latter would result in less coordinatively unsaturated centers, which could undergo chain migration without insertion, whereas lower temperature would allow better discrimination between the two faces of the prochiral monomer. At -10°C and $2x10^5$ Pa propylene pressure, a polymer has been produced which exhibited a rrrr-pentad concentration of ~97 %. The remaining 3 % are mostly distributed on the three pentads arising from mm-triad defect (rrrm, rrmm and rmmr). The rrmr-pentad was also detected in small amounts.

Table 1: Properties of the investigated samples: average molecular weight M_η, molecular weight distribution M_w/M_n, melting temperature T_m, pentad concentrations (m: meso, r: racemic) and the number average sequence length of racemic additions $\overline{r}$ (*: the rrrm-pentad was detected, but not sufficiently separated from the rrrr-pentad to allow quantitative analysis)

	M_η [g/mol]	M_w/M_n	T_m [°C]	rmmr	rrmm	rmrr	rrrr+rrrm*	$\overline{r}$
A	495000	1.7	136	0.8	1.7	1.3	96.2	65
B	292000	1.8	159	0.4	1.0	0.5	98.1	132

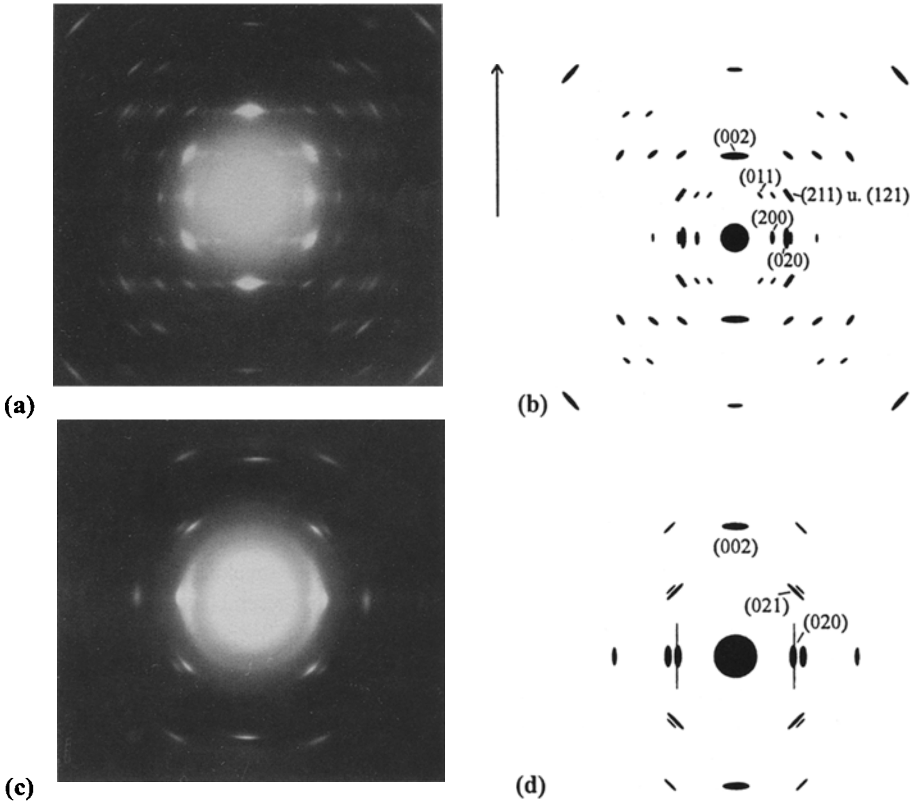
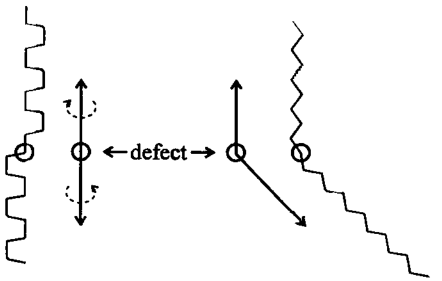


Figure 1: (left) Electron diffraction pattern of the oriented samples **A** **(a)** and **B** **(c)** and (right) the corresponding sketches **(b, d)**; indicated are the drawing direction (arrow) and the main (hkl)-indices. The diffraction patterns of **(a)** and **(b)** are in accordance with the phase III unit cell, while those of **(c)** and **(d)** represents the orthorhombic unit cell of the all-trans chain conformation.

Melt drawing of the samples **A** and **B** results in highly oriented thin films. An electron diffraction pattern of sample **A** and the corresponding sketch is shown in Figures 1a, b. The arrow indicates the drawing and the crystallographic c direction. The pattern is consistent with the helical cell III crystal structure. Many other investigated samples with syndiotacticities equal or less then sample **A** show the same cell III crystal structure formed under elongational deformation from the melt, whereas from a relaxed melt the cell III phase forms only after very long crystallization times under isothermal crystallization conditions. A possible explanation for this surprising result is sketched in reference (23). The elongational deformation of the melt under the preparation conditions of the Petermann and Gohil method favours trans conformation sequences, and the highly ordered cell III crystal structure may be formed readily from these elongated “all-trans“ chains.

Figures 1c, d show an electron diffraction pattern of the melt drawn sample **B** and the corresponding sketch. The diffraction pattern is explained in terms of an orthorhombic unit cell with cell constants a = 0.522 nm, b = 1.117 nm and c = 0.506 nm, and these crystals contain molecules with all-trans conformation according to Chatani et al. (24). The pronounced streaking of the (020) defraction spots in c-direction indicates a high amount of one dimensional lattice defects in the orthorhombic lattice. Similar observations were obtained in



(a) helical conformation (b) all-trans-conformation

Figure 2: **(a)** A tacticity defect in an extended syndiotactic molecule maintains the coaxial direction in its helical conformation (from 26) and **(b)** changes the spatial direction in its all-trans conformation.

the electron diffraction patterns of oriented polyvinylideneflourid (PVF$_2$), and were explained by a clustering of a high number of kink defects (one dimensional agglomeration) in the direction perpendicular to the lattice plane, which exhibits the streaking in the diffraction patterns (25). The chain conformations in PVF$_2$ have very close resemblance to sPP: a (tgtg) and an all-trans chain conformation can exist in their α and β crystalline modification, respectively.

Besides the molecular weight, the main difference between the samples **A** and **B** is the higher syndiotacticity of sample **B**. The different crystallization behaviour of the investigated samples may be explained by a different compensation of the tacticity defects of the molecules during nucleation of the “all-trans“ phase compared to the “helical“ phases (Figure 2).

During polymerization, two main tacticity defects arise: an isolated mm-triad results from insertion of a monomer unit in the energetically less favoured placement analogous to a rr-triad in isotactic polypropylene, and the m-dyad defect is attributed to chain migration without insertion, and is found to be strongly dependent on propylene concentration and temperature (26).

In its helical conformation, a tacticity defect in the syndiotactic molecule changes only the chirality of the chain to the opposite handedness, but maintains the coaxial direction of the chain (Figure 2a) (27). Therefore, a higher amount of those defects can be incorporated into the helical crystal modifications I, II or III as point defects, with the tendency of favouring the crystal modification of lower symmetry (phases I or II). The same tacticity defect in the all-trans conformation results in a change of the spatial direction of the chain (Figure 2b) and this cannot be incorporated into the crystal as a simple point defect. Only perfect molecular sequences longer than the critical nucleus size in the “all-trans“ phase can therefore contribute to its formation.

Crystallite sizes in chain direction and in lateral dimensions are considerably smaller compared to those isothermally crystallized, when crystallization occurs under elongational flow conditions (as in the melt draw method). Due to their small sizes, we were unsuccessful in TEM imaging of these crystals. But their small dimensions may explain, why the “all-trans“ phase appears not in the isothermal crystallized material. And also, the higher amount of tacticity defects in sample **A** hinders the crystallization of the “all-trans“ phase in melt drawn samples, too. Only the high syndiotacticity of sample **B** with an average defectless syndiotactic sequence length of 132 monomers results in the formation of the “all-trans“ phase under elongational flow conditions.

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Literature

1. Natta G, Corradini P, Ganis P (1962) J Polym Sci 58:1191
2. Natta G, Corradini P, Ganis P (1960) Makromol Chem 39:238
3. Corradini P, Natta G, Ganis P, Temussi P A (1967) J Polym Sci, Part C 16:2477
4. Natta G, Pasquon I, Corradini P, Peraldo M, Pegoraro M, Zambelli A (1960) Rend Acc Naz Lincei 28:539
5. Lotz B, Lovinger A J, Cais R E (1988) Macromolecules 21:2375
6. Lovinger A J, Lotz B, Davis D D (1990) Polymer 31:2253
7. Lovinger A J, Davis D D, Lotz B (1991) Macromolecules 24:552
8. DeRosa C, Corradini P (1993) Macromolecules 26:5711
9. Natta G, Peraldo M, Allegra G (1964) Makromol Chem 75:215
10. Tadokoro H, Kobayashi M, Kobayashi S, Yasufuku K, Mori K (1966) Rep Prog Polym Phys Jpn 9:181
11. Chatani Y, Maruyama H, Noguchi K, Asanuma T, Shiomura T (1990) J Polym Sci, Polym Lett 28:393
12. Haftka S, Könnecke K (1991) J Makromol Sci B 30:319
13. Marchetti A, Martuscelli E (1974) J Polym Sci, Polym Phys Ed 12:1649
14. Loos J, Hückert A, Petermann J Colloid and Polym Sci in press
15. Kaminsky W, Lüker H (1984) Makromol Chem, Rapid Commun 5:225
16. Kaminsky W (1984) Naturwissenschaften 71:93
17. Kaminsky W, Engehausen R, Zoumis K,Spaleck W, Rohrmann (1992) J Makromol Chem 193:1643
18. Razavi A, Ferrara J (1992) J Organomet Chem 435:299
19. Randall J C, Polymer Sequence Determination Carbon 13-NMR Method (1977) Academic Press, New York
20. Zambelli A,Locatelli P, Bajo G, Bovey F A (1975) Macromolecules 8:687
21. Scholte T G, Meijerink N L J, Schoffeleers H M, Brands A M G (1984) J Appl Pol Sci 29:3763
22. Petermann J, Gohil R M (1979) J Mater Sci 14:2260
23. Loos J, Buhk M, Petermann J, Zoumis K, Kaminsky W (1996) Polymer 37:387
24. Chatani Y, Murayama H, Noguchi K, Asanuma T, Shiomura T (1990) J Polym Sci: Polym Lett 28:393
25. Gohil R M, Petermann J (1981) Polymer 22:1612
26. Ewen J A, Elder M J, Jones R L, Curtis S, Cheng H N (1991) in: Keii T, Soga K (ed) Catalytic olefin polymerization. Kodansha Ltd., Tokyo (pp 439-481)
27. Auriemma F, DeRosa C, Corradini P (1993) Macromolecules 26:5719