Crystallization of Isotactic Polystyrene from Dilute Solutions

P. J. LEMSTRA and G. CHALLA, Laboratory of Polymer Chemistry, State University of Groningen, Groningen, The Netherlands

Synopsis

The overall rate of crystallization of isotactic polystyrene from dilute solutions, 1% by weight, in trans-decalin and benzyl alcohol was studied as a function of temperature using dilatometry. These solvents were chosen because the dissolution temperatures of crystalline isotactic polystyrene are practically the same in both solvents. The overall rate of crystallization as a function of crystallization temperature showed a maximum in both solvents at about 50°C. At lower crystallization temperatures the rate of crystallization is much lower. The overall rate of crystallization of isotactic polystyrene in benzyl alcohol is far larger than in trans-decalin at the same undercooling throughout the temperature range, which is in apparent contradiction to present crystallization theories. At very large undercooling (T<sub>c</sub> lower than about 0°C) the solutions of isotactic polystyrene in both solvents quickly become “rigid” gels. Surface replicas of freeze-etched gels indicate that a fringed micelle type of crystallization takes place at these low temperatures. The transition from folded chain crystallization to fringed micelle crystallization may be due to a stiffening of the polymer chain below about 50°C, with a reduced rotational mobility of the phenyl groups on the chain. If very dilute solutions, below 0.5% by weight, are crystallized at these low temperatures no gels were formed but fibrous crystals are produced which could be observed under the polarizing microscope.

INTRODUCTION

Isotactic polystyrene (i-PS) is a slowly crystallizing polymer. Due to the low rate of crystallization it is possible to study the kinetics of crystallization over a broad temperature range. Several papers deal with the spherulitic growth rate of i-PS as a function of temperature both in the bulk<sup>1-3</sup> and in concentrated solution.<sup>4</sup> Although the spherulitic growth rate G can be described well by the familiar rate equation proposed by Hoffman and Weeks<sup>5</sup> the preexponential factor G<sub>0</sub>, obtained from fitting the rate equation to the experimental curves, is much smaller than its theoretical limit, b<sub>0</sub>kT<sub>c</sub>/h (T<sub>c</sub> is the temperature at which the growth rate G has its maximal value). Since the i-PS chain in the crystalline phase is a 3<sub>1</sub>-helix,<sup>6</sup> it has been proposed that conformational changes needed for crystallization give rise to this large deviation in the value for G<sub>0</sub> in contrast, for example, to polyethylene<sup>1-3</sup>. The conformation of the i-PS chain might play an important role during crystallization from dilute solutions too. Helms and Challa<sup>7</sup> showed recently that during crystallization from dilute solutions of i-PS in a mixture of toluene and ether, helixes are formed which aggregate to crystals afterwards. Keith, Vadimsky, and Padden<sup>8</sup> observed that at comparable undercoolings, i-PS...
crystals grew much slower in a good solvent (mesitylene) than in a poor solvent (mixture of n-tetradecane and decalin). They suggested that some conformational differences between the molecules in these two solvents caused the difference in growth rate. The conformation of i-PS in dilute solutions has been investigated by different authors in various solvents. The general conclusion has been that helical sequences arise in the polymer chains during the cooling of dilute solutions of i-PS. In this paper we compare the overall rate of crystallization in, respectively, trans-decalin and benzyl alcohol as a function of crystallization temperature. The equilibrium dissolution temperature of i-PS in both solvents is about the same, so that we were able to compare the crystallization rate not only at the same undercooling but also at the same temperature thus reducing the effect of transport factors on the rate of crystallization.

**EXPERIMENTAL**

Our i-PS is the same sample as used previously. It was freed from atactic polystyrene by dissolving the polymer in methylene chloride (1 g/l) and dropping the solution into excess methyl ethyl ketone. After evaporation of methylene chloride, i-PS precipitated quantitatively from the ketone leaving atactic polystyrene in solution. Thus, highly stereoregular i-PS was obtained: $M_n = 18 \times 10^4$ and $M_w = 33 \times 10^4$. $^{13}$C NMR spectra recorded on the Varian XL-100/15 at 25.2 MHz showed that our sample contained 92% isotactic triads. The solvents benzyl alcohol (Baker Chemicals) and trans-decalin (Merck/Schuchardt) were distilled before use at reduced pressure. During dissolution of i-PS in these solvents dry nitrogen was flushed through the solutions and small amounts of antioxidant (2-naphthyl phenyl amine), 1% on weight of polymer were added. The intrinsic viscosity of i-PS in trans-decalin at 30°C is 0.9 dl/g and in benzyl alcohol 0.7 dl/g at the same temperature.

Solution-crystallized samples were obtained by crystallizing dilute solutions of i-PS in trans-decalin or benzyl alcohol at different temperatures in thermostatic baths (temperature control better than 0.05°C). The concentration of the solutions was 0.5% by weight. After complete crystallization the crystals were filtered, washed with toluene, and dried under vacuum. All operations were carried out at room temperature. Due to the low rate of crystallization no further crystallization took place during cooling the solutions to room temperature and subsequent filtration. From the dried crystal "mats," sections were cut for the determination of the long-period spacing of the crystals. The latter was measured with a Kratky/Philips small-angle x-ray scattering unit. Desmearing of the intensity curves was performed using a computer program obtained from Dr. G. C. Vonk (D.S.M.-Geleen, Holland). The orientation of the crystals in the "mats" was determined with a Statton camera (Warhus Co.). The dissolution temperatures $T_d$ of the i-PS crystals as a function of crystallization temperature were determined with a Cenco–T.N.O. light scattering meter. The crystal suspensions, obtained at various $T_c$, were heated directly in the cell of the light-scattering meter. This cell was supplied with a magnetic stirrer, heating mantle, reflux, and thermocouple. The intensity of the scattered light was recorded at 90° ver-
sus temperature with an X/Y recorder (Servogor). When the crystals dissolve, there is a strong decrease in the intensity of the scattered light and the dissolution temperature can be determined easily.

The overall rate of crystallization of i-PS in benzyl alcohol and trans-decalin was determined dilatometrically at various crystallization temperatures. The volume of the solutions in the dilatometers was about 50 ml and mercury was used as the confining fluid. The solvents were thoroughly mixed with mercury at about 75°C for several hours before use. The latter procedure is necessary to avoid the formation of reaction products at the solution-mercury interface in the dilatometers originating from the reaction of mercury and small amounts of impurities in the solvents. In order to obtain reproducible results, the following precautions were taken. All solutions were made by dissolving completely amorphous i-PS powder in benzyl alcohol or trans-decalin containing antioxidant (1% on weight of polymer). Before isothermal crystallization the degassed solutions in the dilatometers were heated at 165°C for 30 min after thermal equilibrium had been achieved. One might argue that this heating time is relatively short for complete dissolution. However, longer heating times at 165°C gave identical results in the isothermal crystallization. After dissolution the dilatometers were transferred to thermostatic baths with very precise temperature control (better than 0.002°C). The crystallization experiments at lower temperatures were performed in thermostatic baths equipped with a cooling unit (Braun/Melunggen Frigomix).

The structure of the gels obtained by crystallizing dilute solutions of i-PS in trans-decalin or benzyl alcohol at very large undercooling (lower than about 0°C) were examined using freeze-etching techniques. The gels were frozen quickly in liquid nitrogen and cut in a Balzers freeze-etching unit at −150°C. After shadowing with platinum and carbon coating, the replicas were studied in a Philips electron microscope (E.M.-300).

**RESULTS**

Figure 1 shows a curve of $(1 - X)$ versus log(time), where $X$ is the degree of transformation of the overall crystallization process calculated from the rela-

![Fig. 1. Curves showing crystallization isotherms of isotactic polystyrene from 1% solutions in benzyl alcohol (curve a) and trans-decalin (curve b) at 50°C (X = degree of transformation).]
TABLE I
Half Times for Crystallization of Isotactic Polystyrene from 1% Solutions in Benzyl Alcohol and trans-Decalin as a Function of Crystallization Temperature $T_c$ |  |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$, °C</td>
<td>$t_{1/2}$ (benzyl alcohol), min</td>
<td>$t_{1/2}$ (trans-decalin), min</td>
</tr>
<tr>
<td>100</td>
<td>$9.0 \times 10^2$</td>
<td>$26.4 \times 10^3$</td>
</tr>
<tr>
<td>75</td>
<td>$1.3 \times 10^3$</td>
<td>$6.6 \times 10^3$</td>
</tr>
<tr>
<td>50</td>
<td>$0.8 \times 10^3$</td>
<td>$3.5 \times 10^3$</td>
</tr>
<tr>
<td>30</td>
<td>$1.6 \times 10^3$</td>
<td>$5.5 \times 10^3$</td>
</tr>
<tr>
<td>10</td>
<td>gelation</td>
<td>gelation</td>
</tr>
<tr>
<td>0</td>
<td>gelation</td>
<td>gelation</td>
</tr>
</tbody>
</table>

The relative height of the mercury column in the capillary of the dilatometer, for i-PS in benzyl alcohol (curve a) and trans-decalin (curve b) at 50°C and concentrations 1 wt-%. In Table I we collected the values of $t_{1/2}$ (time when crystallization process has completed for 50% or $X = \frac{1}{2}$) as a function of temperature. Note the maximum in the overall rate of crystallization at about 50°C and the large difference in rate for both solutions. In Table I no data are reported for the very low crystallization temperatures $T_c = 10°C$ and $T_c = 0°C$. At 10°C no change in the height of the mercury column in the capillary was observed during our period of observation, about 10 days. At 0°C a very small decrease in the height of the mercury column could be observed after

Fig. 2. Electron micrograph of a replica taken from a freeze-etched gel obtained by crystallizing a 1% solution of isotactic polystyrene in benzyl alcohol at −25°C.
some days but it is only a small decrease compared to those at higher crystallization temperatures. Separate test tube experiments showed that the 1% solutions of i-PS in benzyl alcohol and trans-decalin turned into “rigid gels” at about 0°C after a few minutes. At lower temperatures, for example −25°C, this gelation is instantaneous. The gels formed at these low temperatures are transparent but become opaque on standing at room temperature. The transparent gels dissolve at about 50°C. Figure 2 shows an electron micrograph of a replica obtained by freeze etching an i-PS/benzyl alcohol gel.

Fig. 3. Optical micrograph of a suspension of fibrous isotactic polystyrene crystals from a 0.25% solution of isotactic polystyrene in trans-decalin at −10°C (magnification 1200 ×).

Fig. 4. Intensity of scattered light (arbitrary units) at 90° vs. temperature during the heating of suspensions of isotactic polystyrene crystals in benzyl alcohol. The suspensions were obtained by crystallizing 0.5% solutions of isotactic polystyrene in benzyl alcohol at 75°C (curve a) and 25°C (curve b).
This gel was obtained by “crystallizing” a 1% weight solution of i-PS in benzyl alcohol at −25°C. Solutions of i-PS in benzyl alcohol and trans-decalin at lower concentration, for instance 0.25% by weight, do not turn into homogeneous gels at large undercooling but become slightly opaque. In the polarizing microscope we observed that the strongly undercooled solutions contained fibrous crystals as shown in Figure 3.

Figure 4 shows a typical curve of the scattered intensity versus temperature during heating a crystal suspension of i-PS (in this case i-PS/benzyl alcohol originally crystallized at 75°C) in the light-scattering cell. We have chosen rather arbitrarily as dissolution temperature \( T_d \) that temperature at which the scattered intensity dropped to 50% of its original value. In determining \( T_d \) we always used heating rates in the range 3–5°C/min to avoid rearrangements of the crystals during heating. For heating rates of 5 down to 0.1°C/min, \( T_d \) was found to be constant; further reduction leads to higher values of \( T_d \). Figure 5 shows a plot of these dissolution temperatures. To determine \( T_d \) values at higher crystallization temperatures (\( T_c > 100°C \)), a self-seeding technique was used to enhance the overall rate of crystallization. No \( T_d \) values are plotted at the lower crystallization temperatures (\( T_c < 50°C \)) because of the broad dissolution range of the crystals formed at lower \( T_c \). A typical curve is shown in Figure 4 for a crystal suspension of i-PS in...
Fig. 6. Small-angle x-ray scattering curves for isotactic polystyrene crystallized from dilute solutions in benzyl alcohol at various crystallization temperatures $T_c$: (a) $T_c = 30^\circ$C; (b) $T_c = 75^\circ$C; (c) $T_c = 100^\circ$C.

benzyl alcohol, originally crystallized at $T_c = 25^\circ$C. No distinct dissolution temperature can be determined.

Table II shows the long-period spacing of crystalline i-PS mats as a function of crystallization temperature. At lower $T_c$ no diffraction maximum is observed as shown in Figure 6.

**DISCUSSION**

Figure 5 shows that the dissolution temperatures of i-PS in trans-decalin and benzyl alcohol are about the same, and the equilibrium dissolution temperatures $T_d^0$ in both solvents, obtained by extrapolation of the dissolution temperatures $T_d$ to the diagonal $T_d = T_c$, do not differ significantly. So, isothermal crystallizations at the same $T_c$ in both solvents are assumed to occur at comparable undercooling ($T_d^0 - T_c$). Figure 1 and Table I show that the overall rate of crystallization of i-PS from trans-decalin and benzyl alcohol, at the same concentration and temperature $T_c$, is much larger in the latter system. Keith, Vadimsky, and Padden\textsuperscript{8} reported similar observations in crystallizing i-PS from mesitylene (good solvent) and i-PS in a mixture of dekalin and tetradecane (bad solvent). Crystallization in the latter system was much faster than in mesitylene despite comparable undercooling.

We have chosen the solvents benzyl alcohol and trans-decalin in order to compare the rate of crystallization not only at comparable undercooling but also at the same temperature, thus being able to reduce the possibility that transport factors could cause these differences in crystallization rate. As a matter of fact the viscosity of i-PS/benzyl alcohol solutions appeared to be larger than i-PS/trans-decalin solutions (the viscosity of a 1% solution of i-PS in benzyl alcohol is 5.0 cP and that of a 1% solution of i-PS in trans-decalin is 2.6 cP, both at 50°C).
As shown by several authors, i-PS molecules contain helical segments in solution with the number and length depending on temperature and solvent.\(^9,10\) Kobyashi et al.\(^10\) showed that during cooling i-PS/CS2 solutions the intensity of typical “helical bands” in the infrared spectrum increased continuously. This increase in the number of helical segments on cooling i-PS solutions is a general phenomenon observed by different authors in various solvents.\(^9\) Keeping in mind that the i-PS chain in the crystalline phase is a 3_1-helix, it is plausible to assume that the helical conformation of the i-PS molecule is an important factor during crystallization. Keith et al.\(^8\) assumed some conformational differences to be responsible for their observed difference in the growth rate. In our opinion the explanation of the difference in the growth rate might be as follows: With decreasing temperature the helical content of the i-PS molecules increases in both benzyl alcohol and trans-decalin. There is a greater number of helical segments in the more polar solvent benzyl alcohol. These helical segments aggregate to form crystals during isothermal crystallization as shown by Helms and Challa recently.\(^7\) At higher temperatures the helical conformation is less pronounced and so one finds the same dissolution temperature.

An interesting observation is the maximum in the overall rate of crystallization in both solvents at about 50°C and the strong decrease in rate at lower \(T_c\). A decrease in the rate of crystallization with decreasing temperature has been reported\(^12\) for the system i-PS/dimethyl phthalate and the maximum in the overall rate versus temperature was at about the same temperature (60°C). Helms and Challa reported recently\(^11\) that i-PS in toluene showed a transition in various properties at about 50°C which they attributed to a reduced rotational mobility of the phenyl groups. Figure 6 shows that crystals formed at crystallization temperatures below about 50°C do not give a discrete long-period spacing nor a distinct dissolution temperature as shown in Figure 4. At still lower \(T_c\), no crystallization is observed, for example at \(T_c = 10°C\), as shown in Table I. These observations lead us to the conclusion that the rate of “chain-folded” crystallization during isothermal crystallization of i-PS from solution at low crystallization temperatures, \(T_c\) below 50°C, is strongly reduced. We suggest that this reduction in crystallization rate originates from a stronger hindrance of the folding process due to the reduced mobility of the phenyl groups at these low temperatures. At very large undercooling (\(T_c\) below 0°C) the helical molecules do not fold anymore but seem to aggregate locally throughout the solution and form homogeneous network structures even at such low concentrations as we used here: 1% by weight. Instead of folded-chain crystals we obtain a “fringed micelle” crystal structure (Fig. 2). At higher \(T_c\) (lower undercooling) this fringed micelle type of crystallization is highly improbable due to a great loss in entropy in the formation of a bundle-like nucleus.\(^13\)

Concluding, we notice three temperature regions of crystallization: (i) \(T_c > 50°C\): chain-folded crystallization in accordance with classical nucleation theory; (ii) \(0°C < T_c < 50°C\): a transition region with irregular chain folding; and (iii) \(T_c < 0°C\): fringed micelle crystallization. In region (ii) the broad dissolution range of i-PS crystals grown at large undercooling (Fig. 4) and the smeared out diffraction pattern observed at small-angle x-ray scattering (Fig. 6) indicate that at large undercooling a different crystallization mechanism.
starts to take place. In region (iii), gelation due to fringed micelle crystallization is only possible if the concentration of the solutions is sufficiently high; in our case the critical concentration is about 1% by weight. In more dilute solutions, fibrous crystals are formed as shown in Figure 3.

We thank Dr. G. C. Vonk (DSM-Geleen, Holland) for allowing us to use his computer program for desmearing of SAXS curves and Mr. E. Kwak for performing the freeze-etching experiments.

References


Received December 30, 1974
Revised April 9, 1975