Gelation properties of partial benzoylated isotactic polystrene and its implications to the gel structure of isotactic polystyrene

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Isotactic polystyrene (IPS) solution crystals have been benzoylated in heterogeneous medium. By this method, a multi-block copolymer was obtained. The discussed benzoylated IPS crystals (BzIPS) show similar gelation properties as pure isotactic polystyrene. It is proved that the crystalline crosslinks in the gel of the BzIPS polymers are formed by the IPS segments which formed the crystalline core in the original IPS solution crystals. These fringed micellar crystals do not show the familiar 3/1 helical structure of IPS. The proposal is made that at low temperature IPS as well as BzIPS can crystallize in two different crystal structures. A suggestion is made that the formation of the new structure of IPS may be the origin of some anomalies in BzIPS and IPS crystallization at large undercoolings e.g. crystallization rate and annealing behaviour.

INTRODUCTION

The present communication arises from the investigation on the gelation of isotactic polystyrene (IPS). This polymer can be crystallized from different solvents at low concentration over a wide temperature range. It was found that the crystallization rate exhibits a maximum between 60° and 80°C (e.g. 60°C in decalin), unusual for crystallization from solution[1]. The particles formed in suspension are the familiar chain folded crystalline lamellae in the 3/1 helix conformation as reported by Natta *et al.*[2]. However, at higher concentrations (>3%) and large supercooling, an alternative phenomenon of thermally reversible gelation takes place[1]. The initially formed clear gel becomes turbid with time. When heated in the d.s.c. this turbid swollen gel exhibits two melting domains, as does the dried gel. The lower melting peak was related to the melting of fringed micellar crystals, forming the physical crosslinks in the gel. These crystals show in WAXD a sharp meridianal reflection at 5.1 Å, a reflection which is not consistent with the familiar 3/1 helical conformation of IPS. It was suggested that these crystals could be formed by some 'irregularities' in the IPS chains, although ^{13}C n.m.r. analyses did not reveal their presence[1,3].

The high temperature melting endotherm corresponds to the 3/1 helix in the folded chain crystals.

From these observations it can be concluded that IPS can crystallize from solution in two different crystal structures. Until now, the origin of the new structure was still doubtful. The experiments which will be discussed here were carried out to obtain more information about this gelation. They are part of a study on the solution and crystallization properties of partial benzoylated isotactic polystyrene (BzIPS)[4].

EXPERIMENTAL

Isotactic polystyrene was synthesized at 80°C in heptane with $Al(C_2H_5)_3$–$TiCl_4$ as catalyst[5]. The viscosimetric molecular weight was 850 000.

Solution crystals were prepared at different temperatures (*Table 1*) from dilute solutions in dimethylphthalate (1%). The percentage crystallinity was calculated from the area of the melt endotherms, using 8.6 in J/cm^3 as the heat of of fusion of the perfect crystal[6,7].

The IPS crystals were chemically modified by a Friedel–Crafts acylation[8]. To a stirred suspension of 0.5 g IPS crystals in 100 ml nitrobenzene, 0.65 g $AlCl_3$ and 1 ml benzoylchloride were added at room temperature. After one hour at this temperature, the temperature was raised to 60°C and the reaction was continued for an additional 2 h. After cooling to room temperature, another 0.5 ml benzoylchloride was added. The reaction was proceeded overnight at this temperature. The reaction mixture was then poured into a mixture of methanol/0.1 N HCl. After filtration, the col-

Table 1

	Benzoylation (%)		Induction period for gelation at 0°C (5% decalin) (min)	Dissolution temperature of the gel (5% in decalin) (°C)
T_c	a	b		
45	29	40	10	40
54	24	33	10–15	28–32
63	38	53	2–4	35–40
100	18	30	2	50–55

a = total degree of benzoylation, b = degree of benzoylation reduced to the amorphous regions using the degree of crystallinity obtained from d.s.c.

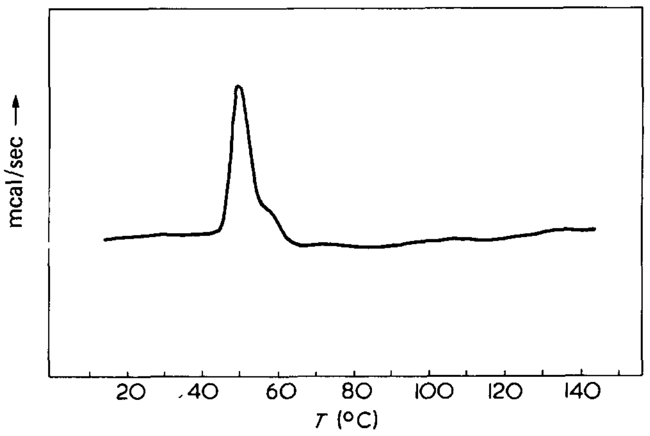

Figure 1 D.s.c.-trace of a gel formed at 8°C in 5% decalin by partial benzoylated IPS solution grown crystals, scan speed 20°C/min. (Original crystallized at 100°C from 0.5% DMP)

lected crystals were washed thoroughly with methanol and ether, and dried under vacuum at 80°C.

The percentage of benzoylation was calculated from i.r. observations, using the ratio of the intensities at υ (C=O) at 1665 cm^{-1} and υ (C–H)$_{\mathrm{aliph}}$ at 2940 cm^{-1}. Poly(vinyl benzophenone) was taken as a reference for 100% benzoylated polystyrene. Calorimetric measurements were made with a Perkin–Elmer DSC-2 instrument.

RESULTS AND DISCUSSION

By benzoylation of IPS crystals below their dissolution temperature, only the chain segments in the amorphous regions will be benzoylated, while the chain segments in the crystalline core remain unaffected[8]. This reaction results in the formation of a multi-block copolymer composed of a large number of alternating sequences of IPS and a random copolymer IPS–BzIPS. The lengths of the IPS sequences are of the same size as the chain segments in the crystalline core of the corresponding crystals. On heating most of the so obtained BzIPS crystals form gels in different solvents and at concentrations $>$5%. Some of these very rigid gels are crystalline while others are amorphous, resulting from a phase separation as a consequence of incompatibility between both sequences[4]. In this study, only those crystals will be used which do not form a gel in 5% concn. in decalin, on heating above the dissolution temperatures of the BzIPS crystals. These BzIPS crystals are tabulated in *Table 1.* In this Table the total degree of benzyolation (a) and the degree of benzoylation reduced to the amorphous phase (b) are reported. Depending on the crystallization conditions, this benzoylation of the amorphous phase amounts from 30 to 53%. These crystals are soluble in decalin when heated above their dissolution temperature. On cooling a 5% solution obtained in this way to below room temperature, clear strong thermally reversible gels are formed. The induction period for gelation is of the same order of magnitude as for pure IPS. On standing, these gels remain clear. On heating, the gels melt and transform into a clear solution, the visible observed melting domains are reported in *Table 1.* In d.s.c. a quite sharp melting endotherm is observed, in the same melting region as with pure IPS gels[1] (*Figure 1*).

The second high temperature melting endotherm observed in pure IPS gels is absent in the BzIPS gels. The WAXD diffraction pattern of the stretched gel shows a sharp meridional reflection at 0.51 nm as observed in the oriented pure IPS gels. The normal 3/1 helical structure is not present in the BzIPS gels, which is the case in pure IPS gels.

On heating the dried gel in the d.s.c., melting of the gel forming crystals is observed at around 120°C, followed by a very fast recrystallization, as shown in *Figures 2a* and *b*. WAXD confirm that the crystals formed during the recrystallization process are the familiar 3/1 helical IPS structure; the 5.1 Å reflection has disappeared.

From these observations, we may conclude that the gel structure formed by pure IPS and BzIPS are of the same origin. This gives strong evidence to the conclusion that the gel forming polymer segments are IPS sequences and not 'irregularities' in the IPS-chains. Irregularities are generally rejected in the amorphous phase during crystallization. By virtue of being excluded from the IPS crystal lamellae, these irregularities are benzoylated.

We may conclude that the IPS sequences, initially incorporated in the crystalline lamellae, form the fringed micellar crystals in the BzIPS gels and are at the origin of the new diffraction pattern. This does not exclude the possibility of the formation from dilute solution of the familiar 3/1 helical structure of IPS with this BzIPS. In dilute solutions (0.5%) in dimethylphthalate at 80°C, crystals are formed, but at a much lower rate compared to IPS (four days for BzIPS instead of a few hours for IPS).

Similar to IPS, BzIPS can crystallize in two distinct conformations from solution. Above the dissolution temperature of the gel crystals in decalin only the 3/1 helix can be formed. In this temperature region the usual crystallization behaviour was also observed with IPS. Crystallization rate and long spacing, change with crystallization temperature as would be expected. At low temperature and higher concentration, a new crystal structure can be formed, eventually to-

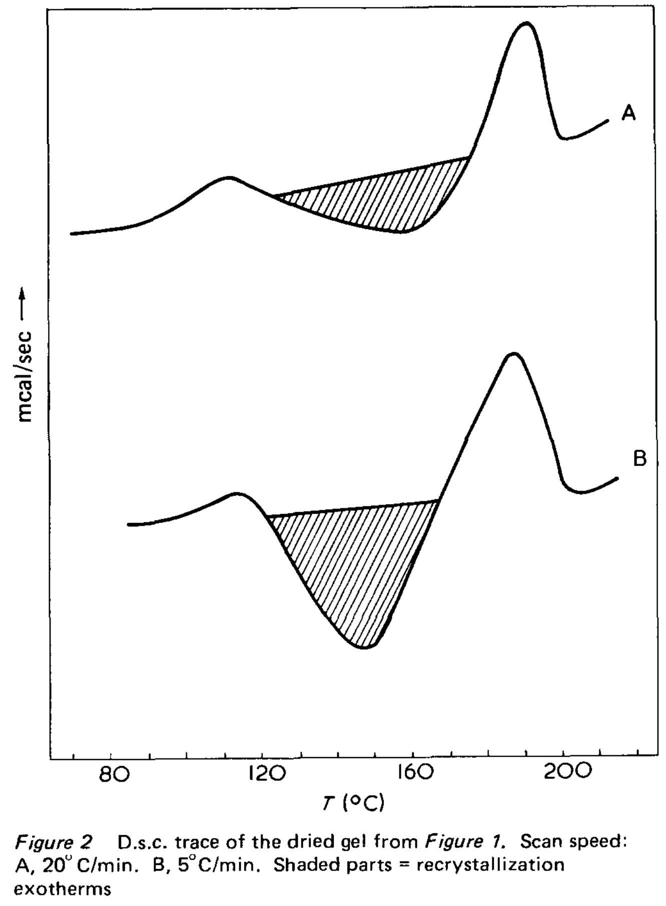

Figure 2 D.s.c. trace of the dried gel from *Figure 1.* Scan speed: A, 20°C/min. B, 5°C/min. Shaded parts = recrystallization exotherms

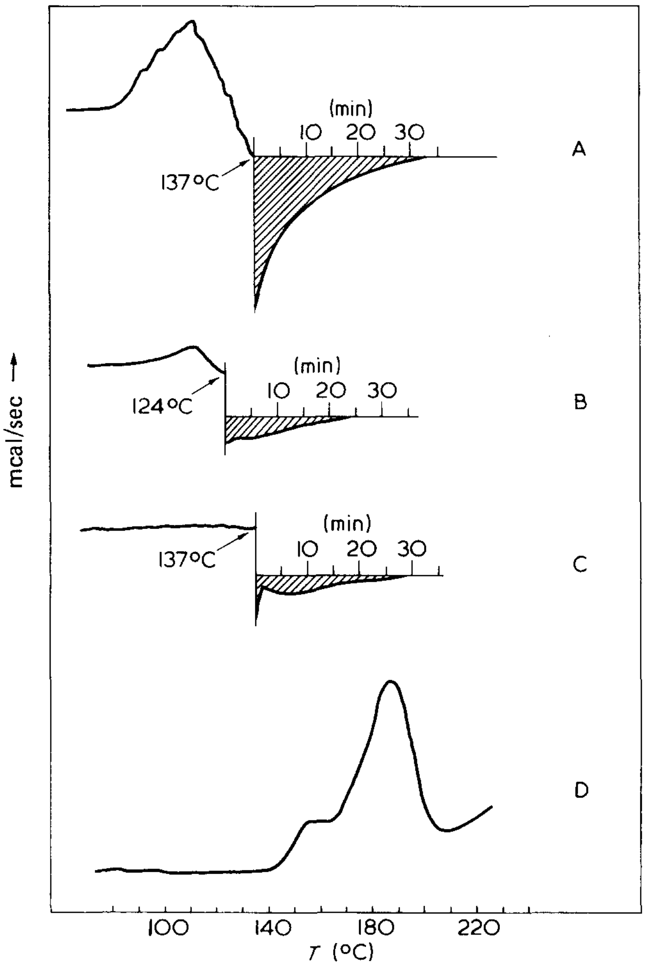

Figure 3 Isothermal recrystallization of the dried gel from *Figure 1*, followed by d.s.c. after heating at 20°C/min to: A, 137°C; B, 124°C; C, after recrystallization for 30 min at 124°C and subsequent heating to 137°C; D, melting of the recrystallized BzIPS at 20°C/min

gether with the 3/1 helix (only for IPS). This structure dissolves at much lower temperature. This new structure is directly related to the formation of fringed micellar crystals[1] as a consequence of intermolecular associations. These fringed micellar crystals are the crosslinks of the gel network. At low temperature, the formation of this new structure seems to be kinetically favoured, a few intermolecular associations being sufficient to obtain a gel network. The periodicity perpendicular to the chain axis seems to be poorly developed as reported in ref 1. The very fast formation of these particles inhibits subsequent crystallization into a 3/1 helix conformation. Even in dilute solution, observations on association of IPS in the low temperature region are widespread[9]. As a consequence of these associations, the viscosity of the solutions increases and lowers the crystallization rate. A close relation between this behaviour and the maximum in the crystallization rate in dilute solution, around the dissolution temperature of this new structure is suggested.

Another important observation is the very fast recrystallization of IPS and BzIPS dried gels on heating in the d.s.c., as represented in *Figure 2*. As already said, the low melting endotherm around 120°C is caused by the melting of the fringed micellar gel crystals. The shaded surfaces represent the crystallization exotherm which follows immediately this low melting endotherm. We have also followed this recrystallization isothermally (*Figure 3*). In *Figure 3a*, the gel was heated to its final melting point around 137°C and kept at this temperature for 30 min. At time zero, recrystallization had already started, as can be deduced from the shape of this exotherm. When the sample is first kept at 124°C (*Figure 3b*), part of the molecules recrystallize isothermally. When this crystallization is completed, subsequent heating of the same sample results in a second isothermal crystallization. It was also observed that no recrystallization occurs when annealing at 100°C, below the onset of the melting endotherm.

These results suggest that this recrystallization consists of a quantitative transformation of the new structure into the 3/1 conformation. This also supposes that quite a large fraction of IPS (corresponding to the crystalline fraction formed by recrystallization) is involved in the formation of the gel crystallites. This transformation is not a true solid state transformation, because this phenomenon is not observed in the swollen gel. When melting the crystals in the presence of a solvent, the chains dissolve immediately and recrystallization becomes very slow. In the dried state, at temperatures not so far above T_g, the diffusion rate of the chains is very low. Owing to this low mobility, chain segments can stay together for quite a time, resulting in a very fast recrystallization.

The crystalline fraction obtained after this fast crystallization amounts to 70% of the total degree of crystallinity obtained by isothermal crystallization of BzIPS from the melt during several days. The additional 30% is obtained by keeping the recrystallized gel at 137°C for several days. The final

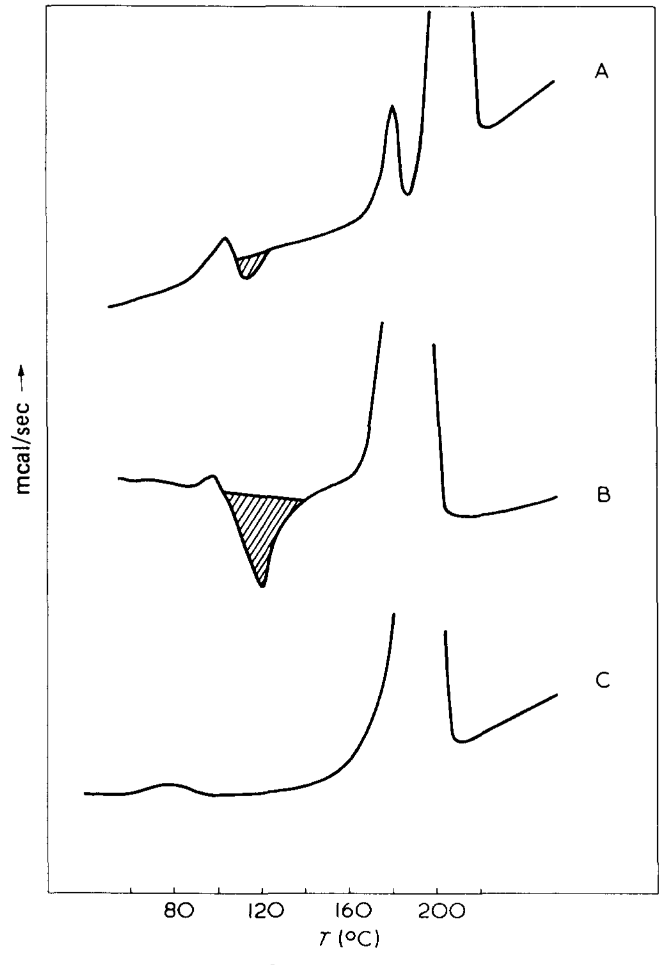

Figure 4 D.s.c.-trace at 10°C/min of: A, IPS crystallized in DMP at 54°C; B, the same crystals as in A after benzoylation; C, IPS crystallized in DMP at 86°C

overall degree of crystallinity of the copolymers is 0.22, which corresponds to about two thirds of the crystallinity of IPS at 137°C. If we take the 70% that are crystallized very rapidly during this recrystallization as a measure for the amount of IPS incorporated in the gel forming crystals, we might conclude that a volume fraction of about 0.15 of the IPS is involved in the formation of the new structure. No experimental verification was, however, possible until now.

A similar fast recrystallization behaviour was also observed with IPS solution crystals formed below the temperature corresponding with the maximum crystallization rate (*Figure 4*). A small exotherm was observed as shown by the shaded parts in *Figures 4a* and *4b*, which was not the case for IPS crystals formed at high temperature in dilute solutions (*Figure 4c*). This may suggest that even in IPS solution grown crystals, formed below this temperature where the maximum of the growth rate is situated, some amount of the new IPS structure may be present. It was also found that crystals formed below this temperature are very similar in stability and annealing behaviour[7]. The changes in long spacings and degree of crystallinity start at around 130°C on annealing. This may be related to the described fast recrystallization phenomenon subsequent to the melting of the new structure..

From our results on the gelation behaviour of partial benzoylated IPS solution crystals, we conclude that the gel crystals in IPS and BzIPS are built up by IPS sequences in another conformation than the familiar 3/1 helix. The suggestion is made that other unusual phenomena observed in the crystallization behaviour of IPS from solution, e.g. crystallization rates, annealing behaviour, could be related to the presence of this new structure.

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