Relation between physical gelation and tacticity in polystyrene

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In order to throw some light on the physical gelation of polystyrene in solution, we have prepared samples of differing tacticities by means of epimerization of an isotactic sample. After careful characterization by ^{1}H nuclear magnetic resonance, light scattering, viscometry and gel permeation chromatography, the gelation propensity has been studied by differential scanning calorimetry and the ball-drop method in carbon disulphide (CS_2) and in diethyl malonate. For a fraction of isotactic triads higher than 58%, gelation characteristics remain those of isotactic polystyrene. Between 58 and 35%, no gelation occurs whatsoever. Below 30%, the gelation characteristics of atactic polystyrene are retrieved only in CS_2. The main conclusion is that the gelation phenomenon in atactic polystyrene in CS_2 is due to the syndiotactic sequences.

(Keywords: physical gelation; polystyrene; isotactic; atactic; epimerization; carbon disulphide; diethyl malonate)

INTRODUCTION

The physical gelation of semi-dilute polymer solutions has received much attention over the past few years. In organic systems, it is generally admitted that such a phenomenon requires two main polymer properties: the presence of long enough stereoregular sequences and the capability of showing a certain amount of crystallinity in the bulk state (for instance, isotactic polystyrene (iPS)[1] and atactic poly(vinyl chloride) (PVC)[2]). From this viewpoint, physical gelation of atactic polystyrene (aPS) solutions, the occurrence of which is supported by several experimental works[3-6], is puzzling.

We have recently shown[6], by means of differential scanning calorimetry (d.s.c.), that gelation of aPS in carbon disulphide (CS_2) may originate from the formation of physical junctions that possess the characteristic of a congruently melting compound. This compound accordingly includes both monomeric units and solvent molecules. This model enables one to understand why the large solvent effect on gelation is not necessarily linked to its thermodynamic quality towards aPS, but rather to its propensity for forming ordered structures with the polymer.

Two questions remain unanswered: does the formation of a congruently melting compound require the existence of stereoregular sequences, and, if such is the case, what is the type of these sequences (iso- or syndiotactic)?

In order to throw some light on this problem, this paper deals with the influence of tacticity on the gelation of polystyrene. For this purpose, we have performed an investigation with polystyrene samples of differing tacticities obtained by epimerization of an iPS sample using the method described by Shepherd *et al.*[7] In the first part, the synthesis and characterization of such polymers is described. Then the d.s.c. study of gelation in different solvents is reported.

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EXPERIMENTAL

Epimerization reaction

The initial iPS sample was prepared by the classical Natta method[8]. It was purified by extraction in boiling heptane at 98°C for 12 h. Finally, the insoluble part was washed with a large excess of methyl ethyl ketone in order to extract the remaining non-isotactic polymer. Its weight-average molecular weight M_w is 3.4×10^5 g mol^{-1} and its polydispersity index is 2.8, as measured by gel permeation chromatography (g.p.c.), under conditions given below.

The iPS epimerization reaction, as described by Shepherd *et al.*[7], was carried out at 100°C under an argon atmosphere for up to 120 h in hexamethyl phosphoramide solutions (100 mg of iPS for 5 ml) containing potassium t-butoxide. The solvent was dried on molecular sieves (13 Å) for several days. The epimerization products (ePS) were recovered by pouring, at different reaction times, a given volume of reaction batch into a methanol–water (50:50) mixture.

Fractionation of the epimerization products

The ePS samples were dissolved in boiling toluene and the fractionation was carried out by addition of methanol as precipitant at 50°C.

Techniques

Nuclear magnetic resonance spectroscopy. ^{1}H n.m.r. spectra of the ePS samples were obtained in deuterated tetrachloroethane ($C_2D_2Cl_4$) solutions (5% weight) by using a Bruker WH90 spectrometer operating at 200 MHz.

Gel permeation chromatography. The different ePS fractions were characterized at 20°C by using a Waters 200 chromatograph coupled with an automatic viscometer[9] with tetrahydrofuran (THF) as elution solvent. The ePS solutions in THF were left at 60°C for 24 h prior to characterization.

Light scattering. Light scattering measurements were performed at 25°C with a Wippler–Scheibling type photogoniodiffusometer[10] operating with a red laser beam (wavelength 632 nm). Freshly distilled THF was used as the solvent. The solutions were prepared near the THF boiling point and clarified by centrifugation at room temperature.

Differential scanning calorimetry. We have used a Perkin–Elmer DSC II microcalorimeter equipped with the thermal analysis data station (TADS) which allows correction of the baseline to be made. This enables one to detect broad melting endotherms such as those drawn in *Figure 7*. Cooling and heating rates ranged from 10 to 80°C min^{-1}.Calibrations were obtained by means of an indium standard.

The polymers were vitrified prior to solution preparation by a quench to room temperature after subsequent heating at 250°C for iPS and ePS samples and at 150°C for aPS samples.

Sheets of about 1 mm thickness were obtained. A desired quantity of these vitrified polymer sheets was introduced into a special pan dedicated to the study of volatile samples. An appropriate volume of solvent was added into the pan, which was then tightly sealed. To ensure thorough homogeneity, the pans were left either at 40°C for several days for samples in CS_2 or at 180°C for several minutes for samples in diethyl malonate (DEM). After these initial thermal treatments, the pans were annealed at room temperature for a minimum of two months. Concentrations (w/w) of the systems were determined before and after each measurement by weighing the pans. The precision on enthalpy values is approximately ± 0.05 cal g^{-1}.

Ball-drop method. We used the ball-drop method, which, although simple, provides the same information as more sophisticated techniques such as the sphere rheometer as far as only the macroscopic sol–gel transition temperature is concerned and regardless of the viscoelastic properties of the system. Known quantities of polymer and solvent were introduced along with a steel ball (60 mg) into a glass tube, and the system was sealed from the atmosphere. Each tube was kept at 70°C for one week to allow for homogeneity prior to any measurements. The ball was then allowed to sink to the bottom of the tube, and the gel was formed by slowly cooling to -60°C. The tube was then turned upside down after gel formation. The temperature was raised at a rate slower than 0.5°C min^{-1}. A magnetic field was applied from time to time to make sure that the ball was still supported by a gel-like material. The temperature at which the ball fell through the sample under a magnetic field was taken as the gel melting temperature.

RESULTS AND DISCUSSION

Characterization of the ePS samples

We have obtained five ePS samples (E_{40}, E_{85}, E_{150}, E_{300} and E_{400}) corresponding to reaction times of 40, 85, 150, 300 and 400 min, respectively. The g.p.c. chromatograms of these unfractionated ePS samples are given in *Figure 1*. Since it is known that tacticity has little influence on hydrodynamic radius of PS[11], the shift towards lower elution volumes for reaction times longer than 80 min indicates significant degradation. It is difficult to say if such degradation is due to the epimerization process or to oxygen that is still present despite the use of an argon atmosphere.

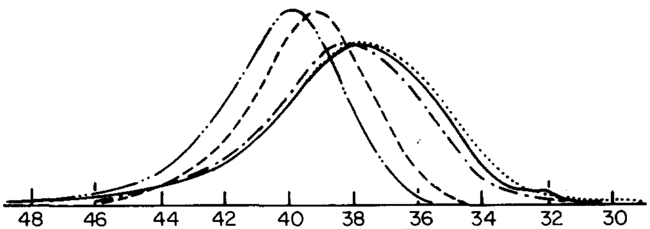

Figure 1 G.p.c. chromatograms of the epimerization products (ePS) after different reaction times: 40 min, E_{40} (·····); 85 min, E_{85} (———); 150 min, E_{150} (-·-·-); 300 min, E_{300} (----); and 400 min, E_{400} (-··-··-)

The molecular characteristics of the ePS fractions are given in *Table 1* and the chromatograms for E_{40} fractions are represented in *Figure 2*. The M_w values, determined from g.p.c. experiments by using the universal calibration method[9], are in rather good agreement with those obtained by light scattering. As can be seen in *Table 1* the polydispersity indices of these fractions range from 1.2 to 2.7 and increase with increasing M_w.

Figure 3 shows the ^1H n.m.r. spectra of the fractions of lowest molecular weight (F_6) for each epimerization product as well as those of aPS (either anionic or radical) and iPS. The resonance of the methine protons consists of two main resonance areas: one at 2.06 ppm (labelled A in *Figure 3a*) characteristic of iPS (mm triads) and another one at 1.78 ppm (labelled B in *Figure 3b*), which is predominant in aPS spectra. The evolution of the ePS samples spectra (*Figure 3b*) shows qualitatively that the epimerization process did take place. Additional experiments carried out on other fractions of a same ePS sample (same reaction time) have not revealed significant molecular-weight dependence of the spectral characteristics; this indicates homogeneous polymer transformation.

There is some controversy as to the assignment of the two main n.m.r. peaks. In order to compare our results with those of Shepherd *et al.*, we have used the attribution they proposed and which seems to be in better agreement with theoretical considerations[12–14]. The A and B resonance areas are assigned to mm and to rr + (rm + mr) triads respectively. In *Figure 4*, we have reported the variation of the fraction of rr + (rm + mr) triads as a function of reaction time. Our experimental results are in very good agreement with those of Shepherd *et al.*[7] These authors have modelled the epimerization reaction through a Monte Carlo simulation. The analysis is based on the difference predicted by Williams and Flory[15] between the probabilities of syndio (0.65) and iso (0.35) arrangements. We have repeated this calculation, which allows predictions of the kinetic variation of fractions of triads, and have shown that they are consistent with n.m.r. results (see *Figure 4*). In addition, we have extended this calculation to the determination of the average fraction of monomer units contained in iso and syndio sequences of given length n (t_{nm} and t_{nr} respectively) and the average length of iso and syndio sequences (n_m and n_r respectively). In *Table 2* are reported these statistical data calculated for the epimerization

Table 1 Characteristics of the fractions of the epimerization products as obtained from gel permeation chromatography, viscometry and light scattering

	Gel permeation chromatography				Viscometry	Light scattering		
Sample	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	$n=\frac{M_w}{M_n}$	$[\eta]$ ($dm^3\,kg^{-1}$)	$[\eta]$ ($dm^3\,kg^{-1}$)	$M_w \times 10^{-5}$	R_g (nm)	A_2 ($m^3\,kg^{-2}\,mol$)
$E_{40}F_2$	4.53	2.5	1.8	148		4.8	43.6	7.7×10^{-4}
$E_{40}F_3$								
$E_{40}F_4$	3.31	2.12	1.58	121				
$E_{40}F_5$	2.43	1.78	1.36	102	106	2.8	38.4	6.3×10^{-4}
E_6	1.7	1.4	1.21	59	68			
$E_{85}F_2$	11.0	4.93	2.23					
$E_{85}F_3$	4.92	2.41	2.04	174	182			
$E_{85}F_4$	3.84	2.26	1.70	133	126			
$E_{85}F_5$	2.4	1.68	1.43	101				
$E_{85}F_6$	1.75	1.25	1.4	63	59			
$E_{150}F_2$	7.56	3.88	1.95		228			
$E_{150}F_3$	4.77	1.83	2.6	156	166			
$E_{150}F_4$				125	126			
$E_{150}F_5$	4.92	2.2	2.22	149				
$E_{150}F_6$	1.69	1.17	1.44	69	71			
$E_{300}F_2$					133			
$E_{300}F_3$	2.75	1.72	1.6	110	115	3.1	26.2	1.76×10^{-3}
$E_{300}F_4$	2.59	1.6	1.6	88	106			
$E_{300}F_5$	2.07	1.46	1.42	85				
$E_{300}F_6$	1.84	1.34	1.37	70		1.5	16.1	3.66×10^{-4}
$E_{400}F_1$	3.4	1.6	2.12					

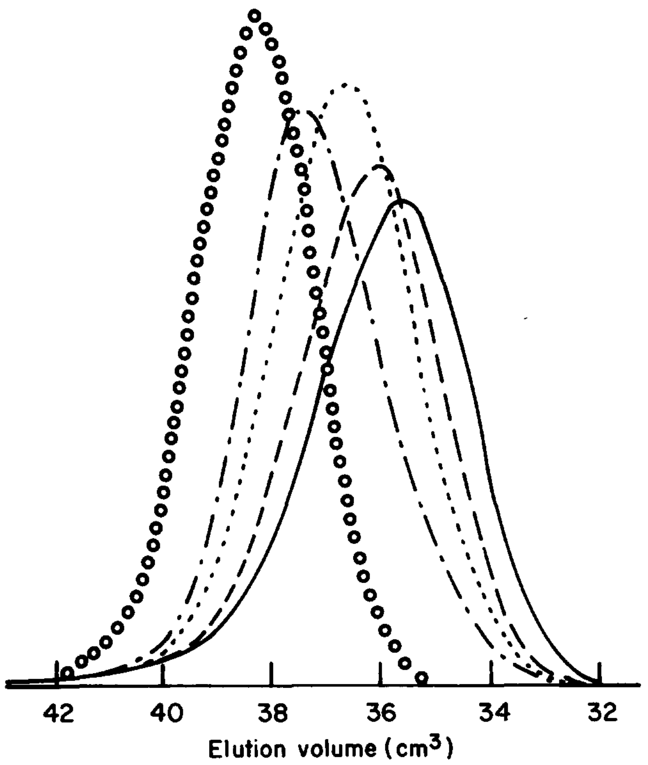

Figure 2 G.p.c. chromatograms of the fractions of the epimerization product E_{40}

products under study. From theoretical results of *Figure 5a*, it turns out that epimerization at low reaction yields should favour the *even* syndio sequences (——) unlike a Bernoullian distribution determined for the same values of dyad fractions (– – –). Conversely, at high reaction yields, one retrieves the distribution obtained for

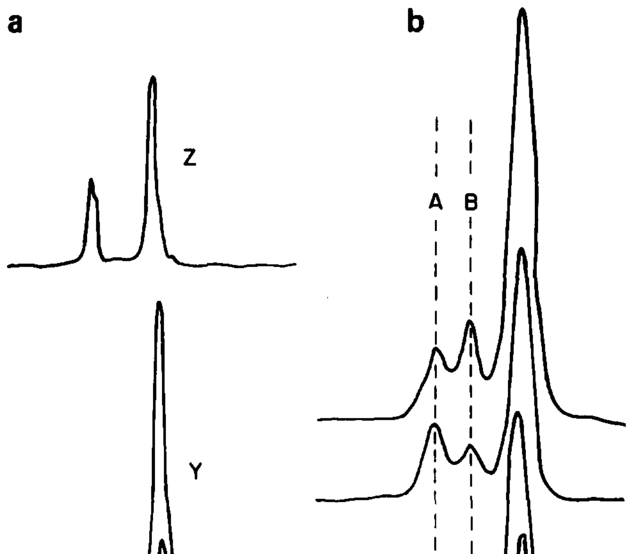

Figure 3 ^1H n.m.r. spectra: (a) radical (X) and anionic (Y) atactic polystyrenes, and isotactic polystyrene (Z); (b) epimerization products, E_{40}, E_{85}, E_{150}, E_{300} and E_{400} from the bottom to the top

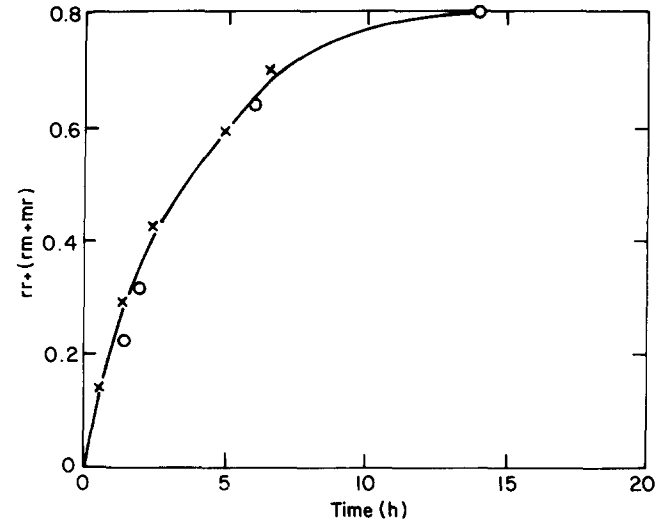

Figure 4 Dyad concentrations in epimerized isotactic iPS as a function of reaction time; (○) results of ref. 7; (×) this work

Table 2 Statistical data for epimerization products[a]

	m	mm	n_m	n_r	$n_{r\,max}$
E_{40}	0.93	0.86	12.7	2.00	2
E_{85}	0.84	0.71	9.1	2.09	4
E_{150}	0.76	0.58	5.4	2.19	6
E_{300}	0.64	0.41	3.3	2.26	8
E_{400}	0.55	0.30	2.4	2.30	10
aPS	0.45	0.20	1.9	2.38	14

[a] m, fraction of isotactic dyads; mm, fraction of isotactic triads (f_{iso}); n_m and n_r, average length of iso- and syndiotactic sequences respectively; $n_{r\,max}$, maximum length of syndiotactic sequences (probability of longer sequences lower than 0.1%)

Bernoullian statistics, which corresponds to the case of polymers prepared by classical polymerization methods (anionic or free-radical) (*Figure 5b*). This analysis will be of further use for the discussion of the gelation phenomena.

Gelation of ePS and iPS samples

We are not concerned in this paper with the kinetics of gel formation. The goal is restricted to discovering the relation between the propensity of polystyrenes to form physical gels and their tacticity. Two solvents have been selected for this purpose: carbon disulphide and diethyl malonate.

Gelation in CS_2. In a systematic study of aPS physical gelation in various solvents, Tan *et al.*[3] found out that the sol–gel transition occurs at higher temperatures in CS_2 than in other 'gelation solvents' for the same polymer concentration. For instance, for a concentration of 15% w/w, the sol–gel transition temperature T_{gel} is near 0°C, but it can reach 25°C for 45% concentration. Although the origin of this particular behaviour is not yet totally clear, this system is by far the most interesting. It is possible to differentiate T_{gel} from the glass transition temperature T_g. Recent d.s.c. experiments carried out on different aPS–CS_2 systems have allowed us to establish temperature–concentration phase diagrams of the type drawn in *Figure 6*[6]. Three domains can be distinguished: domain A, corresponding to a homogeneous solution; domain B, corresponding to the gel; and domain C, corresponding to a glass. In addition T_{gel} was found to be independent of molecular weight but to be dependent on concentration with a maximum around 45%. A maximum for the gel melting enthalpy ΔH is also seen for this concentration. To our knowledge, no investigation has been reported for iPS gelation in CS_2.

We chose to investigate all the systems (aPS and iPS) at a given concentration, 45% w/w, which is expected from aPS data to provide the highest enthalpy values. The thermograms are represented in *Figure 7*. The most noticeable fact is the absence of any endotherms for ePS

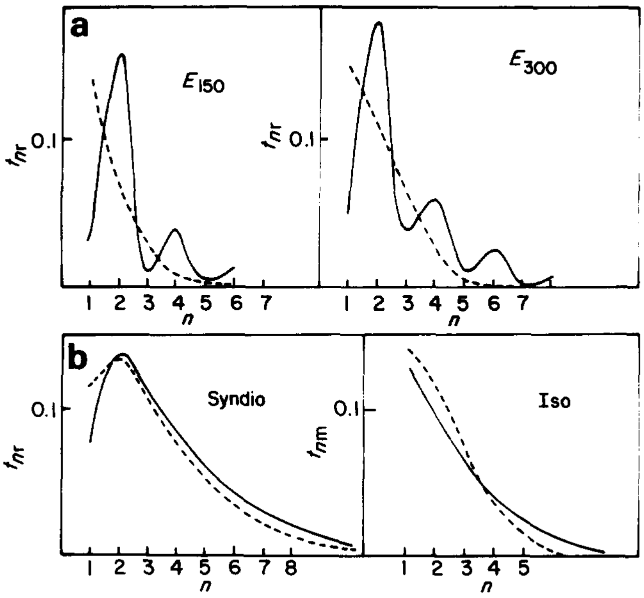

Figure 5 Statistics of the epimerization products as determined through Monte Carlo calculations: (a) fraction of monomer units contained in syndiotactic sequences of length *n*; (b) fractions of monomer units contained in syndiotactic and isotactic sequences of length *n* for E_∞ at total conversion

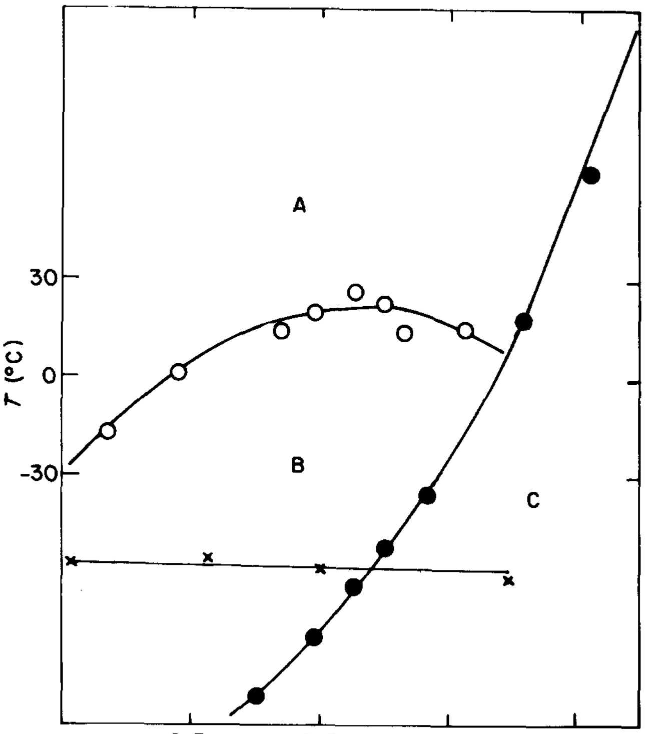

Figure 6 Phase diagram of aPS–CS_2 system: (●) glass transition temperature; (○) sol–gel transition temperature. (Crosses correspond to iPS, see text)

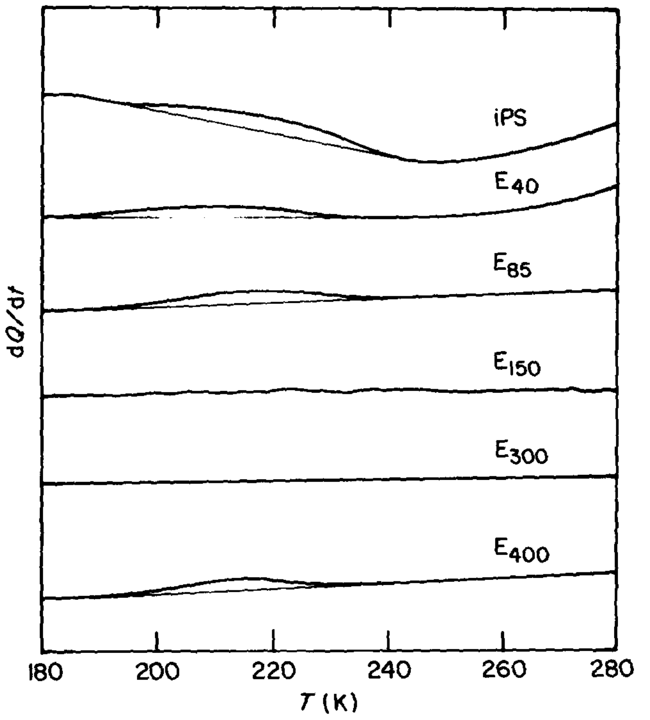

Figure 7 D.s.c. traces for a given polymer concentration ($C=45\%$) in CS_2 but for different contents of isotactic triads

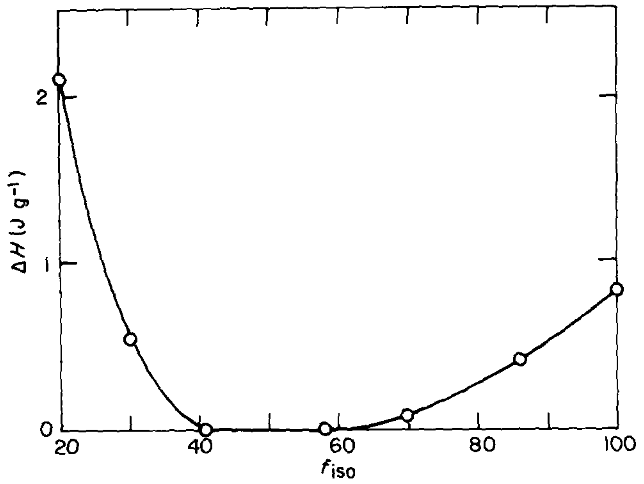

Figure 8 Variation of the melting enthalpy of the low-temperature endotherm as a function of the content of isotactic triads, for polystyrene in CS_2 (45%)

E_{150} and E_{300}. This indicates that gelation does not occur with these systems, a fact confirmed by parallel studies carried out with the ball-drop method. Apparently, this intermediate range of tacticity does not allow gelation while higher degrees of isotacticity or syndiotacticity do. However, in either case, gelation does not have the same characteristics.

(i) The thermograms of iPS, ePS E_{40} and ePS E_{85}, whose fraction of isotactic triads (designated as f_{iso} in what follows) is higher than 0.70, exhibit an endotherm at −50°C, and the associated enthalpy decreases with increasing f_{iso} (see *Figure 8*). Studies by the ball-drop method confirm that these systems are physical gels but their melting point exceeds the boiling point of CS_2 (45°C) and accordingly does not correspond to the temperature domain of the endotherm. Interestingly, in the case of iPS, the endotherm maximum does not vary with concentration (see *Figure 6*). Such an invariance has also been observed in atactic PVC gels and has been assigned to a gel A–gel B transition[16], the nature of which has still not been elucidated. In addition, no glass transition has been observed, unlike for aPS. These preliminary results should be further developed.

(ii) When f_{iso} is lower than 40%, gelation again occurs with characteristics similar to those of aPS. Indeed, the melting point measured by the ball-drop method corresponds to that determined by the endotherm. Yet, T_{gel} for ePS E_{400} gels is far lower than that for aPS gels. Also the gel melting enthalpy is significantly smaller (see *Figure 8*).

This first series of results clearly shows that tacticity is the driving factor for polystyrene gelation in CS_2 as confirmed below by studies in diethyl malonate.

Gelation in diethyl malonate. While gelation of iPS in CS_2 had not so far been reported, its occurrence in other solvents is well documented. Unlike aPS gels, for which the formation process is independent of the cooling rate, iPS gelation requires a rapid quench of the solutions to low temperatures so as to by-pass crystallization under the three-fold helical form (3_1). Until recently, iPS gelation was attributed to the crystallization of another helical form: 12_1 helices[17,18]. Neutron diffraction experiments have called into question such an interpretation[19]. Rather, it is suggested that the structure of the junction points in nascent gels consists of near-3_1 helices the cohesion of which is ensured by the solvent molecules (solvent-mediated interactions). In this view, the gel is not regarded as crystalline[19]. In some solvents such as *trans*-decalin, d.s.c. thermograms on nascent gels reveal only one endotherm, which corresponds to gel melting. Conversely, in other solvents such as diethyl malonate (DEM), the melting behaviour is more complex: two endotherms are observed whose relative proportions are heating-rate-dependent. The low-melting endotherm corresponds to the nascent gel metastable melting point whereas the high-melting endotherm represents the fusion of crystals constituted of 3_1 helices[20]. These crystals ('3_1 crystals') can originate from two processes: either by crystallization from the solution resulting from gel melting, or from transformation of the nascent gel structure into the 3_1 form prior to gel melting[20]. At any rate, DEM is of particular interest since both structures can be observed in a single thermogram and is thus well suited to carrying out an investigation of the effect of tacticity on the gelation propensity.

To our knowledge, no study of aPS gelation in DEM has been reported so far. From this experimental work (d.s.c. and ball-drop method), no gelation occurs if f_{iso} is lower than 58%. For higher values of f_{iso}, the thermograms resemble those obtained for purely isotactic PS, as shown in *Figure 9*. As described above, two endotherms are seen, the melting enthalpy of which decreases with decreasing f_{iso}. *Figure 10* shows the variation of ΔH vs. f_{iso} for the low-melting endotherm. Such a result is expected for both models (12_1 or near-3_1) since the formation of either type of helix requires a minimum isotactic sequence length. While the temperature of the low-melting endotherm does not depend on tacticity, that of the high-melting endotherm decreases by decreasing the isotactic fraction (see *Figure 10*). The explanation of these variations is beyond the scope of this paper. However, if 12_1 helix crystals constituted the nascent gel structure, one would have expected the same behaviour for both endotherms.

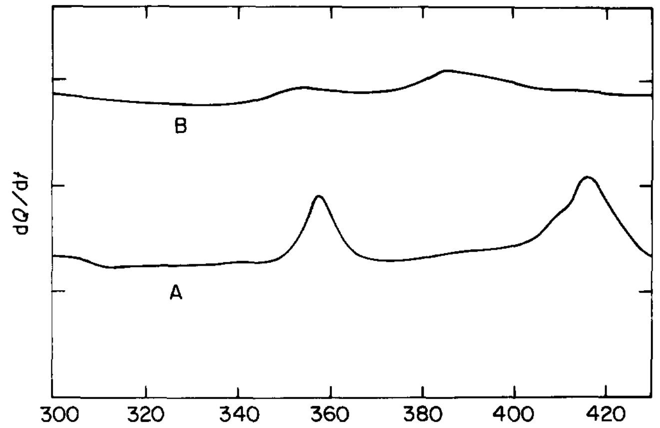

Figure 9 D.s.c. traces of (A) iPS in diethyl malonate (20%) and (B) E_{85} (19%)

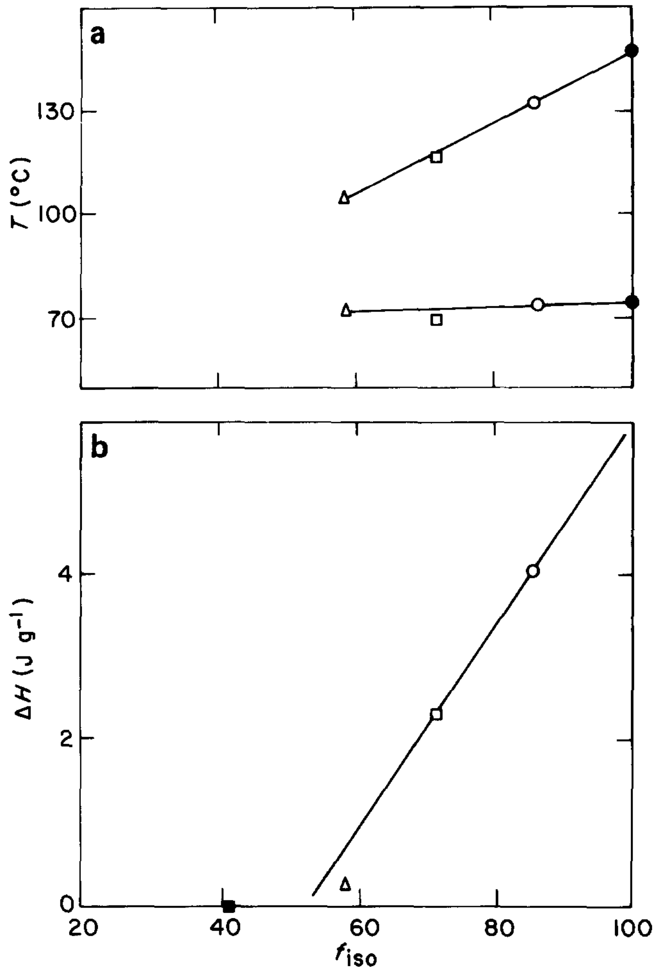

Figure 10 Polystyrene in diethyl malonate: variations of (a) the melting temperatures of the high- and low-melting endotherms and (b) the melting enthalpy of the low-melting endotherm with the content of isotactic triads

Discussion

These results enable one to answer some fundamental questions about the origin of reversible gelation in polystyrene solutions.

(i) Polymer tacticity is the driving force of the gelation phenomenon.

(ii) Gelation of aPS does not originate from remaining isotactic sequences. As a matter of fact, studies carried out in CS_2 have revealed two different types of behaviour: one characteristic of highly isotactic samples and another typical of aPS. In DEM, only samples of high f_{iso} can gel and, interestingly, this capability disappears at the same f_{iso} as in CS_2. Evidently, gelation of ePS of $f_{iso} > 58\%$ can be attributed to the association of either 12_1 or near-3_1 helices as in iPS. If we consider the statistical data of *Table 2*, one realizes that the gelation of isotactic type requires an average length higher than 6 for the isotactic sequences. This result does not necessarily entail that the 12_1 helical form must be definitely ruled out. Indeed, while the average sequence length is 6, one can still find isotactic sequences made up of 12 or more monomers.

(iii) On the basis of the above considerations, we suggest that gelation of aPS is due to the syndiotactic sequences and, ultimately, to their intermolecular associations. If such a statement is correct, it is surprising to find out that atactic type gelation appears for an average length of these sequences as low as 2.3 (E_{400}) and for very low probabilities of long sequences (see last column in *Table 2*). In fact, it is known that the stable form of the syndiotactic chain is the zig-zag conformation where two monomers are enough to form one repeat unit. Accordingly, this may explain why in this type of gelation the minimum sequence length is smaller than in isotactic gelation where the formation of one turn of helix requires a larger number of monomers.

At any rate, further investigations are needed to confirm the major role of the syndiotactic sequences and characterize the structure and size of junction domains.

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