Phase behaviour of syndiotactic polystyrene–decalin

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The phase behaviour of syndiotactic polystyrene–decalin is studied by differential scanning calorimetry, wide-angle X-ray scattering and thermogravimetric analysis. Both the *trans* and *cis* isomers of the solvent have been used. The polymer chain can adopt a helix or a zigzag conformation. The formation of these conformations and their relative contribution to the crystalline structure depend on the initial concentration, the scanning rate and the thermal history of the samples. High cooling rates and low polymer concentrations tend to favour the formation of the helix structure. The conformational transition from the helix to the zigzag conformation can take place on heating. This depends on the experimental conditions.

(Keywords: syndiotactic polystyrene; decalin; solutions; phase behaviour; conformational transition)

INTRODUCTION

The recent developments in the synthesis of highly syndiotactic polystyrene (sPS) have enhanced the interest in this polymer[1–9]. The high melting temperature, chain stiffness, chemical stability and high crystallization rate make sPS an attractive material[10–13].

Structural studies have revealed a very complex polymorphic behaviour[14–23]. The chain can adopt two different conformations, an all *trans* planar zigzag structure (T_4) and a helix structure (T_2G_2). The polymer can crystallize in four major crystalline modifications. The chain adopts the T_4 conformation in the α and β modifications. Both α and β forms can be characterized by a differing degree of structural order intermediate to the two limiting disordered (α' and β') and the two limiting ordered (α'' and β'') modifications. The γ and δ modifications are characterized by a T_2G_2 helix conformation. The γ modification is a completely dried crystalline structure. The δ modification is always prepared in the presence of a solvent and seems to include some solvent molecules. Its exact crystalline structure depends on the nature of the solvent.

EXPERIMENTAL

The polymer was supplied by Idemitsu Kosan Co Ltd, Japan and by Dow Chemical, USA. The samples are referred to, respectively, as sPS1 and sPS2. The weight- and number-average molecular weights, determined by g.p.c. in 1,2,4-trichlorobenzene at 125°C, are 7.9×10^4 and 2.9×10^4 for sPS1 and 18.5×10^4 and 7.2×10^4 for sPS2.

The thermal behaviour was studied with a differential scanning calorimeter Perkin-Elmer DSC-2C equipped with a thermal analysis data station. A cooling and heating rate of 5°C min^{-1} was used. (The use of other rates is specified where appropriate.)

Wide-angle X-ray scattering (WAXS) patterns were obtained using CuKα radiation and recorded with a Philips PW 1729 flat film camera.

Thermogravimetric analysis (t.g.a.) was carried out with a Stanton Redcroft STA 780 series and a Setaram TGDSC 111 instrument.

Trans- and *cis*-decalin (TD and CD, respectively) with a degree of purity of 0.99 were obtained from Aldrich Chemie.

The polymer weight fraction (φ_2) is used to express the polymer concentration.

RESULTS

Phase behaviour of sPS–TD

Construction of the phase diagram: general considerations. The temperature–concentration (T–φ_2) phase diagram of sPS–TD was investigated by differential scanning calorimetry (d.s.c.). On cooling sPS–TD, crystallization takes place. This is reflected in one or several exothermic signals. The temperature at the onset of this signal is reported as the crystallization temperature, T_c. Its position on the temperature scale depends on the cooling rate and on the polymer concentration. The values obtained at different concentrations and at constant cooling rate are used to construct the 'crystallization line' in the phase diagram.

Heating results in the melting of these crystals. Up to three endotherms can be observed in a d.s.c. scan. The temperature at the end of an endotherm is reported as the melting point, T_m. This temperature has to be used because of the two-component nature of the system[24]. The solvent represents one component. The polydisperse polymer is considered in a first approximation as a single component. It represents the second component in the system. The melting point of such a system is monovariant at constant pressure. The temperature at the end of the melting endotherm corresponds to the dissolution of the

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Table 1 WAXS results of sPS crystallized from dilute solution with TD and compared with results obtained from the literature[19]

A		B		C		D	
d (Å)	*i*[a]	*d* (Å)	*i*	*d* (Å)	*i*	*d* (Å)	*i*
12.4	m	11.32	m	7.3	s	7.17	vs
5.5	vs	5.21	vs	6.4	m	6.49	m
3.9	m	3.88	s	5.6	m	5.56	m
3.2	w	3.19	w	2.6	w	2.55	m
				2.1	vw		

A, homogeneous solution quenched in liquid nitrogen, isothermally crystallized at 60°C; B, diffraction results for β phase obtained by Guerra *et al.*; C, homogeneous solution isothermally crystallized at 90°C; D, diffraction results for δ phase obtained by Guerra *et al.*

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong

last crystals. It has to be used to construct the 'melting line' in the phase diagram.

This melting point does not represent an equilibrium value for different reasons. Crystallization takes place at a certain degree of undercooling and the melting point will depend on the crystallization conditions. The experiments are performed at 5°C min^{-1} with rather large samples and this results in a certain degree of superheating. Therefore, the diagrams reported in this paper represent only an approximation of the equilibrium phase behaviour. They nevertheless are very useful in the general discussion of the behaviour of the polymer–solvent system.

Another important parameter is the glass transition temperature (T_g) of the polymer–solvent system. Its position on the temperature scale and its concentration dependence are of great importance in the understanding of the phase diagram.

Structural information on the phase behaviour can be obtained only when the calorimetric data are combined with those obtained from WAXS. The crystal phases are characterized by comparing the most characteristic lattice spacings, experimentally observed, with those reported in the literature. This allows the different crystal phases to be clearly distinguished, in spite of the lower degree of accuracy obtained with the flat film camera recordings. A typical example is reported in *Table 1*.

The interpretation of these results has also to include the crystallization and melting enthalpies of the polymer, obtained by integration of the d.s.c. signals. The values reported in this text are always reduced to the amount of polymer present in the solution.

Dynamic observations. The T–φ_2 phase diagram of sPS1–TD has been studied by d.s.c. The phase diagram is shown in *Figure 1*. Two different concentration regions have to be considered.

(1) Low concentration region ($\varphi_2 < 0.40$)

(i) Crystallization behaviour. Two exotherms are observed on cooling. A typical example of a d.s.c. scan is represented in *Figure 2A*. The T_c of the high temperature exotherm (T_c^β) increases with increasing polymer concentration. The T_c of the lower temperature exotherm (T_c^δ) does not depend on the polymer concentration.

These two transitions represent the formation of two different crystal structures: the β phase in the high temperature region and the δ phase in the low temperature region. This attribution is based on X-ray scattering data obtained with samples isothermally crystallized at two different temperatures.

Annealing of a solution ($\varphi_2 = 0.10$) above T_c^δ, at 90°C for 100 h, results in the formation of a paste-like gel. When this gel is dried at room temperature under reduced pressure, a touch-dry sample is obtained. It still contains ~6% solvent, which can only be eliminated by heating. This has been determined by thermogravimetry (*Figure 3A*). The WAXS pattern corresponds to the one obtained with a sample crystallized from the melt (*Table 1*). In these crystals, the molecules adopt a T_4 planar zigzag conformation. No further detailed analysis has been performed in order to differentiate between the

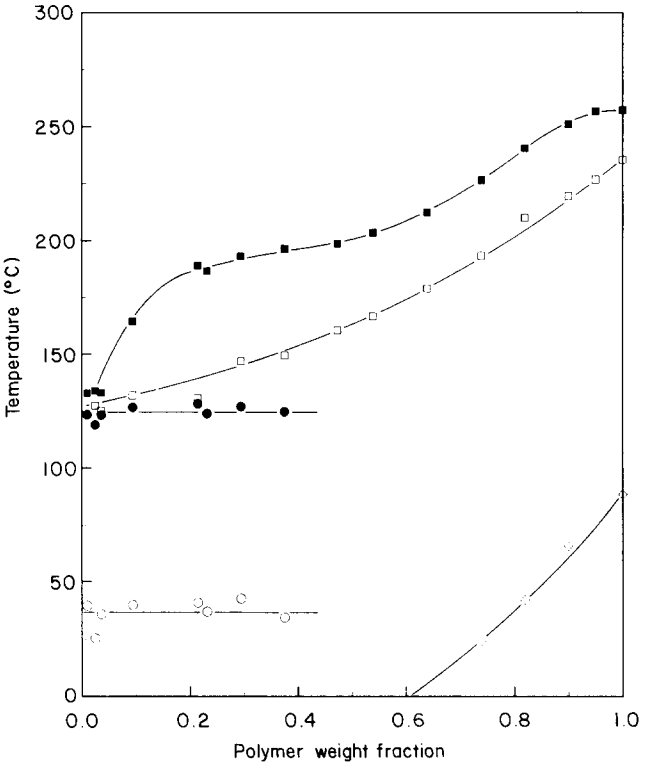

Figure 1 Phase diagram of sPS1–TD: (○) crystallization of helix conformation; (□) crystallization of zigzag conformation; (●) melting of helix conformation; (■) melting of zigzag conformation; (◇) glass transition

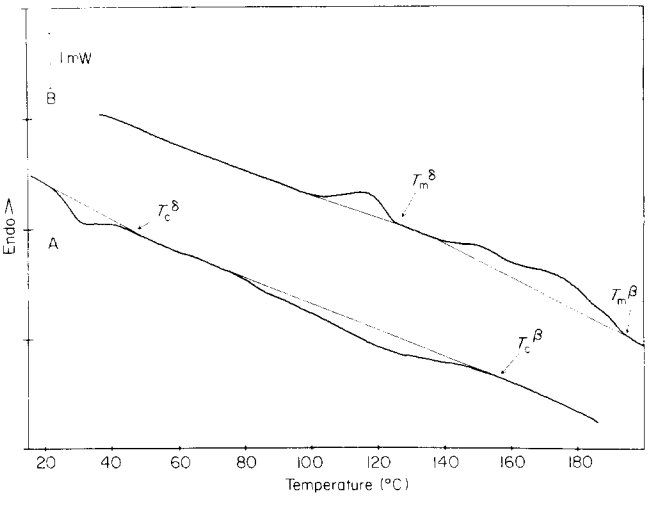

Figure 2 D.s.c. thermograms of sPS1–TD ($\varphi_2 = 0.29$): (A) cooling; (B) heating

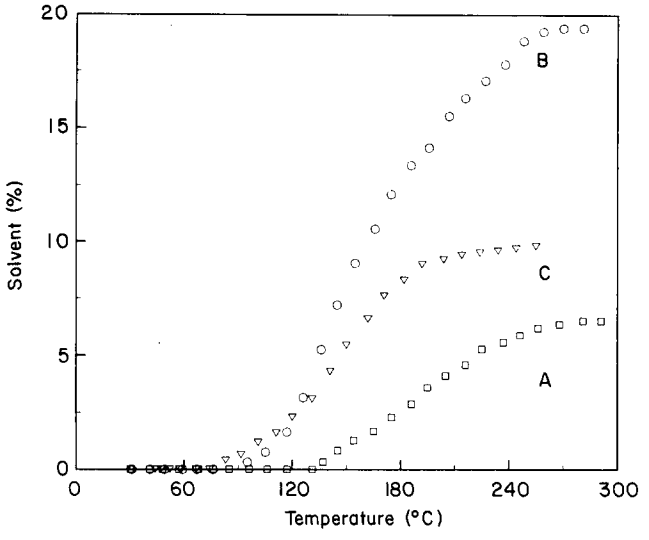

Figure 3 Thermogravimetric analysis of samples dried at room temperature under reduced pressure: (A) β phase sPS; (B) δ phase sPS; (C) aPS

different crystal modifications of the α and β structures. The phase will be called the β phase. Its crystallization temperature will be reported as T_c^{β}. The crystallization of this β phase extends over a very broad temperature range. The temperature at the end of the crystallization exotherm is always situated around 75°C, independent of the initial concentration.

The β phase is not formed when a solution with the same polymer concentration is quenched from the sol state into liquid nitrogen. Annealing at 60°C for 100 h results in the formation of a hazy gel. When this gel is dried at room temperature under reduced pressure, a touch-dry sample is obtained. Its t.g.a. reveals the presence of 20% solvent (*Figure 3B*). An atactic sample, prepared and dried under the same conditions, contains only 10% solvent (*Figure 3C*). The WAXS analysis of the dried sPS sample proves the presence of crystals in which the molecules adopt a T_2G_2 helix conformation. One can conclude therefore that the δ phase has been formed (*Table 1*).

(ii) Melting behaviour. Heating of the crystallized samples results in three melting endotherms. A typical d.s.c. scan is represented in *Figure 2B*. The low temperature endotherm corresponds to the melting of the δ phase that is crystallized in the low temperature region. The corresponding melting temperature, T_m^{δ}, is independent of the polymer concentration (*Figure 1*).

The high temperature endotherm represents the melting of the β phase. It is the only endotherm that is recorded when the samples are crystallized isothermally at 90°C (*Figure 4A*). A different d.s.c. trace is obtained when the sample is heated for the second time after it has been cooled (*Figure 4B*). This corresponds to the one obtained in the dynamic experiments that were carried out to construct the phase diagram (*Figure 1*). The temperature at the end of the high temperature melting endotherm is the same for both experiments. The corresponding melting enthalpy however is different. It is much larger when the samples are crystallized at 90°C. This difference, together with the absence of the low temperature melting signal reveals the important influence of the thermal history.

The occurrence of two endotherms in the high temperature region is ascribed to dynamic recrystallization on heating. The contribution of the melting peak at the highest temperature decreases in favour of the signal at lower temperature when the heating rate is increased (*Figure 5*). This has already been illustrated for pure sPS[11]. The same rate dependence has been found in the polymer–solvent system.

The melting temperature of the β phase, T_m^{β}, increases with increasing polymer concentration (*Figure 1*).

(iii) Melting enthalpy. Integration of the crystallization and melting peaks in this concentration region is rather difficult and the reproducibility is limited. Some scattering is observed in the data. Nevertheless the data reveal a decrease of the melting enthalpy of the δ phase with increasing polymer concentration. The melting enthalpy is zero at $\varphi_2 = 0.40$. A parallel increase of the melting enthalpy of the β phase is observed.

(2) High concentration region ($\varphi_2 > 0.40$)

(i) Crystallization behaviour. Only one exotherm is observed on cooling. It corresponds to the formation of the β phase. This information has been obtained from WAXS experiments, carried out as described earlier. The polymer adopts the same conformation when it is crystallized from the melt. No exotherm, characteristic for the formation

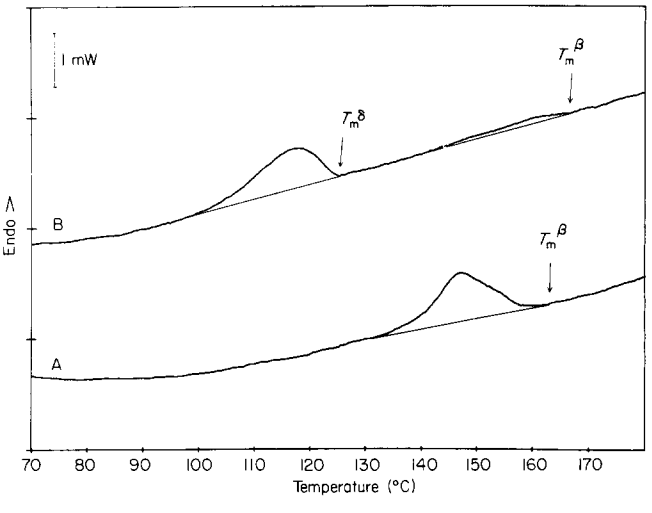

Figure 4 D.s.c. thermograms of sPS1–TD ($\varphi_2 = 0.10$): (A) after isothermal annealing at 90°C; (B) after cooling at 5°C min^{-1}

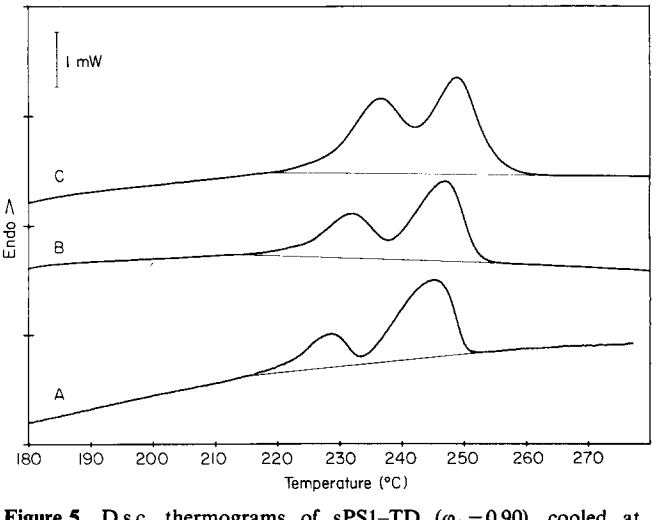

Figure 5 D.s.c. thermograms of sPS1–TD ($\varphi_2 = 0.90$), cooled at 5°C min^{-1} and heated at various scanning rates: (A) 5°C min^{-1}; (B) 10°C min^{-1}; (C) 20°C min^{-1}

Table 2 Influence of cooling rate on the crystallization behaviour of a solution of sPS2–TD ($\varphi_2 = 0.25$)

Cooling rate (°C min^{-1})	T_c^δ (°C)	T_c^β (°C)	ΔH_c^δ (J g^{-1})
−5	55.6	174.7	−11.2
−10	57.0	160.6	−16.5
−20	61.4	139.2	−25.8
−40	58.7	123.2	−31.4

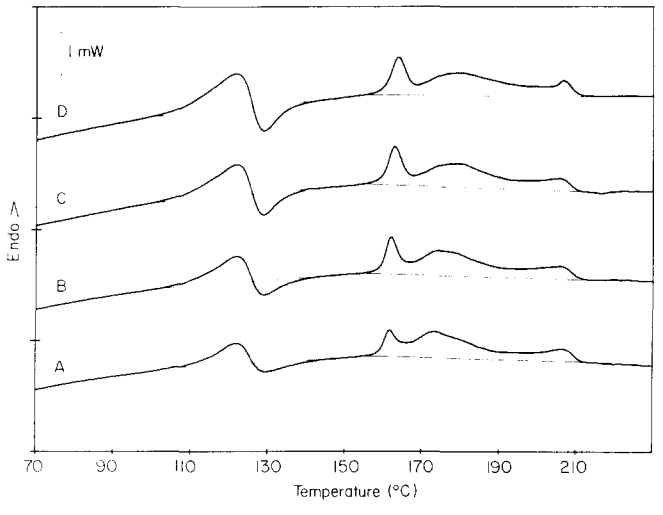

Figure 6 D.s.c. thermograms of sPS–TD ($\varphi_2 = 0.25$) heated at 5°C min^{-1} and cooled at various rates: (A) 5°C min^{-1}; (B) 10°C min^{-1}; (C) 20°C min^{-1}; (D) 40°C min^{-1}

of the δ phase, is observed. WAXS observations confirm the absence of this phase when the samples are cooled at 5°C min^{-1}. The crystallization temperature increases with increasing polymer concentration. Its concentration dependence is the continuation of the T_c^β–φ_2 relationship observed at low concentrations.

(ii) Melting behaviour. Two endotherms appear on heating (*Figure 5A*). They correspond to the melting of the β phase. Recrystallization on heating is responsible for the presence of the two endotherms.

The melting temperature increases with increasing polymer concentration and this T_m^β–φ_2 relationship is the continuation of the one observed in the low concentration region.

The melting enthalpy of the β phase remains almost constant when the polymer concentration is increased. It corresponds to the value observed for the pure polymer.

Influence of the cooling rate. The cooling rate has an important influence on the formation and the relative contribution of the β and δ phases in the low concentration region. A pronounced decrease of T_c^β is observed when the cooling rate is increased. This results in the narrowing of the crystallization exotherm. The crystallization of the β phase stops at 75°C for all scanning rates, independent of the extent of crystallization. The corresponding crystallization enthalpy decreases with increasing cooling rate.

The crystallization temperature of the δ phase is, within experimental error, independent of the cooling rate. The surface of the corresponding crystallization exotherm increases with increasing cooling rate. The data are reported in *Table 2*.

A better insight into the relative contribution of both phases is obtained from melting experiments performed at 5°C min^{-1} with samples cooled at different rates. The corresponding d.s.c. scans are represented in *Figure 6* and the corresponding numerical data are reported in *Table 3*.

The melting enthalpy of the δ phase, ΔH_m^δ, increases with increasing cooling rate but always remains lower than the corresponding crystallization enthalpy, ΔH_c^δ, reported in *Table 2*. This is ascribed to the overlapping of the melting of the δ phase with the recrystallization into the β phase. A crystallization exotherm is observed between the melting endotherm of the δ and β phases. The melting enthalpy of the β phase is almost independent of the cooling rate.

Formation and thermal behaviour of the δ phase. The formation of the δ phase in a cooling experiment is limited to the lower concentration region ($\varphi_2 < 0.40$). However, its formation and existence at higher concentrations is not excluded. This is illustrated by the data obtained from three different series of experiments. The samples have been obtained by quenching, drying or swelling. They were subjected, in the differential scanning calorimeter, to heating (first scan), cooling and further heating (second scan).

(1) Quenched polymer solutions

Samples are quenched in liquid nitrogen and transferred at this low temperature to the d.s.c. cell. A first d.s.c. scan is represented in *Figure 7A* for a sample with $\varphi_2 = 0.75$. A glass transition, two exotherms and one endotherm can be observed.

Table 3 Influence of cooling rate on the melting behaviour of a solution of sPS2–TD ($\varphi_2 = 0.25$, heating rate 5°C min^{-1})

Cooling rate (°C min^{-1})	ΔH_m^δ (J g^{-1})	ΔH_m^β (J g^{-1})	$\Delta H_m^\beta / \Delta H_m^\delta$
−5	10.0	31.8	3.2
−10	13.2	32.5	2.5
−20	16.4	33.4	2.0
−40	21.0	38.2	1.8

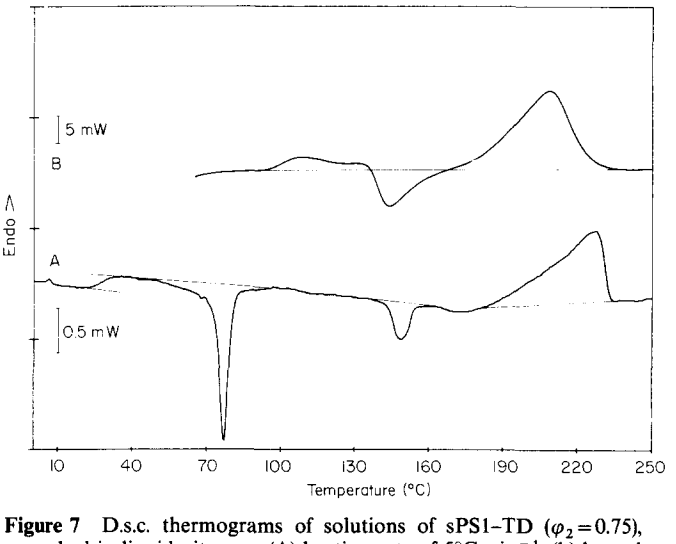

Figure 7 D.s.c. thermograms of solutions of sPS1–TD ($\varphi_2 = 0.75$), quenched in liquid nitrogen: (A) heating rate of 5°C min^{-1}; (b) heated at 5°C min^{-1} to 100°C, cooled at 5°C min^{-1} to room temperature and heated at 40°C min^{-1}

Table 4 Influence of heating rate on the phase behaviour of a quenched, concentrated solution of sPS1–TD ($\varphi_2 = 0.70$)

Heating rate (°C min^{-1})	ΔH_c^δ (J g^{-1})	ΔH_m^δ (J g^{-1})	ΔH_{tr} (J g^{-1})	ΔH_m^β (J g^{-1})
5	−19.3	–	−5.4	31.1
10	−20.7	–	−5.1	30.0
20	−18.8	–	−5.9	27.8
40	−19.1	1.7	−6.4	30.1

Table 5 Influence of heating rate on the transition temperatures of a quenched, concentrated solution of sPS1–TD ($\varphi_2 = 0.70$)

Heating rate (°C min^{-1})	T_g (°C)	$T_c^{\delta min}$ (°C)	$T_m^{\delta max}$ (°C)	$T_c^{\beta min}$ (°C)	$T_m^{\beta end}$ (°C)
5	12	64.4	–	150.0	230.1
10	15	73.1	–	148.0	231.2
20	19	81.5	–	148.5	232.9
40	–	90.0	143.1	154.6	246.9

An amorphous, glassy sample is obtained on quenching. Heating above its T_g results in the formation of the δ phase. This is deduced from WAXS experiments, carried out with samples annealed around 100°C. The small exotherm at higher temperature represents the formation of the β phase. This is confirmed by the WAXS patterns obtained from samples annealed at 190°C. The broad melting endotherm represents the melting of this β phase. No dynamic recrystallization is observed. The melting temperature of the β phase obtained in both experiments is similar. There is no indication for the melting of the δ phase.

The important difference in size between the formation exotherm and the melting endotherm of the β phase, and the absence of the melting endotherm of the δ phase can be explained by the formation mechanism of the β phase. It is proposed that the δ phase melts and recrystallizes into the β phase. Both phenomena will take place simultaneously when this recrystallization is fast enough. Only a small differential exothermic signal is registered. It results from the overlapping of the melting endotherm of the δ phase and the recrystallization of the β phase.

The scanning rate has a pronounced effect on these transitions. The first exotherm (formation of the δ phase) shifts to higher temperatures with increasing scanning rate. The simultaneous melting and recrystallization, resulting in the formation of the β phase, only takes place at scanning rates of 20°C min^{-1} or lower and high polymer concentration ($\varphi_2 > 0.60$). The simultaneity is lost at higher scanning rates. At 40°C min^{-1}, the melting endotherm of the δ phase and the recrystallization exotherm of the β phase become partly separated. This is also demonstrated in *Figure 7B*. *Figure 7B* represents the d.s.c. trace of a quenched sample that undergoes a more complex thermal treatment. The sample is quenched and heated to 100°C at 5°C min^{-1} and then it is cooled to room temperature. This thermal treatment guarantees exactly the same crystallization into the δ phase as the one observed in the dynamic experiment (*Figure 7A*). Then the sample is heated again at 40°C min^{-1}. This results in the d.s.c. trace shown in *Figure 7B*. The simultaneity of the melting of the δ phase and its recrystallization into the zigzag conformation is lost and the two phenomena occur almost separately.

The influence of the heating rate on the transition temperatures and on the crystallization and melting enthalpy of a quenched, concentrated solution is reported in *Tables 4* and *5*.

The overlapping of melting and recrystallization is clearly confirmed by experiments performed on samples with a lower polymer concentration. The formation of the β phase is slowed down and overlapping of the melting of the δ phase and the recrystallization into the β phase is not complete even at low scanning rates. The two thermal transitions are separated to a large extent. The d.s.c. scan of a quenched sample is represented in *Figure 8*. A separate melting of the δ phase and recrystallization into the β phase can be observed for concentrations up to $\varphi_2 = 0.60$.

An increase in polymer concentration results in the decrease of the melting enthalpy of the δ phase and an increase of the melting enthalpy of the β phase. This illustrates the increasing simultaneity of melting and recrystallization.

The thermal crystallization of quenched sPS in the absence of solvent results in the formation of the β phase. The T_g is located at 90°C and crystallization sets in at 140°C. An increasing heating rate has only a secondary influence on the glass transition. It results mainly in a shift to higher temperatures of the temperature at the onset of crystallization.

(2) Dried samples

The thermal behaviour of dried samples, containing only the δ phase, has been investigated.

The d.s.c. trace of a touch-dry δ phase sample reveals a broad exotherm followed, at higher temperature, by a single endotherm in the first scan (*Figure 9A*). The exothermic signal between 120°C and 190°C corresponds to the transition of the δ phase into the β phase. The melting temperature of the β phase is almost 25°C below that of the melt crystallized sPS. This is due to the presence of a large amount of TD, trapped in the touch-dry sample. When the sample is cooled to room temperature and heated for the second time, only the melting of the β phase is registered (*Figure 9B*). The δ phase is not reformed on cooling. The melting enthalpy of the β phase obtained by phase transition (*Figure 9A*) is almost twice the value of the β phase obtained by dynamic cooling (*Figure 9B*).

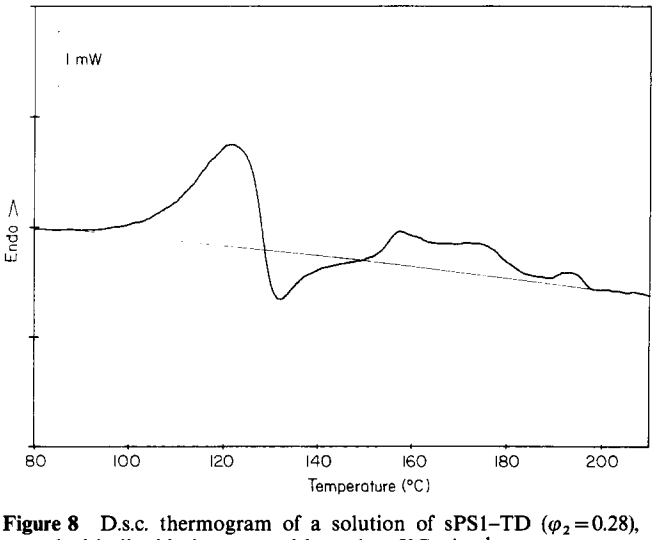

Figure 8 D.s.c. thermogram of a solution of sPS1–TD ($\varphi_2 = 0.28$), quenched in liquid nitrogen and heated at 5°C min^{-1}

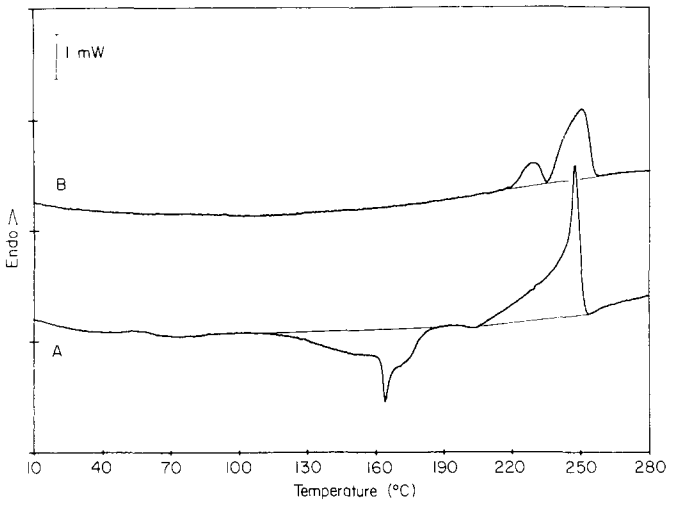

Figure 9 D.s.c. thermograms of a touch-dry δ phase helix structure of sPS2–TD: (A) first scan; (B) second scan

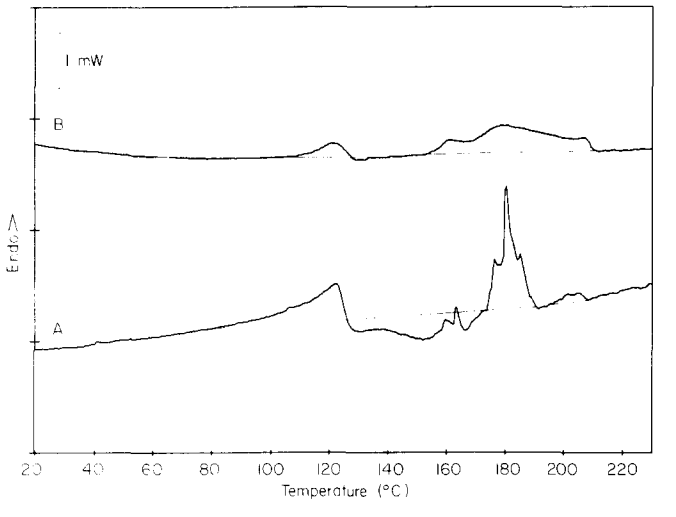

Figure 10 D.s.c. thermograms of a partially dried δ phase structure of sPS2–TD ($\varphi_2 = 0.35$): (A) first scan; (B) second scan

Samples containing a larger amount of solvent, have been prepared by shortening the drying time at room temperature. The behaviour of a sample with $\varphi_2 = 0.35$ is especially interesting. Its solvent content is close to the highest concentration that allows the formation of the δ phase on cooling ($\varphi_2 \approx 0.40$). In the first scan (*Figure 10A*), an endotherm corresponding to the melting of the δ phase is observed. It is abruptly stopped at 125°C by the occurrence of an exothermic signal. This results in the formation of the β phase. This overlapping of two signals also clearly illustrates the melting–recrystallization transition between the δ and β phases. The β phase melts at higher temperature (*Figure 10A*). The second scan reveals the melting of both phases (*Figure 10B*). The melting enthalpy of the δ phase in the second scan is only one-third of the value recorded in the first scan. The melting enthalpy of the β phase is similar in both experiments.

(3) Swelling of amorphous samples

Amorphous, glassy polymer films have been obtained by quenching the polymer from the melt. Stretching in boiling water results in amorphous, oriented films. Swelling in TD has been used as an alternative method for the formation of the δ phase at rather high polymer concentrations. At room temperature, 21% of solvent is absorbed. This has been determined by thermogravimetry and corresponds to the amount of solvent that cannot be removed when a moderately concentrated, gellified solution is dried. No change in the physical aspect of the samples takes place; they remain well oriented and feel touch dry. WAXS observations confirm the formation of the δ phase.

When the samples are heated, the solvent evaporates. A transformation of the δ phase in the solvent-free γ phase takes place. This is reflected in a broad endothermic signal (*Figure 11*). The γ phase helix structure transforms into the β phase zigzag conformation around 190°C. The net result of this conformational transition is a small exothermic signal. It is followed by the melting of the β phase.

Glass transition. The influence of the solvent on the T_g of the polymer–solvent system has been studied. Amorphous samples can be prepared by quenching into liquid nitrogen. The T_g–φ_2 relationship is represented in *Figure 12*, together with the same relationship for the atactic isomer in the same solvent[25]. A much less pronounced decrease of T_g with increasing solvent content is observed for the syndiotactic isomer. The T_g–φ_2 relationship of this last isomer is also reported in *Figure 1*.

Influence of molecular weight. The experiments discussed above have also been carried out with sPS2. An increase in the molecular weight does not change the overall shape of the phase diagram. An increase in T_m^β and T_c^β of ~ 15°C is observed. The increase in T_m^δ is less pronounced (*Figure 13*).

The shape of the d.s.c. scan, observed when a sample with low polymer concentration is heated, is nevertheless more complex. The melting endotherm of the δ phase is followed by a small exothermic signal. This behaviour was also observed with samples of sPS1, quenched in liquid nitrogen. Therefore the same explanation can be used. The melting of the δ phase is followed by a recrystallization into the β phase. The resulting d.s.c. signal is an overlapping of the melting endotherm and a slightly displaced recrystallization exotherm (*Figure 6A*). An additional melting endotherm for the β phase is observed. A direct relationship exists with the recrystallization exotherm. The surface of this particular endotherm increases with increasing extent of recrystallization.

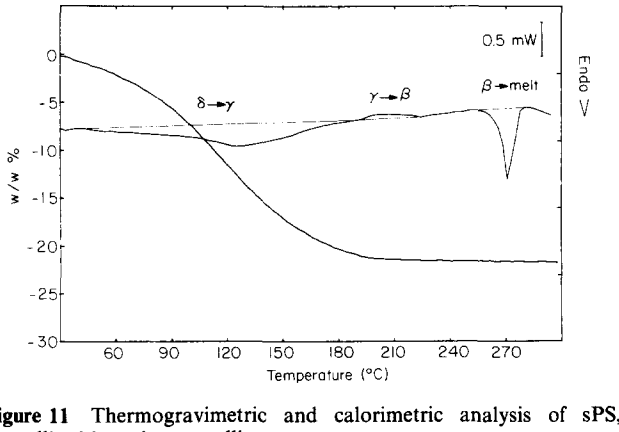

Figure 11 Thermogravimetric and calorimetric analysis of sPS, crystallized by solvent swelling at room temperature

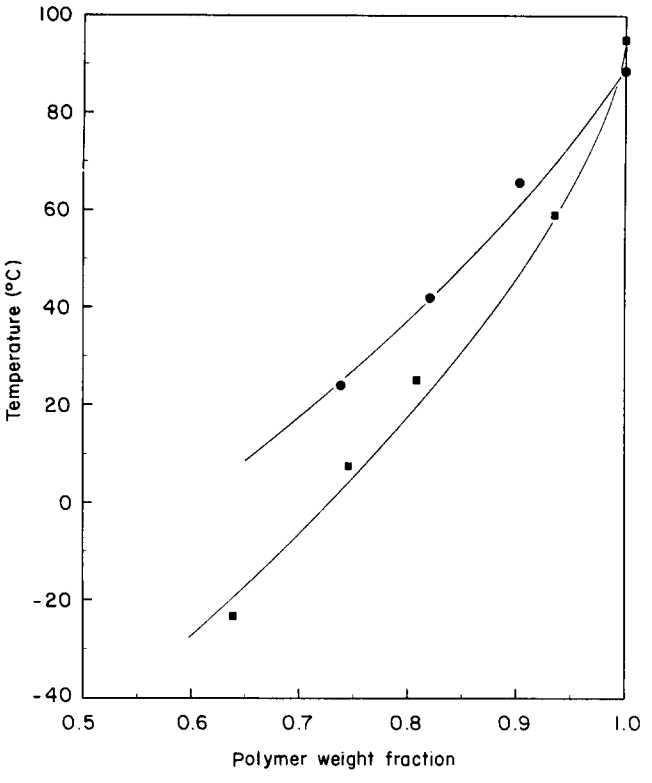

Figure 12 Influence of TD concentration on the T_g of sPS and aPS[25] systems: (●) sPS–TD; (■) aPS–TD

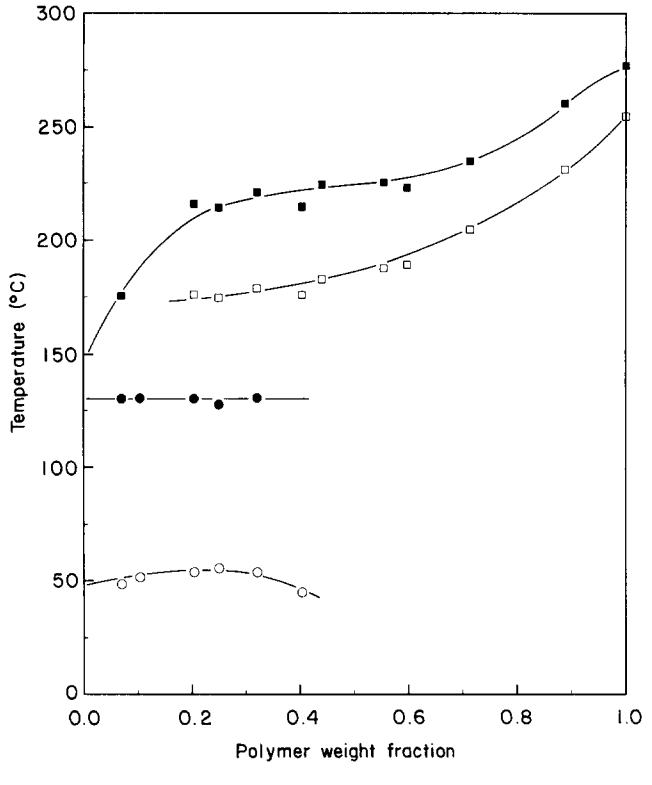

Figure 13 Phase diagram of sPS2–TD: (○) crystallization of helix conformation; (□) crystallization of zigzag conformation; (●) melting of helix conformation; (■) melting of zigzag conformation

Temperature–concentration phase diagram of sPS1–CD

The phase diagram in CD has been constructed in the same way as for the system with TD (*Figure 14*). Its overall shape is similar to the one observed with TD. Some important differences in the thermal behaviour have to be stressed. When melting and crystallization is studied by dynamic experiments, three different concentration regions have to be considered.

Only one exotherm is observed on cooling a sample in the low concentration region ($\varphi_2 < 0.25$). It corresponds to the formation of the δ phase. Heating results in the melting of this δ phase. Concentrated systems ($\varphi_2 > 0.60$) also show one exotherm on cooling but two endotherms on heating. They correspond to the crystallization and melting of the β phase.

In the intermediate concentration region, two exotherms are observed on cooling and three endotherms on melting. In this region, the behaviour is analogous to that observed in TD.

The concentration dependence of the melting and crystallization temperatures of the β phase is very similar to that observed in TD. The formation temperature of the δ phase goes through a maximum. A higher degree of undercooling is needed on both sides of this maximum.

In the low polymer concentration region, the β phase can only be formed by isothermal crystallization at high temperature. The corresponding melting points are well above the melting points of the δ phase.

The integration of the melting and crystallization peaks is easy and very reproducible. This is in strong contrast with the difficulties encountered with sPS1–TD. The melting enthalpy of the δ phase remains constant up to $\varphi_2 = 0.20$. At higher concentrations it rapidly decreases to zero. The melting enthalpy of the β phase shows the opposite concentration dependence. This is represented in *Figure 15*. The concentration dependence of the crystallization enthalpy represents almost the mirror image.

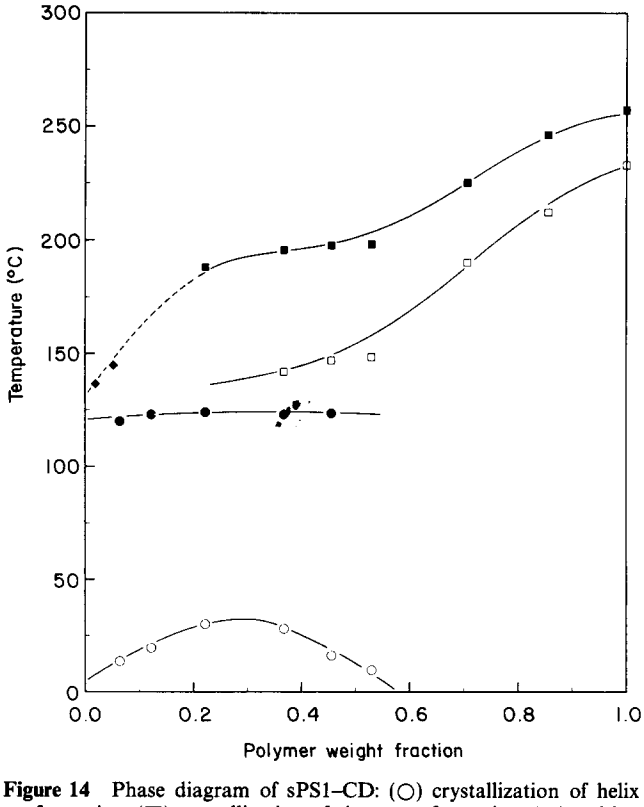

Figure 14 Phase diagram of sPS1–CD: (○) crystallization of helix conformation; (□) crystallization of zigzag conformation; (●) melting of helix conformation; (■) melting of zigzag conformation; (◆) melting of zigzag conformation after isothermal crystallization at 110°C

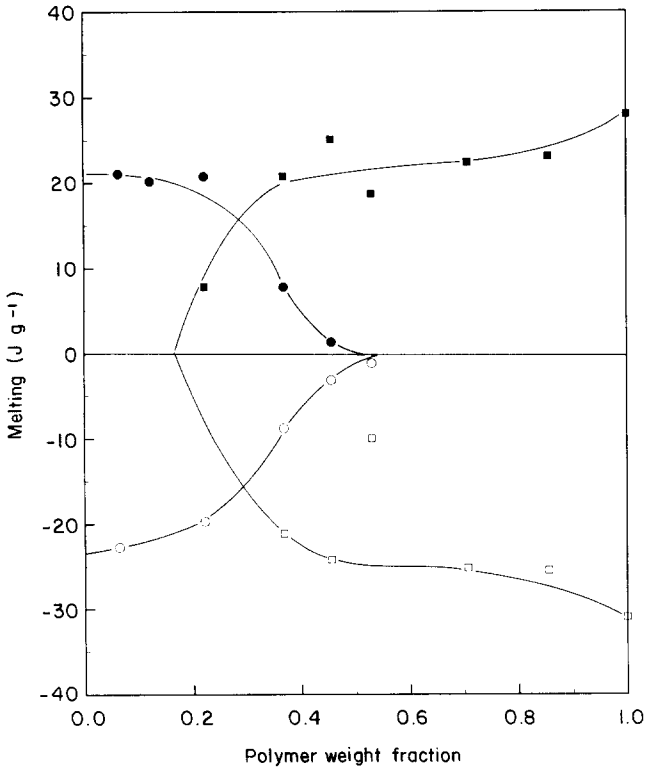

Figure 15 Influence of CD concentration on the crystallization and melting enthalpy of sPS1: (○) crystallization enthalpy of helix conformation; (□) crystallization enthalpy of zigzag conformation; (●) melting enthalpy of helix conformation; (■) melting enthalpy of zigzag conformation

DISCUSSION

The behaviour of sPS–decalin is complex and, in a first approximation, not influenced by the configuration of the solvent (*cis* or *trans*). The discussion can therefore be applied to both systems. Three different phases have been characterized. Their formation and relative contribution to the structure formation is controlled by the experimental conditions.

Formation of the different phases and their interrelationship

Formation of the β phase. The formation of the β phase can take place at any polymer concentration if the crystallization temperature is high enough. The T_m^β–φ_2 relationship is characteristic for the melting of a polymer in the presence of a poor solvent. There is no interference of this crystallization and melting with a liquid–liquid demixing. This last transition is supposed to take place at much lower temperature[25]. It has not been possible however to localize this demixing for sPS–decalin. The formation of the different crystalline phases is too fast and takes place already during a fast cooling operation before the liquid–liquid demixing domain is reached.

The formation of the β phase is a nucleation controlled crystallization phenomenon, strongly influenced by the cooling rate. An increase of this rate shifts the crystallization temperature, T_c^β, to lower temperatures. These experimental observations are in agreement with the general principles of polymer crystallization.

A more surprising result is the influence of the polymer concentration on the degree of transformation into the β phase during a cooling experiment. At high polymer concentrations ($\varphi_2 > 0.40$) the polymer crystallizes almost completely in this β phase when it is cooled down at moderate scanning rates. The degree of crystallinity, reduced to the amount of polymer present, is constant and equal to the value obtained in the absence of solvent. At lower polymer concentrations ($\varphi_2 < 0.40$) a decrease of φ_2 and/or an increase of the cooling rate reduces the degree of crystallinity. This is as a direct consequence of the interruption, at 75°C, of the crystallization process that leads to the formation of the β phase. At this temperature the crystallization exotherms come to an end, independent of the degree of transformation attained. This final temperature is not influenced by the initial concentration or the scanning rate. This limitation is of course only observed during a dynamic experiment. A high degree of transformation into the β phase can be realized at any concentration above 75°C by isothermal annealing. This interruption of the crystallization of the β phase does not take place at higher polymer concentrations ($\varphi_2 > 0.40$). The polymer is completely transformed into the β phase before this temperature threshold is reached as a direct consequence of the higher T_c^β values.

Formation of the δ phase. The formation of the δ phase shows interesting peculiarities. It takes place at low temperature and an important degree of undercooling. This degree of undercooling amounts to 85°C when the experiment is carried out in a differential scanning calorimeter at a cooling rate of 5°C min^{-1}.

The transition can only be realized in a d.s.c. cooling experiment at a high enough cooling rate. Under these conditions, the formation of the β phase is partially or completely suppressed. The degree of transformation into the δ phase increases with decreasing polymer concentration and increasing cooling rate. Fast cooling to a temperature below 75°C results in a complete transformation into the δ phase. A 'temperature gap' of ~35°C exists between the temperature at the end of the formation of the β phase (75°C) and the temperature at the onset of the formation of the δ phase (T_c^δ). A typical example is given in *Figure 2A*.

It is difficult to explain these observations by the accepted principles of polymer crystallization. Therefore, a different mechanism is proposed. It is based on the data reported for syndiotactic poly(methyl methacrylate) in *o*-xylene[26] and isotactic polystyrene in CD[27]. It is a two-step mechanism that has been proposed on the basis of spectroscopic observation and rheological measurements. The first step consists of an intramolecular transition from a random coil to a regular helix. The intermolecular association, leading to the formation of transparent gels, represents the second step.

No direct evidence for the occurrence of this type of two-step mechanism has been found yet. The similarity between the data reported in this paper and those reported in the literature makes it a good candidate for the interpretation of the experimental facts reported here. It is therefore proposed as a possible mechanism requiring further investigation.

A change in molecular conformation from coil to helix is governed by an equilibrium constant[28]. Its change with temperature controls the number of chain segments that is transformed into a regular helix at a certain temperature. This conformational transition sets in around 75°C and slows down or stops completely the formation of the β phase. Cooling of the solution will result in the increase of the helix content. Once

the equilibrium is shifted far enough to the helix side, intermolecular association can take place at an appreciable rate so that it can be detected in a dynamic calorimetric experiment. The extent of intermolecular association, measured at constant scanning rate, will therefore increase with decreasing temperature. The introduction of an equilibrium phenomenon between the crystallization of the β and δ phases has to be considered as the most important factor responsible for the rather large degree of undercooling in a dynamic experiment. It also explains the slow formation of the less stable δ phase in samples that are annealed in the temperature gap. These samples are far below the melting point of the β phase and its rate of formation is expected to be very high: an important degree of undercooling is realized. This does not take place and the less stable δ phase is slowly formed at a low degree of undercooling.

The role of the solvent is not understood. Its involvement in the formation of the δ phase nevertheless has been demonstrated. It is also clear from our experiments that no δ phase can be formed in the absence of solvent. Therefore, the formation of a compound between the polymer and the solvent cannot be excluded. This has been illustrated in the literature[29] for the isotactic isomer.

Formation of the γ phase. This phase can only be established when the solvent is eliminated from the δ phase. It cannot be obtained by quenching the pure polymer into the low temperature region in order to prevent the formation of the β phase at higher temperature. This brings the polymer into the glassy phase where crystallization is impossible.

Phase transitions. No transformation of the β phase into the δ or γ phase takes place on cooling. The δ phase transforms into the β phase on heating by a mechanism of melting and recrystallization. The net result is exothermic. Three phases coexist during this transformation. The δ phase, composed of the polymer and the solvent, the pure solvent and the β phase. This creates an invariant situation for this quasi two-component system at constant pressure. The polymer–solvent compound transforms into the β phase and the pure solvent by incongruent melting. The γ phase transforms into the β phase on heating. This is also an exothermic process.

Interpretation of the phase diagram

The phase diagrams, represented in *Figures 1, 12, 13* and *14*, can be interpreted in view of the previous comments. A schematic representation is given in *Figure 16*. Different domains can be distinguished. A tentative interpretation, based on the data reported in this paper and in the literature on other systems, is given.

At high temperature, the system behaves as a quasi two-component system composed of a polydisperse polymer and a solvent. Cooling results in the formation of the β phase and the solvent.

A transformation from a coil to a helix takes place below 75°C. The solvent can become involved in this step and the result is the formation of a polymer–solvent compound. Its composition is arbitrary and fixed at a molar ratio of styrene/decalin of one. At lower temperature these helices agglomerate into the δ phase. This phase coexists with the solvent. Heating results in the incongruent melting of the compound with the formation of the β phase and release of the solvent. A three-phase equilibrium is established, resulting in an invariant melting point. The β phase melts at higher temperature.

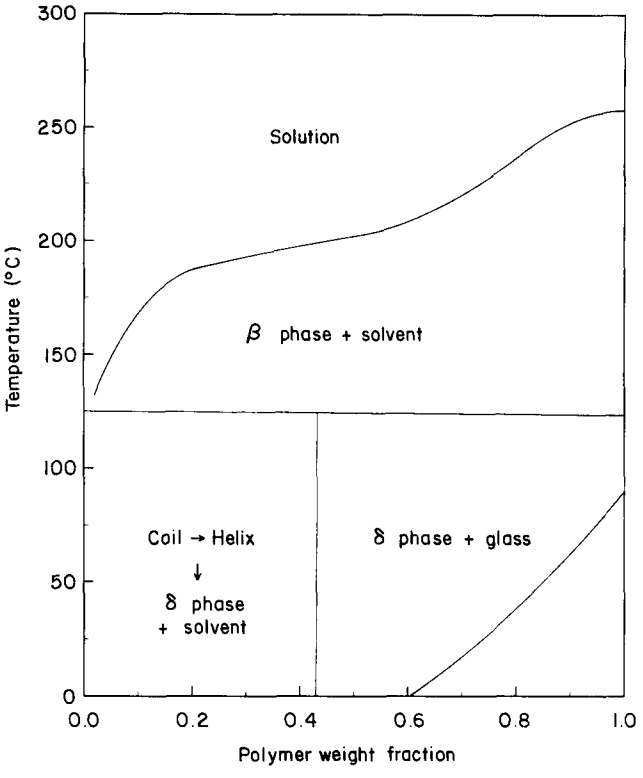

Figure 16 Proposed model for different phase transitions

Drying of the compound–solvent system should establish a new equilibrium between the compound and the pure β phase ($\varphi_2 = 1.00$). This transition however does not take place. The pure polymer axis cannot be reached because of the presence of the glassy region. Elimination of the solvent will force the system into the glassy state and no transition will take place. The δ phase melts on heating and transforms into the β phase with release of the solvent. A three-phase equilibrium is again established and the invariant situation is obtained. Further heating results in the melting of the β phase (variant situation).

Drying at higher temperatures will slowly release the remaining solvent with formation of the stable dry γ phase. It transforms into the β phase at 190°C. The γ phase cannot be formed by a thermal treatment of the melt or the glassy phase.

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