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Crystalline Transitions of the Clathrate (δ) Form of Syndiotactic Polystyrene during Heating: Studies Using High-Temperature X-ray Diffraction

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ABSTRACT: The structural changes occurring during heating in a syndiotactic polystyrene (sPS)−solvent complex were monitored in situ by X-ray diffraction. The room temperature δ form transformed into the γ form on heating above the glass transition temperature of the sPS. The transition temperature showed a linear dependency on the amount of solvent absorbed; the higher the solvent molecules absorbed, the higher the transition temperature. However, the transition temperature does not depend on the nature of the solvent. The emptied clathrate form transformed into the γ form at the glass transition temperature. The γ form transformed into the α″ form at ~200 °C on heating and is independent of the δ to γ form transition. Calorimetric studies showed an endotherm followed by an exotherm during these transitions and indicated that the transitions are first order in nature.The studies provided information on the stability of various crystalline forms of sPS.

Introduction

The sPS in the semicrystalline form shows complex polymorphism. The nature of the polymorphism depends on the conditions of crystallization. It has been shown that sPS has four polymorphic forms, namely α, β, γ, and δ. The α and β forms, both containing planar zigzag chains having the T4 all-trans conformation, can be obtained from the melt or glassy state of sPS under different thermal crystallization conditions.[1−4] In γ and δ forms, the chains have the T2G2 helical conformation and are formed under conditions where solvents are used for crystallization.[5−8] The sPS in the α form has a hexagonal unit cell,[9,10] while the β form exists in the orthorhombic unit cell.[11] The α and β forms are further classified into α′, α″, β', and β'' depending on their structural disorder and order characteristics.[4,5] The α′ and β' are the two limiting disordered modifications, while α″ and β'' correspond to the two limiting ordered modifications. The samples cold crystallized[12] below 200 °C exhibit the α′ form, and α″ has been obtained when the cold crystallization temperature is above 200 °C. The melt crystallization under appropriate conditions yields the β' form,[5] while structurally ordered β'' may be obtained by casting from a suitable solvent.[5,11]

The δ form has a clathrate structure where the guest, low molecular weight molecules, which are most often solvent molecules, are accommodated. The X-ray diffraction peak position and intensity vary depending on the nature and amount of the guest molecules present in the clathrate.[5,7] The clathrate δ form[7] can be obtained by the sorption of suitable compounds (methylene chloride, toluene, chloroform, iodine, dichlorobenzene, decalin, etc.) in amorphous samples or semicrystalline samples having α or γ forms. The guest molecules in the clathrate structure may be extracted out by suitable extraction procedures.[13] The resulting emptied clathrate structure is different from the γ form, which is obtained by annealing the δ form or the emptied δ form, for instance, at ~130 °C.[13] The crystal structure[14] of the sPS−toluene compound is monoclinic, and the space group is $P2_1/a$. The emptied clathrate also has a monoclinic structure, and the space group is $P2_1/a$.[15] However, it has been shown that acetone can crystallize sPS into the γ form, without forming a clathrate.[8]

The polymorphs of sPS are shown to have varying degrees of stability. On annealing above T_g, the δ form transforms into the γ form.[13] The γ form changes into the α form when heated in the temperature range 180−220 °C.[16] On the other hand, the α to β form or vice versa can be achieved by melting and recrystallization under appropriate conditions.[17] Recent studies on the melt-crystallized sPS show that the β form has a higher equilibrium temperature and is more stable than the α form. However, under appropriate conditions the β form can melt at lower temperature than the α form and become metastable.[18]

The impetus for the present work came from the fact that most of the studies that deal with the crystalline transitions in sPS had been carried out at room temperature after annealing or heating the sample at elevated temperatures and not by in-situ measurements during heating. Second, there had been no systematic study on the effect of the nature and amount of solvent present in the clathrate on the transitions. In the present paper we report for the first time the crystalline transitions of sPS−solvent complex that had been followed in situ using a hot stage attached to an X-ray diffractometer during heating and the effect of nature and amount of solvent absorbed in the clathrate structure on these transitions. The results obtained by diffraction studies are corroborated by differential scanning calorimetric (DSC) studies on these samples.

Experimental Section

Syndiotactic polystyrene was kindly supplied by Dow Chemicals. The weight-average molecular weight was 275 000, and the melt index was 4.3. Amorphous films of sPS were obtained by rapidly quenching melted samples in an ice−water bath at 0 °C. These amorphous films were crushed into a fine powder by using a SPEX freezer mill. The crystalline δ form was obtained by immersion of the amorphous powder in dichlo-

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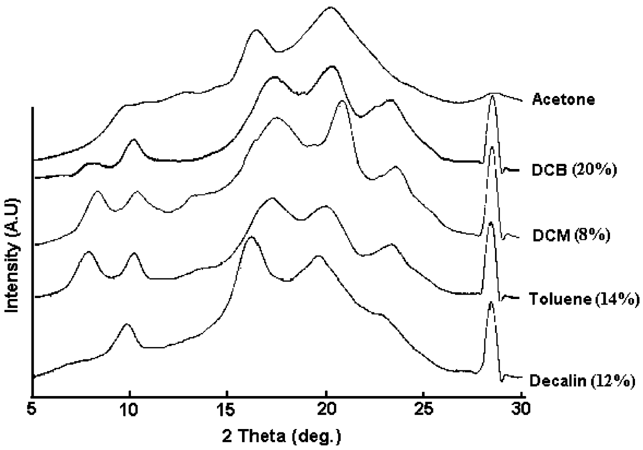

Figure 1. Room temperature wide-angle X-ray diffraction patterns of clathrate δ forms of sPS containing 12% decalin, 14% toluene, 9% DCM, 20% DCB, and acetone crystallized sample having the γ form. The peak at 28.45° shows the silicon (111) reflection, which is used as the internal standard.

romethane and toluene for 2 days and *o*-dichlorobenzene and decalin (cis−trans) for 7 days at room temperature. After the crystallization period, the samples were filtered and kept at ambient temperature and pressure until they became touch dry. Samples with different degrees of clathration were obtained by extraction of the solvent molecules from the clathrate δ form samples in boiling acetone for different intervals of time. The thermal analysis and WAXS experiments were performed on the samples at the same time.

The thermal analyses of the samples were performed using PE TGA-7 and DSC-7 instruments under standard procedures. The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer, and the details were reported elsewhere.[19] The sample holder was a copper block, and a very thin layer of crystallized powder sample was pressed on this block. The copper block with the sample was heated at the rate of 2 °C/min. The diffraction pattern was collected while the sample temperature was held constant within 1 °C of the set temperature, and the data were acquired in 5 min. The sample was kept under vacuum ($\sim 1 \times 10^{-3}$ Torr) during the experiment to avoid thermal degradation. The diffraction data were collected at room temperature and subsequently after every 10 °C to monitor the change in structure during heating. The positions of the peaks were fixed by deconvoluting the peaks using Rigaku multipeak separation software available with the diffractometer system. The amorphous peak profile was assumed to be similar to the diffraction pattern of the melt at 290 °C.

Results

The room-temperature wide-angle X-ray diffraction pattern is shown in Figure 1 for all the clathrate samples crystallized by different solvents as well as the γ form obtained by crystallization in acetone. The amount of solvent present in the clathrate is indicated near the curves and has been determined by TGA analysis. The samples show well-developed crystalline peaks. These peaks correspond to the clathrate δ form and are indexed to the monoclinic unit cell having space group $P2_1/a$.[14,15] The peaks at $2\theta = 7.87°$ and 10.11° are indexed as 010 and $\bar{2}10$ of the monoclinic structure. The variation in the peak positions indicates that the unit cell dimensions depend on the nature and amount of solvent used for crystallization.[5,7]

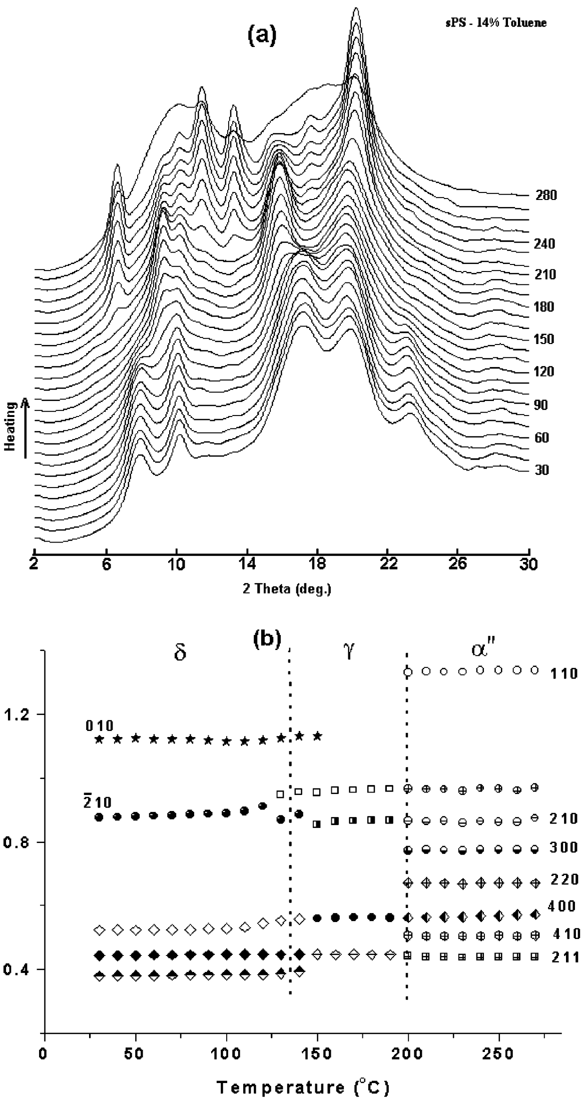

Figure 2. Behavior of (a) X-ray diffraction patterns and (b) *d*-spacings on heating of sPS−toluene (14%) clathrate δ form to melt.

The change in the clathrate structure of the sPS−toluene system (14%) during heating has been followed by X-ray diffraction, and the patterns are shown in Figure 2a. On heating, the clathrate structure does not show any change up to 110 °C. On further heating, the diffraction pattern starts changing and the peaks at $2\theta = 7.87°$, 16.93°, and 23.42° vanish. Simultaneously, new peaks appear at about $2\theta = 9.19°$ and 15.79°. Above 150 °C, the peaks due to the δ form vanish fully, and the new peak positions are due to the γ form only. The variation of the *d* spacings of the various reflections on heating is shown in Figure 2b. It is apparent from Figure 2a,b that the transition occurs over a temperature range starting from about 120 to 150 °C, and the midpoint 135 °C is taken as the transition temperature. On heating above 200 °C, the diffraction pattern shows a rather abrupt change, indicating a second transformation. The new peak positions are at $2\theta = 6.64°$, 9.15°, 10.21°, 11.44°, 12.26°, 13.17°, 13.91°, 15.75°, 17.49°, and 20.09°, and the structure can be identified as the α'' form. The α'' form does not change on further heating and melts at about 280 °C. A cursory inspection of the α'' form indicates that peaks at $2\theta = 6.64°$, 11.44°, 13.17°, and 20.09° show sharpening of the reflection and increase in intensity above 200 °C. The reflections at $2\theta = 9.15°$ and 15.75° show decrease in intensity. This indicates structural organization with crystal perfection at higher temperatures. The decrease in the intensity

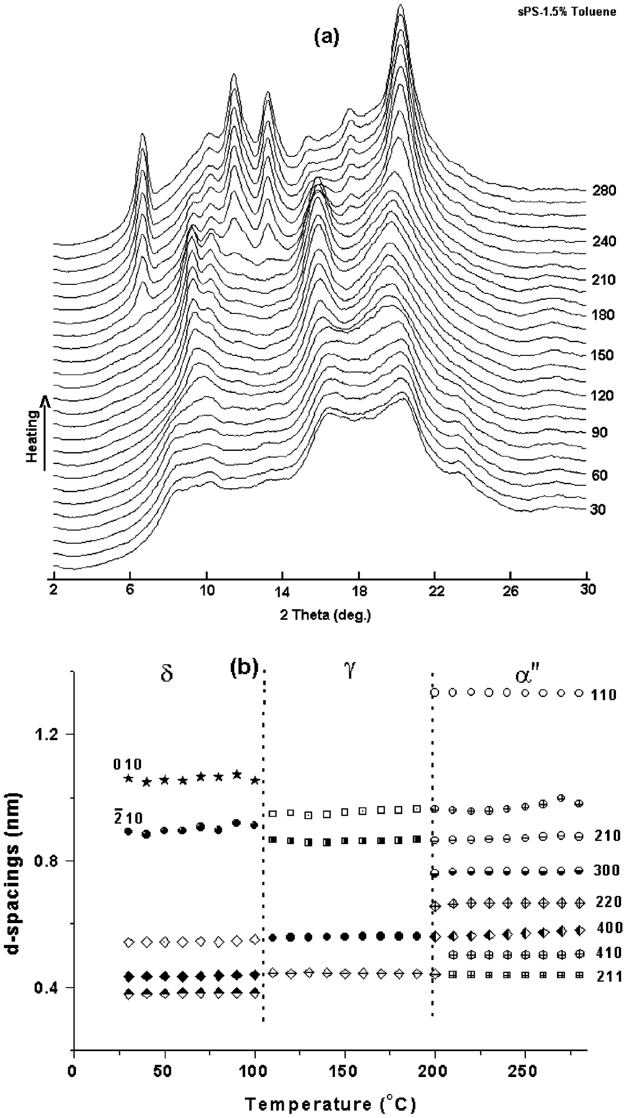

Figure 3. Behavior of (a) X-ray diffraction patterns and (b) *d*-spacings on heating of sPS−toluene (1.5%) clathrate δ form to melt.

of the two reflections indicates that the setting angle of the chain in the unit cell changes with perfection.

Toluene has been emptied from the clathrate by boiling in acetone. Figure 3a shows the diffraction pattern of the emptied clathrate sample containing 1.5% of the solvent on heating. The behavior of the diffraction pattern on heating appears similar to that of the sample with 14% solvent; nevertheless, there are significant differences observed. At room temperature the emptied clathrate has peaks at $2\theta = 8.34°$, 9.92°, 16.33°, 20.45°, and 23. 43°. Upon heating the sample to melting, the peaks at $2\theta = 8.34°$, 9.92°, and 23.43° disappear in the temperature range 100−110 °C, and new peaks appear at about $2\theta = 9.33°$ and 10.22°. The peaks at $2\theta = 16.33°$ and 20.45° shift to 15.85° and 19.96°, respectively. The disappearance of existing peaks and the appearance of new peaks in the temperature range 100−110 °C indicates a phase transition. The new peak position indicates that the transformed structure is in the γ form. The transition temperature has been shifted toward the lower temperature and occurs in a shorter range between 100 and 110 °C when compared with the sample with 14% solvent. On further heating, the γ form transforms into the α'' form at ~200 °C, and the behavior is similar to the sample having 14% solvent discussed above. Figure 3b shows the variation of *d* spacings of various reflections during heating and shows the two transitions clearly. The sample melts in the α'' form at about 280 °C as evident from the broad amorphous halo. On cooling from the melt the samples crystallize in the β form and do not show any transition on cooling to room temperature. Another point noted is that the δ, γ, and α'' forms do not show thermal expansion on heating as the *d* spacings do not change with temperature. Manfredi et al.[13] observed a helical mesophase when the emptied clathrate was annealed at 110 °C. In this work the samples containing 1.5% solvent on heating in the X-ray hot stage do not show any evidence of the mesophase at 110 °C but transform into the γ form between 100 and 110 °C. Such a mesophase may be observed only when the clathrate is fully emptied and has 0% solvent.

The behavior of the clathrates formed by decalin, *o*-dichlorobenzene (DCB), and dichloromethane (DCM) upon heating is similar to that of toluene, and the X-ray diffraction patterns are shown in parts a, b, and c of Figure 4, respectively. However, the low-temperature δ to γ transition temperature and also the peak positions of the clathrate form change for these samples. The transition temperatures are 115, 125, and 140 °C for sPS-DCM (9%), sPS-decalin (12%), and sPS-DCB (20%) systems, respectively. These samples also show the high-temperature transition, γ to α'' form, at about 200 °C. Figure 4d shows the behavior of the X-ray diffraction pattern of the sample crystallized by acetone and having the γ form at room temperature. This sample shows only one transition during heating. The γ form transforms into the α'' form at about 200 °C like other samples. All the above experiments have been performed with sample in a vacuum to minimize the degradation. However, few experiments have been performed without vacuum to study the effect of vacuum on the transition temperatures. The results indicated that the vacuum ($\sim 1 \times 10^{-3}$ Torr) applied has no effect on the transition temperatures.

To understand the role of solvent molecules in the δ to γ to α'' form transitions, the absorbed solvents in the clathrates are extracted in boiling acetone to different levels, and the phase transitions are studied by HT-WAXS. In Figure 5 the δ to γ form and the γ to α'' form transition temperatures are plotted for various samples. The low-temperature δ to γ form transition shows a linear relationship with the amount of solvent present in the system but is independent of the nature of solvent. The samples with higher solvent content show higher δ to γ form transition temperatures. Extrapolation to a totally emptied system (0% solvent in the system) shows a transition temperature of 95 °C, which is the glass transition temperature of sPS. (The T_g obtained by DSC at a heating rate of 10 °C/min is 97 °C.) The γ form to α'' form does not change with the nature of solvent or the amount of solvent present in the system and occurs at ~200 °C.

Discussion

The sPS−solvent complex formation is by the diffusion of solvent molecules into the sample, and the process has been discussed in detail by Tashiro et al.[20,21] The amount of solvent absorbed in the system in the touch dry state is similar to the values reported in the literature,[13] for the δ form with toluene and DCB. These

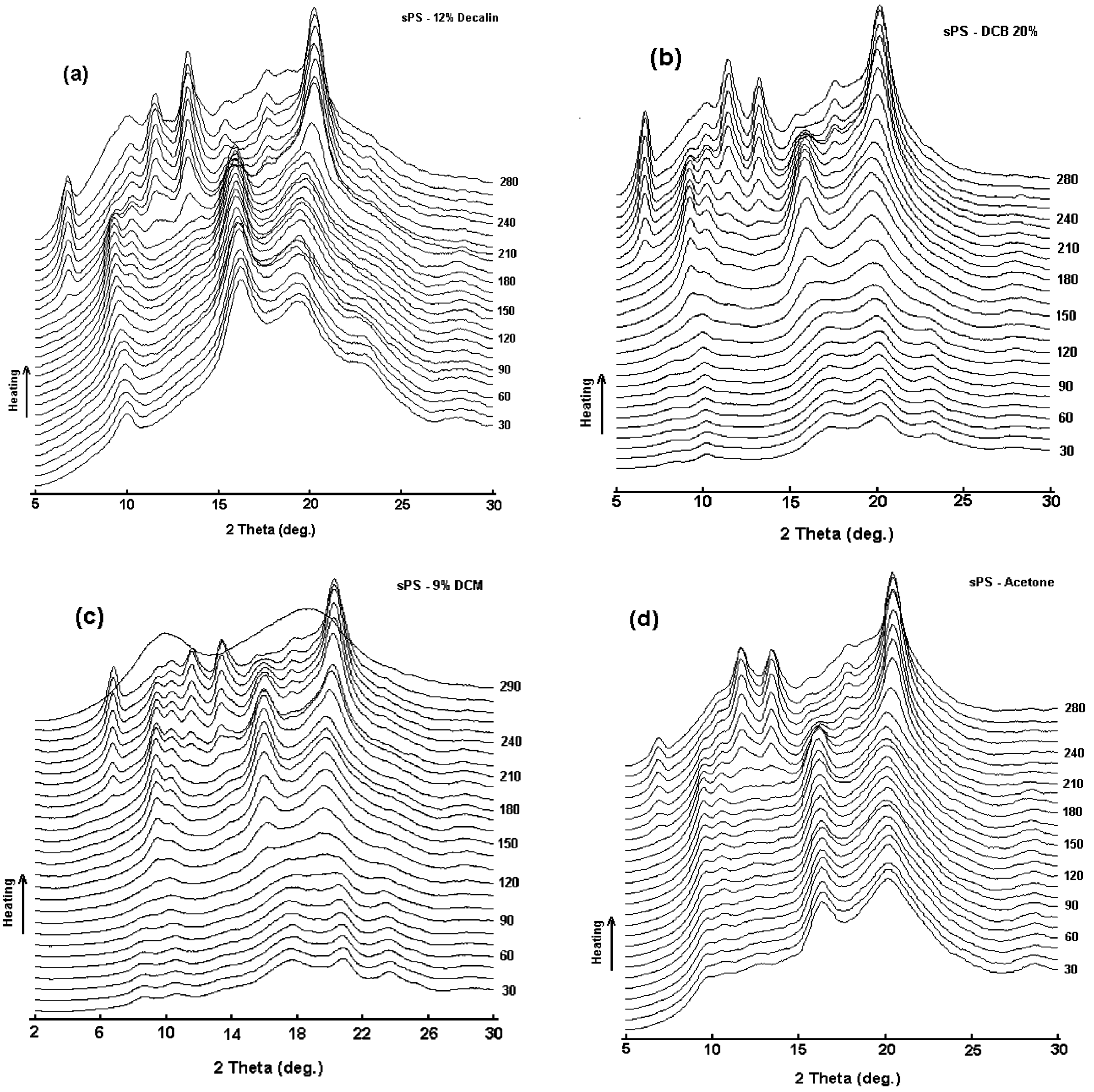

Figure 4. Behavior of X-ray diffraction patterns of clathrate δ forms of sPS containing (a) decalin (12%), (b) DCB (20%), (c) DCM (9%), and (d) acetone crystallized sample on heating to melt.

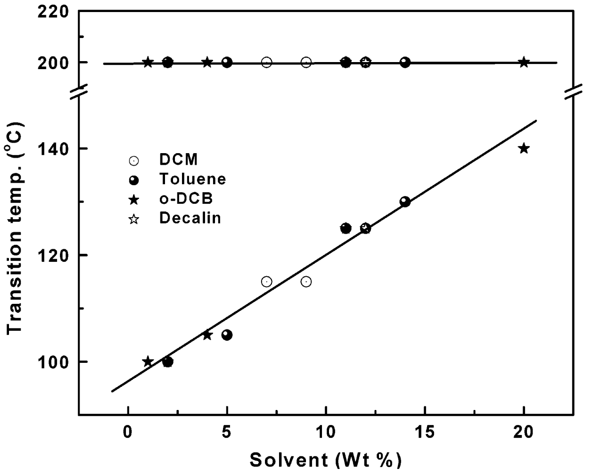

Figure 5. Dependence of amount of solvent absorbed on transition temperatures.

values may be taken as the maximum amount of solvent retained in the system in the touch dry state, as longer periods of crystallization do not increase the amount of solvent absorbed, and it has been suggested that most of the residual solvent is located in the crystalline form.[22]

On heating the clathrate from room temperature to melting, multiple events take place as evidenced by DSC, TGA, and in-situ high-temperature XRD experiments. The clathrate structure changes into the γ form in the temperature range 100−160 °C, and also in this range the solvent molecules leave the system, making the sample dry. At about 200 °C, the γ form transforms into the α'' form, and finally at about 280 °C the sample melts. The δ to γ form transition is mapped clearly in this work using HTWAXS for the first time, though it has been reported in the literature based on room temperature measurements.[13,23] The δ to γ form transition depends on the amount of solvent absorbed in the system. The amount of solvent absorbed has two effects on the transition temperature: (i) The transition temperature increases with increase in the solvent content, and as shown in Figure 5 there is a linear relationship between the two. (ii) The transition temperature range

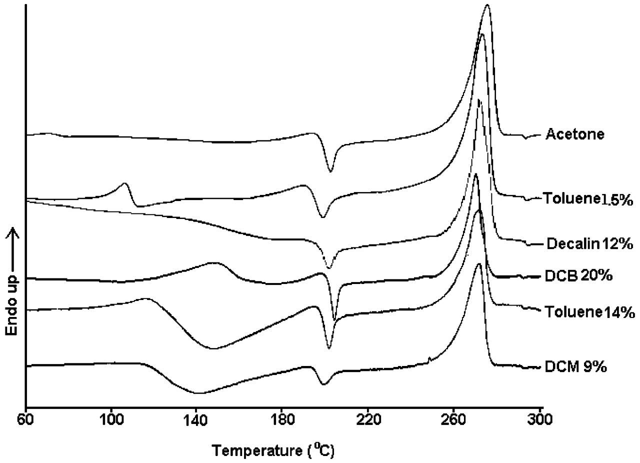

Figure 6. DSC thermograms of clathrate δ forms of sPS containing 9% DCM, 14% toluene, 20% DCB, 12% decalin, 1.5% toluene, and acetone crystallized sample.

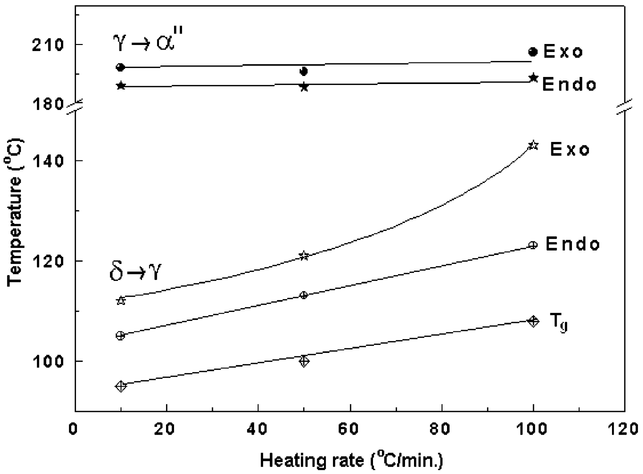

Figure 7. Effect of DSC heating rate on the glass transition temperature and peak positions of the endotherms and exotherms of the δ to γ form and the γ to α'' form transitions.

becomes wider for higher amounts of solvent present in the system. In the sPS–toluene system with 14% solvent the transition occurs over a temperature range of 30 °C, starting from 120 °C. This range shrinks to 10 °C for the sample having 1.5% toluene, and the transition shifts to 105 °C. The observed dependency of the transition temperature on the amount of solvent present in the system, indeed, implies that the intercalating solvent molecules stabilize the helix structure of the δ form. On the removal of the solvent molecules, the structure becomes unstable and converts into the more stable γ form at a lower temperature. The factors responsible for this effect could be the nature of the solvent–sPS interaction,[20,24] solvent molecular volume, and the number of solvent molecules in the clathrate structure.

In the γ form, the solvent is excluded from the crystalline lattice, and consequently, the γ to α'' form transition at 200 °C is independent of the solvent used for the preparation of the clathrate. The transition is rather sharp and occurs over a short temperature range of less than 10 °C. The γ form, which has been obtained directly by treating amorphous sPS in acetone, shows only the γ to α'' form at ~200 °C. Consistent with the WAXS studies, the DSC thermograms of the various samples, shown in Figure 6 on heating, clearly show the γ to α'' form transition as a small endotherm and exotherm at about 200 °C. The well-defined structure change observed by X-ray diffraction studies and the small endotherm and exotherm in DSC traces indicate that the γ to α'' form transition at ~200 °C is a first-order thermodynamic transition and is a characteristic of sPS. The wide-angle X-ray patterns depicted in Figures 2a, 3a, and 4 do not indicate any disordering and ordering of the chains in the crystal during the process of unraveling the helices into planar zigzag conformation during the transition. In the case of sPS–solvent gel systems, it has been suggested that the transformation from the helical to zigzag proceeds through a melting and recrystallization process involving long-range order disruption, while the short-range order is retained.[6,25] Figure 5 also shows that the two lines defining the two transitions meet at 45% of the solvent present in the system and implies that when the absorbed solvent quantity increases above 45%, the δ form transforms into a zigzag planar conformation without going through the intervening γ form. It has been shown[6] in the case of gels that the δ form transforms directly into the β form, and the γ form is not observed.

The DSC measurements could not precisely locate the δ to γ form transition because of the overlapping broad endotherm caused by the solvent evaporation. Nevertheless, the WAXS patterns clearly show the structure change during the heating of the δ form. However, for the sample with 1.5% toluene, the thermogram (Figure 6) clearly shows an endotherm at 105 °C followed by an exotherm at 112 °C corresponding to the δ to γ form transition. The structure change seen in WAXS patterns and the small endotherm and exotherm in DSC are indicative of a first-order transition.

It is interesting to note that the fully emptied clathrate structure transforms at T_g. It is not known at this stage whether it is a just a coincidence or indeed the onset of chain mobility triggers the emptied δ form to change into the more stable γ form. The clathrate samples with 1.5% toluene have been subjected to different heating rates in DSC, and in Figure 7 temperatures of the endotherms and exotherms are plotted along with the glass transition temperature. It can be seen from the figure that the endotherm and exotherm corresponding to the γ to α'' form transition occur at the same temperature and are independent of the heating rate. On the other hand, the δ to γ form transition depends on the heating rate and occurs always above the glass transition temperature. It appears that the first transition is kinetically controlled and can occur at T_g for emptied clathrate sample and at higher temperatures for clathrates with solvent molecules. The high-temperature WAXS experiments could not be paralleled because of the inadequacy of the X-ray diffraction equipment for such fast heating experiments. No further comments can be made at this stage.

All the observed phases of sPS are metastable and have varying degrees of stability. The metastability of the various forms of sPS may be understood from the schematic diagram of free energy with temperature[26] as shown in Figure 8. The β form is the most stable and has a higher equilibrium melting temperature than the α form.[18] The bold lines represent the free energy of the equilibrium crystal and the melt, and these lines intersect at the equilibrium melting temperature of the crystal. The thin lines represent the various metastable

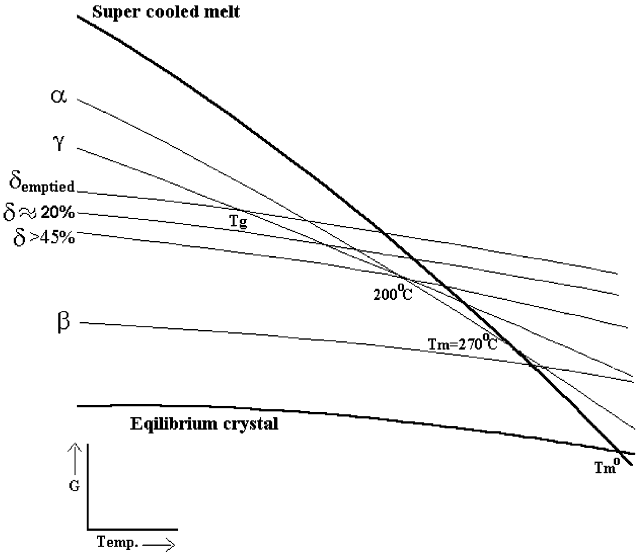

Figure 8. Schematic drawing of free energy vs temperature showing the equilibrium and metastable states of various polymorphs of sPS.

forms. The α form intersects the equilibrium melt at the melting temperature 272 °C. The *γ* form intersects the α form at 200 °C, and above this temperature only the α form is stable. The *δ* form with more than 45% solvent also intersects the lines due to *γ* and α forms at 200 °C. All the three forms can coexist at this temperature. The *δ* form, on losing the entrapped solvent, becomes unstable and moves upward and intersects with the line due to the *γ* form below 200 °C and transforms into the *γ* form. The emptied clathrate will meet the *γ* form at T_g (~95 °C). The samples with solvent between 0 and 45% will meet the *γ* form line between T_g and 200 °C; as an example, a sample with 20% solvent is shown in the figure. As represented in this figure, at room temperature the α form is the least stable form followed by the *γ* form. Indeed, it is possible to convert both α and *γ* forms into the *δ* form by solvent treatment.

Conclusion

The in-situ X-ray diffraction studies on the clathrate structure of sPS provide new information on crystalline transitions on heating. The clathrate *δ* form formed by treating sPS in suitable solvents on heating transformed into the *γ* form above the glass transition temperature. The transition temperature shows a linear relationship with the amount of solvent present in the clathrate and does not depend on the nature of solvent. The transition temperature increases with increase in the amount of solvent absorbed. The emptied clathrate structure without solvent molecule transforms at the glass transition temperature into the *γ* form, indicating that the glassy amorphous phase stabilizes the emptied *δ* form below T_g. The high-temperature *γ* to α'' form transition, on the contrary, is independent of solvent used for crystallization and occurs at 200 °C.

The differential scanning calorimetric studies show an endotherm followed by an exotherm during these two transitions. In-situ monitoring of the structural changes by WAXS patterns indicates that during these two transitions the change in the lattice occurs with least disruption. Based on the results, a schematic free energy diagram has been drawn to understand the metastability of various polymorphs of sPS.

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