Studies on the Clathrate (δ) Form of Syndiotactic Polystyrene Crystallized by Different Solvents Using Fourier Transform Infrared Spectroscopy

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ABSTRACT: Amorphous syndiotactic polystyrene (sPS) was crystallized at room temperature in dichloromethane, chloroform, toluene, *o*-dichlorobenzene, and decalin (cis−trans) to form the clathrate structure (δ form) with respective solvent molecules. Room temperature FTIR spectra are compared for subtle differences, which arise due to the solvent for the first time. The absorbance bands in the regions 590−615, 920−950, and 1130−1400 cm^{-1} are identified to be sensitive to the solvent used for the compound formation. In-situ high-temperature Fourier transform infrared spectroscopic studies were made on these samples, and the spectra showed major changes when the γ form transformed into the α'' form at ~200 °C on heating; the bands due to the helical structure disappear, and bands corresponding to the zigzag conformation appear. On the other hand, the transition of the δ form into the γ form on heating above the glass transition temperature involves spectral changes in weak bands sensitive to the helical conformation.

Introduction

The sPS in the semicrystalline form shows complex polymorphism and has four polymorphic forms, namely α, β, γ, and δ. The α and β forms, both containing planar zigzag chains having a 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 a T2G2 helical conformation and are formed under conditions where solvents are used for crystallization.[5−8] The δ form has a clathrate structure where the guest, low molecular weight molecules, most often solvent molecules, are accommodated in the crystalline lattice. 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 γ form does not include solvent molecules in the crystalline structure. The guest molecules in the clathrate structure may be extracted out by suitable extraction procedures.[9] The resulting emptied clathrate structure is different from the γ form. The γ form may be obtained by annealing the δ form or the emptied δ form, for instance, at ~130 °C.[9] The crystal structure[10] 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 $P2_1/a$.[11] 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, and in situ high-temperature X-ray diffraction studies have shown that the stability of the δ form depends on the amount of solvent present in the clathrate.[12] However, the transition from the γ form to the α form is independent of the solvent used for clathrate preparation[12] and occurs at about 200 °C.

FTIR has been extensively used to study the conformation in the various polymorphs of sPS,[13−18] and specific spectral regions that are sensitive to conformational changes have been identified. Moyses and Spell pointed out the spectral pattern difference between the δ and γ forms in the 920−960 cm^{-1} region.[19] Tashiro and co-workers[20,21] carefully studied the spectral details of the δ, δ_e, and γ forms and found several infrared bands; in particular, the bands in the region 500−800 cm^{-1} are different in their profiles between the δ, δ_e, and γ forms. They have also used in situ FTIR measurements to study the solvent exchange phenomenon in sPS.[21] Tashiro et al.[22,23] have used time-resolved IR spectra measurements to study the molecular mechanism of solvent-induced crystallization of sPS. Guerra and co-workers[24] used time-resolved FTIR to study the mass transport and conformational ordering of the guest molecule in the clathrate.

The impetus for the present work came from the fact that most of the FTIR studies focused on the spectral differences between the various crystalline forms of sPS, but not on the spectral changes due to different solvents. Second, most of the FTIR studies that deal with 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 or annealing. We examined the sPS spectra crystallized by different solvents and also followed in situ the IR spectral changes occurring during the crystalline transitions of the sPS−solvent complex on heating by attaching a hot stage to the FTIR sample compartment. The results obtained are compared with HT WAXS and DSC experiments. These studies also

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showed that the solvents leave their signatures in the spectra, even though the spectra of sPS crystallized by various solvents look similar.

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 thickness about 20−40 μm were obtained by forming a thin melt film and then rapidly quenching in ice−water bath. The amorphous films were crystallized in the clathrate form by immersing in dichloromethane, chloroform, toluene (for 36 h), *o*-dichlorobenzene, and decalin (cis + trans) (for 168 h) at room temperature. The emptied clathrate samples were obtained by extracting the solvent molecules by boiling in acetone for about 15 h. The amorphous sample was also crystallized in acetone at room temperature for 72 h and dried under vacuum at 50 °C for 10 h.

Room temperature and high temperature infrared spectra of these samples were taken using Perkin-Elmer FTIR spectrometer (model PC 16) at a resolution of 2 cm^{-1} in the range 450−4400 cm^{-1}. A total of 32 scans were used for signal averaging. High temperature spectra were obtained by mounting the sample in the Mettler Toledo FP82HT hot stage and placing it in the sample compartment of FTIR and aligned using the red laser light. The sample was heated at a rate of 5 °C/min. The spectra were collected while the sample temperature was held constant. The change in spectra was monitored during heating by scanning at regular temperature intervals until the sample melted. Once the sample started melting at about 270 °C, it moved out of the beam path, and the spectra could not be recorded with further increase in temperature. The selected regions of the spectra were deconvoluted using the Peakfit (Jandell) deconvolution program. The thermal analyses of the samples were performed using a Perkin-Elmer DSC-7 and TGA-7 under standard conditions at the same time using parts of the film used for FTIR studies. The TGA study provided the information about the amount of solvent present in the clathrate structure. In some cases HT WAXS experiments were also performed on the samples at the same time.

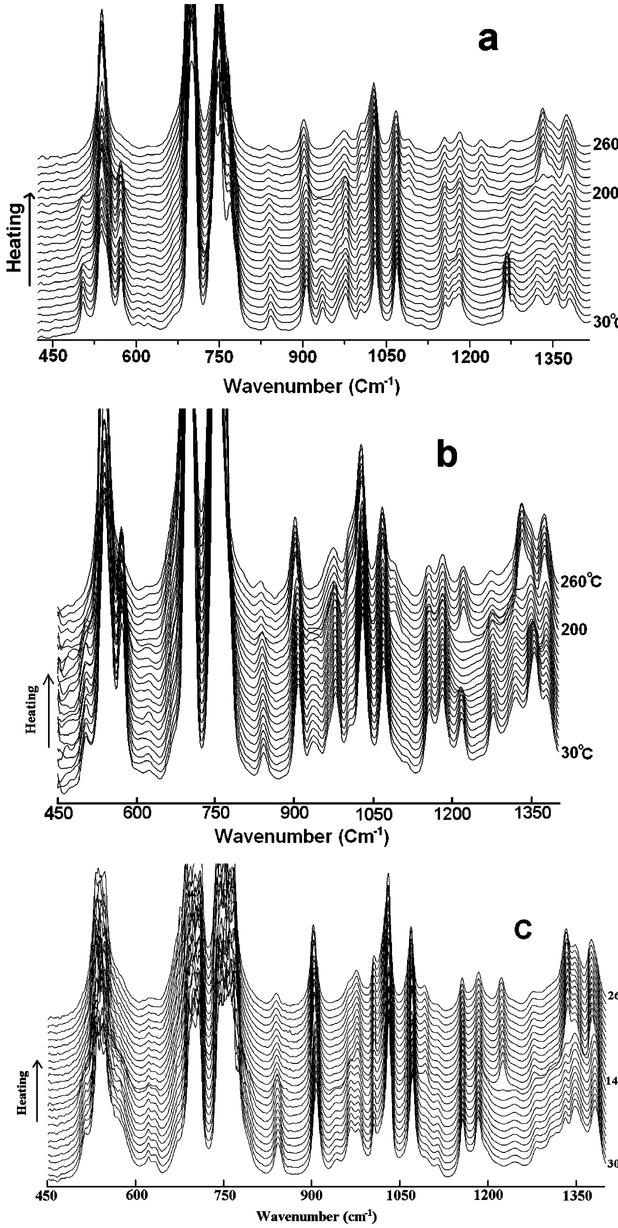

Figure 1. Behavior of IR spectra on heating from room temperature to melt for (a) sPS-DCM (8%) clathrate, (b) γ-form obtained by crystalling sPS in acetone, and (c) an amorphous sample.

Results and Discussion

FTIR spectra of various clathrate samples are expected to show differences due to solvent nature and heating. However, at room temperature, all the clathrates exhibit apparently similar spectra, albeit the characteristic peaks of the solvents. On heating, systematic changes occur in the spectra and will be discussed first. Figure 1 shows the spectra during heating for the clathrate sample with 8% DCM as a representative sample. Also shown are the spectra of the γ form obtained by crystallization of amorphous sPS in acetone and the spectra of amorphous sPS on heating for comparison purpose with that of the δ form. The characteristic bands of the TTGG conformation are seen at 502, 572, 769, 1318, 1353, and 1379 cm^{-1}. The bands at 1090, 1222, and 1333 cm^{-1} are assigned to the 4T conformation and are absent in the room temperature spectra of the clathrates and the amorphous samples. The band at 536 cm^{-1} is very prominent and assigned to a mixture of 4T and TTGG conformations. The bands at 769 and 1353 cm^{-1} are assigned to long and short helical sequences, respectively.[25] Another long helix band at 1168 cm^{-1} appears between the bands at 1155 and 1181 cm^{-1}. The reader may refer to refs 13−18 for detailed assignments of the bands. On heating, the spectra of the clathrate samples show systematic changes in the spectra; however, the changes are subtle until the temperature reaches 200 °C. High temperature WAXS studies[12] on similar samples under similar conditions have distinctly showed the δ to γ form transition by way of distinct changes in the diffraction pattern during the transition on heating above glass transition temperature. It may be kept in mind that the spectra of δ and γ forms are similar, and only a few weak bands show difference between the δ and γ forms and will be discussed later in detail. The spectra show a dramatic change on heating above 200 °C; the characteristic bands of the TTGG conformation either decrease or vanish, and similarly the bands of the 4T conformation either increase in intensity or appear newly. The region 500−600 cm^{-1} is highly sensitive to conformational changes,[17] and as an example, Figure 2a shows the changes occurring in this region during heating in a detailed way for the clathrates that contain 8% DCM and 14% toluene. The region 500−600 cm^{-1} is assigned to out-of-plane modes of the phenyl group.[14] It may be noted that DCM, toluene, and decalin do not

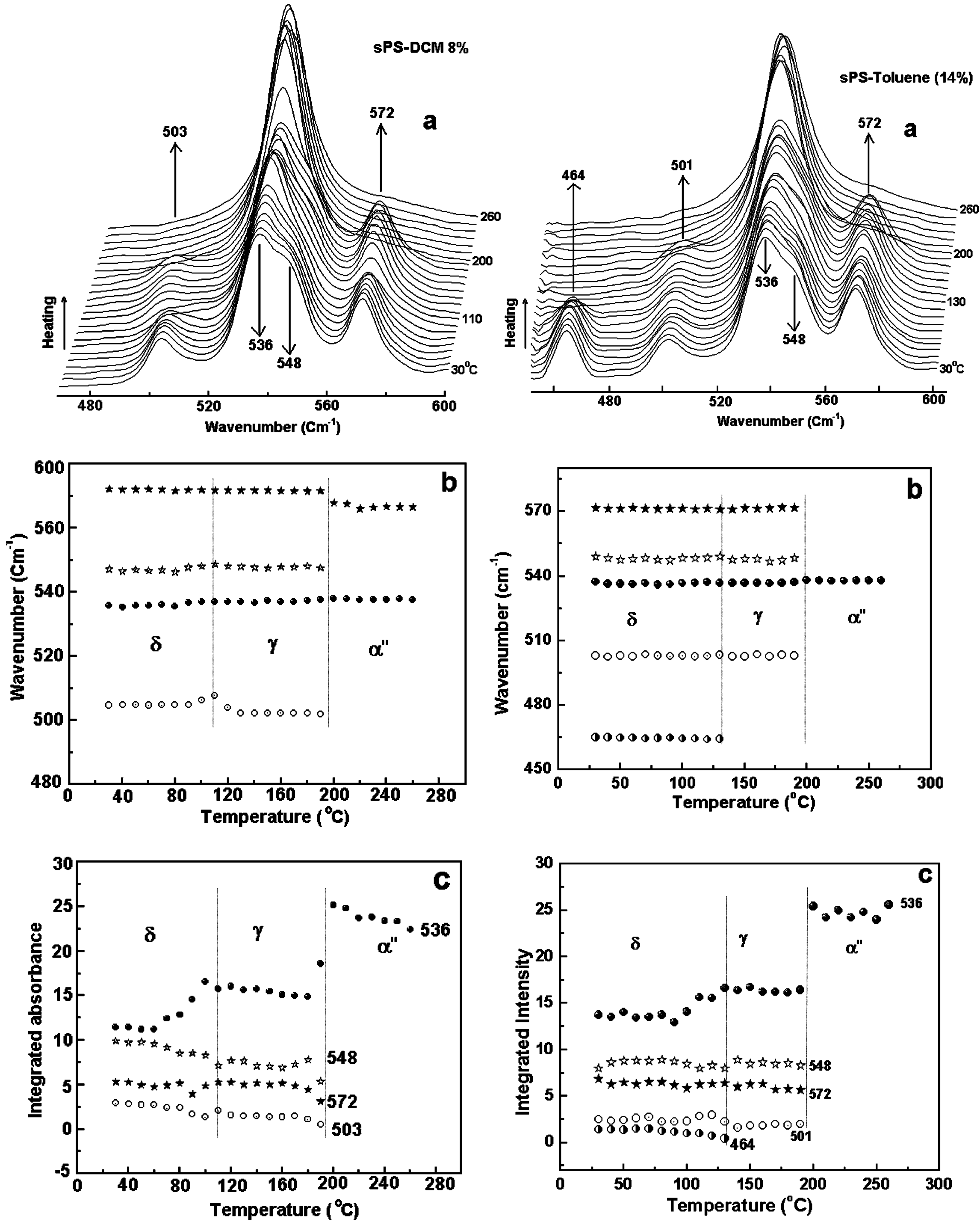

Figure 2. (a) Behavior of IR spectra from 480 to 600 cm^{-1} region during heating for clathrates with 8% DCM and 14% toluene. (b) Variation of band position with temperature. (c) Variation of integrated absorbance.

have solvent spectra in this region, which would otherwise overlap with the sPS spectra. The spectra have been deconvoluted into four peaks centered at 503, 536, 548, and 572 cm^{-1}. The band at 548 cm^{-1} is due to GTTG conformation and appears as a shoulder to the 536 cm^{-1} peak. The change in band position and the integrated absorbance are shown in parts b and c of Figure 2, respectively, for the four bands. The bands at 503, 548, and 572 cm^{-1} disappear at ~200 °C, while the behavior of the 536 cm^{-1} band is more complicated. The integrated absorbance of the 536 cm^{-1} band increases at about 110 °C and then remains unchanged until 200 °C is reached. In the case of clathrate with 14% toluene the band absorbance increases at 130 °C and is attributed to the δ to γ form transition. At about 200 °C, for both the samples, the absorbance of the band 536 cm^{-1} increases rather abruptly and then remains constant until melting.

The other region sensitive to conformational changes is from 1200 to 1400 cm^{-1} and is shown in Figure 3. The band at 1267 cm^{-1} is due to the solvent and vanishes at about 120 °C. Figure 3b,c shows the behavior of wavenumber and integrated absorbance with temperature. The band at 1318 cm^{-1} disappears at about 200 °C, and at the same time the bands due to the 4T conformation start appearing at 1222 and 1332

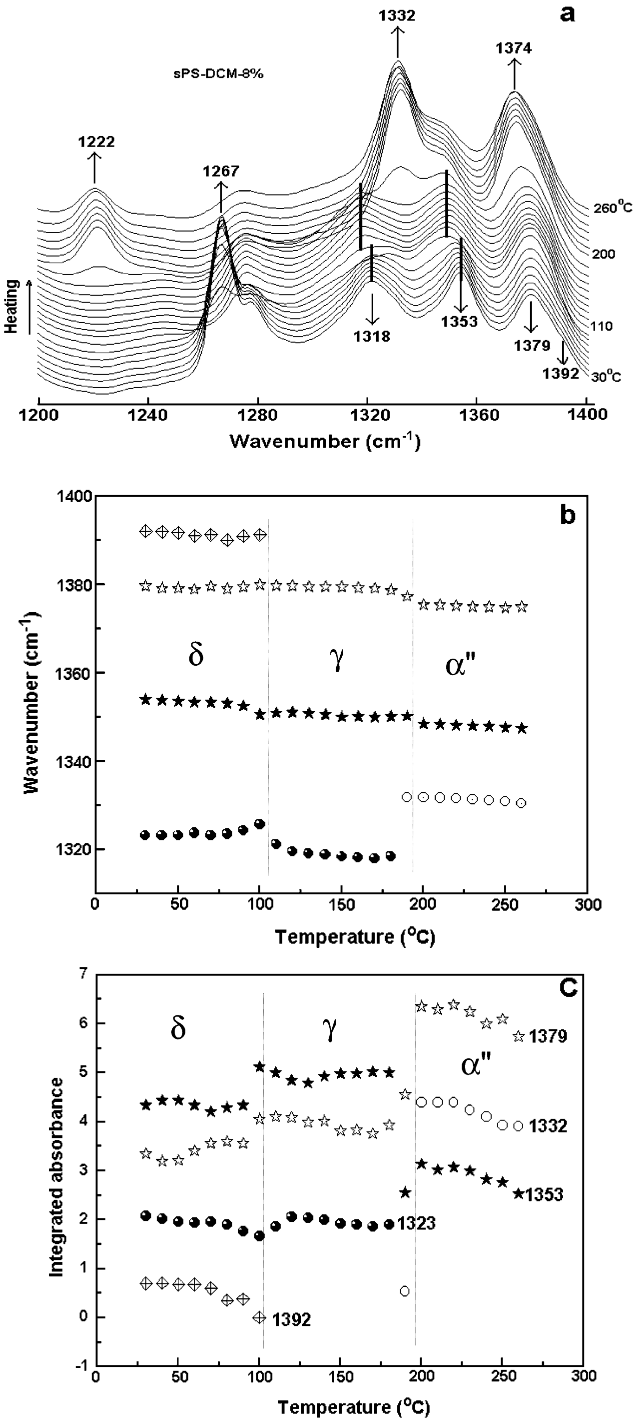

Figure 3. (a) Behavior of IR spectra from the 1200 to 1450 cm^{-1} region during heating for clathrates with 8% DCM (the thick lines indicate the shift in the peak positions before and after transition). (b) Variation of band position with temperature. (c) Variation of integrated absorbance.

cm^{-1}. The absorbance of 1379 cm^{-1} shows behavior similar to the band at 536 cm^{-1}, shows sudden increase at about 110 °C, and again increases after 200 °C. The similarities in the behavior of the 1379 cm^{-1} band with the band at 536 cm^{-1} suggest that 1379 cm^{-1} may be related to a combination of trans and helical conformations. The band at 1392 cm^{-1} appears as shoulder to the band at 1379 cm^{-1} and is shown in Figure 3. On heating, the shoulder disappears when the δ form changes into the γ form at about 110 °C in the case of the clathrate crystallized by DCM. This shoulder appears to be unique to the δ form and is visible in all the clathrates but vanishes after the transition.

All the clathrates exhibit similar behavior, namely the disappearance or decrease in the intensity due to helical conformations at about 200 °C during heating. The conformational changes occurring at $\sim$200 °C may be identified as the transformation of the γ form (TTGG) into the α'' form (4T) on the basis of HTWAXS and DSC studies on these samples.[12] The sample crystallized in the γ form directly also behaves similar to the clathrate samples and transforms into the α'' form on heating above 200 °C. In the case of the amorphous sample, the bands due to the all-trans conformation at 1090, 1222, and 1333 cm^{-1} appear at about 140 °C, as the sample crystallizes into the α'' form. There are no further changes in the spectra on heating, indicating that the sample remains in the α'' form until melting.

As discussed above, the IR spectra are very sensitive to major conformational changes occurring during the γ to α form transition at $\sim$200 °C. On the other hand, the conformational changes are not expected during δ to γ form transition as both have similar helical conformation, and the changes in the spectra occurring during this transition may be attributed to the interaction between the solvent and the sPS helix. Apart from the increase in the absorbance of the bands 536 and 1379 cm^{-1} at this transition, only a couple of weak bands show changes during the transition of δ form into γ form. It may be kept in mind that these bands are in general very weak and not resolved nicely in experiments, probably due to the thin samples used in the experiments. Hence, thicker samples are specifically prepared to study these weak bands.

The doublet at 934 and 943 cm^{-1} is assigned to the helical conformation and is used to study the conformational changes between the δ and γ form transition.[15,19] In the present case, this doublet is deconvoluted into individual peaks, and Figure 4a−c show the spectra, wavenumber, and integrated absorbance for the doublet. In the case of the clathrate with 8% DCM a new peak appears at about 937 cm^{-1} when heated above 110 °C. The spectra do not explicitly show the peak at 937 cm^{-1}; nevertheless, the deconvolution clearly showed the presence of this peak. Moyses and Spells observed this peak in the room temperature spectra of the γ form.[19] The appearance of the 937 cm^{-1} band at 110 and 130 °C on heating for the 8% DCM and 14% toluene clathrate sample, respectively, indicates the change of the δ form into the γ form. The wavenumber and integrated absorbance of the 934 and 943 cm^{-1} bands also show a change at the δ to γ form transition temperatures, $\sim$110 and 130 °C, respectively, for the clathrates having 8% DCM and 14% toluene. It may be worth pointing out that one of the key differences between the two forms is the presence of the 937 cm^{-1} band in the γ form and its absence in the δ form.

Similarly, the band at 1168 cm^{-1}, which is due to the long helix,[25] is assigned to the TTGG conformation, and it also responds to the δ to γ form transition. In the spectra, 1168 cm^{-1} is a weak band visible between 1155 and 1181 cm^{-1}. The region between 1140 and 1200 cm^{-1} has been deconvoluted into three bands at 1155, 1168, and 1181 cm^{-1} and is shown in Figure 5a−d for clathrates having 8% DCM and 14% toluene. The integrated absorbance and the half-width of the band at 1168 cm^{-1} decrease in the δ to γ form transition temperature region and then remain constant. The

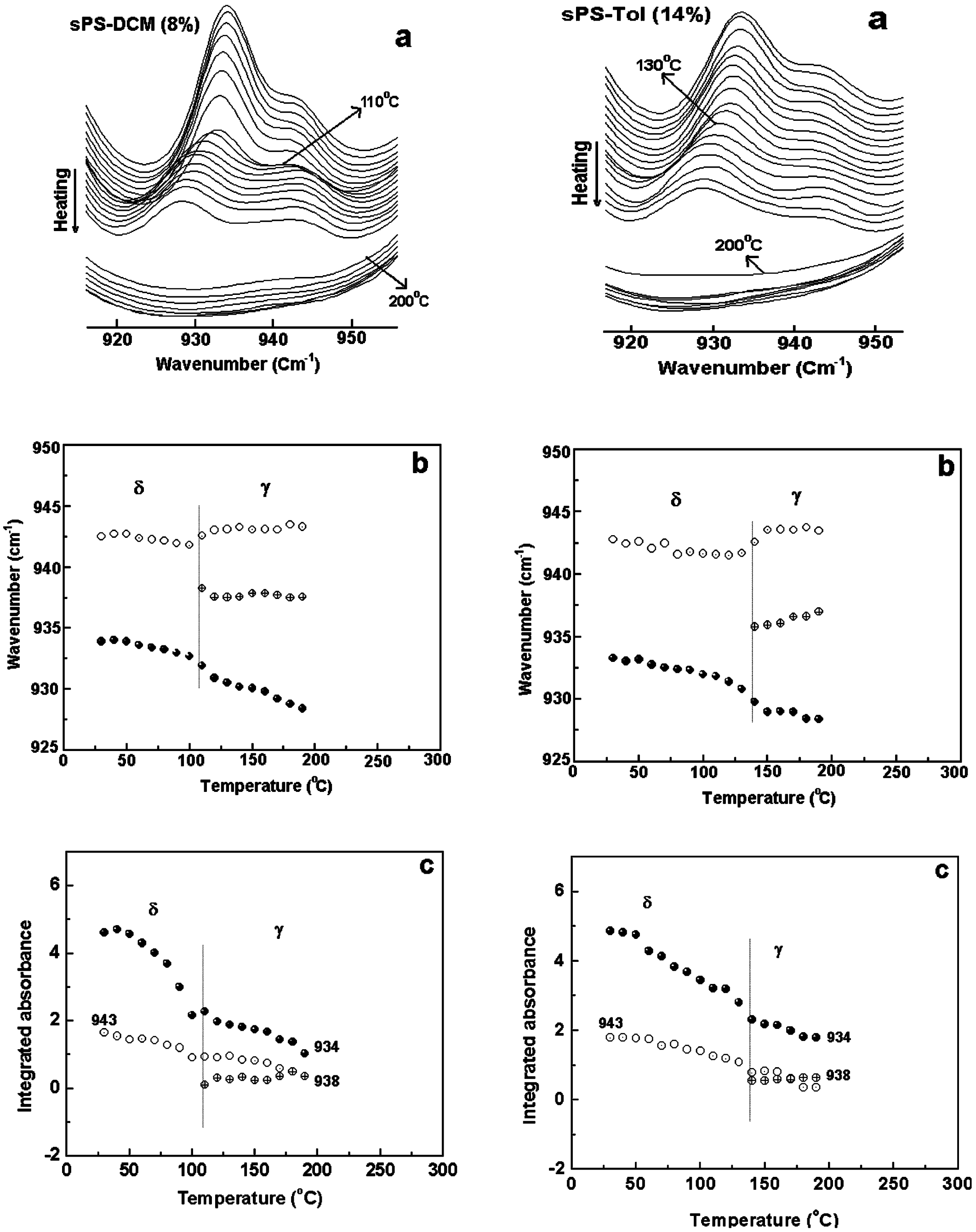

Figure 4. (a) Behavior of IR spectra from the 920 to 950 cm^{-1} region during heating for clathrates with 8% DCM and 14% toluene. (b) Variation of band position with temperature. (c) Variation of integrated absorbance.

transition temperature for the δ to γ form is ~110 °C for clathrate with 8% DCM and ~130 °C for the clathrate with 14% toluene. These values compare very well with the values obtained by HT WAXS studies.[12] The band finally disappears at ~200 °C during heating, when the γ form transforms into the α'' form. The absorbance of 1181 cm^{-1} does not exhibit any major change during the δ to γ form transition but decreases rapidly during the γ to α'' form transition at ~200 °C, while the absorbance of the band at 1155 cm^{-1} remains fairly constant until melting. The ratios between the integrated absorbance of the 1168 and 1181 cm^{-1} bands for various solvents at room temperature and at 160 °C are given in Table 1. It appears that the absorbance of the 1168 cm^{-1} band depends on the solvent present in the clathrate, while in the γ form it is independent of the solvent. This indicates that the band at 1168 cm^{-1} is affected by the interaction between the solvent molecule and the sPS helix in the crystal.

In the foregoing sections the discussion is focused on the changes in the spectra during the crystalline transitions upon heating the clathrate samples from room temperature. The effect of solvent on the spectra is not considered. The following sections will discuss the effect of solvent on the sPS spectra. The bands at 600 and 610 cm^{-1} are identified exclusively with the γ and δ form,[20,21] as these bands are absent in the amorphous and thermally crystallized samples. A careful inspection of the room temperature clathrate spectra shown in Figure 6 will reveal that the separation between the bands at 600 and 610 cm^{-1} is sensitive to the solvent used for crystallization, and the separations between the bands are given in Table 2. Tashiro et al.[20,21] have shown that the emptied δ form has a smaller separation than the δ

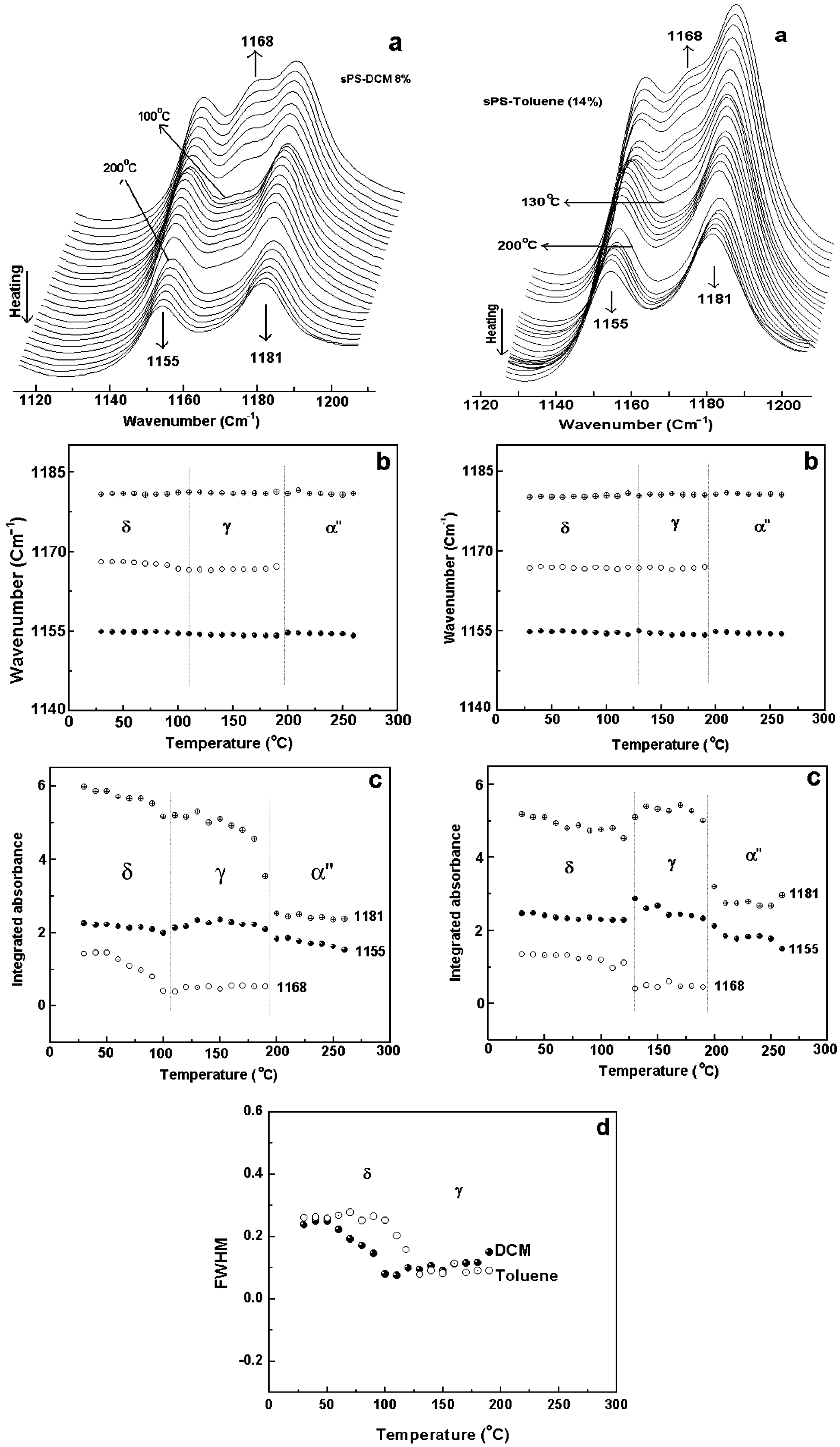

Figure 5. (a) Behavior of IR spectra from the 1120 to 1200 cm^{-1} region during heating for clathrates with 8% DCM and 14% toluene. (b) Variation of band position with temperature. (c) Variation of the integrated absorbance. (d) Variation of half-width of the 1168 cm^{-1} band with temperature.

Table 1. Ratio between the Integrated Absorbance of the 1168 and 1181 cm^{-1} Bands for Various Solvents at Room Temperature (δ Form) and at 160 °C (γ Form)[a]

solvent used	δ (clathrate)	γ
DCM (8%)	0.42	0.30
toluene (14%)	0.73	0.38
decalin (12%)	0.51	0.31
DCB (20%)	0.87	0.45
DCB (0%)	0.33	0.42
acetone	0.21	0.20

[a] The numbers in parentheses indicate the amount of solvent trapped in the clathrate at room temperature.

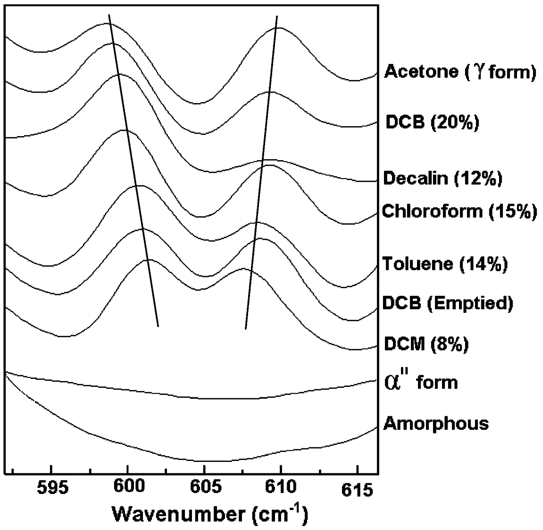

Figure 6. Behavior of the spectral region 595−615 cm^{-1} for various samples at room temperature.

Table 2. Two Bands in the Spectral Region 595−615 cm^{-1} for Various Clathrates at Room Temperature (δ Form) and at 160 °C (γ Form)

	band position (cm^{-1})			
solvent used	30 °C		160 °C	
DCM	601	607	599	610
toluene	600	608	599	610
DCB	599	609	599	609
decalin	599	610	599	610
chloroform	600	609	599	610
DCB (emptied)	601	608	599	610

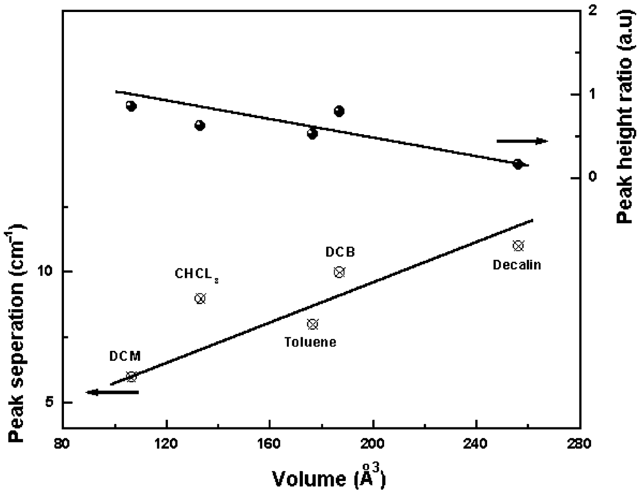

Figure 7. Variation of peak separation and ratio of the absorbance of the 608 to 600 cm^{-1} bands with molecular volume.

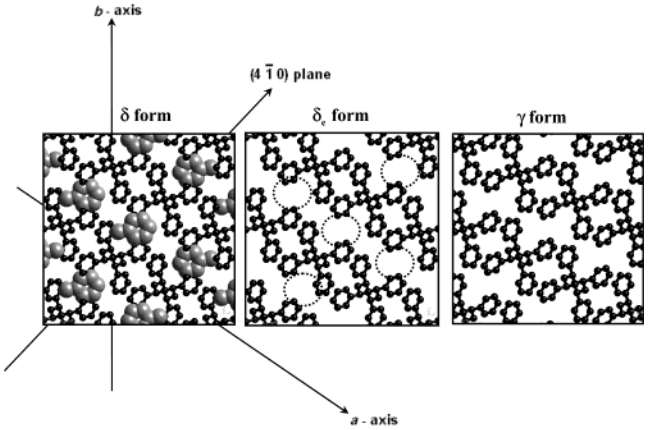

Figure 8. Schematic illustration of the lattice showing sPS and solvent molecules in clathrate, emptied clathrate, and γ form.

form as long as the solvent is of the same type. The γ form has the largest separation between these bands. However, the present result shows that the smallest separation is for the clathrate with DCM (8%). This may be due to the different sizes of the solvent molecules; the distance between sPS and solvent molecule affects the interaction between them. Another noteworthy feature is that the absorbance of 608 cm^{-1} band depends on the nature of solvent. The separation and the ratio of the peak absorbance of the 608 to 600 cm^{-1} bands are plotted against the molecular volume of the solvent molecule in Figure 7. From the plot it appears there is a broad correlation between these two parameters and the molecular volume; the absorbance of 608 cm^{-1} is inversely related to the molecular volume, while the peak separation is related linearly. Two points to be noted here: the γ form has the highest ratio, and the absorbance ratio of the emptied δ form has a lower value than that of the γ form, even though both forms do not include a solvent molecule in the lattice. The variation in the separation between the bands and the ratio of the absorbance with solvent may be explained on the basis of the solvent interaction with sPS. Figure 8 shows the solvent in the lattice, and it is speculated that the interaction between polymer and solvent along the b-axis, to be precise along the $(4\bar{1}0)$ plane, is different between the samples while the interaction along the a-axis is almost common. The interaction along the a-axis reflects the band separation of the empty form, whereas the interaction along the b-axis is negligibly small because no solvent molecules are there between the neighboring chains. In the clathrates the polymer−solvent−polymer interactions are observed along the b-axis, increasing the band separation in addition to the separation determined by the interaction along the a-axis. The polymer−solvent−polymer interactions are different depending on the solvent molecules, giving the different band separation width with various solvents. In the case of the γ form, the closest packing gives the direct interaction along the b axis (polymer−polymer), giving the largest separation. In other words, the 600 cm^{-1} region band profiles are associated with the volume and polarity of the solvent molecule or the interaction strength between sPS and solvent.

These bands also change peak position on heating. The variation of these peaks with temperature is shown for the clathrate with 8% DCM and emptied DCB (0%) in Figure 9a,b. Also shown in the figure is the variation of wavenumber with temperature. It is obvious from the

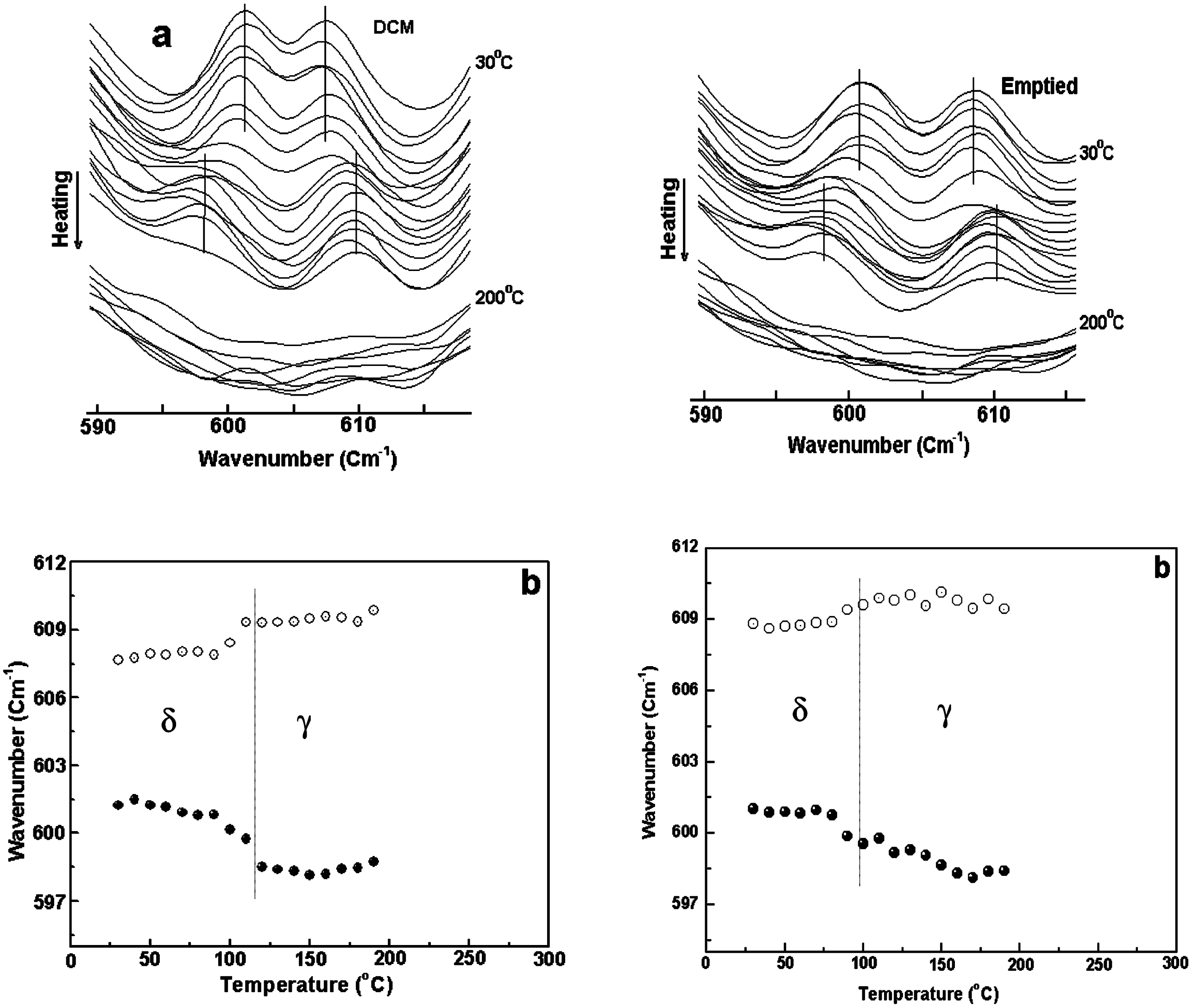

Figure 9. (a) Behavior of IR spectra from the 600 and 608 cm^{-1} bands during heating for clathrates with 8% DCM and emptied clathrate sample. (b) Variation of band position with temperature.

figure that these peaks move away from each other at the *δ* to *γ* form transition. The transition is not readily observable in the clathrates with solvents decalin and DCB because the change in the peak positions for the *δ* and *γ* forms is minimal.

The TTGG band at 1379 cm^{-1} also exhibits a dependence on the nature of solvent used for crystallization and is apparent on heating. Figure 10 shows the variation of peak absorbance on heating for various samples. The clathrate samples with DCM, chloroform, and the emptied sample readily show an increase in absorbance when the structure transforms from the *δ* to *γ* form. On the other hand, toluene- and decalin-based clathrates do not show such an increase in peak absorbance during the *δ* to *γ* form transition and are similar to the behavior of the *γ* form (crystallized by acetone). Irrespective of the solvent used for crystallization, the 1379 cm^{-1} band shows an abrupt increase in the absorbance at about 200 °C, when the structure changes from the *γ* to α form. In the case of thermal crystallization of the amorphous sample, the band increases at about 140 °C, when the sample crystallizes directly into the α form. Though the data are limiting, on the basis of the behavior of the bands at 600 and 608 cm^{-1}, it may be speculated that the 1379 cm^{-1} band is also susceptible to the solvent–sPS interaction outlined in the previous section.

A careful inspection of the spectra of the various clathrates would also reveal that at room temperature few bands show a small but significant shift in the position with the nature of solvent. Also, these bands shift in position after the clathrate transforms into the *γ* form during heating. These bands are at 503, 1323,-1354, and 1380 cm^{-1} for clathrate sample with DCM and shift to 501,1318, 1350, and 1379 cm^{-1}, respectively, after the transition (at 160 °C). Table 3 shows the positions of these bands for clathrate samples with various solvents and after the transition at 160 °C. The data indicate that the room temperature band positions of these bands depend on the solvent in the lattice. However, in the *γ* form the band positions do not show any dependency on the starting clathrate structure.

A cursory look at the data would reveal that the clathrate with DCM shows the maximum shift in position. The behavior of bands 503, 1318, and 1353 cm^{-1} appears complicated during the transition for clathrate sample with DCM. These bands show a sudden perturbation in absorbance at about 110 °C. The bands 503 and 1318 cm^{-1} disappear at 200 °C, but the band at 1353 cm^{-1} remains until the polymer melts but

Table 3. Infrared Bands of Various Clathrates at Room Temperature (δ Form) and at 160 °C (γ Form)

	band position (cm^{-1})							
solvent used	30 °C				160 °C			
DCM	503	1323	1354	1380	500	1318	1350	1379
toluene	501	1321	1352	1380	501	1318	1350	1379
DCB	501	1320	1354	1376[a]	501	1318	1351	1379
decalin	501	1320	1351	1379	501	1318	1351	1379
chloroform	502	1320	1352	1379	501	1318	1350	1379
acetone	501	1318	1355[a]	1378	501	1318	1351	1379
DCB (emptied)	503	1319	1354	1379	501	1318	1350	1379

[a] Solvent band overlaps.

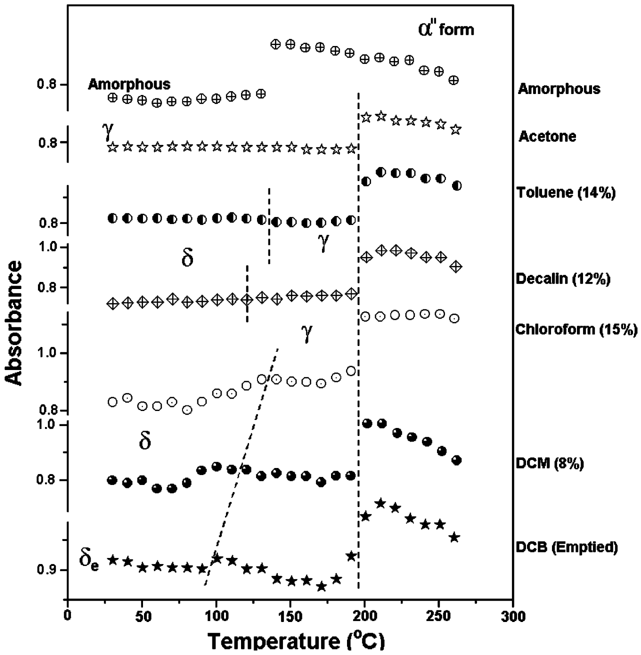

Figure 10. Variation of the peak height of the 1379 cm^{-1} band with temperature for various samples.

with reduced intensity. This perturbation is observed for the sample crystallized with DCM only, and the other clathrates do not exhibit such a perturbation. At this stage no definite explanation is offered for this perturbation; however, it is thought that it arises due the specific interaction between sPS and DCM. In the above discussions the spectra of the γ form at 160 °C has been compared with the clathrate form at room temperature. It is seen from Figure 1 that the spectra of γ form does not change on heating until ~200 °C. Hence, for practical purposes the γ form obtained by heating the clathrate sample to 160 °C may be taken to represent the room temperature γ form spectra. Nevertheless, it may be noted that only the spectral region 920−950 cm^{-1} of the γ form shows change during heating from room temperature. However, these changes are reversible on cooling to room temperature provided the temperature does not exceed the γ to α'' transition temperature.

The present extensive FTIR spectroscopic studies on the sPS samples indicate that few bands arise exclusively from the crystalline region. The bands at 1090, 1222, and 1333 cm^{-1} appear once the γ form transforms into the α'' form at ~200 °C and are assigned to the 4T conformation arising out of the chains within the crystal. These bands do not appear in the spectra of the δ and γ form. In the case of amorphous sPS, however, on heating these bands appear above 140 °C, once the sample crystallizes. The monitoring of these peaks provides an alternative technique to study the thermal crystallization of sPS. The bands at 502, 548, 600, 609, 1169, and 1318 cm^{-1}, on the other hand, appear in the δ and γ form and do not appear in the spectra of amorphous or α form sPS. These bands disappear at ~200 °C on heating and hence are attributed exclusively to the helical s(2/1)2 conformation within the δ and γ form crystals.

Conclusions

The FTIR spectra of clathrate structures of sPS obtained by crystallizing in various solvents are compared for the first time. Examination of room temperature IR spectra obtained from clathrates shows that the bands at 600 and 608 cm^{-1} are very sensitive to the solvents used for crystallization. The clathrate sample with DCM shows the smallest separation while the γ form has the largest separation between these bands. In-situ high-temperature Fourier transform infrared spectroscopic (HT FTIR) studies were used to follow the crystalline transitions in clathrate form of sPS during heating for the first time. The FTIR spectra showed major changes when the γ form transformed into the α'' form at ~200 °C, when the helical conformation changes into a planar zigzag conformation. On the other hand, the transition of the δ form into the γ form on heating above the glass transition temperature is not very obvious, as the spectral changes are only marginal and affectsvery weak bands. The bands at 600, 609, 934, 943, and 1168 cm^{-1} are sensitive to the δ and γ forms and used to follow the δ to γ form transition. These results independently corroborate the HTWAXS results,[12] that the δ to γ form transition depends on the amount of solvent molecules present in the clathrate; the higher the amount of solvent in the clathrate, the higher the transition temperature. These studies also indicate the bands exclusively associated with the sPS crystal.

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