Conformationally Sensitive Infrared Vibrations of the Syndiotactic Polystyrene/Ethylbenzene Complex

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ABSTRACT: The 920−960 cm^{-1} region of the infrared spectrum of the δ phase syndiotactic polystyrene/ethylbenzene predominantly involves bands arising from helical structures and has been studied here as a function of heating temperature. Curve fitting and deconvolution showed the necessity, for annealing temperatures above 120 °C, of adding a third component at 940 cm^{-1} to peaks at 934 and 943 cm^{-1}. The 934 and 943 cm^{-1} peaks behave as a doublet, primarily due to the δ phase, with the splitting increasing on annealing. The 940 cm^{-1} peak is solely due to the γ phase helix. Importantly, these assignments provide the opportunity for using these bands for further studies of complexation/decomplexation in such systems. The reduction in absorbance of 934 and 943 cm^{-1} peaks occurs at a lower temperature than the rise in the 940 cm^{-1} absorbance, and this is attributed to disordering of the δ phase helices prior to reformation as γ phase helices. Similar measurements using deuterated syndiotactic polystyrene also showed helix and zigzag bands, but without a predominantly δ phase helix peak. Solvent peaks in the deuterated syndiotactic polystyrene/ethylbenzene system were used to monitor the δ to γ phase transition. In combination with DSC and TGA data, the melting temperature of the α phase was found to be depressed by 7 °C for the deuterated polymer, while the δ to γ phase transition temperature was shown to be around 24 °C higher.

Introduction

Since the initial synthesis of the polymer in the 1980s, there have been several studies of syndiotactic polystyrene (sPS) using vibrational spectroscopy. The complex polymorphism of sPS, with a helical chain configuration in both the solvent-stabilized δ phase and the solvent-free γ phase (adopting here the notation of Guerra et al.[1]) and a planar zigzag configuration in the α and β phases, has been of widespread interest: spectroscopic characteristics of the different phases were sought. Conformationally sensitive IR bands were soon identified,[2−7] including features from both helical and planar zigzag crystal forms. Normal vibrational analyses have enabled a rationalization of some of the experimental data.[6,8−10]

Conformationally sensitive IR bands have since been used for various purposes. For example, a correlation has been established between the absorbance of the 1222 cm^{-1} zigzag band with sample crystallinity, as obtained from vapor sorption data.[11] The absorbances of helix bands in the region 500−600 cm^{-1} have been studied as a function of annealing temperature for sPS films cast from chloroform solution, showing a loss of helical order simultaneously with decomplexation, followed by a recovery of helix content before the transition to the zigzag form.[12] Similar behavior was later observed by Manfredi et al on heating either the δ phase of sPS/*o*-dichlorobenzene or the "emptied δ phase" (with solvent removed).[13] By comparison with X-ray data from parallel experiments, the minimum in helix content for the emptied δ form was identified with the formation of a mesomorphic form. The formation of a similar form during the decomplexation of sPS/methylene chloride had earlier been suggested by de Candia et al.[14]

Transition kinetics have also been determined using IR spectroscopy with conformationally sensitive bands. The transition from helical to planar zigzag forms has been studied for sPS films cast from toluene, showing a sharp transition followed by crystallization of amorphous material.[15] The kinetics of gelation of sPS in chloroform were followed using bands characteristic of helical forms of sPS.[16]

More recently, Rastogi et al have studied sPS gel systems with the solvents decalin, benzyl methacrylate, and cyclohexyl methacrylate using simultaneous SAXS/WAXS/Raman spectroscopy.[17] Two distinctly different helical δ phase structures, denoted δ' and δ'', were proposed, incorporating ordered and disordered solvent molecules, respectively. Corresponding differences were noted in the conformationally sensitive regions of the polymer Raman spectrum. A phase transition from the ordered δ' to the disordered δ'' phase was observed on heating under conditions where loss of solvent (and formation of the γ phase) was prevented.

We have previously used neutron scattering measurements, in conjunction with computer simulations, to show details of the molecular conformations obtained in the δ phase of sPS/ethylbenzene and the γ phase obtained after decomplexation.[18,19] The sheetlike arrangement of molecular "stems" (the individual traverses of the crystals) in the crystallographic *a* direction was found to become significantly disrupted on decomplexation. The increase in radius of gyration within the plane of the lamellae implies significant molecular mobility, and we therefore sought to attempt a correlation of this behavior with chain conformational details obtainable from IR spectra.

Differences in the 900−1000 cm^{-1} region of the infrared spectrum of sPS have previously been noted for helical and planar zigzag conformations, with a 935 cm^{-1} band associated with the helical δ form.[7] Normal mode calculations indicate a dispersive mode in this

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region for helical sPS, with frequencies of 945 and 929 cm^{-1} corresponding to phase differences (δ) of 0 and π, respectively.[10] This is a complex mode involving backbone CCH bending and C−C stretching components, coupled with a ring C−C stretching. In fact, a doublet at 934/943 cm^{-1} was earlier assigned to the helical conformation.[4] Since interchain interactions are not included in the Rastogi and Gupta calculations, this spectral region would appear to be a good candidate for detecting conformational differences between δ and γ phases. In addition, the availability of fully deuterated sPS allowed us to monitor both polymer and solvent bands during the heating procedure and to study isotopic differences in phase transition temperatures.

Experimental Section

Samples of sPS and fully deuterated sPS were kindly supplied by Professor V. Vittoria (Universita di Salerno) and Dr. J.-M. Guenet (Université Louis Pasteur, Strasbourg). NMR measurements showed tacticity to be in excess of 99% syndiotactic. GPC measurements were supplied by RAPRA Technology Ltd. (Shawbury, UK). Values of $\overline{M_w}$ for HsPS were 85 400 (AH) and 55 700 (BH), while values for the deuterated DsPS were 42 700 (AD) and 144 500 (CD). The sample nomenclature here corresponds to that used previously.[18] Values of $\overline{M_w}/\overline{M_n}$ were generally between 2 and 3.

The ethylbenzene used was Aldrich Chemicals 99% purity grade. Samples were crystallized from dilute solution in ethylbenzene at 40 °C, as previously described,[18] filtered, and allowed to dry to around 14% w/w solvent content. A Mattson 6020 FTIR spectrometer, equipped with an MCT detector, was used at a resolution of 2 cm^{-1}. The transmission measurements typically involved 200 scans. The heating procedure involved heating the sample at 10 °C min^{-1} in a Linkam hot stage to the required temperature, cooling the sample, and removing it to the spectrometer for examination at room temperature, followed by heating to the next (higher) temperature. Measurements at room temperature thus ensured that only irreversible conformational changes were monitored.

DSC measurements were made using a Mettler DSC 30 apparatus, calibrated using indium, at a heating rate of 10 °C min^{-1}. TGA measurements were made with a Mettler TMA 40 thermomechanical analyzer, also at 10 °C min^{-1} heating rate.

Normalization

An "internal thickness" band is required for the normalization of spectra, and this should be unaffected by conformational changes. Various bands have previously been used, including those at 1585[20] and 1183 cm^{-1} [11] for samples in the zigzag conformation. The normalization band(s) used for other work on the helical form were not reported.[12,13] A band at 1181 cm^{-1} has been assigned to a ring in-plane CCH bending mode in the planar zigzag form and to a helix backbone conformation in the helical form.[8] Integrated absorbance measurements of this band, after curve fitting to three or four peaks (depending on temperature) in the region 1135−1210 cm^{-1}, are shown in Figure 1. The fall in absorbance at the γ to α phase transition tends to support the different origins in the two phases. The band is therefore not suitable for use in normalization of spectra over the complete temperature range shown. The 1585 cm^{-1} band has been assigned to a benzene ring stretching vibration. The integrated absorbance after curve fitting is also plotted in Figure 1. Although there is no evidence here of sensitivity to conformation, the scatter in the data points is larger than might be expected for a sample of constant thickness. A band at

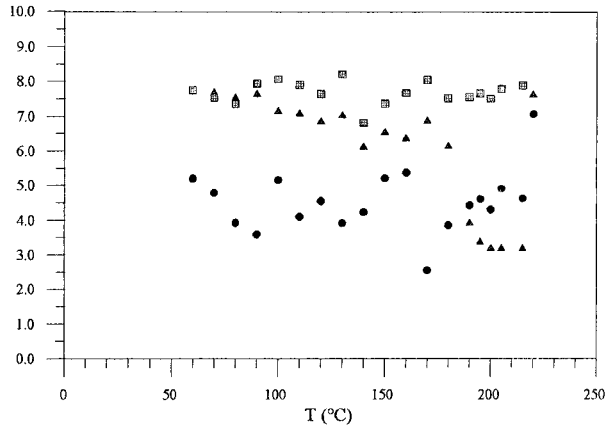

Figure 1. Integrated absorbances of bands considered for spectral normalization. Squares represent the 1069 cm^{-1} peak, triangles the 1183 cm^{-1} peak, and circles the 1585 cm^{-1} peak.

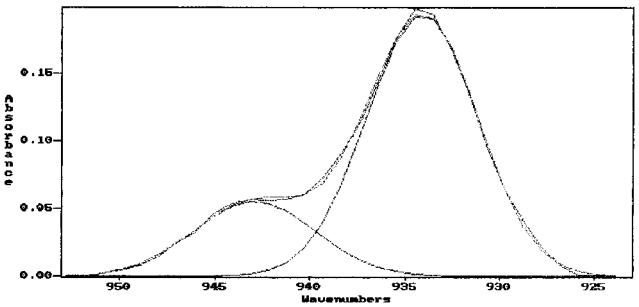

Figure 2. Application of curve fitting to a sample of syndiotactic polystyrene/ethylbenzene as crystallized in the δ phase, without annealing.

1069 cm^{-1}, assigned to a ring in-plane CCH bending vibration for both zigzag and helical conformations,[8] was therefore investigated. In addition to a lack of conformational sensitivity, the band shows much smaller scatter in the data points (Figure 1) and was therefore chosen for the normalization of spectra.

Conformationally Sensitive IR Bands

Previous measurements of helix bands in the region 500−600 cm^{-1} [12] were noted earlier. As outlined previously, we chose to study instead those bands in the range 920−960 cm^{-1}. Curve fitting between 920 and 960 cm^{-1} showed that, up to an annealing temperature of 120° C, two peaks provided an adequate fit to experimental data: an example is shown in Figure 2. The peak positions were approximately 934 and 943 cm^{-1}, although these figures were found to vary somewhat with annealing temperature, as will be discussed shortly. For annealing temperatures above 120 °C, it was found necessary to add a third peak, centered at 940 cm^{-1}. Support for the addition of a third peak was found from both Fourier self-deconvolution (Figure 3) and second-derivative spectra. The resulting peak frequencies and integrated band absorbances are plotted in Figures 4 and 5.

The band initially at 942−943 cm^{-1} and that at 934 cm^{-1} both show a frequency shift (Figure 4), starting below the temperature of 130° C where the third component becomes necessary in fitting the band structure. The shifts continue up to 130° C, with the decreasing frequency of the 943 cm^{-1} band correlated with the increasing frequency of the 943 cm^{-1} band. This points toward a relationship between the two

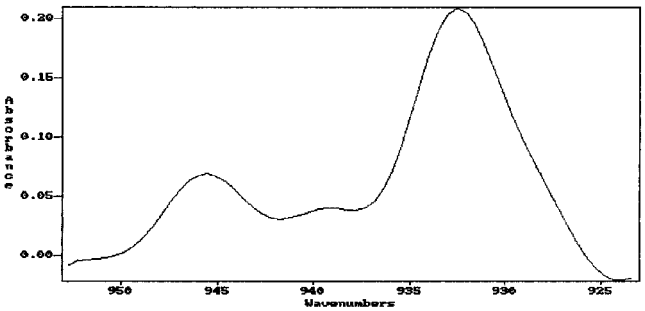

Figure 3. Application of Fourier self-deconvolution to a sample of syndiotactic polystyrene/ethylbenzene which has been annealed at 130 °C, revealing the third component present.

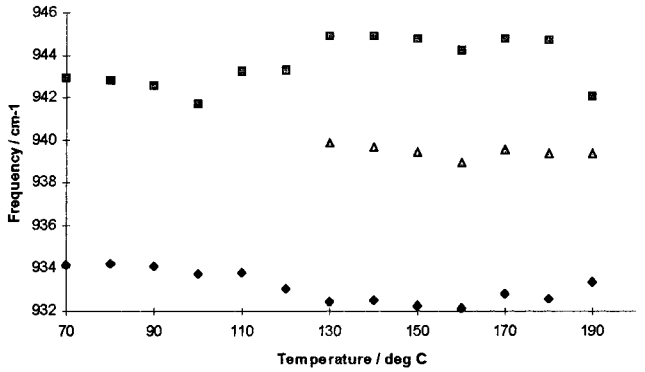

Figure 4. Frequencies of peak components in the 920−960 cm^{-1} region of the FTIR spectrum as a function of annealing temperature for a sample initially in the δ phase.

bands and is consistent with a shift in frequency of both $\delta = 0$ and π limits of the dispersion curve, presumably arising from the increased interchain interaction as the unit cell *b* dimension is reduced during decomplexation. Conversely, the 939−940 cm^{-1} peak stays at approximately the same frequency as a function of annealing temperature.

Regarding the band absorbances shown in Figure 5, the 943 cm^{-1} peak absorbance shows a decrease at the δ to γ phase transition, while finally disappearing at the γ to α transition. The decrease in absorbance at the δ to γ transition is accompanied by the appearance of a band at 940 cm^{-1}. The absorbance of this peak also falls to zero at the γ to α phase transition. Both bands are clearly characteristic of the helical conformation, with the 943 cm^{-1} peak predominantly due to the δ phase and the 940 cm^{-1} peak arising solely from the γ phase. Like the 943 cm^{-1} peak, that at 934 cm^{-1} also shows greater sensitivity to the δ phase, but in this case the difference is less significant. The sharp minimum at 100 °C is noted, but no explanation can be offered at this stage.

In Figure 5, we also show the sum of the absorbances of the bands at 943 and 940 cm^{-1}. While there is no reason to suppose a priori that the absorptivities of both bands are identical, the plot nevertheless shows a remarkable similarity to the behavior of the 571 and 548 cm^{-1} bands of sPS/chloroform observed by Nakaoki and Kobayashi.[12] In each case an initial plateau is followed by a decrease in the region of the δ to γ phase transition, after which an absorbance close to the original value is achieved once more. Finally, a sudden fall in absorbance occurs at the γ to α transition, the latter phase being identified from X-ray diffraction measurements. Conversely, it appears that the 571 and

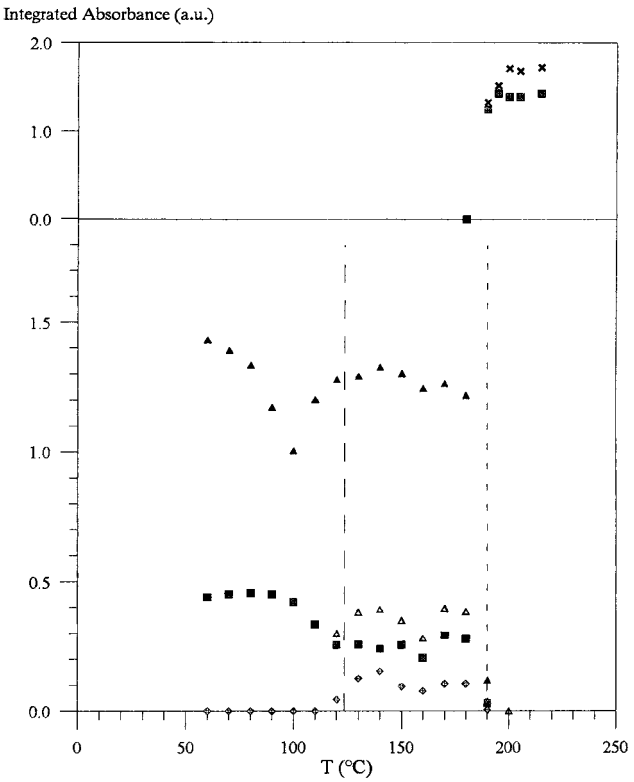

Figure 5. Variation of the integrated absorbance of conformationally sensitive bands with annealing temperature for syndiotactic polystyrene, after normalization using the 1069 cm^{-1} peak. Top plot: crosses, 1222 cm^{-1} peak; squares, 1171 cm^{-1} peak. Bottom plot: filled triangles, 934 cm^{-1} peak; squares, 943 cm^{-1} peak; diamonds, 940 cm^{-1} peak; empty triangles, sum of 943 and 940 cm^{-1} peak absorbances.

548 cm^{-1} peaks are dependent on the total helical content, without discrimination between δ or γ phase structures.

We also monitored the absorbance of bands at 1171 and 1222 cm^{-1}, representative of the planar zigzag chain conformation, and these show the expected increase from zero absorbance at the γ to α phase transition.

From Figure 5, both 934 and 943 cm^{-1} peaks show a reduction in absorbance at a lower temperature than the rise in 940 cm^{-1} absorbance. This indicates an initial disordering of helices and may be related to the mesophase reported, using other solvents.[13,14] From room-temperature wide-angle X-ray measurements, we have no direct evidence of such a phase. We suggest that the disordering allows some segments of crystal stems to move out of the crystallographic planes to which they are confined in the δ phase during the δ to γ phase transition. Small-angle neutron scattering (SANS) measurements of the in-plane radius of gyration of the oriented γ phase mats indicate an increase over values obtained in the δ phase.[18] Earlier work has also led to the suggestion of disordering of the δ phase helices.[12] However, without the benefit of a separation of the contributions from different IR bands, the conclusion was simply that a temporary disordering occurred. Here we have shown that the disordering of δ phase helices is followed at only slightly higher temperatures by the formation of the γ phase helix.

It should be noted that, since the samples were allowed to dry during the course of these experiments, we would not anticipate a transition involving a change in the degree of order of solvent molecules, as was

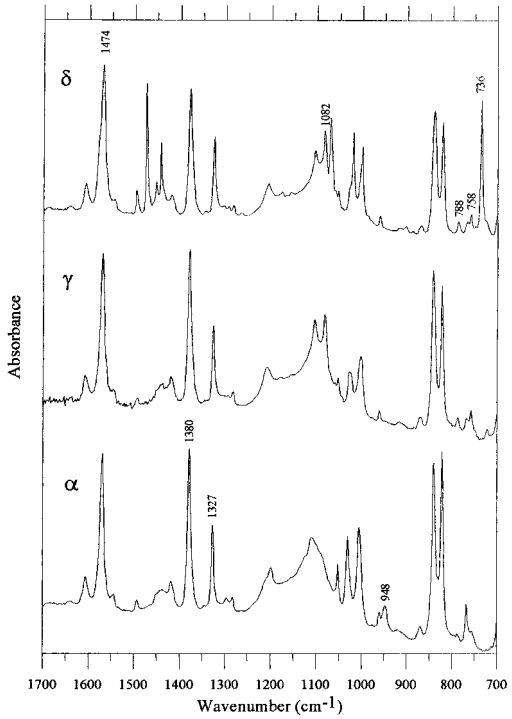

Figure 6. Infrared spectra of deuterated syndiotactic polystyrene in the δ (top), γ (middle, after annealing at 180 °C), and α (bottom, after annealing at 210 °C) phases, with some characteristic peaks labeled.

reported by Rastogi et al.[17] With respect to the bands studied here, there is no evidence of such a transition.

Deuterated Syndiotactic Polystyrene

Samples of the deuterated polymer (DsPS) were also crystallized from ethylbenzene at 40 °C into the δ phase. The spectrum, together with those obtained after heating into the γ and α phases, is shown in Figure 6. From a comparison of the spectra, we identify bands characteristic of a helical conformation at 722, 758, and 788 cm^{-1} and a band from the planar zigzag form at 948 cm^{-1}.

In seeking a band suitable for the normalization of DsPS IR spectra, peaks at 1327 and 1380 cm^{-1} were investigated. In each case the integrated absorbance as a function of temperature is plotted in Figure 7. Although both peaks appear insensitive to phase transitions, the one at 1327 cm^{-1} was preferred because of the smaller degree of scatter in the data. The use of deuterated polymer also allows the identification of solvent peaks. Bands characteristic of ethylbenzene were found at 736 and 1473 cm^{-1}. These have been assigned to an in-phase out-of-plane hydrogen deformation and a C−C ring stretching vibration, respectively, each with probable contributions from CH_2 modes.

The 722, 758, and 788 cm^{-1} peaks all show frequency shifts with annealing temperature, the last of these increasing in frequency with increasing temperature, primarily at the δ to γ phase transition and the other two decreasing in frequency. The integrated absorbances for various conformationally sensitive IR bands of DsPS are shown in Figure 8. The 788 cm^{-1} peak appears insensitive to the δ to γ transition, but the absorbance falls dramatically at the γ to α transition. Bands at 722 and 758 cm^{-1} have greater absorbances in the γ phase than in the δ phase, while both show negligible absorbance in the α phase.

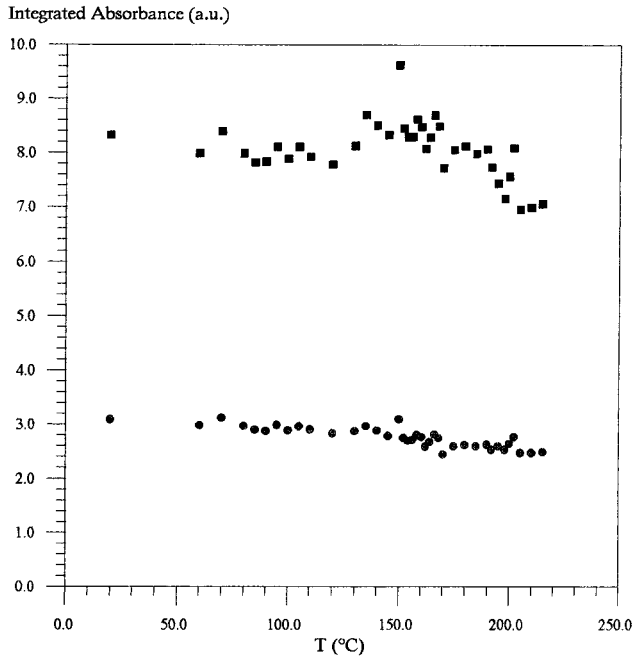

Figure 7. Integrated absorbances of bands considered for use in spectral normalization for deuterated polystyrene: squares, 1380 cm^{-1} peak; circles, 1327 cm^{-1} peak.

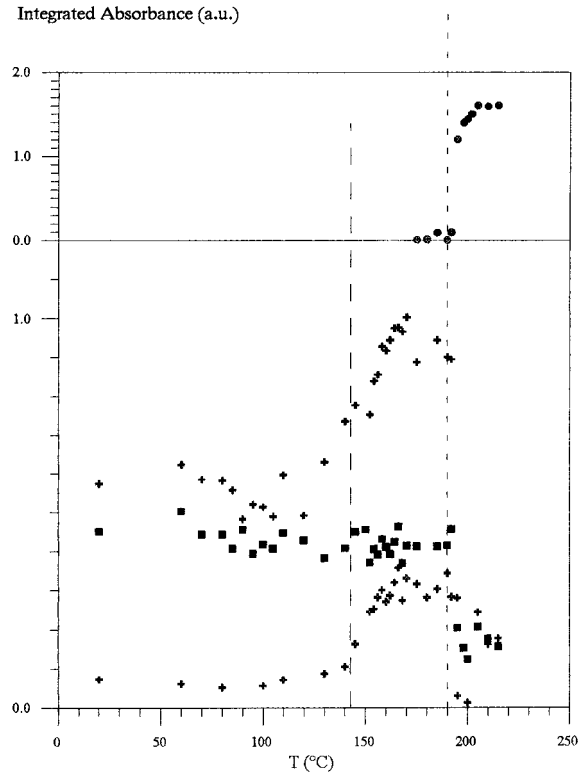

Figure 8. Integrated absorbances of conformationally sensitive bands of deuterated syndiotactic polystyrene, after normalization with the 1327 cm^{-1} peak. Top plot: circles, 948 cm^{-1} peak. Bottom plot: top plusses, 758 cm^{-1} peak; squares, 788 cm^{-1} peak; bottom plusses, 722 cm^{-1} peak.

The behavior previously noted for the 943 cm^{-1} peak of HsPS, namely a significant decrease in absorbance at the δ to γ transition, has not been observed for any of these DsPS peaks. The 722 cm^{-1} peak shows a large increase in absorbance at the δ to γ phase transition, similar to the 940 cm^{-1} peak in the normal polymer (HsPS). The frequency ratio of 1.30 is similar to values

Table 1. Transition Temperatures (°C) for Syndiotactic Polystyrene (HsPS)/Ethylbenzene and Deuterated Syndiotactic Polystyrene (DsPS)/Ethylbenzene

	HsPS/ethylbenzene			DsPS/ethylbenzene			
transition	DSC[a]	FTIR helix/zigzag bands[b]	TGA[b]	DSC[a]	FTIR helix/zigzag bands[b]	FTIR solvent bands[b]	TGA[b]
	AH	BH	BH	AD	AD	AD	AD
$\delta \rightarrow \gamma$	124	100−140 (120)	90−170 (123)	143	130−165 (150)	130−155 (143)	80−180 (126)
$\gamma \rightarrow \alpha$	193	180−190 (185)			190−200 (195)		
$\alpha \rightarrow$ melt	253			246			

[a] Peak positions of DSC endotherms. [b] Temperature range of transition (estimated midpoint).

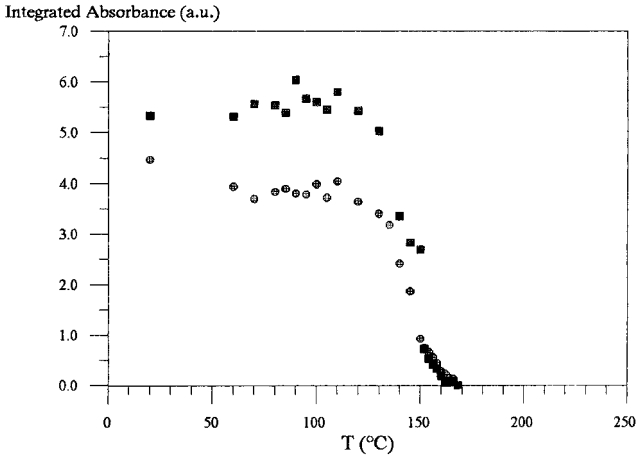

Figure 9. Variation of absorbance of solvent bands in deuterated syndiotactic polystyrene/ethylbenzene as a function of annealing temperature: squares, 736 cm^{-1} peak; circles, 1474 cm^{-1} peak.

expected for various vibrations (see, for example, ref 20), although the complexity of the vibrations precludes an accurate prediction of these frequency shifts. For this reason, it is not possible to unambiguously relate the other helical DsPS peaks to those in HsPS. However, the 948 cm^{-1} zigzag peak in DsPS appears to have the same origin as the 1222 cm^{-1} zigzag peak previously noted for HsPS, the frequency ratio again being close to 1.30. In view of the fact that the frequency of the 788 cm^{-1} band increases at the δ to γ phase transition, while that of the 758 cm^{-1} band decreases, it seems plausible to relate these bands to those at 943 and 934 cm^{-1} in hydrogenous sPS. However, the temperature dependence of their absorbances are clearly different. In addition, the frequency ratios are significantly below 1.30. In the absence of normal mode calculations for the deuterated polymer, a definite assignment cannot yet be made. There is, then, no evidence for a disordering of δ phase helices followed by reformation in the γ phase, as was observed for HsPS. It is possible that stronger polymer/solvent interactions in the DsPS/ethylbenzene system postpone any disordering to higher temperatures, closer to the δ to γ phase transition. At this stage, it is not clear whether the transition mechanisms differ in the two isotopic species. The 948 cm^{-1} peak is evident only in the α phase of DsPS and can thus be related to the zigzag form.

The absorbance of solvent peaks as a function of annealing temperature is shown in Figure 9. Along with the behavior of conformationally sensitive bands noted above, this provides an independent estimate of the δ to γ phase transition temperature. Transition temperatures determined from IR data and from DSC and TGA measurements are listed in Table 1.

Although the different experimental techniques measure different physical properties, the results for HsPS show a close correlation between figures obtained with the different techniques. For DsPS, it should be noted that the γ to α phase transition was not identified from DSC data, principally because of the difficulty in separating melting and recrystallization features. The melting temperature is depressed by 7 °C in DsPS, while the temperature of the γ to α transition is approximately the same. The TGA measurement on DsPS gives a result somewhat out of line with the other data, although the ranges quoted do overlap. The midpoint of the weight loss in TGA shows a dependence on molecular weight, with measurements on sample CD giving a significantly lower transition temperature. It should be noted that TGA and DSC results are both from continuous measurements at the same heating rate. If the TGA result for DsPS is neglected, we conclude that the δ to γ phase transition temperature for DsPS/ethylbenzene is around 24 °C higher than for the complex with the normal polymer.

Isotopic effects in polymer/solvent systems are well-known, as well as in binary isotopic blends of polymers (see, for example, ref 22). Theta temperatures of polystyrene in cyclohexane solutions have long been known to be influenced by isotopic labeling,[23] while the shift in cloud point for the polystyrene/acetone system with solvent labeling has been found to be of the order of 20 °C.[24] Current interpretations view the molar volume isotope effect as arising from the differences in zero point vibrational energy, mainly associated with differing nonbonded intermolecular separations.[25] In view of the findings listed above, it is not entirely surprising that the δ to γ phase transition temperature, being concerned with polymer/solvent interactions, undergoes such a large shift, in the direction shown here, on isotopic substitution.

On the other hand, the γ to α phase transition shows no significant dependence on isotope. The difference of 7 °C in melting temperature is of similar magnitude to, and the same sign as, values previously determined for other polymers. Nevertheless, as we have noted earlier,[18] SANS measurements show the absence of any isotopic fractionation in blends crystallized in the δ form and also after conversion to the γ form. A full analysis of cocrystallization in the DsPS/HsPS/ethylbenzene system could be made under the assumption of equilibrium behavior (see, for example, ref 26), but this assumption is certainly invalid here. We simply note that factors other than the pure isotopic melting temperatures are important.

Conclusions

Making use of the 1069 cm^{-1} IR band as the reference peak for spectral normalization, we have studied the 920−960 cm^{--1} region of the spectrum of δ phase syndiotactic polystyrene/ethylbenzene as a function of heating temperature, for a heating rate of 10 °C min^{-1}.

While peaks at 934 and 943 cm^{-1} provided an adequate fit to experimental data for samples heated to lower temperatures, above 120 °C it was found necessary to include a third band at 940 cm^{-1}. We assign the 943/934 cm^{-1} doublet primarily to the δ phase helical form and the 940 cm^{-1} peak solely to the γ phase helix. The frequencies of the doublet components show related shifts as a function of annealing temperature, adding further support to the assignment as a doublet. The lower temperature observed for the reduction in absorbance of the 934 and 943 cm^{-1} peaks, as compared with the temperature at which the 940 cm^{-1} band appears, is then attributed to a disordering of the δ phase helices prior to reformation as γ phase helices. Whether the 940 cm^{-1} peak is common to γ phase samples prepared from different solvents remains an open question.

Importantly, the assignment of these peaks also provides the potential for time-dependent spectroscopic monitoring of the proportions of the different phases during complexation/decomplexation. Following curve fitting, both frequencies and relative absorbances could be used to characterize such systems.

In deuterated sPS, IR bands characteristic of the helical form have been identified at 722, 758, and 788 cm^{-1} and of the zigzag form at 948 cm^{-1}. The peak at 788 cm^{-1} is insensitive to the phase (δ or γ), while the peaks at 722 and 758 cm^{-1} are more sensitive to the γ phase than to the δ phase. No evidence was found for the loss of helix content prior to the δ to γ phase transition.

Solvent peaks at 736 and 1473 cm^{-1} allowed the decomplexation of DsPS/ethylbenzene to be monitored using IR spectroscopy. Together with the IR data for the helical and zigzag bands and DSC and TGA data, several estimates of the various transition temperatures were obtained for HsPS/ethylbenzene and DsPS/ethylbenzene. Generally, a good correlation was obtained with results from the different techniques. The melting temperature of the α phase was found to be depressed by 7 °C for DsPS, while the γ to α transition temperature was unchanged. Neglecting the surprisingly low figure for the δ to γ transition temperature in DsPS/ethylbenzene as determined by TGA, the transition temperature for DsPS/ethylbenzene was found to be around 24 °C higher than for HsPS/ethylbenzene. This is in line with previous measurements of isotopic effects on the cloud point in polymer/solvent systems.

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