A Spectroscopic Study of Phase-Transition Kinetics in Syndiotactic Polystyrene

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ABSTRACT: The degree and kinetics of a solid–solid phase transition in solution-cast syndiotactic polystyrene films have been measured with infrared spectroscopy. The transformation of crystallites containing a helical chain conformation into those containing an all-trans chain conformation is monitored by measuring the intensity of infrared bands assigned to each phase. The amount of phase transformation above the transition temperature is highly dependent upon sample morphology and therefore their thermal history. Imperfections in films cast from solution cannot be removed by annealing at low temperatures. Extensive phase transformation was observed to occur very rapidly above a critical temperature of 192 °C for cast films annealed at 150 °C. Films annealed at 170 °C display a weak endotherm in differential scanning calorimetric measurements that is associated with the helical to all-trans crystal phase transition, while just above this temperature an exotherm related to the crystallization of amorphous material is found. Increases in the trans content vary linearly with the logarithm of time.

Introduction

Polymers of highly regular configuration and tacticity often display high degrees of crystalline order. Recent reports of syndiotactic polystyrene have shown this material to contain nearly 100% syndiotactic content.[1-4] Depending on the crystallization conditions from melt or solution, polymorphic syndiotactic polystyrene structures exist.[5-15] Samples crystallized from the melt exhibit an all-trans structure, while those cast from dilute solution generally form helices associated with a TTGG chain conformation,[11,13] similar to other syndiotactic polymers such as polypropylene.[16] The helical phase transforms to one containing the all-trans conformation on drawing or on heating to near 190 °C. This transformation is irreversible, unless samples are again exposed to solvent, which will regenerate a helical structure.[6,11-14] The energy barrier to transforming the helical TTGG conformation to the extended trans state has been calculated to be 2–3 kcal/mol from conformational analysis and molecular simulation techniques.[17,18] A melting temperature of 270 °C has been reported for the trans crystalline phase, although with annealing just below the melting point at gradually higher temperatures, a melting point of 285 °C has been observed.[19] Mixtures of the two types of chain conformations can coexist in the same sample. The exact amount of each depends on the thermal history or solvent used.[6,7,12,14]

For syndiotactic polystyrene very little has been reported concerning the morphology, the crystalline kinetics, or the ultimate degree of crystallinity obtained.[20] Such information is essential for a complete understanding of the phase-transition behavior. Electron microscopic studies have shown lamellar structures for annealed films of the trans crystalline phase, while drawn films showed "shish kabob" structures.[9] Very little is known regarding the molecular mechanism responsible for thermally induced phase transformations in syndiotactic polystyrene. This process involves the transition of the helical crystalline phase to the trans and may occur simultaneously with crystallization of amorphous regions to the trans. The fact that the helix to trans transformation is irreversible in bulk material suggests that the helical phase is metastable. In the work reported here, the transformation will be shown to occur over a very narrow range of temperatures. The study of the mechanism responsible for phase transformation in syndiotactic polystyrene is complicated because neither initial nor final states can be characterized easily. It is known that thermal annealing changes the microstructures significantly in that structural defects may be reduced or macroscopic crystalline dimensions altered.

In this study, measurements by infrared spectroscopy of the degree and kinetics of the transformation from the helical to the trans crystalline phase in syndiotactic polystyrene are reported. Infrared spectra of syndiotactic polystyrene contain bands that are assignable to specific conformational sequences. By monitoring the intensity of these bands, the kinetics of the transformation process may be followed. The ultimate goal is to gain an understanding of the mechanism of structural transformation. The structural information obtained complements that provided by electron diffraction studies of larger scale microstructures. Evolution of the trans phase for samples with varying thermal history is reported, and it is found that the kinetics and the extent of phase transformation greatly depend on the annealing history. The exact molecular mechanism is not known and is the subject of current research.

Experimental Section

Polystyrene samples with greater than 98% syndiotactic content (M_n = 125 000, M_w = 660 000) have been obtained from Dow Chemical Co. Films were cast in aluminum pans from a 1.0 wt % solution in toluene and dried under vacuum. Samples were annealed under vacuum at 120, 150, and 170 °C. The absence of solvent in these films was confirmed by the infrared spectrum. Melt-quenched samples were obtained by heating films to 290 °C in a nitrogen atmosphere and quenching into a bath of cyclohexane and liquid nitrogen. The amorphous structure of these films was confirmed by wide-angle X-ray scattering (WAXS) collected with a Siemens D500 diffractometer operating at a 2θ range from 3 to 40°. These X-ray scans appeared identical with those of atactic polystyrene. Infrared spectra were obtained with a Bruker IFS 113v FTIR spectrometer. Samples were heated in a heating cell constructed in our laboratory. In order to obtain spectra rapidly during isothermal measurements, 20–50 scans were collected at a resolution of 2 cm^{-1}. The time interval needed for each measurement can be as short as 15 s. All the spectroscopic

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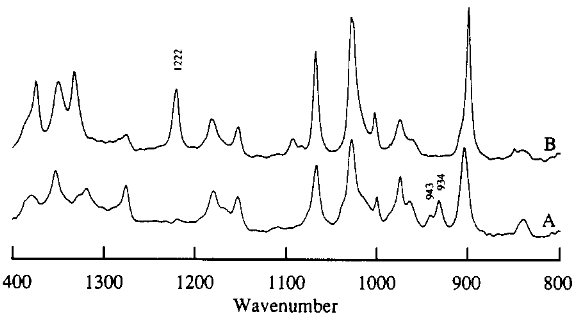

Figure 1. Infrared spectra of syndiotactic polystyrene: (A) cast film; (B) cast film annealed at 290 °C.

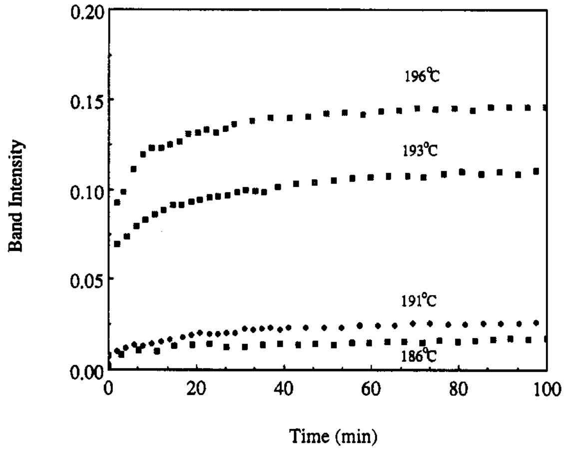

Figure 2. Normalized integrated intensity of the 1222-cm^{-1} band with time at various temperatures for samples annealed at 150 °C.

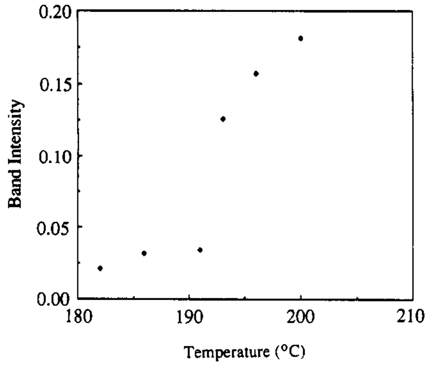

Figure 3. Normalized integrated intensity of the 1222-cm^{-1} band measured at various temperatures for samples annealed at 150 °C.

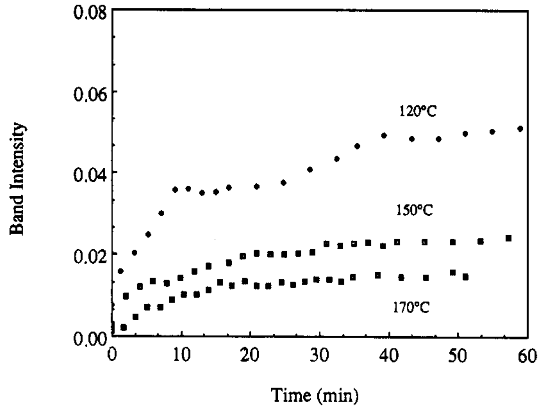

Figure 4. Normalized integrated intensity of the 1222-cm^{-1} band with time at 191 °C for samples annealed at 120, 150, and 170 °C.

data are transferred to PC-based computers to be analyzed using SPECTRAL CALC purchased from Galactic Industries. DSC measurements were made with a Perkin-Elmer DSC-7 calorimeter operating at a scan rate of 20 °C/min.

Results and Discussion

The transition from the helical to the all-trans conformation is followed by monitoring the integrated intensity of the trans infrared active band at 1222 cm^{-1} and of the 943- and 934-cm^{-1} infrared bands assignable to the helical conformation. These features have been identified in previous studies[1,5,8,11,19] and are shown in Figure 1, which displays room temperature spectra of solution-cast films before and after heating above 200 °C. Variations in sample thickness were normalized by measuring the integrated intensities of bands at 1601 and 1585 cm^{-1}. These two bands are assigned to the benzene ring stretching vibrations and are considered to be sufficiently localized, making them insensitive to thermal treatment or chain tacticity. The fact that the 1222-, 934-, and 943-cm^{-1} bands are completely absent in a quenched amorphous sample, which must contain an essentially random distribution of trans and gauche conformations, indicates that these features require the presence of the long conformational sequences found in the all-trans and helical crystalline phases.

The intensity variation of the 1222-cm^{-1} trans band with time at various temperatures is shown in Figure 2 for samples annealed at 150 °C for 1 h. A substantial intensity increase is observed to occur during the first few mintues of heating, followed by a very gradual increase at longer times. The equilibrium band intensity measured at long times for each temperature is shown in Figure 3. This intensity increase occurs simultaneously with a reduction in the intensity of features due to the helical conformation, particularly the 934- and 943-cm^{-1} bands. From Figure 3, it is apparent that the trans content increases significantly at 192 °C. This transition is extremely sharp, which is unusual. Polymers generally exhibit diffuse phase transitions in the solid state. The sharpness of the transition implies that this process involves a high degree of either intra- or intermolecular cooperativity of molecular motion.

The degree and rate of transition is also highly dependent upon the annealing history. The formation of the trans phase at 191 °C for samples annealed at 120, 150, and 170 °C is shown in Figure 4. The increase in trans content is greater for samples annealed at lower temperatures. Lower annealing temperatures generally result in a low degree of crystallinity and small or imperfect crystals. Such structures contain more structural disorder and therefore require less energy for phase transformation than samples annealed at higher temperatures. At an annealing temperature of 170 °C it has been shown previously that a significant increase in the amount and perfection of the helical phase occurs.[10] The critical temperature at which substantial phase transition occurs is then expected to be higher for samples of higher crystallinity.

The volume fraction of the fully trans phase in the samples studied can be estimated by measuring the normalized intensity of the 1222-cm^{-1} band in a sample of known degree of crystallinity. Values for the degree of crystallinity may be determined by measuring the change in the heat capacity at the glass transition. The ratio of this value to that measured for an entirely amorphous sample provides a measure of the amorphous content. This method has been applied to a number of semicrystalline polymers.[21] Syndiotactic polystyrene samples obtained by cooling slowly from the melt contain only the trans crystalline phase. No helical structure was observed in

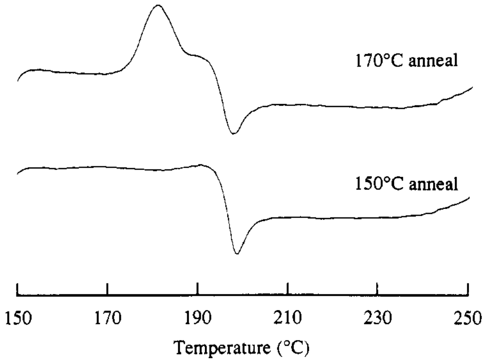

Figure 5. DSC scans of syndiotactic polystyrene samples annealed at 150 and 170 °C.

the infrared spectrum of these samples. Such a sample exhibits a ΔC_p value at T_g of 0.16 J/g °C. For comparison, a melt-quenched amorphous sample shows a value of 0.61 J/g °C. The ratio indicates 74% of the crystallinity for this sample, a value that agrees well with values measured by vapor sorption experiments on samples slowly cooled from the melt.[12] As shown in Figure 3, the trans content estimated by the intensity of the 1222-cm^{-1} band calibrated by ΔC_p values increases approximately 40% between 191 and 193 °C.

This phase transition may also be observed by calorimetry.[6,7,11-13] DSC scans from 150 to 250 °C for samples annealed at 150 and 170 °C are shown in Figure 5. For samples annealed at 170 °C, an endothermic peak with an onset at 174 °C is observed. This is associated with the helical-trans crystalline phase transition. At 195 °C the onset of an exotherm appears that is associated with the crystallization of amorphous material into the trans crystalline phase. The sample annealed at 150 °C does not show the lower temperature endotherm, as it contains very little helical crystalline phase. For samples annealed at 180 °C, the endotherm is more intense and appears at a higher temperature overlapping the crystallization exotherm. The endotherm observed for the sample annealed at 170 °C is quite small, only 4.1 J/g. Thus the two processes that produce the increase in the all-trans phase may be separated by different thermal treatments.

Solid-solid phase transformation from a helix to an all-trans chain conformation occurs very rapidly, particularly at high temperatures. At 186 °C, 62% of the reduction in the intensity of the bands that characterize the helical phase occurs in the first 2 min. The more gradual increase in the trans conformation is dominated by crystallization of amorphous chains and increases in crystal perfection upon annealing. The crystallization kinetics of polymers is often described by the Avrami equation, in which the degree of crystallinity with time $X(t)$ is given by

$$X(t) = 1 - \exp(-Kt^n) \qquad (1)$$

where n is associated with the geometry of the growth process. However the later stages of the crystallization of amorphous material and the perfection of polymer crystals, termed secondary crystallization, have often been described by a logarithmic time dependence.[22-26] Gradual increases in the density and lamellar thickness of polyethylene at very long annealing times have been observed with nonintegral Avrami coefficients, which decreased below 1.0 near the final stages of crystallization.[22,23] Such values are not physically meaningful in the sense of a dimensionality of growth. In this case, a logarithmic time describing increases in the crystal fold length and density was observed over several decades. The overall growth rate is greater for higher crystallization temperatures.

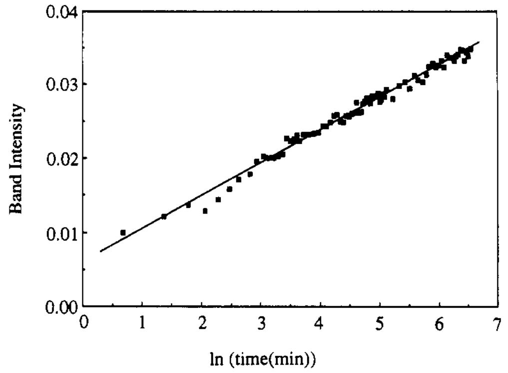

Figure 6. Intensity of the 1222-cm^{-1} band with logarithmic time at 191 °C.

In this study, transition kinetics measured at 186 and 191 °C yielded Avrami coefficients of 0.48 and 0.58, respectively. If the intensity data are plotted versus logarithmic time, as shown in Figure 6, a linear relationship is seen, with a correlation coefficient of 0.994. Thus the majority of the helix-trans phase transition occurs rapidly during the first few minutes and gradual increases in the trans content with time are due primarily to crystallization of the remaining amorphous material and increases in crystalline perfection.

The structures present in the samples used in this study are not known. Undoubtedly the phase-transition mechanism is also complicated by the presence of other polymorphs. However, the infrared data demonstrate the rapid conversion of the helical to the trans phase, with a significant increase in the trans content above a critical temperature of 192 °C. Further increases in trans content involve primarily further crystallization of amorphous material and perfection of crystals. Previous studies have shown crystallization in completely amorphous syndiotactic polystyrene samples to occur at 140 °C.[7,11-13] In the work reported here, the spectroscopic data obtained clearly demonstrate that crystallization of amorphous material occurs just above the phase-transition temperature, although the exact mechanism for the crystallization behavior has not been characterized.

Conclusions

In this study, the solid-solid phase transition in syndiotactic polystyrene has been characterized by infrared spectroscopy. Bands sensitive to specific conformations have been monitored in order to observe the kinetics of the transition from the helical crystalline phase to the all-trans phase at various temperatures and annealing histories. The transition is observed to occur very rapidly. For samples annealed at 150 °C, a sharp increase in the rate of transition occurs above a critical temperature of 192 °C, and approximately 60% of the transformation occurs within 2 min. The rate of structural transformation is highly dependent on the annealing temperature. Samples annealed at lower temperatures show rapid transition, which suggests that a more disordered, less stable structure requires less energy for phase change. By measurement of the infrared band intensity of a sample of known crystallinity (74%), equilibrium intensity data at different temperatures may be converted to the trans crystalline phase content, showing a sharp increase of 40% between 191 and 193 °C.

The phase transition has also been observed by DSC. Annealing at 170 °C prior to DSC scans allows the observation of a weak endotherm associated with the helical to trans crystalline phase transition. Just above this temperature an exotherm is seen, indicative of crystallization of amorphous material. The extension of crystalline chains at the phase transition may allow greater conformational freedom to constrained amorphous chains just above the phase-transition temperature, allowing crystallization to occur. Through monitoring of the isothermal kinetics, the removal of the helical phase is found to occur primarily within the first few minutes of heating at 186 °C. The increase in trans content occurs more gradually and is observed to vary linearly with the natural logarithm of time. Such behavior may be attributed to crystallization of the remaining amorphous material and increases in crystalline perfection.

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