Structural Evolution Process in Solvent-Induced Crystallization Phenomenon of Syndiotactic Polystyrene

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Summary: Structural change has been traced in the solvent-induced crystallization phenomenon of syndiotactic polystyrene through the time-resolved measurements of infrared and Raman spectra and X-ray diffraction. Immediately after the solvent is supplied to the glassy sample, the random coils start a micro-Brownian motion and locally change to short regular helical segments after some induction time. These segments grow longer and gather together to form the crystal lattice. This crystallization occurs even at room temperature far below the original glass transition temperature (Tg = ca. 100°C), because Tg is shifted to ca. -90°C (in the case of chloroform) due to the plasticizing effect, as revealed by the temperature-dependent infrared spectral measurement and the molecular dynamics calculation. The thus-created sPS-solvent complex was found to show a fast and reversible solvent exchange phenomenon between the originally-existing solvent (toluene, for example) and the newly-supplied different type of solvent (chloroform, for example). The time-dependent measurement of wide-angle and small-angle X-ray scatterings using a synchrotron radiation source revealed that the solvent exchange occurs with keeping both the columnar structure of the crystal and the stacked lamellar structure, and that the solvent exchange rate is in the order of chloroform > benzene > toluene, reflecting the difference in diffusion rate of solvent molecules and polymer-solvent interaction.

Keywords: crystallization; infrared spectra; solvent exchange phenomenon; synchrotron X-ray scattering; syndiotactic polystyrene

Introduction

syndiotactic Polystyrene (sPS) is known to form a complex (δ form) with such solvent molecules as toluene, chloroform etc. when the glassy sample is exposed to a solvent atmosphere at room temperature. The molecular chains take a regular helical conformation of TTGG type (T: trans and G: gauche). These helical chains are surrounded by solvent molecules to form a columnar structure as shown in Figure 1.[1] This columnar

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structure is unique in a point that the originally-existing solvent molecules can be exchanged easily with newly-supplied different type of solvent molecules.[2] In order to clarify the formation mechanism of sPS-solvent complex and the fast solvent exchange phenomenon of the complex, the time-resolved measurements of infrared and Raman spectra and wide-angle and small-angle X-ray scatterings were made in these processes. The quantitative analysis of these experimental data in combination with the computer simulation allowed us to make a concrete imagination about the structural changes occurring in these phenomena as functions of time.[2-7]

Structural Evolution in Solvent-induced Crystallization Process

The glassy sample was set into a cell, into which the solvent vapor was supplied at a predetermined constant temperature. Figure 2 shows the infrared spectral changes observed at 20 and 9°C for the case of toluene as a solvent. The absorbances of infrared bands characteristic of helical conformation are plotted against time as shown in Figure 3, where the amorphous band is also plotted for comparison. As reported already the infrared (and Raman) bands can be distinguished depending on the sensitivity to the regular helical segmental length or the so-called critical sequence length (m).[3, 4] In Figure 3 the band at 549 cm^{-1} has an m value of 7 – 12 monomeric units and it was detected for the first time around 6 min after the solvent supply. This means a start of formation of short helical segments consisting of 7 – 12 monomeric units or 2 – 3 helical turns. The band at

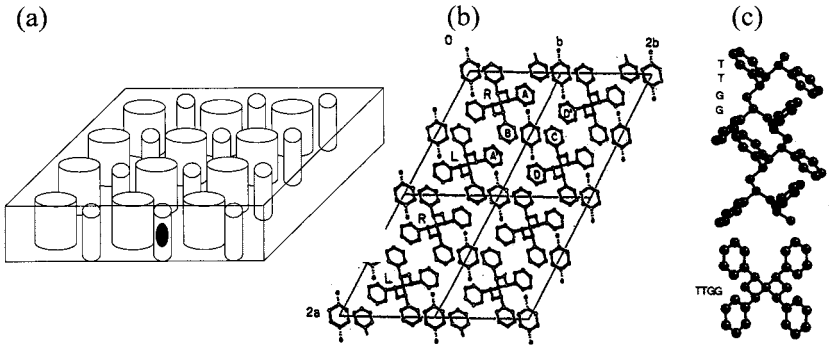

Figure 1. (a) An illustration of sPS-solvent complex crystal. Large cylinders indicate the sPS helical chains shown in (b)[1] and (c). Thin cylinders indicate the columns of solvent.

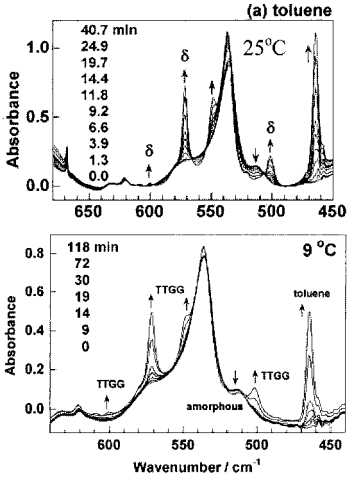

Figure 2. Time dependence of infrared spectra of sPS glass observed in the course of supplying toluene vapor at 25 and 9°C[7].

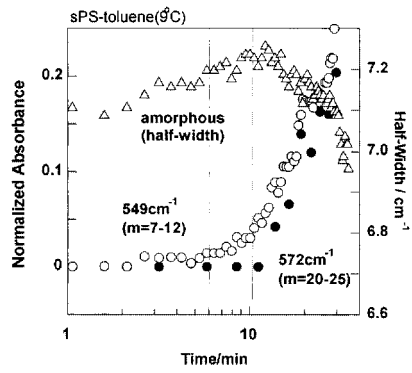

Figure 3. Time dependence of the infrared absorbances estimated for two bands with longer and shorter critical sequence length m and the half width of the amorphous band[7].

572 cm^{-1} corresponding to longer helical length (m = 20 – 25 monomeric units or 5-6 helical turns) was observed later. The difference in time to detect these two bands indicates a growth of short helical segment during this time lag. At the same time it is noticed that the half width of the amorphous band increased rapidly after the supply of solvent. Since the band width is inversely related to the molecular mobility as reported in the previous paper,[4] this increase reflects an activation of molecular motion in the amorphous region. Therefore, the data given in Figure 3 tells us the following structural regularization process as illustrated in Figure 4[7]. (The essentially same picture was presented in a previous paper based on the experimental data at room temperature,[4] but the data taken at 9°C are useful for detecting the structural evolution process more clearly because the

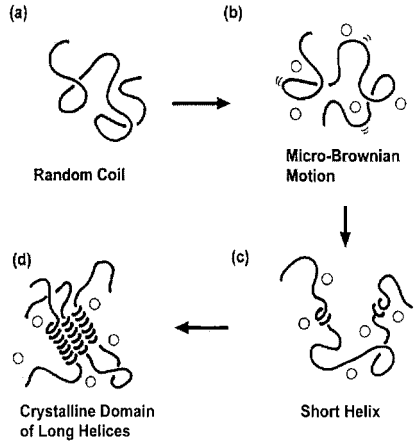

Figure 4. Structural evolution of sPS random coils in the solvent-induced crystallization process [4].

change proceeds more slowly.) (i) Immediately after the supply of solvent, the micro-Brownian motion in the amorphous region is enhanced as known from the increment of half width of the amorphous band. (ii) As a result, the short but regular helical segments are generated and they grow gradually to longer helices. (iii) These helical segments gather together to form a crystalline lattice, as revealed by the X-ray diffraction data[3, 4]. (iv) The measurement of small-angle X-ray scattering revealed the formation of higher order structure with a long period of ca. 100 Å. That is to say, the crystalline domains shown in Figure 4 (d) are stacked along the chain axis with a period of ca. 100 Å.

As seen in Figure 2, a growing rate of crystalline infrared bands decreases remarkably as the crystallization temperature is lower, and the finally-attained crystallinity is relatively low. The time dependence of infrared absorbance was analyzed on the basis of Avrami equation (Absorbance $D = D_0 * \exp[-k(t - t_0)^n]$, where k is a rate constant, t_0 is an induction period and n is an index of crystallization). The rate constant k was plotted against temperature. An extrapolation to $k = 0$ gives the temperature below which solvent-induced crystallization does not occur anymore, or the apparent Tg under an existence of solvent. Similar analysis was made also for the crystallinity *vs* temperature curve. The thus-estimated Tg was -90 ± 10 °C for chloroform, -70 ± 10°C for benzene, and -30 ± 10°C for toluene[6, 7]. In this way the plasticizing effect is remarkable and the Tg is shifted by 130 – 190°C depending on the type of solvent. It is understood why the glassy sPS sample with originally high Tg can be crystallized even at room temperature when the solvent is supplied to the system. This plasticizing effect could be simulated reasonably by performing the molecular dynamics calculation for the model consisting of sPS amorphous chains and solvent molecules at some molar ratios. As shown in Figure 5, a deflection point of the volume or Tg is shifted to lower temperature side depending on the sPS/solvent ratio, where toluene is used as solvent, although the absolute Tg value is rather higher than the observed ones[6, 7].

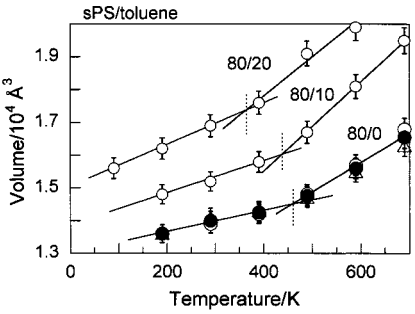

Figure 5. Temperature dependence of volume of sPS/toluene system calculated by molecular dynamics method for the various sPS/toluene molar ratio [7].

Solvent Exchange Phenomena

The thus created sPS-solvent complex was found to show such a characteristic behavior that the solvent molecules originally contained in the complex are easily exchanged with the newly-supplied different type of solvent. In the previous paper [2] we measured the time-dependence of infrared spectra in the course of solvent exchange process between a pair of solvents (chloroform, benzene, and toluene). Recently we have performed the time-resolved measurements of small-angle (SAXS) and wide-angle X-ray scatterings (WAXS) using synchrotron radiation systems (Photon Factory of KEK and Spring-8) for both the uniaxially-oriented and unoriented samples. The as-drawn sample showed the X-ray fiber pattern of planar-zigzag chain conformation and no long period was observed along the draw axis (Figure 6). When this sample was exposed to toluene atmosphere, it changed to the δ form and showed clear meridional SAXS peaks corresponding to the long period of ca. 100 Å. Figure 7 (a) shows the time dependence of meridional SAXS profile measured for the oriented sPS-toluene complex. When chloroform was supplied to this sample, the SAXS peak decreased in intensity due to the X-ray absorption effect by chlorine atoms, during which the WAXS pattern changed correspondingly with keeping the orientation of crystallites unchanged. On supplying benzene to this chloroform-containing sample, the exchange from chloroform to benzene occurred and the SAXS peak increased the intensity

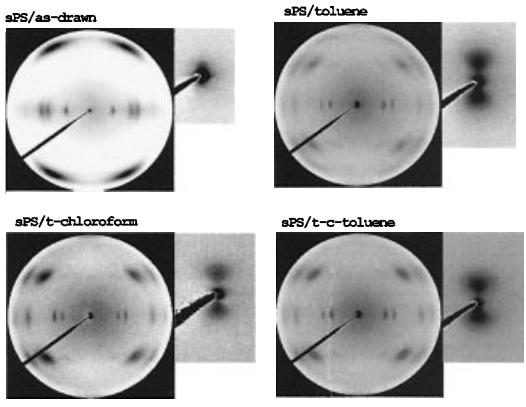

Figure 6. WAXS and SAXS patterns of uniaxially oriented sPS samples. (a) as-drawn sample, (b) exposing (a) into toluene, (c) the sample (b) exposed in chloroform, and (d) the sample exposed again in toluene.

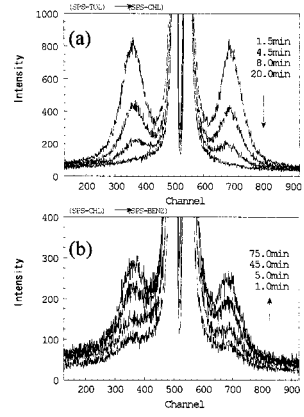

Figure 7. Time dependence of SAXS profile of sPS-solvent complex measured during the solvent exchange process from (a) toluene to chloroform and (b) chloroform to benzene.

again [Figure 7 (b)]. Figure 8 shows the SAXS intensity change during these phenomena observed for an unoriented sample. The solvent-induced crystallization occurred at low rate. But, once the complex was formed, the solvent exchange occurred at higher rate. Among the three solvent exchange processes, the exchange was found to occur in the order of chloroform > benzene > toluene. (In the previous paper[2] we described the infrared spectral data and suggested almost the same solvent exchange rate between the three cases. However, this suggestion must be corrected, and the exchange rate should be different as indicated in Figure 8. In the present experiment of WAXS and SAXS measurements, a thicker sample was used and the crystallization and solvent-exchange phenomena could be traced at longer time scale, giving more confirmative result than the faster infrared experiment using a thinner film.) The order of solvent exchange rate is almost parallel to that of the crystallization rate. The solvent-induced crystallization rate is affected by the solubility of sPS in a solvent and the diffusion rate of solvent molecules in the amorphous phase. Chloroform molecule is small in size and dissolves the sPS more easily than benzene or toluene. Such solvent effect is considered to govern also the solvent exchange rate.

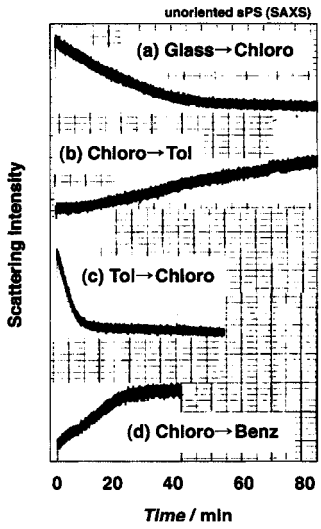

Figure 8. Time-dependence of SAXS intensity measured in crystallization and solvent-exchange processes of an unoriented sPS sample.

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