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Formation of Regular Conformational Sequences in the Gels of Atactic Polystyrenes with Various Stereoregularities

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Introduction. Various types of morphological structures have been proposed as the cross-linking points of gels. Generally, it has been assumed that the gelation of crystalline polymers is accompanied by the formation of microcrystallites. In a series of papers, Kobayashi et al. have investigated the structure and formation mechanism of the gels of syndiotactic and isotactic polystyrenes (abbreviated as sPS and iPS, respectively) by combining infrared spectroscopy with small-angle neutron scattering.[1−6] In these cases, conformational ordering was observed during gelation. However, in contrast with crystalline polymers, gel formation from a noncrystalline polymer involves more complex problems because of the lack of a long stereoregular monomeric sequence along the chain. Wellinghoff et al. reported that noncrystalline atactic polystyrene (aPS) could produce a thermoreversible gel in various solvents.[7] Since then, many investigations of the molecular structure of the aPS gel were carried out by thermal analysis,[8,9] neutron scattering,[10−14] etc.[15−21] Recently, infrared spectroscopy revealed that the gelation of the aPS/CS_2 system was accompanied by a local conformational ordering even in the configurationally irregular atactic chain.[3]

In this study, we will deal with the gelation of aPS samples obtained by epimerization of iPS, i.e., aPS samples with various degrees of configurational regularity. By utilizing these samples, we have been able to study the gelation phenomenon of aPS with a wide range of stereoregularity from a highly isotactic to a highly syndiotactic sequence.

Experimental Section. Samples. A commercial sample of aPS was purchased from Sekisui Chemical Co. Ltd. (Styron 666-7). The racemic diad content (P_r) was estimated to be 0.65 by ^{13}C NMR. Noncrystalline polystyrenes with different tacticity were prepared by epimerization reaction of iPS. The iPS was dissolved in hexamethyl phosphoramide containing potassium *tert*-butoxide. The reaction was conducted by heating this iPS solution at 100 °C.[22,23] The stereoregularity was varied by changing the reaction time. The epimerized samples are referred as ePSn, *n* being the reaction time in hours. The stereoregularity was estimated by ^1H NMR as listed in Table 1.[23] The gels of these samples were prepared by cooling a CS_2 solution (20 wt %) below −50 °C.

Table 1. Stereoregularity of EPS's and Styron 666-7[a]

	P_{mm}	P_m	n_m
ePS1.5	0.80	0.87	11.1
ePS6	0.69	0.80	8.1
ePS10	0.36	0.57	2.9
ePS24	0.14	0.40	1.7
Styron 666-7	0.06	0.35	

[a] P_{mm} and P_m: Probability of meso triad and diad, respectively. n_m: Average length of the isotactic sequence.[23]

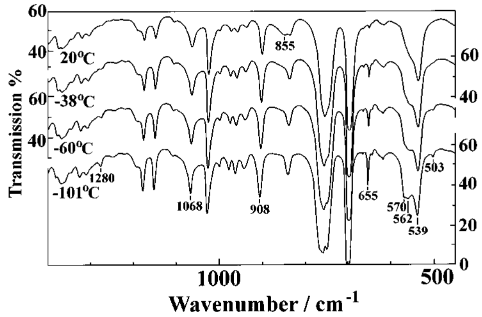

Figure 1. Temperature dependence of the infrared spectra measured in the gelation process of the Styron 666-7/CS_2 system. The bands at 655 and 855 cm^{-1} are due to CS_2.

Measurements. Infrared spectra were measured at 1 cm^{-1} resolution by using a JASCO FT-IR 8000 spectrometer equipped with a DTGS detector. A homemade solution cell was used for the infrared measurement, where a lead spacer of 100 μm thickness was inserted between a pair of KBr windows. For the infrared measurements at low temperature, an Oxford flow-type cryostat was used. ^1H NMR spectra were observed at 400 MHz using a JEOL GSX 400 spectrometer, on a 1,1,2,2-tetrachloroethane-d_2 solution (5 w/w%) at 120 °C.

Results and Discussion. Gel Structure of aPS. In Figure 1, the gelation process of the Styron 666-7/CS_2 system was followed by infrared spectroscopy. The spectral profile at 20 °C corresponds to the noncrystalline state, as found by comparison with the spectrum of the amorphous solid film of Styron 666-7. With decreasing temperature, no change was observed for most of the bands. However, the absorption profile in the 500−600 cm^{-1} region was found to change drastically. The bands in this region are ascribed to the out-of-plane modes of phenyl ring, which are strongly dependent on the local skeletal conformation.[1] This region is very complicated by superposition of several absorption bands, but can be reproduced by summing up the band profiles of sPS and iPS. As reported in a previous paper,[3] the increment in intensity of 572 cm^{-1} band suggests that the gelation is promoted by the formation of a trans−trans−gauche−gauche (ttgg) conformation as part of a short syndiotactic sequence. As the conformational order cannot be observed in the bulk solid-state sample, the solvent is considered to play a significant role in stabilizing the regular conformation.

Kobayashi et al. demonstrated that a particular vibrational mode has its characteristic value of the critical sequence length (m) which is necessary for the corresponding band to be detected in the vibrational spectrum as a conformationally sensitive band.[24] The bands observed in the frequency region of 500−600 cm^{-1}

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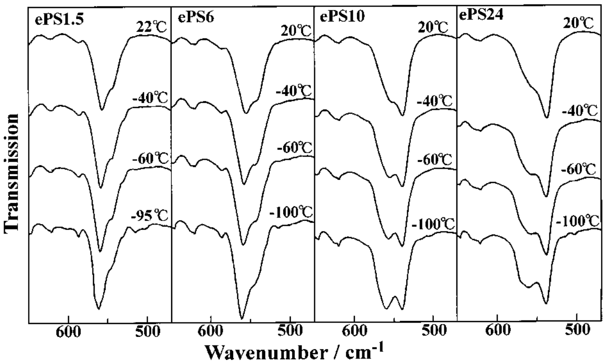

Figure 2. Temperature dependence of the infrared spectra measured for the ePS1.5, ePS6, ePS10, and ePS24/CS$_2$ systems in the frequency region 500−600 cm^{-1}.

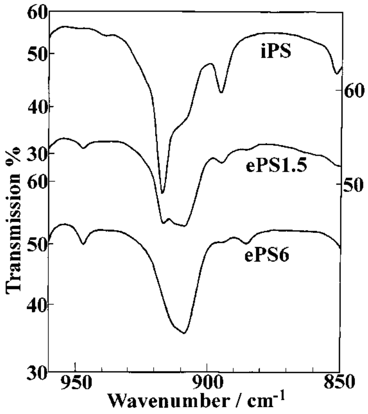

Figure 3. Infrared spectra of the iPS, ePS1.5, and ePS6/CS$_2$ gels measured around −100 °C.

correspond to $m = 6-8$.[25] Therefore, from Figure 1, we may say that the stereoregular sequence length in Styron 666-7/CS$_2$ gel is shorter than eight monomeric units. In other words, two repeating units of a ttgg helical sequence are formed in the gel.

Stereoregularity and Gel Structure. The contents of syndiotactic sequence for Styron 666-7 is as high as $P_r = 0.65$. To clarify the effect of stereoregularity on the gel structure, a series of samples epimerized from iPS were used. Infrared spectra of ePS/CS$_2$ system were measured with decreasing temperature. Since no long stereoregular sequence exists in the ePS samples, the bands characteristic of the gel behave similarly with the case of Styron 666-7. Figure 2 shows the infrared spectral changes in the gelation process of the four types of ePS samples with different stereoregularity (500−600 cm^{-1} region). In the case of isotactic-rich sample such as ePS1.5, the bands at 566 and 582 cm^{-1}, characteristic of the tg sequence of iPS, increase in intensity with decreasing temperature. For the sample with the longer syndiotactic sequence, the 572 cm^{-1} band characteristic of the ttgg sequence of sPS increases in intensity. This indicates that the stable conformation found in the ePS gels closely relates to the stereoregularity of the local monomer sequence. Figure 3 shows the infrared spectra of iPS, ePS1.5, and ePS6 gels observed around −100 °C. The band intensities at 917 and 894 cm^{-1} are very strong in the iPS gel compared with those of the ePS1.5 and ePS6 gels. As reported in ref 24, these bands have a critical sequence lengths of $m = 10$ and $m = 16$, respectively. The observation of these bands in the infrared spectrum of the ePS1.5 gel indicates the presence of sequences with a regular conformation longer than 10−16 monomeric units consistent with the average length of isotactic sequence $n_m = 11.1$ as seen in Table 1. In ePS6 gel, no remarkable increase was observed in the intensity of these bands, because the regular sequence was shorter ($n_m = 8.1$) than the critical sequence lengths of these bands. However, it is sufficiently long for generating the vibrational mode in the 500−600 cm^{-1} region, as shown in Figure 2.

In conclusion, we find that the physical gel of aPS with various stereoregularity exhibits locally ordered conformations at the points of stereoregular sequences. Since such regular conformational sequences are not detected in the bulk solid-state of aPS, the solvent may play an important role to produce the conformationally regular segments in the gel.

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