Gel-Specific Infrared Bands for Isotactic Polystyrene Investigated by Isotope Dilution Using Partially Deuterated Samples

Takahiko Nakaoki,*,† Chikage Katagiri,† and Masamichi Kobayashi‡

Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Otsu, Shiga 520-2194, Japan, and Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received March 25, 2002

ABSTRACT: The stable conformation and the sequential order of isotactic polystyrene (iPS) gel have been investigated by solid-state high-resolution ^{13}C NMR and infrared spectroscopies. The methylene resonance line in the solid-state high-resolution ^{13}C NMR spectrum is very sensitive to the conformation. The same chemical shift observed for both the gel and crystalline form demonstrates the molecular conformation formed in the gel takes a 3/1 helix. The process of conformational ordering during the gelation process of the iPS/CS_2 system has been followed by infrared spectra. In addition to the bands characteristic for a 3/1 helix, the gel-specific bands were observed. The 983 cm^{-1} band is a typical crystallization-sensitive band due to the ring out-of-plane mode with no relation to the main chain mode. This band increased in intensity for the crystalline form, but not for the gel. From the isotope dilution analysis using partially deuterated iPS, this band does not come from either inter- or intramolecular interaction but the disorder of the C(skeletal)−C(ring) axis. This suggests that the solvent molecules are incorporated between polymer chains. The temperature dependence of the absorption intensity has been quantitatively interpreted by a simple statistical model. The trans−gauche regular sequence formed in the iPS/CS_2 gel was estimated to be longer than five turns of the 3/1 helix.

Introduction

Isotactic polystyrene (iPS) is a representative stereoregular polymer, and many studies have been carried out on the molecular structure of the crystalline form, noncrystalline form, and gel, since a highly stereoregular iPS was synthesized by Natta et al.[1] It has been established that the crystalline form takes a 3/1 helical structure consisting of a regular repetition of trans (t) and gauche (g) conformations of the skeletal C−C bond.[2,3] In addition to the investigation of crystallization, gelation is a current topic of study from the viewpoint of molecular structure and morphology. During the recent decade, the gelation of iPS has been given a great deal of attention as a suitable system for studying the molecular mechanism of the formation of a physical gel. Keller et al. reported that the X-ray diffraction pattern taken on partially dried and stretched iPS/decalin gel was different from that of the well-known crystalline phase called the α-form.[4−8] The existence of meridian reflection at the spacing of 0.51 nm suggested the presence of a skeletal conformation having a nearly extended 12/1 helix. Thereafter, Sundaarajan et al. suggested that the crystalline state formed in the gel is solvated.[9−11] A series of neutron diffraction experiments of nascent iPS/decalin gel were carried out for various combinations of deuterated (D) and hydrogeneous (H) species of the polymer and the solvent by Guenet et al.[12−17] They showed that the 0.51 nm reflection is directly concerned with the decalin molecule and proposed a ladder-like model consisting of 3/1 helix that forms a nematic liquid crystal mediated by solvent molecules between polymer chains. After that they revised it to a modified ladder-like model, in which the solvent is intercalated between the phenyl groups to promote the formation of helices.[17] The fluorescence experiments were carried out to elucidate the roll of solvent molecules by Itagaki et al. They showed that the decalin molecules are incorporated into a polymer−solvent compound and the mobility is limited.[18−20]

Infrared spectroscopy is a powerful tool for investigating not only the molecular structure but also the conformational order. Kobayashi et al. revealed that the vibrational mode depends on the conformational order by the analysis of the iPS/carbon disulfide (CS_2) system.[21−24] This analytical method was applied for the gelation of noncrystalline atactic polystyrene (aPS). We revealed that the conformational order takes place at a local stereoregular sequence.[24−26]

In this study, the molecular structure formed in the iPS gel was investigated by means of solid-state high-resolution ^{13}C NMR and infrared spectroscopies. Partially deuterated iPS samples as well as normal hydrated iPS were used for isotope dilution analysis to elucidate the interaction between polymer chains.

Experimental Section

Samples. Polymerization of iPS was carried out with a $TiCl_3$–$Al(C_2H_5)_3$ Ziegler−Natta catalyst in *n*-heptane at 70 °C. The polymer obtained was washed with methanol and then heated in boiling water. The atactic component was extracted with boiling methyl ethyl ketone. The sample was dissolved in hot toluene, and after cooling, the solution was separated from gelatinous precipitate by centrifugation. The polymer was reprecipitated with methanol, and then dried. The diad isotacticity of the iPS sample was evaluated to be over 96% by ^{13}C NMR. Partially deuterated styrene monomers were prepared following the procedure by Kobayashi et al.,[21] and then three different deuterated samples were polymerized, isotactic poly(2-monodeuteriostyrene) with $(CH_2CD(C_6H_5))_n$, poly(1,1-dideuteriostyrene) with $(CD_2CH(C_6H_5))_n$, and poly(phenylpentadeuteriostyrene) with $(CH_2CH(C_6D_5))_n$. In this paper, these samples are abbreviated as iPS-*2-d*$_1$, iPS-1,1-*d*$_2$, and iPS-*r-d*$_5$, respectively. We also synthesized the copolymer

---

* To whom correspondence should be addressed.

† Ryukoku University.

‡ Osaka University.

10.1021/ma020474d CCC: $22.00

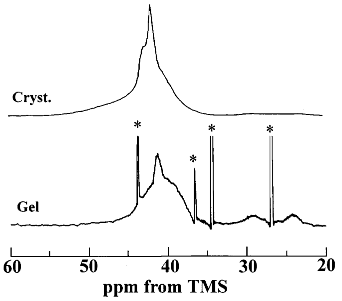

Figure 1. CP/MAS ^{13}C NMR spectra of α-iPS and iPS/decalin gel. Asterisks denote the resonance lines due to decalin.

between styrene and these partially deuterated styrene monomers.

Preparation of the Gel. The iPS/decalin gel was prepared by quenching at 0 °C from a homogeneous solution at 150 °C. This gel was stable at room temperature, so the measurements were carried out at ambient temperature. The iPS/CS_2 gel was prepared by cooling the solution below −50 °C. The polymer concentration of these gels was 20 wt %.

Measurements. Solid-state high-resolution ^{13}C NMR spectra were measured with a Bruker MSL 200 spectrometer, operating at 50 MHz. The ^{13}C chemical shifts were obtained with respect to the signal of tetramethylsilane (TMS). The magic angle spinning of 3 kHz was achieved by the double-bearing system. The measurements were carried out at room temperature. Infrared spectra with 1 cm^{-1} resolution were measured by using a JASCO FT-IR 8000 spectrometer equipped with a DTGS detector. Spectra were accumulated 50 times. A homemade solution cell with a lead spacer of 100 μm thickness inserted between two KBr windows was used. For measurements below room temperature, an Oxford flow-type cryostat was used.

Results and Discussion

Molecular Structure of iPS Formed in the Gel. To make clear the molecular structure formed in the gel, the CP/MAS ^{13}C NMR spectrum was measured for the iPS/decalin gel. Figure 1 shows the methine and methylene resonances, which locate at 41.3 and 42.2 ppm, respectively. Compared with the crystal with regular a t−g sequence, the spectral profile of the gel is very broad, indicating the low crystallinity. It is well-known that the chemical shift of the methylene signal is very sensitive to conformational change due to the γ-gauche effect, which is described by a 5 ppm upfield shift when the methylene group takes a gauche conformation. Although the signals are very broad and overlap those of the noncrystalline component, the chemical shifts for both signals stayed at the same position. There are no signals around 47 ppm due to the planar zigzag conformation. This result indicates that the molecular conformation formed in the gel takes a 3/1 helix, being the same as α-iPS. Decalin has lots of vibrational modes, so it is not suitable for the measurement of the gelation process by infrared spectroscopy. CS_2 is known as another gelation solvent for iPS, but is often difficult to deal with because it is extremely volatile and toxic solvent. However, a simple molecular structure is very convenient for infrared spectral measurement, so CS_2 was chosen as a gelation solvent in this investigation. Figure 2 shows the infrared spectra depending on temperature for the iPS/CS_2 system. This chart exhibits a dramatic thermoreversible change on cooling. The conformation-sensitive bands due to the regular t−g conformation gradually increased with decreasing temperature. This indicates that the gelation accompanies the ordering in the molecular conformation. These characteristic bands for the gel are very close to those for the bulk-crystallized iPS in frequency and relative intensity as well as in shape. Comparing the spectra of α-iPS and the iPS/CS_2 gel, there are some remarkable differences. On the basis of the spectral features, the bands observed in the gel are classified into the following three types: (1) gel-specific bands which disappear in crystalline iPS (1070, 1062, 854, 517, and 503 cm^{-1}), (2) bands providing intensity differing from that of crystalline iPS (1198, 1188, and 983 cm^{-1}), (3) bands shifted from those of the 3/1 helix crystal (917 and 892 cm^{-1}). All these bands are associated with the vibrations due to the phenyl group. The origin of these bands will be discussed in what follows.

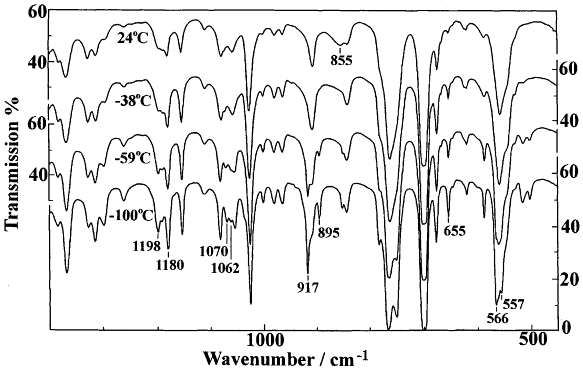

Figure 2. Temperature dependence of the infrared spectra of an iPS/CS_2 solution (20 wt %).

Origin of the Crystallization-Sensitive 983 cm^{-1} Band. The 983 cm^{-1} band is assumed to be a ring C−H out-of-plane mode with no relation to the vibrational mode of the main chain.[27,28] In the crystalline phase, this band is adopted as a crystallization-sensitive band with an intensity increment in proportion to the degree of crystallinity. However, the intensity of this band did not increase through the gelation process but remained at a level as low as in the glassy state. In general, as for the origin of the crystallization-sensitive mode, two different types of inter- and intramolecular interactions are predicted. The intermolecular interaction originates from a specific spatial arrangement of the molecules in the crystalline lattice. In this case, the arrangement of the phenyl ring plays an important role. For the case of intramolecular interaction, the peak intensity would be concerned with a specific conformation of the phenyl ring with respect to the skeletal chain.

To investigate the origin of the crystallization-sensitive character of the 983 cm^{-1} band, the intensity of the band for the isotactic copolymer of styrene and ring-deuterated styrene and the blend of iPS and iPS-*r*-d_5 was investigated. Figure 3 shows the infrared spectra of the blend with 51.2 mol % iPS and the copolymer with 52.1 mol % styrene monomer. As shown in Figure 4, the 983 cm^{-1} band can be assigned to the undeuterated styrene, since there are no peaks around 983 cm^{-1} for the iPS-*r*-d_5 homopolymer. Therefore, this band can be considered as the characteristic band for iPS. For both the copolymer and blend in Figure 3 the 983 cm^{-1} band increased in intensity for the crystalline state compared with the noncrystalline state. For the blend sample, about 50 mol % iPS-*r*-d_5 is high enough for iPS to disappear in the intermolecular interaction. However, the peak intensity was unaltered with the iPS homopolymer. Similarly, the copolymer with ring-deuterated styrene of 50 mol % would make the intramolecular

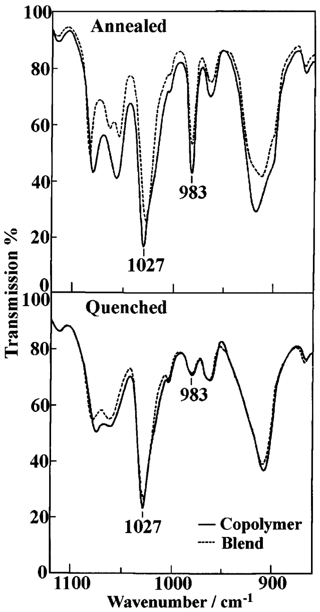

Figure 3. Infared spectra of an isotactic styrene/styrene-*r*-d_5 copolymer (styrene, 51.2 mol %) (—) and an iPS/iPS-*r*-d_5 blend (styrene, 51.2 mol %) (---) in highly crystalline (upper) and glassy (lower) states. On crystallization, the 983 cm^{-1} band gains intensity in both the copolymers and the blend, as in the iPS homopolymer.

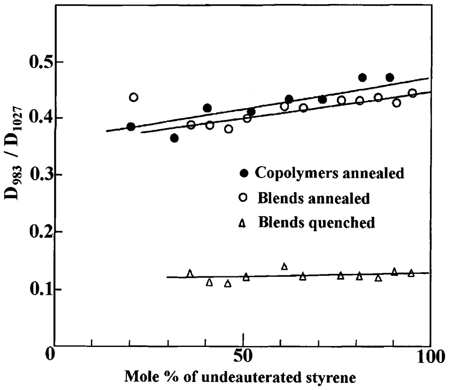

Figure 4. Infrared spectra of iPS (—) and iPS-*r*-d_5 (---) homopolymers in the highly crystalline state.

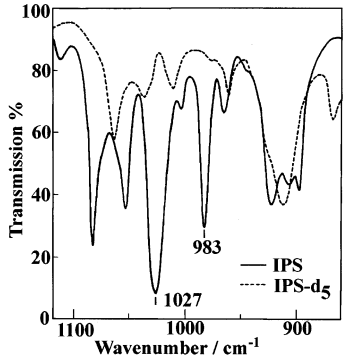

Figure 5. Reduced absorbance of the 983 cm^{-1} band in isotactic styrene/styrene-*r*-d_5 copolymers and an iPS/iPS-*r*-d_5 blend depending on isotope composition.

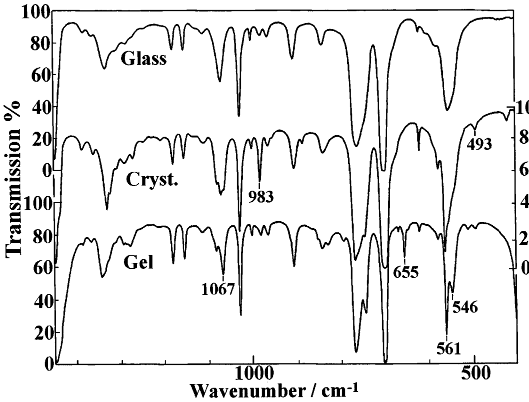

Figure 6. Infrared spectra of noncrystalline, crystalline, and gel CS_2 (measured at −100 °C) for iPS-*2*-d_1.

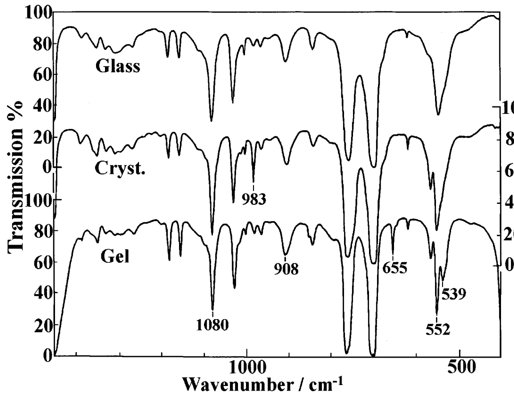

Figure 7. Infrared spectra of noncrystalline, crystalline, and gel CS_2 (measured at −100 °C) for iPS-*1,1*-d_2.

interaction disappear, but the actual spectrum provided the intensity increment at 983 cm^{-1}. To make clear the peak intensity of the 983 cm^{-1} band over the whole isotope concentration, the absorbance for both the copolymer and blend was plotted against the molar concentration of undeuterated styrene units in Figure 5. The absorbance was reduced by using the 1027 cm^{-1} band as an internal standard band. For both the copolymers and blends, the peak intensity remains almost constant over the whole concentration range. A slight reduction with dilution may be due to an experimental artifact in drawing the baseline. This is direct evidence that the crystallization-sensitive character of the 983 cm^{-1} band is in no relationship with either the inter- or intramolecular interactions. A possible explanation is a specific conformation of the C(skeletal)−C(phenyl) bond. Therefore, it is concluded that the intensity depression comes from the disordered orientation of the phenyl ring.

Gel-Specific Bands for Partially Deuterated iPS. The origin of gel-specific bands was investigated by using partially deuterated samples. Figure 6 shows the infrared spectra of the glass, crystalline form, and gel for iPS-*2*-d_1. Most of the crystalline-sensitive bands are the same as those for iPS except the bands concerned with the C−D bond. The peak intensity at 983 cm^{-1} for the gel was comparable with that for the glass, although this band provided a strong intensity for the crystalline form. Other characteristic bands for the gel were observed at 854, 517, and 503 cm^{-1} and so on. These bands come from the ring mode and provide the same behavior as those of the iPS gel. Figure 7 shows the infrared spectra for iPS-*1,1*-d_2 with CD_2 instead of CH_2.

Similar to the case of iPS-*2*-d_1, the intensity of the 983 cm^{-1} band and the appearance of the bands at 854 and 655 cm^{-1} etc. are characteristic behaviors for the iPS gel. Therefore, the vibrations of the methine and methylene groups are hardly influenced by the formation of the gel. This suggests that the main chain conformation takes a 3/1 helix. Figure 8 shows the

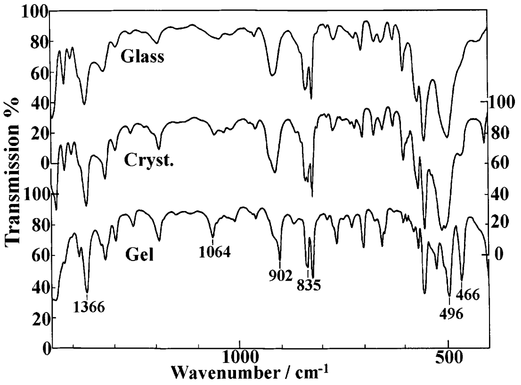

Figure 8. Infrared spectra of noncrystalline, crystalline, and gel CS_2 (measured at −100 °C) for iPS-*r*-d_5.

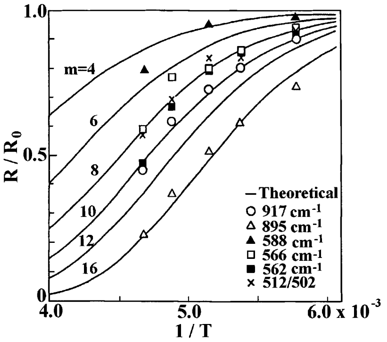

Figure 9. Theoretical curves calculated from the critical length analysis and temperature dependence of the integrated intensities of the characteristic bands observed in the iPS/CS_2 gel.

infrared spectra of the ring-deuterated iPS-*r*-d_5. Contrary to other partially deuterated iPS described above, a dramatic change was observed between the crystalline form and the gel. Especially the 400−800 cm^{-1} region corresponding to the ring out-of-plane mode provided a large difference from the crystalline form. Consequently, only the ring modes are remarkably affected on gelation. It is worth noting that the 983 cm^{-1} band due to the ring mode was unaltered in intensity during the gelation process. Therefore, it is concluded that the gel-specific bands come from the disordered conformation around the C(skeletal)−C(ring) band. Such a disorder may be induced by insertion of solvent molecules into the intermolecular space, while the skeletal chain takes an ordered t−g conformation.

Critical Sequence Length of the Conformation-Sensitive Band. The conformation-sensitive character of the infrared bands originates from the intramolecular vibrational coupling between the monomeric units regularly arranged along the polymer chain. It should be emphasized that the sensitivity of the band intensity differs from band to band depending on the conformational order. The concept of the critical length of the sequence was introduced by Kobayashi et al.[21] It is defined as the shortest length of the regular sequence of a particular conformation such as a t−g conformation. The number of structural units is represented by *m*. In Figure 9, the theoretical curve was drawn following the previous report.[21,22] The *m* values were determined by fitting the experimental result shown in the next section.

In this study, the bands around 900 and 500 cm^{-1} were selected for this analysis because of the characteristic bands for the gel. The absorption profile was separated by Lorentzian components. For example, the integrated intensity of each component in the 500−600 cm^{-1} region was plotted against temperature as shown in Figure 10. On cooling, the intensities of the 566, 562, and 517 cm^{-1} bands due to the t−g form started to increase steeply at the gelation temperature (around −50 °C), while those of the 546 and 562 cm^{-1} bands due to the t−t form decreased. These experimental results were plotted against 1/*T* in Figure 9 together with the theoretical curve. The *m* values estimated by fitting are listed in Table 1. The bands in the 500−600 cm^{-1} region correspond to $m = 4-8$, indicating these bands are very sensitive to the short conformational order. The 917 and 894 cm^{-1} bands correspond to $m = 10$ and 16, respectively. For the gel, the intensity increment of the 894 cm^{-1} band having $m = 16$ indicates that a regular sequence longer than five turns of the 3/1 helix was formed.

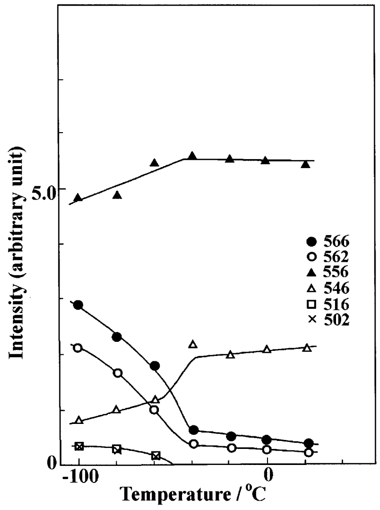

Figure 10. Temperature dependence of the infrared intensities of the helix bands of iPS.

Table 1. Critical Sequence Length (*m*) for Conformation-Sensitive Bands

band/ cm^{-1}	*m* (no. of monomer units)	band/ cm^{-1}	*m* (no. of monomer units)	band/ cm^{-1}	*m* (no. of monomer units)
917	10	566	8	502	6−8
894	16	562	8		
588	4−6	512	6−8		

Recently we reported the gelation of aPS which has a limited stereoregularity.[26] For isotactic-rich aPS, the intensity increment was observed in the 500−600 cm^{-1} region, but the 894 cm^{-1} band was unaltered during the gelation process. This result led to the conclusion that the conformational ordering is very short, less than $m = 16$, because of the local stereospecific sequence. In the case of iPS, the stereoregularity is very high, so the longer conformational order was formed in the gel.

Conclusion

The molecular structure formed through the gelation process of iPS was investigated by solid-state high-resolution ^{13}C NMR and infrared spectroscopies. The conformation-sensitive methylene resonance line observed in the CP/MAS ^{13}C NMR spectrum provided the same chemical shift between the gel and crystal. This indicates that the conformational structure formed in the gel takes a 3/1 helix, which is identical with the conclusion drawn by Guenet et al.

The gelation process depending on temperature was investigated by infrared spectra using partially deuterated iPS. The 983 cm^{-1} band is assigned to the out-of-plane mode with no relation to the skeletal conformation. This band increased in intensity for α-iPS; however, it was unaltered during the gelation process. From the analysis of isotope dilution of the copolymer and blend, it was revealed that the intensity increment of 983 cm^{-1} does not come from either inter- or intramolecular interactions but the disorder of the C(skeletal)−C(ring) axis. This suggests that the solvent molecule causes disorder by locating between polymer chains.

The critical sequence length observed in the infrared spectrum was estimated for conformation-sensitive bands. At the initial stage of gelation, the band intensity in the 500−600 cm^{-1} region increased. These bands correspond to a shorter critical sequence length ($m = 4-8$). After that, the 917 cm^{-1} band with $m = 10$ and 894 cm^{-1} band with $m = 16$ increased in intensity. Therefore, the conformational order longer than five turns of the 3/1 helix was induced through the gelation process. Thus, infrared spectroscopy is a very powerful tool to investigate the conformational ordering on the basis of thermodynamical stability.

References and Notes

(1) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E. *J. Am. Chem. Soc.* **1955**, *77*, 1700.
(2) Natta, G.; Danusso, F.; Moraglio, G. *Makromol. Chem.* **1958**, *28*, 166.
(3) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento, Suppl.* **1960**, *15*, 68.
(4) Girolamo, M.; Keller, A.; Miyasaka, K.; Overbergh, N. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 39.
(5) Atkins, E. D. T.; Isaac, D. H.; Keller, A.; Miyasaka, K. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 211.
(6) Atkins, E. D. T.; Isaac, D. H.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 71.
(7) Atkins, E. D. T.; Keller, A. Shapiro, J. S.; Lemstra, P. J. *Polymer* **1981**, *22*, 1161.
(8) Atkins, E. D. T.; Hill, M. J.; Jarvis, D. A.; Keller, A.; Sarhene, E.; Shapiro, J. S. *Colloid Polym. Sci.* **1984**, *232*, 22.
(9) Sundararajan, P. R. *Macromolecules* **1979**, *12*, 575.
(10) Sundararajan, P. R.; Tyrer, N. J. *Macromolecules* **1982**, *15*, 1004.
(11) Tyrer, N. J.; Bluhm, T. L.; Sundararajan, P. R. *Macromolecules* **1984**, *17*, 2296.
(12) Guenet, J. M. *Macromolecules* **1986**, *19*, 1961.
(13) Guenet, J. M.; McKenna, G. B. *Macromolecules* **1988**, *21*, 1752.
(14) Klein, M.; Guenet, J. M. *Macromolecules* **1989**, *22*, 3716.
(15) Klein, M.; Brulet, A.; Guenet, J. M. *Macromolecules* **1990**, *23*, 540.
(16) Klein, M.; Mathis, A.; Manelle, A.; Guenet, J. M. *Macromolecules* **1990**, *23*, 4591.
(17) Klein, M.; Guenet, J. M.; Brulet, A.; Boue, F. *Polymer* **1991**, *32*, 1943.
(18) Itagaki, H.; Takahashi, I. *Chem. Phys. Lett.* **1993**, *205*, 446.
(19) Itagaki, H.; Takahashi, I. *Macromolecules* **1995**, *28*, 5477.
(20) Itagaki, H.; Nakatani, Y. *Macromolecules* **1997**, *30*, 7793.
(21) Kobayashi, M.; Akita, K.; Tadokoro, H. *Die Makromol. Chem.* **1968**, *118*, 324.
(22) Kobayashi, M.; Tsumura, K.; Tadokoro, H. *J. Polym. Sci., Part A-2* **1968**, *6*, 1493.
(23) Nakaoki, T.; Kobayashi, M. *Rep. Prog. Polym. Phys. Jpn.* **1990**, *33*, 91.
(24) Nakaoki, T.; Kobayashi, M. *J. Mol. Struct.* **1991**, *242*, 315.
(25) Nakaoki, T.; Kobayashi, M. *Rep. Prog. Polym. Phys. Jpn.* **1991**, *34*, 359.
(26) Nakaoki, T.; Tashiro, K.; Kobayashi, M. *Macromolecules* **2000**, *33*, 4299.
(27) Painter, P. C.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1885.
(28) Snyder, R. W.; Painter, P. C. *Polymer* **1981**, *22*, 1633.

MA020474D