Size and Distribution of Free Volume in Thermoreversible Gels of Syndiotactic Polystyrene

Hideyuki Itagaki* and Jun Mochizuki

Department of Chemistry, Graduate School of Electronic Science and Technology and School of Education, Shizuoka University, 836 Ohya, Suruga-ku, Shizuoka 422-8529, Japan

Received August 4, 2005; Revised Manuscript Received September 20, 2005

ABSTRACT: A fluorescence probe technique was used to investigate the role of the solvent in the syndiotactic polystyrene (sPS) thermoreversible gel system. Four probe molecules with different molecular sizes were dispersed throughout the gels, and their fluorescence anisotropy values were examined in detail for a range of sPS concentrations. The results showed that solvent molecules are mobile in the area where solvent gathers in the gels and that, in sPS/chloroform gels consisting of 2_1-helical sPS chains forming a polymer−solvent molecular compound with chloroform, there exists a distribution of free volume in an area where the sPS chains associate and into which molecules smaller than 1,5-dimethylnaphthalene are able to penetrate. The size of the free volume between the sPS chains is consistent with that of the cavity size in the δ-empty crystalline form of sPS solids. However, in the sPS/*trans*-decalin gels having a spherulitic morphology, almost all NP molecules were assumed to be excluded out of the clathrate δ crystalline form not due to their cavity size but rather due to the growing process of the solvated crystalline forms.

Introduction

Fluorescence spectroscopy is growing remarkably as a powerful and effective tool to study the physical and chemical behaviors of macromolecules.[1−3] Because fluorescence techniques are not only highly sensitive but also nondestructive, they are useful for monitoring changes in the microenvironment. Thus far, however, fluorescence techniques have not been employed so effectively for studies on gel systems. We therefore have applied fluorescence techniques to the studies on the gelation processes and the microenvironments inside gel systems including structures of polymer chains and solvent molecules.[4−6]

Syndiotactic polystyrene (sPS) is known to form thermoreversible gels in quite a few solvents, and many papers on sPS gels have been published so far since Kobayashi et al.[7] Because sPS chains can adopt two stable conformations of all-trans planar zigzag (TTTT)[8] and 2_1-helix (TTGG),[9] sPS shows a complex polymorphic behavior of having four different crystalline forms. In solution or after absorption of solvent molecules, it is established that the 2_1-helix conformation can be formed[10] and is responsible for the thermoreversible gelation. The detailed phase diagrams of temperature−sPS concentration have been obtained for sPS gels with solvents such as chloroform,[11,12] toluene,[11,13] benzene,[13,14] bromoform,[15] chlorobenzene,[12] di-, tri-, and tetrachlorobenzenes,[12] *cis*-decalin,[16,17] *trans*-decalin,[16,18,19] naphthalene,[20] and so on. They suggest that solvent molecules are intercalated between sPS chains consisting of the 2_1-helix structure and that the number of solvent molecules forming polymer−solvent compounds with sPS is dependent on gelation solvent itself. However, cooling of sPS solutions with bulky solvents such as octadecyl benzoate[17] and 1-chlorotetradecane[24,25] results in the formation pastelike opaque gels[17] where sPS chains are in the highly ordered all-trans TT skeletal conformation. These gels are mechanically weak[22,24] while gels with sPS chains of 2_1-helical structure are strongly elastic. The conformations of sPS are also reported to depend on the annealing temperature in the case of *cis*-decalin solution of sPS resulting that crystallization competes with gelation.[25]

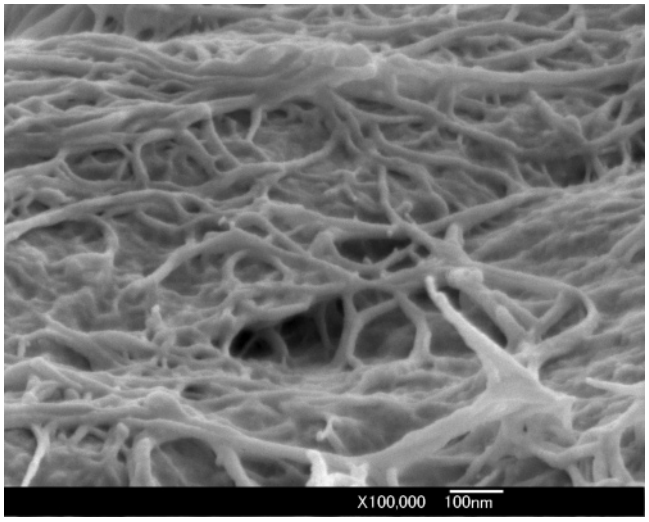

Figure 1. Scanning electron microscopy pictures of sPS/chloroform gel after freeze-drying. The scale bar indicates a distance of 100 nm.

It is quite important to get information on the behavior of solvent molecules in a gel system. However, it is true that there is no decisive tool to monitor it. As a trial for studying the role of the solvent, we applied a fluorescence probe technique to the isotactic polystyrene (iPS)/decalin thermoreversible gel system and successfully obtained the experimental results showing the behavior of solvent molecules.[5] Here we used the same method for observing the mobility and location of the solvent molecules in the sPS gel systems.

Figure 1 shows a picture of the scanning electron microscopy (SEM) of sPS/chloroform gel after freeze-drying. From this picture, the possible location of solvent

* Corresponding author. E-mail: edhitag@ipc.shizuoka.ac.jp.

10.1021/ma051743d CCC: $30.25 © 2005 American Chemical Society
Published on Web 10/20/2005

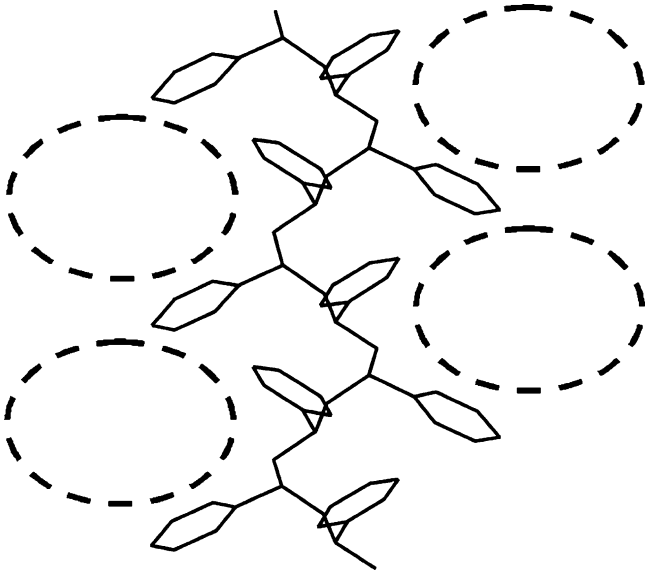

Figure 2. Sketch of possible areas where solvent molecules can remain among the sPS chains in region II. The conformation of the sPS chains is of 2_1-helix form.

molecules within the gel can be divided into two regions: region I is the area where solvent molecules gather while region II is the area where sPS molecules associate together. In Figure 1, all the solvent molecules in region I are gone. If polymer−solvent molecular compounds are formed between sPS chains and solvent, solvent molecules can stay among sPS chains of the 2_1-helix such as Figure 2. Although we can assume another interface area among sPS chains and solvent molecules, it is difficult to be distinguished from region I. We have been interested in investigating whether solvent molecules can exist in region II and whether solvent molecules can move around when in regions I and II or when in an interface region. To answer these questions, we applied a fluorescence probe method in the present paper.

Experimental Section

Materials. Syndiotactic polystyrene (sPS) used for the measurements was kindly supplied from Idemitsu Kosan Co., Ltd. It is 98% syndiotactic with an M_w of 152 000 and an M_w/M_n of 1.9. Chloroform (luminasol grade) was purchased from Wako Pure Chemical Industries and used without purification. *trans*-Decalin was purchased from Tokyo Kasei Co., and its purity was more than 98%. It was purified by passing it through a column packed with alumina (Wako Pure Chemical Industries) to exclude any fluorescent impurities. Fluorescence probe molecules used in the present work are naphthalene (NP), 1-methylnaphthalene (MN), 1,5-dimethylnaphthalene (DMN), and anthracene (AT). All of them were purchased from Wako Pure Chemical Industries. The concentrations of these probe molecules in any sPS gels are strictly adjusted to be the same. They are 1.34×10^{-3} M for NP, 1.37×10^{-3} M for MN, 1.35×10^{-3} M for DMN, and 1.25×10^{-4} M for AT. Even in the case of sPS/*trans*-decalin gels, the concentration of NP in the gels was kept to be 1.34×10^{-3} M. Each gel was prepared by dissolving sPS in chloroform or *trans*-decalin containing the probe molecules and heating the mixture in quartz cells at ca. 80 and 180 °C, respectively. It is not facile to prepare an sPS solution with high concentrations in a quartz cell with an optical path length of 1 mm. However, we could mix a large amount of sPS with solvent in a Pyrex tube jointed to a cell. The concentration of sPS was limited to be at most 15% (w/w) in order to prepare a uniform sPS solution. The solutions in the cell were cooled in a refrigerator (−23 °C) for more than 2 days. The plastic solutions of

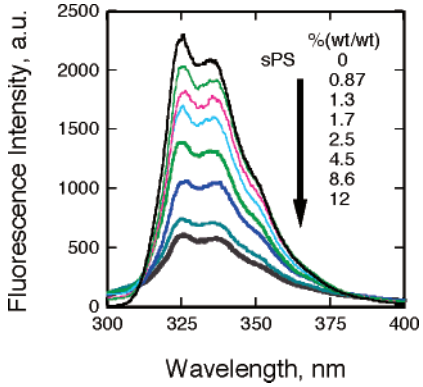

Figure 3. Fluorescence spectra of NP in sPS/chloroform gels with different sPS concentrations. The concentration of NP in each gel was 1.34×10^{-3} M. The excitation wavelength was 280 nm.

fluorescent probe molecules were prepared on quartz disks by using a spin-casting method from a 1% THF solution of atactic polystyrene (aPS: Tosoh Corp.; M_w of 96 400 and an M_w/M_n of 1.01) containing the above compounds and dried by extensive pumping under vacuum for more than 3 days at 40 °C. More than four films for one probe molecule with one concentration were prepared to ascertain the reproducibility.

Measurements. Fluorescence spectra, fluorescence excitation spectra, and fluorescence polarization spectra were measured at 25 °C on a Hitachi F-4500 spectrofluorometer. Fluorescence measurements for the gels were carried out in a quartz cell with an optical path length of 1 mm for their aerated solutions. A cell was set at 45° to the exciting beam. Regarding measurements of fluorescence anisotropy, a Hitachi automatic polarizer was attached to a Hitachi F-4500 spectrofluorometer: the anisotropic values were determined by measuring values for 100 s at some wavelengths more than three times and averaging them. Excitation wavelengths were 280 nm for NP, 286 nm for MN, 290 nm for DMN, and 342 nm for AT.

To determine the intrinsic anisotropy values of probe molecules whose motions are completely suppressed, we measured the fluorescence anisotropy of aPS films doped with some different concentrations of probe molecules. The films were left on the quartz disks for ease of handling during subsequent measurements and were set at 45° to the exciting beam for the measurements.

Scanning electron microscopy pictures were obtained using a JEOL JSM-6300 at Center for Instrumental Analysis of Shizuoka University.

Results and Discussion

Fluorescence Spectra of NP in sPS/Chloroform Gels. Figure 3 shows the fluorescence spectra of NP in sPS/chloroform gels when the concentrations of sPS are from 0 to 12% (w/w). Although the concentrations of NP were exactly the same, the fluorescence intensities of NP were found to decrease with an increase of sPS concentration. This means that the total absorbance of sPS at 280 nm increases at higher concentrations of sPS despite its molar extinction coefficient being quite low, resulting that the possibility for an NP molecule to absorb a 280 nm photon decreases much. The fluorescence spectra of NP in sPS/chloroform gels normalized to the peak were almost identical with each other except the fluorescence between 280 and 320 nm, which are of phenyl groups of sPS. MN, DMN, and AT in sPS/chloroform gels turned out to show the same fluorescence behavior with an increase of sPS. At any rate, since no excimer fluorescences were not observed, all the probe molecules used in the present study were dispersed and not aggregated in sPS/chloroform gels.

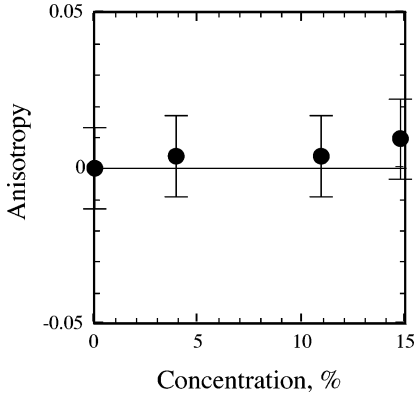

Figure 4. sPS concentration dependence of AT anisotropy (r) in sPS/chloroform gels measured at 25 °C. The excitation wavelength was 342 nm.

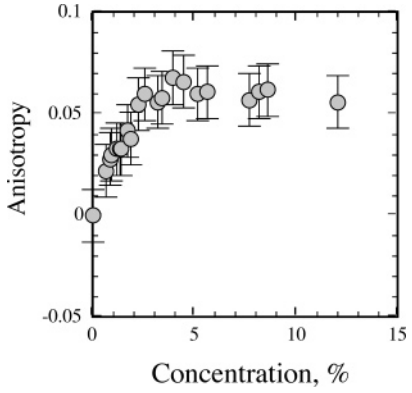

Figure 5. sPS concentration dependence of NP anisotropy (r) in sPS/chloroform gels measured at 25 °C. The excitation wavelength was 280 nm.

Fluorescence Polarization of Probe Molecules in Solid and Fluid Solutions. In general, when a chromophore is excited by polarized light, the emission of the chromophore will be observed to be polarized if (i) the molecular motion of the chromophore is slow enough and (ii) energy transfer and/or energy migration do not take place. Thus, the measurements of the emission anisotropy give information on molecular motions and/or energy transportation. The fluorescence anisotropy, r, is defined as

$$r = (I_p - GI_v)/(I_p + 2GI_v) \quad (1)$$

where the I_p and I_v denote the measured intensities when the observing polarizer is parallel and perpendicular, respectively, to the direction of the polarized excitation, and G is a machine constant. When motion of a chromophore is fast enough or excitation energy can hop among molecules, the anisotropy of the emission falls to zero.

We measured the anisotropy of probe molecules in aPS to determine their inherent values at room temperature. We have already shown that the anisotropy of a dye in plastic solution at 77 K is almost identical with that at room temperature except for the situation where excitation energy migration occurs among dyes.[26] Molecular motion of a probe molecule is assumed to be suppressed in these plastic films. Thus, the r values of probe molecules without molecular motion and energy transportation are determined to be 0.18 for NP, 0.14 for MN, 0.14 for DMN, and 0.20 for AT when they are excited at each wavelength of their absorption peaks.

We also measured the fluorescence anisotropy of NP, MN, DMN, and AT in chloroform and *trans*-decalin. All the fluorescences of probe molecules were found to be completely depolarized, although the viscosity of decalin is not so low.

Finally we obtained the values of anisotropy for several fluorescent molecules in both cases where they are mobile in fluid solution ($r = 0$) and where they are immobile in solid solution. Thus, we examine the motion of probe molecules in gel form by comparing r values.

sPS Concentration Dependence of Anisotropy of AT in sPS/Chloroform Gels. We examined the sPS concentration dependence of anisotropy of AT in the sPS/chloroform gel. Figure 4 shows that the r values of AT were zero or very close to zero in comparison with its inherent anisotropy value (0.20). There is no possibility that AT fluorescence is depolarized due to energy migration among AT molecules because the concentration of AT is so low (1.25×10^{-4} M). Thus, AT molecules are concluded to be mobile in the gels. This behavior was as same as that of larger molecules than NP in iPS/decalin gels.

Let us consider where most AT molecules are. The fraction of region II ought to increase with an increase of sPS, although most solvent molecules are in region I at lower concentrations of sPS. Moreover, the values of r should be high, if AT molecules are in region II and suppressed by sPS chains. Therefore, it is considered from the results shown in Figure 4 that (i) AT molecules staying in region I are mobile and that (ii) the number of AT molecules fixed by sPS chains in an interface area between sPS chains and solvent is very small, and (iii) AT molecules remaining in region II are not suppressed or no AT molecules exist in region II.

If probe molecules exist in the relatively large area of region I where solvent molecules gather together, their fluorescence anisotropy would reflect the motion of the solvent. Thus, it is concluded that (1) solvents in region I are mobile and that (2) motion of solvents near an interface with sPS chains is not limited so much, because the r values do not increase with increasing the fraction of the sPS interface. The average number of solvent molecules in one compartment of region I should decrease with an increase in sPS concentration; therefore, the possibility that both the solvent and probe molecules are fixed by the sPS chains would also increase because the concentration of AT was kept to be the same. However, there is no remarkable change in anisotropy of AT up to 15% (w/w) of sPS. It is therefore concluded that the average volume of region I is still much larger than the volume of an AT molecule and that solvent chloroform molecules in region I are not fixed but can move freely.

sPS Concentration Dependence of Anisotropy of NP in sPS/Chloroform Gels. Next we examined the dependence of the anisotropy of NP (the smallest probe molecule in the study) on the concentration of sPS in the sPS/chloroform gel. It can be seen in Figure 5 that the r value increases as the concentration of sPS increases, leveling off at $r \sim 0.06$ when the sPS concentration had reached 4.5% (w/w). Once again, it should be noted that a higher r value is evidence of the absence of energy transport and of fast moving fluorescent molecules. As was demonstrated above in the last section, any probe molecules remaining in region I should be mobile. This is due to the fact that, since the molecular size of NP is smaller than that of AT, it is very unlikely that any NP molecules in region I are

strongly constrained. We conclude, then, that the observed polarized fluorescence must come from NP molecules located in a different area of the gel.

We noted above that the smallest probe molecule, NP, showed quite high values of r, while the r value for AT, a larger probe molecule, was found to be essentially zero. This does not mean that a molecule in region II is mobile; rather, it implies that no larger probe molecules can exist in region II. This leads us to the conclusion that (1) in the area where some sPS chains associate and line up to become a sort of fiber of the polymer network (region II) there exists a free volume (i.e., a void) into which NP molecules can penetrate and (2) the motion of those NP molecules which have been intercalated among the phenyl groups of the sPS was suppressed. The total amount of NP that is intercalated into region II (which consists of helical sPS chains) should increase with an increase in the sPS content. It is therefore reasonable to assume that the apparent anisotropy value of NP in the gel would increase with increasing concentrations of sPS. Since the response of the aggregated regions such as region II should not be constant (regardless of an increase in the sPS content), we believe that the plateau in the value of r to around ~0.06 is due mainly to the NP molecules being retained in region II: they are fixed, but not perfectly suppressed as they would be in aPS films ($r = 0.18$). As an aside, note that an sPS level of 4.5% (w/w) corresponds to a concentration of the styrene unit of 0.43 M. Since the concentration of NP is 1.34×10^{-3} M (i.e., only 0.3% of the seats available for NP molecules in region II), it is possible for all of the NP molecules added to each gel to remain in region II.

According to Kobayashi et al., the orderliness of the TTGG skeletal conformation, namely the 2_1-helix form, of polymer molecules in sPS/chloroform gels is far less than that in sPS/*o*-dichlorobenzene gels and sPS/carbon tetrachloride gels.[27] The junction point size of sPS gels, which has been estimated using the Tanaka and Stockmayer theory,[28] is also reported to be strongly affected by the choice of solvent: the value for sPS/chloroform gels, in particular, is the smallest of the four solvents tested.[29] This may explain why the concentration at which the r value leveled off (Figure 5) is a little low: the effect could be due to the smallness of the junction points within which the NP molecules can stay among the 2_1-helix sPS chains.

All of this allows us to conclude that, in the case of sPS/chloroform gels, there is enough free space for chloroform molecules to remain among the sPS chains in region II. This must follow since NP molecules, which are larger than chloroform molecules by size, have been shown to occupy such space. This evidence supports the claim for formation of a polymer−solvent molecular compound in sPS/chloroform gels.

Free Volume among sPS Chains in sPS/Chloroform Gels. Figure 6 shows the sPS concentration dependence of the anisotropy of MN and DMN in sPS/chloroform gels. The fluorescence spectra of these substances are identical to those of the same substances in fluid chloroform solutions and do not show excimer fluorescence, which indicates that these probe molecules do not aggregate in the gel at all. In the case of iPS/decalin gels, the r values of MN and DMN were found to be either zero or very close to zero, but in the present case their behaviors proved to be similar to those of the NP molecules described earlier. Their r values increased

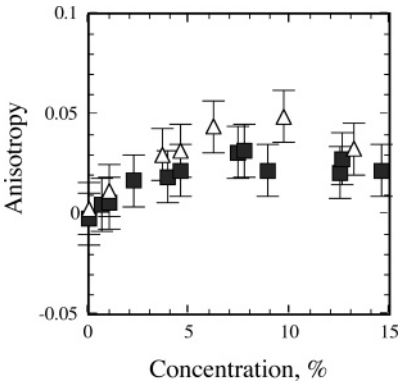

Figure 6. sPS concentration dependence of MN (△) and DMN (■) anisotropy (r) in sPS/chloroform gels measured at 25 °C. The excitation wavelengths were 286 and 290 nm, respectively.

with increasing sPS content in the gels and then leveled off once the amount of sPS reached a particular level. Thus, it is concluded that (1) among the helical sPS rods in region II, there exist free volumes which some MN and DMN molecules can penetrate and (2) the motions of the MN and DMN intercalated among the phenyl groups of the sPS are suppressed. Compared with their inherent r values (0.14), the values measured were quite small. It was therefore assumed that many MN or DMN molecules are in region I.

It is not straightforward to define a molecular size for the probe molecules, but a "molar volume "can be used as a measure of it. The molar volumes of the probe molecules, calculated using the Le Bas group contribution method,[30,31] are 147.6, 169.8, 192, and 197 cm^3/mol for NP, MN, DMN, and AT, respectively. The r values of MN and DMN in sPS/chloroform gels with an sPS content of ~15% (w/w) were much smaller (0.03 and 0.02, respectively) than their inherent values (0.14). In particular, note that the value at which r leveled off for DMN was smaller than the value for MN. We would expect that, for a given amount of free space, the motion of larger probe molecules would be more restricted than that of smaller probe molecules. We have seen, however, that the space for these gels can suppress the motion of NP molecules (see the sketch shown in Figure 2). The results shown in Figures 4−6 therefore suggest that there are free volume whose size is larger than an NP molecule and smaller than an AT molecule and that there is some measurable distribution of the possible volume of such spaces. It is probable that this space is large enough for some DMN molecules to enter into it but small enough that not many can do so. There is only a small difference between the volume taken up by a DMN molecule and that of an AT molecule, but the AT molecules cannot enter region II because its molecular axis is longer than the free space among the sPS chains (Figure 2).

Needless to say, the volume of any space which could accommodate any of the three probe molecules which showed evidence of being constrained within region II (NP, MN, and DMN) should be substantially larger than the size of a chloroform molecule (molar volume: 92.3 cm^3/mol). Therefore, we can conclude that there are free spaces within these gels where sPS chains are aggregated together and which solvent chloroform molecules can populate. In the case of the δ-empty crystal form of sPS solids, each sPS chainis of 2_1-helical form, and the volume of the cavity in the crystal is ~120−160 $Å^3$.[32] The molecular volumes of NP and AT are 127

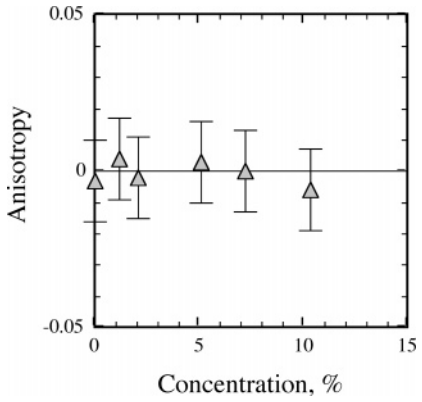

Figure 7. sPS concentration dependence of NP anisotropy (r) in sPS/*trans*-decalin gels measured at 25 °C. The excitation wavelength was 280 nm.

and 170 Å^3, respectively, indicating that our results for sPS/chloroform gels are consistent with the δ-empty crystal results: NP molecules can be found among the sPS chains in both cases, whereas AT molecules are excluded from these regions.

In conclusion, then, we have demonstrated that (1) a polymer−solvent compound is formed between sPS and chloroform in region II of the gel and (2) chloroform molecules can be replaced by naphthalene derivatives because there exists free volumes into which they can penetrate.

sPS Concentration Dependence of Anisotropy of NP in sPS/*trans*-Decalin Gels. Figure 7 shows the sPS concentration dependence of the fluorescence anisotropy of NP in a series of sPS/*trans*-decalin gels. The r values of the NP were found to be zero or very close to zero, although the fluorescence of NP in sPS/chloroform gels was polarized much. The difference between the results may be explained by considering either the conformations of sPS chains or the gel morphologies. There are three possible cases to explain the present data of sPS/*trans*-decalin gels: (A) there are no cavities in region II for NP molecules to stay, (B) there are the cavities in region II for NP molecules to enter but the cavities are too large for the motion of NP molecules to be fixed there, and (C) there are the cavities in region II for NP molecules to stay but they cannot enter there.

Berghmans et al. claim that there are *two* types of sPS gels: elastic and hazy gels consisting of 2_1-helix (TTGG) chains and pastelike, opaque gels consisting of all-trans planar zigzag (TTTT) chains.[17] By carrying out the thermal and structural experiments on sPS in *trans*-decalin, they showed that the conformations of sPS chains depend on the initial concentrations, the heating or cooling rates, and the thermal history of the samples.[16] If our method produced a gel consisting of all-trans planar zigzag sPS chains, it can be assumed that there is no free space among the sPS chains in region II. Thus, all the NP molecules doped into the sPS/*trans*-decalin gel would be excluded from region II and forced to remain in region I, in contrast to their presence in region II of the sPS/chloroform gels described above.

However, the detailed phase diagrams of temperature−sPS concentration obtained for sPS/*trans*-decalin gels demonstrate that the crystallization of β-form consisting of trans planar zigzag conformations takes place only by heating the gels over 120 °C.[16,18,19] Berghmans et al. first showed that the sPS molecules adopt 2_1-helix (TTGG) conformation when sPS/*trans*-decalin gels were dried at room temperature under reduced pressure.[16] Recently, Malik et al. have settled on a conclusion by using neutron diffraction that the conformation of sPS chain in sPS/*trans*-decalin gels is of 2_1-helix form at room temperature.[19] Thus, the NP fluorescence anisotropy results shown in Figure 7 do not seem to be induced by the formation of all-trans planar zigzag sPS chains in sPS/*trans*-decalin gels. Rather, Malik et al. showed that the sPS chain of 2_1-helix structure forms a polymer−solvent compound with a stoichiometry of about one *trans*-decalin molecule per one monomer unit of sPS.[19] Thus, there should be a cavity where NP molecules can enter, and assumption A can be denied.

Assumption B also does not appear to be probable. The characteristic peaks observed through the neutron reflection experiments for *trans*-decalin gels of the deuterium-labeling sPS[19] correspond to the results obtained by X-ray diffraction for the δ-form crystal of sPS where guest molecules such as toluene and 1,2,4-trichlorobenzene form the molecular compounds with sPS, the molar ratio of monomer unit of sPS: guest molecule being 4:1.[33] Daniel et al. reported that the polymer-rich phase in sPS/1,2-dichloroethane gels is a crystalline clathrate phase having a molecular ratio close to the 4/1 styrene unit/guest molecule.[34] Taking into these results, one can assume that the size of the cavity among sPS chains (region II) in *trans*-decalin gels would be at most as large as that of the cavity in the δ-empty crystal form of sPS: the volume of the cavity in the crystal is estimated to be ∼120−160 Å^3 as described above.[32] We measured the r values of NP in s-PS/NP δ clathrate films obtained by exposure of amorphous sPS films to NP vapors at 60 °C:[35] needless to say, the sPS chains were determined to be of 2_1-helix form. The r values were found to be 0.04, which is small but still indicates that the fluorescence of the NP molecules in cavities of the δ-empty sPS crystal form is polarized. Thus, assumption B is concluded to be excluded.

Finally, assumption C is most probable, since the other assumptions A and B can be denied. Let us consider the probability of this assumption. Guenet et al. have demonstrated that sPS/*trans*-decalin gels do not display elastic behavior because the system consists of a packing of spheres with minimum cohesion.[24] Despite having a structure consisting of a polymer−solvent compound with 2_1-helix form, sPS/*trans*-decalin gels did not show the same network morphology as sPS/chloroform does (Figure 1) but rather exhibited a spherulitic morphology with spherulite sizes averaging around 20 μm diameter no matter what polymer fraction is.[19,24] In the case of the gels having a fibrous and network morphology, we have observed that the probe molecules whose sizes are smaller than the cavities among the polymer chains (see Figure 2) can be intercalated among the chains.[5,6]

Here it is quite reasonable that *trans*-decalin molecules possible to stay among sPS chains (region II) can be replaced by NP molecules more easily in the case of a fibrous morphology than in the case of a spherulitic morphology. Thus, the marked difference between the NP anisotropy behavior of the sPS/chloroform gels and sPS/*trans*-decalin gels would therefore be induced by the difference between the gel morphologies. The reason is not so clear, and further investigation is necessary on this subject. However, almost all NP molecules are

supposed to be excluded out of δ clathrate form only when a spherulitic crystalline structure of sPS is growing. There is a possibility that a fibrous and network morphology is induced because crystallization does not proceed three-dimensionally due to the behavior of solvent molecules being mobile and disturbing the isotropic growing of the crystalline structure. On the contrary, the defects of the crystalline region should be least when the spherulitic morphology is formed.

Acknowledgment. This work was supported by Grant-in-aid for Scientific Research (C) (13650948) and (C) (15550183) from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

(1) Itagaki, H.; Mita, I. In *Degradation and Stabilization of Polymers*; Jellinek, H. H. G., Ed.; Elsevier: Amsterdam, 1989; Vol. 2, p 45.
(2) Itagaki, H.; Horie, K.; Mita, I. *Prog. Polym. Sci.* **1990**, *15*, 361.
(3) Itagaki, H. In *Experimental Methods in Polymer Science: Modern Methods in Polymer Research and Technology*; Tanaka, T., Ed.; Academic Press: New York, 2000; Chapter 3.
(4) (a) Itagaki, H.; Takahashi, I. *Chem. Phys. Lett.* **1993**, *205*, 446. (b) Itagaki, H.; Takahashi, I. *Macromolecules* **1995**, *28*, 5477.
(5) Itagaki, H.; Nakatani, Y. *Macromolecules* **1997**, *30*, 7793.
(6) (a) Itagaki, H.; Tokai, M.; Kondo, T. *Polymer* **1997**, *38*, 4201. (b) Watase, M.; Nakatani, Y.; Itagaki, H. *J. Phys. Chem. B* **1999**, *103*, 2366. (c) Itagaki, H. *Macromol. Symp.* **2001**, *166*, 13. (d) Itagaki, H.; Fukiishi, H.; Imai, T.; Watase, M. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 680.
(7) Kobayashi, M.; Nakaoki, T.; Ishihara, N. *Macromolecules* **1990**, *23*, 78.
(8) Doherty, D.; Hopfinger, J. *Macromolecules* **1989**, *22*, 2472.
(9) Guerra, G.; Vitagliano, V.; De Rosa, C.; Petraccone, P.; Corradini, P. *Macromolecules* **1990**, *23*, 1539.
(10) Immirzi, A.; De Candia, F.; Ianelli, P.; Zambelli, A.; Vittoria, V. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 761. (b) Vittoria, V.; De Candia, F.; Ianelli, P.; Immirzi, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 765.
(11) Daniel, C.; Menelle, A.; Brulet, A.; Guenet, J.-M. *Polymer* **1997**, *38*, 4193.
(12) Roels, T.; Deberdt, F.; Berghmans, H. *Macromolecules* **1994**, *27*, 6216.
(13) Ray, B.; Elhasri, S.; Thierry, A.; Marie, P.; Guenet, J.-M. *Macromolecules* **2002**, *35*, 9730.
(14) Daniel, C.; Deluca, M. D.; Guenet, J.-M.; Brulet, A.; Menelle, A. *Polymer* **1996**, *37*, 1273.
(15) De Rudder, J.; Berghmans, H.; De Schryver, F. C.; Bosco, M.; Paoletti, S. *Macromolecules* **2002**, *35*, 9529.
(16) Deberdt, F.; Berghmans, H. *Polymer* **1993**, *34*, 2192.
(17) Roels, T.; Deberdt, F.; Berghmans, H. *Prog. Colloid Polym. Sci.* **1996**, *102*, 82.
(18) Guenet, J.-M. *Macromol. Symp.* **2003**, *203*, 1.
(19) Malik, S.; Rochas, C.; Schmutz, M.; Guenet, J.-M. *Macromolecules* **2005**, *38*, 6024.
(20) Malik, S.; Rochas, C.; Guenet, J.-M. *Macromolecules* **2005**, *38*, 4888.
(21) Li, Y. Q.; Xue, G. *Macromol. Rapid Commun.* **1998**, *19*, 549.
(22) Daniel, C.; Alfano, D.; Guerra, G.; Musto, P. *Macromolecules* **2003**, *36*, 1713.
(23) Daniel, C.; Alfano, D.; Guerra, G.; Musto, P. *Macromolecules* **2003**, *36*, 5742.
(24) Daniel, C.; Dammer, C.; Guenet, J.-M. *Polymer* **1994**, *35*, 4243.
(25) De Rudder, J.; Berge, B.; Berghmans, H. *Macromol. Chem. Phys.* **2002**, *203*, 2083.
(26) Itagaki, H.; Horie, K.; Mita, I.; Washio, M.; Tagawa, S.; Tabata, Y.; Sato, H.; Tanaka, Y. *Macromolecules* **1990**, *23*, 1686.
(27) Kobayashi, M.; Yoshioka, T.; Kozasa, T.; Tashiro, K.; Suzuki, J.; Funahashi, S.; Izumi, Y. *Macromolecules* **1994**, *27*, 1349.
(28) Tanaka, F.; Stockmayer, W. H. *Macromolecules* **1994**, *27*, 3943. (b) Tanaka, F.; Nishinari, K. *Macromolecules* **1996**, *29*, 3625.
(29) Shimizu, H.; Wakayama, T.; Wada, R.; Okabe, M.; Tanaka, F. *Polym. J.* **2005**, *37*, 294.
(30) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; 688 pp.
(31) Le Bas group contribution method: Le Bas, G. *The Molecular Volumes of Liquid Chemical Compounds*; Longmans, Green: New York, 1915.
(32) (a) Milano, G.; Venditto, V.; Guerra, G.; Cavallo, L.; Ciambelli, P.; Sannino, D. *Chem. Mater.* **2001**, *13*, 1506. (b) Tamai, Y.; Fukuda, M. *Polymer* **2003**, *44*, 3279.
(33) Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer* **1993**, *34*, 1620.
(34) Daniel, C.; Guerra, G.; Musto, P. *Macromolecules* **2002**, *35*, 2243.
(35) Venditto, V.; Milano, G.; De Girolamo Del Mauro, A.; Guerra, G.; Mochizuki, J.; Itagaki, H. *Macromolecules* **2005**, *38*, 3696.

MA051743D