Application of Fluorescence Depolarization Method to Monitor Free Volume in Gels of Stereoregular Polystyrene

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Summary: A fluorescence depolarization technique was applied to get the information on free volume among polymer chains in gel form. Four fluorescent molecules with different molecular sizes were doped throughout the gels of syndiotactic polystyrene (sPS) and isotactic polystyrene (iPS) physical gel system, and their fluorescence anisotropy values were examined in detail for a range of polymer concentrations. Consequently, the free volume among sPS chains in sPS/chloroform gels is as large as the size of molecules smaller than 1,5-dimethylnaphthalene and is consistent with that of the cavity size in the δ-empty crystalline form of sPS solids. The cause to produce δ-empty crystalline form of sPS solids and to form cocrystals between sPS and guest molecules is discussed by comparing the molar size of guest molecules with the free volume among sPS chains in gel form.

Keywords: depolarization; fluorescence; free volume; physical gels

Introduction

The application of fluorescence spectroscopy is growing remarkably as a powerful and effective tool to study the physical and chemical behavior of macromolecules.[1–3] The main advantage of spectrofluorometry is its high sensitivity. Ultraviolet/visible (uv/vis) absorption is also known to have a high sensitivity and it can, for instance, effectively be employed to monitor chemical species in blood in medical tests, however, the sensitivity of fluorometry would be 10 to 100 times as much as that of uv/vis absorption spectroscopy. Simply speaking, fluorescence is a photon released from an excited state of a molecule. The excited state can be readily formed by the irradiation of light to a usual molecule in the ground state, but since the duration time of the excited state is usually very short, it goes back to the ground state by releasing the excitation energy as heat and/or fluorescence. What we are interested in is how a molecule behaves during its excited state: for example if it dies normally or associates with another molecule to form another excited species and so on.

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.[4] Because sPS chains can adopt two stable conformations of all-trans planar zigzag (TTTT)[5] and 2_1-helix (TTGG),[6] sPS shows a complex polymorphic behavior of having five different crystalline forms. In solution or after absorption of solvent molecules, it is established that the 2_1-helix conformation can be formed[7] 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,[8,9] toluene,[8,10] benzene,[10,11] bromoform,[12] chlorobenzene,[9] di-, tri-, and tetra-chlorobenzenes,[9] *cis*-decalin,[13,14] trans-decalin,[13,15,16] naphthalene[17] and so

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on. They suggest that solvent molecules are intercalated between sPS chains consisting of 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[14] and 1-chlorotetradecane[18,19] results in the formation paste-like opaque states[14] where sPS chains are in the highly ordered all-trans TT skeletal conformation. These states are mechanically weak[19,20] 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.[19]

The present paper deals with our trial for getting information of free volume in sPS gels by applying fluorescence depolarization method for the first time to these systems. The aim is to study on the relationship between free volume among sPS chains in gel form and cavity size of delta empty crystalline form of sPS. We have actually employed some fluorescent molecules that can be a guest molecule clathrated with sPS crystalline form.

Fluorescence Depolarization Method

Figure 1 demonstrates the general measurement of polarized fluorescence of samples. Two sets of polarizers are used: polarizer 1 is set as Iv shown in the figure and selects the polarized light whose vector of electric field is vertical to the direction of progress as the excitation light of a sample. The excitation light for the polarized fluorescence measurements is always the same as in Figure 1. The polarizer 2 is set in front of the detector as is shown by either Iv or Ih. The fluorescence intensity of a sample is defined to be I0 and I90 when polarizer 2 (fluorescence) is set as Iv and Ih, respectively. I0 and I90 are dependent on how much a sample absorbs the excitation

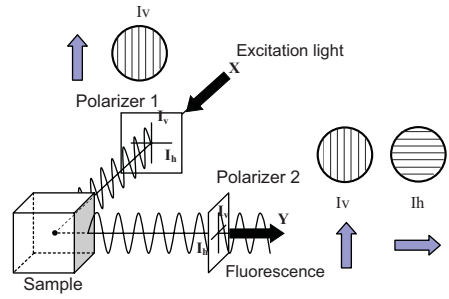

Figure 1.
Sketch of polarized fluorescence measurements. Iv and Ih are vectors of electric field for the polarized light selected by a polarizer. Polarizer 1 is set as to choose a polarized light whose vector of electric field is Iv as the excitation light, while polarizer 2 are automatically set to be either parallel (Iv) or vertical (Ih) to polarizer 1.

light and how much its polarized fluorescence can go through the polarizer 2.

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 does not take place. The fluorescence anisotropy, *r*, which is defined as Equation (1), is convenient for evaluation of how much the fluorescence is polarized.

$$r = (I0 - G \times I90)/(I0 + 2G \times I90) \qquad (1)$$

where G is a machine constant. Usually the comparison between the r values is efficient for obtaining information about the molecular motions and/or energy transportation. When motion of a chromophore is fast enough or excitation energy can hop among molecules, the anisotropy of the emission falls to zero. When a chromophore is doped into amorphous plastic films such as poly (methyl methacrylate) (PMMA), it shows the highest absolute value of r because its molecular motion is perfectly suppressed. The comparison of r with this inherent value, r_0, gives the degree of depolarization.

Energy migration can be avoided if the concentration of fluorescent molecules doped into a system is quite low and the chromophores are not aggregated. Accord-

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ingly, when we dope a small amount of fluorescent molecules into a system and excited them by polarized light, the degree of depolarization would give information on the motion of fluorescent molecules.

Experimental Part

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. Isotactic polystyrene (iPS) used for the measurements is 90% isotactic with Mw of 400,000 (Scientific Polymer Product). Chloroform (luminasol grade) was purchased from Wako Pure Chemical Industries and used without purification. trans- and cis-Decalin was purchased from Tokyo Kasei Co. 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. Each gel was prepared by dissolving polymer in solutions of the probe molecules and heating the mixture in quartz cells with an optical path length of 1 mm having a pyrex tube jointed to a cell. The solutions in the cell were cooled in a refrigerator (−23 °C) for more than 2 days. The plastic solutions of 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 and a film on a quartz disk were 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 sec at some wavelengths more than three times and averaging them. Scanning electron microscopy pictures were obtained using a JEOL JSM-6300 at Center for Instrumental Analysis of Shizuoka University.

Results and Discussion

Fluorescence Polarization of Probe Molecules in Solid and Fluid Solutions

We chose naphthalene (NP: We measured the anisotropy of probe molecules in atactic polystyrene (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.[21] Molecular motion of a probe molecule is assumed to be suppressed in these plastic films. Thus, the r_0 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, 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 relatively high.

Finally we obtained the values of anisotropy for several fluorescent molecules in

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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.

Concept of the Fluorescence Depolarization Method in the Present Study

Figure 2A shows the picture of the scanning electron microscopy (SEM) of sPS/chloroform gel after freeze-drying. The possible location of solvent molecules within the gel can be divided to two: region I is the area where solvent molecules gather while region II is the area where sPS molecules associate together. In Figure 2A, all the solvent molecules in region I are gone. It is already known that polymer-solvent molecular compounds are formed between sPS chains with 2_1-helix structure and solvent molecules.[9] What we would like to get using our depolarization method is how large the free volume (shown as a dotted-line circle in Figure 2B) among sPS chains in region II is. If a fluorescent molecule doped is small enough to enter region II, its molecular motion could be suppressed by side-chains of sPS, resulting that its anisotropy value would be observed not to be zero. However, if the molecular size of a fluorescent molecule doped is so large that it cannot penetrate into region II, it has to be in region I where solvent molecules gather. Here the motion of this large fluorescent molecule must be large, resulting that the anisotropy value must be observed to be 0.

sPS Concentration Dependence of Anisotropy of Naphthalene Derivatives and Anthracene in sPS/Chloroform Gels

We examined the dependence of the anisotropy of NP (the smallest probe molecule in the present study) on the concentration of sPS in the sPS/chloroform gel. It can be seen in Figure 3 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% (wt/wt).[22] Any probe molecules remaining in region I should be mobile, thus their r values would be zero. Because the r values were not zero except the solution with $[sPS] = 0$, we conclude, then, that the observed polarized fluorescence must come from NP molecules located in region II in Figure 2.

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

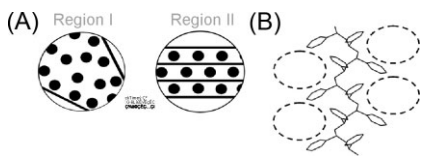

Figure 2.
(A) Scanning electron microscopy pictures of sPS/chloroform gel after freeze-drying. The scale bar indicates a distance of 100 nm. The inside of the gel can be divided into two regions, region I where solvent molecules (black circle) gather together and region II where sPS chains associate together. Solvent molecules can enter region II. (B) 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.

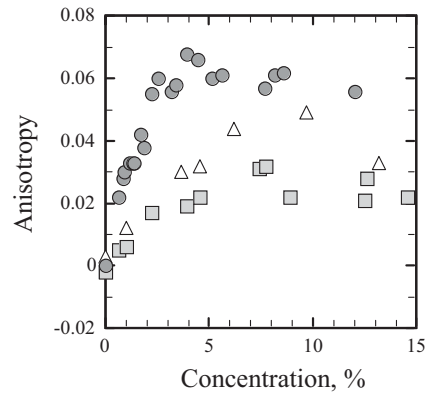

Figure 3.
sPS concentration dependence of anisotropy (r) of NP (●), MN (△), and DMN (■) in sPS/chloroform gels measured at 25 °C. The excitation wavelengths were 280 nm, 286 nm, and 290 nm, respectively.

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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 not due to the total free volume for NP able to enter being limited but rather due 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, notice that an sPS level of 4.5%(wt/wt) 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.

Figure 3 also shows the sPS concentration dependence of the anisotropy of MN and DMN in sPS/chloroform gels. Their behaviors proved to be similar to those of the NP molecules. Their r values increased 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 side-chain phenyl groups of the sPS are suppressed. Compared with their inherent r values (0.14), the values measured were quite small. Because the molecular sizes of MN and DMN should be smaller than those of NP molecules, this decrease in r is considered that the total amounts of MN and DMN molecules possible to enter region II are not so much. It was therefore assumed that many MN or DMN molecules are in region I.

On the contrary, 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. Because it is impossible for the largest AT molecules in the present work to move around in region II where even the smallest NP cannot move so freely, we can conclude that AT molecules cannot stay in region II. The free volume shown in Figure 2B is assumed to be not so roomy that AT molecules cannot remain.

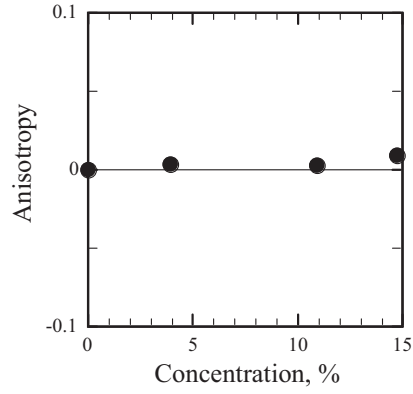

Figure 4.
sPS concentration dependence of AT anisotropy (r) in sPS/chloroform gels measured at 25 °C. The excitation wavelength was 342 nm.

iPS Concentration Dependence of Anisotropy of Naphthalene Derivatives and Anthracene in sPS/Chloroform Gels

Figure 5 demonstrates the isotactic polystyrene (iPS) concentration dependence of the anisotropy of NP and MN in iPS/trans- and cis-decalin gels.[23] Only NP molecules were found to show r values being not zero, but all the r values of MN, DMN, and AT turned out to be zero, meaning that these molecules are in region I where solvent molecules gather together. Thermoreversible gels of iPS/cis- and trans-decalin are concluded to consist of polymer-solvent molecular compounds between solvent decalin and 3_1-helical form of iPS.[24–27] Our photophysical measurements using intramolecular excimer formation have supported these structural models.[28] The results obtained for iPS/cis- and trans-decalin using the fluorescence depolarization method suggest that the free volume among iPS chains in region II is not so

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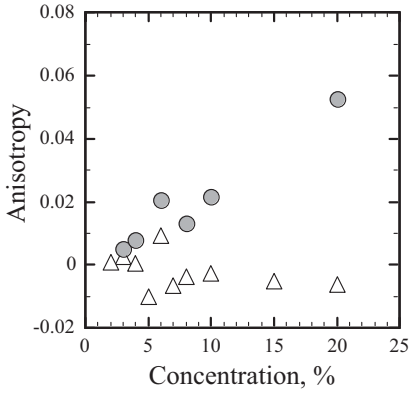

Figure 5.
iPS concentration dependence of anisotropy (r) of NP (●) in iPS/trans-decalin gels and MN (△) in iPS/cis- and trans-decalin gels measured at 25 °C. The excitation wavelengths were 257 nm and 281 nm, respectively.

roomy compared with the free volume among sPS chains in region II of sPS/chroloform gels. This is obviously based on the difference between the structures of sPS and iPS.

How Large is Free Volume Among sPS Chains in Gels and Solids?

Let us summarize our data. In region II of sPS/chloroform gels, there turned out to exist a distribution of free volume in an area where the sPS chains associate and into which molecules smaller than DMN are able to penetrate. However, AT molecules were found not able to penetrate into region II and to remain in region I where solvent molecules gather together. 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. Thus, we can conclude that the free volume between sPS chains in its chloroform gels is at most the space where DMN can stay but AT cannot stay. On the contrary, in region II of iPS/cis- and trans-decalin gels, there was found to exist a small free volume where NP molecules can remain but molecules whose sizes are larger than NP cannot remain: the free space among iPS chains is smaller than the molecular size of MN.

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,[29,30] are 147.6, 169.8, 192, and 197 cm^3/mol for NP, MN, DMN, and AT, respectively. 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).

It is quite interesting that sPS has five crystalline forms. In particular, δ[31] and ε[32] crystalline form have isolated cavities and channels, and their densities ($\rho = 0.98$ g/cm^3) are lower than that of the amorphous sPS ($\rho = 1.05$ g/cm^3). The δ form is monoclinic (space group $P2_1/a$; $a = 1.74$ nm; $b = 1.18$ nm; $c = 0.78$ nm; $g = 117^\circ$) and exhibit per unit cell two identical cavities centered on the center of symmetry and bounded by ten phenyl rings.[33,34] The volume of the cavity in the δ crystalline form is $\sim$120 $Å^3$ to 160 $Å^3$.[33,34] The molecular volumes of NP and AT are 127 $Å^3$ 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.

Considering these results from a different standpoint, the formation of the cavity in the δ-empty crystalline form of sPS solids is assumed to reflect the free volume between sPS chains in region II. The size of the cavity in the δ-empty form is consistent with that of the free volume obtained by our fluorescence depolarization method. It is needless to say that any iPS crystalline forms have no cavity such as δ- and ε- crystalline form of sPS solids.

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As a matter of fact, some of our fluorescent molecules doped into gels can be guest molecules clathrated with sPS δ-type crystalline form. Figure 6 shows a structural model of sPS/NP clathrate phase, whose unit cell is not too different from that of δ-empty crystalline form.[35] However, the crystal structure of sPS with 1,4-dimethylnaphthalene is monoclinic (space group $P2_1/a$; $a = 1.74$ nm; $b = 1.72$ nm; $c = 0.78$ nm; $g = 116.4^\circ$).[36] Note that only the value of b is one and half as much as that of δ-empty form as shown above. This structure is described as intercalates, because they present *ac* layers of polymer helices altered to layers of contiguous guest molecules and a guest/sPS monomer unit molar ratio of 1/2. The average volume of 1,4-dimethylnaphthalene is assumed to be just a little larger than DMN, 1,5-dimethylnaphthalene, which is a sort of limitation of molar size able to enter in region II. We have not examined so far whether 1,4-dimethylnaphthalene can actually stay in region II or whether DMN can be guest molecules clathrated with sPS without forming intercalate structure, however, it is assumed that the molecular size and shape of 1,4-dimethylnaphthalene and/or 1,5-dimethylnaphthalene is the limitation where the molecules can enter among sPS chains in gel or solution form and can be a guest clathrated with sPS to cocrystallize. This is supported by the case of AT: AT is impossible to cocrystallize with sPS[37] or has been reported to have the structure described as intercalate.[38]

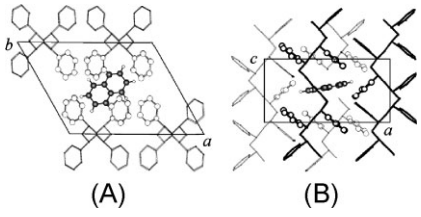

Figure 6.
A model of packing and unit cell for crystal structures of sPS/NP clathrate phase, presenting the calculated minimum energy location of naphthalene. In particular, the unit cells are shown for two different views, along *c* (A) and perpendicular to the *ac* plane (B). The ten phenyl rings which confine the cavity or the NP guest are represented by stick and balls.[35]

Conclusion

Our fluorescence depolarization method to estimate free volume in gels is found to be as efficient as our intermolecular excimer formation method.[39] In conclusion, we have demonstrated that (1) there exists a distribution of free volume in an area where the sPS chains associate (region II) in sPS/chloroform gels, (2) this free volume of the sPS gels is large enough that 1,5-dimethylnaphthalene are able to remain, (3) the size of the free volume between the iPS chains in iPS/cis- and trans-decalin gels is so small that only some portion of NP molecules can barely enter, (4) the size of the free volume between the polymer chains in gel form is a cause to produce a crystalline form with a cavity in sPS solids, and (5) the formation of cocrystals between sPS and guest molecules would be related to the free volume among sPS chains in gel form.

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