# The Role of Solvent Molecules in the Physical Gelation of Isotactic Polystyrene in *cis*- and *trans*-Decalin

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ABSTRACT: A fluorescence probe technique was applied to get information on the role of the solvent in the isotactic polystyrene (iPS−decalin) thermoreversible gel system. Fluorescence anisotropy values of naphthalene, 1-methylnaphthalene, 1,5-dimethylnaphthalene, and anthracene, which were dispersed in the iPS gel, were examined in detail while the concentration of iPS was changed. Probe molecules larger than naphthalene in molecular size were found to be mobile in the iPS gel, indicating that solvent molecules are mobile in the area where solvent gathers and that motion of solvents near the interface with iPS is not limited so much. However, naphthalene, the smallest probe molecule in the present work, showed higher values of fluorescence anisotropy in the iPS gel, and this effect increased with an increase in the concentration of iPS. From these results we conclude that there exists a free volume where naphthalene molecules can break in among iPS helical rods in an area where the iPS chains associate. This means that the possibility is very high for decalin molecules also to be incorporated into a polymer−solvent compound and that their motion is limited, because *cis*- and *trans*-decalin molecules are smaller than naphthalene in size. By means of this fluorescent method there is no large difference detectable among iPS gels formed with *cis*- and *trans*-decalin at concentrations below 20% (w/w).

## Introduction

Thermoreversible gels formed by quenching isotactic polystyrene (iPS) in decalin solutions[1] show typical properties of physical gels of synthetic polymers. Many authors have published papers concerning the gel structure and the mechanism of the gelation.[2] However, a certain aspect of the motion and the orientation of the solvent decalin in such gels is still poorly understood. The present paper deals with the motion and/or location of these solvent molecules by means of a fluorescent probe method.

Concerning the behavior of decalin in iPS gels, Sundararajan et al. suggested that solvation plays an important role in stabilizing a $12_1$ helix, which has near-extended tt chain conformation of iPS.[3] However, Guenet maintained through neutron diffraction experiments[4,5] that the gel structure in the nascent state is not a $12_1$ helix but a near-$3_1$ helical form that is solvated; this model is called a ladder like model.[5,6] In order to prove the appropriateness of the ladderlike model, Guenet and co-workers have presented many experimental results to support it.[2,7−9] However, Pérez et al.[10] demonstrated that the existence of a solvated crystal structure as the ladderlike model is unlikely on the basis of NMR findings that indicate high solvent mobilities and widely dispersed segment mobilities for iPS. Taking into account this mobility, Guenet and co-workers have modified their ladderlike model.[11] In the ladderlike model the chain−chain interaction was considered to be mediated by the solvent which is regarded as the rungs of the ladder. However, in the modified ladderlike model, the solvent does not mediate the interaction between chains but simply promotes the formation of near-$3_1$ helices that associate afterward. Thus, the solvent molecules are not so strictly trapped between two chains in the modified model.

By means of the fluorescence behavior of iPS, we first and directly observed the time change of the iPS chain structure;[12,13] it changes with time for 2 weeks at the gel transition temperature, and the time profile of iPS in *cis*-decalin was found to be different from that in *trans*-decalin and mixed decalin. Our results demonstrated that (1) the local motion of the iPS main chain is restricted to the helical structure and (2) the physical gelation of the iPS-decalin system takes place by the formation of nodes that are a kind of microcrystals made up of oriented helical rods and which can be a cross-linking point for the gel network.

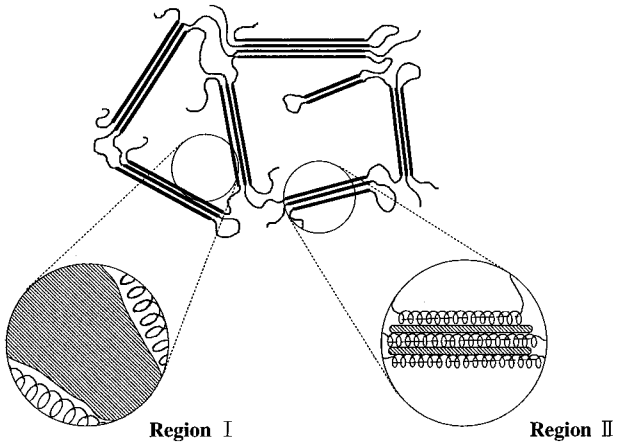


**Figure 1.** Sketch of the iPS chains in the gel form. The hatched areas represent the space in which solvent molecules can be located.

Figure 1 shows the possible location of solvent molecules within the gel. Region I is the area where solvent molecules gather, while region II is the area where helical rods of iPS associate together. We can assume another interface area among iPS chains and decalin molecules; however, it is difficult to distinguish it from region I. We have been interested in investigating whether or not solvent decalin can exist in region II and if solvent decalin can move around when in regions I and II or when in an interface region. In order to answer these questions, we applied a fluorescence probe method in the present paper, since this technique can be an effective tool for investigating the microstructures and motions of polymer molecules, especially because

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**Table 1. Anisotropy (*r*) of NP, MN, DMN, and AT in *cis*-decalin, PS, and PMMA**

| | *r* for given excitation wavelength (nm) | | | | |
|---|---|---|---|---|---|
| | 358 nm | 340 nm | 302 nm | 281 nm | 257 nm |
| NP in *cis*-decalin | | | 0.00 ± 0.01 | 0.00 ± 0.01 | 0.00 ± 0.01 |
| NP in PS | | | 0.15 ± 0.02 | 0.14 ± 0.02 | 0.00 ± 0.01 |
| NP in PMMA | | | 0.15 ± 0.02 | 0.14 ± 0.02 | 0.09 ± 0.03 |
| MN in *cis*-decalin | | | 0.00 ± 0.01 | 0.00 ± 0.01 | 0.00 ± 0.01 |
| MN in PS | | | −0.08 ± 0.02 | −0.07 ± 0.02 | 0.00 ± 0.01 |
| MN in PMMA | | | −0.09 ± 0.02 | −0.07 ± 0.02 | −0.05 ± 0.02 |
| DMN in *cis*-decalin | | | 0.00 ± 0.01 | 0.00 ± 0.01 | 0.00 ± 0.01 |
| DMN in PS | | | −0.09 ± 0.02 | −0.09 ± 0.02 | 0.00 ± 0.01 |
| DMN in PMMA | | | −0.11 ± 0.03 | −0.11 ± 0.03 | −0.08 ± 0.02 |
| AT in *cis*-decalin | 0.00 ± 0.01 | 0.00 ± 0.01 | | | 0.00 ± 0.01 |
| AT in PS | 0.27 ± 0.01 | 0.20 ± 0.01 | | | −0.11 ± 0.02 |
| AT in PMMA | 0.26 ± 0.01 | 0.19 ± 0.01 | | | −0.16 ± 0.02 |

it has the advantage of it being a high-sensitivity method.[14] Thus, we can get information on the microenvironment of the gel without giving any influence on the system even by the addition of fluorescent probe molecules.

## Experimental Section

Isotactic polystyrene used for the measurements is 90% isotactic with an $M_w$, the weight average molecular weight, of 400 000 (Scientific Polymer Products). Decalin was purified by passing it through a column packed with alumina (Wako Co.) to exclude any fluorescent impurities. *cis*-Decalin and *trans*-decalin were purchased from Tokyo Kasei Co., and their purities were more than 98%. Fluorescence probe molecules used in the present work are naphthalene (NP), 1-methylnaphthalene (MN), 1,5-dimethylnaphthalene (DMN), and anthracene (AT). iPS and probe molecules whose concentration was $3 \times 10^{-4}$ M were dissolved in decalin by heating the mixture in quartz cells at ca. 455 K for a few minutes. It is not facile to prepare an iPS solution with high concentrations in a quartz cell with an optical path length of 1 mm. However, we could mix a large amount of iPS with decalin in a Pyrex tube jointed to a cell. The concentration of iPS was limited to be at most 30% in order to prepare a uniform iPS solution. For experiments using the same fluorescence probe, the concentration of the probe was kept constant. The solutions in the cell were cooled in a refrigerator (250 K) for more than 4 days. The plastic solutions of fluorescent probe molecules were prepared on quartz disks by using a spin-casting method from a 10% tetrahydrofuran (THF) solution of poly(methyl methacrylate) (PMMA) or atactic polystyrene (PS) containing the above compounds and dried by extensive pumping under vacuum for more than 3 days at 60 °C.

Fluorescence spectra, fluorescence excitation spectra, and fluorescence polarization spectra were measured at 25 °C on a Hitachi F-4500 spectrofluorometer. Fluorescence measurements for the iPS−decalin gels were carried out in a quartz cell with an optical path length of 1 mm for their aerated solutions. A cell and a plastic film on a quartz disk were set at 45° to the exciting beam. Excitation wavelengths were 257, 281, and 302 nm for NP, MN, and DMN and 257, 326, 340, and 358 nm for AT. The values of anisotropy were determined by averaging the values for each 0.2 nm among 325 and 345 nm for NP, MN, and DMN and among 378 and 382 nm and among 398 and 403 nm for AT. We also employed a Hitachi automatic polarizer to measure the anisotropy of some probe molecules: the values were determined by averaging the values for 60 s at 325 and 337 nm for NP, 326 and 340 nm for MN, and 380 and 401 nm for AT. In order to ascertain the values, the measurements were repeated at least twice.

## Results and Discussion

**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 the motion of a chromophore is fast enough or the excitation energy can hop among the molecules, the anisotropy of the emission falls to zero.

We measured the anisotropy of probe molecules in PMMA and PS 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.[15] The values of *r* are summarized in Table 1. The molecular motion of a probe molecule is concluded to be suppressed in these plastic films, since the anisotropy value of a probe in PMMA precisely coincides with that in PS. Thus, the *r* values of probe molecules without molecular motion and energy transportation are determined to be +0.15 for NP, −0.08 for MN, −0.10 for DMN, +0.20 (excited at 340 nm), and +0.27 (excited at 358 nm) for AT when they are excited at each wavelength of their absorption peaks.

Note that the fluorescence of NP, MN, and DMN in PS excited at 257 nm, which is the UV absorption peak of PS, is perfectly depolarized. This is because the main species absorbing 257 nm light are not NP, MN, and DMN but PS, and there exist singlet energy migration among phenyl moieties of PS and energy transfer from PS to naphthyl moieties. On the contrary, since the extinction coefficient of AT is very large at 257 nm, the fluorescence of AT in PS is observed to be polarized.

Table 1 also demonstrates that all of the fluorescence of the probe molecules in *cis*-decalin solutions is 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.

**iPS Concentration Dependence of Anisotropy of MN, DMN, and AT.** We measured the fluorescence anisotropy of probe molecules that were mixed in a

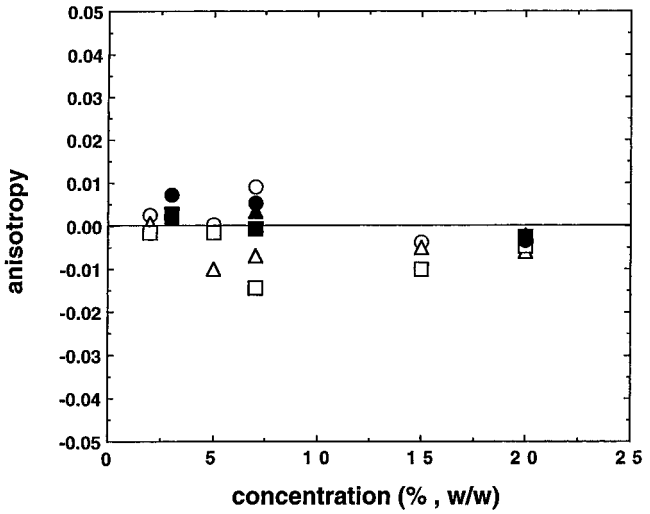


**Figure 2.** iPS concentration dependence of MN anisotropy, *r*, in the iPS−decalin gel measured at 25 °C: obtained for iPS in *cis*-decalin excited at 302 (○), 281 (△), and 257 nm (□), and for *trans*-decalin excited at 302 (●), 281 (▲), and 257 nm (■).

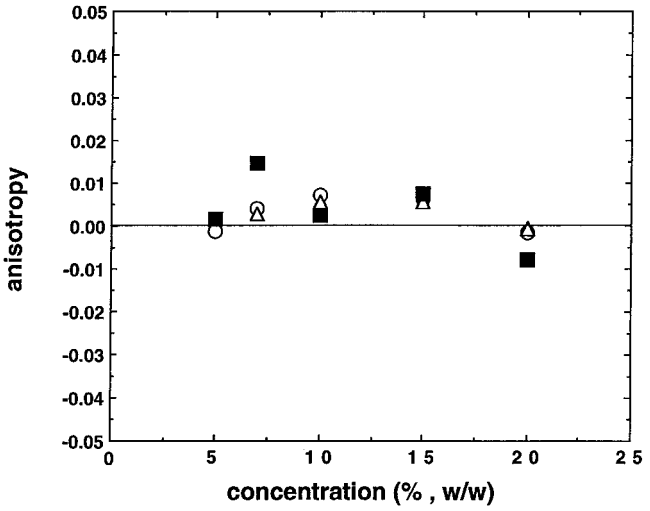


**Figure 3.** iPS concentration dependence of DMN anisotropy, *r*, in iPS/*cis*-decalin gel measured at 25 °C obtained by the excitation at 302 (○), 281 (△), and 257 nm (■).

decalin solution of iPS. The iPS−decalin system forms a gel at room temperature at concentrations greater than 1% (w/w). The fluorescence spectrum of MN in the iPS−decalin gel is perfectly identical with that in a fluid decalin solution without showing excimer fluorescence, indicating that probe molecules do not aggregate at all. Figure 2 shows the iPS concentration dependence of the anisotropy of MN in the iPS−decalin gel. The *r* values of MN are zero or very close to zero in comparison with its inherent anisotropy value (−0.08). There is no possibility that MN fluorescence is depolarized due to energy migration among MN molecules, because the concentration of MN is so low that excimer fluorescence is not detectable. Thus, MN molecules are mobile in the gels. It should be noted that there is no large difference of MN anisotropy between the iPS gels of *cis*- and *trans*-decalin below 20% (w/w) of iPS.

Next we consider where most MN molecules are. The fraction of region II ought to increase with an increase of iPS, although most solvent molecules are in region I at lower concentrations of iPS. Moreover, the values of *r* should be high, if MN molecules are in region II and suppressed by iPS chains. Therefore, it is considered from the results shown in Figure 2 that (i) MN

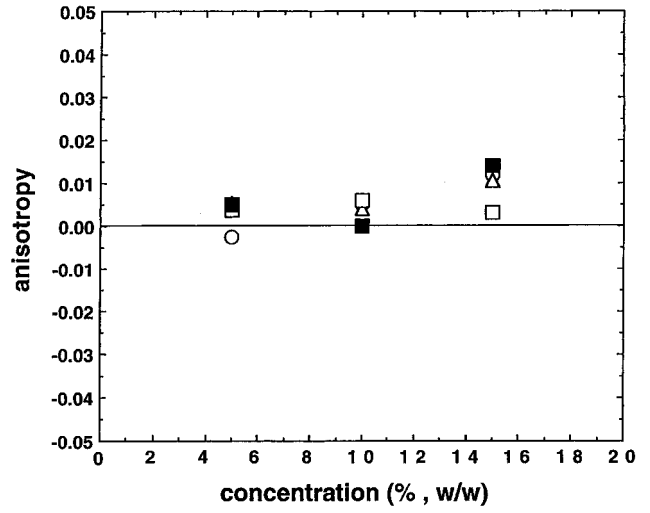


**Figure 4.** iPS concentration dependence of AT anisotropy, *r*, in iPS/*cis*-decalin gel measured at 25 °C obtained by the excitation at 358 (○), 340 (▲), 326 (□) and 257 nm (■).

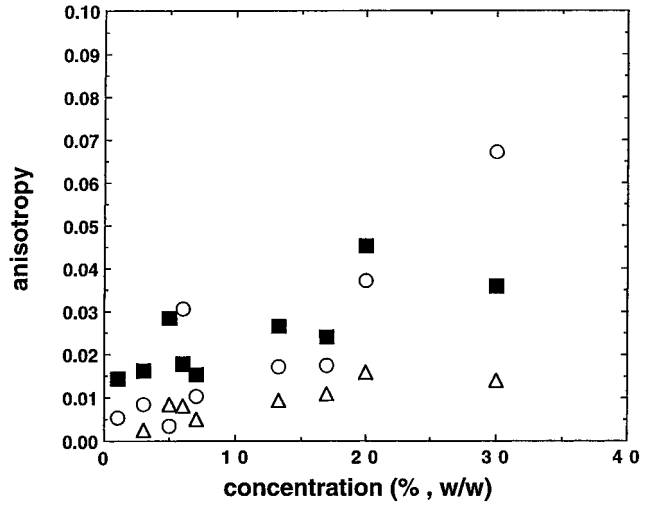


**Figure 5.** iPS concentration dependence of NP anisotropy, *r*, in iPS/*cis*-decalin gel measured at 25 °C obtained by the excitation at 302 (○), 281 (△), and 257 nm (■).

molecules staying in region I are mobile, that (ii) the number of MN molecules fixed by iPS chains in an interface area among iPS chains and the solvent is very small, and that (iii) MN molecules remaining in region II are not suppressed or no MN molecules exist in region II.

If probe molecules exist in the relatively large area of region I in Figure 1 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) the motion of solvents near an interface with iPS chains is not limited so much, because the *r* values do not increase with the increasing fraction of the iPS interface.

The average number of solvent molecules in one compartment of region I should decrease with an increase in iPS concentration; therefore, the possibility that both the solvent and probe molecules are fixed by the iPS chains would also increase. However, there is no remarkable change in anisotropy of MN up to 20% (w/w) of iPS. It is therefore concluded that the average volume of region I in Figure 1 is still much larger than the volume of an MN molecule.

We also examined the iPS concentration dependence of the anisotropy of fluorescent probes whose sizes are

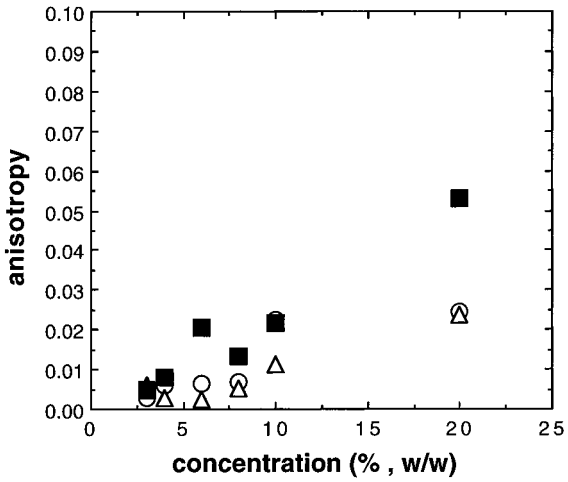


**Figure 6.** iPS concentration dependence of NP anisotropy, *r*, in iPS/*trans*-decalin gel measured at 25 °C obtained by the excitation at 302 (○), 281 (△), and 257 nm (■).

larger than MN in an iPS−decalin gel. The fluorescence spectra of these probes in the iPS gel precisely agree with those in fluid decalin, indicating that aggregation does not take place. Figures 3 and 4 show the anisotropy, *r*, of DMN and AT in iPS/*cis*-decalin gels, respectively. The figures suggest that the motion of these probe molecules is not suppressed below 20% (w/w) of iPS. Since these probe molecules are supposed to be surrounded by solvent molecules in region I, the mobility of the probe molecules indicates that most solvent molecules are mobile.

In conclusion, solvent decalin molecules in region I in Figure 1 are not fixed but can move freely.

**iPS Concentration Dependence of Anisotropy of NP.** Next we examined the iPS concentration dependence of the anisotropy of NP with a concentration identical with that of the other probe molecules in the iPS−decalin gel. The fluorescence spectrum of NP in the iPS−decalin gel is perfectly identical with that in a fluid decalin solution without showing excimer fluorescence, indicating that probe molecules do not aggregate at all. Figure 5, for iPS in *cis*-decalin, shows that the *r* values increase with an increase in the concentration of the polymer. This result was also ensured in the case of iPS in *trans*-decalin (Figure 6). The difference in structure between NP and MN is a methyl group only. Nevertheless, it is clear that the fluorescence of NP in the iPS gel form is polarized. It should be noted once again that a higher *r* value denies not only the existence of energy transport but also that of fast motion of the fluorescent molecules. Shown as above, probe molecules remaining in region I should be mobile. Since the molecular size of NP is smaller than that of MN, it is impossible to assume that NP molecules in region I are fixed very much. Thus, the polarized fluorescence must come from NP located in a different area from that of region I.

The smallest probe molecule, NP, in the present work showed higher *r* values, while larger probe molecules (MN, DMN, and AT) showed zero *r* values. It does not mean that a molecule in region II is mobile but rather that there are no larger probe molecules that can exist in region II. Thus, it is concluded that (1) among iPS helical rods in the area where some iPS chains associate and line up to become a node of the polymer network (region II), there exists a free volume where NP can break into and that (2) the motion of NP that is intercalated among the phenyl groups of iPS is very much suppressed. The total amount of NP that is intercalated into a node consisting of helical iPS chains should increase with an increase in the iPS content. Therefore, the apparent anisotropy value of NP in the gel would increase with increasing iPS: the *r* value of NP fixed completely is 0.15 (Table 1), while that of NP in region I is zero.

The reason that MN, DMN, and AT were not observed to be fixed in the gel is that these fluorescent probe molecules are so large that they cannot penetrate into region II. The discrete change between NP and MN demonstrates that the volume where small probe molecules can exist is limited.

Guenet and co-workers presented their ladderlike model[5,6] and the modified ladderlike model[11] as shown in Figure 7; the gel structure is a near-$3_1$ helical form that is solvated. To form a molecular compound shown in Figure 7, there should be a free volume where decalin molecules can enter among the phenyl groups of the iPS chains. Our fluorescence anisotropy method can demonstrate successfully that the free volume really exists. The size of NP is the same as that of *trans*-decalin: the distance between most separate hydrogen atoms is 0.73 nm for NP, 0.72 nm for *trans*-decalin, and 0.61 nm for *cis*-decalin. Thus, *cis*- and *trans*-decalin molecules are definitely able to penetrate into the location where NP molecules are fixed. This means that the possibility is very high for decalin molecules to be incorporated into a polymer−solvent compound as shown in Figure 7 in the area of nodes (region II in Figure 1). The distinct change of the anisotropy behavior between NP and MN

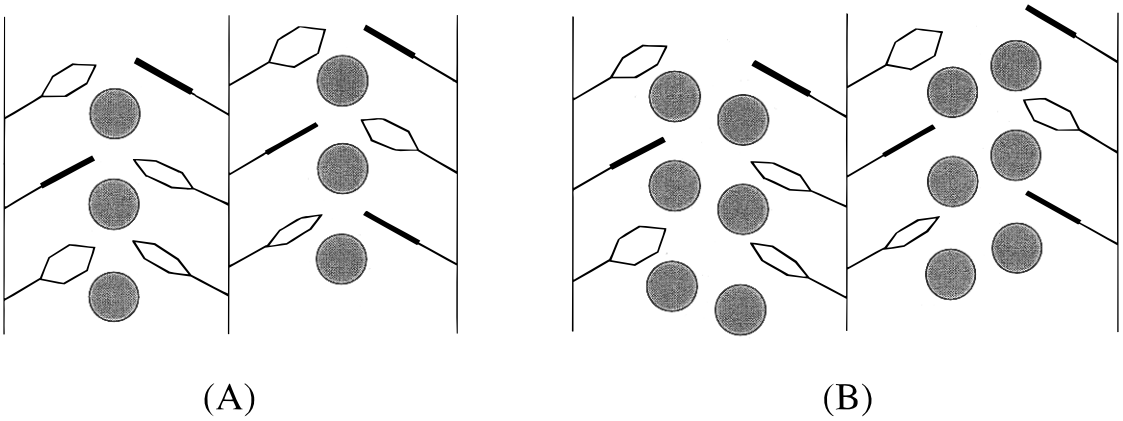


**Figure 7.** Schematic representation of the ladderlike model (A)[5,6] and the modified ladderlike model (B).[11] The black circles represent the solvent molecules. Each iPS molecule has a near-$3_1$ helix arrangement. Every third phenyl group of the middle chain is undrawn because it is situated in the back.

would support the existence of such a distinct structure: i.e., the free volume in region II is larger than the volume of NP and smaller than that of MN. However, we cannot determine strictly whether the solvent is trapped in the intralattice crystalline region (Figure 7A) or in the interlamellar region (Figure 7B). Our conclusion should be limited to the existence of a free volume that makes it possible for solvent molecules possible to remain in region II, although the position of black circles in Figure 7A is more preferable as the place where NP molecules are fixed.

In relation to a ladderlike model, we would like to point out our unexpected results; the *r* values of NP excited at 257 nm, which is the absorption peak of polystyrene, are not zero in iPS gel (Figures 5 and 6), whereas they are zero in PS film (Table 1). As explained above, energy migration among phenyl groups and energy transfer from PS to NP are considered to produce depolarized fluorescence of NP. However, the NP fluorescence was not depolarized in the iPS gel system, although there should exist both energy migration among iPS and energy transfer from iPS to NP when a phenyl moiety is excited. The most possible explanation is that the excitation energy absorbed by iPS is immediately transferred to NP without repeating steps of energy migration, because the average distance is short between the NP and phenyl groups of iPS. Thus, this depolarization behavior would be a further proof that some NP molecules remain in region II.

In conclusion, (1) a polymer−solvent compound is considered to be formed between iPS and *cis*- or *trans*-decalin as shown in Figure 7 (region II), and (2) *cis*- and *trans*-decalin can be replaced by NP because there exists a free volume where decalins and NP can break into the iPS gel. The content of the molecular compound increases with an increase in iPS up to 30% (w/w) in *cis*-decalin and 40% (w/w) in *trans*-decalin,[2,8] so the amount of NP substituted for decalin in the molecular compound increases with an increase in iPS.

Guenet determined the number of solvent molecules adsorbed per iPS monomer unit to be 1.89 for *cis*-decalin and 1.15 for *trans*-decalin by using differential scanning calorimetry.[5] This difference is supposed to be induced by the difference of molecular size between *trans*- and *cis*-decalin: the size of the free volume could be determined inherently by the association of helical iPS rods. When we observed the dynamic process of iPS gelation by monitoring excimer fluorescence,[13] the time constant of gelation in *trans*-decalin (35 h at 290 K for 1.4% (w/w)) is by far smaller than that in *cis*-decalin (92 h at 290 K for 1.4% (w/w)). It is reasonable to assume that it takes a longer time in the case of the *cis*-decalin gel, because smaller *cis*-decalin molecules are more mobile in a limited free volume in region II and the total amount of *cis*-decalin that is intercalated into region II is larger than that of *trans*-decalin.

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