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Physical Gelation Processes Revealed by Fluorescence Technique

Hideyuki Itagaki

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

Summary: The structure of an isotactic polystyrene (iPS) chain in its thermoreversible gel formed with trans- and cis-decalin was determined to be of 3_1-helical form or near 3_1-helical form by monitoring the fluorescence behavior of iPS. The fluorescence depolarization measurements of five fluorescent molecules having different molecular sizes doped into iPS in decalin clearly showed that there is enough space for decalin molecules to intercalate among the iPS helical chains. Our fluorescence data support the idea that a polymer-solvent compound that can be described by a ladder-like model is formed in iPS-decalin gels.

Introduction

The fluorescence probe method is a powerful and efficient technique to detect orientation, aggregation, or self-organization of molecules and/or groups in their microenvironments1,2). A fluorescent molecule or group can easily be labeled for periods as short as 10^{-9} to 10^{-7} sec only by irradiating them, and its behavior can be monitored directly and dynamically in this time range. Therefore, the fluorescence technique provides a nondestructive method to assess microscopic structure in polymer solids and/or polymer aggregation, and a method of dynamic measurement to trace chemical and physical changes such as gelation and liquid crystallization. Nevertheless, this technique has not yet been extensively or intensively applied to polymer science, because fluorescence behavior is not always related to changes of higher order structure and/or orientation of polymer molecules. However, it would be one of the most effective methods once some fluorescent behaviors can be matched to the structure or aggregation of molecules. This could be done by combining fluorescence measurements with other methods, such as x-ray structure analysis, nuclear magnetic resonance, infrared absorption, circular dichroism, and so on. In this paper, we demonstrate some successful examples of using the fluorescence method in gel systems. No other methods are currently capable of providing such information.

Horie et al.3) first applied fluorescence probe methods to polymer chemical gel systems. Since then, quite a few studies have investigated chemical gelation using fluorescence spectroscopy. Isotactic polystyrene (iPS) thermoreversible gels have been used as an example of a typical physical gel in more than 60 studies. In the first of these studies, Girolamo et al.4) demonstrated that quenching of a solution of iPS leads to a solution of a gel. However, since

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the regular structure of iPS chains in gel form has not yet been determined, many characteristics of iPS physical gels are still unclear.

Two basic models of the structure of iPS chains in decalin gels have been proposed: (i) a 12_1 helix form having an extended tt chain conformation[5-7)] and (ii) a near-3_1 (a ladder-like model[8-10)]) or a 3_1 helical (coiled-coil molecular model[11)]) form that consists of g^+t or tg^- conformers. In addition, some physical properties have been found to be distinctly different between gels prepared from cis- and trans-decalin solutions of iPS, although the values of the Flory interaction parameters, χ, are virtually identical for cis- and trans-decalin.

Here we summarize our results obtained with the fluorescent probe method for physical gels formed by iPS in cis- and trans-decalin, and try to draw some conclusions from our experimental data.

Experimental Part

The iPS used for the measurements is 90% isotactic, with a weight average molecular weight of 400,000. Cis- and trans-decalins were purified by passing them through a column packed with alumina to exclude any fluorescent impurities. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-3000 or F-4500 spectrofluorometer. Fluorescence measurements for the 1.4% iPS in decalins (mix, cis-, and trans-), which form 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. iPS was dissolved in decalin by heating the mixture at ca. 450 K for a few minutes. The sample temperature was controlled by an Oxford DN1704 cryostat with an ITC-4 digital temperature controller. Temperature regulation is easily better than ±0.1 K; independent temperature measurement was carried out by means of a second thermocouple and a potentiometer. All samples were kept at each set temperature and spectra were run repeatedly for quite a long time even after perfect duplication was obtained. Consequently it took 100 to 400 hours for the cooling process to reach the equilibrium state, while it took 10 hours at most for the heating process.

Results and Discussion

Photophysical Properties of Stereoregular Polystyrene and Oligostyrenes

An excimer is an excited dimer formed between two molecules of the same species: one is in the singlet excited state, while the other is in the ground state. An excimer turns into two molecules in the ground state after the deactivation of excited energy by either fluorescence or heat. Especially in the case of aromatic compounds, two aromatic groups in an excimer state are in parallel configuration within a distance of 0.35 nm. Thus an excimer is a good probe for getting information on local concentration, mobility, and orientation.

Many authors have reported intramolecular excimer formation in dilute solutions of vinyl polymers containing aromatic pendant groups. Fig. 1 shows the temperature dependence of fluorescence spectra of iPS in tetrahydrofuran (THF). The peaks near 285 and 330 nm have been assigned to phenyl monomer singlet emission and excimer emission, respectively. Intramolecular excimers in such polymer systems are formed between adjacent side-chain chromophores[12-14)] and their formation needs two important processes: one is the formation of excimer conformations (Fig. 2: tt in meso diad; g^-t/tg^- in racemo diad) by local motion, and the other is the influx of excitation energy into a preformed excimer conformation by singlet energy migration[15-17)]. In particular the former process suggests that the transient measurement of intramolecular excimer formation can be used as a direct measurement of dynamic local motion of macromolecules.

In order to elucidate local motion of polystyrene, we measured the dynamic process of intramolecular excimer formation in diastereoisomeric oligostyrenes as shown in Table 1[18-21)]. Table 1 shows the decay parameters obtained for diastereoisomeric oligostyrenes in degassed cyclohexane. Monomer fluorescence of all-racemic isomers was found to decay with a single exponential function: the overlap of the excimer fluorescence was taken into account in the fitting calculation.

$$I_M(t) = \exp(-t/\tau_1) \qquad (1)$$

while that of other isomers was found to decay according to the sum of two exponentials,

$$I_M(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \qquad (A_1 + A_2 = 1) \qquad (2)$$

The excimer dissociation is neglected in styrene oligomer and polymer systems, because the decay profiles of excimer fluorescence agreed very well with one another. Since each

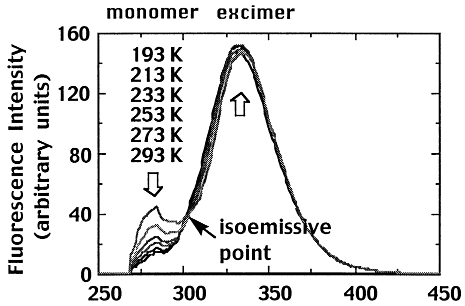


Fig. 1
Temperature dependence of fluorescence spectra of dilute iPS in degassed THF in the temperature region between 193 and 29 3 K (excitation wavelength is 259 nm).

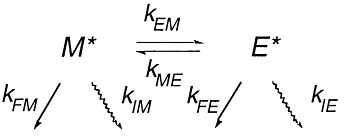


Fig. 3
Kinetic scheme of intramolecular excimer formation taking place in polystyrene. M* is a monomer singlet and E* is an excimer. k_{FM} and k_{FE} are the rate constants for the radiative deactivation from excited monomer and excimer state, respectively. k_{IM} and k_{IE} are those for the nonradiative deactivation, and k_{EM} and k_{ME} are those for excimer formation and dissociation, respectively.

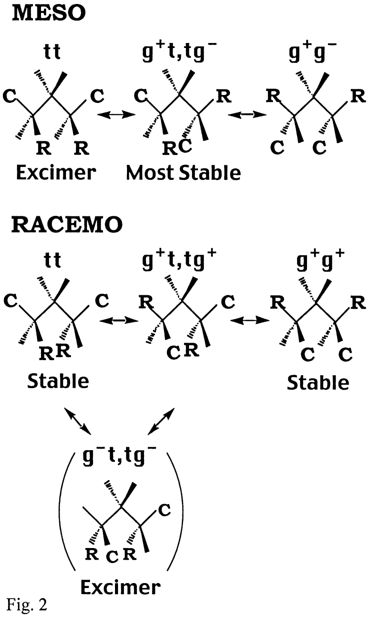


Fig. 2
The main conformational changes for meso (top) and racemic (bottom) diads of a vinyl polymer with side-chain aromatic groups (C, main chain; R, aromatic group).

integration ($\Sigma(A_i\tau_i)$) of monomer fluorescence decay corresponds to each peak in the photostationary fluorescence, the analysis must be acceptable. The kinetic scheme is shown in Fig. 3.

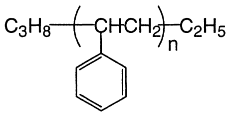
Since Longworth and Bovey's initial study[22)], several authors have reported that an excimer is more easily formed in meso than in racemic dimeric isomers. Almost all meso dimers are at the most stable ground state conformation (g^+t/tg^-) at the initial stage of excitation (Fig. 2). Here the excimer conformation (tt) is easily formed from the g^+t/tg^- conformation by a pathway with small steric hindrance. On the other hand, in the racemic isomers, the excimer conformers (g^-t/tg^-) cannot be formed from the most stable conformers (tt, g^+g^-) without passing over a higher rotational energy barrier.

The results for our oligostyrenes demonstrated that the efficiencies of excimer formation of all racemic isomers (r PS2, rr PS3, and rrr PS4) were far lower than those of the isomers with more than one meso diad. Under the assumptions that (i) the decay constant, $1/\tau_1$, is

Table 1
Decay parameters of monomer fluorescence of diastereoisomeric PS2, PS3, PS4 and atactic oligostyrenes (PS4 to PS) in degassed cyclohexane at 20°C. Fluorescence decays according to the equation $I_M = \sum A_i \exp(-t/\tau_i)$ where $\sum A_i = 1$.

sample	Ref.	A_1	τ_1 (ns)	A_2	τ_2 (ns)	k_{EM}[a] ($10^7 s^{-1}$)	$1/k_c$[b] (ns)
m PS2	18	0.3 ± 0.1	6 ± 1	0.7 ± 0.2	0.5 ± 0.2	13	7.7
r PS2	18	1.0 ± 0.1	11 ± 1	-	-	5.4	19
mm PS3	19	0.3 ± 0.1	4.0 ± 0.5	0.7 ± 0.2	0.5 ± 0.2	21	9.4
mr PS3	19	0.4 ± 0.1	4.0 ± 0.5	0.6 ± 0.2	0.4 ± 0.2	21	9.4
rr PS3	19	1.0 ± 0.1	7.4 ± 0.4	-	-	9.8	20
mmm PS4	20,21	0.4 ± 0.1	2.0 ± 0.4	0.6 ± 0.1	0.7 ± 0.2	46	6.5
mmr PS4	20,21	0.4 ± 0.1	2.0 ± 0.4	0.6 ± 0.1	0.7 ± 0.2	46	6.5
mrm PS4	20,21	0.3 ± 0.1	2.0 ± 0.5	0.7 ± 0.2	0.6 ± 0.2	46	6.5
mrr PS4	20,21	1.0 ± 0.1	2.0 ± 0.4	-	-	46	6.5
rrr PS4	20,21	1.0 ± 0.1	8.2 ± 0.5	-	-	8.5	35

[a] $k_{EM} = 1/\tau_1 - 1/27$ ns (cumene). [b] $1/k_c = k_{EM}/(n-1)$. (-) Not observable.



Structure of PS n

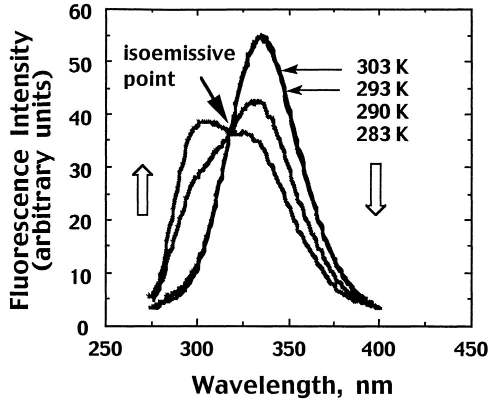


Fig. 4
Temperature dependence of fluorescence spectra of 1.4% iPS in aerated cis-decalin (cis-decalin gels) in the process of cooling from 303 K to 283 K (excitation wavelength is 259 nm).

expressed by the sum of k_{FM}, k_{IM}, and k_{EM} and (ii) the lifetime of cumene in cyclohexane (27 ns) can be substituted into the sum of k_{FM} and k_{IM}, we have obtained the values of rate constant of excimer formation, k_{EM}, to be $5.4\times10^{7}s^{-1}$ (r PS2, $1/k_{EM}$ = 19 ns), $9.8\times10^{7}s^{-1}$ (rr PS3, 10 ns), $8.5\times10^{7}s^{-1}$ (rrr PS4, 12 ns). The value of k_{EM} for rr PS3 is about twice as large as that of r PS2, while that of rrr PS4 is rather smaller than that of rr PS3. The increase in k_{EM} from r PS2 to rr PS3 appears to be reasonable because the possibility of excimer formation is proportional to the number of pairs capable of attaining the excimer conformer between two adjacent phenyl groups (r PS2, 1: rr PS3, 2). However, the decrease in k_{EM} from rr PS3 to rrr PS4 is in contrast with the change from mm PS3 to mmm PS4. This clearly suggests that in polystyrene it is not easily possible for a racemo diad to take an excimer conformer ($g^{-}t/tg^{-}$) due to the higher steric hindrance: the time required for a racemo diad to take an excimer conformer is at least 19 ns. Thus, our results have proved that the excimer is formed mainly as a meso diad, which coincides with the theoretical prediction.

In particular, the most important conclusion deduced from the results with PS3 and PS4 is that the phenyl groups do not rotate independently around the carbon-carbon bonds of the backbone chain, but rather their rotation involves a cooperative motion, such as a crankshaft transition[23,24)] or a three-bond jump motion[25)], in the backbone chain. As described above, the excimer is formed in a meso diad, thus, the excimer formation in mr PS3 and mrr PS4 would give information on the dynamic motion of the phenyl group in a meso structure of the trimer and tetramer, respectively. If side-chain groups could rotate around each carbon-carbon bond of the main chain independently, the efficiency of excimer formation in mm PS3 would be expected to be two times as high as that in mr PS3, and that in mmm PS4 to be three times as high as that in mrr PS4. However, the experimental results show that the longer time constants (τ_l) are identical among the trimers (mm and mr PS3) or the tetramers (mmm, mmr, mrm, mrr PS4). The fact that the efficiency of excimer formation depends not on the number of meso diads, but on the number of phenyl groups (or the number of bonds), indicates that conformational changes take place by a cooperative motion, since the frequency of a cooperative motion in a molecule should be proportional to the number of carbon-carbon bonds in the backbone chain.

Under the same assumption applied to the calculation for all racemic isomers, values of k_{EM} of the isomers having at least one meso diad are calculated and shown in Table 1. Since the number of pairs capable of attaining the excimer conformer of two adjacent phenyl groups is (n-1) for an n-mer (PS2, 1; PS3, 2; PS4, 3), we calculated by dividing each k_{EM} by (n-1) the values of rate constants for conformational change $((g^+t/tg^-)\rightarrow tt)$ for a meso diad by way of a cooperative motion (see $1/k_c$ in Table 1). This coincidence itself suggests the presence of a cooperative motion in the main chain.

Structure of isotactic Polystyrene in a Physical Gel Revealed by Fluorescence Measurements

We have clarified the formation process of intramolecular excimers in polystyrene systems and obtained information on the dynamic process of local motion. Then, we tried to observe the thermoreversible gelation process of iPS in decalin by monitoring polystyrene excimer fluorescence.

Fig. 4 shows the temperature dependence of fluorescence spectra of iPS in cis-decalin, which forms the gel. The fluid solution of iPS (Fig. 1) shows very strong excimer fluorescence, since the excimer is formed in the meso diad as described above: iPS has a stereoregular structure with all meso diads. However, once the gelation takes place, the formation of excimers, i.e., the local motion of side-chains, is restricted so much that a strong monomer fluorescence can be observed. We can present two explanations for why the formation of the helix structure restricts the local motion. First, a higher energy is required to change conformations when an oriented structure having a helical rod is formed, because the total energy of the helical form is thought to be low. Second, the conformational change takes place by way of cooperative motion of the polymer chain as described above. The formation of a helical form would restrain a diad, which is both in a helix and near the helix, from taking part in a cooperative motion of the chain.

Generally speaking, although the fluorescence probe method gives detailed information on the microscopic environment around a probe, it does not yield macroscopic information such as information on the structure. However, in the case of iPS gels, we found that we could obtain information on the structure of the iPS helix. At least we can state that strong excimer emission would be observed if a side-chain phenyl group in the 12_1 helical form rotates freely about the C_{α}-C_{para} axis. This is because almost all diads are in tt (excimer) conformers in the case of the 12_1 helical form and the free reorientation motion of phenyl rings in the tt conformer definitely forms an excimer with small energy. On the contrary, the excimer formation is restricted very much in the case of a 3_1 or near-3_1 helical form, since it needs the

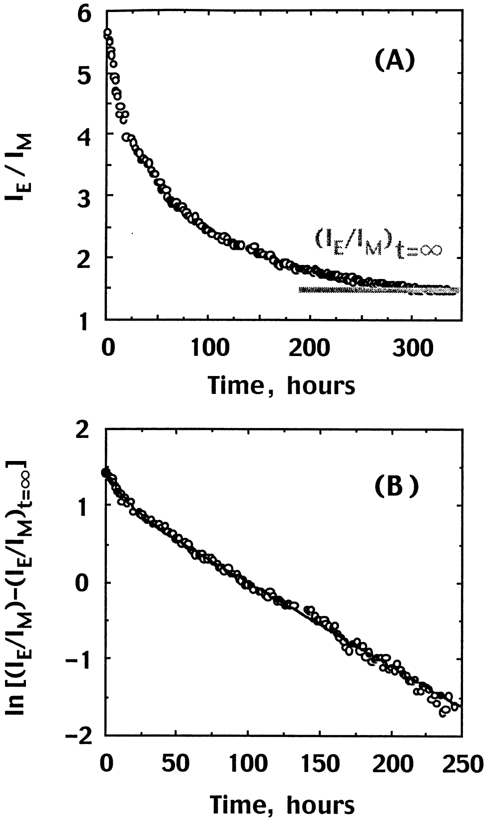


Fig. 5

Time dependence of excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated cis-decalin (cis-decalin gels) at 290 K (excitation wavelength is 259 nm). Variation of I_E/I_M (A) and $\log_e [(I_E/I_M) - (I_E/I_M)_{t=\infty}]$ (B) as a function of time; $(I_E/I_M)_{t=\infty}$ is the equilibrium value. The solid line in (B) shows a model curve of the sum of two exponentials ($[(I_E/I_M)(t) - (I_E/I_M)_{t=\infty}] / [(I_E/I_M)_{t=0} - (I_E/I_M)_{t=\infty}] = 0.68 \exp(-t/ 92\ \mathrm{hrs}) + 0.32 \exp(-t/ 11\ \mathrm{hrs})$).

conformational change from g^+t or tg^- to tt. Thus, our fluorescence data suggest that the 12_1 helix is not likely present in the nascent gel and a 3_1 or near-3_1 helical form is more probable. As a matter of fact, it took more than 2 weeks to obtain the data shown in Fig. 4. In the process of cooling down to 293K, the equilibrium is attained at least within several hours after setting a new temperature of the solution. However, the fluorescence spectra at 290K changed with time for 2 weeks. Fig. 5a shows the time dependence of the fluorescence intensity ratio of excimer, I_E, to monomer, I_M. The I_E/I_M was judged to reach the equilibrium value, $(I_E/I_M)_{t=\infty}$, after 300 hours, since the value of I_E/I_M did not change for 2 days. Fig. 5b shows the logarithm plot of $(I_E/I_M - (I_E/I_M)_{t=\infty})$ against time. This transient curve is found to be the best fit to the sum of two exponentials with time constants of 11 and 92 hours. It is clear that this fluorescence change is not due to a photochemical process, because Fig. 4 shows the isoemissive point. The data in Fig. 5 suggest that some physical properties are different between the nascent gel and the gel stored for some weeks.

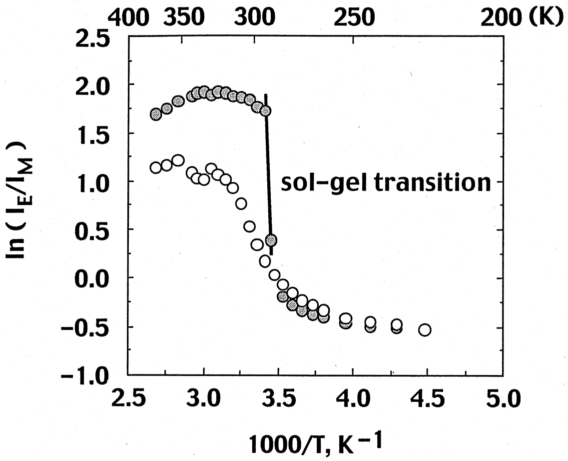


Fig. 6
Temperature dependence of excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated cis-decalin (cis-decalin gels); (●) cooling from 373 K to 223 K, (○) heating from 223 K to 373 K. All the I_E/I_M values are the equilibrium ones. The sol-to-gel transition is observed by cooling from 293 K to 290 K.

The time profile of iPS in cis-decalin was found to be different from that in trans- and mixed decalin: it was found to be a dual exponential function in cis-decalin, while it was found to be a single exponential in trans- and mix-decalin. Guenet[8)] 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, in order to present the proof of his ladder-like model where iPS and decalin forms a polymer-solvent compound. Thus, the difference of time profiles between trans- and cis-decalin is supposed to be induced by their difference of molecular size. 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 the molecular compound formed between iPS and decalin, and the total amount of cis-decalin that is intercalated into iPS helices is larger than that of trans-decalin.

Fig. 6 shows the temperature dependence of I_E/I_M of the 1.4% iPS in cis-decalin, which is obtained by the continuous measurements for a month from 373K to 223K and again from 223K to 373K. All the I_E/I_M values are of the equilibrium state. During the cooling process from 373K to 293K and the heating process from 333K to 373K, iPS-decalin is of the solution form. The continuous increase in I_E/I_M in the heating process to 328K indicates that the local motion that makes it possible to take an excimer conformation (tt) is released gradually although it is still of gel form. Accordingly, it should be stressed again that the strong excimer emission would be observed, if the helix structure of iPS in gel form were of the 12_1 helical form, because the 12_1 helical form consists of tt conformers which are the very excimer conformations.

Flory and coworkers[26)] carried out energy calculations for a separated iPS chain and demonstrated that tt conformation can be stable only due to the attractive interaction of

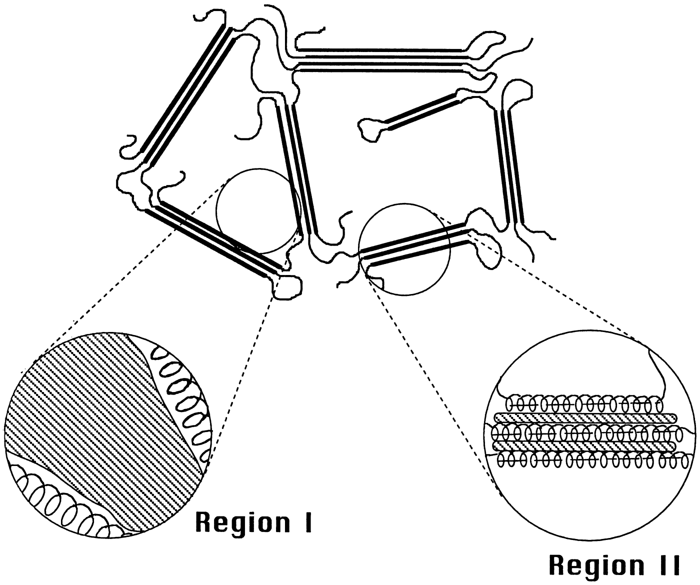


Fig. 7
Sketch of the iPS chains in the gel form. The hatched areas represent the space in which solvent molecules can be located.

neighboring phenyl groups. Since the distance between a pair of adjacent phenyl groups is less than 0.35 nm, if iPS molecules mainly take the 12_1 helical form, we should observe either an excimer or a ground state dimer of phenyl groups. In conclusion, the present fluorescence results showed that iPS molecules in gel form with decalin are of a 3_1 or near-3_1 helical form.

Existence of Polymer-Solvent Compound Revealed by Fluorescence Technique

So far, our results have been based on the inherent fluorescence of polystyrene. Next, we show our results obtained by doping some chromophores into the gel system, because certain aspects of the motion and the orientation of the solvent molecules in such gels are still poorly understood. Fig. 7 shows the possible locations 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 this interface area from Region I. We have been interested in investigating whether solvent decalin can exist in Region II or not, and whether solvent decalin can move around when it is in Region I and II or in an interface region. In order to answer these questions, we doped naphthalene (NP), 1-methylnaphthalene (MN), 1,5-dimethylnaphthalene (DMN), anthracene (AT), and pyrene (PY) into iPS-decalin gels uniformly and measured the iPS concentration dependence of their fluorescence anisotropy.

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 measurements of the emission anisotropy give information on molecular motions and/or energy transportation. The fluorescence anisotropy, r, is defined as

$$r = (I_p - GI_v)/(I_p + 2GI_v) \qquad (3)$$

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 doped in iPS-decalin with changing concentrations of iPS, after their inherent values were determined in plastic film where motion of probe molecules is completely restricted. The anisotropy values of MN, DMN, AT, and PY were measured to be zero even in gels formed with 20%(w/w) iPS (Fig. 8). Thus, probe molecules larger than NP in molecular size were found to be in the relatively large area of Region I in Fig. 7 where solvent molecules gather together, and their fluorescence anisotropy would reflect the motion of the solvent. Thus, it is concluded that (1) solvents in Region I are mobile, and (2) the motion of solvents near an interface with iPS chains is not greatly limited, because the r values do not increase as the interface area between iPS and decalin increases.

Next we examined the iPS concentration dependence of the anisotropy of NP with a concentration identical to that of the other probe molecules in the iPS-decalin gel. The data in Fig. 9, obtained with iPS in cis-decalin, show that the r values increase with an increase in concentration of the polymer. This result was also ensured in the case of iPS in trans-decalin. The structures of NP and MN differ by only a methyl group. Nevertheless, it is clear that the fluorescence of NP in the iPS gel form is polarized. It should be noted once more that a higher r value denies not only the existence of energy transport but also that of fast motion of the fluorescent molecules. As shown above, the 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 strongly fixed. Accordingly, the polarized fluorescence must come from NP located in a different area from that of Region I.

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 into which NP can enter, and (2) the motion of NP that is intercalated among phenyl groups of iPS is greatly 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 while that of NP in Region I is zero. This means that decalin molecules also can be incorporated among iPS chains in place of NP, 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).

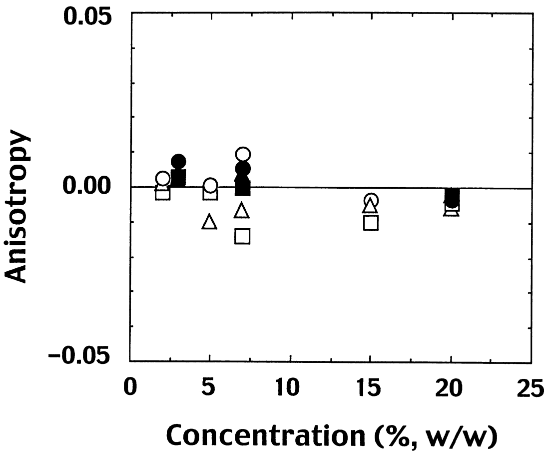


Fig. 8
iPS concentration dependence of MN anisotropy, r, in iPS/cis-decalin gel measured at 25 ° C obtained by the excitation at 302 nm (○), 281 nm (△), and 257 nm (■).

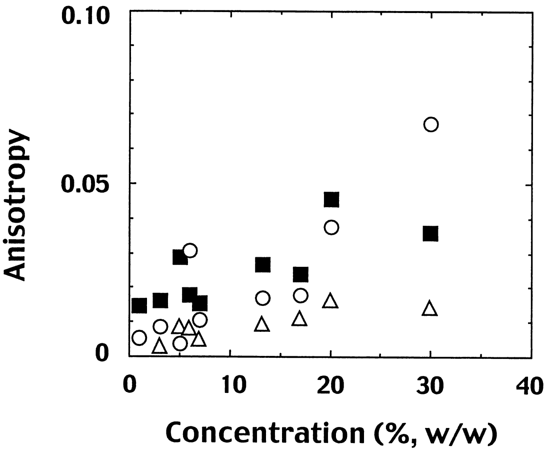


Fig. 9
iPS concentration dependence of NP anisotropy, r, in iPS/cis-decalin gel measured at 25 ° C obtained by the excitation at 302 nm (○), 281 nm (△), and 257 nm (■).

In relation to a ladder-like 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 an iPS gel (see Fig. 9) whereas they are zero in a PS film. As explained above, energy migration among phenyl groups and energy transfer from PS to NP is 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 probable explanation is that the excitation energy absorbed by iPS is immediately transferred to NP without repeating the steps of energy migration, because the average distance is short between NP and the phenyl groups of iPS. Thus, this depolarization behavior would be a further proof that some NP molecules remain in Region II.

In conclusion, our fluorescence results have clearly showed that (1) the structure of iPS chains in gels formed with cis- and trans-decalin is not of the 12_1 helix form but rather a 3_1 or near 3_1 helix form[27,28], and (2) decalin molecules can be intercalated between iPS helical chains[29], and that the possibility is very high for decalin molecules to be incorporated into a polymer-solvent compound.

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