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Helix–Coil Transition and Physical Gelation of Isotactic Polystyrene in *cis*- and *trans*-Decalin Monitored by Fluorescence Measurements

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ABSTRACT: The fluorescence behavior of isotactic polystyrene (iPS) in *cis*- and *trans*-decalin and mixed decalin solutions with some concentrations was measured continuously between 373 and 203 K. A hysteresis loop is observed for the temperature dependence of the fluorescence intensity ratio of excimer to monomer, I_E/I_M, in all the iPS solutions. In particular, I_E/I_M of iPS changes dramatically at temperatures where gelation takes place at high concentrations, and transition from random-coil to helix structure of the iPS chain takes place in dilute solution. It is concluded from the fluorescence data that the local motion of the iPS main chain is restricted in the helical structure. Consequently, the physical gelation of the iPS–decalin system is shown to take place by the formation of the nodes that are kinds of microcrystals made up of oriented helical rods and can be a cross-linking point of the gel network. The formation of helical rods appears to be urged favorably near nodes. Moreover, the time change of the iPS chain structure is first and directly demonstrated by our fluorescence method; it changed with time for 2 weeks at the transition temperature. The time profile of iPS in *cis*-decalin was found to be different from that in *trans*-decalin and mixed decalin, and the difference is due to the interaction between the helical structure of the iPS chain and the decalin isomer. The structure of the iPS chain is also discussed in the present paper.

Introduction

One of the big topics in the condensed polymer system is to clarify the formation mechanism of a thermoreversible physical gel. As a typical example of the physical gel, isotactic polystyrene (iPS) thermoreversible gel has been investigated intensively and has produced more than 60 reports so far since Girolamo et al.[1] first demonstrated that quenching of a solution of iPS leads to a solution of a gel. In relation to the formation mechanism of iPS physical gels, the temperature–concentration phase diagrams have been obtained and discussed by comparing them with theoretical ones: for iPS in *cis*- and *trans*-decalin, in 1-chlorodecane,[2,3] and in nitrobenzene.[4] However, since the regular structure of the iPS chain in gel form is not determined yet, many things about the iPS physical gel are still unclear.

Girolamo et al.[1] showed that the X-ray diffraction pattern of the gel has a meridional reflection of 0.51 nm spacing and a layer line distance of 3.06 nm without having any reflections due to the 3_1 helix that constitutes the usual iPS crystals.[5] Several authors showed by calculations that this reflection pattern was accounted for by the 12_1 helix that contains 12 monomers within the repeat distance of 3.06 nm.[6–11] In particular, Sundararajan et al. suggested that the solvation plays an important role to stabilize this 12_1 helix, which has a near-extended tt chain conformation of iPS.[12] However, the neutron diffraction experiments by Guenet[13,14] for the gel in the nascent state showed that the 0.51-nm reflection is not inherent of the iPS chain but of liquid *cis*-decalin. Thus, Guenet maintained that the appearance of the 0.51-nm reflection is caused by using the dried and the stretched gel and that the gel structure in the nascent state is not the 12_1 helix but a near-3_1 helical form that is solvated; this model is named as a ladderlike model.[14,15] In order to prove the appropriateness of the ladderlike model, Guenet and co-workers have presented many experimental results to support it.[2,3,16–22] However, Pérez et al.[23] demonstrated that the existence of a solvated crystal structure as the ladderlike model is unlikely on the basis of the NMR findings of high solvent mobilities and widely dispersed segment mobilities for iPS. Taking into account this mobility, Guenet and co-workers have modified their ladderlike model.[21] Recently, Chatani and Nakamura[24] proposed a coiled–coil molecular model to explain the 0.51-nm reflection observed for iPS dry gels: the coiled–coil chain is calculated to have basically the same 3_1 helical structure of the $(-TG-)_3$ conformation as in the usual iPS crystals, and the 3_1 helix axis itself again makes a large helix with a long pitch. However, this model is not definitive, since their samples are dried and stretched gels; there are some possibilities that drying brings the sample into the glassy domain in the phase diagram. Consequently, although it is still in the air to establish the structure of the iPS chain in the decalin gel, the models are summarized to two; (i) the 12_1 helix form having an extended tt chain conformation and (ii) the near-3_1 or 3_1 helical form that consists of g^+t or tg^- conformers (the ladderlike model and coiled–coil molecular model).

Meanwhile, the difference of some physical properties has been exhibited distinctly between the 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:[25] X-ray diffraction,[10] differential scanning calorimetry (DSC),[2,14,15,20] NMR,[23] and neutron scattering[17,20,21] together with the phase diagram.[2] Atkins et al.[10] demonstrated that (i) the X-ray diffraction pattern of *cis*-decalin gels is different from that of *trans*-decalin gels, (ii) the *trans*-decalin gel crystals can exist without solvent, while the *cis*-decalin gel crystals rely on the presence of solvent for their existence, and (iii) the DSC behavior of *cis*-decalin gels becomes different after

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complete removal of solvent. Klein et al.[21] concluded through the neutron scattering experiments that the rodlike portions are shorter in *trans*-decalin than they are in *cis*-decalin and that *trans*-decalin does not stabilize the helical form as efficiently as *cis*-decalin. We will compare the fluorescence behavior of *cis*- and *trans*-decalin gels in this paper.

We have studied molecular motion of polystyrene in dilute solution by using stationary and transient photophysical measurements.[26-33] Especially, from the systematic investigations on intramolecular excimer formation of polystyrene and its model stereoregular oligomers, we have clarified that (i) the excimer in polystyrene is formed mainly in meso diad, (ii) there definitely exists singlet energy migration, and (iii) the side-chain phenyl groups do not rotate independently around the carbon–carbon bonds of the backbone chain, but their rotation involves a cooperative motion of backbone chain bonds such as a crankshaft transition or a three-bond jump motion. Thus, there is a possibility that the photophysical technique would give important information on the microstructure and local molecular motion in reversible gels. To our knowledge, no paper has ever dealt with the dynamics of iPS chain motion except Pérez et al.[23] using NMR.

When we started with the project in 1991, no authors had applied photophysical measurements to the study on gels of iPS. However, except our group,[34,35] two groups have published reports about the fluorescence behavior of iPS thermoreversible gels. Wandelt and coworkers[36-38] measured the fluorescence of gel films of iPS in benzyl alcohol; however, the system is too complicated to discuss the gel properties because the emission of the solvent perfectly overlaps that of iPS. Berghmans et al.[39,40] reported the experimental results of the proper fluorescence measurements for iPS decalin gels, which agrees well with our preliminary results. However, our repeated experiments in the present paper clarified that the fluorescence of iPS changes with time even 2 weeks after the preparation of the gel. It means that we have to keep the iPS–decalin at each temperature for quite a long time in order to observe the temperature dependence of iPS fluorescence. Thus this is the first paper to directly observe sol–gel transition by monitoring the fluorescence of iPS, taking into account the time required for the attainment of the equilibrium state. Moreover, we will deal with the temperature dependence of dilute decalin solutions of iPS where gelation does not occur and observe coil-to-helix and helix-to-coil transition of the iPS chain. We believe that our fluorescence probe method gives precious information on the structure and formation mechanism of an iPS–decalin gel.

Experimental Section

Isotactic polystyrene (iPS) used for the measurements is 90% isotactic with M_w, the weight-average molecular weight, of 400 000 (Scientific Polymer Product). Decalin was purified by passing 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%. The mixture of *cis*-and *trans*-decalin (mixed decalin) used for the measurements was purchased from Aldrich, and the fraction of trans content was measured to be 53% using NMR after the purification. iPS was dissolved in decalin by heating the mixture at ca. 450 K for a few minutes. Concentrations of the iPS solutions were varied from 0.05 to 10% (w/w) in order to check whether the gelation takes place or not, and finally 1.4% was chosen for the present measurements because of securing the gelation and excluding the reabsorption effect during the fluorescence measurements. As a control experiment, the temperature dependence of fluorescence spectra of atactic polystyrene (aPS) (Tosoh, $M_w = 9.64 \times 10^4$, $M_w/M_n = 1.01$) was measured in degassed dilute mixed decalin and that of dilute iPS was also measured in tetrahydrofuran (THF). THF (Wako Co., spectrograde) was used without further purification. iPS and aPS dilute solutions were degassed by freeze–pump–thaw cycles under high vacuum.

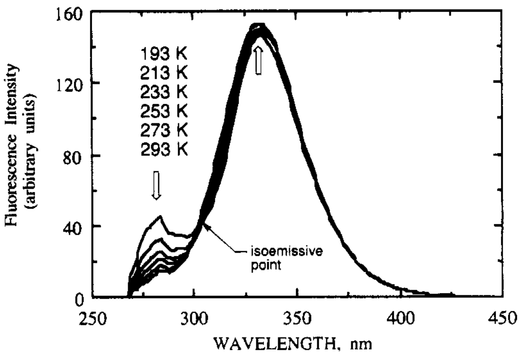


Figure 1. Temperature dependence of fluorescence spectra of dilute iPS in degassed THF in the temperature region between 193 and 293 K (the excitation wavelength is 259 nm).

Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-3000 spectrofluorometer and the emission signal was digitized and transferred into an NEC personal computer system. Fluorescence measurements for the 1.4% iPS in decalins (mixed, *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. All the dilute solutions of iPS and aPS were degassed and measured in a quartz cell with an optical path length of 1 cm. The difference of the $\ln(I_E/I_M)$ values between the dilute solution and the concentrated solution is due to the difference of the measurement methods. The dilute solutions were annealed above 450 K just before the fluorescence measurements. 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, since one of the main aims of the present work is to determine the time required for the equilibrium. Consequently, it took 100–400 h for the cooling process to reach the equilibrium state, while it took 10 h at most for the heating process. The excitation wavelength was chosen to be 259 nm.

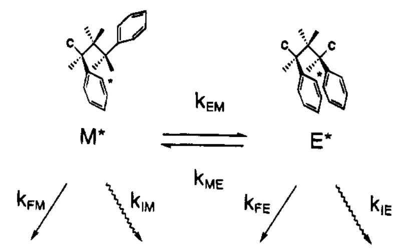
Results

Fluorescence Behavior of Dilute iPS in THF.

Figure 1 shows the temperature dependence (from 303 to 198 K) of fluorescence spectra of 0.05% iPS in THF. As a matter of course, the gelation does not take place in this solution. The peaks near 290 and 330 nm have been assigned to phenyl monomer singlet and excimer emission, respectively. Each fluorescence spectrum is reproducible and identical at each temperature for both heating and cooling processes.

The kinetics of excimer formation in the polystyrene system has been reported to obey the conventional model shown in Scheme 1. The monomer fluorescence of polystyrene is from the excited phenyl moiety in the g^+t or tg^- conformer, while the excimer fluorescence is from the tt conformer. The dissociation of excimer (k_{ME}) is known to be neglected below room temperature. Thus, the ratio of excimer fluorescence intensity, I_E, to

Scheme 1. Kinetic Scheme for Excimer Formation of iPS[a]



[a] M* and E* are the monomer singlet and excimer, respectively. C means the main chain. k_{FM} and k_{FE} are the rate constants for radiative deactivation from excited monomer and excimer states, respectively. k_{IM} and k_{IE} are those for nonradiative deactivation, and k_{EM} and k_{ME} are those for excimer formation and dissociation, respectively. The conformations of M* and E* correspond to g^+t/tg^- and tt.

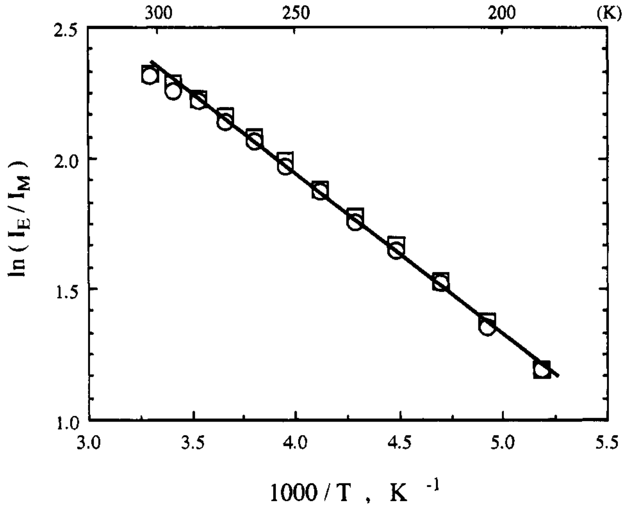


Figure 2. Temperature dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for dilute iPS in degassed THF: (○) heating from 198 K; (□) cooling from 303 K.

monomer fluorescence intensity, I_M, can be expressed as in eq 1.

$$I_E/I_M = k_{FE}k_{EM}/(k_{FM}(k_{FE} + k_{IE})) \tag{1}$$

Accordingly, I_E/I_M should be proportional to k_{EM}. Since k_{FM} and k_{FE} are considered to be independent of temperature,[41] the temperature dependence of I_E/I_M is assumed to be that of k_{EM}. Thus, an Arrhenius plot of I_E/I_M mainly gives the barrier energy (ΔE) to form an excimer conformation.

Figure 2 demonstrates the temperature dependence of I_E/I_M of 0.05% iPS in THF. It clearly shows that the value of I_E/I_M is constant for both cooling and heating processes. All reported I_E/I_M are the ratios of the intensity at the excimer peak to that at the monomer peak. A plot of $\ln(I_E/I_M)$ versus $1/T$ gives a straight line below 300 K and yields a value of 5.0 kJ/mol. The value of 5.0 kJ/mol is reasonable because (1) the barrier energy for excimer formation of aPS is reported to be 5.9 kJ/mol in a mixture of THF and diethyl ether (1:1)[42] and (2) the excimer of aPS is mainly formed in a meso (isotactic) diad.

In conclusion, the results of iPS in THF show that iPS readily forms excimer in the solution state, and the energy required for local motion from the most stable conformer (g^+t or tg^-) to the excimer conformer (tt) is small.

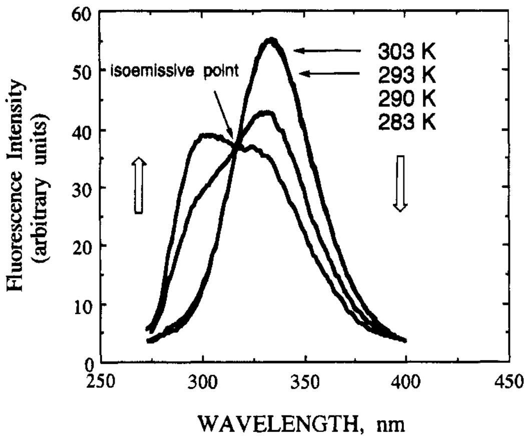


Figure 3. Temperature dependence of fluorescence spectra of 1.4% iPS in aerated *cis*-decalin (*cis*-decalin gels) in the cooling process from 303 to 283 K (the excitation wavelength is 259 nm).

Temperature and Time Dependence of Fluorescence of 1.4% iPS in *cis*-Decalin (*cis*-Decalin Gels). Figure 3 shows the fluorescence spectra of 1.4% iPS in *cis*-decalin which forms a gel. When 1.4% iPS in *cis*-decalin is cooled down, it perfectly remains in the solution form down to 293 K. The spectra were measured at 10 K intervals from 373 to 343 K and at 5 K intervals from 343 to 293 K. As shown in Figure 3, the spectra down to 293 K show the typical spectra of an iPS solution consisting of very strong excimer emission and very weak monomer emission. However, the fluorescence spectrum changes dramatically according to the gelation process which takes place near 290 K; i.e., the intensity of the excimer emission decreases, while that of the monomer emission increases very much. By taking 1.4% iPS in *cis*-decalin out of the cryostat and making an ocular inspection of it, we ascertained that it is of the gel form below 290 K by the above cooling method. Thus, Figure 3 shows that the fluorescence of iPS can be an effective probe to observe the gelation process. Below 283 K, the fluorescence spectra do not change very much with cooling.

As a matter of fact, it took more than 2 weeks to obtain Figure 3. In the cooling process down to 293 K, the equilibrium is attained at least within several hours after setting a new temperature of the solution. However, the fluorescence spectra at 290 K changed with time for 2 weeks. Figure 4A shows the time dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M: the I_M is the peak intensity of the monomer fluorescence, and the I_E is the excimer fluorescence intensity that is derived by subtracting the contribution of monomer fluorescence from the excimer peak intensity. We judged that I_E/I_M reached the equilibrium value, $(I_E/I_M)_{t=\infty}$, after 300 h, since the value of I_E/I_M did not change for 2 days. Figure 4B shows the logarithm plot of $I_E/I_M - (I_E/I_M)_{t=\infty}$ against time. This transient curve is found to be best fitted to the sum of two exponentials with time constants of 11 and 92 h. It is clear that this fluorescence change is not due to a photochemical process, because Figure 3 shows the isoemissive point. Figure 4 suggests that (1) some physical properties are different between the nascent gel and the gel stored for some weeks and (2) there exists two different modes of change process to attain the equilibrium gel form in the case of the iPS gel in *cis*-decalin. By the way, Figure 4 does not mean that the change in the gel structure reaches equilibrium within 350 h, but only means that it takes more than

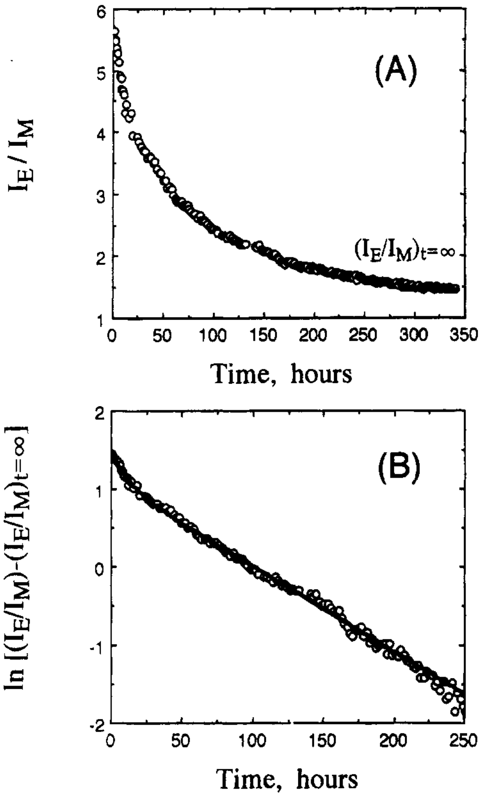


Figure 4. Time dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated *cis*-decalin (*cis*-decalin gels) at 290 K (the excitation wavelength is 259 nm). Variation of I_E/I_M (A) and $\ln[(I_E/I_M) - (I_E/I_M)_{t=\infty}]$ (B) as a function of time; $(I_E/I_M)_{t=\infty}$ is the equilibrium value. The solid line in B shows a model curve of the sum of two exponentials ($[(I_E/I_M)_t - (I_E/I_M)_{t=\infty}]/[(I_E/I_M)_{t=0} - (I_E/I_M)_{t=\infty}] = 0.68 \exp(-t/92\text{ h}) + 0.32 \exp(-t/11\text{ h})$).

300 h to observe the equilibrium value of I_E/I_M, whose change is related to the gel structure. Thus, it is possible that the change in the gel structure still proceeds very slowly over a month, although we cannot detect the slight change in the I_E/I_M value any more.

With regard to the time change of the physical properties of the iPS gel, Guenet et al. showed two experimental results: (i) the differential scanning calorimetry (DSC) thermogram of freshly formed gel is different from that of the gels after annealing at 18 °C for 4 weeks,[15] and (ii) the modulus increases upon aging for gels formed and aged at temperatures above 0 °C.[18] Our fluorescence method clearly and directly shows the transient change of iPS gels in detail.

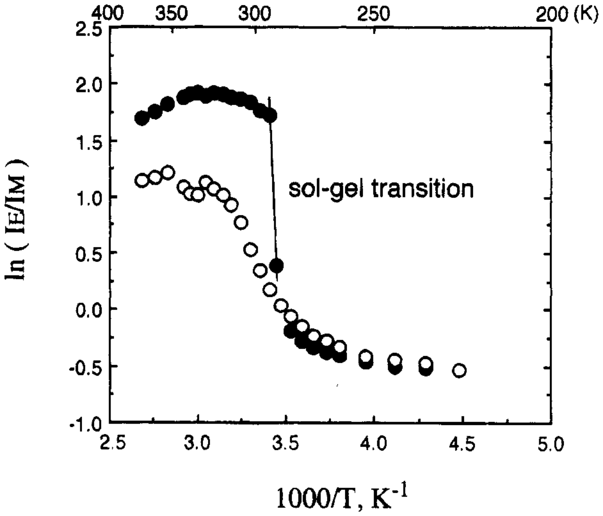


Figure 5. Temperature dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated *cis*-decalin (*cis*-decalin gels): (●) cooling from 373 to 223 K; (○) heating from 223 to 373 K. All the I_E/I_M values are the equilibrium ones. The sol-to-gel transition is observed by cooling from 293 to 290 K.

Figure 5 shows the temperature dependence of I_E/I_M of 1.4% iPS in *cis*-decalin, which is obtained by continuous measurements for a month from 373 to 223 K and again from 223 to 373 K. All the I_E/I_M values are of the equilibrium state. During the cooling process from 373 to 293 K and the heating process from 333 to 373 K, iPS–decalin is of the solution form. The convex curve of the cooling process among 373 and 293 K is not due to gelation or conformational change but is due to the dissociation process of excimer at high temperatures; k_{ME} cannot be neglected in this temperature region. In a gel form, the formation of excimer is restricted very much and the I_E/I_M is low. However, the I_E/I_M increases continuously with an increase in temperature up to 328 K, indicating that the local motion possible to form excimer conformation (tt) is released gradually although it is still of the gel form. Figure 5 demonstrates that (1) a hysteresis loop is observed in the iPS sol–gel transition, (2) the sol-to-gel transition against temperature is observable as the dramatic change of I_E/I_M at 290 K, (3) the gel-to-sol transition is not clearly observable, and (4) after a cycle of cooling and heating of iPS in *cis*-decalin, the value of I_E/I_M at 373 K is lower than the value of I_E/I_M that was first measured at 373 K before cooling.

Table 1 summarizes the temperatures where the dramatic change of I_E/I_M is observed and the time profiles of $I_E/I_M - (I_E/I_M)_{t=\infty}$ at these temperatures together with some reference values.

Temperature and Time Dependence of Fluorescence of 1.4% iPS in *trans*-Decalin (*trans*-Decalin Gels). Figure 6 shows the temperature dependence of

Table 1. Temperatures of Transition (Sol-to-Gel and Coil-to-Helix) Determined by the Fluorescence Measurements and Time Profile of $I_E/I_M - (I_E/I_M)_{t=\infty}$ at Temperatures Where Transition Takes Place

				time profile of $I_E/I_M - (I_E/I_M)_{t=\infty}$[c]				
sample	temp of transition (K)	T_{gel}[a] (K)	Θ_{point}[b] (K)	A_1	τ_1 (h)	A_2	τ_2 (h)	temp (K)
		Sol-to-Gel Transition						
cis-decalin gel (1.4%)	290	290	285	0.68	92	0.32	11	290
trans-decalin gel (1.4%)	293, 290	295	291	1.0	23			293
				1.0	35			290
mixed decalin gel (1.4%)	290			1.0	38			290
		Coil-to-Helix Transition						
cis-decalin solution (0.05%)	283		285	0.38	60	0.62	4.1	283
trans-decalin solution (0.05%)	278		291	1.0	21			278

[a] Temperature of gelation of 15% iPS–decalin detected by DSC.[2] [b] aPS in decalin.[25] [c] Time profiles are from the equation $[(I_E/I_M)_t - (I_E/I_M)_{t=\infty}]/[(I_E/I_M)_{t=0} - (I_E/I_M)_{t=\infty}] = \sum A_i \exp(-t/\tau_i)$ where $\sum A_i = 1$.

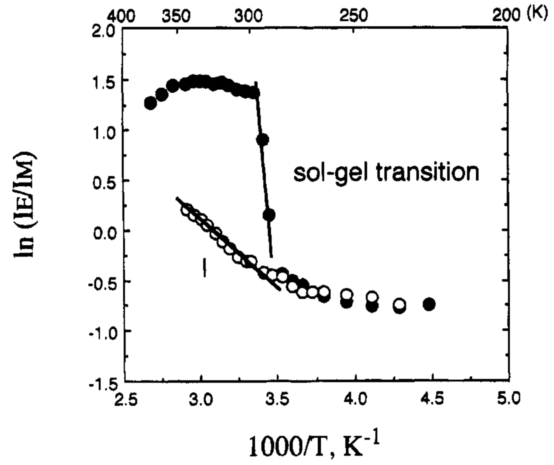


Figure 6. Temperature dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated *trans*-decalin (*trans*-decalin gels): (●) cooling from 373 to 223 K; (○) heating from 223 to 343 K. All the I_E/I_M values are the equilibrium ones. The sol-to-gel transition is observed by cooling from 298 to 290 K. A plot of $\ln(I_E/I_M)$ versus $1/T$ between 298 and 348 K (solid line I) yields a value of 11 kJ/mol.

I_E/I_M of 1.4% iPS in *trans*-decalin, which is obtained by continuous measurements from 373 to 223 K and again from 223 to 348 K at 5 or 10 K intervals. All the I_E/I_M values are of the equilibrium state. The temperature dependence of I_E/I_M of *trans*-decalin gels agrees well with that of *cis*-decalin gels (Figure 5) except some differences: (1) the remarkable change of I_E/I_M in the cooling process takes place at a little higher temperature (293 and 290 K) and the temperature range for the gelation is a little wider, (2) the change of I_E/I_M in the heating process is much slower, and (3) the I_E/I_M value after a cycle of cooling and heating processes is by far smaller than the first measurement value of I_E/I_M.

The largest difference observed in the fluorescence behavior between the *trans*- and *cis*-decalin gels is the time dependence of I_E/I_M at temperatures where the gelation takes place. The I_E/I_M value remarkably changes with time at 293 K until it reaches the equilibrium value. When iPS in *trans*-decalin is, furthermore, cooled down to 290 K, the I_E/I_M value still remarkably changes with time. Figure 7A shows the time dependence of I_E/I_M at 290 K; I_E/I_M reached the equilibrium value, $(I_E/I_M)_{t=\infty}$, after 110 h. Figure 7B shows the logarithm plot of $I_E/I_M - (I_E/I_M)_{t=\infty}$ against time. The transient curve is found to be best fitted to a single exponential with a time constant of 35 h. The same treatment for the time dependence of I_E/I_M at 293 K gives a single exponential with a time constant of 23 h. These results show that (4) there exists only one mode of change process to attain the equilibrium gel form in the case of iPS–*trans*-decalin gels, although there are two modes in the case of iPS–*cis*-decalin gels, and (5) the time required to the equilibrium state of the iPS–*trans*-decalin gels is by far shorter than that of iPS–*cis*-decalin gels.

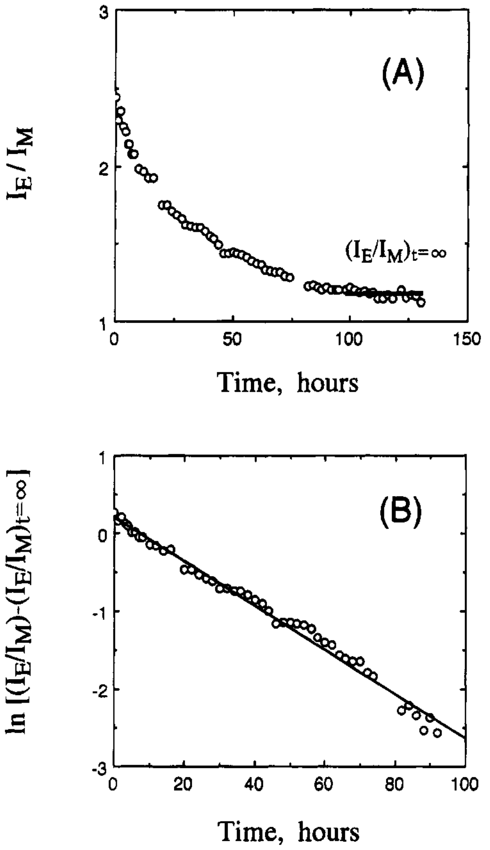


Figure 7. Time dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated *trans*-decalin (*trans*-decalin gels) at 290 K (the excitation wavelength is 259 nm). Variation of I_E/I_M (A) and $\ln[(I_E/I_M) - (I_E/I_M)_{t=\infty}]$ (B) as a function of time; $(I_E/I_M)_{t=\infty}$ is the equilibrium value. The solid line in B shows a model single-exponential curve ($[(I_E/I_M)_t - (I_E/I_M)_{t=\infty}]/[(I_E/I_M)_{t=0} - (I_E/I_M)_{t=\infty}] = \exp(-t/35\ \text{h})$).

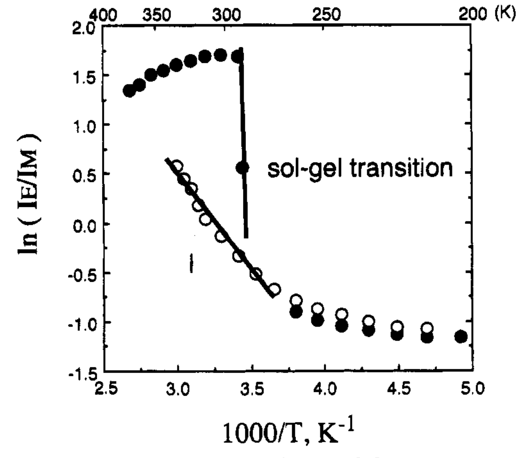


Figure 8. Temperature dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated mixed decalin (mixed decalin gels): (●) cooling from 373 to 203 K; (○) heating from 203 to 333 K. All the I_E/I_M values are the equilibrium ones. The sol-to-gel transition is observed by cooling from 293 to 290 K. A plot of $\ln(I_E/I_M)$ versus $1/T$ between 283 and 333 K (solid line I) yields a value of 17 kJ/mol.

Temperature and Time Dependence of Fluorescence of 1.4% iPS in Mixed Decalin (Mixed Decalin Gels). Figure 8 shows the temperature dependence of I_E/I_M of 1.4% iPS in mixed decalin, which is obtained by continuous measurements from 373 to 223 K and again from 223 to 343 K. We have already showed a similar hysteresis loop curve in our first published letter;[34] however, the old data were not perfectly correct since we kept the sample at each temperature for just several hours. Figure 9 shows the time dependence of I_E/I_M at 290 K together with the logarithm plot of $I_E/I_M - (I_E/I_M)_{t=\infty}$ against time. The transient curve is found to be best fitted to a single exponential with a time constant of 38 h. Although the mixed decalin used for the measurements consists of 53% trans isomer and 47% cis isomer, the fluorescence results demonstrate that the

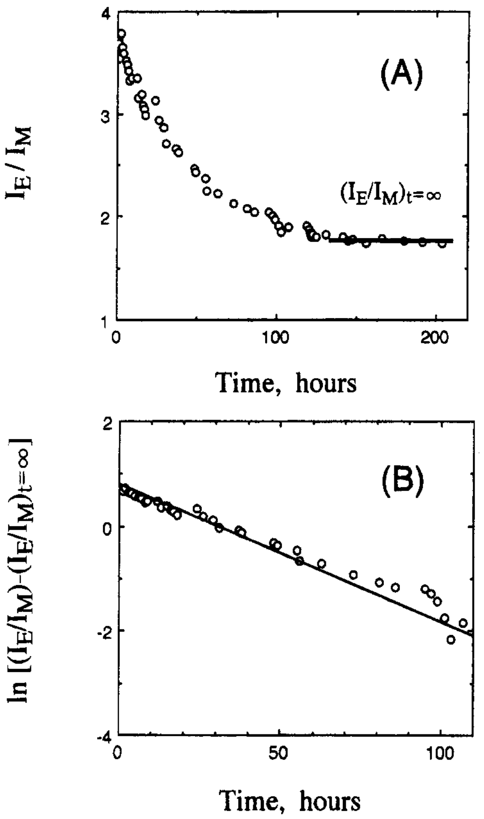


Figure 9. Time dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 1.4% iPS in aerated mixed decalin (mixed decalin gels) at 290 K (the excitation wavelength is 259 nm). Variation of I_E/I_M (A) and $\ln[(I_E/I_M) - (I_E/I_M)_{t=\infty}]$ (B) as a function of time; $(I_E/I_M)_{t=\infty}$ is the equilibrium value. The solid line in B shows a model single-exponential curve ($[(I_E/I_M)_t - (I_E/I_M)_{t=\infty}]/[(I_E/I_M)_{t=0} - (I_E/I_M)_{t=\infty}] = \exp(-t/38$ h)).

behavior of the mixed decalin gels in quite similar to that of the *trans*-decalin gels. This correspondence between the gels prepared from *trans*-decalin and mixed decalin solutions is also observed in the X-ray diffraction pattern.[10]

Temperature and Time Dependence of Fluorescence of Dilute iPS in *cis*-Decalin (*cis*-Decalin Solutions). The concentration of 1.4% was chosen for the fluorescence measurements of gels because of securing the gelation and excluding reabsorption during the measurements. Next, we measured the fluorescence behavior of a dilute decalin solution of iPS where the macroscopic gelation does not occur. We repeatedly measured the temperature dependence of I_E/I_M of iPS in *cis*-decalin: (i) cooling from 313 to 283 K, (ii) heating up to 303 K, (iii) cooling down to 243 K, (iv) heating up to 323 K, (v) cooling down to 243 K, and (vi) heating up to 320 K (Figure 10). Although the macroscopic gelation is not observed in the dilute *cis*-decalin solution, the fluorescence behavior is quite similar to that of iPS–decalin gels; i.e., (1) a hysteresis loop is observed in the cooling and heating cycle, (2) a dramatic change of I_E/I_M is observable in the cooling process, (3) the change of I_E/I_M is continuous in the heating process, and (4) the value of I_E/I_M of the sample once cooled is always lower than the value measured at the same temperature before cooling. In the case of a dilute *cis*-decalin solution, the remarkable change of I_E/I_M is observed at lower temperature (283 K) in the cooling process and the large change is also observed at 309 K in the heating process (process vi).

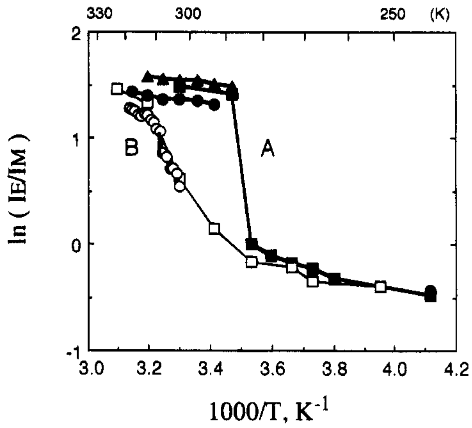


Figure 10. Temperature dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 0.05% iPS in degassed *cis*-decalin (*cis*-decalin solutions): (▲) first cooling from 313 to 288 K, (■) second cooling from 303 to 243 K, (□) heating from 243 to 323 K, (●) third cooling from 323 to 243 K, and (○) final heating from 243 to 319 K. All the I_E/I_M values are the equilibrium ones. A corresponds to a coil-to-helix transition observed by cooling from 288 to 283 K, while B corresponds to a helix-to-coil transition observed by heating from 308 to 309 K in the final heating process.

With regard to item 4, the difference of the I_E/I_M value before and after the cooling is not so large compared to that of the iPS–decalin gels. Since we wanted to observe the strict change of I_E/I_M with temperature, we kept the *cis*-decalin solution of iPS in the cryostat all through the fluorescence measurements as shown in Figure 10. After this measurement, we annealed the iPS solution at about 450 K for a few minutes and measured its fluorescence at some temperatures near 300 K. The I_E/I_M values were almost identical with those of the first measurement (process i).

Figure 11 shows the time dependence of I_E/I_M at 283 K (A) together with the logarithm plot of $I_E/I_M - (I_E/I_M)_{t=\infty}$ against time (B). The transient curve is found to be best fitted to the sum of two exponentials with time constants of 4.1 and 60 h. The function pattern of a dilute *cis*-decalin solution is identical with that of *cis*-decalin gels, although the time constants are relatively short. As described above, the physical properties of iPS gels are reported to change with time.[15,18] However, the information on the transient behavior of the iPS chain structure in a dilute solution is first demonstrated by our fluorescence method.

Temperature and Time Dependence of Fluorescence of Dilute iPS in *trans*-Decalin (*trans*-Decalin Solutions). The temperature dependence of dilute iPS in *trans*-decalin was measured only for the cooling process from 373 to 223 K and found to agree well with that of *trans*-decalin gels. The remarkable change of I_E/I_M in the cooling process takes place at 278 K, and the logarithm plot of $I_E/I_M - (I_E/I_M)_{t=\infty}$ against time at 278 K is found to be best fitted to a single exponential with a time constant of 21 h, which is shorter than the time constant of *trans*-decalin gels (35 h).

Temperature and Time Dependence of Fluorescence of Dilute aPS in Mixed Decalin. In order to observe the behavior of polystyrene or a styrene unit in a decalin solution, we measured the temperature dependence of dilute aPS in a degassed mixed decalin solution. The sample temperature was changed from 323 to 203 K at 5 K intervals. The sample remains as a transparent solution form down to 268 K; however, a turbid suspension appears below 268 K because of aPS becoming insoluble. Here no large increase in the

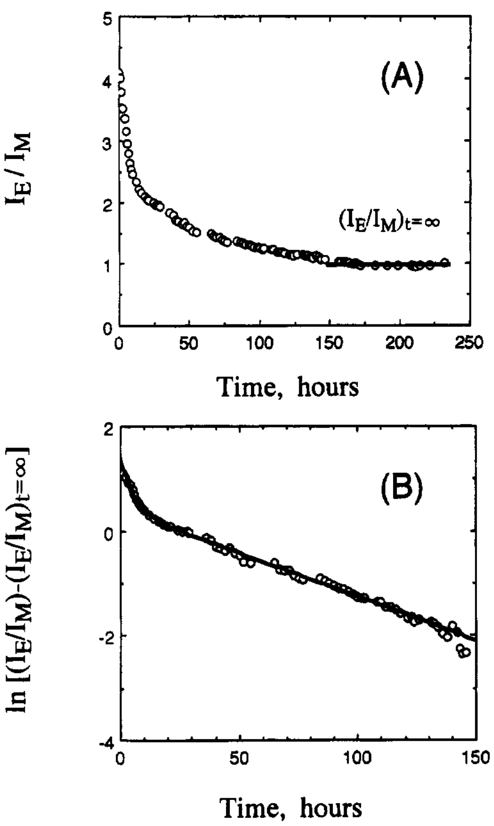


Figure 11. Time dependence of the excimer to monomer fluorescence intensity ratio, I_E/I_M, for 0.05% iPS in degassed *cis*-decalin (*cis*-decalin solutions) at 283 K (the excitation wavelength is 259 nm). Variation of I_E/I_M (A) and $\ln[(I_E/I_M) - (I_E/I_M)_{t=\infty}]$ (B) as a function of time; $(I_E/I_M)_{t=\infty}$ is the equilibrium value. The solid line in B shows a model curve of the sum of two exponentials ($[(I_E/I_M)_t - (I_E/I_M)_{t=\infty}]/[(I_E/I_M)_{t=0} - (I_E/I_M)_{t=\infty}] = 0.38 \exp(-t/60\ \mathrm{h}) + 0.62 \exp(-t/4.1\ \mathrm{h})$).

phenyl monomer fluorescence is observed. Rather a very slight increase in I_E/I_M is observed due to intermolecular excimer formation. The Arrhenius plot of I_E/I_M between 323 and 268 K gives a straight line like in Figure 2 with $\Delta E = 13$ kJ/mol, which is very large compared with dilute iPS in THF (5.0 kJ/mol).

Discussion

Meaning of the Change of I_E/I_M. iPS is known to be a polymer having strong excimer emission in a good solvent (see Figure 1), because iPS consists of only a meso diad where it readily takes an excimer conformer (tt) by local motion from a most stable conformer (g^+t or tg^-) with small barrier energy. Thus, the strong monomer emission observed in the iPS–decalin system should mean that the local motion is restricted very much and the fraction of tt conformer comes to be very small. This restriction of local motion is considered to be induced by the stereoregular polymer chain forming a sort of regular structure such as a helix, because the remarkable restriction of excimer formation at low temperatures is not observed both (1) in the case of iPS in a good solvent such as THF and (2) in the case of atactic polystyrene in a decalin solution.

We can present two explanations for the reason the formation of the helix structure restricts the local motion. First, it requires higher energy 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. We have already demonstrated in the polystyrene system that the phenyl groups do not rotate independently around the carbon–carbon bonds of the backbone but that their rotation involves a cooperative motion of backbone chain bonds.[29,30] 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. Thus, the conformational change is restricted in an oriented structure having a successive sequence of the same conformers (g^+t or tg^-).

On the other hand, the reason the excimer emission is still observed even in the gel form at low temperatures is that the sequence of the helical structure is interrupted by a racemo structure whose fraction is 10% in our iPS sample, and tt conformer in a meso diad is possibly taken in a part of the unfolding chain near racemo diads.

Several authors have presented the hypothesis about the structure of iPS in decalin. Their common conclusion is that iPS in a gel form has a helical structure, although the type of helix is still up in the air: (i) 12_1 helical form having extended tt chain conformation;[6-11] (ii) near-3_1 (Guenet's ladderlike model)[14,15,21] or 3_1 helical form (coiled-coil molecular model)[24] consisting of g^+t or tg^- conformers. With regard to ii, both the models are not conflicting with each other.

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 what the type of helix is. However, in our case, some room for discussion about the structure is left. 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 $C_\alpha - C_{para}$ axis. Because almost all diads are in tt (excimer) conformers, in the case of the 12_1 helical form and the free reorientational motion of phenyl rings in tt conformer possibly forms an excimer with small energy. In particular, once some parts of the 12_1 helical form are unfolded at higher temperatures, the excimer fluorescence should be by far stronger due to the effective migration of excitation energy into this excimer conformer (tt) in the unfolded chain. 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 conformational change from g^+t or tg^- to tt instead of the reorientational motion of the phenyl ring such as in the case of the 12_1 helix. Thus, unless the rotation of phenyl rings around the $C_\alpha - C_{para}$ axis is suppressed, our fluorescence data support recent papers reporting that the 12_1 helix is not likely in the nascent gel and a near-3_1 helical form is more possible.[2,3]

However, we have to emphasize that we do not conclude that the 12_1 helix does not exist or that a near-3_1 helical form is definitive. For example, there exists some possibilities that solvated solvent molecules could interfere with the excimer formation even if almost all diads are in excimer conformations (tt).

In conclusion, our data show either (1) the rotation of the phenyl rings is completely suppressed in the oriented structure of the iPS chains in a gel form or (2) the iPS chains in our gels are in a 3_1 or near-3_1 helical form if the phenyl rings can rotate even in a helix form. In the case of 1, it is not possible to draw any conclusions concerning the molecular structure of iPS from our data except the information on the strict limitation of the phenyl rotation.

Temperature Behavior of Dilute iPS in Decalins. The dramatic change observed at 283 K in Figure 10 is concluded to correspond to the transition from random-coil structure to a helix one of iPS in the cooling process, since the strong monomer fluorescence shows the formation of a helical structure and the restriction of the local motion. The reason a hysteresis loop is observed in dilute iPS in *cis*-decalin (Figure 10) is that the conformation is stuck in a helix form at low temperatures once a helical structure is formed, and it is not perfectly changeable until it is heated up above the temperature for a helical structure to be untied. The measurement for the heating process at 1 K intervals demonstrates that the transition from helix to random-coil structure takes place at 309 K in *cis*-decalin. By the way, we could not observe the dramatic changes along with the transition from the gel-to-sol.

After a cyclic process of the sample being cooled down and heated up, why is the I_E/I_M value at a temperature (>300 K) smaller than that of the first measurements? We believe that it is due to the association of helical rods followed by the formation of a node, which appears to be a part of the crystal structure. A helical rod of an isolated iPS molecule goes back to a random coil at temperatures higher than the temperature where the helix-to-coil transition takes place. However, if some helical rods encounter each other and line up to become a node by an interaction such as the van der Waals force, this association consequently becomes a sort of microcrystal. The energy required for breaking a node into some single helical rods should be higher than that for loosening a helical polymer chain to the random-coil form. In fact, the melting point of iPS is reported to be 480−495 K.[43] Since the helical structure taking part in the formation of a kind of microstructure is not untied and not loosened, the conformational change to tt (excimer conformer) is still restricted at temperatures as high as 330 K. We annealed the iPS solution, whose fluorescence was measured by the repeated cooling and heating, and ensured that the treatment to heat the solution up to 450 K can give the I_E/I_M value back to the value we obtained at the first measurement. The appropriateness of the assumption is demonstrated by the fact that the gap of the I_E/I_M value before and after the cooling is larger in the system of 1.4% iPS, where the gelation occurs, than in the system of dilute solutions: the possibility of the encounter and association of iPS depends on the concentration. We conclude that the gap of the I_E/I_M value before and after the cooling is proportional to the number of the nodes that are made up of the oriented helical rods.

One would suspect that the fluorescence change shown in Figure 10 corresponds to that of an iPS single chain. As described above, it is ascertained that the solution still contains aggregates even if it is diluted. Thus, it is basically impossible to experimentally show that the transition observed in Figure 10 takes place in a definitely isolated single chain. Our fluorescence measurements only show that the helix−coil transition occurs in a part of the iPS chain in both cases of the dilute solution and the concentrated solutions where gelation takes place. However, with regard to the cause of the change in the fluorescence behavior, we would like to stress that the aggregation is not as important as the helix−coil transition. In the case of the mixed decalin solution of 0.05% atactic polystyrene (aPS), the aggregation appears below 268 K by aPS becoming insoluble. Here no large increase in the phenyl monomer fluorescence is observed.

On the contrary, one might suspect the existence of the random-coil state. It is true that intramolecular excimer can be formed in a few diads of unfolded chain, meaning that the excimer formation does not require the helix-to-coil transition all over the whole chain. However, in dilute solution, we can expect the fraction of helix is low, because (1) the Rayleigh scattering decreases much only in the temperatures higher than 309 K and (2) the large increase in I_E/I_M at a temperature in the heating process is observed only in the dilute solution. Both facts could not be observed in the concentrated solutions where gelation takes place. Thus, we conclude that most parts of the iPS chains are of the random-coil form in dilute solutions at the higher temperatures. In opposition, the helix form would be still major in the concentrated solutions where gelation takes place: In fact, Guenet et al. showed by neutron scattering that there is no change of the chain conformation after gel melting.[21]

The present experiment does not give any information on the solvent; therefore, we cannot comment on the role of solvent on the transition from random coil to helix and from helix to random coil. Our data can never deny the existence of the solvated helix form.

Helix−Coil Transition Process and the Gelation Process of iPS in Decalin. We have shown that the temperature dependence of I_E/I_M of dilute decalin solutions (for example, Figure 10) is induced by the transition between helix and random-coil structures. Figures 5, 6, 8, and 10 show that the temperature dependences of I_E/I_M of decalin gels are the same as that of dilute decalin solutions. Thus, the gelation of the iPS−decalin system is concluded to be induced by the formation of helical rods and their association followed by the formation of nodes, since (i) the I_E/I_M value monitors the forming and loosening of the helical structure of iPS chains and (ii) the I_E/I_M value dramatically changes at a temperature where the gelation takes place.

In addition to this important conclusion, the temperature dependence of I_E/I_M can also give information on the gelation process itself. The difference in the fluorescence behavior between *cis*-decalin gels and solutions can be summarized as follows: (1) the inclination of I_E/I_M observed in the heating process is sharp for dilute solutions, while it is slow for gels, (2) the difference of the I_E/I_M value before and after the cooling process is small for dilute solutions, while it is very large for gels, and (3) the transition temperature observed for a gel is higher than that for a dilute solution: 290 K (gel) and 283 K (dilute solution) for *cis*-decalin and 293 K (gel) and 278 K (dilute solution) for *trans*-decalin. The results 1 and 2 suggest that the helical structure becomes fixed once the helical rods associate and form a node such as a microcrystal. The number of the nodes fixing helical rods is supposed to increase with an increase in the concentration. Moreover, on the basis of result 3, we can assume that the formation of helical rods is urged favorably near nodes and crystallization is promoted by the presence of nuclei. In other words, the formation of helical rods increases the nodes, while the nodes urge the formation of helix parts. This is considered to be the main reason for the gelation temperature being higher than the coil-to-helix temperature observed in dilute solution.

Time Dependence of the Helix−Coil Transition and the Gelation Process of iPS in Decalin. We have shown the time dependence of I_E/I_M at the temperature where the coil-to-helix transition (Figure 11) and the gelation (Figures 4, 7, and 9) take place. The features of the time dependence of $I_E/I_M - (I_E/I_M)_{t=\infty}$ are summarized as follows: (1) the time profile is different between the solutions of *cis*-decalin (dual exponential (Figures 4 and 11)) and *trans*-decalin (single exponential (Figure 7)), and (2) time constants for coil-to-helix transition (dilute solution) are shorter compared with those for gelation. We would like to mention that both the time profile and the time constant of 1.4% iPS in mixed decalin are precisely identical with those of 1.4% iPS in *trans*-decalin, while both are completely different from those of 1.4% iPS in *cis*-decalin. Atkins et al.[10] reported that the X-ray diffraction pattern of a mixed decalin gel agrees with that of *trans*-decalin gels while that of *cis*-decalin gels is different. Thus, the time profile should be related to the structural change of the iPS chain.

The dependence of $I_E/I_M - (I_E/I_M)_{t=\infty}$ on time means that it takes a long time for the iPS chain to settle down to the structure at the equilibrium state. It follows that some motion of iPS is possible even in the macroscopic gel form, since the change of I_E/I_M is exclusively induced by the change of the fraction of tt conformers. The transient behavior observed in dilute solution is thought to mainly reflect the behavior of a part of a single chain. Thus, we assume that the time dependence of I_E/I_M over 150 (in *trans*-decalin) to 250 h (in *cis*-decalin) is mainly due to the gradual curling of the helical structure. The requirement of long time to attain the equilibrium state might be due to the coexistence of left-handed helices and right-handed helices and/or the fixing of the racemo diad whose motion is free at the initial stage but comes to be restricted if both neighboring diads take part in each helical structure.

At high concentrations of iPS, the association of helical rods produces the nodes, which are cross-linking points of the gel network, and several diads near the nodes are urged to form a helical structure due to the tight fixing of the nodes. Thus, it is quite reasonable that the time constants for 1.4% solutions, where gelation occurs, are longer than those for dilute solutions, since the formation of a helical structure and node starts randomly at many locations when the concentration is high and a kind of reorientation would be necessary for reaching the most stable state.

Why the time profile of iPS in *cis*-decalin is different from that of iPS in *trans*-decalin and mixed decalin is a big question. Since the time profile is dependent on the formation process of the regular structure of the iPS chain, we assume that this difference is caused by the interaction of decalins with iPS molecules. Although both decalins have the same values of the solubility parameter,[25] their steric structures are quite different from each other. The distance between most separate carbon atoms is 0.52 nm for *trans*-decalin and 0.46 nm for *cis*-decalin, which is more compact than *trans*-decalin. We suppose that the shape and steric structures of *cis*- and *trans*-decalin influence the formation of the stable regular structure of the iPS chain.

It has already been demonstrated that the iPS chain forms different solvated helical structures in each decalin finally. Atkins et al.[10] measured the X-ray diffraction pattern of wet and dried iPS decalin gels. The completely solvent-free *trans*-decalin gels retained the corresponding gel pattern, however, the initially observed *cis*-decalin gel pattern disappeared and the Natta pattern (3_1 helix pattern)[5] took its place after the procedure to remove solvent. Thus, they concluded that the *trans*-decalin gel crystals can exist without solvent while the *cis*-decalin gel crystals rely on the presence of solvent for their existence. Regarding the nascent gel, Guenet et al.[2] demonstrate the temperature–concentration phase diagrams of iPS–decalin gels by means of DSC. Comparison between the phase diagrams revealed the difference between gels prepared from *cis*-decalin and *trans*-decalin. In fact, the shapes of the endotherms recorded on heating at different heating rates for both gels are different: one sharp peak with a broad small tail for the trans gel and two peaks for the cis gel. Guenet[14] 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 DSC in order to support the appropriateness of his ladderlike model.[13] All these data show that *cis*-decalin has a stronger interaction with iPS than *trans*-decalin does, no matter what the gel structure is. Moreover, Guenet and co-workers[20] concluded that there is an intermediate state between the gel and the crystalline state in *cis*-decalin solutions of iPS by the thermal, morphological, and structural investigations of iPS in decalin near the physical gelation threshold. In *trans*-decalin solutions of iPS, there was no intermediate state between the gel and the crystalline state. These experimental results are consistent with our time profile data.

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(43) We do not intend to assign the molecular structure to the 3_1 helix forms. It is just a trial to show how large the interaction energy among the iPS helical rods is.

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