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Reversed Thermal Behaviors of Poly[*N*-(1,3-dioxolan-2-ylmethyl)-*N*-methylacrylamide] and Its Cross-Linked Analogue in Liquids: Water vs Alcohols

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ABSTRACT: Thermal behaviors of poly(*N*-(1,3-dioxolan-2-ylmethyl)-*N*-methylacrylamide [DIOMMA]) and its cross-linked analogue in water or in alcohols have been studied by means of the cloud points (CP) in solutions, temperature dependences of the swelling of gels, and proton NMR spectra. We have deduced relationships between the line widths of proton NMR spectra and the intermolecular polymer−polymer, polymer−solvent, and solvent−solvent interactions. We have then integrated these qualitative relationships to formulate one consistent model. This model qualitatively describes the relative strength and the modes of three intermolecular interactions in water, methanol, or ethanol. Among the macroscopic properties, the CP in polymer solutions and temperature dependences of the swelling of the polymer gels have been elucidated on the basis of the above model. Transient NMR spectral changes observed in water and ethanol around the CP seemed to be caused by reduced motional averaging. This effect is probably associated with polymer aggregation processes, and it can be understood in terms of the state of intermolecular interactions described in the above model.

Introduction

Hydrogels of poly(*N*-isopropylacrylamide[NIPA]) exhibit drastic, thermally reversible volumetric changes in pure water at near 33 °C. For brevity, let these phenomena be called the volumetric phase transition of gels. Since the earliest study by Hirokawa and Tanaka[1] on the volumetric phase transition of NIPA gels, many articles on this subject have been published and recently summarized in a review by Schild.[2] The volumetric phase transition of gels is induced by changes 1) in temperature,[1] (2) in composition of solvents,[3−8] (3) in pH value, and (4) in other factors. The first two cases are as follows. (1) In thermally induced volumetric phase transitions, most macroscopic studies simply investigated how the total volume of gels changed with temperature in pure (a single component) solvent. The results were interpreted by predominantly focusing on differences in the polymer component of gels, even though the polymers only constitute a few percent of gels in weight, the remainder being water or other solvents. In these treatments, the solvents have been considered to act as a passive participant that merely provides an environment for polymers undergoing phase transition processes. (2) Regarding the second means, changes in the total volumes of gels[3−8] were investigated as a function of the composition of binary mixtures, mainly water and organic solvents such as methanol or acetone at one particular temperature. In these cases, the experimental swelling data[5] were theoretically interpreted, for example, in terms of the Flory−Higgins mean-field equation of state.[9] It should be noted that such an approach requires the "single liquid approximation" in which two different solvents are randomly mixed and selective bindings to the polymer are assumed to be absent.[9]

If the above two types of experiments are examined from both experimental and theoretical points of views, it is apparent that the volumetric phase transition has not been studied under one consistent and comprehensive approach. The volumetric phase transition is a physicochemical process. Thus, it is reasonable to think that both cross-linked polymer networks and solvent molecules will seek a state, in response to changes in temperature and/or in solvents. This state will thermodynamically be favorable to the *whole gel system*. Therefore, the nature of the volumetric phase transition of gels cannot be understood without fully appreciating the role of the molecular interactions between polymer and polymer (P−P), polymer and solvent (P−S) as well as solvent and solvent (S−S),[10] all at various temperatures. One of the major obstacles for studying three categorically different intermolecular interactions in the phase separation of polymer solutions, as well as the volumetric phase transition, is the lack of appropriate polymers and corresponding cross-linked analogues. It is most desirable, experimentally and theoretically, if new polymers exhibit thermally sensitive behaviors in various "single-component" solvents.

While investigating the thermal properties of polymers made of many alkyl derivatives of acrylamide, we found that a new polymer consisting of *N*-(1,3-dioxolan-2-ylmethyl)-*N*-methylacrylamide (DIOMMA) exhibits

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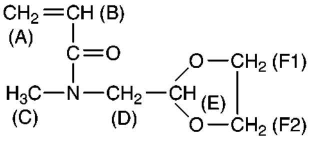
phase separations in either water or alcohols over narrow (few degrees) temperature ranges. In addition, gels of the cross-linked analogue have revealed thermally reversible volumetric changes in water as well as in alcohols, from near 0 °C to a few degrees below their respective boiling points. By using proton NMR spectroscopy, we have first studied how poly(DIOMMA) behaves in either water or alcohols in order to obtain information at the molecular level. Second, spectral profiles of proton NMR spectra have been examined in light of the physical characteristics of the nuclear magnetic dipolar interactions. We have deduced qualitative relationships between the temperature dependences of the line widths and the relative strengths (and the mode) of three intermolecular interactions, P−P, P−S, and S−S, for each solvent as a function of temperature. These qualitative results describing the relative strengths and modes of the intermolecular interactions were integrated to formulate one consistent model. On the basis of this model, we present an explanation of the reversed thermal (macroscopic) behaviors of poly(DIOMMA) and its cross-linked analogue, in water vs that in alcohols. This discussion naturally refers to the role of solvent molecules in phase separation and in volumetric phase transition processes.

Experimental Procedures

1. Monomer Preparation. DIOMMA was synthesized from the following scheme

$$CH_2{=}CHCOCl + NHR_1R_2 + (C_2H_5)_3N \rightarrow CH_2{=}CHCONR_1R_2 + [(C_2H_5)_3N]HCl$$

where $R_1 = CH_3$ and R_2 = 1,3-dioxolan-2-ylmethyl. The reaction was carried out near 0 °C in toluene as solvent. After toluene was removed from the reaction mixture under vacuum, a distillate at 117 °C under 1 mmHg was collected. Next, by means of mass spectrometry as well as IR and proton NMR spectroscopic analyses, the chemical formula of the monomer thus synthesized was identified as



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2. Polymer Preparation. An aqueous solution (61 mL) (O_2-free) of the monomer (2.78 g) was mixed with ammonium persulfate (APS; initiator, 0.01 g) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED; accelerator, 0.02 g). The polymerization was carried out in a sealed tube at 30 °C for 1 h under reduced pressure. Poly(DIOMMA) thus synthesized was then precipitated by slowly pouring the reaction mixture into cold methanol (10 °C), separated by filtration, washed with a large volume of cold methanol, and dried under vacuum. The crude polymer in the form of powder was dissolved in water and dialyzed against a large amount of pure water. The final specimen of poly(DIOMMA) was obtained by lyophilizing the dialyzed solution and then drying the lyophilized polymer under vacuum at 50 °C for 2 days.

3. Gel Preparation. DIOMMA(11.1 g), *N*,*N*′-methylenebisacrylamide (BIS; cross-linker, 0.13 g), APS (0.13 g), and TMED (0.02 g) were dissolved in pure water (89 mL). This pregel solution (15 mL) was transferred to a test tube containing capillaries (0.7 mm ID) and degassed by repeating the freeze−pump−thaw cycles. The gelation was initiated by heating the pregel solution to 30 °C and then continued at 30 °C for 3 h. After completion of gelation, the cyclindrical gels were taken out of the capillaries and used for the swelling experiments, while the rest (bulk gel) was ground to serve as the NMR samples. Each of the gel samples was purified by repeated processes of swelling and deswelling performed in cold (5 °C) and hot (80 °C) water, respectively. The purification was completed when total organic carbon (TOC) was not detected in the washings [with a Beckman TOC analyzer (Model 915B)]. The purified gel was lyophilized and then dried at 50 °C for 3 days under reduced pressure.

4. Determination of Cloud Points and Swelling Degree. The cloud point (CP)[12] was determined by using 1% (w/v) polymer solutions. Transmittance (%) of the polymer solution at 500 nm was recorded by either raising or lowering the temperature at a rate of 1 °C/min. The CP was defined as the temperature at which the transmittance dropped to 50%. The measurements were carried out by using a photometer (Shimadzu Seisaku-sho, Model UV-240) equipped with a thermoregulator.

The degrees of swelling of gels in water or alcohols were determined by measuring the diameters of tiny cylindrical gel pieces as a function of temperature. Gel pieces were immersed in a chosen solvent, subjected to repeated cycles of swelling−deswelling by varying temperature, and then inserted into micropipets with fresh solvent. Both ends of a micropipet were sealed off with a gas flame after freezing the content with liquid nitrogen. The size and shape of a gel piece were monitored with an AVEC image processor (Hamamatsu Photonics, Model C1966). The temperature was maintained to within ± 0.1 °C by circulating water around the cell containing the gel pieces.

5. NMR Experiment. The instruments (housed at the Francis Bitter Magnet Laboratory, MIT) were two homemade multinuclei, Fourier transform, pulsed NMR spectrometers operating at 360 and 500 MHz for proton. Typical 90° pulse widths for proton were 15 and 10 ms at 360 and 500 MHz, respectively.[13] The temperature of the sample was maintained to within less than ±0.1 °C by cryostatic gas flow. To confirm establishment of the phase separation or transition, polymer solutions or gel samples were left overnight (at least 12 h) in the RF probe at temperatures slightly above or below the respective CP or phase transition temperatures. The solvents used in the NMR experiments were fully deuterated chemicals obtained from commercial sources and used without further purification. The atomic deuteron contents (%) in water, methanol, and ethanol were 99.7, 99.9 and 99.0, respectively.

The water (D_2O) and alcohol (CD_3OD or C_2D_5OD) solutions containing a few % (w/w) of poly(DIOMMA) were inserted into 5 mm NMR tubes and degassed thoroughly by repeating the freeze−pump−thaw cycles at least 8 to 10 times. The gel samples were prepared in 5 mm NMR tubes as follows: (1) an appropriate amount of the lyophilized gels was weighed into a 5 mm NMR tube; (2) thoroughly degassed O_2-free solvent was distilled over the gel under vacuum; (3) the tube was filled with O_2-free N_2 gas to about 710 mmHg; (4) the tube was sealed off by a gas flame. All gel samples contain excess amounts of pure solvents.

Experimental Results

1. Poly(DIOMMA) Dissolved in Water or Alcohols. Temperature-Induced Phase Separation of Polymers. An abrupt decrease in the transmittance of 1% aqueous solution was observed at 49.5 ± 0.5 °C (CP) when raising the temperature. In contrast, lowering temperature caused phase separations in alcohol solutions. The CP in methanol and ethanol were 23.5 ± 0.5 and 52.5 ± 0.5 °C, respectively. It is important to mention that the phase separation in alcohol solutions occurred in a completely reversed way to that found in the aqueous solution. Since a small and gradual decrease or increase in the transmittance extended over another 2−3 deg below or above the CP, the actual completion of the phase separation processes seems to occur over a few degrees.

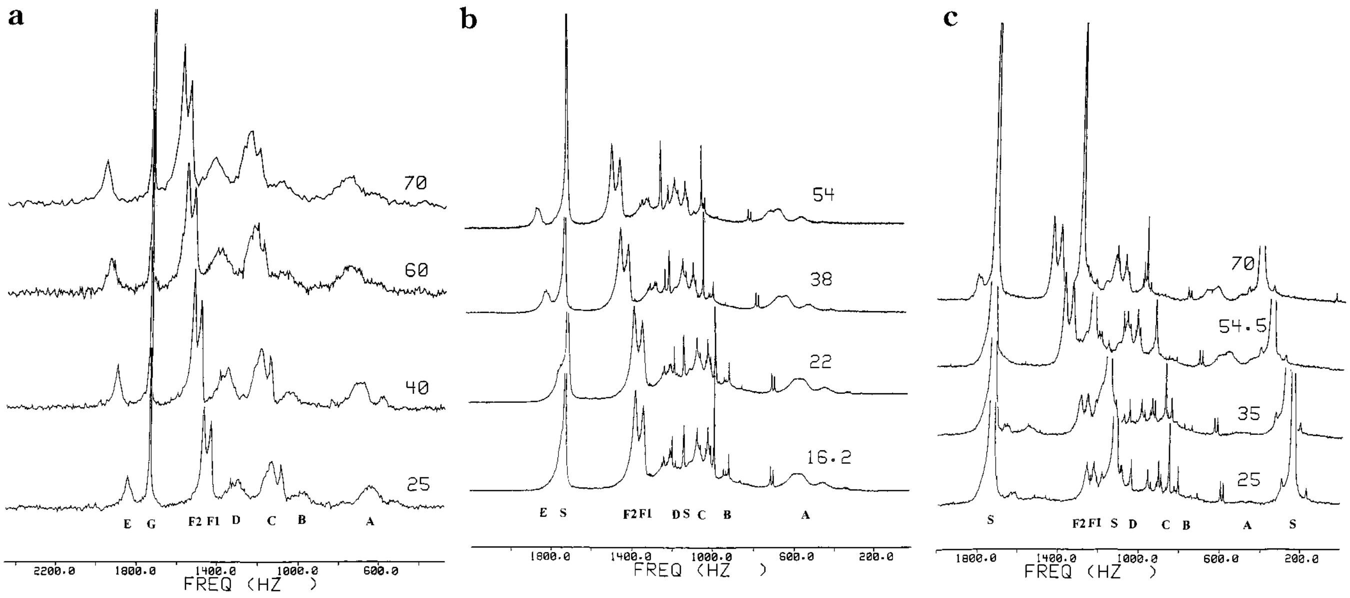

Figure 1. Proton NMR spectra (360 MHz) of poly(DIOMMA) dissolved in (a) D_2O, (b) CD_3OD, or (c) C_2D_5OD obtained at various temperatures (°C). See structure **I** for assignments of A−F. G: HOD (4.80 ppm or 1729.6 Hz in reference to TMS.). S: peaks from liquid CD_3OD or C_2D_5OD.

Overview of Proton NMR Spectra of Poly(DIOMMA). Spectra of the polymer dissolved in D_2O consist of fairly resolved peaks for the chemical groups of DIOMMA residue as shown in Figure 1. Some specific features of the chemical groups were identified in reference to the spectrum of DIOMMA monomer as follows: (1) The spectra of methylene protons (A) of the main polymer chain are made of at least two major, chemically shifted peaks that are accompanied by a small peak at the high-frequency side. (2) The methyne proton (B) appears as an unresolved broad peak. (3) The three protons of the *N*-methyl group (C) seem to be split into triplets through the spin−spin coupling between ^1H and ^{14}N of the amide group, though they are broadened by ^{14}N nuclear quadrupole relaxation. The coupling constant, $J_C(^1H-^{14}N)$ seems to be about 40 Hz. (4) The two protons of the *N*-ylmethyl group (D) is coupled to a single proton (E) which is bonded to the second carbon of the 1,3-dioxolane ring. Thus, the peak becomes a doublet [$J_D(^1H - ^1H)$ is 15−20 Hz] and is further weakly coupled to the same ^{14}N in the amide group through $J_D(^1H-^{14}N)$ (a triplet). The lines are also broadened by the same ^{14}N nuclear quadrupole relaxation as for proton (C). (5) the Proton E is supposed to be a triplet by the above spin−spin coupling [$J_D(^1H-^1H)$] to the ylmethyl protons. This splitting can however, barely be recognized as shoulders at 360 MHz, and the splitting is roughly estimated to be 15−20 Hz from a spectrum at 500 MHz. (6) It is known that a five-membered ring has a nonplanar structure,[14] and thus, four protons (F) attached to the dioxolane ring are chemically and magnetically nonequivalent.[15] From the chemical structure of the DIOMMA residue, it may be presumed that the chemical shift between F1 and F2 protons [δ(F1−F2)] is relatively large as compared to the spin−spin coupling constants among protons. Thus, the spectrum (at 360 MHz) of the DIOMMA monomer may consist of a superposition of the two sets of weakly coupled (AX) rather than strongly coupled (AB) spin systems.[15−17] This is actually the case. Namely, one proton at the fourth position couples to one at the fifth [$J_{F1}(^1H-^1H)$] and another pair of two protons couples each other in the same way [$J_{F2}(^1H-^1H)$]. The values of these two spin−spin coupling constants are very close (about 15 Hz) and thus give two sets of quartets. In other words, the spectra for both F1 and F2 protons appear as closely spaced quartets (not totally symmetrical) separated by δ(F1−F2). However, one should mention that they are not exactly AX systems because δ(F1−F2) is only 80 Hz. In poly(DIOMMA), two broad lines corresponding to four protons (F1 and F2) were observed at temperatures below and above the CP. Therefore, we should interpret that all splittings due to spin−spin couplings are buried within the broad line widths. At temperatures near the CP, four lines transiently appeared in D_2O, as well as in C_2D_5OD. We will discuss the changes that appeared for F1 and F2 protons in a latter section.

The general profile of the spectra for the DIOMMA residue as described above is basically the same in all solvents. However, the temperature dependence of the spectra revealed noticeable differences from one solvent to another. While all the lines in any given solvent shifted toward higher frequency of a similar magnitude (about 3 Hz/K) with increasing temperature, it was found that (1) the line widths in D_2O are, in general, broader than those in alcohols and (2) the line widths in D_2O increase with rising temperature. On the contrary, the line widths in C_2D_5OD narrow with increasing temperature, while those in CD_3OD remain unchanged throughout the entire temperature range. This general trend for the line widths can clearly be seen in the methylene protons (A).

Effects of Temperature and Solvent on F1 and F2 Proton NMR Spectra. To clarify characteristics in the spectral changes of the F1 and F2 protons in D_2O, CD_3OD, and C_2D_5OD, spectra were obtained at both 360 and 500 MHz over a few degrees range around the respective CP. Some representative spectra in D_2O and in C_2D_5OD are shown in Figure 2.

Phenomenologically, a doublet structure below the CP converts to a quartet at slightly above the CP in D_2O. As the temperature is raised further, the quartet returns to a doublet again. The temperature dependence of the spectra was reversed in C_2D_5OD. Namely, a quartet consists of two pairs of doublets with different

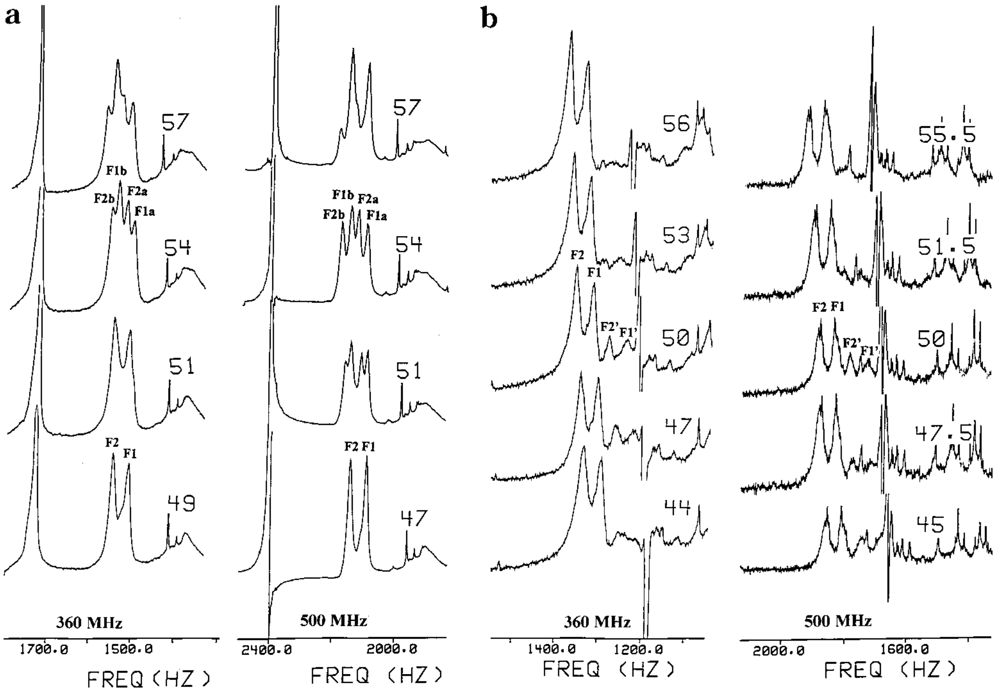

Figure 2. Temperature dependence of ^{1}H NMR spectra (360 and 500 MHz) of poly(DIOMMA) dissolved in (a) D_2O or (b) C_2D_5OD at temperatures around the CP's.

Table 1. Peak Frequencies of a Doublet or Quartet [Four Protons Attached to the Fourth and Fifth Carbons of the 1,3-Dioxolane Ring in poly(DIOMMA)][a]

			Larmor frequency					
solvent	temp (°C)	assignment	360(ν_1)	500(ν_2)	ν_1/ν_2	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_1/\Delta\nu_2$
D_2O	25	F1	1432	1980	0.723	34	53	0.64
		F2	1466	2033	0.721			
	54	F1a	1511	2104	0.718	36	51	0.71
		F1b	1547	2155	0.718			
		F2a	1527	2136	0.715	34	48	0.71
		F2b	1561	2184	0.715			
	60 (70*)	F1	1544*	2123	0.727	39	50	0.78
		F2	1583*	2173	0.728			
CD_3OD	(16–33)	F1	1346–1403	1869–1945	0.720 ± 0.02	39.2 ± 1	55.0 ± 2	0.71
		F2	1385–1443	1923–1998	0.721 ± 0.02			
C_2D_5OD	44 (45*)	F1	1298	1812	0.716	40	54	0.74
		F2	1338	1866	0.718			
	50	F1	1323	1838	0.720	40	53	0.75
		F2	1363	1891	0.721			
		F1′	1246	1740	0.716	40	57	0.70
		F2′	1286	1797	0.710			

[a] All frequencies are in reference to TMS.

intensities just below the CP. Above the CP, a doublet with weaker intensity disappears. No transient change was observed in CD_3OD at both 360 and 500 MHz. The temperature dependent changes in the peak frequencies in water or ethanol are summarized in Table 1. The assignments of peaks, i.e., which peaks form two pairs of doublets (phenomenologically a quartet), are given in Table 1 and Figure 2.

2. Gels of a Cross-Linked Analogue of Poly(DIOMMA) and Water or Alcohols. Temperature Dependence of the Degree of Swelling. Figure 3 shows the temperature dependence of the degree of swelling in either water or alcohols. Here, the degree is expressed in a dimensionless quantity, d/d_0, where d and d_0 denote the diameter of a piece of gel at an arbitrary temperature and the internal diameter of a capillary (0.7 mm), respectively. With increasing temperature, the degree of swelling of the gel in water quasi-monotonically decreases up to near 60 °C and gradually levels off to a constant value at about 70 °C. In the alcohols, the gels exhibit completely reversed

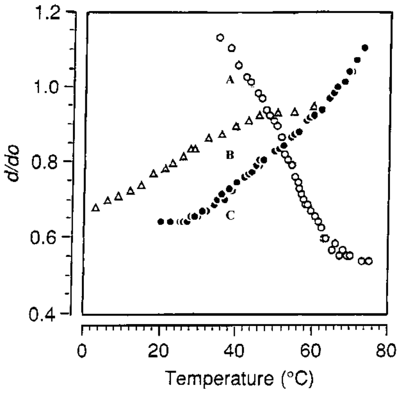

Figure 3. Temperature dependence of the swelling degrees in gels made of the cross-linked analogue of poly(DIOMMA) and water or alcohols.

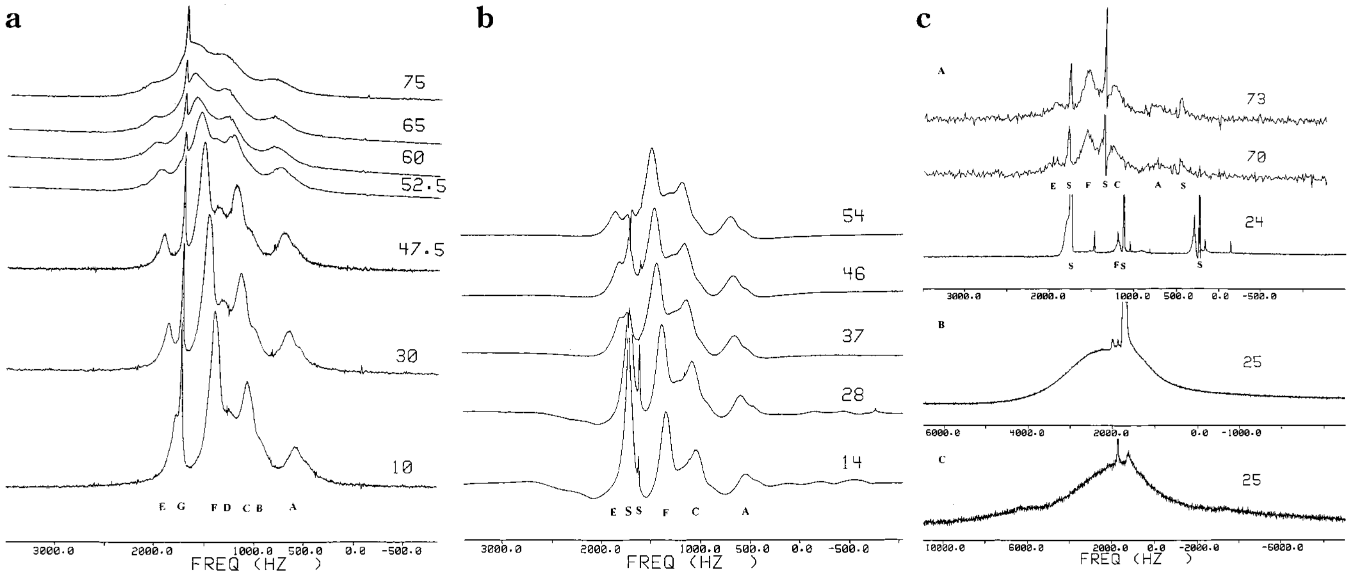

Figure 4. ^{1}H NMR spectra (360 MHz) of gels made of the cross-linked analogue of poly(DIOMMA) and (a) D_2O, (b) CD_3OD, or (c) C_2D_5OD obtained at various temperatures (°C) where A, B, and C denote polymer gel, solid poly(DIOMMA), and its cross-linked analogue, respectively. (Note that the frequency scales of A, B, and C are 23.2_5, 46.5, and 93.0 Hz/mm, respectively.)

trends, i.e., the degree of swelling increases with rising temperature.

In addition, several important features have been found in the temperature dependence of the degree of swelling as seen in Figure 3. They are as follows: (1) The degree of swelling in water was greater than unity at a temperature below 45 °C and the overall change in the degree of swelling is slightly larger than a factor of 2 over a range of 40 °C. (2) The degree of swelling in methanol is greater than that in ethanol. (3) In methanol, the degree of swelling nearly reaches a plateau ($d/d_0 = 0.95$) beyond 50 °C. (4) In ethanol, the degree of swelling has a plateau ($d/d_0 = 0.64$) below 30 °C. (5) At temperatures above 65 °C, the degree of swelling in ethanol exceeds unity, and the overall change reaches a factor of nearly 1.7 over a temperature range of 55 °C. On the basis of the above observations, the phase transition (ph. tr.) temperature in water may be said to be 65 °C. However, it is rather difficult to define the corresponding temperatures in both alcohols.

Overview of Proton NMR Spectra of Cross-Linked Poly(DIOMMA). NMR signals were carefully acquired by varying dwell time (spectral width) in order to detect any fast decaying components (which correspond to broad spectral lines) caused by possible phase transition processes. Some representatives of proton NMR spectra of the poly(DIOMMA) residue obtained at 360 MHz are shown in Figure 4.

As can be seen in Figure 4a, all chemical groups that appeared in the spectra of poly(DIOMMA) dissolved in D_2O can be identified in the gels at temperatures below 50 °C. The CH proton (B) of the main chain appears only as a shoulder to the *N*-methyl protons (C) of the side chain. The *N*-ylmethyl protons (D) are seen as a peak sandwiched by the C and F protons. The doublet structure for the four CH_2 protons in the 1,3-dioxolane ring (F1 and F2) becomes a broad singlet (F) over the entire temperature range. The peak of the CH proton (E) also appeared as a singlet. It should be noted that broad peaks of all chemical groups in the aqueous solution are further broadened in the hydrogel. These eventually coalesced to a broad singlet at 75 °C. Several bumps corresponding to the above peaks can still be seen while the HOD peak remains sharp.

In contrast to these results in D_2O, the spectra in CD_3OD (Figure 4b) resemble to those in D_2O obtained at temperatures below 50 °C but are nearly independent of temperature over the entire temperature range. The NMR signals in C_2D_5OD were hardly detectable at low temperatures (60 accumulations were needed as compared to two averages even at 70 and 73 °C). Considerably broadened peaks of all chemical groups appeared at high temperatures (Figure 4c).

Discussion

First, we discuss how solid poly(DIOMMA) dissolve into water or alcohols. In this process, solvent molecules molecularly separate polymers and retain them in modified liquid structures in the respective liquids. This implies that there is some sort of balance among the intermolecular P−P, P−S, and S−S interactions in order to form polymer solutions. This balance is disturbed when the temperature varies. Therefore, our starting point in order to understand the reversed thermal behaviors of poly(DIOMMA) shown in water vs those in alcohols is *to consider three competitive intermolecular interactions that are agitated by thermal motions of all molecular species involved (a function of temperature).* Both water and alcohols are regarded as hydrogen-bonded dipolar liquid systems, even though water can form a stronger hydrogen-bonded system than alcohols.[18] Because the thermal motions of any kind of molecules increase with rising temperature, all S−S interactions become weak due to the destruction of hydrogen bonds. Namely, the S−S interaction is a weakening function of increasing temperature (T) [$f(1/T)$]. We must experimentally determine the relative strengths and modes of the P−P and P−S interactions for aqueous or alcohol solutions of poly(DIOMMA) as a function of temperature.

Second, we treat gels made of the cross-linked poly(DIOMMA) and water or alcohols under exactly the same consideration as above.

In the following, we will present how the necessary molecular information about the relative strengths and modes of the P−P and P−S interactions can be obtained from the NMR results in aqueous or alcohol solutions of poly(DIOMMA).

1. Relationship between NMR Spectral Widths and the Intermolecular P−P, P−S, and S−S Interactions. Deuterated solvents were used in both solutions and gels. Hence, the line widths of the proton NMR spectra of poly(DIOMMA) arise predominantly from the nuclear magnetic dipole−dipole interactions between protons in various chemical groups of the polymers.[13,21−22] The characteristics of these magnetic interactions are as follows: (A) The interactions are very sensitive to thermal motions of various chemical groups of poly(DIOMMA). In a similar way, they are also sensitive to thermal fluctuations of polymer networks and associations with solvent molecules[13,21−22] (P−S interactions). Hence, the contributions to line widths depend on temperature. (B) The interactions are sensitive to the proximity of neighboring protons.[13,21−22] Any conformational changes occurring in poly(DIOMMA) and/or aggregations of polymers (P−P interactions) will significantly contribute to changes in the line widths. These processes themselves are fundamentally controlled by strengths and modes of the three intermolecular interactions. Thus, this second factor is also indirectly temperature dependent.

We now examine the experimental results obtained in NMR of poly(DIOMMA) in light of the above physical characteristics. We will deduce relationships between features in the NMR spectra in solutions and the intermolecular P−P, P−S, and S−S interactions at the molecular level as a function of temperature, these being as follows. (1) Broadening of the line widths with increasing temperature arises from strong P−P and/or P−S interactions; that is, vigorous thermal motions at high temperatures are overcome by the factor B). (Motional narrowing of the line-width does not occur.) This is the case for water. (2) Insensitivity of the NMR line widths to temperature stems from invariant environments for poly(DIOMMA). In other words, strong and constant P−S interactions prevail over certain temperature range. Methanol fits this description. (3) Vigorous thermal motions are responsible for narrowing of the line widths at high temperatures. This situation is attributable to ever-strengthening P−S interaction [$f(T)$] over either P−P and/or S−S interactions, as temperature increases. This is the situation for ethanol.

Now, let us focus on the case of polymer gels. One major difference between polymer and its cross-linked analogue is the expansion of the covalently bonded polymer networks that are constrained to a certain limit in solvent while polymer can molecularly be dispersed in solvent. This situation enhances the effect of the factor (B) mentioned above. The difference in the effect of factor B is clearly revealed in the NMR spectra of polymer gels. Some examples are as follows: The coalescence of broad spectra of the cross-linked poly(DIOMMA) in water is caused by strong P−P and P−S interactions at high temperatures. The broad spectra of poly(DIOMMA) in methanol solution are furthermore broadened in the corresponding gel. In ethanol, the strong P−P and weak P−S interactions at low temperatures pose difficulties in terms of obtaining spectra (very fast decaying components in the time domain correspond to very broad lines.). This situation is overcome by the ever strengthening P−S interaction with increasing temperature. Thus, broad but thermally narrowed spectra are detectable at high temperatures.

Table 2. Relative Strength and Nature of the Polymer−Polymer (P−P), Polymer−Solvent (P−S), and Solvent−Solvent (S−S) Interactions in Systems Composed of Poly(DIOMMA) or Its Analogue and Solvents

interaction	solvent		
	water	methanol	ethanol
P−P	strong	weak	strong
P−S[a]	strong	strong $\neq f(T)$[b]	weak $\equiv f(T)$
S−S	strong $\equiv f(1/T)$[c]	weak $\equiv f(1/T)$	weak $\equiv f(1/T)$

[a] It may be regarded as solvation interaction of various groups of the polymer component or solvent molecules bound around the polymer chain. [b] $f(T)$: interaction will increase with rising temperature. [c] $f(1/T)$: interaction will decrease with rising temperature.

We can integrate these pieces of information about the relationships to formulate one consistent model. This model qualitatively describes the relative strengths and modes of the intermolecular P−P, P−S and S−S interactions for poly(DIOMMA) in three different solvents as expressed in Table 2. We must emphasize that they were deduced from experimental results obtained at the molecular level (NMR).

2. Role of Solvent Molecules in Phase Separation in Solutions and in Volumetric Phase Transition of Gels. The Reversed Thermal Behaviors of Poly(DIOMMA) in Water vs Those in Alcohols. First of all, we will attempt to explain why the phase separation in water occurs by heating while those in alcohols by cooling. We will apply the aforementioned consistent model for the relative strengths and modes of the intermolecular interactions presented in Table 2. The relative strengths of three intermolecular interactions in aqueous solution are sensitive to temperature changes around the CP (49.5 °C). This sensitivity is associated with changes in the conformations of polymers and thermal motions of the side groups. Subtle changes may occur by heating when the effect of thermal motions slightly exceeds those of the intermolecular P−S and/or S−S interactions, i.e., aggregations of polymers (the P−P and P−S interactions), take place with the aid of weakening S−S interaction. The strong and constant P−S interaction in methanol was however, sustained over the temperature range examined. Hence, further lowering of temperature is needed for aggregations of polymers (CP = 23 °C). When the effect of thermal motions in ethanol slightly decreases around the CP (52 °C), aggregations of polymers may occur because the strong P−P will overcome the ever-weakening P−S, in the presence of strengthening S−S interactions. Thus, the phase separations in alcohols take place by cooling.

On exactly the same basis applied to polymer solutions, we can explain the reversed thermal behaviors of swelling polymer gels in water vs in alcohols. In water, all three interactions are competitively strong enough to maintain the swollen state from 0 up to about 60 °C. An nearly monotonic decrease in the degree of swelling from 30 to 60 °C stems from the ever-increasing thermal motions and thus weakening S−S interaction. At ph. tr. temperature, the strong P−P and P−S interactions finally overcome the thermal motions and the weakening S−S interaction. This situation will probably induce two processes. They are conformational changes in the polymer component and elimination of

Table 3. Some Quantities Derived from Density Determination of Polymer Gels

	temp	poly(NIPA)[a]	poly(DIOMMA)[b]		
	°C	water	water	methanol	ethanol
$v(\mathrm{gel})/m_p$ (cm^3/g)	20	25.2	17.2	8.9	7.4
	34	2.5	16.1	9.5	8.7
	45	2.0	14.0	10.2	8.7
	60		13.6	15.6	11.1
$m_p/m(\mathrm{gel})$ (%)	20	4.0	5.7	13.0	16.0
	34	40.0	6.1	12.0	14.0
	45	47.0	7.0	12.0	14.0
	60		7.0	12.0	11.0
no. of solvent molecules per polymeric residue	20	150	156	35	20
	34	10	146	38	24
	45	7	126	40	23
	60		126	40	30
$m_p/v(\mathrm{gel})$ (g/cm^3)	20	0.040	0.058	0.11	0.14
	34	0.40	0.062	0.10	0.11
	45	0.51	0.072	0.10	0.12
	60		0.073	0.064	0.090

[a] Reference 19. [b] Reference 20.

many water molecules from the gel system. The volumetric contraction from a swollen to a shrunken states is limited to a factor of 2. This is in contrast to more than 1 order of magnitude in the case of poly(NIPA) gel.[1,3] Therefore, a rather large number of water molecules are likely retained even in the shrunken state of poly(DIOMMA). The difference between methanol and ethanol environments arises from the following two factors: The strong and constant P−S interaction exists in the former, and (2) in particular, the strong P−P interaction is prevalent in the latter at lower temperatures. These result in a difference in the degree of swelling, i.e, d/d_0 (methanol) is greater than d/d_0 (ethanol) at lower temperatures. The leveling off of d/d_0 at a constant value near 50 °C in methanol is caused by the first factor with the aid of the weakening S−S interaction (with rising temperature). In ethanol, both strengthening of the P−S interaction [$f(T)$] and vigorous thermal motions with rising temperature promote expansion of the networks and thus maintain ethanol molecules in gels. Finally, d/d_0 (ethanol) exceeds d/d_0 (methanol) at about 60 °C.

Since polymer gels are two-component systems, it is possible to gain further information if we consider how the polymer and solvent components, and not the whole gels, behave with varying temperature even at the macroscopic level. We have approached this problem by studying temperature dependences of the densities of polymer and solvent components in gels. The experimental results for the poly(NIPA)−water system[19] and the above gel systems[20] have just been reported; we judge it to be worthwhile to quote some results as shown in Table 3. The symbols used are: $m(\mathrm{gel})$, $v(\mathrm{gel})$, and m_p representing the mass of gel, the volume of gel, and the mass of the polymer component, respectively. $m_p/v(\mathrm{gel})$ is the density of polymer component in gel. Then, its reciprocal, $v(\mathrm{gel})/m_p$, means the total volume of gel when a unit mass of the polymer component is immersed in solvents. $m_p/m(\mathrm{gel})$ is simply the ratio of two masses expressed in percent. It is apparent that all values in Table 3 support the above conclusion deduced for the three intermolecular interactions. The conclusions drawn from Table 3 are as follows. (1) With regard to the decrease of $v(\mathrm{gel})$ in the aqueous environment with rising temperature, the difference between poly(NIPA) and poly(DIOMMA) arises from a significant loss of water in the former as compared to only a modest decrease of water in the latter. The loss of water caused more than an order of magnitude increase in $m_p/v(\mathrm{gel})$ in the former, while a gradual increase was observed in the latter. (2) Both $m_p/m(\mathrm{gel})$ and the number of methanol molecules per polymeric residue remain nearly constant in methanol over the entire temperature range examined here. These facts support the above conclusion that the strong and constant P−S interaction exists in methanol. (3) The strengthening of the P−S interaction with increase in temperature in ethanol caused a gradual decrease in $m_p/m(\mathrm{gel})$ and an increase in the number of ethanol molecules per polymeric residue. This certainly agrees with tha above conclusion. (4) The stronger P−P interaction in ethanol in comparison to methanol results in larger $m_p/m(\mathrm{gel})$ values in ethanol than methanol. This led to smaller values in both $v(\mathrm{gel})/m_p$ and the number of solvent molecules per polymeric residue in ethanol than methanol.

3. Shrunken State in Hydrogels. The volumetric contraction from the swollen to shrunken state in the hydrogel of poly(DIOMMA) is much smaller than that of poly(NIPA). This difference deserves some attention. In terms of the chemical structure, the strong P−S interaction in the former probably arises from the presence of the 1,3-dioxolane ring. This ring acts as an extra center for binding more water molecules around poly(DIOOMA) as compared to just the amide group in the latter. In the volumetric ph. tr. processes, if the former retains more water around the polymer component in the shrunken state than in the latter, this will result in a smaller contraction in volume. This understanding is substantiated by experimental values of $v(\mathrm{gel})/m_p$ and of the number of water per polymeric residue (Table 3). The difference in the chemical structure must also be reflected for an increase in the ph. tr. temperature (33.5[3]−65 °C).

The most noticeable difference in proton NMR spectra between these two gel systems is the emergence of a broad peak upon the collapse of the hydrogel of poly(NIPA).[13] Eventually, all peaks appearing in the swollen state disappear and merge to the broad peak with a further increase in the temperature. While broadening and merging of all peaks in the hydrogel of poly(DIOMMA) certainly occur at temperatures beyond about 60 °C, conformational changes of the poly(DIOMMA) do not lead to a closely packed situation. Figure 4c shows the line shapes of solid poly(DIOMMA), and solid cross-linked analogue. The full line widths (the width at the half intensity), $\Delta\nu_{1/2}$, for the shrunken state, solid poly(DIOMMA) and solid cross-linked analogue are about 0.64, 2.1, and 3.8 kHz, respectively. These values clearly indicate the shrunken state is not really a closely packed state as compared to the latter two. The values in m_p/v(gel) clearly support this conclusion. In the ph. tr. processes, the bulky and stiff side group in the poly(DIOMMA) rather than that in the isopropyl group may stereochemically hinder changes, leading to a further tight conformation. If one assumes the straight zigzag form (the eclipsed configurations) in the C−C bonds, the straight length of the *N*-(1,3-dioxolan-2-ylmethyl) group is longer than that of the cross-linker, BIS. The stereochemistry of the side group may also contribute to the final outcome (the shrunken state) in the volumetric ph. tr. processes.

In view of the above discussion regarding the shrunken state, the thermal behaviors of the cross-linked poly(DIOMMA) in alcohols should not be regarded as a volumetric phase transition of polymer gels.

4. Consistent Model. We think it is necessary to dispose of our fundamental model that generated the content given in Table 2. First of all, we take a general view that would be applicable to any polymer solutions or gels. Since these systems are two-component systems, there are always three different intermolecular interactions that are subject to changes in temperature. Second, we do not evaluate or estimate the relative strength and the modes of these intermolecular interactions from the theoretical point of views. Instead, we *experimentally* obtain information about these at the *molecular level* as a function of temperatures (at least in a qualitative manner). In the present study, we obtained the information from features of the proton NMR spectra that reflect the states of the intermolecular interactions. The specific results thus obtained (Table 2) are only applicable to the systems made of poly(DIOMMA) and water or alcohols, although the fundamental model and the experimental approach to obtain the results have *generality* in their nature. When we obtain the results for whatever system of interest, we keep the same principles. This is the consistent model in this study.

5. Interpretation of Transient NMR Spectra around CP in Polymer Solutions. Role of the Solvent. The transient changes in proton NMR spectra in both water and ethanol environments around the CP's are noteworthy observations. At temperatures away from the CP, only two lines were observed even though there are four CH_2 protons in the 1,3-dioxolane ring of poly(DIOMMA). This may be interpreted to mean that the motional averaging effect on the spectrum is greater than the splittings caused by the spin−spin couplings among four protons. Or, the latter splittings are much smaller than the line widths by the nuclear dipolar interactions. There may also be a composite influence of both effects.

We first focus on quartet structures that appeared in both D_2O and C_2D_5OD at temperatures around the CP. If they are all chemically nonequivalent and not coupled through the nuclear spin−spin couplings between protons [noncoupled (ABXY) spin system], there should be four separate peaks.[15] In this case, when the spectra were obtained at two different Larmor frequencies, for example, 360 MHz (ν_1's) and 500 MHz (ν_2's), the ratios of frequencies for all peaks, as well as the corresponding ratios of the peak frequency differences between any two peaks, must be the ratio of the two Larmor frequencies of the spectrometers used. This is because the ratios originate only from the chemical shifts.[15,21] The ratio for two spectrometers used in this work is 360.336/501.853 = 0.718012. In addition, the relative intensities of all peaks should remain unchanged at any Larmor frequency.

According to the assignment of peak frequencies at 54 °C (Table 2) for a quartet structure in water, the ratio of ν_1 and ν_2, but also that of $\Delta\nu_1$ and $\Delta\nu_2$ are about 0.72. In addition, the total intensity of the lines remains unchanged. These facts indicate that the quartet structure arises from the same spin system. However, the ratios of $\Delta\nu_1$ and $\Delta\nu_2$ for other combinations, i.e., [$\Delta\nu_1$(F2a−F1a)(=16 Hz)/$\Delta\nu_2$(F2a−F1a)(=32 Hz)], [$\Delta\nu_1$(F2b−F1b)(=14 Hz)/$\Delta\nu_2$(F2b−F1b)(=29 Hz)], [$\Delta\nu_1$(F2b−F1a)(=50 Hz)/$\Delta\nu_2$(F2b−F1a)(=80 Hz)], and [$\Delta\nu_1$(F2a−F1b)(=20 Hz)/$\Delta\nu_2$(F2a−F1b)(=19 Hz)] are 0.5, 0.48, 0.63, and 1.05, respectively. They all deviate considerably from 0.72. Hence, there are some contibutiions from the spin−spin couplings among four protons. If the protons are coupled, the possible coupled spin systems are A_2B_2, AA′BB′, A_2X_2, or AA′XX′, and the spectral patterns do depend on the ratio of chemical shift and spin−spin coupling constant(s).[15−17] Since the spectra are unfortunately not well resolved even at 500 MHz, the best interpretation we can offer is as follows: (1) the four protons likely belong to a AA′XX′ system where AA′ or XX′ protons represents the two protons at the either fourth or fifth carbon; (2) the quartet structure reveals some contributions from the spin−spin couplings that become transiently greater than the motional averaging effect on the spin system or the line widths.

In ethanol, the assignment of peak frequencies at 50 °C (Table 2) for two sets of the doublets show the ratio of ν_1 and ν_2, but also that of $\Delta\nu_1$ and $\Delta\nu_2$, is about 0.72. In addition, it should be noted that one doublet along the low frequency side is much weaker than at higher frequency (Figure 2). The separations between the strong and weak doublets are about 77 and 96 Hz at 360 and 500 MHz, respectively. Thus, the resulting ratio, 0.80, is about 10% higher than the theoretical ratio, 0.72. Therefore, two doublets seem to be unrelated sets that probably represent the CH_2 protons belonging to different 1,3-dioxolane rings in the poly(DIOMMA) molecule.

It is important to notice that transient spectral changes are in concert with the reversing thermal behavior of poly(DIOMMA) in water vs that in ethanol. On the same basis (Table 2) used to explain the latter behavior, the spectral changes (behavior at the molecular level) may be understood in terms of the effects stemming from aggregations of polymers and its associated processes. In water, rapid motions (possibly a ring-puckering or torsional oscillation around the carbon atom) likely average out spin couplings in the AA′XX′ system for four CH_2 protons. This is the situation at temperatures below and far above the CP. When temperature just exceeds the CP however, this motion becomes slower due to aggregation processes between molecules (strong P−P and P−S interactions, see Table 2). Thus, a quartet appears. In ethanol, a subtle difference in the conformations of polymers transiently appears due to retardation of molecular motions around CP. The difference disappears at much lower temperatures because of the strong P−P and P−S interactions.

In methanol, the strong and constant P−S interaction (Table 2) suppresses the effect of thermal motions of the polymer molecules over the entire temperature range examined, and thus, transient effects were not observed.

6. Remarks. At the macroscopic level, "how polymers dissolve in certain solvents and exhibit the CP and/or how and why the cross-linked analogues swell with varying temperature" were the main focus of this study. We cannot elucidate *details* of the above subject on the basis of the *molecularly specific* information about the intermolecular P−P and P−S interactions at this moment. Obtaining the molecular specificity in the interactions will enhance the understanding of the subject. One of the possible experimental approaches is the determination of proton NMR cross-relaxation times[23,24] for various chemical groups of the polymer. These relaxations orignate from *molecularly specific* interactions between a particular chemical group and either polymer or solvent. The experimental determinations of these relaxation times over a wide range of temperatures are presently in progress. By integrating all the experimental results at both macroscopic and molecular levels, we would then be able to elucidate the above subject in a more detailed fashion.

Conclusion

The temperature dependences of the proton NMR spectra of poly(DIOMMA) and its cross-linked analogue have been studied in water, methanol, or ethanol. We have deduced the relationships between the line widths of NMR spectra and the relative strengths (and the modes) of the intermolecular P−P, P−S, and S−S interactions. All information about the temperature dependence of these relationships have been formulated into one consistent model. This model qualitatively describes the relative strengths and modes of the three intermolecular interactions in the poly(DIOMMA) and water or alcohol systems, as given in Table 2. On the basis of this, we have successfully elucidated the reversed thermal behaviors of poly(DIOMMA) in water vs in alcohol.

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