A ^{13}C Nuclear Magnetic Resonance Study of Covalently Cross-Linked Gels. Effect of Chemical Composition, Degree of Cross-Linking, and Temperature to Chain Mobility

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ABSTRACT: A ^{13}C NMR study of various types of covalently cross-linked hydrogels consisting of poly(*N*-vinylpyrrolidone) (PVP), copolymer of *N*-vinylpyrrolidone (NVP) and methyl methacrylate (MMA), and poly(hydroxyethyl methacrylate) (PHEMA) has been performed in order to gain understanding of various factors determining chain mobility in the gels. The ^{13}C resonance peak positions of these gels are found to be essentially the same as those of the uncross-linked polymers in solution. The line widths of the ^{13}C resonances of PVP are primarily determined by water content, which is a function of the degree of cross-linking. For the gel of copolymer of NVP and MMA swollen by water, only the ^{13}C resonances of the NVP component are clearly observed, whereas peak areas of the MMA component are completely lost. However, it is found that the MMA component can be seen by swelling with chloroform or DMSO, which is a good diluent for the hydrophobic segment. The observation of such differential swelling strongly suggests that NVP and MMA constitute separate domains in this gel. Furthermore, a remarkable temperature dependence of the ^{13}C line width is noted in the gel of PHEMA. The extremely large line width (ca. 600 Hz) of the PHEMA gel at ambient temperature is interpreted in terms of restriction of chain mobility as a result of entanglement of polymer chains. Spin–lattice and spin–spin relaxation times and nuclear Overhauser enhancements are also determined to characterize the segmental motions in the gels.

Recently there has been an increasing interest in various types of gels from the viewpoint of biological concern[1-7] and biomedical application.[8] Chemical and physical properties of gels have been known to depend on a number of parameters such as chemical composition, types and numbers of cross-links, presence of functional groups, and variety of diluents. Extensive investigation on the gelation mechanism and thermodynamics of three-dimensional networks held by cross-links has been carried out theoretically and experimentally.[4,9,10] However, molecular architecture and the dynamic aspect of gels are not fully understood.

In this regard, proton-decoupled ^{13}C nuclear magnetic resonance (NMR) has been proved to be a very powerful tool for characterization of polymers including bulk materials such as solid rubber at a temperature above the glass transition,[11-13] swollen gels which are covalently cross-linked,[14] and polysaccharde gels which are physically cross-linked by aggregation of ordered regions of polymers.[3,5-7] In those bulk materials, however, all of the carbons in polymers do not always contribute to high resolution ^{13}C resonances, since sizable loss of peak areas is found to occur due to the presence of immobilized segments such as cross-links or crystalline portions. In some instances, the ^{13}C resonance is completely lost as in the gels of ι-carageenan,[3] collagen,[15] and double-helical polynucleotides.[16] For this reason, to characterize gels by ^{13}C NMR extensive analysis of various factors to determine chain mobility seems to be very important. Therefore, the main purpose of this study was to determine the feasibility of investigating the microstructural features of various types of gels by ^{13}C NMR.

In this paper, we wish to demonstrate the effects of chemical composition, degree of cross-linking (as viewed from water content), and temperature on the ^{13}C resonances of various types of covalently cross-linked gels, consisting of poly(*N*-vinylpyrrolidone) (PVP), poly(hydroxyethyl methacrylate) (PHEMA), and a copolymer of NVP and methyl methacrylate (MMA), swollen by water. It is demonstrated that the line widths of the ^{13}C resonances of gels are primarily influenced by the degree of swelling, which is a function of affinity to diluent and the degree of cross-linking. The temperature at which ^{13}C NMR was carried out is also found to be a very important factor to determine the line widths of a hydrogel consisting of monomeric units of less hydrophilic character but less important for that of a hydrophilic gel. Finally, segmental motions of gels are characterized in terms of a broad distribution of correlation times.

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Experimental Section

Hydrogels. Polymers were prepared by free-radical initiation using azobis(isobutyronitrile) as the initiator for polymerization. Polyfunctional vinyl monomers were used as cross-linking agents for preparation of cross-linked PVP and the copolymer of NVP and MMA. No cross-linking agent was used for preparation of PHEMA gel. These polymers were allowed to swell over deionized water or boiled water more than 24 h to achieve equilibrated water content and to remove residual monomers and oligomers. The degree of swelling was characterized by measurement of water content. In the gel of the copolymer of NVP and MMA and PHEMA, swelling by chloroform or dimethyl sulfoxide was performed by soaking the samples in these diluents. Water content was determined by the ratio of loss of weight by drying to the weight of gel. Uncross-linked polymers, PVP and MMA (syndiotactic), and monomer (HEMA) were obtained from commercial sources.

^{13}C NMR. ^{13}C NMR spectra were measured by a JEOL FX-100 (25.05 MHz) and an FX-60 (15.03 MHz) spectrometer in the pulsed Fourier transform mode. In the former spectrometer, digital quadrature detection was employed. The ^{13}C NMR spectra were obtained under conditions of proton noise decoupling of 2.5 kHz width. A 90° pulse required a pulse duration of 11 and 16 μs for the FX-100 and FX-60 spectrometers, respectively. Free induction decays (FID's) were accumulated in 8192 data points with delay times of 200, 100, and 50 μs after each radiofrequency pulse for spectral range of 5, 10, and 20 kHz, respectively. The accumulated FID's were digitally filtered to improve the signal-to-noise ratio at the expense of added line widths of 1 and 2 Hz. Bulk samples were cut into small pieces, packed into a 10 mm o.d. tube, and confined within the transmitter coil with a Teflon vortex plug. ^{2}H NMR signals of diluents (deuterium oxide or DMSO-d_6) were utilized for field-frequency stabilization. Chemical shifts were expressed in parts per million downfield from external tetramethylsilane (Me_4Si). Temperature was calibrated by a chromel–alumel thermocouple. Spin–lattice relaxation times were determined by the inversion–recovery method,[17] with an estimated accuracy of ±10%. Nuclear Overhauser enhancements were measured by a comparison of the intensity of the fully decoupled spectrum with that obtained by gating the proton noise decoupler only during acquisition of the FID's.[18] A waiting time was usually taken as long as 8–15 times T_1. Some experiments, however, were done with waiting

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Table I
^{13}C Chemical Shifts[a] of Hydrogels and Aqueous Solution of PVP (30 °C)

Assignment	PVP soln	Hydrogels of PVP, water content = 90%	75%	53%
C-2 methylene	18.9 (17.2)[b]	18.9	18.9	18.8*
C-1 methylene	32.6 (31.1)	32.5	32.6	33*
C-β methylene	34.8	34.8	35.1	
C-3 methylene	43.8 (44.4)	43.8	43.9	
C-α methine	45.7	45.7	45.8	45*
	46.9	46.9	46.9	
Carbonyl	178.7 (172.9)	178.8	178.9	179*

[a] Parts per million downfield from external Me_4Si (±0.1 ppm unless otherwise noted, ±0.5 ppm for peaks marked by an asterisk). [b] ^{13}C chemical shifts of NVP in chloroform solution (taken from ref 22).

times of $6T_1$. The estimated accuracy of the NOE is ±10%.[19] Line widths ($\Delta\nu$) were measured as full-width at half-height. Spin–spin relaxation times were calculated from the line width using the relation $T_2 = 1/(\pi\Delta\nu)$. The accuracy of the measurements is usually ±10–±15%. Due to overlap of peaks, the error of some peaks is ±20%. The line widths of overlapped peaks due to unresolved tacticity were determined by the curve-resolving procedure with known separation of peaks observed at elevated temperature (PHEMA, see Figure 4 and Table VI). The error due to the field inhomogeneity in the gels is estimated as less than 2.5 Hz from the measurements of the T_1 values of dissolved sucrose and the condition of $T_1 = T_2$ (PVP gels).

Results

PVP Gels. The ^{13}C NMR spectrum of PVP in aqueous solution is shown in Figure 1A. The assignment has been made on the basis of measurements of the spectrum with off-resonance ^1H decoupling, the spectrum of its monomer, and consideration of additivity rules for chemical shift[21] (Table I). Figures 1B and 1C show the ^{13}C NMR spectra arising from soft and jelly-like hydrogels of water content 90% (0.1 mol % of cross-linking) and of water content 75% (1 mol % of cross-linking), respectively. Spectral features of these gels seems to be identical with that of PVP solution, although the ^{13}C peaks of the gels are slightly broadened. The sample of low water content (53%, 5 mol % of cross-linking) exhibiting brittleness, however, gives rise to very broad ^{13}C peaks (Figure 1D). Nevertheless, no chemical-shift displacement is induced by changing the samples from gels to aqueous solution within experimental error (Table I). By comparing the ^{13}C peak intensity of the PVP gel to that of sucrose of known concentration dissolved in the gel under the condition of suppression of NOE's, it is estimated that only about 55 and 35% of the polymer chain contribute to the observed ^{13}C spectra of the gels of water content 90 and 75%, respectively.

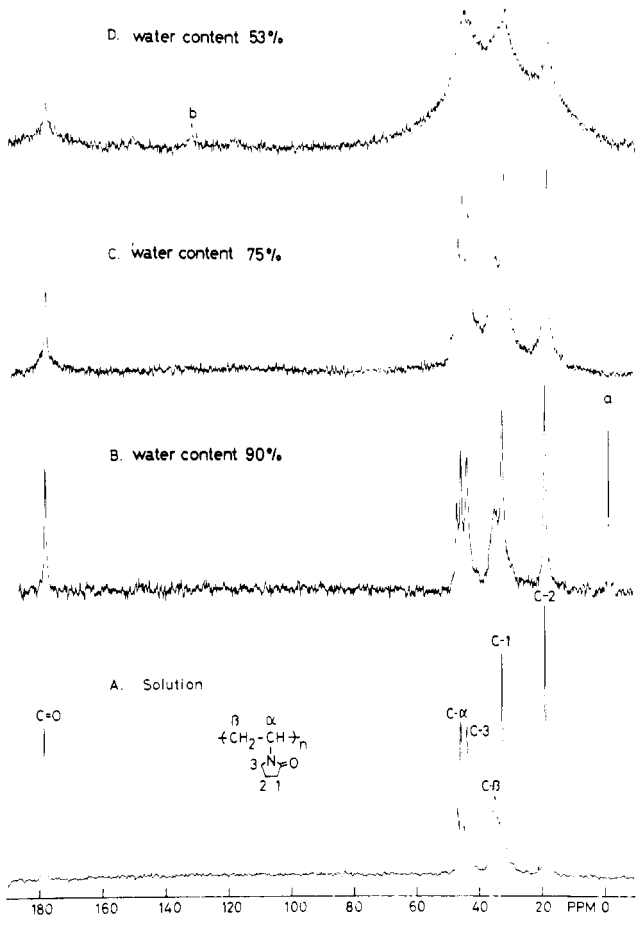

Figure 1. ^{13}C NMR spectra of hydrogels and aqueous solution of PVP at 30 °C (25.05 MHz), 90° pulse, repetition time 1.0 s: (A) aqueous solution (10%), 3600 transients; (B) hydrogel of water content 90%, 3600 transients (the peak a denotes the methyl signal of TSP); (C) hydrogel of water content 75%, 4000 transients; (D) Hydrogel of water content 53%, 10 000 transients (the peak b is due to impurity).

Table II summarizes the line width (T_2), T_1, and NOE of such gels and PVP solution. Interestingly, the line widths are appreciably increased (the T_2's being decreased) in accordance with the decrease of water content. On the contrary, the T_1 and NOE values are found to be unchanged from the solution to the gel of water content 75 and 53%.

Gel consisting of Cross-Linked Copolymer. In Figure 2B is shown the ^{13}C NMR spectrum of a firm resilient opaque gel (water content 46%, 0.1 mol % of cross-linking) of a blend-type copolymer consisting of NVP and MMA (1:1 in weight ratio). The ^{13}C resonance peaks can be clearly ascribed

Table II
^{13}C T_1,[a] Line Width (T_2),[b] and NOE[c] Values of Aqueous Solution and Hydrogels of PVP (25.05 MHz, 30 °C)

	Aqueous sol			Hydrogels 90%			75%			53%		
	NT_1	Line width (T_2)	NOE	NT_1	Line width (T_2)	NOE	NT_1	Line width (T_2)	NOE	NT_1	Line width (T_2)	NOE
C-1 methylene	90	16 (20)	1.8	90	25 (13)*	1.7	94	45 (7.1)*	1.7			
C-2 methylene	134	11 (29)	1.9	134	16 (20)*	1.9	120	25 (13)	1.6	150	250 (1.3)*	1.6
C-3 methylene	96	25 (13)	1.7	96	36 (8.8)*	1.9	92	52 (6.2)*	1.6			
C-α methine[d]	65	17 (18)	1.9	64	31 (10)*	1.8	61	36 (9.2)*	1.6			
		19 (17)			25 (13)*	1.6						
C-β methylene	76		1.8	80		1.6	74		1.5			
Carbonyl		13 (25)			15 (21)			20 (16)			73 (4.4)	

[a] In msec (±10%). [b] Line width in Hz and T_2 in ms (±10%, and ±20% for peaks marked by an asterisk due to overlap of peaks). [c] ±10%. [d] Peak splitting is presumably due to the tacticity of the polymer.

Table III
^{13}C Chemical Shifts[a] of Gels of a Blend-Type Copolymer Consisting of NVP and MMA Swollen by Various Diluents

Swollen by water		Swollen by DMSO		Swollen by $CDCl_3$ (and water)
C-2 methylene (NVP)	18.8 (18.9)[b]	C-2′ methyl (MMA)[c]	19.2 (16.2, 18.5, 20.8)[d]	17.3
C-1 methylene (NVP)	32.4 (32.5)	C-1 methylene (NVP)	32.4	31.0
C-β methylene (NVP)	34.8 (34.8)	C-β methylene (NVP)	35.1	
C-3 methylene (NVP)	43.7 (43.8)	C-α' quarternary (MMA)	45.4 (44.3, 44.6)	44.3
C-α methine (NVP)	45.6 (45.7)	C-1′ methyl (MMA)	53.1 (51.3)	51.5
	46.8 (46.9)	Carbonyl (MMA)	175.4 (176.0, 177.6, 177.9)	
Carbonyl (NVP)	178.8 (178.8)	Carbonyl (NVP)	177.7	

[a] Parts per million downfield from external Me_4Si (±0.1 ppm). [b] ^{13}C chemical shifts of PVP gel of water content 90% (see Table I). [c] Some of the NVP are overlapped to those of MMA components. [d] ^{13}C chemical shifts of PMMA taken in chloroform solution. Assignment based on ref 23.

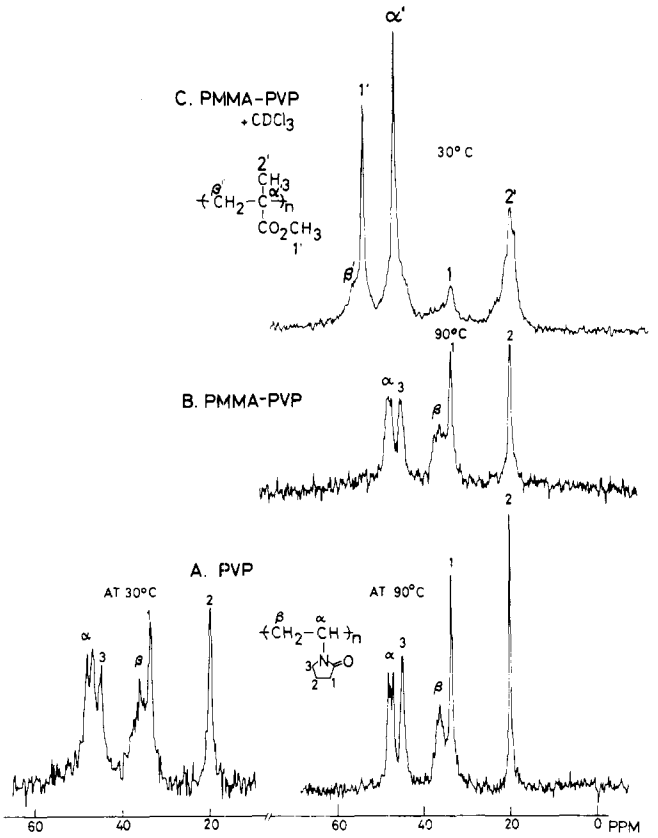

Figure 2. ^{13}C NMR spectra of the PVP gel of water content 90% and a blend-type copolymer of MMA and NVP at 15.03 MHz: (A) PVP gel at 30 °C (left) and 90 °C (right), 45° pulse, 3600 transients, repetition time 1.3 s; (B) hydrogel of copolymer of MMA and NVP (1:1 in weight) at 90 °C (45° pulse, repetition time 1.0 s, 7200 transients); (C) gel of B swollen by mixture of $CDCl_3$ and water, taken at 30 °C (90° pulse, repetition time 1.0 s, 3000 transients).

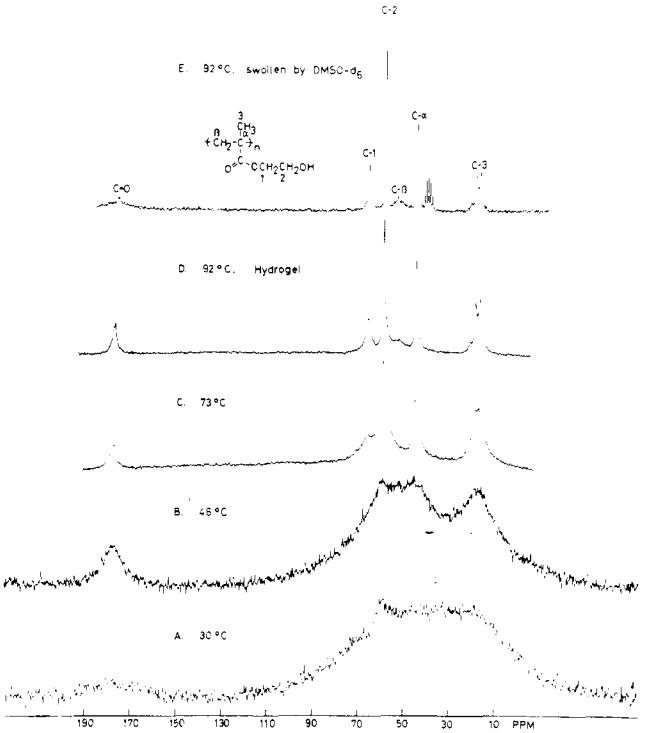

Figure 3. ^{13}C NMR spectra of PHEMA gel swollen by water (water content 37%) or DMSO (90° pulse): (A) swollen by water, at 30 °C (repetition time 0.7 s, 5048 transients); (B) swollen by water, at 46 °C (repetition time 0.9 s, 5048 transients); (C) swollen by water, at 73 °C (repetition time 1.2 s, 3400 transients); (D) swollen by water, at 92 °C (repetition time 2.0 s, 1200 transients); (E) swollen by DMSO-d_6, at 92 °C (repetition time 2.0 s, 1001 transients).

to the NVP component by comparing the peak positions with those of PVP, as shown in Figure 3A. Obviously, peak areas arising from the MMA component are completely lost in this case. However, it is found that the observation of the ^{13}C NMR of MMA component is made possible by swelling with chloroform (Figure 2C) or dimethyl sulfoxide (spectrum not shown). The assignment of the ^{13}C signals is given in Figure 2 and Table III. The difference of the ^{13}C chemical shifts of the MMA component between gels swollen by chloroform and dimethyl sulfoxide may be ascribed to a solvent effect on the ^{13}C resonances. In fact, the ^{13}C resonance peaks of the MMA component of the gel swollen by chloroform are very similar to those of PMMA in chloroform solution.[23] In this case, however, the ^{13}C peaks of C-α, C-3, and C-2 due to the NVP component may be overlapped to the intense signals of the MMA component (Figure 2C). The broad shoulder of the left side of C-1′ (MMA) is assigned to the backbone methylene signal (C-β' of MMA). The rather broad profile of C-2′ might be due to overlap of three signals arising from tacticity.[23] These results indicate that only the hydrophilic NVP component can be swollen by water, while hydrophobic MMA can be swollen by chloroform (in the mixture of chloroform and water) or by dimethyl sulfoxide. Table IV summarizes the T_1's, line widths (T_2's), and NOE's of the gel of cross-linked copolymer. Those are very similar to the values of a PVP gel of 75% water content.

PHEMA Gel. The ^{13}C NMR of a soft and pliable PHEMA gel (water content 37%) is given in Figure 3. The resonances at 30 and 40 °C are considerably broadened. It is noteworthy that the ^{13}C resonances of quaternary and carbonyl groups, which do not have directly bonded protons, are broadened similarly to those of methyl and methylene groups. The line

Table IV
^{13}C T_1, Line Width (T_2), and NOE Values of the Gel of a Blend-Type Copolymer of NVP and MMA Swollen by Water (25.05 MHz, 30 °C)

	NT_1[a]	Line width[b] (T_2)	NOE[c]
C-1 methylene	98	42 (7.5)*	1.6
C-2 methylene	138	35 (9.2)	1.5
C-3 methylene	86	47 (6.7)*	1.5
C-α methine	56	39 (8.2)*	1.5
C-β methylene	83		1.4
Carbonyl		21 (15)	

[a] In ms, with an estimated error ±10%. [b] In Hz, with an estimated error ±10%, and ±20% of peaks marked by an asterisk. [c] ±10%.

width of the carbonyl carbon, for instance, is estimated as ca. 600 Hz at 30 °C. At 72 and 92 °C, it is found that all of the signals are narrowed. The assignment of the peaks has been made on the basis of the peak positions of its monomer (HEMA) and PMMA (Table V). The assignment of C-1 and C-2 of the side chain is determined by taking into account the additivity rule for ^{13}C chemical shifts,[21] displacement of the ^{13}C signals of HEMA in the presence of Eu(DPM)$_3$, and spin–lattice relaxation times. Although the C-β peak is rather broad even at 92 °C and further broadened beyond recognition at 73 °C, the spectrum of the gel swollen with dimethyl sulfoxide gives rise to a distinguishable peak for C-β (Figure 3E). In Figure 3, the most intense signal is the C-2 methylene of the polar end of the side chain. The neighboring C-1 methylene group seems to give broad and less intense signals. Under the condition of suppression of NOE, however, it is found that the peak intensities of C-1, C-2, and C-3 are almost identical within the limit of experimental error. Clearly, splitting of the C-3 peak (and also C-α) can be ascribed to the effect of tacticity of the polymer. Table V indicates that no temperature dependence of the ^{13}C chemical shifts is observed in the PHEMA gel. In Table VI, the relaxation parameters are summarized.

Discussion

Displacement of Chemical Shift Due to Gel Formation. Previously, it was shown that the ^{13}C chemical shifts of the C-1 and C-3 signals of the (1→3)-β-D-glucan from *Alcaligenes faecalis* in the gel state are displaced downfield by amounts of ca. 2–3 ppm with respect to those of the water-soluble acid-degraded low molecular weight fraction, which has a disordered conformation.[6] These downfield shifts are explained in terms of restricted rotamer population around the glucosidic bonds because of assuming a helix form in the gel state. In view of the study of the shift in the absorption maximum of Congo Red complexed with this polymer, the presence of such an ordered conformation was confirmed.[24,25] Furthermore, it was reported that the ^{13}C signal of the α carbon of poly(L-lysine hydrobromide) is displaced downfield (ca. 2 ppm) in the gel phase prepared under the condition of extremely low water content (less than 13 molecules of water per residue).[26] These results strongly support the idea that displacement of the ^{13}C chemical shift might be induced in the carbons of the backbone having in the gel state an ordered (helical) conformation. In this connection, it is worthwhile to examine whether displacement of the ^{13}C chemical shift can be induced as a result of gelation even in the gel consisting of *disordered* conformation as in the cross-linked synthetic gel. Since such a displacement of signals cannot be observed in the gels and solutions of PVP (Table I), NVP, and MMA (Table III), nor in the study of the temperature dependence of the ^{13}C chemical shifts of PHEMA (Table V), the possibility of any special effect causing displacement of the ^{13}C shifts in the gels can be ruled out. This is also in agreement with the ^{13}C NMR study of bulk *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene.[11]

Effect of Cross-Linking (PVP Gel). Since the glass-transition temperature of uncross-linked PVP is reported to be at 105 °C,[27] the observation of high-resolution ^{13}C NMR signals at ambient temperature is satisfactorily explained in terms of the acquisition of rapid molecular motion as in the liquid state as a result of swelling by a good diluent. This is easily anticipated by considering that one monomeric unit is surrounded by 55 water molecules in the case of the PVP gel of 90% water content. It is obvious, however, that segments of cross-links and their vicinities are unable to contribute to high-resolution ^{13}C resonances because of the highly restricted mobility. For this reason, the considerable loss of peak areas is clearly to be ascribed to the carbons of such regions. Consequently, increase of cross-links, accompanying a decrease of water content, would be expected to lead to increased loss of peak areas. This is true for the gels of water contents of 90 and 75%. In addition, the line broadening due to the introduction of cross-links is evident (Table II) and especially manifest at 53% water content (Figure 1D). In the latter, however, loss of peak areas is almost the same as that of 75% water content. Those line broadenings are obviously explained in terms of restriction of chain mobility due to the presence of cross-links and entanglement of polymer chains especially in the vicinity of cross-links, since the line broadening is re-

Table V
^{13}C Chemical Shifts[a] of PHEMA Gel at Various Temperatures

			PHEMA Gel				
			Swollen by	Hydrogel			
Assignment	PMMA[b]	HEMA[c]	DMSO (92 °C)	92 °C	73 °C	46 °C	30 °C
C-3 methyl	16.2		16.7	16.9	16.7		
	18.5	18.2	18.5	18.7	19.4	17.5	
	20.8		20.7	21.0			
C-α quarternary	44.3		44.5				
	44.6		44.7	44.9	44.9	44.8	
C-β methylene	52.4						
	54.2		53.2	52.2			
C-2 methylene		60.6	58.6	59.3	59.3	59.2	
C-1 methylene		66.4	65.9	66.2	66.1		
Carbonyl	176.0						
	177.6	167.8	178.2	177.9	178.1	178.3	182
	177.9						

[a] Parts per million downfield from external Me_4Si. [b] In chloroform solution; assignment based on ref 23. [c] In chloroform solution.

Table VI
^{13}C T_1,[a] Line Width[b] (T_2), and NOE[c] Values of PHEMA Gel at Various Temperatures (25.05 MHz)

	92 °C			73 °C			49 °C			30 °C
	NT_1	Line width (T_2)	NOE	NT_1	Line width (T_2)	NOE	NT_1	Line width (T_2)	NOE	Line width (T_2)
C-1 methylene	294	68 (4.7) 14 (22)[d]	1.7	330	260 (1.2)*	1.7				
C-2 methylene	440	27 (12) 8.9 (35)[d]	2.2	380	94 (3.4)*	2.1				
C-3 methyl	246	41 (7.8) 33 (9.7)	2.5 2.3	171	71 (4.5)*	2.2	150	412[e] (0.77)*	1.9	
C-α quarternary		52[e] (6.2)			68[e] (4.7)*					
Carbonyl		52 (6.2)			65 (4.9)			270 (1.2)		620 (0.51)

[a] In ms, with an estimated error of ±10%. [b] In Hz, an estimated error ±10–±15%, and ±20% for peaks marked by an asterisk. [c] ±10%. [d] Gel swollen by DMSO. [e] Corrected by unresolved separation due to tacticity from the data at 92 °C (5 Hz and 68 Hz for C-α quarternary and C-3 methyl peaks, respectively).

markable in samples of higher cross-linking. Table II shows that the degree of cross-linking does not affect the T_1 and NOE values. In order to characterize the segmental motions and also analyze the effect of cross-links, it seems to be very important to deduce the correlation times as a measure of the mobility of the polymer chains.

Since it is already established that nuclear magnetization of protonated carbons of the backbones and side chains of polymers is relaxed mainly through ^{13}C–^{1}H dipole–dipole interaction,[28,29] the correlation time of isotropic tumbling described either by a single correlation time or a distribution of correlation times can be calculated by the formulas by Doddrell et al.[29] or Schaefer,[30] respectively. Description by single correlation times seems to be insufficient for the present case, since a marked discrepancy of the correlation times based on the T_1, T_2, and NOE is evident as shown in Table VII. The discrepancy is especially remarkable in the gel of low water content (75%). Further, choice of the correlation times, either from the lower or higher temperature side of the minimum of the T_1 curve, cannot be determined in this case. In this connection, the observed T_2 values seem to be much lower for the correlation time of the higher temperature side, the NOE's being higher for that of the lower temperature side. To resolve this discrepancy, it seems more appropriate to adopt the scheme of a distribution of correlation times, according to a log χ^2 distribution, which has been successfully used for the interpretation of the relaxation times of *cis*-polyisoprene[13,30] and elastin fibers.[31]

Following Schaefer,[13,30] the log χ^2 distribution of the correlation times is given by

$$F_p(s) = (ps)^{p-1}e^{-ps}p/\Gamma(p)$$

with

$$s = \log_b (1 + (b - 1)\tau/\bar{\tau})$$

where $F_p(s)$ is the probability density function of the correlation time τ. $F_p(s)$ is normalized to unity by the Γ function $\Gamma(p)$. In this formula, p is used to describe the width of the distribution of the correlation times. As p becomes smaller, the distribution becomes broader. The parameter b describes logarithmic time scale. In this treatment, the average correlation time, $\bar{\tau}$, is computed by

$$f(w_i) = \int_0^\infty \frac{\bar{\tau}F_p(s)\{\exp_b(s-1)\}\,ds}{\{b-1\}\{1 + w_i^2\bar{\tau}^2[\{\exp_b(s-1)\}/(b-1)^2]\}}$$

instead of

$$f(w_i) = \tau^2/(1 + w_i^2\tau^2)$$

The calculated correlation times are found to give consistent values among those obtained from the T_1, T_2, and NOE values

Table VII
Calculated Correlation Times[a] of the Backbone Methine Carbon of PVP Solution and the Gels of PVP

	PVP soln	Hydrogel, water content = 90%	75%
Single correlation time			
From T_1	0.90, 17	0.93, 17	1.0, 16
From NOE	2.1	2.4	3.1
From T_2	9.7	21	22
Log χ^2 distribution,[b] p =	18	16	16
From T_1	1.8, 14	2.1, 13	3.0, 8.4
From NOE	2.0	2.7	7.9
From T_a	1.8	2.0	3.1

[a] In ns. [b] b = 1000.

with the width parameter of p = 18 (PVP solution) and p = 16 (PVP gel) and b = 1000 (Table VII). As the degree of cross-linking is increased, a discrepancy in the correlation times still seems to occur (a factor of 3 at 75%) but is much improved by this treatment. The correlation times $\bar{\tau}$ of 2–3 ns are very similar to those of polystyrene in solution and *cis*-polyisoprene in the solid state.[30] In reflecting the presence of the cross-links in the gel state, a slight increase of the width parameter, and also of the correlation times by a factor of 2, is obtained (Table VII).

Differential Swelling. Copolymer of NVP and MMA. In the gel of the copolymer swollen by water, the hydrophobic MMA component does not give rise to ^{13}C resonances even at 90 °C (the glass-transition temperature of uncross-linked syndiotactic or atactic PMMA being at 105 °C[27]). This component might contain a rigid disordered crystalline region as additional cross-linking. This view is consistent with the opaque macroscopic appearance of the gel. Interestingly, the hydrophobic portion is able to be swollen with the addition of chloroform or in dimethyl sulfoxide, which may be good diluents for the MMA component. It is also interesting to note that the peak heights of the MMA component are at least three times as great as those of the NVP component in the spectrum taken in the presence of chloroform (Figure 2C), although the composition of the copolymer is almost equimolecular in MMA and NVP. This situation may be closely related to the microscopic constitution of the gel. The monomer reactivity ratio of the copolymerization of MMA (M_1) and NVP (M_2) has been given as[33] $r_1 = k_{11}/k_{12} = 4.7 \pm 0.5$ and $r_2 = k_{22}/k_{21} = 0.005 \pm 0.005$, where k_{ij} (i, j = 1, 2) denotes the rate constant of the reaction of $M_i\cdot$ radical with M_j monomer. $M_i\cdot$ represents chain radical having M_i as its terminal. Accordingly, the polymer may predominantly consist of MMA

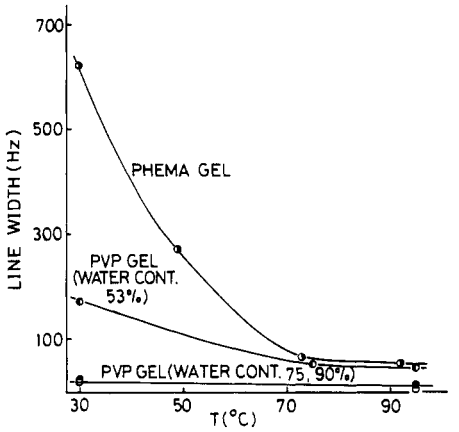

Figure 4. Temperature dependence of ^{13}C line width of PHEMA and PVP gels: (◑) carbonyl carbon of PHEMA gel; (◐) C-2 methylene carbon of PVP gel of water content 53%; (●) C-2 methylene carbon of PVP gel of water content 75%; (○) C-2 methylene carbon of PVP gel of water content 90%.

at an early stage of the copolymerization. In addition, the probability of the addition of NVP monomer to M_2· radical is very low. A GLC analysis of the unreacted monomers is consistent with the expectation. Consequently, a blend-type copolymer in which some of NVP component is dispersed in MMA-rich blocks might be prepared by this procedure. The observation of the reduced peak intensities of the NVP component described above supports this view; some of the NVP chains dispersed in the MMA domain may not gain motional freedom enough to give high resolution ^{13}C NMR signals due to the additional cross-links of the crystalline region of MMA.

Effect of Temperature (PHEMA). Similarly to the case of the PVP of low water content (53%), the extreme broadening of the ^{13}C NMR of PHEMA at ambient temperature is mainly caused by chain entanglement. Although no cross-linking agent is employed for the preparation of the gel, the water content of this sample is very low (37%). This is mainly due to the fact that water is not a good enough diluent to cause swelling. In this regard, DMSO may be more suitable for the purpose of swelling, since rather sharp resonance lines are observed (Figure 3E). The temperature dependence of the ^{13}C spectra of PHEMA gel is in contrast to that of the gel of PVP of water content 90% (Figure 2A) and of water content 53%. As shown in a plot of the line width against temperature (Figure 4), the line widths of PVP gels of 90 and 75% water contents exhibit no temperature dependence, while that of water content 53% shows one-fifth the magnitude of the temperature dependence of PHEMA gel. Consequently, such a marked dependence of the ^{13}C line width on temperature could be attributed to restricted segmental motion caused by chain entanglement, which may be a predominant cause of the extremely large line widths observed at ambient temperature. Because of chain entanglement, not all the spatial orientations of the polymer chain are readily accessible[12] and the residual ^1H dipolar field remaining from the incomplete averaging is likely to broaden the signals of nonprotonated carbons such as the quarternary and carbonyl group to nearly the same extent as the protonated carbons. At higher temperature, in addition to a gain of motional freedom of the polymer chain, it is likely that access of water molecules (or another diluent) to the region of cross-links, which may be formed by a crystalline region instead of covalent bonds, may decrease the extent of the cross-linking. With regard to the role of diluents for molecular motion of the polymer chain, it is of interest to note that a solid gel of PHEMA (not swollen) exhibits an extremely broad envelope of ^{13}C resonance of the line width 2 kHz even at 92 °C, which is above the glass transition (55 °C).

The T_1, T_2, and NOE values (Table VI) clearly indicate that the correlation times of the side-chain motions are on the high-temperature side. Numerical evaluation of the correlation times, however, seems to be very complicated, since motions of the side chains and backbone should be taken into account in the treatment of the distribution of the correlation times. Nevertheless, it follows that the mobility of the C-2 methylene is much higher than that of the C-1 methylene group, reflecting the location of the former at the terminal end of the rather long side chains.

Acknowledgment. The authors are grateful to JEOL Ltd. for providing them opportunity to use FX-60 and PFT-100 spectrometers at an early stage of this work.

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(19) Recently, it was pointed out that unless the T_1 of the proton resonance is much smaller than the T_1 of the ^{13}C, a waiting time of $10T_1$ should be used to avoid systematic errors due to improper waiting times (ref 20). The only data taken with a waiting time of $6T_1$ are for the C-1 and C-2 methylene groups of PHEMA at 73 °C (see Table VI, column seven). By comparing the NOE data with that obtained using waiting times of 8–15 times T_1, it is likely that such a systematic error is not greater than the experimental error (±10%).
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(32) Strictly speaking, a model of isotropic molecular motions might not be applied to our present case, since the NT_1 values of methylene carbons of the aqueous solution and gels of PVP, and of the copolymer of NVP and MMA, are from 17 to 25% and 48% longer than those of the methine carbons, respectively. This implies that molecular motions of the backbone may be anisotropic to some extent. However, the approximation by an isotropic diffusion model, except for copolymer of NVP and MMA, may not be qualitatively misleading, especially in examining the effect of the cross-links.
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