Detection of Spatial Inhomogeneity in Poly(acrylic acid) Gels by Measuring Time-Dependent Diffusion Coefficients of a Probe in NMR Experiments: Effect of the Degree of Cross-Linking and Degree of Swelling

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ABSTRACT: Inhomogeneities in poly(acrylic acid) (PAA) gels differing in their degree of cross-linking were detected as a function of the degree of swelling, Q, defined as the mass of the swollen gel divided by the mass of the dry polymer, $Q = M_{swollen}/M_{dry}$. Q was in the range 2.8−10.0 for the gels studied. The networks were prepared at 70 °C by simultaneous polymerization and cross-linking of a mixture of acrylic acid (AA), sodium carbonate, cross-linker (1,4-butanediol diacrylate), and the redox couple sodium persulfate/sodium isoascorbate as the initiator. Two types of networks were prepared by using the same monomer concentration (30 wt %) and the same amount of sodium carbonate but different amounts of the cross-linker, 1.1 and 0.5 wt %, respectively, in the monomer mixture. The corresponding notation is GEL1 and GEL2. Detection of heterogeneities was based on measuring the diffusion coefficients of the probe molecule poly(ethylene glycol) (PEG) as a function of the degree of swelling and diffusing time, Δ, by means of field-gradient ^{1}H NMR spectroscopy. The inhomogeneities emerged as the degree of swelling of the gels was reduced. For the highly swollen gels (Q = 10.0 and 5.2 for GEL1 and Q = 10.0 and 5.1 and 4.5 for GEL2) only *one* diffusion coefficient was detected, independent of the diffusing time, Δ, in the range 30−500 ms. For less swollen gels (Q = 2.9−4.5 for GEL1 and 2.8−3.9 for GEL2) *two* diffusion coefficients were detected, D_{fast} and D_{slow}, with values that depended on Δ; for these less swollen gels the diffusion distances d_{fast} and d_{slow}, and the relative fractions of the fast and slow diffusion components, f_{fast} and f_{slow}, were calculated. We defined a specific degree of swelling, Q_s, above which the diffusion of the probe in the two gel systems changed from one to two components. A larger value of Q_s in GEL1 was taken as an indicator of a more inhomogeneous gel. Analysis of the effect of Δ on the diffusion coefficients, diffusion distances, and fractions of slow and fast diffusion components indicated that the gels form a highly cross-linked region in a narrow Q range. In this Q range, the polymer chains interact and form a highly restricted diffusion region. The extent and distribution of the cross-links form different restricted diffusion regions in GEL1 and GEL2 systems.

Introduction

Superabsorbent polymers (SAPs) are lightly cross-linked ionic polymers that in aqueous media can absorb several hundred times their dry mass. An important advantage of SAPs, compared to "traditional" absorbent materials such as fiber masses and foams, is their ability to retain the solvent even when pressure is applied.[1] On an industrial scale, acrylic acid (AA) is the monomer of choice; SAPs based on poly(acrylic acid) (PAA) are prepared by copolymerization of partially neutralized AA and a vinyl cross-linker in the presence of an initiator. Typical cross-linkers used in the preparation of SAPs are ethylene diacrylate (EDA) and 1,4-butanediol diacrylate (BDA); the former is more hydrophilic.

The amount of liquid absorbed by the polymer is of considerable practical importance and can be calculated by considering the osmotic pressure Π due to three contributions: the polymer−solvent enthalpy and entropy of mixing, the entropy associated with conformational changes of the polymer network due to swelling, and the ion−solvent and ion−polymer interactions:

$$\Pi = \Pi_{mixing} + \Pi_{network} + \Pi_{ions} \quad (1)$$

For the "phantom model network", which assumes that the constraints on the chains are due only to the presence of cross-links and not to other chains, the osmotic pressure and therefore the swelling capacity can be calculated on the basis of the polymer−solvent interaction parameter, the molar volume of the solvent, the polymer density, the volume of sample when prepared, the molecular weight between cross-links, the molecular weight of the chain, and the concentrations of each ion in the gel and in the swelling solution.[2]

Numerous experiments have suggested that the swelling of real networks is less than that calculated from the Flory−Erman and Flory−Rehner models.[2] Two main factors contribute to the reduced swelling: Manning condensation of counterions[3] and gel heterogeneity; these two topics will be briefly described.

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Manning Condensation. The considerable electrostatic repulsion between neighboring ionic groups with the same charge can be reduced by counterion condensation on the opposite charges attached to the polymer chain. The central parameter of Manning's theory is the dimensionless charge-density parameter $\xi = l_b/l$. The Bjerrum length is $l_b = e^2/(\epsilon k_B T)$, where e is the elemental charge, ϵ the dielectric constant of the solvent, k_B the Boltzmann constant, and T the absolute temperature; l is the distance between two charged groups in the polyion. We note that the Bjerrum length in water is $\approx$7 Å, and the closest distance between two negative charges in PAA, l, is 2.56 Å.

According to this model, in the limit of infinite dilution, the fraction of bound counterions per fixed charge in the polyion, θ_z, depends on the counterion valence, z:

$$\theta_z = \frac{1}{z}\left(1 - \frac{1}{z\xi}\right) \tag{2}$$

The critical value of ξ, $\xi_{critical}$, above which ion condensation occurs also depends on z. For $z = 1$, $\xi_{critical} = 1$; for $z = 2$, $\xi_{critical} = 1/2$; and for $z = 3$, $\xi_{critical} = 1/3$. In the case of PAA neutralized by Na^+ counterions, the critical condition, $\xi_{critical} = 1$, is achieved when $l \approx 7$ Å. Therefore, counterion condensation will be avoided when the degree of neutralization, α, is ≤ 0.3: when about one-third, or less, of the carboxylic groups are neutralized. Most theories of the effect of ionic interactions in polyelectrolytes have assumed the presence of noncoordinating monovalent counterions that are treated as point charges. The specificity of the ionic interactions has been demonstrated repeatedly, however. As early as 1954 it was pointed out that the addition of Ca^{2+} to PAA leads to a larger coil contraction than that of an equivalent amount of Na^+.[4] Moreover, Klooster et al. have shown in a series of papers that the conformational transition in PAA solutions in methanol can be detected for Na^+ but not for Li^+ counterions.[5] More recently, viscosity, light scattering, and small-angle neutron scattering measurements of polyelectrolytes in the presence of divalent cations have indicated that the chain dimensions are reduced, compared to an equivalent amount of monovalent counterion, and that the reduction is sensitive to the specific divalent counterion.[6,7] Work done by some of us has suggested that the coordinating abilities of the counterion are also important and that the binding of the counterion depends on the solvent, the specific ionic group in the polymer, the type of counterion, and the pH.[8] Therefore, estimates of the degree of swelling by polymer gels based on interactions between point charges should be considered as qualitative indicators only.

Gel Inhomogeneity. Numerous experiments have indicated that networks produced by concomitant polymerization and cross-linking contain spatial fluctuations of the cross-link density or even phase-separated domains. Dusek and Prins have demonstrated that polyacrylamide networks become more inhomogeneous as the monomer concentration decreases during the process of gel formation.[9] The parameters that affect the development of gel inhomogeneities during the synthesis of polyacrylamide gels have been studied in a series of papers by Weiss et al.[10] The experimental results were explained by a model that described the gel as a two-phase structure: in the first stage monomers are added around growth centers, thus producing microgel particles with network concentration maxima in the center and containing many unreacted double bonds. These "cores" become loosely linked to each other by a small number of linkages in the second stage of the process, when the concentration of the monomer is lower.

The concept of "osmotically passive" and "osmotically active" counterions has been recently introduced.[11] The degree of swelling was calculated from the two-phase model for the gel, which assumed the existence of inner "cores" formed initially during the polymerization process, separated by a "shell" where the polymer density is lower. The model is similar to that described in ref 10. Counterions residing in the shell are "active" and contribute fully to the osmotic pressure; counterions in the core, however, are "passive" in the sense that their mobility is limited and therefore they do not fully contribute to the osmotic pressure that determines the degree of gel swelling. The degree of inhomogeneity, n, was defined as the ratio of the polymer density in the inner core to that in the shell. For reasonable values of the core and shell sizes and of the corresponding degrees of cross-linking, the gel inhomogeneity can seriously lower the degree of swelling, typically by a factor of $\approx$5.[11]

Imperfections in the network structure may result from additional causes. Differences in reactivity of the monomers cause heterogeneous polymerization, and differences in hydrophilicity between the monomers and the cross-linker may lead to clusters of cross-links. Therefore, the preparation method for superabsorbent polymers (concomitant polymerization and cross-linking) is expected to contain structural inhomogeneities. Reducing and controlling the spatial inhomogeneities in gels is important not only for SAPs but also for control of mechanical and optical properties of numerous gel systems and of mesh (network) size in polymers used in electrophoresis.

Scattering methods such as small-angle X-ray and neutron scattering, SAXS and SANS, respectively, have been widely used for the visualization of inhomogeneities in swollen gels;[12−14] the interpretation of results is complicated because scattering reports not only on time-independent spatial fluctuations but also on time-dependent dynamical effects. The separation of the two components is often achieved by dynamic light scattering (DLS).[14] Initial monomer concentrations in polymerization reactions are known to affect the network structure. The complex relationship between gel inhomogeneity and monomer concentration was studied recently in polyacrylamide gels prepared with four initial monomer concentrations; two swelling states were investigated for the initially prepared gels and for equilibrium swelling in water.[12,13] Surprisingly, a critical monomer concentration that leads to maximum inhomogeneity was detected and assigned to the interplay between two opposing effects: increased inhomogeneity at higher monomer concentrations and decreasing degree of swelling, which reduces the difference between the densely cross-linked and the weakly cross-linked regions in the gel.

A recent SANS study of polystyrene (PS) networks swollen by toluene has shown that the presence of spatial fluctuations in concentration is not limited to networks prepared by simultaneous polymerization and cross-linking.[15] The gels in this study were prepared by cross-linking of well-defined polystyrene chains of low polydispersity, using a trifunctional cross-linker, and the measurements were performed on PS chains with

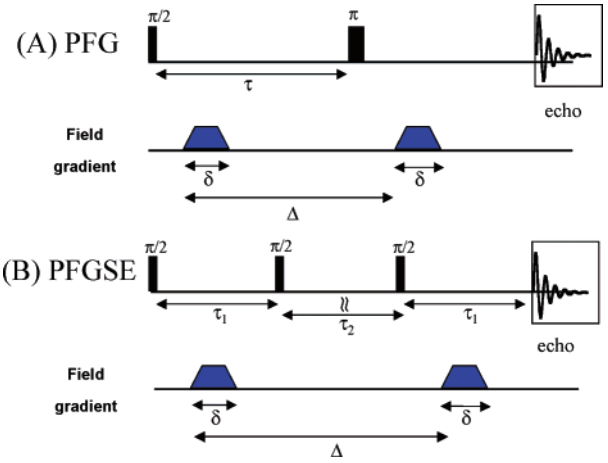
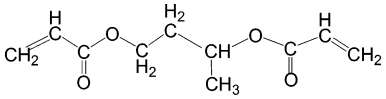


Figure 1. Pulse sequences used for measurement of diffusion coefficients of PEG in PAA gels: The PFG sequence used for $\Delta = 10$ and 30 ms (A) and the PFGSE sequence used for $\Delta = 50-500$ ms (B). δ is the field gradient pulse length ($\approx 1-7$ ms), g is the field gradient strength (up to 1000 G/cm), and Δ is the gradient pulse interval (diffusion time).

Chart 1: Cross-Linker, 1,3-Butanediol Diacrylate (BDA)



different molecular masses. The excess scattering compared to that of semidilute solutions of the same concentration led to the detection of hard-to-swell zones that emerged as the gel was progressively swollen. This important study suggests therefore that the existence of inhomogeneities in swollen networks is a general phenomenon in a large number of gel systems.

Measurement of diffusion coefficients, D, by field-gradient NMR has emerged as a powerful method for detecting inhomogeneities in gels.[16−18] The method is based on the interpretation of the dependence of D on the time Δ ("diffusion time" or "observation time") between the two gradient pulses in the pulsed field gradient (PFG) or pulsed field gradient spin echo (PFGSE) sequences, shown in Figure 1. This time dependence of D is observed in heterogeneous systems. In gels the inhomogeneity is detected from the study of the diffusional behavior of probe molecules. For short diffusion time, probe molecules in inhomogeneous polymer gel systems have two diffusion components; for long Δ values a single diffusion component is observed due to averaging during the diffusion time. In most cases the model used for the interpretation of the results is based on the "two-state system", which assumes that the spatial inhomogeneties can be represented by two types of domains with different mesh sizes.[17,19]

The purpose of the present study was to detect and quantitate spatial inhomogeneity in two PAA gels differing in their degree of cross-linking. The method is based on measuring the diffusion coefficients of poly(ethylene glycol) (PEG) as a probe, as a function of the degree of swelling and diffusing time, Δ, by means of field-gradient ^{1}H NMR spectroscopy. As described below, the inhomogeneities emerged as the degree of swelling of the gels is varied.

Experimental Section

Preparation of PAA Networks. The synthesis was performed in the laboratories of The Dow Chemical Co. The inhibitor, 4-methoxyphenol, in AA and cross-linker was removed before polymerization in order to avoid interference in other spectroscopic measurements, for instance fluorescence. Purification of the acrylic acid was done by vacuum stripping the acid from the inhibitor in a rotary evaporator (pressure 40 mmHg, bath temperature 77 °C). The distilled product was analyzed for inhibitor, using an established liquid chromatographic method;[20] no inhibitor was detected after this procedure. Cross-linkers were separated from inhibitor by passing the mixture through a column packed with activated carbon. The monomers were used immediately after purification.

Polymerization was conducted in a 1 L resin reaction kettle equipped with a glass jacket for temperature control. The glass lid had ground glass fittings for nitrogen gas inlet, gas outlet, and thermocouple. The top and bottom pieces of the reaction kettle were sealed using a small amount of silicone vacuum grease applied to the flat glass flange and held together with a spring-loaded kettle clamp.

The monomer mixture was prepared by adding AA and water to the reactor, followed by addition of an aqueous solution of sodium carbonate. The reagents were stirred by a Teflon-coated magnet. The evolution of carbon dioxide gas served to deoxygenate the mixture. The cross-linker, 1,4-butanediol diacrylate (BDA, Chart 1), was injected into the monomer mixture by a septum, and nitrogen gas was added to keep the monomer mixture oxygen-free. The initiator was the redox couple sodium persulfate and sodium isoascorbate. Both components were added to the reactor as 10 wt % aqueous solutions. The initiator solutions were prepared immediately before use. The polymerization began within a few minutes of the addition of the initiators. After reaching 70 °C, the water bath, prewarmed to 70 °C, was activated to circulate water through the jacket for 120 min. A portion of the resultant hydrogel was cut from the main reactor product, further cut into small pieces, and dried at 100 °C in a circulated-air oven for 16 h. The dried portion was ground to a powder with a kitchen blender. The equilibrium swelling capacity was determined on this dried granular sample. The gel before drying was cut into large chunks and sealed in a zippered plastic bag for storage.

Two types of networks were prepared, using the same monomer concentration (30 wt %) and the same amount of sodium carbonate, but different amounts of the cross-linker, 1.1 and 0.5 wt %, respectively, in the monomer mixture. The corresponding notation is GEL1 and GEL2.

Sample Preparation. The probe polymer, PEG (MW = 1500, $M_w/M_n = 1.05$), was purchased from Polysciences Inc. The solvent was deuterated water (D_2O, D enrichment 99.9%) from Merck. The swollen gels prepared as described above were dried in air at 40 °C for 1 day and over P_2O_5 under reduced pressure at 40 °C for one more day. PAA gels with $Q = 10.0$ and 6.0 were then prepared by soaking the dried gels in the D_2O solution containing 5 wt % PEG. The degree of swelling, Q, of the gels is defined as the mass of the swollen gel ($M_{swollen}$) divided by the mass of the dried gel (M_{dry}): $Q = M_{swollen}/M_{dry}$. Because it is difficult to disperse directly the probe in PAA gels with low Q, the water in gels with $Q = 6.0$ was gradually evaporated at 45 °C until the degree of swelling reached a desired Q value. In this way GEL1 and GEL2 samples with essentially the same Q values were obtained: 2.9, 3.5, 4.0, 4.5, 5.2, and 10.0 for GEL1 and 2.8, 3.9, 4.5, 5.1, and 10.0 for GEL2. The PEG concentrations in each gel were different, but the PEG concentrations in gels with the same Q value were almost identical. Therefore, diffusion coefficients of probes in GEL1 and GEL2 systems with the same Q value can be compared. Moreover, the diffusion behavior of PEG in PAA gels can be examined as a function of Q. The degree of swelling in the GEL1 and GEL2 systems, Q, and the corresponding concentrations of the probe, c_{probe}, are given in Table 1.

The hydrodynamic radius, R_H, of PEG was estimated using the Stokes−Einstein equation

$$D_0 = \frac{kT}{6\pi\eta R_H} \tag{3}$$

Table 1. Degree of Swelling (Q) and Probe Concentrations in the Gels[a]

GEL1	Q	2.9	3.5	4.0	4.5	5.2	10.0
	c_{probe}, wt %	13.4	10.2	8.4	7.2	6.0	5.0
GEL2	Q	2.8		3.9	4.5	5.1	10.0
	c_{probe}, wt %	13.8		8.6	7.1	6.0	5.0

[a] $Q = M_{swollen}/M_{dry}$.

where k is the Boltzmann constant, T is the temperature, η is the viscosity of the solvent, and D_0 is the self-diffusion coefficient of probe molecule in the absence of gel. The self-diffusion coefficient of PEG in 0.5 wt % PEG/D_2O solution at 25 °C, $D_0 = 1.84 \times 10^{-6}$ cm^2 s^{-1}, was measured by pulsed field gradient spin echo (PFGSE) ^{1}H NMR. The hydrodynamic radius, R_H, is 1.33 nm. The probe dimension gives an idea on the length scale that can be investigated.

Measurement of Diffusion Coefficients. Diffusion coefficients, D, of PEG in PAA gels were measured at 25 °C with the Bruker DSX-300 NMR spectrometer operating at 300.11 MHz for ^{1}H, using a pulsed field gradient generator with maximum field strength of 1160 G/cm. The temperature was controlled within ±0.1 °C. Two types of pulse sequences were used for measurements of diffusion coefficients: the pulsed field gradient (PFG) method (π/2 pulse−gradient pulse−τ−π pulse) and the pulsed field gradient stimulated echo (PFGSE) method (π/2 pulse−gradient pulse−τ_1−π/2 pulse−τ_2−π/2 pulse), as shown in Figure 1. The field gradient strength, g, varied in the range 0−1000 G/cm, and the interval between two field-gradient pulses, Δ, was varied in the range 10−500 ms. The spectral width and number of data points were 4.0 kHz and 4096, respectively. The free induction decay (FID) after the echo maximum was recorded and Fourier transformed.

The diffusion coefficients of PEG in the gels were measured as a function of Δ, using the PFG sequence for Δ in the range 10−30 ms, and the PFGSE sequence for Δ in the range 50−500 ms. The echo intensity was measured as a function of g. The D values were determined using the relationship between the echo signal intensity and the field gradient parameters, as shown in eq 4 for the case of several diffusion components.

$$\frac{A(g)}{A(0)} = \sum_i p_i \exp\left[-\gamma^2 g^2 D_i \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \quad (4)$$

In eq 4 $A(g)$ and $A(0)$ are the echo intensities with and without the magnetic field gradient pulse of strength g, respectively; γ is the gyromagnetic ratio of the proton; δ is the field gradient pulse duration (1−7 ms); and Δ is the gradient pulse interval (10−500 ms). When probe molecules have a single diffusion component during measuring time, plots of $\ln[A(g)/A(0)]$ as a function of $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ lead to a straight line with slope $-D$. When the diffusion of the probe consists of several components during measuring time, the total echo attenuation is a superposition of contributions from individual components; D_i is the diffusion coefficients of the ith component, p_i the fractional number of protons of the ith component, and $\sum p_i = 1$. The p_i values are determined by least-squares fitting of eq 4. Typical margins of error for D determination are 5−10%, but could be slightly higher for the case of the component with a low population.

Tables 2 and 3 present the diffusion coefficients of PEG in GEL1 and GEL2, respectively, as a function of Q and Δ at 25 °C, determined as described above. The D values are either independent of Δ or decrease with increase of Δ. The only exception is the slight increase of D_{slow} for GEL1 and GEL2 with $Q = 4.0$ and 3.9, respectively; this effect is most likely due to the higher experimental error, as the fraction of the slow component is low for GEL1 in the entire Δ range (≤0.15) and for GEL2 in the Δ range 30−100 ms (≤0.21).

Results and Discussion

Figure 2 shows typical PFGSE ^{1}H NMR spectra at 25 °C of PEG in GEL2 with $Q = 2.9$ as a function of the field gradient strength, g. The two main peaks, at ≈4.6 and 3.4 ppm, were assigned to HDO and PEG, respectively. Peaks from protons in the polymer chains do not appear in the ^{1}H NMR spectrum due to the slow dynamics of the network chains and the resulting broad lines. The HDO peak decayed rapidly because the diffusion rate is fast; the D value of water in the gels is in the range 10^{-6}−10^{-5} cm^2 s^{-1}. The PEG peak, however, decreased gradually with an increase in g and did not disappear even when for $g = 1000$ G/cm, indicating that the diffusion of PEG in the gel is much slower compared to that of water. The variation of the PEG peak intensity at 3.4 ppm was used for the determination of the diffusion coefficients.

Dependence of Diffusion Coefficients on the Degree of Swelling. Semilogarithmic plots of $[A(g)/A(0)]$ for PEG in GEL1 with $Q = 10.0$ as a function of $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ for Δ = 10, 50, 100, 250, and 500 ms at 25 °C are shown in Figure 3A. The experimental data lie on a straight line, indicating that PEG in this gel has a single diffusion component during the observation time for the entire Δ range. The D values in this Δ range are identical, within experimental error.

Corresponding plots for PEG in the same GEL1 but with $Q = 2.9$ are shown in Figure 3B. We note the gradual deviation from a straight line as Δ increases above 35 ms. The simplest way to interpret the data in Figure 3B is to deconvolute the echo signal into contributions from *two* diffusion components, slow (D_{slow}) and fast (D_{fast}). The fraction of the slow diffusion component can be determined from the intercept of the least-squares fitted straight line at larger g. All D_{fast} and D_{slow} values as well as the corresponding fractions as a function of Δ and Q are shown in Table 2 for GEL1 and in Table 3 for GEL2. From the tables it is clear that the probe has a single diffusion component in gels with large Q values and two diffusion components, fast and slow, in gels with lower Q values.

The variation of the D values for PEG in GEL1 (D_{GEL1}) and GEL2 (D_{GEL2}) with Q for Δ = 500 ms is shown in Figure 4; both D_{GEL1} and D_{GEL2} values increase with an increase in Q. The probability that the diffusion of probe molecules is restrained by the network depends on mesh size: transport through small mesh size in gels with lower Q values is expected to be slower; therefore, D_{GEL1} and D_{GEL2} values depend on Q.

The two diffusion components detected at low Q values are due to spatial inhomogeneity of the gels; weakly restrained diffusing probes contribute to the fast diffusion component, and strongly interacting probes contribute to the slow diffusion component.[18] As seen in Figure 4, probe molecules in GEL1 have two diffusion components for $Q \leq 4.5$ and a single diffusion component for $Q \geq 5.2$. For GEL2, two diffusion components were detected for $Q \leq 3.9$ and a single diffusion component for $Q \geq 4.5$.

We can define a specific degree of swelling, Q_S, above which the diffusion behavior of PEG molecules in the gels changed from one to two components. As seen in Figure 4, the Q_S values are 4.5−5.2 (for GEL1) and 3.9−4.5 (for GEL2). At $Q = 4.5$, for instance, PEG molecules have two diffusion components in GEL1 and a single diffusion component in GEL2. For a given Q value, the difference between the two gels is thought to arise from inhomogeneous distribution of chemical cross-links. Therefore, the difference in the diffusional behavior of the probe shows that GEL1 and GEL2 have different spatial inhomogeneities and distribution of the mesh sizes and that GEL1, with the higher degree of cross-

Table 2. PEG in GEL1: Diffusion Coefficients (D), Diffusion Lengths (d), and Fraction of Fast Diffusion Component (f_{fast})

Q[a]	Δ[b] (ms)	D[c] (cm^2/s)	d[f] (μm)	D_{fast}[d] (cm^2/s)	d_{fast}[f] (μm)	f_{fast}[e]	D_{slow}[d] (cm^2/s)	d_{slow}[f] (μm)
10.0	10	6.9×10^{-7}	1.2					
	30	7.4×10^{-7}	2.7					
	100	7.4×10^{-7}	3.8					
	250	7.3×10^{-7}	6.0					
	500	7.2×10^{-7}	8.5					
5.2	30	2.0×10^{-7}	1.2					
	50	1.9×10^{-7}	2.7					
	100	1.9×10^{-7}	3.8					
	250	1.8×10^{-7}	6.0					
	500	1.8×10^{-7}	8.5					
4.5	30			3.0×10^{-7}	1.3	0.67	9.9×10^{-8}	0.8
	50			3.2×10^{-7}	1.8	0.55	1.1×10^{-7}	1.1
	100			3.2×10^{-7}	2.5	0.54	1.2×10^{-7}	1.5
	250			3.8×10^{-7}	4.4	0.38	1.4×10^{-7}	2.7
	500			2.0×10^{-7}	4.5	0.41	1.3×10^{-7}	3.6
4.0	30			7.1×10^{-8}	0.65	0.85	3.3×10^{-9}	0.14
	50			6.3×10^{-8}	0.79	0.88	3.3×10^{-9}	0.18
	100			5.0×10^{-8}	1.0	0.90	4.2×10^{-9}	0.29
	250			5.2×10^{-8}	1.6	0.90	6.6×10^{-9}	0.57
	500			5.0×10^{-8}	2.2	0.87	7.0×10^{-9}	0.84
3.5	30			9.0×10^{-8}	0.73	0.53	2.7×10^{-9}	0.13
	50			5.8×10^{-8}	0.76	0.54	3.2×10^{-9}	0.18
	100			3.5×10^{-8}	0.84	0.59	1.2×10^{-9}	0.15
	250			1.6×10^{-8}	0.90	0.74	5.8×10^{-10}	0.17
	500			1.2×10^{-8}	1.1	0.81	5.6×10^{-10}	0.24
2.9	35			1.8×10^{-8}	0.35	0.24	2.0×10^{-9}	0.12
	50			1.0×10^{-8}	0.32	0.29	6.6×10^{-10}	0.08
	100			5.8×10^{-9}	0.34	0.33	3.4×10^{-10}	0.08
	250			3.3×10^{-9}	0.41	0.41	1.5×10^{-10}	0.09
	500			2.2×10^{-9}	0.52	0.58	8.5×10^{-11}	0.09

[a] Q is the degree of swelling. [b] Δ is the gradient pulse interval. [c] One diffusion component. [d] D_{fast} and D_{slow} are the fast and slow diffusion components of PEG. [e] f_{fast} and f_{slow} are the fractions of the fast and slow diffusion component of PEG. [f] d_{fast} and d_{slow} are corresponding diffusion distances.

Table 3. PEG in GEL2: Diffusion Coefficients (D), Diffusion Lengths (d), and Fraction of Fast Diffusion Component (f_{fast})

Q[a]	Δ[b] (ms)	D[c] (cm^2/s)	d[f] (μm)	D_{fast}[d] (cm^2/s)	d_{fast}[f] (μm)	f_{fast}[e]	D_{slow}[d] (cm^2/s)	d_{slow}[f] (μm)
10.0	10	6.5×10^{-7}	1.1					
	30	6.9×10^{-7}	2.6					
	100	6.6×10^{-7}	3.6					
	250	6.6×10^{-7}	5.8					
	500	6.8×10^{-7}	8.3					
5.1	30	4.0×10^{-7}	1.6					
	50	4.0×10^{-7}	2.0					
	100	4.0×10^{-7}	2.8					
	250	4.0×10^{-7}	4.5					
	500	3.9×10^{-7}	6.2					
4.5	30	1.9×10^{-7}	1.1					
	50	2.0×10^{-7}	1.4					
	100	2.0×10^{-7}	1.9					
	250	2.0×10^{-7}	3.1					
	500	2.0×10^{-7}	4.5					
3.9	30			7.0×10^{-8}	0.65	0.86	4.8×10^{-9}	0.17
	50			5.5×10^{-8}	0.74	0.85	4.8×10^{-9}	0.22
	100			4.6×10^{-8}	0.96	0.79	7.0×10^{-9}	0.37
	250			3.8×10^{-8}	1.4	0.69	6.8×10^{-9}	0.58
	500			3.5×10^{-8}	1.9	0.48	6.6×10^{-9}	0.81
2.8	30			9.0×10^{-8}	0.54	0.73	4.4×10^{-9}	0.17
	50			5.8×10^{-8}	0.53	0.75	2.5×10^{-9}	0.16
	100			3.5×10^{-8}	0.62	0.70	2.2×10^{-9}	0.21
	250			1.6×10^{-8}	0.77	0.64	1.6×10^{-10}	0.28
	500			1.2×10^{-8}	1.1	0.49	1.7×10^{-10}	0.42

[a] Q is the degree of swelling. [b] Δ is the gradient pulse interval. [c] One diffusion component. [d] D_{fast} and D_{slow} are the fast and slow diffusion components of PEG. [e] f_{fast} and f_{slow} are the fractions of the fast and slow diffusion component of PEG. [f] d_{fast} and d_{slow} are corresponding diffusion distances.

linking, has the more inhomogeneous network. The difference between the two gels becomes evident when the degree of swelling is varied.

Dependence of Diffusion Coefficients on Diffusing Time. The diffusion coefficients can be expressed via the mean-square displacement in the z direction during time Δ, $\langle z^2 \rangle$, by the random walk model of Einstein and Smoluchowki, eq 5. The root-mean-square distance, d, traveled during diffusion time is in eq 6; this value becomes a useful measure of the diffusion spread of probe molecules in three dimensions.

$$\langle z^2 \rangle = 2D\Delta \tag{5}$$

$$d = \sqrt{\langle z^2 \rangle} = \sqrt{2D\Delta} \tag{6}$$

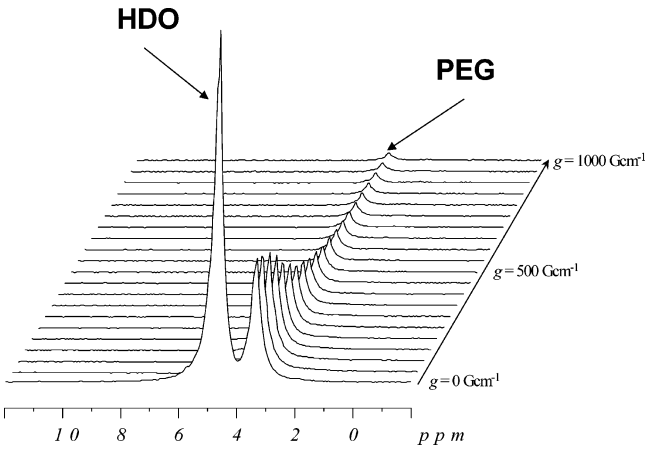


Figure 2. Stimulated echo ^{1}H NMR spectra of PEG in GEL2 with $Q = 2.9$ for $\delta = 3.5$ ms and $\Delta = 500$ ms as a function of the field gradient strength.

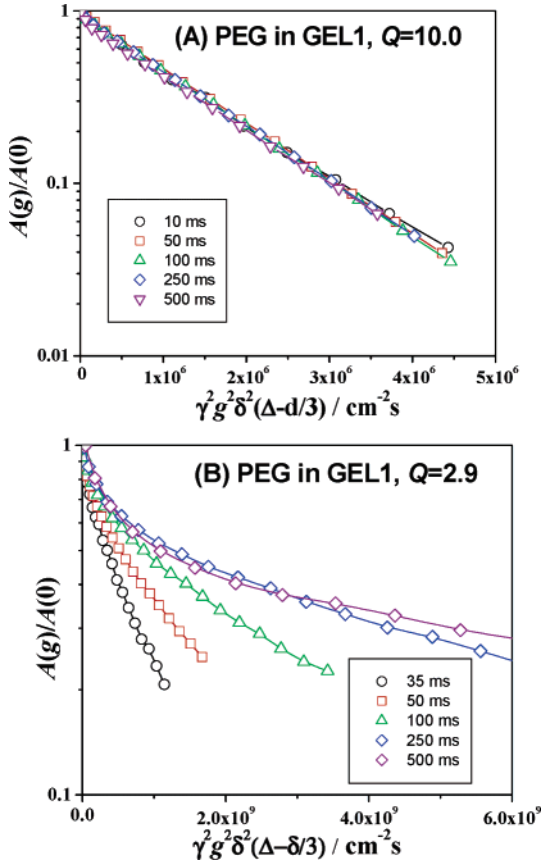


Figure 3. Attenuation of the stimulated echo intensity due to the diffusion of PEG in GEL1, for the indicated values of Δ. (A) $Q = 10.0$; best linear fits to the experimental points were drawn for each set. (B) $Q = 2.9$; experimental points for each Δ were connected by B-splines.

The diffusion distances of PEG in the gels at 25 °C as a function of Δ are also given in Tables 2 and 3. For GEL1 with $Q = 10.0$ and 5.2, and GEL2 with $Q = 10.0$, 5.1 and 4.5, probe molecules in the gels have only one diffusion component. In this regime, for a given Q value, D is independent of Δ in the range 10−500 ms, even though the diffusion distances are different. The diffusion distance in both types of gels for the single diffusion regime is 1−8 μm. Therefore, it appears that probe molecules diffuse to a large distance (compared to their hydrodynamic radius, 1.33 nm) through the network and experience the *same* intermolecular interaction with

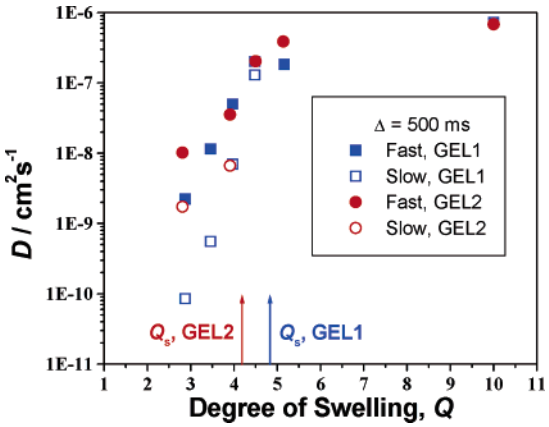


Figure 4. Dependence of the diffusion coefficient of PEG in GEL1 (squares) and GEL2 (circles) on the degree of swelling for Δ = 500 ms. Corresponding fast and slow diffusion coefficients are expressed by solid and open symbols, respectively. Also shown are the approximate specific degrees of swelling, Q_s, for the two types of gels (see text).

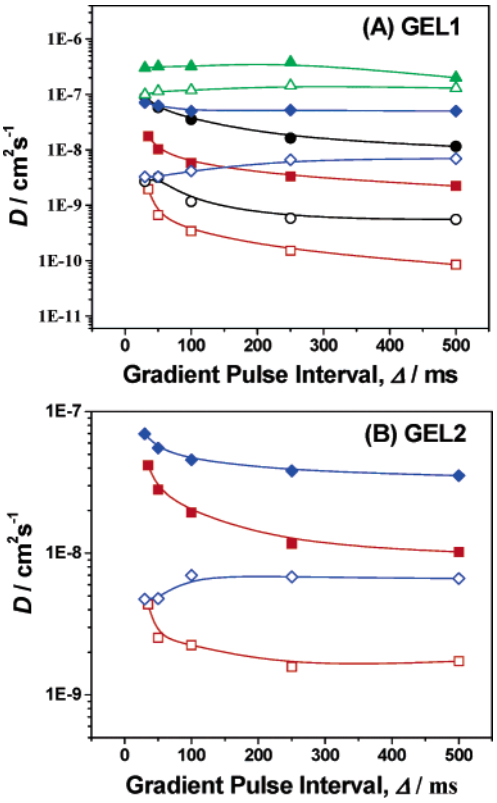


Figure 5. Dependence of the diffusion coefficients of PEG on the gradient pulse interval, Δ. (A) GEL1, for $Q = 4.5$, 4.0, 3.5, and 2.9. (B) GEL2, for $Q = 3.9$ and 2.8. The notation used is as follows. $Q = 4.5$: slow (△), fast (▲); $Q = 3.9$ and 4.0: slow (◇), fast (◆); $Q = 3.5$: slow (○), fast (●); $Q = 2.9$ and 2.8: slow (□), fast (■). Experimental points for each set were connected by B-splines.

network chains; on this scale the PAA gels appear to be spatially homogeneous.

The dependence of the diffusion coefficients on Δ in the Q regime that led to *two* diffusion components is presented in Figure 5A for GEL1 (for $Q = 4.5$, 4.0, 3.5, and 2.9) and in Figure 5B for GEL2 (for $Q = 3.9$ and 2.8). For both gels, the values of D_{GEL1} and D_{GEL2} depend on the diffusion time, Δ, in the range 30−500 ms. In this Δ range, probe molecules diffuse to a large distance through many network cells, but the diffusion distance, d, is not large enough to obtain the single diffusion

component because the scale of the mesh heterogeneity is larger than the diffusing distance. The difference between $D_{GEL1(fast)}$ and $D_{GEL1(slow)}$ values in GEL1 with $Q = 4.5$ is small, and these values tend to get closer as Δ increases; the difference between the two components is not averaged completely even for $d = 4.5$ μm. These experimental results suggest the possibility that two network regions with different mesh size exist in the gel, corresponding to small mesh size region with slow diffusion and to large mesh size region with fast diffusion.

The difference between the two D values in GEL1 with $Q = 4.0$ is much larger: $D_{GEL1(fast)}$ is 22 times larger compared to $D_{GEL1(slow)}$ for $\Delta = 30$ ms and 7 times larger for $\Delta = 500$ ms. These large differences are thought to arise from the large distribution of mesh size in this gel. The difference in diffusion coefficients for GEL1 with $Q = 4.0$ and 4.5 becomes smaller as Δ increases. For PEG in GEL1 with $Q = 2.9$ and 3.5, however, both $D_{GEL1(fast)}$ and $D_{GEL1(slow)}$ values decrease with an increase in Δ, and it is not clear whether the two values will approach each other.

The decrease of $D_{GEL1(slow)}$ with increase of Δ can be explained by the model of restricted diffusion: If PEG diffusion from a specific region is restricted by the network, the observed diffusion coefficient is expected to depend on Δ. If probe molecules are not completely restricted, the observed diffusion coefficient decreases with increase of Δ and is independent of Δ at relatively large Δ values. If PEG molecules are completely restricted, their diffusion distance becomes independent because probe molecules cannot diffuse beyond the restricted region. In analogy with Stejskal and Tanner's report on restricted diffusion in a system of parallel planar barriers of arbitrary permeability,[16] the dependence of the observed diffusion coefficient on Δ can be assigned to the permeability of PEG molecules: GEL1 systems with $Q = 2.9$ and 3.5 have strongly restricted regions from which it is difficult for PEG molecules to escape. From Figure 5A and Table 2 it is clear that PEG molecules in GEL1 with $Q = 2.9$, 3.5, and 4.0 have a broad distribution of the diffusion rate and probe molecules have similar diffusion rates in different swelling gels. We can conclude that the distribution of the mesh size in GEL1s with $Q = 2.9$, 3.5, and 4.0 is broad. This is an important conclusion.

For GEL2 with $Q = 3.9$, $D_{GEL2(fast)}$ is 15 times larger than $D_{GEL2(slow)}$, and the two values get closer gradually as Δ increases. Although the dependence of $D_{GEL2(fast)}$ and $D_{GEL2(slow)}$ values on Δ in GEL2 with $Q = 3.9$ and in GEL1 with $Q = 4.0$ is similar, the difference between the two values of PEG in GEL2 is much smaller than for the GEL1 systems. Therefore, it can be concluded that the distribution of the mesh size in GEL2 with $Q = 3.9$ is much narrower compared to that of GEL1 with a similar Q (4.0). The dependence of D values for GEL1 ($Q = 2.9$) and GEL2 ($Q = 2.8$) is similar, but $D_{GEL2(fast)}$ and the $D_{GEL2(slow)}$ values of PEG in GEL2 with $Q = 2.8$ are larger compared to those of GEL1.

Figure 6 shows the dependence of the diffusion distances of PEG molecules, d_{PEG}, in GEL1 ($Q = 4.0$ and 4.5) and in GEL2 ($Q = 3.9$ and 4.5) on diffusion time, Δ. For $Q = 4.5$, the differences in d_{PEG} values in GEL1 and GEL2 are pronounced. For $Q = 3.9$, the diffusion distances for the slow diffusion components are similar, but the range of d_{PEG} values for the fast component in GEL1 is much larger than that in GEL2.

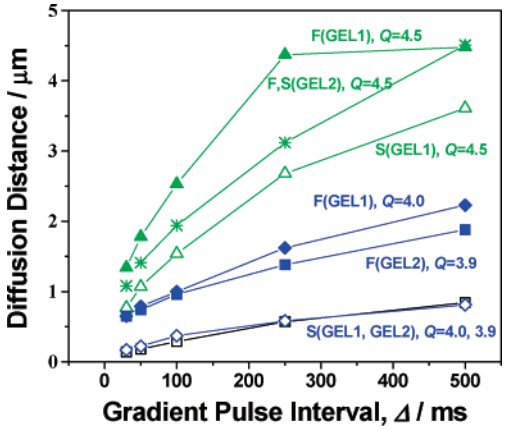


Figure 6. Dependence of the diffusion distances of PEG in GEL1 and GEL2 on the gradient pulse interval, Δ. Experimental points for each set were connected by straight lines, as a guide to the eye. Green: $Q = 4.5$ (GEL1 and GEL2). Blue: $Q = 4.0$ (GEL1 and GEL2). Fast (F) and slow (S) components of the diffusion distance are indicated.

It seems that in this Q range GEL1 systems have a more inhomogeneous distribution of mesh size compared to GEL2.

The dependence of the D values and diffusion distances on the mesh size is clearly seen in the results given in Figures 5 and 6. At this stage, however, it is difficult to determine exactly the mesh size from the D values in gels because the relationship between the D values in gels and the mesh size corresponding to the Q value is not linear, as seen in Figure 4. If this relationship were linear, the distribution of the mesh size as estimated from the distribution of the D values could be compared, even if the D values for GEL1 and GEL2 are different.

Fractions of the Two Diffusion Components as a Function of Q and Δ. The fractions of the fast diffusion component, f_{fast}, in GEL1 and GEL2 are presented in parts A and B of Figure 7, respectively, for Δ in the range 30−500 ms.

For GEL1, f_{fast} values *increase* with increase of Δ and Q, for $Q = 2.9$ and 3.5; are independent of Δ for $Q = 4.0$; and *decrease* with increase of Δ for $Q = 4.5$. The difference between $D_{GEL1(fast)}$ and $D_{GEL1(slow)}$ values at relatively short Δ values can be correlated with the different *distribution* of mesh sizes in the gels; the f_{fast} and f_{slow} values reflect the relative *populations* of mesh size. GEL1 with $Q = 4.5$ has a narrow distribution of the mesh size and a large number of large network cells; $f_{fast} = 0.67$ at $\Delta = 30$ ms. GEL1 with $Q = 4.0$ has a broad distribution of the mesh size, and a large population of large cells, with $f_{fast} = 0.85$ at $\Delta = 30$ ms. GEL1 with $Q = 3.5$ has a large distribution of mesh size, and the number of the large network cells decreases with a decrease in Q, as seen in the large difference in D values between the two diffusion components; $f_{fast} = 0.53$ at $\Delta = 30$ ms. GEL1 with $Q = 2.9$ has a broad distribution of mesh size, and the number of large network cells is smaller than that for $Q = 3.5$, as reflected in the large difference in D between the two diffusion components; $f_{fast} = 0.24$ at $\Delta = 35$ ms.

For GEL2 with $Q = 2.8$ and 3.9, f_{fast} values decrease with increase of Δ. GEL2 with $Q = 3.9$ has a large distribution of the mesh size, and the number of large cells is high, as seen in the large difference in D between the two diffusion components; $f_{fast} = 0.86$ at $\Delta = 30$ ms. GEL2 with $Q = 2.8$ has a broad distribution of mesh

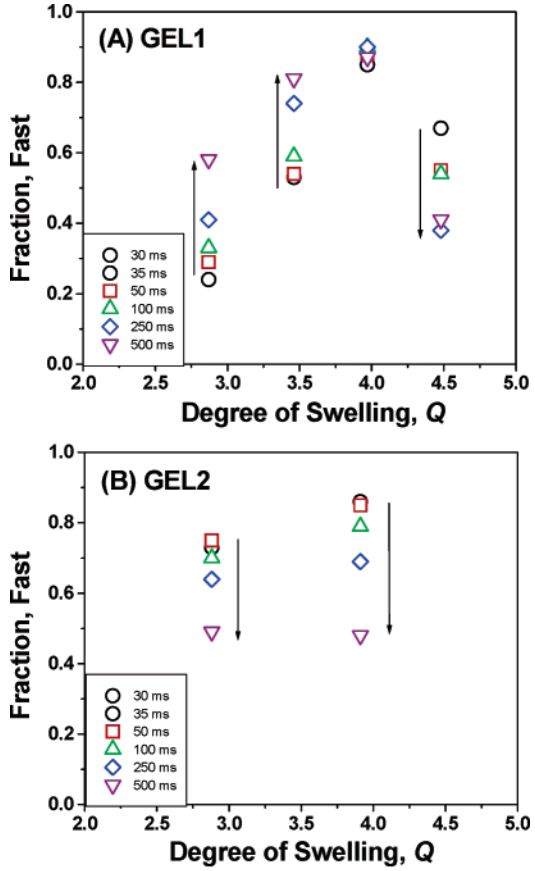


Figure 7. Fraction of the fast (F) diffusion component of PEG as a function of degree of swelling, Q, for the indicated values of the gradient pulse interval, Δ.

size, and the population of large network cells is lower than that for gel with $Q = 3.9$, as reflected in the large difference between the two diffusion components; $f_{fast} = 0.73$ at $\Delta = 30$ ms.

From these results, it appears that in a narrow Q range the gels form a region with a low degree of swelling. In this Q range, the polymer chains interact and form the restricted diffusion regions. The density and distribution of the cross-links form different restricted diffusion regions in GEL1 and GEL2 systems, with different mesh sizes and corresponding populations. For the same degree of swell, GEL1 appears to contain a broader range of mesh sizes.

It is interesting to note that in the SANS method inhomogeneities in gels were detected at high degree of swelling because under these conditions the difference between regions with different mesh sizes became more pronounced.[12−15] In contrast, the NMR method described above was able to detect gel inhomogeneities as the degree of swelling was reduced because the conclusions are a result of the examination of multiple diffusion components and corresponding diffusion distances and relative widths and populations of the mesh sizes.

This study has indicated the type of information that can be obtained using a PEG probe with a fixed molecular weight. Additional questions about gel inhomogeneity could be answered in experiments with PEG probes in a *range* of molecular weights.[21] Moreover, it is important to measure the activation energy for PEG diffusion by measuring the diffusion process as a function of temperature, provided that a constant degree of swelling for the gels is maintained at the different temperatures. Work along these lines is planned in our laboratories.

Conclusions

The goal of this study was to detect inhomogeneities in poly(acrylic acid) (PAA) gels differing in their degree of cross-linking. The networks were prepared at 70 °C by simultaneous polymerization and cross-linking of a mixture of acrylic acid (AA), sodium carbonate, cross-linker (1,4-butanediol diacrylate), and the redox couple sodium persulfate/sodium isoascorbate as the initiator. Two types of networks were prepared, using the same monomer and sodium carbonate concentrations, but different amounts of the cross-linker, 1.1 and 0.5 wt %, respectively, in the monomer mixture. The corresponding notation is GEL1 and GEL2.

Detection of heterogeneities was based on measuring the diffusion coefficients of the probe molecule poly(ethylene glycol) (PEG) as a function of the diffusing time, Δ, by field-gradient ^{1}H NMR spectroscopy. Diffusion measurements were performed as a function of the degree of swelling, $Q = M_{swollen}/M_{dry}$, with Q in the range 2.8−10.0.

The different diffusional behavior of the two gel systems emerged as their degree of swelling was varied. For GEL1 with $Q = 10.0$ and 5.2 and for GEL2 with $Q = 10.0$, 5.1, and 4.5, only *one* diffusion coefficient was detected, independent of the diffusing time, Δ, in the range 30−500 ms. For less swollen gels (Q in the range 2.9−4.5 for GEL1 and 2.8−3.9 for GEL2) *two* diffusion coefficients were detected, D_{fast} and D_{slow}, with values that depended on Δ; for all gels the diffusion lengths, d, d_{fast} and d_{slow}, and the relative fractions of the fast and slow diffusion components, f_{fast} and f_{slow}, were calculated as a function of Δ.

A useful parameter in the interpretation of results was the specific degree of swelling, Q_s, above which the diffusion of the probe in the two gel systems changed from one to two components. A larger value of Q_s in GEL1 was taken as an indicator of a more inhomogeneous gel.

Analysis of the effect of Δ on the diffusion coefficients, diffusion distances, and fractions of slow and fast diffusion components indicated that both gels form a highly cross-linked region in a narrow Q range. In this Q range, the polymer chains interact and form a highly restricted diffusion region. The density and distribution of the cross-links form different restricted diffusion regions in GEL1 and GEL2 systems, and the heterogeneity in terms of mesh size distribution and corresponding populations is higher in the gel with the higher degree of cross-linking.

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