Diffusional Inhomogeneity of Probe Molecules in Chemically Cross-Linked Polymer Gels As Studied by Time-Dependent Diffusion NMR

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ABSTRACT: Inhomogeneity of network size of polymer gels such as polystyrene gel and cross-linked ethoxylate acrylate gel with dimethylformamide as solvent has been studied by using time-dependent diffusion NMR. From the experimental results on the diffusion coefficients of the probe amino acid, *tert*-butyloxylcarbonyl-L-phenylalanine, in the gels, it is found that, in the short diffusion time range, the amino acid in the gels has two components in diffusion as influenced by the distribution of network size, but in the long diffusion time range the amino acid has a single component in diffusion because the diffusion coefficients which come from the distribution of network size are averaged out. Then, inhomogeneity of the gels is elucidated.

Introduction

Polystyrene gels considered in this work have been used as most popular polymer supports in solid-phase peptide synthesis and supports for catalysts, column chromatography, ion-exchange resins, and so on. These functionalities are closely associated with diffusional behavior of probe molecules and solvents, structure and dynamics of polymer gel systems, network size, distribution of network size, and particle size. Especially, the diffusion process of probe molecules must be deeply understood. Further, it can be said that polymer gels have generally inhomogeneity of network size, and then properties of polymer gels depend on their spatial inhomogeneity. The existence of spatial inhomogeneity has been studied by light scattering as speckles.[1−3] One of the clearest manifestations of the inhomogeneity is an appearance of speckle pattern. As for chemically cross-linked polymer gels, the relationship between speckles and spatial inhomogeneity has been elucidated.[4−8] Nevertheless, some problems on intermolecular interactions between network and probe molecules associated with inhomogeneity of the network size in polymer gels remain.

From such a background, in this work we aim to characterize inhomogeneity of the network size in chemically cross-linked polymer gels through observation of the diffusion coefficients (D) of probe molecules, amino acids, in the gels by means of the high-field-gradient spin-echo (PFGSE) ^{1}H NMR method by varying the interval time between two field-gradient pulses (Δ) in the PFGSE pulse sequence corresponding to the diffusing time and to elucidate intermolecular interactions between network and probe molecules associated with inhomogeneity of the network size. Then, as the gel systems Boc-Phe (*tert*-butyloxycarbonyl-L-phenylalanine) and PEO (poly(ethylene oxide)) in Merrifield polystyrene network (MPS) gels,[9,10] cross-linked ethoxylate acrylate (CLEAR) gels[11−13] have been employed.

Experimental Section

Materials. Merrifield polystyrene network (MPS) resin beads are purchased from Nova Biochem Co. Ltd. and Peptide Inc., and cross-linked ethoxylate acrylate (CLEAR) resin beads are from Peptide Institute Inc. MPS resin is cross-linked by divinylbenzene (DVB). Further, two types of resin beads with 1% (MPS1) and 2% (MPS2) cross-linkings are used as for with 1% cross-linking, with 100−200 μm (MPS1) diameters on dry are used. CLEAR resin has an ethoxylate backbone and has been functionalized with amines. The diameter of beads in the dried state is in the range 120−220 μm. PEO (poly(ethylene oxide)) ($M_w = 1500$) purchased from Polysciences Inc. and Boc-Phe (*tert*-butyloxycarbonyl-L-phenylalanine) purchased from Peptide Institute Inc. are used as probe molecules to be diffused in the gels. Deuterated *N*,*N*-dimethylformamide (DMF-d_7) purchased from Merck Co. is used as solvent. The Boc-Phe concentration used in this work is fixed to be 10 wt %. The beads gels are prepared by soaking them in aqueous solution of amino acids for 3 days.

The degree of volume swelling of the polymer network gel (Q) is defined as the ratio of the volume of a swollen polymer network gel at room temperature ($V_{swollen}$) to the volume of a dried polymer network resin (V_{dry}) ($Q = V_{swollen}/V_{dry}$). The volumes of gels are determined by the average diameter of the polymer network gel beads with a microscope.

Measurements. The diffusion coefficient (D) measurements[14−20] on amino acids in polymer gels have been carried out by means of a JEOL GSX-270 NMR spectrometer operating at 270.1 MHz for ^{1}H with a homemade pulse gradient generator (with the maximum field strength of about 2000 G cm^{-1}) and a temperature controller. The temperature control in these experiments is ±0.1 °C. This has been successfully used in our previous works on diffusional behavior in polymer gel systems,[21−25] polymer liquid crystals,[26,27] and n-paraffins.[27,28] As for poly(γ-*n*-octadecyl L-glutamate) thermotropic liquid crystals whose structural inhomogeneity is absent, the echo attenuations were monoexponential decay at diffusion time $\Delta = 4$ ms within the temperature from 60 to 80 °C, and the D values were in the range from ∼10^{-7} to ∼10^{-6} cm^2/s. The D values in this work were in the range from ∼10^{-7} to ∼10^{-6} cm^2/s. Further, we have reported diffusion coefficients elsewhere.[20−28] These diffusion experiments were performed at Δ range from 4 to 100 ms, and the D values were in the range from ∼10^{-7} to ∼10^{-5} cm^2/s. Therefore, the echo attenuations at $\Delta > 4$ ms measured by this NMR system were discussed. In this work, Δ values are from 5 to 100 ms. A field-gradient strength, G, of about 1400 G cm^{-1} is used. The spectral width and number of data points are 4.0 kHz and 4096, respectively.

The D values are determined by using the relationship between echo signal intensity and field gradient parameters:

$$\frac{A(\delta)}{A(0)} = \sum_i p_i \exp\left[-\gamma^2 G^2 D_i \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \qquad (1)$$

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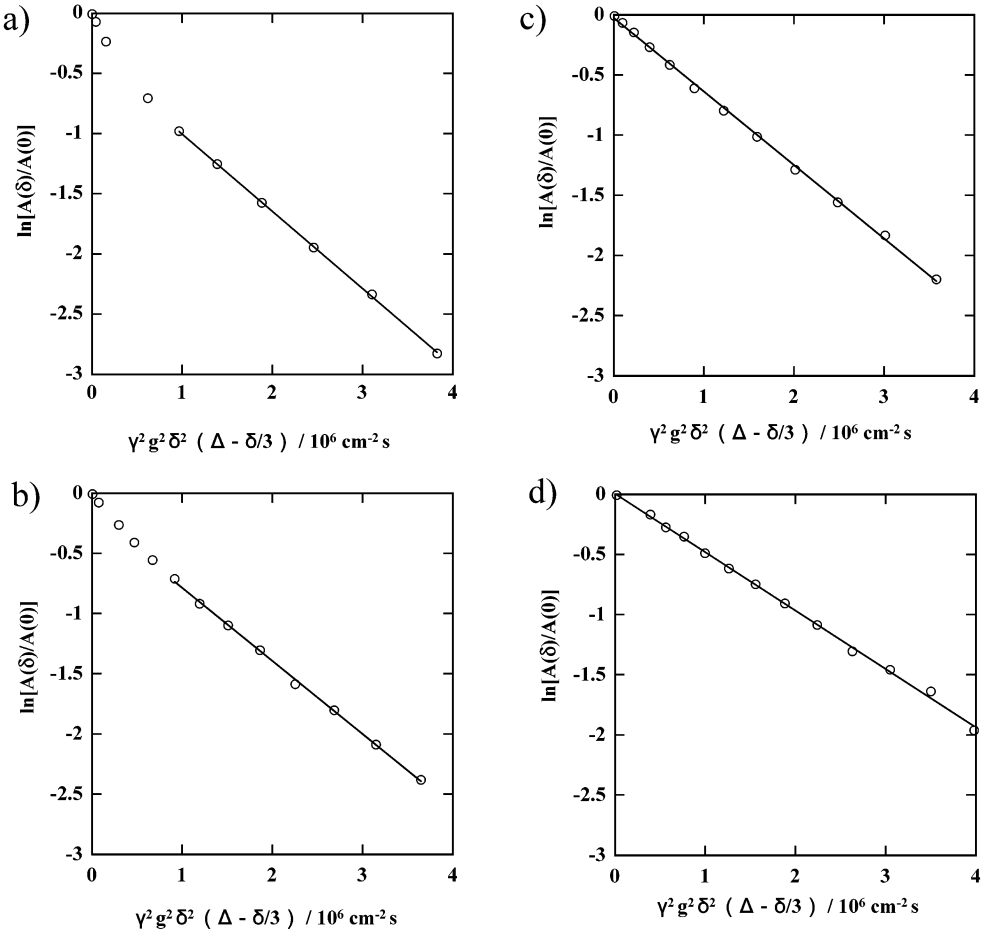

Figure 1. Diffusional spin echo attenuation of Boc-Phe in MPS1 gels with DMF-d_7 as solvent on Δ at 30 °C by varying field gradient pulse duration δ, where the Boc-Phe concentration is 10 wt %. (a) Δ = 10 ms, (b) Δ = 30 ms, (c) Δ = 40 ms, (d) Δ = 100 ms.

where D_i is the diffusion coefficients of the ith component, p_i is the fractional proton number of the ith component, and $\sum p_i = 1$ (in this work, i is one or two). The fraction for the diffusion component can be determined from the intercept of the least-squares fitted straight line at large δ.

It is well-known that the D value in restricted diffusion systems is decreased with an increase in diffusion time. The restricted diffusion in a system with parallel and planar barriers of arbitrary permeability has been studied with emphasis on the results expected from NMR data.[29−31] Recently, the molecular dynamics simulations have reasonably explained with the experimental results on self-diffusivity for a binary mixture adsorbed inside zeolite[32−34] and for zeolite and porous media.[35,36] From these studies the structure of the systems has been elucidated. In this work, however, we have focused on the observation of diffusion coefficients of Boc-Phe in polymer gels, which has two diffusion components, fast diffusion component and slow diffusion component, and their fraction by varying the diffusing time Δ, which is related to the diffusion distance.

Results and Discussion

The diffusion coefficients of Boc-Phe in polymer gels are measured as a function of diffusing time (Δ) (that is, field-gradient pulse-interval time) by the PFGSE ^{1}H NMR method. As for Boc-Phe in MPS1 gels, the plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ at Δ = 10, 30, 40, and 100 ms at 30 °C are shown in Figure 1. As for the plots at Δ = 40 and 100 ms, it is seen that the experimental data lie on a straight line. This shows that Boc-Phe has a single diffusion component in the observation time (Δ) range from 40 to 100 ms corresponding to the diffusing time. On the other hand, as for the plots at Δ = 10 and 30 ms, it is seen that the experimental data do not lie on a straight line. This shows that Boc-Phe in MPS1 gels has two diffusion components such as, for example, the slow diffusion component and fast diffusion component during the observation time Δ. As for echo attenuation curvature at short diffusion times, any diffusant polydispersity, trace solvents, T_2-weighting, and host inhomogeneity of gel could produce curvature at short diffusion times but a single apparent D at longer times. Probe molecules used in this work have monodispersity and single component T_2. In previous works,[21−23] we reported that probe molecules in solution have a single diffusion component. Therefore, we think that echo attenuation curvature is not attributed to diffusant polydispersity, trace solvents, T_2-weighting, and artifacts, but host inhomogeneity. The slow diffusion components to be more sensitive to interactions between gel network and probe molecules than the fast diffusion component because the slow diffusion component comes from strong intermolecular interactions between probe molecule and smaller network in gels. The slow diffusion component increases with an increase in Δ; that is, the averaged D approaches the slow D. Thus, we discussed about the slow and averaged diffusion experimental results. It cannot be said that the fast diffusion component is exactly one component or multicomponents, but the observed diffusion echo signal is approximately deconvoluted by two of the slow and fast diffusion components. Then, the

Table 1. Diffusion Coefficients of Probe Molecules in MPS and CLEAR Gel

		diffusion coefficient/10^{-7} cm^2 s^{-1}				
diffusion time Δ/ms		MPS1 resin DVB 1 mol % Boc-Phe 10 wt %	MPS2 resin DVB 2 mol % Boc-Phe 10 wt %	CLEAR resin Boc-Phe 10 wt %	CLEAR resin Boc-Phe 4 wt %	CLEAR resin PEO 4 wt %
5	D_{fast}	36.4	30.7	33.3	50.6	50.3
	D_{slow}	3.50	2.76	9.46	13.9	7.02
10	D_{fast}	42.7	14.3	45.6	48.3	45.1
	D_{slow}	3.68	2.65	12.3	14.6	4.00
15	D_{fast}	35.8	7.11	44.2	45.2	
	D_{slow}	3.99	2.43	11.7	15.7	
20	D_{fast}	36.8	2.78[a]	27.7	16.3[a]	51.5
	D_{slow}	3.75		12.4		3.73
25	D_{fast}	23.1		23.1	16.5[a]	
	D_{slow}	3.68		12.0		
30	D_{fast}	31.5	2.42[a]	12.0[a]	15.4[a]	50.3
	D_{slow}	3.66				3.63
35	D_{fast}	29.6		11.1[a]	14.4[a]	
	D_{slow}	3.74				
40	D_{fast}	3.42[a]	2.24[a]	11.3[a]	14.3[a]	26.2
	D_{slow}					3.46
45	D_{fast}	3.30[a]		11.2[a]	13.6[a]	
	D_{slow}					
50	D_{fast}	3.24[a]	2.16[a]	10.8[a]	12.5[a]	23.1
	D_{slow}					3.31
60	D_{fast}	3.13[a]		10.6[a]		3.52[a]
	D_{slow}					
70	D_{fast}	2.96[a]		10.4[a]		3.30[a]
	D_{slow}					
80	D_{fast}	2.97[a]		14.2[a]		3.18[a]
	D_{slow}					
90	D_{fast}	2.89[a]		10.6[a]		3.51[a]
	D_{slow}					
100	D_{fast}	2.98[a]		10.4[a]		2.99[a]
	D_{slow}					

[a] D_{fast} is equal to D_{slow}.

echo signals were resolved by two of the slow and fast *D* components. From such plots, the fractions of the slow diffusion component and fast diffusion component can be straightforwardly determined. The fractions of the slow and fast diffusion components (f_{slow} and f_{fast}, respectively) may depend on Δ. This shows that when Boc-Phe molecules are transported in some network cells with different network size during Δ, they have the two diffusion components. This implies that by varying the diffusing time Δ, the diffusion of Boc-Phe molecules with different diffusion coefficients in different network cells is observed. If probe molecules diffuse over a long Δ time, the observed diffusion coefficient may become an averaged value, owing to the diffusion through the network cells with different network size as contributed to the inhomogeneity of network size for gels. Therefore, a series of these experiments give useful information about the diffusion process of Boc-Phe and inhomogeneities of network size. In other words, the slow diffusion component gives useful information about the inhomogeneity of network size for gels through strong intermolecular interactions between probe molecules and network of the gels.

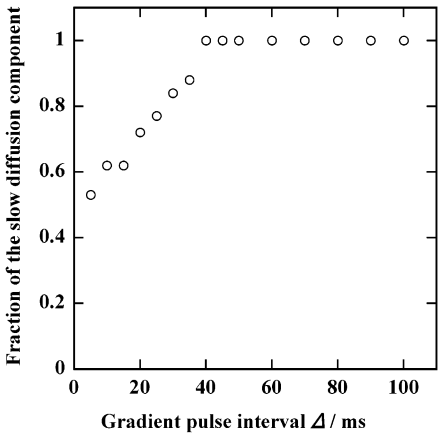

Figure 2. Dependence of the fraction of the slow diffusion component of Boc-Phe (○) in MPS1 gels with DMF-d_7 as solvent at 30 °C on the gradient pulse interval Δ, where the Boc-Phe concentration is 10 wt %.

Figure 2 shows the dependence of the f_{slow} value for Boc-Phe in MPS1 gels DMF-d_7 as solvent on Δ at 30 °C, where the Boc-Phe concentration is 10 wt %. The slow and fast *D* values are shown as Table 1. As seen from this figure, the f_{slow} value increases with an increase in Δ. The f_{slow} value at $\Delta = 5$ ms is about 0.5. In this time scale, the diffusion distance for most of Boc-Phe molecules in MPS1 gels is different from each other. The f_{slow} value at $\Delta > 40$ ms is 1.0. In these time scales, the diffusion distance for all of Boc-Phe molecules in MPS1 gels is almost equal to each other. Therefore, when Boc-Phe molecules in MPS1 gels are diffusing during $\Delta > 40$ ms, the diffusion coefficients to be observed are the single diffusion component. Here, we focus on the Δ in order to understand why the observed diffusion changes from the two components to the single component. Let us name this specified Δ value the "specific" diffusion time (S_{time}).

In the time scale of *t*, the self-diffusion coefficient *D* can be expressed by the mean-square displacement $\langle z^2 \rangle$ in the *z* direction from its starting point after the diffusion time Δ followed by the Gaussian distribution as follows:

$$\langle z^2 \rangle = 2Dt \qquad (2)$$

where t is approximately Δ. As for Boc-Phe in MPS1 gels with DMF-d_7 as solvent, when $\Delta = 5$, 10, 40, and 100 ms, $\langle z^2 \rangle = 0.4$, 0.7, 2.7, and 6.0 μm^2, respectively. These $\langle z^2 \rangle$ values give us information on the diffusion distance d that reflects the experimental results as expressed by the following equation:

$$d = \sqrt{\langle z^2 \rangle} = \sqrt{2Dt} \tag{3}$$

Consequently, the experimental results obtained at $\Delta = 5$, 10, 40, and 100 ms lead to the diffusion distances $d = 0.6$, 0.9, 1.7, and 2.5 μm, respectively. The d values in these experiments are much larger than the network size (12−24 nm) considered here but much smaller than the particle size of swollen gel beads (140−304 μm). The network size in the equilibrium-swollen state is estimated by using the fraction of DVB cross-linking. This is based on the assumption that polystyrene chains between cross-linking points stretch much longer in the equilibrium-swollen state. Therefore, as seen from the obtained S values, it can be said that Boc-Phe molecules go through some network cells during the diffusion time Δ.

As for Boc-Phe in MPS1 gels with DMF-d_7 as solvent at 30 °C, the f_{slow} value increases with an increase in d and changes from the two diffusion components to the single diffusion component at $d = 1.7$ μm. Here, this specified d value is named by the "specific" diffusion distance ($S_{distance}$). In the short Δ range, in which $d < 1.7$ μm, Boc-Phe molecules cannot diffuse to a large distance through many network cells, and so the diffusion distance is not enough to obtain the single diffusion component, but the two diffusion components are observed. On the other hand, in the long Δ range, in which $d > 1.7$ μm, Boc-Phe molecules can diffuse through many network cells, and so the single diffusion component is observed. Therefore, it can be said that a series of time-dependent diffusion experiments give useful information about network structure of polymer gels. If gels systems are formed by larger network size as compared with the $S_{distance}$, the observed diffusion coefficients of Boc-Phe in individual gel beads become the same value. However, if gels systems are formed by smaller network size as compared with the $S_{distance}$, the diffusion coefficients of Boc-Phe in individual gel beads are observed. In other words, all of gel beads with larger size than the $S_{distance}$ have the same function as molecular separation materials, but gel beads with smaller size than the $S_{distance}$ have different functions. Therefore, it is said that $S_{distance}$ is a measure for the diffusional inhomogeneity of probe molecules, the spatial inhomogeneity of network, and the functionalities of network.

Next, let us estimate the $S_{distance}$ for Boc-Phe in CLEAR gels with DMF-d_7 as a function of temperature by the above-mentioned approach, where the Boc-Phe concentration is 10 wt %. This type of gel has no volume transition in the temperature range from 30 to 50 °C. Therefore, we can predict that the $S_{distance}$ is independent of temperature, if intermolecular interactions between Boc-Phe and polystyrene network in this gel system are very negligibly weak in a series of time-dependent experiments, that is, if diffusional behavior of Boc-Phe is independent of temperature. As a result, it is found that the $S_{distance}$ is independent of temperature in the temperature range from 30 to 50 °C. This bears out the foregoing prediction and indicates that the dependence of the f_{slow} value on the Δ value is significantly contributed to the distribution of network size in this gel system. As for Boc-Phe in CLEAR gels with DMF-d_7 as solvent, the $S_{distance}$ at 30, 35, 40, 45, and 50 °C are 2.7, 2.7, 2.8, 2.9, and 2.8 μm, respectively.

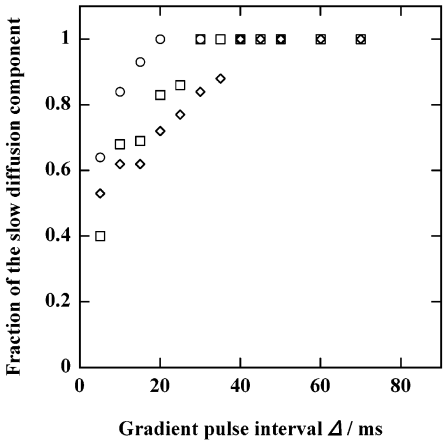

Figure 3. Dependence of the fraction of the slow diffusion component of Boc-Phe in MPS2 gels (○), MPS1 gels (◇), and CLEAR gels (□) with DMF-d_7 as solvent at 30 °C on the gradient pulse interval Δ, where the Boc-Phe concentration is 10 wt %.

Figure 3 shows the dependence of the f_{slow} value for Boc-Phe in MPS2 gels, MPS1 gels, and CLEAR gels with DMF-d_7 as solvent at 30 °C on the gradient pulse interval Δ, where the Boc-Phe concentration is 10 wt %. The slow and fast D values are shown in Table 1. As seen from this figure, the f_{slow} value increases with an increase in Δ and changes from the two components to the single component at larger Δ. The S_{time} as estimated from these plots for Boc-Phe in MPS2 gels, MPS1 gels, and CLEAR gels are 20, 40, and 30 ms, respectively. It is found that the S_{time} depends on the kinds of gels.

As for the $S_{distance}$, it is found that the f_{slow} values for Boc-Phe molecules in three types of gels increase an increase in d and become 1.0 at large d but the dependence differ from each other. As for Boc-Phe in MPS2 gels, MPS1 gels and CLEAR gels at 30 °C, the $S_{distance}$ are 1.1, 1.7, and 2.7 μm, respectively, where the Boc-Phe concentration is 10 wt %. MPS2 gels are cross-linked by 2% DVB, while MPS1 gels are cross-linked by 1% DVB. It can be said that gels with high-density cross-linking have much shorter the $S_{distance}$ than gels with low-density cross-linking, and the $S_{distance}$ depends on the kinds of gels. It can be thought about the network structure of polymer gels as follows. Gels with low-density cross-linking have more cross-linker, of which one side does not react to PS chains as compared with high-density cross-linking. As a result, when the density of cross-linking is low, the distribution of network size in gels becomes broad. Further, it can be thought that distribution of the network size depends on the volume, length, and reactivity of cross-linker. It is found that the $S_{distance}$ of Boc-Phe in CLEAR gels is much larger than that of Boc-Phe in MPS gels. The cross-linker of MPS gels is DVB, and the cross-linker of CLEAR gels is acrylate. The degree of volume swelling for MPS2, MPS1, and CLEAR gels is 1.59, 2.48, and 2.64, respectively.

Figure 4 shows the dependence of the fraction of the slow diffusion component Boc-Phe in CLEAR gels with DMF-d_7 as solvent at 4 and 10 wt % concentrations at 30 °C on the gradient pulse interval Δ. The slow and

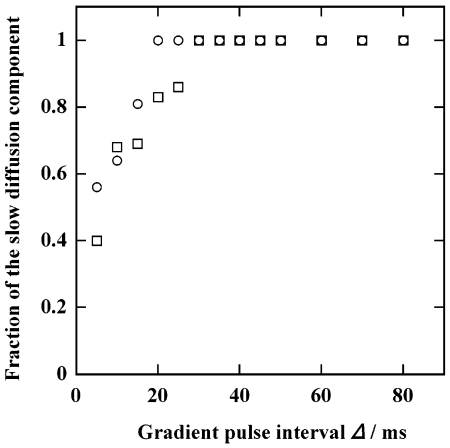

Figure 4. Dependence of the fraction of the slow diffusion component of Boc-Phe in CLEAR gels with DMF-d_7 as solvent at 4 (○) and 10 (□) wt % concentrations at 30 °C on the diffusion distance S for the slow diffusion components in the gradient pulse interval Δ.

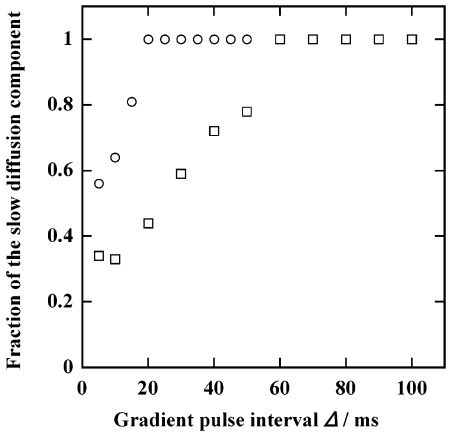

Figure 5. Dependence of the fraction of the slow diffusion component of Boc-Phe (solvent: DMF-d_7) (○) and PEO (M_w = 1500) (□) in CLEAR gels with DMF-d_7 as solvent at 30 °C on the gradient pulse interval Δ, where the Boc-Phe and PEO concentrations are 4 wt %.

fast D values are shown in Table 1. At their concentrations, the S_{time} are 20 and 30 ms, respectively. The S_{time} at 10 wt % are 1.5 times longer than that at 4 wt %.

As the above-mentioned approach, the $S_{distance}$ are estimated. At their concentrations, the $S_{distance}$ are 2.6 and 2.7 μm, respectively. From this result, as for Boc-Phe in CLEAR gels, it is found that the $S_{distance}$ is independent of Boc-Phe concentration between 4 and 10 wt % concentrations. This result indicates that intermolecular interactions between Boc-Phe and polyethoxylate network in this gel are very negligibly weak at the $S_{distance}$ and that diffusional behavior of Boc-Phe in CLEAR gels is independent of Boc-Phe concentration although their averaged diffusion rates are different from each other.

Figure 5 shows the dependence of the fraction of the slow diffusion component for Boc-Phe and PEO (M_w = 1500) in CLEAR gels with DMF-d_7 as solvent at 30 °C on the gradient pulse interval Δ, where the Boc-Phe and PEO concentrations are 4 wt %. The slow and fast D values are shown in Table 1. The S_{time} of PEO are longer than that of Boc-Phe, and the S_{time} are 60 and 20 ms, respectively.

Next, the $S_{distance}$ of PEO are shorter than that of Boc-Phe, and the $S_{distance}$ are 2.1 and 2.6 μm, respectively. As for the same kind of gel, the $S_{distance}$ as contributed to the inhomogeneity of network size for gels must be the same value between different kinds of probe molecules, if the diffusional behaviors of probe molecules are the same. This result can be explained as follows. There is difference between the diffusional behavior of PEO and that of Boc-Phe. Boc-Phe molecules can diffuse all network cells in the size range from the smallest size to the largest size, but PEO molecules cannot diffuse smaller network cells of gels because the network size is not enough large. From this reason, it can be said that diffusional behavior of PEO is not influenced by all of the network cells; therefore, the $S_{distance}$ of PEO are smaller than that of Boc-Phe. It is found that the $S_{distance}$ depends on the diffusional behavior of probe molecules as well as the network structure of gels.

Conclusions

It is concluded that the fraction of the slow diffusion component for amino acids in polymer gels depends on the diffusion time Δ, that in the short Δ range amino acids in polymer gels have the two diffusion components as contributed to the distribution of network size, and, on the other hand, in the long Δ range amino acids have the single diffusion component diffusion because the diffusion coefficient became an averaged diffusion coefficient, and that inhomogeneity of gels are elucidated from the viewpoint of the diffusion process as a function of temperature, kind of gel, degree of the volume swelling, and diameter of gels. Further, it can be said that the diffusion distance has useful information about structure and dynamics of gel as studied by time-dependent diffusion experiments. This method will have potential for applications to characterization of smart membranes, aggregation process, and lattice-forming process as well as gels.

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