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Diffusional Behavior of Solvents and Amino Acids in Network Polystyrene Gels As Studied by ^{1}H Pulsed-Field-Gradient Spin−Echo NMR Method

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ABSTRACT: The diffusion coefficients of *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) in Merrifield network polystyrene gels used as a solid-phase reaction field have been determined as a function of the degree of volume swelling (Q) over the temperature range from 30 to 80 °C by means of the ^{1}H pulsed-field-gradient spin−echo NMR method. From these experimental results, it was found that the D values for DMF in network polystyrene gels linearly increase with an increase of Q in the $Q < 3.2$ range, and a change of the D value for DMF in the $Q > 3.2$ range is smaller than that in the $Q < 3.2$ range. The activation energies of self-diffusion (E) for DMF in network polystyrene gels as determined from the temperature dependence of D are linearly decreased with an increase of Q in the $Q < 1.8$ range, and change of the E value for DMF in the $Q > 1.8$ range is very small. From these experimental results, it was found that the Q dependence of the D value for THF in network polystyrene gels is very similar to that of DMF. Further, it was found that the D values for DMF in network polystyrene gels with $Q < 1.8$ were significantly influenced by the fraction of chloromethylation in the phenyl rings of network polystyrene. Further, from the diffusion coefficient measurements of Boc-Gly(*tert*-butyloxycarbonylglycine) and Boc-Phe(*tert*-butyloxycarbonyl-L-phenylalanine) in network polystyrene gels, it was found that Boc-Gly and Boc-Phe in network polystyrene gels have multicomponents in diffusion by intermolecular interactions between amino acids and polymer network and that the diffusional behavior of Boc-Gly in network polystyrene gels is very close to that of Boc-Phe.

Introduction

It is well-known that Merrifield network polymer systems considered in this work have been applied to a solid-phase reaction field to be used in synthesizing peptides by the reaction of amino acids. The rate of reaction in the solid-phase reaction field is closely associated with structure and dynamics of polymer gels used and intermolecular interaction between the polymer network and amino acids. Further, it can be said that network polymer chains in the gel are more immobile compared with polymer chains in solution at the same polymer concentration because of the existence of chemically cross-linking points.

It has been demonstrated, by the present authors, that NMR gives very useful information about structure and dynamics of polymer gel systems.[1] The spin−lattice relaxation time (T_1) and spin−spin relaxation time (T_2) give information about the microscopic molecular motion of solvent[2−6] and probe polymer in polymer gel systems.[7] Also, ^{1}H NMR imaging can provide spatial information about the diffusion process of molecules in polymer gels.[8−11] Further, the ^{1}H pulsed-field-gradient spin−echo (PFGSE) NMR method has become a useful technique for studying self-diffusion in polymer gels[11−21] in addition to the diffusion studies on substances in polymer gels by the dynamic light scattering (DLS) method,[22−24] and also molecular lateral diffusion in membrane systems has been studied by fluorescence recovery after photobleaching.[25−28] Most recently, by using the PFGSE NMR method, the diffusional behavior of polymer and solvent in polymer gel systems has been systematically elucidated.[29−33]

From such a situation, in this work we aim to elucidate the diffusional behavior of solvent and amino acids in network polystyrene gels as a function of the degree of volume swelling (Q) by means of ^{1}H PFGSE NMR method, as associated with the rate of reaction for amino acids in solid-phase reaction field, to clarify some points for the modification of peptide synthesis in solid-phase reaction field.

Experimental Section

Materials. The Merrifield resin beads purchased from Nova Biochem Co. Ltd., were used as network polystyrene. This resin is cross-linked by divinylbenzene of 1% and has been functionalized with chloromethyl groups. Two types of the resins with the fraction of chloromethylation in the phenyl rings (f_{cm}) being 1.5 (resin A) and 0.3 mmol/g (resin B) were used. The Merrifield resin (C) with the low cross-linking density was synthesized as follows.[34] A solution of acacia gum (2.8 g) and NaCl (1.7 g) dissolved in water (70 mL) is placed in a 200 mL flask. A solution of styrene (3.02 g, 29 mmol), divinylbenzene (0.38 g, 2.9 mmol), and benzoylperoxide (78 mg, 0.32 mmol) dissolved in chlorobenzene (10 mL) was added and rapidly stirred. The reaction flask with the reactants was heated at 85 °C for 24 h. The crude polymer obtained was collected and washed 10 times with 100 mL of water and furthermore 3 times with 50 mL of methanol. Then, network polystyrene resin beads (resin C) were obtained after filtration and drying in a vacuum for 24 h. The average diameters of the beads(resins A, B, and C) were 75−150 μm. The gels of beads (resins A, B, and C) were prepared by soaking them in DMF or THF for 3 days.

The degree of volume swelling of network polystyrene gel (Q) is defined as the ratio of the volume of a swollen network polystyrene gel at room temperature ($V_{swollen}$) to the volume of a dried network polystyrene gel (V_{dry}). The volumes were determined by the average diameter of network polystyrene gel beads, which was measured by a microscope.

$$Q = V_{swollen}/V_{dry} \tag{1}$$

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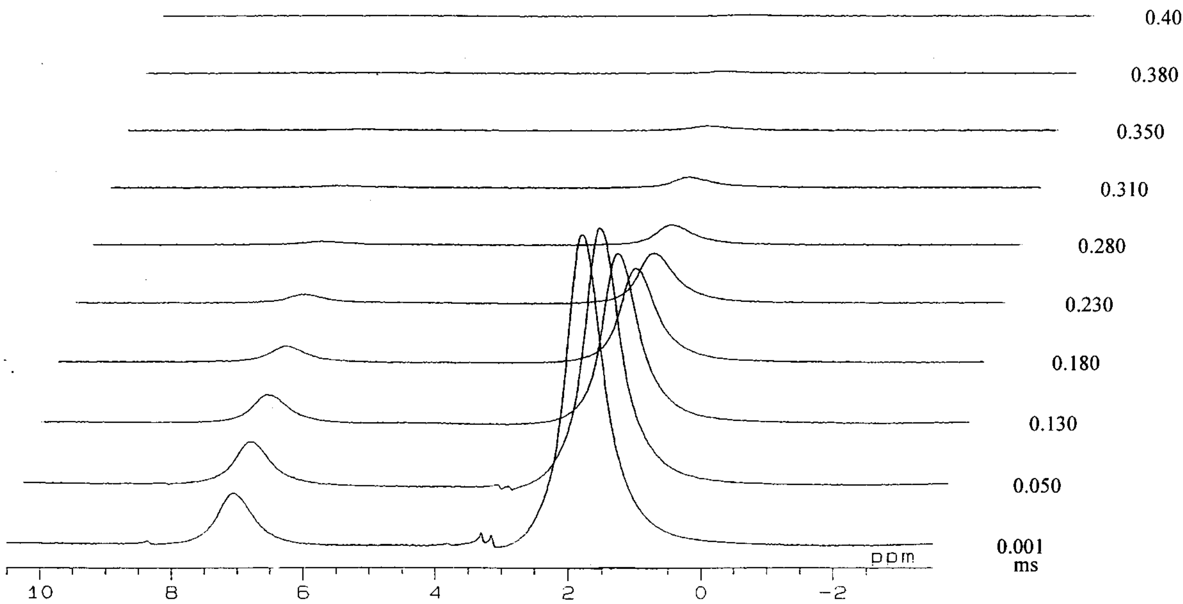

Figure 1. ^{1}H PFGSE NMR spectra of DMF in resin A gel with $Q = 2.20$ by varying field-gradient pulse duration δ at 30 °C.

Boc-Gly(*tert*-butyloxycarbonyl-glycine) and Boc-Phe(*tert*-butyloxycarbonyl-L-phenylalanine) were purchased from Peptide Institute Inc. *N*,*N*-dimethylformamide-d_7(DMF-d_7) from Merck Co. Network polystyrene beads were soaked in a 10 wt % DMF-d_7 solution of Boc-Gly and Boc-Phe for 3 days.

Measurements. The self-diffusion coefficient (D) measurements on solvents and amino acids in network polystyrene gels were carried out over a wide range of temperatures by means of a JEOL GSX-270 NMR spectrometer operating at 270.1 MHz for ^{1}H with a homemade pulse gradient generator and a temperature controller. The temperature control in the D experiments was ± 0.1 °C. The homemade pulsed-field-gradient generator is designed to generate strong field-gradient pulse (with a maximum field strength of about 20 T/m) and to suppress the eddy currents induced. This has been successfully used in our previous works on diffusional behavior in polymer gel systems. In this work, a field-gradient strength G about 13.6 T/m was used. Spectral width and data points were 4.0 kHz and 4096, respectively. Only the free induction decay (FID) was recorded after echo maximum and applied, and then the Fourier transformation was performed (FT).

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

$$\ln[A(\delta)/A(0)] = -\gamma^2 G^2 D \delta^2 (\Delta - \delta/3) \qquad (2)$$

where $A(\delta)$ and $A(0)$ are echo signal intensities at $t = 2\tau$ with and without the magnetic field-gradient pulse, with the length being δ, respectively. γ is the gyromagnetic ratio of proton and Δ is the gradient pulse interval. The echo signal intensity was measured as a function of δ. Plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2 G^2 \delta^2$ (Δ - δ/3) give a straight line with a slope of $-D$. Therefore, the D value can be determined from its slope. The δ and the Δ values employed in these experiments were 0.001−1.0 ms and 10 ms, respectively.

Results and Discussion

(A) Diffusional Behavior of Solvents in Network Polystyrene Gels. ^{1}H PFGSE NMR Spectra and Their Assignments. Figure 1 shows ^{1}H PFGSE NMR spectra of DMF in gel A with $Q = 2.20$ by varying field-gradient pulse duration δ at 30 °C. Two peaks can be assigned to DMF in gel A by using reference data on neat DMF. The rate of diffusion of corresponding DMF molecules influences the peak intensity decay. No peaks which come from gel A appear in the ^{1}H PFGSE NMR experiments. This is due to slow motion of the network chains. Thus, the peaks of gel A decay during echo time (2τ) because these protons have very short T_2. The plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2 G^2 \delta^2$ ($\Delta - \delta/3$) are shown over a wide range of temperatures in Figure 2. It is seen that the experimental data lie on a straight line. This shows that DMF in gel A is a single component diffusion during the observation time because the DMF decay is a mono exponential. The signal of DMF in network polystyrene gels was observed as the restricted diffusion by ^{1}H PFGSE NMR measurements over the Δ range from 5 to 300 ms, but it seems that at $\Delta = 10$ ms the D value determined in this work is close to the real diffusion coefficient.[35−38] As for DMF in resin A gel at 30 °C, at $\Delta = 5$, 10, and 200 ms the determined D values were 9.46×10^{-6}, 8.38×10^{-6}, and 2.38×10^{-6} cm^2/s, respectively. The D values were calculated from the slope of the straight line obtained from the mean least-squares plots, and the experimental error estimated by its standard derivation is less than 5%.

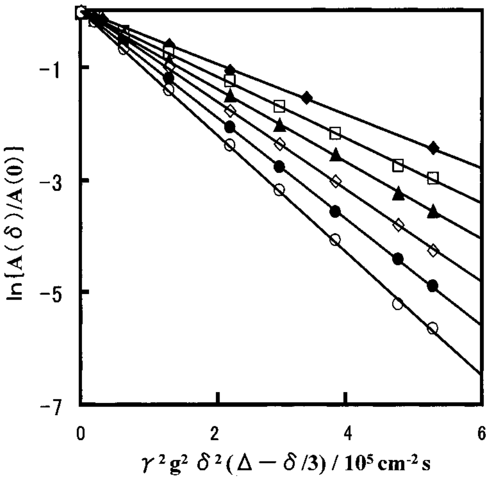

Figure 2. Diffusional spin−echo attenuation of DMF in resin A gel with $Q = 2.20$ in the temperature range from 30 to 80 °C: 30 (◆), 40 (□), 50 (▲), 60 (◇), 70 (●), and 80 °C (○).

Diffusion Coefficient of DMF in Network Polystyrene Gels. The diffusion coefficients of DMF (D^{DMF}) in resin A gel and resin C gel were determined by ^{1}H

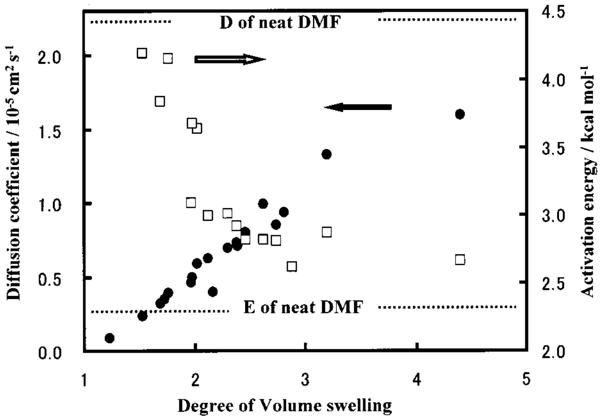

Figure 3. Dependence of the diffusion coefficient of DMF in resin A and resin C gel (●)and activation energy for diffusion (□) on the degree of volume swelling Q at 50 °C.

PFGSE NMR method as a function of Q over the temperatures range from 30 to 80 °C. The D^{DMF} values obtained were plotted against Q at 50 °C as shown in Figure 3.

As seen from this figure, the D^{DMF} value is increased with an increase in Q. The D values for DMF in network polystyrene gels are linearly increased with an increase of Q in the $Q < 3.2$ range, and change of the D value for DMF in the $Q > 3.2$ range is smaller than that in the $Q < 3.2$ range. The D_0^{DMF} value for DMF in neat DMF was 2.26×10^{-5} cm^2/s at 50 °C. Therefore, it can be said that the intermolecular interaction between DMF and polymer network, which depends on the size of the polymer network, restrains the translational motion of DMF molecules.

To understand diffusional behavior of DMF in network polystyrene gels deeply, the activation energy of self-diffusion (E) can be determined by using the following equation

$$D = (a_0^{\,2}/\tau_0)\exp(-E/kT) \tag{3}$$

where a_0 is the interval of the diffusant, τ_0 the time of diffusing, and k the Boltzmann constant. The E value was obtained from the plots of ln D against $1/T$ (the Arrhenius plots) within the temperature range from 30 to 80 °C. The E value was calculated from the slope obtained from the least mean squares fits. As for DMF in resin A gel with $Q = 1.5$ and 2.2, in resin C gel with $Q = 4.4$ and in neat DMF, the determined E^{DMF} values were 4.19, 3.61, 2.66, and 2.36 kcal/mol, respectively. The E^{DMF} values obtained were plotted against Q as shown in Figure 3. As seen from this figure, the E^{DMF} value in the $Q < 1.8$ range is decreased with an increase in Q, and change of the E^{DMF} value in the $Q > 1.8$ range is very small. Further, it is suggested that the probability of intermolecular collisions between DMF and polymer network in network polystyrene gels are changed by an increase of Q in the $Q < 1.8$ range from data of the E^{DMF} value. The probability of intermolecular interactions between DMF and polymer network become higher, that is, intermolecular interactions become stronger.

Diffusion Coefficient of THF in Network Polystyrene Gels. The diffusion coefficients of THF in resin A gel and resin C gel were determined by the same way as DMF solvent. The swelling of network polystyrene by THF is much larger than DMF. The D_0^{THF} value of 2.90×10^{-5} cm^2/s is larger than the D_0^{DMF} value of 1.75×10^{-5} cm^2/s at 30 °C. The D^{THF} values obtained were plotted against Q at 30 °C as shown in Figure 4.

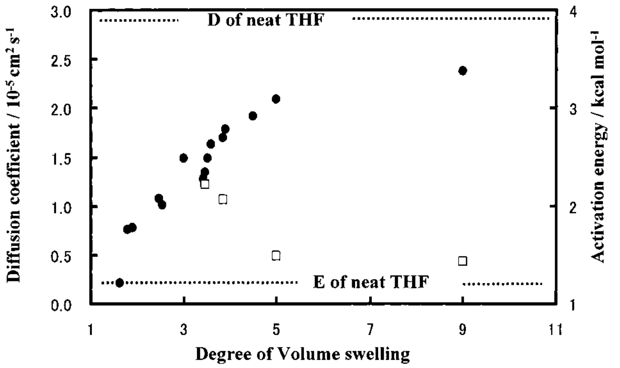

Figure 4. Dependence of the diffusion coefficient of THF in resin A and resin C gel (●) and activation energy of self-diffusion (□) on the degree of volume swelling Q at 30 °C.

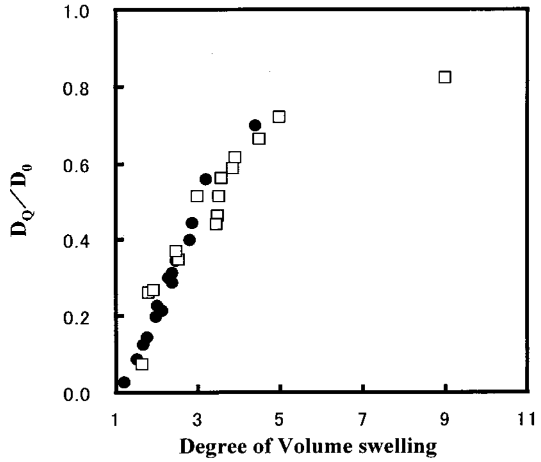

Figure 5. Reduced diffusion coefficient of solvent in resin A and resin C gel dividedby diffusion coefficient of solvent in neat liquid ($D_0^{\mathrm{Solvent}} = D_Q/D_0$ where D_Q is the diffusion coefficient of solvent in gel at Q) was plotted against Q at 30 °C. DMF (●) and THF (□).

As seen from this figure, the D^{THF} value increases with an increase in Q. The change of the D^{THF} value in the small Q region is much larger than that in the large Q region, especially the change of the D^{THF} value in the $Q > 4.8$ range is small. Therefore, as for the diffusional behavior of THF in network polystyrene gels, it can be said that the intermolecular interaction between THF and polymer network, which depends on the size of a network, restrains the translational motion of THF. Thus, the D^{THF} value is larger than the D^{DMF} value at the same Q value.

The reduced diffusion coefficient of solvent in gels A and C divided by diffusion coefficient of solvent in neat liquid($D_0^{\mathrm{Solvent}} = D_Q/D_0$, where D_Q is the diffusion coefficient of solvent in gel at Q) was plotted against Q at 30 °C, to clarify the effect of intermolecular interactions between solvent and polymer network on the diffusion as shown in Figure 5.

From this figure, there is almost no difference in the effect of intermolecular interactions between solvent and polymer network on the diffusion between DMF and THF. It seems that the effect of the network size on diffusion are more important than the effect of intermolecular interactions between solvents and polymer network. Therefore, it can be said that the D^{Solvent} value

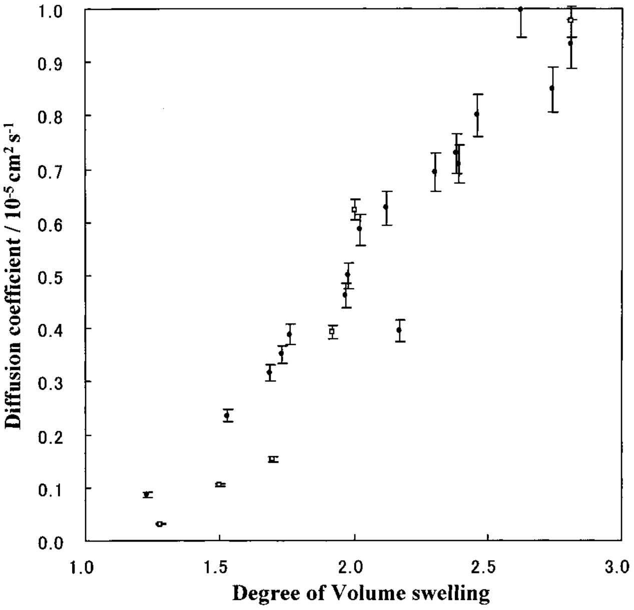

Figure 6. Dependence of the diffusion coefficient of DMF in resin A gel [● ($f_{cm} = 1.5$ mmol g^{-1})] and in resin B gel [□ ($f_{cm} = 0.3$ mmol g^{-1})], on the volume swelling degree Q at 50 °C. f_{cm} is the fraction of chloromethylation in the phenyl rings of network polystyrene.

in network polystyrene gels can be estimated by the $D_0^{Solvent}$ value and the Q value, when there are no strong intermolecular interactions between the solvent molecules and polymer network.

It is known from PFGSE NMR studies that the $D^{Solvent}$ value in polystyrene solutions in the 0−80 wt % polymer range show "universal" behavior among butyl acetate, ethylbenzene, cyclohexane, and toluene, and that the diffusion data from solution can be interpreted with free volume theory, and that the $D^{Solvent}$ value in network polystyrene gels in the $Q = 2.1$, 1.8, and 1.4 are similar to those in polystyrene solutions of the same solvent concentrations.[39−41] In this work, the $D^{Solvent}$ value in network polystyrene gels (called Merrifield resin) in the broad Q range showed "universal" behavior between DMF and THF. The diffusional behavior of solvent in polymer gel systems can be analyzed by the modified free volume theory proposed by Fujita.[42−43] This theory can be applied to solvent in polymer gel systems only when the $E^{Solvent}$ values are nearly equal over a wide range of Q. In this polymer gel system, the $E^{Solvent}$ value increase with a decrease of Q in the small Q region. However, the theoretical curve agrees with the experimental data. From this result and the result that the Q dependence of the D value for THF in network polystyrene gels is very similar to that of DMF, it seems that rapid decrease of the $D^{Solvent}$ value with a decrease of Q can be explained by a decrease of the free volume of solvent.

Effect of the Fraction of Chloromethylation in the Phenyl Rings of Network Polystyrene on the Diffusion Coefficient of DMF in the Gels. We are concerned with the effect of the fraction of chloromethylation in the phenyl rings (f_{cm}) of network polystyrene on the diffusion coefficient of DMF in the gels. The f_{cm} values of resin A and resin B were 1.5 and 0.3 mmol/g, respectively. The determined D^{DMF} values in resin A gel and resin B gel were plotted against Q at 50 °C as shown in Figure 6. Here, the experimental error bars were shown because of detailed comparison of the effect of the f_{cm} on the D^{DMF} values in network polystyrene gels.

As for DMF in the $Q < 1.8$ range, the D^{DMF} values in resin A gel were larger than that in resin B gel. In the $Q > 1.8$ range, there was no difference between them. In other words, the D^{DMF} values in network polystyrene gels in the $Q < 1.8$ range increase with an increase of the f_{cm}, but in the $Q > 1.8$ range, those are almost not affected by f_{cm}. This phenomenon can be explained by weak intermolecular interactions between DMF and polymer chains. It seems that there are weak electrostatic interactions between a DMF molecule and phenyl rings of polystyrene chains, and so the chloromethyl group on phenyl rings prevents approach of a DMF molecule to the phenyl rings. In the small Q range, this leads to effect of f_{cm} on the D^{DMF} value in network polystyrene gels because most of DMF molecules usually contact with polystyrene chains and can interact with polystyrene chains. In this stage, it was not clarified which function of groups in DMF interact with polymer network.

[B] Diffusional Behavior of Amino Acids in Network Polystyrene Gels. ^{1}H PFGSE NMR Spectra and Their Assignments: Figure 7 shows typical ^{1}H PFGSE NMR spectra of Boc-Phe in resin A gel with $Q = 2.48$ by varying field-gradient pulse duration δ at 30 °C. Resin A beads were soaked in a 10 wt % DMF-d_7 solution of Boc-Phe. Two intense peaks can be straightforwardly assigned to the methyl groups and phenyl groups of Boc-Phe molecules in resin A gel from upfield to downfield. The intensity decay for peaks of Boc-Phe is affected by the rate of diffusion. The peaks which come from resin A gel and deuterated DMF (DMF-d_7) molecule do not appear in the ^{1}H PFGSE NMR spectrum. No appearance of the peaks from resin A gel is due to slow motion of the network polystyrene chains.

The plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ are shown in Figure 8. From this figure, it is seen that the experimental data do not lie on a straight line, although the experimental data for Boc-Phe in DMF in the absence of network polystyrene chains lie on a straight line. This means that Boc-Phe in A gels has multicomponents for the diffusion during the observation time. The multicomponents diffusion shows multiexponential decay. Solvent in network polystyrene gel has a single component for the diffusion. It is assumed that Boc-Phe molecules are transported in some sites with different environments during the observation time, in which intermolecular interactions between Boc-Phe and polymer network are largely different from each other and then have multicomponents for diffusion. Here, different environments mean different probabilities of intermolecular interactions between Boc-Phe and polymer network during the observation time. This means that, by adjusting the observation time, that is, the two field-gradient pulse interval, Boc-Phe molecules with different diffusion coefficients in some sites with different environments may be differentiated. In all of the present experiments, Boc-Phe and Boc-Gly in resin A gel have many kinds of components for the diffusion such as a slow diffusion component and the multi-fast-diffusion components. It seems that Boc-Phe molecules interacting strongly with the polymer network contribute to the slow diffusion component, and Boc-Phe molecules interacting weakly with polymer network contribute to the fast diffusion components. These interactions

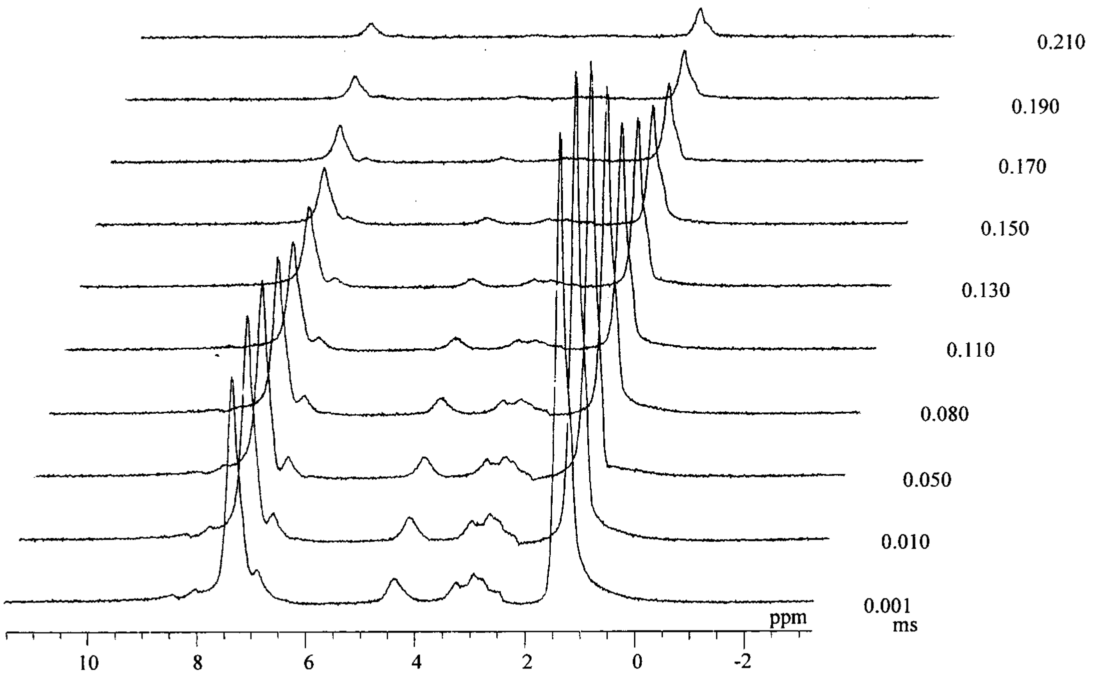

Figure 7. ^{1}H PFGSE NMR spectra of Boc-Phe in resin A gel with $Q = 2.45$ by varying field-gradient pulse duration δ at 30 °C.

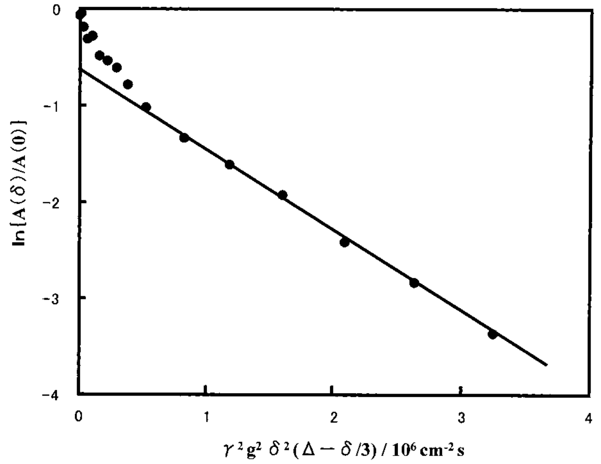

Figure 8. Diffusional spin−echo attenuation of Boc-Phe in resin A gel with $Q = 2.45$ at 30 °C.

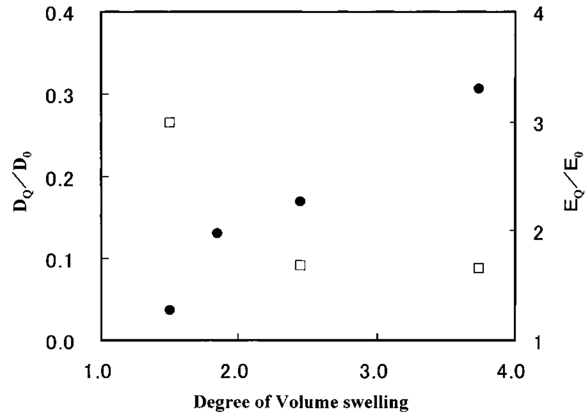

Figure 9. Reduced diffusion coefficient of Boc-Gly 10 wt % (solvent: DMF) in resin A gel divided by diffusion coefficient of Boc-Gly in the absence of resin A ($D_0^{\text{Boc−Gly}} = D_Q/D_0$ (●) where D_Q is the diffusion coefficient of Boc-Gly in gel at Q) was plotted against Q at 30 °C. $E_0^{\text{Boc−Gly}} = E_Q/E_0$ (□).

Table 1. Diffusion coefficient and activation energy of Boc-Gly and Boc-Phe in resin A gel

		diffusion coefficient/10^{-7} cm^2 s^{-1}					activation energy/kcal mol^{-1}
sample	Q	30 °C	35 °C	40 °C	45 °C	50 °C	
Boc-Gly	*a*	48.3	52.6	59.6	61.5	67.2	3.18
	3.74	14.8	18.1	21.9	23.0	25.8	5.26
	2.45	8.14	9.88	11.1	12.8	14.2	5.36
	1.50	1.79	2.38	3.09	3.78	4.81	9.51
Boc-Phe	*a*	48.4	53.1	57.6	61.7	66.9	3.10
	2.48	8.82	9.34	10.9	13.4	14.2	5.14

[a] In DMF solution in the absence of resin A.

depend on intermolecular distance between Boc-Phe molecules and polystyrene chains. The diffusion coefficient and the fraction for the diffusion component can be determined from the slope and the intercept of the least-squares fitted straight line($\delta > 0.11$ ms). The slow diffusion component of the $D^{\text{Boc−Phe}}$ value in resin A gel with $Q = 2.45$ at 30 °C was 8.50×10^{-7} cm^2/s and the fraction for the slow diffusion component was about 0.6.

Diffusion Coefficient of Boc-Gly in Network Polystyrene Gels. We are concerned with the diffusional behavior of Boc-Gly in resin A gel as studied by using the above-mentioned analytical procedure. The $D^{\text{Boc−Gly}}$ values of Boc-Gly in resin A gel as obtained from the slow diffusion component are shown in Table 1. The $D^{\text{Boc−Gly}}$ values going from $Q = 1.50$ to 3.74 are increased from 1.79×10^{-7} to 1.48×10^{-6} cm^2/s and the value of the diffusion coefficient $D_0^{\text{Boc−Gly}}$ of Boc-Gly in DMF-d_7 in the absence of network polystyrene was 4.83×10^{-6} cm^2/s at 30 °C. The reduced diffusion coefficient $D_Q^{\text{Boc−Gly}}$ of Boc-Gly molecules with Q divided by the $D_0^{\text{Boc−Gly}}$ value was plotted against Q at 30 °C, to clarify the effect of intermolecular interactions between Boc-Gly molecule and polymer network on the diffusion as shown in Figure 9.

From this figure and 5, the change of the $D^{\text{Boc−Gly}}$ value in the $1.0 < Q < 4.0$ range is not as large as that of the D^{Solvent} value. Therefore, it can be said that the diffusional behavior of Boc-Gly in network polystyrene gels depends on not only the intermolecular interactions between a Boc-Gly molecule and polymer network, but also the electrostatic interactions between a Boc-Gly molecule and polymer chains.

The diffusion coefficients $D^{\mathrm{Boc-Gly}}$ for Boc-Gly in resin A gel with $Q = 3.74$, 2.45, and 1.50 and in DMF in the absence of resin A as determined as a function of temperature are shown in Table 1.

From this table, it is seen that the $D^{\mathrm{Boc-Gly}}$ values are increased with an increase in temperature. The activation energies of diffusion ($E^{\mathrm{Boc-Gly}}$) for Boc-Gly in resin A gel with $Q = 3.74$, 2.45, and 1.50, and in DMF in the absence of resin A were determined from the Arrhenius plots of ln D against $1/T$. As for Boc-Gly in resin A gels with $Q = 1.50$, 2.45, and 3.74 and in DMF solution in the absence of resin A, the determined $E^{\mathrm{Boc-Gly}}$ values were 9.51, 5.36, 5.26, and 3.18 kcal/mol, respectively. The reduced $E^{\mathrm{Boc-Gly}}$ values obtained with Q divided by the $E_0{}^{\mathrm{Boc-Gly}}$ value was plotted against Q as shown in Figure 9. As seen from this figure, in the $1.5 < Q < 2.5$ range, the $E^{\mathrm{Boc-Gly}}$ values decrease with an increase in Q. This shows that the network size is decreased as Q is decreased, and for this, intermolecular interactions between Boc-Gly and the polymer network are increased. In other words, the environment of Boc-Gly in network polystyrene gels is changed by an increase of Q, especially in the $Q < 2.5$ range. In large Q region, the $E^{\mathrm{Boc-Gly}}$ value with $Q = 3.74$ is 1.7 times larger than that in the DMF-d_7 solution in the absence of resin A ($E_0{}^{\mathrm{Boc-Gly}}$). It can be said that the environment of Boc-Gly in network polystyrene gels is greatly different from that of Boc-Gly in DMF in the absence of network polystyrene. In other words, diffusional behavior of amino acids in peptide solid-phase reaction field differs from that of amino acids in the liquid-phase one. It is thought that this phenomenon may be caused by strong intermolecular interactions between a Boc-Gly molecule and polystyrene chains.

Diffusion Coefficient of Boc-Phe in Network Polystyrene Gels: We are concerned with diffusional behavior of Boc-Phe molecules with that of Boc-Gly. Network polystyrene beads were soaked in a 10 wt % DMF-d_7 solution of Boc-Phe. The $D^{\mathrm{Boc-Phe}}$ values of Boc-Phe in DMF in the absence of network polystyrene and in network polystyrene gels as determined from the Arrhenius plots of ln D against $1/T$. From Table 1, it is shown that there is almost no difference between the $D^{\mathrm{Boc-Phe}}$ value and the $D^{\mathrm{Boc-Gly}}$ value. The $E^{\mathrm{Boc-Phe}}$ value is very close to the $E^{\mathrm{Boc-Gly}}$ value. It is shown that the diffusional behavior of Boc-Phe in network polystyrene gels is very similar to that of Boc-Gly when wt % concentrations are equal to each other. When wt % concentrations are equal, it is assumed that volume fractions are equal. When mole fractions are equal, it is assumed that the $D^{\mathrm{Boc-Gly}}$ value is larger than the $D^{\mathrm{Boc-Phe}}$ value. There is no difference in diffusional behavior between Boc-Phe and Boc-Gly despite the structural difference between them. Therefore, it can be said that strong intermolecular interactions between an amino acid molecule and polystyrene chains come from intermolecular interactions between the carboxyl terminal of an amino acid molecule and polystyrene chains.

Conclusions

The diffusion coefficients for solvents in swollen network polystyrene gels with various Q values were determined by ^{1}H PFGSE NMR method. From these experimental results, it was found that the D values for solvent in network polystyrene gels largely increase with an increase of Q in the small Q region and the change of the D value for solvent in the $Q > 3.2$ range is smaller than that in the $Q < 3.2$ range. There is almost no difference, in the dependence of the D value for solvent on the Q, between DMF and THF. Further, it was found that the D value for DMF in network polystyrene gels with $Q < 1.8$ were influenced by the fraction of chloromethyration in phenyl rings. However, it was found that the motion of amino acids in swollen network polystyrene gels is strongly (more than that of solvent) restrained by the interactions between an amino acid molecule and polystyrene chains and that amino acids in network polystyrene gels have multicomponents diffusion reflecting the distance to polystyrene chains.

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