NMR Characterization of Styrene–Divinylbenzene Gel Beads in Swollen State Using Chloroform as Probe

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SYNOPSIS

Styrene–divinylbenzene copolymer gel beads in a swollen state were characterized with a proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) using chloroform as a probe. The signal of chloroform was observed as doublet peaks and the peak at higher magnetic field was assigned to chloroform inside the gel beads and the other at lower magnetic field to one outside the gel beads. NMR parameters such as signal chemical shift, intensity, line width, and shape were investigated in relation to the characteristics of gel beads such as the swelling ratio, the diameter, pore size, and crosslinking density. The relative intensity of the signal due to chloroform inside the gel beads increased with the amount of diluent used in preparation of the beads. With the decrease of the diameter of the beads, two signals became closer, because the rate of exchange between the solvent molecules inside and outside increased. The pore size also influenced the shape of the doublet peaks. As the pore size increased, the two peaks overlapped due to the decrease of the portion of chloroform that interacts with the polymer matrix. The crosslinking density did not influence the peak shape although the dynamics of chloroform were affected by the crosslinking density.

INTRODUCTION

Styrene–divinylbenzene (St–DVB) copolymer beads are widely used as the packing materials for gel permeation chromatography[1] and reversed-phase chromatography,[2] and as supports for ion-exchange resins and polymeric catalysts.[3] Because the beads are usually used in a solvent swollen state, it is of importance to characterize the beads in a swollen state.

It is difficult to characterize solvent-swollen crosslinked polymers by using NMR spectroscopy, because the gel state is intermediate between the solid and liquid state. As reported by Mohanraj and Ford, high resolution NMR (for solutions) cannot fully cope with the peculiar characteristics of solvent swollen St–DVB gels because of their great dipole broadening.[4] Cross-polarization/magic angle spinning (CP/MAS) method is useful for the characterization of solid polymers. However, it is of limited value for gel state samples, because a rapid local segmental motion of polymer chains of gels may eliminate the dipole coupling required for efficient cross polarization from proton to carbon. The most successful method is the direct polarization/magic angle spinning (DP/MAS) method reported by Stover and Frechet.[5] However, this method can be applied only for lightly crosslinked polymers.

In contrast, solvents in crosslinked polymers give high resolution NMR spectra even if crosslinking density is high. When polymer beads such as St–DVB gel and ion-exchange resins are immersed in organic solvents or water, separate resonances for solvents or ions inside and outside the polymer beads were reported earlier in both ^{1}H- and ^{13}C-NMR spectra.[6–20] This phenomenon has been used to evaluate the dynamics of solvent molecules by the determination of the rate constants for exchange between two sites[11,16,17] and the properties of ion-exchange resins.[6–10,12–14]

In this study, we investigated ^{1}H-NMR spectra of chloroform in the presence of St–DVB gel beads.

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Table I Preparation Conditions and Characteristics of Styrene–Divinylbenzene Gel Beads

Gel	St/DVB[a]	M/DI[b]	PMC[c] (g/mL)	Diameter (μm)	Ex L[d] (× 10^3)
1	80/20	50/50[e]	0.15	50–150	4
2	80/20	67/33[e]	0.24	50–150	3
3	80/20	75/25[e]	0.29	50–150	0.4
4	80/20	100/0	0.36	50–150	0.2
4′-1	80/20	100/0	ND	100–200	ND
4′-2	80/20	100/0	ND	60–100	ND
4′-3	80/20	100/0	ND	30–60	ND
4′-4	80/20	100/0	ND	20–30	ND
4′-5	80/20	100/0	ND	10–20	ND
5	70/30	60/40[e]	0.27	50–150	3
6	50/50	50/50[e]	0.26	50–150	3
7	50/50	50/50[f]	0.24	50–150	50
8	50/50	50/50[g]	0.22	50–150	300

Polym. temp., 80°C, polym. time, 10 h. ND, not determined.
[a] Volume ratio of styrene (St) and divinylbenzene (DVB).
[b] Volume ratio of monomer (M) and diluent (DI).
[c] Polymer matrix concentration swollen in chloroform.
[d] Molecular weight of exclusion limit.
Diluents are:
[e] Toluene.
[f] Toluene + 2 wt % polystyrene (for oil phase).
[g] Isoamyl alcohol.

NMR parameters such as line shape and chemical shift were discussed in relation to the characteristics of the gel beads such as swelling ratio, diameter, pore size, and crosslinking density, which are all important parameters in the applications of beads.

EXPERIMENTAL

Gel Beads Preparation

St and DVB, containing ca. 45% of ethyl vinyl benzene, were obtained from Tokyo Kasei Co., Ltd., and were distilled under reduced pressure before use. St–DVB copolymer beads were prepared by a conventional suspension polymerization at 80°C in the presence of different amounts of a porogenic agent (inert diluent). Swelling ratio and pore size were controlled by changing polymerization conditions such as DVB content, the type, and the amount of a diluent. The obtained gel beads were washed 2–4 times successively with hot water, acetone, and chloroform to remove the suspension stabilizer, unreacted monomers, and the linear polymers, followed by drying *in vacuo*. The fine beads were removed by decantation in acetone. In preparation of gel 4′, a suspension with a wide range of diameter of the oil phase droplet (5–200 μm) was prepared with a Labodisperser (MRK Co.) to obtain beads with wide distribution of size, which were separated into five fractions with sieves based on the size. The polymer matrix concentrations, which represent the swelling ratio, were determined by placing the weighted dry gel beads (typically 1.0 g) in a 10-mL graduated cylinder with excess chloroform followed by measuring the final apparent volume of gel beads (swollen beads plus interstitial volume) after fully swelling. Table I represents the preparation conditions and characteristics of the gel beads used.

Pore Size Determination

The pore size of prepared gel beads was evaluated by gel permeation chromatography (GPC). The gel beads were packed into a stainless steel column (7.6 mm ϕ × 30 cm) to obtain the GPC column with a slurry method. The calibration curves for polystyrene standards (Shodex) were obtained using chloroform as an eluent at room temperature (ca. 25°C).

NMR Sample Preparation and Measurements

Reagent grade chloroform purified by distillation under nitrogen atmosphere was used as an NMR probe. The NMR samples were prepared in 10-mm NMR tubes by placing the dry gel beads in an excess amount of chloroform. After complete swelling, a Teflon plug was inserted to minimize the amount of the interstitial chloroform, and squeezed chloroform was removed by a syringe.

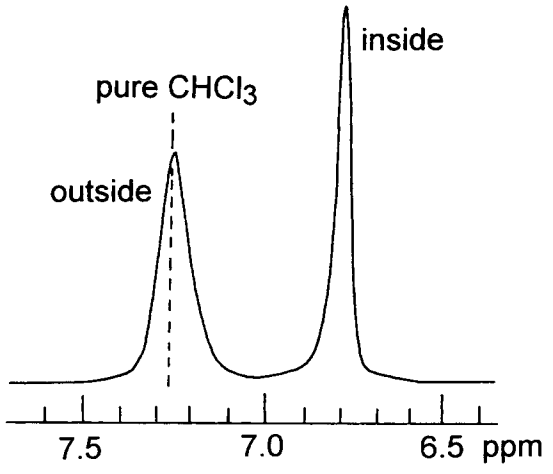

Figure 1 ^{1}H-NMR spectrum of chloroform in the presence of gel 4 (30°C).

All ^{1}H-NMR measurements were made with a JEOL-FX200 NMR spectrometer operating at 200 MHz for protons. A 4000-Hz frequency range (20 ppm), 16 K data points, 10–20 s pulse delay, and 16–32 acquisitions were used. Spin-lattice relaxation time (T_1) measurements were conducted using a conventional inversion recovery method and spin–spin relaxation time (T_2) using the CPMG pulse sequence.

RESULTS AND DISCUSSION

^{1}H-NMR Spectrum of Chloroform in Presence of St-DVB Gel Beads

Figure 1 shows the ^{1}H-NMR spectrum of chloroform in the presence of St–DVB gel beads (gel-4; gel type resin) at 30°C, where two peaks are observed. The chemical shift of the signal at lower magnetic field was almost equal to that of chloroform in the absence of gel beads indicated by the broken line in Figure 1. Therefore, the signals were assigned to chloroform outside and inside the gel beads in the order of increasing magnetic field. No signal of polymer matrix was observed because of high restriction of mobility. It is well-known that the ^{1}H-NMR signal of chloroform in an aromatic solvent is shifted toward higher magnetic field due to the solvent effect.[21] Therefore, chloroform in the polymer matrix is considered to be subjected to the pseudo-solvent effect by the aromatic rings of the matrix that resulted in the appearance of two peaks.

In the case of ion exchange resins, it is also reported that ^{1}H-NMR signals of water or counterions are observed as doublets.[6-15] For example, the signal of water inside sulfonated polystyrene resins appears at a lower magnetic field compared to the external signal,[6-13] and this result is contrary to ours. The shift direction of inside solvents is considered to be determined by the combination of the types of polymer matrix and solvents.

The line width of outside and inside signals at half intensity were 19 and 10 Hz, respectively. If the line width depends only on relaxation times, the inside signal must be broader than the outside one because of the restriction of the mobility by the polymer matrix. Therefore, the observed line widths may be dependent not only on relaxation and exchange rate, but also on heterogeneity and magnetic field gradients within the sample.

Effect of Amount of Diluent

Figure 2 exhibits the effect of the amount of a diluent (toluene) used in preparing the gel on the chemical shifts and relative intensity of the two peaks. The relative intensity of the chloroform inside the gel increased with the amount of the diluent. This can be explained by the fact that with the increase of the amount of the diluent the gel becomes more porous and swells more resulting in the increase of the chloroform inside of the gel. Figure 2 also shows that with the increase of the diluent, the inside signal shifted toward the lower magnetic field, which is attributed to the decrease of polymer matrix con-

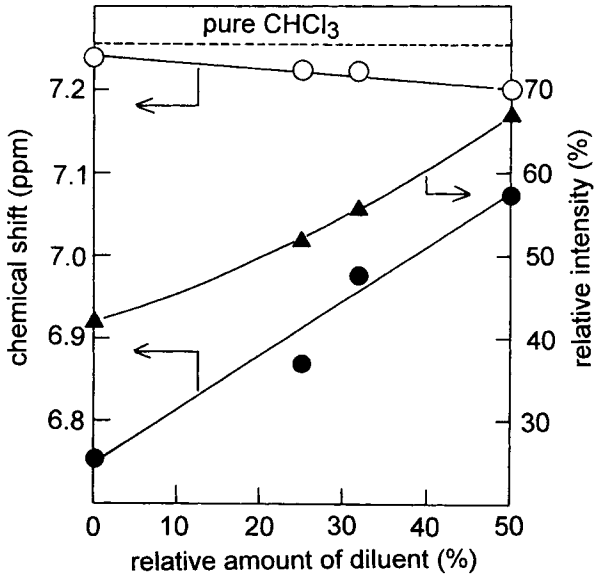

Figure 2 The effect of the amount of diluent on the chemical shift and the signal intensity: (○) chemical shift (open, outside; filled, inside) and (▲) relative intensity of inside signal.

centration inside the gel beads. The outside signal slightly shifted toward the higher magnetic field with the increase of the diluent, which may be due to the increase of exchange rate between two types of chloroform.

Effect of Size of Gel Beads

To examine the effect of the size of the beads, beads with the wide size distribution were prepared, that is, gel 4′ (DVB 20%; no diluent) and separated into five fractions based on the diameter. Figure 3(a) represents the relationship between the chemical shifts of the two peaks and the diameter of the gel beads. The gel with the smallest diameter (fraction 5) shows the overlapped peaks due to the high exchange rate of two types of solvent (the exchange rate is determined by the surface area of beads per unit of volume). As the diameter of beads increases, the inside and outside signals shifted toward the higher magnetic field and lower magnetic field, respectively. These phenomenon can be explained by the increase of the exchange rate with the decrease of the bead size.

As shown in Figure 3(a), it is predicted that the chemical shifts of two types of chloroform coincide with each other at a diameter of about 3.5 μm. When two peaks coalesce, the lifetime of two sites is approximately estimated at 4.5×10^{-3} s from the general equation[22] with the assumption that the frequency difference is 100 Hz, which is based on the observation for fraction 1. The self-diffusion coefficient (D) of chloroform in the gel beads was determined to be 0.30×10^{-5} cm^2/s (30°C) by the pulse gradient spin echo (PGSE) method.[23] The mean square distance [$x = (2Dt)^{1/2}$] in the lifetime was calculated to 1.6 μm. This value is almost equal to the predicted radius of the beads (1.75 μm).

In Figure 3(b), line widths are plotted against the diameter of the beads. As the diameter decreased, line widths of both types of signals increased. This fact also indicates that the exchange rate increases with the decrease of the diameter.

Effect of Pore Size

The pore size of gel beads in a swollen state is dependent on the type and the amount of the diluent used, the crosslinking density, and so forth. The three types of gel beads (gels 6, 7, and 8) were prepared with different types of diluent, where the DVB content and the amount of diluent were constant. The GPC columns packed with gels 6, 7, and 8 showed the molecular weight of exclusion limit of 3

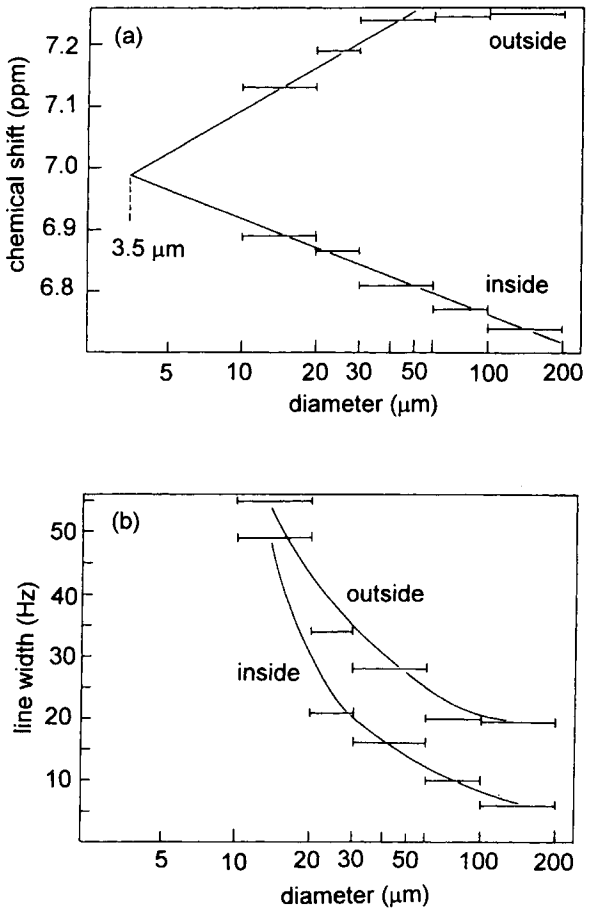

Figure 3 The relationship between the NMR parameters and the diameter of the beads: (a) chemical shift and (b) line width.

$\times 10^3$, 5×10^5, and 3×10^6 (for polystyrene standards), respectively. Figure 4 shows ^{1}H-NMR spectra of chloroform in the presence of these three types of gel beads. Samples in the presence of gels 6 and 7 showed two chloroform peaks inside and outside of the gel. Chloroform with gel 7 showed the smaller chemical shift difference of doublet peaks than one with gel 6. The signal intensity ratio of the two peaks was almost 1 for both samples, which was the same as the in and out solvent ratio estimated from the GPC curves. Gel 8 showed only one peak with a tailing toward the higher magnetic field. The total signal intensity was almost equal among the three samples. Therefore, it is expected that almost all the chloroform inside gel 8 also showed the signals. Thus, it can be said that the inside signal shifted down field and overlapped with the outside signal. The chemical shifts at the center of peaks are 7.11, 7.17, and 7.19 ppm for gels 6, 7, and 8, respectively.

This finding can be explained by the difference of the morphology among the three types of gel beads

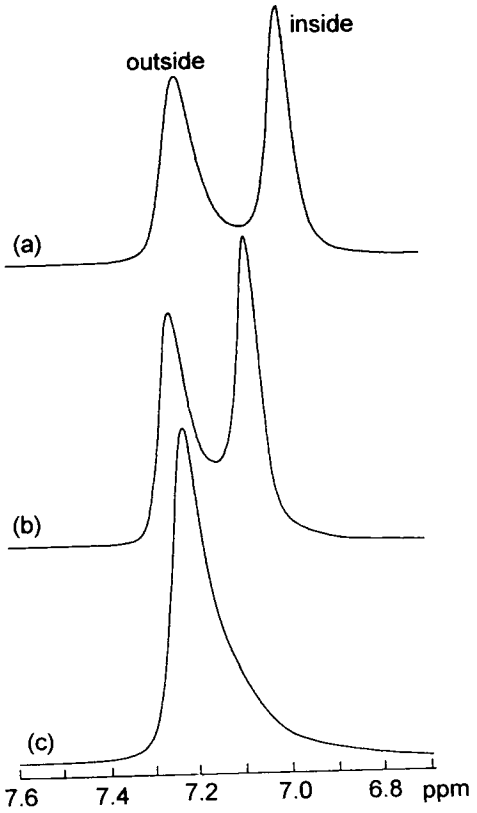

Figure 4 The effect of the pore size on ^{1}H-NMR line shapes: The molecular weight of exclusion limit is (a) 3×10^3 (gel 6); (b) 5×10^5 (gel 7); and (c) 3×10^6 (gel 8).

as shown in Figure 5, which schematically represents the morphology of the three types of gel beads in a swollen state. It is considered that there are two types of chloroform in the pore: one located near the polymer matrix that interacts strongly with it and the other located far from it. The former exhibits the larger shift to the higher magnetic field, and the latter exhibits only a small high magnetic field shift. The amount of the former chloroform decreases with the increase of pore size as shown in Figure 5.

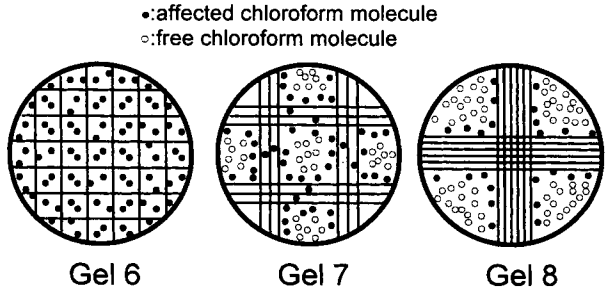

Figure 5 Schematic representations of the swollen networks.

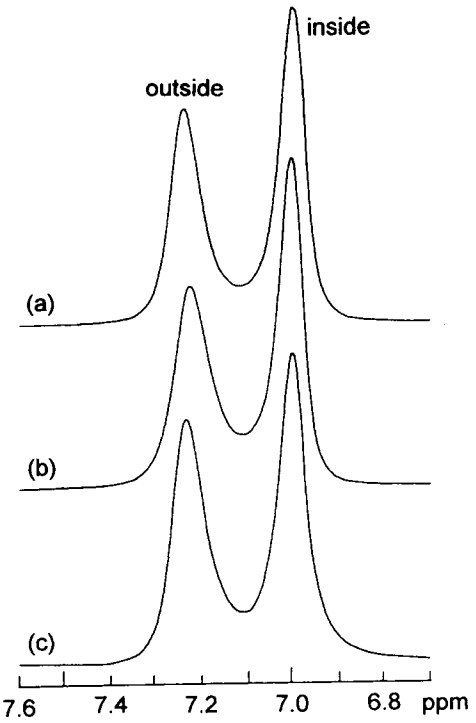

Figure 6 ^{1}H-NMR spectra of chloroform in the presence of gels 2, 5, and 6: (a) gel 2; (b) gel 5; and (c) gel 6.

Effect of Crosslinking Density

Polymer gels with almost the same swelling ratio and different crosslinking density (gels 2, 5, and 6) were prepared by controlling the amount of diluent (toluene) and crosslinking agent (DVB). It is reported that these gel beads have almost the same pore size distribution in a swollen state.[24] Therefore, these gels are suitable to evaluate the effect of the crosslinking density on NMR parameters. Figure 6 shows ^{1}H-NMR spectra in the presence of these gel beads at 30°C. The chemical shifts and the shape of the two peaks are almost the same among the three samples.

Spin–lattice and spin–spin relaxation times of chloroform in the presence of three types of gel beads are tabulated in Table II. As the crosslinking density

Table II Relaxation Data of Chloroform

	T_1 (s)[a]		T_2 (s)[a]	
Gel	Inside	Outside	Inside	Outside
2	7.4	7.6	1.9	1.9
5	3.6	4.8	0.9	1.3
6	2.5	3.0	0.2	0.5

[a] Determined at 30°C.

increased, the relaxation times of inside and outside signals decreased. These values are "apparent" ones because of the exchange between two sites. However, it is suggested that solvent dynamics such as the relaxation and exchange rates are affected by the crosslinking density. The fact that no change of spectra was observed among the gel beads indicates that the line shape depends not on the dynamics but on the polymer structures such as pore size and its distribution as well as the bead size.

CONCLUSION

In the presence of St–DVB copolymer beads, the ^{1}H-NMR signal of chloroform was observed as a doublet assigned to chloroform inside and outside the gel beads. This signal splitting is due to the pseudo-aromatic solvent effect caused by polymer chains. The relative intensity of the inside signal increased with the diluent used in preparation of the gel beads, while the chemical shift of the inside signal shifted toward the outside signal. With the decrease of the diameter of the beads, two signals overlapped with each other, explained by the increase of the exchanging rate between the inside and outside solvents. As the pore size increased, the portion of chloroform in the pore that interacts with the polymer matrix decreased, which resulted in the signal overlapping. As the crosslinking density increased, relaxation times of inside and outside signals decreased, with only a negligible change in the line shape.

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