Image Analysis of the Spatial Distribution of Paramagnetic Pr^{3+} Ions in a Polymer Gel by a ^{1}H-Chemical Shift NMR Imaging Method

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Summary: ^{1}H-chemical shift NMR imaging patterns of a poly(methacrylic acid) gel containing water with paramagnetic praseodymium ions(Pr^{3+}) were successfully observed, in order to elucidate spatial distribution of Pr^{3+} ions in the gel. The ^{1}H chemical shift of water associated with Pr^{3+} ions in the gel moves largely downfield. By analyzing these experimental results, the immersion process of Pr^{3+} ions into the network of the polymer gel was spatially clarified. Further, it is shown that the chemical shift NMR imaging method is a useful means for determining the spatial distribution of paramagnetic metal ions in polymer gels.

Introduction

It has been demonstrated that the NMR imaging method is a useful means for obtaining non-destructively μm-scale spatial information on probe molecules in bulk matter.[1, 2] For this reason, the NMR imaging method has been successfully applied to polymer gel systems.[3-10] In particular, the response of polymer gels under the application of external stimuli, such as stress and electric field,[11,12] has been elucidated at the molecular level and at the macroscopic level by means of NMR imaging method. The target of those efforts was to understand the nature of polymer gels and to discover novel properties. Therefore, the introduction of new NMR methodology to polymer gels leads to new developments in gel science. In addition to the NMR imaging method, most recently, the ESR imaging method has been developed to identify the spatial distribution of radical species in polymer systems.[13,14] Thus, it can be said that both of these methods are useful means for images analysis of spatial distributions in polymer gels.

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From such a background, we aim to elucidate the spatial distribution of paramagnetic praseodymium(Pr^{3+}) ions in a poly(methacrylic acid)(PMAA) gel containing water by using a ^{1}H-chemical shift imaging method, and to establish an NMR methodology for elucidating insight into the nature of polymer gels.

Experimental

Materials

Methacrylic acid (MAA) (Tokyo Kasei Kogyo Co., Japan) was distilled at 299 K under a pressure of 265 Pa. N,N'-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical Industries, Japan) used as the crosslinking monomer, was recrystallized twice from an ethanol solution. $K_2S_2O_8$ (Wako Pure Chemical Industries), used as the polymerization initiator, was recrystallized from an aqueous solution. $Pr(NO_3)_3 \cdot 5H_2O$ as NMR shift reagent is obtained from Apache Chemicals(Illinois, USA)

The PMAA gel was prepared by radical polymerization of MAA(3.0 mol L^{-1}) and MBAA(1.0×10^{-2} mol/L) in an aqueous solution at 318 K for 24 h in a cylindrical tube with an inside diameter of ca. 5 mm. Then, the PMAA gel obtained was soaked in excess deionized water for 3 weeks to remove remaining monomers, linear polymers formed as a by-product, and initiator. The water was changed repeatedly. The degree of swelling of the polymer gel, which was defined by $q = M_{swollen}/M_{dry}$, was 12.4. The diameter of the cylindrical gel was 5.24 mm.

The PMAA gel obtained was placed in aqueous $Pr(NO_3)_3 \cdot 5H_2O$ solution(40 mg/mL) for 3 min. The gel was shrunk to a degree of swelling of 3.3, with cylindrical diameter 3.55 mm.

Measurements

^{1}H chemical shift imaging measurements were carried out in a Bruker DSX 300 NMR spectrometer operating at 300 MHz with an imaging system at 300 K. In these experiments, the ^{1}H chemical shift images of water molecules in the gel were observed. Data processing for two-dimensional images was performed by the Fourier imaging method. In the ^{1}H NMR imaging experiments, the field gradient strengths of 100 G/cm used for the slice selection, phase-enclosing and read-out. The slice thickness was 1 mm. The data points numbered 256x256 for an image and 4000x4000x256 for a spectrum. The number of accumulation for an image was 1.

Results and Discussion

The ^1H chemical shift of aqueous $Pr(NO_3)_3$ solutions as a function of $Pr(NO_3)_3$ concentration: It is known that the ^1H chemical shift of molecules associated with paramagnetic Pr^{3+} ion, a lanthanide shift reagent, moves downfield with an increase in $Pr(NO_3)_3 \cdot 5H_2O$ concentration.[13,14] In Fig. 1 the dependence of the ^1H chemical shift of water in aqueous $Pr(NO_3)_3$ solutions as a function of $Pr(NO_3)_3$ concentration relative to pure water(δ = 4.8 ppm) is shown. It is shown that the ^1H chemical shift of water containing 60 mg/1mL moves largely downfield by about 2.5 ppm as compared with that of pure water. This shows that when Pr^{3+} ions are added into a PMAA gel and are spatially and heterogeneously distributed, water molecules at in the gel have different ^1H chemical shift values from place to place. Thus, it can be expected that the spatial distribution of Pr^{3+} ions in a PMAA gel can be determined by ^1H chemical shift imaging.

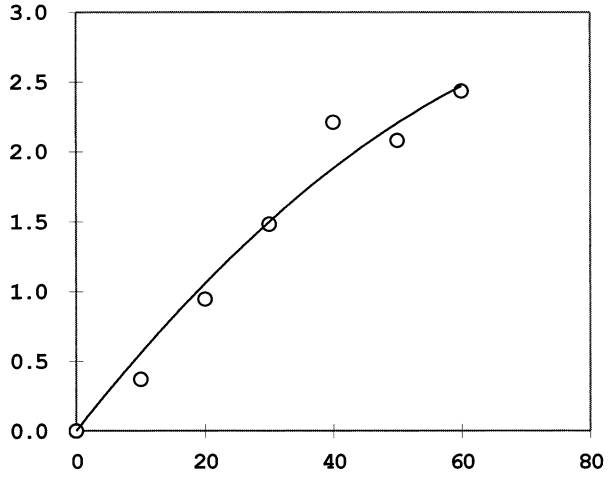

Figure 1. Plots of the ^1H chemical shift δ of water in aqueous $Pr(NO_3)_3$ solutions against $Pr(NO_3)_3$ concentration at 300 K.

^1H NMR images of water in a PMAA gel with $Pr(NO_3)_3 \cdot 5H_2O$: After a PMAA gel was placed in aqueous $Pr(NO_3)_3$ solution(40 mg/mL) for 3 min, the ^1H chemical shift NMR imaging measurements were carried out by placing the gel in an NMR probe. Conditions were set such that the gel consisted of two parts: an outside part containing Pr^{3+} ions, and an inner part containing no Pr^{3+} ions. In Fig. 2 one-dimensional ^1H NMR

spectrum of water in the gel and the ^1H chemical shift imaging patterns spliced transversely for the gel are shown. As seen from this figure, the one-dimensional ^1H NMR spectrum consists of some peaks, which arise from water interactions with Pr^{3+} ions, and without Pr^{3+} ions. The chemical shift range is large. Water having no interaction with Pr^{3+} ions appears at ca. 4.8 ppm, and on the other hand water appears in the range from 4.8 to 5.5 ppm. Probably, there exist network regions with different Pr^{3+} concentrations, as expected from Fig. 1.

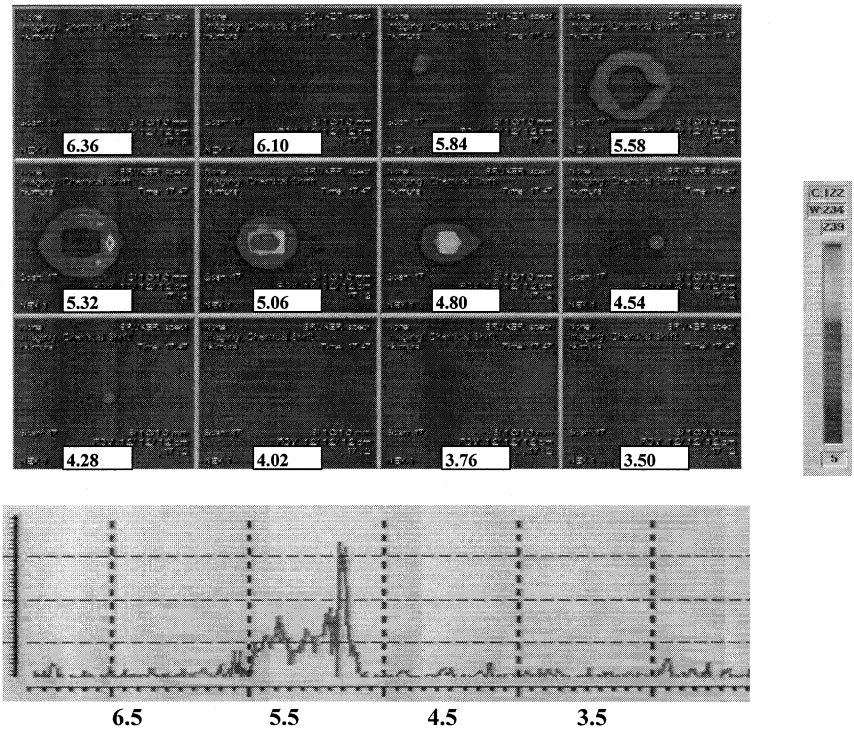

Figure 2. One-dimensional ^1H NMR spectrum of water in a PMAA gel with paramagnetic lanthanide Pr^{3+} ions and ^1H chemical shift imaging patterns of water in the gel spliced transversely to the gel.

If we look at the ^1H chemical shift imaging patterns transversely-sliced with a slice thickness of 1 mm at the central part of the gel (Fig.2), which are expressed as a function of ^1H chemical shift, we can understand that Pr^{3+} ions diffuse from the outside part to the inner part in the gel. For convenience, three-dimensional profiles are shown

as a function of ^{1}H chemical shift in Fig. 3. The profile sliced at 4.8 ppm has an intense peak in the central part of the gel. The profile sliced at lower field than 4.8 ppm has a ring-like peak at the outside of the gel. From these ^{1}H chemical shift image profiles, the spatial distribution of Pr^{3+} ions in the gel is successfully elucidated. This shows that the spatial distribution of paramagnetic lanthanide metal ions in a polymer gel can be determined by ^{1}H chemical shift imaging.

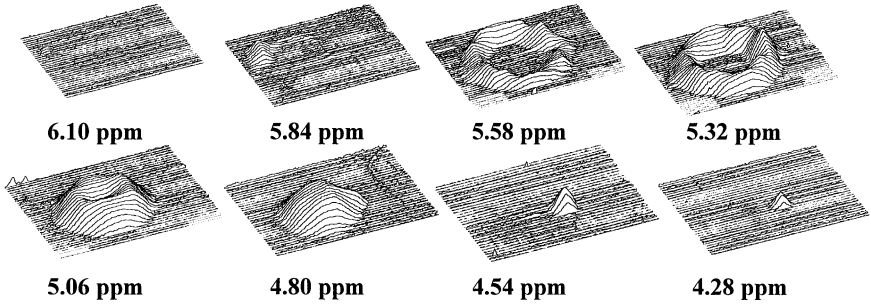

Figure 3. ^{1}H chemical shift imaging profiles of water in a PMAA gel with paramagnetic lanthanide Pr^{3+} ions sliced as a function of ^{1}H chemical shift δ.

We can conclude as follows. ^{1}H-chemical shift NMR imaging patterns of a poly(methacrylic acid) gel containing water with paramagnetic Pr^{3+} ions have been successfully observed and the spatial distribution of Pr^{3+} ions in the gel has been determined. Further, it has been shown that the chemical shift NMR imaging method is a useful means for the determining spatial distribution of paramagnetic metal ions in polymer gels.

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