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Image analysis of the spatial distribution of paramagnetic Mn^{2+} ions in a PMAA gel with the application of an electric field by an ^1H n.m.r. imaging method

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The ^1H T_2 images for a transverse slice of a PMAA hydrogel with paramagnetic Mn^{2+} ions under the application of a 3 V DC electric field were observed as a function of elapsed time by means of 270 MHz ^1H n.m.r. imaging. By using the relationship between the concentration of Mn^{2+} ions and the ^1H T_2 value of water in the gel obtained by ^1H pulse n.m.r., the ^1H T_2 image was converted to the Mn^{2+} ion concentration image. From these experiments, the spatial distribution of paramagnetic Mn^{2+} ions in the gel under the application of a 3 V DC electric field was obtained as a function of the elapsed time.

INTRODUCTION

It is known that water-swollen crosslinked polymer gels deform by the application of an electric field[1]. Recently, application of polymer gels to electrically-activated devices have been widely studied using these deformation properties. Much effort has been put into elucidating the mechanism.

In previous works[2–4], in order to clarify changes in macroscopic structure and dynamics of water molecules in a crosslinked poly(methacrylic acid) (PMAA) gel by the application of external stimuli, such as stress and electric field, through the observation of microscopic information at the molecular level, we have successfully measured ^1H n.m.r. imaging patterns with information about the spatial distribution of ^1H spin density and ^1H spin–spin relaxation time T_2 of water molecules in the polymer gel. From these experimental results, it has been demonstrated that ^1H n.m.r. imaging is a useful means for elucidating the stress–strain process and the shrinkage process by the application of an electric field to the polymer gel, as well as ^1H n.m.r. imaging works in polymer materials[5–7].

As a continuation of our studies, we aim to elucidate the spatial distribution of paramagnetic Mn^{2+} ions in a PMAA gel swollen in an aqueous manganese(II) sulphate solution with the application of a 3 V DC electric field by the images of the spatial distribution of the ^1H T_2 value as measured by ^1H n.m.r. imaging method, and to justify that the ^1H n.m.r. imaging method is a very useful means for elucidating the spatial distribution of paramagnetic ions in a gel by the ^1H n.m.r. imaging method.

EXPERIMENTAL

Materials

Methacrylic acid (MAA) (Tokyo Kasei Kogyo) was distilled at 299 K under a pressure of 267 Pa. N,N′-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical Industries), 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.

PMAA gel was prepared by radical polymerization of MAA (3.0 mol L^{-1}) and MBAA (1.0×10^{-2} mol L^{-1}) in an aqueous solution at 318 K for 24 h. Then, the PMAA gel obtained was soaked in excess deionized water for 3 weeks to remove remaining monomers, linear polymers formed as by-product, and initiator. The water was changed repeatedly. The degree of swelling of the polymer gel (q) is defined by the ratio of the mass of swollen polymer gel ($M_{swollen}$) to that of dried polymer (M_{dry}): $q = M_{swollen}/M_{dry}$. The degree of swelling of the polymer gel used in this work is about 40.

The PMAA gel obtained was dried and swollen in an aqueous manganese(II) sulphate (Kanto Chemical Co., Inc.) solution.

The cylindrical PMAA gel obtained was cut with a diameter of 8.0 mm and 7.0 mm as shown in *Figure 1*.

Measurements

The ^1H spin–spin relaxation time (^1H T_2) was measured by a Bruker minispec PC-20 pulse n.m.r. spectrometer operating at 20 MHz as modified by attaching a home-made interface and a personal computer NEC PC-9801. The relationship between the concentration of Mn^{2+} ions and the ^1H T_2 value of water in the gel was obtained from the ^1H pulse n.m.r. experiments.

^1H n.m.r. imaging was carried out by means of a JEOL GSX-270 n.m.r. spectrometer operating at 270 MHz with a JEOL NM-GIM270 imaging system at 300 K. In these experiments, ^1H spin density and ^1H T_2 weighted images of water molecules in the gel were observed. As reported previously[2–4] this imaging pulse sequence is based on the spin-echo pulse sequence of Hahn[8]. The data processing for

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a two-dimensional image was performed by the Fourier imaging method. In the ^1H n.m.r. imaging experiments, the gradient strengths used for the slice selection, phase-enclosing and read-out are 220, 220 and 220 mT m^{-1}, respectively, and slice thickness is 1.0 mm. Some ^1H n.m.r. images of a composite PMAA gel were measured as a function of the elapsed time after the application of an electric field. The images obtained were analyzed with a PIAS-7 personal image analysis system (PIAS Co. Ltd) and a PC-9801 personal computer (NEC Co. Ltd.) to get profile ^1H spin density images and ^1H T_2 enhanced images.

In applying an electric field to the gel sample, as reported in the previous work[3], the sample was placed at the middle of a cylindrical sealed glass cell which was filled with saturated water vapour in order to prevent evaporation of water from the surface of the gel, as shown in *Figure 2*. Platinum plates as electrode were placed in contact with both sides of a swollen gel and a 3 V electric field was applied for 2 h.

The images of the polymer gel were measured as a function of time with the application of an electric field.

RESULTS AND DISCUSSION

The dependence of ^1H T_2 of water in a PMAA gel on Mn^{2+} concentration

It is known that the logarithm of the ^1H T_2 value of water decreases linearly with an increase of the concentration of paramagnetic Mn^{2+} ions[9,10]. From the ^1H pulse n.m.r. experiments on the gel containing Mn^{2+} ions, we obtained the relationship between the ^1H T_2 value (ms) of water and the concentration of Mn^{2+} ions (C (mol L^{-1})) in the gel, as shown in *Figure 3*, which is expressed by

$$T_2(^1H) = 7.24C^{-0.163} \tag{1}$$

This means that the concentration of Mn^{2+} ions in the gel can be determined through the observation of the ^1H T_2 value of water in the gel.

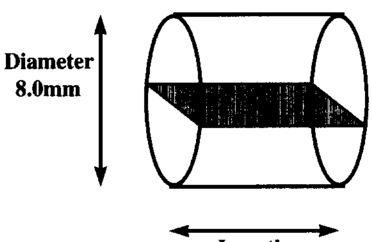

Figure 1 A PMAA gel image of transverse slice to be observed

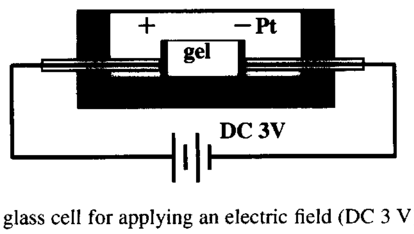

Figure 2 A glass cell for applying an electric field (DC 3 V) to a PMAA gel

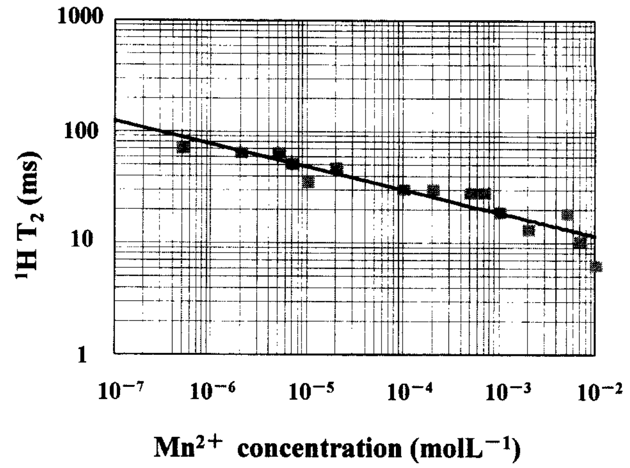

Figure 3 The dependence of ^1H T_2 of water in a PMAA gel on Mn^{2+} concentration

^1H spin density image

The transverse slice to be observed in a PMAA gel is shown in *Figure 1*. The magnitude of the ^1H spin density is differentiated by 256 steps between the lowest and highest densities, and then the observed ^1H spin density image is represented by colours from dark red, representing the lowest density, to white, representing the highest density. The intensity scale indicated by colours is shown in *Figure 4*. The colour scale indicates the relative value of the ^1H spin density.

We are concerned with the shrinkage process of a PMAA gel containing Mn^{2+} ion by the application of an electric field. The application of an electric field to a PMAA gel leads to shrinkage of the gel with exhaustion of water. Shrinkage around the positive electrode is larger than that around the negative electrode. The gel part in contact with the negative electrode is swollen. This result is the same as the shrinkage process of PMAA gel swollen in deionized water reported previously[3].

^1H spin density images for a transverse slice of a PMAA gel containing an aqueous manganese(II) sulphate was measured as a function of the elapsed time (T_e) by the application of a 3 V DC electric field are shown in *Figure 4*. We can clarify the electric field effect on the shrinkage of a PMAA gel, by comparing the ^1H spin density image experiments for the PMAA gel (3 V) with those for PMAA gel (0 V).

The ^1H spin density image experiments for PMAA gel (3 V) is represented in *Figure 4*(b). It is shown that at elapsed time $T_e = 0$ min most of the gel is occupied by the blue region. At $T_e = 15$ min, the magnitude of ^1H spin density increases in going from the positive electrode to the negative electrode as indicated by blue → green → blue → violet. At $T_e = 30$ min, the ^1H spin density changes as indicated by blue → violet → white → violet → blue → green → blue → red. After $T_e = 60$ min, the white region increases. The ^1H spin density image experiments for PMAA gel (0 V) is represented in *Figure 4*(c). It is shown that at elapsed time $T_e = 0$ min most of the gel is occupied by the blue region. Each image of the ^1H spin density from $T_e = 15$ min to 120 min, the magnitude of ^1H spin density is occupied by green region and red region. There is little change in the ^1H spin density image for PMAA gel (0 V).

^1H spin–spin relation time (^1H T_2) image

It is important to know information on the ^1H T_2 value of

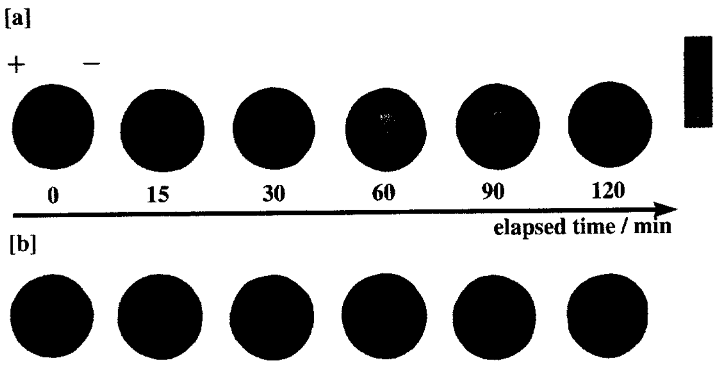

Figure 4 Elapsed-time dependence of image for the ^1H spin density of PMAA gel swollen by an aqueous manganese(II) sulphate solution with (a) and without (b) the application of an electric field

water molecules in a PMAA gel, in order to analyze the distribution of paramagnetic Mn^{2+} ions in the gel under electric stimulus.

The ^1H T_2 images experiment of the gel without the application of an electric field becomes reference data to elucidate the shrinkage process of the gel with the application of an electric field. The ^1H T_2 images for a transverse slice of a PMAA gel containing an aqueous manganese(II) sulphate solution were measured as a function of the elapsed time by the application of a 3 V DC electric field were shown in *Figure 5*.

The ^1H T_2 value of water molecules in a PMAA gel (3 V) is represented in *Figure 5*(a). At $T_e = 0$ min, the ^1H T_2 value of water molecules in a PMAA gel (3 V) distributes homogeneously in the gel. The ^1H T_2 value is about 18 ms. At $T_e =$ 15 min, the *I*H T_2 value of water molecules in a PMAA gel (3 V) decreases from the positive electrode to the negative electrode as indicated by 32 → 33 → 32 → 27 → 15 → 10 ms. At T_e = 30 min, the ^1H T_2 value of water molecules in a PMAA gel (3 V) changes as indicated by 41 → 44 → 45 → 39 → 27 → 14 ms. At T_e = 45 min, 45 → 48 → 45 → 39 → 29 → 14 ms. At T_e = 60 min, 56 → 73 → 67 → 42 → 21 ms. At T_e = 90 min, 71 → 83 → 93 → 65 → 37 → 20 ms. At T_e = 120 min, 55 → 54 → 48 → 36 → 26 → 17 ms.

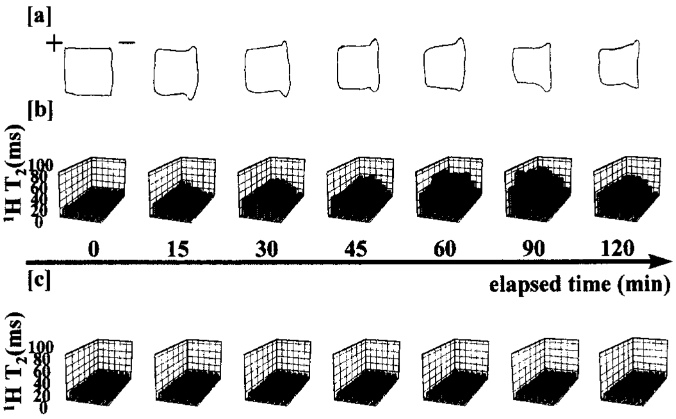

Figure 5 Elapsed-time dependence of the shapes (a) and ^1H spin–spin relaxation time (^1H T_2) distribution for a transverse slice of PMAA gel swollen by an aqueous manganese(II) sulphate solution with (b) and without (c) the application of an electric field

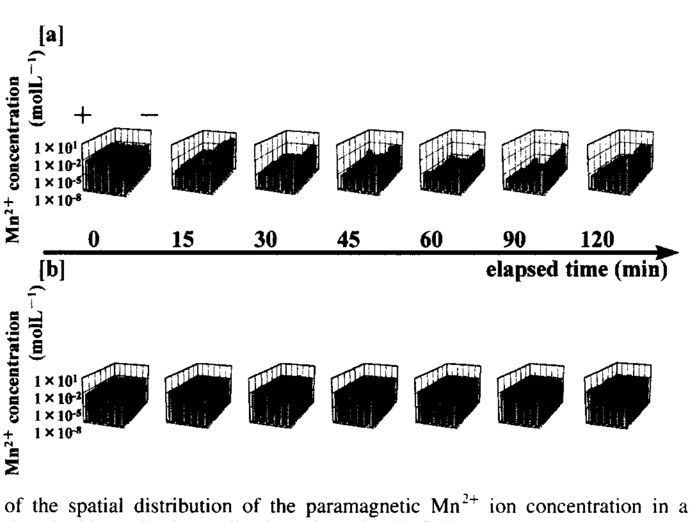

Figure 6 Elapsed-time dependence of the spatial distribution of the paramagnetic Mn^{2+} ion concentration in a PMAA gel swollen by an aqueous manganese(II) sulphate solution with (a) and without (b) the application of an electric field

The ^1H T_2 value of water molecules in a PMAA (0 V) is represented in *Figure 5*(b). As seen from this diagram, the ^1H T_2 values of water molecules in a PMAA gel (0 V) are almost about 18 ms without changing from $T_e = 0$ to 120 min.

Here, it must be paid attention that the change of the spatial parts of ^1H T_2 value is influenced by not only the Mn^{2+} ion concentration but also the mobility of water molecules in a PMAA gel. However, the change of the ^1H T_2 value which is accompanied by the shrinkage of a PMAA gel with the application of an electric field is much smaller than that of the ^1H T_2 value by the influence of paramagnetic Mn^{2+} ions as seen from a comparison of the present work and the previous ^1H n.m.r. imaging work[3] on shrinkage of a PMAA gel without Mn^{2+} ion by the application of an electric field.

In other words, it shows that Mn^{2+} ions in a PMAA gel (3 V) move from the positive electrode side to the negative electrode side. This means that the ^1H T_2 distribution images can be converted to the Mn^{2+} ion distribution images. Their three-dimensional profiles of the spatial distribution of the paramagnetic Mn^{2+} ion concentration in a PMAA gel swollen by an aqueous manganese(II) sulphate solution with (a) and without (b) the application of an electric field were shown in *Figure 6*.

At $T_e = 0$ min, the Mn^{2+} ion distributes homogeneously in the gel. The concentration of the Mn^{2+} ions in the gel is about 3.8×10^{-3} mol L^{-1}. As the elapsed time is increased, the Mn^{2+} ions migrates from the positive electrode side to the negative electrode side. The concentration of the Mn^{2+} ions in the gel at the positive electrode side becomes lower compared with that at the negative electrode side. For example, the Mn^{2+} ion concentration in a PMAA gel (3 V) from the positive electrode side to the negative electrode side increases as indicated by $3.2 \times 10^{-6} \rightarrow 5.3 \times 10^{-7} \rightarrow 1.2 \times 10^{-6} \rightarrow 2.7 \times 10^{-6} \rightarrow 3.3 \times 10^{-5} \rightarrow 1.1 \times 10^{-3}$ mol L^{-1} at $T_e = 60$ min. The Mn^{2+} ions exhaust from the negative electrode side of the gel. By the detailed analysis, quantitative elucidation on the migration of the Mn^{2+} ions, in the gel by the application of an electric field was successfully carried out.

CONCLUSIONS

The ^1H T_2 of water molecules close to Mn^{2+} ions in a PMAA gel is decreased by the effect of Mn^{2+} ions in a gel. As PMAA gel swollen by an aqueous manganese(II) sulphate solution is applied with an electric field, Mn^{2+} ions in the gel move toward negative electrode side and the concentration of Mn^{2+} ions have characteristic spatial distribution. The spatial distribution of the paramagnetic ions in a PMAA gel with application of an electric field is converted by the images of the spatial distribution of the ^1H T_2 values obtained by ^1H n.m.r. imaging method. It can be demonstrated that it is a very useful means for determining the spatial distribution of the paramagnetic ions in a gel by ^1H n.m.r. imaging method.

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