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Spatial Information on a Polymer Gel as Studied by ^{1}H NMR Imaging III. Shrinkage by the Application of an Electric Field to a Composite Polymer Gel

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ABSTRACT: ^{1}H NMR imaging patterns of a composite poly(methacrylic acid) (PMAA) gel being a double cylindrical rod, for which the swelling degrees of the inside and outside gels are different from each other, were measured under the application of an electric field. On the basis of these experimental results the shrinkage process was studied. It was found that the shrinkage process of the composite PMAA gel is different from the case of a homogenous cylindrical PMAA gel as reported previously [*Macromolecules*, **28**, 4377 (1995)]. Details of the shrinkage process were discussed at the molecular level.
    KEY WORDS   Composite Polymer Gel / ^{1}H NMR Imaging Shrinkage / Electric Field /

It is known that water-swollen cross-linked polymer gels deform by the application of an electric field.[1] Recently, applications of polymer gels to electrically-activated devices have been studied widely using these deformation properties. Many efforts have been made on elucidating the deformation mechanism.

In previous works,[2,3] in order to clarify changes in macroscopic structure and dynamics of water molecules in a cross-linked poly(methacrylic acid) (PMAA) gel, we have applied an external stimulus such as stress and an electric field. Through the observation of microscopic information at the molecular level, we have successfully measured ^{1}H NMR imaging patterns with information about the spatial distribution of ^{1}H spin density and ^{1}H spin–spin relaxation time T_2 of water molecules in the polymer gel. From these experimental results, it has been demonstrated that ^{1}H NMR imaging is a useful means of elucidating the stress–strain process and the shrinkage process by the application of an electric field to the polymer gel, as well as other ^{1}H NMR imaging works in polymer materials.[4]

As a continuation of our work, we aim to study the shrinkage process of a composite PMAA gel (that is a double cylindrical rod (Figure 1) in which the swelling degrees of the outside and inside parts are different with each other) by the application of an electric field, and, in addition to our previous work,[2,3] to justify that the ^{1}H NMR imaging method is a useful means for studying stimulus-response behavior in polymer gel systems.[5]

EXPERIMENTAL

Materials

Methacrylic acid (MAA) (Tokyo Kasei Kogyo) was distilled at 299 K under a pressure of 276 Pa. N,N'-Methylenebisacrylamide (MBAA) (Wako Pure Chemical Industries) used as the cross-linking monomer was recrystallized twice from ethanol solution. $K_2S_2O_8$ (Wako Pure Chemical Industries) used as the polymerization initiator was recrystallized from aqueous solution.

PMAA gel was prepared by radical polymerization of MAA and MBAA in aqueous solution at 318 K for 24 h in a glass tube with the inside diameter of 8 mm, at the center of which a glass stick with an outside diameter of 4 mm was put. After the first polymerization for obtaining the outside gel was completed, the inside glass stick was removed from the outside glass tube, and MAA, MBAA, and $K_2S_2O_8$ were added into the resulting cylindrical space to prepare the inside PMAA gel. The structural scheme of a composite PMAA gel is shown in Figure 1. By varying the amount of MBAA used as the cross-linking monomer composite PMAA gels were obtained which consisted of outer and inner gels exhibiting different degrees of swelling. In sample
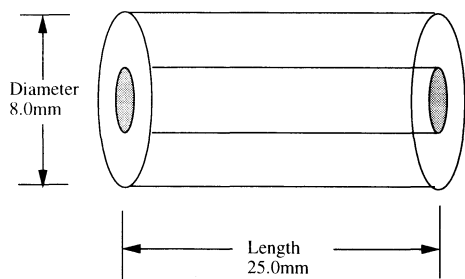
Figure 1. A structural scheme of a composite PMAA gel with the inside gel part (shadowed part) and the outside gel part (light part). The swelling degrees of the inside and outside gels are different from each other.
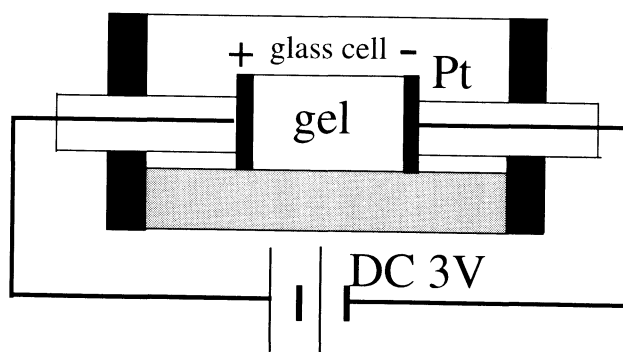
Figure 2. Glass cell for applying an electric field (DC 3 V) to a composite PMAA gel.
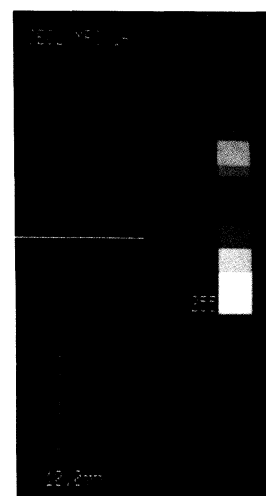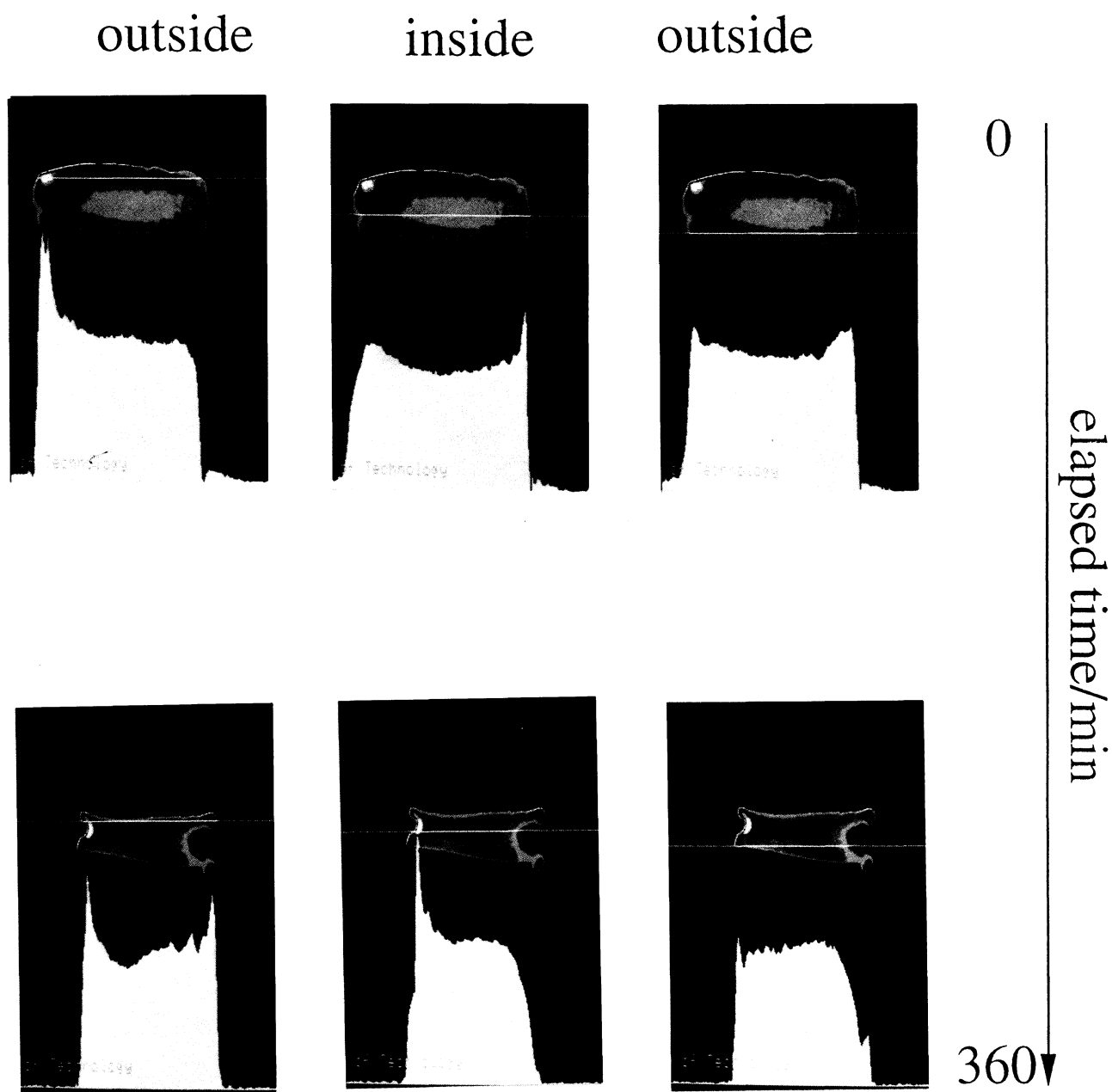
outside   inside   outside

Figure 3. Elapsed-time dependence of images for the ^1H spin density distribution and two-dimensional intensity profile of a composite PMAA gel (sample A) with the application of an electric field, of which the swelling degrees q of the inside and outside gels are 26 and 28, respectively.

A the MBAA concentration was 0.25 mol% for the outside gel and 0.33 mol% for the inside gel, and in sample B was 0.33 mol% for the outside gel and 0.25 mol% for the inside gel.

The PMAA gel samples obtained were soaked in excess deionized water for 3 weeks to remove remaining monomer, linear polymers formed as byproduct, and initiator. The water was exchanged repeatedly. The degree of swelling of the polymer gel (q) is defined by the ratio of the mass of swollen polymer gel to that of dried polymer. The swelling degrees of polymer gels obtained at the MBAA concentrations of 0.33 and 0.25 mol% are 26 and 28, respectively.

Measurements

^{1}H NMR imaging measurements were carried out at 300 K by means of a JEOL GSX-270 NMR spectrometer operating at 270 MHz with a JEOL NM-GIM270 imaging system. In these experiments the ^{1}H spin density and the [1]H T_2 weighted images of water molecules in the gel were observed. As reported previously[2,3] this imaging pulse sequence is based on the spin-echo pulse sequence of Hahn. The data processing for a two-dimensional images was performed by the Fourier
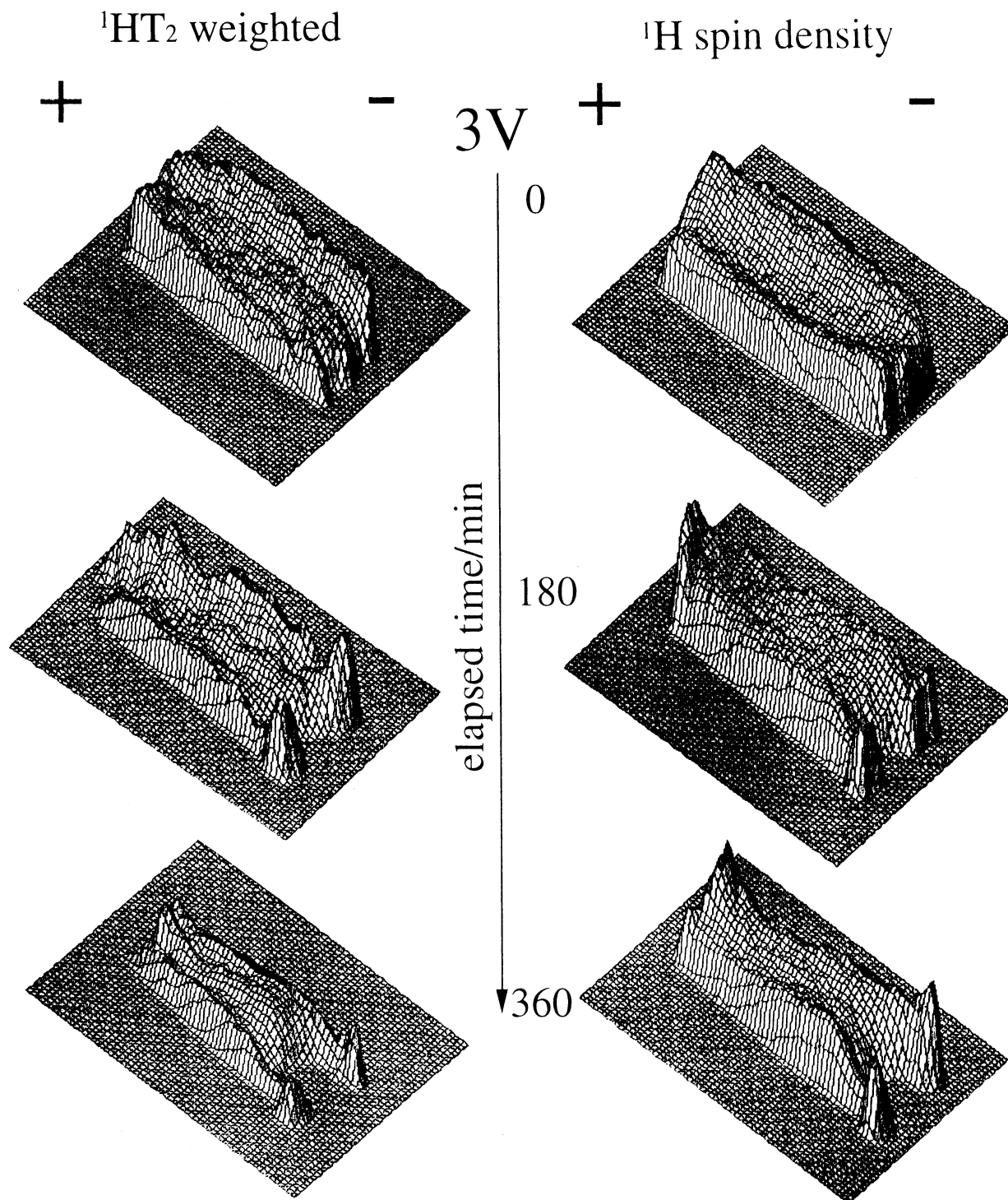
[1]HT₂ weighted

[1]H spin density

Figure 4. Three-dimensional histograms of elapsed-time dependence for the ^{1}H spin density distribution and [1]H T_2 weighted images of a composite PMAA gel (sample A) with the application of an electric field, of which the swelling degrees q of the inside and outside gels are 26 and 28, respectively.

imaging method. Details of ^{1}H NMR image measurements are given in the previous papers. Some ^{1}H NMR 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 images analysis system (PIAS Co., Ltd.) and a PC-9801 personal computer (NEC Co., Ltd.) to get a profile of ^{1}H spin density image and ^{1}H T_2 enhanced image.

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

RESULTS AND DISCUSSION

Shrinkage Process of a Composite Gel (Sample A) for Which the Swelling Degrees of the Inside and Outside Gels are 26 and 28, Respectively

In the ^{1}H NMR imaging experiments, we can detect only ^{1}H signals of water contained in a composite gel due to the removal of dipolar broadening by fast isotropic molecular motion. When protonated water in the gel was replaced by deuterated water, no ^{1}H NMR signals were observed. The transverse slice of the gel is observed in a composite PMAA gel. The observed ^{1}H spin density images as a function of elapsed time (T_e) after the application of an electric field (3 V) are shown in Figure 3. The relative magnitude of the ^{1}H spin density is represented by the colors from dark blue (the lowest density) to white (the highest density). The intensity scale indicated by colors is represented in Figure 3. It is shown that at $T_e = 0$ min most of the inside gel

region is represented by yellow and most of the outside gel region is represented by red. This indicates that the ^{1}H spin density of the outside gel is higher than that of the inside gel. The experimental result is consistent with the fact that the swelling degrees of the inside and outside gels are 26 and 28, respectively. As the elapsed time is increased, most of the inside and outside regions are represented by red except for the gel parts in contact with the negative and positive electrodes. At $T_e = 360$ min in the inside gel the region around the negative electrode becomes white and the region around the positive electrode becomes yellow. On the other hand, in the outside gel the region around both the electrodes remains red.

It is convenient to represent the ^{1}H spin density distribution of a composite gel by a two-dimensional profile. The profiles of the ^{1}H spin density for the inside and outside gels, of which the positions are indicated by a white line on the image, are shown in Figure 3 as a function of elapsed time after the application of an electric field. It is shown that the application of an electric field to a composite gel leads to shrinkage of the gel with exhaust of water from the negative electrode side. The shrinkage rate of the inside gel, which exhibits a smaller degree of swelling than the outside gel, is faster compared with the outside gel. For this, at $T_e = 360$ min it is clear that the inside gel with $q = 26$ shrinks more than the outside gel with $q = 28$, and the shrinkage in the region around the positive electrode is greater when compared with the region around the negative electrode. As seen from the two-dimensional profiles, as the elapsed time after the application of an electric field is increased, the ^{1}H spin density of water in the region around the positive and negative electrodes becomes higher compared with other region. Such a situation can be more clearly illustrated by the three-dimensional histograms as shown in Figure 4. For convenience, the schematic
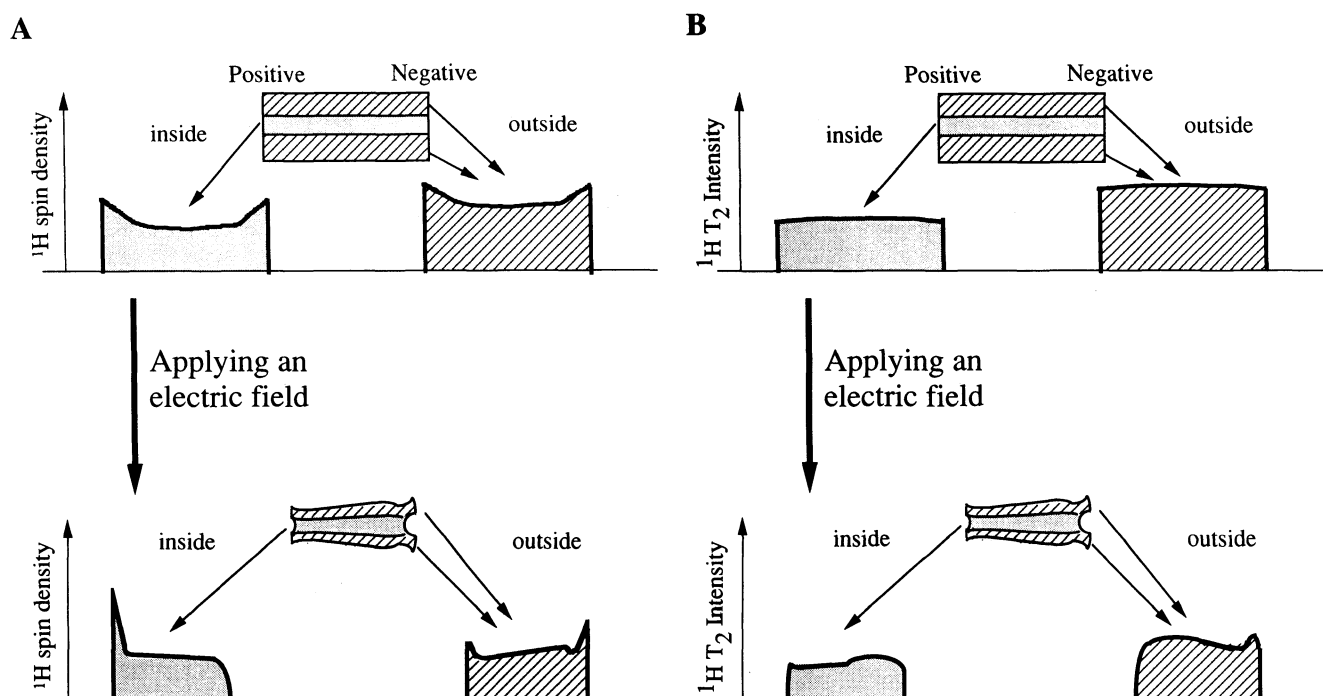
A

B

Figure 5. Schematic diagrams of the shrinkage process of a composite PMAA gel (sample A) by the application of an electric field, of which the swelling degrees q of the inside and outside gels are 26 and 28, respectively, as viewed by ^{1}H spin density (A) and ^{1}H T_2 weighted images (B).

diagram for the ^{1}H spin density distribution of the gel under the shrinkage process is shown in Figure 5(A). The trend for the shrinkage process of the ^{1}H spin density distribution of a homogeneous gel by the application of an electric field as reported previously[2] is very similar to that of the outside gel rather than the inside gel. However, the whole shape of the shrunk composite gel is very different from that of the homogeneous gel which shrinks to form a 'wine-stopper-like' shape at long elapsed time after the application of an electric field.

Next, we are concerned with the ^{1}H T_2 weighted image of a composite gel (sample A). The ^{1}H T_2 weighted image (not shown) provides spatial information on the dynamical behavior of water molecules in a composite PMAA gel under an electric stimulus. The three-dimensional histograms of elapsed-time dependence of the ^{1}H T_2 weighted image of water in the gel after the application of an electric field are shown in Figure 4. For convenience, the corresponding schematic diagram was shown in Figure 5(B). Before the application of an electric field the ^{1}H T_2 weighted intensity is almost constant in the whole region of the gel. This means that the mobility of water in the whole region of the inside and outside gels are almost the same. However, at long
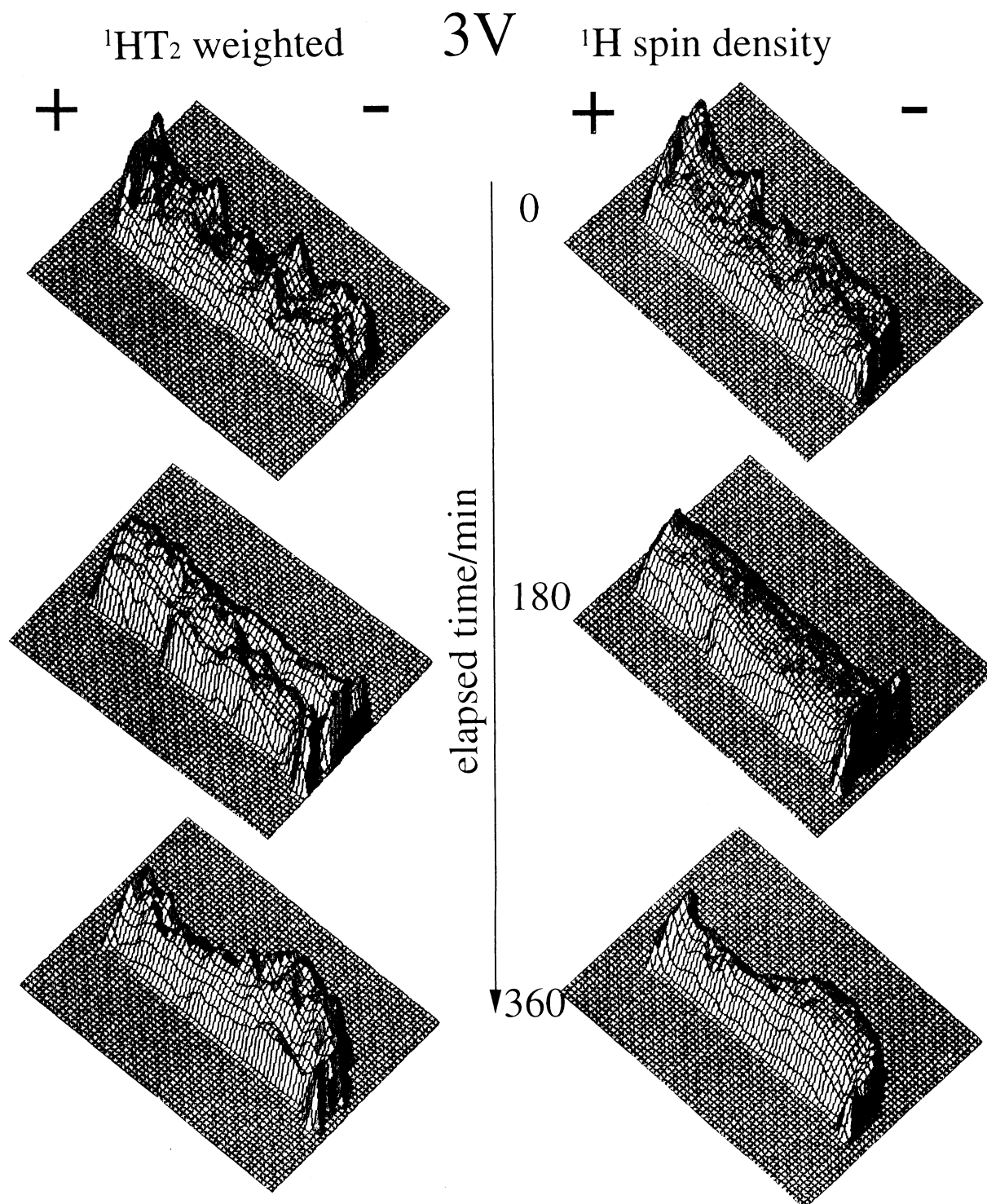

Figure 6. Three-dimensional histograms of elapsed-time dependence for the ^{1}H spin density distribution and ^{1}H T_2 weighted images of a composite PMAA (sample B) with the application of an electric field, of which the swelling degrees q of the inside and outside gels are 28 and 26, respectively.
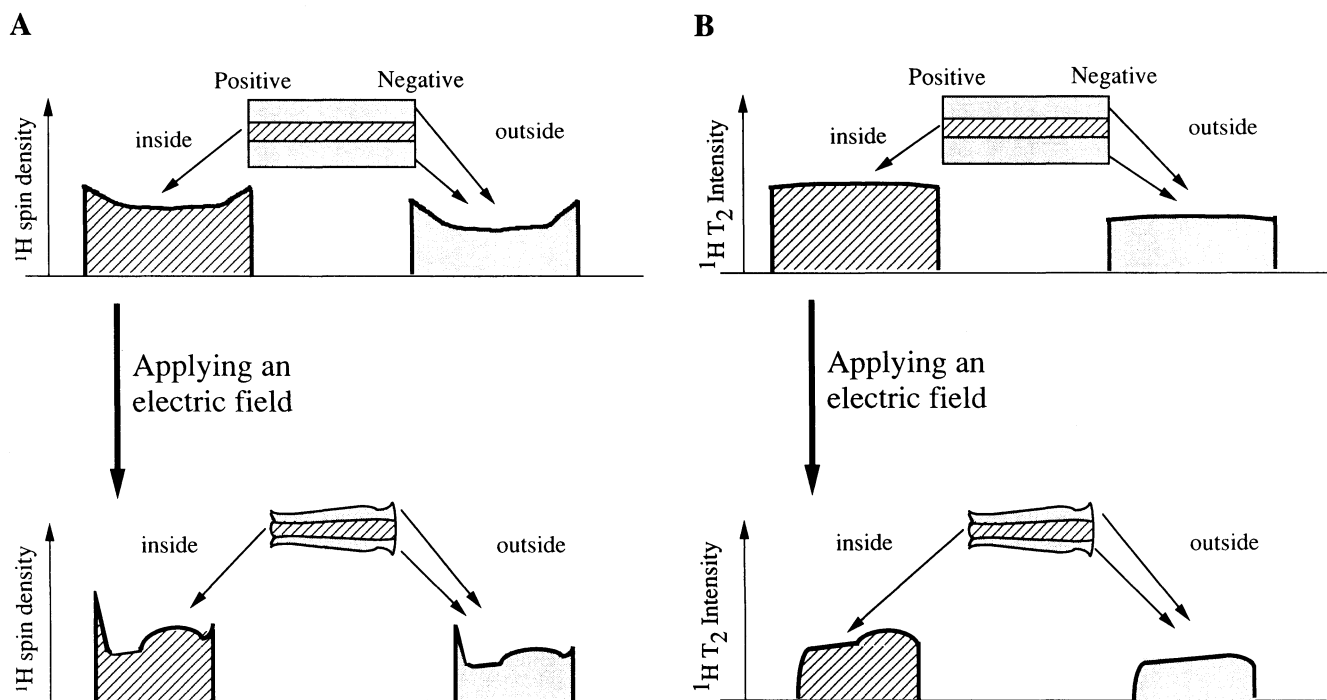
A

B

Figure 7. Schematic diagrams of the shrinkage process of a composite PMAA gel (sample B) by the application of an electric field, of which the swelling degrees q of the inside and outside gels are 28 and 26, respectively, as viewed by ^1H spin density (A) and ^1H T_2 weighted images (B).

elapsed time after the application of an electric field, the ^1H T_2 weighted intensity in the region around the negative electrode in both of the inside and outside gels is somewhat more intense than that around the positive electrode. This means that molecular motion of water in the gel region around the negative electrode is somewhat faster than that in the other region. The trend is very similar to that for the case of a homogeneous PMAA gel reported previously.[2]

Shrinkage Process of a Composite Gel (Sample B) for Which the Swelling Degrees of the Inside and Outside Gels are 28 and 26, Respectively

The swelling degrees of the inside and outside gels for sample B are opposite to those for sample A. Therefore, the swelling degree of the inside gel for sample B is higher than that for sample A. The three-dimensional histogram of the ^1H spin density distribution of a composite PMAA gel (sample B) as a function of elapsed time after the application of an electric field is shown in Figure 6. For convenience, the schematic diagram of the ^1H spin density distribution of the gel is shown in Figure 7(A). It is apparent that the shrinkage process of sample B by the application of an electric field is very different from the case of sample A. At long elapsed time after the application of an electric field the ^1H spin densities of water in the inside and outside gels around the negative and positive electrodes are more intense that those in the other regions. This trend is very similar to that for the homogeneous gel. Also, the shape after shrinkage is similar to that of the homogeneous gel resulting in a wine-stopper like shape at long elapsed time.

In Figure 6 the three-dimensional histograms of elapsed time dependence of the ^1H T_2 weighted image of water in the gel after the application of an electric field are shown. For convenience, the schematic diagram for the ^1H T_2 weighted image of water in the gel after

the application of an electric field is shown in Figure 7(B). Before the application of an electric field the ^1H T_2 intensity is almost constant in the whole region of the inside and outside gels. The mobilities of water in the whole region of the inside and outside gels are almost the same. At long elapsed time after the application of an electric field the ^1H T_2 intensity of water in the inside and outside gels around the negative electrode is more intense compared with that around the positive electrode. This means that the mobility of water in the inside and outside gels around the negative electrode is somewhat higher compared with that around the positive electrode. As reported in the previous paper,[2] the ^1H T_2 of water molecules around the negative electrode in a homogeneous cylindrical gel after the application of an electric field are much longer than that around the positive electrode. Its trend is very similar to that of the composite gel. This means that the shrinkage process is very similar to that of the composite gel.

Finally, it can be said that ^1H NMR imaging provides useful information about the shrinkage process of a composite PMAA gel on applying an electric stimulus. The shrinkage process relates to the translational behavior of water molecules in the gel associated with a change in the size of the network.

REFERENCES AND NOTES

1. T. Tanaka, I. Nishino, S. Sun, and S. Ueno-Nishio, *Science*, **218**, 467 (1982).
2) T. Shibuya, H. Yasunaga, H. Kurosu, and I. Ando, *Macromolecules*, **28**, 4377 (1995).
3) H. Yasunaga, H. Kurosu, and I. Ando, *Macromolecules*, **25**, 6505 (1992).
4) For example: (a) L. A. Weisenberger and J. L. Koenig, *Macromolecules*, **23**, 2445 (1990); (b) L. A. Weisenberger and J. L. Koenig, *Macromolecules*, **23**, 2454 (1990); (c) R. A. Grinsted and J. L. Koenig, *Macromolecules*, **25**, 1229 (1992).