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# Spatial Information on a Polymer Gel As Studied by $^1$H NMR Imaging. 2. Shrinkage by the Application of an Electric Field to a Polymer Gel

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ABSTRACT: $^1$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 a cross-linked poly(methacrylic acid) (PMAA) gel were measured, in order to clarify the translational behavior of water molecules in the gel under shrinkage processes by the application of an electric field. From the experimental result it was found that a cylindrical gel shrank to a wine-stopper-like shape at long elapsed time after the application of an electric field. On the positive electrode side, the $^1$H spin densities were high and the mobilities were low, and on the negative electrode side, the $^1$H spin densities were low and the mobilities high. Further, details of the shrinkage process were discussed at the molecular level.

## Introduction

Hydropolyelectrolyte gels consist of a three-dimensional polymer network and water as the solvent held by the network. They have a lot of attractive physical and chemical properties. For example, hydropolyelectrolyte gels show a discontinuous volume change in response to a change of the external environment, solvent component,[1] pH,[2] ion concentration,[3] and temperature.[4] They can be regarded as nonlinear materials because of such a phase transition. In these reactions water molecules in polymer gels play a significant role and interact with polymer chains. Therefore, in order to elucidate behavior of these water molecules or polymer chains, many investigations have been carried out using DSC,[5] NMR,[6] etc., since Flory's works in the 1940s.[7]

Water-swollen cross-linked polymer gels deform by the application of an electric field because they can convert chemical, electrical, and thermal energies into mechanical energy. Such a reaction is termed the chemomechanical system. The first observation of electric-field-induced deformation was made by Tanaka et al.[8] A rodlike gel of a copolymer of acrylic acid–acrylamide shrinks by the application of an electric field to the gel. A similar phenomenon was also observed by other workers.[9] Recently, applications of polymer gels to electrically-activated devices have been studied widely using these deformation properties. Although a great deal of effort has been made on investigations of the mechanism, it seems that a fundamental approach at the molecular level has rarely been taken. Therefore, it is important to clarify macroscopic structure and dynamics of small-size molecules in a polymer gel through the observation of microscopic information at the molecular level.

In our previous paper,[10] it has been demonstrated that $^1$H NMR imaging is useful for obtaining spatial information on the strain propagation in a polymer gel under stress. The two-dimensional information for a transverse slice of polymer gel sample can be obtained in a noninvasive way with the help of additional magnetic field gradients. Due to this perfect noninvasive characteristic, an NMR imaging method has two advantages: One is that it is possible to measure the time dependence of reaction in a gel sample with one experiment. Another is that it is possible to obtain two-dimensional information on the spatial distribution of the spin density and the relaxation times of molecules in a sample.[11] The signal intensity measured depends on the local concentration of nuclear spins and their spin–lattice ($T_1$) and spin–spin ($T_2$) relaxation times. $T_1$ and $T_2$ are strongly influenced by the mobility of molecules under consideration.[12] It is possible to estimate these parameters from the obtained images by adjusting the appropriate pulse sequence. $^1$H NMR images can enhance the differences in $^1$H density and $^1$H NMR relaxation times among various parts of a gel sample, and the distribution of $^1$H spin density and relaxation times is mapped out. Such a transverse image of the concentration of solvent molecules and the distribution map of $^1$H $T_1$ and $T_2$ give us significant knowledge about the spatial behavior of molecules.

In the present work, we aim to measure $^1$H NMR imaging patterns of the spatial distribution of $^1$H spin density and $^1$H $T_2$ of water molecules in a cross-linked poly(methacrylic acid) (PMAA) gel under an electric stimulus, to clarify the behavior of water molecules in a PMAA gel during the shrinkage process induced by the application of an electric field. This will be carried out using the obtained results on the spatial distribution change of $^1$H spin density and the molecular motion of water molecules. We will also demonstrate the potential applicability of NMR imaging to polymer gel under an outer stimulus.

## Experimental Section

**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 cross-linking 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 (7.5 × 10$^{-3}$ mol L$^{-1}$) in an aqueous

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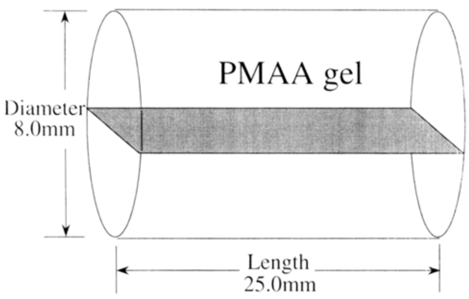

**Figure 1.** PMAA gel and image of transverse slice to be observed.

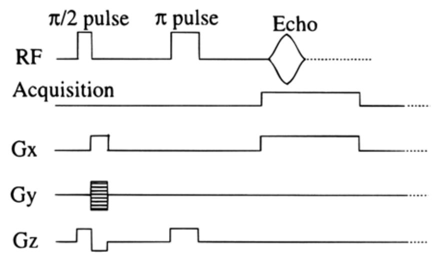

**Figure 2.** Timing diagram for the spin-echo imaging pulse sequence.

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 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 ($M_{\mathrm{swollen}}$) to that of dried polymer ($M_{\mathrm{dry}}$): $q = M_{\mathrm{swollen}}/M_{\mathrm{dry}}$. The swelling degree of polymer gels used in this work is about 40.

A cylindrical PMAA gel obtained was cut with a diameter of 8.0 mm and a length of 25.0 mm as shown in Figure 1.

**Measurements.** $^1$H NMR imaging measurements were carried out by means of a JEOL GSX-270 NMR spectrometer operating at 270 MHz with a JEOL NM-GIM 270 imaging system at 300 K. In this experiment, we measured $^1$H spin density and $^1$H $T_2$ enhanced images of water molecules in the gel.

This imaging pulse sequence is based on the spin-echo pulse sequence of Hahn.[12] The data processing for a two-dimensional image was performed by the Fourier imaging method. The pulse sequence is shown in Figure 2. The slice selection gradient (Gz) and selective radio-frequency pulse determine the position of the region to be observed. The phase-encoding gradient (Gy), which is varied in intensity systematically, serves to obtain the differentiation of the volume elements in the $y$-direction. The phase-encoding period is fixed to be constant. The readout gradient (Gx) is applied in the $x$-direction, and during the phase-encoding period the reversed gradient (Gz) is also applied to refocus the selectively-exited magnetization. During the acquisition period the readout gradient (Gx) is applied to disperse the volume element in the $x$-direction.

In the $^1$H NMR imaging experiments, the gradient strengths used for the slice selection, phase encoding, and readout are 19, 20, and 20 mT m$^{-1}$, respectively, and the slice thickness is 2.0 mm. The $\pi/2$ and $\pi$ radio-frequency pulse lengths are 1.5 ms, but the strength of a $\pi/2$ pulse is half that of a $\pi$ pulse. The number of data points and accumulations are 256 and 2, respectively, to obtain $^1$H NMR image signals with a reasonable signal-to-noise ratio. The experimental errors for $^1$H $T_2$ in the NMR imaging experiments were less than ±10%.

The spin-echo method based on Hahn's pulse sequence is also used to obtain $^1$H $T_2$ enhanced images. Images with different lengths of echo time must be obtained for measurement of $^1$H $T_2$, which provides information about the mobility of the molecule. From these imaging patterns, we can calculate the spatial distribution of the $^1$H $T_2$ value of water molecules in the gel. In our $^1$H NMR imaging experiments, the obtained spin-echo train decays exponentially. This indicates that the addtional diffusion effect on the spin-echo train is not so large. However, it should be thought that our obtained $^1$H $T_2$ is not a real $^1$H $T_2$ but an apparent $^1$H $T_2$ by addition of a small diffusion effect. $T_2$ gives us information about the molecular motion of water in the PMAA gel. According to B.P.P. theory,[13] a larger $T_2$ value corresponds to higher mobility. By using NMR imaging, we can successfully get information on the spatial distribution of $^1$H spin density and $^1$H $T_2$ of water molecules in the PMAA gel.

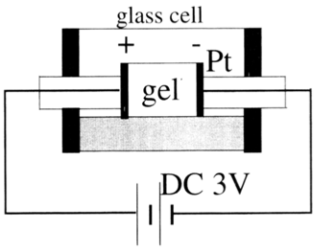

**Figure 3.** Glass cell for applying an electric field to a PMAA gel.

As is shown in Figure 3, a cylindrical PMAA gel 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.

Pt plates as electrodes were placed in contact with both sides of a swollen gel,, and a 3 V dc electric field was applied for 4 and 6 h depending on gel samples. The gel shrinks by exhausting water over a period of time after the application of an electric field. The positive and negative electrodes of Pt plates are moved to remain in contact with the polymer gel during its shrinkage.

Some $^1$H NMR images of a PMAA gel were measured as a function of elapsed time after the application of an electric field. The transverse images were measured along the direction of electric current as shown in Figure 1. Also, the images of the polymer gel were measured as a function of time without the application of an electric field. Except for $^1$H NMR imaging measurements, the gel was put in the absence of magnetic field. Images with and without the application of an electric field were compared with each other, in order to clarify the shrinking process of the polymer gel under 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 a $^1$H spin-density image and a $^1$H $T_2$ enhanced image.

## Results and Discussion

**$^1$H Spin-Density Image.** In the $^1$H NMR imaging experiments we could not detect polymer network of a PMAA gel using the conventional technique due to its large dipole broadening, but we could detect successfully $^1$H signals of water contained in the PMAA gel due to the removal of dipole broadening by fast isotropic molecular motion. Figure 1 shows the transverse slice to be observed in a PMAA gel. The magnitude of the $^1$H spin density is differentiated by 256 steps between the lowest and highest densities, and then the observed $^1$H spin-density image is represented by colors from dark blue, representing the lowest density, to white, representing the highest density. The intensity scale indicated by colors is shown in Figure 4. The color scale indicates the relative value of the $^1$H spin density.

We initiate the shrinkage process of a PMAA gel 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.

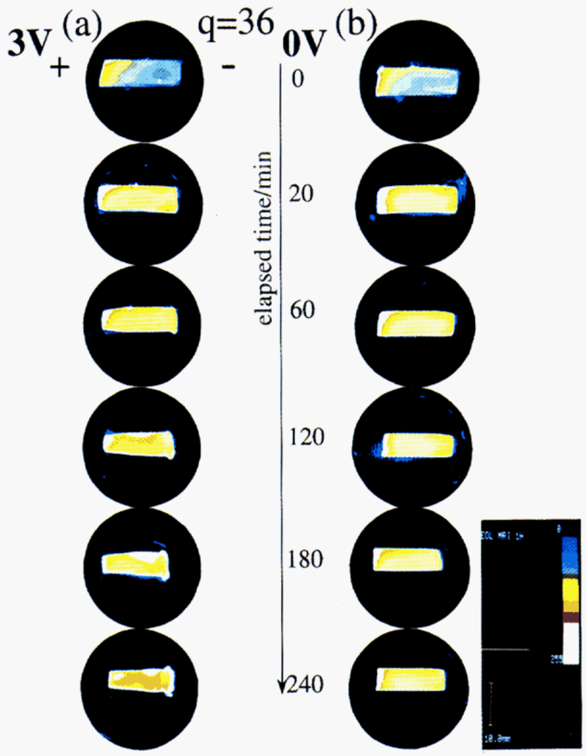

**Figure 4.** Elapsed-time dependence of images for the $^1$H spin-density distribution of a PMAA gel with (a) and without (b) the application of an electric field.

Figure 4 shows the elapsed-time dependencies for the shape and the spatial distribution of $^1$H spin density of the PMAA gel with and without the application of an electric field. Hereafter, PMAA gel samples with and without the application of an electric field (3 V) are expressed by PMAA gel (3 V) and PMAA gel (0 V), respectively.

We can clarify the electric field effect on the shrinkage of a PMAA gel, by comparing the $^1$H spin-density image experiments for PMAA gel (3 V) with those for PMAA gel (0 V). The $^1$H spin-density image experiments for PMAA gel (0 V) is represented in the right side of Figure 4, where some different colored regions from blue to white are distributed. We can recognize from the observed images that the $^1$H spin-density distribution is heterogeneous in the gel at elapsed time $T_e = 0$ min after the application of an electric field and the blue region is quite large. The magnitude of $^1$H spin density increases in going from the right end of the gel to the left end as indicated by blue → green → light green → yellowish green → yellow → bright orange → orange → red → white. At $T_e = 20$ min, the region occupied by yellow becomes large. The magnitude of $^1$H spin density increases in going from the center of the gel to the outside of the gel as indicated by yellow → bright orange → orange → red → white. At $T_e = 240$ min, the change in the magnitude of $^1$H spin density reaches a steady state.

The $^1$H spin-density images for PMAA gel (3 V) are represented in the left side of Figure 4. Before the application of an electric field ($T_e = 0$ min), the polymer gel has the same distribution of $^1$H spin density as PMAA gel (0 V). At $T_e = 20$ min, most of the $^1$H spin-density images on the gel become yellow like the case for PMAA gel (0 V). At $T_e = 120$ min the red region increases. The magnitude of $^1$H spin density changes in going from the negative electrode to the positive electrode as indicated by white → yellow → orange → red → white. At $T_e = 240$ min the red region becomes large. The $^1$H spin density changes in going from the negative electrode to the positive electrode as indicated by white → orange → red → white.

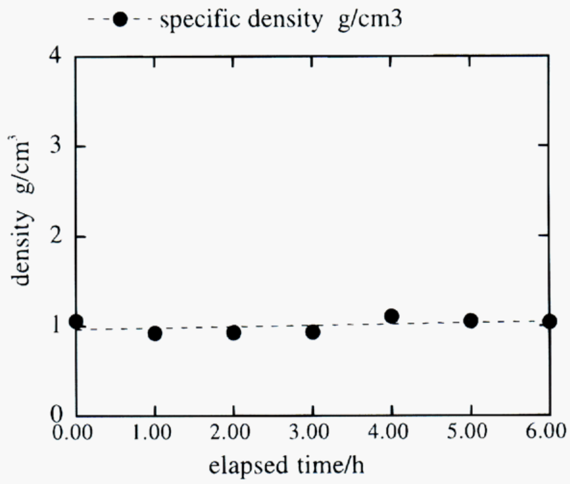

**Figure 5.** Elapsed-time dependence of the specific density of a PMAA gel.

The two kinds of above-mentioned $^1$H spin-density image experiments show as follows: the $^1$H spin-density distributions on PMAA gel (3 V) and PMAA gel (0 V) become uniform with elapsed time. At $T_e = 240$ min the color in the $^1$H spin-density image on PMAA gel (3 V) becomes more uniform compared with that on PMAA gel (0 V). This means that the uniformity of the $^1$H spin-density distribution on PMAA gel (3 V) is greater than that on PMAA gel (0 V).

In the $^1$H spin-density image experiments, the image is represented by colors on the basis of a comparison of the relative $^1$H spin density in a PMAA gel. The region with the highest $^1$H spin density in the gel is represented by white. For this reason, therefore, we cannot compare absolute $^1$H spin-density distributions between different images. Nevertheless, we have tried to compare absolute $^1$H spin-density distributions between different images by the following procedure. The specific density $\varrho$ (g/cm$^3$) is defined by the ratio of the mass of a swollen polymer gel ($M_{\text{swollen}}$) to that of the volume of a swollen polymer gel ($V_{\text{swollen}}$) as

$$\varrho = M_{\text{swollen}}/V_{\text{swollen}} \qquad (1)$$

$M_{\text{swollen}}$ is approximately equal to the mass of water ($M_{\text{water}}$) because the gel used at $q = 36$ contains water of 97 wt % and PMAA of 3 wt % as

$$M_{\text{swollen}} \cong M_{\text{water}} \qquad (2)$$

Thus, the specific density $\varrho$ is expressed by

$$\varrho \cong M_{\text{water}}/V_{\text{swollen}} \qquad (3)$$

Further, the average $^1$H spin density as observed by $^1$H NMR imaging is defined by $M_{\text{water}}/V_{\text{swollen}}$ and so is expressed as

$$\text{average } ^1\text{H spin density} = M_{\text{water}}/V_{\text{swollen}} \cong \varrho \qquad (4)$$

From the above-mentioned relation, the change of the density (g/cm$^3$) of a PMAA gel against the elapsed time after the application of an electric field corresponds to that of the average $^1$H spin density in a PMAA gel (Figure 5). Using these reference data the $^1$H spin-

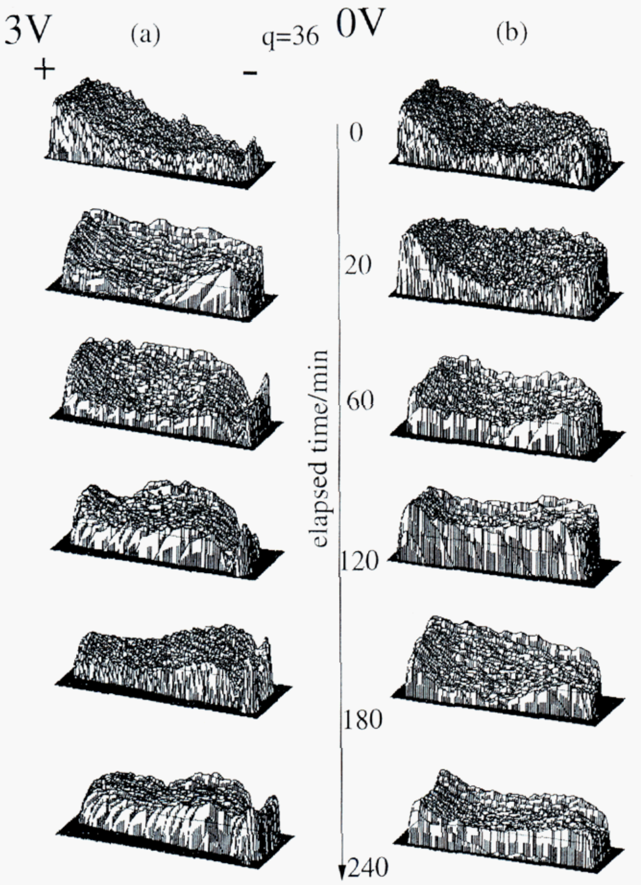

**Figure 6.** Three-dimensional histograms of elapsed-time dependence for the $^1$H spin-density distribution of a PMAA gel with (a) and without (b) the application of an electric field.

density distributions of a PMAA gel between different images can be quantified and compared with each other. As seen from this figure, the average $^1$H spin density of the gel does not change significantly with elapsed time after the application of an electric field.

In order to analyze clearly the $^1$H spin density in detail, the images for the $^1$H spin-density distributions of PMAA gel (3 V) and PMAA gel (0 V) as shown in Figure 6 were represented by a three-dimensional profile. Also, the two-dimensional profile of the $^1$H spin density of PMAA gel (3 V) was shown in Figure 7. The decrease of the $^1$H spin density means a decrease in the population of water molecules in any specified region. In the white region of the image the population of water molecules in the gel is higher than that in the other regions. These profiles show that the observed $^1$H spin-density distribution can be divided into four regions after the application of an electric field. Change of the $^1$H spin-density distribution pattern as a result of the application of an electric field was shown by the schematic diagram in Figure 8. In the schematic diagram, the first region at the left-hand side of the gel (the region around the positive electrode) has the highest $^1$H spin density, the second region occupies most of the gel region and has almost the same $^1$H spin density, the third region has the lowest $^1$H spin density, and the fourth region at the right-hand side of the gel (the region around the negative electrode) has the second highest density.

The above-mentioned results show that an electric stimulus leads to not only the uniformity of the $^1$H spin density distribution but also the unique distribution pattern of $^1$H spin density, and the average $^1$H spin density dose not change significantly at long elapsed time after the application of an electric field.

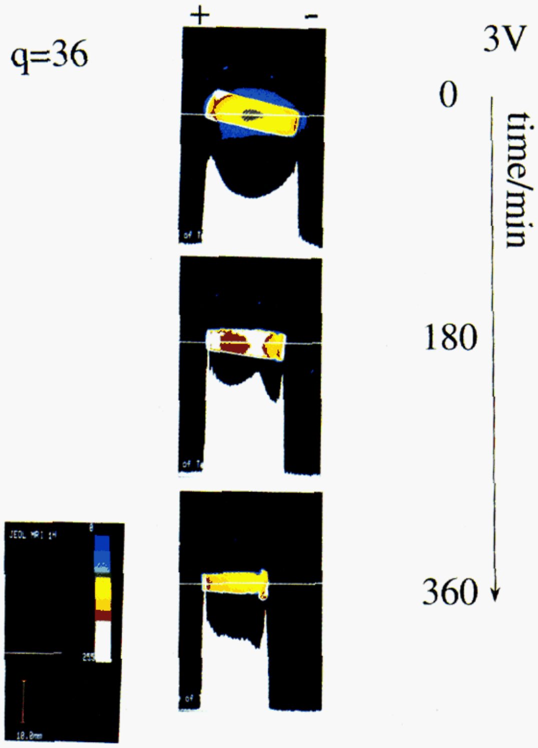

**Figure 7.** Two-dimensional histograms of time dependence for the $^1$H spin-density distribution of a PMAA gel with the application of an electric field.

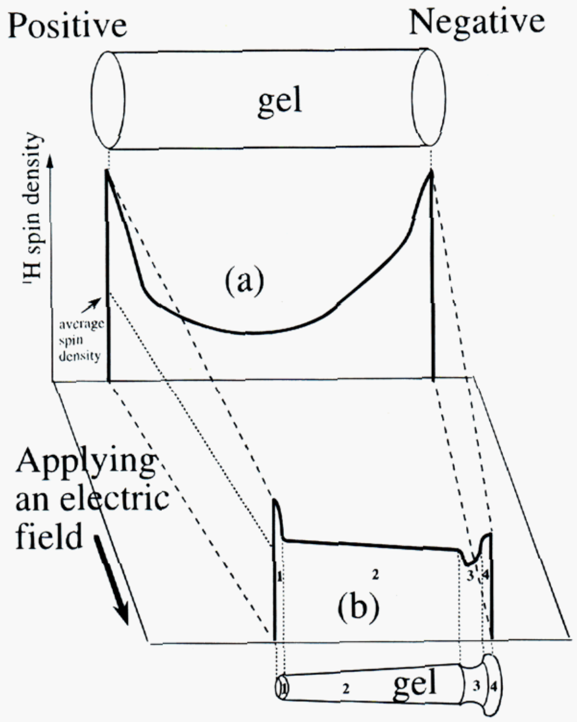

**Figure 8.** Schematic diagram for the $^1$H spin-density distribution in a PMAA gel before (a) and after (b) the application of an electric field.

**Spin–Spin Relaxation Time $T_2$ Image.** It is important to know information on the $^1$H $T_2$ value of water molecules in a PMAA gel, in order to analyze the dynamical behavior of water molecules in the gel under an electric stimulus.

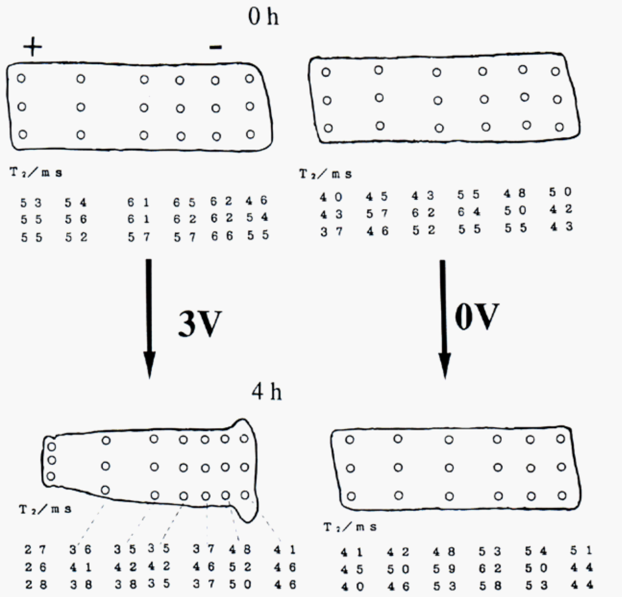

**Figure 9.** ${}^1$H $T_2$ distribution for a transverse slice of a PMAA gel at $T_e = 0$ min and at $T_e = 4$ h with and without the application of an electric field.

The ${}^1$H $T_2$ distributions for a PMAA gel with and without the application of an electric field were measured. The ${}^1$H $T_2$ image experiment on the gel without the application of an electric field becomes reference data to clarify the shrinkage process of the gel with the application of an electric field. Figure 9 shows the ${}^1$H $T_2$ distribution images on PMAA gel (3 V) and PMAA gel (0 V) at elapsed time $T_e = 0$ min and 4 h after the application of an electric field, where figures show $T_2$ values for the part indicated by an open circle in a PMAA gel. This figure shows two significant pieces of information on the shrinkage process. One is that little change of the ${}^1$H $T_2$ value of water molecules in PMAA gel (0 V) is observed during the image experiment but significant change of the ${}^1$H $T_2$ value of water molecules in PMAA gel (3 V) was observed during the image experiment. Another is that by the application of an electric stimulus the ${}^1$H $T_2$ values of water molecules around the positive electrode are decreased to a larger extent than those around the negative electrode. This means that the molecular motion of water molecules in the gel near the positive electrode is strongly restrained.

Further, in order to analyze the elapsed-time dependence of the ${}^1$H $T_2$ distribution change in a PMAA gel under the application of an electric field, the ${}^1$H $T_2$ distribution pattern of PMAA gel (3 V) was represented by colors on the basis of the ${}^1$H $T_2$ value as shown in Figure 10. In this figure ${}^1$H $T_2$ was differentiated by five steps and represented by colors from blue, representing ${}^1$H $T_2$ less than 25 ms, to red, representing ${}^1$H $T_2$ more than 40 ms. The color scale for ${}^1$H $T_2$ is indicated in this figure. This figure shows that the molecular motion of water molecules in the gel is restrained with elapsed time as seen from the observation of the decrease of the ${}^1$H $T_2$ value. In other words, the molecular motion of water molecules in the gel is more restrained with an increase of the degree of shrinkage of the gel by the application of an electric field. From these results the profile of the ${}^1$H $T_2$ distribution image can be divided into four regions in a manner similar to the ${}^1$H spin-density distribution image. For convenience, a rough schematic representation for the ${}^1$H $T_2$ distribution image is represented in Figure 11.

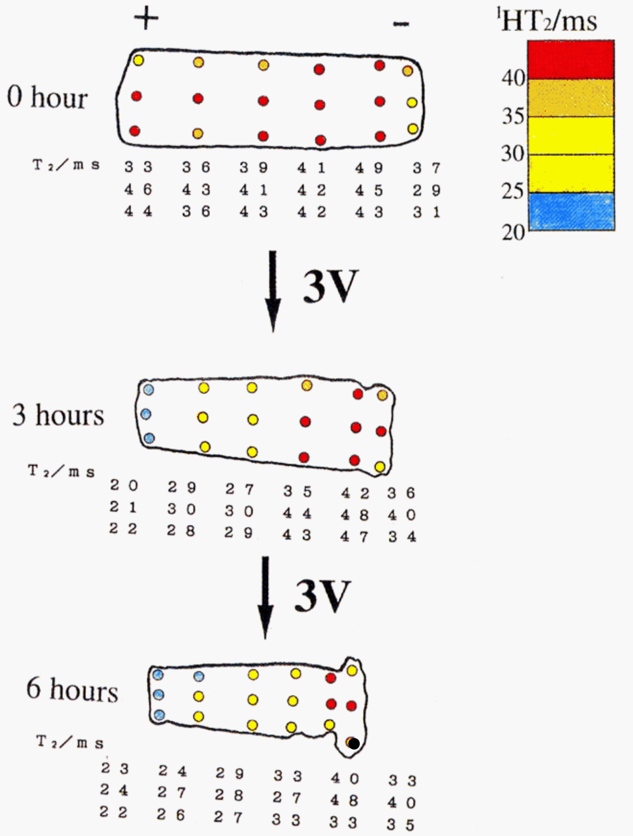

**Figure 10.** ${}^1$H $T_2$ distribution for a transverse slice of a PMAA gel at $T_e = 0$ min, at $T_e = 3$ h, and at $T_e = 6$ h with the application of an electric field.

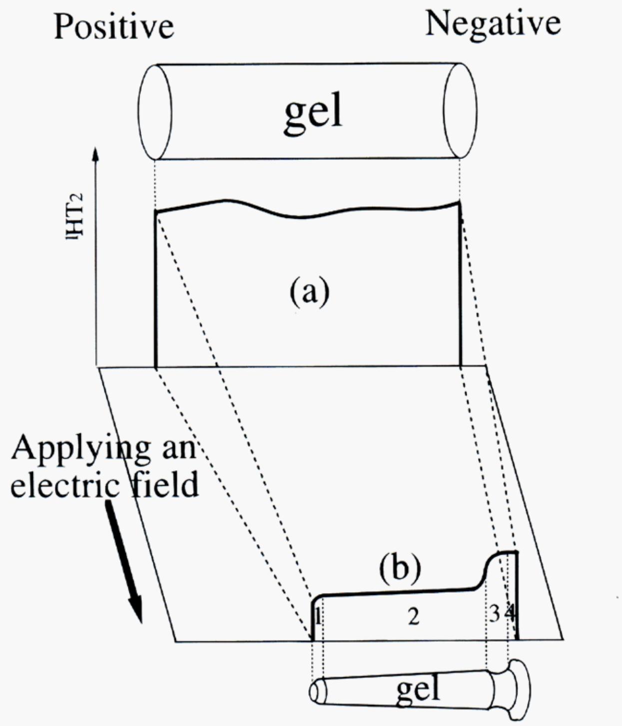

**Figure 11.** Schematic diagram for change of the ${}^1$H $T_2$ distribution image in a PMAA gel before (a) and after (b) the application of an electric field.

In order to compare the ${}^1$H $T_2$ weighted distribution image with the ${}^1$H spin-density distribution image, the three-dimensional histogram of elapsed-time dependence for the ${}^1$H $T_2$ weighted image and the ${}^1$H spin-density image is shown in Figure 12. From this figure it is clear that the region with large shrinkage in a

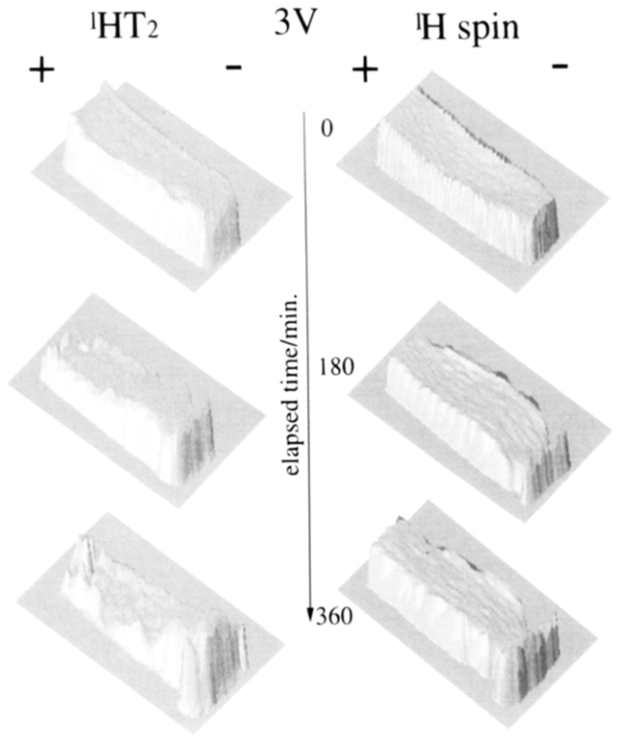

**Figure 12.** Three-dimensional histogram of elapsed-time dependence for the $^1$H $T_2$ weighted image and the $^1$H spin-density distribution image of a PMAA gel with the application of an electric field.

PMAA gel has water molecules with low mobility, but in the third region the mobility of water molecules is high although the fraction of the network is high.

Finally, we conclude as follows. The spatial distribution changes of the $^1$H spin density and $^1$H $T_2$ of water molecules in a PMAA gel under an electric stimulus were successfully observed by $^1$H NMR imaging. It was found, through the observation of spatial information on the behavior of water molecules in a PMAA gel by $^1$H NMR image, that the shrinkage process of a PMAA gel by the application of an electric field is related to the translational behavior of water molecules in the gel associated with a change of the size of the network. It was found that the $^1$H spin density and $^1$H $T_2$ image of the gel have the same distribution pattern which is divided into four regions with different $^1$H spin densities and $^1$H $T_2$. Further, it has been demonstrated that $^1$H NMR imaging is a useful means for obtaining spatial information on the shrinkage process of a polymer gel in response to the application of an electric field.

## References and Notes

(1) Tanaka, T. *Phys. Lett.* **1978,** *40,* 820.
(2) Tanaka, T. *Sci. Am.* **1981,** *244,* 110.
(3) Omine, I.; Tanaka, T. *J. Chem. Phys.* **1982,** *77,* 5725.
(4) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984,** *81,* 6379.
(5) Takizawa, A.; Kinoshita, T.; Nomura, O.; Tsujita, Y. *Polym. J.* **1985,***17,* 747.
(6) Fushimi, H.; Ando, I.; Ijima, T. *Polymer* **1991,** *32,* 241.
(7) Flory, P. J.; Rehner, J., Jr. *J. Chem. Phys.* **1943,** *11,* 521.
(8) Tanaka, T.; Nishino, I.; Sun, S.; Ueno-Nishio, *S. Science* **1982,** *218,* 467.
(9) Osada, Y.; Hasebe, M. *Chem. Lett.* **1985,** 1285.
(10) Yasunaga, H.; Kurosu, H.; Ando, I. *Macromolecules* **1992,** *25,* 6505.
(11) For example: (a) Weisenberger, L. A.; Koenig, J. L. *Macromolecules* **1990,** *23,* 2445. (b) Weisenberger, L. A.; Koenig, J. L. *Macromolecules* **1990,** *23,* 2454. (c) Grinsted, R. A.; Koenig, J. L. *Macromolecules* **1992,** *25,* 1229.
(12) Hahn, E. L. *Phys. Rev.* **1950,** *80,* 580.
(13) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948,** *73,* 679.

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