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Spatial Information on a Polymer Gel As Studied by ^{1}H NMR Imaging. 1. Image Analysis of Stress-Strain

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ABSTRACT: ^{1}H NMR imaging experiments were carried out to obtain spatial information on the propagation of the strain induced by stress in a cross-linked poly(methacrylic acid) (PMAA)/water gel. The ^{1}H spin density and spin-spin relaxation time enhanced NMR imaging patterns for water contained in a PMAA gel under stress were successfully observed. From these results it was found that the spatial distributions of the ^{1}H spin density and the molecular motion of water molecules in the gel are changed by altering the strength of stress and that the ^{1}H spin density and the molecular motion of water in the compressed region become lower and slower, respectively, compared with those in the surrounding uncompressed region.

Introduction

Cross-linked polymer gels have attracted considerable attention from the point of view of their physical and chemical properties. For example, hydropolyelectrolyte gels show a dramatic change in volume in response to change in solvent composition,[1] pH,[2] ionic strength,[3] and temperature.[4] They contract upon application of electric fields[5] and work as electrically-activated devices.[6,7] Water-swollen polymer gels can convert chemical energy into mechanical energy.[8] On the other hand, upon application of stress ionization of the carboxylic groups of poly(methacrylic acid) (PMAA) in water-swollen gels occurs.[7] This shows that stress induces a chemical change in the gel. Therefore, it is important to clarify the effect of stress on a polymer gel.

Water-swollen polymer gels consist of a polymer network and water as solvent. Water molecules play a significant role in the above-mentioned properties of polymer gels. Water molecules in polymer gels specifically interact with polymer chains. For this reason, to elucidate such interactions, many investigations have been done using DSC,[9] NMR,[10,11] etc. Furthermore, it is important to clarify the structure and dynamics of water molecules in polymer gels from a macroscopic point of view through microscopic information at the molecular level to understand the role of water molecules in gels.

Recently, the NMR imaging method[12,13] has been widely used for obtaining information on the spatial distribution of the spin density and the relaxation times in living systems containing a mobile component such as water.[14,15] However, without special techniques it is not easy to obtain such spatial information with high resolution for solid samples due to the large dipolar broadening. For this reason, NMR imaging has been applied to bulk polymer systems containing small molecules with high mobility to obtain information about their diffusion and relaxation times,[16] except for a few works on solid polymer materials.[17] Through these investigations the NMR imaging technique has been demonstrated to be a powerful means to characterize the spatial distribution of the spin density and the molecular motion of the mobile component in polymer systems, for which dipolar broadening is negligible.

The purpose of the present work is to measure the ^{1}H NMR imaging patterns of the spatial distribution of the ^{1}H spin density and the ^{1}H spin-spin relaxation time (T_2) of water molecules in cross-linked PMAA gel by varying stress, to clarify the propagation of strain in the gel induced by stress through the obtained results on the spatial distribution of the ^{1}H spin density and the molecular motion, and to demonstrate the potential applicability of the NMR imaging technique to polymer gel systems.

Experimental Section

Materials. Methacrylic acid (MAA) (Tokyo Kasei Kogyo) was distilled at 299 K under a pressure of 267 Pa. *N,N'*-Methylenebisacrylamide (MBAA) (Wako Pure Chemical Industries), used as the cross-linking monomer, was recrystallized from ethanol solution twice. $K_2S_2O_8$, used as the polymerization initiator, was recrystallized from aqueous solution.

PMAA gel was prepared by radical polymerization of MAA (3.0 mol L^{-1}) and MBAA (9.4×10^{-3} mol L^{-1}) in aqueous solution at 333 K. The PMAA gel obtained was soaked in excess deionized water for 2 weeks to remove the remaining monomer, linear polymers formed as byproduct, and initiator. The water was repeatedly exchanged. 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}): $q = M_{\mathrm{swollen}}/M_{\mathrm{dry}}$.

Measurements. ^{1}H NMR imaging measurements were carried out by means of a JEOL GSX-270 NMR spectrometer operating at 270.1 MHz with a JEOL NM-GIM 270 imaging system at 300 K.

The imaging pulse sequence used is based on the spin-echo pulse sequence[18] of Hahn.[19] The data processing for a two-dimensional image was performed by the Fourier imaging method.[20] The pulse sequence is shown in Figure 1. The slice selection gradient (G_z) and selective rf pulse determine the position of the region to be observed. The phase-encoding gradient (G_y), which is varied in intensity systematically, serves to obtain the differentiation of the volume elements in the y-direction.[21] The phase-encoding period is fixed to be constant. The readout gradient (G_x) is applied in the x-direction, and during the phase-encoding period the reversed gradient ($-G_z$) is also applied to refocus the selectively-excited magnetization. During the acquisition period the readout gradient (G_x) is applied to disperse the volume elements in the x-direction.

In the ^{1}H NMR imaging experiments, the gradient strengths used for the slice selection, phase-encoding and read-out are 19, 20, and 20 mT m^{-1}, respectively, and the slice thickness is 2.0 mm. The $\pi/2$ and π rf pulse lengths are 1.5 μs, but the strength of a $\pi/2$ pulse is half that of a π pulse. The echo time is 36 ms, the phase-encoding time is 4 ms, and the repetition time is 2-15 s. The number of data points is 256. The number of accumulations is 4 to obtain ^{1}H NMR image signals with a reasonable signal-to-noise ratio.

The spin-echo method based on Hahn's pulse sequence is also used to obtain ^{1}H T_2 enhanced images. In this case the echo time is longer than that used for the spin density measurement.

A cylindrical PMAA gel sample with a diameter of 15.0 mm and a height of 5.3 mm at $q = 22$ was placed in a cylindrical sealed

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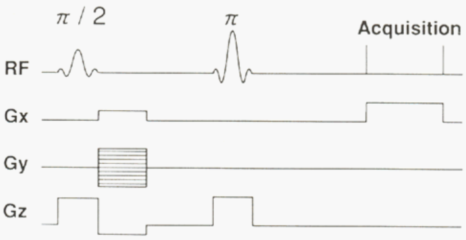


Figure 1. Diagram for the spin–echo ^{1}H imaging pulse sequence used in this work.

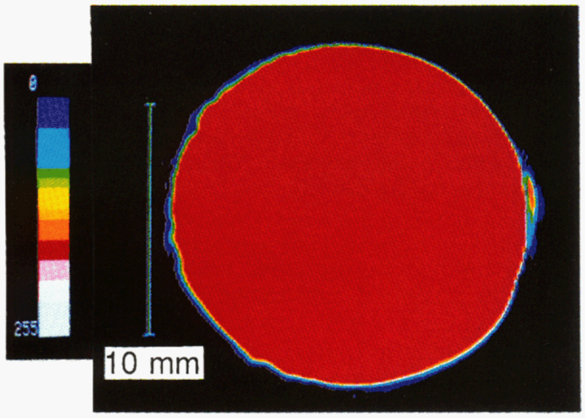


Figure 2. Observed transverse ^{1}H spin density image of PMAA gel at a degree of swelling of 22 without stress at a depth of 1.9 mm from the top surface. The magnitude of ^{1}H spin density is differentiated by 256 steps. The signal variation in the image of uncompressed PMMA gel is 10 steps.

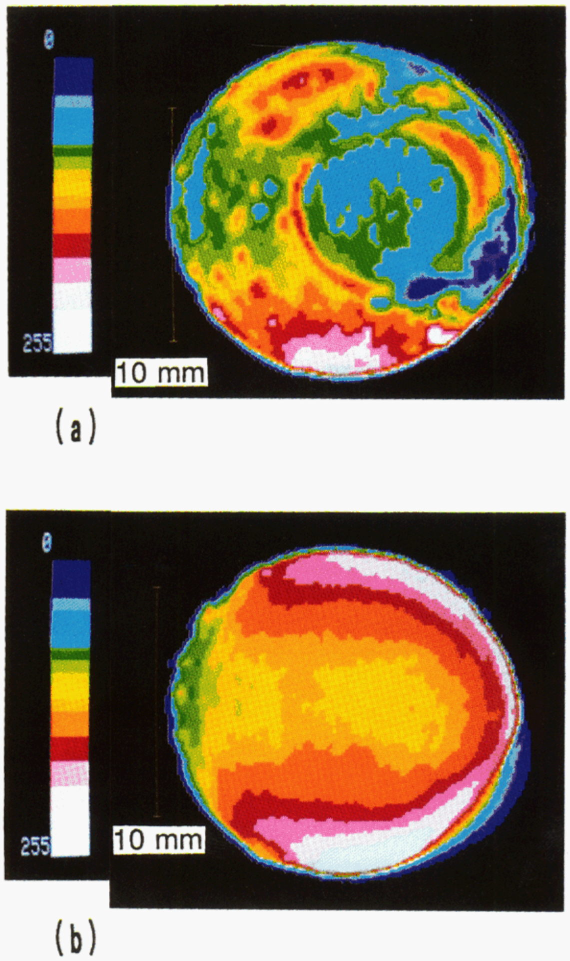


Figure 3. Observed transverse ^{1}H spin density image of PMAA gel at a degree of swelling of 22 under a stress of 4.8 kPa at depth of 1.0 (a) and 1.9 mm (b) from the top surface.

glass cell with an inside diameter of 22.0 mm and a height of 25.0 mm. The stress on the gel sample was applied by a glass piston. The top of the piston is circular and the diameter is 7.7 mm. The strength of the stress is controlled by a weight on the piston. The distance between the center of the circular surface of the PMMA gel with diameter of 15 mm and the center of the circular piston with diameter of 7.7 mm was 1.8 mm.

The obtained images were treated with an LA 525 personal image analysis system (PIAS Co. Ltd.) and a PC-9801 personal computer (NEC Co. Ltd.) to obtain profiles of the NMR image.

The ^{1}H T_2 of water in the PMAA gel was measured with a JEOL GSX-500 NMR spectrometer operating at 500.1 MHz at 300 K, using the CPMG method. A PMAA gel sample with a diameter of 4.0 mm at $q = 89$ was inserted in a glass NMR sample tube with an inner diameter of 5.0 mm.

Results and Discussion

^{1}H Spin Density Imaging. A ^{1}H spin density NMR imaging experiment of a PMMA gel swollen by D$_2$O ($q = 22$) was carried out, but no image was obtained. Therefore, it can be said that, through all the present experiments, no ^{1}H signals of the polymer network of the PMAA gel at $q = 22$ could be detected by the imaging experiments due to its great dipolar broadening, but ^{1}H signals of water contained in the gel could be successfully observed due to its fast molecular motion. Figure 2 shows the observed transverse ^{1}H spin density image of water in the PMAA gel at $q = 22$ with no stress, where the direction of the cross-sectional profile is perpendicular to the direction along a used glass cell. The ^{1}H spin density distribution of the obtained image is approximately homogeneous. This shows that the water molecules are homogeneously distributed in the gel and are undergoing fast molecular motion.

The transverse ^{1}H spin density images of water in the PMAA gel at $q = 22$ under a stress of 4.8 kPa are shown in Figures 3a and 3b, where the latter is the image sliced away from the top surface of the gel compared with the former. The magnitude of ^{1}H spin density is differentiated by 256 steps, and then the observed ^{1}H spin density image is represented by colors from white, representing the highest density, to dark blue, representing the lowest density. The intensity scale indicated by colors is shown in Figure 3. The blue circular portion in Figure 3a shows the compressed region to which stress is applied. As seen from Figure 3b, there are white regions at the top and the bottom of the image, and colored half-circular stripes appear toward the compressed region as white → light pink → pink → red → orange → bright orange → yellow. The yellow region appears in the compressed region. The blue region appears at the periphery of the gel. Further, it is seen that the ^{1}H spin density pattern as shown in Figure 3b is asymmetric, and the ^{1}H spin density of water in the right part of the image (the white region) is higher than that in the left part (the yellow and green regions). The fact that the stress is applied away from the center of the gel induces such an asymmetric pattern.

The detailed ^{1}H spin density profiles of the image with a longitudinal section and a cross section are shown in Figure 4. As seen from these profiles, the ^{1}H spin density of water in the compressed region is lower than that of the uncompressed region, and the ^{1}H spin density gradient which is induced by stress occurs in the gel. The ^{1}H spin density becomes higher toward the outside of the gel and becomes lower in the vicinity of the surface of the gel. The decrease of ^{1}H spin density indicates a decrease in the population of water molecules in any specified region. In other words, the fraction of network polymer in any specified region is increased. In the white region the

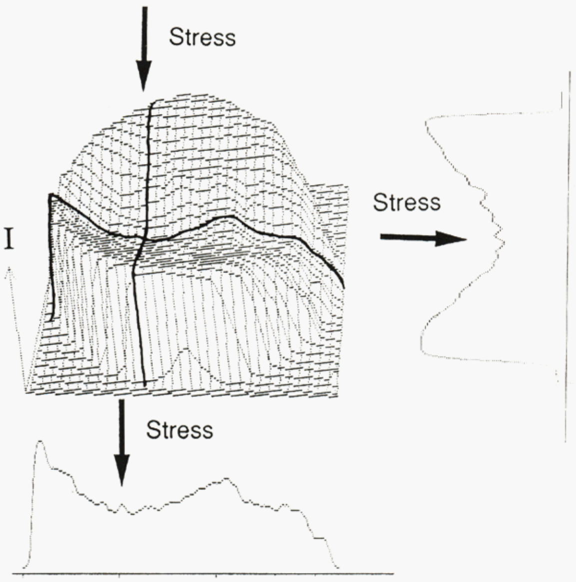


Figure 4. Intensity profile of the transverse ^{1}H image of PMAA gel at a degree of swelling of 22 at a depth of 1.9 mm from the top surface under a stress of 4.8 kPa.

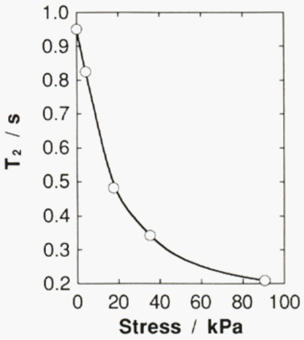
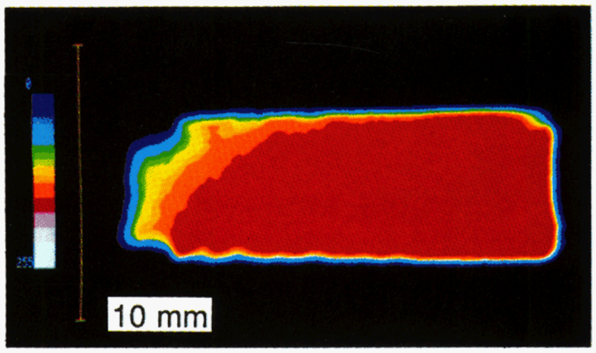


Figure 5. Dependence of ^{1}H T_2 for water in PMAA gel at a degree of swelling of 89 on the applied stress at a resonance frequency of 500.1 MHz.

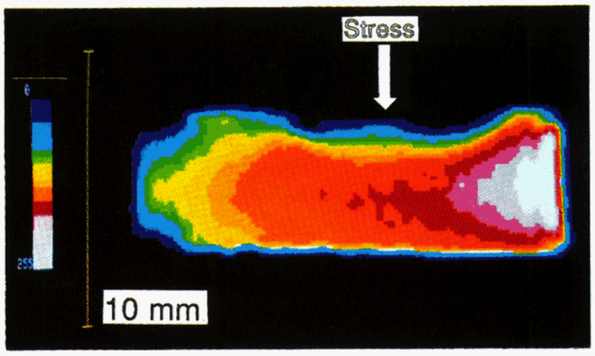
population of water and the fraction of network polymer are higher and lower, respectively, than those in the other regions. This shows that by deformation of the PMAA gel sample due to stress, the uncompressed part of the top surface of the gel rises slightly, and water molecules excluded from the compressed region migrate to the surrounding region.

^{1}H T_2 Enhanced Imaging. Before studying the ^{1}H T_2 enhanced image of the PMAA gel, it may be significant to know information about the ^{1}H T_2 of water in the gel to know the dynamical behavior of water in the gel under homogeneous stress. The ^{1}H T_2 value of water in the PMAA gel (q = 89) compressed homogeneously was measured by means of 500-MHz ^{1}H pulse NMR. The obtained ^{1}H T_2 values are plotted against the strength of the applied stress in Figure 5. It is shown that the T_2 value decreases with increasing stress, and the T_2 value under a stress of 17.6 kPa is half the value under no stress. This shows that the molecular motion of water in the PMAA gel is restrained by the strain induced by stress. Therefore, it is expected that the ^{1}H T_2 enhanced imaging of water in the gel provides useful information on the spatial distribution change for the molecular motion of water by the application of stress.

Figure 6 shows coronal ^{1}H T_2 enhanced images of water in the PMAA gel at q = 22, where the word "coronal" means that the cross-sectional profile is parallel to the direction of the applied stress. In this image, the relative magnitude of the ^{1}H T_2 value of the water is represented by colors. White shows the longest T_2 value and dark blue the shortest T_2 value. The color scale is also shown in Figure 6. In the gel with no stress the ^{1}H T_2 distribution is homogeneous, but in the gel with a stress of 4.8 kPa a gradient pattern in the T_2 distribution is obtained, where the stress is applied away from the center of the gel. The ^{1}H T_2 value of the top surface is short as indicated by dark blue or blue. The color in the compressed region changes from the top of the gel toward the bottom. This indicates that the ^{1}H T_2 value of water in the compressed region increases from the top surface of the gel toward the inner part and decreases from the inner part toward the bottom. The ^{1}H T_2 value increases from the left end of the gel to the right end as indicated by dark blue → blue → green → light green → yellowish green → yellow → bright orange → orange → red → pink → light pink → white. As seen from the above results, the propagation of the strain in the gel which was induced by stress can be observed as the ^{1}H T_2 distribution. In the compressed region, the experimental finding that the ^{1}H T_2 value is not constant from the top of the gel toward the bottom comes from the inhomogeneous strain distribution of the network of the gel. The ^{1}H T_2 value in the right part of the image is longer than that of the left part as shown in Figure 6. As mentioned above, the fact that the stress is applied away from the center of the gel induces such an asymmetric ^{1}H T_2 pattern.



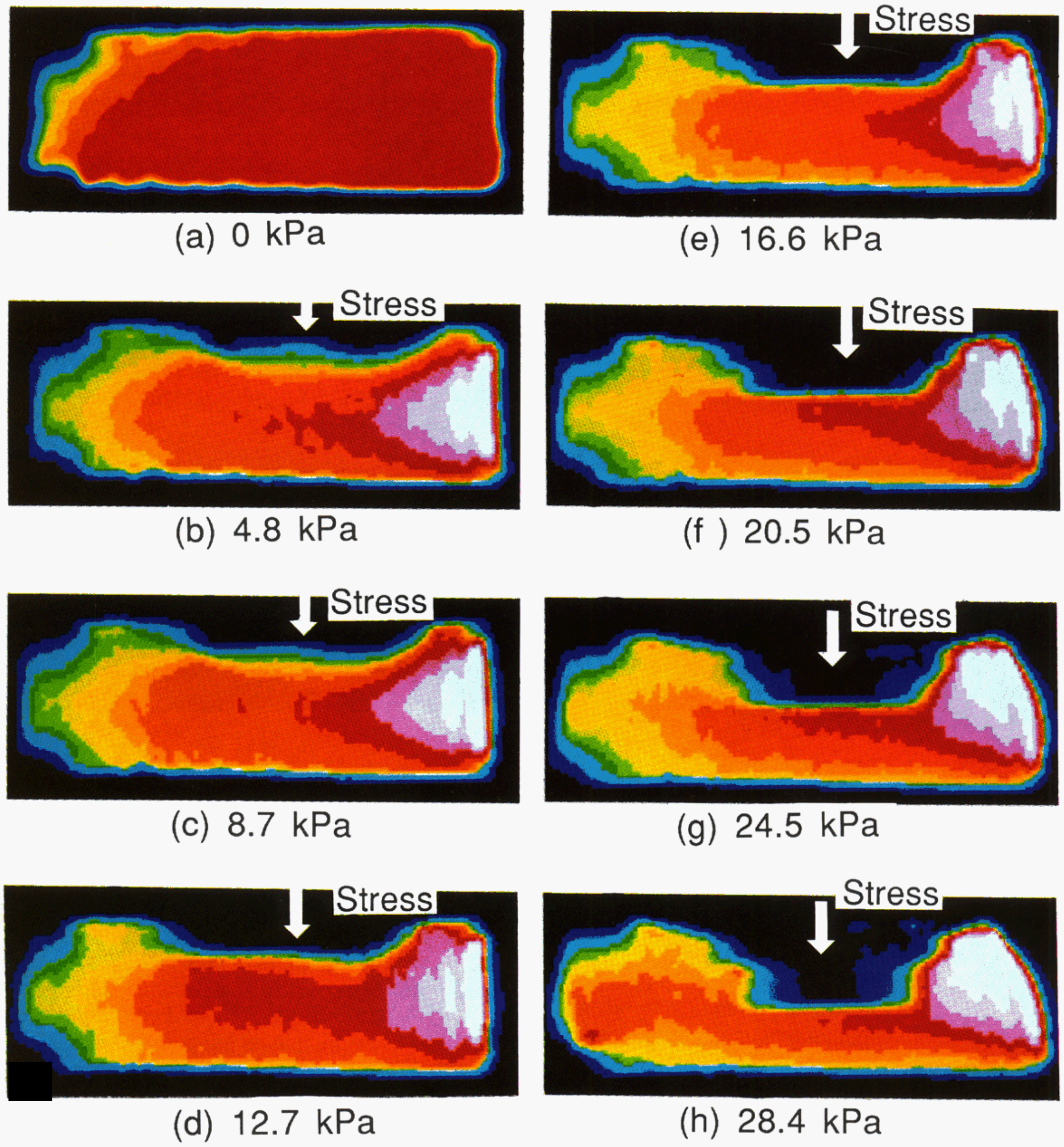
(a) 0 kPa



(b) 4.8 kPa

Figure 6. Observed coronal ^{1}H T_2 enhanced image of PMAA gel at a degree of swelling of 22 under no stress (a) and under a stress of 4.8 kPa (b).

The ^{1}H T_2 enhanced images of the gel as a function of stress are shown in Figure 7. As seen from this figure, the gradient pattern of spatial distribution on ^{1}H T_2 changes with increasing stress. The red and orange regions in the compressed region become narrow with increasing stress, and the bright orange and yellow regions become wide. The white region becomes wide with an increase of the stress from 12.7 to 28.4 kPa. As seen from these results,



(a) 0 kPa

(b) 4.8 kPa

(c) 8.7 kPa

(d) 12.7 kPa

(e) 16.6 kPa

(f) 20.5 kPa

(g) 24.5 kPa

(h) 28.4 kPa

Figure 7. Observed coronal ^1H T_2 enhanced images of PMAA gel at a degree of swelling of 22 as a function of stress.

the molecular motion of water molecules in the compressed region is more strongly restrained with an increase of stress. Further, in the uncompressed region (the right and left parts of the gel) the population of water molecules which are undergoing relatively fast molecular motion increases with increasing stress. This shows that the migration of water in the gel is increased with an increase of stress, and the difference in molecular motion of water in between the compressed and the uncompressed regions becomes large. The central cross-sectional ^1H T_2 profiles of the images along a glass cell are shown in Figure 8. The slope of the right wall for the T_2 gradient pattern of the gel to which the stress is applied becomes steep with increasing stress. while the slope of the left wall does not change so considerably. This shows that the molecular motion of water molecules in the region near the top surface is strongly restrained with an increase of stress. The spatial distribution of molecular motion of water molecules is not homogeneous from the top surface of the gel toward the bottom in the compressed region. This shows that the deformation of network by the stress is not homogeneous in the compressed region.

Finally, we conclude as follows. The spatial distributions of the ^1H spin density and the ^1H T_2 of water contained in the PMAA gel were successfully observed by ^1H NMR imaging. It was found that the water molecules are excluded from the compressed region to which stress was applied and migrate to surrounding region through the polymer network in the gel. The molecular motion of water molecules contained in the gel is restrained by stress, and the spatial distribution of the molecular motion changes

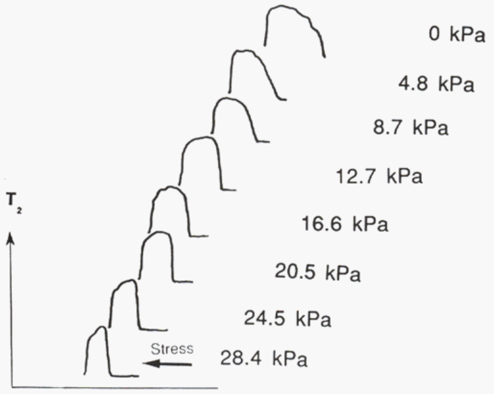


Figure 8. Intensity profiles from the ^1H T_2 enhanced image of PMAA gel as a function of stress.

with the strength of stress. It has been demonstrated that ^{1}H NMR imaging is useful for obtaining spatial information on the strain propagated in a polymer gel under stress.

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