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Proton Magnetic Relaxation Time T_1 of Water in Acrylamide Gel

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Synopsis. Proton magnetic relaxation time T_1 of water in polyacrylamide gel was measured. The results have been interpreted in terms of the contribution from dissolved oxygen and the intrinsic nature of gel. A minimum of $1/T_1$ appears in a system with a *ca.* 2.8% concentration of acrylamide, corresponding to the lowest concentration for gel formation.

The proton spin lattice relaxation time, T_1, of water which is held in a polyacrylamide gel was measured in order to compare the motion of water molecules in the gel with that of bulk water. The gel was prepared by the copolymerization of acrylamide and *N,N'*-methylenebisacrylamide in heavy water, the mole ratio of acrylamide and *N,N'*-methylenebisacrylamide being approximately 80 to 1. The T_1 values of water were measured by the adiabatic rapid passage method using a JNM-C-60H high resolution NMR spectrometer at 60 MHz.

Samples were used under four different conditions: 1) undegassed, 2) degassed at about 10^{-5} mmHg, 3) degassed and polymerized by addition of a small amount of ammonium persulfate to accelerate polymerization, and 4) polymerized without degassing. For samples 3) and 4), no appreciable difference was observed between the values of $1/T_1$ before and immediately after the addition of ammonium persulfate. T_1 measurements were carried out in each case after sufficient elapse of time. The dissolved oxygen in each sample was thus sufficiently in equilibrium with the air pressure contacted (degassed and undegassed conditions).

Plots of $1/T_1$ against the concentration of acrylamide are shown in Figs. 1, 2, and 3. Linearity holds between the acrylamide content and $1/T_1$ of water in acrylamide solutions under atomospheric pressure (Fig. 1). We see that the $1/T_1$ values are considerably shortened by degassing. The paramagnetic effect of dissolved oxygen plays an important role in determining the relaxation.[1,2]

Polymerization causes a remarkable change in the $1/T_1$ values (Fig. 2). The $1/T_1$ values are reduced in a drastic way by polymerization of the solutions at lower concentrations of acrylamide, $1/T_1$ becoming minimum and then increasing.

In marked contrast, no such minimum can be observed in the case of degassed polymer samples (Fig. 3 A). The values of $1/T_1$ observed when the degassed samples are polymerized deviate from a straight line before polymerization (Fig. 3 B). At lower concentrations,

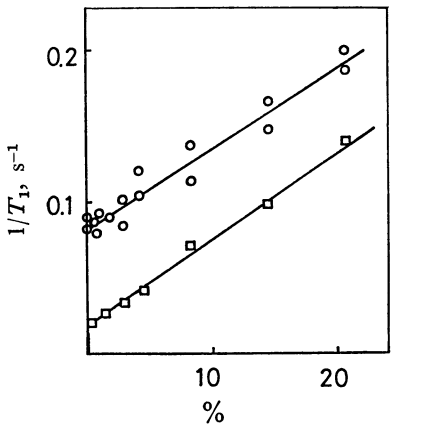

Fig. 1. Plots of $1/T_1$'s of water in acrylamide aqueous solutions *vs.* acrylamide content. —○—: Undegassed samples, —□—: degassed samples.

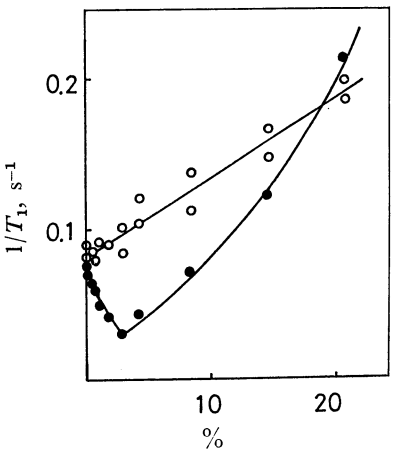

Fig. 2. Plots of $1/T_1$'s of water *vs.* acrylamide content. —○—: Undegassed samples, —●—: Undegassed polymer samples.

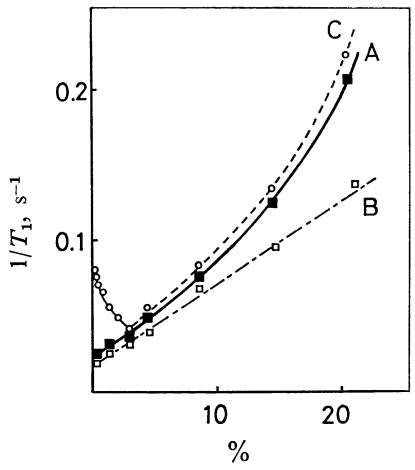

Fig. 3. Plots of $1/T_1$'s of *vs.* water acrylamide content. A —■—: Degassed polymer samples, B —□—: degassed samples, C —○—: undegassed polymer samples.

the line of $1/T_1$ for the polymerized samples (Fig. 3A) nearly coincides with that of samples before polymerization (Fig. 3B), whereas at higher concentrations, the $1/T_1$ values for the polymerized samples (Fig. 3A) increase drastically and are in accord with that for the undegassed polymer samples (Fig. 3C). The fact that very little difference can be observed in the $1/T_1$ values between both polymer samples produced from the degassed and undegassed solutions might indicate that both polymerized samples are essentially the same as regards relaxation of water.

The proton relaxation of water in the polyacrylamide gel is written as

$$(1/T_1)_{obsd} = (1/T_1)_{O_2} + (1/T_1)_{gel},$$

where $(1/T_1)_{obsd}$ is the observed value, $(1/T_1)_{O_2}$ the contribution from the oxygen molecule and $(1/T_1)_{gel}$ the term arising from the intrinsic nature of the gel. It may be concluded that in the sol phase at concentrations lower than 2.8%, the term $(1/T_1)_{O_2}$ dominantly determines T_1, with a negligible contribution from $(1/T_1)_{gel}$. The decrease of $1/T_1$ value with increase in the concentration of acrylamide in this range may be interpreted by the fact that the solubility of oxygen in the polymer solution is reduced with the increase in the concentration of acrylamide.

The above interpretation was deduced from the T_1 data and is not the final conclusion. In the gel phase, $(1/T_1)_{gel}$ becomes dominant, suggesting that the relaxation time T_1 of the water proton in a confined space of the polyacrylamide gel is considerably shortened in comparison with that in bulk water. Two types of water, "bound" and "free" have been assumed to exist in explaining a similar relaxation behavior in biological systems.[3-7] The presence of a small proportion of water having an increased relaxation rate in the bound state can produce a marked reduction in the observed relaxation times.[8-11]

It can be concluded that the minimum point of $1/T_1$ corresponds to the critical concentration at which the gel can be formed.

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