

Ultrasonic Velocity and Absorption Measurements in an Aqueous Solution of Poly(sodium 4-styrenesulfonate)

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Abstract: Both the ultrasonic velocity at 3 MHz and the absorption coefficient in the frequency range from 0.2 to 2 MHz were measured for aqueous solutions of poly(sodium 4-styrenesulfonate) over the concentration range from 5 to 25% (by weight). The pulse echo overlap method was employed to measure the ultrasonic velocity over the temperature range from 10 to 90 °C; the high-Q ultrasonic resonator method was used for the measurement of the absorption coefficient at 20 °C. The velocities exhibited their maximum values at ca. 55, 59, 63, 67, and 71 °C for the 25, 20, 15, 10, and 5% solutions, respectively. The velocity increased with respect to the poly(sodium 4-styrenesulfonate) concentration at a given temperature. A study of the concentration dependence of the both the relaxation frequency and amplitude indicated that the relaxation at ca. 200 kHz is related to structural fluctuations of the polymer molecules, such as the segmental motions of the polymer chains and that the relaxation at ca. 1 MHz resulted from the proton transfer reactions of the oxygen sites of SO₃. Both the absorption and the shear viscosity increase upon increasing the polymer concentration, but they decrease upon increasing the temperature.

Keywords: poly(sodium 4-styrenesulfonate), ultrasonic velocity, absorption, relaxation frequency, relaxation amplitude.

Introduction

Ultrasonic absorption and velocity measurements yield useful information on the behavior of the polymer solutions. A polymer such as poly(sodium 4-styrenesulfonate) may be used as a flocculant to purify water and thus be of practical value. The ultrasonic measurements presented here should be helpful in gaining an understanding of this polymer-water solution. The ultrasonic data reported here should also be a helpful addition to light scattering and other measurements of this polymer solution.¹⁻³ Ultrasound has also been used to study the growth of flocculant particles in polymer solutions. It is hoped that this work may eventually lead to a better understanding of the chemistry of polymer aqueous solution.

In this paper, ultrasonic velocity measurements are made at 3 MHz using the pulse echo overlap method over the temperature range of 10-90 °C and absorption measurements over the frequency range of 0.2-2 MHz using the high-Q ultrasonic resonator method in poly(sodium 4-styrenesulfonate) aqueous solutions, as a function of concentration. In previous years, ultrasonic velocity has been studied in poly(sodium 4-styrenesulfonate)⁴ and other related polymer solutions.⁵ R. Esquivel-Sirvnt, S. S. Yun, and F. B. Stumpf

measured velocity at various concentrations and temperatures (25-45 °C) in the solutions of poly(sodium 4-styrenesulfonate) and water. They suggested that the increase in velocity with concentration was related to the formation of a more rigid structure within the solution due to the presence of a solute. However, they did not explain the phenomenon of velocity increase with temperature. In addition, they did not observe velocity maxima in the solutions, as their measurements were performed at temperatures below 45 °C. Moreover, because they only measured absorption coefficients at 21 MHz, ultrasonic relaxation could not be observed. The measurements in the solutions presented here can be a valuable addition to those studies.

Experimental

The chemical formula for poly(sodium 4-styrenesulfonate) is $[-\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})-]_n$ and its molecular weight is 70,000 g/mol. The monomer has a molecular weight of 206 g/mol. It is known that water can form hydrogen bonds at the oxygen sites of SO₃. The polymer, which is in the form of a fine yellowish-white powder, dissolves in water. The poly(sodium 4-styrenesulfonate) used was obtained from Aldrich Chemical Company and was in the form of fine white powder. The powder had an average molecular weight of 70,000. Concentrations of 5, 10, 15, 20 and 25% by weight

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were carefully prepared. After the polymer was dissolved in pure water, it was stirred for at least 24 h. The weights of water and polymer were carefully determined using a high-sensitivity analytical balance. All concentration values were expressed in percent by weight. The method used in the measurement of ultrasonic velocity at 3 MHz was the pulse echo-overlap method over the temperature range of 10-90°C. The method used in the measurement is shown in Figure 1. This system was, however, partially modified in our laboratory in order to study the velocity. Two transducers of X-cut quartz with a fundamental frequency of 3 MHz is excited by sharp dc voltage with rise time shorter than 10 ns. The rf amplifier can be tuned to 3 MHz and pulse at the fundamental frequency observed. Only the first arriving pulse and the second echo are visualized on CRT. The repetition rate of a CW oscillator is adjusted so that the two pulses are overlapped and matched cycle for cycle. The period of the oscillator which is measured by a counter gives a round-trip time of the pulse, and yields the phase velocity with known path length. The sensitivities of velocity measurements were 0.01%, respectively. This system is very convenient for simultaneous measurements of velocity, and is suitable for the present experiment which are conducted at different temperatures.

The high-Q ultrasonic resonator method was employed for absorption coefficients in 0.2-2 MHz. A block diagram of the resonator method is shown in Figure 2. A resonance cell, which was composed of a quartz transducer and a slightly concave reflector, was filled with a liquid sample, and standing sound waves were established in it. The amplitude of the standing waves is monitored, sweeping the sound frequency, by using Raman-Nath light diffraction and optical heterodyne detection. The bandwidth of the resonance curve provides a measure of acoustic dissipation caused by

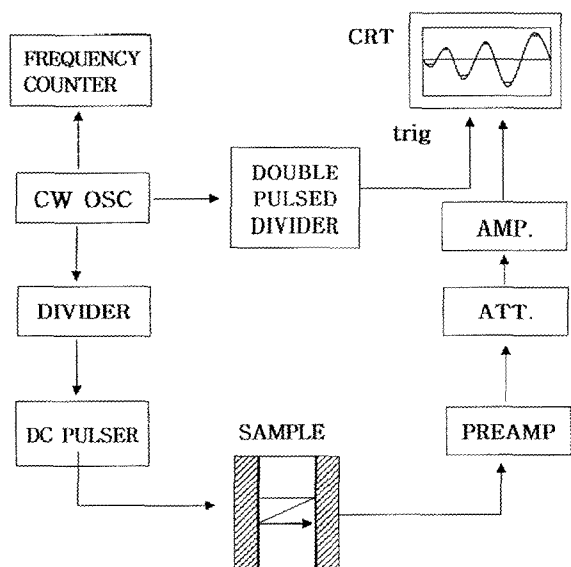


Figure 1. The block diagram of the pulse-echo-overlap method.

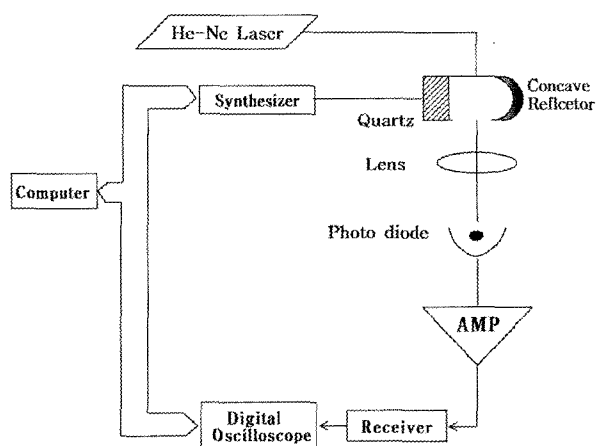


Figure 2. Block diagram of high-Q ultrasonic resonator method.

intrinsic absorption in the sample liquid and instrumental cavity loss. Relative measurement with a standard liquid with known absorption allow us to determine the absorption in the sample. The use of the concave reflector with a curvature radius of 200 mm reduces the instrumental loss and improves the Q factor of the resonator by two orders of magnitude at 300 kHz compared with a conventional resonator of the same diameter.

Water was used as the standard liquid because its acoustic impedance is close to that of poly(sodium 4-styrenesulfonate) solutions. The viscosity using a Brookfield rotating-cylinder viscometer and absorption measurements about 1 MHz using high-Q ultrasonic resonator method over the temperature range of 10-90°C were measured in poly(sodium 4-styrenesulfonate) aqueous solutions. The temperature of the poly(sodium 4-styrenesulfonate) solutions was controlled within 0.2°C.

Results and Discussion

Ultrasonic Absorption and Viscosity Measurements.

The results of the absorption coefficient of ultrasonic wave measurements at 1 MHz are shown in Figures 3 and 4, as a function of temperature and concentration in percent by weight. Figure 3 contains all the data points, whereas Figure 4 has some omitted data points to avoid confusion. It is seen in Figure 3 that α/f^2 decreases monotonically with increasing temperature at a given concentration. The magnitude of the slope of α/f^2 versus temperature tends to decrease more at higher temperatures. In Figure 4, it is seen that α/f^2 for all the temperatures increase exponentially with concentration.

An important factor to be considered for polymer solutions is shear viscosity. Figure 5 illustrates that the measured shear viscosity decreases with temperature for all concentrations. The largest value of the shear viscosity shown at 10°C for the 25% solution is nearly 27 times larger than the value for pure water. The value of α/f^2 for the solution is greater by a

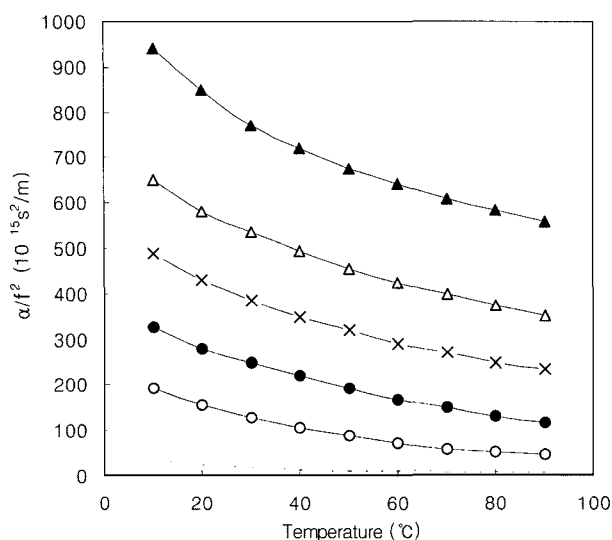


Figure 3. α/f^2 vs. temperature for poly(sodium 4-styrenesulfonate) aqueous solutions. The symbols \circ , \bullet , \times , \triangle , \blacktriangle and \cdots represent the concentration of 5, 10, 15, 20, 25% by weight and pure water, respectively.

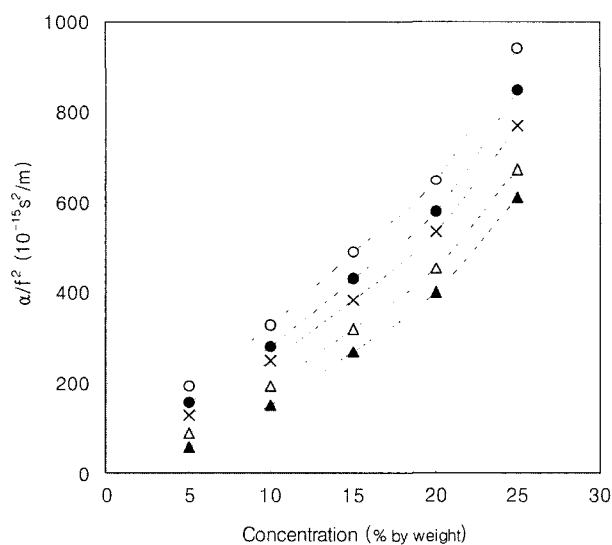


Figure 4. α/f^2 vs. concentration for poly(sodium 4-styrenesulfonate) aqueous solutions. The symbols \circ , \bullet , \times , \triangle and \blacktriangle represent temperature of 10.0, 20.0, 30.0, 50.0 and 70.0°C, respectively.

factor of 25 than that of pure water as shown in Figure 3.

The plot of α/f^2 versus temperature at a given concentration demonstrates the same general trend as viscosity versus temperature. Furthermore, the measurements of α/f^2 versus temperature show that the difference in values for the 25% solution and water at 10°C is 1.6 times the difference at 90°C. This may be related to the fact that the viscosity shows a stronger temperature dependence for the higher concentrations as seen in Figure 5. The reason for any

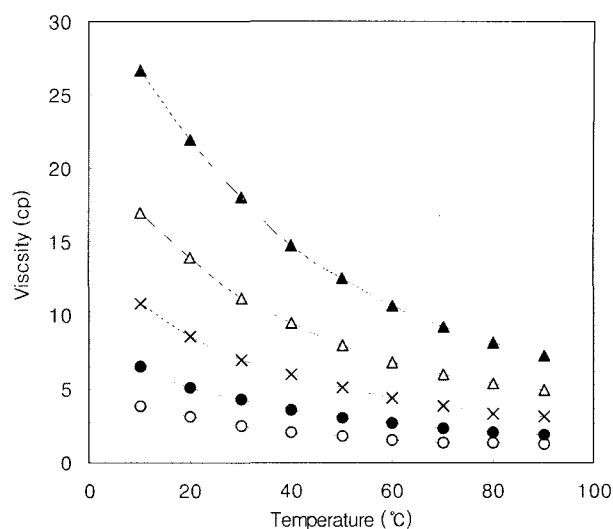


Figure 5. Shear viscosity vs. temperature for poly(sodium 4-styrenesulfonate) aqueous solutions. The symbols \circ , \bullet , \times , \triangle and \blacktriangle represent the concentration of 5, 10, 15, 20 and 25% by weight, respectively.

increase in viscosity upon adding the polymer to water may be due to the interaction of polymer molecules with water molecules. Specifically this might involve the association of water molecules with the oxygen site of SO_3 of the poly(sodium 4-styrenesulfonate). Therefore, these measurements suggest the formation of a more rigid structure with increasing poly(sodium 4-styrenesulfonate) concentration, possibly due to the polymer bonding to water at its oxygen sites. The behavior observed in the poly(sodium 4-styrenesulfonate) aqueous solutions has been observed in other polymer-water solutions.⁵ The association by hydrogen bonding with water can take place at the oxygen site of SO_3 . The similar bonding of metal ions and other ions possible at the oxygen site gives poly(sodium 4-styrenesulfonate) an importance as a flocculating agent.

Figure 6 shows the typical results for the absorption coefficients of ultrasonic waves at 20°C over the frequency range from 0.2 to 2 MHz in poly(sodium 4-styrenesulfonate) aqueous solutions. The data are expressed as α/f^2 vs. logarithmic frequency. The ultrasonic absorption in poly(sodium 4-styrenesulfonate) aqueous solutions can be represented by the equation of double relaxation as follows;

$$\frac{\alpha}{f^2} = \sum_{i=1}^2 \frac{A_i}{1 + \left(\frac{f}{f_{ri}}\right)^2} + B \quad (1)$$

where f represents the measured frequency, f_{ri} the relaxation frequency, A_i the relaxation amplitude, and B the contribution to sound absorption from any other processes that may be occurring at higher frequencies beyond our frequency range. In the case of double relaxation processes, suffixes 1 and 2

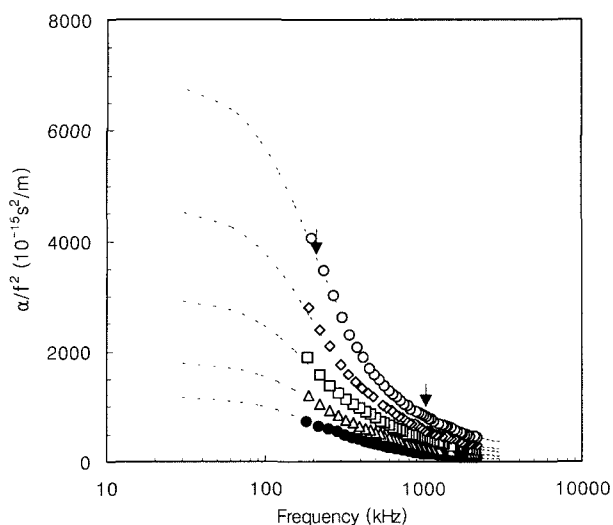


Figure 6. α/f^2 vs. frequency for poly(sodium 4-styrenesulfonate) aqueous solutions at 20°C. The symbols \circ , \triangle , \square , \diamond , and \circ represent the concentration of 5, 10, 15, 20 and 25% by weight, respectively. The lines represent double relaxation curves fitted to the data. The arrows indicate relaxation frequencies for the curve at concentration of 25%.

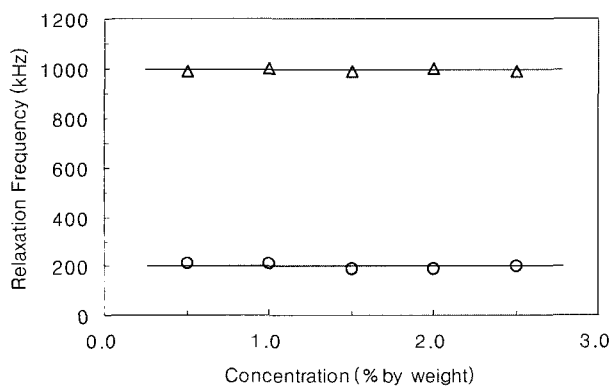


Figure 7. The concentrations dependence of relaxation frequency for the relaxations of $B_1(\circ)$ and $B_2(\triangle)$. The solids lines are drawn for a visual guide.

refer to the low- and higher-frequency processes, respectively. Eq. (1) was fitted by computer to experimental data in the frequency range investigated. Optimal values of the parameters, A_i , f_{ri} , and B , were obtained by assuming double relaxation phenomena. The solid lines in the figure represent the calculated ultrasonic relaxation spectra from Eq. (1) and the arrows show the location of the relaxation frequencies for the curve at concentration 25%. We designate the lower and higher frequency relaxation as B_1 and B_2 , respectively.

Figures 7 and 8 show the concentration dependence of the relaxation frequency (f_{ri}) and amplitude (A_i), respectively. The solid lines are drawn for a visual guide. In Figure 7 the relaxation frequencies around $B_1=0.2$ MHz and $B_2=1$ MHz

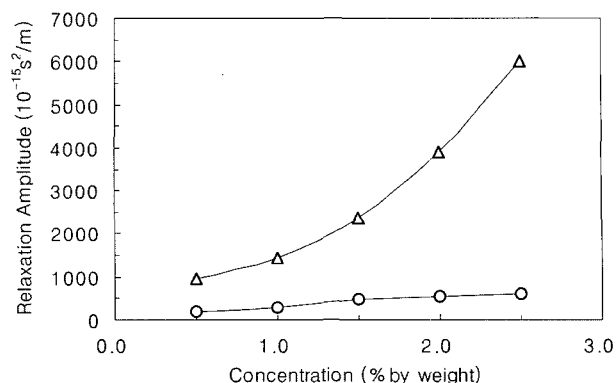


Figure 8. The concentration dependence of relaxation amplitude for the relaxations of $B_1(\circ)$ and $B_2(\triangle)$. The solids lines are drawn for a visual guide.

remain almost constant as a function of concentration, while in Figure 8 the relaxation amplitude increase with concentration. The two relaxations have different concentration dependence as can be seen in Figure 6. In Figure 8 the relaxation amplitude of B_1 increases rapidly in an exponential pattern with B_2 increasing concentration, but that of the increase almost linearly with concentration.

The relaxation mechanisms in poly(sodium 4-styrenesulfonate) aqueous solutions were associated with structural fluctuations of polymer molecules, proton transfer reaction of the oxygen sites of SO_3 , and hydration equilibrium (poly (sodium 4-styrenesulfonate)-water interaction) by sound waves.⁶ In general, the relaxation times related to hydration equilibrium[polymer-water interaction] are distributed over the frequency range from 2 GHz to 0.1 MHz.⁷ In addition, the relaxation frequencies related to proton transfer reaction in the polymer aqueous solution exist around 1-5 MHz.⁶ Shigeo Kato *et al.* reported that the frequency of the ultrasonic relaxation due to segmental motions in aqueous solutions of poly(acrylic acid) was below 1 MHz.⁸ We therefore assume that the mechanism of B_2 is the proton transfer reaction of the oxygen sites of SO_3 . Also, the mechanism B_1 may be attributed to the structural fluctuations of polymer molecules, such as the segmental motion of the polymer chains. However, for a precise understanding of this mechanism, absorption coefficient measurements in the poly(sodium 4-styrenesulfonate) solution should be performed over a wide frequency range, especially over a low-frequency range of 50 to 100 kHz.

Velocity Measurements. Figure 9 shows the ultrasonic velocity in the poly(sodium 4-styrenesulfonate) aqueous solutions. The velocity increases with increasing concentration at a given temperature. Also, the velocity increases as the temperature increases at a given concentration. Since the density should increase as more poly(sodium 4-styrenesulfonate) is added, it signifies the compressibility decreases with concentration. This is seen from the relaxation $\nu=(1/$

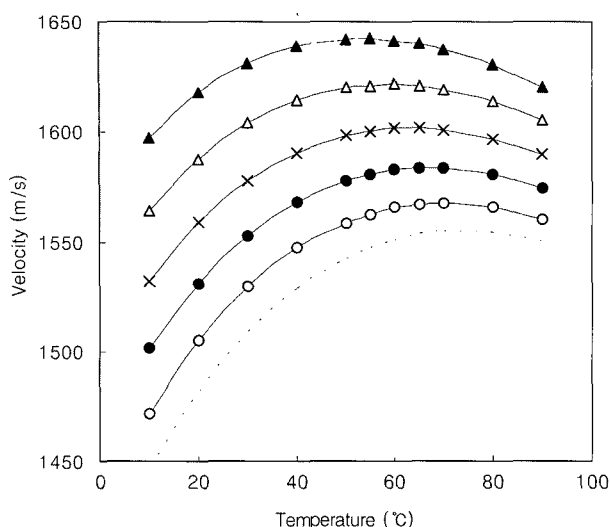


Figure 9. Ultrasonic velocity for poly(sodium 4-styrenesulfonate) aqueous solutions at different concentrations and temperatures (10–90 °C). The symbols ○, ●, ×, △, ▲ and ····· represent concentrations 5, 10, 15, 20 and 25% by weight and pure water, respectively.

$E \cdot \rho)^{1/2}$ between the velocity v , the density ρ , and adiabatic compressibility E . A physical interpretation for the solution is that its molecules may be more strongly bound by polymer-water hydrogen bonding at oxygen sites as the concentration of poly(sodium 4-styrenesulfonate) in water increases.

The velocities at these concentrations show the same temperature dependence as that in water. However, the maximum values of the velocity at these concentrations were found at lower temperatures than that in water. A qualitative explanation can be given as follows. The velocity in water increases with temperature at $dv/dT \sim 3.0 \text{ m/s} \cdot ^\circ\text{C}$ near room temperature, reaches a broad maximum at 74 °C and decreases thereafter.⁹ Here, v and T denote the ultrasonic velocity and temperature, respectively. The ultrasonic velocity in liquids generally decreases with temperature; the only exception is water.⁶ This anomalous behavior is qualitatively explained in terms of the molecular association of water. It is known that icelike clusters, whose size is not yet clear, are constructed of many molecules and coexist with monomers in water. Increase in temperature breaks down the clusters into monomers and decreases the overall compressibility of water near room temperature; the velocity increases since the negative effect of density decrease on the velocity is overwhelmed by the compressibility of water. This increase and the normal effect of a negative temperature gradient, common to all the liquids, cancel out perfectly at 74 °C. The icelike clusters of water have a compressibility higher than that of a simple collection of monomers, resulting in an increase of the velocity with temperature. The collapse of these clusters could be promoted by the foreign molecules

of associated polymers soluble in water, for instance, poly(sodium 4-styrenesulfonate). Thus, small amounts of poly(sodium 4-styrenesulfonate) molecules may seriously change the structure of water, and possibly decrease the temperature of maximum velocity. Therefore, the peak in Figure 8 shifts to a lower temperature as concentrations increase. The velocities in 5, 10, 15, 20, and 25% poly(sodium 4-styrenesulfonate) aqueous solutions had maxima at about 71, 67, 63, 59, and 55 °C, respectively. The maximum velocity tended to shift to higher temperatures with decreasing concentration. The maximum velocity in solutions is approximately 13–90 m/s more than that in pure water.

Conclusions

It is interesting to note that very few, if any, velocity maxima were observed in polymer solutions, such as in poly(sodium 4-styrenesulfonate) solutions. Although previous work suggested that the velocity increased with temperature and attributed the absorption to the shear viscosity, our work on poly(sodium 4-styrenesulfonate) aqueous solutions carried out over a comparatively wide temperature range from 10 to 90 °C demonstrated a velocity maximum for each concentration. Thus, we feel that the behavior of velocity in the polymer solution strongly reflects that in pure water. The concentration dependences of the relaxation frequency and amplitude show that the relaxation at around 200 kHz was related to the structural fluctuations of polymer molecules, such as the segmental motions of the polymer chains and that at 1 MHz resulted from the proton transfer reaction of the oxygen sites of SO_3 for the first time.

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