

Dielectric Investigation of the Sol-Gel Transition in the Acrylamide/*N,N'* Methylenebisacrylamide System

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ABSTRACT: The acrylamide/*N,N'*-methylenebisacrylamide gelation process was studied by time dependent measurement of real ϵ' and imaginary ϵ'' parts of the complex dielectric permittivity. The measurements were carried out in the frequency interval 500 Hz to 13 MHz. Strong relaxation behavior of ϵ' and ϵ'' was observed in all dielectric spectra during the transformation from the sol to the gel state. At all frequencies a maximum in the imaginary part of dielectric constant ϵ'' was observed. The gel point was found by extrapolating this maximum to zero frequency. The behavior of ϵ' and ϵ'' related to the gelation mechanism is discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 463–466, 2000

Key Words: polyacrylamide gels; acrylamide-bisacrylamide gel; free radical gelation

INTRODUCTION

Polyacrylamide gels have useful properties. Their ability to absorb solvents to 50 to 100 times more than their original weight and to retain their durability enhances their use especially in hydrolyzed form in holding aqueous solutions. Their uses extend from controlling humidity of soils to biomedical applications in artificial organs and contact lenses and controlled drug release systems both for human and animal therapy.¹

The acrylamide/bisacrylamide gelation reaction is a free radical crosslinking copolymerization. Formation and properties of polyacrylamide gels and the gelation processes have been studied intensively. These gels are homogeneous and have a clear appearance, but on a molecular scale they are inhomogeneous. This has been demonstrated both theoretically^{2,3} and experimentally.^{4–8}

The aqueous solution of the two monomers, acrylamide and bisacrylamide, together with the initiator and activator undergoes spontaneous

phase transition to the gel state with time. The polymerization and crosslinking reactions proceed simultaneously in many points in the reaction medium. A structural change in the system takes place when finite macromolecules form cluster units, which further coalesce into the gel phase. It is a phase transition, since the reaction changes its nature at this point.

Until the gel point, the length scale within the system is determined by the largest clusters. It increases with time and diverges at the gel point. At this point there is no length scale. Beyond the gel point, the length scale is determined by the size of the voids and the length of unattached loose chains and chain segments between crosslinks. All these lengths decrease as the reaction proceeds and as more and more material is added to the gel phase. The change of the length scale in the pregel regime and the decrease in the postgel regime result in typical frequencies, first decreasing and then increasing after the gel point.

The detection of gel point from rheological measurements is a matter of interest since Flory.^{9,10} In situ, time-dependent impedance spectroscopy is another useful tool in monitoring the gelation

process. The condensation polymerization reaction, namely thermoset curing, has been studied intensely since the 1960s.¹¹⁻¹³ The dielectric behavior of the present system differs greatly from the curing of thermosets. The acrylamide/bisacrylamide reaction is a free radical crosslinking copolymerization reaction. In this system the gel is formed in a swollen state in a highly polar solvent, that is, water. The material is still soft at the end of the gelation reaction.

In this work, the acrylamide/bisacrylamide free radical gelation process was investigated by in situ impedance spectrometry at the 500-Hz to 13-MHz region, and the different regimes occurring during gelation process were differentiated by the ϵ^I and the ϵ^{II} values at different frequencies.

EXPERIMENTAL

Acrylamide was supplied from industry and was used after crystallization from methanol. *N,N'*-Methylenebisacrylamid (Sigma) and ammoniumpersulphate (Merck) and tetramethyl ethylenediamine (TEMED; Merck) were used as supplied. Electrolytic solutions were prepared from ultrapure water (Millipore; Millie Q system). In 100 mL water, a mixture of acrylamide (10 g), bisacrylamide (0.55 g), and ammoniumpersulphate (0.021 g) was deaerated by nitrogen bubbling for 30 min, and after 0.120 mL TEMED was added, the mixture was transferred to the measuring cell.

Measurements were made in a parallel silver electrode, dielectric cell (1 mL) specially designed for this experiment. The electrodes were the flat faces of two silver pistons fitted inside a polymeric cylinder fitted horizontally to the measuring assembly. The diameter of the electrodes were slightly smaller than the inner diameter of the tubing, so that the electrodes were partially immersed in the liquid sample in such a way that no air bubbles were retained in the measuring compartment. The cell was electrically screened and the screen connected to the common ground of the set up. The measurements were carried out using an HP impedance analyzer HP-4192A with a test fixture 16047A connected to the measuring cell. The impedance analyzer was interfaced with a computer for automatic data acquisition. Measurements were started as soon as the cell was filled with the sample. The frequency was auto-

matically scanned in the interval of 500 Hz to 13 MHz during the experiment.

The same reaction was conducted in an identical copy of the reaction vessel, and the reaction mixture stirred with a magnetic stirrer in nitrogen atmosphere. The gel point was determined from the point when the magnet slowed down. The reaction mixture was completely liquid at 10 min and completely solid at 20 min, indicating that the gel point was between 10 and 20 min.

RESULTS AND DISCUSSION

At the beginning of the gelation process there are large numbers of ions and dipoles; therefore, ϵ^I and ϵ^{II} include ionic and dipole contributions. In the pregel regime, the increase of the dissipation loss is related to the growth of the clusters. After the gel point, the infinite macro structure is formed, and further change in the structure is due to the small molecules connecting more and more unreacted groups, thus decreasing the internal length and the dissipation factor.

It is known that electrode polarization can influence the results. The ratio of the thickness of the polarization layer (blocking layer, t_b) to the distance between the plates, L , (t_b/L) is the main parameter in this effect. The observed loss tangent ($\tan \delta_x$) depends on its actual value ($\tan \delta$) and the polarization layer thickness as

$$\tan \delta_x = \tan \delta ((L/2t_b) - 1) / ((L/2t_b) + (\tan \delta)^2).$$

It is seen that, unless $(t_b/L) \leq 1/\tan \delta$, the observed value will be significantly reduced. In our experiments, at intermediate frequencies $\tan \delta_x$ is greater than 100, indicating that $t_b/L < 10^{-2}$. Therefore, we can state that the effect of electrode polarization on ϵ^{II} is negligible.

In Figure 1, the time dependence of the imaginary part of the dielectric constant is plotted in normalized form, $(\epsilon^{II}(t) - \epsilon^{II}(\text{min})) / \epsilon^{II}(\text{min})$ versus time. In the low-frequency part of Figure 1 (upper 3 curves at 500-Hz, 10-kHz, and 100-kHz frequencies), the shapes of curves are almost the same. In the frequency interval of 500 kHz to 13 MHz, the maximum in ϵ^{II} shifts toward later times with increasing frequency. The minimum of $\epsilon^{II}(t)$ occurs when the crosslinking is almost finished. As the crosslink density increases after the gel point, the loose structures are restricted. This restriction damps the mobility of larger struc-

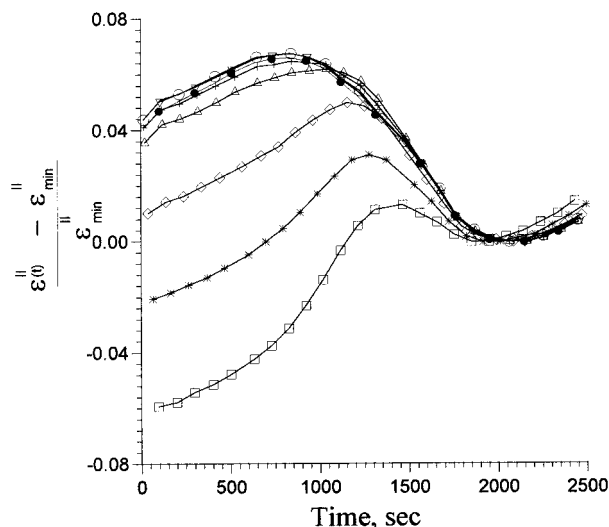


Figure 1 $(\epsilon''(t) - \epsilon''_{min})/\epsilon''_{min}$ values plotted versus time for 500 Hz (\circ), 10 kHz (∇), 100 kHz (\bullet), 500 kHz (+), 1 MHz (\triangle), 4 MHz (\diamond), 8 MHz ($*$) and 13 MHz (\square).

tures, and the effect is seen as a reduction in the loss factor effective at low frequencies. As more and more crosslinks are added, higher frequencies are also damped. Thus, the maximum in occurs later at higher frequencies.

The gel point can be found by extrapolating the results toward lower frequencies. The log of measuring frequency versus the time of the maximum of ϵ'' is plotted in Figure 2. The gelation time can be determined by extrapolation of the plot of log

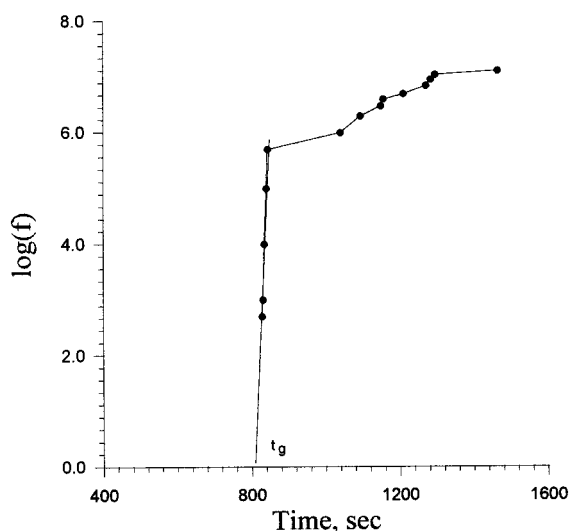


Figure 2 Logarithm of frequency versus observed ϵ'' max times plots from 500 Hz to 13 MHz.

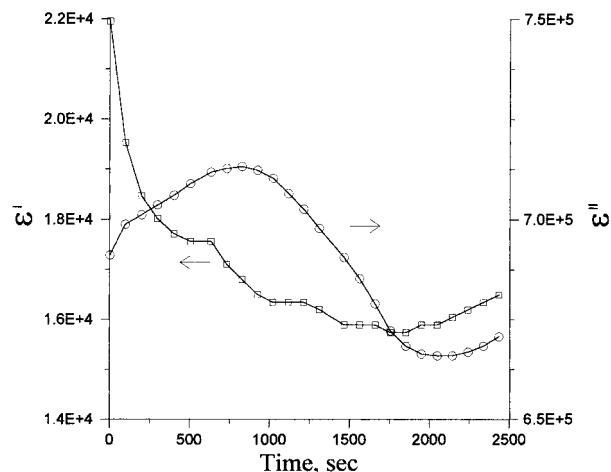


Figure 3 ϵ' and ϵ'' versus time plots at 500 Hz.

(f) versus t_{max} to a very low frequency. This gives the gel point at approximately 810 s, assuming 1 Hz as static point. Note that zero frequency is not meaningful in a finite reaction cell and that the gel point is not sensitive to the arbitrary choice of 1 Hz as the static point. A factor of 100 in this frequency changes the gel point by only 5 or 6 s.

The visual observation of the parallel experiment gave the time of the gel point to be between 10 and 20 min, in accordance with the dielectric measurements.

In Figure 3, ϵ' and ϵ'' values measured at 500 Hz are given. The high values of $\epsilon'(t)$ and $\epsilon''(t)$ arise from ionic and dipole effects. The decrease of $\epsilon'(t)$ is related to the relaxations of dipoles by cluster forming. As seen in Figure 4, $\epsilon''(t)$ undergoes a maximum and the position of ϵ''_{max} at lowest measured frequency (500 Hz) can be considered as the closest measured point to the gel point.

In Figure 4, the real part of the dielectric constant is plotted as a function of time. In this figure, a minimum dielectric constant is observed before the gel point in the interval 100 kHz to 3 MHz. The increase of the dielectric constant after the minimum point is related to the orientational contribution of finite molecules, which becomes more pronounced around the gel point. After the gel point, a peak in the dielectric constant is observed in this frequency range. After the maximum point due to increasing entanglement of the medium, the orientational contribution decreases in this frequency range. The molecules cannot stay in phase with the field and polarization drops. The minimum and maximum smear out in an inflexion point beyond 3 MHz. At frequencies

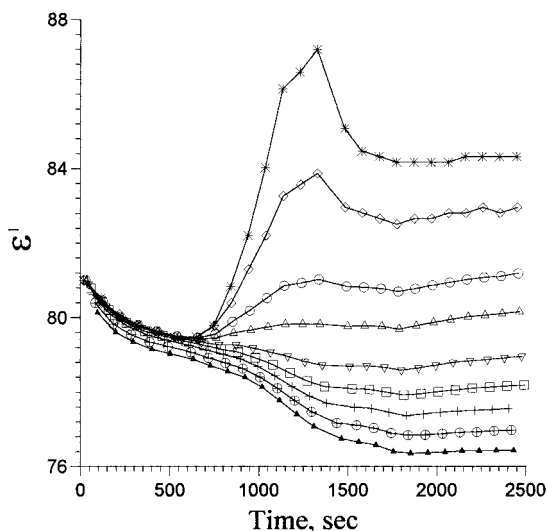


Figure 4 ϵ'' versus time plots at 500 kHz (*), 1 MHz (Δ), 2 MHz (\circ), 3 MHz (\triangle), 4 MHz (∇), 7 MHz (\square), 9 MHz (+), 11 MHz (\oplus), and 13 MHz (\blacktriangle).

higher than 3 MHz, the crossover from orientational to conventional relaxational behavior is observed.

CONCLUSIONS

The gelation reaction is followed by in situ dielectric spectroscopy. A shift at the maximum points of the imaginary part of the dielectric constant is observed from 500 Hz to 13 MHz. The gel point is determined from the extrapolating this maximum

to low frequency as 810 s. Different regimes that dominate the gelation process from the time behavior of the dielectric constant at different frequencies are inferred.

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