Reversible Gelation of Acrylonitrile–Vinyl Acetate Copolymer Solutions. II. Mechanical Properties

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Synopsis

Concentrated solutions of acrylonitrile polymers exhibit reversible gelation. The rate of gelation at 25°C. was determined for various solutions of an acrylonitrile copolymer containing 7.7% vinyl acetate in mixtures of dimethylacetamide (solvent) and water (nonsolvent) by measuring the shear modulus of the forming gel as a function of time. The mechanical properties were also measured on a series of gels formed by cooling solutions to −78°C. It was found that both the rate of gelation at 25°C. and the modulus of gels formed at −78°C. increase very rapidly as either the solids level of the solution or the water content of the solvent is increased. The gelation rate data wree correlated with the gel melting points of the gels. The results are discussed and compared with the analogous but limited data available for other systems.

INTRODUCTION

In an earlier publication[1] the reversible gelation of concentrated solutions of acrylonitrile–vinyl acetate copolymers in various solvents was discussed. The main object of concern in that work was the reversible nature of the transformation from gel to sol (solution) and vice versa. This transition occurs at a reasonably well-defined temperature known as the gel melting point. The gel melting point was shown to depend very critically on the composition of the polymer, the nature of the solvent, and the concentration of the gel. It is usually concluded that reversible gelation is the result of a molecular network formation similar to that in chemically crosslinked systems except that the tie points of the network are not chemical bonds but are physical associations between chains. The observations reported earlier[1] strongly suggest that the tie points are small polymer crystallites in the case of acrylonitrile polymers.

Further studies with an acrylonitrile–vinyl acetate copolymer have been made and are reported here. Two types of experiments were performed, both of which measured mechanical properties of the gels or solutions. In the first, the gels were prepared very quickly by cooling the solutions to −78°C. for about 24 hr. The mechanical properties of the resulting

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gels were measured at 25°C. as a function of the concentration of the gel. In the second experiment the rate of gelation of various solution was determined by measuring the shear modulus of the gelling solution as a function of time while the temperature was held at 25°C.

All of the data shown here were obtained on a single copolymer containing 7.7% vinyl acetate by weight with an $\bar{M}_w$ of about 200,000. Dimethylacetamide (DMAc) was the only solvent used in this work; however, the effect of water in this solvent was studied.

MECHANICAL PROPERTIES OF GELS FORMED AT −78°C.

Experimental Technique

The gels used in this series of experiments were prepared from solutions of the acrylonitrile–vinyl acetate copolymer in various mixtures of DMAc and water by heating and thorough mixing. These solutions were transferred to long cylindrical test tubes. Air bubbles were removed by placing the tubes in a 90°C. bath for 1 hr. or more. The tubes were then immersed in a Dry Ice–acetone bath overnight to allow the solutions to gel. The tubes were removed from the cold bath and allowed to warm up to room temperature. Once at room temperature the gels could be removed from the test tubes by gently pulling on them with a pair of tweezers. The diameter of the cylindrical rod of gel was exactly that of the test tube (1.275 cm.). The gels were left in the test tubes until just before they were tested. This prevented the serious problem of moisture adsorption and the lesser problems of solvent loss. Both of these lead to syneresis of the gel.

The elongational stress–strain relationship for each gel was determined by a simple static method. A rod of gel about 10–12 cm. long was employed. At both ends of the rod, lengths of copper wire were run through the gel (perpendicular to its axis) to serve as clamps. The gel was hung in a vertical position using one of the copper wires. A gage length l_0 of about 6 cm. was marked on the test specimen with ink. Weights were then attached to the lower copper wire clamp in increments of a few grams. After each weight increment was added the new extended length l of the test section was measured by use of a centimeter scale. This, of course, gives the force–elongation curve for the specimen. No creep was observed in the time scale of each observation (from 15 sec. to 5 min.). All samples were stored at room temperature (∼25°C.), and all tests were made at this same temperature.

About two dozen tubes of gel were made from each solution composition. Measurements were made on individual samples at various times after the tubes were removed from the Dry Ice–acetone bath.

Results and Discussion

The results obtained by using the procedure outlined above were the force versus relative length (i.e., $\alpha = l/l_0$). A plot of force versus α gave a curved relation quite similar to that usually observed for crosslinked elas-
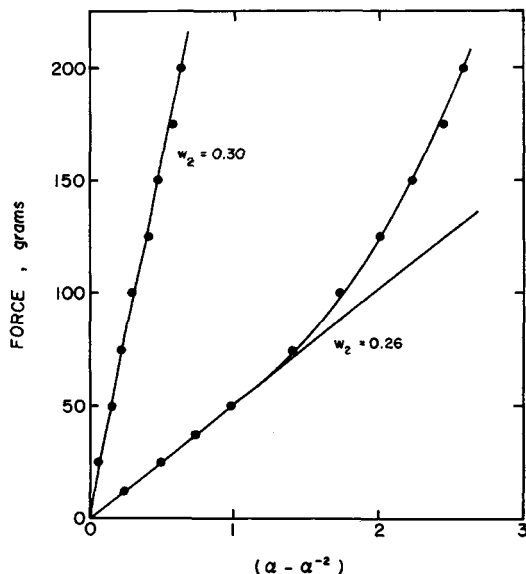
Fig. 1. Elongational stress–strain diagram for gels.

tomers.   Since the long-term elasticity of these gels is attributed to a network, then it seemed reasonable to expect the stress–strain relationship for the gels to be better described by the form of the classical rubber elasticity theory than by a simple Hooke's law relationship.   This means that the strain should be written as $\alpha - \alpha^{-2}$ for the network rather than $\alpha - 1$ as Hooke's law requires.   Plots of force versus $\alpha - \alpha^{-2}$ were found to be more linear than the analogous plots of $\alpha - 1$.   Such a plot is shown in Figure 1 for two different concentrations in pure DMAc, namely, 26% and 30% polymer by weight.   The 26% case is linear up to an α of about 1.6, at which it begins to curve upward.   The 30% case is linear over the entire range measured.   In every case the elongation was found to be reversible up to the point where the stress–strain diagram becomes nonlinear.   This would imply that the nonlinearity is caused by an actual change in the network.   The same phenomenon is observed in crosslinked rubber (at $\alpha > 4$) and is attributed to crystallization.   Since these gels are thought to be partially crystalline, then the nonlinearity here is probably due to additional crystallization induced by the stretching.

An elongational modulus of elasticity can be defined by the rubber elasticity relation as follows

$$F/A_0 = E_0[\alpha - (1/\alpha^2)] \tag{1}$$

where A_0 is the initial cross-sectional area of the sample.   The data obtained here were all plotted in the fashion of Figure 1 and a modulus calculated from the slope of the initial linear region.   To denote this, the modulus was designated by E_0.   At each composition the modulus E_0
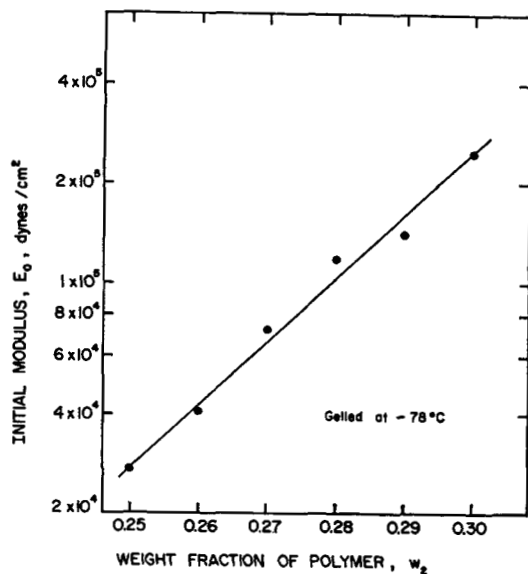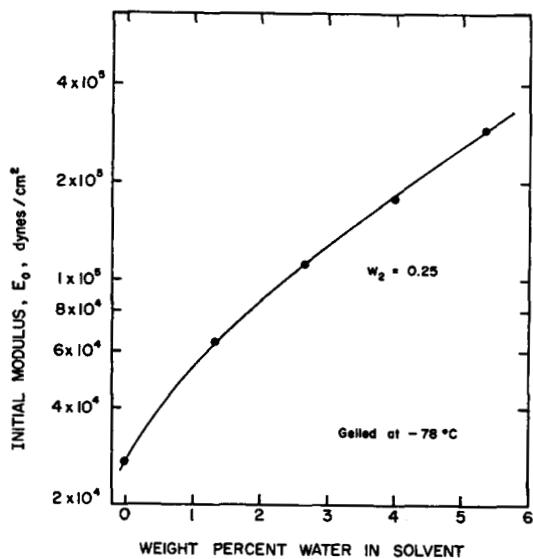
Fig. 2. Initial elongational modulus.

Fig. 3. Initial elongational modulus.

was found to be a slight function of the length of time the gel had been at room temperature, but no real efforts were made to study this change. Apparently the gel structure is changing with time. Most of the measurements were made within a few days after the gels were removed from the Dry Ice bath. The results of these measurements are shown in Figures 2 and 3. Figure 2 shows the effect of solids level on the modulus of the

gels, while Figure 3 shows the influence of water in the solvent (DMAc) at a constant solids level of 25%. Both are very effective at increasing the modulus.

GELATION RATE AT 25°C.

Experimental Technique

The gelation of these solutions at room temperature is first made evident by an increase in the solution viscosity. This proceeds to the point where the viscosity becomes very large, and finally no flow is observed. After this time an elastic modulus would serve as an indication of the state of affairs in the forming gel. By measuring the modulus as a function of time one can determine the rate of gelation. For such measurements it is always necessary to use the same sample and to keep the deformation small to avoid induced crystallization. It is also very important to protect the sample from moisture and solvent loss.

Saunders[2] has suggested a method for measuring the modulus of gelatin gels, and this method was used earlier to measure the temperature dependence of the modulus of a gel formed at $-78°C$.[1] The experimental arrangement is essentially a U tube with one leg of radius R and the other leg a capillary of radius a ($R \gg a$). The U tube was partially filled with mercury. Then a freshly prepared solution was added to the larger leg and the air bubbles were removed by immersing the tube in a 90°C. bath for 1 hr. or more. Once the bubbles were removed, the system was rapidly cooled to 25°C. by immersing the tube into water. This point was marked as zero time for the experiment. A thin layer of paraffin oil was placed on top of the solution to prevent moisture in the air from penetrating the solution. A flexible hose from a nitrogen pressure source was attached to the solution side of the U tube. As pressure is applied to the solution side, one can see the mercury rise on the capillary side. If the solution is still fluid, there will be simple flow until the pressure is equalized on the two sides. However, as the solution gels, the flow ceases, and the gel merely deforms under the shear stress field caused by the pressure differential. This deformation causes the mercury in the capillary to rise. The modulus can be obtained easily by measuring the height of the mercury column in the capillary relative to any arbitrary reference point as a function of the pressure applied to the U tube (measured by a mercury manometer).

The shear stress field set up in the gel by a pressure differential of Δp is given by

$$\tau_{rz} = \Delta p r / 2L \tag{2}$$

where L is the length of gel in the tube. In shear, Hooke's law and the theory of rubber elasticity both give a linear stress–strain relationship

$$\tau_{rz} = -G \, dz/dr \tag{3}$$

where G is the shear modulus and dz/dr is the shear strain. Equations (2) and (3) can be solved to give the volume of mercury displaced from the larger side of the U tube Q:

$$Q = \pi R^4 \Delta p / 8GL \tag{4}$$

The value of Q can be measured by noting the rise in the mercury height h, since

$$Q = \pi a^2 h \tag{5}$$

Rearranging gives an expression for G:

$$G = (R^4/8a^2L)\ \Delta p/h \tag{6}$$

In principle eq. (6) gives G from one pressure and height reading; however, better accuracy can be obtained by using several values. It should be noted here that Δp refers to a pressure differential across the gel and not the pressure read on the manometer and further that h does not refer to an arbitrary datum. As suggested above, if one measures the pressure p exerted on the U tube, and the height of the mercury relative to an arbitrary reference, $h + h_0$, the desired information can be obtained. This is done by plotting p (in centimeters of Hg) versus $h + h_0$ (in centimeters) which gives a straight line if the deformations are kept small. The slope S of this line can be used to calculate $\Delta p/h$ as follows

$$\Delta p/h = 1.33(S - 1) \times 10^{+4} \text{ dynes/cm.}^3 \tag{7}$$

where Δp is expressed in dynes/square centimeter. Equations (6) and (7) can be combined to give

$$G = 1.33(R^4/8a^2L)(S - 1) \times 10^4 \tag{8}$$

where G will have the units of dynes/square centimeter. In the work reported here the following dimensions were typical: $R = 0.73$ cm.; $a = 0.062$ cm.; $L = 14$ cm.; the pressure p was normally varied from 0 to 20 cm. Hg.

A complete set of p and $h + h_0$ data could be obtained in about 10 min. On most samples, readings were made at least once daily and more frequently for faster gelling concentrations. In all cases the deformation was reversible and no indication of creep was seen.

Results and Discussion

By following the procedure outlined above, the shear modulus G was obtained as a function of gelling time for the given solution. This was done for two series of solutions of which one used DMAc as the solvent and the solids level ranged from 25 to 30%, while in the other series the solids level was held fixed at 25% and water was added to the solvent (DMAc) in varying amounts. The data obtained for the first series are shown in Figure 4 while that for the second series is shown in Figure 5.
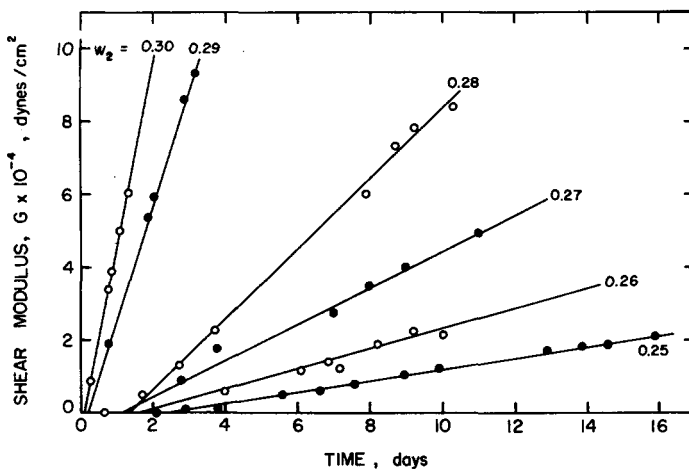
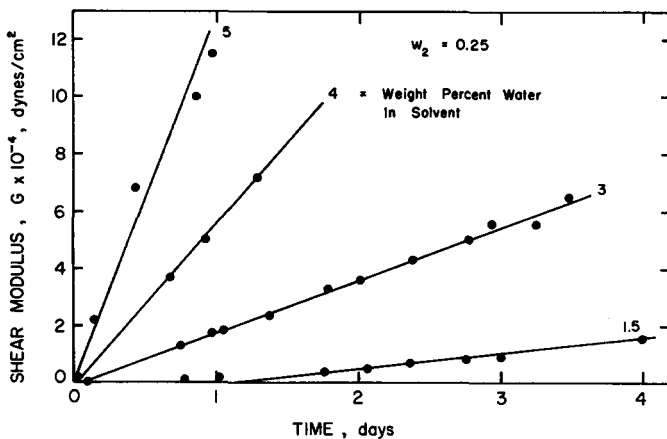Fig. 4. Effect of solids level on gelation rate.

Fig. 5. Effect of water level on gelation rate.

In each case the plot of G versus time took on a characteristic form which can be seen in Figures 4 and 5. A time lag is noted during which the modulus remains essentially zero. After this induction period the modulus increases linearly with the gelation time. A similar result was obtained by Bisschops[3] for pure polyacrylonitrile in DMF.

It seems apparent that it is during this time lag that one observes the increase in solution viscosity. At the point where the modulus starts to increase from zero it is rather likely that the viscosity as measured by, say, a falling ball has just become very large or infinite. Thus by using such a test one would conclude that complete gelation had already occurred at just the point where the test employed here starts to show some changes. The viscosity test is probably of more practical interest for those concerned with problems of solution stability; however, the modulus test is of more
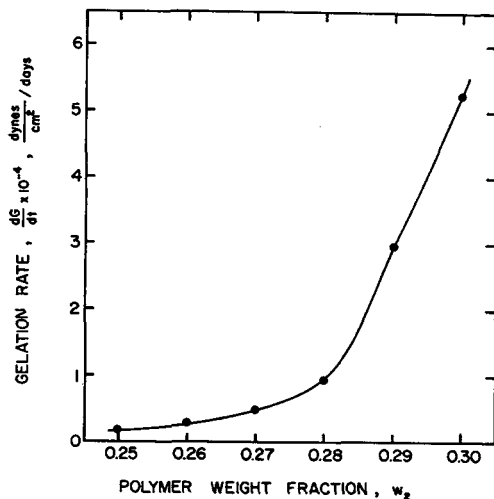
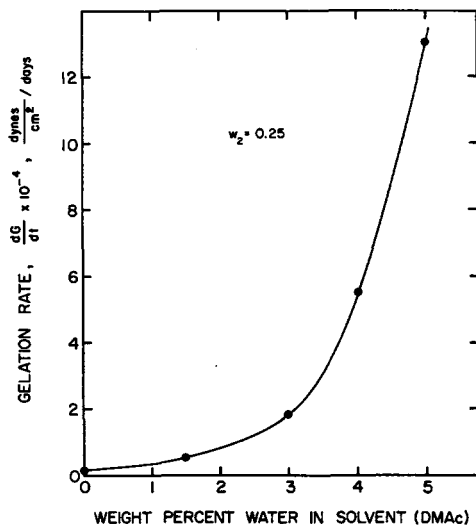Fig. 6. Effect of solids level on gelation rate.

Fig. 7. Effect of water level on gelation rate.

importance when one is concerned with the fundamentals of structure formation during gelation. The two phenomena are very much related and influenced by the same factors. During the induction period, the polymer chains are beginning to become associated with one another (i.e., nucleation); hence there is the rise in viscosity; however, the modulus starts to rise when these regions of association (nuclei) start to connect with one another to form a supermolecular network. The modulus continues to rise as the nuclei become more completely connected and as more polymer

chains become involved.   These ideas tie in very well with the concepts associated with the gel melting point.[1]

It is rather interesting that after the time lag the modulus increases linearly with gelation time.   The slope of this line serves as a very good index of the gelation rate.   Figure 6 shows a plot of this slope versus the solids level for the first series of experiments.   A very slow rise in rate is seen up to about 28% polymer, after which the rate rises very rapidly. This also is very similar to results obtained by Bisschops.[3]   An analogous plot is shown in Figure 7, where the rate is given as a function of the water content of the solvent.   A very rapid increase in rate is seen above 3% water.

It would seem rather unlikely that the modulus could increase linearly with time indefinitely.   However, during the course of these experiments no slowing down was observed.   It would be of interest to see how these modulus values compared with the ones obtained on the gels formed at −78°C.   To do this one must first recognize that the elongational modulus E_0 is approximately equal to three times the shear modulus, i.e., $3G$.   A comparison shows that in each case studied, the gels forming at 25°C. eventually surpass the values obtained for the gels formed at −78°C.   This indicates the difference in the structure formed at the two temperatures.   It was shown earlier that the gel melting point was apparently not affected by the temperature of gelation.   This must indicate that the gel melting point is relatively insensitive to the type and extent of the structure formed.

CORRELATION OF GELATION RATE DATA

It would be instructive to attempt a correlation of the gelation rate data from the solids level series and the water content series with some param-
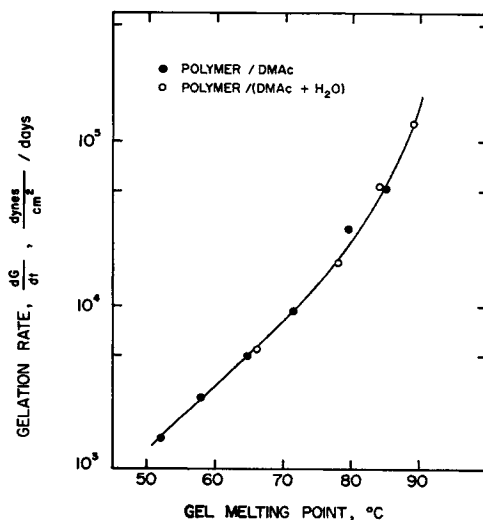

Fig. 8. Correlation of gelation rate with gel melting point.

eter of the gel. The most obvious parameter is the gel melting point reported earlier. Figure 8 shows such an attempt. Here the gelation rates from Figures 6 and 7 are plotted versus the gel melting points for these concentrations (data from the previous paper[1]). Within the accuracy of the data, the rates from the two series are superimposed into a single curve. This fact points up the considerable significance of the gel melting point. One could rationalize this result on the basis of crystallization theory. It would be interesting to see whether this correlation would still hold for a wider and more diverse range of concentrations. It would also be important to take data at other temperatures to see if a correlation could be obtained between rate of gelation and the difference between the gel melting point and the gelation temperature.

COMPARISON WITH OTHER SYSTEMS

Very little information is available on the mechanical properties or the gelation rate of gelled polymer solutions. Such information is essentially limited to the work done on gelatin[4] in water (also ethylene glycol) and the work done by Bisschops on polyacrylonitrile in DMF.[3] In this section the results reported here will be compared to these results.

In a review on the rheology of gelation, Ward and Saunders[4] show the shear modulus G versus gelation time for various concentrations of gelatin in water (2–6% solids). These plots show a very rapid initial increase in modulus with no time lag followed by a slowing down of the rate. The modulus apparently becomes constant after long times. In fact, one experiment showed that when a solution held at 37°C. and a gel formed at 0°C. were both brought to 15°C., the two approached the same modulus but from different directions. This is exactly counter to what was observed here. As mentioned earlier the results reported by Bisschops on the gelation rate of PAN (polyacrylonitrile) in DMF are quite similar to the results given here. However, he worked at a maximum concentration of 23% (of course, PAN is less soluble than the copolymer used here) and never went to a modulus greater than 10^3 dyne/cm.[2]. As a consequence, he never observed gelation rates as fast as shown here. For example, the maximum rate Bisschops reports is 0.40×10^4 dyne/cm.[2]-day (for 23% PAN in DMF at $-10°C.$) which is roughly equivalent to the rate seen for a 27% solution in DMAc at 25°C.

It has been well established for the gelatin–water system that the apparent equilibrium modulus mentioned earlier varies as the square of the gelatin concentration. Hermans[5] has also considered this relationship for carboxymethyl cellulose–water gels. The conclusion is that the square dependence indicates a dimerization type association, i.e., an association between two chains. It would be interesting to test this relationship for the gels used here; however, we are faced with the problem of not being able to see an apparent equilibrium modulus. If the data shown in Figure

2 is used, it is seen that the modulus is not proportional to the square of the polymer weight fraction.   In fact a forced fit of the type:

$$G = kw_2{}^n \qquad (9)$$

gives an n of about 12; however, this form does not fit the data perfectly. If one believes that the value of n gives the stoichiometry of the molecular associations causing gelation, then it can be concluded that in gelatin–water the gelation is caused by the intermolecular forces between two chains (perhaps strong hydrogen bonding), whereas in the system reported here the gelation is caused by the association of perhaps 12 or more chains (perhaps crystallization).   This would explain very nicely the difference in gelation kinetics.   Actually a more realistic equation for the modulus would be

$$G = k(w_2 - w_2{}^0)^n \qquad (10)$$

where $w_2{}^0$ is the minimum concentration for gelation at the temperature in question.   For the system used here at 25°C. one can obtain an extrapolated value of $w_2{}^0$ of about 0.20–0.22.   This will lower the value of n to about 3.   It would be very questionable to draw any conclusions from these arguments.   They are presented here only because they have been used several times by other authors.

References

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Résumé

Des solutions concentrées de polymères acrylonitrile manifestent des gélifications réversibles. La vitesse de gélification à 25°C a été déterminée pour diverses solutions d'un copolymère d'acrylonitrile contenant 7.7% d'acétate de vinyle dans des mélanges de diméthyle acétamide (solvant) et d'eau (non-solvant) en mesurant le module de cisaillement de gels formés en fonction du temps. Les propriétés mécaniques ont également été mesurées pour une série de gels par refroidissement des solutions à −78°C. On a trouvé que à la fois la vitesse de gélification à 25°C et les modules des gels formés à −78°C croissaient très rapidement lorsque, soit la concentration en solution des solides, ou soit la teneur en eau du solvant était augmentée. Les données de la vitesse de gélification ont été mises en rapport avec les points de fusion du gel. Les résultats sont discutés et comparés avec les résultats analogues mais limités, disponibles pour les autres systèmes.

Zusammenfassung

Konzentrierte Lösungen von Acrylnitrilpolymeren zeigen die Erscheinung der reversiblen Gelbindung. Die Geschwindigkeit der Gelbildung wurde bei 25°C an verschiedenen Lösungen eines Acrylnitrilcopolymeren mit Vinylacetatgehalt von 7,7% in Dimethylacetamid (Lösungsmittel)-Wasser (Fällungsmittel)-Gemischen durch Messung des Schubmoduls des entstehenden Gels als Funktion der Zeit bestimmt. Weiters wurden die mechanischen Eigenschaften einer Reihe durch Abkühlung der Lösungen auf −78°C gebildeter Gele gemessen. Es wurde gefunden, dass sowohl die Gelbildungsgeschwindigkeit bei 25°C als auch der Modul der bei −78°C gebildeten Gele sehr rasch bei Steigerung des Festkörpergehaltes der Lösung oder des Wassergehaltes des Lösungsmittels zunimmt. Die Gelbildungsdaten wurden mit den Gelschmelzpunkten der Gele korreliert. Die Ergebnisse werden diskutiert und mit den für andere Systeme vorhandenen, allerdings beschränkten Daten verglichen.