

Reversible Gelation of Acrylonitrile-Vinyl Acetate Copolymer Solutions

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Synopsis

The reversible gelation of acrylonitrile-vinyl acetate copolymers in concentrated solutions has been studied with the use of various solvents. These concentrated solutions gel or become rigid with time, but they become fluid again when heated above a certain temperature called the gel melting point. A technique involving the use of mercury drops was developed to measure this transition. This temperature was evaluated as a function of solids level, water content in the solvent, and the amount of vinyl acetate in the copolymer, dimethylacetamide being used as the solvent. Four other solvents were used to obtain limited data. Gel melting was studied further by differential thermal analysis and shear modulus measurements. The results are discussed in terms of network formation and solubility. The x-ray diffraction results imply that the tie points of the gel are crystalline.

Introduction

It is not uncommon for the viscosity of concentrated polymer solutions to increase with storage time. In some cases the viscosity apparently rises to a new value, and no further change is seen; however, in other cases the viscosity continues to rise until it becomes essentially infinite, and an elastic gel results. In the latter case a modulus of elasticity can be used to characterize the gel. This phenomenon is called gelation but is to be distinguished from the process accompanying chemical crosslinking. This gelation is termed reversible, since the gel structure can be made to disappear by adding solvent or by appropriately changing the temperature. In certain cases shear can destroy the structure. Gelation of this sort is frequently considered a nuisance, but it is also an interesting phenomenon that has received only limited attention in recent years.

Most polymers containing acrylonitrile in rather large proportions show this type of gelation in concentrated solutions. Some results are reported here on a study of the gelation of a series of acrylonitrile-vinyl acetate copolymers in various solvents. All of these polymers had a weight-average molecular weight of about 200,000. Most of the data were obtained on a single polymer sample containing 7.7% vinyl acetate by weight. Unless stated otherwise, all future reference will be to this polymer.

Reversible gelation is by no means a unique property of acrylonitrile copolymers for this behavior has been observed in several polymer-diluent

TABLE I
Gel-Forming Polymer-Diluent System

Polymer	Solvents	Author
Poly(vinyl chloride)	Diethyl phthalate	Walter ¹
Polyacrylonitrile	DMF (dimethylformamide)	Bisschops, ² Jost ³
	DMAc (dimethylacetamide)	Ziabicki ⁴
Nitrocellulose	Ethyl alcohol	Krigbaum ⁵
Methylcellulose	Water	Heyman ⁶
Gelatin	Water, ethylene glycol	Ferry, ⁷ Saunders, ⁸ Flory ⁹
Certain stereoregular mixtures of poly(methyl methacrylate)	DMF	Ryan ¹⁰
Poly(vinyl alcohol)	Water	Khomutov ¹¹

systems. To illustrate this point, a list of gel forming polymer-diluent systems is given in Table I along with some of the authors who have investigated them.

All of these systems form viscous solutions (frequently called sols) which in some temperature regions will not show gelation with time; however the temperature can be changed to some new level at which gelation will occur. In most cases the sol exists at higher temperatures, whereas the gel is formed at lower temperatures. The nitrocellulose and methylcellulose systems shown in Table I are exceptions since the gel is stable at higher temperatures than the sol. This behavior is governed by the temperature dependence of the solution thermodynamic relationships.¹² For all of these systems there is a temperature at which one form is converted to the other and vice versa. This temperature is called the "gel melting point" since it is where the elastic gel is "melted" to form the fluid sol. This term will be used here to designate this transition since it is common practice, but it should not be construed that necessarily any connection with a thermodynamic first-order transition is implied. Observation of this transition by various means constitutes most of the information reported here.

Theories of Reversible Gelation

It is generally agreed that in the case of concentrated high polymer solutions, gelation is the result of a network formation (which gives mechanical strength) analogous to that formed in chemically crosslinked systems, except that the tie points of the network are not chemical bonds. The nature of these tie points is the object of some controversy. The predominant point of view considers them to be small polymer crystallites. These crystallites would then be interconnected by the long-chain molecules that by chance form a part of more than one crystallite. The solvent

apparently surrounds these crystallites, but it is not there in its pure form, as most likely many polymer chains and chain ends would still be dissolved in it. This physical picture of reversible gelation is discussed quite thoroughly by P. H. Hermans.¹³ His discussion is aided by pictorial representations of the envisioned networks. This kind of picture is reminiscent of the "fringed micelle" model of crystalline polymers, but it is not difficult to visualize the crystalline regions incorporating a certain amount of chain folding.

There is not always clear-cut evidence for each system to show that the tie points are crystalline. This is true mainly because these regions are certainly small and constitute only a small fraction of the total mass, thus complicating observations such as x-ray diffraction. However, there seems to be little doubt that the tie points represent a local concentration of polymer chains that is higher than the average. Because these regions are small, the question arises as to whether they are large enough to be called crystalline even if they are ordered. To indicate their small size, these regions are often called crystallization "nuclei."² This is primarily a question of nomenclature and will not be pursued further.

Mandelkern¹² attributes gelation to the copolymeric nature of the polymer molecules. The idea here is that a random copolymer prepared from certain monomers will contain sequences of crystallizable units that will crystallize with similar segments on other chains. The noncrystallizable segments will be free from this ordering but will connect the crystallites with the net result being a supermolecular network that pervades the entire system hence gelation. According to Mandelkern, copolymeric nature is a result of polymerization of two or more monomers, stereoirregularities, incomplete substitution of celluloses, head-to-head polymerization, etc. In this sense nearly all polymers are copolymeric.

The factors favoring gelation are just those that do not favor solubility^{13,14} such as lowering the temperature, adding a nonsolvent, or using a poor solvent. Except in the case of inverted systems mentioned earlier, it is expected that poor solvents or mixtures of a solvent and nonsolvent will result in higher gel melting points than for good solvents alone. This will be shown later to be true. It is not really necessary that the tie points be crystalline for gelation to be considered a solubility phenomenon. The tie points would only have to be regions richer than average in polymer. The gel melting point is then the temperature at which the tie points are redissolved. But are gels to be considered two-phase systems? The gels prepared here and gelatin-water gels look homogeneous to the eye and through the optical microscope. The answer lies in how large the tie points and solvent rich areas must be before they are to be considered as separate phases. Any answer will be arbitrary; hence we probably should not try to be so categorical.

Consider another question. Why do some polymer-diluent systems form two distinct, separable phases when the solubility limits on temperature are surpassed whereas other systems gel and do not show two separable

phases? The answer to this question is uncertain, but an approach is as follows. Due to the long length of the polymer molecules, one chain may form tie points with other chains at several points along its length simultaneously as crystallization or insolubility begins. If the connecting chains are flexible and the intermolecular forces are not too great at the tie points, then the tie points can be disrupted and reformed progressively to permit phase separation. If the chains are stiff and the intermolecular attractions are strong, however, the bonds formed initially will remain intact and a three-dimensional network will result. At the start, the entire lengths of crystallizable sequences will not be contained in the crystallites; hence these crystalline or ordered regions will grow until the mutual entanglement of the chains eventually put an end to this growth. Just as in bulk crystallization, mechanical restraints help determine the ultimately achieved level of crystallinity. This state is one of thermodynamic metastable equilibrium if these restraints are properly considered.

Gels sometimes show syneresis, i.e., they weep or exude solvent. This behavior may be a result of the further growth of the crystallites in some instances to the point where the solvent is mechanically squeezed out. If this is true, then it is not too difficult to think of the gel as a two-phase system. Syneresis is enhanced by large surface-to-volume ratios and the presence of a nonsolvent at the surface such as moisture.

Gelation is a rate process. The rate depends markedly on polymer composition, solids level, the solvent, temperature, and on all of the impurities present. It is of interest to consider the effect of temperature at this point. For gelatin in water, the rate can be greatly increased by lowering the temperature to near 0°C. The same trend has been found for other systems¹⁰ and was true for the systems studied here. For some of the solutions studied here, it took weeks at 25°C. to attain a gel of a certain modulus. This same level of rigidity could be achieved in a few hours by keeping the sample in a Dry Ice-acetone bath (-78°C.). This temperature dependence of the gelation rate highly suggests that gelation is a manifestation of a crystallization process. This is also of great practical significance since it provides a very rapid means of producing gels. Except as noted, the gels used here were prepared overnight at -78°C.

Mercury Drop Penetration Method of Measuring Gel Melting Point

Various methods have been used to measure the melting points of gels.⁷ These methods involve observing the transition from a gel to a viscous solution (or sol) rather than the converse due to the sometimes rather slow rate of gelation. It is usually a good practice in measuring transitions to go from the less mobile state to the more mobile state. Most of the methods for measuring gel melting points employ techniques that are sensitive to changes in the rigidity of the gel. Usually such methods involve slowly warming the gel (if the gel forms at lower temperatures) and noting the temperature at which the gel flows under its own weight, a solid object will

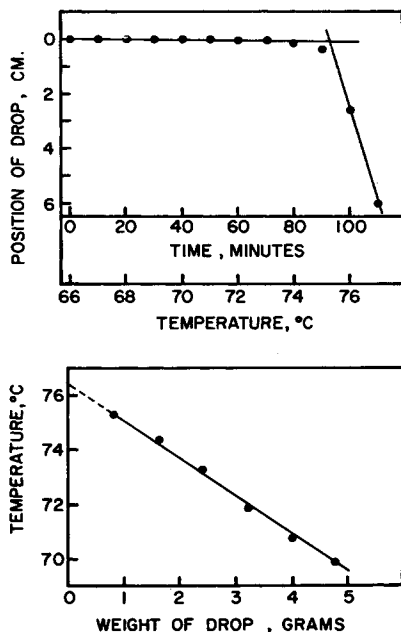


Fig. 1. Illustration of mercury drop penetration technique.

fall through, or bubbles will rise. These methods are simple and easy to use, but they work only for systems in which the gel melts to a low viscosity solution; hence they could not be applied to concentrated polymer solutions often having viscosities above 500 poise.

A method was developed for concentrated polymer solutions and will now be described in detail. Gels were formed in test tubes (usually 25×150 mm.). A drop of mercury of known weight was placed below the surface of the gel in each tube by a dropper. The test tubes (usually five or six) were then immersed in a liquid bath which was at a temperature roughly $15\text{--}20^\circ\text{C}$. below the gel melting point. The temperature was held at this level for at least 1 hr. to insure thermal equilibration. After this, the bath temperature was increased at a constant but slow rate ($\sim 6^\circ\text{C}/\text{hr}$.) by varying the power input to the heaters. During the heating, the position of each drop was noted every 10 min. by using a centimeter scale attached to the test tube. The upper part of Figure 1 shows that the drop remains stationary until a certain region of temperature is reached, and then it begins to fall towards the bottom of the tube. The transition is taken to be the intersection of straight lines drawn through the points before the fall and after the fall has started. This is shown in Figure 1 for a particular weight mercury drop. The yield stress¹² of these gels decreases with increasing temperature. The transition point shown in the upper part of Figure 1 is the temperature at which the yield stress of the gel has been reduced until it is approximately equal to the stress exerted by the mercury drop; hence the drop has started to move. With this in mind, it is

expected that this transition temperature would depend on the weight of the mercury drop used which is just the effect shown in the lower half of Figure 1. Each point on this plot is the intersection of the two lines as illustrated in the upper half of Figure 1 for each particular weight of mercury drop. It has been found that such plots are linear in the weight of the mercury drop. While there is no *a priori* reason why this should be so, it is a convenience. The gel melting point should be the temperature at which the yield stress goes to zero. Therefore, if one extrapolates linearly plots similar to the lower half of Figure 1 to the temperature corresponding to zero weight, a reasonable approximation to the gel melting point should be obtained, since a drop of vanishingly small weight would exert a vanishingly small stress. This extrapolation never amounted to more than 2 or 3°C. and usually less. In all cases, the gel melting points reported here correspond to the zero weight intercept as illustrated in the lower half of Figure 1.

There are two reasons for using mercury drops rather than, say, steel balls. Figure 1 shows that after a drop starts to fall, its rate of descent is slow (~ 0.3 cm./min.) due to the high viscosity of the solution. Since mercury's density is about twice that of steel, steel balls would fall even more slowly making the transition harder to determine. Also, inhomogeneities in the gel (e.g., an air bubble) might completely stop a falling solid object whereas a drop of mercury can easily deform around such an inclusion.

The solutions used in this work were normally prepared in about 2000-g. batches. The solvents were chilled to aid slurring of the polymer. The resulting slurries were heated to several degrees above the estimated gel melting point for that particular composition and mixed well until a clear solution was obtained. In cases where this led to unusually high temperatures, precautions were taken to guard against solvent loss by evaporation. The solution was then transferred to a pot and eventually charged into test tubes through a pipe connected to the bottom of the pot. The test tubes were then stoppered and placed in a bath at roughly 90°C. for 1 or 2 hr. to let the air bubbles that collected during mixing escape. Removal of air bubbles was found to facilitate greatly the ease in performing the experiment as well as offering substantial improvements in the precision attained. After this treatment, the solutions in the test tubes were gelled in one of two ways. The tubes could be left at room temperature to gel; this required a few hours to a few weeks to achieve depending on the composition. Only a few gels were prepared this way, and these will be clearly indicated. Most gels were prepared by immersing the tubes into a Dry Ice-acetone bath ($-78^{\circ}\text{C}.$) for several hours. The tubes sometimes broke after they were removed from the cold bath due to differential expansion. The tubes of solution were frequently opaque after removal from the cold bath. This is due to crystallization of the solvent. In some cases the solution did not become opaque until the tubes started warming up from $-78^{\circ}\text{C}.$ In these cases, small opaque nuclei could be seen to appear and then to grow as perfect spheres, frequently reaching sizes of 1 cm. in diameter depending on the number started. It was found that some minimum

time at -78°C . was necessary for gelation; however no gel property has been found to depend on the time at -78°C . beyond this minimum. In most cases the tubes were left in the Dry Ice-acetone bath overnight. Most of the data presented here were obtained on gels prepared in this way. This was done primarily as a means of speeding up the data gathering process. In all cases extreme care was exerted to prevent moisture from the air, hands, etc. from contacting the gel as this will in effect coagulate it.

Given in the following section are the effects of various variables on the gel melting point as measured by the technique outlined above.

Gel Melting Point Data

Gel melting points were measured as a function of solids level for a 7.7% vinyl acetate copolymer in the solvent DMAc. The results are shown in Figure 2 where the gel melting temperature is plotted versus the weight fraction of polymer in the solution, w_2 . The results were obtained over the most convenient range of w_2 . Below w_2 of about 0.24 the solutions gel with great difficulty, whereas above a w_2 of about 0.36 it is very difficult to make a homogeneous solution due to the high viscosity. All of the data in Figure 2 were obtained by using solutions gelled at -78°C ., except for the two compositions indicated by crosses. These were gelled at room temperature and seem to be in essential agreement with the other points, indicating a small effect, if any, on the temperature of gelation.

The DMAc used in the above experiments was very pure. Additions of nonsolvents such as water to the solvent greatly increase the rate of gelation and the gel melting point. Figure 3 shows this effect by indicating the increase in the gel melting temperature as increasing amounts of water is

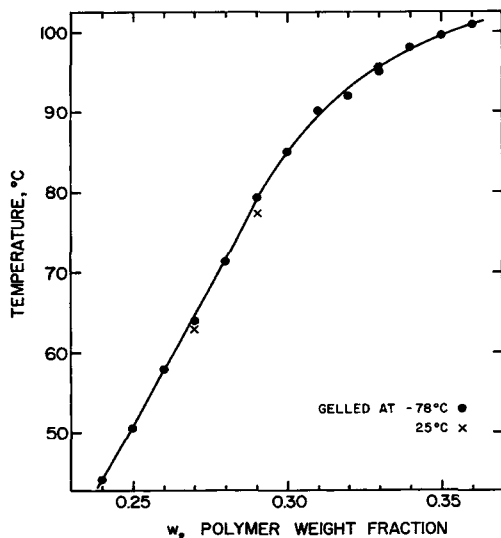


Fig. 2. Gel melting point of copolymer-DMAc gels.

added to the solvent DMAc. Two levels of w_2 are shown, namely, 0.23 and 0.25. The solutions used in obtaining these data were prepared by first adding water to the solvent in the amount shown by the abscissa of Figure 3, and then adding polymer in the amount required to achieve the desired w_2 . The data were extended to as high water levels as practical. Again the circles, both open and filled, represent data for gels formed at

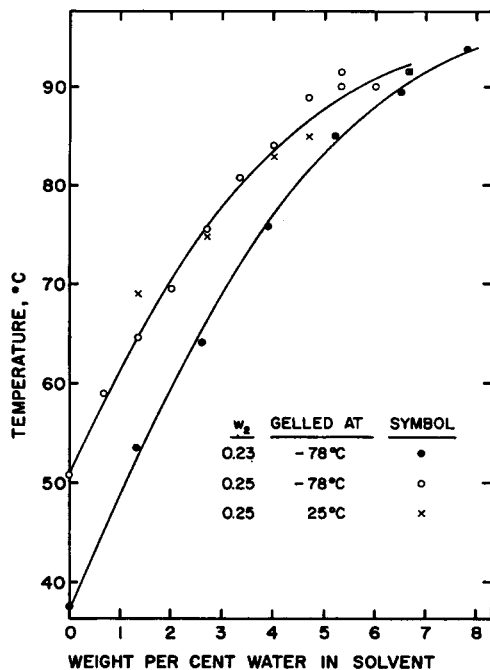


Fig. 3. Gel melting point of copolymer-(DMAc + H₂O) gels.

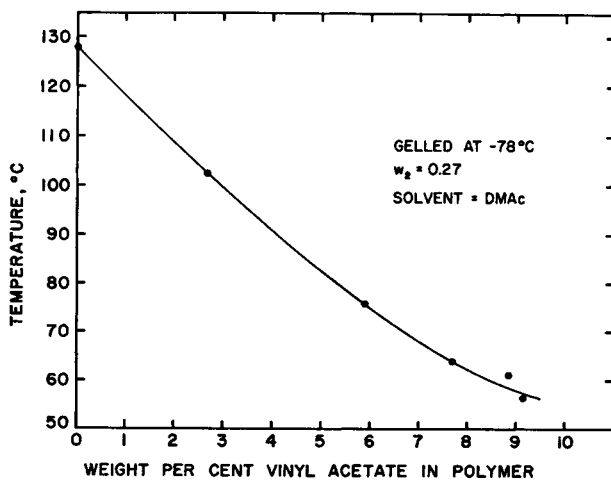


Fig. 4. Effect of vinyl acetate level on the gel melting point.

-78°C ., whereas the crosses represent data for gels formed at room temperature. The trend shown in Figure 3 should be expected on the basis of the discussion above since addition of water makes DMAc a poorer solvent.

Figure 4 shows the effect of copolymer composition (vinyl acetate level) on the gel melting point at a constant w_2 value of 0.27. These data extend from pure polyacrylonitrile to a copolymer of about 10% vinyl acetate by weight. A dramatic decrease in the gel melting point is shown in this range. The presence of the vinyl acetate disrupts the gelling tendency of the acrylonitrile groups. This points out the previously known fact that addition of vinyl acetate makes acrylonitrile polymers more soluble. The

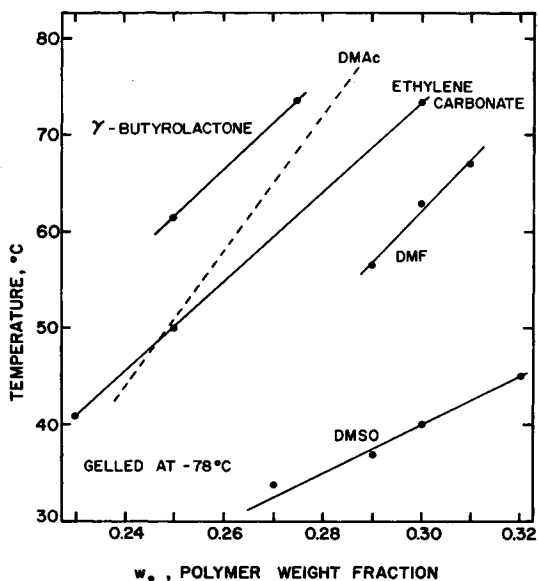


Fig. 5. Gel melting point in various solvents.

gel melting point serves as a good measure of this solubility change. The polymers used to obtain the data in Figure 4 differed only in vinyl acetate content. The solvent used was high-purity DMAc.

The gel melting point-solids level relationship is different for various solvents, as shown in Figure 5. The polymer used contained 7.7% vinyl acetate, and all of the solvents were of quite high purity. The range of w_2 for each solvent except DMAc (the dotted line was taken from Figure 2) is rather limited, and no special significance should be attached to the straight lines drawn through the data points. The gel melting temperature can be used as a measure of solvency power, but comparisons should be made at constant volume fractions for thermodynamic reasons. The five solvents shown in Figure 5 should then be ranked in the following order of decreasing solvent power DMSO, DMF, ethylene carbonate, γ -butyro-

lactone, and DMAc at a constant volume fraction of 0.25. DMSO appears to be a significantly better solvent.

Differential Thermal Analysis of Gels

It seems reasonable that there might be energy changes associated with gel melting since gelation may be thought of as a solubility phenomenon. Changes of this sort are often studied by DTA, but apparently no such measurements have been made on gels. Several gels of the 7.7% vinyl acetate copolymer in DMAc were examined by use of the Du Pont 900 DTA apparatus. Very definite effects were found to be associated with gelation. Some representative DTA thermograms are shown in Figure 6. The usual thermogram conventions are employed in this figure. The top curve is for a solution that was not gelled. It would have gelled in time, but it was run within 1 hr. after preparation. Room temperature gelation would have required about 1 week. The thermogram for this sample shows no energy changes except a gradual endothermic drift at high temperatures (which is just the evaporation of solvent and becomes more pronounced as the boiling point is reached).

The lower curve in Figure 6 is for the same composition as the upper curve, except the sample was gelled. The large differences in the two thermograms can be attributed to gelation. This thermogram is complex, and an exact interpretation is difficult. If the base line is horizontal as it obviously is for the top curve, then there is an endothermic peak at the gel melting point of this gel, i.e., 64°C. On the other hand, if the base line is a line of negative slope, then perhaps this represents only a decrease in the heat capacity rather than a latent energy change. The first explanation seems reasonable in light of the model of gelation discussed earlier, for this would be the energy to melt or dissolve the tie points.

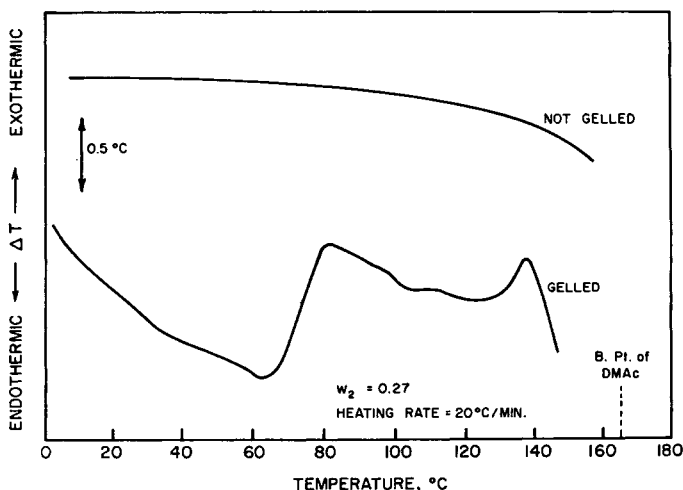


Fig. 6. Differential thermal analysis of gels.

The region above 64°C. is very difficult to understand, especially the apparently exothermic peak at 138°C. This feature was found on a host of scans and always at 138°C. It seems very difficult to associate anything above 64°C. with the breakdown of the gel, since it becomes fluid at this point, and there is no evidence to suggest persistence of this order to these high temperatures. In fact, this gel when heated to 90°C. has the same viscosity as the solution did at 90°C. before it was ever gelled (upper curve of Fig. 6). No attempt will be made to explain this peak. The change at the gel melting point (64°C.) is considered the most significant feature of this thermogram.

Wide-Angle X-Ray Diffraction Studies

At first thought it seems that the question of crystallinity in the tie points of gels could be answered by x-ray diffraction analysis of the gels.^{3,13} However, several factors make such measurements less definitive than desired. Most of the gels studied here contain two to three times more solvent than polymer, and of the polymer present only a small percentage can be expected to exist in the tie points at these compositions. A further difficulty is the poor x-ray response of polyacrylonitrile and its copolymers as they show only one sharp diffraction peak. This peak occurs at $2\theta = 17^\circ$ and can be almost completely masked by the diffuse liquid scattering of DMAc (and other organic solvents) which shows a peak near $2\theta = 18^\circ$.

Many flat plate photographs and diffractometer scans of DMAc gels were found to be indistinguishable from patterns obtained from un-gelled solutions so long as the gels had not undergone syneresis (i.e., solvent loss). In cases where large-scale syneresis occurred, evidence of crystallization was seen. However, gels formed by the system poly(vinylidene fluoride)-DMAc showed crystallinity quite distinctly. In this case the $2\theta = 20^\circ$ crystalline peak of poly(vinylidene fluoride) was seen to emerge after gelation from the broad diffuse scattering caused by the solvent.

Another approach was tried with the acrylonitrile copolymer system, and this was to look for crystalline orientation in a stretched gel. The idea here is that if the tie points are crystalline they should orient upon stretching of the gel, and that the formation of arcs on a flat plate photograph due to this orientation might be detectable even though the un-oriented crystalline peak cannot be detected. Several gels were stretched two to three times their original length (most of the stretch is reversible), and flat plate photographs made in this stressed state. Gels of near 25% solids in DMAc level showed no detectable crystalline orientation; however a 33% polymer gel did show orientation about the equator. Next a stretched gel (25% polymer by weight) was coagulated by water in this oriented position (the sample remained at the stretched length after the clamps were removed). A flat plate photograph of this sample showed very definite signs of crystalline orientation in that arcs were formed about

the equator. Likewise, crystalline orientation was observed in gels that had undergone syneresis either before or after stretching.

From the above observations it is concluded that the tie points are crystalline in these gels. This crystallinity cannot be easily detected at the 25% solids level due to the reasons outlined above. Coagulation, syneresis, or higher solids level increase the amount of the crystalline material to a detectable level when the orientation approach is used. One could argue that the stretching induces crystallization, but the elongations used here, 2 or 3X, do not seem large enough for that.

Mechanical Properties of Gels

Gels of the nature discussed here can be characterized by a modulus of elasticity. This modulus will be determined by the composition, the temperature, and the age or thermal history of the gel. A very ingenious method has been suggested by Saunders⁸ for measuring the shear modulus G of gels. This method involves deforming a sample of gel contained in a tube by a pressure gradient and noting the extent of deformation by the rise of mercury in a capillary connected to the tube containing the gel. From such measurements of deformation at given pressure gradients, the shear modulus defined by Hooke's law:

$$\tau_{rz} = -G(dz/dr)$$

can be calculated from the equation

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

where τ_{rz} is shear stress in the gel, dz/dr is shear deformation of the gel, R is the radius of the tube containing gel, a is the radius of the capillary, L is the length of gel in the tube, Δp is the pressure differential across the gel, and h is the height of mercury rise in capillary. The latter equation can be derived easily in analogy with the Hagen-Poiseuille equation for laminar flow by using Hooke's law of elasticity in the derivation rather than Newton's law of viscosity. A value of G can be obtained by using a single measurement of h at one Δp . Better results were obtained by measuring h at several levels of Δp . When Δp is plotted versus h , a straight line will result if Hooke's law is obeyed. The slope can be used in the calculation rather than $\Delta p/h$.

This method has been used to measure the shear modulus of gels formed by solutions of the 7.7% vinyl acetate copolymer in DMAc. A solution of the desired composition was charged to the apparatus and then gelled by immersing the tube into a Dry Ice-acetone bath for several hours. Modulus measurements were made after removal from the cold bath. No measurements were made until the sample had been at room temperature for several hours. Hooke's law was found to be obeyed up to the highest strains used ($\sim 35\%$). The strain was completely recoverable at least up to this range. The modulus was also independent of the time duration of the stress within the time scale of a few seconds to almost an hour.

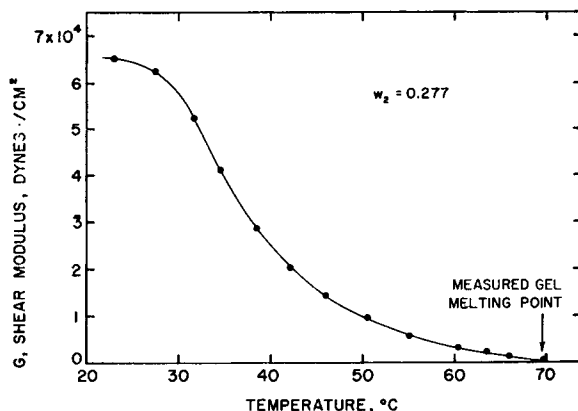


Fig. 7. Shear modulus of a gel.

The shear modulus of a 27.7% solids gel was measured as a function of temperature. The results are shown in Figure 7. The measurements were made on the same gel starting at room temperature and then going to higher levels in steps. The gel was held for a minimum of 1 hr. at each new temperature before a determination of G was made. The gel melting point taken from Figure 2 for this composition is shown in Figure 7 by an arrow. The curve shows that the equilibrium shear modulus approaches zero as the gel melting point is approached. Thus the significance of the gel melting point is clearly indicated. As the temperature is increased the network structure is broken down and this process is effectively complete at the gel melting point.

The shear modulus at room temperature is seen to be about 6×10^4 dyne/cm.² for Figure 7. This is comparable to the modulus of gelatin gels reported by Saunders.⁸ This value is much lower than that for cross-linked elastomers, which have values of the order of 10^7 dyne/cm.². This indicates that the network formed by these gels is not nearly as extensive (or effective) as normally found in chemically crosslinked gels.

The lack of time dependence of the modulus indicates that the tie points are not breaking up and reforming within this time scale but are more or less permanent for a given set of circumstances.

Discussion

It has been stated previously that gelation is believed to be a polymer-diluent solubility phenomenon in which the morphology of the polymer rich material is a three dimensional network that extends throughout the entire system rather than segregating into a distinct, macroscopic and separate phase as is more frequently observed. It would be desirable to correlate all of the gel melting point data given here in terms of some of the well-known thermodynamic solution theories such as that of Flory,⁹ but this does not seem possible. At least two reasons can be given for this difficulty. One is that in order to apply such theories as Flory's to situations

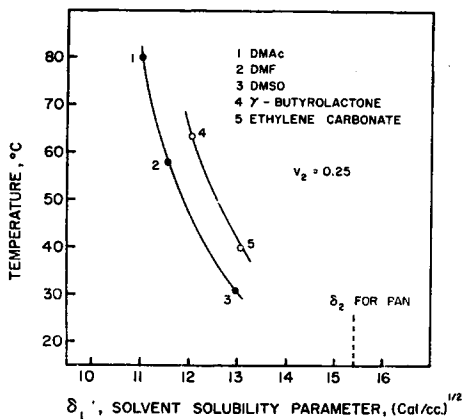


Fig. 8. Effect of solvent cohesive energy density on the gel melting point.

where the undiluted polymer melting point, the enthalpy of polymer crystallization, and the polymer-diluent interaction parameter are all unknown, data must be available over practically the entire composition range to be able to evaluate these unknown quantities. The data given here cover a range of only 12% by weight. The second reason is even more serious, since it deals with the applicability of the usual thermodynamic solution theories. Part of this concern is that the "phases" in a gel must be extremely small, hence leading to possible nonnegligible surface free-energy terms that cannot be properly accounted for with present theories. As mentioned before, these regions may be so small that they should not even be referred to as phases. A second point to note is that even if the surface free-energy terms are negligible, the composition of the phases is unknown and apparently not accessible to experimental determination.

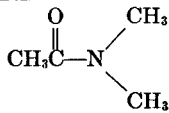
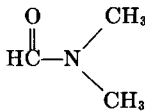
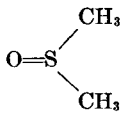
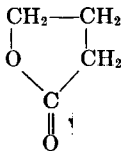
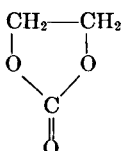
Even though a quantitative correlation does not seem possible, one interesting qualitative correlation can be suggested. Hildebrand¹⁵ has developed a rather successful solubility theory around the concept of the solubility parameter δ , where

$$\delta = (\text{cohesive energy density})^{1/2} \cong (\Delta E_{\text{vap}}/v)^{1/2}$$

The essence of this theory is that the closer the solubility parameter of the proposed solvent, δ_1 , is to the solubility parameter of the solute, δ_2 , then the better solvent it will be. The original theory was developed for nonpolar systems but can be applied to polar systems¹⁶ by the use of appropriate parameters in addition to δ_1 and δ_2 . Since the theory is developed in terms of volume fractions, comparisons of solvents should be made at a constant volume fraction. This is done in Figure 8 by plotting the gel melting point for each of the five solvents used here (at $v_2 = 0.25$) versus the solubility parameter of the solvent δ_1 . The solubility parameter of polyacrylonitrile has been estimated¹⁴ to be 15.4 (cal./cc.)^{1/2}. The value for the copolymer used here might be expected to be slightly less than this. The gel melting temperature would be expected to be lower in better solvents, and Figure 8 shows

as a general trend that as δ_1 nears the estimated δ_2 the gel melting point decreases. Of course, a single curve could not be expected to describe the data for all solvents, since more parameters are needed to describe the effect of polar forces. The two curves are drawn in Figure 8 to suggest that there might be families of curves with a curve for each series of solvents with similar polar natures. Since these forces are a consequence of molecular structure, there might be a curve for each series with similar molecular

TABLE II
Solvent Properties

Solvent	Structure	Molecular weight	Density, g./cc.	δ_1 , (cal./cc.) ^{1/2} ^a
DMAc		87.1	0.938(25°C.)	11.05
DMF		73.1	0.943(25°C.)	11.55
DMSO		78.1	1.101(20°C.)	12.93
γ -Butyrolactone		86.1	1.124(25°C.)	12.05
Ethylene carbonate		88.1	1.322(40°C.)	13.05

^a δ_1 = Solubility parameter of the solvent, defined by $\delta = (\text{cohesive energy density})^{1/2}$, where cohesive energy density $\cong \rho(\Delta\hat{H}_{\text{vap}} - RT/M)$. All of the values of $\Delta\hat{H}_{\text{vap}}$ (heat of vaporization) were calculated from vapor pressure data given by Marsden¹⁷ except for ethylene carbonate, in which case a value of $\Delta\hat{H}_{\text{vap}}$ was taken directly from Marsden.

structure. And indeed the compounds forming the lower curve (DMAc, DMF, and DMSO) do have somewhat similar structures. Likewise the compounds forming the upper curve (γ -butyrolactone and ethylene carbonate) have quite similar structures (see Table II for structures). The idea shown in Figure 8 is very speculative, and much more data would be needed to prove or disprove its merit. It does seem to be a reasonable point of view.

All of the information presented here seem to support the model for gelation discussed earlier. New and novel studies such as these are very valuable in elucidating the nature of gelation, but more elaborate and sophisticated tools could be used to some value in further explaining this important behavior.

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Résumé

La gélification réversible de copolymères acrylonitrile-acétate de vinyle en solution concentrée a été étudiée en utilisant différents solvants. Ces solutions concentrées gélifient ou deviennent rigides avec le temps mais elles deviennent à nouveau fluides lorsqu'elles sont chauffées au-dessus de certaines températures appelées le point de fusion de gel. Une technique utilisant des gouttes de mercure a été développée pour mesurer cette transition. Cette température a été évaluée en fonction du niveau des solides, de la teneur en eau dans le solvant, de la quantité d'acétate de polyvinyle dans le copolymère en utilisant comme solvant le diméthylacétamide. Quatre autres solvants ont été utilisés pour obtenir les limites. La fusion de gel a été étudiée en outre par analyse thermique différentielle et des mesures de module de cisaillement. Les résultats sont discutés en termes de formation de réseaux et de solubilité. Les résultats de diffraction aux rayons-x impliquent que les points d'attache du gel sont de nature cristalline.

Zusammenfassung

Die reversible Gelbildung bei Acrylnitril-Vinylacetat-Copolymeren in konzentrierter Lösung wurde in verschiedenen Lösungsmitteln untersucht. Diese konzentrierten Lösungen gelieren oder werden mit der Zeit steif, bei Erhitzung über eine bestimmte Temperatur, Gelschmelzpunkt genannt, werden sie aber wieder flüssig. Zur Bestimmung dieser Umwandlung wurde ein Verfahren mit Verwendung von Quecksilbertröpfchen entwickelt. Die Umwandlungstemperatur wurde als Funktion von Feststoffgehalt, Wassergehalt im Lösungsmittel und Menge des Vinylacetates im Copolymeren in Dimethylacetamid als Lösungsmittel bestimmt. In vier anderen Lösungsmitteln wurden weniger umfangreiche Daten erhalten. Das Schmelzen des Gels wurde auch mit Differentialthermoanalyse und Schubmodulmessungen untersucht. Die Ergebnisse werden in Zusammenhang mit Netzbildung und Löslichkeit diskutiert. Röntgenbeugungsergebnisse zeigen, dass die Verknüpfungspunkte im Gel kristallin sind.

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