

Thermoreversible Gelation of Cellulose Acetate Solutions Studied by Differential Scanning Calorimetry

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Synopsis

Thermoreversible gels of cellulose acetate can be obtained by cooling concentrated cellulose acetate solutions in solvent-nonsolvent mixtures of dioxane and water. Upon heating the gels, endothermic effects were observed with differential scanning calorimetry. The heat effects are ascribed to the melting of a crystalline phase consisting of cellulose triacetate units. The endothermic peaks appear only after long aging periods of up to several days. Melting points generally decrease and heats of melting increase with increasing polymer concentration and with increasing nonsolvent content. The maximum degree of crystallinity is estimated as 8%. The kinetic effects of varying the water content in the solvent mixture are discussed.

INTRODUCTION

Demixing of a polymer solution by the exchange of solvent with a nonsolvent is the basic formation process of asymmetric membranes which are used in ultrafiltration and hyperfiltration (reverse osmosis). Such membranes are prepared by casting a film of a concentrated polymer solution on a supporting surface or by extruding the solution in hollow-fiber form and by subsequent immersion of the cast solution in a nonsolvent (water) bath. The asymmetric structure of the resulting membrane can be modeled as a dense top layer, with a thickness of about 0.2–0.5 μm , supported by a thick porous sublayer (100 μm thick).

It has previously been suggested by Koenhen et al.¹ that two distinctly different demixing processes are responsible for the formation of the asymmetric structure: (i) a gelation mechanism for the top layer through a fast exchange of a large amount of solvent by a relatively small amount of nonsolvent and (ii) liquid-liquid phase separation as the controlling process for the porous spongelike substructure where phase separation takes place at relatively unchanged overall polymer concentration. This hypothesis was proposed after studying phase separation in an asymmetric membrane-forming ternary system of a polyurethane in a solvent/nonsolvent mixture of dimethylformamide and water. Liquid-liquid phase separation takes place at low and medium polymer concentration and comparatively high nonsolvent content, whereas gelation is operative at high polymer concentration and low nonsolvent content. It was shown that these two different types of phase separation can also be found in the system cellulose acetate/dioxane/water.² Cellulose acetate (with a degree of substitution of about 2.5) is an important membrane material.

A gelation process is thought to be of crucial importance to the formation of the selective top layer. However, at present there is no technique available to study the formation of the asymmetric structure, i.e., in a very short time period, sometimes milliseconds, after immersion in the nonsolvent. Here the approach is taken to study demixing at constant overall composition with change in temperature. It is hoped that this study may provide for a better understanding of the conditions under which phase changes occur and what factors determine the kinetics of the relevant demixing processes.

In this paper the gelation is ascribed to local crystallization of cellulose triacetate units, though other types of crosslinks are not excluded. Evidence for this explanation is thermodynamics, viz., melting points and heats of melting as a function of composition. No structural information is available at present.

EXPERIMENTAL

Materials

The cellulose acetate is from Eastman, catalog number 4644, with acetyl content of 39.8%. By using gel permeation chromatography its molecular weight has been characterized as $M_n = 23,000$, $M_w = 55,000$, and $M_z = 118,000$. Dioxane is 1,4-dioxane, Baker analyzed reagent grade. The water was distilled twice.

Cloud-Point Determinations

Cloud points were determined by using a method described earlier.³ The desired amounts were weighed in small Pyrex glass tubes. The tubes were degassed and sealed under vacuum at liquid nitrogen temperature. The tubes were heated at 90°C for at least 2 days to obtain homogeneous solutions. Most observations of demixing were made in the very concentrated region in the phase diagram. The composition of the sample was preferably outside the (extrapolated) cloud-point lines of the liquid-liquid separation region (cf. Fig. 1).

Differential Scanning Calorimetry

The solutions were prepared by weighing out the appropriate amounts in aluminum sample pans, which were hermetically sealed. Only sample pans were used that showed no weight loss after 2 days at 100°C. The DSC apparatus was a Perkin-Elmer model DSC 2. The low-temperature handling of the samples was considerably improved by making use of an improved cooling head and by careful introduction of liquid nitrogen.⁴

It was shown earlier² that measurable endothermic effects upon heating can only be seen after considerable aging at the gelation temperature. This fact is now used to obtain a quantitative value for the heat effect. The endothermic heat effect, in joules per gram of polymer units, is determined by subtracting the thermogram after aging from the one obtained without aging before reheating. In this way a minimal value for the heat effect is

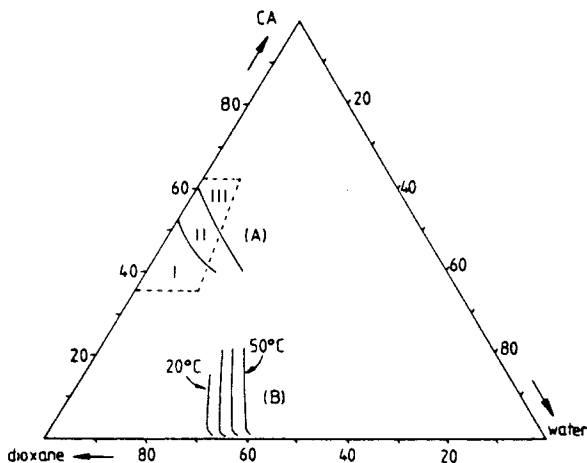


Fig. 1. Gelation (A) and liquid-liquid phase separation (B) in CA/dioxane/water. Coexistence lines for the latter at different temperatures. For explanation of symbols I, II, and III see text. Dashed line indicates region where DSC measurements were made.

determined. If fast cooling and immediate reheating would result in an endothermic effect upon heating, this effect is hidden in the baseline noise. The normal heating rate is $10^{\circ}\text{C}/\text{min}$. The lowest heat value which can be determined with a certain degree of accuracy is about 0.2 J/g polymer units. The melting point is determined as the maximum of the endothermic peak. The accuracy is no better than $\pm 3^{\circ}\text{C}$. The width of the peak is usually around 20°C .

RESULTS

First the location of the region in the ternary system CA/dioxane/water where gelation occurs needs to be established. This is done by determination of cloud points, i.e., the temperatures at which a marked change in turbidity occurs upon changing the temperature at fixed composition of the sample. Selected samples are subsequently subject to differential scanning calorimetry. Melting points (or ranges) and heats of melting are determined from the thermograms. The effect of aging time, aging temperature, and influence of cooling rate on the gelation process are studied in a limited way. Experiments are also performed on samples which undergo both liquid-liquid separation and gelation. This may give rise to interesting results when compared with systems in which only gelation takes place.

Location of Demixing Regions through Cloud-Point Determination

Cloud points of samples having compositions high and low in nonsolvent content were determined (Fig. 1). The DSC samples have a composition located within the dashed region in Figure 1. One can roughly distinguish three different zones in the latter region according to visual observation of these ternary systems: (I) systems homogeneous at 90°C and also homogeneous at 10°C ; (II) systems homogeneous at 90°C , but turbid at 10°C ; (III)

systems turbid over the complete temperature range from 10 to 90°C. Especially at high polymer concentrations the mixing process is tedious.

The general trend seems clear: increasing the nonsolvent content gives turbidity at lower overall polymer concentration. Two important points should be noted. First, systems without nonsolvent, i.e., on the polymer solvent axis, also show demixing. Second, many systems which give an endothermic effect in DSC upon heating are visually clear at low temperature. The systems that are turbid at room temperature have a very elastic gel-like behavior.

Differential Scanning Calorimetry

As was mentioned in the Experimental section, broad endothermic peaks could be observed usually only after considerable aging periods. No exothermic heat effects were found. The samples were quenched to the desired gelation temperature, in most cases 20°C, and were aged at this temperature for a number of days. The sensitivity of the instrument did not allow for the detection of an exothermal effect under isothermal conditions at the gelation temperature.

Melting Points after Aging at Room Temperature

The samples were aged at room temperature (20°C) for a period of three days. The melting point was taken as the maximum of the endotherm in the thermogram. The heat effect was determined as described in the experimental section.

Melting points and endothermic heat effects as a function of polymer weight fraction and at varying nonsolvent content are presented in Fig. 2 and Fig. 3.

It may be observed that the melting points increase slightly with in-

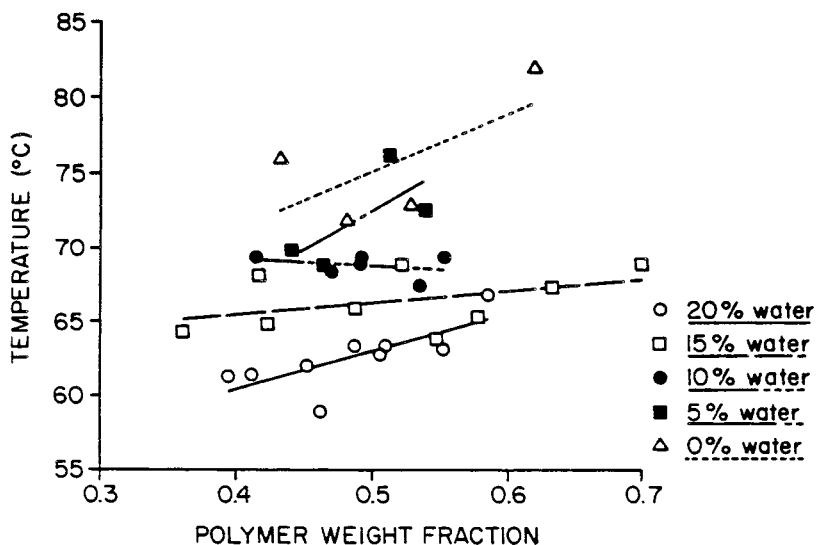


Fig. 2. Melting points from DSC experiments as a function of CA weight fraction in the gel for various water contents water/dioxane mixture: (○) 20, (□) 15, (●) 10, (■) 5, (△) 0% water.

creasing polymer concentration and that there is a trend for the melting point to decrease with increasing nonsolvent content of the solvent mixture. Generally it is found that melting points of gels increase with polymer concentration.

The observed trend that the melting point shows a slight decrease with increasing nonsolvent is not in agreement with a statement of Paul,⁵ who remarks that the melting point of a gel in a solvent/nonsolvent mixture is higher than it is without a solvent. We revert to this point in the discussion section.

Though the points in Figure 2 show considerable scatter, the endothermic heat effect Q generally increases with increasing polymer concentration up to 55%. Above this value low values were again obtained. These low values may be a result of insufficient homogeneity at high polymer concentrations. The dependence of Q on nonsolvent content is rather erratic, and has to be studied further. The lowest values of Q were found with no nonsolvent present.

Influence of Aging Time at 20°C

The results presented in Figure 2 were compared with results obtained from experiments in which the aging time at 20°C was 1 day instead of 3 days. The results indicated that melting points do not differ within the accuracy of the experiment. At relatively high water content of 20% the values for Q after one day of aging were the same as after 3 days. At lower (10%) water content, however, the one-day value was much smaller than that after three days. Hence increasing the water percentage is found to have a positive kinetic influence on the gelation process.

Influence of Cooling Rate on Melting Endotherms

As has been mentioned before, direct reheating after quenching gives no appreciable heat effect. By cooling at sufficiently low cooling rates, however, endothermic heat effects upon reheating (10°C/min) could be seen with samples with polymer concentration of 60% and water content in the solvent/nonsolvent mixture of 15–20%. These small heat effects could be made visible after subtracting the (reheating) curves from quenched samples from the curves for slowly cooled samples (1.25°C/min). The heat effect is located in the same temperature range as presented in Figure 2. No effect could be seen at 10% water content in the mixture.

Thus, at high polymer and relatively high water concentration, the time scale of the gelation process is probably much shorter than at lower polymer concentration.

Influence of Change in Gelation Temperature

Initial experiments on gelation at –10°C were carried out and compared with results from the previous section. Now endothermic effects were situated below 30°C. And again an endotherm could be observed after slow cooling (below 2.5°C/min), even at 10% water. The fact that melting peaks were shifted to lower temperatures when the gelation temperature was lowered prevents us from interpreting the melting points given in Figure

2 as equilibrium values. Equilibrium values for the systems under study can be obtained if an extrapolation procedure is carried out for observed melting points as a function of gelation temperature. An example of such a procedure is given by Borchard et al.⁶

Gelation after Liquid-Liquid Phase Separation

Liquid-liquid phase separation leads to the formation of two liquid phases with large differences in composition. The polymer concentration in the concentrated phase and other conditions may be such that gelation occurs. This was observed with many samples. It is of interest to compare DSC results obtained from thermograms of systems where just gelation and where both liquid-liquid separation and gelation occur.

In systems having compositions within the liquid-liquid phase separation region of the diagram in Figure 1 phase separation sets in immediately after cooling below a certain temperature. For example, at a water content of 40% in the dioxane/water mixture the cloud-point temperature is about 60°C, fairly insensitive to the polymer concentration (in the range of 10–20%). Again the sample was quenched to 20°C for a period of three days and the melting endotherm was taken. In agreement with previous experiments it was again found that the melting points showed a slight increase with polymer concentration, but contrary to earlier experiments Q decreased with increasing polymer concentration. More importantly, very high values for Q , in the range of 5–3 J/g polymer units, were obtained when the polymer concentration was varied from 10 to 20% CA. Visual observation after aging showed a clear dilute liquid phase over a cloudy gel-like phase. The large values for the endothermic heat effect cannot be explained by a heat effect associated with mixing of the dilute and concentrated phases, both differing in polymer concentration and nonsolvent composition. Calculation of heats of dilution using interaction parameters (see Appendix) and extreme values for the concentration difference gave values at least one order of magnitude lower than the observed heat effects.

These results are not yet understood. A complicated phase separation process takes place: first there is liquid-liquid phase separation, resulting in a dilute and a concentrated phase, followed by gelation in the concentrated phase. In terms of membrane formation this combined process of liquid-liquid phase separation and gelation accounts for the formation and solidification of the porous substructure in asymmetric membranes.

DISCUSSION

Evidence for Crystallinity

Thermoreversible gels can be obtained from CA in solvent/nonsolvent mixtures of dioxane and water. A high polymer concentration is necessary for the formation of the gel (see Fig. 1). It is argued that the gelation phenomenon is due to a different type of demixing than the liquid-liquid phase separation found earlier²: (i) The systems under study have a composition outside the (extrapolated) liquid-liquid phase separation coexistence lines. Furthermore, even concentrated solutions of CA in dioxane along

(i.e., without nonsolvent) became turbid and gelatinous when cooled from 90 to 20°C: (ii) It takes long aging periods (sometimes days) to obtain effects of demixing that can be detected by DSC measurements. As we know from earlier measurements liquid-liquid phase separation is a fast process.

Crystalline regions are thought to be responsible for the physical cross-links in the demixing that leads to gelation. However, other types of cross-links are not excluded. So far we have no structural evidence for crystallinity in the systems with high water content in the solvent/nonsolvent mixture.

Dayan et al.⁷ recently reported the formation of liquid crystals in solutions of cellulose and cellulose derivatives. Specifically the formation of a liquid-crystalline phase was studied in the system CA/dioxane in the same concentration and temperature range as the DSC experiments reported here. The reported transition temperatures, obtained from a change in birefringence, are lower than the temperatures given in Figure 2. Experiments to determine whether a change in birefringence can be observed in the presence of water are currently under way.

A value for the degree of crystallinity can be found by using the value for the heat of fusion of 9.9 kJ/mol cellulose triacetate (CTA) units, determined by Takahashi.⁸ Takahashi applied the Flory equation⁹ for the melting-point depression to the melting-point curve of CTA in dibutylphthalate. The above-mentioned value corresponds to 25 J/g polymer units (unit molecular weight $M = 288$). The maximum degree of crystallinity observed ranges from 8 (Fig. 2) to even 20% for systems which undergo liquid-liquid phase separation prior to gelation.

Equilibrium Melting Points

The observed melting-point temperature depends on the gelation temperature. Hence interpretation of melting points determined from melting of systems that gel at the gelation temperature as equilibrium melting points is not possible. To obtain true equilibrium values some kind of extrapolation procedure must be used. Recently Borchard et al.⁶ suggested a procedure for the melting of gelatin gels, and also accounted for the effect of crystal size. In order to test the theory of Borchard the same experiments as presented in Figures 2 and 3 should be performed at different crystallization or annealing temperatures.

Although no equilibrium melting points were determined the observed trend that the melting points decrease with increase of nonsolvent content is in agreement with predictions of the Flory equation for the melting-point depression. In order to apply this equation to crystallization of a polymer in a solvent/nonsolvent mixture, the chemical potential of the polymer unit should be modified to include interaction terms of polymer and solvent with nonsolvent. This is done in the Appendix.

Kinetics of the Gelation Process

Especially at low CA concentrations, the effect of increasing water in the solvent mixture is an increase in the heat of melting: assuming a constant heat of fusion, more material crystallizes. Also, there are results showing

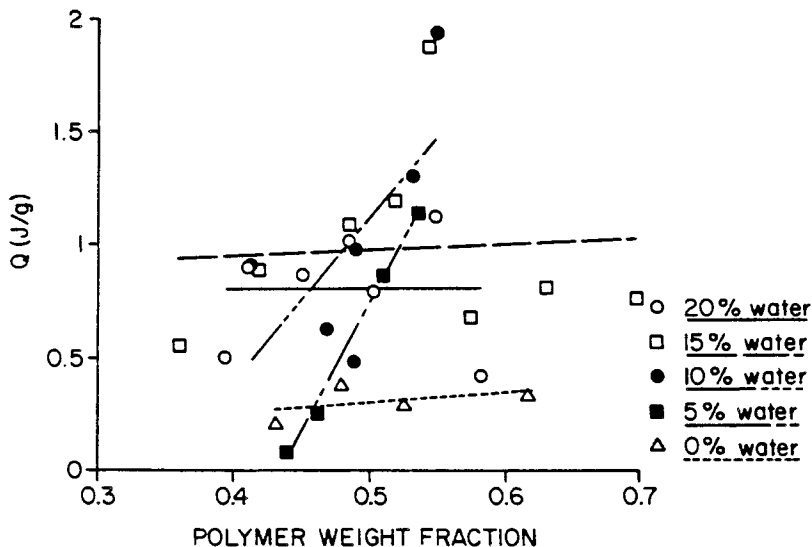


Fig. 3. Heats of melting from DSC as a function of CA weight fraction in the gel for various water contents (key as for Fig. 2) in the water/dioxane mixture.

the positive kinetic influence of water: the area under the endotherm approaches its final value faster.

The gelation process as studied here with DSC is a slow process in the composition regime of the system studied. It is probably also slow on the time scale of the formation of asymmetric membranes, which can be of the order of milliseconds or smaller. Nevertheless, the possible relation of the gelation process studied here and the formation of the dense top layer in asymmetric membranes deserves closer scrutiny. A model recently proposed by Cohen et al.¹⁰ for the formation of porous membranes does not include the possibility of gelation and crystallization in asymmetric membrane formation.

CONCLUSIONS

In the membrane-forming ternary system cellulose acetate/dioxane/water gelation is found to occur at high polymer weight fractions and at relatively low nonsolvent (water) content. Melting points decrease and heats of melting generally increase with polymer concentration and with increase in water content in the solvent/nonsolvent mixture. Gelation through local crystallization is probably the major process leading to the thermoreversible gels.

APPENDIX

The Flory expression for the melting-point depression of a crystalline polymer in the presence of a mixed diluent is derived from (cf. Flory⁹)

$$\mu_u - \mu_u^0 = -\Delta H_u (1 - T_m/T_m^0) \quad (A1)$$

where ΔH_u is the heat of fusion per mole of repeating units, T_m^0 is the equilibrium melting temperature of the pure crystal, and $\mu_u - \mu_u^0$ is the chemical potential difference of the

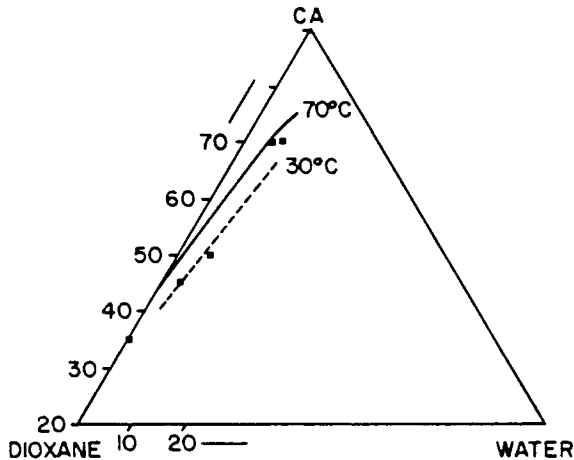


Fig. 4. Composition corresponding to a certain melting point as predicted from the Flory equation for the melting-point depression, modified to include a mixed solvent/nonsolvent. Temperatures 30 (---) and 70°C (—). Experimental points (■) at 70°C.

polymer, per mole of repeating units, in the mixed solvent and the standard (melt) state. An expression for the left-hand side of eq. (A1) is given by Flory⁹:

$$(\mu_u - \mu_u^0)/RT \quad (\text{A2})$$

$$= r \ln w_3 + r(1 - w_3) - w_1 - sw_2 + (g_{13}w_1 + sg_{23}w_2)(w_1 + w_2) - g_{12}w_1w_2$$

where, instead of volume fractions, weight fractions for the three components are used; the free-energy correction factors g_{12} , g_{13} , and g_{23} are those of Koningsveld¹¹; and r and s are the molecular weight ratios M/M_3 and M_1/M_2 , respectively. After insertion of eq. (A2) in (A1) and rearrangement, the melting-point depression in the presence of a mixed diluent is given by

$$\frac{1/T_m - 1/T_m^0}{w_2} = \frac{RM_u}{\Delta H_u M_1} \{-p - s + w_2[p^2g_{13} + p(g_{13} + sg_{23} - g_{12}) + sg_{23}]\} \quad (\text{A3})$$

where $p = w_1/w_2$ is the ratio of weight fractions of the diluents. The following values for the parameters of eq. (A3) are used: (1: water, 2: dioxane, 3: CA) $M_u = 288$, $M_1 = 18$, $M_2 = 88$, $M_3 = M_n = 23,000$, $g_{12} =$ (ref. 13), $g_{13} = 1.4$, $g_{23} = 0.4$, $\Delta H_u = 10$ kJ/mol (ref. 8), $T_m^0 = 579$ K (ref. 12). In Figure 4 the relation between the polymer concentration and composition of the solvent mixture is presented at constant melting points of 30 to 70ldgC. The experimentally found trend that the melting point decreases with increasing nonsolvent content follows the prediction from eq. (A3).

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