The "Cold-Solutioning" Phenomenon in Cellulose Triacetate–Acetone Mixtures

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ABSTRACT: Direct mixing of cellulose triacetate (CTA) in acetone at room temperature produces only an opaque swollen gel at all concentrations. However, cycling the mixture between room temperature and $-78 \pm 3°C$ results in a stable solution at room temperature, if the concentration is less than 6% (w/w). This process has been called "cold-solutioning." Such a process also produces a clear solution at concentrations between 6% (w/w) and 10% (w/w); however, in time, the solution separates slowly into at least two phases, a clear liquid and an opaque gel phase. At concentrations above 10% (w/w) and below 20% (w/w), the system exhibits two phases. A completely opaque swollen gel forms at concentrations of 20% (w/w) and above. The above-described cold-solutioning phenomena are shown to be the coupled kinetic and thermodynamic consequences of (1) the large thermal stresses that would result from thawing a swollen mixture of CTA and acetone, arising from the large differences in their thermal expansion coefficients; and (2) the "bimodal" composition of the cellulose derivative. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1697–1707, 2003

Key words: cellulose acetate; phase behavior; phase separation; thermodynamics; separation of polymers

INTRODUCTION

The influence of the degree of substitution in cellulose acetate (CA) on its solubility characteristics has been investigated by several researchers.[1–5] At low degrees of substitution (0.6–0.8), cellulose acetate is soluble in water. Cellulose diacetate, with a degree of substitution ranging from 2.2 to 2.5, is readily soluble in acetone. However, fully acetylated cellulose [cellulose triacetate (CTA)] is insoluble in water and only partially soluble in acetone. CTA is a highly crystalline polymer and has several applications, such as fibers for tobacco filters,[6] membrane materials for reverse osmosis[7] and for separating chiral isomers,[8,9] and as micro-biosensors for clinical analyses.[10] A significant fraction of the commercially used CTA is in the form of fibers. These fibers are produced by the extrusion of CTA–methylene chloride solutions. The basic nature of CTA also renders it soluble in other acidic solvents, such as chloroform and tetrachloroethane.

Although methylene chloride is a good solvent for CTA, and also has suitable volatility for processing, it is carcinogenic and has been classified as one of 33 draft urban area source hazardous air pollutants by the U.S. Environmental Protection Agency.[11] Efforts are being made to substitute methylene chloride with a solvent or a mixture of solvents that (1) can dissolve CTA up to at least 20% (w/w) in concentration, (2) is relatively nontoxic or capable of being converted to nontoxic products (e.g., through oxidation), and (3) is low boiling so that the solvent can be driven off easily in fabrication processes, such as dry spinning of fibers. One solvent that satisfies the latter two of the three conditions is acetone.

Cowie and Ranson[1] investigated the potential of acetone as a solvent for CTA as early as 1971. Direct mixing of cellulose triacetate with acetone at room temperature results only in a swollen heterogeneous gel phase that is optically opaque at all concentrations. However, upon repeated freezing and thawing of a 2% (w/w) mixture of CTA and acetone between room temperature and approximately $-78°C$, a completely miscible stable solution is produced at room temperature. Other studies have shown that, at higher concentrations [2–10% (w/w)], a single-phase solution is gradually produced with repeated thermal cycling; however, it begins to phase separate and exhibits turbidity over an extended period of time (>20 days).[12] This phenomenon of solubilization has been referred to as "cold-solutioning,"[1] although this term could be misleading in this regard: formation of the solution, if

it occurs, is at the thawing temperature and not at the "cold" temperature in this process.

The work reported here was carried out primarily to address the following two questions.

1. Can acetone serve as a solvent for CTA, with the potential for integration into suitable processing methods?
2. Can the cold-solutioning process be rationalized through thermodynamic/kinetic considerations?

EXPERIMENTAL

Materials

Cellulose triacetate was obtained from Celanese Acetate (Charlotte, NC) and used as received. The average degree of substitution ⟨DS⟩ for this sample was 2.91. Acetone (Spectranal, >99%), methylene chloride (>99.9%), and methanol (>99.5%) were obtained from Aldrich (Milwaukee, WI) and used as received.
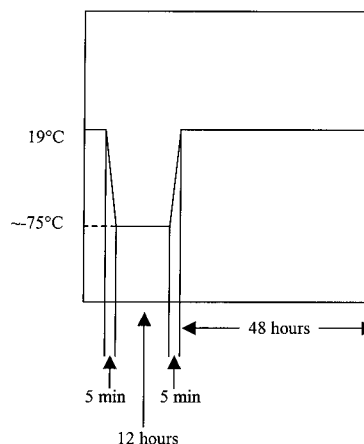
RT–cold-solutioning

Henceforth, the process that constitutes thermal cycling between −78°C and room temperature will be referred to as RT–cold-solutioning. Mixtures of cellulose acetate and acetone of different concentrations were prepared in 15-mL airtight screw-cap vials. These samples were then immersed in a mixture of dry ice and acetone (−78 ± 3°C) and held for about 12 h. The samples were then thawed at room temperature (19°C) for at least 10 h. The mixtures/solutions were not stirred. The thermal cycling was repeated at least three times. Weight measurements showed no detectable loss of acetone. The system was monitored visually to identify any phase separation. In the cases that produced phase separation, the system was found to be composed of two phases, a supernatant liquid and a gelled phase. The two phases were separated and the polymers were recovered from each phase by evaporating the solvent and analyzed for molecular weight and degree of substitution. The polymer concentration in each phase was also measured by weighing before and after solvent evaporation.

Molecular weight

Molecular weights of the polymers in the supernatant and gelled phases were determined by gel permeation chromatography at 19°C, using polystyrene standards. Samples of the polymers were prepared in a 91/9 (v/v) mixture of methylene chloride and methanol solution. The same solvent composition was also used as the mobile phase in chromatography. Because the samples do not absorb in the UV region, an evaporative light-scattering detector was used.
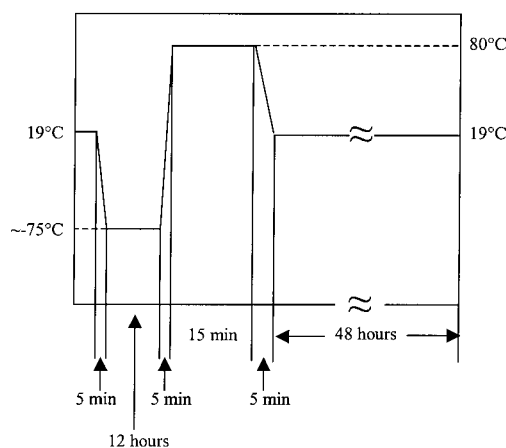
Figure 1 Freeze–thaw cycles for CTA–acetone mixtures: (a) RT–cold-solutioning and (b) HT-RT–cold-solutioning. The plot represents the approximate time–temperature profile used in the experiment.

Degree of substitution (ds)

The degrees of substitution of the polymers isolated from the supernatant and gelled phases were measured by reverse-phase liquid chromatography. Floyd[13] previously provided the details regarding the calibration of retention time versus degree of substitution. The samples were prepared in a 91/9 (v/v) mixture of methylene chloride and methanol. A linear gradient elution of acetone with a mixture of water and methanol (50/45/5 v/v/v) was used as the mobile phase, and an evaporative light-scattering detector was used.

HT-RT–cold-solutioning

CTA–acetone mixtures at four different concentrations [10, 12, 15, and 17% (w/w)] were subjected to the freeze–thaw cycles illustrated in Figure 1. The samples of the mixture were first frozen at the temperature of

TABLE I
Nomenclature Vis-à-Vis the Polymer Fractions
(Original polymer: CTA; ⟨DS⟩ = 2.91)

Polymer	Average degree of substitution, ⟨DS⟩		
	2.58	2.88	2.94
In supernatant phase (SP)	SP-L	SP-H	—
In gel phase (GP)	GP-L	—	GP-H

a dry ice–acetone mixture (−78 ± 3°C) and held for about 12 h. They were then immersed in a water bath maintained at the specified thawing temperatures. The process of gel disappearance was followed visually. The mixtures were held at the thaw temperatures for about 15 min, until the first evidence of boiling of acetone was observed. The samples were then brought to room temperature and monitored for 48 h.

The process in which the initial thawing is carried out at a temperature higher than room temperature will be referred to as HT-RT–cold-solutioning. Because mixtures at concentrations higher than 17% remained mostly gelled even after this process, they were not used further in these experiments.

Nomenclature

The cellulose triacetate, as received, will be referred to as the "original" or "original unfractionated" polymer and will be denoted by the term "CTA." Henceforth the polymer isolated from the clear supernatant phase will be referred to as SP and that isolated from the gel phase as GP. The notation ⟨DS⟩ will be used to indicate the average degree of substitution of all samples, determined by reverse-phase liquid chromatography. Additional nomenclature for the different cellulose acetate fractions is summarized in Table I.

RESULTS AND DISCUSSION

Polymer concentrations

The mixing of CTA and acetone at room temperature produces a swollen gel at all compositions. When mixtures with concentrations of CTA less than 6% (w/w) are subjected to RT–cold-solutioning, clear single-phase solutions are produced. These solutions remain stable over extended periods of time (>3 months). Mixtures in the concentration range 6–12% (w/w) also produce single-phase solutions after three or four freeze–thaw cycles, but ultimately these are found to be unstable, phase separating over a period of 5–6 days. Mixtures in the range of 12% (w/w) to about 20% (w/w) do not produce single-phase solutions even after several freeze–thaw cycles and the 20% (w/w) mixture remains completely opaque under these conditions. The following results show clearly

that a combination of kinetic processes as well as the dictates of equilibrium thermodynamics influence phase separation in CTA–acetone mixtures.

1. Direct mixing of CTA–acetone at room temperature does not produce a solution at any concentration.
2. RT–cold-solutioning of a mixture with <6% (w/w) CTA produces a single-phase solution that is stable over an extended period.
3. RT–cold-solutioning of mixtures with CTA in the intermediate concentration range [6–12% (w/w)] initially produces a single-phase solution, but eventually separates into liquid and gel phases.
4. RT–cold-solutioning produces at least a partially miscible system up to CTA concentrations of 17% (w/w).

To help decipher the phase behavior of CTA–acetone mixtures, the concentrations of the polymer in both the clear and gelled phases were measured as a function of the overall composition of CTA in the mixture. In the event that the phase separation observed in the CTA solutions constituted simple liquid–liquid phase separation of a binary mixture, the concentration within each of the two phases must remain invariant with respect to the overall composition of the mixture. This follows directly from the fact that a binary mixture has a unique free energy versus concentration curve at a given temperature. However, it can be seen from Figure 2 that the concentration of the polymer in the clear phase increases measurably with increasing overall concentration of the mixture. This
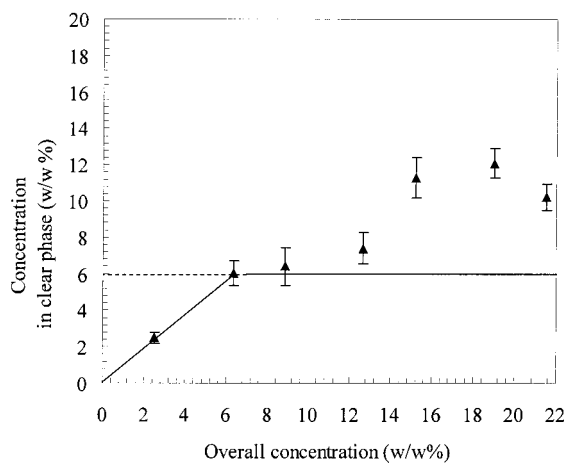
Figure 2 (a) Plot of concentration of the clear phase obtained with RT–cold-solutioning of the CTA–acetone mixture, as a function of overall concentration of the mixture. The full line represents the hypothetical concentration of the clear phase that would have been obtained with liquid–liquid phase separation in a purely binary system, with the extrapolated concentration, shown by the intercept of the dotted line, corresponding to its solubility limit.

observation provided the first indication that the CTA was likely to be heterogeneous with regard to its solution behavior, that is, it consisted of two or more components that differed in chemical nature and/or molecular weight, which precluded it from exhibiting true binary solution behavior. Nevertheless, although a distribution either in the degree of substitution or in molecular weight can cause certain polymer–solvent mixtures to deviate significantly from binary solution behavior, many such cases still do exhibit a pseudo-binary behavior.[14,15] To determine the factors responsible for the observed cold-solutioning behavior of the CTA–acetone mixtures of different overall concentrations and its deviation from binary solution behavior, the polymer was isolated from each of the two phases, by evaporation of acetone, and analyzed.

Degree of substitution and molecular weight

The degree of substitution of the polymers that were isolated from the liquid (SP) and gelled (GP) phases was measured by reverse-phase liquid chromatography. The typical intensity versus retention time plots (Fig. 3) show that each phase is composed of at least two polymer components with distinctly different $\langle DS \rangle$. In both chromatograms, the peak with the lower retention time (R_t) corresponds to a $\langle DS \rangle$ = 2.58. The lower $\langle DS \rangle$ fraction of the polymer in the SP and GP phases will be denoted as SP-L and GP-L, respectively. In the chromatogram of SP, the peak with the higher R_t corresponds to $\langle DS \rangle$ = 2.88 (SP-H), whereas in GP, this component corresponds to $\langle DS \rangle$ = 2.94 (GP-H) (cf. Fig. 3 and Table I). The $\langle DS \rangle$ corresponding to each of the two components in SP and in GP is shown, as a function of the overall concentration of the original mixture, in Figure 4(a). In both SP and GP, the lower $\langle DS \rangle$ component constitutes only a minor fraction [<2.5% (w/w)] of the polymer. The weight fraction of SP-L in SP is slightly higher than that of GP-L in GP [cf. Fig. 4(b)].

The molecular weights of the two fractions were also measured and found to be similar in the clear supernatant liquid and gelled phases [cf. Fig. 5(a)]. The polydispersity of the samples is in the range of 2.5–3.1 [cf. Fig. 5(b)].

To verify whether the small, but measurable, differences in the compositions of the polymers in SP and GP could cause the apparently large differences observed in their solution behavior, the solubility characteristics of the polymer from each phase were determined separately. The polymer in each case was added gradually to acetone under constant stirring and subsequently subjected to cold-solutioning. The solubilities were determined through visual observation of turbidity.

The solubility limit of SP in acetone is 12% (w/w), whereas the solubility of GP is only 5% (w/w) (both at
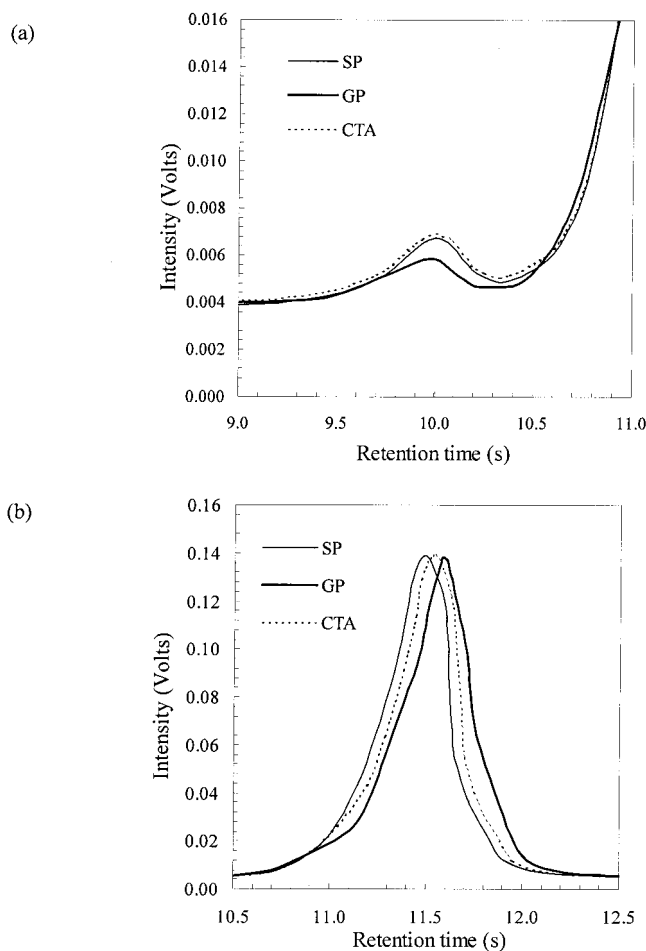
Figure 3 Reverse-phase liquid chromatograms of SP, GP, and the original unfractionated CTA. (a) Peaks corresponding to SP-L, GP-L, and the low $\langle DS \rangle$ fraction in the original CTA. (b) Peaks corresponding to SP-H, GP-H, and the high $\langle DS \rangle$ fraction in CTA.

19°C). SP and GP can be considered as random copolymers with different distributions of acetyl groups along their backbone. The slight difference in the $\langle DS \rangle$ of 0.06 between SP-H and GP-H appears sufficient to influence their solubility in acetone significantly. The fraction of SP-L in the supernatant is slightly higher than the fraction of GP-L in the gel, but the extent to which this affects solubility is not clear. In all subsequent discussions of phase behavior, "CTA" is treated as a binary system, consisting of SP and GP, with cognizance of the fact that each, in turn, is composed of a small fraction of polymer with $\langle DS \rangle$ = 2.58.

Phase behavior of cellulose acetate–acetone mixtures: equilibrium aspects

It is clear from the above results that CTA is composed of a distribution in both degree of substitution and molecular weight (polydispersity). The presence of multiple polymeric components in a mixture complicates the phase behavior of the system. It is well

known that free-energy surfaces have to be invoked to describe phase equilibria in such mixtures.[16-18] The essential elements of such descriptions, with regard to the CTA–acetone mixtures of the present study, are summarized in the following discussion.

Typical free-energy surfaces for polymer/polymer/solvent systems are shown in Figure 6. The free-energy surface for a mixture that separates into two phases is characterized by two minima. A plane can be constructed that is tangential to the surface at two points (M_1 and M_2). The compositions corresponding to these points represent the equilibrium compositions of the two polymeric components in the two phases.

The process of phase separation in a ternary mixture can be understood using the diagram shown in Figure 7. Consider a mixture of two polymeric components, P_1 and P_2, in a solvent S. These two components may differ in one or more aspects, such as chemical nature, molecular weights, and tacticity, for example. The discussions here will be restricted to the case in which P_1 is treated as analogous to the polymer in SP and P_2 to

(a)

(b)
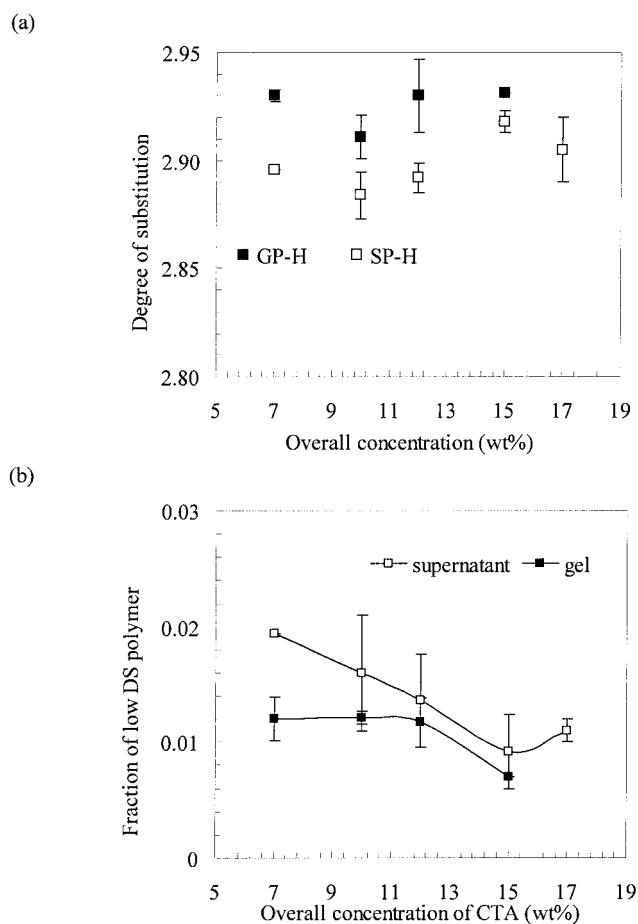
Figure 4 (a) Degree of substitution of cellulose acetate in the supernatant liquid and gel phases, as a function of the overall concentration of the mixture. (b) Weight fraction of the low DS polymer in the two phases as a function of overall concentration.

(a)

(b)
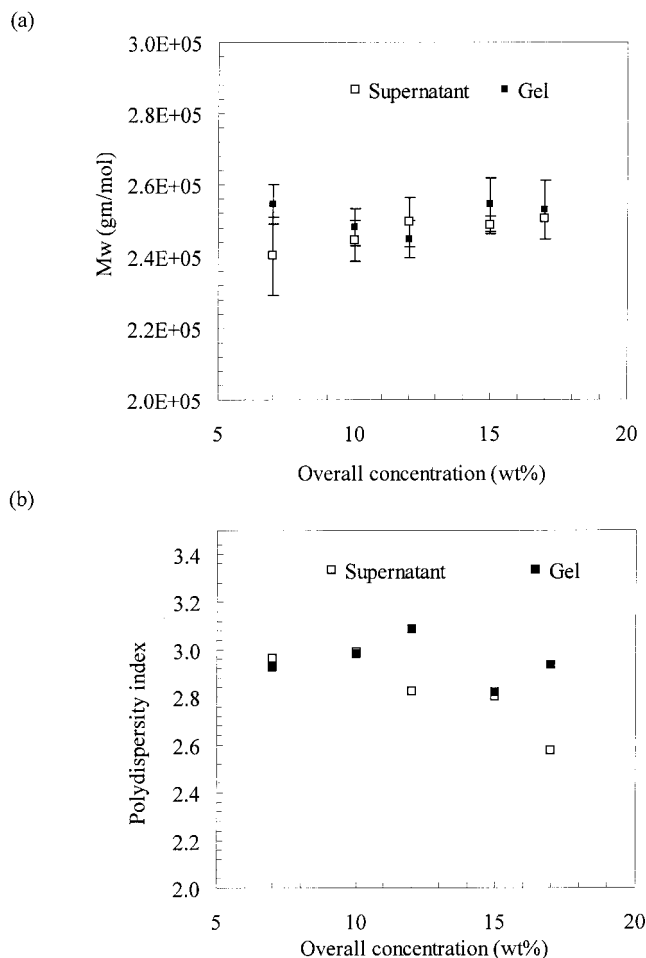
Figure 5 (a) Molecular weights of the polymer isolated from the supernatant liquid and the gel phases, as a function of the overall concentration of the mixture. (b) Polydispersity index of SP and GP as a function of the overall concentration of the mixture.

that in GP. The apices of the triangle in Figure 7 represent the pure components. X in the figure represents the composition variable of the polymer mixture. The line SX will denote all possible solutions consisting of P_1, P_2, and S for a fixed ratio P_1/P_2. A change in P_1/P_2 will change the location of SX, the new compositions being given by SX_1, SX_2, and so forth. For purposes of discussion, the ternary system can be treated as a pseudobinary mixture, composed of a polymeric component, with a given ratio of P_1/P_2, and a solvent. Therefore, at each temperature and for each compositional ratio P_1/P_2, a free-energy curve can be constructed as a function of the overall concentration of the polymer or solvent in the mixture. The equilibrium compositions are obtained by the tangent construction in those cases where the free-energy curve displays two minima. When this procedure is repeated for different P_1/P_2 ratios, binodal curves can be constructed at each temperature. When repeated at different temperatures, this procedure generates the
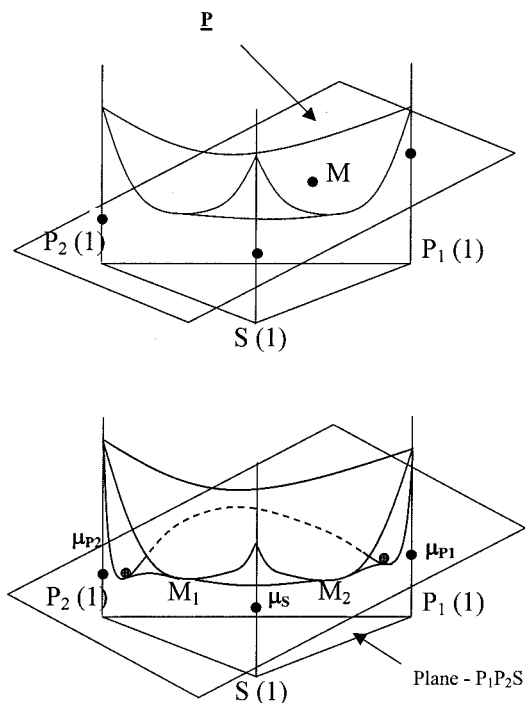
Figure 6 (a) Hypothetical free energy surface for a two-component polymer $(P_1 + P_2)$ + solvent (S) system, with a single minimum in the free-energy (ΔG_m) surface. **P** indicates the plane that is tangential to the free energy surface. M represents the minimum in the free-energy surface. A single minimum in ΔG_m implies a single-phase mixture of P_1, P_2, and S. (b) When the free-energy surface has two minima, a unique plane can be drawn tangential to the ΔG_m surface. The points at which the plane is tangential to the surface (M_1 and M_2), represent the binodal compositions when projected on the plane P_1P_2S. $P_1(1)$, $P_2(1)$, and $S(1)$ refer to pure P_1, P_2, and S, respectively. The corresponding chemical potentials of the three components are denoted by μ, with the appropriate subscripts.

binodal surface. In the case of cellulose triacetate–acetone, it is highly improbable that there exists a ratio P_1/P_2 at which the mixture is a single phase at all compositions because both polymers (in SP and GP) have a finite solubility limit in acetone. This implies that any line SX will necessarily intersect the binodal curve.

The same binodal surface can be generated experimentally by measuring cloud points as follows (cf. Fig. 8). We start with a mixture of solvent, and the pseudosingle polymer component with a composition ratio P_1/P_2 (determined by line SX). Varying the temperature of this mixture and observing the onset of turbidity can generate a liquid–liquid coexistence curve. This is repeated for different P_1/P_2 ratios for a constant overall polymer concentration. Each cloud point curve thus generated will correspond to unique ratios, P_1/P_2, determined by the lines SX_1, SX_2, SX_3, and so forth, and will represent quasi-binary sections of the phase diagram. The envelope of all these binodal curves will produce the binodal surface.

Thus, even under the simplifying assumptions of treating the CTA–acetone system as a ternary mixture,
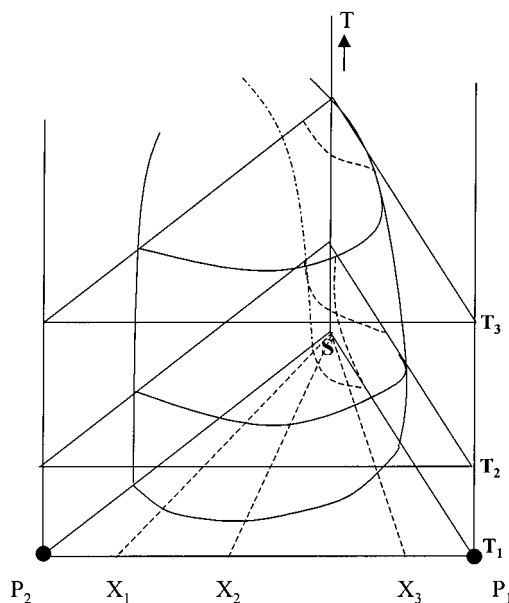
Figure 7 Schematic of the binodal surface of a ternary system (2 polymers + solvent). A unique binodal curve will be present at each temperature for a ternary system. The 3-D envelope is constituted by these individual binodals. In the case shown here, P_1 and P_2 are completely miscible. Both P_1 and P_2 are partially miscible with S. The various points are explained in the text.

it is obvious that a binodal surface is necessary to describe its phase behavior. Although the quantitative aspects of the CTA–acetone system are likely to be more complex than that of even a ternary system, the experimental observations described earlier can still be rationalized using such ternary diagrams. For ex-
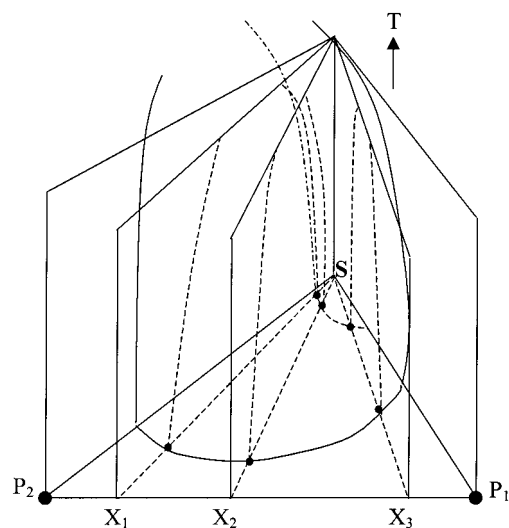

Figure 8 Alternate method of constructing the binodal surface for a ternary mixture. The slices represent the coexistence curves at a constant P_1/P_2. The line SX, in general, represents all possible mixture compositions of constant polymer ratio (P_1/P_2). P_1 and P_2 correspond to SP and GP, respectively.

ample, the change that is observed, within the two-phase region, in the concentration of the polymer in the clear phase at a constant temperature, would be a direct consequence of the ternary nature of the CTA–acetone mixture. Increasing the overall concentration of the polymer corresponds to traversing the gedanken phase diagram (cf. Fig. 8) along the line SX toward the axis P_1–P_2 (Fig. 9). Addition of "CTA" still ensures a constant ratio P_1/P_2. At overall concentrations less than 6% (w/w), the mixture lies in the single-phase region at room temperature. In the two-phase region corresponding to CTA concentrations above 6% (w/w), the compositions of the two phases will be dictated by the tie lines at that temperature. The composition in the clear phase continually changes because different tie lines intersect the line SX at different overall concentrations, as shown schematically at room temperature in Figure 9. A mixture with overall composition given by P' will separate into two phases of composition G_1 and S_1, respectively. When the overall concentration of the polymer is increased to P", the phase-separated mixture will have the compositions given by points G_2 and S_2. Thus, at the same temperature, two phases of varying compositions can be produced. This is most likely the reason for the observed change in the polymer concentration of the SP with increasing overall concentration of CTA above 6% (w/w). After each addition of CTA, partitioning of the low and high DS fractions into the supernatant and gelled phases will occur. Experimental measurements of such phase diagrams are necessary to quantitatively rationalize the solution behavior of cellulose acetate–acetone mixtures.

Cold-solutioning: kinetic and thermodynamic effects

The discussion in the previous section serves to rationalize the following experimental observations.
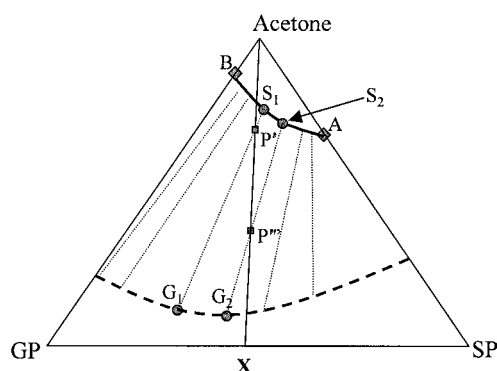
Figure 9 Isothermal phase separation in a ternary mixture. SP refers to the polymer recovered from the supernatant liquid phase and GP refers to the polymer from the gel phase. A and B represent the limits of solubility of SP and GP in S. The line SX represents all possible mixture compositions of constant polymer ratio (SP/GP).
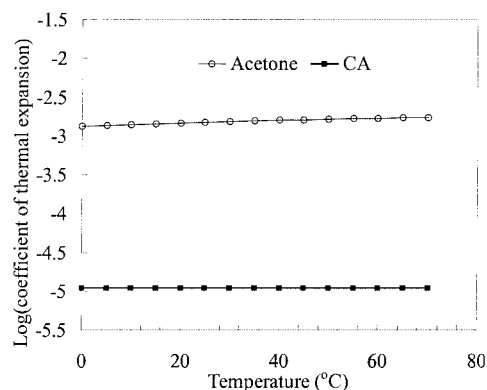
Figure 10 Thermal expansion coefficients of acetone and cellulose diacetate. Data taken from Perry's Chemical Engineers Handbook.[19]

1. The CTA–acetone mixture can exist as a stable single-phase solution at concentrations < 6% (w/w).
2. In the range from 6 to 17% (w/w), the mixture's stable configuration consists of a two-phase mixture, with the concentration of the polymer in each phase changing with the overall concentration of the mixture.

However, the following significant questions still remain to be addressed.

3. At concentrations below 6% (w/w), why does the mixture form a clear solution at room temperature only upon subjecting it to the cold-solutioning process?
4. At concentrations between 6 and 17% (w/w), why does cold-solutioning lead to the formation of a clear single-phase solution initially at room temperature, but phase separates, over an extended period of time, into the gel and liquid phases?

CTA is a highly crystalline polymer. Any solvent for CTA will be effective only if it is able to disrupt/penetrate the crystalline domains of CTA. One way to accomplish this is to establish sufficient thermomechanical stresses within the polymer. The rapid freezing and thawing of CTA–acetone mixtures can cause increased disruption of the crystalline portions of CTA. Because the coefficients of thermal expansion of acetone and CTA differ by more than two orders of magnitude (Fig. 10),[19] rapid freezing and thawing of the swollen semicrystalline polymer can lead to high internal stresses. The fact that, even at low concentrations [<6% (w/w)], a solution is *not* formed when CTA and acetone are mixed directly at room temperature, but does so upon cold-solutioning, can be attributed directly to the large internal stresses that serve to break up the swollen crystalline CTA net-
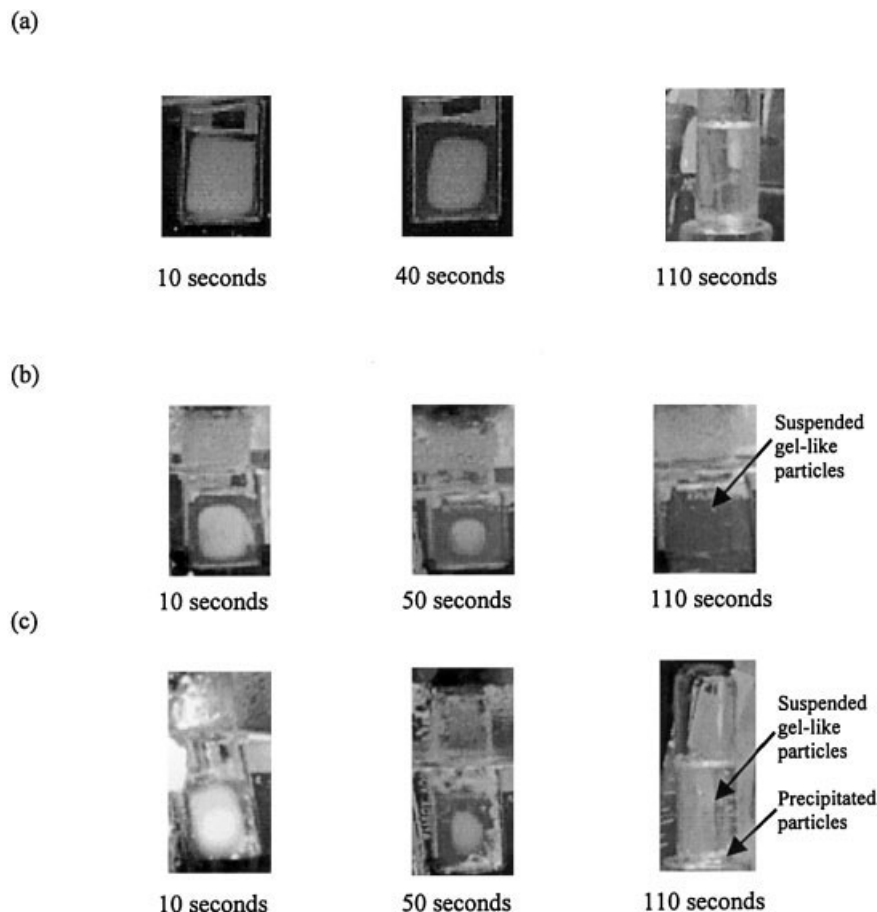
Figure 11 Gel dissolution in (a) 10% (w/w), (b) 15% (w/w), and (c) 17% (w/w) mixture of unfractionated CTA and acetone (HT-RT–cold-solutioning). The freeze–thaw cycle is discussed in the text. The photographs were taken at the indicated times, after the mixture was immersed in the 80°C water bath.

work. The above rationale was verified through the HT-RT–cold-solutioning experiments, changing the temperature at which the frozen mixtures were thawed.
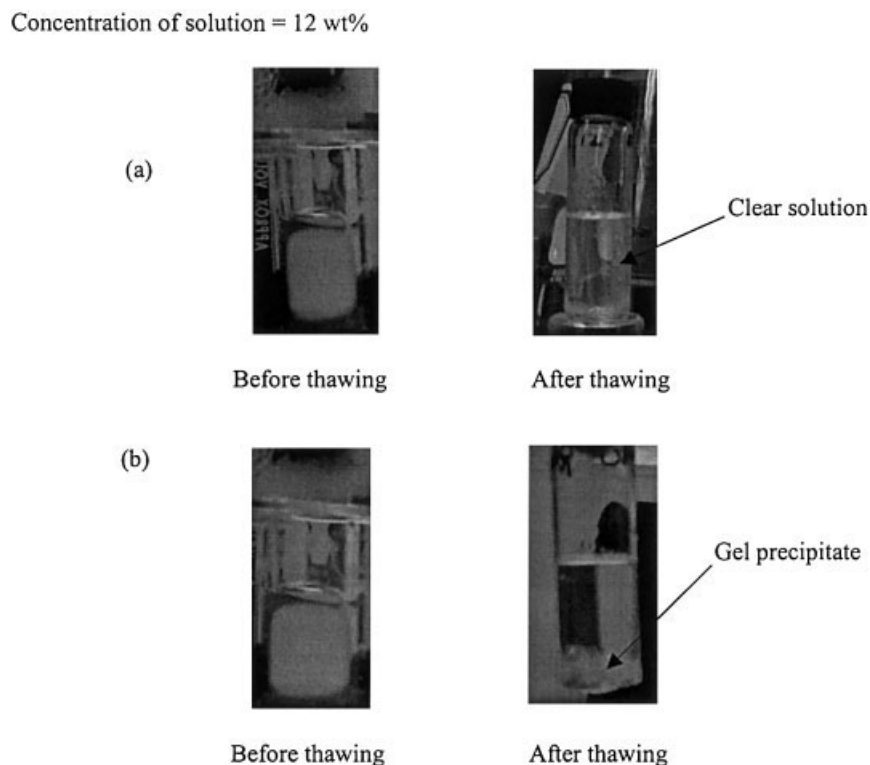
The results of the HT-RT–cold-solutioning experiments are shown in Figure 11(a)–(c). On thawing frozen mixtures of CTA and acetone at 80°C, a progressive disappearance of the gel phase can be observed as a function of time. In the case of the 10% (w/w) mixture, a clear solution forms almost immediately upon thawing at that temperature [cf. Fig. 11(a)]. If these mixtures are brought to room temperature and monitored, a two-phase mixture is formed in all cases after 48 h. As the concentration is increased to 15% (w/w), some gel-like suspended particles are observed upon thawing [cf. Fig. 11(b)]. Even at overall concentrations as high as 17% (w/w) [cf. Fig. 11(c)], almost clear solutions, with only some suspended and precipitated gel-like particles, are formed rapidly at the higher rates of thawing.[20] However, all the "solutions" with concentrations > 10% (w/w) exhibited subsequent phase separation at room temperature in 24 h or longer, showing that the rapid freeze–thaw

cycles produced only a meta-stable state at these concentrations.

The process of rapid thawing was also used with solutions of the polymers that were isolated separately from the liquid and gelled phases (SP and GP). The results are shown in Figure 12 for a solution concentration of 12% (w/w). Even after repeated thermal cycling with rapid thawing, the polymer isolated from GP is not solubilized. However, the polymer isolated from the SP phase is soluble in acetone at this concentration. These results lend strong credence to the conjecture that even small differences in the degree of substitution of cellulose acetate can significantly affect its solubility in acetone.

The phase separation of a random copolymer into two or more daughter phases has been well known[21] and it is also the subject of some recent theoretical investigations.[22,23] Cellulose acetates of different degrees of substitution are actually random copolymers, characterized by an average acetyl content. Upon cold-solutioning, phase separation can occur with fractionation of chains based on differences in ⟨DS⟩, this separation being driven by the differences in com-

Concentration of solution = 12 wt%

(a)

Before thawing   After thawing

Clear solution

(b)

Before thawing   After thawing

Gel precipitate

Figure 12 Results of cold-solutioning of the polymers recovered from the supernatant liquid (SP) and the gel (GP) phases: (a) The SP and (b) the gelled polymer (HT-RT–cold-solutioning). The results after three cycles are shown in the figure. The pictures on the right were taken after cooling the solutions to room temperature and before phase separation set in the solution of the supernatant polymer.

patibility of the respective polymer fractions with acetone. Thus, CTA with $\langle DS \rangle$ = 2.91 phase separates in acetone upon cold-solutioning into a gelled phase consisting predominantly of a polymer with $\langle DS \rangle$ = 2.94 and a liquid phase consisting of a polymer with $\langle DS \rangle$ = 2.88.

The inference that results from the present study regarding a plausible pseudobinary phase diagram for pure cellulose acetate of different degrees of substitution in acetone is shown in Figure 13. This figure represents the overlay of phase diagrams for cellulose acetate of $\langle DS \rangle$ = 2.88, $\langle DS \rangle$ = 2.94, and the original unfractionated "CTA." The solvent in all cases is acetone. Both solid–liquid and liquid–liquid phase separation can occur in these polymers. The location of both the binodal and crystallization curves will depend on the degree of substitution. The lower the $\langle DS \rangle$ in the range 2.0–3.0, the larger would be the single-phase region.

Data on critical temperatures are not available. However, the cloud point data of Cowie and Ranson,[1] reported at concentrations less than 3% (w/w), are included in Figure 13. The data in the single-phase and two-phase regions for samples $\langle DS \rangle$ = 2.88, $\langle DS \rangle$ = 2.94, and "CTA" were obtained by visual inspection. This composite phase diagram reveals that, at room temperature, the original "CTA," and the com-

ponents of $\langle DS \rangle$ = 2.88 and $\langle DS \rangle$ = 2.94, all exist as phase-separated systems, albeit over different ranges of concentration. At concentrations up to 12% (w/w), the $\langle DS \rangle$ = 2.88 polymer forms a single phase in acetone, but this limit is only 5% (w/w) for the $\langle DS \rangle$ = 2.94 polymer. Complete miscibility could not be achieved on heating mixtures of these polymers in acetone at concentrations > 12% (w/w). Thus, there does not appear to be a single-phase region at any temperature in the high concentration regime.

Interplay between equilibrium and kinetic aspects

It is clear from the above-discussed set of results that the following significant kinetic and thermodynamic aspects govern the phenomena observed in cold-solutioning of CTA–acetone mixtures:

1. The effect of the cold-solutioning process is essentially to cause large internal stresses to arise from the fact that the bulk thermal expansion coefficients of CTA and acetone differ by two orders of magnitude, about 10^{-5} K^{-1} for CTA and about 10^{-3} K^{-1} for acetone.
2. The Gibbs energies at room temperature have to be such that the following relations hold at the respective overall concentrations.
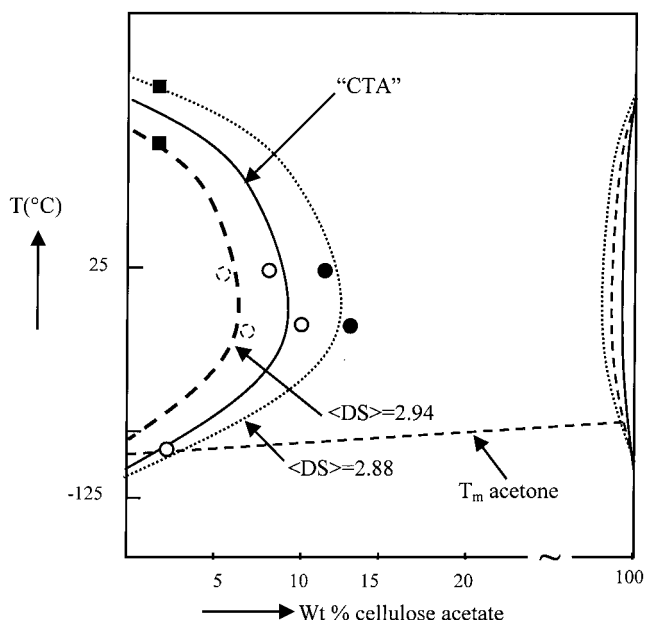
Figure 13 Overlay of possible partial phase diagrams for cellulose acetate of different average degrees of substitution, and acetone. Experimental data are shown by circles. ◌ ⟨DS⟩ = 2.94; ○ "CTA"; and ● ⟨DS⟩ = 2.88. ■ represents cloud point data obtained from Cowie and Ranson.[1]

At low concentrations [i.e., <6% (w/w)],

$$G^*_{CTA+acetone} > G_{CTA+acetone} > G_{"CTA-acetone"\,solution} \quad (1)$$

In the intermediate range from 6 to 17% (w/w),

$$G^*_{CTA+acetone} > G_{CTA+acetone} > G_{"CTA-acetone"\,solution}$$
$$> G_{"CTA1-acetone"\,liquid+"CTA2-acetone"\,gel} \quad (2)$$

At concentrations > 17% (w/w),

$$G_{"CTA-acetone"\,solution} > G^*_{CTA+acetone} > G_{"CTA-acetone"\,gel} \quad (3)$$

In the above equations, CTA refers to the unfractionated polymer and CTA_1 and CTA_2 are, respectively, the fractions with lower and higher average degrees of substitution. Also, "*" refers to the stressed state of the mixture, caused by the substantial thermal expansion mismatch between CTA and acetone.

In the intermediate range, the cold-solutioning process initially produces the CTA–acetone solution because it is thermodynamically favored with regard to phase-separated CTA and acetone, and its formation does not require demixing of the CTA into two (or more) fractions. However, with time for polymer–polymer demixing, this system undergoes separation into a gel phase and a liquid phase, consisting of different fractions of the original CTA in the two phases. In contrast to small molecular systems, the demixing process in polymer solutions can be signif-

icantly influenced by the relatively slow diffusion of the polymeric species.[24–26] In such mixtures (high molecular weight polymer mixture + solvent), it is possible to produce meta-stable single-phase solutions, which remain in that state for extended periods of time, before ultimately undergoing phase separation.

CONCLUSIONS

A large difference is observed in the room-temperature solubilities in acetone of cellulose triacetate polymers. Two fractions of the original CTA polymer that differ in ⟨DS⟩ by only 0.06 exhibit a large difference in their solubility limits (12% versus 5%) in acetone. Also, the original "mixed" polymer has a solubility limit of only 6%. The large differences in solubility, which can arise from relatively small differences in ⟨DS⟩, show that identification of a suitable solvent or solvent system for cellulose triacetate would be greatly facilitated by increasing its compositional homogeneity, that is, reducing its distribution of DS and molecular weight. Within their thermodynamically dictated solubility limits, formation of the solution could be kinetically facilitated by the internal stresses that can be generated through a cold-solutioning process, that is, cycling the swollen polymer–solvent mixture between the solution temperature and a significantly lower temperature.

References

1. Cowie, J. M. G.; Ranson, R. J. Die Makromol Chem 1971, 143, 105.
2. Kamide, K.; Saito, M.; Kowsaka, K. Polym J 1987, 19, 1377.
3. Kamide, K.; Okajima, K.; Saito, M. Polym J 1981, 13, 115.
4. Kamide, K.; Okajima, K.; Kowsaka, K.; Matsui, T. Polym J 1987, 19, 1405.
5. Ilyina, E. E.; Daragen, V. A.; Prisment, A. E. Macromolecules 1993, 26, 3319.
6. Raban, J.; Erxleben, E.; Wildenau, W. Ger. Pat. DE 1923114, 1969.
7. Kesting, R. E. Synthetic Polymer Membranes: A Structural Perspective; Wiley: New York, 1985.
8. Martens, J.; Bhushan, R. J Liq Chromatogr 1992, 15, 1.
9. Lepri, L.; Coas, V.; Desideri, P. G.; Zocchi, A. J Planar Chromatogr-Mod TLC 1994, 7, 103.
10. Tamiya, E.; Karube, I. Sens Actuators 1988, 15, 199.
11. U.S. EPA. Air Toxics, National Air Quality and Emissions Trends Report No. 75, 1997.
12. Brodof, T. Celanese Acetate Company, Charlotte, NC, Personal communication.

13. Floyd, T. R. J Chromatogr 1993, 629, 243.
14. Smartt, W. M. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1993.
15. Akki, R. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1995.
16. Koningsveld, R.; Staverman, A. J. Kolloid Z Z Polym 1967, 218, 114.
17. Koningsveld, R.; Staverman, A. J. Kolloid Z Z Polym 1967, 220, 31.
18. Koningsveld, R.; Kleintjens, L. A.; Schultz, A. R. J Polym Sci A-2 1970, 8, 1262.
19. Perry, R. H.; Green, D. W.; Maloney, J. O., Eds. Chemical Engineers Handbook; McGraw-Hill: New York, 1984.
20. These high overall concentrations produced essentially two-phase mixtures under slow thawing conditions, with the gel phase constituting the major volume fraction.
21. Scott, R. J. J Polym Sci 1952, 9, 423.
22. Sollich, P.; Cates, M. E. Phys Rev Lett 1998, 80, 1365.
23. Evans, R. M. L.; Fairhurst, D. J.; Poon, W. C. K. Phys Rev Lett 1998, 78, 1326.
24. Klenin, V. Thermodynamics of Systems Containing Flexible-Chain Polymers; Elsevier: New York, 1999.
25. He, D. Q.; Nauman, E. B. J Polym Sci Part B: Polym Phys 1997, 35, 897.
26. Miyamoto, T.; Sato, Y.; Shibata, T.; Tanahashi, M.; Inagaki, H. J Polym Sci Part A: Polym Chem 1985, 23, 1373.