Demixing and Gelation Behavior of Ternary Cellulose Acetate Solutions

A. J. REUVERS, F. W. ALTENA, and C. A. SMOLDERS, *Department of Chemical Technology, Twente University of Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands*

Synopsis

The demixing behavior on cooling of ternary systems of cellulose acetate/solvent/water has been examined for CA concentrations up to 40 wt% CA in several solvents. Cloud points have been measured as a function of cooling rate. The rapid process of liquid–liquid demixing can be discriminated from the slow process of aggregate formation by examining the dependence of the cloud point on the cooling rate and by structure analysis of quenched solutions with scanning electron microscopy. The appearance of aggregate formation depends strongly on the type of solvent. Slow cooling of ternary solutions in which acetone is the solvent leads to aggregate formation long before liquid–liquid demixing occurs.

In addition, isothermal sol–gel transitions have been measured for quenched solutions at varying gelation times. It is concluded that gelation is not always preceded by aggregate formation.

INTRODUCTION

This investigation into the demixing behavior of ternary cellulose acetate (CA) solutions has been carried out in order to obtain experimental data, which are necessary to describe the formation mechanism of asymmetric membranes produced by means of the immersion precipitation process.

Asymmetric membranes of CA can be obtained by immersing a film of a binary polymer solution into a water bath. During immersion there is a rapid exchange of solvent and nonsolvent in the polymer film, which leads to the formation of an asymmetric membrane consisting of a dense top layer and a porous substructure. Depending on the specific solvent, the top layer can vary in density and thickness.[1] These structural properties are of great relevance to the transport characteristics of the final membrane, such as the degree of selectivity and the permeability. To understand the influence of the type of solvent used on the top layer structure we must study two characteristic features. First, we must know how the type of solvent influences the concentration profile in the film during the precipitation process. Second, we must know the demixing behavior and the kinetics of demixing as a function of the composition of the ternary system polymer/solvent/nonsolvent.

This study is concerned with the second characteristic. We have focused our attention on the ternary systems CA/solvent/water where the solvent is either dioxane, acetone, or tetrahydrofuran (THF). The solvents are miscible with water in all proportions.

We examined the three systems for the following types of demixing processes.

(1) Liquid–liquid phase separation. On cooling, a polymer solution may become metastable and may then separate into two liquid phases through nucleation and growth of one of the phases.

(2) Formation of aggregates. On cooling, the solution may become metastable and may then demix as a result of aggregation of the polymer molecules, possibly induced by crystallization. One could also call this process precipitation.

These processes can be discriminated by examining the kinetics of demixing. At a low degree of supercooling the formation of aggregates is supposed to be a slower process than liquid–liquid phase separation. Because the CA solutions studied showed a rapid gelation after the demixing process, we could also examine the type of demixing by means of structure analyses of the final product with the aid of electron microscopy.

Besides studying the nature of the demixing processes we also investigated the gelation behavior of the systems.

In the past the demixing behavior and gelation behavior of several ternary polymer solutions have been investigated.[2] Particularly, the system polyacrylonitrile (PAN)/solvent/water has been the object of intensive research.[3-8] Investigations into the demixing behavior of the system CA/solvent/water have been limited to cloud point measurements for CA concentrations less than 25% for several solvents including acetone[10-12] and dioxane.[9-11] Since the kinetics of demixing was not taken into account it was not possible to judge from the results what kind of demixing process caused the turbidity.

Experimental procedures

Materials Used and Preparation of the Samples

CA was obtained from Eastman Kodak with an acetyl content of 39.8% and a viscosity number 3 (ASTM). The solvents were of reagent grade and were used without further purification, except for drying on molecular sieves. The water was demineralized and ultrafiltrated.

Solutions were prepared in glass tubes, which were sealed under vacuum at liquid nitrogen temperature. Solutions for the determination of the sol-gel transitions were provided with a mercury drop of 0.1 g in the tube. Solutions used for quenching to 20°C were prepared in tubes with an inner diameter of 4 mm and a wall thickness of 1 mm. The tubes were rotated and heated at 90°C for at least 2 days to obtain homogeneous solutions.

Determination of the Cloud Points

Both the formation of aggregates and the liquid–liquid phase separation process were accompanied by very strong light scattering; sometimes the solutions became milky white. Therefore, it was sufficient to measure changes in light transmission of the samples instead of changes in light scattering under a certain angle. The light source was a helium–neon laser. The intensity of the transmitted light was monitored on a recorder and was measured as a function of the temperature at two cooling rates: 0.6

and 0.02°C/min. For a detailed description of this technique we refer to the thesis of Wijmans.[3]

The temperature at which the intensity of the transmitted light became less than the intensity of an homogeneous solution was called the cloud point temperature. This temperature was measured within an accuracy of 2°C in the case of aggregate formation and within an error of 0.5°C in the case of liquid–liquid phase separation. We measured the cloud point temperature as a function of the nonsolvent/solvent ratio at constant polymer concentration. Interpolation led to the composition with a cloud point temperature of 20°C. This procedure was repeated for several polymer concentrations.

Determination of the Type of Demixing Process

As mentioned before, the formation of aggregates is supposed to be a slower process than liquid–liquid demixing at a low degree of supercooling. If the cloud point temperature does not depend on the cooling rate we assume that liquid–liquid demixing takes place. When the cloud point temperature measured does depend on the cooling rate we assume that the turbidity is caused by aggregate formation.

As will become clear further on, in the case of CA/acetone/water solutions, in the concentration range of interest the aggregate formation was found to be so rapid that the liquid–liquid demixing gap could not be reached without aggregate formation taking place. Hence, for this system cloud point measurements could not be used to determine the exact position of the liquid–liquid demixing gap, and we had to use a special method to determine its position.

We assumed that a solution having a composition that is situated in the liquid–liquid demixing gap at 20°C is able to separate into two liquid phases upon quenching to 20°C by means of the nucleation and growth mechanism until aggregate formation and gelation in the concentrated phase stop this process. In a solution which has a composition that is situated outside the liquid–liquid demixing gap only aggregate formation occurs upon quenching to 20°C. Structure analysis with scanning electron microscopy (SEM) can reveal the difference in structure due to the different demixing processes.

Therefore, we prepared solutions with a higher nonsolvent/solvent ratio than the cloud point compositions already determined. At constant polymer concentration we prepared several solutions with varying nonsolvent/solvent ratio. After being homogenized at 90°C the solutions were quenched in a 20°C thermostate bath. The tubes were kept at this temperature for 24 h, during which aggregates were formed, which resulted in a stiff gel network. Then the tubes were broken in order to remove the gels. Samples of the gels were treated for structure analysis with SEM in two different ways.

(1) The gels were put in two successive solvent extraction baths with nonsolvent/solvent mass ratios of 50/50 and 100/0, respectively. Then they were quenched in liquid nitrogen, broken, and dried. The baths were necessary to obtain stiff gels that could be dried without destroying the struc-

ture. A thin conductive gold coating was sputtered on the fracture surface, and the samples were examined with SEM.

(2) To avoid possible structure transformations caused by the solvent extraction baths and the drying process we also examined the structure of the gels without any pretreatment. The gels were quenched in liquid nitrogen, broken, and the fracture surfaces were examined at −160°C with SEM equipped with a cryo-unit. A disadvantage of this method is the possibility of destroying the structure by crystal formation and the lower conductivity of the sample surface as compared to the previously mentioned sample preparation procedure where a gold layer was applied.

Determination of the Isothermal Sol–Gel Transition

The ternary systems CA/dioxane/water and CA/acetone/water have been characterized with respect to their gelation behavior. We have measured the position of the sol–gel transition in the ternary diagram by means of the falling ball method.[14] A mercury drop of about 0.1 g was put in the solutions. Homogeneous fluid solutions at 90°C were quenched to 20°C, and after 25 h the tubes were turned upside down. If the mercury drop moved downward we classified the solution as a liquid. If the drop did not move we classified the solution as a gel. We repeated the experiment, with a time allowed for gelation of 100 h. After some preliminary measurements we examined about 50 different solutions with dioxane as the solvent and about 25 solutions with acetone as the solvent with compositions near to the sol–gel transition.

Results

In this section we first discuss the results of the cloud point measurements of the three ternary systems of interest. For the system CA/acetone/water these results gave us no information about the actual location of the liquid–liquid demixing gap. Therefore, we used the special technique as described in the experimental section to determine the liquid–liquid demixing gap for this system. The results are described in the second part of this section. The last part of this section is devoted to the determination of the position of the sol–gel transitions in the systems CA/dioxane/water and CA/acetone/water.

Cloud point measurements

In Figure 1 the cloud point compositions at 20°C have been plotted for the three solvents, determined at two different cooling rates.

For the system CA/THF/water the location of the cloud point curve does not depend on the cooling rate up to 40 wt% CA. In this case the cloud point curve discriminates between homogeneous solutions and solutions which separate into two liquid phases.

For the system CA/dioxane/water the location of the cloud point curve does not depend on the cooling rate up to 26 wt% CA. This is in accordance with the results found by Altena.[9] Above 26 wt% CA the location of the cloud point curve depends on the cooling rate. For a cooling rate higher than 0.6°C/min the location of the cloud point curve does not change any
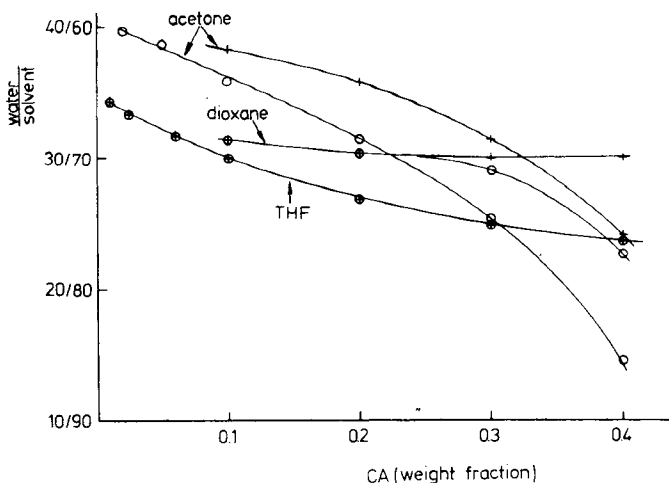
Fig. 1. Cloud point compositions for ternary Ca solutions at 20°C for three solvents. Cooling rate: 0.6°C/min (+) and 0.02°C/min (0).

more. Therefore, we conclude that above 26 wt% CA the cloud point curve at a cooling rate of 0.02°C/min is caused by aggregate formation and that the cloud point curve at a cooling rate of 0.6°C/min is caused by liquid–liquid demixing.

As we can see from Figure 1 the location of the cloud point curve for the system CA/acetone/water depends on the cooling rate for all CA concentrations considered. For a cooling rate higher than 0.6°C/min the location of the cloud point curve changes further. Therefore, we conclude that for both cooling rates the cloud points are caused by aggregate formation.

SEM Analysis

Evidently, more rapid cooling should be carried out to be able to surpass aggregate formation and to enter the liquid–liquid phase separation gap. By carefully choosing the composition, quenching the solution to 20°C, and applying the SEM analysis technique as described in the experimental section we were able to determine at what composition liquid–liquid phase separation occurs at 20°C.

From the micrographs presented in Figure 2 it can be seen that in 30 wt% CA solutions with water/acetone ratios of 40/60 and 38/62, liquid–liquid phase separation has taken place: the large voids are clearly the result of nucleation and growth of the diluted phase. The growth process was stopped because of a consecutive gelation of the concentrated phase surrounding the nuclei. It can also be seen that in the concentrated phase, aggregate formation took place. The aggregates exhibit a fibrous structure. In the solutions with a water/acetone ratio <38/62, only aggregate formation took place.

From Figure 3 we see that solutions containing 20 wt% CA with a water/acetone ratio >38/62 are situated inside the liquid–liquid demixing gap. Comparison of Figure 3(d) and 3(b) shows that in case 3(d) the concentrated phase is denser than in case 3(b). This is to be expected since liquid–liquid
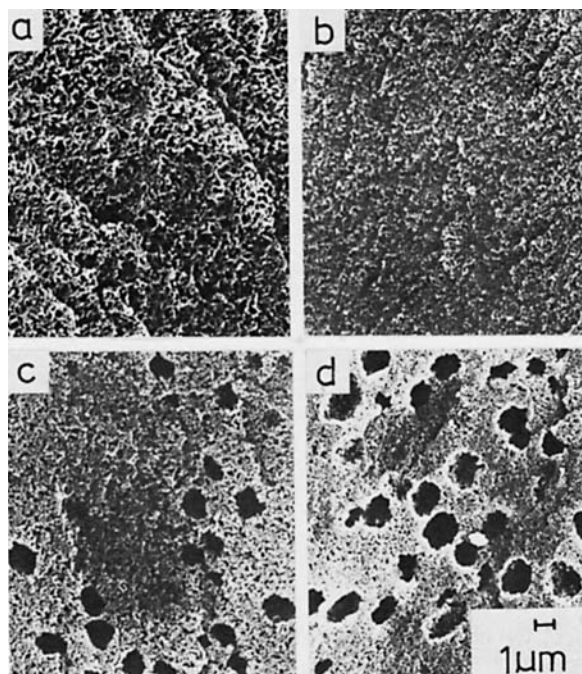
Fig. 2.   SEM micrographs for 30 wt% ternary CA solutions quenched to 20°C. Water/acetone ratio: (a) 36/64; (b) 37/63; (c) 38/62; (d) 40/60.
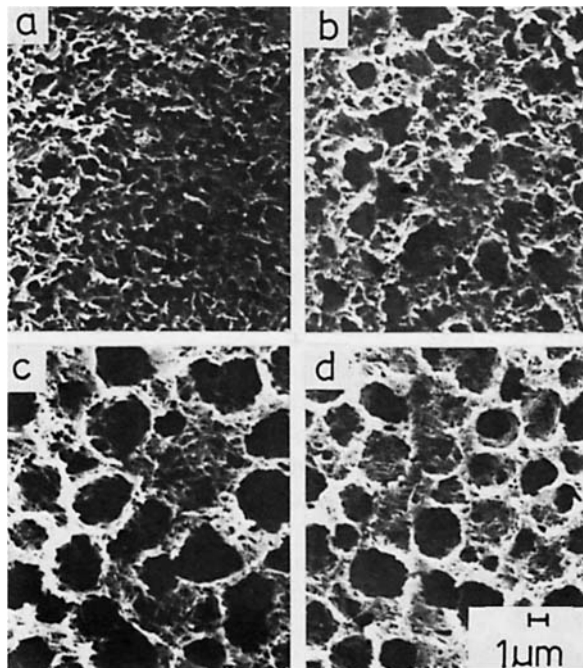

Fig. 3.   SEM micrographs for 20 wt% ternary CA solutions quenched to 20°C. Water/acetone ratio: (a) 38/62; (b) 39/61; (c) 40/60; (d) 42.5/57.5.

phase separation is likely to lead to a higher polymer concentration in the concentrated phase when the demixing gap is entered further.

All micrographs shown in this paper originate from gels that have been put in two successive solvent extraction baths and have been dried before examination with the SEM, except the micrograph represented in Figure 4(a). This micrograph represents a gel analyzed using the SEM in combination with the cryo-unit. Comparison of Figure 4(a) with 4(b) leads to the conclusion that both ways of preparing the samples for SEM analysis give the same picture and therefore do not lead to serious changes of the structure.

At lower CA concentrations [Fig. 4(c) and (d)] the droplets which consist of the diluted phase have coalesced to form larger droplets before gelation of the concentrated phase took place. This can be understood since it takes more time before the aggregates in the concentrated phase form a continuous network which could oppose further coalescence.

From Figure 5 it can be seen that for a 10% CA solution with a water/ acetone ratio of 40/60 coalescence of the diluted phase took place, whereas a solution with a water/acetone ratio of 39/61 did not separate into two liquid phases, so that coalescence could not take place here. Again, this shows that with the combination of quenching and SEM analysis described in this paper an accurate and reliable determination of the location of the liquid–liquid demixing gap is possible.

The results of the cloud point measurements and the SEM analysis can be combined to give isothermal (20°C) representations of ternary phase
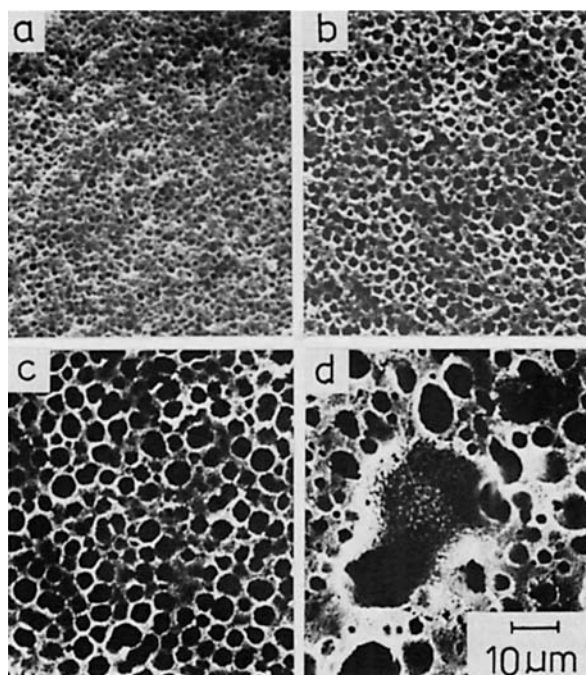

Fig. 4. SEM micrographs for ternary CA solutions quenched to 20°C. Water/acetone ratio: 42.5/57.5 wt% CA: (a) 20 (sample prepared without solvent leaching); (b) 20; (c) 15; (d) 12.5.
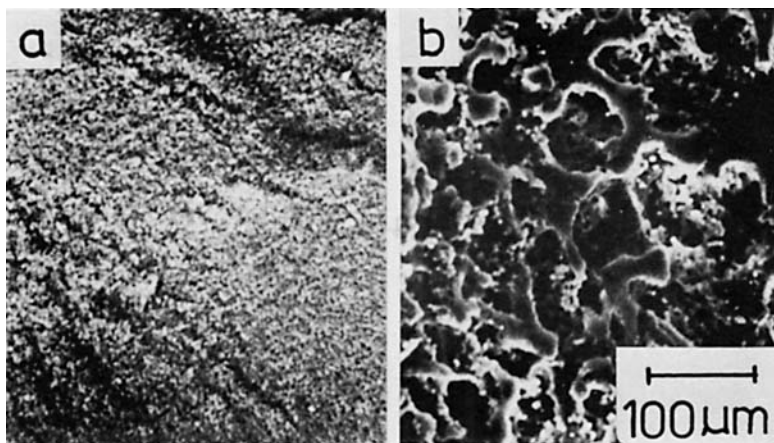
Fig. 5. SEM micrographs for 10 wt% ternary CA solutions quenched to 20°C. Water/acetone ratio: (a) 39/61; (b) 40/60.

diagrams for both CA/acetone/water (Fig. 7) and CA/dioxane/water (Fig. 6).

Sol–Gel Transitions

For the system CA/dioxane/water we have determined the sol–gel transition from 10% CA until 52% CA. For the system CA/acetone/water we have determined the sol–gel transition from 10% CA until 40% CA. For all experiments done the upper limit for the CA concentration of the examined solutions is given by the fact that no homogeneous solution could be obtained within 2 days at 90°C. Longer exposure to this temperature leads to a degradation of the polymer. The results of the investigation into the location of the sol–gel transition are represented in Figures 6 and 7. It can be concluded that the time allowed for the gelation process influences
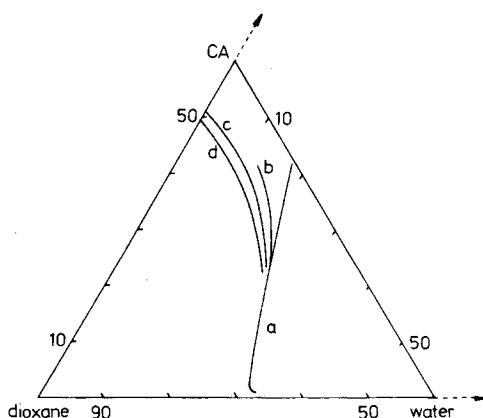

Fig. 6. Isothermal phase behavior for the system CA/dioxane/water at 20°C. (a) Liquid–liquid demixing gap (determined by cloud point measurements). (b) Cloud point curve (cooling rate: 0.02°C/min). (c) Sol–gel transition (time allowed for gelation: 25 h). (d) Sol–gel transition (time allowed for gelation: 100 h).
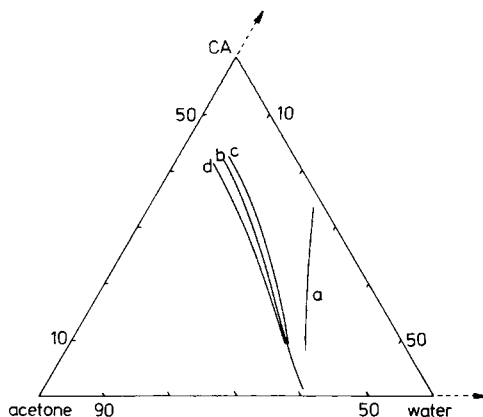
Fig. 7. Isothermal phase behavior for the system CA/acetone/water at 20°C. (a) Liquid–liquid demixing gap (determined by structure analysis). (b) Cloud point curve (cooling rate: 0.02°C/min). (c) Sol–gel transition (time allowed for gelation: 25 h). (d) Sol–gel transition (time allowed for gelation: 100 h).

the position of the sol–gel transition. The measured sol–gel transitions and sol–aggregate transitions are nonequilibrium transitions. The liquid–liquid demixing curves represent the transition between equilibrium phases because the location of these curves does not depend on the cooling rate.

Discussion

By varying the cooling rate (CA/dioxane/water) and examining the structure of quenched solutions (CA/acetone/water) we were able to discriminate between aggregate formation and liquid–liquid demixing. It was found that aggregate formation strongly depends on the kind of solvent. With acetone, aggregates are formed even at very low CA concentrations (2 wt%). On the contrary, with THF, aggregate formation only takes place at very high CA concentrations (>40 wt%). By cooling ternary solutions of PPO[16] and PAN[3,4] it was also found that aggregate formation sets in before liquid–liquid demixing takes place. In our opinion, the methods described in this paper could be used to determine the actual position of the liquid–liquid demixing gap for these systems. In points (1)–(3) we give some further comments.

(1) In Figure 8 our results for the system CA/acetone/water are presented together with the results given by Strathmann,[12] Frommer,[11] and Guillotin.[10] The results given by Frommer and Guillotin are cloud points determined by titration of water. The authors do not give quantitative information about the time effects of their observations. The cloud point curve given by Strathmann is partly determined by means of titration of water. The upper and lower part of the curve given by Strathmann are determined by adding a specific amount of water to a CA solution and separating the concentrated part of the demixed solution from the diluted part. The compositions of the concentrated and diluted part form the upper and lower part of the cloud point curve given by Strathmann.

The cloud points given in the literature differ to a large extent. In our opinion this is caused by the fact that different times were allowed for the
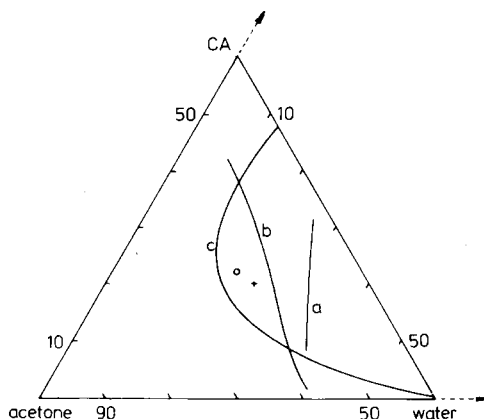
Fig. 8. Isothermal phase behavior for the system CA/acetone/water at 20°C. (a) Liquid–liquid demixing gap (this work). (b) Cloud point curve (this work, cooling rate: 0.02°C/min). (c) Cloud point curve Strathmann.[12] (0) Cloud point Guillotin.[10] (+) Cloud point Frommer.[11]

solutions to demix. In the ternary phase diagram the cloud points are situated at the left of the liquid–liquid demixing gap determined with our quenching technique. This means that the cloud points are probably caused by aggregate formation and not by liquid–liquid demixing. The upper and lower parts of the cloud point curve given by Strathmann are not identical to the liquid–liquid demixing curve, as he supposes, since he ignores the influence of aggregate formation and gelation on this type of experiment.

(2) In this paper we do not intend to explain the mechanism of aggregate formation. Nevertheless, some remarks can be made on this phenomenon. We think that microcrystallites are responsible for the solid structure of the aggregates because of the following reasons.

(a) We observed a large difference between the temperature at which the aggregates are formed and gelation sets in and the temperature at which the aggregates dissolve and the sturcture becomes fluid. We measured that this temperature difference is 40°C for a 30 wt% CA solution with a water/acetone ratio of 25/75. According to Tan[15] this temperature difference only occurs when microcrystallites are formed.

(b) Crystallization is a slow process in comparison with liquid–liquid demixing because of the time needed for orientation of the polymer molecules, both for nucleus formation and for growth.

(c) Aggregate formation also occurs in solutions of PPO[16] but does not occur in (even very concentrated) solutions of polysulfone. PPO is a semicrystalline polymer just like CA; polysulfone is a completely amorphous polymer. To get more information about the role of crystallization during aggregate formation it is necessary to do DSC experiments.[17]

Labudzinska[3,4] has examined the interrelation between aggregate formation and gelation for ternary solutions of PAN and PVA by means of light scattering and viscosity measurements. She concludes that gelation is not necessarily preceded by aggregate formation. This is in agreement with our observations. We observed that all examined CA/acetone/water gels were turbid, whereas clear CA/dioxane/water gels could be obtained. So we conclude that the gelation of the examined CA/acetone/water gels

is always preceded by aggregate formation, while CA/dioxane/water solutions also form gels without the formation of large, strongly light scattering aggregates.

(3) In order to draw conclusions about the role of aggregate formation during the membrane formation process it is necessary to know more about the kinetics of aggregate formation at high CA concentrations. The concentration changes in the precipitating polymer film are so rapid that the slow process of aggregate formation at low CA concentrations can be easily surpassed. Liquid–liquid demixing certainly plays a role during membrane formation. This phase separation process is responsible for the formation of the porous substructure of the membrane. As already mentioned by Ziabicki[1] it is also important to know more about the kinetics of liquid–liquid demixing in ternary polymer solutions. In combination with knowledge about the diffusion behavior during membrane formation we hope to be able to say more about the thickness of the top layer of the membrane. Further investigations will be carried out on the kinetics of liquid–liquid phase separation.

Conclusions

For the interpretation of turbidity measurements it is necessary to examine the influence of the cooling rate on the location of the cloud point compositions. As long as the location of the cloud point compositions does not depend on the cooling rate we assume that liquid–liquid phase separation takes place.

For the system CA/acetone/water we used a new method to determine the liquid–liquid demixing gap. By quenching homogeneous solutions to 20°C and analyzing the structure of the demixed and gelled solution by means of electron microscopy we were able to discriminate between the two demixing processes. This method can also be applied to other rapidly gelling systems. For the system examined by us this method leads to a considerable improvement of the accuracy of the phase diagram.

References

1. R. Bloch and M. A. Frommer, *Desalination,* **7**, 259 (1970).
2. A. Ziabicki, *Fundamentals of Fibre Formation,* Wiley, New York, 1976.
3. A. Labudzinska, A. Wasiak, and A. Ziabicki, *J. Polym. Sci.,* C **16**, 2835–2844 (1967).
4. A. Labudzinska and A. Ziabicki, *Kolloid Z. Z. Polym.,* **243**, 21–27 (1971).
5. J. Bisschops, *J. Polym. Sci.,* **12**, 583–597 (1954).
6. J. Bisschops, *J. Polym. Sci.,* **17**, 89–98 (1955).
7. P. Lagerkvist, and P. Flodin, *J. Polym. Sci, Polym. Lett. Ed.,* **19**(3), 125–130 (1981).
8. H. Strathmann and H. D. Saier, *Proceedings of the 4th International Symposium on Fresh Water from the Sea,* **4**, 381–394 (1973).
9. F. W. Altena and C. A. Smolders, *Macromol.,* **15**, 1491–1497 (1982).
10. M. Guillotin, C. Lemoyne, C. Noël, and L. Monnerie, *Desalination,* **21**, 165 (1977).
11. M. A. Frommer and D. Lancet, *Reverse Osmosis Membrane Research,* H. K. Lonsdale and H. E. Podall, Eds., Plenum, New York, 1972, p. 85.
12. H. Strathmann, P. Scheible, and R. W. Baker, *J. Appl. Polym. Sci.,* **15**, 811 (1971).

13. J. G. Wijmans, Thesis, ch. 3, 1984.

14. D. R. Paul, *J. Appl. Polym. Sci.,* **11**, 439 (1967).

15. H. M. Tan, B. H. Chang, E. Baer, and A. Hiltner, *Eur. Polym. J.,* **19**, 1021 (1983).

16. J. G. Wijmans, Thesis, ch. 4, 1984.

17. F. W. Altena, J. S. Schröder, R. van de Hulst, and C. A. Smolders, *J. Polym. Sci., Polym. Phys.,* in press.