The Construction of a Phase Diagram for a Ternary System Used for the Wet Spinning of Acrylic Fibers Based on a Linearized Cloudpoint Curve Correlation

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ABSTRACT: A phase diagram for the commercially significant ternary system poly(acrylonitrile-*co*-methylacrylate-*co*-sulfonic acid), sodium thiocyanate, and water, used to wet-spin textile acrylic fibers, was constructed from a linearized cloudpoint curve correlation. Experimental cloudpoints in the accessible low polymer content range were evaluated and used to extrapolate to higher polymer concentrations to produce a full-phase diagram. Although the correlation only holds for systems undergoing liquid/liquid demixing, the fact that the relation holds for this system despite evidence for PAN crystallization is discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2131–2139, 1997

INTRODUCTION

Acrylic textile fibers are an important commodity, with worldwide sales topping 2.5 million tonnes in 1994. There are a number of quite different production routes used commercially, which can be classed into general methodologies of dry spinning, wet spinning, and dry/wet spinning (melt spinning is generally not commercially feasible since polyacrylonitrile thermally degrades before it melts). In dry spinning, the acrylic polymer solution is forced through spinneret holes into a heated column where the solvent evaporates from the filaments. The solid fibers are washed free from solvent and further processed. In the case of wet spinning, the extruded polymer solution is brought into contact with a liquid nonsolvent for the polymer, such that solvent and nonsolvent exchange takes place until the polymer precipitates. Dry/wet spinning is a modification of wet spinning whereby the freshly extruded polymer solution passes through an inert gas, before entering a nonsolvent bath. In each case, the formation of fibers from the solution is of paramount importance since this first-formed structure dictates to a large extent the nature of subsequent changes on further processing and, ultimately, finished fiber properties and performance.

An idea of the vast range of morphologies accessible by altering formation conditions in the wet-spinning case was demonstrated as far back as 1963 the work of Knudsen.[1] Additionally, a range of morphologies possible with the specific wet-spinning system using aqueous sodium thiocyanate, operated commercially by Courtaulds under the trade name Courtelle, was demonstrated by the authors of this article in a previous publication.[2] Attempts have been made since the early days of commercialization to describe coagulation phenomena and to link a unifying formation mechanism to the diversity of structure obtainable from a wet-spinning system.[3–5] To date, however, a good description of the processes operating in a wet-spinning precipitation bath and their relationship to subsequent morphology has not materialized.
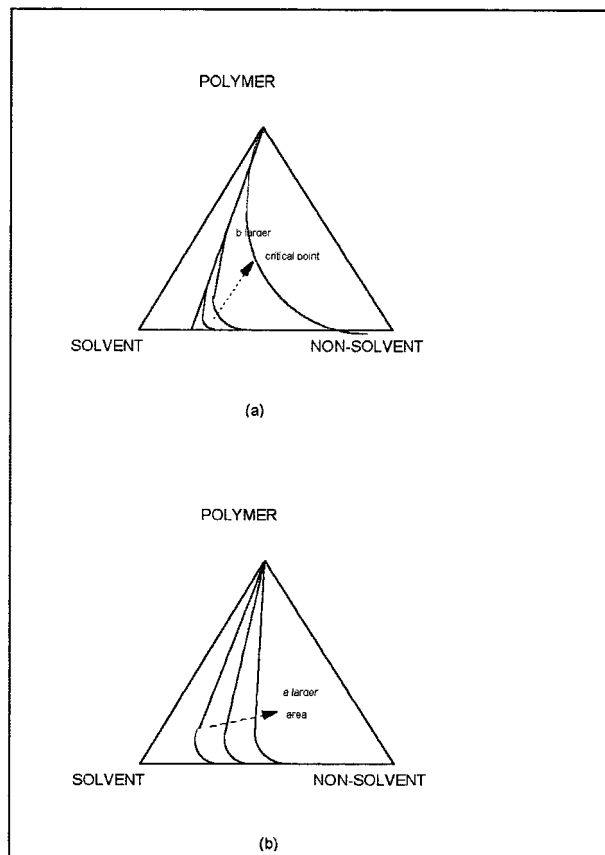
Figure 1   Variation of LCP: (a) gradient b; (b) intercept a.

In contrast, over the last 15 years or so, membrane researchers have set about the task of developing such a framework for phase-inversion membrane systems, recognizing the importance of both the thermodynamics and kinetics of a phase-separating polymer solution. These efforts have culminated in attempts to derive mathematical models to describe the phase-separation process.[6,7] To verify such models, experimental evidence of phase behavior and the kinetics of phase separation of the system in question under a range of conditions are required.

Phase Diagram

The phase diagram which describes the limit of stability and the composition of separated phases at equilibrium can usually be partly obtained experimentally for a particular system. This involves measuring (usually by turbidimetric titration) the cloudpoint curve which represents the border be-

tween compositions which are completely stable in a single phase and those which are unstable or only metastable. This is an experimental curve which closely matches the binodal curve in most practical situations. Deviations occur because polymer solutions are rarely monodisperse and some fractionation in molecular weight will occur. In practice, wet-spinning fiber and phase-inversion membrane systems comprise a very strong nonsolvent element, so even low molecular weight species tend not to reside in the polymer lean phase, thus minimizing fractionation.

This technique is applicable to solutions which contain low levels of polymer. However, compositions beyond the critical point (often around 5% polymer) are generally difficult to assess. This is because the viscosity of the solution is rising sharply and complete mixing of the nonsolvent titrant is extremely difficult. Localized, premature phase separation is usually the result. To circumvent this problem, compositions beyond the critical point and in the two-phase region at the required temperature are formed at higher (or lower in the case of L.C.S.T. systems) temperature, and phase-separated by a change in temperature. The compositions of each phase is then evaluated and these represent compositions at each end of a tie line spanning the binodal. Such experimentation, however, is demanding and time-consuming.

Recently, an article emerged describing a linearized cloudpoint curve correlation (LCP) function which applies to membrane-forming ternary systems.[8] The LCP is interpreted in terms of the various thermodynamic parameters appearing in the Flory–Huggins theory; the slope of the LCP plot gives information on entropic parameters (i.e., molar volumes), while the intercept yields data exclusively on the concentration-independent interaction parameters. The relation holds only for phase separation by liquid/liquid demixing, so it can be used to distinguish crystallization-induced separation from the former process without further experiments. Finally, from a few cloudpoint measurements (in the limit only one cloudpoint if certain assumptions are made), a full (isothermal) binodal can be calculated for the system in question.

In this article, a phase diagram is constructed for the ternary system polyacrylonitrile/NaSCN/ water used for the production of textile acrylic fiber, utilizing the LCP approach. It is noted that
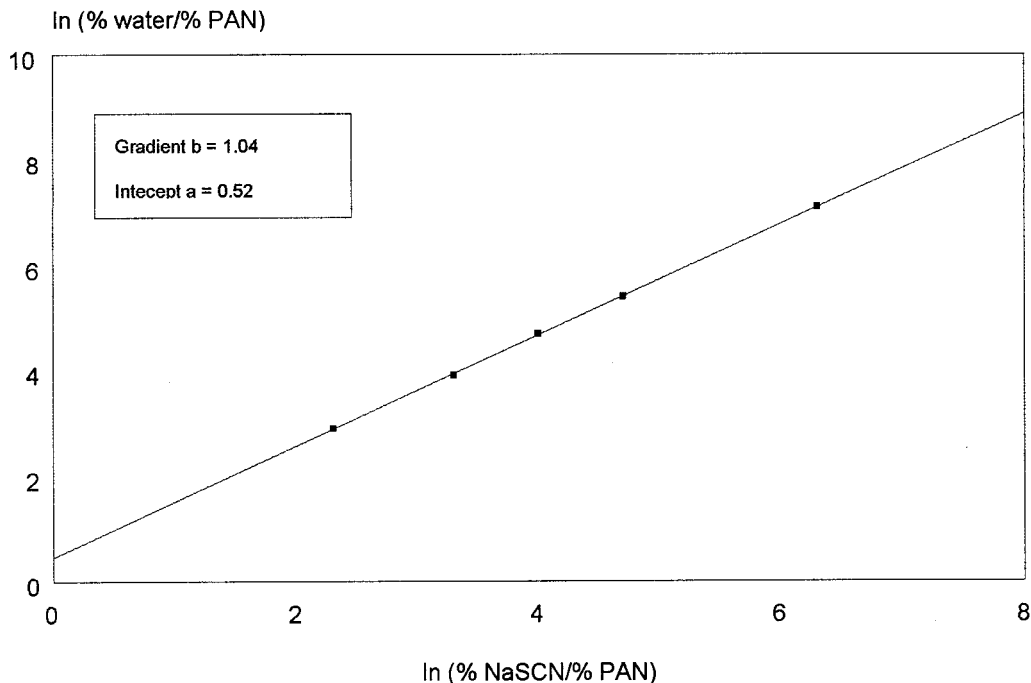
Figure 2 LCP plot for the PAN/NaSCN/water system.

a published phase diagram for the PAN/NaSCN/Water ternary system is not in existence.

Linearized Cloudpoint Curve Correlation (LCP)

Flory–Huggins theory can give the free energy of mixing for a ternary system as a function of the concentrations. When the relation is differentiated with respect to the number of moles of each component, pairs of compositions at equilibrium (same chemical potential) are evaluated which give rise to the binodal. This binodal coincides with the cloudpoint curve of the system providing that the polymer is monodisperse. However, in the special case of a membrane-forming or wet-spinning system, it still approximates the cloudpoint curve because the polymer is very incompatible with the nonsolvent. Low molecular weight fractions present in a polydisperse polymer solution are therefore unlikely to migrate into the polymer lean phase which would lead to early fractionation.

In the absence of experimentally determined concentration-dependent interaction parameters, the entire cloudpoint/binodal curve has to be produced experimentally. Several attempts have been made to fit simple relations to the cloudpoint curve data. Some treat the high polymer content

side of the critical point, while others, the dilute end. However, they all break down near the critical point. Recent work by Boom et al.[8] was based on a combination of these approaches and described the concentrations in any single phase that is on the verge of demixing; thus,

$$\ln \frac{F_1}{F_3} = b \ln \frac{F_2}{F_3} + a$$

where F_i is the weight fraction of component i, a and b are constants, and 1, 2, and 3 are the nonsolvent, solvent, and polymer, respectively.

It was shown by Boom et al. that the relation holds for a polymer/solvent/nonsolvent system over the entire concentration range (up to 50% polymer has been verified experimentally), even in the region of the critical point, provided that two conditions are met:

(i) The polymer is strongly incompatible with the nonsolvent.
(ii) Liquid/liquid demixing is the mode of phase separation.

If there is deviation from the relation at some polymer concentration (usually high) leading to
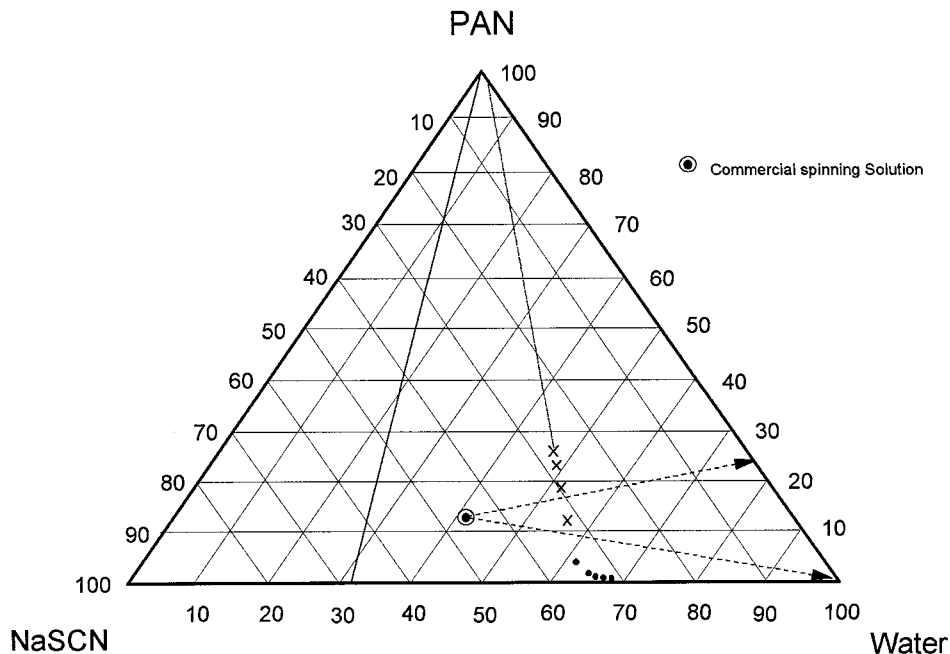
Figure 3   Phase diagram for the PAN/NaSCN/water system, based on (●) experimental and (×) calculated cloudpoints.

an asymptote, there is good evidence for crystallization. This can be probed further by monitoring the dependence of the cloudpoint on the rate of cooling (if temperature is being used to induce phase separation). Because crystallization is generally a much slower phenomenon than is liquid/liquid demixing, a temperature dependence is noted for crystallization, which disappears for the latter process.

A plot of ln F_1/F_3 against ln F_2/F_3 at the cloudpoint compositions will therefore give a straight line with slope b and intercept a. It has been found that the slope b for a system satisfying the above provisions is invariably just greater than 1, while the intercept can be positive or negative. This means that, in principle, accepting the aforementioned assumptions, it is possible to derive a complete cloudpoint curve from a single experimental point. Furthermore, this data point can originate from the experimentally accessible low polymer concentration region.

The parameters a and b have been described in terms of the Flory–Huggins theory. It turns out that the gradient b is a function only of the molar volumes, i.e., the entropic parameters, while the intercept a contains the interaction parameters with molar volumes, i.e., the enthalpic parameters. This decoupling of entropic and enthalpic parameters is highly unique.

In support of this derivation, the intercept does seem to represent the area covered by the demixing gap, which is classically dictated by enthalpic effects, while the gradient is determined by the position of the critical point, i.e., the overall shape of the demixing gap, which, of course, is a function of molecular weight and, hence, molar volume. A slope of 1.0 represents the limiting case with the critical point located on the solvent/nonsolvent axis and represents a polymer of infinite molecular weight. A low molecular weight species gives rise to a large value of b and a critical point near the middle of the binodal curve (see Fig. 1).

EXPERIMENTAL

Cloudpoints

A 5% stock solution of acrylic polymer [poly(acrylonitrile-*co*-methylacrylate-*co*-sulfonic acid)] was prepared by diluting a 13% polymer dope with 52% aqueous sodium thiocyanate (NaSCN) solution. The stock solution was further diluted with appropriate amounts of 52% NaSCN to give polymer solutions of 2.0, 1.0, 0.5, and 0.1%, respectively. Each solution was then titrated against demineralized water at 22°C until the first permanently cloudy product was obtained. The solutions

were stirred vigorously to ensure thorough mixing of the nonsolvent.

X-ray Diffraction

The LCP correlation has been shown to be applicable only to those systems undergoing phase separation by liquid/liquid demixing. To test for crystallization of the polymeric phase after precipitation, samples of PAN copolymer from low and higher polymer content solutions were subjected to X-ray diffraction analysis. In addition, as a comparison, a diffractogram of powdered oriented fiber derived from the same polymer composition was obtained. The details are outlined below:

Polymer precipitate collected from the cloud-point titration of 1% polymer solution was washed exhaustively with demineralized water and subsequently dried to constant weight in a vacuum oven at 50°C. An approximately 450 μm-thick film of a 13% polymer solution was cast onto a glass plate and then precipitated in a demineralized water bath at 22°C. The film was exhaustively washed with water then dried at 50°C in a vacuum oven until constant weight. A powder was then produced from the film by grinding in a pestle and mortar.

Washed and dried oriented acrylic fiber of the same polymer composition which was made under commercial conditions was cut into very short lengths to produce a powder. All three powders were then subjected to X-ray diffraction for an evaluation of the level of crystallinity. The powders were contained in 1.5 mm Pantak capillary tubes, which were held vertically in a fiber sample holder. Examination was carried out on a Philips PW 1130 generator, using CuKα radiation. Equatorial scans were carried out in 0.1° 2θ steps over the range 5°–60° 2θ.

Curve fitting was carried out by subtracting background scatter, then by manually subtracting an amorphous peak, assumed to be Gaussian in nature. The extent of ordering was evaluated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where D is the mean crystallite dimension; β, the width in radians of the diffraction peak at half-height; θ, the Bragg angle with a wavelength λ; and k, a constant usually given a value of unity.

RESULTS AND DISCUSSION

Figure 2 shows a plot of ln(% water/% PAN) vs. ln(% solvent/% water), derived from the cloud-point compositions. The gradient b is 1.04 with intercept 0.52. Clearly, the LCP relation holds for the PAN/NaSCN/water system, at least over the concentration range studied. Obtaining data for higher polymer concentrations would be very difficult as the solutions are becoming too viscous for sensible titrations to be carried out. However, if we assume that the relation holds at higher concentrations (as it does for other poorly crystallizing ternary systems), the cloudpoint compositions at these higher, more commercially useful polymer concentrations can be calculated. This can be done by choosing x and y values of points which lie on the LCP line and solving for the compositions. Thus,

$$\ln \frac{\% \text{ water } (W)}{\% \text{ polymer } (P)} = x, \quad \ln \frac{\% \text{ solvent } (S)}{\% \text{ polymer } (P)} = y$$

and

$$\% \text{ water} + \% \text{ polymer} + \% \text{ solvent} = 100$$

so

$$\frac{W}{P} = e^x, \quad \frac{S}{P} = e^y, \quad \text{and} \quad W + S + P = 100$$

$$Pe^x + Pe^y + P = 100$$

$$P = \frac{100}{(1 + e^x + e^y)} \tag{1}$$

then

$$W = Pe^x \quad \text{and} \quad S = Pe^y \tag{2}$$

where the combination of eqs. (1) and (2) gives the quantity of polymer, solvent, and nonsolvent at any cloudpoint.

Figure 3 shows the experimentally determined cloudpoints on a ternary phase diagram (shown as dots) along with several extracted from the LCP relation (crosses). In the limit, the LCP relation predicts that the binodal terminates at the 100% polymer apex. In reality, most polymers swell to some extent in water, and it is known that the equilibrium moisture content of acrylic
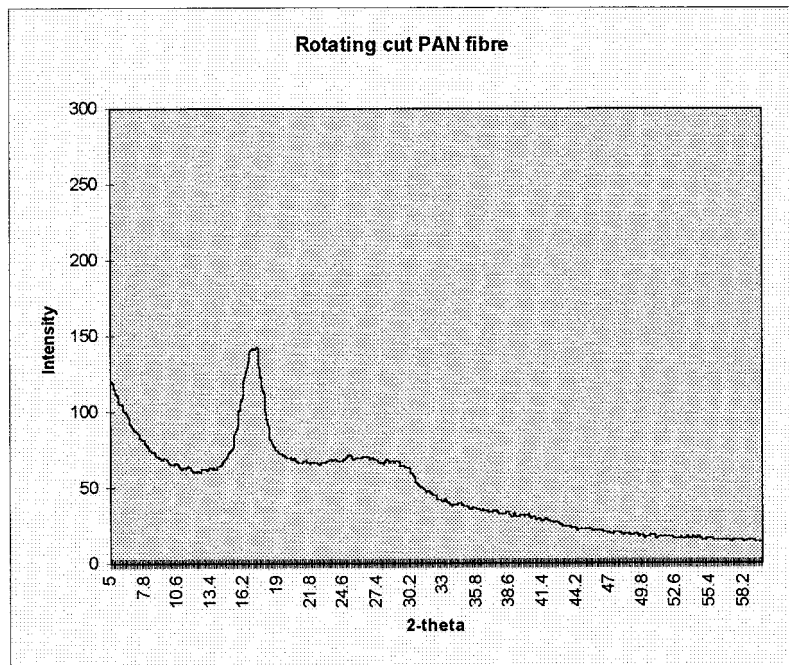
Figure 4 X-ray diffractogram of rotating cut PAN fiber.

fiber is about 1–3.5%, dependent on the humidity.[9] The binodal should therefore terminate just below the polymer apex on the polymer/water axis.

The composition of a typical acrylic spinning dope is shown on the diagram (nominally 13% polymer, 45.2% NaSCN, 41.8% water). The two lines emanating from this point represent extreme possibilities during coagulation, i.e., exclusively water diffusion into the nascent filament, and at the other extreme, only solvent outflow from the filament. (These fluxes arise from the chemical potential gradients, simplistically concentration gradients existing at the filament/bath interface.) In reality, both processes will occur so the "precipitation trajectory" will lie somewhere between these limits. It follows that traversing into the two-phase region can theoretically occur between two limiting polymer concentrations, 9 and 17% for this standard composition at this temperature. According to Knudsen,[1] the effect of higher polymer solids is to produce more homogeneous, less porous as-formed structures. It is therefore expedient to control the route taken into the two-phase region such that phase separation at and beyond the binodal is from a desirable polymer concentration.

The LCP relation relies on liquid/liquid demixing being the mode of phase separation. Crystalli-

zation is indicated by deviation from the relation. The "crystallinity" of acrylic fiber has been well documented.[10] While distinct diffraction is present in X-ray diffractograms, it is restricted to equatorial reflections indicating lateral order without regularity along the polymer axis. (This restricts the applicability of the term crystallinity to PAN, where order is probably a better descriptor.) The diffractogram shown in Figure 4 of powdered acrylic fiber indicates that a not insignificant level of order exists in an oriented PAN polymer precipitated from reasonably high polymer concentration (13%). The level of "crystallinity" evaluated for this sample was 23%.

The diffractogram for 13 and 1% powders are shown in Figures 5 and 6, respectively. One cannot easily experimentally determine whether the LCP relation holds at high polymer concentrations where crystallization is more likely to occur. However, the level of order in the film precipitated from 13% polymer concentration is no higher than that for the powder produced from a 1% polymer solution, in a region where the LCP has been shown to be valid (the powder produced from 1% polymer solution will have been formed by nucleation of the polymer phase, while the film from 13% polymer solution will have derived from nucleation of the polymer lean phase and, hence, has mechanical integrity). The level of order has been
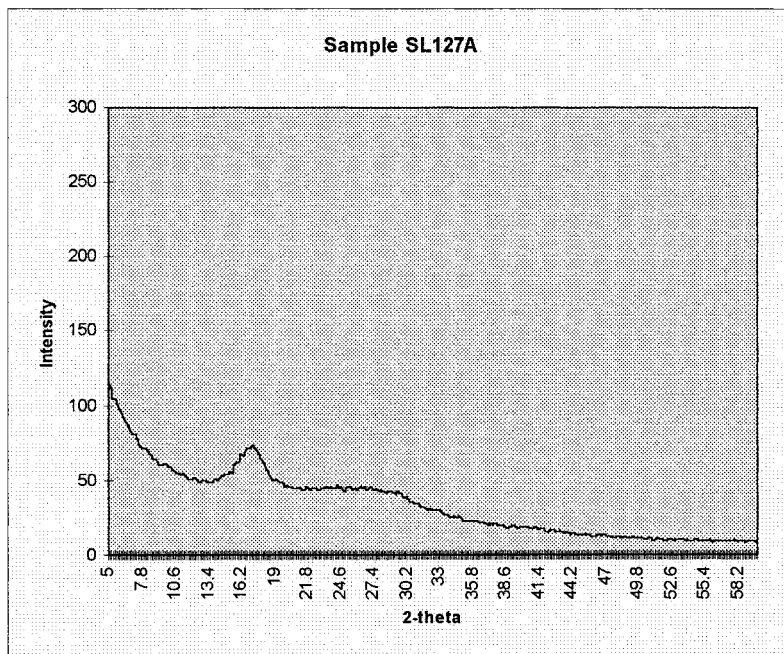
Figure 5 X-ray diffractogram of 13% PAN powder.

estimated from these scans to be 14 and 12%, respectively. The extent of lateral order is summarized in Table I, along with the other XRD data. These data suggest that no significant increase in "crystallinity" is expected at higher polymer concentrations, so the LCP is likely to be valid in this region.

Comparing these figures with the value for powdered oriented fiber shows how the downstream processes in this particular textile acrylic
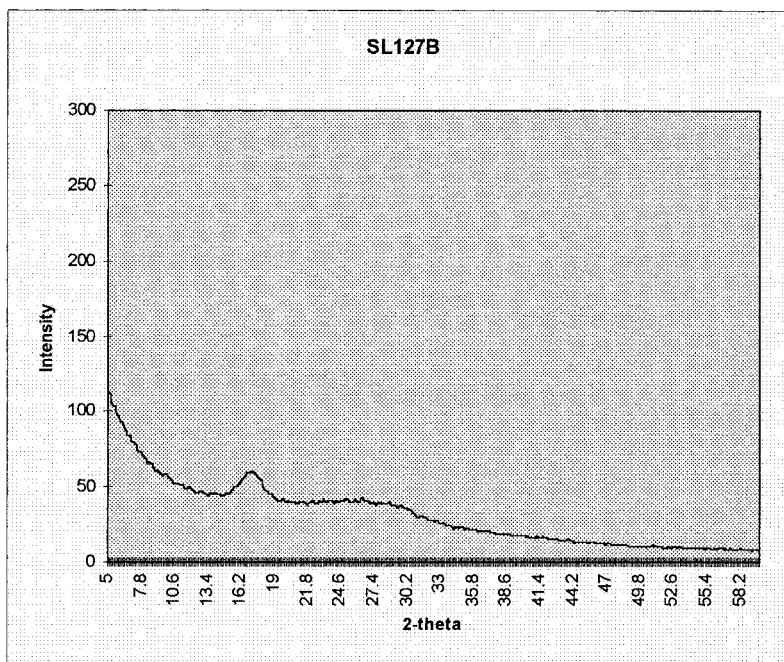

Figure 6 X-ray diffractogram of 1% PAN powder.

Table I   X-Ray Diffraction Data for Powdered Oriented Fiber, Film Derived from 13% Polymer Solution, and Powder Derived from 1% Polymer Solution

Sample Description	d-Spacing (Å)	Crystal Size (Å)	% Crystallinity
Powdered film from			
13% polymer	5.22	39	14
	3.38		
Powder from			
1% polymer	5.22	45	12
	3.38		
Powdered oriented	5.22	32	22
Fiber	3.44		

fiber manufacture, particularly stretching, serve to increase the level of ordering beyond the first-formed structure. This is in contrast to the findings of Bell and Dumbleton[11] who observed no increase in order as a function of draw for acrylic fiber spun from the dimethylacetamide system.

It is known for certain polymers to undergo crystallization during nonsolvent-induced phase separation (e.g., Refs. 12 and 13). It is assumed that crystallization and liquid/liquid demixing compete, the latter usually being the more rapid process so tends to dominate. However, under conditions which favor crystallization, such as high polymer concentration, high level of nonsolvent in the polymer solution, and significant supersaturation of the solution during nonsolvent immersion, all of which tend to increase the density of nuclei, crystallization can be dominant. That crystallization can occur at all at temperatures well below the melting point of the pure polymer is due to the melting point depression effect of the solvent and nonsolvent diluents. In a study by Bulte et al.,[14] differential scanning calorimetry (DSC) was used to probe the crystallization phenomena of phase-separated nylon 4, 6 structures through melting behavior. They found that crystallization through solid/liquid demixing was favored for this easily crystallizable polymer when a high initial polymer and/or water (nonsolvent) content was used. Melting endotherms indicated a significant level of inherent crystallinity, compared to the bulk polymer which has a crystallinity of about 50%.[15] At polymer contents lower than 17%, the structures formed were said to be a result of liquid/liquid demixing. This conclusion was based on observation of films imaged by SEM, where a cellular morphology resulted, as opposed to aggregations of spheres said to be a result of crystalliza-

tion at higher concentrations. Accompanying DSC experiments were not reported for the former materials. Unfortunately, to corroborate XRD data, this type of analysis is not possible for PAN since it will thermally decompose before melting behavior can be examined in typical DSC experiments.

CONCLUSIONS

The ternary polymer system poly(acrylonitrile-co-methylacrylate-co-sulfonic acid)/sodium thiocyanate/water used to commercially wet-spin acrylic fibers has been shown to obey a linearized cloudpoint curve correlation reported recently by researchers in the membrane field. Using experimentally determined cloudpoints in the accessible low polymer content region, the correlation function has been fitted and used to extrapolate into the higher and more commercially relevant region. Such a methodology has revealed a full (isothermal) phase diagram for this system. This can be used to help interpret relationships between fiber formation conditions and the structures which result.

In the original work, the correlation was found to hold only for those systems which phase separate by nucleation and growth. "Crystallization" in oriented acrylic fibers is well documented, albeit only lateral in nature—distinct axial ordering is generally not present. For unoriented polymer precipitated from both low and high solids, order has been shown to be present. Thus, the LCP holds for the PAN copolymer system studied here, despite "crystallization" of the polymer across a polymer content range of 1 to 13%.

Examples of phase separation in ternary systems by either liquid/liquid demixing or solid/liq-

uid demixing can be found in the literature. Whether the PAN copolymer studied in this work truly undergoes solid/liquid demixing is open to conjecture, particularly in light of its nonclassical solid-state structure. Further experimentation around the kinetics of phase separation is needed.

REFERENCES

1. J. P. Knudsen, *Text. Res. J.,* **33,** 13 (1963).
2. S. J. Law and S. K. Mukhopadhyay, *J. Appl. Polym. Sci.,* **62,** 33 (1996).
3. A. Rende, *J. Appl. Polym. Sci.,* **16,** 585 (1972).
4. D. R. Paul, *J. Appl. Polym. Sci.,* **12,** 383, 2273 (1968).
5. A. Ziabicki, *Fundamentals of Fibre Formation,* Wiley-Interscience, New York, 1976.
6. A. J. Reuvers, *J. Mater. Sci.,* **34,** 67 (1987).
7. Y. Termonia, *J. Polym. Sci. B Polym. Phys.,* **33,** 279 (1995).
8. R. M. Boom, T. van den Boomgaard, J. W. A. van den Berg, and C. A. Smolders, *Polymer,* **34,** 11 (1993).
9. J. R. James, P. J. Akers, and J. Picker, *J. Text. Asia,* **70,** 2348 (1988).
10. C. R. Bohn, J. R. Shaefgen, and W. O. Statton, *J. Polym. Sci.,* **55,** 531 (1961).
11. J. P. Bell and J. H. Dumbleton, *Text. Res. J.,* **41,** 196 (1971).
12. A. Keller, *J. Polym. Sci.,* **17,** 447 (1955).
13. J. G. Wijmans, H. J. J. Rutten, and C. A. Smolders, *J. Polym. Sci. Polym. Phys. Ed.,* **23,** 1941 (1985).
14. A. M. W. Bulte, B. Folkers, M. H. V. Mulder, and C. A. Smolders, *J. Appl. Polym. Sci.,* **50,** 13 (1993).
15. *Encyclopedia of Polymer Science and Engineering,* 2nd ed., Vol. 11, Polyamides, Wiley, New York, 1985.