### A Framework for Morphological Evolution vis-à-vis Phase Transitions in Polymer Solutions

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ABSTRACT: When a polymer crystallizes from solution, it is well known that the resulting morphology depends on whether any liquid-liquid phase separation (LLPS) has preceded crystallization. In addition to the dense morphology that results when crystallization occurs directly from a homogeneous solution, at least three other distinctly different morphologies are produced if crystallization follows LLPS. Although much work has been reported in this regard, a framework that can relate the path that a process might follow across a phase diagram to the consequent morphology is lacking. We report here the fundamental elements of a simple thermodynamic framework that serves to identify the driving forces that produce these different morphologies. It is based on identification of the nucleating phase, if any, in LLPS and coupling it with the domain in which nucleation of crystallization occurs. The essential elements of the framework for morphological evolution are demonstrated by relating the sequence of phase transitions to the morphology which can result in the crystallized polymer when a polymer solution is cooled from a homogeneous state at a high temperature. Four distinctly different morphologies are shown to evolve, depending on whether crystallization occurs (a) directly from a homogeneous solution (dense); (b) following binodal liquid-liquid phase separation, LLPS, with nucleation of the polymer-rich phase (GMP-globular microporous); (c) following spinodal LLPS (FMP-fibrillar microporous); or (d) following binodal LLPS with nucleation of the solvent-rich phase (CTMP-cell-tunnel microporous). An important implication of the framework is that a predictable sequence of "dense  $\rightarrow$  GMP  $\rightarrow$  $FMP \rightarrow CTMP \rightarrow dense$ " morphologies has to arise with increase in overall polymer concentration in such solutions. The framework also serves to identify conditions, such as passage through specific temperature/concentration regions in the phase diagram, that would increase the likelihood of forming mixed or coexisting morphologies. However, it is still necessary to develop appropriate kinetic models to predict sizes of the morphological components within each of the four morphologies. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1343-1355, 1999

**Key words:** phase transitions in solutions; liquid–liquid phase separation; polymer morphology; globular microporous; cell-tunnel microporous; fibrillar microporous

#### INTRODUCTION

Knowledge of phase transitions in polymer solutions can serve to identify mechanisms for simpli-

Journal of Applied Polymer Science, Vol. 73, 1343–1355 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/081343-13 fication of processing paths and also for controlled generation of useful morphologies. Extensive research has been conducted in recent years on the morphological implications of phase transitions. Of significant interest in this regard are liquid– liquid phase separation and solidification via crystallization or glass transition.<sup>1,2,7–20</sup> Membrane technology is dependent on such phase transitions in polymer solutions, induced either

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thermally<sup>1</sup> or through diffusion of a nonsolvent.<sup>9,11</sup> The phase transitions have been utilized to generate spherical particles, 1,11,12,15,17,18 closed-cell microporous morphology,<sup>10,11,18</sup> opencell (denoted here as cell-tunnel) microporous morphology,<sup>9,11,17,20</sup> as well as bicontinuous morphology.<sup>18</sup> Kinetics of phase separation<sup>14,16,19</sup> and generation of morphological features<sup>14,16,20</sup> have been studied qualitatively, in semicrystalline $^{9-17,20}$ as well as amorphous<sup>18</sup> polymers. Binary solvent/ nonsolvent systems<sup>10-13</sup> have been effectively used to demonstrate the impact of thermodynamic and kinetic aspects on the evolution of different morphologies. Although it is well known that microporous morphologies with different pore morphologies and sizes would result if crystallization of a polymer from solution is preceded by LLPS, the fundamental processes that lead to the formation of different morphologies have not been clearly enunciated. For example, we have seen through an earlier study<sup>1</sup> that solutions of polyacrylonitrile in a binary solvent system [water and dimethyl formamide (DMF)] exhibit one or both of two phase transitions, liquid-liquid phase separation (LLPS) and crystallization, as a function of binary solvent composition, polymer composition, and cooling rate. Three distinctly different morphologies, cell-tunnel (CTMP), fibrillar (FMP), and globular (GMP), have been seen to result if LLPS precedes crystallization. Relatively denser morphologies are obtained if crystallization occurs directly from a homogeneous polymer solution. However, as with other studies, these results were presented and discussed with respect to their implications regarding process modifications and potential applications, but without a clear enumeration of the path across a phase diagram, which causes the evolution of each of the microporous morphologies, especially CTMP and GMP.

We report here the results from an extensive study of phase transitions and the consequent morphologies in solutions of polyacrylonitrile in binary solvents, comprising of water with N,Ndimethyl formamide (DMF), N-methyl pyrrolidone (NMP), or dimethyl sulfoxide (DMSO). The emphasis is on relating the morphological features in the solidified polymer to the sequence of observed, or inferred, phase transitions that occur when these solutions are cooled to room temperature from a homogeneous single phase at a higher temperature. Well-established theories are used to identify the nucleating phase in LLPS and to incorporate these in a generally consistent framework for prediction of morphological features. This framework can be used to simplify solution-based processing of polymers, while simultaneously offering pathways for versatile generation of useful morphologies. It should be noted here that the morphological features in this regard are on a scale from  $\sim 0.01$  to  $\sim 10 \ \mu$ m, pertaining to features that would be governed by the presence or absence of LLPS prior to crystallization of the polymer.

The likelihood of formation of different morphologies through LLPS followed by crystallization has been widely observed.<sup>5–28</sup> However, with the exception of the consequences of spinodal decomposition, the underlying nucleation process in LLPS and how it dictates, in combination with crystallization, the class of microporous morphology that evolves through these phase transitions have not been reported.

# FRAMEWORK FOR THE EVOLUTION OF MORPHOLOGY

#### **Overall Phase Diagram**

A typical Gibbs free-energy–polymer concentration relationship that can lead to the formation of two solution phases is shown in Figure 1. Separation of a homogeneous polymer solution<sup>3</sup> into two liquid phases (LLPS) can occur in the compositional range from A to B via one of two mechanisms: nucleation and growth (for polymer concentration between A and C; between D and B) and spinodal decomposition (between C and D). The latter consists of spontaneous decomposition of the homogeneous solution into two liquid phases. The necessary condition for each of the two mechanisms of LLPS is that the change in Gibbs free energy with concentration of the polymer solution should be negative. This condition tends to be inherently satisfied in spinodal decomposition. It is met in the case of nucleation and growth only when a fluctuation larger than a certain critical size is formed.

At a critical temperature, the spinodal (locus of points C and D for different temperatures) and binodal curves (locus of points A and B for different temperatures) have the same solution composition (Fig. 2). Because the spinodal process is spontaneous, a solution of this composition, which passes through the critical temperature, invariably undergoes phase separation via this mechanism under all conditions. When the polymer con-



**Polymer** Concentration

**Figure 1** Typical Gibbs free energy of the two-phase region. A and B are the equilibrium compositions based on the common tangent construction. Points C and D are the inflexion points representing metastable states at the boundary of the spinodal region. The tangent at M corresponds to the path for local fluctuations at constant chemical potential. The point N, situated inside the spinodal and having the same chemical potential as M, represents the critical composition for a solution of composition corresponding to M. (Hillert et al.<sup>4</sup>).

centration is not at the critical point, the solution has to pass through the nucleation and growth regime before it can enter the spinodal regime, causing the homogeneous solution to phase separate via nucleation and growth prior to entering the spinodal regime. Thus, unless the cooling rates are high enough to render the nucleation and growth process negligible, spinodal decomposition does not occur in solutions of such composition.

If a polymer solution does not undergo LLPS prior to crystallization of the polymer, the crystallization temperature would increase with polymer concentration. However, if a polymer-solvent system exhibits LLPS prior to crystallization, the phase with the higher polymer concentration invariably reaches its crystallization temperature first. As a consequence, an invariant crystallization temperature is observed within the range of polymer concentration in which LLPS precedes crystallization (Fig. 2). At polymer concentrations that are below or above those corresponding to LLPS, crystallization occurs from a homogeneous solution and an increase in crystallization temperature is observed with polymer concentration. Thus, by examining for invariance in the crystallization curve, it is possible to predict whether LLPS precedes crystallization in these solutions.

(The analysis presented here is valid only for systems in which the composition of the binary solvent is the same in both the solution phases that form through LLPS, i.e., systems that behave as pseudobinary solutions. Such behavior arises, at least as an approximation, usually when the two solvent components, for example, DMF and water, are miscible in all proportions. If the binary solvent should tend to have different compositions in different phases of the polymer solution, LLPS would no longer lead to the same two compositional pathways. Invariance of crystallization temperature may not arise in such solution systems. An example of this kind has been seen in solutions of a PAN terpolymer in succinonitrile and water.<sup>5</sup>)

#### **Evolution of Morphology**

An important aspect in morphological evolution, if LLPS occurs by nucleation and growth mechanism, is the phase that nucleates.<sup>4</sup> The nucleating phase is dictated by the change in molar Gibbs free energy as a function of polymer concentration. If a tangent is drawn on the molar Gibbs free-energy curve at an overall concentration of the solution in this compositional range (Fig. 1), it



Polymer Concentration, wt.%

**Figure 2** Typical phase diagram of a solution exhibiting liquid–liquid phase separation and crystallization. Binodal curve is obtained from the common tangent construction and spinodal from the locus of inflexion points in the Gibbs free energy vs. concentration curves (Fig. 1). Arrows represent the path taken by a solution across the phase diagram and the resulting morphologies. (a–c) These represent typical cell-tunnel microporous (CTMP), globular microporous (GMP), and fibrillar microporous (FMP) morphologies, respectively.

represents the free energy of an infinite solution whose local concentration fluctuations can adopt various configurations without changing the chemical potential of the solution. Consider phase separation of such a solution into the equilibrium concentrations denoted by the two points, A and B, of the common tangent to the free energycomposition curve. The point N, situated inside the spinodal, has the same chemical potential as M. In a solution of overall composition corresponding to M, if a compositional fluctuation should exceed that corresponding to N, it will grow spontaneously. Also, when the overall concentration (point M) is below that of the lower spinodal point, C, a decrease in Gibbs free energy results if the higher concentration phase (B) nucleates from a local fluctuation. On the other hand, nucleation of the lower concentration phase (A) would lead to an increase of Gibbs free energy in this case. Thus, when the overall concentrations are below the lower spinodal point (point C), the higher concentration phase, B, nucleates. The distance between the two parallel lines, measured along the free energy axis, represents the activation energy for nucleation in a solution of composition corresponding to M. A similar analysis shows that the lower concentration phase nucleates when the overall concentrations are above the higher spinodal point (point D). However, if the overall solution concentration is anywhere between the spinodal points, both the phases form spontaneously (Fig. 1).

Thus, we see that the path traversed with respect to the phase diagram would dictate the evolution of morphology. It can range from microporous to dense, depending on whether LLPS precedes crystallization or crystallization occurs from a homogeneous phase. The nature of microporous morphology that evolves would depend on the nature of LLPS, which can be either spinodal or binodal. If LLPS should occur via binodal decomposition, the resulting morphology would also be determined by whether the higher or lower polymer concentration phase nucleates as the discrete phase.

Solutions that have concentrations below the critical concentration (in the range from A to C in Fig. 1), phase separate such that the polymer-rich phase nucleates. Upon further cooling of this solution, crystallization is initiated in the higher polymer concentration phase, i.e., in the same phase that nucleated in LLPS, and gives rise to globular microporous (GMP) morphological features (Fig. 2).



**Figure 3** Mechanism of formation of the cell-tunnel microporous morphology from an initially homogeneous solution. LLPS with nucleation of a solvent-rich phase (step 1) produces the cell domains; initiation and propagation of crystallization in the polymer-rich phase (step 2) leads to a solvent-rich front that forms the connecting tunnels between the cells (step 3).

If the overall polymer concentration is higher than the critical polymer concentration (C to B in Fig. 1), the solvent-rich phase nucleates and the morphologies resulting from subsequent crystallization of the polymer-rich phase have "cell-tunnel" microporous (CTMP) characteristics (Fig. 2). (This morphology was termed "cell-pore" microporous (CPMP) morphology in a previous report.<sup>1</sup> It has been changed here to provide a more appropriate name, and to eliminate the confusions that arise with "cell-pore" terminology.) The tunnels, i.e., the connection between cells, in CTMP morphology evolve subsequent to LLPS, i.e., during crystallization. In this case, the "solvent fronts," which are produced during the propagation of crystallization in the continuous polymerrich phase, connect the discrete solvent-rich cells. previously formed during LLPS (Fig. 3). This mechanism has been verified through measurement of electrical conductivity in a polymer-solvent system with a substantially higher conductivity of the solvent.<sup>6</sup> A pronounced drop in conductivity occurs in this case with the onset of predominantly solvent-nucleated  $(T > T_{critical})$ LLPS. It is followed by a sharp reversal with the onset of crystallization, due to the connecting solvent-rich tunnel-like structures that are established between the initially discrete cells.

When the polymer concentrations are around the critical point, LLPS occurs via spontaneous spinodal decomposition, with subsequent crystallization leading to the formation of fibrillar microporous (FMP) morphologies. Even at a concentration other than the critical concentration, kinetic limitations with nucleation and growth can cause the solution to enter the spinodal regime and phase separate spontaneously, with little or no prior binodal decomposition. This can happen especially if the cooling rate is high. On the other hand, if the cooling rate is low enough, the same solution would undergo phase separation via nucleation and growth, and the two polymer concentrations that evolve would follow the binodal curve until the onset of crystallization. The scale on which LLPS-dictated evolution of morphology occurs is determined by its nature, i.e., spinodal or binodal, with nucleation of the polymer-rich or solvent-rich phase. The globular structures that evolve through nucleation of the polymer-rich phase in LLPS are on a finer scale ( $\sim$  0.01 to  $\sim$  0.1  $\mu m)$ than the cells that arise through nucleation of the solvent-rich phase (~ 1 to ~ 10  $\mu$ m), due to the much slower diffusion rates associated with the former process.

#### **Summary of Framework**

It is clear from the preceding analysis that the following morphological sequence has to evolve, if solutions of successively increasing polymer concentration are cooled at a slow rate from a homogeneous single phase (Fig. 2). (a) At very low polymer concentrations, crystallization occurs directly from a homogeneous solution (Region I), leading to relatively dense morphological features. (b) In the regime where LLPS precedes crystallization (Region II): (i) Globular Microporous (GMP) morphologies evolve when the polymer concentration is below the critical point (Region IIG), through nucleation of the polymer-rich phase in LLPS, followed by crystallization of this phase. (ii) Fibrillar Microporous (FMP) morphologies arise when polymer concentrations are close to the critical point (Region IIF), through spontaneous spinodal decomposition into polymer-rich and solvent-rich phases, followed by crystallization of the former. (iii) Cell-Tunnel Microporous (CTMP) morphologies are formed when polymer concentrations are above the critical point (Region IIC), through nucleation of the solvent-rich phase in LLPS, followed by crystallization of the polymer-rich phase. It is known that the cells in this microporous morphology result from the discrete spherical domains of the solvent-rich phase that



**Figure 4** Typical phase diagrams of solutions exhibiting LLPS and crystallization. The consequences, visà-vis morphological evolution, of these phase diagrams are discussed in the text.

form during LLPS, while the tunnels (connection between cells) are formed by the solvent front that arises during subsequent crystallization (Fig. 3). (c) At polymer concentrations that are above the region where LLPS precedes crystallization, i.e., where crystallization occurs directly from the homogeneous phase (Region **III**), relatively dense morphologies are again produced.

Thus, the sequence of morphologies that should arise with increasing polymer concentration in binary solution systems that contain a LLPS regime is "dense-GMP-FMP-CTMP-dense." The range of polymer concentration corresponding to each of these morphologies would depend on the phase diagram for the specific solution system. It is possible that certain regimes, especially the spinodal, might be too narrow, requiring finely spaced experimentation in polymer concentrations to see the manifestation of their corresponding morphological features. Some of the typical phase diagrams that can arise are shown in Figure 4. It can be seen clearly that each of these conditions can lead to the predominance of a different morphological feature within the prescribed sequence.

#### **EXPERIMENTAL**

The following is a brief description of the materials and the experimental methods. Additional details can be found in ref. 1.



**Figure 5** Results from direct visualization of homogeneous phase, LLPS, and crystallization in solutions of PANt in 25 : 75 w/w of water/DMF at different temperatures upon cooling. A temperature range has been specified when transitions were observed to indicate the uncertainty in recording the onset temperatures; Cooling rate =  $5^{\circ}$ C/min; Crystallization temperatures obtained from visual recording of solution are compared with the onset of crystallization temperatures obtained from DSC, indicated by  $\bullet$ .

The acrylonitrile-based terpolymer (PANt) used in this research contained 1% itaconic acid and 6% methyl acrylate ( $M_v = 117,000$  g/mol). The solvents in this study were N,N-dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), and dimethyl sulfoxide (DMSO). Each of these solvents was combined with water to generate a series of binary solvents, with diminishing solvent power for PANt as the water concentration was increased.

Calorimetric measurements were carried out in hermetically sealed high-pressure stainless steel pans. The polymer was packed in the pans and a known quantity of solvent was added. Heating and cooling rates of either 20°C/min or 5°C/ min were used. Each thermal analysis experiment consisted of two cycles of heating and cooling.

The samples obtained from DSC pans at the end of the second cooling cycle were used to determine the morphological features of the crystallized polymer. Transverse sections of the dried polymer were examined with a Hitachi Model 800 high-resolution SEM at accelerating voltages ranging from 5 to 20 kV.

Direct visual monitoring of LLPS in these polymer solutions is difficult due to the degradation that occurs when the solutions are held for a long time at high temperatures. Therefore, only a limited set of experiments were conducted to observe LLPS and crystallization directly, primarily to verify the inference from calorimetric experiments regarding the occurrence of LLPS prior to crystallization. These experiments were set up in a high-pressure vessel (70 mL) with borosilicate glass windows. The vessel containing the polymer and solvents was immersed in a silicone oil bath, for controlled heating and cooling. The bath had coils for water cooling and cooling rates up to 5°C/min could be achieved. The large difference in polymer concentrations, and in the corresponding densities of the two liquid phases produced by LLPS, led to gross separation of the two phases in these relatively large scale experiments. In every case that was studied, the development of a distinct interface between the two phases could be observed visually when LLPS occurred.

#### **RESULTS AND DISCUSSION**

## Direct Verification of Inferences Regarding LLPS from Calorimetric Results

Because PAN solutions undergo detectable degradation when kept at high temperatures



Figure 6 Crystallization curves of PANt–DMF–water solutions at 5°C/min cooling rate, depicting the regions where dense, GMP, FMP, or CTMP morphologies were observed. (a) 80% water–20% DMF, (b) 60% water–40% DMF, (c) 40% water–60% DMF, (d) 20% water–80% DMF.



7(a)





7(c)

**Figure 7** SEM micrographs corresponding to Figure 6, depicting the typical morphologies of (a) GMP (2% PANt), (b) CTMP (40% PANt), and (c) relatively dense regions (77% PANt) in 80 : 20 water : DMF.

(above 200°C) in a relatively short time ( $\sim 15$  min), direct observation of the onset of LLPS prior to crystallization was precluded in most cases. As discussed earlier, much of the evidence for occurrence of LLPS prior to crystallization came from observed invariance of crystallization temperature with polymer concentration. Verification of this inference was obtained with solutions of PANt, for example, in 25 : 75 of water : DMF. Formation of two distinct phases with a clear-cut interface was seen

because global phase separation occurred in these solutions under gravity, due to the large size of the high pressure cell. The regions corresponding to crystallization from two-phase and single phase solutions in this experiment were seen to correspond to those obtained via calorimetric measurement of crystallization (Fig. 5). This provided direct validation for associating prior LLPS in the range of polymer concentration that exhibited invariance of crystallization temperature.





8 (b)



8 (c)



8 (d)



#### Morphological Evolution

Verification of the framework relating the phase transitions to the consequent morphologies has been obtained from solutions of PANt in different binary solvent systems. One such solvent system, as discussed in the previous report,<sup>1</sup> is DMF + water, which allows versatile manipulation of phase transitions by changing the ratios of water to DMF.

Because the experimental observations have been made only at discrete polymer concentrations, there are sequences in which one or more of the morphological features may be missing in the results. In the absence of rate effects, the FMP morphology can evolve only if the solution is almost exactly of the critical concentration. It is thus likely to be absent in experiments that are conducted at low rates of cooling. Also, the polymer concentration range corresponding to the evolution of a particular morphology can be so narrow as to be not seen in these experiments. This can be seen in the results from experiments with a series of solutions in 80/20 water/DMF at different polymer concentrations, even with



**Figure 9** Crystallization curves depicting the regions where dense, GMP, FMP, or CTMP morphologies were observed for PANt–water–NMP solutions with varying ratios of water to NMP. (a) 80% water–20% NMP, (b) 60% water–40% NMP, (c) 40% water–60% NMP, (d) 20% water–80% NMP.

closely spaced experiments in the appropriate polymer concentration range, i.e., at low polymer concentrations in this solvent system (Figs. 6 and 7). At 2 and 5% polymer concentrations, traces of GMP and FMP were observed along with CTMP morphological features. As the polymer concentration was increased further, only CTMP structures were observed. Upon increasing the polymer concentration to 80%, dense morphological features were seen.

Significant changes occur in the phase diagram and the consequent "dominant" morphology when the solvent power of a binary solvent is changed through its composition. For example, solutions of PANt in water (Fig. 8) produced predominantly GMP structures in the range from  $\sim 4$  to  $\sim 85\%$ polymer concentration. Traces of FMP appeared along with the GMP morphology in a broad range from 39 to 85% polymer concentration. CTMP morphology was not observed in these solutions, even at polymer concentrations as high as 85%. indicating that the corresponding region between spinodal and binodal is extremely narrow. Relatively dense morphologies were formed from a 95% polymer solution, which depicted crystallization from a homogeneous solution. The crystallization data showed that PANt-water solutions have a broad invariant region, from  $\sim 2$  to  $\sim 85\%$ 

in polymer concentration, where LLPS precedes crystallization. Much of this broad region is at polymer concentrations lower than that of the critical point, thus producing a GMP morphology. Existence of a broad range in which FMP is mixed with GMP also showed that the binodal and spinodal curves are both relatively flat. The inferred phase diagram in this case corresponds to that shown in Figure 4(a), with the critical point around 90% polymer concentration.

As exemplified earlier in solutions of PANt in 80 : 20 of water : DMF (Fig. 6), the dominant morphology changed from GMP to CTMP as DMF was added to water, beginning with a relatively low ratio of DMF to water. Thus, addition of DMF to water dramatically alters the phase transitions in these polymer solutions by changing the relative positions of binodal and spinodal curves and the associated critical point.

As the ratio of DMF to water was further increased, the range of polymer concentration where LLPS preceded crystallization decreased consistently, with the dominant morphology within this regime remaining as CTMP (Fig. 6). The crystallization curves and the predominance of CTMP structures observed in these systems imply together that the phase diagram is skewed towards lower polymer concentration, with a narrow spinodal region, as shown in Fig. 4(c). Solutions of PANt in DMF exhibit only crystallization from a homogeneous solution, resulting in a monotonic increase of crystallization temperature with polymer concentration and a dense morphology.

Phase behavior was also studied in solutions of PANt in binary solvent systems of water with NMP and DMSO. As seen with DMF, they also exhibit a decrease in crystallization temperature as the ratio of NMP or DMSO to water is increased. Invariance of crystallization temperature, exhibiting the presence of LLPS, was also observed in these solvent systems (Figs. 9-12). The range of polymer concentration over which this invariance was observed depended, as with DMF, on the composition of the binary solvent. However, unlike DMF, the polymer crystallized from these solutions exhibited a predominance of GMP morphology over much of the binary solvent composition. FMP structures were seen, but only in trace quantities at certain compositions, only in combination with GMP structures. The NMPwater system exhibited CTMP along with GMP at certain concentrations and CTMP along with dense structures at higher concentrations, both conforming to the sequence in the framework out-



10 (a)





#### 10 (c)

**Figure 10** SEM micrographs corresponding to Figure 9(a), depicting the typical morphologies of (a) GMP (20% PANt), (b) FMP (49% PANt), and (c) relatively dense regions (79% PANt) in 80% : 20% water : NMP.

lined earlier. The inference from the observed crystallization temperatures and the corresponding morphologies is that solutions of PANt in binary solvents of water with NMP and DMSO produce, respectively, phase behaviors that correspond to Figure 4(b) and (d).

The crystallization and morphological data pertaining to solutions of PANt in water, and in binary solvents containing water, show how the solvent system controls the thermodynamics of phase transitions and causes the relative positions of binodal and spinodal to shift. Four distinctly different phase diagrams have been inferred to exist in these solutions. The inferences are that a solution of PANt in (a) water has a flat binodal curve and a broad spinodal along with it [Fig. 4(a)]; (b) DMF with water shifts the spinodal to a significantly lower polymer concentration [Fig. 4(c)]; (c) water-DMSO moves the spinodal towards the higher end of polymer concentrations [Fig. 4(d)]; (d) water-NMP exhibits an intermediate spinodal regime [Fig. 4(b)]. Thus, it can be seen that the solvent interactions play an important part in dictating the phase transitions. All



**Figure 11** Crystallization curves depicting the regions where dense, GMP, FMP, or CTMP morphologies were observed for PANt-water-DMSO solutions with varying ratios of water to DMSO. (a) 80% water-20% DMSO, (b) 60% water-40% DMSO, (c) 40% water-60% DMSO, (d) 20% water-80% DMSO.

the solutions follow the general framework that has been proposed for generation of morphological features (Fig. 2). The morphological features are formed in a well-defined specific sequence as the polymer concentration is changed in these solutions. If LLPS precedes crystallization of the polymer, the progression occurs from GMP to FMP to CTMP as the polymer concentration is increased within the range of LLPS. Changing the solvent system changes the breadth of the regimes of polymer concentration where each of these morphologies is generated.

#### **Coexisting Morphologies**

In solutions that exhibit LLPS prior to crystallization, up to three phases can coexist at certain temperatures and overall concentrations. The phases that coexist are obtained through a horizontal line drawn at a given temperature. The phases that correspond to the intersection of this line with the phase diagram can coexist. If the overall concentration of the polymer is such that it is very close to the boundary of two adjacent regions, then concentration fluctuations could cause the typical morphologies of these two regions to coexist. Another mechanism by which two morphologies that are typical of two different regions can coexist is when the already formed phases undergo phase separation within their domains, thus giving rise to phases within phases.<sup>5</sup> Here, the microstructure can appear as patches of regions of very different morphological features. It should be noted that most of the solutions studied here produced only the morphology dictated by a single sequence of phase transitions at a given overall polymer concentration. It is, however, important to recognize the solution compositions that can result in mixed morphologies in the crystallized polymer so that they can be avoided in processes where a single uniform morphology is desired. An example of PANt solution in a binary solvent that has a propensity to form mixed morphologies is described by Akki.<sup>5</sup>

#### SUMMARY AND CONCLUSIONS

Polymer solutions that undergo LLPS and crystallization generate morphological features that depend on the sequence and magnitude, i.e., time duration and temperature range, of transitions that lead to a solidified polymer. Depending on the polymer-solvent system, the underlying phase diagram can have distinctly different characteristics pertaining to the binodal and spinodal (flat or narrow, symmetric, or asymmetric with a skew towards low or high polymer concentrations, etc.) as well as crystallization transitions. A framework has been developed here to relate the path of a process across the phase diagram for a polymer solution to the resulting morphology in the crystallized polymer. The morphological features of interest are in the range of 0.01 to 10  $\mu$ m, features that arise from any LLPS that might precede crystallization of the polymer. Four distinctly different morphologies result from crystallization (a) directly from a homogeneous solution (dense), (b) following binodal LLPS with nucleation of the polymer-rich phase (globular microporous-GMP), (c) following spinodal LLPS (fibrillar microporous-FMP), or (d) following binodal LLPS with nucleation of the solvent-rich phase (cell-tunnel microporous-CTMP). The underlying nucleation processes dictate that the morphologies that arise from increasing the overall polymer concentration in such solutions follow the sequence, "dense  $\rightarrow$  GMP  $\rightarrow$  FMP  $\rightarrow$  CTMP  $\rightarrow$ dense." The framework also serves to identify conditions (narrow temperature/concentration regions in the phase diagram) that can increase the









12 (c)

**Figure 12** SEM micrographs corresponding to Figure 11 depicting the typical morphologies of (a) GMP (28% PANt), (b) FMP (68% PANt), and (c) relatively dense regions (79% PANt) in 80 : 20 water : DMSO.

likelihood of forming mixed or coexisting phases and the consequent morphologies.

PANt solutions in binary solvents, containing water and DMF, NMP, or DMSO, showed that the solvents affect the phase behavior significantly. The evolution of morphology in these different binary solvent systems has been seen to be consistent with the proposed thermodynamic framework. This framework can be used for rational design of processes to generate suitable morphologies for specific applications.

The morphologies that evolve in these solutions also differ in sizes. The scale of morphological features in GMP are smaller than CTMP morphology by at least an order of magnitude, again consistent with the inferred mechanisms of phase separation in their formation, namely, nucleation and growth of polymer- or solvent-rich phases, respectively, in LLPS. To make quantitative predictions of these morphological features, it is necessary to analyze the underlying kinetics of nucleation and the transport processes during LLPS and any subsequent structural coarsening<sup>26,27</sup> that can occur. The thermodynamic framework presented here can serve to formulate appropriate kinetic models for quantitative modeling of these processes. The authors gratefully acknowledge partial funding of this research through a grant from the DuPont Company. Additional funding was provided by the High Performance Polymers and Ceramics (HiPPAC) Center, funded by NASA.

#### REFERENCES

- Akki, R.; Desai, P.; Abhiraman, A. S. J Appl Polym Sci 1994, 54, 1263.
- Lee, H. K.; Myerson, A. S.; Levon, K. Macromolecules 1992, 25, 4002.
- 3. Tager, A. A. Fluid Mech Soviet Res 1991, 20, 80.
- 4. Hillert, M. In Lectures on the Theory of Phase Transformations; Aaronson, H., Ed.; American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.: New York, 1986.
- Akki, R. Ph.D. Thesis, Georgia Institute of Technology (1995).
- 6. Abhiraman, A. S. unpublished work (1978).
- Van der Witte, P.; Dijkstra, P. J.; van den Berg, J. W. A.; Feijen, J. J Membr Sci 1996, 117, 1.
- Schugens, Ch.; Maquet, V.; Grandfils, Ch.; Jerome, R.; Teyssie, Ph. J Biomed Mater Res 1996; 30, 449.
- Han, M. J.; Bummer, P. M.; Jay, M.; Bhattacharyya, D. Polymer 1995; 36, 4711.
- Cheng, L.-P.; Dwan, A.-H.; Gryte, C. C. J Polym Sci Part B Polym Phys 1995, 33, 211.
- Han, M. J.; Bhattacharyya, D. J Membr Sci 1995, 98, 191.

- Damman, P.; Fougnies, C.; Dosiere, M.; Wittmann, J. C. Macromolecules 1995, 28, 8272.
- Vadalia, H. C.; Lee, H. K.; Myerson, A. S.; Levon, K. J Membr Sci 1994, 89, 37.
- Laxminarayan, A.; McGuire, K. S.; Kim, S. S.; Lloyd, D. R. Polymer 1994, 35, 3060.
- Nicholes, M. E.; Robertson, R. E. J Polym Sci Part B Polym Phys 1994, 32, 573.
- Zyrd, J. L.; Burghardt, W. R. Polym Mater Sci Eng 1993, 69, 347.
- Bulte, A. M. W.; Folkers, B.; Mulder, M. H. V.; Smolders, C. A. J Appl Polym Sci 1993, 50, 13.
- Vandeweerdt, P.; Berghmans, H.; Tervoort, Y. Macromolecules 1991, 24, 3547.
- 19. Bansil, R. J Phys IV 1993, 3, 225.
- Smartt, W. M. Ph. D. Thesis, Georgia Institute of Technology (1991).
- Kaneba, G. T.; Soong, D. S. Macromolecules 1985, 18, 2538.
- Aubert, J. H.; Clough, R. L. Polymer 1985, 26, 2047.
- Williams, J. M.; Moore, J. E. Polymer 1987, 28, 1950.
- 24. Aubert, J. H. Macromolecules 1988, 21, 3468.
- 25. Kinzer, K. E. U.S. Pat. # 4,867,881 (1989).
- Tsai, F. J.; Torkelson, J. M. Macromolecules 1990, 23, 775.
- 27. Aubert, J. H. Macromolecules 1990, 23, 1446.
- Lloyd, D. R.; Kim, S. S.; Kinzer, K. E. J Membr Sci 1991, 64, 1.