

Morphological Implications of Phase Transitions in Polymer Solutions: Study of Polyacrylonitrile-Based Solutions

RASHI AKKI, P. DESAI,¹ and A. S. ABHIRAMAN^{2,*}

Polymer Education and Research Center, ¹School of Textile and Fiber Engineering and ²School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

SYNOPSIS

Solution-based processing of infusible polymers usually involves large quantities of undesirable solvents and transport-limited morphological evolution that is often difficult to control. The present study constitutes a rational exploration of the phase transitions in polymer solutions to form the basis for new processes that would diminish the above-mentioned problems and also identify appropriate mechanisms for controlled generation of useful morphologies. The fundamental concepts in this regard are exemplified through solutions of acrylonitrile-based homopolymer and copolymers, with important inferences drawn regarding their potential implications for the formation of fibers, films, and membranes. Thermodynamic and kinetic manipulation of transitions such as liquid-liquid phase separation and crystallization is shown to be effective in controlled generation of morphologies ranging from microporous to dense. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Processing of infusible polymers, such as polyacrylonitrile (PAN), cellulose, and aromatic polyamides and polyesters, is carried out of necessity via solution-based routes. In addition, solution-based paths are also followed in many instances with fusible as well as infusible polymers to generate morphologies that are inaccessible via bulk-processing routes. Predominant among familiar examples of this kind is the formation of membranes in which desired microporous morphologies are generated by virtue of liquid-liquid phase separation induced by coagulation in a nonsolvent medium, concentration changes via controlled evaporation of solvent, or a controlled change in temperature. If relatively homogeneous morphological features are wanted in the final product, thermally induced phase transitions (TIPT) are preferred because diffusion-controlled¹ global morphological gradients are usually encountered in evaporation or non-solvent-induced coagulation processes.

The estimated melting temperature of polyacrylonitrile is around 320°C,^{2,3} but it is well-known that degradation of the polymer occurs before the onset of melting^{4,5} unless heating rates in excess of 1,000°C/min are used. Even under such extreme conditions, rapid degradation of this polymer occurs immediately following melting. Homopolymers and copolymers of acrylonitrile (AN) are therefore processed necessarily from their solutions. Commonly used solvents for solution-based processing of PAN [solubility parameter,⁶ $\delta = 12.5$ (cal/mL)^{1/2}] are dimethyl formamide [DMF; $\delta = 12.1$ (cal/mL)^{1/2}], dimethyl acetamide [DMAc; $\delta = 10.8$ (cal/mL)^{1/2}], and dimethyl sulfoxide [DMSO; $\delta = 12.0$ (cal/mL)^{1/2}]. These solvents are considered good solvents of polyacrylonitrile because their solubility parameters are very close to the polymer. Solutions of PAN in these solvents have subambient melting/crystallization points.

A route that has been recently explored for processing of PAN is from solutions made in water⁷ at a relatively high temperature, around 200°C. A useful feature of this processing route is the fact that precipitation of the polymer from solution is via a thermally induced phase transition (crystallization) that occurs well above room temperature. Because

* To whom correspondence should be addressed.

it is *not* a large-scale diffusion controlled process, it would allow a faster rate of processing. If local diffusional instabilities can be avoided during the phase transition, a homogeneous morphology would be obtained in the final product. Since water [$\delta = 23.4$ (cal/mL) $^{1/2}$] 6 is not as good a solvent for PAN as DMF or DMAc, solutions of PAN in water have high melting/crystallization temperatures, higher than the normal boiling point of water, as has been shown experimentally by Frushour. 8 A major difficulty that is encountered in processing PAN from its solution in water arises because the crystallization temperature is much higher than the normal boiling temperature of the solvent. Min et al. 9 extruded filaments from a solution of PAN in water under supercooled conditions (at 150°C) after melting (at 170°C), and found that supercooling helped reduce foaming problems caused by high pressures in fiber spinning. They also recognized that incorporation of a solvent, such as ethylene carbonate, with water in a ternary solution with PAN decreased the melting and crystallization temperatures. Solutions of PAN in water-DMF binary solvent have also been shown to decrease the gelation (crystallization) time compared to solutions in DMF alone. 10

The study reported here is part of a comprehensive effort 11,12 to rationalize the role of phase transitions that can occur in polymer solutions, with respect to the evolution of morphology and properties in solution-based processing. The goal is to apply such knowledge to facilitate the development of new processes that would offer one or more of the following advantages: versatile generation of morphology, control of morphological evolution, simple processing and solvent recovery schemes, and elimination/reduction of toxic solvents.

The phase transitions in polymer solutions that are of interest, in relation to processing and evolution of morphology, are liquid-liquid demixing and crystallization. If a single-phase, homogeneous solution phase separates due to crystallization of the polymer, an increase in the crystallization temperature is observed with an increase in the polymer concentration. On the other hand, if liquid-liquid phase separation (LLPS) precedes crystallization, an invariance of crystallization temperature with polymer concentration is observed within that specific regime (Fig. 1). This is due to the occurrence of crystallization from a two-phase solution which, according to phase rule, causes a reduction in the degree of freedom. In solutions with extreme polymer concentrations, where crystallization precedes and thus precludes liquid-liquid demixing, there

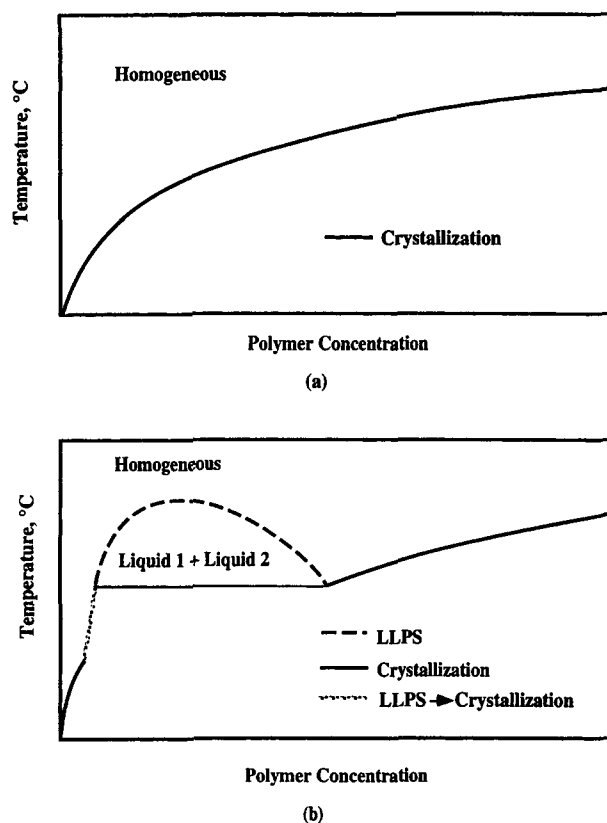


Figure 1 Phase behavior of polymer solutions undergoing crystallization and liquid-liquid phase transition: (a) when crystallization occurs from a homogeneous solution, and (b) when liquid-liquid demixing precedes crystallization.

would still be an increase of crystallization temperature with polymer concentration. The behavior of the crystallization curve in the phase diagram, with respect to polymer concentration, would thus allow us to infer whether crystallization is occurring from a single- or a two-phase liquid solution. As early as 1945, Richards 13 had noticed this kind of phase behavior for polyethylene in various solvents ranging from good to poor. Burghardt 14,15 has experimentally measured, and also calculated, these phase diagrams based on the Flory-Huggins theory for binary and ternary systems [poly (2,6-dimethyl-1,4-phenylene oxide) in binary solvent systems], and predicted the invariant crystallization temperature with polymer compositions for systems showing LLPS and crystallization. Frushour 8 has also shown that the melting temperature of PAN in water remained invariant above a weight fraction of water ≈ 0.3 , at least up to a weight fraction of 0.6. However, no inferences regarding any preceding transitions or consequent morphologies were drawn from these data.

It is obvious that the morphology of a polymer that crystallizes from a solution will depend on any phase transition that might precede crystallization itself. Of particular interest in this regard are the consequences of liquid-liquid phase transition prior to crystallization. Distinctly microporous morphologies, ranging from cell-pore microporous (CPMP)¹⁶ structures, through globular microporous¹⁷ (GMP), to fibrillar microporous (FMP) structures have been obtained in such cases. The CPMP and GMP morphologies are usually consequences of liquid-liquid phase transition via nucleation and growth of the low polymer concentration and the higher polymer concentration liquid phases, respectively, followed by glass transition or crystallization of the polymer in the higher concentration phase. The scale of such structures is typically $> 0.1 \mu\text{m}$. Microporous structures of a smaller scale are also typically seen *within* the CPMP and GMP structures. The FMP morphologies arise often from spinodal decomposition into two continuous liquid phases prior to crystallization. Structures that reflect a combination of both (i) spinodal decomposition and (ii) nucleation and growth¹⁸ are also seen in many cases. It is clear that kinetics of these phase transitions¹⁹ would influence the nature of morphological evolution in such cases. It is especially important to know the relative influence of each governing factor on these phase transitions. For example, the rate of cooling of a solution can have a pronounced influence on the onset of crystallization, especially in concentrated solutions. If the kinetic influence of the same factor on liquid-liquid phase separation is less pronounced, then the gap between the onset of the two transitions would be widened,

with important consequences to the evolution of topological features in the resulting material. The study reported here is meant to address such issues and produce generalized inferences regarding mechanisms for controlled generation of useful morphologies. The fundamental knowledge gained is also shown to be potentially relevant in designing simplified solution-based polymer processes.

EXPERIMENTAL

Materials

The acrylonitrile-based polymers used in this research were a homopolymer from Polysciences Inc. (PAN-H; $\bar{M}_v = 79,800 \text{ g/mol}$), a copolymer with 2% itaconic acid (PAN-IA2; $\bar{M}_v = 204,300 \text{ g/mol}$), a copolymer with 6% itaconic acid (PAN-IA6; $\bar{M}_v = 269,100 \text{ g/mol}$), and a terpolymer with 1% itaconic acid and 6% methyl acrylate (PAN-T; $\bar{M}_v = 117,000 \text{ g/mol}$). The viscosity-average molecular weights were obtained from measurement of intrinsic viscosity in DMF at 30°C. The Mark-Houwink-Sakurada equation, $[\eta] = K(\bar{M}_v)^a$, with $K = 0.0335 \text{ mL/g}$ and $a = 0.72$ at 30°C, was used for PAN-T, and $K = 0.0392 \text{ mL/g}$ and $a = 0.75$ at 25°C, were used for all the other polymers in this study.⁶

Calorimetry

Calorimetric measurements were carried out using Seiko (SSC/5200) and Perkin-Elmer System 4 differential-scanning calorimeters (DSC). The samples were made in hermetically sealed stainless-steel pans

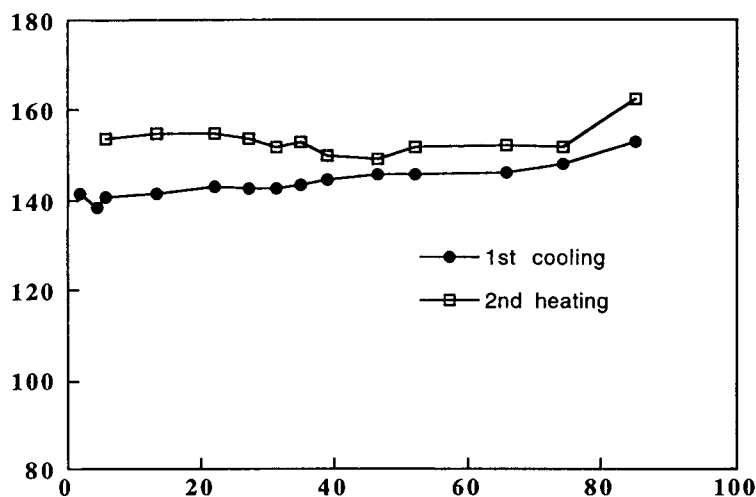
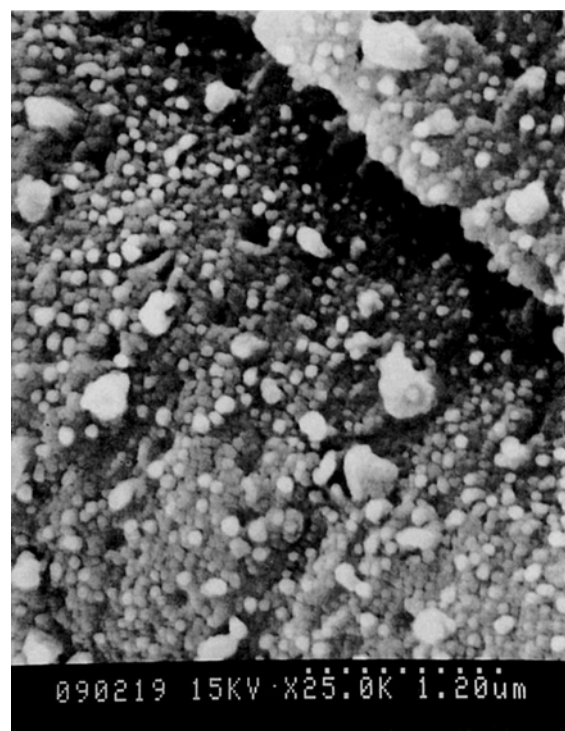
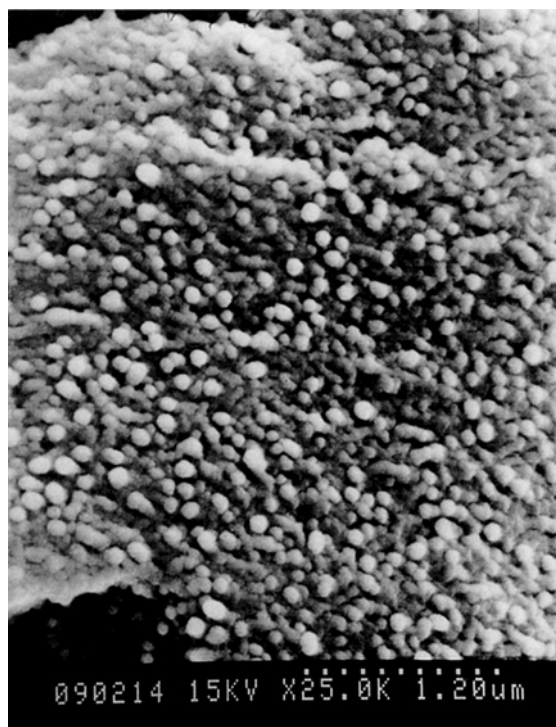


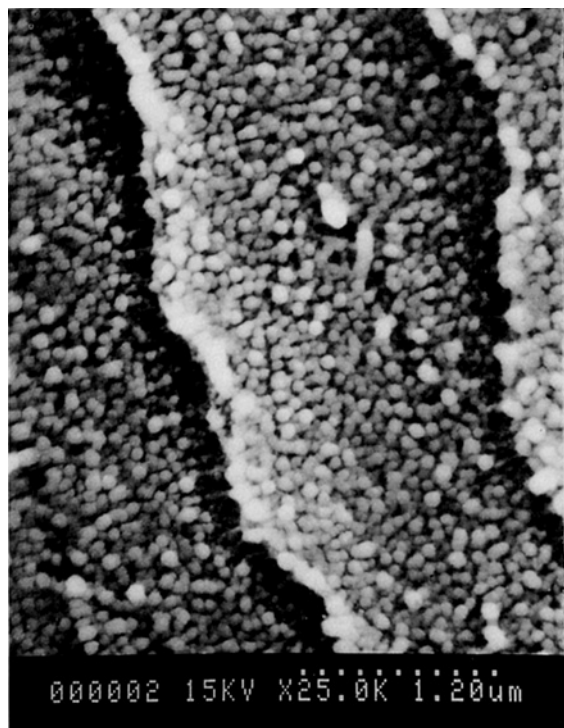
Figure 2 Crystallization and melting temperatures of solutions of PAN-T in water.



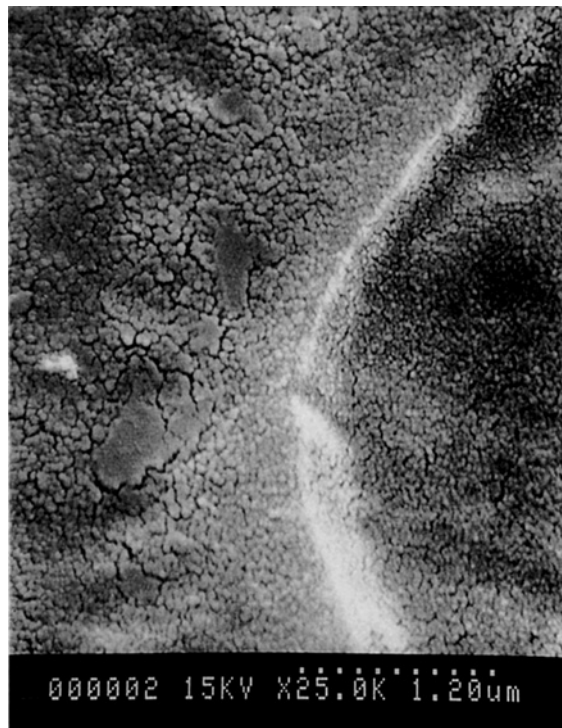
(A)



(B)



(C)



(D)

Figure 3 Micrographs of solutions containing (a) 6%, (b) 35%, (c) 52%, and (d) 85% w/w PAN-T in water. (a), (b), and (c) depict GMP morphology; (d) shows dense morphological features with cracks due to nonuniform cooling.

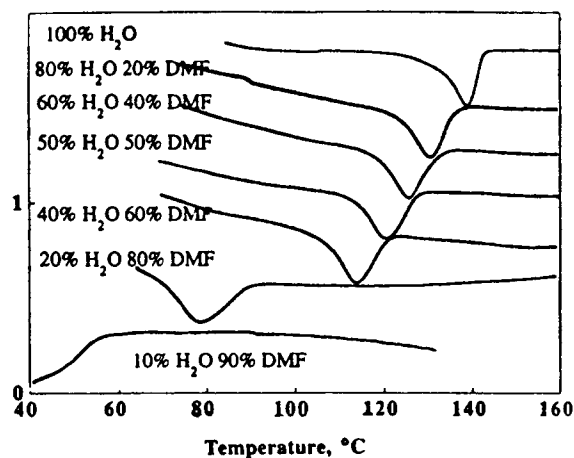


Figure 4 DSC thermograms of PAN-T solutions in binary solvent systems containing water and DMF in different relative concentrations.

(Seiko, part T560005), which can sustain up to 50 atm pressure, or large-volume stainless-steel capsules (Perkin-Elmer, part 319-0218), which can sustain 25 atm pressure. The polymer was packed in the bottom of the pans, and a known volume of binary solvent was added to the polymer using a microsyringe. Exact masses were measured at each stage to estimate the composition of the mixture. The Seiko pans could easily sustain the pressures generated by water alone at temperatures up to 230°C. To provide a margin of safety, i.e., avoid rupture of a capsule, the thermal scans with Perkin-

Elmer pans were not taken beyond 200°C. The program generally consisted of two cycles of heating and cooling scans. To avoid anomalies due to differences in initial morphologies, data from the first heating ramp were not used in the analysis. Heating and cooling rates in the range from 1°C/min to 40°C/min were used to study the effect of rates, but most of the studies were carried out at 5°C/min and 20°C/min. The sealed DSC pans were weighed at the end of each thermal analysis to ensure that no loss of solvent had occurred during the experiment.

Prior to conducting the measurements on phase behavior of the polymers in solutions, studies were carried out to determine if significant degradation would occur at the high temperatures to which the solutions would be exposed. One would like to raise the temperature as high as possible and stay at the high temperature long enough to ensure that all the initially present crystallites have been allowed to melt completely and that a homogeneous solution is obtained, before cooling it to determine the onset of liquid-liquid phase separation and/or crystallization. An obvious constraint in this regard arises from any degradation that can occur if the solution is kept at a high temperature for a long time. Thus, a detailed study to determine the optimum combination of time and temperature was conducted. Detection of degradation was carried out through visual examination of any discoloration because it offered much greater sensitivity than spectroscopic methods. A series of experiments were conducted at which solutions of PAN-T were raised to, and kept at,

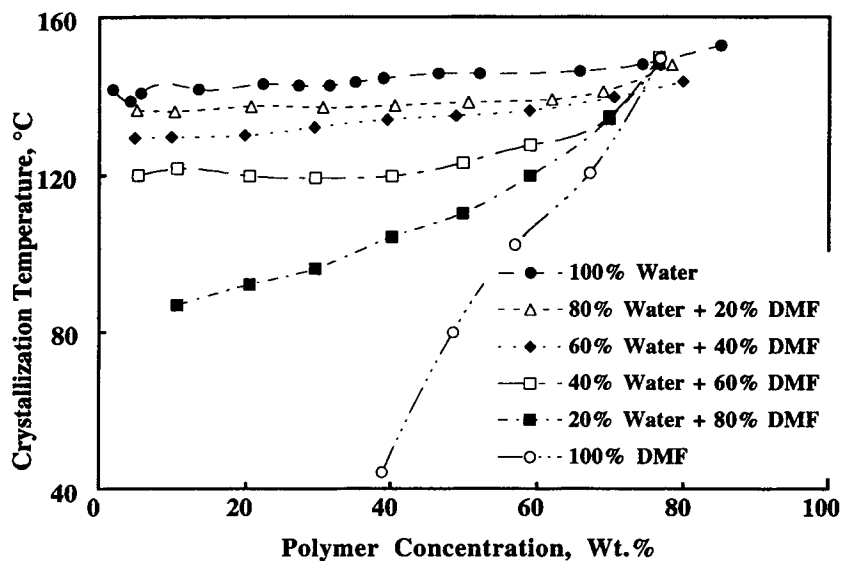


Figure 5 Partial phase diagram depicting crystallization of PAN-T in binary solvent system containing water and DMF in various compositions.

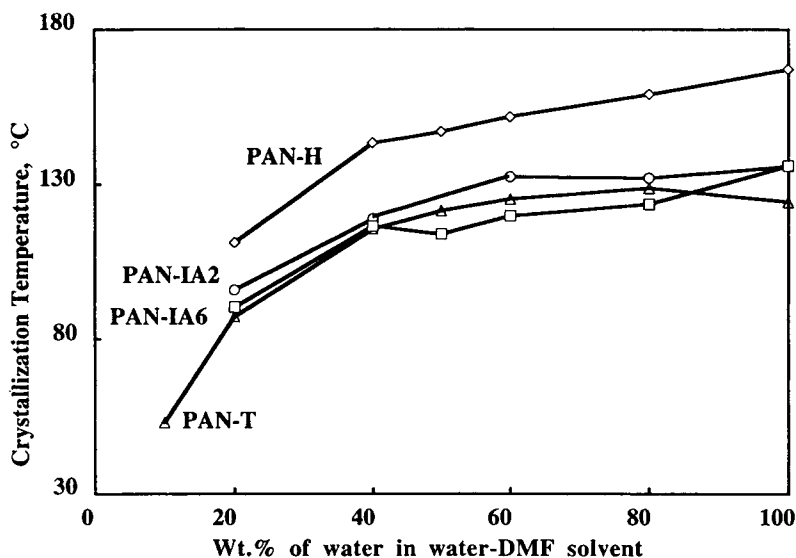


Figure 6 Effect of copolymerization on crystallization temperature. Cooling rate = 20°C/min; polymer concentration = 10 wt %.

temperatures ranging from 200°C to 230°C for 5 min to 15 min. The pans were then opened and any discoloration noted. It was found that the samples taken up to 230°C for 15 min degraded to such an extent that the solution did not crystallize, and stayed in a liquid form even at room temperature. The solutions that were taken to 220°C for 5 min and 15 min, and to 210°C for 15 min, were all brownish gels. The samples that were taken to 210°C for 5 min did not go into solution completely, and remnants of initial fibers were still seen when examined subsequently by scanning electron microscopy. The combination of a maximum temperature of 210°C and a soak time of 10 min was determined to be the most appropriate for PAN solutions in water.

Table I Effect of Cooling Rate on the Onset of Crystallization and Morphology in PAN-T 20% w/w Solutions in 40 : 60 Water/DMF

| Maximum Temp (°C) | Cooling Rate (°C/min) | Crystallization Temp (°C) | Morphology |
|-------------------|-----------------------|---------------------------|--------------|
| 210 | 1 | — | GMP |
| 210 | 5 | 117 | GMP and CPMP |
| 210 | 20 | 100 | CPMP |
| 210 | 40 | 82 | CPMP |

Temp = temperature.

The conditions established above were further verified for the absence of significant degradation by examining crystallization in successive cycles of calorimetric analysis. If significant degradation should occur, it would be reflected through a change in the temperature and/or enthalpy of crystallization. Additional confirmation in this regard was obtained by ensuring invariance of morphology of the crystallized polymers from these solutions. It is quite possible that degradation is still occurring to a small extent in all the samples under the conditions established through these experiments. However, its influence on the phase transitions of interest and the consequent morphologies has been negligible in the thermal studies.

Based on thermal, morphological, and visual assessment of degradation, the scans were chosen to be from room temperature to 210°C, with a soak time of 10 min at 210°C for PAN-water systems. Similar studies were carried out as a function of DMF content in the binary solvent. The maximum temperature was set at 190°C, with a soak time of 10 min at DMF concentration $\geq 60\%$ w/w in the binary solvent system.

Scanning Electron Microscopy (SEM)

The samples obtained from DSC pans at the end of the second cooling cycle were used to study the morphology of the crystallized polymer. These samples were soaked in a large amount of water for 24 h at room temperature to dilute the DMF. The second

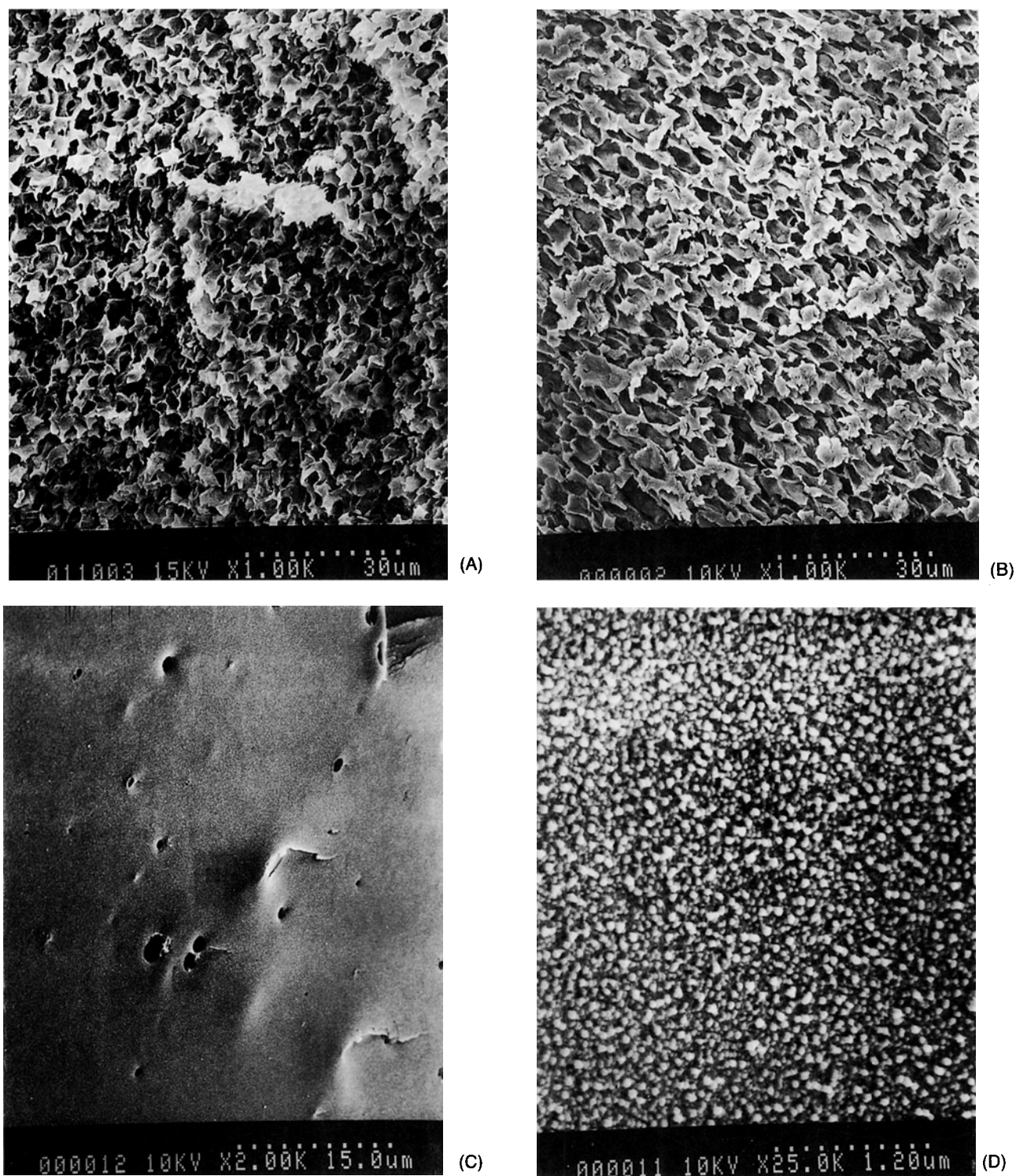


Figure 7 Morphological features obtained at different cooling rates from solutions containing 20% w/w PAN-T in binary solvent ratio of 40 : 60 water/DMF. Cooling rates of (a) 40°C/min, (b) 20°C/min, (c) 1°C/min at low resolution, and (d) 1°C/min at high resolution have been shown.

Table II Effect of Solution-Forming Temperatures on Crystallization Temperature and Morphology in PAN-T 21% w/w Solutions in 40 : 60 Water/DMF

| 1st Scan T_{\max} (°C) | 2nd Scan T_{\max} (°C) | Crystallization Temperature | | Morphologies |
|-----------------------------|-----------------------------|-----------------------------|---------------|-------------------------------|
| | | 1st Scan (°C) | 2nd Scan (°C) | |
| 190 | 190 | 123.5 | 122.1 | CPMP |
| 190 | 170 | 124.1 | 125.1 | CPMP |
| 190 | 160 | 123.0 | 130.7 | Inhomogeneous, mostly CPMP |
| 190 | 150 | 123.2 | 131.9 | Inhomogeneous, mostly CPMP |

Heating and cooling rates used were 5°C/min.

step involved soaking in fresh water for 24 h again to remove the remaining DMF. The polymer was then allowed to dry for another 48 h. Transverse sections of the sample were cut, glued to aluminum stubs, and then gold plated in an International Scientific Instruments sputter coater for 4 min at a voltage of 1.2 kV and current of 12 mA. They were examined in a Hitachi high-resolution SEM (model 800) at accelerating voltages ranging from 10 kV to 20 kV.

RESULTS AND DISCUSSION

PAN-Water Solutions

Melting and crystallization temperatures measured in PAN-T and water solutions exhibited a broad region of invariance with respect to polymer concentration (Fig. 2). The results are similar to those of Frushour,⁸ who had shown that the melting temperature of these solutions was depressed with an increase in water concentration to a certain limit, beyond which it remained invariant. The scans were made at 5°C/min, the lowest cooling rate required to obtain the appropriate sensitivity in the DSC thermograms; at lower rates, the peaks broadened to such an extent that assessment of the onset temperature became impossible. At a scan rate of 5°C/min, it was found that the crystallization temperature of these solutions remained the same from 2% up to 75% w/w in polymer concentration, beyond which an increase in the crystallization temperature was observed. The inference from phase rule regarding this invariance is that crystallization is occurring from a two-phased system. Thus, liquid-liq-

uid phase separation (LLPS) occurs prior to crystallization in these solutions. A uniformly globular morphology, with the size of the globules depending on polymer concentration, was observed as a consequence in all cases up to 75% polymer concentration (Fig. 3). Solutions containing 85% polymer were heterogeneous, and yield a dense morphology in most of the areas and some partially globular characteristics, most likely because this composition was close to the boundary between direct crystallization from a single-phase solution and liquid-liquid phase separation prior to crystallization. Morphology of the crystallized polymer from higher concentration solutions was essentially dense within the scale of resolution used in this analysis. Experiments at high polymer concentrations also revealed some evidence of degradation of the polymer, as indicated by discoloration of the solution.

PAN-Binary Solvent Systems

The DSC thermograms obtained with 10% w/w of the terpolymer in different compositions of the DMF-water binary solvent system are shown in Figure 4. As expected, the exotherm corresponding to crystallization of the polymer is shifted to lower temperatures with increasing DMF concentrations. The drop in crystallization temperature is especially pronounced when the DMF concentration in the binary solvent is increased above 60% w/w. The data shown with respect to the onset of crystallization at different polymer concentrations and solvent compositions provide an important clue in this regard (Fig. 5). Whereas the crystallization temperature appears to be invariant over a broad range of polymer concentration in binary solvents with 60% w/

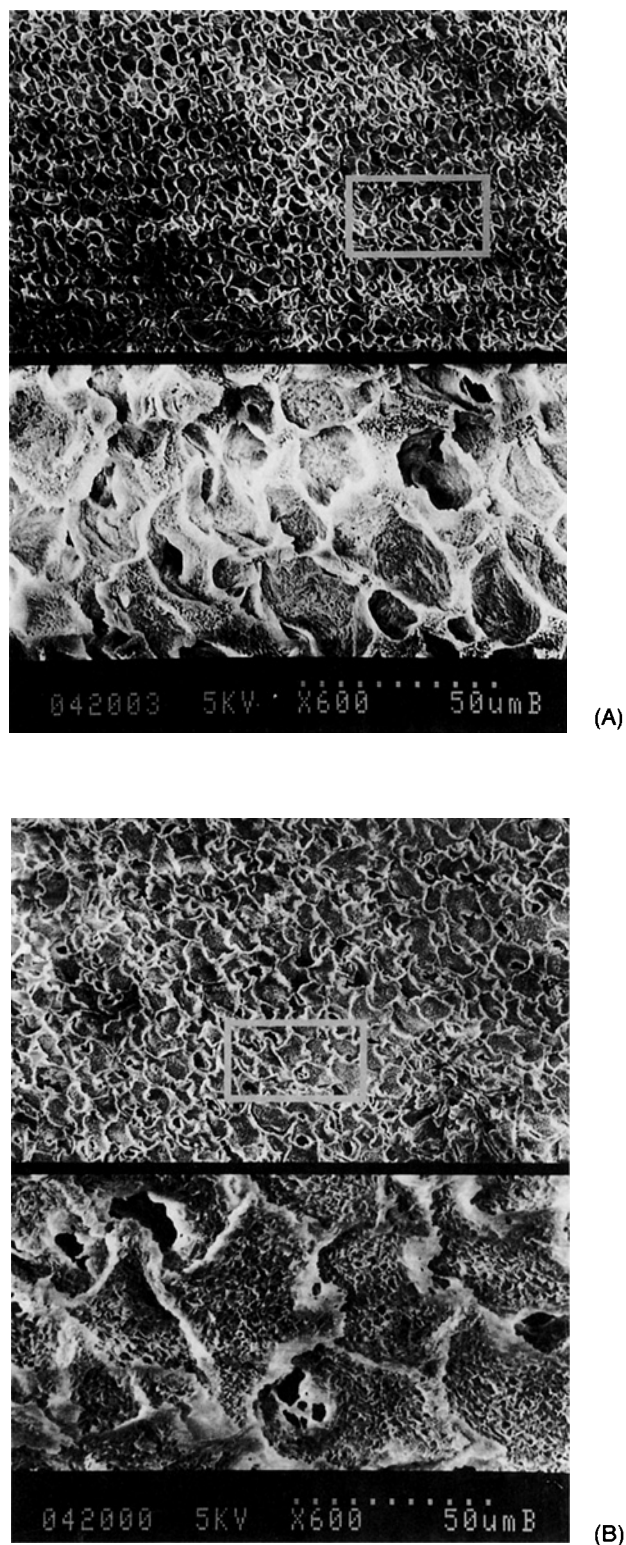


Figure 8 Effect on morphology of solution-forming temperature (a) $T_{\max} = 190^{\circ}\text{C}$, and (b) $T_{\max} = 160^{\circ}\text{C}$; 20% w/w PAN-T in 40 : 60 w/w of water/DMF. Cooling rate = $5^{\circ}\text{C}/\text{min}$.

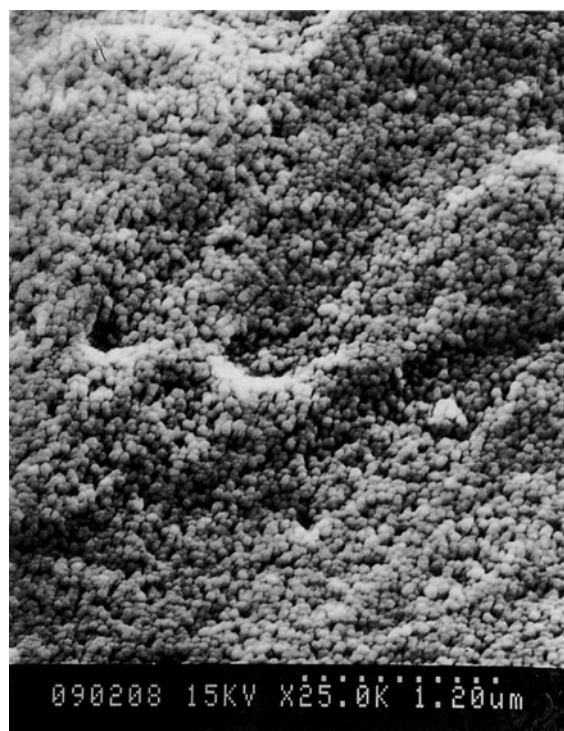
w DMF or less, one observes a monotonic decrease in this temperature with a decrease in polymer concentration at compositions of 20 : 80 and 0 : 100 w/w water/DMF. As described earlier, the data from solutions with relatively lower DMF concentrations reflect the occurrence of LLPS prior to crystallization over a broad range of overall polymer concentration in solution. Crystallization in these cases will be initiated in the phase with high polymer concentration, thus resulting in a significant elevation of its onset temperature. There is no evidence of such LLPS in the crystallization data corresponding to 20 : 80 and 0 : 100 w/w water/DMF solvents. It should be noted here that these data were obtained at a cooling rate of $5^{\circ}\text{C}/\text{min}$. Since the kinetic influence is likely to be much greater on the onset of crystallization than LLPS, it is possible for these characteristics to change with factors such as the rate of cooling. This aspect will be addressed further in a later section.

An interesting aspect in the data shown in Figure 5 is that, by choosing the appropriate binary solvent composition, crystallization of the polymer can be made to occur between room temperature and the normal boiling point of the solvent. This feature can provide two significant advantages in processing the polymer:

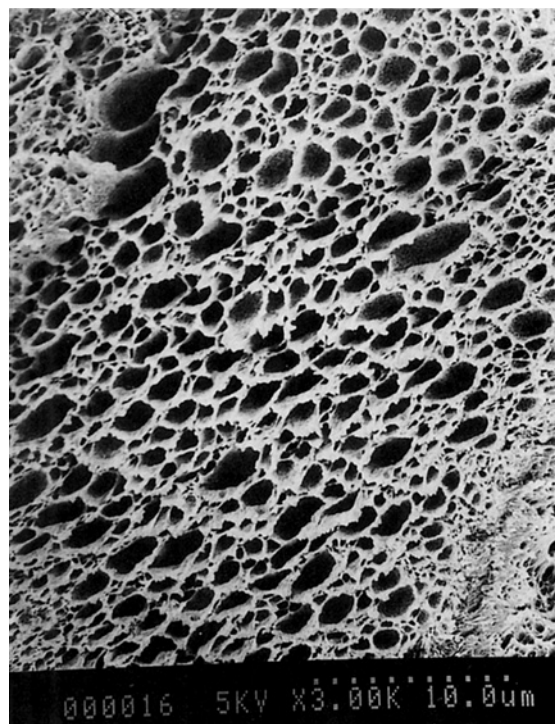
1. Thermally induced crystallization above room temperature can be used to eliminate the need for coagulation of the solution in a nonsolvent or rapid evaporation of the solvent to cause solidification via crystallization. Both these processes present significant disadvantages in solvent recovery and in the generation of homogeneous morphologies.
2. Reducing the crystallization temperature to below the normal boiling point of the solvent would allow solidification of the polymer under conditions with relatively low vapor pressure of the solvent. High vapor pressures during crystallization of the polymer, such as those in the PAN-water systems, can lead to diffusional instabilities and thus result in the formation of significant defects in the solidified polymer structure.

Copolymerization

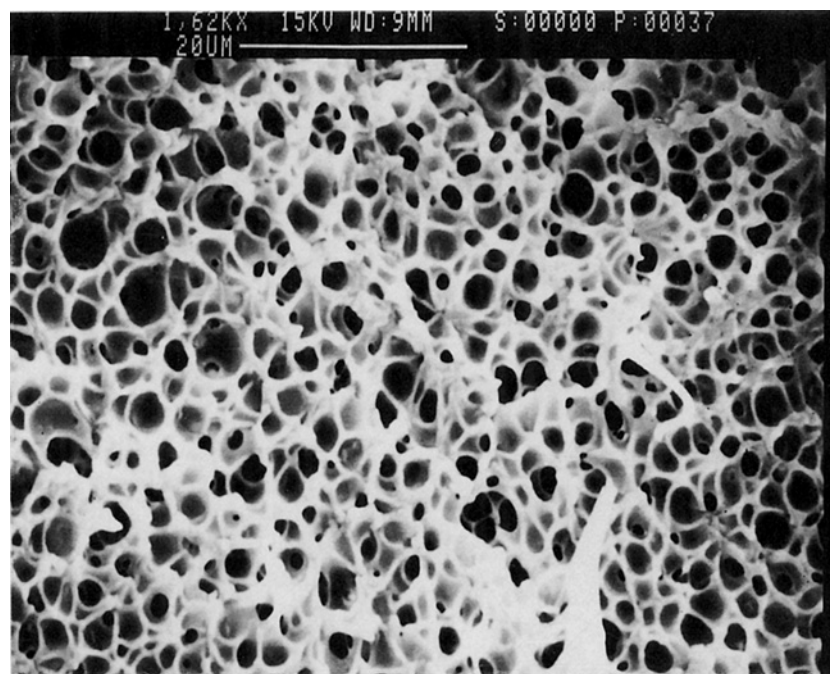
An effective mechanism for changing (decreasing) the crystallization/solution temperature of the polymer, without adversely affecting the potential mechanical properties of the solid polymer, is



(A)



(B)



(C)

Figure 9 Effect of binary solvent composition on morphology of 20% w/w PAN-T. Water/DMF ratio: (a) 100 : 0, (b) 80 : 20, (c) 60 : 40, (d) 50 : 50, (e) 40 : 60, and (f) 10 : 90. Cooling rate = 20°C/min.

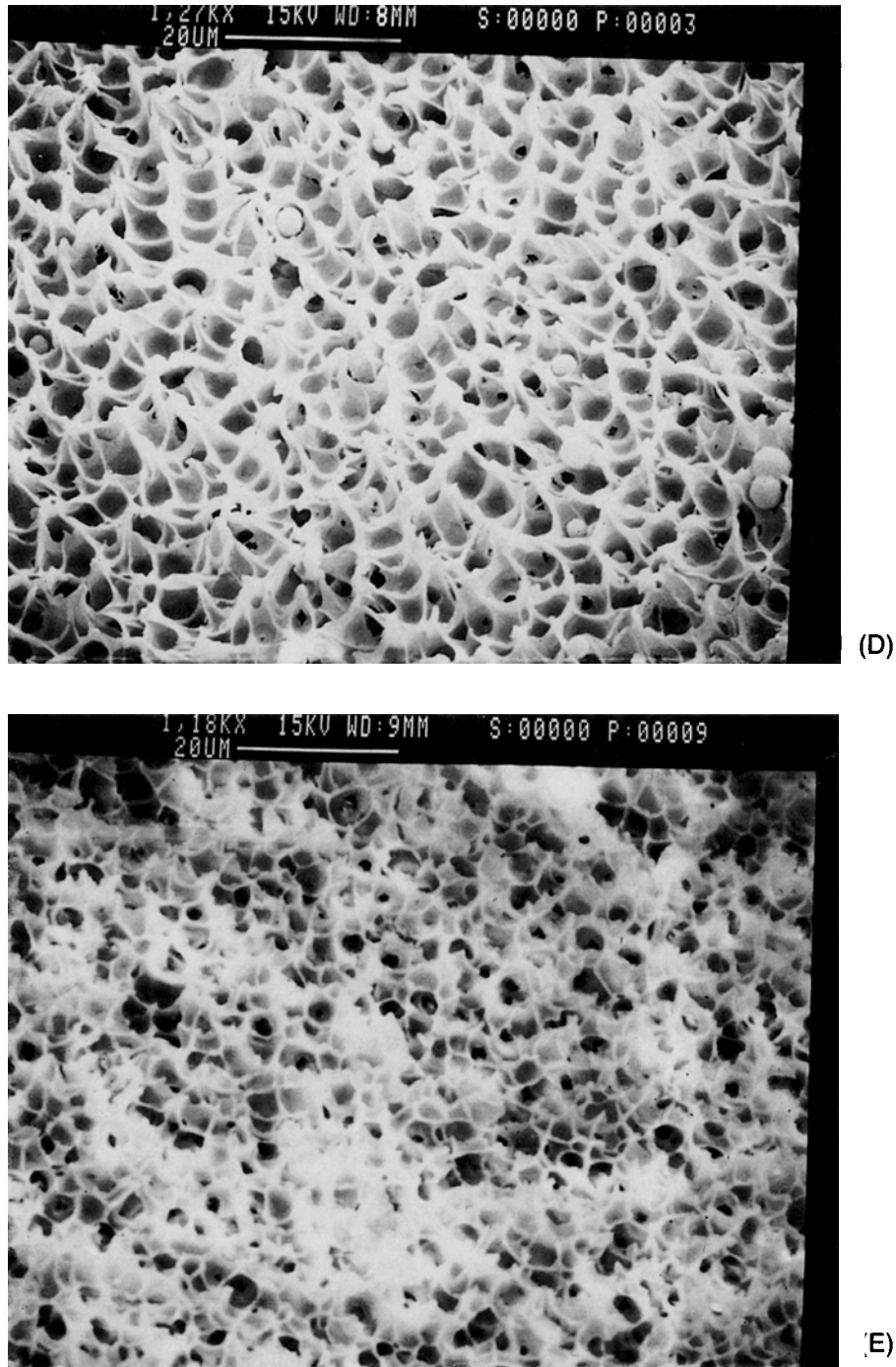


Figure 9 (Continued from the previous page)

through copolymerization at very low comonomer concentrations. For example, the data from 10% w/w solutions of the different polymers (Fig. 6) show clearly that this mechanism is extremely effective in lowering the temperature of initiation of crystal-

lization in these solutions. It is particularly effective at very low comonomer concentrations, e.g., 2% IA, with only a marginal effect at higher concentrations. It is also fortuitous that comonomers (such as itaconic acid and methyl acrylate) are usually incor-



Figure 9 (Continued from the previous page)

porated in PAN to make it more suitable for applications as textile fibers and carbon fiber precursors. Comonomer sequence distributions, as dictated by composition of monomers in polymerization and their reactivity ratios, and the compositions of the two liquid phases (if LLPS precedes crystallization) will govern together the magnitude of change in crystallization behavior in these solutions. It is clear that the desirable effect on the onset of crystallization, i.e., causing it to occur within a convenient range between room temperature and the normal boiling point of the solvent, can be achieved easily through copolymerization at low comonomer concentrations. This should allow simplification of the process schemes as described earlier, especially in combination with appropriate choice of binary solvent compositions.

Morphology

Rate Effects

It is important to control the “phase history” in solution-based processing of a polymer. In addition to its influence on potential process configurations, it also dictates the morphology and properties of the resulting polymer. Typically, the polymer that crys-

tallizes directly from a concentrated homogeneous solution shows dense morphological features. Crystallization of the polymer from two-phased solutions usually leads to morphologies that are either microporous “cell-pore” (CPMP) or globular (GMP) upon extraction of the solvent, the two features arising from nucleation of the solvent-rich phase and the polymer-rich phase, respectively, during LLPS. Such structures arise at low to intermediate cooling rates if no anisotropic stress fields are present during the process. This hypothesis was verified by examining the morphologies of the polymers obtained from the DSC analysis.

Since the morphology of polymer obtained after crystallization would depend on the path traversed on the phase diagram, it would be influenced by the rate of cooling. At higher rates, the onset of LLPS as well as crystallization would move to lower temperatures, with crystallization being affected to a greater extent than LLPS. A consequence here is widening of the temperature gap between the two transitions. Since the time per unit change in temperature is inversely proportional to the rate of cooling, the overall time for LLPS prior to crystallization will be dictated by the combination of the two opposite influences. An additional important aspect here is the increasing likelihood of spinodal decomposition, instead of nucleation and growth, being the mechanism of LLPS at higher rates of cooling. Experiments were conducted to examine these effects of cooling on the kinetics of phase transition and, therefore, on the morphological evolution in the process. The rate of cooling was changed in the range from 1°C/min to 40°C/min (Table I). In samples cooled at 1°C/min, the morphology observed was globular, which is the kind of structure observed when the nucleating phase in LLPS is the phase of higher polymer concentration, and thus the phase that would begin to crystallize first. However, when the same composition solution was cooled at 40°C/min, the resulting morphology was CPMP, indicating that the continuous phase of the two-phase solution in this case was of high polymer concentration and crystallized first. A cooling rate of 20°C/min also resulted in CPMP morphologies, but cooling at 5°C/min resulted in a combination of globule-like and CPMP structures (Fig. 7). It is clear from these results that the relative kinetics of liquid-liquid phase transition and crystallization play an important role in dictating the final morphology of crystallized polymer.

A set of experiments was also conducted to determine the effect of maximum temperature, and

the time at this temperature, on crystallization during subsequent cooling. It is well-known that initially present primary crystalline nuclei can survive for a considerable period of time during dissolution/melting of a polymer, and thus contribute to spontaneous athermal nucleation upon cooling. To ensure that this effect was observed with minimum influence of any *previous* thermal history, all the samples were initially taken to 190°C, maintained at that temperature for 10 min, and then cooled to 50°C at 5°C/min. These samples were then taken to different maximum temperatures in the range from 150°C to 190°C, held for 10 min, and cooled at 5°C/min to determine the onset of crystallization temperatures and the resulting morphologies. The results obtained from a 20% w/w solution of PAN-T in a DMF/water (40 : 60) binary solvent are summarized in Table II. The polymer did not dissolve completely in 10 min at 150°C and 160°C and, when cooling, the crystallization temperatures were much higher (130.7°C and 131.9°C, respectively) than was obtained in the cooling scan of the sample preparation cycle. The morphology of the resulting sample was highly inhomogeneous, with a predominance of CPMP structure. Uniform CPMP structures were obtained at 190°C (Fig. 8), with crystallization temperatures similar to those in the cooling scan of the sample preparation cycle.

Solvent Power and Polymer Composition

The most convenient mechanism for generating different morphologies within a processable range of polymer concentration is by changing the overall solvent power through the composition of the binary solvent system. Progressive changes in the solvent power, from good to poor, can be used to generate a dense structure, CPMP or globular (GMP) morphology. As described earlier, these are direct consequences of the change in the path traversed by the polymer solution on the phase diagram.

The influence of solvent power on morphologies is exemplified through a 20% w/w solution of the terpolymer in the binary DMF/water system. These studies were conducted at a cooling rate of 20°C/min, after holding the solution at 200°C for 5 min to minimize any influence from the initial morphology of the polymer. Scanning electron micrographs of the morphologies obtained from different binary solvent compositions (DMF/water) are shown in Figure 9. A dense morphology results from crystallization of the terpolymer in high DMF/water solvents. The transition in morphology occurs

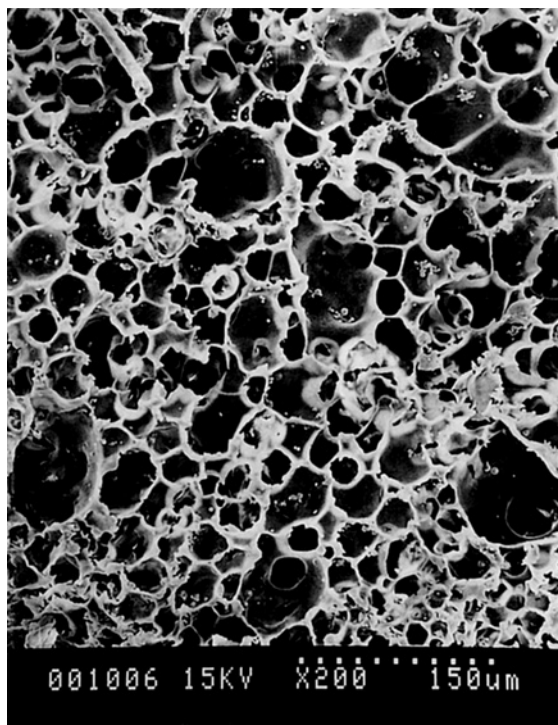
around 80 : 20 w/w DMF : water. It should be noted here that solutions of AN-based polymers in 100% DMF are common in the production of dense fibers for applications in textile materials and as precursors for high-strength carbon fibers. Depending on whether a dry or wet (coagulation) spinning method is used, the solid/gel filament is generated via either evaporation of the solvent or coagulation in a DMF-rich (60% w/w or higher) medium. It is clearly necessary in these cases to avoid any LLPS and the consequent evolution of microporosity in the crystallized polymer. Reducing the solvent power with increasing ratios of water/DMF leads progressively to the generation of different morphologies in the "dense polymer → CPMP → GMP" sequence (Fig. 9). GMP morphology invariably results from crystallization in solutions of AN-based polymers in water over a very broad range of processable polymer concentrations. This aspect is probably a primary reason for the lack of success in adopting this system for commercial production of dense fibers and films.

Whether crystallization occurs directly from a homogeneous solution or after LLPS, i.e., from a two-phase solution, depends on the polymer concentration as well as the binary solvent composition. As mentioned earlier, inferences regarding the path to crystallization can be made from " T_c -polymer concentration" data. The morphological consequences are, once again, seen clearly in the examples shown in Figure 10, obtained from solutions of PAN-T in 60 : 40 water/DMF (w/w) at a cooling rate of 20°C/min.

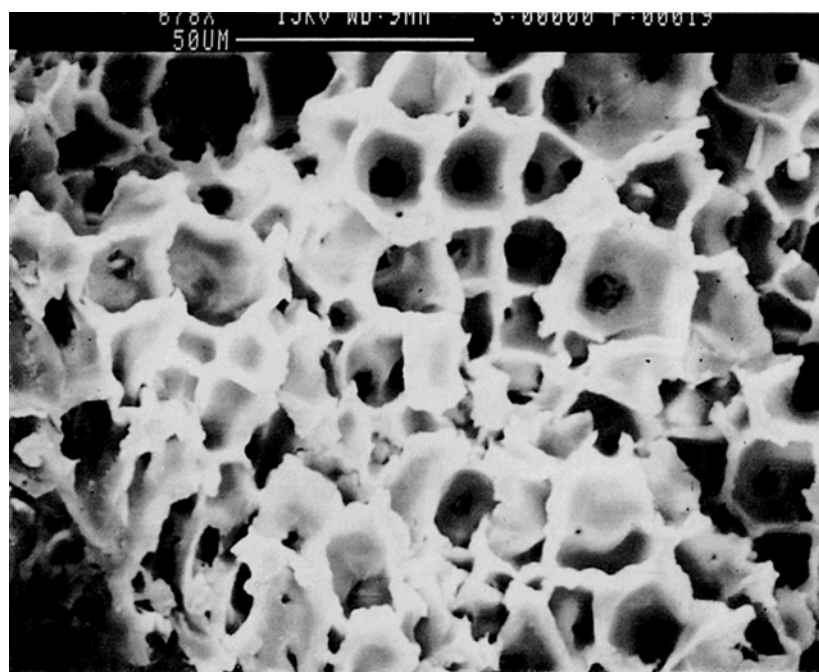
CONCLUSIONS

We have demonstrated several positive consequences for potential advances in processing schemes and versatile generation of morphologies through this fundamental study of crystallization, and any implied LLPS, in concentrated solutions of acrylonitrile-based copolymers and homopolymer. Of primary significance in this regard are:

1. The ease with which useful morphologies, ranging from dense structures to microporous morphologies, can be created *from the same polymer-binary solvent system*, through a facile combination of stoichiometry (polymer/solvent 1/solvent 2), copolymer composition (at low comonomer compositions that would leave potential mechanical properties unchanged), and rate of cooling.



(A)

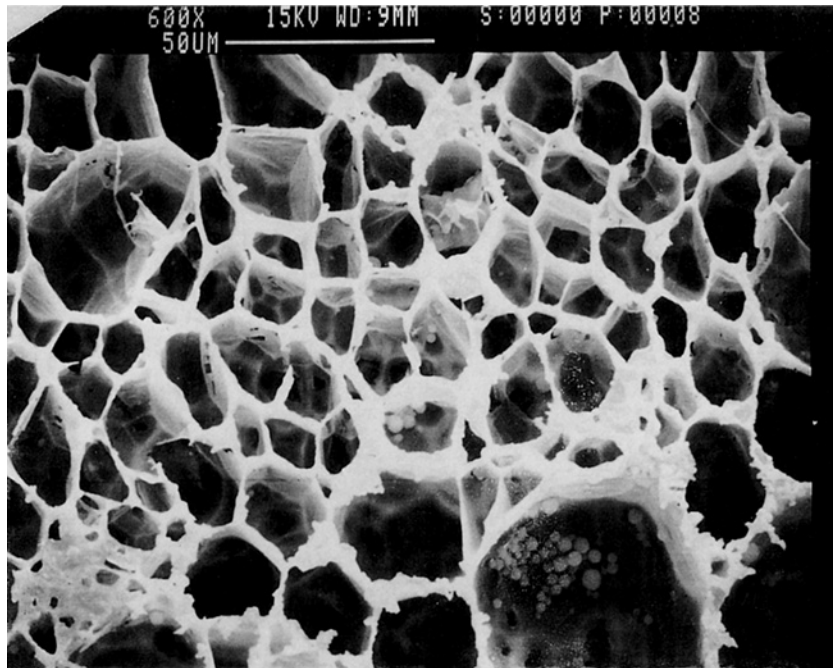


(B)

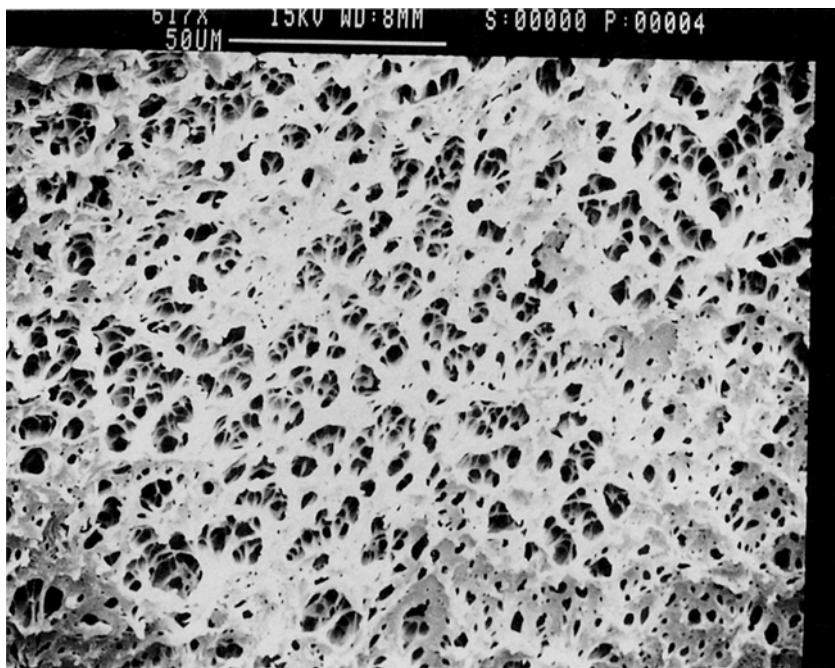
Figure 10 Effect of polymer composition on morphology of PAN-T. Water/DMF 60 : 40 w/w. Polymer concentration: (a) 10%, (b) 20%, (c) 30%, (d) 40%, and (e) 60% PAN-T. Cooling rate = 20°C/min.

2. The potential for gross simplification of processing schemes by causing crystallization to occur below the normal boiling point of the

binary solvent system, but significantly above room temperature. The former eliminates mass-transfer instabilities that can arise be-



(C)



(D)

Figure 10 (Continued from the previous page)

cause of crystallization at high pressures, and the latter eliminates the need for coagulation. Recovery of the solvents from the solidified polymer/binary solvent is a relatively simpler operation.

3. The formation of a continuously connected cell-pore microporous (CPMP) morphology

in polyacrylonitrile that can serve as a precursor in new methods to form microporous carbon, ceramic, and metal structures. These possibilities arise from the potential to convert microporous PAN to microporous carbon via oxidative stabilization and carbonization,^{16,20} with subsequent infiltration of the

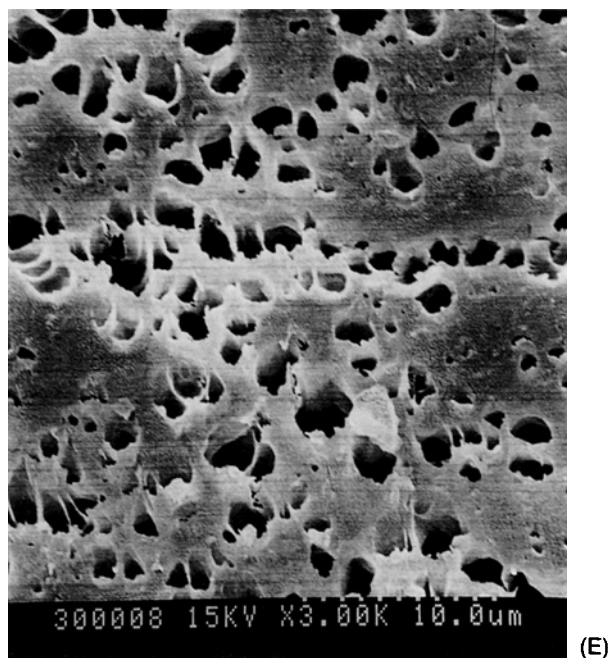


Figure 10 (Continued from the previous page)

porous carbon domains with high-temperature melts or precursors to high-temperature materials.

This study has primarily dealt with morphological features in the $\geq 0.1 \mu\text{m}$ scale that arise because of phase transitions in polymer solutions. It is clear that in the hierarchy of morphologies from the polymer chains to these superstructures, there are finer structures that are equally important in governing bulk- and surface-properties of polymers. Quantitative characterization of these aspects is currently being carried out in our laboratories.

Note added in proof: The specific nomenclature for porous materials that has been recommended by IUPAC refers to materials' with pore diameters greater than 500 \AA as "macroporous" and those with less than 20 \AA as "microporous." However, we have retained here the terminology that is commonly used with polymer morphology, i.e., "microporous" to describe pore sizes of the order of $0.1 \mu\text{m}$.

The authors gratefully acknowledge partial funding of this research through a grant from the DuPont Company. Additional support was provided by the NASA-HiPPAC Center.

REFERENCES

1. É. R. Alieva, Yu. P. Kozhevnikov, V. A. Medvedev, et al., *Khimicheskie Volokna*, **5**, 6 (1990).
2. G. Hinrichsen, *Angew. Macromol. Chem.*, **20**, 121 (1974).
3. W. R. Krigbaum and N. Tokita, *J. Polym. Sci.*, **18**, 213 (1960).
4. N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).
5. G. Hinrichsen and H. Orth, *Kolloid Z.*, **247**, 844 (1971).
6. M. Kurata, Y. Tsunashima, M. Iwama, et al., in *Polymer Handbook*, 2nd ed., Chap. 4, J. Bandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1975, p. 1.
7. C. D. Coxe, U. S. Pat. 2,585,444 (1952).
8. B. G. Frushour, *Polymer Bulletin*, **7**, 1 (1982).
9. B. G. Min, T. W. Son, B. C. Kim, et al., *Polym. J.*, **24**, 841 (1992).
10. É. A. Pakshver, I. A. Barsukov, N. K. Kireeva, et al., *Khimicheskia Volokna*, **1**, 25 (1992).
11. W. M. Smartt, Ph.D. thesis, Georgia Institute of Technology, Atlanta, GA (1991).
12. W. M. Smartt and A. S. Abhiraman, *2nd Topical Conf. in Emerging Technologies in Materials*, AIChE National Mtg., San Francisco, CA, Nov. (1989).
13. R. B. Richards, *Trans. Faraday Soc.*, **41**, 10 (1945).
14. W. R. Burghardt, L. Yilmaz, and A. J. McHugh, *Polymer*, **28**, 2085 (1987).
15. Janice L. Zyrd and W. R. Burghardt, *PMSE*, **69**, 347 (1993).
16. A. P. Sylwester, J. H. Aubert, P. B. Rand, et al., *Proc. ACS PMSE Div.*, 113 (1987).
17. P. Schaff, B. Lotz, and J. C. Wittman, *Polymer*, **28**, 193 (1987).
18. A. Prasad, H. Marand, and L. Mandelkern, *J. Polym. Sci. Part B: Polym. Phys.*, **32**, 1819 (1993).
19. W. Stoks and H. Berghmans, *J. Polym. Sci. Part B: Polym. Phys.*, **29**, 609 (1991).
20. Girish Deshpande, unpublished results, private communication (1994).

Received May 27, 1994

Accepted June 6, 1994