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PHENOMENA AFFECTING MORPHOLOGY OF MICROPOROUS POLY(ACRYLONITRILE) PREPARED VIA PHASE SEPARATION FROM SOLUTION*

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ABSTRACT

This paper is concerned with controlling the morphology of microporous polymers prepared via thermal demixing of solutions. 2 wt% solutions of poly(acrylonitrile) in maleic anhydride, a poor solvent, are first cooled to produce separated polymer-rich and solvent-rich phases. Removing the solvent by freeze drying then produces a microporous material having a density of 33 mg/cm^3, a void fraction of 97%, and a pore size of about 10μm. We find that the morphology cannot be explained by existing models, which focus on phase diagrams and kinetics of phase transformations during cooling of the solution. In conflict with those models, we find that two radically different morphologies can be produced even when the polymer concentration and cooling path are held strictly constant. A hypothesis that polymer degradation causes the different morphologies is not supported by GPC, ^{13}C NMR, and FTIR experiments. Instead, we offer evidence that the different microporous morphologies are caused by different polymer conformations in solutions having the same concentration and temperature.

*This work performed at Sandia National Laboratories, supported by the U. S. Department of Energy under Contract DE-AC04-76DP00789.

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INTRODUCTION

Microporous polymers are useful for applications as diverse as separation membranes and physical supports for chemically active species. One of the most important preparation methods employs thermal demixing of solutions(1,2). Cooling the polymer solution causes separation into polymer-rich and solvent-rich phases. Removing the solvent leaves a three-dimensionally interconnected polymer structure, if the process conditions are chosen correctly. When the solvent is removed by freeze-drying (as in this work), the porous polymer has nearly the same morphology as the polymer-rich phase in the solvent filled precursor. This work is concerned with selecting process conditions to control the morphology of high porosity materials (97% void). The cell structure must be controlled very precisely in these materials in order to produce adequate strength for technical applications.

Efforts to understand the morphology of thermally demixed solutions have invariably focussed on equilibrium phase diagrams and on the phase transformations occurring during cooling (1-5). For a crystallizable polymer, such as poly(acrylonitrile) (PAN), the most important transformations are liquid-liquid phase separation and crystallization. A schematic phase diagram(4) illustrating the equilibrium boundaries for these two transformations is shown in Fig. 1. At temperature-concentration conditions below the equilibrium melting line, the free energy can be lowered by crystallization of the polymer. If the solution is cooled at a rate greater than the rate of crystallization, it can reach the binodal, below which the lowest free energy would be achieved by separation into two liquid phases. Liquid phase separation occurs either by nucleation and growth or spinodal decomposition, yielding different morphologies(1-5).

A necessary consequence of the above model is that fixing the concentration and initial temperature (i.e., fixing the initial condition, point A) and fixing the cooling

path will fix the morphology of the demixed solution. Our results on 2 wt% solutions of a poly(acrylonitrile) polymer are inconsistent with this model, because we produce radically different morphologies even when the initial solution temperature and the cooling path are fixed. We conclude that the phase transformations during cooling are affected by another variable in addition to concentration and the initial temperature. We speculate that this additional variable is related to the conformation of the polymer chains in solution, which is slow to reach equilibrium. There is special interest in the microporous PAN materials studied here because they can be converted into microporous carbon materials having novel electrical, chemical, and mechanical properties(6,7).

EXPERIMENTAL

Materials. The poly(acrylonitrile) (from Aldrich) has a ^{13}C NMR spectrum representative of an atactic polymer (see below). GPC analysis yielded polystyrene equivalent M_w of 700,000 and a polydispersity of 3. The maleic anhydride solvent was purified by sublimation. The major impurity, maleic acid, was thereby reduced to 0.06 wt%. Maleic anhydride is a moderately poor solvent because its solubility parameter is about 1.0 $(cal/cm^3)^{1/2}$ higher than that of PAN.

Procedure. The PAN was processed into a microporous material following the three step method developed by Sylwester and co-workers(6). First, 2.0 wt% of the polymer was dissolved in maleic anhydride at 162±2C under vacuum. Second, the solution was cooled to 140C and then poured into a heated mold. The mold was then quenched on a water cooled copper plate held at 26C. Finally, the solvent was frozen and then removed by vacuum sublimation, leaving microporous PAN having density 33±2 mg/cc. Small variations in cooling rate between experiments had no effect on the morphology of the microporous PAN. Similarly, variations of ±0.1 wt% in PAN concentration had no effect on the morphology.

GPC characterization was performed using two Shodex KD-80M columns in a Waters 150C instrument operating at 50C. The solvent system was dimethylformamide (DMF) containing 0.01M LiBr(8,9). 50 MHz decoupled ^{13}C NMR spectra of PAN were obtained on 5 w/v% solutions in deuterated dimethyl sulfoxide (Fig. 2). Three methine carbon peaks near 27 ppm are assigned to iso-, syndio-, and hetero-tactic triads, consistent with an atactic polymer.

RESULTS

Two samples of microporous PAN prepared using the same concentration (2.0 wt%) and cooling path have completely different morphologies (Fig. 3). Sample 98 is composed of 3μ

spheres loosely connected together, while sample 95 is composed of similar sized sheets that appear highly interconnected. This difference in morphology causes a drastic difference in mechanical strength. Sample 98 is so weak that a 4 g piece cannot be handled without damaging it. In contrast, sample 95 is strong enough to be machined into complex shapes. The Shore 000 hardness (1/2 in. spherical indenter) is 85 for the sample having the interconnected sheet morphology and 35 for the sample having the sphere morphology.

The spherical structure in sample 98 has been observed before in other microporous crystallizable polymers prepared from demixed solutions(Ref. 4 and references therein). This structure has been explained in terms of crystallization of the polymer prior to liquid phase separation. We know that crystallization occurred during preparation of the spherical structure, because we observed the strong 220 plus 400 reflection of crystalline PAN in x-ray diffractograms. Interestingly, the same reflection appeared in the sample with the sheet structure.

Different morphologies in thermally demixed solutions are usually explained by different mechanisms of phase separation during the cooling step. The explanation relies on phase diagrams of the kind shown in Fig. 1 plus consideration of the rate of the phase transformations relative to the rate of cooling(1-5). That analysis would predict that two solutions with the same composition and initial temperature (same initial condition A in Fig. 1) would produce the same morphology if they were cooled via the same path. That prediction is inconsistent with the different morphologies observed in samples 95 and 98 (Fig. 3). We therefore hypothesize that prior to the cooling step, the solutions used to make the two microporous samples were actually different, even though they had the same concentration and temperature.

We first hypothesized that polymer degradation caused the difference in the solutions. We have not, however, found any evidence for degradation in either sample. Molecular weights measured by GPC for the strong and weak microporous materials were statistically identical to those of the PAN raw material. The shapes of the GPC chromatograms are also indistinguishable (Fig. 4). ^{13}C NMR as well as FTIR spectra for the two microporous materials were also indistinguishable from each other and from those of the raw material (Figs. 2 and 5). Any change in molecular weight or molecular structure of the PAN that occurred during preparation of the microporous materials was too small to be detected by GPC or spectroscopy.

We now speculate that differences in the conformation of the polymer chains in the solution prior to the cooling step caused the difference in morphology. We have not been able to characterize conformational differences due to difficulties in making rheological or scattering measurements at elevated temperatures with the volatile, hazardous maleic anhydride solvent. Many of our observations, however, are at least, consistent with our speculation.

First, we have observed that the preferred sheet morphology (Fig. 3b) is consistently produced when the dissolution step leaves tiny amounts of undissolved PAN. (Since the undissolved bits of polymer float to the top when the solution is poured into the casting mold, they do not perturb the bulk morphology.) In contrast, greater agitation during dissolution produces a more visually homogeneous solution, which invariably favors production of the weak, sphere morphology. These differences in visual homogeneity are believed to be an indicator of differences in polymer conformation.

To further demonstrate that the severity of polymer dissolution affects the microporous morphology, we performed strictly replicated experiments where the only variable was an extra ingredient added to the dissolution flask. 0.1 wt% of PAN in the form of a compressed pellet was added in addition to the standard 2 wt% of PAN powder. Since only half of the pellet dissolved, the increase in PAN concentration was too small to have any effect on the morphology (see Experimental section.) All other process conditions remained strictly constant, and all solutions were visually homogeneous, except for the pellet. Even though the PAN pellet was filtered out of the solution prior to the cooling step, it invariably caused the sheet morphology to form. The same preparation process without the pellet consistently produced the sphere morphology. In fact, the only difference between the two samples shown in Fig. 3 is that sample 95 was made with the PAN pellet and 98 without the pellet. These findings are consistent with our speculation focussing on the physical structure of the polymer chains in solution rather than the chemical structure of the molecules.

DISCUSSION

Two physical phenomena that may affect the microporous morphology are a)aggregation of the PAN chains in the moderately poor maleic anhydride solvent or b) variation in the radius of gyration of the molecules. PAN has long been known to have anomalous properties in dilute solution, even in a good solvent, DMF(8-10). For example, unusual GPC and light scattering results have been explained by

intermolecular aggregation or intramolecular variations in the polymer coil size. The precise cause of the anomalous solution properties of PAN remains unresolved(11). Addition of LiBr (0.01M) to dilute solutions of PAN in DMF are believed to mediate some of these anomalous effects, perhaps by screening inter- or intra- molecular associations between the polar nitrile side groups. Interestingly, addition of LiBr to the PAN/maleic anhydride solutions invariably produces the sheet morphology(11). All of these findings are consistent with our physically based explanation for the morphology differences in the microporous PAN, even though the behavior of PAN in solution is understood neither by us nor by other investigators. In our presentation at the symposium, we intend to report on rheological or scattering experiments aimed at characterizing the differences between the PAN solutions that produce the sheet and sphere morphologies.

CONCLUSIONS

Differences in the morphology of thermally demixed 2 wt% solutions of PAN in maleic anhydride cannot be explained by existing models, which are based on phase diagrams. An explanation based on degradation of the polymer is not supported by GPC, NMR, or FTIR experiments. We speculate that the physical structure of the polymer in solution, involving either intramolecular dimensions or intermolecular aggregation, has an important effect on the morphology.

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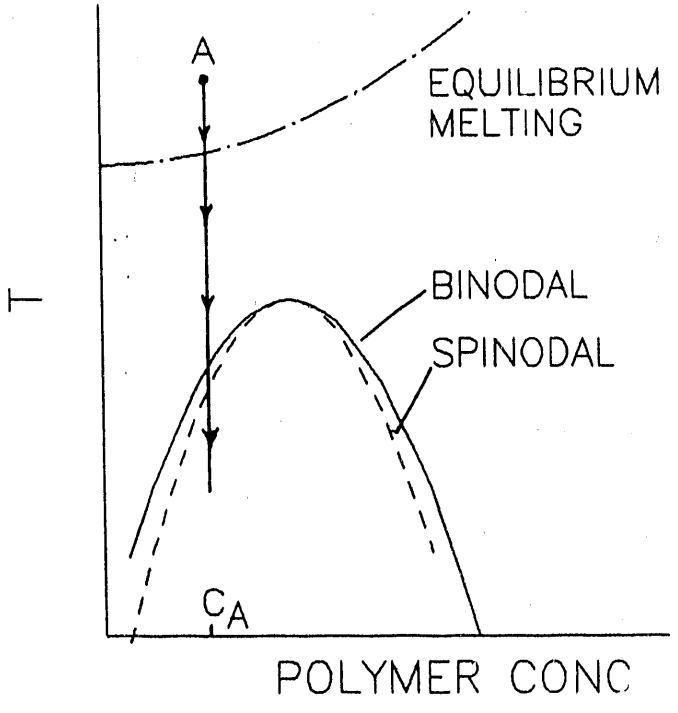

FIGURE 1. Schematic phase diagram showing thermal demixing at concentration C_A.

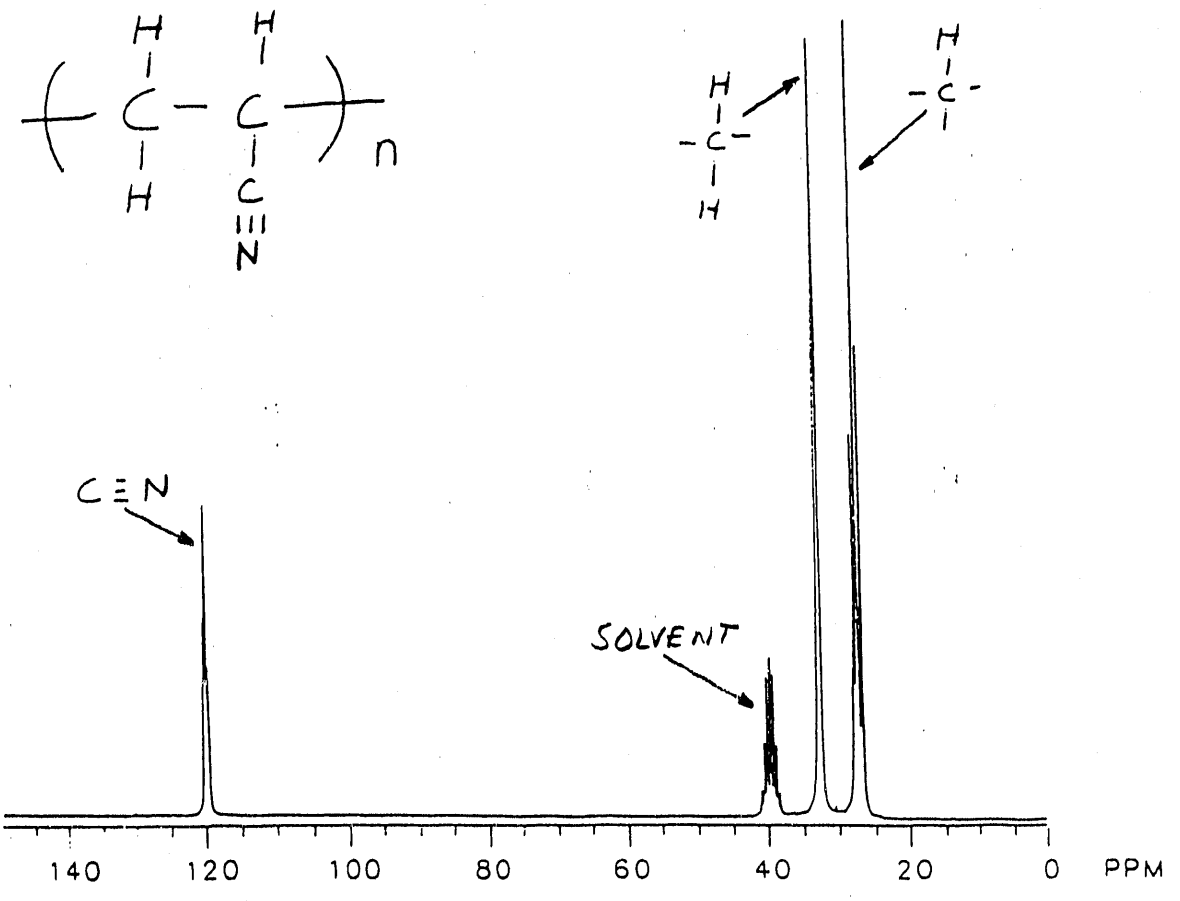

FIGURE 2. 50 MHz ^{13}C NMR spectrum of PAN raw material.

(a)

(b)

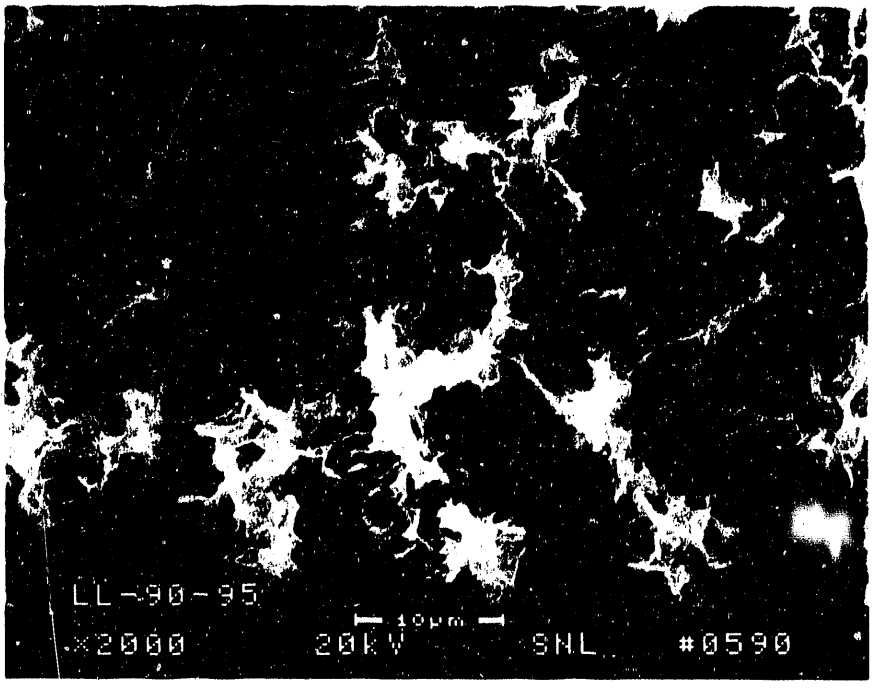

FIGURE 3. SEM photos of fracture surfaces showing (a) weak, sphere morphology and (b) strong, sheet morphology in microporous PAN materials.

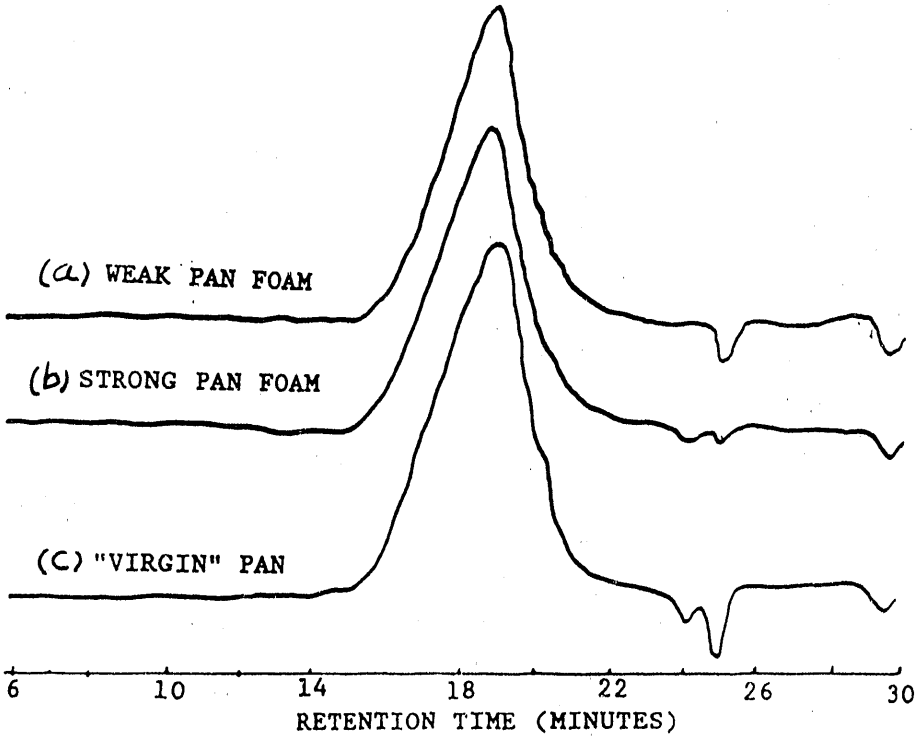

FIGURE 4. GPC chromatograms of (a, b) microporous PAN materials and (c) unprocessed polymer.

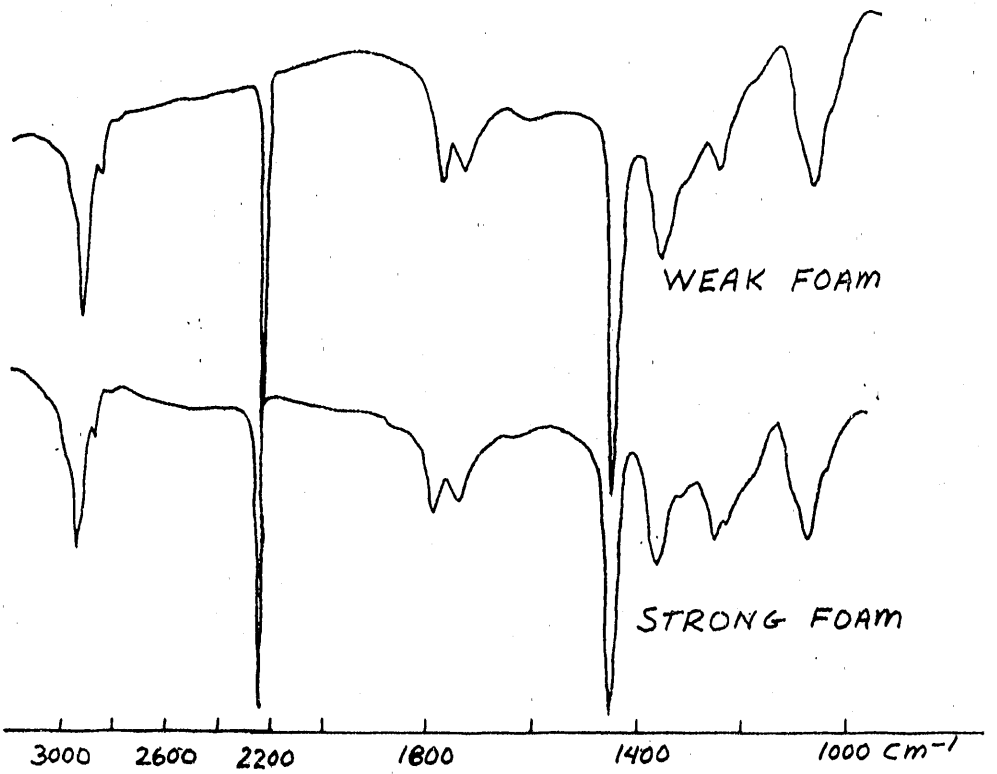

FIGURE 5. FTIR transmission spectra obtained using KBr pellets.

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