TMGa:NH_3 were observed. The strongest absorption appears at 1136 cm^{-1}, corresponding to CH_3 symmetric deformation. The Ga–C stretching appears at 559 cm^{-1}, and the corresponding peak for TMGa appears at 583 cm^{-1}. When TMGa was mixed with NH_3 at 150 °C, chemical equilibrium was reached between the gaseous adduct TMGa:NH_3 and the reactants. By assuming reversible bimolecular reaction, a forward rate constant of 5.89×10^{-3} (Torr s)$^{-1}$ was measured for the predeposition reaction between TMGa and NH_3 at 150 °C. There was no evidence of a reaction between NF_3 and TMGa at either room temperature or 150 °C. Therefore, NF_3 could be used as an alternative source of nitrogen in order to limit predeposition reaction.

Acknowledgment. This research is sponsored in part by a subcontract from the University of Floride (Grant No. MDA972-88-J-1006) and the Engineering Experiment Station at Kansas State University. Their support is gratefully acknowledged.

Registry No. TMGa, 1445-79-0; GaN, 25617-97-4; NH_3, 7664-41-7; NF_3, 7783-54-2.

Phase Separation in Poly(enaminonitrile) Solutions and Blends

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Received December 17, 1990. Revised Manuscript Received March 28, 1991

The solubility behavior of poly(enaminonitrile) (PEAN) solutions and blends has been investigated by using light scattering. PEANs are soluble in a series of polyether solvents (glymes), and those solutions show cloud points as the temperature is raised. The same behavior was observed from miscible blends of PEAN with poly(ethylene oxide). Cloud points were determined by laser light scattering measurements.

Introduction

One of the more interesting aspects of miscible polymer blend studies is the finding that many of these systems show cloud points on heating. The equation-of-state theory that describes this behavior for small molecules also successfully interprets this behavior for a mixture of polymers with specific interactions (e.g., hydrogen bonding), leading to a negative heat of mixing.[1-6] Poly(enaminonitriles) (PEANs) are new high molecular weight, film-forming polymers that exhibit excellent thermal stability and good mechanical properties.[7] We have been studying blends of PEAN with several commercial polymers. It was found that PEAN forms miscible blends with good hydrogen-bond acceptors such as poly(ethylene oxide) (PEO), poly(4-vinylpyridine), poly(ethyloxazoline), and poly(*N*-vinylpyrrolidone).[8,9] Strong hydrogen bonding evidenced by FT-IR spectroscopy was suggested as the driving force that favors miscibility. The blends of PEAN with PEO showed particularly interesting lower critical solution temperature (LCST) type phase behavior. An endothermic transition associated with the phase separation was observed clearly by differential scanning calorimetry. In this article, we describe independent measurements of the cloud points of PEAN solutions in a series of polyether solvents (glymes) and polymer blends with PEO using the laser light scattering technique. Cloud point curves were established, which were in good accord with previous data.[9]

Experimental Section

Materials. PEANs were synthesized by using the procedure we developed for condensation polymerization of the chosen monomers with 4,4′-oxydianiline or 1,4-bis(4-aminophenoxy)benzene in 1-methyl-2-pyrrolidinone (NMP) in the presence of DABCO as the acid acceptor.[7] Their structures and molecular characteristics are shown in Table I. A sample of 1,3-ODA–PEAN with intrinsic viscosity of 0.47 dL/g was found to have a weight-average molecular weight of 34 000 daltons by low-angle laser light scattering (LALLS). PEO with an average molecular weight of 100 000 daltons was purchased from Aldrich and used without purification. A series of ethylene glycol dimethyl ether (glyme) solvents (mono-, di-, tri-, and tetraglyme) was purchased from Aldrich. Penta-, hexa-, and heptaglyme were obtained from Parish Chemical Co. Poly(ethylene glycol) dimethyl ether samples with average molecular weights of 500 and 1000 daltons, were obtained from Hoechst Chemikalien. All glyme solvents were used as received without further purification.

Preparation of PEAN Solutions and Blends. The solutions were prepared by dissolving measured amounts of the polymers in glyme solvents and filtering through 0.45-μm microfilters. Blends were prepared by solution casting from DMF solutions. The solvent was evaporated slowly under N_2 flow at 60 °C. The resulting films were further dried in vacuo at 120 °C for 2 days and then slowly cooled to room temperature and stored in a

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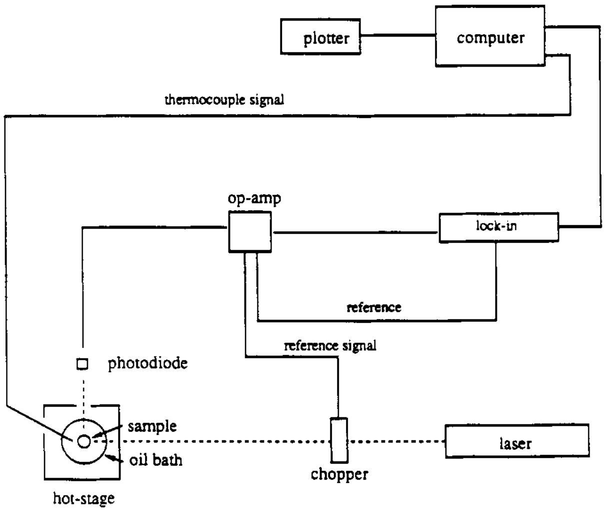


Figure 1. Apparatus for cloud point measurements of PEAN solutions.

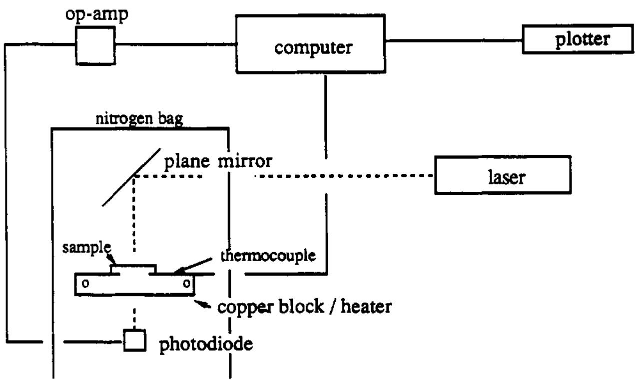


Figure 2. Apparatus for cloud point measurements of PEAN/PEO blend films.

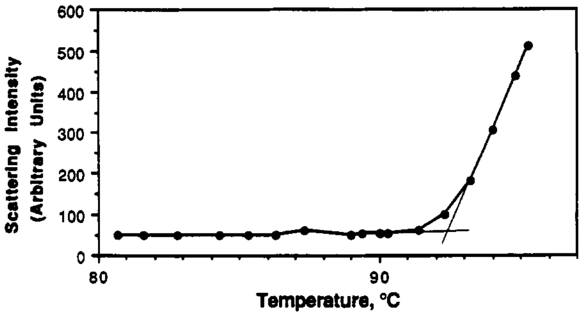


Figure 3. Typical scattering intensity vs temperature curve.

desiccator over P_2O_5 for 1 week prior to measurement. The film thickness was about 20 μm.

Instrumentation and Cloud Point Measurements. The polymer solution was placed in a stoppered test tube immersed in an oil bath that was heated at a rate of approximately 1 °C/min. A 2-mW He–Ne laser light source (6328 Å) was used. A photodetector was placed at an angle of 90° to the incident light. The voltage signals from the detectors were amplified with variable-resistor, operational-based, current-to-voltage amplifiers, which were made for this work. Lock-in amplifiers were used to filter the chopped signal, eliminating 60-Hz background signals and other interference. The signal voltage from the photodiode and the thermocouple was processed with a DEC microcomputer (called MINC). (See Figure 1). Several programs to collect and manipulate the data were written. A plotter program that involved interfacing the MINC with a Hewlett-Packard plotter using an IEEE bus interface was also written. The temperature at which the extrapolation of the increased scattering intensity intersected the base line was taken as the cloud point. A typical scattering vs temperature curve is shown in Figure 2. The cloud points of blend films were determined by a method similar to that described above. A thin film on a glass slide was heated on a copper block with four heaters mounted horizontally. A thin thermocouple was placed near the film sample. The laser light was directed vertically by using a mirror, in this case. The photodetector was mounted above the sample to detect the transmitted light. After phase separation, the sample scatters more light, decreasing the intensity transmitted through the film, as detected by the photodiode. This voltage drop was directly related to the amount of light scattered. A nitrogen-filled bag was placed over the copper heating block and sample to prevent oxidation of the sample at high temperature. (See Figure 3).

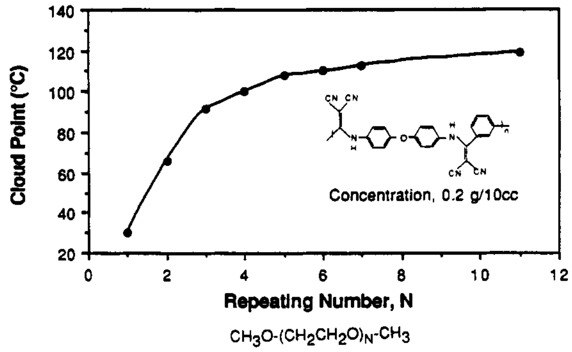


Figure 4. Cloud point of 1,3-ODA–PEAN in glyme solvents as a function of solvent size (concentration, 0.2 g/10 cm^3).

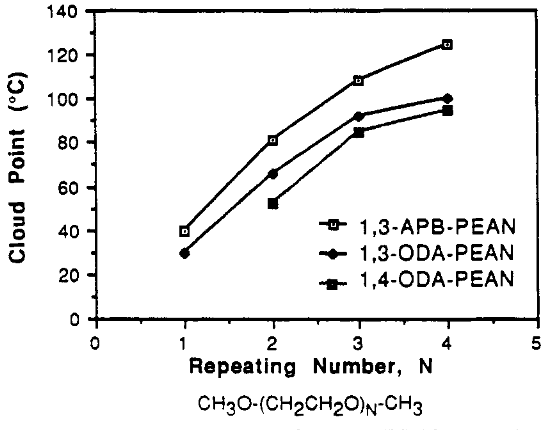


Figure 5. Cloud points of three different PEANs as a function of solvent size (concentration, 0.1 g/10 cm^3).

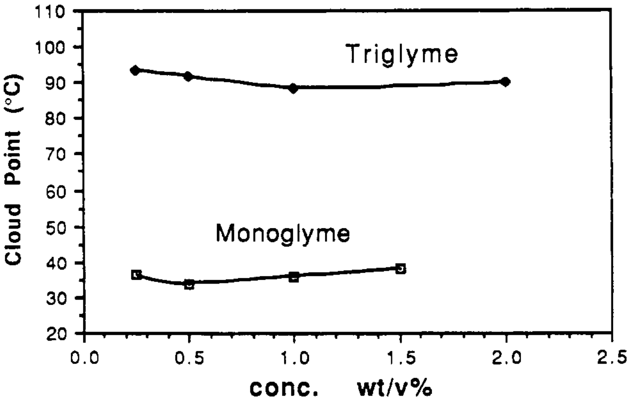
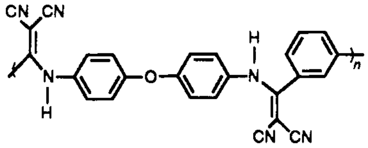
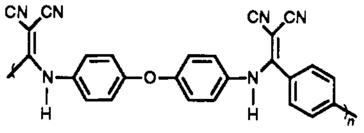
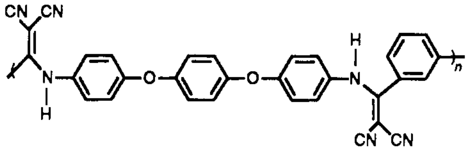


Figure 6. Cloud point curves of 1,3-ODA–PEAN in glyme and triglyme.

Results and Discussion

Various PEAN polymers exhibited cloud points in polyether solvents, and this behavior appears to be quite general. At the cloud point and above, the solution became more and more turbid by continuous separation of polymer from solution. Figure 4 shows how the cloud point of

Table I

designation	structure	intrinsic viscosity[a]
1,3-ODA-PEAN		0.47
1,4-ODA-PEAN		0.70
1,3-APB-PEAN		0.51

[a] Viscosity was measured with a Cannon-Ubbelohde viscometer at 25 °C in DMF and is reported in units of dL/g.

1,3-ODA-PEAN varies with increasing solvent size. As the number of oxyethylene repeating units increases in the solvent, $CH_3O(CH_2CH_2O)_NCH_3$, the cloud point increases and then tends to level at higher values of N. The same trend was observed for the two other polymers as shown in Figure 5. The monotonic increase of cloud points may be caused by the increase of the solubility parameter of the glymes as N increases.[10] Cloud points of 1,3-ODA-PEAN were determined for several different concentrations as shown in Figure 6. Only small differences in the cloud points as a function of concentration were observed within this narrow solubility range. The turbid solution became clear when the solution was cooled below the cloud point; in other words, the process was totally reversible except for the case of the 1,4-ODA-PEAN solutions. At the earier stages of separation, 1,4-ODA-PEAN solutions in glyme solvents behaved the same as other solutions, i.e., the slightly turbid solution became clear upon cooling. However, the solution, after a certain degree of separation, remained turbid upon cooling (irreversible), and the precipitated polymer was totally insoluble in the glyme solvents that were used for the cloud point measurements and also in THF. The development of partial crystallinity during the separation process may be responsible for this change in solubility. The polymer precipitated in this manner was still soluble in DMF, and films cast from DMF could be redissolved in glymes.

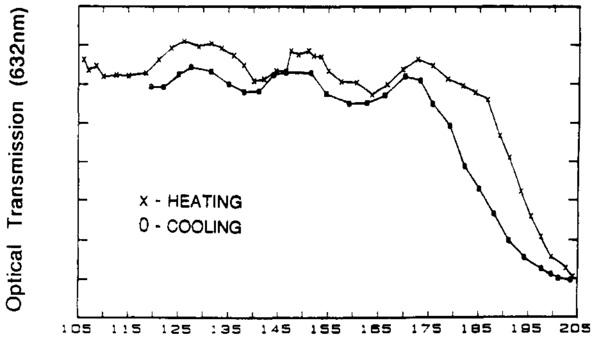


Figure 7. Optical transmission vs temperature curve of 50/50 (1,3-ODA-PEAN/PEO) blend.

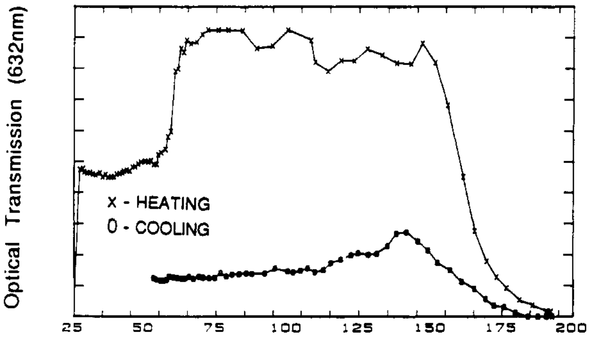


Figure 8. Optical transmission vs temperature curve of 30/70 (1,3-ODA-PEAN/PEO) blend.

As may be expected from the good solubility of PEAN in polyether solvents and the lower consolute type of phase behavior, PEANs form miscible blends with high molecular weight PEO even though crystallization of PEO was observed at higher contents of PEO in the blend.[9] Films containing up to 50 wt % PEO were transparent, but films containing more than 50 wt % PEO became increasingly less transparent as PEO content increased because of the growth of PEO crystallites. Thus, the blend may be viewed in terms of crystallites of PEO embedded in a compatible amorphous matrix of two polymers. At higher temperature these blends undergo phase separation because of the existence of the LCST. Figure 7 shows the temperature dependence of the intensity of light transmitted through a 50/50 (PEAN/PEO) blend film. Upon heating, the intensity begins to decrease at about 175 °C and continues decreasing gradually until it levels off at about 205 °C. At this point, the sample is completely opaque. As this is cooled, the intensity of transmitted light increases almost to the original level and the sample becomes transparent, although hysteresis is apparent. Hence, the phase separation process for this blend is reversible. A two phase morphology of the 50/50 (PEO/PEAN) blend with modulated structure was observed under a hot-stage optical microscope above the cloud point temperature. When the temperature was lowered below the cloud point, the image contrast of the modulated structure gradually weakened, and finally the image disappeared.

Figure 8 shows the temperature dependence of a 30/70 (PEAN/PEO) blend film. The original sample was already slightly turbid because PEO crystallites developed in the film as was observed through an optical microscope. As this is heated the light intensity increased abruptly at around 60 °C, indicating the melting of PEO. After the

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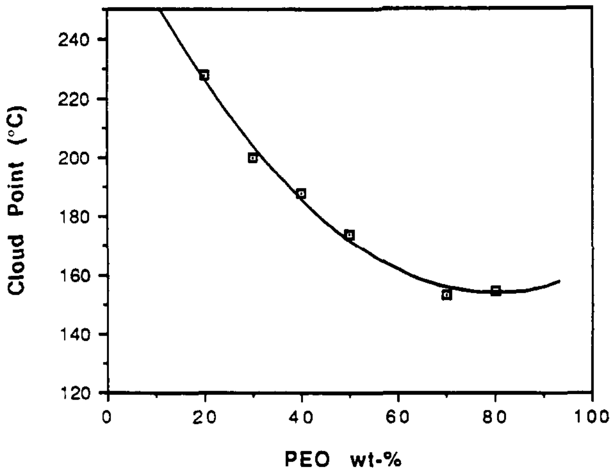

Figure 9. Cloud point curve established by light-scattering measurements.

PEO crystallinity is eliminated, the blend resembles an amorphous, compatible system. Consequently, the degree of scattering should be markedly reduced, and the intensity of transmitted light should remain high until the temperature of the cloud point is reached. The light intensity then decreases gradually because of phase separation, and the sample becomes opaque. As this is cooled, the light intensity increases slowly but does not reach the original level, which indicates that the phase redissolution is not complete at this composition. More detailed study of the kinetics of phase separation and redissolution and subsequent crystallization behavior of PEO are interesting but are beyond the scope of this paper. Similar observations were obtained for the 20/80 (PEAN/PEO) blend.

On the basis of light scattering experiments, a cloud point curve was obtained as shown in Figure 9. The data up to 50 wt % PEO were in good agreement with those obtained by DSC as reported in our previous publication.[9]

Acknowledgment. This work was supported, in part, by a grant from the Office of Naval Research. We thank Dr. P. D. Persans for providing equipment and help with the light scattering experiments. Molecular weight measurement of a PEAN sample was performed by Dr. Thomas Mourey of the Eastman Kodak Research Laboratory, and we gratefully acknowledge his willing assistance. P. Seidel participated in this work initially as part of the N.S.F. Young Scholars Program (Summer 1988) and also as a Summer Research participant (Summer 1989) sponsored by the E. I. du Pont Co.

Registry No. PEO, 25322-68-3; 1,3-ODA–PEAN, 117371-55-8; 1,4-ODA–PEAN, 103083-29-0; 1,3-APB–PEAN, 126143-79-1; monoglyme, 110-71-4; diglyme, 111-96-6; triglyme, 112-49-2; tetraglyme, 143-24-8; pentaglyme, 1191-87-3; hexaglyme, 1072-40-8; heptaglyme, 1191-91-9; poly(ethylene glycol) dimethyl ether, 24991-55-7.