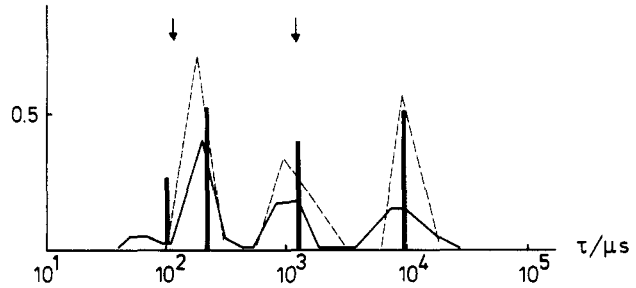

Figure 5. Distribution of decay times using various methods[12] for data obtained on solutions of PS ($\bar{M}_w = 15 \times 10^6$) in cyclopentane (21 °C) at a concentration of 4.7% (w/w) (measurements at $\theta = 60°$): (a) CONTIN[13] (continuous line); (b) linear-programming method,[14] which uses fixed components equidistant on a logarithmic scale and minimizes the sum of absolute values of residuals (result shown as the broken line); (c) positive-coefficient exponential sum (PES) method,[15] which fits the experimental curve to the expression $(\sum_{i=1}^{N} c_i e^{-t/\tau_i})^2 + b$, with all c_i, τ_i, and b adjusted by least squares with $c_i > 0$ and $\tau_i > 0$. Components N are increased until no new τ_i with positive c_i can be added. These values are illustrated as the vertical bars. The two vertical arrows shown are the results of bimodal analysis as described in ref 3.

dynamics, not the least because it is difficult to obtain asymptotic conditions even with very high molecular weight fractions. We have endeavored to meet this need, as shown by the data in Figure 3. It is apparently necessary to exceed $C \simeq 10\%$ (the often-used limit for semidilute solutions owing to monomer-friction complications) if a limiting exponent for the gel mode is to be established. However, the experimental difficulties are formidable in obtaining a precise description of the various components involved in the relaxation behavior. The degree of nonexponentiality is considerable, and substantial ambiguity attaches to the components regardless of the data-analysis technique employed. It is also possible that the slower modes couple to some extent with the faster motions of the transient gel at the highest concentrations.[7]

Acknowledgment. The author is grateful to Dr. Petr Štěpánek, Czechoslovak Academy of Sciences, for helpful discussions and for performing correlation function analysis.

Registry No. PS, 9003-53-6.

References and Notes

(1) Hecht, A.-M.; Bohidar, H. B.; Geissler, E. *J. Phys. Lett.* **1984**, *45*, L-121.
(2) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760.
(3) Brown, W. *Macromolecules* **1986**, *19*, 387.
(4) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(5) Brochard, F. *J. Phys.* (*Les Ulis, Fr.*) **1983**, *44*, 39.
(6) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(7) Chu, B., personal communication.
(8) Brown, W.; Johnsen, R. M. *Macromolecules* **1985**, *18*, 379.
(9) Noda, I.; Higo, Y.; Ueno, N.; Fujimoto, T. *Macromolecules* **1984**, *17*, 1055. These authors show, using osmotic pressure measurements, that the crossover to the concentrated region occurs at between 15 and 20%, irrespective of molecular weight.
(10) Brown, W. *Macromolecules* **1985**, *18*, 1713.
(11) ALV-Langen Co., F.R.G.
(12) Štěpánek, P.; Koňák, Č.; Jakeš, J. *Polym. Bull.* (*Berlin*) **1986**, *16*, 67.
(13) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(14) Zimmerman, K.; Delaye, M.; Licinio, P. *J. Chem. Phys.* **1985**, *82*, 2228.
(15) Jakeš, J.; Štěpánek, P., to be published.

Wyn Brown
Institute of Physical Chemistry
University of Uppsala
751 21 Uppsala, Sweden

Received June 18, 1986

Spinodal Decomposition of Polymer Mixtures with a Thermotropic Liquid Crystalline Polymer as One Component

The mechanism and kinetics of phase separation of polymer mixtures have been the subject of extensive studies in recent years.[1-13,35-39] The studies involve time-resolved analyses of structural evolution from the mixtures in the molten, isotropic liquid state[1-8,11,13,35-39] or in a neutrally good solvent[9,10,12] (i.e., phase separation into polymer A solution and polymer B solution), induced by quenching the systems to a thermodynamically metastable or unstable state.

In this paper we present novel experimental evidence on phase separation into a liquid crystalline phase and a molten, isotropic, liquid phase via spinodal decomposition.[2,7,14] During the course of the isothermal phase separation we observed the following: (i) We found an evolution of periodic concentration fluctuations with correlation length Λ_m which increases with time spent for phase separation. (ii) The time evolution of the concentration fluctuations results in a bicontinuous, periodic network-type structure: one type of phase is rich in liquid crystal forming polymer and forms the liquid crystalline phase, and the other type of phase is rich in molten, isotropic polymers and forms the optically isotropic phase. (iii) At a sufficiently late stage, a "self-similarity"[16,17] was found between the structures obtained at different times.

Observations i–iii are essentially the same as those reported for unmixing processes of critical mixtures of metallic alloys,[18-20] small-molecule liquids,[21,22] inorganic glasses,[23] and binary liquid polymers.[24,40] It is our objective in this paper to report that this common phenomenon can also be found in the unmixing process of binary mixtures between thermotropic, liquid crystalline polymers and isotropic liquid polymers.

The system used in this study was a 50:50 mixture (by weight) of a commercial poly(ethylene terephthalate) (PET) and a copolyester of 60 mol % *p*-oxybenzoate (OBA) units and 40 mol % ethylene–terephthalate units (X-7G; Tennessee Eastman Co.). The number-average molecular weights of these polymers are both ca. 2×10^4. X-7G is among the first thermotropic liquid crystalline polymers, and its synthesis and properties have been reported by Jackson and Kuhfuss.[25] These two polymers were dissolved in *o*-chlorophenol at 60 °C, and the insoluble part, which probably consists of crystalline poly(*p*-oxybenzoate), was removed by filtration. The test specimens were prepared by casting one or two droplets of 1–5 wt % solutions on microscope cover glasses. The solvent was quickly evaporated by placing the cover glasses onto a hot plate preheated at 60 °C in a vacuum chamber. The film-casting seemed to be completed within a few minutes but the test specimens were kept under vacuum for an additional 3 h. The films thus prepared had average thicknesses of 1–10 μm at the centers of the droplets and thicker peripheries. The as-cast films were clear and exhibited no optical anisotropy under a cross-polarized optical microscope. Time evolution of the structure was observed by a Nikon Optiphot-Pol XTP-11 polarizing microscope equipped with a TH-600 heating stage (LINKAM Scientific Co.). The temperature of the heating stage was calibrated for the melting points of various standards of small molecules. The observations were started as soon as the test specimens on the cover glasses were placed on the heating stage controlled at the preset temperature. The time required for a temperature jump (T jump), i.e., the time necessary for the test specimens to reach the preset temperature, was less than a few seconds. The

0024-9297/86/2219-3008$01.50/0

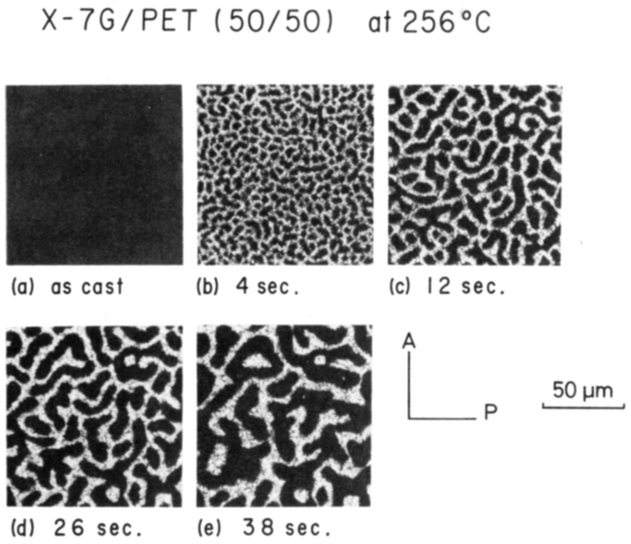

Figure 1. Polarized optical micrographs of X-7G/PET (50/50) mixture film: (a) observed at room temperature (as-cast film) and observed at 256 °C after (b) 4, (c) 12, (d) 26, and (e) 38 s of isothermal phase separation at 256 °C.

polarized optical micrographs were taken with the increment of annealing time. The light scattering patterns were obtained, however, from specimens quenched after various annealing times on a metal block at room temperature.

Figure 1 shows the structure evolved by the isothermal phase separation of the mixture at 256 °C. The isothermal phase separation was initiated by a T jump from room temperature to 256 °C for the as-cast films. The as-cast films are optically isotropic and homogeneous on a spatial scale of 50 μm as shown in Figure 1a. The temperature 256 °C is above the melting point of the crystallites of the PET sequence in X-7G and pure PET[41] so that PET homopolymer and the PET sequence in X-7G are in the molten liquid state. X-7G forms liquid crystals at 256 °C.[25]

Shortly after the *T* jump, unmixing between the optically isotropic phase and the anisotropic phase was observed to occur, as shown in the pictures obtained 4 and 12 s after the *T* jump (Figure 1b,c, respectively). The phase separation appears to form periodic, bicontinuous network structure, and the periodicity or the correlation length appears to increase with time. With a further lapse of time, a coarsening of the network pattern occurs, while "self-similarity" of the patterns seems to be maintained throughout the process. The fine structures observed within the optically anisotropic networks are believed to originate from a polydomain structure[26] in the thermotropic liquid crystal phase. The polydomain structure in turn is believed to arise from the spatial distribution of the disclination lines[27] and hence to represent regions of the correlated orientations[26] of the OBA optical axes. Except for the novelty associated with one phase being liquid crystalline, the general trends observed in the time evolution of the unmixing structures are typical of those for unstable critical mixtures in small-molecule liquids, metallic alloys, inorganic glasses, and binary liquid polymers.

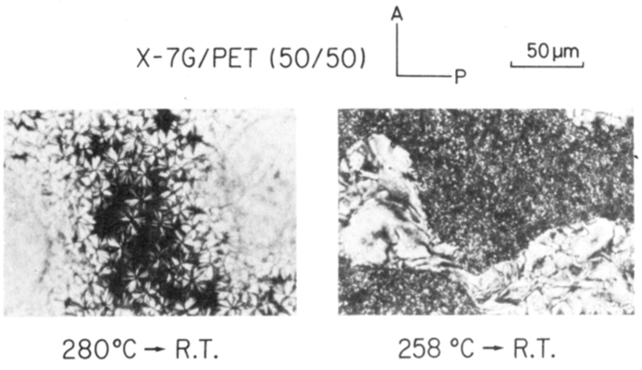

Figure 2. Polarized optical micrographs of X-7G/PET (50/50) mixture film: slowly cooled to room temperature after phase separation at 280 °C (left) and rapidly cooled to room temperature after phase separation at 258 °C (right).

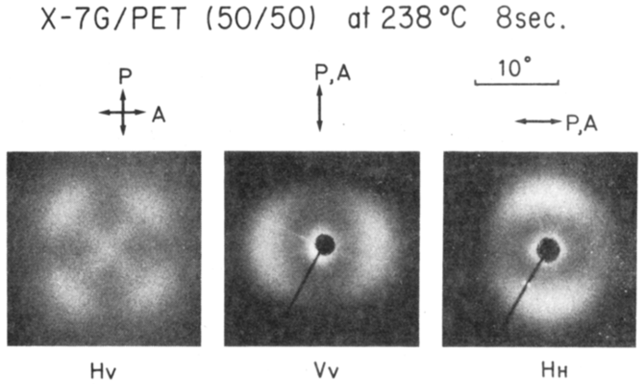

Figure 3. Light scattering patterns taken under H_V (left), V_V (center), and H_H (right) conditions from an X-7G/PET (50/50) mixture film isothermally phase separated at 238 °C for 8 s and quenched to room temperature. The directions of the polarizer and analyzer are shown by arrows.

Figure 2 demonstrates that the isotropic phase in Figure 1 indeed corresponds to a liquid PET phase. The left picture was obtained by slowly cooling the mixture subjected to a certain stage of unmixing at 280 °C to room temperature, while the right picture was obtained by rapidly cooling the mixture subjected to another stage of unmixing at 258 °C to room temperature. In the left picture, the defocused regions located in the left and right corners of the pictures correspond to a part of the liquid crystalline networks which are frozen in the glassy state. Between the liquid crystalline regions one can clearly observe the PET spherulites that grow from the isotropic liquid phase during the cooling process. In the right picture, a part of the glassy liquid crystalline networks is observed in the lower part of the picture, and small PET spherulites or crystallites are observed in the matrix.

The time evolution of the light scattering patterns during the isothermal phase separation was also investigated.[28] During phase separation ring-like scattering patterns typical of what is called a "spinodal-ring"[9] was observed, and the peak position was found to shift toward the incident beam axis. The time evolution of the ring-like scattering reflects growth of periodic concentration fluctuations originating from the spinodal decomposition and its coarsening process. The light scattering technique was found to be especially powerful in the investigation of the early stage of unmixing where the periodic network structure cannot be clearly resolved under the optical microscope due to overlap of the structure in the thickness direction. Of course, good agreement between the correlation length Λ_m's measured from the light scattering technique and optical microscopy was clearly found in the late stage of unmixing where the network structure is clearly distinguished under the microscope.

Figure 3 shows a unique feature of the spinodal ring that results from one phase being optically anisotropic due to the liquid crystal nature. The anisotropy gives rise to the strong depolarized (H_V) pattern. The orientations of the polarized and depolarized patterns are expected from scattering theory for anisotropic systems[26,29–32] and indicate preferential orientation of the OBA molecules in the liquid

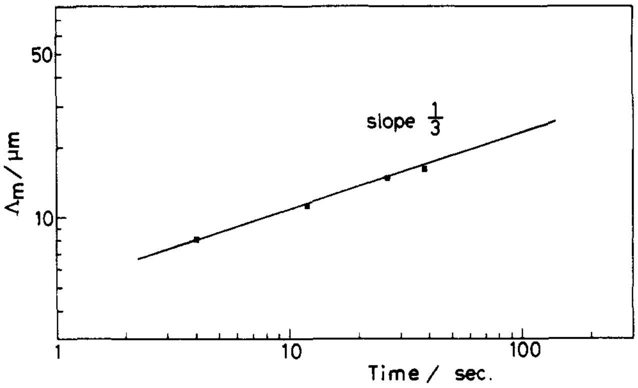

Figure 4. Logarithmic plot of the correlation length Λ_m vs. time spent for the isothermal phase separation of X-7G/PET (50/50) mixture film at 256 °C.

crystalline networks. Detailed analyses on the scattering patterns will be described elsewhere.[28]

Figure 4 shows the time evolution of the correlation length Λ_m's during isothermal phase separation at 256 °C. Λ_m's were measured by image processing of the optical microscopic pictures obtained in the late stage of the unmixing so that the network structure could be unequivocally distinguished with the dynamic image analyzer built in our laboratory.[33] Details of the dynamic image analyzer[33] and the method of extracting Λ_m's will be reported elsewhere.[28] Preliminary experimental results show the power law

$$\Lambda_m \sim t^{1/3} \tag{1}$$

The $^1/_3$-power law is the one familiar for the droplet growth caused by the hydrodynamic effect[16,17,34] or by the Lifshitz–Slyozov process.[15] The growth of the droplets occurs as a consequence of their diffusion and coalescence so that

$$R^2(t) \sim D(t)t \tag{2}$$

where $R(t)$ is the size of the droplet and $D(t)$ is time-dependent diffusivity of the droplet, which, in turn, is given by

$$D(t) \sim k_B T/\eta R(t) \tag{3}$$

where $k_B T$ is the thermal energy and η is the viscosity. From eq 2 and 3 one obtains the $^1/_3$-power law

$$\Lambda_m \sim R(t) \sim (k_B T/\eta)^{1/3} t^{1/3} \tag{4}$$

Needless to say, further investigation is required as to whether the $^1/_3$-power law observed in the preliminary study of the unmixing dynamics of the liquid crystalline component and isotropic liquid component exactly corresponds to the $^1/_3$-power law in the growth of patterns caused by hydrodynamic interactions of the Lifshitz–Slyozov process found for the isotropic liquid or solid mixtures. Moreover, the $^1/_3$-power law itself has to be further investigated over a much wider time scale and temperature range. Further work along this line is currently in progress in our laboratory. However, all evidence presented in this paper indicates that spinodal decomposition and subsequent coarsening processes similar to those for isotropic liquids and solids occur even when one component is a liquid crystalline polymer and forms a liquid crystal phase.

Acknowledgment. We are grateful to Dr. S. Suehiro for help in the image processing of the optical micrographs with the dynamic image analyzer. Part of this work was supported by the Japanese Ministry of International Trade and Industry (MITI).

References and Notes

(1) Nishi, T.; Wang, T. T.; Kwei, T. K. *Macromolecules* **1975**, *8*, 227.
(2) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.
(3) Nojima, S.; Tsutsumi, K.; Nose, T. *Polym. J. (Tokyo)* **1982**, *14*, 225.
(4) Nojima, S.; Ohyama, Y.; Yamaguchi, M.; Nose, T. *Polym. J. (Tokyo)* **1982**, *14*, 907.
(5) Hashimoto, T.; Kumaki, J.; Kawai, H. *Macromolecules* **1983**, *16*, 641.
(6) Snyder, H. L.; Meakin, P.; Reich, S. *Macromolecules* **1983**, *16*, 757.
(7) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(8) Gelles, R.; Frank, C. W. *Macromolecules* **1983**, *16*, 1448.
(9) Hashimoto, T.; Sasaki, K.; Kawai, H. *Macromolecules* **1984**, *17*, 2812.
(10) Sasaki, K.; Hashimoto, T. *Macromolecules* **1984**, *17*, 2818.
(11) Izumitani, T.; Hashimoto, T. *J. Chem. Phys.* **1985**, *83*, 3694.
(12) Inoue, T.; Ougisawa, T.; Yasuda, O.; Miyasaka, K. *Macromolecules* **1985**, *18*, 57.
(13) Russel, T. P.; Hadziioannou, G.; Warburton, W. K. *Macromolecules* **1985**, *18*, 78.
(14) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.
(15) Lifshitz, I. M.; Slyozov, V. V. *J. Phys. Chem. Solids* **1961**, *19*, 35.
(16) Binder, K.; Stauffer, D. *Phys. Rev. Lett.* **1974**, *33*, 1006.
(17) Furukawa, H. *Prog. Theor. Phys.* **1978**, *59*, 1072; *Phys. Rev. Lett.* **1979**, *43*, 136; *Phys. Rev. A* **1981**, *23*, 1535; *Physica A: (Amsterdam)* **1984**, *123*, 497.
(18) Hennion, M.; Ronzaud, D.; Guyot, P. *Acta Metall.* **1982**, *30*, 599.
(19) Komura, S.; Osamura, K.; Fuji, H.; Takeda, T. *Phys. Rev. B* **1984**, *30*, 2944.
(20) Furusaka, S.; Ishikawa, Y.; Mera, M. *Phys. Rev. Lett.* **1985**, *54*, 2611.
(21) Chou, Y. C.; Goldburg, W. I. *Phys. Rev. A* **1981**, *23*, 858.
(22) Knobler, C. M.; Wong, N. C. *J. Phys. Chem.* **1981**, *85*, 1972.
(23) Craievich, A.; Sanchez, J. M. *Phys. Rev. Lett.* **1981**, *47*, 1308.
(24) Hashimoto, T.; Itakura, M.; Hasegawa, H. *Polym. Prepr. Jpn., Soc. Polym. Sci., Jpn.* **1985**, *34*, 2773; *J. Chem. Phys.*, in press. Hashimoto, T.; Itakura, M.; Shimidzu, N. *J. Chem. Phys.*, in press.
(25) Jackson, W. J.; Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043.
(26) Hashimoto, T. *J. Appl. Polym. Symp.* **1985**, *41*, 83.
(27) Demus, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: New York, 1978.
(28) Nakai, A.; Shiwaku, T.; Hasegawa, H.; Hashimoto, T., to be submitted.
(29) Stein, R. S.; Rhodes, M. B. *J. Appl. Phys.* **1960**, *31*, 1873.
(30) Rhodes, M. B.; Stein, R. S. *J. Appl. Phys.* **1968**, *39*, 4903.
(31) Hashimoto, T.; Ijitsu, T.; Yamaguchi, K.; Kawai, H. *Polym. J. (Tokyo)* **1980**, *12*, 745.
(32) Hashimoto, T.; Ebisu, S.; Inaba, N.; Kawai, H. *Polym. J. (Tokyo)* **1981**, *13*, 701.
(33) Suehiro, S.; Takebe, T.; Izumitani, T.; Hashimoto, T., to be submitted.
(34) Kawasaki, K.; Ohta, T. *Prog. Theor. Phys.* **1978**, *59*, 362.
(35) McMaster, L. P. *Adv. Chem. Ser.* **1975**, *No. 142*, 43.
(36) Gilmer, J.; Goldstein, N.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2219.
(37) Hill, R. G.; Tomlins, P. E.; Higgins, J. S. *Macromolecules* **1985**, *18*, 255.
(38) Han, C. C.; Okada, M.; Muroga, Y.; McCrackin, F. L.; Bauer, B. J.; Tran-Cong, Q. *Polym. Eng. Sci.* **1986**, *26*, 3.
(39) Yang, H.; Shibayama, M.; Stein, R. S.; Shimidzu, N.; Hashimoto, T. *Macromolecules* **1986**, *19*, 1667.
(40) Takahashi, M.; Horiuchi, H.; Kinoshita, S.; Ohyama, Y.; Nose, T. *J. Phys. Soc. Jpn.* **1986**, *55*, 2687.
(41) Wide-angle X-ray diffraction and small-angle X-ray scattering showed the melting point of the pure PET is close to 275 °C, slightly higher than 256 °C. However, the crystallinity of the PET homopolymer in the mixture, if it existed, appears to make an insignificant contribution to the anisotropy of the PET-rich phase.

Akemi Nakai, Toshio Shiwaku, Hirokazu Hasegawa, and Takeji Hashimoto*

Department of Polymer Chemistry
Faculty of Engineering
Kyoto University, Kyoto 606, Japan

Received July 25, 1986