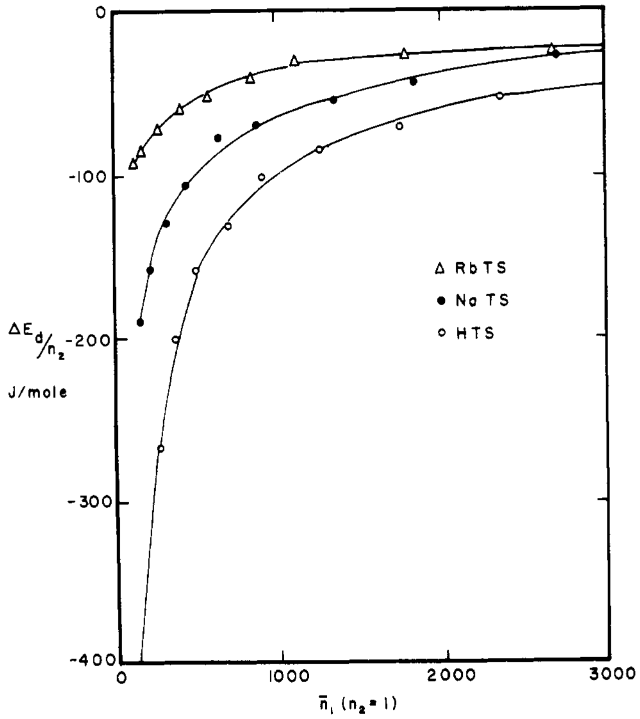

Figure 2. Variation of intermediate molal heats of dilution with the average number of moles of water for 1 mol of *p*-toluenesulfonic acid and its sodium and lithium salts at 25 °C.

dissociation. In the case of the monomer, the aliphatic group, which is less "soluble" than the aromatic group,[23] is exposed to water molecules inducing the formation of icebergs[24] which might extend over the entire anion. Hydration shells around *p*-toluenesulfonic anion are creating a screening effect, such as in the case of small cations, explaining the complete dissociation of all its alkaline salts over the concentration range covered here.

Acknowledgment. The support of this work by the National Research Council of Canada is gratefully acknowledged.

References and Notes

(1) S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions", Academic Press, New York, N.Y., 1961.
(2) W. Schulze, *Z. Elektrochem.*, **58,** 165 (1954).
(3) F. Vaslow, Abstracts of the 145th Meeting of the American Chemical Society, New York, N.Y., Sept 1963.
(4) J. Skerjanc, D. Dolar, and D. Leskovsek, *Z. Phys. Chem. (Frankfurt am Main)*, **56,** 207 (1967).
(5) J. Skerjanc, D. Dolar, and D. Leskovsek, *Z. Phys. Chem. (Frankfurt am Main)*, **56,** 218 (1967).
(6) J. Skerjanc, D. Dolar, and D. Leskovsek, *Z. Phys. Chem. (Frankfurt am Main)*, **70,** 31 (1970).
(7) J.-P. Cartier and H. Daoust, *Can. J. Chem.*, **49,** 3935 (1971).
(8) H. Daoust and A. Lajoie, *Can. J. Chem.*, to be published.
(9) L. Kotin and M. Nagasawa, *J. Am. Chem. Soc.*, **83,** 1026 (1961).
(10) S. Lapanje and S. A. Rice, *J. Am. Chem. Soc.*, **83,** 496 (1961).
(11) See ref 1, Chapter 9.
(12) L. M. Gross and U. P. Strauss, "Chemical Physics of Ionic Solutions", B. E. Conway and R. G. Barradas, Ed., Wiley, New York, N.Y., 1966, Chapter 17.
(13) G. S. Manning, *J. Chem. Phys.*, **51,** 924 (1969).
(14) U. P. Strauss and Y. P. Leung, *J. Am. Chem. Soc.*, **87,** 1476 (1965).
(15) A. Caillé and H. Daoust, *J. Polym. Sci., Polym. Symp.* **No. 45,** 153 (1974).
(16) J. S. Muirhead-Gould and K. J. Laidler, ref 12, Chapter 6.
(17) O. Yo. Samoilov, "Water and Aqueous Solutions: Structure, Thermodynamics and Transport Process", R. A. Horne, Ed., Wiley, New York, N.Y., 1972, Chapter 14.
(18) H. L. Friedman and C. V. Krishnan, "Water, a Comprehensive Treatise", Vol. 3, F. Franks, Ed., Plenum Press, New York, N.Y., 1973, Chapter 1.
(19) E. R. Nightengale, Jr., ref 12, Chapter 7.
(20) M. Eigen and E. Wicke, *J. Phys. Chem.*, **58,** 702 (1954).
(21) S. Lifson and A. Katchalsky, *J. Polym. Sci.*, **13,** 43 (1954).
(22) K. Mita and T. Okubo, *J. Chem. Soc., Faraday Trans. 1*, **70,** 1546 (1974).
(23) F. T. Wall and M. J. Eitel, *J. Am. Chem. Soc.*, **79,** 1550, 1556 (1957).
(24) G. E. Boyd, F. Vaslow, A. Schwarz, and J. W. Chase, *J. Phys. Chem.*, **71,** 3879 (1967).
(25) R. E. Robertson, S. E. Sugamori, R. Tse, and C.-Y. Wu, *Can. J. Chem.*, **44,** 487 (1966).
(26) F. Franks and H. F. Smith, *J. Phys. Chem.*, **68,** 3581 (1964).
(27) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24,** 133 (1957).

Morphological Studies on the Viscous Crystalline Phase of Poly(diethylsiloxane) Including the Dynamics of Phase Formation and the Relationship of Viscous Crystalline Structure and Crystalline Structure

J. M. Pochan,* D. F. Hinman, and M. F. Froix

Xerox Corporation, Rochester, New York 14644. *Received March 3, 1976*

ABSTRACT: A morphological study on the viscous crystalline phase of poly(diethylsiloxane) and its effects on the crystalline phase of the polymer has been done. It has been shown via optical microscopy and light scattering that formation of the phase, prior to crystallization, has a profound effect on the morphology of the crystalline phase. Normal spherulitic texture can be generated via quenching (elimination of the viscous crystalline phase) and an isotropically oriented birefringent structure can be obtained if the viscous crystalline phase is permitted to form (nonoriented rods?). The kinetics of formation of the viscous crystalline and crystalline phase have also been studied. Viscous crystal formation from the amorphous phase is Arrhenius activated with an energy of 47 kcal/mol. Kinetic studies of the crystalline formation have shown that the interaction parameter between the crystalline phase and surrounding material is small compared to normal semicrystalline polymer systems. These small interaction parameters are thought to be indicative of preordering of the crystal structure by the viscous crystalline phase.

Polymers are generally considered to exist in two phases: the amorphous and the crystalline.[1] The type of phase as well as the morphologies of the crystalline phase have been shown to be controlled by chemical composition, tacticity, and methods of crystallization. In addition, crystalline polymers contain amorphous and crystalline components and are called semicrystalline to denote the mixed state. Recently, two new ordered polymeric phases, which exhibit intermediate order between the amorphous and crystalline phases, have been investigated and have been named liquid crystal[2-9] and viscous crystalline.[10,11] To a first approximation, both could be considered identical as x-ray diffraction studies exhibit a single sharp diffraction peak characteristic of one-dimensional ordering. The similarity ends with the x-ray data, however. The liquid-crystalline polymers form as a single-phase system from polymeric materials which might normally be amorphous (for example, atactic poly(*p*-biphenyl acrylate)). The viscous crystalline phase of poly(diethylsiloxane) (PDES), on the other hand, has been shown to exist as a two-phase system similar to semicrystalline material with a partially ordered phase and an amorphous phase.[10,11] In our original studies on PDES,[10-13] four calorimetric events were observed: a glass transition at −135 °C, a crystal–crystal transformation at −70 °C, a crystal melt at ca. −5 °C, and a possible endothermic transition at $\sim$20 °C. With wide line and pulsed NMR, dielectric, and x-ray techniques, it was shown that at the crystal melt an intermediate phase (which shows one-dimensional ordering) is formed from the crystal phase. The amount of ordered phase was shown to be a function of temperature, decreasing with increasing temperature above the crystal melt until the entire sample became amorphous at $\sim$20 °C. NMR experiments also showed that the formation of the viscous crystalline phase from the amorphous phase could be kinetically limited (i.e., cooling the sample quickly from the amorphous phase caused only amorphous relaxations to occur in the temperature range −5 to +20 °C). With this kinetic data and the implications of preordering prior to crystallization, it becomes important that the morphological characteristics of the viscous crystalline phase be investigated. The following investigation is the result of optical and light-scattering studies on the viscous crystalline phase of PDES. In addition, the kinetics of formation of the viscous crystalline phase from the amorphous phase and kinetics of formation of the crystalline phase and structural interpretation of the crystalline phase, as formed from the amorphous and viscous crystalline phase, are presented.

Experimental Section

The PDES used in these experiments was obtained from C. L. Lee, Dow Corning Corp., Midland, Mich. It was reprecipitated from toluene into cold methanol ($\bar{M}_w = 250\,000$; MWD = 2.0).

An Ortholux microscope (200× magnification) with a Mettler temperature control stage was used for the optical and kinetic experiments. An acetone–dry ice slush was used to cool the stage. The Mettler stage was calibrated with a copper–constantan thermocouple. The temperature could be programmed or manually set with an accuracy of ±0.1 °C.

For the crystal nucleation and growth studies, an E.G. & G. S6D-100A Silicon photodiode was mounted in the eyepiece of the microscope. Light transmission with cross-polarizers (birefringence) was monitored as a function of time after the sample was introduced at a given Mettler temperature setting. The sample was heated to 50 °C (the amorphous phase) and then placed in the Mettler. Temperature equilibration was achieved within 10 s of insertion. The phototube output was plotted on a strip chart recorder so that the induction period as well as initial growth rate could be obtained. Two separate sets of experiments produced similar data. Unfortunately, there was no means at our disposal to quench samples below the crystallization temperature from the viscous crystalline phase temperature region so that all data were obtained with quenching from the amorphous phase.

For crystallization the above experiment was sufficient for obtaining data; however, the viscous crystalline phase of PDES is not highly birefringent and formation and growth curves of this phase were determined as follows. Samples were quenched from 50 °C to a temperature in the viscous-crystalline region. At specific times, photomicrographs (200×, cross-polarizers) were taken with 3000 speed Polaroid film. These were usually 15-s exposures taken every one or two minutes. The optical densities of the photographs were then taken with a colorimeter and the formation of the phase determined in arbitrary light intensity units/minute. Three sets of data were taken at each temperature.

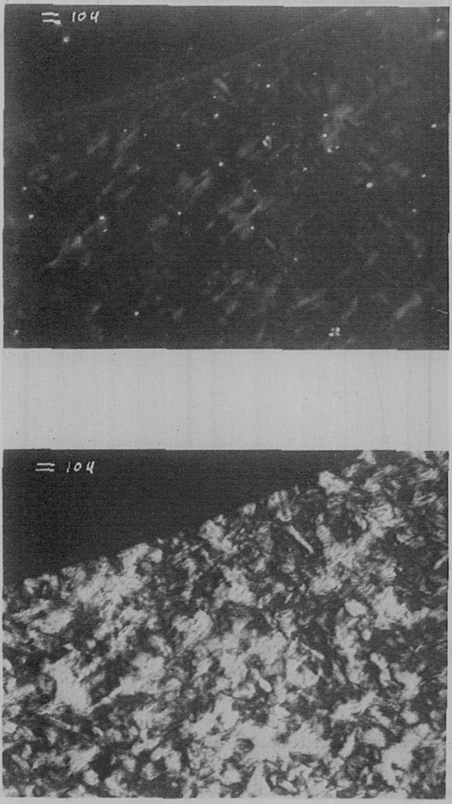

Figure 1. (a, top) PDES at 0.0 °C (cross polarizers) at 200× (viscous-crystalline temperature).
(b, bottom) PDES at −4.0 °C (crossed polarizers) at 200× (temperature of crystallization).

Light-scattering experiments were conducted by placing the sample 8.9 cm from the laser light source (Spectra Physics helium–neon laser) with a cross-polarizer placed 8.9 cm on the opposite side of the sample from the light source. A red filter was used on the source during all experiments. A photographic plate was placed 25.4 cm from the sample. Two experiments were done: (1) a slow quench from $\sim$30 °C via blowing compressed nitrogen passed through a dry ice–acetone slush over the sample (time duration for crystallinity approximately 90 min); (2) heating of the sample to $\sim$60 °C and quenching in liquid nitrogen. The temperature was then maintained below the crystal melt via the above cooling method while light-scattering experiments were conducted. Light-scattering photographs were generated with an exposure time of approximately 0.5 s.

Results and Discussion

Optical Microscopy. Shown in Figure 1 is a photomicrograph of PDES in the viscous crystalline phase at 0.0 °C and the same region of material immediately after crystallization at −4.0 °C. The viscous-crystalline phase is slightly birefringent, with rather large areas of birefringence noted ($\sim$10 μ). This birefringence is indicative of the ordering observed by other experimental techniques.[10,11] Of greater significance is the crystallization of the sample from the viscous-crystalline phase. If Figures 1a and 1b are compared, the birefringent areas of Figure 1a give way to the birefringent crystals of Figure 1b. The orientations and dimensions are similar. When crystallization takes place it occurs as a development of the birefringent viscous crystalline areas rather than a growth front as is observed in normal spherulitic growth. We feel that this is an indication of the viscous-crystalline phase preordering the amorphous structure (one dimensionally) and facilitating crystallization with similar orientations. This will be discussed in depth in the kinetic section of this study. The preordering feature is reversible in that a crystalline phase can

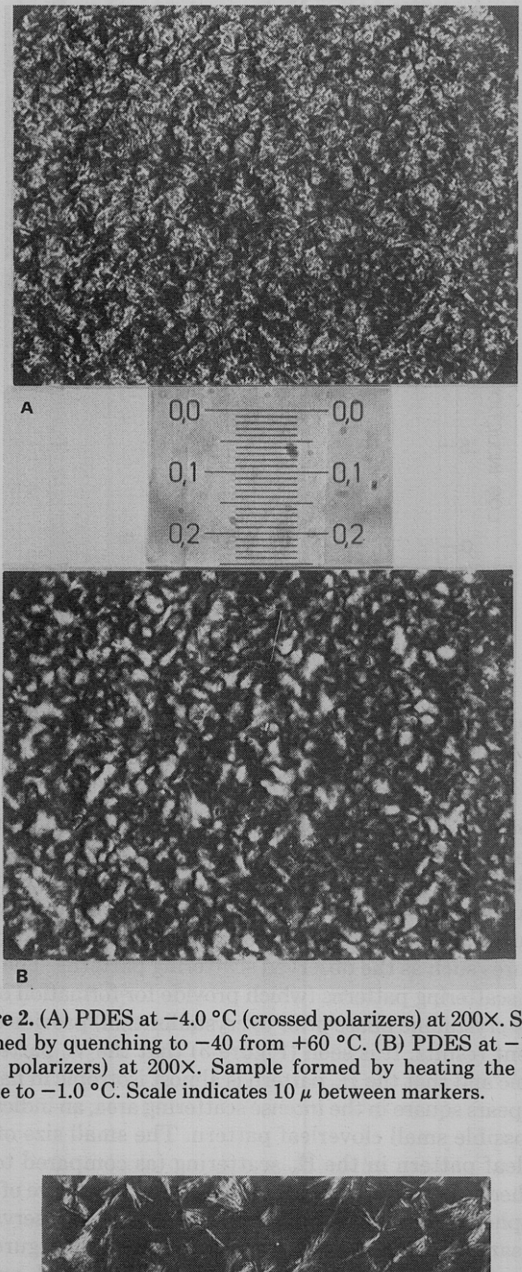

Figure 2. (A) PDES at −4.0 °C (crossed polarizers) at 200×. Sample obtained by quenching to −40 from +60 °C. (B) PDES at −1.0 °C (cross polarizers) at 200×. Sample formed by heating the above sample to −1.0 °C. Scale indicates 10 μ between markers.

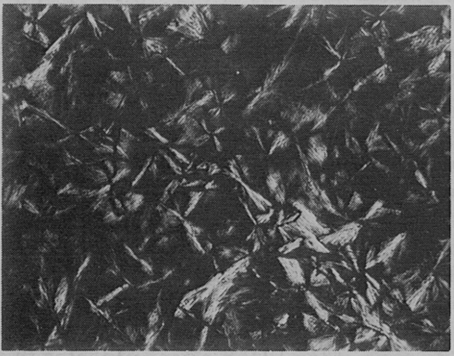

Figure 3. PDES at −18.4 °C (crossed polarizers) at 200×. Sample quenched from 20 °C. Same scale as Figures 1 and 2.

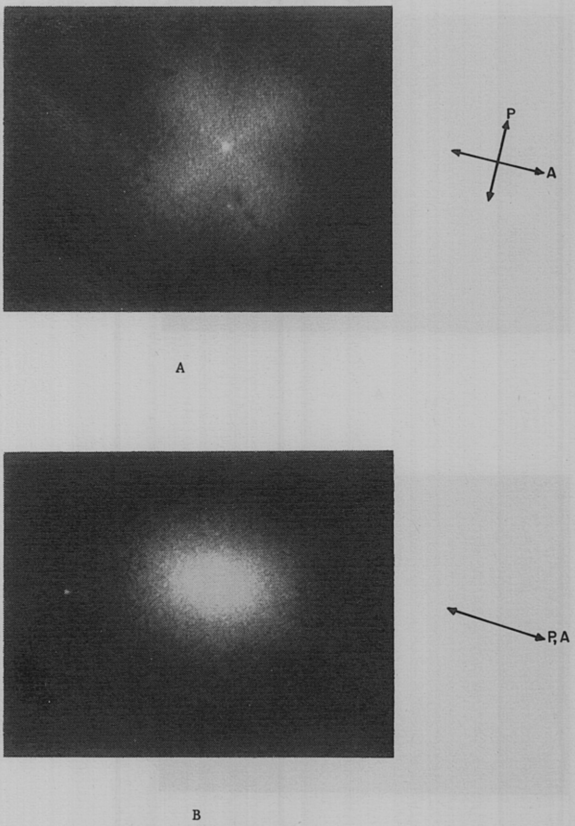

Figure 4. (A) H_v light-scattering pattern for rapidly quenched PDES. (B) V_v light-scattering pattern for rapidly quenched PDES. Conditions of crystallization listed in the Experimental Section.

be formed via quenching (thus minimizing or eliminating the viscous-crystalline phase) and then melted to yield a preordered viscous-crystalline phase. This is seen in Figures 2A and 2B which show the quenched-crystalline state at −4 °C and the viscous-crystalline phase formed from the crystals upon melting. Note that the birefringent areas are similar. The intensity of the birefringent viscous-crystalline phase formed in this way is much greater than that formed upon cooling. It appears from these observations that although the viscous-crystalline region is a thermodynamically allowed phase, the kinetics governing its formation are slow (see below) and that any preordering of the polymer chains (in this case via crystallization) is maintained in the viscous crystalline phase. In earlier work,[10] it was postulated that the phase is one in which the polymer chains maintain a unique interchain distance (8.7 Å), but that lattice registry along the chain is not maintained. Figures 1 and 2 lend credulence to this postulate. When the viscous crystalline phase forms from the amorphous phase a large degree of orientational disorder must be overcome for some type of chain alignment. Thus, low birefringence might be expected. In the case of quenching the amorphous material into the crystalline phase, and then melting the crystals, the ordered crystal structure gives way to the less ordered viscous-crystalline structure. The preordering caused by crystallization produces a more highly ordered viscous-crystalline phase and, thus, higher birefringence. This effect could be due to the melting of the crystalline phase in which lattice registry is not maintained. In fact, NMR results[11] show translational motion and partial hindered rotation about the chain axis in the viscous crystalline state, and, thus, orientational disorder in the partially ordered state. Whether the above two methods would produce identical equilibrium birefringent phases at long enough times has not been tested.

Various morphologies of the crystalline material can be observed. This is seen by comparing Figures 1 and 3. In Figure 3 banding occurs, which is characteristic of lamellar twisting during crystallization.[14] This effect is not observed in Figure 1. If a free surface of the polymer is observed during viscous-crystal formation, buckles (surface ripples) occur as the phase is formed. These are indicative of an increase in density although density measurements have not been done at this time.

Light Scattering. These experiments were done to ascertain what, if any, effect the viscous-crystalline phase has

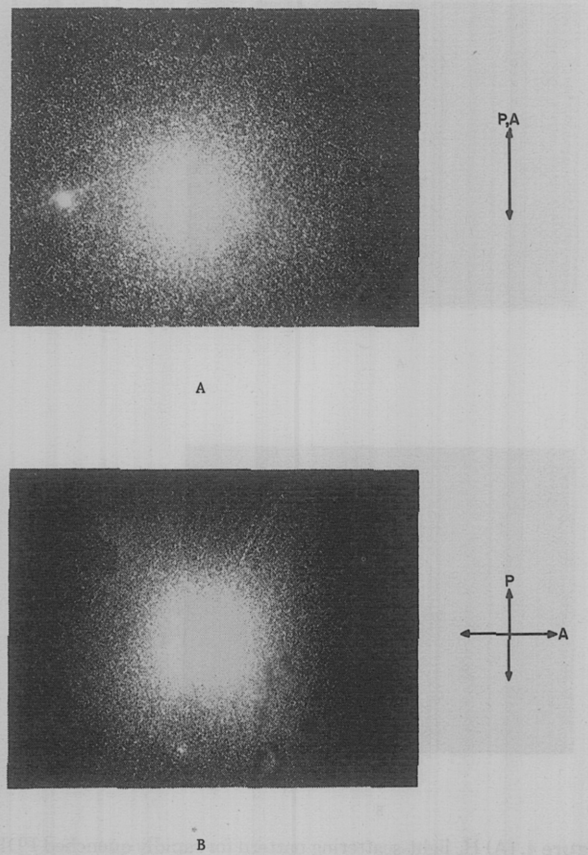

Figure 5. (A) V_v light-scattering pattern for a slowly cooled PDES sample. (B) H_v light-scattering pattern for a slowly cooled PDES sample. Conditions of crystallization in the Experimental Section.

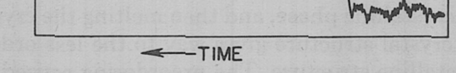

Figure 6. Phototube response as a function of time for the crystallization of PDES after quenching to −6 from 50 °C. Time scale approximately 6 min for (A) and 40 min for (B): 6 °C (A), and −10 °C (B).

on crystal formation. To do this, scattering patterns were taken of samples which were either quenched from 50 °C (totally amorphous) to liquid nitrogen temperature or which were cooled slowly through the viscous-crystalline region and crystallized. The results of these experiments are shown in Figures 4 and 5. Differences in the patterns are evident. The rapidly quenched sample exhibits a H_v pattern similar to those observed by Stein et al.[15–17] and Samuels[18,19] for unoriented spherulitic textures. The pattern does not exhibit the well-*developed lobes of normal spherulitic textures and appears* similar to those observed by Stein and Misra[15] during the early crystallization steps of poly(ethylene terephalate). This incomplete development has been characterized as rodlike development of the crystals which transforms to spherulitic textures at longer times. The V_v pattern is elliptic in nature and could also be described as a typical V_v pattern that has not developed. Both patterns indicate, as expected, that quenching the polymer from +60 °C to liquid nitrogen temperature does not allow enough time for stable equilibrium structures to form. This would provide imperfect crystal structures such as the observed scattering patterns. The slow cooled scattering patterns (which provide for formation of the *viscous-crystalline phase prior to crystallization)* provide quite different results. It is seen (Figure 5) that the V_v pattern is isotropic and that the H_v pattern is almost isotropic in nature, but appears square in the intense scattering area, an indication of a possible small cloverleaf pattern. The small size of any cloverleaf pattern in the H_v scattering (as compared to the quenched sample's H_v scattering) would be indicative of very large spherulitic scattering. However, microscopic observation of the sample revealed a texture similar to that in Figure 1 in *which no spherulites were observed. The fact that* H_v and V_v scattering are observed would indicate that there are correlated dipoles within the sample (crystallites), but that these crystallites are isotropically oriented. The differences between the quenched sample and the slowly cooled sample also indicate that the formation of the viscous-crystalline phase changes the morphological character of the PDES crystals.

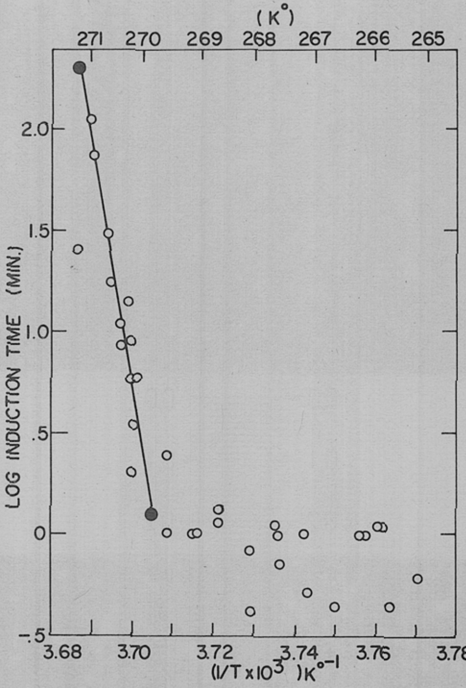

Figure 7. Log induction time (min) vs. inverse temperature for PDES heated to 50 °C and quenched to specific temperature.

Nucleation and Growth of the Crystalline Phase. As described earlier, these studies were conducted by monitoring *the birefringence of the PDES after quenching to a specific* temperature from 50 °C. Typical phototube responses are shown in Figure 6. Two parameters are obtainable from such plots: (1) induction time (nucleation time) and (2) initial relative growth rate of the birefringence (initial slope of the change in transmission). Two other effects were also noted during some measurements: a decrease in transmission vs. time after the initial fast rise in the growth curve (see Figure 6B). We feel that the former effect is due to turbidity ac*companying crystallization and that the latter effect at longer* times is due to secondary nucleation phenomena.

Figure 7 is a plot of log induction time vs. inverse temperature. The high-temperature portion of the curve is linear and represents a very narrow temperature range. Data at temperatures below 269 °C are not accurate because the

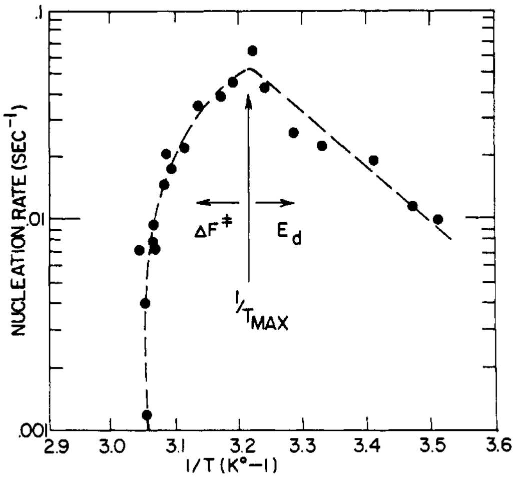

Figure 8. Log nucleation rate vs. $1/T$ (K^{-1}) for cholesteryl nonanoate. Data taken from ref 20.

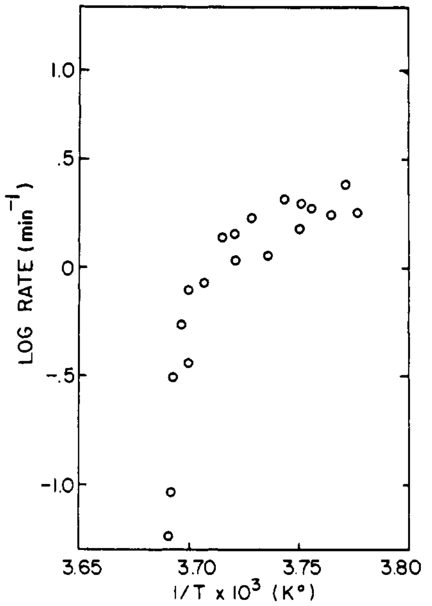

Figure 9. Log (initial growth rate/T) vs. $1/T$ (K^{-1}) for PDES heated to 50 °C and quench to the specified temperature.

quenching time of the sample is greater than the nucleation rate. The activation energy described by the linear portion of the curve is quite high (>500 kcal/mol) and we believe it represents only a small portion of the theoretical curve that can be generated for such data. Nucleation and growth can be described by similar equations of the form,[20–23]

$$P = P_0e^{+E_d/RT_e + \Delta F/RT} \qquad (1)$$

where P_0 represents the rate at infinite temperature, E_d represents the viscosity barrier for molecular transport across the amorphous (or viscous crystalline)/crystalline interface, and ΔF represents the change in internal free energy upon crystallization. ΔF is usually written in terms of a supercooling equation[20–23] and in final form produces a plot similar to Figure 8. In that plot the effects of free energy and microscopic viscosity are apparent on either temperature side of the maximum rate. We believe that our data occur on the thermally activated portion of the curve in the temperature region near T_m (see Figure 8). With the nucleation occurring in this region a very steep slope leading to an apparently high activation energy would be found. Note that the data in Figure 7 were taken over a two-degree temperature span. It is interesting to note that the time scale for the experiments does permit formation of the viscous crystalline phase prior to nucleation. This was obvious microscopically after a few minutes at the quench temperature when the birefringent phase was seen. The process that is being monitored is more than likely the viscous crystalline-to-crystalline transformation rather than the amorphous–crystalline transformation.

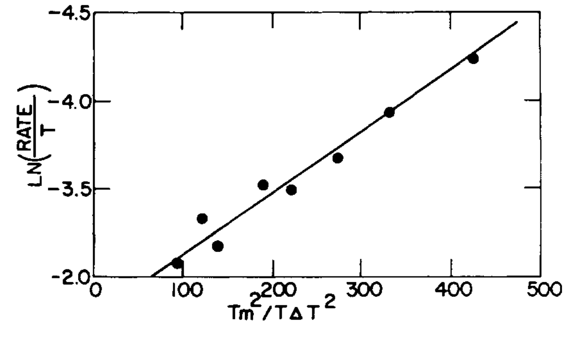

Figure 10. Log (initial growth rate/T) vs. $T_m^2/T\Delta T^2$ for PDES.

In light of this, the use of eq 1 to analyze our data must be considered. The formalism involved in deriving eq 1 considers nucleation and growth in terms of critical nuclear sizes and growth boundaries, respectively. It has already been stated that crystallization from the viscous crystalline phase occurs as an intensification of the viscous crystalline areas of the polymer. If these viscous-crystalline regions can be considered as crystal nuclei the application of eq 1 is directly understood. If, on the other hand, crystallization involves large-scale reorganizations throughout the preordered phase, where increased birefringence with time is due to increasing perfection and ordering, the application of eq 1 must be made with caution. The observed phenomena could be explained in terms of microviscosity and activation energy, as in eq 1, but the specifics, as acquired from eq 2, could be in error. Our analysis of the formation kinetics of the crystalline phase is done in terms of eq 1 and 2 but the above reservations must be kept in mind.

A plot of the initial slope of the growth curve vs. inverse temperature is shown in Figure 9. It is apparent that the curve is similar to the nucleation curve and that the data correspond to the thermally activated temperature portion of the kinetic curve. The theory of Mandelkern et al.[22–24] can be applied to the rate data to determine an interfacial interaction parameter/molecule. We have applied the conventional nucleation rate theory in which the quantity log (rate/T) is plotted against $T_m^2/T(\Delta T)^2$ where T_m is the crystal melting point, T is the absolute temperature, and ΔT is the degree of supercooling of the material below the crystal melt. Such a plot of our data is shown in Figure 10. The slope of this plot is equal to

$$8\pi\sigma_\mu^2\sigma_e/\Delta H^2R\rho^2 \qquad (2)$$

where σ_μ is the lateral surface energy of a growing crystal boundry, σ_e is the end surface energy, ΔH is the heat of fusion of the crystal, ρ is the density, and R is the universal gas constant. The value of surface energy obtained from such an equation is the cubic ($\sigma_\mu^2\sigma_e$). Using these data and a value of 10 J/cm as the heat of fusion[12] a value of 0.06 ergs/cm^2 is obtained for the average value of the molecular surface energy. This value could be in error because chain length has not been taken into account,[23,24] and the value of dp (2000) could affect the results. The value obtained for σ_{av} is much lower than those reported for other polymer systems.[23] It is felt that this low value is due to the preordering of the viscous-crystalline

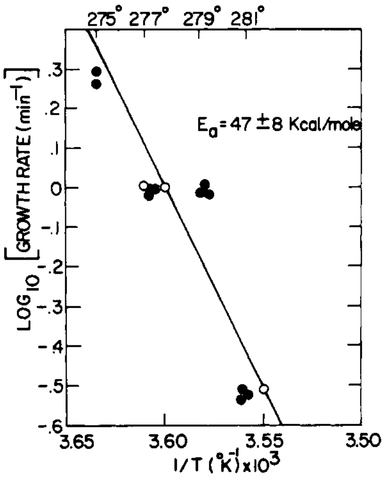

Figure 11. Log (rate of formation of viscous-crystalline phase) vs. inverse temperature. Sample heated to 50 °C and quenched to the specified temperature.

phase. Such preordering would require less reorientational energy for the molecular chains forming the crystalline structure from the viscous-crystalline structure and would provide less interactive free energy during the molecular transformation. It is interesting to note that the preordering decrease in σ is similar to that observed during crystal nucleation phenomena of liquid crystals in which the preordered phase (liquid crystal) facilitates crystallization and lowers the interfacial barrier term.[20,21]

Kinetics of Formation of the Viscous-Crystalline Phase. The experimental set-up for monitoring the formation characteristics of the viscous-crystalline phase has already been presented. Results of those experiments are shown in Figure 11, a plot of arbitrary growth units vs. inverse temperature. In this region the growth appears barrier activated with an activation energy of 47 ± 8 kcal/mol. The kinetics of formation of the ordered phase is similar to "normal" systems showing an increase in formation rate with increased supercooling. Since crystallization takes place readily below T_m of the material, no low-temperature data could be taken to assess the possibility of a viscosity-controlled region of growth. It is also noted that "growth" of the phase does not result from the growth of texture in the normal sense of the word (as with spherulitic growth of crystalline systems). The birefringent areas of the material develop (over a region $>1\mu$) and intensify with time. The intensification process is the subject of this study. The value of the activation energy is relatively large and may indicate that most ordering in the system takes place in the viscous crystalline region of the sample if enough time is permitted. Unfortunately, the heat of formation (as measured via DSC above the crystal melt) of the phase is questionable (as to whether the transition is first or second order) and molecular theories could not be applied to learn anything about the physical interactions of the molecules during formation of the phase. Note is also made that formation of the viscous-crystalline phase is slow compared to that of the crystalline phase and thus quenching experiments (as reported above in the light-scattering studies) can easily be done.

Summary

A morphological study on the viscous-crystalline phase of PDES and its effects on the crystalline phase of the polymer has been done. It has been shown via optical microscopy and light scattering that formation of the phase, prior to crystallization, has a profound effect on the morphology of the crystalline phase. Normal spherulitic texture can be generated via quenching (elimination of the viscous crystalline phase) and an isotropically oriented birefringent structure can be obtained if the viscous crystalline phase is permitted to form (nonoriented rods?). The kinetics of formation of the viscous-crystalline and crystalline phase have also been studied. Viscous crystal formation from the amorphous phase is Arrhenius activated with an energy of 47 kcal/mol. Kinetic studies of the crystalline formation have shown that the interaction parameter between the crystalline phase and surrounding material is small compared to normal semicrystalline polymer systems. These small interaction parameters are thought to be indicative of preordering of the crystal structure by the viscous-crystalline phase.

Acknowledgments. The authors wish to acknowledge the helpful discussions of Drs. R. S. Stein (University of Massachusetts) and P. F. Erhardt and the helpful discussions and sample of Dr. C. Beatty.

References and Notes

(1) F. Billmeyer, "Textbook of Polymer Science", McGraw-Hill, New York, N.Y.
(2) B. A. Newman, V. Frosini, and P. L. Magagnini, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 87 (1975).
(3) E. F. Jordan, Jr., D. W. Feldersen, and A. J. Wrigley, *J. Polym. Sci., Part A-1*, **9**, 1835 (1971).
(4) N. A. Plate, V. P. Shibaev, B. S. Pekruklin, and V. A. Kargin, *J. Polym. Sci., Part C*, **23**, 37 (1968).
(5) J. H. Wendorff, private communication.
(6) V. N. Tsevetkov, T. N. Shtennikova, Y. I. Ryumtsev, G. F. Kolbina, I. L. Konstantinov, Y. B. Amerik, and B. A. Krentsel, *Vysokomol. Soedin., Ser. A*, **11**, 2528 (1969).
(7) V. N. Tsevetkov, Y. I. Ryumtsev, I. I. Konstantinov, Y. B. Amerik, and B. A. Krentsel, *Vysokomol. Soedin., Ser. A*, **14**, 67 (1972).
(8) V. N. Tsevetkov, Y. I. Ryumtsev, I. N. Shtennihova, Y. B. Konstantinov, Y. B. Amerik, and I. I. Konstantinov, *Vysokomol. Soedin., Ser. A*, **15**, 2158 (1973).
(9) V. N. Tsevetkov, Y. I. Ryumtsev, I. N. Shtennihova, Y. B. Konstantinov, Y. B. Amerik, and B. A. Krentsel, *Vysokomol. Soedin., Ser. A*, **15**, 2270 (1973).
(10) C. L. Beatty, J. M. Pochan, M. F. Froix, and D. F. Hinman, *Macromolecules*, **8**, 4, 547 (1975).
(11) M. F. Froix, C. L. Beatty, J. M. Pochan, and D. F. Hinman, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 7, 1269 (1975).
(12) C. L. Beatty and F. E. Karasz, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 971 (1975); *Bull. Am. Phys. Soc.*, **18**, 461 (1973).
(13) J. M. Pochan, C. L. Beatty, and D. F. Hinman, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 977 (1975); *Bull. Am. Phys. Soc.*, **18**, 461 (1973).
(14) Reference 1.
(15) R. S. Stein and A. Misra, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 109 (1973).
(16) T. Hashimoto, R. E. Prud'homme, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 709 (1973).
(17) D. Y. Yoon and R. S. Stein, *J. Polym. Sci., Poly. Phys. Ed.*, **12**, 635 (1974).
(18) R. J. Samuels, *J. Polym. Sci., Part A-2*, **9**, 2165 (1971).
(19) R. J. Samuels, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1417 (1971).
(20) J. M. Pochan and H. W. Gibson, *J. Am. Chem. Soc.*, **94**, 5573 (1972).
(21) J. M. Pochan and H. W. Gibson, *J. Am. Chem. Soc.*, **93**, 1279 (1971).
(22) L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York, N.Y., 1964.
(23) L. Mandelkern, J. G. Fatou, and C. Howard, *J. Phys. Chem.*, **69**, 956 (1965).
(24) L. Mandelkern, J. G. Fatou, and C. Howard, *J. Phys. Chem.*, **68**, 3386 (1964).