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Liquid Crystalline Type Order in Polydiethylsiloxane

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ABSTRACT: Polydiethylsiloxane has been demonstrated via calorimetric, dielectric, NMR, and X-ray techniques to exist in a two-phase structure for approximately 20° above its crystalline melting point, 270°K. One phase is amorphous and the other partially ordered. Analogies are drawn between polymer and liquid crystal morphology and behavior. The properties of the partially ordered phase are stable and intermediate between the amorphous and crystalline states suggesting that the term viscous crystalline is more descriptive of this phase.

The fact that some polymers do crystallize has resulted in extensive studies of the supramolecular texture and the mechanism of crystallization. Conventionally, crystallinity has come to be associated with a regular spatial repeat in three dimensions over some long range. However, it has been found that sharp diffraction intensities are observed for spatial repeats in only one or two dimensions.[1] This phenomena occurs in liquid crystals (low molecular weight materials) which may possess order in one or two dimensions. Several polymers have been studied which show one- and two-dimensional order. Stratton[2] concluded from a study of several of these polymers that two-dimensional order could be attributed to a regular lateral packing of linear molecules with no order along the chain direction, and one-dimensional order to longitudinal periodicity with no lateral order.

Recently the synthesis and characterization of poly(*p*-biphenyl acrylate) (PPBA) was reported.[3] Subsequent X-ray[4,5] and calorimetric studies[5] on PPBA, poly(*p*-cyclohexylphenyl acrylate) (PPCPA), and poly(*p*-biphenyl methacrylate) (PPBMA), all of which are atactic, showed PPBA and PPCPA to produce single sharp X-ray peaks, while PPBMA gave an amorphous halo. Annealing increased the intensity of the diffraction peaks of PPBA and PPCPA. DSC data also showed distinct melting over 5° ranges for PPBA and PPCPA while PPBMA showed no distinct melting range. The combined results for PPBA and PPCPA are explained in terms of a high degree of order, yet they are not crystalline in the convential sense, showing long-range order only in one direction. However, when the same thermodynamic considerations applied to semicrystalline polymers are used, "degrees of crystallinity" determined from heats of fusion and specific heat measurements are in good agreement for both polymers although the crystallinity of PPCPA is less than PPBA.

It was concluded that the formation of ribbon-like macromolecules in the solid PPBA is energetically favorable if the substituents are sufficiently long.[5] That is, the lowest free energy is found for molecular conformations in which the side groups are arranged in a plane passing through the main chain.

Despite the dissimilarity of PPBA and PPCPA and because PPCBA contains the flexible cyclohexyl ring, it is reasoned that the mobility of the cyclohexyl ring is severely reduced when bound to the benzene ring and as a result PPCPA is more like PPBA than expected, making the side chains fairly rigid. It has also been demonstrated that the order observed in the copolymerization of the monomers of PPBA and PPCPA is very sensitive to its copolymer partner.

It has also been reported that dilute solutions of methacrylylphenyl polyesters of alkoxy benzoic acids exhibit mesomorphic type order in which side chains form a mobile liquid-crystal structure.[6–9] Cooling of the macromolecules in a thermodynamically poor solvent is accompanied by an improvement in the orientational order of the side groups because of the reduction in polymer–solvent interaction which competes with the interaction between side chains within the polymer molecule. For the poly(phenylmethacrylyl ester of hexyloxybenzoic acid), PEHA, larger absolute birefringence of PEHA solutions than the EHA monomer indicated that larger "intrinsic units" were responsible for the observed birefringence in polymer solutions. There is also a high degree of orientational polar ordering within the structure of these units. Negative birefringence of PEHA solutions is a consequence of the orientation of the dipole molecules of the polymer, and the increase in this effect as the temperature is lowered is a result of the improvement in the intramolecular ordering within the side groups which have a tendency toward the formation of a liquid-crystal phase. Prolonged thermostating of the solutions led to a large positive value of the Kerr constant. This increase in K with time is due to the formation of molecular aggregates with an ordered internal structure whose dimensions increase with time.

Wendorff et al.[10] have also observed a nematic liquid-crystalline type order in 4-acryloxybenzylidene-4^1-ethoxyaniline. All of the systems mentioned above appear to have the following common features: (1) they are composed of fairly stiff shift chains, (2) they are not potentially crystallizable, and (3) they can exist in a single phase exhibiting liquid-crystalline type order. Recent utilization of block copolymers of stiff liquid-crystalline type ordered systems to obtain highly oriented, high strength materials demonstrates the need to understand the factors which lead to molecular ordering.[11] As a result we have undertaken a series of studies on polydiethylsiloxane incorporating widely varying experimental techniques. Our results suggest that a similar liquid-crystalline type order exists in polydiethylsiloxane as observed in other polymer systems. However, polydiethylsiloxane is crystallizable, flexible by comparison to previously studied liquid-crystal type ordered polymers, and heterogeneous in supramolecular texture.

Experimental Section

The PDES used in these experiments was obtained from C. L. Lee, Dow Corning Corporation, Midland, Mich. The sample was initially reprecipitated from toluene into cold methanol ($\bar{M}_n$ = 112,000, $\bar{M}_w/\bar{M}_n$ = 2.5) and will be referred to as PDES-I.[12] Another reprecipitation led to fractionation of the system ($\bar{M}_n$ = 250,000, $\bar{M}_w/\bar{M}_n$ = 2.0), yielding sample PDES-II.[13] Molecular weights were determined using membrane osmometry and gel permeation chromatography. At room temperature, PDES-I was transparent and liquid like in nature, while PDES-II was translucent and more viscous. A Perkin-Elmer Differential Scanning Calorimeter, Model 1-B, was used to confirm previously obtained adiabatic calorimetric results.

The wide-angle X-ray diffraction data on PDES-II were obtained using Ni-filtered Cu radiation from a Phillips wide-angle X-ray diffractometer. A stream of cooled nitrogen flowing past electrically heated coils was used to control temperature.

Dielectric measurements were made using a General Radio 1615-A bridge with the necessary accessories. As PDES is a viscous liquid at room temperature, no attempt was made to vacuum deposit electrodes on the polymer. A Balsbaugh-type MC-100 stainless steel liquid cell with spring loading was used on all measurements. All dielectric measurements on the initial sample, PDES-I, were corrected for thermal changes in cell dimensions above T_g(~133°K) of PDES.

Spin lattice and spin–spin relaxation time (T_1 and T_2) of PDES-II were measured using a Bruker SXP pulsed spectrometer. Measurements of proton relaxation times were made by the 180–τ–90° pulse technique.[14] All T_1 measurements were made at 90 MHz. The 90° pulse widths for protons were in the range 1.5 to 2.0 msec.

The magnetic field was generated by a 12 in. Bruker shimmed electromagnet and operated in the current-regulated mode. Temperature was controlled by a gas flow cryostat and monitored with a thermocouple to an accuracy of about ±1°.

The values of T_1 were derived from a least-square analysis of plots of log $[A(\infty) - A(t)]$ as a function of the time interval, τ, between the 90 and 180° pulses in accordance with the equation

$$\ln [A(\infty) - A(t)] = \ln [2A(\infty)] - t/T_1$$

where $A(t)$ is the amplitude of the free induction decay following the 90° pulse at time t; $A(\infty)$ is the limiting value of $A(t)$ for a very long time interval between the 180 and 90° pulse. No significant deviations from exponential behavior were observed and the slope of the straight line was given by $1/T_1$. Spin–spin relaxation times were obtained from the free induction decay following the 90° pulse. T_2 is given by $t_{1/2}/\ln 2$, where $t_{1/2}$ is the time required for the free induction decay to fall to one-half its initially observed value.

Results

A. Calorimetric. The differential scanning calorimetric, DSC, results for PDES-II (Figure 1) are similar to those previously observed via adiabatic calorimetry with the exception of results above 293°K.[12] These higher-temperature data were obtained via adiabatic calorimetry[15] but not reported previously as confirmation via other techniques was desired.

The transition at about 297°K is not as sharp as those of liquid crystal to isotropic melt transitions and polymeric first-order thermodynamic transitions.[16–18] If domains of an ordered phase of different stability existed, then the transformation of the phase to an isotropic melt could occur continuously over a range of temperatures. These domains may be variable in stability because of their varying dimensions, such as the melting temperature of polymer crystals which is directly dependent upon their thicknesses.[19] Polymeric lamellae thickness is in turn dependent upon crystallization temperature and subsequent annealing.[20,21] Transformation of regions of varying stability, therefore, could result in a relatively broad diffuse peak as a result of a first-order thermodynamic transition without displaying the characteristic shape of a first-order peak.

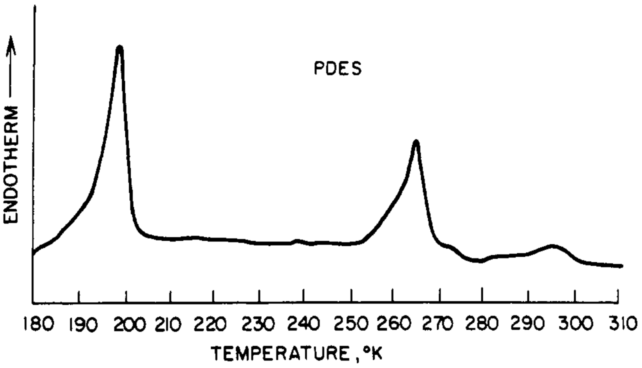

Figure 1. Heat capacity of PDES-I as a function of temperature via differential scanning calorimetry.

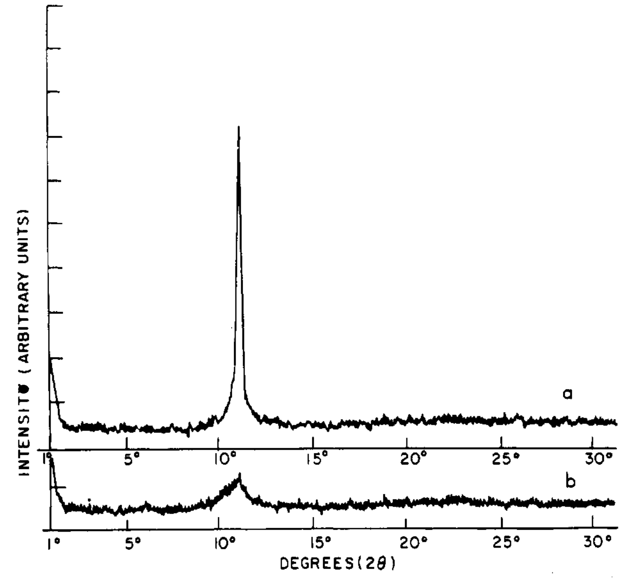

Figure 2. Wide-angle X-ray diffraction traces of (a) the partially ordered phase and (b) the isotropic melt at 288 and 303°K, respectively, for PDES-II.

Adiabatic calorimetric results on PDES-I also indicate a diffuse transition similar to those observed via DSC. However, the size of the peak indicates a greater percentage of the phase that causes the transition in PDES-II than in PDES-I.

B. X-Ray Diffraction. The wide-angle X-ray diffraction patterns of PDES-II at 288 and 303°K (Figure 2) are different. The single peak observed at 288°K for PDES is similar to those observed and theoretically explained in nematic and smectic liquid crystalline structures.[18,22] Location of the peak at 11.8 Å 2θ corresponds to an average spacing of approximately 8.7 Å between PDES chains in the partially ordered state. The presence of the same diffraction peak at 303°K (although of considerably reduced intensity) indicates that (1) the spacing between chains in

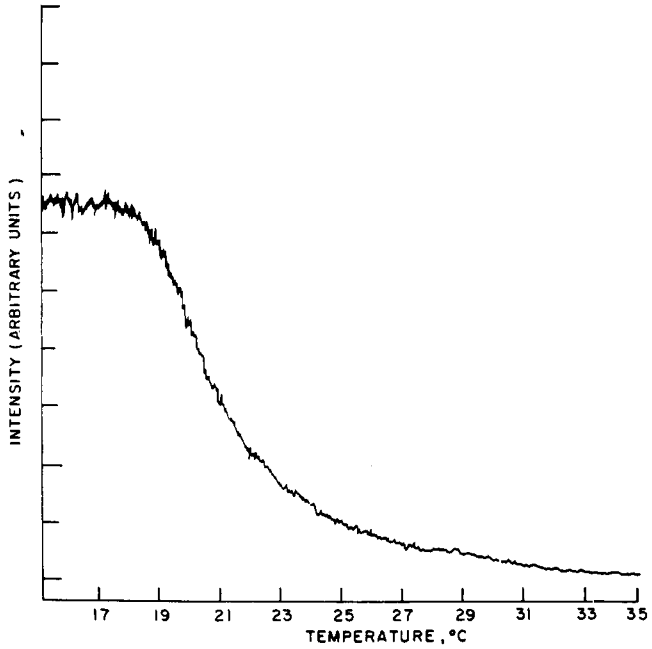

Figure 3. Decrease of singlet maximum peak intensity as temperature is increased from 288 to 303°K.

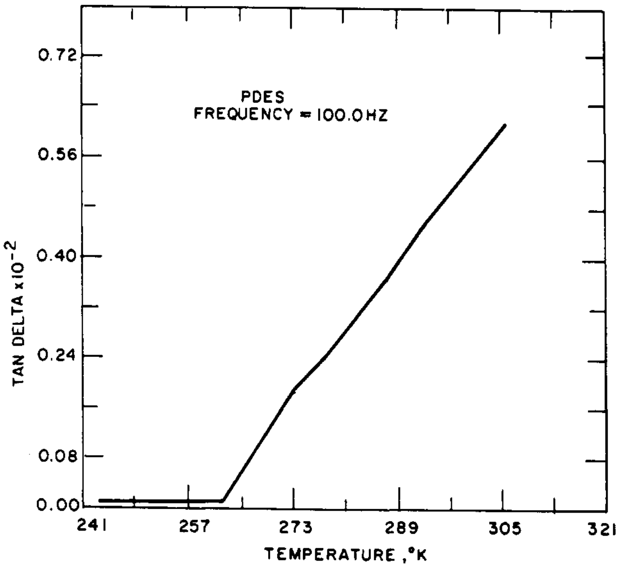

Figure 4. Dielectric tan δ vs. temperature for PDES-II.

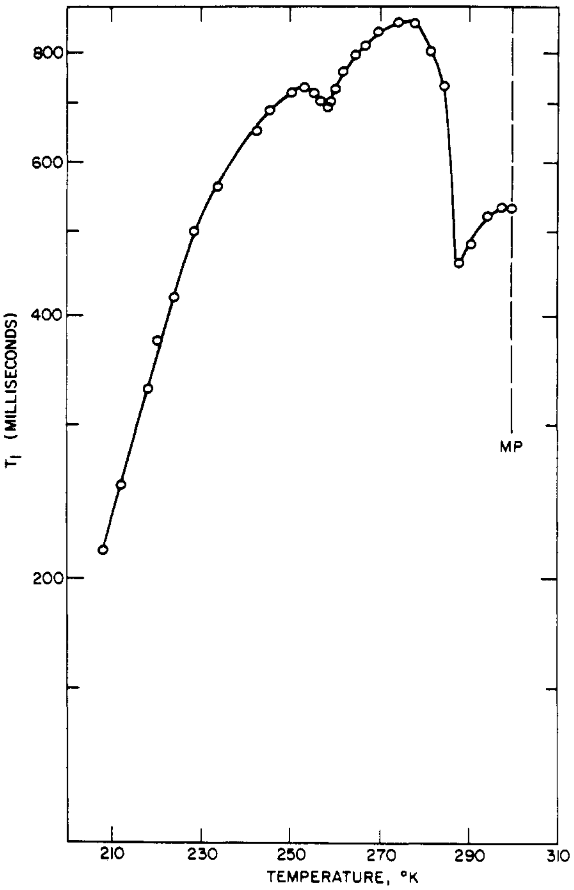

Figure 5. Spin–lattice relaxation times of PDES-II as a function of temperature.

the melt is similar to the spacing in the partially ordered region, or (2) some ordered regions remain at this elevated temperature. The former is a better model since the reduction of peak intensity above 303°K (Figure 3) is slight. The breadth of the transition may be due to poor heat transfer and thermal equilibration of the improvised apparatus used for the temperature scanning study.

C. Dielectric Relaxation. Dielectric results for PDES in the vicinity of the partially ordered phase are shown in Figure 4 (a plot of tan δ increases essentially linearly with temperature throughout the regime of the partially ordered phase). This behavior could be due to one of two possibilities: dc conduction or a gradual change in the partially ordered structure with temperature. The former probably can be eliminated because of the low conductivity of siloxane polymers of this type. The conductivity has not been specifically measured, although a representative value for polydimethylsiloxane is $\sim 10^{15}$ Ω cm.[23] The latter presents two varieties of proposed structure. One is a homogeneous partially ordered structure which becomes dielectrically more mobile with increasing temperature. The other is a mixed structure consisting of partially ordered and amorphous regions whose relative size is dependent on temperature. That is, the partially ordered texture decreases in amount with increasing temperature.

D. Nuclear Magnetic Resonance. Figures 5 and 6 are plots of log T_1 and log T_2 vs. temperature, respectively. In Figure 6, two components are discernable around 250°K. The longer T_2 is attributed to the amorphous component while the shorter T_2 is ascribed to the crystalline component of the polymer.[24] T_1 (Figure 5) shows a transition at 258°K which corresponds to an increase in T_2 for the amorphous phase of the polymer. T_2 for the crystalline component stays constant. At about 268°K, T_2 for the crystalline component increases while T_1 begins to decrease rather rapidly.

Figure 7 shows the wide-line proton resonance of PDES-II at 258°K where the polymer is known to be semicrystalline.[12] At this temperature the resonance line consists of two components, a broad component due to the crystalline region and a narrow component due to the amorphous phase. The crystalline resonance is much narrower than one would expect for a rigid lattice. At this temperature, side chain rotation of the ethyl group would be too fast to contribute to T_1. Rotation of the side chains about the O–Si–O bonds is not likely to produce either of the transitions at 258 or 268°K since the important interproton distances would be those of the ethyl group and this relaxation would be much more efficient than those at hand.

At temperatures between 268°K and the melting point,

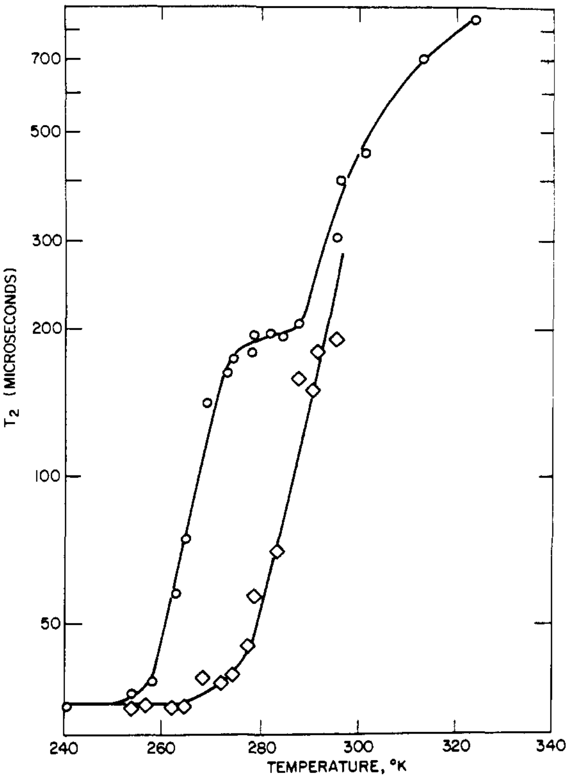

Figure 6. Spin–spin relaxation times of PDES-II as a function of temperature.

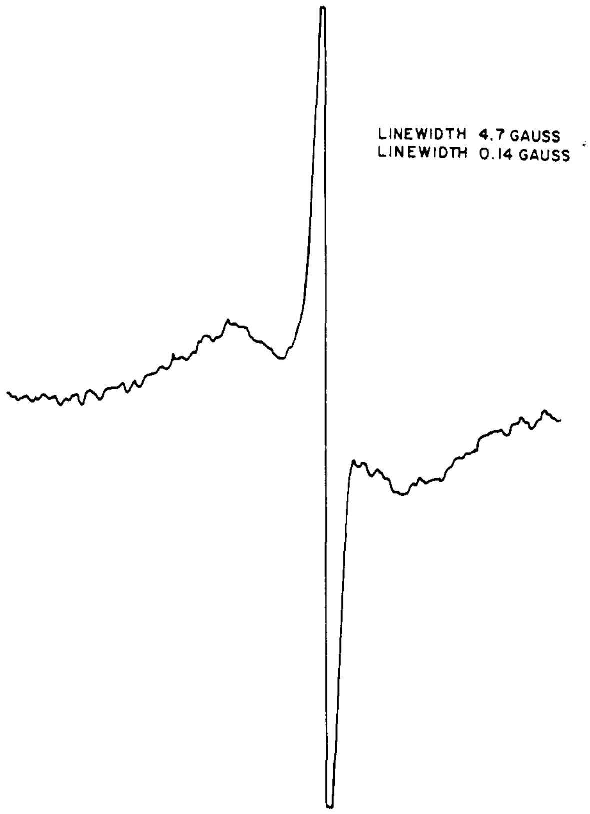

Figure 7. Wide-line proton resonance of PDES-II at 258°K.

the solid has an even narrower resonance line consisting of two components, the narrower of which is due to the amorphous component (see Figures 6 and 8). The ratio of the amorphous to the viscous-crystalline component steadily increases as the melting point is approached. The ratio was determined from the relative heights of the intercepts of the components of the free induction decay following a $\pi/2$ pulse. The transitions at 258 and 268°K may be ascribed to the translational motion of the chains with respect to each other. The T_2 data suggest that this motion is experienced in the amorphous regions before the crystalline portions where it only begins to take place on melting of the crystallites at around 268°K. In light of the greater interproton distances involved in a translational motion, one might expect this to be a somewhat less efficient relaxation mechanism than rotation of the side chain or rotation about the Si–O bonds. At temperatures just below the melting point, T_1 increases slightly. This is probably a premelting phenomenon in the ordered melt.

Activation energies were determined from the straight-line portions of the T_1 vs. temperature data according to the relations[25]

$$1/T_1 \propto \tau_c/(1 + \omega_0{}^2\tau_c{}^2) \qquad (1)$$

$$\tau_c = \tau_0 \exp(E_a/RT) \qquad (2)$$

$$2.3 \log T_1 = E_a/RT + f(\tau_c) \qquad (3)$$

where τ_c is the correlation time for molecular motions, τ_0 is the inverse frequency dependence, and ω_0 is the resonance angular frequency.

The low-temperature relaxation (i.e., semicrystalline material) has an activation energy of 4.1 kcal/mol and the high-temperature activation energy is 2.5 kcal/mol.

Discussion

The dielectric data indicate that either (1) molecular mobility increases or (2) phase volume reduction occurs throughout the partially ordered phase as temperature increases. However, NMR line width measurements show that two phases do exist in this temperature domain with a reduction in quantity of the ordered phase as temperature is increased. These measurements are in agreement with calorimetric measurements which demonstrate a rounded diffuse peak attributable to melting of a greater percentage of the partially ordered phase as temperature is increased. These combined results indicate that a mixture of a partially ordered phase exists in an amorphous matrix similar to the existence of crystalline regions in an amorphous matrix in semicrystalline polymers.

Birefringent areas are observed between crossed polars in the optical microscope and the semiordered material in the 263–293°K region is qualitatively more viscous than the isotropic melt. Therefore, in analogy to the liquid-crystal nomenclature, we prefer to think of this type of material as viscous crystalline. To lend insight into the organization, properties, and behavior of the viscous-crystalline phase, it may be useful to draw analogies to existing phases of polymeric and liquid crystalline materials.

Molecular liquid crystalline materials exist in smectic, nematic, and cholesteric phases as illustrated in Figure 9. The wide-angle X-ray diffraction patterns of these materials yield a single peak characteristic of the average distance between molecules or molecular planes. In many respects, these materials may be considered to be the oligomeric analogs of paraffins. Compared to the folded chain morphology of polymeric crystals paraffins exist in extended chain conformations,[26] a state normally obtained only by high-pressure crystallization.[27,28] Extending this analogy, it is probable that a polymeric viscous-crystalline material will exist in a chain-folded state similar to conventional polymers (Figure 9). The extent and type of chain folding has obviously not been determined as folding has not been

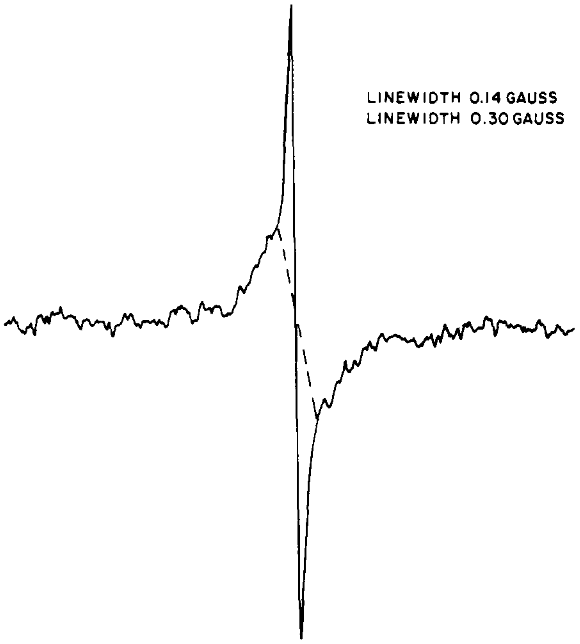

Figure 8. Proton resonance of PDES-II at 283°K.

proven for this partially ordered state. However, it is suspected that semiconstant thickness lamellae may initially exist upon melting the relatively constant thickness lamellar crystalline material. The thermodynamic stability of semicrystalline polymers is related to lamellae thickness. Consequently, if individual domains in the viscous-crystalline phase exist in some distribution of sizes dependent upon formation temperature, the reduction in quantity of viscous-crystalline material throughout the viscous-crystalline region may be explained by melting fractions of different quasi-lamellae thicknesses. An alternate mechanism incorporates the concept that continued annealing of the viscous-crystalline domains forms more stable regions that would melt at higher temperatures in a fashion similar to that observed for polymer lamellae.

In conclusion, a semiordered polymeric state has been observed in PDES. This state, which is a two-phase system consisting of a one-dimensional ordered phase and an amorphous phase, exists between the semicrystalline phase (268°K) and the amorphous phase (293°K). The relative amounts of these two phases are temperature dependent with the amorphous phase prevalent at higher temperatures. NMR, dielectric, X-ray diffraction, and calorimetric data have been used to verify the existence of this phase. X-Ray data indicate one or two dimensional ordering, with the order dimension remaining constant throughout the temperature range of the semiordered state. This order dimension is also characteristic of the amorphous phase. It is felt that the partially ordered phase, which we call the viscous-crystalline phase, is a polymeric phase existing between the amorphous and crystalline phases and is the polymer analog of the liquid crystal phase in monomeric materials.

Although the existence of lamellae in the partially ordered state is not known, the question of supramolecular structure such as spherulites naturally arises, as illustrated in Figure 9. PDES is birefringent as observed between crossed polars. However, the field is not homogeneous, indicative of relatively large-scale two-phase behavior.

The existence of a phase such as the reported viscous-crystalline state raises the question, "Is it a precursor to the crystalline state?" Or alternately, "Does this state exist for all semicrystalline polymers, but on a greatly reduced time/temperature scale?" If the answer to either question is "yes", then this polymer may serve as a model for understanding the crystallization behavior of semicrystalline polymers.

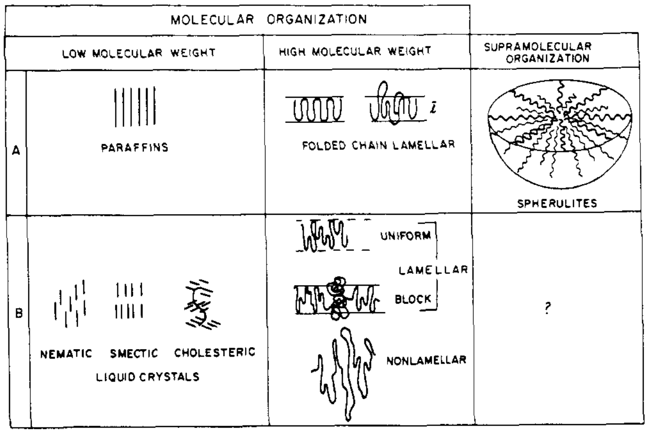

Figure 9. (a) Variation of morphological structures as molecular weight is increased. (b) Possible analogous variations in morphology as liquid crystal molecular weights are increased.

These and other questions concerning molecular and supramolecular organizational and transitional behavior are currently being investigated and will be the subject of subsequent publications.

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