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Thermotropic Anthraquinone Polymers: Structure and Enthalpic Relaxation

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The existence of a mesogenic state for certain low molecular weight species has been recognized for decades. Only recently, however, have a variety of polymers that melt to an ordered liquid been developed. In a previous publication, the author reported on the crystallization kinetics of aromatic polyesters from ordered melts.[1] Not all thermotropic polymers crystallize, however, particularly those that contain bulky side groups or bulky or asymmetric backbone entities or lack a regular backbone sequence. These polymers typically lack three-dimensional order in the solid state, lack a strong melting endotherm, have a strong glass transition (T_g) and flow with stress above T_g. Hence, they may be more closely modeled as amorphous polymers than as semicrystalline polymers.

The phenomenon of enthalpic relaxation in glassy polymers is well documented and it is generally accepted that it is due to a loss in free volume rather than to an increase in the local ordering.[2,3] Enthalpic relaxation can be easily detected by using differential scanning calorimetry (DSC), but it also parallels changes in mechanical properties, density, etc.[3]

Theoretically, enthalpic relaxation may occur in amorphous or semicrystalline thermotropic polymers even though they possess two-dimensional order. Petrie, indeed, has shown that enthalpic relaxations can be observed for glassy, nonpolymeric mesogens.[3]

It is generally accepted that the rate of enthalpic relaxation is determined by the self-diffusion coefficient and, hence, is dependent on the reduced temperature and the departure from equilibrium.[2,3] Consequently, small changes in experimental conditions (viz., temperature) can produce dramatic changes in the rate of diffusive transport.

The diffusion tensor of an amorphous unoriented polymer is isotropic. With oriented vitreous or liquid crystalline polymers, however, the diffusion coefficients are not independent of direction. Moreover, and particularly in the case of polymers with stiff molecules in a frozen-in nematic texture, a large number of atoms must move cooperatively for effective long-range self-diffusion. Motion on a scale of ångstroms, however, should not be much more difficult in the anisotropic glass as compared with that in the isotropic glass. Motion associated with enthalpic or volume relaxation is expected to be short range and, hence, ought not be affected by orientation.

Several difficulties are encountered when one attempts to study relaxation in oriented amorphous polymers: (1) The density of the material may change significantly with drawing. (2) Strong shrinkage forces may develop during low-temperature annealing. (3) Orientation changes the glass transition temperature.

Despite these difficulties some authors have succeeded in producing some data which suggest that the rate of relaxation is not changed dramatically by orientation once corrected for density and glass transition temperature.[4,5]

As described in this paper, the aforegiven problems have been circumvented by the use of liquid crystal polymers and it has been found that the rate and magnitude of enthalpic relaxation is comparable to that of conventional (flexible) amorphous or semicrystalline polymers.

Experimental Section

The polymers utilized in this study were prepared by the usual melt polymerization techniques, using 1,4-acetoxybenzoic acid, 2,6-dihydroxyanthraquinone, terepthalic acid, and isophthalic acid, and will be described in detail in a subsequent paper.[6,7] A variety of compositions were synthesized and all the polymers investigated show qualitatively the same behavior. The data in this paper are derived from a single polymer with the nominal composition being 50/25/12.5/12.5 mol %, respectively, and the intrinsic viscosity in 0.1% pentafluorophenol being 1.91 dL/g. Samples employed were fibrous, having been spun with the use of a micromelt unit at about 360 °C to a denier of 3.7 and a birefringence of 0.367. The details of spinning will be presented in a subsequent paper.[7]

Annealing was generally conducted in a circulating air oven at 125 °C for various times. Fibers were mounted free to shrink to accomodate the negative thermal expansion coefficient. There is virtually no entropic shrinkage.

When samples were to be analyzed by thermal analysis, they were annealed directly in the differential scanning calorimeter, Perkin-Elmer DSC 2.

X-ray diffraction patterns were obtained with a Rigaku-Denki rotating anode unit, Ni-filtered Cu radiation, and recorded by using a Unicam S27. A Joyce-Loeb microdensitometer was employed when semiquantitative data were needed; aluminum powder was used for calibration purposes.

Glass transition temperatures (T_g) were determined with the use of a DuPont 990 Thermal Analyzer (DTA) and specific heats obtained with the use of a sapphire standard.[7] The DSC was calibrated by using indium and used at 20 °C/min. The purge gas was nitrogen. Excess enthalpy was determined by the method of Petrie.[3]

Density measurements were achieved by the use of columns filled with calcium nitrate and water. Because of slight porosity in the fibers, the accuracy provided by the columns could not be fully utilized.

Mechanical properties were determined with the use of an Instron Testing Machine. A gauge length of 2.54 cm and a strain rate of 20%/min were employed. The data have not been corrected for gauge length (i.e., uncorrected for compliance or grip effects) which typically results in an incremental increase in modulus of about 20%, no change in tenacity, and only a minor

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Table I
Mechanical Properties of Anthraquinone-Based Polyester

	tenacity, g/denier	stand dev	modulus, g/denier	stand dev	elong, %	stand dev
virgin	6.9	0.36	664	31	1.13	0.10
annealed for 18 h at 125 °C	6.3	1.31	671	44	0.93	0.19

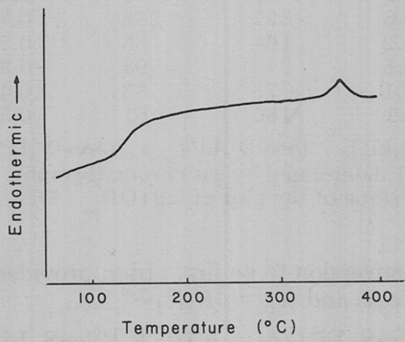

Figure 1. Differential thermal trace of the anthraquinone polymer.

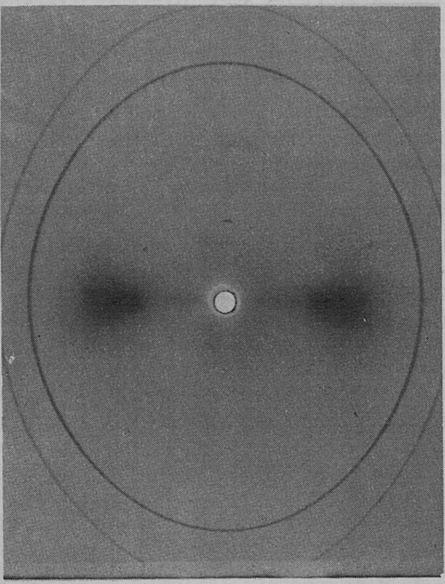

Figure 2. Wide angle X-ray diffraction pattern from the anthraquinone fiber tilted 6° from vertical.

decrease in elongation. Values given represent the average of ten breaks. The denier was determined for each break.

Results

Thermal Behavior of AQ Polymer. The DSC trace of the AQ polymer is shown in Figure 1. Evident are the strong glass transition occurring at 130 °C and a weak endotherm (1.25 cal/g) peaking at 355 °C. The upper transition may represent melting, or alternatively a crystal-crystal transition. There was no visual evidence (hot-stage microscopy) that the material became isotropic at this transition. Most importantly, above 130 °C the polymer deforms with pressure much like any amorphous material. In any event, Bair and others[8] have shown that enthalpic relaxation can occur in semicrystalline as well as amorphous polymers.

X-ray Diffraction. The X-ray diffraction pattern from fibers is reproduced in Figure 2. The fiber axis is canted 6° from vertical in order to reveal the meridianal spots corresponding to intramolecular distances. The diffuse nature of the equatorial scattering is characteristic of an oriented amorphous polymer.

Annealing Studies. A thermogram for an annealed sample is shown in Figure 3 along with the reheating curve.

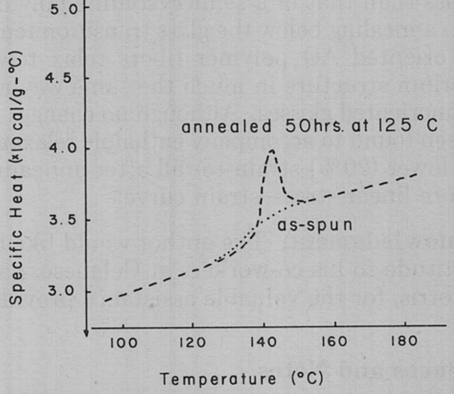

Figure 3. Effect of annealing below the glass transition temperature on the specific heat for the anthraquinone fiber.

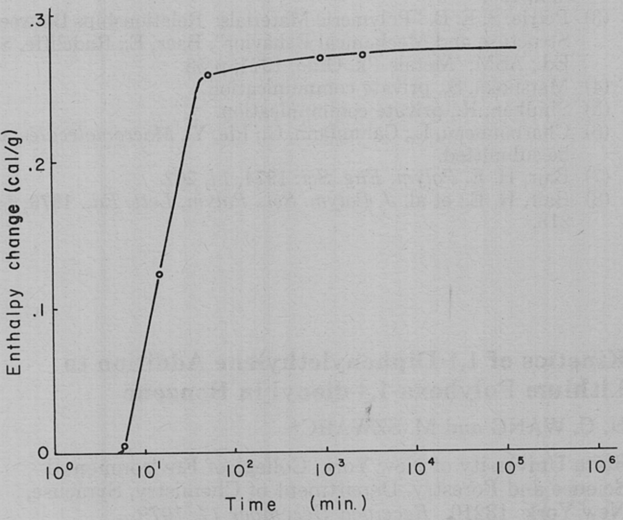

Figure 4. Effect of annealing time at 125 °C of the anthraquinone fiber on the enthalpy associated with relaxation.

The T_g as observed under the experimental conditions described here increases about 8 °C with prolonged annealing. A summary of the data obtained by holding a sample at 125 °C for various times is shown in Figure 4. The structure begins to reach equilibrium after only an hour at 125 °C. (The relaxation process cannot be modeled by a single relaxation time.)

The recorded density of the virgin fiber is 1.443 g/cm^3 and that of the fiber annealed for 18 h at 125 °C is 1.441 g/cm^3. The difference is well within experimental error and any increase in density would be obscured by the presence of the needle shaped voids. Such voids have been observed with the use of polarized light microscopy.

The mechanical properties both before and after annealing are summarized in Table I. The stress/strain curves for the annealed samples are perfectly Hookean, but the as-spun samples have a characteristic deflection from linearity of about 0.1% at break. The initial moduli are virtually identical.

Discussion and Conclusions

The anthraquinone-based polyesters described here show light transmission under crossed polars at 400 °C and variable transmission upon shear and, therefore, are thermotropic. Using wide angle X-ray diffraction, optical microscopy, and a variety of other techniques, one can demonstrate that, upon cooling, the bulk of the polymer retains its nematic texture and morphology.[1] Consequently, the rheological and mechanical behavior of the material as well as its structure resembles more closely that of a glass than that of a semicrystalline polymer.

Upon annealing below the glass transition temperature, highly oriented AQ polymer fibers relax toward their equilibrium structure in much the same way as conventional unoriented glasses. Although no changes in density have been found to accompany enthalpic relaxation, fibers have a lower (20%) strain-to-fall after annealing as well as a more linear stress–strain curve.

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Kinetics of 1,1-Diphenylethylene Addition to Lithium Polyhexa-1,4-dienyl in Benzene

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Addition of 1,1-diphenylethylene (D) to lithium polystyryl ($\sim\mathrm{S^-,Li^+}$) in benzene was studied in the past[1] and similar reactions of this kind were investigated later.[2] The following mechanism accounts for the findings. The addition involves the monomeric, nonassociated form of the polystyryl, viz.,

$$\sim\mathrm{S^-Li^+} + \mathrm{D} \xrightarrow{k} \sim\mathrm{SD^-,Li^+}$$

However, the monomeric salt of polystyryl and that of the $\sim\mathrm{SD^-}$ anions are in equilibrium with the respective homo and mixed dimers, i.e.,

$$2\sim\mathrm{S^-,Li^+} \rightleftarrows (\sim\mathrm{S^-,Li^+})_2 \qquad {}^1/_2K_1$$

$$\sim\mathrm{S^-,Li^+} + \sim\mathrm{SD^-,Li^+} \rightleftarrows (\sim\mathrm{S^-,Li^+},\sim\mathrm{SD^-,Li^+}) \qquad K_{12}$$

$$2\sim\mathrm{SD^-,Li^+} \rightleftarrows (\sim\mathrm{SD^-,Li^+})_2 \qquad {}^1/_2K_2$$

Concentrations of the monomeric species are assumed to be much smaller than those of the dimeric ones, and the absorbance of the latter, per unit of the pertinent anion, seems to be unaffected by the mode of dimerization, i.e., whether homo or mixed type.

Table I

$[\sim\mathrm{H^-,Li^+}]_0 \times 10^4$,[a] M	$[\mathrm{D}] \times 10^4$,[b] M	$k_i \times 10^4$,[c] $\mathrm{S^{-1}}$	$(k_i/[\mathrm{D}])$, $\mathrm{M^{-1}\ s^{-1}}$
1.0	74	80	1.09
1.1	217	208	0.96
2.0	64	58	0.91
3.6	54	35	0.65
3.6	327	235	0.72
7.2	104	55	0.53
8.5	246	93	0.38
10.1	78	33	0.42
13.1	186	61	0.33

[a] $[\sim\mathrm{H^-,Li^+}]_0 = [\sim\mathrm{D^-,Li^+}]_\infty$; $\epsilon_{435}(\sim\mathrm{D^-,Li^+}) = 2.2 \times 10^4$. [b] [D] determined by gas chromatography. [c] $k_i = 2.3$ (initial slope of the plot of log $(\mathrm{OD}_\infty - \mathrm{OD}_t)_{435}$ vs. time).

Progress of the addition was followed spectrophotometrically by monitoring the absorbance at $\lambda_{\max}$ of either of the respective anions. The proposed mechanism predicts the conversion to be first order, provided that D is in large excess and $K_{12} = (K_1K_2)^{1/2}$, i.e.,

$$\mathrm{d}\ \ln\ [\sim\mathrm{S^-,Li^+}]/\mathrm{d}t = k[\mathrm{D}]/K_1^{1/2}[\sim\mathrm{S^-,Li^+}]_0^{1/2}$$

The first-order plot becomes curved when $K_{12} \neq (K_1K_2)^{1/2}$, but the initial slope is still inversely proportional to $[\sim\mathrm{S^-,Li^+}]_0^{1/2}$.

Our approach has been applied lately by the Akron team to the system lithium polyhexadienyl in benzene.[3] The reported results intrigued us and it was decided to re-investigate this problem. Our findings, however, diverge from those reported by the other group.

Experimental Section

2,4-Hexadiene (mixture of isomers, Aldrich) was distilled twice from calcium hydride, and 1,1-diphenylethylene was freed from traces of benzophenone by vacuum distillation of the compound kept for a few hours over sodium mirror. The distilled olefins were sealed in ampules and never exposed to the air.

Lithium polystyryl was prepared in benzene using *sec*-butyl lithium as the initiator. Its molar absorbance at $\lambda_{\max} = 335$ nm is 1.3×10^4, while that of $\sim\mathrm{SD^-,Li^+}$ at $\lambda_{\max} = 435$ nm is 2.2×10^4. The molar absorbance of polyhexadienyl salt is $\sim 1.0 \times 10^4$ at 290 nm, based on the ϵ_{435} of $\sim\mathrm{SD^-,Li^+}$.

The lithium polystyryl capped by 2,4-hexadiene was prepared by adding about 100-fold excess of the diene (in respect to the concentration of living polystyryl) to the solution of lithium polystyryl in benzene and observing the decay of the original absorbance. It disappears in a few hours and thereafter the reagents were kept for about 24 h before being used in the kinetic or viscometric studies.

All the operations and kinetic studies were carried out in evacuated all-glass equipment with an attached quartz cell that allowed us to determine the initial concentrations of the reagents and to follow the progress of the reaction spectrophotometrically. The viscosity measurements were carried out following the procedures reported by Yamagishi and Szwarc.[2]

Purification of Diphenyl Ether. The degassed phenyl ether (Aldrich Chemical Company) was stirred and vacuum pumped over potassium mirror for about 24 h. The color of the solvent turned greenish-brown. Next diphenyl ether was slowly distilled under high vacuum pumping at ~70 °C into evacuated vials with break seals.

Results

For each run the plots of log $(\mathrm{OD}_\infty - \mathrm{OD}_t)_{435}$ vs. time are curved as exemplified by Figure 1. The values of k_i = 2.3(initial slope) are listed in Table I. The nonlinearity of the plots implies the inequality $K_{12} \neq (K_1K_2)^{1/2}$. The ratios of the initial slope to the respective, extrapolated slope at infinity are substantially greater than unity, implying a high tendency for formation of the mixed dimers.

All the kinetic results are summarized in Table I, and the plot of the log of normalized pseudo-first-order constants determined at the onset of the reaction, i.e., $(k_i/[\mathrm{D}])$, vs. the log of $[\sim\mathrm{H^-,Li^+}]$ is shown in Figure 2. The slope

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