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Glass Transition of Polyquinoline

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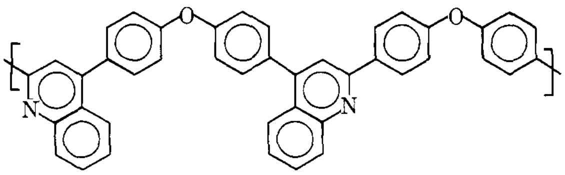
ABSTRACT: The glass transition interval of a polyquinoline (T_g = 251 °C and T_m = 483 °C) has been studied by calorimetric, dilatometric, and dynamic mechanical techniques. The behavior of this polymer in the T_g interval has been quantitatively examined as a function of thermal history. Specifically it was of interest to determine (1) the effects of annealing temperatures at constant heating and cooling rates, (2) the effect of cooling rates at constant annealing temperatures, (3) the effect of heating rates at constant cooling rates, and (4) the effect of annealing time at constant annealing temperature and heating rate. The data show that widely different nonequilibrium structures result as a consequence of variable formation histories. Overlapping the normal second-order T_g, there are heat absorptions which exhibit distinct first-order character in addition to residual hysteresis effects (i.e., time-dependent configurational rearrangements).

In the course of studies relating to the thermal behavior of fully aromatic polymers[2] we have investigated the glass transition interval of polyquinolines, a new class of aromatic-heterocyclic polymers which has recently been synthesized.[3–5] Like numerous other aromatic polymers, certain of the polyquinolines are largely amorphous solids in that no long-range periodicity is observed by x-ray techniques and they exhibit viscoelastic properties typical of amorphous materials.[6] Because of their high stiffness energies, polyquinolines show glass transition intervals at relatively high temperatures. Depending on chemical repeat unit structures, high molecular weight polyquinolines show T_g's ranging from 250 to 400 °C. It is also possible to synthesize symmetrical and unsymmetrical geometric isomers for a given polymer with the symmetrical structure always exhibiting the higher T_g. The introduction of flexibilizing groups into the chains produces a pronounced lowering, while incorporation of fused rings causes a substantial increase in T_g. All these observations suggest that intramolecular effects seem to dominate the thermal behavior of these polymers. Unlike many other aromatic-heterocyclic polymers, polyquinolines can be synthesized into single isomers and in that sense they exhibit configurational regularity. Therefore, at least on a "local level", say up to 20 Å, these polymers are capable of spacial ordering. However, attempts to crystallize polyquinolines, i.e., produce regular conformation either from the melt or from solution to a high degree have failed to date.

DSC of six different polyquinolines resulted in complex scans in the T_g interval showing in addition to discontinuities of C_p, minima just below T_g, followed by overlapping single and at times multiple maxima in the form of relatively sharp endothermic peaks. It was the main objective of this study to examine these peaks with respect to formation histories (i.e., quenching, annealing) and it was hoped that a quantitative analysis of the results would offer explanation to the nature of these thermal processes.

Experimental Section

The polyquinoline used in this study, poly[2,2′-(oxydi-*p*-phenylene)-4,4′-(oxydi-*p*-phenylene)diquinoline], had the following repeat structure:



The material had an intrinsic viscosity of 0.44 in chloroform (for complete characterization see ref 4 and 5). Films were cast from chloroform solutions and dried under reduced pressure at 100 °C for 4 h. Most experiments reported here were made on a Du Pont Thermal Analyser Model 990. For DSC measurements a heat transfer analysis was performed according to a method described by Strella and Ehrhardt.[7] Accordingly, the heating rate dependence of the glass transitions is a result of: (a) a time lag in the sample, (b) a time lag in the heat path through the sample, and (c) free volume effects. The instrument error involved because of time lag to the sample was estimated from a plot of maximum rate of melting vs. heating rate for a 0.03-mg sample of indium. The maximum error over a 100 °C/min heating rate range was 8.5 °C. An estimate of the combined temperature error due to machine and sample can be obtained from the following equation:[8]

$$\Delta\Theta \sim \beta \frac{l_{sc}^2}{2k_{sc}} + \frac{4l_s^2}{\pi^2 k_s}$$

where β = heating rate; l_{sc} = sample chamber thickness; l_s = sample thickness; k_{sc} = thermal diffusivity of sample chamber; k_s = thermal diffusivity of sample. The first term in brackets which is the time interval by which the sample chamber surface lags the heated surface

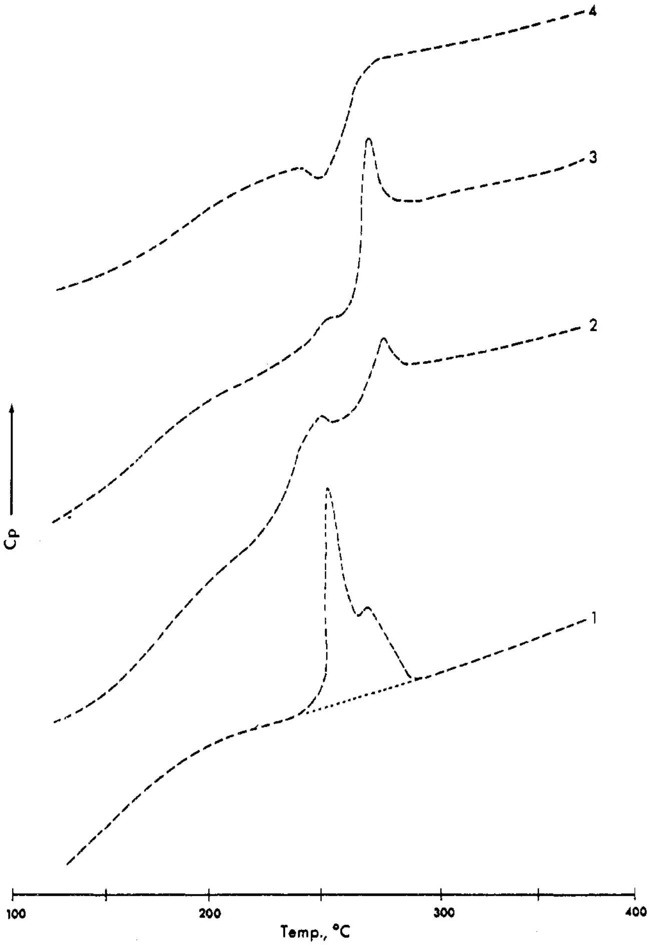


Figure 1. DTA recorder traces of polyquinoline cooled at 5 °C/min from different temperatures and heated at a rate of 50 °C/min. (1) Original film annealed for 30 days at 30 °C; (2) cooled from 200 °C; (3) cooled from 300 °C; (4) cooled from 400 °C.

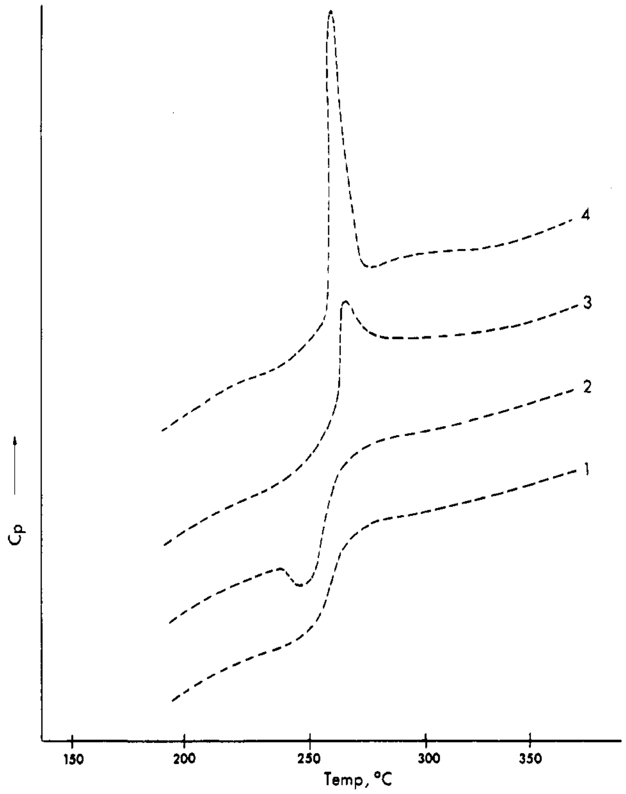


Figure 2. DSC recorder traces of polyquinoline cooled from 400 °C at different cooling rates and heated at 50 °C/min (1) 100 °C/min; (2) 10 °C/min; (3) 1 °C/min; (4) 0.1 °C/min.

was, as already mentioned, determined experimentally from the maximum melting temperature vs. heating rate plot of indium. The second term, which is the heat lag through the sample, was estimated by assuming a thermal diffusivity of 0.001 (for polymers) and an l of about 1 mm (for a 12-mg sample). Linear cooling experiments were carried out directly in the DSC cell. Specific heat measurements were made as previously described,[2b] by using a sapphire disk as the calibration standard. Under the program conditions employed the accuracy of C_p was ±0.003 cal/(g K). Determinations of the energy absorbed in the glass transition interval (Figures 1 and 2) were made based on the area under the curve obtained by assuming a sigmoidal line extending the curve below and above the T_g interval. For the sample sizes used in these experiments (10–20 mg) the accuracy of ΔH measurements was ±0.008 cal/g. In all annealing experiments the sample temperature in the DSC cell could be maintained within ±0.1 °C.

Thermal expansion measurements were made on specimens of compression molded powder (applied pressure 10 000 psi, temperature 320 °C). The TMA was calibrated using a slab of pure aluminum and the linear thermal expansion coefficients were calculated based on the relationship given in the manufacturer's instrument manual (Du Pont 990). The specific volumes at a given temperature were calculated from the following equations:

$$V_{s,g} = V_{s,25} + \alpha_g \Delta T$$

$$V_{s,L} = V_{s,25} + \alpha_L \Delta T$$

where the specific volume at 25 °C was 0.768 cm^3/g.

Results

In Figure 1 are shown recorder traces for polyquinoline samples which were exposed to different temperatures, cooled at a linear rate of 5 °C/min and heated at a linear rate of 50 °C/min. Curve 1 was obtained from a sample which was annealed for 30 days at room temperature. The glass transition interval occurred between 250 and 285 °C and was marked by a jump in heat capacity. The shapes of these endothermic curves were drastically different ranging from double peaks to sigmoidal, depending on the temperature from which cooling was started.

The effect of cooling rate on the shape of DSC curves is illustrated in Figure 2. In all cases samples were heated to 400 °C in a helium atmosphere and cooled, and recordings were made at a heating rate of 50 °C/min. Rapid cooling at a rate of 100 °C/min produced a perfectly symmetrical sigmoidal shape with an inflection point of 260.5 °C (curve 1). Several, additional polyquinoline samples with thermal histories identical with that of curve 1 were prepared and DSC scans were made at different heating rates. A plot of the log of the apparent T_g (the temperature of half-freezing of holes) vs. heating rates was constructed and extrapolated to zero heating rate, from which a rate-independent glass-transition temperature of 251 °C was established.

Cooling at a rate of 10 °/min results in a DSC scan (Curve 2) similar to that of curve 1 except that a minimum in heat capacity just prior to the T_g was observed.

Slow cooling (curves 3 and 4) at linear rates of less than 1 °C/min results in curves which in addition to the typical heat capacity jump show peaks whose magnitude increases with decreasing cooling rate. The effect of heating rate on the magnitude of 0.1 °C/min cooled material (curve 4) is shown in Figure 3. Within the limits of these experiments it was noted that these peaks increase in proportion to the heating rate. However, the apparent enthalpy calculated from these areas increases from 0.8 cal/g at a heating rate of 5 °C to 1.02 cal/g at 100 °C/min, suggesting that the process giving rise to these peaks involves in addition to an apparent heat of transition, also an overlapping hysteresis (superheating). Furthermore, it is apparent that these glassy peaks are shifted to higher temperature with increasing heating rate in a similar

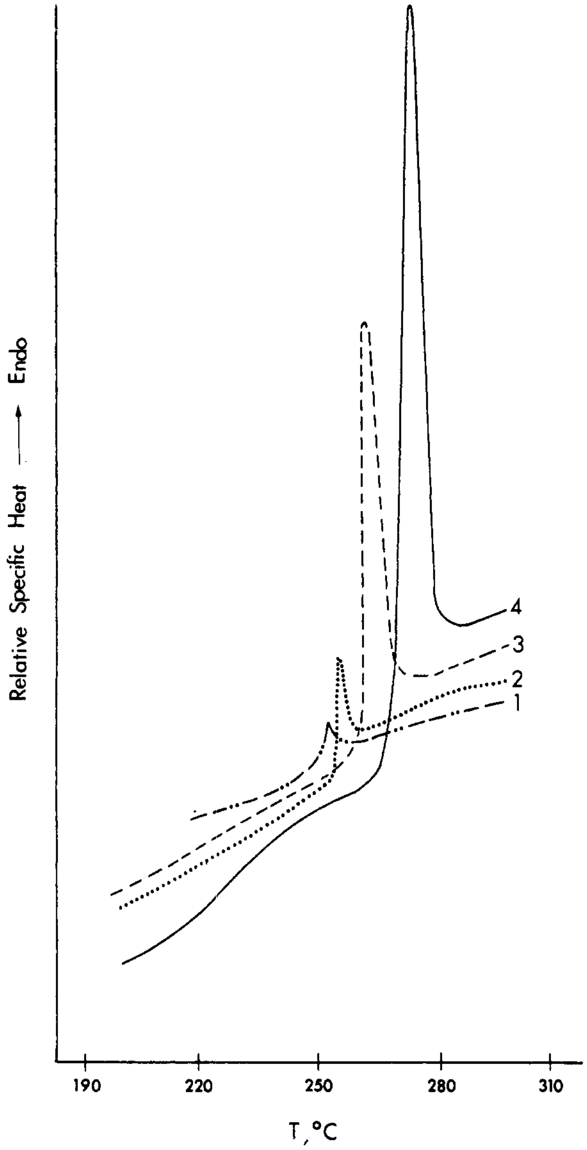


Figure 3. DSC recorder traces of polyquinoline cooled from 400 °C at a rate of 0.1 °C/min and heated at various linear rates (curve 1, 5 °C/min; 2, 10 °C/min; 3, 50 °C min; 4, 100 °C/min).

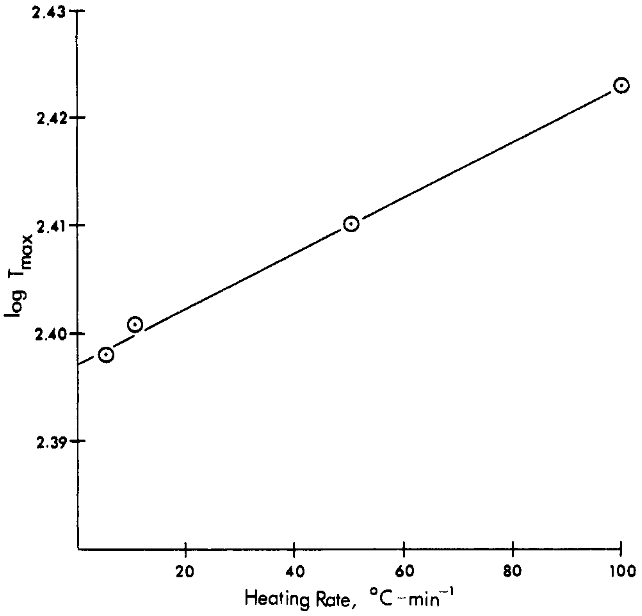


Figure 4. Effect of heating rate on peak temperature of rapidly cooled polymer (cooling rate = 100 °C/min).

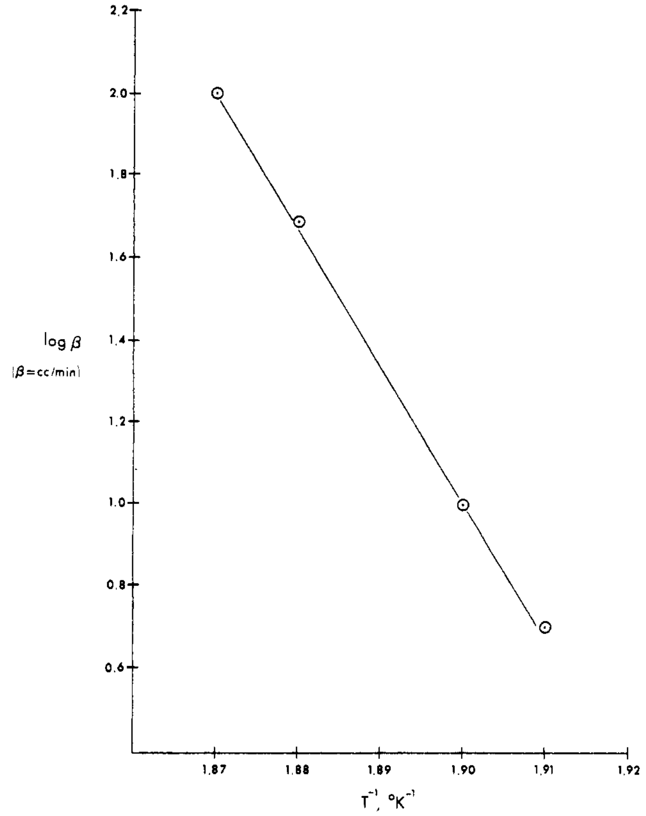


Figure 5. Plot of log β vs. $1/T_{\max}$ (E_a = 149 kcal/mol, $f = 2 \times 10^{-46}$ min/deg).

way to that of the glass transition temperature (Figures 4 and 5).

The linear thermal expansion of bulk polymer with a thermal history similar to that in Figure 3 is shown in Figure 6. The T_g interval is apparent by a jump in probe displacement in the temperature range between 260 and 300 °C. As can be seen by the complex shape of the curve, an increase in α in the T_g interval is followed by a temporary contraction of the sample preceding the liquid region above 300 °C. A second contraction at 475 °C is due to the melting of the crystalline phase, which causes a partial collapse in the sample geometry. Figure 7 is a plot of specific volume as a function of temperature. Because of the instability of the thermal expansion curves in the T_g interval no calculations of V_{sp} were carried out between 250 and 300 °C, and therefore, the $V_{sp}(T_g)$ (=0.818 cm^3/g) had to be extrapolated. In a plot of C_p vs. temperature (Figure 8), in order to permit a valid estimate of $\Delta C_p(T_g)$ the sample chosen had a thermal history similar to that in curve 1 of Figure 2. As shown in Figure 8, C_p is a smooth monotonic function of temperature exhibiting sigmoidal character at T_g with a ΔC_p of 39.6 cal/(mol deg) or 5.0 cal/(mol segment deg) (based on 8 rotatable segments per repeat unit structure). This value is considerably higher than would be predicted from the rule of constant ΔC_p at T_g, but is consistent in magnitude to those obtained for other aromatic heterocyclic polymers. Figure 9 is a plot of the amount of heat absorbed at the glass transition temperature as a function of annealing time at 30 °C. The sample used for this experiment was a film cast from chloroform which was placed in an air circulated oven preset to 30 °C and samples were removed periodically for DSC measurements. Since the DSC curves obtained showed the development of a second peak as shown in curve 1, Figure 1, the total area under the peaks above the baseline was taken for calculating ΔH except that the time base of the instrument was used to provide for a more accurate area determination.

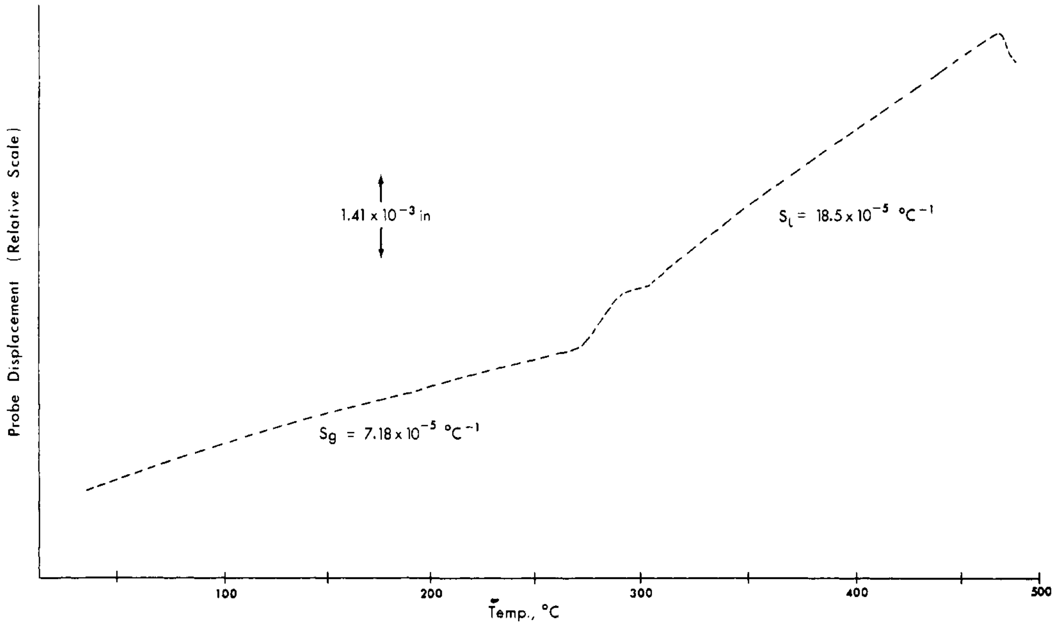


Figure 6. Thermal expansion (linear) of polyquinoline (heating rate 5 °C/min, He atmosphere).

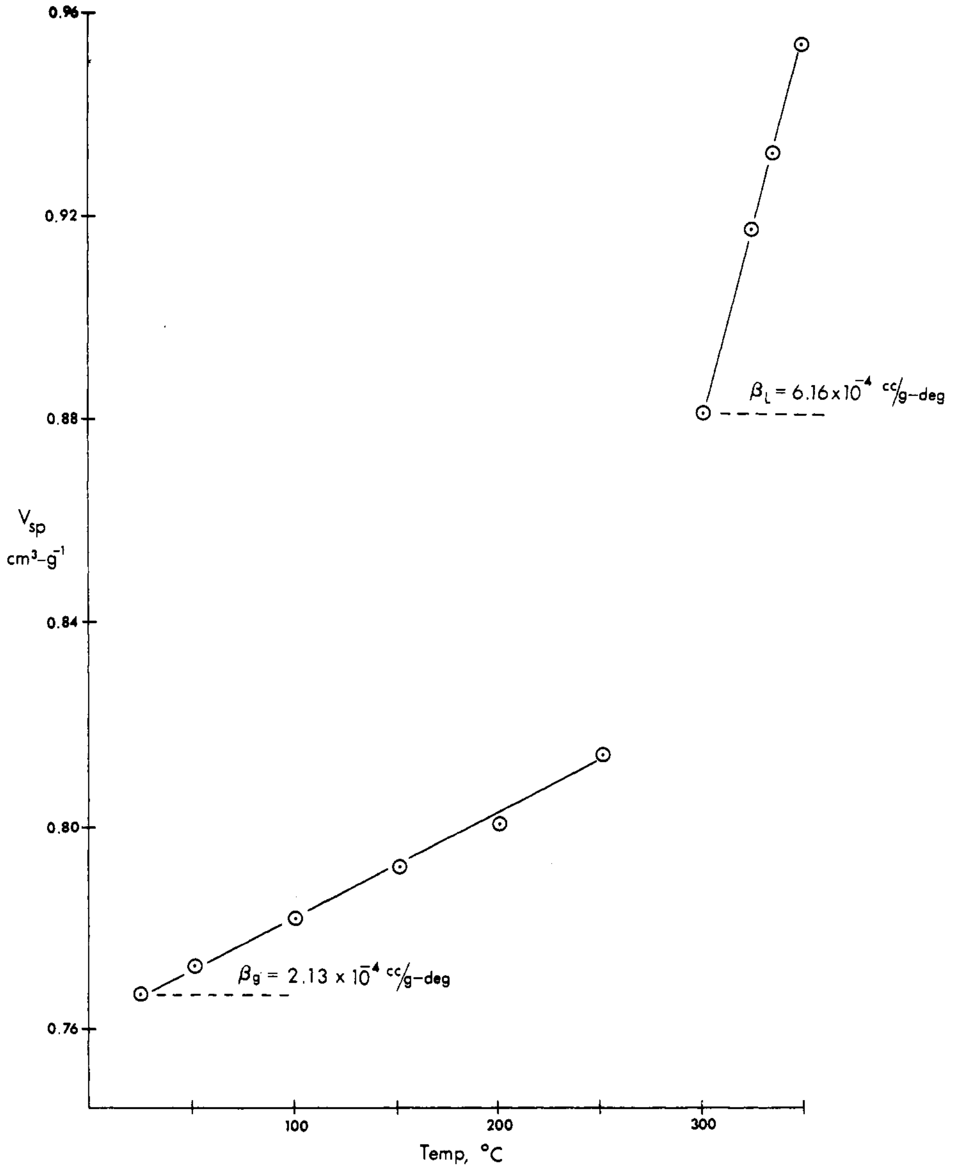


Figure 7. Dependence of specific volume on temperature.

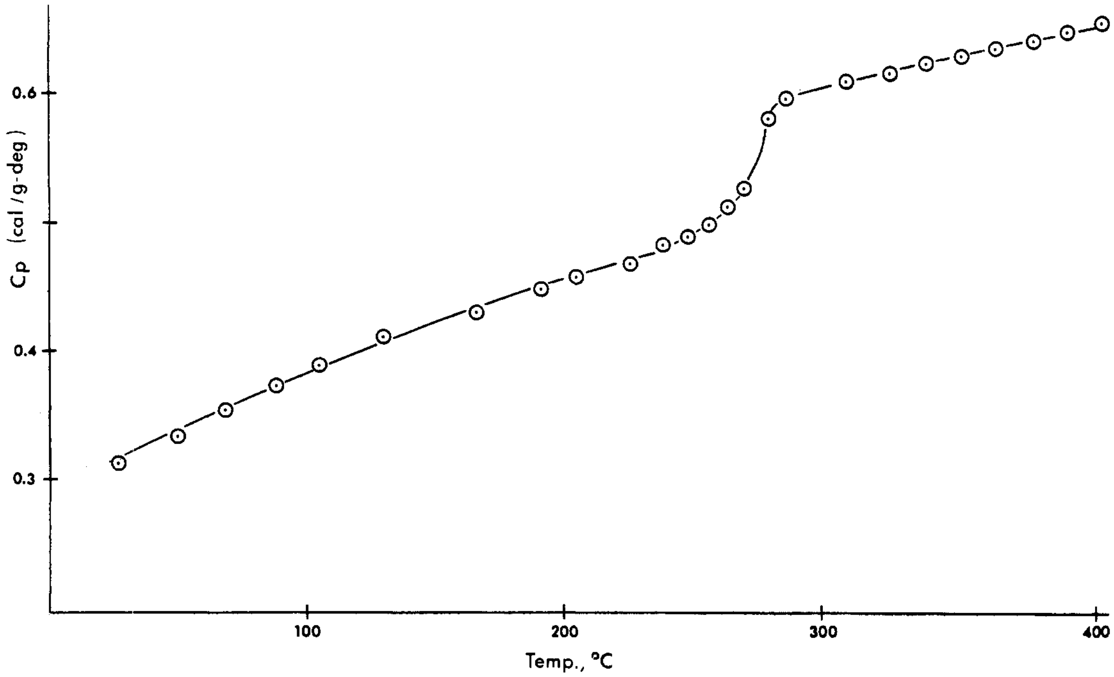


Figure 8. Specific heat as a function of temperature.

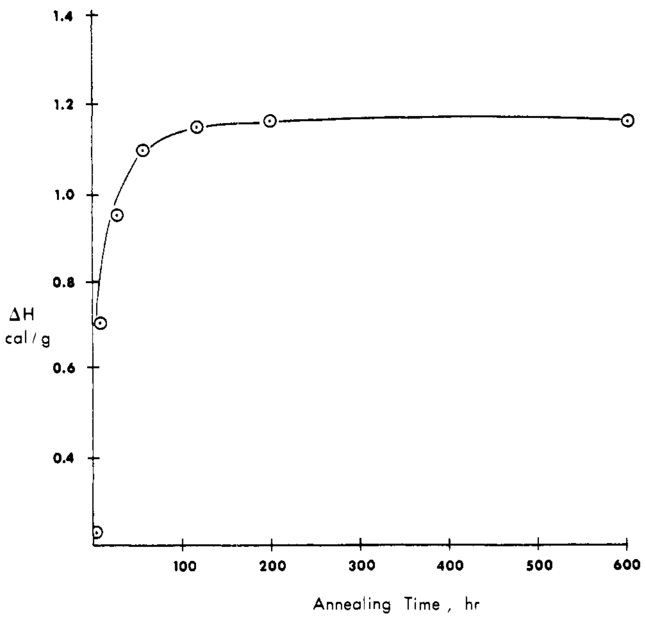


Figure 9. Heat absorbed in the glass transition interval as a function of annealing time at 30 °C.

X-ray diffraction patterns between 2θ of 5 to 45 °C of samples with different thermal histories exhibited essentially amorphous character, although some crystallinity (less than 10%) was noted by the presence of peaks of weak intensity.

A summary of thermophysical data for polyquinoline is given in Table II.

Discussion

The thermal behavior of polyquinolines in the glass-transition region is similar to that observed with polycarbonates, PVC, PMMA, polystyrenes, and glucose in that in addition to the normal second-order process one observes endothermic peaks which have been attributed to first-order phenomena in the Ehrenfest sense, and alternatively have been interpreted as hysteresis effects. The objective of this study was to assess thermophysical properties of a polyquinoline and to examine the consequences of different thermal histories on these properties. In this respect it was of interest to determine (1) the effect of annealing temperature at constant heating and cooling rate, (2) the effects of cooling rates at constant maximum temperature and heating rate, (3) the effect of heating rates at constant maximum cooling rate, and (4) the effect of annealing times at constant temperature and heating rate. Overall, the data presented here show that widely different structures result as a consequence of variable formation histories.

The existence of "excess enthalpies" which in our case appear in various forms ranging from minima (curve 2, Figure 2) to single maxima (curves 3 and 4, Figure 2) to double maxima (curves 1, 2, and 3, Figure 1) of varying intensities of C_p and which are overlapping the normal free volume effects as shown in Figure 2 and which can be produced without any apparent second-order jump in C_p as in curve 1, Figure 1, requires explanation.

Several explanations have been offered.[9-13] Illers investigated the influence of temperature on the calorimetric behavior of partially crystalline PVC and found that annealing below T_g results in enthalpy relaxations in the form of overlapping endothermic maxima (superheating) similar to the ones found in this work. This maximum was interpreted as being a consequence of a decrease in the hole concentration of the amorphous regions. In another study,[11] the effects of molecular weight on these overlapping endothermic maxima in the T_g interval of polystyrene was investigated. It was found that these excess enthalpies decrease somewhat with increasing molecular weight. Matsuoka, et al.,[13] investigated the effects of tensile drawing on the specific heat of ABS polymers in the T_g interval and found that stretching samples produced endothermic peaks similar to the ones observed in this study. The following questions of concern here follow: (1) Are the "apparent" excess enthalpies strictly hysteresis effects, that is, nonequilibrium effects due to time-dependent configurational rearrangements of molecules (i.e., volume and enthalpy relaxations)? (2) Are they phase transformations, and if so, what is being transformed? (3) Are the observed peaks actually superposed endothermic enthalpy changes of preordered structures which dissolve just below the transition temperature and melt during dissolution? (4) Is the magnitude of these

Table I
Experimental Results from DSC Runs of a Polyquinoline Cooled at a Rate of 0.1 °C/min from 400 °C

β, heating rate, °C min^{-1}	T_{max}, °C	ΔT_{max}, °C	$\Delta\Theta_\beta$, °C	$(T_{max} - \Delta\Theta_\beta)$, °C	log β	$1/T_{max}$, $10^3 \times$ K^{-1}	A, rel area	A_β, corrected area	$(\Delta H)_{T_g}$, cal/g
0	248.8			248.8					
5	252.2	3.4	1.3	250.9	0.699	1.908	8	160	0.80
10	257.5	8.7	2.1	255.4	1.000	1.904	18	180	0.90
50	268.0	19.2	9.5	258.5	1.699	1.881	95	190	0.95
100	275.0	26.2	14.5	260.5	2.000	1.874	204	204	1.02

peaks influenced or even masked by exothermic heats resulting from the release of mechanical stress which could have been frozen in during rapid cooling from temperatures far above T_g? For example, the exothermic shoulder in curve 4, Figure 1, could well represent the onset of "stress heat", whose magnitude could have been depressed by the main glass transition endotherm.

In the discussion following an attempt will be made to clarify some of these points based on the experimental evidence available. It is understood that in the absence of morphological data the thermal analysis results presented are only indirect evidence for possible secondary morphological processes which, in polymers, may continue over many decades of logarithmic time. Unfortunately such secondary rate processes which could lead to ordering are inaccessible to direct observation by any of the presently available techniques, so microscopy is of not much use.

A distinction between hysteresis effects and heats of transitions can be made by drastically changing heating rates as was done for a sample of polyquinoline which was annealed at 400 °C and cooled at a linear rate of 0.1 °C/min (Figure 3). Hysteresis effects are time dependent; heats of transition are not. Thus, if the peak areas remain constant with increasing heating rate, then it would appear that a heat of transition rather than thermal hysteresis is responsible for the apparent enthalpy changes. The results in Table I show that the heat absorbed in the T_g interval between a heating rate of 5 and 100 °C/min increase from 0.8 to 1.0 cal/g, a change which is beyond experimental error. However, the relative constancy of these areas with increasing heating rates, β, and also an increase in the peak temperature ($T_{max} - \Delta\Theta_\beta$ after correction for thermal lag $\Delta\Theta_\beta$) with increasing β suggest the coexistence of a first-order transition with a residual hysteresis effect. Moreover, the peaks in Figure 1 clearly show multiple transitions analogous to those in melting curves of crystalline polymers.

It is significant to note that the magnitude of the first peak decreases approximately in proportion to an increase in the second peak with increasing annealing temperature, and both peaks eventually disappear when the material is annealed above T_g. It is not unreasonable to consider the possibility of two types of ordered phases coexisting at lower annealing temperatures which merge into a higher, more stable, temperature form with increasing annealing temperature, a phenomenon similar to reorganization in crystalline polymers prior to melting. At annealing temperatures substantially above T_g (curve 4, Figure 1) these phases apparently dissolve and on subsequent "slow" quenching (cooling at 5 °C/min) a "normal" glass is generated. However, at least the higher temperature peak can be regenerated on annealing above T_g provided the melt is linearly cooled at rates of <10 °C/min (Figures 2 and 3). A linear inverse temperature dependence (corrected for thermal lag) of this peak with heating rate (Figure 5) leads to an apparent overall activation energy of 149 kcal/mol. This value is considerably higher than those observed for other polymers (using DTA measurements), but it is considerably below the theoretical value of 400 kcal/mol which was derived from the WLF equation.[14] The large discrepancy between the theoretical and apparent activation energy is surprising and implies that a mechanism other than a normal viscoelastic relaxation process gives rise to the observed excess enthalpy in the T_g interval. The well-resolved double maxima in C_p of film samples annealed at 30 °C for 30 days which was not observed with freshly cast films of polyquinoline was subject to a more detailed analysis. It was of interest to determine the time-dependent increase in the area under the curve as shown in Figure 1, curve 1, which represents the amount of heat absorbed for both thermal processes. The resolution of each peak area was considered too risky in light of the fact that the first peak decreased at the expense of the second peak with increasing time. Therefore, the amount of heat absorbed as a function of time was calculated based on the total area under the curves. As shown in Figure 9 there is a steep increase in ΔH up to 50 h, followed by a very gradual, almost constant ΔH with time up to 600 h. X-ray data of material annealed for this period of time exhibited only an amorphous halo characteristic of glasses.

An estimate of the extent to which the polyquinoline film was displaced from an equilibrium glassy state[15] was obtained from the following equation, $Q_{eq} = (\Delta C_p)(T_g - T_a)$, where Q_{eq} is the maximum amount of heat absorbed in the glass transition interval of a glass in its equilibrium glassy state, ΔC_p is the jump in specific heat in the T_g interval, and T_a is the annealing temperature. The value of ΔC_p was taken from specific heat measurements made by DSC (Figure 8) of material which was rapidly quenched into liquid nitrogen from 400 °C, and the inflection point in the C_p–T curve was taken as T_g. A value of Q_{eq} of 26 cal/g was obtained. On the assumption that such a calculation is valid within the limits of our experiment, it suggests that after annealing for 600 h at 30 °C the material has reached only about 5% of its maximum value at this temperature, meaning that it would take an almost infinitely long time to approach equilibrium under these conditions. It is to be noted, however, that we have not specified a process where the energy is due to an enthalpy relaxation, that is, a configurational rearrangement of molecules. On the contrary, we prefer to attribute the increase in ΔH to the formation of new conformations resulting in paracrystalline type structures. In such an ordering process equilibrium between phases could be established in much shorter periods of time. In this connection we point out that samples of films become increasingly opaque with annealing time at 30 °C, and also increasingly brittle. Yet at no time was there any evidence of crystallinity developing with these samples as observed by X-ray diffraction. Certainly these physical changes must have been more than a densification of the amorphous polymer, i.e., decrease in holes concentration is observed for PVC by Illers.[10] Moreover, when brittle material, which was previously annealed below T_g, was subsequently heated above T_g, the brittleness and opaqueness disappeared and a flexible, clear film was regenerated. This phenomenon is similar to one observed by Hentze for poly(ethylene terephthalate) and polycarbonate,[16] polymers which incidently all contain aromatic rings in their chains.

Under conditions such as specified for curve 1 in Figure 2 one generates what may be called a normal glass, normal in the sense that specific heat (Figure 8) and volume curves are

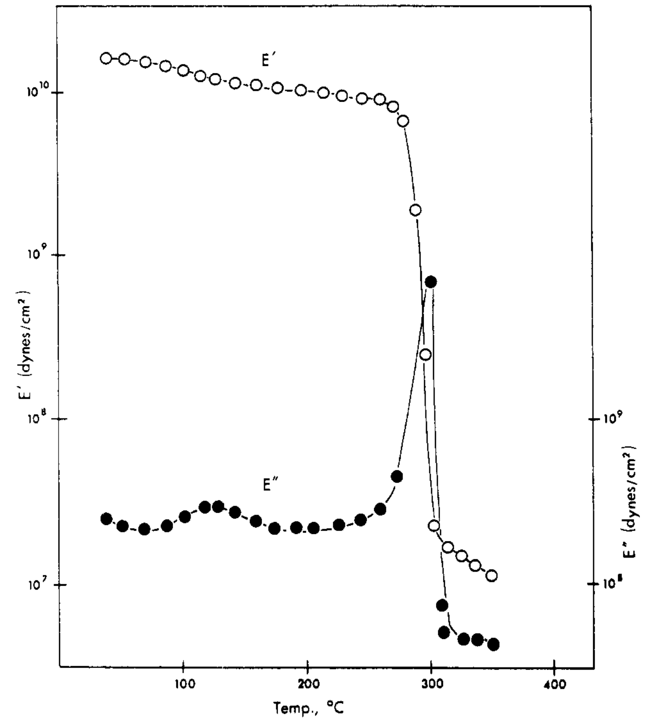


Figure 10. Plot of dynamic storage and loss modulus vs. temperature of polyquinoline (heating rate, 5 °C/min, He atmosphere, frequency 35 cycles/s).

well behaved and exhibit only second-order transitional behavior at T_g. Since the lifetime of such a material in this case was relatively short (see Figure 9) it was important that the assessment of thermal properties (C_p, V_{sp}, α's, etc.) was made immediately after its formation. The thermophysical properties of "normal" polyquinolines are summarized in Table II, and a dynamic mechanical relaxation spectrum obtained on a Rheovibron (Model DDVII) is given in Figure 10. Correlation between C_p, V_{sp}, and mechanical loss spectra in locating T_g was relatively good. The maxima in mechanical loss modulus (E'') occurred at 300 °C, about 50 °C above T_g. This temperature difference is substantially larger than that which can be accounted for by frequency and heating rate effects which would amount to about 20 °C. We offer no explanation for this difference, but we like to point out that the film sample used for mechanical measurements was in a mildly prestressed state which may have produced some orientation and possibly resulted in anisotropic behavior.

The data given in Table II are suitable for testing numerous empirical and theoretical relationships of glasses which have recently been reviewed.[9] We have not done this because our normal glass requires rather abnormal formation histories, it has a short life time, and we doubt that any existing glass theories would be capable of predicting its behavior.

Table II
Thermophysical Data for "Normal" Polyquinoline

Glass transition temperature T_g, °C	251
Melting point of crystalline phase[a] T_m, °C	483
Thermal decomposition temperature $T_d{}^i$, °C	565
T_g/T_m	0.73
Change in heat capacity at T_g [$\Delta C_p(T_g)$], cal/(mol segment deg)	4.95
Linear thermal expansion coefficient	
Below T_g (α_g, °C^{-1})	2.15×10^{-4}
Above T_g (α_L, °C^{-1})	5.55×10^{-4}
Specific vol at T_g (V_g, cm^3 g^{-1})	0.818
Ratio of hole vol to free vol $\Delta\alpha/\Delta_L$	0.61
Ratio of vibrational vol to free volume α_g/α_L	0.39
Hole energy ϵ_n, cal/mol	3017

[a] % crystallinity is about 10.

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