Polymer Bulletin 23, 83–88 (1990)

Polymer Bulletin

Physical ageing in glassy liquid crystalline poly(p-hydroxy-benzoic acid-co-ethylene terephthalate)

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SUMMARY

Glassy liquid crystalline poly(p-hydroxy-benzoic acid-co-ethylene terephthalate) is after rapid cooling from temperatures above T_g in a non-equilibrium state and exhibits physical ageing. It is shown that enthalpy and volume decrease with increasing annealing time. At the same undercooling, with respect to middle temperature of the major glass transition (T_{gl}), the rate of the equilibration process is significantly slower in the studied polymer than in an ordinary glassy amorphous polymer. The presence of a constraining ETP-rich phase exhibiting a 25 K higher glass temperature than T_{gl} may be the cause for this retarded enthalpy relaxation.

INTRODUCTION

Thermotropic liquid crystalline polymers most frequently exhibit a glass transition and therefore should display physical ageing at temperatures between the glass transition temperature (T_g) and the sub-glass transition temperature (T_β). Only a few papers have been published on physical ageing in thermotropic liquid crystalline polymers. Warner (1) studied physical ageing in an oriented thermotropic liquid crystalline copolymer based on 1,4-acetoxybenzoic acid (50 mole%), 2,6-dihydroxy antraquinone (25 mole%) and terephthalic acid (12.5 mole%) and isophthalic acid (12.5 mole%). From thermal analysis on annealed samples the appearance of enthalpy relaxation was confirmed in this copolymer.

Physical ageing has been reviewed by Struik (2) and a great number of papers have been published on physical ageing in a variety of different polymers and non-polymeric materials: glassy amorphous polymers (e.g. refs. 2-6), filled rubbers (e.g. refs. 2) and semicrystalline polymers (refs. 2,7,8). It is well-known that physical ageing results in a decrease in volume, enthalpy and entropy of the material (2). The change in these primary properties has a major influence on a number of other properties, e.g. creep compliance, impact strength, transport properties and electric properties (2).

Our work has been focused on the physical ageing in the thermotropic liquid crystalline copolymer poly(p-hydroxy-benzoic acid (HBA)-co-ethylene

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*To whom correspondence should be addressed terephthalate (ETP)) with HBA/ETP molar ratio of 0.6:0.4. In this paper data are presented, mainly by differential scanning calorimetry (DSC) measurements on samples annealed at temperatures between the glass transition temperature and the sub-glass transition temperature. Physical ageing has also been studied by density measurements of annealed samples.

Earlier work have shown that this material is a two-phase system with 2 μm globuls rich in ETP and a matrix phase enriched in HBA (9). Dielectric measurements revealed the presence of three dielectric relaxations at the following temperatures: 364 K (α'), 337 K (α) and 223 K (β), measured at 50 Hz (10). Relaxation strength measurements indicated that the α (and α') process may be assigned to the ETP-rich phase and the β process to both phases (10). The presence of a β process is a prerequisite, thus fulfilled in the present case, for the occurrence of physical ageing in a material (2). A recent study by Amundson et al (11) showed that P(HBA-ETP) 0.6:0.4 is biphasic and contains both nematic and isotropic fractions.

EXPERIMENTAL

The polymer studied is a copolyester based on p-hydroxybenzoic acid (HBA) and ethylene terephthalate (ETP), with a molar ratio HBA/ETP of 0.6:0.4. The synthesis and structure of this polymer is described elsewhere (9,12).

Annealing: Isotropic samples were heated to 380 K, cooled at a rate of 80 K(min)$^{-1}$ to 280 K and annealed for times ranging from 75 s to almost 4 months (10^7 s) at the following temperatures: 308.1 K, 317.7 K, 322.0 K, 327.0 K and 331.0 K. The majority of the heat treatments were carried out in a temperature calibrated Perkin-Elmer DSC-2. The long-time annealing was carried out in a temperature calibrated hot stage.

Differential scanning calorimetry (DSC) was carried on the annealed samples in a Perkin-Elmer DSC-2, which was energy and temperature calibrated according to standard procedures. The annealed samples were heated from 280 K to 380 K at a rate of 10 K(min)$^{-1}$ while the differential heat flow was recorded. Then the samples were immediately quenched to 280 K at a rate of 80 K(min)$^{-1}$. By subsequently reheating the sample to 380 K at 10 K(min)$^{-1}$ while recording the differential heat flow a reference thermogram was obtained.

Density measurements: The room temperature density of both the annealed samples and reference (quenched) samples was measured in a density gradient column based on water solutions of calcium nitrate. The column was calibrated with glass beads of known density.

RESULTS AND DISCUSSION

Typical DSC thermograms of annealed samples are presented in Fig. 1. It is evident that the glassy LC polymer exhibits enthalpy relaxation. The growth of the peak associated with the glass transition is qualitatively similar to the behaviour of glassy amorphous polymers. The glass transition temperature

(T_g) is also shifted to higher temperatures on prolonged annealing. This is a well-known feature for glassy amorphous polymers and is attributed to a non-equilibrium behaviour *(superheating)* occurring during the heating scan. The sample which was annealed for $1.7x10^{-6}$ s (Fig. 1) displays two endothermal peaks above the main glass transition. The cause of these peaks is not clarified but may be due to the presence of the upper glass transition (α′) of the ETP rich phase.

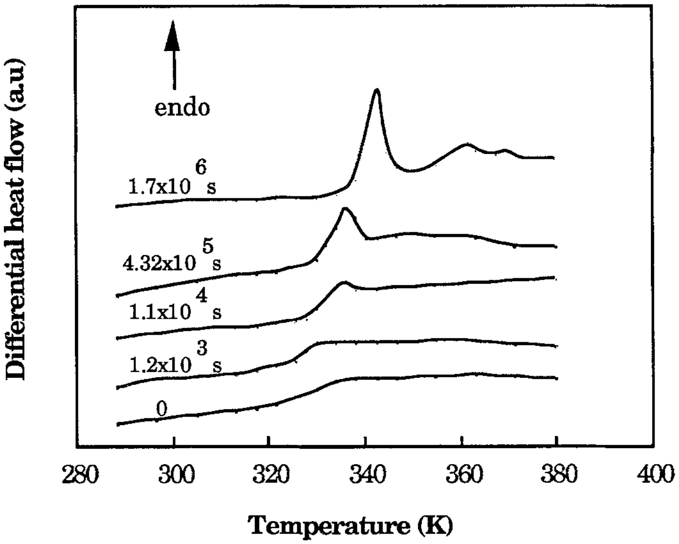

Figure 1. Thermograms obtained during the heating scan of samples annealed at 322.2 K for different periods of time as indicated in the figure.

The enthalpy of any specific annealed sample is related to a reference state which is defined on the basis of the rapidly cooled (80 $K(min)^{-1}$) sample. The enthalpy difference ΔH is compared with the enthalpy difference (ΔH_e) between the reference state and the equilibrium state. The equilibrium state is not reached within a reasonable experimental time at all the temperatures and its enthalpy difference value was therefore calculated according to eq. (1). This equation is based on the assumption that that the equilibrium value can be determined by an extrapolation of enthalpy data of the rubbery state:

$$\Delta H_e = \Delta C_p[T_g - T_a] \qquad ....(1)$$

where ΔC_p is the difference in specific enthalpy between the rubber state material and the glassy polymer, T_g is the glass transition temperature for the reference sample (330 K) and T_a is the annealing temperature. In Fig. 2, the enthalpy difference between the equilibrium state and the annealed sample, i.e. ΔH_e - ΔH is plotted versus the logarithm of the annealing time for three different temperatures. The curves presented in Fig. 2 may be extrapolated to ΔH=ΔH_e in order to estimate the time required for reaching equilibrium.

From a comparison of the data for the equilibration time (log t_e) for the liquid crystalline polymer with data by Struik (3) for glassy amorphous polymers (according to eq. 2), it appears that enthalpy relaxation in the liquid crystalline polymer is significantly slower than in a normal glassy amorphous polymer at the same reduced temperature, $T_g - T$ (Table 1).

$$t_e = 100\ e^{0.77(T_g-T)} \qquad \ldots.(2)$$

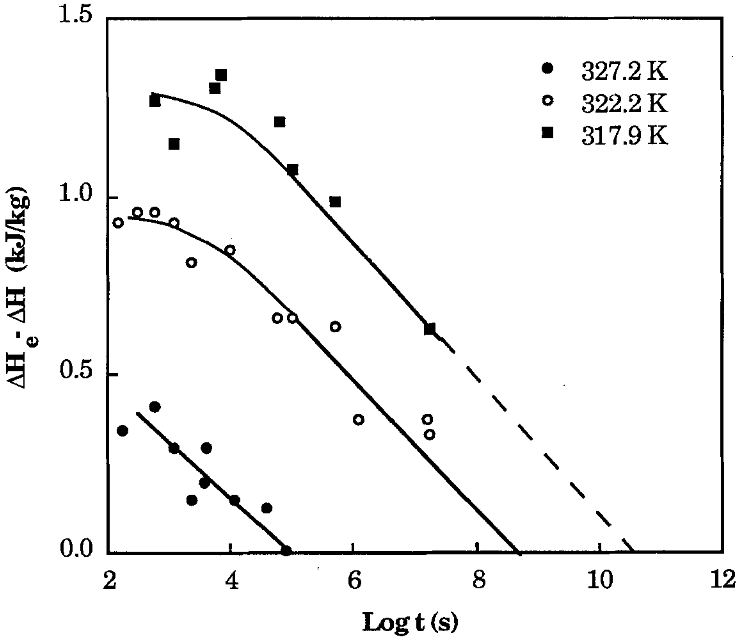

Figure 2. Enthalpy relaxation expressed as ΔH_e - ΔH as a function of the logarithm of the annealing time for samples annealed at the temperatures shown in the graph.

This seems not be a general characteristic for thermotropic liquid crystalline polymers, since Warner (1) has published results demonstrating that the enthalpy relaxation in another liquid crystalline polymer has the same rate and magnitude as in conventional glassy amorphous polymers. This was explained by the fact that the motion of chains associated with the enthalpy relaxation is in the range of nanometers and that this motion should not be more difficult for anisotropic glasses than for conventional isotropic glassy polymers.

A possible explanation to the slow enthalpy relaxation in our liquid crystalline polymer may be the heterogeniety in composition and the presence of a double T_g of the ETP-rich phase. The double T_g may be due to the biphasic nature, i.e.

the presence of nematic and isotropic fractions in this polymer. The reduced temperature value (ΔT) is obtained in reference to the middle point of the lower T_g of the ETP-rich phase. The upper T_g indicates a constraining component in the ETP-rich phase which may retard enthalpy relaxation.

Table 1. Equilibration time (s)- comparison between liquid crystalline and amorphous polymers.

T_g - T (K)	Amorphous [a]	Liquid crystalline
3	10^3	10^5
8	$10^{4.6}$	10^9
12.3	10^6	10^{11}

a. From data by Struik (2).

Density measurements indicated a density increase of the order of 1‰ for annealing times of $6x10^6$ s. As the sensitivity of the density measurement technique is obviously of the same order of magnitude as the measured increase, no relevant analysis could be performed. This was also concluded by Warner (1).

ACKNOWLEDGEMENTS

The reported study has been sponsored by the Swedish National Science Research Council (NFR), grants no K-RT 1910-100 and K-KU 1910-300 and the National Swedish Board for Technical Development (STU), grant no 85-3593. The authors wish to thank Dr. W.J. Jackson Jr., Tennessee Eastman Co., USA, for providing the polymer studied.

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Accepted November 3, 1989 C