Thermally stimulated depolarization of a copolymer of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid

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A liquid crystal copolymer containing poly(ethylene terephthalate) (PET) and 0.6 mole fraction of *p*-hydroxybenzoic acid (PHB) was studied. There is a large amount of information available for this material, which has been obtained by techniques other than thermally stimulated depolarization (t.s.d.). Hence the usefulness of this latter method can be evaluated for the characterization of polymer liquid crystals. First, by applying the same field of 13.3 MV m^{-1} in each case, effects caused by varying the polarization temperature were determined. Second, for a constant polarization temperature of 90°C, the polarizing field was varied between 3.3 MV m^{-1} and 13.3 MV m^{-1}. Third, for the same polarization temperature and fixed field, the storage time was varied between 0 h and 125 h. In the temperature range studied (20–190°C) the PET-rich phase contributes more to t.s.d. than the PHB-rich phase. High temperatures and strong fields produce similar effects of randomization of dipole orientations, or more generally of destruction of low-temperature structures. There is a competing effect of removal of restrictions on angular motions of dipoles along with increasing free volume. Longer storage times enable relaxation of electric stress created during electret formation. T.s.d. is one of several methods used for the determination of locations of phase transitions. However, in contrast to most other characterization techniques, t.s.d. permits the determination of effects of annealing on resulting structures at lower (e.g. ambient) temperatures. In particular, it is found that annealing shifts the cold crystallization process to higher temperatures.

(Keywords: copolymer; thermally stimulated polarization; PET; PHB)

INTRODUCTION

Polymer liquid crystals (PLCs) represent a rapidly expanding field of research due to their fundamental behaviour and their practical applications. The applications are related to their properties; compared to usual engineering thermoplastics, PLCs show clear superiority[1,2] with regard to chemical resistance, low flammability, outstanding mechanical properties, applicability at elevated temperatures, low isobaric expansivity, and often unusual ease of processing. Non-linear optical properties of PLCs have been found and their applications as optical storage media have been explored.

PLCs exhibit more complex types of behaviour than flexible polymers. A variety of techniques is used to study the mechanical, thermophysical, rheological, optical, electrical and other properties of PLCs. The aim of this paper is to study the use of the method of thermally stimulated depolarization (t.s.d.) in the determination of collective chain dynamics and phase transitions. In another paper[3], we intend to explore the use of the internal friction method in the study of PLCs.

METHOD

Many polymers are dielectric and in an electric field accumulate electric charges. Some dielectrics can form electrets: after polarization by an external field they retain the charge for a long time, sometimes for several years. Studies of macromolecular electrets and application of the t.s.d. method to polymeric materials is largely due to the pioneering work of van Turnhout[4,5].

The procedure is basically as follows. An electret becomes polarized at an elevated temperature T_p by the application of a sufficiently high electric field E_p for a time t_p. Usually T_p is higher than the glass transition temperature (T_g) of the material. For a given chemical structure, the magnitudes of E_p and t_p determine the extent of orientation of dipoles in the material. Free charges drift towards the electrodes during this time. When the sample is cooled to a desired (often ambient) temperature and the field switched off, the resulting material is a thermoelectret. In these experiments the thermoelectret is kept in the shorted position for 10 min to remove stray charges. The sample is subsequently heated at a constant rate; this produces a gradual discharge of the thermoelectret and a t.s.d. current flows. Maxima of t.s.d. current observed at various temperatures

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are related to relaxations of electric charges in the sample as a function of events taking place at the molecular and supermolecular (phase) level. The depolarization current is measured with a sensitive electrometer. The apparatus is shown schematically in *Figure 1*. *Figure 2* shows the t.s.d. procedure as a plot of temperature *versus* time.

The t.s.d. method has already provided useful information on the storage and transport of charge carriers in a variety of insulators and semiconductors. Characteristic of the method is the relative experimental simplicity that provides a high sensitivity with currents as low as 10^{-14} A. Electret stability, that is the extent of preservation of the dipole polarization at a given temperature, is naturally obtained from t.s.d. scans.

The simplest assumption that can be made consists of assigning a single relaxation time τ to dipoles in the material. At a constant temperature the rate of depolarization and the t.s.d. current are given by:

$$i(t) = \frac{dP(t)}{dt} = -\frac{P(t)}{\tau} \qquad (1)$$

where P is the residual polarization at time t. The temperature dependence of τ is often represented by an Arrhenius-type equation:

$$\tau = \tau_0\, e^{E/kT} \qquad (2)$$

where τ_0 is a constant, E is the activation energy, k is the Boltzmann constant and T is the thermodynamic temperature. In spite of the simplification involved in assuming a single relaxation time, the parameter E is a convenient measure of magnitudes of structural changes (and their energetic consequences) that occur in various transitions. A discussion of E is provided by Kovarskii[6].

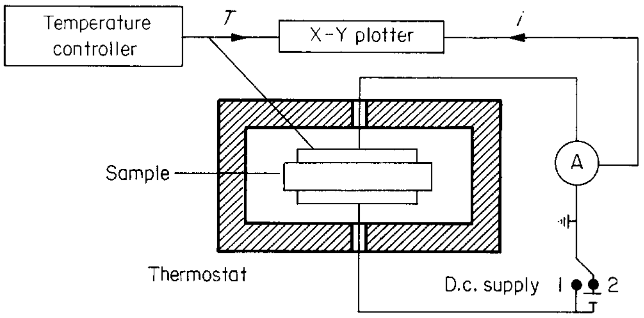

Figure 1 Schematic diagram of the t.s.d. apparatus

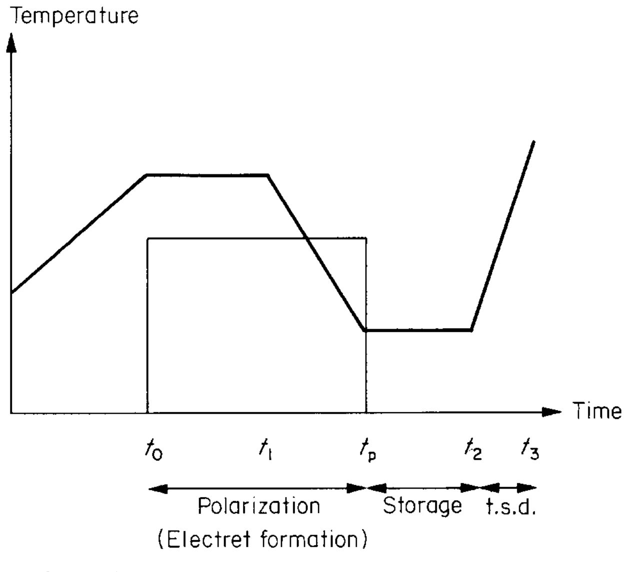

Figure 2 T.s.d. procedure represented schematically as temperature and electric field manipulations as a function of time: T_0, initial temperature; T_p, polarization temperature; t_0, start of polarization; t_1, start of cooling; t_p, time of switching off the field; t_2, start of heating; t_3, end of heating

If the temperature increase varies linearly with time, that is

$$T = T_0 + bt \qquad (3)$$

where T_0 is the initial temperature and b a proportionality factor, integrating equation (1) with respect to time we obtain:

$$i(T) = -\frac{P_0}{\tau_0}\exp\left(-\frac{E}{kT} - \frac{1}{b\tau_0}\int_{T_0}^{T} e^{-E/kT}\, dT\right) \qquad (4)$$

where P_0 is the initial polarization.

The t.s.d. technique is useful in studies of the ageing of polymers[7,8]. For isotactic polypropylene, Myslinski and Kryszewski[9,10] found t.s.d. current maxima dependent on the spherulite size in their samples. Moreover, material purity can be checked by t.s.d. Impurities generally increase the number of ionizable carriers and therefore promote considerably the temporary storage of charge. High sensitivity of t.s.d. is useful in studying the changes in dielectric properties induced by chemical degradation, atomic radiation, swelling, moisture and other agents[11]. Crazing and craze healing are also shown well in t.s.d.[12].

To our knowledge there has been just one attempt to apply t.s.d. to PLCs: Simon[13] studied four one-row combs, which are all in the subclass $\varepsilon 0$ in the PLC classification developed by one of us[1,2]. There is ample proof that PLCs belonging to different classes have different properties. Simon[13] found that t.s.d. provided a reliable determination of T_g. It is known that in combs the dynamics of mesogenic side chains is to a considerable extent decoupled from the motions of the flexible main chain. It was decided to study a longitudinal PLC[1,2]; where the liquid crystal sequences are in the main chain and oriented along the chain direction. The second property distinguishes these PLCs from other classes, such as orthogonal or stars. Currently, longitudinal PLCs are the most frequently studied.

EXPERIMENTAL

A copolymer of poly(ethylene terephthalate) (PET) and *p*-hydroxybenzoic acid (PHB) was studied. This will be referred to as PET/0.6PHB, where 0.6 represents the mole fraction x of liquid crystalline PHB sequences in the copolymer. Samples were supplied by Eastman Kodak (Kingsport, TN) and by Unitika (New York City, NY) as flakes and thin sheets. PET/xPHB copolyesters were first obtained and studied by Jackson and Kuhfuss[14], which prompted a new line of extensive research. (For a review and predictions of future trends see reference 15.) Methods other than t.s.d. have been used to study the same materials[3,14,16–18]. Determination of the tensile strength, flexural modulus and notched Izod impact strength for PET/xPHB copolymers with varying x and for blends of PET with PET/0.6PHB show[14,16] that all these properties have a maximum around $x = 0.6$. D.s.c.[16,19–21] and SEM of fracture surfaces[16,20] show that PHB sequences form nearly spherical second phase regions in the solid state. These regions have been called islands[16] and their structure is being studied[17].

For t.s.d. purposes, circular samples (area ~3 cm^2) were cut from 150 μm thick sheets, and then vacuum-coated on both sides with aluminium electrodes. The results reported below pertain to new samples used in each run. However, in a few cases the same sample was studied under the same conditions several times; locations of the transitions did not change significantly from one run to the next.

The general method described in the preceding section was applied. Polarization temperatures (T_ps) were applied in the range 30–150°C at 20°C intervals and E_p values in the range 3.3–13.3 MV m^{-1} with steps of 1.7 MV m^{-1} were used. Ageing times between 0 h and 125 h were applied. Quick cooling to 20°C was achieved with an air fan for all samples in the same manner. The t.s.d. current was measured at a uniform heating rate of 2 K min^{-1} from 20 to 200°C.

A series of t.s.d. spectra for $T_p = 90°C$ but for different E_p values were compared. Surface areas under the t.s.d. current *versus* temperature curves were evaluated and found to be linearly dependent on E_p. This confirms the dipolar relaxation character of processes up to 90°C which appear as maxima on the curves.

POLARIZATION TEMPERATURE DEPENDENCE OF t.s.d. CURRENTS

Depolarization currents as a function of temperature are shown in *Figure 3*, with each curve corresponding to a defined T_p at an E_p of 13.3 MV m^{-1}.

For the lowest T_p of 50°C two peaks were found: one at 65 ± 2°C and the other at 101 ± 2°C, referred to as α and α' peaks, respectively. Coburn and Boyd[22] determined the dielectric constant and dielectric loss over several decades of frequency for pure PET, while Gedde *et al.*[23] made similar measurements on two PET/PHB copolymers including PET/0.6PHB. Gedde *et al.* report maxima in dielectric loss for 50 Hz at −50°C(β), 64°C(α) and 91°C(α'). We cannot comment on the β transition since our experiments did not go below room temperature. Clearly the α transition determined using dielectric studies agrees with our t.s.d. value within limits of the experimental accuracy; it also reasonably agrees with the glass transition at ~60°C determined by d.s.c.[16,23]. Since the glass transition or pure PET occurs at 69°C[15,24], the α transition is the T_g of the PET-rich phase. This is further confirmed by the fact that Gedde *et al.*[23] found that the relaxation strength increases with increasing PET content.

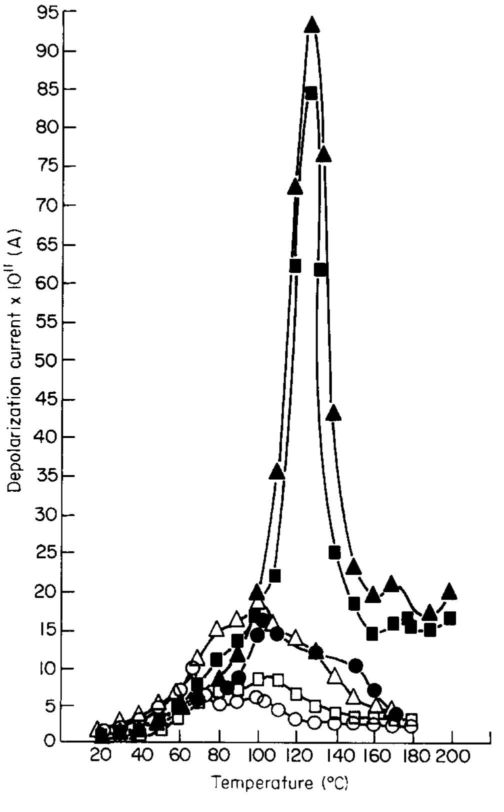

Figure 3 T.s.d. spectra of PET/0.6PHB samples polarized with a 13.33 MV m^{-1} field for several polarization temperatures: (○) 50°C; (□) 70°C; (△) 90°C; (●) 110°C; (■) 130°C; (▲) 150°C

In turn, consider the α' transition: the t.s.d. value is 10 K higher than the dielectric loss value. Seemingly, the t.s.d. technique is equally sensitive as the dielectric method to the α transition, but shows retardation at the α' transition. Therefore, consider the nature of the α' process. Coburn and Boyd[22] report for pure PET the onset of crystallization at 100°C for what they call the amorphous sample, witnessed by a fall of the dielectric constant and by the appearance of a new peak at a higher temperature. It is known from d.s.c. and SEM that the system is biphasic[16]; the PET-rich phase has its own glass transition. We infer that the same phase also undergoes cold crystallization, similarly as pure PET, and this is the α' transition found by Gedde *et al.*[23] and by us. Now we note that maintaining the t.s.d. sample at $T_p > T_g$ is equivalent to annealing, with the additional imposition of an electric field. Structural relaxations take place during annealing[25], a process common to materials of all types. When an annealed sample is brought from T_p down to room temperature, recrystallization becomes more difficult. Hence the cold crystallization process starts in t.s.d. experiments at a higher temperature than in dielectric ones.

The Stockholm group[26] studied PET/0.6PHB by d.s.c. and wide-angle X-ray scattering (WAXS) but at temperatures higher than used here (they show d.s.c. scans starting at 130°C, some 30°C above the α' transition here). They found two sizes of crystals in the PHB-rich phase. They assigned the existence of larger crystals to transesterification reaction induced crystallization, and the formation of smaller ones to cold crystallization.

To see whether our interpretation of the α' process is correct, the t.s.d. curves in *Figure 3* corresponding to higher T_p values were analysed. In the T_p range of 70–110°C the α' is shifted upwards as expected, but only slightly, to no more than 105°C. The activation energy $E(\alpha') = 0.43$ eV [see equation (2)]. For the highest T_ps, 130 and 150°C, there is a dramatic jump in the α' transition to 128°C; the $E(\alpha')$ is then 0.69 eV. This clearly confirms our hypothesis: the higher the temperature at which the sample is annealed/polarized, the greater the destruction of the low-temperature structure, and it is more difficult for the PET-rich phase to 'reorganize', and cold crystallization begins at a higher temperature.

We do have a fairly good idea of what happens during cold crystallization of PET at the molecular level. The ethylene glycol linkage exists in two conformations; an extended form which is *trans* and a more compact form which is *gauche*. Crystalline regions of PET contain the *trans* form only. N.m.r. and i.r. spectra and current glow curves[27–30] indicate that the amorphous regions contain both forms. We infer that at a temperature above the glass transition, namely at the α' transition, the amount of free volume present becomes sufficient for a partial *gauche* to *trans* conversion of the ethylene glycol linkages, and hence for cold crystallization.

Returning now to the α transition. Compared to what has been identified as $T_g = 65°C$ for $T_p = 50°C$, the glass transition goes up to the PET $T_g = 80°C$ for T_p in the range 70–110°C. It appears that what we have called the annealing mechanism is operative here also: high-temperature structure reorganization at T_p destroys, in part, the low-temperature structure (in the present case the glassy PET-rich phase). Moreover, some PET crystallization occurs during annealing; the number of dipoles contributing to the α transition decreases. The remnants of the PET glass undergo the transition at a higher temperature. Moreover, the transition is weaker: a shoulder on each t.s.d. curve, as contrasted to a fairly sharp peak for low T_p. For the highest T_ps, 130 and 150°C, the annealing destroys the glass in the PET-rich phase completely, and the α transition disappears. Such disappearances for polymeric materials subjected to higher T_ps have been previously reported[31–33]. We conclude that the present annealing model agrees with the earlier results, and explains the present results for both the α and α' transitions.

The peak current i_m for the α transition increases with T_p up to 90°C and then decreases slowly. Belana *et al.*[34] studied t.s.d. of amorhphous PET and found a maximum for i_m at 70°C. The existence of such a maximum can result from simultaneous operation of at least two factors. One factor is the restriction of angular motion of the dipoles. A model of such restricted motions has been developed by Wang and Pecora[35], while experimental work on dielectric relaxation in lyotropic PLC solutions has been carried out by Moscicki *et al.*[36,37]. This restriction should become less and less pronounced along with free volume increase on increasing temperature, particularly above the glass transition. However, higher temperature provides also additional thermal energy to the dipoles – which moreover operate in larger volume; hence the randomizing effect. The randomization in competition with gradual removal of restrictions on dipolar motions jointly produce the i_m extremum.

As for our determination of the α' transition, no extremum is observed and the peak current scales with the T_p.

FIELD DEPENDENCE OF t.s.d. CURRENTS

Since the peak current for the α transition shows a maximum for $T_p = 90°C$, subsequent studies were all carried out at this T_p. The E_p values were varied between 3.3 MV m^{-1} and 13.3 MV m^{-1}. The resulting family of curves is shown in *Figure 4*.

The same two peaks, α and α', that were found in the T_p series of measurements are found here. The location of the α peak clearly moves to higher temperatures along with an increase in the field strength E_p. It seems that E_p increase plays a similar role as temperature increase: more destruction of the low-temperature structure of the PET-rich phase takes place. However, in the field strength range studied that destruction is not complete and even at the highest E_p the α peak is observed.

The α' peak appears at ~100°C; i_m increases along with E_p for both kinds of peak, but the effect is more pronounced for α' peaks. We note that our α' peak corresponds to the dielectric α' determined at 50 Hz by Gedde *et al.*[23].

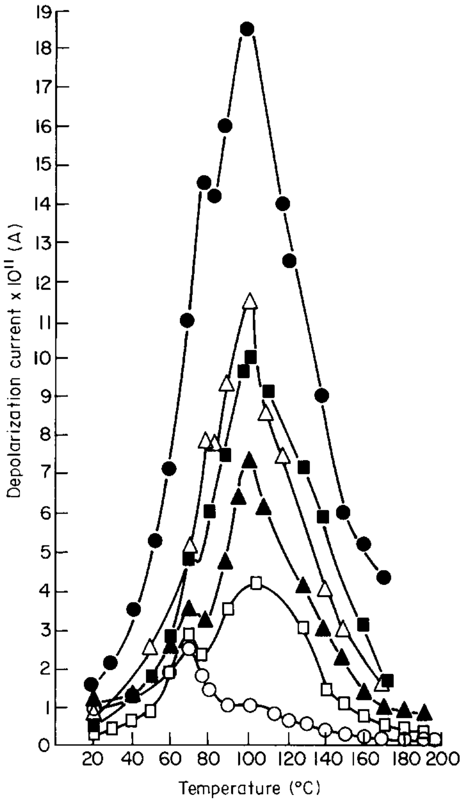

Figure 4 T.s.d. spectra of PET/0.6PHB samples polarized at 90°C at various electric fields: (○) 3.33 MV m^{-1}; (□) 5.00 MV m^{-1}; (▲) 6.66 MV m^{-1}; (■) 8.33 MV m^{-1}; (△) 10.00 MV m^{-1}; (●) 13.33 MV m^{-1}

STORAGE TIME EFFECT

We have also determined the thermograms of PET/0.6PHB thermoelectrets stored for different times t_s after formation. In this series the T_p was also 90°C and E_p was 13.3 MV m^{-1}. The samples, after cooling to room temperature (25°C), were short-circuited, stored at that temperature for different times, and then the t.s.d. currents were measured. The results are shown in *Figure 5*.

We find in *Figure 5* that i_m decreases when t_s increases; this applies to both α and α' peaks. During electret formation the material is under electrical stress. Once the electric field is removed, the dipoles tend to rotate. Hence longer storage time necessarily brings about a lowering of the peak current. This agrees with an earlier observation for cellulose nitrate[33].

As for *Figures 3* and *4*, the α peak is explained by the glass transition of PET in the PET-rich phase, modified to a certain extent by the presence of PHB as a minor component in that phase. There is a transition shown by d.s.c. around 195°C[17], but this is just at the end of the experimental range studied.

CONCLUSIONS

High temperatures and strong fields lead to randomization of dipole orientations, or more generally to destruction of low-temperature structures. A competing

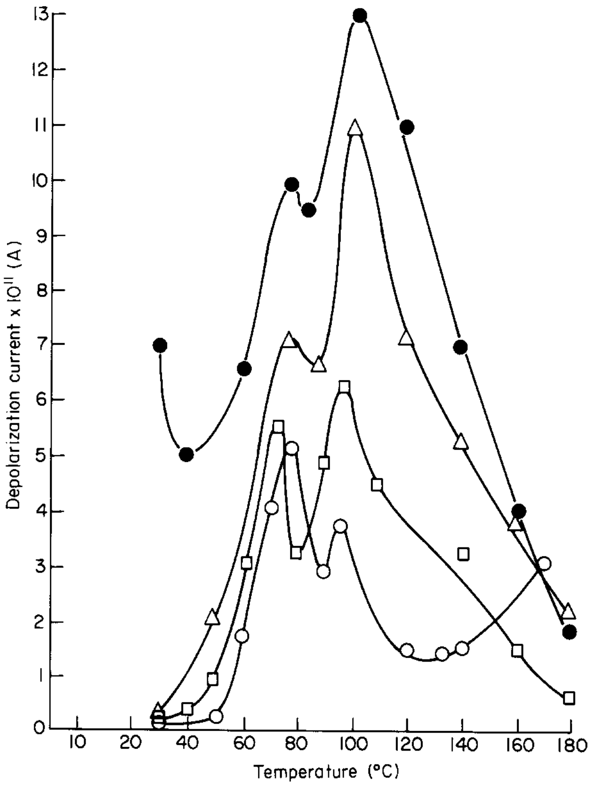

Figure 5 T.s.d. spectra of PET/0.6PHB samples polarized at 90°C and stored for varying ageing times: (○) 125 h; (□) 25 h; (△) 5 h; (●) 0 h

effect seems to be that of removal of restrictions on angular motions of dipoles along with increasing free volume; however, this effect is overwhelmed by randomization above 90°C. The effect of storage time contributing to lowering of the peak current fits into the same coherent picture.

There are several methods of locating phase transitions. Simon[13] found that t.s.d. served well in the determination of T_gs of his comb PLCs and also of blends of a comb with a highly dipolar dye. The same is true for our longitudinal PLC. We infer that t.s.d. can be used to determine transitions in PLC systems either as a substitute for or complementary to dielectric relaxation. The latter method has been applied to PLCs by Kresse[38] and used since with good results for combs[39,40], longitudinal[41] and cross-shaped star PLCs[42]. Other alternative methods, namely thermomechanical analysis (linear isobaric expansivity determination), dynamic mechanical testing and d.s.c. ought to be noted.

The t.s.d. method has an advantage which other methods, including those above, do not have. The results depend naturally on what above has been called annealing – the imposition of an elevated temperature for a period of time while the electric field is applied. Contributions to crystallization at the highest annealing temperatures were noted. It is known that a variety of processing technologies include annealing periods: to remove at least in part internal mechanical stresses[25], to allow partial or complete network formation reactions, or for other reasons. The t.s.d. method allows phase transitions to be located. It also makes inferences possible on the consequences of annealing on the resulting structures. Effects of varying annealing temperatures can be determined. In turn, this knowledge should help in better definitions of processing conditions. This is applicable to polymeric materials in general, but seems particularly pertinent for PLCs because of relatively high complexity of their multiphase structures.

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