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Study of the thermal relaxation effects in polymers by a conjugated use of thermally stimulated depolarization and polarization current methods [a]

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Abstract

Among the various thermally stimulated current methods used for analyzing the relaxation behavior of polymers, the thermally stimulated polarization current (TSPC) technique is rarely used because the classical theory provides for obtaining spectra having relaxational characteristics similar to those obtained from the more familiar thermally stimulated depolarization current (TSDC) technique. In fact, a number of factors such as the temperature dependence of equilibrium polarization, the effect of thermal expansion, the annealing process necessarily associated with TSDC experiments, or the existence of a temperature-dependent structure, can lead to very dissimilar results. This is especially the case in polymers, where the use of TSDC and TSPC methods in conjunction is very useful, e.g., for differentiating between various polarization processes, for studying the physical aging phenomenon or the behavior of thermally unstable structures, and for revealing non-equilibrium intermediate relaxations.

INTRODUCTION

The method of thermally stimulated depolarization currents (TSDC), which consists of measuring, with a definite heating scheme, the currents generated by the release of a polarized state in a dielectric, is now a very well established technique of studying the thermal relaxation properties in the solid state, especially because of (1) its high sensitivity (allowing, for example, detection of dipole concentrations of less than 0.1 ppm or carrier concentrations of $\approx 10^8$–10^9 cm^{-3}, (2) its very low equivalent frequency (10^{-2}–10^{-4} Hz), leading to a high resolution of coexisting relaxation processes, and (3) its rather exceptional ability for resolving multicomponent or distributed peaks by analysis techniques such as partial cleaning and fractional or "windowing" polarization [1–5]. The method of thermally

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stimulated polarization currents (TSPC), which is based on the opposite process, i.e., measuring the currents generated by the buildup of a polarization state in a dielectric, is more rarely used for two main reasons: (1) the classical theory provides for obtaining TSPC spectra having relaxational characteristics similar to those obtained from TSDC [6], and (2) in the high temperature range, the TSPC spectra are usually less well resolved because the relaxational current can be superimposed onto (or eventually masked by) the normal d.c. conduction current [2]. In fact, however, it seems intuitively obvious that, at least in certain materials, a number of factors can potentially lead to the observation of very dissimilar TSDC and TSPC results at the relaxational level, the most important of which should be the temperature dependence of equilibrium polarization, the effect of thermal expansion, the annealing process associated with the TSDC procedure, or the existence of a temperature-dependent structure. In the following, we present some characteristic examples of polymers giving rise to such significant differences, showing that the conjoint use of these two methods and the comparison of spectra could be particularly useful, e.g. for identifying and quantifying non-equilibrium phenomena, for detecting thermally unstable entities, or for differentiating between various possible polarization mechanisms.

EXPERIMENTAL

Commercial samples of polydian carbonate (PC) were obtained from Bayer (Makrolon). The isoprene–styrene–isoprene (ISI) and styrene–isoprene–styrene (SIS) block copolymers were prepared at the Ecole d'Application des Hauts Polymères (Strasbourg, France) from *n*-butyllithium catalysts in benzene as described elsewhere [7]. Their properties have been reported in a previous paper [8]. Ionomers based on commercial poly(*n*-butyl methacrylate) (Aldrich) were obtained with various degrees of neutralization by adding calculated amounts of methanol solutions of alkali bases to isopropanol solutions of the acid copolymers [9]. The alkaline dicarboxylatopolybutadienes were prepared by neutralization of the carboxy-telechelic polybutadiene commercialized by B.F. Goodrich under the trade name Hycar CTB 2000 × 156. The synthesis is described in detail elsewhere [10].

Samples for TSDC and TSPC measurements of undrawn polymers were used in the form of square sheets 3×3 cm^2, obtained either directly from the commercial material (PC, for the study of nonequilibrium relaxations in as-received specimens), or from compression molded materials (block copolymers, ionomers and halato-telechelic polymers). The cold-drawing conditions used for PC samples were described in a previous paper [11]. The drawn regions were cut, starting from the middle of the "neck" formed, into square samples 2×2 cm^2.

All specimens were silver or aluminum coated, with two measuring electrodes and a guard ring in order to prevent surface leakage currents, and they were then short-circuited and kept over phosphorus pentoxide at room temperature. The measurements were carried out with a three-terminal electrode system under a controlled nitrogen flow (25 cm^3 min^{-1}) in a home-modified dielectric test cell of a relaxation spectrometer (Unirelax, Tetrahedron) provided with a stabilized d.c. generator (VG Electronics Ltd) and a current detector (Keithley electrometer, type 616). The heating and cooling rates were controlled by an automatic temperature programming system (Wizard 1501, Tetrahedron). The electrical connections between the metal coated samples and the electrodes of the cell were made using silver-pasted thin copper wires. Thus the samples were held freely in the cell with no pressure exerted on them during the measurements. This procedure was found necessary to obtain reproducible results and to avoid the presence of spurious or exceedingly noisy currents, which often accompanied volume variations of the samples during thermal cycling.

TSDC curves were recorded by using a standard procedure [11] with a heating rate of $b = 6°C\ min^{-1}$. For TSPC measurements, the sample was first cooled to $-150°C$ while short-circuited. An electric field identical to the polarization field used in TSDC experiments was then applied and the polarization current was measured during linear heating at $b = 6°C\ min^{-1}$.

RESULTS AND DISCUSSION

Thermal dependence of equilibrium polarization and effect of thermal expansion

With the same basic assumptions as are used in the usual theoretical formulation of TSDC [2], i.e. by considering that the temperature dependence of the equilibrium polarization P_e can be neglected during the nonisothermal step of the poling process, the classical theory of TSPC provides for obtaining, in the molecular relaxation region, current peaks characterized by the same position, height and shape as the corresponding TSDC peaks, the only difference being that the polarization current is obviously of opposite sign [6]. In fact, model calculations, initially based on the simple bistable model of Fröhlich [12] and then extended to the case of more realistic systems characterized by a distribution of relaxation times [13], show that taking into account the $P_e(T)$ function carries with it important consequences for the analysis and interpretation of both TSDC and TSPC experiments. These calculations imply, in particular, that (1) the TSPC peaks must be smaller than the corresponding TSDC peaks, (2) a current reversal must occur in TSPC measurements ("negative" TSPC peak) at the temperature for which the buildup polarization curve joins the temperature-dependent equilibrium polarization curve, and (3) during a

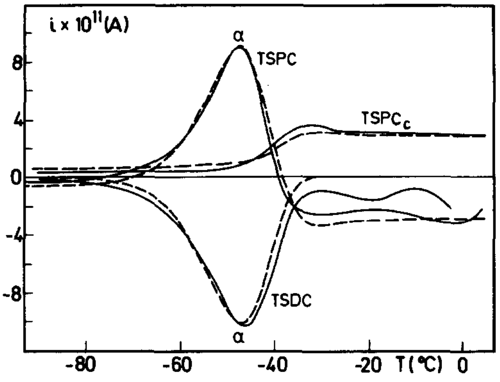

Fig. 1. TSDC, TSPC and $TSPC_c$ observed in a SIS block copolymer (———) and compared with the theoretical curves (- - - - - -) computed by taking into account the temperature dependence of the equilibrium polarization and the contribution of thermal expansion in the glass transition range of the polyisoprene phase (normalization at the maximum temperature of the experimental α TSDC peak). The values of material constants chosen for model calculations are given in Ref. 15.

subsequent cooling step with the field still applied ($TSPC_c$), a small relaxational peak must appear in the same temperature range [13]. By further considering the contribution of thermal expansion (especially important in the glass transition range of polymers, where the thermal expansion coefficient β_v increases markedly from the glassy state into the rubbery one [14]), we have recently shown that the amplitude ratio of the TSPC current reversal and main positive precursor peak must significantly increase (up to about one third for typical β_v values of elastomers) and that a negative current must also appear in the low temperature range of a given TSPC relaxational process [15].

It is obvious, however, that rigorously testing the predictions of such model calculations can be attempted only in materials for which the various relaxation processes are well resolved and the bulk conductivity remains negligible for the temperature region of interest (otherwise the differences in TSDC and TSPC peak intensities could be unnoticed and the TSPC reversals could be masked by the conduction current or superimposed relaxation processes). These conditions are fulfilled satisfactorily in several polymers, and especially in block copolymers of the styrene–diene type (i.e. copolymers where one of the components is essentially non-polar) up to temperatures several tens of degrees higher than the glass transition temperature (T_g) of the diene phase [8]. Figure 1 shows the spectra of TSDC, TSPC and $TSPC_c$ observed in the glass transition region of the elastomeric phase of a SIS block copolymer and compared with the curves obtained from numerical calculations. These were based on a temperature dependence of P_e of the Langevin type, a linear temperature dependence of the thermal expansion coefficient β_v in a temperature range of 10°C from T_g, and a value of 4 is

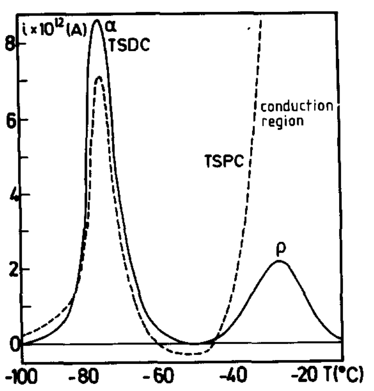

Fig. 2. TSDC (———) and TSPC (- - - - -) curves of carboxy-telechelic polybutadiene (field $= 10^6$ V m^{-1}; polarization temperature in the TSDC case = 25°C). For convenience of comparison, TSPC is reported in the same direction as TSDC.

chosen for the ratio $\beta_v(T > T_g)/\beta_v(T < T_g)$, which corresponds to that observed in most elastomers [14,16]. If we except the small deformation of the main current reversal due to the presence of a small secondary relaxation [8] (which is obviously not considered in the corresponding computed curve), it can be seen that a full agreement is obtained with the theoretical predictions, i.e., a weak negative component is apparent in the low-temperature TSPC range, the amplitude of the main current reversal is close to that expected, the intensity of the main positive TSPC peak is slightly smaller than that of the corresponding TSDC peak, and the polarization current obtained during a TSPC$_c$ sequence also fits quite well the computed curve. Similar results are obtained with ISI copolymers, in which it is also possible to fit quite well the theoretical and experimentally observed currents [15]. In several other polymers, reversals are also commonly observed in the high temperature range of the TSPC peak corresponding to T_g, but they are usually weaker owing to the superimposition of the conduction current (Fig. 2). Whatever the case, these results show that the temperature dependence of both equilibrium polarization and thermal expansion cannot be neglected *a priori* for analyzing thermally stimulated currents, and that the TSPC–TSDC comparison is particularly useful for determining the relative importance of these effects.

Non-equilibrium relaxations and internal stresses

Relaxation regions associated with a non-equilibrium state have been reported in a number of polymers, either freshly molded, or subjected to more or less severe mechanical treatments such as cold and hot drawing and rolling [17–20]. These relaxations, which disappear more or less rapidly when annealing the sample, are usually designated as "intermediate" or α' relaxations because they are located between the glass transition (α relaxa-

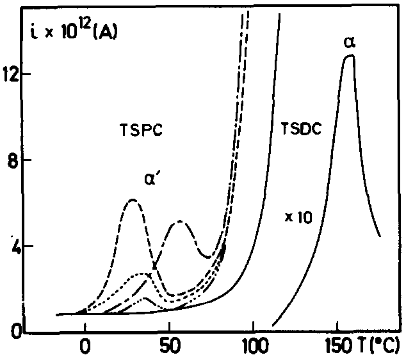

Fig. 3. TSDC and TSPC observed in as-received samples of Makrolon PC (field $=10^6$ V m^{-1}; polarization temperature in the TSDC case = 160°C). The four TSPC curves refer to various samples cut at different places of a given original sheet. For convenience of comparison, TSPC is reported in the same direction as TSDC.

tion) and the first (in order of decreasing temperatures) local mode β transition. They have been associated mainly with internal, residual stresses frozen in the polymer glass during manufacture or deformation treatment but little is known about their molecular origin. In polydian carbonate, in particular, such a relaxation has been clearly evidenced by numerous mechanical [17,18,21], dielectric [17,18,22] and DSC [23] measurements in a temperature range extending approximately from room temperature up to 100°C, depending on the measuring frequency and the type of mechanical treatment performed. In most of the results reported in the literature, however, this relaxation is difficult to quantify because it is comparatively small in amplitude, often manifesting itself in the shape of a simple shoulder in the initial slope of the α relaxation. On the other hand, the high sensitivity and resolution of the thermally stimulated methods generally allow the α' relaxation to be observed in the shape of a well-defined peak, and thus any variation of properties due to differences in initial treatment or annealing process [11,19] are easily followed. Since such a relaxation is, by nature, very sensitive to thermal cycling, large differences in TSDC and TSPC results can also be expected, and the comparison of the spectra can thus lead to a better understanding of the non-equilibrium process.

As shown in Fig. 3, the TSPC method is the only one allowing the observation of such intermediate relaxations in as-received samples of commercial PC sheets. This is so because the corresponding stresses are released during heating, and thus cannot give rise to TSDC peaks (which necessarily result from a previous polarization at high temperature). It is seen that the properties of the α' TSPC peaks can vary markedly from sample to sample and batch to batch, showing that they could possibly be used as fingerprints of spatial stress heterogeneities and/or previous thermomechanical history [24].

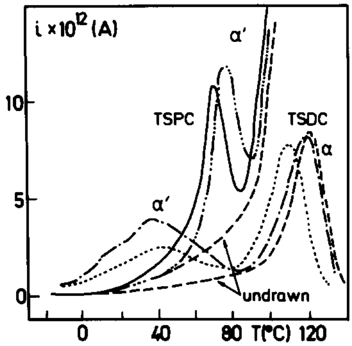

Fig. 4. TSDC and TSPC of undrawn and cold-drawn (25°C) PC (two samples cut at different places of a given original sheet). Field = 25×10^5 V m^{-1}; polarization temperature in the TSDC case = 125°C. For convenience of comparison, TSPC is reported in the same direction as TSDC.

In cold-drawn specimens of the same PC polymer, the intermediate relaxation is particularly well demonstrated in TSPC as well as in TSDC experiments following the TSPC run (and on condition that the maximum polarization temperature remains some tens of degrees below T_g); but the relaxation characteristics of the two spectra appear to be appreciably different (Fig. 4). As a matter of fact, the TSPC process, which can be ascribed to a field-induced orientation of chain segments made possible by the increase in free volume occuring in cold-drawn materials [11,25], always appears in the 60–80°C range as a well-defined, narrow peak superimposed onto the monotonously increasing conduction current. The TSDC peak, on the other hand, is markedly broadened, occasionally structured and shifted to the 40–60°C range, and its amplitude is drastically lowered. This is a clear indication that structural variations have occurred during the polarization step. In fact, this is not surprising in view of the non-equilibrium phenomena involved, since this polarization step is equivalent to annealing, under field, the drawn sample up to the maximum polarization temperature reached before cooling. This procedure is expected to have complex consequences at the TSDC level because it first involves a dipolar orientation (α' TSPC relaxation) and then, at higher temperatures, a variation in free volume involving a progressive change in dipolar environment. This probably explains the shift and widening of the relaxation in subsequent TSDC measurements as a result of widening of the distribution function of relaxation times [11]. Generally speaking, this kind of intermediate relaxation should probably be considered as a more or less proximate non-equilibrium precursor of the glass transition [26]. It should also be emphasized that the characteristics and properties of these α' TSDC and TSPC peaks depend on the drawing conditions (drawing rate, ratio and temperature) and the place where the specimen was cut, relative to the starting point of the neck [11], which confirms that the thermally stimulated current method is a very

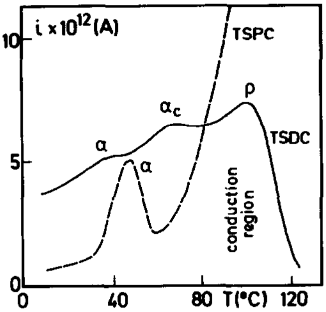

Fig. 5. TSDC and TSPC of 75% neutralized *n*-butyl methacrylate–methacrylic acid copolymer (K ionomers). Field $= 10^6$ V m^{-1}; polarization temperature in the TSDC case = 100°C. For convenience of comparison, TSPC is reported in the same direction as TSDC.

sensitive tool for investigating the thermal and mechanical history of polymers.

Temperature-dependent structures: the ionomer and halato-telechelic cases

In ionomers giving rise to formation of ionic clusters, a specific transition sometimes appears, due to molecular relaxation or ionic migration processes taking place in or at the cluster boundaries [9]. Since clusters are generally thermally breakable structures, it is obvious that their transition properties must be predominantly influenced by the thermal and electrical history of the samples, which implies that TSDC and TSPC measurements must, by nature, lead to significantly different results. This is particularly well exemplified in highly neutralized *n*-butyl methacrylate based ionomers, for which a cluster relaxation α_c appears clearly in TSDC spectra between the classical α glass transition and the space-charge process corresponding to the conduction region, but is totally absent in TSPC spectra (Fig. 5). The presence of a TSDC peak could be explained by the fact that orientation and/or migration effects occur in or at the boundaries of the cluster entities formed during the cooling step (i.e. polarization step) of the experimental procedure. During the heating step, the opposite process, i.e. dipolar disorientation and/or charge recombination, takes place, thus giving rise to a depolarization peak. On the other hand, the TSPC process does not induce any specific cluster peak because the starting structure is unoriented and the thermal breaking of clusters does not occur before the conduction region is reached (so that any dipolar motion consecutive to this thermal breaking will be masked by the conduction current).

In alkali-containing halato-telechelic polymers, which can be considered as model ionomers [10], the ionic associations are usually smaller in size (multiplets) and their thermal breaking occurs at lower temperatures. So, a specific peak related to these entities can become evident in TSDC as well as in TSPC experiments, where it appears more or less superimposed onto the normal conduction current, depending on the type of cation and degree of neutralization [27] (Fig. 6).

CONCLUSIONS

It has now been extensively demonstrated that the thermally stimulated depolarization current method can be considered as a very sensitive probe of kinetic transitions and molecular relaxation processes in polymers. In this paper, we have shown by means of some characteristic examples, that a full understanding of the underlying mechanisms, especially in connection with the thermal and mechanical history of the samples, requires in fact a conjugated use of both depolarization (TSDC) and polarization (TSPC) current methods. This is particularly true for studying relaxations related either to non-equilibrium intermediate processes (such as those resulting from previous, more or less severe, thermal or mechanical treatments) or to thermally unstable structures (such as clusters and multiplets in ionomers and halato-telechelic polymers).

In addition, the TSPC method, in spite of some experimental difficulties resulting from the possible interference of conduction or injection phenomena, has the advantages that it avoids overheating the samples and allows us, in favorable cases, to obtain direct information on the thermal expansion effects, and the importance and type of the temperature dependence characterizing the equilibrium polarization.

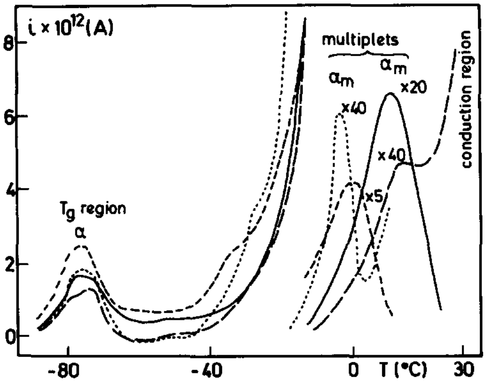

Fig. 6. TSDC and TSPC curves of Na-containing halato-telechelic polymers for two degrees of neutralization. Field $=10^6$ V m^{-1}; polarization temperature in the TSDC case = 25°C. (------) TSDC 80%; (———) TSDC 100%; (······) TSPC 80%; (— — —) TSPC 100% neutralization. For convenience of comparison, TSPC is reported in the same direction as TSDC.

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