Thermally Stimulated Discharge Current Studies on Low-Temperature Relaxations in Polycarbonate

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Synopsis

The β-relaxation in polycarbonate has been investigated by the thermally stimulated discharge current (TSC) technique. The polarization of the β-peak in polycarbonate is shown to be uniform. Two broad peaks centered at 130° and 200°K were observed. Furthermore, two single relaxation processes were resolved for the lower temperature peak. The high temperature peak was also resolved into two peaks, however, only one of them was a single relaxation process. The individual peaks satisfied the dipolar theory, and the three peaks are associated with activation energies of 0.24, 0.27, and 0.47 eV, and temperatures of the peak maxima were 121°, 131°, and 193°K, respectively. The mechanism attributed to each peak is discussed and does not appear to contradict the results of conventional dielectric and mechanical relaxation and NMR measurements on the β-relaxation in polycarbonate.

INTRODUCTION

Polycarbonates are members of the class of polyesters which contain phenyl groups in the main chain. The polycarbonate used in the present study is the commercially available polyester prepared by the condensation of bisphenol A (4,4'-dihydroxydiphenyl-2,2-propane) with phosgene in pyridine.[1,2]

The commercial importance of the material is due to its relatively high glass transition, its superior ductility, and high impact strength below T_g. The high impact strength has been attributed to molecular motions of the main chain at low temperatures.[3,4] Those motions are evidenced by a low-temperature secondary relaxation (β-relaxation).

Mechanical and dielectric relaxations on the β-relaxation in polycarbonate have been extensively studied.[3–11] From extensive studies of dielectric relaxation on solid polymers with polar group, Ishida[12–14] and Havriliak[15] assigned the low-temperature β-relaxation to the motion of polar groups. However, from investigations on phenyl-containing polyurethanes, Kajiyama and MacKnight[16] assigned the β-relaxation to the torsional motion of the phenyl groups. From dielectric relaxation and nuclear magnetic resonance studies on polycarbonate, Matsuoka and Ishida[6] suggested that the β-relaxation should be attributed to the combination of its polar groups and phenyl groups. Using several different techniques on polycarbonate (mainly NMR, dielectric, and mechanical) in the temperature range of −150°C to room temperature, Locati and Tobolsky[4] resolved the broad β-relaxation process into

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two components. They assigned one of the two processes (the peak at lower temperature) to relaxation of carbonate groups and the other (the peak at higher temperature), to some restricted motions of the phenyl groups.

The investigation of the dielectric relaxation by the alternating field method and the dynamic mechanical relaxation is, in general, complicated when several relaxation processes coexist at the same temperature. The contribution of different relaxation mechanisms can be distinguished in the dispersion curve only if the corresponding relaxation times differ appreciably. Furthermore, the dielectric measurement by the alternating field method has another complication where there is a nonvanishing electric conductivity within the material, because it builds up a space charge on the interfaces between a sample and electrodes which can stimulate an additional polarizing mechanism superimposed with the true dielectric dispersion.

A new method of studying dielectric relaxation which eliminated the complications mentioned above was introduced by Bucci and co-workers.[17-19] Although nonisothermal dielectric relaxation has been investigated since 1936, it was not until 1966 that its theoretical basis was given by them. The theory is very similar to that of thermoluminescence[20-23] or electrical glow[24-27] (see theory section). This method allows a precise analysis of the single relaxation process and gives a complete picture of the temperature-dependent relaxation. It also allows the parameter of dipole relaxation time and activation energy to be determined from a single measurement with higher accuracy than the conventional dielectric relaxation measurements. The method has been widely used in studies of alkali halides.[17-19] Recently, Perlman,[28-29] Creswell,[30] Turnhout,[31] Gross,[32] and others[33-35] have applied it for studying the electret effect and the relaxation mechanism in polymers quantitatively and they called it Thermally Stimulated Discharge Current (TSC or TSD) Method.

Thermally stimulated discharge current measurements have now become a powerful tool for observing the molecular motion in polymers. Takamatsu and Fukuda[33] have found several peaks for low-density and high-density polyethylene and Teflon by means of the TSC method. They have been able to associate molecular motion to several peaks, although a few peaks remain unidentified. Furthermore, Perlman has succeeded in separating the overlapping bands into several individual peaks by a peak cleaning method[28] and the individual peaks satisfied the TSC theory.

The objective of the present study was to promote a better understanding of the relaxation mechanism of the β-relaxation in polycarbonate by using the recently developed TSC method. The relaxation time and the activation energies have been calculated for the β-peaks in polycarbonate and a theoretical fit to the present data has been performed.

THEORY

The TSC theory is summerized here. For the temperature-dependent relaxation time of the dipoles in a dielectric, an Arrhenius equation is appropriate and given as

$$\tau(T) = \tau_0 \exp (U/kT) \tag{1}$$

where τ_0 is constant, k is the Boltzmann constant, and U is the potential barrier between a normal state and an activated state (the activation energy).

The rate of change of the polarization P is related to $P(t,T)$ and the relaxation time $\tau(T)$ by the equation

$$dP(t,T)/dt = -P(t,T)/\tau(T) \tag{2}$$

Since $\tau(T)$ is also a function of time for nonisothermal measurements, the solution of eq. (2) satisfies

$$P(t,T) = P_0 \exp\left(-\int dt/\tau(T)\right) \tag{3}$$

Here, P_0 is given by

$$P_0 = Np^2\alpha E_p/kT_p \tag{4}$$

where N is the number of dipoles per unit volume, p is the dipole moment, E_p is the polarizing field, T_p is the polarizing temperature, and α is a geometrical factor which is $\frac{1}{3}$ for freely rotating dipoles.

The depolarization current is expressed as

$$I(t,T) = -P(t,T)/\tau(T) \tag{5}$$

or

$$I(t,T) = -(P_0/\tau(T)) \exp\left(-\int dt/\tau(T)\right) \tag{5'}$$

If the dielectric is warmed at a uniform rate, then

$$T = a + bt \tag{6}$$

where T is the temperature, t is the time, and a and b are constants.

Combining eqs. (1), (4), (5'), and (6), one has an expression for the TSC curve, i.e.,

$$I(T) = (Np^2\alpha E_p/kT_p\tau_0) \exp\left[-U/kT\right.$$
$$\left. - (1/b\tau_0) \int_{T_0}^{T} \exp(-U/kT)dT\right] \tag{7}$$

The temperature T_m at which the maximum current occurs $(dI(T)/dT = 0)$ can be written as

$$\tau_0 = \frac{kT_m^2}{bU \exp(U/kT_m)} \tag{8}$$

and the low-temperature tail from eq. (7) is given by

$$\ln I(T) = \text{const} - U/kT \tag{9}$$

Thus, the activation energy U can be determined from a semilogarithmic plot of $I(T)$ versus $1/T$ (this is the initial rise method of Garlick and Gibson[27]), and then τ_0 can be determined from eq. (8).

The activation energy U and τ_0 can also be obtained by utilizing the whole curve $I(T)$ and the following equation:

$$\ln \tau(T) = \ln \tau_0 + U/kT = \ln\left[\int_{t(T)}^{\infty} I(t)dt\right] - \ln I(T) \tag{10}$$

By plotting $\log \tau(T)$ versus $1/T$, the slope and intercept give the activation energy U and τ_0. The total charge released is given by

$$Q = \int_0^\infty I(t)dt \tag{11}$$

Cowell and Woods[36] proposed an approximate form of eq. (7). By putting $s = U/kT$, eq. (7) can be written as

$$I(s) = A \exp\left[-s + B \int_{s_0}^s \exp(-s)s^{-2}ds\right] \tag{12}$$

where $A = Np^2\alpha E_p/kT_p\tau_0$ and $B = U/kb\tau_0$. Repeated integration by parts of the integral in eq. (12) leads to a convergent infinite series for $I(s)$:

$$I(s) = A \exp[-s - B\{\exp(-s)s^{-2} - 2\exp(-s)s^{-3} + 6\exp(-s)s^{-4}\ldots\}^s_{s_0}] \tag{13}$$

Since s is large in practice, in the range of 15–40 (20–30 in the present work), $I(s)$ can be approximated by dropping all but the first three terms in the series; then

$$I(s) \simeq A \exp[-s - B\{\exp(-s)(s^{-2} - 2s^{-3} + 6s^{-4})\}^s_{s_0}] \tag{14}$$

Differentiating eq. (14) to obtain the maximum of the TSC curve leads to

$$B' = \exp(s^*)\frac{(s^*)^5}{(s^*)^3 + 24} \tag{15}$$

where B' is the approximate value of B and $I(s)$ is a maximum at s^*. The true value of B can be obtained by differentiating eq. (12):

$$B = \exp(s^*)(s^*)^2 \tag{16}$$

The fractional error between the true B and B' is

$$\frac{B - B'}{B} = \frac{24}{(s^*)^3 + 24} \tag{17}$$

The lowest value of s^* in the present work is about 20, so that the largest error between B and B' is within 0.01%, which is negligible. The value A can be obtained by normalizing $I(s)$ in eq. (14) to the experimental curve at maximum current. All calculations have been made on a CDC 6000 and compared to the experimental data.

EXPERIMENTAL

The polymer selected for this work was polycarbonate supplied by General Electric Co. Films were cast onto a Pyrex substrate from a solution of 150 g polycarbonate per liter solvent, methylene chloride. The 5-mil-thick films were allowed to dry in air for several hours. The films were then put into an oven and the temperature was gradually increased to 120°, held for 1 hr, and cooled to the room temperature. Test specimens for TSC measurements were cut in the form of a flat disk $1\frac{1}{8}$ in. in diameter.

Evaporated silver electrodes $\frac{3}{4}$ in. in diameter were used for eliminating homocharging.[30] All silver evaporated specimens were kept in an evacuated
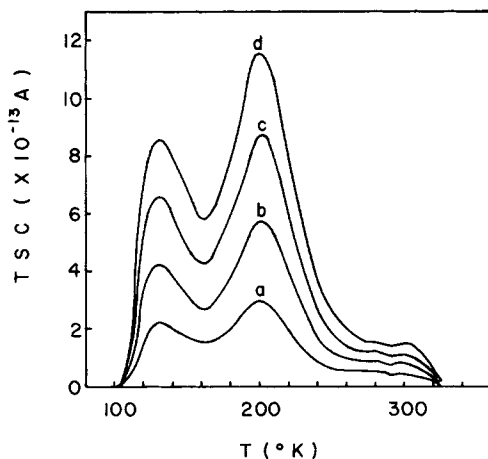
Fig. 1. Thermally stimulated current vs. temperature for various polarizing fields E_p. (a), (b), (c) and (d) correspond to $E_p = 7.87$, 15.7, 23.6, and 31.5 kV/cm, respectively.

desiccator for several weeks before use in order to eliminate residual solvent and water. Copper was used for the specimen holders and the guard ring. A copper–constantan thermocouple was inserted into the one of the specimen holders for temperature monitoring.

A static electric field was applied to the specimen in a capacitor configuration at room temperature. The specimen was then cooled down to about 100°K with the electric field sustained. The electric field was removed and specimens were short-circuited for about 20 min in order to eliminate the rapid discharge. The TSC spectrum was detected by a vibrating capacitor electrometer (Keithley Model 640) at a constant heating rate. The linear heating rate was accomplished by using a nichrome wire heater which was located around the specimen holders, controlled by R. I. Thermac Controller and R. I. Data-Trak. An X-Y recorder (Moseley Model 135) was used to trace the TSC versus temperature, and an X-Time recorder was also used to trace temperature versus time and check the constant heating rate.

The TSC measurement was carried out in a small amount of the dry high-purity nitrogen in order to facilitate the heat transfer. Most of the TSC measurements were carried out at a heating rate of 3°C/min. This rate ensured a good resolution of the spectrum and gave current values which were sufficiently high to make the background current negligible. To assist in the analysis of the TSC spectrum, partial heating,[28] peak cleaning,[30] and theoretical fitting were also performed.

RESULTS

The TSC spectra obtained from polycarbonate charged at 20°C for periods of 10 min for different polarizing fields and a heating rate of 3°C/min are shown in Figure 1. All curves show two prominent peaks. The maximum temperatures of those peaks are independent of the polarizing field. One maximum occurs at 130°K and the other, at 200°K. The relationship between the maximum current of the TSC peak and the polarizing field is
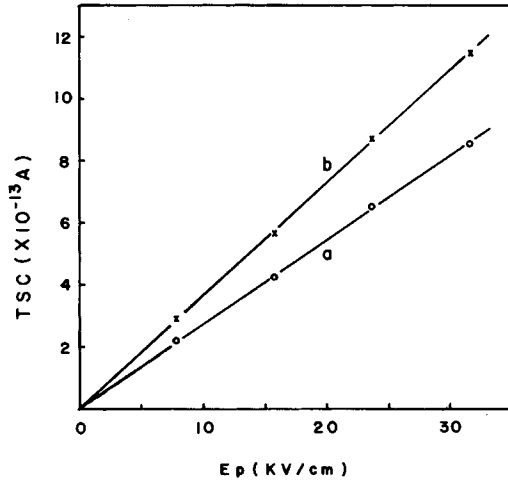
Fig. 2. Maximum current in the TSC peak vs. polarizing fields: (a) and (b) correspond to the peak at 130°K and the peak at 200°K, respectively.
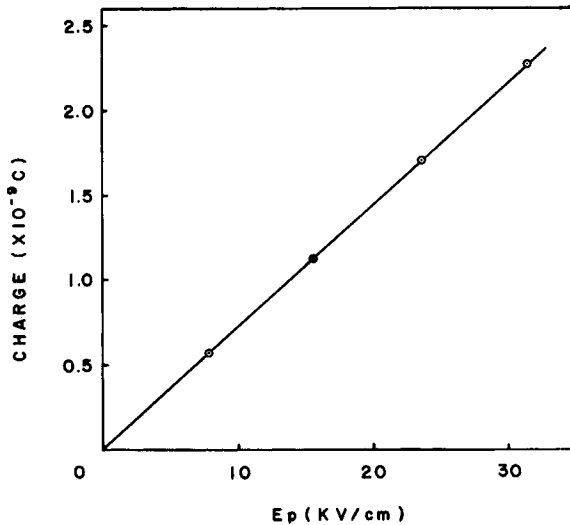

Fig. 3. Charge released to external current vs. polarizing field.

shown in Figure 2. The relationship is seen to be linear for 130° and 200°K peaks, respectively.

Figure 3 shows the polarizing field dependence on the total charge released to the external current which can be obtained by integrating the TSC spectrum in terms of time from $t = 0$ to $t = \infty$. A linear relationship was also found between them. Figure 4 shows the TSC spectra for constant polarization field (31.5 kV/cm) and polarizing temperature (20°C for 10 min) but varying heating rate. Both peaks are seen to be increased in strength and to be shifted slightly to higher temperature on increasing the heating rate. If one assumes that each peak consists of a single relaxation, a plot of $\ln (b/T^2{}_m)$ versus $1/T_m$, where T_m is the temperature at which TSC spectrum shows a maximum, can be used along with eq. (8) to obtain the activation energy.
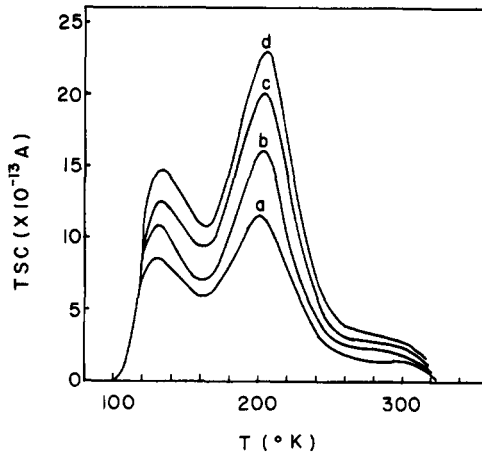
Fig. 4. Thermally stimulated current vs. temperature for various heating rates: (a), (b), (c), and (d) correspond to $b = 3°$, $4°$, $5°$, and $6°C/min$, respectively; $E_p = 31.5$ kV/cm and $T_p = 20°C$.
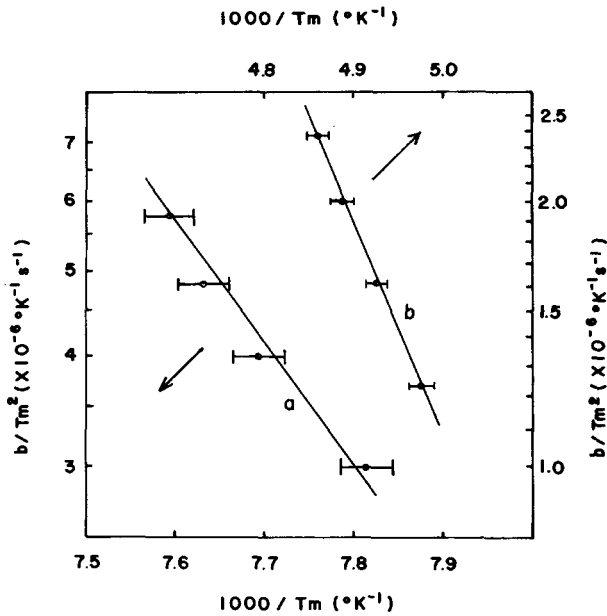

Fig. 5. Plot of $\ln (b/T_m^2)$ vs. $1000/T_m$: (a) and (b) correspond to the peak at 130°K and the peak at 200°K, respectively.

The slopes in Figure 5 give the activation energies for the two peaks, 0.27 ± 0.05 eV for the lower temperature peak ($T_m \simeq 130°K$) and 0.5 ± 0.1 eV for the higher temperature peak ($T_m \simeq 200°K$).

In order to isolate the individual peak from all others, a partial heating method and a peak cleaning method were applied. The complete TSC spectrum was obtained for polycarbonate polarized with 31.5 kV/cm at 20°C for 10 min at a heating rate of 3°C/min (TSC spectrum d in Fig. 1). Then, in order to apply the partial heating method, the specimen was charged and
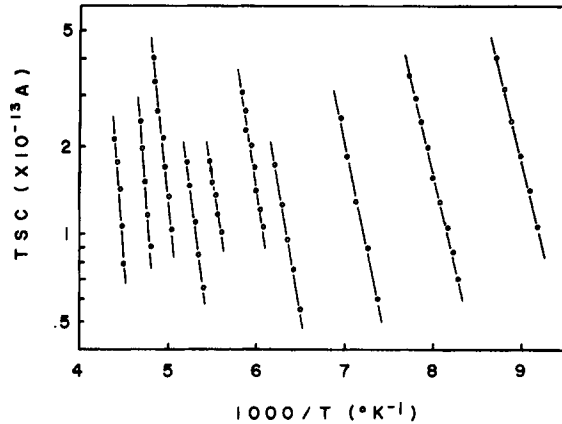
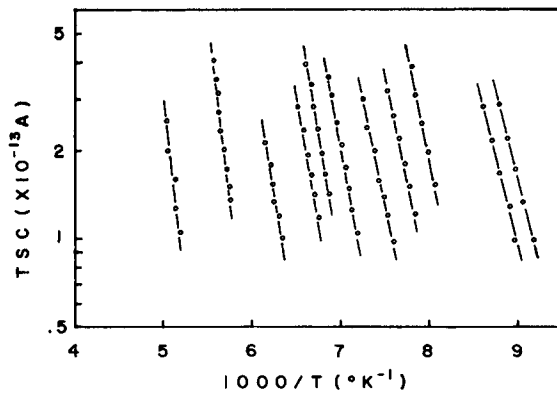Fig. 6. Plot of ln (TSC) vs. 1000/T for partial heating experiments (first run).

Fig. 7. Plot of ln (TSC) vs. 1000/T for partial heating experiments (second run).

cooled down again under the same conditions as the initial run. The specimen was then discharged by successively heating from low temperature (~100°K) to an elevated temperature of 5° ~ 10°C higher than the previous maximum and cooling down the specimen between each step. These procedures were repeated many times. The partial heating method was applied twice to the same specimen.

The results of the first and second experiments are shown in Figures 6 and 7, respectively. The activation energy calculated from the slope of the straight line in Figures 6 and 7 is plotted against the maximum temperature reached in each partial heating in Figure 8. There are four flat spots on the curve corresponding to activation energies of 0.24, 0.27, 0.35, and 0.47 eV. The results of a peak cleaning experiment are shown in Figure 9. After polarizing at room temperature and cooling to 100°K, the temperature was increased to about the temperature (130°K) where the first constant activation energy ended and curve a was obtained. The specimen was again cooled and the TSC redetermined by heating up to the temperature (140°K) where the second constant activation energy ended. To obtain curve b, one has to normalize the data to subtract the contribution made by this peak cleaning pro-
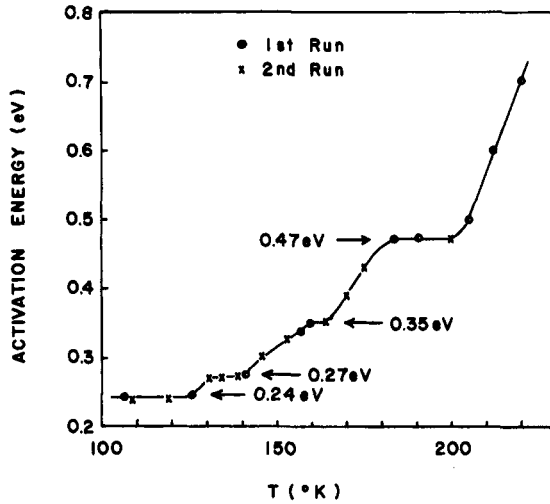
Fig. 8. Determination of activation energies U from partial heating experiments in Figs. 6 and 7.
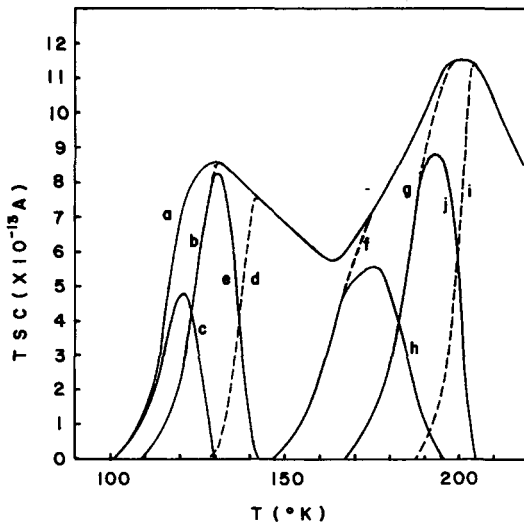

Fig. 9. Thermally stimulated current vs. temperature for peak cleaning: (c), (e), (h), and (j) are the isolated peaks.

cedure.   Peak c results from subtracting b from a.   These procedures were repeated for the other three peaks.   Finally, peaks c, e, h, and j were obtained.

In order to analyze each isolated peak, a theoretical fit was applied and is shown in Figures 10 and 11.   Peaks 1 and 2 in Figure 10 and peak 2' in Figure 11 satisfy the TSC theory very well, while peak 1' in Figure 11 does not.   The parameters P_0, U, and τ_0 were calculated for those three peaks which satisfied the theory and are shown in Table I.   From the relaxation time at $T = 293°K$ (20°C) in Table I, the polarizing time 10 min at 20°C in our experiments is seen to be long enough to saturate the polarizations of three peaks.
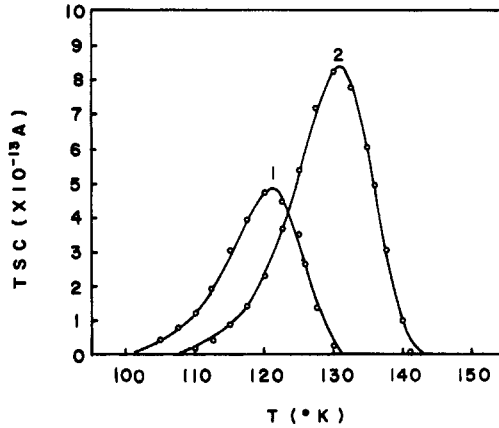
Fig. 10. Curve fit by Cowell and Woods method: (O) experimental points and solid line is theoretical fit; (1) and (2) correspond to peaks (c) and (e) in Fig. 9, respectively.
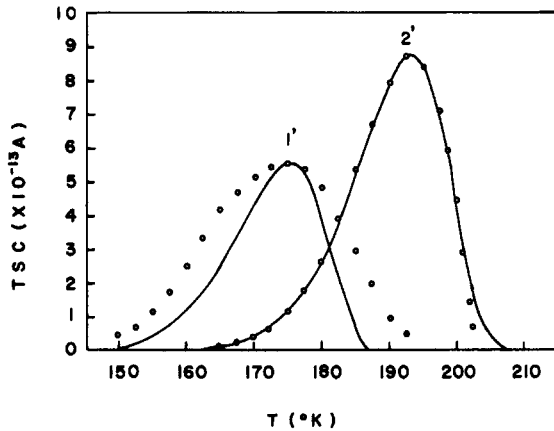

Fig. 11. Curve fit by Cowell and Woods method: (O) experimental points and solid lines are theoretical fit; (1') and (2') correspond to peaks (h) and (j) in Fig. 9, respectively.

DISCUSSION

Polarization of solid dielectrics can be produced by two different mechanisms. One is a heterocharge and the other, a homocharge (the Gross two-charge theory[38,39]). The heterocharge is a uniform volume polarization and can be produced by dipole alignment or migration of ions over microscopic distances with trapping.[28] The homocharge is an ionic surface charge (non-uniform volume polarization) and can be produced by space charge buildup associated with migration of ions over macroscopic distances or charge injection from the electrodes. Since we are interested in the molecular movements inside materials, only a uniform volume polarization should be distinguished from a surface charge. The charge injection can be eliminated by using evaporated metal electrodes,[31] and the space charge due to ions can be neglected by applying a relatively low electric field to electrodes.[40]

The results shown in Figures 2 and 3 indicate that the polarization in polycarbonate from 100° to 320°K with the present experimental conditions is

TABLE I
Numerical Results of TSC for Polycarbonate[a]

	T_m, °K	$P_0 \times 10^{-11}$, C/cm²	$I(T_m) \times 10^{-13}$, A	U, eV	$\tau_0 \times 10^{-11}$, sec	$\tau(T = 293°\,K) \times 10^{-4}$, sec	U, eV	$\tau_0 \times 10^{-11}$, sec	$\tau(T = 293°\,K) \times 10^{-4}$, sec
					Initial rise method			Whole curve method	
Peak 1	121	4.42	4.75	0.24	1060	1.43	0.23	3190	2.89
Peak 2	131	8.04	8.30	0.27	448	1.98	0.28	195	1.28
Peak 2'	193	10.8	8.80	0.47	7.26	88.3	0.48	3.60	65.6

[a] E_p = 31.5 kV/cm, T_p = 293° K, and b = 3° C/min.

uniform. Namely, the charge injection from electrodes or the space charge due to ions (nonuniform polarization) is not detected by using the evaporated silver electrodes and applying an electric field up to about 32 kV/cm to polycarbonate below room temperature.

According to Jonscher,[40] the activation energy associated with migration of ions over microscopic distances in amorphous materials is 0.6–0.8 eV or higher. Since the activation energies of the β-relaxation process in polycarbonate are about 0.8 eV or less, the polarization of polycarbonate at low temperature must be mainly produced by dipole alignment.

Nuclear magnetic resonance measurements on polycarbonate in the temperature region where it exhibits the β-relaxation have been investigated by many workers.[6,41-43] From their studies, it can be seen that the protons of methyl groups undergo a motional narrowing of line width in the temperature region from 110° to 130°K, while the protons of the phenyl group undergo a narrowing of line width in the region from 165° to 220°K. The former narrowing is centered at about 120°K and the latter, at 193°K. Comparing the results from NMR measurements to those from TSC, we may assign peak 1 (maximum at 121°K) and peak 2' (maximum at 193°K) to local motions involving methyl groups and phenyl groups, respectively.

The methyl group relaxation originates from a change in the distribution of angular displacement of methyl groups. The characteristics of the methyl group relaxation are expressed by its narrow distribution of the relaxation time and as a single relaxation process. The activation energy of the relaxation process for methyl groups in polymers like polycarbonate is about 0.2 to 0.3 eV.[44] The relaxation process of peak 1, Figure 10, observed from 100° to 130°K in our TSC measurement is centered at 121°K with the activation energy 0.24 eV and is expressed as a single relaxation process which satisfies the TSC theory. Calculation of the dipolar polarization by methyl groups using eq. (4), assuming a reasonable dipole moment $0.4D$,[45] results in a value of 11 $\times$ 10^{-11}C/cm², which is very close to the experimental value of 4.42 $\times$ 10^{-11}C/cm² in Table I. Thus, we may conclude that the peak whose maximum is at 121°K in polycarbonate is associated with local motions of methyl groups.

It has been generally accepted by all recent workers in this field that the

β-relaxation in polycarbonate is mainly attributed to molecular motions of phenyl groups and carbonate groups. From investigations of polycarbonate by stress relaxation experiments, Locati and co-workers[4] have resolved two peaks in the β-relaxation. One is at 150°K and the other at 190°K with activation energies 0.35 and 0.56 eV, respectively. They have suggested that the lower temperature component of the β-relaxation in polycarbonate is associated with movements of the carbonate groups, while the higher one is associated with some restricted motions of the phenyl groups. Since the NMR investigations on polycarbonate as mentioned before indicate that the phenyl groups initiate their molecular motions around 165°K, the relaxation process for peak 2 (maximum at 131°K) cannot be attributed to the motion of phenyl groups.

In their work on polycarbonate, Matsuoka and Ishida[6] and others[4,11] reported an activation energy for the dielectric β-relaxation of approximately 7 kcal/mole (≈ 0.3 eV). Since the carbonate group offers the only dipolar group except the methyl group (which has a much smaller dipole moment than the carbonate group) in the main chain, it is plausible that the dielectric relaxation is due mainly to the movement of this group. The activation energy obtained by a TSC measurement for peak 2, Figure 10, is 0.27 eV, which agrees very well to the activation energy of the carbonate group determined from the conventional dielectric measurements. Therefore, we propose that the peak at 131°K is associated with the movement of the carbonate groups. Since the movement of the carbonate group is restricted by the phenyl group in the main chain,[4,6] the polarization produced by the carbonate groups in our TSC measurement seems to be much smaller than the theoretical value assuming that the polar group can move freely. Calculation of the polarization produced by the carbonate group, taking the dipole moment to be $1.4D$,[45] results in a value of $P_0 = 1.6 \times 10^{-9}$ C/cm^2, which is much larger than the experimental value 8.04×10^{-11} C/cm^2. Thus, the peak at 131°K appears to be associated with the movement of the carbonate groups restricted by the phenyl groups in the main chain.

From extensive work on low-temperature mechanical and dielectric relaxation in polymers containing aromatic groups, Chung and Sauer[46] and Rigby and Dew-Hughes[47] have determined the activation energies associated with various types of aromatic groups and observed values of $U = 8 \sim 11$ kcal/mole ($0.3 \sim 0.5$ eV). The NMR investigations on polycarbonate as mentioned before indicate that phenyl groups initiate their molecular motions around 165°K. Hence, the relaxation of the peak at 193°K associated with the activation energy 0.47 eV is reasonably attributed to the movements of phenyl groups accompanying molecular motions of the carbonate groups in the main chain of polycarbonate.

Although additional peaks appear to exist between 140° and 180°K, the mechanisms for those peaks have not been well defined. They are probably complex relaxations associated with the peculiar movement of the carbonate groups restricted by the phenyl groups in the main chain. The peaks above 210°K which have activation energies larger than 0.6 eV, as shown in Figure 8, can probably be assigned to the migration of ions over microscopic distances with subsequent trapping inside polycarbonate, because an activation energy which is larger than 0.6 eV shown would normally be associated with ionic transport, as suggested by Jonscher.[40]

CONCLUSIONS

In conclusion, the TSC technique has been found to be a very powerful tool for investigating the molecular motions in polymers. The apparent activation energies for the peaks has been estimated by changing the heating rate, as shown in Figure 5. The values 0.27 ± 0.05 eV and 0.5 ± 0.1 eV for two β-peaks in polycarbonate from our TSC measurements are very close to the values 0.35 and 0.56 eV obtained by Locati and co-workers[4] from their stress relaxation experiments. Furthermore, an individual relaxation process with a single relaxation time can be resolved by the application of the partial heating and peak cleaning techniques to broad relaxations. The activation energy and the relaxation time for individual peaks have been obtained by the two methods and shown in Table I. The activation energy $\cdot U$ and τ_0 determined by the two methods are very consistent with each other and are found to be in good agreement with the theoretical values within the experimental error. The error produced by the experimental limitation of the TSC measurements has been found to be much smaller than that of the conventional dielectric and mechanical relaxation measurements.

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