Thermally stimulated current study of relaxation in glassy polycarbonate

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The transitions/relaxations of polycarbonate around its glass transition temperature, T_g, have been investigated by differential scanning calorimetry and thermally stimulated current spectroscopy. A sub-glass transition/relaxation has been observed with higher intensity in the quenched sample. This precursor of T_g is characterized by relaxation times following a Fulcher–Vogel equation. It might be explained by the diffusion of conformational defects all along the chain. The glass transition/relaxation is constituted of two components: (i) The lower-temperature component is associated with a distribution of relaxation times obeying a compensation law. It corresponds to cooperative movements of sequences of various length in the 'true' amorphous regions. (ii) The upper-temperature component is enhanced by annealing above T_g. It has been attributed to the 'constrained' amorphous regions. Note that such domains with high local order have been previously observed by electron microscopy and X-ray diffraction.

(Keywords: thermally stimulated currents; polycarbonate; vitreous state; annealing; polarization)

INTRODUCTION

Polycarbonate has a particular place among thermoplastics because of its excellent impact strength properties[1–4]. Several studies have reported their evolution with time, temperature and thermal history[5,6]. The corresponding structural evolution probably involves conformational changes towards a more stable state. Such modifications can be studied by thermal techniques[7], dielectric relaxation[8–10] and mechanical experiments[11,12]. They have a strong influence on the secondary transition/relaxation located in the 60–100°C range and designated as the sub-glass transition/relaxation. They also modify the glass transition/relaxation significantly.

In fact, the evolution of both transitions/relaxations reveals that they are complex. The aim of this work is to explore the fine structure in order to determine precisely the nature of molecular or morphological entities that are involved. Two thermally stimulated techniques have been applied to this study: differential scanning calorimetry (d.s.c.) and thermally stimulated current (t.s.c.).

MATERIALS AND METHODS

Materials

Bisphenol A polycarbonate, Lexan, from General Electric has been studied. Samples have been used first in their initial state, i.e. after quenching: they will be designated as quenched polycarbonate. Two annealings have also been performed: the first series has been annealed for 2 min at 190°C; the second series has been annealed for 5 min at 230°C.

Methods

Thermally stimulated current principle. The principle of the t.s.c. technique is as follows. The sample is polarized by a static electric field E at temperature T_p. When the polarization P has reached its equilibrium value, the temperature is decreased till $T_0 \ll T_p$ in order to freeze this configuration. Then, the field is cut off. The polarization recovery is induced by increasing the temperature in a controlled manner. The depolarization current j flowing through the external circuit is measured by an electrometer and the 'dynamic conductivity' $\sigma \equiv j/E$ can be calculated.

Let us consider an elementary polarization P that varies exponentially with time, at a given temperature T:

$$\mathrm{d}P/\mathrm{d}t = -P/\tau \qquad (1)$$

where τ is the relaxation time and $j \equiv |\mathrm{d}P/\mathrm{d}t|$ is the depolarization current. During a thermal stimulation, which can be considered as a series of equilibrium states at a given temperature, the temperature dependence of the relaxation time can be calculated from:

$$\tau(T) = |P(T)/j(T)| \qquad (2)$$

In polymers, the polarization P is complex. By using fractional polarization, it is possible to isolate an elementary polarization P_i such that:

$$P = \sum_i P_i \quad \text{with} \quad \frac{\mathrm{d}P_i}{\mathrm{d}t} = -\frac{P_i}{\tau_i} \qquad (3)$$

Fractional polarization principle. The principle of the fractional polarization procedure is the following:

(i) The sample is subjected to the electric field for a time (2 min) at a temperature (T_p) allowing the polarization of the dipolar entities having relaxation times $\tau \leqslant \tau_i$.

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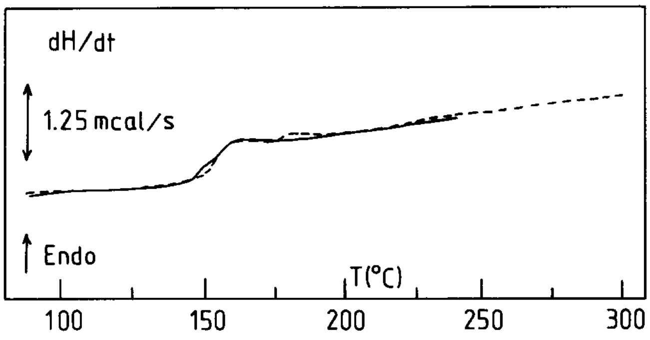

Figure 1 D.s.c. thermograms of polycarbonate: (——) quenched; (– –) annealed

(ii) Then the temperature is decreased by 10°C and the field is cut off. The temperature is maintained constant for another 2 min for allowing disorientation of the dipoles having a relaxation time $\tau < \tau_i$.

This configuration is frozen and a classical t.s.c. scan shows the response of a monokinetic process giving an elementary t.s.c. spectrum. Then equation (2) can be used for calculating the relaxation time. By shifting the 'temperature window' along the temperature axis, the whole relaxation-time spectrum can be explored.

Relaxation map analysis (r.m.a.). The temperature dependences of the various relaxation times are plotted on an Arrhenius diagram to give the relaxation map of the material. The analysis is performed automatically on the TSC/RMA spectrometer from Solomat that has been used for the experiments.

EXPERIMENTAL RESULTS

Differential scanning calorimetry

A comparative study of reference and annealed polycarbonate has been performed on a differential scanning calorimeter DSCII from Perkin-Elmer. *Figure 1* shows the time derivative of the enthalpy $\mathrm{d}H/\mathrm{d}T$ *versus* temperature T for reference (full curve) and annealed (broken curve) polycarbonate. In both samples, the classical step of the glass transition is observed around 150°C. For the reference polycarbonate we note at the glass transition onset a shoulder that disappears after annealing: this thermal event has been associated with the sub-T_g mode. Moreover the annealing reveals an endothermic phenomenon around 25°C above the glass transition. These results are in good agreement with data previously published by Enns and Boyer[13].

Thermally stimulated currents

The depolarization of polycarbonate is of course strongly dependent upon its thermal treatment. The corresponding t.s.c. spectra have been resolved, experimentally, by the technique of fractional polarization.

Complex spectra. Figure 2 shows the variation of the dipolar conductivity (σ) *versus* temperature (T) of polycarbonate with different thermal history: the full curve is for quenched polycarbonate, the chain curve corresponds to polycarbonate annealed at 190°C and the broken curve is for polycarbonate annealed at 230°C. The three spectra have been polarized according to the same procedure: the electric field ($E = 10^5\ \mathrm{V\ m^{-1}}$) was applied for 2 min at the polarization temperature indicated by an arrow on *Figure 2* ($T_p = 175$°C). It is important to note that the t.s.c. spectrum of quenched polycarbonate is perfectly reproducible if the temperature of the sample is lower than 175°C. This t.s.c. peak is situated at 155°C, i.e. in the vicinity of the glass transition temperature T_g (cf. *Figure 1*). So, it has been associated with the dielectric manifestation of the glass transition. After thermal treatment at 190°C, an additional t.s.c. peak appears above the glass transition temperature (chain curve on *Figure 2*). After a thermal treatment at 230°C (broken curve on *Figure 2*) its temperature position remains stable at 175°C. At the same time the sub-T_g mode decreases.

Fine structure of complex spectra. The resolution of the fine structure of the complex t.s.c. spectra of polycarbonate has been performed using the fractional polarization technique[14]. The polarizing field is the same as that for the complex t.s.c. spectrum; a temperature window of 10°C shifted by 5°C has been used. In these conditions, the elementary t.s.c. peaks are uniformly shifted along the temperature axis. *Figure 3* shows as an example the elementary peaks isolated in quenched polycarbonate around the glass transition, indicating a wide distribution of relaxation times. The maximum temperature T_m of elementary peaks obtained in the quenched polycarbonate and in the polycarbonate annealed at 230°C are listed respectively in *Tables 1a* and *1b*. Each elementary peak has been analysed and the relaxation times have been calculated from equation (2). Then, the experimental points have been plotted on an Arrhenius diagram: *Figures 4a* and *4b* correspond respectively to the quenched polycarbonate and to the polycarbonate annealed at 230°C.

Relaxation map analysis

Arrhenius relaxation times. T.s.c. peaks situated at $120°\mathrm{C} < T_m < 173.5°\mathrm{C}$ (*Table 1a*) and at $133.5°\mathrm{C} < T_m < 176.5°\mathrm{C}$ (*Table 1b*) are characterized by relaxation times following an Arrhenius equation:

$$\tau = \tau_{0a} \exp(\Delta H / kT)$$

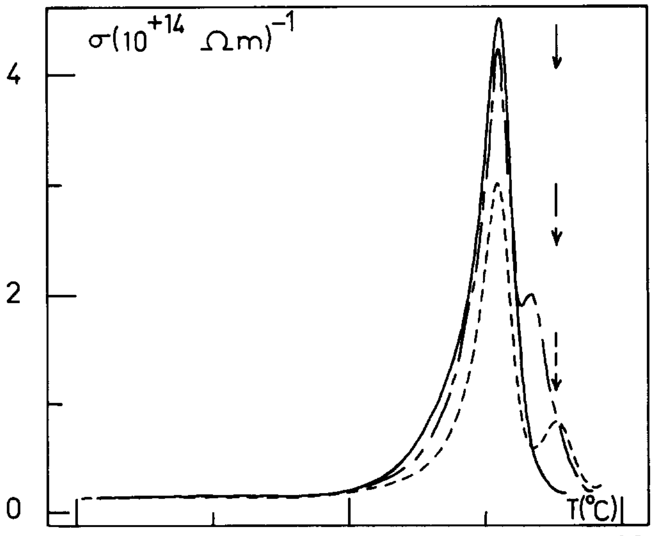

Figure 2 T.s.c. spectra of polycarbonate: (——) quenched; (– —) annealed at 190°C; (– –) annealed at 230°C

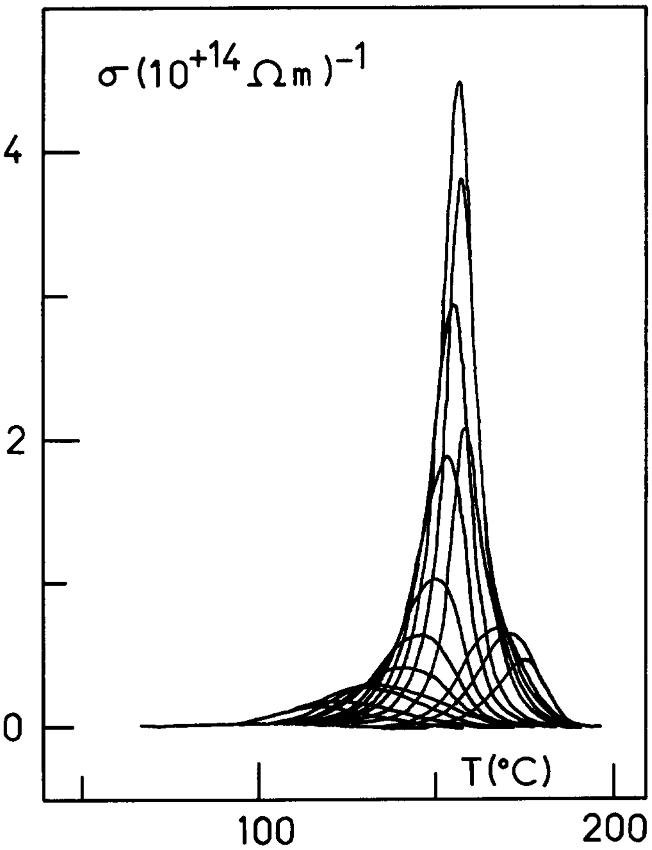

Figure 3 Elementary peaks isolated in reference polycarbonate

Table 1 Activation parameters of relaxation times: (a) in the quenched polycarbonate; (b) in the annealed polycarbonate
(a) Quenched PC

T_m (°C)	ΔH (eV)	τ_{0a} (s)
116	1.64 ap	3.60×10^{-20} ap
120	1.63	9.65×10^{-20}
128.5	1.60	5.65×10^{-19}
131	1.62	4.90×10^{-19}
139.5	1.72	5.85×10^{-20} C
144.5	1.94	2.00×10^{-22} C
149.5	2.02	3.80×10^{-23} C
152.5	2.33	1.30×10^{-26} C
155	2.55	3.80×10^{-29} C
156.5	2.64	5.55×10^{-30} C
157	2.96	1.25×10^{-33} C
158	3.29	2.40×10^{-37} C
166	3.02	9.45×10^{-34}
170	2.94	1.25×10^{-32}
173.5	2.94	2.85×10^{-32}

(b) Annealed PC

T_m (°C)	ΔH (eV)	τ_{0a} (s)
128	1.61 ap	2.95×10^{-19} ap
133.5	1.65	2.50×10^{-19}
141	1.75	2.70×10^{-20}
145.5	1.87	1.25×10^{-21} C
151	1.91	9.00×10^{-22} C
152.5	2.28	3.80×10^{-26} C
155	2.60	1.00×10^{-29} C
156.5	3.17	3.05×10^{-36} C
157.5	3.63	1.55×10^{-41} C
158.5	4.59	9.35×10^{-53} C
176.5	3.00	9.15×10^{-33}

where τ_{0a} is the pre-exponential factor, ΔH is the activation enthalpy and k is the Boltzmann constant.

The correlation coefficients are higher than 0.95. The corresponding pre-exponential factors τ_{0a} and activation enthalpies ΔH have been listed in *Tables 1a* and *1b* respectively.

Compensation law. For quenched polycarbonate, peaks isolated at $139.5°\text{C} < T_m < 158°\text{C}$ have the same relaxation time $\tau_c = 0.7$ s at the particular temperature $T_c = 182°\text{C}$. So, they obey a compensation equation:

$$\tau(T) = \tau_c \exp\left[\left(\frac{\Delta H}{k}\right)(T^{-1} - T_c^{-1})\right]$$

where the compensation time τ_c and the compensation temperature T_c are constants. The corresponding elementary processes are defined by only one parameter: the activation enthalpy. They are indicated by letter C on *Table 1a*.

For annealed polycarbonate, the calculated values of the compensation temperature and time for peaks isolated at $145.5°\text{C} < T_m < 158.5°\text{C}$ are $T_c = 165°\text{C}$ and $\tau_c = 6.2$ s. They are designated by letter C on *Table 1b*.

Vogelian relaxation times. T.s.c. peaks situated at 116°C in quenched polycarbonate and at 128°C in annealed polycarbonate have correlation coefficients of 0.95 with 'apparent' parameters indicated on *Tables 1a* and *1b* (designated ap). A best fit of experimental points

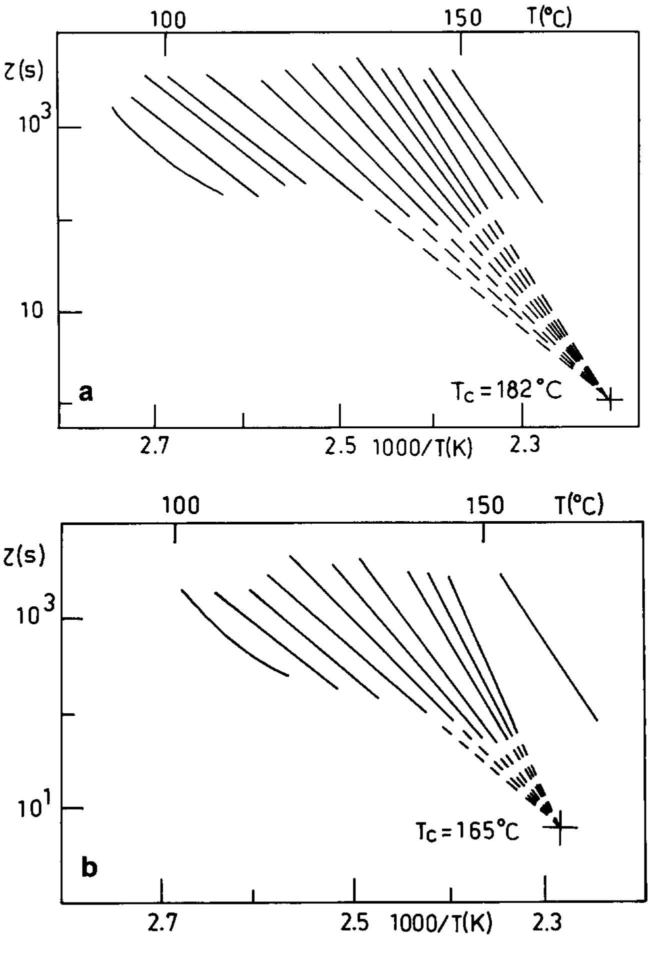

Figure 4 Arrhenius diagram of the dielectric relaxation times isolated (a) in the quenched polycarbonate and (b) in the annealed polycarbonate

Table 2 Parameters of Vogelian relaxation times

Polycarbonate	T_m (°C)	T_∞ (°C)	α_f (10^{-3} deg^{-1})	τ_{0v} (s)
Quenched	116	44	2.4	0.23
Annealed	128	77	8.25	10

is obtained from the Cohen and Turnbull theory[15]. In such free-volume theory, the molecular mobility is frozen below a finite 'critical' temperature T_∞; above T_∞, the fractional free volume f expands with a thermal expansion coefficient α_f so that:

$$T < T_\infty \qquad f = 0$$

$$T \geqslant T_\infty \qquad f \equiv \alpha_f(T - T_\infty)$$

Then, the dielectric relaxation time obeys a Fulcher–Vogel equation:

$$\tau(T) = \tau_{0v} \exp[\alpha_f(T - T_\infty)]^{-1}$$

where τ_{0v} is the pre-exponential factor. The experimental values of the parameters of the Fulcher–Vogel equation have been listed in *Table 2*.

DISCUSSION

Polarization phenomena observed in polycarbonate in the glass transition temperature region are complex. Two relaxation modes have been distinguished:

(i) The glass relaxation mode that is the most intense is situated around 155–175°C.

(ii) The sub-glass relaxation mode is located around 50°C.

Glass relaxation mode

As shown on *Figure 2*, this mode is constituted of two components: the lower-temperature component, α_l; the upper-temperature component, α_u.

Lower-temperature component. The corresponding t.s.c. peak is situated at 155°C, i.e. around the glass transition temperature (*Figure 1*). Its temperature position is independent of the thermal treatment of the polycarbonate. This component is constituted of elementary processes characterized by relaxation times following a compensation law. The activation enthalpies ΔH agree pretty well with the values obtained by Aoki[16] (2 to 4.1 eV) by the same technique on the same material.

Such a compensation law has been observed in amorphous polymers where local order is chemically[17] or mechanically[18] induced. A similar phenomenon has also been found in semicrystalline polymers[19–22]. It is interesting to note that in various semicrystalline polymers like polyolefins[23], polyamides[19] and polyurethanes[24], $T_c - T_g \sim 20$°C, i.e. the value recorded for polycarbonate. This relationship reflects local order induced either by crystallites in semicrystalline polymers or by 'ordered domains' in polycarbonate. The existence of such 'ordered domains' will be discussed in the next paragraph.

At a molecular level, the compensation law is indicative of cooperative movements of sequences of various length: the larger is the activation enthalpy, the larger the sequence.

Upper-temperature component. Upon annealing above T_g, the intensity of the upper-temperature component increases as shown on *Figure 2*. This component has been assigned to a constrained amorphous phase where local order is induced by the stiffness of the bisphenol A sequence.

At the same time, the d.s.c. trace exhibits a step in the corresponding temperature range. It is important to note that no trace of crystallization is found. In semicrystalline polycarbonate, the melting point is around 280 to 300°C[25,26]: at 190°C crystallization requires one day[27,28] to form crystallites and at least eight days to develop spherulites of about 2 μm[25–28]. Even for temperatures above 190°C, the crystallization time is comparable[27].

This upper-temperature component of the glass relaxation mode of polycarbonate has been assigned to a 'constrained' amorphous phase that would segregate under annealing. This assumption is coherent with the existence of ordered nodules of some 40 Å postulated by Yeh[29] for explaining electron microscopy[5,6,30] and X-ray diffraction data[31].

Sub-glass relaxation mode

The sub-glass relaxation mode can be easily seen on *Figure 5* where the complex t.s.c. spectrum, after normalization, of quenched and annealed polycarbonate has been plotted. It is important to note that, according to the literature[4,32], the intensity of this mode decreases significantly after annealing. As shown by d.s.c. thermograms (*Figure 1*) the corresponding sub-glass transition has the same behaviour.

In the same temperature zone, a sub-T_g mode has been observed by dielectric[8–10] and mechanical[12] relaxation. It is interesting to note that the same behaviour upon annealing has been reported for these relaxations.

The analysis of the fine structure of the sub-T_g mode shows that the relaxation times obey Arrhenius or Vogel equations.

(i) For Arrhenius relaxation times, the activation enthalpies have been indicated on *Table 3* together with the maximum temperatures of the peaks. Those values are in good agreement with the one (1.75 eV) obtained by Hong and Brittain[4] with the same technique, on the same polycarbonate.

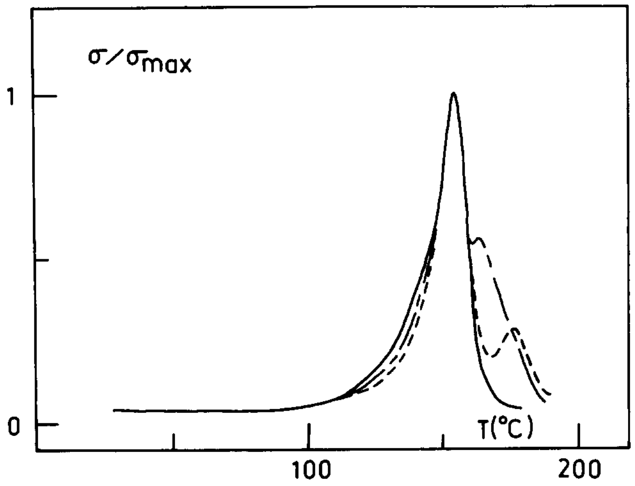

Figure 5 Normalized complex t.s.c. of quenched (——) and annealed polycarbonate at (– —) 190°C and (– –) 230°C

Table 3 Maximum temperatures and activation enthalpies in quenched and annealed polycarbonate

Polycarbonate	T_m (°C)	ΔH (eV)
Quenched	116–131	1.60–1.64
Annealed	128–141	1.61–1.75

Table 4 Fractional free volume at temperature T_m for quenched and annealed polycarbonate

Polycarbonate	$f(T_m)$	T_m (°C)
Quenched	0.168	116
Annealed	0.421	128

(ii) For Vogelian relaxation times, the fractional free volume (f) has been calculated as a function of T_m and the corresponding values are listed in *Table 4*. It is interesting to compare these data with the ones of polystyrene: at the liquid–liquid transition (160°C), $f = 8.3 \times 10^{-2}$ (ref. 18). So, the fractional free volume obtained 50°C above T_g in polystyrene is lower than the one found at the sub-T_g mode in polycarbonate.

This more liquid-like environment in polycarbonate relative to most glassy polymers provides a high degree of motion. A relatively simple model consistent with the previous data has been proposed by Jones[33]. The polycarbonate chain in the glass can be considered as composed of large *trans–trans* units with respect to the carbonate group with an occasional *cis–trans* or *trans–cis* unit. The fundamental notion is the exchange of *cis–trans* (or *trans–cis*) conformation of the carbonate with a *trans–trans* conformation of a neighbouring carbonate. The bisphenol A unit of the polymer is not significantly reoriented except for a flip of a phenylene group. The bispenol A unit between the two carbonates which interchange conformation is translated and slightly reoriented. This translation can diffuse along the chain as the *cis–trans* or *trans–cis* unit migrates down the backbone and this migration is typical of diffusional motion along the backbone of the chain.

The role of the free volume in sub-T_g process is well predicted by the molecular model of Robertson[34,35] for the relaxation of internal energy and volume in polymer glasses. In this model, chain configurational changes are responsible for local free-volume variations by a diffusion process. This free-volume diffusion process is characterized by Vogelian relaxation times. It is favoured by the presence of excess free volume in the 'true' amorphous phase. Since annealing decreases the magnitude of this phase, the magnitude of the sub-glass relaxation decreases in the same time as the α_1 component of the glass relaxation mode.

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