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Secondary Retardation/Relaxation Processes in Bisphenol A Polycarbonate: Thermostimulated Creep and Dynamic Mechanical Analysis Combined Investigations

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Abstract: Thermostimulated creep (TSCr) and dynamic mechanical analysis (DMA) have been used to analyze the complex secondary retardation/relaxation mode of bisphenol A polycarbonate (PC). TSCr and DMA studies have been combined to extend the frequency range using the very low equivalent frequency of TSCr measurement ($\approx 10^{-3}$ Hz). The dielectric spectra revealed a bimodal β retardation/relaxation mode with two overlapped components β_2 and β_1 . A thermal sampling (TS) protocol has been applied to TSCr measurements to obtain this β_1 mode fine structure. TSCr has proved to be a powerful tool to analyze the two overlapped contributions.

Keywords: Polycarbonate; Thermostimulated creep; Secondary retardation/relaxation mode; Dynamic mechanical analysis

INTRODUCTION

The great interest in polycarbonate (PC) is due to its excellent impact strength properties^[1–4] over a temperature range of more than 250°C below its glass transition temperature ($T_g \approx 145^\circ\text{C}$).^[5] Moreover, it has

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been shown that most glassy polymers exhibiting a good impact resistance have a prominent β secondary relaxation.^[6] In fact, some relationships seem to exist between the bulk mechanical properties and the rapid and extensive motions in the glass.^[6]

The β relaxation in polycarbonate has been extensively studied. Dynamic mechanical analysis and dielectric spectroscopy studies at 1 Hz reveal a very intense and broad secondary relaxation peak centred around -100°C for PC.^[7,8] Some authors found that this broad β relaxation may be resolved into more than one process,^[9–11] while others do not show any evidence of an existing structure within the relaxation.^[12,13] So, the origin of the molecular mobility of this secondary relaxation mode is not yet clearly understood. The aim of this work is to explore the fine structure of the β relaxation mode in order to investigate the molecular or morphological entities involved.

Thermostimulated creep (TSCr), developed by Lacabanne and coworkers,^[14] is derived from the thermostimulated current (CTS) technique developed by Bucci et al.^[15] and applied to polymers study by Chatain et al.^[16] The great interest of this technique is overall the low equivalent frequency associated with its measurements: $\approx 10^{-3}$ Hz.^[17] It allows extending the frequency range classically used for mechanical spectroscopy within a reasonable experimental time frame. A second interest of TSCr is the possibility to experimentally extract the activation parameters associated with a retardation mode. This extraction is possible thanks to the application of the thermal sampling (TS) protocol, which is extensively explained by several authors.^[18,19] This protocol is derived from the same TS protocol applied to TSC.^[20,21]

In this article we investigated the bisphenol A polycarbonate (PC) secondary retardation mode. The TSCr technique, coupled with the TS protocol, has been used to obtain the characteristic parameters and the activation enthalpy distribution associated with this retardation mode. We will compare these results with those obtained with dynamical mechanical analysis (DMA) in a similar temperature range with different measurement frequencies. The large frequency range used in this study is expected to give us a good overview of the weak molecular mobility associated with the secondary retardation mode at low temperature.

EXPERIMENTAL

Material

The studied material was bisphenol A polycarbonate (PC). General Electrics supplied this polymer grade, LEXAN 141. Before molding, PC pellets were dried at 110°C . PC samples were then molded at 250°C to

obtain sheets 0.5 mm thick for TSCr experiments and 1 mm thick for DMA measurements.

For TSCr experiments, samples are 70 mm long and 0.6 mm wide. For DMA, samples are 50 mm long and 10 mm wide. Before carrying out the experiments, each sample was heated to an annealing temperature (T_a) above the glass transition temperature (T_g): $T_a = 160^\circ\text{C}$, to erase the effects of previous thermal treatment.

Methods

TSCr experiments were performed in an apparatus developed in our laboratory.^[22] The secondary retardation mode measurements were carried out with the application of the complex measurement protocol. As represented in Figure 1, complex measurements were recorded by applying a shear stress of 1.5 MPa at a stress application temperature: $T_\sigma = 0^\circ\text{C}$, for two minutes. Then the sample was cooled down at $30^\circ\text{C}/\text{min}$ to a temperature $T_0 = -150^\circ\text{C}$ where the stress was released and the sample annealed 2 minutes. During a heating ramp at $7^\circ\text{C}/\text{min}$ the values of the temperature (T), the strain (γ) and the derivate strain time x ($d\gamma/dt$) were recorded.

The strain, γ , is defined according to the Timoschenko relationship^[23] by:

$$\gamma = \frac{\theta \cdot a}{L} \tag{1}$$

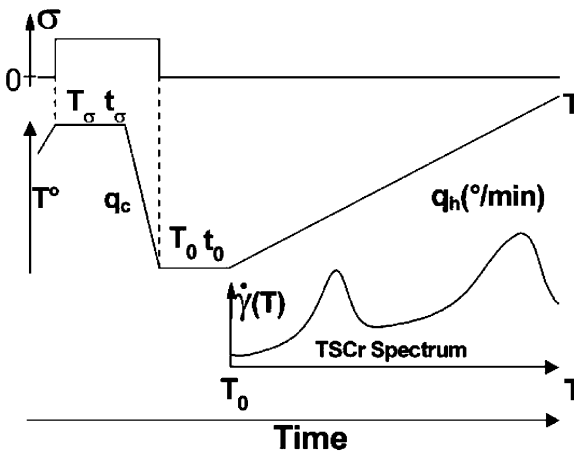


Figure 1. TSCr complex spectrum protocol.

where θ is the rotation angle, a is the sample thickness, and L is the sample length.

The data $\dot{\gamma} = d\gamma/dt$, plotted as a function of the temperature, represents the TSCr complex spectrum.

As shown in Figure 2, thermal sampling (TS) protocol is realized by applying the stress during a narrow temperature window of 5°C ($T_{\sigma 1} - T_{\sigma 2} = 5^\circ\text{C}$). Then, the stress is released and the sample is cooled down to $T_0 = T_{\sigma 1} - 40^\circ\text{C}$. The sample is heated at a rate of $7^\circ\text{C}/\text{min}$ and $\dot{\gamma}(T)$ is recorded. The variation of $\dot{\gamma}$ with temperature is called an elementary spectrum. Shifting $T_{\sigma 1}$ on the temperature axis gave us all the β retardation mode elementary spectra. This represents its fine structure.

Each elementary retardation process has Debye-like behavior with a unique retardation time.^[24] This retardation time variation versus the temperature is defined by the Arrhenius relation:

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta H}{RT}\right) \tag{2}$$

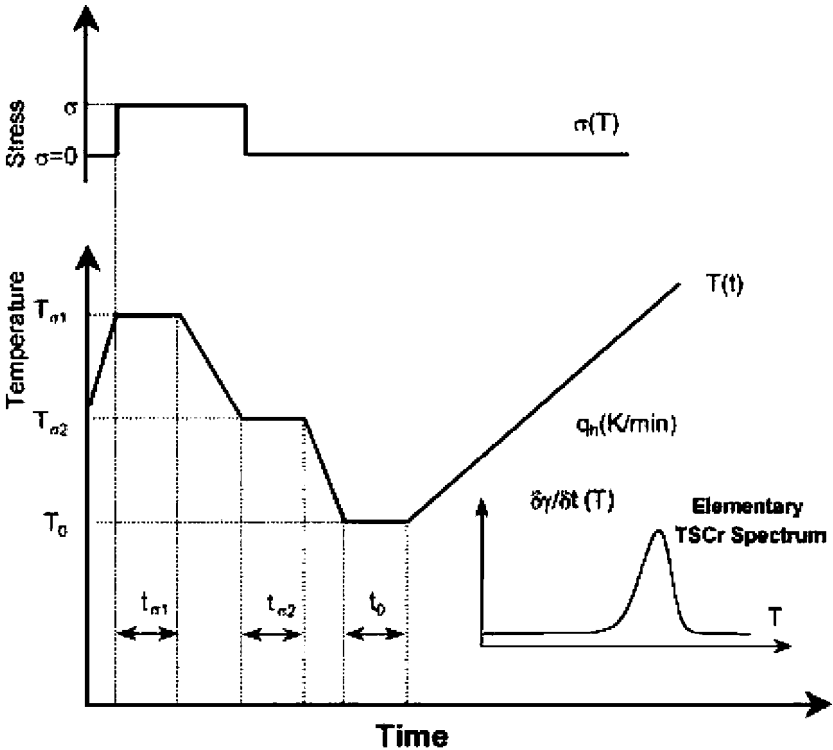


Figure 2. TSCr elementary spectrum protocol.

with ΔH as the activation enthalpy of the elementary process and τ_0 as the pre-exponential factor.

The temperature dependency of the retardation time (τ) is calculated with the experimental data:

$$\tau(T) = \frac{|\dot{\gamma}(T)|}{|\dot{\gamma}'(T)|} \tag{3}$$

The parameters τ_0 and ΔH are calculated from the plot of $\tau(T)$ in an Arrhenius diagram from the intercept and the slope of its linear regression respectively.

DMA experiments were performed on a ARES spectrometer (Advanced Rheometric Expansion System) of Rheometrics System.

Measurements of the complex shear modulus ($G^* = G' - iG''$) were done with an isothermal measurement protocol with a pulsation strain ranging from $\omega = 0.1$ to $100 \text{ rad} \cdot \text{s}^{-1}$. These experiments were carried out in a temperature range from -130° to 0°C with steps of 10°C . The maximal strain applied for these measurements was $\gamma_{\text{max}} = 2.10^{-3}$.

RESULTS

TSCr Results

Measurements carried out with the TSCr technique for complex and elementary spectra were normalized to the applied stress at T_σ . The TSCr complex spectrum presented in Figure 3 shows a large and

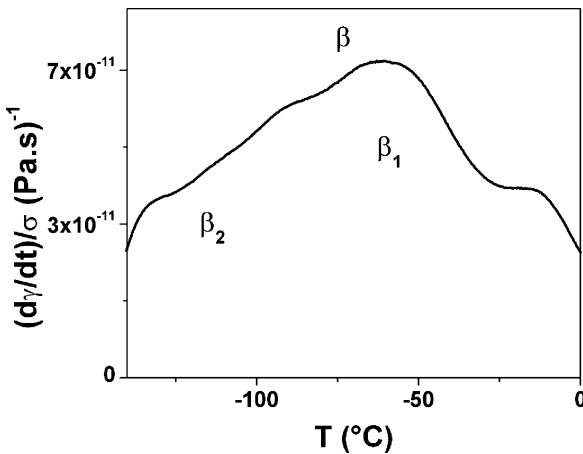


Figure 3. PC secondary retardation mode TSCr complex spectrum with $T_\sigma = 0^\circ\text{C}$ and $\sigma = 1.5 \text{ MPa}$.

nonsymmetrical process for a temperature between -140° and -30°C . At low temperatures, the signal rises from -150° to -130°C , showing a weak contribution under the shape of a little shoulder. A slow and continuous increase of the intensity signal can be observed from this weak contribution to the β retardation mode maximum at -60°C . Above this temperature, the signal rapidly decreases to a non-null value. For temperatures around T_{σ} and above, the dramatic signal decrease is due to the TSCr measurement protocol. So TSCr does not allow the observation of a signal above T_{σ} .

This mode appearing in a large temperature range has also been observed by the thermostimulated current technique applied to polycarbonate.^[25] It has been attributed to a secondary relaxation mode and labeled β mode. Several authors^[9,11] hypothesized that the PC secondary relaxation mode was composed of two separated contributions. Concerning our measurements, the TSCr complex spectrum in Figure 3 reveals a broad component centred around -120°C labeled β_2 and a pronounced maximum associated with the component named β_1 .

The fine structure of this complex spectrum, reported in Figure 4, has been obtained by the technique of fractional loading, performed in a temperature range from -115° to 0°C . This enables us to observe the elementary spectra in the β_1 retardation mode temperature range. The fine structure of the β_2 retardation mode could not be obtained because of its maximum situated around -120°C , and we cannot technically monitor the elementary spectra for $T_{\sigma} \leq -130^{\circ}\text{C}$.

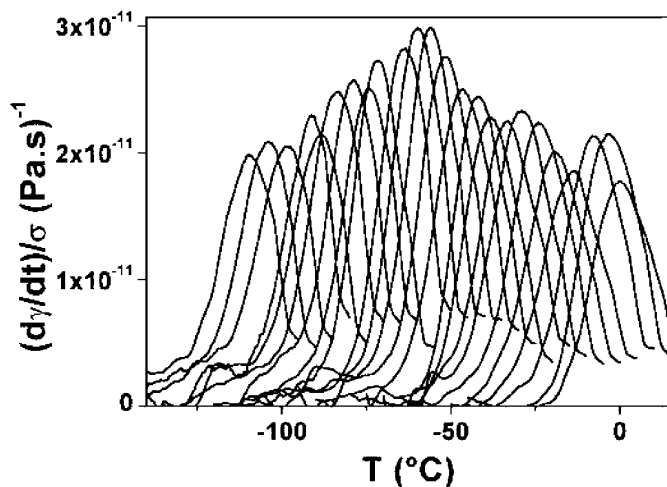


Figure 4. PC secondary retardation mode fine structure, $T_{\sigma 1}$: -115°C ; 0°C , with a temperature incremental step of 5°C , $\sigma = 1.5\text{ MPa}$.

So, in this temperature range, the complex retardation mode β was resolved in a set of elementary processes. The shape of the fine structure presented in Figure 4 is comparable to the complex spectrum in Figure 3. We can observe an increase from -115° to -60°C , where the maximum of the fine structure is in the same temperature range as the maximum of the complex spectrum. For temperatures above -60°C , the intensity of elementary spectra decreases to reach non-null values.

The set of elementary spectra presented in Figure 4 has been analyzed using Equation (3). So we obtained the temperature dependencies of the retardation time for each process associated with each elementary response.

The solid lines plotted in Figure 5 represent the set of the retardation time temperature dependencies associated with the fine structure in Figure 4. Each variation is linear in the Arrhenius diagram, confirming its thermally activated behavior. As shown in Figure 5, the extrapolations of the $\tau(1/T)$ variations for the processes in the temperature range of the

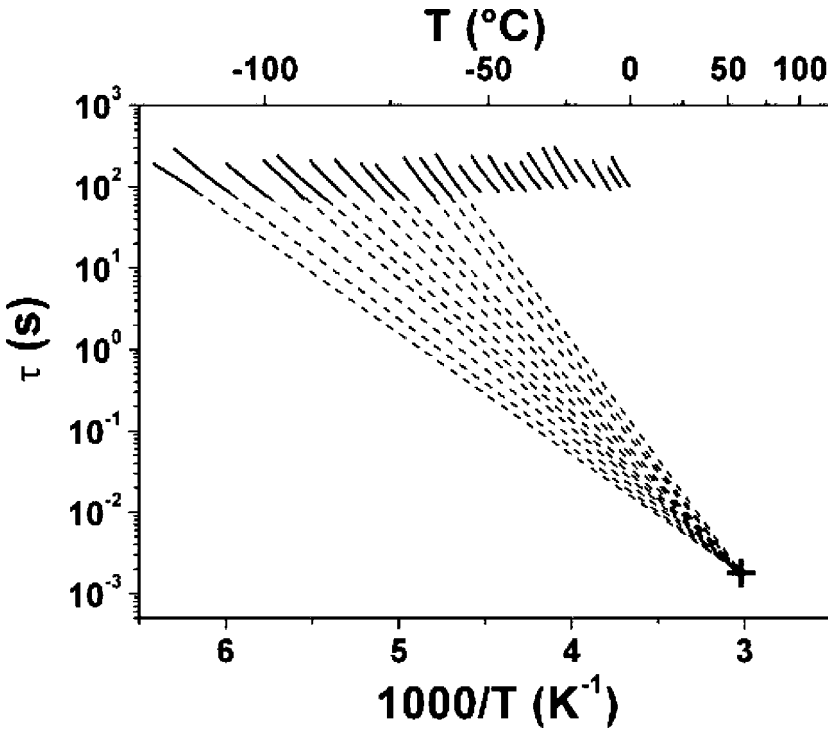


Figure 5. τ vs. $1000/T$ variations obtained from Equation (3) (solid lines) for each elementary spectrum of Figure 4. The compensation point (cross) coordinates are: $(1000/T_c), \tau_c$.

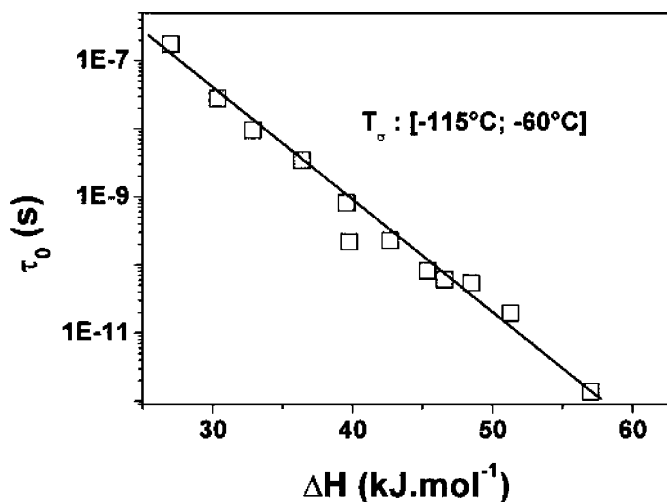


Figure 6. Compensation diagram of (τ_0 , ΔH) values for elementary processes in temperature range, $T_{\sigma 1}$: -115°C , -60°C .

retardation mode β_1 , $[-115^\circ\text{C}; -60^\circ\text{C}]$ converge to a single point. This is characteristic of a compensation phenomenon. In this temperature range, the activation parameters τ_0 and ΔH were calculated for each process with Equation (2), and are reported in the compensation diagram (Figure 6).

In Figure 6, we can observe the parameters associated with the β_1 process showing a linear evolution. This activation enthalpy linear dependency as a function of the activation entropy highlights the common origin of all of this elementary process set. These processes can be defined with the compensation parameters; the compensation temperature (T_c) and time (τ_c); calculated from a linear regression of this set. The data calculated are: $T_c = 58^\circ\text{C}$ and $\tau_c = 1.8 \times 10^{-3}$ s. It can be noted that a similar behavior has been observed for the secondary relaxation mode of PET studied by TSC.^[26] This study shows a compensation phenomenon associated with the β_1 contribution of the secondary retardation mode.

DMA Results

Figure 7 shows a three-dimensional representation of the loss modulus G'' of the complex shear modulus G^* for PC in the pulsation range of $[10^{-1}-10^2 \text{ rad} \cdot \text{s}^{-1}]$ and for a temperature range of $[-130-0^\circ\text{C}]$. The difference between the temperature ranges of the two techniques is due to technical limitations of the DMA.

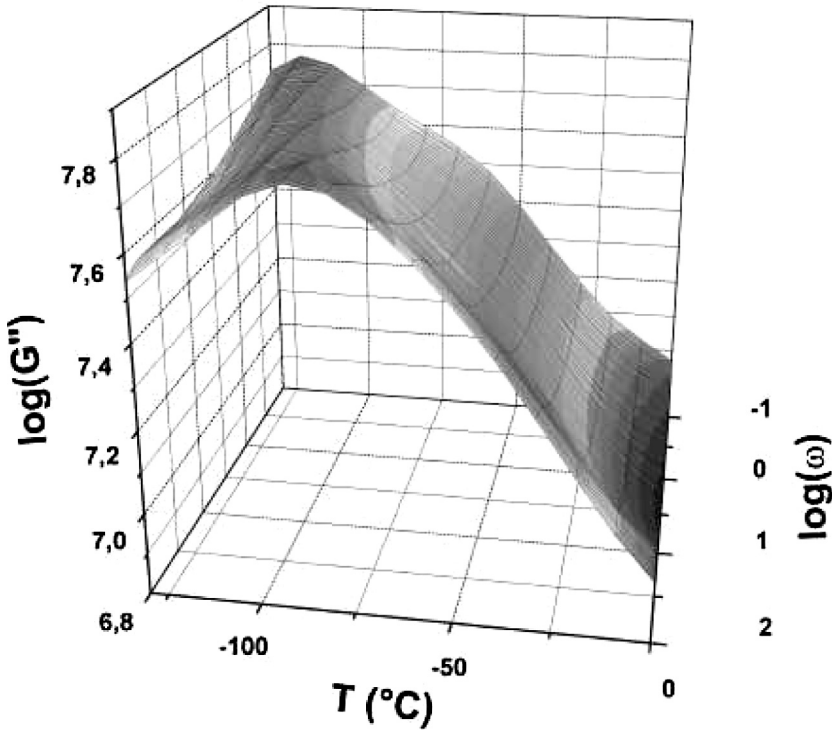


Figure 7. Values of PC loss modulus, G'' , versus temperature and pulsation for T : -130°C , 0°C , with a temperature incremental step of 10°C . Pulsation in the range from 0.1 to $100 \text{ rad} \cdot \text{s}^{-1}$.

Figure 7 represents the broad secondary relaxation mode β . The study of the temperature and pulsation dependencies of this mode enables us to characterize it by a macroscopic relaxation time:

$$\tau = \frac{1}{\omega_{\max}} \tag{4}$$

where ω_{\max} is given by the peak position of $G''(\omega)$. The corresponding temperature dependency $\tau(T)$ is reported in the Arrhenius diagram in Figure 8.

The characteristic relaxation time of the β mode is well described by an Arrhenius equation. This behavior is characteristic of the molecular mobility in a glassy state. A linear regression allows us to calculate τ_0 and ΔH from the $\tau(T)$ variation obtained by DMA. The following parameter values were calculated: $\Delta H = 51.3 \text{ kJ} \cdot \text{mol}^{-1}$ and $\tau_0 = 10^{-16} \text{ s}$. These activation parameter values are consistent with the ones presented in the literature.^[13]

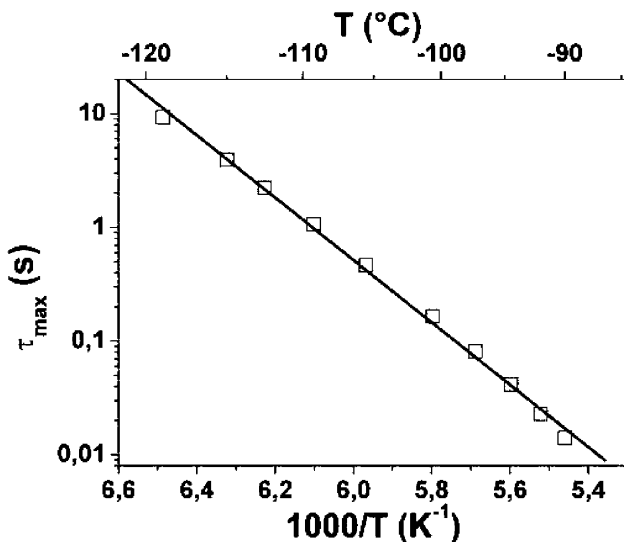


Figure 8. Relaxation time-temperature dependence calculated with DMA data.

DISCUSSION

The comparison of the β mode, recorded by TSCr and DMA techniques, reveals a difference of behavior due to the different experimental protocols of these two techniques. TSCr is based on the measurement of shear strain recovery after the application of a constant shear stress, corresponding to the compliance (J), while DMA experiments measure the shear stress allowing the calculation of the modulus G^* . Because of these different experimental protocols, the results obtained have been compared with the J'' compliance calculated from DMA data with the relation:

$$J'' = \frac{G''}{(G')^2 + (G'')^2} \quad (5)$$

where J'' is the loss part of the complex compliance J^* .

As an example of the DMA analysis, the temperature dependence of J'' has been calculated from the set of data $G''(T)$ recorded with a strain pulsation of $0.1 \text{ rad} \cdot \text{s}^{-1}$. For comparison purpose, the $G''(T)$ spectra reported in Figure 9 are included with the corresponding calculated $J''(T)$.

This comparison reveals quite different behavior between $G''(T)$ and $J''(T)$. Hence, the β_1 component appears on $G''(T)$ as a weak shoulder of the β complex relaxation mode on the high temperature side of the

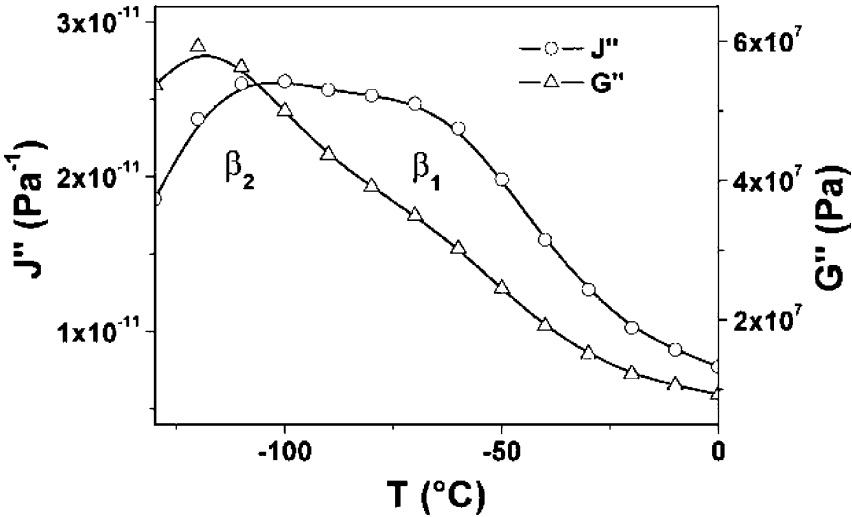


Figure 9. Values of $G''(T)$ and $J''(T)$ (calculated with Equation (5)) for $\omega = 0.1 \text{ rad} \cdot \text{s}^{-1}$.

diagram. On the $J''(T)$ spectrum, the β_1 component creates a broadening of the β complex retardation mode. These spectra show the bimodal behavior of the complex secondary relaxation/retardation mode in the PC. However, the secondary retardation mode observed on the $J''(T)$ spectrum and obtained by DMA presents differences from the mode obtained by TSCr (Figure 3). The low equivalent frequency ($\approx 10^{-3} \text{ Hz}$) of the TSCr technique allows observing molecular mobility for lower frequencies than those used during a DMA measurement, so we studied the frequency dependency and the evolution of the relative intensity of each contribution β_2 and β_1 by DMA.

The β complex retardation mode recorded by this method has been decomposed by a numerical method into two components, β_2 and β_1 , using the hypothesis of two Gaussian components. As an example, the β_2 and β_1 peaks for $\omega = 10 \text{ rad} \cdot \text{s}^{-1}$, obtained with a correlation coefficient of 0.9998, have been reported in Figure 10.

This numerical method has been applied for pulsations ranging from $\omega = 0.1$ to $100 \text{ rad} \cdot \text{s}^{-1}$. The evolutions of β_2 and β_1 retardation modes obtained for the different pulsations are presented in Figures 11 and 12.

As is made clear by these figures, the evolution of the two retardation modes as a function of the pulsation is quite different. In fact, with the increase of ω from 0.1 to $100 \text{ rad} \cdot \text{s}^{-1}$, the intensity maximum of β_2 increases while the intensity maximum of β_1 decreases. At the same time, the maximum temperature of each process is shifted towards the higher temperatures when ω increases.

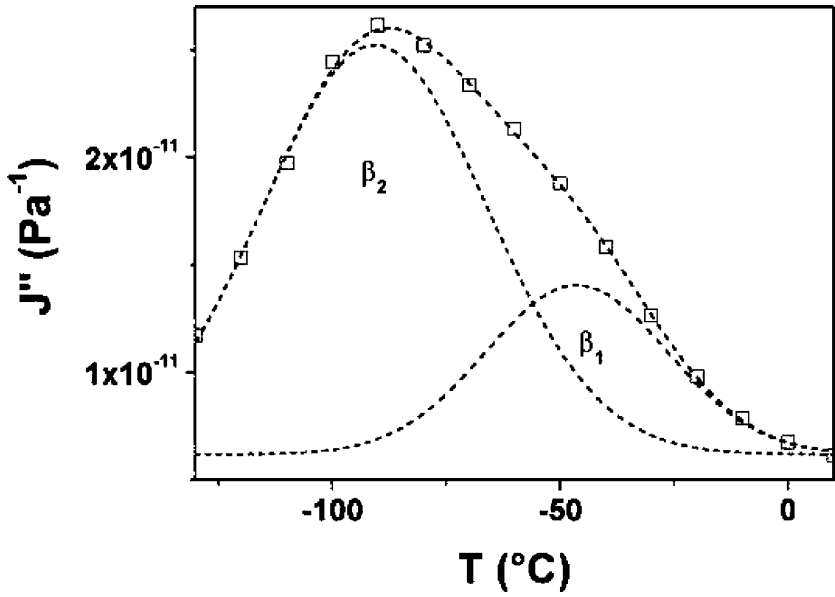


Figure 10. Mathematical decomposition of $J''(T)$ in two Gaussian contributions, β_2 and β_1 , for $\omega = 10 \text{ rad} \cdot \text{s}^{-1}$.

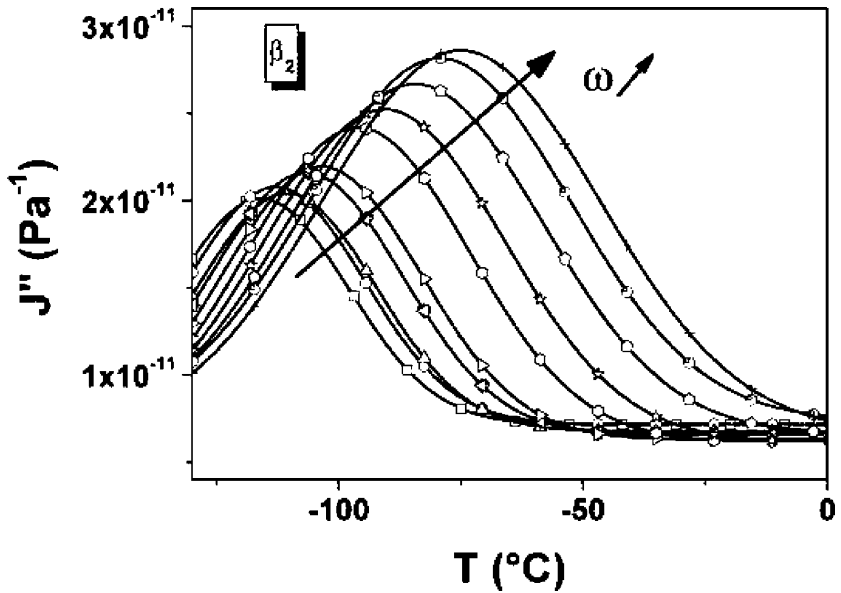


Figure 11. Evolution of β_2 contribution for ω values between 0.1 and $100 \text{ rad} \cdot \text{s}^{-1}$.

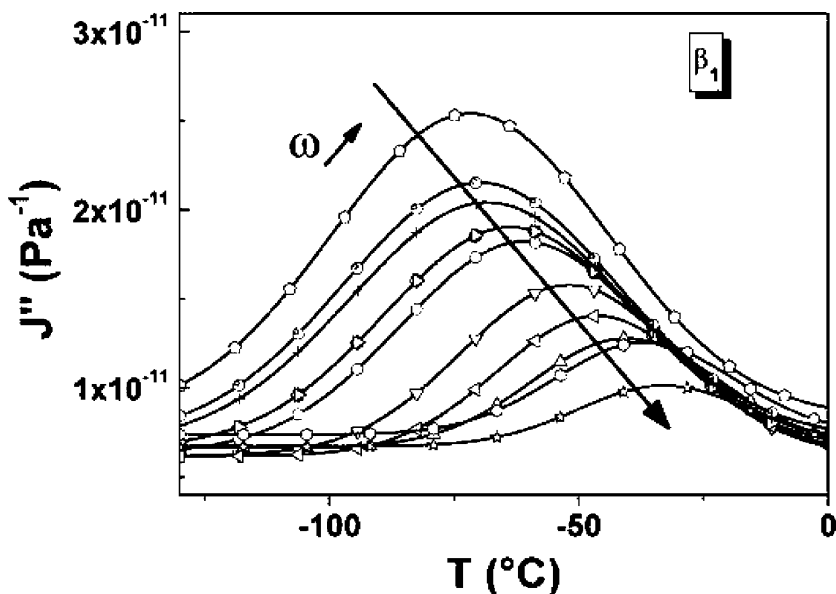


Figure 12. Evolution of β_1 contribution for ω values between 0.1 and 100 $\text{rad} \cdot \text{s}^{-1}$.

For the low frequencies, the $J''(T)$ DMA spectra in Figures 11 and 12 reveal a predominant relative intensity of β_1 compared to β_2 . Thus, these evolutions with the frequency show that the analysis of $J''(T)$ from DMA spectra is consistent with the secondary retardation mode obtained by TSCr. Moreover, the maximum activation enthalpy calculated with the TS protocol by $57 \text{ kJ} \cdot \text{mol}^{-1}$, is in the same range as the one obtained by DMA by $51 \text{ kJ} \cdot \text{mol}^{-1}$. Thus, the TSCr technique is a very good complement to a DMA study, especially to study overlapped relaxation processes at very low frequencies, since DMA measurements at very low frequencies are not satisfying in practice due to the long experimental time needed to get good data accuracy.

Elementary processes isolated by the experimental TSCr technique in the temperature range of β_1 are well described by a compensation law. According to the model proposed by Hoffman et al.^[27] to describe dielectric relaxation in paraffins, the activation enthalpy and entropy vary like the size of the mobile sequence. So, the linear dependency of the activation enthalpy and entropy increase with temperature is associated with the size increase of the mobile sequence. The β_1 mode has been attributed to a local conformation change due to phenyl and carbonyl groups cooperative motions.^[11] This observation is in good agreement with the compensation phenomenon observed for the β_1 process by the TS protocol. Several authors have attributed the molecular mobility associated with

the β_2 relaxation mode to the motion of carbonyl groups.^[9,11] Therefore, with the increase of ω , the phenyl ring cooperative motions associated with the β_1 process seem to be penalized while the noncooperative motions of the carbonyl groups associated with the β_2 process are not. It is interesting to note that the β complex mode becomes more symmetric with increase of frequency and seems to lose its bimodal behavior. This phenomenon has also been observed for PET, whose bimodal behavior disappears for high frequencies.^[28]

CONCLUSION

In this work, we have shown the interest of thermostimulated creep for the mechanical characterization of an amorphous polymer (polycarbonate). In the very low frequency range, this technique is a good complement to more classical techniques like DMA. First, it extends the frequency range studied, giving a good tool to observe overlapped retardation modes. Then, the TS protocol allows experimental access to the characteristic parameters of a retardation process, like activation enthalpy and entropy.

The TSCr and DMA results obtained on PC secondary retardation/relaxation mode are in good agreement. The correlation of these two techniques allowed us to observe the evolution of the relative intensity with the frequency of the two overlapped contributions, β_2 and β_1 , constituting the secondary retardation/relaxation mode of PC. The TSCr measurements, realized at very low frequencies, made the bimodal behavior observation of the PC β retardation mode possible. This result is consistent with the hypothesis of a β_1 contribution associated with phenyl ring cooperative motions.

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