Study by Thermostimulated Currents of Dielectric Relaxations through the Glass Transition in an Amorphous Polymer: Poly(*n*-butyl methacrylate)

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ABSTRACT: The study of poly(*n*-butyl methacrylate) (PnBMA) by thermostimulated currents has been performed in order to give a better definition of the molecular mobility when crossing the glass transition. It reveals the existence of two dipolar relaxation modes: α, ascribed to the glass−rubber relaxation, and α', which might be the dielectric manifestation of the liquid−liquid transition. The distribution of relaxation times and the evolution of the activation enthalpies when increasing the temperature have been studied by the fractional polarizations technique. It appears that the α and α' modes behave differently, showing the crossover from an Arrhenian to a Vogelian behavior. Furthermore, up to T_α, the cooperativity of molecular mobility is highlighted by the existence of a compensation law in agreement with Starkweather's criterion, and above T_α, results might be explained by the existence of an intermediate state neither glassy nor completely liquid.

Introduction

The amount of studies on the β relaxation in polymers that have been performed in the past decades has permitted to establish analysis models that are now generally accepted.[1] On the other hand, although a lot of research has been realized on molecular mobility around the glass transition in amorphous polymers, its proper nature still remains unclear.

The analysis of molecular mobility above the glass−rubber transition, in the liquid state, revealed that it can be described by a behavior of Vogel−Tamman−Fulcher type. Nevertheless, the behavior at the crossing of the glass−rubber transition is a subject of controversy. Indeed, just below T_g, experimental observations show the existence of molecular mobility of Arrhenius type generally reported only in the sub-T_g region.

In this work, we used the thermostimulated currents (TSC) technique on account of its ability for describing the dielectric relaxation times distribution from the glassy state to the liquid state, thanks to its high-resolution power and its low equivalent frequency ($\sim 10^{-3}$ Hz).

Considering the prominent role of the free volume in this evolution, an amorphous poly(methacrylate) with a bulky side group was chosen for this work. Since the glass transition of this material had to be high enough not to be hidden by a secondary mode, we adopted the poly(*n*-butyl methacrylate) (PnBMA).

There are two different approaches to describe the TSC spectra, namely a homogeneous scenario[2] (Kohlrausch−Williams−Watts function) or a heterogeneous scenario[2] (distribution of processes of Debye type) as presented by some authors.[3] We chose to follow an experimental approach and so to use the fractional polarizations technique to explore the dielectric relaxation times distribution in order to determine precisely the nature of involved molecular movements.

Experimental Section

1. Materials. PnBMA used in this study was furnished by PolymerExpert. It was polymerized at −78 °C in THF and was heated to 130 °C, the temperature at which it was pressed under a pressure of 1 bar for 2 min in order to prepare the samples in the form of films.

Size exclusion chromatography with polystyrene standard indicates a number-average molecular weight of 105 000 g/mol and a polydispersity index of 1.1.

Differential scanning calorimetry experiments were carried out in a DSC 2920 instrument from TA-Instrument.

A 9.38 mg sample of PnBMA was enclosed in an aluminum pan. The as-received sample was heated at 10 °C/min from −40 to 120 °C and annealed at this temperature for 2 min in order to erase the effects of previous thermal histories. Then, PnBMA was quenched to −40 °C, and the DSC spectrum was recorded with a heating rate of 10 °C/min to 120 °C. The obtained thermogram is reported in Figure 1. A jump of heat capacity, characteristic of the glass transition, can be seen at 33 °C using the inflection point method. It should be noted that this value is in agreement with previous studies.[4]

2. Methods. **a. Complex TSC Spectra.** Initially, the thermostimulated currents technique was introduced by Bucci and Fieschi in 1964[5] to study point defects in crystals. Later, it has been applied to the characterization of molecular mobility in polymers. This method consists of recording the depolarization current after removal of a static electrical field.[6]

In the TSC technique, a sample is polarized by an electrical field E at a temperature T_p for a time t_p ($t_p = 2$ min). This time is long enough to orient all dipolar units having relaxation time $\tau(T_p)$ lower than t_p. The sample is then quenched to a temperature $T_0 \ll T_p$ with liquid nitrogen, which freezes the orientation of dipoles. At this temperature, the electrical field is cut off, and the sample is short-circuited for t_0 ($t_0 = 2$ min). Upon heating at 7 °C/min, dipolar units return to equilibrium. It gives rise to a depolarization current, which is recorded with a Keithley 642 electrometer with a precision of 10^{-16} A.[6]

The recorded global spectrum is generally complex because it results from the distribution of species with different relaxation times. To improve its resolution, the fractional polarizations technique is used.

b. Elementary TSC Spectra. In this procedure, after polarization at T_p for t_p ($t_p = 2$ min), the sample is short-circuited for t_d ($t_d = 2$ min) at T_d some degrees below the

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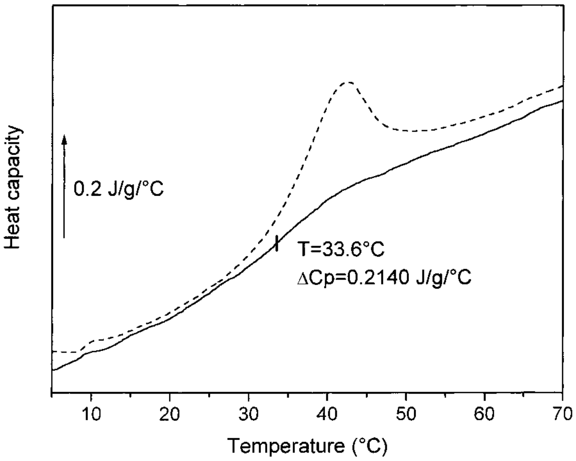

Figure 1. First (- - -) and second (—) DSC scans of PnBMA performed at 10 °C/min.

polarization temperature. So dipolar units characterized by relaxation times τ, such that $\tau(T_p)$ is inferior to t_p and $\tau(T_d)$ is superior to t_d, are oriented and experimentally isolated. The film is then quenched, and as for the TSC experiment, the depolarization current is recorded upon a linear increase of temperature. By shifting the polarization window ($\Delta T = T_p - T_d$) along the temperature axis, a series of elementary spectra are obtained.[6,7]

If the polarization window is small enough ($\Delta T = 5$ °C), each elementary spectrum can be analyzed by assuming a single relaxation time which can be established from the polarization $P(T)$:

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

Since

$$I(T) = -s\frac{\mathrm{d}P}{\mathrm{d}t} \qquad (2)$$

where $I(T)$ is the depolarization current and s is the sample area, the relaxation time is deduced from the depolarization current by the following relation:

$$\tau(T) = \frac{1}{qI(T)}\int_T^{\infty} I(T)\,\mathrm{d}T \qquad (3)$$

where $q = \mathrm{d}T/\mathrm{d}t$ is the heating rate.

Results

TSC Complex Spectrum. The TSC global spectrum of PnBMA is shown in Figure 2. The polarizing field of 4.1×10^5 V/m was applied at the temperature $T_p = 105$ °C. Then, the sample was quenched to −120 °C and reheated to 120 °C at 7 °C/min.

Although this spectrum is complex, two peaks can clearly be seen: the first one (α) is located at $T_\alpha = 25$ °C and the second one (α′) at $T_{\alpha'} = 90$ °C.

To identify these peaks, the field dependence of the TSC spectrum has been studied. The whole polarization P_0 corresponding to the α and α′ peaks has been calculated from the following equation

$$P(T) = \frac{1}{sq}\int_T^{\infty} I(T)\,\mathrm{d}T \qquad (4)$$

and reported vs the applied electrical field in parts a and b of Figure 3, respectively. For each peak, the diagram reveals a linear increase of polarization upon increasing of the field. These two peaks have then been ascribed to dipolar relaxation processes since the polarization saturation value of a group of dipoles depends linearly on E as

$$P_0 = \frac{N\mu^2}{3kT_p}E \qquad (5)$$

where N is the number of dipoles, μ is the dipolar moment, and k is the Boltzmann constant. Furthermore, since the α peak maximum temperature is of the same order of magnitude as the glass transition temperature obtained by differential scanning calorimetry (Figure 1), it has been associated with the dielectric manifestation of the glass transition.

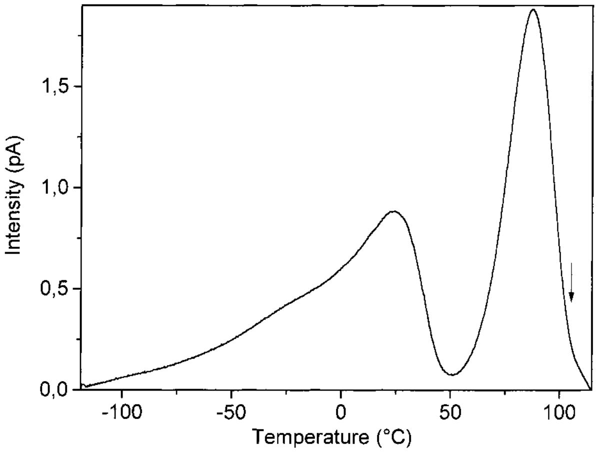

Figure 2. TSC complex spectrum of a sample of PnBMA of 70 μm thickness obtained under an applied voltage of 29 V. The polarization temperature ($T_p = 105$ °C) is indicated by the arrow.

It is worth noting that this mode shows a shoulder near −25 °C. This phenomenon is ascribed to the β mode, which is assigned by some authors to 180° flips of the ester group accompanied by the rotation of the backbone around the local chain axis.[8,9] It is known that the main transition α shifts to lower temperatures with increasing side chain length whereas the β relaxation is only weakly influenced.[10,11] This explains why, in the case of PnBMA, these two relaxations merge to such a degree. In this work, the β relaxation will not be considered even if it deserves further investigations.

Fine Structure of TSC Spectra. The resolution of the fine structure of the complex TSC spectrum of PnBMA has been performed by fractional polarizations. Figure 4 reports the elementary spectra obtained for a PnBMA sample polarized by an electrical field of 1.2×10^6 V/m at temperatures varying from −75 to 97.5 °C. The polarization window of 5 deg was shifted along the temperature axis by 5 deg for the α mode and by 2.5 deg for the α′ mode.

As can be seen, the elementary spectra isolated for the α mode extend over an important range of temperatures, which reveals a wide distribution of relaxation times.

On the contrary, the temperature of the maximum of each elementary spectrum isolated for the α′ mode is independent of polarization conditions. Indeed, the temperature of this maximum is nearly constant, indicating that the relaxation times distribution of this mode is narrow.

a. Temperature Dependence of Relaxation Times. These elementary spectra can be analyzed by assuming

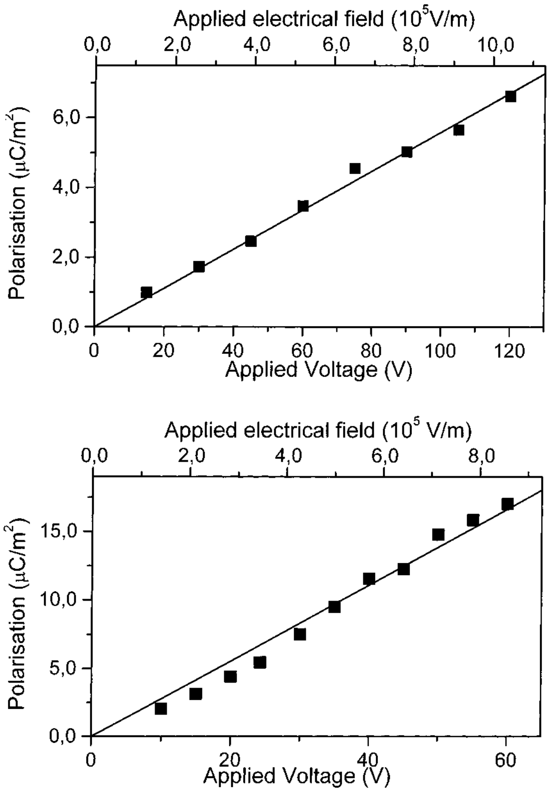

Figure 3. Polarization variation as a function of the applied electrical field for the (a) α and (b) α′ mode, respectively.

the existence of a single relaxation time. This allows us to define the relaxation time variation as a function of temperature for each isolated process. Figure 5 shows the temperature dependence of these relaxation times on the Arrhenius diagram.

(i) α mode: For $T_p < 30$ °C, relaxation time variations of elementary processes are linear on the Arrhenius diagram, which means that they can be described by an Arrhenius equation:

$$\tau(T) = \tau_{0a} \exp\left[\frac{\Delta H_a}{RT}\right] \tag{6}$$

where τ_{0a} is the preexponential factor, ΔH_a is the activation enthalpy, and R is the perfect gas constant.

Moreover, for -10 °C $< T_p < 30$ °C, $\tau(T)$ vs reciprocal temperature variations converge, by extrapolation, at a given temperature T_c: they obey a compensation law:[6,12]

$$\tau(T) = \tau_c \exp\left[\frac{\Delta H_a}{R}\left(\frac{1}{T} - \frac{1}{T_c}\right)\right] \tag{7}$$

where τ_c is the compensation time and T_c is the compensation temperature.

So, at the temperature T_c, all these elementary processes would have the same relaxation time τ_c. The obtained compensation parameters are $T_c = 65$ °C and $\tau_c = 7 \times 10^{-2}$ s. These values are analogous with values recorded for other amorphous polymeric materials.[6]

As will be discussed later, this compensation phenomenon highlights the cooperativity of molecular movements in the glass−rubber relaxation range.

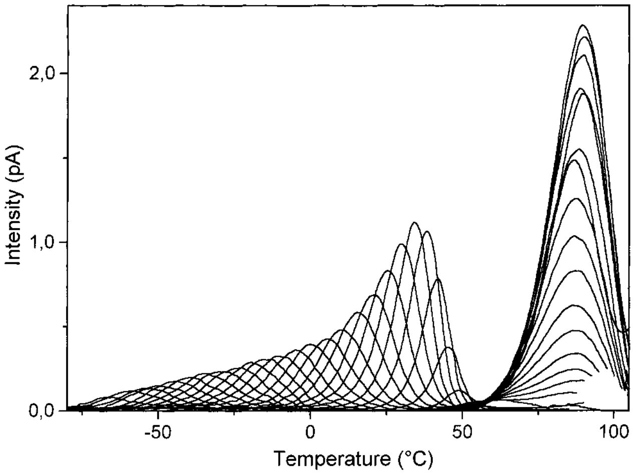

Figure 4. Fine structure of a sample of PnBMA of 95 μm thickness performed by fractional polarizations technique. Experimental conditions: applied voltage of 120 V and polarization window of 5 deg shifted along the temperatures axis by 5 deg for the α mode and by 2.5 deg for the α′ mode.

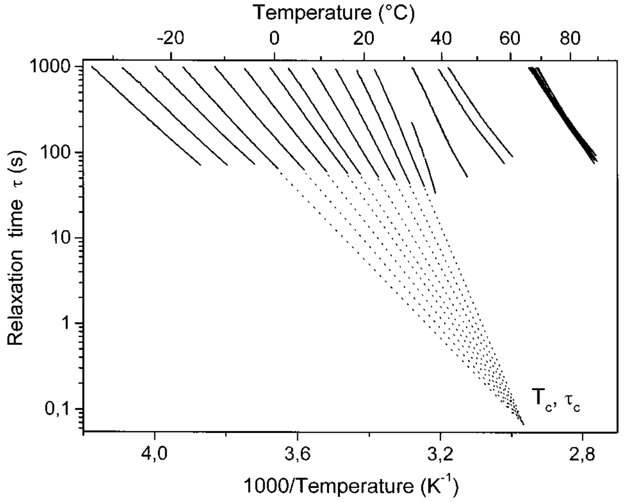

Figure 5. Arrhenius plot of relaxation times of processes isolated by fractional polarizations. The dashed lines represent the extrapolation which gives rise to the compensation point (T_c, τ_c).

It should be noted that, for 30 °C $< T_p <$ 50 °C, relaxation time variations vs T^{-1} are more difficult to analyze due to some overlapping of the α′ mode and to the weak intensity of the corresponding elementary spectra. Nevertheless, they would be assumed, in a first approximation, to be Arrhenian.

(ii) α′ mode: For $T_p > 50$ °C, relaxation time variations are almost analogous. In this temperature range, each variation of $\tau(T)$ is well described by a Vogel−Tamman−Fulcher equation:

$$\tau(T) = \tau_{0v} \exp\left[\frac{1}{\alpha_f(T - T_\infty)}\right] \tag{8}$$

where τ_{0v} is the preexponential factor, α_f is the thermal expansion coefficient of the free volume, and T_∞ is the critical temperature at which any mobility is frozen.

It yields for the highest temperature elementary spectrum ($T_p = 87.5$ °C) the following Vogel−Tamman−Fulcher parameters: $\alpha_f = 4.4 \times 10^{-4}$ K^{-1} and $T_\infty = -44$ °C.

b. Distribution of the Activation Enthalpy. We studied the activation enthalpy evolution toward the α mode.

In Figure 6, the variation of activation enthalpies of processes isolated for the α mode is represented as a

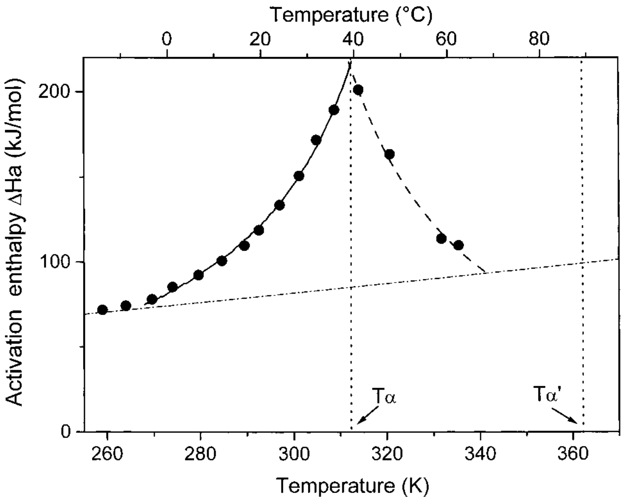

Figure 6. Variation of α mode activation enthalpy as a function of peak maximum temperature. The solid line (—) represents the compensation law. The dash line (- - -) is a guide for the eyes. The dash dot line (— • —) is Starkweather's "line" of $\Delta S = 0$ (calculated with $f_{eq} = 5 \times 10^{-3}$ Hz).

function of the peaks maxima temperature T_m. The Starkweather's "line" corresponding to the theoretical activation enthalpy associated with a null activation entropy has been added. It is expressed[13,14] as

$$\Delta H_0 = RT\left[1 + \ln\left(\frac{kT}{2\pi h f_{eq}}\right)\right] \tag{9}$$

where h is the Planck's constant and f_{eq} is the equivalent frequency ($\approx 5 \times 10^{-3}$ Hz).

According to this criterion, the α mode is divided into two zones.

(i) On one hand, for 0 °C $< T_m < T_\alpha$, the activation enthalpies deviate from the Starkweather's "line", and this strong increase of ΔH_a as a function of T_m is associated with a compensation phenomenon previously described. Indeed, from the compensation equation (eq 7) and from the expression of the Arrhenian relaxation time at the maximum temperature[12]

$$\tau(T_m) = \frac{R{T_m}^2}{q\Delta H_a} \tag{10}$$

we deduce a relationship describing the experimental parameters as shown in Figure 6.

(ii) On the other hand, for $T_\alpha < T_m < T_{\alpha'}$, the enthalpy decreases exponentially upon increasing T_m until the Starkweather's "line".

It should be noted that we have not plotted the activation enthalpies of processes isolated for the β mode as we focused on the α relaxation. Nevertheless, these activation enthalpies follow the Starkweather's "line". So the observed deviation for $T_m >$ 0 °C appears as a rough change of behavior which points out the beginning of the α mode and which underlines the capacity of the fractional polarizations technique to separate the two processes.

Discussion

This work emphasized the existence of two dipolar relaxation modes in the region around and above the glass transition temperature.

Let us consider the α′ mode: the maximum temperature of this peak is 90 °C. The value of $T_{\alpha'}$ (K)/T_α (K) ratio obtained by TSC (low equivalent frequency) is 1.20 ± 0.02.

We can note that this value obtained by TSC agrees with the value reported by Boyer for T_{ll} (K)/T_g (K) ratio[15] for a frequency value close to zero, where T_{ll} is the liquid−liquid relaxation temperature and T_g is the glass relaxation temperature.

Since $T_{\alpha'}$ is in good agreement with the liquid−liquid transition temperature of PnBMA found by this author,[16] the α′ mode may be the dielectric manifestation of the liquid−liquid transition.

It is noteworthy that other workers who performed DSC experiments on different glass-forming liquids and polymers like Murthy[17] or TSC experiments on different amorphous polymers, especially PMMA,[18] PVC,[19] atactic PS,[20] and who reported the existence of this mode had the same interpretation.

The fractional polarizations technique allowed us to establish that in PnBMA the temperature dependence of the relaxation time is varying from an Arrhenian behavior (α mode) toward a Vogelian one (α′ mode) as temperature is increased. This result is coherent with previous works from Colmenero[21] and Alegria et al.,[22] who reported the same crossover across the glass transition by combination of either dielectric spectroscopy and the isothermal depolarization current technique or dielectric spectroscopy and the transient current method.

Moreover, the experimental resolution of the complex dielectric response highlighted three zones.

(i) On the low-temperature side of the α mode ($T < T_\alpha$), the isolated elementary processes are characterized by relaxation times following a compensation law. Then, the activation enthalpies depart from the Starkweather's "line" with increasing temperature: they have been associated with cooperative mobility of chain sequences according to Starkweather's works.[13,14]

The compensation phenomenon reveals a linear relation between ΔH_a and the activation entropy ΔS defined from τ_{0a}:

$$\Delta S = R \ln\left(\frac{h}{kT\tau_{0a}}\right) \tag{11}$$

Figure 7 emphasizes the linear relationship between ΔS and ΔH_a for processes isolated around the α mode.

An interesting interpretation of the compensation law is based on the model proposed by Hoffman, Williams, and Passaglia to describe crystalline relaxations in *n*-paraffins.[23] Indeed, they found a linear variation of both the activation enthalpy and the activation entropy as a function of the length *n* of the molecule.

When this model is applied to polymers, the activation enthalpy of an elementary process reflects the length of the mobile unit. Thus, the increase of ΔH_a as the temperature increases up to T_α reflects the involvement for the α relaxation of hierarchical cooperative movements of longer and longer mobile units. It should be noted that this phenomenon has been observed in all amorphous polymers investigated just below the glass transition temperature.[24]

(ii) In the temperature range $T_\alpha < T < T_{\alpha'}$, we have seen that both ΔH_a and ΔS of isolated processes decrease. As the temperature increases, the activation entropy decreases: the drop of the number of accessible

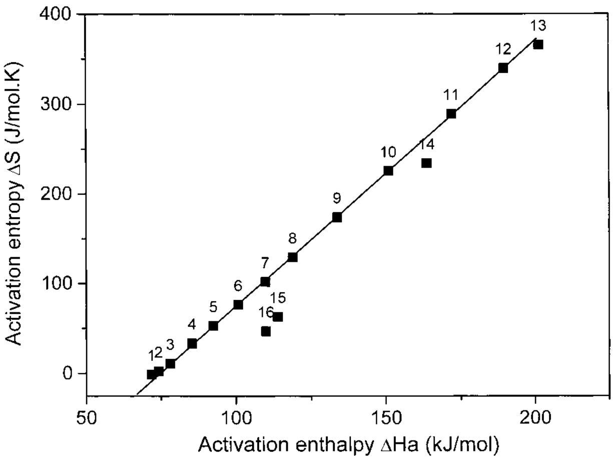

Figure 7. Variation of ΔS as a function of ΔH_a for the processes isolated by fractional polarizations. The indices correspond to increasing values of T_p by 5 °C (for 1, $T_p = -75$ °C). The solid line is a linear fit of experimental points 4−12.

sites Ω deduced from the Boltzmann equation $\Delta S = R \ln \Omega$ indicates that the molecular mobility takes place in more ordered regions. Such local order might be due to the inter- and intramolecular segment−segment interactions described by the Privalko and Lipatov's model.[25]

(iii) At T_{ll}, according to Boyer's interpretation,[15] those interactions break and liberate the molecular mobility all along the entire chains. The α′ mode appears as the dielectric manifestation of this phenomenon since the obtained Vogelian behavior indicates the vanishing of any molecular interactions. Note that α_f has a value close to the one obtained by Williams, Landel, and Ferry for a wide variety of polymeric materials while a very low value of T_∞ is obtained.

In that manner, just below T_g, in the glassy state, delocalized and cooperative movements of longer and longer sequences would take place. At T_g, only a part of the interactions between chains would be broken, giving rise to a liquid state with anchorage points (called "fixed liquid state" by Boyer). Between these points, the free volume would allow the mobile units to reorganize without energy loss (decrease of ΔH_a) and without a perturbation of the environment (decrease of ΔS). Finally, at approximately T_g + 60 °C (T_{ll}) all these interactions would disappear, resulting in a pure liquid state and the movement would then be delocalized along entire chains.

Conclusion

This study by thermostimulated currents of poly(*n*-butyl methacrylate) allowed us to show the existence in the glass transition temperature range of a glass−rubber relaxation mode, α, and, 65 deg above this mode, of an other dipolar relaxation mode which might be assigned to the dielectric manifestation of the liquid−liquid transition.

Furthermore, this work pointed out three steps in the crossover from the glassy state to the liquid state, the intermediate zone being neither glassy nor completely liquid, as well as a crossover from an Arrhenian behavior to a Vogelian one. These different dielectric relaxation phenomena revealed a hierarchy in the molecular movements: localized in the glassy state and more and more delocalized when increasing the temperature until the whole chain would be involved, in the liquid state.

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