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Dynamic mechanical and dielectric absorptions in poly(2-*tert*-butylcyclohexyl methacrylate) and poly(4-*tert*-butylcyclohexyl methacrylate)

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Abstract

Dynamic mechanical and dielectric relaxations of poly(2-*tert*-butylcyclohexyl methacrylate) (P2tBCHM) and poly(4-*tert*-butylcyclohexyl methacrylate) (P4tBCHM) have been measured. The *tert*-butyl group inhibits the chair-to-chair motions in the cyclohexyl ring. However, small motions of the cyclohexyl group are still possible giving rise to subglass relaxations in both polymers. The dielectric response is more sensitive than the mechanical one to the corresponding applied force fields © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanical relaxations; Dielectric absorptions; Activation energies

1. Introduction

The effect of the side-chain structure on the solution as well as in the solid state behavior of vinyl polymers has been studied previously for a number of poly(methacrylates) [1–5]. The conformational study of polymers containing aromatic, aliphatic and saturated cyclic side chains has demonstrated that the nature, volume and chemical structure of the substituents notably influence the conformation and rigidity of the polymer chain [6,8]. The rigidity of the chain in these kinds of polymers depends, in a significant way, on the spatial volume of the side groups and on their specific interactions [3,4,9,10]. Polymers containing bulky side chains show high characteristic ratio (C_∞) and rigidity coefficients ($(r_0^2/r_{0f}^2)^{1/2}$), due to the steric hindrance to rotation of the main chain [1,8]. Owing to the bulky side groups, these polymers also present high T_g values [6,8]. However, in spite of this characteristic, the mobility of the side chain is large enough to produce dielectric as well as mechanical activity [11–15]. On the contrary, the polymers containing cyclohexyl rings are able to show several conformational states [11–15]. These chains have a large number of degree-of-freedom that produce several molecular motions. This structural fact produces a great variety of transitions and relaxations when the material is affected by mechanical or dielectric force fields.

The flexibility of the saturated ring also allows flipping (chair-to-chair) motions of the cyclohexyl group, which has been attributed as the molecular origins that produce rapid relaxation processes in dynamic mechanical and dielectric measurements. It is well known that the chair-to-chair motions in the cyclohexyl ring produce a mechanical relaxation at about −80°C at 1 Hz, as reported by Heijboer [11]. Recently we have reported the dielectric and mechanical behavior of poly(cyclohexylmethyl methacrylate) (PCHMM) and poly(cyclohexylethyl methacrylate) (PCHEM) [12–16]. These polymers show a variety of absorptions due to the versatility of their structural moieties. The question is open in the sense that if the substitution of bulky groups in the saturated rings inhibit or not this relaxational behavior. In this framework, polymers with *tert*-butyl groups as substituents of hydrogens in the cyclohexyl ring are good candidates to analyze this effect.

The aim of the present work is to study and compare the dielectric and dynamic mechanical behavior of poly(2-*tert*-butylcyclohexyl methacrylate) (P2tBCHM) and poly(4-tert-butylcyclohexyl methacrylate) (P4tBCHM) (see Scheme 1)

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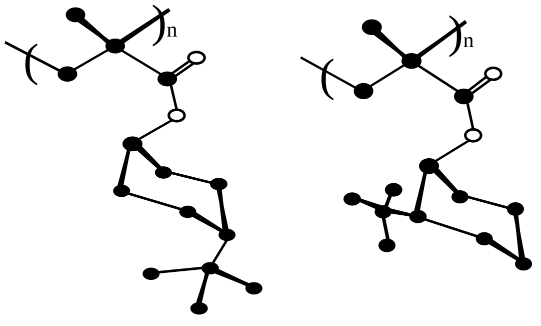

P4tBCHM P2tBCHM

Scheme 1.

2. Experimental

2.1. Monomer and polymer preparation

2-*tert*-butylcyclohexyl methacrylate (2tBCHM) and 4-*tert*-butylcyclohexyl methacrylate (4tBCHM) were obtained by reaction of methacryloyl chloride with the corresponding *tert*-butylcyclohexyl alcohol using triethylamine as acid acceptor at reflux temperature in toluene solutions following a procedure previously reported for related monomers [7,11–15]. Radical polymerization was achieved in toluene solution under vacuum using α, α' azobisisobutyronitrile as initiator at 50°C for a period of 72 and 96 h for 4tBCHM and 2tBCHM, respectively. The polymers were purified by successive reprecipitation in THF as solvent and methanol as the precipitant. The calorimetric glass transition temperatures (T_g) measured at 10°/min were 174 and 163.4°C, respectively.

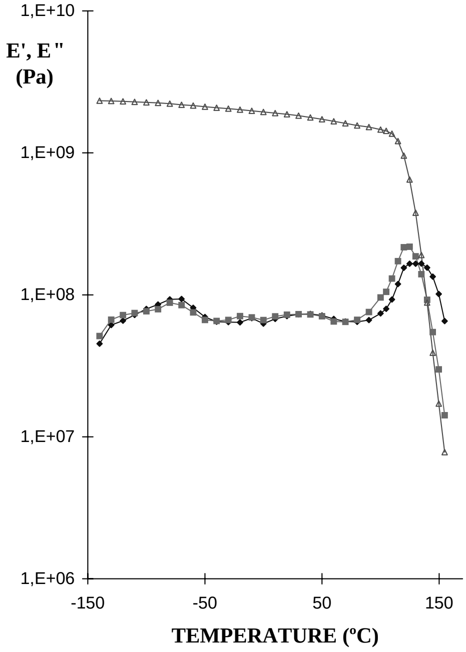

Fig. 1. Storage modulus (1 Hz) (△) and loss modulus (1 Hz) (■); (10 Hz) (◆), for P2tBCHM.

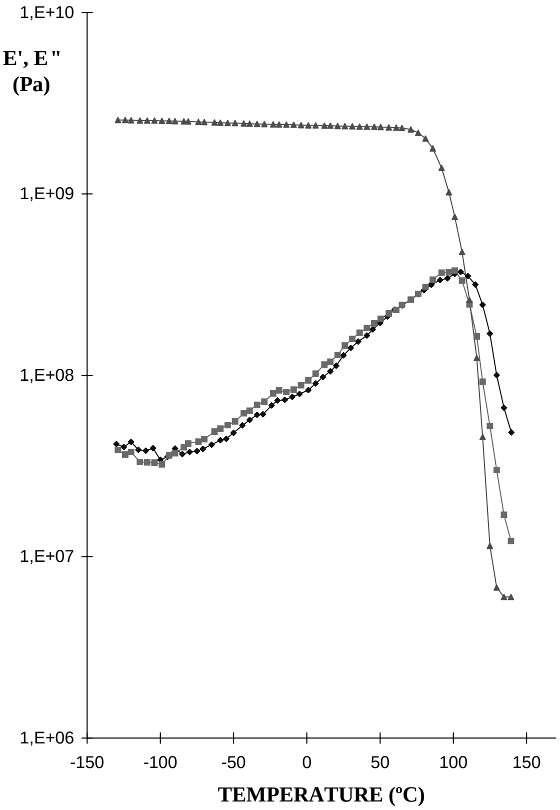

Fig. 2. Storage modulus (1 Hz) (△) and loss modulus (1 Hz) (■); (10 Hz) (◆), for P4tBCHM.

2.2. Dynamic mechanical measurements

The storage and loss components of the complex relaxation modulus E^* were obtained using a Rheometric DMTA MarkII apparatus in a double cantilever flexural mode. The experiments were carried out on moulded samples of $1 \times 10 \times 8.5\ \text{mm}^3$ at a heating rate of 1°/min at 0.3,1,3,10 and 30 Hz from -140°C up to a temperature close to the glass transition. In order to warrant a good thermodynamic equilibrium, close to the glass transition and in the vicinity of T_g, the measurements were made in isothermal conditions at 5° steps.

2.3. Dielectric measurements

The real and imaginary parts of the complex dielectric permittivity ϵ^* were measured under dry nitrogen atmosphere with a DEA 2970 apparatus from TA instruments. The heating history was similar to that used in the mechanical measurements and the range of frequencies was 10^0–10^4Hz.

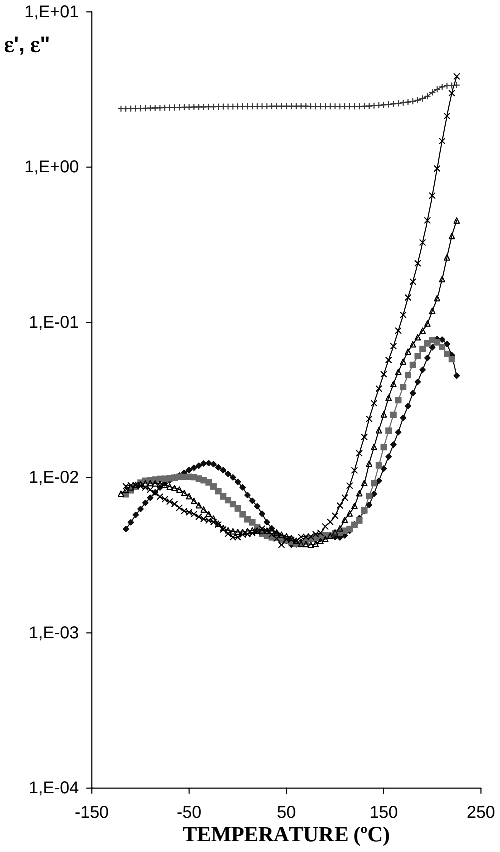

Fig. 3. Dielectric permittivity (100 Hz) (+) and loss (10 Hz) (×), (10^2Hz) (△), (10^3Hz) (■), (10^4Hz) (◆), for P2tBCHM. Only a few frequencies are shown for sake of clarity.

3. Results

3.1. Dynamic mechanical measurements

Figs. 1 and 2 show the storage and loss tensile moduli for poly(2-*tert*-butylcyclohexyl methacrylate) (P2tBCHM) and poly(4-*tert*-butylcyclohexyl methacrylate) (P4tBCHM), respectively. In these figures, it can be observed that the mechanical loss for P2tBCHM is more complex than that for P4tBCHM, which is relatively featureless except in the zone corresponding to the glass transition temperature. Both polymers show a strong relaxation at about 120 and 100°C for P2tBCHM and P4tBCHM, respectively. Moreover, P2tBCHM shows a complex secondary relaxation at about −80°C and a remainder of the mechanical activity at about −20 and 30°C, respectively. The first of these remaining peaks has a counterpart in P4tBCHM, and the second one corresponds to the shoulder observed in the low temperature side of the α peak in P4tBCHM. It is noteworthy that the α relaxation associated with the dynamic glass transition in both polymers seems to have structure. In fact it is possible to observe that in both polymers the α peak is split with increasing temperature and frequency. At low temperatures and low frequencies in the α zone, only a single peak is apparent. However, with increasing frequency and temperature a new peak appears that becomes dominant at higher temperatures. This phenomenon was attributed to the humidity present in the sample irrespective of the previous drying procedure and was impossible to avoid.

3.2. Dielectric measurements

Dielectric permittivity and loss for both polymers under study can be observed in Figs. 3 and 4. In these figures for both polymers, a prominent peak corresponding to the dynamic glass transition can be observed, which at low frequencies is overlapped by conductivity effects. Moreover, in both polymers a broad secondary peak is observed at about −50°C. This peak is more prominent in P2tBCHM, which is in good agreement with the mechanical measurements. It is also possible to observe a remaining dielectric activity in both polymers in the temperature range between 50 and 100°C. This remaining activity is enhanced by the conductivity in the case of P4tBCHM.

4. Discussion

In order to characterize the relaxational behavior of both polymers, the activation energy parameters of the secondary relaxation should be determined. For this purpose an Arrhenius plot has been obtained, Fig. 5, from which the

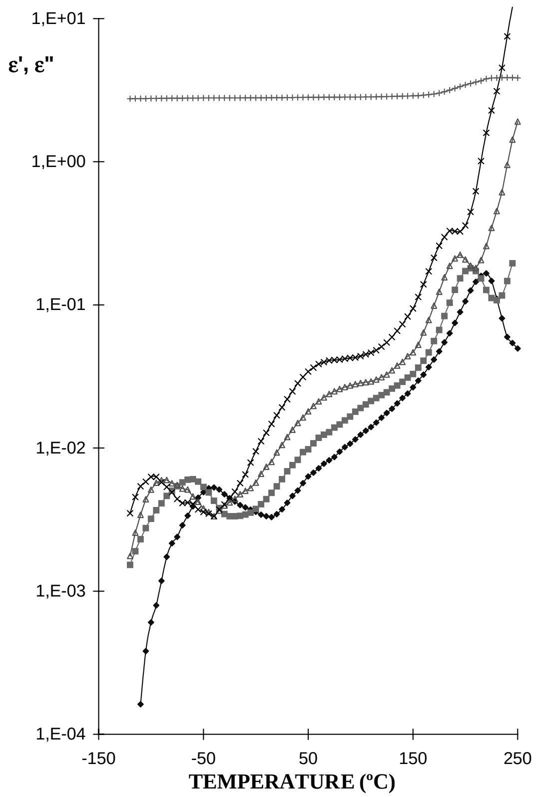

Fig. 4. Dielectric permittivity (100 Hz) (+) and loss (10 Hz) (×), (10^2Hz) (△), (10^3Hz) (■), (10^4Hz) (◆), for P4tBCHM. Only a few frequencies are shown for sake of clarity.

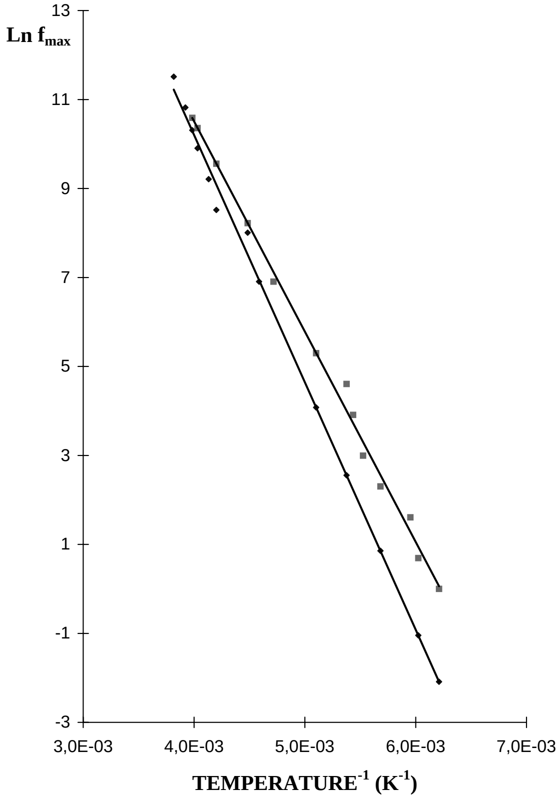

Fig. 5. Arrhenius plot for the β dielectric relaxation for P2tBCHM (◆) and P4tBCHM (■).

activation energies (E_a) can be obtained from the slope of the straight lines. The values obtained are 38.6 ± 0.5 kJ mol^{-1} for the mechanical sub-T_g relaxation of P2tCHM and 46.0 ± 0.5 kJ mol^{-1} and 39.3 ± 0.5 kJ mol for the dielectric sub-T_g relaxations for P2tBCHM and P4tBCHM, respectively.

In the α zone, it is important to separate the conductive contribution of the loss permittivity. For this purpose, a *hopping model* for the conductive effects is proposed as described previously [17] according to the equation:

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega^s} \qquad 0.5 \leq s \leq 1 \tag{1}$$

where ω is the angular frequency, ε_0 the permittivity of the vacuum and σ the conductivity. The values obtained for each polymer are compiled in Table 1, where the bimodal structure of the conductivity can be observed. The activation energy of the conductivity obtained from a plot of $\ln \sigma$ against T^{-1} (Fig. 6) reflects the presence of two zones, presumably associated to the different types of charge carriers. The values of the activation energy are 57 and 162 kJ mol^{-1} for P2tBCHM, and 53 and 178 kJ mol^{-1} for P4tBCHM for low and high temperature zones, respectively.

Table 1
s parameter of Eq. (1) to P2tBCHM and P4tBCHM

P2tBCHM			P4tBCHM		
T (°C)	s	σ_0 (Ω^{-1}m^{-1})	T (°C)	s	σ_0 (Ω^{-1}m^{-1})
220	0.9314	1.2819×10^{-9}	220	0.8618	5.2353×10^{-10}
200	0.827	1.8224×10^{-10}	200	0.8909	8.6704×10^{-11}
180	0.6819	2.879×10^{-11}	180	0.6984	2.3288×10^{-11}
160	0.6482	7.4858×10^{-12}	160	0.6504	1.3581×10^{-11}
140	0.6599	3.1589×10^{-12}	140	0.6616	6.6656×10^{-12}

Table 2
Parameters of de Havriliak–Negami equation for P4tBCHM

T (°C)	ε_∞	$\Delta\varepsilon$	α	β	τ_0
195	2.76	1.03	0.55	0.61	0.0032
190	2.77	1.07	0.53	0.60	0.0090

After subtracting this contribution, a clean α peak can be observed in Figs. 7 and 8 for the two polymers under study. Afterwards it is possible to fit an empirical Havriliak–Negami equation [18]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + (j\omega\tau)^\alpha)^\beta} \qquad \alpha \leq 1, \alpha\beta \leq 1, \tag{2}$$

to the experimental data following the usual procedure. The parameters for P4tBCHM are summarized in Table 2. For the other polymer, i.e. P2tBCHM, after subtracting the conductivity contribution, the results are

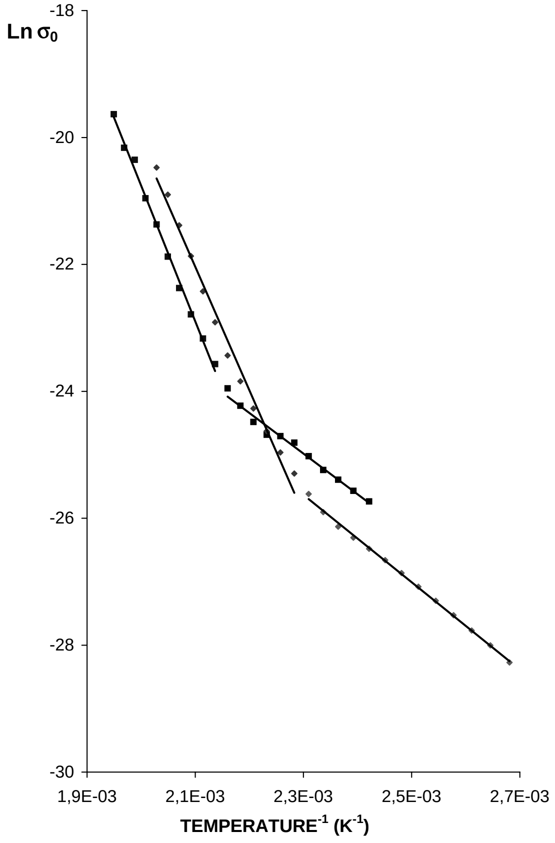

Fig. 6. Arrhenius plot for the conductivity of P2tBCHM (◆) and P4tBCHM (■), showing the bimodal structure in each case.

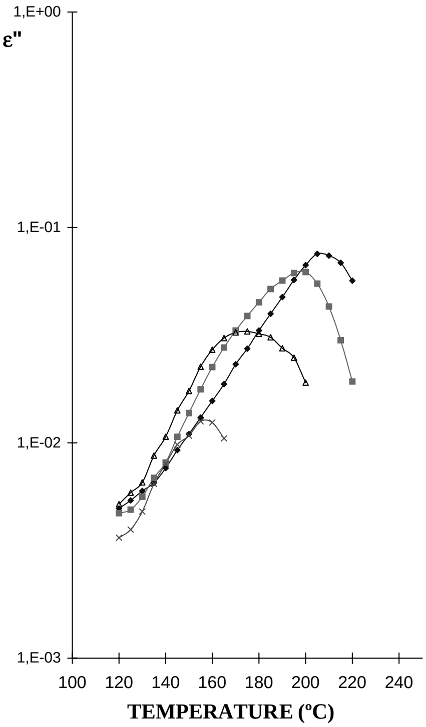

Fig. 7. Loss permittivity in the α relaxation zone, after subtracting conductivity at different frequencies: (10 Hz) (×), (10^2Hz) (△); (10^3Hz) (■); (10^4Hz) (◆); for P2tBCHM.

qualitatively consistent, but they do not allow a good fit of the Havriliak–Negami equation [18] due to the high values of conductivity.

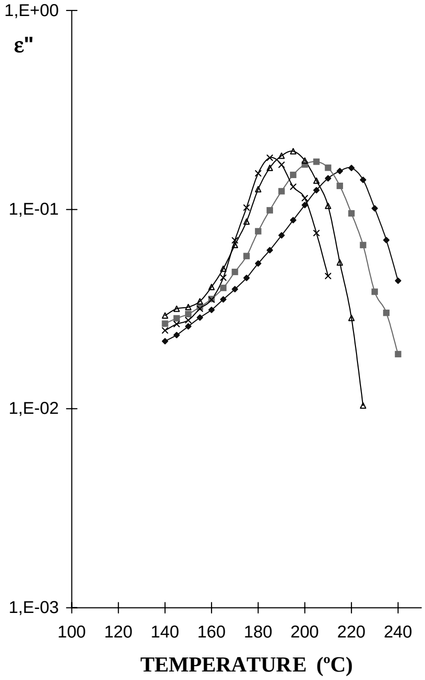

Fig. 8. Loss permittivity in the α relaxation zone after subtracting conductivity at different frequencies: (10 Hz) (×); (10^2Hz) (△); (10^3Hz) (■); (10^4Hz) (◆); for P4tBCHM.

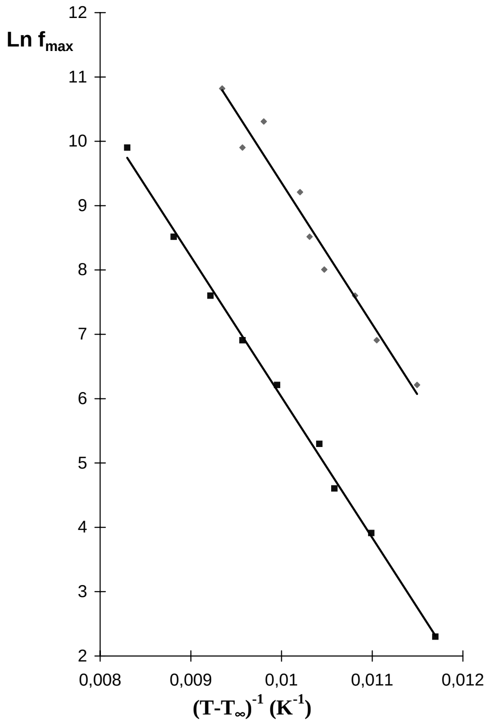

Fig. 9. Vogel–Fulcher–Tamman–Hesse plots for P2tBCHM (◆) and P4tBCHM (■).

The temperature dependence of the α relaxation in the frequency domain can be conveniently analyzed by means of the Vogel–Fulcher–Tamman–Hesse (VFTH) equation [19–21] formulated empirically by these authors as

$$\ln f_{\max} = A' - \frac{m'}{T - T_\infty} \tag{3}$$

T_∞, in this equation, is an empirical parameter related to the Kauzman temperature or the temperature at which the conformational entropy is zero. The best fit of the dielectric experimental results to Eq. (3) were obtained for values of T_∞ equal to 381 and 373 K for P2tBCHM and P4tBCHM, respectively. The value of m' amounts to 2197 and 2186 for P2tBCHM and P4tBCHM, respectively (Fig. 9).

Comparison of the VFTH equation with the Doolittle equation yields

$$\frac{\phi}{B} = \frac{T - T_\infty}{m} \tag{4}$$

which relates the free volume that appears in the Doolittle equation with the value of m' in the VFTH relationship. By using the values of m' given above, one finds that the relative free volume at T_g, (ϕ_g/B), amounts to 3.0 and 2.9% for P2tBCHM and P4tBCHM, respectively, in relatively good agreement with the free volume theory.

Despite the chain rigidity of both polymers under study and the high values observed for the glass transition temperature, significant dielectric subglass activity is present in both polymers. In fact, the *tert*-butyl group is essentially located in the equatorial position inhibiting the chair-to-chair motion but not wholly supressing. This activity is more important in the case of P2tBCHM. The bond that links a substituent in the 4-position to the ring retains its direction in space, shifting parallel to itself during the transition, as pointed out by Heijboer [11]. However, a substituent in the 2-position is turned through an angle of 109° [11]. As a result, the dielectric effect of the remaining chair-to-chair transition should be much larger for a substituent in the 2-position than for one in the 4-position. On the contrary, the mechanical sub-T_g activity is lower than the dielectric one. In the case of P4tBCHM, there are no clearly defined sub-T_g peaks. This means that these two polymers are more easily activated by electric force fields than by the mechanical ones. Owing to the fact that the only relevant dipolar group is the ester in both polymers, it can be concluded that in the molecular origin of the dielectric subglass relaxation, some contribution of this group is expected. This contribution is more important in P2tBCHM than in P4tBCHM for the reasons given above. The mechanical subglass activity is also in good agreement with the fact that higher mobility is found in the polymer with the substitution in the 2-position.

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