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Comparative study of poly(2,3 and 4 methyl cyclohexyl methacrylate)s. Dielectric relaxation spectroscopy (DRS)

Gustavo Domínguez-Espinosa[a], Maria J. Sanchis[a], Ricardo Díaz-Calleja[a,*], Claudia Pagueguy[b], Ligia Gargallo[b], Deodato Radić[b]

[a]*Departamento de Termodinámica Aplicada, ETSII, Universidad Politécnica de Valencia, Camino de Vera s/n, 46071 Valencia, Spain*
[b]*Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile*

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Abstract

The relaxation properties of poly(methyl cyclohexyl methacrylate)s (P2MCHMA), (P3MCHMA), (P4MCHMA) were analyzed. Dielectric spectroscopy (DS) techniques were used for this purpose. These polymers exhibit prominent α peaks, associated to the dynamic glass transitions, and then poorly defined β-relaxations and two other relaxation zones labelled as γ- and δ-relaxation in order of decreasing temperatures. The α relaxation processes were analyzed by means of the free volume theory, using the Vogel–Fulcher–Tammann–Hesse (VFTH) equation and in terms of the Havriliak–Negami (HN) empirical equation. Previously to these analyses, conductive contributions to the loss permittivity were subtracted. The apparent activation energies for the secondary processes under study have been calculated by means of Arrhenius. Comparison with previous relaxation results of poly(cyclohexyl methacrylate) (PCHMA), i.e. the polymer without substituents in the cyclohexyl ring, has been also carried out. In this way, changes in the glass transition absorptions as well as in the secondary processes have been discussed.

Keywords: Poly(methyl cyclohexyl methacrylate)s; Relaxation processes; Dielectric analysis

1. Introduction

The study of the response of glass formers, as for example amorphous polymers, to perturbations due to weak mechanical or electric force fields, is a subject of increasing interest in condensed matter physics. Generally speaking, the frequency response shows a cascade of relaxations revealing different modes of molecular mobility. The complexity of these motions increases as the frequency of the disturbance field decreases. At very low frequencies, the response of polymers to these fields display a normal mode associated with motions of the chain as a whole and strongly dependent of the molecular weight. Dielectric normal mode relaxation is only present in polymers having dipoles partially oriented along the backbone. The α-relaxation or segmental mode, is related to the glass transition and the response at shorter times is reflected in secondary relaxations named in the increasing order of frequency as β, γ, δ, etc. These sub glass absorptions have been traditionally associated to local molecular motions [1,2]. Obviously, these secondary molecular motions take place at nano-scale level. In the present context, acrylic polymers containing cycloaliphatic rings in the ester moiety have higher mechanical as well as dielectric activity than their counterparts with aromatic groups [3–5]. The relaxational behaviour of poly(cyclohexyl methacrylate) (PCHMA) has been widely studied [6,7] by means of mechanical, as well as dielectric techniques. The aim of this work is to analyze the dielectric relaxation behaviour of the three polymers resulting from the methyl substitution in the cyclohexyl ring of PCHMA, that is, (P2MCHMA), (P3MCHMA), (P4MCHMA) (Scheme 1). Dielectric spectroscopy (DS) was used to characterize these polymers and to elucidate the molecular motions involved in the observed relaxation processes.

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* Corresponding author. Tel.: +34 963 879 324; fax: +34 963 877 329.
E-mail address: rdiazc@ter.upv.es (R. Díaz-Calleja).

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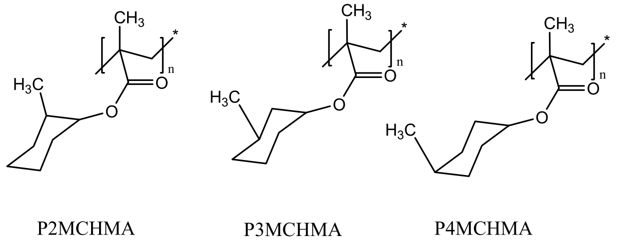

Scheme 1. Schematic diagrams of P2MCHMA, P3MCHMA and P4MCHMA.

2. Experimental section

2.1. Monomer and polymer preparation

Methacrylates were obtained by reaction of methacryloyl chloride with the corresponding alcohols (50/50% *cis–trans* conformations) in toluene using triethylamine as acid acceptor, following a procedure previously reported [8,9]. Monomers were polymerized under vacuum, in toluene solutions at 323 K using α,α'-azo-bisisobutyronitrile as initiator. Polymers were purified by successive reprecipitations with methanol. Samples were vacuum dried at 303 K during several days. The calorimetric glass transition temperature (T_g), measured at 20 K min^{-1} in DSC-Q10 from TA Instruments, were 371, 374 and 394 K, for P2MCHMA, P3MCHMA and P4MCHMA, respectively.

2.2. Dielectric measurements

Dielectric measurements were performed on moulded disc-shaped probes of about 0.1 mm thickness and 20 mm diameter by means of NOVOCONTROL Dielectric Spectrometer based on Alpha analyzer and a Quatro temperature controller. Isothermal measurements were carried out at several frequencies between 10^{-1} and 10^6 Hz from 133 to 463 K at 5 K intervals.

3. Results and discussion

The results dealing with dielectric relaxations measurements for P2MCHMA, P3MCHMA and P4MCHMA are shown in Fig. 1. An isochronal representation of the data has been choosing for sake of clarity.

Fig. 1(a)–(c) show the dependence of the permittivity and loss factor with the temperature for the polymers under study at several frequencies. Fig. 1(d) has been introduced in order to compare the dependence of permittivity and loss factor as function of the temperature, at 2 kHz for the three polymers under study and with previous results obtained for PCHMA. These spectra show several relaxation zones. Starting at low temperatures, at 160 K a weak relaxation peak labelled δ peak has been observed. Unfortunately, the δ-relaxation falls just on the low temperature limit for measurements and merges as a shoulder of the γ peak. This makes difficult the corresponding analysis. Moreover, the height of the δ maximum is only about 1/3 of those of the γ peak. The determination of the activation energy for the δ-peak, according to the Arrhenius plot was only possible for P4MCHMA, and it results 24.8 ± 0.9 kJ mol^{-1}.

When the temperature increases another peak, labelled as γ, is observed for all the polymers under study. Fig. 1(d) shows that this relaxation has a minor intensity than in the case of the polymer with non-substituted cyclohexyl ring, (PCHMA). It has been also observed that this γ peak is broader in the case of the three poly(methylcyclohexyl methacrylate)s than in PCHMA. We notice that the methyl group in the cyclohexyl ring can be either in *cis* or *trans*, relative to the bond that links the cyclohexyl ring to the main chain. According to that, the γ peak observed in the three polymers under study, can be the result of the overlapping of the relaxations corresponding to the *cis* and *trans* co-monomers. Premonitory activation energies calculated from an Arrhenius type plots (Fig. 2), for P2MCHMA, P3MCHMA and P4MCHMA were 50.1 ± 0.2, 43.2 ± 0.4 and 46.9 ± 0.4 kJ mol^{-1}, respectively, that compares well with those for PCHMA which is 43.1 ± 1.7 kJ mol^{-1}. As usual the whole analysis of this relaxation peak was carried out by means of the Fuoss–Kirkwood empirical equation, which is [10]

$$\varepsilon'' = \varepsilon''_{\max} \operatorname{sech}\left[m \ln\left(\frac{f_{\max}}{f}\right)\right] \tag{1}$$

where $f_{\max}$ is the frequency at which the loss attains to a maximum $\varepsilon''_{\max}$, m is a broadness factor, which is the unit for a single frequency relaxation peak, and the relaxation strength is calculated by $\Delta\varepsilon = 2\varepsilon''_{\max}/m$.

The corresponding parameters for P2MCHMA, P3MCHMA and P4MCHMA are presented in Fig. 3. The values of the m parameter are lower than those corresponding to other polymers containing cyclohexyl groups [6], which is indicative that the process is very distributed. This fact is reasonable taking into account the presence of *cis* and *trans* units into the polymer. The m factor has the following tendency: P2MCHMA > P4MCHMA > P3MCHMA, which is the same tendency than that for the activation energy.

A very broad β-relaxation appears at temperatures between those of α and γ processes. In order to analyze β-relaxation, the empirical Havriliak–Negami model (HN) [11,12] was used

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = [1 + (i\omega\tau_0)^\mu]^{-\nu} \tag{2a}$$

where ε_∞ is the relaxed permittivity, ε_0 is the unrelaxed permittivity, and the parameters μ and ν $[0 < \mu, \mu\nu \leq 1]$ define the symmetrical and asymmetrical broadening of the loss peak, respectively, τ_0 is the characteristic relaxation time, and

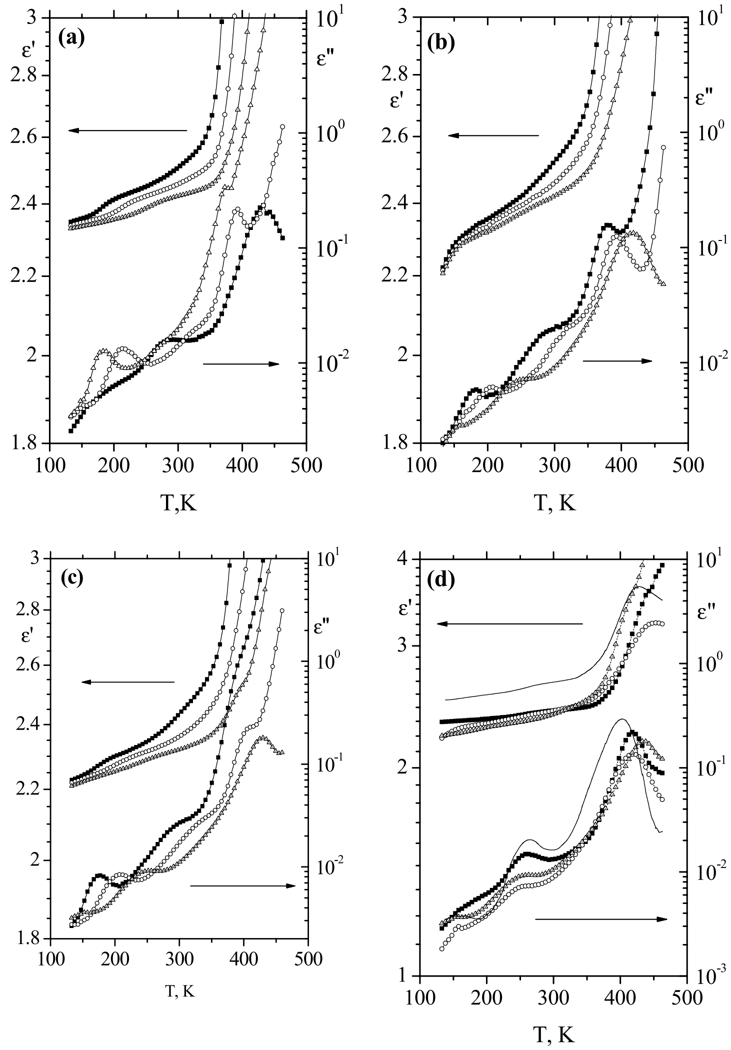

Fig. 1. Permittivity (ε') and loss (ε'') of (a) P2MCHMA, (b) P3MCHMA and (c) P4MCHMA; at several frequencies as a function of temperature: (■) 0.109 Hz, (○) 12.95 Hz, (△) 1040 Hz. (d) Comparison of permittivity and loss factor as a function of the temperature at 2 kHz for the followings polymers: (—) PCHMA, (■) P2MCHMA, (○) P3MCHMA, (△) P4MCHMA.

$$f_{\max} = f_0 \left[\frac{\sin\left(\frac{\pi\mu}{2(1+\nu)}\right)}{\sin\left(\frac{\pi\mu\nu}{2(1+\nu)}\right)} \right]^{\frac{1}{\mu}} \tag{2b}$$

is the frequency at which ε'' passes through the maximum. The splitting of Eq. (2a) in real and imaginary parts gives:

$$\varepsilon'(\omega) = \varepsilon_\infty + r^{-\nu/2}(\varepsilon_0 - \varepsilon_\infty)\cos \nu\theta \tag{3a}$$

$$\varepsilon''(\omega) = r^{-\nu/2}(\varepsilon_0 - \varepsilon_\infty)\sin \nu\theta \tag{3b}$$

where

$$r = \left[1 + (\omega\tau_0)^\mu \cos\left(\frac{\mu\pi}{2}\right)\right]^2 + \left[(\omega\tau_0)^\mu \sin\left(\frac{\mu\pi}{2}\right)\right]^2 \tag{4}$$

$$\theta = \operatorname{arctg}\left[\frac{(\omega\tau_0)^\mu \sin\left(\frac{\mu\pi}{2}\right)}{1 + (\omega\tau_0)^\mu \cos\left(\frac{\mu\pi}{2}\right)}\right]$$

For the three polymers under study, the ν parameter was equal to unity (according to Eq. (2b), $f_0 = f_{\max}$). For this reason, in this case, the β-relaxation can be adjusted in terms of the Cole–Cole equation, which in fact is a symmetric HN-equation. As usual, the relaxation strength for the β relaxation increases with the temperature in all the polymers under study. The shape parameter (μ) for the β-relaxation process keeps almost constant, in values of 0.20, 0.25 and 0.35 for, respectively, P4MCHMA, P3MCHMA, and P2MCHMA in the range of temperatures analyzed. This parameter takes account of the broadness of the process, and for this reason, the position of the substituted methyl group in the cyclohexyl ring affects the broadness of the β-relaxation process.

The obtained values of $f_{\max}$ at each temperature analyzed were used in order to evaluate the activation energy associated at this β-relaxation (Fig. 2). So, activation energies calculated from an Arrhenius type plots, for P2MCHMA, P3MCHMA and P4MCHMA were 82.3 ± 0.6,

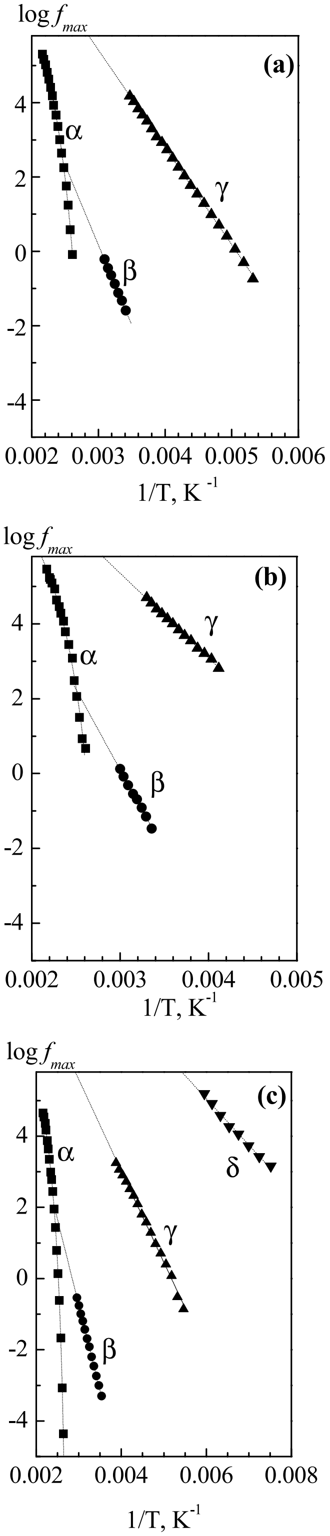

Fig. 2. Dependence of $\log f_{\max}$ with inverse temperature in the range of δ (▼), γ (▲), β (●) and α (■) relaxations for (a) P2MCHMA, (b) P3MCHMA and (c) P4MCHMA.

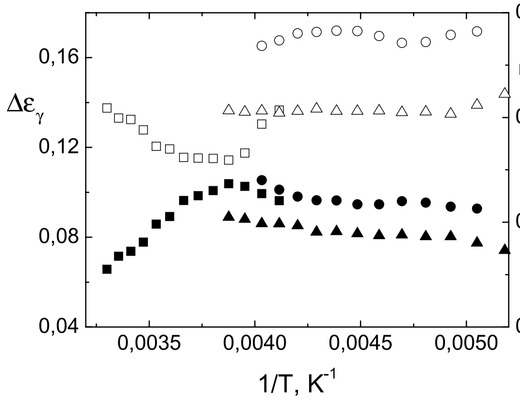

Fig. 3. Relaxation strength, Δε (full symbols) and shape parameter m, (open symbols) for the gamma relaxation as a function of the inverse of temperature, for the P2MCHMA (●, ○), P3MCHMA (■, □) and P4MCHMA (▲, △).

82.3±1.7 and 92.0±0.3 kJ mol^{-1}, respectively. These values are close to the corresponding values for the β-relaxation of PMMA. Taking into account that the β-relaxation in PMMA is attributed to the partial rotation of the lateral chain as a whole hindered by the α-methyl group, we can assign the observed β-relaxation in the polymers under study to the same molecular origin.

At higher temperatures the α-relaxation related to the glass transition temperature appears. This main relaxation process can be associated to the dynamic glass transition of the polymers. In the case of polymers with methyl groups in the cyclohexyl ring a shift of the α-relaxation peak towards higher temperatures with respect to the case of PCHMA is shown (Fig. 1(d)). It can also be observed a systematic increase of the loss permittivity when the temperature increases. This behaviour suggests the presence of significant conductivity contributions which are dominant over the dipolar contributions in this range of frequencies and temperatures.

In order to analyze the glass transition temperature, and due to the asymmetric character of this last relaxation, the empirical Havriliak–Negami model (HN) [11,12] was used. In order to take into account the conductive contributions to the loss permittivity, a term $(\sigma/(\varepsilon_{\mathrm{vac}}\omega))^s$ can be added to Eq. (3b) to give,

$$\varepsilon''(\omega) = r^{-\nu/2}(\varepsilon_0 - \varepsilon_\infty)\sin\nu\theta + \left(\frac{\sigma}{\varepsilon_{\mathrm{vac}}\omega}\right)^s \qquad (5)$$

where σ is a constant, $s \leq 1$, and $\varepsilon_{\mathrm{vac}}$ is the vacuum permittivity (=8.854 pF m^{-1}).

After subtracting the conductivity contribution to the loss permittivity, the ε'' frequency dependences of α-relaxation were described by a HN function. The values of relaxation strength and HN shape parameters obtained for all polymers at several temperatures are summarized in Fig. 4 (relaxation strength) and Fig. 5 (shape parameters) for the alpha and beta relaxation process.

The α-relaxation strength values, follow the tendency, $(\Delta\varepsilon)_{\mathrm{P2MCHMA}} > (\Delta\varepsilon)_{\mathrm{P4MCHMA}} > (\Delta\varepsilon)_{\mathrm{P3MCHMA}}$, suggesting that the mean square dipole moment of these polymers have the same tendency.

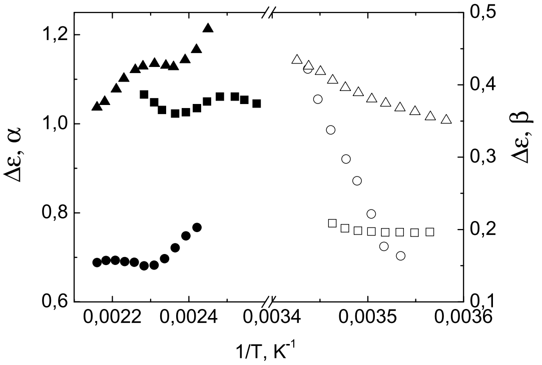

Fig. 4. Relaxation strength, $\Delta\varepsilon$, for the α (full symbols) and β (open symbols) process, as a function of the inverse of temperature, for the P2MCHMA (■, □), P3MCHMA (●, ○) and P4MCHMA (▲, △).

The temperature dependence of the α-relaxation was analyzed in the context of the free volume theory by means of the Vogel–Fulcher–Tamman–Hesse (VFTH) equation [13–15]

$$\ln f_{\max} = A - \frac{M}{T - T_{\infty}} \tag{6}$$

where A and M are constant and T_{∞} in this equation is an empirical parameter related to the Kauzmann temperature or the temperature at which the conformational entropy is zero.

The comparison of VFTH equation with the Doolittle [16,17] equation yields

$$\frac{\phi}{B} = \frac{T - T_{\infty}}{M} \tag{7}$$

this relates the free volume in the Doolittle equation, with the values of M in Eq. (6). From the values of M, the relative free volume at T_g, (ϕ_g/B), can be obtained. The experimental data were analyzed in terms of these equations. The temperature dependence of the α-relaxations with the frequency for the three polymers under study is shown in Fig. 2. The values obtained for the relevant parameters are shown in Table 1. After inspection of these values, it is concluded that the values of relative free volume are in good agreement with the free volume theory. It is interesting to note that both the free volume and glass transition temperature increase with the sequence (P2MCHMA < P3MCHMA < P4MCHMA). The differences between the polymers analyzed in the present study are closely related to the position of the methyl substituted in the cyclohexyl ring. In fact, according to preliminary molecular calculations to be developed in a subsequent paper, the volume occupied by the lateral chain, tend to increase in the sequence P2MCHMA → P3MCHMA → P4MCHMA. At the same time, the rigidity of the lateral chain also increases. These facts can explain the simultaneous increase of the free

Table 1
Parameters of the VFTH equation and relative free volume

	P2MCHMA	P3MCHMA	P4MCHMA
M	1407 ± 78	1195 ± 59	971 ± 29.7
A	22.0 ± 0.4	21.4 ± 0.3	18.9 ± 0.3
T_{∞} (K)	320 ± 2	326 ± 2	345.7 ± 0.7
T_g (K)	371	374	394
ϕ_g/B (%)	3.6 ± 0.3	4.0 ± 0.4	5 ± 0.1

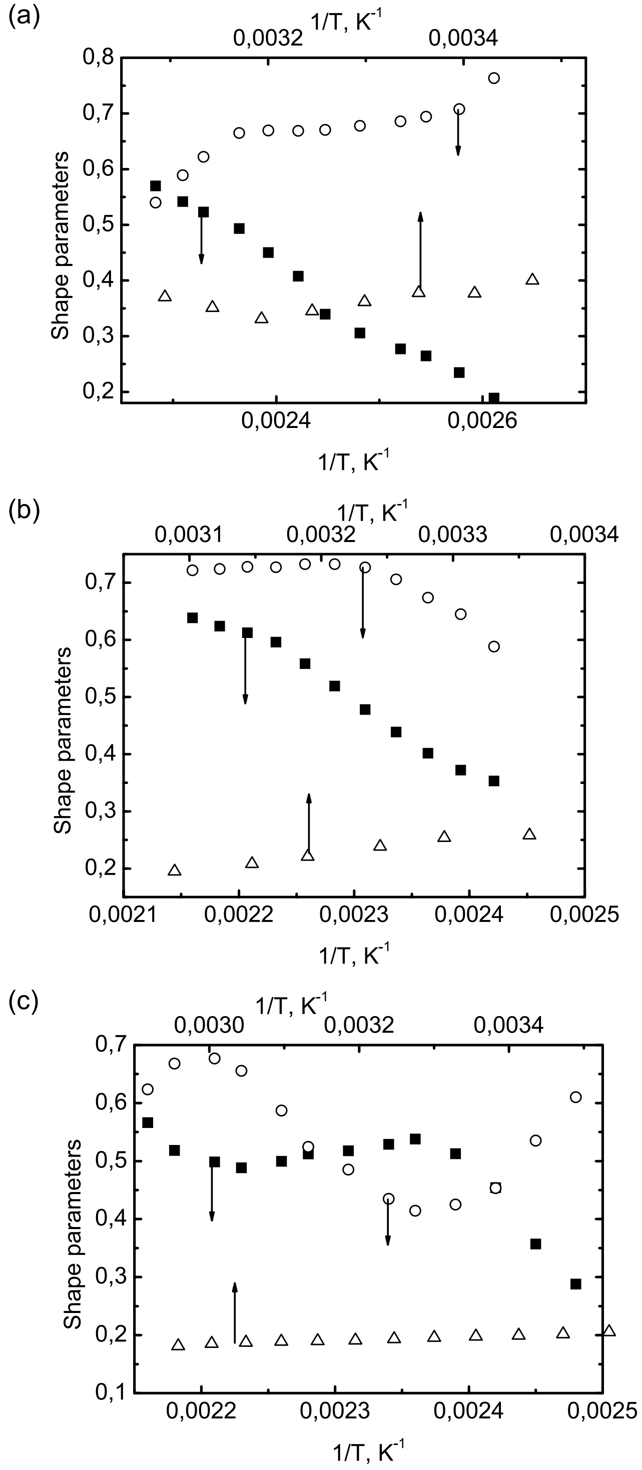

Fig. 5. Shape parameters μ (■), ν (○) for the alpha and μ (△) for beta process as a function of the inverse of the temperature, for the (a) P2MCHMA, (b) P3MCHMA, and (c) P4MCHMA.

volume as well as the glass transition temperature observed in Table 1 in the aforementioned sequence.

The behaviour of the α-relaxation follows the VFTH equation only for some range of temperatures near the glass transition, for higher temperatures Arrhenius behaviour could appear. This behaviour is also reflected in the HN parameters where is possible to observe both tendencies. For this reason the error associated to the VFTH equation are relatively higher.

In any case, both the position and the intensity of the maxima of γ, β and α peaks, shift to higher temperature and their height increases when the frequency increases. The corresponding Arrhenius plots are presented in Fig. 2.

4. Conclusions

Methacrylic polymers like P2MCHMA, P3MCHMA and P4MCHMA show complex dielectric relaxation spectra. In fact at least four relaxations zones labelled α, β, γ and δ in decreasing order of temperature are observed.

By DRS spectroscopy at temperatures about the glass transition, dipolar data are contaminated by spurious conductivity contributions. For this reason these conductive contributions are removed from the experimental curves in order to analyze the α-relaxation in terms of a Havriliak–Negami equation. A poorly defined β-relaxation zone is also observed between α and γ peaks. Moreover, according to our experimental data, the β-relaxation is symmetric. As in the case of poly-*n*-alkyl methacrylates, we attribute the molecular origin of the relaxation to librations of the lateral chain as a whole.

The main effect of the methyl substitution on the cyclohexyl group is to decrease the height of the γ peak. Small increases in the broadness and in the activation energies are also observed. This is in agreement with the assumption that motions in the cyclohexyl ring are responsible of this γ peak. This is because the height of this peak is related to the proportion of cyclohexyl groups in the moiety, and the presence of the methyl substitute tends to diminish this density. On the other hand, the broadening of these γ peaks can be attributed to the presence of two γ-relaxations. These two relaxations should be due to *cis* and *trans* cyclohexyl units in the lateral chain.

Information about the activation energy of the δ-relaxations is given. The molecular origin of this relaxation process can be attributed to several different mechanisms, as for example methyl group rotation, pendant group reorientation or others. Because this relaxation is absent in polymers with pendant phenyl groups, this relaxation peak should be probably caused by a motion precursor of the more pronounced motion causing the γ-relaxation. A specific study of the γ-relaxation by TSDC and molecular modelling is in progress.

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