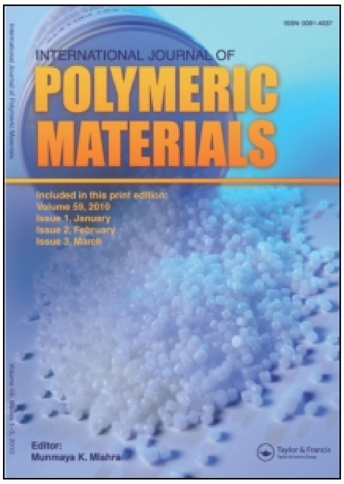

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Dielectric and Mechanical Relaxational Behavior of Poly (Chlorobenzyl Methacrylate)s

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Dielectric and Mechanical Relaxational Behavior of Poly (Chlorobenzyl Methacrylate)s

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Dielectric relaxational behavior of poly(monochlorobenzyl methacrylate)s (PMClBM) and poly(dichlorobenzyl methacrylate)s (PDClBM) has been analyzed. The study was carried out by determining the components of the complex dielectric permittivity ε^*. *Two relaxation processes, labelled as* α *and* β *relaxations, which were analyzed in terms of the Havriliak-Negami and Cole-Cole equations, respectively, have been experimentally observed. The relative position of the chlorine substitute in the benzyl ring determines the characteristic parameters of the relaxations. Complementary dynamic mechanical measurements on these polymers have been carried out. The relationship between the macroscopic measurements with the dipolar moment of the relaxing entities has been analyzed in terms of the Onsager-Kirkwood-Fröhlich equation.*

Keywords: dielectric properties, dipolar moment, mechanical properties, poly (chlorobenzyl methacrylate)s, subglass relaxation

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INTRODUCTION

The spectrum of the loss response of supercooled liquids to perturbation fields displays several absorptions in the frequency domain. In cooling the material from the melt, a temperature, called the glass transition temperature, is reached at which the free volume collapses and a slow process appears. This absorption is associated with cooperative molecular motions and is called α relaxation [1–3]. Although molecular mobility is severely restricted below the glass transition temperature, a cascade of subglass relaxation phenomena may occurs revealing different modes of mobility. These processes called secondary relaxations, are labelled as β, γ, ... in order of decreasing temperatures [1–3]. The temperature at which a structural group undergoes a relaxation usually depends on both the polymer structure and the local environment. On the other hand, the α relaxation also depends on the molecular structure, and still today it is a challenge to make reliable predictions on the glass transition temperature and the associated α relaxation. For this reason, in order to study this complex relaxational behaviour it is advisable to compare polymers with small differences in the chemical structure of their molecular moiety.

In the present article, the dielectric relaxation properties of a family of poly(monochlorobenzyl methacrylate)s (PMClBM) and poly(dichlorobenzyl methacrylate)s (PDClBM) are reported and these properties are related to the relative position of the chlorine atom in the benzyl ring. Additionally, the mechanical behaviors have been analyzed and compared with the dielectric properties. The nomenclature of the polymers used in this work is poly(2-monochlorobenzyl methacrylate) (P2MClBM), poly(3-monochlorobenzyl methacrylate) (P3MClBM), poly(4-monochlorobenzyl methacrylate) (P4MClBM), poly(2,3-dichlorobenzyl methacrylate) (P2,3DClBM), poly(2,4-dichlorobenzyl methacrylate) (P2,4DClBM), poly(2,5-dichlorobenzyl methacrylate) (P2,5DClBM), poly(2,6-dichlorobenzyl methacrylate) (P2,6DClBM), poly (3,4-dichlorobenzyl methacrylate) (P3,4DClBM), and poly(3,5-dichlorobenzyl methacrylate) (P3,5DClBM). The chemical structure of the polymers is schematized in Figure 1.

EXPERIMENTAL

Monomer and Polymer Preparation

Mono- and dichlorobenzyl methacrylates were prepared by reaction of methacryloyl chloride with the corresponding alcohols in toluene solutions and N,N-dimethylaniline at reflux temperature during 32 to 36 h

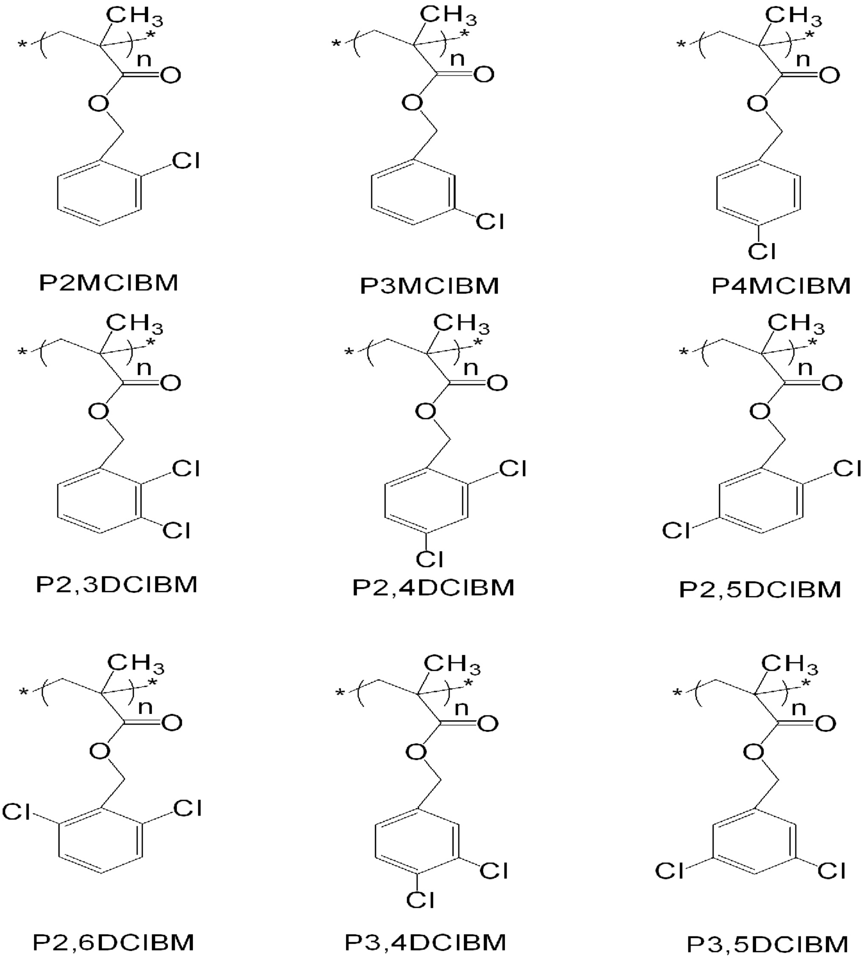

FIGURE 1 Chemical structures for PMClBM and PDClBM.

depending on the monomer, according to the technique described by Burtle and Turek [4]. Purification was achieved by distillation under vacuum.

Monomers were polymerized in toluene solutions under vacuum in sealed tubes, in presence of $5 \cdot 10^{-4}$ to 10^{-2}% (w/w) α,α'-azobisisobutyronitrile (AIBN) as previously reported [5].

Polymers were fractionated by solubility in toluene/methanol as a solvent–nonsolvent pair. Three fractions were obtained and the middle fraction was selected for the present study.

Molecular Characterization

Monomers and polymers were characterized by FT-IR measurements recorded in a Vector 22 Bruker Fourier Transform infrared Spectrophotometer. The spectra were recorded with a resolution of 1 cm^{-1}. The samples were prepared directly in KBr pellets. ^{1}H NMR spectra were recorded in a Bruker AC 200 Spectrometer using TMS as internal standard and deuterated chloroform as solvent. The weight average molecular weight (M_w) were determined by static light scattering measurements using a Dawn-F light scattering instrument from Wyatt Technology containing 15 permanently mounted detectors and a He-Ne laser at $\lambda = 632.8$ nm, connected with a Knauer chromatograph and a OPTILAB DSP interferometric refractometer. Polydispersity indices were obtained directly from the software of the instrument (see Table 1).

DSC Measurements

The glass transition temperatures (T_g) of the polymers were measured with a Mettler TA-3000 system equipped with a TC-10A processor and a DSC-20 cell and a Mettler 821 calorimetric system using the STAR^e program. Polymer samples were dried under reduced pressure in a vacuum oven prior to measurements. Dry nitrogen was used as purge gas and thermograms were measured in the range 308 to 523 K at a scan rate of 20 K · min^{-1} (see Table 1).

Density Measurements

The density of polymers was measured by immersion in water at 294.7 K using a pycnometer. The volume of the pycnometer was

TABLE 1 Characteristics of Polymers

Polymer	Density (g·cm^{-3})	T_g (K)	M_w (kD)	M_w/M_n	DP
P2MClBM	1.230 ± 0.002	327.2	225	2.8	1071
P3MClBM	1.264 ± 0.001	290.0	145	2.5	690
P4MClBM	1.216 ± 0.002	316.7	310	3.0	1476
P2,3DClBM	1.451 ± 0.004	313.2	100	2.2	408
P2,4DClBM	1.543 ± 0.009	293.4	65	2.0	265
P2,5DClBM	1.450 ± 0.002	299.1	60	1.8	245
P2,6DClBM	1.463 ± 0.002	332.0	150	1.9	612
P3,4DClBM	1.423 ± 0.002	307.9	70	2.2	286
P3,5DClBM	1.440 ± 0.002	304.9	80	2.0	327

calibrated with water. The measurements of density were repeated tree times and averaged (see Table 1).

The glass temperature (T_g), density and molecular weight of the polymers are summarized in Table 1.

Dielectric Measurements

The real and imaginary parts of the complex dielectric permittivity ε^* were measured in dry nitrogen atmosphere with a DEA 2970 apparatus from TA Instruments. The heating rate was $1\,\mathrm{K \cdot min^{-1}}$ at 26 frequencies in the range of 10^{-1}–10^5 Hz from 123 K up to a temperature 20 K above to the glass transition.

Dynamic Mechanical Measurements

The storage and loss components of the complex relaxation modulus E^* were obtained with a Rheometric DMTA MarkII in double cantilever flexural mode. The experiments were carried out on molded samples of $1 \times 10 \times 8.5\,\mathrm{mm}^3$ at a heating rate of $1\,\mathrm{K \cdot min^{-1}}$ at 0.3, 1, 3, 10, and 30 Hz from 153 K up to a temperature close to the glass transition.

RESULTS

Dielectric Measurements

Figure 2 shows the dielectric permittivity and loss for PMClBM and PDClBM as function of temperature. In all the cases the α relaxation associated to the dynamic glass transition can be observed and the β relaxation that in some cases is observed as a shoulder of the α relaxation. At low frequencies and high temperatures, a conductive contribution can be observed. In order to analyze the α and β relaxations it is necessary to split these effects. The conductive contribution of the dielectric loss ϵ'' can be described by using the hopping model [6]

$$\epsilon'' = \frac{\sigma}{\epsilon\omega^s} \tag{1}$$

where σ is the conductivity, ϵ is dielectric permittivity of the vacuum, ω is the angular frequency, and s a parameter to be determined. In this case, according to Table 2 the observed values for s ranges between 0.94–0.99. This result indicates that pure ionic conductivity predominates over partial blocking phenomena. The activation energies can be calculated from Arrhenius plot of ln σ against T^{-1}. These values are summarized in Table 2.

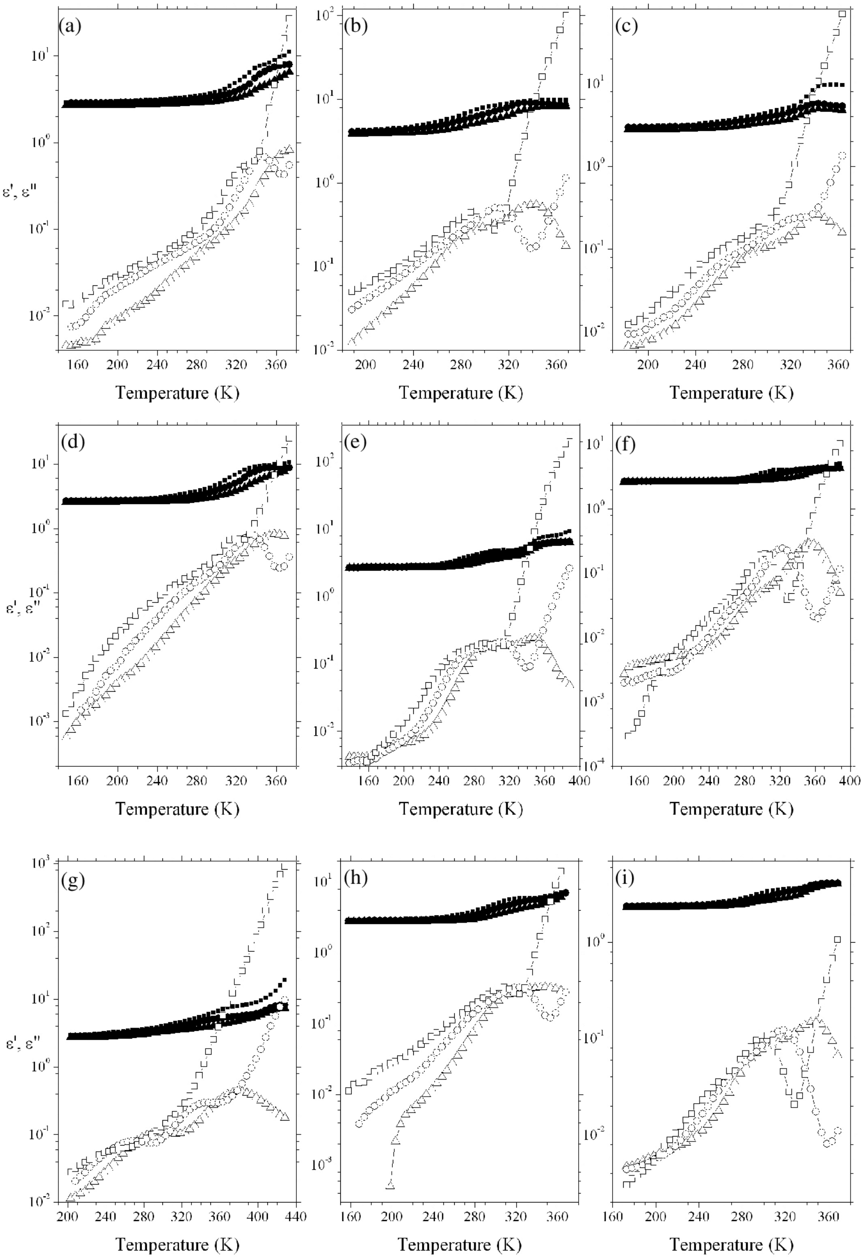

FIGURE 2 Dielectric permittivity (solid) and loss (open). (triangle) 10^4 Hz, (circle) 10^2 Hz, and (square) 10^0 Hz. (a) P2MClBM, (b) P3MClBM, (c) P4MClBM, (d) P2,3DClBM, (e) P2,4DClBM, (f) P2,5DClBM, (g) P2,6DClBM, (h) P3,4DClBM, and (i) P3,5DClBM.

TABLE 2 Activation Energy for Conductive Contribution for PMClBM and PDClBM

Polymers	E_a conductive ($kJ \cdot mol^{-1}$)	s	Temperature (K)
P2MClBM	146.7	0.94	373
P3MClBM	105.0	0.97	368
P4MClBM	108.8	0.95	368
P2,3DClBM	97.9	0.94	373
P2,4DClBM	104.2	0.98	388
P2,5DClBM	112.1	0.99	388
P2,6DClBM	105.4	0.99	428
P3,4DClBM	114.6	0.94	363
P3,5DClBM	112.1	0.98	368

After eliminating the ionic conductivity, the asymmetric α relaxation can be analyzed by using the asymmetric Havriliak-Negami equation (HN) [7]

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (j\omega\tau)^a)^b} \tag{2}$$

where $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ is the strength of the relaxation, ε_0 and ε_∞ are the relaxed and unrelaxed permittivity, a and b are two parameters related to the shape and skewness of the Cole-Cole plot and τ is the relaxation time. When the b parameter is equal to unity, Eq. 2 reduces to the Cole-Cole equation (CC) [8].

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (j\omega\tau)^a} \tag{3}$$

This means that the relaxation is symmetric in shape, which is the actual situation for many secondary relaxations.

In the present case, the α and β relaxations are in general very close, and the analysis should be done by using a combination of Cole-Cole and Havriliak-Negami equations according to:

$$\epsilon^* = \epsilon_{\beta\infty} + \frac{\Delta\epsilon_\beta}{1 + (j\omega\tau_\beta)^{a_\beta}} + \frac{\Delta\epsilon_\alpha}{(1 + (j\omega\tau_\alpha)^{a_\alpha})^{b_\alpha}} \tag{4}$$

where $\Delta\epsilon_\beta = \epsilon_{\beta 0} - \epsilon_{\beta\infty}$ and $\Delta\epsilon_\alpha = \epsilon_{\alpha 0} - \epsilon_{\alpha\infty}$, and $\epsilon_{\alpha\infty} = \epsilon_{\beta 0}$.

The obtained parameters by using Eq. 4 are shown in Tables 3 for PMClBM and 4 for PDClBM.

TABLE 3 Parameters of Havriliak-Negami and Cole-Cole and Kohlrausch-Williams-Watts equations for PMClBM

T (K)	$\varepsilon_{\beta\infty}$	$\Delta\varepsilon_\beta$	a_β	τ_β (s)	$\Delta\varepsilon_\alpha$	a_α	b_α	τ_α (s)	b_{KWW}	τ_{KWW} (s)
P2MClBM										
338	3.38				4.11	0.58	0.37	2.86×10^{-2}	0.260	3.55×10^{-3}
343	3.67				4.57	0.42	0.70	4.08×10^{-3}	0.265	3.32×10^{-3}
348	3.83				4.43	0.41	0.86	8.66×10^{-4}	0.303	1.55×10^{-3}
P3MClBM										
288	4.31	0.97	0.43	6.28×10^{-6}	3.79	0.31	0.82	4.77×10^{-1}	0.201	8.06×10^{-1}
293	4.32	1.01	0.41	2.97×10^{-6}	3.81	0.34	0.71	2.40×10^{-1}	0.212	2.04×10^{-1}
298	4.29	1.02	0.43	5.13×10^{-7}	3.91	0.35	0.66	6.90×10^{-2}	0.215	5.98×10^{-2}
P4MClBM										
333	4.02				1.87	0.35	0.98	1.04×10^{-4}	0.253	3.07×10^{-4}
338	4.25				1.68	0.40	0.99	4.11×10^{-5}	0.294	1.05×10^{-4}
343	4.37				1.42	0.45	1.02	1.96×10^{-5}	0.339	4.61×10^{-5}

On the other hand, the dielectric permittivity obtained in the frequency domain, can be related to the correlation function in the domain time by the Laplace transformation, according to

$$\frac{\epsilon^*(\omega)-\epsilon_\infty}{\epsilon_0-\epsilon_\infty}=\Phi^*(\omega)=L\left[-\frac{d\varphi(t)}{dt}\right] \tag{5}$$

where $\Phi^*(\omega)$ and $\varphi(t)$ are correlation functions in the frequency and time domain, respectively. For an asymmetric relaxation, the function on the time domain can be described by using the Kohlrausch-Williams-Watts (KWW) equation [9]

$$\varphi(t)=\exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{b_{KWW}}\right] \tag{6}$$

where b_{KWW} is the shape parameter and τ_{KWW} is the characteristic time.

The parameters arising for this analysis for the PMClBM and PDClBM are shown in Tables 3 and 4.

As can be seen in these tables, in some cases, P2MClBM, P4MClBM, P2,3DClBM and P2,5DClBM, the α and β relaxations overlap, thus precluding the analysis of the β relaxation. In other cases, the β and α relaxations are close and the strengths of relaxation are similar. This is the situation for P3MClBM, P2,4DClBM, P3,4DClBM, and P3,5DClBM where the analysis has been carried out by means of Eq. 4. P2,6DClBM is the only polymer where the β and α relaxations are enough separated to permit a quantitative analysis for both relaxations.

TABLE 4 Parameters of Havriliak-Negami and Cole-Cole and Kohlrausch-Williams-Watts Equations for PDClBM

T (°C)	$\varepsilon_{\beta\infty}$	$\Delta_{\varepsilon\beta}$	a_β	τ_β (s)	$\Delta\varepsilon_\alpha$	a_α	b_α	τ_α (s)	b_{KWW}	τ_{KWW} (s)
P2,3DClBM										
343	3.10				6.06	0.56	0.29	1.69×10^{-3}	0.213	8.86×10^{-5}
348	3.05				5.99	0.64	0.25	7.27×10^{-4}	0.214	2.74×10^{-5}
353	3.20				5.83	0.65	0.25	3.05×10^{-4}	0.223	1.31×10^{-5}
358	3.35				5.62	0.70	0.24	1.46×10^{-4}	0.226	5.90×10^{-6}
P2,4DClBM										
293	2.50	1.73	0.23	7.60×10^{-6}	1.13	0.36	0.88	0.54	0.250	1.065
298	2.29	1.86	0.22	1.07×10^{-6}	1.28	0.35	0.71	0.44	0.220	3.95×10^{-1}
303	2.27	1.89	0.20	8.28×10^{-7}	1.33	0.32	0.64	0.39	0.191	2.27×10^{-1}
P2,5DClBM										
333	2.82				1.25	0.71	0.47	7.23×10^{-4}	0.378	2.06×10^{-4}
338	2.82				1.24	0.76	0.44	3.47×10^{-4}	0.393	8.86×10^{-5}
343	2.83				1.24	0.80	0.41	1.82×10^{-4}	0.406	4.29×10^{-5}
348	2.92				1.19	0.82	0.45	8.74×10^{-5}	0.451	2.55×10^{-5}
353	3.07				1.10	0.83	0.54	4.26×10^{-5}	0.506	1.70×10^{-5}
P2,6DClBM										
253	2.75	0.71	0.24	3.66×10^{-3}						
258	2.77	0.73	0.25	1.67×10^{-3}						
263	2.78	0.77	0.26	7.92×10^{-4}						
268	2.78	0.82	0.26	3.46×10^{-4}						
273	2.77	0.82	0.27	1.29×10^{-4}						
278	2.77	0.87	0.27	5.64×10^{-5}						
283	2.74	0.91	0.28	2.33×10^{-5}						
288	2.75	0.91	0.29	1.02×10^{-5}						
293	2.75	0.92	0.31	4.94×10^{-6}						
328	3.61				1.20	0.56	0.39	1.25×10^{-2}	0.256	1.69×10^{-3}
333	3.60				1.32	0.58	0.39	7.29×10^{-3}	0.266	1.04×10^{-3}
338	3.60				1.49	0.54	0.54	3.77×10^{-3}	0.265	7.16×10^{-4}
343	3.54				1.66	0.55	0.55	2.30×10^{-3}	0.258	3.59×10^{-4}
P3,4DClBM										
308	3.13	0.46	0.57	1.32×10^{-5}	3.56	0.24	0.95	1.26×10^{-1}	0.176	5.84×10^{-1}
313	3.15	0.39	0.61	8.90×10^{-6}	3.54	0.25	0.85	5.02×10^{-2}	0.167	1.43×10^{-1}
318	3.17	0.27	0.69	6.04×10^{-6}	3.46	0.25	0.82	1.06×10^{-2}	0.162	2.48×10^{-2}
323	3.17	0.14	0.84	4.31×10^{-6}	3.35	0.27	0.76	2.38×10^{-3}	0.166	3.44×10^{-3}
P3,5DClBM										
313	2.37	0.60	0.35	4.58×10^{-7}	0.69	0.39	0.98	5.06×10^{-3}	0.268	1.41×10^{-2}
318	2.40	0.61	0.35	4.11×10^{-7}	0.62	0.43	0.96	1.85×10^{-3}	0.313	3.90×10^{-3}
323	2.45	0.61	0.36	3.81×10^{-7}	0.55	0.47	0.93	7.35×10^{-4}	0.342	1.26×10^{-3}

It can be assumed that the temperature of the maximum of the α relaxation at 1 Hz nearly agrees with the glass transition temperature. According to that, in Table 5, the temperatures of these maxima and the calorimetric glass transition are compared. In some cases this

TABLE 5 Comparison of Calorimetric Glass Transition Temperature and Temperature of the Maximum of the α Relaxation at 1 Hz

Polymer	T_g (K)	T_{max} [1Hz] (K)
P2MClBM	327.2	[a]
P3MClBM	290.0	292.7
P4MClBM	316.7	[a]
P2,3DClBM	313.2	318.2
P2,4DClBM	293.4	291.7
P2,5DClBM	299.1	302.7
P2,6DClBM	332.0	[a]
P3,4DClBM	307.9	307.2
P3,5DClBM	304.9	301.2

[a] Hidden for conductivity.

comparison has proved not to be possible, due to the overlap of the conductivity and the α dipolar contributions at 1 Hz. In general, conductivity contributions tend to shift the peak maxima to high temperatures.

The obtained values are in fairly good agreement.

The analysis of the frequency dependence of the α relaxation on the temperature and the corresponding free volume can be performed by means of a Vogel-Fuchel-Tamman-Hesse (VFTH) Eq. 10

$$\ln(f_{\max}) = B - \frac{DT_\infty}{T - T_\infty} \tag{7}$$

where T_∞ is the temperature at which the conformational entropy is zero, D is the so-called Angell parameter or fragility index that measures the departure of supercooled liquids from Arrhenius behavior, and B is a pre-exponential factor.

The VFTH equation is related to the free volume by means of the following equation:

$$v_f = \frac{T - T_\infty}{DT_\infty} \tag{8}$$

which relates the fractional free volume to the value of fragility index in the VFTH equation.

The temperature dependence of the secondary relaxations in the frequency domain can be conveniently analyzed by means of the Arrhenius equation:

$$\ln(f_{\max}) = A - \frac{E_a}{RT} \tag{9}$$

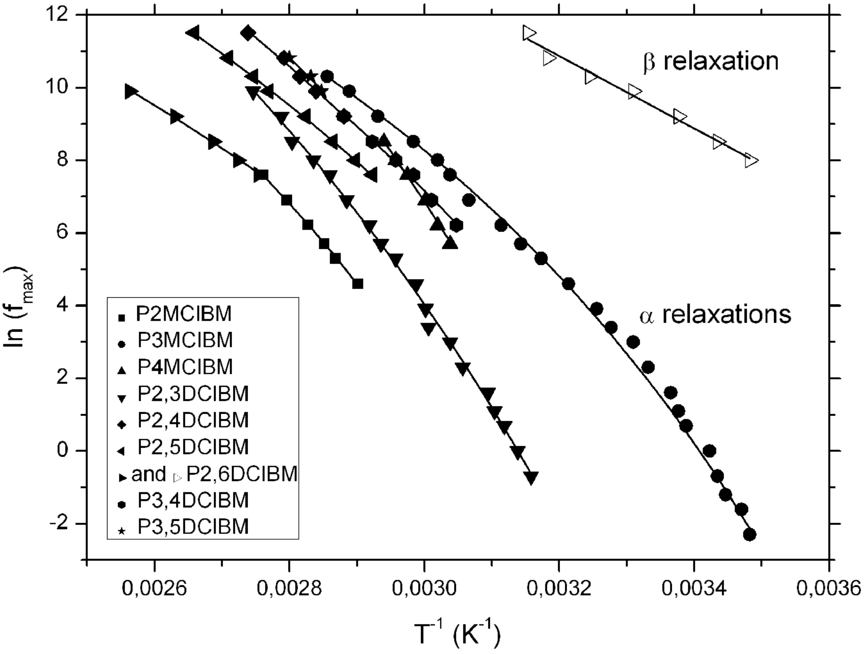

FIGURE 3 Arrhenius plot for PMClBM and PDClBM.

where E_a is the activation energy for sub-glass relaxation. The only system where the activation energy of the β relaxation has been estimated is P2,6DClBM. The corresponding values is $74.7\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$.

The frequency-temperature plots for α and β relaxation are shown in Figure 3 and the parameters of Arrhenius and VFTH equations together with the fractional free volume are summarized in Table 6.

As can be seem in Table 6, the fractional free volumes for poly(chlorobenzyl methacrylate)s are in relatively good agreement with those predicted by the free volume theory (2.5%).

Dynamic Mechanical Measurement

Figure 4 shows the storage and loss tensile modulus for PDClBM at 1 Hz. Measurements on monosubstituted polymers were not performed due to the low glass transition temperatures exhibited by these polymers, which precludes the preparation of the samples. In this figure two relaxations can be also shown: the high temperature one, corresponding to the dynamic glass transition or α relaxation, and the β relaxation which in nearly all the cases is observed as a shoulder

TABLE 6 Parameters from Arrhenius Equation, from VFHT Equation and Fractional Free Volume at Glass Transition, Temperature

Polymer	B	D	T_∞ (K)	v_f (%)
P2MClBM	25.58	9.10	240.58	3.95
P3MClBM	24.40	8.80	215.67	3.92
P4MClBM	36.53	15.67	218.14	2.89
P23DClBM	32.71	15.96	214.00	2.90
P24DClBM	28.97	13.80	197.96	3.48
P25DClBM	27.98	14.76	198.41	3.43
P26DClBM	24.39	15.00	191.39	4.90
P34DClBM	27.67	11.87	211.03	3.87
P35DClBM	31.70	14.37	211.42	3.08

of the α relaxation. This fact and the short frequency range of the dynamic mechanical measurements precludes the analysis of the β relaxation. Only in the case of P2,6DClBM, the β relaxation is very well separated from the α relaxation, as in the dielectric measurements.

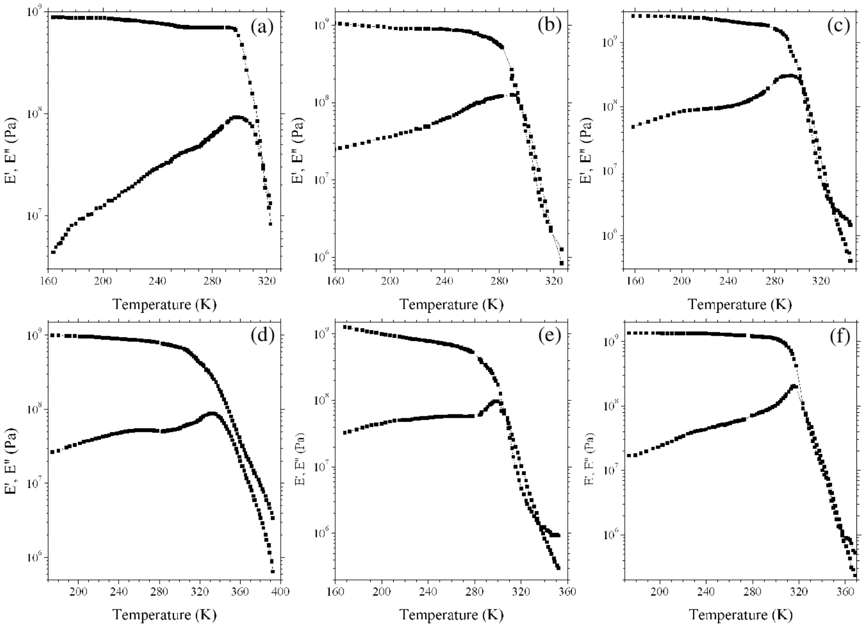

FIGURE 4 Storage and loss modulus for (a) P2,3DClBM, (b) P2,4DClBM, (c) P2,5DClBM, (d) P2,6DClBM, (e) P3,4DClBM, and (f) P3,5DClBM at 1 Hz.

DISCUSSION

The dielectric and mechanical relaxational behavior of these polymers is fairly complex. In particular, the sub-glass zone shows indications of several overlapped processes. This means that there are significant dielectric as well as mechanical activities below T_g. However, the continuous increase in the loss precludes a detailed analysis of the secondary relaxation processes. For this reason, a global comparison of the behavior of these polymers is pertinent.

As is well known, the dipole moment of the polymer is related to the relaxation strength by means of the Onsager-Fröhlich-Kirkwood equation (OFK) [11–12]. By considering the combined contributions of the β and α relaxations, one can write the OFK equation as:

$$\Delta\epsilon_\alpha + \Delta\epsilon_\beta = \frac{3\epsilon_{\alpha 0}}{(2\epsilon_{\alpha 0} + \epsilon_{\beta\infty})} \frac{4\pi N}{3kT} \left(\frac{\epsilon_{\beta\infty} + 2}{3}\right)^2 \langle \mu_0^2 \rangle g \qquad (10)$$

where the subindices 0 and ∞ refer, respectively, to the relaxed and unrelaxed permittivities, k is the Boltzmann constant, T the absolute temperature, N is the number of the monomer units per unit volume and $\langle {\mu_0}^2 \rangle$ is the mean-square dipole moment in vacuum and g is the Kirkwood correlation factor. This factor is a measure of the local order in the molecule, which depends on the structure of the material and gives information about the local forces. These local forces can be of intra and intermolecular in origin. The intramolecular forces are dominant in diluted solution. However, both intra and intermolecular contributions are present in the bulk. For this reason the correlation factor takes into account intra as well as intermolecular contributions.

The product of $\langle {\mu_0}^2 \rangle$ and g is the mean-square dipole moment in the condensed state, $\langle \mu^2 \rangle$.

$$\langle \mu^2 \rangle = g \langle \mu_0^2 \rangle \qquad (11)$$

From Eq. 10 and the experimental data a rough estimation of the correlation factor can be done. On the other hand, the mean-square vacuum moments were calculated by using the Austin model-1 (AM1) molecular orbital method [13] for monomeric structures. The mean-square dipole moment in the liquid state, mean-square vacuum moment, and the Kirkwood correlation function are summarized in Table 7.

Typical values of g for poly(methacrylate)s in solution are 0.6 [14]. In the case of poly(4-chlorophenyl methacrylate) [15] and poly(dichlorophenyl methacrylate) [16] Kirkwood correlation function

TABLE 7 Mean-Square Dipole Moment and Kirkwood Correlation Factor

Polymer	T(K)	$\langle\mu^2\rangle$(D^2)	$\langle\mu_0\rangle$(D)	$\langle\mu_0^2\rangle$(D^2)	g
P2MClBM	338	3.14	3.042	9,254	0.34
P3MClBM	288	2.33	2.716	7,377	0.32
P4MClBM	333	1.77	1.719	2,955	0.32
P23DClBM	343	4.62	3.637	13,228	0.35
P24DClBM	293	2.66	2.695	7,263	0.37
P25DClBM	333	1.14	1.783	3,179	0.36
P26DClBM	328	2.40	2.701	7,295	0.33
P34DClBM	308	2.72	2.861	8,185	0.38
P35DClBM	313	1.41	1.798	3,233	0.38

has also been reported in solution, and their values are respectively 0.35 and 0.38. These values are similar to those estimated for poly(chlorobenzyl methacrylate)s in bulk as shown in Table 6. This indicates that the intermolecular contributions do not significantly affect the correlation factor at these temperatures as suggested by Williams [17–18].

CONCLUSIONS

This study reveals the complexity of the relaxational behavior of PMClBM and PDClBM. In general, these polymers show two relaxations. The first one corresponds to the dynamic glass transition, that is α relaxation and then the diffuse relaxation, named as β. It seems clearly that the relative position of the chlorine atoms in the benzyl ring influences directly the position and the strength of the secondary relaxation. This indicates that the benzyl ring takes part on the β relaxation. In addition, the relative position of the chlorine atom also determines the glass transition temperature. The mechanical measurements of PDClBM confirm these conclusions.

The mean-square dipole moment depends on the relative position of the chlorine atom. In this sense, the mean-square dipole moment for the P3MClBM and P2,4DClBM are similar, and the same is true for P4MClBM and P3,5DClBM. By using the OFK equation, a rough estimation of the correlation factor for the combined α and β relaxations has been made. The results indicate that the correlation factor is similar for all the systems under study. Moreover, a comparison of these correlation factors with those obtained in solution for polymers with similar structure, suggests that intramolecular correlations are dominant in these systems.

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