Dipolar correlation coefficients in the time and frequency domains for low molecular weight models of acrylate polymers

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The temperature dependence of the components of the complex relative permittivity of 2-biphenyl isobutyrate (OBPI) and bis(biphenyl-2-yl) 2,4-dimethylglutarate (OBPG), model compounds of a single repeating unit and a dimer of poly(biphenyl-2-yl acrylate), respectively, is reported in the frequency range 10^{-4}–10^{2} kHz. The relaxation spectra of both compounds at 0.1 Hz exhibit glass–liquid relaxations with maxima located at −61.2 and −8.8 °C, respectively, for OBPI and OBPG. Subglass absorptions are not detected in the glassy state down to −120 °C. The free volume fraction at T_g is calculated to be 0.024 and 0.028 for OBPI and OBPG, respectively. Molecular dynamics (MD) simulations give the following values for the mean-square dipole moment of OBPI: 4.01, 2.92 and 2.80 D^2 at 1000, 500 and 300 K, respectively. The values of $\langle\mu^2\rangle$ at 500 and 300 K are in rather good agreement with the experimental result, 2.69 ± 0.13 D^2, at 303 K. The time dependence of the dipolar autocorrelation coefficient $\varphi(t)$ is calculated by MD at several temperatures. Transformation of the autocorrelation coefficient from the time to the frequency domain permits the determination of the components of the complex permittivity for these compounds. At low temperatures, the mobility of the molecules is not large enough to cover the whole conformational space within a reasonable computing time. At temperatures lying in the neighbourhood of 500 K, the molecules already visit the whole conformational space, and the values of the complex permittivity in the frequency domain obtained from the $\varphi(t)$ of OBPI and OBPG are in good agreement with the experimental results. These results suggest that the intermolecular cross-correlation terms, although present, do not alter in a significant way the time dependence of $\varphi(t)$.

Introduction

The response of liquids to external perturbations depends on the interactions between the constituent particles (atoms, ions or molecules). These interactions, conditioned by the chemical nature of the particles, their relative position in the space, *etc.*, are embodied in a energy potential function which includes contributions from electrostatic multipoles and polarization effects, covalency and hydrogen bonding, intramolecular force fields, short-range electron-cloud-overlap repulsions and longer range dispersion attractions, *etc.*[1] Knowledge of this function in combination with the classical Newton equations may provide a suitable description of the dynamics of liquids.

When a noncrystallizable liquid is cooled, a temperature is reached in the vicinity of which a dramatic change in the properties of the system occurs. At this temperature, called glass transition temperature T_g, the response of the liquid to a perturbative force field is very slow, and it loses its ability to flow. The phenomenological theories of linear viscoelasticity predict that the mean relaxation time of amorphous condensed matter is given by the ratio between the viscosity and the infinite frequency shear modulus. As the temperature of the liquid approaches T_g, the viscosity of the system undergoes an anomalous increase and the mean relaxation time of the system becomes very large.[2] Liquids do not exhibit Arrhenius behaviour in the vicinity of T_g, and the temperature dependence of the mean-relaxation time, $\tau(T)$, is described by the Vogel–Fulcher–Tammann–Hesse (VFTH) empirical equation given by eqn. (1),[3–5] where T_0, a temperature roughly 50 °C below T_g, lies

$$\tau(T) = \tau_0 \exp\left[\frac{m}{T - T_0}\right] \qquad (1)$$

in the vicinity of the Kauzmann temperature,[1,6] that is, the temperature at which the conformational entropy of the glass vanishes. As long as the relaxation time is shorter than the time scale of the experiment, the liquid will remain in a state of quasi-equilibrium with the molecular particles visiting the conformational space of local energy minima. But as the temperature declines, coming close to T_g, the mean relaxation time increases and crosses the time scale of the experiment at T_g. Consequently, below T_g the system falls out of equilibrium.

The relaxation spectra obtained at temperatures just above T_g show peaks, presumably associated with local conformational transitions, located in the very short times region, while at longer times, the correlation function of the relaxation, $\varphi(t)$, displays a Kohlrausch–Williams–Watts (KWW) stretched exponential decay given by eqn. (2),[7,8] where $0 < \bar{\beta} \leqslant 1$ and

$$\varphi(t) = \exp\left[-(t/\tau^*)^{\bar{\beta}}\right] \qquad (2)$$

τ^* is comparable to the mean-relaxation time when T is near T_g. For simple Debye relaxations, $\bar{\beta} = 1$; that is, the process is described by a single relaxation time. A decrease in the value of the stretch exponent leads to an increase of the breadth of the distribution of relaxation times. Transformation of the KWW equation from the time to the frequency domain makes explicit the increase of the breadth of the distribution with the decrease of $\bar{\beta}$.

Molecular dynamics (MD) has proved to be a useful tool to predict the equilibrium dipolar autocorrelation function of low molecular weight compounds. The value of this quantity was calculated for esters of alcohol residues containing phenyl groups in their structure from the trajectories described by the dipole moments of these compounds in the conformational space, finding good agreement between experimental results and those obtained from the simulations.[9,10] These studies were further extended to the evaluation of the equilibrium dipolar

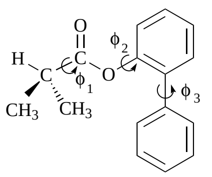

Fig. 1 The molecule of biphenyl-2-yl isobutyrate (OBPI) shown in its planar conformation, for which all the rotational angles were taken to be 180°

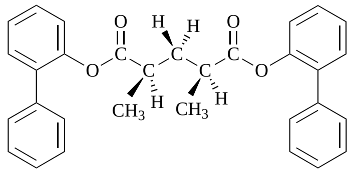

Fig. 2 The molecule of bis(biphenyl-2-yl) 2,4-dimethylglutarate (OBPG) in its planar conformation

autocorrelation function of esters with substituted cyclohexane and dioxane moieties in the alcohol residue.[11–13] Again calculations gave a good account of the experimental results for these compounds. MD simulations were even used to evaluate barrier energies involved in the chair-to-chair conformational transitions occurring in the cyclohexane and dioxane rings of the later compounds. The values of the barriers obtained were in rather good agreement with those reported in the literature for similar compounds.[11–13]

This paper goes a step further in the use of molecular dynamics in permittivities. It tries to simulate the dipole-moment time-correlation function of biphenyl-2-yl isobutyrate (OBPI) and bis(biphenyl-2-yl) 2,4-dimethylglutarate (OBPG), model compounds of a single repeating unit and a dimer of poly(biphenyl-2-yl acrylate). Schematic representations of both OBPI and OBPG are shown in Figs. 1 and 2, respectively. The frequency dependence of the components of the complex dielectric permittivity ε^* of these compounds is further evaluated by transforming the dipole-moment time-correlation function from the time to the frequency domain. The results thus obtained are compared with those experimentally measured in order to assess the capability of MD simulations to predict the response of molecular compounds to electric force field perturbations. This work forms part of a more general investigation into the influence of the structure on the relaxation behaviour of flexible polymer chains.

Experimental

Biphenyl-2-yl isobutyrate (OBPI) and bis(biphenyl-2-yl) 2,4-dimethylglutarate (OBPG) were obtained by condensation of 2-biphenol with isobutyric acid and 2,4-dimethylglutaric acid, respectively, in a solution of refluxing toluene, using an equimolecular amount of toluene-*p*-sulfonic acid and boric acid (2%) as catalyst. The solvent was evaporated and the products were isolated by column chromatography (Kiesel-gel 60, Merck) using a mixture of chloroform–ethane (75:25, v/v) as eluent.

The static relative permittivity ε of benzene solutions of biphenyl-2-yl isobutyrate was measured at 30 °C with a capacitance bridge (General Radio, type 1620 A) and a three terminal cell, using a frequency of 10 kHz. The value of the mean-square dipole moment of this compound was further evaluated by means of the method of Guggenheim and Smith,[14,15] eqn. (3),

$$\langle \mu^2 \rangle = \frac{27k_BTM}{4\pi\rho N_A(\varepsilon_1 + 2)^2}\left[\frac{d\varepsilon}{dw} - 2n_1\frac{dn}{dw}\right] \quad (3)$$

where k_B is the Boltzmann constant, N_A is Avogadro's number, w and M represent the weight fraction and molecular weight of the solute, while ρ and ε_1 are the density and the permittivity of the solvent at the temperature of interest. Values of the increments of the index of refraction of the solution n with respect to that of the solvent n_1 were measured with a refractometer (Chromatix, Inc.). From plots of these increments against the weight fraction of solute, the term dn/dw of eqn. (3) was obtained. The value of the mean-square dipole moment thus obtained was 2.69 ± 013 D^2.

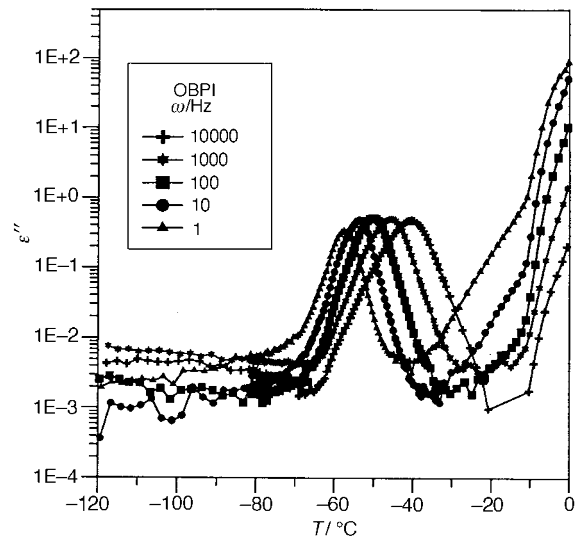

Fig. 3 Temperature dependence of the permittivity loss ε'' for OBPI at the frequencies indicated

Experimental values of the loss ε'' and real ε' components of the relative permittivity of both OBPI and OBPG were obtained with a capacitance apparatus TA-DEA 2970 operating in the frequency range 10^{-4}–10^2 kHz. The technique involves exposing the sample to an alternating electrical field created by applying a sinusoidal voltage to one of the electrodes. The phase angle shift is measured by comparing the applied voltage to the measured current, and the admittance is separated into the capacitance and conductance components. A ceramic single-surface sensor is used that is based on a coplanar interdigitated-comb configuration of electrodes, consisting of a ceramic substrate, metal ground plate high temperature insulating layer, screen-printed gold electrode arrays, a platinum resistance temperature detector and electrical contact pads. Gain and phase data are sent to a calibration table stored in computer memory, where they are used to determine the permittivity and loss. In the glassy region, the experiments proceeded from low to high temperature at the heating rate of 1 °C min^{-1}. In the glass–liquid transition, ε' and ε'' were measured under isothermal conditions at steps of 5 °C. The error involved in the determination of the components of the complex relative permittivity was estimated to be lower than 5%.

Results

The temperature dependence of the loss $\varepsilon''(\omega)$ component of the complex relative permittivity $\varepsilon^*(\omega)$ for OBPI and OBPG are shown at several frequencies in Figs. 3 and 4, respectively. The isochrones exhibit prominent absorptions associated with the glass-liquid relaxation process whose maxima span from -35.0 to -61.2 °C in the case of OBPI and from 23.6 to -8.8 °C in OBPG; the range of measured frequencies covers from 10^{-4} to 10^2 kHz. The values of the glass transition temperatures, taken as the temperatures at the maximum of the peaks for the lowest measured frequency, were found to be -61.2 and -8.8 °C for the former and latter compounds, respectively. Subglass absorptions were not detected in the glassy state down to -120 °C.

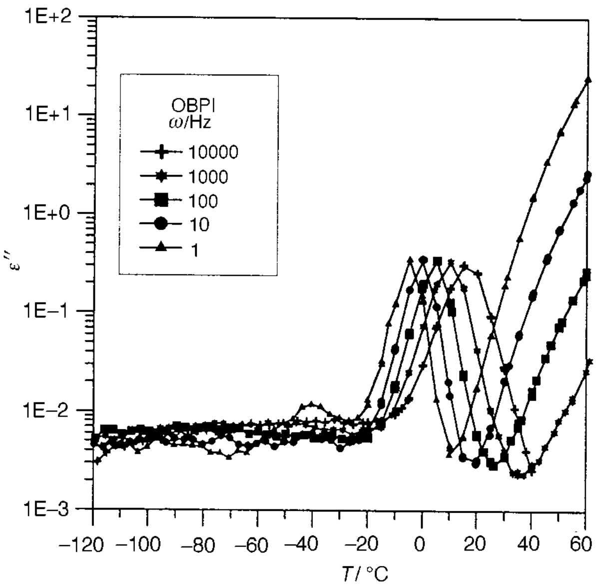

Fig. 4 Same as Fig. 3 for OBPG

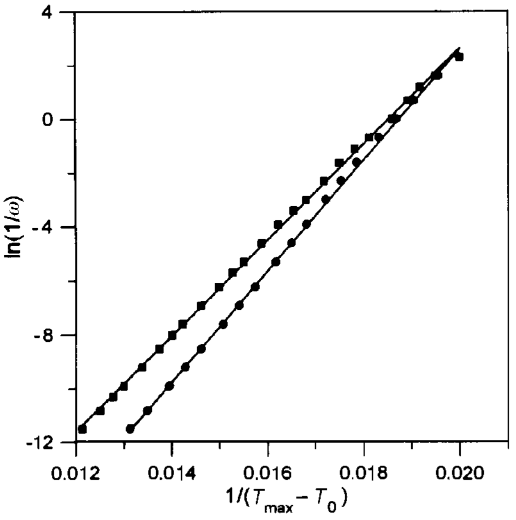

Fig. 5 Natural logarithm of the reciprocal of the experimental frequencies *versus* the reciprocal of $T_{max} - T_0$, where T_{max} is the temperature at which the maximum of ε'' is reached for each frequency while T_0 was taken to be $T_g - 50$ (■, OBPG; ●, OBPI)

For thermorheological simple systems, the mean relaxation time associated with the glass–liquid transition is assumed to be related to the free volume by eqn. (4).[16] In this expression,

$$\tau = A \exp\left[\frac{B}{\Phi}\right] \tag{4}$$

empirically formulated by Doolittle, Φ [$= (v - v_o)/v_o$ where v_o is the occupied specific volume] is the relative free volume, and B is an empirical constant of the order of the unity; this latter parameter is believed to be related to the ratio between the critical volume required for a relaxation process to take place and the volume of the segments intervening in the relaxation.[17] The assumption that the specific volume is a linear function of temperature leads to eqn. (1). By comparing eqns. (1) and (4), one obtains the relative free volume at T_g given by eqn. (5).

$$\frac{\Phi_g}{B} = \frac{T_g - T_0}{m} \tag{5}$$

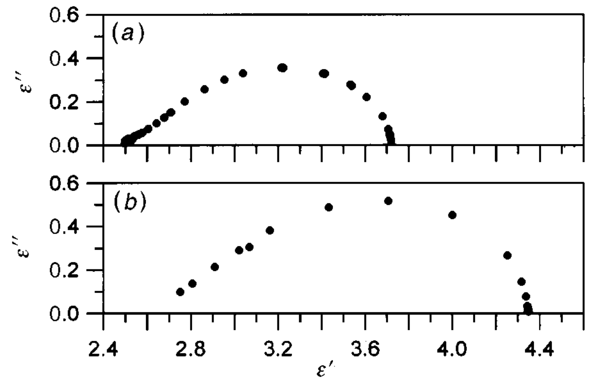

Fig. 6 Complex plane representation of ε^* (*i.e.* loss ε'' *versus* real ε' components) for (*a*) OBPG at 0 °C (*b*) OBPI at −50 °C in the range of frequencies 10^{-4}–10^2 kHz

The analysis of the experimental results in terms of eqn. (1) was performed by plotting the natural logarithm of the reciprocal of the measured frequencies as a function of $(T_{max} - T_0)^{-1}$, where T_{max} represents the temperature of the peak in ε''. The plots of OBPI and OBPG, shown in Fig. 5, fit to straight lines with slopes $m = 2062$ and $1781\ K^{-1}$, respectively, with values for T_0 of 162 and 214 K, respectively. These values in conjunction with eqn. (5) suggest that the relative free volume at the glass transition temperature are 0.024 and 0.028 for OBPI and OBPG, respectively, in good agreement with the results obtained for most viscoelastic liquids which lie in the range[18] 0.025 ± 0.005.

Complex plane plots of ε'' against ε' give skewed arcs whose intercepts with the abscissas axis give the values of the relaxed ε_0 and unrelaxed ε_∞ permittivities. Illustrative plots of this kind at −50 °C (for OBPI) and 0 °C (for OBPG) are shown in Fig. 6. The values of the relaxed ($\omega \rightarrow 0$) permittivity for OBPI ($T = -50$ °C) and OBPG ($T = 0$ °C) are 4.35 and 3.72, respectively; these values drop to 2.65 and 2.49 for the unrelaxed relative permittivity of the former and latter compounds, respectively.

The α relaxation in the frequency domain was obtained from isothermal dielectric measurements. An example of the α relaxations thus obtained for OBPI at −50 °C is shown by circles in Fig. 7 and 8. With the aim of investigating the effect of nonthermal equilibrium conditions on the shape of the curve of this relaxation, this curve was further determined from isochrones measured in nonthermal equilibrium. For comparative purposes these results are plotted as triangles in Figs. 7 and 8. It can be seen that the curves obtained from both procedures are identical indicating that, when the temperature sweep is slow enough, both measurements provide the same results. Results obtained for OBPG at 0 °C under isothermal conditions are shown in Figs. 9 and 10.

Theoretical analysis

MD simulations for single molecules of both OBPI and OBPG *in vacuo* were performed according to standard procedures[19] employing the SYBYL molecular modelling package[20] and the TRIPOS force field.[21] Coulombic contributions to the force field were computed from the partial charges assigned to each atom of the molecule calculated by using the AMPAC package and the AM1 procedure.[22] The leap-frog algorithm was employed to integrate the equations of motion for every atom on the studied molecules with time steps $\delta = 1$ fs (*i.e.* 10^{-15} s), and the conformations reached by the molecules every $\Delta = 500$ cycles were saved for further analysis. The calculations were performed at several temperatures ranging from 300 to 1000 K. The conformational energy was minimized with respect to all bond lengths, bond angles and rotational angles, thus providing an optimized molecular geometry that was used as a starting point for the MD trajectories that began with a thermostatted period along which the molecule was warmed up from 0 K to the working temperature with 20 K incre-

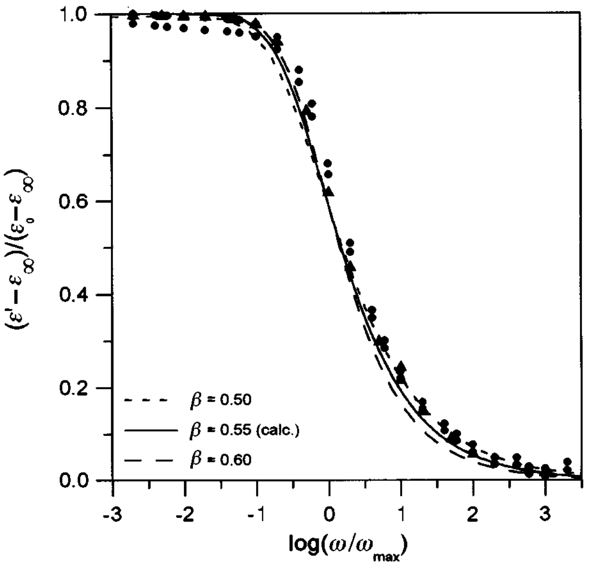

Fig. 7 Normalized values of the real component ε' of the complex relative permittivity ε^* of OBPI measured at -50 °C as function of frequency. Circles indicate results obtained under isothermal conditions, triangles correspond to measurements performed with slow temperature sweep. The lines display theoretical values computed according to eqns. (8) and (9) with $\beta = 0.55 \pm 0.05$, which is the result obtained for this parameter by means of MD simulations performed at 500 K.

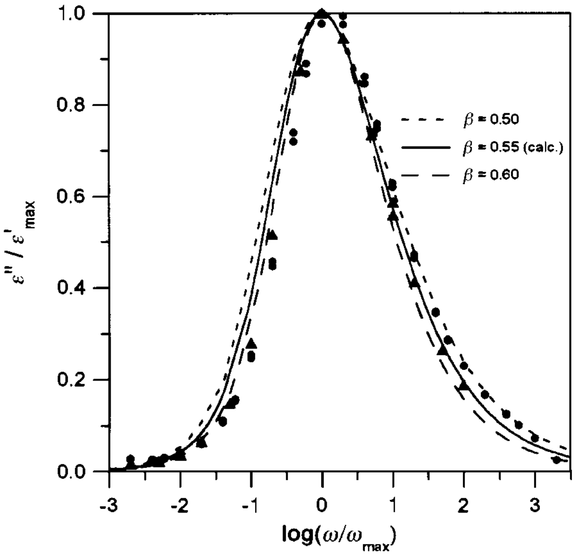

Fig. 8 Same as for Fig. 7 for the loss component ε''

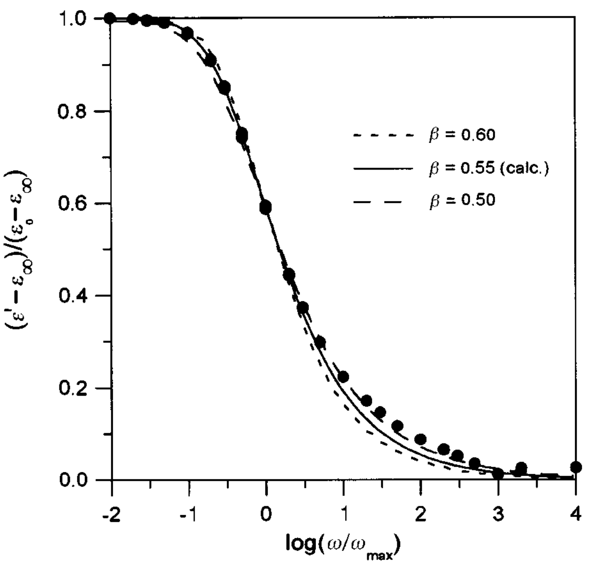

Fig. 9 Same as Fig. 7 for OBPG at 0 °C. No sweep temperature measurements were performed in this case.

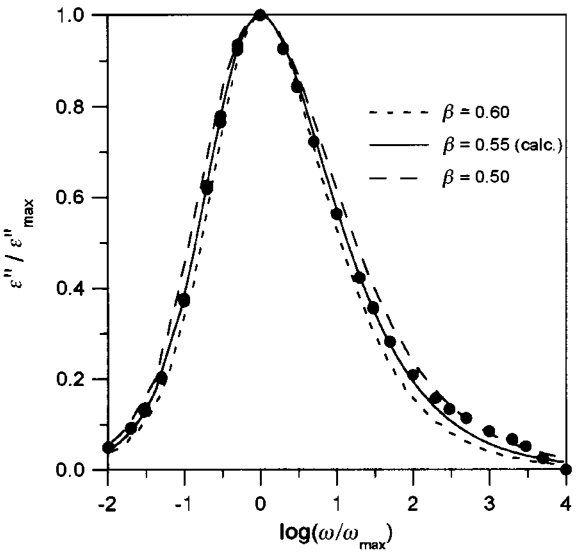

Fig. 10 Same as Fig. 9 for the loss component ε''

ments allowing an equilibration interval of 500 fs on each intermediate temperature. Once the molecule reached the working temperature, the data collection step was initiated and maintained for 5×10^6 integration cycles, thus providing a total number of 10 000 recorded conformations, covering a time span of 5 ns.

Dipole moments of the analysed conformations were obtained from the partial charges associated with the atoms of the molecules. The results of μ for OBPI are shown as a function of time in Fig. 11 for the three temperatures of interest. As this figure indicates, the values of μ at 300 K oscillate roughly within the limits 1.5 ± 0.5 D. As the temperature increases, the mean value of μ is not substantially modified, but the amplitude of the oscillations increases, mainly due to deformations of bond lengths and bond angles produced at high temperatures. Averaged values computed from the data shown in Fig. 14 are: $\langle|\mu|\rangle = 1.91$ D, $\langle\mu^2\rangle = 4.01$ D^2 at 1000 K, $\langle|\mu|\rangle = 1.68$ D, $\langle\mu^2\rangle = 2.92$ D^2 at 500 K, $\langle|\mu|\rangle = 1.65$ D, $\langle\mu^2\rangle = 2.80$ D^2 at 300 K. This last value, computed at 300 K, is in good agreement with the experimental results obtained in the vicinities of this temperature.

If the relaxation strength of the secondary or β process is negligible as occurs for the compounds studied in this work, the normalized decay function in the time domain for the α relaxation can be expressed in molecular terms by eqn. (6).[23–25]

$$\varphi(t) = \frac{\langle\mu_i(0)\mu_i(t)\rangle + \sum_j\langle\mu_i(0)\mu_j(t)\rangle}{\mu_i^2 + \sum_j\langle\mu_i(0)\mu_j(0)\rangle} \tag{6}$$

Though the intermolecular cross correlation terms in this equation may have a significant magnitude and their signs may be either positive or negative, theoretical considerations and the critical interpretation of the relative permittivity data for polar–non polar random copolymers suggest that the auto and the cross correlation functions may have the same time dependence.[25–27] According to this reasoning, the cross-correlation terms, although present, do not significantly alter the time dependence of the decay function,.[28] This assumption is backed by a wealth of experimental work carried out by Williams and co-workers[29] in low molecular glass forming liquids. Recent experimental work[30,31] carried out on the relaxation behaviour of 2-chlorocyclohexyl acetate (liquid) and poly(2-chlorocyclohexyl acrylate) (amorphous solid) shows that the exponent for

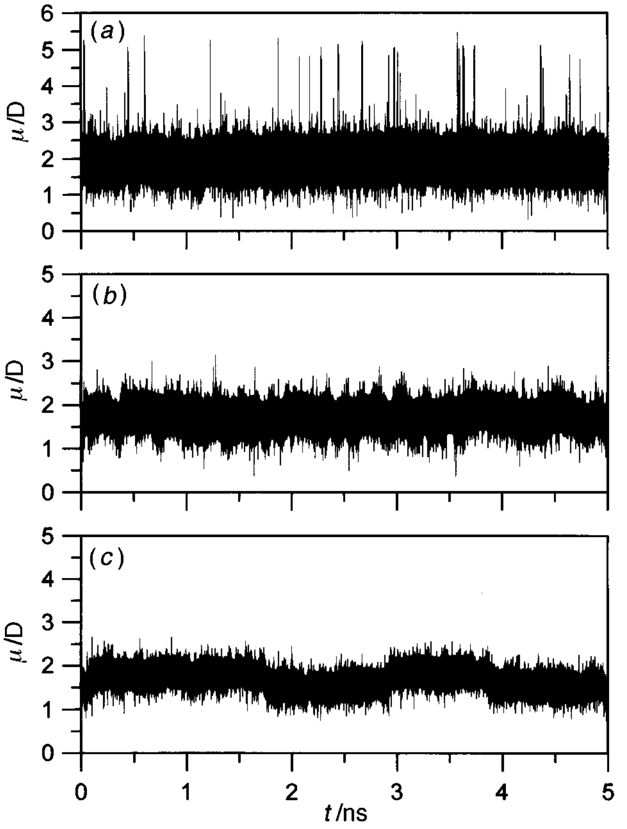

Fig. 11 Dipole moment of OBPI as function of time, obtained through MD simulations performed at (*a*) 1000, (*b*) 500 and (*c*) 300 K

the stretch function of the α relaxation is nearly similar in both cases.

The normalized dipole-moment time-autocorrelation coefficient was computed by means of eqn. (7),[31] where N repre-

$$\varphi(n\Delta) = \frac{1}{\langle \mu^2 \rangle (N-n)} \sum_{i=1}^{N-n} \boldsymbol{\mu}[i\Delta]\boldsymbol{\mu}[(i+n)\Delta] \qquad (7)$$

sents the total number of conformations studied. This equation represents an average over the $(N - n)$ values of φ obtained with all the pairs of conformations that are separated by a time increment equal to $n\Delta$ (*i.e.* $500n$ fs). The value of the autocorrelation function decreases rather fast with increasing time, thus $\varphi(n\Delta) \approx 0$ for values of n which are much smaller than N and therefore $N - n$ is very large, which ensures a good sampling of φ over all the conformational space.

The dipole-moment time-autocorrelation coefficient computed at several temperatures is shown in Fig. 12 for OBPI and Figs. 13 and 14, respectively, for the meso and racemic configurations of OBPG. It is worth noting that $\varphi(t)$ decreases much faster with increasing time in OBPG than in the case of the OBPI molecule. These curves should allow the determination of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ at the temperatures of interest. However, preliminary calculations showed that the treatment of the data is more efficiently done if the noise that appears in the autocorrelation curves is eliminated. For that purpose, the curves were fitted to the KWW relationship[7,8] [eqn. (2)]. The quality of the fitting can be observed in Figs. 12–14 where dotted and solid lines represent, respectively, the fitting functions and the actual values of $\varphi(t)$ computed from the MD trajectories.

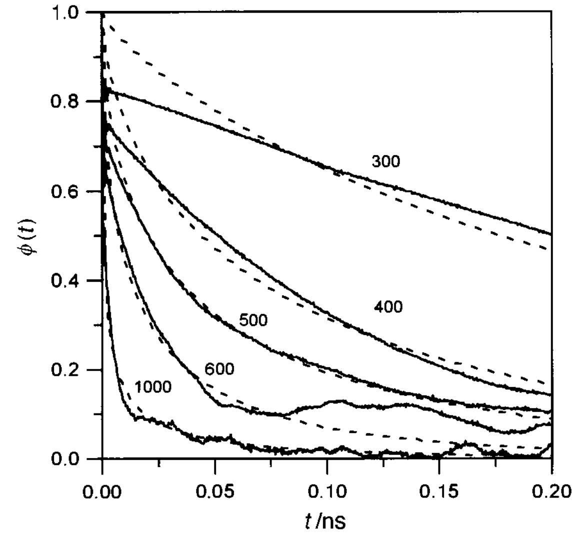

Fig. 12 Dipole-moment time-autocorrelation function $\varphi(t)$ as a function of time for the OBPI molecule obtained at the indicated temperatures (in K). Solid lines represent values computed from MD trajectories while broken lines represent least squares fittings to the KWW function [eqn. (2)].

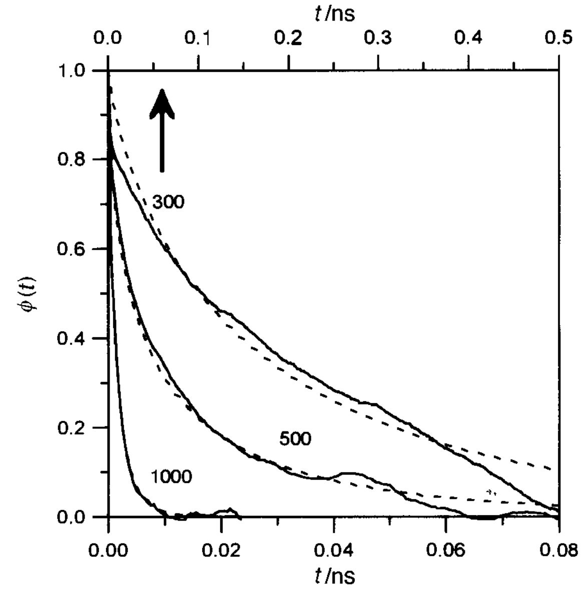

Fig. 13 Same as Fig. 12 for the *meso* OBPG molecule

Fig. 12 indicates that the fitting is rather poor at low temperatures (*i.e.* 300 and 400 K). The reason may be that the mobility of the molecule is not large enough to cover the whole conformational space with the frequency required for the evaluation of the autocorrelation functions at reasonably short times [*i.e.* $\varphi(t)$ for times on the order of 0.5 ns that require simulation of MD trajectories of *ca.* 5 ns]. Of course, the fitting procedure provides the best choice for τ^* and β parameters, but the computed values of $\varphi(t)$ do not follow the KWW function. On the contrary, at high temperatures (*i.e.* 600–1000 K), the mobility of the molecule is too large and $\varphi(t)$ drops very quickly to values close to zero, where the uncertainty in the calculation (*i.e.* the oscillations shown by the solid lines on Figs. 12–14) becomes important. Therefore, even if the quality of the fitting is very good (probably because there are less points to be fitted), the reliability of the function is smaller. It is possible that intermediate temperatures of about 500 K may be the best choice for the evaluation of $\varphi(t)$ for these molecules. At this temperature, the parameters obtained in the fitting are:

OBPI:	$\tau^* = 0.0402$ ns, $\beta = 0.55 \pm 0.05$
meso OBPG:	$\tau^* = 0.0075$ ns, $\beta = 0.55 \pm 0.05$
racemic OBPG:	$\tau^* = 0.0103$ ns, $\beta = 0.55 \pm 0.05$

It should be pointed out that the correlation functions of the three molecules studied in the present work, namely OBPI, *meso* OBPG and racemic OBPG, can be fitted employing

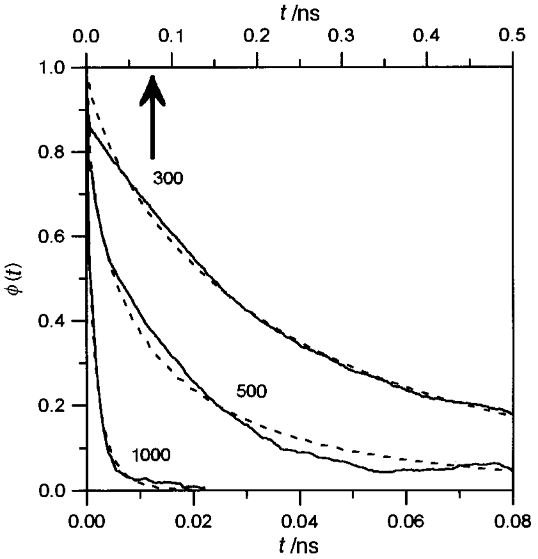

Fig. 14 Same as Fig. 12 for the racemic OBPG molecule

the same value of the $\bar{\beta}$ parameter, *i.e.* $\bar{\beta} \approx 0.55$ with a estimated uncertainty of *ca.* 0.05.

The theoretical calculation of $\varepsilon'/(\varepsilon_0 - \varepsilon_\infty)$ and $\varepsilon''/\varepsilon''_{\max}$ can be performed by means of eqn. (8):[32]

$$\frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = 1 - \int_0^\infty \varphi(t) \cos \omega t \mathrm{d}t$$
$$\frac{\varepsilon''(\omega)}{\varepsilon''_{\max}} = \frac{1}{\varepsilon''_{\max}} \int_0^\infty \varphi(t) \sin \omega t \mathrm{d}t \tag{8}$$

Values of these integrals were obtained by the method outlined by Williams *et al.*,[33] [eqn. (9)], for high frequencies [*i.e.* $-1 \leqslant \log(\omega\tau_0) \leq +4$ when $\beta > 0.25$], and eqn. (10) for low

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{(\omega\tau_0)^{n\beta}} \frac{\Gamma(n\beta + 1)}{\Gamma(n + 1)} \left[\cos\left(\frac{n\beta\pi}{2}\right) - i \sin\left(\frac{n\beta\pi}{2}\right)\right] \tag{9}$$

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{(\omega\tau_0)^{n-1}}{\Gamma(n)} \Gamma\left(\frac{n + \beta - 1}{\beta}\right) \left[\cos\left(\frac{(n-1)\pi}{2}\right) + i \sin\left(\frac{(n-1)\pi}{2}\right)\right] \tag{10}$$

frequencies. Theoretical values of these magnitudes computed with $\bar{\beta} = 0.55 \pm 0.05$ (which was obtained at 500 K from the autocorrelation functions shown in Figs. 12–14 through the KWW function indicated above) are shown in Figs. 7–10. The agreement between the experimental values and the theoretical results is excellent.

The assumption stated above that the cross-correlation terms do not alter in a significant way the time dependence of the decay function suggests that the $\bar{\beta}$ exponent obtained for this equation in the MD simulations should be independent of temperature, provided that the computing time at the temperature of interest is large enough for the molecules to visit all the conformational space. The temperature would mainly affect the value of the mean-relaxation time, τ^*, and, as a result, the location of the relaxation curves in the frequency or time domains. Consequently the plot of the normalized components of the complex relative permittivity against log $(\omega/\omega_{\max})$ should be independent of temperature. This assumption is backed by the good agreement between theoretical and experimental results observed in Figs. 7–10 for low molecular weight model compounds of acrylate polymers. The good agreement also observed between experimental and MD computed results for other model compounds, specifically 2-chlorocyclohexyl isobutyrate[31] and *cis*/*trans*-2-phenyl-5-(acetoxymethyl)-5-ethyl-1,3-dioxacyclohexane,[34] also support the assumptions used in this work. However, we are aware of the fact that further calculations in which intermolecular cross-correlations terms are considered may be of interest to eliminate any hint of doubt. We are working in this line at present.

Acknowledgements

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