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Molecular Mobility in Poly(butyl methacrylate) and Poly(methyl methacrylate)

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Molecular mobility is studied in poly(butyl methacrylate) and poly(methyl methacrylate) (PMMA) with molecular dynamics simulations in order to understand the effect of the α – β crossover on the β relaxation activation energy and co-operativity. In the high frequency range investigated, the estimated β process activation energy is decreased as compared to the low frequency value. This deviation is stronger in poly(n butyl methacrylate) (PnBMA) than in PMMA. The intra-molecular co-operativity related to the β process is also higher in PnBMA than in PMMA. These results could be related to the relative position of the simulation temperature range and of the extrapolated α – β crossover temperature.

Keywords: Molecular mobility; β relaxation; PMMA; PnBMA

INTRODUCTION

Several relaxation processes are often observed in polymers like the α relaxation associated with the glassy transition and secondary relaxation processes corresponding to local rearrangements (β and γ relaxations). A distinction has been introduced between two types of glass formers. The so-called “type-A” glass formers exhibit excess intensity in the high frequency side of the α relaxation peak, while “type-B” glass formers clearly reveal a higher frequency process, the Johari-Goldstein β relaxation [1,2]. Yet many crucial points are still debated. It is not clear what happens in the frequency and temperature range where the unique high temperature process, noted a or $\alpha\beta$ process, splits into two processes. This temperature range is associated with many properties changes [3,4]. Nevertheless, until now, there is no general understanding of the extent

to which the local secondary relaxation processes change near the junction with the cooperative α process. The Arrhenius behaviour of τ_β is well established below the glass transition temperature T_g , however, above the T_g it remains a matter of controversy. On the one hand, some studies suggest a simple physical picture of a β relaxation with a characteristic time τ_β following an Arrhenius dependence until the merging with the α process [5]. On the other hand, some dielectric spectroscopy measurements have suggested that, in the crossover region between the α and β relaxations, the β process dynamics could be changed [6,7]. A possible explanation for this change is that a part of the potential barrier of the β process originates from inter-molecular interactions which may be decreased near the merging temperature $T_{\alpha\beta}$ [8,9]. It must be emphasized that there is still no agreement about the relative contributions of inter- and intra-molecular interactions to the activation energy of the β process. The magnitude of the co-operativity of this relaxation phenomenon also remains a matter of debate. To address such problems, molecular dynamics simulations may provide interesting information, since correlation times associated to a definite molecular motion can be obtained from runs performed on bulk or isolated structures [8,10].

The α – β splitting and the junction temperature $T_{\alpha\beta}$ where it occurs are very sensitive to the monomer structure. Polymers having more rigid backbones or sterically-hindering pendant groups are often associated with large fragility indexes and marked separation between the α and β processes [11]. That is the reason why we tried to compare with molecular dynamics simulations of

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the poly(butyl methacrylate) isomers which are characterized by a very similar secondary β process and very different α relaxations [12]. We suggested that the secondary processes activation energy may be decreased near the junction with the main α process. Yet the effect of the monomer structure, is not evident on this decrease and on the relative contributions of inter- and intra-molecular interactions. We have found that the β process, which involves flips of the lateral carboxyl side group, is accompanied by rotational rearrangements around the main chain axis, limited to one torsion angle in a large temperature range. We suggested that this intra-molecular co-operativity was marked more in the linear side chain isomer, poly(n butyl methacrylate) (PnBMA), than in the hindered side chain isomers [12]. Nevertheless, the role played by the temperature was not extensively studied. In this work, we try to clarify the validity of these conclusions and we investigate the influence of the lateral chain length. We intend to get a better characterization of the β process intra-molecular co-operativity and to get a parallel between the effects of the chain length and of the steric hindrance. To this purpose, we complement our first study and we compare poly(methyl methacrylate) (PMMA) and poly(n butyl methacrylate) (PnBMA).

The present contribution uses the same conceptual frame as the one presented in our former study [12]. It relies on the calculation of two correlation functions based on the ϕ_β side chain dihedral, which is assumed to be the relevant quantity to study the β process. This paper is structured as follows: in the first section, we summarize some of the relaxational properties of the polymers studied, which have been obtained experimentally. Then, we detail the simulations performed, and we present the calculated quantities. We then report the results concerning the β process in PMMA and PnBMA and its intra-molecular co-operativity.

MATERIALS AND METHODS

Relaxational Properties of PMMA and PnBMA

The chemical structure of PMMA and PnBMA is displayed in Fig. 1. The glass transition temperatures, as measured by DSC with a heating rate of 10 K/min are $T_g = 300$ and 360 K for PnBMA, and PMMA, respectively [12,13]. A relaxational diagram, as obtained with low frequency mechanical spectroscopy measurements, which compares the α and β process in PMMA and PnBMA, is displayed in Fig. 2 [12,13]. When the α and β relaxations are resolved, the activation energy of the β process is weakly dependent on the length of the lateral chain but the junction temperature between the α and β relaxation processes and the glass transition temperature decrease with increasing length of the alkyl side chain. From the former relaxation diagram, the extrapolated junction temperature $T_{\alpha\beta}$ between the α and β process can be estimated to 300 and 450 K for PnBMA and PMMA, respectively. RMN studies have demonstrated that in both polymers, the β process involves flips of the lateral carboxyl side group [14]. The torsion angle involved in this relaxation is displayed in Fig. 1 and will be denoted by ϕ_β . These flips are associated with localized main chain rearrangements and thus we shall use the torsion angles numbered along the chain and denoted by ϕ_i (Fig. 1) [12]. The index $i = 0$ corresponds to the dihedral under consideration, $\phi_0 = \phi_\beta$.

Simulation Methodology

Molecular dynamics calculations were performed using CVFF95 force field as integrated in the Cerius program (Molecular Simulation Inc., San Diego, CA, USA). This force field is devised for organic polymers and small organic molecules and described in detail elsewhere [12,15]. The initial structures construction and the relaxation strategy have been described extensively in our former work [12].

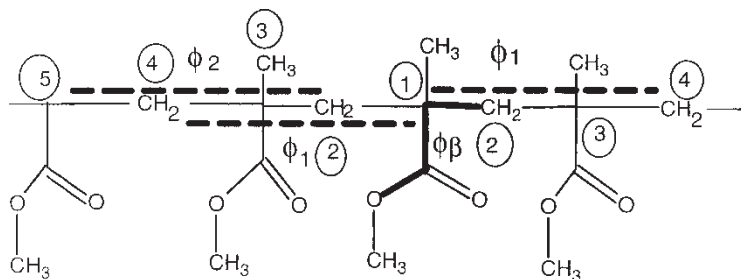


FIGURE 1 Chemical structure of PMMA (a) and PnBMA (b). Schematic drawing of the torsion angles associated to the β process, ϕ_β , and of the torsion angles ϕ_i involved in the CCF function. The torsion angle ϕ_1 involves the carbon atoms 1,2,3 and 4, the torsion angle ϕ_2 , the carbon atoms 2, 3, 4 and 5.

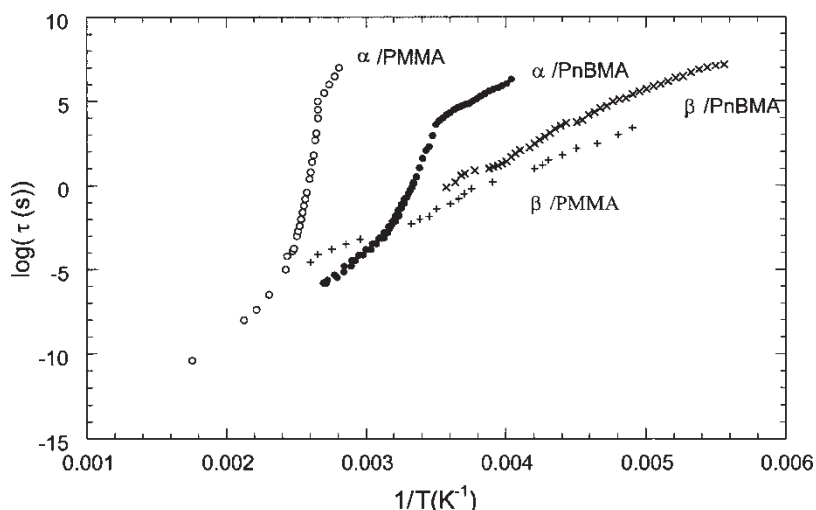


FIGURE 2 Relaxation diagram of PnBMA and PMMA as obtained with mechanical spectroscopy: α relaxation of PnBMA (●) and PMMA (○), β relaxation of PnBMA (×) and PMMA (+).

For both polymers, a single atactic chain of 30 repeat units was generated with the Monte-Carlo method as implemented in the Amorphous Builder module of Cerius. It must be emphasized that a higher number of monomers does not significantly modify the calculated correlation times. Such a small system is thus assumed to be sufficient to catch the relaxation behaviour studied. Isolated polymers and bulk polymers with periodic boundary conditions were prepared in order to separate the intra-molecular and inter-molecular contributions of the activation energy of the β process. For each polymer, six separate cells were independently built to ensure that a range of conformations of the amorphous polymer were sampled. The isolated polymers structures were optimized using steepest descent and conjugate gradients algorithms. The amorphous bulk structures were simulated with cubic periodic boundary conditions and the initial cell densities were given the values measured experimentally at 300 K, 1.053 and 1.19 g cm⁻³ for PnBMA and PMMA, respectively [12,16,17]. In order to relax these structures, we have followed a procedure similar to that used by Mattice *et al.* [18,19]. After minimization with a 100000 steps steepest descent algorithm, the structures are heated by steps of 100 K from 300 to 800 K. Each step of this heating procedure consists of a 10 ps run performed in the NVT statistical ensemble. The conformation with the lowest total potential energy during the latest molecular dynamics run is selected and its potential energy is minimized. Such a high simulation temperature is necessary to give the system enough energy to overcome energy barriers between local minima. It is only a computational technique and no comparison is possible with real polymer systems at 800 K.

At the end of this first step, a molecular dynamics run in the NPT statistical ensemble at 200, 250, 300, 350, 400, 450, 500, 550 and 600 K, and with the pressure set to 1 atm, is then performed until a constant density and energy is obtained. At 300 K, the deviation of the densities of the equilibrated polymers from the experimental values is less than 2%. Concerning the other temperatures, the structures obtained at the end of this relaxation strategy are considered as reasonable low-energy states because, in the subsequent additional molecular dynamics runs, their total energy and density fluctuate less than 0.5%. The validation of the force field and of the relaxation procedure is based on a comparison of the experimental densities and of the simulated ones and on the calculation of the ester methyl group dynamics in PMMA consistent with neutron scattering experiments [12]. Since the two polymers have exactly the same force field parameters, the changes in the activation energies detailed in the following will directly be linked to changes in their molecular characteristics. Moreover, molecular dynamic trajectories calculated using the Dreiding 2.21 force field [20] yield correlation times and apparent activation energies that can not be distinguished from the ones obtained with the CVFF95 force field, in view of the error bars. Only the results obtained with the CVFF force field will be detailed here.

We have then used the relaxed structures obtained in order to perform 100 ps and 1 ns molecular dynamics runs at 200, 250, 300, 350, 400, 450, 500, 550 and 600 K in the NVT statistical ensemble for subsequent analysis. Positions and velocities are recorded at time intervals of 0.1 and 1 ps, respectively, depending on the simulation length.

The longer simulation runs were used to capture the main features of the β process assumed to be related to the ϕ_β dihedral dynamics, and to calculate:

$$G(t) = \frac{[3\langle \cos^2[\phi_\beta(t) - \phi_\beta(0)] \rangle - 1]}{2} \quad (1)$$

For the calculation of these correlation functions, an average is taken over the time, with a shift of the initial conformation. To improve statistical efficiency, an average is also taken over the monomers of the polymer. The shorter runs were devoted to the calculation of the cross-correlation function (CCF) associated to the ϕ_β and ϕ_i pair of bonds, and describing the intra-molecular co-operativity of the β process, as suggested by Mattice *et al.* [18,19]:

$$\text{CCF}(i, t) = \langle \sin[\phi_\beta(t) - \phi_\beta(0)] \sin[\phi_i(t) - \phi_i(0)] \rangle \quad (2)$$

The same calculation procedure is used for this correlation function. The index $i = 0$ corresponds to the dihedral involved in the β process, $\phi_0 = \phi_\beta$, and thus to the ϕ_β self-correlations investigated with $G(t)$. The advantage of this CCF is that it excludes uncertainties caused by introducing any definition of the ϕ_β conformational transition. The results obtained for the six equilibrated structures like correlation time are averaged. Error bars have been estimated from the dispersion of the results from the six conformations used.

RESULTS AND DISCUSSION

Torsion Angles ϕ_β Dynamics

As an example, Fig. 3a and b display some semi-logarithmic plots of $G(t)$ obtained for the temperature $T = 500$ K, for the torsion angle ϕ_β in isolated and bulk PMMA and PnBMA. The average over the six independent samples is presented for these plots. In order to evaluate a single characteristic time from this decrease, we have used the same approach for the analyzing of the data as in our former work [12]. The fast decay of the first picoseconds which can be ascribed to librations is neglected, and the $G(t)$ decrease is fitted to the Kohlrausch–Williams–Watts stretched exponential function:

$$G(t) = \exp(-(t/\tau)^\beta) \quad (3)$$

In the temperature range studied, constant values, $\beta = 0.85 \pm 0.05$ for the bulk structures, and $\beta = 0.9 \pm 0.05$ for the isolated ones, were obtained from the simulations. No trend as a function of the temperature or as a function of the monomer structure can be found. On the basis of this methodology, we have determined the temperature dependence of the averaged correlation times, $\tau_{\phi_\beta}(T)$ associated to the isolated and bulk PMMA and

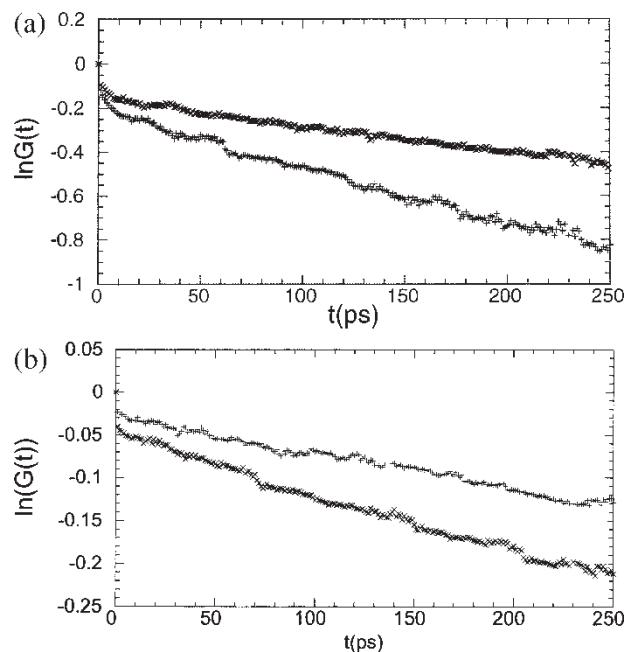


FIGURE 3 (a) Semi-logarithmic plots of $G(t)$ for the torsion angle ϕ_β in isolated PnBMA (\times) and PMMA($+$) at $T = 500$ K. (b) Semi-logarithmic plots of $G(t)$ for the torsion angle ϕ_β in bulk PnBMA(\times) and PMMA($+$) at $T = 500$ K.

PnBMA, which are displayed on Fig. 4. In order to take into account the low simulation times and the limited decay of the correlation functions, error bars were estimated for the correlation times τ_β . At low temperature, some correlation times are too high to be evaluated with accuracy. It is well known that, in the high temperature range, above the crossover temperature $T_{\alpha\beta}$, the temperature dependence of the characteristic time of the $\alpha\beta$ merged process can be accounted for by a Vogel–Fulcher–Tamman law [21]. Moreover, it has been shown that the distribution of the characteristic times of the β process is rather wide in PMMA [22]. Yet as a first approximation and in view of the restricted temperature range investigated, a simple Arrhenius law gives a correct description of the temperature dependence obtained, for the bulk and isolated structures. The apparent activation energies should of course be considered with caution. The apparent activation energies obtained for the bulk or isolated polymers are summarized in Table I, together with the mechanical spectroscopy values. Figure 4 and Table I illustrate several results which complement our former study of the poly(butyl methacrylate) isomers:

- the activation energy value in the isolated PMMA is significantly lower as compared to the one obtained for the isolated PnBMA. In PMMA, the inter-molecular contribution is the dominant part of the total activation energy. With the same simulation methodology, no

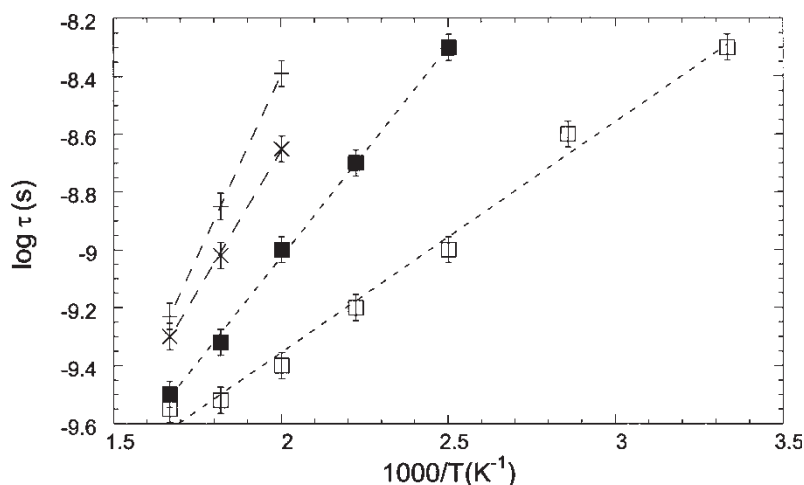


FIGURE 4 Temperature dependence of the average correlation times $\tau_{\phi\beta}$ obtained in bulk PnBMA (x), isolated PnBMA (■), bulk PMMA (+) and isolated PMMA (□). The dashed lines correspond to the estimated activation energies.

significant differences in the intra-molecular contributions have been evidenced between the various poly(butyl methacrylate) isomers [12].

- the activation energies for the bulk simulated polymers deviate significantly from the values derived from the low frequency mechanical spectroscopy and the values are lower in PnBMA than in PMMA. Consequently, the value of the calculated activation energy of the ϕ_β motion in PMMA compares better with one obtained with low frequency mechanical spectroscopy.

As concerns the first result, the short lateral chain of PMMA is likely to induce stronger inter-molecular interactions and an easier packing of the chains, while the bulky PnBMA side group may induce high intra-molecular barriers. Moreover, the molecular complexity differences are more marked between PnBMA and PMMA than between the poly(butyl methacrylate) isomers. Distinct intra-molecular and inter-molecular contributions to the activation energy are thus obtained when the chain length is varied. The differences in structure and free volume size and distribution between the two polymers and between the bulk and isolated conformations will be investigated in detail in a forthcoming work. Yet at this point it is of interest to have information about the conformation differences between the bulk

and isolated polymers. The atomic radial distribution function, $g(r)$, gives the probability of finding a pair of atoms with a separation r , relative to the probability expected for a uniform distribution at the same density. The radial distribution function $g_{\text{CH}_3-\text{CH}_3}(r)$ based on the carbon atoms of the methyl group located at the end of the ester side chain is calculated as:

$$g_{\text{CH}_3-\text{CH}_3}(r) = \frac{N_{\text{CH}_3-\text{CH}_3}(r)}{4\pi r^2 \Delta r} \frac{V}{N}$$

where $N_{\text{CH}_3-\text{CH}_3}(r)$ is the average number of ester side chain methyl carbon atoms pairs in the spherical shell between r and $r + \Delta r$, N is the total number of pairs and V the simulation cell volume of the bulk structure. The radial distribution functions averaged over the whole set of conformations obtained from the runs are displayed in Fig. 5 for the isolated and bulk PnBMA. In the isolated structure, the pair distribution function exhibits a relatively broad peak between 5 and 8 Å, which corresponds to methyl groups located on different but nearby ester groups of the single main chain. The decrease of the pair distribution function for larger distances is due to the rather extended conformation of the polymer chain, which prevents close contacts between ester side groups, which are not first-neighbors. This conformation results in a high amount of free volume. In the bulk polymer, the peak around 9 Å is attributed to methyl groups located on ester side groups of different PnBMA chains. This peak indicates the higher local chain packing in the dense PnBMA system. The higher activation energy value found in the bulk polymers can thus be related to a more compact system.

At last, a possible interpretation of the low calculated apparent activation energies is that, for the highest temperatures investigated, the α and β relaxations have merged, and that the potential barrier hindering the rotation of the ϕ_β

TABLE I Activation energies related to the ϕ_β motion obtained for bulk or isolated PMMA and PnBMA, and low frequency mechanical spectroscopy values associated to the β process

Structure	PMMA (kJ/mol)	PnBMA (kJ/mol)
Isolated polymer-simulation	15 ± 3	28 ± 3
condensed state-simulation	56 ± 5	42 ± 5
mechanical spectroscopy	67 ± 5	67 ± 5

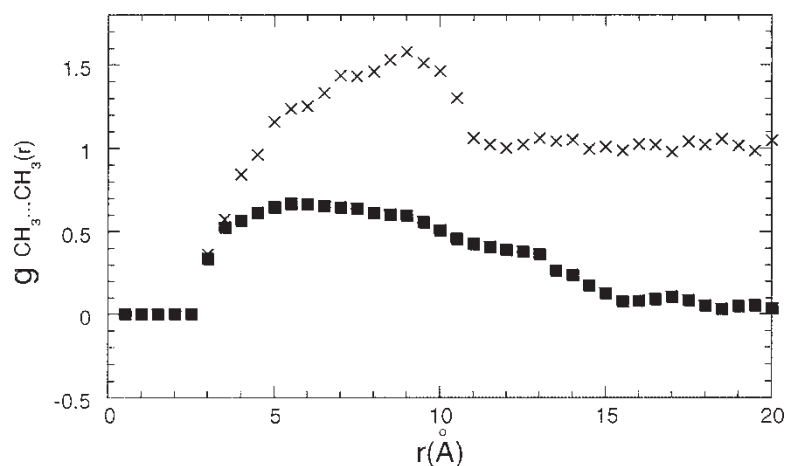


FIGURE 5 Pair correlations functions related to the ester side chain methyl group obtained in isolated (■) and bulk (×) PnBMA.

angle is decreased. This decrease may originate from a higher flexibility of the main chain and from vanishing inter-molecular interactions. From this point of view, it is worth noting that the decrease of the ϕ_β motion activation energy is more marked in PnBMA. Comparing the junction temperatures $T_{\alpha\beta}$ estimated in PMMA ($T_{\alpha\beta} = 450$ K) and PnBMA ($T_{\alpha\beta} = 300$ K), it is tempting to infer that the extent to which the activation energy is modified is in correlation to the position of these junction temperatures in the temperature range investigated with simulations for the bulk structures. Between 400 and 600 K, the crossover between the α and β processes is expected to have occurred in PnBMA, while it takes place only for the highest simulated temperatures for PMMA. This explanation would be in agreement with the results obtained for the poly(butyl methacrylate) isomers [12].

Co-operativity of the β Relaxation Process

Molecular dynamics simulations in the bulk are an interesting tool to investigate the coupling of the various degrees of freedom involved in the β process in relation with the junction between the α and β processes [12]. With the CCF functions presented above, we focus our attention on the intra-molecular correlations associated to the motions of the main chain torsion angles ϕ_i , induced by the motion of the ϕ_β dihedral, on the same polymer chain. The characteristic length scales and temperature dependences of these correlations are investigated in the following.

Figure 6 displays the evolution of CCF time dependence maximum as a function of the index of the dihedral i along the main chain PMMA and PnBMA at 400 K. The index $i = 0$ corresponds to self-correlations of the ϕ_β dihedral. In PnBMA and PMMA, the correlations disappear and the value of the cross correlation function becomes negligible over the whole time range after the first main chain

torsion angle ϕ_1 . Between 200 and 600 K, the distortion and rearrangements of the bond angles along the main chain are thus localized on a short length scale corresponding to about two backbones atoms. This is an agreement with the NMR results [14]. In the following, we will focus on the CCF values obtained for the index $i = 1$ corresponding to the correlations obtained for the first torsion angle along the chain since we can not extract information from the CCF values obtained for $i = 2$. In Fig. 7, it is apparent that the intra-molecular co-operativity, as studied by the CCF function, is higher in PnBMA. This point will be developed in the following.

On Figure 7a and b are plotted examples of the CCF evolutions as a function of time for PMMA and PnBMA, for the index $i = 1$. The averages over the six independent runs are presented. The calculated CCF values displayed significant scatter and the error bar can be estimated to 0.004. Yet the main trends of the CCF, evolution as a function of temperature or as a function of the monomer length

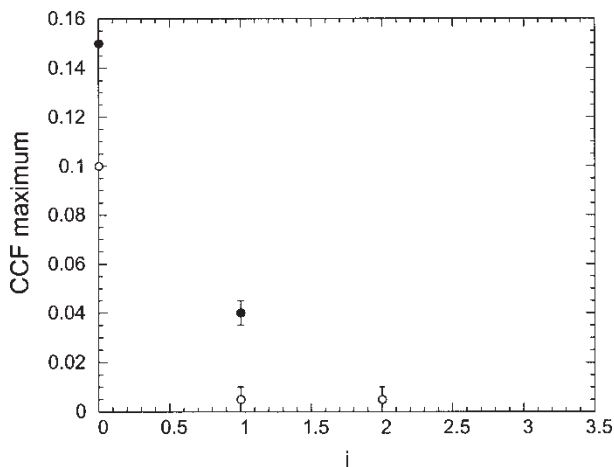


FIGURE 6 Evolution of the CCF maximum obtained at $T = 400$ K as a function of the index i along the main polymer chain in PMMA(○) and PnBMA (●).

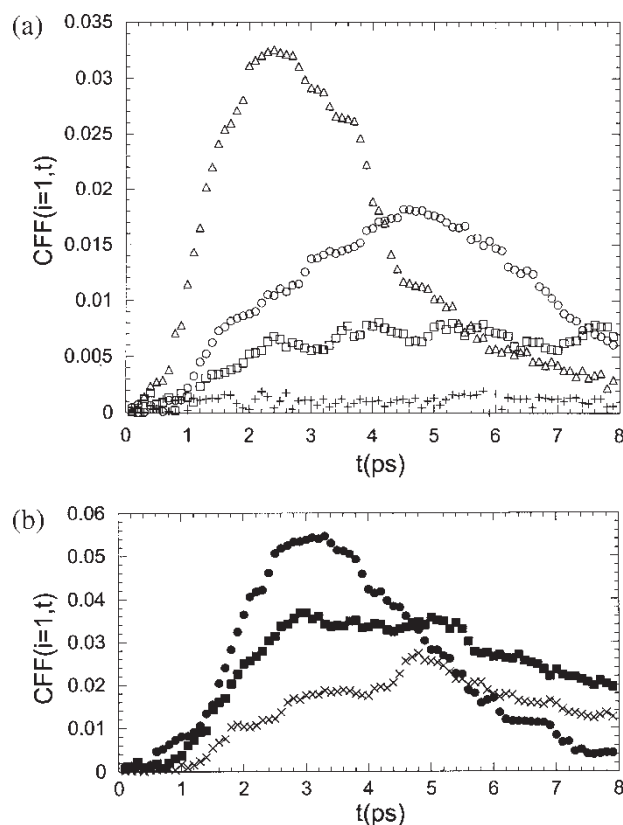


FIGURE 7 (a) Evolution of the CCF function as a function of time in PMMA for the index $i = 1$ and the temperatures $T = 300$ K(+), $T = 400$ K(Δ), $T = 500$ K(\square) and $T = 600$ K(\circ). (b) Evolution of the CCF function as a function of time in PnBMA for the index $i = 1$ and the temperatures $T = 200$ K(\times), $T = 400$ K(\blacksquare) and $T = 600$ K(\bullet).

can be extracted. The CCF variations are not displayed for $i = 0$ since the behavior obtained corresponds to the decrease of the self-correlations for the torsion angle ϕ_β observed on the correlation function $G(t)$. The time evolution of the CCF function is qualitatively similar to the one obtained by Mattice *et al.*, for conformational transitions in polybutadiene

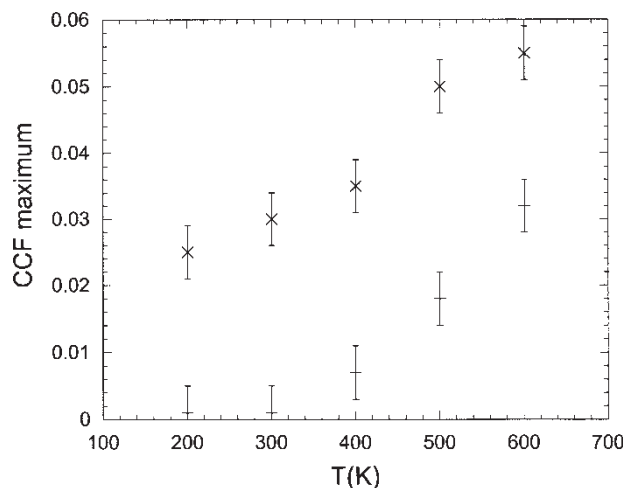


FIGURE 8 Evolution of the CCF maximum as a function of temperature in PMMA (+) and PnBMA (\times) for the index $i = 1$.

[18,19]. An initial increase of the $CCF(i = 1, t)$ value is observed for the shorter simulation times followed an asymptotic decrease to zero value corresponding to the loss of correlations between the ϕ_β and ϕ_i motions for long times. Characteristic peaks are observed in the intermediate time range. For both polymers, the maximum in the time evolution of $CCF(1, t)$ is shifted to lower times and its magnitude increase for increasing temperatures. Moreover, the loss of correlation is faster with a higher simulation temperature. Fig. 8 displays the evolution of the mean CCF maximum as a function of temperature for PnBMA and PMMA. This value is assumed to be related to the strength of the intra-molecular co-operativity, i.e. the main chain motion induced by some ϕ_β motion. For both polymers, the strength of the intra-molecular co-operativity increases with temperature as suggested by NMR studies [14]. Yet in spite of these similarities, the co-operativity observed is very weak below 400 K in PMMA contrary to what is observed in PnBMA where significant correlations are founded at 300 K. The intra-molecular co-operativity is higher in PnBMA than in PMMA on the whole temperature range.

A possible interpretation of these results is that the strength of the coupling between the motions of the pairs of bonds considered is determined by the relative positions of the simulated temperature and of the junction temperature between the α and β processes, $T_{\alpha\beta}$. This could explain the increase of the intra-molecular co-operativity with temperature. Moreover, in the framework of this interpretation, the shift towards the high temperature range of the beginning of correlations in PMMA as compared to PnBMA may be related to the higher junction temperature $T_{\alpha\beta}$ in this polymer.

CONCLUSION

In this paper, we have studied with molecular dynamics simulations the lateral chain length effect on the microscopic dynamics of the torsion angle ϕ_β related to the β relaxation in PMMA and PnBMA like in the poly(butyl methacrylate) isomers, and found that the calculated value of the ϕ_β motion activation energy in PMMA deviated from the low temperature value of the activation energy of the β process. Yet the decrease obtained is less marked in PMMA than in PnBMA and this result is consistent with a decay associated to an effect of the α relaxation on the β process. Moreover, the intra-molecular contribution of the β relaxation is found lower in PMMA than in PnBMA. This result can be attributed to a denser packing of the polymer chains in PMMA.

The chain length also plays a role in the co-operativity of the ϕ_β motion, and the intra-molecular

co-operativity is higher in PnBMA than in PMMA. The temperature range where this co-operativity is apparent is shifted to higher temperatures in PMMA. On account of these results, a correlation is proposed between the intra-molecular co-operativity of the β process, as studied with cross correlation functions, and the junction temperature between the α and β process. It is suggested that, when the α and β processes are resolved, large frequency or temperature distance from the crossover corresponds to a weak intra-molecular co-operativity of the β process.

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