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Cooperativity in stereoregular PMMAs observed by molecular simulation

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Abstract

The motion correlation along the backbone and between the side-chain and the backbone for the two PMMA chains of opposite tacticity, are investigated using molecular dynamics simulations. According to the coupling model (CM), the index of fragility, which can be considered as a measure of the cooperativity, can be related to the Kohlrausch–Williams–Watts (KWW) exponent. This exponent actually stems from the computation of the correlation time of different bonds inside the polymer chains. From suitably selected bonds, its behavior with temperature can thus unveil cooperativity along the backbone and between the side-chain and the backbone. Compared with experimental data and present theories, these simulation data show that at a relative temperature above the glass transition temperature, T_g, both configurations exhibit the same behavior for the backbone, but a different coupling is clearly observed between the side-chain and the backbone. Such a behavior tends to explain the difference in T_gs between the two configurations in PMMA.

Keywords: Glass transition; Coupling model; Relaxation

1. Introduction

Among glass forming materials, several liquids and polymers exhibit striking and conceptually unresolved properties. A specific case is poly(methyl methacrylate), PMMA, whose glass transition temperature, T_g, depends on the tacticity of the polymer chains. The bulk T_g ranges from 40 °C for isotactic, to 130 °C for syndiotactic PMMA. Gibbs and DiMarzio (GD) [1] claimed that the conformational energy difference in energies between trans and gauche conformations is the primary factor in determining the T_g of a polymer. From a static point of view, the conformation and packing of the side groups have also been envisaged as an important factor in the determination of the T_g [2].

From a dynamics approach, Allen et al. [3] calculated from neutron scattering and NMR relaxation studies the rotation barriers of the α-methyl, which is 32 and 23 kJ/mol for solid s- and i-PMMA, respectively. Several workers [4,5] suggested that a certain population of isotactic sequences relax in a cooperative fashion well below the T_g of a conventional PMMA. Moreover, using 2-D NMR spectroscopy, Kuebler et al. [5] demonstrated that the unusual main-chain mobility below T_g is coupled to the β-relaxation process in the atactic PMMA, a-PMMA. However, even if a certain amount of isotactic triads is present in the atactic chains, no mention is made to the possible influence of the tacticity in the cooperativity of the relaxation process. According to Rault [6], the so-called, α–β bifurcation, corresponding to a cross-over temperature above which the α transition and the β relaxation merge together may be a significant parameter in the cooperativity.

Adam and Gibbs [7] argued that glass formers above T_g are characterized by a length, ξ, describing a cooperatively rearranging region (CRR). In the framework of this theory, dynamic heterogeneity is expressed by an increasing number of molecular groups whose motion is coupled when temperature decreases and approaches T_g. The average size of this CRR is of the order of 2–4 nm but the predominant inter or intra-molecular character of this cooperativity in polymers has never been envisaged to our knowledge. Moreover, no distinction is made between polymer possessing side groups or not. This cooperativity concept may be necessary in addition to conformational property and local dynamics to solve the differences in T_g of stereoregular PMMA.

Actually, the cooperativity of molecular motion can be gleaned from the non-exponentiality of the relaxation,

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characterized by β_{KWW}, the Kohlrausch exponent [8]. A near unity exponent describes a 'strong liquid', since the behavior can be described by an Arrhenius plot. As it departs from unity, the polymers become more and more fragile [9]. Relaxation times thus display a non-Arrhenian behavior. The fragility is usually described by a fragility, or steepness parameter, *m*. It is quantified by the slope of the logarithm of the relaxation time versus the inverse of the relative temperature, at T_g. A direct correlation exists between this parameter and β_{KWW} [10] from experimental data and derived from the coupling model (CM) [11]. Rault states that the $1/\beta_{\mathrm{KWW}}$ ratio can be considered as the number of individual units (of β type) participating to the α cooperative motion at a given temperature above T_g [6]. The computation of this exponent is thus a key to exploring the cooperativity behavior of geometrical parameters.

Consequently, an accurate simulation of the difference in T_gs between isotactic and syndiotactic chains of PMMA, could lead to a better understanding of such a variation. It has been shown that this difference is clearly obtained using the simulated dilatometry technique [12]. Further investigations were then carried out to understand the reason of such a variation: differences in non-bond energy, intradiade angle [13] and local dynamics [14] have been reported. In this article the focus is directed towards the observation of the cooperativity along the backbone, and between the side-chain and the backbone, by the study of the β_{KWW} behavior with temperature.

2. Procedure

A polymer chain is first generated using a self-avoiding walk procedure based on a modified RIS conditional probability [15] to take into account long-range interactions [16]. This chain is then embedded into a cubic cell whose volume is determined from the knowledge of the mass and the density of the simulated polymer. The periodic boundary conditions are then imposed: each atom coming out from one face is automatically entering through the opposite face. The force field is *pcff* and the software used are Amorphous_Cell and Discover_3 in the InsightII environment, from Accelrys. All the details of the simulation can be found in a previous publication [12].

A series of molecular dynamics simulations were carried out in the NPT ensemble, i.e. the number of atoms, the pressure and the temperature were kept constant. The duration of a simulation was 110 ps with a 10 ps equilibration stage. The integration step using the Verlet-leapfrog algorithm was 1 fs. The temperature was controlled using a Nosé–Hoover thermostat bath, and the pressure was kept constant using a Parrinello–Rahman algorithm [17]. To access to the T_g, a simulated dilatometry procedure was carried out: at particular temperature and pressure, the specific volume, i.e. the inverse of the density, is reported on a graph versus the temperature. The T_g is then determined by the intersection of the lines joining the points of the vitreous and rubbery phases [18]. Such a technique was applied to the two PMMA stereomers [12]. The simulated T_g for s-PMMA is found to be 212 °C, while for i-PMMA it is 157 °C, yielding to a difference between T_gs of +55 °C. This result is in good agreement with +69 °C, experimentally expected. It has to be mentioned that the T_gs are higher than those expected in agreement with the time–temperature superposition principle.

It has to be pointed out that configurations at 307, 267, 247, 227, 167, 127, 67 and 27 °C, were kept, and are used in the present study, with a prolonged MD simulation time of 1 ns at the corresponding temperature. Configurations are saved every 0.5 ps [13].

3. Results and discussion

3.1. Data treatment

The second term of the Legendre polynomial, $P_2(t)$, tends to give a picture of the local dynamics of polymers [19]. Actually it measures the loss of the orientational correlation of a molecular segment, represented by the vector **u**, at a time *t* with respect to its initial orientation at $t = 0$. The actual correlation is represented by the autocorrelation function, $\langle \mathbf{u}(t)\cdot\mathbf{u}(0)\rangle$, extracted from molecular dynamics trajectories. The second term of the Legendre polynomial is used instead of the first term because of the anisotropy of the system.

$$P_2(t) = \frac{3\langle(\mathbf{u}(t)\cdot\mathbf{u}(0))^2\rangle - 1}{2} \tag{1}$$

The shape of $P_2(t)$ can be fitted with a stretching exponential function, a Kohlrausch–Williams–Watts (KWW) function [20]: $\exp[-(t/\tau)^{\beta_{\mathrm{KWW}}}]$, where τ is the averaged relaxation time, and β_{KWW} represents the departure from a simple exponential decay ($0 < \beta_{\mathrm{KWW}} < 1$). The correlation time is then acquired by the integration of $P_2(t)$ in all the time domain. Since this dynamics order parameter can be fitted with a KWW function, the correlation time, τ_c, at a specific temperature directly stems from the determination of the fitting parameters τ and β_{KWW}. To specifically study the link between the motions responsible for the local dynamics with molecular processes accountable for the glass transition, this procedure has to be carried out at different temperatures, and the correlation times versus the temperature are fitted using the VFT relation. A WLF equation can also be used, since the equations are mathematically equivalent [14].

$$\tau_c(T) = A \exp\left(\frac{B}{T - T_0}\right) \tag{2}$$

T_0 is the temperature at which the configurational entropy vanishes. B is often referred as the apparent activation energy. Actually, the B parameter is not an activation energy since the equation clearly shows a non-Arrhenian behavior at temperatures above T_g.

The KWW function contains information about the detailed mechanisms of the local dynamics. β_{KWW} can be directly correlated to the cooperativity, or the fragility of the compound: lower is β_{KWW}, higher is the fragility, and higher is thus the cooperativity. Consequently, the knowledge of the KWW exponent behavior with temperature can give insight to the cooperativity motion between the different geometrical parameters it refers to. The time correlation and β_{KWW} have to be reported versus the temperature in order to get acquainted of the local dynamics. Fig. 1 shows the repeat unit of PMMA and the two bond vectors that are chosen to characterize specific local dynamics.

3.2. Cooperativity along the backbone

The first chosen bond vector is the C–H bond vector (Fig. 1) which is directly linked to the polymer backbone, and thus will give a picture of its motion. Information about its motion gives insight to the backbone local dynamics. As already reported, the two backbone of different configuration present the same dynamics relatively to their T_g, as shown in Fig. 2 [14]. This behavior is also revealed by their approximately same apparent activation energy, B, 11.8 kcal mol^{-1} for s-PMMA, and 12.5 kcal mol^{-1} for i-PMMA.

Fig. 3 shows the behavior of the KWW exponent representative of the backbone dynamics with respect to T_g/T. According to Rault [6], a linear relationship exists between the KWW exponent and the reciprocal temperature. Such a representation ensures a better comparison between the different curves, and the different behavior of the chains. In agreement with previous results, the two figures display the same behavior for the two backbone of different PMMA configuration [14]. The curve shown in Fig. 3 unveils the same cooperativity along the backbone chain at a relative temperature above T_g.

Since the T_g of s-PMMA is superior to the T_g of i-PMMA, the correlation times and therefore the cooperativity at a specific temperature above T_g are higher for the s-PMMA backbone than for the i-PMMA one. To try to understand these differences, the study of the side-chain has been investigated. Actually, experimental observations have shown that the side-chain motion influences the backbone mobility [5].

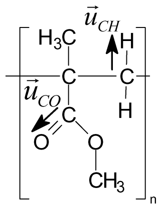

Fig. 1. PMMA repeat unit with the two vectors, $\vec{u}_{CH}$ and $\vec{u}_{CO}$, which reveal the backbone and side-chain/backbone local dynamics, respectively.

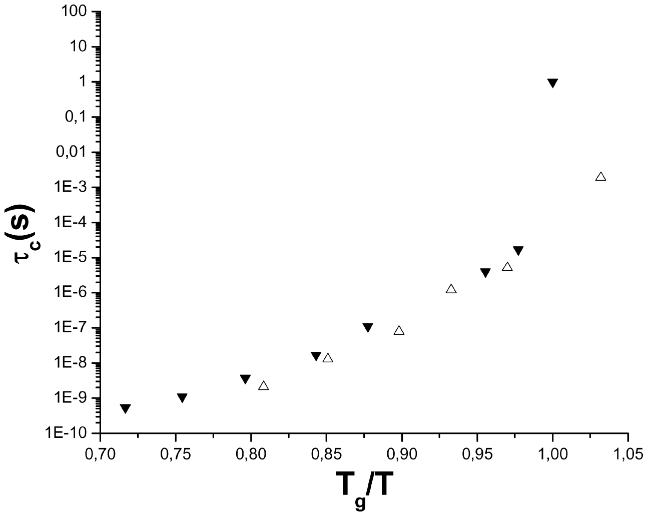

Fig. 2. Correlation times of the i-PMMA (▼), and s-PMMA (△) C–H bond vector orientation, with respect to the T_g/T ratio.

3.3. Cooperativity between the backbone and the side-chain

The second study concerns the C=O bond vector (Fig. 1) behavior. Its response actually unveils the coupling between the side-chain and the backbone. The reason for this coupling representation stems from the fact that the study of the C=O bond, according to the determination of the autocorrelation function, reveals three kind of motion

- the librational motion;
- the motion due to the side-chain;
- the motion due to the backbone.

The first motion is actually eliminated by the use of the stretching function. Although the two other motions are more difficult to separate, studies are presently carried out to differentiate them. A different approach was thus

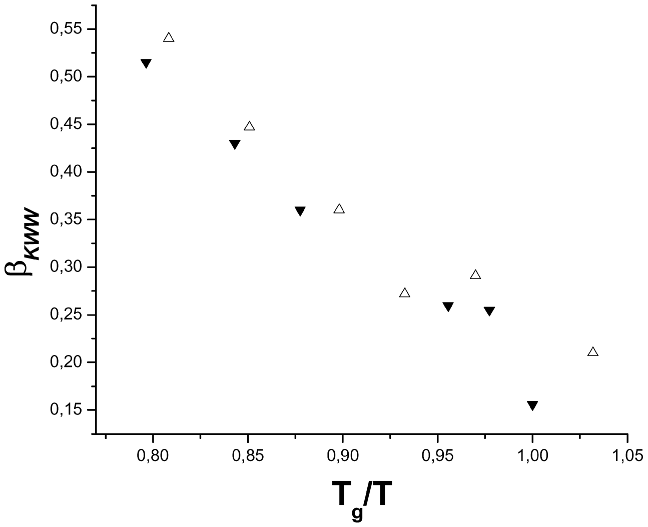

Fig. 3. KWW exponent, β_{KWW}, of the i-PMMA (▼), and s-PMMA (△) C–H bond vector orientation, with respect to the T_g/T ratio.

investigated, to extract specific observations from the comparison between the two configurations behavior.

The correlation time corresponding to the local dynamics of the C=O bond is reported for both configurations versus T_g/T in Fig. 4. The two different behaviors reveal different molecular motions. The local dynamics depicted by the C=O bond corresponds to an interpenetration of the overall motions of the side-chain and the backbone. To actually differentiate the motion of the side-chain from the motion of the backbone, the number of transitions between the 'up' and 'down' states [21] were computed, and reported versus T_g/T (Fig. 5) for both configurations. From this figure, the syndiotactic side-chains clearly exhibit the lowest number of transitions between the two states, at a relative temperature above and below T_g compared to the isotactic side-chains. In fact, to show cooperativity, analysis of this figure has to be coupled with Fig. 6. Fig. 6 shows the KWW exponent, β_{KWW}, related to the local dynamics of the C=O bond versus T_g/T.

As the temperature increases, the number of side-chain rotations of s-PMMA tends to approach that of i-PMMA (Fig. 5). In the case of the KWW exponent, it is the inverse: β_{KWW} tends to be equal when the temperature is lowered to T_g (Fig. 6) At high temperatures, the two configurations tend to present the same number of transitions between the two states of the side-chain (Fig. 5), moreover the mobility of both backbones are equivalent (Fig. 2), but the difference in the KWW exponent is undoubtedly observed (Fig. 6). At these temperatures, β_{KWW} clearly represents the motions of the backbone and the side-chain since they are both very mobile. Consequently the KWW exponent really exhibits the coupling between the side-chain and the backbone since the two times could not be separated.

Consequently, since at a relative temperature above T_g both polymer configurations display the same behavior, and the number of side-chain rotations tends to be equal, the variation of β_{KWW} could only be explained by a stronger cooperativity between the side-chain and the backbone. This is consistent with the existence of a $\alpha-\beta$ crossover temperature, T^*, generally 30 °C above T_g, above which the two motion modes merge. Since the correlation time of the two motion processes is of the same order of magnitude, coupling between the two modes cannot be excluded. This might especially be the case when the side-group motions are involved in the β process and may not vanish at T^*. However, no theory exist which allow to definitively conclude if this temperature T^* can be related to the presence of a side group in the polymer chain or not.

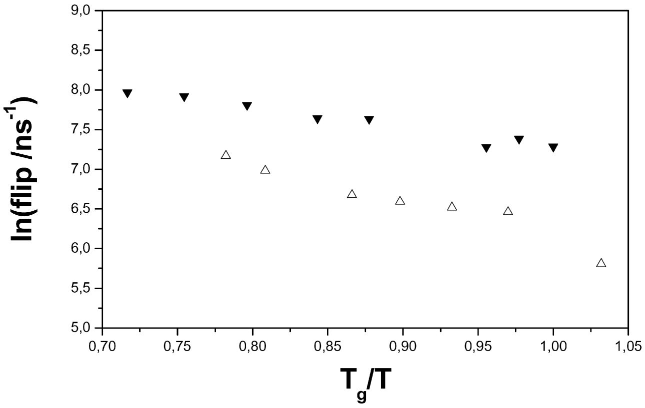

Fig. 5. Neperian logarithm of the transition frequency of the side-chain of i-PMMA (▼), and s-PMMA (△), with respect to the T_g/T ratio.

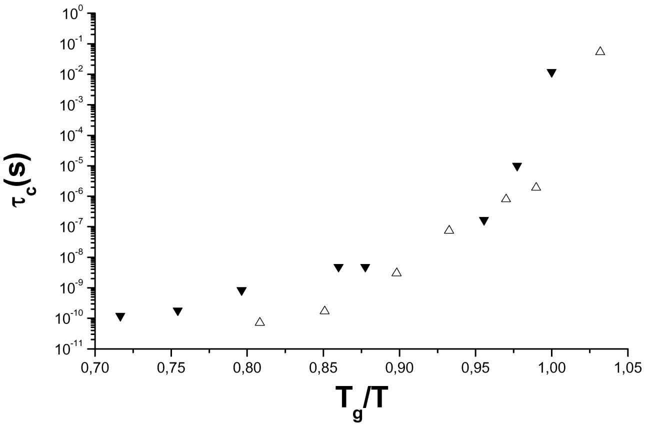

Fig. 4. Correlation times of the i-PMMA (▼), and s-PMMA (△) C=O bond vector orientation, with respect to the T_g/T ratio.

The analysis to demonstrate the correlation between the backbone and the side-chain is based on the important mobility encountered at high temperatures. However, it could not be pursued as the temperature approaches the T_g: the number of side-chain rotations reduces more for the s-PMMA than for i-PMMA, while for the KWW exponents, they tend to be equal for the two stereoisomers. Therefore, this exponent does not clearly reveal the cooperativity between the backbone and the side-chain since the backbone becomes increasingly rigid. Consequently, the influence of each kind of relaxation cannot be well documented unless

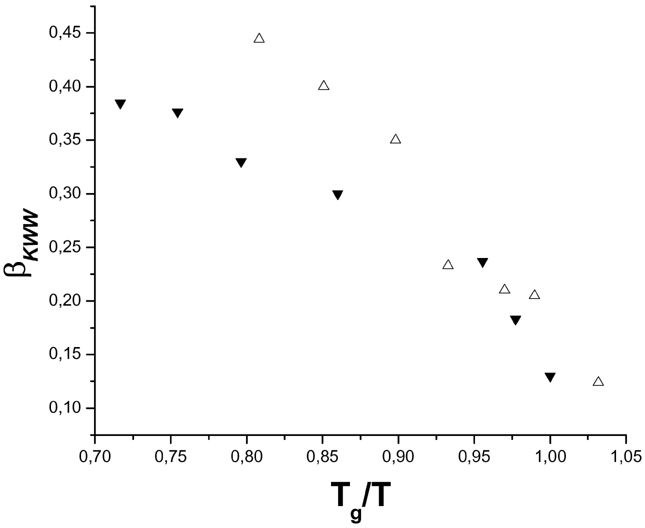

Fig. 6. KWW exponent, β_{KWW}, of the i-PMMA (▼), and s-PMMA (△) C=O bond vector orientation, with respect to the T_g/T ratio.

the different motions can be undoubtedly separated. Further studies are presently carried out in this way.

3.4. Cooperativity and T_gs difference

At a relative temperature above T_g, both PMMA configurations display comparable rotations of the side-chain (Fig. 5), but at higher temperatures, the coupling between the side-chain and the backbone is found greater for the i-PMMA than for the s-PMMA. This cooperativity influences the mobility of the backbone: the side-chain rotation drives the backbone mobility. Looking at a relative temperature compared with the T_g, the cooperativity along the backbone is the same for both configurations, but it is different at an equal temperature. This difference stems from the difference in the coupling between the side-chain and the backbone. Such a behavior is perfectly in accordance with the interpretation, according to the free volume theory, of the difference in T_gs : a greater dynamic mobility of the chain induces a lower T_g.

These results highlight the difficulties in handling the concept of cooperativity in polymers and especially in PMMA. Intramolecular coupling between side-group and backbone motions, computed in this study, exist in agreement with experimental data obtained by Kuebler et al. [5]. However, these concerted motions may only refer to local scale restricted cooperativity. These investigations open many fundamental questions. Is the local scale cooperativity observed here consistent with the CRR theory? Can the size or the shape of the CRR be affected by the PMMA tacticity? This very up-to-date debate is reinforced by the recent investigation on the thermal properties of polymers in thin films. The effect of PMMA tacticity on T_g, indeed, seems to vanish for film thickness below 20 nm as reported by several workers [22,23]. The tacticity dependent size or anisotropic shape of the CRR may be a crucial point revealed by chain confinement. Further investigations will be performed on this topic in light of our molecular dynamics results.

4. Conclusion

The KWW exponent extracted from the computation of the time correlation of selected chain backbone or side-group bonds motion yield some new results concerning the cooperativity in stereoregular PMMAs. Although, according to the coupling model, the cooperativity along the chain backbone is tacticity independent, some coupling is revealed between side-group and backbone motion. These concerted motions are much more present in the isotactic isomer as compared to the syndiotactic one. This result might be used to explain the difference in the T_g between the two stereoisomers but also for a better understanding of the particular thermal behavior of PMMA confined in thin films.

In conclusion, according to the experimental results [5], higher is the rotation of the side-chain, higher is the mobility of the backbone. Consequently, a greater rotation of the i-PMMA side-chain involves an increase in the backbone mobility, comparatively to the s-PMMA backbone, resulting in a lower T_g. Such a coupling has been envisioned by the lower Kohlrausch exponent value for i-PMMA at high temperatures.

Acknowledgements

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