Modeling of Methyl Group Rotations in PMMA

T. M. Nicholson and G. R. Davies*

IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, U.K.

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ABSTRACT: This paper explores a simple quasi-static approach to the study of conformational changes in polymers in condensed phases. Essentially, a conformational change is driven in steps by a forcing potential and the change in energy of the system is monitored as the transition path is followed. The technique is of interest since it has the potential of yielding the distribution of activation energies for processes which occur on time scales too long for study by molecular dynamic (MD) techniques. In order to test its validity, however, we have applied it to the study of the rotation of the ester methyl group in poly(methyl methacrylate) (PMMA) and compared its predictions with those of direct molecular dynamics simulations and experimental quasi-elastic neutron scattering data. Since the experimental data were analyzed in terms of a Kohlrausch−Williams−Watts (KWW) correlation function, the simulation data are analyzed in terms of fitted KWW τ and β values. We find that the quasi-static approach yields values of β similar to those obtained from the molecular dynamics data and also to the experimentally observed values. Activation energies, deduced from the temperature dependence of the fitted τ values, are also in reasonable agreement for the two different simulation methods. The simulated mean energies do not agree with the most recent analysis of the quasi-elastic neutron scattering data, but they are in agreement with earlier analyses and with the observed values for similar systems such as poly(vinyl methyl ether) (PVME). We therefore conclude that the quasi-static technique is valid and can confidently be applied to the study of slower motions in other systems such as the motion of the α methyl group in PMMA, which is inaccessible by MD techniques.

Introduction

There is a great deal of interest in modeling molecular motions in condensed phases. However, many of these motions take place over quite long time scales (maybe $\sim 10^{-3}$ s), while molecular dynamics are limited to $\sim 10^{-9}$ s since typically a time step of less than 1 fs is required.

This paper explores an alternative "quasi-static" approach to obtaining information about a condensed phase motion without using dynamics. The method, which has been used by others,[1,2] involves the direct driving of the mode of motion of interest. The system used is the rotation of the ester methyl group in poly(methyl methacrylate) (PMMA). This was chosen because these rotations are fast, so the process can be modeled using molecular dynamics, thus enabling a comparison between the dynamics and the alternative approach to be made. In addition, experimental data from neutron scattering[3,4] are available for this process with which the simulations can be compared.

In the neutron scattering experiments it is assumed that the methyl group can be in one of three states, with the dihedral angle C−O−C−H_1 (see Figure 1) approximately 0° or ±120° and that the observed motion is jumps between these states. The quasi-elastic spectral width, which is related to a jump rate, is measured as a function of temperature and hence yields a barrier height. A conformational correlation function is calculated and empirically fitted to a Kohlrausch−Williams−Watts (KWW) function, which is a stretched exponential function:[5]

$$f(t) = \exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right) \tag{1}$$

where the relaxation time τ and the width of the function β are determined. We have therefore developed our simulations in these terms to allow comparison with experimental data.

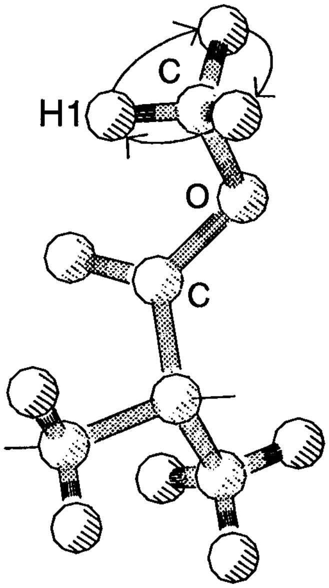

Figure 1. One unit of PMMA showing the mode of motion of the ester methyl group.

At low temperatures quantum tunneling through the barrier is the dominant process, but as the temperature is increased, the rate of quantum tunneling decreases[6] while the rate of thermally activated jumping over the barrier increases until this is the dominant process above about 70 K. The motion at 200 K and above can therefore be safely considered in classical terms.

Model Construction

Simulations were carried out using the Insight and Discover programs from MSI[7] using the Polymer Consortium Force Field (PCFF). In particular the powerful BTCL programming language in Discover allowed the rapid development of the modeling strategy.

The model system used in these simulations was built using the MSI Amorphous Cell Builder. A cubic cell containing 30 syndiotactic MMA units was constructed

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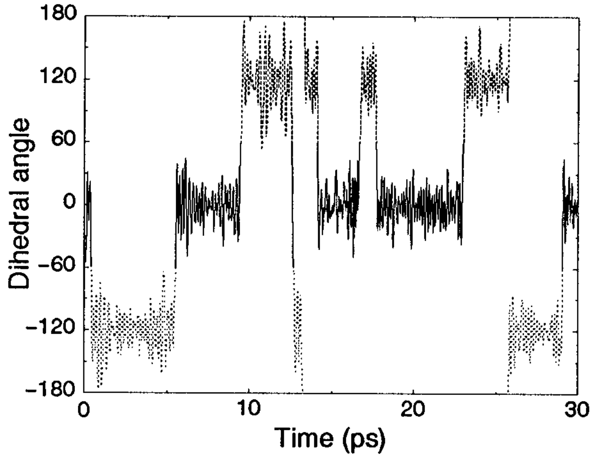

Figure 2. Typical plot of methyl group orientation as a function of time during a dynamics run. The assignment of orientation to the three states is shown by different gray levels of the line.

at a density[8] of 1.18 g cm^{-3} and a temperature of 298 K, leading to a cell dimension of 16.06 Å. Periodic boundary conditions were employed in order to model a bulk system. The range of the nonbonded interactions considered between atoms was smaller than half the cell edge so no atom interacts with an image of itself. Five separate cells were independently built to ensure that a range of conformations of the amorphous polymer were explored. A second set of five cells of isotactic PMMA were also built, at a density of 1.21 g cm^{-3}, to allow the effect of tacticity to be investigated. For brevity, the figures in this paper show results for the syndiotactic cells only, but results from both syndiotactic and isotactic cells are included in the final tables.

Dynamic Modeling

Molecular dynamics at 298 K was run using the MSI Discover program on each of the constructed cells. Initially, the atoms of the system are assigned velocities from a Boltzmann distribution corresponding to the temperature of interest. Then Newton's laws of motion are solved numerically in 0.5 fs time steps, using the Velocity Verlet algorithm to follow the evolution of the conformations. A NVT ensemble was used with the Velocity Scaling algorithm to keep the temperature constant. 10 000 steps (5 ps) were used to equilibrate the energy of the system (i.e., to allow the potential energy to reach a plateau value) and then a further 100 000 steps (50 ps) run, during which data were collected. Each run took 2 h on a SGI R4000 Indigo workstation.

The dynamics runs were also repeated at a lower temperature (198 K).

Results. During the dynamics run the dihedral angle of each of the ester methyl groups was recorded at 10 fs intervals. Figure 2 shows an excerpt of the record for a typical group. It is clear that the assumption that the group makes transitions between three distinct states holds. The frequency of transitions was clearly much lower than the sampling frequency, so the sampling frequency was increased to 100 fs and the probability that a methyl group makes more than one transition between samples was neglected. The number of transitions for each methyl group was determined and a histogram of the distribution of transition rates obtained (Figure 3).

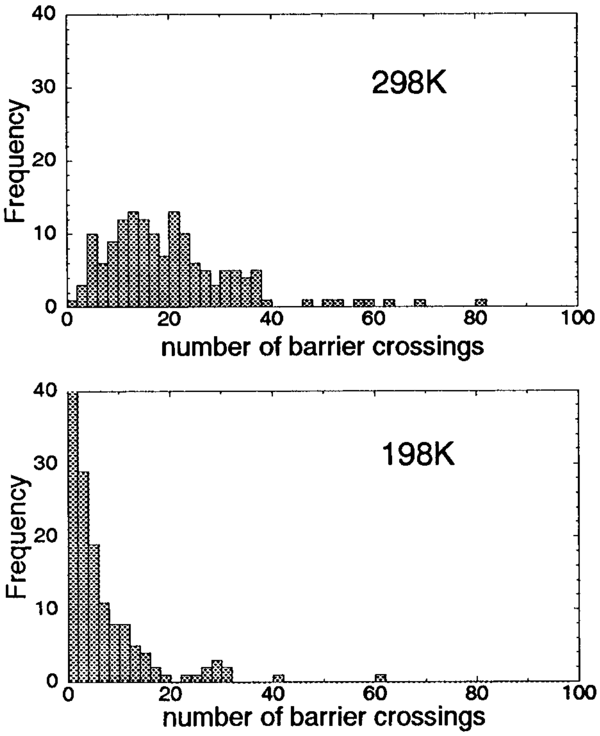

Figure 3. Frequency distribution of the number of barrier crossings made by individual methyl groups during 50 ps of dynamics simulation at the two indicated temperatures.

The distribution of transition rates is broad. Some groups hardly change conformation during the simulation run while others are performing barrier crossings 1 order of magnitude faster. At the lower temperature fewer transitions are observed as might be expected, but there are still some groups that are undergoing significant numbers of transitions.

Fitting of Data. To fit these data to the empirical function (eq 1) a correlation function $c(t_1,t_2)$ was defined, which is 1 if a dihedral is in the same state at times t_1 and t_2 and 0 otherwise. Then a conformational correlation function is given by

$$f(t) = \langle c(t',t'+t)\rangle \tag{2}$$

where the angle brackets denote an average taken over all methyl groups and all time origins t'. This is a similar process to one used by Brown and Clarke[9] to describe conformation relaxations in butane. $f(t)$ varies from 1 at short t to $^1/_3$ at long t so it was normalized using

$$F(t) = \frac{f(t) - f(\infty)}{f(0) - f(\infty)} \tag{3}$$

to produce a function that varied from 1 to 0.

Figure 4 shows the calculated $F(t)$ for syndiotactic PMMA at the two temperatures together with a weighted least squares fit to the stretched exponential. Note that the data for long time intervals are less accurate since there are fewer such intervals available to be sampled from the data. The fitting procedure used takes this into account. From this fit, values of the time constant τ and width parameter β are obtained.

E_{barrier}, a mean activation energy for the transition process, can then be calculated from the ratio of τ at two temperatures using

$$\frac{\tau_1}{\tau_2} = \exp\left(\frac{E_{\text{barrier}}}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \tag{4}$$

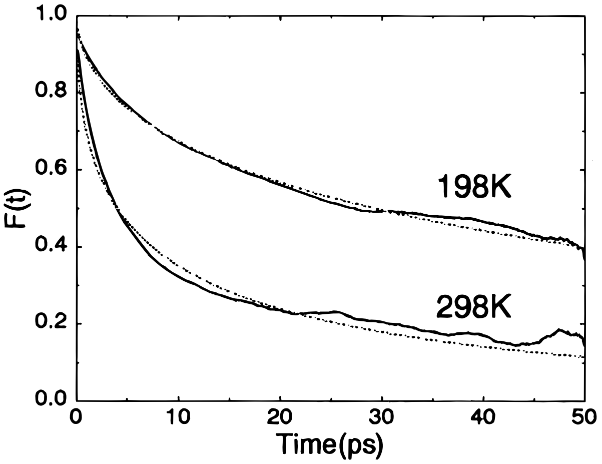

Figure 4. Fitting of the dynamic data to the stretched exponential (eq 1). The dark lines are the decay of correlation information calculated using eqs 2 and 3, and the lighter lines are a weighted least squares fit to these data.

Table 1. Average Methyl Group Energy Barriers (in kcal/mol) Calculated by the Various Methods Described in the Text[a]

	syndiotactic	isotactic
dynamic		
empirical fit		
ratio of τ's	2.20	1.85
quasi-static		
histogram average	2.33	2.39
empirical fit		
ratio of τ's	2.20	2.29
298 K	2.32	2.48
198 K	2.40	2.40
neutron scattering		
quasi-static[3]	1.27	
inelastic[4]	2.10	

[a] Experimental values for comparison are taken from the indicated references.

Table 2. Width Parameter (β) of the Stretched Exponential Fit to the Methyl Group Rotation Data Calculated by the Various Methods Described in the Text[a]

	syndiotactic	isotactic
dynamic		
298 K	0.45	0.42
198 K	0.52	0.54
static		
298 K	0.58	0.55
198 K	0.59	0.54
experiment		
198 K	0.65	
150 K	0.57	

[a] The experimental value is taken from ref 3.

Values of E_{barrier} and β calculated for both syndiotactic and isotactic PMMA are given in Tables 1 and 2.

Quasi-Static Modeling

As an alternative to running dynamics, the barrier height for a methyl group was estimated directly by explicitly rotating the group and monitoring the energy of the system. This is similar to the method described by Suter et al.[1] who studied the rotation of phenyl rings in amorphous polystyrene and Tiňo et al.[2] who investigated conformational barriers in polyethylene. Here we employed two variants of the method.

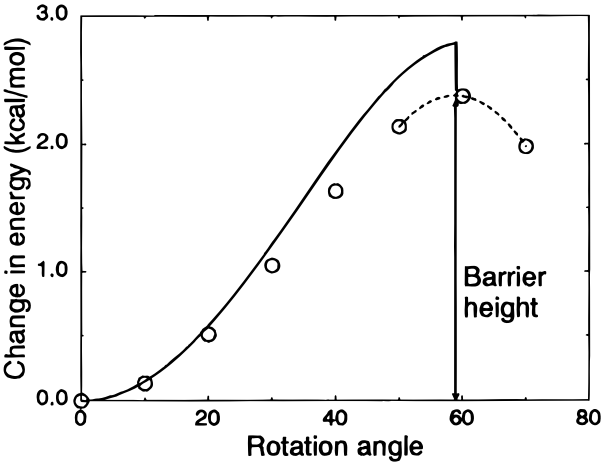

Figure 5. Schematic illustration of the two driven methods employed to calculate the methyl group barrier heights. Circles and dotted line correspond to method 1, and the solid line to method 2.

In method 1 the system was initially minimized and the system energy recorded. Then one methyl group was chosen at random and rotated in 10° steps. At each step the dihedral angle that described the orientation of the group (i.e., the C−O−C−H_1 dihedral angle in Figure 1) was restrained at its new value and the rest of the system minimized to calculate a new energy. When the calculated energy began to fall, the maximum energy for the group rotation was calculated by a quadratic fit to the last three points, and hence a measure of the barrier height was obtained. This is illustrated by the circles and dotted line in Figure 5. The process was then repeated on all the other methyl groups in the cell, chosen in a random order.

On a SGI Indigo R4000 workstation this took 8 h per methyl group. The method was only used on one syndiotactic cell, and a faster method was sought.

In method 2, the chosen methyl group was rotated in 1° steps, but the system energy was evaluated without allowing the rest of the system to be minimized. When the maximum energy position for the methyl group was found, the dihedral angle was restrained to this position and the rest of the system minimized, to obtain the barrier height. This is illustrated by the full line in Figure 5.

This second method was 4 times faster than the first, since only two rather than typically eight minimizations per methyl group were required. The results for the two methods for one cell of syndiotactic PMMA were compared and found to be similar. This second method was used on all 10 constructed cells.

The process was then repeated with the density of the cells increased to 20% more than normal to investigate the effect of surrounding atoms on the barriers to rotation.

Results. The barrier heights of all the individual methyl groups were recorded and histograms illustrating the distribution produced (Figure 6). The means and standard deviations calculated from these histograms are given in Table 3. The means can be compared with the barrier height of rotating a methyl group in an isolated MMA segment of 2.10 kcal/mol.

There is a wide spread of barrier heights. The effect of neighboring chains is not, as might have been expected, to simply raise the energy barriers; in fact some barriers are lower than for an isolated chain. As the density is increased, the distribution broadens; the mean increases but the number of low barriers also increases. This may be explained by the fact that the

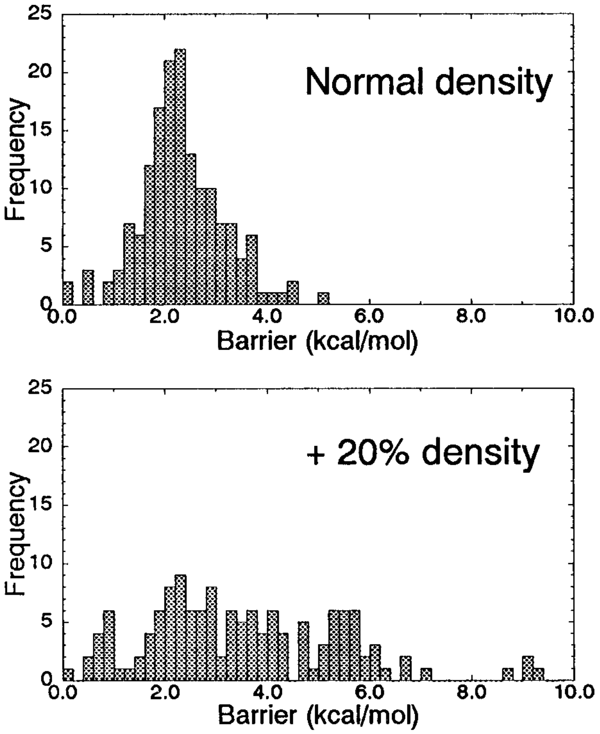

Figure 6. Distribution of barrier heights calculated by the driven rotation of methyl groups using method 2 described in the text.

Table 3. Mean and Standard Deviations (in kcal/mol) of Barrier Heights of Methyl Groups Calculated by Direct Rotation of the Groups[a]

	syndiotactic		isotactic	
	mean	sd	mean	sd
method 1	2.40	0.85		
method 2	2.33	0.82	2.39	0.85
method 2 + 20% density	3.61	2.04	3.79	1.95

[a] The "method 2" results correspond to the histograms in Figure 6.

presence of adjacent chains need not raise the energy at the maximum point of a rotation but may destabilize the minimum energy conformation, to reduce the overall barrier. A simple model of this process has been proposed by Bicerano.[10] This effect increases at higher densities, leading to a broadening of the distribution.

Fitting of Data. To fit the static data to the same empirical function as used previously, a correlation function needs to be defined. First a time constant τ' for each methyl group was calculated from the barrier heights E. Assuming a constant τ_0 and a given temperature T, this is given by:

$$\tau' = \tau_0 \exp\left(\frac{E}{kT}\right)$$

In principle τ_0 could vary for each methyl group. At present, however, this has been ignored and a single arbitrary constant used.

Assuming that the methyl groups move independently a global conformational correlation function can then be defined:

$$G(t) = \left\langle \exp\left(\frac{-t}{\tau'}\right)\right\rangle \qquad (5)$$

where the angle brackets indicate an average over all methyl groups. This is in fact a function of both T and τ_0. The function was then fitted by the stretched exponential (eq 1) to give values for τ and β.

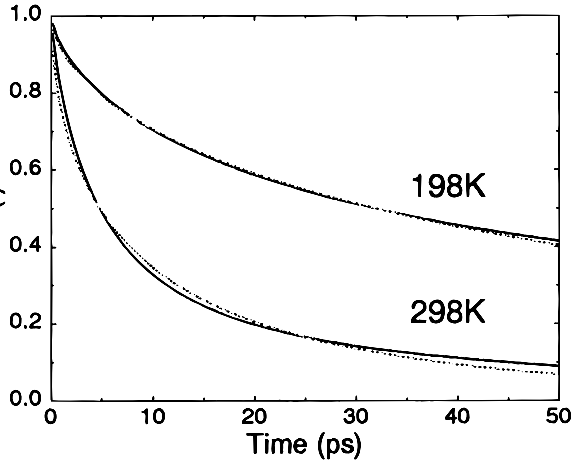

Figure 7. Fitting of the driven rotation data to the stretched exponential (eq 1). The dark lines are the decay of correlation information calculated using eq 5, and the lighter lines are a weighted least squares fit to these data.

Figure 7 shows both the correlation function $G(t)$ and the least squares fit at two temperatures for syndiotactic PMMA. The time axis has been scaled by choosing a value of $\tau_0 = 6.5$ ps such that the fitted τ for normal density PMMA at 298 K is the same as that which was calculated from the dynamic data.

The ratio of data from two temperatures can be used as before to calculate E_{barrier} (eq 4), or alternatively, since τ_0 is fixed and known, data from a single temperature can be used by using

$$\tau = \tau_0 \exp\left(\frac{E_{\text{barrier}}}{kT}\right)$$

Results of all three calculations are given in Table 1 with values of β calculated from the fit in Table 2.

Discussion

The comparison of the results for the energy barrier to methyl group rotation shown in Table 1 shows good agreement between the methods. While in this case the quasi-static approach was much slower (about 30 times!) than the dynamic approach, for other systems in which the characteristic time for transitions is much longer this quasi-static approach will be useful. Using BTCL it would also be possible to investigate the energy barriers in more complicated systems where more than one dihedral angle is involved, such as the rotation of a carbonyl group in an aromatic polyester.

The results are of a similar order to experimental results, agreeing quite well with an analysis of the inelastic neutron scattering data for PMMA.[4] This paper also analysed quasi-elastic neutron scattering data using a simple exponential function (which implies a single barrier energy) and obtained an anomalous temperature dependence of the activation energy with temperature, decreasing from 1.7 kcal/mol at 300 K to 0.24 kcal/mol at 150 K. Recently, Arrighi et al.[3] have analyzed the quasi-elastic data using the KWW function (which implies a range of barrier energies), obtaining a mean barrier energy of 1.27 kcal/mol. It is interesting to note that this same paper reports a value for the barrier in poly(vinyl methyl ether) (PVME), a similar polymer, of 1.68 kcal/mol, which is closer to our calculated values.

Colmenero et al.[11] report values for the barrier heights in PVME, measured by time of flight neutron scattering techniques, of 2.0 kcal/mol at 300 K, which is comparable with our calculations for PMMA. They also show a distribution of barrier energies that is not temperature dependent, which suggests that our quasi-static simulation, which is effectively being performed at 0 K, is predicting the same barrier distribution seen at the MD temperatures. The distribution of barrier energies is clearly the main origin for the distribution in jumping rates.

The comparisons of model data with the KWW function shows systematic deviations, which suggest that this function may not be a good choice for expressing their data. This can also be seen from the distribution of barrier energies, which is asymmetric with a tail in the high-energy region for the quasi-static model while the distribution corresponding to a KWW function should show a tail in the low-energy region. A better approach would be to reanalyze the PMMA quasi-elastic scattering data to directly obtain a distribution of energy barriers, but this has not been done for this system. We are currently simulating methyl rotation in PVME and these data will be compared with the experimentally derived spread of barrier heights.

The effect of other methyl groups on the energy barrier of a particular methyl group in the quasi-static simulation is to some extent included by way of the relaxation of the surrounding structure during the minimizations. It is probable, however, that since thermal motions are neglected, the method will almost certainly overestimate the environmental constraints, but if this method shows that the motion could occur, it almost certainly will in some form.

The broadening of the distribution of barrier heights at increasing pressure is an interesting prediction. The β parameter for syndiotactic PMMA by the dynamic method at 298 K reduces from 0.45 to 0.40 and at 198 K from 0.52 to 0.43. We have attempted to test this by neutron scattering measurements under pressure, but the broadening was so great in our initial experiments that the effects of the methyl group rotation could not be resolved. It is worth noting that the simulation pressure, as calculated from the virial coefficient during the NVT dynamics simulations, is higher than expected (0.8 GPa). NPT dynamics simulations at atmospheric pressure after allowing for the tail correction[12] show the equilibrium simulation density to be about 4% less than the experimental density. This implies that the modeled system is being constrained as if already at a higher density and so the degree of broadening at a reduced simulation density will be expected to be less than we have calculated.

Conclusions

The quasi-static method has been shown to give results similar to those from molecular dynamics simulations and therefore can confidently be applied to slower motions such as the the backbone methyl group in PMMA or other systems that are inaccessible by MD techniques.

The primary effect of the environment on the ester methyl group in PMMA is to broaden the range of conformational barrier energies. A significant shift in the mean barrier energy is only produced at high densities. These high densities further increase the breadth of the distribution.

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