A molecular mechanics investigation into the mechanism of the low temperature relaxations of three poly(alkyl methacrylates)

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The enthalpy curves for the rotation of the ester groups around the O–alkyl bonds in three-unit all-*anti* models of syndiotactic poly(ethyl methacrylate), poly(isopropyl methacrylate) and poly(cyclohexyl methacrylate) have been calculated using molecular mechanics. The abundance of conformers and the enthalpies of activation for their interconversion at 50 K have been related to the mechanical loss processes at low temperature with Hoffman's theory for a three site model with two equienergetic sites. The calculated activation energies compare well with the experimental values of the δ relaxations. The mechanical loss process is in all cases caused by the exchange of ester side chain positions by partial rotation around the O–alkyl bond.

(Keywords: molecular mechanics; poly(ethyl methacrylate); poly(isopropyl methacrylate); poly(cyclohexyl methacrylate); conformational analysis; mechanical loss; barriers to rotation; side group motions)

INTRODUCTION

Wada and co-workers reported extensively on the low temperature relaxations in poly(ethyl methacrylate)[1] (PEMA) and poly(isopropyl methacrylate)[2] (PIPMA). The δ relaxation was attributed to the internal rotation in the side chain around the O–alkyl bond. They also calculated these motions in an isolated side chain and in a side chain attached to the main chain of a 5_1 helix with a geometry taken from the crystal structure of isotactic poly(methyl methacrylate) (PMMA). Using a simple rigid model, they give potential energy maps for two torsion angles (O–C_α and C_α–C_β) calculated from interactions between non-bonded atoms and a three-fold torsion potential for the C_α–C_β bond. Cowie[3] had already noted that in these calculations the restrictions of the main chain on the motions in the side chain are probably much too severe. Now molecular mechanics affords a refined model with full relaxation of bond distances, bond angles and torsion angles and with more accurate empirical force fields. Therefore, it seemed worthwhile to recalculate the rotational barriers around the O–alkyl bonds to further the insight into the molecular processes of low temperature relaxations in glassy amorphous polymers. We included poly(cyclohexyl methacrylate) (PCHMA) in the calculations, both for its structural proximity to the isopropyl derivative and because new mechanical relaxation data are available[4]. *Figure 1* gives these data together with those for PEMA, both obtained at the Centre d'Etudes Nucleaire, Grenoble.

EXPERIMENTAL

The molecular mechanics calculations were carried out on model compounds of the polymers. We used a main chain of seven carbon atoms with side chains on positions two, four and six, i.e. three methacrylate units terminated by a hydrogen atom on one side and a methyl group on the other (*Figure 2*). We chose the syndiotactic configuration, since in the polymers on which the relaxation measurements have been carried out, syndiotactic sequences are predominant. The calculations were performed on the all-*anti* (all-*trans*) forms of the main chains. Apart from small variations this form of the main chain was retained during all rotations around the O–C_α bond of the middle ester group. Both to reduce the size of the model compounds and to simplify the conformational complexity of the models only the ester alkyl group of the middle unit was varied from ethyl to isopropyl and cyclohexyl, while methyl ester groups were taken for the outer units. The calculations were confined to the rotations around the O–C_α bond of the middle unit, because our previous calculations on PMMA[5] show that other barriers to rotation in the ester side chain are much too high to be related to the δ relaxation. Rotations of methyl groups are excluded, because they lead at best to very weak mechanical relaxations. For obvious reasons we placed the cyclohexyl group in its chair form and attached it to the ester oxygen via an equatorial bond.

The calculations were performed using DELPHI, the Delft computer program for molecular mechanics[6], with the MM2 empirical force field[7]. Rotations around O–C_α were carried out using the Lagrange multiplier method[6] with complete relaxation. The mean value of three corresponding torsion angles around this bond was constrained in a stepwise manner. The minima and transition states were calculated without any constraint, all showed six zero eigenvalues of the final force constants matrix. The program gives the enthalpy, H, at 298 K and

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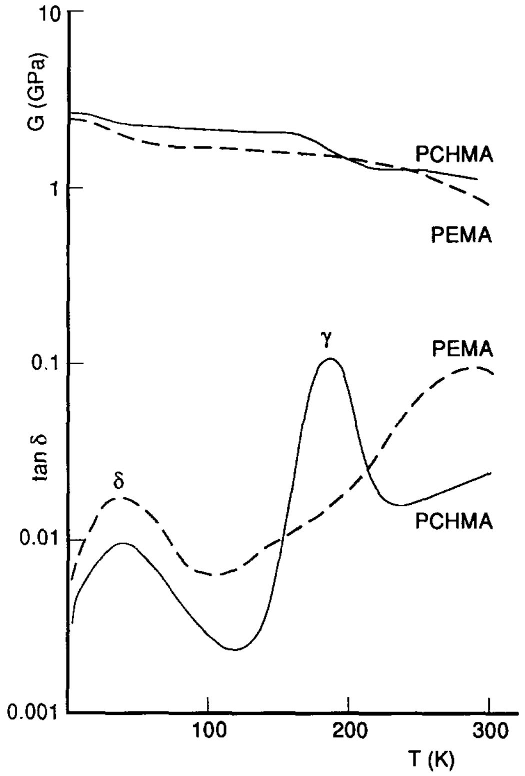

Figure 1 Shear modulus, G, and damping, tan δ, at ~1 Hz as a function of temperature for PEMA and PCHMA

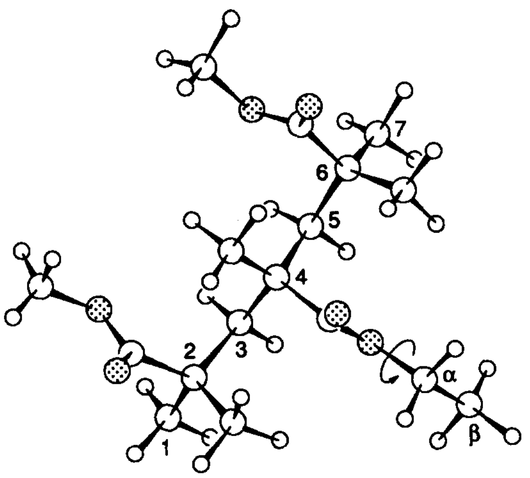

Figure 2 Ball and stick representation of the three-unit model compound of PEMA (coordinates of the global minimum, lone pairs on oxygen deleted)

the heat content, HC, for a series of temperatures. Since the loss processes are located in the region of 50 K, we calculated the enthalpies at 50 K from $H(50) = H(298) - HC(298) + HC(50)$. The conformational energies, ΔH, were obtained by subtracting the enthalpy of the global minima.

RESULTS AND DISCUSSION

The conformational energies, $\Delta H(298)$, *versus* the O–C_α rotation angles for the three model compounds are shown in the *Figures 3*, *4* and *5*. Data on the minima and transition states are given in *Table 1*. The conformations with a torsion angle C–O–C_α–C_β (PEMA) or C–O–C_α–H (PIPMA and PCHMA) of 0 and 180° have a plane of symmetry (C_{1h}). This symmetry is also expressed in the energy curves. In each case three minima and three transition states are met during a full rotation. The minima appear when the geometry around O–C_α is staggered, the transition states when it is eclipsed. The transition states are relatively high when a C_α–C_β bond passes the O–C bond (d, d′) and relatively low when this

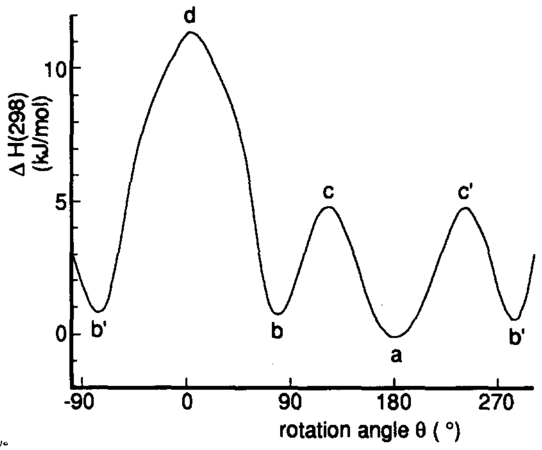

Figure 3 Conformational energy, $\Delta H(298)$, *versus* rotation angle, θ, around O–C_α for PEMA (θ is the mean value of the torsion angles C–O–C_α–C_β, LP–O–C_α–H and LP′–O–C_α–H′ with about equal values; LP = lone pair)

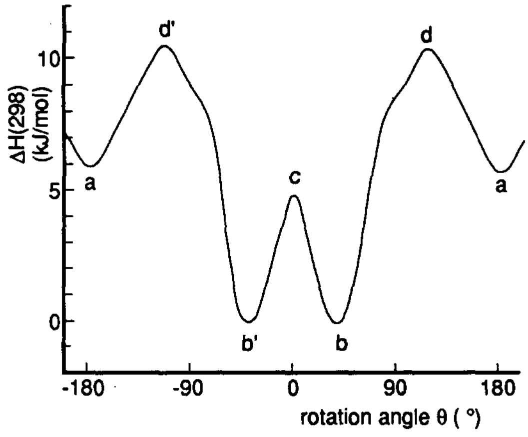

Figure 4 Conformational energy, $\Delta H(298)$, *versus* rotation angle, θ, around O–C_α for PIPMA (θ is the mean value of the torsion angles C–O–C_α–H, LP–O–C_α–C_β and LP′–O–C_α–C'_β with about equal values; LP = lone pair)

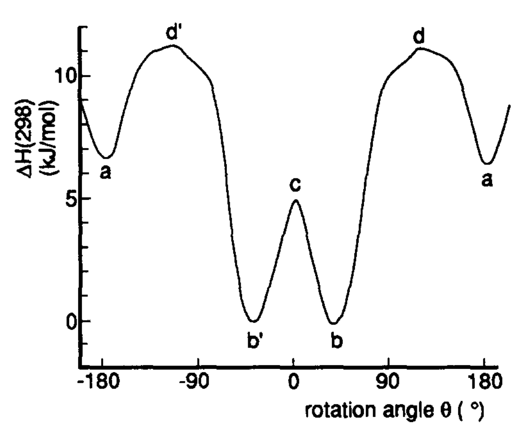

Figure 5 Conformational energy, $\Delta H(298)$, *versus* rotation angle, θ, around O–C_α for PCHMA (θ is the mean value of the torsion angles C–O–C_α–H, LP–O–C_α–C_β and LP′–O–C_α–C'_β with about equal values; LP = lone pair)

Table 1 Conformational energies, ΔH (kJ mol^{-1}), at 50 and 298 K of the minima and transition states for the rotation of the middle ester alkyl groups $-CH_2CH_3$ (Et), $-CH(CH_3)_2$ (iPr) and $-CH(CH_2)_5$ (cHex) in the three-unit models of syndiotactic poly(alkyl methacrylate)

R	Conformation[a]		Point group	Rotation angle (°)[b]	ΔH(298)	ΔH(50)
Et	a	min	C_{1h}	180.0	0.0	0.0
	c	ts	C_1	120.1	4.9	7.1
	b	min	C_1	77.9	0.8	1.3
	d	ts	C_{1h}	0.0	11.4	14.1
iPr	a	min	C_{1h}	180.0	5.9	6.0
	d	ts	C_1	115.8	10.6	13.1
	b	min	C_1	39.2	0.0	0.0
	c	ts	C_{1h}	0.0	5.0	6.9
cHex	a	min	C_{1h}	180.0	6.6	6.7
	d	ts	C_1	117.3	11.3	13.6
	b	min	C_1	38.7	0.0	0.0
	c	ts	C_{1h}	0.0	5.1	6.9

[a] Conformations are denoted by the letters in *Figures 3, 4* and *5*. For mirror image pairs only one conformation is given; min = minimum, ts = transition state

[b] See legends of *Figures 3, 4* and *5*

is the case for a C_α–H bond (c, c′). Inspection of the geometries d (d′) shows unfavourable non-bonded interactions between C_β with its hydrogen atoms and the carbonyl group. The shape of the curves near these higher transition states is rather different for the three compounds. The maximum is much broader for the cyclohexyl ester. This is caused by the restriction of the rotation around C_α–C_β. When a methyl group of the isopropyl ester passes the O–C bond it moves ~14° to both sides; the corresponding methylene group of the cyclohexyl derivative moves only ~6°.

During the rotations around C_α–O the interactions of the ester alkyl groups with the methyl groups of the adjacent units on the main chain are relatively small; these methyl groups hardly rotate. The small value of the energy difference between the minima a and b (b′) in the ethyl ester supports this point. In this ester the interaction is further diminished by small rotations around the C_4–CO and CO–O bonds when C_β and a main chain methyl group interact unfavourably. The same small rotations stabilize the lower energy minima b and b′ of the isopropyl and cyclohexyl esters but are for symmetry reasons not present in the higher energy minima a. This explains why the energy difference between the minima in the isopropyl and cyclohexyl esters is much larger than twice the value found in the ethyl ester.

Finally, we also performed a rotation of the ethyl group with the torsion angles of the main chain fixed at their values in the global minimum (173.6, 174.0, −174.0 and −173.6°). The effect on the height of transition state d was negligible, transition state c (c′) increased 0.1 kJ mol^{-1} in energy and minimum b (b′) 0.2 kJ mol^{-1}. These very minor changes confirm that the interactions between the ester alkyl groups and the main chain are small during the rotations of the former groups around O–C_α.

Of the results of Wada *et al.*[1] on models of PEMA only those for the isolated side chain can be compared, since the interactions for the isotactic main chain configuration will be much higher than for our syndiotactic configuration. Their energy difference between geometries corresponding to a and b of 1.0 kJ mol^{-1} is in good correspondence with our ΔH(298) value of 0.8 kJ mol^{-1}. Their lowest barrier between b and a of 8.8 kJ mol^{-1} is considerably larger than our value of 4.1 kJ mol^{-1}. The most serious discrepancy is found for the barrier corresponding to our transition state d: according to the contour map of Figure 8a in reference 1 it is larger than 200 kJ mol^{-1}, whereas we obtained only 10.6 kJ mol^{-1}. This indicates that the rigid model applied in reference 1 to calculate the barriers to rotation is too crude.

Relation with relaxation data

We will try to relate the conformational energy curves with mechanical properties, using the theory of the site models applied by Hoffman[8] to dielectric relaxation. This theory gives the number of groups, N_i, in each site and the molecular relaxation time, τ. It starts from the elementary transition probabilities, k, between the sites and allows only transitions between adjacent sites. The three site model with sites 1 and 2 equienergetic (*Figure 6*) is characteristic for the compounds studied in this investigation.

The differential equations for the number of groups in each site are:

$$dN_1/dt = -(k_1 + k_2)N_1 + k_1N_2 + k_3N_3$$
$$dN_2/dt = +k_1N_1 - (k_1 + k_2)N_2 + k_3N_3$$
$$dN_3/dt = +k_2N_1 + k_2N_2 - 2k_3N_3$$

The solution of these simultaneous equations is of the form:

$$N_i = C_{i1} + C_{i2}\psi_2 + C_{i3}\psi_3 \qquad (i = 1, 2, 3)$$

with $\sum C_{i1} = N$ (the total number of groups), $\sum C_{i2} = 0$ and $\sum C_{i3} = 0$. ψ is a decay function of the form $\exp[-f(k)t]$ and C_{i1} is the number of groups in each site at equilibrium. For the present case we obtain $C_{22} = C_{12}$, $C_{32} = -2C_{12}$, $C_{23} = -C_{13}$, $C_{33} = 0$ and finally:

$$N_1 = [k_3/(k_2 + 2k_3)]N + C_{12}\exp[-(k_2 + 2k_3)t] + C_{13}\exp[-(2k_1 + k_2)t]$$
$$N_2 = [k_3/(k_2 + 2k_3)]N + C_{12}\exp[-(k_2 + 2k_3)t] - C_{13}\exp[-(2k_1 + k_2)t]$$
$$N_3 = [k_2/(k_2 + 2k_3)]N - 2C_{12}\exp[-(k_2 + 2k_3)t] + 0$$

It is generally accepted that external stress disturbs the conformational equilibrium of energetically different sites. When the sites are identical the conformational equilibrium cannot be disturbed and as a consequence

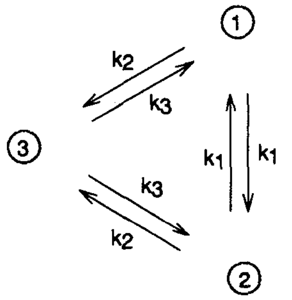

Figure 6 Definition of the k values in the three site model with sites 1 and 2 equienergetic

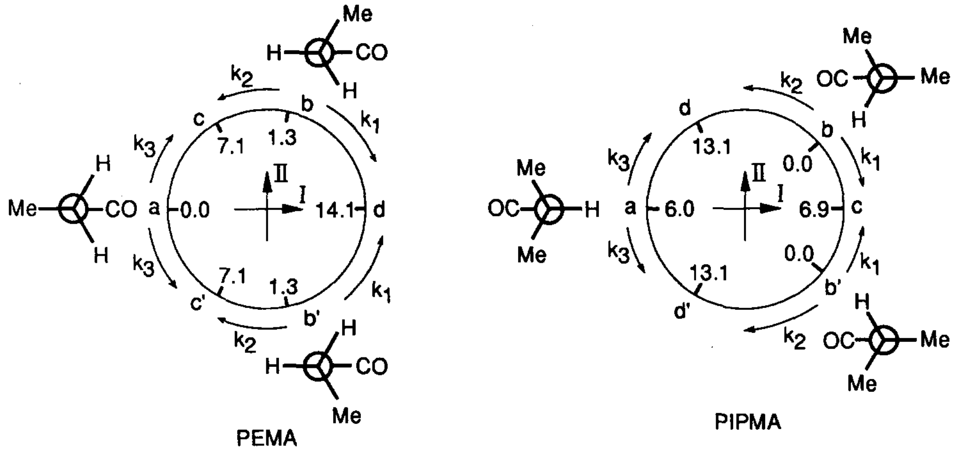

Figure 7 Schematic representation of the directions of the external stress I and II with respect to the positions of the side chains. The conformations are denoted by the letters from *Figures 3* and *4*, the k values correspond to *Figure 6*

theory predicts that no relaxation can be observed. This is, for instance, the case for the three rotamers of a methyl group. The minima b and b′ are equienergetic but not identical because the side chains do not occupy the same position in space. In each orientation of the O–C_α bond with respect to the applied external stress the two sites are affected differently and the random partitioning of the side chains over the originally equienergetic sites is disturbed. The above equations show that there are two ways to restore the disturbed equilibria: mode A, an exchange between site 3 on the one hand and sites 1 and 2 on the other; and mode B, a net exchange between sites 1 and 2. The relaxation times of these modes are $\tau_A = (k_2 + 2k_3)^{-1}$ and $\tau_B = (2k_1 + k_2)^{-1}$.

The occurrence of these two modes can also be explained by considering the effect of the external stress on a single side chain by means of *Figure 7* (a scheme for PCHMA is not given as it is very similar to that of PIPMA). We suppose that a conformation with a methyl group in the direction of the stress is more favourable than one with the smaller hydrogen atom pointing in that direction. A stress in the direction of the axis of rotation O–C_α will hardly affect the conformational equilibrium, because the movements of the methyl group(s) and the hydrogen atom(s) in that direction are very small during the rotation. A stress perpendicular to the axis of rotation and lying in the plane of symmetry (*Figure 7*, direction I) favours the positions b and b′ at the cost of a. This corresponds to mode A. A stress perpendicular to the plane of symmetry (direction II) favours position b at the cost of b′, while the abundance of conformer a is hardly changed. This corresponds to mode B.

In the case of PEMA the transitions from a to b and b′ and vice versa (mode A) occur via the single low barriers c and c′. On the basis of the calculated enthalpy difference at 50 K, $k_3 = 0.044k_2$ and $\tau_A = (1.09k_2)^{-1}$. It also follows from the Boltzmann relation that the transitions from b to b′ and vice versa (mode B) occur via the consecutive passage of the low barriers c and c′ and only to an extremely small extent via the high barrier d, since at 50 K $k_1(\mathrm{b} \rightarrow \mathrm{b}') \approx 5 \times 10^{-8} k_2(\mathrm{b} \rightarrow \mathrm{a})$. Thus $\tau_B = k_2^{-1}$ and cannot be distinguished from τ_A. On the basis of the abundance of the conformers, mode A will predominate.

The situation for PIPMA and PCHMA is different: the two high barriers d and d′ separate unequivalent sites. The transition from a to b and b′ or vice versa (mode A) cannot be observed at 50 K because the abundance of groups in site a is extremely low at this temperature. The transition from b to b′ and vice versa (mode B) takes place exclusively via transition state c, since at 50 K $k_2(\mathrm{b} \rightarrow \mathrm{a}) < 10^{-6} k_1(\mathrm{b} \rightarrow \mathrm{b}')$ and $\tau_B = (2k_1)^{-1}$. In this case mode B will be the only effective one.

Comparison with relaxation measurements

We will now compare the calculated conformational energy barriers, ΔH^*, with activation energies, E_a, obtained from mechanical and dielectric relaxation measurements, keeping in mind that $E_a = \Delta H^* + RT$. Secondary transitions generally obey an Arrhenius equation:

$$\nu_m = \nu_0 \exp(-E_a/RT_m)$$

with $\nu_0 \sim 10^{13}$ Hz. The absolute temperature of the loss maximum at a frequency ν_m is T_m. When T_m is only available at a single frequency ν_m, E_a can be estimated from:

$$E_a = (0.25 - 0.0083 \ln \nu_m) T_m$$

A more accurate way to obtain E_a is the determination of the slope of the Arrhenius plot of log ν_m *versus* T_m^{-1} over a broad frequency range[9]:

$$\ln(\nu_1/\nu_2) = (E_a/R)(T_2^{-1} - T_1^{-1})$$

Figure 8 gives the Arrhenius plots of the δ relaxations of the polymers investigated. Part of this figure has been taken from Figure 6 of reference 1. However, the slope of the line of that figure does not correspond with the given E_a of 2.1 kcal mol^{-1} (8.8 kJ mol^{-1}); it should be 1.6 kcal mol^{-1} (6.7 kJ mol^{-1}). The points for PIPMA have been estimated from Figure 14 of reference 2, by subtracting the background. The data obtained from *Figure 8* are given in *Table 2*.

It is seen that the values obtained from molecular mechanics calculations, E_{MM}, compare well with the experimental values, E_a. We conclude that a rotation over the lower barriers is the cause of the mechanical loss process. The kinetic considerations presented above

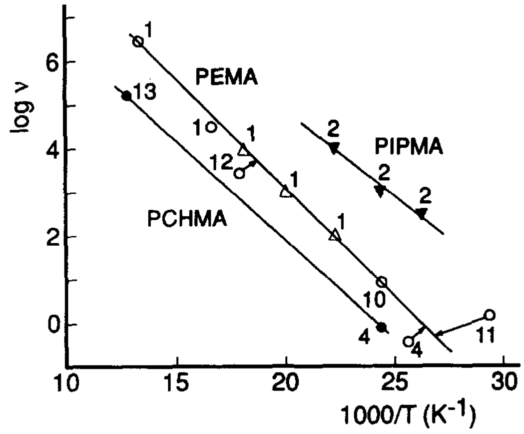

Figure 8 Arrhenius plots of the δ relaxations of PEMA, PIPMA and PCHMA (○, ●, mechanical loss peaks; △, ▼, dielectric loss peaks; the numbers refer to references)

Table 2 Experimental activation energies, E_a, of low temperature relaxations of poly(alkyl methacrylates) compared with the energies, E_{MM}, obtained from the potential energy curves ($E_{MM} = \Delta H^* + RT$)

Polymer	$E_a{}^a$	$E_a{}^b$	$E_{MM}{}^c$
PEMA	9.6	9.6	6.2
PIPMA	≈7.7	≈7.5	7.3
PCHMA	8.8	10.3	7.3

[a] From frequency dependence
[b] From T_m
[c] From the enthalpies at 50 K (see *Table 1*)

show that a rotation with passage over the higher barrier(s) cannot be the molecular mechanism.

It should be noted that the present calculations neglect intermolecular interactions. Struik[14] has shown that losses cannot occur without intermolecular interactions. However, the calculation of the intermolecular contribution to secondary loss processes in glassy polymers is an unsolved problem.

CONCLUSIONS

The molecular mechanics calculations strongly support the idea that the molecular mechanism of the δ relaxation is a limited rotation around the O–alkyl bond, passing only the lower transition state(s). The rigid model previously applied gives far too high conformational energy values for the high transition states.

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