

# A molecular mechanics investigation into the $\gamma$ -relaxation of poly(propyl methacrylate)

J. Heijboer

Plastics and Rubber Research Institute TNO, Schoemakerstraat 97,  
2628 VK Delft, The Netherlands

and J. M. A. Baas, B. van de Graaf and M. A. Hoefnagel

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136,  
2628 BL Delft, The Netherlands

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Molecular mechanics calculations are reported on barriers to rotation in model compounds for poly(propyl methacrylate). The results present strong evidence that the so-called  $\gamma$ -maximum in the mechanical loss measurements must be attributed to hindered rotation around the  $\text{OCH}_2\text{-CH}_2$  bond of the propyl group.

(Keywords: molecular mechanics; poly(propyl methacrylate); mechanical loss;  $\gamma$ -relaxation; conformational analysis; side group motions; barriers to rotation)

## INTRODUCTION

In a recent paper<sup>1</sup> the molecular mechanisms of the low-temperature relaxations of poly(ethyl methacrylate), poly(isopropyl methacrylate) and poly(cyclohexyl methacrylate) have been discussed on the basis of molecular mechanics calculations. For these relaxations only the rotation around the oxygen-alkyl bond had to be considered as the molecular mechanism. For poly(propyl methacrylate) (PPMA), besides this rotation, the rotation around the  $\text{OCH}_2\text{-CH}_2$  bond also has to be examined.

PPMA has a mechanical loss peak at about 90 K, 1 Hz. This so-called  $\gamma$ -transition was first observed by Hoff *et al.*<sup>2</sup> in 1955. Pertinent data can also be found in references 3 to 7. Figure 1 shows the shear modulus  $G$  and damping  $\tan \delta$  obtained from measurements at the Centre d'Etudes Nucléaires, Grenoble<sup>7</sup>. Waterman *et al.*<sup>6</sup> calculated from measurements extending over five decades of frequency an activation energy of  $22 \text{ kJ mol}^{-1}$  for this  $\gamma$ -relaxation. The  $\gamma$ -loss peak is also found in the poly(*n*-alkyl methacrylates) containing a longer alkyl group (butyl, pentyl, hexyl); these peaks are broader and lie at a somewhat higher temperature<sup>7</sup>. Illers<sup>8</sup> found a similar loss peak for poly(propyl acrylate) lying at about the same temperature.

## EXPERIMENTAL

The molecular mechanics calculations were performed as described in a previous paper<sup>1</sup>. They were carried out on two model compounds (Figures 2 and 3). As a one-unit model compound the propyl ester of trimethylacetic acid was used to study the behaviour of the propyl group without interference with the main chain. For this compound a contour map of the conformational energy at 298 K was constructed with the rotation angles around the  $\text{O-C}_\alpha$  bond ( $\theta_1$ ) and the  $\text{C}_\alpha\text{-C}_\beta$  bond ( $\theta_2$ ) as coordinates. To this end the conformational manifold of

the ester group was explored by stepwise constraints on  $\theta_1$  and  $\theta_2$  using the Lagrange multiplier method<sup>9</sup>. The minima, transition states and maxima in this map were calculated without constraints. All stationary points showed six zero eigenvalues of the final force constants matrix; the transition states showed also one and the maxima two negative eigenvalues. The calculations give the enthalpies  $H$  at 298 K; the conformational energies  $\Delta H$  were obtained by subtracting the enthalpy of the global minimum.

As in the previous investigation<sup>1</sup>, the polymer was also approached by a three-unit model: a main chain of seven carbon atoms with side chains placed in the syndiotactic configuration on positions two, four and six, and the three methacrylate units terminated by a hydrogen on one side and a methyl group on the other side (Figure 3). The main chain had an all-*anti* (*trans*) form and only the middle unit carried a propyl group; methyl esters were taken for the outer units. Only the minima, transition states and maxima were calculated. They were obtained starting from the corresponding conformations of the one-unit model compound.

Since the loss peak is located near 90 K, calculations were also made of the enthalpies at 98 K from  $H(98) = H(298) - HC(298) + HC(98)$ , in which  $HC$  is the heat content. This was given by the program at a series of temperatures, of which 98 K is the nearest to 90 K.

## RESULTS AND DISCUSSION

Figure 4 shows the contour map of the conformational energy of the one-unit model compound at 298 K as a function of the rotation angles  $\theta_1$  and  $\theta_2$ . The region around  $(0^\circ, 0^\circ)$  is inaccessible because of severe steric hindrance between the carbonyl oxygen and the terminal methyl of the propyl group. The contour map shows nine minima, indicated by capital letters. E ( $180^\circ, 180^\circ$ ) is a

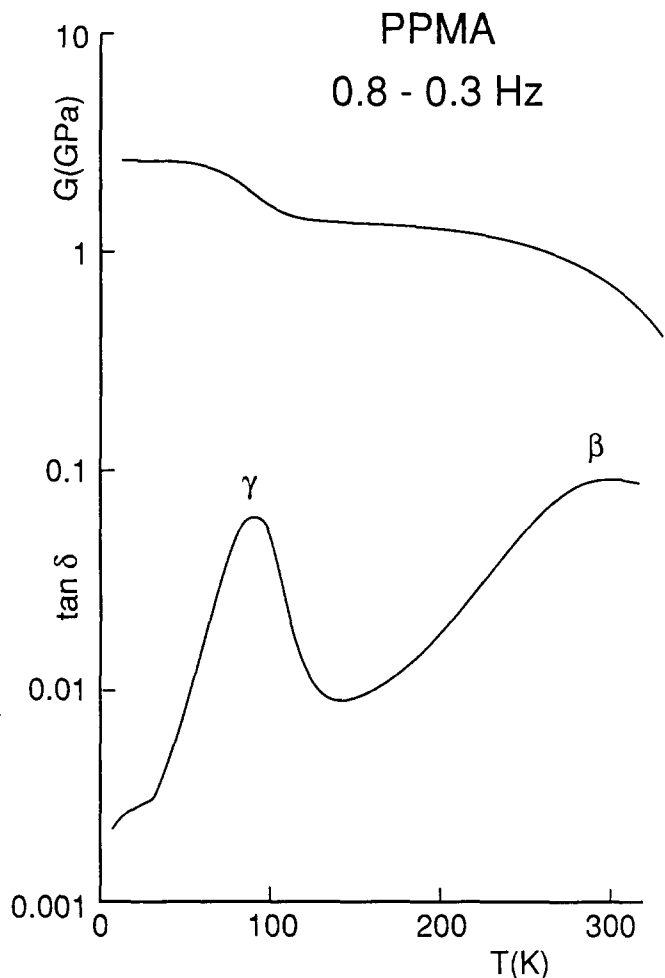


Figure 1 Shear modulus  $G$  and damping  $\tan \delta$  at  $\approx 1$  Hz as a function of temperature for PPMA

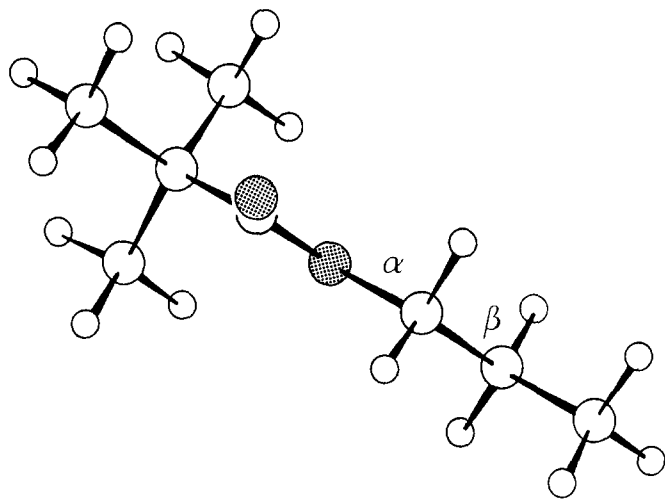


Figure 2 Ball-and-stick representation of the one-unit model compound of PPMA, minimum E ( $\alpha$  and  $\beta$  label carbon atoms of the ester group)

centre of symmetry; A and J, B and H, C and G, and D and F are mirror images.

Table 1 lists the coordinates and the conformational energies  $\Delta H$  at 298 K of the minima, transition states and maxima in two quadrants. It contains also the locations of the corresponding conformations calculated for the three-unit model compound; the global minimum is

changed from E to H. The difference between the coordinates of the one-unit and the three-unit model compounds is most pronounced for A and G; the difference for the transition states is in general not important ( $6^\circ$  or less). The former difference is caused by the interaction between the terminal methyl group of the ester side chain and the methyl group attached directly to the main chain in the case of the three-unit model compound.

In the discussion of the kinetics, the conformational energies of the three-unit model compound at 98 K are used; these are also given in Table 1. The conformational energies increase with decreasing temperature except for E.

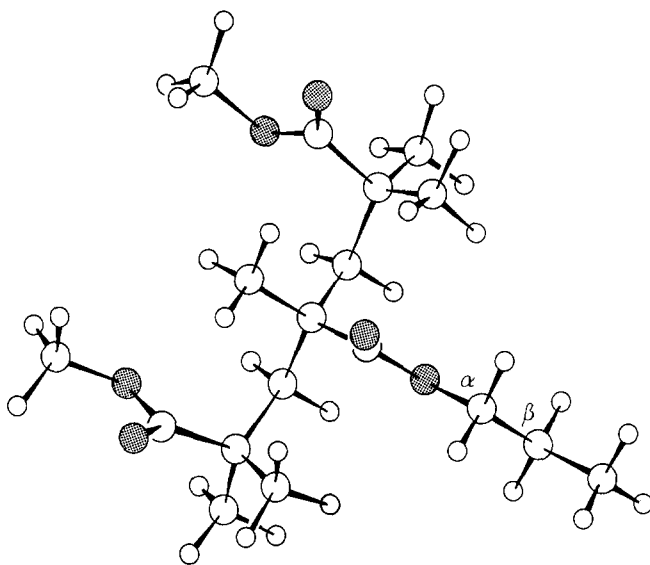


Figure 3 Ball-and-stick representation of the three-unit model compound of PPMA, minimum E ( $\alpha$  and  $\beta$  label carbon atoms of the ester group)

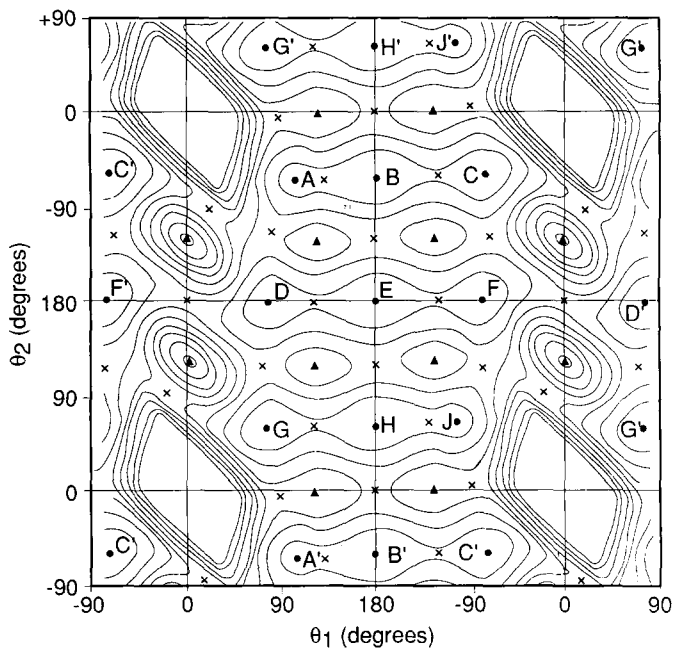


Figure 4 Contour map of the conformational energy  $\Delta H$  of the propyl ester of trimethylacetic acid at 298 K as a function of the rotation angles around the  $O-C_\alpha$  bond ( $\theta_1$ ) and the  $C_\alpha-C_\beta$  bond ( $\theta_2$ ). Contour lines, from 5 to 40  $\text{kJ mol}^{-1}$ , are spaced 5  $\text{kJ mol}^{-1}$ ;  $\bullet$ , energy minimum;  $\times$ , transition state;  $\blacktriangle$ , energy maximum

**Table 1** Rotation angles  $\theta$  and conformational energies  $\Delta H$  of stationary points of the model compounds

Conformation <sup>a</sup>		One-unit model				Three-unit model			
		$\theta_1$ (°)	$\theta_2$	$\Delta H(298)$ (kJ mol <sup>-1</sup> )	$\Delta H(98)$	$\theta_1$ (°)	$\theta_2$	$\Delta H(298)$ (kJ mol <sup>-1</sup> )	$\Delta H(98)$
ts	C <sub>1h</sub>	0	180	12.8	14.7	0	180	13.8	15.5
D	min	78	177	0.9	1.1	80	178	2.4	2.4
ts		122	178	4.5	6.4	121	176	6.5	8.0
E	min	180	180	0.0 <sup>b</sup>	0.0 <sup>b</sup>	180	180	1.5	1.2
max		1	122	40.7	44.1	-2	123	41.7	44.8
ts		71	116	12.5	14.4	69	119	16.2	17.8
max		122	118	18.4	21.9	114	116	20.0	23.3
ts		-180	120	13.1	14.7	-176	122	14.1	15.5
ts		-20	94	22.0	24.0	-25	97	22.0	23.7
G	min	75	59	0.8	1.3	85	64	2.8	3.1
ts		121	61	4.8	6.7	124	57	5.7	7.4
H	min	180	62	0.2	0.4	-174	62	0.0 <sup>b</sup>	0.0 <sup>b</sup>
ts		87	-6	16.6	18.7	89	0	27.9	29.7
max		123	-2	20.0	23.6	102	-2	28.5	31.9
ts	C <sub>1h</sub>	180	0	14.4	16.0	180	0	14.7	16.2
ts		20	-94	22.0	24.0	25	-97	20.0	23.7
A	min	102	-65	2.9	3.5	98	-82	8.8	9.1
ts		126	-65	3.7	5.8	124	-76	12.5	14.0
B	min	-180	-62	0.2	0.4	174	-62	0.0	0.0
max		-1	-122	40.7	44.1	2	-123	41.7	44.8
ts		80	-115	13.2	15.1	82	-120	16.8	18.4
max		124	-123	18.0	21.5	113	-128	18.5	21.8
ts		180	-120	13.1	14.7	176	-122	14.1	15.5

<sup>a</sup>min = minimum, ts = transition state, max = maximum. The capital letters alongside the minima correspond to those given in Figure 4

<sup>b</sup>Global minimum

Based on a Boltzmann distribution of the groups over the nine minima and using a pre-exponential factor of  $10^{13}$  in all cases, the relative transition rates are calculated at 98 K from the Arrhenius activation energies  $E_a$ :

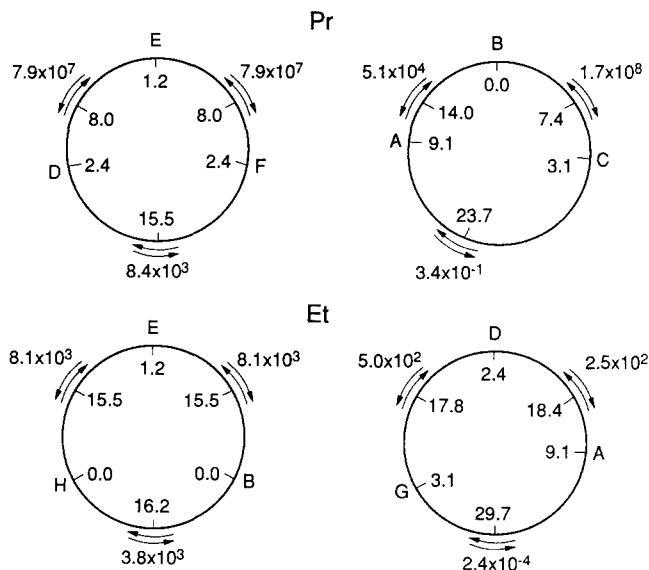
$$-(dx_i/dt)_j = x_i 10^{13} \exp(-(E_a)_{ij}/RT)$$

with<sup>10</sup>  $(E_a)_{ij} = \Delta H_{ij} + RT$ ;  $x_i$  is the fraction of the groups in minimum  $i$ . The rates are shown in Figure 5 for the rotation itineraries of the propyl group ( $\theta_1$ ) and the ethyl group ( $\theta_2$ ). For the propyl group the partial rotations from B to C and from E to D and F are the most important, for the ethyl group those from E to B and H. At 98 K the reorientation of the propyl group is more frequent by a factor of  $\approx 10^4$  than that of the ethyl group.

To gain an insight into the effect of mechanical stress on the relaxation, it has to be estimated to what extent the stress changes the distribution of the groups over the different potential wells. As a first approximation, the effect of a change  $\Delta E_j$  in the energy of a potential well on the fractions  $x_i$  of the groups in all the potential wells has been calculated. It follows from the Boltzmann distribution that

$$dx_i/dE_j = -x_i(\delta_{ij} - x_j)/RT$$

with  $\delta_{ij} = 1$  ( $i = j$ ) or  $\delta_{ij} = 0$  ( $i \neq j$ ). The effect relative to that in the deepest well  $dx_B/dE_B$  is given in Table 2. Only the changes in B, H and E are larger than 10%. F



**Figure 5** Schematic representation of the rotational itineraries of the propyl (Pr) and ethyl (Et) groups, with their relative transition rates and the conformational energies at 98 K

and D play a minor role. The changes in C and G are still smaller: less than 5% of those in B and H.

It is concluded that after disturbance of the potential wells the redistribution takes place mainly by rotation

**Table 2** Relative changes in the partition of the groups over the potential wells induced by changed energies of the wells<sup>a</sup>

Potential well	Energy change								
	$E_A$	$E_B$	$E_C$	$E_D$	$E_E$	$E_F$	$E_G$	$E_H$	$E_J$
A	–	–	–	–	–	–	–	–	–
B	–	–1.00	0.02	0.04	0.17	0.04	0.02	0.73	–
C	–	0.02	–0.04	–	–	–	–	0.02	–
D	–	0.04	–	–0.09	0.01	–	–	0.04	–
E	–	0.17	–	0.01	–0.36	0.01	–	0.17	–
F	–	0.04	–	–	0.01	–0.09	–	0.04	–
G	–	0.02	–	–	–	–	–0.04	0.02	–
H	–	0.73	0.02	0.04	0.17	0.04	0.02	–1.00	–
J	–	–	–	–	–	–	–	–	–

<sup>a</sup>Only values differing more than 0.005 from zero are given

of the ethyl groups between B and H. From the relative transition rates (*Figure 5*) it can be seen that this redistribution goes about half directly and half via E (transmission coefficient  $\kappa = 0.5$ ). From the total rate  $(3.8 + 8.1 \times 0.5) \times 10^3$ , the effective activation energy  $E_a$  is calculated to be  $16.4 \text{ kJ mol}^{-1}$ . The experimental  $E_a$  is  $22 \text{ kJ mol}^{-1}$ . Thus the calculated value compares well with the experimental one; the difference may be attributed to effects of intermolecular interactions.

The rotation of the ethyl group may be combined with a complete rotation of the propyl group starting from E. The mechanical manifestation of the partial rotation of the propyl group from D to F is expected to be hardly observable (*Table 2*). The calculated barrier for this motion is  $5.6 \text{ kJ mol}^{-1}$ ; the corresponding loss peak must be expected in the region of 40 K, 1 Hz. The small lump in the damping curve near 20 K (see *Figure 1*) might be related to this motion.

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