The side-group reorientations of polypropylene and poly(methyl acrylate) during conformational state transition

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Conformational contour maps of polypropylene and poly(methyl acrylate) have been examined by using full relaxation minimization under MM2 force field. Low energy paths along the potential surface were found for the *meso* and the *racemic* dyads. The side-group reorientation along the low energy pathways for both polymers was obtained. A 20° rotation was found for each methyl group of polypropylene. A large cooperative rotation, ~130°, is needed for the two ester groups of poly(methyl acrylate) to climb the energy barrier.

(Keywords: side-group reorientation; polypropylene; conformational energy)

INTRODUCTION

The conformational state transition of polymer chains relates to crystallization processes, migration of the chains in solution, fluctuation of the end-to-end distance of random coils and the relaxation and phase transitions of polymers. A description of the conformational state transition requires information about: (1) the number of stable conformational states for a specific σ bond; (2) the barriers between the states; (3) the mechanism of the conformational transition; (4) any cooperative behaviour during the transition. Flory and co-workers made excellent studies on the statistical mechanics of polymer chains and determined some of this information[1]. On the other hand, the side-groups must reorientate during conformational state transition, and it is important to understand this cooperative behaviour. In early studies, with a rigid model, this cooperative behaviour could not be described, therefore a different model needs to be used.

Molecular mechanics has developed from Lifson and Warshel[2] to Allinger[3], and from CFF and MM2 to MM3[4] and DREIDING[5]. Although it is an adiabatic mapping method, molecular mechanics is used extensively to obtain a good approximation of the conformational energy and the low energy path between conformational states. We think it can be used to study the reorientation of side-groups.

There have been some conformational transition studies of the zigzag chain[6,7] and the conformational transition of the helix has recently been receiving more attention. This is because both the phase transition behaviour between crystals[8] and the transition of the chiral helical chain from the left hand to the right hand[9] need to be understood. Polypropylene (PP) and poly(methyl acrylate) (PMA) have typical helical chain structures. In the present work, their conformational energies, low energy paths and the side-group reorientation have been investigated using molecular mechanics.

METHOD

A modified program was used with MM2 parameters. PP and PMA have been examined by full relaxation minimization in this study. Every internal coordinate, such as the bond lengths, the bond angles and the dihedral angles, is released to vary along the potential surface. Dyads of the polymers were adopted as models (*Figure 1*). A pair of bonds, ϕ_i and ϕ_{i+1}, along the backbone was set from 0° to 360° with an interval of 30° as generally scanning, and with an interval of 5° around the minimum. The low energy path was re-examined by adding more points along the path calculated in the first step. The orientations of the side-groups can then be calculated from the trajectory files along the low energy path. The orientations of the side-groups were determined by measuring the dihedral angles of the first bond of the side-group linking to the backbone, χ_i, χ_{i+1}. The 0° position of the side-group was defined as the ester group being perpendicular to the main chain.

The dihedral angle along the backbone atoms I, J, K, L is used to label the conformational states, for example 180° is the *trans* state represented by *t*. The other symbols are: *g* and *g'* representing 60° and $-60°$, respectively; g^*, 0–60°; g'^*, 300–360°; g'', 60–120°; g''', 240–300°; t^*, 120–180°; t'^*, 180–240°: this is shown in *Figure 2*.

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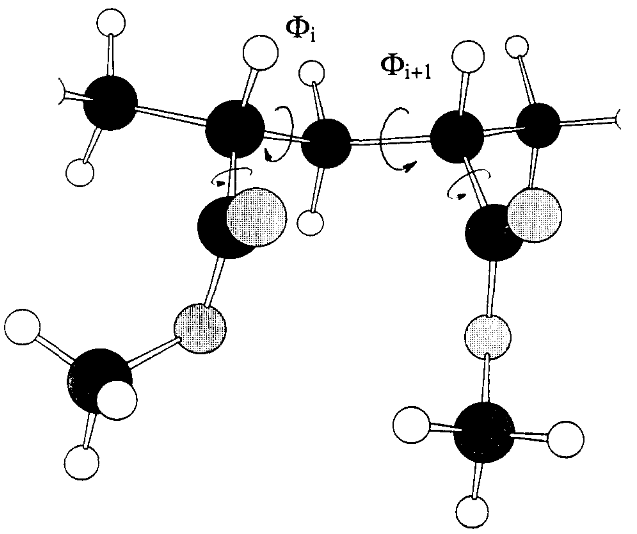

Figure 1 Dyad of poly(methyl acrylate) in certain torsional angles Φ_i, Φ_{i+1} along backbone and with side-group rotations in χ_i, χ_{i+1}

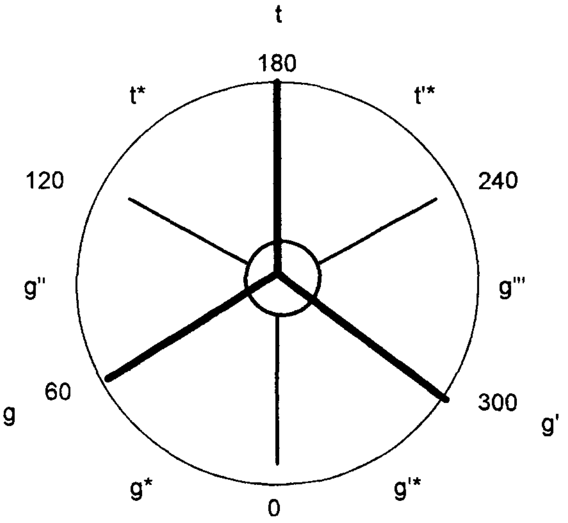

Figure 2 Representation of conformational states

RESULTS AND DISCUSSION

Conformational states

Table 1 and *Figure 3a* show the obtained data and contour map of the PP *meso* dyad; these are similar to the earlier results[10,11]. The major minima occur at 180, 60° (*tg*), 300, 180° (*g't*), 300, 90° (*g'g''*), 270, 60° (*g'''g*), 225, 165° (t'*t*), 195, 135° (t'*t*) for the *meso* dyad; the last four states have a higher energy difference of 1.97 kcal mol^{-1} compared to *tg* and *g't*, and are located between them. For the *racemic* dyad (*Figure 3b*), the major minima are 60, 60° (*gg*), 180, 180° (*tt*), 135, 60° (t*g), 180, 90° (*tg''*), 60, 135° (gt*), 90, 180° (*g''t*). The *gg* and the *tt* state are 1.92 kcal mol^{-1} more stable than the last four states (*Table 2*).

For PMA, more energy minima were found than in the earlier study[12]. As listed in *Table 3*, the conformational states of the *meso* dyad at 60, 180° (*gt*), 180, 300° (*tg'*), 160, 200° (t*t'*), 60, 270° (*gg'''*) and 90, 300° (*g''g'*) are very close to those found before, but new conformational states are located at 160, 60° (t*g), 300, 200° (g't'*), 80, 70° (*g''g''*), 290, 280° (*g'''g'''*), 60, 50° (gg*), 315, 300° (g'*g'), 280, 60° (*g'''g*) and 300, 80° (*g'g''*). These new minima cannot be recognized without the full relaxation minimization and the side-group rotation. The total 13 states have a pair symmetry to the axis through 0, 360° and 360, 0° (*Figure 4a*). Compared to the lowest energy, where the *gt* and *tg'* states are located, the t*t'* amounts to 1.30 kcal mol^{-1}, the *gg'''* and *g''g'* to 2.74 kcal mol^{-1}, the t*g and g't'* to 1.40 kcal mol^{-1}, the *g''g''* and the *g'''g'''* to 2.08 kcal mol^{-1}, the gg* and g'*g' to 2.31 kcal mol^{-1} and the *g'''g* and *g'g''* to 2.37 kcal mol^{-1}.

Table 1 Geometries and energies of conformational states for the *meso* dyad of polypropylene

Backbone torsions, Φ_i, Φ_{i+1} (deg)	Symbol	Conformational energy (kcal mol^{-1})	Side-group torsions, χ_i, χ_{i+1} (deg)
180, 60	*tg*	0.00	−62.6, −55.5
300, 180	*g't*	0.00	−55.4, −60.3
300, 90	*g'g''*	1.97	−57.8, −60.3
270, 60	*g'''g*	1.97	−60.3, −57.8
225, 165	t'*t*	1.97	−63.4, −56.0
195, 135	t'*t*	1.97	−55.9, −63.4

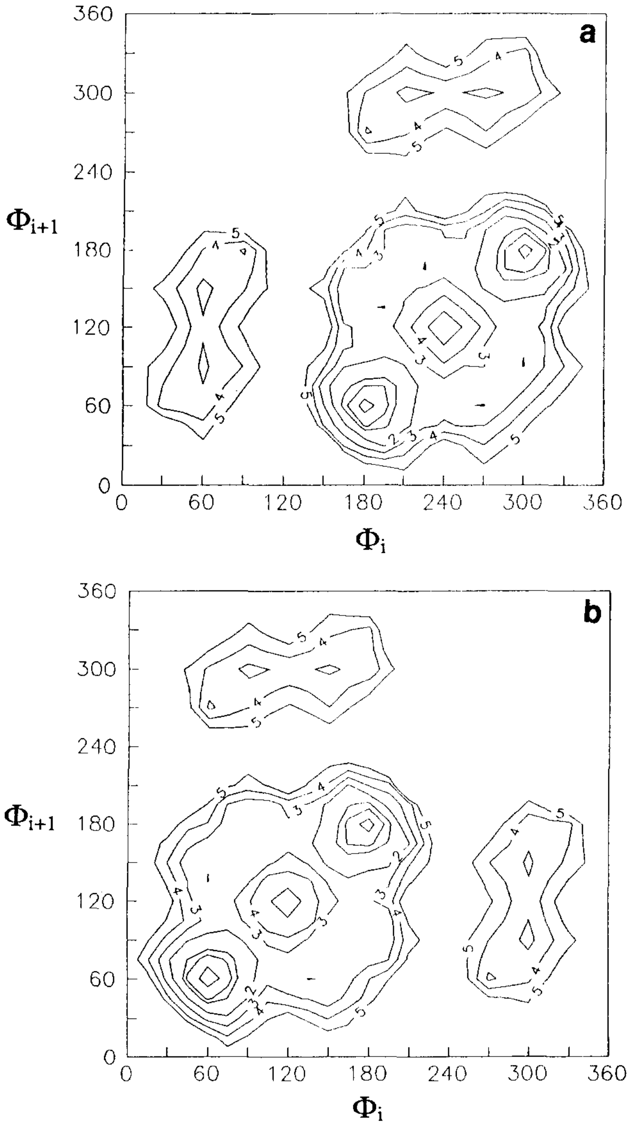

Figure 3 Potential energy contours for bond pair *i*, *i*+1 of polypropylene, expressed in 0–5 kcal mol^{-1}: (a) the *meso* dyad; (b) the *racemic* dyad

Table 2 Geometries and energies of conformational states for the *racemic* dyad of polypropylene

Backbone torsions, Φ_i, Φ_{i+1} (deg)	Symbol	Conformational energy (kcal mol^{-1})	Side-group torsions, χ_i, χ_{i+1} (deg)
60, 60	gg	0.01	−60.5, −60.4
180, 180	tt	0.00	−56.1, −55.9
135, 60	t^*g	1.92	−63.4, −59.9
180, 90	tg''	1.92	−52.7, −55.7
60, 135	gt^*	1.92	−60.3, −63.5
90, 180	$g''t$	1.92	−57.8, −52.6

Table 3 Geometries and energies of conformational states for the *meso* dyad of poly(methyl acrylate)

Backbone torsions, Φ_i, Φ_{i+1} (deg)	Symbol	Conformational energy (kcal mol^{-1})	Side-group torsions, χ_i, χ_{i+1} (deg)
60, 180	gt	0.00	−46, −38
180, 300	tg'	0.00	4, −57
160, 200	$t^*t'^*$	1.30	−34, −38
160, 60	t^*g	1.40	29, −60
300, 200	$g't'^*$	1.40	−60, 29
80, 70	$g''g''$	2.08	−41, 55
290, 280	$g'''g'''$	2.08	55, −41
60, 270	gg'''	2.74	−45, −45
90, 300	$g''g'$	2.74	−45, −45
60, 50	gg^*	2.31	−50, −78
315, 300	g'^*g'	2.31	−78, −50
280, 60	$g'''g$	2.37	−36, −94
300, 80	$g'g''$	2.37	−94, −36

Although the truncated Lennard–Jones potential was not used in the present study, the calculated potential energies for the first five states are almost the same as in the earlier study[12]. Surprisingly, for the *racemic* dyad of PMA the lowest energy states were found at 290, 170° ($g'''t^*$) and 170, 290° (t^*g''') (*Table 4*), even lower than the tt state at 180, 180° by 0.18 kcal mol^{-1}. The energy of the gg state amounts to 0.67 kcal mol^{-1}. For the $t''g$ and the gt'' state, the conformational energy increases to 1.62 kcal mol^{-1}. The contour map of the *racemic* dyad is shown in *Figure 4b*.

The lowest energy states found in the present study draw support from the side-group rotation. For the tt state, the carbonyl groups have just 2–3° departure from the initial geometry, where the carbonyl group is perpendicular to the backbone of the polymer chain. In the $g'''t^*$ and the t^*g''' state, the two carbonyls have undergone larger turns: one turns 16° and the other −44°. This rotation changes the dipole moment within the molecule and makes a tremendous difference in the electrostatic energy term from the rigid model, where the torsion angle of the carbonyl is fixed. As mentioned above, eight new conformational states were found for the *meso* dyad and two new states for the *racemic* dyad. The existence of the new states may perturb the statistical properties of the chain dimensions to a certain extent. This will be discussed in a separate publication.

Low energy paths

The low energy paths between the conformational states have been obtained in the present study. For the *meso* dyad of PP, the conformational transition (*Figure 5a*) goes through: $tg(180, 60°) \rightarrow g'''g(270, 60°) \rightarrow g'g''(300, 90°) \rightarrow g't(300, 180°)$ or $tg(180, 60°) \rightarrow t'^*t^*(195, 135°) \rightarrow t'^*t^*(225, 165°) \rightarrow g't(300, 180°)$. The barrier of the first step and the final step is 2.65 and 0.7 kcal mol^{-1}, respectively. For the second step, the barrier is 0.5 kcal mol^{-1}, which is almost 2 kcal mol^{-1} lower than

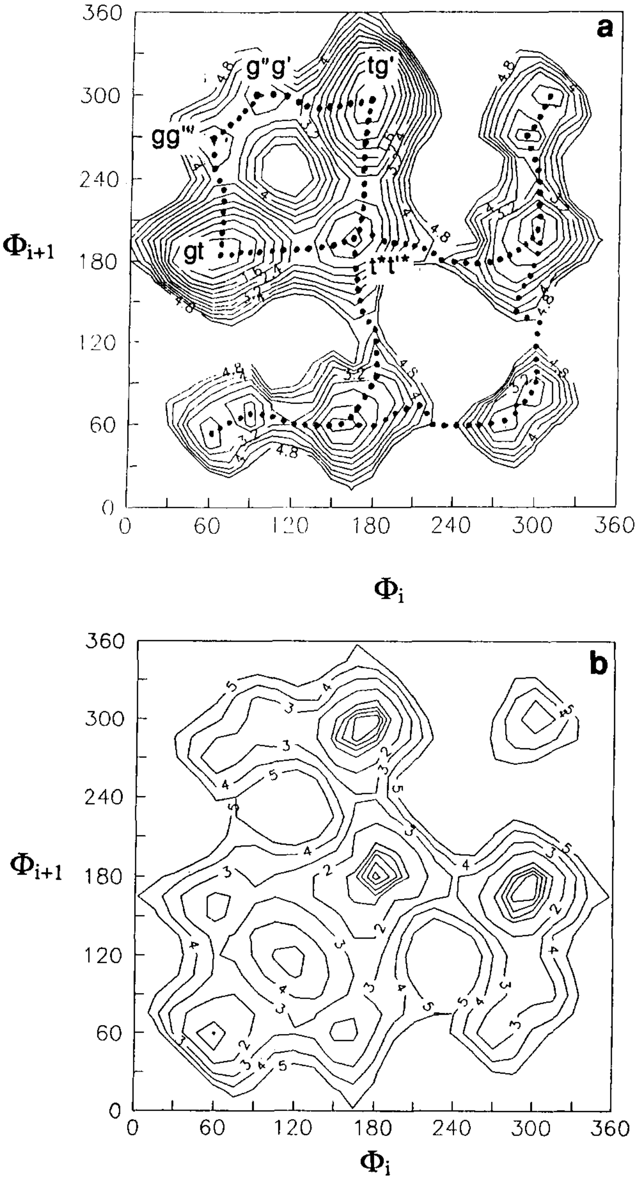

Figure 4 Conformational energy contours for bond pair i, $i+1$ of poly(methyl acrylate) in 0–5 kcal mol^{-1}: with low energy paths for (a) the *meso* dyad; (b) the *racemic* dyad

Table 4 Geometries and energies of conformational states for the *racemic* dyad of poly(methyl acrylate)

Backbone torsions, Φ_i, Φ_{i+1} (deg)	Symbol	Conformational energy (kcal mol^{-1})	Side-group torsions, χ_i, χ_{i+1} (deg)
60, 60	gg	0.67	47, −50
180, 180	tt	0.18	2.5, −3
160, 60	t^*g	1.62	51, 36
60, 160	gt^*	1.62	36, 51
290, 170	$g'''t^*$	0.00	16, −44
170, 290	t^*g'''	0.00	−44, 16

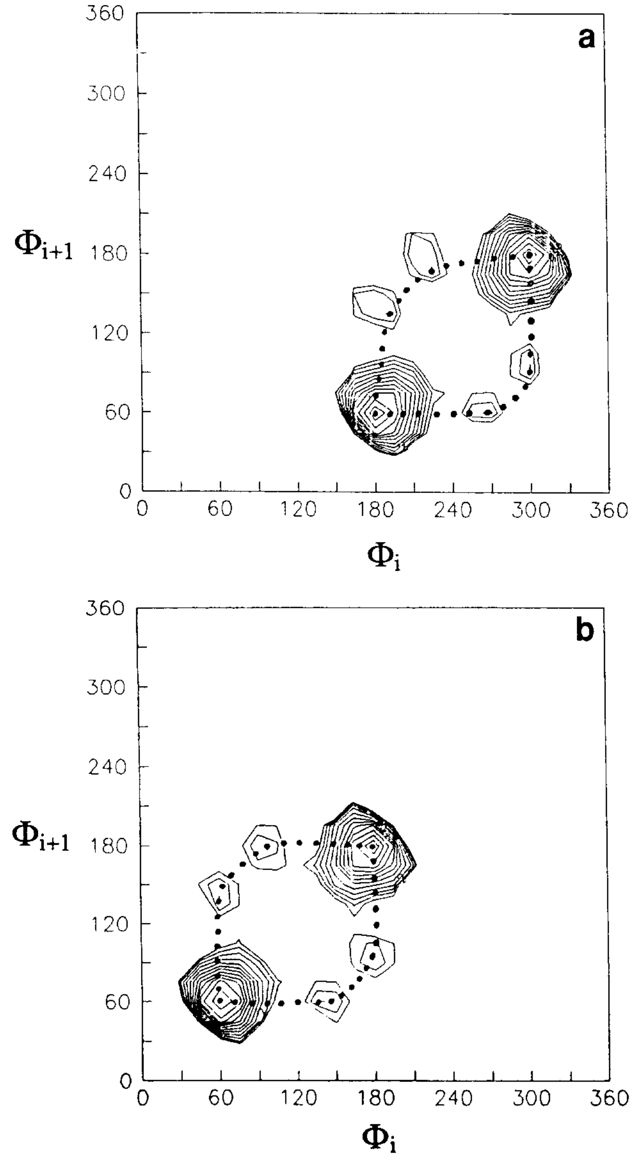

Figure 5 Low energy path along the potential energy contours for bond pair *i*, *i*+1 of polypropylene, expressed in 0–2.4 kcal mol^{-1} with 0.2 kcal mol^{-1} intervals: (a) the *meso* dyad; (b) the *racemic* dyad

that in the earlier study[11]. The calculated low energy path of the *racemic* dyad is along $gg(60, 60^\circ) \rightarrow t^*g(135, 60^\circ) \rightarrow tg''(180, 90^\circ) \rightarrow tt(180, 180^\circ)$ or $gg(60, 60^\circ) \rightarrow gt^*(60, 135^\circ) \rightarrow g''t(90, 180^\circ) \rightarrow tt(180, 180^\circ)$ as shown in *Figure 5b*.

In order to make this clearer, we define a new axis for plotting the low energy paths. Evidently, every point on the potential surface along the low energy path can be projected to the two-dimensional plane of Φ_i, Φ_{i+1}. We extend the projection that measures the conformational state displacement as the new axis in degrees. Thereby, the energy data are plotted along the axis as a function of the displacement. The energy curves of *Figures 6a* and *b* are obviously very similar. In the case of the *racemic* dyad, the barrier of the first peak has the same value as the final peak, which amounts to 2.48 kcal mol^{-1}. For the middle peak, the barrier is 0.56 kcal mol^{-1} which is also lower than Suter and Flory's result[11] by about 2 kcal mol^{-1}. The decrease is attributable to the full relaxation minimization.

In the *meso* dyad of PMA there are also two low energy paths available for conformational transition between the two lowest energy states. Path 1 is $gt(60, 180^\circ) \rightarrow t^*t'^*(160, 200^\circ) \rightarrow tg'(180, 300^\circ)$; path 2 is $gt(60, 180^\circ) \rightarrow gg'''(60, 270^\circ) \rightarrow g''g'(90, 300^\circ) \rightarrow tg'(180, 300^\circ)$ (*Figure 7a*). *Figure 7b* shows the low energy paths for the *racemic* dyad of PMA.

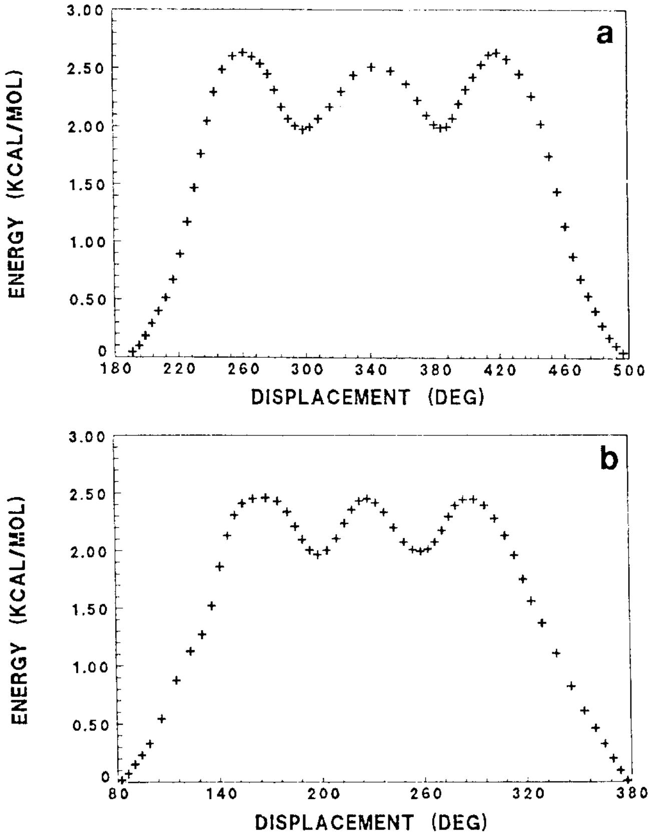

Figure 6 Extended low energy paths for polypropylene: (a) the *meso* dyad; (b) the *racemic* dyad

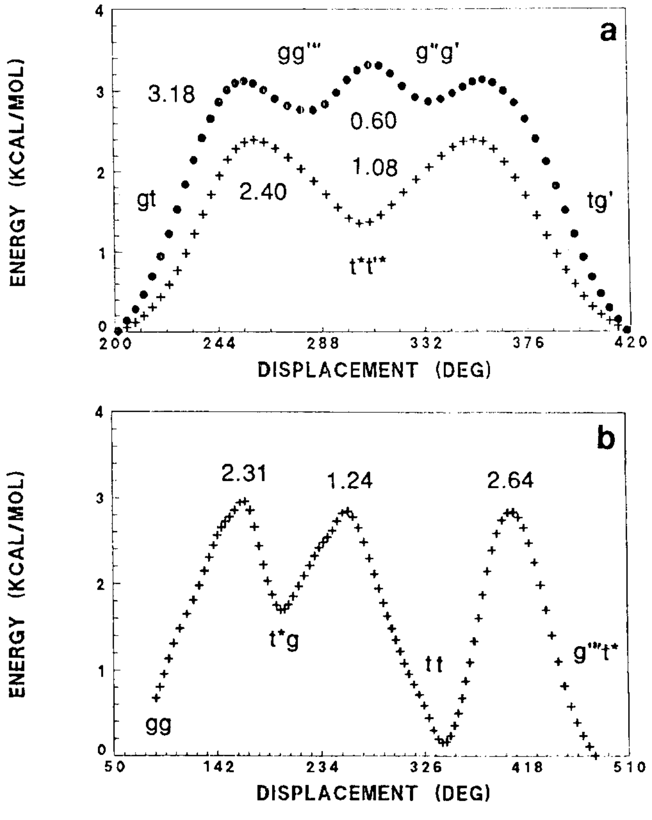

Figure 7 Extended low energy paths for poly(methyl acrylate): (a) the *meso* dyad; (b) the *racemic* dyad. +, Path 1; ●, path 2

Side-group reorientation

The side-group reorientation during the conformational state transition has been examined. χ_i, one of the torsion angles of the side-group, ranged from -52 to -72° and χ_{i+1} from -48 to -72° for the *meso* dyad of PP. In the case of the *racemic* dyad, χ_i, χ_{i+1} are all in the range from -50 to -70°. The plots of χ_i and χ_{i+1} as a function of displacement along the low energy path are shown in *Figure 8*.

The torsion angles of the side-groups of PMA underwent remarkable turns, from -80 to 50°, to pass the low energy pathway. This change amounts to 130° and is shown, reduced by a factor of four, in *Figure 9a* for the *meso* dyad. Obviously, the two side-groups made a very cooperative rotation during the conformational state transition. When the conformer reaches the top of the barrier in *Figure 9a*, the two torsional angles have a maximum difference. Thus the two carbonyls point in different directions by about 130°. For the *racemic* dyad (*Figure 9b*), the two side-groups have the same amount of change, but not such regular and symmetric traces of reorientation.

In the present study, we found several new conformational states for PMA. In the conformational transitions for both polymers we seldom found a single barrier but usually encountered multiple barriers along the low energy path. In addition, when a conformer evolves through the pathway, side-group reorientation plays a very important role. In the case of a small side-group, such as methyl in PP, the dihedral angle of the side-group has a small amplitude rotation, 20° or so, as found here and by Suter and Flory[11]. In the case of a large side-group, such as methyl ester in PMA, the dihedral angle of the ester groups has a much larger rotation of 130°. The two carbonyls must coordinate their orientations in a cooperative motion to make the low energy pathway. During the transition, the difference between the two torsions of the carbonyls is 130°. The traces of the two torsions are symmetric for the *meso* dyad, but asymmetric for the *racemic* dyad.

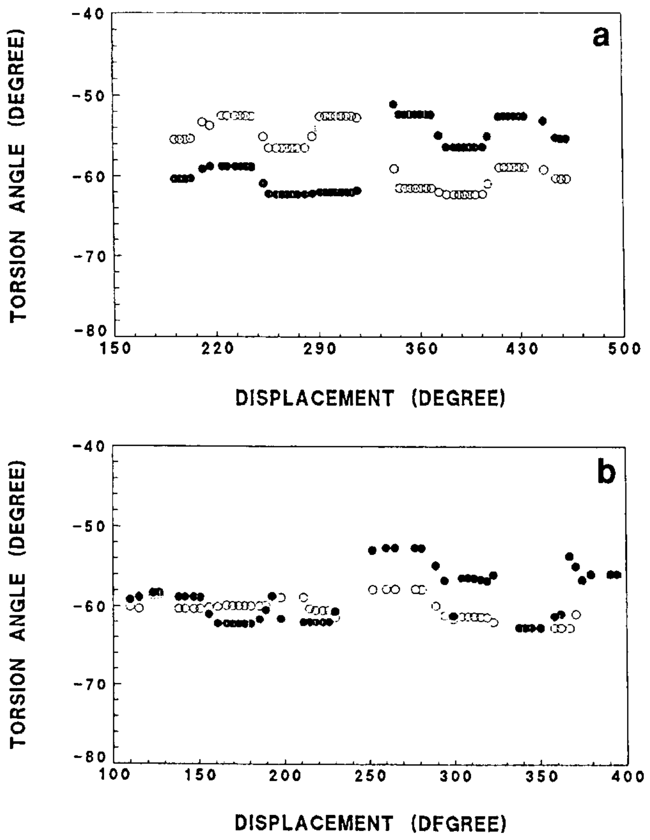

Figure 8 Reorientation of the side-groups of polypropylene: (a) the *meso* dyad along the low energy path from *tg* to *g't*; (b) the *racemic* dyad along the low energy path from *gg* to *tt*. ○, Torsion 1; ●, torsion 2

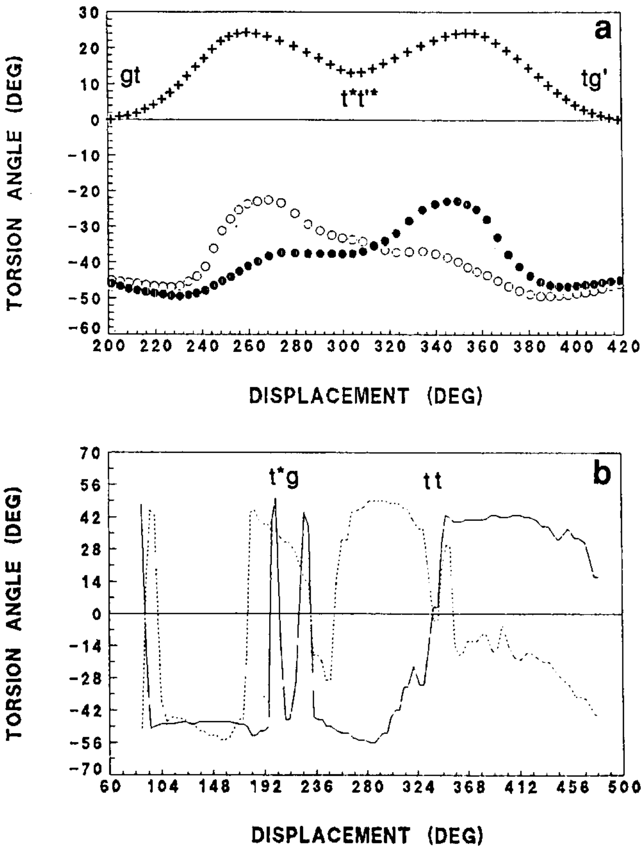

Figure 9 Reorientation of the side-groups of poly(methyl acrylate). (a) The *meso* dyad along the low energy path from *gt* to *tg'*; torsion angles (○, torsion 1 and ●, torsion 2) are reduced by a factor of four and energy (+) is increased by a factor of 10. (b) The *racemic* dyad along the low energy path from *gg* to *g'''t**: ——, torsion 1; ---, torsion 2

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