A molecular mechanics study on rotational motions of side groups in poly(methyl methacrylate)

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(Received 28 July 1986; accepted 13 October 1986)

Molecular mechanics has been applied to model compounds of syndiotactic poly(methyl methacrylate) (PMMA). The results for the energy minimum correspond with the conformation derived in literature from wide-angle X-ray scattering. Barriers to rotation calculated for the ester and the main-chain methyl groups correspond well with available experimental data. The barrier to rotation obtained for the alkoxy group is much higher than usually expected, but the two-well potential model rules this rotation out as the molecular process responsible for the β-maximum of PMMA. The barrier to rotation obtained for the alkoxycarbonyl group is much too low to correspond to the β-maximum. Constraint of the main-chain torsion angles brings the barrier near to the activation energy of this process. We conclude that about half the experimental barrier can be attributed to matrix effects.

(Keywords: molecular mechanics; poly(methyl methacrylate); conformation; β-maximum; side group motions; barriers to rotation; matrix effects)

INTRODUCTION

The detailed molecular processes responsible for secondary loss peaks in glassy amorphous polymers have in most cases not been identified unequivocally. Many arguments have been given that secondary loss peaks result from specific intramolecular motions (see e.g. refs. 1, 2 and 3). On the other hand it has also been argued that the so-called β-maximum, the first loss peak below the glass-transition, originates from intermolecular interactions and does not require a specific intramolecular motion[4,5]. Participation of the main chain in a secondary loss mechanism is of practical importance, because main-chain motions contribute to the impact strength of glassy polymers[6].

In the study of secondary loss peaks, systematic variation of the chemical structure and comparison of dielectric and mechanical losses have been used to obtain information about the group responsible for a given loss peak. In matching specific molecular motions to loss peaks, activation energies are determined from the temperature and frequency dependence of the mechanical and dielectric loss peaks, and the activation energies are compared with known rotational barriers in small molecules. For the β-maximum of ordinary poly(methyl methacrylate) (PMMA), which is observed mechanically at ~280 K and 1 Hz, and dielectrically at ~320 K and 60 Hz, the respective activation energies E_a are ~70 kJ mol^{-1} and ~85 kJ mol^{-1}. It is generally believed that this maximum is due to the hindered rotation of the $-COOCH_3$ group about the C–C bond linking it to the main chain[1]. The hindrance to this rotation mainly arises from interaction with the main-chain methyl groups of the adjacent units. Arguments in favour of this mechanism are:

(a) Dielectrically the β-maximum of PMMA is much more pronounced than the α-maximum, whereas mechanically it is the other way around. This constitutes strong evidence that the β-maximum is related to reorientation of the polar part (ester side groups) of the polymer. This argument is supported by measurements on poly(methyl α-chloroacrylate) (PMClA)[7].
(b) When the methyl groups on the main chain are replaced with hydrogen atoms, the β-maximum shifts to a lower temperature[8,9].
(c) The β-maximum is strongly depressed if intermolecular interactions are increased by replacement of the ester methyl group with a bulky and rigid group, e.g. cyclohexyl or tert-butyl. The effect on the β-maximum of replacement with a flexible alkyl group (ethyl, n-propyl, n-butyl) or by addition of a plasticizer is only small[1,2,10,11].

The supposition of Havriliak and Roman[12] that the β-maximum of PMMA is due to a main-chain motion and the α-maximum to a side-chain motion is in our opinion not correct. It conflicts with the effects of plasticizer and the relative heights of the mechanical and dielectric α- and β-maxima of PMMA and PMClA[2,7].

Although it is likely that the β-maximum is due to

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reorientation of the ester side group, the detailed mechanism of this reorientation is not completely understood; in particular, it is not clear whether, or to what extent, it involves the main chain[1]. Recently Boyd, Robertsson and Jansson[13] and, more explicitly, Robertsson[14], expect from mechanical measurements on PMMA a larger volume of the reorienting unit than corresponds to the rotation of the ester side group only.

High-resolution n.m.r. of solid polymers can in principle give direct information on the motion of carbon and hydrogen atoms, but results obtained by two groups of investigators[15,16] are conflicting and do not relate directly to the reorientation of the ester group.

Another approach is the application of molecular mechanics, energy calculations using empirical force fields. Using such methods Grigoreva and Gotlieb[17] studied the rotation of the $-COOCH_3$ side group in PMMA as early as 1968, but their approach was rather crude: they kept bond lengths and angles fixed, considered only Van der Waals interactions, and used no separate torsional barriers. In 1975 Shimizu, Yano and Wada[18], using a similar method but including a torsional barrier for the C–C bond, found barriers to rotational motions in alkyl side groups of poly(alkyl methacrylates) that correlate well with mechanical and dielectric data.

At present molecular mechanics is mostly used with complete relaxation of the geometry. The energy is calculated using an empirical force field with potential functions for bond stretching, angle bending and for Van der Waals, torsional and electrostatic interactions. It seemed promising to apply this kind of molecular mechanics to PMMA, in particular to investigate the molecular mechanism of its β-maximum. From molecular mechanics calculations on esters of 2-ethylbutanoic acid, Cowie and Ferguson[19] recently concluded that this transition could be assigned to the rotation around the carbonyl-oxygen bond. However, results for these model compounds do not relate to the β-maximum of PMMA, since the main-chain methyl groups on the adjacent units in PMMA are not present. This objection also holds for the model compound with the $-COOR$ group attached to a tertiary carbon atom[20].

For the present study we have chosen syndiotactic PMMA, because ordinary PMMA, which has been the subject of most mechanical and dielectric measurements, is nearly syndiotactic. According to Lovell and Windle[21] the average monomeric unit is situated in a series of about seven racemic diads. Moreover, the β-maximum of syndiotactic PMMA is very close to that of ordinary PMMA, whereas that of isotactic PMMA is much lower and occurs at a lower temperature[1].

Since the main-chain methyl groups are indispensable for the β-maximum of PMMA, calculations on poly(methyl acrylate) (PMA) have also been performed for purposes of comparison.

EXPERIMENTAL

Syndiotactic sequences of up to five monomer units were taken as model compounds for PMMA. The main chain was terminated by hydrogen at one end and by a methyl group at the other. For PMA a syndiotactic sequence of three units terminated in the same way was taken. In addition the ester methyl group of the middle unit was replaced with a tert-butyl group in the PMMA model of three units. A diagram of the model compounds of three units is shown in *Figure 1*.

The calculations were performed using DELPHI, the Delft Computer Program for Molecular Mechanics[22], and the MM2 empirical force field[23]. The conformations of minimum energy were found starting from the extended all-*anti* (all-*trans*) form of the main chain. These conformers were the starting points for the calculation of the barriers to rotation of the various side groups on the middle unit. To this end the respective torsion angles were driven stepwise with increments of 5° or 10°, using the Lagrange multiplier method[22], with complete relaxation of all other internal coordinates. In this way graphs were obtained of the steric energy vs. the constrained angle. The transition states were found from unconstrained optimization of geometries corresponding to the highest values of the steric energy.

At a later stage, some of the barriers to rotation were also calculated while the C_1–C_7 distance was kept constant, and also with constraints on the torsion angles of the main chain.

RESULTS AND DISCUSSION

Conformation of syndiotactic PMMA

Table 1 lists data on the minimum-energy conformation of model compounds comprising one to five monomeric units. Clearly, increasing the number of units beyond three makes little difference.

Interactions between the methyl and ester side groups of adjacent units cause a large increase of the bond angle at the secondary carbon atoms in the main chain, whereas the angle at the quaternary carbon atoms C_α is less than the tetrahedral value. The C–C bond length in the main chain is increased slightly. Torsion angles are defined in accordance with the IUPAC rules[24], which specify a positive sign for the right-handed screw. For the configuration shown in *Figure 1* the sequence of the torsion angles for three units is 173°, 173°, −173°, −173°, for five units −173°, −173°, 174°, 174°, −174°, −174°, 173°, 173°. As can be seen in *Figure 2*, these values imply that the adjacent methyl groups are nearer each other and the adjacent ester groups farther apart than in a perfect all-*anti* conformation.

A search for other energy minima near the all-*anti* conformation was made from two other starting points with three units: torsion angles in the main chain of −165°, −165°, 165°, 165° (twisting of the main chain in the opposite direction) and of 173°, 173°, 173°, 173° (helix). In both cases the minimum already described was obtained again. A different minimum was found starting from a conformation with the C=O bond in the middle unit *anti* to the C_α–CH_3 bond ($\theta_d = 180°$). This conformer, also of C_{1h} symmetry, has a steric energy of 154.5 kJ mol^{-1} (i.e. only 2.4 kJ mol^{-1} higher than the other minimum) and

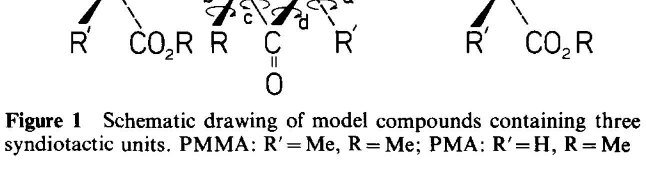

Figure 1 Schematic drawing of model compounds containing three syndiotactic units. PMMA: R′ = Me, R = Me; PMA: R′ = H, R = Me

Table 1 Data[a] on the minimum energy conformations[b] of model compounds of syndiotactic PMMA

No. of monomeric units	1	2	3	4	5
Point group	C_{1h}	C_2	C_{1h}	C_2	C_{1h}
Steric energy (kJ mol^{-1})	36.7	92.2	152.2	213.1	274.3
Increase of steric energy per unit (kJ mol^{-1})		55.5	60.0	60.9	61.2
Main-chain bond angles (°)[c]					
$C-C_\alpha-C$	110.3	108.6	107.1	106.9	106.6
$C_\alpha-C-C_\alpha$	–	121.2	122.5	123.8	124.0
Absolute value of main-chain torsion angles (°)[c]	–	173.3	173.5	173.7	173.7
C–C bond length, in the main chain (Å)[c]	1.541	1.551	1.561	1.563	1.565

[a] Energy minima are characterized by six zero eigenvalues of the final force constants matrix

[b] In all conformations the C=O and C_α–CH_3 bonds are eclipsed

[c] At the middle of the chain

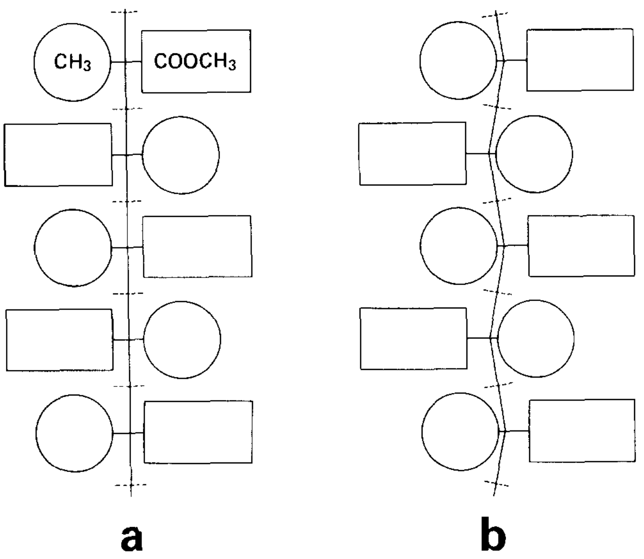

Figure 2 Schematic drawing of the relative positions of the main-chain methyl and ester groups in syndiotactic PMMA in the perfect all-*anti* (a) and the minimum energy (b) conformations

main-chain torsion angles of 174°, 174°, −174°, −174°. The calculation with five units gave main-chain torsion angles of −173°, −173°, 175°, 174°, −174°, −175°, 173°, 173° and an energy difference between the two minima of 1.4 kJ mol^{-1}.

Sundararajan and Flory[25] calculated the conformation of syndiotactic PMMA assuming fixed bond lengths and angles. They took $C-C_\alpha-C$ 110° and $C_\alpha-C-C_\alpha$ 122.0°. With θ_d fixed at 0°, the global energy minimum was obtained at about the 170°, 170°, −170°, −170° conformation (10°, 10°, 10°, 10° in their notation). By contrast, Tanaka and Ishida[26] found a minimum close to the all-*anti* conformation, which has an energy about 80 kJ mol^{-1} higher than their global minimum, which is close to an *anti–anti–gauche–gauche* conformation. From wide-angle X-ray scattering experiments, Lovell and Windle[27] conclude that syndiotactic PMMA has mainly conformations close to all-*anti*. Starting with main-chain bond angles of 110° and 128° and a C–C distance of 1.54 Å, their data fit best to conformations $+\phi$, $+\phi$, $-\phi$, $-\phi$ with ϕ between 170° and 175°. Recently, both Flory and Sundararajan published a refinement of their calculations. Vacatello and Flory[28] now vary the bond angles of the main chain, but still keep the bond lengths constant (1.53 Å). They find that the syndiotactic configuration prefers the all-*anti* conformation with small energy differences depending on the orientation of the ester groups ($\theta_d = 0$ or $\sim 180°$). They obtain main-chain bond angles of 106° and 123° or 124°, and torsion angles of 171°, 171°, −171°, −171°. Sundararajan[29] still keeps the angle $C-C_\alpha-C$ constant at 110° and obtains in the all-*anti* energy minimum a value for $C_\alpha-C-C_\alpha$ of 123.4° and torsion angles of 170°, 170°, −170°, −170°. Our results agree rather well with those of Flory, Sundararajan and Vacatello and those of Lovell and Windle.

The energy difference of the two minima at $\theta_d = 0°$ and 180° has been derived from dielectric[30], stress relaxation[31] and i.r.[32] measurements; the values obtained for ordinary PMMA were ca. 2.9, 3.3 and 2.7 kJ mol^{-1}, respectively. These data have to be compared with the calculated values of 2.4 kJ mol^{-1} (three units) and 1.4 kJ mol^{-1} (five units).

Barriers to rotation

Table 2 summarizes the barriers to rotation of the various side groups on the middle unit. The results for five units do not differ significantly from those for three.

Rotation of the main-chain methyl group (a). This results in a threefold potential barrier between sterically identical conformers. The two-well potential model (two-site model) predicts no mechanical loss maximum for conformers that do not differ in energy or occupied volume. Nevertheless, Williams and Eisenberg[33] find a minor mechanical loss maximum near 270 K at 13 MHz. They attribute it to rotational motion of the main-chain methyl group in syndiotactic sequences, and propose a tunnelling mechanism for this process at low temperatures. An alternative[34] in terms of an imperfect threefold potential barrier has recently been proposed. From the frequency dependence of the maximum near room temperature, Williams and Eisenberg obtained an activation energy E_a of 28 kJ mol^{-1}. From inelastic neutron scattering experiments, Higgins[35] derived a barrier of 29.1 kJ mol^{-1} to rotation of α-methyl in predominantly syndiotactic PMMA, and from n.m.r. measurements a barrier of 23.3 kJ mol^{-1} in pure syndiotactic PMMA. From n.m.r. experiments, Wada *et al.*[36] derived a value of 27 kJ mol^{-1} as the barrier to rotation of a methyl group attached to a quaternary carbon atom*. These values in our opinion agree satisfactorily with the value of 28 kJ mol^{-1} obtained from our molecular mechanics calculations.

The barrier to rotation of the ester methyl group or tert-butyl group (b). This also has threefold symmetry with sterically identical conformers. For this rotation we find a much lower barrier than for the rotation of the main-chain methyl group. This is in good qualitative agreement with n.m.r. results: Wada *et al.*[36] quote an activation energy of 10 kJ mol^{-1} for the rotation of the ester methyl groups, and it is well established that the rotation persists at much lower temperatures than that of the main-chain methyl groups[37,38]. A reliable quantitative comparison of the value from molecular mechanics with experimental data is not possible, because neutron scattering

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*The activation energy of 23 kJ mol^{-1} derived from the ultrasonic measurements given in *Figure 2* of the same paper is not reliable, because the pronounced maximum in that figure is probably due to an impurity; it is not observed in pure PMMA.

Table 2 Barriers[a] to rotation (kJ mol^{-1}) of the side groups in the middle unit of model compounds of syndiotactic PMMA and PMA

Rotation[b]	C–R′(a)	O–R(b)	OC–OR(c)	C–COOR(d)
R = R′ = Me				
1 unit	18.4	5.4	51.3	5.5
3 units	28.7	5.5	62.2	30.8
5 units	28.0	5.5	62.0	30.6
R′ = Me, R = tBu[b]				
3 units	30.1	4.5	113.3	29.5
R′ = H, R = Me				
3 units	–	5.3	50.5	8.9

[a] Obtained from unconstrained molecular mechanics calculations; transition states are characterized by six zero and one negative eigenvalue of the final force constants matrix

[c] Only in the middle, other ones Me

experiments have shown that the motion of the ester methyl group is of a non-Arrhenius type[39]. The apparent activation energy ranges from 7 kJ mol^{-1} above room temperature to 1 kJ mol^{-1} at 150 K. The information that can be obtained from mechanical measurements is even more vague. Mechanical losses attributed to motion of the ester methyl group in PMMA are very small, and occur at temperatures below 20 K[40–42]. As in the case of the main-chain methyl groups rotational tunnelling has been invoked to explain the measurements[42]. No relation between these mechanical measurements and our calculated potential barrier is apparent.

The rotation of the alkoxy group (c). This has the highest barrier. Some investigators[43,44] have failed to realize this. In ref. 44, it is assumed that barrier (c) is lower than barrier (d). This assumption is based on experimental data for esters, in which the –COOR group is not linked with a tertiary carbon atom, which are therefore unrepresentative of polymethacrylates. For this reason the suggestion that the absorption of methacrylates in the 110–170 K range is an alkoxy group relaxation is not justified.

Rotation (c) cannot be responsible for the β-maximum of PMMA, in spite of the fact that the calculated value of its barrier is not very far from the activation energy for this maximum. In the two-well potential model it does not even give rise to a loss process, because there is only one conformation of low energy (*Figure 3*). Moreover, the barriers calculated for the different structures do not agree qualitatively with the data of the β-maximum: the barrier of the tert-butyl substituted model should be equal to that of its methyl analogue, whereas it is calculated to be much higher; and the barrier of the acrylate should be much lower, whereas it is calculated to be only slightly lower.

The rotation of the alkoxycarbonyl group (d). This is of most interest to us, because it is generally held responsible for the β-maximum of PMMA. Our results for this rotation satisfy the two-well potential model: there are two conformers differing only about 2 kJ mol^{-1} in energy; the high-energy well is therefore sufficiently populated to give rise to a loss maximum. Moreover, in agreement with experimental data, the barrier calculated for this rotation changes only slightly when methyl is replaced with tert-butyl, and is much lower for the acrylate than for the methacrylate.

There is, however, a serious discrepancy between the calculated height of the barrier (about 30 kJ mol^{-1}) and the activation energy of the β-process of PMMA observed experimentally (about 75 kJ mol^{-1}). The reason might be that the model is not realistic, because it neglects matrix effects or intermolecular interactions. We have attempted to simulate intermolecular interaction by putting constraints on the model. During the rotation of the alkoxycarbonyl group, the calculated length of the main chain changes slightly: the distance C_1–C_7 which, at the potential minima, is 7.38 Å and 7.37 Å, passes a minimum of 7.19 Å. Keeping the distance C_1–C_7 at 7.38 Å leads only to a slight increase of the calculated barrier, viz. from 30.8 to 32.5 kJ mol^{-1} for the three unit model.

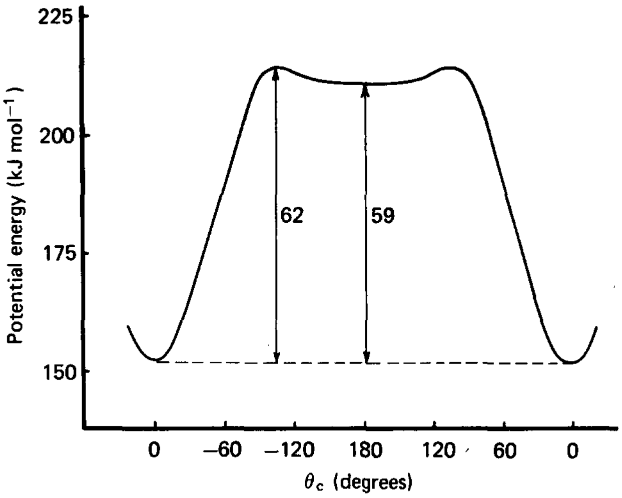

Figure 3 Potential energy profile for rotation of the middle –OMe group in a syndiotactic PMMA model of three units. Driven angle O=C–O–C (θ_c)

The considerable torsional deformation of the main chain during rotation (d) is, perhaps, of more importance (*Figure 4*). With complete relaxation, changes in the torsion angles of the main chain of up to 37° are calculated. These changes are not strongly affected with the constraint on the distance C_1–C_7 mentioned above.

Constraining the four main-chain torsion angles to the values of the global minimum raises the barrier to 69.2 kJ mol^{-1} in the three-unit model (*Figure 5*). The energy difference of the two minima remains 2.4 kJ mol^{-1}. The barrier calculated in this way differs little from 75 kJ mol^{-1}, the activation energy of the β-maximum of PMMA.

It is interesting to compare our results with the views of Mashimo *et al.*[45], who ascribe about half the activation energy of the β-maximum to friction with neighbouring molecules. They base their conclusion on the decrease of this activation energy on copolymerization of MMA with styrene or *p*-chlorostyrene; the decrease is explained by the screening of the MMA ester side groups by the phenyl and *p*-chlorophenyl groups, preventing the ester side groups from interacting with neighbouring molecules. However, they have not taken account of the fact that, in the glassy state, replacement of the methyl group on the main chain in adjacent monomeric units with hydrogen already decreases the activation energy of the β-maximum. In addition, their conclusion is incompatible with the finding that copolymerization of MMA with α-methylstyrene leaves the activation energy of the β-maximum constant[46].

Constraining the torsion angles in the main chain may not be the right way of accounting for matrix effects. It is nevertheless clear that matrix effects play an important

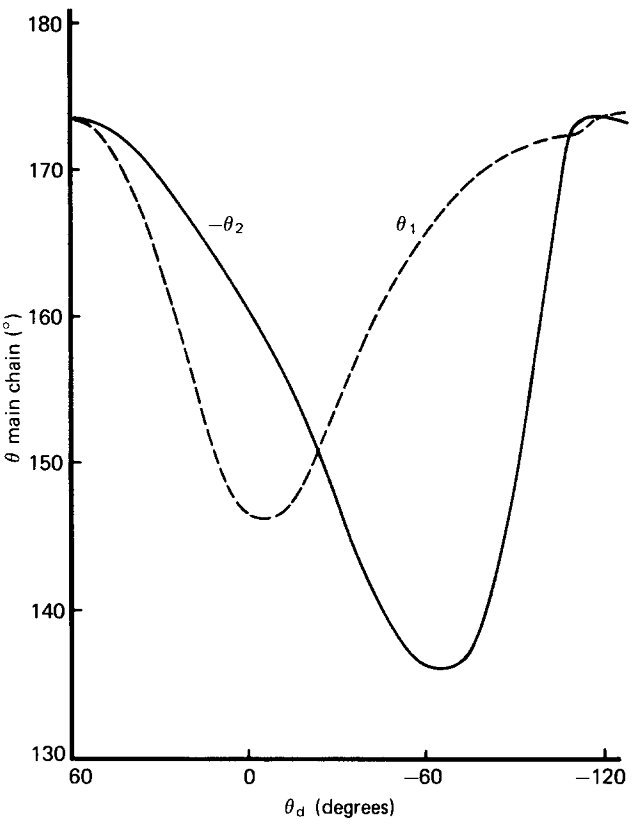

Figure 4 Cooperative motion of the main chain on rotation of the middle -COOMe group with complete relaxation in a syndiotactic PMMA model of three units. Torsion angles C_2-C_3-C_4-C_5 (θ_1) and C_3-C_4-C_5-C_6 (θ_2) as a function of the driven angle C_5-C_4-C-O (θ_d)

role in restraining torsional motion of the main chain. Our calculations show that they are responsible for about half the activation energy of the β-maximum.

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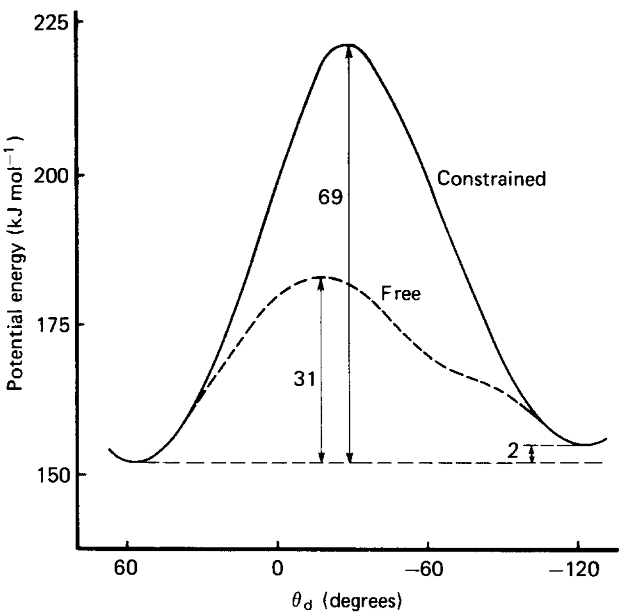

Figure 5 Potential energy profile for rotation of the middle -COOMe group in a syndiotactic PMMA model of three units. Free: complete relaxation. Constrained: torsion angles of the main chain kept constant. Driven torsion angle C_5-C_4-C-O (θ_d)

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