Possible origins of the β-relaxation in poly(methyl methacrylate) and related structures from molecular mechanics calculations*

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Molecular mechanics calculations using the Allinger 'MM2' force field have been carried out on several selected model compounds in an attempt to gain some insight into possible origins of the β-relaxation processes which occur in poly(alkyl methacrylate)s, poly(alkyl acrylate)s and poly(alkyl itaconate)s. Restrictions on the movement of the model compound(s) (or parts of) in response to the movement of the rotating ester side group were introduced in order to simulate some of the conditions which would be present in the glassy state. It was found that, in all cases, the molecular mechanism of oxycarbonyl side group rotation combined with reasonable constraints on movements of the neighbouring side groups gave theoretical activation energy requirements which were in good agreement with those determined from experiment.

(Keywords: molecular mechanics; poly(methyl methacrylate); relaxation)

INTRODUCTION

The identification of relaxation processes in the glassy state of amorphous polymers, which are mechanically or dielectrically active, is of considerable interest as it has been suggested that these may have some bearing on the 'toughness' of a polymer. While location of these sub-glass transition phenomena is relatively straightforward, elucidation of the actual molecular origin may not be quite so simple.

In the alkyl methacrylate polymers, a number of workers have identified a broad mechanically active damping peak in the vicinity of 280 K. This lies below the glass transition temperature, T_g, of the methyl, ethyl, propyl and butyl derivatives and the temperature of the peak maximum remains unchanged with increasing side chain length whereas T_g is decreased[1]. This transition has been called the β-relaxation and is generally thought to be caused by the onset of oxycarbonyl group rotation in the side chain. The activation energy $\Delta H^{\ddagger}$ for the process has been determined and while the values vary somewhat the most commonly quoted is about 75 kJ mol^{-1}.

The β-relaxation has also been studied using dielectric loss measurements and a very large dispersion has been reported in atactic samples[2] around 280 K while at T_g the dispersion is very small. This implies that the polar parts of the alkyl methacrylate polymers are active below T_g and that the whole oxycarbonyl unit must be in motion. The activation energy calculated from dielectric measurements has been determined to lie between 80 and 95 kJ mol^{-1}, which is slightly higher than the mechanically measured values but as the peak is normally quite broad it can be expected that $\Delta H^{\ddagger}$ will be in the range 70–95 kJ mol^{-1}.

The influence of neighbouring alpha-methyl side groups on the β-relaxation in PMMA has been commented upon by Shindo[3], and when one considers the effect of replacing the alpha-methyl side groups with hydrogens, as in poly(methyl acrylate), one finds that this polymer exhibits a broad mechanical damping peak around 150 K[3], which is some 130 K lower than the β-relaxation in PMMA. The corresponding relaxation process has an activation energy requirement of about 36–40 kJ mol^{-1}.

Studies[4] on the structurally related poly(alkyl itaconate)s have revealed a damping shoulder in the mechanical spectra for the dimethyl, diethyl and dipropyl derivatives, again centred on 280 K. Although the intensity of this damping peak is not quite so pronounced in the itaconate series, it is believed that the molecular origins of this β-peak are the same in all three of the polymer series discussed above. It was decided to try to obtain more substantial evidence for considering that the relaxation of the oxycarbonyl unit was responsible for this feature. One way of approaching the problem is to use the molecular mechanics technique to calculate the theoretical energy requirements of a bond rotation in a model compound which simulates part of the polymer chain. This technique has already been used by us with reasonable success[5] and is extended here to study the β-relaxation.

MOLECULAR MECHANICS METHOD

Strain energy calculations were carried out on a VAX 11/780 computer using the force field method developed by Allinger and coworkers[6]. The program (MM2) can handle up to a maximum of 100 atoms but for realistic computational times to be achieved model compounds with between 40 to 50 atoms were used in the study.

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Application to polymer structures requires the selection of a realistic small molecule analogue as a model compound and the trimer units for each polymer were chosen. The first step in the calculations is to establish an initial geometry from a set of suitable atomic coordinates generated from the appropriate bond lengths and angles, and also by inspection of molecular models. In addition, the program requires information on the connectivity in the model compound and each atom type must be identified by suitable parameters. From this information the program can be used to minimize the strain energy of this initial geometry by making spatial readjustments of all the atoms. This provides a new set of atomic coordinates for the model. With this strain minimized geometry as a starting point a bond is selected for rotation and is driven through 360° in 10° intervals. At each of these intervals the strain energy is again minimized until finally a potential energy curve for the complete rotation is produced. Only one bond rotation and group of attached atoms may be driven at a time but the method allows all the other atoms to readjust their spatial positions, as the geometry is minimized, either by torsional oscillation or by small translational motions.

In some of our previous attempts[5] to simulate low temperature relaxation processes in polymers, we used a simplified rigid force field model which did not allow the rest of the molecule to adjust itself while the side group under investigation was rotated about a given bond, and this gave unacceptably large values for the activation energy for oxycarbonyl rotations in some of the simple model compounds which were previously studied. It is also possible to jump to the other extreme, and use a simulation which is much too flexible, i.e. one which imposes no constraints whatsoever on the possible movements of the rest of the molecule while a side group rotation is being performed, and the value of the energy barrier which is obtained will also be unrealistic and probably too low. The best compromise for this situation is to use a computer simulation which can apply constraints on the motions of any part (or parts) of the target molecule being studied, and such a facility exists in the Allinger MM2 program. Thus one can now begin to take account of 'matrix effects' in a more controllable manner.

In practice, these constraints are applied by progressively 'locking' in space the other atoms in the molecule which would normally move in response to the rotation of the given side group about a specified bond. Hence some of the restrictions of the glassy state can be simulated, and the energy requirements for side group rotation altered. The parameters used for our calculations were those quoted in the Allinger 1977 'MM2' program[6].

RESULTS AND DISCUSSION

The alkyl methacrylates

The model compounds used for the investigation of the alkyl methacrylates were trimers of methyl methacrylate of different stereochemistries. An atactic unit was treated first according to the Allinger method and gave the minimized geometry shown in *Figure 1a*. As the dielectric measurements suggest that all the dipoles are active below T_g, the (C_1–C_2) bond was selected as the one most likely to rotate all of the oxycarbonyl unit. Progressive restrictions were placed on the other atoms in the trimer by 'locking'

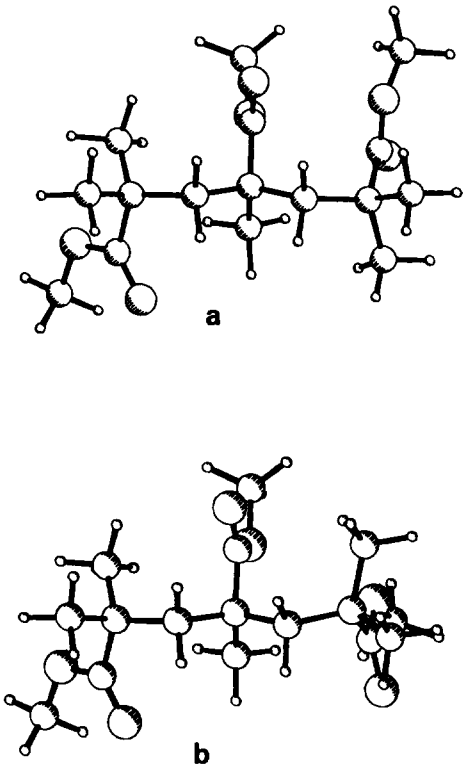

Figure 1 (a) Atactic methyl methacrylate (MMA) triad in minimized geometry, and (b) syndiotactic MMA triad in planar-zig-zag form

these marked with a black dot in *Figure 2a* and *b* and the strain energy of the molecule as a function of the (C_1–C_2) bond rotation angle was calculated for each case. *Figure 3* is a plot of the results for both the unconstrained and the constrained case shown in *Figure 2a*. It is gratifying to note the effect that these constraints have upon the size of the calculated activation energy requirements, which increase markedly when compared with the completely free model. The atactic unit was then forced into another geometry, *Figure 1b*, in which the side group, when rotated, would encounter methyl units on either side (i.e. a syndiotactic structure) and the most appropriate restricted motions are illustrated in *Figures 2c,d*.

The procedure was repeated with a zigzag isotactic conformation shown in *Figure 4*, and two likely restricted rotations are illustrated in *Figures 5a* and *b*. It was found that the rotating side group must force the two adjacent ester side groups to undergo torsional oscillations of $\pm 16°$ to relieve the stress during rotation of the central group, but in order to achieve energies in the 70–90 kJ mol^{-1} range the C_1 backbone atom and its attached methyl group must also be allowed to relax. When these are fixed in space the activation energy rises to *ca.* 110 kJ mol^{-1}.

The β-relaxation in both the mechanical and dielectric spectra is seen as a broad peak and this probably means that there is a distribution of relaxation times and energies associated with the process. The calculations suggest that if there are differing degrees of freedom in limited sections of the main chain then this could account for a variation in the energy requirements for oxycarbonyl group rotation and could reflect differing 'matrix effects' which would restrict movement in adjacent parts of the chain.

The 'matrix effect', i.e. the influence of atoms from other chains in the bulk polymer on specific group

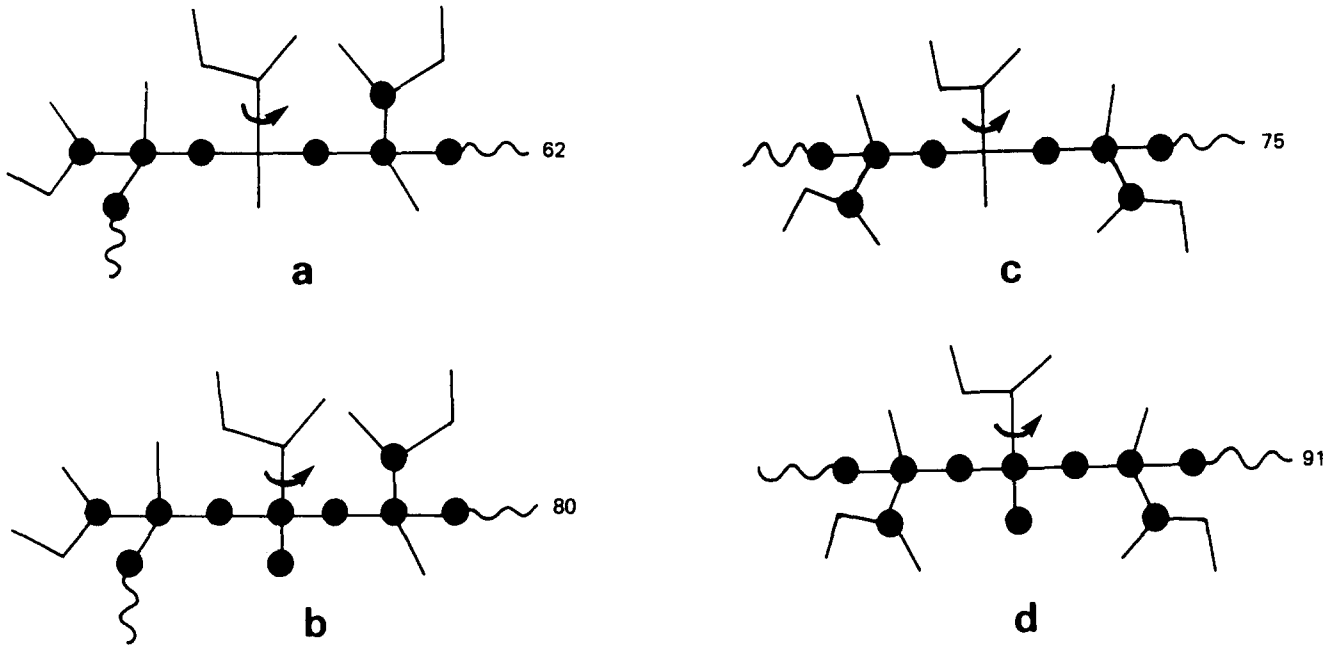

Figure 2 Two types of MMA triad showing atoms locked in space (—●—) and energy requirements for rotations about the (C_1–C_2) bond

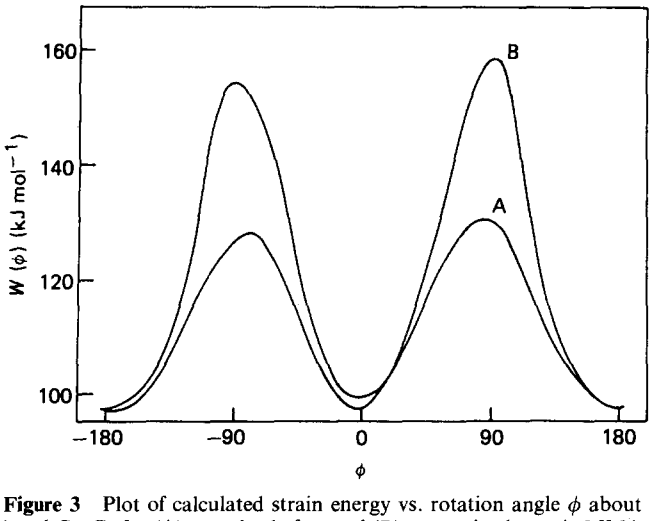

Figure 3 Plot of calculated strain energy vs. rotation angle ϕ about bond C_1–C_2 for (A) completely free and (B) constrained atactic MMA trimer structure shown in *Figure 2a*

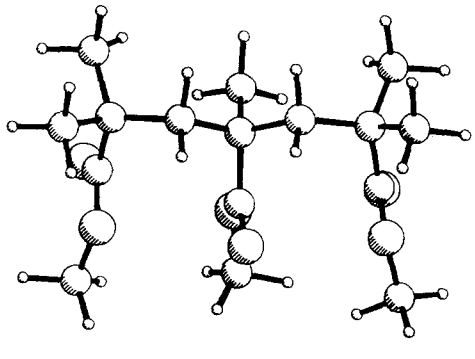

Figure 4 Isotactic MMA triad in planar zig-zag conformation

rotation, is difficult to simulate accurately in amorphous polymers and some of the geometries explored here may not be entirely realistic from that point of view. However, the general conclusion that one can draw from these calculations is that if an isolated side group movement, driven by rotation of the (C_1–C_2) bond is considered, the

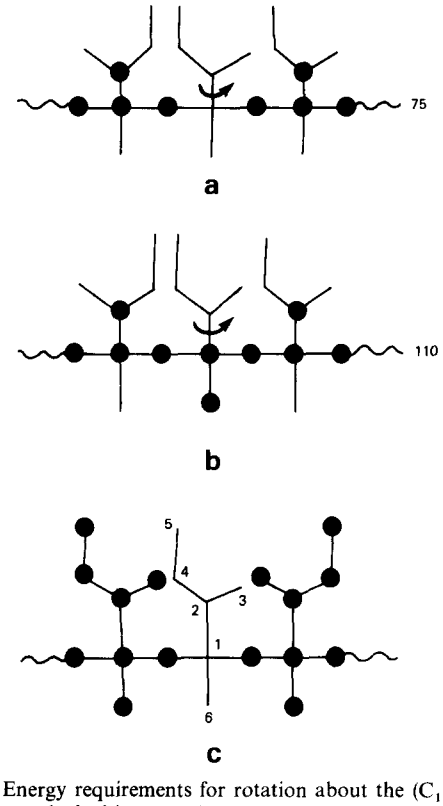

Figure 5 Energy requirements for rotation about the (C_1–C_2) bond showing atoms locked in space (—●—)

energy requirements can be made to match the experimental values by holding the majority of neighbouring atoms quite rigid and allowing only relatively few spatial readjustments of selected contiguous atoms to take place. Thus if the adjacent side groups are allowed to oscillate through $\pm 16°$, and if the C_1 backbone carbon and its attached methyl group can make small lateral movements if required, then sensible values of $\Delta H^{\ddagger}$ are obtained from a number of geometries. Clearly, quite a large number of permutations are possible in the restricted geometries of model

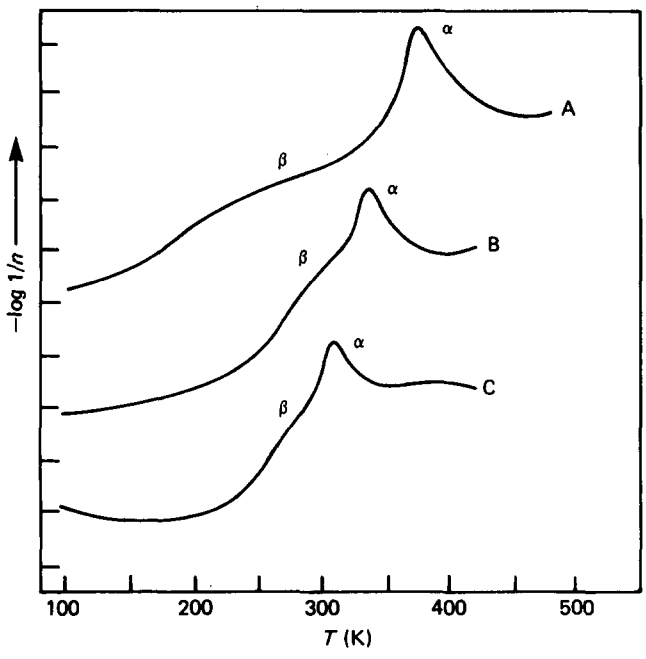

Figure 6 Mechanical damping spectra for poly(alkyl itaconate)s: (A) poly(dimethyl itaconate); (B) poly(diethyl itaconate); (C) poly(dipropyl itaconate)

compounds; those illustrated here represent only a few of these but are thought to be realistic possibilities.

Alkyl acrylates

When one considers the effect of replacing the alpha methyl group with a hydrogen atom, as in the case of poly(methyl acrylate), then one might expect the energy requirements for oxycarbonyl rotation to be somewhat lower than that calculated for the methyl methacrylate trimers above. The three model compounds used in this part of our study were obtained by replacing the alpha-methyl groups of the MMA trimers by hydrogens and then searching for these geometries which gave minimum energy conformations. These starting energies were found to be on average only one third of the energies calculated for the corresponding MMA trimer. The constraints which were applied to the methyl methacrylate trimer shown in *Figure 2a* were also used for the calculations involving the three methyl acrylate trimers.

The energy barrier for oxycarbonyl rotation about the (C_1–C_2) bond in the unconstrained syndiotactic trimer model compound was found to be 18 kJ mol^{-1}, whereas the value for the constrained case was 22 kJ mol^{-1}. The syndiotactic trimer is not the most realistic model compound to use in the case of PMA, as there are less 'nearest neighbour matrix effects' than in the previously discussed case of PMMA. The energy requirements for the same bond rotation in the other two constrained model compounds used were 33 kJ mol^{-1} for the atactic trimer, and 43 kJ mol^{-1} for the isotactic trimer. These would correspond to T_{max} peaks in mechanical damping spectra of 130 K and 172 K respectively. Finally, if one allows the carbonyl carbon atoms on the adjacent side groups to move, then the calculated energy requirement for the isotactic case is lowered to 40 kJ mol^{-1}. This shows that, again, given a reasonable set of constraints, it is possible to account for the experimentally observed energy requirement of 38 kJ mol^{-1} for the β-relaxation process in poly(methyl acrylate) and that oxycarbonyl group rotation is a likely molecular mechanism.

Alkyl itaconates

It is of interest to examine the analogous poly(alkyl itaconate) structures which also show a β-relaxation, although this seems to be a much weaker spectral feature as can be seen in *Figure 6*. The model trimer chosen to represent the itaconates was a dimethyl itaconate trimer with an atactic configuration, as shown in two projections in *Figures 7a* and *b*. The molecule appears to be quite crowded and may then be a reasonably realistic representation of the bulk glassy state and account for any matrix effect. Several bonds were rotated in this model while keeping a variety of other atoms stationary and a number of examples are shown in *Figure 8*. The energy requirements for the rotation of the (C_6–C_7) bond (*Figure 8a*) were quite low and well outside the β-relaxation energy requirements.

More likely candidates are rotations about the (C_1–C_2) bond with oscillation of the two neighbouring side groups and some freedom for lateral movement of the C_1 atom and attached side group. The situations illustrated in *Figures 8c* and *d* are only two permutations of restrictions which could be applied to this more complex molecule. However, many more sets of suitable constraints could still be found producing an activation energy which would match with what is obtained experimentally. This is similar to the situation examined in the methacrylates. Restriction of the side group atoms attached to C_1 raised the $\Delta H^{\ddagger}$ value, but not outwith the expected limits. If the other side groups are also frozen the energy requirements

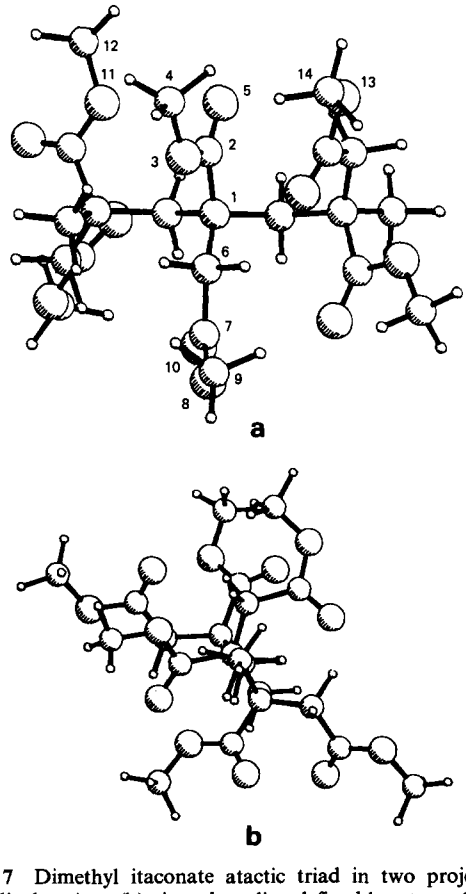

Figure 7 Dimethyl itaconate atactic triad in two projections: (a) perpendicular view; (b) view along line defined by atoms C_1 and C_7

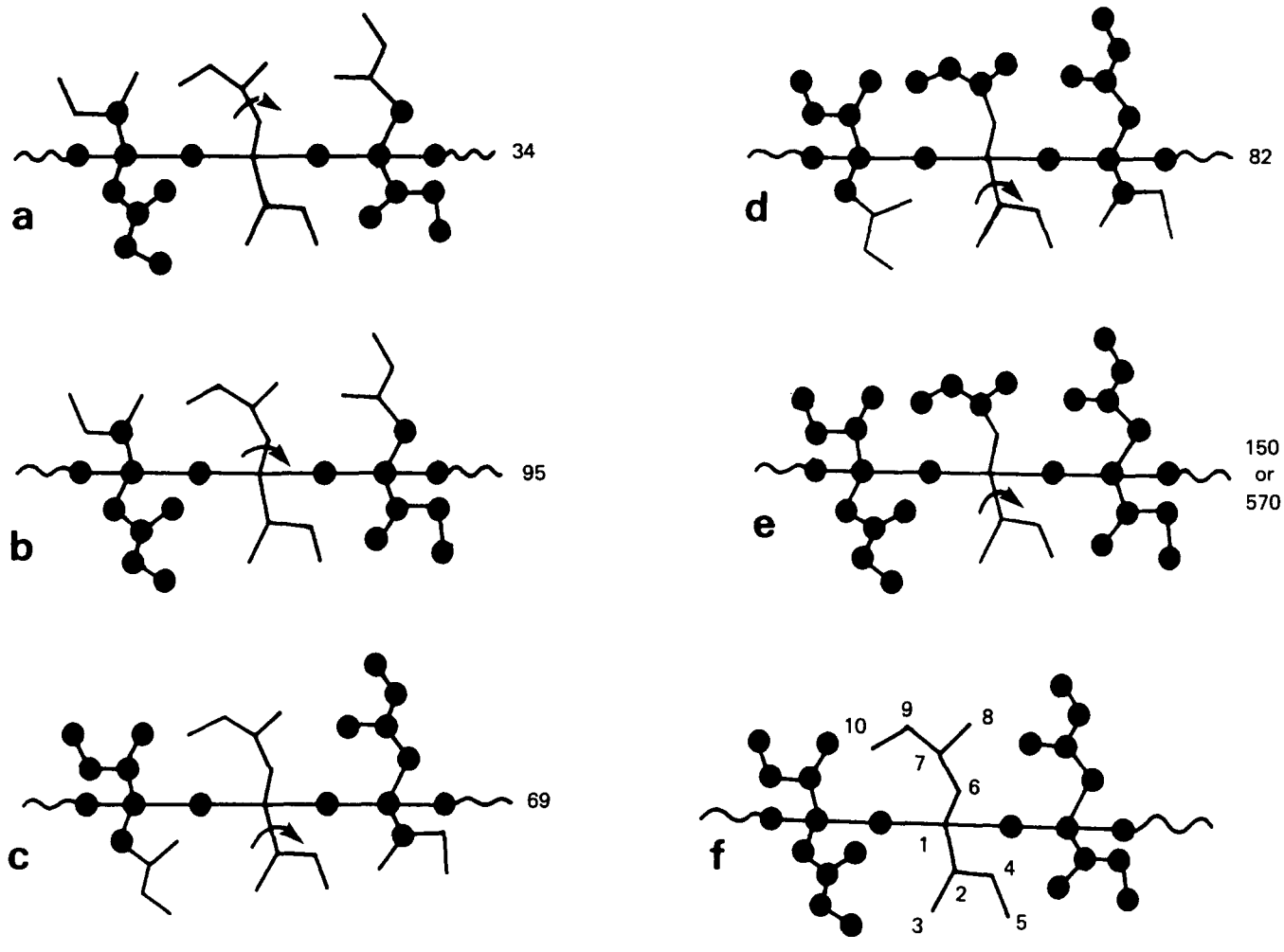

Figure 8 Dimethyl itaconate triad, showing atoms locked in space (—●—), and energy requirements for rotation about (a) bond (C_6–C_7); (b) bond (C_1–C_6); (c), (d) and (e) bond (C_1–C_2) with increasing restrictions imposed; (f) numbering system

become very high indeed, being 750 kJ mol^{-1} for complete rotation and 150 kJ mol^{-1} for a partial rotation (*Figure 8e*). This implies that oxycarbonyl motion can only be responsible for the β-relaxation if there is some freedom of movement in neighbouring side groups which will relax during the rotation. The effect of rotating the (C_1–C_6) bond was also examined and arrangements could be obtained which resulted in suitable $\Delta H^{\ddagger}$ values; one example is shown in *Figure 8b*.

CONCLUSION

The calculations carried out show that the β-relaxation processes observed in the poly(alkyl methacrylate)s, poly(alkyl acrylate)s, and poly(alkyl itaconate)s can be explained by rotation of the oxycarbonyl unit driven through the (C_1–C_2) bond. The energetic requirements of the process can be made to match the experimentally obtained apparent activation energies without invoking unrealistic models or excessive movement of adjoining portions of the polymer. In most models tested for the methacrylates and itaconates, the oxycarbonyl unit can rotate with an energy input of between 70 and 90 kJ mol^{-1} if the side groups in the immediate vicinity of the rotating group are allowed to move out of the way by oscillating over a small angular range. This is not unreasonable as the bonds subjected to this have much lower barriers to rotation than the β-relaxation and are probably already in motion. In addition, if the carbon atom in the main chain to which the pendant group is attached is also given the freedom to make small spatial adjustments, then again suitable energies of rotation can result. Of the atomic movements which are not driven directly by bond rotation, none are in any way excessive or unrealistic. This indicates that the β-relaxation, if it has its origins in this oxycarbonyl motion, can be quite localized and while there may be limited coupling with the main chain this will not involve it in significant movement.

The Allinger program can also deal with the effects of reducing some of the nearest neighbour steric hindrance to oxycarbonyl bond rotation, as seen in poly(methyl acrylate) for example, and the calculated activation energy requirement for the β-relaxation in poly(methyl acrylate) can be made to match the experimentally determined energy requirement to within a few per cent by applying reasonable restrictions to the movement of neighbouring side groups.

We are currently investigating the energy requirements for restricted molecular motions in several helical forms of isotactic PMMA, and are also trying to improve our modelling of 'matrix effects'.

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