

The γ relaxation in polymers containing ether linkages: conformational dynamics in the amorphous phase for a series of polybibenzoates containing oxyethylene spacers

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Restricted conformational transitions in oxyethylene chains have been investigated using a molecular mechanics approach. Geometries and energies of transition pathways have been evaluated for kink inversion and formation, and for crankshaft type motions which are feasible in anisotropic glassy matrices. Barrier heights for these processes are found to be similar to those determined for the corresponding processes in polyethylene chains although geometries of the conformations at the energy minima are significantly different. Results of the calculations are broadly consistent with dynamic mechanical measurements which indicate a γ relaxation in the amorphous phase of thermotropic liquid crystal polymers containing oxyethylene spacers. They support the hypothesis that kink formation, inversion and migration are primarily responsible for the low temperature relaxation in these polymers. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Dynamic mechanical relaxation studies of thermotropic liquid crystal polymers provide evidence of a broad relaxation process which occurs in the amorphous phase at low temperature (<170 K)^{1,2}. The relaxation strength is found to increase with the spacer length¹ which indicates that the relaxation is associated with restricted chain motion. These results are reminiscent of the γ process which is commonly observed in polymers containing polymethylenic chains³. Despite the vast amount of work which has now been published concerning γ relaxation in polyethylene, there remains no clear consensus concerning the details of the underlying motional process^{4,5}. There is, however, a body of opinion which supports one or more of the various models for restricted conformational transitions such as kink inversion and formation, and crankshaft motions involving either three or five chain bonds^{6–10}. These motions have been proposed as candidates for the γ process on the grounds that they are localized within small sections of the chains, consistent with the experimental observation that the measured relaxations depend little, if at all, on molecular weight. They also produce a minimum distortion of the overall chain orientation and position on either side of the defect undergoing the transition, thus complying with the steric

restrictions imposed on individual chains by the surrounding glassy matrix.

Experimental studies have also been carried out pertaining to the low temperature γ process in polymers containing ether linkages. However, results are in many cases qualitatively different from those found for polyethylene. In particular for poly(oxyethylene), the mechanical γ relaxation is barely visible and it is evident that in this polymer the dynamics is fundamentally different from that in polyethylene. In fact, it has been suggested that those polymers containing $(\text{CH}_2)_n$ segments with $n \geq 3$ will display relaxations due to restricted motion of this sequence and therefore bear a strong resemblance to polyethylene with regard to the dynamics at low temperatures¹¹.

This hypothesis, however, is at odds with the relatively clear mechanical relaxation observed at low temperatures (~ 160 K) for thermotropic polybibenzoates containing oxyethylene spacers¹. The intensity of the relaxation is found to increase as the number of $[(\text{CH}_2)_2\text{-O-}]$ units in the spacer is increased, indicating that the responsible motion is associated specifically with the flexible chains. The corresponding polymers containing all methylene instead of oxyethylene spacers exhibit very similar relaxation behaviour, suggesting that the two types of spacer chain undergo the same type of motions. The apparent activation energy for the relaxation, $30\text{--}50$ kJ mol⁻¹, is somewhat lower than that usually assigned to the γ process for amorphous regions in

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polyethylene, but falls within the overall range of values found for the low temperature relaxation.

Whilst the early experimental results for polyethers appear to indicate that oxygen atoms do not participate in kink and crankshaft type motions, the underlying physical reasons for this remain unclear. One possible interpretation of the experimental findings is that the intramolecular potentials for ether linkages, which are known to be quite different from that for linear all-methylene chains, prohibit this type of conformational transition. In the case of isolated chains, the intramolecular potential entirely determines the transition pathways for conformational dynamics and it should be possible to interpret experimental observations of these processes solely in terms of this potential. However, for real condensed phases, conformational dynamics are governed not only by the direct influence of the intramolecular potential but also by the equilibrium conformational distribution, which is determined by both intramolecular and intermolecular interactions. This is undoubtedly the case for glassy and crystalline polymers where the chain structure is partially frozen in.

One of the principal questions addressed in this study concerns the relative importance of the conformational distribution in determining the conformational dynamics in oxyethylene chains. More specifically, we investigate whether restricted conformational transitions such as kink or crankshaft processes might be responsible for the low temperature relaxations which have been observed in thermotropic polybiphenyls containing oxyethylene spacers. We have adopted a molecular mechanics approach similar to that followed by Boyd and co-workers in their studies of conformational dynamics in polyethylene^{9,10}. Results obtained for oxyethylene chains are discussed with reference to similar calculations carried out for all-methylene chains and compared with experimental results of dynamic mechanical studies performed for these materials. We finally draw some conclusions concerning the feasibility of the various processes investigated in different environments.

COMPUTATIONAL DETAILS

A molecular mechanics FORTRAN program has been developed specifically for linear hydrocarbon and ether linkage chains. The program, which performs energy minimization with respect to internal coordinates (bond lengths, bond angles and torsion angles, $\Omega = \sum_i r_i, \theta_i, \phi_i$) employs the MM2 force field^{12,13}. This force field takes account of *gauche* effects in -O-C-C-O- segments, which are thought to play an important role in conformational behaviour of polyethers¹⁴. Minimization is carried out using the full matrix Newton-Raphson (NR) method, the block diagonal NR method¹⁵, or a linear constraints minimization routine¹⁶. The latter approach was used in most cases since, for chains with more than seven skeletal (i.e. carbon or oxygen) atoms, this converged most efficiently. In all cases, first derivatives of the energy are calculated analytically. The program was tested by comparing bond lengths, bond angles and torsion angles evaluated for specific conformations (e.g. *cis*, *anti*) in small alkanes and ethers, with those reported in the literature for the MM2 force field^{12,13}.

Fixing of internal coordinates is straightforward, either by removing the corresponding rows and columns

from the second derivatives matrix (for the NR methods) or by setting the upper and lower parameter bounds to be equal (linear constraints minimization). Transition pathways were investigated by choosing one of the bonds involved in the transition as the drive bond and incrementing its torsion angle successively through the transition from the initial to the final conformation. This torsion angle is maintained fixed during minimization. Initial conformations are determined by allowing all coordinates to vary (i.e. no fixed parameters) during energy minimization, including the selected drive bond torsion angle. The program allows for the possibility of anchoring the end stems (defined by three or more atoms) by including pseudo stretching potentials which tie designated atoms to their initial (or other specified) locations in cartesian space. Fixing of end bonds was employed in the early simulations of polyethylene¹⁰ but is probably too severe, even for modelling crystalline systems⁹. A more rigorous treatment of the surrounding matrix would require explicit inclusion of the neighbouring molecules^{9,17}. However, in the present case, we have little knowledge regarding the relative disposition and conformational distribution of the polyesters and such a detailed approach is not feasible. We have, therefore, devised an alternative means of constraining the molecule to physically realistic conformations. In this procedure, the end to end chain length and the end stem orientations are constrained by harmonic potentials to their initial conformation values.

It should be stressed that the drive bond method usually follows the desired transition pathway but this transition route is not necessarily unique. That is to say, other routes across the potential energy surface effecting the desired transition may also be feasible. Situations have also been found in which the desired transition was *not* obtained simply by driving a single torsion angle. This is because the drive bond procedure follows the *local* minimum energy pathway at each fixed value of the torsion angle. However, it is conceivable that the *most probable* transition pathway does not derive from the minimum energy route determined in the vicinity of the starting conformation. In other words, the transition coordinate is not, in general, described by a single torsion angle. In order to unambiguously determine the overall minimum energy transition path, a global search covering the entire conformational energy surface would be required, which is not feasible for any but the smallest of molecules. These problems are well-known and discussed in more detail in ref. 15.

Finally, we note that the internal coordinate approach offers some advantages over the more usual cartesian coordinate method of parameterization for transition pathway problems, since it provides a very simple means of applying external constraints such as fixing the drive bond torsion angle. It also allows for the imposition of symmetry constraints on the structure, helpful for following the *correct* transition pathway if the symmetry of the transition is known *a priori*¹⁵. It has also been suggested recently that internal coordinates should be suitable for the study of extremely large macromolecules where it may be necessary to fix many of the bond lengths and angles¹⁸.

MATERIALS AND METHODS

The polymers discussed in this study were obtained by

transesterification of the diethyl ester of *p,p*-dibenzoic acid with the corresponding glycol spacer using isopropyl titanate as catalyst. Samples were purified by precipitation from solutions in chloroform on addition of methanol. All polymers display either smectic A or C phases depending on the type of spacer^{19,20}. Glass transition temperatures, measured by differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.), range from 40° to 52°C for the polymers with all-methylene spacers and from 0° to 50°C for the series of polymers with oxyethylene spacers. Values obtained by d.s.c. were found to be similar to or, in some cases, even slightly higher than those derived from d.m.t.a. measurements for all compounds in these series studied to date^{1,21}.

Samples used for dynamic mechanical measurements were prepared by moulding in a Collin press equipped with smooth-polished plates, and hot-pressed (~20°C above isotropization temperatures) for about 5 min at a pressure of 1 MPa. The liquid crystal glasses were obtained by quenching from the isotropic melt. For the series of polyesters containing oxyethylene spacers, the quenching process effectively suppresses crystal formation. In the case of the series containing all-methylene spacers, the degree of crystallinity for quenched samples, estimated by X-ray diffraction, was found to be less than 17%²². The effect on crystal formation and liquid crystalline behaviour of incorporating oxygen in the flexible spacers has been discussed previously^{19,20}.

Dynamic mechanical measurements were carried out with a Polymer Laboratories MK II dynamic mechanical thermal analyser operating in the tensile mode. The complex modulus and loss tangent have been measured at 3, 10 and 30 Hz at a heating rate of 2°C min⁻¹. Further details concerning the characterisation and properties of the polymers may be found in previous publications^{1,2,23}.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the loss modulus, E'' , and loss tangent, $\tan \delta$, between -150° and 0°C, measured at 3 Hz for a series of polyesters having all-methylene spacers in the main chain. The corresponding results obtained for a similar series with oxyethylene spacers are plotted in Figure 2^{1,2,23}. For both series, two relaxations are clearly observed in this temperature range. At higher temperatures (between 0° and 50°C—not shown in Figures 1 and 2) the α relaxation, related to the glass transition, is also observed. The β relaxation, which occurs between -50° and -80°C, is believed to be associated with complex motions involving the carboxyl groups, phenyl rings and the spacer chains²⁴⁻²⁶. A γ relaxation appears below -100°C for all the polymers investigated. The intensity and temperature location of the relaxation are affected by the length of the spacer chain and the degree of crystallinity. It is evident that the polymer with an 8-methylene group spacer displays a much weaker γ relaxation than other members of this series. It is not yet clear why polymers containing this spacer do not follow the general trends apparent in the rest of the series. However, the anomalous behaviour of the 8-methylene group spacer has now been observed in a variety of different samples, including copolymers and it seems that the effect is quite general^{2,27}. For the remainder of the materials investigated in this study, a clear tendency was found for those polymers with longer

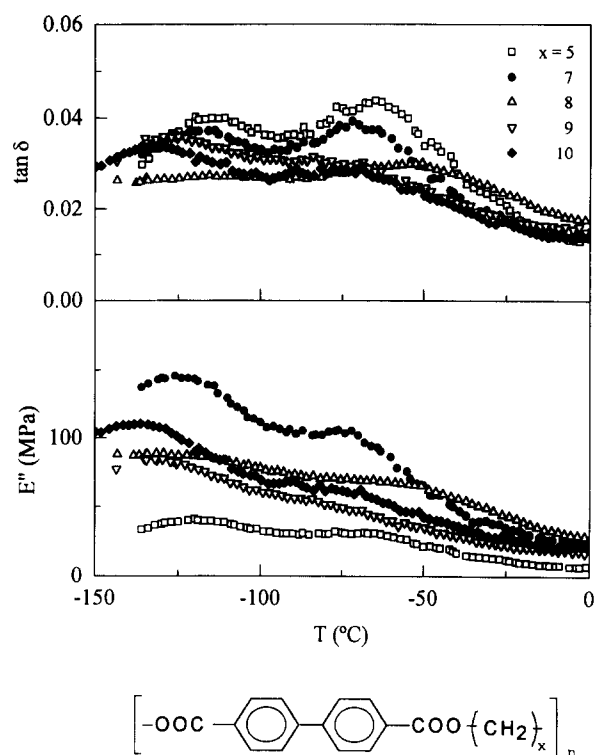


Figure 1 Loss modulus, E'' , and loss tangent, $\tan \delta$, measured at low temperatures for a series of main chain thermotropic polyesters having all-methylene spacers

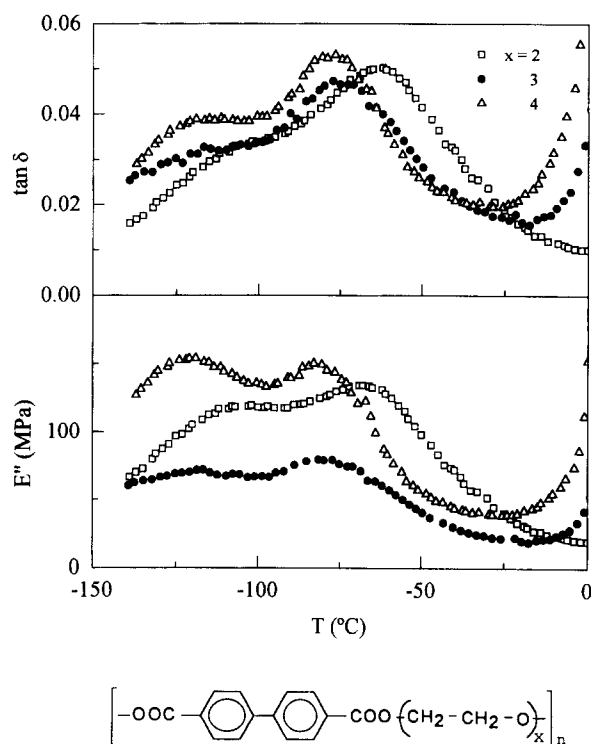


Figure 2 Loss modulus, E'' , and loss tangent, $\tan \delta$, measured at low temperatures for a series of main chain thermotropic polyesters having oxyethylene spacers

spacers to exhibit a more intense and better defined γ relaxation. This observation, together with the measured activation energies, which lie in the range from 30 to 50 kJ mol⁻¹, suggest that the relaxation is associated with restricted conformational transitions, similar to those believed to be responsible for the γ relaxation in

polyethylene. This hypothesis, based on the experimental results presented in Figure 1, implies that restricted conformational transitions may occur in spacers consisting of oxyethylene subunits. Such processes would require the active participation of oxygen atoms in large amplitude cooperative motion with neighbouring carbons, a situation which has generally been discounted in dynamic studies of polyethers and related polymers. It is this apparently anomalous behaviour exhibited by the thermotropic polyesters which has stimulated the present study of conformational energetics in oxyethylene spacers. It is worthwhile pointing out at this point that for crystalline poly(oxyethylene), this type of motion is not expected (nor, apparently, it is observed) since it is incompatible with the 7_2 helix structure based on the *tg* (*trans gauche gauche*) sequence for consecutive OCCO, CCOC and COCC segments²⁸. However, there is no reason to expect the thermotropic polyesters reported here to adopt this type of helical structure either in crystalline or non-crystalline regions.

We have investigated three types of conformational transition in oxyethylene chains. These are (a) five bond crankshaft motions proposed by Schatzki⁶, (b) kink formation and inversion⁹, and (c) three bond crankshaft process such as kink migration⁷. The three types of transition studied are pictured schematically in Figure 3. In all cases, the transitions take place within a relatively short chain segment causing a minimum disturbance in the orientation and position of the chain at either end of the segment. Accounting for all possible variations in the initial conformations of the end chain segments, the total number of distinct transitions is clearly quite large, even for this limited set of pathways. The situation is complicated further in the case of oxyethylene spacers since rotations about C-C and C-O bonds are not equivalent. This implies that each of the processes mentioned above can occur in two different ways reflecting the different combinations of individual C-C and C-O bonds which undergo rotational transitions in the course of the motion. For this reason we have focused the study primarily on these conformations expected to be most populated. For main chain liquid crystal polymers or oligomers, the interactions experienced by the polymer chains due to the anisotropic environment in the mesophase favour those conformers in which the mesogenic groups are approximately parallel. Conformational analysis and X-ray studies of these polymers indicate that highly extended conformers predominate^{19,20}. Similar results have been found for nematic main chain polymers^{29,30} and have been interpreted with models based either on anisotropic steric interactions^{29,31} or long range dispersion forces³². For present purposes, it is important to recognize that the thermotropic polyesters preferentially adopt linear extended conformations. This conclusion is in fact consistent with the existence of kink sequences g_+tg_- , or g_-tg_+ , in the spacer chains. These sequences produce a small lateral displacement of the chain without significantly modifying its orientation and causing only a small reduction in the end-to-end spacer length. Note that it is precisely these sequences which are also thought to be involved in restricted conformational transitions such as those described above.

Energy profiles for the five bond crankshaft process (see Figure 3a)⁶ are shown in Figure 4. For oxyethylene

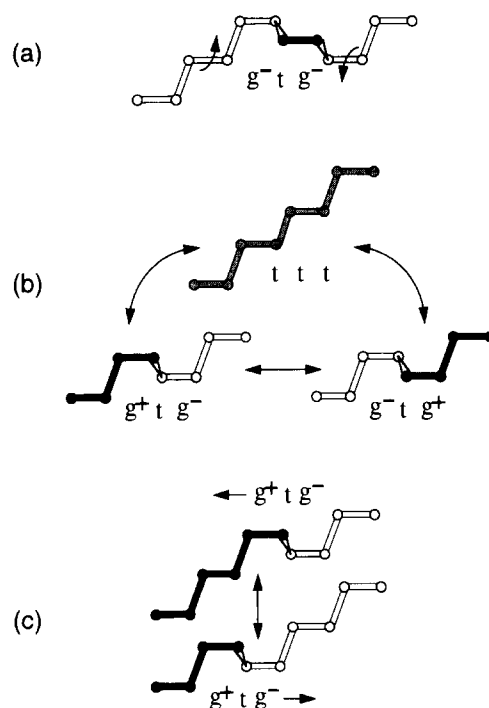


Figure 3 Crankshaft and kink motions in linear chains: (a) five bond crankshaft motion; (b) kink formation and inversion; (c) kink migration

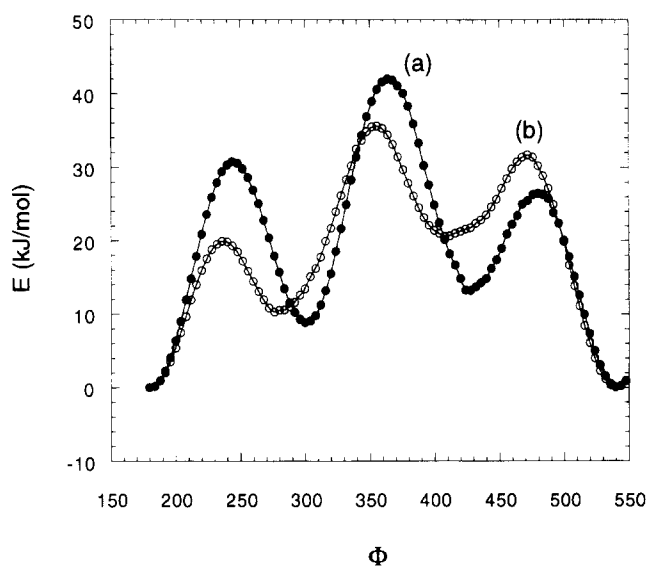


Figure 4 Minimum energy profiles for five-bond crankshaft motions in (a) C-C-O-C-C-O-C-C and (b) O-C-C-O-C-C-O-C chain segments as a function of the drive bond torsion angle, Φ . The initial conformation is $tg_+tg_+tg_+$, which approximately maintains the orientation of the main polymer chain at either end of the crankshaft. For both cases, the first bond of the sequence was employed as the drive bond

spacers, the process can occur in a -C-C-O-C-C-O-C-C- segment (Figure 4a), with rotation occurring about the two end -C-C- bonds, or it might involve a -O-C-C-O-C-C-O-C- section with rotations occurring about -O-C- bonds (Figure 4b). Calculations were performed by starting with the chain in the $tg_+tg_+tg_+$ conformation. In this conformation, the main chain orientation is virtually undisturbed by the presence of the crankshaft segment, and hence allows for approximately parallel orientation of mesogenic groups and extended

conformations favoured in the liquid crystal phase. Similar results, however, are obtained for other combinations containing the tg_+tg_+ chain section. Calculations carried out on all-methylene chains yield similar values for the barrier heights which lie in the range from 20 kJ mol^{-1} to about 35 kJ mol^{-1} . In order for calculations to follow the desired transition trajectory, it was necessary in some cases to maintain the end stems of the five bond sequence parallel, which was achieved by including a pseudo bending potential operating on the two stems. This potential causes only a minor increase in the conformational energy since the resulting distortion can easily be accommodated by small adjustments in the torsion angles about their minima. The procedure serves simply to guide the chain through the desired transition during the torsion angle driving. For all-methylene chains, the end stems are in any case virtually collinear as a result of the approximately tetrahedral geometry of the chain carbon atoms. Oxyethylene chains, on the other hand, deviate substantially from the tetrahedral lattice, and the end stems for such five-bond chain sequences may deviate significantly from collinearity. This is most notable in the case of the $-O-C-C-O-C-C-O-C-$ fragment. Although feasible energy pathways can be found for the conformational transitions, the likelihood of the oxyethylene chains initially existing in a suitable starting conformation (i.e. with end stems collinear) is presumably small. In any event, as Boyd and Breitling have remarked¹⁰, five-bond crankshaft motions involve a large swept-out volume and are for this reason improbable in glassy or crystalline environments. Whilst it is not possible to entirely discount this process as a contributor to the γ relaxation, the somewhat intuitive physical arguments outlined above suggest that it does not represent the principal mechanism.

The simplest conformational sequences which approximately maintain the overall chain orientation are g_+tg_- and g_-tg_+ kinks. The formation of kinks from *all-trans* fragments and the related process of kink inversion has been proposed as the dominant mechanism for the γ relaxation in polyethylene^{5,9}. This process involves the simultaneous counter-rotation about two bonds separated by one intervening bond (see *Figure 3b*). In all-methylene chains and $-C-O-C-C-O-C$ fragments, the local symmetry of the chain is preserved during the transition. In $O-C-C-O-C-C$ fragments, on the other hand, rotations about the $-C-C-$ and $-O-C-$ bonds are clearly different and the process follows no obvious symmetrical pattern. The formation of a kink from an initial *all-trans* fragment results in a shortening of the fragment which will lead to strains in the remainder of the chain and also in the surrounding lattice⁹. Interconversion between g_+tg_- and g_-tg_+ sequences does not involve any overall change in the chain length but rather a translational shift of one of the chain stems with respect to the other. Such shifts must give rise to fluctuating stresses and strains which would be effective in mechanical relaxation. The relationship between molecular structure and macroscopic mechanical behaviour is extremely complex requiring detailed knowledge of intermolecular interactions¹⁷ over long ranges. In the absence of such detailed information concerning the intermolecular interactions, we have adopted the simplified approach of maintaining the overall chain length fixed during the transition. The pseudo potential which is included to

constrain the chain length may be regarded as a crude representation of the interactions between the *trial* segment and the remainder of the chain and with the surrounding matrix. In a real sample we should expect a significant variation in these interactions, reflecting the heterogeneity of local environments throughout the amorphous materials.

The energy profiles for the overall $g_+tg_- \leftrightarrow g_-tg_+$ process calculated for $C-O-C-C-O-C$ and $O-C-C-O-C-C$ fragments are shown in *Figure 5*. Calculations were carried out for (a) the free chain and with the chain length fixed at (b) its *all-trans* value and (c) its value for a kink conformation. Equivalent calculations performed for all-methylene chains yield transition profiles (not shown) similar to those obtained for $C-O-C-C-O-C$ fragments (*Figures 5a-c*). Results for $O-C-C-O-C-C$ fragments (*Figures 5d-f*) however, indicate a higher barrier in the eclipsed form (torsion angle = 0°) for the fully extended chain (i.e. with the chain fixed at its *all-trans* length). For both types of fragment, kink conformations no longer represent stable states in fully extended (i.e. *all-trans*) chains. The relative destabilization of kink sequences is evident also for all-methylene chains. It is, of course, to be expected, since kink sequences in the free chain are shorter than the corresponding *all-trans* conformation sequences. The unsymmetrical transition profile for the $O-C-C-O-C-C$ fragment (*Figure 5f*) was obtained by initializing the transition with the fragment in the kink conformation and with the chain length held fixed at its initial (i.e. kink) value. This profile may not be unique but is probably one of several feasible transition routes which traverse the potential energy surface between the different kink and extended conformations. It does, however, give an idea of the approximate barrier heights which are likely to be encountered in this process. The chain length restrictions imposed during the evaluation of the transition pathways may be considered as extreme limiting cases. In real systems, both the remaining polymer chain and the surrounding lattice are able to relax to some extent and it is reasonable to assume that realistic transition profiles lie somewhere between the free chain profiles and those obtained for the fixed chain lengths. This supposition is lent some support by detailed calculations performed for polyethylene chains confined in ordered matrices, which indeed yield profiles with kink conformations of reduced stability and increased barrier heights relative to those in the free chain⁹.

The crankshaft motion proposed by Boyer⁷ (*Figure 3c*) involves rotations about approximately parallel—but not collinear—stems and results in the simultaneous transitions of three bonds. Of particular relevance in extended chains is the $ttg_+tg_- \leftrightarrow g_+tg_-tt$ transformation. Note that the spatial locations of the end bonds remain largely unaffected by the transition. This process then involves the shifting of a g_+tg_- kink along the chain by two chain segments. In all-methylene chains, the translation of a kink leaves the remainder of the chain (i.e. the part not directly involved in the transition) entirely unaffected. This is clearly not the case in oxyethylene chains which have a repeat unit involving three segments—i.e. an oxygen atom and two methylene groups. Nevertheless, it is possible to envisage kink migrations occurring in oxyethylene chains, although initial and final conformations will not be geometrically

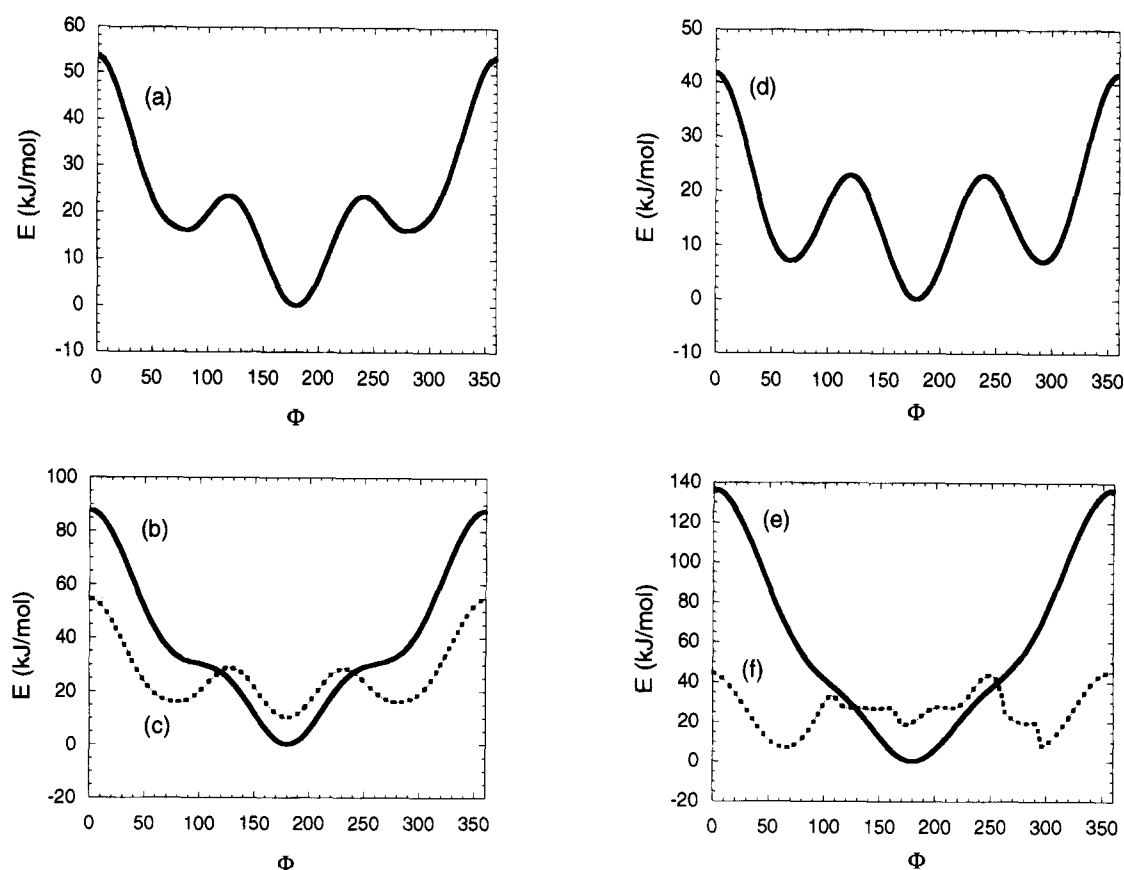


Figure 5 Minimum energy profiles for kink formation and inversion ($g_+tg_- \leftrightarrow tt \leftrightarrow g_-tg_+$) as a function of the drive bond torsion angle, Φ . The drive bond may be taken to be either of the two bonds whose conformation is modified during the transition: (a) C–O–C–C–O–C segments with no constraints (i.e. free chains); (b) same as (a) but with segment length fixed at its value for the *all-trans* conformation; (c) same as (a) but with segment length fixed at its value for the free chain kink conformation. Profiles (d)–(f) refer to calculations performed for O–C–C–O–C–C segments. Profile (d) corresponds to the free chain, (e) with the segment length fixed at its *all-trans* value and (f) with the segment length constrained to the kink conformation value

or energetically equivalent. Energy profiles have been evaluated for symmetrical kink shifts in C–C–O–C–C–O–C–C with the 4th bond (C–C) employed as the drive bond, and for unsymmetrical kink migrations in C–O–C–C–O–C–C–O–C using bond 5 (O–C) as the drive bond. The results are plotted in *Figure 6*. Note that the kink migration is represented here by the change in the central bond torsion angle (i.e. the abscissa parameter in *Figure 6*) from $\Phi \sim 60^\circ$ to $\Phi \sim 300^\circ$. Calculations for the unsymmetrical transition were carried out on C–O–C–C–O–C–C–O–C chains rather than O–C–C–O–C–C–O–C segments in order to avoid the complications of hydroxyl groups (which are not relevant to the polymers) or unsaturated terminal oxygen atoms. For both types of chain segment, the end-to-end chain length and the end bond orientation were held constant during the transition. Barrier heights of ~ 20 – 25 kJ mol^{-1} are found for the C–C–O–C–C–O–C–C fragment (*Figure 6a*) and ~ 10 – 15 kJ mol^{-1} for the C–O–C–C–O–C–C–O–C chain (*Figure 6b*). Results obtained for all-methylene chains (not shown) are similar to those obtained for the C–C–O–C–C–O–C–C fragment, both in the general form of the profile and with respect to the calculated values of the barrier heights.

The kink migration process involves cooperative transitions in three of the five bonds which define the relevant chain fragment. This is actually a special case of the three bond crankshaft motion initially proposed by Boyer⁷ as the mechanism for the γ relaxation in

polyethylene. *Figure 7* shows the torsion angles for each of the relevant bonds as a function of the drive bond angle. Whereas the penultimate bonds (Φ_3 and Φ_5 for the C–C–O–C–C–O–C–C segment; Φ_4 and Φ_6 for the C–O–C–C–O–C–C–O–C segment) display only minor variations from their minimum energy *trans* conformations throughout the transition, the remaining *active* bonds undergo large amplitude cooperative transitions. The strong correlation between the segment and bond torsion angles (i.e. Φ_2 and Φ_6 for the C–C–O–C–C–O–C–C) is a reflection of the approximate symmetry of the chain and its force field about the central (drive) bond. However, for neither of the oxyethylene chain cases investigated here is the kink migration process entirely symmetric as it should be in the case of an ideal polyethylene chain under the same conditions. For the C–O–C–C–O–C–C–O–C segment transition (*Figures 6b* and *7b*), this is to be expected since the initial and final conformations are distinct, even for a free chain. For the C–C–O–C–C–O–C–C case, on the other hand, the initial and final kink conformations have the same distribution of *trans* and *gauche* states amongst C–C and O–C bonds. In this case, however, the overall chain orientation would be significantly modified by the transition, were it not for the restrictions imposed on the chain by the neighbouring molecules. The difference ($\sim 4 \text{ kJ mol}^{-1}$) between the two kink conformations at $\Phi \sim 60^\circ$ and $\Phi \sim 300^\circ$ in *Figure 6a* thus reflects the degree of distortion imposed on the chain by the

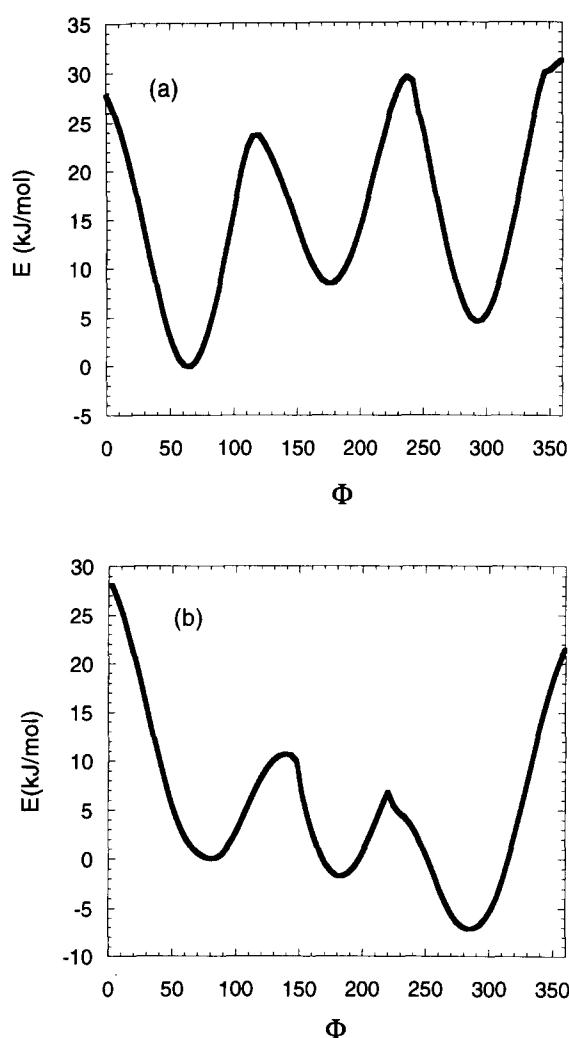


Figure 6 Minimum energy profiles for kink migration in oxyethylene spacers as a function of the drive bond torsion angle, Φ . Profile (a) refers to C-C-O-C-C-O-C-C segments with the central C-C bond (i.e. 4th bond) as the drive bond and profile (b) was evaluated for C-O-C-O-C-C-O-C segments with the 5th bond (O-C) used as the drive bond

constraints of the surrounding matrix. The fact that the end stems are not collinear (in fact they are also not parallel in the case of oxyethylene chains) does not appear to significantly affect the energetics of the process. For the kink migration process, the energy surface is relatively uncomplicated and apparently contains well defined minimum energy pathways for the transition which are rather tolerant of variations in the geometry of *gauche* conformations and consequent deviations of the chain from the tetrahedral lattice. Note that this result contrasts with that found for the five-bond crankshaft process discussed above where the shape of the potential energy surface is sensitive to the geometry of the chain.

CONCLUSIONS

The molecular mechanics calculations described here indicate that restricted conformational transitions such as kink formation, inversion and migration are feasible processes in non-crystalline polymers containing linear spacers involving oxyethylene units. In fact the overall

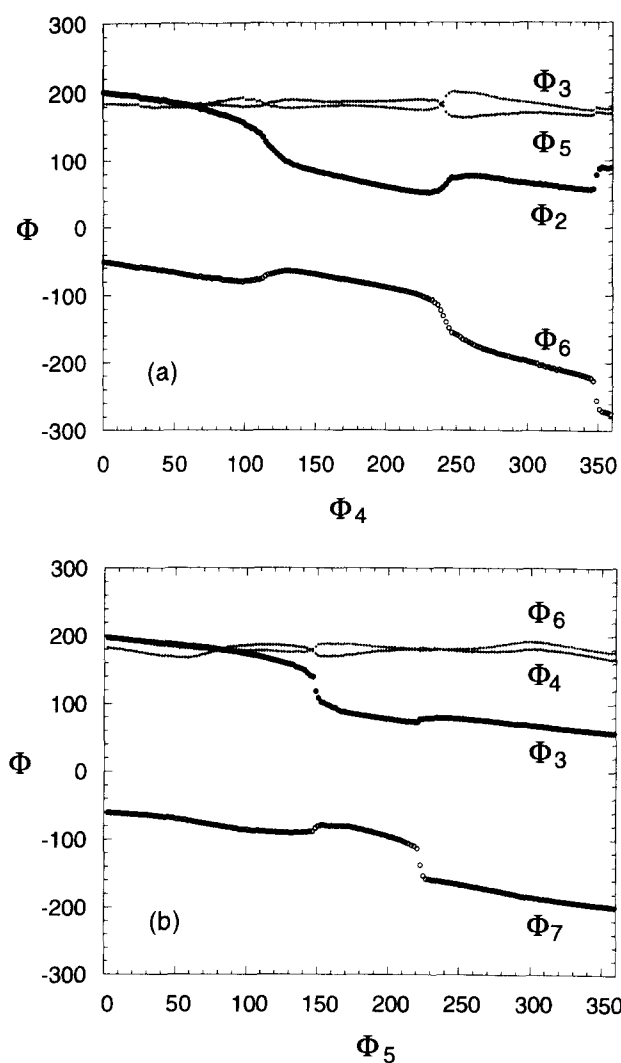


Figure 7 Variation of the torsion angles, Φ_i , for each of the segment bonds, i , during kink migration in (a) C-C-O-C-C-O-C-C and (b) C-O-C-C-O-C-C-O-C segments. These plots correspond to the energy profiles shown in Figure 6

transition profiles obtained are similar to those found for polyethylene chains and suggest that this type of process may be responsible for the γ relaxation observed in a series of main chain thermotropic polyesters having oxyethylene spacers^{1,2,23}.

Although the intramolecular potential and resulting geometry for chains composed of oxyethylene units are significantly different from those for the corresponding all-methylene chain, this in itself is not sufficient to preclude the possibility of kink motions occurring. In hindsight, this may not seem altogether surprising in view of the broad similarities (although some notable differences are also observed) in many other physical properties (e.g. liquid crystalline transitions) between polymers having oxyethylene and all-methylene spacers^{19,20}. However, it is at odds with the conclusions of previous studies of the γ process in polyethers¹¹, which maintain that only those sequences containing three or more consecutive carbon atoms are capable of supporting such processes. Our calculations provide no reason to suspect that oxygen atoms located in the chain cannot actively participate in restricted conformational transitions. It is stressed, however, that these results are strictly valid only for non-crystalline polymers or crystalline material in which the

polymer chains adopt extended conformations which allow for the possibility of introducing kink sequences. Other well defined structures such as the ttg_+ adopted by poly(oxyethylene)²⁸, should not be expected to display the same behaviour. In such cases, the formation of kinks are geometrically incompatible with the overall chain and lattice structure. This is not the case in polyethylene or in highly extended all-methylene spacers, where the tetrahedral chain geometry permits such transitions to occur without significantly distorting the surrounding lattice. It is significant that all those linear polyethers with repeat units containing three or more consecutive methylene groups adopt predominantly all-*trans* conformations in the crystalline and amorphous phases. These polymers are, therefore, highly extended and hence can be expected to permit kink formation and exhibit a γ relaxation of the polyethylene type, as is indeed observed experimentally. The fundamental requisite for kink motions thus appears to be the equilibrium conformational distribution of the chain rather than the presence and location of oxygen atoms. Chains which are highly extended allow for the formation of kink sections which may invert and migrate. These processes are apparently responsible for the γ relaxation observed in the series of thermotropic polybenzoates investigated here.

The barrier heights evaluated for the various transitions typically lie in the 20–35 kJ mol⁻¹ range. Experimental values for the activation energy of the mechanical γ relaxation in thermotropic polybenzoates^{1,2,23} fall between 30 and 50 kJ mol⁻¹. Bearing in mind the rather simplistic way in which lattice interactions have been included in the calculations, as well as possible inaccuracies in the force field itself, the discrepancy between calculated barrier heights and experimental values for the γ process activation energy are not irreconcilable. Even in the case of polyethylene, for which the γ relaxation has been investigated in considerable detail, simple molecular models are unable to completely account for experimental results⁵. It is not surprising that the same models cannot provide a detailed fully quantitative description of the observed relaxations in the polyesters discussed here. What has been shown here, principally, is that kink motions such as those proposed in all-methylene chains may also occur in oxyethylene spacers and that this simple model provides a semiquantitative description of the dynamic mechanical behaviour of a series of thermotropic polyesters.

Further information concerning the molecular origin of the γ process can be gleaned from dielectric relaxation and n.m.r. studies. Detailed evaluation of the effects of spacer length and the degree of crystallinity on the γ

relaxation should also shed more light on the conformational dynamics in these polymers. Work along these lines is currently underway in our laboratory.

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