polymer review

Relaxation processes in crystalline polymers: Molecular interpretation – a review

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Recently, the experimental facts concerning relaxation processes in semi-crystalline polymers have been reviewed (ref. 1). Here, in a companion to that review, progress in interpretation of the molecular processes underlying the relaxations is considered.

(Keywords: crystal phase; amorphous fraction; molecular mechanism; dielectric relaxation; mechanical relaxation; nuclear magnetic resonance)

INTRODUCTION

Because the physical properties of semi-crystalline thermoplastics are dominated by the presence of relaxation processes there is considerable interest in the study and interpretation of these phenomena. Recently, the experimental facts concerning relaxation processes have been summarized in a review with the same general title as the present one but subtitled, 'Experimental Behaviour' (see Ref. 1). The purpose of the present article is to extend that review by summarizing the progress in the molecular interpretation of the processes. There have been many mechanistic suggestions for the molecular processes underlying relaxations. However, translating these into models that are sufficiently detailed or a priori in their construction to be useful in checking their consequences with experimental results is another matter. Only for the α process has model development reached the stage of successful detailed comparison with experiment. For the other processes it is nevertheless a very useful exercise to discuss what kind of model the experimental data seem to call for and what improvements are needed in both theory and experiment to clarify molecular mechanisms.

THE α RELAXATION

As detailed in Ref. 1, the dielectric and n.m.r. processes in PE occur directly in the crystals. The mechanical process is more complicated in that although it requires the presence of the crystals its relaxation strength is assigned to the amorphous fraction. The mechanical process is broader and has a larger central relaxation time than the dielectric one. The activation energies however are similar. For both processes the relaxation times are dependent on crystal thickness. The mechanism of the dielectric process is taken up first because of the direct association with the elementary or fundamental molecular process in the crystal fraction and because quantitive relaxation parameters are available experimentally for comparison with model results.

### Dielectric relaxation and the mechanism of the elementary crystal process

As discussed in Ref. 1, the dielectric relaxation strength implies that typical crystal chains are involved, not just a few that perhaps contain a conformational defect. The fact that the process is narrow in the frequency domain, nearly single relaxation time, makes a model involving reorientation of a single chain at a time over a barrier between two sites the plausible one. This reorientation then must involve a symmetry operation of the crystal, bringing the typical chain back into crystallographic register. To achieve dielectric activity a screw rotation about the 'c' axis of 180° that advances the chain by half a unit cell ($c/2$) must then be involved. This results in reorientation of a perpendicular dipole (e.g. occasional C=O in lightly oxidized PE) by 180° and return to register of the chain. As was seen in Ref. 1, n.m.r. experiments indicate the same chain reorientation. This reorientation accounts for the initial and final states of the motion. The path between the sites gives rise to the barrier and defines the detailed mechanism. It is clear that a rigid motion of the reorienting chain is not involved in thick crystals as the following argument shows. The barrier, ΔH^*, for a two site, single relaxation time process is related[2,3] to $\log f_{max}$ as $2\pi f_{max} = 1/\tau = 2k_R$. The rate constant, k_R, is given by absolute rate theory (at T_{max}) as,

$$\ln \pi f_{max} = \ln k_R = \ln k_B T_{max}/h + \Delta S^*/k_B - \Delta H^*/k_B T_{max} \quad (1)$$

For a rigid chain motion, with all the CH_2 units in a given reorienting cyrstal chain turning simultaneously, ΔH^* would be proportional to crystal thickness. Hence $\log f_{max}$ (at constant T_{max}) would decrease linearly with thickness and T_{max} (at constant $\log f_{max}$) would increase nearly linearly. The data (Figure 1, see also Figure 30 of Ref. 1) show, rather, a drop off toward T_{max} or $\log f_{max}$ becoming nearly independent of thickness for very thick crystals. Long ago it was proposed that the chains in paraffins[3,4] must be internally flexible and develop a twist that moves through the crystal (Figure 2). The details of the twist and
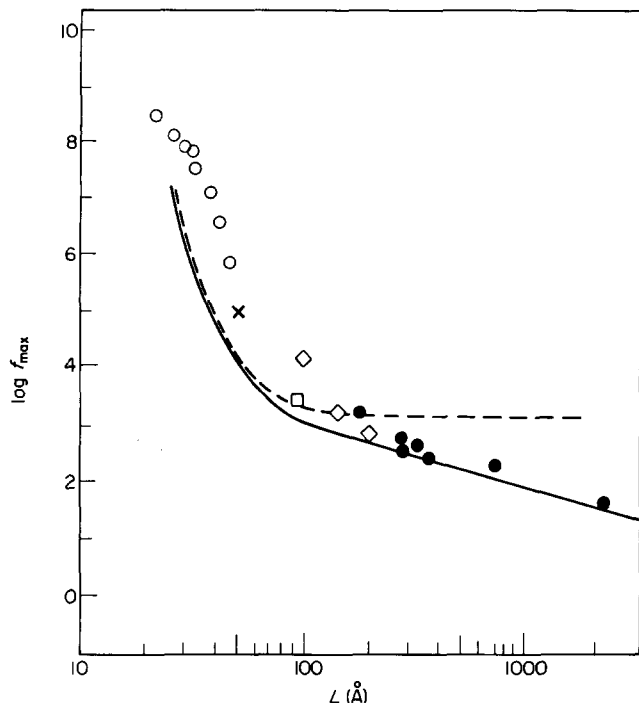
Figure 1 Comparison of experimental and calculated dielectric loss peak locations vs. crystal thickness for a variety of dipole decorated polyethylenes and paraffins[14]. The points are experimental and the curves are calculated on the basis of the localized smooth twist model. The solid curve contains a correction for scattering or trapping of the propagating twist that the dashed curve does not
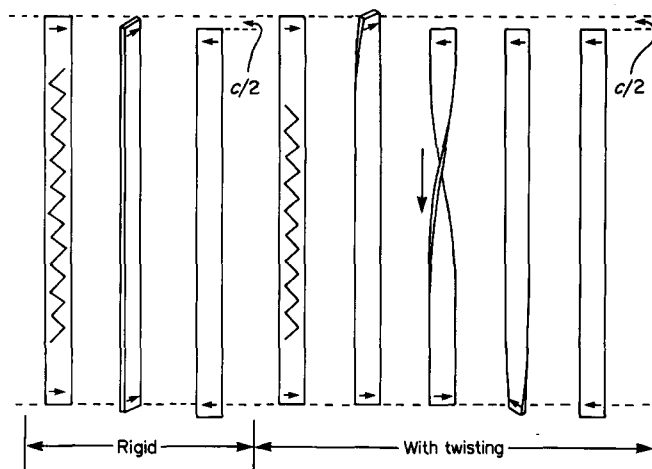

Figure 2 Idealized rendering of a planar zig-zag chain turning rigidly and turning via a twist[14]

how it moves then define the mechanistic path. There are two extreme structures for the twist. The first one is a very gradual twist involving only torsional angle distortions. It has been modelled using elasticity theory or continuum mechanics[4-7]. In their improvement on Froehlich's model, Williams et al.[7] proposed a gradual twist whose length is of the same order as a moderate sized crystal thickness in PE. They did not address a problem that arises in this model when only torsional angle distortions are included. That is, one end of the chain is out of crystallographic register in this model since both 180° rotation (accomplished by the twist) and $c/2$ translation must be accommodated to achieve register. At the other extreme is a model[8,9] based on the Reneker defect[10] where the twist has collapsed into a relatively short buckled section of the chain. The buckling is accomplished in a

manner that shortens the chain by $c/2$ and hence gives crystallographic register on both sides of the twist. Motion of this twist from one site to the next ($c/2$ translation) requires passage over a barrier ($\sim 17\ \mathrm{kJ\ mol^{-1}}$) in addition to the creation energy ($\sim 54\ \mathrm{kJ\ mol^{-1}}$). Eventual motion of a twist created at one surface through the crystal by hopping over the local barrier at each CH_2 site (diffusive passage) results in the desired overall chain reorientation. It is to be emphasized that in the present context this twist cannot be a steady-state or equilibrium defect (subject to creation and disappearance) in the sense of there being an appreciable concentration of such entities (the creation energy is far too high). Rather it must be regarded as the conformational description of a transition state where creation and hopping energies are activation energies. This mechanism suffers from a serious flaw[11]. Since the conformationally defective region is quite limited along the 'c' axis (~ 1 nm), the energetics are independent of crystal thickness even for very thin crystals. Thus the only dependence of relaxation time on crystal thickness would be from the length of the diffusive path rather than from activation energy *per se*. Diffusive crossing of a barrier[12,13] leads to the relaxation time being proportional to the path length across the barrier top, or, $\log \tau = C + \log l$ wher l is the crystal thickness (and C is a constant). The experiments however, *Figure 1*, (see also Figure 30, Ref. 1) show a stronger dependence of $\log \tau$ (or $\log f_{max}$, T_{max}) on thickness in the region $1 < 10$ nm.

As a result of extensive conformational energy calculations another model has been proposed that appears to meet the salient experimental requirements[14]. In result, it incorporates some of the features of the two extremes above. In this model the chain has a twisted region that is quite limited in extent ($\sim 12\ CH_2$ units) but is smooth in structure, in that it involves relatively uniform, modest torsional angle distortions at each bond and no buckling (and little shortening). The smooth twist fits into the lattice much better (lower defect energy) than the buckled one. Taken as an isolated entity this twist, like the long one above[7], generates lattice mismatch at one stem. However it was shown that the lattice forces from surrounding chains distort the mismatched stem elastically (either shortening or lengthening it through valence angle distortions) and gradually bring it back into register away from the twist (*Figure 3*). The dependence of the activation energy on crystal thickness was found to result from this elastic distortion effect. It was further found that the twist (when far enough away from the crystal surface
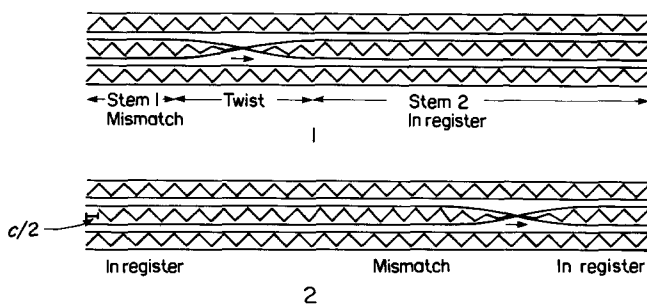
Figure 3 Propagation of a localized smooth twist along the chain. As the twist starts (1) it leaves behind it a translational mismatch. As the twist proceeds (2) the mismatch becomes attenuated at large distances from the twist by elastic distortion of the stem valence angles and bond lengths[14]

for the elastic mismatch energy to reach the asymptotic value) moves with no further expense of energy. Thus there is no local hopping or diffusive character to the motion across the crystal but rather it is largely free-streaming in nature. A correction for trapping of the moving twist in very thick crystals was made. *A priori* calculated activation energies were found to give rise to log f_{max} values in good agreement with the experimental ones (*Figure 1*). The dielectric and n.m.r. processes seem well accounted for by this mechanism and model. In later refinements of the free streaming nature of the twist motion it has been proposed that it has the character of a solitary wave (soliton)[15,16]. Skinner and Park[17] have recently carried out a detailed analysis of α process dielectric data at various specific volumes[18] in terms of the soliton model. A good accounting of the shape (Cole–Cole plots) of the process was achieved.

The mechanical α process

The question of why it is the mechanical process behaves somewhat differently and its relaxation strength is to be assigned to the amorphous rather than the crystalline fraction is now taken up. It is instructive to review the predictions of site or defect theories for anelastic relaxation processes with respect to relaxation strength. Such models for a two-site process (see *Figure 4*) result[19,20] in an expression for the compliance (reciprocal modulus) change through the relaxation $\Delta J = (J_R - J_U)$ as

$$\Delta J = (\bar{N}/RT)(N_a V \Delta \varepsilon)^2 \exp(-\Delta U/RT)/ \\ (1 + \exp(-\Delta U/RT))^2 \tag{2}$$

where ΔU is the energy associated with reorientation of the relaxing entity, $\bar{N}$ is the mole density of entities, N_a is Avogadro's number, and $\Delta \varepsilon$ is the change in strain, on reorientation of the entity, of a volume, V, surrounding it. In other words, for mechanical activity to be present the reorientation (*under zero applied stress*) must involve a strain change. However the dielectric and n.m.r. mechanism detailed above finds the reorienting chain in crystallographic register before and after the reorien-
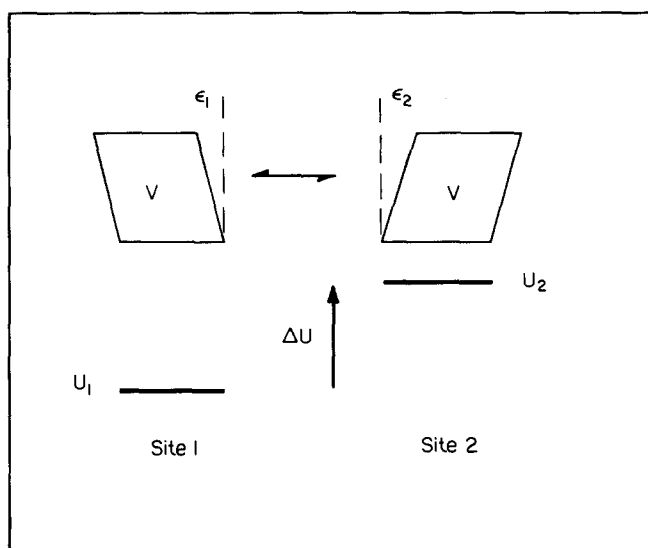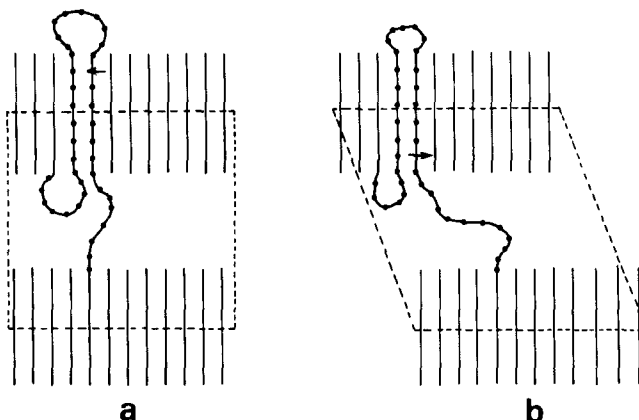
Figure 5 Further relaxation of the amorphous fraction resulting from translational mobility in the crystal (the latter acquired in the α process). Illustrated in this case is reorganization of the interface in (a) through shortening of two loops that in (b) permits lengthening of a tight tie chain which in turn permits more deformation of the amorphous fraction. Also shown is a decorating dipole in the crystal which moves through a number of translational, rotational steps. One such step suffices for dielectric activity
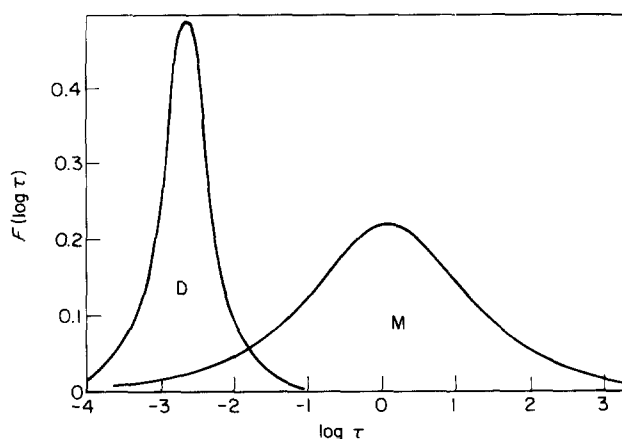
Figure 6 Comparison of the distribution of dielectric (D) and mechanical (M) relaxation times for the α process in similar PE specimens at 50°C[22]

tation. There is no crystal strain induced by it and hence no direct mechanical activity in the crystal. McCrum suggested, however, that the crystal process can couple to the amorphous fraction[21]. The translational component of the motion does lead to the possibility of reorganizing the crystal surface and hence the connections of the amorphous layer chains to the crystal. As shown in Ref. 1, for the amorphous fraction in all semi-crystalline polymers the *relaxed* modulus associated with the glass-rubber relaxation is very high due to the constraints by the crystals. Achievement of crystal stem mobility in the α region through repeated or accumulated $c/2$ translational steps can lead to redistribution of the tight and loose folds, cilia and intercrystalline links that make up the amorphous layer (see *Figure 5*). As a result, further softening of the interlamellar material takes place at a rate controlled by the rate of crystal stem translation (and therefore with the same activation energy). Since repeated translational steps are required it is reasonable that the mechanical process should be somewhat slower and broader than the dielectric or n.m.r. ones as they monitor the individual elementary steps directly. Comparison of the spectrum of dielectric and mechanical relaxation times[22] in similar PE specimens is shown in *Figure 6* and reinforces the

Figure 4 Mechanical relaxation via a two-site jump process. In site 1 the relaxing local entity has energy U_1 and induces a strain ε_1 over the volume, V, in the surrounding matrix. In site 2 it has energy U_2 and induces strain ε_2

hypothesis that, in the time domain, the dielectric process lies at the beginning of a broader mechanical one.

Criteria for the presence of a crystal related alpha process

Finally it is of interest to discuss the molecular structural reasons why a crystalline α process occurs in some polymers and not in others. In the mechanism described above for PE[14] the essential feature is the ability to form a mobile localized structure (i.e. a localized smooth twist) whose motion across the crystal advances the chain translationally and leaves it in crystallographic register. The mobile entity must have low enough creation energy (i.e. activation energy in the attendant rate process) to lead to relaxation times short enough to give rise to an observable process below the melting point. The localized character is necessary to allow motion through increasingly thick crystals without continued increase in activation energy. In POM, IPP and POE (which have mechanical α processes), although the requisite calculations have not been made, it seems reasonable that a localized structure can be formed with reasonable energy that permits advancement by one monomer unit along the chain helix and return to register. For example, in POM the local entity would require a twist of $200°$ about the 'c' axis accompanied by a compression or extension of 0.19 nm (i.e. the helix parameters) in order to form a structure whose motion advances the chain. These parameters seem reasonable in comparison to PE ($180°$ and 0.127 nm) especially since the POM helix is more extensible than the PE planar zig-zag leading to amelioration of the elastic compression or extension energy. An obvious reason for the lack of an observable process is that the local entity creation or advancement energies are too high. Polymers with bulky repeat units would be likely to fall into this category. PET and isotactic polystyrene (which do not have α processes) are to be presumed good examples. There is however an interesting third category that deserves discussion. Aliphatic polyamides and some aliphatic polyesters have planar zig-zag conformations in the crystal and hence are somewhat similar to PE. However the chemical repeat units are much longer. It obviously would not be possible to form a localized mobile structure that incorporates shortening by a whole chemical repeat unit. It is possible to think of the chain advancing by one CH_2 unit at a time by the same mechanism as in PE (see *Figure 7*). However until enough steps had accumulated to advance the chain one repeat unit the chain would be out of register crystallographically. This would give rise to barrier systems like those illustrated in *Figure 8*. The energy associated with the out of register chain (after advancement by CH_2) is denoted as ΔM. The latter energy depends on the misfit energy of one 'X' unit (in a —[$(CH_2)_4$-X]—chain) in the out of register chain and is proportional to the number of such units in that particular crystal stem and hence is proportional to the crystal thickness. The two cases (a) and (b) can be illustrative of the same chemical structure but with the crystal thickness much greater for (b). More to the point here, the two cases can also be illustrative (for the same crystal thickness) of two different chemical structures with the misfit energy of a single 'X' unit being higher for the (b) case than for the (a). Let it be assumed that case (b) represents an overall barrier ($\Delta E^* = V + \Delta M$) that is too high for an observable process to take place but for case (a) it is not. Then it is probable that polyamides (where no
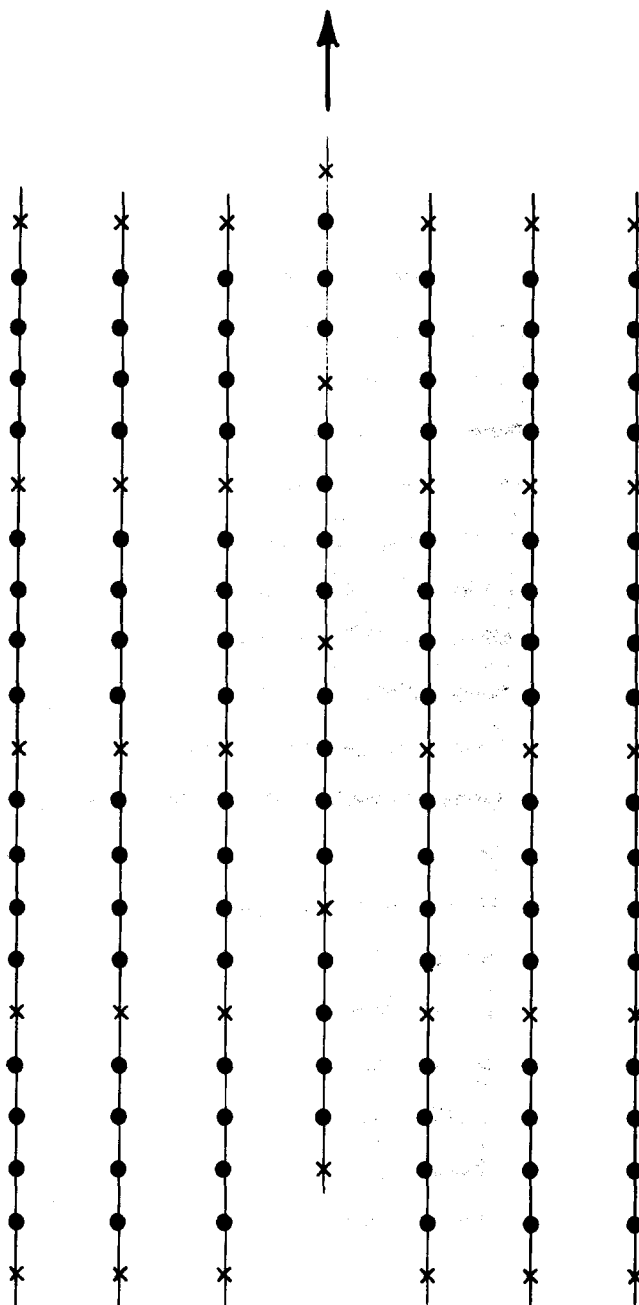
Figure 7 Schematic representation of the translational movement of a chain of structure [—$(CH_2)_4$-X-], ($\bullet$)=CH_2, X could be an amide or ester moiety) through a crystalline array. Translation by one CH_2 at a time leaves the chain in a local energy minimum but with a defect energy proportional to the number of -X- groups in the chain and which are now not in crystallographic register

α process is experimentally observed) represent an example of case (b) behaviour due to high misfit energy. The hydrogen bonding energy associated with the amide groups leads to sheets or layers of the groups in the crystal structure and the disruption of this bonding for advancement of a chain presumably leads to a quite high value for ΔM for ordinary crystal thicknesses. Since there are of the order of 20 amide groups in a typical crystal, a misfit energy of only $5–10$ kJ mol^{-1} per amide group would give rise to $\Delta M = \sim 100–200$ kJ mol^{-1}, enough to raise ΔE^* to a range where the process cannot be observed below the melting point (ΔE^* for LPE is ≈ 100 kJ mol^{-1}). However the aliphatic polyesters may well represent an example of case (a) behaviour. It is certain that disruption of 'c' axis register in aliphatic polyesters is much less costly energeti-
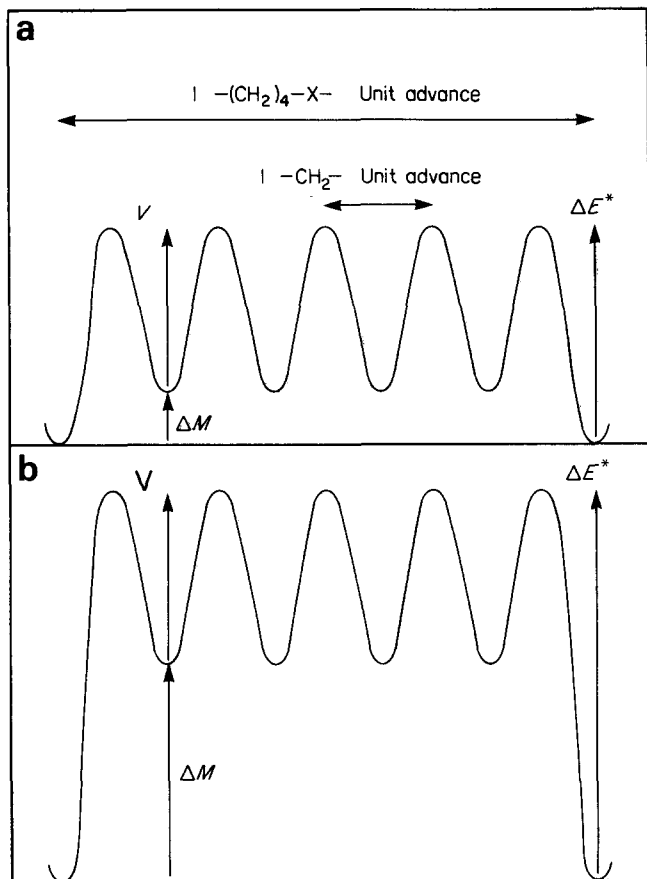
Figure 8 Schematic α process energetics in a chain of structure of [–(CH₂)₄–X–] (see *Figure 7*). As the chain advances by one –CH₂– the energy goes through a local maximum and minimum and after five steps regains crystallographic register. The misfit energy, ΔM, depends on how many –X– groups misfit and hence crystal thickness. Case (a) could be for a thin crystal and (b) for a thick one, both for the same type of chain. Since ΔM depends on the size and structure of the –X– group, case (a) could also represent a relatively well fitting –X– group and case (b), a relatively poor fitting group –X'–, both for the same crystal thickness

cally than in polyamides. In fact there is experimental X-ray diffraction evidence that 'c' axis disordering occurs easily in samples that are not carefully annealed[23,24]. Although the experimental situation with respect to observation of α processes in aliphatic polyesters is not yet completely clear it is apparent that some members do exhibit one[25,26].

The above mechanism provides mechanical activity via the effect of crystal chain translation on the constrained amorphous fraction. However the return to register of crystal chains precludes the direct observation of the crystal process dielectrically in any but defective or irregular chains (like dipole decorated IPE). This feature seems to be in accord with experiment. No dielectric α process has been found in POM or POE[27], both of which have mechanical ones[1,28]. Poly(vinylidene) fluoride (PVDF) shows a crystalline dielectric process[29], and it may be that the well-known head-to-tail defects are necessary for its activity.

THE β OR α_a RELAXATION

In Ref. 1 the background for associating the β relaxation (or α_a relaxation in polymers where there is no crystal related α process) with the amorphous fraction glass–rubber relaxation was developed. This relaxation differs

from that in wholly amorphous polymers in being much broader in the frequency domain than in the latter type. Mechanically the limiting relaxed amorphous phase modulus is very high (of the order of 100 MPa) due to the constraining influence of the crystals. Dielectrically this immobilization can result in the inability of amorphous phase dipoles to relax over all spatial directions as manifested by a reduced dipole relaxation correlation factor. Both the relaxed modulus and the relaxed dielectric constant are strongly temperature dependent, the former decreasing and the latter increasing. These circumstances are to be presumed to be the result of amorphous chain configurations that are relatively unfavourable energetically due to constraints imposed by the crystals becoming thermally populated. In wholly amorphous polymers the glass–rubber relaxation involves generalized segmental motion. The equilibrium relaxed modulus associated with the relaxation in a crosslinked material is treated by the theory of rubber elasticity. In uncrosslinked materials the relation between the temporary plateau modulus and entanglement density is a subject of current interest in rheology. Although the longer range dynamic modes may be represented by the Rouse–Zimm theory there is no comprehensive molecular theory of the kinetics of the glass transition. In semicrystalline polymers the situation is obviously even more complicated and a molecular theory for the amorphous fraction glass–rubber relaxation cannot be expected at present. There has been some work on treating limiting static properties such as the relaxed modulus. There have been attempts to model the relaxed modulus using rubber elasticity concepts. Some years ago Krigbaum et al.[30] treated the immobilizing effect of the crystals on the amorphous fraction by finding the effect of further crystallization on an amorphous segment that is initially laid down as a tie chain between two advancing crystal surfaces. The originally deposited chain was assumed to have unperturbed conformations but subsequent crystallization was found to greatly extend the segment (requireing inverse Langevin statistics). In fact the extension was found to limit the degree of crystallization and an expression for the equilibrium degree of crystallinity as a function of temperature was obtained as was an expression for the equilibrium relaxed modulus as a function of temperature. The resulting modulus equation was equivalent to handling the crystal–amorphous mechanical connectivity or composite problem by assuming additive compliances (Reuss lower bound behaviour) and assigning zero compliance to the crystals. Most important however was the finding that parameters consistent with measured dependence of degree of crystallinity on temperature were also consistent with measured moduli and their temperature dependence. The equilibrium amorphous modulus was calculated to be very high and to decrease strongly with increasing temperature. More recently Lohse and Gaylord[31] have presented detailed calculations using Gaussian statistics of the contribution to the modulus of folds of various lengths, cilia, floating chains and tie chains all in the presence of the confining effect of lamellar surfaces. Without knowing the proper mix of these entities it is not possible to calculate an amorphous phase modulus but it is apparent that reasonable mixtures give very high equilibrium moduli.

Several attempts have been made to model the effects of the contraining influence of the crystals on amorphous

chain reorientation in order to interpret n.m.r. relaxation experiments. Schmedding and Zachmann[32] treated the case of segments of various lengths reorienting under the restraining effect of the ends being tied to fixed points. Rosenke *et al.*[32] applied similar methodology in their study of deuteron n.m.r. line shapes. Douglass and coworkers have considered the constraining effects of folds and cilia[34,35].

In the context of understanding the morphology of semicrystalline polymers there has been a great deal of interest in describing how the amorphous fraction is connected to the crystals. Guttman *et al.*[36] have given a statistical argument for arriving at the relative number of loops, bridges and tight folds. It has been possible to carry out a Monte Carlo simulation of the interconnection[37,38]. A detailed lattice theory description of the problem has also recently been carried out[39,40]. As yet none of these treatments have application to relaxation properties as such questions as relaxed moduli have not been addressed.

With respect to dynamics it is obvious that little can be done at present to theoretically model the segmental motion. However in view of the narrowness of the relaxation width in wholly amorphous polymers compared to the very wide relaxation in the amorphous fraction in semicrystalline polymers it is interesting to speculate as to whether there is some approximate correspondence between portions of the relaxation time spectrum and topological entities related to the amorphous phase and its interaction with the crystals. For example it might be that the shortest times are associated with motions of very loose folds and relatively non-extended tie chains, longer times with tighter or more extended tie chains and perhaps relatively not so loose folds and that tight folds are unable to relax in this region. As stated above, the temperature dependence of the relaxed modulus and dielectric constant are probably manifestations of significant energy differences between multiple conformations of the same constrained entity such as a relatively tight loop. It is to be emphasized however that, as far as is now known, the relaxation spectrum is a smooth one with all of these relaxing entities, from those closely associated with the crystal surface to those associated with unconstrained amorphous segments, contributing to the same process. There is no experimental evidence for treating an interfacial region as a separate structure as far as relaxation behaviour is concerned. For example, in many semicrystalline polymers the dielectric spectrum can be measured directly over wide frequency and temperature ranges and in these cases although it is very broad there is no evidence for structure in it (see Ref. 1). In n.m.r. studies a number of workers, especially in interpreting T_2 values from time traces in pulse experiments, have invoked contributions from three components, the crystals, the amorphous fraction and an interfacial region. No doubt the introduction of the third component (the interlayer region) is a useful improvement over representing the amorphous fraction by just a single T_2 contribution. However doubtless if the dielectric spectrum is any clue and considering the limited extent of the n.m.r. time traces this is in turn just a first approximation to a very broad distribution, one that results from amorphous phase segmental motion in general and includes the constraining influence of the crystals.

The β relaxation is considerably more prominent in bPE than in lPE. This can be given a reasonable explanation in terms of their chemical structural differences. First, in mechanical experiments the difference can be traced phenomenologically to the fact that the relaxed β process modulus is significantly lower in bPE than in lPE (see Table 2 in Ref. 1). This increases the relative intensity of the β process and decreases that of the α in bPE (a further but more minor effect is that the unrelaxed γ process modulus in bPE is slightly lower in bPE, thus decreasing the γ intensity slightly). On a molecular basis the reason for the lower relaxed β process modulus in bPE is not hard to see. Inevitably, the rejection of branches during the crystallization process will lead to a more loosely organized amorphous fraction with larger loops, less tight folds, less taut tie chains etc. This less constrained amorphous fraction is capable of relaxing to a lower limiting rubbery modulus. Similar considerations would hold for the effect of more limiting mobility in increasing the strength of the β process in n.m.r. and dielectric experiments.

Finally, it is perhaps appropriate to comment on some alternative interpretations of the glass–rubber relaxation since historically they have received considerable attention and it now appears that the major points of difference have largely been resolved. The alternative arguments could be expressed something like the following. The β relaxation in highly crystalline polymers such as lPE is rather diffuse and difficult to resolve from the neighbouring γ and α relaxations. This led some investigators[41] to question its existence and therefore assign the γ relaxation as the glass–rubber relaxation. However as the result of further admirable experimentation there is now agreement that there is a β relaxation in lPE[42]. The only remaining point of contention is the interpretation of the β *versus* the γ processes. It has been proposed[43] that the β relaxation in both lPE and bPE arises in the interfacial region between the crystal and amorphous phases. However, as detailed in Ref. 1, in a number of important examples (including bPE, see Figures 33 and 34 in Ref. 1) β relaxations can be traced (through crystallinity variation) clearly and unambiguously directly to the glass–rubber relaxation in the completely amorphous polymer where no interfacial region exists. As commented on in Ref. 1 and above, there are profound changes in the relaxation parameters with the onset of crystallinity but the process itself is present in both the completely amorphous and semi-crystalline forms of the polymer. Similarly, γ processes are directly traceable between the completely amorphous and semi-crystalline conditions (and in this case with very little sensitivity to the onset of crystallinity). Whatever general interpretation is given to the β and γ processes in semi-crystalline polymers it must hold in the completely amorphous state as well. A view has been expressed[44] that correlation times deduced from T_1 values from n.m.r. measurements on lPE and bPE are not consistent with the β relaxation being a glass–rubber relaxation. Actually when the correlation times found (approximately 3×10^{-7} to 1×10^{-10} s, $-35°C$ to $0°C$) are compared via a 'relaxation map' with other measurements (mechanical, dielectric and proton n.m.r., see, for example, Ref. 1 Figure 29 and Ashcraft and Boyd[45], it is seen that the values agree well and correspond to a relaxation region to be described as largely merged β and γ processes. (The high temperature merging is typical of all

polymers showing glass–rubber and sub-glass relaxations.) The overall relaxation maps for IPE and bPE are quite characteristic of polymers showing high activation energy glass–rubber and low activation energy sub-glass processes. The role of specific heat measurements in describing the relaxation processes in IPE[46,47] has also been controversial and was discussed in Ref. 1. There it was pointed out that although inherently a relatively low resolution 'integral-like' method (as opposed to 'derivative-like' dynamic loss peaks) heat capacity does indeed show the presence of relaxations in each of the α, β and γ regions in a manner similar to other low frequency relaxation methods (see Figure 35, Ref. 1). Thus the measurements are consistent with the interpretation of the β process given here. The use of thermal expansion measurements in studying relaxations has been discussed in the literature[41,48] but only mentioned in passing in Ref. 1. Again this is inherently a low resolution method and in view of the agreement now that there is a β process in IPE this discussion will not be developed further here. It need only be emphasized that thermal expansion or heat capacity like other properties can be expected to give rise to an increment with any relaxation process and the size of the increment will probably correlate with the relaxation strength of the process as measured by other methods. Thus with respect to the β relaxation in semi-crystalline polymers immobilization of the amorphous phase by the crystals can be expected to broaden and make more diffuse the change in thermal expansion and reduce the increment in a manner analogous to modulus or dielectric constant. There is a context in which comment on thermal expansion is of interest with respect to amorphous phase organization and relaxation. In single crystals of IPE Fischer and Kloos[49] found via small angle X-ray diffraction measurements that the difference in thermal expansion coefficient between crystal and amorphous phases was rather independent of temperature down to the γ relaxation where a break occurred. It is probably true that the amorphous layer in single crystals is more immobilized than in bulk crystallized polymers (the relative proportion of more confined surface associated entities being enhanced). This would lead to even less prominence of the β process than in bulk crystallized specimens.
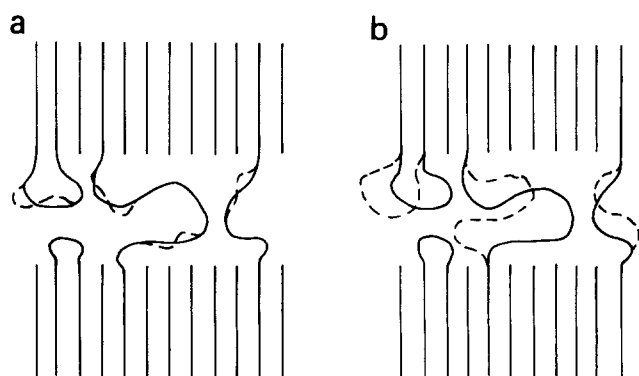
THE γ RELAXATION

As developed in Ref. 1, γ relaxations (or designated β if no crystalline phase associated α process is present) are characterized by occurring in the amorphous fraction, by the location, width and phase relaxation strength being quite insensitive to morphological factors such as the presence or degree of crystallinity or degree of deformation in oriented specimens and by having Arrhenius temperature behaviour of the central relaxation time with modest activation energy. The higher temperature β process, associated with amorphous phase segmental motion characteristic of a glass–rubber relaxation, is quite sensitive to the presence of the crystal phase, especially with respect to relaxation breadth and relaxed mechanical modulus, and to a lesser extent, relaxation location and dielectric relaxation strength. The temperature dependence of the central relaxation time is Williams–Landel–Ferry-like with higher activation energy and entropy than for the γ relaxation. A γ relaxation whether in a wholly amorphous polymer or in the amorphous fraction in a semicrystalline polymer is extremely broad in the frequency or time domain. This contrasts with the β relaxation which is similarly broad in semicrystalline polymers but much narrower in wholly amorphous ones.

Localized conformational transitions

The above features indicate that γ processes are to be regarded as 'sub-glass' relaxations. They further suggest that γ processes involve molecular motions that are relatively short range in character in comparison with those associated with the glass–rubber (β) relaxation. That is, they involve relatively simple conformational motions that are possible in an otherwise glassy matrix that is quiescent with respect to the generalized longer-range segmental motions characteristic of the glass–rubber relaxation (see Figure 9). Efforts have been made to identify conformational transitions in a PE chain that would be local in nature (leaving the attached molecular stems adjacent to the bonds undergoing transition *relatively* undisturbed) and in addition would have favourable energetics in the sense of leading to a modest activation barrier. The energetics would include an internal or intramolecular contribution as well as one of intermolecular origin sensitive to the swept-out volume accompanying the conformational transition. With respect to the first requirement, there are two simple conformational transitions that are local in nature and leave the stems disturbed not at all. The first of these is a 'three bond' motion. The conformational sequence TGT permits the move to TG'T (see *Figure 10*) without disturbing the stems[50,13,51]. The next one is a 'five bond' motion involving the sequence TGTGT[52–54]. Here the stems are colinear and the internal sequence of bonds does not change conformation, just the adjacent stem bonds (see *Figure 10*). Because the five bond motion involves conformational changes only at the stem junctions, it is popularly referred to as a 'crankshaft' motion. There has been a tendency to generalize the term to mean any motion that leaves the stems undisturbed. The Boyer (three bond) and Schatzki (five bond) motions can be viewed as the simplest allowed moves of a tetrahedrally bonded chain on a diamond lattice that leave the stems in place. These transitions obviously satisfy the first requirement, leaving the stems relatively undisturbed. With respect to the second, that the swept-out volume and the internal energetics lead to modest energy requirements, the situation is less favourable. The internal energetics of


Figure 9 (a) Schematic representation of molecular motion localized or confined to certain portions of amorphous chains and postulated to be of the type responsible for γ relaxations. (b) More general amorphous phase segmental motion underlying the β (glass–rubber) relaxation
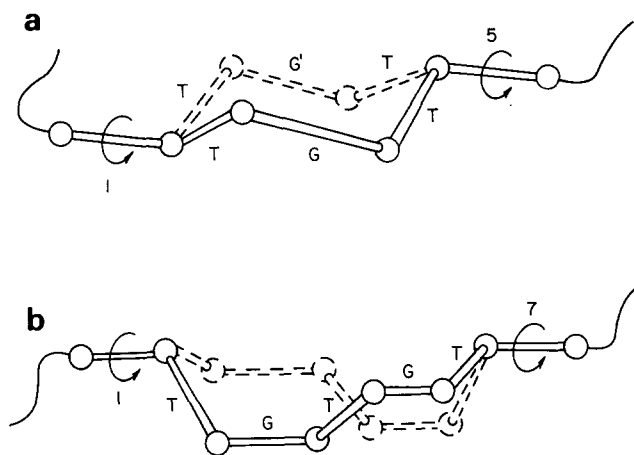
Fifure 10 (a) A three bond crankshaft motion. The conformational sequence TGT (full bonds) can, along with conformational changes in bonds 1, 5, undergo transition to TG'T (= = = = =) without disturbing the stems. The before and after portions form a cyclohexane ring. (b) A five bond crankshaft motion. The conformational sequence TGTGT can undergo rotation about the colinear stem bonds 1, 7 (without change in conformation of the centre five bonds)

the five bond transition are modest. However the transition clearly appears to require too much volume to be allowed in the context of a motion in a glassy matrix. In the three bond transition direct crankshaft-like rotation about the stem bonds involves a double barrier system with an intermediate energy minimum[51]. The internal motion over one of the barriers requires very little swept-out volume and should be rather insensitive to the presence of the matrix. The motion associated with the other barrier does require significant volume and is thus inhibited by the matrix. Thus a complete three bond move via stem bond rotation is not a favourable motion. Just as important, neither the three or five bond motions can be expected to give rise to significant mechanical activity. The latter is associated with stress biasing of strains (i.e. changes in shape). The three and five bond moves relocate a section of a chain locally but do not induce a shape change.

There is a motion closely related to the 3 bond one above that does accomplish shape change along with fulfilling the requirements with respect to intra- and intermolecular energetics. The conformational sequence GTG' occurring in an otherwise all *trans* chain (e.g. ...TTTGTG'TTT...) has the effect of leaving the planar zig-zag all *trans* portions parallel to each other but non-coplanar or displaced from each other, see *Figure 11*[55,13]. This conformational entity has been called a kink[55]. Interchange of the senses of the *gauche* bonds,
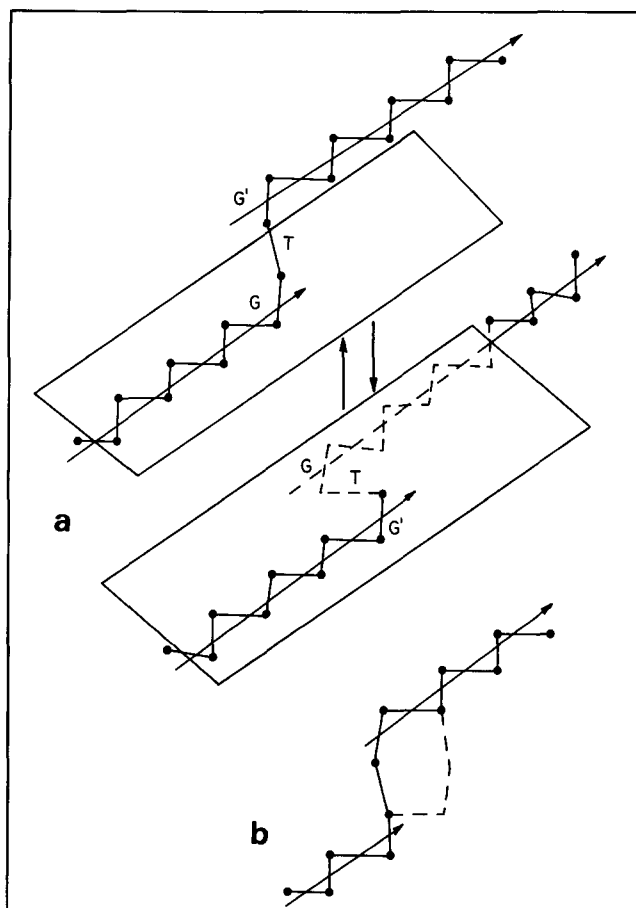
...TTTGTG'TTT...→...TTG'TGTTT...
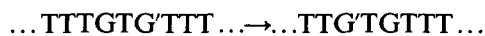
converts the kink into a mirror image of itself (*Figure 11*). Left-hand–right-hand kink inversion or interconversion involves very little swept-out volume and requires a modest activation energy[51,56,57]. Very importantly, although the stems are relatively undisturbed by interconversion they are displaced somewhat. This allows the possibility of mechanical activity. The change in stem displacement gives rise locally to a change in shape that can be propagated through the specimen as a shear strain field (see *Figure 12*). It is important to realize that the state produced on kink interchange involves stem displacement and therefore is not an allowed move in a strict

diamond lattice simulation (with ends fixed) of chain motions. Such simulations[58,33] miss kink inversion.

Kinks can advance via a 3 bond crankshaft move (see *Figure 11*) allowed on the diamond lattice (with chain ends fixed). Since advance is allowed on the lattice it will not contribute significantly to mechanical activity. Kinks can rather easily unkink ...TGTG'T...→...TTTTT...[56]. It seems very probable[56,18] that a concerted kinking unkinking process can lead to quite high mobility of the kinks in predominately *trans* chains. It is to be noted that kinking, unkinking would induce a tensile strain (the kinked section is shorter than the all *trans* sequence) and hence be mechanically active. However because of the differing numbers of *gauche* and *trans* bonds in the kinked and unkinked states there should be site energy differences that would limit relaxation strength (see below). To summarize, three and five bond crankshaft motions, per se, do not appear to be promising candidates for a localized motion mechanism for the γ relaxation of the grounds of excessive swept-out volume and lack of mechanical activity. Kink inversion however does appear to have the requisite properties.

Application in models

After having sorted through various possibilities for a satisfactory localized conformational transition in a PE

Figure 11 Kinks and kink inversion. (a) The conformational sequence ...TTTGTG'TTT... has parallel offset planar zig-zag stems (indicated by arrows) on either side of the GTG' portion. The transition TGTG'T→TG'TGT (called here kink inversion) creates a mirror image of the kink about the displaced stems. (b) A three bond crankshaft move is shown at a kink site (as dashed lines). This move results in advancing the kink along the chain by 2CH$_2$ units
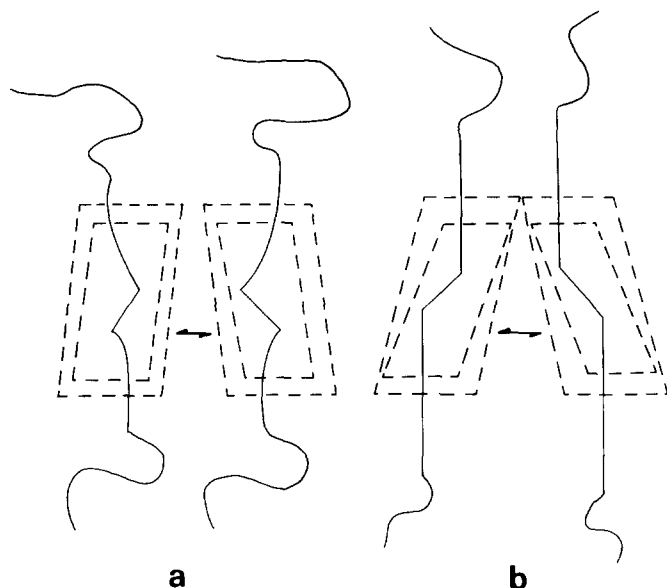
Figure 12 (a) Strain fields set up by stem displacement accompanying kink inversion. (b) Possible more complete relaxation of stems following 'adiabatic' transition in (a)

chain and found that there is a possible candidate the question of whether a satisfactory model or theory can be built around this candidate must be addressed. The answer is, this has not been accomplished. So far modelling has been restricted to independent site models. The activation energy of the PE γ relaxation can probably be accounted for by an independent site model incorporating inversion of isolated kinks. This is stated as probable because although it seems clear that the swept-out volume in the matrix is small enough to permit the process, the interaction with the matrix does contribute to the activation energy. Indeed, the mechanical activity depends on the strain induced by the stem displacement on conformational transition (inversion in the case of kinks), a matrix effect. This interaction can be only crudely simulated at present. The activation energy is however only one characteristic of the relaxation and the others are more difficult to account for. The relaxation is very broad and narrows with increasing temperature. The activation entropy, although not nearly as high as for glass–rubber relaxation is nevertheless quite large, of the order of 150–250 J K^{-1} mol^{-1} (dielectrically). Both of these facts indicate considerable cooperativity and that therefore an independent site model is inadequate. However, it is possible that the temperature dependent broadness and the activation entropy could be manifestations of the effects of fluctuations in packing environments expected in a glassy matrix on localized conformational transitions and that the independent site model could be a useful first approximation.

Comparison of estimated relaxation strengths of the mechanical and dielectric processes in localized site models with experiments is an important test. To carry out such comparisons the consequences of a localized conformational transition must first be considered more carefully. In a strict interpretation of the stems being imbedded in a glassy matrix the transition might be considered as 'adiabatic'. That is, no disturbance of the matrix takes place beyond a more or less instantaneous elastic distortion after the conformational jump. In the case of a mechanically active transition, such as kink

inversion is postulated to be, this leaves the stems in a stressed state uncharacteristic of a quasi-equilibrated glass. The question is then, do they remain in this state or is it possible through accumulation of fluctuations (including those arising from other similar transitions elsewhere in the matrix) to dissipate this stress and for the stems to relax to an unstressed state. For example, in *Figure 12* (a) could represent the adiabatic transition but this could be followed by relaxation to an unstressed kink such as represented by *Figure 12* (b). The stem relaxation would not compromise the mechanical activity. In fact it could be greatly enhanced if, as seems reasonable, the stem displacements still serve as strain markers.

In pursuing relaxation strength comparison the dielectric case is taken up first. In a dilute independent site model the correlation factor, g, appearing in the Kirkwood–Onsager equation,

$$\varepsilon_R - \varepsilon_U = \frac{3\varepsilon_R}{2\varepsilon_R + \varepsilon_U}\left(\frac{\varepsilon_U + 2}{3}\right)^2 \bar{N}\mu^2 g/3k_B T \qquad (3)$$

(where R and U refer to relaxed and unrelaxed dielectric constants, μ to dipole moment and $\bar{N}$ to number concentration of relaxint entities) can be expressed as (for two sites),

$$g = 2(1 - \cos\gamma)F \exp(-\Delta U/RT)/(1 + \exp(-\Delta U/RT))^2 \qquad (4)$$

In the latter equation, F is the fraction of dipoles capable of relaxation, i.e. properly situated at the proposed relaxing conformational entity such as a kink, ΔU is the site energy difference and γ is the angle through which the dipole relaxes in traversing between the two sites. In the case of kink inversion ΔU is expected to be zero. In the strictly adiabatic interpretation, the maximum angular excursion for a dipole would be for one located at either end of the centre bond in the sequence GTG'. This excursion would be about 120°. These considerations lead to $g = \sim 3/4F$. Allowing for some relaxation from dipoles situated not at this site but at nearby bonds suggests the approximation $g \approx F$. The number of relaxing entities can be estimated from statistical mechanics if some temperature where the conformational population is frozen-in can be assumed and if the population is not grossly perturbed by the crystal imposed constraints. This temperature presumably is to be taken somewhere in the β relaxation region. For an energy of 2500 J mol^{-1} and $T = 240$ K the statistical weight (Boltzmann factor), f, of a *gauche* bond is 0.285. If it is assumed that the minimum conformational sequence necessary for an invertible link is –TGTG'T– then in the independent bond approximation the chance of a position in an inverting kink pair occurring at a given chain atom is $f^2/(1 + 2f)^5 = 0.0085$. However incorporating the suppression of GG' sequences in the near-neighbour bond-pain interaction model increases this number to 0.012. If the fraction of dipoles relaxing is taken to be the same as the chance that a given chain atom is favourably located (i.e. assuming that a dipole decorated chain atom has the same conformational statistics) then $F = 0.024$ since there are two positions for the dipole to be located (at either end of the centre T bond). Experimentally measured values of F (under the approximation $F = g$) lie in the range 0.08–0.20 for PE[45]. For aliphatic polyesters measured values of F are 0.05–0.10[59]. The effect of an ester group participating in a kink

in altering the conformational statistics of a PE chain are likely to be more profound than for a decorating carbonyl or chlorine and have not yet been worked out. However it is likely that kink concentration in aliphatic polyesters is higher than in PE since *gauche* bonds occur with higher probability adjacent to the ester group. On balance however it would appear that the values of dielectric strength estimated from a model incorporating kink inversions in the strictly adiabatic interpretation are low in comparison with in experiment. The adiabatic case incorporates only the immediate angular excursion accompanying the idealized transition. Since it is very possible that further significant rearrangement of the packing environment ensues, accumulation of these rearrangements attending many localized conformational transitions could appreciably enhance the total average angular excursion of a typical dipole. [On a larger scale an analogy might be the rotation of a pendant dipole about a single bond in a three state chain. If only one bond were considered it might be concluded that complete spatial relaxation does not accompany the three site motion. It is obvious that the accumulation of these rotations from all bonds does result in complete relaxation even though it is difficult to theoretically describe in detail how this happens, even in molecules of a few bonds.] It is not yet known whether more extensive dipole excursion than indicated by the adiabatic interpretation would in fact result from a proper model of localized conformational transitions. However the inadequacy of the strictly adiabatic interpretation is apparent.

A similar comparison for mechanical relaxation strength can be attempted. However the difficulties in doing so are much more severe. In equation (2), in the case at hand, $\bar{N}$, the kink concentration, can be taken to be the concentration of CH_2 units times the chance, F, that a chain atom is properly situated in a kink or $\bar{N} = FN(CH_2)$. Thus F is the same factor introduced in the preceding paragraph. In the dielectric case a good estimate of the change in moment when the dipole reorients between sites (i.e. leading to $2\mu^2(1 - \cos \gamma)$) can be made. In the mechanical case the analogous quantity is the strain change at a given volume (i.e. $(\Delta \varepsilon V)^2$). It is much more difficult to estimate the latter. About all that is known concerning it in the strictly adiabatic context is a calculation of the strain induced by a kink in a *crystalline* environment in PE[56]. This calculation led to a shear strain between the '*a*', '*b*' diagonal and the '*c*' axis of 0.04 measured at one unit cell surrounding the centre T bond of the kink. Actually equation (2) applies only to the situation where the defects (strain sources) have the same orientation, the matrix is isotropic and surface effects are neglected. In the case of randomly oriented defects a factor of 4/15 is introduced on averaging and surface or image forces increase the strength by ~4[60]. In the crystal, or locally in the amorphous phase, the environment is far from isotropic. The effect of this anisotropy is not known. Applying equation (2) as is, using the same value of F as above (0.024), setting $\Delta \varepsilon = 2 \times 0.04 = 0.08$ and $V = 92$ Å^3 (the unit cell volume) results in (at 175 K) $\Delta J = \sim 0.006$ GPa^{-1}. Experimentally for the γ process in PE the relaxed amorphous phase shear compliance is about 2.8 GPa^{-1} and the unrelaxed is about 0.3 GPa^{-1}.[22] Obviously the model result is far less than the experimental value of 2.5 for ΔJ. If the kink relaxes completely after inversion then the strain will be considerably higher (cf. *Figure 12(a)* and

(*b*)). This would bring calculated values of the strength closer to experiment (especially considering the square dependence on strain) but whether sufficiently close for satisfactory agreement remains problematic.

Next the implications of n.m.r. measurements for model considerations are discussed. Olf and Peterlin[11] in their analysis of proton broad-line spectra concluded that kink reorientation underestimates the degree of narrowing actually found through the γ process in PE. Sillescu and Spiess and their coworkers in their deuterium quadrupole studies on PE[33,61-63] have interpreted the line shapes in terms of rigid bonds, reorientations of C–D bonds moving between 2 sites separated by the tetrahedral angle, between 3 such sites, and, more general motions. The 2-site jumps were interpreted as arising from kink advance (i.e. one of the three bond crankshaft motions, see above). The 3-site jumps arise from five bond crankshaft motion. Rigid bonds, 2- and 3-site tetrahedral jumps each have characteristic line shapes. They concluded that in going through the γ region in temperature the line shape remained that of a highly motionally hindered material but that a majority of the C–D bonds acquired 2-site mobility. This is obviously not consistent with the estimate from conformational statistics referred to above that only about 2% of the CH (or CD) groups are associated with kinks. The question of kink inversion was not addressed in the n.m.r. interpretation. There do appear to be some technical difficulties in assessing the degree of motional freedom from the line shapes. In the γ region the 2- and (3-) site fast exchange limiting line shapes are not observed. The degree of participation of 2-site processes has to be inferred from a rather minor decrease in intensity in the centre of a two line spectrum that results from the near slow exchange limit. However again it appears that the degree of motional freedom exceeds that possible from reasonable estimates of the number of kinks inverting or, as interpreted in this case, kinks advancing (three bond motion).

There is information from n.m.r. concerning sub-glass secondary relaxation in other polymers. Jelinsky *et al.*[64] have studied deuterium resonance in poly(butylene terephthalate) with the centre two methylene groups of the butylene sequence deuterium labelled. They concluded that the motional process was consistent with a 2-site jump of the C–D bonds that would accompany a torsional transition about the connecting C–C bond of 103°. They speculated that the most likely source of this transition was kink inversion.

It is apparent that in the dielectric, mechanical and n.m.r. cases experiments show that motion is highly hindered. However direct application of independent site models for conformational transition, especially in the adiabatic interpretation, underestimates observed relaxation strength (degree of motional freedom). Obviously the question arises as to whether it is the concept of localized transitions that is wanting or rather the ability of independent site models to adequately represent the consequences of localized motions. In any event it must be concluded that although localized conformational transitions might be the proper concept underlying the γ relaxation satisfactory models for quantifying the concept are yet to be developed. Such models must address the very broad frequency spectrum and high activation entropy nature of the process as well as relaxation strength.

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