(15) P. J. Flory and S. Fisk, *J. Chem. Phys.*, **44,** 2243 (1966).
(16) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.
(17) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940.
(18) E. F. Casassa and T. A. Orofino, *J. Polym. Sci.*, **35,** 553 (1959).
(19) R. F. Hoffman, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pa., 1969.
(20) S. K. Gupta, R. F. Hoffman, R. E. Hughes, and W. C. Forsman, in preparation.

The Conformational Analysis of Crankshaft Motions in Polyethylene[1]

Richard H. Boyd* and S. M. Breitling

Department of Chemical Engineering and Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112. *Received March 26, 1974*

ABSTRACT: Conformational changes involving sequences of only a few bonds (crankshaft motions) in chain segments residing in amorphous domains have for some time been proposed as the basis for the γ relaxation in polyethylene. The energetics of the Schatzki (five bonds between stem bonds) and Boyer (three bonds between stem bonds) crankshaft motions have been investigated here by means of conformational energy calculations. In the isolated chain the five-bond motion is found to be as Schatzki proposed, a single barrier determined by the sum of the barriers in the rotating colinear stem bonds. The Boyer crankshaft motion in the isolated chain is found to involve two barriers separating a strained stable intermediate state from the initial and final states. One of the barriers can be described as semirigid motion about the stem bonds much in the manner of the Schatzki motion. The other barrier, passage over which is required to complete the motion, can be described as a "flip–flop" of two gauche bonds of opposite sense separated by a trans bond $\cdots$ G′(TGT)– $\rightarrow$ $\cdots$ G(TG′T)– where the first gauche bond is one of the stem bonds and the other is the center bond in the three-bond sequence interior to the stem bonds. Calculations of the effect of a surrounding matrix indicate that motion over the flip–flop barrier to the stable strained intermediate requires very little swept out volume and is not significantly influenced by the matrix. The motion over the other barrier involves considerable swept out volume and is significantly inhibited by the matrix. From these results, it is also concluded that the Schatzki motion cannot take place in a glassy matrix. A model for the amorphous component of the γ relaxation in polyethylene is proposed in terms of the motion between $\cdots$ G′TGT sequences (frozen in at the glass temperature, or β transition) and the strained intermediate state over the flip–flop barrier (and perhaps also influenced by the complete motion over both barriers). The breadth of the transition is ascribed to several relaxation times associated with differing barrier systems resulting from several possible conformations adjacent to the $\cdots$ G′TGT sequences and perhaps also to the double barrier nature of each system. The height of the calculated barriers is consistent with the location of the γ process in the T, ν domain. The increase in intensity of the transition with temperature is ascribed to the energy differences between the initial and intermediate states. The energy of the strained intermediate state should be sensitive to mechanical deformation and thus the flip–flop barrier motions should be mechanically active.

The identification of molecular mechanisms associated with the relaxation behavior of polymers has suffered from a lack of tractable models for which comparisons of predicted and measured properties can be made. In particular a useful quantitative description of the highly cooperative long-range segmental motions associated with the glass–rubber transition seems to be highly elusive. A number of suggestions of varying degrees of completeness have been made concerning the nature of other transitions. The α transition in polyethylene is thought to be a process taking place within the chain-folded crystalline lamellae.[2] Hoffman, Williams, and Passaglia[3] have proposed a site model involving a rotation of the chain as a nearly rigid unit. McCullough[4] has presented a more detailed and sophisticated treatment of this motion. Other proposed motions associated with the crystalline phase have involved defect structures such as chain-end induced row vacancies,[3,5] motion of a defect chain twist[3] (Reneker defect[6]), and fold reorientations.[7] Another mechanistic suggestion involves the amorphous phase contribution to the γ transition in polyethylene (and other linear polymers). The low temperature (−120°, 1 Hz) at which this transition occurs and its modest activation energy (∼11–15 kcal/mol[2]) suggests that it must involve a molecular motion of a particularly simple type[8–11] (crankshaft motions) uncoupled from the longer range highly cooperative segmental motion usually associated with glass–rubber transitions (and considered by many to be responsible for the β transition on polyethylene[2,3]).

Recently, computational methods have been developed that permit the calculation of the minimum energy path for conformational changes involving the cooperative motion of a number of bonds.[12–14] In addition, advances in conformational computational methods[15] have resulted in much improvement in the energy functions and parameters for hydrocarbons to be used in quantitative conformational calculations.[16] Thus, it now seems opportune to undertake the calculation of the energetics of the conformational changes associated with mechanisms proposed as underlying relaxations in polymers. In the present work we have undertaken the investigation of crankshaft motions in polyethylene in an attempt to answer some of the questions outlined below concerning them.

Inquiring into what might be the shortest range motion energetically feasible in polyethylene, Schatzki[8] presented a very specific model for the γ mechanism. He proposed that the conformational transition that could take place with the least energy barrier between stable strain-free conformations in the amorphous phase is of the type depicted in Figure 1. Since the initial and final states together represent a ring structure, it is helpful to visualize the conformational situation as a substituted *cis*-decalin. The substituent bonds 1 and 7 are colinear and Schatzki pointed out that the transition from the initial to the final state can be accomplished by simultaneous rotation about bonds 1 and 7 with the rest of the bonds held rigid. Further, the overall barrier to the motion should be well approximated by the sum of the two individual barriers to rotation of

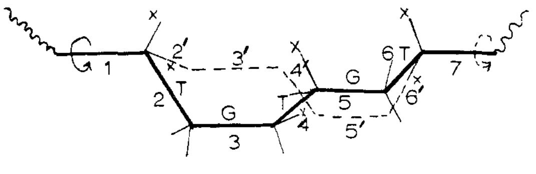


Figure 1. The Schatzki crankshaft motion is conveniently visualized by reference to *cis*-decalin (*cis*-bicyclo[4.4.0]decane). The bonds 2, 3, 4, 5, and 6 (heavy solid lines) which are in the conformational sequence TGTGT go around one side of the ring and represent the chain before the motion. Rotation about the colinear bonds 1 and 7 carries bonds 2–6 rigidly to the new positions 2′, 3′, 4′, 5′, and 6′ (dashed lines) which complete the *cis*-decalin ring. Schatzki proposed that chains with substituents in the positions marked by X's would not increase the volume swept out by the motion and hence could have such motions.

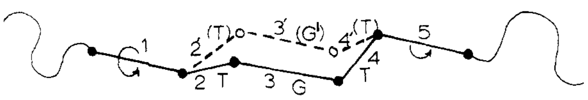


Figure 2. The Boyer crankshaft motion is conveniently visualized by reference to the equatorial, equatorial conformer of 1,4-dimethylcyclohexane. The bonds 2, 3, and 4 (solid lines) go around one side of the ring, 2′, 3′, and 4′ (dashed lines) go around the other. The sequence TGT for bonds 2, 3, and 4 represents the polyethylene chain before the motion, the sequence TG′T for 2′, 3′, and 4′ (dashed lines) represents the chain after the motion. Bonds 1 and 5 are parallel but only approximately colinear. In contrast to the Schatzki motion rotation about the stems (bonds 1 and 5) is accompanied by conformational change of the interior bonds (2, 3, and 4), which go from TGT to TG′T.

bonds 1 and 7. Schatzki[8b] asserted that this motion would be energetically the most feasible as far as the intramolecular energy is concerned. He suggested that the volume swept out by the motion might be sufficiently small that intermolecular interference (matrix effect) would not preclude it. He further suggested[8b] that substituents at some positions would not increase the volume swept out and thus would exhibit γ transitions whereas substituents at others would increase the volume and prevent the motion.

Boyer[9] has proposed another model for the motion of a small segment of the polyethylene chain. It is depicted in Figure 2 and the initial and final states together can be visualized as a substituted cyclohexane. The equatorial substituent bonds 1 and 5 are parallel and approximately colinear. Boyer actually described this model as involving the motion about exactly colinear stems of three intermediate bonds (two atoms). However, this exact colinearity is not possible without the initial and final states being strained. We regard Figure 2 as the generalization of the three-bond crankshaft to unstrained initial and final states and thus the stems are only approximately colinear. Inspection of models suggests the conformational change can take place by rotation about bonds 1 and 5 (and accompanied by changes in bonds 2, 3, and 4) with energetics primarily determined by bond rotational barriers and without extremely large bond length or bond valence angle distortions. This motion would appear to have a higher barrier than the Schatzki mechanism. However, since fewer bonds are involved, it might be that the intermolecular interference is less and this motion could compete with or even be favored over the Schatzki motion.

Both of these mechanisms belong to a general class of especially simple conformational transitions that have become known as "crankshaft" motions. Both have in common an attempt to describe a motion between stable strain-free conformations in a glassy matrix that has a particularly low barrier and is likely to be uncoupled from other more cooperative motions. They invoke conformational transitions in short segments of the chain with the stems held fixed by the matrix. Whether or not such conformational mechanisms are the molecular basis for the γ relaxation in polyethylene has been the subject of much speculation and controversy. An obvious uncertainty has been a lack of knowledge concerning the energetics of such motions. Arguments against this association include the possibility that even though this mechanism involves the shortest possible segmental motion, the volume swept out by the bonds during the conformational change is too large to be energetically feasible in a matrix of glassy polymer. Another objection is that such a simple motion might be expected to have an energy profile with a simple single maximum separating the initial and final states. As such it would be expected to have a single relaxation time whereas experimentally the relaxation is found to be broad. Other objections have included observations of the presence or absence of similar transitions in polymers of differing chemical structures.[11]

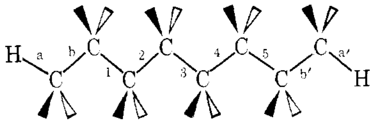
Table I
Conformational Notation[a]

$\phi \sim 60° =$ gauche, G
$\phi \sim 180° =$ trans, T
$\phi \sim 300° =$ gauche′, G′
$\phi \sim 0, 120, 240° =$ eclipsed, E

[a] Bond rotational angles, ϕ, are measured relative to carbon eclipsing carbon as zero. A clockwise rotation of the far bond relative to the near one looking along (parallel to) the center bond is taken as a positive rotation. A subscript + or − indicates substantial distortion from the standard values 60, 180, 300° in the direction indicated (*i.e.*, $G_+ = \phi > 60°$, etc.).

Calculations on Isolated Chains

Boyer Crankshaft. A number of calculations (using previously developed potential function parameters[16]) were carried out on *n*-octane



where the numbering of the bonds corresponds to that in Figure 2. As an example, starting from the conformational sequence TTGTT (see Table I for conformational notation), bonds a, b, a′, and b′ were held fixed in space and bond 1 was designated as the "driving bond" and driven from T toward G the "long way around" (through eclipsed, G′, and eclipsed, a total of 240°). At each step of the way, the energy was minimized with each atom, including the hydrogens (but not the three atoms at each end defining bonds a, b, a′, and b′) free to move. Each bond distance, valence angle, and bond torsional angle was thus free to adjust, subject to the restraints of bond 1 torsional angle being fixed at the desired values and bonds a, b, a′, and b′ being fixed. The restraint to bond 1 torsion was applied by using an artificially high barrier and a false minimum in the potential function for this torsional coordinate. Bonds a, b, a′, b′ were held fixed by deleting the rows and columns of the X, Y, Z coordinates of the constrained atoms from the coefficient matrix in the minimization calculation.[15]

Although the sequence of bonds 2, 3, and 4 must be TGT and TG′T (or *vice versa*) at the start and end of this crankshaft motion, bonds 1 and 5 can be in any of the conformations T, G, or G′. In addition, either bond 1 or bond 5 can be driven the "long way around" (240°, rather than 120°)

Table II
The Six Distinct Boyer Crankshaft Barrier Systems[a]

Calculation	Initial state	1st barrier	Intermediate minimum	2nd barrier	Final state
(1) Approximate conformation Energy	$\overset{*}{\mathrm{T}}$TGTT 0.0	$\overset{*}{\mathrm{E}}$TGT_E 6.5	$\overset{*}{\mathrm{G}}$'TGT_G 3.8	$\overset{*}{\mathrm{E}}$TETG 11.0	$\overset{*}{\mathrm{G}}$TG'TG 1.5
(2a)	$\overset{*}{\mathrm{T}}$TGTG 0.0	$\overset{*}{\mathrm{E}}$TGTE 9.3	$\overset{*}{\mathrm{G}}$'TGT_G' 3.9	$\overset{*}{\mathrm{E}}$TETG' 11.7	$\overset{*}{\mathrm{G}}$TG'TG' 0.8
(2b)	TTGT$\overset{*}{\mathrm{G}}$ 0.0	ETGT$\overset{*}{\mathrm{E}}$	GTGT$\overset{*}{\mathrm{T}}$	GTET$\overset{*}{\mathrm{E}}$ 10.3	GTG'T$\overset{*}{\mathrm{G}}$' 0.7
(3a)	$\overset{*}{\mathrm{T}}$TGTG' 0.0	$\overset{*}{\mathrm{E}}$TGTE 5.6	$\overset{*}{\mathrm{G}}$'TGTT 1.5	$\overset{*}{\mathrm{E}}$TETT 10.1	$\overset{*}{\mathrm{G}}$TG'TT 0.0
(3b)	TTGT$\overset{*}{\mathrm{G}}$' 0.0	TTET$\overset{*}{\mathrm{E}}$ 9.2	TT_G'T$\overset{*}{\mathrm{G}}$ 1.4	ETG'T$\overset{*}{\mathrm{E}}$ 5.6	GTG'T$\overset{*}{\mathrm{T}}$ 0.0
(4)	$\overset{*}{\mathrm{G}}$TGTG 0.0		(Maximum, 12.0)		$\overset{*}{\mathrm{G}}$'TG'TG' 0.0

[a] Note: an asterisk indicates the "driving" bond, energies in kcal/mol.

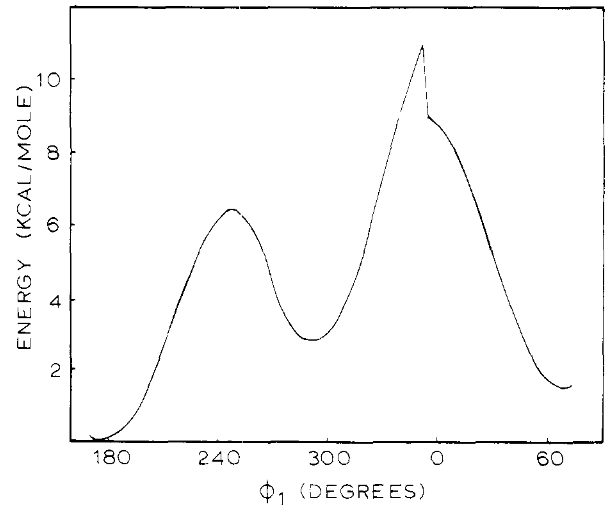


Figure 3. The minimum energy path for the Boyer crankshaft motion in an isolated chain as represented by the conformational change TTGTT to GTG'TG in n-octane with the end bonds restrained (a, b, and a'b' of the n-octane diagram). Type 1 of Table II.

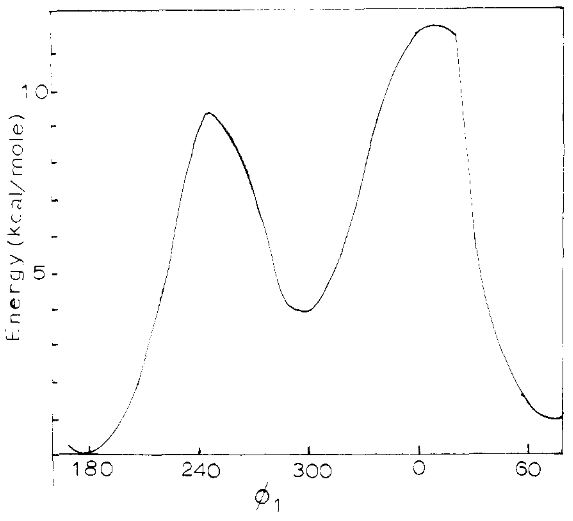


Figure 4. Minimum energy path for type 2a isolated chain Boyer crankshaft of Table II.

while the other one goes the "short way" (through 120°). Of these 18 possibilities only six are distinct in the sense of having differing energetics. These six systems are listed in Table II. Calculations were made on all six of these and are summarized in Table II and the resulting energy curves are shown in Figures 3–8.

Schatzki Crankshaft. Calculations were made on n-decane with bond 1 of Figure 1 as the driving bond. This motion involves no conformational change for bonds 2 through 6 which are TGTGT. Bonds 1 and 7 may each be in any of the conformations T, G, or G' so that there are actually nine such transformations in each direction from the starting conformation (there are only six distinct ones if the energetics depends only on the end bonds). Results of a typical one are shown in Figure 9. As anticipated by Schatzki, there is very little change in the values of the torsional angles of bonds 2 through 6 through the motion. Table III lists values of the barriers calculated by driving bond 1 for several conformations of bonds 1 and 7. Also demonstrated in Table III and as conjectured by Schatzki this crankshaft barrier is quite accurately approximated by the sum of the individual bond barriers traversed by the end bonds.

Calculations on the Effect of Surrounding Chains

Boyer Crankshaft. Simulation of the packing in the amorphous phase is a difficult problem and, in fact, the general question of the amorphous structure is a question in which there is much interest. However, for our purpose of assessing the "collision diameters" of the crankshaft rotations, the following scheme proved feasible and we believe realistic. The conformational sequence ··· TTTGTG'TTT ··· has planar zig-zag stems which are parallel but somewhat displaced (see Figure 10). The effect of the complete crankshaft motion (see crankshaft 3 in Table II) is to move the GTG' sequence along the chain by two atoms, *i.e.*, to ··· TTTTTGTG'T ··· . It seemed possible that the environment of such a segment could be simulated by inserting it into the crystal.[10] It was found that a relatively short segment could indeed be incorporated into the crystal without undue expense of energy. Its location in the cell was determined by energy minimization with the entire ten-atom crankshaft center chain free. Then the ends were fixed for the drive calculation. It is to be empha-

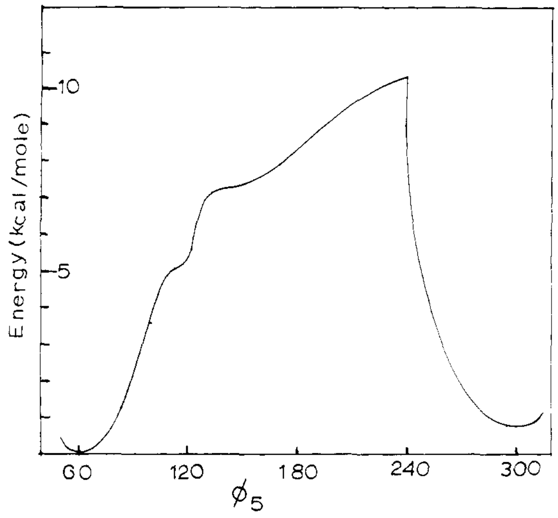


Figure 5. Minimum energy path for type 2b isolated chain Boyer crankshaft of Table II.

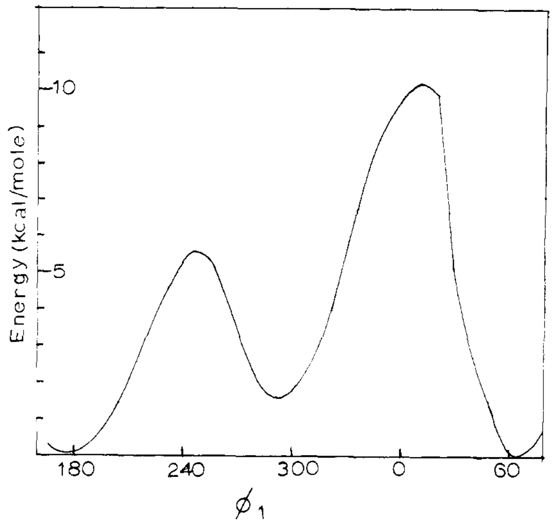


Figure 6. Minimum energy path for type 3a isolated chain Boyer crankshaft of Table II.

sized that this is not a crystallographic defect, the stems are not in crystallographic register. The model adopted is described in Figures 11 and 12. In order to handle it computationally, however, it was necessary to reduce the number of atoms by approximating each CH_2 group as a force center[17] and deleting the hydrogens explicitly. The following $(CH_2) \cdots (CH_2)$ nonbonded potential function was derived by fitting the unit cell *a* dimension[18] (and approximately the *b* dimension) and the heat of sublimation of polyethylene at 0°K[19]

$$V(R) = 5.216 \times 10^6/R(\text{Å})^{12} - [1571.8/R(\text{Å})^6] \quad (1)$$

The following torsional, valence angle, and stretching functions were also used

$$V(\phi) = (3.2/2)(1 + \cos 3\phi) + 0.8/2(1 + \cos \phi) \quad (2)$$

$$V(\theta) = (158.4/2)(\theta - 111.6°)^2 \quad (3)$$

$$V(R) = (633.6/2)(R - 1.53 \text{ Å})^2 \quad (4)$$

All of the above functions are in terms of kcal mol^{-1}.

For the drive the volume of the unit cell was adjusted to match that of the amorphous phase at 188°K (1.065 cm^3/gm) estimated from the thermal expansion data discussed

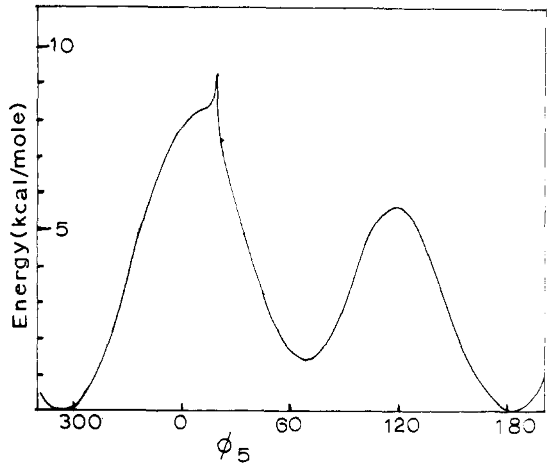


Figure 7. Minimum energy path for type 3b isolated chain Boyer crankshaft of Table II.

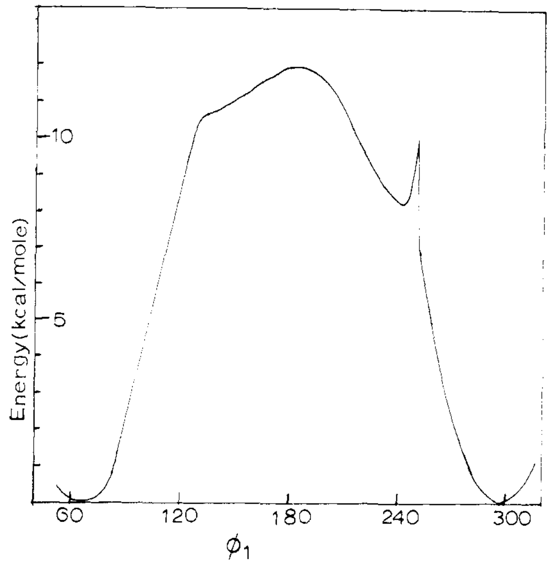


Figure 8. Minimum energy path for type 4 isolated chain Boyer crankshaft of Table II.

by Stehling and Mandelkern[20] and by Boyer[21] by taking *a* = 7.66 Å, *b* = 5.10 Å, and *c* = 2.534 Å. Using the model of Figures 11 and 12 with the crankshaft 3b of Table II, the drive was carried out in the crystal. The results are shown in Figure 13. Also shown for comparison is the isolated chain calculation using the (CH_2) group approximation and the functions of eq 1–4 above. The results of the isolated chain calculation are similar to but differ somewhat from the calculation using hydrogen atoms (*cf.* Figure 7). We regard the isolated chain calculations using the hydrogen atoms and the parameters of ref 16 as more reliable, but the differences in the two curves of Figure 13 indicating the packing effects should be meaningful.

Schatzki Crankshaft. As will be discussed below, the experience gained from the matrix calculation indicated that the Schatzki motion cannot take place adiabatically in an environment of surrounding chains (glassy matrix) without extreme expense of energy and no calculation was attempted.

Discussion and Conclusions

Although the isolated chain barrier energetics of the six Boyer motions of Table II, and as shown in Figures 3–8, seem at first glance to be rather complicated, they can be

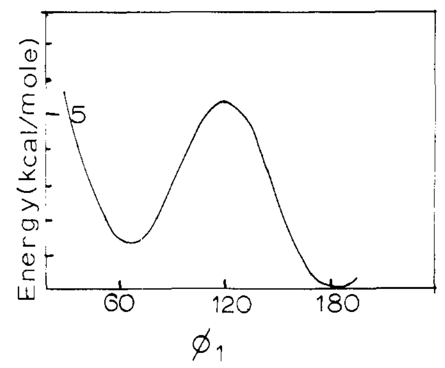


Figure 9. Minimum energy path for an isolated chain Schatzki crankshaft GTGTGTG′ → TTGTGTT.

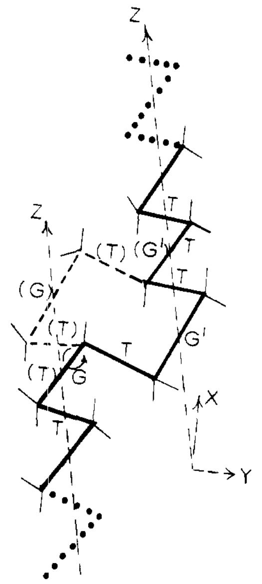


Figure 10. TGTG′TTT (type 3b, Table II) crankshaft used for matrix effect calculation. The planar zig-zag stems are parallel but displaced.

Table III
Barriers for Schatzki Crankshaft Rotation[a]

Starting conformation	Barrier, kcal mol^{-1}	Final conformation
TTGTGTT	5.3 (5.4)	G′TGTGTG
TTGTGTG′	6.6 (6.8)	GTGTGTG
TTGTGTG	4.7 (4.8)	GTGTGTT

[a] The values in parentheses were calculated by adding together individual bond barriers for the two end bonds taken from rotational calculations on *n*-hexane (ref 12: V_0(T → G) = 2.7, V_0(G → T) = 2.1, V_0(G → G′) = 4.1 kcal mol^{-1}).

interpreted quite simply. Taking the motion 1 of Table II (and Figure 3) as an example, we plot in Figure 14 the responses of the torsional angles ϕ_2 − ϕ_5 (Figure 2) to changes in ϕ_1 along the minimum energy path. It is apparent from Figure 14 that the first barrier in Figure 3 (at 240°) corresponds to the simultaneous rotation of the end bonds (ϕ_1 and ϕ_5) of the crankshaft through the eclipsed positions. This motion is much the same as the Schatzki motion but in the Boyer case does involve appreciable, though not severe, distortion of other torsional (and valence) angles. The minimum between the barriers corresponds to what would be the strain-free conformation G′TGTG reached by rotation of the end bonds through 120° if it were not for the restraint of the stems being fixed. This restraint causes this sequence to be strained and Figure 14 indicates that bond 4 bears the bulk of this by being distorted ~30° toward the 120° eclipsed position. The second barrier (near ϕ_1 = 0) corresponds to a "flip-flop" of

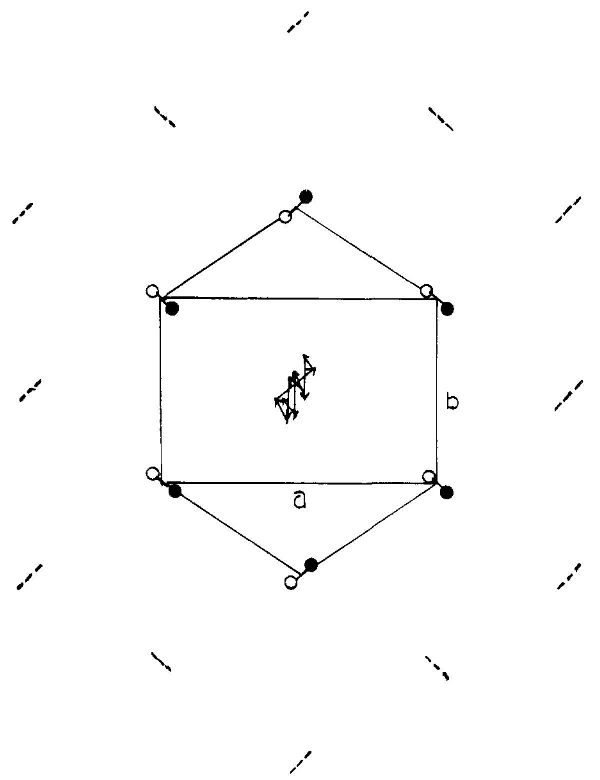


Figure 11. Model used for calculation of the effect of embedding the crankshaft in a matrix of surrounding chains. Each line represents a polyethylene chain 10 atoms long. The solid lines are chains restrained at the ends to fixed positions (three atoms at each end) but otherwise free to deform subject to the appropriate conformational energy functions (including internal valence angle and torsional angle functions and intermolecular nonbonded potentials). The dotted lines are chains completely rigidly fixed and interact with the other chains by means of nonbonded potentials. The simplification of regarding the $-CH_2-$ group as a single force center for nonbonded interaction was made. By replacing the center chain of the orthorhombic unit cell with a crankshaft defect, an estimate of the effect of the matrix on the crankshaft motion was made. The cell volume was adjusted to that of the amorphous phase.

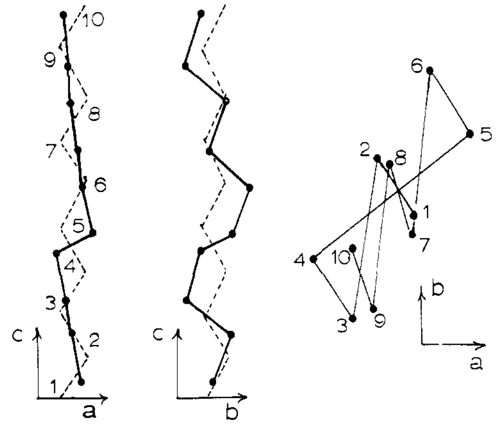


Figure 12. The ac, bc, and ab projections of the crankshaft defect in Figure 11. The ab projection is enlarged 4 × over the ac and bc. The dashed lines are the positions of a normal planar zig-zag chain in the unit cell.

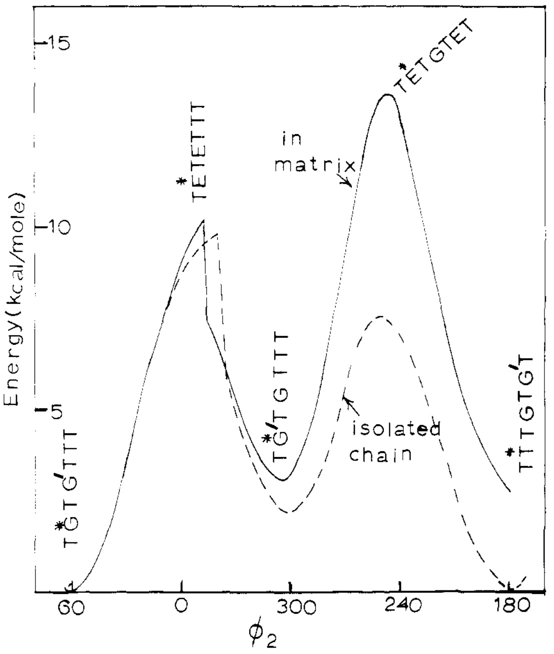


Figure 13. The Boyer crankshaft (Figure 10) motion in the crystal matrix of Figure 11 compared with isolated chain motion. Both cases use (CH_2) force center approximation and hydrogens are deleted (parameters of eq 1–4).

bonds 1 and 3 as they "trade" conformations. As bond 1 proceeds toward G, bond 3 undergoes a sudden almost discontinuous displacement near the top of the barrier from a distorted G value over to the G′ side. The near discontinuity in the energy in Figure 3 is a result of this flip–flop. This near discontinuity appears to be an unavoidable consequence of the molecular dynamics and not a computational artifact. In some of the calculations, the flip–flop occurred smoothly as a result of the driving angle changes (as was the case in Figure 3), but in other cases, it had to be induced by driving ϕ_3 from G_- to G_+' holding ϕ_1 fixed near 0°. Such cases are drawn as spikes in the energy diagrams. The energy surface, however, is fairly flat with ϕ_1 approaching the barrier so that such paths appear to approximate the minimum energy path over the barrier well.

The barrier systems of motions 1, 2a, 3a, and 3b of Table II (Figures 3, 4, 6, and 7) are all very similar and conform to the above description of motion. Motions 2b and 4 (Figures 5 and 8) differ from these in that the minimum between the barriers no longer exists. This is the result of the fact that although in the above cases in the region between barriers the restraints of the fixed stems can be accommodated by modest torsional angle distortions, types 2b and 4 cannot adjust to the stem restraint by torsional distortion. Fairly severe valence angle distortion is required. The latter is quite costly energetically and the intermediate minimum is wiped out. The flip–flop discontinuity at $\phi = 240°$ (Figures 5 and 8) is still apparent, however.

With this background, we are in a position to understand the results in Figure 13 concerning the matrix effect. It is apparent that one barrier shows almost no effect of the surroundings but the other one is quite sensitive, the barrier being now considerably higher. The matrix sensitive barrier corresponds to the motion about the end bonds, the second barrier of type 3b of Table II and Figure 7. This motion carries the three included bonds more or less rigidly and sweeps out significant volume. However, the matrix insensitive barrier involves the flip–flop exchange of the conformation ··· GTG′ ··· → ··· ETE ··· → ··· G′TG ··· and requires very little swept out volume. Based on the matrix sensitivity of the second barrier in the Boyer case, we believe the Schatzki motion which requires two additional bonds in the rigid motion and considerably more swept out volume can be ruled out as a contributor to the low-temperature γ processes.

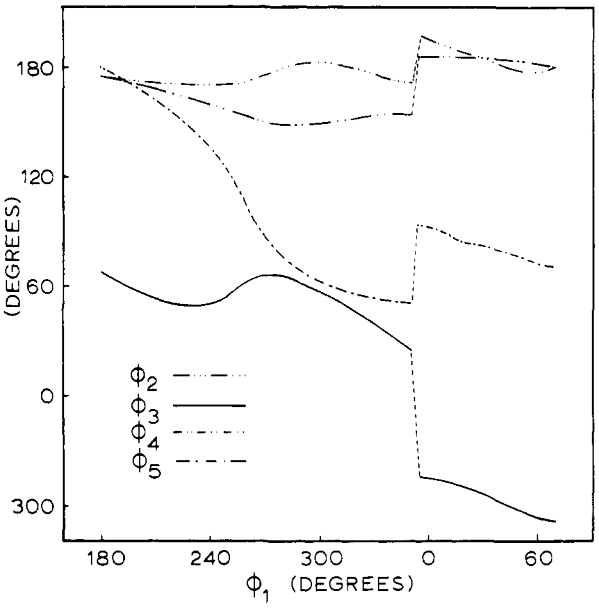


Figure 14. The response of bonds 2, 3, 4, and 5 (see Figure 2) to changes in the driving bond, 1, along the minimum energy path for the crankshaft motion of Figure 3, type 1, Table II.

Although it is not our intention to attempt here a quantitative interpretation of the γ mechanism in terms of the energetics developed, it does seem appropriate to make some general observations. First of all, we suggest that the γ mechanism involves the barrier systems of the Boyer crankshaft motion for types 1, 2a, 3a, and 3b of Table II where a stable minimum exists between barriers. Further it is presumed that in the matrix the flip–flop barrier and intermediate minimum is similar to the isolated chain barriers of Table II but that the other barrier corresponding to the ETGTE semi-rigid motion between stems is displaced to a value significantly higher than the flip–flop barrier. In other words, it is supposed that the barrier systems for the above types look like that of Figure 13. According to the site theory of relaxation[22] such a barrier system will have two relaxation times

$$1/\tau_{1,2} = (b \pm \sqrt{b^2 - 4c})/2 \tag{5}$$

where

$$b = k_1 + k_2 + k_3 + k_4$$

$$c = k_1k_3 + k_1k_4 + k_2k_4$$

and

$$k_1 = (k_BT/h)\ \exp(-E_1/k_BT) \tag{6}$$

$$k_2 = (k_BT/h)\ \exp(-(E_1 - V')/k_BT) \tag{7}$$

$$k_3 = (k_BT/h)\ \exp(-(E_2 - V')/k_BT) \tag{8}$$

$$k_4 = (k_BT/h)\ \exp(-(E_2 - V)/k_BT) \tag{9}$$

with the k's as defined in Figure 15.

If the barriers are of unequal height (E_2 significantly greater than E_1) then the two relaxation times will approach a short one, $\tau_1 \approx 1/k_2$, and a longer one determined primarily by the higher barrier into the intermediate minimum. We suggest that the short relaxation time dominates the contribution to the γ process. If it were not for the strain on the final state of the complete motion over both

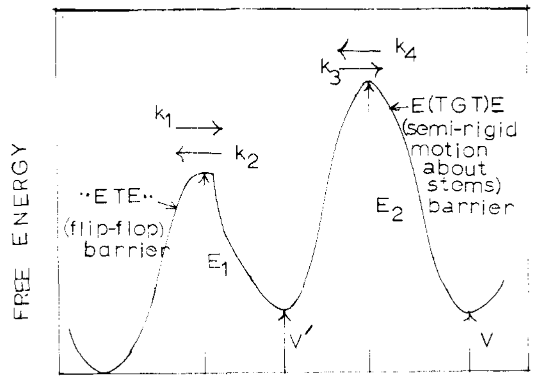


Figure 15. Schematic rendering of Boyer crankshaft barrier system (appropriate for motion in matrix) defining rate constants.

barriers (···TGTG′TTT··· → ···TTTGTG′T···; see Figure 13) induced by the matrix, the sequences ···GTG′T··· could achieve mobility along the chain by means of the crankshaft rotation. However, it is presumed that they are effectively trapped thermodynamically by this strain and also perhaps kinetically by a longer relaxation time associated with motion over the second barrier (dominated by k_4 of Figure 15). An interesting hypothesis is that successive motions of crankshafts in neighboring chains cooperatively relieves this strain and allows ···GTG′T··· mobility as a prerequisite for the onset of the glass–rubber transition (and in our view associated with the β transition). In any event, for present purposes, we will assume that the amorphous γ process is dominated by the four relaxation times $1/k_2$ (eq 7) from each of the four types of motion 1, 2a, 3a, and 3b (Table II). In addition, we assume that the number of ···G′TG′T··· sequences is determined by freezing in at the β transition and that they are not in thermodynamic equilibrium with respect to gauche bond distribution.

The γ process in polyethylene definitely occurs in both crystalline and amorphous domains.[3,20] Unfortunately, the process has never been adequately resolved into these two components to allow the relaxation parameters of the amorphous process to accurately be derived for comparison with our model. Furthermore, the best information comes from dielectric measurements on slightly chlorinated or oxidized (carbonyl group containing) specimens. It is not yet known what effect the chlorine or carbonyl group has on the barrier systems of Table II. However, it should be possible in the future to calculate similar curves for the various possible placements of substituents. However, comparison of predicted and experimental values of $T_{\max}(\nu)$, the location of the loss peak, should be interesting. To do this we will make the presently arbitrary assumption that each of the four barrier systems contributes the same inherent intensity to the total process. We further assume that the intensity of each relaxation is affected by temperature through a Boltzmann weighting of the initial and intermediate states (a result that follows from site theory of relaxation[22]). The factors $E_1 - V'$ in eq 7 (and Figure 15) are actually free energies and the question of the entropy of activation arises since the calculated barriers are energy or enthalpy curves. The methods used[12-16] to calculate the minimum energy paths can also be used to calculate the vibrational frequencies of the chain in the ground and transition state. Thus, a direct application of the classic but seldom employed partition-function formulation of absolute rate theory[23] can be made.[14] That is

$$k = \frac{k_{\mathrm{B}}T}{h}\frac{Q^*}{Q_0}e^{-\Delta E_0^*/k_{\mathrm{B}}T} \tag{10}$$

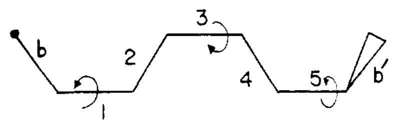


Figure 16. The transition state for the flip–flop barrier (···G′TG···→···ETE···→···GTG′···) is approximately planar. The reaction coordinate corresponds to an imaginary frequency with ϕ's for bonds 1 and 3 moving in opposite directions. Another very low-frequency vibration involves nearly free simultaneous rotation about bonds 1 and 5.

where Q_0 and Q^* are the vibrational partition functions of the ground and transition states. In the present case, the calculation was complicated by the fact that for the transition state in addition to the imaginary frequency corresponding to the barrier translation, one of the vibrations had a frequency that was extremely low. It was too low in fact to have confidence in treating it as a harmonic oscillation in the partition function. This vibration was treated in the following way. Figure 16 shows the flip–flop transition state. Consideration of the eigenvectors indicates that the very low-frequency vibration can be considered approximately as a simultaneous rotation about bonds 1 and 5. Whereas motion across the barrier (reaction coordinate) involves simultaneous lowering of the energy in bonds 1 and 3 (imaginary frequency), the low-frequency mode involves decreasing energy in bond 1 but increasing in bond 5 leading to a very low frequency. For purposes of entropy estimation, we have considered this motion to be a free rotation about bonds 1 and 5. The situation boils down to this. The frequencies of the ground and transition states match fairly well except for the "missing" barrier translational frequency and the low-frequency vibration described above. Thus, not considering these, the ground state has two extra frequencies, giving it about 5 eu more entropy at 150°K. However, the free-rotation treatment indicates about 5 eu for the low-frequency vibration of the transition state. Therefore, we surmise that $\Delta S \approx 0$. Similarly, we conclude that the vibrational contribution to ΔH should, at most, amount to a few hundred calories at 150°K.

Calculations of $T_{\max}$ under the above assumptions from the maximum loss using

$$E'' = C\sum_{n=1}^{4} P_1{}^nP_2{}^n\omega\tau_n/(1 + \omega^2\tau_n{}^2) \tag{11}$$

where

C = arbitrary constant

$P_1 = 1/(1 + \beta_n)$

$P_2 = \beta_n/(1 + \beta_n)$

$\beta_n = e^{-V_n'/kT}$

$\tau_n = 1/k_2{}^n$ (k_2 from eq 7 for the four types of motion, 1, 2a, 3a, and 3b)

are shown in Table IV. The experimental values in Table IV were selected as representing low crystallinity, largely amorphous polyethylene, or, in the case of dielectric measurements on chlorinated linear polyethylene, because the chlorine atoms are believed to be largely confined to the amorphous domains.[24] The agreement on the location of the peak is quite good. Perhaps it is even fortuitously so, since uncertainties in the calculated barriers of 1–2 kcal/mol are to be expected. The experimental activation energy of 10 kcal/mol (values of 10 and 14 kcal/mol have been found[25,26] for partially crystalline carbonyl containing branched polyethylene where, since the carbonyls are incorporated in the crystals, both the crystalline and amorphous γ contribute) is in reasonable agreement also.

Table IV
Calculated Values of $T_{\max}$ (loss) for the Combined Barrier Processes (1, 2a, 3a, 3b of Table II[a]) at Several Frequencies Compared with Experiment

	$T_{\max}$, °K		ΔH^*, kcal/mol	
ν, Hz	Calcd	Exptl	Calcd	Exptl
1	147			
1		160[b] (mechanical)		
10^3	196		8.3	
10^3		193[c] (dielectric)		10
10^3		193[d] (dielectric)		

[a] The values 7.2, 7.8, 8.6, and 7.8 for $E_1 - V'$, respectively, were used in eq 7 for k_2 along with the values 2.3, 3.1, 1.5, and 1.4, respectively, for V' for Boltzmann weighting of the relative intensities (eq 11). [b] Low crystallinity partially chlorinated branched polyethylene: K. Schmieder and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953). [c] Slightly chlorinated linear polyethylene: Matsuoka, Roe, and Cole, ref 24. [d] G. P. Mikhailov, S. P. Kabin, and T. A. Krylova, *Sov. Phys. Tech. Phys.* 2, 1899 (1957); *J. Tech. Phys. (USSR)*, **27**, 2050 (1957); low crystallinity quenched oxidized branched polyethylene.

It is important to note that when an activation energy is determined for an overall composite process which consists of a number of relaxation times, this activation energy may not be representative of the average of the activation energies of the various relaxation times. Consider a collection of pairs of sites and barriers between them that have the property of the highest barriers ($E_1 - V'$) having the smallest energy differences between sites (V') and *vice versa* and further that the energy differences between sites are comparable to kT. Such a collection will have an apparent activation energy for the composite process (as determined from $\nu_{\max}$ *vs.* T) that is strongly displaced toward or can even easily exceed the activation energy for the highest barrier. This point is raised in two connections. First, although the composite calculated activation energy of Table IV is not strongly displaced from the average of the individual ones, a minor adjustment of the site energy differences could increase the composite activation energy significantly. Second, the calculation of a composite ΔS^* from an experimental value of the loss peak location (T, ν) and an activation energy (from $\nu_{\max}$ *vs.* T) may well result in a rather large activation entropy for the γ process (and especially for the composite of the amorphous and crystalline ones). We suggest that this may be unrealistic since the composite activation energy is probably biased toward the high end of the range of individual ones.

As remarked earlier the above considerations depend on the site energy differences (V') being comparable to kT in the γ region. Direct evidence that this is so comes from the intensity of the γ process. The latter increases strongly with temperature indicating site differences of ≈ 1 kcal/mol.[24] This, of course, does not necessarily imply a correlation of increasing barrier height with decreasing site energy difference. In any event the increase in intensity of the amorphous γ process with temperature has a natural explanation in the site energy differences found here for the barrier motions proposed.

Finally we comment on the likelihood of mechanical activity. For both the five- and three-bond crankshafts, the complete motion between strain-free initial and final states, of course, involves no strain involving the stems. As such the accumulation of local strain into a macroscopic one would be a very weak effect indeed. Thus, the mechanical intensity should be very weak. However, for the strained intermediate of the flip–flop barrier, the stems are strained. Under stress biasing, these strains can be envisioned as accumulating into a macroscopic strain. Phrased alternatively, the energy of the strained intermediate state of the flip–flop barrier system can be expected to be sensitive to applied deformation leading to a strain sensitivity of the energy difference V' and hence possess mechanical activity. In contrast, the applied deformation sensitivity of the energies of the conformationally strain-free initial and final states should be quite low. Thus, the picture emerges here as flip–flop motions rather than complete crankshaft motions as previously envisioned as responsible for the mechanical relaxation.

Acknowledgment. The authors are indebted to the U.S. Army Research Office (Durham) and to the National Science Foundation for support of this work. They are also grateful to Dr. J. D. Hoffman, National Bureau of Standards, for his encouragement of this work.

References and Notes

(1) Presented in part at the Division of Polymer Chemistry Meeting, American Chemical Society, Detroit, May 1–4, 1973; see *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, **14(1)**, 192 (1973).
(2) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic Efforts and Dielectric Effects in Polymeric Solids," Wiley, New York, N.Y., 1967.
(3) J. D. Hoffman, G. Williams, and E. Passaglia, *J. Polym. Sci., Part C*, **14**, 173 (1966).
(4) R. L. McCullough, *J. Macromol. Sci., Phys.*, **9**, 97 (1974).
(5) P. Predecki and W. O. Statton, *J. Appl. Phys.*, **37**, 4053 (1966).
(6) D. H. Reneker, *J. Polym. Sci.*, **59**, 539 (1962).
(7) P. E. McMahon, R. L. McCullough, and A. A. Schlegel, *J. Appl. Phys.*, **38**, 4123 (1967).
(8) (a) T. F. Schatzki, *J. Polym. Sci.*, **57**, 496 (1962); (b) 150th Meeting of the American Chemical Society, Atlantic City, N.J., *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **6**, 646 (1965); (c) *J. Polym. Sci., Part C*, **14**, 139 (1966).
(9) R. F. Boyer, *Rubber Chem. Tech.*, **34**, 1303 (1963).
(10) A proposal closely related to crankshaft motions is that of "kink" motions (W. Pechold, S. Blasenbrey, and S. Woerner, *Kolloid-Z. Z. Polym.*, **189**, 14 (1963)). As is discussed in the present work under matrix modelling, there are conformational sequences of bonds that allow the possibility of three-bond crankshaft motions that also have parallel planar zig-zag extended stems. However, the stems are not colinear and the phases of the two zig–zag stems are not in register. Pechold and his coworkers proposed that these are incorporated into the crystal latice and the stems brought into crystallographic register (along the same *C* axis) by steric distortion (and perhaps aided by the occurrence of two such defects nearby in the same chain). The resulting defects were called kinks. In the present work we do not address ourselves to the question of these sterically strained crystal kinks but only to unstrained initial state conformational sequences which we presume to be appropriate for the amorphous phase. In our modelling of the matrix the conformational sequence in question is not brought into crystallographic register.
(11) R. F. Boyer, *Macromolecules*, **6**, 288 (1973), and references therein.
(12) R. H. Boyd and S. M. Breitling, *Macromolecules*, **5**, 1 (1972).
(13) R. H. Boyd and S. M. Breitling, *Macromolecules*, **5**, 279 (1972).
(14) K. B. Wiberg and R. H. Boyd, *J. Amer. Chem. Soc.*, **94**, 8426 (1972).
(15) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).
(16) S. J. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Amer. Chem. Soc.*, **92**, 3109 (1970).
(17) W. Brandt, *J. Chem. Phys.*, **26**, 262 (1957).
(18) M. Shen, W. Hansen, and P. C. Romo, *J. Chem. Phys.*, **51**, 425 (1969).
(19) F. Billmeyer, *J. Appl. Phys.*, **28**, 1114 (1957).
(20) F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).
(21) R. F. Boyer, *Macromolecules*, **6**, 288 (1973).
(22) J. D. Hoffman, *J. Chem. Phys.*, **23**, 1331 (1955).
(23) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N.Y., 1941.
(24) S. Matsuoka, R. J. Roe, and H. F. Cole, "Dielectric Properties of Polymers," F. Karasz, Ed., Plenum Press, New York, N.Y., 1972, p 255.
(25) C. A. F. Tuijnman, *Polymer*, **4**, 259 (1963).
(26) P. J. Phillips, G. L. Wilkes, B. W. Delf, and R. S. Stein, *J. Polym. Sci., Part A2*, **9**, 499 (1971).