Energetics of Strain-Induced Conformational Transitions in Polymethylene Chains

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Received October 16, 1989; Revised Manuscript Received February 23, 1990

ABSTRACT: Deformation potentials have been calculated for highly extended polymethylene chains containing simple torsional defects. The calculations were performed by using molecular mechanics techniques. The deformation potentials show abrupt discontinuities, which have been identified as gauche-trans transitions of chains containing strained defects into chains in the fully extended zigzag form. The reverse trans-gauche transition was observed during compression of all-trans chains. The observed discontinuity in the conformational transition is a direct consequence of the input of mechanical energy into the torsional angles and also into the bond lengths and bond angles in the chain. The transition point imposes a limit on the amount of energy stored in chains containing defects; the energy is fully recovered at the transition. It is suggested that abrupt conformational transitions may occur upon drawing crystalline and glassy polymers as a mechanism of avoiding large translational movements of atoms under the conditions of strong constraints from neighboring chains. The Hookean behavior of single chains containing a conformational defect was tested and the effect of this defect on the chain modulus was estimated.

Introduction

The molecular mechanism of the transmission of macroscopic forces applied to solid polymers to individual chains is still poorly understood. In crystalline and semicrystalline polymers the process of orientation and extension of polymer chains by shear and elongation is affected mainly by the polymer morphology and by the conformation of the polymer chain. In the ordered regions of a polymeric solid lattice constraints drastically reduce the number of available conformations to a select few, which can be accommodated in the lattice without major energy requirements. For example, in polymethylene chains, in addition to the preferred all-trans conformation, some highly but not completely extended conformations involving "conformational defects" are observed. A typical representative of this category is a chain segment ...g^+tg^-... containing a "kink", a three-bond defect with two coupled gauche bonds of opposite orientation. In kinks and in similar structures such as jogs, folds, etc., the two all-trans portions of a chain flanking the defect are parallel and fit into lattice registration.

Apart from the conformational equilibrium, the length (end-to-end distance) of a given structure must be considered in the elongational force field. Generally, conformations with the larger dimension in the direction of the stretching force are favored; a fully extended zigzag is the ultimate result of stretching a chain. Consequently, partially extended polymethylene segments in a crystalline polymer are gradually converted by stretching into all-trans structures until all conformational defects are eliminated. The resulting entropically "unfavorable" zigzag is stabilized by lattice forces involving neighboring chains.

The energetics of conformational interconversions brought about by stretching crystalline polymers was first described by Kausch,[1] who emphasized the irreversible nature of the transition and suggested that this irreversibility can explain numerous phenomena observed during polymer stretching, for example, the difference between the first and subsequent cycles (hysteresis) of stress-strain measurements of semicrystalline polymers such as polyethylene or polyamides. It is believed that irreversible conformational interconversions are especially important in those portions of the chains that connect the individual lamellar or fibrillar blocks in crytalline polymers. Since the stress between the individual blocks in crystals is transmitted by these relatively few "tie" molecules, the latter must be quite highly extended and at higher stresses may become overstrained.

It has been suggested[2,3] that in tie molecules and in similarly partially extended chains the overall strain in the molecules is given by the sum of two terms: $\epsilon = \epsilon_1 + \epsilon_2$, where ϵ_1 represents the elongation of a molecule due to a continuous change of torsional angles from the gauche to trans states and ϵ_2 is the elongation due to the subsequent (energy-elastic) deformation of a fully extended zigzag. This reasoning[2,3] is based on the assumption that the torsional angles are the only valence parameters that change in the first phase of stretching during conformational interconversion. However, data accumulated in recent years suggest that the valence bond angles and bond lengths are more deformable than previously believed and their change during deformation cannot be neglected.

At present two theoretical approaches are available for the energetic and structural characterization of the deformation of alkane molecules, namely, the quantum chemical[4] and molecular mechanical[5,6] computation methods. For complex lower molecular weight hydrocarbons and for macromolecules the molecular mechanics approach is the only sufficiently reliable and economically feasible method. The molecular mechanics method is inherently well suited for the description of

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molecular deformation because it expresses the "strain" energy of a molecule relative to a "strainless" reference state even in the absence of external force.[5] Boyd's version[5] of the method has been extensively applied in investigations of conformational energetics and dynamics of hydrocarbon chains, and the procedure is readily adaptable for calculations of molecular deformation brought about by external forces.[6-10]

We have used this methodology in our previous contributions[11-13] dealing with the mechanism of deformation of hydrocarbon chains. In these studies, which involved segments containing kink and gauche defects, we have observed a discontinuity in the deformation potential indicating a conformational transition of the defect into an all-trans structure. Since this phenomenon is of direct relevance to the mechanism of deformation of macromolecules in various situations of interest, the focus of the present paper is on the detailed description of the energetics of strain-induced transitions in simple polymethylene structures. In this paper we show that the discontinuity at the transition is a direct consequence of variations in bond lengths and bond angles during deformation and we have also determined the elastic energy that can be accumulated in a chain prior to the conformational transition.

Computational Method and Model

In molecular mechanics calculations the total potential energy of a molecule is expressed as the sum of several contributions[5]

$$V = V_r + V_\theta + V_\phi + V_{nb} \tag{1}$$

The bond length deformation potential is expressed by a harmonic approximation as $V_r = (1/2)k_r(r_{ij} - r_{ij}^\circ)^2$, where r_{ij} is the bond length between atoms i and j, r_{ij}° is an analogous reference (relaxed) bond length, and k_r is the bond stretching force constant. The energy of deformation of bond angles is $V_\theta = (1/2)k_\theta(\theta_{ijk} - \theta_{ijk}^\circ)^2$ where the symbols are analogous to those in the V_r term. The inherent torsional potential of an ethanelike bond of the form $V_\phi = (1/2)V_0(1 + \cos 3_{\phi i})$ exhibits minima at 180° and in the vicinity of 60 and 300° for the trans (t) states and the gauche (g^+ and g^-) states, respectively. The term V_{nb} expresses the summation of all nonbonded pair interactions of atoms in the molecule. The optimization of the energy by a numerical iterative method yields the equilibrium valence geometry and the static potential energy of the molecule.

The calculations were performed for *n*-hexadecane in several conformations, which are shown in Figure 1. The introduction of a conformational defect into the all-trans form brings about a decrease in chain length to different degrees as schematically shown in Figure 1. We recall that only the zigzag structure is planar and that all the other structures shown in Figure 1 project from the plane of the paper. In the calculations a molecule of given geometry fixed at one end is stretched by a force acting at the other end. The direction of the stretching force is collinear with a line connecting the end carbon atoms of the hexadecane molecules. The C_1–C_{16} distance in the undeformed molecule is denoted as h_0.

Chains containing several kinds of defects (Figure 1) were investigated. Two types of kink defects differing in the localization of the ...g^+tg^-... sequence were studied. Molecules with ϕ_3 and ϕ_5 torsional angles in the gauche position are denoted as kink A chains while those with ϕ_{12} and ϕ_{14} gauche bonds are denoted as kink B chains.

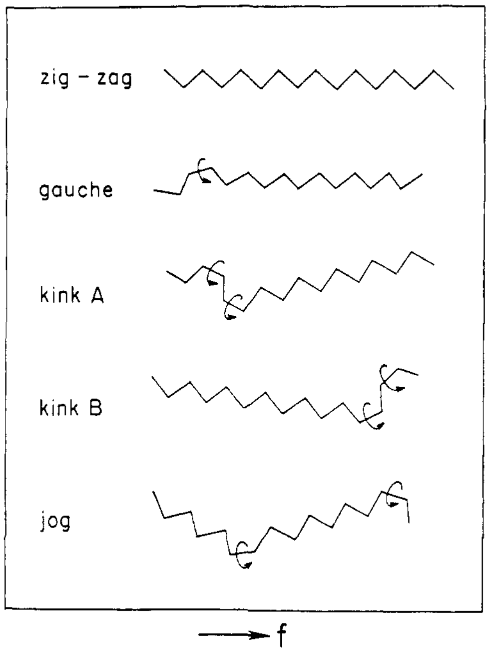

Figure 1. Hexadecane chains with torsional angles ϕ_i in the defect indicated: the zigzag conformation; the gauche (ϕ_3) conformation; the kink A structure with the (ϕ_3, ϕ_5) defect; the kink B structure with the (ϕ_{12}, ϕ_{14}) defect; the jog structure with the (ϕ_6, ϕ_{14}) defect.

In addition, a molecule having a "jog" defect ...tg^+t...tg^-t... with gauche angles at the ϕ_6 and ϕ_{14} bonds was also investigated. A third type of defect was represented by a chain containing a single gauche bond at ϕ_3. Molecules containing pairs of gauche bonds coupled with kink defects are believed to be present in highly ordered phases of solid polymers, while molecules containing gauche bonds loosely coupled in jogs or in isolated gauche defects are more typical for disordered zones in polymer chains either in bulk or in solution.

The external stretching force was simulated as previously described[11-13] by the additon to eq 1 of a deformation term, $V_{ex} = (1/2)k_{ex}(h_s - h)^2$, where k_{ex} is the relevant force constant, h_s is the present distance of the terminal carbon atoms C_1 and C_{16} in the molecule, and h is an analogous distance after optimization by the Newton–Raphson method. The additional deformation term serves only as a constraint during optimization and does not contribute to the total potential energy V. In most of the calculations the optimization was carried out with the force constant k_{ex} = 500 N/m; in some cases the values 10 and 80 N/m were used. The chain elongation (strain) is $\epsilon = (h - h_0)/h_0$ where h_0 is the distance between the end carbon atoms in the undeformed molecule. In addition, all-trans molecules were compressed by forced reduction of the distance between the end atoms;[13] the effects are briefly considered below. The Young's moduli, E, of single chains in elongation were determined from Hooke's law, assuming a constant value of 0.1824 nm^2 for the undeformed cross-sectional area of all the structures shown in Figure 1.

Results and Discussion

Effects of Deformation. The static potential energy, V_0, and the undeformed length, h_0 (the C_1–C_{16} distance), of each of the conformations shown in Figure 1 are listed in Table I. The introduction of a conformational defect decreases the length of the hexadecane molecule and destabilizes the chain with respect to the all-trans structure. The energy of destabilization (the conformational energy), ΔV_0 (about 5.6 kJ mol^{-1}), of the kinks is about twice that of the gauche state. In the kink conformations the energy ΔV_0 depends slightly on the location of the defect within the chain; in addition, the equilibrium lengths h_0 of the

Table I
Parameters of the Deformation Potential of Hexadecane Models[a]

	V_0, kJ mol^{-1}	ΔV_0, kJ mol^{-1}	h_0, nm	ΔV_{tr}, kJ mol^{-1}	ϵ_{tr}	E, GPa	E/E_{zz}
all-trans zigzag (zz)	19.37		1.9123			200.4	1.0
all-trans zigzag[b]	19.37		1.9123	37.5	8.5		
gauche defect	22.10	2.73	1.8385	21.4	5.1	70.1	0.35
kink defect A[c,d]	25.12	5.65	1.8364	33.8	5.1	110.5	0.55
kink defect B[e]	25.03	5.56	1.8195	25.0	4.7	90.0	0.45
jog defect[f]	24.59	4.22	1.6897	8.4	6.9	15.8	0.08

[a] V_0 is the static potential energy in the undeformed state and ΔV_0 is the related difference with respect to the zigzag structure; h_0 is the C_1–C_{16} distance in the undeformed molecule; ΔV_{tr} is the energy relieved at the gauche–trans transition at the strain ϵ_{tr}; E is the Young's modulus of the chain upon unilateral elongation, and E/E_{zz} is its relative value with respect to the zigzag structure. [b] Deformation on compression.[13] The trans–gauche transition. [c] Gauche bonds ϕ_3 and ϕ_5. [d] Reference 11. [e] Gauche bonds ϕ_{12} and ϕ_{14}. [f] Data for the first transition.

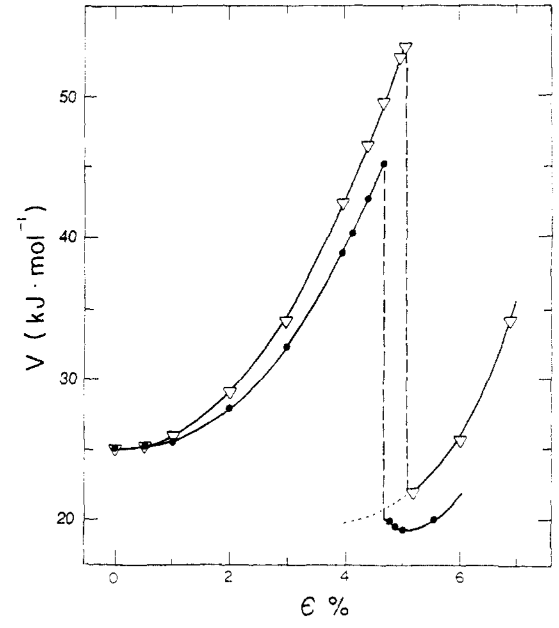

Figure 2. Conformational transition upon elongation for the kink A (▽) and the kink B (●) chains. The dotted line indicates the oversaturation region (see text).

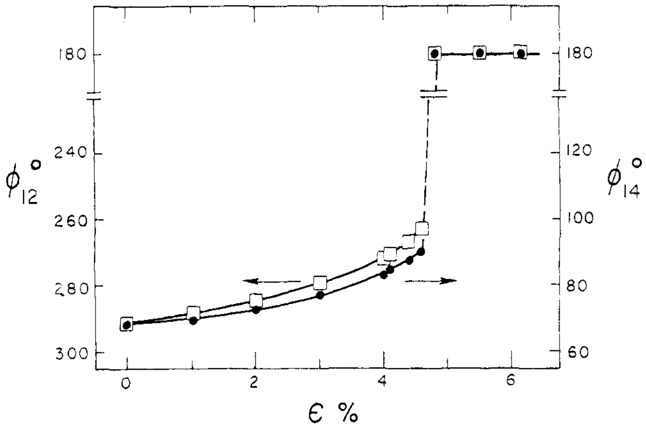

Figure 3. Variation of the torsional angles ϕ_{12} (□) and ϕ_{14} (●) with strain for the kink B chain.

kink structures A and B also differ (Table I). The chain containing a jog defect displays the smallest value of h_0 (a decrease in chain length of 0.22 nm with respect to the all-trans conformation, i.e., a change of 11.6%). The jog-containing chains are also more stable than the kink-containing chains, indicating that the separation of two gauche bonds of opposite sign by a longer sequence of trans bonds enhances the stability of an alkane molecule.

The stretching of chains containing defects at first results in an increase in the static energy V because of the contribution of the elastic energy stored in the molecule, $V = V_0 + V_{se}$. This is shown in Figure 2 for the kink A and B chains. However, at about 5% strain an abrupt decrease in energy is observed and the molecule undergoes a "flip-flop" transition into an all-trans conformation. At this point further conservation of the kink form destabilized by stored elastic energy is no longer favorable and the accumulated energy is released. The sharpness of the transition is best illustrated by the change in the torsional angles ϕ_{12} and ϕ_{14} in the kink B chain (Figure 3). Both torsional angles are at first continuously displaced by stretching from their equilibrium gauche values. At the transition point characterized by the strain ϵ_{tr} the two angles change discontinuously in a concerted way to 180°; the deformed kink B chain "jumps" into a zigzag conformation. Overall, the deformation of the two torsional angles shows a symmetrical "mirror image" pattern.

The energy released at the transition, ΔV_{tr} (Table I), *corresponds mainly to the V_{se} term, i.e., to the elastic* energy stored in the chain during the deformation ("the activation" energy in Figure 2). However, the term V_{se} also includes as a minor contribution the conformational energy, ΔV_0, due to the change of the ground state from the kinked to the all-trans conformation. Of the conformations investigated, the kink A chain sustains the maximum accumulation of deformation energy before it is converted to the all-trans state. Because of the location of the defect, closer to the stretched end of the molecule, the kink B chain shows a slightly lower ΔV_{tr}. The two model chains differ also in ϵ_{tr} since their undeformed length h_0 is not identical. However, a special "kinetic" effect contributes to this difference. The transition from the energy hypersurface corresponding to the deformed kink molecule into the hypersurface corresponding to the all-trans structure occurs when the length of the deformed structure h^{kink} becomes close to the equilibrium length of the undeformed zigzag $h^{zz}{}_0$ or in other words when the decrease in length of the molecule due to the defect is approximately compensated by chain elongation. Figure 2 shows that in the kink B chain the lengths $h^{zz}{}_0$ and h^{kink} are equal at about 5.0% strain and the transition occurs "prematurely" at slightly lower values of strain; i.e., the molecule is converted into a slightly compressed zigzag structure. However, in the kink A chain the undeformed zigzag length is attained at 4% strain, but the transition occurs at higher value, at 5.1%. Both the premature transition in the kink B chain and the deferred transition in the kink A chain are related to the problem of finding the optimum path of transition by the constrained optimization. In the kink A chain the optimization procedure manifests a tendency, perhaps artificial, for conservation of the structure of the deformed kink. This inertia brings about, in the region between 4 and 5.1% strain, an "oversaturation" of the molecule by the elastic energy. In other words, in the kink A chain the transition from the hypersurface of the deformed kink to *the hypersurface of the all-trans chain is separated by an* energy barrier.

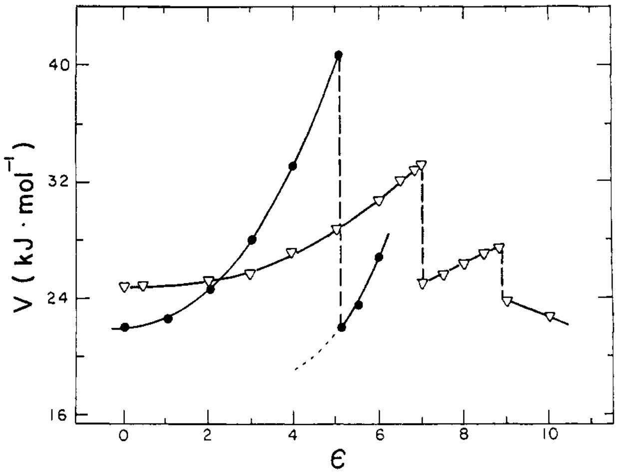

Figure 4. Conformational transitions in the gauche chain (●) and in the jog-containing chain (▽). The dotted line indicates the oversaturation region (see text).

The deformation potential for stretching the gauche and jog-containing chains is shown in Figure 4. The energetics of gauche chain deformation are similar to those of the kink conformations; the only difference is the reduced value of the energy ΔV_{tr} accompanying the gauche–trans transition. Again, an energy oversaturation of the deformed gauche chain is observed, implying that the molecule is transformed into a slightly stretched all-trans structure. The elastic behavior of a molecule containing two gauche bonds coupled in a kink and that of a molecule containing a single gauche bond seem to be similar; hence, the deformation properties of kink chains in the present case cannot be reconstructed by the summation of results for two independent gauche bonds. The subsequent stretching of the all-trans conformation resulting from the transition follows the prediction of the deformation potential of the isolated zigzag structure reported previously.[13]

In contrast to the case of the kink-containing chains, two discontinuous transitions were observed for the jog-containing molecule (Figure 4), indicating a much "looser" connecton between changes of the torsional angles ϕ_6 and ϕ_{14} upon stretching the molecule. In the first transition the gauche bond containing the torsional angle ϕ_6 is transformed into the trans state while the other defect bond ϕ_{14} rotates only slightly and remains in the range of the gauche conformation. The second, less distinct transition converts the molecule into a partially compressed zigzag conformation, which becomes fully planar after additional stretching. In comparison with the kink-containing chains, the interconversion in a jog-containing molecule is more facile and the molecule can accommodate only a small amount of elastic energy.

Distribution of Stored Energy. The elastic energy stored in the chain displaces all valence coordinates from their equilibrium values. In molecular mechanics calculations in addition to the torsional angles ϕ_i, changes in bond lengths r_i and bond angles θ_i are permitted upon stretching chains with torsional defects. The results show that the presence of "soft" parameters ϕ_i in a molecule does not automatically imply that the response of "hard" parameters r_i and θ_i to stress can be neglected. Recently, the importance of the bond angle and bond length terms was pointed out for the rate of conformational interconversions.[14] The flexibility of these degrees of freedom lowers the trans–gauche barrier of interconversion. In a zigzag structure with only r_i and θ_i as the variable parameters, the widening of the skeletal CCC angles on stretching brings about a slight change in the orbital hybridization on those carbon atoms, which results in the reduction of the CCH and HCH bond angles. In other words, the effective "thickness" of the zigzag ribbon is reduced by stretching.

Table II
Variation of the Energy and the Selected Valence Coordinates in the Kink A Chain as a Function of the Strain ε up to the Transition Point

	ε					
	0.0	0.99	2.94	4.71	5.05	5.18
E, kJ mol^{-1}	25.11	25.90	34.19	50.18	53.74	21.89
ϕ_3, deg	292.5	289.5	283.8	274.4	264.2	180.7
ϕ_4, deg	180.7	177.7	175.5	175.1	175.1	181.6
ϕ_5, deg	68.3	70.2	78.6	91.3	103.7	181.1
ϕ_6, deg	175.5	174.0	171.7	170.0	170.8	181.3
θ_4, deg	113.2	113.6	114.6	115.3	114.7	113.0
θ_5, deg	113.3	114.1	115.6	116.6	116.0	112.5
θ_{10}, deg	111.8	112.0	113.1	114.1	114.1	113.0
r_4, pm	154.2	154.2	154.5	155.0	155.1	154.5
r_5, pm	154.1	154.3	155.0	155.8	155.8	154.5
r_{10}, pm	153.8	154.0	154.8	155.5	155.4	154.5

The change in the valence parameters is especially notable in the vicinity of the defect. Table II shows the variation of some of the valence parameters with strain for the kink A chain up to the transition point ϵ_{tr}. It is seen that, in addition to the critical change in the angles ϕ_3 and ϕ_5 from the gauche to trans position, the angles ϕ_4 and ϕ_6 are also modified during stretching. Similarly, Table II illustrates the major changes in the bond angles θ_4 and θ_5 and in the bond lengths r_4 and r_5 pertaining to the defect as compared to the parameters θ_{10} and r_{10}, which exemplify the all-trans portion of the chain. The changes in the valence parameters in the kink A chains induced by stretching gradually dampen with increasing distance from the defect along the chain. An odd–even alternation in these changes was observed, similar to that described previously.[12,14] Overall, the structural data for the deformation of chains with torsional defects show the partial delocalization of the defect and its coupling with the adjacent parts of the chain. Hence, the summation of the properties of the "defect" and "all-trans" portions of the chain in the evaluation of the properties of the whole chain is only a first approximation. At the transition point all the stored elastic energy is released and the valence parameters relax from strained values to their equilibrium values for the all-trans chain.

Since all three types of valence coordinates change with stress, the overall chain strain is given as a sum, $\epsilon = \epsilon_r + \epsilon_\theta + \epsilon_\phi$. In chains containing conformational defects the torsional contribution ϵ_ϕ dominates the overall chain strain. However, the observation of a discontinuous strain-induced conformational transition is connected with the nonzero terms ϵ_r and ϵ_θ. For example in a sufficently long chain containing a kink the elongation of the chain by Δh_0 brings the chain length h^{kink} close to the length $h^{zz}{}_0$ of the undeformed zigzag. This situation may occur well in advance of any significant changes in the torsional angles pertaining to the defect so the molecule can still be in a deformed kink state; a flip-flop jump to the hypersurface of the all-trans conformation follows. When the variation in r_i and θ_i with strain is neglected, the chain strain is given by its torsional component only and the conformational interconversion proceeds by a smooth "dekinking" process with continuous changes in the torsional angles as originally envisioned.[2,3]

The precise value of ϵ_{tr} for a given defect depends on the chain length and on the bond angles and bond length parameters. In general, an abrupt transition occurs in those cases when the contribution of the latter two parameters

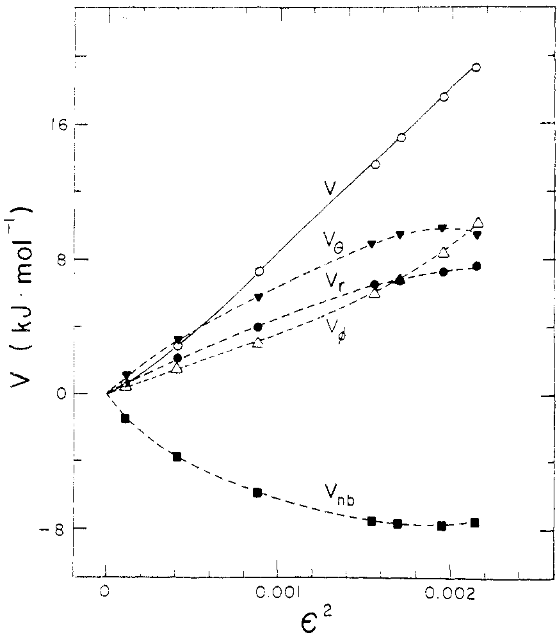

Figure 5. Variation of the potential energy and its components according to eq 1 with square of the strain for the kink B chain up to the transition point ϵ_{tr}.

to the chain length just compensates the chain shortening due to the defect, Δh_0, but the defect torsional angle is still in the ascending part of the gauche–trans barrier. Recent calculations[15] for a simple four-atom gauche segment using differing force-field potentials also feature an abrupt jump into the energy hypersurface of the trans state.

The significance of the bond length and bond angle terms is also indicated by the resolution of the stored energy into contributions according to eq 1. Figure 5 illustrates this point for the kink B chains in a plot of total energy and its distribution into components as a function of the square of the strain up to the transition point. It is seen that except in the vicinity of the transition point the torsional term is not a major contribution to the deformation energy. This is a contradiction to the traditional view, which associates the deformation of chains involving conformational defects only with purely torsional dekinking. The energy contributions of the bond and angle strains in Figure 5 are roughly equivalent. Since stretching reduces unfavorable nonbonded interactions between atoms in close contact, the change in the term V_{nb} with stretching stabilizes the molecule.

The transition point poses a limit on the amount of energy that can be mechanically "pumped" into molecules containing a torsional defect. The energy released at the transition ΔV_{tr} can be contrasted with the gauche–trans barrier in undeformed paraffin molecules: 8.2 kJ mol^{-1} was found from calculations using Boyd's method.[16] The latter figure gives a maximum of the energy that can be stored in the torsional mode, and the remaining portion of ΔV_{tr} represents the energy accumulated in the strained bonds and bond angles. The amount of accumulated (and released) energy can be significant (Table I); for example, for the kink A chains, the term ΔV_{tr} is about 2.1 kJ mol^{-1} per CH_2 group or about 150 J cm^{-3} assuming unit density. The latter value represents about one-third of the cohesive energy density of typical liquid paraffins.

Abrupt Conformational Transitions in Bulk Polymers. In the usual "continuum" picture of a conformational transition the mechanical force provides the energy to elongate the chain by pulling segments over conformational barriers that would be insurmountable by thermal energy only. In this process the change of the torsional angle from the gauche to trans state proceeds through the whole range from 60° to 180° and requires the translation of segments on a large scale. Recent calculations[15] showed that sufficiently strong interchain constraints present in the glassy state can effectively prohibit conformational transitions of this kind. Thus the importance of interconversions via the abrupt transitions described in this paper is stressed. The stretching of a chain in the presence of strong constraints from neighboring molecules in crystalline or glassy polymers distributes the deformation energy into all three types of valence coordinates, r_i, θ_i and ϕ_i, and the process is accompanied by a lower transitional displacement of atoms. Thus in contrast to polymer materials above T_g and T_m where most of the mechanical energy is stored entropically, by a shift in the equilibrium conformational distribution in favor of longer conformations, the elastic energy in crystalline and glassy polymers is stored in the alteration of all valence coordinates. The stored energy can be recovered by relieving the interchain constraints, for example, by heating; this phenomenon can be observed by calorimetric techniques.

The results of model calculations should be of direct relevance to the molecular mechanism of drawing crystalline polymers involving polymethylene segments. Crystalline polymers such as polyethylene or polyamides can be modeled as series arrangements of crystalline and amorphous regions where the latter are traversed by highly extended tie molecules of various degrees of tautness. The irreversible conformational transitions within tie molecules have been invoked[1,2] to explain the difference between the first and subsequent stress–strain cycles. One can envision that the drawing of already rather extended chains is accompanied by an abrupt, irreversible gauche–trans transition with the dissipation of the elastic energy as heat. The amount of stored (and dissipated) energy can be estimated by resolution of the deformation energy from cyclic experiments into elastic, anelastic, and plastic components.[17] The anelastic component is believed to be a consequence of the stress-releiving conformational transitions. The anelastic component determined for polyamide 6,6, about 10 J cm^{-3} at 15% strain, steadily increases with the strain.[17] It is probable that at this point the tie molecules in the material are still coiled and that the energy released is much lower than that shown in Table I. However, at higher macroscopic strains the structure of the taut tie molecules in polyamide 6,6 should closely resemble the models shown in Figure 1, and the anelastic part of the deformation energy determined from experiment may reach values comparable to those listed in Table I.

The role of the stress-bearing interfibrillar tie molecules is particularly critical in high-strength/high-modulus polyethylene fibers. The extraordinary material properties of these polymers are a consequence of perfect alignment of macromolecules in crystalline aggregates connected by taut tie molecules. The kink structures shown in Figure 1 and the process of their interconversion discussed above may represent a realistic model for the response of a polyethylene fiber to stretching.

To complete the picture of conformational transitions induced by mechanical deformation of the chains, Table I also includes the data for the opposite trans–gauche interconversion observed previously[13] upon compression of all-trans chains. The single planar zigzag chain without constraints of neighboring molecules in a lattice was subjected to compression by a gradual decrease in the C_1–

C_{16} distance from the equilibrium distance h^{zz}_0. The originally rodlike chain at first undergoes a process of being gradually bent and buckled by small deviations in the torsional angles from 180° as well as by variations in the skeletal bond angles since the zigzag structure is planar only when two neighboring CCC angles are identical. Further increases in the compression to about 8.5% strain bring about a decrease in energy due to the formation of a gauche defect in the CC bond located fourth from the chain end. The stored elastic energy is thus released by a conformational interconversion, this time, however, of the opposite, trans–gauche direction. The remaining torsional angles relax to 180°, and the bond angles and bond lengths also return to equilibrium values.

The compressional transition can be compared to the inverse process due to stretching of the gauche chains shown in Figure 4 even though the latter data refer to the transition at the third bond from the chain end. The comparison (Table I) shows a large difference in the energy ΔV_{tr} and strain ϵ_{tr} for these two processes, indicating existence of a large hysteretic effect in the path of the mechanically induced conformational transitions.

The potential for the distortion by compression of torsional angles from values of approximately 180° in the zigzag structure is responsible for the asymmetric parabolic shape of the deformation potential of the zigzag in stretching and in compression.[13] This unique structural feature of single chains has striking consequences in the material properties of high-performance polymers based on rigid-rod molecules such a aromatic amides or on the more flexible chains such as in high-modulus polyethylene. Typically, these materials have high axial strength and modulus but low compressional strength. By compression of extended chains in these materials, the discontinuous jump in torsional angles and the loading of elastic energy into all valence parameters should be expected. Because of the neighboring chain constraints, the trans–gauche transition appropriate for single-chain compression would be amended to a trans–kink interconversion. The phenomenon of conformational transitions occurring on compression may be incorporated into the model of compressional failure[18] based on the concept of chain microbuckling. Recent molecular dynamic simulations[19] of the assembly of polymethylene segments also predicts a reduction of bond angles and the formation of gauche bonds under compression.

When the deformation force is relieved and the constraints of neighboring chains are weak, the conformational transitions are reversible and presumably proceed in both directions by a discontinuous path. This may be the situation observed for low-density polyethylene[20] where annealing was explained by the transformation of tie molecules from the extended into a more coiled, rubbery state.

In general, the concept of abrupt conformational transitions at elongation or compression is not limited to paraffinlike chains but may occur in any macromolecule with single bonds in the backbone. In some cases such as in vinyl polymers or poly(oxymethylene), which prefer helical conformations, stress induces the conformational transformation of chains into the higher energy zigzag conformation.

Defect Chain Moduli. The plot of energy as a functon of ϵ^2 permits a test of the Hookean behavior of model chains since in the energy representation Hooke's law is written as

$$V = (1/2)Eh_0A\epsilon^2 \qquad (2)$$

where E is the Young's modulus for unilateral elongation and A is the cross-sectional area of an undeformed chain. As is seen from Figure 5 the kink B chains obey Hooke's law at strains above about 1.5%; in the region of small strains the curve shows positive deviation from a straight line. This is a result of a fortuitous cancellation of contributions since neither of the individual components of the total energy in Figure 5 follows Hooke's law.

The Young's modulus of the kink B chain, 90 GPa, was determined from the linear part of the curve for the total energy in Figure 5 assuming a value of 0.1824 nm^2 for the cross-sectional area of a paraffin chain. By similar graphic representations of eq 2 Young's moduli for other model chains were determined and results are listed in Table I. In all cases deviation from Hooke's law in the range of small strains was observed, indicating that the initial moduli (for $\epsilon \to 0$) are smaller than those listed in Table I. The compression of the zigzag chain showed non-Hookean behavior in the whole range of strains investigated.

The calculated moduli correspond to a force acting in the direction of a line connecting and end carbon atoms of the chain. Even for the all-trans form, this direction is not exactly collinear with the long axis of molecule. The deviation is more noticeable for chains containing conformational defects. With respect to the modulus, the mutual orientation of the acting force and of the torsional axis, for example, the bond C_3C_4 or C_5C_6 in the kink A chain, is a major factor. If the orientation of the force and the torsional axis is identical, a minimal value of modulus will result. On the other hand in situations where the force acts almost perpendicularly on the axis of torsion, as in the present cases, the modulus attains a fairly large value.

The data in Table I suggest that introduction of a defect considerably diminishes the chain modulus E to about half or one-third the value of the zigzag element, E_{zz}, for kink or gauche defects, respectively. The ratio E/E_{zz} should be preferred as a relative measure of the influence of the defect on the modulus over the absolute values. The absolute values of the calculated chain modulus for the polymethylene zigzag differ considerably depending on the method used and are in the range of about 200–400 GPa.[1,4,7,11] Our calculations (Table I) suggest that the Boyd parametrization[5] of molecular mechanics calculations gives an all-trans modulus in the lower limit of the above range presumably because of an overestimation of the "softness" of the bond angle deformation. Recently, a modulus of 267 GPa was reported[8] for the paraffin zigzag using a new parametrization[21] of Boyd's method with modified parameters in the V_θ term. We believe that the use of the ratio E/E_{zz} to assess the impact of defects on the chain modulus allows circumvention of the question of which version of the method should be favored. Nevertheless, it seems that future developments of reliable force fields in molecular mechanics would certainly benefit from the inclusion of the stress–strain properties of single molecules into the process of selection and balancing of parameters.

Formally one can evaluate the elastic modulus of a "bare" defect in a chain assuming additivity of the reciprocal moduli (compliances) of the structural elements of a chain

$$1/E = \sum_{i=1}^{\infty} x_i/E_i \qquad (3)$$

For example, for the kink B chains, the chain compliance, E^{-1}, is a compositional average of the bare kink defect

$\ldots g^+tg^-\ldots$: and the remaining all-trans portion of the chain. When the data from Table I, 90.0 and 200.4 GPa for the kink B chain and the all-trans modulus, respectively, are used, eq 3 yields 28.9 GPa for the bare modulus of the three -bond kink sequence. This indicates that the kink defect yields an element about 7 times more elastic than that of the all-trans structure. The bare defect modulus effectively includes all changes in the deformational response of the zigzag segment that were brought about by an introduction of the defect into the segment.

Very little information is available on the moduli of chains with conformational defects. An unrealistically high modulus of 245 GPa was calculated[22] for the three-bond kink defect assuming a strictly symmetrical (i.e., $\phi_3 = -\phi_5$) deformation of torsional angles. Using the original parametrizaton of Boyd's method, Reneker and Mazur[9] calculated moduli in the range of 30–70 GPa or several six- or seven-bond crystallographic defects characterized by a full reentry of the chain ends into the lattice points of the original all-trans chain. It is our expectation that calculations of moduli for the some additional segments involving torsional defects will be useful in the interpretaton of the mechanical properties of polymeric materials.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research, Grant No. 88-001.

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Registry No. Polymethylene, 25038-57-7; hexadecane, 544-76-3.

Molecular Aspects of Latex Film Formation: An Energy-Transfer Study[1]

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Received October 5, 1989; Revised Manuscript Received March 14, 1990

ABSTRACT: Poly(butyl methacrylate) (PBMA) latex labeled with either phenanthrene or anthracene derivatives in low concentrations (1 or 2 mol %) was prepared by semicontinuous emulsion polymerization. The latex film formation process was studied by analysis of the nonradiative energy transfer from phenanthrene (donor) to anthracene (acceptor). Initially, when the latex film dries, there is little energy transfer, indicating that the particles conserve their individual identity. With increasing time at temperatures above the glass transition temperature of PBMA, the extent of energy transfer increases. This is a clear indication that interdiffusion of polymer chains across particle boundaries occurs. The diffusion coefficient D of the polymer was evaluated by using models based upon Fick's second law. In each sample, the magnitude of D decreases with time. Initial D values increase with increasing temperature, taking values between 1×10^{-14} to 1×10^{-18} cm^2/s, yielding an apparent activation energy of 38 kcal/mol. The diffusion data also fit well to the Williams–Landel–Ferry equation. The results demonstrate the great potential of fluorescence techniques in the study of polymer diffusion processes during latex film formation.

Introduction

The topic of film formation from aqueous latex dispersions is of both fundamental and technological importance.[3,4] Recent concern about the deleterious environmental impact of solvent-based coatings has led to an even more intense effort to develop high-performance coatings based upon aqueous dispersions. Much of the early work on latex film formation focused on the early stages of the process: particle concentration accompanying water evaporation followed by particle coalescence and deformation to produce continuous and transparent films.[5,6] Particle deformation occurs only above a certain temperature, the minimum film formation temperature (MFFT), which is usually close to the glass transition temperature of the polymer.

The drying of aqueous latex to produce a film usually takes from several minutes to several hours, depending on the film thickness and the environmental conditions. After this period, both film aspect and film properties often improve with time.[7,8] This phenomenon is referred to as "further coalescence". One explanation of this process is the interdiffusion of polymer chains across particle

0024-9297/90/2223-4082$02.50/0