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Calculation of Three-Dimensional Elastic Constants of Polymer Crystals. 3. α and γ Forms of Nylon 6

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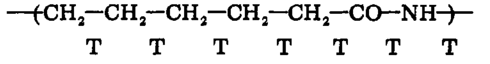
ABSTRACT: Three-dimensional elastic constants of the α and γ crystal forms of nylon 6 have been calculated and showed fairly good agreement with values observed by X-ray methods. The Young's modulus in the direction normal to the chain axis has been found to have a large anisotropy, different from the cases of orthorhombic polyethylene (PE) and atactic poly(vinyl alcohol) (PVA) reported earlier; the Young's modulus is much larger in the hydrogen-bonded sheets of the plane (about 15 GPa) than in the direction normal to the sheets, governed by van der Waals forces (about 7 GPa). Such circumstances are also seen in the cases of anisotropic linear compressibility. The elastic constants have been calculated with and without taking into consideration the intermolecular hydrogen bonds, making clear the roles of van der Waals interactions and hydrogen bonds upon the mechanical anisotropy. The calculated Young's modulus along the chain direction, E_l, for the α form of nylon 6, about 312 GPa, is too large to explain the observed value at room temperature, about 100 GPa, but corresponds well with the value observed at −150 °C, about 270 GPa. These values are interpreted by the contraction of the molecular chain from the planar–zigzag conformation, as revealed by the calculation of E_l as a function of the internal rotation angle of CH_2–amide bonds. The calculated Young's modulus E_l for the γ form is about 54 GPa, the observed value being about 27 GPa. Intermolecular interactions have been found to greatly affect the Young's modulus E_l for the contracted chain of the γ form but not for the planar-zigzag chains of PE, PVA, and the α form.

In the previous two papers we developed a method for calculating three-dimensional elastic constants and discussed the anisotropy of Young's modulus and linear compressibility for orthorhombic polyethylene (PE) and poly(vinyl alcohol) (PVA).[1,2] Hydrogen bonds of OH···O type in PVA crystal were found to have a large effect on the values of mechanical constants, in contrast to the case of PE, governed mainly by van der Waals interactions. The α and γ forms of nylon 6 have three different kinds of interactions in three different directions, respectively; i.e., the molecular chains constructed by strong covalent bonds are linked to each other by hydrogen bonds of NH···O type to form a series of sheets, which are stacked together by weak van der Waals interactions (Figure 1).[3,4] Thus we can expect a pronounced anisotropy of mechanical constants in different directions of nylon 6 crystals. Additionally the α form of nylon 6 differs from the γ form in chain conformation as well as in packing mode, reflecting on the difference in mechanical anisotropy between them.

In this paper we report the calculated results of elastic constants of the α and γ forms of nylon 6 and discuss their mechanical anisotropy in comparison with the cases of PE and PVA reported in the previous paper.[2]

Crystal Structures and Potentials

α Form of Nylon 6. Although this polymer has been said to experience a slight crystal structural change depending on the annealing conditions,[5] we will employ here the crystal structure model proposed by Holmes, Bunn, and Smith.[3] It belongs to the space group $P2_1$-C_2^2 and has cell parameters of a = 9.56 Å, b (fiber axis) = 17.24 Å, c = 8.01 Å, and β = 67.5°. A unit cell contains four molecular chains of conformation



$$\begin{array}{c}-\!\!\left(CH_2-CH_2-CH_2-CH_2-CH_2-CO-NH\right)\!\!-\\ \mathrm{T}\quad\mathrm{T}\quad\mathrm{T}\quad\mathrm{T}\quad\mathrm{T}\quad\mathrm{T}\quad\mathrm{T}\end{array}$$

Table I
Nonbonded Interatomic Force Constants for Nylon 6[a]
f (mdyn/Å) = A exp($-Br$) − Cr^{-D}

atomic pair	A	B	C	D
H···H	257.66	3.74	7.96	8
H···C	1342.77	3.67	54.66	8
H···O H···N			−3887.10	14
C···O			−2332.23	14

[a] Intermolecular interatomic distance r in units of Å.

which form two sheets of hydrogen-bonded planes as shown in Figure 1. The number of atoms contained in one crystallographic asymmetric unit is 76 and the order of the matrices necessary for calculation of the elastic constants approaches 230, too large to perform a numerical calculation of the elastic constants even with a computer, due to excessively long computational times and cumbersome data processing. Therefore we will assume here the crystal structure model shown in Figure 1 as a first approximation; only one sheet of the plane is contained in the unit cell with parameters of a' = 9.56 Å, b' = 5.45 Å, c' (fiber axis) = 17.24 Å, α' = 47.3°, β' = 90.0°, and γ' = 73.7° and this sheet is brought to the next sheet of the plane by the translation of 3/14 b along the chain axis. In this model the relative positions of the methylene and amide groups are displaced gradually from the original ones as the molecular chains locate far from the position of the basic chain (Figure 1). But, as understood from the values of intermolecular force constants, only the intermolecular interactions between the nearest-neighboring chains determine the anisotropy of mechanical properties of the crystals where there is negligibly small contribution from the electrostatic long-range interactions, different from the cases of ionic crystals. This means that the crystal structure model employed here may be acceptable for the present calculation. The positions of hydrogen atoms were determined by assuming HCH = 109.5° and C–H = 1.09 Å and that they might pass through the bisectors of skeletal bond angles. Intramolecular potentials are of the valence-force-field type and their values are transferred directly from ref 6. The intermolecular force constants of the central-force-field type are given as the second derivatives of the potential functions listed in Table I for the atomic pairs H···H, H···C, H···O, H···N, and C···O, with interatomic distances shorter than 4 Å.[7] For the NH···O hydrogen bond, with a distance of 2.81 Å, a force constant of 0.3 mdyn/Å was assumed.[8]

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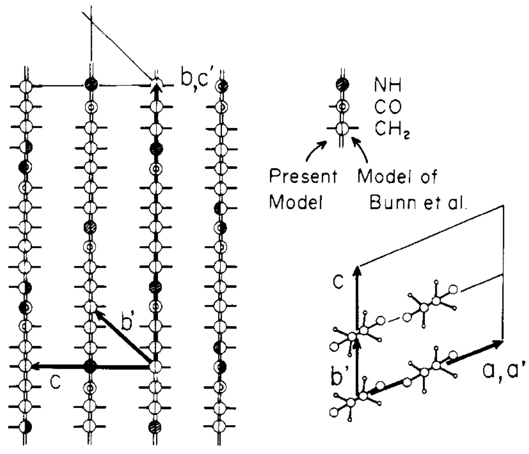


Figure 1. Crystal structure of the α form of nylon 6. The right-half side of the circles of the chain represents the atomic arrangements proposed by Bunn et al.[3] (cell axes of a, b, and c) and the left-half side the arrangements utilized in the present calculation (cell axes of a', b', and c').

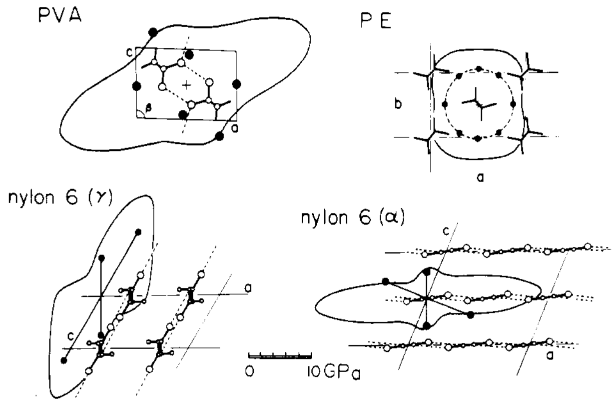


Figure 2. Anisotropy of Young's modulus in the plane normal to the chain axis. The solid circles are the values observed by Sakurada et al.[10] and the solid curves show the calculated results.

The calculations of the elastic constants are based on the equations derived in the previous paper.[1]

γ Form of Nylon 6. The crystal structure proposed by Arimoto et al.[4] was employed (Figure 2): the cell parameters are $a = 9.33$ Å, b (fiber axis) $= 16.88$ Å, $c = 4.78$ Å, and $\beta = 121°$, the space group is $P2_1/a\text{-}C_{2h}^5$, and the molecular conformation is

$$\begin{array}{c} -\!\!(\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CO{-}NH})\!\!- \\ \mathrm{T\quad T\quad T\quad T\quad S\quad T\quad \overline{S}} \end{array}$$

The intramolecular and intermolecular potentials are the same as used for the α form. The force constant of the NH···O hydrogen bond (2.82 Å) was also assumed to be 0.3 mdyn/Å.

The reasonableness of these potentials was checked by comparison of the calculated lattice vibrations of the α and γ forms with the observed frequencies, with results reported later.

Results and Discussion

The calculated elastic constant tensor **C** and compliance constant tenson **S** for the α and γ forms of nylon 6 are shown in eq 1–4. The Cartesian coordinate axes were assumed as follows: z axis = the chain axis; y = the c axis; x normal to the zy plane.

α Form of Nylon 6:

$$\mathbf{C} = \begin{bmatrix} 12.44 & 2.68 & 2.00 & 0 & 0 & 4.40 \\ 2.68 & 5.20 & 0.75 & 0 & 0 & 0.82 \\ 2.00 & 0.75 & 312.33 & 0 & 0 & 0.06 \\ 0 & 0 & 0 & 2.33 & -0.39 & 0 \\ 0 & 0 & 0 & -0.39 & 0.95 & 0 \\ 4.40 & 0.82 & 0.06 & 0 & 0 & 3.65 \end{bmatrix} \text{ GPa} \qquad (1)$$

$$\mathbf{S} = \begin{bmatrix} 15.27 & -5.15 & -0.08 & 0 & 0 & -17.24 \\ -5.15 & 21.66 & -0.02 & 0 & 0 & 1.34 \\ -0.08 & -0.02 & 0.32 & 0 & 0 & 0.10 \\ 0 & 0 & 0 & 46.13 & 19.11 & 0 \\ 0 & 0 & 0 & 19.11 & 113.05 & 0 \\ -17.24 & 1.34 & 0.10 & 0 & 0 & 47.86 \end{bmatrix} \times 10^{-2} \text{ GPa}^{-1} \qquad (2)$$

γ Form of Nylon 6:

$$\mathbf{C} = \begin{bmatrix} 5.27 & 1.77 & 0.80 & 0 & 0 & -0.96 \\ 1.77 & 17.52 & 4.47 & 0 & 0 & 0.67 \\ 0.80 & 4.47 & 54.96 & 0 & 0 & -0.44 \\ 0 & 0 & 0 & 4.44 & -0.63 & 0 \\ 0 & 0 & 0 & -0.63 & 2.35 & 0 \\ -0.96 & 0.67 & -0.44 & 0 & 0 & 2.75 \end{bmatrix} \text{ GPa} \qquad (3)$$

$$\mathbf{S} = \begin{bmatrix} 21.23 & -2.43 & -0.05 & 0 & 0 & 7.98 \\ -2.43 & 6.17 & -0.49 & 0 & 0 & -2.43 \\ -0.05 & -0.49 & 1.86 & 0 & 0 & 0.40 \\ 0 & 0 & 0 & 23.41 & 6.29 & 0 \\ 0 & 0 & 0 & 6.29 & 44.23 & 0 \\ 7.98 & -2.43 & 0.40 & 0 & 0 & 39.87 \end{bmatrix} \times 10^{-2} \text{ GPa}^{-1} \qquad (4)$$

Anisotropy of Young's Modulus in the Plane Normal to the Chain Axis

In Figure 2 are shown the calculated results of the anisotropy of Young's modulus in the plane normal to the chain axis for the α and γ forms of nylon 6, in comparison with those of PE and PVA reported in the previous paper.[2] Young's modulus $E(\theta)$ in the direction of an angle θ from the Cartesian x axis is represented as follows in the case of a monoclinic system:[9]

$$1/E(\theta) = s_{11}\cos^4\theta + s_{22}\sin^4\theta + (2s_{12} + s_{66}) \times \cos^2\theta\sin^2\theta + 2(s_{16}\cos^2\theta + s_{26}\sin^2\theta)\cos\theta\sin\theta \qquad (5)$$

The solid circles in the figure represent the values observed by Sakurada et al., using X-ray diffraction.[10] The magnitude of Young's modulus in the direction θ is represented by a distance between the point on the curve and the center point along this direction. The agreement between the observed and calculated results is fairly good. As discussed in the previous paper, the anisotropy of Young's modulus for PE crystals is not so clear although the modulus in the b direction is somewhat larger than that in the a direction, reflecting nearly uniform van der Waals interactions in all directions. In the case of PVA, the maximal and minimal Young's moduli are directed to the bisectors of the two kinds of hydrogen bonds and the anisotropy is not so large. The magnitude itself of Young's modulus is much larger than that of PE crystals. Different from these two cases of PE and PVA, the hydrogen-bonded chains in the unit cells of the α and γ forms of nylon 6 form a series of sheets held together by van der Waals interactions. Such a structural feature reflects on the large anisotropy of Young's modulus: that is, Young's modulus within the hydrogen-bonded sheet is almost of the same order as that of PVA, while the modulus normal to the sheet plane is about the same magnitude or even smaller than that of PE.

Anisotropy of Linear Compressibility in the Plane Normal to the Chain Axis

Figure 3 shows the anisotropy of linear compressibility

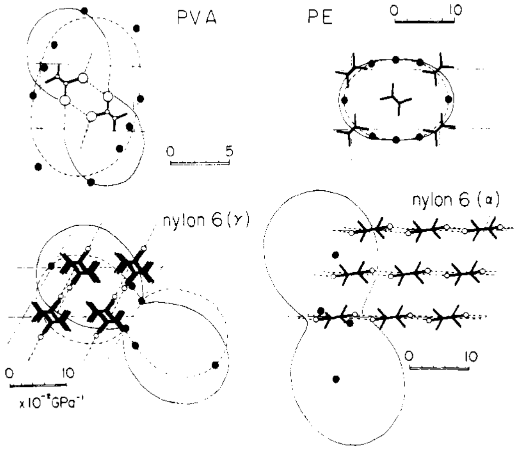
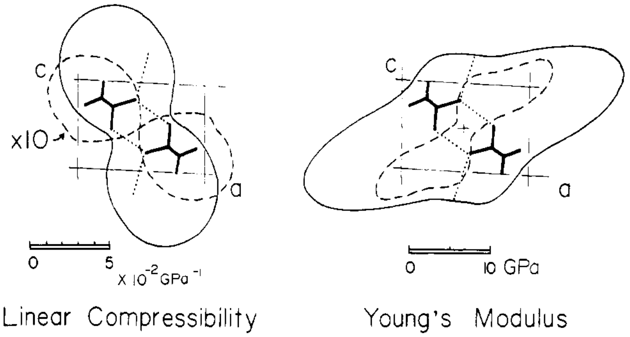


Figure 3. Anisotropy of linear compressibility in the plane normal to the chain axis. The solid curves show the calculated results and the broken lines with the solid circles are the values observed by Ito et al.[11]

in the plane normal to the chain axis for PE, PVA, and the α and γ forms of nylon 6. Linear compressibility $\beta(\theta)$ in the direction of an angle θ from the x axis is represented as[9]

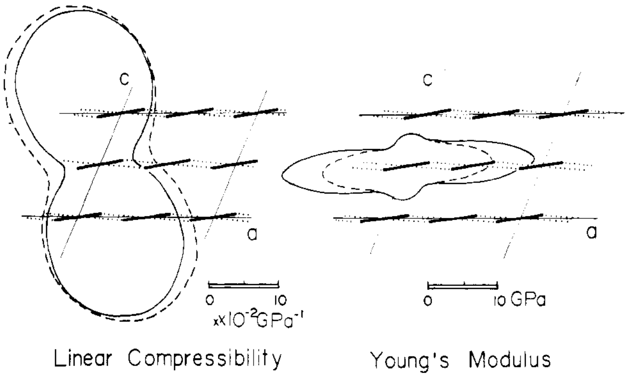
$$\beta(\theta) = (s_{11} + s_{12} + s_{13}) \cos^2 \theta + (s_{21} + s_{22} + s_{23}) \sin^2 \theta + (s_{16} + s_{26} + s_{36}) \sin \theta \cos \theta \quad (6)$$

The broken lines represent the curves fitted to the values observed by Ito et al. (solid circles)[11] and the solid lines are the calculated results. Just as for the Young's modulus, the anisotropy of linear compressibility may be also understood reasonably from the structural features of these crystals. In the case of PE, the linear compressibility along the b direction is a little smaller than that along the a axis, although the anisotropy is not so pronounced. In the case of PVA, the linear compressibility is appreciably small in whole compared with that of PE because of the strong hydrogen bonds. But the anisotropy is not so clear. For the α crystal of nylon 6, the anisotropy of linear compressibility is remarkable; the compressibility in the direction normal to the hydrogen-bonded sheets is of the same order as those for PE, while the compressibility in the sheet planes is of the same order as those of PVA. The calculated result gives an anisotropy similar to the observed one but the absolute values are about 2 times larger than the latter. Mechanical constants in the direction normal to the sheet planes are almost governed by the H···H nonbonded interatomic interactions. In the crystal structure proposed by Bunn et al.,[3] some of the H···H atomic pairs are extremely short, about 1.7 Å, unacceptable from a crystallographic point of view. Recently, Malta et al.[12] refined the crystal structure of the α form of nylon 6 but the H···H distances are not yet revised so reasonably. It may be necessary to thoroughly analyze the crystal structure of the α form of nylon 6 with the more reasonable interatomic distances. For the γ form of nylon 6, we obtain good agreement between the observed and calculated results of linear compressibility as well as Young's modulus. The linear compressibility in the direction normal to the sheet planes is somewhat larger than that of PE, while the linear compressibility within the sheets is of the same order as those of PVA and the α form of nylon 6.



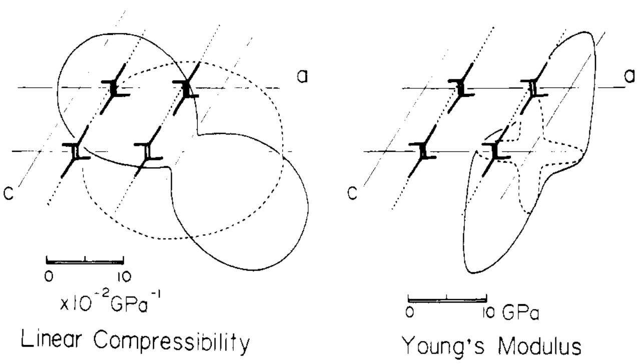
Linear Compressibility Young's Modulus

Figure 4. Effect of the intermolecular van der Waals interactions and hydrogen bonds on the mechanical anisotropy of atactic poly(vinyl alcohol). The solid lines represent the calculated result, taking into consideration all the intermolecular interactions, and the broken lines represent the result calculated without the hydrogen bonds.



Linear Compressibility Young's Modulus

Figure 5. Effect of intermolecular van der Waals interactions and hydrogen bonds on the mechanical anisotropy of the α form of nylon 6. Refer to the caption of Figure 4 for the meanings of the solid and broken lines.



Linear Compressibility Young's Modulus

Figure 6. Effect of intermolecular van der Waals interactions and hydrogen bonds on the mechanical anisotropy of the γ form of nylon 6. Refer to the caption of Figure 4 for the meanings of the solid and broken lines.

Effect of Intermolecular Hydrogen Bonds on the Young's Modulus and Linear Compressibility in the Plane Normal to the Chain Axis

In order to investigate to what extent the intermolecular hydrogen bonds affect the anisotropy of Young's modulus and linear compressibility, we calculated the elastic and compliance constants both with and without taking into consideration the hydrogen bonds. Figures 4–6 show the calculated results of Young's modulus and linear compressibility in the plane normal to the chain axis for PVA and the α and γ forms of nylon 6. In all cases the Young's modulus is substantially reduced in the direction of the hydrogen bonds. The effect is much more pronounced for linear compressibility. In the case of PVA, the calculated compressibility without taking into account the hydrogen bonds is about 10 times larger than that with hydrogen bonds, indicating that the mechanical property of PVA is almost determined by the strong hydrogen bonds. As for the α form of nylon 6, the linear compressibility curve does not show so great a change, although the compressibility

Table II
Crystallite Modulus in the Chain Direction (GPa)

	PE	PVA	nylon 6	
			α	γ
observed value				
X-ray method[10]	235	250	165 100[14]	27
longitudinal acoustic mode	358[16] 290[17]			
neutron scattering	329[18]			
calculated value	315.5	287.4	311.5	53.7

in the direction of the a axis or within the sheet planes is reduced somewhat more than that along the direction normal to the sheet plane. In this case, van der Waals interactions may govern the anisotropy. For the γ form of nylon 6, the role of hydrogen bonds is interesting in that the van der Waals interactions give almost an isotropic curve of compressibility and the hydrogen bonds deform the curve into a quite anisotropic curve along the direction of the hydrogen bonds.

Young's Modulus and Linear Compressibility along the Chain Axis

In Table II are shown the observed and calculated Young's moduli along the chain direction for PE, PVA, and the α and γ forms of nylon 6.[10] PE, PVA, and the α form of nylon 6 have the calculated moduli characteristic of the planar-zigzag conformation, about 300 GPa. The molecular conformation of the γ form of nylon 6 is, on the other hand, contracted about 3.3% from the fully extended conformation,[4] so that the crystallite modulus is lower by one figure than the case of the planar-zigzag chain. The agreement between the calculated and observed values is good except for the α form of nylon 6. The molecular chain of the α form has been said to be contracted slightly from the extended structure by some torsional rotations about the CH_2–amide bonds due to the thermal motion[13] or due to the interaction among the sheet planes.[5] Miyasaka et al.[14] measured the stress–strain curve of the α crystal form by X-ray diffraction and showed that the slope gradually becomes steeper as the chains are stretched; that is, the crystallite modulus of about 100 GPa for the initial slope increases to a value of about 300 GPa when the fiber is stretched by the tensile stress of about 3000 kg/cm^2. They also measured the temperature dependence of the crystallite modulus in the range +20 to −150 °C and revealed that the initial Young's modulus increases to 270 GPa at −150 °C from the value of 100 GPa at room temperature, The fiber period was found to increase from 17.28 to 17.32 Å under free tension as the temperature was lowered, indicating that the molecular chain extends close to the planar-zigzag conformation at low temperature. From these results they concluded that the chain in the α form is not completely extended but somewhat twisted at room temperature and the extraordinarily small crystallite modulus observed at room temperature is due to such a twisting. We calculated the Young's modulus of nylon 6 isolated chain as a function of the fiber period by varying the internal rotation angles of CH_2–amide bonds. The result is shown in Figure 7, where the crystallite modulus is plotted against the amount of contraction from the planar-zigzag chain. The modulus is very sensitive to the contraction of the chain; it is reduced to half the value for the planar-zigzag chain for a contraction of only about 0.3%, corresponding well to the observed result of the relation between the Young's modulus and the fiber period by Miyasaka et al.[14]

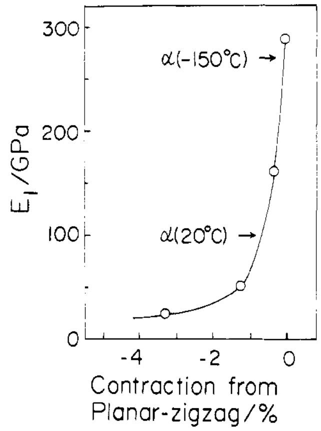


Figure 7. Calculated Young's modulus along the chain axis of nylon 6 isolated chain as a function of the contraction of the fiber period from the planar-zigzag conformation. The arrows show the values observed by the X-ray diffraction method.[10,14]

Table III
Influence of Intermolecular Interactions on the Crystallite Modulus along the Chain Direction (GPa)

	PE	PVA	nylon 6	
			α	γ
calcd with all intermol interactions	315.5	287.4	311.5	53.7
calcd without hydrogen bonds		287.4	311.5	51.8
calcd without intermol interactions	315.4	287.2	288.6	24.9

The linear compressibility along the chain direction is calculated as follows: α form of nylon 6, $\beta_c = 0.22 \times 10^{-2}$ GPa^{-1}; γ form of nylon 6, $\beta_c = 1.33 \times 10^{-2}$ GPa^{-1}. The volume compressibility is calculated to be $\kappa_{\text{calcd}} = 26.8 \times 10^{-2}$ GPa^{-1} for $\kappa_{\text{obsd}} = 13.1 \times 10^{-2}$ GPa^{-1} for the α form of nylon 6 and $\kappa_{\text{calcd}} = 23.3 \times 10^{-2}$ GPa^{-1} with $\kappa_{\text{obsd}} = 17.9 \times 10^{-2}$ GPa^{-1} for the γ form.[11]

In Table III are listed the calculated crystallite moduli in the chain direction of the four polymers with and without taking into consideration the intermolecular interactions. The influence of intermolecular interactions on the crystallite modulus along the chain axis is hardly detected for planar-zigzag PE, PVA, and nylon 6 α form. The modulus of the γ form of nylon 6, on the contrary, is affected largely by intermolecular interactions, especially by van der Waals interactions. For the planar-zigzag chains, the crystallite modulus along the chain direction is almost determined by the bond stretching and the bond angle deformation of the skeletal linkages, as understood from the distribution of the strain energy shown in Figure 8. The intermolecular force constants are smaller by 2 or 3 orders than the force constants of bond stretching and bond angle deformation, so that they affect only negligibly the modulus along the chain direction. For the contracted chain of the γ form of nylon 6, the potential energy of strain distributes mainly to the torsional deformations of the CH_2–amide bonds. Such torsional deformations are, in general, influenced greatly by the intermolecular forces because of the small force constants of the internal rotations. This is frequently seen in the cases of molecular vibrations of helical chain coupled with the external lattice vibrations. But we should not always say that the crystallite modulus of contracted chain conformation is necessarily influenced by the intermolecular interactions. In the case of isotactic polypropylene,[15] for example, the crystallite modulus is almost unaffected by the intermo-

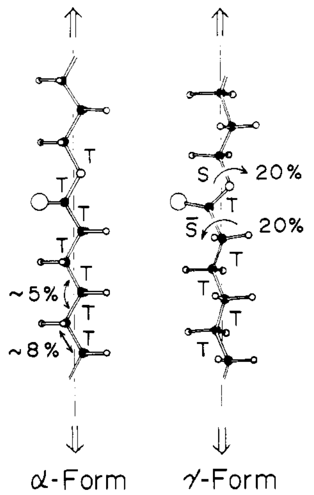


Figure 8. Calculated distribution of the strain energy when the nylon 6 chain is stretched along the chain axis.

lecular forces because the internal and external interactions do not strongly couple with one other. This is because the intermolecular interactions are almost restricted to the nonbonded methyl–methyl pairs and the skeletal chains are affected by the intermolecular interactions only through such side group interactions. In the case of the γ form nylon 6, the intermolecular forces influence directly the skeletal chains, different from the case of i-PP. A detailed discussion for i-PP will be reported soon.[15]

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Activation Energy Insensitivity to Barrier-Crossing Correlations in Long-Chain Molecules[1]

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ABSTRACT: Recent experiments by Morawetz et al. show that the activation energy for rotational barrier crossings in a long-chain molecule in solution is the same as for an analogue molecule with only a single rotational barrier. We present the results of computer simulation studies of this process which use the technique of Brownian dynamics applied to a model of a polymer chain regarded as a system of linked rigid bodies. The computer simulation results parallel qualitatively the experimental results of Morawetz et al. We consider also a model system with two degrees of freedom, each representing the motion of a dihedral angle, and a tensor viscosity which permits a controlled degree of correlation between the motion of these angles over rotational barriers. This model also exhibits insensitivity of the activation energy to the degree of correlation and an examination of its trajectories provides some insight into the process.

Introduction

A linear long-chain molecule in solution undergoes frequent conformational transitions by rotations about bonds of the backbone chain. These rotations are opposed by a rotational energy barrier (one associated with each bond) due to side-group interactions, and the overcoming of this barrier is a thermally activated process.

A question of long standing concerns the degree of correlation that exists among the times at which the various bonds along the chain undergo rotations over their respective barriers. That some correlation should exist is seen by considering the situation in which a rotation over the barrier takes place about a bond near the chain center while the dihedral angles describing the conformations of the remaining bonds remain unchanged. In this case the chain ends would experience a rapid, large excursion through the solvent, commonly referred to as whipping motion. Since this whipping motion would bring into play large viscous forces, suggestions have been put forward conjecturing various types of correlated motions such as the crankshaft of Schatzki,[2] the gauche migration of Helfand,[3] the three-bond motion,[4,5] and others which would serve to limit chain-end excursions.

A closely related question is the effect of correlated motions upon the activation energy for thermally activated conformational transitions. If rotations about bonds occur in an uncorrelated manner so that only one rotational energy barrier is crossed at a given time, the theory of thermally activated processes indicates that the activation energy for the process should be E_b, the height of the

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