by solving this quadratic equation, using the values of τ_k. Consequently two sets of solutions are obtained for the parameters τ_1 and τ_k, if

$$[X(k+1)^2 + Y(k+1)^2 + Z(k+1)^2]^{1/2} \leqq d$$

This procedure could save a lot of computation for setting up molecular models of (2/1) helical chains such as poly(ethylene oxybenzoate) α form.

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Elastic Moduli and Molecular Structures of Several Crystalline Polymers, Including Aromatic Polyamides

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ABSTRACT: The relationship between the elastic moduli and the molecular structures has been investigated for three typical aromatic polyamides, poly(*p*-phenyleneterephthalamide), poly-*p*-benzamide, and poly(*m*-phenyleneisophthalamide), and related polymers, poly(ethylene terephthalate), etc. Potential energy calculations of the aromatic polyamides indicate very high potential barrier hindering conformational changes and suggest the presence of extended molecules in noncrystalline regions for poly(*p*-phenyleneterephthalamide) and poly-*p*-benzamide, causing the very high values of the measured macroscopic moduli. The calculated crystallite moduli agree well with the observed values. The distributions of the strain potential energy to the internal coordinates, that is, the changes of the bond lengths, bond angles, and internal rotation angles, have been calculated. The relation between the crystallite moduli and macroscopic moduli for various polymers is discussed in connection with the molecular conformations in the crystalline region and the orderness and mobility of the molecules in the amorphous region.

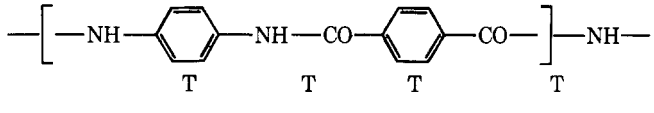
Fibers made of poly(*p*-phenyleneterephthalamide) (commercial name of du Pont Kevlar or Fiber B) and poly-*p*-benzamide (PRD-49 Type I, abbreviated as PRD-49 hereafter) have characteristic properties such as high tensile strength, high elastic modulus, and high thermal resistance, as shown in Table I. Poly(*m*-phenyleneisophthalamide) fiber (Nomex) is excellent in heat stability, although it shows an elastic modulus and tensile strength similar to usual fibers.[1,2] These characteristic features can be reasonably interpreted by the results of structure analyses.

In this paper we focus our attention mainly into the elastic moduli of these aromatic polyamides and related polymers including poly(ethylene terephthalate) and poly(ethylene oxybenzoate), which have the benzene rings in the skeletal chains. The crystallite modulus was first measured by Dulmage and Contois[9] on poly(ethylene terephthalate) based upon the assumption of series model. Thereafter the study was extended for a wide variety of polymers by Sakurada and his co-workers.[4] In Table I are shown the measured crystallite moduli (CM) of several polymers including Kevlar and Nomex by Sakurada et al.[5] The crystallite modulus can be calculated theoretically if the geometrical structure is known and the suitable force constants can be assumed. This calculation was first made by Mark[10] for straight-chain hydrocarbon and also by Meyer[11] for cellulose. Then, Treloar,[12] Shimanouchi,[13] Miyazawa[14] and the others made the calculations for many polymers. We calculated the crystallite moduli of the single molecular chains of the aromatic polyamides and related polymers based on the crystal structures determined by x-ray analyses and examined the relationships among the elastic moduli, the molecular conformations, and the flexibility of the chains.

Chain Conformations and Flexibility

The crystal structures of Kevlar,[1] PRD-49,[1] and Nomex[2] are reproduced in Figures 1, 2, and 3, respectively, and their crystallographic data are given in Table II.

The molecular conformation of Kevlar in the crystalline region is fully extended all trans.



Here we replace N–Ph–N or C–Ph–C by a virtual bond after Flory.[15] The internal rotational angles (ω) of the benzene ring measured from the amide plane are about 30°.

Table I
Properties of Various Fibers[3]

Fiber	Strength, (g/D) kg/mm²	Elongation, %	Macroscopic modulus (MM), (g/D) dyn/cm²	Crystallite modulus Obsd (CM)[4,5]	Crystallite modulus Calcd	CM/MM	T_g, °C[7,8]	Mp, °C (dec point)
Kevlar	(25) 330	5	(850) 111 × 10^{10}	153[a] × 10^{10}	182 × 10^{10}	1.4	345	(500)
PRD-49, Type I	(15) 200	3	(1050) 134		163	1.2[b]	>230	(500)
Nomex	(5.5) 68	35	(82) 10	88	90	8.8	>230	(415)
PET	(9.0) 110	7	(160) 19.5	108	95, 122[c]	5.4	81	260
it-PP	(9.0) 74	15	(120) 9.6	34	28[c]	3.4	−35	170
PE	(9.0) 78	8	(100) 8.5	235	296[c]	26	−21	135
Nylon 6 (α)	(9.5) 97	16	(50) 5.0	165	244[c]	33	50	225
PEOB (α)	(5.3) 64	25	(75) 8.9	5.9	2.4	0.7	84	225

[a] Most recently Gaymans et al. reported the value 200 × 10^{10} dyn/cm².[43] [b] Value from the observed macroscopic modulus and calculated modulus. [c] These calculated values are quoted from the literature: PET,[12] it-PP,[14] PE,[14] and Nylon 6 (α).[6]

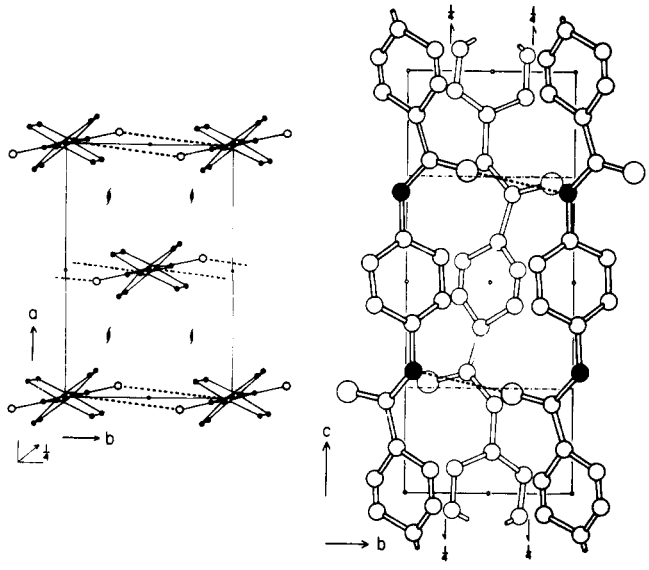


Figure 1. Crystal structure of Kevlar.[1]

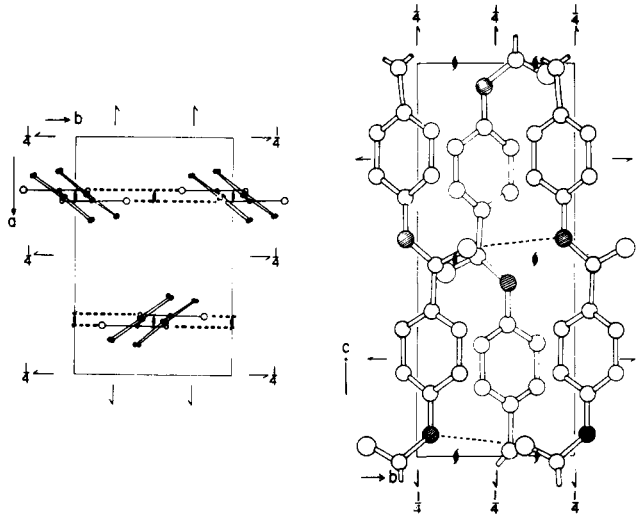
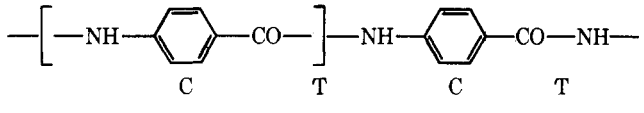
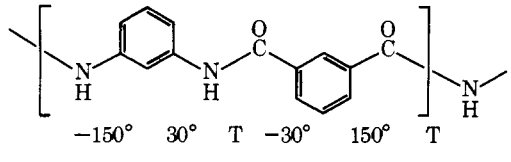


Figure 2. Crystal structure of PRD-49.[1]

PRD-49 has a conformation with twofold screw symmetry, consisting of the cis and trans internal rotational angles. The dihedral angles ω are also about 30°.



The Nomex molecules are contracted from the fully extended conformation by about 9% (fiber period 11.3 Å). Assuming a dummy atom A in the center of the benzene ring and regarding the N–A or C(O)–A as a chemical bond, the internal rotation angles are given as follows;



The dihedral angles (ω) in the three polymers are commonly about 30°, which is similar to those of the related low-molecular-weight compounds: *p*-Br–Ph–NHCOOR (24.2°),[16] *p*-Br–Ph–NHCOOR′ (37.0°),[17] *m*-NH_2–Ph–$CONH_2$ (27°),[18] Ph–$CONH_2$ (24.6°),[19] and *p*-NH_2CO–Ph–$CONH_2$ (23°).[20]

The factors governing the internal rotation angles ω may be classified into two components. One is the tendency to keep the coplanarity of the benzene rings and the amide planes owing to the partial double bond characters. This potential energy function may be represented as

$$V_\pi = V_\pi^0 (1 + \cos 2\omega)/2$$

where V_π^0 is the height of the barrier and was assumed to be −16 kcal/mol. This value was estimated based upon the π-bond energies for the model structures of aromatic polyamides calculated by Belyakov et al.[21] (see Appendix). This potential energy is represented by dotted lines in Figure 4.

The other component is the steric interaction mainly between the orthopositioned hydrogen atoms of the benzene ring and the hydrogen and oxygen atoms of the amide group. These interaction energies were calculated by using the Lennard-Jones type potential function,

$$V_{nb} = \sum_i (A_i/r_i^{12} - B_i/r_i^6)$$

where the summation is made over the four H(ortho)···H(amide) pairs [A_i = 4470 kcal Å¹²/mol, B_i = 47 kcal Å⁶/mol] and the four H(ortho)···O(amide) pairs [A_i = 25370 kcal Å¹²/mol, B_i = 125 kcal Å⁶/mol].[22] Figure 5 shows the molecular parameters used in this calculation. These potential energies are shown with broken lines in Figure 4. The solid lines are the sums of these two components ($V = V_\pi + V_{nb}$). The minimum is found at ω = ca. 30° for both the bonds Ph–N and Ph–C and

Table II
Crystallographic Data of Three Aromatic Polyamides

	Kevlar[1]	PRD-49[1] type I	Nomex[2]
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$–C_{2h}^5	$P2_12_12_1$–D_2^4	$P1$–C_1^1
Lattice constants	a = 7.80 Å	a = 7.71 Å	a = 5.27 Å
	b = 5.19 Å	b = 5.14 Å	b = 5.25 Å
	c(f.a.)[a] = 12.9 Å	c(f.a.) = 12.8 Å	c(f.a.) = 11.3 Å
	γ = 90°		α = 111.5°
			β = 111.4°
			γ = 88.0°
No. of chains in a unit cell	2	2	1
Density Obsd	1.49 g/cm³	1.48 g/cm³	1.38 g/cm³
Calcd	1.50 g/cm³	1.54 g/cm³	1.45 g/cm³

[a] f.a. = fiber axis.

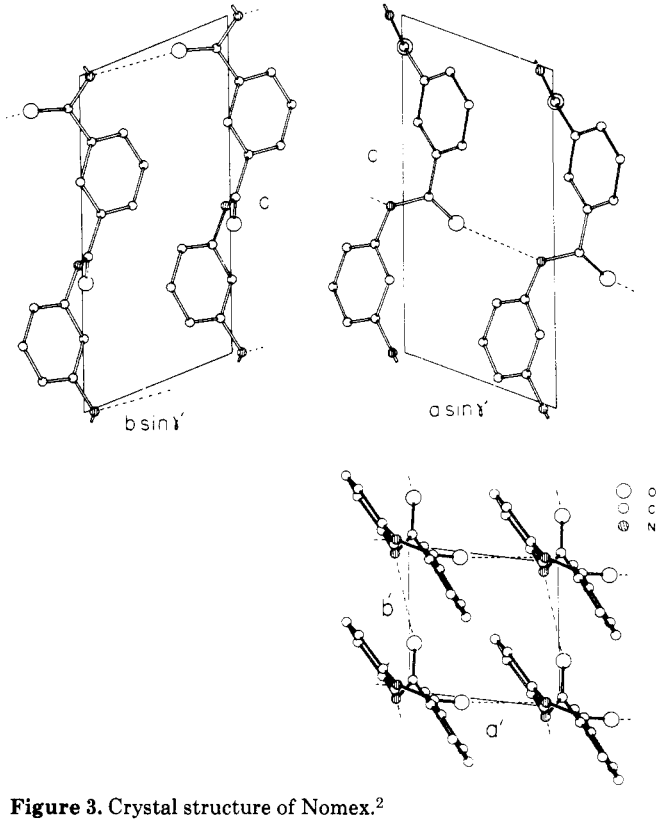
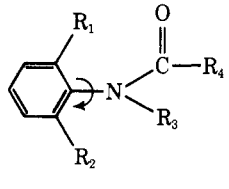


Figure 3. Crystal structure of Nomex.[2]

it agrees well with the values found by x-ray analyses as stated above.

As shown in Figure 4, the potential barriers are 6–12 kcal/mol, much higher than the value 3 kcal/mol estimated for the benzene–carbon bond of poly(ethylene terephthalate).[23] The barrier 6–12 kcal/mol seems to be reasonable compared with the values estimated by NMR measurements for the compounds



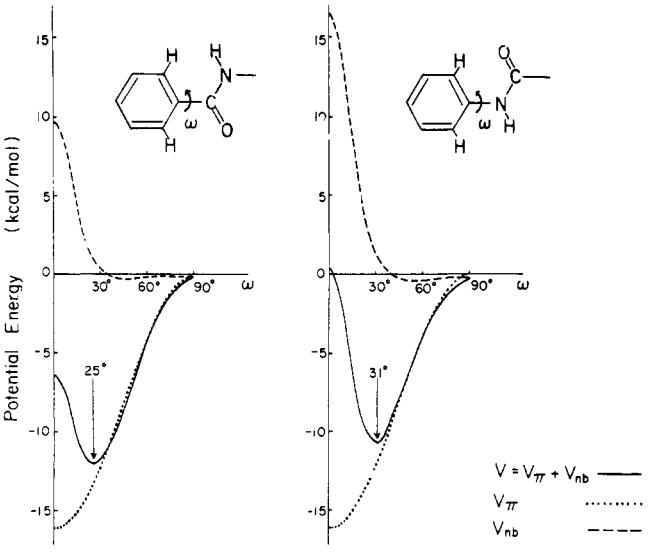


Figure 4. Potential energies vs. dihedral angles (ω) of Ph–C and Ph–N.

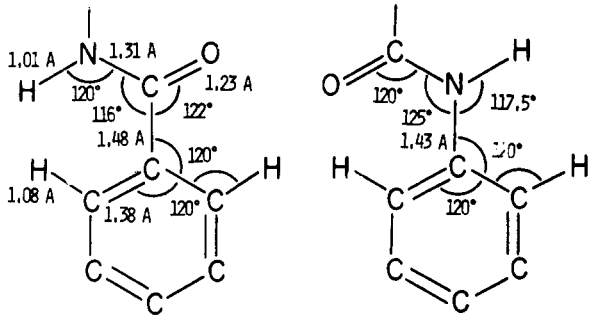


Figure 5. Bond lengths and bond angles used in the calculation of rotational barriers.

15–32 kcal/mol for the case with bulky substituents of R, and possibly lower than 10 kcal/mol for R = H.[24] The rotational barrier of the amide C–N bonds was reported to be about 20 kcal/mol from the NMR measurements.[24]

The force constant 0.65 mdyn Å/rad² on the average for the internal rotation of N–benzene or C(O)–benzene was obtained as the second derivatives of the solid lines in Figure 4 with respect to ω at the minimum point. This value is close to that of the amide group (0.67 mdyn Å/rad²) reported by Jakes and Krimm[25] and much larger than that of Ph–C(O) of aromatic ester (0.23 mdyn Å/rad²)[26] or CH_2CH_2 of n-paraffins (0.24 mdyn Å/rad²).[27]

For Kevlar and PRD-49, the internal rotation angle of the virtual bond is reasonably interpreted by taking into account the angles ω calculated above. The possible internal rotation angles of the virtual bond are nearly the cis, gauche, and trans forms by the combination of a pair of rotation angles ω, which can take one of the four energetically minimum positions (±30°, ±150°). Among these, all-trans and cis-trans conformations may not transform easily to the others because of high barriers of the virtual bonds and also of the amide C–N bonds. In other words, Kevlar and PRD-49 chains have very low flexibility.

For Nomex, all the dihedral angles of the benzene rings measured from the amide planes are about 30°, which are the most stable angles as stated above. Therefore the molecular conformation found by the x-ray analysis (±30°, ±150°) corresponds to the most stable one from the viewpoint of the

Table III
Force Constants used for Crystallite Moduli Calculations of Aromatic Polyamides, Polyesters and Polyethers, and Polyethylene

Related coordinates [common atoms]	Values	Related coordinates [common atoms]	Values
(a) Aromatic Polyamides[a]			
Stretching		CC, CC(b) (meta) [C]	−0.320
CC(b)[b]	6.433	CC, CC(b) (para) [C]	0.309
C=O	8.780	CO, C(O)C(b) [C(O)]	0.764
N–H	5.980	NC(O), C(O)C(b) [C(O)]	0.638
N–C(O)[b]	6.118	NC(O), CO [C(O)]	0.230
C(O)–C(b)	4.500	NC(O), NC(b) [N]	0.352
N–C(b)	4.500	Stretching–bending	
Bending		C(b)NH, C(O)N [N]	−0.375
CCC(b)	0.934	C(b)C(O), C(O)C(b)C(b) [C(O)C(b)]	0.313
C(b)CO	2.000	C(b)C(b), C(b)C(b)C(O) [C(b)C(O)]	0.316
C(b)C(O)N	2.000	CC, CCC(b) [CC]	0.164
C(b)NC(O)	2.000	C(b)C(O), C(b)CO [C(b)C(O)]	0.258
C(b)NH	1.154	C(b)N, C(O)NC(b) [NC(b)]	0.615
C(b)C(b)C(O)	0.930	C(b)N, C(b)NH [C(b)N]	0.324
C(b)C(b)N	0.930	CO, NC(O)C(b) [C(O)]	−0.495
NH o.p. bend[c]	0.080	C(O)N, C(b)C(O)N [C(O)N]	0.438
CO o.p. bend	0.580	C(b)N, NC(b)C(b) [C(b)N]	0.312
Torsion		C(b)C(b), NC(b)C(b) [C(b)C(b)]	0.325
CCCC(b)	0.300	C(O)N, C(b)NC(O) [C(O)N]	−0.483
C(b)NC(O)C(b)	0.671	CO, C(b)CO [CO]	−0.117
C(O)NC(b)C(b)	0.65	Bending–bending	
NC(O)C(b)C(b)	0.65	C(b)C(O)N, C(b)CO [C(b)C(O)]	1.495
Stretching–stretching		C(b)NH, C(b)NC(O) [C(b)N]	0.848
CC, CC(b) (ortho) [C]	0.750		
(b) Aromatic Polyesters and Polyethers[d]			
Stretching		C(b)C(b)OC(H)	0.03
CC(b)	6.433	OC(H)C(H)C(b)	0.03
C=O	12.4	Stretching–stretching	
C(b)C(O)	4.5	CC, CC(b) (ortho) [C]	0.750
C(H)O	5.09	CC, CC(b) (meta) [C]	−0.316
C(b)O	5.09	CC, CC(b) (para) [C]	0.342
C(H)C(H)	4.26	C=O, C(O)O [C(O)]	0.3
C(O)O	6.18	C(H)O, C(O)O [O(et)]	0.1
Bending		C(b)O, C(H)O [O]	0.288
CCC(b)	0.934	C(H)C(H), C(H)O [C(H)]	0.1
C(O)C(b)C(b)	0.934	Stretching–bending	
OC(O)C(b)	0.8	CC, CCC(b) [CC]	0.164
C(H)OC(O)	1.62	COC(es), C=O [C=O]	0.65
C(H)C(H)O(et)[e]	1.18	C(b)CO(es), C=O [C=O]	0.65
C(b)OC(H)	1.3	C(O)O, OC(O)C(b) [C(O)O]	−0.3
OCO(es)[e]	1.0	C(O)O, C(O)OC(H) [C(O)O]	−0.3
O(es)CC(b)	0.6	C(H)OC(O), C(O)O [C(O)O]	0.48
Torsion		C(b)OC(H), C(H)O [C(O)O]	0.48
CCCC(b)	0.300	C(H)C(H), C(H)C(H)O(et) [C(H)C(H)]	0.4
C(H)OC(O)C(b)	0.23	C(H)O, C(H)C(H)O(et) [C(H)O]	0.62
OC(O)C(b)C(b)	0.23	Bending–bending	
OC(H)C(H)O	0.03	C(b)CO(es), C(O)C(b)C(b) [C(b)C(O)]	0.11
C(H)C(H)OC(O)	0.03		
(c) Polyethylene[f]			
Stretching		Stretching–stretching	
CC	3.948	CC, CC [C]	0.231
Bending		Stretching–bending	
CCC	1.523	CC, CCC [CC]	0.216

[a] The values are referred to Jakes and Krimm[25] and Patel et al.[26] The stretching constants have units of mdyn/Å; the stretch–bend interactions have units of mdyn/Å; and the bending constants have units of mdyn Å/rad^2. [b] C(b) and C(O) represent the carbon atoms of benzene and carbonyl group, respectively. [c] "o.p. bend" means the out of plane bending mode. [d] The values are refered to Snyder and Zerbi,[27] Patel et al.,[26] and Susi and Scherer.[33] [e] C(H), O(es), and O(et) represent the methylene carbon, oxygen of the C=O bond, and oxygen of the C–O bond, respectively. [f] In this calculation, only skeletal carbons are considered.

intramolecular interactions. Owing to the high barriers of internal rotations of Ph–amide and C–N bonds, Nomex is also expected not to be easily transformed into the other conformations.

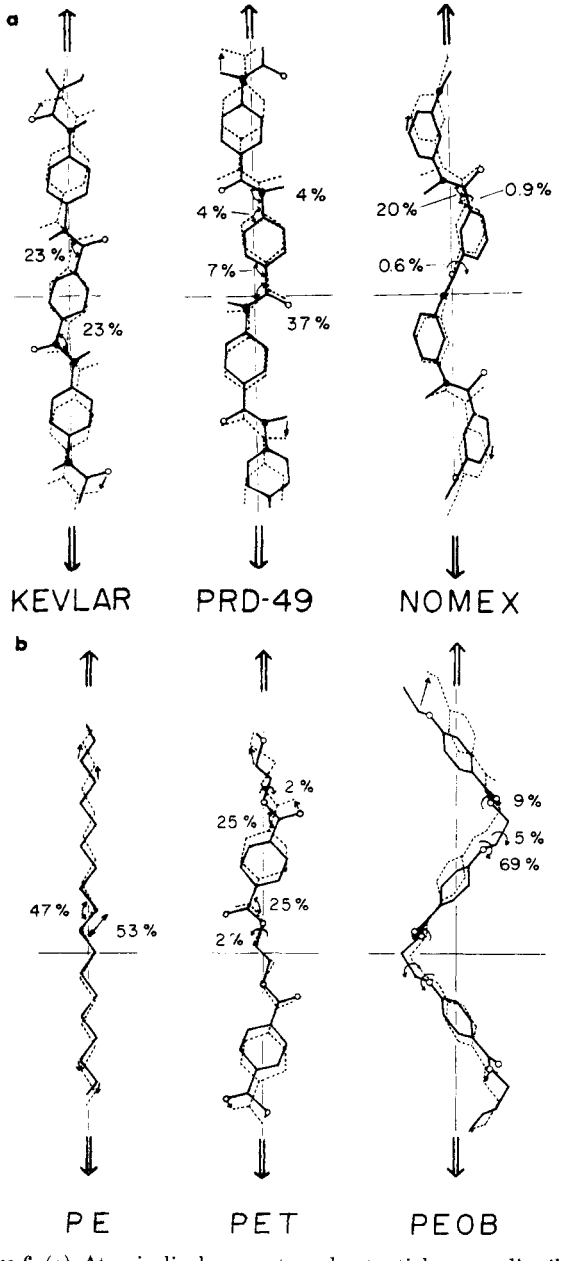


Figure 6. (a) Atomic displacements and potential energy distributions for aromatic polyamides, when the chains are stretched 10%. (b) Atomic displacements and potential energy distributions for PE, PET, and PEOB (α), when the chains are stretched 10%.

Crystallite Moduli and Chain Conformations

In this paper the calculation of the crystallite moduli was made for single chains by the method of Miyazawa et al.,[28] neglecting the intermolecular interactions and keeping the rotation angles about the helical axis constant, that is, preserving the helical symmetry. The atomic coordinates determined by x-ray analyses were used for Kevlar and PRD-49,[1] Nomex,[2] poly(ethylene terephthalate),[29] polyethylene,[30] and poly(ethylene oxybenzoate) α form.[31] The force constants of valence force field (VFF) type were used and given in Table III. These values were transferred from those used in low-molecular-weight compounds with a little modification.[25–27,32,33] The calculated elastic moduli are tabulated in Table I.

Figure 6 shows schematically the calculated displacements of the atoms, by assuming hypothetically large elongation of 10%. The deformation should occur so as to minimize the potential energy of strain as a whole. We can calculate the distribution of the strain potential energy to the internal coordinates (PED) by using the following equation;

$$(\mathrm{PED})_i = 100 \times F_{ii} \times \Delta R_i^2 / \sum_i F_{ii} \times \Delta R_i^2 (\%)$$

where ΔR_i is the ith internal displacement coordinate, F_{ii} is the diagonal element of the symmetrized force constant matrix, and the summation is made over all the internal coordinates defined.

(1) Kevlar. Kevlar has the all-trans extended molecular conformation, which can explain the high modulus of one single chain. In the case of the all-trans conformation, the changes of bond lengths and bond angles can contribute to elongation of the molecular chain, but the change of internal rotation angles cannot. As shown in Table III, the bond stretching force constant K is 6–4 mydn/Å, the bond angle bending force constant H is lower by one order of magnitude, about 0.8 mdyn/Å, and the internal rotation force constant F_τ is furthermore lower, about 0.1–0.3 mdyn/Å. The calculated potential energy distributions show that the bond angles Ph–C–N have about 46% elastic energy, which causes the large crystallite modulus of Kevlar.

The calculated crystallite modulus is 182×10^{10} dyn/cm^2 in good agreement with the observed value of 153×10^{10} dyn/cm^2. Fielding-Russell[34] already calculated the crystallite modulus of Kevlar by assuming the all-trans planar conformation and reported 200×10^{10} dyn/cm^2. This is similar to the present value, because the structure and the force constants used by him are not so different from ours.

The crystallite modulus is contributed not only by the modulus of a single chain but by the intermolecular interaction in crystallite. In the case of Kevlar the strong intermolecular interaction is expected owing to the good packing of the benzene rings and the strong interchain forces of hydrogen bonding. These effects will be discussed in a later paper.

For the macroscopic modulus of the fiber sample, the modulus of the amorphous part is more important than the crystallite modulus. For Kevlar the sample with the density of 1.49 g/cm^3 was obtained by heat treatment for 5 h at 450 °C under tension,[35] whose density is very close to the crystal density 1.50 g/cm^3. Furthermore in the small-angle x-ray scattering (SAXS) no meridional reflection is observed, according to Dr. Mochizuki of Kurare Co.[36] This means that the electron density difference of the repeat along the direction of fiber axis is too small to be detectable. Strong equatorial scattering observed in SAXS of Kevlar reveals poor regularity and remarkable electron density fluctuation along the radial direction due to voids and others. This is in accordance with the characteristic feature of the wide-angle x-ray diagram in which the meridional reflections are sharp in contrast to the other reflections (Figure 7). From all these results, in addition to the low flexibility of the chain, the extended chain structure or oriented amorphous structure may be reasonably considered for Kevlar. This is consistent with Flory's theory[37] that the random arrangement of the chains with low flexibility in the concentrated solution is disadvantageous statistically even if the intermolecular interactions are not considered and so the rodlike chains arrange fairly well aligned parallel to a common axis (tactoidal phase).

Kevlar has the high macroscopic modulus 850 g/D or 111 $\times 10^{10}$ dyn/cm^2. In Table I are shown the ratios of crystallite and macroscopic moduli for various polymers. For Kevlar the ratio is about unity. This may be understood by an oriented amorphous structure mentioned already. Besides we can easily

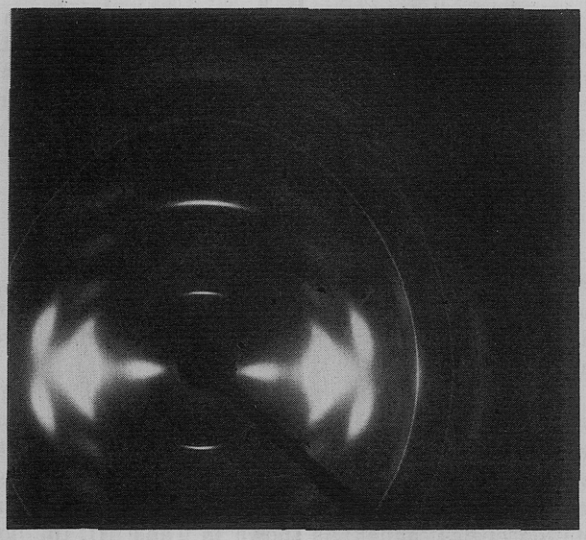


Figure 7. Fiber diagram of Kevlar. The arcs are from aluminum powder for correction of radius of cylindrical camera.

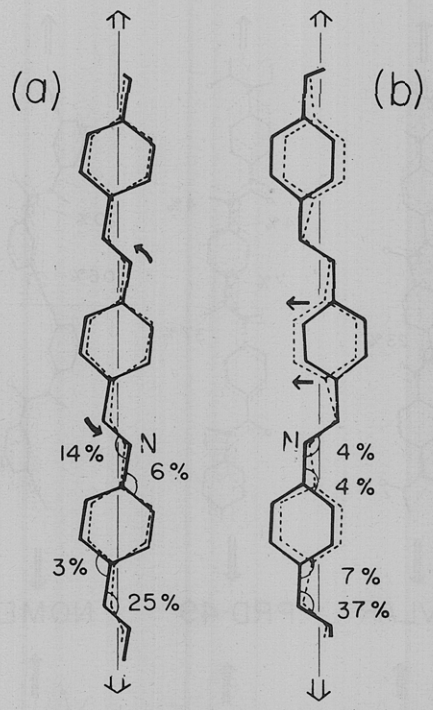


Figure 8. Comparison of the geometrical changes and potential energy distributions of two models of PRD-49: (a) all-trans conformation, (b) cis-trans conformation.

understand the liquid crystal formation of concentrated solution and the difficulty of chain folding for Kevlar.

(2) PRD-49. PRD-49 has the conformation with the alternating sequence of cis and trans. The calculated crystallite modulus is 163×10^{10} dyn/cm^2, smaller than the value of Kevlar (182×10^{10} dyn/cm^2). For comparison, the modulus of a molecular model of PRD-49 with the all-trans conformation, using the same parameters as the cis-trans model, was calculated to be 238×10^{10} dyn/cm^2, much larger than the cis-trans conformation which in turn is larger than Kevlar. When the molecule is deformed by stretching, the virtual bonds N–Ph–C of the cis-trans structure are bent as shown in Figure 8, but those of the all-trans structure are caused to rotate so as to become parallel to the elongation direction by deforming the bond angles ∠Ph–C–N and ∠Ph–N–C. The force necessary to bend the virtual bond is clearly smaller than that to deform the bond angles ∠Ph–C–N and ∠Ph–N–C. The smaller crystallite modulus of the cis-trans conformation is thus explained.

The macroscopic modulus of PRD-49 is a little larger than that of Kevlar, unexpected from the calculated results. The coexistence of the molecules of all-trans conformation in the amorphous region of PRD-49 may be one of the reasons for this high macroscopic modulus.

(3) Nomex. The observed crystallite modulus of Nomex was 88×10^{10} dyn/cm^2.[5] Fielding-Russell[34] calculated the crystallite modulus of Nomex under the assumption of the fully extended structure to be 127×10^{10} dyn/cm^2. But the value for the fully extended form should be ca. 253×10^{10} dyn/cm^2, since the cross-sectional area he assumed seems to be too large, 42.3 Å^2 instead of 23.8 Å^2 (x-ray value). Either way, however, these values of crystallite modulus are too large. The fully extended structure is incorrect and may be difficult to find because of the high potential barrier at the rotation angle 0° as already discussed. Hence we recalculated the crystallite modulus of Nomex based upon the crystal structure determined by x-ray analysis, 90×10^{10} dyn/cm^2, in good agreement with the observed value.

The calculated potential energy distributions are shown in Figure 6. The Nomex chain is contracted from the extended structure and therefore it is necessary to consider the changes of the internal rotation angles when the chain is deformed. The potential energy distribution is, however, only 0.9% or less to the internal rotations. Thus the internal rotations are not effective in this case. This is due to two factors, the geometry and the force constants of Nomex chain. The elastic potential energy distributions are approximately proportional to the product of $(\partial d/\partial R_i)^2$, geometrical factor, and the diagonal term of the compliance matrix ($\simeq 1/F_{ii}$), where d is the axial advancement per one monomeric unit, R_i is the ith internal coordinate, and F_{ii} is the diagonal force constant for R_i.[38] For Nomex chain, the calculated values of $(\partial d/\partial R_i)^2$ for the internal rotations (ca. 0.01) are much smaller than those for the bond stretchings (ca. 0.7) and bond-angle deformations (ca. 0.5), which compensates the large values of the compliances for the internal rotations ($1/F_{ii}$ for the internal rotations are about 1/0.2 Å/mdyn, about 1/0.5 for the bond angles, and about 1/5 for the bond stretchings). In this way we can understand the low-energy distributions for the internal rotations for Nomex.

Nomex has the check-patterned hydrogen bonds as shown in Figure 3 and therefore the crystallite modulus along the chain direction must be considerably affected by such strong intermolecular interactions, which will be reported in a later paper.

From the contracted conformation in crystal, more or less disordered structure is considered in the amorphous part of Nomex, where the bonds neighboring the benzene ring may assume one of the stable and high-barriered internal rotation angles ±30° and ±150°. It may be reasonable to think that such a contracted molecule cannot form a liquid crystal. As shown in Table I, the ratio of the crystallite and macroscopic moduli of Nomex is 8.8, which is similar to the value of PET, 5.4. It may be understood by assuming from the above-mentioned structure in the amorphous part that these ratios are intermediate between Kevlar and polyethylene.

(4) Polyethylene, Poly(ethylene terephthalate), and Poly(ethylene oxybenzoate). Polyethylene (PE) is one of the polymers with the highest crystallite moduli. The bond stretching and the bond angle deformation have almost the same contributions to the potential energies (Figure 6). This is characteristic of the planar zigzag polymer chain. As shown in Table I, PE has the very large ratio of crystallite and mac-

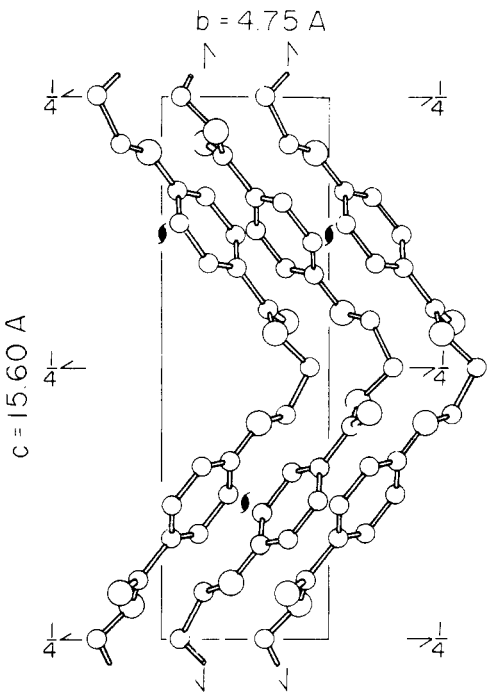


Figure 9. Crystal structure of poly(ethylene oxybenzoate) α form.

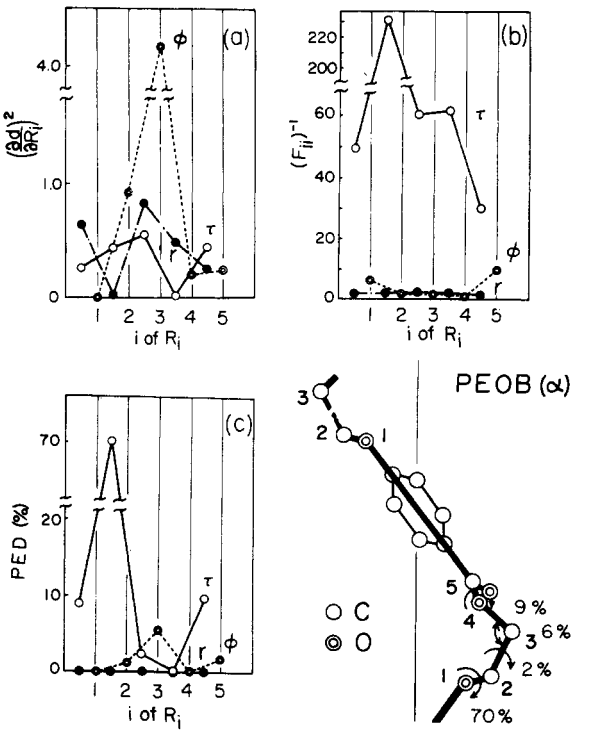


Figure 10. $(\partial d/\partial R_i)^2$, compliances $(F_{ii})^{-1}$ (Å/mdyn), and potential energy distributions for PEOB α form. When the ith atom is represented by M_i, the bond $r_{i-1,i}$ is defined as $M_{i-1}M_i$, the bond angle ϕ_i is $\angle M_{i-1}M_iM_{i+1}$, and the internal rotation angle $\tau_{i-1,i}$ is around the bond $M_{i-1}M_i$.

roscopic moduli, similar to the case of Nylon 6. This can be explained by the random structure in the amorphous part due to the high flexibility of the molecular chain with no side group. Recently polyethylene samples with "ultra-high" macroscopic modulus (ca. 70×10^{10} dyn/cm^2) were obtained with the high-pressure extrusion method by Weeks and Porter,[40] or with the cold-drawing method by Capaccio and Ward[41] and by Kiho and Asai.[42] The ratio for these samples is about 3, near to that for Kevlar. Weeks and Porter[40] attributed this high modulus to the existence of the extended chain crystal embedded in a matrix of highly drawn PE. This situation may be very similar to that of Kevlar with the oriented amorphous structure.

Poly(ethylene terephthalate) (PET) is slightly contracted from the fully extended chain by the internal rotations of the O–CH_2 bonds.[29] Only 2% of the total energy is distributed, however, to the internal rotations of the O–CH_2 bonds and about 25% is preferentially distributed to the bond angle deformation of Ph–C(O)–O (Figure 6). Therefore, the modulus of the fully extended molecule is supposed to be not so much different from that of the actual structure. In fact, both the all-trans and the contracted structures give essentially the same value of modulus (95×10^{10} dyn/cm^2). Here we should notice that the above circumstance differs from that of Nomex in which the chain is contracted from the all-trans conformation, although the internal rotations do not contribute appreciably to the elastic modulus in both cases of PET and Nomex. PET takes the conformation deviated slightly from the fully extended form and preserves the essential form of the all-trans chain, but Nomex remarkably differs from the extended structure by the large rotations of Ph–N and Ph–C(O) bonds. So the calculated modulus of all-trans structure differs so much from that of the actual one for Nomex but not for PET. The small potential energy distribution for internal rotations in Nomex is special and characteristic of its chain form, as explained in the preceding section.

The potential energy distributions and atomic displacements of PET are similar to those of Kevlar because the parts around the benzene rings are very similar to each other in the two polymers, resulting in comparably similar values of crystallite modulus.

Poly(ethylene oxybenzoate) (PEOB) has two crystal forms α and β. The conformation of the α form is a large scale zigzag, one monomeric unit being one zigzag unit (Figure 9).[31] The observed crystallite modulus of the α form is 6×10^{10} dyn/cm^2, lower than the macroscopic modulus of 8.9×10^{10} dyn/cm^2. Such a low crystallite modulus can be understood from the molecular structure of Figure 9. The length of the arm, the component of the moment of force, is about 6 Å, much larger than the value of 0.9 Å in polyethylene. The calculated potential energy distributions are concentrated to the internal rotations as shown in Figure 6 and so the deformation of the large zigzag occurs mainly owing to such internal rotations. Because of the two factors, that is, the long length of the arm and the small values of the internal rotation force constants, the crystallite modulus of the PEOB α form is small.

For considering in more detail, $(\partial d/\partial R_i)^2$ for the α form was calculated as shown in Figure 10. The used model is simplified as indicated by the bold line. The bond C(O)–Ph–O is replaced by the virtual bond. The internal coordinate ϕ_3, for example, is very effective in changing the helical pitch, but has a very small $(F_{ii})^{-1}$, resulting in a low-energy distribution as shown in Figure 10. For the internal coordinate τ_{12}, on the contrary, $(\partial d/\partial R_i)^2$ is appreciable and $(F_{ii})^{-1}$ very large so that it takes a very high distribution of strain energy. These circumstances illustrate clearly that the potential energy distributions are mainly determined by the efficiency for stretching the chain and the flexibility of the internal coordinates.

Since the large units move on stretching, the intermolecular interactions should play an important role in the measured elastic modulus. Now we are going to calculate this effect.

The β form of PEOB consists of the almost extended chain conformation[39] and the calculated modulus is 57×10^{10} dyn/cm^2, much larger than that of the α form. This is because the bond angle deformations take charge of potential energies but the internal rotations do not. The fact that the crystallite modulus of α form is smaller than the macroscopic one (Table

Table IV
π-Bond Energies for the Various Structures of Aromatic Polyamides

No.	Structures	E_π, eV[a]	E_π (Ph–amide), eV
1	Alkyl–NHCO–Alkyl	4.908	
2	Ph–NHCO–Ph	26.327	0.745
3	Ph–CONH–Ph–NHCO–Ph	42.603	0.723
4	Ph–CONH–Ph–NHCO–Ph–CONH–Ph	58.870	0.714
5	Ph–[–CONH–Ph–NHCO–Ph–]$_2$–H	75.145	0.711

[a] After Belyakov et al.[21]

I) may be due to the coexistance of the β form. In fact, in the x-ray photograph of the PEOB sample with the higher macroscopic modulus, there appears a considerable number of the spots due to the β form.

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Appendix. Evaluation of the π-Bond Energy of the Bond between the Benzene Ring and the Amide Plane

The value of π-bond energy (V_π^0 in the text) of the bond between the benzene ring and the amide plane [E_π (Ph–amide)] has not yet been reported as far as we know. We derived this value from the π-bond energies E_π for various aromatic polyamide compounds calculated by Belyakov et al.[21] (Table IV). The E_π (Ph–amide) can be calculated approximately as

$$E_\pi\,(\text{Ph–amide}) = [E_\pi - \sum_{\text{Ph}} E_\pi(\phi) - \sum_{\text{amide}} E_\pi\,(\text{amide})]/n$$

where E_π(amide) is the π-bond energy for the CO–NH bond of the amide group, 4.908 eV (No. 1 in Table IV), E_π(Ph) is the π-bond energy inside the benzene ring, 9.965 eV, estimated from the heat of hydrogenation of benzene,[44] and n is the number of the benzene–amide π bonds contained in a molecule. The calculated values of E_π(Ph–amide) for various structures (No. 2–5) are found to be almost constant as shown in Table IV. E_π(Ph–amide) is, therefore, about 0.7 eV, i.e., 16 kcal/mol on the average.

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