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Relationships between Ring Substitution, Chain Conformation in Solution, and Polymer Properties in Aramids

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ABSTRACT: Minimum energy conformers produced by relative rotation of phenylene and amide planes in poly(1,4-phenyleneterephthalamide) (PPD-T) and its ring-substituted analogs were determined by semiempirical and *ab initio* quantum mechanical calculations. Overall twist of 360° across the repeat unit, at lowest energy conformations, is necessary to provide chain linearity conducive to lyotropy in concentrated solutions and high chain alignment, strength, and stiffness in extrudates. Substituted terephthaloyl or 2,2′-disubstituted 4,4′-biphenylene units usually prevent this. Selected experimental examples to demonstrate various conformation-related effects are discussed, e.g., size, number, and placement of ring substituents, internal hydrogen bonding effects due to methoxy substituents, and terephthalamides from 2,2′-disubstituted benzidines including an unusual case with trifluoromethyl substituents in the presence of dissolved salts.

Introduction

The key role of polymer chain conformation in solution in determining polymer properties is well illustrated by the contrasting cases of poly(1,4-phenyleneterephthalamide) (PPD-T) and its meta isomer, poly(1,3-phenyleneisophthalamide) (MPD-I). The high strength and stiffness of PPD-T fibers[1] (Kevlar aramid) is characteristic of good alignment of extended polymer chains in the axial direction, which is the direct consequence of lyotropy in the precursor solutions. By contrast, MPD-I fibers (Nomex aramid) possess a considerably lower degree of chain alignment, manifested as lower strength and stiffness but greater toughness, stemming from random coil conformations in precursor solutions. MPD-I does not have adequate chain straightness or stiffness to form lyotropic solutions. The differences in solution behavior of PPD-T and MPD-I, at comparable molecular weights, may be measured in terms of persistence length (25 and 2 nm, respectively) and inherent viscosity (6 and 1.8 dL/g, respectively).[1] Intermediate degrees of chain stiffness, as with poly(1,3-phenyleneterephthalamide), is reflected by intermediate inherent viscosity values ($\eta_{\text{inh}} \sim 3$ dL/g). Higher values indicate greater chain stiffness, e.g., poly(1,4-benzobenzthiazole) with $\eta_{\text{inh}} \sim 30$ dL/g.[2]

Alterations to the composition of PPD-T, which diminish its rod-shaped character in solution, may ultimately inhibit lyotropy, good chain alignment, and high mechanical property levels. Examples are N-substitution[3] or copolymerization with ether-containing monomers. Less obvious are similar effects with certain ring substituents. Thus, Sweeny[2] reported lyotropy in the case of F only, for a PPD-T series containing halogen substituents in the acid moiety, in sulfuric acid solutions. ClPPD-T, with chlorine on the diamine moiety, gave distinctly lyotropic sulfuric acid solutions;[4] in dimethylacetamide (DMAc)/LiCl solutions of ClPPD-T became isotropic at higher LiCl concentrations.[5] Phenyl substituents in diamine or acid moiety of PPD-T enhanced solubility in DMAc/LiCl to as high as 50% but solutions remained isotropic.[6] This contrasts with the strong thermotropic character of the corresponding ester, poly(2-phenyl-1,4-phenyleneterephthalate) in the melt[7] or in dichlorobenzene[8] (45%; 250 °C under pressure). The isomeric poly(1,4-phenylene-2-phenylterephthalate) was also anisotropic in the melt.[9] Jadhav *et al.*[6] speculated that absence of lyotropy in phenyl-substituted PPD-T was the consequence of decreased chain stiffness caused by destruction of conjugation between amide and phenylene groups when the phenyl-substituent forces the carbonyl out of coplanarity with the phenylene ring. They also attributed low inherent viscosity of substituted PPD-T, relative to unsubstituted PPD-T, to steric hindrance during amide bond formation. In this context it seems anomalous that PPD-ClT, despite lower inherent viscosity (3.74 dL/g) suggesting lower molecular weight, gave fibers of strength comparable to PPD-T.[4]

Aramids containing 2,2′-disubstituted 4,4′-biphenylene units, including poly[2,2′-bis(trifluoromethyl)-4,4′-biphenyleneterephthalamide] (DCF$_3$PP-T), do not provide lyotropic solutions and exhibit little crystallinity in the solid state.[10,11] The suggested reason[11] was a weakening of intermolecular attractive forces, especially hydrogen bonding, by a combination of poor packing ability and dipolar repulsion. However, for lyotropic solutions of certain polyimides based on DCF$_3$PP-T, hydrogen bonding cannot be a factor bearing on lyotropy.[12] The picture is further obscured by the observation of lyotropy in solutions of poly(2,2′-dimethyl-4,4′-biphenyleneterephthalamide) and certain related copolymers.[13]

For elucidation of the effect of ring substituents in PPD-T and its 4,4′-biphenylene analogs on solution behavior and polymer properties we have applied computer-assisted modeling to determine minimum energy rotational conformers representing segments of the macromolecule. Selected specific polymer examples, illustrating the connection between modeling predictions and solution behavior, are discussed.

Experimental Section

Materials. 2,5-Bis(methoxycarbonyl)terephthaloyl Chloride.[14] Pyromellitic dianhydride, treated with methanol under reflux for 18 h gave a solution of mixed 2,5-bis(carbomethoxy)-terephthalic acid and the isomeric isophthalic acid. Concentration and cooling gave a precipitate of the desired isomer (38%): ^{1}H NMR (60 MHz). Treatment with SOCl$_2$ in presence of dimethylformamide at reflux gave, on cooling, a precipitate of the diacid chloride (57%): mp 137.0–138.5 °C. Anal. Calcd for $C_{13}H_8O_6Cl_2$: C, 45.17; H, 2.53; Cl, 22.22. Found: C, 45.22; H, 2.49; Cl, 22.22.

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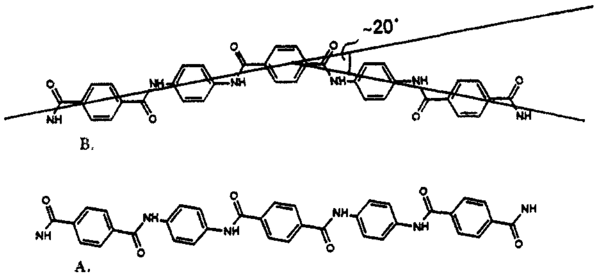


Figure 1. Rigid rodlike aromatic polyamides: A, fully *anti*-conformation; B, a single *syn* conformer in an otherwise fully *anti* chain.

2,5-Bis(2-methoxyethoxycarbonyl)terephthaloyl chloride[14] was prepared by the same general procedure as the preceding compound. The terephthalic acid, mp 181–4 °C, was easily separated from the isomeric isophthalic acid, mp 111–115 °C. The diacid chloride of the former was crystallized from ether at −30 °C: mp 52–3 °C. Anal. Calcd for $C_{10}H_{16}O_8Cl_2$: C, 47.20; H, 3.96; Cl, 17.41. Found: C, 47.34; H, 4.00; Cl, 17.25.

2,2′-Dichlorobenzidine was prepared[14,15] by hydrazo-coupling of 3-chloronitrobenzene, followed by a benzidine rearrangement: mp 166–8 °C. Anal. Calcd for $C_{12}H_{10}Cl_2N_2$: C, 56.94; H, 3.98; Cl, 28.01; N, 11.07. Found: C, 56.98; H, 4.00; Cl, 28.03; N, 11.06.

2,2′-Bis(trifluoromethyl)benzidine was prepared[11,14] by coupling of 2-bromo-5-nitrobenzotrifluoride[16] over copper, hydrogenation over PtO_2, treatment of the dihydrochloride in water with NaOH, and recrystallization from $CHCl_3$: mp 179–181.5 °C (lit.[11] 181–2 °C).

2,2′-Dicarboxybenzidine was prepared[14] by nitration of diphenic acid, separation of 4,4′-dinitrodiphenic acid by crystallization from EtOH (mp 253–5 °C), hydrogenation over PtO_2,[17] isolation of free diamine by treatment of dihydrochloride solutions with NaOAc, and treatment with refluxing toluene in a Dean Stark separator to remove water of hydration: mp 264–5 °C (lit.[17] 254.5–255.5 °C).

2,2′-Dibromo-3,3′-dimethoxybenzidine was prepared by conversion of 3,3′-dimethoxybenzidine to the diacetamide (mp 243.5–246 °C) by acetic anhydride, bromination,[18] sulfuric acid hydrolysis, and recrystallization from EtOH: mp 168 °C.

Aromatic polyamides were prepared, as described by Bowen *et al.*[19] In cases where product was a fluid solution as distinct from an immobile gel, it was extruded directly to form fibers[20] after neutralization of byproduct HCl by $Ca(OH)_2$. Otherwise, it was isolated and redissolved in sulfuric acid.[19] For preparation of excessively viscous solutions, a Helicone Model 2CV mixer[21] with intersecting helical blades in a conical vessel was used.

Polyterephthalamides of 2,2′-bis(trifluoromethoxy)benzidine, 2,2′-bis(1,1,2,2-tetrafluoroethoxy)benzidine, and 2,2′-bis[2-(*n*-heptafluoropropoxy)tetrafluoroethoxy]benzidine were supplied by A. E. Feiring and E. Wonchoba of Du Pont.

Molecular Modeling. The preferred *ab initio* quantum mechanical calculations were made using either HONDO[22] or GRADSCF[23] with double-zeta valence basis set plus polarization functions on the amide group (DZ+D).[24] The preferred semiempirical molecular orbital calculations (MOPAC)[26] used the AM1 approximation of Dewar *et al.*[25]

Discussion

Molecular Modeling. PPD-T. The planar trans configuration of the amide group in aramids[27] indicates that the C(O)–N(H) bond has partial double bond character (confirmed by its length, 1.355 Å in benzanilide)[28] and rotation around this bond in solution is thus inhibited; cis conformers in significant amounts have never been reported.[27] Rotation about the C(aryl)–N(H) and C(aryl)–C(O) bonds, being far less restricted, allows aramids to exhibit some degrees of random coil character. A two-dimensional representation of PPD-T in its most extended form is an essentially linear, fully *anti* conformation (Figure 1). Introduction of a single *syn* conformer, i.e., rotation of a single C(aryl)–C(O) bond through 180°, produces a bend of about 20°. Smaller rotations produce smaller bends with directionality (+ or −) determined by direction of rotation.

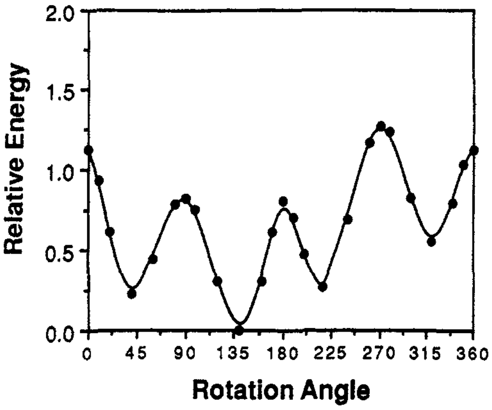


Figure 2. Conformational energies (kcal/mol) for terephthalamide calculated as a function of rotating one amide group from AM1 results.

Assumptions regarding applicability of conformations in the crystal to solution conformation, comparative planarity of the macromolecule, invariability of bond lengths and angles, and neglect of π electron contributions to force fields colored earlier conclusions on the molecular structure of aramids. Previous calculations of preferred rotation angles between phenyl and amide planes varied widely,[29–31] and intervening energy barriers between 0.7 and 12 kcal/mol, represented a wide range of stiffness. Earlier models do not explain why many PPD-T analogs fail to show lyotropy and other characteristics of the parent.

A variety of methods[30] were evaluated for the calculation of preferred conformers for various PPD-T "fragments"—benzamide, benzanilide, terephthalamide, formanilide, and 1,4-phenylenediformamide—to determine which provided the most realistic three-dimensional model for PPD-T. While the preferred *ab initio* methods[32–34] can provide results rivaling experimental values, semiempirical calculations,[25] judiciously calibrated by *ab initio* data, can provide results adequate to support key conclusions in a fraction of the Cray computer time otherwise necessary. For this work it was assumed that solvation effects are absent.

AM1 semiempirical calculations[25] gave a 40° dihedral angle between phenyl and amide groups (O–C–N plane) in terephthalamide. Then with one amide group arbitrarily fixed at a dihedral angle of 40°, the relative energy may be plotted as the second amide group is rotated through 360° (Figure 2). The lowest and highest energy conformers may be likened to the *anti* and *syn* conformers of the two-dimensional model (Figure 1), while the other two energy minima represent intermediate degrees of helical twist, as applied to the PPD-T macromolecule. Energy barriers between minima arise from steric interaction between ortho-hydrogen of phenylene rings and amide hydrogens or loss of conjugative π electron stabilization at high dihedral angles and are low (≤1.3 kcal/mol). The twist angle across the phenylene group in terephthalamide is the sum of $\theta + \psi$. Table I shows the twist angle and relative energies (AM1) for terephthalamide with ψ arbitrarily fixed at 40°. Each of the "helical"

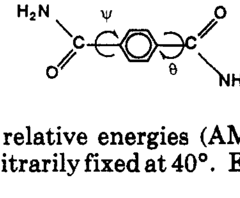


Table I. Torison Angles (deg) and Relative Energy (kcal/mol) for Four Unique Terephthalamide Conformations from AM1 Calculations

(ψ Arbitrarily Fixed)

Ψ	θ	relative energy	twist	conformers	comment
40	−40	0.55	0	0	crank
40	−140	0.27	−100	±100	helical
40	40	0.22	80	±80	helical
40	140	0.00	180	180	step

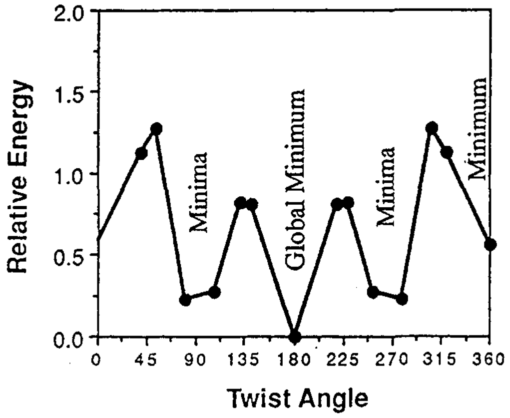


Figure 3. Relative conformational energies for the terephthalamide moiety in the polymer chain as a function of the twist imparted to the chain (AM1 results).

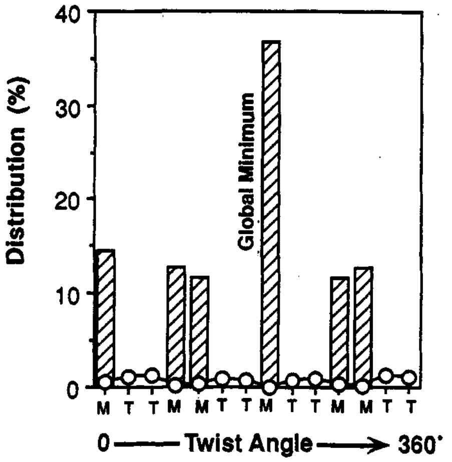


Figure 4. Probability distribution of terephthalamide conformers in a polymer chain at ambient temperature from AM1 results (M = minimum; T = transition state).

conformers, as part of a PPD-T chain, has a nonsuperimposable enantiomer, so that there is a total of six different helical twist possibilities through the terephthalamido moiety in the PPD-T chain. Figure 3 shows the amount of twist each of the terephthalamido conformers (Table I) would impart to a polymer chain and the relative energies of each with intervening transition states. The global minimum of 180° is the lowest energy state and is conducive to a linear polymer chain. Since ψ has available three minima additional to the 40° considered in Table I, a total of 16 conformers, neglecting enantiomeric forms, need to be considered.

Using the concepts of statistical thermodynamics and a Boltzmann distribution, the probability distribution of different conformer populations in dilute solution (neglecting solvation effects) may be calculated (Figure 4, with relation to Figure 3). A preponderance of units will be in the minimum energy (180°) linear conformation, but there remains a considerable population of units at higher energy minima, to provide helical twist to a PPD-T chain. Increasing the concentration of polymer increases the proportion of conformer populations in the lowest energy states (Figure 5). Thus, as concentration increases, the linear, lowest energy, form, is dominant and at an appropriate point chain linearity is sufficient to engender the formation of thermotropic phases.

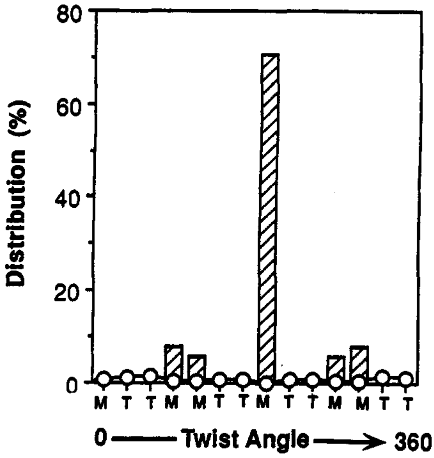


Figure 5. Probability distribution of terephthalamide conformers in a polymer chain at high concentration from AM1 results (M = minimum; T = transition state).

Table II. Torsion Angles (deg) and Relative Energy (kcal/mol) for the Four Unique Terephthalamide Conformations and Transition States from *ab Initio* DZ+D Calculations

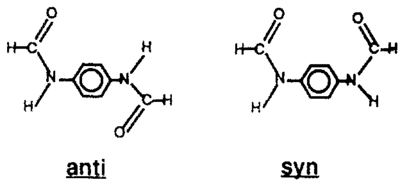
(ψ Arbitrarily Fixed)

angle 1	angle 2	energy	twist	conformers	comment
22.4	−22.4	0.56	0	0	crank
23.8	23.8	0.31	48	±48	helical
21.1	−160.4	0.22	−139	±139	helical
22.0	158.7	0.00	180	180	step
18.7	0.0	1.60	19		transition
22.5	94	2.90	116		
21.5	180	1.08	−158		
22.1	−87	3.55	−67		
90	90	8.3	180		ring flip

While semiempirical methods such as AM1 permit the same general conclusions as *ab initio* methods, the latter are necessary for accurate torsion and energy level computations. The DZ+D results summarized in Table II may be compared with AM1 data (Table I). The dihedral angles of about 22° for terephthalamide agree well with the crystal structure (23°).[32] The energy difference between "step" and "crank" forms is remarkably similar. The torsional barriers are larger than with AM1 (Table I) showing lower flexibility. The six energy minima in relationship to the twist angle and probability distribution of terephthalamide conformers in PPD-T in dilute solution at ambient temperature are broadly comparable to the data for AM1 (Figures 3 and 4).

The phenylene ring of the diamino moiety in PPD-T may be modeled by 1,4-phenylenediformamide. The extent of coplanarity between phenylene and amide planes, previously calculated, varies from 0°[33] in solution to over 40°[30] in some crystal structures. Previous PPD-T models[29-31] predicted a twisted conformation for lowest energy.

Both AM1 and DZ+D *ab initio* calculations showed only two conformations for 1,4-phenylenediformamide, wherein the phenyl and amide groups were coplanar. A 180° twist (*anti* form) gave lowest energy while zero twist (*syn* form) minimum was 0.94 kcal/mol higher (DZ+D), with 2.3 kcal/mol the transition state (DZ+D). A total of 80% of the conformers in dilute solution at ambient temperature are



in the *anti* mode. The amide moiety has considerable rotational flexibility and can be rotated up to 40° in either direction at a cost of about 1 kcal/mol. The decrease in π conjugation and stability with twisting (to a maximum of ca. 8 kcal/mol (DZ+D) at ±90°) is partly offset by strain relief in the C–N–C bond angle (123° vs 128°). The noncoplanarity often observed in the crystalline state results from crystal packing forces and hydrogen-bond formation (2–3 kcal/mol).

The key conclusion from modeling PPD-T conformations is that a twist angle of 180° across the terephthaloyl moiety, or 360° across the entire PPD-T repeat unit, for minimum energy conformations, is necessary for macromolecular linearity with consequent solution lyotropy and well-aligned molecular chains and attendant high strength and modulus in polymer extrudates. Mild random coil character in dilute solutions resulting from a minor population of helical conformers diminishes with increasing concentration (or decreasing temperature) to some critical concentration where lyotropic phase appears, e.g., at 12% PPD-T concentration in 100% sulfuric acid, with accompanying characteristic drop in solution concentration (Figure 6).

The behavior of a large number of lyotropic aramids related to PPD-T, i.e., based on paraphenylene rings, synthesized in these laboratories and elsewhere, is consistent with a fully-extended, ribbonlike chain conformation, wherein successive amide groups are mutually coplanar, i.e., show a 360° twist across the repeat unit. This model correlates well with the crystal structure of as-coagulated PPD-T and related lyotropic extrudates or fibers (cf. Figure 19). The same crystal structure is observed when extrudates are instantly frozen in liquid nitrogen and solvent subsequently removed. There can be little question that the planes of coplanar, hydrogen-bonded amide groups in Kevlar (PPD-T) fibers reflect planar amide conformations of chains in the precursor solutions.

Certain polymers such as L-benzylglutamate form regular helices to give an overall rod-shape and solution lyotropy but cannot be termed rodlike because they lack the high stiffness (modulus) characteristic of rods. The high levels of fiber modulus achievable with PPD-T (650–1400 gpd) approach theoretical values calculated for straight rodlike molecules and substantially exceeds that for helical rod-shaped chains such as certain liquid crystal polyesters. An example is poly[(3,4′-carbonyldiphenyl)-terephthalate] with a modulus of 450 gpd. The modulus of L-benzylglutamate is extremely low. The low solution viscosity of aramid solutions at high MW (DP ~100) and high concentration (35% by volume in sulfuric acid; chain separation of one to two solvent molecule diameters) would hardly be likely with chains that are not fully extended, e.g., consist of mutually canceling nonlinear units.

A few probable anomalies are known where the chains may well not be extended ribbons, but which we have not addressed in this paper. One such is the Russian "SVM" fiber composition in which asymmetric repeat units contain a bend of 45°. To achieve solution lyotropicity it is clearly necessary that adjacent units must, in large measure, mutually cancel out their respective non-linearities. There obviously can be facile rotation at the imidazole-phenylene bond. The derived fibers are non-crystalline.

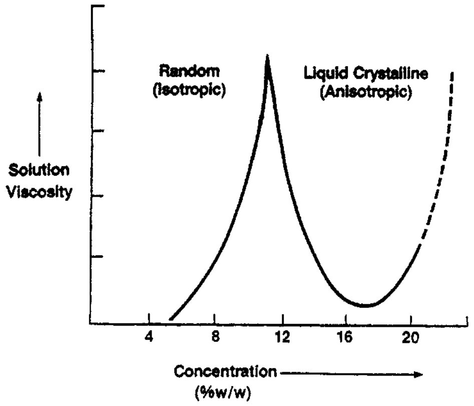


Figure 6. Viscosity of PPD-T (η_{inh} = 8.0) in 100% sulfuric acid at various concentrations at 75 °C.

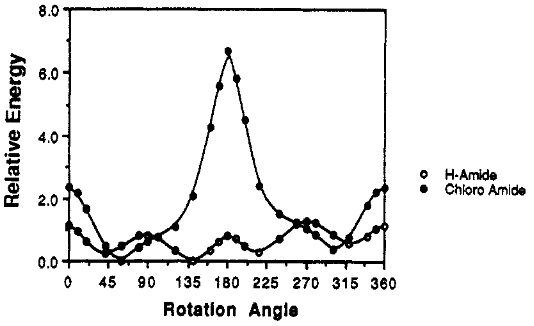
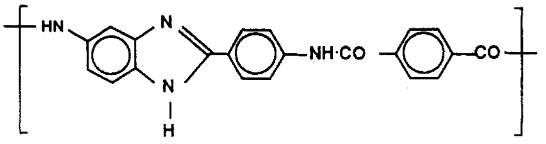


Figure 7. Conformational energies for chloroterephthalamide calculated as a function of rotating one amide group (AM1).



We have found that the calculated lowest energy conformations for a PPD-T and analogs correlate very well with the phase and structural characteristics. Examples are provided in the second part of this paper. We have not attempted to deal with the much more complex actual situation wherein aramid chains are solvated by sulfuric acid or organic solvents. However, we believe the same general principle emerges, that availability of ribbonlike conformation facilitates lyotropic phase formation, and vice versa.

Substituted PPD-T. Apart from diminishing monomer symmetry, terephthaloyl ring monosubstituents change the number, level, and intervening barriers for rotational energy minima.

Figure 7 shows a plot of rotational conformational energy (AM1) for 2-chloroterephthalamide wherein (a) one dihedral angle is fixed at the minimum energy position and the second dihedral angle is varied through 360° and (b) vice versa. With that angle adjacent to the chlorine fixed, the plot for rotating the second amide group (with no ortho-chlorine) is the same as in Figure 2 for terephthalamide. Twist angles for 2-chloroterephthalamide are shown in Table III; allowing for enantiomeric forms this unit, as a component of PPD-ClT, can accommodate eight different helical twists. Figure 8 shows the relative conformational energies in the polymer chain as a function of twist and Figure 9 shows the probability distribution of conformers in a PPD-ClT chain in dilute solution at ambient tem-

Table III. Torsion Angles (deg) and Relative Energies (kcal/mol) for Four Unique Chloroterephthalamide Conformations from AM1 Calculations (Angle 1 Corresponds to the Amide Adjacent to the Chloro Group)

angle 1	angle 2	energy	twist	conformers	comment
57	-40	0.33	17	±17°	helical
56	-143	0.30	-87	±87	helical
58	41	0.01	100	±100	helical
57	140	0.00	-163	±163	helical

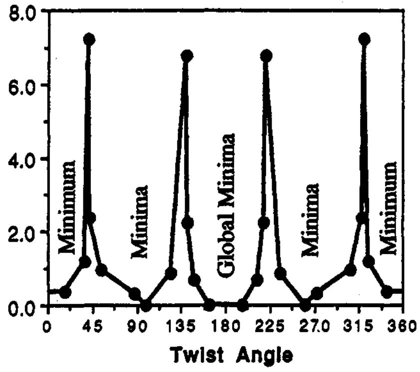


Figure 8. Relative conformational energies for the chloroterephthalamide moiety in the polymer chain as a function of the twist imparted to the chain (AM1 results).

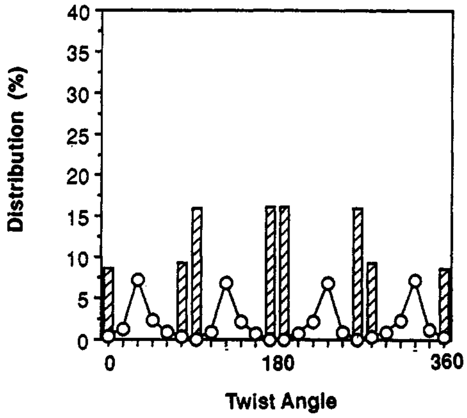


Figure 9. Probability distribution of chloroterephthalamide conformers in a polymer chain at ambient temperature from AM1 results.

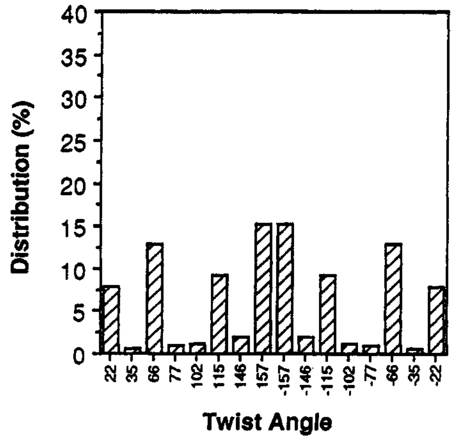


Figure 10. Probability distribution of chloroterephthalamide conformers in a polymer chain at ambient temperature from *ab initio* results.

perature (AM1). The latter has similar character to the same data calculated by *ab initio* DZ+D (Figure 10) but reveals the existence of 16, rather than 8 (AM1), unique conformations available to impart helical twists across the chloroterephthalamide moiety in PPD-ClT: ±22°; ±35°; ±66°; ±77°; ±102°; ±115°; ±157°; ±168°. At higher concentrations (Figure 11), no single minimum energy conformation, of twist angle 180°, is clearly dominant as is the case with PPD-T (Figure 7). Figure 11 indicates that about 60% of PPD-ClT conformers at an arbitrarily chosen high concentration show a twist angle of 157°, which is not too far removed from the 180° need for absolute chain straightness. Also some of the more pronouncedly helical minima conformers may be adjacently sited in the chain such as to cancel each other out, e.g., + and −66° enantiomers. Nevertheless, it seems, qualitatively, a borderline situation as to whether, at highest possible concentrations, PPD-ClT can achieve the degree of linearity necessary for lyotropy, although such might be expected with higher levels of input as might be provided by fiber stretching or crystallization. Flory *et al.*[35] have defined as a requirement for liquid crystallinity that length: diameter ratio should be at least 8 which, in the case of PPD-ClT, indicates linearity over at least three repeat units (assuming the chain width to be 5 Å).

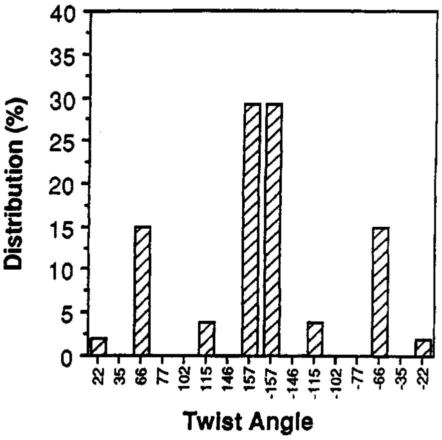


Figure 11. Probability distribution of chloroterephthalamide conformers in a polymer chain at high concentration (or low temperature) from *ab initio* results.

Table IV. Dihedral Angles for Ortho-Substituted Benzamides

ortho-substituent	AM1 twist (deg)	ortho-substituent	AM1 twist (deg)
H	36	NO$_2$	78
F	40	CH$_3$	60
Cl	58	CF$_3$	78
Br	66	CO$_2$H	65
I	74	CO$_2$CH$_3$	65
OH	36*[a]	C$_6$H$_5$	51
OCH$_3$	42		

[a] Reflects internal hydrogen bonding.

A change in the size of substituent on the terephthalamide changes the dihedral angle with the amide group adjacent to the substituent, and to alter rotation barriers. Dihedral angle correlates (AM1) broadly with substituent size (Table IV). The effect of these changes on macromolecular linearity depends on whether the planes of the two amides in the terephthalamide residue approaches a 180° twist. As an example of a larger substituent iodoterephthalamide, a model for PPD-IT, provides twist and energy differences as shown in Table V. Energy barriers are high. Figures 12, 13, and 14, respectively, show this relationship of relative energy to twist level and probability distribution for conformers at low and high concentrations. It is evident that a linear PPD-IT conformation is not possible. Similar conclusions may be adduced with bromine or CF$_3$ substituents.

Table V. Torsion Angles (deg) and Relative Energies (kcal/mol) for Four Unique Iodoterephthalamide Conformations from AM1 Calculations (Angle 1 Corresponds to the Amide Adjacent to the Iodo Group)

angle 1	angle 2	energy	twist	conformers	comment
79	−143	0.49	−64	±64	helical
82	−40	0.43	52	±42	helical
81	138	0.10	−141	±141	helical
81	42	0.00	123	±123	helical

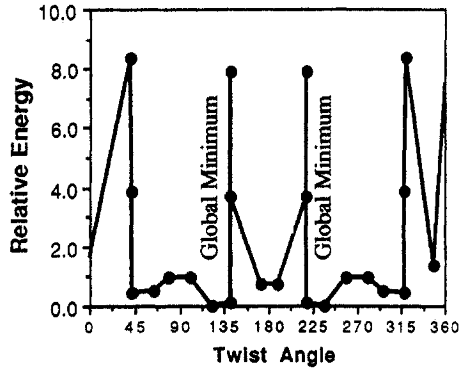


Figure 12. Relative conformational energies for the iodoterephthalamide moiety in the polymer chain as a function of the twist imparted to the chain (AM1 results).

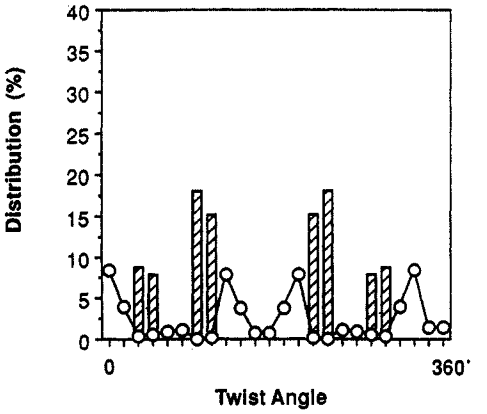


Figure 13. Probability distribution of iodoterephthalamide conformers in a polymer chain at ambient temperature (AM1).

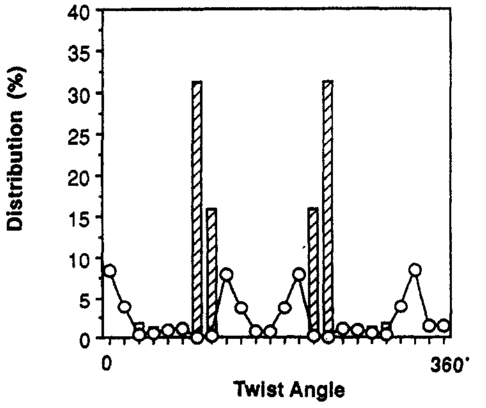


Figure 14. Probability distribution of iodoterephthalamide conformers in a polymer chain at high concentration (AM1).

Fluorine is the smallest substituent of practical importance. Among the conformational preferences shown in Table VI is a twist of 180° at lowest energy level, indicative that, despite 10 different helical twist possibilities in PPD-FT, a linear polymer chain and solution lyotropy are possible. (The 180° conformer is absent in *ab inito* results but this is because hydrogen bonding involving fluorine is considered, such as unlikely in a solvent as sulfuric acid.)

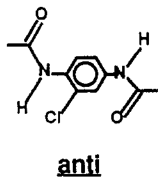
Table VI. Torsion Angles (deg) and Relative Energies (kcal/mol) for the Six Unique Fluoroterephthalamide Conformations from AM1 Calculations (Angle 1 Corresponds to the Amide Adjacent to the Iodo Group)

angle 1	angle 2	energy	twist	comment
124	−38	2.41	86	helical
119	42	2.02	161	helical
40	−40	0.26	0	crank
37	−142	0.19	−105	helical
40	41	0.05	81	helical
40	140	0.00	180	step

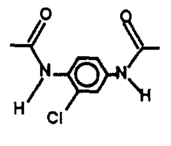
Table VII. Torsion Angles (deg) and Relative Energies (kcal/mol) for the Two Unique Chloro-*p*-phenylenediformamide Conformations and Transition States from AM1 Calculations (Angle 1 Corresponds to the Amide Adjacent to the Chloro Group)

angle 1	angle 2	energy	twist	comment
0	0	0.18	0	syn
0	180	0.00	180	anti
0	90	3.5	90	transition
180	180	11.9	0	transition
180	0	11.1	180	transition

Moderately-sized substituents on the phenylene ring derived from PPD do not disturb coplanarity with adjacent amide groups. Thus, chloro-1,4-phenylenediformamide is planar in both *syn* and *anti* conformations



anti

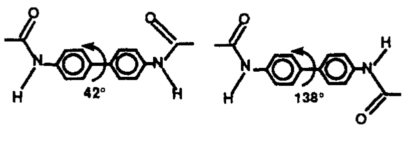


syn

There is little energy difference between minima in these two conformations (Table VII). The energy barrier to 180 °C rotation is, however, very high (11 kcal/mol) for the amide next to the substituent. Comparable data were obtained for trifluoromethyl-1,4-phenylenediformamide. With 2,5-disubstituted 1,4-phenylenediformamides, the *anti* conformer is preferred. With larger substituents such as mono-SO_3H, significant dihedral angles of −150° (*anti*) and 13° (*syn*) are created.

Thermotropic Polyester Analogs. The oxygen atom of the ester group is much smaller than the NH in aramid analogs such that terephthalate groups are planar, even when bearing substituents as large as phenyl, as evidenced by their thermotropy.[9] The *syn* and *anti* conformers are of nearly equal energy but separated by a significant rotation barrier of 6.0 kcal/mol (*ab initio*).

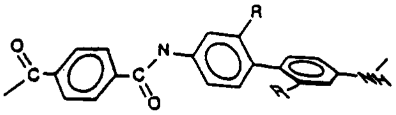
PPD-T Analogs Containing 4,4′-Biphenylene Units. Biphenyl is planar in the crystal[36] but noncoplanar in the gas phase[37] (dihedral angle 41.6°). Nonbonded interactions between ortho-hydrogens[38] produce a rotation barrier of less than 5 kcal/mol. *Ab initio* methods gave minimum energy dihedral angle of 41.9° with a 3.4 kcal/mol barrier for the planar (0°) transition state and 1.5 kcal/mol for the 90° transition state (arising from loss of π electron conjugation between rings). Thus the minimum energy forms of benzidine diformamide are



The 138° twist is the lower energy form. Taking account of enantiomers there are four possible helical twists through the benzidinediformamide moiety in poly(4,4′-benzidineterephthalamide) (PP-T): ±42° and ±138°.

The key to linearity is for the twists across the PP-T unit or analogs to add up to 360° in low energy conformers. In PP-T the terephthalamide twist of −139° twist is followed by a benzidine moiety with 138° twist.

Substituents in the 2,2′-positions in biphenyls increase the dihedral angle.



Thus with CF_3 groups the helical twists through the biphenylene group become ±51° and ±111° which inhibit the formation of a zero net twist in a lowest energy form, so that the absence of a low energy linear macromolecular conformation and lyotropy are predictable under normal circumstances, as observed by Gaudiana and co-workers.[10,11] The latter also noted that in the solid state, aramids from 2,2′-disubstituted biphenyls are essentially noncrystalline, which might be expected from their stiff nonlinear conformations.

Applications of Models

Monosubstituted PPD-T. Behavior of PPD-T with a substituent on the terephthaloyl unit, as reported in the literature, is consistent with our macromolecular conformational models. The preferred linear chain conformation of PPD-T in the more concentrated solutions used for fiber spinning, made possible by minimum energy twist angle of 360° for the repeat unit, is the basis for lyotropy and the remarkable mechanical properties of the highly oriented fibers therefrom. Sweeny[2] demonstrated lyotropic solutions of PPD-FT in sulfuric acid under conditions comparable to those used for PPD-T fiber spinning (Kevlar aramid) and obtained comparable fiber strength and modulus, indicative of very good chain alignment. This is in line with our model wherein the fluorine substituent does inhibit a twist angle of 360° (Table VI).

The "borderline" nature of PPD-ClT in terms of its ability to attain a high degree of linearity is reflected in the conflicting reports that sulfuric acid solutions therefrom are lyotropic[19] and isotropic[2] at similar high concentrations (19.4%). Hartzler[39] observed a reversible lyotropic to isotropic phase transition for a 20% PPD-ClT solution at 80–95 °C. The lower η_{inh} values, relative to PPD-T, of apparently high MW PPD-ClT, cited earlier,[4] results from the greater nonlinear character of the polymer chains under the conditions of η_{inh} determinations (0.5% concentration) compared with its much more linear character at the higher, lyotropic spin-dope concentrations (correlate with Figures 10 and 11). The same phenomenon was also observed[19] in a series of PPD-T/ClT copolymers wherein the η_{inh} diminished with increasing ClT content, while fiber tenacity and modulus, reflecting respectively comparable levels of MW and chain alignment, remained more or less constant (Table VIII).

Table VIII. Inherent Viscosity, Fiber Tenacity, and Fiber Modulus (Undrawn) for a Series of PPD-T/ClT Copolymers[19]

ClT (% molar)	η_{inh} (dL/g in H_2SO_4	tenacity (gpd)	modulus (gpd)
0	6.3	23.5	706
20	5.9	25.0	720
40	5.4		
50	4.7	20.6	650
70	3.9		
100	4.2	17.2	601
100[4]	3.7	21.0	640

With larger substituents such as iodine, phenyl, or nitro groups in the terephthaloyl group, the random helical character of the polymers in both dilute and concentrated solutions is considerably increased and conformational minima with 360° twist are no longer available. It is therefore not possible for these polymers to adopt rodlike conformations in solution. Increased helical nature of these chains is reflected in respective η_{inh} values of 2.0,[40] 0.63,[6] and 2.13[41] dL/g in sulfuric acid (the low value for PPD-PhT probably also indicates lower MW). Again, the progressive increase of nitroterephthalic acid (NO_2T) units in copolymers with PPD-T causes a marked reduction in η_{inh} values. Thus, 0, 10, 30, 40, 50, and 100 mol % NO_2T gave polymer having, respectively, η_{inh} of 6.0, 5.3, 4.9, 3.9, 3.1, and 2.1 dL/g.[41] Inhibition of lyotropy and decreased rodlike character reduce fiber properties to quite low levels, e.g., PPD-BrT and PPD-IT gave tenacity/modulus values of 3.6/251 and 3.8 gpd/171 gpd, respectively.[2]

Modeling predicts that with moderately-sized substituents such as chlorine in the phenylenediamino ring macromolecular linearity should be similar to PPD-T itself. In fact, ClPPD-T solutions in sulfuric acid are less viscous than PPD-ClT solutions of comparable MW and concentration (20%),[39] due to differences in linearity. (Similar effects can be produced by copolymerizing PPD-T with nonlinear monomers such as 4,4′-oxydianiline.) The relatively lower η_{inh} values reported for substituted PPD-T, such as 3.1 dL/g for ClPPD-T,[4] as well as for PPD-ClT[4] (previously discussed), have prompted speculation that this is the result of steric hindrance during polymerization. In the case of the diamines, limited MW appears to be the result of lowered purity because of exceptionally high sensitivity of substituted phenylenediamines to atmospheric oxidation. We have demonstrated high $\eta_{inh} \geq 6$ dL/g easily from ClPPD·2HCl by liberating the free diamine in solution by reaction with the equivalent amount of tertiary amine, just before treatment with terephthaloyl chloride.[42] With the even more air-sensitive MePPD, carefully distilled monomer gave η_{inh} approaching 5 dL/g, while purified ClPPD also can provide $\eta_{inh} \geq 6$ dL/g.[39]

The unusual capability of ClPPD-T solutions in organic solvents such as dimethylacetamide to transition from lyotropy to isotropy, when the amount of dissolved LiCl is increased, has been ascribed to altered interchain associations.[5] However, our conformational models suggest that increased ionic associations with amide NH create a significant dihedral angle between amide and phenylene planes, thus introducing sufficient helical character into the polymer chains as to inhibit ability to align in solution.

Disubstituted PPD-T. The original stimulus for this modeling study was the observation that poly[1,4-phenylene-2,5-bis(carboalkoxy)terephthalamides] (PPD-DRO_2CT) in NMP failed to afford solution lyotropy, in contrast to PPD-T.[43] With R = CH_3 or C_2H_5 the polymers, formed from reaction of diamine and diacid chloride in 20% solution, precipitated out during polymerization. Complete solubility was achieved with R = $CH_3OC_2H_5$ or, more conveniently, by replacing 50–100% of the PPD by ClPPD. As discussed, the latter is not expected to provide reduced chain linearity. Unlike alkoxy substituents (discussed later), carboalkoxy substituents are not expected to diminish solubility by internal hydrogen bonding, according to *ab initio* calculations.

The polyamide esters such as ClPPD-$DMeO_2$CT at 15–20% in DMAc, with or without added LiCl or $CaCl_2$ salt, were clear yellow. The color indicates extended π electron conjugation, as in PPD-T itself. Inherent viscosity values

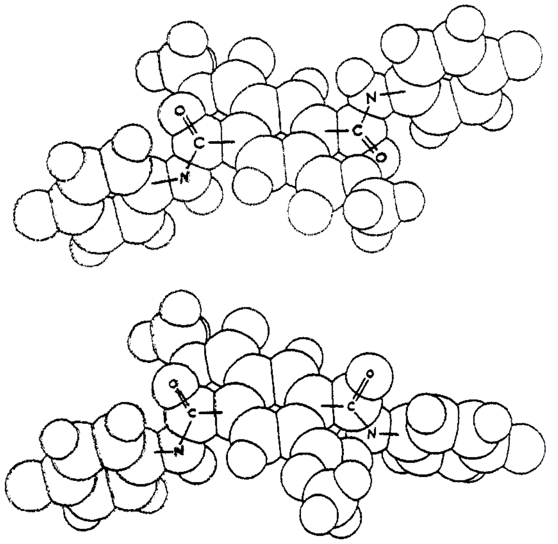


Figure 15. (a, top) *anti*-Periplanar conformation of 2,5-bis(carbomethoxy)terephthalamide. The nitrogen atoms are on *opposite* sides of the phenyl ring. (b, bottom) *syn*-Periplanar conformation of 2,5-bis(carbomethoxy)terephthalamide. The nitrogen atoms are on the *same* side of the phenyl ring.

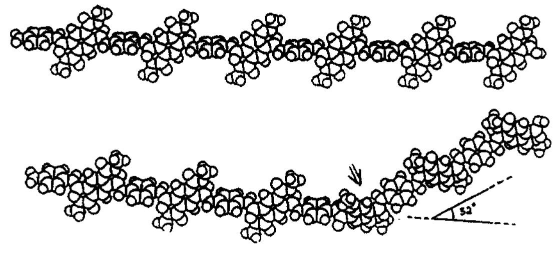


Figure 16. (a, top) Linear oligomer of poly[*p*-phenylene-2,5-bis(carbomethoxy)terephthalamide] having all monomeric units in the *anti*-periplanar conformation. (b, bottom) Kinked oligomer poly[*p*-phenylene-2,5-bis(carbomethoxy)terephthalamide] with one terephthalamide unit in the *syn*-periplanar conformation.

were low −1.0–2.3 dL/g. No lyotropic phase was present although anisotropy was temporarily induced by shear and observed by a temporarily bright field when the cover slide above a solution specimen, mounted between crossed polarizers on a microscope stage, was pressed down. Extruded dopes provide fibers of modest tenacity (3.2 gpd), not subject to improvement by stretching.

Modeling data indicate that these polymer chains are relatively stiff and extended, but not rodlike and thus unable to form lyotropic solutions. The carboalkoxy groups are coplanar with the phenylene ring to which they are attached, are not hydrogen bonded with the amide hydrogen, and cause twisting of the adjacent amide groups, randomly to one side or the other with equal probability. Unlike PPD-T, these two forms are not interconvertible under normal constraints of concentration, temperature, and fiber stretching which might be applied. The precise conformer present in a given molecular unit is determined at the instant when the amide bond is formed. Figure 15a shows the antiperiplanar conformation of 2,5-bis(carbomethoxy)terephthalanilide, which may be regarded as a fragment of PPD-$DMeO_2CT$. This conformer provides a twist angle of 180° because the dihedral angle occasioned by one MeO_2C substituent is exactly cancelled out by an equal and opposite dihedral angle caused by the second MeO_2C substituent. In the *syn*-periplanar conformation (Figure 15b), the twisting effect of the two MeO_2C substituents is additive, such that a pronounced bend is introduced into the chain. Figure 16a shows the hypothetical linear chain which would result from a catenation of *anti*-periplanar conformers. Figure 16b shows the effect of introducing a single *syn*-periplanar conformer into such a linear chain. A dihedral angle of 40° was used for these models. For an actual case of PPD-DRO_2CT or an analog, comparable amounts of randomly-sited *syn*- and *anti*-periplanar forms are present, wherein the former may provide a right-handed or left-handed helical twist. The result is a nonlinear, generally extended chain as represented in Figure 17.

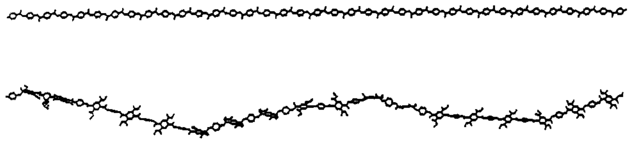


Figure 17. Random coil shaped conformation of poly[1,4-phenylene-2,5-bis(carbomethoxy)terephthalamide] (lower) compared with linear conformation of PPD-T (upper).

While mono- and disubstituted PPD-T such as PPD-ClT and PPD-DClT (from 2,5-dichloroterephthalic acid) both provide randomly helical chains, as discussed, there is a key difference. Whereas each ClT unit may make a moderate contribution to helical twisting, with DClT about half such units provide zero twist while the other half provides a sharper twist (relative to ClT). In practice the copolymerization of 20 mol % ClT into PPD-T reduced η_{inh} from 6.3 to 5.9 dL/g whereas 18% 2,5-DClT reduced it from 6.3 to 4.8 dL/g.[19] However, fiber tensile strength of the two copolymers was similar to that of PPD-T, indicating comparable MW levels.[19] The fiber moduli were similar but lower than for PPD-T, reflecting comparable overall effects of random twist. The differences in chain conformation at 0.5% concentration, implied by the differences in η_{inh}, are elided by the constraints of higher concentration and fiber formation.

2,2′-Disubstituted Biphenylene Analogs of PPD-T. Consistent with modeling predictions, poly(3,3′-dimethyl-4,4-biphenyleneterephthalamide) (3,3′-DMePP-T) provides lyotropic solutions at 20% in sulfuric acid.[44] The ortho-methyl groups do not diminish coplanarity of adjacent phenyl and amide rings, while the dihedral angle of the biphenyl group is complemented by a terephthalamido conformer to provide a twist angle across the repeat unit of 360°. For polymer chains of similar length, as judged by fiber strengths, the inherent viscosity of 3,3′-DMePP-T, containing the stiffer biphenylene unit, is higher than for PPD-T (9 vs 6 dL/g).

Polyterephthalamides from 2,2′-disubstituted benzidines also exhibit very high levels of inherent viscosity in sulfuric acid or amide solvents, indicating high levels of molecular stiffness and extension. Compared with η_{inh} = 6 dL/g for PPD-T, values of >9 dL/g were attained readily with polyterephthalamide of 2,2′-dibromo-3,3′-dimethoxybenzidine (2,2′-DBr-3,3′-DMeOPP-T), 2,2′-dicarboxybenzidine (3,3′-DHO_2CPP-T), and 2,2′-bis(trifluoromethylbenzidine) (DCF_3PP-T), while 2,2′-dichlorobenzidine (2,2′-DClPP-T) gave 6 dL/g. (DHO_2CPP-T was best polymerized as the dihydrochloride, treated with a tertiary amine to liberate free diamine *in situ*, then with terephthaloyl chloride;[45] free diamine, on storage, tended to form internal salt bonds which prevented it from polymerizing quantitatively or even could render it insoluble.) Despite considerable chain stiffness, none of these polymers gave lyotropic solutions under normal circumstances. This was consistent with the observations of Rogers *et al.*[11] that aramids in general, containing a 2,2′-disubstituted biphenylene unit, including 2,2′-DCF_3-PP-T, did not form lyotropic solutions. Rogers *et al.*[11] attributed this to diminished hydrogen bonding and other

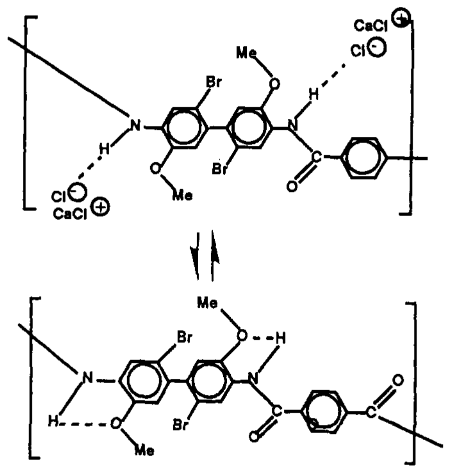
Table IX. Inherent Viscosities of 2,2′-DBr-3,3′-DMeOPP-T in Various Solutions

solvent	$CaCl_2$ (% by wt)	molar ratio [$CaCl_2$]:[polymer]	η_{inh}, dL/g (0.5% by wt)
100% H_2SO_4			7.9
NMP			9.8
NMP/$CaCl_2$	0.5	1:1	9.9
	3.0	5:1	10.8
	4.3	29:1	11.0

intermolecular attractions. Modeling, by contrast, indicated that polyterephthalamides from disubstituted benzidines resembled crooked rods in solution and were unable to attain the degree of alignment in solution necessary for lyotropy. This was supported by their higher solution viscosities compared with PPD-T. Thus, whereas PPD-T of η_{inh} = 6.0 provides readily extrudable 20% solutions in sulfuric acid at 80 °C, 2,2′-DClPP-T of considerably lower MW (η_{inh} = 3.7) gave an extremely viscous, clear 17% isotropic solution capable of anisotropy while under shear. For 2,2′-DClPP-T of η_{inh} = 6.0, a concentration as low as 11% was necessary to obtain a viscosity conducive to spinnability at 80 °C. The low tensile strength and modulus of 2,2′-DClPP-T fibers as extruded (2 gpd and 60 gpd, respectively; cf. 23 gpd and 500 gpd for PPD-T), their lack of crystallinity and high X-ray orientation angle (54°; cf. 10–23° for PPD-T) are characteristic of quite unexceptional chain alignment. On the other hand, low response (4%) to high temperature (425 °C) stretching accompanied by a significant modulus increase (60 to 240 gpd) and a more modest strength increase (2.0 to 3.5 gpd) indicates significant directionality of chains in the fiber axial direction wherein hydrogen bonding is a strong deterrent to drawing.

Compared with 2,2′-DClPP-T which, like PPD-T, was poorly soluble in organic solvents and formed a stiff gel in NMP/$CaCl_2$ under standard polymerization conditions, 2,2′-DBr-3,3′-DMeOPP-T provided fluid 5–10% solutions in NMP at high η_{inh} levels (to at least 10 dL/g). While η_{inh} values are lower for this polymer in sulfuric than in NMP, added $CaCl_2$ produces increases in η_{inh} (Table IX). In sulfuric acid internal hydrogen bonding between amide hydrogen and methoxy oxygen is unlikely but is probable in NMP to form a ring which increases the stiffness of the chain. However, increase in η_{inh} values with increased $CaCl_2$ content can hardly be thus explained, but rather indicates a shift in equilibrium toward a bulkier complex with $CaCl_2$.

When 2,2′-DBr-3,3′-DMeOPP-T solutions in NMP/$CaCl_2$ (5.6% solids; η_{inh} = 6.6 dL/g in sulfuric acid) were stored at 21 °C for several weeks, $CaCl_2$ (identified by X-ray analysis) progressively precipitated even though the original concentration of $CaCl_2$ was well below the solubility limit usual for aramid solutions. (Solubility of $CaCl_2$ in aramid/NMP solutions is considerably higher than in NMP alone because it can complex with amide bonds.) Subsequently, polymer began to precipitate in a form which was not redissolvable in hot NMP or NMP/$CaCl_2$. Polymer precipitated by addition of a nonsolvent such as water was likewise not redissolvable. The cause of these phenomena appears to be equilibration of the polymer from a soluble form which is solvated and/or complexed with $CaCl_2$ towards a non-solvated, internally hydrogen bonded form as shown.



In the absence of the 2,2′-dibromo substituents, i.e., with 3,3′-DMeOPP-T, solubility is considerably reduced. In the course of the usual diacid chloride polymerization in NMP/$CaCl_2$ polymer precipitated at quite low MW (η_{inh} ~1.3 dL/g in sulfuric acid; estimated M_n < 4000). Kwolek[44] previously achieved η_{inh} = 0.99. At this point chain growth ceased. It seems clear that solvation or complexation is inhibited once again by internal hydrogen bonding. Under identical circumstances the analogous 3,3′-DMePP-T, which is incapable of internal hydrogen bonding, can attain a high MW (~9 dL/g in sulfuric acid). A somewhat analogous situation to the 3,3′-DMeOPP-T case occurs when PPD-T is formed in NMP in absence of $CaCl_2$. Because of diminished solvent power, PPD-T polymer precipitated at η_{inh} ~ 1.0 (estimated M_n ~ 4000). Shifts in infrared absorption frequencies for 3,3-DMeOPP-T, compared with PPD-T (1670 vs 1649 cm^{-1} for C=O stretching and 3320 vs 3320 cm^{-1} for NH stretching, respectively) are presumably caused by internal hydrogen bonding.

Internal hydrogen bonding involving methoxy groups causes lowered melting points in related monomeric compounds, by preventing intermolecular hydrogen bonding (Table X). Similar melting points for the three benzidine diamines indicate negligible intramolecular hydrogen bonding. With the fully acetylated diamines no hydrogen bonding of any sort is possible and melting points are again similar. The melting point of 3,3′-dimethoxybenzidinediacetamide is similar to those of the completely acetylated analog because intermolecular hydrogen bonding is not possible but is considerably lower than for benzidinediacetamide and 3,3′-dimethylbenzidinediacetamide. A comparable situation occurs with the benzamides. Turner[46] also ascribed lowered melting points in various aramids from 2-methoxyterephthalic acid to intramolecular hydrogen bonding.

In freshly polymerized 2,2′-DBr-3,3′-DMeOPP-T, wherein intramolecular hydrogen bonding is not yet extensive, the solubilizing effects of 2,2′- and 3,3′-substitution appear to act synergistically. Separately, as in 2,2′-DClPP-T or 3,3′-DMePP-T, solubility in organic solvents is quite limited.

Dissolution of 2,2′-DBr-3,3′-DMeOPP-T of fairly high MW (η_{inh} = 6.55 dL/g) in 100% sulfuric acid, using a high efficiency mixer, gave a hard gel at 21 °C. This required heating (briefly) to 170–180 °C (well above decomposition temperature) for fluidity. To achieve fluid solutions below the decomposition range (~90 °C), the concentration of the same polymer had to be reduced to 5%. These solutions were isotropic. At much lower MW (η_{inh} = 3.7 dL/g) it was possible to prepare an extremely viscous, but nevertheless fluid solution, at 20% solids. This solution was lyotropic. Anisotropy diminished considerably on heating to 100 °C but, under shear, birefringence was very high. At this level of MW, dilution to 7.5% was nevertheless necessary for increasing fluidity enough for fiber

Table X. Melting Points (°C) of Aramid-Related, Methoxy-Substituted Monomers and Their Analogs

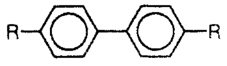
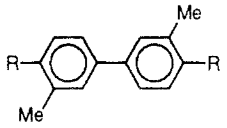
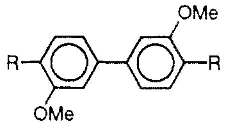
R			
$-NH_2$	128	132	138
$-N(OCOCH_3)_2$	215	217	246
$-NHOCOCH_3$	317	319	244
$-NHOCOC_6H_5$	352	265	236

Table XI. Inherent Viscosities of 2,2′-DCF$_3$PP-T in Various Solvents

solvent	equiv of Cl$^-$ per amide group (after dilution to 0.5% concn)	η_{inh}
H_2SO_4		2.95
DMAc	0	2.55
DMAc/HCl	2	8.97
DMAc/$CaCl_2$	2	10.18
	4	6.87
	33	2.78
	84	2.95

spinning; lyotropy was lost at this dilution but high shear birefringence remained.

The behavior of 2,2′-DBr-3,3′-DMeOPP-T illustrates that, although the lowest energy conformations may not provide the 360° repeat unit twist angle needed for complete chain linearity, nevertheless under the constraints of high concentration (coupled with reduced MW to accommodate solution fluidity rather than gelation) combinations of conformers approaching a 360° twist angle per repeat unit, adequate for lyotropy, are achievable. Even with lyotropy, the very high viscosities in sulfuric acid show that chains are less rodlike than PPD-T. In sulfuric acid, internal hydrogen bonding is not an important factor. While such an approximation to 360° twist angle is apparently more difficult with 2,2′-DClPP-T, it appears to be more facile with 2,2′-DMePP-T because Schmidt and co-workers[13] observed lyotropy in solutions of this polymer and certain of its copolymers at fairly high concentrations.

Poly[bis(2,2′-trifluoromethyl)-4,4′-biphenyleneterephthalamide] (2,2′-DCF$_3$PP-T) has enhanced solubility in organic solvents, compared with previously-discussed analogs; at η_{inh} = 3.5 dL/g at up to about 11% concentration in NMP or DMAc, it provided fluid, viscous isotropic solutions. Attainment of higher inherent viscosity values presented difficulty. When limited amounts of LiCl, $CaCl_2$, or HCl (0.75–4.0 equiv/amide group) were additionally present in these polymer solutions, they became strongly lyotropic.[47] At higher levels of additives lyotropy disappeared. Induction of lyotropy in aramid solutions by ionic species has not previously been reported.

Isotropic solutions of 2,2′-DCF$_3$PP-T, whether containing little, no, or large amounts of $CaCl_2$, when diluted to 0.5% concentration by pure solvent (NMP or DMAc) gave modest η_{inh} values of about 3 dL/g, commensurate with values obtained by redissolving preisolated polymer in sulfuric acid. By contrast, η_{inh} values from dilution of the same polymer in solutions containing intermediate amounts of $CaCl_2$ gave very high η_{inh} values (Table XI).

Modeling calculations indicate that with energy minima at dihedral angles of ±51° and ±111° for 2,2′-bis(trifluoromethyl)biphenylene groups there is no minimum energy combination with a terephthalamide conformer which will yield a repeat unit twist angle of 360°. This is consistent with the observation of solution isotropy at low and high chloride levels. The appearance of lyotropy when limited amounts of $CaCl_2$, LiCl, or HCl are present may be explained by the formation of an electrostatic bridge between a fluorine atom of an electronegative CF_3 group and an oxygen atom of an adjacent carbonyl, thus enabling the biphenylene unit to attain a modified dihedral angle such as to allow an aggregate 360° twist across the total repeat unit (Figure 18). With low amounts of cation insufficient alteration of rotation angles occurs for production of lyotropy. With excess cation the electronegative F and O atoms are subject to additional non-directional electrostatic attractions by other cations, which diminish unique bridge formation. The unusually high inherent viscosity values for polymer solutions derived from the lyotropic solutions at higher concentrations may be explained in terms of enhanced straightness and stiffness of the polymer chains when complexed with critical amounts of H$^+$, Li$^+$, or Ca^{2+}; 5% concentration is lower than the critical concentration of better known aramids such as poly-1,4-benzamide[48] in DMAc/LiCl (ca. 7%), but a biphenyl group is expected to contribute to stiffness more than a p-phenylene group, if the chains are well extended. The possibility that high inherent values are the consequence of aggregation of several individual molecules, held together by residual electrostatic attraction across cationic bridges, cannot be excluded.

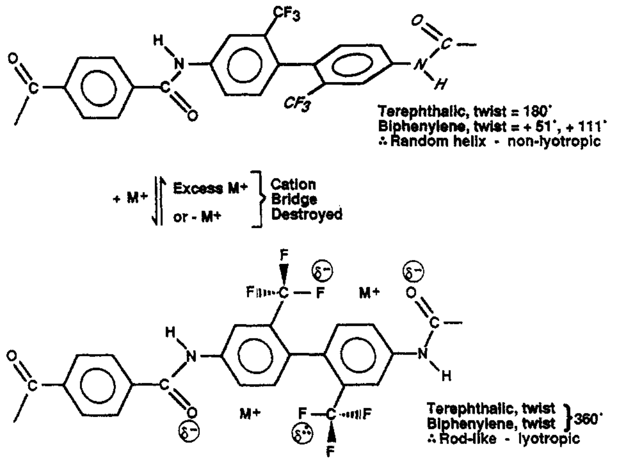


Figure 18. Conformation of 2,2′-DCF$_3$PP-T in solution.

Table XII. Lyotropic Character and Inherent Viscosity Behavior of DC$_2$F$_4$HOPP-T in DMAc/CaCl$_2$

equiv of $CaCl_2$ per amide group	η_{inh} by dilution (dL/g)	anisotropy (6%)
0.0	1.67	–
0.9	1.47	+
2.8	3.72	+
4.6	3.30	+
6.5	5.50	–

The only other example of ion-induced lyotropy and inherent viscosity increase is with poly[2,2′-bis(1,1,2,2-tetrafluoroethoxy)-4,4′-biphenyleneterephthalamide] in DMAc/$CaCl_2$ (Table XII). With CF_3O substituents, polymer solubility is excessively low in the same solvent while with soluble, large $C_3F_7OCHFCF_2O-$ groups, lyo-

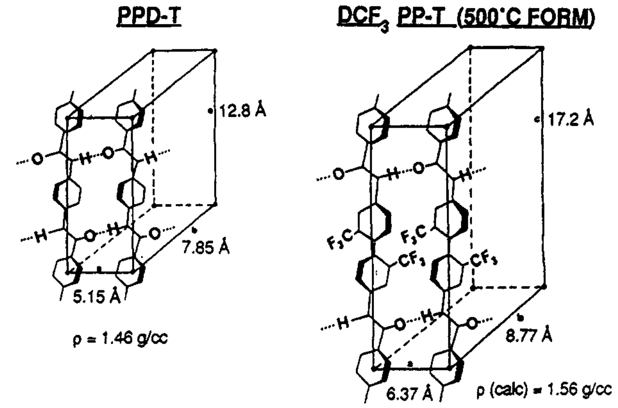


Figure 19. Unit cells of PPD-T and DCF$_3$PP-T.

tropy is absent. In any case, the phenomenon is associated with the presence of aliphatic fluorine in the substituent groups.

The 5% lyotropic solutions of DCF$_3$PP-T (η_{inh} = 2.5 in H_2SO_4) in DMAc/$CaCl_2$ were wet-spun into water to provide a moderately well-oriented (30° X-ray orientation angle) amorphous fiber. In contrast with PPD-T, these could be stretched about 12% at 300 °C to a much higher degree of orientation (12°) and highly crystalline structure, with an accompanying 2-fold increase in tensile strength and modulus (10 gpd and 400 gpd, respectively). Chain alignment in the fiber is evidently very good. When fiber stretching was performed above 450 °C, a distinctly different crystal structure was produced (Figure 19).[49] This contrasts with previous experience that aramids with 2,2′-disubstituted biphenylene groups are essentially amorphous[10,11] 2,2′-DCF$_3$PP-T had considerably greater thermal stability than 2,2′-DClPP-T or more especially 2,2′-DBr-3,3′-DMeOPP-T. Unfortunately, 2,2′-DCF$_3$PP-T may not be processed from sulfuric acid in the manner of Kevlar aramid because aryl–CF_3 groups are thus converted to aryl–CO_2H groups which, in the present context, are subject to further reactions in sulfuric acid.

Summary and Conclusions

Semiempirical molecular orbital calculations, which generally agreed well with much more computer-intensive *ab initio* quantum mechanical results, provided a profile of the energy changes associated with mutual rotation of phenylene and amide planes in key "fragments" of PPD-T, especially as terephthalamide and 1,4-phenylenediformamide. From a knowledge of minimal energy rotational conformers and the intervening energy barriers, the relative rectilinearity of the PPD-T macromolecules at low and high solution concentrations was inferred. The basic condition for chain linearity is that the overall twist angle across a repeat unit of the polymer, at lowest energy conformations, be 360° or thereabouts. Comparative rectilinearity controls lyotropicity, bulk viscosity, and ability to extrude very highly aligned polymer forms, having high tenacity and modulus.

With PPD-T, ring substituents of moderate size in the PPD-based moiety do not disrupt the coplanarity of phenylene and amide groups, but in the terephthaloyl moiety they increase the dihedral angle for rotational energy minima and increase the transition state energy barriers such that overall twist angles may deviate considerably from 360°. Consequently lyotropicity cannot ordinarily be achieved with substituents on the terephthaloyl ring which is larger than chlorine and capability for good chain alignment diminishes with increasing substituent size. Replacement of a 1,4-phenylene ring in PPD-T by a 2,2′-disubstituted-4,4′-biphenylene provides additional twist and high energy barriers which, again, create the likelihood that overall twist angles will diverge from 360°.

The foregoing principles are discussed in terms of actual examples. Thus, lyotropicity and high chain alignment are not possible with 2,5-dicarboalkoxy polyterephthalamide, or with monosubstituents as large as I. Whereas ClPPD-T behaves like PPD-T in providing lyotropic solutions capable of giving strong, well-oriented fibers, isomeric PPD-ClT solutions, except at extreme concentrations in sulfuric acid, are not lyotropic and alignment and properties are somewhat lower. The lower inherent viscosity, obtainable with certain substituted terephthalic acids, is a consequence of nonlinear chains (substituted PPD have often given lowered inherent values, but only because of the difficulty of maintaining high purity with these oxygen-sensitive monomers).

Poly[2,2′-bis(trifluoromethyl)-4,4′-biphenyleneterephthalamide] and analogs present a unique situation whereby dopes are isotropic in organic solvents without or containing high levels of $CaCl_2$, LiCl, or HCl, but lyotropic with about 0.75–4.0 equiv chloride per amide and provides unusually high values of inherent viscosity. Modeling indicates that with limited additives, attraction between Li^+ or other cation and neighboring electronegative O and F atoms makes possible a twist angle of 360° and may also cause some aggregation of macromolecules in dilute solution. With poly(2,2′-dichloro-4,4-biphenyleneterephthalamide) very high solution viscosities were demonstrated; high inherent viscosity values suggested "crooked rod" conformation. An additional complication affecting solubility and chain stiffening due to internal hydrogen bonding, with methoxy groups ortho to the amide group, is discussed for the cases of polyterephthalamides from 3,3′-dimethoxybenzidine and 2,2′-dibromo-3,3′-dimethoxybenzidine.

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