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Highly Amorphous, Birefringent, Para-Linked Aromatic Polyamides

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ABSTRACT: The synthesis and properties of a class of high molecular weight, film- and fiber-forming, rodlike, aromatic polyamides containing all-para-linked substituted-biphenylene and/or -stilbene repeat units are described. Substituents are placed on the aromatic rings (or double bond of the stilbene moiety) so as to force them into a noncoplanar conformation. The effect of this noncoplanarity is to reduce the crystallinity (to ≤10%) of even highly oriented films, enhance solubility, and reduce or completely eliminate absorption of visible radiation. Another consequence of this noncoplanar conformation is to confer a substantially cylindrical electron density distribution about the long axis of the polymer backbone which in many examples enhances the repeat unit anisotropy and may contribute to the unusually high birefringence.

Introduction

Several years ago a series of patents[1-3] issued which described optical devices, e.g., polarizers, filters, etc., utilizing birefringent polymeric films as the primary element(s). The usefulness of the devices was greatly limited by the availability of polymeric materials exhibiting the extremely high birefringence ($\Delta \eta \geq 0.4$) required to maximize polarization efficiency. The most useful polymer available was poly(ethylene terephthalate) which, when undirectionally oriented, exhibited a birefringence of approximately 0.17.[4]

In the last decade the development of processable, highly oriented aromatic polyamides was realized.[5-7] The combination of high inherent polarizability, rodlike geometry, and high orientation of these materials generated unusually high birefringence ($\Delta \eta = 0.761$[8]). Unfortunately, the crystallinity, the biaxial optics, and strawlike color of these polymers precluded their use for most optical applications.

The goals of this investigation were to design and synthesize aromatic polyamides that could be processed into highly oriented, optically uniaxial, colorless, transparent (noncrystalline) films and fibers suitable for optical applications. In addition, the interrelationships of molecular geometry and polarizability were to be delineated so as to maximize birefringence.

Results and Discussion

The structures of 17 polyamides are given in Table I; a summary of the corresponding physical and optical data is given in Table II.

Synthesis and General Polymer Properties. The synthesis of the diacid chloride and diamine monomers and the methods used for purification are given in the Experimental Section. For the compounds which were found in the literature, experimental details are given only in those examples where significant procedural changes were made; the method of purification and physical data are given, however, for every monomer.

The procedure used for the polymerizations was the low-temperature solution condensation technique developed for poly(*p*-phenyleneterephthalamide) and homologues.[9,10] Typically, the polymerization was started at −5 to 0 °C and over several hours was allowed to warm to 25 °C. It was determined that heating (up to 80 °C) overnight did not increase the inherent viscosity over that obtained by reaction at room temperature.

The inherent viscosity of the polymers was significantly affected by the solvent used in the polymerization reaction[11] and the concentration of the reactants.[10] The solvent system which generated consistently high inherent viscosities was tetramethylurea/*N*-methylpyrrolidone (TMU/NMP) (at a volume ratio of 1:1 to 2:1) containing LiCl which ranged in concentration from 2% to 6% (w/v), 3% being the optimum. The polymer concentration was always adjusted to 2–3% (w/v). If the concentration was greater than approximately 3%, the solution could not be stirred effectively, which is particularly important at the early stage of the reaction. Below 2% polymer concentration, side reactions may have become significant, thus enhancing chain termination reactions which resulted in lower viscosity.[10]

In every case these procedures were meticulously followed and this resulted in polymers which exhibited inherent viscosities (in 5% LiCl/dimethylacetamide (DMAc) at 30 °C) greater than 1 dL/g even when synthesized on a 1-g scale. Several polymers exhibited optical properties which were particularly significant, and hence these polymers were synthesized several times on a much larger scale in an attempt to increase the molecular weight. Many of the latter polymers exhibited inherent visocisities in the 4–5 dL/g range, and a few had viscosities in excess of 9 dL/g. For example, several batches of polymer II were synthesized with inherent visocisities in the 9.3–9.8 range; this corresponds to an intrinsic viscosity of 12.9 ($\eta_{INH} = 9.3$). The molecular weight (M_w) of this polymer, determined by low-angle light scattering, was 2.98×10^4 ($\overline{DP} = 54$). The exponent (a) in the Mark–Houwink equation was 1.05 ($K = 2.04$), which is indicative of the rodlike nature of the polymer in LiCl/DMAc.

The thermal stability of these polymers is typical of the aromatic polyamide class; namely, the onset of decomposition in nitrogen and air was in the 400 and 350 °C range, respectively. Polymers containing the stilbene moiety darkened when heated in air to 250 °C or when subjected to direct sunlight for extended periods. Differential scanning calorimetry (Perkin-Elmer Model 2, 5 °C/min) on either fibrous powders or films showed weak but reproducible endotherms between 150 and 200 °C for several polymers. Thermal mechanical analysis (Du Pont Model 943, 5 °C/min) showed a reproducible, gradual relaxation which began at approximately 150 °C and continued to increase up to 290 °C; at the latter temperature an abrupt relaxation and rupture occurred. This behavior is probably due to the gradual weakening of intermolecular forces as the temperature increased. At the upper temperature limit

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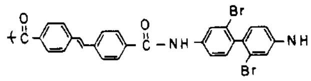
Table I
Molecular Structures of the
Aromatic Polyamides Prepared for This Study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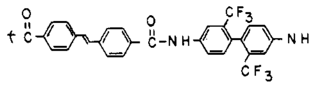
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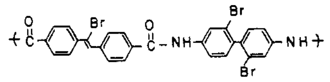
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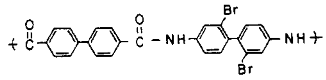
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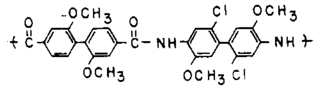
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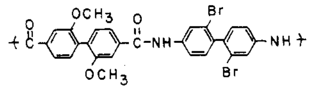
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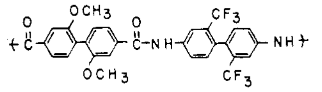
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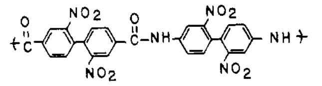
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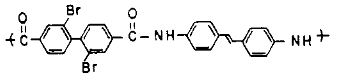
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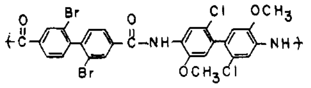
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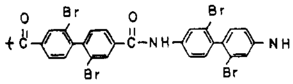
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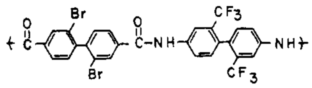
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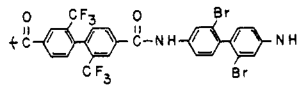
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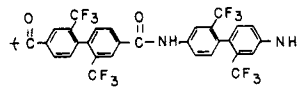
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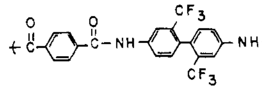
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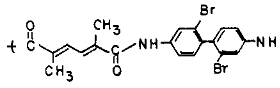
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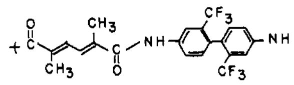
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Table II
Physical and Optical Properties of Aromatic Polyamides

polymer	η_{INH}[a]	T_g,[b,c] °C	λ_{max},[e] nm	η_{iso}	$\Delta\eta_{max}$
I	9.04	225[b]	350 (62800) light yellow	2.05[g]	0.865[g]
II	9.80	185[b] 290[c]	350 (76000) light yellow	1.89[f]	0.801[f]
III	7.81	195[b]	light yellow	2.07[g]	0.849[g]
IV	3.54	d	320 (75000) colorless	1.93[h]	0.293[h]
V	2.36	155[b]	colorless		
VI	4.16	188[b]	colorless	1.89[g]	0.58[i]
VII	3.77	180[b]	315 (25880)	1.69[g]	0.58[i]
VIII	1.40	190[c]	280 (46400) yellow	1.72[h]	0.33[i]
IX	4.62	225[b]	370 (62800) yellow	1.82[h]	
X	5.75	110[b]	colorless	1.87[g]	0.20[g]
XI	2.04	120[c]	305 (31900)	1.84[g]	0.48[g]
XII	3.82	d	colorless	1.66[g,h]	0.45[i]
XIII	3.00		colorless	1.67[f] 1.65[g,h]	
XIV	5.74	d	290 (54800)	1.57[f]	0.13[f]
XV	3.53	294[c]	310 (31200) colorless	1.76[f]	0.57[f]
XVI	4.69	185[b]	333 (33600)	1.91[h]	0.58[i]
XVII	5.85	d	colorless	1.77[f]	0.385[f]

[a] 0.5 g of polymer/5% LiCl/DMAc at 30 °C. [b] DSC. [c] TMA. [d] Not detectable. [e] Solvent: 5% LiCl/DMAc. [f] Brewster angle (at 633 nm). [g] Jamin-Lebedeff interferometry (at 589 nm). [h] Becke-line analysis. [i] Quartz-wedge compensator (at 589 nm).

Table III
Wide-Angle X-ray Analysis of Polyamide Films

polymer	% crystallinity	$\Delta\eta$
I	<5	0.44
	5–10	0.52
VIII	5–10	0.26
XI	<5	0
	<5	0.29

the thermal energy is sufficient to overcome all of these forces, and the rodlike chains slipped past each other, resulting in film breakage.

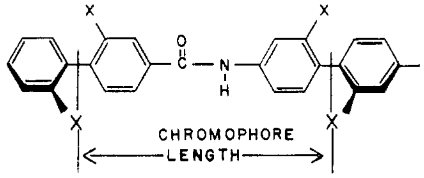
At room temperature, the films are quite strong. For example, analysis of stress–strain curves obtained from partially oriented films (65% by IR dichroism using the carbonyl–amide transition) gave a Young's modulus of 4 × 10^6 psi. This was particularly surprising in view of the fact that neither unoriented nor highly oriented films exhibited greater than 10% crystallinity by wide-angle X-ray scattering[12] (Table III).

Ultraviolet/Visible Absorption Characteristics. A highly desirable property of these optical-quality polymers is that they should not exhibit absorption bands (or tails of UV bands) in the visible region of the spectrum. In addition, it is desirable that the position of the absorption bands in the UV region occur at the shortest possible wavelength in order to diminish the refractive index dispersion. It is well-known that the various aromatic polyamides, such as poly(*p*-phenyleneterephthalamide), and the aromatic polyhydrazides are yellow in solution and generate pale-yellow films and fibers the color of which intensifies on heat treatment.[5–7,13] The former class, for example, exhibits an absorption band in the 300–320-nm region which tails out to well beyond 400 nm in solution. The very large bathochromic shift relative to benzanilide (λ = 267 nm) is due to the very strong double-bond character of the amide C–N bond (the rotation barrier is approximately 20 kcal/mol[14]) which extends the conjugation between adjacent phenyl/amide moieties. The absorption would appear at even longer wavelength were it not for the fact that the amide group and the adjacent phenyl rings are noncoplanar; the dihedral angles, as measured by X-ray crystallography, are 30° in model compounds and polymers.[15] This noncoplanarity is due to steric effects between the ortho hydrogens of the phenyl rings and the oxygen and hydrogen of the amide groups. The rotational barriers between these groups are estimated to be at most 2.6 kcal/mol.[15a] The combination of low dihedral angle, which diminishes but does not eliminate multi-repeat-unit conjugation, and low rotational barriers, which provide low-energy pathways for interconversion of conformers, contributes to band broadening and long-wavelength tailing.

In order to prevent extended conjugation and eliminate tailing of the absorption band, the interplanar dihedral angle must approach 90°, and the rotational barriers must be raised, thereby locking in an orthogonal conformation.

Two possible solutions to this problem were envisioned. The first is to substitute, on at least one of the carbon atoms of the phenyl ring ortho to the amide group, a sterically bulky group such as methyl or chloro. The literature contains many examples of polyamides with this type of substitution, but in every example the degree of polymerization, as indicated by the visosity, is adversely affected.[16-19]

The second approach, which was demonstrated experimentally to be correct, involved the placement of sterically bulky substituents on the 2,2′-positions of the phenyl rings of biphenylene polyamides. This substitution does not interfere with the polymerization reaction as evidenced by the viscosity data in Table II. Furthermore, the size and electronic nature of the substituents directly affect the rotational barriers around the 1,1′-bond and diminish the extent of multi-repeat-unit conjugation by limiting p-orbital overlap of the 1,1′-carbon atoms.

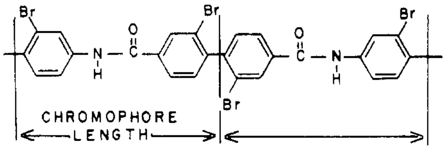


The effect of 2,2′- and 6,6′-substitution on the dihedral angles and the rotational barriers of biphenyls is well documented.[20] Many unsymmetrical, tetra-ortho-substituted biphenyls have been resolved into optically active enantiomers which are stable indefinitely at room temperature. The dihedral angles in these compounds are close to 90°, and the rotational barriers are high even when the substituents are relatively small such as, for example, 2,2′-difluoro-6,6′-dimethoxybiphenyl ($E_{rot} \simeq$ 35–39 kcal/mol[21]). Disubstituted biphenyls are much more difficult to resolve because of their lower rotational barriers, which are in the 18–21 kcal/mol range for 2,2′-dibromo, 2,2′-diiodo, and 2,2′-bis(trifluoromethyl)[22] ($t_{1/2} \simeq$ 58 s, 39° for 2,2′-bis(trifluoromethyl)benzidine[23]).

The dihedral angles of 2,2′-disubstituted biphenyls in the vapor phase, in solution, and in the crystalline state range from 60° for 2,2′-difluorobiphenyl to 79° for 2,2′-diiodobiphenyl.[24] From Raman spectroscopy the dihedral angles of biphenyl, 2-methylbiphenyl, and 2,2′-dimethylbiphenyl are 25°, 60°, and 70°, respectively.[25] The intensity of the 1600-cm^{-1} band, which is indicative of the amount of conjugation between the phenyl rings, is nearly equal to that of benzene itself for the 2,2′-dimethyl compound. This implies that there is very little conjugation through the 1,1′-bond.

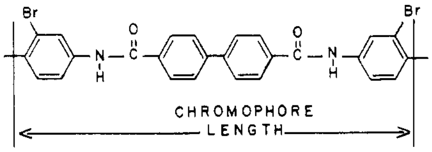
This conclusion was confirmed by UV spectroscopy of 2,2′-bridged biphenyls[26,27] and 2,2′-disubstituted biphenyls. In the latter class, even the 2,2′-difluoro compound exhibits a hypsochromic shift to λ_{max} = 234 nm from λ_{max} = 249 nm for biphenyl itself.[28] In addition, the long-wavelength edges (or tails) of the adsorption bands of 2,2′-difluoro-, -dichloro-, -dibromo-, and -dimethylbiphenyl all appear at shorter wavelength than biphenyl; this suggests that the higher rotational barriers have diminished absorptions of the low-energy conformers.

Examples of colorless polymers composed of diacid and diamine moieties, both of which contain 2,2′-substituents, are V–VII and X–XIV. The substituents are either very large, nonconjugated trifluoromethyl groups (4.90-Å diameter—measured from space-filling models) or weakly conjugaed bromines (3.90-Å diameter), chlorines (3.60-Å diameter), or methoxy groups in various combinations. Polymer IV, which is also colorless, has no substituents other than hydrogen on the diacid moiety. Since the dihedral angle of biphenyl is 20° in solution,[29] conjugation through the diacid–biphenyl results in a bathochromic shift of the absorption band by 15 nm relative to polymer XI, but the 2,2′-substituents on the diamine moiety prevent further conjugation as shown by the following:



XI

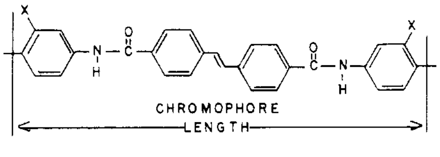
λ_{max} = 305 nm



IV

λ_{max} = 320 nm

Increasing the conjugation of this repeat unit by incorporating a double bond between the phenyls (polymers I and II) shifts the absorption band an additional 30 nm. Since the bands tail beyond 400 nm, both polymers are yellow.



I, X = Br, λ_{max} = 350

II, X = CF_3, λ_{max} = 350

In polymer IX, the amide nitrogen is in conjugation with the stilbene moiety and this results in an additional 20-nm bathochromic shift (λ_{max} = 370 nm) and a yellow polymer. Polymer VIII, which contains a yellow, noncoplanar diamine, is also yellow. Obviously, incorporating a colored monomer into a polymer generates a colored material.

Crystallinity. In addition to being colorless, optical-grade polymers must also be completely nonscattering. There are two ways to prevent scattering: either the polymers have to have extremely large or extremely small crystals (much greater or much smaller than the wavelength of visible radiation), or they have to be completely amorphous.

From the standpoint of practicality, the latter approach was considered the most feasible even though it is known that completely aromatic, rigid-rod polyamides readily form lyotropic solutions[5,6,10,30] and highly crystalline fibers.[7,31,32] It is generally believed that the propensity of this class of polymers to crystallize is enhanced not only by the rigidity of the backbone but also by intermolecular hydrogen bonding and van der Waals forces; the combined interaction energy of these two intermolecular forces contributes an estimated 14.6 kcal/mol to the crystal energy.[15c,33]

A unique approach to the elimination of crystallinity in this polymer class again centers around the incorporation

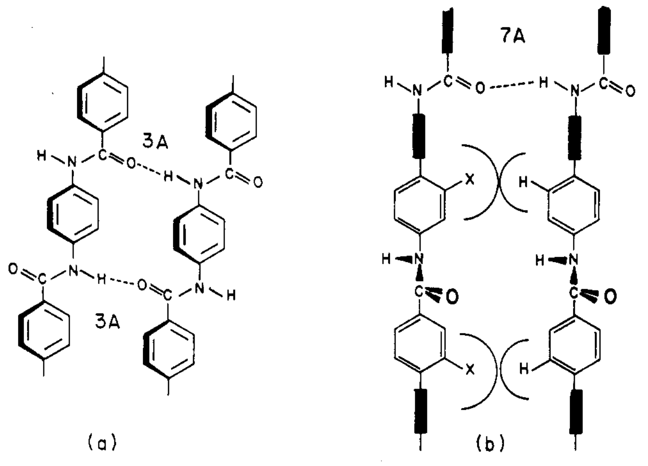


Figure 1. Hydrogen bonding in aromatic polyamides: (a) single phenyl ring allowing close packing; (b) substituted biphenyls preventing close packing and amide groups in different planes.

of 2,2′-disubstituted biphenyl moieties into the polymer backbone. In the previous section it was shown that 2,2′-substituents larger than hydrogen force the biphenyl rings into a highly noncoplanar conformation ($\Phi \geq 60°$) which affects the position and shape of the absorption band. This noncoplanarity also affects the crystallinity by weakening van der Waals forces and hydrogen bonding and by lowering the symmetry of the repeat units.

In regard to van der Waals forces, data from the liquid crystal literature show that nematic and smectic phase stability, as evidenced by the magnitude of the liquid crystal temperature range and the crystal/liquid crystal transition temperature, is greatly decreased or eliminated when the biphenyl moiety of the molecules contains 2,2′- or 2,2′,6,6′-substituents.[34,35] The smectic phase, which is more dependent on lateral forces, is affected to a greater extent than the nematic phase. It was suggested that this destabilization is the result of the diminution of lateral van der Waals forces of attraction caused by the noncoplanar phenyl rings.

In the 2,2′-disubstituted biphenyl polyamides, hydrogen bonding should also be weakened, if not completely eliminated, as a result of the noncoplanar phenyl rings. For example, in single-phenyl polyamides, all of the amide groups lie in the same plane, and the phenyl rings rotate out of the plane of the amide group by 30° (Figure 1), thus allowing an intermolecular hydrogen-bond distance of approximately 3 Å[31] (bond energy = 7 kcal/mol[33]). Molecular models of the biphenyl polyamides show that when the polymer chains are parallel to one another, the hydrogen-bond distance is increased to 7 Å. Furthermore, the amide groups themselves are noncoplanar, and the probability that the amide groups of one chain are in the correct registration to hydrogen bond to amide groups of neighboring chains, generating a three dimensional network, is extremely small.

It should be noted that hydrogen bonding in polyamides can also be significantly reduced by extensive methylation of the amide-nitrogen atoms, and N-methylation in aliphatic[36] and aromatic/aliphatic[37] polyamides results in polymers which are completely amorphous. The problem with this substitution in rodlike polyamides, such as poly(*p*-phenyleneterephthalamide), is that the equilibrium rigidity (in solution) is reduced by more than a factor of 10.[38,39] Additional evidence for increased flexibility of these polymers is obtained by a comparison of the exponent (a) in the Mark–Houwink equation which, for *N*-methyl-*p*-phenyleneterephthalamide in H_2SO_4, is 0.96 vs. 1.76 for the unsubstituted polymer.[40] The polymers are more flexible because the steric interaction between the N substituent and the ortho hydrogen atoms of the phenyl ring reduces the double-bond character of the carbonyl carbon–nitrogen bond, thereby lowering its rotational barrier. A consequence of the diminished rodlike character of the polymer backbone is reduced birefringence.

Table IV
Solubility of Substituted Biphenylene Polyamides

polymer[a]	class	solvents[b]
I, III–VI, VIII, IX, XI, XVI	1	LiCl/DMAc, LiCl/TMU, LiCl/NMP, etc., strong acids
II, X, XV	2	DMAc, TMU, NMP, etc., w/o LiCl
VII, XII, XIII, XIV, XVII	3	"common" solvents—THF, acetone, methoxyethanol

[a] The inherent viscosities are listed in Table II. [b] Solvents were dried over molecular sieves before testing.

The final consideration in regard to eliminating crystallinity is symmetry. It should be noted that each chain of the biphenyl polyamides is composed of randomly distributed mixtures of enantiomers due to the presence of 2,2′-disubstituted biphenyls. Once again, the registration of appropriate conformations necessary for ordered close packing in crystals is extremely unlikely.

The fact that this approach actually results in amorphous, nonscattering materials was demonstrated when the polymers were cast or extruded from solution. The films were oriented by mechanical stretching while they were swollen with solvent or by heating and stretching after removal of solvent. When the film thickness was less than approximately 25 μm (1 mil), the films, whether oriented or unoriented, appeared glassy and completely nonscattering. Wide-angle X-ray analysis[12] of both oriented and unoriented films (in this thickness range) of polymers I, VIII, and XI showed that they contain at most 10% crystallinity (Table III).

Films cast from LiCl-containing solvents which were above approximately 60 μm in thickness developed noticeable scattering and in fact could be made nearly opaque depending on the method of processing. Examination of these highly scattering films by electron microscopy showed that they contain large voids and stratified, layered cross sections; in addition, there exist dense, uniform top layers on both film faces and much less dense, open structures in the various layers below the surface. It was observed that the uniformity of the cross section is dependent on the rate of extraction, gel formation, and coagulation, all of which are affected by the solvent used in the coagulating bath.

Solubility. In the previous section it was shown that subtle manipulation of the molecular structure affects intermolecular forces to such a large extent that gross morphological changes result. As a consequence, rigid-rod polyamides, which as a class normally exhibit a high propensity for crystallization, are obtained which are almost completely amorphous. On this basis alone it was anticipated that these polymers would exhibit higher rates of dissolution compared to other aromatic polyamides, and this was observed for all of the polymers presented in this study. Specifically, polymers of class 1 (Table IV) dissolved quickly, with stirring and heating to not more than 100 °C, in LiCl-containing amide solvents and strong acids, such as concentrated sulfuric, up to a maximum concentration of approximately 7–9% (w/v). Polymers of class 2 were soluble in amide solvents, such as TMU, without LiCl; in fact, polymers II and XV were completely soluble up to 10% and 30%, respectively. Although solubility in amide solvents in the absence of LiCl is unusual, there are a few examples of para-linked, rodlike polyamides in the literature which are soluble in DMF. These polymers are composed of 2,2′-diiodobiphenyldicarboxylic acid copolymerized with unsubstituted phenylene or biphenylene diamines,[41] the solubility limit and solution properties were not investigated.[42,43]

Extremely unusual solubility is exhibited by 5 of the 17 polymers synthesized for this study. The polymers in this group, designated as class 3, are soluble in THF, ketone solvents such as acetone, or methoxyethanol. Polymer XVII, for example, is soluble in THF up to 17% (w/v). Solubility in common solvents has not been exhibited by any other aromatic, para-linked, rigid-rod polyamide known to date, but the solubility of these polymers is similar to that exhibited by the oligomeric[44] and low molecular weight, substituted, rigid-rod polyphenylenes which are soluble in toluene.[45,46] It should be noted that all of the class 3 polymers have the bis(trifluoromethyl)biphenyl moiety in at least one of the comonomers. The incorporation of this moiety into the polymer is a necessary but not a sufficient condition for this unusual solubility since at least two of the polymers of class 2 also contain this moiety. The solubility-enhancing effect of the trifluoromethyl group[47] and that of 2,2′-disubstituted biphenylenes[41] are suggested in the literature, but the polyamides presented in this paper are the first examples which combine both of these effects.

Rather surprisingly, not one of the polyamides of this study exhibits lyotropic behavior in any of the solvents in which they were soluble even up to the limit of solubility. When the concentration limit is reached, the polymer solutions form either translucent or transparent gels or the polymer precipitates as a swollen mass. When stressed, the solutions instantaneously develop streaming birefringence (when observed between crossed polarizers) but not stir opalescence. When the stress is removed, the solutions became isotropic and completely transparent, i.e., nonscattering. The inability to form lyotropic solutions obtains in spite of the fact that all of the known prerequisites for such behavior have been met. Namely, the materials are rodlike, have high molecular weights, and are capable of being dissolved to very high concentrations in solvents which are known to yield anisotropic solutions for other polyamides.

The most reasonable explanation that can be offered at the present time in regard to the unprecedented solubility and unusual solution behavior of these polymers is similar to the rationale forwarded for lack of crystallinity, namely, reduction of the cohesive energy density by diminution of interchain van der Waals forces and hydrogen bonding.

Birefringence. Two of the goals of this work were the maximization of optical anisotropy (birefringence) with preferrably uniaxial optics and the elucidation of molecular factors affecting this property.

It was realized at the outset that morphology, which is dependent in a very complex way on molecular structure, intermolecular correlations, and macroscopic manipulation, contributes significantly to the optical properties of a film or fiber. Polymer films are either amorphous or semicrystalline. In order to prevent scattering, a semicrystalline polymer film would have to have crystallites which are smaller than the wavelength of visible radiation. In addition, the polymer crystals themselves must be uniaxial, e.g., tetragonal,[48] hexagonal, or trigonal, and completely unidirectionally oriented. This combination would impart to the film a single isotropic axis which would be coincident with the orientation direction. As a result, the birefringence would be maximized, and it would be invariant for incident radiation impinging on the film or fiber along any line perpendicular to that direction (Figure 2). Alternatively, if the crystal optics were biaxial (e.g., monoclinic, triclinic, or orthorhombic—each of which by definition has two isotropic axes[48]) and complete unidirectional orientation were attained, the birefringence would be strongly dependent on the angle of incidence (Figure 3).

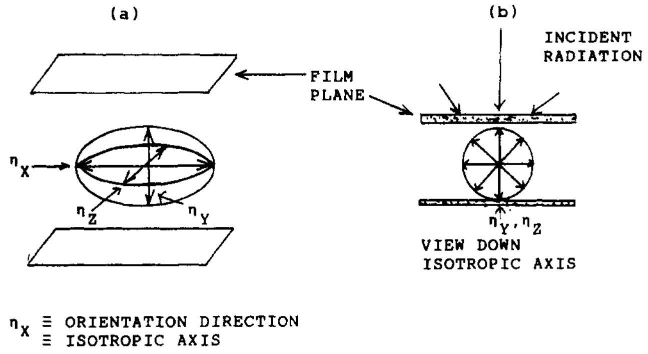


Figure 2. Positive uniaxial refractive index ellipsoid ($\eta_X > \eta_Y = \eta_Z$): (a) orientation direction and isotropic axis coincident; (b) incident radiation perpendicular to η_X has birefringence which is independent of incident angle.

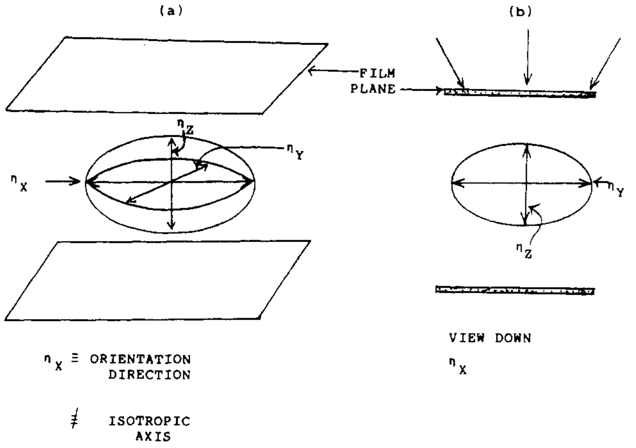


Figure 3. Positive biaxial refractive index ellipsoid ($\eta_X \gg \eta_Y > \eta_Z$): (a) orientation direction and η_X coincident—two isotropic axes not shown; (b) incident radiation perpendicular to η_X has birefringence which is angle dependent.

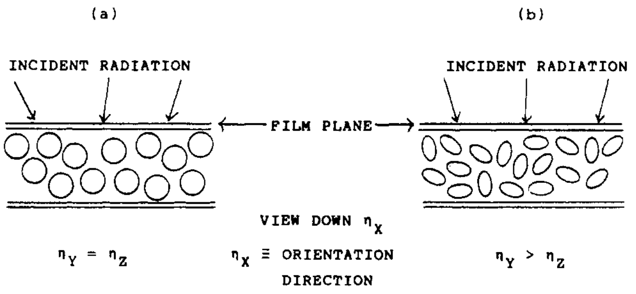


Figure 4. Ensemble of refractive index ellipsoids: (a) positive uniaxial ellipsoids; (b) uncorrelated positive biaxial ellipsoids. The birefringence is independent of incident angle in both examples.

There is a circumstance, however, by which biaxial crystals could generate uniaxial optics. The film or fiber would have to be composed of small nonscattering domains of completely oriented biaxial crystallites, the conformations of each of which around the orientation direction, i.e., the major axis of the indicatrix, n_X, are uncorrelated (Figure 4). It must be emphasized that, in a film, any degree of orientation between 1% and 99% would result in a biaxial indicatrix independent of crystalline class.[49]

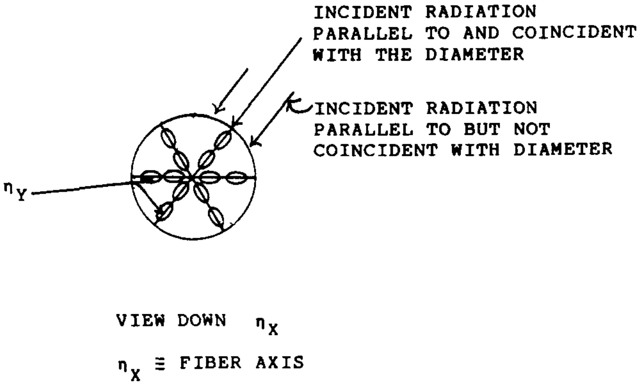


Figure 5. Radial distribution of η_Y about the fiber axis (η_X).

For completeness one other possibility should be considered in regard to correlated biaxial crystals. The literature indicates that highly oriented poly(*p*-phenyleneterephthalamide) fibers are composed of monoclinic or pseudoorthorhombic) crystallites, the major transverse axis, η_Y, of each of which is radially distributed about the orientation direction (Figure 5).[32,50] In this specific case, incident radiation impinging on the fiber parallel to and coincident with the diameter will experience a uniaxial field. However, radiation which is parallel to the diameter but not coincident with it will experience a biaxial field.

In light of these morphological complexities, it was anticipated that the most straigtforward approach to the attainment of high-quality films with controllable optical properties would be to synthesize completely amorphous polymers (cf. Crystallinity section). With this morphology the optics and the birefringence depend almost exclusively on controllable molecular factors such as orientation, interchain correlation, molecular geometry, and electron polarizability and distribution.

In the interest of aiding the synthetic effort and quantifying the rather intuitive approach taken in the early stages of this work, computations were made based on the Lorentz–Lorenz theory with the goal of predicting the refractive indices of candidate polymers. The well-known Lorentz–Lorenz equation (eq 1)

$$\left(\frac{\eta^2 - 1}{\eta^2 + 2}\right)\left(\frac{M}{d}\right) = \frac{4}{3}\pi N\alpha \tag{1}$$

where $\eta \equiv$ refractive index, $M \equiv$ molecular weight, $d \equiv$ density, $N \equiv$ Avogadro's number, and $\alpha \equiv$ polarizability, relates bulk refractive index or, in a modified form, birefringence (eq 2)

$$\Delta\eta = \frac{2\pi}{9}\frac{(\eta^2 + 2)^2}{\eta}\left(\frac{Nd}{M}\right)\Sigma(\alpha_\parallel - \alpha_\perp) \tag{2}$$

where $\Delta\eta$ = birefringence = $\eta_\parallel - \eta_\perp$, and $\alpha_\parallel$ and $\alpha_\perp \equiv$ molecular polarizabilities parallel and perpendicular to the major molecular axis, respectively, to molecular polarizability. However, these equations were not developed for polymers and are based on the model of a point dipole in a spherical cavity composed of identical point dipoles. It is far beyond the goal and scope of this paper to review the numerous attempts to establish adequate modifications of the Lorentz–Lorenz equations, which would have been applicable to polymers.[51] Attempts to calculate accurately the refractive index or birefringence of poly(*p*-phenyleneterephthalamide)[8,52] and the polyamides presented in this work from bond and group polarizabilities utilizing such modifications were completely unsuccessful.

Regardless of the shortcomings of the Lorentz–Lorenz equations in regard to predicting bulk optical properties of polymers, calculations of repeat unit polarizability values are in themselves instructive.

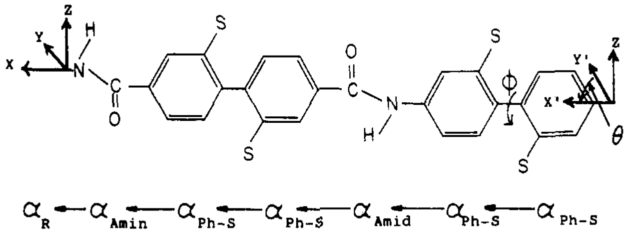


Figure 6. Transformation of the polarizability tensor, α' of the various components of a repeat unit (in coordinates X', Y', Z') into a repeat unit polarizability tensor, α_R (in coordinates X, Y, Z). The X, Y, Z coordinates are coincident for all repeat units.

The calculation procedure was as follows. Bond and group polarizability tensors for the various components of the repeat unit of the polymers in question were found in the literature;[53] if a particular substituted phenyl was not found, the tensor was calculated from group and/or bond polarizabilities. The tensor for the first member of a repeat unit was expressed in the X',Y',Z' coordinate system (Figure 6) and then transformed into the coordinate system of the second member by a rotation about X' (Φ) and Z' (θ), thus generating a new polarizability tensor. The procedure was repeated until all of the components of the repeat unit were transformed into a reference coordinate system (X,Y,Z) generating a repeat unit polarizability, α_R.[54] The three diagonal terms of α_R, after the diagonalization procedure

$$\alpha_R = \begin{bmatrix} \alpha_X & & \\ & \alpha_Y & \\ & & \alpha_Z \end{bmatrix}$$

removed off-diagonal elements, are the polarizability values on each of the three axes and were used to generate polarizability ellipsoids analogous to the refractive index ellipsoids of Figures 2–4.

It was hypothesized that in order to maximize birefringence, the repeat unit polarizability along the X axis, α_X, must be maximized while simultaneously minimizing the polarizabilities along the Y axis (α_Y) and Z axis (α_Z). In other words, maximizing the repeat unit anisotropy, $\Delta\alpha$, defined as

$$\Delta\alpha_R = \alpha_X - (\alpha_Y + \alpha_Z)/2 \tag{3}$$

would also maximize the inherent birefringence, $\Delta\eta$, defined analogously as

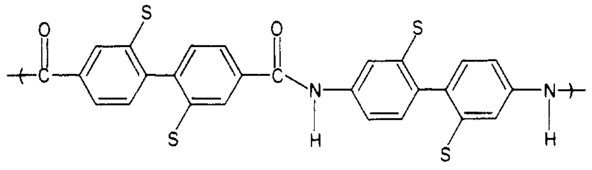
$$\Delta\eta = \eta_X - (\eta_Y + \eta_Z)/2 \tag{4}$$

Specifically, three structural factors were identified by which polarizability, and hence birefringence, could be manipulated; two of these were partially confirmed by the calculations.

First, the polymer must have a rigid, rodlike backbone composed of nonconjugated repeat units—aromatic polyamides are one of the obvious choices.

Second, atoms with nonbonded electron pairs, such as sulfur, phosphorus, the halogens (particularly Br and I), and groups with highly polarizable π-electron density, such as arenes, alkenes, and alkynes, must be incorporated into the polymer repeat unit. Whatever combinations of atoms and groups are chosen, they must not diminish the rigidity, disrupt the rodlike geometry of the polymer chain, or add significantly to the transverse polarizability. The choices of groups placed directly in the polyamide backbone are limited to para phenylenes, trans double bonds, and alk-

Table V
Calculated Polarizability Data for Selected Biphenyl Polyamides



S (angle[b])	α_X	α_Y	α_Z	$\Delta\alpha_R$
H (20°)	6.473	5.845	3.305	1.898
F (60°)	6.475	4.242	4.998	2.005
Cl (72°)	7.201	5.223	5.386	1.904
Br (75°)	7.563	5.718	5.820	1.794
I (85°)	8.711	6.598	6.511	2.156
CF_3 (90°)[c]	7.216	5.280	5.280	1.937

[a] The units are 10^{-23} cm^3. [b] Dihedral angles between the amide N and phenyl and amide C and phenyl are 31° and 25°, respectively (cf. Crystallinity section). [c] Models show that I has a diameter of 4.30 Å while that of CF_3 is 4.90 Å and therefore the choice of 90° for the dihedral angle is justified.

Table VI
Effect of Dihedral Angle on the Repeat Unit Anisotropy of Polymers XI and XIV

dihedral angle,[a] deg	α_X[b]	α_Y	α_Z	$(\alpha_Y + \alpha_Z)/2$	$\Delta\alpha_R$
		Polymer XI			
0	7.555	7.697	3.850	5.774	1.781
c	7.563	5.718	5.820	5.774	1.794
90	7.629	5.775	5.698	5.747	1.892
		Polymer XIV			
0	7.214	6.552	4.010	5.281	1.933
c	7.216	5.279	5.279	5.279	1.937
90	7.215	5.280	5.280	5.280	1.935

[a] Including the dihedral angles between the amide groups and adjacent phenyl rings. [b] The units are 10^{-23} cm^3. [c] Angles from literature sources.

ynes. All other atoms and groups are placed in lateral positions.

Third, lateral substituents contribute to both the longitudinal and the transverse polarizability. The relative magnitude of the contribution made by a substituent to these axes depends not only on its polarizability and the angle of its attachment to the rod axis, but also on the dihedral angle between the group to which it is bonded and neighboring groups.

The effects of the second and third factors are exemplified by the data in Tables V and VI for the halogen series. The longitudinal polarizability of the repeat unit was predictably enhanced by the presence of highly polarizable substituents. Hence, α_X increases in the series from F to I with CF_3 being approximately equal to Cl. Quite unexpectedly, the corresponding values for $\Delta\alpha_R$ do not follow the same trend; in fact, $\Delta\alpha_R$ decreases from F to Br. The value for Br was actually lower than that for H. This is due to the fact that the incremental increase in the transverse polarizability exceeds that in the longitudinal direction. For some unknown reason, the trend reverses itself for I, which exhibits the highest $\Delta\alpha_R$ value in this series.

It was also observed that the calculated repeat unit anisotropy is affected by a change in the dihedral angle between the various groups in the backbone. In several cases an increase in angle results in an increase in anisotropy; polymer XI is a typical example (Table VI). When the dihedral angles between the various groups of this polymer are increased from 0° to 90°, the longitudinal polarizability increases while the transverse polarizabilities simultaneously decrease; the result was an increase in $\Delta\alpha_R$. It was noted that, in general, deviations from 0° change the class of the repeat unit ellipsoid from negative uniaxial to negative biaxial, and, as the dihedral angles approach 90°, the ellipsoid becomes either positive biaxial or positive uniaxial, i.e., $\alpha_Y = \alpha_Z$. The latter corresponds to cylindrical electron distribution about the polymer backbone. Initially, it was theorized that the repeat unit anisotropy and, most importantly, the birefringence might be maximized when a positive uniaxial ellipsoid was generated. Unfortunately, there are several examples, one of which is polymer XIV (Table VI), for which the $\Delta\alpha_R$ values increase and then decrease as the dihedral angles are increased even though both nonzero entries generate a uniaxial ellipsoid. Hence, the relationship between cylindrical electron density, i.e., uniaxiality, and enhanced repeat unit anisotropy can only be partially correlated.

Table VII
Calculated Polarizabilities for Selected Polyamides

polymer[b]	α_X	α_Y	α_Z	$\Delta\alpha_R$
I	7.274	6.069	4.913	1.782
XI	7.563	5.718	5.820	1.794
II	7.119	5.940	4.534	1.881
XIV	7.216	5.280	5.280	1.937

[a] The units are 10^{-23} cm^3. [b] Dihedral angles are given in Table V; dihedral angles for stilbene were 0°.

Table VIII
Comparison of Polarizability and Inherent Birefringence

polymer	$\Delta\alpha_R$[a]	$\Delta\eta_{max}$[b]
I	1.782	1.20
II	1.881	0.98
XI	1.794	0.51
XIV	1.937	0.70
PPD-T	1.033	0.84[c]

[a] The units are 10^{-23} cm^3. [b] Extrapolated from IR dichroism of the carbonyl-amide vs. birefringence data. [c] Using orientation and birefringence data found in the literature.[7,52]

Another instructive result was found when a biphenyl moiety was replaced by a stilbene moiety. It was anticipated that the incorporation of a double bond into the backbone of a polymer parallel to the major axis would enhance the repeat unit polarizability and the birefringence, since the double bond extends the conjugation of the repeat unit, increases the longitudinal polarizability, and contributes very little to the transverse polarizability. Comparison of polymer I with XI and II with XIV (Table VII) shows that the repeat unit polarizability decreases for the stilbene-containing polymers. A comparison of $\Delta\alpha_R$ values and $\Delta\eta_{max}$ values (inherent birefringence) are listed in Table VIII. The inherent birefringence values were obtained by plotting percent orientation, determined by infrared dichroism,[55] of stretched polymer films and their corresponding birefringence values and extrapolated to 100% orientation. According to the repeat unit anisotropies, polymer XIV should have a higher inherent birefringence than polymer XI—this was found to be the case. However, the predicted inherent birefringences for polymers I and II are opposite to that indicated by their polarizability values, and, in addition, the $\Delta\eta_{max}$ values for these two stilbene-containing polymers are higher than the all-biphenyl polymers contrary to the predictions of their respective $\Delta\alpha_R$ values. For comparison purposes the polarizability[56] and inherent birefringence values for poly(*p*-phenyleneterephthalamide) (PPD-T) are also listed. The data show that the $\Delta\alpha_R$ values for the biphenyl- and stilbene-containing polyamides are significantly higher than that for PPD-T; however, the inherent birefringence values for XI and XIV are much lower while those for I and II are much higher. While broad generalities and trends within a homologous series can be identified, precise correlations between repeat unit anisotropy and inherent birefringence are not always possible.

It should be noted that with the exception of one report on polybenzothiazole,[57] the experimental birefringence values (at 80–90% orientation by IR dichroism) for polymers I–III (see Table II) are the highest known for any polymer to date.

Summary

The incorporation of 2,2′-disubstituted biphenylene moieties into rigid-rod polyamides results in colorless (or nearly colorless), transparent, highly birefringent films and fibers. The combination of these properties in the polyamides or any other rigid-rod polymers was previously unreported, and it has made these materials extremely useful for certain optical devices.

Although complete orientation was not attained, the polymers were oriented to such a high degree that any departure from uniaxial optics was not apparent. Work is continuing on attaining higher orientation and also on measuring the 2V angle which in these films exceeds 90°.

The ability to calculate accurately the refractive index and birefringence of these polymers from polarizability data has not yet been accomplished, but many intriguing and instructive results were obtained from this attempt.

From the standpoint of the field in general perhaps the most interesting findings center around the unique solution properties of these materials: high solubility in "common" solvents and lack of lyotropic behavior. Work is continuing in this area on polyamides and is presently being expanded to other polymer classes in order to delineate further the molecular properties upon which these phenomena are based.

Experimental Section

Monomer Synthesis. 2,2′-Bis(trifluoromethyl)-4,4′-dinitro-1,1′-biphenyl[58] (XVIII). Activated copper[59] (45 g) was added to a solution of 50 g of 2-bromo-5-nitrobenzotrifluoride (from Marshallton) in DMF (100 mL) and the mixture was refluxed with stirring for 5 h. It was cooled and poured into excess water, and the brown precipitate was filtered off, washed with water, and dried. Chromatography over silica gel gave XVIII, recrystallized as shiny yellow prisms from ether (25 g, 71%): mp 138–140 °C; IR (KBr) 1620, 1540, 1360, 1300, 1170 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.50 (d, 2 H, J = 2 Hz), 8.40 (dd, 2 H, J1 = 9 Hz, J_2 = 2 Hz), 7.40 (d, 2 H, J = 9 Hz); mass spectrum (70 eV), m/e 380 ($\mathrm{M^+}$), 350 ($\mathrm{M^+ - 2NO_2 - 2CF_2}$).

Anal. Calcd for $\mathrm{C_{14}H_6F_6N_2O_4}$: C, 44.21, H, 1.58; F, 30.0; N, 7.37. Found: C, 44.12; H, 1.79; F, 28.9; N, 7.30.

Filtrates from removal of XVIII gave 2,2′-bis(trifluoromethyl)-4,6′-dinitro-1,1′-biphenyl (XIX) arising from the isomeric contaminant 2-bromo-3-nitrobenzotrifluoride in the starting material. This biphenyl crystallizes as cream-colored needles from ether–hexane (1.3 g, 4%): mp 114–115 °C; IR (KBr) 1620, 1540, 1360, 1300, 1190 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.55 (d, 1 H, J = 2 Hz), 8.45 (dd, 1 H, J_1 = 9 Hz, J_2 = 2 Hz), 8.35 (d, 1 H, J = 9 Hz), 8.10 (d, 1 H, J = 9 Hz), 7.80 (t, 1 H, J_1 = 9 Hz, J_2 = 9 Hz), 7.50 (d, 1 H, J = 9 Hz); mass spectrum (70 eV), m/e 380 ($\mathrm{M^+}$), 350, 334, 288, 238, 188.

Anal. Calcd for $\mathrm{C_{14}H_6F_6N_2O_4}$: C, 44.21; H, 1.58; F, 30.0; N, 7.37. Found: C, 44.13; H, 1.55; F, 31.4; N, 7.18.

2,2′-Bis(trifluoromethyl)benzidine (XX).[58] To a solution of XVIII (1.9 g, 5 mmol) in ethanol (5 mL), stannous chloride dihydrate (8 g) was added; while the mixture was stirred at room temperature, concentrated HCl (12 mL) was added carefully. The mixture was refluxed overnight and ethanol was removed. Water was added to the residue and basified with 20% NaOH. The white precipitate was filtered off, washed with water, dried, and extracted in a Soxhlet with acetone for 4 h. Removal of acetone gave XX as a white residue that could be recrystallized from $\mathrm{CHCl_3}$–hexane as white short needles (1.2 g, 74%): mp 181–182 °C; sublimes 120–130 °C (at 0.0012 mm; IR (KBr) 3450, 3350, 1640, 1490, 1330 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 6.85 (d, 2 H, J = 2 Hz), 6.75 (d, 2 H, J = 9 Hz), 6.70 (dd, 2 H, J_1 = 9, J_2 = 2 Hz); mass spectrum (70 eV), m/e 320 ($\mathrm{M^+}$).

Anal. Calcd for $\mathrm{C_{14}H_{10}F_6N_2}$: C, 52.50; H, 2.63; F, 35.6; N, 8.75. Found: C, 52.74; H, 3.23; F, 35.0; N, 8.67.

2,2′-Bis(trifluoromethyl)-4,4′-diiodobiphenyl (XXI). Ten grams of 2,2′-bis(trifluoromethyl)benzidine (31.2 mmol) was dissolved in water (100 mL) and concentrated sulfuric acid (60 mL) and the solution was cooled to 0 °C. A solution of sodium nitrite (4.5 g; 65.2 mmol) in water (10 mL) was added dropwise with stirring. The resulting cold tetrazonium salt solution was added slowly to a stirred solution of sodium iodide (20 g) and iodine (20 g) in water (20 mL) maintained at a temperature of 0 °C. During the addition, methylene dichloride was added to keep the product in solution. After the mixture was stirred overnight at room temperature, excess iodine was destroyed by adding sodium bisulfite and the product was extracted with methylene dichloride. The organic phase was washed with aqueous sodium bisulfite, dried, and evaporated to yield 13.3 g (78%) of product i.e., 2,2′-bis(trifluoromethyl)-4,4′-diiodobiphenyl, having a melting point of 119–122 °C. Recrystallization from methanol yielded white prisms having a melting point of 121–123 °C: IR (KBr) 1470, 1400, 1300, 1180, 1130 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 6.98 (d, 2 H, J = 8 Hz), 7.87 (dd, 2 H, J = 8 Hz, 2 Hz), 8.07 (d, 2 H, J = 2 Hz); mass spectrum (70 eV), m/e 542 ($\mathrm{M^+}$), 415 ($\mathrm{M^+}$ – I), 288 ($\mathrm{M^+}$ – 2I), 271 ($\mathrm{I - Ph - CF_3)^{+\cdot}}$, 238 ($\mathrm{M^+}$ – 2I – 2CF), 221 ($\mathrm{I - Ph - F)^{+\cdot}}$.

Anal. Calcd for $\mathrm{C_{14}H_6F_6I_2}$: C, 31.02; H, 1.12; F, 21.03; I, 46.83. Found: C, 31.03; H, 0.93; F, 20.13; I, 47.71.

Dimethyl 2,2′-Bis(trifluoromethyl)-4,4′-biphenyldicarboxylate (XXIII). 2,2′-Bis(trifluoromethyl)-4,4′-diiodobiphenyl (7 g, 12.9 mmol), 183 mg (0.26 mmol) of dichlorobis(triphenylphosphine)palladium(II), 5.5 mL (39 mmol) of triethylamine, and 65 mL of methanol were stirred at 55 °C under 1 atm of carbon monoxide for 18 h. The solvent was evaporated and the residue was dissolved in hexane, treated with Norit (activated carbon), and filtered in a Soxhlet extractor. Flash chromatography of the filtrate over silica gel with methylene dichloride/hexane (1:1 by volume) yielded an amber oil which was crystallized from methanol at –60 °C to yield 3.8 g (73%) of white product having a melt point of 71–72 °C: IR (KBr) 1730 $\mathrm{cm^{-1}}$; UV ($\mathrm{CH_2Cl_2}$) $\lambda_{\max}$ 281 nm, (ϵ 3880), 273 (4280), 238 (29400); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 4.00 (s, 6 H), 7.36 (d, 2 H, J = 8 Hz), 8.21 (dd, 2 H, J = 8 Hz, 2 Hz), 8.42 (d, 2 H, J = 2 Hz); mass spectrum (70 eV), m/e 406 ($\mathrm{M^+}$), 375 ($\mathrm{M^+ - OCH_3}$).

Anal. Calcd for $\mathrm{C_{18}H_{12}F_6O_4}$: C, 53.21; H, 2.98; F, 28.06. Found: C, 53.10; H, 2.74; F, 27.98.

2,2′-Bis(trifluoromethyl)-4,4′-biphenyldicarboxylic Acid (XXIII). Two grams (4.9 mmol) of dimethyl 2,2′-bis(trifluoromethyl)-4,4′-biphenyldicarboxylate was dissolved in 20 mL of methanol and 4 mL of 50 wt % aqueous sodium hydroxide. The solution was heated to boiling with stirring and 100 mL of water was added over a 1-h period to maintain a clear solution as methanol was distilled off. When the vapor temperature reached 99 °C, the solution was cooled and acidified with concentrated hydrochloric acid to yield a course precipitate which was filtered, washed with water, and dried. The product, obtained in an amount of 1.77 g (95%), had a melting point greater than 300 °C: IR (kBr) 1702 $\mathrm{cm^{-1}}$; ^{1}H NMR $\mathrm{(CD_3)_2CO}$ δ 7.62 (d, 2 H, J = 8 Hz), 8.37 (dd, 2 H, J = 8 Hz, 2 Hz), 8.47 (d, 2 H, J = 2 Hz), 8.5 (broad, 2 H).

2,2′-Bis(trifluoromethyl)-4,4′-biphenyldicarbonyl Chloride (XXIV). A reaction mixture composed of 2.5 g (6.6 mol) of 2,2′-bis(trifluoromethyl)-4,4′-biphenyldicarboxylic acid, 30 mL of thionyl chloride, and 1 drop of dimethylformamide was stirred under reflux for 4 h. Excess thionyl chloride was then distilled off and the residual oil was dissolved in pentane, filtered, and blown dry with nitrogen to effect crystallization of the product. Drying in vacuo provided 2.6 g (95%) of product exhibiting a melting point of 52–54 °C. Molecular distillation at 80–100 °C (5 μm) provided white crystals (2.3 g, 84%) exhibiting a melting point of 55–56 °C: IR ($\mathrm{CCl_4}$) 1760 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CCl_4}$) δ 7.39 (d, 2 H, J = 8 Hz), 8.27 (dd, 2 H, J = 8 Hz, 2 Hz), 8.44 (d, 2 H, J = 2 Hz); mass spectrum (70 eV), m/e 414 ($\mathrm{M^+}$), 379 ($\mathrm{M^+ - Cl}$).

Anal. Calcd for $C_{16}H_6Cl_2F_6O_2$: C, 46.29; H, 1.46; Cl, 17.08; F, 27.46. Found: C, 46.24; H, 1.82; Cl, 17.17; F, 27.39.

2,2′-Dibromo-4,4′-dinitrobiphenyl[60,61] **(XXV).** To a four-neck 2-L round-bottom flask equipped with a mechanical stirrer, a pressure-equalizing dropping funnel (with a needle-valve stopcock), a thermometer, and a Dewar condenser (filled with ice–salt), containing 1 L of concentrated H_2SO_4, was added 76.67 g (314 mmol) of 4,4′-dinitrobiphenyl while stirring vigorously. After the latter was dispersed, the temperature was lowered to 0 °C and 293.7 g (942.1 mmol) of Ag_2SO_4 was added to the reaction vessel. While the temperature was carefully maintained at 0 °C, Br_2 (117 g, 731 mmol, 17% excess) was added at the rate of 1 drop/s; after the final addition of Br_2, cooling and stirring were continued for 6 h. The ice bath was removed and the reaction was stirred overnight at room temperature. The mixture was filtered by means of a sintered glass funnel; the solid was washed thoroughly in the funnel with concentrated H_2SO_4, and the washings were combined and poured onto crushed ice whereupon a light yellow precipitate formed. The solid was filtered, washed with water, and dissolved in THF. The THF solution was washed with saturated aqueous NaCl and dried with Na_2SO_4; evaporation of the solvent gave an orange oil (106.6 g, 84% crude yield). Column chromatography (dry column), using 2:1 benzene/hexane as eluant, separated three materials, 72% of which was the desired product (XXV). One recrystallization from methanol yielded a pale yellow crystalline solid: mp 129–130 °C (lit.[61] mp 126 °C); IR (KBr) 1535, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.45 (2 H, d, J = 2 Hz), 8.18 (2 H, dd, J = 9 Hz, J_2 = 2 Hz), 7.30 (2 H, d, J = 9 Hz); mass spectrum (70 eV), m/e 402, (M^+ – NO), 356 ($M^+ - NO_2$), 320 (M^+ – Br), 150 ($M^+ - 2NO_2$ – 2Br).

Anal. Calcd for $C_{12}H_6Br_2N_2O_4$: C, 35.85; H, 1.50; Br, 39.75; N, 6.97. Found: C, 35.81; H, 1.49; Br, 40.79; N, 6.91.

2,2′-Dibromo-4,4′-diaminobiphenyl[62] **(XXVI).** To a 1-L, three-necked round-bottom flask, equipped with a mechanical stirrer, a reflux condenser, and a thermometer was added at 25 °C 68 g (168 mmol) of 2,2′-dibromo-4,4′-dinitrobiphenyl and 379.77 g (1.68 mol) of stannous chloride. The mixture was stirred and 400 mL of concentrated HCl was slowly added. The temperature was raised to 100 °C and was maintained at this temperature for 6 h. The temperature was then lowered to 40 °C and the reaction mixture poured into 600 mL of ice water. The solution was neutralized with NaOH and at pH 7 a white, finely divided precipitate appears. The solid was filtered and washed thoroughly with ethyl acetate in order to remove the product from the tin salts. The ethyl acetate extract was washed with saturated NaCl (aq) and dried with Na_2SO_4. After the solvent was stripped, 55.37 g (96% crude yield) of an off-white powder (XXVI) was obtained. One recrystallization from ethanol–H_2O yielded 47.73 g (83.1%) of a white microcrystalline solid: mp 152–156 °C (lit. mp 150–151.5 °C); sublimes 140 °C/30 μm; IR (KBr), 3420, 3320, 1630, 1610 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 8.90 (4 H, broad s), 7.80 (2 H, s), 7.50 (2 H, d, J = 9 Hz), 7.40 (2 H, d, J = 9 Hz); ^{13}C NMR 148.9 (C-4), 131.8 (C-6), 129.0 (C-1), 124.0 (C-2), 116.5 (C-3), 112.8 (C-5) ppm; mass spectrum (70 eV), m/e 344 (M^+), 182 (M^+ – 2Br).

Anal. Calcd for $C_{12}H_{10}Br_2N$: C, 42.13; H, 2.95; Br, 46.73; N, 8.15. Found: C, 42.16; H, 2.90; Br, 46.63; N, 8.14.

2,2′-Dibromo-4,4′-biphenyldicarbonyl Chloride (XXVII). The bromination of 4,4′-dicarbomethoxy-1,1′-biphenyl (described in ref 60) followed by column chromatography and acidic hydrolysis was the procedure used to generate 2,2′-dibromo-4,4′-biphenyldicarboxylic acid.

A reaction mixture composed of 3.50 g (14.7 mmo) of 2,2′-dibromo-4,4′-biphenyldicarboxylic acid and 50 mL of thionyl chloride (no DMF) was stirred and refluxed for 18 h. The excess thionyl chloride was distilled off and the viscous residual oil was recrystallized by using hexane, yielding 3.20 g (91%) of white crystals exhibiting a melting point of 88–90 °C: IR (KBr) 1750 cm^{-1}; ^{1}H NMR (CCl_4) δ 8.30 (2, H, d, J = 2 Hz), 8.15 (2 H, dd, J = 8 and 2 Hz), 7.55 (2 H, d, J = 8 Hz); mass spectrum (70 eV), m/e 400 (M^+).

Anal. Calcd for $C_{14}H_6Br_2Cl_2O_2$: C, 38.48; H, 1.38; Br, 36.58; Cl, 16.23. Found: C, 38.43; H, 1.32; Br, 36.74; Cl, 16.12.

2,2′-Dinitro-4,4′-biphenyldicarbonyl Chloride (XXVIII). The Ullmann coupling of methyl 4-iodo-3-nitrobenzoate[22,63] followed by hydrolysis yielded 2,2′-dinitro-4,4′-biphenyldicarboxylic acid.

A reaction mixture composed of 10.0 g (31.0 mmol) of the diacid, 100 mL of thionyl chloride, and 1 mL of DMF was stirred and refluxed for 18 h. The excess thionyl chloride was distilled off. The residual oil was recrystallized once each from CCl_4 and THF/hexane; the yield of colorless, needlelike clusters was 8.23 g (72% yield): mp 111–112 °C; IR (KBr) 1750 cm^{-1}; ^{1}H NMR nMe_2SO-d_6) δ 8.78 (2 H, s), 8.4 (2 H, d, J = 8 Hz), 7.7 (2 H, d, J = 8 Hz).

Anal. Calcd for $C_{14}H_6Cl_2N_2O_6$: C, 45.55; H, 1.64; Cl, 19.21; N, 7.59; O, 26.00. Found: C, 45.70; H, 1.60; Cl, 19.44; N, 7.47.

2,2′-Dinitrobenzidine (XXIX). 2,2′-Dinitro-4,4′-biphenyldicarbonyl chloride (XXVIII) was converted to 2,2′-dinitro-4,4′-biphenyldicarbonylazide in 78% yield by treatment of the former with freshly activated sodium azide. The dicarbonylazide was rearranged with acetic anhydride in concentrated sulfuric acid to 4,4′-diacetamido-2,2′-dinitrobiphenyl in 37% yield.

A reaction mixture composed of 15.0 g (41.9 mmol) of 4,4′-diacetamido-2,2′-dinitrobiphenyl acid in 90 mL of 50% aqueous sulfuric acid was stirred and refluxed for 4 h whereupon gas evolution ceased. The reaction mixture was poured onto crushed ice; the resulting yellow precipitate was dissolved in THF. The THF solution was washed with aqueous base and saturated NaCl and dried. The solution was filtered through a neutral alumina column (activity grade III). By removing the solvent and recrystallizing from ethanol, we obtained 5.20 g (45% yield) of the product (XXIX): mp 210–217 °C with decomposition to a red oil; IR (KBr) 3400, 1615 cm^{-1}; mass spectrum (70 eV), m/e 274 (M^+); UV/vis (95% ethanol) λ 245 nm (ϵ 35 800), 375 (3200).

Anal. Calcd for $C_{12}H_{10}N_4O_4$: C, 52.56; H, 368; N, 20.43; O, 23.34. Found: C, 57.75; H, 3.72; N, 20.37.

2,2′-Dimethoxy-4,4′-biphenyldicarbonyl Chloride (XXX). 2,2′-Dimethoxy-4,4′-biphenyldicarboxylic acid was obtained from hydrolysis of the dimethyl ester[64] with NaOH/ethanol.

The diacid (1.5 g, 5 mmol), thionyl chloride (25 mL), and DMF (5 drops) were stirred and refluxed for 1 h. Removal of the excess thionyl chloride and DMF in vacuo resulted in a pale-yellow, oily solid; two recrystallizations from THF gave 1.60 g (95% yield) of white, needlelike clusters: mp 212–213 °C; IR (KBr) 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$ and Me_2SO-d_6) δ 7.40–7.55 (4 H, m); 7.10 (2 H, d, J = 8 Hz), 3.70 (6 H, s); mass spectrum (70 eV), m/e 339 (M^+), 304 (M^+ – Cl), 213 (M^+ – 2COCl).

Anal. Calcd for $C_{16}H_{12}Cl_2O_2$: C, 56.63; H, 3.54; Cl = 20.94. Found: C, 56.63; H = 3.86; Cl = 21.63.

4,4′-Biphenyldicarbonyl Chloride (XXXI). The synthesis of XXXI from the diacid as described in ref 65 regenerated mixtures which were difficult to separate and gave much lower yields than reported.

In the preferred procedure[66] 4.19 g (17.3 mmol) of the diacid 10.8 g (51.9 mmol) of PCl_5 and 25 mL of toluene were stirred and refluxed for $2^1/_2$ h. The solution was cooled to room temperature and filtered, and then the $POCl_3$ and toluene were removed by vacuum distillation. The pale-yellow residue was recrystallized from hexane/THF and then THF. The yield of light-beige needles was 2.75 (55.8%): mp 187–189 °C (lit. mp[65] 184 °C); IR (KBr) 1780 cm^{-1}; mass spectrum (70 eV), m/e 279 (M^+).

Anal. Calcd for $C_{14}H_8Cl_2O_2$: C, 60.25; H, 2.87; Cl, 25.41. Found: C, 60.40; H, 2.94; Cl, 25.70.

4,4′-Stilbenedicarbonyl Chloride (XXXII). A mixture containing 200 g (748 mmol) of stilbenedicarboxylic acid, 1.8 L of thionyl chloride, and 7 mL of DMF was stirred and refluxed for 48 h. The green mixture was cooled to room temperature and filtered; the solid was washed thoroughly with anhydrous ether and dried in a vacuum oven for 2 h at 110 °C. The greenish-gold, needlelike crystals weighed 177 g (61.3%) and were used for polymerization witout further purification.

The product (XXXII) could be recrystallized from a large volume of anhydrous THF which generated dark yellow needles: mp 239–240 °C; IR (KBr) 1750 cm^{-1}; ^{1}H NMR (THF) δ 8.08 (4 H, d, J = 8 Hz), 7.83 (4 H, d, J = 8 Hz), 7.50 (2 H, s); UV (p-dioxane) λ 347 (ϵ 54 800), 365 (39 200); mass spectrum (70 eV), m/e 305 (M^+).

Anal. Calcd for $C_{16}H_{10}Cl_2O_2$: C, 62.98; H, 3.30; Cl, 23.24; O, 10.49. Found: C, 62.83; H, 3.21; Cl, 23.33.

α,α'-Dimethylmuconyl Chloride (XXXIII). A mixture containing 116 g (555 mmol) of PCl_5 and 100 mL of $POCl_3$ was stirred at 65–70 °C for 10 min, and then 45 g (264 mmol) of muconic acid followed by 20 mL of $POCl_3$ was added cautiously. As the reaction progressed a vigorous exotherm occurred which necessitated cooling. After about 2 h, $POCl_3$ was vacuum distilled (aspirator) and the residue was recrystallized from hexane. The white rhombic crystals weighed 49.20 g (90.0% yield): mp 76.5–77.7 °C; IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90 (2 H, s), 2.10 (6 H, s); mass spectrum (70 eV), m/e 207 (M^+).

Anal. Calcd for $C_8H_8Cl_2O_2$: C, 46.41; H, 3.89; Cl, 34.24; O, 15.45. Found: C, 46.54, H, 3.89; Cl, 34.15.

2,2′-Dichloro-5,5′-dimethoxybenzidine (XXXIV). This compound was purchased from Eastman Chemicals and was purified by recrystallization from THF/hexane and then sublimed. The small white crystals melted at 182–4 °C; IR (KBr) 3400, 1610 cm^{-1}; mass spectrum (70 eV), m/e 313 (M^+).

Anal. Calcd for $C_{14}H_{14}Cl_2N_2O_2$: C, 56.69; H, 4.51; Cl, 22.64; N, 8.95; O, 10.22. Found: C, 56.75; H, 4.55; Cl, 22.90; N, 8.81.

Polymer Synthesis. The procedure for the best studied polymer is given below and is representative of that used for all of the polymers listed in the table.

Poly[2,2′-bis(trifluoromethyl)-4,4′-biphenylene-*trans*-*p*,*p*′-stilbenedicarboxamide]. Anhydrous NMP and TMU were obtained by first fractionally distilling at atmospheric pressure (N_2), and then distilling from CaH_2 (N_2) just prior to use.

A 100-mL resin kettle equipped with a mechanical stirrer, a nitrogen inlet tube, a calcium chloride drying tube, and 1.5 g of lithium chloride was flamed with a Bunsen burner and simultaneously flushed with nitrogen. After the reaction vessel had cooled to room temperature, 0.517 g (1.615 mmol) of recrystallized 2,2′-bis(trifluoromethyl)benzidine was added while maintaining a positive nitrogen pressure. A thermometer and a rubber stopper were put in place and 10 mL of anhydrous, distilled *N*-methylpyrrolidone (NMP) and 10 mL of anhydrous, distilled tetramethylurea (TMU) were carefully added to the vessel by means of syringes. The mixture was stirred and warmed to 40 °C until all the solids dissolved. When the solution was cooled to −5 °C with an ice–salt bath, a small amount of lithium chloride precipitated. Recrystallized *trans-p*,*p*′-stilbenedicarbonyl chloride (0.4923 g, 1.615 mmol) was added through a funnel to the stirred benzidine solution as quickly as possible. An additional 10 mL of TMU (T = 0 °C) was added to the reaction mixture through the funnel. The temperature of the reaction mixture did not rise above +5 °C and then fell rapidly to −3 °C. After the solution was stirred for 30 min, it began to thicken, and streaming birefringence (but not stir opalescence) was observed. Stirring was continued for an additional 30 min at 0 °C. The ice bath was removed, and when the temperature reached 15 °C (30 min), the solution was very viscous. Over the next 75 min, the completely colorless, transparent solution was warmed to 72 °C. After being stirred at this temperature for the next 18 h, the mixture was cooled to 40 °C. It was then poured into 200 mL of ice water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water, acetone, and ether; it was dried in a vacuum oven at 15 mm pressure and 90 °C for 18 h. The product obtained (in 99.5% yield) was a very light-yellow fibrous solid. The inherent viscosity of the polymer dissolved in 5% lithium chloride/dimethylacetamide at 30 °C was 4.735 dL/g. The polymer was synthesized 9 times at the 35-g scale by using this procedure. The inherent viscosity of these batches ranged from 6.239 to 9.80 dL/g. The molecular structure was confirmed by infrared spectroscopy of polymer films. Ultraviolet/visible spectroscopy in 5% LiCl/DMAc exhibited a peak at 350 nm with a shoulder at 366 nm.

Anal. Calcd for $C_{30}H_{18}F_6N_2O_2$: C, 65.22; H, 3.28; F, 20.64; N, 5.07. Found: C, 64.54; H, 3.00; F, 20.25; N, 5.22. Thermogravimetric analysis showed that the onset of degradation in nitrogen occurred at 500 °C and in air at 410 °C. Differential scanning calorimetry detected a reproducible transition at approximately 185 °C.

Films of this material were prepared by casting solutions onto glass plates; the solvent used was dimethylacetamide containing 5% LiCl (w/v). The concentration of polymer ranged from 1.0% to 5% (w/v). In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water before significant evaporation of solvent had occurred. The polymer film was observed to gel and a transparent, colorless unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone, and dried in a vacuum oven at 90 °C and 15 mm pressure. Refractive index, measured by interferometry and Brewster angle, was 1.997 and 1.897, respectively.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were stretched in acetone and then in air at 220 °C to about 60–65% elongation. The stretched films were optically transparent. Typical bifringence, measured with the aid of a quartz wedge, was 0.54.

Solutions of the polymer in lithium chloride/dimethylacetamide were also formed into films by the "wet-jet" method whereby the polymer solution was extruded into an aqueous coagulation bath for gelling of the polymer material. The resulting transparent, colorless film strips were soaked in water and cut to about 1–2 in. for testing. The partially oriented strips of film produced by the extrusion were further oriented by stretching in the manner described above. Stretching was carried out to an elongation of less than 20%. The stretched strips were optically transparent. Infrared dichroism indicated that the films were 85–90% oriented. Measurement of birefringence by means of a quartz wedge provided a birefringence value of 0.879. Several other highly oriented films gave birefringence values ranging from 0.750 to 0.801 (when measured by the Brewster angle technique).

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