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HIGH REFRACTIVE INDEX POLYMERS

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ABSTRACT

Rodlike polymers with repeat units composed of groups with high π -electron density directly on the backbone, such as linearly conjugated double bonds and aromatic heterocyclic rings, exhibit high isotropic refractive indexes and high birefringence values when oriented. Typical polyamide birefringence values for oriented films far exceed 0.5 and several are as high as 0.85; the corresponding parallel and perpendicular indexes for these polymers are in the 2.2–2.4 and 1.5–1.7 range, respectively, depending on the molecular structure and degree of orientation. The isotropic index values may be as high as 1.8–2.0.

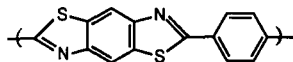
In order to make optical devices utilizing these highly birefringent films, it is frequently necessary to bond them to films or glass, which necessitates the use of index-matching, optical-quality bonding agents. We devised two synthetic strategies to obtain polymers that exhibit these properties. In one approach, we synthesized a series of colorless, nonbirefringent, polyacrylates (and methacrylates) containing halogenated carbazole rings; these results will be reported in a forthcoming paper that is currently being prepared. We have also modified rodlike polyamides by substituting index-enhancing groups directly on the amide nitrogen; the refractive index values of the resulting materials are in the 1.60–1.67 range. The most important finding of the latter research was the realization that rodlike polyamides not only exhibit unusually high bire-

fringence, but also greatly enhanced isotropic refractive indexes, which is directly related to their rodlike conformation.

INTRODUCTION

In a series of papers spanning the last several years [1-4], we have reported the development of melt or solution-processable, rodlike polymers which have a unique combination of properties. The optical properties of these polymers, for example, are particularly unusual in that they are colorless, noncrystalline, and hence nonscattering. The latter attributes, when combined with high refractive index and, in oriented films and fibers, high birefringence, make them very useful in certain optical applications.

Wholly aromatic, rodlike polymers having high molecular polarizability can be formed into oriented, highly birefringent fibers and films. The optical anisotropy of these polymers is related not only to their rodlike geometry, but also to the concentration of highly polarizable, π -electrons located directly on the backbone. Aromatic rings contain polarizable



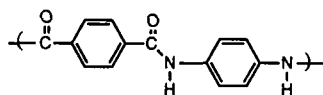
Polybenzthiazole [PBT]

$$\Delta n = 1.09$$

$$n_{\parallel} = 2.6$$

$$n_{\perp} = 1.5$$

highly crystalline, yellow-orange



Poly(p-phenylene)terephthalamide

$$\Delta n = 0.80$$

$$n_{\parallel} = 2.50$$

$$n_{\perp} = 1.65$$

highly crystalline, yellow

FIG. 1. Optical data for two rodlike polymers.

electrons and in rodlike polymers are typically joined by functional groups such as amides, thiazole, or oxazole rings (Fig. 1). Unfortunately, these functional groups enhance multirepeat unit conjugation, which causes color due to absorption of visible radiation. In addition, films of these polymers are characteristically semicrystalline, which causes scattering, poor solubility, and very high, or nonexistent, processing temperatures. The occurrence of any one of these properties severely limits the use of these materials in optical applications.

During the course of our research, we developed three types of rodlike or semirodlike polymers, e.g., polyamides [1, 2], polyesteramides [3], and polyesters [4], which contain the combination of properties alluded to above, thus making them particularly suitable for optical applications. The common molecular feature of all these polymers is the presence of some level of a 2,2'-disubstituted biphenylene comonomer. Substitution of the 2,2'-positions forces the rings into a noncoplanar conformation resulting in asymmetry, e.g., atropism. If the substituents are large enough, or if all four ortho positions are substituted with groups as small as methoxy and fluorine [5], the enantiomers may be resolved and characterized. We used a fairly wide variety of substituents during this investigation, such as the halogen, nitro, alkoxy, and fluorocarbon groups. The molecular structures of several examples of these polyamides are given in Fig. 2; Table 1 contains relevant data for six of these polymers. Figure 3 lists a variety of data for the best characterized of our polyamides.

Although all the substituted, biphenylene-containing polymers exhibit noncrystalline morphology and significantly enhanced solubility, the substituent that imparts the most dramatic effect on these properties is the trifluoromethyl group. For example, a direct comparison of solubilities of a bromo- or methoxy-substituted polyamide with the analogous trifluoromethyl substituted polymer reveals a significant improvement for the latter (Table 2). Similar results are realized for polyester solubilities, and additionally, a significant decrease of the glass-to-nematic phase transition temperatures is also obtained.

In regard to refractive index, the fluorine atom, and hence the trifluoromethyl group, imparts significantly lower polarizability to the polymer than the bromine atom as generally evidenced in the isotropic refractive index of the corresponding polymers (Table 1). Experimental birefringence values also reflect this difference albeit to a lesser extent. Caution must be exercised in making this comparison, however, due to the difficulty encountered in measuring refractive indexes above about 1.80. Standard microscope techniques such as Becke line analysis and

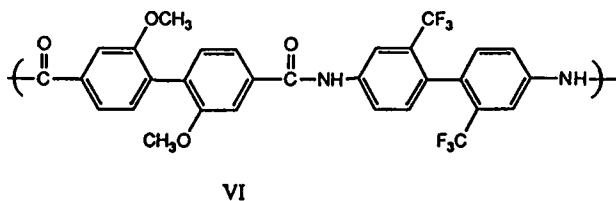
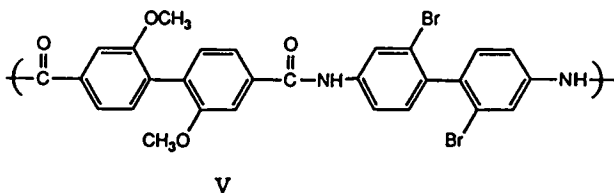
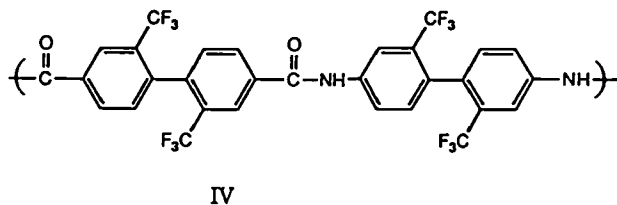
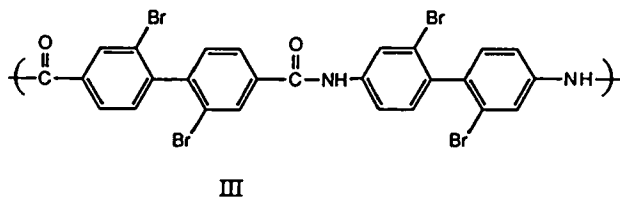
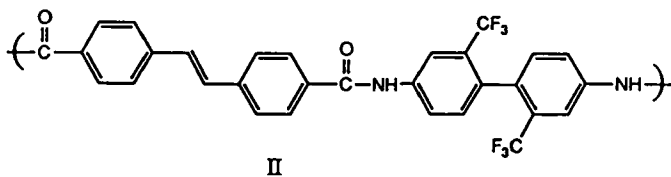
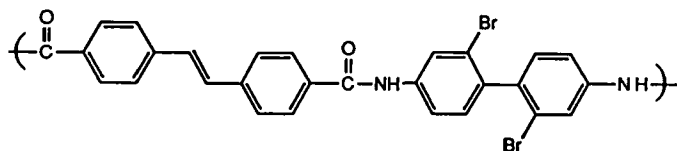


FIG. 2. Polyamide structures referred to in text.

TABLE 1. Physical and Optical Properties of Aromatic Polyamides

Polymer	η_{INH}^a	$T_g(^{\circ}\text{C})^{b,c}$	$\lambda_{\text{max}}(\text{nm})^c$	η_{iso}	$\Delta\eta_{\text{max}}$
I	9.04	225 ^b	350 (62,800) light yellow	2.05 ^g	0.865 ^g
II	9.80	185 ^b 290 ^c	350 (76,000) light yellow	1.89 ^f	0.801 ^f
III	2.04	120 ^c	305 (31,900)	1.84 ^g	0.48 ^g
IV	5.74	^d	290 (54,800)	1.57 ^f	0.13 ^f
V	4.16	188 ^b	Colorless	1.89 ^g	0.58 ^h
VI	3.77	180 ^b	315(25,880)	1.69 ^g	0.58 ^h

^a0.5 g of polymer/5%LiCl/DMAc at 30°C.

^bDSC.

^cTMA.

^dNot detectable.

^eSolvent: 5% LiCl/DMAc.

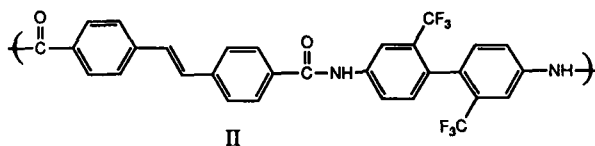
^fBrewster angle (at 633 nm).

^gJamin-Lebedeff interferometry (at 589 nm).

^hQuartz-wedge compensator (at 589 nm).

index matching which require immersion oils are completely inadequate due to the fact that high index oils cause the polymer films to swell, and the highest refractive index oil obtainable has a $\eta_D = 2.1$, which greatly limits the utility of this technique. An interference technique, i.e., Jamin-Lebedeff interferometry, is much more reliable but somewhat subjective at very high retardation values, i.e., high refraction values. Our preferred method is the purely optical Brewster angle technique, which can be used with good precision after making an incident angle correction. However, we have not been able to develop a second reliable technique to check the results.

It is intuitively obvious that high refraction should be inherent in structures that possess a high concentration of polarizable electrons on the backbone of the polymer. Any substituents placed perpendicular to the backbone contribute to the transverse polarizability and the perpendicular refractive index which will lower the birefringence. Extending this reasoning beyond the individual repeat unit leads to the realization that flexible chains likewise contribute to transverse polarizability which accounts for the extremely high parallel refractive index values and high



$$\eta_{\text{INH}} = 9.80$$

$$[\eta] = 12.75$$

$$[\eta] = 4.8 \times 10^{-5} \text{M}^{1.3}$$

$$M_w = 49,500; M_n = 26,500$$

$$\text{Persistence Length} = 200 - 300 \text{ \AA}$$

$$T_g = 185^\circ\text{C (DSC)}; 290^\circ\text{C (TMA)}$$

Solubility : amide solvents : DMAc, etc., w/o LiCl

Solutions : nonlyotropic

Morphology : noncrystalline

$$\Delta n_{\text{max}} = 0.801$$

$$n_{\text{iso}} = 1.89; n_{\parallel} = 2.4; n_{\perp} = 1.6$$

$$\lambda = 350 \text{ nm (76 000)}$$

pale yellow

FIG. 3. Optical and physical data for polymer II.

TABLE 2. Solubility of Substituted, Biphenylene Polyamides

Polymer ^a	Solvents ^b
I, III, V	LiCl/DMAc, LiCl/TMU LiCl/NMP, strong acids
II	TMU w/o LiCl
IV, VI	"Common" solvents – THF, acetone, methoxyethanol

^aFor inherent viscosities and additional data, see Ref. [1].

^bSolvents were dried over molecular sieves before testing.

birefringence typically exhibited by rodlike polymers. For example, polybenzthiazole (PBT), which is one of the most rodlike of the synthetic polymers (persistence length = 640 Å [6], has a parallel index equal to 2.60 and a birefringence of 1.09, the highest of any polymer reported to date [7]. Polymers I and II, which are among the most polarizable of the polyamides due to the incorporation of a double bond in the backbone parallel to its long axis, gave the largest parallel indexes (~ 2.4) and the largest extrapolated maximum birefringence and experimental birefringence values, $\Delta\eta = 0.865$ and 0.801 , respectively. The lower refraction values of these polymers compared to the PBT type reflect a decrease in persistence length of the polyamides (200–300 Å range [1] and Fig. 3). An additional decrease in refraction is observed for the thermotropic polyesters, reflecting their lower persistence length (~ 100 Å [8]).

As an aid to design and synthesis, we also attempted to calculate bulk refractive indexes, and ultimately birefringence, of potentially useful polymers from group and atom polarizability values. Unfortunately, clear trends relating molecular structure to refraction were not obtained, which reflects the inadequacy of equations relating molecular parameters to bulk reaction. Several modifications to the fundamental Lorentz-Lorenz equation may be found in the literature which give fairly close correlations between calculated and experimental refraction values for small molecules and for simple polymers such as polyethylene. However, these modifications are not accurate for the calculation of birefringence of rodlike polymers. The major shortcoming of the modified L-L theories is their inability to account for intermolecular interactions [9]. In fact, even trends in polarizability are counterintuitive. For example, the incorporation of a double bond into the backbone of a polymer parallel to the major axis should enhance repeat unit polarizability and birefringence, since the double bond extends the conjugation of the repeat unit, increases the longitudinal polarizability, and contributes very little to the transverse polarizability. However, comparison of polymer I with III or II with IV (Table 3) shows that the calculated repeat unit polarizability ($\Delta\alpha_R$) is lower for the stilbene-containing polymers. Inherent birefringence values ($\Delta\eta_{\max}$) track with the anticipated trend but not with the calculated polarizabilities.

To further emphasize the importance of rodlike conformation on refraction, we should mention the effect of incorporation of substituents, even those which are highly polarizable, on the amide nitrogen.

One of the strategies developed for the attainment of polymers exhibiting high isotropic refractive index required the modification of the

TABLE 3. 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
III	1.794	0.51
IV	1.937	0.70

^aThe units are 10^{-23} cm^3 .

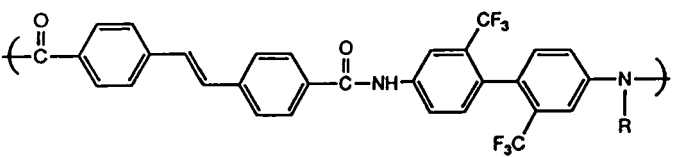
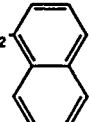
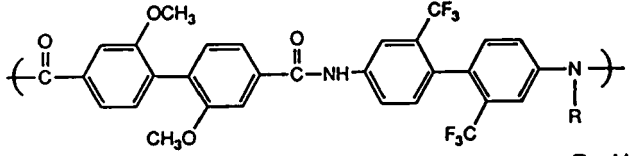
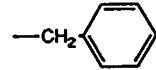
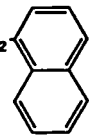
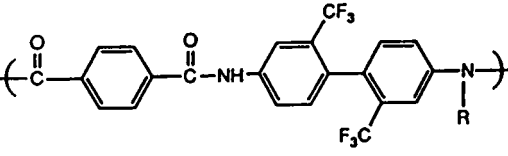
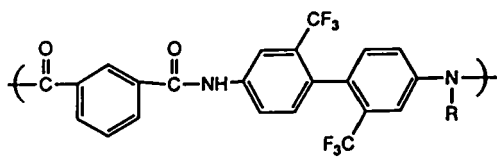
^bExtrapolated from IR dichroism using the carbonyl-amide vibrational tensor vs. experimental birefringence data.

highly birefringent polyamides described above. Polymer (I) was chosen as the starting material due to the fact that it has a very high isotropic index (Fig. 3). Since the literature indicates that N-substitution significantly lowers the persistence length of polyamides to 60–70 Å [11], it was anticipated that substitution would increase solubility and, depending on the nature of the substituents, might generate polyamides that exhibit melting points.

Table 4 lists the isotropic refraction values for several unsubstituted polyamides along with several examples of 50% N-substituted polymers. Benzyl and naphthylmethylene groups were chosen as the substituents because of their high polarizability and synthetic utility [11]. Quite surprisingly, the placement of a naphthylmethylene group lowered the refractive index from 1.89 to 1.67. A similar result was obtained when the benzyl or naphthylmethylene group was substituted in polymer VI. In this example the index decreases from 1.68 to 1.60 for the former substituent but only decreases to 1.67 for the latter. The refraction values for the substituted versions of polymer VI reflect the index-enhancing capability of the naphthalene ring relative to the phenyl ring, but the general decrease in index for both polymers I and VI upon substitution is very likely due to a significant change in conformation. In other words, the conversion from a rodlike (200–300 Å persistence length) to a nonrodlike conformation (60–70 Å) drastically lowers the index of refraction, which must reflect a decrease in molecular polarizability.

Additional support for this hypothesis was obtained from the data shown for the last three entries of Table 4. The unsubstituted, rodlike

TABLE 4. Isotropic Refractive Index Values for Selected Polyamides

		n_{Iso}	
		50% SUBST	
 <p style="text-align: center;">II</p>	R = H	1.89	
		R = 	1.67
 <p style="text-align: center;">VI</p>	R = H	1.68	
		R = 	1.60
		R = 	1.67
	R = H	1.76	
	R = H	1.60	
	R = CH ₃	1.57	

polymer has an index of 1.76. However, the use of isophthalic acid instead of terephthalic acid in the polymer generates a nonrodlike polyamide which exhibits an index of 1.60. N-substitution of the latter lowers the index even further.

Although the refractive index values of the substituted polyamides are quite high, they were still disappointing since index values in the 1.8 region had been anticipated, and the desired melting properties were not realized. At this point we directed our research to the polyacrylates which contain halogenated carbazoles; these results will be reported in another paper currently being prepared.

One of the simplest optical devices for which both birefringent films and index-matching, nonbirefringent, melttable polymers would find utility is the polarizing beam splitter (Figs. 4 and 5). Figure 4 is a schematic representation of such a device made from calcite prisms cut along a basal section so as to maximize the birefringence ($n_{\parallel} = 1.66$; $n_{\perp} = 1.48$). The prisms are cemented together with Canada Balsam ($n_D = 1.48$) which matches the perpendicular index of the prism. In the figure, unpolarized light enters the prism from the left along a line parallel to the axis of maximum birefringence. Light in the vertical plane experiences an index equal to 1.48 and that in the horizontal plane an index of 1.66. Since the prism/Canada balsam interface for the vertically polarized wave is optically nonexistent due to the index match, the wave has no reflection component and passes through the second half of the prism with an unaltered line of travel. The horizontally polarized wave undergoes total internal reflection at the interface since there is a large refractive index mismatch. Hence, a single unpolarized beam impinging one face of the prism is converted into two divergent, oppositely polarized beams emerging from different faces.

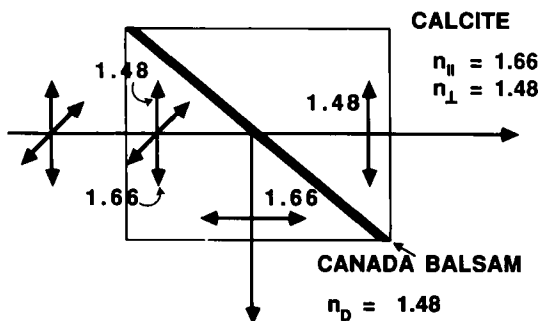


FIG. 4. Schematic of a calcite beam splitter.

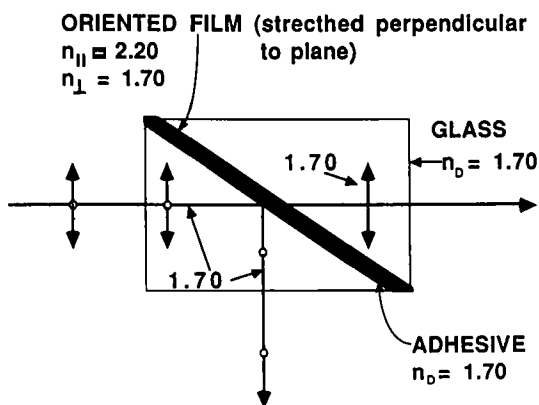


FIG. 5. Schematic of a beam splitter using a birefringent polymer film.

Figure 5 shows a schematic of a polarizing beam splitter that uses a highly birefringent film ($n_{\parallel} = 2.20$; $n_{\perp} = 1.70$; oriented perpendicular to the plane of the page) sandwiched between glass prisms ($n_D = 1.70$). An adhesive with a refractive index equal to 1.70 is used since it provides a convenient means of making good optical contact between the film and the prisms. In this example, when an unpolarized light beam enters the prism, both the horizontal and vertical components experience a refractive index equal to 1.70, and therefore the beam remains unpolarized. For the vertical component, the interface between the glass, the adhesive, and the film is optically nonexistent due to the index match, and this component traverses the entire prism undeviated from its original path. Conversely, the horizontal component is completely reflected at the adhesive/film interface due to the large refractive index mismatch between the adhesive and the parallel index of the film. In analogy to a calcite beam splitter, the unpolarized impinging radiation is converted to two divergent, polarized beams.

There are many other applications for optical devices using highly birefringent films, which are described in detail in a series of patents issued to the Polaroid Corporation [12].

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