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Consequences of Chemical Modification on Optical and Solution Properties of Rodlike Polyamides

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ABSTRACT

Rodlike polyamides were substituted to 50-55% on the nitrogen atom of the amide group with benzyl, 1-naphthylmethyl, and 4-(1,3,6,8-tetrabromo-9-carbazolyl)-1-butyl groups using a standard literature procedure. The resulting polymers exhibit significantly lower isotropic refractive indices and enhanced solubility. Polymers composed of the isophthaloyl moiety, with or without N-substitution, also exhibit lower refractive indices and enhanced solubility when compared to their rodlike analogs. These differences in properties are due to a great extent to the large difference in conformational rigidity between the two polymer types.

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INTRODUCTION

Over the past several years we have been investigating molecular structure/refractive index relationships, as well as solubility, of rod-like polyamides. In the first two papers of this series [1, 2], we demonstrated that extremely high refractive index and birefringence values can be attained in this class of polymers and that the experimental values significantly exceed those calculated from the Lorentz-Lorenz equation by use of group and atom polarizabilities. We speculated that the calculated repeat-unit polarizabilities should be treated in such a way that only the parallel component was multiplied by some as yet undetermined factor. In addition, we suggested that the significant deviation from theory is due to the rodlike conformation of the polymer backbone coupled with a large π -electron density, and this deviation would probably be observed in all polymers which are at least as rodlike as the para-linked aromatic polyamides.

We also demonstrated that the solubility of rodlike aromatic polyamides can be enhanced by incorporating 2,2'-disubstituted biphenyl moieties into the polymer without changing its rodlike conformation. The 2,2'-substituents force the biphenyl rings into a noncoplanar conformation which lowers the symmetry of the backbone, thus diminishing crystallinity and hydrogen bonding.

There are two other approaches to solubility enhancement in aromatic polyamides. The first incorporates meta-substituted diacids or diamines into the polymer [3, 4] which destroys the rodlike conformation [5, 6] and significantly lowers crystallinity. In the second approach the hydrogen atom of the amide group is replaced by alkyl groups. The N-alkyl substituent diminishes or completely eliminates interchain hydrogen bonding [7-10], and it also converts the rodlike conformation of the original polymer into a Gaussian coil [11].

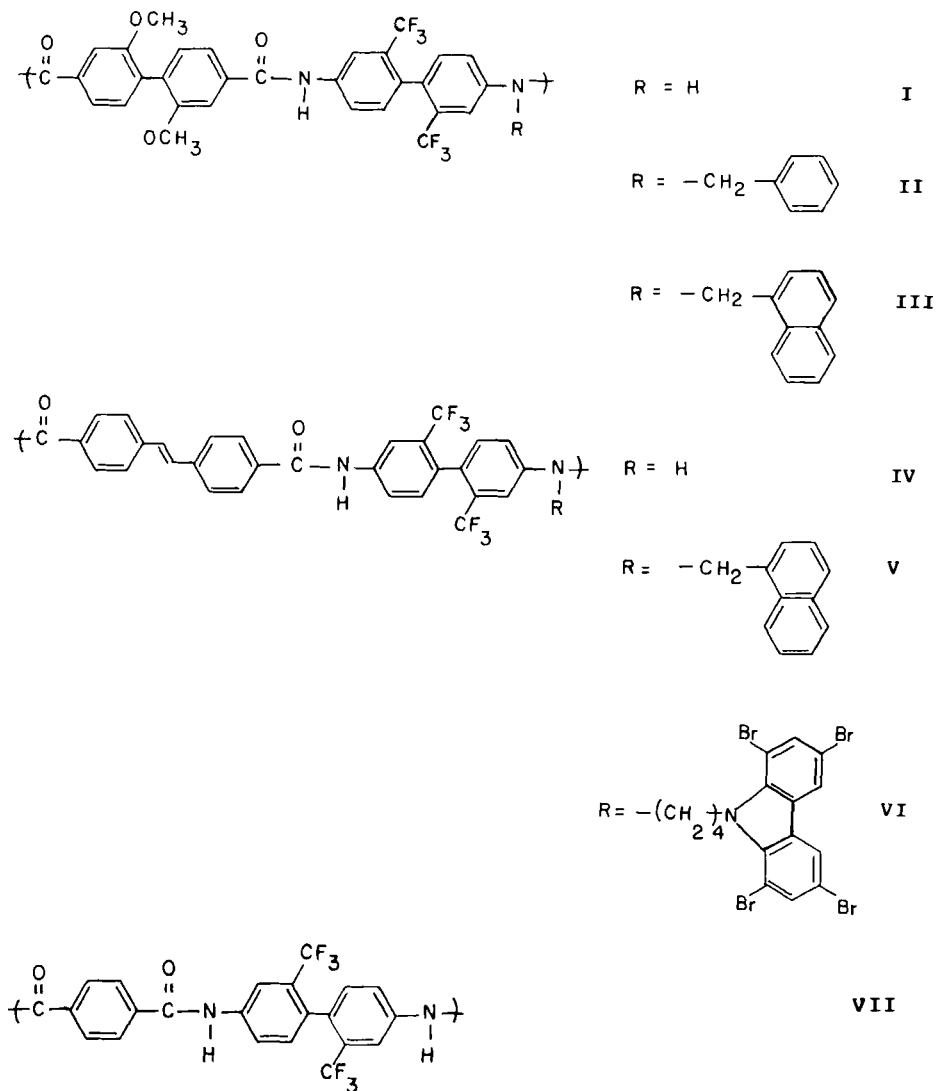
Our continuing interest in processability and the molecular factors controlling refraction in polymers led to an examination of the optical properties of Gaussian-coil polyamides. In this paper we compare refraction and solubility properties of the latter, represented by polyamides composed of N-substituted amide groups and/or meta-substituted diacids, with their rodlike homologs.

EXPERIMENTAL

The synthesis and purification of monomers prepared for this study are given in detail in the literature [1, 2].

The polymers were prepared by low-temperature solution condensation; the structures are given in Table 1. N-Substituted polymers were prepared by reacting the parent polymer with the sodium salt of the dimethylsulfoxide anion followed by the appropriate alkyl halide [9]. Table 2 lists all of the pertinent data.

TABLE 1. The Molecular Structures of the Rodlike and Nonrodlike Aromatic Polyamides Used for Comparison in This Study



(continued)

TABLE 1 (continued)

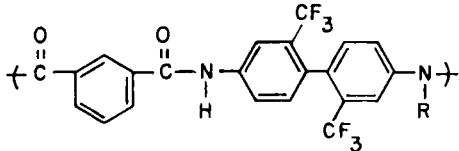
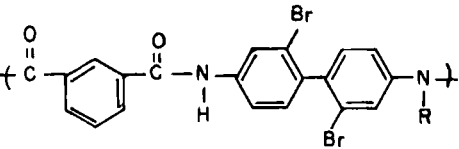
	R = H	VIII
	R = CH ₃	IX
	R = H	X
	R = CH ₃	XI

TABLE 2. Polymer Properties

Polymer	η_{inh} , dL/g ^a	η_{iso} ^b	Percent substitution
I	1.47	1.68 ^c	0
II	1.12	1.60 ^d	55 ^f , ~50 ^g
III	1.21	1.67 ^d	54 ^f , ~50 ^g
IV	4.51	1.89 ^d	0
V	1.62	1.67 ^d	~50 ^g
VI	1.24	- ^e	~50 ^g
VII	3.53	1.76 ^d	0
VIII	1.20	1.60 ^d	0
IX	1.15	1.57 ^c	~50 ^g
X	1.31	1.67 ^c	0
XI	1.10	1.66 ^c	~50 ^g

^a0.5% Polymer (w/v) in 5% LiCl/dimethylacetamide (w/v).

^bIsotropic refractive index.

^cJamin-Lebedeff interferometry at 589 nm.

^dBrewster-angle measurement at 633 nm.

^eFilms too scattering to measure.

^fBy ¹³C-NMR ($\pm 5\%$).

^gEstimated from IR spectra of films.

The inherent viscosities ($\eta_{inh}^{30^\circ}$, 0.5 dL/g) were determined in a Ubbelohde viscometer with 5% LiCl/dimethylacetamide (w/v) as the solvent.

Refractive index measurements were made on a Zeiss polarizing microscope by Jamin-Lebedeff interferometry and by Brewster angle analysis using a 633-nm He-Ne laser.

Polymer Synthesis

The following procedure is representative of the technique used for the synthesis of Polymers I, IV, VII, VIII, and X.

Synthesis of Polymer X

A resin kettle was equipped with a mechanical stirrer, a nitrogen inlet tube, and a calcium chloride drying tube. To this was added LiCl (2.034 g) and the vessel was flamed with a Bunsen burner and simultaneously flushed with nitrogen. The reaction vessel was cooled to room temperature and a solution of 2,2'-dibromobenzidine (1.104 g, 3.22 mmol) in 25.4 mL anhydrous 2:1 tetramethylurea (TMU)/N-methylpyrrolidone (NMP) was added. This was stirred and warmed gently to dissolve LiCl. The mixture was then cooled to 0°C in an ice salt bath and isophthaloyl chloride (0.656 g, 3.22 mmol) was added as a solid through a narrow-necked funnel. The funnel was washed with 25.4 mL of 2:1 TMU/NMP solvent mixture. The mixture was stirred for 30 min at each of the following temperatures (0, 5, 10, 25°C). The temperature was raised to 65°C; stirring was continued overnight. No apparent increase in viscosity was noted. The polymer solution was poured into H₂O and mixed in a blender. It was filtered and washed twice with H₂O, then with ether. The white solid was placed in a vacuum oven for 18 h at 100°C (< 1 torr). The yield was 1.414 g (93% yield).

The infrared spectrum was determined from a film cast from diglyme (cm⁻¹): 3 300 (N-H, amide), 3 075 (=C-H, aromatic), 1 660 (C=O, amide).

The following procedure [9, 10] is representative of that used for the synthesis of the substituted polyamides: II, III, V, VI, IX, XI.

Synthesis of Polymer XI

A round-bottomed, 3-necked flask was equipped with a condenser, thermometer, and N₂ inlet. To this flask was added powdered NaH (30.7 mg, 1.278 mmol) and 30 mL of freshly distilled DMSO. The reaction mixture was heated to 65°C and stirred under N₂ for 1 h.

The solution was cooled to room temperature, and poly(2,2'-dibromo-4,4'-biphenylene)-1,3-isophthaloyldicarboxamide (600 mg, 1.278 mmol)

was added and stirred for 4 h. Iodomethane (181.5 mg, 1.278 mmol) was then added to the vessel and stirred overnight. The reaction mixture was poured into cold H₂O and a gel-like precipitate formed. The precipitate was filtered and washed with H₂O and ether. The polymer was dried in a vacuum oven at 120°C (1 torr) overnight. The resulting white solid weighed 453.6 mg (74% yield.)

The molecular structure is consistent with the IR spectrum of a film cast from diglyme (cm⁻¹): 3 300 (N-H); 3 075 (=C-H, aromatic); 2 960, 2 870 (CH₃, asymmetric and symmetric); 1 690 (C=O, substituted amide); 1 640 (C=O, unsubstituted).

RESULTS AND DISCUSSION

The purpose of this work is to compare solubility and refraction of rodlike and nonrodlike polyamides. In order to make this comparison, we chose two routes of investigation. The first and most direct was the synthesis of aromatic polyamides containing isophthalic acid. The second was the substitution of an alkyl group on the nitrogen atom of the amide group. To insure that the results could be reasonably compared, each polymer was substituted to approximately 50%. We chose this level of substitution because we wanted to examine the optical effect of a randomly alternating rodlike/nonrodlike conformation.

Synthesis and Characterization

The literature indicated that the most successful and controllable method of polyamide N-substitution, without actually synthesizing N-substituted A-B comonomers [13], is a procedure which uses sodium hydride/DMSO [9, 10]. The precise number of moles of NaH (based on the desired degree of substitution of the polymer) is reacted with DMSO to form the methyl sulfonium carbanion in DMSO. Sequential addition of the polyamide and the primary alkyl bromide results first in deprotonation of amide-hydrogen bonds and then nucleophilic substitution which effects N-alkylation.

Infrared and ¹³C-NMR spectral analyses were used to determine the degree of N-alkyl substitution of the polymers. The results of elemental analysis were much too variable in our polymers to be used diagnostically although some unspecified elemental technique has been successfully used by others [9, 10]. NMR analysis (in THF) was particularly advantageous for Polymers I-III. The parent polymer (I) has two methyl groups which exhibit carbon frequencies (56.6 ppm) remote from any other carbon atom of the repeat unit, and the methylene carbon of the benzylated (40.3 ppm) and naphthylated (41.9 ppm) amide was also well resolved. Polymer I was benzylated to the 20, 40, and 50 mol% level: NMR analysis of the resulting polymers indicated that

the actual percentages were 19, 38, and 54, respectively. Infrared analysis of these materials agreed with these percentages. Since the reaction was nearly quantitative, we concluded that the level of substitution could be easily effected by careful control of the reactant concentrations. The actual level of substitution could be quantified by monitoring the amide N-H, the methylene C-H, and the carbonyl stretching bands. The results of these analyses indicate that 50-55% substitution was obtained for each polymer.

One of the consequences of N-alkyl substitution is the diminution of solution viscosity which is caused by a conformational change from rodlike to nonrodlike. For example, it was found that incorporation of either naphthylmethyl groups (Polymer V) or tetrabromocarbazoyl-butyl groups (Polymer VI) lowered the inherent viscosity of Polymer IV from 4.51 to 1.62 and 1.24, respectively. A similar but less dramatic effect was observed for Polymer I on substitution. The polymerization of isophthalic acid in place of terephthalic acid has the same effect on viscosity (compare, for example, Polymer VII and VIII). Methyl substitution of the amide group of Polymer VIII has a very small effect on viscosity since VIII itself has a nonrodlike conformation. Similar results can be found in the literature for N-substituted poly(p-phenylene terephthalamide) (PPTA) [3, 10, 13].

Solubility

The parent rodlike polymers, e.g., I, IV, and VII, exhibit very unusual solubilities. For example, Polymer I is soluble in glyme and to 5% (w/v) in THF, and Polymers IV and VII are readily soluble in amide solvents such as tetramethylurea (without LiCl) up to 10 and 20%, respectively [1, 2]. When these polymers are converted to their nonrodlike analogs, the solubility, particularly that of Polymers IV and VII, increases dramatically. For example, Polymers V and VI are soluble in THF, and Polymer VIII is soluble in THF, acetone, and diglyme. The methylation of Polymer VIII has very little effect on solubility. The observed solubility enhancement in these polymers is similar to that exhibited by N-substituted PPTA [9, 10]. It should be noted, however, that unsubstituted PPTA not only has a rodlike conformation but it also exhibits a high level of crystallinity and hydrogen bonding, and the enhanced solubility of the N-substituted polymer is expected. For Polymers I, IV, and VII, the solubility enhancement is due solely to a conformational change since these polymers are highly amorphous and have, at most, very weak hydrogen bonding.

Refraction

At the initial stages of the investigation of optical properties of polymers, we postulated that refractive index, and particularly birefringence, could be maximized by the manipulation of certain molecular

structural parameters. As the work progressed, several guidelines were formulated relating molecular and macroscopic properties. For example, refractive index enhancement of polyamides could be realized by incorporating groups and atoms with high polarizability, such as phenyls, alkenes, and alkynes, into the repeat unit; all these moieties obviously have significant π -electron density. Atoms which exhibit high polarizability are halogens, sulfur, phosphorus, etc.; these atoms have nonbonded electrons. In order to generate polymers with high birefringence, these groups and atoms must be incorporated into the polymer repeat units in such a way that they enhance only the longitudinal polarizability while contributing very little to the transverse polarizability. This can be accomplished by avoiding the placement of these moieties pendent to the backbone.

An additional, but very significant, experimental result was the observation that the refractive index and the birefringence were significantly higher than intuitively expected or mathematically predicted. For example, the calculated refractive index and birefringence from the Lorentz-Lorenz equation, which relates group and atom polarizabilities to refractive index, and several empirical, less rigorous mathematical procedures [13] gave much lower values than those found experimentally. We postulated that this large deviation was directly related to the rodlike conformation of the polyamides in question.

As a test of this concept, the refractive index and birefringence of the polyamides shown in Table 1 were determined. As discussed in previous sections, the viscosity and solubility evidence, along with ample literature corroboration, strongly suggests that both the N-substituted and meta-linked polyamides possess a nonrodlike conformation. As a consequence of this conformation, very low birefringence ($\Delta n < 0.1$) is exhibited by these polymers when they are stretched and oriented; by comparison the rodlike parent Polymers I, IV, and VII gave experimental maximum birefringence values of 0.33, 0.80, and 0.57, respectively [1].

In regard to the isotropic refractive index, every nonrodlike polymer exhibits a lower value than its respective parent (Table 2). For example, Polymer II, which is substituted with a benzyl group, has a 0.08 lower index than the parent. The substitution of a 1-naphthylmethyl group decreases the index by only 0.01 units; a smaller decrease is expected because this substituent is much more polarizable than a benzyl group. Polymer V, which is also substituted with a 1-naphthylmethyl group, exhibits a 0.22 unit decrease in index relative to its parent (IV). Unfortunately, Polymer VI, which contains the highly polarizable tetrabromocarbazole moiety, yielded films which showed so much scattering that its index could not be measured.

A comparison of Polymer VII with Polymer VIII also shows a significant decrease in index for the latter which has a nonrodlike conformation by virtue of the fact that its repeat unit is composed of an isophthaloyl moiety. The refractive index of Polymer X is higher than VIII because the more polarizable bromine atoms are substituted on the biphenyl in place of the trifluoromethyl group. The N-methyl-

ation of VIII and X, Polymers IX and XI, respectively, has a small effect on refractive index. This is so because the unsubstituted polymers already exist in nonrodlike conformations and the methyl group has a very small polarizability.

These results strongly suggest that a polymer backbone composed of very short rodlike segments, i.e., with persistence length approximately equal to the repeat unit length, is unable to generate the multi-repeat unit interaction required for the attainment of extremely high refractive index and concomitant birefringence.

We are aware of the fact that density is an important factor in refraction, and we have made many attempts to measure this parameter by density gradient techniques. In every case, the polymer was swollen by the immersion solvent to such an extent that the data obtained were unreliable. It is very likely that density differences between the two conformational types are small since the rodlike polymers themselves are amorphous [1], and it is anticipated that this morphology will be predominant in the nonrodlike conformation.

CONCLUSIONS

We have converted three rodlike polyamides into their nonrodlike analogs by N-substitution and by use of meta-linking comonomers. Every example exhibited a decrease in inherent viscosity and an increase in solubility.

We have clearly shown that the refractive index and, particularly, the birefringence are significantly decreased by this conformational change.

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