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Depolarization Ratios and Rigidity of Aromatic Polyamides

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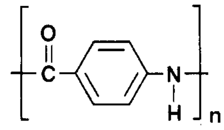
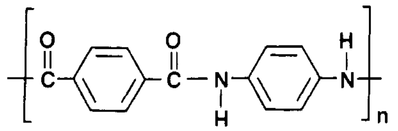
ABSTRACT: Monodisperse oligomers and several unfractionated polymers of poly(*p*-benzanilide–terephthalamide) (*p*-BT) were prepared and characterized. Their depolarization ratios were measured in concentrated (96%) sulfuric acid and they produced optical anisotropy values essentially the same as those of poly(*p*-phenylene terephthalamide) (*p*-PT) of comparable M_w. A numerical fit to our *p*-BT data and literature data for fractionated *p*-PT yielded a persistance length of 113 Å. The unfractionated *p*-PT, particularly at high molecular weights, tended to yield higher depolarization ratios and, consequently, higher persistance lengths than equivalent fractionated material, possibly due to high polydispersity.

Introduction

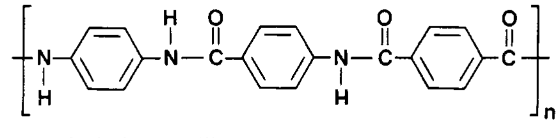
Due to the remarkable tensile properties and thermal stability of their fibers, there is a great deal of practical and theoretical interest in the properties of para-substituted aromatic polyamides, particularily poly(*p*-benzamide) (*p*-BA) and poly(*p*-phenylene terephthalamide) (*p*-PT). Recently, one of us has studied[1] the behavior of monodisperse oligomers and higher molecular weight homologues of the polymer poly(*p*-benzanilide–terephthalamide) (*p*-BT), which can be considered to be a 1:1 copolymer of *p*-BA and *p*-PT.



poly (p-benzamide) (p-BA)



poly (1,4-phenylene terephthalamide) (p-PT)



poly (p-benzanilide terephthalamide) (p-BT)

The properties of *p*-BA and *p*-PT in dilute solution have not been extensively measured, chiefly because of the following: (a) in *N,N*-dimethylacetamide (DMAc)/LiCl solvent mixtures, the aromatic polyamides show strong effects of molecular aggregation; (b) other useful solvents, such as concentrated sulfuric acid or chlorosulfonic acid, are highly corrosive and possess high viscosity; (c) a protracted exposure to these strong acids results not only in a slow degradation of the aromatic polyamides but also in the sulfonation of their aromatic rings.

The existing measurements have indicated that the above aromatic polyamides are very rigid, as one would expect. From intrinsic viscosity ($[\eta]$) and molecular weight (M_w) measurements, the Mark–Houwink exponent (a) in

$$[\eta] = K[M]^a \qquad (1)$$

falls in the interval $1.0 < a \le 1.85$, with the most common values obtained being around 1.1–1.2. Because they are higher than the theoretically expected values ($a = 1.7$) for monodisperse completely rigid rodlike molecules of comparable lengths,[1-3] values of, say, $a = 1.85$[4] appear to reflect the strong aggregation effect of *p*-BA in DMAc/3% LiCl and not the true behavior of individually disperse *p*-BA macromolecules.

Furthermore, persistence lengths (q) from viscosity, depolarization ratio, radius of gyration, electric birefringence, and flow birefringence measurements cover a huge range of values. Even when measured only in concentrated (96%) sulfuric acid, where aggregation effects are presumably eliminated, one gleans from the literature values of $325 \le q \le 1050$ Å for *p*-BA and $150 \le q \le 650$ Å for *p*-PT.[5-16] The q values are tabulated in Table I. Diffusion and sedimentation experiments appear not to be suffi-

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Table I
Persistence Length (q) in Å, Measured in 96% Sulfuric Acid

technique (ref)	p-BA	p-PT
light scattering, R_g (5)	400	200
light-scattering depolarization ratio (6)		150
flow birefringence (7)		185
light scattering (8)	600	200
viscosity (8)	400	150
flow birefringence (9)	325	
light-scattering depolarization (10)		287
electric birefringence, Kerr effect (11)		300
light scattering (12)		≥450
flow birefringence (13)	1000	
flow birefringence (14)		650
flow birefringence (15)	1050	650
flow birefringence (16)	435	275

ciently sensitive to yield even a rough estimate of q.[15,17,18] Changes in the nature and strength of the solvent acid, manifested by variations in the protonation level of the amide groups along the chain and in the consequential changes in chain extension and rigidity, were also reported to affect the exponent a,[19,20] the persistence length q,[18] and the radius of gyration R_g.[19]

Plots by Arpin and Strazielle[5,8] of intrinsic viscosity and radius of gyration against weight-average molecular weight (M_w) show the same dependencies and the same data scatter for unfractionated as for fractionated p-PT. This indicates that viscosity and the usual light-scattering measurements are insensitive to the polymer polydispersity, if it is not very large. The determination of the persistence length from the optical anisotropy of wormlike chains appears, however, to be influenced by polydispersity, as well as by the solvent nature. These effects are clearly demonstrated in the values of optical anisotropy obtained from the depolarization of light scattered from solutions of fractionated and unfractionated p-PT in concentrated sulfuric acid and chlorosulfonic acid.[6,19]

In this study, we compare our depolarization ratio results on monodisperse oligomers and modest molecular weight p-BT with previous studies[6,8] on p-PT, thus attempting to establish whether there is any significant difference in rigidity between the two polyamides. We shall, furthermore, contribute another value for the persistence length of these molecules.

Theory

For a wormlike chain of contour length L, consisting of N segments each of projected length b, $L = Nb$, it was shown by Benoit and Doty[21] that the mean-square radius of gyration can be obtained from the relationship

$$\langle R_g^2 \rangle = q^2[x/3 - 1 + 2/x + 2[1 - \exp(-x)]/x^2] \quad (2)$$

where $x = L/q$. The optical anisotropy Δ^2 for such a chain was calculated[6] to be

$$\Delta^2 = \delta_0^2[2/x' - 2[1 - \exp(-x')]/x'^2] \quad (3)$$

where $x' = 3L/q$ and δ_0^2 is the optical anisotropy for the structural segment. The values of δ_0^2 are usually obtained by extrapolation of the values of Δ^2 determined for chains of decreasing length to their values at $N = 1$:

$$\delta_0^2 = \Delta^2 \quad (N = 1) \quad (4)$$

The optical anisotropy Δ^2 is calculated from the measured depolarization ratio (ρ). The relationship between Δ^2 and ρ depends on the nature of the incident light. In the case of unpolarized incident light, the depolarization ratio ρ_u at a scattering angle $\theta = 0°$ relates to Δ^2 as[6,8]

$$\Delta^2 = 5\rho_u/(6 - 7\rho_u) \quad (5)$$

but in the case of vertically polarized incident light[22] at $\theta = 0°$,

$$\Delta^2 = 5\rho_v/(3 - 4\rho_v) \quad (6)$$

In our case, vertically polarized incident light was used. Data were collected at seven different scattering angles (θ), ranging from about 10° to 152°, and corrected to zero angle by the use of the equation

$$\rho_v = \rho_\theta(1 + \cos^2(\theta))/[2 - \rho_\theta(1 - \cos^2(\theta))] \quad (7)$$

Persistence lengths and radii of gyration are obtainable, hence, from measurements of depolarization ratios of scattered light, provided L is known.

Experimental Section

Six monodisperse aromatic amide oligomers were used in this study. They were all phenyl end capped. The lowest homologue in this series is benzanilide (MW = 197), which was purchased from Aldrich Chemical Co. The other oligomers contained only para substitutions. The p-triphenylene diamide (MW = 315) was prepared according to the Yamazaki[23] procedure from 2 mol of aniline and 1 mol of terephthalic acid. Using the same procedure, the reaction of benzoic acid with 4,4′-diaminobenzanilide produced p-tetraphenylene triamide (MW = 434). For p-pentaphenylene tetraamide (MW = 553), 2 mol of 4-aminobenzanilide was reacted with 1 mol terephthalic acid. To obtain p-hexaphenylene pentaamide (MW = 672), benzoyl chloride was reacted with p-aminobenzoic acid under Schotten–Baumann conditions, and the product was then reacted with 4,4′-diaminobenzanilide under Yamazaki conditions in 2:1 molar ratio. The p-heptaphenylene hexaamide (MW = 791) was made by reacting terephthaloyl chloride with p-aminobenzoic acid in 1:2 molar ratio, under Schotten–Baumann conditions, and then using the Yamazaki procedure to react each mole of the product with 2 mol of 4-aminobenzanilide. The oligomers synthesized by these methods are essentially monodisperse; i.e., they have a polydispersity index (M_w/M_n) of exactly one.

Higher molecular weight p-BT fractions were all prepared by the Yamazaki procedure from terephthalic acid and 4,4′-diaminobenzanilide and were not end capped. Increasing molecular weights were obtained by allowing the reaction to progress for increasing durations prior to quenching and workup. All structures were confirmed by carbon-13 NMR. This method of synthesis usually yields fairly low polydispersity ($M_w/M_n < 2$).

To avoid aggregation effects, all solution work was conducted in concentrated (96%) sulfuric acid. The molecular weight of the monodisperse oligomers was calculated from their structures. In this case, the number-average and weight-average molecular weights are the same. The weight-average molecular weight (M_w) of the higher M p-BT homologues was determined by light-scattering measurements using a custom-made Langley-Ford LSA II photon correlation spectrometer, the details of which are described elsewhere.[24] From M_w, the molecular weight per repeat unit ($M_0 = 119$), and its monomer length ($b \approx 5.5$ Å), the chain length (L) is calculable. Because of the high optical anisotropy, it was necessary to correct the M_w values for the depolarization ratio by dividing by the Cabannes factor at zero angle ($C_0 = 1/(1 - 7\rho_u/6)$).

Depolarization ratios were measured in the same photon correlation spectrometer equipped with a polarizer at each of the seven angles of measurement. Each angle was calibrated for absolute Rayleigh ratio measurements by measuring the light-scattering intensity of a pure solvent of known Rayleigh ratio (toluene). The depolarization ratio is the ratio of the horizontally polarized and vertically polarized intensities (after subtracting the corresponding values for the solvent), which were measured at each of the seven scattering angles.

At least four different concentrations in concentrated sulfuric acid were prepared of each p-BT and filtered with Millex filter units (0.2 micro pore diameter) from Millipore. To avoid degradation, the solutions were prepared and measured on the same day. For the samples measured, no angular dependence was found, due to their small size. Thus, only an extrapolation to zero concentration was needed to determine the molecular weight of

Table II
Optical Anisotropy of Aromatic Polymers Polymer Fractionation

no.	sample i.d.	types	level	M_w, g/mol	N	ρ_v	Δ^2
			This Work				
1	benzanilide	*p*-BT	monodisperse	197	2	0.192	0.430
2	A0500-9E	*p*-BT	monodisperse	315	3	0.180	0.395
3	A0500-9D	*p*-BT	monodisperse	434	4	0.090	0.170
4	A0500-9C	*p*-BT	monodisperse	553	5	0.173	0.375
5	A0500-9B	*p*-BT	monodisperse	672	6	0.174	0.378
6	A0500-9A	*p*-BT	monodisperse	791	7	0.151	0.315
7	A0500-13A	*p*-BT	unfractionated	1400	12	0.119	0.236
8	A0500-13B	*p*-BT	unfractionated	2300	19	0.117	0.231
9	A0500-13C	*p*-BT	unfractionated	2700	23	0.110	0.215
10	A0500-13D	*p*-BT	unfractionated	2900	24	0.101	0.195
11	A0969-85B	*p*-BT	unfractionated	6300	53	0.073	0.135
			Arpin et Al.[a]				
12		*p*-PT	fractionated		13		0.290
13		*p*-PT	fractionated		18		0.223
14		*p*-PT	fractionated		23		0.184
15		*p*-PT	fractionated		29		0.154
16		*p*-PT	fractionated		38		0.130
17		*p*-PT	fractionated		55		0.103
18		*p*-PT	fractionated		66		0.094
19		*p*-PT	unfractionated		18		0.270
20		*p*-PT	unfractionated		36		0.177
			Arpin and Strazielle[b] Polymer 1977, 18, 591				
21	A50	*p*-PT	unfractionated	1680	14	0.25[c]	0.294
22	A26	*p*-PT	unfractionated	4500	38	0.175[c]	0.183
23	A27	*p*-PT	unfractionated	9350	78	0.16[c]	0.164
24	A28	*p*-PT	unfractionated	19700	166	0.115[c]	0.111
25	A30	*p*-PT	unfractionated	35000	294	0.11[c]	0.105
26	A33	*p*-PT	unfractionated	43500	366	0.10[c]	0.094
27	A32	*p*-PT	unfractionated	63000	529	0.09[c]	0.084

[a] Arpin; et al. *Polymer* **1977**, *18*, 262. [b] Arpin; Strazielle *Polymer* **1977**, *18*, 591. [c] ρ_{μ}.

Table III
Results of Fits to Eq 3

data pts. fit	description	δ_0^2	q Å
1–27	all data	0.439	142
1–6, 12–18	fractionated, oligomers	0.472	107
1–11, 12–18	fractionated, all *p*-BT	0.463	113
7–11, 19–27	unfractionated *p*-PT	0.266	1020
7–11, 19–23	unfractionated *p*-PT, $N < 100$	0.357	306

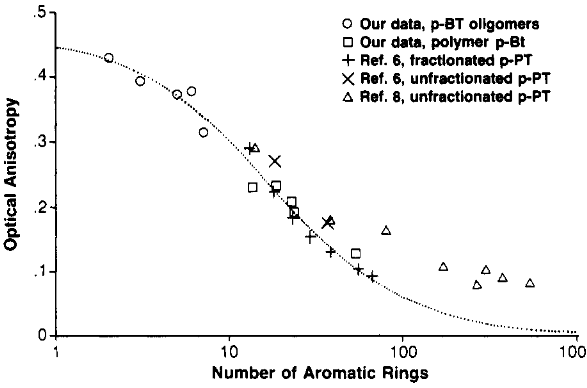

Figure 1. Optical anisotropy of aromatic polyamides vs. the number of aromatic rings. The dotted line is a fit to the wormlike coil model for the *p*-BT oligomers and fractionated *p*-PT ($\delta_0^2 = 0.463$, $q = 113$ Å).

the unfractionated *p*-BT and the depolarization ratios of all the *p*-BT samples.

Results and Discussion

Our results are summarized in Table II, entries 1–11. The optical anisotropies for our results in the table were calculated according to eq 6 from our measured values of ρ_v. Entries 12–20 in Table II were extracted from the graphs in the paper by Arpin et al.[6] It should be noted that in their treatment each repeat unit contains two aromatic rings, while in our case each unit is treated as having only one such ring. Entries 21–27 in the table were taken from Arpin and Strazielle[8] and their code numbers are used to identify the various samples. In this case, the optical anisotropies were calculated from the given depolarization ratios (ρ_u) by using eq 5. The values of Δ^2 thus obtained are comparable to the values in the rest of the table.

In Figure 1, the data are plotted in terms of optical anisotropy (Δ^2) against the number of aromatic rings (N) in the polyamide chain. It is obvious that the data are virtually superimposable, particularly if only our *p*-BT and the fractionated *p*-PT samples are considered. Table III shows the results of nonlinear least-squares fits of various subsets of the data to eq 3. If only the monodisperse *p*-BT oligomers and fractionated *p*-PT samples were used, the largest value for the segment optical anisotropy ($\delta_0^2 = 0.472$) and the smallest value for the persistence length ($q = 107$ Å) were obtained; the addition of the *p*-BT polymers did not change the values much ($\delta_0^2 = 0.463$, $q = 113$ Å). The fit to the *p*-BT data and fractionated *p*-PT data is shown by the dotted line in Figure 1. In general, the unfractionated samples had higher optical anisotopies than one would expect for a monodisperse sample of equivalent molecular weight; this deviation becomes more pronounced at higher molecular weights. The inclusion of unfractionated, high molecular weight polyamides in the fits decreases the apparent value of δ_0^2 and increases the apparent value of q; this is especially evident when the fractionated *p*-PT and our *p*-BT data are omitted from the fit (see the last two entries in Table III). If the higher molecular weight unfractionated samples are omitted ($N > 100$), a persistence length of 306 Å is obtained for the unfractionated samples, rather similar to some of the more recent *p*-PT values in the literature.[10,11,16] Our values of δ_0^2 for the fractionated samples appear to be in excellent agreement with the values (0.4–0.45) reported in the literature for *p*-PT.[6,8,19]

In a previous publication,[1] it was shown that, for comparable molecular weights of unfractionated samples, *p*-BT follows the relationship

$$[c] = (5.25 \times 10^{-5})[M_{\mathrm{w}}]^{1.217}; \qquad 1800 \leq M_{\mathrm{w}} \leq 18\,500$$

while *p*-BA follows the relationship

$$[\eta] = (2.14 \times 10^{-5})[M_{\mathrm{w}}]^{1.203}; \qquad 3100 \leq M_{\mathrm{w}} \leq 13\,000$$

both in concentrated H_2SO_4 at 25 °C and the viscosity measured in deciliters per gram. These *a* values are in excellent agreement with the value of $a = 1.237$ reported by Lavrenko and Okatova[18] for *p*-PT. In light of this great similarity in the a values of *p*-BT, *p*-BA, and *p*-PT and in the behavior of the optical anisotropy of the *p*-BT and *p*-PT polymers, it is unlikely that *p*-BA would be much different. This is especially so in light of the fact that *p*-BT can be considered as an alternating copolymer of *p*-benzamide and *p*-phenyleneterephthalamide. It should be noted, however, that the substantial behavioral similarity of the three polymers appears to hold only in dilute solutions. In concentrated solutions, it was clearly demonstrated[1] that *p*-BA behaves as a measurably more rigid molecule than *p*-BT; this behavior may be attributed to aggregation effects.

A study by Millaud and Strazielle[19] indicated that *p*-BA molecules tend to aggregate rather strongly. When one compares, however, the depolarization ratios (ρ_u) for *p*-BA molecules[19] with those reported by Arpin and Strazielle[8] for *p*-PT, one finds them to be reasonably close to each other for comparable M_{w}. This indicates to us that the molecular rigidities of *p*-BA and *p*-PT are rather similar and the large differences in *q* (Table I) might arise from aggregation effects.

As previously stated, and clearly shown by Figure 1 and Table III, polydispersity plays a significant role in the value obtained for the persistence length. We have no data correlating Δ^2 with the breadth of the molecular weight distribution, but it is clear that unfractionated samples produce larger Δ^2 values (and *q* values) than fractionated samples of comparable M_{w}. In their monograph, Tsvetkov and Andreeva[16] show that the equilibrium rigidity of rigid chain polymers is independent of the molecular weight in the high-*M* region when the limiting value of $([\mu]/[\eta])_\infty$ is reached. This independence of rigidity from *M* prevents errors in the determination of *q* caused by polydispersity. Most importantly, however, it is a fact[7,16] that at lower molecular weights the ratio of $[\mu]$, the characteristic value of flow birefringence, to $[\eta]$, the intrinsic viscosity, is rather strongly dependent on the molecular weight, causing marked effects of polydispersity on the calculated chain rigidity and persistence length. The strong effects of polydispersity on the orientation angle of flow birefringence (α),

$$\tan \alpha = (\tan \alpha_{\mathrm{c}})(M_z/M_{\mathrm{n}})^{3a(1+a)}$$

$$\tan \alpha = (\tan \alpha_{\mathrm{c}})(M_{\mathrm{w}}/M_{\mathrm{n}})^{3a(1+a)/2}$$

were previously demonstrated by Chaffey.[25] Here $\tan \alpha_{\mathrm{c}}$ is calculated by assuming the sample to be monodisperse with molecular weight of M_{w}. It is possible, hence, that a neglect of the dependence of chain rigidity on the molecular weight of relatively low-*M* polymers contributed to the excessively high *q* values obtained from flow birefringence and reported in the early literature.[13-15] Just as in the case of flow birefringence, the effects of polydispersity on the determination values of *q* might vanish in the region of very high M when the backbone rigidity becomes independent of molecular weight.

It may be possible to experimentally assay the effect of polydispersity by making mixtures of monodisperse model compounds. Unfortunately, our *p*-BT oligomers, the only truly monodisperse compounds, do not cover a very wide range of ρ_{v} values and thus would not give an accurate assessment of the effect. A quick measurement on a 50:50 mixture of the two extremes (AO500-9A and benzanilide) yields a ρ_{v} value of about 0.17, roughly halfway between the values for the pure compounds.

Conclusions

The depolarization ratios and optical anisotropies of *p*-BT are essentially the same as those of *p*-PT in the literature. The calculated persistence lengths appear to have a qualitative dependence on sample polydispersity—the higher the polydispersity is, the larger *q* is. Thus, for *p*-BT data and *fractionated p*-PT data, $q = 113$ Å. For *all* samples, $q = 142$ Å and for only the *unfractionated* ones, $q = 1020$ Å (306 Å for $N < 100$).

Registry No. *p*-BT (copolymer), 29153-47-7; $C_6H_5CONHC_6H_5$, 93-98-1; *p*-triphenylene diamide, 7154-31-6; *p*-tetraphenylene triamide, 87706-91-0; *p*-pentaphenylene tetramide, 35701-91-8; *p*-hexaphenylene pentaamide, 109034-61-9; *p*-heptaphenylene hexamide, 108773-38-2.

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