Characterization and conformation of aromatic polyamides: poly(1,4-phenylene terephthalamide) and poly(*p*-benzamide) in sulphuric acid

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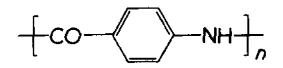
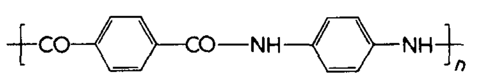
The dilute solution properties of two aromatic polyamides, poly(1,4-phenylene terephthalamide) (PPDT) and poly(*p*-benzamide) (PBA) in 96% sulphuric acid, have been investigated by measurements of the intrinsic viscosity, by light scattering and by gel permeation chromatography (g.p.c.). The Mark–Houwink relation for PPDT indicates that the conformation is intermediate between a coil and a rod-like particle. The conformations of both aromatic polyamides have been determined precisely by coupling g.p.c., light scattering and viscosity and it was found that PPDT and PBA in 96% sulphuric acid are not very rigid particles. The rigidity has been characterized in terms of a worm-like chain. The persistence lengths q which evaluate the rigidity of the chain are q = 175 ± 25 Å for PPDT and q = 500 ± 100 Å for PBA; PBA has the more rigid polymer chain.

INTRODUCTION

Recently a number of patents have appeared[1] which describe a series of new synthetic fibres with interesting physical properties, such as high thermal stability and elastic modulus much higher than the elastic modulus of conventional fibres such as nylon and polyesters. These materials, called high modulus fibres or high performance fibres, are generally derived from aromatic polymers, especially poly(*p*-benzamide) (PBA):



and poly(1,4-phenylene terephthalamide) (PPDT):



Several Du Pont patents and some recent papers[2–5] discuss, in detail, synthesis, spinning procedures and some physical properties of these fibres. It has been shown that these *para*-substituted aromatic polyamides are able to form anisotropic phases in selected amide solvents or strong acids. Anisotropic phases, when obtained at one critical concentration, are nematic, but little is known about the structure of these mesomorphic phases.

We have studied by optical microscopy and X-ray diffraction the anisotropic phases of concentrated solutions of one PPDT sample in pure sulphuric acid[6]. A thread-like texture, which characterizes the nematic phases of crystalline liquids, has been observed, and the lateral distance of the macromolecules has been determined as a function of dilution. These observations indicated that the chains of aromatic polyamides in concentrated solution are almost as extended as in the crystal.

Much less work has been done on the properties of these aromatic polyamides in dilute solution[7–9], because of the difficulty of dissolving them in classical solvents. They can only be dissolved in polar solvents, such as *N*,*N*-dimethylacetamide (often only in the presence of lithium salt), or strong acid, such as concentrated sulphuric acid or chlorosulphonic acid.

In our recent papers we have published preliminary results[10–12], the present paper reports a detailed study of the conformation of dilute solutions of PPDT in 96% sulphuric acid, as well as similar data for PBA.

CHARACTERIZATION OF POLY(1,4-PHENYLENE TEREPHTHALAMIDE)

The samples of PPDT and PBA were prepared according to methods described earlier[2–5]. PPDT was prepared by low temperature polycondensation of 1,4 phenylene-diamine and terephthaloyle chloride in methylpyrrolidone (N-MP) or hexamethylphosphoryl-triamine (HMPT), or a mixture of both solvents, in the presence or absence of lithium chloride, with vigorous stirring. The degree of polymerization depended upon the concentration of reactants, the solvent composition, the presence of salt, the temperature and the rate of stirring. The inherent viscosities of the PPDT samples varied between 0.5 and 8 dl/g[*].

The polymerization reaction[2–5] of PBA from *p*-aminobenzoylchloride was more complex.

The measurements (viscosity, light scattering) were made in 96% sulphuric acid ('Prolabo'). The concentration of the sulphuric acid was maintained at 95.7% ± 0.15 and controlled by density measurements.

The intrinsic viscosities, $[\eta]$, (ml/g) were calculated by extrapolating the reduced viscosity measured in a capillary viscosimeter (ϕ = 0.7 mm) to zero concentration; the flow

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[*] As an indication of the degree of polymerization, one can determine the inherent viscosity: $\eta_{inh} = (1/c)\log(\eta/\eta_0)$ in 100% sulphuric acid at a concentration of c = 0.5 g/dl.

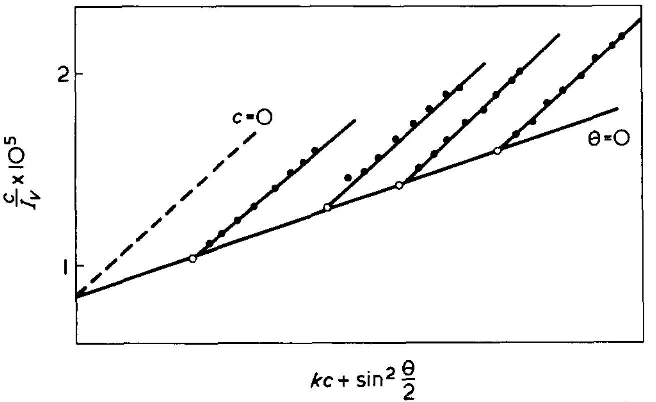


Figure 1 Zimm plot of PPDT sample A_{32} in 96% sulphuric acid (the incident light is vertically polarized)

times were obtained with a precision of 1/100 sec. The weight-average molecular weights, M_w, were determined by light scattering with a Fica 50 apparatus at $\lambda = 540$ nm using non-polarized or vertically polarized light. The values of M_w were obtained by the double extrapolation method (Zimm plot). *Figure 1* shows the Zimm plot for the sample A_{32} of the highest inherent viscosity. The molecular weights were corrected by the Cabannes factor for the anisotropy of the molecules. The refractive index increments were found to be 0.309 ml/g for PPDT and 0.360 ml/g for PBA. For light scattering measurements, solvents and solutions were clarified by coupling filtration with a glass filter G5 and by centrifugation for 2 h at 25 000 xg. The initial concentrations were about 0.2–0.3% for low inherent viscosity samples and 0.05–0.1% for high inherent viscosity samples.

Molecular characterization of PPDT

Table 1 lists, for eight PPDT samples, viscosity data and light scattering measurements: intrinsic viscosities, $[\eta]$; weight-average molecular weights M_w; depolarization factors ρ_u; radii of gyration $\langle R^2\rangle^{1/2}$; and second virial coefficients of osmotic pressure A_2.

The weight-average molecular weights, M_w, range from 1650 to 63 000. All samples show a depolarization factor ρ_u which is not negligible; ($\rho_u = I_H/I_V$ is the ratio of scattered lights of solute when the incident light is horizontally and vertically polarized). The ρ_u factor for sample A 34 is very high, owing to the presence of a residual fluorescence. To determine the true value for M_w, the intensity of the scattered light has been corrected for fluorescence according to some correction formulae derived from data in the literature[13,14].

The graphs of the reduced viscosity η_{sp}/c *versus* the concentration exhibit a 'polyelectrolyte effect' only at low concentration ($c \leqslant 0.4$ mg/ml) for the samples of high inherent viscosity ($\eta_{inh} > 3$ dl/g); η_{sp}/c increased rapidly with decreasing concentration for concentrations less than 0.4 mg/ml. This behaviour was simular to that described by Schaefgen *et al.*[7]. On the other hand, this effect was not observed in light scattering experiments, if we consider the angular distribution of the intensity I of the scattered light under the same condition: high molecular weight in the low concentration range (see *Figure 1*). The variations of I/c *versus* $\sin^2(\theta/2)$ (θ is the scattered angle) were regular and linear. One could explain this phenomenon by a real 'polyelectrolyte effect', but an identical effect considering an elongational viscosity at the top of the capillary is also possible. Complementary studies, changing the nature of the solvent for example, will be necessary for adequate understanding of this effect.

The viscosity/molecular weight relationship (Mark–Houwink relation) for PPDT has been given in a preceding paper[10]. From the data obtained on unfractionated samples (see *Table 1*), the Mark–Houwink relation was regular; below $M_w = 35\,000$ we obtained $[\eta] = 8 \times 10^{-3}M^{1.09}$. A more precise determination of this relationship on fractions especially of higher molecular weight is given below.

Gel permeation chromatography of PPDT

Polydispersities and molecular weight distributions have been studied by gel permeation chromatography on a simplified apparatus of the Waters type in glass and Teflon with a porasil packed column (four types of gel with different porosities). The eluated polymer was detected with a u.v. photometer at $\lambda = 330$ nm. The flow time of 1 ml/min is given by the nitrogen pressure. For each fraction of 5 ml, concentration, elution volume and reduced viscosity were determined directly after elution.

Initially, we have determined the calibration curve $\log M = f(V_e)$ with monodisperse samples of polystyrene in tetrahydrofuran (THF) and have obtained good selectivity for the column in the molecular weight range from 10^4 to 8×10^5. The parameter $(\sigma^2/a^2)_{\text{dif}}$ which characterizes the efficiency of the column has been found to be 0.2 (σ is the half-width of the chromatogram for a monodisperse sample and a is the slope of the calibration curve $V_e = a \log M + b$).

The PPDT samples have been studied in 96% sulphuric acid using the same column but replacing the THF progressively with sulphuric acid. *Figure 2* shows the chromato-

Table 1 Molecular parameters (intrinsic viscosity, molecular weight, depolarization factor ρ_u, radius of gyration $\langle R^2\rangle^{1/2}$ and second virial coefficient A_2) for PPDT in 96% sulphuric acid

Sample	η_{inh} (dl/g)	$[\eta]$ (ml/g)	ρ_u	M_w	$\langle R^2\rangle^{1/2}$ (Å)	A_2 (mol mlg^{-2})
A 50	0.51	26	0.25	1680	–	2×10^{-2}
A 26	0.76	69	0.17_5	4500	–	2.4×10^{-2}
A 27	1.84	180	0.16	9350	–	9×10^{-3}
A 28	3.06	400	0.11_5	19 700	–	8×10^{-3}
A 34	4.40	550	0.28_5	24 300	–	–
A 30	5.12	770	0.11	35 000	–	7.5×10^{-3}
A 33	6.00	820	0.10	43 500	(375)	8.3×10^{-3}
A 32	7.94	1250	0.09	63 000	(430)	9×10^{-3}

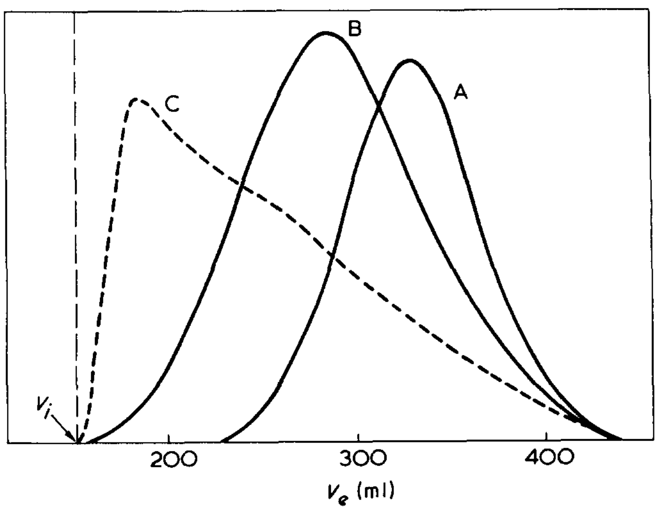


Figure 2 Chromatograms of some PPDT samples in H_2SO_4 at 96%. A, $\eta_{inh} = 0.5$ dl/g; B, $\eta_{inh} = 1.83$ dl/g; C, $\eta_{inh} = 5.1$ dl/g (V_i is the dead volume)

Table 2 Characterization of PPDT samples by g.p.c. in 96% sulphuric acid. Comparison with the direct determination of M_w and $[\eta]$

Sample	$[\eta]$ (ml/g)	M_w	V_e (ml)	$[\eta]$ peak (ml/g)	M_{peak}	$[\eta]_{g.p.c.}$ (ml/g)
A 50	26	1680	330	27.3	1700	–
A 26	69	4500	320	51	3100	62
A 27	180	9350	283	188	10 000	192
A 57	240	12 000	278	220	10 900	237
A 28	400	19 700	242	380	17 500	392
A 30	770	35 000	(185)	–	–	740
A 33	820	43 500	(178)	–	–	850
A 32	1250	63 000	(164)	–	–	–

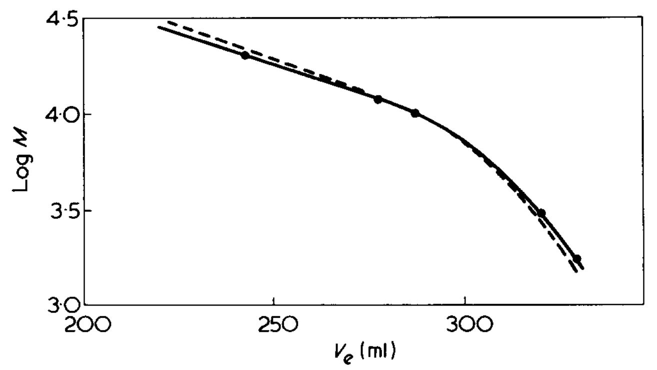


Figure 3 Calibration curve log *M versus* elution volume V_e for PPDT in 96% sulphuric acid: ●, experimental points; — — —, curve calculated from the calibration curve of PS in THF according to equation (1)

grams for three samples with inherent viscosities 0.5 dl/g (curve A), 1.83 dl/g (curve B) and 5.1 dl/g (curve C). For the samples of low inherent viscosity ($\eta_{inh} \leqslant 3$ dl/g), the chromatograms were regular, symmetric and showed a nearly Gaussian distribution (curves A and B). For the samples which had an inherent viscosity higher than 3, the chromatograms were not well defined and the curves were very asymmetrical. This type of curve can be explained by the loss of selectivity of the column in the range of low elution volumes and consequently for the highest molecular weights; the 'dead' volume of the column has been estimated to be V_e = 160 ml. Very similar chromatograms have been obtained for PPDT and also for PBA in the same range of η_{inh} ($\eta_{inh} \geqslant 4$) by Schaefgen *et al.*[7]; these authors have explained the observed behaviour by considering a bimodal distribution, especially for PBA, but no characteristics of the columns ('dead' volume, for example) were given.

In a previous communication[11], we reported good agreement between the viscosities determined directly on the whole samples and the viscosities obtained by coupling measurements of g.p.c. and viscosity:

$$[\eta]_{g.p.c.} = \frac{\Sigma c_i \eta_i}{\Sigma c_i}$$

where c_i and η_i are the concentration and viscosity of the fraction *i* respectively. Data for g.p.c. and viscosity are given in *Table 2*. The molecular weights M_{peak} have been calculated from the viscosities at the peak. From the M_{peak} values, it was shown that the variations of log(ηM) *versus* V_e for PPDT samples in sulphuric acid and polystyrene in THF lead to a unique curve for both systems. This result confirms the validity of the universal calibration for polymers of different structure in various solvents[15–18].

The calibration curve $\log M = f(V_e)$ for PPDT in sulphuric acid obtained in the range of selectivity of the column (V_e > 220 ml) is reported in *Figure 3* and compared with the calibration curve calculated from the curve $\log M = f(V_e)$ for PS in THF under the assumption of validity of the universal calibration. For a given elution volume V_e, one can write:

$$\log M_2 = \frac{1+\alpha_1}{1+\alpha_2}\log M_1 + \frac{1}{1+\alpha_2}\log\frac{K_1}{K_2} \qquad (1)$$

where the subscripts 1 and 2 are for PS and PPDT respectively, and α and K are the parameters of the Mark–Houwink relation (for PS in THF, the relation is $[\eta] = 14 \times 10^{-3} M^{0.7}$). This procedure allows us to define the calibration curve $\log M = f(V_e)$ for PPDT in the range of low elution volumes.

To obtain some indication of the polydispersity of the samples, a simple and direct method has been proposed by Tung[19] from the half width σ_{chrom} of the chromatogram:

$$\left(\frac{\sigma^2}{a^2}\right)_{chrom} = \gamma^2 + \left(\frac{\sigma^2}{a^2}\right)_{dif} \qquad (2)$$

where $\gamma^2 = \ln(M_w/M_n)$, a_{chrom} is the slope of the calibration curve $V_e = a \ln M + b$ for PPDT, and $(\sigma^2/a^2)_{dif}$ the characteristics of the column (efficiency and axial dispersion) were determined previously with monodisperse PS samples. The determination of M_w/M_n from Tung's relation assumes a chromatogram with a nearly Gaussian distribution. The polydispersities M_w/M_n calculated in this way for PPDT, which present a symmetrical chromatogram in the range of V_e upon 220 ml, are given in *Table 3*.

If we now consider that the chromatograms are the result of the product of the molecular weight distribution and a Gaussian distribution due to the axial dispersion, we can write, assuming a Weslau distribution[20,21]:

$$H_e(M) = H_0 \exp\left(-\frac{1}{\gamma'^2}\ln^2\frac{M_e}{M_0}\right) \qquad (3)$$

where $H_e(M)$ and M_e are the height of the chromatogram and the molecular weight deduced from the curve $\log M = f(V_e)$ for a given elution volume V_e; H_0 and M_0 are the same quantities at the peak.

The analysis of the chromatograms, after the linearization of equation (3), for elution volumes ranging from 220 to 350 ml allows us to calculate the polydispersity:

$$\gamma^2 = \ln\frac{M_w}{M_n} = \gamma'^2 - \left(\frac{\sigma^2}{a^2}\right)_{dif}$$

and the molecular weight $M_w = M_0 \exp(\gamma^2/2)$. The results

Table 3 Determination of the polydispersity for PPDT by g.p.c. from Tung's relation (equation 2)

Sample	η_{inh}	M_w	$\left(\frac{\sigma^2}{a^2}\right)_{chrom}$	γ^2	$\frac{M_w}{M_n}$
A27	1.84	9350	0.55	0.35	1.42
A57	2.30	12 000	0.91	0.71	2.04
A28	3.06	19 700	1.19	0.99	2.68

Table 4 Determination of the polydispersity and molecular weight M_w from the analysis of chromatogramms for PPDT in 96% sulphuric acid (equation 3)

Sample	η_{inh}	$M_{w_{l.s.}}$	γ^2	$\left(\frac{M_w}{M_n}\right)_{g.p.c.}$	$M_{w_{g.p.c.}}$
A 27	1.84	9350	0.41	1.51	10400
A 57	2.30	12000	0.61	1.84	13500
A 28	3.06	19700	0.84	2.31	22800
A 30	5.12	35000	1.105	3.00	35000
A 33	6.00	43500	1.15	3.20	50000

of this analysis are reported in *Table 4* for five PPDT samples for which the inherent viscosity varied from 1.86 to 6 dl/g. For the intermediate inherent viscosities (η_{inh} = 2–3 dl/g), the ratio M_w/M_n was approximately 2, but the polydispersity increased with molecular weight: M_w/M_n = 3.2 for the sample with η_{inh} = 6 dl/g.

Finally, the following conclusions could be made from the g.p.c. viscosity measurements:

(1) It was possible to fractionate PPDT by g.p.c. with sulphuric acid as eluent and to study each fraction after elution

(2) The universal calibration curve log $(\eta M) = f(V_e)$ established for PS samples in THF was also valid for PPDT in 96% sulphuric acid.

(3) The analysis of chromatograms allowed us to estimate with good approximation the polydispersity of the samples. The ratio M_w/M_n differed from the theoretical value M_w/M_n = 2 for some samples, especially when the molecular weight was high. This result is not surprising if we consider the procedure of polymerization, which is not a classical polycondensation.

(4) The molecular parameters determined by g.p.c., such as weight-average molecular weight M_w and intrinsic viscosity $[\eta]$, were in good agreement with the values obtained on unfractionated samples using classical methods.

CONFORMATION OF AROMATIC POLYAMIDES: EVALUATION OF THEIR RIGIDITY

Study of poly(1,4-phenylene terephthalamide)

The viscosity law of unfractionated PPDT dissolved in 96% sulphuric acid showed an exponent α of the Mark–Houwink relation of 1.09, in agreement with recent results[7] for molecular weights above 12000. This α value is also near the value obtained for poly (n-alkyl-isocyanate) and indicates that an intermediate conformation exists between a rod-like particle (α = 1.7) and a flexible chain (α = 0.8 in a good solvent). This intermediate conformation can be described by considering the model of a worm-like chain, or a chain with a finite persistence length.

To obtain more accurate information about the conformation of the aromatic polyamides and estimate the rigidity of the molecules, it was necessary to isolate fractions of a wide molecular weight range. Therefore, we have fractionated the PPDT by g.p.c. and characterized each fraction by combining the techniques of g.p.c., light scattering and viscosity measurements. In order to obtain larger quantities of material, a 'semipreparative' g.p.c. fractionation was carried out by injecting a larger volume of solution (ten times the volume used previously); we have fractionated five PPDT samples with η_{inh} values of 0.76, 2.95, 3.06, 5.12 and 7.9 dl/g respectively. For each fractionation, 10 or 12 fractions were collected and studied directly after elution by light scattering, or by viscosity measurements, or by both methods simultaneously; the concentration of polymer in the eluate was determined by u.v. at 330 nm. The high value of dn/dc (0.309 ml/g) and the good clarification of solvent and solutions after elution through the column allowed us to obtain very precise light scattering measurements. It should be noted that, for low inherent viscosity samples which were more concentrated, the results were obtained at zero concentration by direct dilution in the cell or in the viscosimeter.

The results for all the fractionations (molecular weights, radii of gyration and viscosities) are reported in *Figures 4* and *5*. *Figure 4* shows the variations of the radius of gyration as a function of the molecular weight in a log/log plot and *Figure 5* gives the viscosity law. Both variations are very well defined. On the plot of log $[\eta]$ *versus* log M_w, a linear

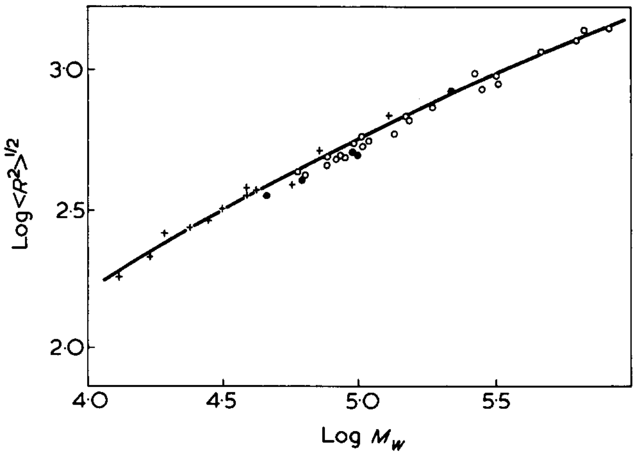


Figure 4 Variation of the radius of gyration $(R^2)^{1/2}$ *versus* molecular weight for the fractions of PPDT in 96% sulphuric acid: ○, fractions from sample of η_{inh} = 7.9 dl/g; ●, fractions from sample of η_{inh} = 5 dl/g; +, fractions from sample of η_{inh} = 3.06 dl/g

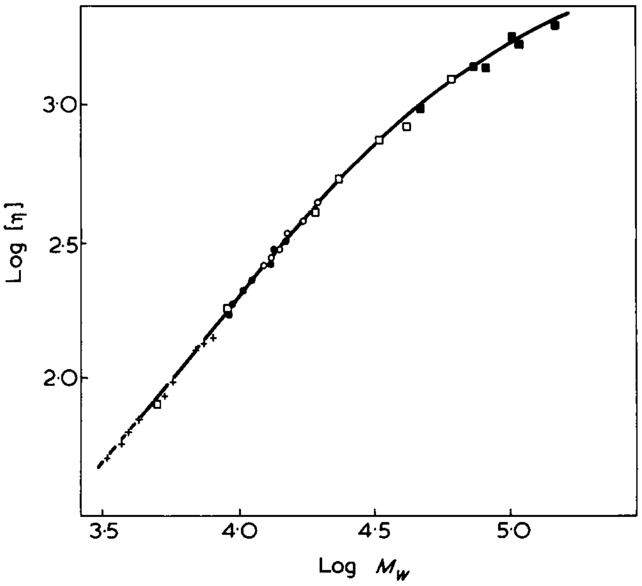


Figure 5 Viscosity–molecular weight relationship of PPDT in H_2SO_4 at 96% (fractions and unfractionated samples): ■, fractions from samples of η_{inh} = 7.9 dl/g; ○, fractions from samples of η_{inh} = 3.06 dl/g; ○, fractions from samples of η_{inh} = 2.95 dl/g; +, fractions from samples of η_{inh} = 0.76 dl/g; □, unfractionated samples

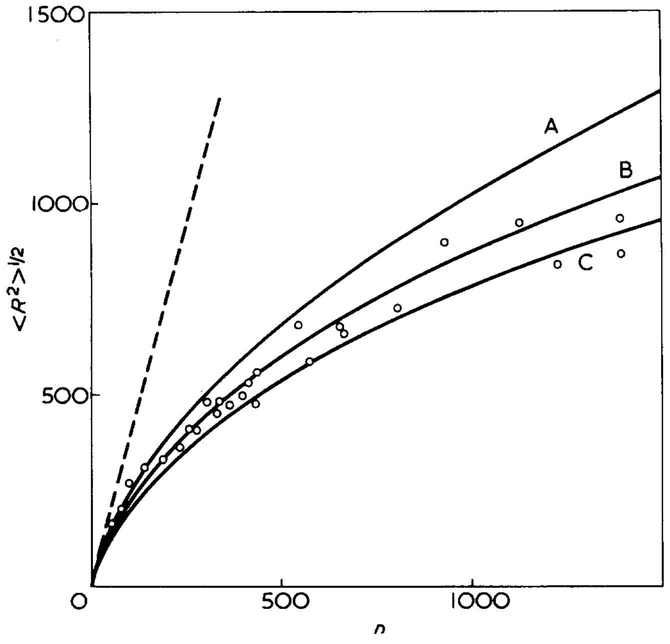


Figure 6 Relation between the radius of gyration $\langle R^2\rangle^{1/2}$ and degree of polymerization n_w for PPDT in H_2SO_4 at 96%. The curves are calculated according to equation (5) for a = 12 Å, and q = 150(C), 200(B) and 300(A) Å. — — —, rodlike particle; ○, experimental points

section was observed for fractions of low molecular weight ($M_w < 25\,000$) with a slope α of 1.20: this value is slightly higher than the value of $\alpha = 1.09$ which was determined on unfractionated samples. In the range of higher molecular weights ($M_w > 25\,000$) the coefficient α became lower as the molecular weight increased. This behaviour is characteristic for worm-like chain polymers[23].

Interpretation of results: evaluation of the persistence length

Molecular dimensions. The concept of the worm-like chain molecule, first introduced by Kratky and Porod[24], has often been used to explain the behaviour of stiff chain macromolecules such as DNA, cellulose derivates, nylon-1.

The mean square distance $\langle r^2\rangle$ for a worm-like chain is given by:

$$\langle r^2\rangle = q^2\left\{2x - 2[1 - \exp(-x)]\right\} \qquad (4)$$

and the mean square radius of giration is obtained by the relation[25]:

$$\langle R^2\rangle = q^2\left\{\frac{x}{3} - 1 + \frac{2}{x} + \frac{2}{x^2}[1 - \exp(-x)\right\} \qquad (5)$$

In both relations, q is the persistence length which characterizes the flexibility of the worm-like chain ($2q = \lambda^{-1}$, if λ is the reciprocal of the Kuhn statistical segment); $x = L/q$ where $L = Na$ represents the contour length, N being the number of repetitive segments and a the projection of this segment on the contour length.

To determine both parameters q and a for *para*-substituted aromatic polyamides, the experimental data for $\langle R^2\rangle^{1/2}$ as a function of the average degree of polymerization n_w were compared with the theoretical curves derived from equation (5) for different values of q and a. The length of the structural element was determined as 12.9 Å by X-ray diffraction studies[26]. The parameter a for the structural element in solution was only slightly lower and a value of 12–12.5 Å was determined. The theoretical curves with a = 12 Å and q = 150, 200 and 300 Å and the experimental points are reported in *Figure 6;* the best fit was obtained for q = 200 Å and the most probable value of q is 200 ± 50 Å. It was shown also that the choice of the value a (a = 11.5 and 12.5 for example) did not affect the determination of q. It was not possible to determine the radius of gyration for the low molecular weight fractions ($M_w < 12\,000$); the determination of the parameter q was not accessible from the molecular dimensions. However, these fractions exhibited an optical anisotropy Δ^2 which was not negligible; the depolarization factor ρ_u varied between 0.05 and 0.2. The relation between the optical anisotropy Δ^2 and the ratio ρ_u is given by:

$$\rho_u = \frac{6\Delta^2}{5 + 7\Delta^2} \qquad (6)$$

with

$$\Delta^2 = \frac{(\alpha - \beta)^2}{9\bar{\alpha}^2}$$

α and β being the principal polarizability of the particle and $\bar{\alpha}$ its average polarizability.

The optical anisotropy Δ^2 for a worm-like chain has been calculated elsewhere[27]. One can write:

$$\Delta^2 = \delta_0^2\left\{\frac{2}{x'} - \frac{2}{x'^2}[1 - \exp(-x')]\right\} \qquad (7)$$

where $x' = 3L/q$; $\delta_0^2 = (\alpha_0 - \beta_0)^2/9\bar{\alpha}_0^2$ is the optical anisotropy for the structural segment.

The analysis of the experimental results presented in a recent paper, leads to a value of persistence length, in the molecular weight range of 1200 to 8000, of q = 150 Å and for δ_0^2 a value of 0.4[27].

Intrinsic viscosity. Several theories have been developed which take into account the hydrodynamical properties (including viscosity, sedimentation coefficient, and rotatory diffusion constant) of rigid particles, stiff-chain macromolecules and worm-like chains[28–32]. These theories, such as Hearst's theory, give some relations which are valuables for limiting cases:

$\lambda L \gg 1$ (chain) and $\lambda L \ll 1$ (rod-like particle).

Recently, Yamakawa and Fujii[33] have proposed a new method to determine the intrinsic viscosity and the translational friction coefficient of worm-like chains without excluded volume by applying the Oseen–Burgers procedure to worm-like cylinder models. The parameters involved in the calculation are the contour length L($L = Na$), the persistence length q (or the Kuhn statistical segment length $\lambda^{-1} = 2q$), and the molecular diameter b. These calculations applied to DNA have also been used for stiff-chain macromolecules, such as PLGB, and poly(n-alkylisocyanates)[34].

The relations proposed by Yamakawa and Fujii for the viscosity are:

$$[\eta] = \frac{\phi_\infty L^{3/2}}{M} \times \frac{1}{1 - \sum_{i=1}^{4} C_i L^{-i/2}} \quad \text{for } L \geqslant 2.28 \qquad (8)$$

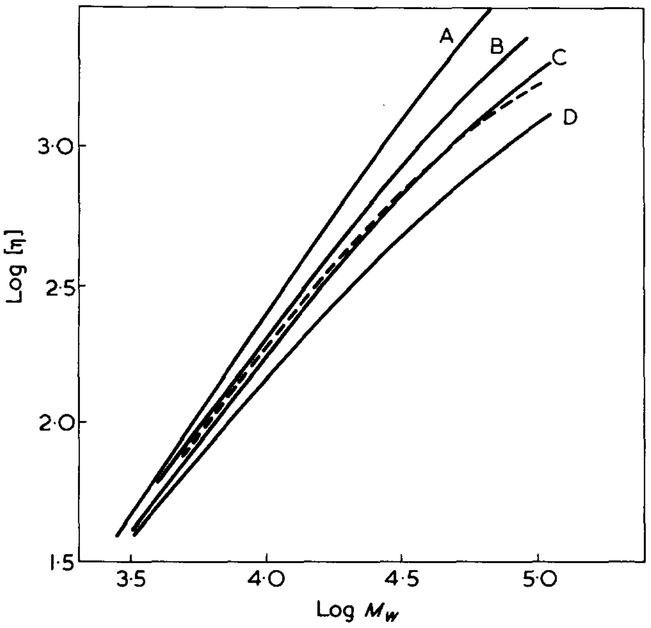


Figure 7 Viscosity law of PPDT in H_2SO_4 at 96%. Comparison between the experimental curve (— — — —) and calculated curves according the Yamakawa and Fijii theory (equation 8) with a = 12 Å, b = 6 Å and q = 100, 150 and 400 Å. A, q = 400; B, q = 200; C, q = 150; D, q = 100

where $\phi_\infty = 2.87 \times 10^{23}$ (if the viscosity is expressed in ml/g) and C_i are coefficients dependent on the molecular diameter b (see ref 33), and

$$[\eta] = \frac{\pi N_a L^3}{24M \ln (L/b)} \times \frac{f(L)}{1 + \sum_{i=1}^{4} A_i \ln (b/L)^{-i}} \quad \text{for } L < 2.28 \tag{9}$$

where $f(L) = (3/2)L^4\,[\exp(-2L) - 1 + 2L - 2L^2 + (4/3)L^3]$; N_a is Avogadro's number and A_i are constants independent of L and b: $A_i = 1.84, A_2 = 8.24, A_3 = 32.86$ and $A_4 = 41.10$.

In equations (8) and (9), $[\eta]$ represents the reduced intrinsic viscositic viscosity, because all lengths are expressed in units of Kuhn statistical element length λ^{-1}.

To determine the parameter of the worm-like chain from viscosity measurements, equations (8) and (9) were used to calculate the theoretical curves for various values of q, a and b. *Figure 7* shows the curves deduced from equation (8) with a = 12Å (the value which was determined previously), b = 6 Å (which is nearly of 5Å, the geometrical diameter derived from X-ray diffraction studies) and q = 100, 150, 200 and 400 Å.

By comparing these theoretical curves calculated for the non-reduced intrinsic viscosity and the experimental results (broken line), the best fit was obtained for q = 150 ± 20 Å, a = 12 Å and b = 6 Å in the range of molecular weights between 4000 and 100 000; in this range, the calculated curves from equations (8) and (9) were obtained with an accuracy of 1–1.5%.

Another representation proposed by Yamakawa and Fujii from equation (8) is to plot log ($[\eta]\ M^{-1/2}$) *versus* log M according to the relation:

$$[\eta] M^{-1/2} = \phi_\infty \left(\frac{2aq}{M_0}\right)^{3/2} \Gamma_1(L,b) \tag{10}$$

where

$$\Gamma_1 = \phi/\phi_\infty = \frac{1}{1 + \sum_{i=1}^{4} C_i L^{-i/2}}$$

M_0 is the molecular weight of the structural element (M_0 = 238). This representation is given in *Figure 8*; the curves are calculated for q = 150 and 200 Å. Good agreement was obtained for q = 150 Å, except perhaps for the highest molecular weights; this deviation can be explained by considering the presence of aggregates in the high molecular weight fractions which affected the molecular weight determination more than the viscosity measurements.

Another hydrodynamic property, the rotatory diffusion constant D_r, can be used to characterize the stiff-chain macromolecules. A recent study by flow birefringence has been carried out on unfractionated PPDT samples[35]. The information obtained from birefringence measurements (the rotatory diffusion D_r and the intrinsic birefringence $[n_i]$) confirm the proposal of the worm-like chain model for PPDT. From the D_r determination using Hearst's theory[31], and from the intrinsic birefringence $[n_i]$ according to the theory of Tsetkov[36], a value of q = 185 Å has been obtained.

*Study of poly(*p*-benzamide) PBA*

A similar study, as reported in the previous section on PPDT samples, was carried out on some fractions of PBA by combining g.p.c., light scattering and viscosity measurements. The variations of the radius of gyration and of intrinsic viscosity were investigated on only three PBA samples which had inherent viscosities of 1.65, 2 and 3 dl/g and were fractionated by g.p.c.

In the molecular weight range between 4000 and 16 000 the exponent of the Mark–Houwink relation was 1.5, indicating a more pronounced rigidity of the molecule. The variations of the intrinsic viscosity and the radius of gyration as a function of the molecular weight or the degree of polymerization were compared with the theoretical curves calculated from equations (5) and (8) for different values of q. The results are shown in *Figures 9* and *10*. The curves are calculated with values of b = 6 Å and a = 12 Å for PBA, which is

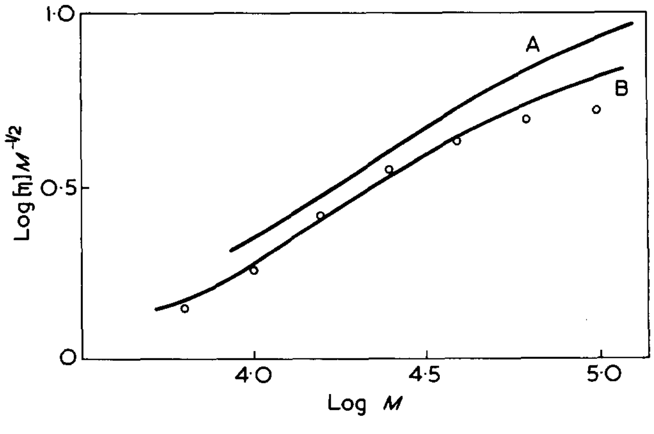


Figure 8 Plot of log $[\eta] M^{-1/2}$ *versus* log M for PPDT in 96% sulphuric acid: ○, experimental data. The curves are calculated according to equation (10) with a = 12 Å, b = 6 Å and q = 150 (B) and 200 Å (A)

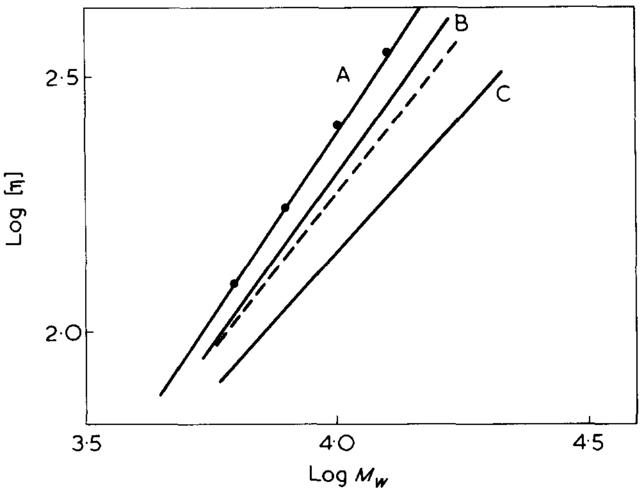
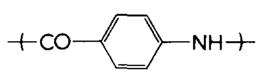


Figure 9 Intrinsic viscosity of PBA in H_2SO_4 at 96%. Comparison between experimental results (●) and calculated curves according to equation (8) with a = 12 Å, b = 6 Å and q = 100 (C), 200 (B) and 400 (A) Å (— — —, experimental curve for PPDT)

twice the length of the structural segment:



and which corresponds more closely to the repeat unit for PPDT. The analysis of the results indicate a longer persistence length q for PBA than we found for PPDT; the value of q of about 400–600 Å was determined from viscosity measurements and the determination of the molecular dimensions.

CONCLUSIONS

A model of a worm-like chain, which is a chain with a persistence length, seems to be the best to describe the properties of aromatic polyamides dissolved in a relatively good solvent such as 96% sulphuric acid. The determination of the persistence length q which characterizes the rigidity of the chain has been determined from molecular parameters, such as molecular dimensions (or radii of gyration), optical anistropy and hydrodynamical properties (intrinsic viscosity and rotatory diffusion coefficient). Values for the persistence lengths of PPDT and PBA determined by several different methods are summarized in *Table 5*.

The q values for PPDT obtained from different methods vary little and were found to be between 150 Å (from viscosity measurements) and 200 Å (from molecular dimension calculations).

The persistence lengths are 175 ± 25 Å for PPDT and 500 ± 100 Å for PBA, both measured in 96% sulphuric acid. The q parameter or the Kuhn statistical segment length is different for the two aromatic polyamides, but these q values are lower than the value determined for a rigid macromolecule such as PLBG which has q = 800 Å[34].

The difference between the q values for both aromatic polyamides, determined under the same conditions, is significant. This difference could be caused by a more effective conjugation or greater percentage of double-bond character of the amide group of the PBA molecule. Another hypothesis may be a difference in the degree of solvation for both polymers; additional studies are necessary to verify these questions.

A comparison of our results with some data from the literature, obtained by flow birefringence measurements for example, gave a q value of 1050 Å (λ^{-1} = 2100 Å) for PBA in sulphuric acid[9]. On the other hand, the persistence length has been evaluated to be 195 Å (λ^{-1} = 390) from sedimentation measurements using DMAc + LiCl as a solvent[37], but in this case, the system is different from our system (96% sulphuric acid).

From the viscosity–molecular weight relationship, Schaefgen *et al.*[7] have deduced a q value of 240 Å for both aromatic polyamides. It seems that the problem of the determination of conformation for aromatic polyamides is directly related to the difficulty of obtaining very precise values of the molecular weights by the direct and classical methods such as light scattering.

Another very important point is that the study of anisotropic, concentrated solutions of PDDT in 100% sulphuric acid by means of optical microscopy and X-ray diffraction shows that these macromolecules are nearly extended in the nematic phase[6]. Other stiff-chain macromolecules, for example poly(n-alkyl isocyanate)[38] exhibit in dilute solution the conformation of a worm-like chain with an identical or higher persistence length than that of the aromatic polyamides, but do not seem to give nematic phases. This difference can be explained because the chain–chain interactions are totall different.

It is not only the existence of nematic phases in concentrated solutions, but also the conformation of molecules in dilute solutions, which indicate that the role played by the solvent is not negligible. Recent information indicates that aromatic polyamides can exhibit intrinsic viscosity values in 100% sulphuric acid[39] or in chlorosulphonic acid[40] which are higher than those determined in 96% sulphuric acid. This behaviour is related to a more pronounced rigidity of the aromatic polyamides in the first two solvents.

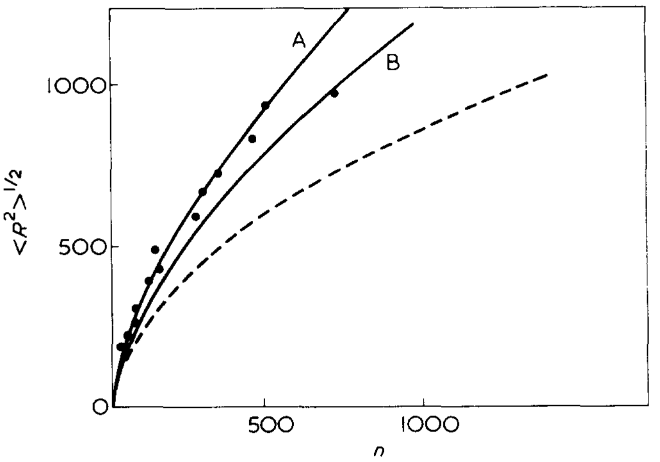


Figure 10 Variation of radius of gyration *versus* the degree of polymerization M_w for PBA in H_2SO_4 at 96%. ●, experimental points. The curves are calculated according to equation (5) with a = 12 Å and q = 400 (B) and 600 (A) Å. (— — —, experimental curve for PPDT)

Table 5 Persistence length q obtaining by various methods for PPDT and PBA in 96% sulphuric acid

Methods		q(Å) PPDT	q(Å) PBA
Light scattering	molecular dimensions	200	400–600
	anisotropy	150	–
Hydrodynamical properties	viscosity	150	400
	flow birefringence	185	–

The problem of the relation between the nature of solvent and the polymer conformation in dilute solution is very important and is expected to be a clearer insight of the vehaviour of stiff chain molecules in solution.

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