Dilute solution properties of thermotropic polymers: aromatic polyazomethines

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The dilute solution properties of some polyazomethines have been investigated. Poly(nitrilo-2-methyl-1,4-phenylene nitrilomethylidine-1,4-phenylene methylidine) (MePNPM) was studied. The measurements of intrinsic viscosities, molecular weight and depolarization ratio were made in 96% sulphuric acid and in methane sulphonic acid for these polymers. A side by side aggregation is observed with time in the second solvent. In order to obtain a well defined law of viscosity, fractionation by gel permeation chromatography was made. A small amount of aggregated particles was observed for the samples which have been submitted to a thermal treatment. Nevertheless, a well defined law of viscosity has been obtained. From the viscosity law and the variation of the apparent molecular anisotropy, the rigidity of the molecule has been evaluated; the persistence length q which characterizes this rigidity has been found to equal 150 Å ± 25 Å.

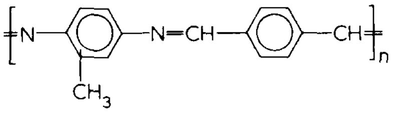
INTRODUCTION

Recently, a new class of polymers has appeared in the patent literature[1,2], called thermotropic polymers and exhibiting an anisotropic phase without solvent. Such phases are obtained by increasing the temperature. Two groups of these polymers are now known: the aromatic polyesters and the aromatic polyazomethines. The second group is considered herein. An anisotropic melt is obtained at a temperature which is generally superior to 250°C. A great tenacity is observed from the fibres or the films obtained with these anisotropic melts. From a fundamental point of view, these polymers are important, because they are the first macromolecules to present liquid–crystal structure in the absence of solvent. Consequently, the molecular parameters, which are related with this property must be known. Strong acids, like sulphuric or methane sulphonic acid are apparently the only solvents for these aromatic polyazomethines. In the patent, the synthesis is described, but the only given characteristic is the inherent viscosity at 0.5% by weight of polymer in 96% sulphuric acid or methane sulphonic acid. In order to characterize these systems more precisely, it seemed important to measure the fundamental molecular parameters such as the molecular weight, the intrinsic viscosity, the relation between the viscosity and molecular weight, the rigidity of the molecule, and to ask whether they present a rigid rod configuration, like poly(γ-benzyl-L-glutamate)[3], or worm-like chain configurations like aromatic polyamides[4] which give nematic mesophases in sulphuric acid[5].

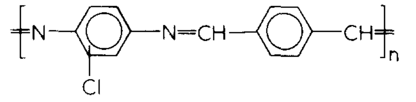
All these points and also the influence of the nature of the solvent on properties in dilute solution are considered herein.

The aromatic polyazomethines which are known to give mesophasic behaviour have substituents like methyl or chloride on the phenylene ring. The poly(nitrilo-2-methyl-1,4-phenylene nitrilomethylidine-1,4-phenylene methylidine) which we have called Me-PNPM has been mainly studied:

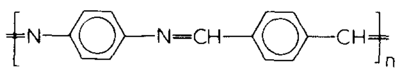
Me—PNPM :



Another product has also been envisaged: the poly(nitrilo-2-chloro-1,4-phenylene nitrilomethylidine-1,4-phenylene methylidine) called Cl-PNPM:



A further polymer, which is not itself thermotropic, but which is chemically similar to the previous products has also been studied. The poly(nitrilo-1,4-phenylene nitrilomethylidine-1,4-phenylene methylidine) or PNPM:



SYNTHESIS AND EXPERIMENTAL METHODS

Synthesis of the samples

All the samples were synthesized using the methods described in the United States patent of 'Du Pont de Nemours'[2] The polycondensation of the paraphenylene diamine or its chlorinated or methylated derivatives with terephthalic aldehyde gives these products.

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Synthesis of the Me-PNPM samples. The polycondensation of the 2-methyl-paraphenylene diamine with terephthalic aldehyde has been carried out first in a mixture of hexamethylphosphorotriamide (HMPT), N-methylpyrrolidone (NMP) and 4% of lithium chloride. The polymer thus obtained is denoted M_{11}. A second sample was made in absolute ethyl alcohol (M_{14}). A portion of these two samples was taken. The other portion was then submitted to a thermal treatment at 300°C, in an inert atmosphere. Two series of samples were then obtained: M_{12}, M_{13} and M_{15}, M_{16}, M_{17} respectively from M_{11} and M_{14}. The conditions of the post-polymerization are given in *Table 1.* Two samples were furnished by the Rhone-Poulenc Company. The first (M_{10}) was obtained in HMPT, NMP + LiCl (5%); a chain inhibitor (4-amino acetanilide) was added at the end of the polymerization. The second was prepared at 300°C like M_{12} or M_{13} (post-polymerization during 25 minutes of a sample prepared in HMPT, NMP + LiCl 4%). In order to examine the efficiency of the chain inhibitor, sample M_{10} was post-polymerized at 300°C for 10 min, to obtain M_{10}^{*}.

Synthesis of the samples of PNPM and Cl-PNPM. A sample of Cl-PNPM was prepared by polycondensation of 2-chloroparaphenylene diamine and terephthalic aldehyde in dimethyl acetamide with 4% of LiCl. The post-condensation of this polymer can be obtained at 310°C. Two samples of PNPM were also prepared: M_2 (in HMPT, NMP and LiCl), and M_4 (in absolute ethyl alcohol).

All these polycondensations were effected by stirring at room temperature. The samples were then washed with water (twice) and methanol (thrice), and dried for 24 h under vacuum at room temperature.

Table 1 Experimental post-polymerization conditions of Me-PNPM.

Sample	duration of the post-polymerization
M_{11} (HMPT+NMP+LiCl)^a	0 (initial polymer)
M_{12}	30 min at 300° from M_{11}
M_{13}	75 min at 300 from M_{11}
M_{14} (absolute ethyl alcohol)^a	0 (initial polymer)
M_{15}	15 min at 300° from M_{14}
M_{16}	35 min at 300° from M_{14}
M_{17}	50 min at 300° from M_{14}

^{a}Solvent of the initial polycondensation

The original samples were an orange to red brown powder. The products resulting from the post-polymerization are very hard and grain like. These were ground to a powder.

In dilute solution (H_2SO_4 96% or methane sulphonic acid), a red brown colour is obtained. An important absorption peak is observed in the visible spectra with a maximum at 400–450 nm.

Experimental methods

All the measurements for characterization of the unfractionated samples were made in 96% sulphuric acid (Prolabo). By extrapolation at $c \rightarrow 0$ of the reduced viscosity or of the inherent viscosity the intrinsic viscosity was determined. These viscosities were realized using a Ubbelhode type capillary viscosimeter (0.7 mm diameter).

Because of the absorption and of a strong fluorescence of the solution when illuminated with green (λ = 546 nm) or yellow (578 nm) light, the scattering measurements were made using red light (λ = 632 nm). The light scattering apparatus, a FICA 42000, was modified with its light source replaced by a He-Ne gas laser (5 mw) that gave vertically polarized radiation at 632 nm[6].

The solutions were clarified by centrifugation (3–4 h at 25000 g).

The refractive indices increments dn/dc were measured at 632 nm using a Brice Phoenix differential refractometer, the light source was also replaced by a He-Ne gas laser.

The fractionation of the samples was obtained by gel permeation chromatography (g.p.c.). The same apparatus which was used for the study of the aromatic polyamides[4], is a simplified Water's type apparatus, using nitrogen under pressure to obtain a 1 ml/min flow. The polymer concentration is detected by ultra-violet measurements at 280 nm. The 8 ml fractions were then studied by viscosity and light scattering measurements.

RESULTS AND INTERPRETATION

Characterization of unfractionated Me-PNPM samples

Intrinsic viscosity. The intrinsic viscosities $[\eta]$ of all the samples of Me-PNPM were determined at 25°C in 96% H_2SO_4. The intrinsic viscosity increases with the time of post-polymerization (see *Table 2*). The Huggins constant has abnormally high values (between 0.8 and 3.2 and even more for M_{17}).

Table 2 Molecular characteristics of unfractionated samples of MePNPM in 96% H_2SO_4 (intrinsic viscosities, molecular weight, depolarization ratio and dissymmetry)

Samples	$[\eta]$ ml.g^{-1}	M_w	ρ_v	Z
M_{10}	–	4500	0.24	1.06
M_{11}	48	3550	0.29	1.04
$M_{12}{}^a$	118	6900	0.14	1.1
$M_{13}{}^a$	210	39 000 27 000^b	0.06	1.78
M_{14}	28	1850	0.34	1.02
$M_{15}{}^a$	110	5300	0.18	1.09
$M_{16}{}^a$	150	10 000 8000^b	0.105	1.35
$M_{17}{}^a$	170	17 700 12 500	0.072	1.55
$M_{CF}{}^{113a}$	235	47 000 30 000^b	0.025	1.70

^{a}post-polymerized samples
$^b M_w$ calculated using the values of c/I at high angles

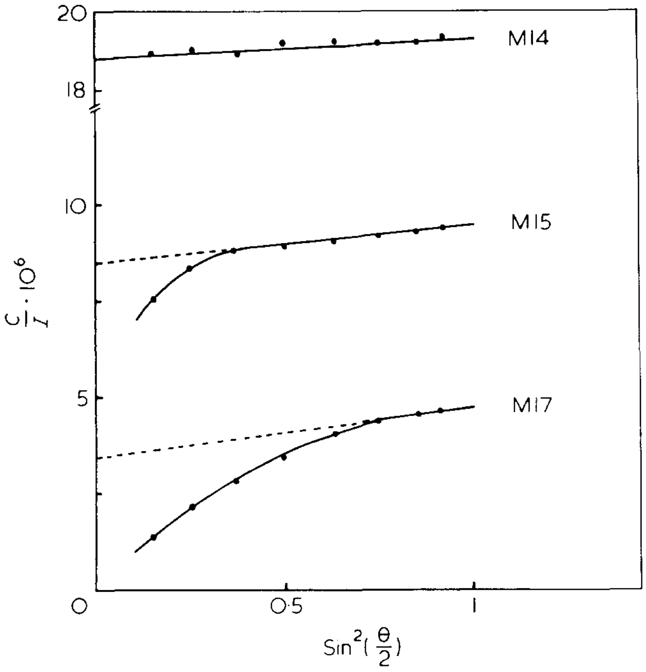

Figure 1 Variation of the scattered intensity versus the angle of observation for some samples of MePNPM in 96% sulphuric acid

Molecular weight and anisotropy. The dn/dc value at 632 nm was found to be equal to 0.62 ± 0.01 for all the samples. The angular distribution of the scattered intensity (variation of c/I versus $\sin^2(\theta/2)$) was determined.

A linear angular distribution with a very low dissymetry (Z = 1.02; 1.05) was found for the samples which are not post-polymerized. On the contrary, for post-polymerized samples a curvature in the angular distribution appears at small angles. This curvature which corresponds to a higher scattered intensity increases with the time of post-polymerization. The evolution of the angular distribution is given in *Figure 1* for samples M_{14}, M_{15} and M_{17}.

The solutions also give rise to a non-negligible apparent optical anisotropy. The depolarization ratio ρ_v varies between 0.025 and 0.36 (ρ_v is the ratio of the scattered intensity horizontally and vertically polarized with the incident light vertically polarized). The results of the measurements on unfractionated samples are reported in *Table 2.* The molecular weights were calculated using the scattered intensity at $\theta = 90°$ and the anisotropy correction (Cabanne's factor: $3 + 3\rho_v/3-4\rho_v$) was made. For the samples which give a large curvature, the values of the molecular weight calculated using the extrapolation at high angles are also given, along with the evolution of the depolarization factor and the dissymmetry.

The intrinsic viscosity versus the molecular weight is shown in *Figure 2.* Two domains can be observed. For the initial samples and for some of the post-polymerized ones, a linear variation is observed. A Mark–Houwink relation can be defined: $[\eta] = 4.32 \times 10^{-3} M^{1,15}$.

In fact, the constants 'K' and 'α' are not well defined (α = 1.15 ± 0.1). For the higher molecular weight, the intrinsic viscosities $[\eta]$ are lower than those calculated with the earlier relation.

The viscosities and the angular distribution obtained for these samples seem to indicate the presence of highly aggregated particles. These have little influence on the viscosity, but they lead to high molecular weight values.

FRACTIONATION AND CONFORMATION OF MePNPM

Fractionation by g.p.c. In order to define more accurately the law of viscosity of the fractions for a large molecular weight range and to clarify the problem of the post-polymerized samples (i.e. are there aggregated particles or a high polydispersity), a semi-preparative g.p.c. fractionation was made. For all fractionations of 4 ml samples in solution in H_2SO_4, fractions were collected (8 ml) and then studied by light scattering and viscosity measurements. The concentrations were determined by ultra-violet absorption at 280 nm, using a calibration curve.

Figure 3a shows the result of the fractionation of the non post-polymerized M_{11} sample.

We give the chromatogram of the variation of the concentration Δc (in optical density: DO) of the scattered intensity (ΔI measured at 90°) versus the elution volume. These two chromatograms give the molecular weight distribution (curve a), the intrinsic viscosity is assumed to be equal to the specific viscosity (the concentrations are low) and its variation is represented by the curve b. The variation of the depolarization ratio (ρ_v) is given by the curve c.

The molecular weight M_w and the intrinsic viscosity $[\eta]$ decrease regularly with the elution volume V_e. The molecular weights vary from 8000 to 1750 and the intrinsic viscosity from 78 to 18.5.

A different behaviour is observed for the post-polymerized samples. *Figure 3b* shows the fractionation of the sample M_{16}. The chromatogram $\Delta c = F(V_e)$ appears to be regular, but, in the small elution volume, macromolecules with high molecular weight and high molecular dimensions exist. Also, a low intrinsic viscosity is another peculiarity of these macromolecules. The higher curve gives the variation of M_w versus V_e for the fractions that have an elution volume larger than to 200 ml. (For these fraction there is no angular disymmetry). The first fractions probably give rise to aggregated particles (their molecular weights vary from 120 000 to 500 000), rather than molecularly dispersed fractions of high molecular weight. For this sample, the quantity of aggregates can be evaluated to be 5%. This point will be studied further.

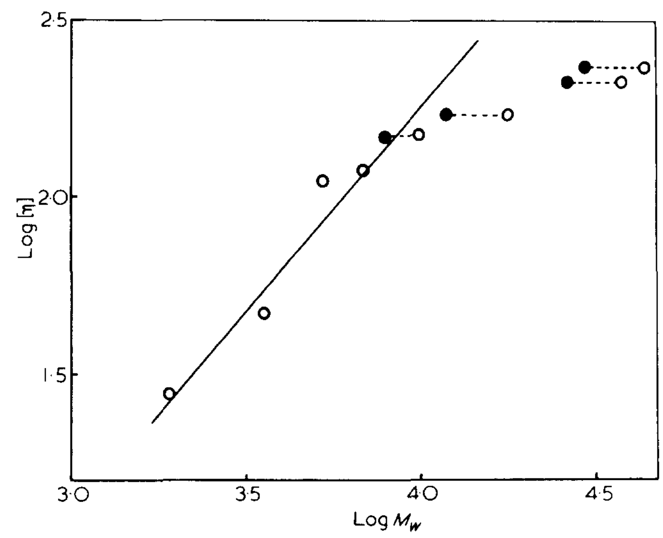

Figure 2 Viscosity law of the unfractionated samples of MePNPM in sulphuric acid. ○, molecular weight determined at θ = 90°; ●, molecular weight obtained using the extrapolation at high angles

Using the results obtained for the fractions (without the first fractions of the post-polymerized samples), the law of viscosity log $[\eta] = f(\log [M])$ can be determined: *Figure 4*. A well defined law is obtained for molecular weights varying from 1250 to 28 000 and the Mark–Houwink relation $[\eta] = KM^{\alpha}$ can be written as:

$$[\eta] = 1.9 \times 10^{-3} M^{1.20}$$

It is remarkable that the law of viscosity of the unfractionated samples for molecular weights varying from 1850 to 10 000 has the same exponent 'α' as the law for fractionated samples. On the other hand, the parameter K is lower for the fractionated than for the unfractionated samples and this can be explained by the value of the 'α' exponent which is greater than one.

G.p.c. behaviour, properties of the peak fractions. As for the aromatic polyamides[4] (polyparaphenylene terephthalamide), we have tried to observe the independence of the universal calibration curve (log $[\eta M] = f(V_e)$ with the polymer and the solvent used. The calibration of the column has been realised first, using monodisperse samples of polystyrene in solution in tetrahydrofuran (their molecular weight were chosen between 6000 and 1.6×10^6). The characteristic of the column (efficiency and selectivity) is given by σ^2/a^2 (σ is the half width of the chromatogram of a monodisperse sample and a is the slope of the calibration curve $V_e = a \log M + b$; σ^2/a^2 found to be equal to 0.54 i.e. relatively middle efficiency). The calibration curve of the Me–PNPM can be calculated using that of the polystyrene, if the law of viscosity of the two systems are known and if the universal calibration curve is respected[7]. A MePNPM of molecular weight M_2 gives the same elution volume as a polystyrene of molecular weight M_1 if:

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

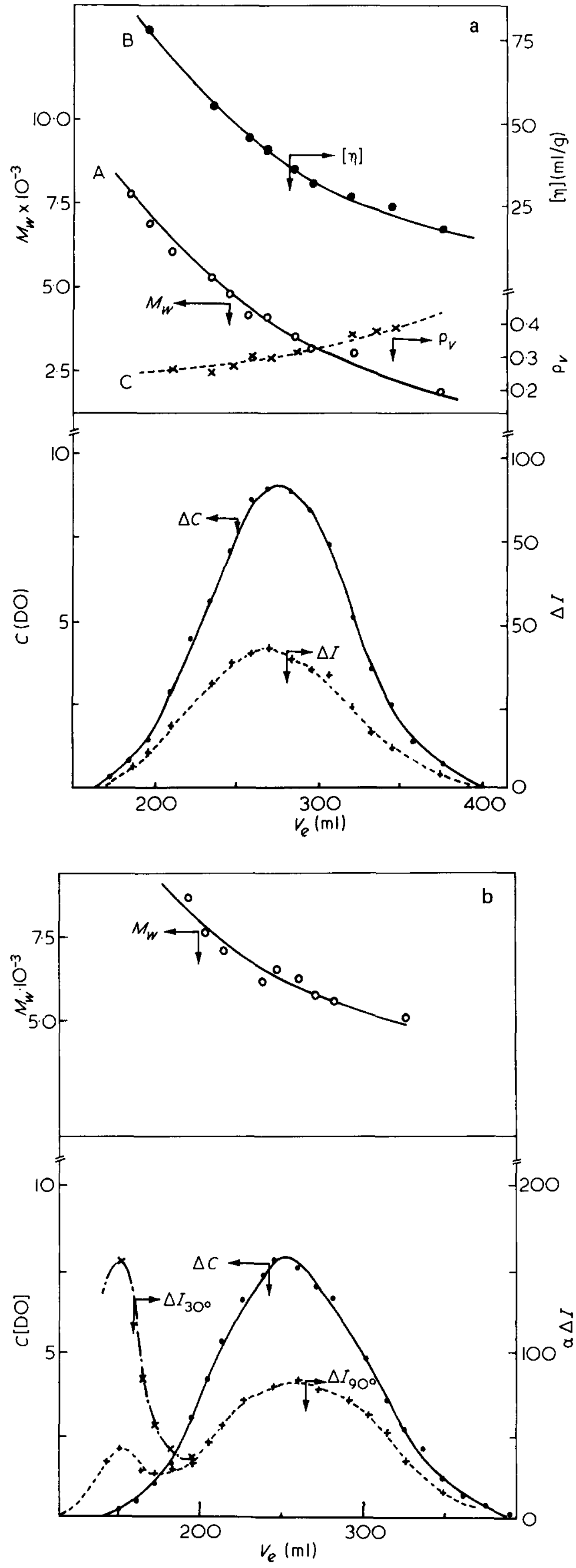

Figure 3a and b: Chromatogram of a non-post polymerized (3a) and of a post-polymerized (3b) sample of ME-PNPM. *c*, concentration in arbitrary units (optical density); Δ*I*, scattered intensity of the fractions; M_w, molecular weight, [η] intrinsic viscosity; ρ_v, depolarization ratio

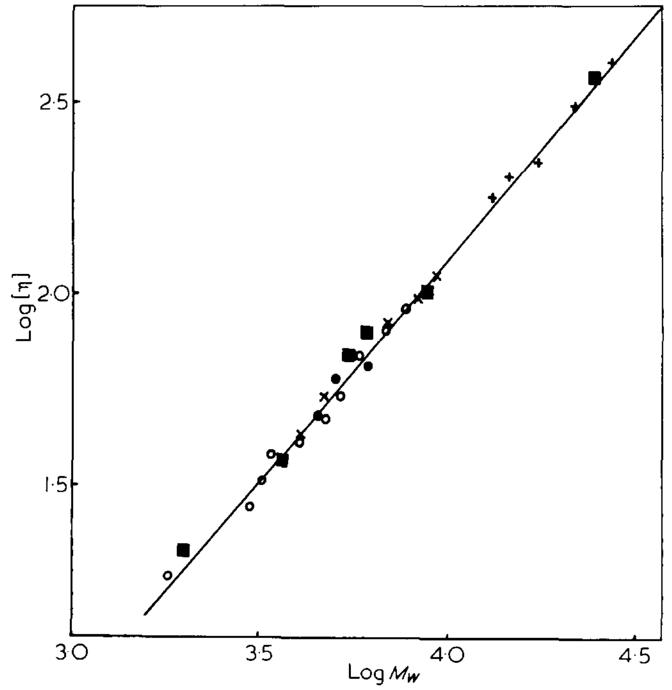

Figure 4 Viscosity law of the Me-PNPM in 96% sulphuric acid. ○, fractions of samples M_{11}; ×, fractions of sample M_{16}; +, fractions of sample M_{CF113}; ■, peak fractions

where α_1, K_1 and α_2, K_2 are respectively the parameters of the laws of viscosity of polystyrene in THF and of MePNPM in H_2SO_4. This calculated calibration curve is given in *Figure 5* and can be compared to the experimental results obtained for the fractions at the peak of the chromatogram.

All of these results i.e.: elution volume V_e, molecular weight M_w, depolarization ratio ρ_v and intrinsic viscosities of the fractions to the peak are summarized in *Table 3*. The molecular weight of the unfractionated samples and the percentage of the aggregated particles (this quantity is approximated using the variation of the concentration and of the scattered intensity with the elution volume) are also given in this table.

The experimental curve of the distribution of molecular weight versus the elution volume for MePNPM is also given in *Figure 5*. A shift from the calibration curve to the higher elution volume is observed. This shift increases with decreasing the molecular weight. This behaviour can be explained by an adsorption of the polymer on the support of the column. This can be due to the difference of the affinity of the solvents and of the polymers considered with the gel[8].

The polydispersity is difficult to estimate, because of this adsorption, and the Tung's Method[9] cannot be used without correction. Nevertheless, the polydispersity of the smaller sample has been estimated to be 1.7 to 2, and the polydispersity of the larger samples from 2 to 2.4.

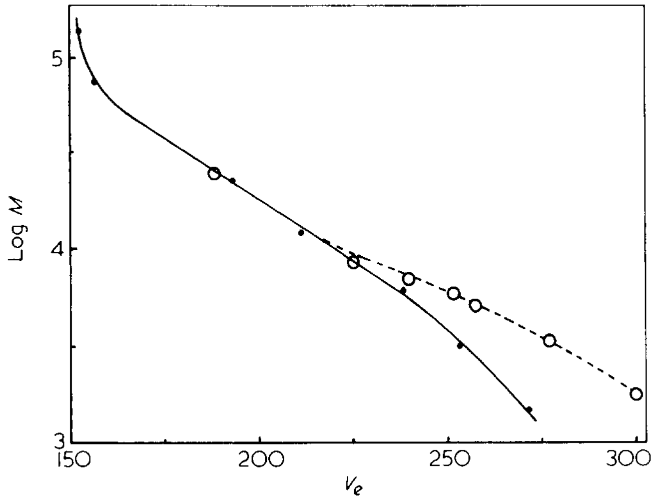

Figure 5 Calibration curve of the MePNPM in 96% sulphuric acid. log M_w versus the elution volume V_e. ○, experimental points; ●, theoretical curve obtained for the MePNPM using the universal calibration curve determined with samples of polystyrene in tetrahydrofuran

Study of the aggregated fractions

As can be seen from *Figures 4a* and *4b*, a very different behaviour is observed for the non post-polymerized and the post-polymerized samples. For the latter, the first fractions are characterized by high molecular weight, and non negligible molecular dimensions but low viscosities. The hypothesis of the presence of compact aggregates, with a low friction coefficient (thus a low viscosity) fits the experimental results.

In order to have more precision with these high molecular weight fractions, some of these were collected for further study (especially the 3 first fractions from M^*_{10}, which give a high scattered intensity). These 3 fractions were thermally treated: 2 h at 40°C and then 12 h at 40°C. The light scattering measurements (molecular weight M_w, radius of gyration $(\overline{R^2})^{1/2}$ and depolarization ratio ρ_v) initially and after the both thermal treatment are given in *Table 5*, along with the intrinsic viscosities at the end of the thermal treatments. The molecular weight and the radius of gyration decreased rapidly by this treatment. On the other hand, the viscosities do not vary significantly and they remain low at 95, 96 and 106 ml/g for the molecular weight of 140000, 50000; 25500 respectively. This evolution cannot be explained by a degradation of molecularly dispersed particles with high molecular weight because: firstly, the viscosities do not vary simultaneously with the molecular weight, and secondly, the middle fractions (fraction to the peak for example) are not sensitive to the thermal treatment. The most realistic hypothesis is the presence of aggregates which

Table 4 Thermal treatment of the first fractions of a post-polymerized sample M^*_{10}. Evolution of M_w, radius of gyration $(R^2)^{1/2}$, ρ_v with the thermal treatment and intrinsic viscosity after the treatment

Fractions		Thermal treatment at 40° C $t = 0$	$t = 2h$	$t = 12h$
F_1	M_w	830 000	195 000	140 000
	$(R^2)^{1/2}$	1825	1350	700
	ρ_v	0.02	0.02	0.04
	$[\eta]$	–	–	96
F_2	M_w	170 000	82 000	49 500
	$(R^2)^{1/2}$	1050	804	540
	ρ_v	0.03	0.03	0.06
	$[\eta]$	–	–	95
F_3	M_w	65 000	38 000	25 500
	$(R^2)^{1/2}$	810	660	430
	ρ_v	0.04	0.05	0.1
	$[\eta]$	–	–	105

Table 3 Properties of the peak fractions (elution volume V_e intrinsic viscosities $[\eta]$, molecular weight M_w and depolarization ratio)

Sample	V_e (ml)	$[\eta]$ ml.g^{-1}	M_w	ρ_v	% aggregate	M_w[a]
M_{14}	300	22	1900	0.34	0	1850
M_{11}	276	38	3400	0.31	0	3850
M_{10}	257	74	5300	0.25	0	4500
M_{16}	252	86	6200	0.20	~5	10 000
M_{17}	240	–	7000	0.10	15–18	17 700
M_{16}	250	105	9000	0.10_5		–
	–	–	14 800[c]	0.085[b]		
$M_{CF_{113}}$[c]	195	314	23 400	0.026	~30	47 000

[a] Molecular weight of unfractionated samples
[b] Molecular weight and depolarization ratio of a fraction, before the peak
[c] Sample obtained after two post polymerizations.

Table 5 Behaviour of Me-PNPM in methane sulphonic acid. Evolution of the parameters with the time; —light scattering measurements: molecular weight M_w and depolarization ratio ρ_v — Intrinsic viscosity $[\eta]$ — Refractive index increment dn/dc — $\bar{n}$ is the degree of association

Sample	time (in h)	dn/dc (ml.g^{-1})	M_w	ρ_v	$[\eta]$	$\bar{n}$
M_{11}[a] $\eta = 48$ $M_w = 3550$ $\rho_v = 0.29$	3	0.55	3500	0.24	69	~1
	24	0.495	24 100	0.35	36	~7
	48	0.45	40 600	0.385	18	~11.5
	120	0.43	—	—	—	—
	24 + 12 (at 40°C)	0.45	67 000	0.38	15.5	~19
M_{14}[a] $\eta = 28$ $M_w = 1850$ $\rho_v = 0.34$	3	0.55	2550	0.32	44	~1.4
	12	0.50	8000	0.35	38	~4.5
	48	0.45	46 600	0.385	18.5	~25
M_{12}[a] $\eta = 118$ $M_w = 6900$ $\rho_v = 0.14$	3	0.55	7600	0.13	185	~1
	48	0.45	41 500	0.39	16.3	~6

[a] characteristics in H_2SO_4 at 96%

are sensitive to thermal treatment. The model of an ellipsoid with a high density of polymer (very compact) seems to be the more probable description for the aggregates found in the first fractions.

Conformation of the Me-PNPM

The exponent α of the viscosity law ($\alpha = 1.20$) indicates a semi-rigid conformation, intermediate between the flexible chain ($\alpha = 0.8$ in a good solvent) and the rigid rod ($\alpha = 1.6$). The semi-rigid chain can be described by a worm-like chain model; this worm-like chain is characterised by its persistence length q. Numerous methods are available for the determination of this parameter: from the molecular sizes, the intrinsic viscosity, translation or rotation diffusion constant, molecular anisotropy etc.

To measure the rigidity of the Me-PNPM, two methods are used:

(1) *Viscosity law:* the intrinsic viscosity of a worm-like chain has been calculated by Yamakawa and Fujii[10] using a curved continuous cylinder model. The parameters involved in the calculations are the contour length ($L = Na$, N and 'a' being the number and the length of the element), the persistence length q or the Kuhn statistical segment $\lambda^{-1} = 2q$ and the diameter b of the cylinder. The proposed relations by the authors are:

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

where ϕ_∞ is the Flory's constant and C_i are numerical constants depending on b; or

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

where $f(L) = 3/2L^4\{\exp(-2L) - 1 + 2L - 2L^2 + (4/3)L^3\}$ and A_i are numerical constants. In both expressions, all the lengths are expressed in the Kuhn statistical segment λ^{-1}.

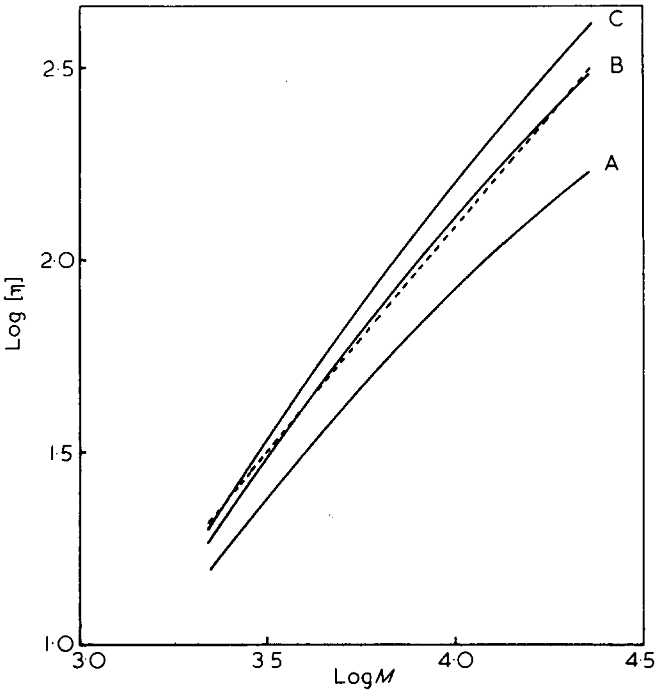

Figure 6 Viscosity law of the MePNPM plotted with the theoretical curve calculated using the Yamakawa Fujii equations for the persistence lengths q = 50Å (curve a), q = 100Å (curve b), q = 150Å (curve c); dotted line: experimental curve

The chain diameter of Me-PNPM can be estimated to be equal to 5 Å. The calculated curves for $b = 4$ Å, $a = 11$ Å and $q = 50{,}100$ and 150 Å are given in *Figure 6* and compared with the experimental curve (dotted line). The best argreement is obtained for $b = 4$–5 Å, $a = 11$–12 Å and $q = 125$ Å ± 25 Å. The experimental molecular weights are less than 30 000; these values are not sufficiently high to observe the decreasing of the α exponent of the viscosity law for the higher molecular weight, this behaviour being characteristic of a worm-like chain.

(2) *Apparent molecular anisotropy as measured by light scattering.* The apparent optical anisotropy Δ^2 of a molecule can be determined from the depolarization ratio ρ_v by the relation $\Delta^2 = 5\rho_v/3 - 4\rho_v$ when the incident light is vertically polarized. On the other hand, the relation between the optical anisotropy and the persistence length q for a worm-like chain is[11]:

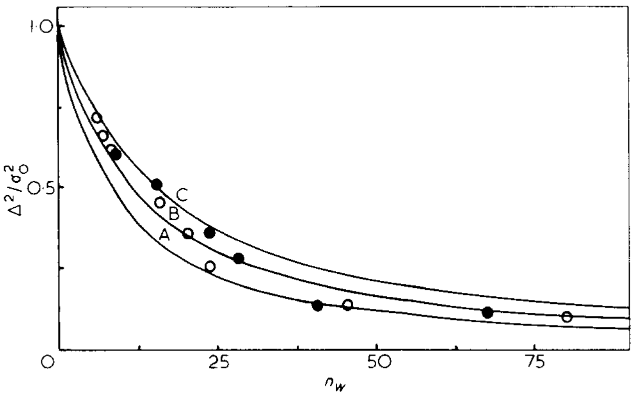

Figure 7 Ratio of the apparent optical anisotropy of samples of MePNPM on the apparent optical anisotropy of the monomer (Δ^2/δ_0^2) versus the number in weight of monomer, plotted with the theoretical curve determined for q = 100Å (curve a), q = 150Å (curve b), q = 200Å (curve c). ○, unfractioned samples; ●, peak fractions

$$\Delta^2 = \delta_0^2 \left\{\frac{2}{x'} - \frac{2}{x'^2}(1 - e^{-x'})\right\}$$

where $x' = 3Na/q$ and δ_0^2 is the optical anisotropy extrapolated to the monomer unit. The experimental variations of ρ_v versus the weight number of monomer units gives an extrapolated value of $\rho_v = 0.43 \pm 0.02$. *Figure 7* shows the calculated curves with a = 11 Å, $\delta_0^2 = 1.68$ ($\rho_v = 0.43$) and q = 100, 150 and 200 Å. The experimental points (for some unfractionated samples and fractions at the peak: see *Tables 2* and *3*) are also plotted on this diagram and show a fit between 100 and 200 Å; thus the persistence length can be evaluated to be q = 150 Å ± 50. This value is consistent, but slightly higher than that found from the viscosity law (q = 125 Å ± 25).

BEHAVIOUR OF THE Me-PNPM IN METHANE SULPHONIC ACID

Substituted or unsubstituted polyazomethines are also soluble in some derivatives of sulphonic acid (chloro sulphonic acid: $ClSO_3H$ and methane sulphonic acid: CH_3SO_3H). Therefore it seemed important to examine the influence of the nature of solvent on physico-chemical properties of thermotropic polymers. For this study, measurements by light scattering and viscosity were carried out on samples of Me-PNPM in methane sulphonic acid. A very peculiar behaviour is observed in this solvent. All the studied parameters are functions of time and probably of temperature. The refractive index increment dn/dc which is equal to 0.58 when measured 1 h after dissolution, decreases with time to attain 0.50–0.52 after 6 h and 0.43 after 120 h. This variation of dn/dc with the time can be explained considering the evolution of the absorption spectra in ultra violet and visible light* (i.e. in relation with the abnormal dispersion). The variation with the time for the different parameters (i.e. molecular weight M_w, depolarization factor ρ_v and intrinsic viscosity $[\eta]$) are given in *Table 5*. An increase of the molecular weight with a decrease of the viscosity and an increase of the apparent optical anisotropy is observed. We must note that it is impossible to measure a radius of gyration even for the highest molecular weight: the angular distribution of the scattered intensity ($C/\Delta I = f(\sin^2\theta/2)$) is independent of the angle, the disymmetry Z is of the order of 1 to 1.05, so the radius of gyration must be lower than 100 Å. The most probable model is of side by side aggregation of rod ($\bar{n}$ being the average number of molecules per aggregate or the degree of association). This behaviour in methane sulphonic acid seems to be very general, because it was observed with Me-PNPM, Cl-PNPM and also PNPM samples.

In order to be more explicit, we have tried to estimate theoretically the intrinsic viscosity of such a system. An expression of the intrinsic viscosity of a solution of rods has been given by Hearst[12]:

$$[\eta] = \frac{\pi N_a L^3}{90M}\left\{\frac{1}{\log\left(\frac{L}{a}\right) - 2.72 + 0.66\left(\frac{a}{b}\right)} + \frac{3}{\log\frac{L}{a} - 2.72 + 1.33\left(\frac{a}{b}\right)}\right\}$$

where L is the contour length of the molecule, b the hydrodynamic diameter, 'a' the projection of the monomer unit on the contour length and M the molecular weight of the rod.

Using the characteristics of the sample M_{11} (see *Table 5*) we can find the hydrodynamic diameter of these aggregates; if we let the hydrodynamic diameter of the aggregate be proportional to the square root of the number $\bar{n}$, we find b = 7 Å. Inserting this value into the equation, we have calculated the variation of the viscosity as a function of the degree of assocaition $\bar{n}$.

Figure 8 shows such a curve for sample M_{11}. The experimental points fit quite well with the theoretical curve, and we note that the extrapolated viscosity to $\bar{n}$ = 1 is very near to the experimental value. This value is higher than those determined in sulphuric acid.

A difficulty was encountered in the characterization of the ClPNPM sample. For this polymer, the aggregation phenomena observed for the MePNPM in methane sulphonic

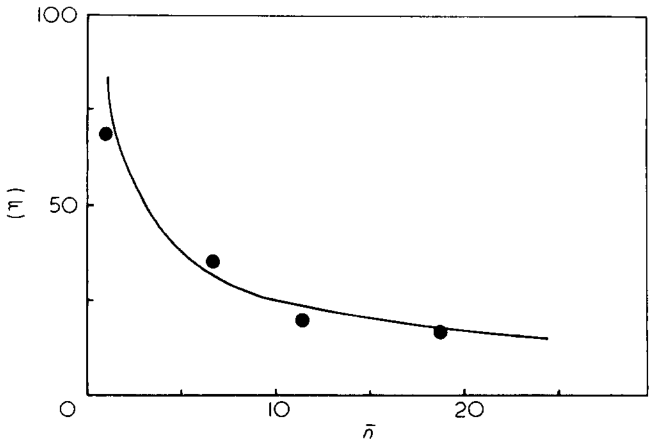

Figure 8 Curve of the intrinsic viscosity of samples M11 in methane sulphonic acid versus the aggregation number $\bar{n}$, using the Hearst equation. ●, experimental points

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* A detailed analysis of the relation between the high values for dn/dc observed here and the absorption spectra will be given in a future paper.

acid occurs in sulphuric and in methane sulphonic acid. So the determination of the molecular parameters is practically impossible.

CONCLUSIONS

In this paper, the measurements of the characteristics of some thermotropic polyazomethines were carried out. Samples of MePNPM were primarily studied. Some difficulties have been encountered in this characterization.

The first was in the fluorescence of these polymers and so, the molecular weights were measured using red light. The refractive index increments were also measured at the same wavelength. The observed values are exceptionally high and as a very strong absorption peak exists in the blue spectral region, these high values were explained by the abnormal variation of indices due to this absorption peak.

Also the molecular weight and the viscosities in two solvents like sulphuric or methane sulphonic acid are very different. An aggregation in methane sulphonic acid occurs with time. If the molecular weights are measured just after the dissolution of the polymer in methane sulphonic acid, the values are very near of those measured in sulphuric acid. This aggregation process seems very general, and it was observed with the three polymers MePNPM, Cl-PNPM, PNPM. For the aggregation phenomena in methane sulphonic acid, a model was made, the law of viscosity versus the association degree was calculated and the experimental values showed a reasonably good fit to this model.

For methane sulphonic acid, the intrinsic viscosity in the absence of aggregates, is higher than in sulphuric acid, such a phenomenon was also observed for the aromatic polyamides[13]. The solvation shell (i.e. the hydrodynamic diameter) is probably greater in the methane sulphonic acid than in sulphuric acid.

By g.p.c. measurements, it has been verified that the curvature observed in the Zimm-plot of post-polymerized samples is due to an amount of large aggregates, the number of these aggregates depending on the time of post polymerization. When the samples are not too post polymerized, an approximated molecular weight of the samples can be obtained by extrapolating the Zimm-plot to $\theta = 180$ where the aggregates influence is so much smaller.

A well defined law of viscosity has also been found for the MePNPM.

The rigidity of the Me-PNPM was measured using the law of viscosity and the optical anisotropy of the macromolecules. By these two methods, a value of the persistence length: $q = 150$ Å ± 25 Å is obtained for the MePNPM. So the structure of this polymer is not rod-like (Like PBLG[3]) and a worm-like chain representation seems better for this polymer. The rigidity is near to that measured for polyparaphenylene terephthalamide, which does not melt but gives lyotropic nematic phases[5]. Thus the intrinsic rigidity of the polymer is not a criterion for differentiation between the thermotropic and lyotropic polymers.

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