

# Characterization of polyazomethines in dilute solution. Correlation between the light scattering parameters and the u.v.-visible absorption spectrum

Bernard Millaud, Claude Strazielle and Gilbert Weill

Centre de Recherches sur les Macromolécules, CNRS et Université L. Pasteur, Strasbourg, France

(Received 27 March 1979; revised 13 September 1979)

The high values (up to  $1 \text{ cm}^3 \text{ g}^{-1}$ ) of the refractive index increments  $dn/dc$  of sulphuric and methane sulphonic acid solutions for a series of polyazomethine compounds at 546 and 628 nm are related quantitatively to the existence of a strong absorption band around 400 nm. The frequency dependence is well explained by the anomalous dispersion calculated from the decomposition of the absorption band into Gaussians. The blue shift and hypochromic effect, and the correlated decrease in  $dn/dc$ , resulting from an aggregation process in methane sulphonic acid can be interpreted by a side-by-side arrangement of aggregates. This result is substantiated by a calculation of the optical anisotropy from the depolarized part of the scattered light.

## INTRODUCTION

The dilute solution characterization of semi-rigid polymers, giving thermotropic liquid crystals, is an important step in the understanding of the correlation between molecular stiffness and mesogenic character<sup>1</sup>.

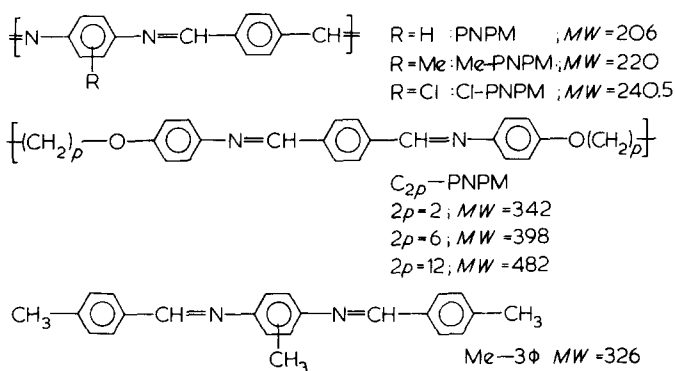
In a recent paper<sup>2</sup>, we studied a series of polyazomethines in 96% sulphuric and/or in methane sulphonic acid by light scattering. Due to their extended conjugation, they have a broad u.v.-visible absorption band. In order to avoid absorption and fluorescence, light scattering experiments were performed at the wave length of an He-Ne laser (632.8 nm) where the molar extinction coefficient is negligible. However, the refractive index increments are abnormally high, with values between 0.32 and 0.78. This has been attributed qualitatively to anomalous dispersion close to the absorption band. In some instances with methane sulphonic acid, a slow aggregation process takes place, where the change of scattered intensity results from both the true change in molecular weight and from the change in the refractive index increment. The latter is attributed to the change in absorption spectrum resulting from the association.

It is the purpose of this paper to show that the correlation between the absorption spectrum and the value of the refractive index increment is quantitative. We discuss the type of association which can be derived from the changes in both the depolarization of the scattered light and the u.v.-visible absorption spectra.

## MATERIALS AND METHODS

The absorption spectra between 230 and 600 nm were obtained on a Beckman DB spectrophotometer. The refractive index increments  $dn/dc$  with either a mercury lamp or an He-Ne laser as a light source. All experiments were carried out at room temperature ( $\sim 22^\circ\text{C}$ ).

Several thermotropic polymers were studied. Their formulae and the molecular weight ( $MW$ ) of the structural unit are given below. The synthesis and physicochemical properties of some of these polymers have already been described<sup>2</sup>.



The abbreviation PNPM stands for poly(nitrilo 1,4-phenylene nitrolo methyldine 1,4-phenylene methyldene), with an eventual indication of the ring substituent. Three polymers in which conjugation is broken every three phenyl rings by a flexible aliphatic sequence of  $2p \text{ CH}_2$  have been included, together with the low molecular weight model labelled Me-3 $\phi$ .

## CORRELATION BETWEEN REFRACTIVE INDEX INCREMENT AND ABSORPTION SPECTRUM

### (i) Theoretical background

When measuring the light scattered by solutions of absorbing molecules, it is necessary to correct the intensities for absorption and to use the sum of the terms corresponding to the real and imaginary part of the complex refractive

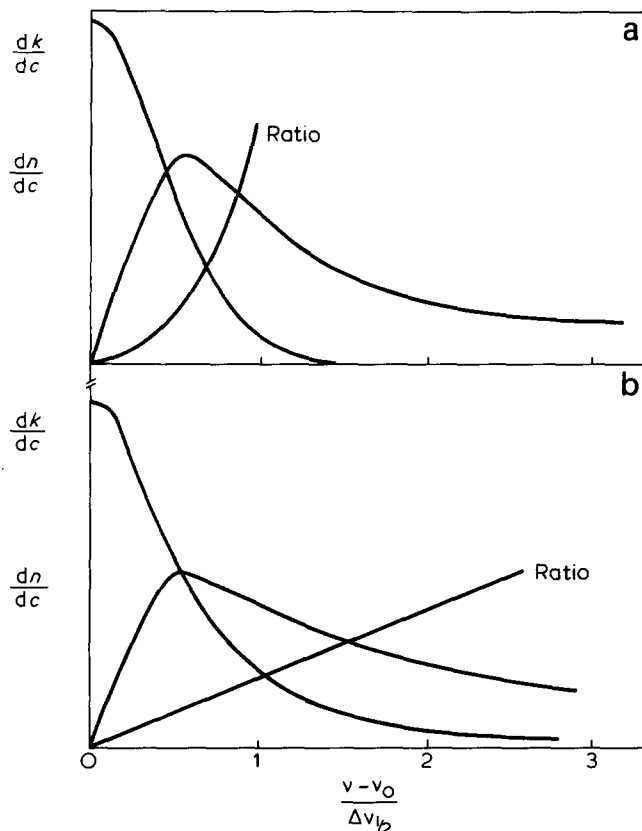


Figure 1 Frequency variation of the real ( $dn/dc$ ) and imaginary ( $dk/dc$ ) parts of the refractive index increment (and of their ratio) resulting from an absorption band  $k(\nu)$  with a, a Lorentzian line shape; b, a Gaussian line shape

index, as the square of the refractive index increment in the calculation of molecular weight, i.e.<sup>3</sup>:

$$\left(\frac{dn}{dc}\right)^2 + \left(\frac{dk}{dc}\right)^2$$

The imaginary part  $k$  is related to the molar extinction coefficient  $\epsilon$  by:

$$k(\lambda) = \frac{2303 \epsilon(\lambda) \lambda}{4\pi} \frac{c}{m} \quad (1)$$

where  $\lambda$  is the wave length of the light *in vacuo* and  $c$  the concentration in  $\text{g ml}^{-1}$ .  $n$  and  $k$  are related by Kramers–Kronig relations which, taking into account equation (1) can be written<sup>4</sup>:

$$n(\bar{\nu}) - n_0(\bar{\nu}) = \frac{2303 c}{2\pi^2 m} \int_0^{\infty} \frac{\epsilon(\bar{\nu}')}{(\bar{\nu}'^2 - \bar{\nu}^2)} d\bar{\nu}' \quad (2)$$

where  $n_0$  is the solvent index of refraction and  $\bar{\nu}$  the wave number ( $\bar{\nu} = \lambda^{-1}$  in  $\text{cm}^{-1}$ ).

If one assumes a Lorentzian line shape:

$$\frac{dk(\bar{\nu})}{dc} = \frac{2303}{4\pi m} \frac{\epsilon_0}{\bar{\nu}} \frac{1}{1 + 4(\bar{\nu} - \bar{\nu}_0/\Delta\bar{\nu}_{1/2})^2} \quad (3)$$

where  $\epsilon_0$  is the molar extinction coefficient at the wave number  $\nu_0$  of the maximum of the band, and  $\Delta\nu_{1/2}$  the band

width at  $1/2 \epsilon_0$ . The corresponding increment of the real part of the refractive index is then:

$$\frac{dn(\bar{\nu})}{dc} = \frac{2303}{4\pi m} \frac{\epsilon_0}{\bar{\nu}} \frac{2(\bar{\nu} - \bar{\nu}_0/\Delta\bar{\nu}_{1/2})}{1 + 4(\bar{\nu} - \bar{\nu}_0/\Delta\bar{\nu}_{1/2})^2} \quad (4)$$

The frequency dependence of  $dk/dc$ ,  $dn/dc$  and of their ratio is plotted in Figure 1.  $dk/dc$  cannot be neglected up to values of  $\bar{\nu} - \bar{\nu}_0/\Delta\bar{\nu}_{1/2} \sim 3$ . However, it is more realistic to consider a Gaussian line shape:

$$\frac{dk(\bar{\nu})}{dc} = \frac{2303}{4\pi m} \frac{\epsilon_0}{\bar{\nu}} \exp(-q^2) \quad (5)$$

where

$$q = 1.6651 \frac{\bar{\nu} - \bar{\nu}_0}{\Delta\bar{\nu}_{1/2}} \quad (5)$$

Then equation (4) becomes:

$$\begin{aligned} \frac{dn(\nu)}{dc} &= \frac{2303}{2\pi^2 m} \epsilon_0 \int_0^{\infty} e^{-q^2} \frac{d\bar{\nu}'}{\bar{\nu}'^2 - \bar{\nu}^2} \\ &= \frac{2303}{2\pi^2 m} \frac{\epsilon_0}{\bar{\nu}} = \pi^{1/2} \left[ (e^{-q^2} \int_0^q e^{x^2} dx) - \frac{\Delta\bar{\nu}_{1/2}}{3.33(\bar{\nu} + \bar{\nu}_0)} \right] \end{aligned} \quad (6)$$

The Dawson integral

$$D(q) = e^{-q^2} \int_0^q e^{x^2} dx$$

is tabulated<sup>5</sup> and has two extrema, equal to  $\pm 0.54$  for  $\bar{\nu} = \bar{\nu}_0 \pm 0.54 \Delta\bar{\nu}_{1/2}$ . The frequency dependences of  $dk/dc$ ,  $dn/dc$  and of their ratio are plotted in Figure 1.  $dk/dc$  can be neglected for  $(\bar{\nu} - \bar{\nu}_0/\Delta\bar{\nu}_{1/2}) > 1.5$ .

We now show how these relations can be applied to our polymers.

#### (ii) Experimental results

The spectra of all the compounds studied present a clearly resolved u.v. band around  $36\,000 \text{ cm}^{-1}$  (280 nm) and a broader dissymmetric band in the visible, extending up to  $20\,000 \text{ cm}^{-1}$ . Figure 2 shows as an example the spectrum of Me–PNPM in 96% sulphuric acid. The experimental line shapes are in most cases far from Gaussian but can be analysed visually as a small number of Gaussian bands, using a Dupont 310 curve resolver. Examples of such analysis are given in Figure 2. The values of  $\bar{\nu}_0/\Delta\bar{\nu}_{1/2}$  and  $\epsilon_0$  for each of the resolved Gaussian bands are given in Tables 1 and 2, together with the corresponding oscillator strength  $F$  calculated according to<sup>4</sup>:

$$F = 4.6 \times 10^{-9} \epsilon_0 \Delta\bar{\nu}_{1/2} \quad (7)$$

Whether the analysis corresponds to a true overlap of different electronic or vibrational transitions is irrelevant for the calculation of the dispersion of  $dn/dc$  based on Kramers–Kronig relations<sup>6</sup>.

Table 3 gives the values of  $(dn/dc)$  measured at 546 and 632.8 nm (18 315 and 15 803  $\text{cm}^{-1}$ ) where the absorption is negligible. In the cases where the spectrum changes with time, the absorption spectra and refractive index increments have been measured at the same time.

### (iii) Discussion

Consideration of the values of  $dn/dc$  together with the solvent index of refraction in Table 3 shows that not only are they exceptionally high but also that the variation for two close wavelengths is very large. The contribution

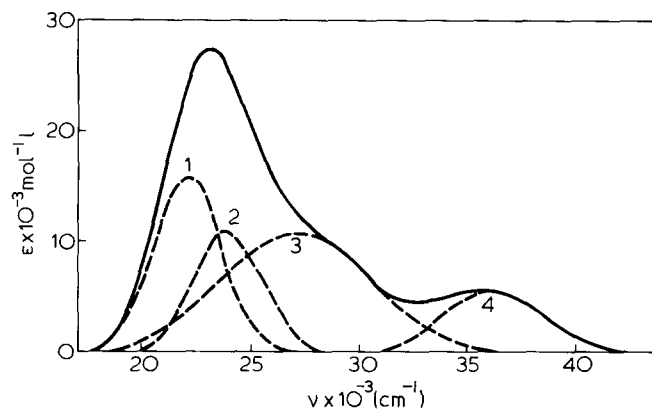


Figure 2 U.v.-visible spectrum of Me-PNPM in 96% sulphuric acid. Decomposition in Gaussian bands

of the near u.v.-visible absorption band to the refractive index increment at these wavelengths has been calculated using equation (6) and the analysis into Gaussians (Tables 1 and 2). Results are given in Table 3 as  $(dn/dc)_{\text{near}}$ . Subtraction from the experimental value gives  $(dn/dc)_{\text{far}}$ , the contribution from far u.v. transitions. It is seen that the values calculated from the measurements at 546 or 632.8 nm are equal, within experimental accuracy. The wavelength dependence of  $dn/dc$  is fully explained by anomalous dispersion on the low frequency side of the absorption band.

The value of  $(dn/dc)_{\text{far}}$  decreases when passing from PNPM to Me and Cl-PNPM and to Me-3 $\phi$  and C<sub>2p</sub>-PNPM. This is related to the low polarizability of the substituents and/or to the decrease of the conjugation which is reflected in the total oscillator strength of the broad u.v.-visible band as given in Tables 1 and 2. The structural unit in PNPM and its methylated and chlorinated derivatives contains two phenyl rings while that of 3 $\phi$  and C<sub>2p</sub>-PNPM contains three phenyl rings. The progressive decrease of oscillator strength brought by aggregation in methane-sulphonic acid is correlated to the decrease of  $(dn/dc)_{\text{near}}$  and to  $(dn/dc)_{\text{far}}$ , which takes a value similar to that observed in the model compound Me-3 $\phi$  which has a limited extent of conjugation.

### TIME EVOLUTION OF OPTICAL PROPERTIES OF Me-PNPM IN METHANE SULPHONIC ACID AND ASSOCIATION

The time evolution of the absorption spectra and molecular weight (calculated from light scattering using the values of  $dn/dc$  measured at the corresponding time<sup>2</sup>) can be correlated to other molecular characteristics such as the intrinsic

Table 1 Analysis of the u.v.-visible spectra into Gaussian bands. Position, band width, molar extinction coefficient and oscillator strength of the bands

Sample	Solvent	$\nu_0 \times 10^3$ ( $\text{cm}^{-1}$ )	$\epsilon_0 \times 10^3$ ( $\text{mol}^{-1}$ l)	$\Delta\nu_{1/2} \times 10^3$ ( $\text{cm}^{-1}$ )	$F$
PNPM	$\text{H}_2\text{SO}_4$	21.5	23.6	2	0.217
		23.0	14.6	1.9	0.128
		24.3	20.8	4.5	0.431
		29.2	10.0	6.6	0.304
		36.4	6.6	6.8	0.206
					1.08
Me-PNPM	$\text{H}_2\text{SO}_4$	22	15.8	3.6	0.262
		23.9	11.0	3.4	0.172
		27.3	11.0	7.7	0.390
		36.2	5.6	5.3	0.137
					0.824
Me-3 $\phi$	$\text{H}_2\text{SO}_4$	26.4	18.4	5.1	0.432
		29.4	11.5	4.8	0.294
		34.7	5.4	7.0	0.174
					0.726
C <sub>2</sub> -PNPM	$\text{CH}_3\text{SO}_3\text{H}$	20.6	16	2.8	0.206
		22.7	5.6	2.7	0.070
		24.3	18	7.5	0.621
		32.2	4.6	5.8	0.123
					0.897
C <sub>6</sub> -PNPM	$\text{CH}_3\text{SO}_3\text{H}$	21.1	25.2	4.2	0.487
		24.2	9.0	3.5	0.145
		27.2	8.0	6.4	0.236
		36.2	13.0	6.4	0.383
					0.868
C <sub>12</sub> -PNPM	$\text{CH}_3\text{SO}_3\text{H}$	21.1	14.2	3.9	0.255
		24.4	10.2	8.2	0.385
		24.9	4.5	8.6	0.178
		36.3	13.2	7.2	0.437
					0.876
C <sub>12</sub> -PNPM	$\text{H}_2\text{SO}_4$	22.7	10.8	4.5	0.224
		26.2	13.6	8.0	0.500
		36.2	10.8	9.7	0.482
					0.724

Table 2 Analysis of the u.v.-visible spectra into Gaussian bands. Time evolution of the parameters of bands

Sample	Solvent	t (h)	$\nu_0 \times 10^3$ (cm <sup>-1</sup> )	$\epsilon_0 \times 10^3$ mol <sup>-1</sup> l	$\Delta\nu_{1/2} \times 10^3$ (cm <sup>-1</sup> )	F
Cl-PNPM	H <sub>2</sub> SO <sub>4</sub>	3	23.1	24.2	4.9	0.545
			26.7	4.5	6.3	0.130
			28.7	11.4	7.8	0.409
			36.5	9	6.5	0.269
		48	27.7	14	3	0.193
			34	6	3.2	0.193
39.5	3		2.5	0.035		
Me-PNPM	CH <sub>3</sub> SO <sub>3</sub> H	2	23.2	25.8	4.5	0.534
			27.4	11.4	6.8	0.357
			29.4	1.6	5.9	0.043
			35.8	5.8	6.9	0.184
		6	24.5	22.6	5.5	0.572
			29.2	10.8	5.6	0.278
			36	6	5.6	0.155
		9	24.5	16.8	5.1	0.394
			28.4	10.2	6	0.282
			35.7	6.6	7.5	0.228
		24	25.1	12	4.2	0.232
			28.5	10.8	5.8	0.288
36.0	6.6		8.0	0.243		
48	26.7	14.5	7.2	0.480		
	35.5	6.8	9.0	0.282		
120	27.6	13.6	7.4	0.463		
	35.5	6.8	8.0	0.250		

Table 3 Experimental values of the refractive index increment and calculated contribution from the near u.v.-visible bands. The index of refraction  $n_0$  of H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>SO<sub>3</sub>H at 578 nm are respectively 1.429 and 1.432

Sample	Solvent	$\lambda$ (nm)	$(dn/dc)_{exp}$ (cm <sup>3</sup> g <sup>-1</sup> )	$dn/dc_{near}$ (cm <sup>3</sup> g <sup>-1</sup> )	$dn/dc_{far}$ (cm <sup>3</sup> g <sup>-1</sup> )
PNPM	H <sub>2</sub> SO <sub>4</sub>	632	0.78	0.31	0.47
		546	1.05	0.55	0.50
Me-PNPM	H <sub>2</sub> SO <sub>4</sub>	632	0.62	0.23	0.39
		546	0.80	0.42	0.38
Me-3 $\phi$	H <sub>2</sub> SO <sub>4</sub>	632	0.38	0.08	0.30
		546	0.42	0.11	0.31
C <sub>2</sub> -PNPM	CH <sub>3</sub> SO <sub>3</sub> H	632	0.42	0.22	0.20
C <sub>6</sub> -PNPM	CH <sub>3</sub> SO <sub>3</sub> H	632	0.38	0.21	0.17
C <sub>12</sub> -PNPM	CH <sub>3</sub> SO <sub>3</sub> H	632	0.34	0.15	0.19
C <sub>12</sub> -PNPM	H <sub>2</sub> SO <sub>4</sub>	632	0.32	0.10	0.22
		546	0.39	0.17	0.22
Cl-PNPM					
t = 3 h	H <sub>2</sub> SO <sub>4</sub>	632	0.55	0.24	0.31
t = 48 h	H <sub>2</sub> SO <sub>4</sub>	632	0.40	0.07	0.33
Me-PNPM					
t = 2 h	CH <sub>3</sub> SO <sub>3</sub> H	632	0.58	0.25	0.33
		546	0.72	0.19	0.30
t = 6 h	CH <sub>3</sub> SO <sub>3</sub> H	632	0.50-0.52	0.19	0.31-0.33
t = 9 h	CH <sub>3</sub> SO <sub>3</sub> H	632	-	0.15	-
t = 24 h	CH <sub>3</sub> SO <sub>3</sub> H	632	-	0.10	-
t = 48 h	CH <sub>3</sub> SO <sub>3</sub> H	632	-	0.10	-
t = 120 h	CH <sub>3</sub> SO <sub>3</sub> H	632	0.43	0.09	0.34

viscosity  $[\eta]$  and the optical anisotropy  $\delta^2$  derived from the depolarization ratio  $\rho_v$  in vertically polarized incident light:

$$\delta^2 = 5\rho_v / (3 - 4\rho_v) \quad (8)$$

The results are summarized in Table 4 for samples of Me-PNPM of increasing molecular weight. It can be remarked

that:

- the molecular weight increases from a value close to that measured in sulphuric acid up to a limiting degree of association  $\bar{n}$  which decreases with increasing initial molecular weights;
- the viscosity decreases towards a value which is nearly independent of the initial molecular weight;

the depolarization ratio increases from a value which decreases with the initial molecular weight up to a value of  $0.385 \pm 0.005$ , independent of the initial molecular weight and final degree of association;

the spectrum of the aggregates (Figure 3) tends towards a limit, with the broad visible band shifted towards the u.v. region, and a total oscillator strength about half that of the single molecule. For low degrees of association,  $\bar{n}$ , the oscillator strengths, and, therefore,  $dn/dc$ , are a decreasing function of  $\bar{n}$ . Thus, the calculated molecular weight and degree of association in Table 4 can be underestimated because of the polydispersity in  $\bar{n}$ .

The relation between degree of association and viscosity has been shown to be consistent with a side by side aggregation<sup>2</sup>. We can substantiate this result from the depolarization ratio and absorption spectrum measurements.

In the hypothesis of an aggregate of parallel rods,  $\delta^2$  and  $\rho_v$  should remain constant. For our non-aggregated polymers,  $\delta^2$  is a function of the molecular weight because of the flexibility of the molecules<sup>5</sup>. The fact that  $\rho_v$  increases upon aggregation to a value independent of the initial molecular weight and final value of  $\bar{n}$  indicates that the process of association stiffens the molecule.

We can calculate<sup>6</sup> the difference in polarizability of the structural unit ( $\alpha_0 - \beta_0$ )<sup>6</sup>:

$$\delta_0^2 = (\alpha_0 - \beta_0)^2 / (9\Delta\alpha^2) \quad (9)$$

Table 4 Time evolution of molecular weight, intrinsic viscosity and depolarization ratio of Me-PNPM in methane sulphonic acid (initial values are those obtained in H<sub>2</sub>SO<sub>4</sub>)

Sample	Time (h)	$M_w$	$\bar{n}$	$[\eta]$ cm <sup>3</sup> g <sup>-1</sup>	$\rho_v$
M <sub>14</sub>	(0)	(1850)	—	(28)	0.340
	3	2550	~1.4	44	0.320
	12	8000	~4.5	38	0.350
	48	46 600	~25	18.5	0.385
M <sub>11</sub>	(0)	(3550)	—	(48)	0.290
	3	3500	~1	69	0.240
	24	24 100	~7	36	0.35
	48	40 600	~11.5	18	0.385
	24 + 12 at 40°C	67 000	~19	15.5	0.380
M <sub>16</sub>	(0)	(6900)	—	(118)	0.14
	3	7600	~1	18.5	0.13
	48	41 500	~16.3	16.3	0.39

Table 5 Optical anisotropy parameters at 632.8 nm

System	Conformation	$\left(\frac{dn}{dc}\right)$	$(\alpha_0 - \beta_0)$ Å <sup>3</sup>	$(\alpha_0)_{near}$ Å <sup>3</sup>	$(\alpha_0 - \beta_0)_{far}$ Å <sup>3</sup>
Aromatic polyamide (PPDT), H <sub>2</sub> SO <sub>4</sub>	Worm like chain $\delta_0^2$ extrapolated	0.31	38.7	—	—
Me-3φ, H <sub>2</sub> SO <sub>4</sub>	Rigid	0.38	134	21.5	113 (for 3 phenyls)
Me-PNPM, H <sub>2</sub> SO <sub>4</sub> Me-PNPM, CH <sub>3</sub> SO <sub>3</sub> H $t \rightarrow 0$	Worm like chain $\delta_0^2$ extrapolated	0.62	147	43	104
		0.61	131	46	85
Me-PNPM, CH <sub>3</sub> SO <sub>3</sub> H $t = 7.6$ h	Rigid Aggregated	0.51	94.5	35	59.5

where  $\delta_0$  is the apparent anisotropy (extrapolated to the length of the structural unit for partly flexible molecules),  $\Delta\alpha$  is the excess of average polarizability with respect to the solvent of refractive index  $n_0$ :

$$\frac{4\pi}{3} \frac{\mathcal{N}}{m} \Delta\alpha = 2n_0 \frac{(dn/dc)}{n_0^2 + 2} \quad (10)$$

where  $\mathcal{N}$  is Avogadro's number.

The values of  $\alpha_0 - \beta_0$  are given in Table 5. Since the transition moment of the u.v.-visible band is essentially parallel to the direction of maximum conjugation, it will only contribute to  $\alpha_0$ . We have calculated this contribution from the value of  $(dn/dc)_{near}$  in Table 3:

$$\frac{4\pi}{3} \frac{\mathcal{N}}{m} \frac{(\alpha_0)_{near}}{3} = 2n_0 \frac{(dn/dc)_{near}}{n_0^2 + 2} \quad (11)$$

The values are reported in Table 5. The change in  $(\alpha_0)_{near}$  due to the correlated changes of spectrum and  $dn/dc$  accounts semi-quantitatively for the change in the value of  $(\alpha_0 - \beta_0)$ . Comparison with an aromatic polyamide<sup>6</sup> (paraphenylene polyterephthalamide PPDT) with less conjugation and no visible absorption band shows that the changes in the far u.v. band should also contribute to the changes in  $(\alpha_0 - \beta_0)$ . (Note that the value given here is different from that previously<sup>6</sup> where a mistake was made in the application of equations (9) and (10).

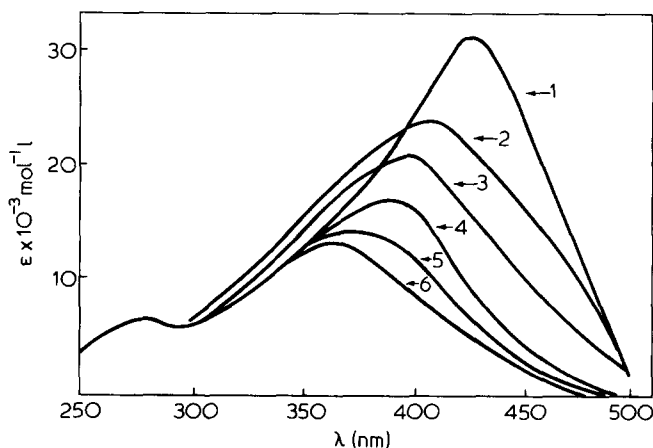


Figure 3 Time evolution of the u.v.-visible spectrum of Me-PNPM in methane sulphonic acid.  $t = 2$  h; 6 h; 9 h; 24 h; 48 h; 120 h

The change in the absorption spectrum can be understood as a simple result of a side-by-side aggregation process. The theory of the shifts and hypochromic effects in aggregates has been developed to explain the optical properties of dimers, dye aggregates or helical biopolymers e.g. polypeptides or DNA<sup>7,8</sup>. The lifting of the degeneracy of the optical transitions of the isolated chromophore through dipolar interaction leads to a splitting of the excited levels into an exciton band, whose width is proportional to the interaction energy. For a side-by-side arrangement of the transition moments, the dipolar interaction is repulsive. Selection rules show that the allowed transition is towards the top of the band, involving a displacement of the absorption band of the aggregates towards higher energy. The change in oscillator strength can be understood as an internal field effect<sup>9</sup>. The replacement of an isotropic solvent by parallel polymer molecules with a high polarizability along their axis is expected to lead to an hypochromic effect (i.e. a decrease in oscillator strength). The effect is similar to that produced by the parallel arrangement of base pairs in the DNA molecule.

The evolution of the absorption spectra (*Figure 3, Table 2*) fits these qualitative predictions of hypochromism and the shift towards the u.v. region satisfactorily. The optical properties of the aggregates bring additional and conclusive arguments for a side-by-side aggregation process.

## REFERENCES

- 1 Millaud, B., Thierry, A. and Skoulios, A. *J. Phys. Paris* 1978, **39**, 1109
- 2 Millaud, B. and Strazielle, C. *Polymer* 1979, **20**, 563
- 3 Miller, G. A. *J. Phys. Chem.* 1978, **82**, 616
- 4 Fredericq, E. and Houssier, C. 'Electric dichroism and electric birefringence', Clarendon Press, Oxford, 1973
- 5 'Handbook of Mathematical functions' (Eds. M. Abramowitz and I. Stegun) Dover, New York, 1965
- 6 Arpin, M., Strazielle, C., Weill, G. and Benoit, H. *Polymer* 1977, **18**, 262
- 7 Tinoco, I. *Adv. Chem. Phys.* 1967, **9**, 113
- 8 Geoffroy, M. and Weill, G. *J. Chem. Phys.* 1970, **67**, 139
- 9 De Voe, H. *Biopolymers Symp.* 1963, **1**, 251