which determine an upper and lower limit for $\langle\cos^4\theta\rangle$. If one refers to the middle of the allowed $\langle\cos^4\theta\rangle$ range, one obtains, according to the same concept as in *Table 1*, the results shown in *Table 2*. The data in *Table 2* shows the experimental accuracy limit, i.e. error bars given in %, resulting from the mathematically well defined limits, e.g. $\langle\cos^4\theta\rangle = 0.375 \pm 0.125$ at $\langle\cos^2\theta\rangle = 0.5$.

It follows from the data in *Table 2*, that even in the case of moderate accuracy, e.g. 10%, considerable reductions of the allowed range of $\langle\cos^4\theta\rangle$ can be received. In such a way the type of the odf may be limited, allowing for discrimination between deformation models, provided they are sufficiently different.

Conclusions

The fpm is an efficient and valuable tool in discriminating types of odf and types of deformation schemes if one selects photophysically ideal chromophores ($p_m \rightarrow 0$) and if one investigates samples showing only moderate scattering depolarization. It is necessary to calculate and realize experimentally the required accuracy in the light intensity measurements and in the determination of the correcture parameter *p*, provided that the involved symmetry conditions of the sample and of the chromophore hold.

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Intrinsic viscosity of cellulose derivatives and the persistent cylinder model of Yamakawa

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By using the chain model proposed by Yamakawa, intrinsic viscosity measurements allow characterization of cellulose derivatives in dilute solution by persistence length and hydrodynamic diameter as a function of different parameters such as temperature of solvents, degree of substitution and type of substituent.

Keywords Intrinsic viscosity; polymer; solution; persistence length; cellulose derivatives

Anisotropic phases are formed in concentrated solutions of certain rigid polymers. The best known examples are the aromatic polyamides which have been studied with the help of various physico-chemical methods[1-7]. Recently, it has been demonstrated that polymer chains of lesser rigidity, such as the cellulose derivatives, can also form mesomorphic solutions at high concentrations, between 20 and 50 wt%[8-13]. The concentration at which the anisotropic phase appears depends not only on the type of solvent but also on characteristics of the chain such as degree of substitution, type of substituent and so on.

In these discussions a parameter of some importance is the chain rigidity. To gain an insight into the concentration dependence of the rigidity, we firstly studied dilute solutions and have investigated the intrinsic viscosity for a number of cellulose derivatives.

Over a sufficiently small range of polymer molecular mass the intrinsic viscosity $[\eta]$ can be fitted to the empirical Mark–Houwink equation[14]:

$$[\eta] = K.M^{\alpha} \tag{1}$$

where K and α are constants for a given polymer–solvent system. Qualitatively, α increases with increasing chain rigidity, but for a more complete analysis, it is necessary to consider a more detailed theoretical model such as that proposed by Yamakawa[15]. Some authors have used this model and graphical methods to estimate the persistence length of flexible chains[16-18] and of α-helical polypeptides[19]. Following ideas first proposed by Arpin[20], we have calculated the hydrodynamic diameter and the persistence length from experimental values of intrinsic viscosity and molecular mass for a large variety of polymer systems. By refining and extending the method of Arpin, we have been able to obtain a systematic analysis of cellulose derivatives in solution.

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Yamakawa Model

Given a system of monodisperse chains of contour length L, Yamakawa calculates the intrinsic viscosity with a method based on the ideas of Kirkwood and Riseman[21] for flexible chains. It is thereby expressed as a sum of terms which depend on the friction coefficients of the individual segments. For each segment, the friction is given by the local segment velocity, the local fluid velocity in absence of the segment and the perturbation of the fluid velocity due to all other segments (method of Oseen–Burgers)[21]. These frictional forces are solutions of an integral equation which depends on the equlibrium conformation of the chain. In the Yamakawa model, the Gaussian distribution of the flexible chain is replaced by a chain of persistence length q and the discrete linear model is replaced by a three dimensional continuum by introducing the hydrodynamic diameter D. The results obtained for $[\eta]$ are approximated by the following analytical expressions[15]:

For $L \geqslant \sigma = 2.278$

$$[\eta] = \frac{\varphi_\infty L^{3/2}}{M} \cdot \frac{1}{1 - \sum_{i=1}^{4} C_i L^{-i/2}} \tag{2}$$

where $\varphi_\infty = 2.87\ 10^{23}$, $L = 1/2q$ and C_i are functions of $d = D/2q$.

For $L < \sigma$

$$[\eta] = \frac{\pi N_A L^3}{24 M \mathrm{Ln}(L/d)} \cdot \frac{f(L)}{1 + \sum_{i=1}^{4} A_i [\mathrm{Ln}(d/L)]^{-i}} \tag{3}$$

where N_A is the constant of Avogadro, A_i are constant coefficients and

$$f(L) = (3/2.L^4)(e^{-2L} - 1 + 2L - 2L^2 + (4/3)L^3)$$

Application of the Yamakawa model

Expressions (2) and (3) of Yamakawa lead to an equation with three unknown parameters for a sample of given molecular mass and intrinsic viscosity. These three parameters are a, the projection of the monomeric unit on the contour length with $l = (M/m_0).a$, the hydrodynamic diameter D and the persistence length q. To a first approximation, the values of a and D can be estimated by values obtained from X-ray scattering in compounds of the same family and the persistence length is a calculated value. But if we assume that D and q are characteristics of the polymer–solvent system (independent of the mass), we can apply equations (2) or (3), to solutions of different mass leading to a system of equations in two unknowns for a chosen value of a. This system is solved by iteration with minimization of the relative mean square deviation:

$$\delta^2 = \frac{1}{N} \cdot \sum_{i=1}^{N} \left(\frac{[\eta]\mathrm{exp}_i - [\eta]\mathrm{th}_i}{[\eta]\mathrm{exp}_i} \right)^2 \tag{4}$$

with N number of samples and $[\eta]$ exp_i, $[\eta]\mathrm{th}_i$ are respectively the experimental and theoretical (Yamakawa) values of the intrinsic viscosity for the sample i of mass M_i. The method is sensitive to experimental errors in M_i and $[\eta]_i$, and to minimize this effect we have found it is necessary to consider a large number of samples (of the order of ten) in a wide range of mass. All the molecular masses used are weight average ones, M_w.

Results and Discussion

As a first step, we have tested our method on aromatic polyamides, using the results given by Arpin[20] for the paraphenylene polyterephthalamide in a 96% solution of H_2SO_4. Arpin derives values of the persistence length within the Yamakawa model taking values of a and D from crystallographic data. He obtains $q = 150$ with $a = 12$ and $D = 6$ Å. Our calculations lead, for $a = 12$, to a similar result, $D = 9$ and $q = 116$ for $\delta^2 = 0.72$. For the parameters of Arpin, we obtain $\delta^2 = 2$. These results are shown in *Figure 1*.

Our interest is mainly in the cellulose derivatives and in a preliminary study, we have selected published results on the intrinsic viscosity of cellulose nitrate CN[22,23], cellulose di- and tri-acetate CDA, CTA[24–28] and cellulose tricarbanilate CTC[29–32] in solution. We assume $a = 5.15$ Å for this entire group of compounds.

Influence of the solvent. The influence of the solvent on the chain rigidity is given by *Tables 1a* and *2a* and in *Figures 2* and 3, for two compounds, the CTA[28] and the CTC[29] each in solution in some of the following solvents: dimethylacetamide (DMAc), acetone, trifluoroacetic acid (TFA), tetrachloroethane (TCE), trichloromethane (TCM), dioxane and pyridine. For CTA in five different solvents we find:

$$q_{\mathrm{DMAc}} > q_{\mathrm{Acetone}} > q_{\mathrm{TFA}} > q_{\mathrm{TCE}} = q_{\mathrm{TCM}}$$

and for CTC in three different solvents:

$$q_{\mathrm{Dioxane}} > q_{\mathrm{Pyridine}} > q_{\mathrm{Acetone}}$$

For CTC, these results confirm the observation of Noordermer *et al.*[33] The authors have noted that the

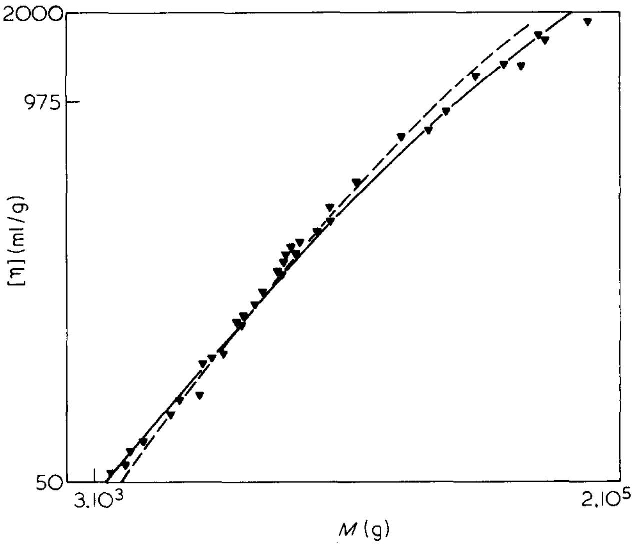


Figure 1 Intrinsic viscosity $[\eta]$ as a function of molecular mass M, in a log–log plot for samples of polyterephthalamid of paraphenylene in solution in H_2SO_4 (96%). $T = 25°C$. Experimental points, Arpin[20]: ▲, theoretical curves from the theory of Yamakawa, Arpin[20]: (— — —); present study: (——)

Table 1 Influence of the solvent on the hydrodynamic diameter, D, and the persistence length, q, for CTA samples[28] at 25°C, except with dichloromethane (T = 20°C): (a) assuming monodisperse samples, (b) taking into account the polydispersity of the samples

	(a) Monodisperse			(b) Polydisperse		
Solvents	D (Å)	q (Å)	δ^2	D (Å)	q (Å)	δ^2
DMAc	8	66	0.079	8	69	0.082
Acetone	6	57	0.225	6	59	0.232
TFA	10	55	0.115	11	56	0.116
DCM	6	39	0.046	5	42	0.056
TCE	8	35	0.237	9	36	0.235
TCM	8	35	0.017	10	35	0.024

Table 2 Influence of the solvent on the hydrodynamic diameter, D, and the persistence length, q, for CTC samples[29]. T = 20°C. (a) Assuming monodisperse samples, (b) taking into account the polydispersity of the samples

	(a) Monodisperse			(b) Polydisperse		
Solvents	D (Å)	q (Å)	δ^2	D (Å)	q (Å)	δ^2
Dioxane	15	146	0.410	14	154	0.312
Pyridine	10	96	0.455	9	102	0.403
Acetone	14	86	0.264	14	89	0.186

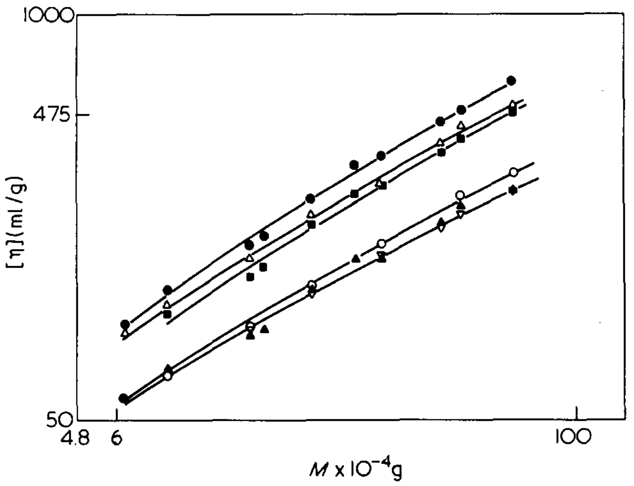


Figure 2 Intrinsic viscosity [η] as a function of molecular mass M, in a log–log plot for samples of CTA[28] in solution in various solvents. Experimental points in DMAc (●), TFA (△), Acetone (■), TCE (▲) and TCM (△) at 25°C and in DCM (○) at 20°C. Theoretical curves from the Yamakawa theory: (——)

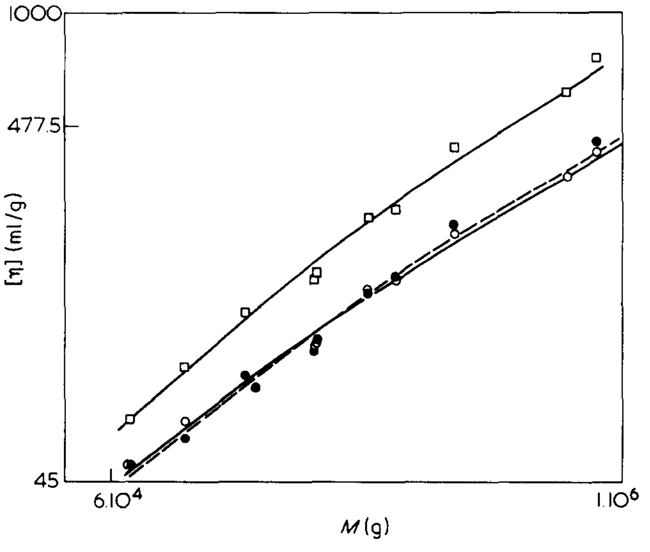


Figure 3 Intrinsic viscosity [η] as a function of molecular mass M for samples of CTC[25]. T = 20°C. Experimental points in dioxane (□), acetone (○) and in pyridine (●). Theoretical curves from the theory of Yamakawa: dioxane or acetone (——), pyridine (– – –)

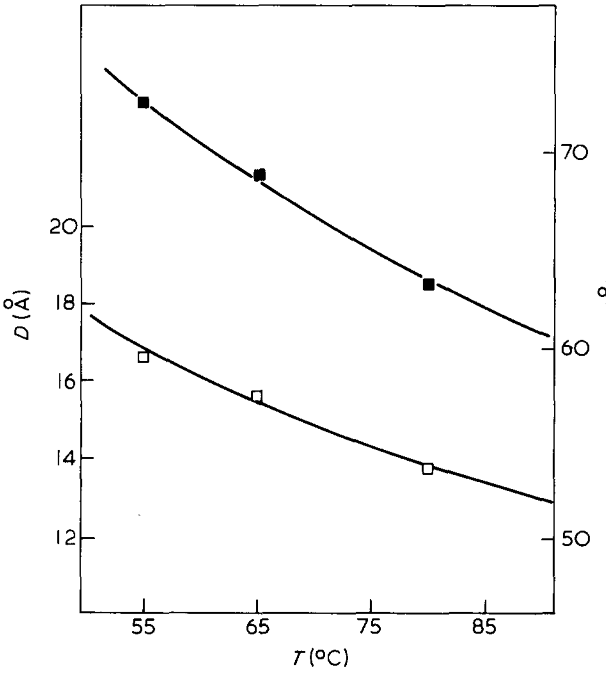


Figure 4 Variations of D (□) and q (■) as a function of temperature for CTC in solution in benzophenone[32]

polymer is more rigid in ether solvents than in esters and in ketones.

Influence of temperature. Experiments on CTC in solution in benzophenone[32] are used to indicate the variations of D and q as a function of temperature. In *Figure 4*, we note that D and q decrease with increasing temperatures as expected from an increase in free rotations and resulting decrease in rigidity. These variations are relatively weak.

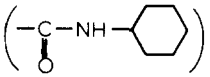
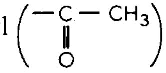
Influence of substituant. For a CN/Acetone solution[22] at 20°C we calculate $D = 11$ Å, $q = 156$ Å and $\delta^2 = 0.713$. For the same solvent, we can compare with the values for CTC at 20°C and CTA at 25°C given in *Tables 1a* and *2a* (this comparison is justified due to the weak dependence on temperature as discussed previously).

It follows that:

$$q_{\mathrm{CN}} > q_{\mathrm{CTC}} > q_{\mathrm{CTA}}$$

and

$$D_{\mathrm{CTC}} > D_{\mathrm{CN}} \geqslant D_{\mathrm{CTA}}$$

The hydrodynamic diameter increases with increasing size of the radical, the phenylisocyanate group  being much longer than the nitrate or the acetyl  $\left(\begin{array}{c}-\mathrm{C}-\mathrm{CH_3}\\ \| \\ \mathrm{O}\end{array}\right)$ groups.

Influence of the degree of substitution. We have used the experimental results of Kamide on CDA and CTA[26-28] in solution to establish the influence of the degree of substitution (*DS*) on *D* and *q*. For CDA we have assumed the same values of *D* as obtained for CTA in *Table 1a*. If we then calculate *q* in CDA for the various solvents, we find that for an increase in *DS* there is a decrease in *q*. This can be understood by the greater ability of forming intramolecular hydrogen bonds and thereby making the chain structure more rigid at a lower degree of substitution.

However, if we try to apply the procedure we have used all along by looking for the optimum *D* and *q* values, we obtain a result that is quite difficult to understand as *D* is then very large (>20 Å) and so a *DS* decrease leads to a large increase in *D* and a decrease in *q*. This unexpected result may be explained by the formation of aggregates which has been observed for the CDA/THF system[37] and this point is actually under investigation.

Influence of polydispersity. Implicitly, we have assumed until now that the samples are monodisperse. In reality, polydispersity will be present and must be taken into account. We assume a Schulz type distribution $P(M)$ of polymer length (or mass) and calculate $[\eta]$ for each sample as the average:

$$[\eta] = \int [\eta](M)P(M)\mathrm{d}M \qquad (5)$$

where $[\eta](M)$ is the intrinsic viscosity of a chain of mass M,

$$P(M) = \frac{M}{M_n} \cdot \frac{y^k M^{k-1} e^{-yM}}{\Gamma(k)}$$

where $k = \dfrac{1}{h-1}$ and $y = \dfrac{1}{M_w - M_n}$

With M_n and M_w, respectively the number and weight average molecular mass and h the index of polydispersity. In the samples studied, h is smaller than 1.8.

A comparison between the mono (a) and poly (b) disperse parts of *Tables 2* and *3* show only a weak sample polydispersity influence on the *D* and *q* values. We obtain:

$$q_h \gtrsim q_{h=1} \quad D_h \sim D_{h=1}$$

with $\dfrac{\Delta q}{q} < 6\%$ and $\dfrac{\Delta D}{D} < 10\%$, the latter being of the order of magnitude of the calculation precision. This relative insensitivity vanishes when the calculations assuming the samples monodispersity ($h = 1$) are done with number instead of weight average molecular mass as was mentioned in ref. 18.

As expected, the calculation taking into account the sample polydispersity is equivalent to a calculation which assumes the samples mono dispersity with the average molecular mass M_v of each sample expressed by:

$$[\eta]_{\text{measures}} = \underset{\text{Yamakawa theory}}{[\eta]\ (D,q,M_v)} = \int \underset{\text{Yamakawa theory}}{[\eta](D,M,q)} P(M)\,\mathrm{d}M$$

We know that $M_n \leqslant M_v \leqslant M_w$, M_v being not far from M_w. We can therefore conclude that calculations assuming a monodisperse sample of mass M_w and intrinsic viscosity $[\eta]$ will lead to a good approximation for *D* and *q*.

Influence of parameter 'a'. We have also performed the calculations in the case of three unknowns *a*, *D* and *q*. As shown in *Table* 3, there is no appreciable change in the results for an appreciable increase in computer time. For example in the cellulose compounds, a comparison of the calculation with a fixed at 5.15 Å and with a variable gives only small relative deviations:

$$\frac{\Delta a}{a} < 3\% \quad \frac{\Delta q}{q} < 1\% \quad \frac{\Delta D}{D} < 10\%$$

An application of the theory of Yamakawa on intrinsic viscosity provides information on the hydrodynamic diameter and the persistence length of the polymer chain in a given solution.

Then, we can:

(1) apply the quantitative results on chain rigidity in dilute solutions to calculate phase diagrams and phase transitions at higher concentrations[34].

(2) calculate the translational diffusion coefficient within the Yamakawa theory[35] and the scattering

Table 3 Influence of the parameter '*a*'. Comparison of the values of the hydrodynamic diameter, *D*, and of the persistence length, *q*, of some polymer–solvent system in two types of calculations: (a) *a* constant (= 5.15 Å for the cellulosic compounds and 12 Å for the polyterephthalamid paraphenylene). *D* and *q* variables. (b) *a*, *D* and *q* variables

		(a)				(b)	
Polymer/Solvent	*D* (Å)	*q* (Å)	δ^2	*a* (Å)	*D* (Å)	*q* (Å)	δ^2
CTC/Dioxane 20°C	13	154	0.3352	5.20	12	154	0.3349
NC/Acetone 20°C	11	156	0.713	5.00	13	157	0.681
CTA/Acetone 25°C	6	57	0.225	5.00	7	58	0.223
/TFA 25°C	10	55	0.115	5.35	10	52	0.097
Polyterephthalamide paraphenylene/H_2SO_4 96% 25°C	9	116	0.718	12.10	9	114	0.705

intensity and compare with experimental results.

We must point out though, that a change of conformation of the molecule has been observed in CTC in dioxane and ethylacetate as a function of temperature. The conformation of the molecule at a given temperature has also been shown to be dependent on the molecular mass[36]. In the discussion given previously this conformational change was not taken into account (the persistence lengths obtained are averaged over all conformations). But this conformational change is only slightly cooperative and the previously obtained persistence length is a good approximation. This can be seen if we calculate D and q for the system CTC/Dioxane[29] at 20°C taking only polymers of mass $\geqslant 300\,000$ into account we find with $a = 5.15$ Å:

$$D = 13 \text{ Å} \quad q = 154 \text{ Å} \quad \delta^2 = 0.335 \text{ (mono)}$$

$$D = 12 \text{ Å} \quad q = 162 \text{ Å} \quad \delta^2 = 0.237 \text{ (poly)}$$

According to ref. 36 such a system should be fairly rigid. If we compare with the values of *Table 2*, we find as expected somewhat smaller values of persistence length in the average system. We think that there is only a weak difference between the two conformations and not a drastical variation like in helix–coil transition.

We expect the conformational change at low concentration to be a general phenomena in other cellulose compounds. In a future publication, we will report on intrinsic viscosity measurements we have performed in these systems and will analyse our results along the same lines presented here.

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