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Conformational Change Studies by Intrinsic Viscosity of Cellulose Tricarbanilate as a Function of Temperature

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SUMMARY

The experimental variation of the intrinsic viscosity $[\eta]$ as a function of temperature for various molecular weights of cellulose tricarbanilate in solution in dioxane displays a S-shaped character with two plateau regions, respectively at low and high temperatures. The use of the Yamakawa model leads to two distinct values for the chain stiffness q, one which may be associated to a rather "rigid" conformation of the macromolecule (q=139 Å), the other which may correspond to a rather "flexible" conformation (q = 84Å).

INTRODUCTION

Gupta, Marchal and Burchard (1), have shown by dielectric relaxation and static permittivity measurements, that a reversible thermally induced conformational change takes place for solutions of cellulose tricarbanilate (CTC) in dioxane and in ethylacetate (from a less to a more flexible conformation with increasing temperature). In both solvents, this conformational change is molecular weight dependent. Their results are reproduced on figure 1. For a given molecular weight, M_w, the variation of $\eta_0 f_c/T$ (f_c is the critical frequency of the hertzien spectra of the dielectric relaxation) displays a S-shaped curve with two plateau regions.

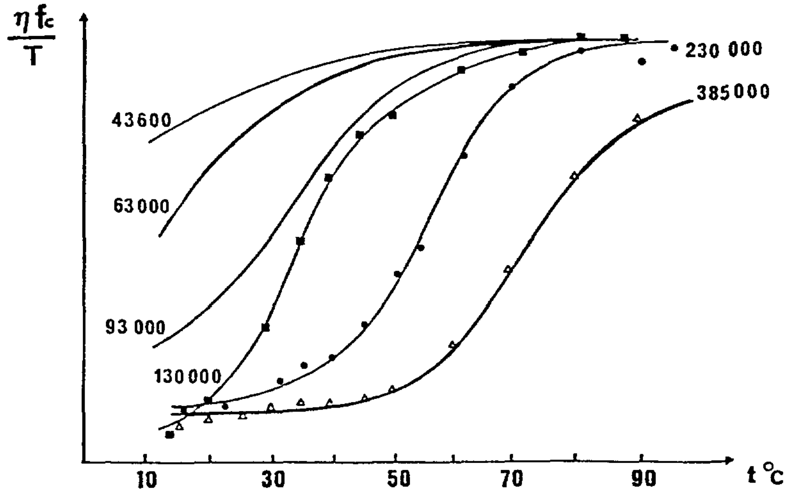

Figure 1. Variation of $\eta_0 f_c/T$ as a function of temperature for CTC samples of various molecular weights in solution in dioxane.

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In a previous study (2a, 2b), we have used the persistent cylinder model of Yamakawa (3) to deduce, from intrinsic viscosity measurements $[\eta]$ on cellulose derivatives solutions, the characteristics of each polymer chain in a given solvent, i.e., its persistence length q and its hydrodynamic diameter D. For example, from values of $[\eta]$ obtained on solutions of CTC in dioxane, at room temperature, we find q = 146 Å and D = 15 Å (2a). However, in all these calculations, we don't have taken into account the possible existence of a conformational change of the macromolecule.
So, the purpose of this work is :

- first, to perform experimental measurements of $[\eta]$ as a function of temperature, for CTC samples with various molecular weights in solution in dioxane, and to see whether it is possible or not to find a S-shaped curve for $[\eta] = f(T)$ as it has already been found for $\eta_o f_c/T = f(T)$. These two quantities depend on the macromolecular friction (through translational and rotational diffusion coefficients) and may be both sensitive to a possible conformational change.
- then, to use the previously mentioned treatment (2a) (based on the theory of Yamakawa) for respectively the CTC samples which have a high and a low value (plateau regions where the macromolecule has respectively the rigid and the flexible conformation) of their $[\eta]$ as a function of temperature, to characterise the two macromolecular conformation, through their persistence length q and their hydrodynamic diameter D.

I - Experimental results :

We wish to thank E. Marchal and W. Burchard who kindly supplied the CTC samples. The molecular weight of these samples ranges from 59700 to 910000, and the polydispersity, h, is about 1.10. Rhône-Poulenc has provided us with 571000 molecular weight CTC sample, with a polydispersity h = 2.25.

Table I

h	T°C Mw	20,1	26,0	35,8	44,4	52,8	68,7	more rigid conformation	more flexible conformation
1,1	59 700	0,5103	0.4629	0,5083	0,4123	0,4247	0,3994	T ⩽ 35,8°C	T ⩾ 44,4°C
1,1	83 000	0,8592	0,8019	0,7315	0,6839	0,6383	0,6139		T ⩾ 53,8°C
1,1	162 000	1,1005	1,1052	1,0841	1,0533	0,9484	0,8658	T ⩽ 39,3°C	T ⩾ 63,8°C
?	230 000	2,1424	2,0929	1,8794	1,6949	1,6496	1,4077	prefiguration of "plateau"	
?	385 000	3,513	3,334	2,950	-	2,426	1,9833	$[\eta]$ = linear and decreasing function of T	
2,25	571 000	7,1764	6,5570	5,9367	5,4710	5,1628	4,2250	$[\eta]$ = linear and decreasing function of T	
?	910 000	8,577	7, 946	7,217	_	5,873	-	$[\eta]$ = linear and decreasing function of T	

Experiments where achieved by using an Ubbelhode viscosimeter, at fixed temperatures (+ 0.1°C), for concentrations of CTC in dioxane ranging from 2 to 10.10^{-4} g/cc. Specific viscosities $(\eta - \eta_0)/\eta_0 c$ extrapolated at zero concentration give us the intrinsic viscosity values in dl/g which are reported on table I and figure 2.

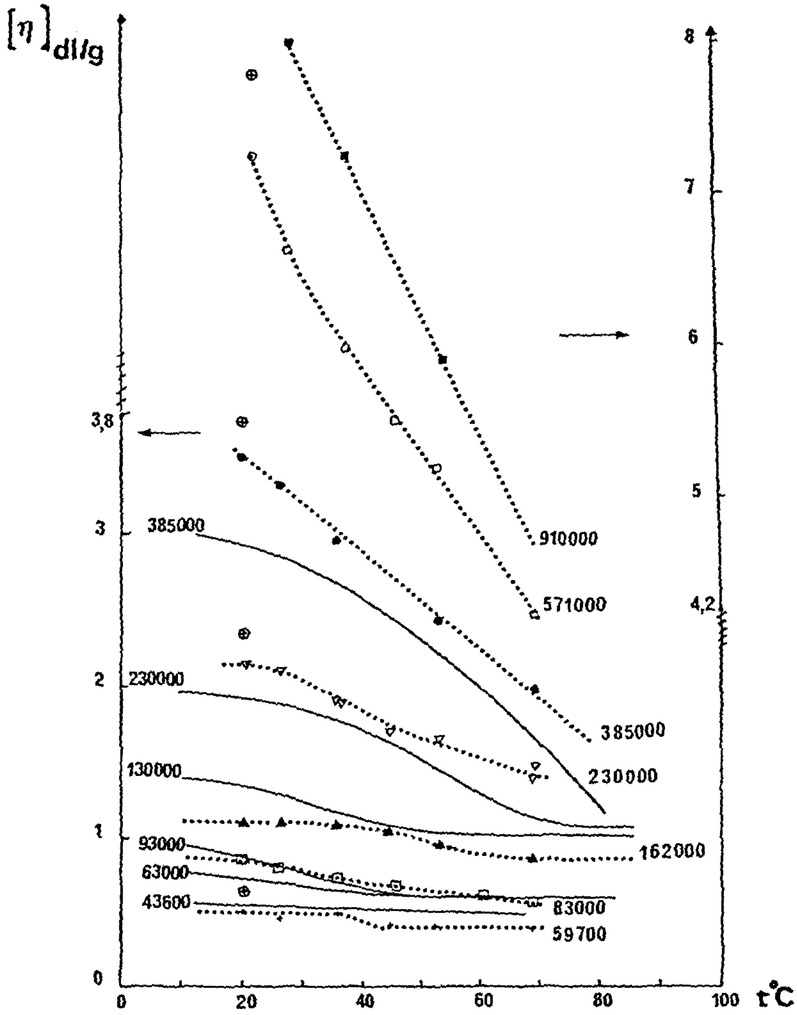

Figure 2. Intrinsic viscosity $[\eta]$ (dl/g), as a function of temperature t°C, for CTC samples of various molecular weight

———— $[\eta]$ calculated from the experimental values of $\eta \cdot f_c/T$ given by Marchal (1)

.... $[\eta]$ our measurements

⊕ experimental points of Marchal

II - Comparison with previously published results :

The curves of the experimental values of $[\eta]$ as a function of temperature do not show, so distinctly, the existence of these two plateau regions. We may notice that the range of temperature is 10°C narrower (from 20 to 70°C).
As a comparison, Marchal's results were exploited by applying Kirkwood-Riseman model (5). The relation :

$$D_R = \pi . f_c = \frac{N_A \, k \, T}{4 \, M [\eta] \eta_o}$$

with D_R, the rotationnal diffusion coefficient
f_c, the dielectric critical frequency
N_A, the Avogadro number
k , the Boltzman constant
T , the temperature
M , the molecular weight of polymer
$[\eta]$, the intrinsic viscosity value
η_o, the solvent viscosity
gives the $[\eta]$ values from the inverse of the quantity $(\eta_o f_c/T)$ measured by Marchal and all. So, we have :

$$[\eta] = \frac{N_A \, k}{4\pi} \cdot \frac{1}{M} \cdot \frac{T}{\eta_o \, f_c}$$

These calculated values are displayed on figure 2. Although the quantitative agreement is not really good, which has to be expected because of the choice of the chain model, the qualitative behavior of the calculated and experimental values of $[\eta]$ as a function of temperature is the same. A few experimental values of $[\eta]$ for various molecular weight of CTC at 20°C given by Marchal have also been shown on this figure.
As previously mentionned by these authors, the higher the molecular weight, the higher the temperature of this conformational change is.

III - Discussion :

In the temperature range under investigation, and within the limits of experimental determinations, $[\eta]$ is a decreasing and linear function of temperature for the samples of CTC whose M_w do not belong to the range $\}50000 - 300000\{$.
In this molecular range, the variation of $[\eta]$ as a function of T displays a S-shaped behavior. The plateau regions, which correspond respectively with the rather rigid and rather flexible conformations of the macromolecule, seem to be obvious only for the samples where molecular weight are M_w = 59700, 83000, 162000 and 230000. On figure 3, is shown the temperature of appearance of the most flexible conformation as a function of the CTC molecular weight.
The characteristic parameter q of the chain stiffness, obtained by applying the Yamakawa model to all our experimental results without taking into account the previous remark, decreases quite linearly with increasing temperature, but the dispersion of the experimental points is more important than usual. For comparison, the case of solutions of CTC in benzophenone (6) is given on figure 4, and one may expect to have a less pronounced conformational change for CTC in this solvent. Moreover, the experimental

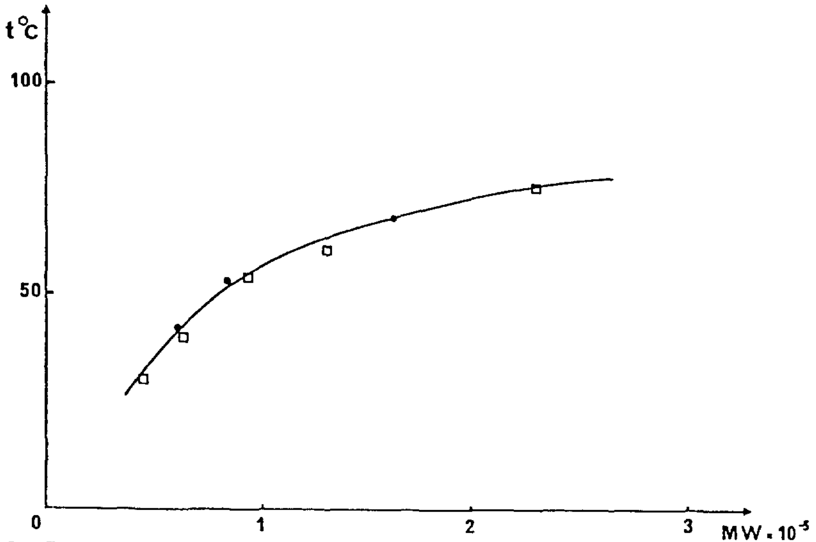

Figure 3. Temperature of appearance of the coil conformation as a function of the molecular weight M_W of CTC samples

- □ experimental points from Marchal (1)
- • present work

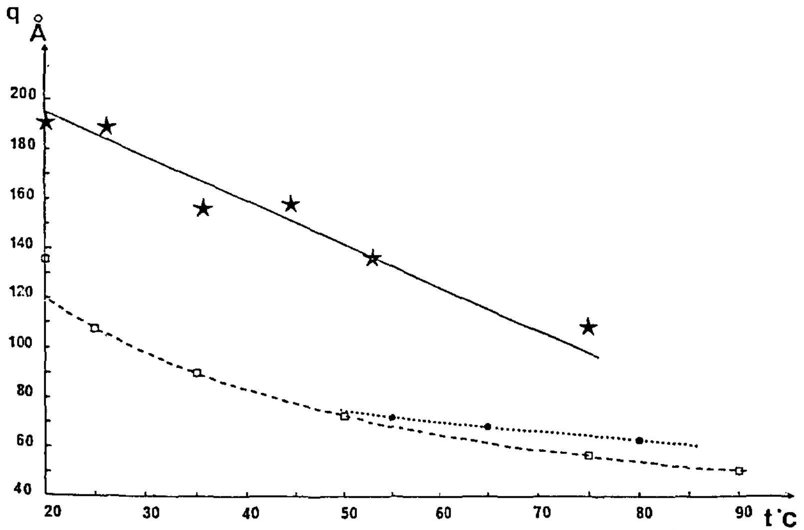

Figure 4. Evolution of the chain rigidity q as a function of temperature for :

- ★ Marchal samples of CTC - this work.
- • CTC/benzophenone solutions (6)
- □ CTC/dioxane solution Marchal (1)

variation of q as a function of the inverse of the temperature is three times more important than which can be expected with the only linear dependance of q with the inverse of the temperature mentioned elsewhere for the cellulosic solutions (7). The curve decreases in a monotonous way because we are dealing with averaged values of q and one must keep in mind that the presence of a high molecular weight sample has a great influence on the q value. So, before studying a weight range, $50000 < M_W < 300000$, we have taken care to place our experimental values (stars) by comparing them with the ones of Burchard-Husemann (4) (15 points -cross-shaped) and Burchard-Sutter (8) (11 points - circles-shaped).

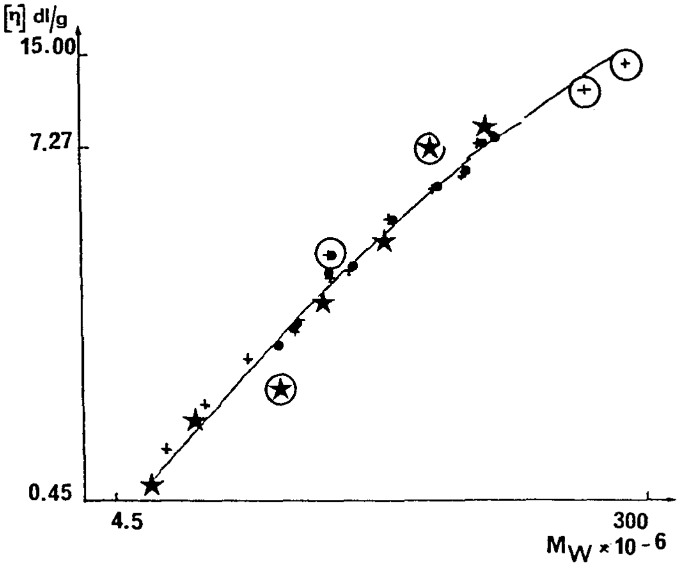

Figure 5. Intrinsic viscosity [η] (dl/g), as a function of M_W in log log scale
+ Burchard-Husemann (4) at 20°C
★ this work
● Burchard-Sutter (8)

On figure 5, we can see the distribution of these 33 points all around the calculated curve of ln [η] as a function of ln (M_W) which is obtained for D = 10 Å and q = 161 Å, the values which give the better fit. One can notice that 6 points (large circles) are quite far from the mean curve, among which two from ours, $M_W = 162000$ and $M_W = 571000$. They are not considered in the following.

So, for the remaining 27 points, at 20°C, the better fit for a molecular weight range of 59700 to 950000, leads to D = 10 Å and q = 164 Å. For our experimental points, i.e.,for CTC samples of same origin, in a weight range of 59700 to 910000, we find a good agreement : D = 9 Å and q = 170 Å. By restricting the weight range, i.e. by omitting the high weights, we obtain a decrease of the value of the persistence length. For example, for the experimental values of Burchard-Husemann (4), the treatment of a range of mass, $67200 < M_W < 950000$ gives D = 16 Å and q = 154 Å, while the same calculation on a range of mass, $67200 < M_W < 230000$, gives D = 21 Å and q = 120 Å .

By reducing our weight range to $50000 < M_W < 300000$, we obtain at 20.1°C the following values : D = 13 Å and q = 139 Å .

When the thermally induced conformational change is taken into account, the parameters for the chain stiffness become at 68.8°C : D 14 Å and q = 84 Å. (the relative accuracy of the calculations is always better than 10%).

This result clearly shows the conformational change from a semi-rigid form to a flexible form of the CTC macromolecule with increasing temperatures.
However, it is difficult to specify the physical nature of this change : is it a weakly cooperative helix-coil transition or a stiffness loosening due for example, to the breaking of hydrogen bonding ? Unfortunately, an independent measurement of the mean square end to end distance $\bar{R}^2$ could not give the answer : indeed the Yamakawa model implies a simultaneous variation of these two parameters $\bar{R}^2$ and q.

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