ELSEVIER

PII: S0144-8617(97)00041-6

Carbohydrate Polymers 34 (1997) 91–94

0144-8617/97/$17.00 + .00

Derivatization of cellulose in homogeneous condition: 1-cellulose propionate

E. Bianchi[a], **E. Marsano**[a], **L. Ricco**[a] and **G. Conio**[b]

[a]*Dipartimento di Chimica e Chimica Industriale, Università Via Dodecaneso 31, 16146 Genova,Italy*
[b]*IMAG, CNR, Via De Marini 6, 16149 Genova,Italy*

(Received 9 August 1996; revised version received 8 January 1997; accepted 11 February 1997)

Samples of cellulose propionate were prepared by reaction of propionyl chloride with cellulose dissolved in dimethylacetamide/5% LiCl. The values of the substitution degree (DS) as well as the purity of the products were determined. The trend in chain rigidity in terms of the persistence length as a function of DS was obtained by applying the Yamakawa–Fujii method to the intrinsic viscosity values. The rigidity progressively decreases with DS. All the samples keep mesogenic behaviours. Copyright © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Aliphatic esters of cellulose belong to a class of derivatives whose macromolecular behaviours are scarcely known, except for acetates (Kamide and Saito, 1987a; Doelker, 1993) which have been widely employed in industrial processes.

One of the reasons for this lack of knowledge is probably based on the difficulty in preparing reliable products from reactions performed with cellulose fibers in heterogeneous conditions; in fact the cellulose molecules behave differently depending whether they are or are not on the fiber surface. The derivatives are heterogeneous and, when the substitution degree is low, cannot be easily separated from the unreacted cellulose (Marsano *et al.*, 1993). Moreover the samples, having intermediate substitution degree, are generally obtained by hydrolysis of the completely substituted and soluble cellulose derivative.

Discovery of new solvents (Philipp *et al.*, 1986) now allows one to perform derivatization processes in homogeneous conditions where all the molecules have the same probability of reacting. Unfortunately the majority of these solvents are not suitable for this kind of process, due to their chemical reactivity. Mixtures of *N,N*-dimethylacetamide (DMAc) and *N*-methylpyrrolidone (NMP) with LiCl appear to be, at present, the most promising solvents, as both of them dissolve cellulose even at high concentration, and do not interfere with other chemical agents (Diamantoglou and Kundiger, 1995). Dawsey and McCormick (1990), Diamantoglou and Kuhne (1988), Schempp *et al.* (1984), and Edgar *et al.* (1995) synthesized in this way various different cellulose derivatives (ethers, carbamates, acetates, acetoacetates) partially substituted without the need of an additional hydrolysis step.

In this paper we describe the derivatization of cellulose dissolved in DMAc containing 5% of LiCl (w/w) with propionyl chloride. The macromolecular properties as a function of the substitution degree (DS) were studied as well as the retainment of mesogenic properties, peculiar to nonderivatized cellulose in the same solvent.

EXPERIMENTAL

A sample of regenerated cellulose, DP = 250, was supplied by Stazione Sperimentale per la Cellulosa, Carta e Fibre Tessili Vegetali ed Artificiali (Milan). Propionyl chloride (Janssen) and Methanol (Fluka) were used as received. *N,N*-Dimethylacetamide (Fluka) was distilled under vacuum and stored under nitrogen atmosphere over Riedel type 4A molecular sieves. Lithium chloride (Fluka) was dried at 200°C under vacuum before use.

Potentiometric titrations were performed by using a Radiometer Phmeter PHM 84 equipped with combined electrode GK2401C and temperature automatic compensator T701. The intrinsic viscosity $[\eta]$ was determined by using a suspended-level Ubbelhode viscometer (solvent flow time > 100 s) in the concentration range 0.1–0.4 g/100 ml, at $T = 25 \pm 0.05$°C.

The concentrated solutions for liquid crystallinity tests were prepared by mixing suitable amounts of polymer and solvent. About one month was necessary in order to obtain an equilibrium state. The sample was observed under polarized light between crossed nicols using a Microscope Polivar Pol. Reichert Jung. Density measurements were performed by using a gradient column.

RESULTS AND DISCUSSION

Six samples of cellulose propionate (CEP) were synthesized according to the following route. A suitable amount of solution containing 2.5% (w/w) of cellulose in DMAc/5 LiCl was cooled down to 0°C under a nitrogen atmosphere. Propionyl chloride was then added under stirring, in a proportion ranging between 0.4 and 5.8 mol of chloride per mole of cellulose repetition unit. After 2 h, the product was precipitated with ethanol, washed with acetone and dried under vacuum at 50°C. The DS was determined by the increase in weight of the product (w_{CEP}) with respect to that of cellulose (w_{CE}), according to the equation:

$$DS = w_{CEP} - w_{CE}/(57 - 1)n_{CE} \tag{1}$$

where n_{CE} is the number of moles of cellulose repetition units, 57 is the molecular weight of the residue CH_3-CH_2-CO- and 1 is the molecular weight of the substituted -H.

A different method for DS determination is based on the use of water as precipitant agent. In this case the unreacted propionyl chloride immediately hydrolyzes and the propionic acid may be titrated with NaOH. Thus the reacted propionyl chloride is evaluated and DS easily deduced.

The agreement between the results of the two methods is fairly good, except when a colloidal form of the precipitate causes a poor separation of the polymer from the solution and interferes with the titration. For this reason we assume as more generally reliable the results of the ponderal method and report the corresponding DS values in Table 1 column 3.

Figure 1 illustrates the trend of DS as a function of the ratio RCOCl/CE. Curve (a) gives the theoretical trend at yield = 1, when the whole chloride is supposed to react with the cellulose. Curve (b) gives the trend of experimental values. Its progressive divergence from (a), is strongly evident when DS > 2, which probably reflects the different reactivity of -OH functions on the repetition unit of cellulose. This fact has been already observed for other derivatives, e.g. the synthesis of carboxymethylcellulose where a preferential substitution on C_6 of a sample of cellulose II was deduced (Kamide and Saito, 1987b).

Table 1. **Synthesis and properties of cellulose propionate**

Sample	RCOCl/CE (mol/mol)	DS	[η] (dl/g)[a]
CE	—	0	2.90
CEP 1	0.4	0.27	2.36
CEP 2	1.8	1.01	1.62
CEP 3	2.0	0.80	1.47
CEP 4	2.9	1.11	1.33
CEP 5	5.7	1.30	1.19
CEP 6	8.9	1.76	0.88

[a] Measured in DMAc / 5 LiCl at 25°C.

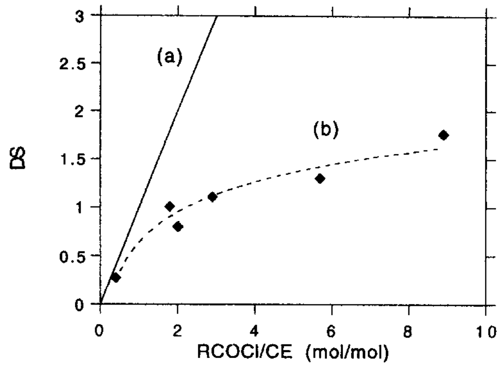

Fig. 1. Substitution degree of cellulose propionate versus the ratio RCOCl/CE.

Viscosity values in DMAc/5 LiCl at $T = 25$°C are reported in the last column on Table 1. Figure 2 gives the intrinsic viscosity as a function of DS. The smooth decrease of [η] up to DS≈2 involves a priori a number of factors, such as the residual intramolecular hydrogen bonds along the main chain, the steric hindrance of the substituents, the interactions of solvent with cellulosic units as well as with lateral groups.

Data reported in the literature only concern mixed esters of propionic acids with other aliphatic acids (Yuichiro *et al.*, 1987), besides some properties of the tripropionate in the solid state and in chloroform

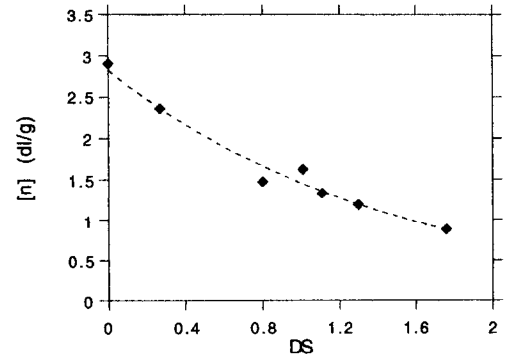

Fig. 2. Intrinsic viscosity in DMAc / 5 LiCl at 25°C of cellulose propionate versus DS.

solution (Farvardin and Howard, 1979). The relationship $[\eta]/M_v$ in chloroform allows calculation of the intrinsic viscosity of an hypothetical tripropionate sample having the same DP as our cellulose. The value $[\eta] = 0.75$ dl/g agrees well with the viscosity of the curve in Fig. 2 extrapolated to DS = 3, in spite of the different solvent.

On the whole, the data in Fig. 2 are consistent with a progressive decrease in the chain rigidity as a function of DS. This decrease may be quantitatively expressed through the persistence length q, calculated by applying the Yamakawa–Fujii (YF) method (Yamakawa and Fujii, 1974) to the viscosity data. Yamakawa and Fujii put forward an equation for the dependence $[\eta]/M_v$ in the case of a wormlike chain:

$$[\eta] = \Phi(L')^{3/2}.(2q)^3/M_v \tag{2}$$

where $L' = M/M_L$ is the reduced contour length of the chain, M_L the mass per unit length, Φ a function of L' and d' (reduced diameter) tabulated by the authors, q the persistence length, and $2q$ the Kuhn segment.

For our case M_L was calculated from the average value of the molecular weight of the repetition unit M_0 divided by the projection of the length L_0 of the unit itself onto the chain axis. L_0 is supposed to be constant and equal to that of the pure cellulose (5.14 Å) (Bianchi *et al.*, 1985) irrespective of DS. (Fig. 3)

The unreduced diameter d was obtained from the equation (Flory, 1984)

$$d = (M_0/\rho N_A L_0)^{1/2} \tag{3}$$

where ρ is the polymer density and N_A the Avogadro number; M_0 and L_0 have the same meaning as previously defined.

ρ Values for the samples in Table 1 are listed in Table 2 together with the d values. Finally M_v may be calculated from the polymerization degree (DP) of cellulose multiplied for the molecular weight of the monomeric unit. Notwithstanding the decrease in q and the concomitant increase of d with DS (see sixth and fifth columns on Table 2), the value of the axial ratio of the Kuhn segment $2q/d$ is sufficiently high to entail the formation of lyotropic phases. In fact, according to Flory (1956), when the ratio $2q/d$ is higher than 6.4, anisotropic phases may occur in solution at suitable concentrations. The theory predicts the polymer volume fraction ν'_{th} at which anisotropy may be first observed. The calculated values of ν'_{th} are reported in column seven.

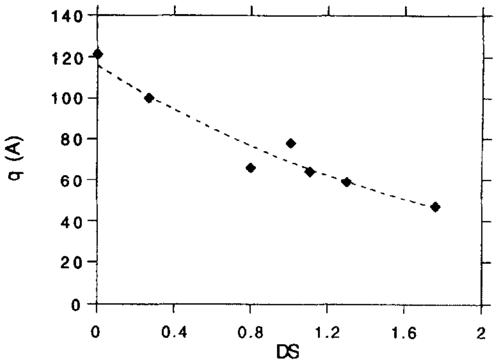

Fig. 3. Persistence length of cellulose propionate as a function of DS.

Experimental studies on the mesogenic behavior of propionate derivatives have been performed for samples CEP 3 and CEP 5 according to the procedure reported in the experimental section. Column eight reports the data together with the ν'_{exp} value for pure CE, previously determined (Bianchi *et al.*, 1985). Figure 4 is a picture of the biphasic system of sample 3 close to the ν'_{exp} condition. Finally Fig. 5 gives the ν'_{th} and ν'_{exp} trend versus DS.

The condition $\nu'_{th} > \nu'_{exp}$, clearly illustrated in Fig. 5, is common to many mesogenic systems and has been widely examined in a previous paper (Ciferri and Marsano, 1987). Different factors were considered. Firstly the possible indetermination of d values. Secondly, q_{YF} itself may be underestimated with respect to the actual persistence length. Finally the polydispersity of the polymer may play an important role.

These considerations clearly indicate a non-negligible indetermination of data in column six. In the case of pure cellulose in DMAc/LiCl (Ciferri and Marsano, 1987) the possibility of association phenomena in order to explain the discrepancy that $\nu'_{exp} < \nu'_{th}$ was also suggested. Alternatively the presence of anisotropic soft interactions (Warner and Flory, 1980) may be evoked, but they were considered of minor significance for cellulose in Ciferri and Marsano (1987). Similar considerations appear valid for propionate derivatives.

Table 2. Persistence length and mesogenic behavior of cellulose propionate

Sample	M_0	M_v	ρ (g/cm^3)	d (Å)	q (Å)	ν'_{th}	ν'_{exp}
CE	162	40 500	1.52	5.8	121	0.19	0.08
CEP 1	177	44 250	1.45	6.3	100	0.24	—
CEP 2	219	54 750	1.32	7.3	78	0.36	—
CEP 3	206	51 500	1.35	7.0	66	0.40	0.23
CEP 4	224	56 000	1.31	7.4	64	0.44	—
CEP 5	235	58 750	1.29	7.7	59	0.49	0.40
CEP 6	261	65 250	1.28	8.1	47	0.77	—

Fig. 4. Micrograph of a biphasic solution of sample 3 in DMAc.

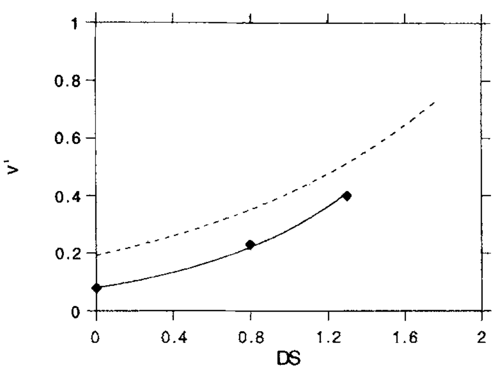

Fig. 5. Experimental and theoretical volume fraction of cellulose propionate versus DS: ◆, experimental values; dashed line, theoretical values

In conclusion and on the base of the above discussion, we believe that our results supply a good knowledge of the macromolecular behavior of cellulose propionate as a function of DS. Moreover the retention of mesogenic properties has also been assessed.

REFERENCES

Bianchi, E., Ciferri, A., Conio, G., Cosani, A. and Terbojevich, M. (1985) *Macromolecules* **18**, 646.

Ciferri, A. and Marsano, E. (1987) *Gazzetta Chimica Italiana* **117**, 567.

Dawsey, T. R. and McCormick, C. L. (1990) *Rev. Macromol. Chem. Phys.* **30**, 405.

Diamantoglou, M. and Kuhne, H. (1988) *Das Papier* **42**, 690.

Diamantoglou, M. and Kundiger, E. F. (1995) In *Cellulose and Cellulose Derivatives: Physico-chemical Aspects and Industrial Applications*, ed. J. F. Kennedy, G. O. Phillips and P. A. Williams. Woodhead Publishing, 141–152.

Doelker, E. (1993) *Adv. Polym. Sci.* **107**, 199.

Edgar, K. J., Arnold, K. M., Blount, W. W., Lawniczak, J. E. and Lowman, D. W. (1995) *Macromolecules* **28**, 4122.

Farvardin, J. R. and Howard, P. (1979) *Polymer* **20**, 667.

Flory, P. J. (1984) *Adv. Polym. Sci.* **59**, 1.

Flory, P. J. (1956) *Proc. Roy. Soc. (London), Ser. A* **234**, 73.

Kamide, K. and Saito, M. (1987) *Adv. Polym. Sci.* **83**, 1.

Kamide, K. and Saito, M. (1987) *Adv. Polym. Sci.* **83**, 5.

Marsano, E., Tamagno, M., Bianchi, E., Terbojevich, M. and Cosani, A. (1993) *Polym. Adv. Tech.* **4**, 25.

Philipp, B., Lukanoff, B., Schleicher, H. and Wagenknecht, W. (1986) *Z. Chem.* **26**, 50.

Schempp, W., Krause, T., Selfried, U. and Koura, A. (1984) *Das Papier* **38**, 607.

Yamakawa, H. and Fujii, M. (1974) *Macromolecules* **7**, 128.

Yuichiro, S., Shuto, Y., Sugiyama, J., Harada, H. and Okamura, K. (1987) *Macromolecules* **20**, 2317.

Warner, N. and Flory, P. J. (1980) *J. Chem. Phys.* **73**, 6327.