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# Crosslinking of Methylolcellulose During Acetylation in the Dimethylacetamide–Paraformaldehyde System

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*SUMMARY*

*This paper describes the physicochemical characterization of methylcellulose acetate obtained by acetylation of methylcellulose. Dilute polymer solutions were investigated by means of light scattering and hydrodynamic techniques. Several samples were examined, with* $DS(COCH_3) = 2{\cdot}5\text{–}2{\cdot}7$ *and* $DS(CH_2O) = 1{\cdot}3\text{–}2{\cdot}2$. *The polymers are soluble in most common organic solvents, except for a certain amount of material (4–15%) which swells without dissolving. Light scattering measurements in acetone, acetonitrile, ethyl acetate, tetrahydrofuran and 2-butanone indicate no aggregation for the polymer in the examined concentration range. On the other hand,* $DP_W$ *values are obtained 2 to 4 times higher than the values of the starting cellulose. These findings are interpreted in terms of crosslinking reactions to yield acetal derivatives between two or more cellulose chains.*

*Viscosity measurements also indicate lack of aggregation, thus supporting the above hypothesis.*

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Johnson and co-workers (Johnson *et al.*, 1976) introduced a solvent system for cellulose, consisting of dimethyl sulphoxide containing excess paraformaldehyde (in comparison to hydroxyl groups of the macromolecule). The dissolved cellulose was then derivatized in a homogeneous phase, giving ethers (Nicholson & Johnson, 1977), esters (Seymour & Johnson, 1978; Miyagi & Young, 1982) and oxidation products (Basso *et al.*, 1982).

Remarkable improvements in cellulose acetylation were obtained in dimethyl formamide–paraformaldehyde (DMF–PF) or in dimethylacetamide–paraformaldehyde (DMAC–PF) solvent mixtures using acetic anhydride in the presence of an alkali metal oxide or acetate as a catalyst (Leoni *et al.*, 1980; Leoni & Baldini, 1982).

Acetylated methylol and/or polyoxymethylene chains are present in these products, possibly together with acetylated and free cellulose hydroxyls, the extent of acetylation depending on the acetylation time, the temperature and the amount and nature of the catalyst. The oxymethylene/cellulose ratio in the acetylated products seems strictly related to the formaldehyde/cellulose ratio in the starting solutions.

In this paper we report investigations of the physicochemical properties of the dilute methylolcellulose acetate (MCA) solutions obtained in the DMAC–PF system and attempt a comparison with the corresponding properties of cellulose acetate (CA) at the same degree of substitution. (For a preliminary report, see Cosani *et al.* (1983).)

## EXPERIMENTAL

### Materials

Solvents and reagents were of reagent grade and were used without further purification. Prehydrolysed kraft pulp cellulose with weight average degree of polymerization ($DP_W$) = 500 ± 25 was obtained from Snia Fibre, Italy. The degree of polymerization was calculated by intrinsic viscosity measurements in 0·5 M cupriethylenediamine (CED) at 25·0°C using the method introduced by Marx (Marx, 1955; Marx Figini & Schulz, 1962).

CED was purchased from Carlo Erba, Milan, Italy, as a 1 M solution in water; it was then diluted to 0·5 M.

## MCA preparation

The following general method has been used. Cellulose solution in DMAC–PF (30 g), containing 8·4% $CH_2O$ and 9·5% cellulose, was heated to 60°C. A solution of 0·3 g potassium acetate in 30 g acetic anhydride, containing a few drops of acetic acid, was then added under vigorous stirring and an inert gas atmosphere over a period of about 15 min. The temperature was subsequently raised to 120°C and the reaction mixture stirred for a further 60 min. The clear solution was allowed to cool to room temperature. Sixty millilitres of 1:1 (v/v) water/methanol were finally added with stirring. A white precipitate was obtained, which was collected in a fritted glass funnel and washed several times with the water/methanol mixture.

After drying to constant weight at 80–100°C, 5·69 g of white powder were obtained. The product has been characterized by elemental analysis, i.r., u.v., $^1$H-n.m.r., analysis of acetate groups (hydrolysis) (degree of substitution (*DS*) = 2·2 ± 0·1) and analysis of oxymethylene groups ($CH_2O$) (decomposition by $H_3PO_4$ and distillation of formaldehyde) (*DS* = 2·3 ± 0·1). The above method allows variation of cellulose % from 2·2 to 12·9% and the formaldehyde % from 2·8 to 15·1%.

If double the amounts of acetic anhydride and potassium acetate are used, the *DS*($COCH_3$) per glucosidic residue is increased from 2·2 to 2·6.

## MCA solutions

The sample (~1 g) was dried for 24 h at 90°C. It was then swollen in 100 ml of solvent at room temperature and shaken for 2 days in a Stuart–Flask shaker. The opalescent mixture was finally centrifuged to yield a clear solution.

Concentrations were determined by weighing the dry residue obtained after removal of the solvent from a known amount of polymer solution.

## Methods

Viscosities were determined using suspended level Ubbelohde viscosimeters at 20 ± 0·1°C having flow times for the solvent greater than 120 s

and relative viscosities between 1·2–1·8. Newtonian behaviour of solutions was observed. Intrinsic viscosity $[\eta]$ values were obtained by means of the Huggins (Huggins, 1942) and Kraemer (Kraemer, 1938) equations.

Light scattering measurements were performed at room temperature using a Sofica Model 42000 photometer with cylindrical cells immersed in toluene. Non-polarized light with wavelength ($\lambda$) = 436 and 546 nm was used covering scattering angles ($\theta$) between 30 and 150°. The instrument was standardized using pure dust-free benzene as a reference liquid, taking the values $15{\cdot}8 \times 10^{-6}$ and $45{\cdot}6 \times 10^{-6}$ cm$^{-1}$ at 546 and 436 nm (Utiyama, 1972) as the Rayleigh ratio of benzene, $R_B$.

Solutions and solvents were clarified by centrifugation at 25 000$g$ for 1 h. The light scattering data were plotted as $c/H_\theta$ vs. $\sin^2\theta/2 + Kc$, where $K$ is an arbitrary constant chosen so as to provide a convenient spread of the data on a piece of graph paper (Tanford, 1961), and $c$ is the concentration of polymer in g ml$^{-1}$. $H_\theta$ is defined as

$$H_\theta = \frac{(I - I_0)\sin\theta}{1 + \cos^2\theta}$$

where $I_0$ and $I$ are intensity of scattered light for solvent and solution, respectively.

The molecular weight was calculated from the relationship

$$\frac{1}{M_W} = \frac{2\pi^2 n_B^2}{\lambda^4 N R_B} \cdot \left(\frac{dn}{dc}\right)^2 \cdot I_B \left(\frac{c}{H_\theta}\right)_{\substack{c=0 \\ \theta=0}}$$

where $M_W$ is the weight average molecular weight, $N$ is Avogadro's number, and $n_B$ and $I_B$ are, respectively, the refractive index and the scattered intensity (at 90°) of benzene.

The virial coefficient, $B$, can be determined from the limiting slope of the $(c/H_\theta)_{\theta=0}$ vs. $c$ line.

$$B = \frac{1}{2M_W} \cdot \frac{|(c/H_0)_c - (c/H_0)_{c=0}|/(c/H_0)_{c=0}}{c}$$

while the radius of gyration $\langle R_G^2\rangle_z^{1/2}$ is determined from the slope/intercept ratio of the $(c/H_\theta)_{c=0}$ vs. $\sin^2\theta/2$ line

$$\langle R_G^2\rangle_z = \frac{3\lambda^2}{n^2 16\pi^2} \cdot \frac{|(c/H)_{\theta=180} - (c/H)_{\theta=0}|}{|c/H|_{\theta=0}}$$

Values of $dn/dc$ were determined using a Brice–Phoenix differential refractometer, at wavelengths of 436 and 546 nm. Three to five polymer solutions were usually employed in the concentration range $3\text{–}20 \times 10^{-3}$ g ml$^{-1}$.

Infrared measurements were performed on KBr discs using a Perkin–Elmer model 580 instrument.

## RESULTS AND DISCUSSION

The polymer samples investigated in the present work and their $DS(COCH_3)$ and $DS(CH_2O)$ are reported in Table 1.

All were obtained using $DP_W = 500 \pm 25$ cellulose as the starting material at a concentration ranging between 9·3 and 9·6%. For samples (1) to (4) the formaldehyde percentage in the reaction mixture was 8·4% while it was 4·5% in the last sample (sample (5)). For the latter, the $DS(CH_2O)$ value dropped accordingly from 2·2 to 1·3.

MCA is soluble in many systems. We have chosen a number of solvents used in a similar study on cellulose acetate ($DS$ = 2·4–2·8) (Tanner & Berry, 1974), which exhibited favourable $dn/dc$ values ($\geqslant$0·05 ml g$^{-1}$) and did not induce polymer association. Acetone, ethyl acetate, acetonitrile, tetrahydrofuran and 2-butanone were the most suitable.

Polymer solutions were obtained as reported in the experimental section. The percentage of undissolved material reported in Table 1

**TABLE 1**
Characteristics of Samples Investigated

| *Polymer sample* | $DS(COCH_3)$[a] | $DS(CH_2O)$[a] | *Mo*[b] | *% Insoluble* |
|---|---|---|---|---|
| (1) MCA25 | 2·6 | 2·0 | 331 | 16 |
| (2) MCA25/19 | 2·6 | 2·2 | 337 | 5 |
| (3) MCA25/14 | 2·5 | 2·0 | 326 | 2 |
| (4) MCA25/40 | 2·6 | 2·2 | 337 | 3 |
| (5) MCA25/4 | 2·7 | 1·3 | 314 | 4 |

[a] Estimated error ±5%.
[b] Mo = weight residue.

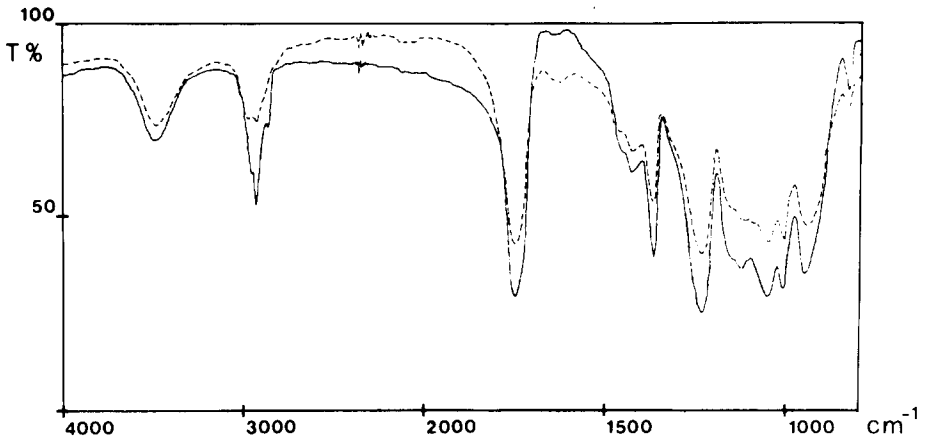


**Fig. 1.** Infrared spectra of MCA25: ——, fraction soluble; – – –, fraction insoluble.

was strictly related to the examined sample and *not* to the solvent properties. In particular MCA 25 showed a relatively high insoluble fraction, while all other samples were much more soluble. Elemental analysis and i.r. data (Fig. 1) strongly suggested that the undissolved fraction was substantially composed of methylolcellulose acetate, i.e. material quite similar to the soluble fraction.

## Refractometry

As expected from the theory, in all solvents examined a linear $n$ vs. $c$ relationship was obtained.

The $dn/dc$ values at 20°C and a wavelength of 546 nm for samples at comparable *DS* are reported in Fig. 2 as a function of the solvent refractive index at the same temperature and 589 nm. The plot relative to cellulose acetate (*DS* = 2·41) (Tanner & Berry, 1974) is also shown for comparison. A linear pattern is observed, in accordance with the Dale–Gladstone empirical equation (Tanner & Berry, 1974):

$$\frac{dn}{dc} = \frac{1}{d_2}(n_2 - n_1)$$

where $d_2$ is the polymer density, $n_1$ the solvent refractive index and $n_2$ the polymer refractive index. According to the above data, other

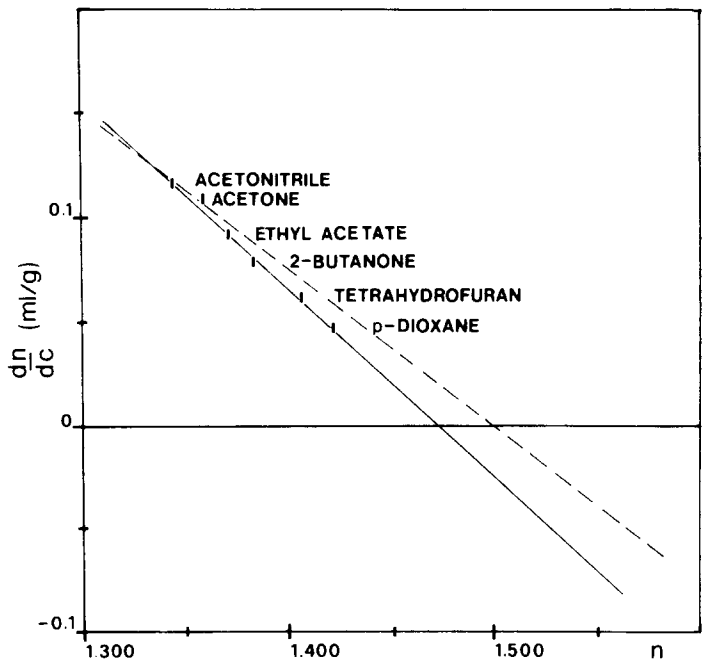


**Fig. 2.** Refractive index increment of MCA ($DS(COCH_3) = 2{\cdot}5\text{-}2{\cdot}7$; $DS(CH_2O) = 2{\cdot}0\text{-}2{\cdot}2$) and CA ($DS = 2{\cdot}45$) solutions as a function of refractive index of the solvent: ——, MCA; – – –, CA (Tanner & Berry, 1974).

solvents suitable for LS measurements should exhibit refractive index values lower than 1·42 or higher than 1·52.

Unfortunately, dimethyl sulphoxide, which was initially considered for this investigation, has an $n$ value of 1·4795. In fact the $dn/dc$ values were exceedingly low ($\simeq 0{\cdot}01$) and rendered quite difficult both detection of the scattered light and a visual estimation of the swollen polymer fraction. Furthermore, MCA tends to aggregate in dimethyl sulphoxide forming stable transparent gels. Using the Dale-Gladstone equation we estimated the refractive index for MCA to be $1{\cdot}473 \pm 0{\cdot}005$ and its density $1{\cdot}11 \pm 0{\cdot}03$ g ml$^{-1}$.

These values are different when compared to those corresponding to cellulose acetate (1·499 and 1·31 g ml$^{-1}$, respectively). In particular, the density change cannot be easily explained, as it is related to several

factors, amongst which chemical structure, crystal structure and degree of crystallinity play major roles.

## Light scattering measurements

The Zimm plot of a representative MCA sample in acetone is reported in Fig. 3. Similar plots were obtained for MCA25/19 and MCA25/14 in the same solvent.

The values of $M_W$, $B$ and $\langle R_G^2 \rangle_z^{1/2}$ are reported in Table 2.

Although all samples exhibited the same chemical properties, as they were prepared under identical experimental conditions, only for MCA25 and MCA25/19 the same $DP$ value is found. MCA25/14 gave, in fact, values corresponding to about 60% of the above. Moreover, while $M_W$ should not exceed 150–170 000 for molecularly dispersed materials (the starting cellulose had a $DP_W = 500$), the authors always found values 2 to 4 times higher. These results possibly reflected multimerization of MCA in acetone as is often found for polysaccharides and derivatives (Elias, 1972).

In particular, Tanner & Berry (1974) found varying degrees of multimerization for cellulose acetate in almost all solvents, giving two substantially different scattering envelopes. Multimerization could be limited to a small fraction of the polymer, giving rather high $M_W$ species

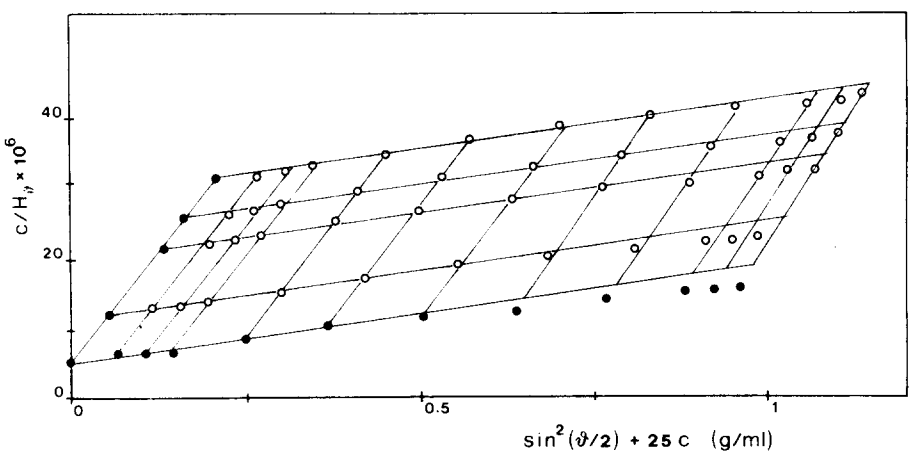


**Fig. 3.** Typical Zimm plot for MCA25 in acetone. $\lambda = 546$ nm.

**TABLE 2**
Dilute Solution Parameters for MCA

| *Polymer* | *Solvent* | $M_W \times 10^{-3}$ [a] | $DP_W$ [a] | $B \times 10^4$ [a] *(mol ml g$^{-2}$)* | $\langle R_G^2 \rangle_z^{1/2}$ [a] *(Å)* |
|---|---|---|---|---|---|
| MCA25 | Acetone | 580 | 1750 | 5·7 | 850 |
| | Acetonitrile | 500 | 1510 | 5·0 | 830 |
| | Tetrahydrofuran | 480 | 1450 | 3·7 | 720 |
| | Ethyl acetate | 520 | 1570 | 1·7 | 810 |
| | 2-Butanone | 530 | 1600 | 0·15 | 890 |
| MCA25/19 | Acetone | 580 | 1720 | 5·3 | 970 |
| | Acetonitrile | 480 | 1430 | 4·6 | 730 |
| | Tetrahydrofuran | 490 | 1450 | 3·0 | 630 |
| MCA25/14 | Acetone | 340 | 1040 | 5·8 | 640 |
| | Acetonitrile | 350 | 1070 | 3·3 | 640 |
| | Tetrahydrofuran | 400 | 1220 | 3·8 | 670 |
| MCA25/40 | Acetonitrile | 480 | 1430 | 4·8 | 740 |
| MCA24/4 [b] | Acetonitrile | 280 | 890 | 5·7 | 690 |

[a] Estimated error ±5%.
[b] $dn/dc = 0{\cdot}123$ ml g$^{-1}$ at $\lambda = 546$ nm.

(microgels). This fact would introduce remarkable uncertainty into the initial slope and intercept of the Zimm plot, due to high curvature at low angles.

Since plots $c/H_\theta$ vs. $\sin^2\theta/2$ at different concentrations were parallel and linear in all cases (Fig. 3), the above possibility should be ruled out. Our experimental results might be better explained in terms of small multimers formed by the majority of the polymer chains. On the other hand, the slope $d(c/H_0)/dc$, related to the virial coefficient $B$, was positive (Fig. 3 and Table 2). MCA multimers should accordingly behave as stable, undissociable entities even at high dilution.

To shed light on these apparently conflicting results, scattering measurements were repeated in other solvents, where different polymer–solvent interactions are expected. In particular, sample MCA25 was investigated in acetonitrile, tetrahydrofuran, ethyl acetate and 2-

butanone; MCA25/19 and MCA25/14 in acetonitrile and tetrahydrofuran; and MCA25/40 in acetonitrile. The Zimm plots obtained in all cases (Fig. 4) did not show evidence of high-curvature scattering envelopes or of negative $d(C/H_0)/dc$ slopes. Moreover, the $M_W$ data are seen to be in reasonable agreement with the acetone values (samples MCA25, MCA25/19 and MCA25/14). In particular, in 2-butanone where $B$ is rather low (Suzuki *et al.*, 1982) (and thus polymer-polymer interactions more likely) the $DP_W$ obtained is practically identical to the corresponding values in thermodynamically better solvents. The results reported in Table 2 should therefore refer to *true* molecular weights free from multimerization.

This hypothesis is further confirmed by measurements of MCA25 in tetrahydrofuran. Whilst at low ($<2 \times 10^{-3}$ g ml$^{-1}$) MCA concentrations plots as described in Fig. 4 were obtained, at higher amounts of dis-

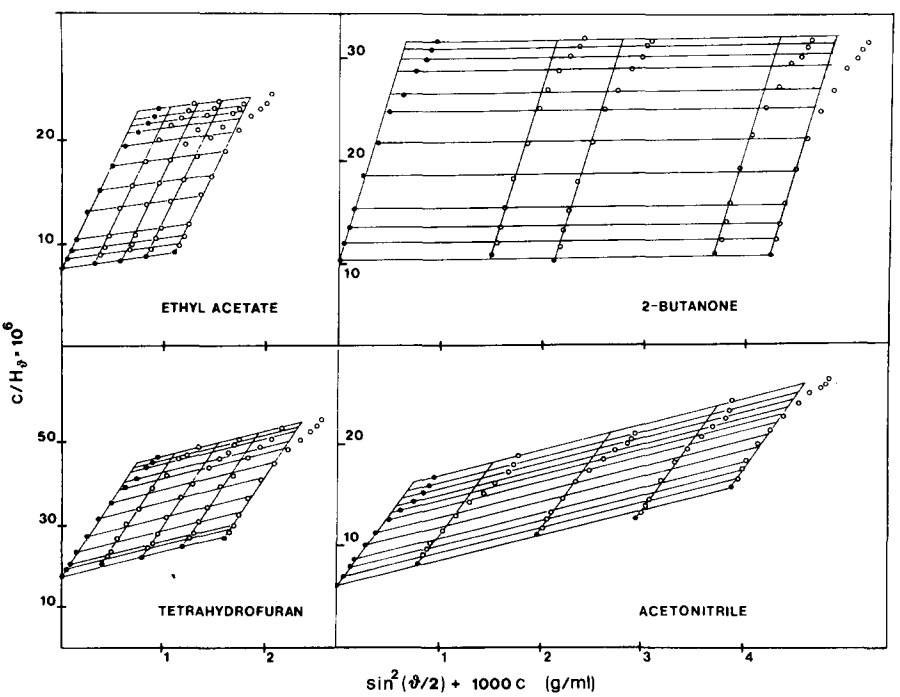


**Fig. 4.** Zimm plots for MCA25 in acetonitrile, ethyl acetate, 2-butanone and tetrahydrofuran.

solved polymer plots were no longer parallel and the corresponding intercepts decreased on increasing concentration, indicating appreciable multimerization under these experimental conditions (Fig. 5). It was therefore concluded that the difference of $DP_W$ observed on comparing the cellulose sample before and after derivatization was most probably due to intermolecular bond formation among cellulose chains during derivatization. It is conceivable in fact that the methylol derivative reacts with hydroxyl groups of a different polymer chain to yield the corresponding acetal. Further extensive crosslinking may lead to a tridimensional network and to insolubility of the material.

Interestingly, the derivatized polymer is partially insoluble in all solvent systems investigated by the authors, as reported in the previous section (see Table 1).

Obviously, intermolecular crosslinking does not exclude the corresponding intramolecular phenomena, which cause conformational changes in the macromolecule (Mancier & Vincendon, 1981).

Crosslinking of cellulose by formaldehyde is a well-known reaction (Parikh, 1967) which has been investigated as far as mechanism and the effects on the macromolecule are concerned (Rowland, 1966; Guthrie,

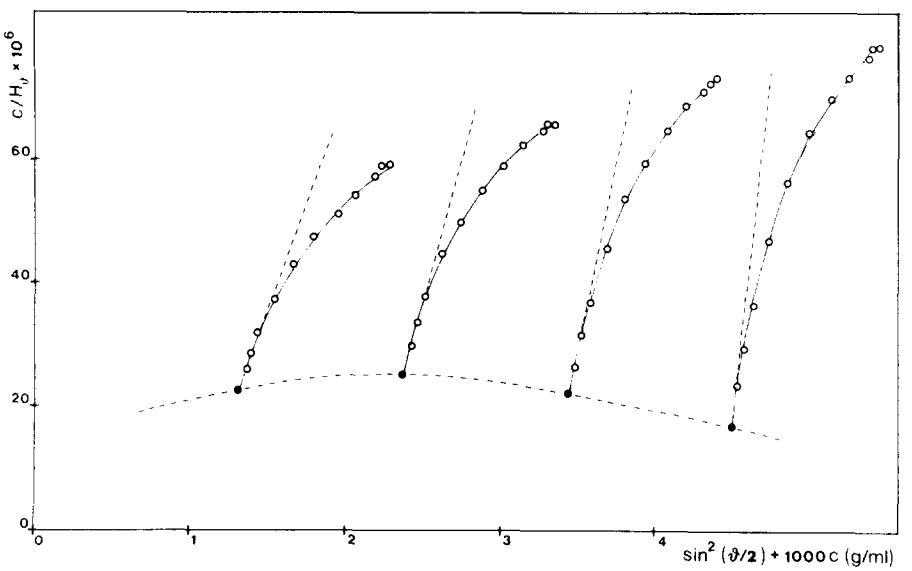


**Fig. 5.** $c/H_\theta$ vs $c$ at different concentrations for MCA25 in tetrahydrofuran.

1967; Smith, 1972). Since acetylation is performed under acidic conditions, crosslinking is more likely to occur during derivatization rather than during cellulose solubilization. Sample MCA25/4, treated in the presence of lower formaldehyde concentrations, exhibits, in fact, a $DP_W$ value remarkably lower than other samples (but higher than the starting material).

Since the soluble fraction of MCA, obtained as described, is probably composed of chains containing long branching as well as intramolecular bands, a direct comparison between cellulose acetate and methylolcellulose acetate is not possible. For the same reason no conformational data are deducible by means of the usual relationships relating $B$, $\langle R_G^2 \rangle_z^{1/2}$, $[\eta]$ and $M_W$.

It is indeed rather unusual that the average dimensions in a linear polymer remained unchanged in different polymer–solvent systems, as we observed for MCA25. In fact, while the virial coefficient $B$ ranges from $5{\cdot}7 \times 10^{-4}$ to $0{\cdot}5 \times 10^{-4}$, spanning over one order of magnitude, we always found $\langle R_G^2 \rangle_z^{1/2} \cong 800$ Å. Sample MCA25/19 behaved somewhat differently as lower $B$ values correspond to lower $\langle R_G^2 \rangle_z^{1/2}$ values. The authors conclude that in the first sample intramolecular crosslinking took place to a higher extent, thus increasing chain rigidity.

It is worth recalling that for this sample a substantial amount of insoluble material was also found, which is also indicative of extensive tridimensional crosslinking reactions.

## Viscometry measurement

Intrinsic viscosities in different solvents and $K'$ and $\beta$ values are reported for all compounds in Table 3.

The intra- and intermolecular bonding proposed according to the LS results are further confirmed by hydrodynamic measurements (Bohdanecký and Kovář, 1982). Viscosity values were rather low, when compared to the values found for cellulose acetate at comparable $DS$ and $M_W$. By means of the equation (Johnston & Sourirajan, 1972)

$$[\eta] = 1{\cdot}5 \times 10^{-4} M_V^{0.83}$$

we obtain, for $M_W = 500\,000$ and $350\,000$, $[\eta] = 8{\cdot}06$ and $6{\cdot}13$ dl g$^{-1}$, respectively. Moreover, in keeping with the previously reported LS results, the viscosity data did not show a clear-cut dependence on the solvent used and on $M_W$. The latter finding is best understood if we

**TABLE 3**
Viscometric Data for MCA

| *Polymer* | *Solvent* | $[\eta]^a$ *(dl g$^{-1}$)* | $K'^{a,b}$ | $\beta^{a,c}$ | $M_W \times 10^{-3}$ *a,d (LS)* |
|---|---|---|---|---|---|
| MCA25 | Acetone | 2·67 | 0·87 | 0·06 | 520 |
| | Acetonitrile | 3·33 | 0·47 | 0·10 | |
| | Tetrahydrofuran | 2·91 | 0·53 | 0·07 | |
| | Ethyl acetate | 2·77 | 0·56 | 0·07 | |
| MCA25/19 | Acetone | 2·51 | 0·89 | 0·12 | 500 |
| | Acetonitrile | 3·08 | 0·67 | 0·03 | |
| | Tetrahydrofuran | 3·52 | 0·47 | 0·09 | |
| MCA25/14 | Acetone | 2·55 | 0·82 | 0·17 | 360 |
| | Acetonitrile | 2·89 | 0·63 | 0·04 | |
| | Tetrahydrofuran | 3·11 | 0·5 | 0·09 | |
| MCA25/40 | Acetonitrile | 3.33 | 0.57 | 0.06 | 480 |
| MCA25/4 | Acetonitrile | 2·97 | 0·63 | 0·03 | 280 |

[a] Estimated error ±5%.
[b] $\eta_{sp}/c = [\eta] + K'[\eta]^2 c$.
[c] $\ln \eta_{rel}/c = [\eta] + \beta[\eta]^2 c$.
[d] The data refer to average values in the various solvents.

consider that samples prepared under practically identical conditions may contain different amounts of intra- and intermolecular bonds. As a result, remarkably different materials are obtained and no comparison can be made.

Huggins' $K'$ values, ranging between 0·45 and 0·90, are relatively high, if compared to the theoretically expected values of 0·35 (Tanford, 1961) in thermodynamically good solvents. This effect has to be ascribed to long branching phenomena, as experimentally reported for amylopectin and styrene–divinylbenzene copolymers (Bohdanecký & Kovář, 1982).

## CONCLUSIONS

Light scatttering and hydrodynamic measurements lead to the conclusion that during cellulose derivatization, in the DMCA–PF system, which yields methylolcellulose acetate, acetal crosslinks are formed.

Under the experimental conditions of this study, a moderate increase in $DP_W$ is found (2–4 times the cellulose starting value) along with the formation of a partially insoluble material, due probably to tridimensional crosslinking reactions. Both phenomena are somewhat random and not easily controlled.

Unfortunately, simultaneous inter- and intramolecular bond formation does not allow a conformational analysis in solution, using the above techniques. Consequently a direct comparison with cellulose acetate at the same *DS* is not possible at present. Further studies are therefore needed to unravel oxymethylene group effects on the solution properties of derivatized cellulose chains.

## ACKNOWLEDGEMENT

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