Preparation and characterization of water soluble and crosslinkable cellulose acrylate

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The reaction of cellulose with acryloyl chloride in LiCl/*N*,*N*-dimethyl acetamide resulted in a water soluble cellulose acrylate. The degree of substitution per anhydroglucose unit was determined from the titration of the double bond with bromine. Crosslinking of the acryloyl moieties was carried out in aqueous solution using $K_2S_2O_8/FeSO_4$ as redox initiator. The original cellulose, cellulose acrylate and the crosslinked cellulose acrylate were characterized by i.r., wide-angle X-ray diffraction, d.s.c., t.g.a. and solid state ^{13}C n.m.r. Crosslinked cellulose is insoluble in water and the gel fraction was measured with a Soxhlet extractor. The fundamental properties of the crosslinked cellulose acrylate films were evaluated. Experimental results indicated that this water soluble and crosslinkable cellulose acrylate is a promising candidate as a water-borne coating material.

(Keywords: cellulose; crosslinking; water soluble)

INTRODUCTION

Cellulose is the most abundant naturally occurring polymer. Cellulose and its derivatives are of great industrial importance. However, the regularity of the cellulose chain and the extensive hydrogen bonding between hydroxy groups in adjacent chains cause cellulose to be a tightly packed crystalline material[1]. As a result, it is insoluble, even in hydrogen-bonding solvents. Furthermore, although cellulose is a linear polymer, it is infusible, with decomposition occurring before a sufficient number of hydrogen bonds are broken[2]. Thus, cellulose cannot be processed in the melt or in solution. In spite of this, several cellulose derivatives with less hydrogen bonding can be processed. Most of these commercially interesting derivatives are chemically modified from the native cellulose in heterogeneous reaction mixtures. The reaction conditions are normally difficult to control. In recent years, several solvent mixtures for cellulose have been reported[3–6]. In this paper, we report a water soluble cellulose derivative, cellulose acrylate, prepared from the esterification of cellulose with acryloyl chloride in homogeneous LiCl/*N*,*N*-dimethyl acetamide (DMAc) solution. This product is crosslinkable and is a promising candidate as a water-borne coating material.

EXPERIMENTAL

Materials

Cellulose, acryloyl chloride, LiCl, DMAc and pyridine were purchased from Merck Co. Cellulose, LiCl and pyridine were used without further purification. Acryloyl chloride and DMAc were purified by distillation under reduced pressure. $K_2S_2O_8$ and $FeSO_4$ were used as received from Janssen Co.

Preparation of cellulose acrylate

Cellulose (4 g, 0.025 mol, based on the anhydroglucose (AHG) unit) was added to a solvent mixture which was prepared by dissolving LiCl (6 g) in DMAc (100 ml). The mixture was stirred and heated to 160°C under nitrogen atmosphere for 1.5 h and the resultant mixture became a homogeneous gold coloured solution. The solution was then cooled down to room temperature and charged into a three-necked flask equipped with a stirrer. Pyridine (6 ml) in DMAc (20 ml) was added to the flask as an acid acceptor. DMAc solution (60 ml) containing acryloyl chloride (12.08 ml, 0.149 mol) was then added dropwise with constant stirring. Different batches were prepared for various reaction times (12, 36 and 48 h, respectively). The reaction mixture was then diluted with water and poured into a vessel containing methanol (500 ml). White cellulose acrylate was coagulated in quantitative yield. The product was filtered, washed with methanol and dried at 60°C under vacuum for 2 days.

Degree of substitution

The degree of substitution (*DS*) per AHG unit was calculated from titration data for the double bond. Titration was carried out by dissolving the cellulose acrylate (0.5000 g) in deionized water (120 ml), and titrating with bromine. The end point was taken as when the bromine colour persisted. The *DS* per AHG unit was calculated according to the relationship:

$$DS \times \left[\frac{W(1-a)}{159+(3-DS)+55DS}\right] = \frac{W'}{159.8}$$

where W is the precise weight of cellulose acrylate, a is the fraction of water in the cellulose acrylate, which can be read directly from the t.g.a. thermogram, and W' is the exact weight of bromine consumed in the titration.

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Crosslinking of cellulose acrylate

The dried cellulose acrylate (1 g, 4.57×10^{-3} mol, based on the AHG unit) was dissolved in deionized water (30 ml) containing $FeSO_4$ (0.0161 g, 5.77×10^{-5} mol). To this clear solution, $K_2S_2O_8$ (0.0156 g, 5.77×10^{-5} mol) in water (10 ml) was added to induce the crosslinking reaction of the acryloyl moiety. A portion of this reaction mixture was put into an i.r. liquid cell (CaF_2 window) and the decreasing absorption of the double bond at 1610 cm^{-1} was monitored. The change in solution viscosity during crosslinking was measured with a Brookfield viscometer. For a coating solution, the pot-life is defined as the time from the initial cure to the point where the solution viscosity increases abruptly so that the flow becomes difficult, and poor brushing of the coating is observed. The gel fraction was measured with a Soxhlet extractor, and the uncrosslinked portion of cellulose acrylate was continuously extracted with water for 60 h.

Film properties

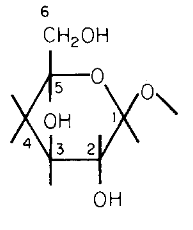
Clear film was obtained by casting the cellulose acrylate onto a glass plate from its aqueous solution containing the $K_2S_2O_8/FeSO_4$ redox initiator. The film properties of the crosslinked cellulose acrylate were evaluated according to ASTM standard test methods[7].

Instruments

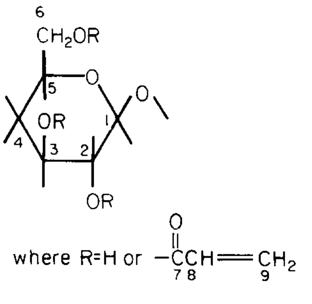
Solid state ^{13}C n.m.r. spectra were recorded with a Bruker MSC 200 using a 54.7° magic angle at 3500 rev min^{-1}. Tetramethylsilane was used as the internal standard. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Shimadzu X-ray diffractometer (model XD-5). D.s.c. scans and t.g.a. thermograms were recorded with DuPont 1090 and DuPont 951 instruments, in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The solid state ^{13}C n.m.r. spectra of the original cellulose, cellulose acrylate and crosslinked cellulose acrylate are shown in *Figures 1a*, *b* and *c*, respectively. For the original cellulose, C-1, C-4 and C-6 have chemical shifts at 105.9, 89.3 and 65.1 ppm, respectively, while C-2, C-3 and C-5 have chemical shifts at ~72–75 ppm[8]. The cellulose acrylate shifts the substituted C-1, C-4 and C-6 peaks to 104.5, 83.0 and 57.9 ppm, respectively, while the substituted C-2, C-3 and C-5 are overlapped at 35.9 ppm. The unsubstituted C-2, C-3 and C-5 are overlapped at 73.1 ppm. New peaks at 170.6, 145.9 and 129.5 ppm are assigned as C-7, C-8 and C-9 on the acryloyl moiety as shown below:



Cellulose



where R=H or $-\overset{\overset{\large O}{\|}}{C}CH{=}CH_2$ (7 8 9)

Cellulose acrylate

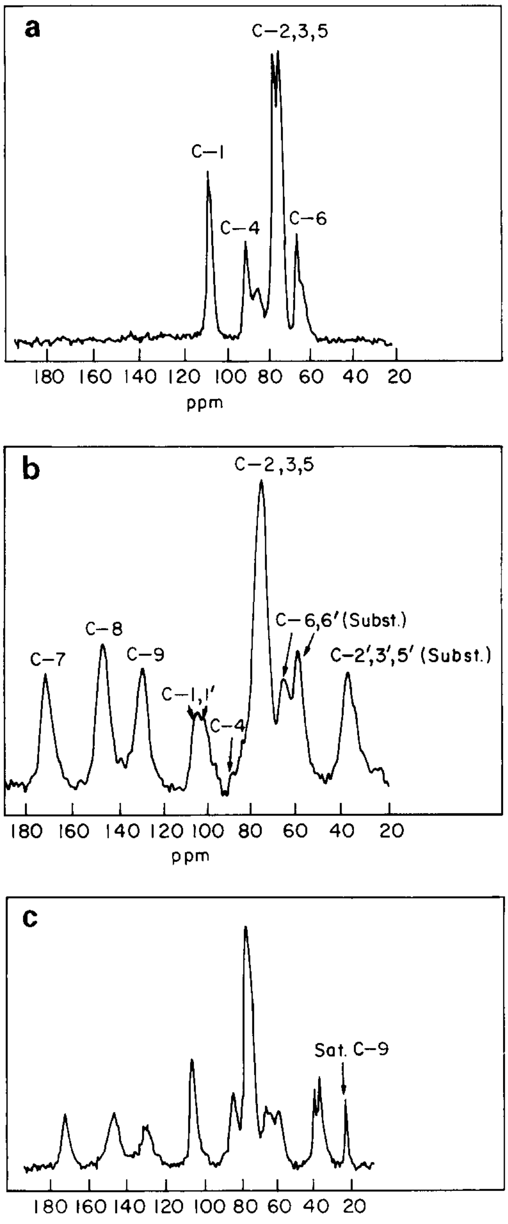


Figure 1 Solid state ^{13}C n.m.r. spectra of (a) cellulose, (b) cellulose acrylate and (c) crosslinked cellulose acrylate

For the crosslinked cellulose acrylate (*Figure 1c*), the newly developed peak at 22.4 ppm is believed to be due to saturated C-9. The peak around 35.9 ppm now splits into a doublet, presumably because of incomplete cure.

The *DS* values per AHG unit for various batches of cellulose acrylate obtained at different reaction times are given in *Table 1*. The i.r. spectra of cellulose and cellulose acrylate are shown in *Figures 2A* and *B*, respectively. Absorption of the carbonyl group and the double bond in the cellulose acrylate can be observed at 1730 and 1610 cm^{-1}. The WAXD patterns of cellulose and cellulose acrylate are given in *Figures 3A* and *B*, respectively. The diffractogram of the original cellulose shows crystalline peaks at $2\theta = 14.8$, 16.4 and 22.5°, which are characteristic of cellulose I[9,10]. The cellulose acrylate shows no characteristic peak in the diffractogram, indicating loss of crystallinity and, therefore, is soluble in water. This amorphous polymer was also evidenced by the transparency of the cast film.

Table 1 Measured *DS* per AHG unit for cellulose acrylate by titration

Reaction time (h)	*DS*
12	1.05
36	1.75
48	1.80

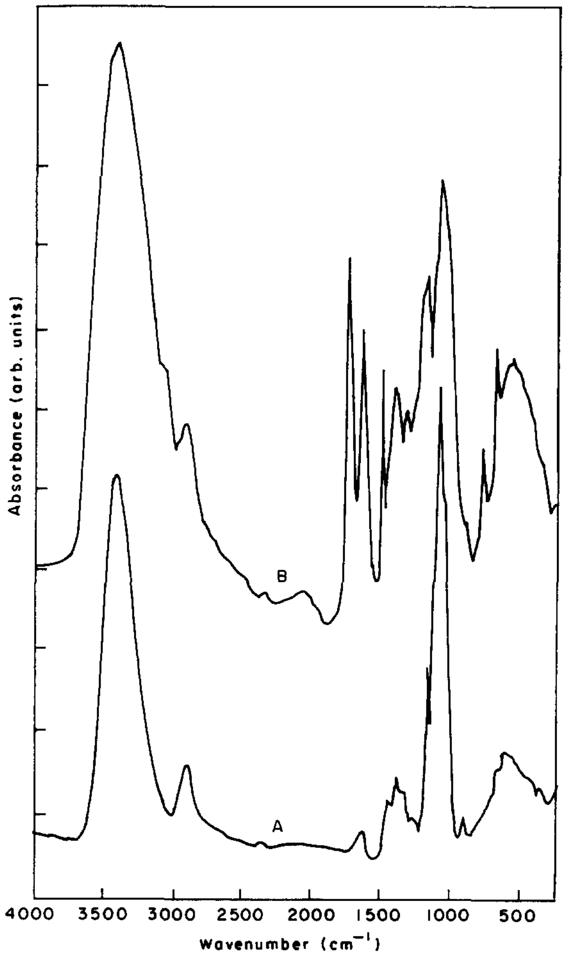


Figure 2 I.r. spectra of (A) cellulose and (B) cellulose acrylate

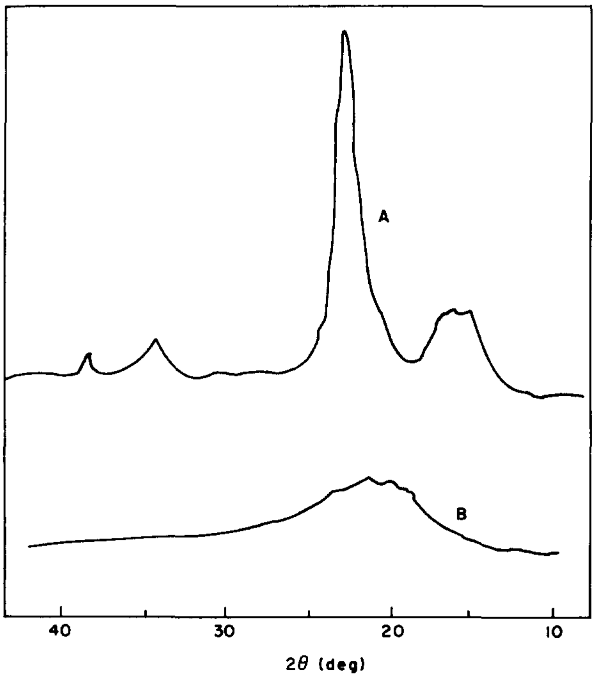


Figure 3 WAXD patterns of (A) cellulose and (B) cellulose acrylate

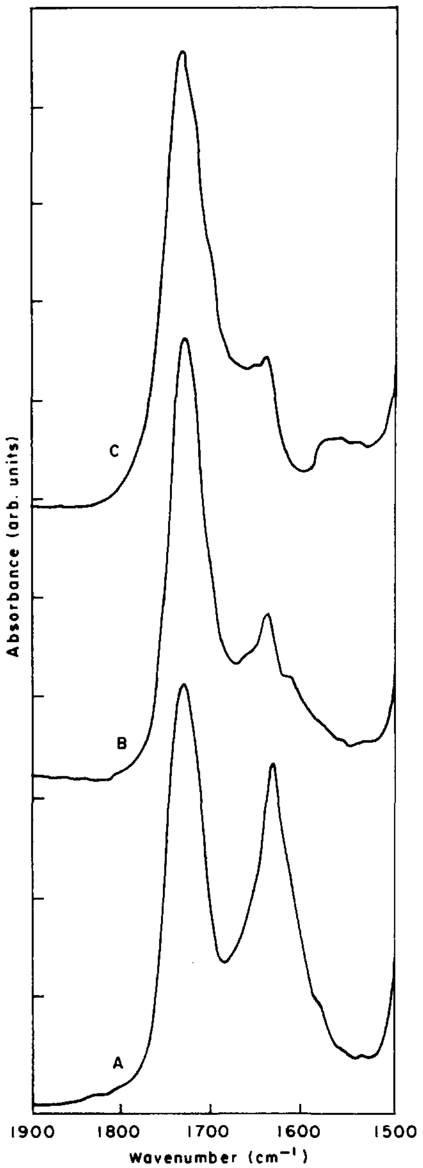


Figure 4 I.r. absorption change of the C=C bond at 1610 cm^{-1} in cellulose acrylate: (A) before crosslinking; (B) during crosslinking; (C) after crosslinking

The crosslinking reaction of the cellulose acrylate in aqueous solution was induced by the redox initiator $FeSO_4/K_2S_2O_8$. *Figure 4* shows the successive changes in i.r. absorption for the C=C bond at 1610 cm^{-1} during crosslinking. A residual absorption peak at 1610 cm^{-1} after gelation is observed (*Figure 4C*).

The thermal characterization of cellulose, cellulose acrylate and crosslinked cellulose acrylate is shown in *Figures 5a–f*. Eventually all of the samples contained ~6–8% water which was very difficult to remove. The property of moisture absorption for cellulose acrylate is believed to be due to incomplete esterification of the original cellulose, leading to some residual hydroxy groups as indicated by the i.r. spectrum in *Figure 2B*. *Figures 5a* and *b* show the d.s.c. scan and t.g.a. thermogram for cellulose, where the onset of melting temperature occurs at 305°C, followed immediately by decomposition. *Figures 5c* and *d* show the d.s.c. scan and t.g.a. thermogram of amorphous cellulose acrylate, where no apparent melting point can be identified. The first

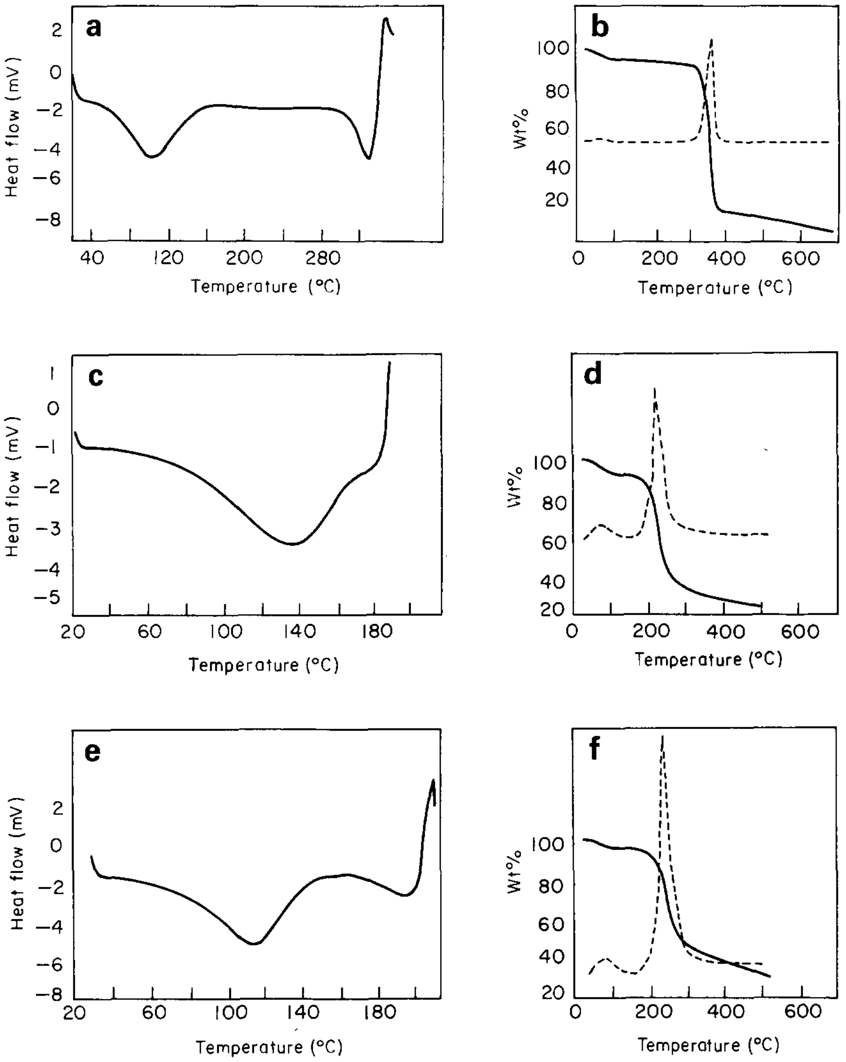


Figure 5 D.s.c. scans and t.g.a. thermograms, respectively, of (a, b) cellulose, (c, d) cellulose acrylate and (e, f) crosslinked cellulose acrylate

onset of decomposition temperature occurs at 186°C, followed by a second stage of decomposition. The d.s.c. scan and t.g.a. thermogram of crosslinked cellulose acrylate are shown in *Figures 5e* and *f*, where the onset of decomposition temperature occurs at 194°C, slightly higher than the 186°C for the uncrosslinked precursor. The broad exothermic peaks around 100°C in the d.s.c. scans are believed to be due to the evaporation of the absorbed water, which can be confirmed from the initial weight loss in the corresponding t.g.a. curves.

Figure 6 shows the plot of viscosity *versus* curing time for cellulose acrylate (1 g) for various amounts of $K_2S_2O_8$ in water (30 ml). The molar ratio of the redox pair, $FeSO_4/K_2S_2O_8$, was kept at a 1:1. This clearly demonstrated that the pot-life is dependent on the level of curing agent. A pot-life of 45 min was found when 0.0156 g of $K_2S_2O_8$ (5.77×10^{-5} mol) was used in conjunction with 0.0161 g of $FeSO_4$ (5.77×10^{-5} mol) as initiator (*Figure 6B*). *Figure 7* shows the plot of gel fraction *versus* the amount of $K_2S_2O_8$ for cellulose acrylate with a *DS* of 1.05. The gel fraction increases with increasing amount of curing agent. A gel fraction of 80% or higher can be reached.

The cellulose acrylate thus obtained is soluble in water,

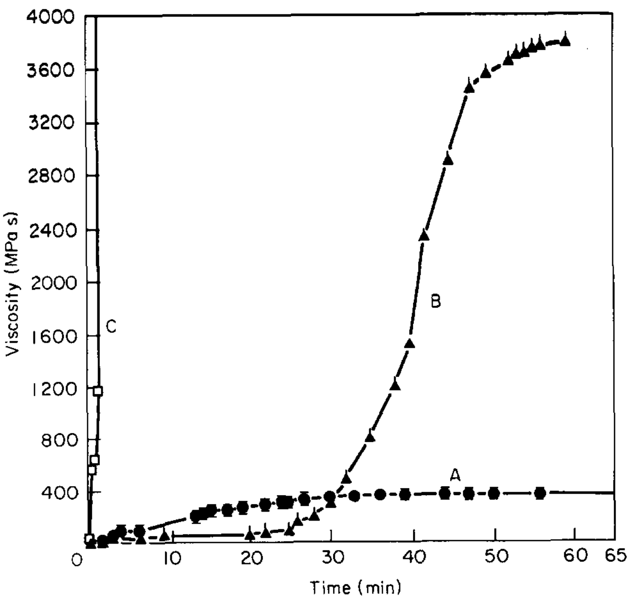


Figure 6 Plot of viscosity *versus* curing time for cellulose acrylate (1 g) in water (30 ml) containing various amounts of $K_2S_2O_8$: (A) 0.0088 g; (B) 0.0156 g; (C) 0.0278 g

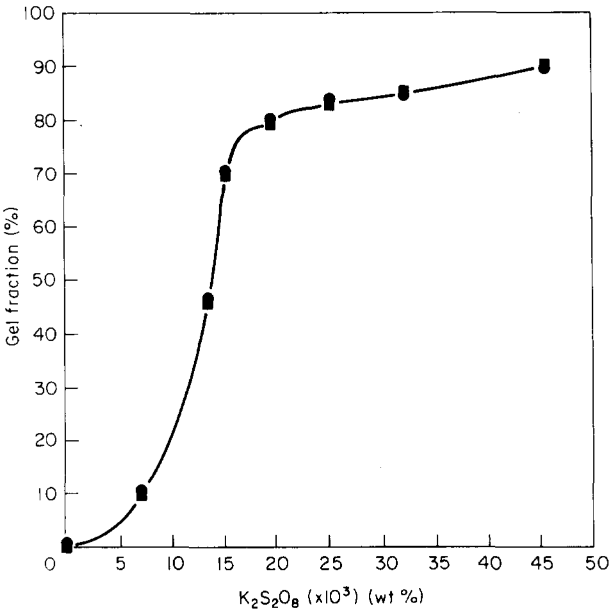


Figure 7 Plot of gel fraction *versus* the amount of $K_2S_2O_8$ for cellulose acrylate (1 g) in water (30 ml)

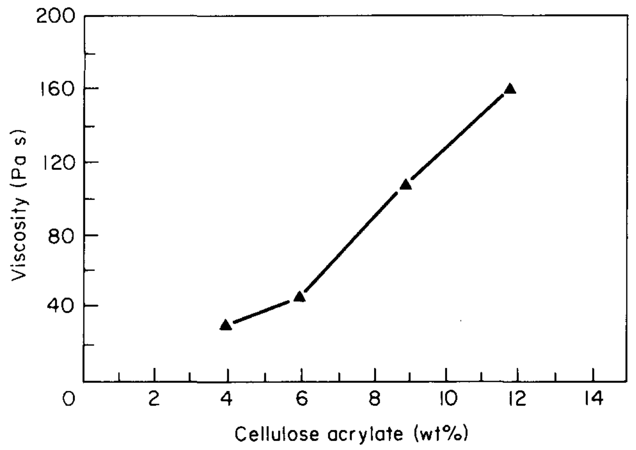


Figure 8 Plot of viscosity *versus* cellulose acrylate concentration in aqueous solution

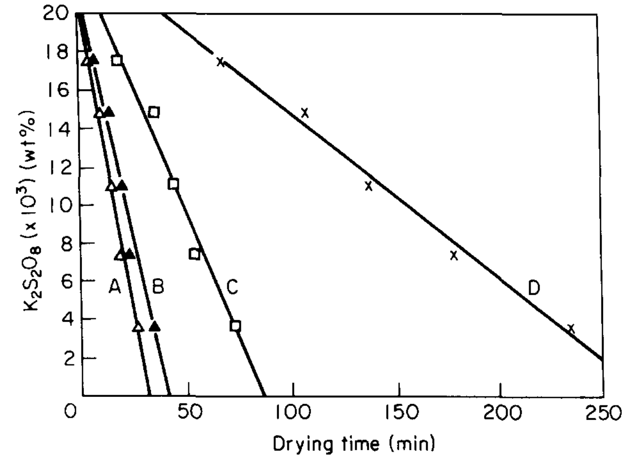


Figure 9 Dependence of drying time on the amount of $K_2S_2O_8$ at various temperatures: (A) 80°C; (B) 60°C; (C) 40°C; (D) 18°C

Table 2 Film properties of crosslinked cellulose acrylate

Test	Result
Resistant to:	
Alcohol	Good
Water (*DS* = 1.05)	Fair
Water (*DS* = 1.75)	Good
Water (*DS* = 1.80)	Good
Benzene	Good
Aliphatic hydrocarbons	Good
Acids (HCl, H_2SO_4)	Slight yellowing
Alkalis	Yellowing
U.v.	Good
Heat	Good
Adhesion to glass	Good
Hardness	84.2 Shore A
Gloss (°)	30

water/methanol (50/50 v/v) and water/ethanol (50/50 v/v), but insoluble in methanol, ethanol, chloroform, ethyl acetate, ethyl ether, acetone, DMAc and *N,N*-dimethylformamide. *Figure 8* shows the plot of viscosity *versus* cellulose acrylate concentration in aqueous solution. Its aqueous solution shows good flow property. Some water-borne coating recipes were formulated and tested. For example, the plot of an aqueous solution of cellulose acrylate (1 g) in water (30 ml) containing different amounts of $K_2S_2O_8$ at various temperatures *versus* the drying time is shown in *Figure 9*. The crosslinked cellulose acrylate film was evaluated according to ASTM test methods[7] and its film properties are listed in *Table 2*. The water resistance of the crosslinked cellulose acrylate film with a *DS* of 1.05 per AHG unit was found to be fair with wrinkles being observed after the test. When the *DS* was raised to 1.75 or higher, the water resistance was good and no apparent defect was found after the test.

CONCLUSIONS

The homogeneous reaction of cellulose with acryloyl chloride in LiCl/DMAc resulted in an amorphous cellulose acrylate which was both water soluble and crosslinkable. Clear film can be cast from its aqueous solution. When the *DS* per AHG unit is 1.75 or higher, the crosslinked film demonstrated good water resistance and other film properties and, therefore, is a promising candidate for a water-borne coating material.

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REFERENCES

1 Simon, I., Glasser, L. and Scheraga, H. A. *Macromolecules* 1988, **21**, 990
2 Dawsey, T. R. and McCormick, C. L. *J. Macromol. Sci., Rev. Macromol. Chem.* 1990, **30**, 4005
3 McCormick, C. L. and Licvhatowich, D. K. *J. Polym. Sci., Polym. Lett. Edn* 1979, **17**, 479
4 McCormick, C. L. *US Pat. 4 278 790*, 1981
5 Hudson, S. M. and Cuculo, J. A. *J. Macromol. Sci., Rev. Macromol. Chem.* 1980, **18**, 1
6 Isogai, A., Ishizu, A. and Nakano, J. *J. Appl. Polym. Sci.* 1984, **29**, 2097
7 Sward, G. G. (Ed.) 'Paint Testing Manual', 13th Edn, ASTM, Philadelphia, 1972
8 Kondo, T., Isogai, A., Ishizu, A. and Nakano, J. *J. Appl. Polym. Sci.* 1987, **34**, 65
9 Lewin, M. and Roldox, L. G. *Text. Res. J.* 1975, **45**, 308
10 Dobb, M. G. and Sefain, M. Z. *Text. Inst.* 1976, **67**, 229