Preparation and water sorption properties of cellulose–polypropylene glycol block copolymers

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A series of cellulose-polypropylene glycol block copolymers have been prepared by techniques described previously. The chain extension reactions used for their preparation were confirmed by i.r. and intrinsic viscosity data. The water sorption of films of the blocks was determined and the results, calculated on the cellulose content, compared with various forms of pure cellulose. It was found that lower crystallinity of the blocks was indicated by the higher water sorption values. As the size of the cellulose blocks was decreased the water sorption also decreased but the smallest block sample gave a higher value. It is believed that the polypropylene glycol blocks exert a restraining influence on the water sorption which is eventually overcome by the decrease in the crystallinity of the cellulose blocks as their size decreases.

INTRODUCTION

In previous papers the preparation and properties of two cellulose–polypropylene glycol block copolymers have been described[1,2]. In particular the biodegradability of the polymers was demonstrated. Indeed the cellulose blocks were found to be more degradable than normal cellulose. This was interpreted as an indication of greater accessibility, i.e. lesser crystallinity, of the short cellulose blocks. This would also, in principle, be reflected in the water sorption behaviour and such studies would be clearly of interest. In this paper the preparation of a further series is described and the water sorption behaviour of films prepared from the block copolymers presented.

EXPERIMENTAL

Materials

Cellulose triacetate was obtained from the Eastman Chemical Co., 2,3-tolylene diisocyanate (TDI) from Aldrich, polypropylene glycol (PPG) (Niax Polyol, PPG 3025) from Union Carbide and stannous octoate from the Witco Chemical Co.

Depolymerization of cellulose triacetate. Cellulose triacetate (acetyl value – 46.0%; $[\eta] = 1.60$ in $CHCl_3$ at 30°) was depolymerized in 99.4% acetic acid solution following the procedure of Steinmann[3] but the hydrolysed products were precipitated with 2-propanol instead of petroleum ether. Aliquots of the hydrolysis mixture were withdrawn at 3, 4, 6 and 8 h. Total yield was 81%, the acetyl and $[\eta]$ values and i.r. data are presented in *Table 1*.

Preparation of block terpolymers. PPG was dissolved in 1,2-dichloromethane contained in a 250 ml, three-necked round bottom flask with a magnetic stirrer, distillation column and a condenser. The flask and contents were heated with agitation and azeotropically distilled to dry the system. The TDI was added under N_2, followed by stannous octoate (0.05 ml) and the mixture agitated for 4.5 h at 50°C. The weights employed are given in *Table 2*.

Infra-red spectra showed an absorption at 3280 (N–H stretching), 1620 (aromatic ring deformation) and

Table 1 Hydrolyzed cellulose triacetate data

	1 (3 h aliquot)	2 (4 h aliquot)	3 (6 h aliquot)	4 (8 h aliquot)
$[\eta]$, dl g^{-1}	0.14*	0.10*	<0.08*	0.08**
Acetyl value, %	44.59	43.63	43.99	–
OH-stretching peak at 3350 cm^{-1}	Yes	Yes	Yes	Yes
Molecular weight	7557	5367	3952	1977

* In $CHCl_3$ solution at 30°C
** In CH_2Cl_2 (CH_3OH (9/1) solution at 30°C

Table 2 Weights employed in block terpolymer preparation using PPG

PPG (mmol)	TDI (mmol)	Sn octoate (ml)	1,2-dichloromethane (ml)	
			Used	Distilled
1.99	4.77	0.05	24	12
5.00	10.38	0.05	60	30
5.00	10.37	0.05	60	30
5.00	10.37	0.05	60	30

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1550 cm^{-1} (N–H deformation). The PPG had an [η] of 0.10 and the capped glycol 0.14 dl g^{-1} in $CHCl_3$ at 30°C.

Hydrolyzed cellulose triacetate (CTA) was dissolved in 1,2-dichloromethane, contained in a 350 ml, three-necked round-bottom flask, equipped with a magnetic stirrer, an N_2 inlet tube and a distillation column and azeotropically distilled. The weights employed are given in *Table 3.*

The dried CTA solution was added to the dried, capped glycol solution, prepared as above, and the mixture heated and stirred at 50° for 8 h, additional Sn octoate (0.5 ml) was added and reaction continued for another 8 h. The resulting viscous solution was poured into agitated and chilled 2-propanol. A highly swollen precipitate formed which was collected by centrifugation and dried under vacuum at 35°C. The yields were 79, 89, 94 and 68 percent respectively. Infra-red spectra data are given in *Table 4* and the intrinsic viscosity data in *Table 5.* The terpolymers were coded 1, 2, 3 and 4.

Deacetylation of the block terpolymers

The terpolymers were cast into thin films from methylene chloride solution. Sample 1 gave a tough leathery film, the other films were slightly brittle. The films were used directly for deacetylation.

A modification of Vink's procedure[4] was used. Sodium (2.0 g) was added to anhydrous methanol (500 ml) under N_2. The terpolymers were added to aliquots of this solution (see *Table 6* below) contained in a three-necked flask equipped with an agitator and N_2 inlet and outlet tubes. The heterogeneous mixtures were stirred continuously at room temperature for 3 h.

The films were washed with methanol and water and dried at 35°C under high vacuum. The yields were 56, 69 58 and 59% respectively. The intrinsic viscosity data are given in *Table 5.* The original films were clear and transparent, after deacetylation they become somewhat cloudy and more brittle. The terpolymers after deacetylation had diminished absorption peaks at 1750 cm^{-1} (C=O stretching) and at 1390 cm^{-1} ($-CO-CH_3$ deformation).

Moisture absorption

The deacetylated films were dried under high vacuum. Weighed amounts were placed in desiccators containing saturated aqueous solutions of $MgCl_2$ (33% r.h.) and $NaNO_3$ (73.8% r.h.) and pure water. Films were also placed in a 65% r.h. standard test room. After seven days the films were removed and weighed and the percent moisture regain calculated.

RESULTS AND DISCUSSION

The success of the chain-extension reactions used to prepare the block copolymers is confirmed by the infra-red spectral data in *Table 4* and the intrinsic viscosity data in *Table 5.* The spectrum of each of the CTA/TDI/PPG terpolymers had absorption peaks corresponding to the block components. The intrinsic viscosities of the terpolymers increased by a factor of 2–4 compared to that of the TDT/PPG prepolymers and by 2–8 compared to the intrinsic viscosity of the hydrolysed CTA.

The terpolymers deacetylated smoothly using NaOMe in methanol as evidenced by the decrease in the intensities of the 1700 and 1390 cm^{-1} peaks in the i.r. spectra. The

Table 3 Weights employed in block terpolymer preparation using CTA

CTA		1,2-dichloromethane (ml)	
mmol	Molecular weight	Used	Distilled
1.99	7557	75	20
5.00	5367	135	35
5.00	3952	150	50
5.00	1977	150	50

Table 4 Infra-red absorption peaks

Group	Adsorption (cm^{-1})	Assignment
–OH stretching	3440	CTA
C=O stretching	1750	CTA
$-CO-CH_3$ deformation	1390	CTA
$-CH_2-$ stretching	2850	PPG
NH stretching	3320	TDI
NH deformation	1550	TDI

Table 6 Terpolymers added to NaOMe solution

Terpolymer	Wt of terpolymer	NaOMe solution (ml)
1	4.1	124
2	4.0	120
3	4.2	126
4	4.1	124

Table 5 Intrinsic viscosity data

Terpolymer	Hydrolysed CTA	PPG*	PPG/TDI*	CTA/TDI/PPG*	After deacetylation***
1	0.14*	0.10	0.14	0.23	0.25
2	0.10*	0.10	–	0.36	0.21
3	0.08*	0.10	–	0.62	0.45
4	0.08**	0.10	–	0.47	0.39

* In $CHCl_3$ solution at 30°C
** In CH_2Cl_2/CH_3OH (9/1) solution at 30°C
*** In DMSO solution @ 30°

Table 7 Moisture absorption (regains) calculated on cellulose content only

	Sample						
Percent r.h.	1	2	3	4	Cellophane	Rayon	Cotton
50	11.0	8.1	6.5	8.3	10.2	10.2	4.7
75	18.2	15.5	11.5	15.7	15.7	15.3	7.0
90	28.2	25.5	21.7	27.7	22.0	22.1	11.0
100	45.2 (44.1)	37.7 (36.4)	30.4 (28.9)	40.0 (38.1)	33.0	42.3	18.0
Percent cellulose	62.0	53.0	46.0	30.0			

Number in parentheses have been corrected for the PPG sorption

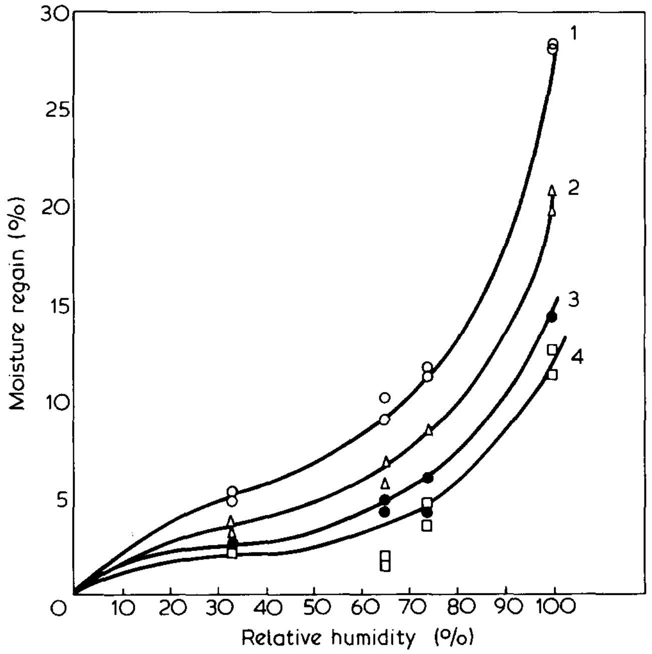

Figure 1 Moisture regain *versus* relative humidity (%)

intrinsic viscosities of the deacetylated products were reasonably high but different from those of the acetylated terpolymers due to the change in solvents from $CHCl_3$ (or CH_2Cl_2/CH_3OH) to DMSO.

The moisture regains are presented in the form of sorption isotherms in *Figure 1*. The values calculated on the cellulose content only, taken directly from the curves, are given in *Table 7*. The values at 100% r.h. are also given corrected for the sorption by the PPG blocks. Typical literature values for cellophane, viscose rayon and cotton are included for purposes of comparison. Neither vacuum nor circulation was used in the present measurements and the actual relative humidities, especially the 100% value, are probably slightly lower than given. The regains themselves are therefore probably slightly on the low side and are, in any case, quite interesting.

The largest cellulose block sample has considerably higher water sorption than normal cellulose samples. This presumably reflects a lower crystallinity in the blocks than most pure forms of cellulose. The shorter blocks probably have even lower crystallinity, however, the water sorption values decrease with decreasing block length except for the shortest block when the regains increase again. It is believed that the PPG blocks exercise a growing influence in preventing the swelling and water sorption, counteracting the possible decreasing crystallinity. The shortest blocks presumably have sufficiently low crystallinity to overcome the restraining influence of the PPG blocks. Although reasonable, these explanations are largely speculative and need independent verification. These and other experiments will be carried on on higher molecular weight samples, presently being prepared. It is hoped that a wide range of biodegradable water sorbing polymers can be prepared in this manner.

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