Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Biodegradable Cellulose Graft Copolymers. I. Condensation-Type Graft Reactions

B. G. Penn[a]; V. T. Stannett[a]; R. D. Gilbert[a]
[a] Fiber and Polymer Science Program North Carolina State University, Raleigh, North Carolina

To cite this Article Penn, B. G. , Stannett, V. T. and Gilbert, R. D.(1981) 'Biodegradable Cellulose Graft Copolymers. I. Condensation-Type Graft Reactions', Journal of Macromolecular Science, Part A, 16: 2, 473 — 479

To link to this Article: DOI: 10.1080/00222338108058484

URL: http://dx.doi.org/10.1080/00222338108058484

J. MACROMOL. SCI.–CHEM., A16(2), pp. 473-479 (1981)

Biodegradable Cellulose Graft Copolymers.
I. Condensation-Type Graft Reactions

B. G. PENN, V. T. STANNETT, and R. D. GILBERT

Fiber and Polymer Science Program
North Carolina State University
Raleigh, North Carolina

ABSTRACT

The synthesis of cellulose graft copolymers using condensation reactions to graft onto the cellulose backbone is described. Cellulose acetate (D.S. 2.27) was grafted with MDI and TDI. The cellulose acetate-MDI copolymer was further reacted with hydroxy-terminated poly(butadiene-styrene) copolymer and polyethylene glycol. Grafting was confirmed by Pmr and IR spectroscopy. The copolymers were easily deacetylated with NaOMe. The deacetylated products were readily degraded by cellulysin, faster than cellulose itself.

INTRODUCTION

It has been previously demonstrated that biodegradable block copolymers can be prepared by the incorporation of cellulose [1-3] or amylose [4] oligomeric blocks into the polymer backbone. Briefly, cellulose (or amylose) is acetylated, hydrolyzed by hydronium ions to give a hydroxyl-terminated cellulose (or amylose) triacetate oligomer, which is reacted with diisocyanates or with hydroxyl-terminated noncellulose (or nonamylose) oligomers using diisocyanates as coupling agents. Deacetylation yields cellulose or amylose block copolymers that are degraded by enzymes. This is a quite straightforward but fairly tedious procedure. Graft polymerization potentially offers a simpler route as previously suggested [2, 3]. In this paper the preparation of biodegradable cellulose graft copolymers is described using condensation reactions to graft to the cellulose backbone.

EXPERIMENTAL

Materials

Cellulose acetate (CA) was obtained from Tennessee Eastman Co., diphenyl methane diisocyanate (MDI) from Upjohn Co., hydroxy-terminated poly(butadiene-styrene) copolymer from Arco Chemical Co., and polyethylene glycol from Union Carbide. The enzyme Cellulysin was from Calbiochem Co.

Preparation of Graft Copolymers

CA (D.S. 2.37, 0.033 mmole, $[\eta]$ 1.55 dL/g in acetone at 30°C, M.W. 61,450) was dissolved in dioxane (125 mL), the solution heated at 50° under N_2 for 1 h, then MDI (3.2 mmol) and Et_3N (0.2 mL) in dioxane (5 mL) added and the heating continued for 26 h. The reaction product (I) was precipitated and washed with isopropyl alcohol (isoProH) and dried overnight under vacuum, yield 1.9 g (66%).

The reaction was repeated using a CA/MDI mole ratio of 1:10. The yield of product (II) was 3.32 g (80%).

Similarly, CA (0.065 mmole) was reacted with toluene diisocyanate (TDI) (1.66 mmole) to yield 2.7 g (65%) of Product III.

CA (0.05 mmole) was dissolved in pyridine (75 mL) with stirring and heating. HO-terminated poly(butadiene-styrene) copolymer (OH value 0.65, 0.05 mmole) was dissolved in pyridine (50 mL) in a 3-neck flask fitted with a stirrer, condenser, and N_2 inlet and outlet tubes. The mixture was heated at 70° under N_2 for 1 h. MDI (1.05 mmol) and ET_3N (0.2 mL) were added, and the mixture heated at 70° for 18 h with stirring. The CA solution in pyridine was added and the reaction allowed to continue at 70° for 49 h. The reaction mixture was then poured into isoProH, the reaction product (IV) isolated, and dried under vacuum to yield 3.43 g (69%).

Polyethylene glycol (0.33 mmol) was dissolved in dioxane contained in a 250-mL 3-neck flask equipped with a condenser, magnetic stirrer, thermometer, and N_2 inlet and outlet tubes. The mixture under N_2 was heated to 60°, MDI (0.72 mmol) and ET_3N (2 mL) were added, and the mixture was heated for another 12 h. CA (D.S. 2.37, 0.067 mmol) was added and heating continued for another 50 h. The product (V) was precipitated and washed with isoProH and dried under vacuum. Yield 3.33 g (69%).

Deacetylation of the Copolymers

The graft copolymers were solvent cast into films, placed in screw-cap bottles containing NaOMe (0.4 g Na/100 mL CH_3OH), and allowed to stand at R.T. for 24 h, the films washed with isoProH, and dried under vacuum. All the copolymer films were opaque, semi-flexible, and quite strong before deacetylation. After deacetylation their flexibility was reduced, but not to the point of brittleness.

Enzymatic Hydrolysis

Either 0.1 or 0.5% buffered (pH 5) enzyme (Cellulysin) solutions were prepared using 0.05 M Na acetate and HOAc. The deacetylated graft copolymer films were weighed and added to the enzyme solution (10 mL) in a screw-cap bottle, and the bottles and contents incubated at 50° for various times. The films were collected, washed several times with H_2O and isoProH, and dried under vacuum at 50°. The degree of enzymatic hydrolysis was determined by the film weight loss and the presence of a friable powder. The copolymer films became brittle and fragile in all cases. Control samples were run in each case in the absence of the enzyme.

Infrared spectra were obtained with a P.E. 337 IR Grating Spectrometer at R.T. Pmr Spectra were obtained with a Varian HA-100 spectrometer and $CDCl_3$ or DMSO as solvent. TMS was used as an internal lock signal. Chemical shifts are on the τ scale. Thermograms were obtained using a P.E. DSC-1B differential scanning calorimeter at a scan rate of 20°/min or with a DuPont 990 thermal analyzer.

RESULTS AND DISCUSSION

Two CA-MDI (I and II), a CA-TDI (III), a CA-MDI-poly(butadiene-styrene) (IV) and a CA-MDI-poly(propylene glycol) (V) graft copolymers were prepared using partially acetylated (D.S. 2.37) CA. No gelation was encountered during their preparation, probably because of the high D.S. value of the CA and because an excess of diisocyanate was employed to block the majority of the accessible cellulose hydroxyl groups. The success of each reaction was confirmed by Pmr and IR spectroscopy. These data are summarized in Tables 1 and 2, respectively. The IR data in particular demonstrate grafting occurred by the presence of the following peaks: deformation vibrations of NH bonds at 1550 cm^{-1}, C=O bond stretching at 1750-1770 cm^{-1}, and out-of-plane bending of aromatic C–H bonds at 850-870 cm^{-1}. Copolymer IV also had the expected C=C absorption peak at 950 cm^{-1} and aromatic C–H peaks from the styrene phenyl group at 3000 and 3070 cm^{-1}. Thus each reaction product had absorptions characteristic of each component expected in the graft copolymers.

TABLE 1. Pmr Peak Assignments

	Values					
Polymer	OH	Acetyl	–NH–	$-O-CH_2-$	$-C_6H_4-CH_2-C_6H_4-$	Vinylic
I	3.6	2.9	8.8	-	-	-
III	3.5	2.9	8.3	-	-	-
IV	3.5	2.9	-	-	-	4.7
V	3.6	2.9	-	4.5	3.9	-

TABLE 2. IR Peak Assignments

	Absorption peaks (cm^{-1})					
Polymer	OH	NH	Aromatic C–H[a]	$-\overset{O}{\overset{\|}{C}}-CH_3$	C=C	Aromatic C–H
I	3500	1550	870	1750		
II	3461	1550	870	1770		
III	3500	1550	860	1760		
IV	3500	1550	850	1760	950	3000, 3070
V	3500	1550	850	1760		

[a] Out-of-plane bending.

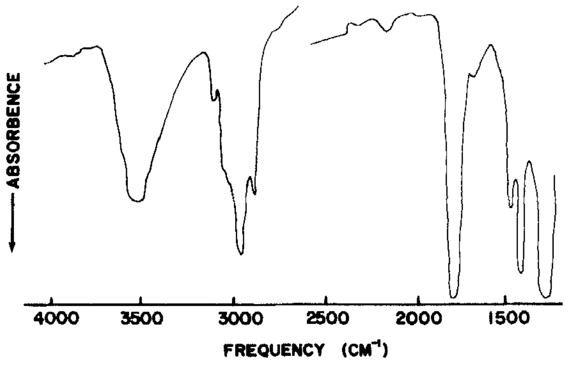

FIG. 1. Infrared spectrum of reaction product IV, before deacetylation.

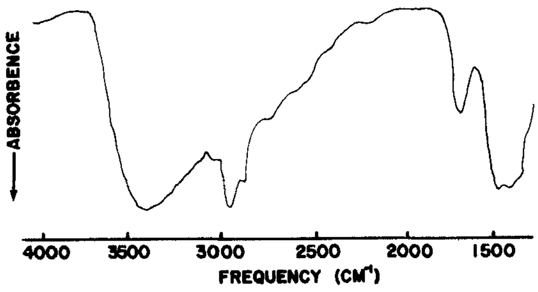

FIG. 2. Infrared spectrum of reaction product IV, after deacetylation.

TABLE 3. DSC Results

Polymer	Endothermic transitions (°C)
I	85, 190
III	85, 200
IV	85, 148, (205[a]), 260
V	85, 260

[a] Exothermic transition.

In addition, each copolymer showed an acetyl resonance at 2.9 τ in the pmr spectra. Copolymers I and III showed an NH peak at 8.8 and 8.3 τ, respectively. This peak was not present in IV and V, presumably due to the relatively low concentration of these protons after the attachment of the poly(butadiene-styrene) and poly(ethylene glycol) segments. Copolymer IV did exhibit a vinylic proton signal at 4.7 τ and V a methylene adjacent to an oxygen at 4.5 τ and a methylene due to the MDI segment at 3.9 τ.

The copolymers in film form were easily deacetylated by NaOMe to form copolymers with cellulose backbones. Infrared spectra of the polymer films before and after treatment with NaOMe showed the deacetylation was essentially complete. Representative IR spectra for copolymer IV are shown in Figs. 1 and 2. The disappearance of the acetyl absorption at 1770 cm^{-1} and the concurrent increase in the hydroxyl peak of 3500 cm^{-1} (Fig. 2) show deacetylation occurred.

DSC thermograms of the deacetylated products confirm grafting occurred on the cellulose acetate. The DSC results are summarized

TABLE 4. Enzymatic Hydrolysis, 0.1% Cellulysin Solution Copolymer IV

Time (h)	Weight (g)	Weight loss (%)
0	0.2	0
6	0.162	19
78.5	0.152	24

TABLE 5. Enzymatic Hydrolysis, 0.5% Cellulysin Solution

Polymer	Time (h)	Initial weight (g)	Final weight (g)	Weight loss (%)
I	15.75	0.0114	Film disintegrated	-
II	15.75	0.0368	0.0300	18.5
III	15.75	0.0128	0.0110	22
IV	15.75	0.0234	0.0171	26
V	15.75	0.0364	0.0273	25
Deacetylated CA	15.75	0.0166	0.0155	6.6
Deacetylated CA	15.75	0.0114	0.0114	0
I[a]	15.75	0.0055	0.0052	5.5
IV[a]	15.75	0.0036	0.0036	0

[a] Control runs at pH 5 in absence of Cellulysin.

in Table 3. The MDI and TDI graft copolymers (I and III) had endothermic transitions at 85 and 190-200°. The 85° transition is probably due to disruption of H-bonding between the urethane secondary amine groups and cellulose OH groups. Interurethane H-bond disruption is most likely responsible for the 190 and 200° transitions.

Copolymer IV and V also exhibited the 85° endothermic transition. The 148° transition for IV may be due to interurethane H-bonding disruption. The 260° transition may be due to poly(styrene)-MDI and poly(ethylene glycol)-MDI segments. The exothermic peak at 205° in IV possibly originates from the poly(butadiene) MDI linkages. An exothermic transition at 150° has been reported for poly(butadiene) [5].

The deacetylated copolymer films were incubated at 50° with either a 0.1 or 0.5% aqueous solution of Cellulysin buffered at pH 5. Enzymatic degradation was followed by weight loss as no suitable solvent was found for these cellulose copolymers for intrinsic viscosity determinations. The results are summarized in Tables 4 and 5. Biodegradation was also indicated by the appearance of a white friable powder in the enzyme solution.

A preliminary incubation of Copolymer IV with 0.1% Cellulysin showed an initial rapid degradation followed by a leveling-off of the rate as noted previously [1-4]. Increasing the concentration of Cellulysin to 0.5% (Table 4) did result in a more rapid rate of degradation but the total amount was not appreciably greater. However, in each case the film was considerably weakened and, as noted above, a white friable powder was produced. There was little weight loss nor the presence of the friable powder for controls run in the absence of the enzyme.

As observed with block copolymers of cellulose [1, 2], the graft copolymers degrade faster than cellulose itself–presumably due to the greater accessibility of the copolymers. Recent work [6] concerning the water sorption of cellulose-polypropylene glycol block copolymers strongly indicates the low crystallinity of the cellulose component.

REFERENCES

[1] S. Kim, V. T. Stannett, and R. D. Gilbert, J. Polym. Sci., Polym. Lett. Ed., 11, 731 (1973).
[2] S. Kim, V. T. Stannett, and R. D. Gilbert, J. Macromol. Sci.–Chem., A10(4), 671 (1976).
[3] S. Kim, V. T. Stannett, and R. D. Gilbert, U.S. Patent 3,950,282 (1976).
[4] M. M. Lynn, V. T. Stannett, and R. D. Gilbert, Polym. Prepr., 19(2), 106 (1973).
[5] B. Ke, in Encyclopedia of Polymer Science and Technology, Vol. 5, 1969, p. 37.
[6] R. Amick, V. T. Stannett, and R. D. Gilbert, Polymer, 21, 648 (1980).

Accepted by editor December 27, 1979
Received for publication March 5, 1980