Graft Copolymerization of Cellulose with Structopendant Unsaturated Ester Moieties in Homogeneous Solution

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ABSTRACT: Cellulose esters of cinnamic acid, vinyl acetic acid, and fumaric acid monoethyl ester with moderate degrees of substitution were copolymerized with styrene, butyl methacrylate, and acrylic acid, respectively. Although high grafting ratios were obtained, crosslinked systems were formed despite attempts to manipulate pendant group reactivity vs. that of the grafting comonomer or the polymerization time and temperature. However, addition of a simple thiol chain-transfer agent resulted in soluble, noncrosslinked graft copolymers with moderate conversion (>40%) and grafting ratios to 170%. Structural elucidation of the graft copolymers was accomplished by FTIR and NMR spectroscopy. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 307–317, 1997

INTRODUCTION

Cellulose or poly(1 → 4, β-D-anhydroglucose) is the most abundant naturally occurring polysaccharide. Intrinsic properties of this renewable resource have made cellulose one of the most studied polymers, having been derivatized into a large number of commercially important products.[1–3] Among the most successful techniques targeted at improving physical, morphological, and mechanical properties of cellulose has been grafting onto native forms, including cotton, wood fiber, or derived products, such as textiles or pulp.[4–7] Many free-radical and ionic grafting procedures have been utilized with varying degree of success. A host of side reactions including chain cleavage and crosslinking, as well as the necessity in many cases for heterogeneous reaction conditions, limit precise tailoring and complicate structural analysis.

Free-radical grafting techniques are most often used in which a macroradical is formed through an oxidation–reduction reaction with transition metals such as cerium and vanadium or by irradiation.[8–12] The grafting comonomer is often present in the reaction mixture or is added after radical formation. In cases which rely on hydrogen abstraction from the cellulose backbone, success is possible only in those systems in which homopolymerization and termination can be controlled.[13,14] Other techniques include anionic grafting utilizing alkali metal alkoxide[15–17] or postcondensation reactions.[18–20]

In most grafting procedures of cellulose reported to date, heterogeneous reaction conditions have been employed. Typically, cellulose is dispersed in a reaction mixture containing a monomer(s) and an initiator. Since grafting relies on diffusion of reagents to the backbone site, swelling is crucial. Otherwise, surface grafting and/or homopolymerization of the monomer might occur, resulting in nonuniform substitution and separation problems, respectively. In an attempt to avoid the above problems, we synthesized a series of cellulose esters of unsaturated carboxylic acids,[21] which are easily initiated under free-radical conditions. These reactive cellulose esters are uniformly substituted and are readily soluble in di-

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methyl sulfoxide (DMSO). Our objective in this work was to maximize grafting efficiency and yield by anticipating favorable kinetics in this homogeneous system. A fundamental understanding of this process could have utility in applications ranging from soluble cellulose derivatives for rheological modifiers to interpenetrating networks for stimuli-responsive membranes.

EXPERIMENTAL

Materials

Cellulose esters of cinnamic acid (CEOC), degree of substitution (DS) ~ 0.4; fumaric acid monoethyl ester (CEOF), DS ~ 0.4; and vinyl acetic acid (CEOV), DS ~ 0.5, were prepared utilizing reaction procedures recently reported by our group.[21] Samples (0.5–1.0 g) were dissolved in 100 g DMSO and allowed to age for 1 day. The resulting viscous solutions were filtered prior to use.

The grafting monomers styrene (S), butyl methacrylate (BMA), and acrylic acid (AA) were purchased from Aldrich Chemical Co. and were distilled under vacuum prior to use. Azobisisobutyronitrile (AIBN) was obtained from Eastman Kodak Co. and recrystallized from methanol prior to use. Other reagents and solvents were reagent grade and utilized as received.

Graft Copolymerization

Graft Copolymerization and Isolation

The unsaturated cellulose ester solutions in DMSO were degassed under a vacuum (30 min) and then the grafting monomer(s) and initiator were sequentially added. A typical procedure is given below. Styrene (1.8 g), butyl methacrylate (1.8 g), and 0.5 mol % AIBN were added to the prepared solution containing 0.12 g of the cellulose ester of cinnamic acid (CEOC) in 20 g DMSO in a 50 mL, three-necked flask equipped with a thermometer, nitrogen inlet and outlet tube, and mechanical stirrer. After degassing, the mixture was allowed to react at 60°C for 36 h under nitrogen.

The cellulose graft copolymer and the copolymer of S/BMA were isolated from the crude solution by precipitation into methanol. The polymer fraction was then dried under a vacuum and weighed to determine total conversion. The graft copolymer was separated from the linear S/BMA copolymer by extraction (24 h) with chloroform ($CHCl_3$) utilizing a Soxhlet apparatus. The S/BMA was recovered from the chloroform solution by reprecipitation into methanol. Finally, the two separated products were again dried under a vacuum and weighed to determine monomer conversion as well as grafting parameters.

Kinetic Experiments of Grafting

Basic kinetic experiments of graft copolymerization were conducted with the same polymerization and separation procedures as previously mentioned. Samples of the reaction mixture were taken at specific time intervals. In kinetic experiments, a higher molar concentration of cellulose esters and comonomers were used relative to the AIBN concentration. For example, 0.65 g cellulose ester and 9.0 g S/BMA (1 : 1 by wt) with a lower initiator concentration at 0.3 mol % AIBN based on moles of vinyl monomers and a lower monomer concentration in DMSO (10 wt %) were utilized.

The percentages of monomer conversion (C_m) and grafting ratio (G_r) and grafting efficiency (G_e) were calculated as follows:

$$C_m = \frac{W_2 - W_1 + W_3}{W_4} \times 100 \qquad (1)$$

$$G_r = \frac{W_2 - W_1}{W_1} \times 100 \qquad (2)$$

$$G_e = \frac{W_2 - W_1}{W_2 - W_1 + W_3} \times 100 \qquad (3)$$

where W_1, W_2, W_3, and W_4 represent weights of vinyl cellulose added, grafted cellulose obtained, vinyl polymer obtained, and vinyl monomers added, respectively.

Characterization

Solubility of the Grafted Cellulose

About 10–20 mg of the grafted cellulose sample was added to the 1.5–2.0 mL (1 : 1 volume) THF/DMSO mixture to test solubility.

Spectroscopy

FTIR was conducted with a Galaxy 2020 spectrometer (Mattson Instrument Co.). Grafted cellulose samples were prepared by casting films with THF/DMSO (1 : 1 vol) mixture solvents. For NMR characterization, samples were dissolved in DMSO-d_6/chloroform-d (1 : 1 volume) solvent. ^{1}H-

NMR spectra were recorded with a Bruker AC-200 spectrometer.

Differential Scanning Calorimetry Analysis

DSC was performed on a Mettler TA 400 calorimeter from −50 to 300°C at a heating rate of 10°C/min. under a nitrogen atmosphere. Films cast from solutions were also used for DSC analysis.

Viscosity Measurements

A Contraves LS-30 rheometer was used with measurements performed at 25°C. The solutions of grafted celluloses and vinyl copolymer were prepared by dissolving a known amount of the dry sample in THF/DMSO (1 : 1 by volume) and methyl ethyl ketone (MEK), respectively, and diluting for testing. Intrinsic viscosities were evaluated using the Huggins equation.

RESULTS AND DISCUSSION

Selection of Monomers and Unsaturated Cellulose Esters for Graft Copolymerization

Three cellulose ester derivatives with residual unsaturation were chosen for graft copolymerization studies. These cellulose esters of cinnamic acid (CEOC, DS ~ 0.4), fumaric acid monoethyl ester (CEOF, DS ~ 0.4), and vinyl acetic acid (CEOV, DS ~ 0.5) meet our criteria. The reactive alkenyl functional groups are directly attached to the relatively rigid cellulose backbone by an ester group which restricts their mobility. The reactivity ratios of the pendant unsaturated groups and the concentration of the vinyl monomer favor cross-addition (grafting) over homopolymerization (crosslinking). Simple fumarate and cinnamate esters possess β-substitution, which also sterically retards or inhibits homopropagation. The ester of vinyl acetic acid does not have a β-substituent; however, this allylic monomer would be prone to degradative chain transfer at high concentrations.[22]

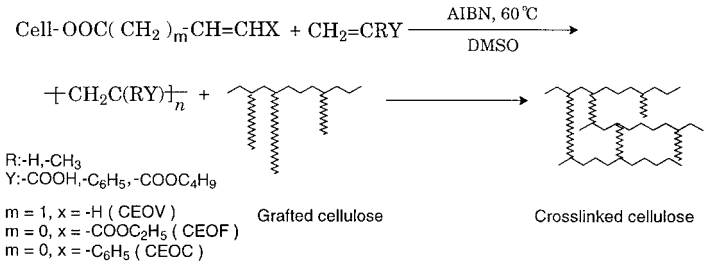
Grafting is also favored by choosing comonomers, M_2, with appropriate reactivity compared to the pendant cellulose alkenyl group, M_1, and by maintaining relatively high molar ratios of M_2 to M_1 in the grafting reactions. Reactivity ratios for cinnamate (similar to CEOC) and fumarate (similar to CEOF) derivatives with styrene based on literature data for simple esters are shown in Table I; these are used as guides for the selection of relative substrate and monomer composition in the feed.[23,24] For optimal grafting, we would expect $r_1 r_2 < 1$ ($r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$), where r_1 and r_2 represent the respective reactivity ratios of the alkenyl pendant group, M_1, and grafting comonomer, M_2. The rate constants for the four possible propagation reactions are given by k_{11}, k_{12}, k_{22}, and k_{21}.

Inspection of Table I reveals r_1 values for the fumarate (M_1)/styrene (M_2) and the cinnamate (M_1)/styrene (M_2) pairs of 0.07 and 0.10, respectively, for the ethyl esters. Under conditions of sufficient swelling of CEOF and CEOC, we would expect that once these moieties are incorporated during propagation reactivity with styrene would be greatly favored in the next step. The lack of mobility of the unsaturated esters, the r_2 values (0.3 and 1.5), and the relative concentrations favor grafting. It should be noted that cross-propagation (if it were to occur at all) would be largely intermolecular due to chain stiffness of the cellulose and would require higher concentrations of the cellulose esters than are present at the DS levels in our experiments. However, such cross-propagation should be more predominant in CEOF than in CEOC.

Table I Reactivity Ratios of Fumaric and Cinnamic Esters with Styrene (60°C)[a]

	R—	r_1	r_2
Fumaric esters (M_1)/styrene (M_2)			
(ROOC—CH=CH—COOR)	—H	0.25 ± 0.10	0.18 ± 0.10
	—Et[2]	0.07 ± 0.007	0.30 ± 0.02
Cinnamic esters (M_1)/styrene (M_2)			
(C_6H_5—CH=CH—COOR)	—nBu	0.08 ± 0.03	1.96 ± 0.03
	—Et	0.10 ± 0.03	1.50 ± 0.03

[a] Data from Ref. 23; no reference data are available for vinyl acetic ester with styrene.
[b] $r_1 = 0.02$, $r_2 = 0.29$ (60°C, benzene), data from Ref. 24.



Scheme 1 Graft copolymerization of the structopendant unsaturated ester moieties of cellulose with vinyl monomers.

Large incorporation of styrene might be expected to limit flexibility and hydrophilicity of the resulting graft copolymer. In that regard, we incorporated the comonomers, BMA and AA. These monomer pairs copolymerize readily with reactivity ratios of $r_1 = 0.47$ and $r_2 = 0.52$ for BMA/S (60°C). Reactivity ratios for AA (M_1) with S and BMA (M_2) are $r_1 = 0.15$, $r_2 = 0.25$ (60°C) and $r_1 = 0.29$, $r_2 = 3.67$ (50°C), respectively.

Graft Copolymerization

Graft copolymerization of CEOF, CEOC, and CEOV with DS values of ~ 0.4, ~ 0.4, and ~ 0.5, respectively, were conducted as described in the Experimental section utilizing the comonomers S, BMA, and AA. Scheme 1 illustrates the reaction pathway and the three major products expected: graft copolymers, nongrafted linear homo- or copolymers, and crosslinked systems for free-radical-induced graft copolymerization. Experimental conditions and the resulting data from the grafting studies of CEOC with S, CEOV with BMA or BMA/AA, and CEOF with S or S/BMA are summarized in Tables II and III, respectively.

As anticipated, the reaction parameters and the reactivity of pendant functionality with comonomers determined the grafting efficiency (G_e) and grafting ratios (G_r). For example, the grafting ratios (G_r) increased from ~ 75 to ~ 250%, as the monomer concentration to cellulose ester was increased to about 2.5 times by weight in reactions GP-1 and GP-2. However, these values decreased substantially upon incorporation of a second monomer. Addition of AA, e.g., to the CEOV–BMA system reduced G_r from 300 to 275% (GP-3 and GP-4). A more substantial decrease of 850 to 520% was obtained when BMA was added to the CEOF–S system (GP-5 and GP-6). Grafting efficiency, however, remained the same (approximately 25%) for the CEOC–S at different styrene concentrations.

Monomer conversion (C_m) depends upon the relative reactivity of the pendant unsaturated groups on cellulose and the comonomer(s) as well as on the reaction time for all systems (Table III). For the CEOC–S system, C_m can be pushed to ~ 40% and grafting ratios > 200%; however, at this extended reaction time, crosslinked systems were obtained.

Table II Graft Copolymerization of Unsaturated Cellulose Esters with Vinyl Monomers[a]

Series No.	Cellulose Esters[b] W_1 (g)	Vinyl Monomers W_4 (g)	Temp (°C)	Time (h)
GP-1	CEOC, 0.202	S, 2.2	60	24
GP-2	CEOC, 0.123	S, 3.3	60	36
GP-3	CEOV, 0.127	BMA, 3.6	60	36
GP-4	CEOV, 0.123	BMA/AA, 3.6 (5 : 1 wt)	60	36
GP-5	CEOF, 0.127	S, 3.6	70	24
GP-6	CEOF, 0.121	S/BMA, 3.6 (1 : 1 wt)	70	24

[a] Copolymerization conditions: monomer concentrations 15 wt % in DMSO; initiator: AIBN 0.5 mol % based on moles of monomers added.

[b] CEOC, CEOV, and CEOF represent cellulose esters of cinnamate, vinyl acetate, and fumarate, respectively; S, BMA, and AA: styrene, butyl methacrylate, and acrylic acid, respectively.

Table III Data for Graft Copolymerization of Unsaturated Cellulose Esters with Vinyl Monomers[a]

Series No.	Grafting Systems[b]	W_2 (g)	W_3 (g)	C_m (%)	G_r (%)	G_e (%)
GP-1	CEOC–S	0.357	0.454	27.7	76.7	25.5
GP-2	CEOC–S	0.427	0.890	36.2	246	25.4
GP-3	CEOV–BMA	0.517	2.720	86.9	307	15.8
GP-4	CEOV–BMA/AA	0.464	1.326	41.3	278	23.6
GP-5	CEOF–S	1.202	0.894	54.7	846	54.6
GP-6	CEOF–S/BMA	0.750	1.471	58.4	523	30.2

[a] Graft copolymerization conditions are given in Table II.
[b] CEOC, CEOV, and CEOF: cellulose esters of cinnamate, vinyl acetate, and fumarate, respectively.

Basic Kinetic Studies

To understand the time dependence of monomer conversion (C_m) and grafting parameters (G_r, G_e) as well as to attempt to control the process of the graft copolymerization, basic kinetic experiments of copolymerization with these unsaturated cellulose esters and vinyl monomers were conducted. The resulting kinetic data are illustrated in Figures 1–3 for the CEOC–S/BMA, CEOV–S/BMA, and CEOF–S/BMA, respectively.

These figures show that C_m slowly increases with polymerization time with ultimate conversion reached at no more than 30% under the conditions of the experiments. The rate of graft copolymerization is relatively low for all systems. In the CEOF–S/BMA case, phase separation occurred after 7 h, adversely affecting sampling and accurate data analysis.

C_m and G_r values indicate that the sequence of reactivity of unsaturated cellulose esters with S/BMA is CEOF > CEOV > CEOC, particularly in the early stage of copolymerization. According to the solubility tests, differences in time required for crosslinking were also demonstrated. For the CEOF–S/BMA system, the grafted cellulose was crosslinked at the very beginning of copolymerization while in the other two systems crosslinking occurred after 5 h for the CEOC–S/BMA and 20 h for the CEOV–S/BMA systems, respectively.

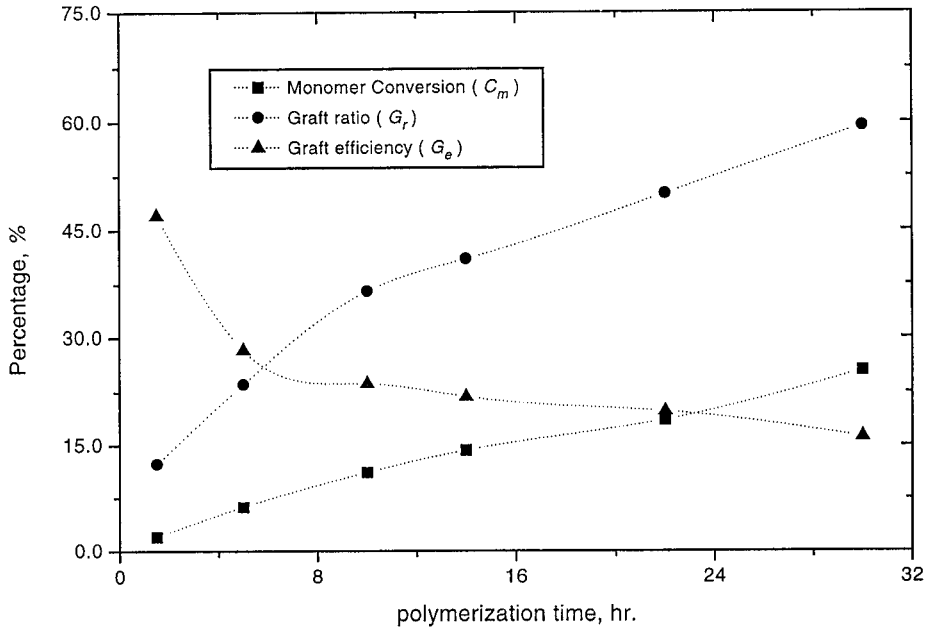


Figure 1 Grafting parameters (G_r, G_e) and C_m vs. polymerization time for CEOC–S/BMA graft copolymerization. Conditions: CEOC 0.666 g; S/BMA 9.0 g (5 : 1 wt); AIBN 0.3 mol % on moles of monomers; DMSO 90 g at 60 ± 1°C.

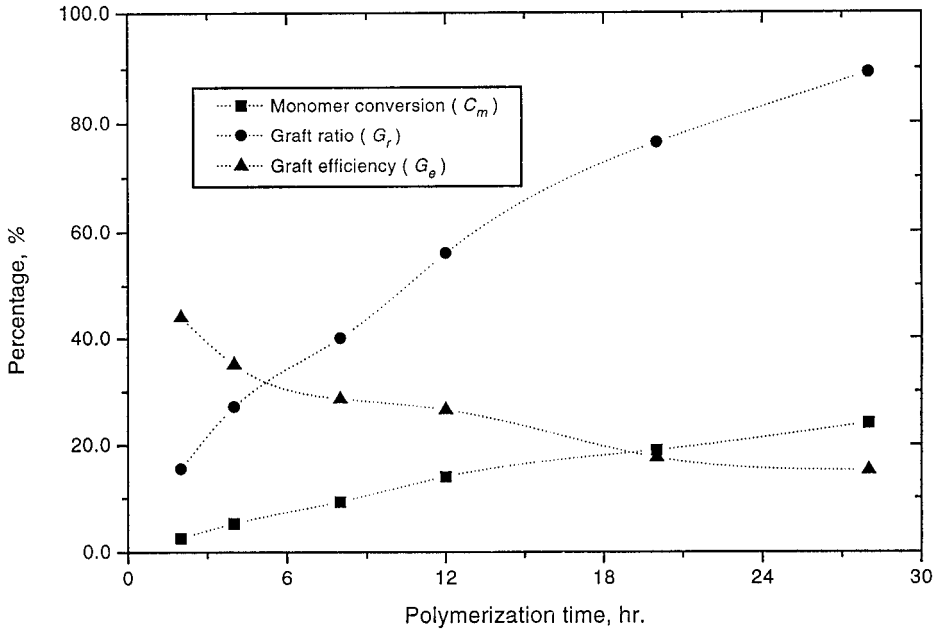


Figure 2 Grafting parameters (G_r, G_e) and C_m vs. polymerization time for CEOV–S/BMA graft copolymerization. Conditions: CEOV 0.788 g; S/BMA 9.0 g (5 : 1 wt); AIBN 0.3 mol % on moles of monomers; DMSO 90 g at 60 ± 1°C.

The grafted CEOV remained uncrosslinked at relatively long polymerization times, probably due to the chain-transfer behavior of the allyl group.

G_r increases remarkably but G_e decreases as the polymerization time increases for all grafting systems. At extended times, less of the pendant functional groups are available on cellulose and monomer homo- or copolymerization is substan-

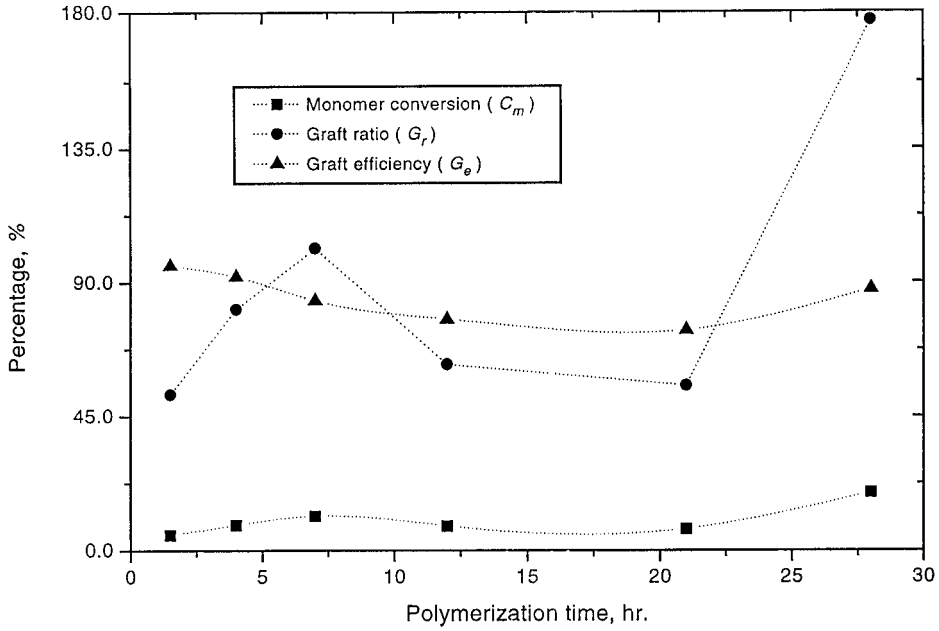


Figure 3 Grafting parameters (G_r, G_e) and C_m vs. polymerization time for CEOF–S/BMA graft copolymerization. Conditions: CEOF 0.788 g; S/BMA 9.0 g (5 : 1 wt); AIBN 0.3 mol % on moles of monomers; DMSO 100 g at 60 ± 1°C.

Table IV Transfer Constants of Chain-transfer Agents for Polymerization[a]

	C_s (for Polymerization)			
	Styrene		Methyl Methacrylate	
	60°C	80°C	60°C	80°C
Benzene	0.28×10^{-5}	1.5×10^{-5}	0.4×10^{-5}	2.4×10^{-5}
Carbon tetrachloride	0.0092	0.013	0.0005	0.0024
Carbon tetrabromide	1.78	2.3	0.27	0.33
1-Octanethiol	19.0 (50°C)	—	—	—
1-Dodecanethiol	14.8	—	—	—

[a] Data from Ref. 23.

tially favored. Regardless of the extent of crosslinking, G_r and G_e values can reach reasonably high values. This is especially evident for the reactive CEOF (Table III).

From the basic kinetic studies, it may be concluded that merely controlling the monomer conversion during graft copolymerization is insufficient to prevent crosslinking, especially for CEOC– and CEOF–S/BMA. However, the results with CEOV suggested that further experiments with chain-transfer agents might be helpful in controlling the crosslinking reaction.

Graft Copolymerization in the Presence of Chain-transfer Agents

For most free-radical polymerization systems, chain-transfer reactions inevitably exist to some extent. The kinetic chain may be prematurely terminated by the transfer of a hydrogen or other species from the monomer, initiator, solvent, or polymer.[22] Obviously, the extent of termination reactions including coupling and disproportionation may be affected by chain-transfer reactions, if an effective chain-transfer agent is used. For example, the weak S—H bond of thiol is often used to control kinetic chain length by terminating a propagating chain:

$$\sim\sim\sim\sim\sim\sim\sim\sim\cdot + \mathrm{RSH} \xrightarrow{R_{tr}} \sim\sim\sim\sim\sim\sim\sim\sim\mathrm{H} + \mathrm{RS}\cdot$$

The chain-transfer constant ($C_{tr} = k_{tr}/k_p$, or simply C) is adopted to measure the effectiveness of the existing chain-transfer reaction. The chain-transfer constant (C_s for solvents and chain-transfer agents) of benzene, carbon tetrachloride, carbon tetrabromide, and alkyl thiol for styrene and methyl methacrylate (MMA) polymerization are cited in Table IV.[23] It is also shown that the weak carbon–halogen bond also leads to high C_s values.

For our studies, carbon tetrachloride (CCl_4) and 1-dodecanethiol were employed as transfer agents in the graft copolymerization of CEOV and CEOC with S/BMA. The polymerization conditions and results of these studies are shown in Tables V and VI, respectively. Based on the solubility tests, all the grafted celluloses (GPT-2–GPT-8) are uncrosslinked, except under conditions of GPT-1.

For grafting systems with CCl_4, C_m, G_r, and G_e, are low, indicating that a very limited amount of monomer is grafted to the cellulose backbone. The trichlorocarbon radicals ($^{\bullet}CCl_3$) are not efficient in reinitiating polymerization ($k_a \ll k_p$).[22] The ratio of CCl_4 to the monomer and the reactivity of the vinyl monomer also have significant influence (see reactions GPT-2/GPT-3, GPT-3/GPT-4).

For the grafting systems with RSH, C_m reaches comparably high values ($> 40\%$) and is less affected by the variation of the polymerization conditions. This indicates that the rate of constant of reinitiation (k_a) with the regenerated radical $RS^{\bullet}$ is of the same order of magnitude, compared to the rate constant of propagation ($k_a \cong k_p$). In addition, the thiol behaves as a more effective chain-transfer agent than does CCl_4 ($k_{tr} > k_p$, $C_s > 1$, and $k_a \cong k_p$) in these graft-polymerization systems.

Apparently, individual C_m values are determined by the pendant cellulose species and its ratio to vinyl monomers as well as by the polymerization conditions (GPT-5–GPT-8). In the cases of GPT-7 and GPT-8, C_m, G_r, and G_e reached reasonable values. Obviously, polymer molecular weight is also affected by the number of chain-transfer reactions and the magnitude of C_{tr}. In many cases, a compromise must be reached to yield adequate side-chain grafting and DS while eliminating the crosslinking reaction.

Table V Graft Copolymerization of Unsaturated Cellulose Esters and Vinyl Monomers with Chain-transfer Agents[a]

Series No.	Cellulose Esters[b] W_1 (g)	Vinyl Monomers W_4 (g) (Ratios by Wt)	CTA[c] (mol %)	Temp (°C)	Time (h)
GPT-1	CEOV, 0.125	S/BMA, 3.6 (1 : 1)	CCl_4, 100	60	36
GPT-2	CEOC, 0.121	S/BMA, 3.6 (1 : 1)	CCl_4, 100	60	48
GPT-3	CEOC, 0.123	S/BMA, 3.6 (2 : 1)	CCl_4, 100	60	36
GPT-4	CEOC, 0.123	S/BMA, 3.6 (2 : 1)	CCl_4, 50	60	36
GPT-5	CEOC, 0.124	S/BMA, 3.6 (2 : 1)	RSH, 1×10^{-3}	60	36
GPT-6	CEOV, 0.549	S/BMA, 6.0 (1 : 1)	RSH, 5×10^{-4}	70	24
GPT-7	CEOC, 0.512	S/BMA, 6.0 (1 : 1)	RSH, 5×10^{-4}	70	24
GPT-8	CEOC, 0.430	S/BMA/AA, 6.0 (1 : 1 : 0.22)	RSH, 5×10^{-4}	70	42

[a] Monomer concentrations 15 wt % in DMSO; initiator: AIBN 0.5 mol % based on moles of monomers.
[b] CEOV and CEOC represent cellulose esters of vinyl acetate and cinnamate, respectively; S, BMA, and AA: styrene, butyl methacrylate, and acrylic acid, respectively.
[c] CTA: chain-transfer agent, mol % based on moles of vinyl monomers; CCl_4: carbon tetrachloride; RSH: 1-dodecanethiol.

Characterization of Grafted Celluloses

Solubility and Intrinsic Viscosity of Grafted Celluloses

Generally, graft copolymers consisting of substantially different structural backbone and side chains have unusual dissolution requirements. Solvation of the diverse segments is accomplished by manipulating the solubility parameter (δ) of the solvent. In some cases, microphase separation of the segments allows preferential swelling and often micellelike behavior.

For the CEOV and CEOC derivatives grafted with S/BMA, the solubility is substantially different from their DMSO-soluble parent celluloses as well as the THF-soluble S/BMA copolymer (the latter is also soluble in MEK and $CHCl_3$). The solubility parameters of PS, PBMA, and 56% acetylated cellulose are 9.1, 8.8, and 13.6, respectively. Either THF δ = 9.5 or DMSO δ = 12.9 alone will not dissolve the grafted celluloses; only swollen opaque or transparent gels were obtained. Solubility can be achieved, however, utilizing the binary solvent mixture in relationship to the grafting ratios.

The intrinsic viscosities [η] for typical samples (GPT-8) of the grafted cellulose and the S/BMA–AA copolymer are 2.7 in THF/DMSO and 0.15 in MEK, respectively. These data indicate that the backbone of cellulose is grafted with short-chain segments of the comonomers.

FTIR Spectroscopic Characterization

The IR spectrum of the grafted cellulose film (from GPT-8) cast from the binary solvent THF/

Table VI Data for Graft Copolymerization of Unsaturated Cellulose Esters and Vinyl Monomers with Chain-transfer Agents[a]

Series No.	Grafting Sytems[b]	W_2 (g)	W_3 (g)	C_m (%)	G_r (%)	G_e (%)
GPT-1	CEOV–S/B–CCl_4	0.185	1.943	49.3	49.4	3.0
GPT-2	CEOC–S/B–CCl_4	0.128	0.981	27.4	5.8	0.7
GPT-3	CEOC–S/B–CCl_4	0.131	0.381	14.0	6.5	1.4
GPT-4	CEOC–S/B–CCl_4	0.148	1.044	29.7	20.3	2.4
GPT-5	CEOC–S/B–RSH	0.189	1.554	45.0	52.5	4.0
GPT-6	CEOV–S/B–RSH	0.685	2.534	44.5	24.7	5.1
GPT-7	CEOC–S/B–RSH	0.889	2.580	49.3	73.7	12.8
GPT-8	CEOC–S/B/A–RSH	1.175	1.910	44.3	173	28.1

[a] Graft copolymerization conditions are given in Table IV.
[b] CEOV and CEOC: cellulose esters of vinyl actate and cinnamate, respectively; CCl_4 and RSH: carbon tetrachloride and 1-dodecanethiol, respectively.

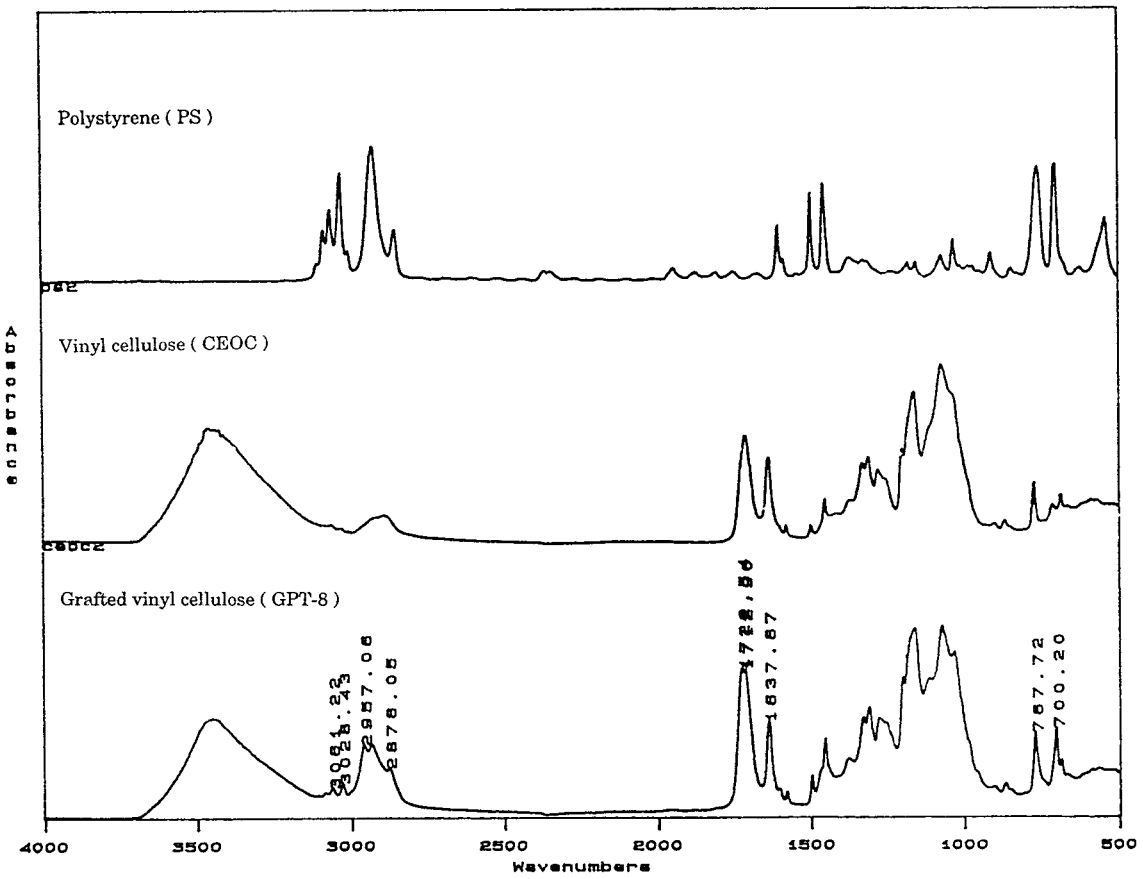


Figure 4 IR spectra of grafted cellulose ester (GPT-8), unsaturated cellulose ester (CEOC), and polystyrene (PS).

DMSO (1 : 1 volume) and the reference spectra of pendant alkenyl cellulose (CEOC) and polystyrene (PS) are shown in Figure 4. Additional absorbances in four regions which should be related to the chain units of S/BMA–AA are seen. These are at 702 and 767 cm^{-1} (the C—H deformation of aromatic in CEOC and PS), 1712 and 1722 cm^{-1} (the C=O stretching related to CEOC and BMA/AA units), and the multiple peaks between 2870 and 2960 cm^{-1} (CH, CH_2, and CH_3 stretching of CEOC and S/BMA–AA units) as well as 3028 and 3061 cm^{-1} (CH stretching of aromatic in CEOC and PS). These additional absorbances reflect the existence of S/BMA–AA chain units in the grafted cellulose.

NMR Spectroscopic Characterization

A typical ^{1}H-NMR spectrum of grafted cellulose with S/BMA–AA (GPT-8) is contrasted with the spectra of the unsaturated cellulose and the S/BMA copolymer in Figure 5. The chemical shifts of the copolymer of S and BMA are 1.1–2.4 (broad and overlapped, three protons of CH and CH_2), 6.6 and 7.06 (five aromatic protons) for PS, and 0.5–2.5 (broad and complex, 12 protons of CH_2 and CH_3), 0.95 (terminal CH_3), and 3.96 (broadened triplet, CH_2 bonded to O atoms) for PBMA, respectively.[25] For the CEOC-substituted cellulose, the chemical shifts are 3.0–5.0 (protons attached to carbon on the anhydroglucose ring), 5.1–5.9 (protons of residual hydroxyls), and 6.6 and 7.4–7.7 (two vinyl and five aromatic protons), respectively.[21] Obviously, these chemical shifts all exist in the spectrum of the grafted cellulose.

DSC Characterization

DSC analysis was employed for the grafted celluloses to characterize the thermal properties of resultant materials. DSC thermograms for the grafted cellulose (GPT-8) and original pendantly

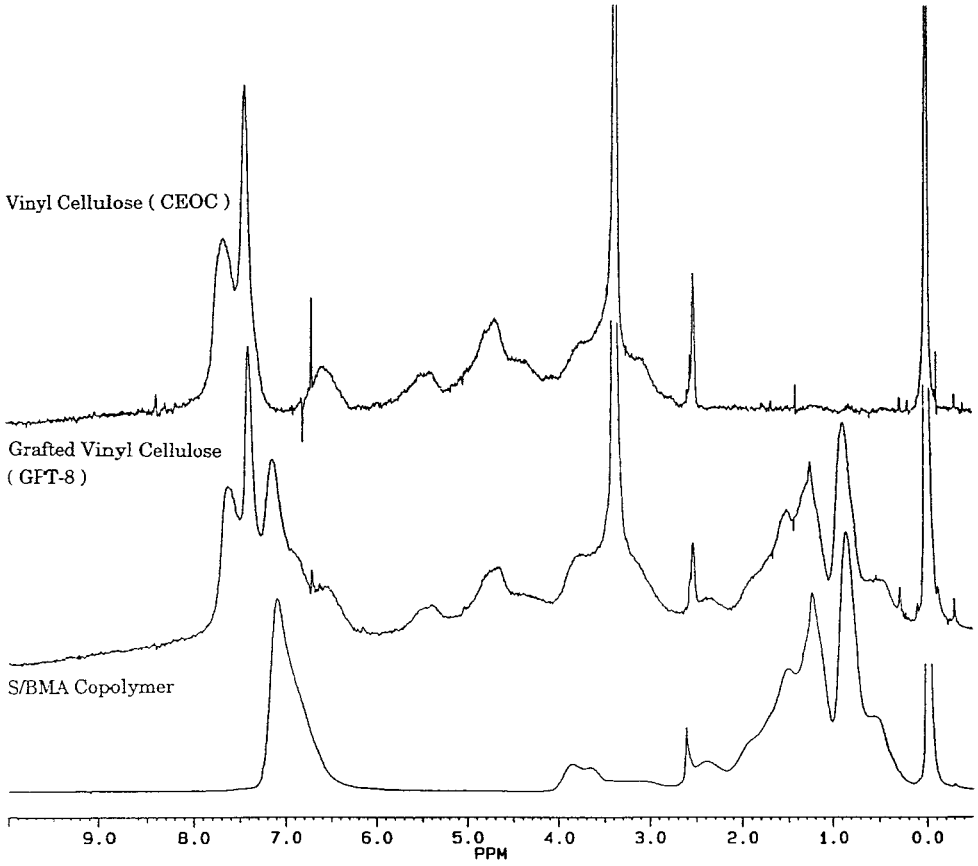


Figure 5 ^{1}H-NMR spectra of grafted cellulose ester (GPT-8), unsaturated cellulose ester (CEOC), and S/BMA copolymer.

substituted cellulose (CEOC) are presented in Figure 6. The thermograms show similar features for both grafted cellulose and the unreacted cellulose. The molecular motion of cellulose is strongly restricted by inter- and intramolecular hydrogen bonding; therefore, any kind of phase transition is not observed for dry cellulose at a temperature below the decomposition temperature.[26] Thus, the shallow endotherm found by DSC in the temperature range 20–120°C should be due to dehydration of absorbed water. The differences in the integrated endotherm area appear to correspond to the differences in hydrophilicity of the grafted and ungrafted celluloses. An endotherm occurs at 220°C for the sample of grafted cellulose from depolymerization of S/BMA–AA chain segments.

CONCLUSIONS

Substituted ester derivatives of cellulose, CEOC, CEOV, and CEOF are shown to undergo facile graft copolymerization with the vinyl monomers styrene, butyl methacrylate, and acrylic acid by free-radical initiation. Reasonably high grafting ratios (more than 200%) in most cases are obtained due to the careful selection of pendant cellulose functionality and comonomers. However, the grafted celluloses undergo a crosslinking reaction at high conversion. Results of basic kinetic studies show that the manipulation of only polymerization time and monomer conversion is not sufficient to avoid the formation of crosslinked networks. By utilizing an effective chain-transfer agent such as a thiol graft copolymerization proceeds satisfactorily, resulting in the soluble, uncrosslinked grafted celluloses with fairly high C_m (>40%) and moderate G_r (up to 170%) values. The structural identification of grafted celluloses was made by solubility testing as well as by IR and NMR spectroscopy. Further studies will be directed toward investigation of physical and morphological properties of films cast from solutions of these graft copolymers.

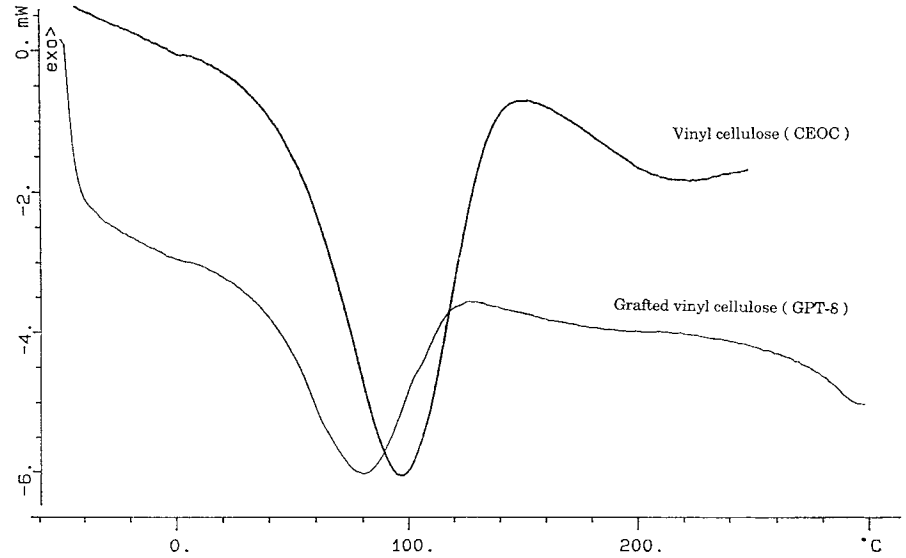


Figure 6 DSC thermograms of grafted cellulose ester (GPT-8) and unsaturated cellulose ester (CEOC).

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