(Photo) Graft Copolymerization of Methyl Methacrylate (MMA) on Polyamine-Modified Oxycellulose in a Limited Aqueous System

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Synopsis

Graft copolymerization of methyl methacrylate (MMA) on oxycellulose modified with a polyamine [diethylene triamine (DETA)] was studied in a limited aqueous system under photoactivation in visible light using $K_2S_2O_8$ as the initiator. No polymerization was observed in the dark or in presence of light in 80 min in the case of DETA-treated cellulose; however, ready graft copolymerization resulting in high percent grafting and grafting efficiencies took place in the case of DETA-modified oxycellulose system under photoactivated conditions. DETA-modified oxycellulose prepared from oxycellulose corresponding to low degrees of oxidation (copper nos. 1.5–3.5) produced optimum grafting. The grafting parameters under different sets of conditions were studied and compared, and the mechanism of graft copolymerization was discussed.

INTRODUCTION

Graft copolymerization of vinyl monomers on cellulose has been extensively investigated in recent years.[1-8] The present trend involves modification of the cellulose prior to grafting, which often leads to improved grafting effects and rate in the subsequent graft copolymerization process.[9-10] The present report involves studies on modification of oxycellulose (periodate-treated cellulose)[9-11] by treatment with a polyamine, diethylene triamine (DETA), and subsequent graft copolymerization of methyl methacrylate (MMA) monomer on the (poly) amine-modified oxycellulose in a limited aqueous system using potassium persulfate ($K_2S_2O_8$) as the initiator under photo conditions at room temperature, keeping the volume of water $\leq$ volume of the monomer. Results of the effect of variation of process conditions on the grafting parameters are reported.

EXPERIMENTAL

Materials

Cotton cellulose (absorbent cotton), obtained from the local market, was purified by standard procedures.[9] Monomer MMA, obtained through the kind courtesy of Western Chemical Corporation, Calcutta, was purified by the usual procedures and distilled prior to use. $NaIO_4$ and $K_2S_2O_8$ obtained from BDH, India, were of A.R. grade.

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Oxidation of Cellulose and Further Modification of Oxycellulose by DETA

Selective oxidation of cellulose leading to limited transformation of the hydroxyl groups in the 2 and 3 positions of the glucosidic rings to aldehyde groups without chain breakage was accomplished by treatment with 0.05*M* aqueous solution of $NaIO_4$.[11] Extent of oxidation, expressed in terms of copper number,[12] was varied by varying the time of periodate treatment. The oxycellulose samples thus prepared will be written as oxycellulose (x), the value of x in the parentheses denoting its copper number.

The oxycellulose samples were then treated with 0.05*M* aqueous solution of DETA (liquor ratio 1:50) at room temperature for 24 h.[13] Thereafter, the samples were washed repeatedly with water to amine-free condition, squeezed to a limiting water content, and finally dried in air. The polyamine-modified oxycellulose samples thus prepared will henceforth be referred to as DETA-modified oxycellulose (x).

Graft Copolymerization

A weighed amount of the cellulose substrate was placed in a Corning borosilicate glass ampoule (1-in. diameter), to which was added requisite volumes of an aqueous solution of $K_2S_2O_8$ and MMA under nitrogen-flushed conditions. Polymerization experiments were generally studied under photoactivated conditions by placing the test tubes between a pair of fluoresent tube lamps (40 W) for a specified time period at 32 + 0.5°C.

After polymerization, the contents of the test tube were quantitatively transferred to a beaker containing methanol. The gross polymer was then washed thoroughly with water, methanol, and finally with petroleum ether, and dried in vacuum at 50°C. For isolation of the homopolymer PMMA, the gross polymer of known weight was allowed to swell and partially dissolve in excess of benzene containing 5% methanol for over 24 h—under occassional stirring conditions at room temperature. The solvent containing dissolved PMMA only was then decanted off. Any more free PMMA still remaining in the residue was then extracted out using the same solvent mixture under boiling condition for about 6 h. This hot extraction step was repeated a number of times, if necessary, till the extract gave no turbidity on addition of excess petroleum ether. The residue was then dried in a vacuum oven at 40°C and weighed. The amount of free PMMA was given by the loss in weight due to extraction; % grafting, grafting efficiency, and total conversion (%) were calculated in the usual manner.[9]

RESULTS AND DISCUSSION

Preliminary data on the graft copolymerization of MMA on oxycellulose (x = 21.81) and DETA-modified oxycellulose (x = 21.81) at room temperature (32 ± 0.5°C) in a limited aqueous system are given in Table I, which clearly indicates that, under comparable conditions, the grafting parameters are significantly higher in the DETA-modified systems. Graft copolymerization of MMA on the DETA-modified oxycellulose proceeds at a faster

TABLE I
Graft Copolymerization of Methyl Methacrylate on Oxycellulose (x = 21.81) and DETA-Modified Oxycellulose (x = 21.81): A Comparative Study[a]

Substrate and conditions of experiment	Time of polymerization (min)	Total conversion (%)	% Grafting	Grafting efficiency (%)
Oxycellulose (in presence) of light)	20	—	—	—
	40	1.30	3.70	20.33
	60	1.93	3.86	14.26
DETA-modified oxycellulose (in presence of light)	20	11.56	93.32	57.54
	40	19.45	109.86	40.61
	60	27.14	134.83	35.63
	80	37.94	161.36	30.49
DETA-modified oxycellulose (in the dark)	20	—	—	—
	40	1.26	4.15	33.58
	80	2.24	13.65	43.84
	120	23.78	85.91	25.60

[a] Substrate = 0.10 g; MMA = 1.5 mL; water = 1 mL; $K_2S_2O_8$ = 27 mg; temperature = 32 ± 0.5°C.

rate in the light than in the dark as revealed by % conversion–time data (Table I). In case of the DETA-modified cellulose (x = 0.22) system, no polymerization took place under similar conditions.

Results of (photo) graft copolymerization of MMA on DETA-modified oxycellulose showing the effect of variation of time of polymerization for various x values of oxycellulose, concentration of $K_2S_2O_8$ and monomer content are given in Tables II and III and Figures 1 and 2.

Effect of Variation of Time of Polymerization using DETA-Modified Oxycellulose Corresponding to Different x Values

Related results are shown in Table II and Figure 1. Increasing the time of polymerization results in an initial increase of % conversion and % grafting followed by a levelling-off trend. The levelling-off effect becomes apparent at progressively earlier states (time) of the reaction as the value of x increases. The grafting efficiency and its variation with time of polymerization is dependent on the copper number (x) of the oxycellulose intermediate. For a DETA-modified system corresponding to a low value of x (x = 1.60), the grafting efficiency increased gradually with time, while for systems corresponding to higher values of x (x = 3.30–21.81), the grafting efficiency exhibits a sharp initial uptake [over the broken line zone, Fig. 1(c)] followed by a levelling-off or a decreasing trend.

Effect of Variation of x

The effect of variation of x (and hence the degree of polyamine incorporation or the total number of amine moieties in a given mass of DETA-modified oxycellulose) at a fixed time of polymerization on the grafting parameters can be evaluated from the results of Table II and Figure 1. The % conversion and grafting parameters generally pass through a maximum.

TABLE II
(Photo) Graft Copolymerization of MMA onto DETA-Modified Oxycellulose: Effect of Variation of Time of Polymerization and Copper Number x of the Oxycellulose Intermediate

Time of polymerization (min)	x	Total conversion (%)	% Grafting	Grafting efficiency (%)
25	1.60	1.51	4.76	22.50
	3.30	1.27	11.74	65.09
	6.10	1.91	20.00	74.91
	10.26	9.52	95.21	71.74
	12.68	10.06	106.14	75.64
	17.40	8.82	78.05	63.16
	21.81	9.51	69.68	52.60
50	1.60	10.72	49.23	32.99
	3.30	4.48	54.56	87.05
	6.10	17.81	203.99	82.15
	10.26	25.17	178.43	50.92
	12.68	18.33	158.93	62.34
	17.40	16.79	105.24	44.98
	21.81	16.48	92.49	40.13
75	1.60	22.48	212.29	67.98
	3.30	34.00	419.56	89.00
	6.10	31.37	355.40	81.46
	10.26	39.10	274.44	50.11
	12.68	33.21	186.81	40.27
	17.40	23.06	134.81	41.95
	21.81	22.03	117.32	38.09
100	1.60	32.19	399.14	89.16
	3.30	59.45	740.15	90.23
	6.10	55.00	494.92	74.48
	10.26	67.96	413.00	43.66
	12.68	35.31	204.98	41.66
	17.40	32.38	181.60	40.25
	21.81	25.30	117.92	33.00
125	1.60	58.91	717.71	87.78
	3.30	60.29	774.38	93.32
	6.10	63.75	586.62	66.30
	10.26	72.67	427.89	42.09
	12.68	44.48	246.76	39.99
	17.40	42.84	188.12	31.61
	21.81	32.71	135.70	29.69

[a] Substrate = 0.10 g; MMA = 1.5 mL; water = 1 mL; $K_2S_2O_8$ = 5.4 mg; temperature = 32 ± 0.5°C.

Total Conversion

The maximum for % conversion corresponds to a moderate value of $x (x = 10.26)$ for times of polymerization ranging from 50 to 125 min. For a low time of polymerization (25 min), the maximum is attained at a point corresponding to $x = 12.68$.

% Grafting

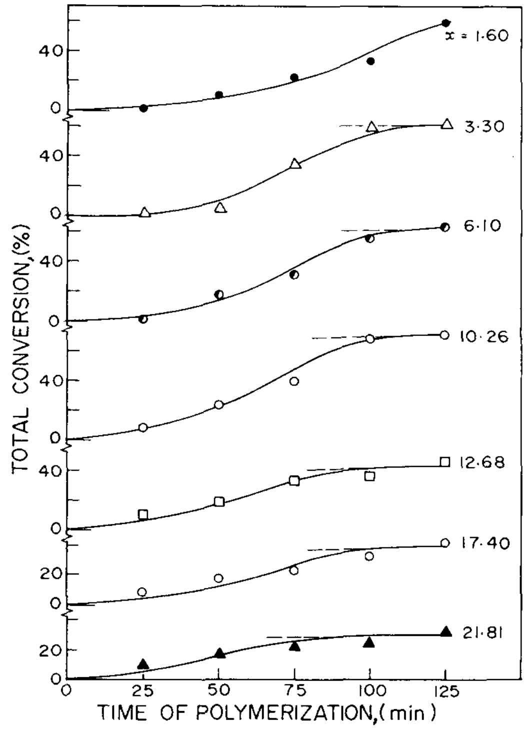
For % grafting, the maximum corresponds to a low value of x $(x = 3.30)$ for longer times of polymerization (75–125 min). The maximum is shifted to some higher values of x for shorter times of polymerizatin (e.g., to

TABLE III
(Photo) Graft Copolymerization of MMA on to DETA-Modified Oxycellulose ($x = 10.26$): Effect of Variation of $K_2S_2O_8$ Content

$K_2S_2O_8$ (mg)	Total conversion (%)	% Grafting	Grafting efficiency (%)	[η] (dL/g)	
				Free PMMA	Grafted PMMA
0[b]	—	—	—	—	—
1.55	10.12	107.71	76.19	4.82	—
5.40	25.17	179.04	50.92	4.59	8.52
6.80	25.22	188.94	53.63	4.32	7.80
15.20	25.43	185.90	52.33	—	—
29.45	25.65	163.32	45.58	4.13	5.71
41.65	26.08	158.92	43.62	3.97	5.70

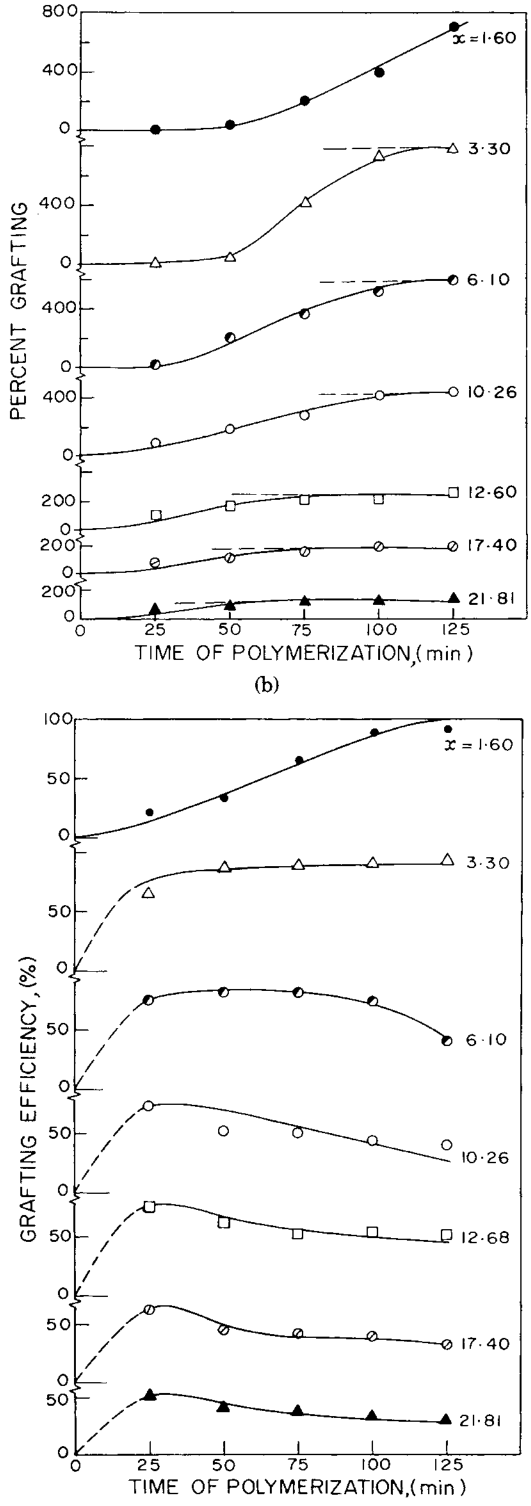
[a] DETA-modified oxycellulose = 0.10 g; MMA = 1.5 mL; water = 1 mL; time of polymerization = 50 min; temperature = 32 ± 0.5°C.

[b] No polymerization.



(a)

Fig. 1. Photograft copolymerization of MMA (1.5 mL) on DETA-modified oxycellulose (0.1 G) at 32 ± 0.5°C. Plot of (A) % total conversion, (B) % grafting, (C) grafting efficiency (%), against time of polymerization. Water: 1.0 mL, $K_2S_2O_8$ = 5.4 mg, copper number (x) varies.



(b)

(c)

Fig. 1. *(continued from previous page)*

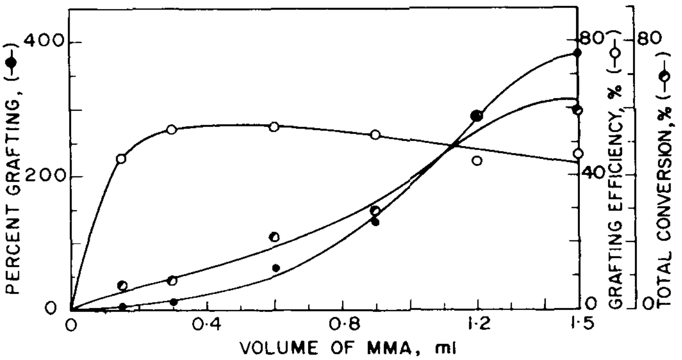


Fig. 2. Photograft copolymerization of MMA on DETA-modified oxycellulose (x = 6.10): Plot of grafting parameters against monomer content. DETA-modified oxycellulose: 0.1 g, $K_2S_2O_8$ = 18.9 mg, water = 1 mL, total volume = 2.5 mL, balancing diluent = toluene.

x = 6.10 for 50 min of polymerization and to x = 12.68 for 25 min of polymerization.

Grafting Efficiency

The maximum corresponds to x = 3.30 for times of polymerization ranging from 50 to 125 min. For a low time of polymerization (25 min), the maximum is attained over the range x = 6.10–12.68.

Effect of Variation of Monomer Content

Related results are shown in Figure 2. % conversion and % grafting showed a slow increasing trend with increasing monomer content till a point coresponding to about 0.6–0.8 ML of MMA in the system. It was then followed by a zone of sharper gain in the parameters up to about 1.2–1.3 ML of MMA. Grafting efficiency (%) apparently increases over the low monomer range and then follows a levelling off or even a slow decreasing trend as monomer content is increased.

Effect of Variation of $K_2S_2O_8$ Content

Related results using DETA-modified oxycellulose (x = 10.26) as the substrate are given in Table III. Increasing the $K_2S_2O_8$ content results in a sharp initial increase in the % total conversion followed by a levelling-off effect: % grafting passes through a maximum corresponding to about 6–10mg $K_2S_2O_8$ and decreases gradually thereafter. Grafting efficiency (%) apparently attains a maximum value at a still lower $K_2S_2O_8$ content ($\leq$ 1.55 mg) as can be understood from Table III.

Comparison of Chain Length of Grafted and Free PMMA Fractions

The grafted PMMA fractions from some selected experiments were isolated by procedures described before.[9] Intrinsic viscosities [η] of the isolated grafted PMMA fractions and of the corresponding free PMMA fractions were determined from benzene solution at 30°C and compared (Table III).

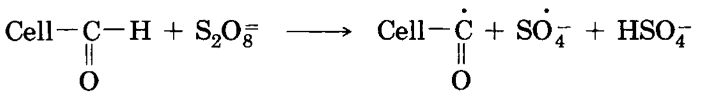
The [η] value (and hence molecular weight) of the grafted PMMA fractions are significantly higher than those of the corresponding free PMMA fractions. This is believed to accrue from much more delayed termination of the growing grafted in PMMA chains as compared to the termination of the growing free PMMA chains owing to the greatly diminished mobility of the grafted—in chains on account of the cellulosic chain network acting as an additional physical barrier.[9]

Mechanism

The radical generation process in the present graft copolymerization system is complicated because of the multiplicity of factors controlling them including the heterogeneous nature of the system. The likely radical generating reactions in a cellulose/oxycellulose/$K_2S_2O_8$ system are as follows[10]:

$$S_2O_8^{=} \longrightarrow 2\,SO_4^{\bullet} \qquad (1)$$

$$\text{Cell}-OH + S_2O_8^{=} \longrightarrow \text{Cell}-\dot{M} \times S\dot{O}_4^{-} + HSO_4^{-} \qquad (2)$$



$$\text{Cell}-\underset{\underset{O}{\|}}{C}-H + S_2O_8^{=} \longrightarrow \text{Cell}-\underset{\underset{O}{\|}}{\dot{C}} + S\dot{O}_4^{-} + HSO_4^{-} \qquad (3)$$

$$\text{Cell}-NH-R + S_2O_8^{=} \longrightarrow \text{Cell}-\dot{N}-R + HSO_4^{-} + S\dot{O}_4^{-} \qquad (4)$$

Each of these reactions are photosensitive. Radicals may also be generated on the cellulosic substrate via chain transfer. In the DETA-modified oxycellulose, reaction (3) is inconsequential considering complete transformation of aldehyde groups when allowed to react with large excess of the polyamine. In view of grafting of PMMA on DETA-modified oxycellulose (Cell—NH—R)[13] being possible also in the dark, reaction (4) is considered more important in the present system.

In view of relatively poor grafting on oxycellulose as compared to DETA-modified oxycellulose under otherwise identical conditions (Table I), it is indicated that generation of radical sites on the DETA-modified oxycellulose substrate occurs principally via reaction (4). Homopolymerization is initiated through $SO_4^{\bullet -}$ radicals.

Besides the activating or chain initiating role of the polyamine sites in the DETA-modified oxycellulose, they are also likely to produce some retardation effects, particularly in higher concentrations as for systems characterized by high x values; some of the levelling-off effects in % conversion or overall grafting may be partly understood on this basis.

Table III clearly shows that % conversion for a given time does not practically vary with $K_2S_2O_8$ content over a wide range beyond a very low initial $K_2S_2O_8$ content for a DETA-modified oxycellulose of a fixed x value; the chain lengths of the poly (methyl methacrylate) formed (free and grafted), however, decrease largely with increase in $K_2S_2O_8$ content. It is indicated thereby that the present graft copolymerization system is characterized by chain termination by primary radicals including those derived from the polyamine moieties of the DETA-modified oxycellulose.

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