Graft Copolymerization of Methyl Methacrylate (MMA) on Hydrazine Treated Oxycellulose in Limited Aqueous System

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Synopsis

Graft copolymerization of methyl methacrylate (MMA) on oxycellulose modified with hydrazine treatment was studied in a limited aqueous system using $K_2S_2O_8$ as the initiator. Hydrazine modified oxycellulose prepared from oxycellulose corresponding to low degrees of oxidation (copper nos. 2–6) produced the best grafting effects. Grafting parameters under different sets of conditions were studied and compared and the mechanism of graft copolymerization discussed.

INTRODUCTION

On chemical modification, cellulose often leads to higher rates and extents of grafting when graft copolymerization of a vinyl monomer is done on it. Reports on grafting of vinyl polymers on amine-treated cellulose or oxycellulose are very scanty.[1,2] In the present paper we report results of graft copolymerization of methyl methacrylate (MMA) on hydrazine-treated oxycellulose employing potassium persulfate ($K_2S_2O_8$) as the initiator under different conditions.

EXPERIMENTAL

Materials

Cellulose

Cellulose in the form of absorbent cotton was used after the following treatment. A 10 g portion of the cotton sample was boiled briskly in 500 mL dilute NaOH solution (0.08%) containing 0.1 g of a nonionic surfactant for 3 min. The sample was then washed successively with hot water, cold water, HCL solution (1%), and finally with cold water until it was acid free. The scoured cellulose thus obtained was dried at room temperature in a current of dust free air. Cellulose sample thus treated will be called unmodified cellulose in this paper.

Preparation of Oxycellulose

Selective oxication of unmodified cellulose to oxycellulose was carried out using $NaIO_4$ solution according to procedure published earlier.[3]

Hydrazine Treatment of Oxycellulose

Oxycellulose prepared (oxidation accomplished at 2 and 3 position of the glucoside rings, transforming the respective hydroxyl groups to aldehyde groups) was treated with hydrazine[4] in a subsequent step using 0.05 molar hydrazine hydrate solution with a liquor ratio of 1:50 for 24 hrs. The hydrazine-treated products were then washed with cold water until free from hydrazine, squeezed to a limiting water content, and then dried at room temperature in a current of dust-free air. The extent of hydrazine intake by oxycellulose was dependent on its copper number (i.e., its degree of oxidation), which was determined following the standard procedure[5] given by Heyes.

Other Reagents

Monomer MMA was purified following the usual procedures.[3] Analytical-grade $K_2S_2O_8$ from E Merek was used in polymerization experiments.

Graft Copolymerization

A weighed amount of hydrazine-treated oxycellulose was taken in a corning brand borosilicate glass test tube (0.8 in. diam). To this a requisite amount, of MMA and aqueous solution of $K_2S_2O_8$ were added. The test tube was then flushed with purified nitrogen for about 5 min. The N_2-flushed test tube was then stoppered tightly and put in a thermostatic water bath at a specified temperature. After polymerization for a fixed time period, the gross polymer was taken out, washed profusely with water, methanol, and petroleum ether, and finally dried under vacuum to constant weight. The extraction and isolation of the free polymethyl methacrylate (PMMA) in this gross product and calculation of % grafting, grafting efficiency, E_M (%), and total conversion (%) were done in the usual manner.[3] Some graft copolymerizations were also done on oxycellulose and its derivatives obtained by reacting it with ethylene diamine, phenyl hydrazine and hydroxylamine separately.

RESULTS

Preliminary Studies

Preliminary studies indicated that, for thermal polymerization done under comparable conditions at 50°C, the rate of polymerizations judged from yield at a given time (2h) was substantially higher in the case of hydrazine- and ethylene-diamine-treated oxycellulose than that for simply oxycellulose or for hydroxylamine- or pheny-hydrazine-treated oxycellulose (Table I). Data in Table I clearly show that hydrazine-treated oxycellulose produced the best grafting effects, and hence subsequent studies were made on hydrazine-treated oxycellulose and related results are described below.

Graft Copolymerization Using Hydrazine-Treated Oxycellulose

The results of graft copolymerization of MMA hydrazine-treated oxycellulose showing the effect of variation of monomer content and initiator concentration are given in Figures 1 and 2, respectively, and those showing the effect of variation of extent of hydrazination (judged from the copper

TABLE I
Graft Copolymerization or MMA on Oxycellulose and Some of Its Derivatives[a]

Base polymer type	Base polymer (g)	Total conversion (%)	Grafting (%)	Grafting efficiency E_M (%)
Oxycellulose	0.2002	9.04	17.28	27.13
Hydroxyl-amine-treated oxycellulose	0.2001	3.64	2.39	9.33
Phenyl-hydraxine-treated oxycellulose	0.2013	24.08	40.73	24.15
Ethylenediamine-treated oxycellulose	0.2015	65.99	226.6	49.07
Hydrazine-treated oxycellulose	0.2007	77.60	444.04	81.43

[a] MMA = 1.5 mL; H_2O = 1.5 mL; $K_2S_2O_8$ = 9 mg; time = 2 h; temp = 50°C; copper no. 17.12.

number of oxycellulose). Sulfuric acid concentration and temperature are given in Tables II, III, and IV, respectively. Table IV also shows variation of overall rate of polymerization (R_p) (mol L^{-1} S^{-1}) with variation of temperature. The overall activation energy was found to be 5.71 k cal/mol.
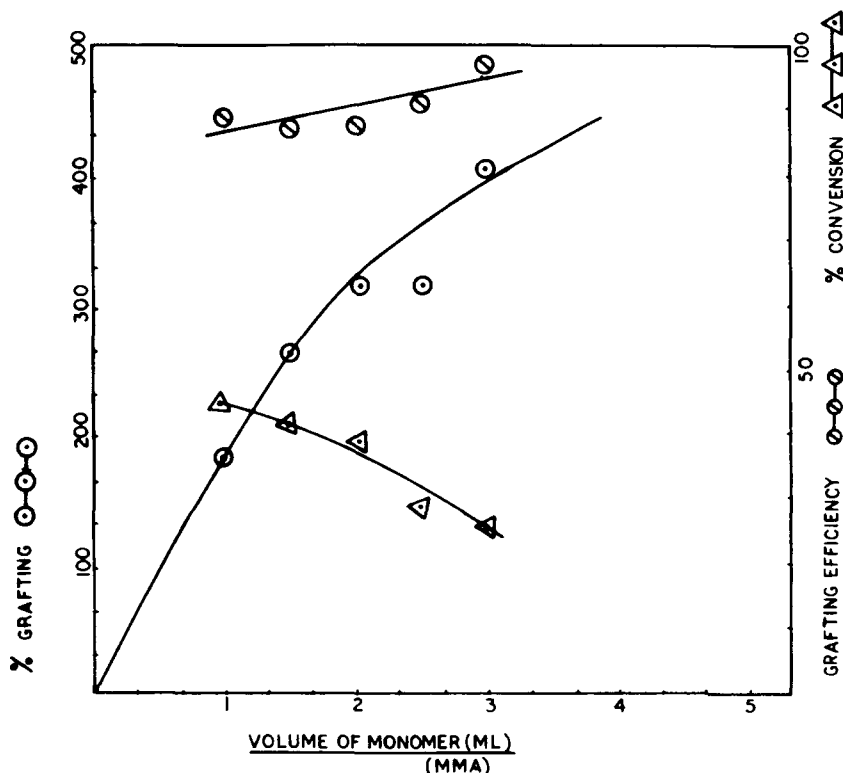

Fig. 1. Graft copolymerization of MMA on hydrazine-treated oxycellulose (copper no. 17.12). Effect of variation of monomer content: temperature=40 + 0.1°C; time= 2 h; $K_2S_2O_8$=9 mg; water=1.5 ML; the cellulosic substrate=0.2 g.
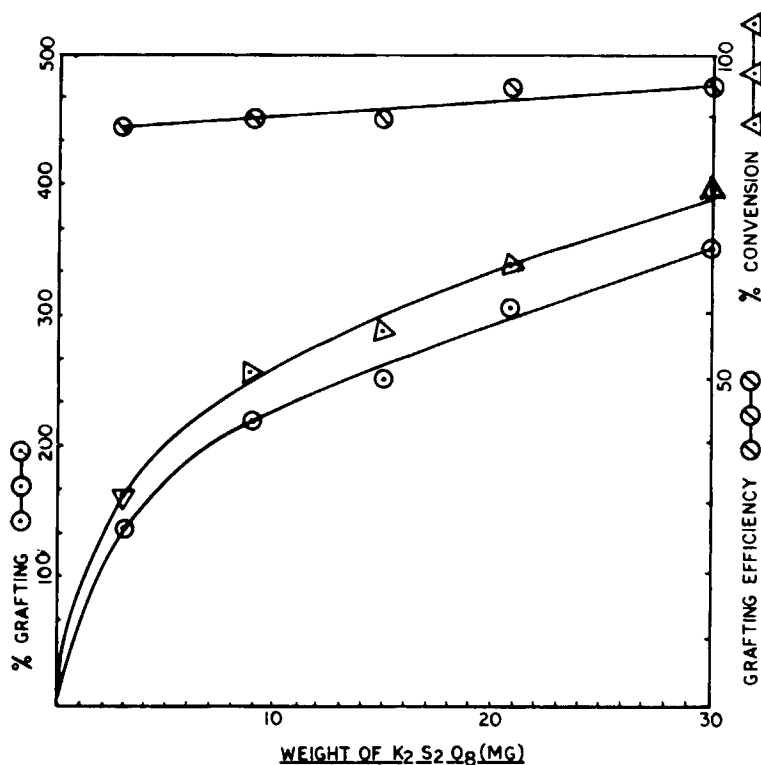
Fig. 2. Effect of variation of $K_1S_2O_8$ concentration on graft copolymerization of MMA on hydrazine-treated oxycellulose (copper no. 12.97): temperature 40 + 0.1°C; MMA = 1 mL; time = 2 h; water = 1.5 ML; the cellulosic substrate = 0.2 g.

Effect of Variation of Degree of Oxidation of Oxycellulose

It may be seen from Table II that, for a given time of polymerization (2 h), improved grafting effects and conversion were observed in hydrazine-treated oxycellulose having low copper number (2–6). With oxycellulose of

TABLE II
Graft Copolymerization of MMA on Hydrazine-Treated Oxycellulose: Effect of Variation of Hydrazine Incorporation Given by the Copper Number of the Oxycellulose

Copper no.	Total conversion (%)	Grafting (%)	Grafting efficiency E_M (%)
0.28[b]	2.67	9.27	74.1
0.28[c]	13.1	55.23	90.5
1.70	43.07	198.7	98.5
2.93	71.91	337.56	100.0
5.10	75.37	353.54	100.0
8.39	62.73	278.35	94.87
12.97	51.0	219.01	91.55
17.12	45.17	172.46	88.56
16.6	36.98	145.19	83.80
33.82	12.95	27.11	44.66

[a] MMA = 1 mL; H_2O = 1.5 mL; $K_2S_2O_8$ = 9 mg; time = 2 h; temp = 40°C; hydrazine-treated oxycellulose 0.2 g.
[b] Unmodified cellulose without hydrazination.
[c] Unmodified cellulose treated with hydrazine.

TABLE III
Effect of Variation of Added H_2SO_4 in the Graft Copolymerization
of MMA on Hydrazine-treated Oxycellulose[a]

H_2SO_4 (M/L)	Total conversion (%)	Grafting (%)	Grafting efficiency E_M (%)
4×10^{-5}	42.60	177.2	88.48
4×10^{-4}	68.92	285.73	88.42
4×10^{-3}	80.23	327.09	87.08
4×10^{-2}	72.91	249.35	73.12
2×10^{-1}	72.43	199.11	66.23

[a] MMA = 1 mL; H_2O = 1.5 mL; $K_2S_2O_8$ = 9 mg; time = 2 h; temp = 40°C; hydrazine-treated oxycellulose (copper no. 17.12) = 0.2

still higher copper number, the grafting effects and % conversion tend to fall off significantly (Table II).

Effect of Variation of Monomer Content

In most of the experiments, 0.2 g of the cellulosic sample was used for 1 mL of MMA, and total liquid volume, including the aqueous solution of $K_2S_2O_8$ was 2.5 mL. For studies of the effect of variation of monomer content, the total liquid volume varied between 2.5 and 4.5 mL.

Effects of variation of monomer content (1–3 mL) are shown in Figure 1. For a given time of polymerization, percent grafting and grafting efficiency increase with increasing monomer content but % conversion, expectedly, follows a decreasing trend.

TABLE IV
Effect of Variation of Time and Temperature in the Graft Copolymerization
of MMA on Hydrazine-treated Oxycellulose[a]

Temp (°C)	Reaction time (h)	Total conversion (%)	Grafting (%)	Grafting efficiency E_M (%)	R_p (M L^{-1} s^{-1})	Activation energy (k$_{cal}$/mol)
35	0.5	4.21	14.25	71.97		
35	1.0	31.61	132.66	89.66		
35	1.5	42.9	186.01	92.33	2.82×10^{-4}	
35	2.0	62.73	278.35	94.87		
35	3.0	74.76	297.62	85.37		
40	0.5	21.57	97.42	95.06		
40	1.0	45.19	194.78	92.35		
40	1.5	52.17	221.33	90.53	4.28×10^{-4}	
40	2.0	59.88	245.89	87.67		
40	2.25	71.0	275.31	82.87		
45	0.5	25.87	120.8	99.34		5.71
45	1.0	61.45	281.56	97.8		
45	1.5	76.20	311.39	87.33	5.7×10^{-4}	
45	2.5	77.53	317.83	87.78		

[a] Hydrazine-treated oxycellulose 0.2 g; MMA = 1.0 mL; $K_2S_2O_8$ = 9 mg; H_2O = 1.5 mL; copper no. = 8.39.

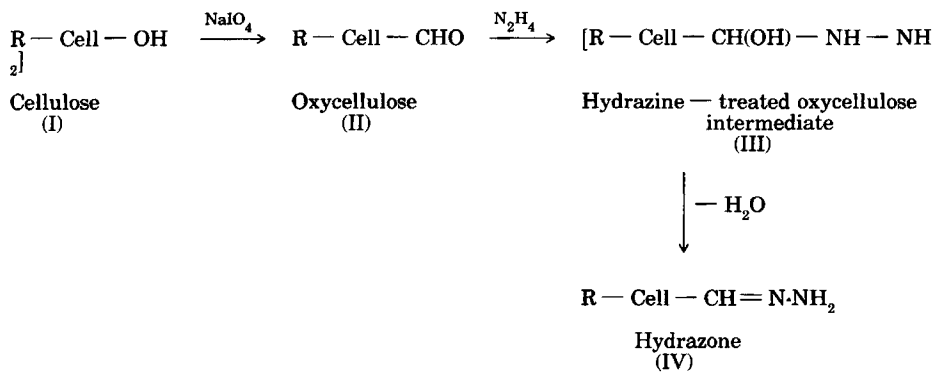## Effect of Variation of $K_2S_2O_8$ Content

Results showing variation of $K_2S_2O_8$ content (3–30 mg) (Fig. 2) indicate that percent grafting and % conversion follow increasing trends with increasing $K_2S_2O_8$ content and grafting efficiency, remaining close to the 90–95% range, also show a slow increasing trend.

Effect of Variation of Acidity of the Medium

In the presence of added H_2SO_4 (4×10^{-5}–2×10^{-1} mol L^{-1}) percent grafting and % conversion tend to pass through a maximum at H_2SO_4 concentration of about 4×10^{-3} mol L^{-1} while grafting efficiency (%), remaining practically constant upto this level of acid concentration, follows a dropping trend on further increase in acidity of the medium Table III.

Mechanism

Controlled oxidation of cellulose with $NaIO_4$ produces oxycellulose of different degrees of oxidation depending on the reaction condition leading to limited generation of —CHO groups on the C_2 and C_3 positions of the anhydro-β glucose units. Treatment with excess of hydrazine transforms the aldehyde groups to the corresponding hydrazones (IV) via the intermediate addition product (III). The sequence of reactions may be represented as:

$$R - Cell - OH \xrightarrow{NaIO_4} R - Cell - CHO \xrightarrow{N_2H_4} [R - Cell - CH(OH) - NH - NH_2]$$

Cellulose   Oxycellulose   Hydrazine — treated oxycellulose
(I)   (II)   intermediate
                    (III)

$$\downarrow - H_2O$$

$$R - Cell - CH = N \cdot NH_2$$
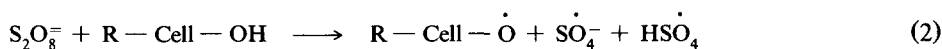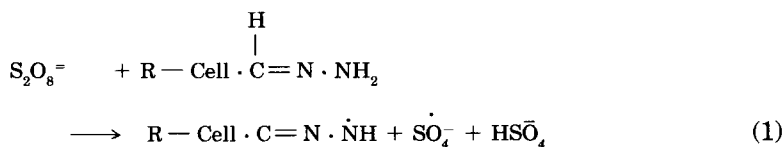
Hydrazone
(IV)

Under the present conditions of reaction between oxycellulose of low copper number (0.3–15) and a large excess of hydrazine in the heterogeneous system, the initially favored reaction product is the hydrozone (IV). In presence of excess of aldehyde groups, particularly in a homogeneous system, however, the favored product would be the corresponding azine formed through further reaction between the hydrazone and excess aldehyde groups.

Stabilities and different structural aspects of amine- and hydrazine-treated oxycellulose have been studied and reported.[4] On storage, the oxycellulose–hydrazone turned yellowish, and the depth of the color slowly increased with time. Graft copolymerization of MMA on (IV) using $K_2S_2O_8$ initiator took place by a radical mechanism. All grafting experiments were done on fresh hydrazine-treated oxycellulose samples to avoid complication due to structural changes on aging. The aged or stored samples usually gave much lower % conversion and grafting parameters. It is possible that,
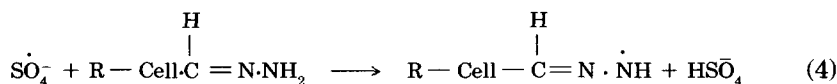
on storage, the active hydrazones in the initial hydrazine-treated samples slowly transformed into less reactive products including those having azine structures; further studies in this respect are beyond the scope of the present communication.

Extent of hydrazination was judged from the copper number of oxycellulose, assuming quantitative reaction. Independent studies made in this laboratory by conductometric analysis of cationic starch obtained through reaction between oxystarch (dialdehyde starch) and pyridinium acetohydrazide chloride indicated that the reaction was quantitative when a large excess of the hydrazine derivative was used.

The radical generation process in the graft copolymerization system of the present kind is complicated due to multiplicity of factors controlling them, including the heterogeneous nature of the system. The primary radical forming reactions here include the following:

$$S_2O_8^= \quad + R - Cell \cdot \overset{\overset{\textstyle H}{\textstyle |}}{C} = N \cdot NH_2$$

$$\longrightarrow \quad R - Cell \cdot C = N \cdot \dot{N}H + \dot{S}O_4^- + HS\bar{O}_4 \tag{1}$$

$$S_2O_8^= + R - Cell - OH \longrightarrow R - Cell - \dot{O} + \dot{S}O_4^- + H\dot{S}O_4 \tag{2}$$

$$S_2O_8^= \longrightarrow 2 \dot{S}O_4^- \tag{3}$$

Formation of graft copolymers occurs due to initiation of polymerization of MMA through the cellulosic macro radicals obtained in reactions (1) and (2), and formation of free PMMA occurs through the agency of SO_4^- radicals formed in reactions (1), (2), and (3). Due to the strong reducing nature of the hydrazinated oxycellulose, reaction (1) is far more significant than the other two reactions. Very high grafting efficiency (nearly 100%) and high % grafting with hydrazine-treated oxycellulose of low degrees of oxidation (copper nos. 2–6) (Table II) clearly show that (homo) vinyl polymerization is practically prohibited, and the following radical transfer reaction generating more of cellulosic macroradicals assumes overwhelming significance under this

$$\dot{S}O_4^- + R - Cell \cdot \overset{\overset{\textstyle H}{\textstyle |}}{C} = N \cdot NH_2 \longrightarrow R - Cell - \overset{\overset{\textstyle H}{\textstyle |}}{C} = N \cdot \dot{N}H + HS\bar{O}_4 \tag{4}$$

condition, leaving very little SO_4^- in the system to carry on homopolymerization.

DISCUSSION

Table II clearly shows that hydrazinated samples corresponding to oxycellulose of low degrees of oxidation (copper nos. 2–6) provide optimum concentration of radical generating (hydrazone) sites on them in the presence of $S_2\overline{\overline{O}}_8$. Falling trends in % conversion and grafting parameters with increase in copper number beyond about 5–6 appears to be due to a rela-

tively low-efficiency initiation process under such conditions, they hydrazone sites in higher concentrations acting as additional consequential sites of primary radical generation as well as producing more effective retardation competitively, higher hydrazone concentration producing more pronounced retardation and poorer grafting effects. The initiating and retarding roles of the hydraine-treated oxycellulose closely follow those of hydrazine hydrate in aqueous polymerization of MMA.[6]

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