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Photograft Copolymerization of Methyl Methacrylate on Cellulose and Oxycellulose Using Oxalic Acid-Permanganate Redox Initiator in a Limited Aqueous System

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ABSTRACT

Graft copolymerizations of methyl methacrylate (MMA) on cellulose and oxycellulose were studied mostly under photoactivation with visible light using oxalic acid/$KMnO_4$ redox initiator in a limited aqueous system. Polymerization in the dark (40-60°C) produced little graft copolymer, while that in the light at 32°C produced significant or efficient grafting at reasonable rates. Cellulose, modified to degrees of oxidation corresponding to copper number 20-35, produced optimum grafting. Percent grating and grafting efficiency under different sets of conditions were studied and compared, and the mechanism of polymerization and graft copolymer formation discussed. Generation of grafting sites (radical centers) on cellulose/oxycellulose was consequential only in the presence of light. Generally higher percent grafting and grafting efficiency in oxycellulose systems (as against cellulose systems) appear to be due to more easy and effective generation of radical sites on oxycellulose through oxidation of the aldehydic sites present in them in higher concentrations.

INTRODUCTION

Graft copolymerization of vinyl monomers on cellulose has been the subject matter of many investigations in recent years [1-7]. In the present paper we report results of graft copolymerization of methyl methacrylate (MMA) on cotton cellulose (with or without modification with periodate treatment) employing a combination of oxalic acid and potassium permanganate as redox initiator [8] under various conditions, particularly under photoactivation.

EXPERIMENTAL

Materials

Celluose

Mechanically processed Egyptian cotton was obtained through the courtesy of Textile Technology College, Berhampur, West Bengal. The cotton cellulose sample was used after the following treatment. A 10-g portion of the 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. For the present paper the cellulose sample thus treated will be called "unmodified cellulose." The molecular weight of the unmodified cellulose determined viscometrically following a nondegradative nitration procedure [9] was 9.52×10^5.

Oxidation of (Unmodified) Cellulose

Selective oxidation of cellulose leading to transformation of the hydroxyl groups in the 2 and 3 positions to aldehyde groups without chain breakage was accomplished by treatment with 0.05 mol/L $NaIO_4$ solution with a liquor ratio of 1:50 in neutral pH [10]. The periodate oxidation was done for different lengths of time (0-50 h) to achieve varied extents of oxidation without chain breakage. The oxidized samples were then washed until free from $NaIO_4$, squeezed to a limiting water content, and then dried in air. The extent of oxidation of each oxidized sample was expressed in terms of its copper number [11].

Monomer MMA, obtained from the local market, was purified following the usual procedures. Analytical grade oxalic acid and potassium permanganate from E. Merck were used in polymerization experiments without further treatment.

Graft Copolymerization

A weighed amount of cellulose, unmodified or modified by periodate oxidation, was placed in a Corning borosilicate glass ampule (1 in. diam) and was intimately mixed with a known volume of an aqueous solution of oxalic acid of known concentration for 5-10 min under flowing nitrogen. A measured amount of MMA was then added and finally a known volume of a dilute aqueous solution of $KMnO_4$ of known concentration was added under a blanket of nitrogen and the test tube was tightly stoppered. Polymerization experiments were mainly studied under photoactivation with visible light by placing the test tubes between a pair of tube lamps (40 W) for specified time periods. Initially a few polymerization experiments were also done in similar systems in the dark at 40 and 60°C.

After polymerization, the contents from each experiment were transferred quantitatively into a round-bottom flask of a refluxing unit. The free vinyl polymer (PMMA homopolymer) formed was extracted from the gross product in four successive stages allowing long reflux times and using benzene as the solvent in excess. No homopolymer PMMA was detectable in the extracts after the fourth stage of extraction. The free PMMA was isolated from the mixture of the extracts from successive stages by precipitation with petroleum ether and drying in vacuum at 50°C. The residues from the final benzene extraction, containing a mixture of the cellulose-PMMA graft copolymers and corresponding unreacted (free) cellulose, were treated with a petroleum ether-methanol mixture to collapse their swollen structure, which were then dried in air and finally in vacuum. This dried residue is termed the apparent graft copolymer. The true graft copolymer may be obtained only if the free or unreacted cellulose portion could possibly be separated from the overall residue. The percent grafting, grafting efficiency (%), and total conversion (%) were calculated as follows:

$$\%\ \text{grafting} = \frac{\text{PMMA in the apparent graft copolymer (g)}}{\text{cellulose sample taken (g)}} \times 100$$

$$\text{Grafting efficiency, } E_M\ (\%) = \frac{\text{PMMA in the apparent graft copolymer (g)}}{\text{total PMMA formed (g)}} \times 100$$

$$\text{Total conversion } (\%) = \frac{\text{total PMMA formed (g)}}{\text{MMA taken (g)}} \times 100$$

TABLE 1. Polymerization of MMA in the Presence of Cellulose and Oxycellulose (initiator system: $KMnO_4$ (0.1-20 mg), oxalic acid (2.0-10.0 mg), MMA, (1 mL), water (2.5 mL).

Base polymer	Condition of polymerization	Formation of PMMA[c]	
		Free	Grafted
Cellulose, 0.2 g, (copper number: 0.25)	Dark, 40°C, 3 h	+	-
	Dark, 60°C, 3 h	+	-
	Photo, 32°C, 3 h	+	++
	Photo, 32°C, 3 h[a]	-	-
	Photo, 32°C, 3 h[b]	-	-
Oxycellulose, 0.2 g, (copper number: 27.94)	Dark, 60°C, 3 h	+	-
	Photo, 32°C, 3 h	+	++
	Photo, 32°C, 3 h[a]	+	-
	Photo, 32°C, 3 h[b]	+	+

[a] Only $KMnO_4$ and no oxalic acid.
[b] Only oxalic acid and no $KMnO_4$.
[c] + = reasonable to appreciable, ++ = high, - = nil.

RESULTS

Preliminary studies indicated that for polymerizations done in the dark at 60°C, the rate of polymerization, judged from yield at a given time, was appreciably lower than what was observed for photopolymerization at 32°C. For polymerization in the dark, there was practically no graft copolymer formation (Table 1). All successive experiments were therefore carried out under photoactivated conditions.

The results of photograft copolymerization of MMA on cellulose (both unmodified and modified with periodate oxidation) showing the effect of variation of time and monomer content are given in Figs. 1 and 2, respectively, and those showing the effect of variation of degree of oxidation (copper number) and concentrations of the redox components ($KMnO_4$ and oxalic acid) are given in Tables 2 and 3.

It may be seen from Table 2 that for a given time of polymerization, 3 h, the photografting process generally produces better results [% grafting, % total conversion, and grafting efficiency, E_M (%)] for cellulose samples with higher degrees of oxidation (copper number). However, the improving effect tends to level off beyond a copper number of about 35, the copper number of the unmodified cellulose

TABLE 2. Photograft Copolymerization of MMA on Cellulose. Effect of Variation of Degree of Oxidation (copper number) of Cellulose (cellulose sample, 0.2 g; $KMnO_4$ (aq), 0.68 mg; oxalic acid (aq), 5.4 mg; MMA, 1 mL; water, 2.5 mL; temperature, 32 ± 1°C; time, 3 h)

Copper number of cellulose	Total conversion (%)	% Grafting	Grafting efficiency (E_M, %)	$[\eta]$	
				Free PMMA	Grafted PMMA
0.25[a]	50.90	141.70	60.80	3.20	5.40
16.50	60.65	160.00	58.00	3.01	4.60
27.94	62.50	175.60	64.40	-	-
35.16	68.80	209.30	67.90	3.20	5.03
42.50	72.70	210.36	66.50	-	-
46.40	72.50	209.95	66.32	3.80	5.61

[a] Unmodified cellulose (without periodate treatment).

being 0.25. In all successive experiments with modified cellulose, an oxycellulose sample with copper number 27.94 was used.

In most of the experiments, 0.2 g of the cellulosic sample (modified or unmodified) was used for 1 mL of MMA, and the total liquid volume, including the aqueous solutions of $KMnO_4$ and oxalic acid, was 3.5 mL. For studies of the effect of variation of monomer content, the total liquid volume varied between 2.7 and 4.5 mL.

Effects of variation of monomer content (0.2 to 2.0 mL) are shown in Fig. 2. Percent grafting tends to pass through a maximum at about 1 mL MMA for unmodified cellulose and 1.5 mL for oxycellulose, the latter showing a higher % grafting in general. Monomer variation does not bring about much change in the grafting efficiency in either case. Percent conversion is generally higher with oxycellulose than with unmodified cellulose and in either case the % conversion expectedly follows a decreasing trend with increasing monomer content.

Results of variation of $KMnO_4$ content (0.1-2.0 mg) at a fixed oxalic acid content (5.4 mg) and vice versa ($KMnO_4$ content, 0.68 or 1.0 mg, fixed; and oxalic acid content variable, 2-20 mg) are shown in Table 3. High grafting effects were obtained for the oxycellulose sample with about 1.0 mg $KMnO_4$ and with oxalic acid in the range of 15-25 mg as the initiating system, giving about 70-80% conversion in 3 h with about 250-300% grafting of PMMA and close to 80% grafting efficiency (E_M).

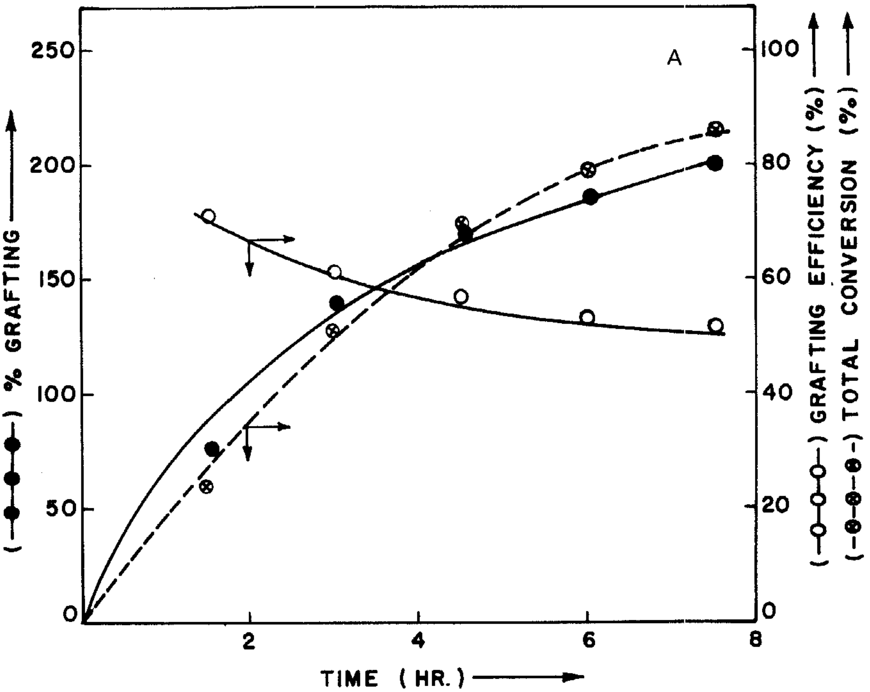


FIG. 1. Effect of variation of time on photograft copolymerization of MMA on cellulose (A) and oxycellulose (B). Temperature: 32 ± 1°C, MMA: 1 mL, oxalic acid (aq): 5.4 mg, $KMnO_4$ (aq): 0.68 mg, total liquid volume: 3.5 mL, cellulose/oxycellulose: 0.2 g.

Mechanism

The radical generation process in the present graft copolymerization systems is complicated because of multiplicity of factors controlling them including the heterogeneous nature of the systems. On addition of dilute aqueous $KMnO_4$ on cellulose or oxycellulose samples soaked in dilute aqueous oxalic acid/MMA system, the color of the permanganate was discharged almost instantaneously. Photografting was studied by placing the colorless system under N_2 in visible light. The exact mechanism of the instantaneous reactions involving $KMnO_4$ and oxalic acid in the presence of MMA and the preformed polymer (cellulose/oxycellulose) is uncertain, but it is likely that colorless complexes of manganese in its intermediate oxidation states (Mn^{4+}, Mn^{3+}, etc.) and oxalic acid are formed through the initial reactions. The most likely primary radicals to be generated in the system are carboxyl and oxalate ion radicals [8, 12]:

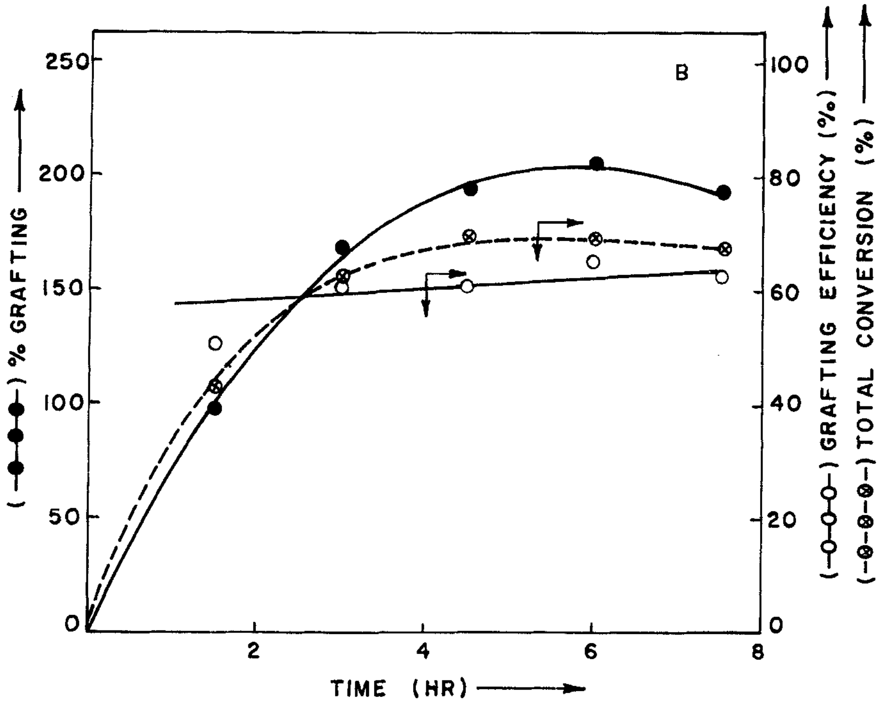
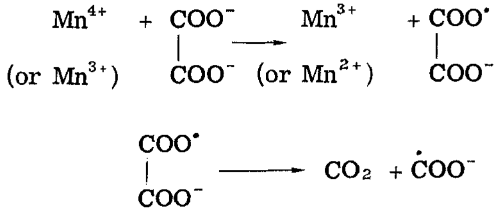


FIG. 1 (continued)



$$\underset{(\text{or } Mn^{3+})}{Mn^{4+}} + \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \longrightarrow \underset{(\text{or } Mn^{2+})}{Mn^{3+}} + \begin{matrix} COO^\bullet \\ | \\ COO^- \end{matrix}$$

$$\begin{matrix} COO^\bullet \\ | \\ COO^- \end{matrix} \longrightarrow CO_2 + \dot{C}OO^-$$

Moreover, photolysis of oxalic acid would also take place readily to give carboxyl radicals:

$$C_2O_4^{2-} \xrightarrow{h\nu} 2\dot{C}OO^-$$

$$C_2O_4^{2-} + H_2O \xrightarrow{h\nu} C_2{}^\bullet O_4^- \ (\text{or } CO_2 + \dot{C}OO^-) + H^\bullet + OH^-$$

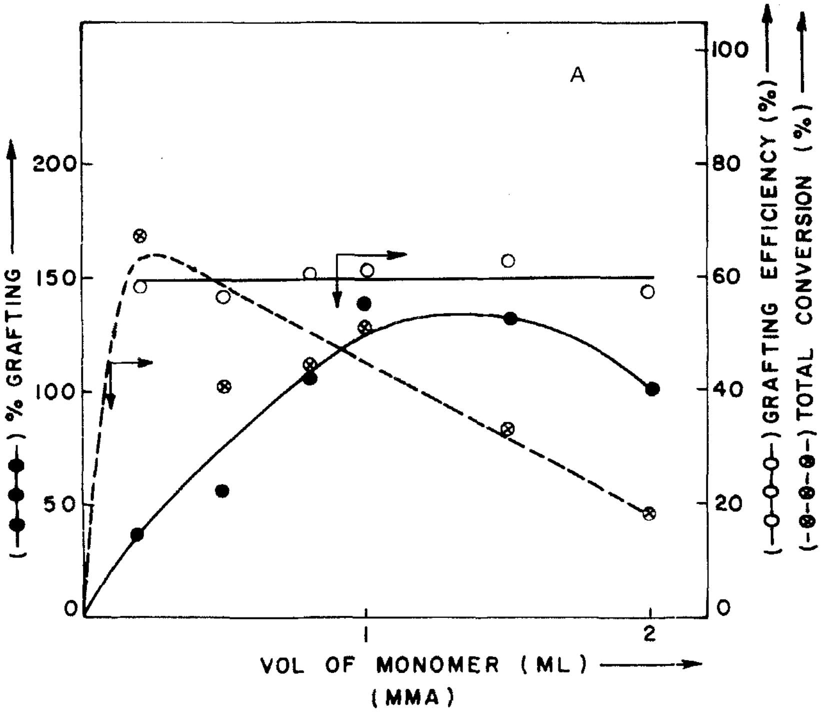


FIG. 2. Effect of variation of monomer content on the photograft copolymerization of MMA on cellulose (A) and oxycellulose (B). Temperature: 32 ± 1°C, oxalic acid (aq): 5.4 mg, $KMnO_4$ (aq): 0.68 mg, water: 2.5 mL, cellulose/oxycellulose: 0.2 g, time: 3 h.

The photolysis of oxalic acid is known to be largely activated by manganese ions, particularly Mn^{2+}. Other radical generation reactions are also likely to be prone to photoactivation. Generally better conversions under photolytic condition can be understood from this consideration. It is not altogether unlikely that the above radical generation reactions would be modified via radical transfer reactions due to the presence of the preformed polymers, giving radical sites on the respective macromolecules.

Further, generation of radical sites on the preformed polymer, cellulose (R–cell–OH) may be considered to take place as follows:

$$Mn^{+n} + R\text{–cell–OH} \longrightarrow Mn^{+(n-1)} + R\text{–cell–O}^{\bullet} + H^{+}$$

In oxycellulose, concentration of oxidized, i.e., aldehydic $(-\overset{\overset{O}{\|}}{C}-H)$, sites

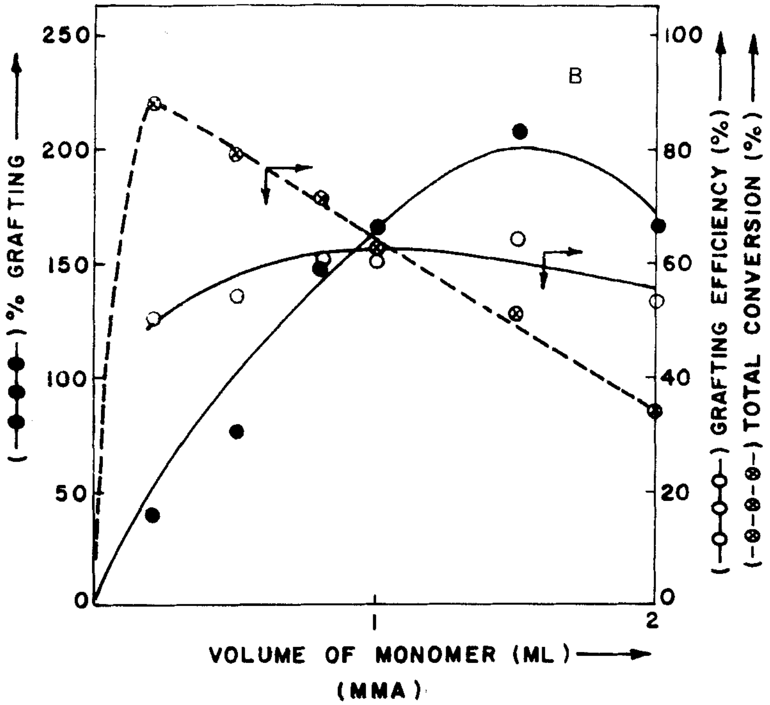
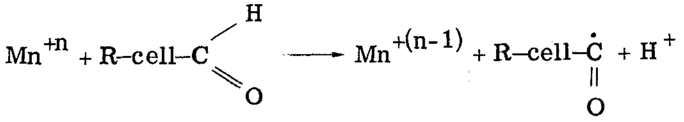


FIG. 2 (continued)

being relatively high, the following reaction will be expected to assume some prominence in addition:



$$\mathrm{Mn}^{+n} + \mathrm{R{-}cell{-}C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown\!\!\diagdown \mathrm{O}\end{smallmatrix} \longrightarrow \mathrm{Mn}^{+(n-1)} + \mathrm{R{-}cell{-}}\underset{\underset{\mathrm{O}}{\|}}{\dot{\mathrm{C}}} + \mathrm{H}^{+}$$

Due to the much stronger reducing character of aldehydes than of alcohols, the above redox reaction is expected to produce a somewhat higher rate (conversion at a given time), percent grafting, and efficiency of grafting for oxycellulose systems as compared to the cellulose (unmodified) systems, provided that the oxycellulose system does not produce any retardation effect. Reactions leading to generation of radical sites on cellulose/oxycellulose chains are consequential only

TABLE 3. Effect of Variation of $KMnO_4$ and Oxalic Acid Contents on Photograft Copolymerization of MMA in Visible Light (cellulose/oxycellulose, 0.2 g; MMA, 1 mL; water, 2.5 mL; time, 3 h; temperature, 32 ± 1°C)

					[η]	
$KMnO_4$	Oxalic acid	Total conversion (%)	% Grafting	Grafting efficiency (E_M, %)	Free PMMA	Grafted PMMA
	A. Cellulose (unmodified; copper number 0.25)					
0.13	5.4	54.26	98.84	38.37	3.20	5.60
0.68	"	50.94	141.70	60.80	3.15	5.60
0.81	"	58.70	152.00	56.00	-	-
1.62	"	68.31	125.63	37.95	3.00	5.10
0.68	2.56	59.10	103.40	39.34	2.60	4.80
"	3.84	55.10	130.20	54.00	-	-
"	10.24	62.56	198.44	62.20	4.60	7.20
	B. Oxycellulose (copper number 27.94)					
0.25	5.4	13.74	32.00	50.93	1.50	2.80
0.50	"	30.90	85.00	59.80	-	-
0.68	"	62.01	170.25	60.10	-	-
1.00	"	60.22	183.56	66.71	3.50	5.10
2.00	"	76.60	197.11	56.07	-	-
2.50	"	65.80	143.93	47.80	3.00	4.40
1.00	2.0	42.98	61.50	31.30	2.00	4.77
"	4.0	61.88	175.73	61.30	-	-
"	13.5	67.27	233.84	76.15	-	-
"	18.0	69.92	250.27	77.92	4.20	6.00
"	22.5	80.69	285.30	78.80	-	-

under photoactivation because no graft copolymer formation and only formation of homopolymer PMMA was observed in experiments done in the dark.

DISCUSSION

On examination of the effect of variation of degree of oxidation (copper number) of cellulose, Table 2, it was found that oxycelluloses with degrees of oxidation corresponding to copper numbers 20-35 provide the optimum concentration of free radicals, generating (aldehydic) sites on them in the presence of the initiator used. The leveling-off effect of the improvement of rate or % conversion with an increase in copper number beyond 35 appears to be due to the relatively low efficiency-rate of initiation under such conditions, aldehydic sites in higher concentrations acting as additional consequential sites of primary radical generation as well as producing more effective retardation competitively. The retarding effect of the aldehydic sites in a given oxycellulose system is more apparent at lower initiator concentrations, giving relatively low conversion, percent grafting, grafting efficiency, and chain length for the polymers formed when compared with those for the (unmodified) cellulose system, Table 3. In either case, grafting parameters improve more in the presence of a higher proportion of oxalic acid for a given $KMnO_4$ content than in the presence of a higher proportion of $KMnO_4$ for a given oxalic acid content.

Comparison of Chain Lengths of Grafted and Free PMMA

The grafted PMMA fractions from some selected experiments were isolated by destructively dissolving the cellulose portions of the respective apparent graft copolymer using 72% H_2SO_4 at room temperature, following the usual procedures. The bound PMMA thus isolated was dried, dissolved in benzene, filtered, precipitated with excess methanol and petroleum ether, collected, and dried under vacuum at 50°C.

Intrinsic viscosities $[\eta]$ of the PMMA fractions thus isolated and of the corresponding free PMMA fractions isolated before were determined from benzene solutions at 30°C and compared. In each case the $[\eta]$ value (and hence the molecular weight) of the grafted PMMA fraction was found to be significantly higher than that of the corresponding free PMMA fraction, Tables 2 and 3. It is believed that, in the present heterogeneous system, the cellulose/oxycellulose chain networks act as additional and more effective physical barriers for the mobility of the growing grafted-in PMMA chains, resulting in delayed termination for them and hence giving rise to much higher molecular weights for them in comparison with the molecular weights of the corresponding free PMMA chains.

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