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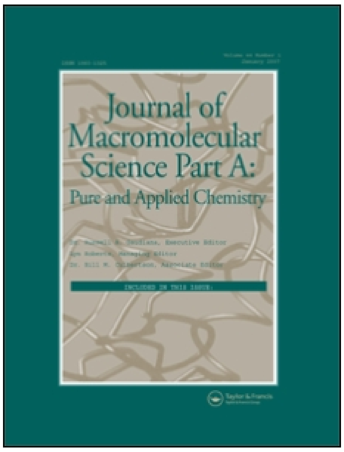

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Photograft Copolymerization of Methyl Methacrylate, Acrylonitrile, and Acrylamide on Oxycellulose Using Potassium Persulfate as the Initiator in Limited Aqueous Systems

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ABSTRACT

Graft copolymerization of methyl methacrylate (MMA), acrylonitrile (AN), and acrylamide (AA) on cellulose of low degrees of oxidation (effected through periodate treatment) was studied under photoactivation with visible light in limited aqueous systems. The degree of oxidation of the cellulose sample given in terms of copper number was between 0.25 (for the native cellulose) and 46. Increasing degree of oxidation initially produced higher overall % conversion or rate of polymerization. Overall grafting effects, i.e., % grafting and grafting efficiency, were also generally higher in oxycellulose than in unmodified cellulose. Effects of variations of time of polymerization, initiator content, and monomer content on overall grafting were also studied, and related data for the three monomer systems have been presented and compared. Percent grafting as high as 300-500% and grafting efficiency of the order of 80-95% were easily obtained.

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INTRODUCTION

Graft copolymerization of vinyl monomers on cellulose has been widely studied [1-8]. It has been recently shown from our laboratory [8] that significantly improved grafting is readily effected through prior oxidation of cellulose by periodate treatment and employing methyl methacrylate as the monomer in the presence of a combination of oxalic acid and potassium permanganate as redox initiator, particularly under photoactivation. In the present paper we report the results of photograft copolymerization of methyl methacrylate (MMA), acrylonitrile (AN), and acrylamide (AA) on (cotton) cellulose and oxycellulose of varying degrees of oxidation (effected through periodate treatment) employing $K_2S_2O_8$ initiator in limited aqueous systems.

EXPERIMENTAL

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Mechanically processed Egyptian cotton was the source of cellulose for the present experiments. The cellulose sample was scoured and subsequently treated with sodium periodate for different time periods, causing practically no chain length degradation according to procedures described before [8]. The scoured cellulose is called "unmodified cellulose" and the periodate-treated cellulose is termed "oxycellulose" in the present paper. The degree of oxidation of each oxidized cellulose sample is expressed in terms of its copper number.

Monomers MMA and AN were purified by vacuum distillation following standard procedures. Reagent grade AA obtained from E. Merck was used without purification. Analytical grade $K_2S_2O_8$ from E. Merck was used in polymerization experiments without further treatment.

Cellulose or oxycellulose (0.2 g) was soaked in an excess of 1-3% aqueous solution of $K_2S_2O_8$. It was then squeezed to bring down the water content to a limiting value and the $K_2S_2O_8$ content was then calculated from the gain in weight due to absorption of its solution. A known volume of monomer (MMA or AN) or of monomer solution (AA in water, 75-80%) was then added into the squeezed cellulose/oxycellulose sample taken in a borosilicate ampule under flowing nitrogen. The ampule was then stoppered and the monomer was allowed to polymerize under specified conditions.

After polymerization, the overall polymer product was isolated by precipitation with methanol and petroleum ether. The product was then dried in vacuum and weighed. Total conversion (%) of monomer to polymer, % grafting, and grafting efficiency, E_M (%), with respect to the vinyl polymer formed in the respective systems were determined following the usual procedures [8]. Solvents used for extracting the homopolymer formed in the respective systems were benzene for polymethyl methacrylate (MMA system), dimethylformamide for polyacrylonitrile (AN system), and water for polyacrylamide (AA system). Each extraction was done in four successive stages, allowing long reflux times to ensure complete extraction of homopolymer. In each case the residue after solvent extraction, considered as the apparent graft copolymer, was treated with a methanol-petroleum ether mixture to collapse its swollen structure which was then dried and weighed. The true graft copolymer may be obtained only if the free or unreacted cellulose portion could possibly be separated out from the overall residue.

RESULTS

Preliminary studies indicated that in each case the rate of polymerization as judged from the % conversion for a given time and grafting parameters were much higher in the presence of visible light (40 W tube lamp) than in the dark, and overall grafting of the vinyl polymers was much higher with oxycellulose than with unmodified cellulose. All successive experiments were, therefore, done with oxycellulose under photoactivated conditions [8] and their results are given in Tables 1-4.

Effect of Variation of Time of Polymerization

This study was done with an oxycellulose sample having copper number 35.16, the copper number of unmodified cellulose being 0.25. The results are given in Table 1. Total conversion (%) improves with time very significantly in the case of MMA and quite reasonably with AN up to about 7-8 h, but in the case of AA, the water soluble monomer, the said trend of improvement appears limited to within 2-3 h and thereafter % conversion tends to level off. The trend in improvement of % grafting is also similar in the respective systems. Over a low time of polymerization (up to about 3 h), MMA gives close to 100% grafting efficiency (E_M) which then exhibits a slow falling trend with a further increase in time. Grafting efficiency increases initially from a low value (20%) with a leveling-off tendency (70%) at a later stage for the AN system. For the AA system the E_M value is quite high (80%) initially and remains so without showing any definite pattern of change with an increase in time.

Effect of Variation of Degree of Oxidation (Copper Number) of Cellulose

Related results are given in Table 2. For the MMA and AN systems, % conversion is low with unmodified cellulose (<10%) but it is

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TABLE 1. Effect of Variation of Time on Photopolymerization of MMA, AN, and AA in the Presence of Oxycellulose (copper number 35.16) at 32 ± 1°C in Limited Aqueous Systems Using $K_2S_2O_8$ as the Initiator [total liquid volume (liquid monomer + water): 1.5 mL; MMA, 1 mL; AN, 1 mL; AA, 0.765 g. $K_2S_2O_8$: for MMA system, 14.5 mg; for AN system, 10.2 mg; for AA system 9.4 mg. Oxycellulose: 0.2 g]

Time of polymerization (h)			Total conversion (%)			% Grafting			Grafting efficiency, E_M (%)		
MMA	AN	AA	MMA	AN	AA	MMA	AN	AA	MMA	AN	AA
1.5	1.5	2.0	5.58	19.40	63.94	25.60	15.65	185.75	100.00	20.80	79.70
3.0	3.0	3.0	18.66	39.80	80.01	83.00	75.63	232.66	97.03	47.80	77.18
4.0	4.5	4.5	25.60	69.63	87.04	108.00	175.31	245.08	92.03	66.40	95.19
6.0	6.5	6.5	43.28	72.60	78.04	175.00	199.60	207.39	88.00	69.24	71.03
7.5	8.5	8.5	79.20	77.38	85.10	290.67	198.19	225.32	80.03	68.02	70.26

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TABLE 2. Effect of Variation of Degree of Oxidation (copper number) of Cellulose on Photopolymerization of MMA, AN, and AA with $K_2S_2O_8$ Initiator at 32 ± 1°C in Limited Aqueous Systems [$K_2S_2O_8$ in mg and time of polymerization in h: for MMA system, 14.5 and 7.0; for AN system, 10.2 and 6.5; for AA system, 9.4 and 4.5. Total liquid volume (liquid monomer + water): 1.5 mL. Monomer: MMA, 1.0 mL; AN, 1.0 mL; AA, 1.072 g. Cellulose/oxycellulose: 0.2 g]

Copper number	Total conversion (%)			% Grafting			Grafting efficiency, E_M (%)		
	MMA	AN	AA	MMA	AN	AA	MMA	AN	AA
0.25[a]	8.0	9.1	49.6	30.0	24.6	142.8	98.0	34.6	59.7
16.50	78.9	22.3	67.3	277.9	140.4	280.5	77.3	79.3	84.6
27.94	79.3	42.7	73.9	275.4	284.3	314.8	77.2	83.0	84.3
35.16	79.9	63.2	94.4	287.7	390.1	407.9	79.4	76.1	85.2
46.50	79.8	71.6	94.6	309.6	380.9	408.8	84.5	66.8	87.6

[a] Cotton cellulose (without periodate treatment).

about 50% for the AA system. For the MMA system, % conversion increases sharply to a high value (80%) even with a limited degree of oxidation of the cellulose sample, but % conversion remains practically unchanged with a further increase in the degree of oxidation. For the AN and AA systems, % conversion shows a regular increasing trend with an increase in the degree of oxidation of cellulose. However, % grafting shows increasing trends in each of the three monomer systems with an increase in the degree of oxidation of the cellulose, the initial value for unmodified cellulose being much higher in the AA system than in the other two monomer systems. Grafting efficiency is quite high in all the systems. For the MMA system it is close to 100% for unmodified cellulose and around 80-85% for oxycellulose samples. For the AN and AA systems the grafting efficiency increases initially with an increase in the degree of oxidation but remains more or less steady thereafter.

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Effect of Variation of $K_2S_2O_8$ Content

Related results are given in Table 3. Increasing initiator ($K_2S_2O_8$) content generally shows an enhancement in % conversion and % grafting in the MMA and AN systems. However, for the AA system an improvement in % conversion with in increase in $K_2S_2O_8$ content is marginal or practically insignificant as shown in Table 3, while % grafting remains close to a high value (400%) after an initial uptake in the low range of initiator content. Grafting efficiency is in the range of 70-80% for the MMA system with a falling trend in the higher range of $K_2S_2O_8$ content, and it remains practically constant around 90% after an initial enhancement from a low value (30%) for the AA system. For the AN system an increase in the initiator content produces a slowly increasing trend in grafting efficiency.

Effect of Variation of Monomer Content

Related results are given in Table 4. Percent total conversion passes through a maximum in each monomer system. The water-soluble monomer, AA, gives much higher conversions in general. With close to 1 g of monomer for 0.2 g of oxycellulose (copper no. 35.16), % grafting is in the range of 400-500% for the AA system and around 300% and 200% for the MMA and AN systems, respectively, and the corresponding grafting efficiency values are about 90% for the AA system, between 80 and 90% for the MMA system, and about 70% for the AN system.

DISCUSSION

Under all conditions, AA gives the best conversion figures. This may be understood from the complete solubility of both the initiator

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TABLE 3. Effect of Variation of $K_2S_2O_8$ Content on Photopolymerization of MMA, AN, and AA in the Presence of Oxycellulose at 32 ± 1°C in Limited Aqueous Systems [Copper Number of oxycellulose: 35.16; weight of oxycellulose: 0.2 g. Time, monomer content, and total liquid volume (water and liquid monomer) are: for MMA: 7.5 h, 1 mL, and 1.5 mL; for AN: 6.5 h, 2 mL, and 2.5 mL, for AA: 4.5 h, 1.02 g, and 1.5 mL]

$K_2S_2O_8$ (mg)			Total conversion (%)			% Grafting			Grafting efficiency, E_M (%)		
MMA	AN	AA	MMA	AN	AA	MMA	AN	AA	MMA	AN	AA
3.30	2.02	2.18	13.07	33.26	91.60	47.68	173.72	138.75	80.80	62.56	29.68
7.00	6.66	4.99	38.50	29.03	94.15	144.08	201.52	415.82	82.76	69.35	89.49
14.00	10.02	9.50	79.20	63.21	94.39	290.67	390.13	431.58	80.03	76.10	92.59
20.34	12.41	11.05	89.50	70.17	94.69	283.60	550.38	424.57	70.50	85.24	90.68
33.83	22.08	21.64	73.70	83.64	95.42	235.69	564.88	403.80	71.17	85.85	88.37

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TABLE 4. Effect of Variation of Monomer Content on Photopolymerization of MMA, AN, and AA Using $K_2S_2O_8$ Initiator in the Presence of Oxycellulose (copper number 35.16) at 32 ± 1°C in Limited Aqueous Systems [Oxycellulose: 0.2 g; $K_2S_2O_8$: 14.46 mg in MMA system, 10.2 mg in AN system, and 9.5 mg in AA system. Time: 7.5 h in MMA system, 6.5 h in AN system, and 4.5 h in AA system. Volume of water in each case: 1.5 mL]

Monomer content			Total conversion (%)			% Grafting			Grafting efficiency, E_M (%)		
MMA (mL)	AN (mL)	AA (g)	MMA	AN	AA	MMA	AN	AA	MMA	AN	AA
0.25	0.25	0.128	64.40	25.84	70.03	45.13	5.66	16.04	61.06	23.45	35.94
1.00	0.50	0.255	79.20	39.98	86.31	290.67	60.48	78.35	80.03	51.23	71.19
1.50	1.00	0.765	49.00	72.60	87.04	300.74	199.60	245.08	88.87	69.24	75.19
2.50	2.00	1.021	38.00	63.21	94.39	380.29	390.13	431.58	87.22	76.10	92.59
3.00	2.50	1.275	41.10	57.04	92.25	440.31	381.60	497.78	77.87	75.89	88.02

($K_2S_2O_8$) and the monomer (AA) in a limited volume of water. Overall, grafting parameters are significantly higher in the MMA system than in the AN and AA systems when the monomer contents are low under more or less comparable conditions otherwise. Polymerization is considered to proceed radically through direct photodecomposition of $S_2O_8^{2-}$ ions absorbed in the cellulose or oxycellulose samples taken and photoactivation of the redox reaction between $S_2O_8^{2-}$ ions and alcoholic groups of cellulose/oxycellulose. In oxycellulose systems the redox reaction between $S_2O_8^{2-}$ ions and the –CHO groups of oxycellulose also assumes prominence, more so with an increasing degree of oxidation of cellulose.

$$S_2O_8^{2-} \longrightarrow 2\ \dot{S}O_4^- \qquad (1)$$

$$S_2O_8^{2-} + \text{R cell OH} \longrightarrow \dot{S}O_4^- + \text{R cell O}^\bullet + HSO_4^- \qquad (2)$$

$$S_2O_8^{2-} + \text{R cell CHO} \longrightarrow \dot{S}O_4^- + \text{R cell }\dot{C}\text{O} + HSO_4^- \qquad (3)$$

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All these reactions are photoactive and hence there are always higher rates of polymer formation in light than in the dark. For grafting, Reactions (2) and (3) are more consequential than Reaction (1). $\dot{S}O_4^-$ ion radicals generated in the above reactions, being unable to largely diffuse out in the limited aqueous systems present, are likely to further interact with the nearby –OH and –CHO groups of cellulose and oxycellulose to produce more radical sites on them for further grafting of vinyl polymers:

$$\dot{S}O_4^- + \text{R cell OH (or R cell CHO)} \longrightarrow HSO_4^- + \text{R cell O}^\bullet \text{ (or R cell }\dot{C}\text{O)} \qquad (4)$$

Very high % grafting and grafting efficiencies in some of the experiments can be understood on the basis of Eq. (4) which substantially limits the scope of homo(vinyl) polymerization under favorable conditions.

Besides the activating role of –CHO groups, they are also likely to produce some retardation effects, particularly in higher concentrations as in oxycelluloses of higher degrees of oxidation [8]. Some of the leveling-off effects in % conversion or overall grafting may be partly explained on this basis.

The present photografting of cellulose with a limited degree of oxidation in limited aqueous systems provides an interesting and novel approach of a general nature toward achieving high rates of conversion along with very high percent grafting (up to 300-500%) and grafting efficiencies (up to 80-95%) at a low temperature.

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REFERENCES

[1] M. Imoto and K. Takemoto, Makromol. Chem., 110, 31 (1967).
[2] J. C. Arthur, Jr., Adv. Chem. Ser., 91, 574 (1969).
[3] H. Kobuta and Y. Ogiwara, J. Appl. Polym. Sci., 17, 2427 (1973).
[4] H. Kobuta, Y. Murata, and Y. Ogiwara, J. Polym. Sci., Polym. Chem. Ed., 11, 485 (1973).
[5] N. S. Hon, Ibid., 13, 955, 1347, 1933 (1975).
[6] M. Imoto, S. Kushibu, and T. Ouchi, J. Macromol. Sci.–Chem., A11, 321 (1977).
[7] B. N. Misra, R. Dogra, I. Kaur, and J. K. Jassal, J. Polym. Sci., Polym. Chem. Ed., 17, 1861 (1979).
[8] P. Ghosh and T. K. Ghosh, J. Macromol. Sci.–Chem., A17, 847 (1982).

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