Grafting of Methyl Methacrylate to Nitrocellulose by Ceric Ions

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Synopsis

Studies were carried out on grafting of various vinyl monomers to nitrocellulose by ceric ions. It was observed that graft copolymerization occurred only with methyl methacrylate (MMA) and methyl acrylate monomer. The variables such as initiator concentration, monomer concentration, time of grafting, and nitrocellulose content on grafting of MMA are discussed. By hydrolyzing away the nitrocellulose backbone, the grafted poly(methyl methacrylate) branches were isolated and the $>c=o$ peak at 1740 cm^{-1} in the infrared spectra of these isolated branches gave definite evidence of grafting. The molecular weight of isolated branches has been determined by viscometry. The probable mechanism of grafting may be at the α-carbon atom of primary alcohol or at a C_2-C_3 glycol group of the anhydro glucose unit or at the hemiacetal group of the end unit of nitrocellulose, as nitrocellulose is formed by the partial nitration of cotton cellulose.

INTRODUCTION

The graft copolymerization of vinyl monomers onto cellulose in the presence of oxidizing agents and ceric ions,[1-3] as well as under irradiation,[4,5] has been the subject of much discussion, and the mechanism of grafting has been discussed by a number of workers.[3,5,6] The graft copolymerization of methyl methacrylate and acrylonitrile onto methyl cellulose in the absence of the radical initiators[7] and by the persulphate ion[8] and of styrene onto cellulose acetate[9] has also been reported. No effort has been made so far to modify nitrocellulose, despite its versatile applications in surface coating and leather finishes. Modification of nitrocellulose by graft copolymerization of methyl methacrylate in solution using benzoyl peroxide[10] has been reported in our earlier paper. The ultimate objectives of these investigations were to produce a nitrocellulose lacquer and lacquer emulsions which would yield a flexible film of high mechanical properties, high elasticity, good gloss, and high water repellency. The present investigation deals with the grafting of vinyl monomers to nitrocellulose with ceric ammonium nitrate (CAN) in heterogeneous medium. The variables such as initiator concentration, time of grafting, monomer concentration, and nitrocellulose content on grafting are presented in this paper.

EXPERIMENTAL

Materials

Commercially available nitrocellulose (½ sec) with 11.8%–12.2% nitrogen supplied by Ashahi Chemical Industry Co. Ltd., Japan, was purified by washing with water and dried.

0021-8995/79/0023-2923$01.00

Methyl methacrylate was made free of inhibitor by washing with aqueous sodium hydroxide solutions, dried over anhydrous sodium sulfate, and distilled under reduced pressure. All the other monomers used were also purified by standard procedures.

CAN, analytic reagent grade (E. Merck) was used without purification. A stock solution of $0.1N$ ceric solution in $1N$ nitric acid was prepared and stored in a refrigerator.

Grafting Procedure

The requisite amount of nitrocellulose was dispersed in 300 ml of water in a Waring blender after allowing it to swell for 30 min. The heterodispersed solution was then transferred to a three-necked flask equipped with a glass stirrer and nitrogen inlet. Purified nitrogen was passed for about 30 min and then the required quantities of monomer followed by catalyst were added. The reaction was carried out at 30°C under nitrogen atmosphere. Hydroquinone was added at the end of the required reaction time to arrest polymerization. The products were separated by filtration and were washed with distilled water repeatedly.

RESULTS AND DISCUSSION

Initial experiments were carried out to graft various vinyl monomers (styrene, vinyl acetate, acrylic acid, acrylonitrile, acrylamide, methyl methacrylate, methyl acrylate) to nitrocellulose. No graft copolymerization was found to occur with styrene, vinyl acetate, acrylic acid, acrylonitrile, or acrylamide, whereas with methyl acrylate and methyl methacrylate grafting took place when nitrocellulose was used as the backbone polymer. Brauer and Termini[11] have also carried out studies on the grafting of a variety of monomers onto protein (collagen) with ceric ions. These authors have also observed the absence of grafting with a number of monomers, but no explanation has been offered. This abnormal behavior of vinyl monomers to the specific backbone is not clear at present. The grafting efficiency of methyl methacrylate was observed to be higher compared to methyl acrylate, and hence the present paper deals with graft copolymerization of methyl methacrylate to the nitrocellulose backbone.

Isolation and Characterization of the Grafted Product

The products separated by filtration were first soxhlet extracted for 72 hr with benzene to remove poly(methyl methacrylate) homopolymer. The remaining products were soxhlet extracted with methanol for 72 hr to remove the unreacted nitrocellulose. The remaining product is a true graft copolymer. This is one of the few instances in graft copolymerization where complete separation of the individual polymer takes place by extraction.

Infrared Spectra. The infrared spectrum of the graft copolymer, after removal of poly(methyl methacrylate) homopolymer and the unreacted nitrocellulose, has shown a small intensity peak for the $>c{=}o$ group at 1740 cm^{-1}, indicating the attachment of poly(methyl methacrylate) chains onto the nitrocellulose backbone. This graft copolymer was hydrolyzed with $6N$ HCl at 105°C to separate poly(methyl methacrylate) chains attached to nitrocellulose. The

infrared spectrum of this sample gave a more pronounced $>c=o$ peak at 1740 cm^{-1}. The formation of a polyblend between nitrocellulose and poly(methyl methacrylate) does not take place as reported earlier.[10]

Viscosity. The viscosity measurements of the graft copolymer (after hydrolysis) were carried out in benzene at 30°C using Ubbelohde dilution viscometer, and the number-average molecular weight of the grafted chains was calculated using the following equation[12]:

$$[\eta] = 8.69 \times 10^{-5} \, \overline{M}_n^{0.76}$$

Grafting Percentage. The percent grafting was calculated by

Percent grafting

$$= \frac{\text{Weight of nitrocellulose-g-poly (MMA)} - \text{Weight of nitrocellulose}}{\text{Weight of nitrocellulose}} \times 100$$

and the values are reported in Tables I–IV.

Effect of Variables on Grafting

Effect of Grafting Time. The effect of grafting time on molecular weight and grafting percentage is shown in Table I and Figure 1. In the initial stages of the graft copolymerization reaction (up to 75 min), the ceric ion initiates a large number of growing PMMA branches. This is reflected by an increase in the grafting percentage up to 75 min, with grafting time greater than this, the grafting percentage remains more or less constant. The number-average molecular weight of the grafted chains also increased up to 75 min and then remains constant.

Effect of Initiator Concentration. The effect of initiator concentration on the grafting percentage and on the number-average molecular weight of grafted chains is shown in Table II. A significant increase in grafting was achieved when the CAN concentration was 1.7×10^{-3} mol/l, and at higher concentration the degree of grafting decreased considerably. The number-average molecular weight of the grafted chains also increased up to CAN a concentration of 1.7×10^{-3} mol/l, further increases causing a decrease in the number-average molecular weight of the grafted chains. The obvious reason for this trend is that a greater number of grafting sites are created by increases in the ceric ion concentration; at the same time the termination by ceric ions may also be prevalent at these high concentrations, resulting in shorter grafted chains.

TABLE I
Effect of Grafting Time on Percentage Grafting and Molecular Weight[a]

No.	Time (min)	Grafting, %	Ungrafted polymer	Molecular weight, $\overline{M}_n \times 10^5$
1	30	10.0	0.1	0.7
2	75	25.0	0.3	1.5
3	120	21.7	0.6	—
4	180	22.0	1.0	1.7
5	300	25.0	1.2	1.8

[a] Nitrocellulose, 6 g; grafting temperature, 30°C; MMA, 0.25 mol/l; CAN, 1.7×10^{-3} mol/l; total volume, 300 ml.
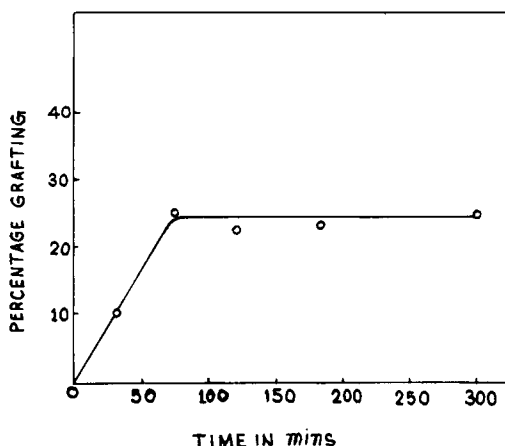
Fig. 1. Effect of grafting time on the graft copolymerization of methyl methacrylate onto nitrocellulose.

TABLE II
Effect of Initiator Concentration on Percentage Grafting and Molecular Weight[a]

No.	[CAN], mol/l $\times 10^{-3}$	Grafting, %	Molecular weight, $\overline{M}_n \times 10^5$
1	1.0	10.0	0.8
2	1.7	25.0	1.5
3	2.7	13.3	1.3
4	3.3	23.3	1.2

[a] Nitrocellulose, 6 g; grafting temperature, 30°C; time, 75 min; MMA, 0.25 mol/l; total volume, 300 ml.

Effect of Variation of Monomer. The effect of varying monomer concentration on the grafting percentage is shown in Table III and Figure 2. As the monomer concentration is increased, the grafting percentage and the number-average molecular weight increase, reach a maximum value at a concentration of 0.22 mol/l, and then decrease. The addition of higher monomer content caused agglomeration of nitrocellulose, resulting in the formation of a lump.

Effect of Nitrocellulose Content. The effect of nitrocellulose on the grafting percentage is shown in Table IV and Figure 3. The grafting percentage increased up to 6 g nitrocellulose in 300 ml of water and then decreased with further in-

TABLE III
Effect of Monomer Concentration on Percentage Grafting and Molecular Weight[a]

No.	[MMA], mol/l	Grafting, %	Molecular weight, $\overline{M}_n \times 10^5$
1	0.06	Trace	—
2	0.09	4.0	—
3	0.16	10.0	1.1
4	0.22	20.0	2.1
5	0.25	16.0	0.8

[a] Nitrocellulose, 5 g; grafting temperature, 30°C; time: 75 min; CAN, 1.7×10^{-3} mol/l; total volume, 300 ml.
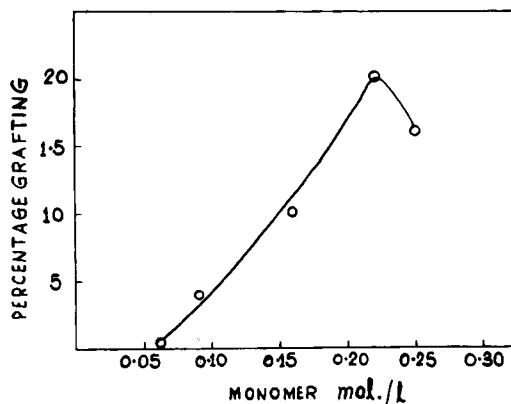
Fig. 2. Effect of monomer concentration on the graft copolymerization of methyl methacrylate onto nitrocellulose.

creases in nitrocellulose. This is attributed to the change in the relative ratio of nitrocellulose to the ceric ion.

Mechanism of Grafting. Nitrocellulose is formed by partial nitration of cotton cellulose, leaving some of the primary alcohol and the glycol units unaffected. The probable mechanism may be that grafting takes place at the residual
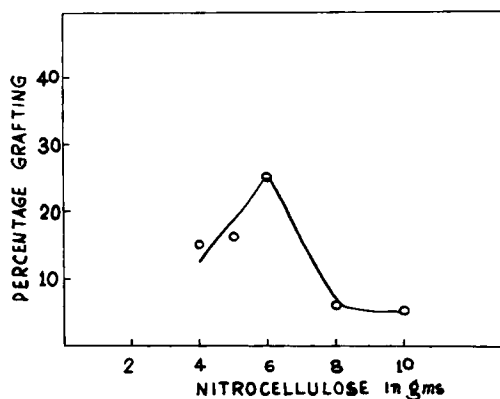

Fig. 3. Effect of nitrocellulose content on the graft copolymerization of methyl methacrylate onto nitrocellulose.

TABLE IV
Effect of Nitrocellulose Content on Percentage Grafting and Molecular Weight[a]

No.	Nitrocellulose, g	Grafting, %	Molecular weight, $\overline{M}_n \times 10^5$
1	4	15.0	—
2	5	16.0	0.8
3	6	25.0	1.5
4	8	6.3	1.9
5	10	5.0	—

[a] MMA, 0.25 mol/l; grafting temperature, 30°C; time, 75 min; CAN, 1.7×10^{-3} mol/l; total volume, 300 ml.

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α-carbon atom of primary alcohol or at the C_2-C_3 glycol group of the anhydro glucose unit or at the hemiacetal group of the end unit of nitrocellulose molecule, as proposed in the case of cellulose by different investigators.[1,6,13–15]

CONCLUSION

The present investigation has revealed that even though grafting of vinyl monomers onto the nitrocellulose backbone is rather difficult with most of the monomers tried, some degree of grafting can be achieved with methyl methacrylate and using ceric ions for initiation in aqueous medium.

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