# Grafting of methyl methacrylate onto cellulose nitrate initiated by benzoyl peroxide

**D. Sudhakar, K. S. V. Srinivasan*, K. Thomas Joseph and M. Santappa****
*Polymer Division, Central Leather Research Institute, Adyar, Madras* 600 020, *India*
(*Received* 10 *September* 1979; *revised* 5 *August* 1980

It has been observed that grafting of vinyl monomers onto cellulose nitrate in solution takes place using benzoyl peroxode. The graft copolymer was isolated from the unreacted backbone and homopolymer by selective solvent extraction. The effect of variables, such as the initiator concentration, the monomer concentration and the reaction time on the percent grafting and the grafting efficiency, were discussed. A probable mechanism for grafting of vinyl monomers to cellulose nitrate in solution has been proposed.

## INTRODUCTION

Chemical modification of cellulose and cellulose derivatives by graft copolymerization has been the subject of much discussion[1-3]. Until recently no references appeared in the literature dealing with the modification of cellulose nitrate by graft copolymerization, in spite of its applications in the surface coating industries. Cellulose nitrate is made flexible by the addition of plasticizers. The drawback with such plasticizers is their tendency towards migration on ageing which makes the film brittle. One of the ways of making cellulose nitrate flexible may be by graft copolymerization. In our earlier papers we have reported the grafting of vinyl monomers onto cellulose nitrate initiated by $C^{IV}$ ion[4] and by benzoyl peroxide[5]. In this paper, we have studied the effects of variables such as the initiator concentration, the monomer concentration and the reaction time on the percent grafting and the grafting efficiency.

## EXPERIMENTAL

### *Materials*

Commercially available cellulose nitrate, NC ($\frac{1}{2}$ sec-grade supplied by the Ashahi Chemical Industry Co. Ltd., Japan) was washed with water and dried *in vacuo* at 55°C to constant weight. Methyl methacrylate, MMA (Rohm and Haas, Philadelphia, USA) was washed with sodium hydroxide (5% solution to remove the inhibitor), then washed with water, dried over anhydrous sodium sulphate and distilled under vacuum. Benzoyl peroxide, BPO (LR, BDH) was recrystallized from chloroform. All solvents were purified and distilled before use.

### *Graft polymerization procedure*

A known weight of cellulose nitrate was dissolved in methyl isobutyl ketone in a polymerization tube and then the required amounts of monomer and initiator were added. Purified nitrogen was passed through the solution for 15 min. The reaction tube was then sealed and transferred to a thermostat maintained at 70±0.1°C. After the required reaction time, the reaction tube was removed from the thermostat, immediately cooled in ice–salt mixture to arrest the reaction and the contents were precipitated by pouring into an excess of petroleum ether (60–80°C). The gross polymer was filtered and dried to a constant weight *in vacuo* at 60°C.

### *Isolation of the graft copolymer*

The gross polymer was Soxhlet extracted with benzene for 72 h to extract poly(methyl methacrylate), PMMA. The remaining polymer was Soxhlet extracted again with methanol for 72 h to remove the unreacted cellulose nitrate. The remaining residue is then considered to be the true graft copolymer. Evidence of graft copolymerization from infra-red spectra has been discussed in earlier papers[4-6]. The percent grafting and the efficiency of grafting (GE) were calculated using the relation

$$\% \text{ grafting} = \frac{\text{wt of (NC-g-PMMA)} - \text{wt of NC}}{\text{wt of NC}} \times 100$$

$$\text{GE} = \frac{\text{wt of PMMA grafted}}{\text{total wt of PMMA formed}}$$

### *Nitrogen analysis*

Estimation of the percent nitrogen in cellulose nitrate and the grafted sample was carried out by the volumetric method described by Stalcup and Williams[7].

### *Viscosity*

The graft copolymers after thorough extraction were suspended in 6 M HCl in hydrolysis tubes. The hydrolysis tubes were evacuated, sealed and kept in an oven at 105–110°C for 48 h. The cellulose nitrate part in the graft copolymer was completely hydrolysed in the process. The insoluble grafts were removed by filtration then washed with water and methanol. The isolated grafts were purified by reprecipitation from a benzene solution with methanol and the intrinsic viscosities were measured in benzene at 30±0.1°C. The molecular weights were then

* Department of Chemistry, University of Wisconsin, Madison, Wisconsin 58706, USA.
** Vice-Chancellor, S.V. University, Tirupati 517 502, A.P. India.

0032-3861/81/040491-03$02.00

*Table 1* Effect of variation of BPO concentration. Reaction condition: cellulose nitrate, 1.00 g; [MMA], 0.63 mol $l^{-1}$; temperature, 70 ± 0.1°C; reaction time, 3 h; total volume, 15 $cm^3$

| Sample no. | [BPO] mol $l^{-1} \times 10^2$ | % grafting | Grafting efficiency | $MW$ $\bar{M}_n \times 10^{-4}$ |
|---|---|---|---|---|
| 1 | 0.69 | 19.2 | 0.64 | 1.4 |
| 2 | 1.39 | 27.3 | 0.71 | 1.3 |
| 3 | 2.08 | 38.7 | 0.73 | 1.2 |
| 4 | 2.77 | 42.7 | 0.77 | 1.2 |
| 5 | 3.46 | 46.8 | 0.81 | 1.2 |
| 6 | 4.16 | 42.8 | 0.73 | 1.2 |
| 7 | 4.85 | 41.4 | 0.83 | 1.2 |

*Table 2* Effect of variation of MMA concentration. Reaction conditions: cellulose nitrate, 1.00 g; temperature, 70 ± 0.1°C; reaction time, 3 h; [BPO], $2.77 \times 10^{-2}$ mol $l^{-1}$; total volume, 15 $cm^3$

| Sample no. | [MMA] mol $l^{-1}$ | % grafting | Grafting efficiency | $MW$ $\bar{M}_n \times 10^{-4}$ |
|---|---|---|---|---|
| 1 | 0.31 | 10.8 | 0.43 | 0.4 |
| 2 | 0.63 | 42.8 | 0.77 | 1.2 |
| 3 | 0.94 | 68.9 | 0.82 | 1.5 |
| 4 | 1.25 | 58.5 | 0.53 | 2.2 |
| 5 | 1.57 | 57.0 | 0.36 | 3.7 |
| 6 | 1.88 | 59.9 | 0.34 | – |

calculated using the relationship[8]:

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

The intrinsic viscosities of cellulose nitrate samples were measured in ethyl acetate at 20±0.1°C [9].

## RESULTS AND DISCUSSION

*Initiator concentration*

*Table 1* shows the effect of the BPO concentration on the % grafting and the grafting efficiency. The % grafting and the grafting efficiency have their maxima at $3.46 \times 10^{-2}$ mol $l^{-1}$ of BPO. It seems that a BPO concentration beyond $3.46 \times 10^{-2}$ mol $l^{-1}$ both benzoyl peroxide radicals and radicals formed on cellulose nitrate are wasted by recombination and other termination processes. It is observed that the molecular weights of the grafted chains decreased with the increase in initiator concentration in the beginning and then remains more or less constant. At higher initiator concentrations, the number of grafting sites reaches a maximum value. Hence the molecular weights of the grafted chains are little affected by further increase in the BPO concentration.

*Monomer concentration*

*Table 2* shows the dependence of grafting parameters on the methyl methacrylate concentration. Both the % grafting and grafting efficiency reach a maximum value at 0.94 mol $l^{-1}$ of monomer. Further increase in the monomer concentration decreases both the % grafting and the grafting efficiency. As the MMA concentration is increased, the number of homopolymer radicals formed are more than the number of radicals on the cellulose nitrate backbone. Therefore both the % grafting and the grafting efficiency decrease at higher monomer concentrations. The molecular weights of the isolated grafted chains were found to increase steadily with increase in monomer concentration. As the monomer concentration increases, the chain length of the grafted polymer and therefore the molecular weight increases.

*Grafting time*

*Table 3* shows the effect of time on the % grafting, the efficiency of grafting and the molecular weight of the isolated poly(methyl methacrylate) chains. The total conversion, the % grafting and the efficiency of grafting increased with increase in reaction time. This agrees with the earlier observation with free radical initiated polymerization.

## GRAFTING MECHANISM

*Nitrogen analysis*

Conventional methods such as the nitrometer and Kjeldahl methods were not suitable for the estimation of nitrogen content in the cellulose nitrate samples. We adopted the method of Stalcup and Williams[7], developed for the determination of percent nitrogen in cellulose nitrate samples where the conventional methods are either inapplicable or inaccurate. A difference of 4.9% in nitrogen was found between samples of original and grafted cellulose nitrate. Cellulose nitrate, when treated under identical conditions of the graft copolymerization reaction in the absence of monomer also showed some loss of nitrogen (2.3%). However, the significant reduction of nitrogen content in the grafted samples exceeding 2.3% can be attributed to the effect of grafting on cellulose nitrate. The loss of nitrogen from cellulose nitrate molecule under the conditions of grafting also indicate that some changes are taking place in the structure of cellulose nitrate. This is also supported by the observation of Kolova *et al.*[10] who found that the heating of cellulose nitrate in a suitable solvent removes some of the nitro groups giving unsaturated polysaccharides.

*Unsaturation*

Cellulose nitrate is a saturated compound. However, cellulose nitrate treated in the graft copolymerization reaction in the absence of monomer was found to be unsaturated, as revealed by the bromination method[11]. The amount of unsaturation was estimated as 0.14 per anhydroglucose unit, AGU, using the bromination method. The blank experiments conducted with backbone, monomer and solvent in the absence of catalyst showed that the backbone itself cannot initiate graft copolymerization. This experiment reveals that the formation of unsaturation may be a factor in the formation of graft copolymer.

*Table 3* Effect of reaction time. Reaction conditions: cellulose nitrate, 1.00 g; [MMA], 0.63 mol $l^{-1}$; temperature, 70 ± 0.1°C; [BPO], $2.77 \times 10^{-2}$ mol $l^{-1}$; total volume, 15 $cm^3$

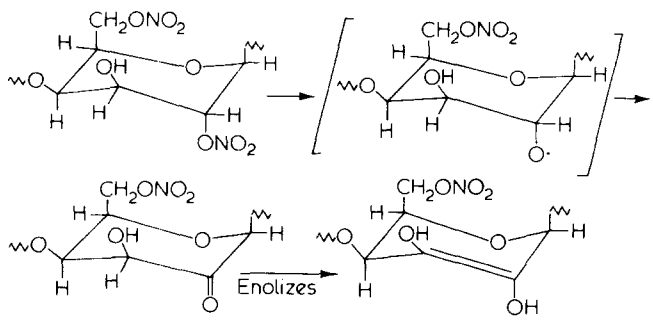
| Sample no. | Reaction time (min) | % grafting | Grafting efficiency | $MW$ $\bar{M}_n \times 10^{-4}$ |
|---|---|---|---|---|
| 1 | 60 | 9.0 | 0.44 | 1.0 |
| 2 | 90 | 23.2 | 0.65 | 1.1 |
| 3 | 120 | 23.3 | 0.69 | 1.2 |
| 4 | 180 | 42.7 | 0.77 | 1.2 |
| 5 | 210 | 45.6 | 0.81 | 1.2 |

*Viscosity and degradation*

Studies have been carried out aimed at an understanding of the degradation of the backbone chains during grafting. The intrinsic viscosity of the backbone polymer before and after the treatment as in a grafting experiment in the absence of monomer, was the same (0.61 dl/g) which shows that no degradation of the backbone polymer has taken place under these conditions.

*Possible mechanism*

The cellulose molecule does not have labile atoms (as in the case of PVC or chlorinated rubber etc.) which can be abstracted to create grafting sites on it by free radical initiators like benzoyl peroxide[12]. The possibilities of grafting sites on the cellulose nitrate molecule must be either (a) at the free hydroxyl group, (b) at the nitro group, or (c) by some rearrangement in the AGU. The hydroxyl group in cellulose molecule can form reactive sites only with redox initiators such as Ce(IV), Mn(III) etc. but have been totally ineffective with initiators such as benzoyl peroxide. The elimination of nitro groups and the absence of polymerization without the initiators, under the polymerization conditions, show that the $NO_2$ elimination alone is not enough for graft polymerization. The elimination of nitro groups and the detection of unsaturation under the experimental conditions show the formation of an unsaturated polysaccharide which may provide a reactive site for graft copolymerization. Under mild conditions of oxidation of cellulose, it has been suggested that a ketone group is formed at $C_2$ without a $C_2$–$C_3$ bond cleavage[13]. McGee *et al.*[14] concluded that the ketone group in the AGU, resulting from the oxidation of celluronic acid by nitrogen dioxide, would enolize to an unsaturated structure. The AGU in the cellulose nitrate molecule may result in the enol structure as shown:




It is possible that graft polymer results from the direct attack on the unsaturated AGU by primary initiator radicals derived from BPO. The following reactions, given in equations (1) to (9) leading to the formation of graft and homopolymer, appear to be important:

*Production of radicals*

$$\text{Catalyst (BPO)} \xrightarrow{k_{dj}} 2\text{C}\cdot \qquad (1)$$

*Initiation*

$$\text{C}\cdot + \text{M} \xrightarrow{k_1} \text{R}\cdot \qquad (2)$$

$$\text{C}\cdot + \text{P} \xrightarrow{k_2} \text{P}\cdot \qquad (3)$$

*Chain transfer*

$$\text{R}\cdot + \text{P} \xrightarrow{k_3} \text{P}\cdot + \text{RH} \qquad (4)$$

(Termination of homopolymer radicals is insignificant in this case.)

*Propagation*

$$\text{Homopolymer: R}\cdot + \text{M} \xrightarrow{k_4} \text{R}\cdot \qquad (5)$$

$$\text{Graft polymer: P}\cdot + \text{M} \xrightarrow{k_5} \text{P}\cdot \qquad (6)$$

*Termination*

$$\text{Graft + graft P}\cdot + \text{P}\cdot \xrightarrow{k_6} \text{high molecular weight graft} \qquad (7)$$

$$\text{Graft + homo P}\cdot + \text{R}\cdot \xrightarrow{k_7} \text{graft-homopolymer composite} \qquad (8)$$

$$\text{Homo + homo R}\cdot + \text{R}\cdot \xrightarrow{k_8} \text{homopolymer} \qquad (8)$$

C· and R· refer to the catalyst radicals and homopolymer radicals respectively and P· refers to the backbone radicals as well as graft polymer radicals, both the reactivities being assumed to be the same while reactivity of homopolymer radicals R· was different from P·.

## REFERENCES


1 Immergut, E. H. in 'Encyclopedia of Polymer Science and Technology' (Eds. H. F. Mark, N. G. Gaylord and N. M. Bikales) Interscience Publishers, New York 1965, Vol 3, p 242
2 Stannett, V. T. and Hopfenberg, H. B. in 'High Polymers' (Eds. N. M. Bikales and L. Segal) Wiley-Interscience, New York, 1971, Vol 5, Part V, p 907
3 'Proceedings of the Symposium on Graft Polymerization onto Cellulose' (Ed Jett C. Arthur Jr.) *J. Polym. Sci.* 1972, **C37**
4 Sudhakar, D., Srinivasan, K. S. V., Joseph, K. T. and Santappa, M. *J. Appl. Polym. Sci.* 1979, **23**, 2923
5 Sudhakar, D., Srinivasan, K. S. V., Joseph, K. T. and Santappa, M. *J. Polym. Sci., Polym. Letts. Edn.* 1978, **16**, 457
6 Srinivasan, K. S. V. and Sudhakar, D. *Polymer Bulletin* 1980, **2**, 321
7 Stalcup, H. and Williams, R. W. *Anal. Chem.* 1955, **27**, 543
8 Fox, T. G., Kissinger, J. B., Mason, H. F. and Schule, E. M. *Polymer* 1962, **3**, 71
9 Alexander, W. J. and Mitchell, R. L. *Anal. Chem.* 1949, **21**, 1497
10 Kolova, A. F., Snezhko, V. A., Khomyakov, K. P., Virmik, A. D. and Rogovin, Z. A. *Izv. Vyssh, Uchebu, Zaved., Khim. Khim. Technol. 1974*, **17**(12), 1890
11 Siggia, S., in 'Quantitative Organic Analysis via Functional Groups', John Wiley and Sons Inc., New York, 1963, 300
12 Mechell, G. and Richards, G. N. *J. Chem. Soc.* 1961, 3308
13 Hebeish, A. and Mehta, P. C. *J. Appl. Polym. Sci.* 1968, **12**, 1625
14 McGee, P. A., Fowler, Jr, W. F., Unruh, C. C. and Kenyan, W. O. *J. Am. Chem. Soc.* 1948, **70**, 2700