# Free Radical Copolymerization of Poly(*n*-butyl Methacrylate) onto Polychloroprene

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## Synopsis

Graft copolymerization of *n*-butyl methacrylate onto polychloroprene was carried out in toluene using benzoyl peroxide as an initiator. The polychloroprene-g-poly(*n*-butyl methacrylate) was isolated from the copolymerization product by extracting with hexane. Infrared (IR) spectra and nuclear magnetic resonance (NMR) of graft copolymer showed the occurrence of grafting. Percentage of grafting and grafting efficiency calculated under different experimental conditions were discussed. The mechanism of grafting seems to occur by chain transfer, as evidenced by a decrease in chlorine content during the experiment.

## INTRODUCTION

The discovery of new polymers is a rarity these days and many attempts are being made to modify the existing polymers either through the blend formation[1] or by graft copolymerization.[2,3] By these processes many new materials have been formed which differ completely in both physical and chemical properties from that of the parent material.[4,5] Polychloroprene finds extensive applications as an adhesive and in moulded articles, and it is usually used by blending with other components. These processes have certain advantages as well as disadvantages. Little has been reported on the modification of polychloroprene, and this article deals with the graft copolymerization of poly(*n*-butyl methacrylate) onto polychloroprene using benzoyl peroxide as an initiator in solution medium. The effect of variables such as monomer concentration, initiator, temperature, and backbone on graft copolymerization have been studied. The probable mechanisms for this graft copolymerization have been discussed. The graft copolymers obtained on subsequent hydrolysis are likely to yield carboxylated polychloroprenes, which are likely to find applications as adhesives for bonding metal to rubber.

## EXPERIMENTAL

### Materials

Polychloroprene PCP (Bayprene 321 supplied by Bayers, W. Germany) with 38% chlorine content was used. Polychloroprene was purified by dissolving in toluene and precipitating by methanol. The precipitation was carried out twice and the product was dried in vacuum at 50°C.

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The monomer, *n*-butyl methacrylate (BDH Chemicals, England) was freed on inhibitors by washing successively with 5% aqueous sodium hydroxide, drying over anhydrous $CaCl_2$, distilling under vacuum, and storing in a refrigerator at 4°C. This monomer was used throughout the experiments.

Benzoyl peroxide (BPO) BDH was recrystallized from chloroform. Toluene, benzene, tetrahydrofuran, methanol, and hexane used were all of reagent grade.

### Grafting Procedure

Polychloroprene was dissolved by stirring conditions overnight in toluene medium. The required quantity of this solution was transferred into a flask, which was immersed in a thermostatic bath maintained at a required temperature. Known quantity of monomer and initiator was added, and slow-stream nitrogen was passed throughout the experiment. After required polymerization time, the polymerization tube was removed from the thermostat and immediately cooled in ice to arrest the reaction. The total contents in the tube were poured into excess of methanol to precipitate the polymers. The polymer suspension was placed in a refrigerator for 24 h, after which it was filtered and washed in a weighed sintered glass crucible. The gross polymer obtained was dried in vacuum at 50°C until a constant weight was obtained.

### Isolation of Graft Copolymer

In the synthesis, the gross polymer obtained consists of ungrafted polychloroprene, graft copolymer, and unbound homopolymer. Poly(*n*-butyl methacrylate) homopolymer was separated from the rest of the polymer by extracting the gross polymer in hexane for 72 h by Soxhlet extraction method. The remaining weight of the polymer in the crucible after drying was taken as polychloroprene and polychloroprene-g-PBMA. From these results, the amount of graft copolymer was calculated. The percent grafting and grafting efficiency were calculated using the following equations

$$\text{Percent grafting (PG)} = \frac{\text{Weight of polymer grafted}}{\text{Weight of backbone}} \times 100$$

$$\text{Grafting efficiency (GE)} = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

### Chlorine Estimation

A weighed quantity of polychloroprene was taken in a porcelein crucible and swollen with a little benzene: 6 g of mixture of 2 parts sodium nitrate, 1 part sodium carbonate, and 1 part potassium carbonate was added and mixed with the swollen polychloroprene. The benzene was evaporated at 100°C; 4 g of sodium carbonate was placed on top of mixture in the crucible and the latter was covered with a porcelein cover. The crucible was then heated, first over a low flame, gradually increasing to a full flame. After 3 h heating, the material was allowed to cool and subsequently transferred to a beaker first

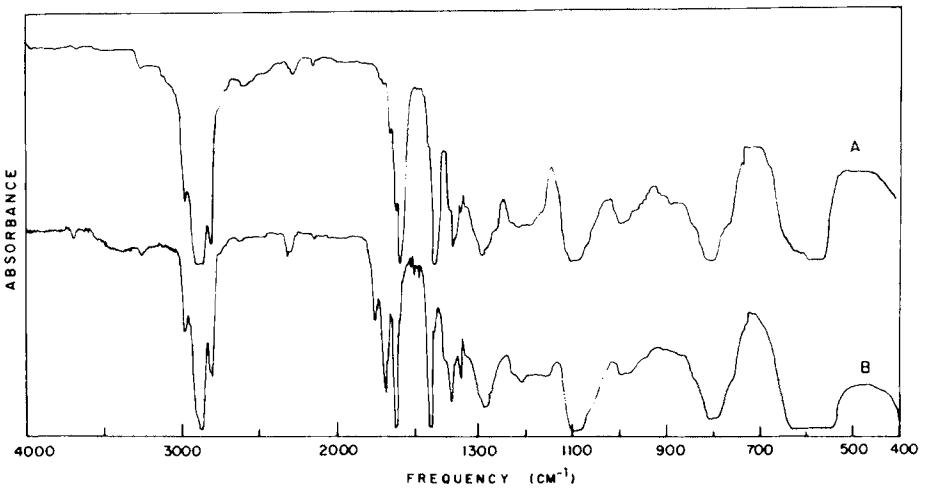



Fig. 1. IR spectrum of *A*, polychloroprene, *B*, polychloroprene-g-poly(*n*-butyl-methacrylate).

with warm distilled water and, then 13 mL of concentrated nitric acid was added on a steam bath to dissolve all the materials.

To the solution, diluted to about 150 mL, was added an excess of standard silver nitrate solution. The precipitated silver chloride was filtered off and washed with silver nitrate, and then finally with distilled water. The filtrate and washings were combined and titrated with standard thiocyanate solution.

The filtrate from the precipitated chloride was treated with 5 mL of the ferric solution and the excess silver determined by addition of the thiocyanate until a permanent reddish-brown color was produced and the amount of chloride was estimated using the standard procedure.[6,7]

## RESULTS AND DISCUSSION

### Characterization of Graft Copolymer

**IR spectra of polymers.** The isolated polychloroprene-g-PBMA dissolved in toluene was poured into a mercury bed and allowed to dry in vacuum. The IR spectra of films were recorded by Perkin-Elmer 337, and are shown in Figure 1. The graft copolymer showed an absorption band at 1730 $cm^{-1}$, a characteristic of the C=O peak present in poly(*n*-butyl methacrylate). This showed that poly(*n*-butyl methacrylate) chain was grafted to polychloroprene.

**NMR spectra of polymers.** Polychloroprene and the isolated graft copolymers were dissolved in deuterated benzene and the NMR spectra of these samples were recorded using Perkin-Elmer R-32 (90 MHz) instrument, and are shown in Figure 2. The graft copolymer shows the $-OCH_2$ proton peak at 4.07 ppm and $\alpha$-$CH_3$ proton at 1.39 ppm. The presence of these signals in the isolated graft copolymer sample clearly indicates that poly(*n*-butyl methacrylate) has been grafted onto polychloroprene.

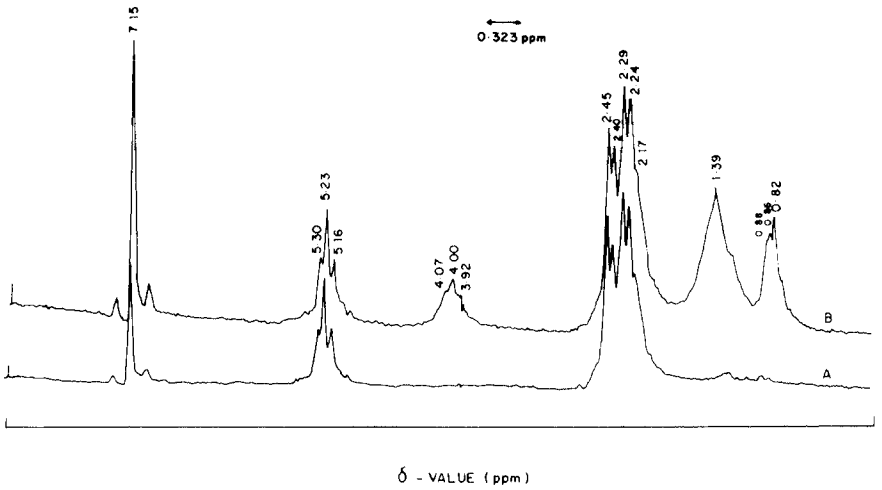



Fig. 2. NMR spectrum of *A*, polychloroprene, *B*, polychloroprene-g-poly (*n*-butylmethacrylate).

## Effect of Variables on Grafting

**Effect of grafting time.** The polymerization was carried out in toluene medium at 70°C for 3, 4, 5 h with constant concentration of polychloroprene, *n*-butyl methacrylate, and benzoyl peroxide. The results of grafting percentage and grafting efficiency are shown in Table I. As can be seen the grafting percent increased with increase in time and the grafting efficiency decreased up to 5 h, and then increased. The increase in the ratio of homopolymer to grafted polymer up to 5 h showed a decrease in grafting efficiency. After 5 h, the amount of homopolymer formed is less, and hence the grafting efficiency was found to be higher.

**Effect of initiator concentration.** Polymerization was carried out with various concentrations of initiator at 70°C for 6 h and the results are given in Table II. The grafting percentage increased with increase in the concentration of benzoyl peroxide up to $2.7 \times 10^{-2}$ mol/L, and then decreased. The obvious

TABLE I
Effect of Time Variation in Graft Copolymerization of *n*-BMA onto Polychloroprene

| Time (hr) | Total weight of polymer formed (g) | Weight of graft copolymer formed (g) | Percent grafting (%) | Grafting efficiency (%) |
|---|---|---|---|---|
| 3 | 0.183 | 0.145 | 14.5 | 79.2 |
| 4 | 0.279 | 0.212 | 21.2 | 76.0 |
| 5 | 0.364 | 0.274 | 27.4 | 75.3 |
| 6 | 0.406 | 0.352 | 35.2 | 86.7 |

[PCP], 0.511 mol/L; grafting temperature, 70°C; BPO, 0.015 mol/L; *n*-BMA, 0.319 mol/L; total volume, 22 mL.

TABLE II
Effect of Initiator Concentration in Graft Copolymerization of *n*-BMA onto Polychloroprene

| [BPO] × $10^2$ mol/L | Total weight of polymer formed (g) | Weight of graft co-polymer formed (g) | Percent grafting (%) | Grafting efficiency (%) |
|---|---|---|---|---|
| 2.1 | 0.146 | 0.113 | 11.3 | 77.4 |
| 2.7 | 0.220 | 0.186 | 18.6 | 84.5 |
| 2.9 | 0.157 | 0.129 | 12.9 | 82.2 |
| 3.2 | 0.125 | 0.087 | 8.7 | 69.6 |

PCP, 0.511 mol/L; grafting temperature, 70°C, time, 6 h; *n*-BMA, 0.319 mol/L; total volume, 22 mL.

reason for this trend is that greater number of grafting sites are created by increase in initiator concentration.

**Effect of polychloroprene content.** Polymerization was carried out with various concentrations of polychloroprene at 70°C for 5 h, and the results are shown in Table III. The weight of polymerized *n*-butyl methacrylate and the grafting percentages decreased with increases in the concentration of polychloroprene. With higher concentrations of polychloroprene, more active centers are formed in the system, and thus, the degree of polymerization of poly(*n*-butyl methacrylate) is lower. On the other hand, the lower the concentration of polychloroprene, the fewer active centers, and thus the higher degree of polymerization of poly(*n*-butyl methacrylate). Therefore, the percentage of grafting increased.

**Effect of variation of monomer.** Polymerization was carried out with various concentrations of *n*-butyl methacrylate, keeping the concentration of polychloroprene and benzoyl peroxide constant at 70°C for 5 h. The results are shown in Figure 3. The percentage grafting increased with the concentration of monomer, but the grafting efficiency decreased. The decrease in grafting efficiency with increase in monomer concentration can be explained by assuming that the grafted chains acting as the diffusion barrier, inhibited the diffusion of monomer into the backbone. As a result, less monomer will be

TABLE III
Effect of Poly(chloroprene) Concentration in Graft Copolymerization of *n*-BMA onto Polychloroprene

| [PCP] mol/L | Total weight of polymer formed (g) | Weight of graft copolymer formed (g) | Percent grafting (%) | Grafting efficiency (%) |
|---|---|---|---|---|
| 0.256 | 0.284 | 0.203 | 40.6 | 71.5 |
| 1.023 | 0.494 | 0.422 | 21.1 | 85.4 |
| 1.534 | 0.367 | 0.288 | 9.6 | 78.5 |
| 2.045 | 0.317 | 0.218 | 5.5 | 68.8 |

*n*-BMA, 0.319 mol/L; grafting temperature, 70°C; time, 6 h; BPO, 0.015 mol/L; total volume, 22 mL.

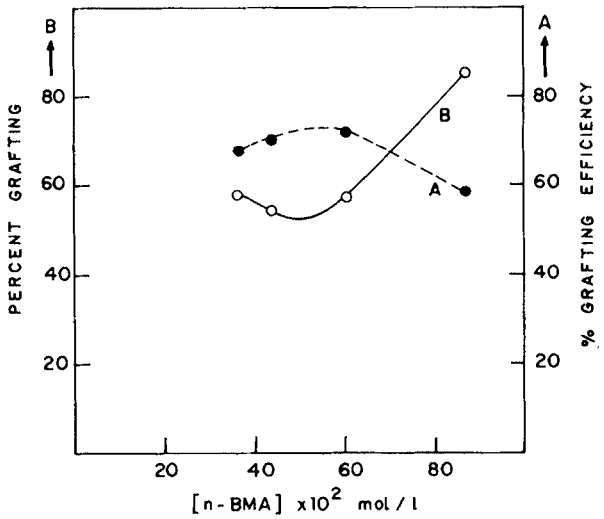



Fig. 3. Effect of monomer concentration on the graft copolymerization of *n*-butyl methacrylate onto polychloroprene.

available for grafting active centers, and hence, most of them are used for the formation of homopolymer. The grafting percentage reached 86% at $8.6 \times 10^{-3}$ mol/L.

**Effect of reaction time.** Polymerization was carried out at 60, 65, 70, and 75°C, keeping all the variables constant. The results are given in Table IV. Both the percentage of grafting and grafting efficiency increased up to 70°C, followed by a tendency to decrease further with increase in temperature. The increase in temperature showed an increase in percentage of grafting and grafting efficiency, indicating the formation of more graft polymer than the homopolymer. Further increase in temperature favors the formation of more homopolymer, and consequently, there is a decrease in grafting percentage and grafting efficiency.

## Mechanism of Grafting

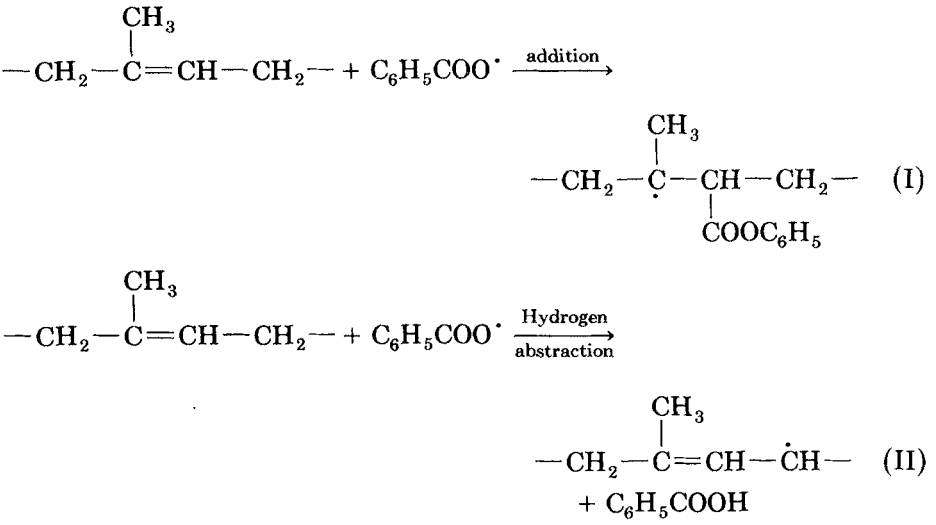
In the system of grafting of methyl methacrylate onto natural rubber using benzoyl peroxide, free radical centers are created either by the opening of the double bonds in natural rubber by benzoyloxy radicals (from benzoyl perox-

TABLE IV
Effect of Temperature Variation in Graft Copolymerization of *n*-BMA onto Polychloroprene

| Temperature (°C) | Total weight of polymer formed (g) | Weight of graft copolymer formed (g) | Percent grafting (%) | Grafting efficiency (%) |
|---|---|---|---|---|
| 60 | 0.252 | 0.031 | 3.1 | 12.3 |
| 65 | 0.272 | 0.192 | 19.2 | 70.6 |
| 70 | 0.406 | 0.352 | 35.2 | 86.7 |
| 75 | 0.455 | 0.279 | 27.9 | 61.3 |

PCP, 0.511 mol/L; *n*-BMA, 0.319 mol/L; BPO, 0.015 mol/L; time, 6 h; total volume, 22 mL.

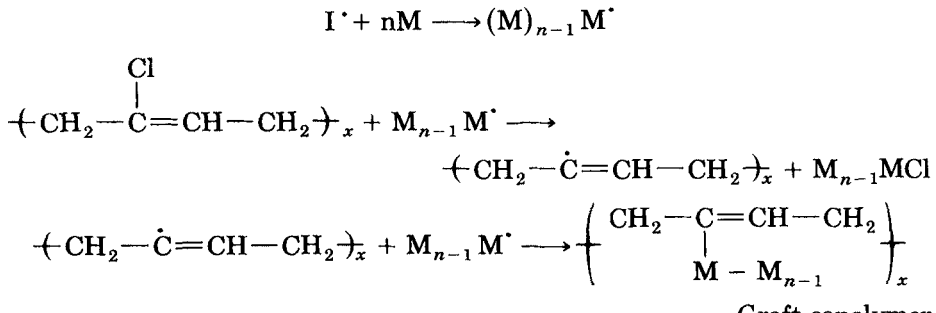
ide) attack (I) or by abstraction of α-methylene hydrogen atom in rubber (II).[8,9]



Later studies by Ghosh and Sengupta on graft copolymerization of methyl methacrylate and natural rubber indicated that the loss of unsaturation was marginal and the graft copolymer appeared to be primarily due to polymer growth on isoprenyl radicals formed in the system by the abstraction of labile hydrogen atoms of α-methylene groups in the rubber chains by primary radical derived from benzoyl peroxide.[10]

The estimation of chlorine in polychloroprene was found to be 38%, which tallies with the literature value for polychloroprene. The analysis of graft copolymer (taking into consideration the weight of grafted chain) gave a reproducible value of 33% chlorine. This indicates the elimination of chlorine to create potential sites for grafting. If the two previous mechanisms are operative, then there should be no elimination of chlorine from polychloroprene.

The polychloroprene is very stable and direct elimination of chlorine creating a radical site is also eliminated in the present experimental conditions. Alternatively, the elimination of chlorine by chain transfer reaction creating a radical site is a possibility and the probable mechanism of graft copolymerization in the present study is given below:



Graft copolymer

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