# Grafting of Acrylate Monomers onto Chlorinated Rubber*

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## Synopsis

Grafting of chlorinated rubber with ethylacrylate and butyl methacrylate in xylene solution has been studied using benzoyl peroxide as the initiator. It is observed that the grafting reaction follows conventional kinetic behavior under the present experimental conditions. The energies of activation obtained for both monomers were 10.8 and 10.95 K.cals, respectively. The grafting efficiency and percent grafting were calculated. Additional proof for grafting onto chlorinated rubber was also obtained by characterization of the graft copolymer by gel permeation chromatography.

## INTRODUCTION

Graft copolymerization of chlorinated rubber (CR) with ethylacrylate using benzoyl peroxide (BPO) in xylene medium was presented as a short communication.[1] In the present article, the detailed investigation of the grafting of CR using both ethylacrylate and butyl methacrylate is given with regard to the synthetic variables such as temperature, monomer concentration, etc., and characterization of graft copolymer with gel permeation chromatography (GPC), IR, and NMR. Rate of polymerization with respect to monomer and initiator concentration and temperature was determined to understand the kinetic behavior of the system.

## EXPERIMENTAL

### Materials

Chlorinated rubber (Chlorub 40, ~65% Cl), marketed by Rishiroop Polymers Pvt. Bombay, was purified by dissolving in ethyl methyl ketone and precipitation by excess methanol. The precipitation was carried out twice and the product was dried before use. Ethylacrylate and butyl methacrylate were washed with 5% NaOH and distilled water successively and distilled under vacuum. The middle cut of the monomer sample was stored in a freezer. Benzoyl peroxide was recrystallized and used in the grafting reactions. Xylene (BDH, AR grade), ethyl methyl ketone, methanol, and petroleum ether were purified as per standard procedures and used.

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## Polymerization Procedure

Grafting was conducted in closed corning glass ampuls in nitrogen atmosphere. Specified amounts of CR, monomer, and BPO were dissolved in xylene to get a homogeneous phase and the solution was flushed with a slow stream of nitrogen for about 10 min. The ampuls were closed and thermostated immediately for polymerization. The times of polymerization depended upon the experimental conditions and the aim of the experiments. Reactions were terminated by pouring the contents into excess petroleum ether. The gross polymer was recovered by filtration, dried, and weighed.

## Polymer Characterization

### Isolation of Graft Copolymer

The gross polymer was a physical mixture of ungrafted CR, grafted CR, and free homopolymer. The isolation of graft copolymer was achieved by fractional precipitation technique using ethyl methyl ketone as a solvent and methanol as a nonsolvent. The solubility characteristics of the CR and homopolymers in ethyl methyl ketone were found to be widely different. The $\gamma$-values (volume fraction of the nonsolvent required to separate the particular polymer) were found out for each polymer namely, CR, graft copolymers, poly(butyl methacrylate) (PBMA) and poly(ethyl acrylate) (PEA). It was found that PEA could not be precipitated from ethyl methyl ketone and could be recovered almost quantitatively after the removal of grafted polymer. The precipitation ranges in terms of volume fractions of methanol were as follows: for CR: $\gamma$ 0.2–0.35; for CR-g-PEA: $\gamma$ 0.30–0.65; and for CR-g-PBMA: $\gamma$ 0.30–0.58. Since ethyl methyl ketone is comparatively good solvent for homopolymers, the precipitation range ($\gamma$) for PBMA is above 0.6 and PEA is not precipitated with the addition of methanol. The pure graft copolymer, thus isolated, was purified again and subjected to analysis.

### Gel Permeation Chromatography

Gel permeation chromatograms were obtained on a Waters Associates ALC (244 Model, high pressure liquid chromatograph) using dilute polymer solutions (0.02%) in toluene and a flowrate of 1 ml/min. The chromatograph was equipped with four microstyragel columns in series (pore size $10^6$, $10^5$, $10^4$, $10^3$ Å).

### Molecular Weight Determination

The molecular weight of the homopolymers, poly(ethyl acrylate) and poly(butyl methacrylate), separated from the crude mixture were calculated by determining the intrinsic viscosity $[\eta]$ in benzene at 30°C ± 0.05, using an Ubbelohde dilution viscometer. The dilution was effected by adding specified amount of solvent to the solution in the viscometer itself. The viscosity average molecular weight $\overline{M}_v$ of the samples was calculated[2,3] using the Mark–Houwink equation $[\eta] = K\overline{M}_v^a$.

TABLE I
Effect of Temperature and Time in Grafting of CR with PEA[a]

| Time (hr) | Temperature (°C) | Percent Grafting | Percent G.E. | $\overline{M}_v \times 10^{-4}$ |
|---|---|---|---|---|
| 3 | 60 | 4.08 | 14.92 | — |
| 6 | 60 | 5.9 | 16.10 | 1.3545 |
| 8 | 60 | 10.14 | 17.55 | 1.3670 |
| 3 | 70 | 8.03 | 15.06 | — |
| 6 | 70 | 11.01 | 15.72 | 0.8886 |
| 8 | 70 | 14.09 | 18.98 | — |
| 3 | 80 | 8.49 | 12.07 | 0.7723 |
| 6 | 80 | 11.28 | 13.43 | 0.8352 |
| 8 | 80 | 14.00 | 15.67 | — |

[a] EA = 0.924 mole/liter; CR = 0.1995 mole/liter; BPO = 2.9 × 10⁻³ mole/liter; xylene = 20 ml.

## RESULTS AND DISCUSSION

As pointed out in our earlier work[1] evidence for grafting was established as follows:

(i) The graft copolymer fraction, after the isolation of homopolymer and ungrafted polymer, was subjected to IR and NMR spectroscopic analyses (Fig. 7). The characteristic band of —C=O, at 1720–1722 cm⁻¹ from IR spectra of graft copolymer fraction indicates the presence of acrylate chains. The graft copolymer also shows a strong absorption at 1601 cm⁻¹, which is attributable to small residual unsaturation,

$$( -C = C - Cl )$$
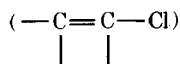
in chlorinated rubber.[4] A peak at 3.8–3.9 $\delta$ of the NMR spectra of graft copolymer fraction is due to —OCH₂ protons of acrylate systems.

(ii) The graft copolymer fraction, completely isolated from homopolymer and ungrafted CR, was subjected to GPC analysis. Figure 6 represents the GPC curves of CR (control) and pure graft copolymer fraction. It is seen that the graft copolymer sample has lower elution counts compared to that of control, thereby indicating the increase in the molecular weight. This increase is due to the presence of PEA chains attached to the parent backbone polymer.

Table I indicates the effect of variation of time and temperature on the grafting of ethyl acrylate to CR. The data also include the viscosity average molecular weight from the Mark–Houwink equation. Table II represents the variation of ethyl acrylate concentration at 60°C.

TABLE II
Effect of Monomer Concentration in Grafting of CR with PEA[a]

| Monomer concentration (mole/liter) | Percent grafting | Percent G.E. | $\overline{M}_v \times 10^{-4}$ |
|---|---|---|---|
| 0.924 | 6.00 | 11.14 | 1.67 |
| 1.386 | 18.48 | 22.19 | 2.3 |
| 1.848 | 21.22 | 15.09 | 3.9 |
| 2.2176 | 25.15 | 12.74 | 3.95 |

[a] Time = 4 hr; temperature = 60°C; CR = 0.1329 mole/liter; BPO = 3.875 × 10⁻³ mole/liter; xylene = 20 ml.

For butyl methacrylate, the data are tabulated in Tables III–VI.

The total weight of polymer obtained as a function of polymerization time is shown in Figure 1. In both monomer systems, the initiator BPO was used for the grafting reactions. It was already established that grafting of CR with vinyl monomers takes place through a chain transfer process when free radical initiators are used.[5] The rate of polymerization ($R_p$) when plotted against monomer concentration, gives a straight line, indicating the first-order dependence on monomer concentration. The plot of $R_p$ versus monomer concentration is shown

TABLE III
Effect of Initiator Concentration in Grafting of CR with PBMA[a]

| BPO $\times 10^3$ (mole/liter) | Percent grafting | Percent G.E. | $\overline{M}_v \times 10^{-5}$ |
|---|---|---|---|
| 3.87 | 26.80 | 25.35 | 6.670 |
| 6.46 | 25.44 | 22.32 | 6.140 |
| 10.34 | 22.88 | 21.29 | 4.7629 |
| 12.90 | 19.24 | 12.400 | 4.053 |

[a] BMA = 1.68 mole/liter; CR = 0.067 mole/liter; xylene = 15 ml; time = 2.5 hr; temperature = 70°C.

TABLE IV
Variation of Polymerization Time in Grafting of CR with PBMA[a]

| Time (hr) | Percent grafting | Percent G.E. |
|---|---|---|
| 2.0 | 11.86 | 16.87 |
| 4.0 | 19.86 | 24.07 |
| 6.0 | 24.64 | 23.55 |
| 7.5 | 24.40 | 21.58 |

[a] BMA = 1.261 mole/liter; CR = 0.067 mole/liter; xylene = 15 ml; BPO = 1.94 $\times 10^{-3}$ mole/liter.

TABLE V
Effect of Monomer Concentration in Grafting of CR with PBMA[a]

| Monomer concentration (mole/liter) | Percent grafting | Percent G.E. | $\overline{M}_v \times 10^{-5}$ |
|---|---|---|---|
| 0.8404 | 14.6 | 24.94 | 3.84 |
| 1.6807 | 30.18 | 35.70 | 6.54 |
| 2.101 | 48.3 | 38.52 | 9.80 |
| 2.524 | 50.58 | 35.90 | 9.98 |

[a] CR = 6.7 $\times 10^{-2}$ mole/liter; BPO = 2.258 $\times 10^{-3}$ mole/liter; time = 3 hr; temperature = 70°C; xylene = 15 ml.

TABLE VI
Effect of Temperature in Grafting of CR with PBMA[a]

| Sl. No. | Temperature (°C) | Percent grafting | Percent G.E. |
|---|---|---|---|
| 1. | 60 | 15.06 | 23.776 |
| 2. | 70 | 24.14 | 22.74 |
| 3. | 80 | 26.54 | 16.65 |

[a] BMA = 1.261 mole/liter; CR = 6.7 $\times 10^{-2}$ mole/liter; time = 4 hr; xylene = 15 ml.
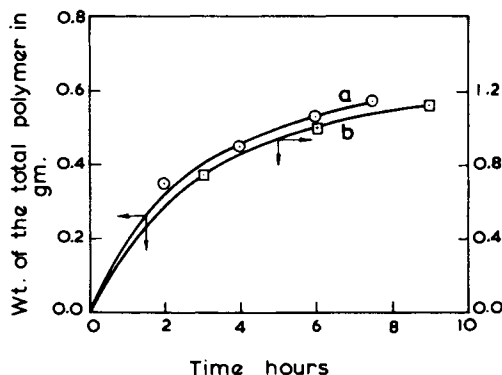
Fig. 1. Weight of total polymer formed versus time in hours.   (A) Ethyl acrylate; (B) butyl methacrylate.

in Figure 2.   Figure 3 shows the linear dependence of $R_p$ on the square root of the initiator concentration.   These results demonstrate that this system follows normal kinetic behavior, which is unaffected by the presence of backbone polymer.

The log rate of polymerization is plotted against $1/T$ (Fig. 5) in order to calculate the energy of activation.   The values obtained from the plots of PEA and PBMA are about 10.8 and 10.95 kcal/mole, respectively.   The overall activation energy in the case of chemical grafting, should account for the following processes:

(i) Energy of activation for the decomposition of catalyst; (ii) energy of activation for the growing radical to chain transfer with the backbone to form a initiating species; (iii) energy of propagation; and (iv) activation energy for ter-
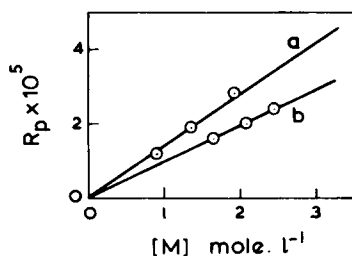


Fig. 2. Rate of polymerization $R_p$ versus monomer concentration.   (A) Ethyl acrylate; (B) butyl methacrylate.
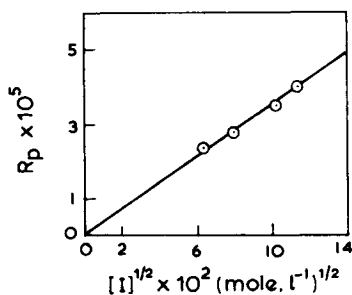


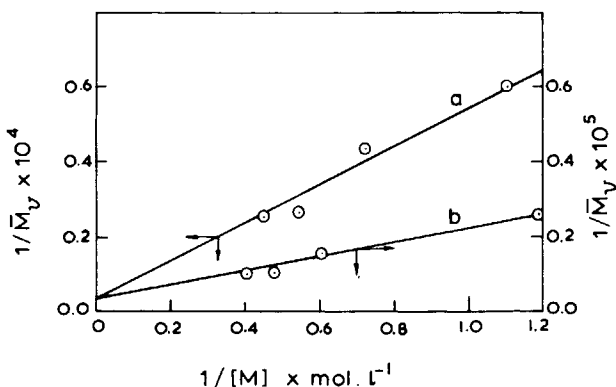Fig. 3. Rate of polymerization $R_p$ versus square root of initiator concentration.

Fig. 4. Reciprocal viscosity average molecular weight versus reciprocal monomer concentration. (A) Ethyl acrylate; (B) butyl methacrylate.

mination process.   It can be represented as

$$E_a = E_d/2 + E_{tr}/2 + (E_p - E_t/2)$$

where $E_d$ is the energy of activation for decomposition of catalyst; $E_{tr}$ is the activation energy for transfer process; $E_p$ is activation energy for propagation; and $E_t$ is the activation energy for termination.

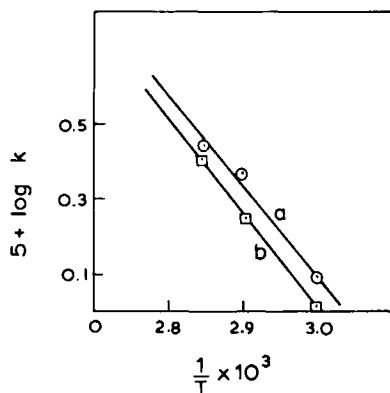$(E_p - E_t/2)$ for PEA is about 6.8 kcal/mole,[6] and for PBMA it is 4.00 kcal/



Fig. 5. Relation between log $k$ versus $1/T$.   (A) Ethyl acrylate; (B) butyl methacrylate.
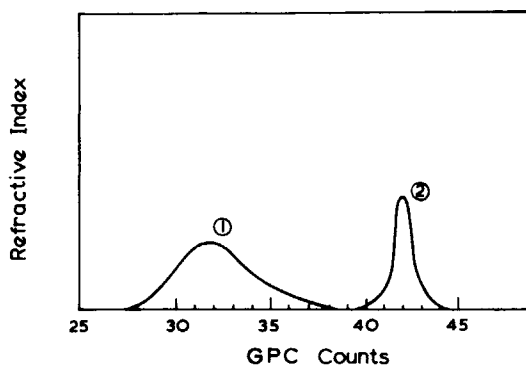


Fig. 6. Curve (1), chlorinated rubber-g-PEA; curve (2), chlorinated rubber.
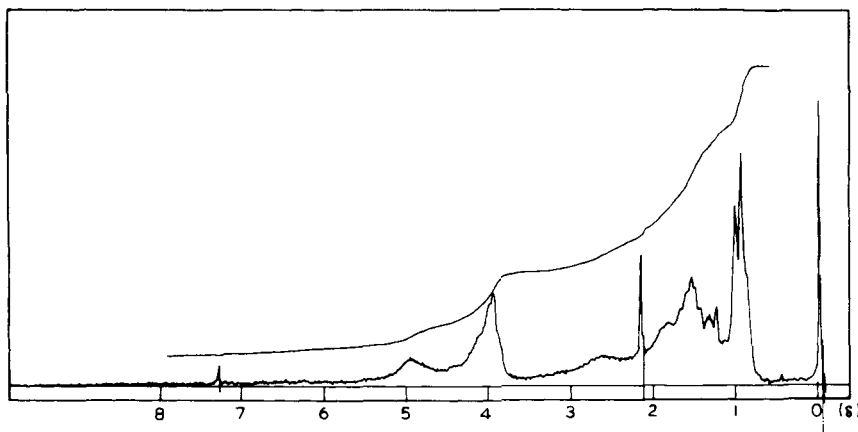
Fig. 7. NMR spectra of CR-g-PEA.

mole.[7]   When all the parameters are taken into account, the overall activation energy can be computed as 25.1 kcal/mole.   However, the energy of activation determined appears to be less by $E_d/2$ (14.8 kcal/mole).   This clearly indicates that, in this BPO initiated grafting system, the initiator species appears to be only the growing homopolymer chain radical, which by abstracting labile chlorine atoms from the backbone, initiates the grafting reaction.   In the case of acrylic acid grafting on polyester[8] fiber and the grafting of glycidyl methacrylate on poly(ethylene terephthalate)[9] using BPO as initiator, the reported values of activation energy are about 10.7 and 14.7 kcal/mole, respectively.   The investigators attributed these lower values for grafting of backbone by means of a chain transfer process.   Similarly, the lower action energy values obtained in our present system led us to assume the occurrence of chain transfer process in the grafting reaction.

Moreover, from the point of view of Lenz,[10] the exclusive involvement of initiator radical in creating transfer sites could be attributed to the prevention of growing polymer chains from taking part in chain transfer reactions with the substrate polymer molecule, because of the incompatibility of two different
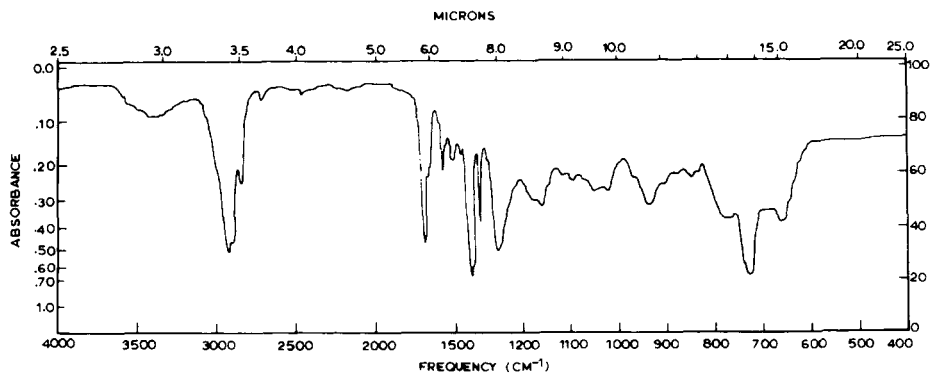


Fig. 8. IR spectra of CR-g-PEA.

homopolymers. Unlike natural rubber, the CR is mostly free from unsatura-tion[11] (in the case of natural rubber,[12,13] BPO radical is actively involved in creating grafting sites by abstracting allylic hydrogen atom) and compatible with the homopolymers used in this investigation.[14] It is, therefore, appropriate to assume that the involvement of growing polymeric chains in creating active centers is more likely than the initiator radical itself.

The chain transfer constants $(C_p)$ of CR in the presence of ethyl acrylate as well as butyl methacrylate were evaluated and the values are $0.7 \times 10^{-3}$ and $1.1 \times 10^{-3}$, respectively.[15] The $C_p$ values for the same substrate with other acrylate monomer systems were of the same order.[16] The observed high values of $C_p$ indicate the occurrence of chain transfer process in this system.

## Grafting Efficiency

To augment the effectiveness of grafting of the backbone chain with monomers employed, one should evaluate the grafting efficiency and percentage grafting.

The grafting efficiency (GE) was calculated using

$$\text{percent grafting efficiency} = \frac{\text{weight of grafted PEA}}{\text{weight of grafted PEA} + \text{weight of homo PEA}} \times 100$$

The percentage grafting was calculated as follows:

$$\text{percent grafting} = \frac{\text{weight of grafted PEA}}{\text{weight of backbone polymer}} \times 100$$

The grafting efficiency for ethyl acrylate is given in Tables I and II, while that for butyl methacrylate is given in Tables III–VI. The effect of monomer con-centration on grafting efficiency are presented in Tables II and V. The per-centage of grafting and the molecular weights were increased as monomer con-centration was increased. Since the percentage grafting depends on the amount of grafted polymer, the added monomer evidently increases the percentage grafting and molecular weight. The percent grafting efficiency decreases with the increase in the concentration of the monomer. The decrease in grafting ef-ficiency may be attributed to the predominance of chain transfer to monomer with increase of monomer concentrations. This leads to more of the homo-polymer formation.

The influence of initiator concentration on grafting has been studied (Table III). Both percentage and percentage grafting efficiency decrease with the in-crease in initiator concentration. From this observation, it can be concluded that the maximum grafting efficiency may be obtained with the lower amount of initiator concentration in both the cases. The decrease of grafting efficiency also supports the occurrence of chain transfer process.

The grafting reactions were carried out between 60 and 80°C (Tables I and VI). The percentage grafting increases and percentage grafting efficiency de-creases with the increase in temperatures. The chain transfer reactions usually have higher activation energy and at higher temperature chain transfer to polymer will be more. Consequently there will be increase in percentage grafting (Tables I and VI). The decrease of grafting efficiency may be due to acceleration of the termination process, which leads to formation of higher amount of ho-mopolymer.

## Molecular Weight of Homopolymers

Since the present system follows the conventional kinetic behavior, the molecular weight of PEA and PBMA should, therefore, show a linear relationship with reciprocal monomer concentration. The plot shows (Fig. 4) good straight lines and gives support for the observed kinetic behavior of the system. The ordinate intercept shows the effect of chain transfer process observed in the present system.

It would be of great interest to remove branches by the selective cleavage of backbone polymer. Unfortunately, this is not possible in the present case and a direct determination of molecular weight of branches cannot be made. However, the molecular weights of the branches are assumed to be equivalent to the molecular weights of the homopolymers formed along with the grafted polymer. Similar cases are reported in literature.[12] $\overline{M}_v$, the viscosity average molecular weights of separated homopolymers of PEA and PBMA, were given in tables, which represent the chain length of both free and grafted polymers in general.

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