# Grafting of Methyl Methacrylate onto Guar Gum by Hydrogen Peroxide Initiation

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## Synopsis

Graft copolymerization of methyl methacrylate (MMA) onto guar gum (GG) in aqueous slurry has been carried out using hydrogen peroxide ($H_2O_2$) as initiator. The copolymers were characterized by infrared spectroscopy. The grafting parameters like percent grafting, grafting efficiency, percent add-on, and the grafting frequency were determined, and the effect of reaction time, concentration of initiator, and [GG]/[MMA] ratios on the grafting parameters have been discussed. The decrease in % add-on at increasing concentration of $H_2O_2$ indicated enhancement in the rate of homopolymerization of methyl methacrylate.

## INTRODUCTION

The grafting of thermoplastics onto cellulosic materials is useful in obtaining moldable products with high concentrations of relatively inexpensive naturally occurring cellulosic polymers. Otey[1] has reviewed the biodegradable plastics and films in terms of their use and technical importance. The studies on compatibility of unmodified starch,[2] as well as vinyl monomers such as acrylonitrile and methyl methacrylate (MMA) grafted starch fillers,[3] with the synthetic resins revealing the fact that the use of unmodified starch which is hydrophilic has poor compatibility with the hydrophobic resins. PVC resins filled with such graft copolymers yielded high strength plastic products that appear to have industrial significance.

Hebeish and Guthrie[4] have reviewed the grafting behaviors of different starch and celluloses in detail.

There are many reports that the cellulosic materials can initiate graft copolymerization when they were heated with vinyl monomer and water, even in the absence of a radical initiator.[5-10]

As far as the guar gum (GG) and other important polysaccharides are concerned, no one has drawn proper attention regarding grafting behavior. As such, GG is not found to initiate graft copolymerization. Considering the oxidation state of cellulosic material responsible for initiating the graft copolymerization, oxidized GG has been employed, and the grafting behavior of MMA on to oxidized GG has been comprised in the present investigation. The object of this work was to determine the grafting parameters and to study the influence of various reaction conditions on them. The copolymers were also characterized by infrared spectroscopy.

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RAVAL, PATEL, AND PATEL

## EXPERIMENTAL

### Materials

All the chemicals and solvents used were analytical grade reagents. MMA was washed with 5% aqueous alkali to remove phenolic inhibitor and then distilled. Fresh distillate was used for each reaction. The solvents methanol and benzene were distilled and middle fractions were collected for the use. Hydrogen peroxide (30% w/w) was used as received. Commercially available high purity, food-grade guar flour of single lot was employed for the grafting reactions. A 500 mL three-necked round-bottom flask equipped with a thermometer, a stirrer, and a condensor was employed as the reaction vessel.

### Graft Copolymerization

Guar was slurried in water to a 1% concentration, oxidized by a desired concentration of hydrogen peroxide ranging from $5.0 \times 10^{-3}M$ to $20 \times 10^{-3}M$ at 60°C for 30 min. Required amount of MMA (0.1 mol) was charged at a time, and the copolymerization was carried out at 85°C for different time intervals. The temperatures were maintained by thermostatically controlled waterbath. The polymerization was stopped by adding a small amount of hydroquinone. The reaction mass was cooled and coagulated by the addition of methanol, filtered, washed, and dried. Homopolymer was separated by benzene extraction till no precipitates were found by adding methanol to the extracted solvent. The grafting parameters like percent grafting, grafting efficiency, percent add-on, and grafting frequency were calculated by applying their standard definitions as described below[11]:

% grafting       = ratio of wt increase to wt of initial GG

$$= \frac{\text{wt extracted product} - \text{initial wt GG}}{\text{initial wt cellulose}} \times 100$$

grafting efficiency = ratio of the amount of grafted monomer to the total weight of monomer that was polymerized

$$= \frac{\text{wt extracted product} - \text{initial wt of GG}}{\text{wt crude product} - \text{initial wt GG}} \times 100$$

percent add-on    = amount of pure copolymer

$$= \frac{\text{wt extracted product} - \text{initial wt GG}}{\text{wt extracted product}} \times 100$$

$$\text{grafting frequency} = \frac{\text{anhydroglucose units (mol)}}{\text{grafted PMMA (mol)}}$$

The grafted side chains were separated by employing a fast technique to hydrolyze the polysaccharide.[12] The grafted poly(methyl methacrylate)

TABLE I
Reproducibility of the Grafting Reactions[a]

| No. | Total conversion (g) | Copolymer yield (g) | Percent grafting | Percent add-on | $\overline{M}_n$ of grafted chain | Frequency of grafts (AGU/mol) |
|-----|------|------|-------|-------|---------|------|
| 1 | 4.01 | 3.23 | 61.50 | 38.10 | 198,000 | 1987 |
| 2 | 4.10 | 3.15 | 57.56 | 36.51 | 185,000 | 1986 |
| 3 | 4.38 | 3.20 | 60.09 | 37.50 | 189,000 | 1944 |

[a]GG = 2.0 g (dry basis); MMA = 10 g = 10.65 mL; $H_2O_2$ = 5 × $10^{-3}M$; reaction time = 1 h; temp = 85°C.

(PMMA) remains as a white insoluble mass on the water. The polymer so obtained was dissolved in benzene and reprecipitated in methanol to remove any impurities. The number average molecular weight was obtained from the intrinsic viscosity in benzene at 30°C by means of the following equationU1[3]:
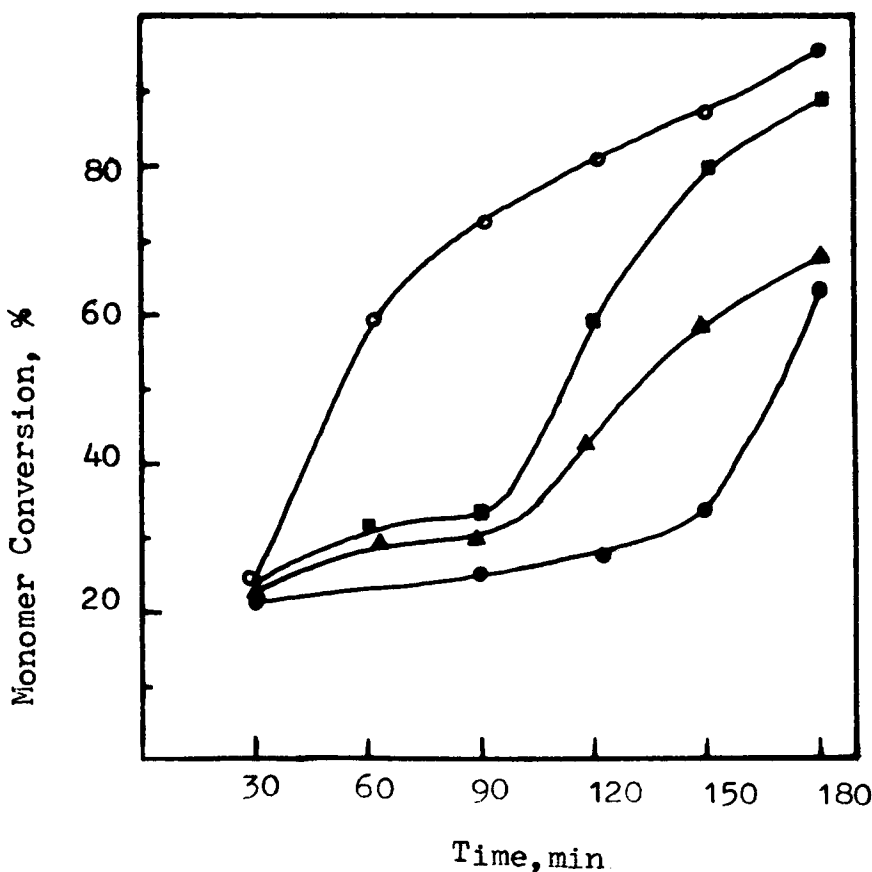
$$[\eta] = 8.69 \times 10^{-5}\overline{M}_n^{0.76}$$



Fig. 1. Total conversion of monomer in grafting of MMA onto GG. Reaction conditions: GG = 2.0 g (dry basis), MMA = 10 g, $H_2O_2$ = 5 × $10^{-3}M$ (●), 10 × $10^{-3}M$ (▲), 15 × $10^{-3}M$ (■), and 20 × $10^{-3}M$ (○), and temperature = 85°C.

## RESULTS AND DISCUSSION

Three reactions were conducted under identical conditions, and the results are presented in Table I. The reproducibility of these experiments within 5% of total conversion appears to be adequate for our purposes. Experiments performed under other reaction conditions were not repeated. It was of interest to observe the effects of $H_2O_2$ concentration, amount of guar gum (GG), and reaction time on the grafting parameters. The initiator concentration was varied from $5 \times 10^{-3}M$ to $20 \times 10^{-3}$ mol/L. The concentration of anhydroglucose units was varied by increasing the amount of GG charged per batch from 2 to 10 g on a moisture free basis. The amount of MMA used was 10 g (10.65 mL) for grafting in each batch.

The percent add-on values, weight of synthetic polymer grafted per 100 g of copolymer produced, vary between 20 to 52%, yielding low to moderately high grafting efficiency from 7 to 61% along with the considerable amount of homopolymer PMMA. The total conversions of MMA to polymer with respect
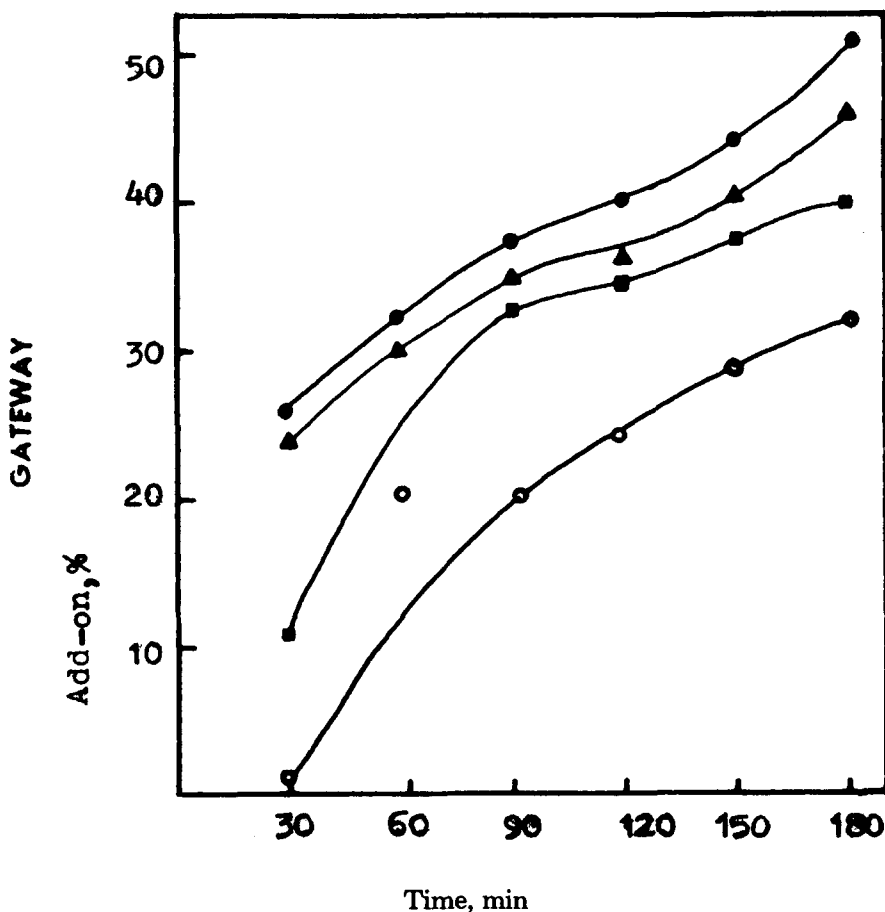


Time, min

Fig. 2. Percent add-on in grafting of MMA onto GG. Reaction conditions: GG = 2.0 g (dry basis), MMA = 10 g, $H_2O_2$ = $5 \times 10^{-3}M$ (●), $10 \times 10^{-3}M$ (▲), $15 \times 10^{-3}M$ (■), and $20 \times 10^{-3}M$ (○), and temperature = 85°C.

to initiator concentrations and reaction time are shown in Figure 1; a higher percent conversion was observed with a higher concentration of initiator. The percent conversion peculiar to each concentration of initiator appeared to be almost attained after 3 h of reaction time. The decrease in percent add-on at higher concentration of H$_2$O$_2$, as revealed from Figure 2, indicates enhancement in the rate of homopolymerization. Even after polymerization period of 3 h, only 33% add-on has been achieved at $20 \times 10^{-3}M$ H$_2$O$_2$, while 52% add-on has been achieved by $5 \times 10^{-3}M$ H$_2$O$_2$. This might be viewed as the severe oxidation states of GG reduce the grafting efficiency. The situation favoring homopolymerization rather than grafting at higher H$_2$O$_2$ concentration might be attributed to the greater availability of free radicals. It has also been observed that in aqueous polymerization, the growing PMMA chains are more compatible with MMA monomer,[14] and this in turn increases the rate of termination of the growing grafted chains by monomer, resulting in lower
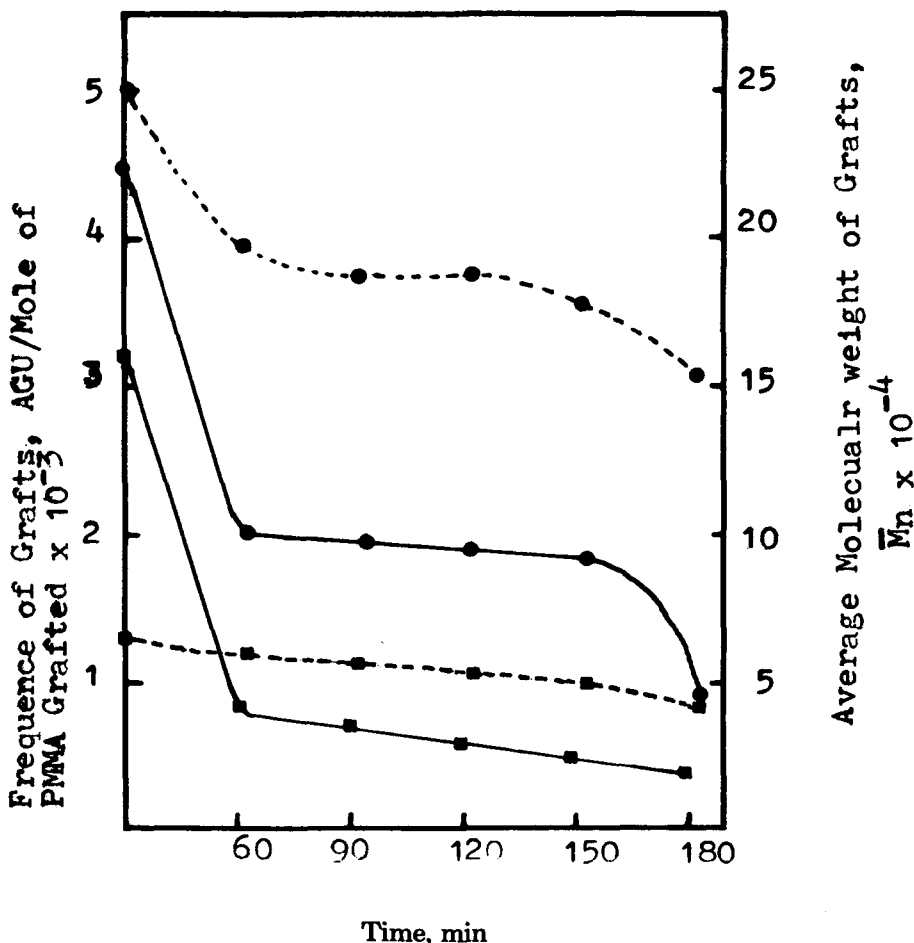


Fig. 3.  Average molecular weight of grafts (---) and frequency of grafts (—) in grafting of MMA onto GG. Reaction conditions: GG = 2.0 g (dry basis), MMA = 10 g, H$_2$O$_2$ = $5 \times 10^{-3}M$ (●), and $15 \times 10^{-3}M$ (■), and temperature = 85°C.
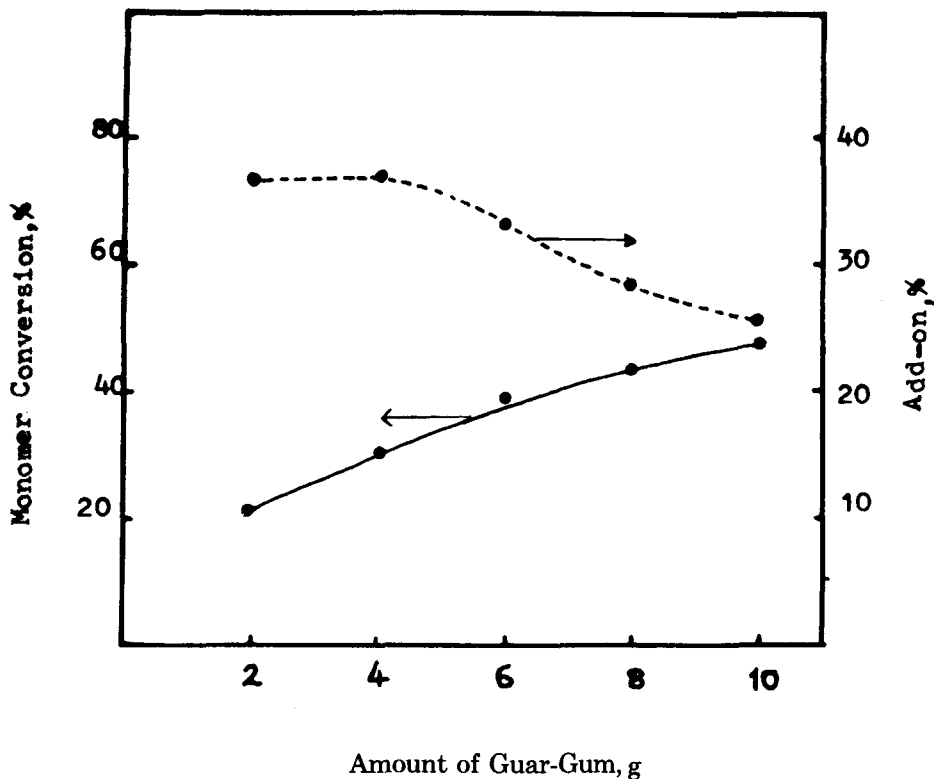
Fig. 4. Total conversion of monomer (—) and % add on (---) in grafting of MMA on to GG. Reaction conditions: MMA = 0.1 mol = 10 g, $H_2O_2 = 5 \times 10^{-3}M$, reaction time = 1 h; temperature = 85°C.

grafting. Thus the role of monomer–polymer compatibility may also be considered for the lower grafting efficiency.

The variation in grafting frequencies and molecular weights of the grafted PMMA chains with reaction time for $5 \times 10^{-3}M$ and $20 \times 10^{-3}M$ $H_2O_2$ has been plotted in Figure 3. At $H_2O_2$ concentrations of $5 \times 10^{-3}$–$20 \times 10^{-3}M$, the average molecular weights of PMMA grafts are found to be decreased. This appears to be due to higher propagation rates at lower $H_2O_2$ concentrations, caused by higher ratios of MMA to the total number of radicals initiating grafting. A fact that increase in percent add-on decreases the molecular weights of grafted PMMA peculiar to each $H_2O_2$ concentrations (Figs. 2 and 3) clearly indicates that the increased conversion of monomer to the grafts was due to the formation of more frequent grafts during the course of reaction. This has been observed as the decrease in grafting frequency, AGU per mole of PMMA grafted as shown in Figure 3.

Increase in the amount of GG charged per batch, keeping $H_2O_2$ and MMA concentrations constant, means increase in the GG to $H_2O_2$ and GG to MMA ratios. The amount of GG was varied fivefold, from 2 to 10 g. Figure 4 depicts that net conversion of MMA to PMMA increased from 21 to 47.8% as the amount of GG was increased from 2 to 10 g, whereas percent add-on decreased from 36.5 to 25.9% in the same range. The increase in monomer conversion
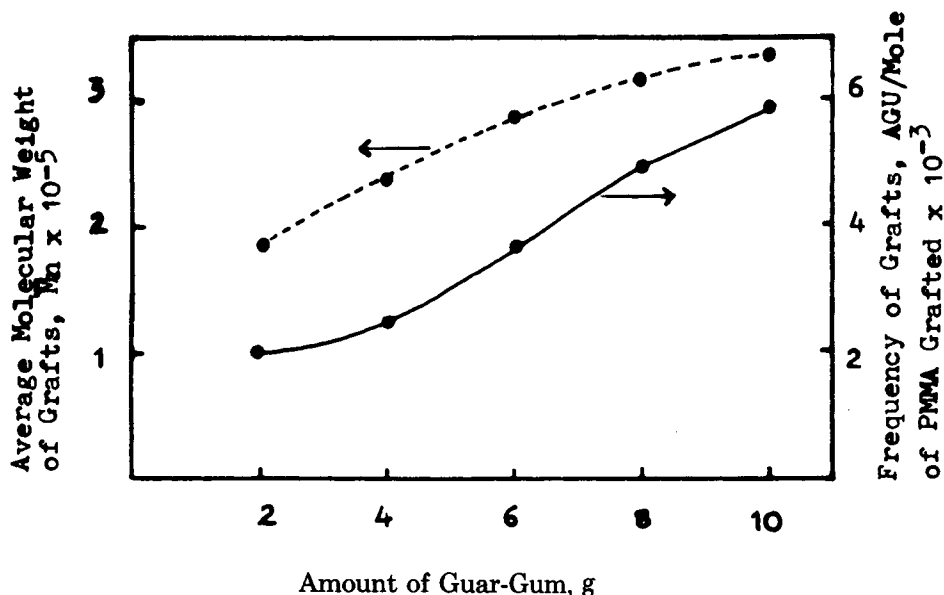
Fig. 5. Average molecular weight of grafts (---) and frequency of grafts (—) in grafting of MMA on to GG. Reaction conditions: MMA = 0.1 mol = 10 g, $H_2O_2 = 5 \times 10^{-3}M$; reaction time = 1 h; temperature = 85°C.

with increase in GG appears to be due to a larger number of initiation sites. The percent add-on shows a decreasing tendency with increasing the amounts of GG. This might be explained as the increase in the amount of GG charged decreases the monomer to GG ratio.

As shown in Figure 5, increasing the [GG]/[$H_2O_2$] and [GG]/[MMA] ratios by a factor of 5 increase the frequency of grafts, AGU per mole of polymer grafted, almost proportionately. This may be interpreted as the higher [GG]/[$H_2O_2$] ratio produces less active sites for grafting causing increase in grafting frequency by a factor of 3. The increase in molecular weights of the grafts suggests that polymerization of MMA onto GG, with the abundance of GG in medium, takes place preferentially in the GG matrix. Hence the integrated surface area of the GG greatly affects the diffusion of the monomer and free radical species.

The infrared spectra recorded on a Perkin-Elmer IR 983 spectrophotometer using KBr pellets for the comparative study of the spectra for PMMA (a), GG-g-PMMA (b), and GG (c) (Fig. 6) yielded the sound evidence of grafting. In the spectra of GG-g-PMMA presence of the peaks at 1740 and 2960 cm$^{-1}$, respectively, due to the carbonyl stretching and asymmetric stretching of methyl group clearly indicated the presence of PMMA grafted to GG.

Our attempts to obtain high grafting efficiencies with vinyl monomers by $Ce^{+4}$ initiation without $N_2$ atmosphere failed. Although prescribed $H_2O_2$ initiation has been successfully employed to other monomers also. Results of evaluation of properties of GG graft copolymers with acrylonitrile, methyl acrylate, and acrylamide and TGA studies of the graft copolymers may be published in forthcoming papers.
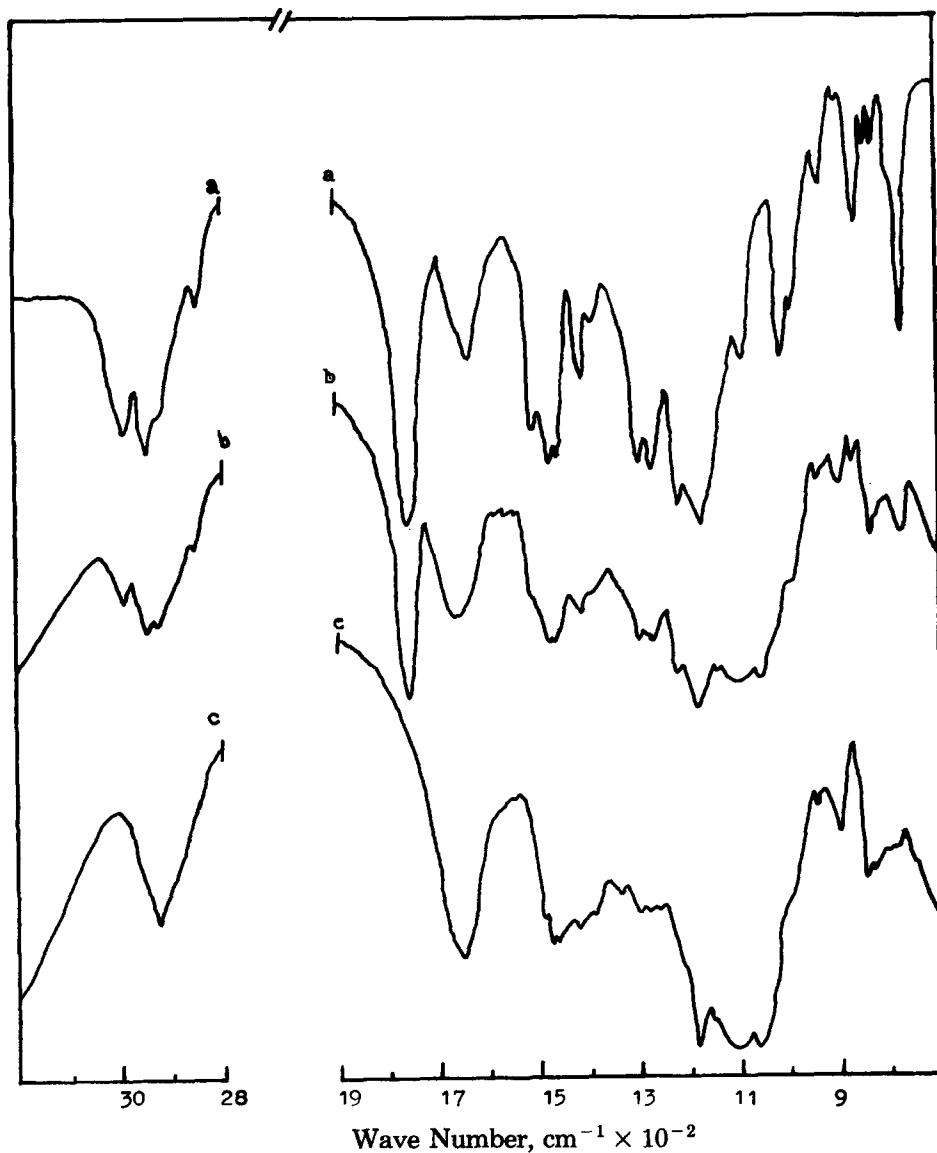
Fig. 6.   Infrared spectra of (a) PMMA, (b) GG-g-PMMA, and (c) GG.

## CONCLUSIONS

MMA can be graft-copolymerized onto GG efficiently in aqueous slurry under a wide range of reaction conditions. Changes in the reaction time and concentrations of $H_2O_2$ and GG influence appreciably the grafting parameters like add-on, conversion of MMA monomer to polymer, and frequency of grafts (AGU/mol PMMA grafted).

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