

## Graft Copolymerization of Methyl Methacrylate and Natural Rubber

PREMAMOY GHOSH\* and PRANAB K. SENGUPTA, *Department  
of Applied Chemistry, University College of Science and Technology,  
Calcutta, India*

### Synopsis

Graft copolymerization of natural rubber and MMA was carried out in the presence of  $Bz_2O_2$  or AIBN as thermal initiator and hydrogen peroxide or benzophenone as photosensitizer. From the overall copolymerization product, the rubber-PMMA graft copolymer fraction was isolated from unreacted rubber and free PMMA fractions and composition characterization of the separated fractions was done by determination of rubber unsaturation. The efficiency of grafting under different conditions has been calculated and compared.

### INTRODUCTION

The graft copolymerization of methyl methacrylate (MMA) with natural rubber provides a unique system involving a naturally occurring polymer and a synthetic polymer, in that it can be carried out in solution, in emulsion using the latex rubber or by swelling the rubber in bulk monomer, by thermal or photochemical means with or without sensitizers, or by mechanochemical processes.<sup>1-4</sup> Characterization of the copolymerization product depends largely on an elaborate and precise separative procedure which would separate the unreacted rubber hydrocarbon and the free poly(methyl methacrylate) (PMMA) from their graft copolymer.

Selective extraction and fractional precipitation have been usually employed in order to separate the overall graft copolymerization product to the above three polymeric entities and ozonolysis, has generally been employed<sup>5,6</sup> in determining the composition of the graft copolymer fraction. Perbenzoic acid oxidation or infrared spectroscopy has also been used for the analysis of rubber in the copolymer.<sup>7</sup> In this paper we report the results on the composition characterization of natural rubber-PMMA graft copolymerization products prepared under varied conditions. Our results are based on the above separative procedure and on a simple method of determination of rubber unsaturation by additive bromination.

\* Present address: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York.

## EXPERIMENTAL

### Materials

Pale yellow crepe (natural) rubber of 93.7% assayed hydrocarbon content and intrinsic viscosity of 3.7 dl./g. in toluene solution at 30°C. was used in all experiments without any purification and processing. Stabilized MMA was freed of stabilizers and dried by the usual procedures and was distilled under reduced pressure before use.

### Polymerization Procedure

Rubber solution of known concentration in toluene, known amounts of an initiator (benzoyl peroxide,  $Bz_2O_2$ , or azobisisobutyronitrile, AIBN, both recrystallized) and MMA were mixed together in clean Pyrex tubes which were then sealed under vacuum. Some experiments were done in nitrogen atmosphere, and they showed no appreciable difference in polymerization rate. In some experiments a known amount of rubber was allowed to swell in a fixed volume of the monomer containing the catalyst for about 24 hr. in the dark at room temperature under nitrogen atmosphere and then the contents were sealed under vacuum. Polymerization was allowed to proceed at a specified temperature for a specified time and was arrested by precipitating the whole polymer in a large excess of methanol.

MMA containing hydrogen peroxide ( $H_2O_2$ ), which was extracted in MMA from 30% hydrogen peroxide by the method of Nandi and Palit,<sup>8</sup> was also used with rubber solution in toluene; polymerization was carried out at 30°C. in sunlight under nitrogen. Some polymerization experiments under nitrogen were also done in presence of ultraviolet light in a system containing known amounts of rubber, MMA, and benzophenone, the latter being used as a photosensitizer.<sup>9</sup>

### Separation of the Graft Copolymerization Product into Constituent Polymeric Entities

The polymers precipitated in methanol were filtered after long standing (>15 hr.), washed with methanol, and dried at 40–45°C. in vacuum and weighed. A sample of this dried polymer will be termed gross polymer. The gross polymers were separated into unreacted rubber, rubber-PMMA graft copolymer, and free PMMA fractions by a method of selective extraction and fractional precipitation similar to that described by Allen and Merrett<sup>10</sup> with some modifications.

Free soluble rubber was extracted from a known amount of the gross polymer with a benzene-petroleum ether (b.p. 80–100°C.) mixture at room temperature for 24 hr. and then at 40–45°C. for about 1 hr. About 80 ml. of the solvent mixture was used per gram of gross polymer. The ratio of benzene to petroleum ether was adjusted and the maximum percentage of benzene used was 50%. When a large proportion of rubber was present in the graft copolymer, a much lower percentage of benzene was used

(25–35%), as a 1:1 mixture of the solvents caused part of the graft copolymer to dissolve, which was evidenced by the cloudy or turbid nature of the extract. When the extract made with 1:1 solvent mixture was cloudy or turbid, the right proportion of the two solvents was attained by slowly adding just enough petroleum ether so as to clarify the solvent phase on stirring and standing. After extraction with the solvent mixture, the residual polymer was treated successively with 20 ml. portions of petroleum ether of boiling range 60–80°C. and 40–60°C. under reflux to remove the last traces of free soluble rubber. All these extract solvents were mixed together and evaporated under vacuum at near room temperature. The residue left after evaporation was the free soluble rubber.

After extraction of the free soluble rubber, the residual polymer was dried and weighed and was then dissolved in benzene to give an apparently clear solution (2–5%) and was fractionally precipitated with methanol at room temperature. On addition of 2–5 ml. of methanol a very faint turbidity appeared, and the solution was centrifuged (8000 rpm) at this stage for 15–20 min., and a very small amount of crosslinked, insoluble rubber was usually found to separate out. More methanol was slowly added with stirring to the decanted centrifugate until flocculation of the graft copolymer just started. The system was then cooled by 5–10°C. for 10 min. and then allowed to stand at room temperature. The graft copolymer fraction was thus completely separated. The clear supernatant solution did not show an increase in turbidity on further addition of 0.5–1 ml. methanol. It was then decanted out and the last (free PMMA) fraction was precipitated out with a large excess of methanol and a little petroleum ether.

The separated polymer fractions were all dried in vacuum at 40°C. and weighed. Known amounts of these fractions (except the insoluble free rubber fraction) were then dissolved in benzene and brominated by the modified bromination method of Gowans and Clark,<sup>11</sup> iodine bromide in carbon tetrachloride being used as the reagent. The method of bromination and isolation of the product have been described elsewhere.<sup>12</sup> This has been found to be a method of exclusively additive bromination at rubber unsaturation, and the gain in weight on bromination was used to calculate the rubber hydrocarbon content in a given fraction.<sup>11,12</sup> Pure PMMA gave no increase in weight on treatment with the brominating solution. The spectrophotometric method<sup>12</sup> developed in our laboratory for the determination of traces of rubber unsaturation (the method being based on the color reaction between brominated rubber and phenol) was used to check the separative procedure and the rubber content of some of the graft copolymer fractions.

## RESULTS AND DISCUSSION

Tables I–IV show the results of graft copolymerization and subsequent composition characterization experiments. Almost all gross polymer

TABLE I  
 Graft Copolymerization of Natural Rubber and Methyl Methacrylate<sup>a</sup>

System	Wt. rubber hydrocarbon, g.	Temperature, °C.	Initiator	Initiator concn., mole/l.	Time of polymerization, hr.	$E_M$	Grafting efficiency, % $E_R$
A <sup>b</sup>	0.0707	60	Bz <sub>2</sub> O <sub>2</sub>	0.0056	1	15.6	7.6
				"	2	33.3	12.7
				"	3	62.2	30.3
				"	4	62.5	44.4
				"	5	60.4	68.1
B	0.0981	60	Bz <sub>2</sub> O <sub>2</sub>	0.0041	5	60.4	55.9
				0.0124	5	60.0	82.2
				0.0248	5	43.4	92.2
				0.0413	5	39.0	92.8
				0.0081	3	20.8	13.3
C <sup>c</sup>	0.0736	60	AIBN <sup>d</sup>	"	5	38.4	19.2
				0.0244	5	19.4	36.8
				0.0375	3	—	—
				"	5	36.3	21.5
				"	7	24.7	31.5
D	0.0761	30	H <sub>2</sub> O <sub>2</sub> , sunlight	"	10	39.6	34.6
				"	15	26.8	52.4
				"	15	—	—

<sup>a</sup> Toluene, 4 ml.; MMA, 3 ml.

<sup>b</sup> Observed values of  $x = (\text{bound PMMA})/(\text{free PMMA})$  range from 0.18 to 1.5; assuming simple chain transfer as the only graft copolymer producing reaction, the calculated value of  $x$  is about 0.12, the degree of polymerization of PMMA prepared in rubber free system in an otherwise fixed condition being 4800.

<sup>c</sup> With 0.0081 mole/l. AIBN, the observed values of  $x$  range from 0.25 to 0.6; assuming simple chain transfer as the only graft copolymer producing reaction, the calculated value of  $x$  is about 0.046, the D.P. of PMMA prepared in a rubber-free system (other conditions being fixed) being 1500.

<sup>d</sup> In AIBN-initiated system, although appreciable polymer was formed in the first hour, the formation of graft copolymer was negligible.

TABLE II  
Effect of Variation of Monomer Concentration and Temperature on Graft Copolymerization<sup>a</sup>

System	Wt. rubber hydrocarbon, g.	Volume, MMA, ml.	Temperature, °C.	Grafting efficiency, %	
				$E_M$	$E_R$
A	0.0674	0.5	60	56.6	52.8
	0.0674	1.0	60	42.7	63.2
	0.0674	2.0	60	55.1	72.3
B	0.0707	3.0	45	No polymer formation	
	0.0707	3.0	60	60.4	68.2
	0.0707	3.0	70	77.8	95.0
	0.0707	3.0	80	54.0	96.0

<sup>a</sup> Initiator,  $Bz_2O_2$ , 0.0056 mole/l.; time of polymerization, 5 hr.; total volume (rubber solution + MMA), 7 ml.

TABLE III  
Effect of Variation of Rubber Concentration on Graft Copolymerization<sup>a</sup>

Wt. rubber hydrocarbon, g.	Grafting efficiency, %	
	$E_M$	$E_R$
0.0958	58.4	79.2
0.1901	53.9	68.2
0.2860	75.9	46.0
0.4770	82.9	46.0
0.7610	81.9	45.9

<sup>a</sup> MMA, 3 ml.; toluene, 4 ml.; temperature, 60°C.;  $Bz_2O_2$ , 0.0056 mole/l.; time of polymerization, 6 hr.

TABLE IV  
Ultraviolet-Induced Graft Copolymerization of Natural Rubber and MMA in Presence of Benzophenone as Sensitizer<sup>a</sup>

Time of polymerization, hr.	Grafting efficiency, %	
	$E_M$	$E_R$
4	66.8	42.7
6	81.6	50.0
9	89.0	62.5

<sup>a</sup> Rubber hydrocarbon, 0.0937 g.; MMA, 5 ml.; benzophenone, 0.055 mole/l. based on MMA; temperature, 30°C.

samples were found to contain some free unreacted rubber. The grafting efficiency based on rubber  $E_R$  is expressed as the percentage of total rubber hydrocarbon appearing in the graft copolymer and that based on PMMA,  $E_M$  is expressed as the percentage of total PMMA appearing in the copolymer.

The amount of insoluble rubber obtained in most of the experiments was rather small, and precise determination of the insoluble form of rubber

in the gross polymer was not attempted in all the experiments. The insoluble rubber separating out at the early stage of fractional precipitation with methanol was centrifuged out and was usually rejected.

During thermal polymerization catalyzed by  $Bz_2O_2$  in the presence of a fixed low concentration of rubber,  $E_M$  values increase with time in the beginning and then level off or decrease, while  $E_R$  values show a continuously increasing trend over the same overall period of polymerization (5 hr.) (Table IA). The effects of variation of initiator ( $Bz_2O_2$ ) concentration, monomer concentration, and temperature on graft copolymer formation are shown in Table IB and Table II. Under the given conditions in Table IIB, the  $E_M$  values pass through a maximum of about 80% at nearly 70°C. and then fall off with further rise in temperature, while  $E_R$  values rise much more sharply with rise in temperature at the beginning and then level off at nearly 100%  $E_R$  value in the higher temperature range. Increased proportions of rubber in an otherwise fixed condition enhance retardation of polymerization, and  $E_M$  values show an increasing trend while  $E_R$  values follow the opposite trend (Table III).

It has been reported earlier<sup>6,10</sup> that when AIBN is used as the initiator, formation of rubber-PMMA graft copolymer is insignificant or negative. Our observations stand in contradiction to this. We have been able to isolate graft copolymer in significant quantities in AIBN-initiated systems under the conditions given in Table IC, although the grafting efficiency ( $E_M$  or  $E_R$ ) is much less than that observed in equivalent experiments with  $Bz_2O_2$  as the initiator.

Hydrogen peroxide, when used as a photoinitiator in presence of sunlight, yields graft copolymer with relatively low grafting efficiency (Table ID), but benzophenone, when used as the photosensitizer in presence of ultraviolet light in a system of rubber swelled in MMA, yields graft copolymer with relatively high grafting efficiency; in this case  $E_M$  values are much higher than corresponding  $E_R$  values (Table IV). Appreciable unreacted free rubber appears in insoluble form, particularly with increasing period of photosensitization in presence of benzophenone. In the absence of benzophenone very little graft copolymer is formed. When dilute toluene solution of rubber (2-4%) is used in presence of benzophenone and MMA and the system placed in ultraviolet light, little polymerization is observed in about 5 hr.

The separative procedure for the gross polymer products has been found to be reproducible. Precise separation of graft copolymer fractions from free PMMA fractions was easily checked by testing for the color reaction between the respective brominated samples and phenol. For free PMMA samples the color test was negative or negligible.

It appears from composition characterization experiments, based on determination of rubber unsaturation, that very little unsaturation in rubber is lost; it is assumed that in the crosslinked free rubber fraction, however small, unsaturation is not lost to any significant extent.

The NMR spectra of a purified natural rubber sample, a pure PMMA sample (initiated by  $Bz_2O_2$  at 60°C.), and a purified natural rubber-PMMA

graft copolymer of 17.3% rubber hydrocarbon content as determined by bromination method (graft copolymerization initiated by  $Bz_2O_2$  at  $60^\circ C$ .) are shown in Figure 1. The spectra were taken with about 15% solution of the polymers in deuteriochloroform in a Varian A-60 NMR spectrometer. The proportion of methylene, methoxy, and methyl protons of the copolymer, calculated and observed, are given at the top of the spectrum of the graft copolymer, the NMR analysis being based on calculation of areas

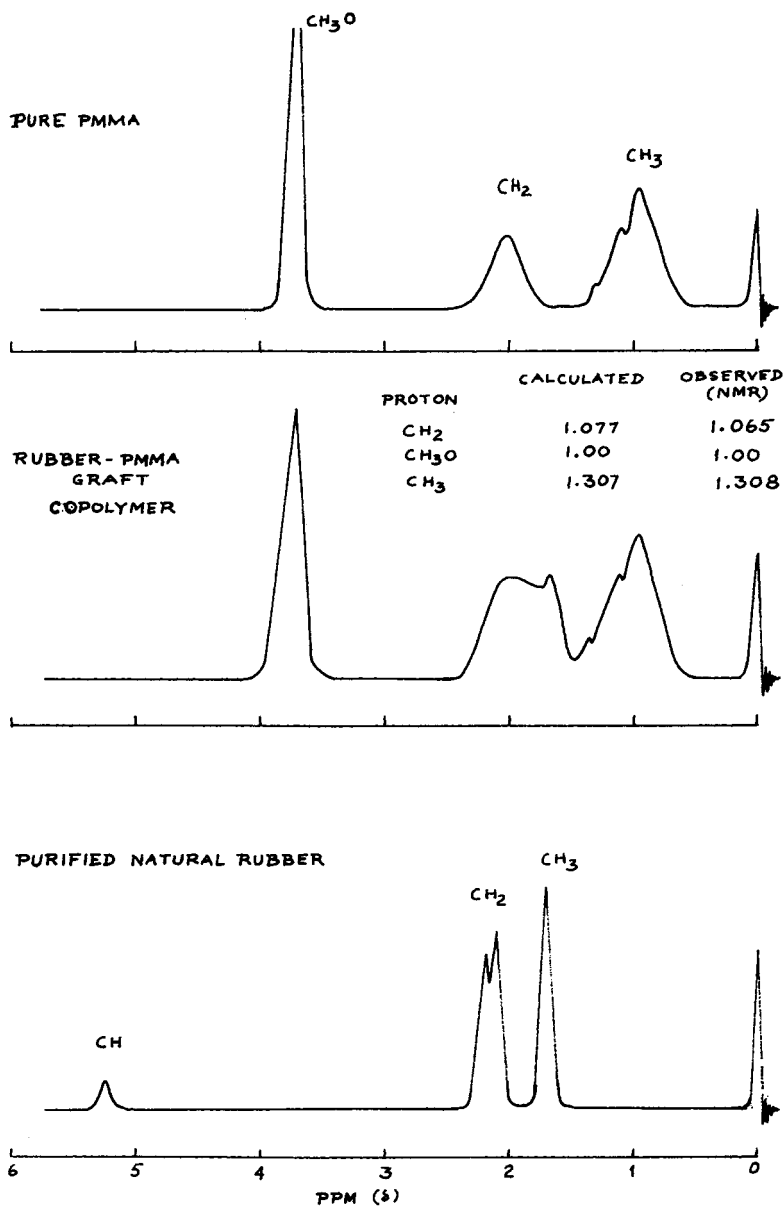


Fig. 1. NMR spectra of natural rubber, PMMA, and the graft copolymer.

under respective peaks given by the signal integrator of the Varian A-60. The calculated and observed values are in good agreement.

### Mechanism

Our results on  $Bz_2O_2$ -catalyzed graft copolymerization are in agreement with those of Scheele and Rhode<sup>13</sup> on rubber vulcanization. Loss of unsaturation is very slight,<sup>14</sup> and in some cases it may be within the limits of experimental error; the amount of crosslinked rubber formed is also relatively small. The ratio  $x$  of bound PMMA to free PMMA in the grafting experiments is generally much higher than the same calculated on the basis of grafting reaction, being entirely due to transfer reaction between growing PMMA chains and isoprene units of the rubber chains; e.g., under experimental conditions of Table IA the value of  $x$  calculated on the basis of the transfer reaction alone is about 0.12, but the observed values range from 0.18 to 1.5. Thus it is indicated that transfer reaction has only a minor contribution, if it contributes at all, to the formation of graft copolymer. Graft copolymer formation thus appears to be primarily due to polymer growth on isoprenyl radicals,  $-\dot{C}H-C(CH_3)=CH-CH_2-$ , formed in the system by the abstraction of relatively labile hydrogen atoms of  $\alpha$ -methylene groups in rubber chains by the primary radicals derived from  $Bz_2O_2$ .<sup>13</sup>

Likewise, in AIBN-catalyzed systems the observed ratio of bound PMMA to free PMMA is much higher than that calculated on the basis of transfer reaction. This indicates that primary or secondary radicals derived from AIBN abstract  $\alpha$ -methylene hydrogens from rubber chains to a significant extent to give rise to radical sites for the growth of PMMA grafted chains in presence of MMA. A rubber-MMA system with AIBN as the catalyst, when placed in ultraviolet light at room temperature, gave a hard product within 2-3 hr. which could not be properly characterized due to its near insolubility in benzene or other common solvents. In view of the disproportionation reaction of primary isobutyronitrile radicals,<sup>15</sup> their reported reactivity toward halogenated benzenes,<sup>16</sup> and absence of significant initiator effect<sup>17</sup> in graft copolymerization of vinyl acetate and PMMA, the reactivity of isobutyronitrile radicals or unstable reaction products derived from them [dimethyl-*N*-(2-cyano-2-propyl)ketenimine] with rubber molecules would not be altogether unexpected. Hammond et al.<sup>18</sup> reported that the ketenimine intermediate formed in the decomposition of AIBN easily reacted by a free-radical mechanism with mercaptans and halogenated compounds. Although graft copolymer has been isolated in AIBN-initiated systems, our experiments show that the effectiveness of AIBN in producing rubber-PMMA graft copolymer is much less than that of  $Bz_2O_2$ , and this is perhaps due to higher stability of the isobutyronitrile radicals due to resonance than the benzoyloxy radicals.

Formation of graft copolymer in the photosensitized systems presumably takes place by the same mechanism as above. Formation of higher proportions of insoluble rubber in the presence of benzophenone appears to be due



to significant crosslinking of natural rubber induced by ultraviolet light and aided by the presence of the photosensitizer.<sup>9</sup>

P. K. SenGupta is grateful to the University Grants Commission, India for financial support. The interest of Dr. P. K. Chowdhury in this work is sincerely acknowledged. Thanks are due to Prof. F. W. Billmeyer, Jr. for reviewing the manuscript.

### References

1. F. M. Merrett, *Trans. Faraday Soc.*, **50**, 759 (1954).
2. W. Cooper, W. Vaughan, S. Miller, and M. Fielden, *J. Polymer Sci.*, **34**, 651 (1959).
3. E. G. Cockbain, T. D. Rendle, and D. T. Turner, *J. Polymer Sci.*, **39**, 419 (1959).
4. D. T. Angier and W. F. Watson, *J. Polymer Sci.*, **20**, 235 (1956).
5. W. Kobryner and A. Banderet, *J. Polymer Sci.*, **34**, 381 (1959).
6. P. W. Allen, G. Ayrey, and C. G. Moore, *J. Polymer Sci.*, **36**, 55 (1959).
7. J. A. Blanchett and L. E. Nielson, *J. Polymer Sci.*, **20**, 317 (1956).
8. U. S. Nandi and S. R. Palit, *J. Polymer Sci.*, **17**, 65 (1955).
9. G. Oster, G. K. Oster, and H. Moroson, *J. Polymer Sci.*, **34**, 671 (1959).
10. P. W. Allen and F. M. Merrett, *J. Polymer Sci.*, **22**, 193 (1956).
11. W. J. Gowans and F. E. Clark, *Anal. Chem.*, **24**, 529 (1952).
12. P. K. SenGupta and P. Ghosh, *Anal. Chem.*, **38**, 505 (1966).
13. W. Scheele and E. Rohde, *Rubber Chem. Technol.*, **39**, 768 (1966).
14. F. H. Farmer and S. E. Michael, *J. Chem. Soc.*, **1942**, 513.
15. J. C. Bevington, *J. Chem. Soc.*, **1954**, 3707.
16. D. B. Anderson, G. M. Burnett, and A. C. Gowan, *J. Polymer Sci. A.*, **1**, 1465 (1963).
17. G. Smets, J. Roovers, and W. Van Humbeek, *J. Appl. Polymer Sci.*, **5**, 149 (1961).
18. G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *J. Am. Chem. Soc.*, **81**, 4878 (1959).

### Résumé

La copolymérisation greffée du caoutchouc naturel et du méthacrylate de méthyle a été effectuée en présence de peroxyde de benzoyle ou d'asobisisobutyronitrile comme initiateurs thermiques et de peroxyde d'hydrogène ou benzophénone comme photosensibilisateurs. Au départ du produit de copolymérisation totale, la fraction de copolymère greffé caoutchouc-PMMA a été isolée et séparée du caoutchouc qui n'a pas réagit et des fractions de PMMA libre et la caractérisation de la composition des différentes fractions séparées a été effectuée par la détermination de l'insaturation en caoutchouc. L'efficacité de greffage dans diverses conditions a été calculée et comparée.

### Zusammenfassung

Die Pfropfcopolymerisation von MMA auf Naturkautschuk wurde in Gegenwart von  $Bz_2O_2$  oder AIBN als thermische Initiatoren und Wasserstoffperoxyd oder Benzophenon als Photosensibilisatoren durchgeführt. Im Bruttocopolymerisationsprodukt wurde die Kautschuk-PMMA-Pfropfcopolymerfraktion vom nicht umgesetzten Kautschuk und den freien PMMA-Fractionen isoliert und die getrennten Fractionen durch Bestimmung ihrer Kautschukdoppelbindungen in Bezug auf die Zusammensetzung charakterisiert. Die Pfropfausbeute wird für verschiedene Bedingungen berechnet und verglichen.

Received February 2, 1967

Revised February 27, 1967

Prod. No. 1589