

## **Radiation-Induced Block or Graft Copolymers of Methyl Methacrylate with Isobutylene and Ethylene-Propylene Rubbers**

JOSEPH PELLON and KENT J. VALAN, *Chemical Department,  
Central Research Division, American Cyanamid Company,  
Stamford, Connecticut*

### **Synopsis**

Attempts to prepare block or graft copolymers of isobutylene rubbers by radiation in the presence of methyl methacrylate gave low yields of copolymer with only 20% of the rubber entering into the copolymer. The remainder of the rubber is degraded during the process. A single experiment describes the graft copolymerization of methyl methacrylate with ethylene-propylene rubber in which 45% of the rubber is copolymerized.

### **INTRODUCTION**

The object of the present study was to investigate the preparation of graft (or block) copolymers by irradiating mixtures of isobutylene rubbers and methyl methacrylate. While this procedure is known to give high percentages of graft copolymers when diene rubbers are used, comparative data were lacking on isobutylene rubbers. Previously published studies of radiation grafting onto polyisobutylene are those of Henglein, Schnabel, and Heine<sup>1</sup> and of Sebban-Danon<sup>2</sup> with styrene and those of Odian and Bernstein<sup>3</sup> using poly-functional monomers. This paper presents results of product separation and analysis of irradiated mixtures of methyl methacrylate with polyisobutylene and also with butyl rubber latices. In addition the preparation and properties of an ethylene-propylene rubber graft copolymer are presented.

### **EXPERIMENTAL**

#### **Materials and Apparatus**

Commercial rubbers were purchased from Enjay Chemical Co. The polyisobutylene (Vistanex MML-140) had a viscosity of 3.73-4.30 dl./g. in diisobutylene (according to Enjay Co. literature). Based on this viscosity the polymer had a calculated viscosity-average molecular weight of  $1 \times 10^6$ .<sup>4</sup> Bulk polyisobutylene was sliced and cut into small wafers before use. The butyl rubber latex (a copolymer of isobutylene and isoprene,

Enjay Butyl 80-20) was described in the Enjay Co. literature as having 1.5-2 mole-% unsaturation. The latex was used as a 50% solids. The butyl rubber was found to have an intrinsic viscosity of 1.69 in  $\text{CCl}_4$  at  $30^\circ\text{C}$ ., corresponding to a calculated viscosity-average molecular weight of 339,000 from values<sup>5</sup> of  $K$  and  $\alpha$  of  $2.9 \times 10^{-4}$  and 0.68, respectively. The copolymer of ethylene and propylene (Enjay EPR MD-260) was stated to contain  $58 \pm 5$  mole-% ethylene. The bulk rubber was cut into small wafers for use. Inhibitor-free methyl methacrylate was used as received. The x-ray source was a 3 M.e.v. Van de Graaff accelerator employing a gold target.

### Experimental Procedure

The general procedure used in this study was to soak the rubber overnight in monomer or solvent-monomer mixtures, deaerate by purging with nitrogen, and irradiate. The product was isolated by a methanol precipitation and fractionated to give a hexane-soluble fraction, an acetone-soluble fraction, and a residue not soluble in hexane or acetone. The methacrylate content of the three fractions was determined either from oxygen analysis or from standardized infrared analysis. Intrinsic viscosities and inherent viscosities, i.e.,  $\eta_{\text{inh}} = \ln \eta_{\text{R}}/C$  at  $C = 0.5$  g./100 ml. were determined by standard methods at  $30^\circ\text{C}$ .

Sample preparation and fractionation for the isobutylene rubber series was handled as follows. A 5-g. portion of rubber or 10 g. of latex was placed in a  $1\frac{1}{2}$ -oz. wide-mouthed bottle along with weighed monomer or monomer-solvent mixture. This mixture was allowed to remain for 6-7 hr. at room temperature and overnight at  $5^\circ\text{C}$ . in a refrigerator in order to permit maximum penetration. The system was then deaerated by purging for 15 min. with nitrogen. The bottle was closed with a screw cap lined with Mylar polyester film. Samples were then irradiated at ambient temperature while being rotated.

The physical state of the bulk samples after radiation depended on the total dose. After 8 Mrad the reaction mixture was quite fluid, while at lower doses it appeared essentially unchanged. Polymer was isolated by precipitation in a large excess of methanol (in some cases the bulk mixtures were diluted initially with benzene to get a fluid mass) while being stirred in a Waring Blendor. The isolated product was dried at room temperature for 24 hr. and then overnight in a vacuum oven at  $65^\circ\text{C}$ .

After weighing, the dried reaction product was transferred to a 1-pt. wide-mouthed jar, covered with 250-300 ml. of hexane, and after sealing it was rotated on rolls for about 2 days. After several additional days of standing, the hexane layer was carefully syphoned off from the solids and the cycle repeated. The number of hexane extractions varied from 7 to 12. Extractions were continued until the hexane extract gave no precipitate in methanol.

Hexane extracts were combined and their volume was reduced by evaporation to  $\sim 200$  ml. The solution was centrifuged and decanted into a

tared bottle. Solids obtained from centrifuging were combined with the hexane-insoluble residue. An aliquot (usually  $\frac{1}{5}$  of the hexane solution) was transferred into a tared flat-bottomed evaporating dish, and hexane was evaporated in a hood. Gentle warming was used to prevent excessive cooling and water condensation into the sample. To complete the removal of hexane the product, a thin transparent film, was transferred to a vacuum oven at 65–70°C. and dried to constant weight. An average of 36–48 hr. was necessary to accomplish this. Samples were analyzed for methacrylate content by oxygen analysis or infrared.

Hexane-insoluble residue was dried at room temperature and transferred to a 1-pt. wide-mouthed jar and covered with 300–400 ml. of acetone. The acetone extraction procedure was the same as that described for hexane. An average of four extraction cycles (each with 5–10 days of soaking) was involved. Acetone extract was processed by combining all fractions and reducing their volume by evaporation to  $\sim 75$  ml. Acetone-soluble polymer was isolated by precipitation in hexane. This polymer was dried for 24 hr. at room temperature and then in a vacuum oven for 24 hr. at 70°C.

The residue from the acetone extraction was isolated and dried to a constant weight.

A further fractionation of this polymer by a fractional precipitation procedure was attempted. In order to permit a fractional precipitation analysis of the residue, precipitation ranges for solutions of polyisobutylene and of poly(methyl methacrylate) and combinations of the two were determined.

Titration of a 1% benzene solution of poly(methyl methacrylate) with hexane gave a 92% precipitation of the poly(methyl methacrylate) at a hexane:benzene ratio of 1:1. Titration of a 1% 50:50 benzene-hexane solution of polyisobutylene with acetone gave a sharp 100% precipitation of the polyisobutylene at an acetone to solvent ratio of 0.35. Based on these results, 200 ml. of benzene solution containing 1% polyisobutylene and 1% poly(methyl methacrylate) was prepared and 200 ml. of hexane were slowly added; the precipitated polymer was isolated and found to represent an 89% recovery of poly(methyl methacrylate). A 160-ml. portion of acetone was slowly added to the resultant solution, and the precipitated polymer represented 98% recovery of polyisobutylene.

Titration of 100 ml. of 1% benzene solution of the residues resulting from the hexane and acetone extraction of the reaction products with 100 ml. of hexane and with 100 ml. of acetone failed to give any isolable precipitates. The solutions were cloudy, but no precipitation occurred at the precipitation ranges for the pure homopolymers. An additional 200 ml. of hexane was then added in an attempt to get a further subfraction of the copolymer. Following the final hexane addition the solution was allowed to stand for several days and the soluble and insoluble copolymer fractions were isolated.

In the preparation and isolation of a methacrylate graft copolymer of ethylene-propylene rubber, two 16-oz. wide-mouthed jars were each charged with 100 g. of Enjay EPR, 200 ml. of heptane, and 50 ml. of methyl

methacrylate and the mixture permitted to stand for 48 hr. to allow maximum swelling of the polymer. The resultant mass was kneaded for 15 min. in a Sigma mixer with nitrogen flush, returned to the jar, and, after flushing with nitrogen, the cover was screwed on over a Mylar film. Each sample was then irradiated for 2 hr. at a dose rate of 4 Mrad/hr. Additional methyl methacrylate (50 ml.) was then added and the sample further irradiated for 4 hr. at 1 Mrad/hr., giving a total dose of 12 Mrad. The reaction product, a soft, opaque rubbery mass, was cut into small chunks with scissors and added individually to an operating 1-gal. Waring Blendor containing 2.3 liters of methanol. (Care should be taken not to permit the methanol vapors to be drawn into the housing of the blender, as on one occasion this resulted in a fire, after which a separate air-intact device was designed for the blender.) After air and vacuum drying, the resultant product was a white, nontacky powdery material having a total weight of 336 g. The overall product composition (two jars) was 200 g. of rubber and 136 g. of poly(methyl methacrylate).

Heptane extraction on a portion of the product was carried out by placing 180 g. of product in 1-gal. wide-mouthed jar with 2 liters of heptane. Heptane-solubles, acetone-solubles, and residue were obtained by the method previously described, three heptane extractions and two acetone extractions being used.

## RESULTS AND DISCUSSION

Tables I-III summarize the results of product analysis on irradiated mixtures of polyisobutylene or butyl latex with methyl methacrylate. The radiation products were isolated by methanol precipitation and fractionated by extraction to give a hexane-soluble fraction, an acetone-soluble fraction, and a residue not soluble in either hexane or acetone.

Oxygen content of the hexane soluble fractions derived from polyisobutylene (Tables I and II) was found to be at the lowest limits of detection ( $\sim 0.3\%$ ) and indicated that these fractions were generally free from methacrylate, i.e.,  $0.3\%$  O is equivalent to  $1\%$  poly(methyl methacrylate). The hexane-soluble butyl rubber fractions (Table III) also showed less than  $6\%$  methacrylate content.

The oxygen analysis for the acetone-soluble material gave a value of  $>29\%$  O at the low doses, indicating a minimum of  $90\%$  poly(methyl methacrylate); higher doses showed a tendency to somewhat lower oxygen values, indicating increased polyisobutylene residues in the acetone solubles.

The total amount of hexane- and acetone-insoluble residue isolated was found to reach a maximum at intermediate doses (1-4 Mrad). As indicated above, an attempt was made to further subfractionate the residues by fractional precipitation processes. Samples were dissolved in benzene and titrated with hexane followed by acetone: no precipitates were isolated at precipitation ranges previously shown to precipitate the homopolymers.

TABLE I  
 Fractionation Results of Irradiated Mixtures of Polyisobutylene and Methyl Methacrylate<sup>a</sup>

Dose, Mrad <sup>b</sup>	Wt. of product isolated, g.	Wt. of various fractions, g.				Oxygen, %			Inherent viscosity		MMA in copolymer, %
		Hexane-soluble	Acetone-soluble	Residue	Total	Hexane-soluble	Acetone-soluble	Residue <sup>c</sup>	Hexane-soluble <sup>d</sup>	Acetone-soluble <sup>e</sup>	
0 <sup>f</sup>	9.84	5.34	4.67	0	10.01	<0.3	29.18	—	—	—	—
0.25	5.32	5.02	0.12	0.22	5.36	0.34	30.72	17.70	2.48	1.71	55
0.50	5.74	4.62	0.36	0.56	5.64	0.47	30.40	14.95	2.11	1.41	47
0.50*	6.28	4.58	0.80	0.66	6.04	0.31	29.33	17.80	1.94	1.96	56
1.0	6.40	4.60	0.80	0.92	6.32	<0.3	30.01	14.65	1.70	1.56	46
1.0*	11.40	4.40	6.20	0.84	11.40	<0.3	30.80	16.26	2.72	—	51
2.0	7.52	4.19	1.85	0.87	6.91	0.42	—	18.20	1.26	0.60	57
4.0	13.00	4.52	7.69	0.53	12.74	<0.3	29.30	15.80	0.86	1.18	50
8.0	14.81	4.70	10.26	0.14	15.10	<0.3	28.64	13.70	0.56	0.68	43

<sup>a</sup> Charge: 5 g. polyisobutylene and 10 g. methyl methacrylate.

<sup>b</sup> Dose rate 4 Mrad/hr.

<sup>c</sup> These values represent an average of the per cent oxygen from the soluble and insoluble fractions which resulted from the attempted subfractionation of the residue.

<sup>d</sup> In CCl<sub>4</sub> at 0.5 g./100 ml. at 30°C.

<sup>e</sup> In benzene at 0.5 g./100 ml. at 30°C.

<sup>f</sup> Solution containing 5 g. polyisobutylene (Vistanex 140) and 5 g. poly(methyl methacrylate) (Lucite) in 10 ml. of hexane.

<sup>g</sup> Sample allowed 24 hr. post-irradiation period before opening.

TABLE II  
 Fractionation Results of Irradiated Mixtures of Polyisobutylene, Hexane, and Methyl Methacrylate<sup>a</sup>

Dose, Mrad <sup>b</sup>	Wt. of product isolated, g.	Wt. of various fractions, g.			Total	Oxygen, %		Inherent viscosity		MMA in copolymer, %
		Hexane-soluble	Acetone-soluble	Residue		Hexane-soluble	Acetone-soluble	Residue <sup>c</sup>	Hexane-soluble <sup>d</sup>	
0	5.08	4.78	0	0	4.78	<0.3	—	—	—	—
0.25	5.01	4.83	0	0	4.83	<0.3	—	—	—	—
0.5	5.01	4.92	0	0	4.92	<0.3	—	—	—	—
0.5 <sup>f</sup>	4.94	4.63	0	0.15	4.78	<0.3	—	—	—	12
1.0	5.43	4.27	0.28	0.67	5.22	<0.3	30.50	1.41	1.55	18
1.0 <sup>f</sup>	5.57	4.52	0.35	0.63	5.52	0.46	30.17	1.33	0.61	20
2.0	6.62	3.98	1.25	1.32	6.55	0.47	29.64	1.27	0.59	29
4.0	9.13	3.78	4.32	1.33	9.43	0.71-1.04	26.94	0.59	0.46	27
8.0	9.62	4.09	4.82	0.32	9.23	<0.3	28.06	0.37	0.41	33

<sup>a</sup> Charge: 5 g. polyisobutylene, 10 ml. hexane, 5 g. methyl methacrylate.

<sup>b</sup> Dose rate 4 Mrad/hr.

<sup>c</sup> No insoluble fraction was formed on attempted subfractionation of the residue.

<sup>d</sup> In CCl<sub>4</sub> at 0.5 g./100 ml. at 30°C.

<sup>e</sup> In benzene at 0.5 g./100 ml. at 30°C.

<sup>f</sup> Sample allowed 24 hr. post-irradiation period before opening.

TABLE III  
 Fractionation Results of Irradiated Mixtures of Butyl Latex and Methyl Methacrylate<sup>a</sup>

Dose, Mrad <sup>b</sup>	Wt. of product isolated, g.	Wt. of various fractions, g.			Total	Oxygen in residue, % <sup>c</sup>	PMMA in hexane- soluble, % <sup>d</sup>	MMA in copolymers, %
		Hexane- soluble	Acetone- soluble	Residue				
0	5.00	—	—	—	—	—	—	—
0.5	6.77	4.27	1.45	1.07	6.79	14.08	3.5	44
0.5 <sup>e</sup>	7.37	4.29	—	—	—	—	5.1	—
2.0	7.48	4.30	1.72	1.30	7.32	8.16	6.5	26
4.0	7.69	3.97	2.10	1.19	7.26	9.31	3.0	29
4.0 <sup>e</sup>	7.40	4.26	—	—	—	—	2.9	—
8.0	7.29	4.34	2.02	0.94	7.30	8.48	1.4	27

<sup>a</sup> Charge: butyl latex (10 g. containing 5 g. butyl rubber), and 2.5 g. methyl methacrylate.

<sup>b</sup> Dose rate 4 Mrad/hr.

<sup>c</sup> Average oxygen value from soluble and insoluble subfractions of the residue.

<sup>d</sup> By infrared analysis.

<sup>e</sup> Sample allowed 24 hr. post-irradiation period before opening.

TABLE IV  
Radiation Stability of Isobutylene Rubbers<sup>a</sup>

Dose, Mrad <sup>b</sup>	Viscosity data	
	Intrinsic viscosity, irradiated butyl latex <sup>c</sup>	Inherent viscosity, irradiated polyisobutylene <sup>d</sup>
0	1.69	3.7
0.5	1.70	2.1
1	1.62	1.50
2	1.29	1.38
4	0.99	0.38
8	0.64	0.41

<sup>a</sup> Deaerated Butyl latex was irradiated directly: 5 g. polyisobutylene (Vistanex 140) was dissolved in 15 ml. hexane; the solution deaerated and irradiated.

<sup>b</sup> Dose rate  $\approx$  4 Mrad/hr. (3 M.e.v. x-rays, 10 in. scan, 1000 Hm. A, 6.9 cm. to target).

<sup>c</sup> In CCl<sub>4</sub> at 30°C.

<sup>d</sup> In CCl<sub>4</sub> at 0.5 g./100 ml. at 30°C.

Additional hexane was then added. In some cases insoluble material resulted, while in others no insolubles were formed. It was obvious from this and from an analysis of the separations which were achieved that the residue, while being essentially free from homopolymer, was complex and variable in composition. A complete description of the residue would therefore have required refined separation of each sample on an individual basis, and for that reason only the overall composition of the residue is reported. This was derived either by analysis of the isolated single fraction or by averaging of the analysis of two fractions.

Solubility, fractional precipitation results, and also chemical and spectral analysis showed that the residues are copolymers.

The average composition of the copolymers was different in the three systems studied. Bulk irradiation of polyisobutylene with methacrylate (Table I) gave copolymer mixtures having an overall composition with 46–57% methacrylate.

Copolymers resulting from the irradiation of polyisobutylene with hexane-methacrylate mixtures (Table II) had lower (10–30%) percentages of methacrylate. It is expected that the reduced methacrylate to polyisobutylene ratio used in this series would give copolymers containing less methacrylate than those described in the previous paragraph.

Similarly the results of the butyl latex copolymerization (Table III) show that with certain exceptions the copolymers have methacrylate concentrations in the 20–50% range.

The solution viscosities for the hexane- and acetone-soluble materials were found to decrease with increasing dose. The degradation was so serious at 2–8 Mrad as to make the extraction procedures less certain. A separate check was made on the radiation stability of the isobutylene rubbers under the conditions used. As shown in Table IV, butyl rubber was



not degraded up to about 1 Mrad, but polyisobutylene degradation resulted at the lowest radiation doses studied.

A comparison of the viscosity data for the polyisobutylenes isolated from the reaction mixtures with those of the control mixtures points up the fact that the degradation is not significantly retarded by the presence of the monomer, indicating a low degree of polyisobutylene radical combination with monomer. The finding that greater amounts of copolymer were obtained at lower doses with butyl rubber is consistent with the greater radiation stability and greater grafting reactivity of this rubber due to the presence of low percentages of allylic unsaturation.

As indicated in the introduction, our primary concern in this study was the determination of copolymerization efficiency. The poor yields of copolymer obtained is illustrated by the fact at their maximum the copolymers represented only about 20% of the product and also at the maximum about 80% of the polyisobutylene was degraded but not copolymerized.

TABLE V  
Fractionation Results of Irradiated Mixtures of  
Ethylene-Propylene Rubber and Methyl Methacrylate<sup>a</sup>

Fractions	Wt. isolated, g.	Viscosity	Material Balance of Components, g.	
			MMA	EPR
Heptane-soluble	52.8	1.6 <sup>b</sup>	1.0	51.8
Acetone-soluble	42.5	0.27 <sup>c</sup>	42.5	0
Residue (copolymer) <sup>d</sup>	61	2.14 <sup>c</sup>	18.3	42.7
Total				
Found	156.3	—	61.8	94.5
Theory	180	—	72	108

<sup>a</sup> Total initial weight = 180 g., based on feed; this consisted of 108 g. of ethylene-propylene rubber and 72 g. of poly(methyl methacrylate) (see theory).

<sup>b</sup> Intrinsic viscosity in cyclohexane at 30°C.

<sup>c</sup> Inherent viscosity in benzene at 30°C. at 0.5 g./100.

<sup>d</sup> Chemical analysis: C, 77.61%; H, 12.24%; O, 9.72%; Refractive index, 1.481. Properties of unvulcanized sheet: Durometer hardness, 70; Microtensile, 115 psi at break; elongation on break, 22%.

The physical appearance of the copolymers depended somewhat on their methacrylate content, those having 25% methacrylate being transparent and rubbery but those having 50% methacrylate being transparent, hard, tough films.

The synthetic aspects of the preparation of graft copolymers of ethylene-propylene rubbers was also explored, and the results of a single scaled-up preparation and fractionation are presented in Table V. The percentage composition of the product in this experiment is 39% copolymer, 27% poly(methyl methacrylate), and 34% degraded ethylene-propylene homopolymer. In this experiment 45% of the initial rubber has been copolymerized.

The findings of this study are generally consistent with the known radiation behavior of these saturated hydrocarbon systems<sup>6,7</sup> and with the results of studies by others.<sup>1-3</sup> Low reactivity (relative to allylically activated butadiene rubbers) and high degradative tendencies would be expected to make polyisobutylene rubbers poor candidates for graft copolymerization. Our findings also indicate that block copolymerization is also minimal. Ethylene-propylene polymers, having enhanced reactivity (by virtue of a tertiary hydrogen) and less degradative tendencies than isobutylene polymers, allow preparation and ready isolation of methacrylate graft copolymers.

The authors wish to acknowledge the valuable assistance provided by N. B. Colthup (infrared), R. R. Fiala (viscosities), C. F. Spiers (radiation), and P. Stehman (oxygen analysis).

### References

1. Henglein, A., W. Schnabel, and K. K. Heine, *Angew. Chem.*, **70**, 461 (1958).
2. Sebban-Danon, J., *J. Chim. Phys.*, **58**, 246, 263 (1961).
3. Odian, G., and B. S. Bernstein, *J. Polymer Sci.*, **B2**, 819 (1964).
4. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953; Fig. 50, p. 311.
5. Fox, T. G., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949).
6. Bovey, F. M., *The Effects of Ionizing Radiation on Natural and Synthetic High Polymers*, Interscience, New York, 1958.
7. Chapiro, A., *Radiation Chemistry of Polymer Systems*, Vol. 15, High Polymer Series, Interscience, New York, 1962.

### Résumé

Les tentatives de préparation de copolymères en bloc ou greffés par irradiation de caoutchoucs d'isobutylène en présence de méthacrylate de méthyle ont fourni de faibles rendements en copolymère, avec seulement 20% de caoutchouc dans le copolymère. Le caoutchouc restant est dégradé pendant le processus. Une seule expérience décrit la copolymérisation par greffage de méthacrylate de méthyle sur du caoutchouc éthylène-propylène dans lequel 45% du caoutchouc est copolymérisé.

### Zusammenfassung

Versuche, Block- oder Pfropfkopolymere aus Isobutylenkautschuk durch Bestrahlung in Gegenwart von Methylmethacrylat darzustellen, lieferten niedrige Ausbeuten eines Kopolymeren, das nur 20% des Kautschuks enthielt. Der restliche Kautschuk wird während des Prozesses abgebaut. In einem Einzelversuch wurde die Pfropfkopolymerisation von Methylmethacrylat mit Äthylen-Propylenkautschuk durchgeführt und dabei 45% Kopolymerisation des Kautschuks erhalten.

Received January 13, 1965

Revised April 1, 1965