

# Block Copolymers Obtained by Free Radical Mechanism. II. Butyl Acrylate and Methyl Methacrylate

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## Synopsis

Block copolymers were synthesized using methyl methacrylate and butyl acrylate as the monomers and a multifunctional initiator, di-*t*-butyl 4,4'-azobis(4-cyanoperoxyvalerate). The polymerizations for the formation of the block copolymers were carried out in two stages. First the poly(methyl methacrylate) polymeric initiator was synthesized and isolated. In the second stage, the thermally activated azo group in the polymer backbone initiated the polymerization of butyl acrylate. Upon termination by combination a tri-block results. Selective solvent fractionation was used to separate the block from the homopolymers.

## INTRODUCTION

In a previous publication, Piirma and Chou<sup>1</sup> reported on the synthesis of styrene and methyl methacrylate block copolymers using a multifunctional initiator, di-*t*-butyl 4,4'-azobis(4-cyanoperoxyvalerate). Their system served as a model to study the feasibility of such polymerizations.

In this present study, the same initiator was used and butyl acrylate was used as the comonomer with methyl methacrylate. The reactions were carried out in two stages. In the first stage, the poly(methyl methacrylate) polymeric initiator was prepared by perester group initiation at room temperature with tetraethylenepentamine as the reducing agent. This yielded a polymer with an azo group in the center of the backbone. In the second stage, this azo group was activated to initiate the polymerization of the second monomer, butyl acrylate, to form the block copolymer. The first stage reactions were carried out in bulk, the second stage polymerizations were done either in bulk, solution, or emulsion. The mechanism and kinetics of these reactions will be published in a separate report. This present article will deal with the synthesis, separation, and characterization of the butyl acrylate-*b*-methyl methacrylate copolymers.

## EXPERIMENTAL

Methyl methacrylate (Matheson, Coleman and Bell Company) was distilled under nitrogen at 50°C (120 mm) after washing first with 10% NaOH aqueous solutions and subsequently with water.

Butyl acrylate was freed from inhibitor by washing with 10% NaOH aqueous solution and water. Dried over Na<sub>2</sub>SO<sub>4</sub> and finally distilled twice in vacuo (28°C at 10 mm Hg).

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Di-*t*-butyl 4,4-azobis(4-cyanoperoxyvalerate) (RS-604) obtained from Lucidol Division, Pennwalt Corporation, (95% pure melting at 95°C) was used as received.

### Preparation of PMMA Polymeric Initiator

Reactions were carried out in 4-oz. bottles having screw caps lined with self-sealing butyl rubber gaskets. Methyl methacrylate monomer and the initiator, RS-604, were charged into the bottles and the bottles were tightly capped. After complete solution of the RS-604 in the methyl methacrylate monomer, N<sub>2</sub> was purged through a long needle into the bottle for about 5 min. The required amount of tetraethylenepentamine was carefully added and the reaction was timed. Bottles were placed in a thermostatted bath and rotated at 45 rpm for desired periods of time at 25°C. The reaction solution was diluted with acetone prior to coagulation in methanol in order to obtain a fluffy powder. The product was filtered and washed several times with methanol to remove the unreacted initiator and reducing agent. The product was dried under vacuum, stored in the refrigerator at 0°C, and used within one week. The preparation conditions employed for the preparation of the poly(methyl methacrylate) (PMMA) polymeric initiator is shown in Table I. All conversions were 25% of the initial monomer charged.

Three different molecular-weight PMMA polymeric initiators were prepared by this method. The molecular weights, as determined by GPC and from the nitrogen analysis results, are in Table I, and the GPC curves are shown in Figure 1.

### Fractionation of Poly(methyl Methacrylate) Polymeric Initiators

Polymeric initiators were fractionated using acetone-methanol mixtures to determine the molecular weight distributions of the individual fractions and their nitrogen contents. Poly(methyl methacrylate) polymeric initiator with  $\bar{M}_n = 1.7 \times 10^5$  (BG-105), 15.0 g, was dissolved in a round flask in 1000 ml acetone in order to give a 1.5% solution at 25°C. Methanol was added dropwise into the solution with rapid stirring until the first turbidity was observed. At this point, the turbid solution was heated to redissolve the polymer, then the solution was

TABLE I  
Synthesis of PMMA Polymeric Initiator

	BG-103 <sup>a</sup>	BG-105	BG-107
MMA, g	75.0	75.0	75.0
RS-604, g	1.5	3.0	4.5
RS-604, mol $\times 10^3$	3.54	7.08	10.6
TEPA, g	0.75	1.5	2.25
([Initiator]/[M]) $\times 10^3$	4.91	9.83	14.7
Reaction temp., °C	25	25	25
Reaction time, min	180	150	105
Wt % nitrogen in polymer	0.15	0.33	0.54
$\bar{M}_n \times 10^{-5}$	2.18	1.71	1.20

<sup>a</sup> Sample number.

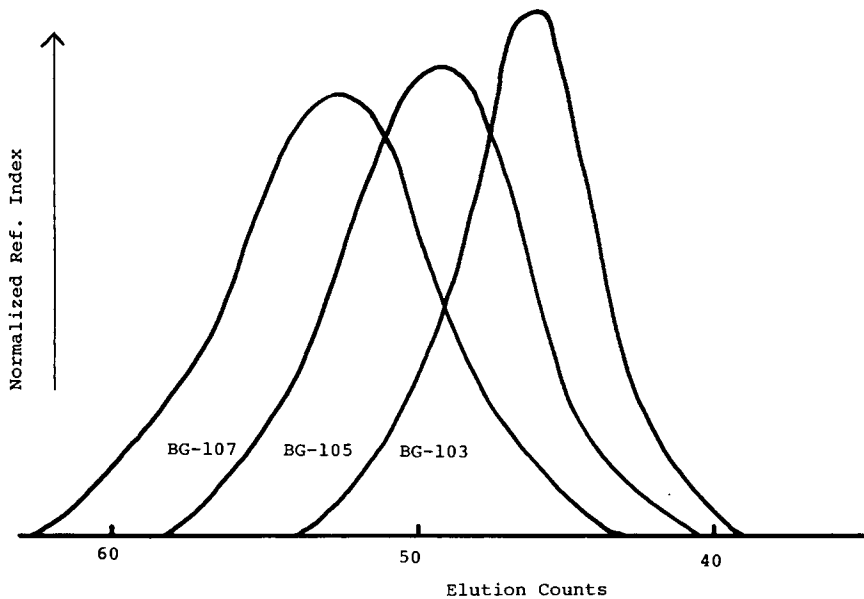


Fig. 1. GPC curves of MMA polymeric initiator with different  $\bar{M}_n$  values.

kept for 24 h at 25°C. The next day the clear supernatant solution was decanted into another flask. The precipitate was washed with methanol, filtered, and dried under vacuum. Additional methanol was added into the supernatant liquid until the next appearance of turbidity, and the same procedure was repeated. Four different fractions were collected by this method. These fractions were dried in a vacuum oven at 25°C until constant weight. Each fraction was analyzed by GPC and Dorman analyzer to determine the MWD and the nitrogen content. The results are shown in Figure 2 and Table II, respectively.

### Preparation of Poly(methyl Methacrylate-*b*-Butyl Acrylate)

The block copolymerizations with butyl acrylate monomer were carried out in bulk, solution, and emulsion initiated by the PMMA polymeric initiator.

**Bulk Polymerization.** The required amount of PMMA polymeric initiator and the butyl acrylate monomer were charged into 2-oz. bottles which were tightly capped. After purging with  $N_2$ , a sample was taken to determine the initial solids content. The bottles were then placed into a thermostatted water bath at 60°C and rotated at 45 rpm. The final product was precipitated from methanol and washed with it several times. The precipitate was then filtered and dried in vacuum at room temperature. The mole charge ratios of the butyl acrylate monomer to the PMMA polymeric initiator were varied tenfold from  $[M]/[I] = 5.7 \times 10^3$  to  $5.7 \times 10^4$ . The systems became viscous very fast, and accelerated rates were observed beyond 25% conversion.

**Solution Polymerization.** When solution polymerization was used in the second stage, the required amount of the PMMA polymeric initiator was dissolved in a mixture of benzene and butyl acrylate monomer. The reaction was

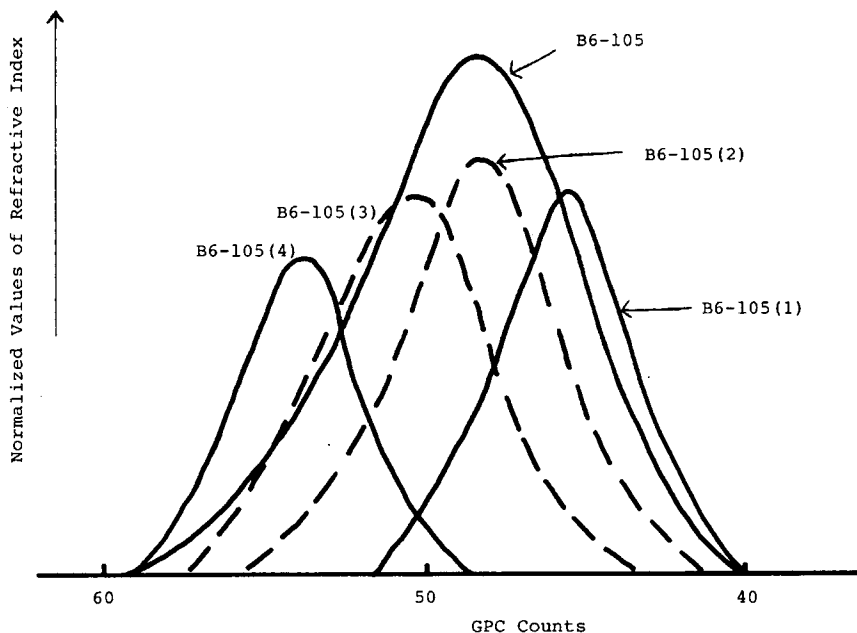


Fig. 2. GPC curves of BG-105 and its three fractions.

carried out in 4-oz. bottles. The techniques for polymerization and purification were as described above.

The molar charge ratios for the second-stage solution polymerization of butyl acrylate initiated by the MMA polymeric initiators of three different number-average molecular weights are shown in Tables III and VI.

**Emulsion Polymerization.** When the second-stage polymerization of butyl acrylate with the PMMA polymeric initiator was carried out in emulsion, the following technique was used: The required amount of polymeric initiator was dissolved in enough benzene to obtain a clear solution. This clear solution was then emulsified in sodium dodecyl sulfate aqueous solution by stirring (400 rpm) for 18 h. This emulsion was then charged into 4-oz. bottles, and the bottles were tightly capped and nitrogen purged as described before. Butyl acrylate monomer was charged via a hypodermic syringe. Table VII illustrates the polymerization conditions.

TABLE II  
Fractionation and Nitrogen Analysis Results, Sample BG-105,  $\bar{M}_n = 1.7 \times 10^5$

Fraction	$\gamma$ Value <sup>a</sup>	BG-105, wt %	Nitrogen content, Wt %
1	0.68	15.0	0.182
2	0.76	47.2	0.350
3	0.82	27.4	0.301
4	0.90	10.1	0.051

$$^a \gamma = \frac{\text{volume of nonsolvent}}{\text{volume of solvent} + \text{volume of nonsolvent}}$$

TABLE III  
Block Copolymer Synthesis in Benzene Solution

	BZ-12	BZ-13	BZ-17	BZ-28-B	BZ-30	BZ-31
Polymeric initiator $\bar{M}_n \times 10^{-5}$	2.1	2.1	1.7	1.7	1.2	1.2
Concn., mol $\times 10^5$	0.95	0.95	1.176	1.176	0.83	2.5
Butyl acrylate, mol	0.0938	0.0703	0.0975	0.0312	0.0468	0.0468
M/PI, mol ratio $\times 10^3$	9.87	7.4	8.29	2.6	5.6	1.8
Time at 60°C	6	9	5	4	10	8
Conversion, %	50.9	47.5	62.1	31.9	44.9	47.9
Block copolymer, wt %	84.0	85.8	84.1	49.6	88.1	75.4
Block copolymer $\bar{M}_n \times 10^{-5}$	(75.1)	7.3	(21.0)	6.1	6.1	3.65
Butyl acrylate in block copolymer, mol %	85.8	74.4	91.9	73.5	77.6	62.9
Unreacted PI, wt %	14.8	12.8	14.9	49.7	10.8	23.8

### Separation of Poly(butyl Acrylate-*b*-Methyl Methacrylate) from Homopolymers

Selective solvent extraction methods were used. At room temperature, *n*-butanol is a solvent for poly(butyl acrylate) but a nonsolvent for PMMA. The reaction product from second-stage polymerization, 2 g, was dissolved at 65°C in 100 ml *n*-butanol. This solution was then cooled to room temperature, and precipitation was observed. This precipitate was separated by filtration and was washed with *n*-butanol. The supernatant portion was then fractionally treated with methanol to separate the block and the homopolymer of butyl acrylate. The dropwise addition of methanol was maintained until a  $\gamma$  value of 0.5 was reached. The precipitate collected between  $\gamma = 0.5$  and 0.6 was poly(butyl acrylate-*b*-methyl methacrylate). Further addition of MeOH to the supernatant produced no more precipitate.

The blank tests carried out with poly(butyl acrylate) in *n*-butanol-methanol system showed that at  $\gamma = 0.70$ – $0.90$ , the poly(butyl acrylate) with  $\bar{M}_n 7 \times 10^4$  to  $2.5 \times 10^5$  was separated out completely. In all these block and homopolymer separations even at  $\gamma = 0.90$ , no precipitation was observed, and further evaporation of filtrate did not give any solid, indicating the absence of the homopolymer of butyl acrylate.

The cast films of the block polymer were completely clear.

### Polymer Characterization

Nuclear magnetic resonance spectroscopy was used to obtain the microstructure of the polymers. The instruments used were Varian T-60 and HR-300 NMR.

The molecular weights and molecular weight distributions were done by osmometry (Hewlett-Packard High-Speed Osmometer 503) and by gel permeation chromatography (Waters Ana-Prep).

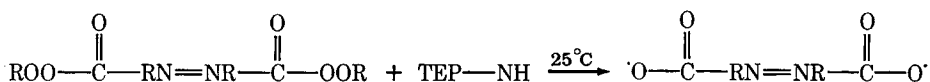
The latex particles were characterized by electron microscopy (JEM-120U).

## RESULTS AND DISCUSSION

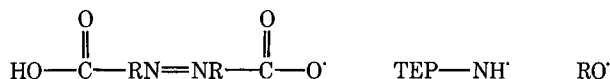
## Preparation of MMA Polymeric Initiator

For the synthesis of the methyl methacrylate polymeric initiator, di-*t*-butyl 4,4'-azobis(4-cyanoperoxyvalerate) was used. This sequential initiator is manufactured by Lucidol Division of Pennwalt Corp. and carries the code name RS-604.

The methyl methacrylate polymerization was carried out in bulk and involved the activation of perester groups located at both ends of the initiator molecule:

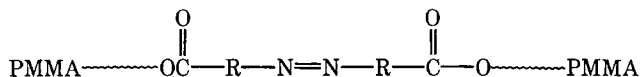


The mechanism of this redox system which used tetraethylenepentamine as the reducing agent has not been explained clearly. There is, of course, the possibility of some monoradical formation such as



and these radicals can initiate methyl methacrylate polymerization. Diradicals, however, are considered to be the principal intermediate radicals (evidence: see  $\text{N}_2$  content shown in Table II).

Since it has been established<sup>2,3</sup> through end group analysis that MMA primary mode of termination is by disproportionation, it is justified to assume that the polymeric MMA initiator will have the following structure:



i.e., an azo group in the center of the molecule.

The molecular weights of the polymeric initiators were controlled by the proper choice of the initial charge ratio of the RS-604 to monomer. The polymerization rates and molecular weights were found to be proportional to the square root of the initiator concentration, as shown in Figures 3 and 4. The three different molecular weight polymeric initiators (Table I) were subjected to fractionation, and each fraction was analyzed for nitrogen content. Table II gives the results for sample BG-105, where it can be seen that the fraction at  $\gamma = 0.90$  has a very low nitrogen content. This fraction must have been formed by the initiation of the  $\text{RO}\cdot$  or  $\text{RNH}\cdot$ -radicals and thus constitutes the inactive portion of the polymeric initiator. Later in the block copolymer separation, it was found that homopoly(MMA) was an unavoidable impurity.

## Block Copolymers

The preparation of block copolymers of butyl acrylate and methyl methacrylate was achieved by utilizing the poly(methyl methacrylate) polymeric initiator (PI). Three different chain-length polymeric initiators were used (Table I).

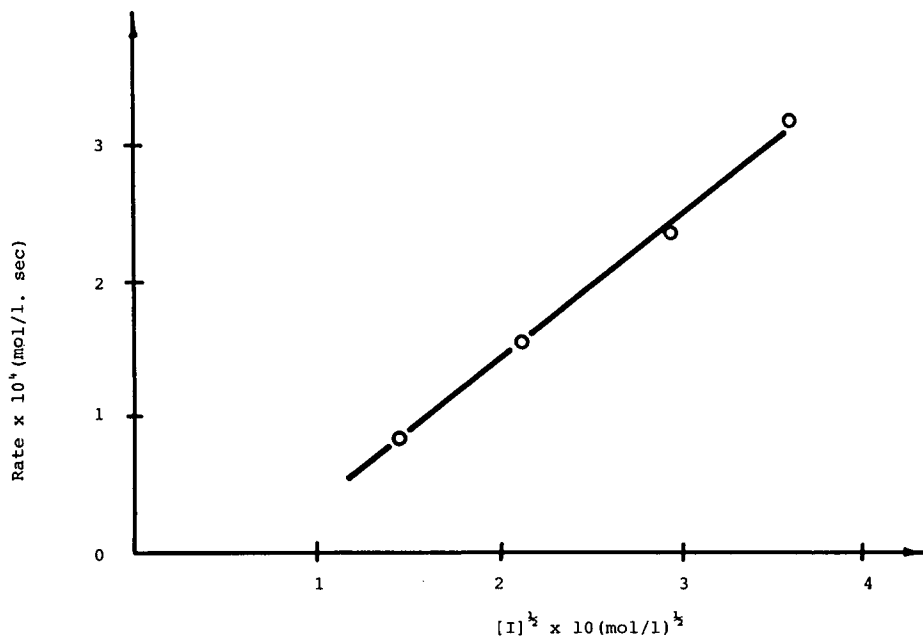


Fig. 3. Bulk polymerization of methyl methacrylate at 60°C with RS-604 as initiator.

Polymerizations were carried out in bulk, in solution, and in emulsion. Under all three polymerization conditions, the formation of homopoly(butyl acrylate) was found to be negligible. The explanation for this could be that chain transfer to the butyl acrylate monomer or the solvent is very infrequent. The chain

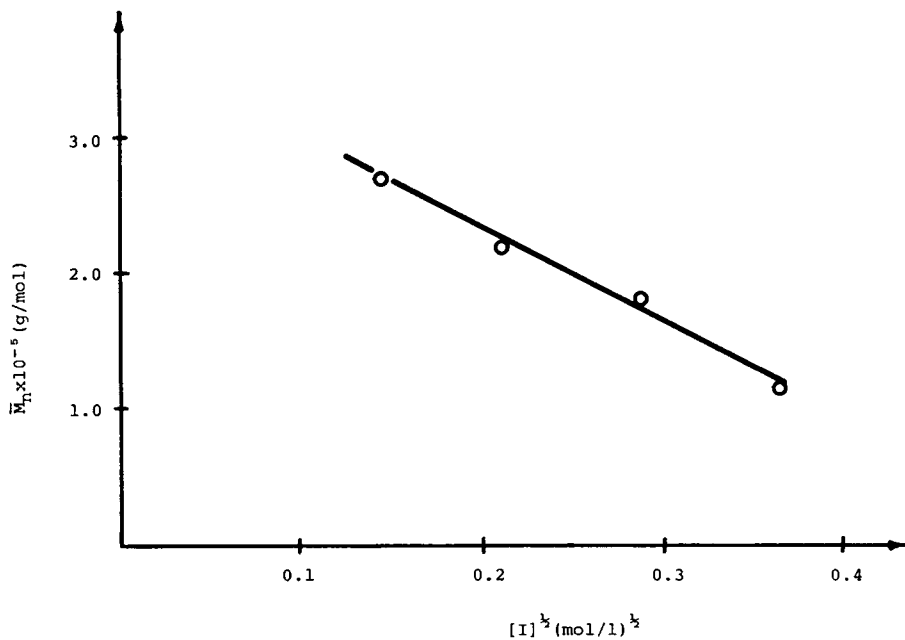


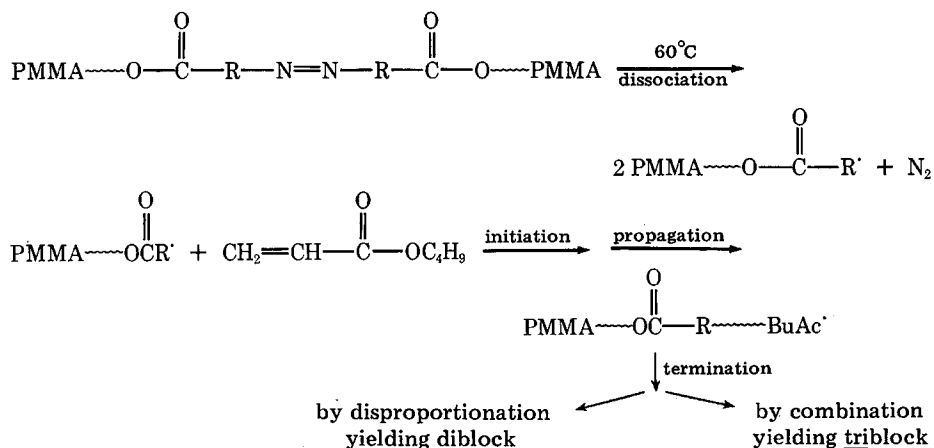
Fig. 4. Effect of initiator (RS-604) concentration on the number-average molecular weight in MMA bulk polymerization.

transfer constant values for this monomer have been reported to be very low, somewhere in the range of  $3 \times 10^{-5}$ . The same applies for the solvent benzene. In the polymerization product, therefore, the only impurity found was the unreacted poly(methyl methacrylate).

Our kinetic studies showed that bulk polymerization was not practical to use for the formation of the block copolymer due to the increase in viscosity in the early stages of conversion. The polymerization rates were very fast due to the decrease in the termination rate, and the percent of the diazo groups cleaved in the polymeric initiator was very small before the onset of the viscosity problem. Therefore, although the percent of butyl acrylate in the final block copolymer was high, the number of segments was low.

Further utilization of our kinetic studies showed that the factors which affect the composition and the percentage of block copolymer are the ratio of the monomer to the polymeric initiator, the amount of solvent used, the reaction time, and the molecular weight of the initial polymeric initiator, which relates directly to the active diazo concentration. A higher solvent level decreased the rate of polymerization; but when coupled with a higher percentage of diazo groups, it resulted in less homopoly(methyl methacrylate) formation as a side product.

The proposed reaction mechanism for the block polymerization is as follows:



Every variation in the charge composition, i.e., in the monomer to PI concentration ratio, affected the yields and compositions of block copolymers. This is illustrated in Table III, in which we can compare samples BZ-12 with BZ-13, BZ-17 with BZ-28-B, and BZ-30 with BZ-31. These three groups of block copolymers were synthesized using three different molecular-weight polymeric initiators. BZ-12 has a higher M/PI molar charge ratio than does BZ-13. Even though the polymerization times for these polymers are not exactly the same, one can still see that BZ-12 has a higher butyl acrylate content in the block copolymer. Same kind of observations can be made with the other two sets of samples. In general, it was also observed that the higher the M/PI ratio, the larger the butyl acrylate segments in the block copolymer.

The length of time of polymerization and the extent of conversion were also



TABLE IV  
 Polymerization Conversion and Time Effect<sup>a</sup>

	BZ-28-A	BZ-28-B
Polymerization time, h	9	4
Conversion, %	50.1	31.9
Final product, wt %	75.8	49.6
Block copolymer $\bar{M}_n \times 10^{-5}$	4.8	6.1
Butyl acrylate in block, mol %	61.4	73.5
Unreacted PI, wt %	23.8	49.7

<sup>a</sup> Polymerization conditions: BuAc =  $3.125 \times 10^{-2}$  mol and BG105 =  $1.17 \times 10^{-5}$  mol, both in benzene solution; temp. = 60°C.

important factors which affected the yields and the compositions of block copolymers. Our kinetic studies, which will be discussed in a subsequent paper, showed that the longer the polymerization time, the lower was the percent unreacted PI, which appeared as the by-product with the block copolymer. The results in Table IV show, however, that the molecular weight of the block and the poly(butyl acrylate) content in the block copolymer were higher at the shorter reaction times, i.e., at lower conversions. This distinct difference observed in these two samples given as examples can be explained as being due to broadening of the molecular weight distribution as the reaction proceeds. Initiation of chains

 TABLE V  
 Effect of Initiator Concentration

	BZ-32	BZ-34
BG-107, mol $\times 10^5$	5.0	6.66
M/PI $\times 10^{-3}$ , mol ratio	1.06	1.28
Conversion, %	48.1	57.5
Block, wt %	50.2	52.6
Block copolymer $M_n \times 10^{-5}$	3.20	2.69
Butyl acrylate in block, mol %	57.5	50.2
Unreacted BG-107, wt %	48.9	46.7

<sup>a</sup> Polymerization conditions: BuAc =  $4.68 \times 10^{-2}$  mol; time, 5 h; in benzene.

 TABLE VI  
 Example of BuAc-MMA Block Synthesis

	BZ-1 <sup>a</sup>	BZ-45	BZ-27	BZ-40	BZ-20 <sup>b</sup>
PI Type	BG-103	BG-105	BG-105	BG-107	—
[PI] $\times 10^5$ , mol	0.47	1.76	3.52	2.5	2.2
[BuAc], mol	0.23	0.023	0.039	0.023	0.0468
Conversion, % BuAc	30.9	54.9	56.8	46.9	48.1
Time, h	1.5	13	10	10	7.5
Block copolymer, wt %	89.6	67.9	66.9	68.5	48.1
Block copolymer $\bar{M}_n \times 10^{-5}$	*NA	3.28	3.01	2.1	3.89
Butyl acrylate in block (from NMR), mol %	97.6	46.3	42.6	40.7	75.5
Unreacted (BG-107), wt %	8.7	31.6	32.7	31.5	24.7

<sup>a</sup> BZ-1 reaction was carried out in bulk.

<sup>b</sup>  $M_n = 9 \times 10^5$ .

TABLE VII  
 Synthesis of Block Copolymers in Emulsion<sup>a</sup>

	BZ-101	BZ-110	BZ-119
Butyl acrylate, mol	0.0313	0.0625	0.0938
SDS Emulsifier, g	1.25	5.0	2.5
Water, g	48.75	45.0	47.5
Conversion, % BuAc	42.6	55.2	40.1
Time, h	16.0	10.0	5.0
Block copolymer, wt %	81.3	80.2	87.5
Block $\bar{M}_n \times 10^{-5}$	3.9	—	—
BuAc, mol %	51.2	81.9	88.3
Unreacted BG-105, wt %	18.2	19.3	21.7

<sup>a</sup> [BG-105]  $\times 10^5 = 1.176$  mol; temp. = 60°C; solvent = 16 ml benzene; SDS = sodium dodecyl sulfate.

is a time-dependent process in this system, and the chains initiated early in the reaction have a chance to grow longer than the ones initiated later. One reason for this could be the depletion of the monomer in the system through polymerization.

Utilization of the kinetic data suggested that in order to obtain block copolymers with reasonable average molecular weights, i.e.,  $\bar{M}_n \approx 300,000$ , initial PI concentration had to be increased and M/PI mol ratio had to be kept as low as possible. For example, samples of BZ-32 and BZ-34 are good examples for the above. Final molecular weights of the block copolymers were  $3.2 \times 10^5$  and  $2.69 \times 10^5$ , respectively, with butyl acrylate contents equal to methyl methacrylate with 57.5 vs. 50 mol %, respectively (Table V). In both samples, the unreacted PI content was approximately the same, 47 to 49 wt %, since the reaction time was not long enough to use up all the initiator.

As shown in Table VI, a number of block copolymers were synthesized by varying the charge compositions of monomer to polymeric initiator, the polymerization time, as well as the molecular weight of the polymeric initiator. For example, sample BZ-1 bulk polymerization was not successful due to the increase in viscosity and acceleration in the rate of polymerization. The final product was not easily characterized, and the unreacted polymeric initiator concentration was much lower than expected.

Table VII lists some of the block copolymers obtained by emulsion polymerization technique. The final molecular weights and the butyl acrylate contents were very high in emulsion; the monomer to PI ratio was kept always high compared to solution systems in order to increase the rate of diffusion of monomer into the emulsified polymeric initiator particles. Therefore, emulsion block copolymers had very long butyl acrylate and short PMMA blocks. When low butyl acrylate concentrations were used as in BZ-101, conversions at 16 h was much lower than expected. As will be discussed in a subsequent report, the kinetics of emulsion for the second-stage block copolymerization of the butyl acrylate with the MMA polymeric initiator was completely different than conventional emulsion system. This, of course, was reflected in the yields and compositions of block copolymers obtained in this system.

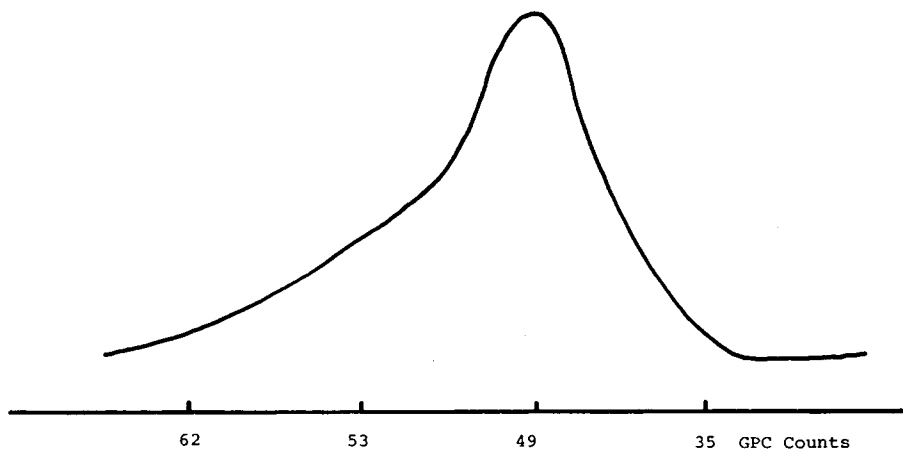


Fig. 5. GPC curve of sample BZ-32 (block copolymer and homopolymer mixture).

### Separation and Characterization

As explained in the experimental section, the *n*-butanol-methanol solvent system was used to separate the block copolymer from the homopolymers. Each fraction was characterized by NMR for composition, by osmometry for the molecular weights, and by GPC for the molecular weight distributions of these polymers. Figures 5-7 show the GPC curves of the polymerization product, the separated block copolymers, and the homopolymers, respectively. GPC was also used as the instrument which allowed a closer look into the molecular weight to show the behavior of the development in the second-stage polymerization. PMMA polymeric initiators time-dependent initiation as observed by the disappearance of the homopolymer, and the formation of the block copolymer was easily followed by GPC. For this particular study, samples were taken from the polymerization bottle at three different conversions and prepared for GPC analysis. Figure 8 shows that at an early conversion of butyl acrylate (7.8%), the peak representing the methyl methacrylate is the predominant one and is

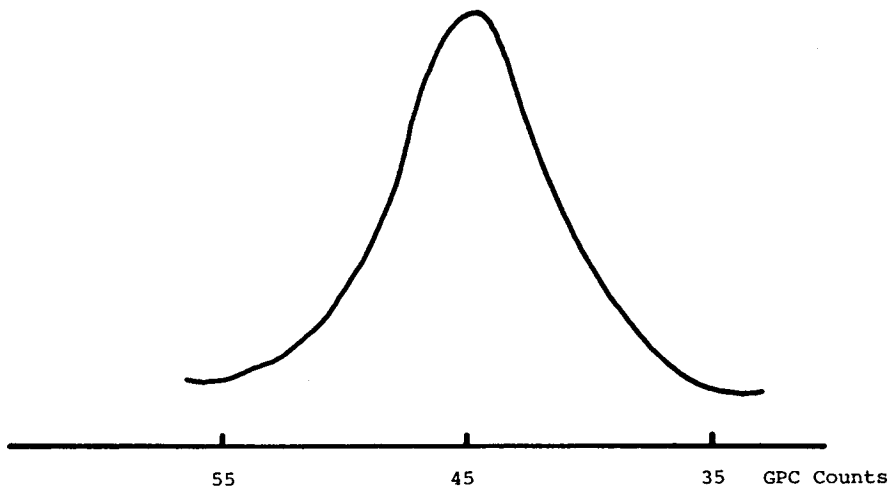


Fig. 6. GPC curve of sample BZ-32 after fractionation: separated block copolymer.

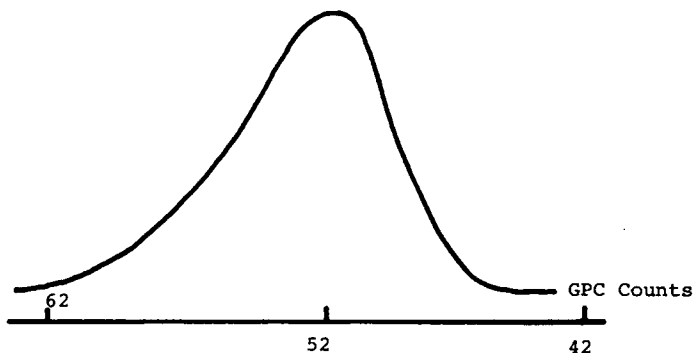


Fig. 7. GPC curve of sample BZ-32 after fractionation: separated PMMA homopolymer.

accompanied with a slight peak at lower counts. As conversion proceeds, the polymeric initiator peak decreases, and at 32% it becomes the tail on the block copolymer peak, which appears at lower counts.

Glass transition ( $T_g$ ) temperatures were determined for several of the separated block copolymers. A du Pont DSC instrument with Chromel-Alumel electrodes at  $10^\circ\text{C}/\text{min}$  heating rate was used. As shown in Figure 9, the endothermic slope changes were observed in two regions. One region was between  $-45$  and  $-38^\circ\text{C}$ . The second region was between  $113$  and  $129^\circ\text{C}$ . The  $T_g$  for poly(butyl acrylate) under the same conditions was  $-52^\circ\text{C}$  and for poly(methyl methacrylate),  $128^\circ\text{C}$  (also shown in Fig. 9).

## DISCUSSION

The sequence reported in this investigation for the formation of the block copolymer turned out to be more efficient than the one reported in Ref. 1. It totally eliminated the formation of one of the homopolymers, in this case homopoly(butyl acrylate). With the utilization of redox initiation in the first stage of the polymerization, all of the active perester chain ends were used up. Selection of a proper monomer for the center block was important. One requirement was that the monomer would not undergo any appreciable extent of chain transfer; the second, that termination by combination was preferable. The se-

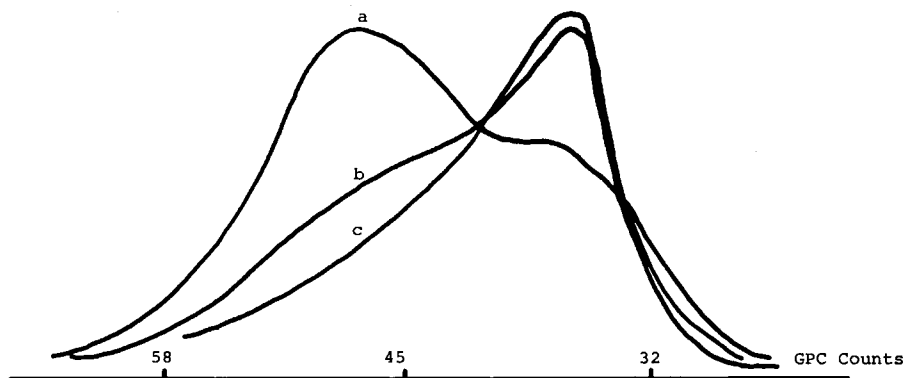


Fig. 8. GPC curves of sample BZ-28 block copolymer formation at: (a) 7.8% conversion, (b) 31.9% conversion, (c) 50.1% conversion.

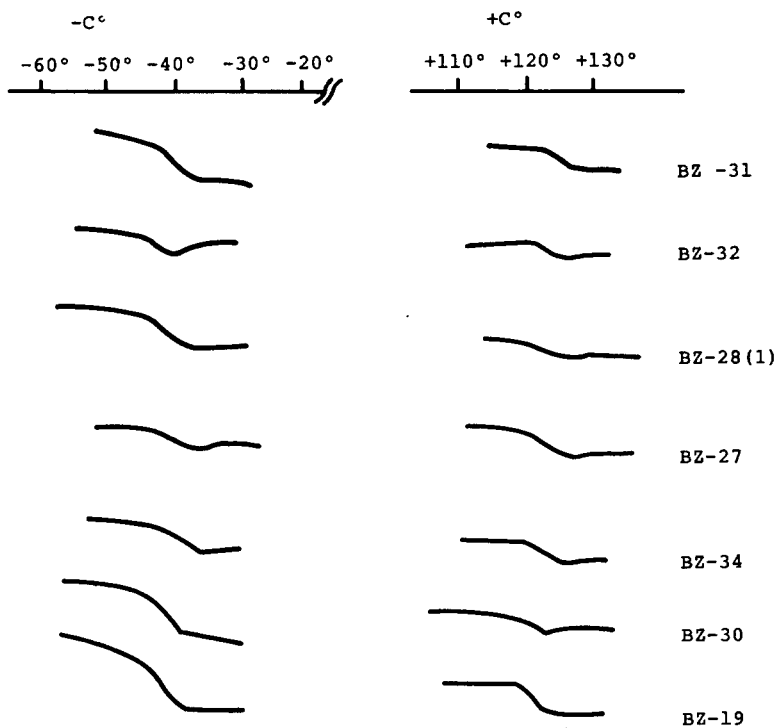


Fig. 9. Glass transition temperatures of poly(butyl acrylate-b-methyl methacrylate).

lection of end block monomer was also important, i.e., it was necessary that the monomer would terminate primarily by disproportionation since any recombination termination would have led to the formation of segmental block copolymers.

There was always a certain percentage of inactive polymeric initiator present during polymerization, and it had to be later separated from block copolymer.

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