

Block Copolymers Obtained by Free-Radical Mechanism. I. Methyl Methacrylate and Styrene

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Synopsis

Block copolymers were synthesized using styrene and methyl methacrylate as the monomers and a multifunctional initiator, di-*t*-butyl 4,4'-azobis(4-cyanoperoxyvalerate). The unique feature of this sequential initiator is the fact that the formation of the free radicals can be achieved thermally and/or by a redox system at different stages. The polymerizations for the formation of the block copolymer were carried out in two stages. First, a polymeric initiator was synthesized, which was then used in the second stage to initiate the polymerization of the second monomer. Styrene and methyl methacrylate were used as the comonomers. Selective solvent fractionation was used for the separation of the block from the homopolymers. The separation technique was found to be efficient, giving pure block copolymers which could subsequently be characterized by GPC, NMR, IR, and EM techniques.

INTRODUCTION

Block copolymers have become more and more important in recent years. The reason for the importance stems from the fact that their special chemical structure yields unusual physical properties which are related to their solid-state morphology. Block copolymers frequently exhibit phase separation which gives rise to a dispersed phase consisting of one block type in a continuous matrix of the second block type. The colloidal and mechanical properties that result from a block copolymer molecule able to participate in different types of phases include, among other things, modification of surface activity, elasticity, and impact strength. Several important classes of block copolymers have found significant commercial applications as raw materials for elastomers, fibers, adhesives, surfactants, thermoplastics, and elastoplastics.

A number of synthetic methods have been developed for the preparation of block copolymers. These methods include mechanochemical synthesis, condensation polymerization, polymerization with Ziegler catalysts, and anionic, cationic, and free-radical polymerizations.

In the free-radical polymerization process, homopolymers are unavoidably produced together with block copolymers; and for quantitative evaluation of the process, separation procedures are necessary to isolate the block copolymer fractions.

Multifunctional free-radical initiators have been used with some success in block polymerization. Orr and Williams¹ made use of *p*-diisopropylbenzene dihydroperoxide with ferrous pyrophosphate as the reducing agent and produced polymeric dihydroperoxide. These polymers were then used to polymerize a second monomer to form block copolymers. Yerigova and Ivanchev² studied

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under nitrogen at 30°C (20 mm). Methyl methacrylate, reagent-grade material from Fisher Scientific Company, was distilled at 50°C (120 mm). Both monomers were stored under nitrogen at 0°C for no longer than one week before use.

Distilled water was freshly redistilled, deaerated, and charged with nitrogen.

Di-*t*-butyl 4,4'-azobis(3-cyanoperoxyvalerate) (R-S604), obtained from Lucidol Division, Pennwalt Corp., was 95% pure, melting at 95°C.

Preparation of Polymeric Initiators

Polystyrene. In 8-oz. bottles, destabilized styrene and the initiator were charged separately, and the dissolution of the R-S604 was sped up by shaking the bottles while nitrogen was used to expel the air. The tightly capped bottles were then clamped and rotated in the thermostated water bath at 60°C. This temperature was sufficient to activate the azo group in the initiator molecule yet leaving the perester groups intact. After the required time period of polymerization, the bottles were quickly cooled and the contents diluted with benzene and coagulated into methanol. The precipitates were filtered with suction. Coagulations and filtrations were repeated twice, after which the polymers were dried under vacuum at 25°C until they reached constant weight. The polymers were stored refrigerated until further use. The preparation conditions employed and the properties of the resultant polystyrene polymeric initiators are listed in Table I.

Poly(methyl Methacrylate). The bulk polymerization for the preparation of the polymeric initiator in this case utilized a 20% benzene solution of tetraethylenepentamine to activate the perester groups of the R-S604 initiator. A 25°C polymerization temperature was used, and the polymers were precipitated from methanol. Table II shows the preparation conditions employed and the molecular weight (M_n) values of these three polymeric initiators.

Fractionation

In order to obtain a series of different molecular weight polymeric initiators with narrow molecular weight distributions, fractionations of the original polymers were necessary. A liquid-liquid phase precipitation technique was employed. A solution containing 10 g polystyrene in 500 cc benzene was mixed in a round-bottom flask equipped with a stirrer. The flask was then placed in a 30°C water bath, and methanol was added slowly with rapid stirring at a rate that maintained a clear solution. The addition of methanol, dropwise at the end, was stopped at the first sign of permanent turbidity. Then exactly 20 cc of methanol was added, and the flask with the precipitate was kept in a 50°C water bath until the turbidity disappeared. Next, the solution was transferred into a 1000-cc separatory funnel and kept in a 30°C water bath for precipitation of the fraction.

After the precipitate had settled and the supernatant liquid was reasonably clear, the separation of the fraction was carried out as follows. The liquid precipitate was allowed to run through the stopcock of the separatory funnel into rapidly stirred methanol. The supernatant liquid was then transferred out of

TABLE I
Synthesis of Polystyrene Polymeric Initiator

	No. 100	No. 200	No. 300	No. 400	No. 500	No. 600	No. 700	No. 800
Wt. styrene, g	200.0	135.0	60.0	10.0	10.0	150.0	150.0	135.0
Wt. R-S604, g	1.0	1.0	1.0	1.0	1.0	0.75	0.75	1.0
Mole ratio M/I	815.4	550.4	244.6	40.8	40.8	815.4	815.4	550.4
Temperature, °C	60.0	60.0	67.0	75.0	75.0	60.0	65.0	65.0
Time, min	240.0	240.0	180.0	180.0	75.0	180.0	180.0	180.0
Conversion, %	13.2	15.0	52.0	90.0	63.5	10.0	20.0	21.2
Intrinsic viscosity, dl/g	0.70	0.54	0.33	0.10	0.098	0.70	0.50	0.42
\bar{M}_w, \bar{M}_n	2.05	1.92	—	—	—	—	1.75	2.15
$\bar{M}_w \times 10^{-3} \pm 10\%$ ^a	150.0	110.0	57.5	11.5	11.2	150.5	100.9	79.1
$\bar{M}_w \times 10^{-3} \pm 10\%$	210.0	125.0	—	—	—	—	107.8	79.6
$\bar{M}_n \times 10^{-3} \pm 10\%$	102.5	65.0	—	—	—	—	61.6	36.9

^a Flory's equation: $\log [\eta] = -4.021 + 0.744 \log M; M = 3 \times 10^4 - 6 \times 10^5$.

TABLE II
 Poly(methyl Methacrylate) Polymeric Initiator Synthesis

	No. 1100	No. 1200	No. 1300
Wt. MMA, g	50.0	25.0	50.0
Wt. R-S604, g	0.5	1.0	1.0
Mole ratio <i>M/I</i>	424	106	212
Wt. TEPA, g	0.05	0.1	0.1
Temperature, °C	25	25	25
Time, hr	18.0	2.5	2.5
Conversion, %	—	32.5	—
\bar{M}_n	1.22×10^6	2.17×10^5	1.9×10^5

the top of the separatory funnel and was ready for the next fractional precipitation. Four additional fractions were separated in the same manner using 10-, 15-, 20-, and 65-cc additions of methanol consecutively. The dried polymer fractions were subsequently used for the determination of molecular weight, molecular weight distribution, and further block copolymer synthesis.

Preparation of Poly(styrene-*b*-Methyl methacrylate)

Using Polystyrene Polymeric Initiator. For each reaction 2.5 g polystyrene polymeric initiator and 5.0 g methyl methacrylate monomer were placed in a bottle and dissolved by shaking the bottle. After the polymer was completely dissolved, nitrogen was used to deaerate the solution. The bottles were then tightly capped with a punched cap and sealed with a self-sealing butyl rubber gasket. When the above reaction was carried out in solution instead of in bulk, 30 g benzene was added. To activate the perester groups, 0.25 g tetraethylenepentamine was added using a hypodermic syringe and needle. Vigorous shaking of the bottle was necessary to obtain homogeneity of the mixture. The polymerization of the methyl methacrylate at 25°C took 24 hr. The contents of the bottle were then dissolved in 100 cc benzene and slowly coagulated in methanol to obtain a finely divided precipitate. Coagulations and filtrations were repeated twice, after which the polymer was dried under vacuum at 25°C.

The polymerization in emulsion was carried out in 8-oz. bottles; 2.5 g sodium dodecyl sulfate was dissolved in 50.0 g freshly distilled and deaerated water. In another container 2.5 g of the polystyrene initiator was dissolved in 5.0 g methyl methacrylate (in some cases 15.0 g benzene was added). These two solutions were then mixed together in the 8-oz. bottle and capped with a punched cap sealed with a butyl rubber gasket. The bottle was clamped and rotated in a 25°C water bath in order to obtain a homogeneous emulsion. After the equilibrium was reached, 2.5 g tetraethylenepentamine (as a 20% aqueous solution) was transferred with a hypodermic syringe and needle into the reaction bottle. The bottle was then rotated in the 25°C water bath for a desired period of time. The same precipitation and drying procedures were applied as in bulk polymerization. The block copolymer synthesis conditions are listed in Tables III and IV.

Using Poly(methyl Methacrylate) Polymeric Initiator. In the bulk polymerization of the block polymer a 1.5-g poly(methyl methacrylate) polymeric initiator was dissolved in styrene monomer. The polymerization conditions are shown in Table V.

TABLE III
No. 100 Series Block Copolymer Synthesis

	No. 101	No. 102	No. 103	No. 106	No. 107
Wt. initiator, g	3.0	3.0	3.0	4.0	3.0
Wt. MMA, g	9.5	9.5	3.0	8.6	9.0
Wt. TEPA, g	0.12	0.36	0.3	0.3	0.3
Temperature, °C	25.0	25.0	25.0	30.0	25.0
Polymerization type	bulk	soln. ^a	soln. ^a	soln. ^a	emul. ^b
Time, hr	68.0	24.0	24.0	65.0	29.0
Conversion of MMA, %	78.9	51.0	47.0	71.5	82.8
Styrene content, %	28.5	39.2	68.0	39.4	28.7

^a 30.0 g benzene used as solvent.

^b 2.5 g SLS and 50.0 g water used.

TABLE IV
No. 200 Series Block Copolymer Synthesis

	No. 201	No. 202	No. 203	No. 204
Wt. initiator, g	3.0	3.0	2.0	2.0
Wt. MMA, g	5.0	8.0	5.0	5.0
Wt. TEPA, g	0.3	0.3	0.3	0.3
Temperature, °C	25.0	25.0	28.0	28.0
Polymerization type	bulk	emul. ^a	bulk	emul. ^a
Time, hr	24.0	24.0	24.0	24.0
Conversion of MMA, %	75.0	88.2	73.7	89.1
Styrene content, %	47.0	29.8	35.2	31.0

^a Emulsion polymerization, 50.0 g water and 2.5 g SLS used.

TABLE V
Block Copolymer Synthesis and Separation Using Poly(methyl Methacrylate) Polymeric Initiator

	No. 1102	No. 1104	No. 1201	No. 1202	No. 1203
	Synthesis				
Wt. initiator, g	1.5	1.5	1.5	1.5	1.5
Wt. styrene, g	12.0	12.0	12.0	7.5	12.0
Temperature, ± 1°C	50	65	50	50	65
Time, hr	36	27	24	24	27
	Separation				
Wt % PS	22.5	27.0	22.0	35.2	50.6
Wt % PMMA	46.6	14.3	51.5	45.9	22.0
Wt % Block copolymer	30.9	58.7	16.5	18.9	27.4
Styrene molar content, % in block copolymer	18.8	26.3	—	—	78.3

Separation of the Polymers

A selective solvent extraction method was used to separate the block copolymers from the homopolymers of methyl methacrylate and styrene. About 2 g polymer mixture was extracted at one time using an extraction thimble and a Soxhlet extraction apparatus. The separation is best followed on the separation flow chart shown in Figure 1.

The separation efficiency by this extraction method was checked by mixing

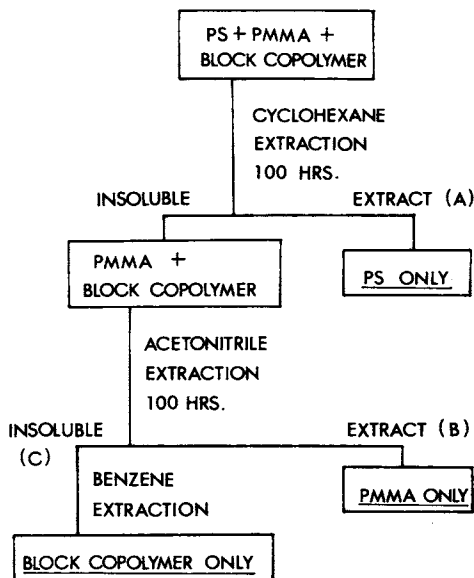


Fig. 1. Separation flow chart.

together polystyrene, poly(methyl methacrylate), and their block copolymer in ratios of 1:1:1 and 1:1:2. The results are shown in Table VI.

Polymer Characterization

Infrared and nuclear magnetic resonance spectroscopies were used to obtain the microstructure of the polymers. The molecular weights and molecular weight distributions were done by osmometry, viscometry, and gel permeation chromatography. The emulsion particle sizes were determined using electron microscopy.

RESULTS AND DISCUSSION

Preparation of Polymeric Initiators

For the synthesis of the styrene and methyl methacrylate polymeric initiators, di-*t*-butyl 4,4'-azobis(4-cyanoperoxyvalerate) was used. This sequential initiator is manufactured by Lucidol Division of Pennwalt Corporation and carries the code name R-S604.

In the synthesis of the styrene polymeric initiator, use was made of styrene's primary mode of chain termination, namely, termination by combination. The polymerization in bulk involved the thermal activation of the azo groups which then yielded a polymeric initiator with perester groups at both ends of the polymeric chain:

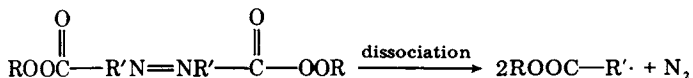


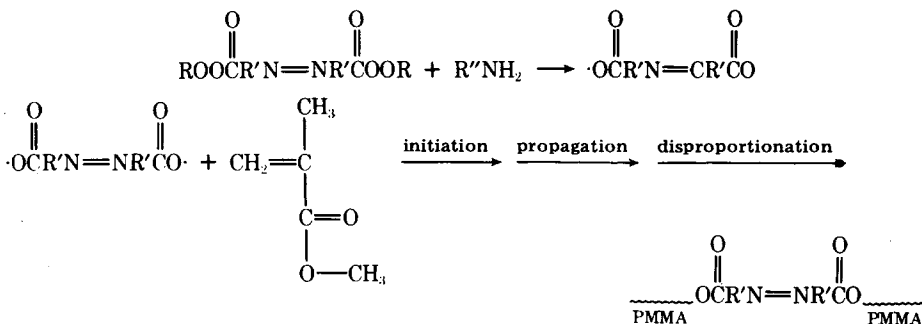
TABLE VI
Separation Efficiency by Extraction Method^a

	1			2		
	Feed, g	Ext., g	Rec., %	Feed, g	Ext., g	Rec., %
PS (\bar{M}_n 75,400)	1.102	1.078	97.82	1.094	1.084	99.09
PMMA (\bar{M}_n 21,700)	1.093	1.082	98.99	1.015	0.990	97.54
Block S/MMA (73,300/21,700)	0.945	0.948	100.32	2.253	2.260	100.31
		3			4	
	Feed, g	Ext., g	Rec., %	Feed, g	Ext., g	Rec., %
PS (\bar{M}_n 150,000)	0.522	0.512	98.08	0.463	0.458	98.92
PMMA (\bar{M}_n 1,220,000)	0.540	0.552	102.22	0.475	0.458	98.92
Block S/MMA (150,000/1,120,000)	0.489	0.480	98.16	1.012	1.002	99.01

^a Cyclohexane, acetonitrile, and benzene used as selective solvents.

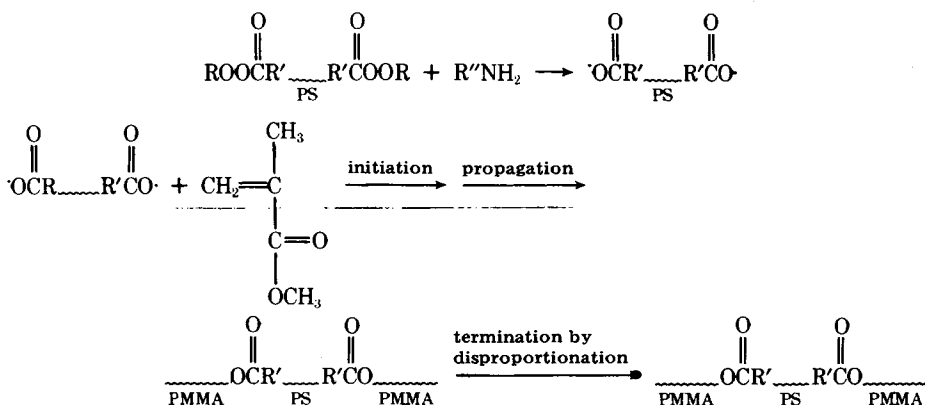
S604 initiator follows first-order kinetics. The straight lines when extrapolated do not pass through the origin, however, suggesting chain transfer, in this case induced decomposition of perester groups.

The poly(methyl methacrylate) polymeric initiator was synthesized by making use of the methyl methacrylate's primary mode of termination, in this case termination by disproportionation. The R-S604 initiator perester endgroups were activated by tetraethylenepentamine (TEPA). This reaction produced a poly(MMA) molecule with an azo group in the backbone:



Block Copolymers

The polymeric initiators were used in the synthesis of the block copolymers. These second-stage polymerizations were carried out in bulk, in solution, and in emulsion. In the present discussion, the polymerization of methyl methacrylate initiated by the styrene polymeric initiator will be presented in greater detail, and less emphasis will be placed on the block formation using MMA polymeric initiator. The primary emphasis of this investigation was to establish the feasibility and practicability of a free radical-initiated block polymer using a multifunctional initiator of the azo perester type. The main reactions involved in the block copolymer preparation with the polystyrene polymeric initiator are



where $\text{R}''\text{NH}_2 =$ tetraethylenepentamine.

The No. 100 series styrene polymeric initiator had a viscosity-average molecular weight of 150,000, and since in the second-stage bulk and emulsion polymerizations the MMA was also to be the solvent, a minimum monomer-to-initiator ratio of 3:1 could be used. In No. 200 series with a \bar{M}_v of 110,000,

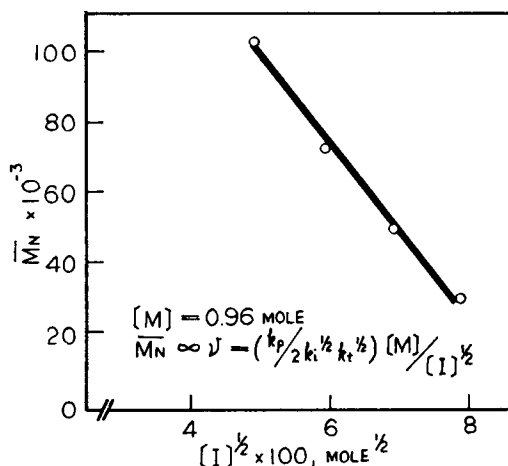


Fig. 3. Effect of initiator RS-604 concentration on molecular weight of styrene polymeric initiator.

the ratio could be lowered to 2.5:1. This ratio was very important in controlling the styrene content in the final block copolymer. Higher MMA concentrations in the ratio result in a lower styrene content.

In the quantitative phase of the study of the block copolymer formation, several experiments were carried out to gain better insight into the mechanism. For one of these, the No. 700 series polymeric initiator with M_v 100,000, was fractionated into five fractions. The by GPC determined molecular weights of the fractions are listed in Table VII. For a block synthesis reaction in bulk with these fractions, the amounts of the MMA monomer and the styrene polymeric initiator were the same. The actual molar concentrations of the initiator varied, of course, depending on the molecular weight of the initiator. TEPA was used to activate the perester groups which then initiated the MMA. After 24 hr of reaction time, conversion of the MMA was 80% with the lower molecular weight fractions. With the higher molecular weight fraction (M_w 167,000) yield was only 25%. When the unfractionated polystyrene was used as initiator, the conversion of MMA to polymer was more than 80% in the same time period.

The No. 800 series polystyrene initiator was used to start block reactions in emulsion. Although the molecular weight of this polymer was relatively low, M_v 79,000, its solubility in MMA was still limited. For this reason benzene was added to the reaction mixture. Table VIII lists the reaction conditions. The recipes of these emulsion systems were designed in such a way that the solid contents before polymerization were approximately 4%. At the end of the reaction, i.e., at 100% conversion of MMA, the solid content was around 10%. The total organic phase was about one third of the total charge, which is equivalent to a common emulsion polymerization charge ratio. The results of these reactions are also listed in Table VIII where it can be seen that high conversions of MMA could already be reached after 2.5 hr of reaction. The conversion-versus-time plot for one of the experiments in emulsion is shown in Figure 4. The polymerization rates were found to be fast and constant up to about 70% to 80% conversion. In this modified emulsion system the styrene polymeric initiators were already in the particles protected by the emulsifier molecules before the

TABLE VII
No. 700 Series Block Copolymer Synthesis (in Bulk)

	No. 700II	No. 700III	No. 700IV	No. 700V	No. 700VI	No. 701	No. 702
Molecular weight of styrene polymeric initiator							
\bar{M}_w	167,000	115,000	78,000	55,000	36,500	—	—
\bar{M}_n	129,000	88,000	58,000	43,000	28,000	—	—
Wt. initiator, g	1.2	1.2	1.2	1.2	1.2	2.5	2.5
Initiator concn., moles $\times 10^6$	7.2	10.4	15.4	21.8	32.9	—	—
Wt. MMA, g	2.4	2.4	2.4	2.4	2.4	3.0	5.0
Wt. TEPA, g	0.07	0.10	0.15	0.22	0.33	0.30	0.30
Temperature, °C	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Time, hr	24.0	24.0	24.0	24.0	24.0	24.0	24.0
Conversion of MMA, %	25.0	39.6	52.5	85.0	79.2	87.6	86.5
Styrene content, %	66.7	55.8	48.8	39.0	38.7	48.8	36.6

TABLE VIII
No. 800 Series Block Copolymer Synthesis (in Emulsion)^a

	No. 801	No. 802	No. 804
Wt. initiator, g	2.5	2.5	2.5
Wt. MMA, g	5.0	7.5	5.0
Wt. benzene, g	15.0	15.0	15.0
Wt. SLS (emulsifier), g	2.5	2.5	2.5
Wt. water, g	50.0	50.0	50.0
Wt. TEPA, g	0.3	0.3	0.2
Temperature, °C	25.0	25.0	25.0
Time, hr	24.0	24.0	2.5
Conversion of MMA, %	95.0	98.5	90.2
Styrene content, %	34.7	25.3	35.7

^a Rate of agitation = 40 rpm.

polymerization commenced. Due to the low temperature (25°C), the reaction could not start until the water-soluble activator TEPA entered the particles. The particle sizes of the latex after complete conversion were in the range of 500 to 2000 Å.

Separation and Characterization

Before subjecting the block copolymers to actual selective solvent separations, the efficiency of the extractions was tested, and the results are shown in Table VI. These results indicate that the separation efficiency is excellent: at least

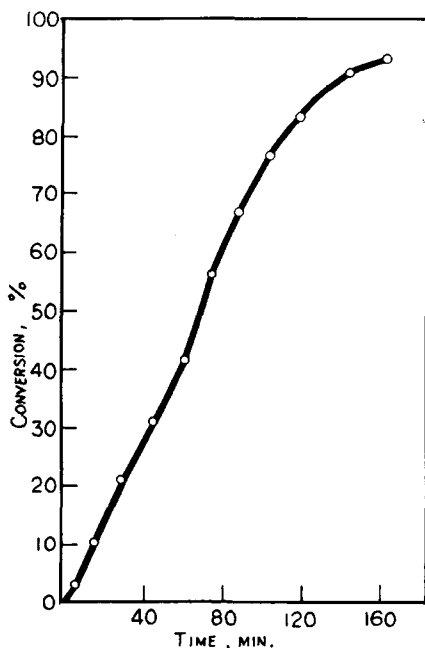


Fig. 4. Conversion-vs.-time curve (preparation of No. 802 in emulsion system): Recipe: precursor no. 800, 2.5 g; benzene, 15.0 g; MMA, 7.5 g; SLS, 2.5 g; water, 50.0 g. TEPA, 0.3 g; water, 1.2 g.

TABLE IX
Separation Results. Block Synthesis in Bulk and Solution

	Bulk						Solution	
	No. 101	No. 201	No. 203	No. 701	No. 702	No. 102	No. 103	No. 106
Wt % PS	16.6	32.3	15.7	37.0	21.9	16.6	58.2	30.0
Wt % PMMA	16.8	18.7	35.7	33.9	27.2	16.8	26.0	34.8
Wt % block	66.6	49.0	48.6	29.1	50.9	13.1	15.8	35.2
Styrene molar content in block copolymer, %	17.4	27.4	26.2	40.5	28.8	33.6	40.2	38.0
$\bar{M}_n \times 10^{-3}$ S/MMA	103/468	65/140	65/176	62/88	62/147	103/195	103/147	103/161

TABLE X
Separation Results. Block Synthesis in Emulsion

	No. 107	No. 202	No. 204	No. 801	No. 802	No. 804
Wt % PS	22.5	25.6	26.1	30.5	20.9	32.8
Wt % PMMA	28.5	40.5	43.7	28.6	19.7	8.6
Wt % Block	49.0	33.9	30.2	40.9	59.4	58.6
Moles S in block, %	11.6	24.4	24.3	10.3	8.1	10.0
$\bar{M}_n \times 10^{-3}$ S/MMA	103/751	65/195	65/195	37/310	37/404	37/320

TABLE XI
Separation Results. No. 700 Series Block Copolymer—Molecular Weight Effect^a

	No. 700II	No. 700III	No. 700IV	No. 700V	No. 700VI	No. 701	No. 702
Polystyrene Initiator $\bar{M}_n \times 10^{-3}$	129	88	58	43	28	62 ^b	62 ^b
Wt % PS	32.1	30.4	31.8	29.2	35.0	37.0	21.9
St % PMMA	12.4	17.9	19.9	20.1	17.8	33.9	27.2
Wt % Block	55.5	51.7	48.3	50.7	47.2	29.1	50.9
Styrene molar content in block copolymer, %	62.3	49.2	35.2	21.3	16.6	40.5	28.8
$\bar{M}_n \times 10^{-3} \pm 10\% \text{ S/MMA}$	129/75	88/87	58/103	43/153	28/135	62/88	62/147

^a Synthesis in bulk data refer to Table XI.

^b Unfractionated.

TABLE XII
Separation Results, No. 700 Series Block Copolymer—Time of Conversion Effect

	No. 703	No. 704	No. 705	No. 706	No. 707	No. 708
Time of pzn, hr	2.0	5.0	8.0	16.0	25.0	168
Conversion of MMA, %	49.5	55.1	57.6	61.0	66.1	75.0
Wt % PS	34.8	34.6	33.3	32.3	31.2	29.8
Wt % PMMA	24.6	25.3	25.9	27.8	29.9	32.2
Wt % block	40.6	40.1	40.8	39.9	38.9	38.0
Styrene molar content in block copolymer, %	38.0	32.3	32.5	31.9	30.5	26.3
$\bar{M}_n \times 10^{-3} \pm 10\% S/MMA$	62/97	62/125	62/124	62/127	62/136	62/167

^a Solution polymerization at 25°C using No. 700, 2.0 g; MMA, 4.0 g; and TEPA, 0.2 g in 20.0 g benzene.

98% of the original polystyrene and poly(MMA) homopolymers was recovered. These extracted homopolymers were also tested by infrared and NMR spectroscopy for purity and found clean, thus proving excellent separation by this technique.

The selective solvent separations of the block copolymers from the concomitantly formed poly(MMA) were carried out to determine the material balance between these two and the polystyrene from the unreacted or for other reasons dead polymeric initiator. Table IX shows the results for the blocks synthesized in bulk and solution, and Table X lists the results for emulsion polymerization. The percent block in the analyzed material varied from 13% up to 67%. The molar content of styrene in the block as calculated from NMR spectra of the blocks was lowest when the block synthesis was carried out in emulsion. This is to be expected since in emulsion the reaction is very fast, and high molecular weight is created almost at the beginning of the reaction. The molecular weight data provided in Tables IX and X were based on the molecular weights of the styrene polymeric initiator, the final molecular weight of the block, and the styrene molar content data.

In a quantitative study of the effects of the molecular weight of styrene polymeric initiator on the formation of the block copolymer, the fractions shown in Table VII resulted in blocks which after selective solvent separation gave the material balance as listed in Table XI. These results show that the amount of block formed decreases with decreasing molecular weight with no great variations in the homopolymer yields. The number-average molecular weights of methyl methacrylate segments in the block copolymers were quite dependent on the molecular weight of the polymeric initiator. The \bar{M}_n of the MMA segments increased with decreasing initiator molecular weight.

A study of the effect of reaction time gave the results shown in Table XII. The conversion of MMA reached 50% in 2 hr in this solution polymerization, after which the rates started leveling off. The analysis results show that the 40% block was produced during these first 2 hr, with no change thereafter.

DISCUSSION

It is obvious from the results discussed above that the reaction scheme used in this investigation creates a number of avenues for homopolymer formation. In the first stage of reaction, i.e., in the polymeric initiator preparation, the main reactions involved are the formation of the polystyrene with either one or two perester chain ends. The decomposition of the perester groups, either thermal or radical induced, is possible and results in the formation of an unreactive polystyrene chain. The observed pseudozero-order rates of polymerization and the molecular weight distribution data support the assumption of a premature decomposition of the perester groups. These polystyrene molecules with no active endgroups are, of course, unable to initiate any block polymerization and add to the formation of the large amounts of homopolystyrene found in the final polymer mixture. It is possible also for the primary radicals in the second stage of polymerization to abstract a hydrogen from RNH radical, for example, and terminate creating a homopolystyrene molecule. Besides the $\cdot\text{OOCR}\sim\text{RCOO}\cdot$ and $\text{HOOCR}\sim\text{RCOO}\cdot$ which would initiate tri- and diblock formation, spec-

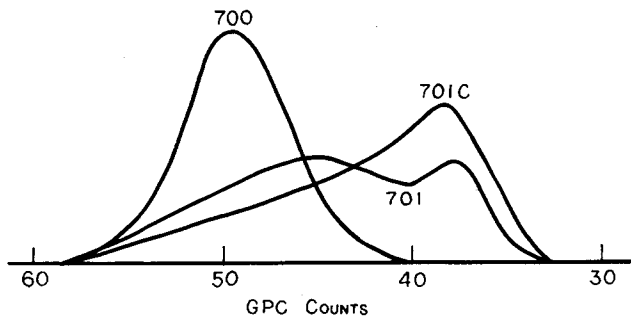


Fig. 5. GPC curves of styrene polymeric initiator (700) and block copolymer (701 and 701C).

tively, the amine radicals $R\dot{N}H$ and the alkoxy radical $RO\dot{O}$ would create only homopoly(MMA).

An attempt was made in this investigation to analyze the distribution of diblock and triblock copolymers. In Figure 5 the GPC curve 700 represents sample No. 700 polymeric initiator with \bar{M}_n 6.2×10^4 and a distribution index \bar{M}_w/\bar{M}_n of 1.75; curve 701 represents the reaction product from sample No. 700 bulk reaction with MMA. After extractions of the homopolymers, this two-hump curve gives curve 701C, which suggests that the lower molecular weight peak of curve 701 corresponds to homopolystyrene and the block copolymer has a very wide distribution. Although GPC techniques have sometimes been used to analyze the distribution of diblock and triblock copolymers,⁷ our GPC curves did not give any information on the structures of the block copolymers. This was probably due to the broad distribution of the polystyrene initiator.

The fractionated polystyrene initiators were thus prepared, and the GPC results of one of them are shown in Figure 6. Curve 700II represents the polystyrene initiator with \bar{M}_n 1.29×10^5 and a distribution index of 1.30. The 700II-1C curve represents the block copolymer only. As can be seen, there is a molecular weight shift from the lower elution counts to the higher ones for the block copolymers, but the broad distribution with the long tail fails to give any indication to what percentage the block is a di- or triblock.

The alternate approach for the synthesis of styrene-MMA block copolymer was mentioned at the beginning of this paper. One of the advantages of this approach is that only a very small amount of homopolystyrene should be formed

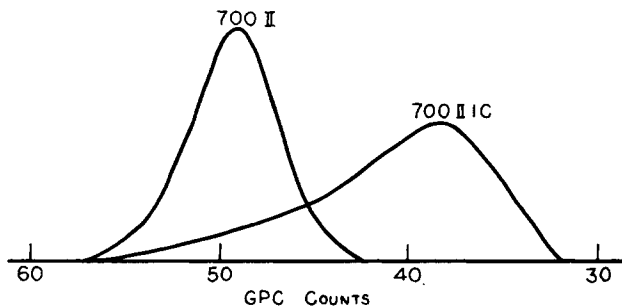


Fig. 6. GPC curves for a fractionated polystyrene initiator.

