

Block Copolymers Obtained by Free Radical Mechanism III. Synthesis in Emulsion

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Synopsis

Block copolymers were synthesized by a sequential free radical polymerization method with the use of di-*t*-butyl-4,4'-azobis(4-cyanoperoxyvalerate) as the trifunctional initiator. The polymerizations were carried out in two stages. First, the poly(methyl methacrylate) and poly(butyl methacrylate) polymeric initiators were synthesized by activating, at room temperature, the perester groups of the initiator with tetraethylenepentamine. For the second stage, the reaction ingredients were pre-emulsified, then the azo groups of these polymeric initiators were activated thermally in the presence of either styrene or *p*-methylstyrene. It was found that the reaction in the emulsion particles followed bulk kinetics, although the average size of the particles was small, 50–100 nm.

INTRODUCTION

It has been quite a number of years, that certain copolymers particularly the di-block or tri-block type have steadily gained industrial importance.^{1,2} This significant commercial development of these polymers has been due to the fact that they possess special properties which are not attainable in simple homopolymers or random copolymers. Most of these block copolymers have been synthesized by initiation mechanisms other than free radical.

In two previous papers in this series, Piirma and co-workers^{3,4} reported syntheses of block copolymers using a trifunctional free radical initiator, di-*t*-butyl-4,4'-azobis(4-cyanoperoxyvalerate). These studies included monomers such as styrene, methyl methacrylate, and butyl acrylate. The reactions were carried out in two stages. First, a polymeric initiator was produced by the activation in the initiator of either the azo group or the perester end groups. The unused active group in the initiator, now lodged in the polymer, was then activated in the second stage to form a di- or tri-block copolymer.

In the present study, two polymeric initiators, poly(methyl methacrylate) and poly(butyl methacrylate) were prepared in bulk by the activation at room temperature of the initiator perester groups with tetraethylenepentamine. This polymerization resulted in a polymeric initiator with a center azo group. In the second stage, this azo group was activated thermally in the presence of styrene or *p*-methylstyrene as monomers. Prior to this second-stage polymerization the polymeric initiator was dissolved in the appropriate second monomer and the system emulsified using an aqueous solution of sodium dodecyl sulfate stabilizer. Hence, this article will deal with the kinetic parameters of the pre-emulsified polymerization system, their dependence on each other, and the particle size. Although, the styrene–methyl methacrylate combination of monomers was chosen as the model for most of the experiments, the results with other monomers are included whenever necessary.

TABLE I
 Polymeric Initiator Preparation

Run #	MRA-2	MRA-3	MRA-4	MRA-7	MRA-9
Methyl methacrylate (g)	240	240	240	120	200
RA-604 initiator ^a	4.0	6.0	8.0	6.0	6.0
[I]/[M] × 10 ³	3.9	5.9	7.9	11.8	7.1
Conversion (%)	8.1	10.8	12.0	17.2	11.7
$\bar{M}_n \times 10^{-5}$	6.1	4.3	3.1	2.2	3.5
Run #	BRA-1	BRA-2	BRA-3	BRA-7	BRA-8
Butyl methacrylate (g)	240	240	240	120	60
RA-604 initiator ^a	4.0	6.0	8.0	4.0	4.0
[I]/[M] × 10 ³	6.0	9.0	11.9	11.95	23.9
Conversion (%)	13.0	15.6	18.3	18.3	28.6
$\bar{M}_n \times 10^{-5}$	4.1	3.3	2.2	2.2	1.3

Polymerization temp. 25°C.

Polymerization time 3 h for MMA series, 4 h for BMA series.

^a1 g Tetraethylene pentamine.

EXPERIMENTAL

Styrene, reagent grade (Eastman Kodak Company) and *p*-methyl-styrene (Mobil Oil Co.) were washed with 10% NaOH aqueous solution and then dried over Na₂SO₄, followed by vacuum distillation under nitrogen at 30°C (20 mm). Methyl methacrylate and butyl methacrylate reagent grade (Matheson, Coleman and Bell Company) were washed with 10% NaOH aqueous solution then dried over Na₂SO₄, followed by a vacuum distillation under nitrogen at 50°C (120 mm). All monomers were stored under nitrogen at 0°C.

Di-*t*-butyl-4,4'-azobis(4-cyanoperoxyvalerate), RS-604, provided by Lucidol Chemical Company, in 92–98% purity was used as received.

Preparation of Polymeric Initiator

The distilled methyl methacrylate (MMA) or butyl methacrylate (BMA) monomer and the multifunctional initiator were charged separately under N₂ into 100 cm³ bottles having screw caps lined with self-sealing butyl rubber gaskets. Tetraethylenepentamine (TEPA), which served as the reducing agent for initiation, was charged with a syringe and needle through the bottle cap. The bottles were clamped tightly to a shaft in a 25°C thermoregulated water bath and rotated at 45 rpm. After the required polymerization time periods, bottles were removed from the bath and the contents precipitated in methanol. The recovered polymer samples were vacuum dried to a constant weight for conversion analysis. Table I lists the polymerization conditions and results for various initiator and monomer concentrations for both methyl methacrylate and butyl methacrylate.

Fractionation of Polymeric Initiator

The polymeric initiators PMMA and PBMA were fractionated using benzene and methanol as the solvent nonsolvent system to provide a narrower molecular weight distribution sample for further work. This was carried out

by adding methanol dropwise to a 1.0% polymer benzene solution until turbidity started to develop at 25°C. The first fraction from sample number MRA-3 was chosen for further use, it had a number average molecular weight of 5.05×10^5 . Sample number BRA-1 first fraction with an $\bar{M}_n = 3.94 \times 10^5$ was the poly(butyl methacrylate) polymeric initiator for further study.

Pre-emulsification for the Second-Stage Polymerization

The second-stage block copolymer synthesis was carried out in emulsion. For this, a pre-emulsification process was applied whereby to a monomer solution containing styrene and the polymeric initiator was added an aqueous solution of a sodium dodecyl sulfate. This was carried out in 100 cm³ bottles using different concentration of the surfactant solution. The bottles were clamped to a shaft in a 250°C temperature bath and rotated at 45 rpm for 2 h. Through this pre-emulsification procedure, a fine emulsion can be created by phase transition from water-in-oil (w/o) to oil-in-water (o/w). For the purpose of determining the size of the emulsion particles before polymerization, the monomer swollen particles were hardened with osmium tetrachloride. This usually required two to three drops of 1% (w/v) OsO₄ in distilled water. All the particle size analyses were carried out on dilute emulsions by transmission electron microscopy.

Preparation of Block Copolymers

From 30 g to 70 g of the polymeric initiator was dissolved in 100 g monomer, then emulsification was carried out using 240 mL of aqueous sodium dodecyl sulfate (SDS) solution. The concentration of the SDS solution was varied from 1% to 5% aqueous phase. The bottles containing all the pre-emulsified ingredients were clamped onto the shaft of a 60°C water bath and rotated end-over-end at 45 rpm. The conversion time relationships of these reactions

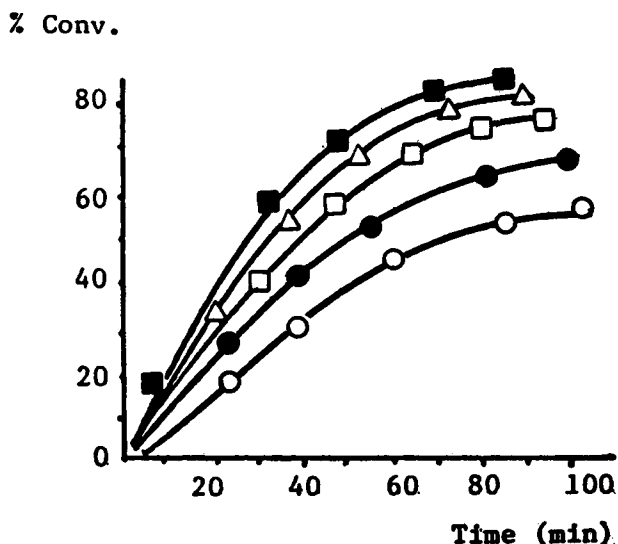


Fig. 1. Conversion time curves for poly(MMA-b-STY-b-MMA) at various polymeric initiator amounts: ○ 3 g, ● 4 g, □ 5 g, △ 6 g, ■ 7 g.

% Conv.

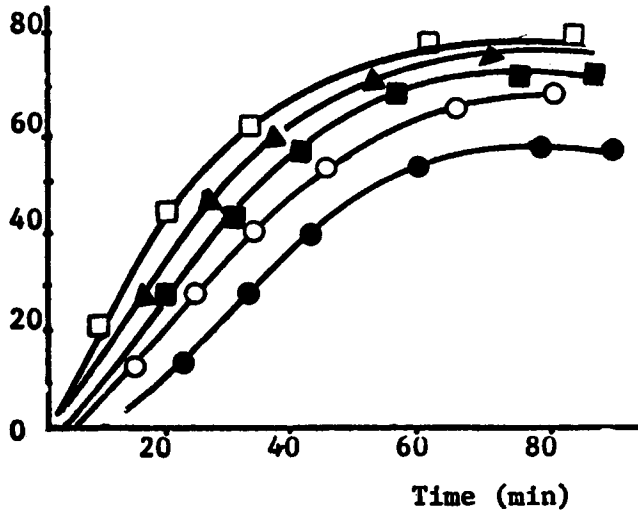
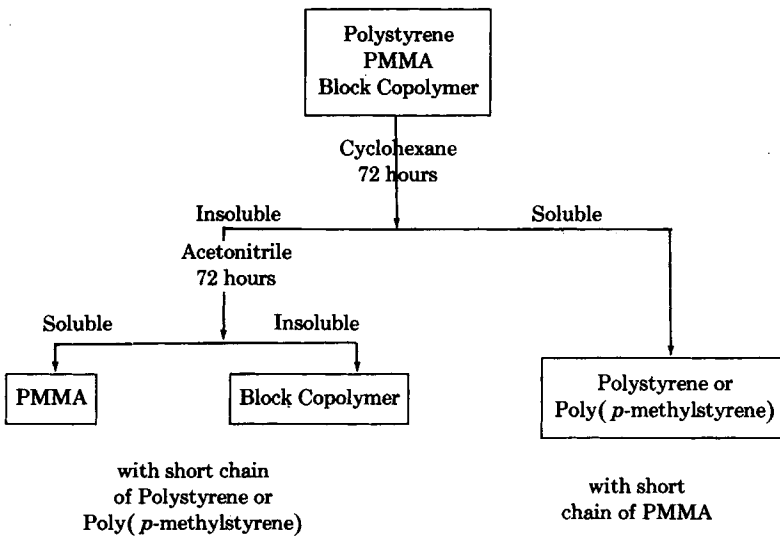


Fig. 2. Conversion time curves for poly(MMA-b-STY-b-MMA) at various surfactant amounts: ● 1% SDS, ○ 2% SDS, ■ 3% SDS, ▲ 4% SDS, □ 5% SDS.

TABLE II
Extraction Scheme for Poly(MMA-b-Sty-b-MMA) and Poly(MMA-b-PMS-b-MMA)



are shown in Figures 1 and 2 for the PMMA styrene block combination for different initiator and surfactant concentrations, respectively.

Block Copolymer Separation and Purification

Since free radically initiated block copolymers always contain some homopolymers in the reaction mixture, and, in order to gain any information on the blocking efficiency, a fractional separation has to be carried out. In this study, the extractions were carried out in a Soxhlet apparatus. The separation scheme is shown in Table II.

Polymer Characterization

The following analyses were carried out to characterize the block copolymers. Varian 7-60 nuclear magnetic resonance (NMR) and infrared (IR) for structure analysis; membrane osmometry (Hewlett-Packard High-Speed Osmometer 503) and gel permeation chromatography (Waters Ana-Prep) for molecular weight and molecular weight distribution. Electron microscopy and hydrodynamic chromatography for latex particle characterization.

RESULTS AND DISCUSSION

Block Copolymer Synthesis in Emulsion

Four different block copolymers were synthesized in this study. The combinations were poly(MMA-b-Sty-b-MMA), poly(MMA-b-PMS-b-MMA), poly(BMA-b-Sty-b-BMA), and poly(BMA-b-PMS-b-BMA). The polymeric initiators containing the azo group were dissolved in the appropriate monomers, then emulsified by the slow addition of an aqueous solution of sodium dodecyl sulfate. This created at first a water-in-oil emulsion, which upon further addition of the aqueous SDS solution, inverted to an oil-in-water emulsion. It was observed that this kind of procedure provided an emulsion with a rather narrow particle size distribution, and a particle diameter in the range of 50 to 100 nm.

The polymerization rate dependence on surfactant and polymeric initiator concentrations were taken from Figures 1 and 2. The calculated data from log-log plots for the four block copolymers are listed in Table III. There is, obviously, a direct relationship between the rate of polymerization and the

TABLE III
Dependence of the Rate of Polymerization on the Surfactant and Initiator Concentrations $R_p \propto [S]^a [I]^b$

Block copolymers	<i>a</i>	<i>b</i>
Poly(MMA-b-sty-b-MMA) ^a	0.68	0.53
Poly(MMA-b-PMS-b-MMA) ^a	0.56	0.38
Poly(BMA-b-Sty-b-BMA) ^a	0.57	0.40
Poly(BMA-b-PMS-b-BMA) ^b	0.25	0.26

Polymeric initiator: ^a poly(methyl methacrylate); ^b poly(butyl methacrylate).
Surfactant: Sodium dodecyl sulfate.

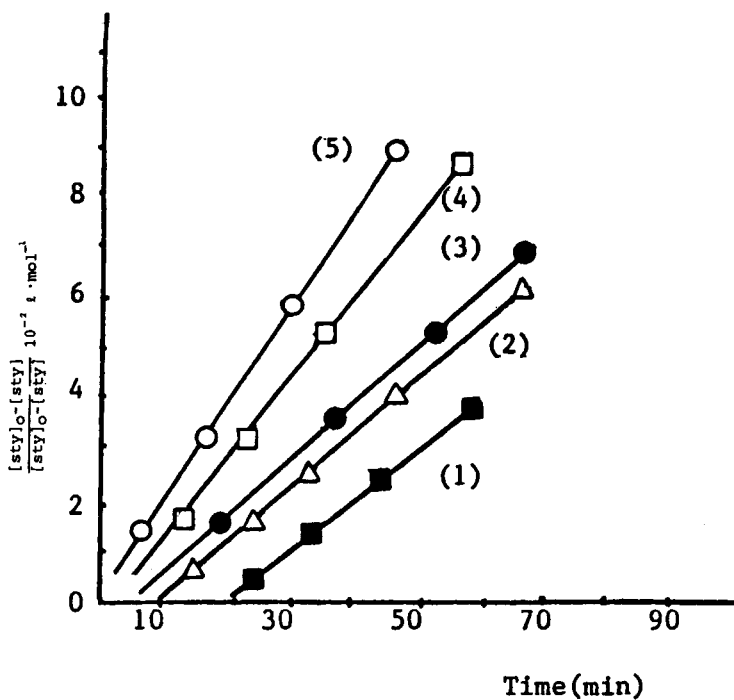


Fig. 3. Second-order kinetics of poly(MMA-b-STY-b-MMA) during second-stage reaction: (1) ■ MRAS-1; (2) △ MRAS-2; (3) ● MRAS-3; (4) □ MRAS-4; (5) ○ MRAS-5.

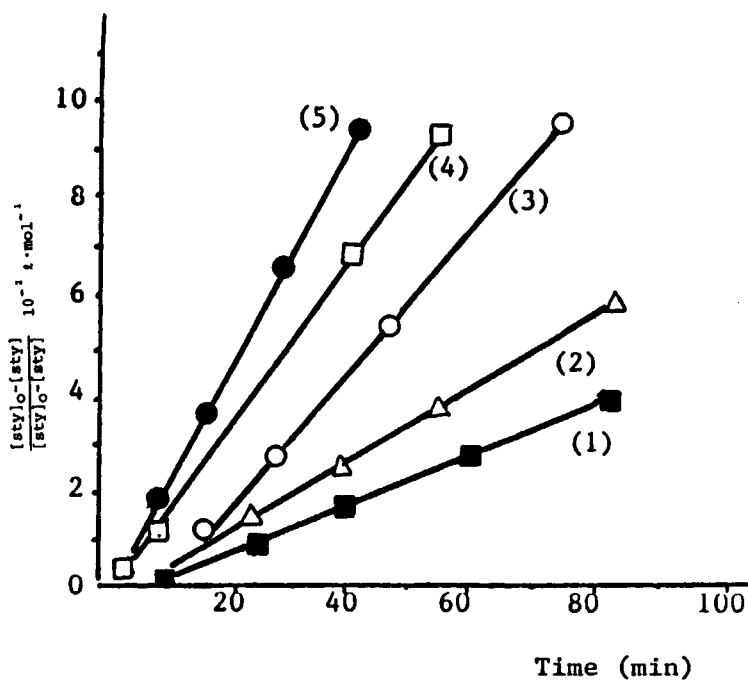


Fig. 4. Second-order kinetics of poly(MMA-b-STY-b-MMA) during second-stage reaction: (1) ■ MRAS-6; (2) △ MRAS-7; (3) ○ MRAS-8; (4) □ MRAS-9; (5) ● MRAS-10.

surfactant concentration, since each particle-containing monomer and polymeric initiator can be considered to be one bulk polymerization site. Hence, the higher the surfactant concentration, the higher the number of particles that this surfactant can stabilize and consequently the higher the number of reaction sites. The monomer is in the vicinity of the initiator molecules due to the pre-emulsification process. Once the azo group is activated, there is competition between the newly formed radicals to recombine or to initiate polymerization. However, since most of the monomer is held inside the particles by the surfactant, the probability of forming the second block segment is higher than recombination. Each particle can be regarded as a reaction site and obeys bulk polymerization kinetics. The bulk kinetics is further verified by treatment of the rate data in Figures 1 and 2 in terms of second-order kinetics. Figures 3 and 4 exhibit the recalculated experimental data according to the second-order treatment and as can be seen the data fit well on a straight line in the region between 10 to 80% conversion. At higher conversions it is expected that the conversion curves start to level off due to monomer depletion.

It should be noted here that of the four systems studied the polymerization for the synthesis of the poly(MMA-*b*-Sty-*b*-MMA) has the fastest rate and shortest induction period. This might be due to steric hindrance of the butyl and *para*-methyl groups for the other combinations.

Separation and Characterization of Block Copolymers

Using the selective solvent separation scheme shown in Table II, the block copolymers were separated from other products. Table IV lists the results which indicate that the methyl methacrylate-styrene combination has the highest block yield while the other three pairs exhibit only 40 to 50% block formation. In addition, the highest homopolymer producers were PMMA and PBMA. This probably is due to combination of polymeric radicals after the azo group had been thermally activated.

Qualitative characterizations of the block copolymers before and after separation were carried out by ^1H NMR and IR spectroscopic analyses shown in Figures 5 and 6. For IR, the absorption at 1730 cm^{-1} is characteristic for the carbonyl stretching mode in MMA, while the absorption at 1603 cm^{-1} indicates the presence of styrene. The mole ratios for each block segment were quantitatively determined by ^1H NMR (by integrating the peak area) and by membrane osmometry (\bar{M}_n). Table V lists the results from these two types of measurements and, as can be seen, the results are fairly close.

TABLE IV
Block Copolymer Yields

	Polystyrene	PolyPMS (%)	PolyMMA (%)	PolyBMA (%)	Block (%)
Poly(MMA- <i>b</i> -sty- <i>b</i> -MMA)	2.85	—	22.98	—	73.92
Poly(MMA- <i>b</i> -PMS- <i>b</i> -MMA)	—	10.80	44.00	—	44.70
Poly(BMA- <i>b</i> -sty- <i>b</i> -BMA)	5.08	—	—	39.38	51.10
Poly(BMA- <i>b</i> -PMS- <i>b</i> -BMA)	—	9.50	—	46.70	43.40

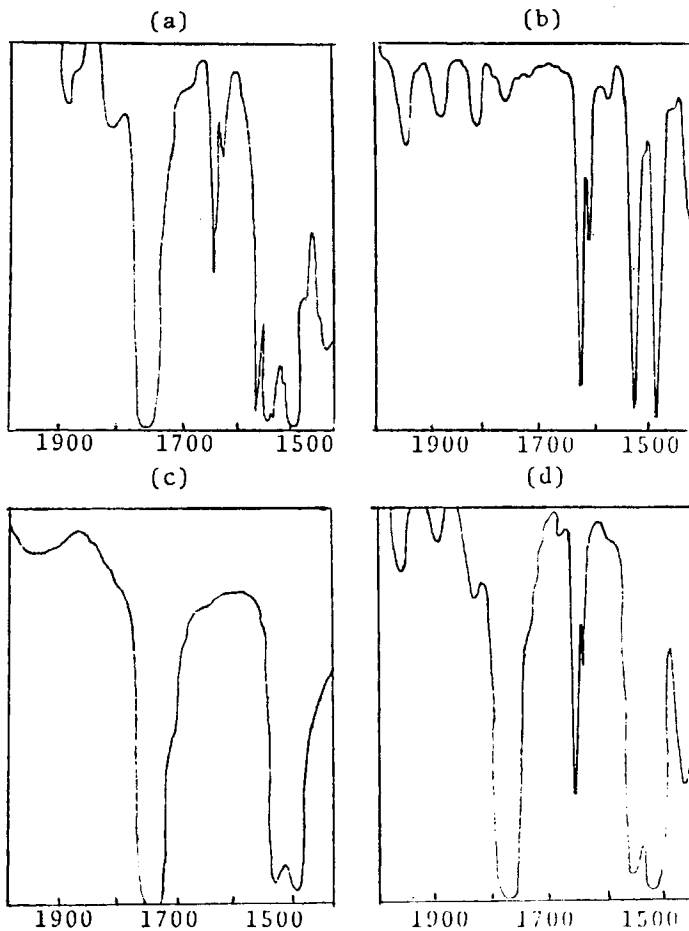


Fig. 5. I.R. spectra of poly(MMA-b-Sty-b-MMA) (a) before solvent extraction; (b) after cyclohexane extraction: polystyrene; (c) after acetonitrile extraction: poly(methyl methacrylate); (d) block copolymer.

Particle Size Analysis

One of the important measurements in this research was the latex particle analysis. Because the monomer droplets containing polymeric initiator created were by pre-emulsification, it is expected that the number of particles will remain constant throughout the reaction unless these particles start to show coalescence. Transmission electron microscopy was used to examine the latexes and Table VI lists the results of poly(MMA-b-Sty-b-MMA) prepared with various SDS concentrations. As discussed previously, each particle may serve as a reaction site if it contains both the monomer and polymeric initiator. In this respect, the higher number of particles should result in a faster rate of polymerization. An argument that was reinforced by the results shown on Figure 2. Table VII lists the results for the relationship between particle size and conversion. As expected, the number of particles remain fairly constant throughout the reaction and close to the number created by the pre-emulsification process.

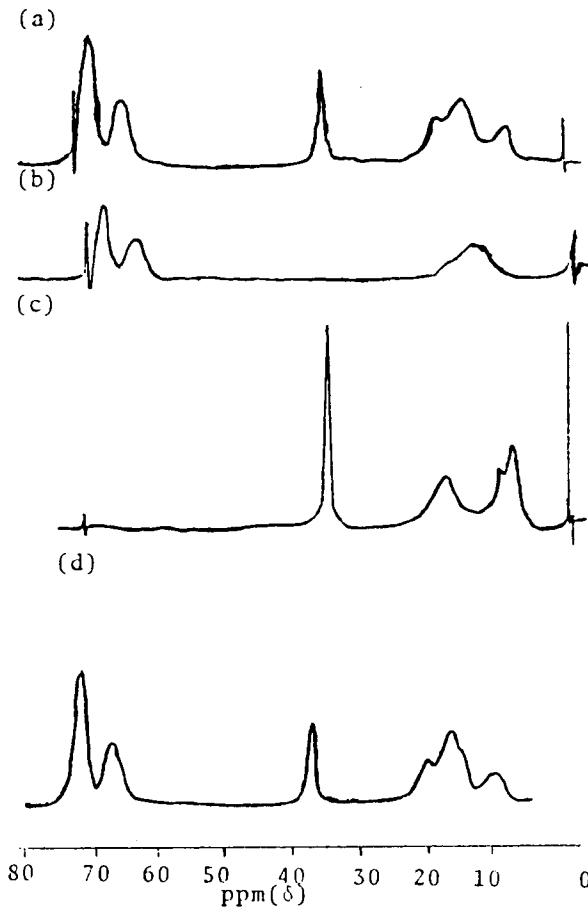


Fig. 6. ^1H NMR spectra of poly(MMA-b-Sty-b-MMA): (a) before solvent extraction; (b) after extraction with cyclohexane: polystyrene; (c) after extraction with acetonitrile: poly(methyl methacrylate); (d) block copolymer.

TABLE V
Block Ratios Determined from Membrane Osmometry (\bar{M}_n) and ^1H NMR Data

Block copolymer before separation	Poly(MMA) $\bar{M}_n \times 10^{-5}$	Poly(BMA) $\bar{M}_n \times 10^{-6}$	Polysty $\bar{M}_n \times 10^{-6}$	Poly(PMS) $\bar{M}_n \times 10^{-6}$	Mole ratio		Block copolymer after separation $\bar{M}_n \times 10^{-6}$	Mole ratio
					1st stage	2nd stage		1st stage 2nd stage
$\bar{M}_n \times 10^{-6}$								^1H NMR analysis
1	2.3	4.32	—	0.7	—	0.22/0.78	2.03	0.26/0.74
2	2.97	4.32	—	—	1.04	0.38/0.62	1.85	0.33/0.67
3	1.94	—	3.98	0.8	—	0.29/0.71	1.08	0.26/0.74
4	1.72	—	3.98	—	0.75	0.26/0.74	0.926	0.35/0.65

^a1 Poly(MMA-b-sty-b-MMA).

2 Poly(MMA-b-PMS-b-MMA).

3 Poly(BMA-b-sty-b-BMA).

4 Poly(BMA-b-PMS-b-BMA).

TABLE VI
Particle Sizes of Poly(MMA-b-Sty-b-MMA) Latexes at 50%
Conversion and at Various SDS Concentrations

Surfactant	1%	2%	3%	4%	5%
D(N) (nm)	91	87	84	81	74
D(W)/D(N)	1.05	1.07	1.04	1.12	1.07
Vol. of particles, $\times 10^{16}$ (cm ³)	4.21	3.69	3.21	3.10	2.20
No. of particles/cm ³ $\times 10^{14}$	4.53	5.16	5.93	6.14	8.60

TABLE VII
Particle Sizes of Poly(MMA-b-Sty-b-MMA) at Various Conversions

Conversion	20%	35%	50%	60%	70%
D(N) (nm)	62	74	84	85	91
D(W)/D(N)	1.10	1.07	1.04	1.07	1.05
Vol. of particles, $\times 10^{16}$ (cm ³)	1.5	2.2	3.2	3.4	4.2
No. of particles/cm ³ $\times 10^{14}$	5.08	6.06	5.95	6.72	6.35

Surfactant amounts: 3% SDS.
Method: electron microscopy.

TABLE VIII
Final Particle Size for the Four Block Copolymers
(EM and HDC Results)

	1	2	3	4
D(N) (nm)	85	113	101	123
D(W) (nm)	90	120	105	129
D(W)/D(N)	1.07	1.06	1.04	1.05
D(HDC) (nm)	79	118	106	130

Surfactant amounts = 3% SDS.
Conversion = 50%.

- 1) Poly(MMA-b-sty-b-MMA).
- 2) Poly(MMA-b-PMS-b-MMA).
- 3) Poly(BMA-b-sty-b-BMA).
- 4) Poly(BMA-b-PMS-b-BMA).

Although the method of preparation of the emulsion particles was the same for all four block copolymer synthesis, there was a slight particle size difference in the final latex for each as can be seen in Table VIII. The pre-emulsification method has thus proven to be a useful way to prepare latex from concentrated monomer-polymer solutions. The diameter of the latex particles was found to decrease with increasing surfactant concentration, which allows some control in the variation of the particle size.

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