

SYNTHESIS OF STYRENIC TONER PARTICLES BY SPG EMULSIFICATION TECHNIQUE

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Abstract This research studied the initiator efficiency for producing polymeric particles of poly(styrene-co-methyl methacrylate) copolymers by a Shirasu porous glass membrane (SPG) emulsification technique followed by suspension copolymerization. BPO, ADVN, and AIBN were used as initiators and we found that BPO is the most suitable initiator. Copolymers for various feed ratios of styrene/methyl methacrylate were thus synthesized by benzoyl peroxide, and their copolymer particle size, molecular weight distribution and particle size distribution were characterized. Then *n*-BMA or 2-EHMA was added as the third monomer to decrease the terpolymer glass transition temperature. This article describes the preparation technique, recipes and polymerization conditions for producing both copolymer and terpolymer particles, particle size changes, the corresponding particle morphologies and glass transition temperatures.

Keywords Shirasu porous glass, Emulsification, *n*-Butyl methacrylate, 2-Ethylhexyl methacrylate, Toner binder

INTRODUCTION

Polymeric microspheres of controlled size with a narrow size distribution have attracted steady attention because of increasing demand in many scientific and industrial applications. Chromatographic packing materials^[1, 2], dry and liquid toners for electrophotography^[3, 4] and support for medicines^[5] are just a few of their applications.

For electrophotographic printing, a conventional toner comprises a colorant, charge control agent, and additives dispersed in a polymeric binder. The particle size of the polymeric binder is of prime importance for controlling image or printing quality. The conventional toner particles are melt mixed and crushed in an air jet impinging on a polished metal plate to obtain as small particle sizes as possible as well as a relatively narrow size distribution. Commercial toner particles range from 5 to 14 μm depending on desired printer quality. The crushed, large polymeric particles produce ragged lines, uneven dots, and otherwise poor fusing performance. As a consequence, toners having a smaller particle size, which give superior color reproduction and noise reduction, are desired.

Omi *et al.*^[5] have extensively investigated an SPG technique for the synthesis of microspheres of crosslinked porous polystyrene and poly(methyl methacrylate) controlled either by solubility parameters or a two-stage emulsion technique. Hatate *et al.*^[3] prepared poly(styrene-co-divinylbenzene) microspheres as dry toner particles containing a colorant and a charge control agent using the SPG emulsification technique.

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EXPERIMENTAL

Emulsification

A Shirasu Porous Glass (SPG) membrane of 0.9 μm or 1.42 μm pore size was used for making emulsion droplets in the emulsification kit shown in Fig. 1. The dispersion phase containing a mixture of monomers, hydrophobic additives, and an initiator was stored in a 20 mL oil storage tank. Precisely controlled nitrogen pressure was applied to the oil storage tank. A three-digit pressure gauge was used. The dispersion phase was allowed to permeate through the microporous membrane; the module was completely immersed in an emulsion storage tank containing the continuous phase. The droplets were stabilized by the adsorption of poly(vinyl alcohol) (PVA) and cosurfactant sodium lauryl sulfate (SLS) dissolved in the continuous phase, which was stirred gently at 300 rpm with a magnetic bar to prevent the creaming of the droplets. After the emulsification of the dispersion phase, the emulsion was transferred to the reactor and polymerized. The monomer droplets before polymerization were examined with an optical microscope. The diameters of 200 droplets were measured to calculate the average diameter and the size distribution.

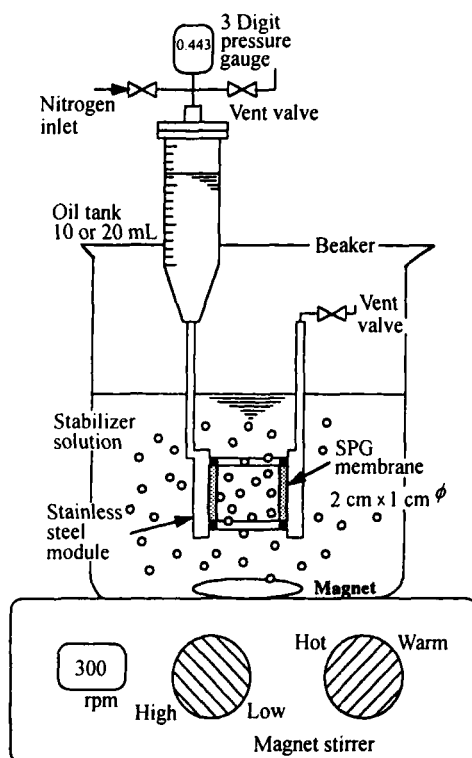


Fig. 1 Shirasu porous glass membrane (SPG) installed in the emulsification kit

The preparation conditions for the polymerization using the 0.9 μm SPG membrane were as follows. Nitrogen pressure in the range of 0.45–0.7 kgf cm^{-2} (4.4×10^4 – $6.7 \times 10^4 \text{ N m}^{-3}$) was applied. The oil droplets were dispersed in the continuous phase containing PVA-217 as a stabilizer, SLS, and Na_2SO_4 in the concentrations of 1.5, 4×10^{-2} and $5 \times 10^{-2} \text{ g mL}^{-1}$ of water, respectively. For the 1.42 μm membrane, nitrogen pressure in the range of 0.30–0.45 kgf cm^{-2} (2.9×10^4 – $4.4 \times 10^4 \text{ N m}^{-3}$) was applied. The oil droplets were dispersed in the continuous phase containing PVA-217 stabilizer, SLS, and Na_2SO_4 in concentrations of 6.50×10^{-3} , 1.74×10^{-4} , and $2.2 \times 10^{-4} \text{ g mL}^{-1}$ of water, respectively.

Polymerization

The emulsion so obtained was transferred to a three-necked glass separator flask of 300 mL connected with a semicircular anchor-type blade for agitation, a spiral condenser, and a nitrogen inlet nozzle. The nitrogen gas was

gently bubbled into the emulsion for 1 h. The nozzle was then lifted above the emulsion surface and the temperature was increased to 75°C. Polymerization proceeded for 24 h under the nitrogen atmosphere. After the completion of polymerization, polymer particles were removed from the latex by centrifugation at 3000 rpm, washed repeatedly with methanol and dried under vacuum at room temperature for 24 h. The polymer particles were observed using a scanning electron microscope to calculate the average diameter and the size distribution.

Characterization

The percentage conversion of the monomers was determined by a gravimetric method. The polymer latex (5 mL) was collected in a 20 mL weighing bottles, and 10–15 mL of methyl alcohol was added to precipitate the polymer. They were separated by centrifugation at 3000 rpm, and washed repeatedly with methyl alcohol 2–3 times. They were then dried in a vacuum oven at room temperature and weighed.

The average molecular weight (M_w) and molecular weight distribution (MWD) of the polymer particles were obtained using Tosoh GPC model HLCH820. The dried polymer sample of 1 mg was dissolved in 2 mL of THF to an approximate concentration of 0.1 wt%. The polymer solution was injected into the chromatographic column at a flow rate of 0.5 mL min⁻¹.

Measurements of the T_g of the polymer were made using a MAC Science model 3100 differential scanning calorimeter with a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Effect of the Type of Initiator

The SPG pore size of 0.90 μm was used to prepare emulsion droplets. The dispersion phase containing St (styrene) and MMA (methyl methacrylate) in a 50:50 weight ratio was studied with different types of initiators: benzoyl peroxide (BPO with 25 wt% moisture content), 2,2'-azo-bis-isobutyronitrile (AIBN), and 2,2'-azo-bis-2,4-dimethylvaleronitrile (ADV N) or V-65. Table 1 shows the results for St-MMA copolymer particles newly synthesized with half-lives ($t_{1/2}$) of the initiators and dissociation rate constant (k_d) at the reaction temperature of 70°C in toluene.

Table 1. Effect of the initiator type on the particle size and size distribution M_w and MWD of poly(styrene-co-methyl methacrylate)

Properties	Run No.		
	131	132	134
Initiator	BPO	AIBN	ADV N
k_d in toluene (s ⁻¹)	1.1×10^{-5}	4.0×10^{-5}	2.0×10^{-5}
$t_{1/2}$ in toluene (min)	1049	289	58
Results			
D_e (μm)	5.82	6.13	4.85
σ (μm) in emulsion	0.68	0.81	0.50
CV(%) in emulsion	11.70	13.24	10.37
D_p (μm)	5.40	-	3.89
σ (μm) in polymer	0.64	-	0.45
CV(%) in polymer	11.85	-	11.69
Conversion (%)	49	-	75.7
M_n	23,100	144,500	10,950
M_w	45,210	579,300	112,500
M_w/M_n	1.96 ^a	4.90 ^a	10.27 ^b

Dispersion phase: styrene 8.00 g, MMA 8.00 g, methyl palmitate 1.50 g, and initiator 0.45 g for the three runs;

Continuous phase: water 230 g, PVA-217 1.50 g, SLS 0.04 g, Na₂SO₄ 0.05 g, and hydroquinone 0.016;

In Run 134, NaNO₂ 0.03 g was used instead of hydroquinone in the continuous phase.

^a Unimodal MWD; ^b Bimodal MWD

Droplet and particle size histograms for the St-MMA copolymers from different types of initiators are given in Figs. 2 and 3. Addition of methyl palmitate to the dispersion phase produced higher stability of the emulsion

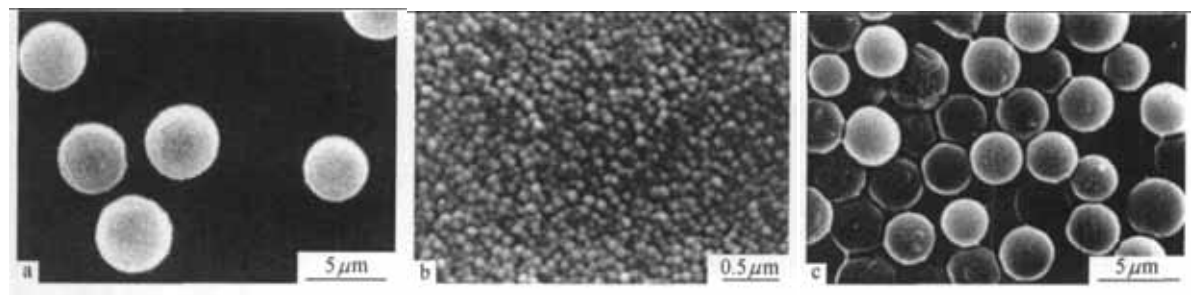


Fig. 2 SEM photographs of poly(styrene-co-MMA) particles for different initiators
a) BPO (Run 131); b) AIBN (Run 132); c) ADVN (Run 134)

for the three runs as illustrated in Table 1. Polymerization by the ADVN initiator with the fastest decomposition rate (a half-life of 58 min at 70°C) yielded a narrow particle size distribution and the smaller particle diameter in the presence of NaNO₂. On the other hand, BOP initiator with a slow decomposition rate (half-life of 1049 min at 70°C) yielded a narrow particle size distribution, but a larger average droplet size. The particle size distribution is related to both the decomposition rates of the initiator and the particle diameter. This implies that oligomers produced by a quickly decomposing initiator tend to propagate and form particle nuclei of various chain lengths, most probably short chains. The initiator radical generation rate is possibly faster than the rate of stabilizer adsorption onto the droplets for stabilization. The shrinkage of particles is thus higher as shown in Fig. 3, with a

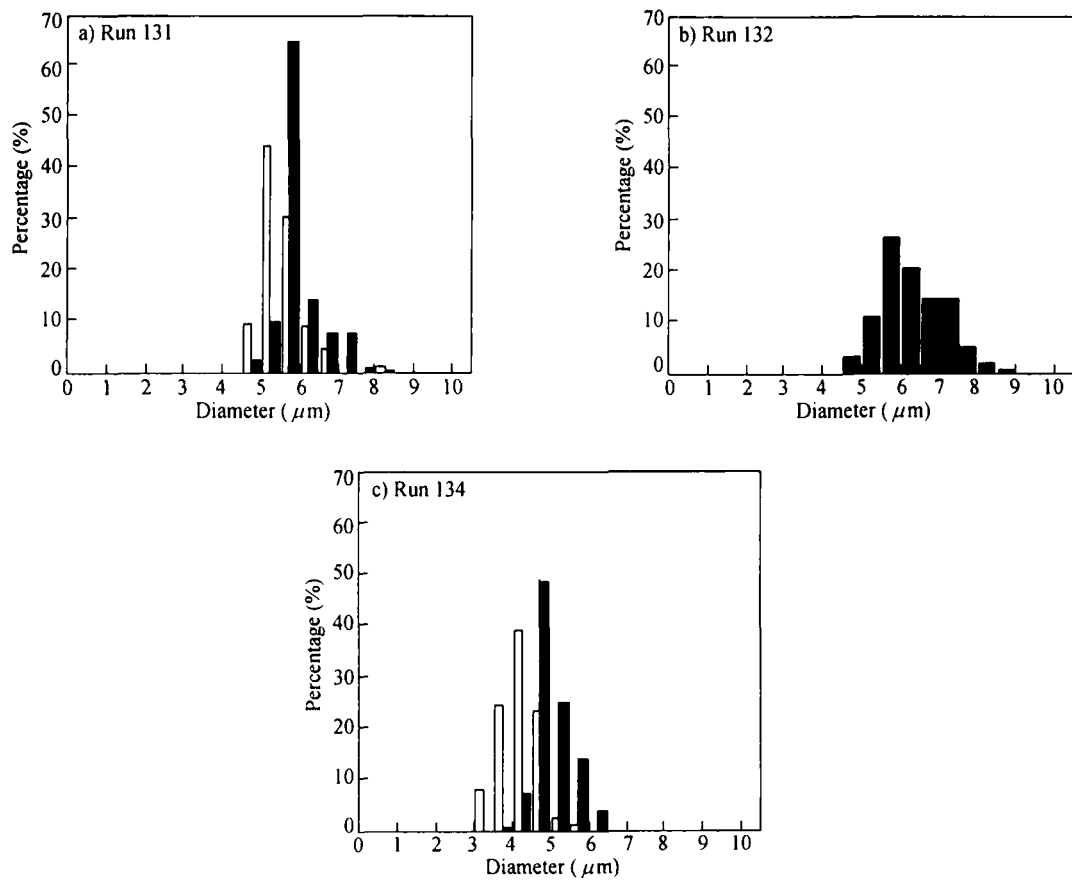


Fig. 3 Histograms of the size distribution of emulsion droplets and polymer particles using a) BPO, b) AIBN, and c) ADVN as initiator
□ Polymer particles; ■ Emulsion droplets

tendency to separate apart from the histogram of the droplets. As the k_d is high, the initiator radicals may escape into the aqueous phase so that a portion of the monomers was used in secondary nucleation formation. Therefore, the copolymer particles initiated by ADVN are smaller than normally expected. In contrast, a slowly decomposing initiator generates oligomer radicals at a much slower rate. For a longer reaction time, a more uniform chain length of the polymer was resulted. Thus, a narrow MWD was obtained shown in the GPC chromatogram in Fig. 4. The bimodal MWD with a high M_w (see Table 1) and a broad MWD resulted from ADVN initiation in Run 134.

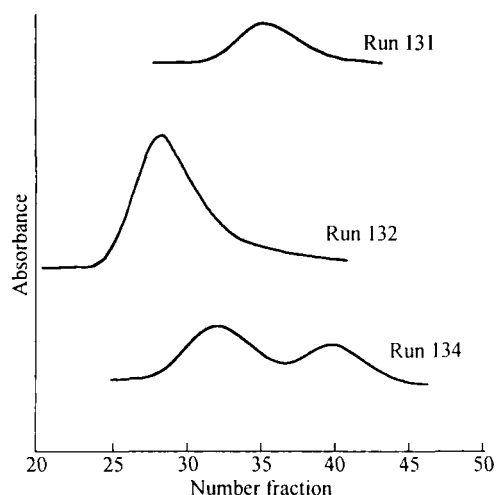


Fig. 4 GPC chromatograms of poly(styrene-co-MMA) for different initiators BPO (Run 131), AIBN (Run 132), and ADVN (Run 134)

The action of AIBN as an initiator is different from those of the other two initiators. Although AIBN is regarded as an oil-soluble initiator, it in fact dissolves appreciably in water. It can thus initiate emulsion polymerization instead of suspension polymerization as we would expect. It has been observed previously that oil-soluble initiators could behave similarly as aqueous-phase initiators in emulsion polymerization. We also found this similar phenomenon in our present work. As shown in Fig. 2b (Run 132), an average particle size lower than $0.1\ \mu\text{m}$ was obtained at a high degree of conversion (86%). Considering the monomers used, a relatively polar MMA has a higher water solubility ($160\ \text{mg mL}^{-1}$) than St ($4\ \text{mg mL}^{-1}$)^[6], it can then partly dissolve in the aqueous phase. Partitioning of the AIBN initiator into the aqueous phase is insufficient due to its low water solubility (0.1%). However, the greater solubility at higher reaction temperature along with the presence of a surfactant, for example, SLS, could promote the initiation ability of AIBN. When the SLS concentration exceeds its critical micelle concentration (CMC), the surfactant molecules aggregate together to form small colloidal clusters, i.e. micelles. When the initiator is present in the aqueous phase, the initiating radicals will be generated and diffuse into the micelles. The reaction occurs mostly within the micelles and all the monomer droplets, large and small, which are used as a reservoir for the reaction ($D_c = 6.13\ \mu\text{m}$). Emulsion polymerization results in M_w of 579,300 and a broad MWD (M_w/M_n) of 4.9. From the above observation, AIBN may not be a good initiator of suspension polymerization.

Effect of the Copolymer Composition of Poly(styrene-co-MMA)

Poly(styrene-co-methyl methacrylate) particles were prepared using an SPG membrane with a pore size of $1.42\ \mu\text{m}$. Nitrogen pressure was applied in the range of $0.30\text{--}0.34\ \text{kgf cm}^{-2}$ ($2.9 \times 10^{-4}\text{--}3.2 \times 10^{-4}\ \text{N m}^{-2}$) for making stable emulsion droplets. Polymerization was then carried out for 24 h under a nitrogen atmosphere at 75°C with an agitation speed of 180 rpm. The preparation conditions and the results of polymerization are shown in Table 2. Size distributions of the emulsion droplets and polymer particles of St and MMA homopolymers and St-MMA copolymers are shown in Fig. 5. The pressure applied in the range of $0.30\text{--}0.34\ \text{kgf cm}^{-2}$ ($2.9 \times 10^{-4}\text{--}$

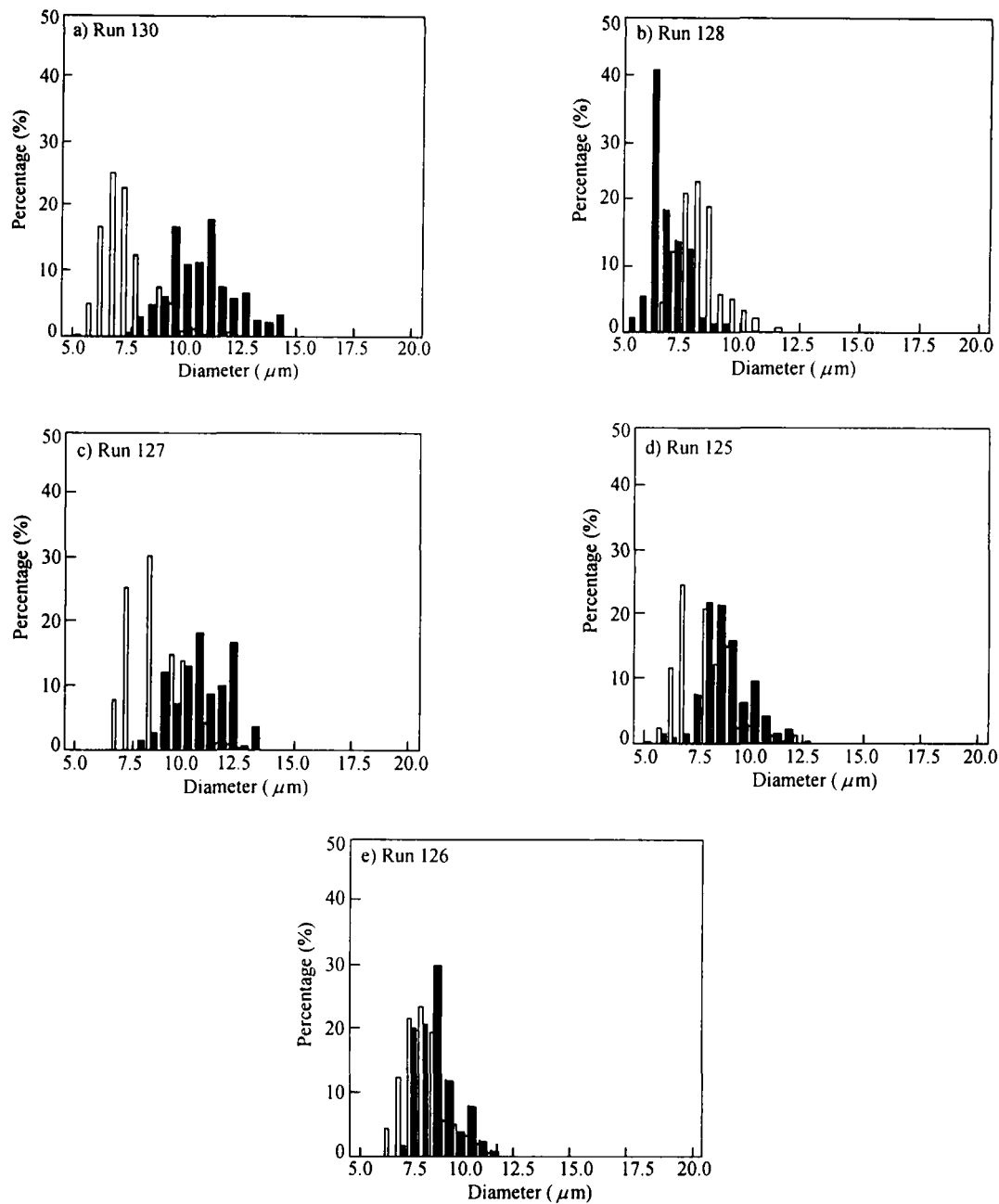


Fig. 5 Histograms of the size distribution of homopolymers and St-MMA copolymers showing the effect of the copolymer composition of St/MMA in the feed: a) polystyrene, b) PMMA, c) 75:25, d) 50:50, and e) 25:75 wt% ratios
□ Polymer particles
■ Emulsion droplets

$3.2 \times 10^{-4} \text{ N m}^{-2}$) has a major effect on the particle size distribution. One can observe that the histogram of polystyrene is not superimposed with that of emulsion droplets in Run 130. Likewise, the histogram of the copolymer prepared with the St/MMA ratio of 75:25 in Run 127 appears sooner than its precursor, i.e., the particles of the copolymer are smaller. The St-MMA copolymer prepared from the monomer feed ratio of 50:50 by weight in Run 125 gives an intermediate profile. The copolymer from the 25:75 feed ratio of St/MMA and

PMMA homopolymer produce overlapping histograms, i.e., their particle sizes are of the same magnitude as those of the emulsion droplets in Runs 126 and 128. Additionally, the particle diameter decreases with an increasing amount of MMA. As shown in Table 2, the T_g values of the two homopolymers are similar, and the compatibility of methyl palmitate (MP) with the copolymer chains may affect free volumes in the polymer particles. When the comonomer droplets are rich in styrene segments, MP cannot mix well in the emulsion droplets, leaving a high interstitial volume in the particles. When MMA-rich emulsion droplets mix well with MP, a lower interstitial volume results, which leads to smaller emulsion droplets. However, the particle sizes of PMMA are found to be larger than those of its emulsion droplets (Run 128). Partly water-soluble MMA monomer and its rather hydrophilic polymer chains are surrounded by water in the dispersion phase. These water molecules, which are entrapped in the intramolecular chains during polymerization, behave as a plasticizer. During the drying interval, the entrapped water or moisture is driven out and leaves microvoids in the particles or dimples on the soft surfaces. Therefore, the volume enclosed by the polymer particles is increased to give the larger particle diameter as shown in Table 2.

Table 2. Polymerization recipe and yield of poly(styrene-co-MMA) particles with various monomer compositions

Item	Run No.				
	130	127	125	126	128
Dispersion phase					
Styrene (g)	16.00	12.00	8.00	4.00	0
MMA (g)	0	4.00	8.00	12.00	16.00
Methyl palmitate (g)	1.50	1.50	1.50	1.50	1.50
BPO (g)	0.45	0.45	0.45	0.45	0.45
Results					
Emulsion droplets					
D_c (μm)	10.75	10.67	8.93	8.56	6.48
σ (μm)	1.46	1.22	1.23	1.00	0.71
CV (%)	13.57	11.41	13.76	11.73	11.02
Polymer particles					
D_p (μm)	7.56	8.76	7.98	8.15	7.86
σ (μm)	1.10	1.21	1.18	1.06	0.93
CV (%)	14.58	13.87	14.80	13.03	11.88
Conversion (%)	43.3	55.8	59.1	66.4	64.7
M_n	14400	17000	24100	19000	105700
M_w	33800	36100	59600	46300	514300
M_w/M_n	2.35 ^a	2.12 ^a	2.47 ^a	2.43 ^a	4.86 ^b
T_g (calc) (K)	373	374.2	375.5	376.7	378
T_g (obs) (K)	351	361	374.4	680.4	380.4

Dispersion phase: H₂O 230 g, PVA-217 1.50 g, SLS 0.04 g, Na₂SO₄ 0.05 g and hydroquinone 0.016 g

In Run 128, 0.03 g of NaNO₂ was added in the continuous phase as an inhibitor in place of hydroquinone.

^a Unimodal MWD

^b Bimodal MWD

Effect of Copolymer Composition on the Morphology of Polymer Particles

As shown in Fig. 6, polystyrene is spherical while poly(methyl methacrylate) particles are dented (dimpled) on the surface. Addition of methyl palmitate has a favorable influence on the styrene polymer. Similarly, almost all the St-MMA copolymers have the same morphology. The appearance of low conversion of the polymers indicates that unreacted monomers are trapped inside the particles. During the cleaning process, the unreacted monomers are extracted and the particles become stressed leading to the dented (dimples) surfaces. Secondary nucleation of the smaller particles on the bigger particle surfaces was observed, especially in the case of polystyrene and the St-MMA copolymer particles, despite the addition of hydroquinone (HQ) to the aqueous phase. Generally, the inhibitor in the aqueous phase for preventing the formation of secondary nucleation should have the following properties: 1) eliminating particle formation in the aqueous phase by preventing the

propagation of any free radicals in this phase; 2) not obstructing polymerization in the droplets by introducing any induction period, or annihilating free radicals either for initiation or propagation; and 3) not affecting the stability of the polymer particles^[7].

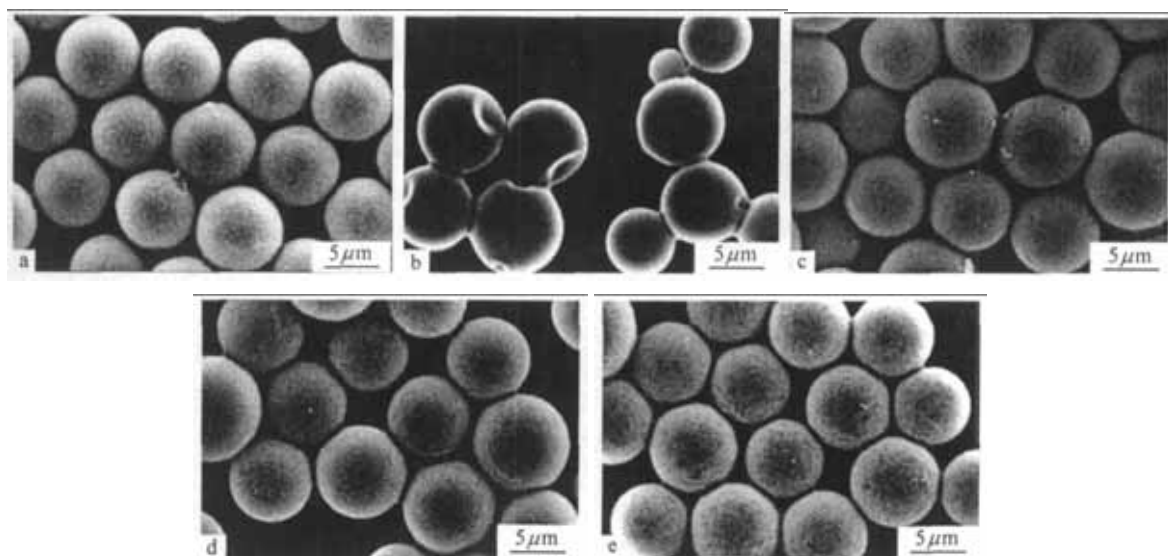


Fig. 6 SEM photographs of polymer particles synthesized from a) polystyrene, Run 130; b) poly(methyl methacrylate), Run 128; c) St:MMA 75:25, Run 125; d) St:MMA 50:50, Run 125; e) St:MMA 25:75, Run 126

HQ, a non-electrolyte compound, causes both an induction period and retardation of polymerization in an oil phase. The partition of the inhibitor between the oil and water phases is responsible for the occurrence of secondary nucleation. The inhibiting ability of HQ has been attributed to its oxidized form of quinone, which is an effective inhibitor. If this is the case, then more oil-soluble benzoquinone could diffuse into the oil phase. The extent of secondary nucleation of the higher content of styrene monomer was consequently increased, producing polymer with lower molecular weight. To suppress the nucleation of polymer particles in the aqueous phase, sodium nitrite (NaNO_2) was used instead of HQ in the case of PMMA synthesis because HQ causes coloring of the emulsion. Fitch suggested that NaNO_2 might undergo hydrolysis and form nitrous acid, which dissociated into nitric acid and nitric oxide as follows^[8]:



Uneven electrons of the nitric oxides and nitrous oxide promote their coupling with polymer radicals. These radicals are also soluble in the oil phase, and inhibit the polymerization to some extent.

Effect of Adding Third Monomer without a Crosslinking Agent

Since the introduction of toner in the 1950s, there has been a continuous demand of toners with smaller particle size for finer electrophotographic images. The reduction in particle size causes a sharp increase in production costs due to an increase in energy consumption for pulverization. Terpolymerizations of styrene, methyl methacrylate and *n*-butyl methacrylate (*n*-BMA) or styrene, methyl methacrylate and 2-ethylhexyl methacrylate

(2-EHMA) were carried out. Considering energy conservation and the fusion temperature of the images from this type of binder, *n*-BNA having a T_g of 293 K or 2-EHMA with a T_g of 263 K could lower the T_g of the terpolymers. In view of the low T_g of *n*-BMA, it is possible to prepare toners with lower fusing temperature by using *n*-BMA. The first series was studied by adding *n*-BMA into the standard recipe. Dispersion phases composed of St/MMA/*n*-BMA in the weight ratios of 50:40:10, 50:35:15, 50:30:20, 50:20:30 and 50:10:40 based on the monomer concentrations were prepared without a crosslinking agent. The same approach was applied to the St/MMA/2-EHMA system. Likewise, MP was used as a hydrophobic additive with BPO as the initiator. The emulsification was carried out with the precisely controlled nitrogen pressure of $0.335 \text{ kgf cm}^{-2}$ ($3.2 \times 10^4 \text{ N m}^{-2}$) for each recipe. The recipes and their corresponding results are shown in Table 3.

Table 3. Copolymerization recipe and experimental results for the non-crosslinked terpolymers of poly(styrene-*co*-MMA-*co*-*n*-BMA) and poly(styrene-*co*-MMA-*co*-2-EHMA)

Run No.	1402	1401	1403	1404	1405	1602	1601	1603	1604	1605
Dispersion phase										
Styrene (g)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
MMA (g)	6.40	5.60	4.80	3.20	1.60	6.40	5.60	4.80	3.20	1.60
<i>n</i> BMA (g)	1.60	2.40	3.20	4.80	6.40	0	0	0	0	0
2EHMA (g)	0	0	0	0	0	1.60	2.40	3.20	4.80	6.40
Methyl palmitate (g)	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
BPO (g)	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Results										
Emulsion droplets										
D_e (μm)	10.37	9.88	13.68	11.41	12.47	10.82	9.65	12.30	11.52	12.57
σ (μm)	1.62	1.29	1.67	1.55	1.58	1.59	1.07	1.79	1.52	1.50
CV(%)	15.66	13.07	12.24	13.55	12.68	14.73	11.08	14.54	13.23	11.90
Polymer particles										
D_p (μm)	7.28	7.93	11.75	9.54	10.19	9.04	7.36	9.54	9.98	13.23
σ (μm)	1.29	1.32	1.53	1.50	1.44	1.40	1.10	1.59	1.20	0.83
CV(%)	17.70	16.67	13.06	15.69	14.14	15.49	15.02	16.69	12.00	6.30
Conversion (%)	36.42	79.26	71.33	66.62	57.62	81.60	50.34	48.84	50.14	69.07
M_n	23470	23080	24720	26940	22270	16310	21710	19220	22870	23320
M_w	44330	45810	50170	51440	47970	34300	44920	44000	52710	56020
M_w/M_n	1.89	1.99	2.03	1.91	2.15	2.10	2.07	2.29	2.30	2.40
T_g (calc) (K)	364.9	359.9	355.0	345.6	336.7	359.8	352.5	345.5	332.2	319.9
T_{g1} (obs) (K)	-	-	303.0	298.7	300.6	293.2	-	290.4	287.8	316.5
T_{g2} (obs) (K)	352.8	346.6	340.7	332.6	327.3	-	343.6	317.1	-	-

Continuous phase: H₂O 230 g, PVA-217 1.50 g, SLS 0.04 g, Na₂SO₄ 0.05 g, and hydroquinone 0.016 g

Effect of Various Alkyl Methacrylate Monomer Compositions on the Particle Size and Size Distribution of the Terpolymers

Histograms of size distributions in Figs. 7 and 8 reveal similar overlapping profiles of emulsion droplets and polymer particles for both terpolymers. Changing the ratios of MMA-*n*-BMA or MMA/2-EHMA, or in other words, changing the chain length of alkyl methacrylate, does not affect the particle sizes, but the percentage of small particle sizes of the terpolymers of St/MMA/*n*-MBA increased substantially.

Effect of Various Alkyl Methacrylate Monomer Compositions on Morphology of the Terpolymer

The SEM photographs of the terpolymer particles of St/MMA/*n*-MBA and St/MMA/2-EHMA are shown in Figs. 9 and 10, respectively. They reveal that the amount of *n*-BMA or 2-EHMA influences the morphology of the particles formed. In the series of St/MMA/*n*-BMA (see Fig. 9), when the content of *n*-BMA in the terpolymer is lower than 40%, the terpolymer particles are spherical. The difference in the length of the side chains of MMA and *n*-BMA imposed on the particle morphology is not significant. When the terpolymer contain 40 wt% of *n*-BMA, the particles are deformed and stick together due to a high proportion of *n*-BMA. The addition of 2-

EHMA (Fig. 10) at less than 20% produces deformed and distorted particles. The hemi-spherical distorted particles fused and connected together like a thin and flattened wave are found when the content of 2-EHMA is higher than 30%.

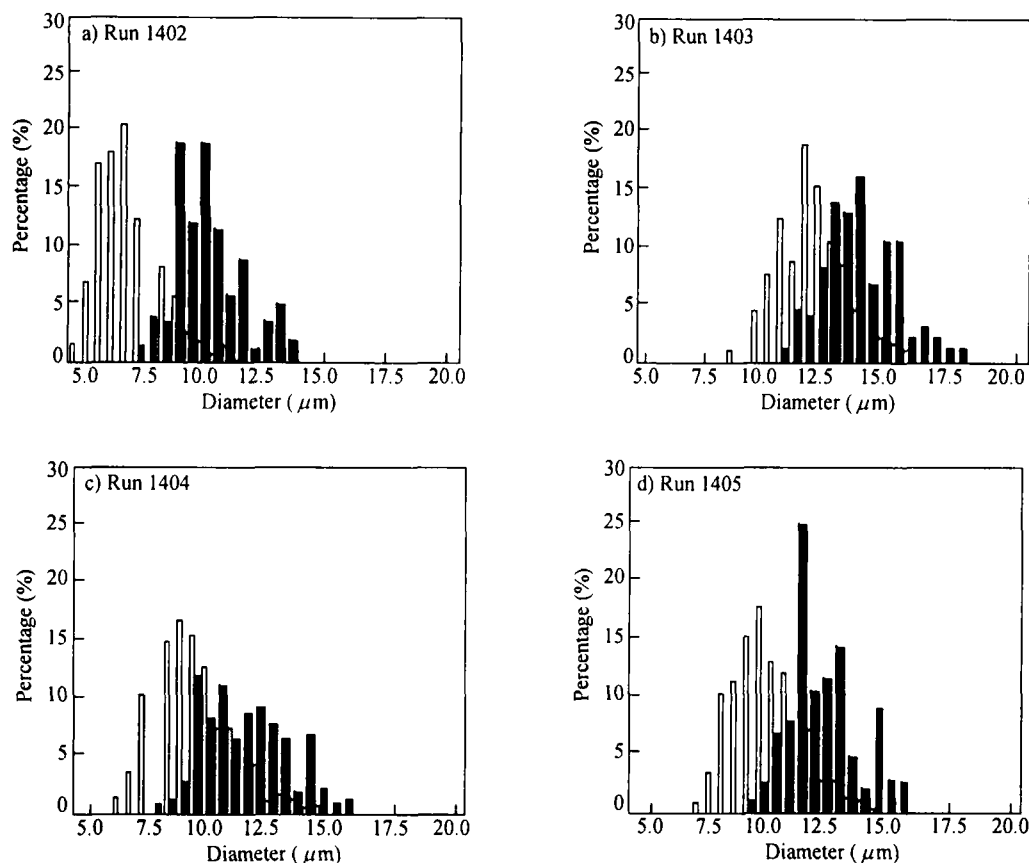


Fig. 7 Histograms of the size distribution of emulsion droplets and polymer particles, using the weight fractions of St/MMA/*n*-BMA in the feed: a) 50:40:10, b) 50:30:20, c) 50:20:30, d) 50:10:40

□ Polymer particles
■ Emulsion droplets

Effect of Adding the Third Monomer with a Crosslinking Agent

To improve the spherical shape of the terpolymer, EGDMA, a crosslinking agent was added at a concentration of 0.1 wt% based on the monomer concentration. In our previous work^[9], we found that a higher concentration of the crosslinking agent added caused a phase separation of the highly crosslinked network from the base polymer. In this case, a lightly crosslinked terpolymer was obtained. The results of the polymerizations are shown in Table 4. The systems containing St/MMA/*n*-BMA or St/MMA/2-EHMA with a weight ratio of 50:40:10 gave coagulum particles, which does not occur in the terpolymers having higher contents of alkyl monomers. A low conversion resulted (30%), which may indicate that the unreacted monomers have been trapped inside the particles during polymerization. The terpolymer is rubbery-like, composed of mostly soft segments of oligomers or monomers, and sticks together easily.

Effect of Various Alkyl Methacrylate Monomer Compositions on the T_g

The glass transition temperature of terpolymers is observed to be between the transition temperature of each homopolymer. The observed T_g values of St/MMA/*n*-BMA and St/MMA/2-EHMA (uncrosslinked and crosslinked) are shown in Tables 5 and 6. The trends of changing T_g of the terpolymers are in good agreement with the values calculated from Fox's equation, Increasing the *n*-BMA content lowers the T_g in the same direction

for the observed and calculated values. This terpolymer might form a random terpolymer with a single T_g . However, when the ratio of *n*-BMA is higher than 30%, two transition temperatures are observed. For St/MMA/2-EHMA terpolymers, the observed T_g is different from the calculated one; two T_g values are found in some cases.

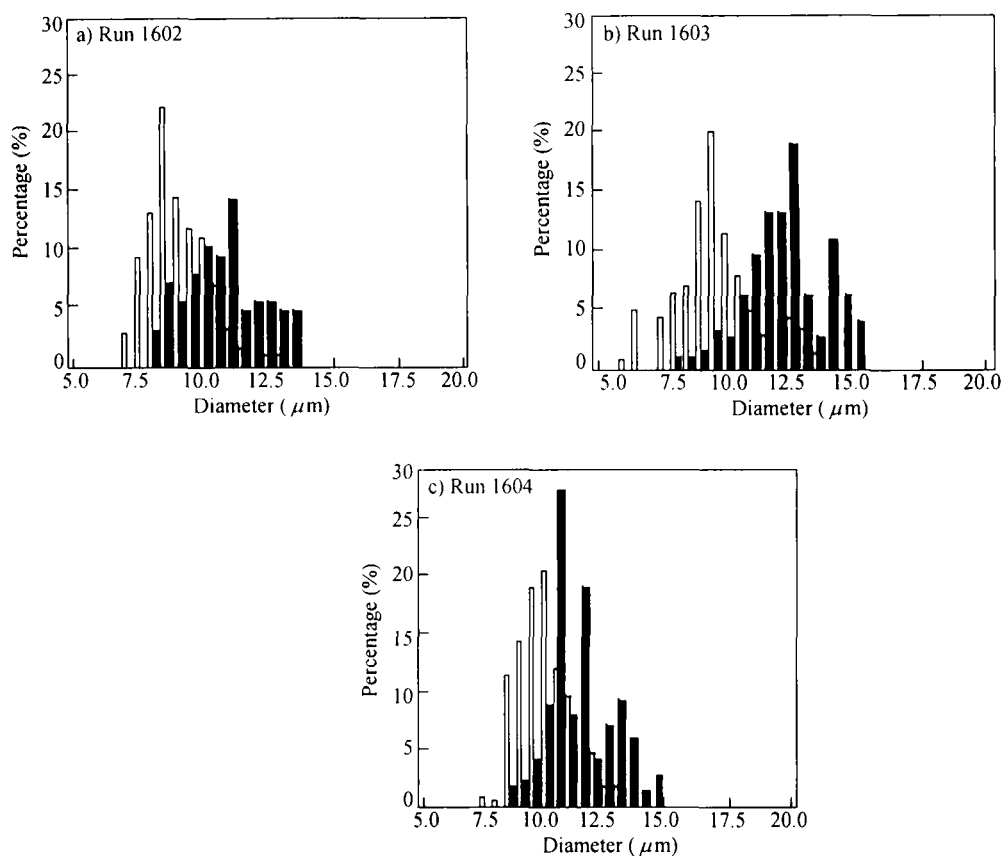


Fig. 8 Histograms of the size distribution of emulsion droplets and polymer particles using the weight ratios of St/MMA/2-EHMA in the feed: a) 50:40:10, b) 50:30:20, c) 50:20:30
 □ Polymer particles
 ■ Emulsion droplets

The differences between the two types of terpolymers are probably due to the longer side chains of 2-EHMA that hinder mixing among the terpolymer chains. This behavior may give variations in thermal properties, which are found for both types of crosslinked terpolymers (St/MMA/*n*-MBA or St/MMA/2-EHMA).

CONCLUSIONS

The types of thermal initiators used for preparing St-MMA copolymers revealed that BPO produced relatively large polymeric particles with a narrow MWD due to its slow decomposition rate, so that less secondary nucleation took place compared with that for ADVN. We found that both BPO and ADVN initiators could be used for preparing St-MMA copolymers with a narrow size distribution. AIBN is not so suitable for such a suspension polymerization, but it is better for emulsion polymerization. Regarding the effect of the St:MMA feed ratio, increasing the MMA feed decreases the size of the polymer particles. Methyl palmitate additive favors the MMA fraction due to its ester functionality. The copolymer particles are spherical for all compositions of St/MMA when methyl palmitate is used instead of hydroquinone to suppress the secondary nucleation of PMMA.

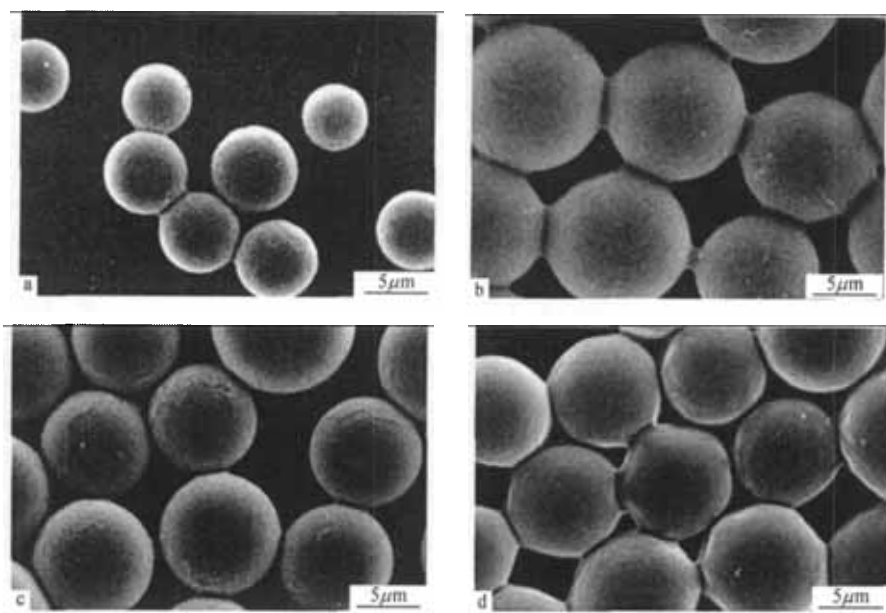


Fig. 9 SEM photographs of poly(styrene-*co*-MMA-*co*-*n*-BMA) particles for the weight ratios of St/MMA/*n*-BMA in the feed: a) 50:40:10 (Run 1402), b) 50:30:20 (Run 1403), c) 50:20:30 (Run 1404), d) 50:10:40 (Run 1405)

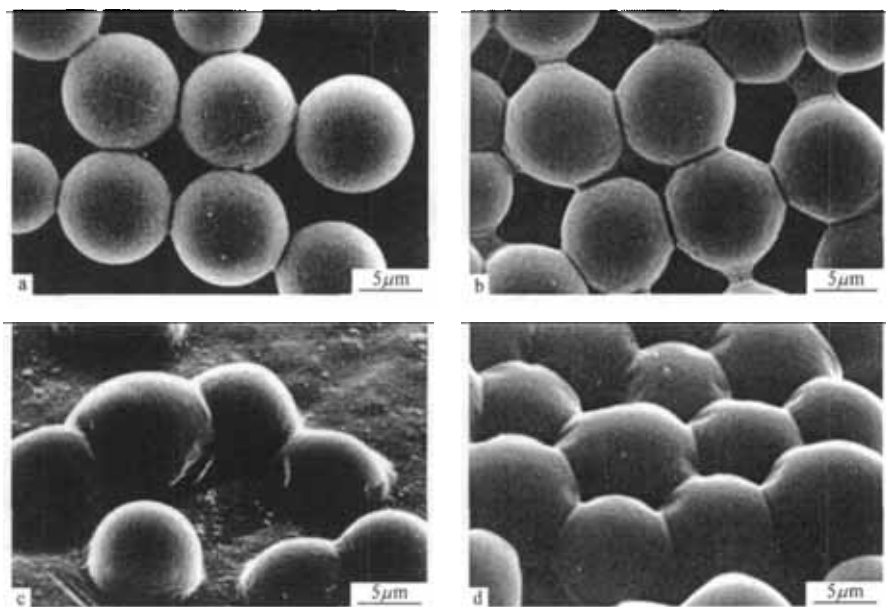


Fig. 10 SEM photographs of poly(styrene-*co*-MMA-*co*-EHMA) particles for the weight ratios of St/MMA/2-EHMA in the feed: a) 50:40:10 (Run 1602), b) 50:30:20 (Run 1603), c) 50:20:30 (Run 1604), d) 50:10:40 (Run 1605)

The addition of low glass transition temperature monomers, *n*-BMA or 2-EHMA, lowers the T_g of the terpolymers. In this research, we were able to synthesize various small particles of poly(styrene-*co*-methyl methacrylate), and poly(styrene-*co*-methyl methacrylate-*co*-butyl methacrylate) and poly(styrene-*co*-methyl methacrylate-*co*-2-ethylhexyl methacrylate) with thermal properties suitable for electrophotographic printing.

Table 4. Copolymerization recipe and experimental results for the crosslinked terpolymers of poly(styrene-co-MMA-co-*n*-BMA) and poly(styrene-co-2-EHMA)

Run No.	1407	1408	1409	1410	1607	1608	1609	1610
Dispersion phase								
Styrene (g)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
MMA (g)	6.40	4.80	3.20	1.60	6.40	4.80	3.20	1.60
<i>n</i> -BMA (g)	1.60	3.20	4.80	6.40	0	0	0	0
2-EHMA (g)	0	0	0	0	1.60	3.20	4.80	6.40
EGDMA (g)	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Results								
Emulsion droplets								
<i>D_e</i> (μm)	13.16	13.46	13.67	13.17	12.76	11.62	12.65	12.62
σ (μm)	1.68	1.79	1.55	1.60	1.79	1.40	1.56	1.74
CV(%)	12.73	13.29	11.37	12.12	14.01	12.04	12.30	13.82
Polymer particles								
<i>D_p</i> (μm)	Coagulum	10.80	11.22	9.96	Coagulum	9.55	9.70	10.71
σ (μm)		1.58	1.82	1.36		1.18	1.28	1.60
CV(%)		14.62	16.22	13.63		12.33	13.22	14.94
Conversion (%)	43.86	51.53	55.55	51.22	33.59	59.08	54.09	67.27
<i>M_n</i>	13900	9413	4435	3788	17150	10510	10860	12810
<i>M_w</i>	31800	25130	22650	21710	36750	29070	29240	30840
<i>M_w</i> / <i>M_n</i>	5.11	2.67	5.11	5.81	2.14	2.77	2.69	2.44
<i>T_g</i> (calc.) (K)	359.9	355.0	345.6	336.7	359.9	355.0	345.6	336.7
<i>T_{g1}</i> (obs) (K)	285.9	283.9	292.7	288.6	317.7	291.0	299.3	284.8
<i>T_{g2}</i> (obs) (K)	344.8	338.1	336.5	325.8	349.7	337.0	333.9	333.9

Methyl palmitate as additive 1.50 g, and BPO 0.45 g as initiator were added in the dispersion phase
Continuous Phase: H₂O 230 g, PVA-217 1.50 g, SLS 0.04 g, Na₂SO₄ 0.05 g, and hydroquinone 0.016 g

Table 5. Characterization of the non-crosslinked terpolymers with various compositions of monomers

Run No.	<i>M_n</i>	<i>M_w</i>	<i>M_w</i> / <i>M_n</i>	<i>T_g</i> (calc.) (K)	<i>T_{g1}</i> (obs) (K)	<i>T_{g2}</i> (obs) (K)
1402	23500	44300	1.89	364.9	-	352.8
1401	23100	45800	1.99	359.9	-	346.6
1403	24700	50200	2.03	355.0	303.0	340.7
1404	26900	51400	1.91	345.6	298.7	332.6
1405	22300	48000	2.15	336.7	300.6	327.3
1602	16300	34300	2.10	359.8	293.2	-
1601	21700	44900	2.07	352.5	-	343.6
1603	19200	44000	2.29	345.5	290.4	317.1
1604	22900	52700	2.30	332.2	287.8	-
1605	23300	56000	2.40	319.9	316.5	-

Table 6. Characterization of the crosslinked terpolymers with various compositions of monomers

Run No.	<i>M_n</i>	<i>M_w</i>	<i>M_w</i> / <i>M_n</i>	<i>T_g</i> (calc.) (K)	<i>T_{g1}</i> (obs) (K)	<i>T_{g2}</i> (obs) (K)
1407	13900	31800	5.11	359.9	285.9	344.8
1408	9400	25100	2.67	355.0	283.9	338.1
1409	4400	22600	5.11	345.6	292.7	336.5
1410	3800	21700	5.81	336.7	288.6	325.8
1607	17100	36800	2.14	359.9	317.7	349.7
1608	10500	29100	2.77	355.0	291.0	337.0
1609	10900	29200	2.69	345.6	299.3	333.9
1610	12800	30800	2.44	336.7	284.8	333.9

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