Dependence of Morphological Changes of Polymer Particles on Hydrophobic/Hydrophilic Additives

R. NUISIN,¹ G.-H. MA,² S. OMI,² S. KIATKAMJORNWONG³

¹ Multidisciplinary Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

² Bio-Application and System Engineering, Graduate School, Tokyo University of Agriculture and Technology, Nakamachi, Koganei, Tokyo 184-8588, Japan

³ Department of Photographic Science and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

ABSTRACT: Fairly uniform microspheres of poly(styrene-*co*-methyl methacrylate) were prepared by employing a microporous glass membrane [Shirasu porous glass (SPG)]. The single-step SPG emulsification, the emulsion composed mainly of monomers, hydrophobic additives, and an oil-soluble initiator, suspended in the aqueous phase containing a stabilizer and inhibitor, was then transferred to a reactor, and subsequent suspension polymerization followed. The droplets obtained were polymerized at 75°C under a nitrogen atmosphere for 24 h. The uniform poly(styrene-*co*-methyl methacrylate) microspheres with diameters ranging from 7 to 14 μm and a narrow particle-size distribution with a coefficient of variation close to 10% were prepared by using SPG membrane with a pore size of 1.42 μm. The effects of the crosslinking agent and hydrophobic additives on the particle size, particle-size distribution, and morphologies were investigated. It was found that the particle size decreased with a narrower size distribution when the additives were changed from long-chain alkanes to long-chain alcohols and long-chain esters, respectively. Various microspheres with different morphologies were obtained, depending on the composition of the oil phase. The spherical poly(styrene-*co*-methyl methacrylate) particles without phase separation were obtained when using an adequate amount of the crosslinking agent and methyl palmitate as an additive. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1013–1028, 2000

Key words: morphology; phase separation; hexadecane; hexadecanol; methyl palmitate; beeswax

INTRODUCTION

The need for polymeric microspheres of controlled size with a narrow size distribution has grown

steadily because they are used in scientific and industrial applications such as chromatographic packing materials,[1,2] dry and liquid toner for electrophotography,[3,4] and support for medicines.[5] For electrophotographic printing, the conventional dry toners consist of a colorant and additives, such as a charge control agent, dispersed on a polymeric material. The polymeric microspheres are the most important component of the toner. The particle size of the toner generally ranges from 7 to 14 μm.[6] The toner particles are

usually produced by the melt-mixing and crushing method. It is very difficult to synthesize toner particles having a narrow size distribution and with *in situ* incorporation of a charge control agent, colorant, and additives. This toner is known as the polymerized toner. The crushed, large particles produce ragged lines, uneven dots, and other poor fusing performance. As a result, a smaller size was found to be superior for color reproduction and noise reduction. Thus, uniformity of the toner particles is very attractive. The other feature of the toner is rheology. Rheology, thermal behavior, and performance of the toner depend on the selection of the polymerization method.[7]

To produce uniform particles in a simple and easy procedure using two immiscible liquids, one liquid, termed as a dispersed phase, is permeated through the Shirasu porous glass (SPG) membrane into the other liquid, named a continuous phase. The stabilization of the emulsion droplets is controlled by using surfactants and stabilizers. The SPG emulsification is then followed by suspension polymerization. The uniform microspheres with sizes ranging from 1 up to 100 μm are normally obtained depending on the SPG pore size and monomer type.[8,9] Omi et al.[5,10] extensively investigated the SPG technique for the syntheses of microspheres of crosslinked porous polystyrene[10,11] and poly(methyl methacrylate)[12–14] controlled either by solubility parameters or a two-stage emulsion technique. Hatate et al. prepared poly(styrene-*co*-divinylbenzene) microspheres as dry toner particles containing a colorant and a charge-control agent by using the SPG emulsification technique.[3,4] They were able to measure the toner triboelectric properties.

The nonaqueous phase-dispersion copolymerization of acrylate monomers and styrene (St) requires an organic solvent as the continuous medium.[15] As for the green issue, an aqueous dispersion system is performed to avoid the release of organic solvents. The SPG technique allows the addition of wax or plasticizers essential to the toner powder to stabilize the emulsion droplets and function properly as toner.

The present article involves the preparation of emulsion droplets of St/acrylate monomer in the presence of a crosslink agent and hydrophobic/hydrophilic additives. Suspension copolymerization is then carried out to obtain the prospective polymeric particles.

EXPERIMENTAL

Preparation of Emulsion Droplets of Monomers

An SPG membrane of 1.42-μm pore size was used for emulsification.[16] The preparative conditions for a one-step emulsification are shown in Table I. The dispersion phase containing a mixture of St (commercial grade, Kishida Chemical, Osaka, Japan), methyl methacrylate [MMA (commercial grade, Kishida Chemical)], hydrophobic additives, and an initiator, benzoyl peroxide [BPO (25 wt % moisture, reagent grade, Kishida Chemical)], was prepared. In a continuous phase, the stabilizer, poly(vinyl alcohol) [PVA (degree of polymerization, DP = 1700, 88.5% saponification)], surfactant, sodium lauryl sulfate [SLS (biochemical grade, Merck)], Na_2SO_4 (commercial grade, Kokusan Chemical Works, Tokyo, Japan), and inhibitor, hydroquinone [HQ, reagent grade, Kishida Chemical)] were dissolved. The droplets were stabilized by PVA and SLS and dissolved in the continuous phase through adsorption onto the surfaces of the droplets. To prevent the creaming of the droplets, the continuous phase was stirred gently at 300 rpm with a magnetic bar. The details of SPG emulsification were described elsewhere.[16]

Suspension of the Emulsion of Monomers

The emulsion obtained was transferred to a three-necked glass separator flask with a capacity of 300 cm^3 connected with a semicircular anchor-type blade for agitation, a spiral condenser, and a nitrogen inlet nozzle. Nitrogen gas was gently bubbled into the emulsion for 1 h; the nozzle was lifted above the emulsion level; the temperature was increased to 75°C, and the emulsion was polymerized for 24 h under the nitrogen atmosphere.

Characterization

Monomer droplets before polymerization and polymer particles were observed with an Olympus DP-10 optical microscope. Diameters of about 200 droplets were measured to calculate an average diameter and a size distribution.

Percentage conversion of the monomer was determined by gravimetric method. Methyl alcohol (commercial grade, Kishida Chemical) was added to precipitate the polymer. Polymer particles were separated by centrifugation and washed repeatedly with methyl alcohol 2–3 times. The poly-

Table I Polymerization Recipe of Poly(styrene-*co*-MMA) and Experimental Results with and without a Crosslinking Agent Using an SPG Pore Size of 1.42 μm

	Run No.						
	106	108	107	110	111	113	143
Dispersion phase							
Styrene (g)	12.80	8.00	7.50	7.27	6.67	5.60	8.00
MMA (g)	3.20	8.00	7.50	7.27	6.67	5.60	8.00
DVB (g)	0	0	1.00	0	0	0	0
EGDMA (g)	0	0	0	1.46	2.66	4.80	0
Hexadecane (g)	1.50	1.50	1.50	1.50	1.50	1.50	0
BPO (g)	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Results							
Emulsion droplets							
$\bar{D}_e$ (μm)	14.8	15.3	16.2	13.7	8.6	9.7	broad
σ (μm)	2.0	2.1	2.5	1.6	1.2	1.4	
CV (%)	13.7	13.6	15.6	11.8	14.3	14.0	
Polymer particles							
$\bar{D}_p$ (μm)	12.6	13.1	13.7	12.9	7.0	8.8	
σ (μm)	1.8	2.5	3.9	2.2	1.0	1.2	
CV (%)	16.4	19.0	28.5	17.1	13.6	13.3	
Conversion (%)	63.5	70.3	80.8	89.7	73.4	84.4	

Continuous phase: H_2O, 230 g; PVA-217, 1.50 g; SLS, 0.04 g; Na_2SO_4, 0.05 g; and hydroquinone, 0.016 g.

mer particles were dried in vacuum at room temperature and their weight was measured.

The external morphology of polymer particles was determined by a Jeol scanning electron microscope (Model JSM-5310). The specimens were prepared by dilution of the polymer latex. The diluted latex was dropped on an aluminum stub surface and coated with a thin layer of gold under reduced pressure ($<10^{-2}$ Pa) by using a fine coater Jeol (Model JFC-1200). On average, the diameters of 200 polymer particles were determined from SEM images.

RESULTS AND DISCUSSION

Effect of Crosslinking Agent

The effect of the crosslinking agent [divinylbenzene (DVB), Kishida Chemical Co., containing 55% active isomeric DVB, 40% ethyl vinylbenzene, and 5% saturated hydrocarbons] on the copolymer morphology was the first parameter studied using the SPG membrane with a pore size of 1.42 μm. The polymerization recipe and experimental results are summarized and classified in

Table I, based on preparation with and without the crosslinking agent.

Noncrosslinked Poly(styrene-*co*-MMA) Microspheres

Figure 1 shows two SEM photographs of uniform microspheres of poly(styrene-*co*-MMA) in Runs 106 and 108 having a few tiny holes. In Run 106, the particles produced by the dispersion phase contained an 80 : 20 weight ratio of St-MMA and had two small, uniform holes. In the dispersion phase containing a 50 : 50 weight ratio of St–MMA in Run 108, the extent of the phase separation became enhanced and particles with large uniform holes were also obtained. All the copolymers were prepared by using hexadecane (HD) as an additive. The polymeric spheres with holes are created by the phase separation of hydrophobic HD. To form the spheres, the hydrophobic additive began to separate out from the main domain inside the spheres at an early stage of polymerization. Before the reaction was completed, HD had been partially trapped inside the voids or between the polymer chains of the noncrosslinked spheres. The extraction of the spheres with
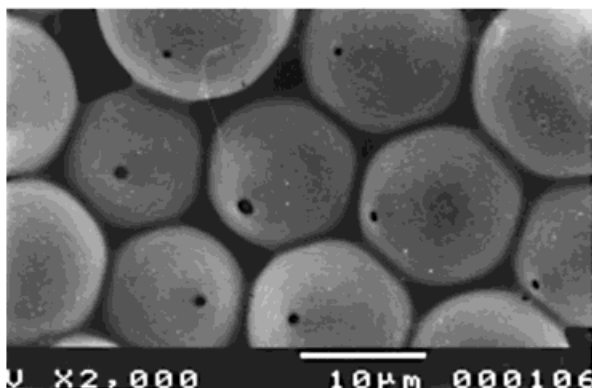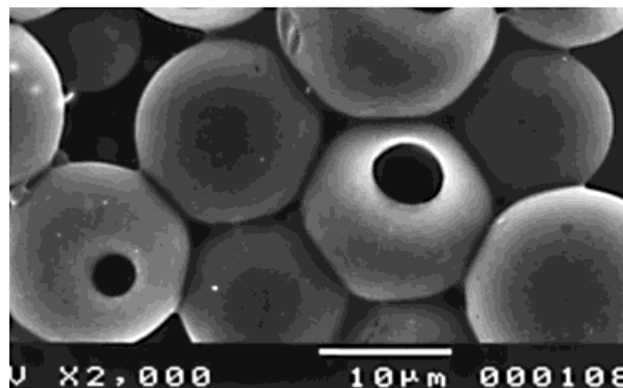
Figure 1 SEM photographs of noncrosslinked poly(styrene-*co*-MMA) particles; St/ MMA: (a) 80 : 20 wt % ratio, and (b) 50 : 50 wt % ratio in monomer.

methyl alcohol enabled the solvent to remove the unreacted comonomers or additives from the spheres to form holes.

## Synthesis of Solid, Uniform Crosslinked Poly(styrene-*co*-MMA) Microspheres

The crosslinking agents, DVB and ethyleneglycol dimethacrylate (EGDMA, commercial grade, Kishida Chemical Co.), were added in the dispersion phase at various concentrations. The polymerization recipe and experimental results are summarized in Table I.

On addition of the crosslinking agent, an apparent phase separation was also observed. The crosslinking agent DVB at a concentration of 6.7 wt % based on the monomer was added in Run 107, and EGDMA in various concentrations of 10, 20, and 42 wt % based on the monomer was also added in St–MMA copolymers in Runs 110, 111, and 113, respectively. SEM photographs in Figure 2 reveal snowmanlike microspheres, whereas the highly crosslinked particles of Run 113 were dented when particle sizes became smaller. Such a phenomenon suggests that the difference in propagation rate of St, MMA, and crosslinking agent (DVB or EGDMA) radicals may be attributed to the phase separation. EGDMA-rich copolymers composed of –COOCH₃ pendant groups were formed in the early stage of the polymerization, because DVB or EGDMA is more reactive than St and tends to be consumed earlier. The reaction of EGDMA formed the nuclei of the crosslinked copolymer. When the monomer mixture contains a crosslinking agent, the crosslinked copolymer becomes insoluble both in

the monomer and hydrophobic additive. Phase separation occurs between the St- and MMA-rich phase, which yields hemispheric particles. The spherical particles were attributed to the crosslinked networks formed during the polymerization, and the amorphous matrix to the noncrosslinked polymer. Thus, the crosslinked polymer network comprised both crosslinked and noncrosslinked fractions. In Figure 2(a,b), the lightly crosslinked network and the head of snowman were the partially noncrosslinked fraction. Considering the incompatibility of the hydrophobic additive, HD plays a vital role for a strongly hydrophobic additives in an emulsion process, which stabilized the emulsion droplets. HD was isolated in the MMA-rich phase domain, which was formed in the later stage of polymerization. Because the microspheres contain a low degree of crosslinking, after polymerization HD was extracted by methyl alcohol in the purification process. The head of the snowman can then form at a hole in the St-rich phase.

The highly crosslinked microspheres of St–MMA copolymer also gave a snowmanlike morphology such as the spheres in Runs 111, 113 shown in Figure 2(c,d), respectively. The particle surface looks harder and thicker because of the higher density of the crosslinked network. In other words, the higher the crosslink density of the particles, the smaller the noncrosslinked fraction. The size of the separated phase domain becomes smaller. The particles have a good tendency to be spherical as the head of the snowman is smaller, and dimples were observed instead of holes, because hexadecane and the unreacted
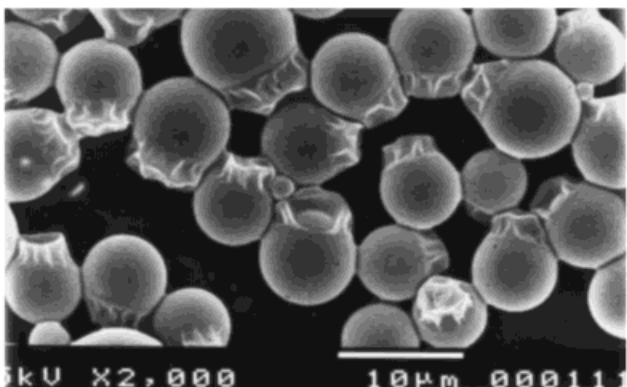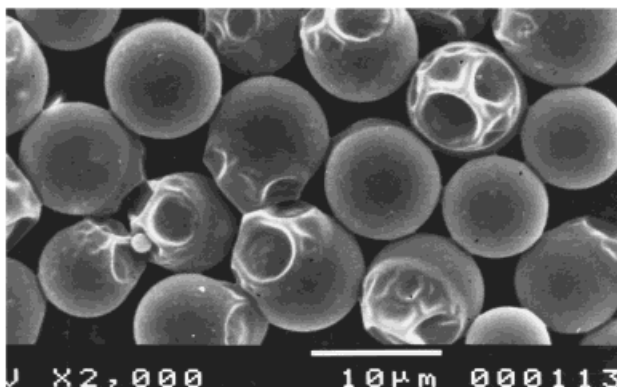
a) Run 107
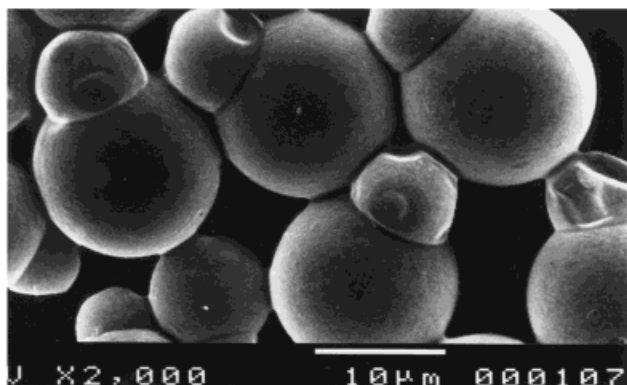
b) Run 110
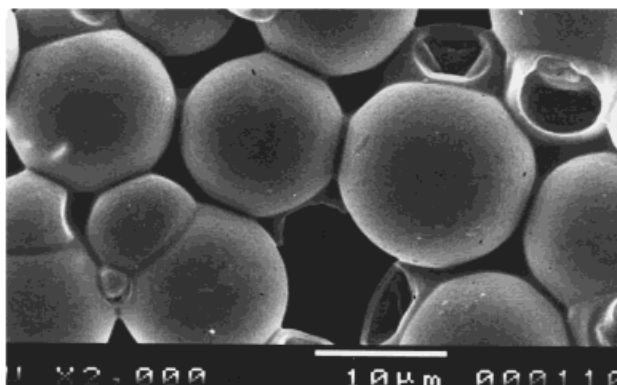
c) Run 111

d) Run 113

Figure 2   SEM photographs of crosslinked poly(styrene-*co*-MMA) particles: (a) DVB, 6.67 wt %, Run 107; (b) EDGMA, 10 wt %, Run 110; (c) EDGMA, 20 wt %, Run 111; and (d) EDGMA, 42 wt %, Run 113, of monomer in the feed, respectively.

comonomer were expelled onto the particle surface completely because of the high crosslinking density of EGDMA in the microspheres.

Effect of Additive Types

Particle morphology is affected by the structure of polymer particles which is strongly dependent on the density of crosslinking. Development of the phase separation with the progress of polymerization is enhanced by the incompatibilities between polymer chains and other ingredients initially added in the dispersion phase. In this polymerization system, water-insoluble or hydrophobic additives, HD, 1-hexadecanol (HD–OH), methyl palmitate (MP), and beeswax (BW, white with the number of carbon atoms ranging from 24 to 36 atoms), were used. The polymerization recipe and experimental results are summarized in Table II. The study was conducted as follows: Run 109 was

with HD, Run 114 with HD–OH, Run 118 with MP, and Run 122 with BW; the concentration of additives for each run was 10 wt %, and a crosslinking agent concentration of 5 wt % of EGDMA was added based on the monomer content. The SEM photographs of the polymer particles are shown in Figure 3.

In Run 109, the crosslinking network of the particles begins to develop among the growing chains of each monomer due to the high interfacial tension of HD and the incompatibility of St and MMA. The particles might be distorted in some way to account for the effect of additives. Such a formation yielded nonspherical microspheres with a snowmanlike morphology. We compare the particles resulting from the polymerizing system with the added HD without the crosslinking agent in Run 108 with those resulting from changing the additive type from HD to

Table II Polymerization Recipe and Experimental Results for Poly(styrene-*co*-MMA) with Various Hydrophobic Additives Using an SPG Pore Size of 1.42 μm

	Run No.										
	109	114	116	117	118	119	120	121	122	123	124
Dispersion phase											
Styrene (g)	7.50	7.60	7.62	7.62	7.62	7.62	7.62	7.62	7.62	7.62	7.62
MMA (g)	7.50	7.60	7.62	7.62	7.62	7.62	7.62	7.62	7.62	7.62	7.62
EGDMA (g)	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Hexadecane (g)	1.50	0	0.75	1.12	0	0.75	0.38	0	0	0	0
1-Hexadecanol (g)	0	1.50	0.75	0.38	0	0	0	0.75	0	0	0
Methyl palmitate (g)	0	0	0	0	1.50	0.75	1.12	0.75	0	0.75	1.12
Beeswax (g)	0	0	0	0	0	0	0	0	1.50	0.75	0.38
BPO (g)	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Results											
Emulsion droplets											
$\bar{D}_e$ (μm)	12.2	10.8	11.0	9.28	9.0	9.4	8.4	10.6	8.8	9.9	6.8
σ (μm)	1.7	1.7	1.5	1.2	1.0	2.4	0.9	1.6	1.1	1.5	0.7
CV (%)	14.1	16.0	13.8	13.4	10.8	25.7	10.4	15.0	12.1	14.8	10.3
Polymer particles											
$\bar{D}_p$ (μm)	9.5	9.2	9.1	7.8	7.4	8.0	6.8	9.1	7.5	8.8	6.3
σ (μm)	1.6	1.7	1.2	1.1	1.0	1.7	1.0	1.5	0.9	1.4	0.8
CV (%)	19.0	18.2	13.5	14.5	14.2	21.6	14.9	11.7	11.7	16.2	12.5
Conversion (%)	53.3	86.3	88.1	43.4	74.3	56.4	55.6	63.5	63.5	50.8	56.6

Continuous phase: H_2O, 230 g; PVA-217, 1.50 g; SLS, 0.04 g; Na_2SO_4, 0.05 g; and hydroquinone, 0.016 g.

the long-chain alcohol, HD—OH, in Run 114. Comparing results for the same number of carbon atoms of the alkyl group with different functional groups is interesting because spherical particles with plateletlike debris attached to each particle surface were obtained. Considering the interfacial tension among St–MMA, St–(HD–OH), and MMA–(HD–OH), the hydroxyl end groups of HD–OH probably have better affinity with the ester group of MMA than St. Also, because alcohol has a lower interfacial tension than alkane, 1-HD–OH becomes a good pair with MMA and may slightly dissolve in the continuous phase. The MMA-rich phase was probably expelled to the surface, as reflected by small flakes on the surface. The spherical microspheres were prepared by using MP as an additive in Run 118. The ester group of MP has an affinity for the ester group of MMA. Thus, the perfectly spherical shape developed. Run 122 used a large molecule with higher numbers of carbon atoms ranging from 24 to 36 atoms. Nonspherical particles were obtained as shown in Figure 3(d), probably because the long alkyl chain has a higher affinity for

St and MMA. Consequently, the crosslinking agent pushed out the BW during the crosslinking reaction. Also, the MMA-rich copolymers moved with BW because of their higher affinity than that of MMA and that of the additive containing the hydroxyl group as a functional group. The platelets in Figure 3(b) changed to the solid head of the hemisphere in Figure 3(d), whereas the wax remains on the particle surface as detected by the FTIR technique.

Effect of Composition of Hydrophobic Additives

To determine the effects of the functional group and polarity on morphology of the polymer particles, the mixture of HD and HD–OH was the first effect under study in terms of the mixed HD/(HD–OH) 50 : 50 and 75 : 25 weight ratios for Runs 116 and 117, respectively. As shown in Figure 4(a,b), the polymer particles reveal dual morphologies of which one has a trace of circular area on the surface, and the other forms spheres with some debris. Due to the hydrophobicity of HD, HD is mixed with a polar additive such that the amount of polymer in the
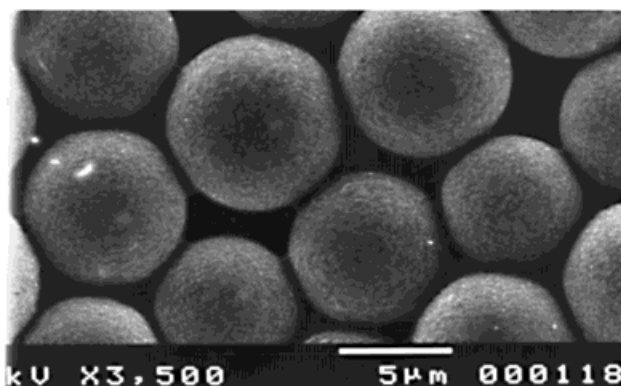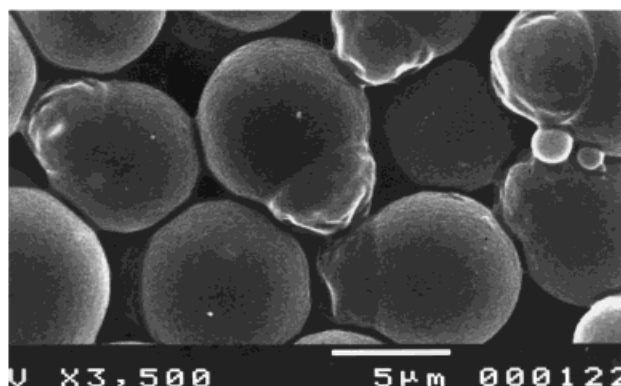
a) Run 109
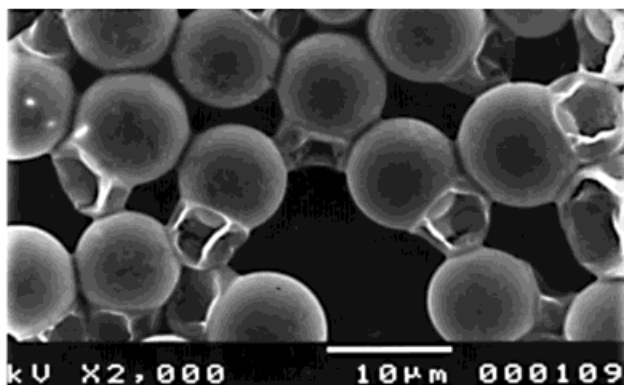
b) Run 114
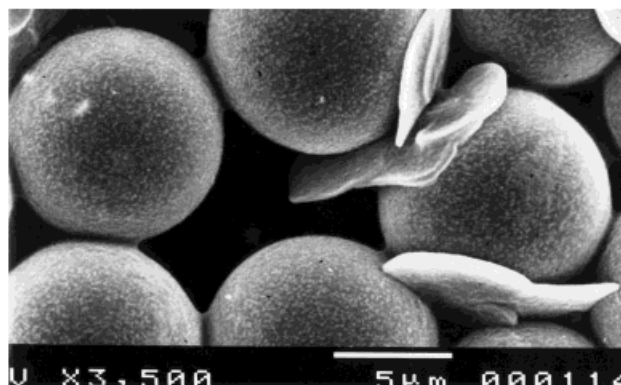
c) Run 118

d) Run 122

Figure 3 SEM photographs of poly(styrene-*co*-MMA) particles by various additives: (a) hexadecane, (b) 1-hexadecanol, (c) methyl palmitate, and (d) beeswax, respectively.

domain is not enough to form a strong filmy skin from which the HD bursts out in the extraction process. However, if the amount of HD is higher, the morphology shifts to hemispheric particles, and only the phase separation of HD on the surface is observed. The homogeneous spheres were obtained when MP was used as a coadditive. The ratio of HD/MP was selected at 50 : 50 and 25 : 75 in Runs 119 and 120, respectively. The particle appearance is similar to that in Run 116, with an appreciable amount of the circular area on the surface, which also resulted in Run 119 when 50% of HD was used. After decreasing the amount of HD to 25%, the particles showed very tiny holes resulting from the minute phase separation of HD. Therefore, MP is more dominant in forming the holes than HD, especially when the amount of MP is higher than 50%. The mixtures of MP and BW were studied at the MP/BW ratios of 50 : 50 and 75 : 25 in Runs 123 and 124, respectively. BW is more dominant in the two runs than is MP. The compatibility of MP with

the St-rich phase and with the MMA-rich phase developed the spherical domain, whereas BW, a long-chain ester, has a higher affinity than does the low-molecular-weight ester in which the phase separation may enhance in the MMA-rich phase. The snowmanlike morphology was obtained in both runs. The results of Runs 121 to 124 are shown in Figure 4(e–g). Extension of phase separation due to the presence of different hydrophobic additives controls the morphology of the polymeric particles of St–MMA copolymers. Addition of MP provides the perfect spheres; the addition of the polar compound, such as HD–OH, gives plateletlike debris attached to the particle surface. With the hydrophobic additive, HD, and the mixture of hydrophobic and hydrophilic additives, a range of particle morphology is obtained.

Average Diameter of Poly(styrene-*co*-MMA)

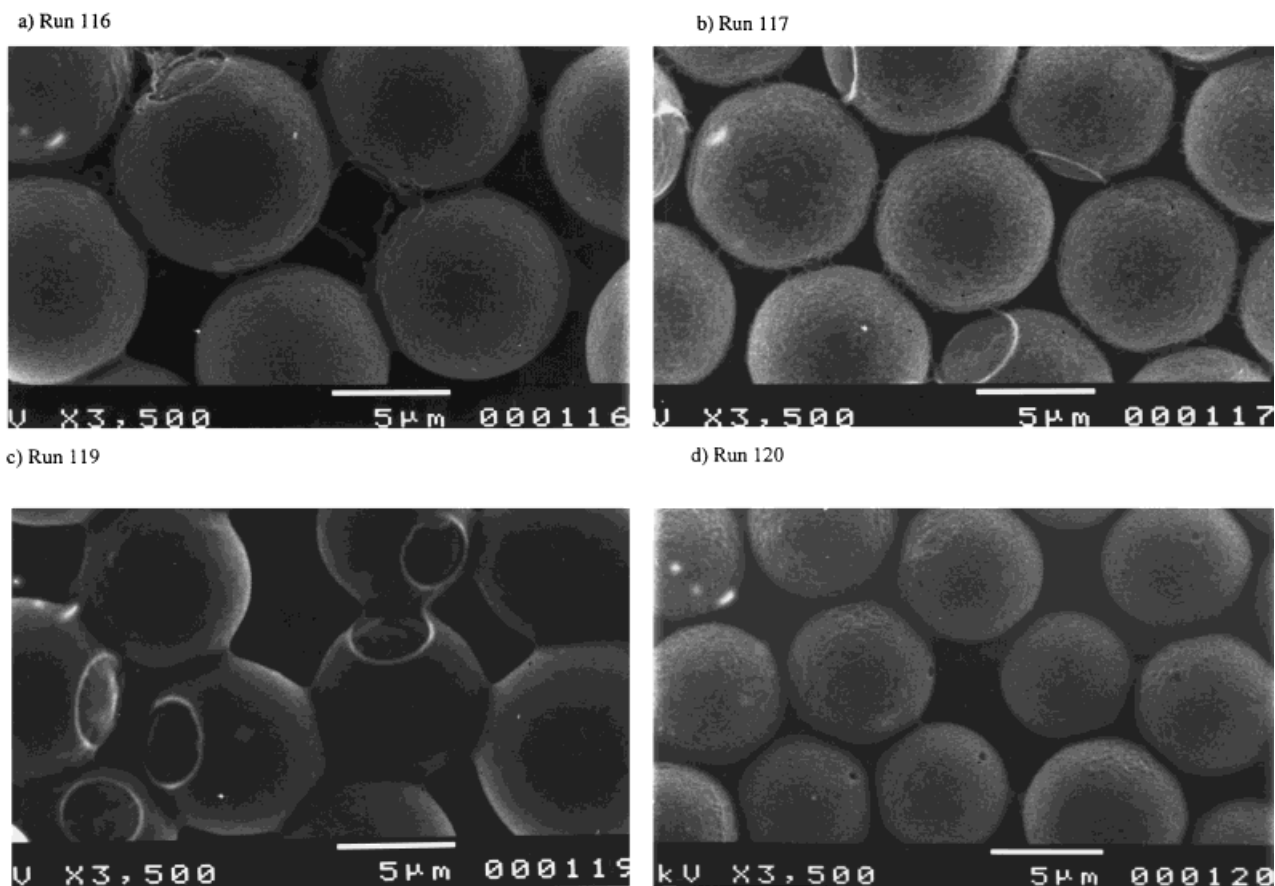As shown in Figure 5, the particle size decreased with a narrow particle-size distribution when the

Figure 4 SEM photographs of poly(styrene-*co*-MMA) particles by various compositions of additives: (a) HD/(HD–OH) 50 : 50 wt % ratio, (b) HD/(HD–OH) 25 : 75 wt % ratio, (c) HD/MP 50 : 50 wt % ratio, (d) HD/MP 25 : 75 wt % ratio, (e) (HD–OH)/MP 50 : 50 wt % ratio, (f) MP/BW 50 : 50 wt % ratio, and (g) MP/BW 75 : 25 wt % ratio, respectively.

hydrophobic additive was changed from HD to-HD–OH, MP, and BW. The distribution of the particle diameters was roughly 6–16 μm. For the hydrophobic additions of HD, MP, and BW, the average particle diameters are around 8, 7.5, and 6.5, respectively. The particle-size distribution imposed by the addition of HD–OH is rather broad but the peak diameters are located at 7.5, 8, and 10 μm, respectively. Considering a system of two different kinds of liquids, a liquid–liquid system, one is termed as an oil phase and the other is termed as an aqueous phase. In the syntheses of the St–MMA copolymer without any additive, the experiment was carried out with a dispersion phase containing 50 : 50 weight ratio of St–MMA as shown in Run 143. The polymer particles with a broad particle-size distribution were obtained as shown in Figure 6. Besides the main population of the particles of 8.1-μm diameter, another

population of larger particle sizes > 100 μm was found. The lack of additives causes a low interfacial tension between the monomer phase and the water phase. In other words, MMA monomer which is partially water-soluble (the solubility in water is 16 g/dm^3 at 298 K)[16] dissolves in water. Also, the collision of droplets occurred due to the stirring force during the polymerization process. To obtain the smaller polymer particle size, a higher interfacial tension is necessary through the addition of the hydrophobic additive.

The hydrophobic additives affect the boundary between two phases. In the case of HD (16 carbon atoms in the alkyl group), the molecules of the alkanes at the surface exhibit a dependence on the hydrophobic chain length. Due to the low polarity, the additives may not be present in the aqueous phase. Therefore, HD can yield the large emulsion droplets with an average droplet diam-
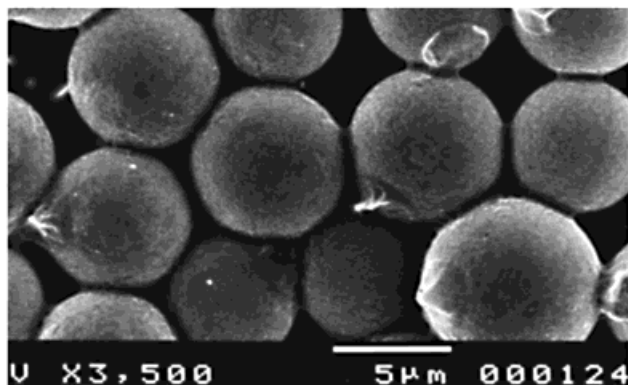
e) Run 121
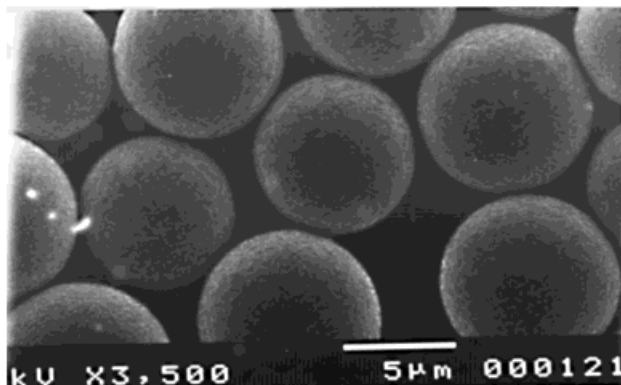
f) Run 123
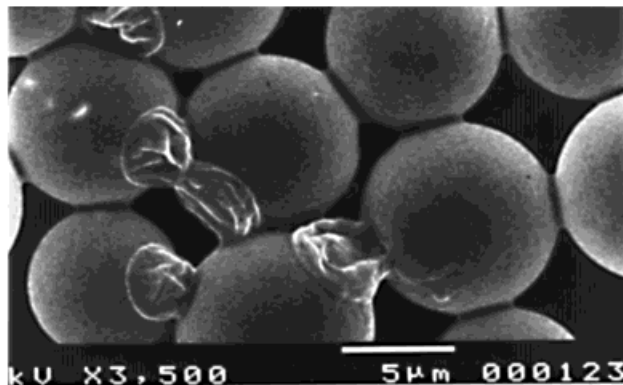
g) Run 124

Figure 4.   (*Continued from the previous page*)

eter of 12.2 μm and a coefficient of variation of 14.0% shown in Run 109. The different homologous series provide valuable information about the stabilizing forces in the fluid. Note that HD–OH has more polarity than HD because of the functional group of alcohol. Thus the additive can come out to the surface of droplets and affect the interfacial tension between two phases exhibiting a lower interfacial tension due to the greater affinity for water. Therefore the use of HD–OH as an additive shows that the droplet size distribution tends to be narrow and gives smaller emulsion droplets (i.e., an average droplet diameter of 10.8 μm was obtained in Run 114). MP exhibits great compatibility with the St–MMA copolymer, and in particular with the MMA segment according to the suitable alkyl chain length and the influence of the functional group. The smaller droplet diameter of 9.0 μm was obtained with a narrow size distribution. The stability of droplets due to the hydrophobicity of the alkyl group might enhance the compatibility with St, and the ester

group of the additive also promoted the compatibility with the ester group of MMA. Because the ester functional group can undergo hydrogen bonding, MP can diffuse to the surface of droplets for the formation of hydrogen bonding. The lower the interfacial tension, the smaller the particle sizes. Then, the additive was switched from MP to methyl laurate to evaluate the effect of the chain length in the alkyl group. To increase the hydrophilicity, a shorter alkyl chain length of methyl laurate (reagent grade, Tokyo Chemical Industry Co., Ltd., Japan) was used because methyl laurate is more hydrophilic than MP. The lower affinity with the monomer may increase, in which the emulsion droplets with an average diameter of 11.2 μm were obtained. Addition of more hydrophobic additives containing long-chain alkyl groups of hydrocarbons (24–36 carbon atoms in the alkyl group) with the ester functional group, such as BW, led to much more finely dispersed emulsions, and greatly increased the stability of the emulsion. This possibly resulted from higher
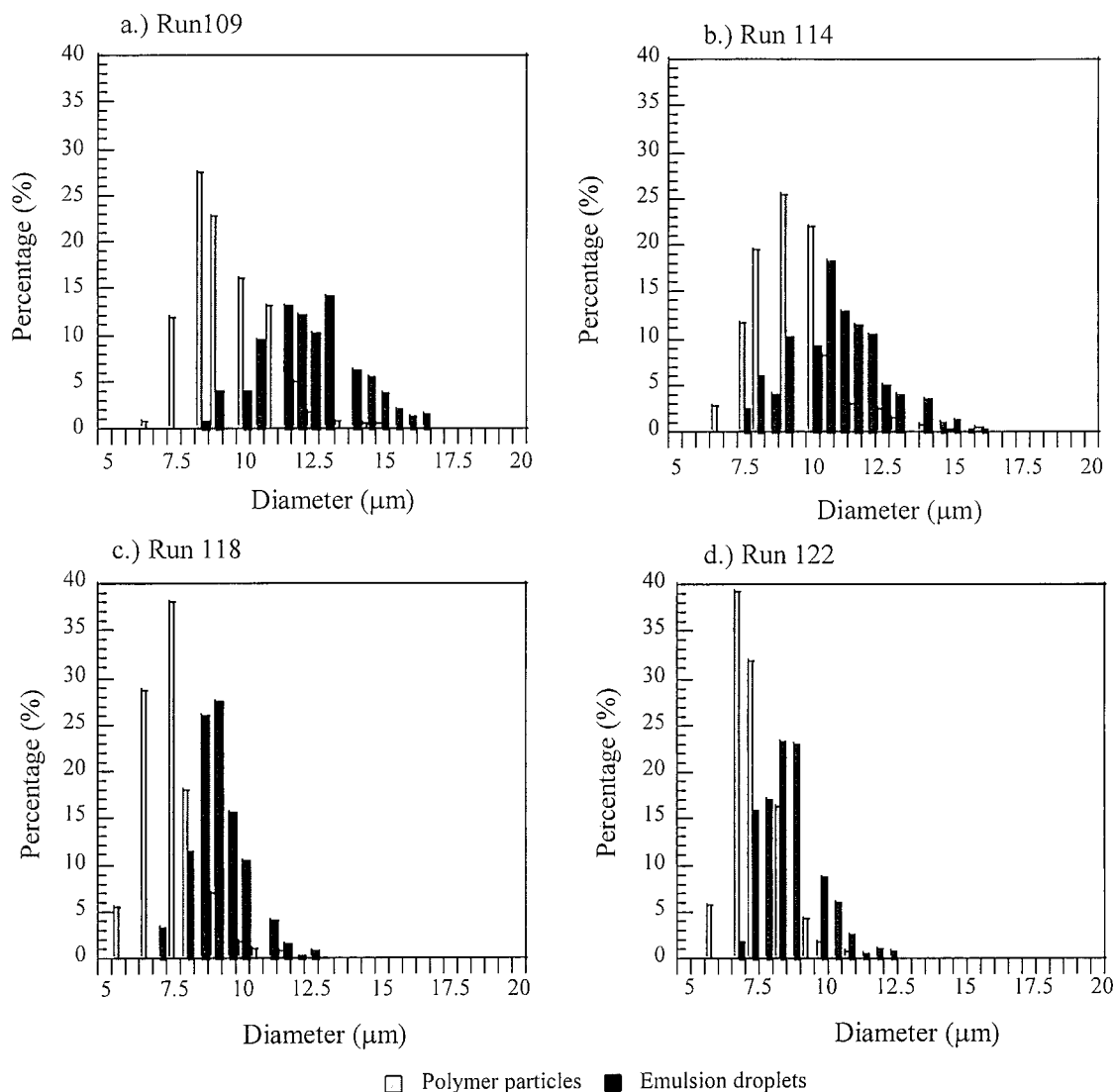
Figure 5 Histograms of size distribution of poly(styrene-*co*-MMA) showing the effect of additives: (a) hexadecane, Run 109, (b) 1-hexadecanol, Run 114, (c) methyl palmitate, Run 118, and (d) beeswax, Run 122.

alkyl chain lengths. The smaller droplet diameter of nearly 7 μm and a narrow droplet size distribution with a coefficient of variation of 12.1% were obtained. Furthermore, due to the higher viscosity of the dispersion phase containing BW, it is difficult to permeate the dispersion phase through the membrane; hence the size of droplets was smaller.

Figure 7 shows the relationship between the average diameters of particles and the fraction of a particular additive. In the mixture of HD and HD–OH, the smaller polymer particles are obtained when the mixture contains 25 wt % of HD in Run 117. An average particle diameter of 7.8 μm was

thus obtained. The molecules of the alkanes at the surface may exhibit some interesting phenomena depending on the chain length, which can be related to van der Waals interactions between chains. However, it is quite a weak interaction. Therefore, the alcohols would be mainly stabilized by both van der Waals force and hydrogen bonds,[18] the latter being stronger than the former. The molecular arrangement of HD and HD–OH for this composition revealed the dominant effect of HD–OH at the droplet surface relative to HD. Smaller droplets were thus obtained. Run 116 with the mixture of 50 wt % of HD gave polymers with an average particle-size diameter of 9.1 μm. Such a composition may not
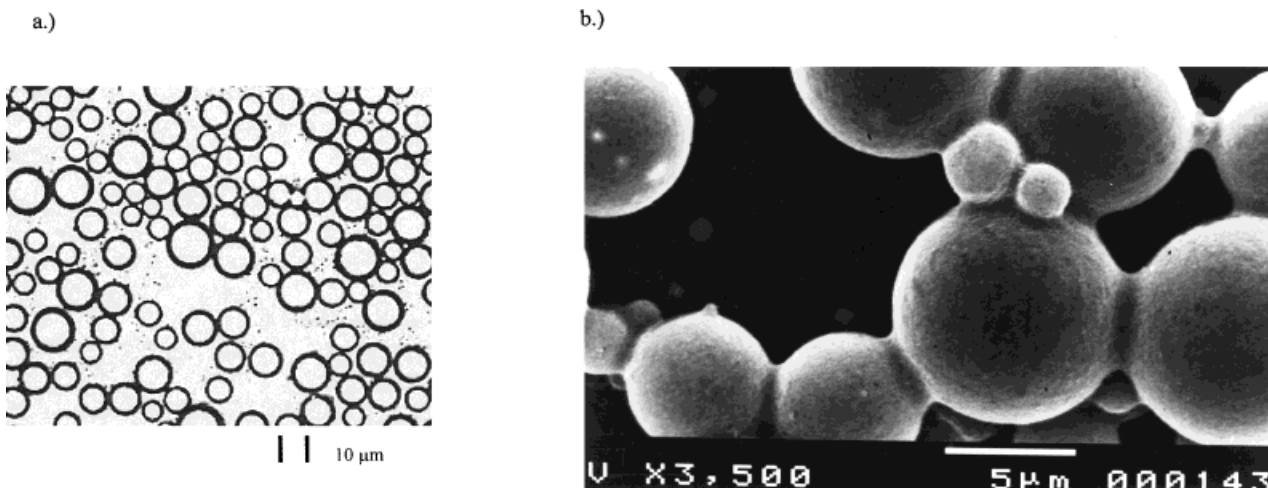
Figure 6 Photomicrographs of the poly(styrene-co-MMA) in Run 143 without additives: (a) photograph of the droplets taken by an optical microscope; (b) SEM photograph of the particles; CV = 20.2%, and $\bar{D}_p$ = 8.12 μm.

possibly be a favorable ratio for the additives. However, the particle size increased and became close to that obtained with 100% HD–OH. The particles prepared by using the mixed additives between HD and MP clearly show the significant change in interfacial tension due to the presence of additives.

The particle size decreased with an increasing amount of MP, which also increased the interfacial tension of the monomer and disperse phases. In Run 120, an emulsion droplet diameter of 6.8 μm with a narrow size distribution and a coefficient of variation of 10.4% were obtained.
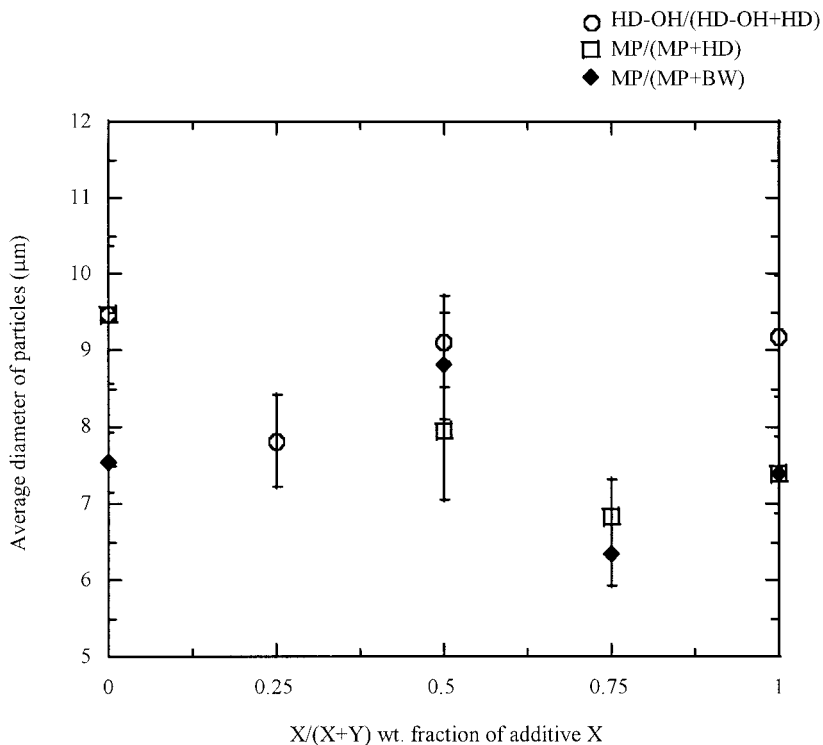

Figure 7 Average diameter of the polymer particles with various compositions of hydrophobic additives.

Table III   Polymerization Recipe and Experimental Results for Poly(styrene-*co*-*n*-BMA) and Poly(styrene-*co*-2-EHMA) with Various Hydrophobic Additives Using an SPG Pore Size of 1.42 μm

	Run No.							
	401	403	404	406	601	603	604	606
Dispersion phase								
Styrene (g)	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
n-BMA (g)	8.00	8.00	8.00	8.00	0	0	0	0
2-EHMA (g)	0	0	0	0	8.00	8.00	8.00	8.00
Hexadecane (g)	1.50	0	0	0	1.50	0	0	0
1-Hexadecanol (g)	0	1.50	0	0	0	1.50	0	0
Methyl palmitate (g)	0	0	1.50	0	0	0	1.50	0
Beeswax (g)	0	0	0	1.50	0	0	0	1.50
BPO (g)	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Results								
Emulsion droplets								
$\bar{D}_e$ (μm)	10.9	12.6	11.5	12.7	13.2	11.6	12.3	12.6
σ (μm)	1.1	1.6	1.4	1.5	1.8	1.3	1.3	1.8
CV (%)	10.3	12.6	12.5	12.1	13.4	11.0	10.7	14.3
Polymer particles								
$\bar{D}_p$ (μm)	9.6	10.8	9.5	10.6	13.1	10.2	10.8	10.2
σ (μm)	1.3	1.5	1.3	1.5	2.4	1.4	1.6	1.8
CV (%)	13.4	14.2	13.9	14.2	18.2	14.2	14.2	17.5
Conversion (%)	71.6	72.3	54.4	96.7	67.7	64.0	73.8	49.2

Continuous phase: H_2O, 230 g; PVA-217, 1.50 g; SLS, 0.04 g; Na_2SO_4, 0.05 g; and hydroquinone, 0.016.

The mixture of additives of the same functional group was added using MP and BW. The mixtures containing 50% of BW in Run 123 and 25% of BW in Run 124 produced average particle sizes of 8.8 and 6.3 μm, respectively. Compared with the mixed additives containing the other functional groups of alkane or alcohol, a small-sized polymer was obtained because of the interaction between hydrogen bonding of the ester groups. Miller et al.[19] in their mini-emulsion polymerization of St claimed that the highest number of polymer particles and a solid emulsion were obtained when a 1 : 3 molar ratio of SLS and hexadecanol was employed. Yuyama et al.[20] reported the very complex behavior of the interfacial tension between the droplets and the continuous phase when they employed PVA and SLS as a mixed stabilizer in the aqueous phase, and HD as a hydrophobic additive in their emulsion of St and DVB. The results of the present system are by no means directly comparable with their results. However, it can be said that the complex behavior of droplet size in Figure 8 is certainly due to the complex formation of the two additives on the interface between the droplets and the aqueous phase.

To summarize the morphological changes of poly(styrene-*co*-MMA) particles due to the effect of additives, the extent of phase separation along with different particle morphologies is graphically presented in Figure 8. Based on the feed (wt ratio) of St : MMA of 50 : 50, the monomer system is rather hydrophilic because MMA is relatively polar due to the acrylate functionality. The additive to the single phase should be rather hydrophilic. Increasing the additive hydrophobicity usually enhances the phase separation. These two concepts correspond to the matched solubility parameters for single-phase solution. The smaller the phase separation, the greater the result in perfect polymer particles [see Fig. 8(a,b)]. The smaller the phase separation between the MP, and the base polymer shown in Figure 8(a) for Run 118, resulted in the spherical particles of poly(styrene-*co*-MMA). The addition of more hydrophobic addition of HD–OH enhanced the phase separation, yet it is sufficient to produce the spherical particles. The phase separation occurred as shown in Figure 8(b,c) when the mixture of additive contains HD. HD plays a role as a strongly hydrophobic additive, and its mixture
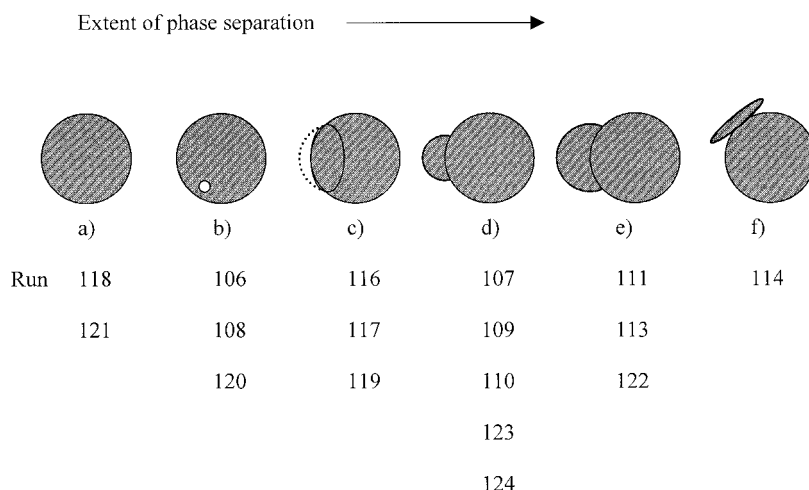
Extent of phase separation ⟶

a)	b)	c)	d)	e)	f)

Run	118	106	116	107	111	114
	121	108	117	109	113	
		120	119	110	122	
				123		
				124		

Figure 8 Schematic diagram for the morphology classification in the preparation of poly(styrene-*co*-MMA), the weight ratio of St/MMA in the feed of 50 : 50; except Run 106, St/MMA in the feed of 80 : 20.

with HD–OH or MP produce the hemisphere on the polymer particles. The crosslinking agent imposes the same tendency as shown in Figure 8(d,e) (Runs 107, 109, 111, and 113). In the other case of BW or the mixture of MP and BW containing different hydrocarbon chain lengths, increasing the chain length can increase the phase separation. Therefore, the bigger portion of the snowman's head was developed. On the other hand, when the more hydrophilic additive of HD–OH was added as shown in Figure 8(f), less phase separation was revealed. Only a protrusion of debris (like a platelet) on the surface of the particles was developed.

Effect of the Additives on Morphologies of Poly(styrene-*co*-*n*-butyl methacrylate) (St-*n*-BMA) and Poly(styrene-*co*-2-ethylhexyl methacrylate) (St-2-EHMA) Particles

The effect of the additives on the morphologies of copolymers obtained from different monomers was carried out by employing the dispersion phase containing a 50 : 50 weight ratio of St-*n*-BMA and St-2-EHMA. To evaluate the effect of additives on a series of alkyl methacrylate, the noncrosslinked polymers were prepared in which the experimental recipe and results are shown in Table III and Figures 9 and 10.

In Run 401, St-*n*-BMA particles retained a smooth surface and were spherical in shape with small dimples when HD was added. On the other hand, the effect of HD on St-*n*-BMA is similar to the cases of St–MMA copolymer particles in Runs

106 and 108 discussed previously. *n*-BMA is more hydrophobic than MMA due to the long side chain of the alkyl group. The side chain of *n*-BMA can be partially compatible with HD due to their similar hydrophobicity. A trace amount of HD was expelled to the surface and could simply be extracted by methanol to yield the dimples on the surface. However, when using 2-EHMA as a comonomer, the dimples were not observed. The particle distortion from the spherical shape occurred because the monomer possesses a lower glass transition temperature (T_g) than does *n*-BMA. Thus, the St-2-EHMA particles have a softer and rubberlike morphology and are unable to keep the spherical shape. The hemispheric and flattened particles sticking together can be observed on the SEM photographs in Figures 9(a) and 10(a). St-*n*-BMA and St-2-EHMA copolymer particles prepared in the presence of HD–OH still showed the phase separation. The spherically shaped particles with some plateletlike debris morphologies in Figure 9(a) and the depressed and soft surfaces in Figure 10(a) sticking together were obtained. The amount of the debris on both copolymer particles increased more than those observed on St–MMA particles. The increase in the separated domains indicates a poor compatibility of HD–OH with the monomers because they are more hydrophobic than MMA. MP still revealed a relatively good compatibility, yielding the spherical shape of St-*n*-BMA and St-2-EHMA copolymer particles. However, both types of particles stuck together and deformed due to the low
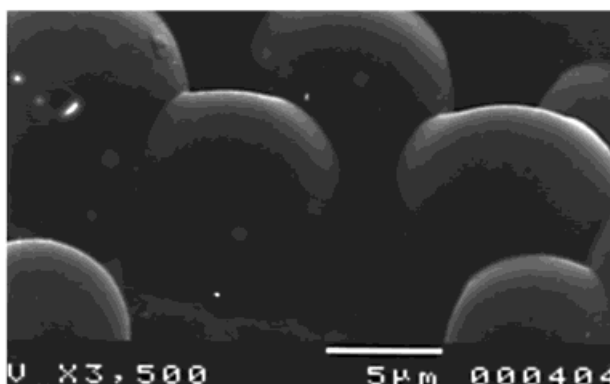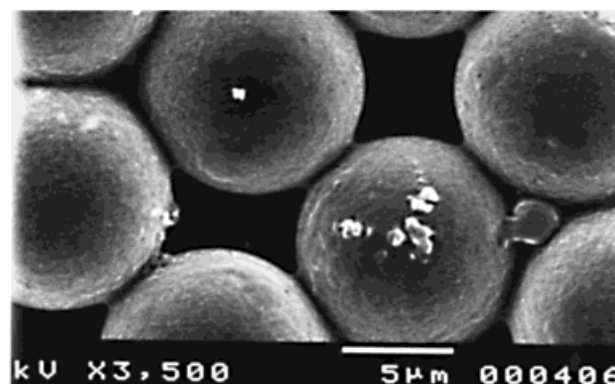
a) Run 401
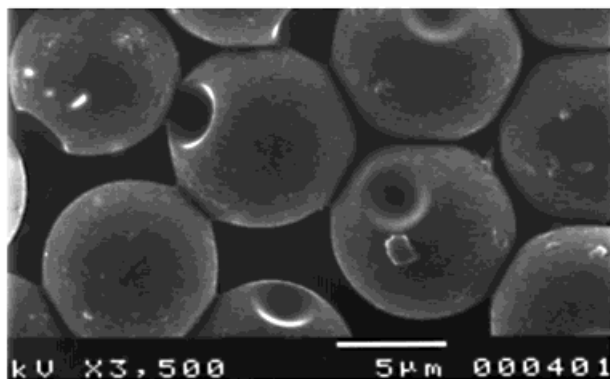
b) Run 403
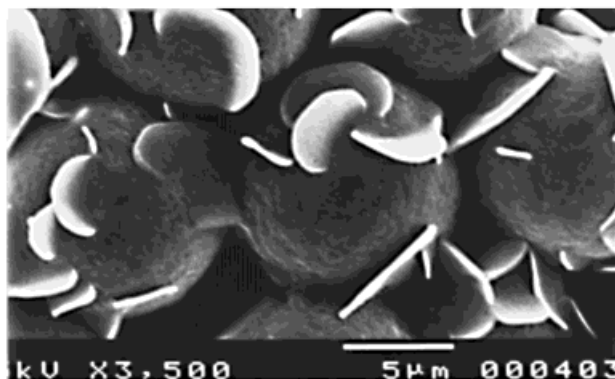
c) Run 404

d) Run 406

Figure 9   SEM photographs of poly(styrene-*co*-BMA) particles by various additives: (a) hexadecane, (b) 1-hexadecanol, (c) methyl palmitate, and (d) beeswax, respectively.

T_g. BW represents a good additive in the synthesis of the St-n-BMA and St-2-EHMA copolymers. The tiny flakes on the surface may suggest the partial phase separation of BW and its expulsion to the surface of the polymer particles.

Effect of Additives on the Particle Size and Size Distribution of Poly(styrene-*co*-*n*-BMA) and Poly(styrene-*co*-2-EHMA) Particles

The particle-size distribution of both St-n-BMA and St-2-EHMA copolymer particles revealed similar behavior of interfacial tension when changing the additive type as discussed for St–MMA copolymer particles in the previous section. The exception is in the case of BW, which resulted in a broad distribution, probably because of the very slow droplet protrusion through the SPG membrane. Considering the molecular structure of n-BMA and 2-EHMA, both monomers have relatively large side chains: —$COOC_4H_9$ and —$COOCH_2CH(CH_2CH_3)(CH_2)_3CH_3$, respectively.

The monomer with the higher viscosity is more difficult to permeate through the membrane. Furthermore, the hydrophobic alkyl group of BW does not dissolve in the water. Thus the wax may plug up the membrane pores. The emulsion droplets become smaller when the SPG emulsification takes a long time. As a result, a broad particle-size distribution resulted.

CONCLUSION

The preparation of uniform poly(styrene-*co*-MMA) microspheres was successfully accomplished by using the SPG emulsification technique. Monodisperse St–MMA copolymer microspheres with an average particle size from 7 to 14 μm were obtained, employing the SPG pore size of 1.42 μm under a precisely controlled nitrogen pressure. The effect of the crosslinking agent showed the amount of EGDMA required to give crosslinked networks in
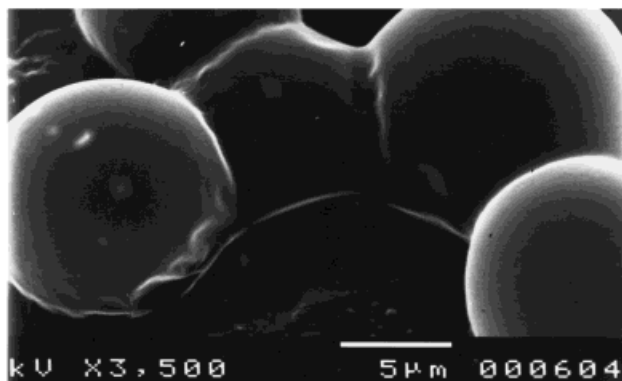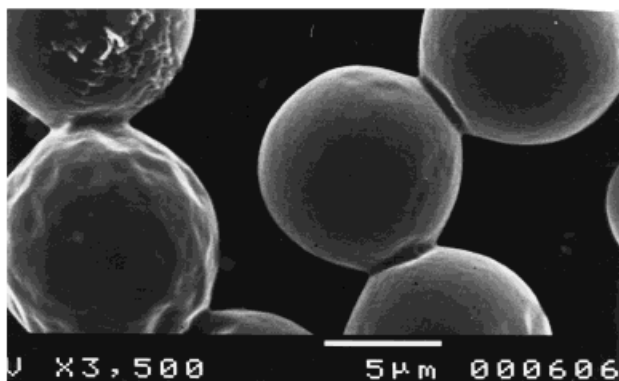
a) Run 601
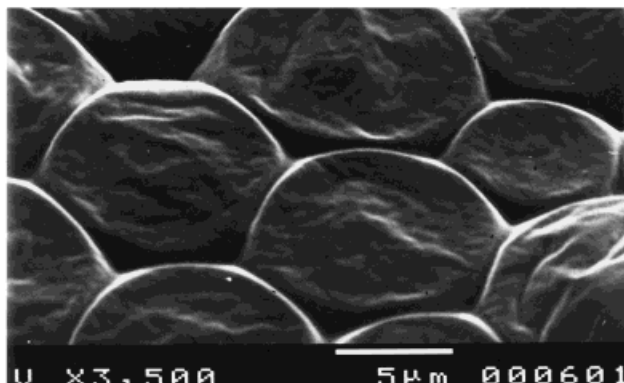
b) Run 603
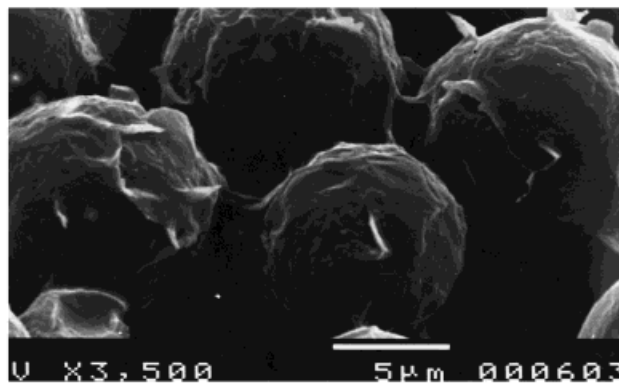
c) Run 604

d) Run 606

Figure 10 SEM photographs of poly(styrene-*co*-2-EHMA) particles by various additives: (a) hexadecane, (b) 1-hexadecanol, (c) methyl palmitate, and (d) beeswax, respectively.

particles. However, the use of EGDMA with a coadditive, HD, caused phase separation and produced various morphologies of the resulting particles such as nonspherical particles. Increasing the crosslinking density enhanced the degree of phase separation. The use of different additive types resulted in different sizes of the droplets and particles, and their size distribution. The particle size decreased when changing the additive from long-chain alkane, HD, to long-chain alcohol, HD–OH, and to long-chain esters, MP and BW. The influence of additives on morphology and particle size was via the interfacial tension between the disperse phase (monomer and additive) and aqueous phase that depended on the functional group and the alkyl chain length. The additives containing the ester group, such as MP and BW, yielded a smaller particle size and higher droplet stability because of the hydrogen bonding and the long-chain alkyl moiety of the molecules. The physical appearance of St–MMA, St-*n*-

BMA, and St-2-EHMA copolymer particles by the effect of additives demonstrates that the compatibility between the hydrophobic additives and the monomers provides various morphologies of particles. The mixed additives with varying compositions were studied for the preparation of St–MMA copolymer particles. The results revealed particles with different morphologies. The formation of phase separation was affected by the dominance of one additive over the other. We identified suitable additive fractions and types for providing spherical particles.

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