Influence of Compositions and Polymerization Processes on Morphologies, Molar Mass Distributions, and Phase Structures of n-Butyl Acrylate–Methyl Methacrylate Copolymers

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ABSTRACT: The target of the research is to examine influence of a polymerization process and monomer ratio on structures and compositions of phases in an emulsion copolymerization of n-butyl acrylate (BA) and methyl methacrylate (MMA). Emulsion copolymerizations are performed using three different BA/MMA weight ratios (60%/40%, 50%/50%, and 40%/60%) and two different processes, statistical batch and seeded emulsion polymerizations. Phase structures, monomer compositions, and morphological stabilities of copolymers are investigated by differential scanning calorimetry, ^{1}H-NMR, and scanning electron microscopy. Gel permeation chromatography is used to follow the changes in the molar mass distribution during syntheses. The gel content and backbiting level of end products are measured by extraction and ^{13}C-NMR, respectively. Copolymerizations give products with a bimodal molar mass distribution and three or two separate phases having different BA/MMA compositions. The morphological stability of particles decreases with the increasing BA fraction in the feed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41467.

INTRODUCTION

Dispersions of emulsion polymers usually consist of polymer particles with sizes in tens of nanometers up to a few micrometers. Emulsion polymers are extensively used in many applications such as adhesives, in coatings, and in some products as an impact modifier.[1–3] Acrylic polymers form a large group of emulsion polymers and they have numerous interesting properties, such as a broad range of glass transition temperatures (T_g) and excellent chemical and optical properties. One of the most studied monomer pair is methyl methacrylate (MMA) and n-butyl acrylate (BA) because the T_g of the forming copolymer can be controlled over a wide range between -50 and 110°C by adjusting the monomer ratio in the feed.[4,5] Pure poly(methyl methacrylate) (PMMA) is a hard and transparent material with a good environmental stability, whereas polybutyl acrylate (PBA) is a soft material at room temperature and is used as an adhesive material. Both are important commercial polymers.

Emulsion copolymers may contain many different separate phases or domains, which can lead to variable mechanical properties.[6,7] Copolymer particles with a soft core and a hard shell have a more stable morphology at higher temperatures than particles without the shell. Such particles have enhanced

dispersing possibilities and can be used as an impact modifier.[8,9] However, copolymer particles having a gradually changing composition and a soft exterior can be used as pressure-sensitive adhesives.[7,10] One of the most important way to tailor the polymer phases or domain structures is the polymerization process. The seeded and statistical batch emulsion polymerizations are the basic processes for the synthesis of the above-mentioned copolymers.[11]

Furthermore, some acrylates have a tendency to form cross-linked fractions and gels. A gel form of the polymer can also be desirable in some technical applications where special mechanical properties, such as impact strength, are required.[8,9] In the emulsion polymerization of BA, the branching of BA polymer chain is well known, and it can take place by an intra- (so-called backbiting) or intermolecular chain transfer to polymer. Backbiting make short-chain branches, whereas the intermolecular chain transfer produces long-chain branches. The gel is formed by termination of long chain-branched polymer chains by radical combination.[12,13] In addition, Sayer et al.[14] have observed in emulsion copolymerization of BA and MMA that a higher gel fraction was obtained in a starved process in comparison to semi-starved processes. However, González et al.[15] found

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Table I. Feed Compositions of the Syntheses

| | | | Statistical and seeded copolymers Weight ratios of BA/MMA | | |
	PMMA	PBA	40%/60%	50%/50%	60%/40%
Component	(g)	(g)	(g)	(g)	(g)
MMA	20	—	13.5	9	6
BA	0	20	9	9	9
Initiator (APS)	0.05	0.05	0.05	0.05	0.05
Emulsifier (SDS)	0.03	0.03	0.03	0.03	0.03
Deionized water	180	180	180	180	180

that the presence of MMA decreases both branching and gel forming of BA in several ways. MMA reduces the formation of BA–BA–BA triads necessary for the intramolecular chain transfer. Gel forming and intermolecular chain transfer are decreased because of the ability of PMMA radicals to make termination by disproportionation.

The main target in the current research is to examine influence of a polymerization process (seeded or statistical) and the monomer ratio on structures and compositions of phases formed in an emulsion copolymerization of BA and MMA. In the seeded emulsion polymerization, the seed (core) is prepared from BA and the second-stage polymer (shell) by copolymerization from MMA and BA monomers. The composition during the synthesis is evaluated for the statistical copolymers and the second-stage copolymers of the seeded process on the basis of the conversion and ^{1}H-NMR results. The size and morphology of emulsion particles are analyzed by scanning electron microscopy (SEM), and molar mass distributions during synthesis are measured with gel permeation chromatography (GPC). Changes in the glass transition temperatures of thermally separate phases are followed during the synthesis by a differential scanning calorimetry (DSC). The gel content and backbiting level of the emulsion particles are also measured.

The emphasis in our research is to show how the composition, molar mass distribution, and morphological stability of polymer particles change during the synthesis using these two different polymerization processes and how the composition and polymerization process will affect the gel and backbiting contents of copolymer. The results indicate that copolymerizations of MMA and BA give products with a bimodal molar mass distribution and three or two separate phases with different compositions. Furthermore, the morphological stability of emulsion particles decreases as the fraction of BA in the feed increases.

EXPERIMENTAL

Materials

MMA (Fluka, 99.0+%), BA (Acros Organics, 99.0+%), sodium dodecyl sulfate (Sigma-Aldrich, 98.5+%), ammonium persulfate (APS, Sigma-Aldrich, 98.0+%), and chromium (III) acetylacetonate [Cr(C$_5$H$_7$O$_2$)$_3$, Aldrich, 97%] were used as received. Dialysis tubes were Spectra/Por® 6 (MWCO 25,000 Da). Deionized water was used in the syntheses and in the purification of the final products.

Synthesis

Pure homopolymers (PMMA and PBA) and statistical copolymer poly(BA-co-MMA) were synthesized by a free-radical bath emulsion polymerization using APS as an initiator and SDS as an emulsifier. Seeded copolymers were prepared by a seeded emulsion polymerization using the same monomer ratios as in the statistical copolymerization. The amounts of reagents used in synthesis are given in Table I. The polymerizations were performed in a conical flask equipped with a Glenfeliz magnetic stirrer head and the flask was heated in an oil bath for 4 h under a nitrogen atmosphere.

Homopolymerizations and Statistical Copolymerizations. At first, deionized water and SDS were added in a reaction vessel and the solution was stirred at 70°C using a twin-paddled overhead stirrer operating at 300 rpm. Monomer was added in the flask and stirred for 30 min at 70°C. In the copolymerizations, three different BA/MMA compositions were used. The amount of BA was kept constant in the copolymer syntheses and the amount of MMA was varied according to the BA/MMA weight ratio. Then, initiator (APS) was dissolved in deionized water and added in the reaction vessel. The reaction was allowed to proceed for 4 h. The resulting polymerization products were purified by dialysis.

Seeded Copolymerizations. Measured amounts of deionized water and SDS were added in a reaction vessel, and the solution was stirred at 300 rpm with heating at 70°C. BA was added in the vessel and stirred for 30 min at 70°C. Then, a deionized water solution of the initiator (APS) was added in the vessel for 10 min. The reaction was allowed to proceed for 75 min, and after that time, the conversion of BA was around 65%. In addition, the color of the mixture had changed from transparent to milky. After a 75-min polymerization of BA, MMA was added in the reaction mixture with an addition speed of 1.5 g/min. The reaction was allowed to proceed for 4 h. The resulting polymerization products were purified as in the statistical polymerization case. For the second stage copolymer, the theoretical weight ratios of BA/MMA are 34%/66%, 26%/74%, and 19%/81%, and the corresponding theoretical shell/core weight ratios are 1.6/1, 2.1/1, and 2.8/1, respectively. The weight ratios were obtained assuming that the conversion of BA before addition of MMA is 65% and the total conversion is 100%. The weight values of monomers given in Table I were used in the calculation of the weight ratios.

Purification of Emulsion Polymer Products

The final products of polymerization were purified to remove excess of surfactant and water-soluble ionic materials by dialysis. Before the dialysis, cellulose membranes were purified in deionized water to remove sodium azide and others impurities. Then, emulsion mixture was placed in the tube, and it was immersed in deionized water. The purification took 1 week and water was replaced every 24 h.

Characterization

Conversion measurements were made by taking samples (about 5 mL) from the reactor during polymerization, and the samples were weighed to determine the overall conversion according to the method by Silvestri et al. (see section S1 in Supporting Information).[16]

Four hundred-megahertz ^{1}H NMR measurements were performed with a Bruker Avance 400 NMR spectrometer. The polymer solutions were prepared in CDCl$_3$, and the solvent was used as an internal standard in the chemical shift measurements. The polymer concentrations were about 5 wt %, and number of scans were 30 and the delay time was 10 s.

The morphology and average diameter of polymer spheres were measured using a Hitachi SEM S-4800 scanning electron microscope. Samples were prepared by placing a small amount of dried emulsion on a carbon tape and coated with 4 nm gold layer (Au) by using a sputter coater (Cressington 208HR, high-resolution sputter coater).

Molar mass distributions were measured by a GPC instrument (Waters, Alliance GPCV 2000) equipped with a Waters 510 pump, a Rheodyne loop injector, and viscometry and differential refractive-index detectors. Styragel HT 3, HT 4, and HT 5 columns packed in tetrahydrofuran (THF) were used. The calibration of the instrument was performed with 12 different PS standards between 3070 and 3.250×10^6 Da. Samples were dissolved in THF, and the polymer concentrations were about 2 wt %. The sample size was 250 μL, and the flow rate of THF eluent was 1.0 mL/min. Temperature in the measurements was 35°C.

Glass transition temperature measurements were performed on a DSC instrument (Mettler Toledo DSC823^e). Program included two cooling–heating cycles between −80 and 160°C. Measurements were performed under a nitrogen gas flow (50 mL/min) with a heating rate of 10°C/min and a cooling rate of −10°C/min. The first cooling–heating cycle was used to remove the thermal history of the sample and the second heating was used to determine the glass transition temperatures.

The gel content of copolymers was measured in two different ways. The solvent extraction method using the filter paper technique was adapted from the study by Tamai et al.[17] It was made by dissolving 200 mg of a final product in 100 mL of THF at 30°C for 24 h. After filtration and drying, the filter paper was weighed to evaluate the gel content (see section S5 in Supporting Information). The Soxhlet extraction method was adapted from the work by Elizalde et al.,[18] and the extraction was performed at 67°C under a N$_2$ atmosphere for 48 h. The sample size and solvent used were 70 mg and THF, respectively. After extraction, the dried extraction thimble was weighed to find out the gel content with the same procedure as in the solvent extraction method using the filter paper technique.

^{13}C-NMR measurements were performed on a Bruker AMX 400 NMR spectrometer. Samples were measured with an inverse-gated decoupling pulse program. The polymers were dissolved in toluene-D8, and the toluene-D8 was used as an internal standard in the chemical shift measurements. Cr(C$_5$H$_7$O$_2$)$_3$ was used to decrease the relaxation time of the carbon nuclei of the polymers and the concentration of Cr(C$_5$H$_7$O$_2$)$_3$ in toluene was 20 mmol/L. The polymer concentrations were about 100 mg/mL, and the number of scans was more than 25,000 and the delay time was 2 s. The theoretical calculations of backbiting and branching contents are explained in section S6 of Supporting Information.

RESULTS AND DISCUSSION

Emulsion copolymerizations of BA and MMA were performed with a statistical and a seeded copolymerization processes, and the used monomer feed weight ratios of BA/MMA were 60%/40%, 50%/50%, and 40%/60%. The total weight of BA was kept the same in all of the copolymerizations, whereas the amount of MMA varied (Table I). Homopolymerizations of MMA and BA were performed for comparison.

In the seeded copolymerizations, the seeds were made up of PBA, which is soft at room temperature. The conversion of BA in seeds was adjusted to around 65% to produce seeds possessing the same volume. The second-stage copolymerization was used to produce a shell on the seeds. The addition of the second-stage monomer was started before the conversion of BA was complete to allow further propagation of BA polymer chains. This enabled the seeds and the second-stage monomer to form covalent bonds. The second-stage copolymer consisted of the rest of unreacted BA and a varied amount of MMA and assuming that the BA conversions before addition of MMA and the total conversions are 65 and 100%, respectively, the theoretical weight ratios of BA/MMA of 34%/66%, 26%/74%, and 19%/81% and the corresponding theoretical shell/core weight ratios of 1.6/1, 2.1/1, and 2.8/1, respectively, are expected.

Conversion of the Syntheses

Conversions were obtained with a gravimetric method (see section S1 in Supporting Information). The conversion of copolymerizations was close to 100% after a 120-min reaction, whereas homopolymerizations of MMA and BA were complete in 60 and 180 min, respectively (Supporting Information Figure S1). According to these results, the polymerization rate decreased of pure MMA, copolymers, and pure BA. The experimental weight ratios of the shell/core in the seeded copolymerizations were calculated according to the conversion measurements (the BA conversions before addition of MMA and the total conversions) and the exact weight values of monomers in the feed. The experimental values were 1.4/1, 2.0/1, and 2.8/1, which are close to the theoretical values.

Composition of the Statistical and the Second-Stage Copolymer (Shell) During the Synthesis

^{1}H-NMR was used to determine the compositions of copolymer particles by an integration of the resonances of —OCH$_3$ of
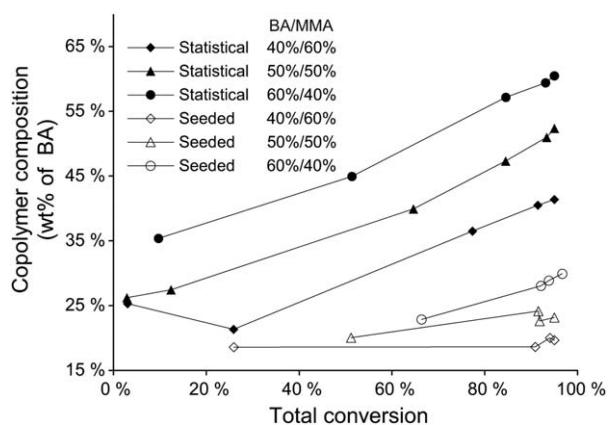
Figure 1. BA weight compositions of the statistical copolymers and the second-stage copolymers (shell) of the seeded copolymerization as a function of the total conversion. The weight ratios of BA/MMA in the feed were 40%/60%, 50%/50%, and 60%/40%.

MMA and ─OCH$_2$─ of BA, according to the method by de la Fuente et al.[19] The average molar fractions of BA and MMA obtained from ^{1}H-NMR was used to determine the weight composition of copolymer particles (see section S2 in Supporting Information). The BA weight contents of the statistical and the second-stage copolymers are presented in Figure 1 as a function of the total conversion. The composition curves indicate a slower incorporation of BA in the copolymer chains because of the higher reaction rate of MMA.[20–23] The final compositions of the formed copolymers correspond to the initial feed ratios of the monomers. A similar trend has been reported in the literature.[19,24]

Morphological Stability of the Emulsion Particles During the Synthesis

Polymer particles, which were stable at room temperature, were observed to self-assemble in the face-centered cubic (FCC) close-packed structure. This indicates that the morphology of the particles was uniform and the size distribution narrow. As can be seen in Table II, the morphology and size of spheres changed during the reaction. The PBA synthesis did not produce particles morphologically stable at room temperature and

a similar phenomenon was observed in the case of copolymers containing 60 wt % of BA.

In the middle stage of the statistical polymerization, it was observed that the emulsion particles were spherical and their morphology was stable [Figure 2(1a,1b)]. As the reaction went on the surface of emulsion particles became more obscured and simultaneously their visible appearance in the dried state changed from opaque to translucent. This indicates that the outer interface of the particles became soft and the particles merged together to a condensed material [Figure 2(1c)]. The change from opaque to translucent was observed especially in the case of the samples with the high BA content.

In the seeded copolymerization case, as the second-stage copolymerization went on the morphological stability of particles increased as shown in Table II. Simultaneously, as stable particles were formed, the visible appearance of emulsion particles in the dried state changed from translucent to opaque. During the outer shell formation, the surface of the particles became hard and this enabled the formation of particles morphologically stable at room temperature. An example of such surface change is shown in Figure 2(2a–2c). When the weight ratio of (BA/MMA) in the feed was 60%/40%, the synthesis did not produce stable particles, probably due to the small thickness of the outer shell. The weight ratio of shell/core in (60%/40%) case was 1.4/1, whereas in (50%/50%) and (40%/60%) cases, the weight ratios of shell/core were 2.0/1 and 2.8/1, respectively.

Molar Mass Distribution During Synthesis

Changes in molar mass distributions were followed during the polymerizations (Supporting Information Table SI). The molar mass distributions of the homopolymer of MMA gave only a monomodal signal during the synthesis. In the case of PBA, the bimodal distribution was detected already from the start of synthesis (Supporting Information Figure S2). The molar mass distributions of PBA and PMMA differ due to the difference in the chain termination mechanisms. For PBA, the termination by combination is favorable increasing the possibility for formation of higher molecular weight (MW) polymers, whereas in the case of PMMA, the termination by disproportionation is favored.[15] For statistical polymerizations, the GPC results indicate that the first polymer fractions formed possessed the

Table II. The Size and the Morphological Stability of Spheres Produced by the Two Synthesis Processes Using Different Monomer Ratios

Time (min)	PMMA (nm)	PBA (nm)	Statistical, particles diameter (nm) Weight ratios of BA/MMA			Seeded, particles diameter (nm) Weight ratios of BA/MMA		
			40%/60%	50%/50%	60%/40%	40%/60%	50%/50%	60%/40%
30	120 ± 3	a	38 ± 6	65 ± 5	55 ± 4			
60	125 ± 4	a	90 ± 4	110 ± 7	95a			
75						a	a	a
90	125 ± 6	a	135 ± 5	116a	a	a	114a	a
120	125 ± 4	a	133a	123a	a	154 ± 3	134 ± 4	a
150	—	—	—	—	—	153 ± 6	131 ± 6	a
240	125 ± 5	a	133a	123a	a	155 ± 4	134 ± 5	a

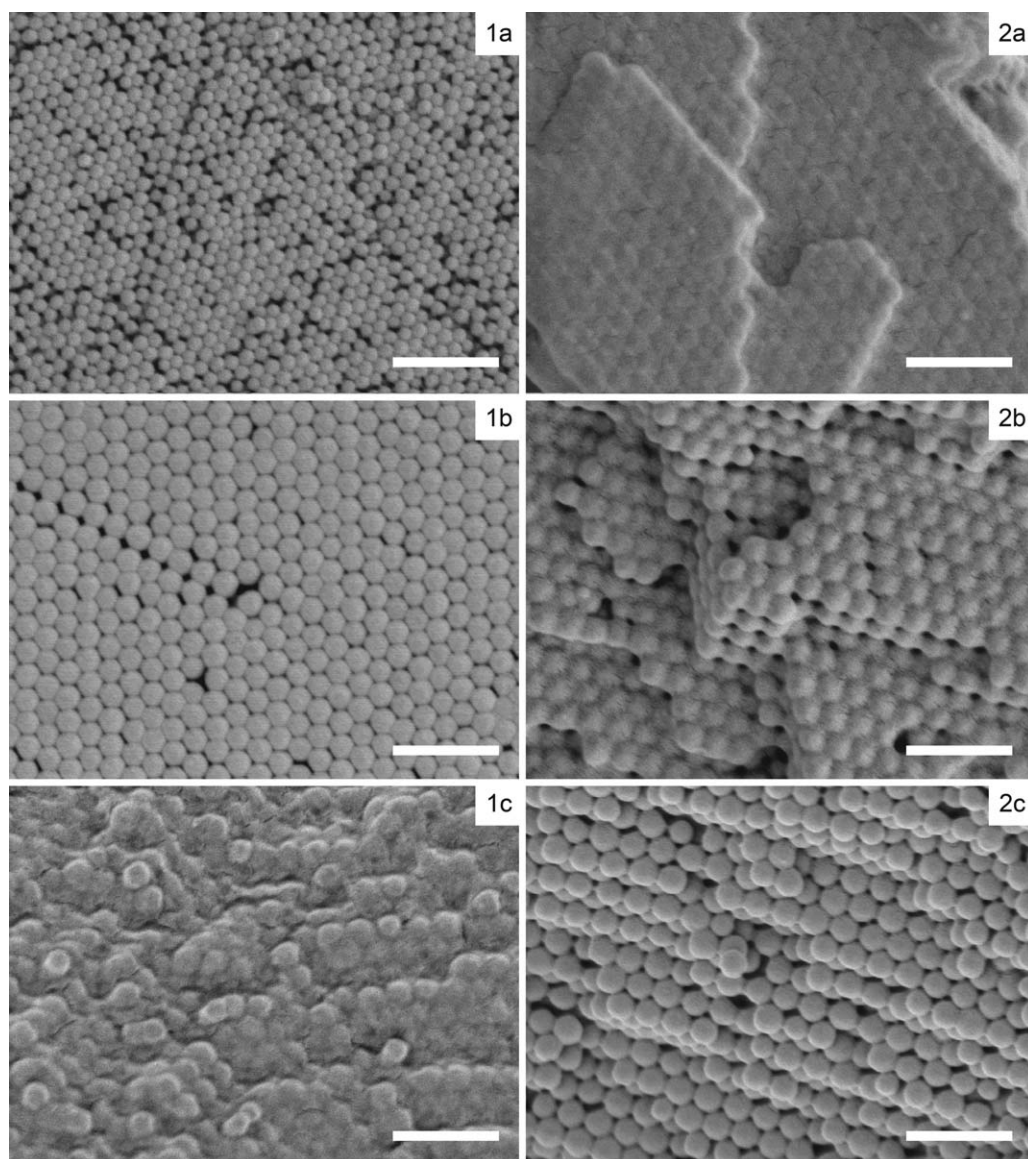^{a} Surface of particles are obscure or nonexistent.

Figure 2. SEM images of the morphological stability of copolymer spheres during the synthesis. Samples of the statistical copolymerization (1) with different total conversions (a = 15%, b = 65%, c = 95%) and samples of the seeded copolymerization (2) with different second-stage copolymer conversions (a = 50%, b = 85%, c = 95%), respectively. The weight compositions of the feed were 50%/50% (BA/MMA). Each scale bar represents 500 nm.

monomodal molar mass distribution (Supporting Information Figure S3). During the synthesis, the molar mass of the product increased and the distribution of molar mass was observed to get broader. The bimodal signal appeared after the total conversion was 80%. The intensity of the high molar mass signal was increasing as the reaction went on.

In the seeded copolymerizations, pure PBA was formed during the first 75 min, and the bimodal signal was observable, like in the homopolymer PBA case (Supporting Information Figure S4). After addition of MMA, the intensity of the lower molar mass signal was increasing, and the relative intensity of the higher molar mass signal started to decrease. Moreover, the higher molar mass signal was not shifting like in the PBA case. The molar mass distributions of the seeded and statistical copolymers with weight composition 50%/50% (BA/MMA) and

PBA in Figure 3 show that the seeded copolymer affords the narrowest molar mass distribution when compared with the statistical polymer or PBA homopolymer.

Changes in the Glass Transition Temperature During Synthesis

Glass transition temperatures (T_g) were measured during the copolymerizations. In the statistical cases, three different T_g signals were detected (Figure 4; Supporting Information Table SII). T_{g1} at a low temperature (Figure 4) was observed only when the conversion of polymerization was higher than 80%, whereas the T_{g2} and the T_{g3} were observable throughout the synthesis. The glass transition range of T_{g2} decreased (Supporting Information Table SIII) and become wider with the increasing polymerization time, whereas the glass transition ranges of T_{g1} and
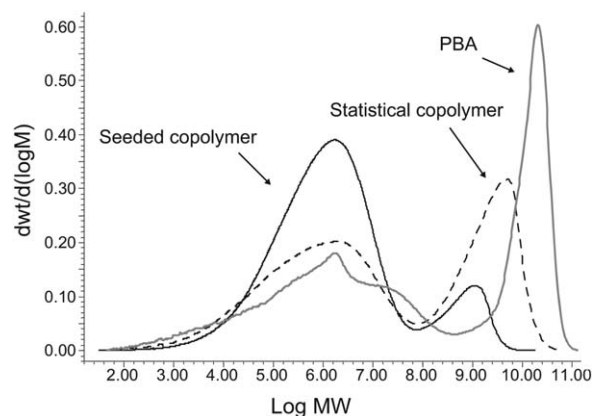
Figure 3. Molar mass distributions of BA/MMA copolymers and PBA. In the copolymer cases, the weight ratio of BA/MMA in the feed was 50%/50%.

T_{g3} stayed constant. An example of the T_{g2} drifting can be seen in Figure 4.

Products of the seeded copolymerization gave two different T_gs, which are more distinct than the T_g signals in the statistical case. The T_{g1} signal is the glass transition temperature of the
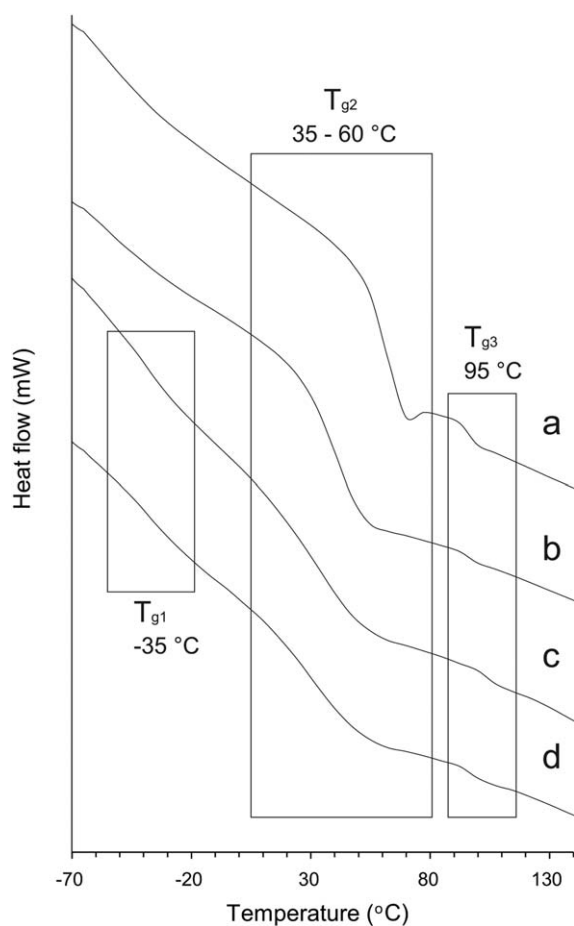

Figure 4. DSC results of a statistical copolymerization (the BA/MMA weight composition of the feed was 50%/50%) with different total conversions (a = 15%, b = 65%, c = 85%, d = 95%) and total BA/MMA compositions (a = 26%/74%, b = 34%/66%, c = 47%/53%, d = 51%/49%).
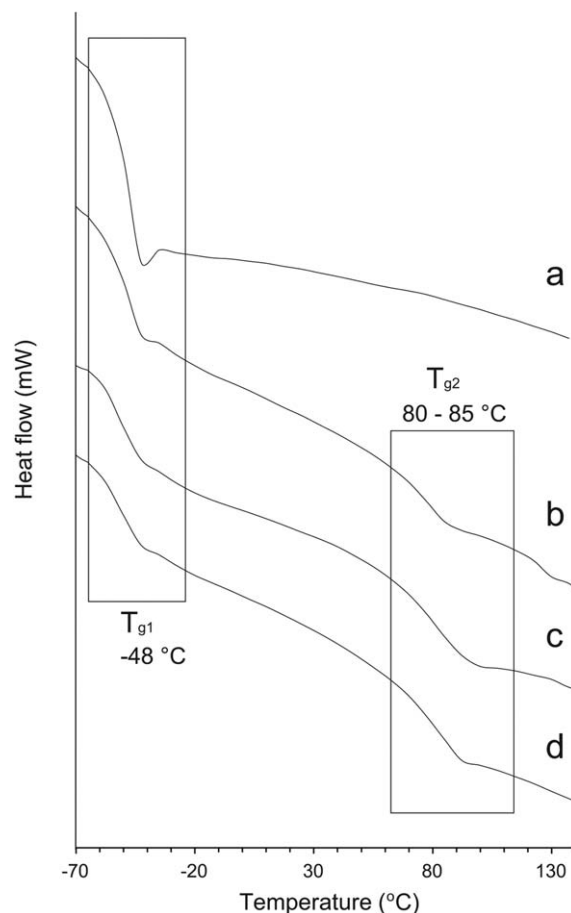

Figure 5. DSC results of a seeded copolymerization (the BA/MMA weight composition of the feed was 50%/50%) with different second-stage copolymer conversions (b = 50%, c = 85%, d = 95%) and the BA/MMA weight compositions of the second-stage copolymer (b = 24%/76%, c = 23%/77%, d = 23%/77%). Curve (a) is the DSC profile of the seed polymer (PBA).

seeds and is the same as T_g of pure PBA, and it stayed the same during the synthesis. On the contrary, the T_{g2} appears after addition of MMA and its glass transition range changes slightly, which can be seen in Figure 5 and Supporting Information Table SIII. A similar signal like T_{g3} in the statistical cases was not detected.

Copolymers with several glass transition signals well apart indicate a presence of separate, thermally stable phases with different monomer compositions.[25] The composition of these phases can be estimated with Gordon-Taylor equation (see section S4.1 in Supporting Information).[5] In the statistical copolymerization cases, the T_{g1} and T_{g3} signals are the glass transition temperatures of BA-rich and MMA-rich phases, respectively (Supporting Information Table SIV). Because of the high reactivity ratio of MMA with BA,[20–23] MMA-rich phases are formed in the beginning of the synthesis illustrated by T_{g3}. The T_{g2} signal corresponds to the glass transition of the main product possessing a composition close to the theoretical weight ratio of the monomers in the feed. When the amount of MMA is depleted, more BA monomers are added in the polymer chain and the total BA content increases and that changes the composition of the
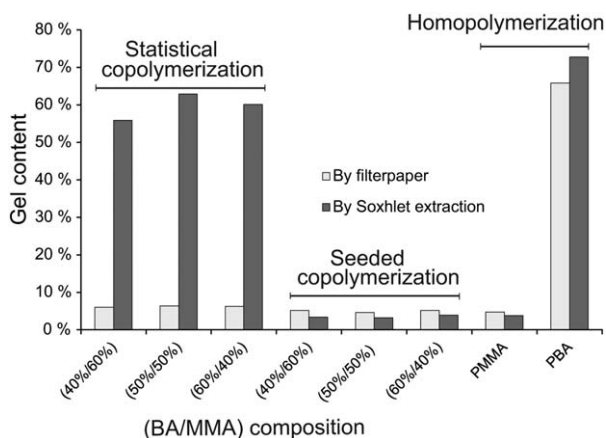
Figure 6. Gel contents of copolymers and homopolymers in the end of the syntheses.

copolymer during the synthesis. The temperature range of T_{g2} was observed to shift to lower temperatures and to become wider with the increased BA fraction in the copolymer.

The low temperature T_{g1} signal appeared when the conversion of the statistical copolymerization was more than 80% and the number of free monomers was limited causing a starved condition. Simultaneously, the bimodal molar mass distribution appeared, and the particle morphology, stable up to this point, disappeared. The value of T_{g1} is close to the glass transition temperature of pure PBA, indicating that this polymerization stage produces BA-rich polymer sequences with an increasing tendency for the termination by combination. Polymer chains with a high molar mass are formed by combination. In this way, the statistical copolymerization of BA/MMA can produce emulsion particles containing thermally separate phases and possessing a soft BA-rich exterior as observed in the SEM analysis (Figure 2).

Two different glass transitions observed in the seeded copolymerization cases correspond to two separate phases. The phases formed are the PBA seed (core) and the second-stage copolymer (shell). A similar signal like T_{g3} in the statistical cases was not detected agreeing with the SEM results. According to the DSC results, addition of MMA did not cause new nucleation and did not produce MMA-rich phases, but it gave a poly(MMA-co-BA) shell on seed particles. In the seeded copolymerizations, the molar mass distribution became bimodal already during the seed synthesis. On addition of MMA, the feed ratio of MMA increased, and it became more probable that the end group of reactive chains was MMA rather than BA. Addition of MMA reduces termination by combination and also diminishes formation of the high molar mass copolymers. So, this copolymerization process leads to particles having a rubbery soft core and a glassy hard shell and possessing a stable particle morphology as indicated by the SEM images in Figure 2.

Gel Content and Backbiting Content of the End Product

In our study, when using a solvent extraction with the filter paper method, the gel contents of the final products were almost the same for all copolymers (4–7 wt %) except for PBA, as shown in Figure 6. A Soxhlet extraction method was also used for determination of the gel content because the extraction

thimbles have smaller pores. In statistical copolymerization case, the Soxhlet extraction gave higher gel contents (55–65 wt %) compared with paper filtration probably due to the different size exclusion (pore sizes of the thimble and filter paper are 6–10 μm and 16 μm, respectively). However, the gel content results of the seeded copolymerizations were the same, regardless of the determination method used. The results of gel contents are supported by GPC results, which indicated that the molar mass decreased of pure PBA, statistical and seeded copolymers (Figure 3).

Determination of the branching and the backbiting levels of the polymers presented in Table III was performed on the basis of ^{13}C-NMR results (see section S6 in Supporting Information). For copolymers, only the backbiting content could be determined. However, the backbiting content provides a semi-quantitative information about the branching content, because backbiting (Supporting Information Scheme S1) is the predominant mechanism in branching.[15,26]

The branching and backbiting contents are at high level in the PBA case. Both copolymerization processes produced copolymers with the similar backbiting contents, which were lower than in the pure PBA. The presence of MMA reduced slightly the backbiting level in all copolymer cases regardless of the polymerization process.

Even the both copolymerization processes produced copolymers with a similar backbiting content, only the statistical process produced gels. In the end part of statistical synthesis, the BA content of the remaining feed was high that enabled termination by combination and further the formation of the high MW copolymer. Branched chains and termination by combination favored formation of high molar mass products having high gel

Table III. Results of the Branching and the Backbiting Contents (mol %)

	Branching		Backbiting
	C_q[a]	$CH + CH_2$[b]	End BA[c]
PBA	2.8%	3.2%	3.3%
Statistical 60%/40% (BA/MMA)			2.1%
Statistical 50%/50% (BA/MMA)			1.9%
Statistical 40%/60% (BA/MMA)			1.8%
Seeded 60%/40% (BA/MMA)			2.1%
Seeded 50%/50% (BA/MMA)			2.2%
Seeded 40%/60% (BA/MMA)			1.7%

[a] Branching content evaluated with the quaternary carbon, $\delta_{Cq} = 49.0$ ppm.
[b] Branching content evaluated with the carbons adjacent to quaternary carbon, $\delta_{Cq + CH} = 40.2$ ppm; $\delta_{Cq + CH2} = 38.8$ ppm.
[c] Backbiting content evaluated with the $CH_2\underline{CH_2}COOBu$ end group, $\delta_{End BA} = 31.9$ ppm.
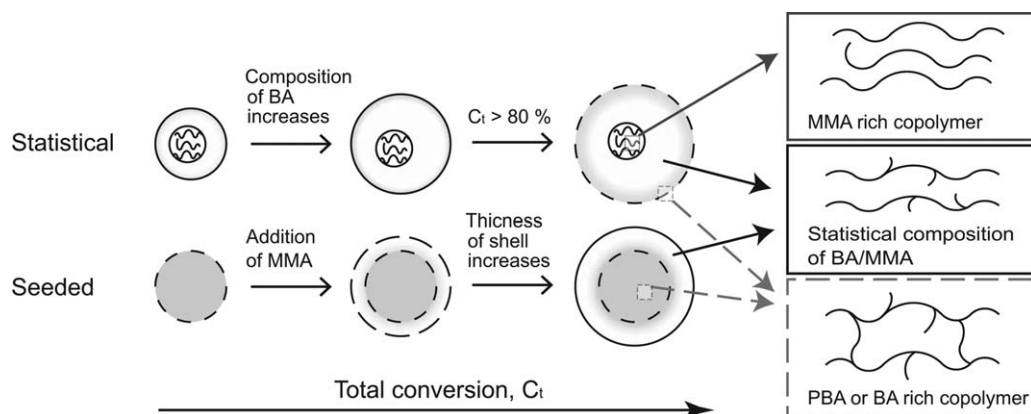
Scheme 1. Evolution of the morphology of copolymer particles during the synthesis in the seeded and statistical copolymerizations. Dashed and solid lines correspond to unstable and stable particles, respectively.

contents. This is further supported by GPC results, which show that the statistical copolymerizations produced higher MW products compared with the seeded copolymerizations. In addition, the SEM imaging and DSC measurements support this conclusion. In the seeded copolymerization, the free MMA monomer content was high at the final stage of the synthesis and termination by disproportionation was favored. This reduced the possibility for formation of a high molar mass copolymer and hence decreased the gel content, even though the polymer was as branched as the statistical copolymers.

Proposed mechanisms for development of the morphology of copolymer particles during the synthesis are shown in Scheme 1 for the seeded and statistical copolymerizations. In the statistical copolymerization case, the particles contain two separate domains in the beginning of the synthesis (a MMA-rich phase and a phase with a statistical composition of BA/MMA), because of the high reactivity ratio of the two monomers. As the conversion increases, the particles are growing and the weight ratio of BA in copolymers and the amount of branched copolymer chains increase. As the total conversion is more than 80%, BA-rich copolymers under the starved conditions are formed. The high BA content causes the increases in the molar mass and the gel content of copolymers and induces obscure particle interfaces. In the seeded copolymerization case, the seeds were formed from a PBA homopolymer possessing a high molar mass and branched polymer chains. After addition of MMA, a shell of mostly PMMA was formed decreasing the possibility of termination by combination. The stability of the particles was observed to increase with the MMA/BA weight ratio of the shell/core.

CONCLUSIONS

MMA/BA copolymers produced with different monomer compositions and synthesis processes were investigated. The phase structures, molar mass distributions, and morphologies of copolymers changed during the synthesis. The statistical and seeded copolymerizations gave copolymers with three and two separate phases having different compositions, respectively. The composition of the phases was evaluated on the basis of their glass transition temperatures obtained with DSC.

The molar mass distribution during the synthesis of statistical copolymers changed clearly at the end of synthesis. Because of the starved condition and high BA content in feed, the termination by combination was favored and bimodal molar mass distribution was observed. Combination of branched chains led to the high gel content. However, in the seeded copolymerization case, when the content of MMA monomer in the feed was high in the final stage of synthesis, lower yields of combination products and reduced gel contents were observed.

The composition and phase structure together with the molar mass distribution affect the morphology of emulsion copolymer particles. The particle morphology of the statistical copolymer at room temperature vanished when the BA content of copolymers increased. This was due to the continuous change in the composition of copolymer particles from MMA-rich to BA-rich that led to particles with a soft outer interface. However, in the seeded copolymerization cases, when the thickness of MMA-co-BA shell formed on PBA seed was large enough, the particle morphology was stable at room temperature. Our results show that the final application properties can be controlled with the copolymerization process and the monomer composition.

REFERENCES

1. Urban, D.; Takamura, K. Polymer Dispersions and Their Industrial Applications; Wiley-VCH: **2002**; Chapter 4–15.

2. EI-Aasser, M. S.; Tang, J.; Wang, X.; Daniels, E. S.; Dimonie, V. L.; Sudol, E. D. *J. Coating. Technol.* **2001**, *73*, 51.

3. Lili, Q.; Dubé, M. A. *Eur. Polym. J.* **2010**, *46*, 1225.

4. Chauvet, J.; Asua, J. M.; Leiza, J. R. *Polymer* **2005**, *46*, 9555.

5. Penzel, E.; Riegel, J.; Schneider, H. A. *Polymer* **1997**, *38*, 325.

6. Grunlan, J. C.; Ma, Y.; Grunlan, M. A.; Gerberich, W. W.; Francis, L. F. *Polymer* **2001**, *42*, 6913.

7. Zhao, C. L.; Roser, J.; Heckmann, W.; Zosel, A.; Wistuba, E. *Prog. Org. Coat.* **1999**, *35*, 265.

8. Hassan, A.; Haworth, B. *J. Mater. Process. Tech.* **2006**, *172*, 341.

9. Wu, G.; Zhao, J.; Shi, H.; Zhang, H. *Eur. Polym. J.* **2004**, *40*, 2451.

10. Xu, H.; Wang, N.; Qu, T.; Yang, J.; Yao, Y.; Qu, X.; Lovell, P. A. *J. Appl. Polym. Sci.* **2011**, *123*, 1068.

11. Urban, D.; Takamura, K. Polymer Dispersions and Their Industrial Applications; Wiley-VCH: **2002**; Chapter *2*.

12. Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. *Macromolecules* **2000**, *33*, 4.

13. Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. *Macromolecules* **2000**, *33*, 5041.

14. Sayer, C.; Lima, E. L.; Pinto, J. C.; Arzamendi, G.; Asua, J. M. *J. Polym. Sci. Pol. Chem.* **2000**, *38*, 1100.

15. González, I.; Asua, J. M.; Leiza, J. R. *Polymer* **2007**, *48*, 2542.

16. Silvestri, D.; Gagliardi, M.; Cristallini, C.; Barbani, N.; Giusti, P. *Polym. Bull.* **2009**, *63*, 423.

17. Tamai, T.; Pinenq, P.; Winnik, M. A. *Macromolecules* **1999**, *32*, 6102.

18. Elizalde, O.; Arzamendi, G.; Leiza, J. R.; Asua, J. M. *Ind. Eng. Chem. Res.* **2004**, *43*, 7401.

19. de la Fuente, J. L.; Fernández-Garsía, M.; Fernández-Sanz, M.; Madruga, E. L. *Macromolecules* **2001**, *34*, 5833.

20. Carraher, C. E. Jr. Seymour/Carraher's Polymer Chemistry: An Introduction; Marcel Dekker: New York, **1996**; Chapter 10.

21. Hutchinson, R. A.; McMinn, J. H.; Paquet, D. A. Jr.; Beuermann, S.; Jackson, C. *Ind. Eng. Chem. Res.* **1997**, *36*, 1103.

22. Dubé, M. A.; Penlidis, A. *Polymer* **1995**, *36*, 587.

23. Lowell, P. A.; El-Aasser, M. S. Emulsion Polymerization and Emulsion Polymers; Wiley: New York, **1997**; Chapter 1.

24. Brar, A. S.; Kaur, S. *J. Polym. Sci. Pol. Chem.* **2005**, *43*, 1100.

25. Yu, H.; Peng, J.; Zhai, M.; Li, J.; Wei, G.; Qiao, J. *Radiat. Phys. Chem.* **2007**, *76*, 1746.

26. Britton, D. J.; Lovell, P. A.; Heatley, F.; Venkatesh, R. *Macromol. Symp.* **2001**, *175*, 95.