Miniemulsion Copolymerization of *n*-Butyl Methacrylate with Crosslinking Monomers

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ABSTRACT: Miniemulsion copolymerization of *n*-butyl methacrylate and crosslinking monomers such as a macromonomer crosslinker (Mac), ethylene glycol dimethacrylate (EGDMA), or an aliphatic urethane acrylate macromonomer (AUA) was utilized to obtain crosslinked latex particles. The crosslinking monomers were added at 0.2 mol %, on the basis of the amount of *n*-butyl methacrylate utilized in a polymerization. The development of the gel content during the copolymerization reaction differs depending on the type of the crosslinking monomer. In addition to the crosslinking reactions between the *n*-butyl methacrylate and the crosslinking monomers, other kinetic events, such as microphase separation, may have occurred, giving rise to different particle morphologies, dependent on the type of initiator used (i.e., oil-soluble or water-soluble). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1721–1730, 2001

INTRODUCTION

A variety of possible copolymer microstructures such as statistical, random, alternating, periodic, block, graft, star, crosslinked, and interpenetrating copolymers[1–3] may be obtained by combining more than one type of monomeric unit. The copolymerization process allows for a great deal of synthetic flexibility in the alteration of the final copolymer properties. In many instances, it is desirable for the copolymer to be crosslinked; crosslinked copolymers typically exhibit good mechanical strength and integrity and offer good chemical resistance. Copolymers may be synthesized by step condensation or radical chain polymerization processes. For the radical chain copolymerizations, the preparation of the copolymers can be carried out by homogeneous polymerization, for example, by bulk and solution copolymerization, or by heterogeneous copolymerization processes, such as emulsion, dispersion, or suspension copolymerizations.

Three different categories of emulsion polymerization processes exist[4]: macroemulsion (i.e., conventional emulsion polymerization), microemulsion, and miniemulsion, which differ in terms of their formulation, kinetic, and mechanistic details. The resulting copolymer latexes that result from these different processes represent dispersions of polymer particles in water. Macroemulsion droplets are unstable and typically range in size from 1 to 100 μm; the final latex particle size is usually in the submicron size range. The use of the miniemulsion technique gives both droplet and latex particles in a size range from 50 to 500 nm, with much better emulsion droplet stability compared to macroemulsions. Microemulsions, on the other hand, have the highest stabilities (i.e.,
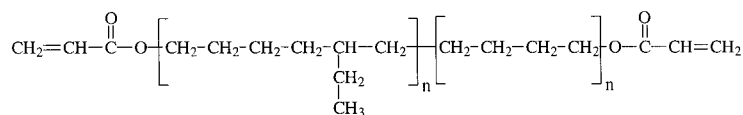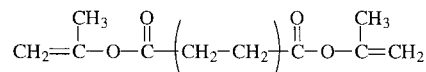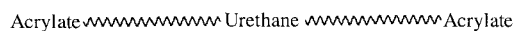
Macromonomer Crosslinker (M_n = 3480 g/mol; M_w = 4000 g/mol; PDI = 1.1-1.2, n~ 21)

Ethylene Glycol Dimethacrylate (M_n = 198 g/mol)

Acrylate wwwwwwwwww Urethane wwwwwwwwww Acrylate

Aliphatic Urethane Acrylate (exact structure is not known; M_n = 3728 g/mol; M_w = 6300 g/mol; PDI = 1.7)

Figure 1   Chemical structures of the crosslinking comonomers used in the synthesis of the *n*-butyl methacrylate copolymers.

they are thermodynamically stable) and result in the formation of latex particles with very small particle sizes of 10–50 nm.

This article describes the preparation of latexes by the miniemulsion copolymerization of *n*-butyl methacrylate (*n*-BMA) with three different types of crosslinking comonomers, [i.e., a novel macromonomer crosslinker (Mac), ethylene glycol dimethacrylate (EGDMA), or an aliphatic urethane acrylate (AUA) comonomer]. The primary reason for employing the miniemulsion approach was the very low water solubility of some of the crosslinkers employed in the synthesis. Miniemulsion polymerization is an ideal approach for the preparation of such copolymers because the droplet sizes are small enough to be the principal loci of copolymerization. Because the water solubility for some of the crosslinkers used is limited, and therefore diffusion of this comonomer through the aqueous phase during copolymerization would be highly restricted, copolymerization must occur at the sites where the crosslinkers are found.

EXPERIMENTAL

Materials

n-BMA and EGDMA (both obtained from Aldrich, Milwaukee, WI) were purified to remove residual inhibitor prior to copolymerization using an inhibitor-removal column (Aldrich). The monomers were passed through these columns twice according to the manufacturer's recommendations. The AUA (Sartomer, West Chester, PA) was purified in a column packed with De-hibit-100 macrorecticular ion exchange resin (Polysciences, Inc., Warrington, PA). The resin was first washed with 10 wt % aqueous sodium chloride solution (minimum volume equal to 4 times the volume of the column) to remove any residual amine which might be present in the resin. The column containing the resin was then washed with 600 mL of deionized water. Methanol (2.5 times the volume of the resin in the column) was then passed through the column for 1 h. The AUA was first diluted fourfold with toluene and then passed through the column. Evaporation of the toluene in the AUA was carried out by placing the mixture in a shallow pan with a large surface area in a vacuum oven at room temperature until attaining a constant weight. The synthesis, purification, and characterization of the Mac macromonomer crosslinker is described elsewhere.[5–6] The chemical structures of all three crosslinkers are shown in Figure 1. The initiators, either water-soluble potassium persulfate (KPS; Aldrich) or oil-soluble 2,2′-azobis(2-methylbutyronitrile) (AMBN; DuPont, Wilmington, DE), were used as received. The surfactant, sodium lauryl sulfate (SLS; J. T. Baker, Phillipsburg, NJ), and costabilizer, hexadecane (HD; Aldrich), were used as received. Deionized (DI) water was used in all experiments.

Table I   Recipe Used for the Preparation of the *n*-Butyl Methacrylate Copolymer Latexes with the Three Crosslinking Monomers

Component	Amount (g)
Macromonomer crosslinker (Mac) or	2.00
Ethylene glycol dimethacrylate (EGDMA) or	0.14
Aliphatic urethane acrylate (AUA)	2.15
n-Butyl methacrylate (*n*-BMA)	38.0
Hexadecane (HD)	1.81 (50 m*M*, based on aqueous phase)
2,2′-Azobis(2-methylbutyronitrile) (AMBN)[a] or	0.04
Potassium persulfate (KPS)[b]	
Sodium lauryl sulfate (SLS)	1.18 (12 m*M*, based on aqueous phase)
Deionized water	160.0

[a] 5 m*M* on oil phase.
[b] 1 m*M* on aqueous phase.

Preparation of Miniemulsions

Miniemulsions were prepared from *n*-BMA with the Mac, EGDMA, or AUA. The crosslinkers were used at a ratio of 1 : 500 crosslinker/*n*-BMA (~ 0.2 mol % crosslinking comonomer). The recipe used for the preparation of the miniemulsions is given in Table I. HD was used as the costabilizer. An oil phase consisting of a mixture of the monomers (*n*-BMA with Mac, EGDMA, or AUA), HD, and the oil-soluble AMBN initiator was first prepared by stirring the reaction components for 30 min using a magnetic bar. The mixture was kept covered and chilled in an ice bath. A separate aqueous phase consisting of DI water and SLS was also prepared and stirred with a magnetic bar for 15 min. The aqueous phase was then slowly added into the oil phase and the mixture was stirred with a magnetic bar for 30 min (keeping the mixture chilled in an ice bath) to give the crude emulsion. The crude emulsion was then sonified for 3 min using a Branson Sonifier (Model 450; Branson Ultrasonics) in a pulsed mode with a 50% duty cycle and a power level of 7. In the case where the water-soluble KPS initiator was used, the initiator solution was added to the miniemulsion and further stirred using a magnetic bar for 15 min. It should be noted that the miniemulsion was kept chilled in an ice bath during the sonification process to minimize any heating of the miniemulsion that could occur during the sonification process.

Miniemulsion Latex Synthesis

The resulting miniemulsion was then transferred to bottles of appropriate sizes (e.g., 8 oz). Each bottle was purged with nitrogen gas and the bottles were then sealed. The bottles were placed in a thermostated bottle polymerization unit where the bottles were tumbled end-over-end at 70°C for different lengths of time.

Determination of Gel Content

Latex samples were withdrawn from the bottles immersed in the bottle polymerizer unit for different intervals of time and the gel content was determined for each latex as follows. Approximately 0.5 g of the latex was added to 25 g of tetrahydrofuran (THF; VWR Scientific, Bridgeport, NJ). The mixture was placed in a bottle, which was equipped with a magnetic stir bar. The latex particles were swollen in THF for a minimum of 24 h. The mixture was then placed in a preweighed centrifuge tube and then centrifuged (using a Beckman L8M ultracentrifuge) at 37,000 rpm for 1.5 h at 5°C. The supernatant soluble fraction of the sample is thus separated from the gel fraction. The gel content is expressed on the amount of polymer present in the sample. Determination of the gel content directly from the latex particles reflects the extent of crosslinking achieved within the latex particles themselves, which should provide a more accurate picture of the state of crosslinking as compared to the determination of gel content from a latex film. Nonhomogeneous swelling may occur in the film; for example, further crosslinking may occur during film formation, resulting in inaccurate gel content values.

### Determination of Latex Particle Size and Particle Size Distribution

Particle size and size distributions were determined using several different techniques [i.e., by electron microscopy and by dynamic light scattering (DLS)]. A Philips 400 transmission electron microscope (TEM) was used to examine the latex particle morphology and also to determine the particle size. Two DLS instruments were utilized to determine the particle size: Nicomp Submicron Particle Sizer (Model 370, Nicomp Particle Sizing Systems) and the Brookhaven Photon Correlation Spectroscopy B12030 AT Digital Correlator equipped with an argon ion laser of 488-nm wavelength. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Effect of the Type of Initiator on the Development of Gel Content as a Function of *n*-Butyl Methacrylate Conversion

Oil-Soluble Initiator (5 mM AMBN)

Stable miniemulsions and latexes were obtained with all three systems [i.e., P(BMA-*co*-Mac), P(BMA-*co*-EGDMA), and P(BMA-*co*-AUA)], prepared using either AMBN or KPS initiators. The development of gel content as a function of *n*-BMA conversion for these three copolymer systems prepared using the oil-soluble initiator, AMBN, is shown in Figure 2. The rates of gel development were found to differ between the three copolymers. Faster rates of gel formation
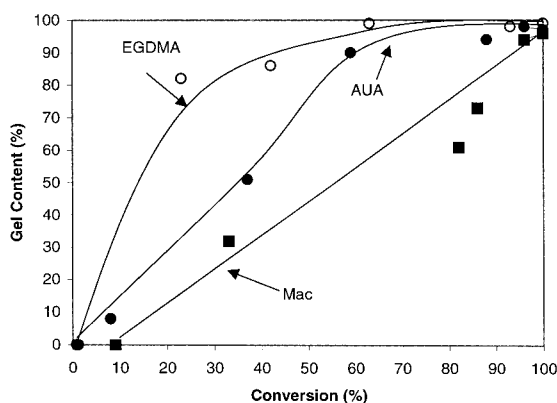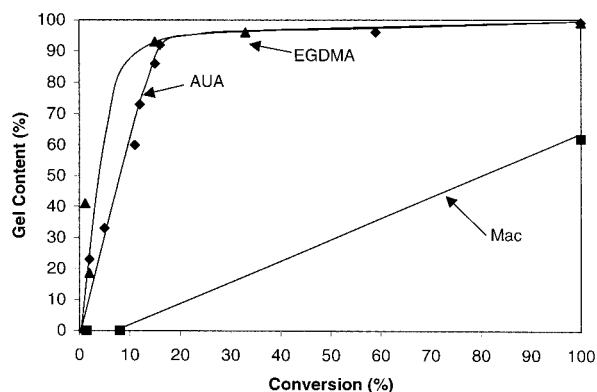

Figure 2 Development of the gel content as a function of *n*-BMA conversion for copolymers (Mac, EGDMA, or AUA) prepared using 5 mM AMBN initiator.

were observed for the copolymers crosslinked with EGDMA and AUA compared with Mac; the latex prepared by copolymerizing *n*-BMA with EGDMA exhibited the fastest rate of gel formation. For all three crosslinkers, the ultimate gel content (at full polymer conversion) was very high (> 95%). For the P(BMA-*co*-Mac) copolymer latex system, unlike the other copolymer systems, approximately 10% of linear polymer was formed before any appreciable gel content was obtained. The formation of the linear polymer was then followed by a progressive and steady increase in the gel content until the end of the copolymerization when *n*-BMA was fully converted (100%) after 4–5 h of reaction. However, in the case of EGDMA and AUA, the gel content was significant from the beginning of the copolymerization reaction; high gel content (> 95%) was obtained when a significant fraction of the *n*-BMA monomer remained unreacted (~ 45% *n*-BMA was unreacted for the EGDMA system, whereas ~ 35% *n*-BMA was not yet reacted at this gel content for the AUA system). In copolymerization reactions, compositional drifts are inevitable,[2] and the more reactive monomer can be consumed earlier in the reaction, leaving the copolymer richer in the slower reacting monomer at the end of the reaction. Detection of the residual amount of crosslinker proved to be difficult; powerful tools such as infrared spectroscopy or nuclear magnetic resonance spectroscopy cannot detect the presence of the crosslinker at 0.2 mol %; hence, it was not possible to determine the amount of crosslinker that was reacted during the course of the reaction.[5] For the Mac and AUA, the amount of converted *n*-BMA can be easily determined from gravimetric analysis. The determination of the conversion of *n*-BMA in the copolymerization with EGDMA may include the amount of EGDMA; however, this amount is very small on a weight basis (0.3 wt %) (i.e., within the experimental error); hence, it is assumed to be negligible compared to the increase in the gel content. However, the high gel content obtained for all three copolymer systems is an indication that most of the monomers used were incorporated during the copolymerization reaction, and this in turn indicates that the miniemulsion technique can be successfully applied to obtain high copolymer yields for highly water-insoluble monomers such as Mac and AUA.

The reactivity ratios of *n*-BMA and Mac were previously estimated.[5] Solution polymerizations (in toluene), initiated with 0.5 wt % 2,2′-azobis-

(isobutyronitrile) (AIBN), for 1 h were carried out; r_1 (*n*-BMA) was found to be ~ 13 and r_2 (Mac) was ~ 0.1, as calculated using the reduced copolymerization equation which was first developed by Jaacks.[7] These values suggest highly nonequivalent reactivities of the *n*-BMA and the Mac monomers. The propagating PBMA chain prefers reacting with its own BMA monomer before it reacts with a Mac molecule. Thus, the development of the gel content in the *n*-BMA and Mac miniemulsion copolymerization reaction may be explained by the differences in the reactivity ratios between the two species. The high gel content for this system implies that the Mac chains did participate in the copolymerization; because the initiator is oil-soluble, the likelihood of the Mac chain bearing the radical appears to be likely. Differences may exist in the copolymerization kinetics of these monomers between the solution and miniemulsion polymerization systems; a preferential location of the macromonomer may also play a significant role in the kinetics and on the resulting microstructure. In the miniemulsion copolymer system, because Mac is highly water-insoluble, more of the *n*-BMA may be found on the surface of the miniemulsion droplets and particles and the Mac may be located within the core of the droplets and in the resulting particles. The Mac chains may orientate and adopt conformations where the less hydrophobic portion (which is actually the reactive group bearing the vinyl groups) is closer to the particle surface. This postulation was put forth from the experimental data gathered from the homopolymerization of Mac when water- (KPS) and oil-soluble (AIBN) initiators were compared.[6] It was found that the homopolymerization of Mac using water-soluble initiator was very rapid (< 1 h at 70°C) compared to the homopolymerization carried out using the oil-soluble initiator (> 12 h at 70°C).

The high gel content obtained (almost 100%) for the P(BMA-*co*-EGDMA) and P(BMA-*co*-AUA) copolymers when there was still some unreacted *n*-BMA present may contribute to variations in the polymer chain microstructure and the particle morphology. At this point, there may be fewer crosslinked chains present or none at all, which means that when the rest of the *n*-BMA became reacted, the polymer chains that were formed were more linear or lightly crosslinked, although they are attached to the existing network. For all of the systems, a nonuniform extent of crosslinking may also be possible within the particles (i.e., different particles may have different extents of

Figure 3 Development of gel content as a function of *n*-BMA conversion for copolymers (Mac, EGDMA, or AUA) prepared using 1 mM KPS initiator.

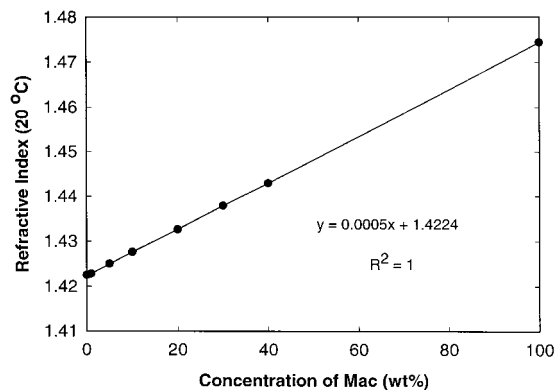crosslinking). It should be noted that the gel content for the homopolymer PBMA latex particles was < 5%.

Water-Soluble Initiator (1 mM KPS)

Figure 3 shows the development of gel content as a function of the *n*-BMA conversion for copolymers prepared using the KPS water-soluble initiator. The gel content development profiles for these copolymer systems are similar to those obtained when the copolymers were prepared using the oil-soluble initiator; however, there were some significant differences. In the case of P(BMA-*co*-Mac), although the observed trend in gel formation was similar whether water- or oil-soluble initiators were used (i.e., some linear polymer had formed before the gel content became appreciable followed by crosslink formation); the final amount of gel formed only reached 60% in the case where the water-soluble initiator was used, in contrast to 100% gel formation when the oil-soluble initiator was used. The conversion of *n*-BMA after the initial formation of linear polymer to 100% conversion was very rapid. This observation may still be explained by the dramatic differences in the reactivity ratios of these two monomers (BMA and Mac); in addition, the site where the radicals were generated may also be crucial in influencing the copolymerization kinetics for these systems. In the case of the water-soluble initiator, the persulfate radicals were formed in the aqueous phase, presumably after reaching the j-critical mer length, the *n*-BMA oligoradical (*n*-BMA monomer has a water solubility[8] of 2.5×10^{-3} mol/dL; hence, a small amount of dissolved monomer may be present in

the aqueous phase) would selectively react at a much higher rate with n-BMA monomer compared to Mac. The location of the reactive endgroups of the Mac would appear to be equally important. If these endgroups were located further away in the core of the growing particles, they would react later in the polymerization. When $\sim$ 100% conversion of the n-BMA monomer was reached, only 60% gel was obtained. This may reflect the formation of an increased amount of n-BMA homopolymer, or else microphase separation within the particles had occurred such that $\sim$ 40% linear polymer was formed. Formation of linear polymer is possible because n-BMA does possess some water solubility and homogeneous nucleation could result. Microphase separation within the particles may also be possible. To test the possibility of microphase separation, a separate experiment was carried out in which a ternary mixture of PBMA, n-BMA, and Mac were mixed together in a vial. The PBMA used had a molecular weight of 2.5×10^5 g/mol. The amount of Mac in the ternary mixture was kept approximately constant at 5 wt %. When the concentration of PBMA was $>$ 10%, phase separation was clearly observed at room temperature and at 70°C. Table II shows the phase separation results for different combinations of ternary mixtures. As a control experiment, a binary mixture of n-BMA and Mac was prepared; they appeared to be completely miscible up to 40 wt % of Mac in the mixture as concluded from refractive index measurements (Abbe-Fischer Scientific refractometer) as shown in Figure 4. If all of the crosslinker chains added were in the crosslinked or gel fraction, then there were more crosslink points rela-
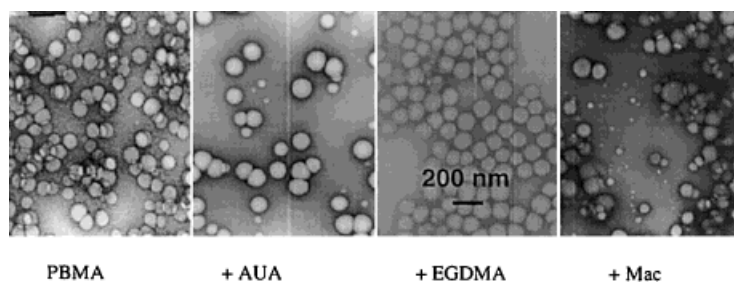

Figure 4 Measurement of the refractive indices of solutions of macromonomer crosslinker in n-BMA at various concentrations at 20°C. The data also include neat n-BMA (0% concentration of Mac) and neat macromonomer crosslinker (100% concentration of Mac).

tive to the n-BMA units in the case of the P(BMA-co-Mac) prepared with KPS (60% gel) compared with P(BMA-co-Mac) prepared with AMBN ($>$ 95% gel). It is equally likely that more of the crosslinker was not used up or that dangling ends of vinyl groups were present at the end of the copolymerization in the P(BMA-co-Mac) copolymer latex prepared with KPS initiator.

For the P(BMA-co-EGDMA) and P(BMA-co-AUA) copolymers prepared with KPS initiator, faster rates of gel development were obtained compared to the AMBN-initiated systems. For P(BMA-co-EGDMA), a high gel content was achieved when 70–80% of n-BMA remained unreacted and for P(BMA-co-AUA) some 40% of n-BMA was still available. Again, when these points were reached (i.e., at a very high gel content), the amount of crosslinker remaining unreacted is questionable. If most of the crosslinker had reacted at this point, then the rest of the PBMA units which had added onto the existing network were primarily linear and for both P(BMA-co-EGDMA) and P(BMA-co-AUA) copolymer latexes prepared using KPS, the ultimate gel contents were also $>$ 95%.

Particle Size and Size Distributions of PBMA Homopolymer and Copolymer Latexes Prepared with AMBN and KPS Initiators

Figure 5 shows the transmission electron micrographs of the n-BMA homopolymer latex as well as the three types of copolymer latex particles prepared with 5 mM AMBN initiator, whereas

Table II Effect of the Amount of PBMA on the Phase Separation of Ternary Mixtures of Macromonomer Crosslinker (Mac), n-BMA, and PBMA

PBMA (wt %)	Mac (wt %)	PBMA : Mac	Observations
0.4	5.3	0.08	Clear solution
1.2	4.9	0.24	Clear solution
4.5	5.5	0.82	Clear solution
5.4	5.1	1.06	Clear solution
10.6	5.2	2.04	Cloudy solution (also at 70°C)
13.3	5.3	2.50	Very cloudy
16.7	4.1	4.07	Phase separated mixture

Figure 5 Transmission electron micrographs of PBMA homopolymer and copolymer latexes prepared with different crosslinkers (AUA, EGDMA, and MAC) using 5 mM AMBN initiator.

Table III gives the particle size and the size distributions for the different latex particles.

The crosslinkers used vary in terms of their endgroups and molecular weight. Mac has a molecular weight of $\sim$ 3500 g/mol; EGDMA has a molecular weight of 198 g/mol, and AUA has a molecular weight of $\sim$ 3700 g/mol. Mac and AUA have similar endgroups and molecular weights; however, the polydispersity of the molecular chain distribution differs. Mac has a much narrower molecular weight polydispersity index (1.2) compared to AUA ($>$ 1.7). Comparison of the particle size distributions of the copolymer latexes show that when copolymers of *n*-BMA were prepared with longer molecular weight crosslinker, the particle size polydispersity index, PDI, increased dramatically. The PBMA homopolymer and the copolymer of *n*-BMA prepared with EGDMA exhibited a relatively narrower particle size distribution. The increase in the polydispersity of the copolymer latex particle size when the longer molecular weight crosslinkers were used (i.e., Mac and AUA) may be due to the ability of these molecules to confer additional stability to

the droplets against Ostwald ripening by retarding molecular diffusion of the monomer; thus, this may also preserve the number of droplets created during the formation of the miniemulsion.

Figure 6 shows the TEM micrographs of the homopolymer and copolymer latexes prepared with the three types of crosslinkers utilizing KPS as initiator; the corresponding details of the average particle size and particle size distributions are given in Table IV. Similar trends were observed as in the case of the AMBN-initiated system, except that the particle sizes of the latexes prepared with KPS were slightly smaller.

Comparison of Unswollen and Swollen Copolymer Latex Particles and Derivation of M_c

The average particle size and size distributions for both the swollen and the unswollen copolymer latexes prepared using 5 mM AMBN and 1 mM KPS initiators were also determined using the Brookhaven DLS instrument at room temperature. The unswollen weight-average diameters were determined in water. The particle size for

Table III   Particle Size and Size Distribution Data for PBMA Homopolymer and Copolymer Latexes Prepared Using 5 m*M* AMBN Initiator

Latexes	TEM			DLS		
	D_w (nm)	D_n (nm)	PDI	D_w (nm)	D_n (nm)	PDI
PBMA	166.0	156.0	1.06	169.0	138.0	1.20
P(BMA-*co*-Mac)	138.0	88.0	1.60	170.0	110.0	1.60
P(BMA-*co*-EGDMA)	175.0	168.0	1.04	199.0	171.0	1.20
P(BMA-*co*-AUA)	160.0	136.0	1.20	171.0	137.0	1.30

D_w = weight-average particle diameter; D_n = number-average particle diameter; PDI = polydispersity index ($=D_w/D_n$).
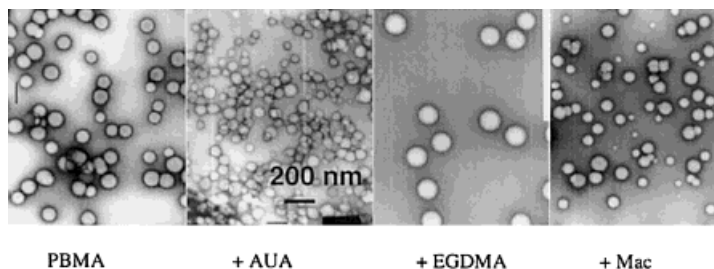
Figure 6 Transmission electron micrographs of PBMA homopolymer and copolymer latexes prepared with different crosslinkers (AUA, EGDMA, or Mac) using 1 mM KPS initiator.

the swollen latex particles were determined from latex samples which had been swollen in THF for 3 months. Approximately 0.5 g of latex was added to 25 g of THF. The swollen latex mixture was further diluted with THF (5 times more THF) when the particle size analysis was carried out. Table V shows the average unswollen radii (r_0) and swollen radii (r_s) of the particles and the derived M_c values for the different copolymers. The Flory–Rehners equation[9] was used for the derivation of M_c as follows:

$$-Hv^2\ln\left(1 - \frac{1}{Hv}\right) - Hv - \left(\frac{V_m\rho}{M_c}\right)\left(Hv^{5/3} - \frac{Hv}{2}\right)$$
$$= \chi + \left(\frac{2V_m\gamma}{RT}\right)\left(\frac{Hv^{5/3}}{r_0}\right) \quad (1)$$

where ρ is the density of polymer (copolymer) which was taken as 1.07 g/cm^3, V_m is the molar volume of solvent, H_v is the volume swelling ratio $= (r_s/r_0),^3$ and χ is the interaction parameter. γ is assumed to be very small because the amount of THF to water is large ($\sim$ 98%); hence, the term on the right-hand side reduces to only χ. The χ for

the polymer pairs were determined by estimating their solubility parameters (δ) from the Group Molar Attraction Constants.[10] The equations used to calculate the value of χ are

$$\delta = \frac{\rho \sum G}{M} \quad (2)$$

$$\chi = \frac{V_r(\delta_1 - \delta_2)}{RT} \quad (3)$$

where ρ is the density, δ is the solubility parameter, ΣG is the sum of the molar attraction constants, V_r is the molar volume of solvent, R is the gas constant, T is the temperature in Kelvin, and M is the molecular weight of the repeating mer.

The swelling data for the copolymer latexes show that the P(BMA-co-Mac) latex particles tend to swell more than the other copolymer latex particles. This behavior can be explained by the formation of a loosely crosslinked network or else the linear chains which exist at the particle surfaces are long. These chains become extended in the solvent (THF); hence, the hydrodynamic volume

Table IV   Particle Size and Size Distribution Data for PBMA Homopolymer and Copolymer Latexes Prepared Using 1 m*M* AMBN Initiator

	TEM			DLS		
Latexes	D_w (nm)	D_n (nm)	PDI	D_w (nm)	D_n (nm)	PDI
PBMA	142.0	134.0	1.06	150.0	133.0	1.10
P(BMA-co-Mac)	113.0	82.0	1.40	132.0	80.0	1.70
P(BMA-co-EGDMA)	168.0	160.0	1.05	172.0	150.0	1.20
P(BMA-co-AUA)	215.0	103.0	1.20	171.0	137.0	1.30

D_w = weight-average particle diameter; D_n = number-average particle diameter; PDI = polydispersity index ($=D_w/D_n$).

Table V   Unswollen (r_0) and Swollen (r_s) Radii of Copolymer Latex Particles, Volume Swelling Ratios, and Derived M_c Values

Latexes (10 h)	r_0 (nm)	r_s (nm)	$(r_s/r_0)^3$	M_c (g/mol)
5 mM AMBN				
PBMA + Mac	75	140	6.6	3275
PBMA + EGDMA	80	120	3.4	869
PBMA + AUA	69	100	2.9	—
1 mM KPS				
PBMA + Mac	47	115	14.7	13,823
PBMA + EGDMA	68	118	5.3	2178
PBMA + AUA	55	85	3.7	—

of the particles is increased. The volume swelling ratio $(r_s/r_0)^3$ of P(BMA-*co*-Mac) copolymer latex particles prepared with KPS initiator was higher than the ratio for the P(BMA-*co*-Mac) copolymer latex particles prepared with AMBN initiator. This implies that either longer linear PBMA chains are attached to a smaller crosslinked network or else the network is more heterogeneous (with higher concentrations of dangling vinyl groups), which resulted in a greater ability of the network to swell. For this copolymer, 40% of linear polymer was extractable, where the linear polymer was present either as separate particles of linear PBMA homopolymer or else was present within the existing particles due to microphase separation. Thus, the swelling values which were obtained may not just be a reflection of the swelling capacity of the network formed, but may also be due to the presence of linear chains which became extended out into the solvent.

P(BMA-*co*-AUA) copolymer latex particles exhibited the lowest degree of swelling, which suggested a tighter crosslinked network, whether the copolymer latex was prepared using AMBN or KPS initiator. On the other hand, the swelling behavior of the P(BMA-*co*-EGDMA) copolymer latex particles exhibited a more obvious dependence on the type of initiator employed. The P(BMA-*co*-EGDMA) copolymer latex prepared using KPS showed a greater ability to swell, similar to the case of P(BMA-*co*-Mac) latex prepared using AMBN. If the plots of gel content as a function of the *n*-BMA conversions are examined (Figs. 2 and 3), it can be seen that there was a higher rate of gel development for the KPS-initiated system. If there was a higher degree of crosslinking of poly-

mer chains at the particle surfaces, then the extent of swelling would be limited, even though there was more linear or lightly crosslinked PBMA chains present in the particle (i.e., the linear chains would be present within the particles, but may not contribute to the degree of swelling since this will be controlled by the presence of a crosslinked network closer to the particle surfaces). The fact that there was an observed higher degree of swelling for the P(BMA-*co*-EGDMA) copolymer latex particles prepared using KPS despite the more rapid formation of gel content may signify that there were more linear or lightly crosslinked PBMA chains present closer to the particle surfaces. A possible explanation for this is that microsyneresis[11] may occur, where the crosslinked network becomes the discrete phase and the linear PBMA chains become the continuous phase in the particle; hence, differences in particle morphology would be expected. This phase separation was induced by the formation of a large amount of gel ($> 95\%$) when the majority of the *n*-BMA remained unreacted. If the particle morphologies for the AMBN- and KPS-initiated systems are different, then differences in film properties may be expected. In general, the copolymer latexes prepared with AMBN initiator exhibited a lower degree of swelling compared to those latexes prepared with KPS. If swelling is primarily governed by the particle morphology, then the derivation of M_c for the copolymers is not accurate. Figure 7 shows a series of schematic representations of the possible proposed particle morphologies which could explain the observed swelling behavior.

The M_c value calculated for the P(BMA-*co*-Mac) copolymer latex was very high (see Table V), which would indicate that there were only a few crosslinked points and that there would be more linear PBMA units present between each crosslink. This in turn would imply that either the crosslinker was not effectively copolymerized or that the network that was formed was more heterogeneous, or, as previously mentioned, this might be a consequence of the presence of longer linear PBMA chains or lightly crosslinked network chains which affected the swelling measurements. The presence of any Mac macromonomer crosslinker cannot be determined in the extracted soluble fraction because it was below the limit of NMR detection (i.e., either all of the Mac chains were present in the gel phase or the amount of residual Mac chains was too small to be detected). However, the majority of the linear polymer frac-
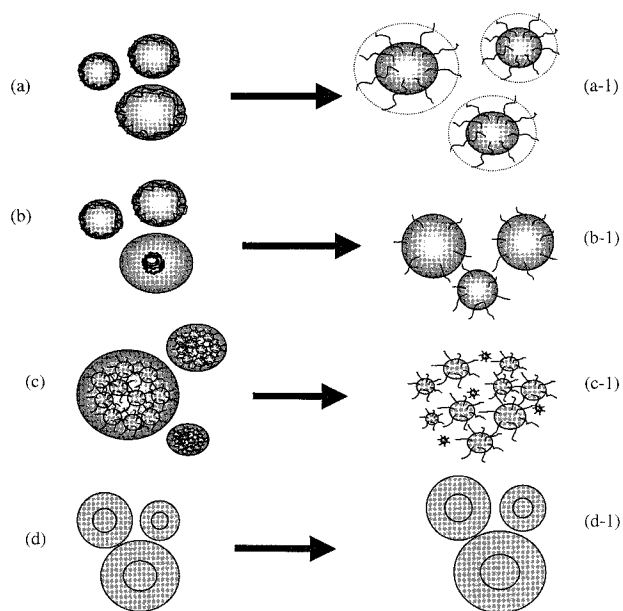
Figure 7 Schematic representation of unswollen (a, b, c, and d) and swollen (a-1, b-1, c-1, and d-1) particle morphologies: (a) represents particles with linear or lightly crosslinked polymer chains which reside closer to the particle surface and are connected to the crosslinked network. The corresponding swollen particle (a-1) represents a structure where the chains become extended out into the swollen medium, increasing the hydrodynamic volume and therefore reflecting an increase in swelling; (b) depicts a situation where linear polymer chains are not connected to the network chains; the linear polymer becomes dissolved when the particles are swollen; the swollen diameter largely reflects the swelling of the network; (c) particle morphology where microdomains exist within the particles; the particle size and size distribution before and after swelling can be completely different; and (d) is a morphology where the linear polymer has become microphase-separated, but is not able to diffuse through the network chains because the mesh size of the network is too small. The linear polymer might also exist in the form of discrete phases, surrounded by crosslinked regions.

tion must comprise PBMA homopolymer since the total amount of Mac used in a recipe was only 5 wt %. Contributions of linear PBMA homopolymer or lightly crosslinked polymer chains to the swelling values appear to be very likely and this would also be consistent with the P(BMA-*co*-EGDMA)

copolymer latex results. The properties of the films obtained from these copolymer latexes are expected to differ according to the different morphologies of the latex particles.

CONCLUSION

Copolymer latexes of *n*-BMA and three different crosslinkers [macromonomer crosslinker (Mac), ethylene glycol dimethacrylate (EGDMA), and aliphatic urethane acrylate (AUA)] with varying molecular weights were prepared. The gel development as a function of *n*-BMA conversion for these copolymer latexes was found to be dependent on the type of crosslinker and the type of initiator used. The particle size distributions of these copolymer latexes increased irrespective of the type of initiator that was used for the longer molecular weight crosslinkers. The swelling behavior of the copolymer latex particles suggested that the particle morphologies for the three types of copolymers were different.

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