

Properties of *n*-Butyl Methacrylate Copolymer Latex Films Derived from Crosslinked Latex Particles

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ABSTRACT: Films obtained from copolymer latexes of *n*-butyl methacrylate (BMA) with a series of crosslinking monomers [i.e., a macromonomer crosslinker (Mac), ethylene glycol dimethacrylate (EGDMA), and aliphatic urethane acrylate] exhibited differences in their tensile properties and swelling behaviors. For P(BMA-*co*-EGDMA) copolymer, a dependence on the initiator type was obtained. It is postulated that the network microstructures for the various copolymers evolved as the result of the copolymerization reactions between the monomer pairs during the synthesis in the miniemulsion free-radical copolymerization. These network microstructures are, therefore, hypothesized to influence the mechanical properties of the resultant films. Copolymers prepared with Mac were tough in comparison with copolymers made with EGDMA. The presence of longer linear or lightly crosslinked poly(*n*-butyl methacrylate) (PBMA) chains and the looseness of the crosslinked network structures in the PBMA-*co*-Mac copolymers appear to be the factors responsible for the differences. All of the copolymer films disintegrated into swollen individual microgels when they were immersed in tetrahydrofuran. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 42–49, 2003

Key words: crosslinking; films; latexes; mechanical properties

INTRODUCTION

Films formed from crosslinked latex particles often are not useful because such latexes are not able to form coherent films with good mechanical properties. The crosslinking process involves the linking of polymer chains to obtain a network; therefore, the dynamics of the chains that are connected in a network are different from those of linear polymer chains. The reptation of the interconnected chains (which are initially confined within the latex particles) across the latex particle boundaries during the film formation process is, therefore, reduced. Polymer chains are viscoelastic in nature, and crosslinking will increase the rigidity of the chains, which will retard their segmental motion. The development of appreciable cohesive strength in a latex polymer film is dictated by the ability of the interconnected polymer chains to participate in the interdiffusion process that occurs during annealing and in which polymer chain entanglements occur between polymer chains of neighboring latex particles. The reptation of linear polymer chains is facilitated in comparison with the crosslinked chains. When

crosslinking reactions take place within the latex particles, depending on the extent of crosslinking, the interdiffusion of the crosslinked chains has been shown to be greatly hindered,^{1–8} and this results in poor film formation. Failure to form a film becomes crucial when the molecular weight between crosslink points (M_c) is less than the molecular weight between chain entanglements (M_e). Other than the crosslinking process, the molecular weight of the polymer chains and their architecture may also affect reptation. Linear chains that interdiffuse by reptation are depicted by a snakelike motion of the chain in a tube, as first proposed by deGennes,⁹ whereas nonlinear chains such as star, branched, or cyclic polymer chains have greater difficulty in reptating. The reptation of these nonlinear chains is theorized to occur by an adoption in a change in entropy so that a branch will lie parallel to the main polymer chain in an adjacent tube, causing one end of the chain to move forward, thereby pulling the other end of the chain, as it translates in the same tube. The branch can also retract to renew its conformation by retracing its path along the confining tube to the center of the chain and then adopt a new conformation.^{10,11} For network or crosslinked polymer chains, reptation will be more difficult, especially when the network mesh is tight. Despite the network formation of polymer chains in crosslinked latex par-

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ticles, some mixing of the chains among the particles can take place; this is often attributed to the presence of dangling chains due to imperfections in the crosslinked network.¹²

The crosslinking of polymer chains can be initiated in many different ways,¹³ including free-radical polymerization involving crosslinking monomers. This article describes the physical and mechanical properties of films obtained from latexes prepared from the emulsion copolymerization of *n*-butyl methacrylate (BMA) monomer with crosslinking monomers of different types and molecular weights.

EXPERIMENTAL

Latex synthesis

Copolymer latexes of BMA with three different crosslinking monomers were prepared with the mini-emulsion technique.¹⁴ The crosslinkers were (1) a novel crosslinker called a macromonomer crosslinker (Mac; based on an ethylene-butylene diol with reactive acrylate end groups that was synthesized in our laboratories^{15,16}), (2) ethylene glycol dimethacrylate (EGDMA; Sigma-Aldrich, Milwaukee, WI), and (3) an aliphatic urethane acrylate macromonomer (AUA; Sartomer, Exton, PA). The crosslinkers were employed at 0.2 mol % (i.e., a molar ratio of 1:500 crosslinker/BMA). Also, for each crosslinker, there are two terminal reactive groups; therefore, 1 mol of crosslinker was expected to react with 2 mol of BMA. The type of initiator used, water-soluble (potassium persulfate) or oil-soluble [2,2'-azobis(methyl butyronitrile) (AMBN)], was also investigated. The details of the copolymerization, kinetics, and developments of the gel contents of the copolymers are given elsewhere.^{15,17} Mac and AUA had similar functional groups (two terminal acrylate groups) and also had comparable molecular weights (~3500 and ~3700 g/mol, respectively). However, their chain length distributions differed, with a narrower molecular weight distribution for Mac (1.2) than for AUA (>1.7). EGDMA, however, had a much lower molecular weight (198 g/mol) with two terminal methacrylate groups.

Preparation and testing of film specimens

The copolymer latexes were coagulated by subjection to several freeze-thaw cycles. The polymer was then isolated and washed thoroughly with water and then with methanol. The polymer flakes were initially dried at room temperature in a hood and then in a vacuum oven, also at room temperature, until a constant weight was attained. The dried polymer was then compression-molded with a Tetrahedron press at 120°C for 30 min under a pressure of approximately 2000 psi so that polymer films could be obtained. The

trimming of some of the compression-molded test samples was necessary; therefore, all of the compression-molded copolymer films or test pieces were first heated to 100°C for 5 min and then trimmed.

Type V microtensile specimens with the dimensions specified in ASTM D 638 were prepared by the compression molding of the films as previously detailed. The stress-strain behavior of the microtensile specimens was determined with an Instron 5565 instrument at 25°C at a relative humidity of 50%, with a crosshead speed of 25 mm/min. A 100-lb load cell was used for the measurements. Each reported data set was obtained from the averaging of the results obtained from a minimum of three microtensile specimens.

RESULTS AND DISCUSSION

Stress-strain properties of copolymer latex films

Copolymer films derived from latexes prepared with 5 mM AMBN

Figure 1 shows the stress-strain plots for the poly(*n*-butyl methacrylate) (PBMA) homopolymer and the three crosslinked copolymer films in which the corresponding latex was prepared with 5 mM AMBN as an initiator. Table I gives the corresponding details for the tensile strength (TS), elongation at break (E_B), and the toughness [i.e., expressed as the work expended to break the film (W_B)] for all films.

P(BMA-*co*-Mac) copolymer latex films exhibited stress-strain behavior similar to that of the PBMA homopolymer film. This behavior is typical of a tough and ductile polymer. A yield point was observed, and an ultimate E_B value greater than 600% was obtained. A slight upturn in the curves, which may indicate the state of packing of the polymer chains, was obtained in both cases before failure. In contrast, P(BMA-*co*-EGDMA) and P(BMA-*co*-AUA) copolymer latex films exhibited brittle failure. The corresponding latexes exhibited very high gel contents, greater than 95%, for all of these copolymer films.^{15,17}

The development of the crosslinked polymer network formed during the copolymerization of BMA with the three crosslinking monomers differed, depending on the type of crosslinker and the type of initiator used. There was a delay in the formation of the crosslinked network for the P(BMA-*co*-Mac) latex prepared with the oil-soluble AMBN initiator. This delay, resulting from the unequal reactivity between BMA and Mac, was postulated to have resulted in the formation of longer sequences of linear or lightly crosslinked PBMA chains at the particle surface connected to a more fully crosslinked polymer network located within the core of the latex particles. These linear or lightly crosslinked polymer chains located at the particle surface were capable of interdiffusing as a result of favorable reptation to form a more coherent

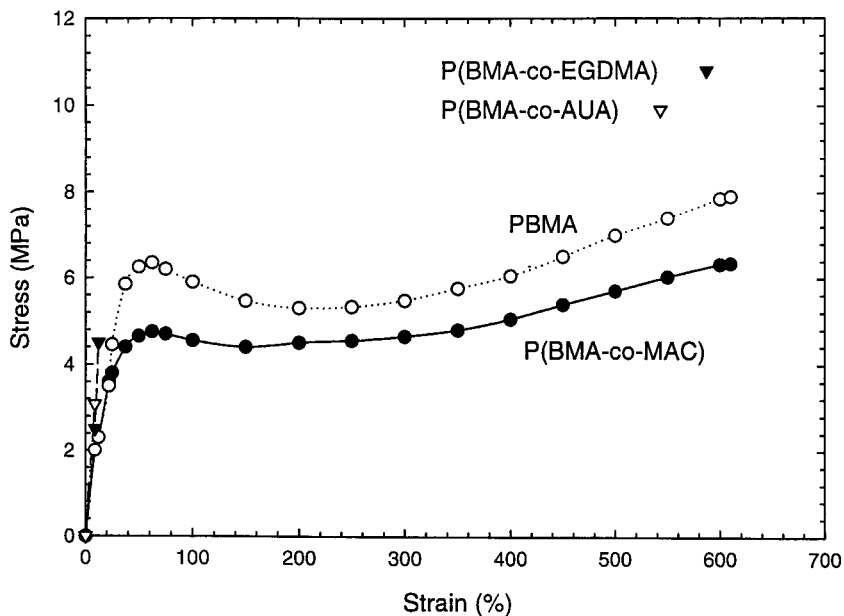


Figure 1 Stress–strain plots of PBMA and crosslinked PBMA copolymer microtensile specimens for which the latexes were prepared with 5 mM AMBN as an initiator.

P(BMA-*co*-Mac) film. The high extensibility of the P(BMA-*co*-Mac) copolymer films before they broke suggested that a lightly crosslinked network with long linear chain sequences was present. These chains could disentangle and slide over one another during the tensile test. The P(BMA-*co*-Mac) copolymer latex films exhibited a considerable degree of cohesive strength, similar to the PBMA homopolymer films with no crosslinked network present (i.e., high molecular weight homopolymer with many chain entanglements). These results would suggest that the crosslinked latex particles, with greater than 95% gel content, underwent a significant degree of stitching across adjacent latex particle boundaries during the film formation process. The major mechanism of fracture due to tensile extension appears to be largely macrodeformation of the long chains being pulled out after extending, disentangling, and sliding. The linear polymer chains (which must be connected to the network) made up the continuous phase of the films. Therefore, the toughness of the P(BMA-*co*-Mac) copolymer films was comparable to the toughness of the

PBMA homopolymer films, despite a greater than 95% gel content in the copolymer. This would also imply that domains of the crosslinked polymer chains or network (95% gel content) existed within the latex particles and that the network domain sizes within the crosslinked particles were small (smaller than the latex particles, which were 100–160 nm in diameter). It may also be possible that the observed behavior resulted from network imperfections that were far more significant for the P(BMA-*co*-Mac) copolymer, despite its very high gel content. Favorable interactions between the linear or lightly crosslinked PBMA chains and a rather loose PBMA-*co*-Mac crosslinked network may also contribute to this behavior.

In a perfect network, the use of high molecular weight crosslinkers such as Mac would indicate that the molecular weight of the crosslinker (M_x), which is the length of one side of the network mesh (schematic given in Fig. 2), is relatively longer than the mesh size of P(BMA-*co*-EGDMA) because M_x for EGDMA is much lower, that is, 198 g/mol compared to 3500 g/mol, for a mesh with a similar value of M_c . A bigger mesh size would imply that the interdiffusion of a linear polymer chain through the network mesh is more likely if the diameters of the reptating polymer chains are smaller than the diagonal size of the mesh. In addition, the entanglement of the network with the linear polymer chains is enhanced. Larger M_x or M_c values for the network mesh may also result in greater flexibility for deformation under a load (i.e., the mesh behaves like a spring), particularly when the glass-transition temperature of the crosslinker is low

TABLE I
Stress–Strain Properties of PBMA Homopolymer and Copolymer Films Derived from Latexes Prepared with 5 mM AMBN as the Initiator

Film	TS (MPa)	E_B (%)	W_B (MPa)
PBMA	7.0 ± 1.0	650.0 ± 50.0	40.0 ± 5.0
P(BMA- <i>co</i> -Mac)	6.5 ± 0.5	650.0 ± 50.0	34.5 ± 4.5
P(BMA- <i>co</i> -EGDMA)	4.0 ± 1.0	12.0 ± 3.0	0.2 ± 0.1
P(BMA- <i>co</i> -AUA)	2.5 ± 0.5	15.0 ± 5.0	0.3 ± 0.1

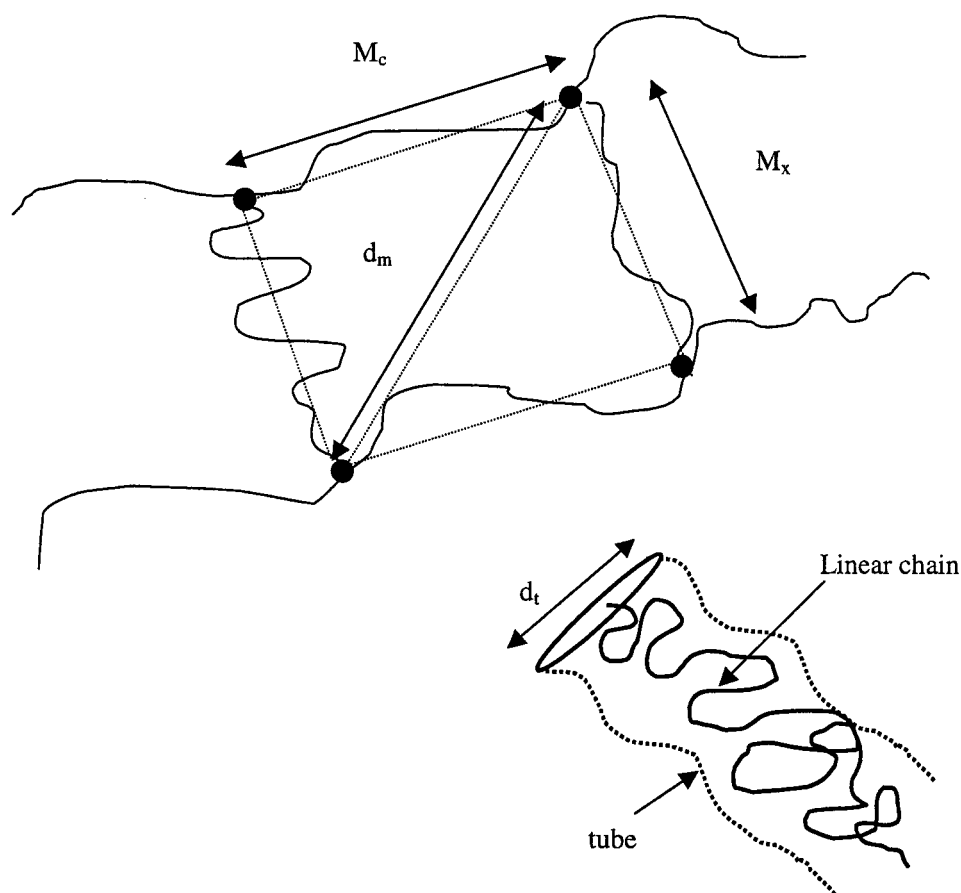


Figure 2 Simplified diagram of the tetrafunctional AB type of crosslinked network microstructure. The dashed lines indicate the mesh size with a diagonal dimension of d_m . d_t is the tube diameter, denoting the reptation⁹ of a single polymer chain.

enough that the crosslinker chains exhibit elastomeric characteristics at the test temperature.

For the P(BMA-*co*-EGDMA) and P(BMA-*co*-AUA) copolymer latex films, the rapid formation of the gel content as a function of the *n*-BMA conversion indicates that the chain ends present before the formation of the network were shorter. Subsequently, when the films were formed, these chain ends were not long enough to intermix to obtain good film coherence and strength. The linear or lightly crosslinked PBMA chains that were postulated to form later in the copolymerization could not form the continuous phase of the resulting film because they were confined within the particle core. However, these chains might still have been able to interpenetrate the network mesh if they were long enough and if the network mesh size was large enough to allow the linear chains to interpenetrate through the network and extend into the neighboring particles. The situation is clearly different when the behavior of the P(BMA-*co*-EGDMA) copolymer film is compared to that of the P(BMA-*co*-Mac) films. This, in turn, suggests that the kinetics of the copolymerizations for these two systems resulted in different chain architectures of the network within the latex particle, which was expected to control the formation

of the film and, subsequently, the resulting film properties. Therefore, tighter chain networks appear to have been present at the particle surfaces for P(BMA-*co*-EGDMA) and P(BMA-*co*-AUA) copolymer systems, and so there was little polymer chain interdiffusion among the particles, particularly at the particle interfaces. Chain breakage was, therefore, facilitated in these regions in which less chain mixing occurred or there was mixing of shorter polymer chains.

Copolymer films prepared from latexes synthesized with 1 mM KPS

The stress-strain behavior of the copolymer films that were obtained from latexes prepared with 1 mM KPS as an initiator are shown in Figure 3, and the corresponding TS , E_B , and W_B values are given in Table II. Similar plots were obtained for the Mac and AUA systems, but the P(BMA-*co*-EGDMA) copolymer films exhibited an entirely different behavior; that is, a dependence on the type of initiator was observed. Although the P(BMA-*co*-EGDMA) copolymer film prepared with the oil-soluble initiator exhibited brittle behavior as previously shown, the copolymer films prepared with the water-soluble KPS initiator were

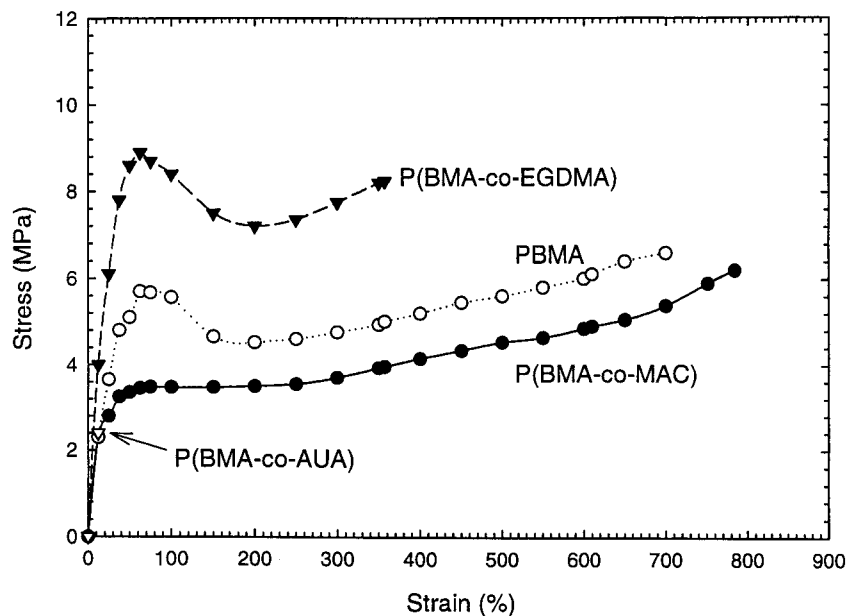


Figure 3 Stress-strain plots of microtensile specimens of PBMA and PBMA copolymers prepared with 1 mM KPS.

tougher. This was surprising, particularly because the rate of development of the gel (or the amount of gel formed) was more rapid when the water-soluble initiator was used. Very high gel contents (>95%) were obtained. It follows that the high gel content development in the latex particles began when a substantial amount of *n*-BMA was still present during the copolymerization. We had previously noted that, at the point at which a high gel content was first attained, most of the crosslinker appeared to have been consumed. When this was the case, the remaining unreacted *n*-BMA must then have formed linear or lightly crosslinked PBMA chains during the remainder of the copolymerization reaction.

Although the development of the gel content for P(BMA-*co*-AUA) was similar to that for the EGDMA system, the behavior of the films was different; P(BMA-*co*-AUA) copolymer latex films were extremely brittle when copolymerization was carried out in the presence of either one of the initiators.

TABLE II
Stress-Strain Properties of PBMA Homopolymer and Copolymer Films Prepared with 1 mM KPS as the Initiator

Film	TS (MPa)	E_B (%)	W_B (MPa)
PBMA	6.5 ± 0.5	700.0 ± 50.0	37.0 ± 5.0
P(BMA- <i>co</i> -Mac)	6.5 ± 0.5	750.0 ± 50.0	35.0 ± 5.5
P(BMA- <i>co</i> -EGDMA)	8.5 ± 0.5	350.0 ± 50.0	25.0 ± 5.0
P(BMA- <i>co</i> -AUA)	3.5 ± 0.5	17.5 ± 2.5	0.45 ± 0.15

Behavior of copolymer films toward a solvent

Exposure of films to solvent vapor

The compression-molded copolymer latex films prepared with AMBN and KPS were subjected to swelling by exposure to tetrahydrofuran (THF; VWR Scientific, Bridgewater, NJ) vapor in a sealed container. PBMA homopolymer films prepared with AMBN or KPS flowed toward the bottom of the glass container as expected. This occurred because there were no crosslinks to hold the polymer chains together, and so the polymer chains were free to flow in the presence of the solvent. In contrast, all of the PBMA copolymer films retained their integrity after exposure to the solvent vapor because of the presence of crosslinked networks. Photographs of swollen films of the copolymers prepared with AMBN are shown in Figure 4. Cracks were observed in the P(BMA-*co*-AUA) films: the THF solvent molecules had penetrated the films in some regions and completely separated the polymer chains. The extent of swelling of these films must have been controlled by the state of the polymer chains that existed in the films. The amounts of solvent present in the swollen polymer films were determined, and these are shown in Table III. The films exhibited different behaviors when similar amounts of the solvent were present. P(BMA-*co*-Mac) copolymer films prepared with KPS bulged after exposure to the THF solvent vapor. This was not surprising because there was 40% linear polymer present in the copolymer; despite this, the film remained intact. The 40% linear polymer did not separate out from the network chains, probably because there were intimate interactions among them.

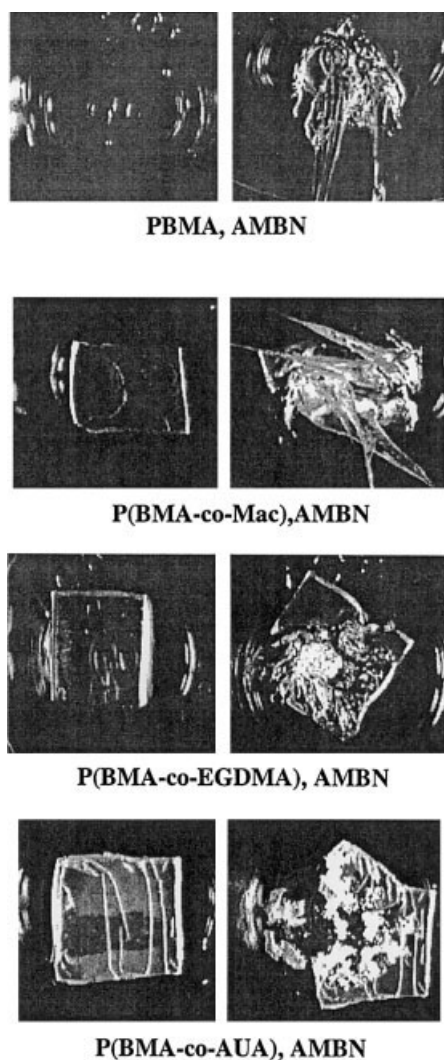


Figure 4 Photographs of swollen samples (left) and disturbed (by stretching) swollen samples (right).

Even more dramatic behavior was observed when a glass rod was used to stretch the swollen copolymer films. This was done very quickly to avoid a loss of the solvent when the lid to the solvent chamber was removed. The swollen mass of the PBMA homopolymer could be stretched a long distance, and this was com-

parable to the behavior observed when P(BMA-co-Mac) swollen copolymer films (AMBN or KPS) were stretched. However, P(BMA-co-EGDMA) films prepared with KPS exhibited less stretching when disturbed. Much less stretching was observed for the P(BMA-co-EGDMA) swollen copolymer film that was prepared with AMBN (resembled vacuum grease). P(BMA-co-AUA) films again exhibited a completely different behavior; that is, the swollen films crumbled when disturbed in both cases (prepared with either AMBN or KPS).

Immersion of films in a solvent

Despite the high gel contents (>95%) for most of the copolymers [except for P(BMA-co-Mac) prepared with KPS with a gel content of 60%], the compression-molded films disintegrated to give very small particles (with sizes on the order of the individual latex particles) when they were completely immersed in the THF solvent (Fig. 5). This indicates that there were latex particles present that contained crosslinked networks in the films. The latex particles were held together by linear or lightly crosslinked chains, as postulated earlier from the tensile property data and a study of the gel content as a function of the *n*-BMA conversion. During swelling, the polymer chains that held the crosslinked domains (latex particles) together completely separated from one another to give microgels. The particle sizes of the microgels were on the order of the original latex particle sizes after they were swollen in an excess of THF (0.5 g of copolymer latex in 25 g of THF), except for P(BMA-co-AUA) films, for which larger pieces of films were obtained after immersion in THF. Table IV shows the results of the unswollen (latex particles dispersed in distilled water) and swollen (latex particles dispersed in THF solvent) copolymer latex particles. In Table IV, different swelling behaviors can again be noted among the copolymer latexes, which also showed a dependency on the type of initiator employed for the copolymerization. The use of the water-soluble KPS initiator resulted in the formation of films that exhibited higher swelling ratios

TABLE III
Amount of Solvent Imbided by the Copolymer Films After Exposure to THF Solvent Vapor for 120 h at Room Temperature

Film	Unswollen weight, W_o (g)	Swollen weight, W_s (g)	Swelling ratio, $W_s - W_o/W_o$
PBMA, AMBN	0.051	0.157	2.08
P(BMA-co-Mac), AMBN	0.083	0.247	1.98
P(BMA-co-EGDMA), AMBN	0.073	0.215	1.95
P(BMA-co-AUA), AMBN	0.093	0.290	2.12
PBMA, KPS	0.118	0.362	2.07
P(BMA-co-Mac), KPS	0.126	0.383	2.04
P(BMA-co-EGDMA), KPS	0.090	0.265	1.94
P(BMA-co-AUA), KPS	0.110	0.343	2.12

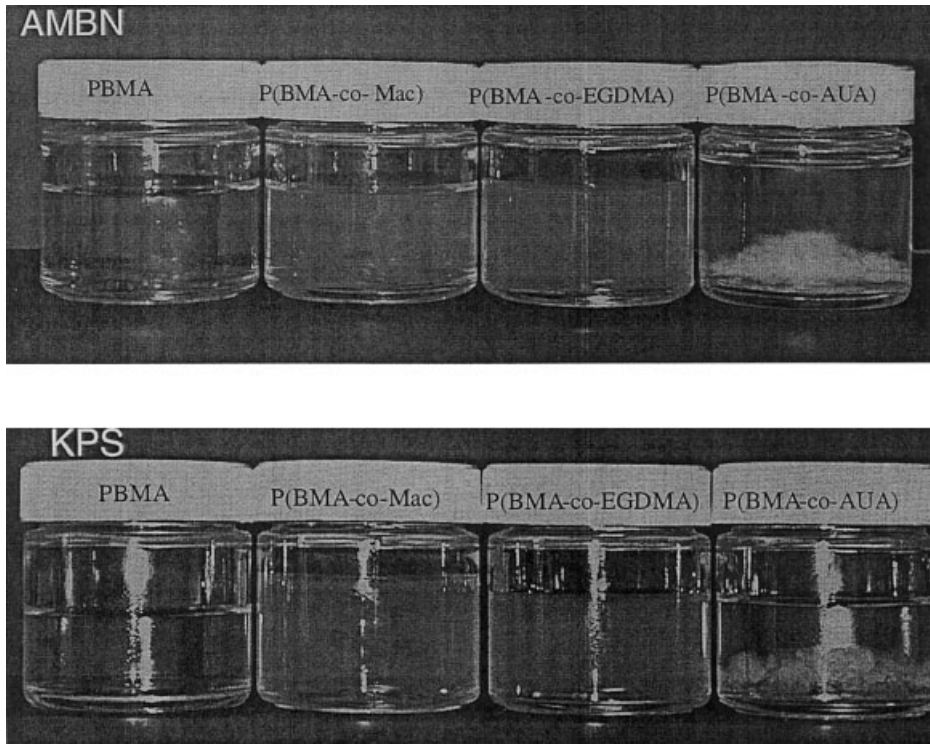


Figure 5 Photographs of swollen, compression-molded films immersed in THF (used as a solvent).

than the films prepared with the oil-soluble AMBN initiator. The volume swelling ratio for the P(BMA-co-EGDMA) copolymer latex particles prepared with KPS appeared to be similar to the volume swelling ratio of P(BMA-co-Mac) copolymer latex particles prepared with AMBN. Therefore, this again offers evidence that the polymer chains in the network had similar architectural profiles in these two cases; that is, long linear or lightly crosslinked chains made up the continuous phase of the film, which conferred coherence to the film, and this explains the relatively high toughness values that were obtained when the samples were deformed for the P(BMA-co-EGDMA) copolymer films prepared with KPS.

During the P(BMA-co-EGDMA) copolymerization, a phenomenon associated with microphase separation¹⁸ known as microsinerisis could have taken place as a

TABLE IV
 r_0 r_s $(r_s/r_0)^3$ 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	74.5	140	6.6	3275
PBMA + EGDMA	80	120	3.4	869
PBMA + AUA	69	99.5	2.9	—
1 mM KPS				
PBMA + Mac	47	115	14.7	13823
PBMA + EGDMA	67.5	118	5.3	2178
PBMA + AUA	55	85	3.7	—

result of the high extent of crosslinking achieved when the majority of the *n*-BMA molecules were still present. The smaller *n*-BMA molecules moved outward to the particle surfaces on which they continued to react after the crosslinker had been used up in the formation of the crosslinked network (gel). The swelling and extraction processes applied to the latexes should have been able to remove any unconnected linear chains. However, because the gel contents were high for these latexes, the linear chains had to be connected to the network chains. Therefore, longer chain segments were present near the particle surfaces; these longer chain segments represented the continuous phase during film formation. These chains were able to interact and contribute to the overall cohesive strength of the film in comparison with the situation in which the chains could not interact at the particle–particle interfaces. The Flory–Rehner equation¹⁹ was applied in an attempt to estimate M_c for the copolymer latex films:

$$\begin{aligned}
 -H\nu^2 \ln\left(1 - \frac{1}{H\nu}\right) - H\nu - \left(\frac{V_m \rho}{M_c}\right) \left(H\nu^{5/3} - \frac{H\nu}{2}\right) \\
 = \chi_{12} + \left(\frac{2V_m \gamma}{RT}\right) \left(\frac{H\nu^{5/3}}{r_0}\right) \quad (1)
 \end{aligned}$$

where $H\nu$ is the volumetric swelling ratio $(r_s/r_0)^3$, r_s is the radius of the swollen particles, and r_0 is the radius of the unswollen particles; V_m is the molar volume of

the solvent; ρ is the density of the (co)polymer; χ is the Flory interaction parameter; γ is the interfacial tension; R is the gas constant; and T is the temperature (K).

The group molar attraction constants²⁰ based on the repeat units of the chemical structure of the copolymer were used to estimate the solubility parameter (δ) needed to calculate χ . The estimation of M_c with the Flory–Rehner equation gave lower values for P(BMA-*co*-EGDMA) than those for the P(BMA-*co*-Mac) copolymer latex particles. The M_c values, which represented an average value, suggested the formation of a tighter network for the P(BMA-*co*-EGDMA) copolymer in comparison with the P(BMA-*co*-Mac) network.

CONCLUSIONS

The copolymerization of small amounts of different types of crosslinking monomers with BMA resulted in the formation of films that exhibited different tensile properties and swelling behaviors. In one instance (with EGDMA used as a crosslinking comonomer), a dependence on the type of initiator employed was observed. The evolution of the copolymer structure during the copolymerization reaction is thought to be responsible for the differences in the film behavior (i.e., some films were brittle, whereas others were quite tough). The toughness of the P(BMA-*co*-Mac) copolymers resulted from the higher extent of mixing of longer linear or lightly crosslinked PBMA chains connected to the crosslinked polymer network as well as the looseness of the network structure, which constituted the continuous phase of the films. A lack of long linear chains and a tighter network, particularly for the P(BMA-*co*-EGDMA)

copolymer prepared with AMBN as an initiator, resulted in less mixing of the polymer chains in the continuous phase of the films and, therefore, resulted in the brittle behavior of these films.

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