Glycine Derived Polymerizable Cosurfactant in the Synthesis of Functionalized Poly(butyl acrylate) Nanolatexes

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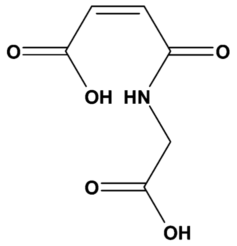
The approach of employing *N*-glycinylmaleamic acid (NGMA) as an efficient cosurfactant to provide microemulsion polymerization of butyl acrylate using a weight ratio of sodium dodecyl sulfate (SDS)/butyl acrylate (BA) at ≤1.5, which is lower than that employed in previous experiments, has been demonstrated. The narrow polydispersity index at 1.36−1.48 of poly(butyl acrylate) copolymers from investigated microemulsion polymerization reactions evidences the promotion of a controlled polymerization reaction, in contrast to the solution polymerization method generating polymers with higher polydispersity index at 3.15−4.23. The enhanced incorporation of NGMA at ∼0.35 *m* in the copolymer demonstrates the merits of the proximity effect enabled in the microemulsion polymerization reaction. The incorporation of NGMA promotes rigidity of the polymer chain as suggested by a higher T_g of −16.8 °C for the copolymer in comparison to that of the poly(butyl acrylate) homopolymer.

Introduction

Polymerization in microemulsion allows the synthesis of well-defined polymeric nanolatexes in the size range 10−100 nm with narrow size distribution.[1−3] The polymerized nanolatexes in view of their immense potential in industrial and pharmaceutical applications are expected to be environmentally friendly, nontoxic, and biodegradable. However, the majority of the investigated oil-in-water microemulsion polymerization reactions of styrene/butyl acrylate use large quantities of cationic surfactants such as cetyl trimethylammonium bromide (CTAB), which are toxic in nature. [4−7] The four-component microemulsion aided by the alcohol cosurfactants requires a large amount of anionic surfactant and results in very low activity material.[8−10]

There is a growing interest in development of a microemulsion phase using natural surfactants derived from proteins, sugar, fatty acids, and lipids.[11−15] Antonietti et al.[16] have demonstrated the scope of a combination of lecithin and sodium cholate in microemulsion polymerization of styrene. Kaler and co-workers have investigated in detail the phase behavior of a microemulsion formulated by biodegradable nonionic surfactants derived from alkyl polyglucosides.[17−19] In our efforts to develop microemulsion polymerization with an environmentally friendly formulation, we have identified a polymerizable compound, viz., *N*-glycinylmaleamic acid (NGMA) (Scheme 1), that can be employed in place of alcohols as a cosurfactant. The cosurfactant activity of NGMA for sodium dodecyl sulfate (SDS) micellar assemblies has been recently established by us.[20] Glycine in the side chain of NGMA is expected to provide merits of biodegradability and functionalization by virtue of a free −COOH group, while the maleyl group could participate in the copolymerization reaction. The functionalized latex could provide a cross-linking reaction, finding applications in drug delivery as demonstrated by Wooley and co-workers.[21] We report here the oil-in-water microemulsion polymerization of butyl acrylate using the SDS surfactant in the presence of NGMA cosurfactant, completely replacing the medium-chain alcohol. We investigate the merits of NGMA as a cosurfactant in a microemulsion copolymerization reaction with butyl acrylate and the effect of functionalization of NGMA on the thermal and interfacial organizational characteristics of poly(butyl acrylate).

Scheme 1. Structure of *N*-Glycinylmaleamic Acid (NGMA)



Experimental Section

Materials. Glycine 98% and maleic anhydride 98% used in the synthesis of NGMA were from s.d.fine Chemicals Ltd., India. NGMA was synthesized using the reported procedure.[22] Sodium dodecyl sulfate (SDS) 99% and *n*-butyl acrylate (BA) 98% from Aldrich were used as such. Potassium persulfate 98% was obtained from s.d.fine Chemicals Ltd., India. 2,2′-Azobisisobutyronitrile (AIBN) 98% was obtained from Aldrich, U.S.A.

Microemulsion Polymerization. The microemulsion phase compositions consisting of different mole fractions of BA and NGMA (Table 1) were transferred into a polymerization tube and degassed. About 1 wt % of $K_2S_2O_8$ initiator based on the weight of the monomers was added, and the mixture was placed in a constant-temperature water bath at 80 °C under nitrogen atmosphere. The reaction was performed for a period of 8 h. In the photopolymerization reactions, the polymerization tubes containing microemulsion solutions were placed in Heber multilamp photoreactor model HML-compact-LP-MP-812, 8 W medium-pressure UV lamp. About 0.1% $K_2S_2O_8$ initiator based on the weight of the monomers was added, and the polymerization was carried out at 365 nm and 30 °C under nitrogen atmosphere for a period of 8 h.

Solution Copolymerization. The identical feed compositions of BA and NGMA used in microemulsion polymerization were dissolved in dimethyl sulfoxide and taken in a polymerization tube. About 1% and 0.1% AIBN initiator based on the weight of monomers was added for thermal polymerization and photopolymerization, respectively, and the polymerization reaction carried out for 24 h under nitrogen atmosphere.

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Table 1. Microemulsion Phase Compositions Chosen for Polymerization Reaction

system	NGMA (M)	SDS (M)	BA (M)	NGMA/BA mole ratio	SDS/BA (wt. ratio)
GMA1	0.507	0.458	1.02	0.34:0.66	1.008
GMA2	0.636	0.386	0.640	0.50:0.50	1.360
GMA3	0.572	0.119	0.333	0.64:0.36	0.807
GMA4	0.677	0.010	0.167	0.80:0.20	0.128
GMA5	0.628	0.013	0.073	0.90:0.10	0.391

The duration of the reaction was maintained the same for thermal and photo reactions, and this period was identified to provide good yield of polymers under experimental conditions of the polymerization reaction from several preliminary experiments.

Characterization of the Latexes. The particle size and zeta potential measurements were made on the latexes using a Malvern particle size analyzer 1000HS/3000HS at a fixed scattering angle of 90°. The samples were freed of excess surfactant and cosurfactant by dialysis using low molecular weight cutoff membranes. The dialysis was performed for about a week with repeated change of water. The samples were filtered using 0.45 micron filter paper before measurements. The number of particles has been estimated using the reported equation.[23] The surface tension measurements of the latexes before and after polymerization were made on a Nima DST9005 tensiometer where a platinum DuNouy ring was used as a probe. Each measurement was made several times to obtain coherent values, allowing a rest time of almost 15 min between the sample addition and surface tension measurement to allow surface adsorption equilibrium to be achieved.

Characterization of the Copolymers. The polymers from the microemulsion and the solution polymerization reaction were isolated by the solvent precipitation method using methanol as a precipitating solvent, washed several times with water to ensure complete removal of surfactant, and dried under vacuum until a constant weight was obtained. ^{1}H NMR measurements for the characterization of the copolymers were performed in $CDCl_3$ solvent on a JEOL ECA 500 (500 MHz) NMR spectrometer employing tetramethylsilane as the internal standard. Molecular weight estimations of the polymers were performed on a JASCO GPC chromatograph model MX-2080-31 fitted with PL gel 5 μm Mixed-C columns, 300 × 7.5 mm, in tetrahydrofuran with a flow rate of 1 mL min^{-1} at 30 °C using a refractive index detector. The copolymer composition has been estimated from the pH titration method using alcoholic potassium hydroxide as titrant. Differential scanning calorimetric (DSC) measurements were performed on NETZSCH DSC200PC DSC with the heating rate of 5 °C/min. The thermogravimetric analysis (TGA) of the copolymers was done using NETZSCH STA 409PC TGA with a heating rate of 10 °C/min.

Conditions of Surface Pressure (π)−Area (A) Isotherm Measurements using Langmuir Film Balance (LFB). $\pi - A$ isotherm experiments of the copolymers were performed on a NIMA 611 single-barrier trough fitted with a Wilhelmy balance (accuracy 0.01 mN/m). The monolayers were spread from chloroform (Merck HPLC grade) solution on Milli-Q deionized water from the Millipore system using a microsyringe. Typically, 30 μL of a chloroform solution of the copolymer (1 mg/mL) was slowly spread on the water subphase. Ten minutes after spreading, when the solvent had completely evaporated, the monolayers were compressed at a speed of 2×10^{-1} nm^2/(mol/min). Each measurement was repeated at least three times to check the reproducibility of the isotherms. All measurements were carried out at a temperature of 25 ± 0.1 °C. The absence of surface-active impurities in the solvent was confirmed by performing a blank run with the solvent. The $\pi - A$ isotherms of the copolymers were measured at the suphase pH values of 6.5 and 10.2.

Results and Discussion

Microemulsion Polymerization of BA and NGMA. The structure of NGMA is represented in Scheme 1. The microemulsion phase compositions generated using NGMA cosurfactant and the anionic surfactant SDS are presented in Table 1. With an aim to minimize SDS surfactant, we have chosen to restrict the SDS/BA weight ratio to ≤1.5. It is noted that most of the reported microemulsion systems employ surfactant/monomer weight ratios of ≥2. Since NGMA exhibits a solubility limit of about 12% in water, we have taken care to keep the concentration of NGMA at <12%. We inferred that it is possible to generate microemulsion phase structures over a mole fraction range of NGMA/BA from 0.36:0.64 to 0.90:0.10. It is significant to note that, using NGMA, the microemulsion phase could be formed with an SDS/BA weight ratio as low as 0.128, thus demonstrating the cosurfactant activity of NGMA. We have selected these microemulsion compositions for investigations of the polymerization reaction. The polymerization reactions were carried out under (1) thermal and (2) photo conditions especially to explore the possible scope for reorganization of microemulsion phase structures under these conditions and their effects on the polymerization reaction. The reactions were performed under nitrogen atmosphere, and therefore, inhibition due to oxygen from the atmosphere is ruled out.

The polymers from microemulsion and solution polymerization reactions were characterized using ^{1}H NMR spectroscopy. The complete absence of peaks due to CH═CH at δ 5.5−6.5 ppm ensures the removal of unreacted monomer and also the occurrence of the polymerization reaction due to addition across the double bond as anticipated. In molecular weight estimations using gel permeation chromatography (GPC), THF was used as the preferred solvent. It is significant and interesting to note that thermal polymerization and photopolymerization reactions performed in the microemulsion phase resulted in polymers with high molecular weight in the range (1.18−1.57) × 10^6 g/mol and narrow polydispersity index of 1.36−1.48 (Table 2). On the contrary, the solution polymerization method under thermal and photo conditions resulted in polymers with high polydispersity indexes of 3.15−4.23 (Table 3). The formation of polymers with narrow polydispersity index from microemulsion polymerization demonstrates the occurrence of polymerization under controlled conditions typical of microemulsion polymerization.

Table 2. Characteristics of the Copolymers from Microemulsion Polymerization[a]

	thermal (1% $K_2S_2O_8$)				photo (0.1% $K_2S_2O_8$)			
system	NGMA (m)	BA (m)	$M_n/10^5$ g/mole	M_w/M_n	NGMA (m)	BA (m)	$M_n/10^5$ g/mole	M_w/M_n
GMA1	0.04	0.96	13.64	1.48	0.08	0.92	13.18	1.46
GMA2	0.06	0.94	12.56	1.44	0.10	0.90	15.74	1.42
GMA3	0.16	0.84	13.43	1.36	0.16	0.84	12.87	1.40
GMA4	0.20	0.80	12.67	1.42	0.22	0.78	13.12	1.42
GMA5	0.33	0.67	11.87	1.44	0.35	0.65	12.34	1.43

[a] Thermal initiator, 1% $K_2S_2O_8$, $T = 80$ °C. Photo initiator, 0.1% $K_2S_2O_8$, $T = 30$ °C.

Table 3. Characteristics of Copolymers from Solution Copolymerization

	thermal (1% AIBN)				photo (0.1% AIBN)			
system	NGMA (m)	BA (m)	$M_n/10^5$ g/mole	M_w/M_n	NGMA (m)	BA (m)	$M_n/10^5$ g/mole	M_w/M_n
GMA1	0.02	0.98	4.10	3.78	0.02	0.98	4.18	4.23
GMA2	0.02	0.98	2.75	4.09	0.02	0.98	5.74	4.15
GMA3	0.05	0.95	3.43	4.16	0.04	0.96	2.87	3.76
GMA4	0.07	0.93	2.67	3.15	0.04	0.96	3.24	3.55
GMA5	0.07	0.93	2.87	3.44	0.06	0.94	1.87	4.05

Table 4. Characteristics of Latexes from Thermal Polymerization, 1% $K_2S_2O_8$

system	particle size (nm)	number of particles (N_P/L)	zeta potential (mV)	surface tension (mN m^{-1})
GMA1	152	9.63×10^{16}	−31.8	25.6
GMA2	128	1.82×10^{17}	−32.5	26.2
GMA3	44	3.20×10^{18}	−32.9	27.6
GMA4	40	4.15×10^{18}	−33.2	28.1
GMA5	35	5.93×10^{18}	−33.8	28.8

The incorporation of NGMA in the poly(butyl acrylate) chain has been estimated from a titration method wherein the acid group equivalent to the NGMA component is estimated. The characteristics of the polymers from thermal polymerization and photopolymeriztion methods are presented in Table 2. From the composition of the polymers (Table 2), it could be seen that incorporation of NGMA in the copolymer, although less than the feed ratio, increases significantly in line with feed composition. It is understood from previous reports[24] that the incorporation of monomer in the polymer chain is dependent on reactivity of the monomer, as controlled by the structural features and the polymerization reaction conditions. It is possible that the lower reactivity of NGMA accounts for its poor incorporation, and this issue is to be studied in detail. However, it is significant to note that, with an increase in concentration of NGMA up to 0.90 *m*, the maximum incorporation at 0.33−0.35 *m* could be achieved from thermal and photopolymerization methods (Table 2). In sharp contrast to this, a very low incorporation to the extent of 0.06−0.07 *m* of NGMA could be afforded from the solution polymerization method, both under thermal polymerization and under photopolymerization conditions (Table 3). These results establish the proximity effect provided by the microemulsion phase. This is possible due to solubilization of BA and NGMA at the interface in the microemulsion phase, and this must play a significant role in promoting the incorporation of NGMA.

Characterization of the Latexes. The aqueous polymer latexes have been characterized for particle size distribution, zeta potential, and surface tension after dialysis using low molecular weight cutoff membranes. The characteristics of the polymer latexes are presented in Table 4. The particle size of the latex serves as an indirect index of the particle number and interfacial area. It could be seen that the decrease in particle size indicative of an increase in particle number and interfacial area occurs with an increase in concentration of NGMA and decrease in concentration of BA and SDS. For example, on increasing the concentration of NGMA from 0.507 to 0.572 M, particle size decreases from 153 to 44 nm, which amounts to an increase in particle number per liter from 9.63×10^{16} to 3.20×10^{18} (Table 4) and an increase in interfacial area from 6.98×10^7 to $21.52 \times 10^7 cm^2$/L. It is significant to observe that this is observed under conditions of small changes in SDS/BA weight ratio from 1.0 to 0.807. The trend of an increase in particle number and interfacial area with increasing NGMA and decreasing SDS concentrations substantiates cosurfactant activity of NGMA. Zeta potential estimations are expected to provide information on the charge characteristics of the particle. The zeta potential has been estimated to be −31 ± 2 mV for the latexes GMA1, 2, 3, 4, and 5 (Table 4). The negative zeta potential is indicative of the anionic nature of the particle, and this is probably provided due to the adsorption of NGMA along with SDS surfactant on the latex surface. The small variation in zeta potential among latexes indicates the complete coverage of the latex particle in all the microemulsion compositions. The surface tension of the latexes was estimated as 25 ± 2 mN/m. The equilibrium surface tension of 0.1 M SDS in the absence and presence of NGMA was found to be about 28 mN/m. Surface tension of the latex is indicative of interfacial tension at the particle−air interface. The close values of the surface tensions of the latex and the SDS surfactant solution in the presence of NGMA support complete coverage of the latex particles, in agreement with zeta potential estimations. The stability of the latex over a period of about a year is further established by negligible changes in zeta potential values.

Thermal Characteristics of Copolymers of Poly(butyl acrylate) (PBA) and NGMA. The polymers GMA1 and GMA3 have been investigated for thermal characteristics in comparison with the homopolymer. PBA shows T_g of −55 °C in accordance with the literature value.[24] From the DSC curves of the polymers GMA1 and GMA3 (Figure 1a and b), it is shown that polymer GMA1 (4% functionalized) and GMA3 (16% functionalized) exhibit T_g of −34.6 °C and −16.8 °C. The T_g of a polymer is indicative of flexibility of the polymeric chain. The negative T_g of PBA is known to arise from the flexibility of the polybutyl side chain. The increase in T_g of polymers GMA1 and GMA3 suggests restriction of mobility of PBA chains. In this case, it is possible that the promotion of intermolecular interactions provided by NGMA, especially by virtue of the free COOH group, might contribute to restricted mobility and hence the observed increase in T_g. Thus, it is interesting to note that the polymer GMA3 consisting of a higher proportion at 16 mol % NGMA contributes to greater rigidity of the polymeric segments, as indicated by higher T_g in comparison to polymer GMA1. The thermogravimetric analysis (Figure 2a and b) performed on these polymers suggests that the polymers GMA1 and GMA3 show nearly similar features to those of homopolymer PBA. The onset temperature for decomposition is 302 ± 2 °C. The polymers exhibit single-step decomposition wherein maximum

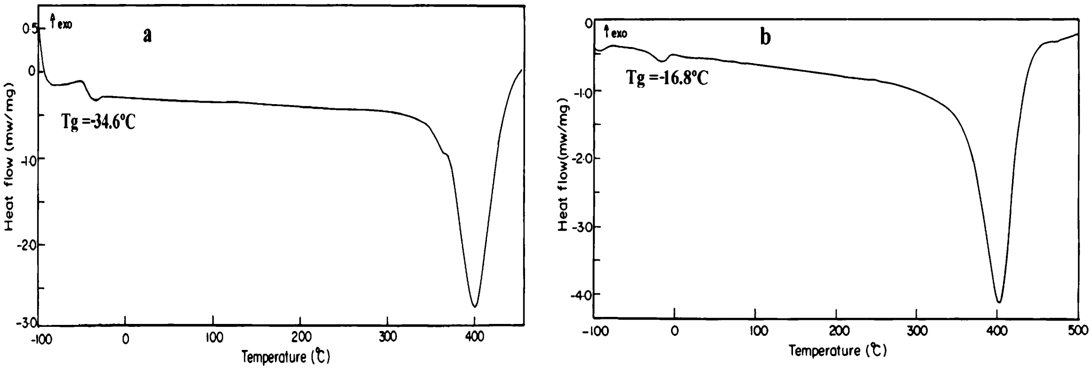

Figure 1. DSC traces of the copolymers (a) GMA1 and (b) GMA3.

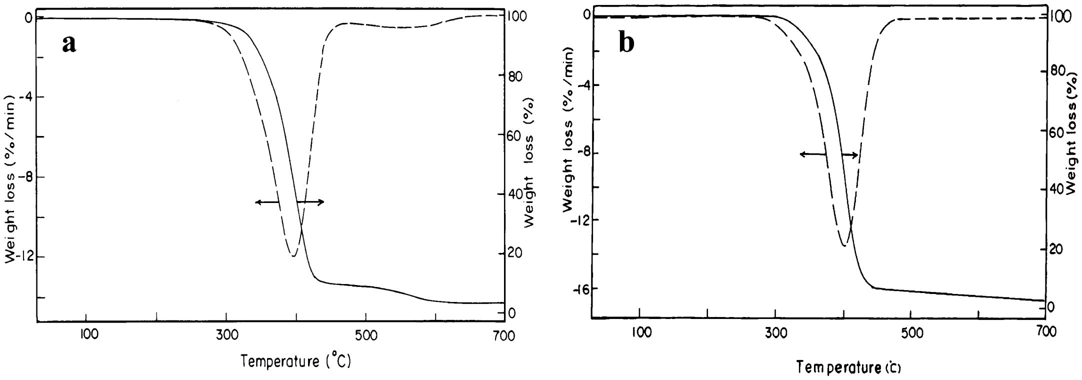

Figure 2. TGA curves of the copolymers (a) GMA1 and (b) GMA3.

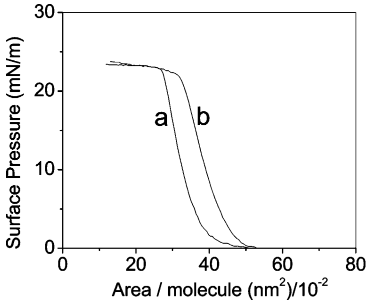

Figure 3. Surface pressure (π)−surface area (A) isotherms of copolymers from microemulsion on aqueous subphase, pH 6.5, at 25 °C. (a) GMA1 and (b) GMA3.

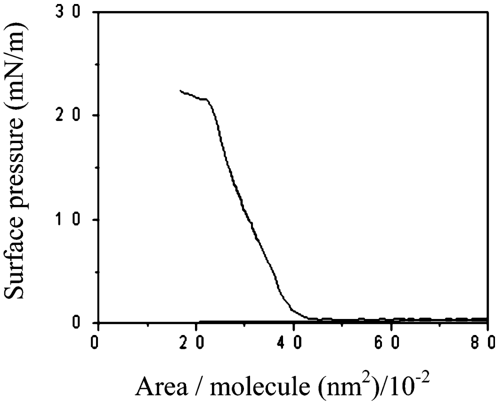

Figure 4. Surface pressure (π)−surface area (A) isotherms of PBA homopolymer.

loss in weight to an extent of 91 ± 2% occurs at temperature of 398 ± 2 °C. The introduction of NGMA essentially brings about changes in mobility of the segments and does not affect the thermal stability of the PBA polymer.

Interfacial Organizational Characteristics of NGMA Functionalized PBA Polymer Films. The polymers GMA1 and GMA3 have been characterized at the air/water interface in comparison with neat PBA using the LFB technique. All isotherms have been found to be reproducible under the conditions of the experiment. The $\pi-A$ isotherms of the copolymers GMA1 and GMA3 measured in the aqueous subphase (pH = 6.5) are presented in Figure 3. The standard deviation in area measurements is about 0.01 nm^2/molecule. The $\pi-A$ isotherms suggest that the polymer remains at the air/water interface after spreading and compression by the barrier. This suggests that the polymers are surface-active, i.e., amphiphilic having the hydrophobic and hydrophilic parts in fair balance for film formation. It could be seen that the extrapolated area (A_0) indicative of minimum surface area at the closest packing estimated for the poly(butyl acrylate) (PBA) (Figure 4) remains almost invariant at 33.87 Å^2/molecule with the incorporation of a very small mole fraction of NGMA at 0.04 m (Figure 3a). On the other hand, A_0 increases considerably to 44.40 Å^2/molecule for the polymer consisting of 16 mol % NGMA (Figure 3b). This increase in A_0 of GMA3 might arise either from loose packing of molecules or from packing of NGMA in the copolymer film adsorbed at the interface. The homopolymer PBA and the copolymers GMA1 and GMA3 show maximum π of 23.0 ± 0.5 mN m^{-1}. On further compression, π increases to a very small extent, <5%. This behavior is indicative of phase transition and also suggests that this maximum π corresponds to equilibrium π (π_{eq}). The compressibility coefficient (K) at different surface pressures is estimated by employing eq 1 [25]

$$K = 1/A_o(\delta A/\delta\pi) \qquad (1)$$

where A_o is the extrapolated area and $\delta A/\delta\pi$ is the slope of the $\pi-A$ isotherm. The standard deviation in the estimation of K has been found to be about 1 × 10^{-3} m/mN. It is interesting to observe that K of the copolymer films GMA1 and GMA3 in the high-pressure regions of 10, 15, and 20 mN/m are consistently lower than that of neat PBA film. For example, at π = 15 mN m^{-1}, K values for PBA, GMA1, and GMA3 are 1.98, 1.02, and 1.16 × 10^{-2} m/mN, respectively (Table 5). This is suggestive of the promotion of close-packed structures by NGMA comonomer at the air/water interface. The $\pi-A$ isotherms of the copolymers measured at pH 10.2 are given in Figure 5. The increase in pH of the subphase brings about a large increase in A_o from 36.45 to 43.29 Å^2/molecule for the polymer film GMA1 (Figure 5a), whereas for GMA3, A_o remains almost invariant. However, for both GMA1 and GMA3 a small increase in K is observed at this pH. This is indicative of a small expansion in the packing arrangement of the monolayer, which might arise from the neutralization of −COOH to −COONa under alkaline conditions. Hysteresis experiments on monolayer films are well-known to provide information on stability characteristics. Hysteresis experiments were performed thrice to check reproducibility. The results of the third hysteresis cycle performed on the polymers GMA1 and GMA3 at pH 6.5 are shown in Figure 6a and b. Both GMA1 and GMA3 form a stable film at the interface as indicated from the good reproducibility of the $\pi-A$ isotherm characteristics in the compression and expansion cycle. The loss in surface area estimated to be 6−8% at different π values of 10−20 mN m^{-1} for both GMA1 and GMA3 is suggestive of viscoelastic characteristics, typical of polymer film.[25]

Table 5. Minimum Area of Packing (A_0) and Compressibility Coefficient (K) on Aqueous Subphase at Different Surface Pressures of Copolymers from Microemulsion Polymerization ($T = 25$ °C)

		K (m/mN) 10^{-2} at different surface pressures (π)			
polymer	A_0 nm^2/mol/10^{-2}	$\pi = 5$ mN/m	$\pi = 10$ mN/m	$\pi = 15$ mN/m	$\pi = 20$ mN/m
PBA	33.87 ± 0.01	2.35 ± 0.1 (pH 6.5)	2.15 ± 0.1 (pH 6.5)	1.98 ± 0.1 (pH 6.5)	1.38 ± 0.1 (pH 6.5)
GMA1	36.45 ± 0.01	2.18 ± 0.1 (pH 6.5)	1.36 ± 0.1 (pH 6.5),	1.02 ± 0.1 (pH 6.5)	1.02 ± 0.1 (pH 6.5)
	43.29 ± 0.01	2.27 ± 0.1 (pH 10.2)	1.82 ± 0.1 (pH 10.2)	1.28 ± 0.1 (pH 10.2)	1.28 ± 0.1 (pH 10.2)
GMA3	44.40 ± 0.01	2.02 ± 0.1 (pH 6.5)	1.31 ± 0.1 (pH 6.5)	1.16 ± 0.1 (pH 6.5)	1.16 ± 0.1 (pH 6.5)
	42.92 ± 0.01	2.21 ± 0.1 (pH 10.2)	1.66 ± 0.1 (pH 10.2)	1.30 ± 0.1 (pH 10.2)	1.23 ± 0.1 (pH 10.2)

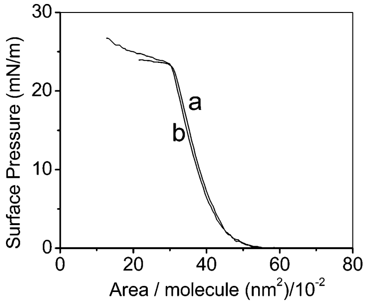

Figure 5. Surface pressure (π)−surface area (A) isotherms of copolymers from microemulsion on aqueous subphase, pH 10.2, at 25 °C. (a) GMA1 and (b) GMA3.

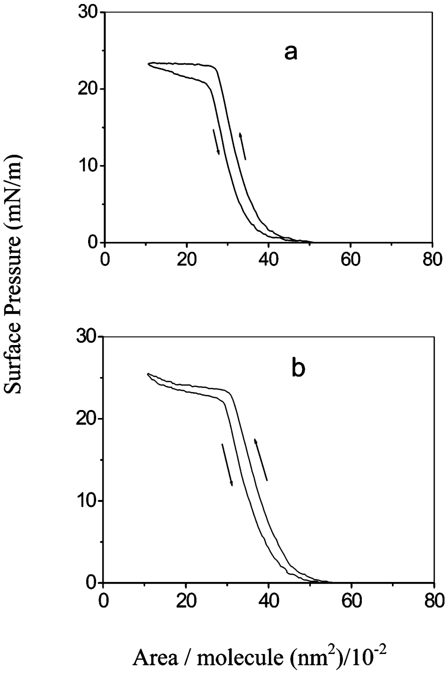

Figure 6. Hysteresis π−A isotherm curves of copolymers from microemulsion on aqueous subphase, pH 10.2, at 25 C. (a) GMA1 and (b) GMA3.

Conclusion

The use of polymerizable NGMA in the microemulsion polymerization of BA is realized not only as an environmentally friendly alternative to alcohol cosurfactant, but also an efficient cosurfactant capable of reducing the amount of SDS. The increase in the concentration of NGMA contributes to a decrease in particle size and an increase in particle number from 9.63 × 10^{16} to 5.93 × 10^{18} per liter. The polymeric latex remains stable throughout the polymerization reaction. The coverage of polymeric particles with SDS in combination with NGMA is evidenced from the zeta potential of about −32 mV. The promotion of controlled conditions for the polymerization reaction inside the microemulsion phase is further evidenced by the narrow polydispersity index (PDI) of 1.40 for the polymers in contrast to those from the solution polymerization reaction showing PDI as high as 3.15−4.23. The functionalization of poly(butyl acrylate) with 16 mol % of NGMA is able to bring significant changes in the thermal and interfacial organizational characteristics.

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