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Preparation of Polyurethane/Acrylic Hybrid Nanoparticles via a Miniemulsion Polymerization Process

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ABSTRACT: Nanosized polyurethane/poly(*n*-butyl methacrylate) (PU/PBMA) hybrid latex particles (∼50 nm) with various compositions were successfully prepared using a redox-initiated miniemulsion polymerization process. Studies were carried out on the miscibility of PU prepolymer and BMA monomer, PU/BMA droplet formation, and polymerization kinetics. This process provides a new method to synthesize nanosize hybrid latex particles using a relatively small amount of surfactant. A suitable chain extension process was developed, where a hydrophobic chain extender was used to introduce intraparticle cross-linking while maintaining the original small particle size of the nanosize PU/PBMA hybrid latexes. The ratio of PU to BMA, the amount of grafting agent (hydroxyethyl methacrylate; HEMA), and the presence of the hydrophobic chain extender have little influence on the particle size of the final latexes compared to the seeded emulsion polymerization processes. This illustrates the advantage of this process, whereby the final particle size is less sensitive to the composition and amount of cross-linking agent or chain extender.

Introduction

Polyurethane (PU) dispersions are used in a wide range of industrial coatings and adhesives applications. More than 1000 patents have been filed over the past five decades, and these have been well reviewed and documented.[1−3] To obtain cost/performance benefits, polyurethane dispersions, which are relatively expensive, are blended with polyesters, alkyds, acrylics, and other waterborne polymers. The most widespread combination are the PU/acrylic emulsion blends, where the aim is to upgrade the performance of the acrylic polymer with respect to toughness, flexibility, abrasion resistance, and film-forming properties. However, there are some inherent limitations to blend systems because of the incompatibility between the polyurethane and acrylic dispersions, which results in phase separation, gel formation, or discoloring upon storage. Furthermore, the homogeneity of the polyurethane/acrylic blends is questionable, both in the wet state and most importantly in the final dried coating. Therefore, efforts are being made to combine urethane and acrylic polymers in single-component hybrid systems, which is expected to result in a superior balance of properties compared to physical blends. This can be achieved by a number of routes, such as seeded emulsion polymerization,[4−8] preparation of interpenetrating polymer networks (IPN),[9] cross-linking,[10] and graft copolymerization of PU onto acrylic polymer chains.[7,11−14]

Recently, the preparation of nanosized latex particles has become more attractive both in research and for end-use application. It is expected that films with better appearance and mechanical properties would be obtained by using small-size latex particles.[15] Usually, microemulsion polymerization is utilized to prepare nanosize latex particles. However, obvious disadvantages hinder its application, such as the requirement of a high PU/acrylic ratio, low solids content, and high emulsifier level resulting in either high cost or poor film formation.[14,16] The target of the current work is to prepare stable nanosize (∼50 nm) urethane/acrylic hybrid latexes via redox-initiated miniemulsion polymerizations carried out at low temperatures, which facilitates the attainment of small-size latex particles using a limited amount of surfactant.[17] Moreover, the unique droplet nucleation mechanism of miniemulsion polymerization aids in the preparation of hybrid latex particles by generating monomer droplets that contain polymer (or prepolymer) prior to polymerization. Miniemulsion polymerization using a hydrogen peroxide/ascorbic acid redox initiator pair was therefore utilized for the preparation of PU/acrylic hybrid nanoparticles. To attain the intimate molecular mixing between the PU and acrylic components, PU chains were grafted onto the acrylic chains via the incorporation of a hydroxy functional acrylic monomer (i.e., hydroxyethyl methacrylate) in the synthesis of the PU component (prepolymer). An intraparticle chain extension process for the urethane prepolymer was developed, which not only extended the polyurethane chains to increase the molecular weight of the PU but also served as a “cross-linker-like” moiety by tying the pendant urethane chains together. Moreover, it exhibited no influence on the particle size of the hybrid latexes. In this article, the development of the polymerization process and the chain extension of the urethane prepolymer will be discussed in detail.

Experimental Section

Materials. *n*-Butyl methacrylate (BMA; Aldrich; reagent grade) was used after distillation under reduced pressure. Hydroxyethyl methacrylate (HEMA; Aldrich; reagent grade) was purified by passing it through an inhibitor removal column filled with an appropriate inhibitor removal packing material (Aldrich). Hexadecane (HD; Aldrich), sodium lauryl sulfate (SLS; Fisher), ascorbic acid (Aldrich), 30% hydrogen peroxide (H_2O_2; Acros), 2-methyl-1,5-pentanediamine (Aldrich), Bisphe-

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Table 1. Recipe for the Preparation of PU/PBMA Hybrid Miniemulsion Nanoparticles[a]

ingredient	parts by weight (g)	comment
oil phase		
urethane prepolymer	2.0–8.0	10–40%
n-butyl methacrylate (BMA)	18.0–12.0	90–60%
hexadecane (HD)	0.54	
hydrophobic chain extender[b]	0–varies[c]	
dibutyltin dilaurate	0.0004–0.0016	0.02 wt %[d]
aqueous phase		
sodium lauryl sulfate (SLS)	0.17	7.5 mM[e]
deionized water	78.9	
10% hydrogen peroxide (H_2O_2)	0.69	25.2 mM[e]
10% ascorbic acid (H_2A)	0.39	2.77 mM[e]

[a] Polymerization temperature: 30.0 ± 0.1 °C. [b] Bisphenol A, 4,4′-ethylenedianiline, 4,4′-methylenebis(cyclohexylamine), NH_2-terminated poly(propylene oxide). [c] A stoichiometric amount based on the free isocyanate groups remaining in the system. [d] Based on prepolymer. [e] Based on aqueous phase.

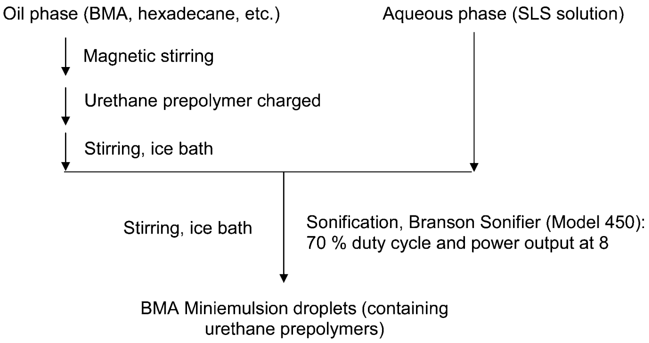


Figure 1. Procedure for the preparation of BMA miniemulsions containing urethane prepolymers.

nol A (Aldrich), dibutyltin dilaurate (DBTDL; Aldrich), tetrahydrofuran (THF, Aldrich), uranyl acetate (UAc; Polysciences, Inc.), and phosphotungstic acid (PTA; Fisher) were all reagent grade and used as received without further purification. Urethane prepolymers were synthesized and characterized according to the methods described previously.[17] In brief, the polyurethane prepolymers were prepared from poly(propylene glycol) 2000 (80 parts by weight) and methylene-di-*p*-phenyldiisocyanate (MDI; 20.5 parts by weight) or isophorone diisocyante (IPDI; 19.10 parts by weight) catalyzed with 10 wt % dibutyltin dilaurate. In addition, 1.5 wt % (based on the total number of hydroxyl groups) hydroxyethyl methacrylate (HEMA) was utilized in order to incorporate reactive acrylic double bonds into the polyurethane chains.

Preparation of Polyurethane/PBMA Hybrid Latexes via Miniemulsion Polymerization. The general recipe used for the preparation of PU/PBMA hybrid miniemulsion nanoparticles is listed in Table 1. Prior to polymerization, BMA miniemulsion droplets containing urethane prepolymer were prepared according to the procedure described in Figure 1. The oil phase and the surfactant (SLS) solution were prepared separately and then mixed by magnetic bar stirring. A Branson Sonifier (model 450) was used to emulsify the mixture at a duty cycle of 70% and a power output of 8 for 4 min. The beaker containing the miniemulsion mixture was immersed in an ice bath to reduce any rise in temperature that may occur during the emulsification process, and the magnetic bar stirring was continued throughout the sonification procedure. Stable BMA miniemulsion droplets containing urethane prepolymer were obtained by this process. The miniemulsion was then transferred to a four-neck flask or the 1 L Mettler RC1 MP10 reactor. When using the RC1 reactor, the ingredients listed in Table 1 were scaled up 6-fold. Miniemulsion polymerizations were carried out under nitrogen at 30 °C by charging the redox initiator components by a batch addition mode (i.e., hydrogen peroxide was added first, followed by the ascorbic acid after the reactor reached 30 °C) into the system. The stirring speed was 180 rpm for the reactions carried out in the flask and 400 rpm for the RC1. The polymerization time was 90–120 min for all experiments. In the case where hydrophilic chain extension agents, such as 2-methyl-1,5-pentanediamine, were used, a stoichiometric amount (based on the quantity of free isocyanate groups remaining in the system) of chain extender solution was added into the system with mild stirring after the polymerization.

Table 2. Miscibility of Urethane Prepolymer with BMA Monomer

urethane[a] in mixture (wt %)	25	50	75
shelf life[b] at room temp	>15 days	7 days	5 days

[a] Urethane prepolymers were prepared using PPG-diol and MDI. [b] Numbers of days when no visible phase separation was observed.

Characterization of Miniemulsion Droplets and Hybrid Latex Particles. Miniemulsion droplet sizes were determined using dynamic light scattering (Nicomp, model 370). Miniemulsion samples were diluted using a BMA-saturated SLS solution. The amount of free isocyanate groups remaining in the system was measured using a conductometric titration method involving the reaction of dibutylamine with the isocyanate and the back-titration of the excess amine with standard hydrochloric acid in 2-propanol solution.[17] The particle size and particle size distributions of the latexes were measured by capillary hydrodynamic fractionation (CHDF, model 1100, Matec Applied Sciences). Transmission electron microscopy (TEM, Philips model 400T) was employed to study the morphology of the hybrid latex particles. For the TEM experiments, an acceleration voltage of 100 kV was used. A cold stage with liquid nitrogen coolant was employed to maintain the soft particles in their original spherical shapes during the TEM imaging process. The particles were treated with an aqueous solution of uranyl acetate or phosphotungstic acid (PTA) for negative staining.[18]

Fourier transform infrared spectroscopy (FTIR, Mattson Sirius model 100 spectrophotometer) was used to monitor the reactions between the chain extension agents and the isocyanate groups.

Results and Discussion

Preparation of BMA Miniemulsion Droplets Containing Urethane Prepolymer. a. Miscibility of Urethane Prepolymer with BMA Monomer. To increase the efficiency of hybridization, the urethane prepolymer should at least have good miscibility with the acrylic monomer. A series of prepolymer/BMA mixtures were prepared. The weight percent of urethane prepolymer in the mixture was varied: 0, 25%, 50%, and 75%. All of the mixtures exhibited good shelf stability at room temperature, as evidenced by a clear solution and a lack of phase separation over 5 days (Table 2). This indicates that the urethane prepolymer can be dissolved in BMA monomer, and a homogeneous oil phase is obtained over a wide range of compositions.

b. Preparation of BMA Miniemulsion Droplets Containing Urethane Prepolymer. BMA miniemulsion droplets containing urethane prepolymer were prepared according to the procedure described in Figure 1. The droplet size was monitored by dynamic light scattering as a function of the sonification power, which resulted in the data plotted in Figure 2. The sonification power is defined here as the product of the power output, duty cycle, and sonification time (min) per 100 g of emulsion. It was found that the droplet size (the number-average droplet size, D_n, and the volume-average droplet size, D_v) first decreased substantially during the initial input of the sonification energy and then increased. After passing through a minimum, the

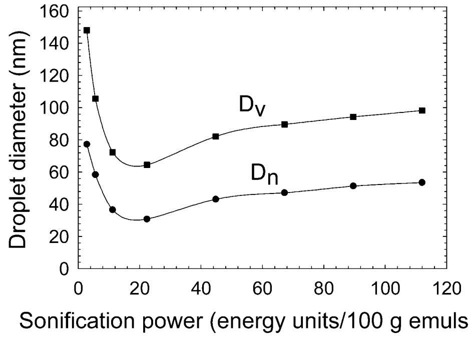


Figure 2. Miniemulsion droplet size as a function of sonification power for urethane prepolymer (prepared using MDI and PPG diol) in BMA monomer dispersed in water; urethane/BMA = 25/75 (wt %); total oil phase = 20 wt %; sonification duty cycle = 70%; power output of 8; SLS = 7.5 mM, based on the aqueous phase; HD = 3.6 wt % based on the monomer (40 mM based on aqueous phase).

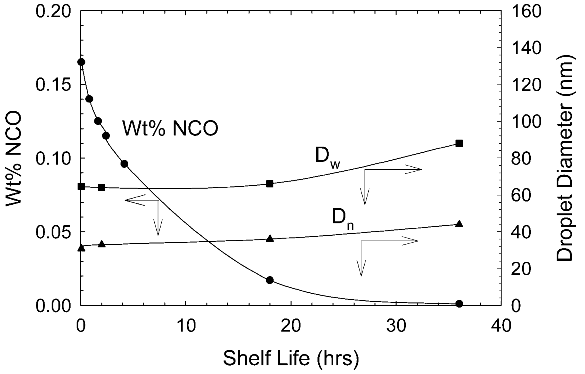


Figure 3. Wt % NCO in the miniemulsion and the droplet size vs shelf life; the initial miniemulsion was prepared using urethane prepolymer (prepared using MDI)/BMA = 25/75 wt/wt; total oil phase = 20%.

droplet size began to increase slowly. This indicates that the shear energy provided by the sonifier is effective in breaking down large droplets, but further shear energy applied to the pseudostable miniemulsions containing small-size droplets results in droplet coalescence instead of reducing their size. This suggests that there are optimum sonification conditions where miniemulsion droplets with minimum size can be produced. The minimum in droplet size could also be due to the high viscosity of the droplets.

As there are a considerable number of isocyanate groups remaining in the prepolymer, which are sensitive to water, it is inevitable for some of these groups to react with water after the oil phase is mixed with the aqueous phase. Therefore, it is necessary to determine the loss of isocyanate groups and the stability of the BMA droplets containing the urethane prepolymer.[19] The wt % of isocyanate groups in a miniemulsion and the droplet size were monitored with aging time (Figure 3). A measurement was made immediately after sonification, which was considered to be time zero. It was found that the concentration of isocyanate groups decreased from an initial value of 0.165 wt % (based on the weight of miniemulsion) to near zero (almost complete disappearance of the NCO groups) after sitting undisturbed on a shelf for 36 h. The drop in wt % NCO during the sonification was only 0.004%, which is considered negligible. The value of the wt % NCO of the dispersion before sonification (0.169%) was calculated by using the wt % NCO of the urethane prepolymer used in the preparation. It was found that around 20% of the isocyanate groups were lost after aging the miniemulsion for 2 h, and the droplets were stable (in terms of retaining their original size) for at least 2 h, during which time the subsequent polymerization reaction would be completed. However, the reaction of isocyanate groups with water, which occurs at the interface between the miniemulsion droplets and the aqueous phase, could gradually change the homogeneity of the oil phase by pulling the prepolymer to the interface. The accumulation of the urethane near the interface would be especially significant before or during the polymerization of the acrylic monomer due to the mobility of BMA molecules. To increase the hybridization efficiency in the final latex particles, the reaction of the isocyanate groups with water should be minimized before and during polymerization. One of the possible solutions is to rapidly polymerize the acrylic monomer at a relatively low reaction temperature that also minimizes the side reaction of the NCO groups with water. It was previously shown that the use of a redox initiation system in the miniemulsion polymerization of BMA at 30 °C results in a faster polymerization rate compared to the corresponding conventional emulsion polymerization (the miniemulsion polymerization can reach ~100% conversion within 25 min) and the formation of small-size latex particles.[17] Therefore, the redox initiator system, comprised of hydrogen peroxide/ascorbic acid, was employed to initiate the polymerization at 30 °C.

Preparation of PU/PBMA Hybrid Miniemulsion Nanoparticles. a. Development of Polymerization Process. In most of the reported literature,[4−8] PU/acrylic hybrid latexes were prepared via seeded emulsion polymerization processes, where a water-dispersible polyurethane dispersion was used as "seed" and the acrylic polymer was formed around these seed particles. Intimate molecular mixing of the acrylic and polyurethane could not be achieved in a single hybrid particle. In addition, a considerable amount of acrylic polymer may not be incorporated into the hybrid particles because of the secondary nucleation of pure acrylic latex particles. To overcome the drawbacks from this traditional approach, miniemulsion polymerization was employed in this study to prepare PU/PBMA hybrid latexes, as illustrated in Figure 4. Since the urethane prepolymer exhibits good miscibility with the acrylic monomer (BMA) over a wide range of compositions (Table 2), the use of the miniemulsion polymerization technique could promote the mixing of the polyurethane and polyacrylate components at the molecular level within each hybrid latex particle by generating acrylic monomer droplets containing the urethane prepolymer prior to polymerization. These miniemulsion droplets become the locus of the polymerization by the entry of free radicals after the initiator is charged. Thus, the unique droplet nucleation mechanism of miniemulsion polymerization (including homopolymerization of the acrylic monomer and its copolymerization with the urethane prepolymer containing polymerizable end groups by reaction with hydroxyethyl methacrylate) would significantly increase the degree of hybridization/compatibilization between these two polymers. Copolymerization of BMA with the HEMA units contained in the PU chains will generate in situ "comb-type" compatibilizing agents that ensure a good compatibility and certain miscibility of the polymer phases in the hybrid particles. The extent of phase separation is

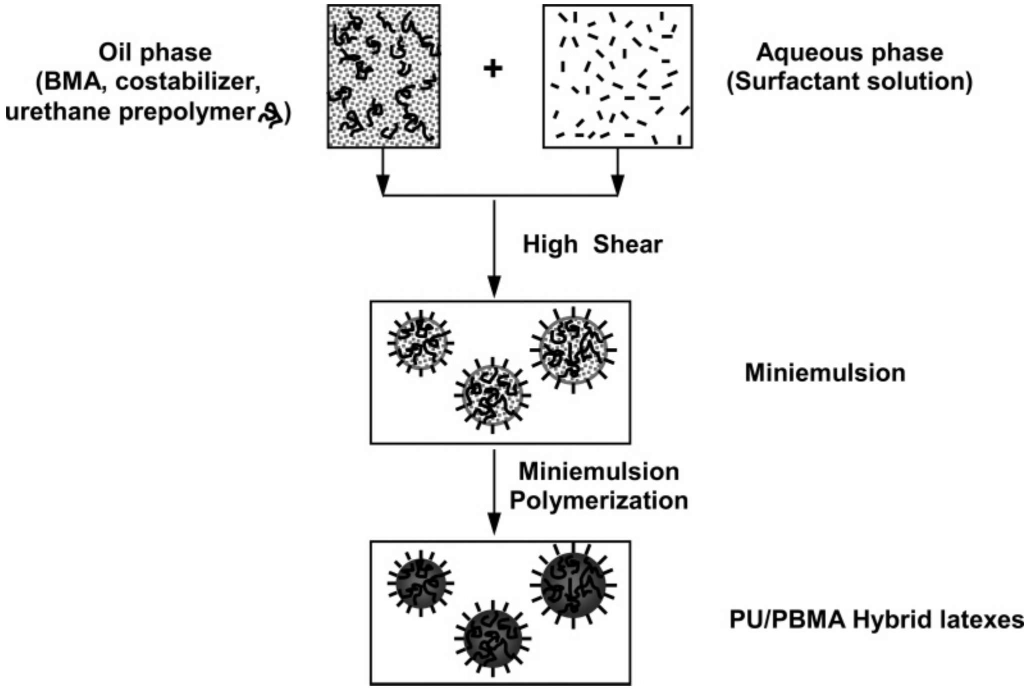


Figure 4. Schematic illustration of the use of the miniemulsion polymerization process for the preparation of PU/PBMA hybrid latex particles.

Table 3. Effect of Costabilizer and Aging Time Prior to Polymerization on the Preparation of PU/PBMA Hybrid Latexes[a]

	before polymerization			after polymerization		
	hexadecane	sonification	aging time	D_v (nm)	PDI = D_w/D_n	stable?
miniemulsion polymerization						
	yes	yes	<10 min[b]	52.1	1.28	yes
	yes	yes	1−1.5 h[c]	61.5	1.07	yes
homogenized emulsion polymerization						
	no	yes	<10 min[b]	64.7	1.31	yes
	no	yes	1−1.5 h[c]	66.7	1.26	coagulum

[a] Reaction temperature = 30 ± 0.1 °C; hybrid composition: PU/PBMA = 25/75 (wt %); total solids content = 20%. [b] Polymerizations were carried out in a flask reactor. [c] Polymerizations were carried out in the RC1 reactor, where it took 1−1.5 h for systematic calibration of the reactor in the presence of the emulsion before initiator was charged.

kinetically controlled and depends on polymerization conditions. In this case, the particles appear to be homogeneous with no evidence for phase separation in the electron micrographs.

The objective of this work is to prepare nanosized (~50 nm) hybrid latexes using a limited amount of surfactant. As discussed elsewhere,[17] in order to obtain latexes with similarly small particle sizes via a miniemulsion polymerization approach, stable miniemulsion droplets with small sizes need to be prepared first (i.e., by applying high shear forces), and then, the droplet size must be maintained by minimizing droplet degradation before the droplets are nucleated. The incorporation of a costabilizer with low water solubility and low molecular weight (such as hexadecane) effectively retards the diffusional degradation of the monomer droplets producing a relatively stable miniemulsion. It has been reported that a small amount of polymer (highly water-insoluble but soluble in the monomer) could be used as a hydrophobe (somewhat analogous to a costabilizer) to prepare kinetically stable miniemulsions.[20,21] However, those polymeric hydrophobes are rather poor costabilizers in terms of their ability to stabilize miniemulsion droplets against diffusional degradation, as conceded by the authors. Table 3 lists the effect of costabilizer, as well as aging time before the initiation of polymerization, on the resulting particle size of the PU/PBMA hybrid latexes. Small and stable particles were produced when hexadecane acted as costabilizer. Even when the polymerization was initiated after aging the BMA miniemulsion containing urethane prepolymer for 1−1.5 h, hybrid latexes of relatively small sizes and good stability were obtained. In the case of homogenized emulsion polymerizations, where no costabilizer was employed in the recipe, nanosized PU/PBMA hybrid latexes with good stability could only be attained if there was immediate initiation of the polymerization after the sonification process was complete. Coagulum was observed in the PU/PBMA latexes prepared after aging the emulsion which was preemulsified using a sonifier prior to polymerization. As schematically illustrated in Figure 5, BMA miniemulsion droplets containing urethane prepolymer were initially created by the miniemulsification process regardless of the presence of costabilizer. If the costabilizer was present in the oil phase, then BMA monomer diffusion between the miniemulsion droplets would be greatly retarded.[22,23] The miniemulsion was shown to exhibit an improved stability with aging at 30 °C in terms of the droplet size.[17] As a result, PBMA would be incorporated into the

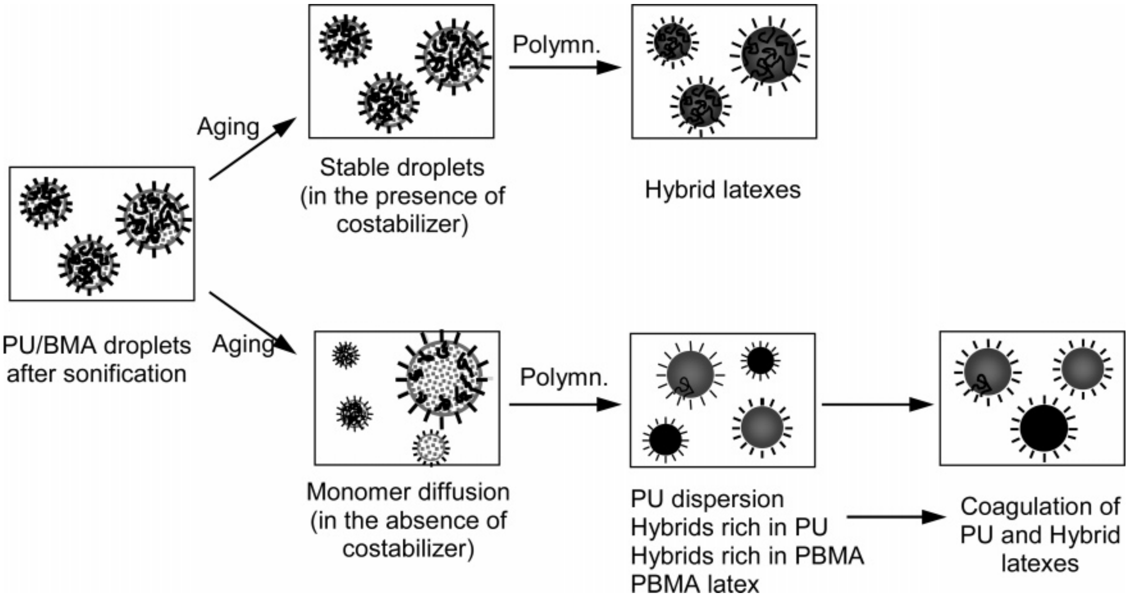


Figure 5. Schematic illustration of the effect of costabilizer on the preparation of PU/PBMA hybrid nanoparticles.

hybrid latex particles along with the PU prepolymer during the subsequent polymerization. However, in the system where no hexadecane costabilizer was present, the urethane prepolymers (number-average molecular weight of 4000−5000 g/mol) could serve as a poor "costabilizer" instead. Although Ostwald ripening between the miniemulsion droplets wound be more significant, apparently the presence of the urethane prepolymer can confer a limited kinetic stability that results in the formation of stable hybrid nanoparticles via polymerization within 10 min of preparing the miniemulsion. Upon longer aging (1−1.5 h), diffusional degradation would result in the redistribution of BMA monomer among the miniemulsion droplets. After polymerization of this emulsion, a latex would result which could be comprised of a PU dispersion, hybrid particles rich in PU, hybrid particles rich in PBMA, and PBMA homopolymer particles. Some coagulation of the latexes occurred, primarily among the PU dispersion and hybrid particles rich in PU, resulting in an unstable emulsion system, where a solid mass of PU was separated from the emulsion. Referring to the work of Gooch, Ding, and Schork,[24] who used oil-modified PU in the preparation of their hybrid acrylic latexes, in our case the PU prepolymers possess a less hydrophobic character and therefore exhibit poorer "costabilizer" properties.

b. Kinetics of Hybrid Miniemulsion Polymerization in the RC1 Reaction Calorimeter. Figure 6 shows the kinetics of the polymerizations of BMA in a urethane prepolymer/BMA miniemulsion and in a BMA miniemulsion, obtained using the Mettler RC1 reaction calorimeter. It is first noted that the polymerizations are fast in both cases. The reaction reached ∼100% conversion within 5 min for the hybrid miniemulsion polymerization and 26 min for the miniemulsion homopolymerization. As discussed elsewhere,[17] the fast free radical generation rate by the redox initiator system at the low polymerization temperature accelerates the nucleation of the miniemulsion droplets, which results in the formation of small latex particles. Droplet nucleation is the primary nucleation mechanism in the redox-initiated miniemulsion polymerization of BMA. The polymerization rate of BMA in the presence of urethane prepolymer is even faster than that observed in the BMA miniemulsion system, even though a lower amount of surfactant (7.5 mM) was employed in the hybrid system compared to the homopolymer system (10 mM). The difference in the number of initial miniemulsion droplets was considered to be the reason for this phenomenon. In the presence of urethane prepolymer, which is more hydrophilic than BMA monomer, the

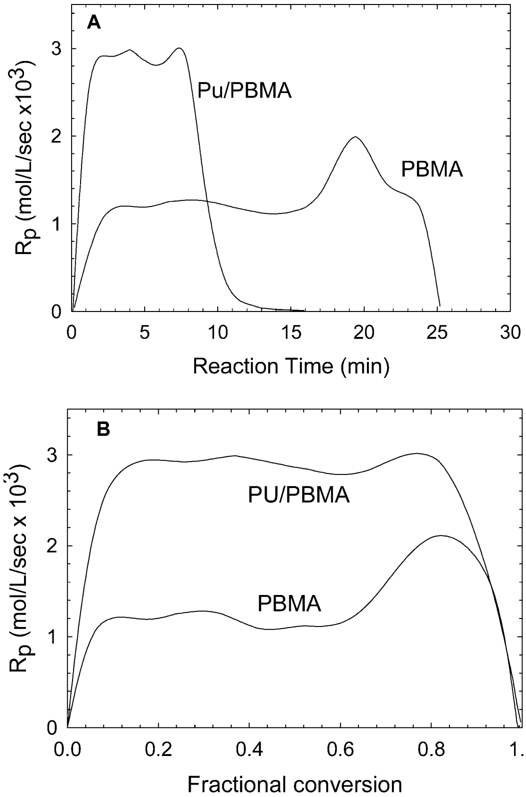


Figure 6. Polymerization rate (R_p) vs (A) reaction time and (B) fractional conversion of BMA for the miniemulsion polymerization of BMA in the presence or absence of urethane prepolymer. Total solids content = 20%; T_r = 30 °C; [HD] = 3.62 wt % based on the BMA monomer; [SLS] = 7.5 mM for hybrid miniemulsion polymerization and 10 mM for miniemulsion homopolymerization (both based on the aqueous phase).

Table 4. Characterizations of Initial Miniemulsion Droplets and Final Latex Particles

sample	type[a]	[SLS] (mM)	$D_{v,\text{droplet}}$ (nm)	$N_d \times 10^{-17}$ (L^{-1})	$D_{v,\text{particle}}$ (nm)	$N_p \times 10^{-17}$ (L^{-1})
PBMA		10.0	72.2	10.35	78.7	7.53
PU/BMA hybrid	IPDI	7.5	50.1	33.1	47.1	35.1
PU/BMA hybrid	MDI	7.5	55.2	24.7	52.4	25.5

[a] Type of diisocyanate used in synthesis of urethane prepolymer.

initial urethane prepolymer/BMA droplets were smaller than the corresponding BMA droplets, resulting in a greater number of droplets in the hybrid system (Table 4). As droplet nucleation is the predominant nucleation mechanism in the miniemulsion system, there would be more polymerization loci present in the hybrid system. Urethane/acrylic hybrid latexes with sizes of approximately 50 nm were obtained after the subsequent rapid miniemulsion polymerization initiated with the redox system.

c. Chain Extension of the Free Isocyanate Groups Remaining in Urethane Prepolymer. Although the use of urethane prepolymers with relatively low molecular weight (i.e., less than 10 000 g/mol) would facilitate the miniemulsification step since the prepolymer could easily be dissolved in the monomer with low viscosity to obtain small-size miniemulsion droplets, better mechanical properties of the resulting film might be obtained by using higher molecular weight polyurethanes. Therefore, a further chain extension reaction step for the isocyanate groups that remain in the prepolymer is critical to increase the polyurethane molecular weight. Aliphatic di- or triamines react with the isocyanate groups 1 order of magnitude faster than does water. These are usually used as chain extension agents to extend the NCO-terminated urethane prepolymers in the form of dispersions. In addition, urethane prepolymers may also be extended with diols and water.

After preparation of the nanosized (~50 nm) urethane/PBMA hybrid latexes, it was observed (see Figure 7) that their particle size increased from the initial 50 to 70−80 nm after several days of aging at room temperature. In these cases, no additional chain extension agents were used in the preparation recipe. This implies that the urethane prepolymers in the PU/PBMA hybrid particles were actually chain extended by water in the medium. The reaction of isocyanate groups (remaining in the urethane prepolymer) with water, which should occur primarily at the hybrid particle/aqueous phase interface, resulted in some limited bridging flocculation of the particles and a subsequent increase in particle size. Figure 8 shows a TEM image of the PU/PBMA hybrid latex, which was prepared in the absence of additional chain extension agent, after 5 days of aging. The hybrid latex particles may possess a spherical shape right after the hybrid miniemulsion polymerization; however, the reaction of the isocyanate groups with water during aging results in the formation of larger, irregularly shaped particles consisting of two to four smaller coalesced particles. Thus, a crucial step in obtaining nanosized urethane/acrylic hybrid latexes is to find a suitable chain extension agent (other than water) to react with the free isocyanate groups remaining in the system, while maintaining particles whose size does not change with time.

At first, a water-soluble diamine was used to chain-extend the remaining isocyanate groups in the PU/PBMA hybrid latex. Aqueous 2-methyl-1,5-pentane diamine solution (10%) was added to the hybrid latexes drop by drop with mild stirring. The latex particle size increased immediately after the addition of diamine and finally resulted in total coagulation of the hybrid latexes. As illustrated schematically in Figure 9A, the hybrid latexes are stabilized using anionic surfactant (SLS), and the surfaces of the latexes are therefore negatively charged. The addition of 2-methyl-1,5-pentanediamine,

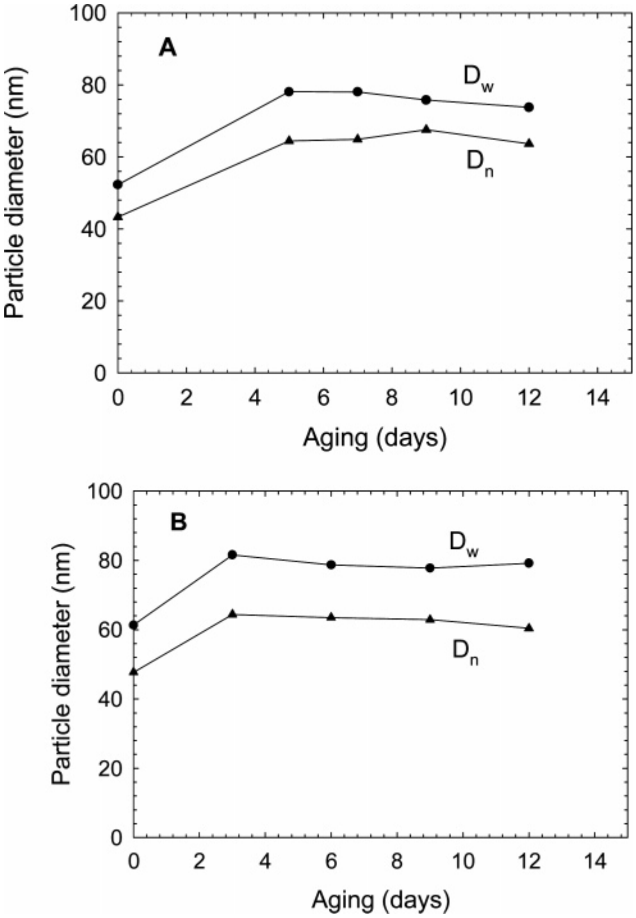


Figure 7. PU/PBMA hybrid latex particle diameter as a function of aging time: hybrid latexes were prepared in the absence of additional chain extension agents; urethane prepolymers were prepared using (A) IPDI and (B) MDI.

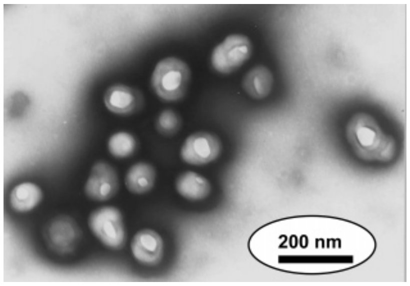


Figure 8. TEM micrograph of PU/PBMA hybrid miniemulsion latex particles, which were prepared in the absence of additional chain extension agents, after 5 days of aging; PU prepolymer/BMA = 25/75 (wt %); latexes were stained with phosphotungstic acid (PTA).

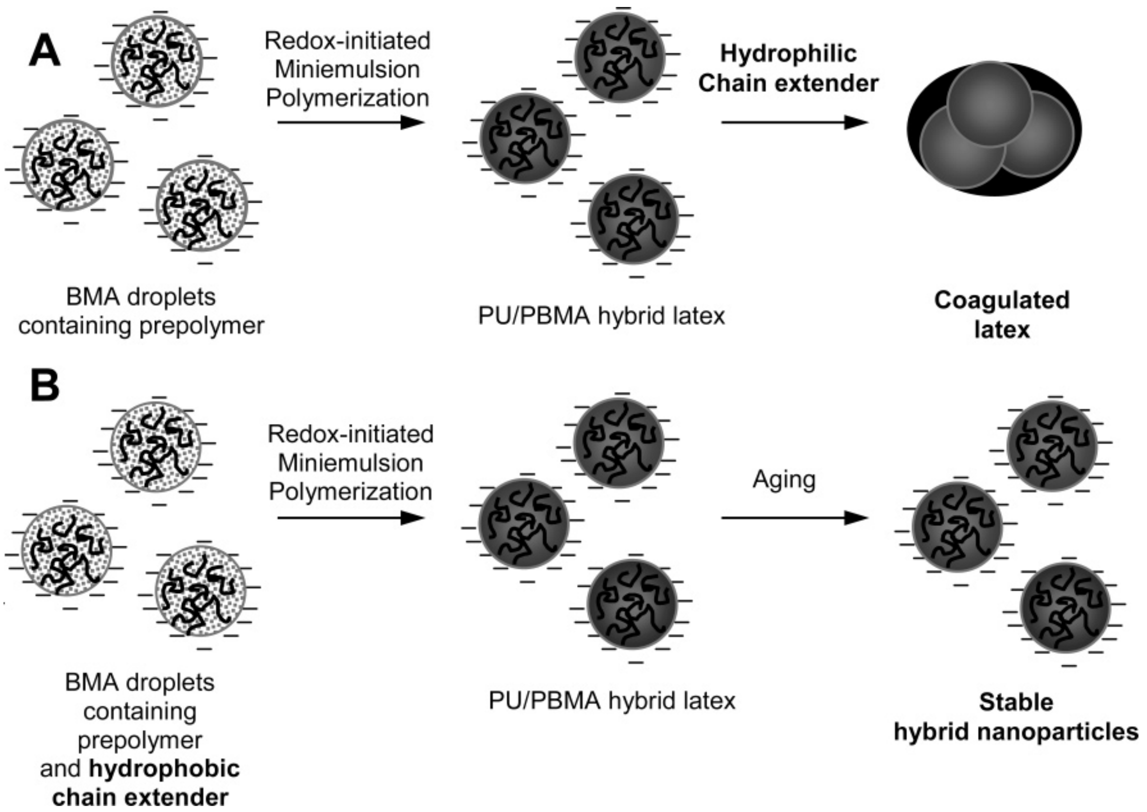
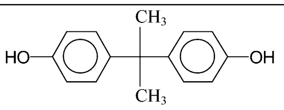
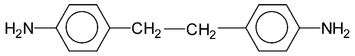
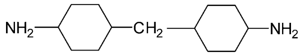
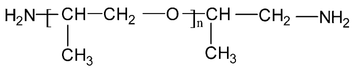


Figure 9. Schematic diagram showing the chain extension process for NCO-terminated urethane prepolymer in PU/PBMA hybrid latexes: (A) using hydrophilic chain extender and (B) using hydrophobic chain extender.

Table 5. Hydrophobic Chain Extension Agents Used for the NCO-Terminated Urethane Prepolymer in Miniemulsion Systems

Chain Extender	Chemical Structure
Bisphenol A	
4,4’-Ethylenedianiline	
4,4'-Methylenebis(cyclohexylamine)	
NH_2-Terminated polypropyleneoxide	 $H_2N-[CH(CH_3)-CH_2-O]_n-CH(CH_3)-CH_2-NH_2$

which is cationically charged, resulted in flocculation of the latex particles. In fact, hydrophilic chain extension agents are not appropriate for this system. Unlike a seeded emulsion polymerization process, the hybrid latexes prepared via miniemulsion polymerization were expected to possess a more uniform composition in each particle as a result of the unique droplet nucleation mechanism. When the hydrophilic chain extender was used, the chain extension reaction of free −NCO groups would primarily occur at the interface between the latex particles and aqueous phase. Consequently, the urethane moiety would tend to be pulled toward the interface, resulting in a type of “core (PBMA)/shell (PU)” morphology. In addition, this would increase the likelihood that the hybrid latex particles aggregate by bridging flocculation, resulting in extensive coagulation.

On the contrary, the use of a hydrophobic chain extender, such as bisphenol A, 4,4′-ethylenedianiline, 4,4′-methylenebis(cyclohexylamine), or NH_2-terminated poly(propylene oxide) (Table 5), should allow the chain extension reaction of the free isocyanate groups to be carried out inside the miniemulsion latex particles (see Figure 9B). Figure 10 illustrates the molecular structure of the resulting PU/PBMA hybrid. The amount of the grafting agent, hydroxyethyl methacrylate, and an efficient chain extension agent are the important parameters needed to ensure intimate mixing between polyurethane chains and poly(n-butyl methacrylate) chains at a molecular level. The degree of grafting of the urethane prepolymer to the PBMA backbone is controlled by the amount of double bonds in the urethane prepolymer (as end groups), which are introduced by HEMA in the prepolymer synthesis recipe. As the molecular weight of the urethane prepolymer is less than 10 000 g/mol, which is insufficient to provide good mechanical properties, the chain extension reaction

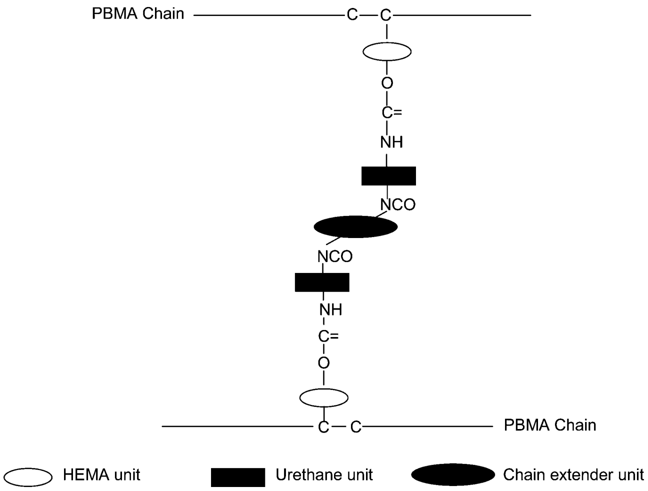


Figure 10. Schematic structure of the polyurethane/PBMA hybrid. "HEMA" represents the grafting unit (hydroxyethyl methacrylate).

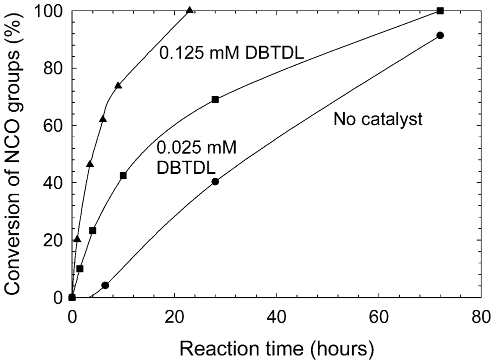


Figure 11. Conversion (in terms of the isocyanate group) vs reaction time for the reaction between 0.5 M bisphenol A and 0.5 M MDI at room temperature (25 °C): 0−0.125 mM dibutyltin dilaurate (DBTDL) was used as catalyst. Anhydrous tetrahydrofuran was used as solvent.

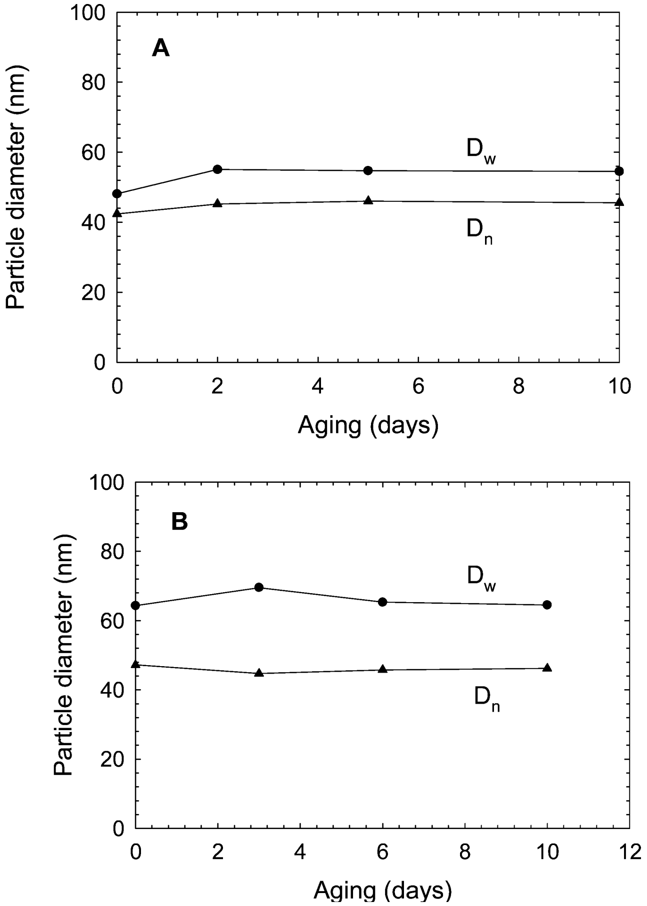


Figure 12. Particle diameter as a function of aging time for PU/PBMA hybrid miniemulsion latex particles prepared using bisphenol A as chain extender: urethane prepolymer/BMA = 25/75 (wt %); urethane prepolymer was synthesized using: (A) IPDI and (B) MDI.

would increase the molecular weight of the polyurethane and serve as a "cross-linker-like" moiety by tying the pendant urethane chains together. In practice, bisphenol A was chosen here as the chain extender to prepare the PU/PBMA hybrid miniemulsion latexes.

To determine the rate of reaction between the urethane and chain extender, reactions between bisphenol A and the isocyanate (MDI) were performed and monitored. Figure 11 shows the reaction kinetics between bisphenol A and MDI at room temperature. FTIR was used to monitor the concentration of free isocyanate groups, which has a sharp absorbance peak at 2273 cm^{-1}. It was found that the reaction rate could be controlled by the amount of catalyst, dibutyltin dilaurate (DBTDL). By adding bisphenol A and a certain amount of catalyst to the recipe for the preparation of the hybrid nanoparticles, the particle size was successfully maintained at ∼50 nm, the same as the initial particle diameter, even after days of aging (Figure 12). Both types of urethanes were successfully used as illustrated in Figure 12A,B. These results also suggest that bisphenol A efficiently competes with water to react with the isocyanate groups. TEM images, shown in Figure 13A,B, also confirmed that the PU/PBMA hybrid latex particles remained stable, with an average diameter of ∼50 nm, by the use of the hydrophobic chain extender. Consequently, nanosize (∼50 nm) hybrid latexes with good shelf life and uniform composition were obtained via the miniemulsion polymerization process.

Preparation of PU/PBMA Hybrid Miniemulsion Latex Particles with Different Compositions. PU/PBMA hybrid latexes with various compositions were prepared via the H_2O_2/ascorbic acid redox-initiated miniemulsion polymerization process. Characterization results are reported in Table 6. Three variables were investigated: (1) the ratio of PU to PBMA in the hybrid, (2) the amount of grafting agent, hydroxyethyl methacrylate (HEMA), incorporated in the synthesis of the urethane prepolymer, and (3) the addition of hydrophobic chain extender, bisphenol A, in the miniemulsion formulation. It was found that hybrid latexes with a larger particle size (∼70 nm) were obtained at lower PU/PBMA ratios (10/90). These results indicate that the concentration of the PU prepolymer affected the surface properties. The lower concentration of the PU resulted in a more hydrophobic surface of the PU/BMA droplets. This consumed (by adsorption) much of the surfactant, resulting in larger droplets. In contrast, higher concentrations of the PU lead to somewhat smaller droplets and, thus, smaller hybrid particles. However, the extent of the change is small, especially when compared to other hybridization processes such as the PU seeded process. For example, Hirose and co-workers[7,14] found that in seeded or conventional emulsion polymerization processes the urethane and acrylic composition ratio

Table 6. PU/PBMA Hybrid Latexes Prepared via Redox-Initiated Miniemulsion Polymerization Process[a]

sample	U10B90 _B_HH	U25B75 _B_HH	U40B60 _B_HH	U25B75 _0_HH	U25B75 _B_HL
composition (PU/PBMA)	10/90	25/75	40/60	25/75	25/75
HEMA (wt %) in urethane prepolymer	1.5	1.5	1.5	1.5	0.5
addition of bisphenol A[b]	yes	yes	yes	no	yes
D_v (nm)	68.3	53.6	56.6	68.3	56.2

[a] Polymerization temperature = 30 ± 0.1 °C. [b] Stoichiometric amount based on the amount of free isocyanate groups remaining in the system.

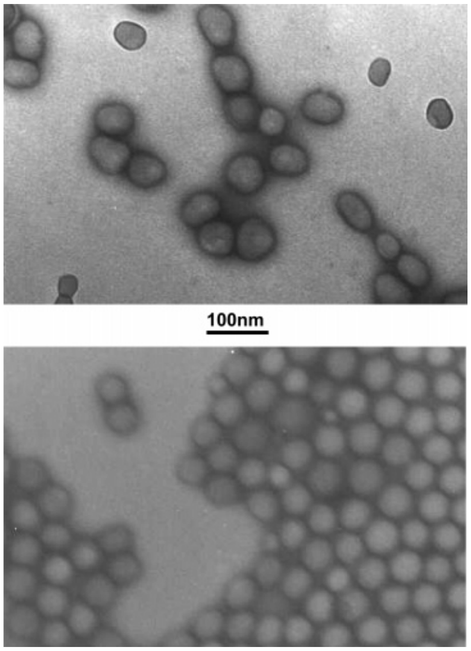


Figure 13. TEM micrographs of PU/PBMA hybrid miniemulsion latex particles prepared using bisphenol A as the chain extension agent. The images were taken after 10 days of aging. Urethane prepolymer/BMA = 25/75 (wt %); latex was stained with phosphotungstic acid (PTA). Urethane prepolymer prepared using (A) IPDI and (B) MDI.

substantially changed the particle size and size distribution of the resulting PU/acrylic hybrid latexes. When the acrylic/urethane ratio was increased from 20:80 to 50:50 and then further to 70:30, the average particle size of the hybrid emulsions increased from 22 to 101 nm and then to 180 nm. Similar results were also reported by Kukanja et al.[8] The authors explained that when using the seeded or conventional polymerization process the particle size of the hybrid emulsions was almost the same as that of the polyurethane dispersion when the amount of acrylic components introduced was small. However, a further increase in the amount of acrylic monomer made it difficult for the micelle-forming polyurethane component to contain acrylic polymer and form stable hybrid emulsion particles. Consequently, larger emulsion particles were formed, presumably by the aggregation of several particles, resulting in multimodal size distributions. Compared with these other hybridization processes, the miniemulsion process can sustain more dramatic changes in the composition without severely affecting the final particle size (Table 6).

The results presented in Table 6 also show that the amount of grafting agent (HEMA) incorporated in the synthesis of the prepolymer has no obvious influence on the particle size of the PU/PBMA hybrid latexes. This implies that the presence of HEMA had no significant effect on the surface properties of the PU/BMA droplets. Nevertheless, the particle size increased in the absence of bisphenol A in the miniemulsion system, as discussed earlier.

Conclusions

This work demonstrates that the miniemulsion polymerization process initiated by a redox initiator system, such as H_2O_2/ascorbic acid, is a very powerful method to prepare nanosize (~50 nm in diameter) PU/PBMA hybrid latex particles. A relatively small amount of surfactant is shown to be sufficient to obtain the small hybrid latex particles by this process, which may be technologically important with respect to the preparation of nanosize hybrid latex particles.

It was found that the urethane prepolymer exhibits good miscibility with the acrylic monomer (BMA) over a wide range of compositions. In the miniemulsification of the urethane prepolymer/BMA droplets, the energy supplied per unit weight of the miniemulsion is the parameter that controls the droplet size. The droplets were stable (in terms of retaining their original size) for at least 2 h. However, the free isocyanate groups present in the miniemulsion gradually decreased due to the reaction with water in the media. Thus, immediate and rapid polymerization is recommended.

It was found that the polymerization rate of BMA in the presence of the urethane prepolymer is faster than that observed in the BMA homopolymer miniemulsion system, even with less surfactant employed in the hybrid system (7.5 mM vs 10 mM SLS). Here, the presence of the urethane prepolymer was considered likely to result in a decreased droplet size because of its hydrophilic nature and presence at the droplet/water interface. A greater number of polymerization loci in the hybrid system results in higher R_p and final N_p. It was demonstrated that shorter aging times prior to the polymerization and the use of hexadecane as costabilizer result in the formation of stable PU/PBMA hybrid miniemulsion.

The particle size of the PU/PBMA hybrid latex particles prepared without chain extender increased substantially after several days of aging. The increase in the particle size during aging was caused by the flocculation of the particles resulting from the chain extension reaction of NCO groups with water.

Studies on the chain extension of the PU/PBMA hybrid latex particles indicate that the chain extension agent has to be carefully selected to maintain the stability of the nanosize hybrid particles while the PU chains are extended; otherwise, coagulation can occur. Hydrophilic chain extenders such as 2-methyl-1,5-pentanediamine result in an immediate particle size increase of the newly obtained PU/PBMA hybrid miniemulsion latexes, followed by coagulation. It was found that hydrophobic chain extenders, such as bisphenol A, can both extend the PU chains and maintain the stability of the hybrid latex particles at their original size (~50 nm).

The particle size of the PU/PBMA hybrid miniemulsion latexes depends much less on the PU/PBMA ratio than those reportedly prepared via seeded emulsion polymerization processes. The use of the grafting agent, HEMA, or the hydrophobic chain extender, bisphenol A, did not significantly influence the particle size of the PU/PBMA hybrid miniemulsion latexes.

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