Hybrid Acrylic–Polyurethane Latexes: Emulsion Versus Miniemulsion Polymerization

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ABSTRACT: Two kinds of hybrid acrylic–polyurethane (PUA) latexes are compared according to their synthesis and properties. The acrylic part is a copolymer of styrene, methyl methacrylate, and butyl acrylate. The PUAs are based on the polycondensation of isophorone diisocyanate and poly(propylene glycol) using butanediol and ethylene diamine as chain extenders. The first class result from the polymerization of miniemulsions of solutions of PU in the mixture of monomers using benzoyl peroxide as an initiator at 80°C. In the second class PUs modified by neutralized dimethylolpropionic acid are used as seeds and emulsifiers for emulsion polymerization of the monomer mixtures initiated with azobisisobutyronitrile at 75°C. The polymerization kinetics are compared, as well as the morphology of the latex particles. Films are obtained upon coalescence of these latexes, and the surface composition of these films and their tensile properties are studied. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3927–3941, 2006

Key words: hybrid latex; acrylic copolymers; polyurethane; miniemulsion polymerization; seeded emulsion polymerization; kinetics; morphology; mechanical properties

INTRODUCTION

Waterborne coatings are being used in increasing frequency, and numerous efforts are still being made to improve their properties. The main products are based on acrylic or vinylic latexes from emulsion polymerization of the corresponding monomers, but polycondensates such as polyurethanes (PUs) or alkyd resins are also dispersed in water to produce waterborne coatings. Each class of products has advantages and disadvantages. Obviously, combinations of products of these two classes are expected to add their good properties without keeping their drawbacks.

Several trials toward this objective have been described during the last decade. A study by Hegedus and Kloiber[1] compared a set of so-called hybrid aqueous acrylic–PU dispersions to the basic compounds and their blends, showing the interest in the hybrids. However, the preparation of these hybrids was not described, except for references to a few patents. In the same year as the latter study, Okamoto et al.[2] pub-lished an article about blends of acrylic latexes and PU dispersions. The acrylic latex was a copolymer of ethylhexyl acrylate, methyl methacrylate (MMA), styrene (St), and acrylic acid, with or without a ketone-containing monomer, diacetone acrylamide (DAAM). The PU dispersion contained adipic acid, dimethylolpropionic acid (DMPA), and an excess of diisocyanate (DI). It was a chain-extended ether with a reactive hydrazine or a nonreactive piperazine. Then, the two dispersions were or were not crosslinked through specific interactions of the keto-hydrazine chemistry. The crosslinking reaction was followed by FTIR. Although this reaction could be observed even at room temperature, the mixed dispersions displayed good storage stability without crosslinking. In contrast, the crosslinked resulting films exhibited synergistic effects between the two polymers, including good solvent resistance, flexibility at low temperature, and good abrasion resistance. A similar approach with blends of modified crosslinkable systems was described in the field of alkyd resins.[3]

A few groups have published results about true hybrid acrylic–PU latexes. One typical approach was based on core–shell hybrid latexes.[4] Three different kind of hybrid latexes were described: A/U, U/A, and A/UgA. In these products, a PU was produced first from an ethyl acetate solution of polyester polyol reacted with isophorone DI (IPDI), which can be modified by DMPA. After neutralization of the acid, the

solution was poured into a large amount of water to cause phase inversion and water dispersion; further addition of adipic dihydrazide was carried out before the elimination of the solvent. To the polymer-containing dispersion were added the components of an acrylic copolymer, including DAAM, and polymerization was carried out (A/U type). The U/A type was obtained upon addition and polymerization in a solution of the component of the acrylic copolymer containing a rather high amount of acrylic acid before emulsification and elimination of the solvent. For the A/UgA type, the PU chains were end capped with hydroxyethyl methacrylate (HEMA) before dispersion in water. A core–shell morphology was obtained in the three cases, with a trend to have the modified PU in the shell. Crosslinking was obtained from the reaction of the hydrazide groups and the ketone groups, one of the components sometimes being added after the preparation of the latex, and then reacting during the formation of the film. Careful characterizations of the film surfaces were done and the adhesive properties were measured, showing improvements versus blends of latexes. A study of the structure of these hybrid emulsions was published more recently by the same group,[5] using ^{13}C-NMR, electron spectroscopy for chemical analysis, and contact angle measurements. They showed that the shell part of these core–shell latexes is preferentially oriented toward the surface layers of the dried films and the interface with plastic films when adhesion on these plastic films was tested. In a similar approach, a Korean team studied the emulsion polymerization of St[6] and MMA[7] in the presence of PU seed particles obtained upon polycondensation of IPDI, DMPA, and poly(propylene glycol) (PPG). The grafting efficiency of the acrylic monomer onto the PU was shown to be related to the amount of hard segments constituted of IPDI and DMPA via a transfer reaction on the NH moiety. The same researchers also published[8] a study on the chain extension of the neutralized PUs with similar structures by hexamethylene diamine using FTIR and GPC measurements. More recently,[9] the same team published a study of the influence of the degree of neutralization of the carboxylic acid of the seed on the kinetics of the emulsion polymerization of St. The rate of polymerization, average number of radicals per particle, and ability to solubilize pyrene molecules were shown to be dependent on the degree of neutralization, which varied between 85 and 110%. The explanation of these results lies in the state of aggregation of the PU seeds and their swelling behavior in water.

The subject was further treated by a Slovenian team, who carried out semibatch emulsion copolymerization of acrylic monomers from PU seed particles. The PU dispersions were commercial anionic polyester carbonate. In their first study,[10] the authors compared the hybrids resulting from the seeded emulsion copo-

lymerization with blends of the PU dispersion and acrylic latexes; they showed that the improved compatibility of the hybrids causes improvements of the chemical and mechanical properties. However, the main interest of this team seems to be in the kinetics of the seeded emulsion polymerization[11] and the influence of the various parameters (concentrations, nature of the monomers) on both the kinetics and the mechanism of the process. They stated that the final seeded hybrids do form structured particles.

Another interesting study was published by Zhang et al.[12] The PU that they used was a polycondensate of toluene diisocyanate, PPG, and DMPA, the NCO end groups of which being reacted with hydroxypropyl acrylate (HPA). They were used as seeds in the emulsion polymerization of MMA, initiated by sodium persulfate under soap-free conditions at 80°C. The influence of the sodium persulfate and MMA concentrations and the composition of the PU (DMPA, HPA) on the kinetics, particle size, and degree of crosslinking was studied. The mechanical properties of the cast films were strongly dependent on the composition of the seeds, the tensile strength being increased by the increase of both DMPA and HPA, at the expense of the elongation at break. Finally, phosphonated PU from condensation of a phosphonated polyester macroglycol, DMPA, and a DI was used after neutralization as a seed for the emulsion polymerization of a set of acrylic monomers.[13] The rheological properties of the latexes were studied and shown to exhibit Newtonian behavior, whereas contact angle measurements carried out on the cast films displayed good hydrophobicity.

A second and more recent approach to obtain hybrid latexes was published, which used miniemulsion polymerization of a solution of PU in acrylic monomers.[14] In the first study based on this approach, the PU was modified by end capping with an unsaturated linseed oil with alkenyl double bonds of low reactivity. Some retardation of the polymerization was observed, and limited grafting of the acrylic copolymer on the PU took place as well as a few percent crosslinking, but the majority of the double bonds were preserved for further curing reactions. We recently published a three studies based on the miniemulsion approach.[15–17] Our PUs were based on the reaction of IPDI with PPG, using butanediol (BD) as a chain extender. We initially studied[15] the basic kinetics of polymerization of the miniemulsions obtained through sonication of PU solutions in acrylic (or styrenic) monomers and demonstrated that the PU behaves as a good hydrophobe for the stabilization of the miniemulsion against Ostwald ripening. In our second study[16] the PU was end capped either with a methoxy group or a polymerizable moiety by reacting with either methanol or HEMA. In the second case, the hybrids resulting from the polymerization were

crosslinked and in stress–strain experiments on films from the latexes they showed elastomeric behavior, with a much lower elongation at break than the corresponding noncrosslinked materials. Finally, in our third study[17] we did a comparison of noncrosslinked materials with blends of the basic materials from the viewpoints of both the surface morphology of the films and their mechanical properties. We confirmed the better compatibility and better mechanical properties of the hybrids.

The purpose of this article is to compare the two approaches: seeded emulsion copolymerization and miniemulsion polymerization. A variety of PUs was prepared for the seeds and for the miniemulsions. The latter were based upon condensates of IPDI and PPG, with chain extension by BD. The PUs for the seeds were composed of condensates of IPDI, PPG, and DMPA, which were neutralized with triethylamine (TEA) and further chain extended by a diamine and in some cases also by BD. Some products were end capped with hydroxyethyl acrylate. The comparison was done in terms of polymerization kinetics, surface morphology, and mechanical properties.
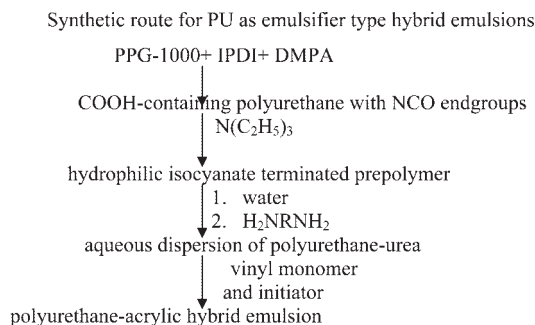
EXPERIMENTAL

Materials

PPG-1000 (Aldrich) was dried at 80°C and 0.1 mmHg for 4 h. 1,4-Butanediol (BDO, Aldrich) was purified by vacuum distillation. IPDI, dibutyltin dilaurate (DBTDL), MMA, butyl acrylate (BA), HEMA, benzoyl peroxide (BPO), BD, ethylene diamine (EDA), and DMPA were used as received from Aldrich. Sodium dodecyl sulfate (SDS, Acros) was used without further purification. Deionized water was used for all experiments.

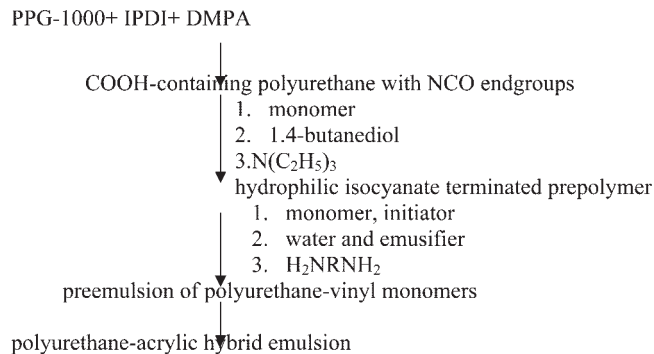### PU synthesis for miniemulsions

A 1000-mL four-necked flask with a separable glass reactor was used, which had a mechanical stirrer, thermometer, condenser, and nitrogen purge. The reaction was carried out in an N_2 atmosphere in a constant-temperature water bath. IPDI and DBTDL were first charged into the reactor and heated to 50°C with agitation, and PPG was dropped into the reactor while keeping the temperature at 80°C. The reaction proceeded over approximately 2 h. BD was subsequently charged into the reactor, and the reaction proceeded for another 4 h at 70°C upon obtaining the theoretical NCO/OH value. Then, the mixture was cooled to 50°C. After dissolution in ethyl acetate, end capping was carried out upon reaction of the solution at 60°C with methanol to produce a reference compound or with an excess of HEMA to obtain a reactive PU. Otherwise the crude product was dipped in water,

Synthetic route for PU as emulsifier type hybrid emulsions

PPG-1000+ IPDI+ DMPA

↓

COOH-containing polyurethane with NCO endgroups

$N(C_2H_5)_3$

↓

hydrophilic isocyanate terminated prepolymer

1. water
2. H_2NRNH_2

↓

aqueous dispersion of polyurethane-urea

vinyl monomer and initiator

↓

polyurethane-acrylic hybrid emulsion

Scheme 1 The sequence of operations for route I hybrids from PU seeds.

where it precipitated in fine particles that were soft enough to produce films.

PU synthesis for seeds

Route I

A 1000-mL four-necked flask with a separable glass reactor was used, which had a mechanical stirrer, thermometer, condenser, and nitrogen purge. The reaction was carried out in an N_2 atmosphere in a constant-temperature water bath. IPDI and DBTDL were first charged to the reactor and heated to 50°C with agitation, and then PPG and DMPA dissolved in N-methyl-pyrrolidinone were dropped into the reactor while maintaining the temperature at 80°C. The reaction proceeded over approximately 2 h. The mixture was cooled to 60°C and the carboxylic groups were neutralized with TEA. An aqueous dispersion was obtained by adding water under vigorous stirring. Chain extension was carried out with diethyl amine (DEA)/water for a period of 1 h. Route I to the PU precursor before the synthesis of the hybrid copolymer is illustrated in Scheme 1.

Route II

IPDI, PPG, DMPA, and DBTDL were poured into the reactor. After a 3-h reaction at 80°C, 7% of the monomer mixture was charged into the system. Then, BD was added and the mixture was allowed to react for another 2 h at 70°C. The system was neutralized with TEA at 60°C and cooled to 25°C. Scheme 2 illustrates this second route.

Route III

IPDI, PPG, DMPA, and DBTDL were poured into the reactor. After a 3-h reaction at 80°C, the desired amount of BD was added and reacted for 1 h. HEA was added and the system was allowed to react for 1 h at 70°C. Then, the system was neutralized with TEA at 60°C and cooled to 25°C. Chain extension was carried

PPG-1000+ IPDI+ DMPA

COOH-containing polyurethane with NCO endgroups
1. monomer
2. 1,4-butanediol
3. N(C₂H₅)₃
hydrophilic isocyanate terminated prepolymer
1. monomer, initiator
2. water and emusifier
3. H₂NRNH₂
preemulsion of polyurethane-vinyl monomers

polyurethane-acrylic hybrid emulsion

Scheme 2 Synthetic route II for the monomer as the solvent for prepolymer-type hybrid emulsions.

out with DEA/water for period of 1 h. Scheme 3 illustrates route III.

Miniemulsification of monomer solutions

Miniemulsions were prepared as follows: the desired amount of SDS was dissolved in about 300 g of deionized water. The BPO organophilic initiator was dissolved in PU dissolved in the monomer mixture of St, MMA, and BA. Then, the oil phase was added to the SDS solution and sheared for 12 min at 1000 rpm. The preemulsion was sonicated for 10 min at 95% output with a Branson ultrasonifier.

Polymerizations of miniemulsions

The monomer miniemulsion was transferred to a 1000-mL four-necked flask. The system was purged for 15 min with nitrogen and brought to the polymerization temperature. Approximately 30 g of sample were taken at intervals during polymerization. Monomer conversion was determined gravimetrically from these samples. The data for the average monomer particle sizes were obtained from the dynamic light scattering method, and the molecular weight measurements were carried out using size exclusion chromatography (SEC) from THF solutions. A Waters instrument and polystyrene standards were used to calibrate the elution volume scale.

Emulsions polymerizations from seeds

The PU–acrylate (PUA) hybrid emulsion was prepared by semibatch emulsion polymerization of acrylate monomers in the presence of a PU seed dispersion as an emulsifier. The same reactor used for the preparation of the PU dispersion was charged with an amount of aqueous PU dispersion and 7% acrylate monomers. In routes I and III the PU dispersion was allowed to swell overnight with this limited amount of monomers. Then, the system was purged for 15 min

with nitrogen and brought to the polymerization temperature. The preemulsion was made by dissolving SDS emulsifier in water, followed by a slow addition of the remaining monomers and azobisisobutyronitrile (AIBN) under constant stirring at 200 rpm. Then, the preemulsion was fed into the PU dispersion at a constant flow rate for 3 h. This feeding step is illustrated as the last step in Schemes 1–3. In route II the swelling step was omitted and instead a limited amount of monomers was allowed to polymerize so that the seed was already a hybrid latex with low solid contents.

Approximately 10 g of sample were taken at intervals during polymerization. Monomer conversion was determined gravimetrically from these samples. The data for the average monomer particle size were obtained from the dynamic light scattering method. The reported data represent an average of at least 10 measurements.
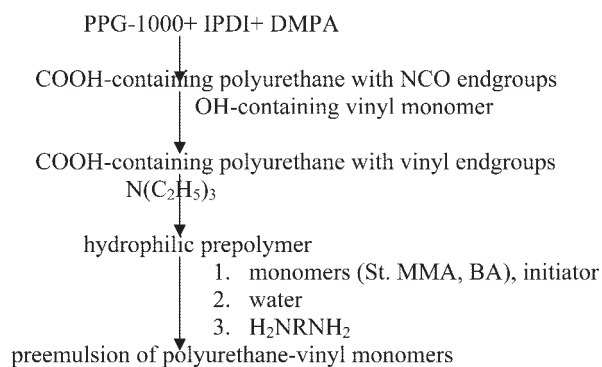
Polymer characterization

High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C. Spectra were obtained with a 5-mm QNP probe at 353 K from dimethylsulfoxide-d_6 (DMSO-d_6) solutions at 80°C. Chemical shift values were given in reference to internal tetramethylsilane. The SEC analysis of the same samples were obtained from solutions in dimethylformamide (DMF + LiBr) at 70°C.

Differential scanning calorimetry was carried out using a PerkinElmer Pyris 1 apparatus.

Films were prepared from dry casting at 20°C in a flat Teflon capsule to obtain a 0.75-mm homogeneous film.

The tensile tests were performed at ambient temperature using an Instron 8150 machine at a constant crosshead rate of 50 mm/min. The dumbbell-shaped samples were 2 × 15 mm (width × length). Nominal

PPG-1000+ IPDI+ DMPA

COOH-containing polyurethane with NCO endgroups
OH-containing vinyl monomer

COOH-containing polyurethane with vinyl endgroups
N(C₂H₅)₃

hydrophilic prepolymer
1. monomers (St, MMA, BA), initiator
2. water
3. H₂NRNH₂
preemulsion of polyurethane-vinyl monomers

Scheme 3 Synthetic route III for PU–acrylate graft-type hybrid emulsions.

TABLE I
Molecular Weights of Polyurethanes for Miniemulsions

Run	IPDI/PPG	BD	NCO/OH	End cap	M_n	M_w/M_n
PU 18F	3	1.5	1.2	OMe	5600	2.3
PU 18E	3	1.5	1.2	Acryl	5900	2.2
PU 18H	3	1.5	1.2	W	11100	5.4

strain (ε_n) and nominal stress (σ_n) are given by the relationships

$$\varepsilon_n = (L - L_o)/L_o \quad \text{and} \quad \sigma_n = F/S_o$$

where F is the applied force, L is the sample length during the test (L_0 at $t = 0$), and S_0 is the initial cross section. In the assumption of constant volume, true stress can be deduced from nominal data by

$$\varepsilon = \ln(\lambda) = \ln(1 + \varepsilon_n)$$

where $\lambda = L/L_0$ is the stretching ratio and

$$\sigma = F/S = (1 + \varepsilon_n)\sigma_n$$

The morphology of the films containing polystyrene was studied using TEM after staining the St units with uranyl acetate solutions. The composition of the film surface was determined using X-ray photoelectron spectroscopy (XPS) analysis. The XPS spectra were recorded using a VG ESCALB MK apparatus. The surface composition (atom %) of the hybrid polymer samples was determined by considering the integrated peak area of the C(1s) at 289 eV, O(1s) at 563 eV, and N(1s) at 404 eV and their respective sensitivity factors.

RESULTS AND DISCUSSION

Synthesis and structure of PU as hydrophobe for miniemulsions

When the PU after chain extension with BD was dipped into water and not end capped through a reaction with an alcohol, its molecular weight was increased by a factor of 2, as shown in Table I (three first lines). Before dipping, residual NCO groups remain that are able to react with water with elimination of CO_2 and formation of an NH_2 end group. If this reaction is not immediate, these new end groups can react further with other residual NCO groups, leading to urea bonds and further chain extension, thus explaining the nearly twofold increase of the number-average molecular weight (M_n) between the three first lines of Table I. In addition, the polymolecularity index (M_w/M_n) also increases by a factor of more than 2, depending on the local concentration of NCO and NH_2 end groups.

### Synthesis and structure of PU as seeds

A variety of PUs were prepared to use them as seeds for further emulsion copolymerization of the mixture of monomers. All of them contained IPDI (4 parts), PPG-1000 (1 part), and various amounts of DMPA. They were chain extended with EDA (and a few of them with BD). All were made hydrophilic upon neutralization of the carboxylic groups with stoichiometric amounts of TEA. Their composition and some structural data are reported in Table II.

The data in the last column of Table II were obtained from a quantitative analysis of the C=O region of the ^{13}C-NMR spectra. This region exhibited several peaks that are attributed to the C=O group from urea (signals between 157.3 and 159.7 ppm) and urethane (signals between 154.0 and 157.3 ppm). Urea and urethane groups are also characterized by their NH proton resonances found from 5 to 6.2 ppm for urea and from 6.2 to 7 ppm for urethane. The corresponding ^{13}C- and ^1H-NMR spectra for the precursor PU 7 are

TABLE II
Structure and Molecular Weights of PUs Used as Seeds

| Run	IPDI/PPG	BDO	DMPA (g)	EDA	NCO/OH	End cap	M_n	M_w/M_n	Urethane/urea
PU 5	4	0	0.9	0	2.1	NH_2	3,750	1.6	0.28
PU 7	4	0	0.9	2.1	2.1	NH_2	51,000	2.0	1.3
PU 9	4	0.77	0.9	1.33	1.5	NH_2	Gel		0.53
PU 11	4	0	0.9	1.33	1.5	HEA (1)	15,400	1.7	0.56
PU 12	4	0	0.6	2.4	2.5	NH_2	—	—	1.35
PU 13	4	0.77	0.6	1.33	2.4	NH_2	42,000	1.17	0.40
PU 14	4	0	0.6	1.33	1.5	HEA (2.2)	25,000	2.8	1.16

The acid groups are neutralized with equivalent amounts of triethylamine.
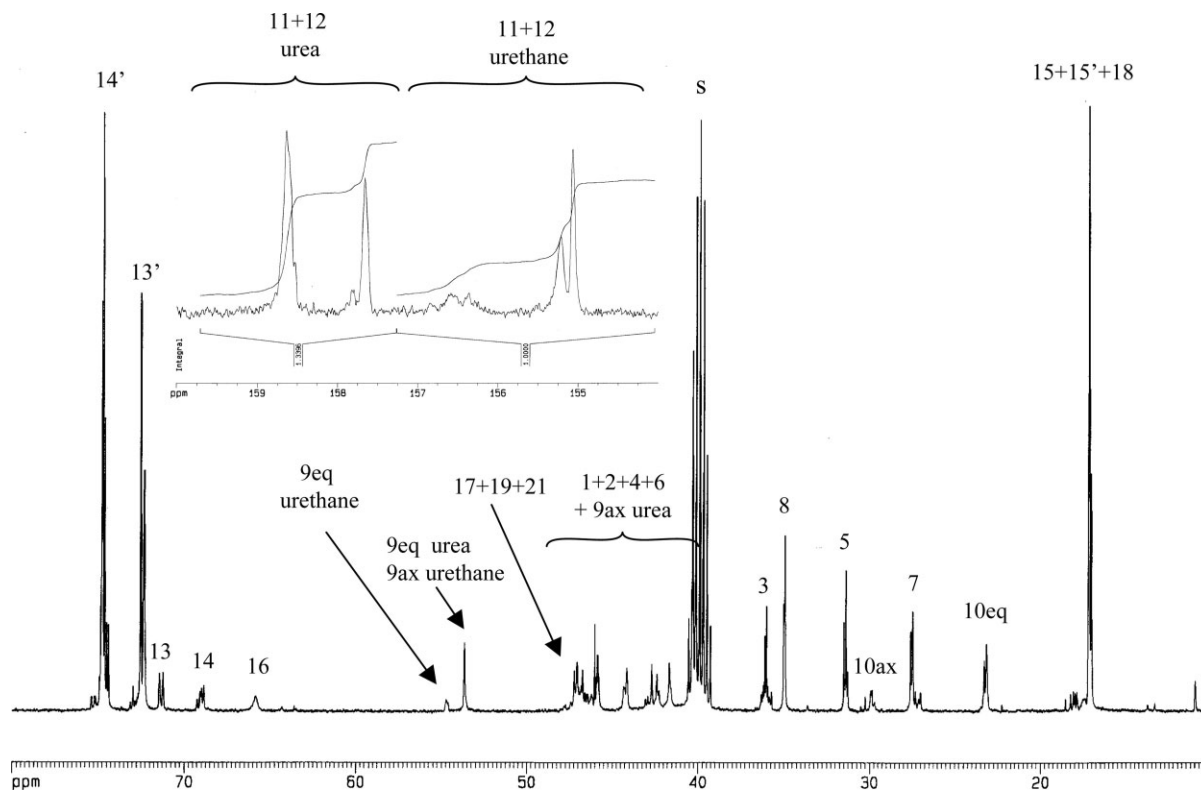
Figure 1 The ^{13}C-NMR spectrum of precursor PU 7 in DMSO-d_6 (s) at 353 K.
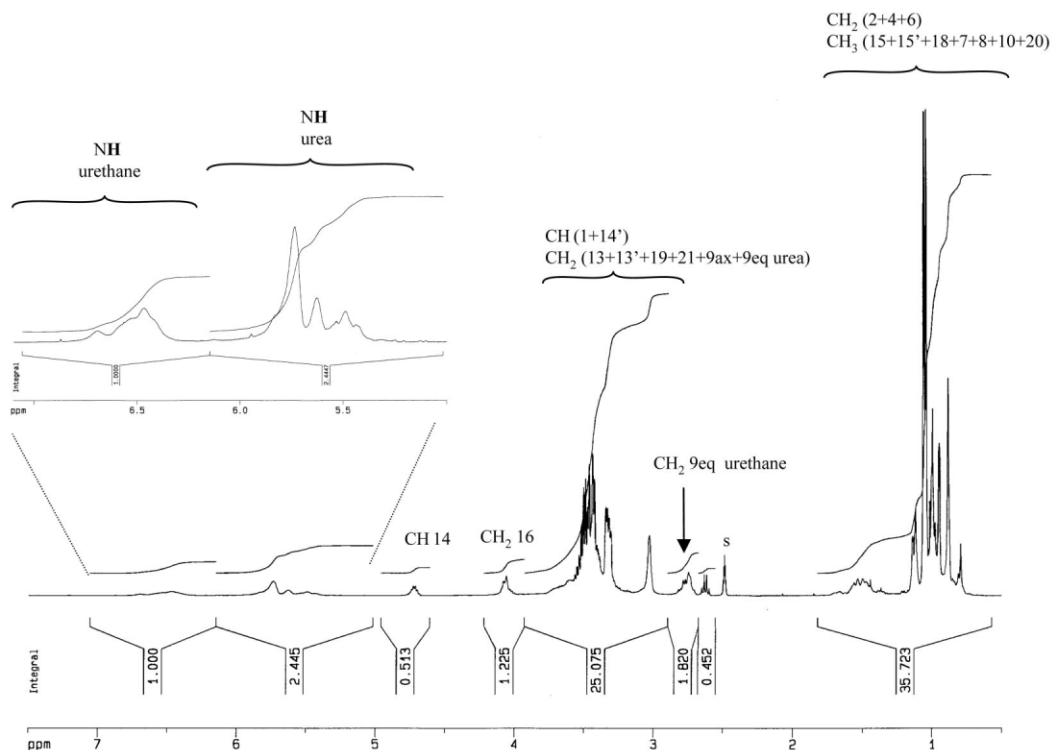
Figure 2 The ^{1}H-NMR spectrum of precursor PU 7 in DMSO-d_6 at 353 K. (inset) An enlargement of the 5.0–7.1 ppm region attributed to the NH proton resonances (s, protonated residue of DMSO-d_6).
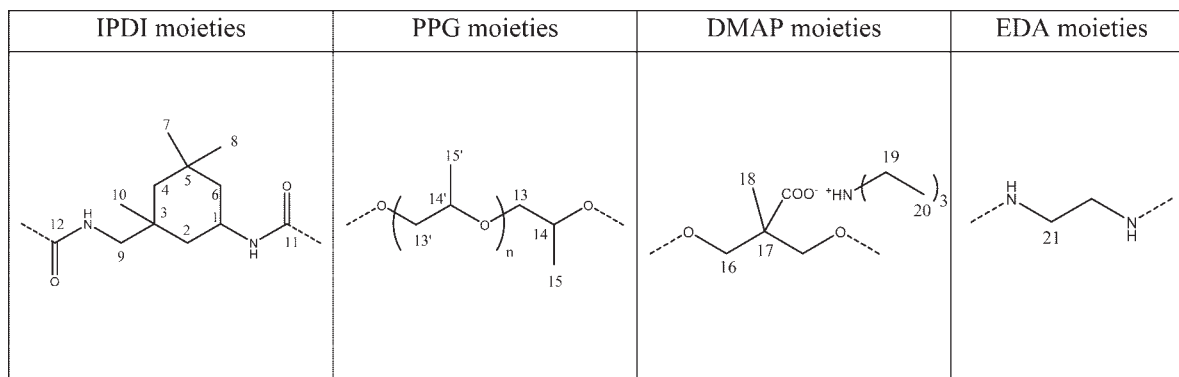
Figure 3 Proton and carbon labels used for NMR peak attribution in the case of precursor PU 7. Although the observed chemical shifts have few differences, the same labels are used for PPG, DMAP, and DEA moieties reacted either with a primary or a secondary isocyanate function. When it is not clearly noted in the spectra, the same labels are also used for IPDI moieties linked through urea or urethane functions.

shown in Figures 1 and 2, respectively. Assignment of both ^{1}H and ^{13}C resonances were from literature values[18] and from NMR spectra of model compounds especially prepared by reacting IPDI with PPG, DMAP, EDA, and BDO. Corresponding proton and carbon labels are summarized in Figure 3.

The assignments of the NMR bands were obtained from the literature[18] or from model compounds especially prepared (e.g., PU 5) by reacting a mixture of IPDI, PPG, and DMAP with an excess of OH groups and without chain extenders (see Fig. 3).

SEC analyses were carried out in DMF with LiBr at 70°C. However, because of difficult solubilization, some samples may be fractionated upon passing through the filter protecting the column. The lack of solubility seems to be due to the salt character of the neutralized acids. Thus, the molecular weight data may be not totally reliable.

Polymerization of miniemulsions

These polymerizations have been thoroughly described in our previous articles.[15–17] Therefore, we only mention a few data about those hybrid latexes that will be discussed further for a comparison of the polymerization kinetics and the mechanical properties

of films from these polymers. These data are reported in Table III.

Emulsion polymerizations from PU seeds

Three sets of hybrid copolymers were prepared using the PU precursors of Table II and following routes I, II, and III. The recipes used for these syntheses are given in Table IV.

Although the latexes prepared using routes I and II are soluble polymers, those from route III are more or less crosslinked. Some of the structural data for these hybrid polymers are reported in Table V.

Comparison of polymerization kinetics (emulsion vs. miniemulsion)

This comparison is not straightforward, because the initiators are different. In the case of miniemulsion BPO is used at 75°C whereas for seeded emulsion polymerizations AIBN is used at 80°C.

The conversion curves of the whole monomers for the terpolymerization St/MMA/BA (30/30/40) are shown in Figure 4 for the overall conversion starting from monomer solutions of PU with different end groups, either reactive (methacryl) or nonreactive

TABLE III
Structural Data of Hybrids Prepared Using Miniemulsion Polymerization

Hybrid	PU	End cap (%)	PU (%)	St (%)	MMA (%)	BA (%)	M_n	M_w/M_n	M_x
PUA 88	18H	NH$_2$	60	0	60	40	38,3000	2.7	—
PUA 89	18F	OMe	60	0	60	40	49,3000	2.6	—
PUA 96	18	Acryl	60	0	60	40	—	—	1,650
PUA 135	18F	Ome	60	30	30	40	—	—	—
PUA 136	18E	Acryl	60	30	30	40	—	—	1,400
PUA 137	18H	NH$_2$	60	30	30	40	—	—	—

TABLE IV
Recipes for PU-Acrylate Hybrid Emulsion

Run	DMPA (%)	End group	PU (g)	St (g)	MMA (g)	BA (g)	Emulsifier (g)	Water (g)	Route
PUA 101	6.2	NH_2	100	30	30	40	1	466.7	I
PUA 103	6.2	NH_2	100	30	30	40	4	466.7	II
PUA 104	6.2	Acryl	100	30	30	40	1	466.7	III
PUA 201	6.2	NH_2	100	10	10	13.3	0.3	310.3	I
PUA 203	6.2	NH_2	100	10	10	13.3	1.2	310.3	II
PUA 204	6.2	Vinyl	100	10	10	13.3	0.3	310	III
PUA 301	4.2	NH_2	100	30	30	40	1	466.7	I
PUA 303	4.2	NH_2	100	30	30	40	4	466.7	II
PUA 304	4.2	Acryl	100	30	30	40	1	466.7	III

Routes I–III are PU as are emulsifier-type hybrid, monomer as a solvent for prepolymer-type hybrid, and PU–acrylic graft-type hybrid emulsion polymerizations, respectively.

(NH_2 or OCH_3). The corresponding evolution of particle sizes is displayed in Figure 5.

Whatever the end group of the PU, the kinetics are very similar with an acceleration period followed by a deceleration period. The particle sizes are also not very dependent on the end groups of the PU; they tend to decrease during the acceleration period and then remain stable. There is probably some renucleation process during that acceleration period. However, the stability of the particle sizes, which is not very different from the initial monomer droplets, tends to support the idea that, whatever their composition, the PUs are good hydrophobe stabilizers of the miniemulsions of their monomer solutions, a conclusion already reported in previous works.[14–17]

In the case of the seeded emulsion polymerizations, using the modified PU particles as seeds, Figure 6 shows that the conversion kinetics are almost independent of the route followed. The main difference results from the amount of emulsifier used in the recipe. Run 103 is slightly more rapid than runs 101 and 104 because this amount was higher. In fact, the evolution of the particle size (Fig. 7) is rather different in run 103 compared to the two other runs. In run 103, the size increases smoothly whereas it remains constant for about 30 min in the two other cases before a rather sudden increase. There is possibly some floccu-

lation process because of the smaller amount of surfactant used.

The evolution of the number of particles is shown in Figure 8, which deserves comments because the behavior in the case of run 103 is very different from the other two runs. The particle number for run 103 remains fully constant. In the two other cases, it goes to a maximum after an initial renucleation period; then there is a rather important limited flocculation resulting in a rather low particle number, which seems to correspond to the sudden increase of the particle size.

In the first period the particle size seems to remain almost constant, but the particle number is strongly increased. However, this apparent contradiction can be explained because the dynamic light scattering method is much more sensitive to the largest particles and practically does not see the small particles recently nucleated. These particles become apparent when they begin to flocculate. This flocculation event is retarded in route II, where a larger amount (4 times more) of emulsifier is engaged. Another difference that can be observed lies in the interface between the aqueous phase and the particles. In routes I and III the interfacial region involves mainly the PU, which plays the role of emulsifier; at the beginning of the polymerization this interfacial layer may hinder the entry of

TABLE V
Structural Data of Hybrids Prepared Using Seeded Emulsion Polymerization

| Hybrid	PU	End cap	PU (%)	St (%)	MMA (%)	BA (%)	M_n	M_w/M_n	M_x
PUA 101	7	NH_2	100	30	30	40	71,000	2.5	—
PUA 103	9	NH_2	100	30	30	40	Gel	—	—
PUA 201	7	NH_2	100	10	10	13.3	—	—	—
PUA 203	9	NH_2	100	10	10	13.3	39,000	2.4	—
PUA 301	12	NH_2	100	30	30	40	—	—	—
PUA 303	13	NH_2	100	30	30	40	50,000	2.8	—
PUA 104	11	HEA	100	30	30	40			900
PUA 204	11	HEA	100	10	10	13.3			700
PUA 304	14	HEA	100	30	30	40			1,100
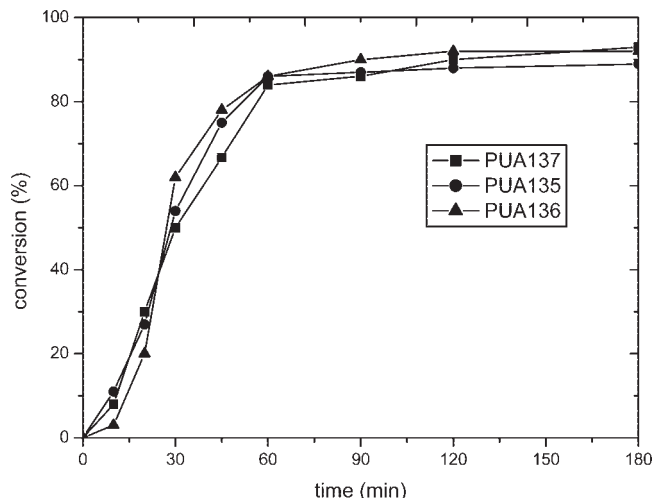
Figure 4 The evolution of the conversion in the PU–acrylate hybrid miniemulsion polymerization stabilized by PU with different end groups as hydrophobes at 75°C and initiated by BPO: (■) —NCO, (●) —OCH$_3$, and (▲) methacryl. The PU molar ratios (w/w) are 3/1/1.5 IPDI/PPG-1000/DBO and 100/30/30/40 PU/St/MMA/BA.

the oligomeric radicals coming from the water phase, as shown schematically in Figure 9.

In contrast, for route II the PU seed is already enlarged and the interfacial region involves a mixture of SDS and PU as the emulsifier, which makes the entry of the oligoradicals easier.

In the case of route I, Figure 10 illustrates the influence of the PU/monomer ratio and the amount of DMPA on the polymerization kinetics with the overall and instantaneous conversions. The polymerization
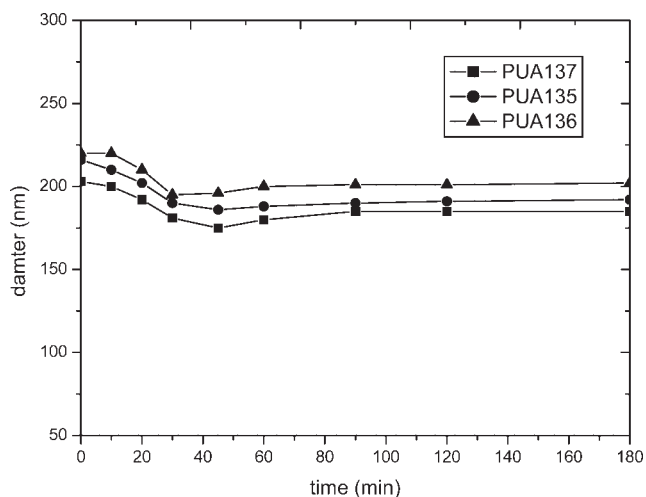
Figure 5 The evolution of the average diameter in the PU–acrylate hybrid miniemulsion polymerization stabilized by PU with different end groups as hydrophobes at 75°C and initiated by BPO: (■) —NCO, (●) —OCH$_3$, and (▲) methacryl. The PU molar ratios (w/w) are 3/1/1.5 IPDI/PPG-1000/DBO and 100/30/30/40 PU/St/MMA/BA.
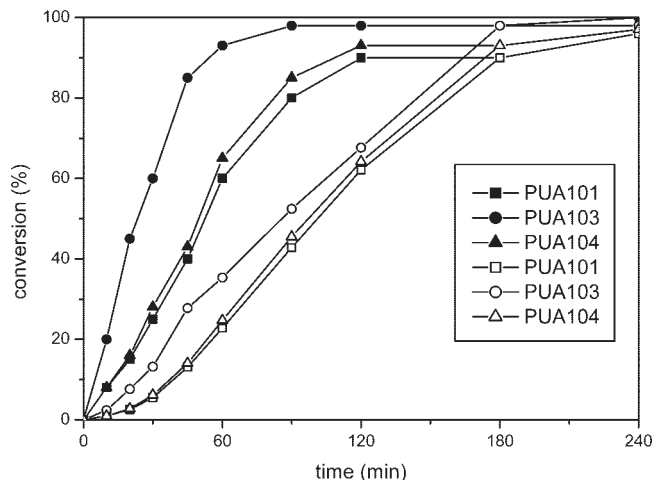
Figure 6 The influence of different polymerization methods on the (□, ○, △) overall and (■, ●, ▲) instantaneous conversion of the hybrid emulsion while employing a 100/100 PU/monomer weight ratio.

rates are decreased not only when the amount of DMPA is decreased from 6.2 to 4.2% (run 301) but also when the relative amount of monomers was decreased by a factor of 3 (run 201). The corresponding influence of these two parameters on the particle sizes is shown in Figure 11.

In both figures it can be seen that the amount of DMPA shows the strongest effect. For route III, similar effects can be observed for the rates, particle sizes, and particle numbers. Figure 12 provides the number of particles for the three experiments where route III was followed.

In the case of route II, the effect can be observed only on the particle size, not for the polymerization rates, and only small effects for the particle numbers. Figures 13 and 14 illustrate these features.
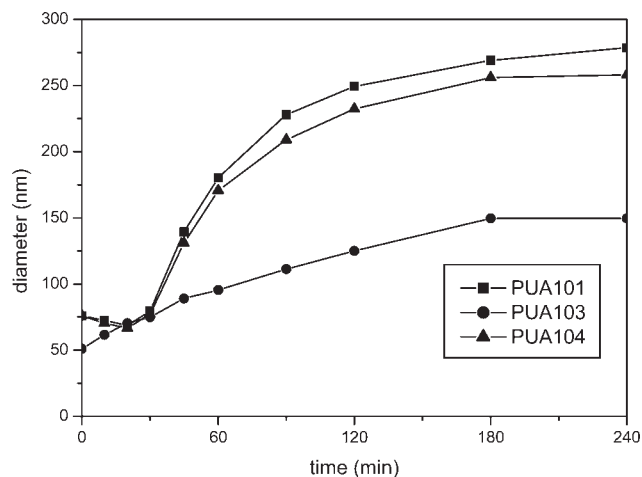
Figure 7 The influence of different polymerization methods on the average diameter of the hybrid emulsion while employing a 100/100 PU/monomer weight ratio.
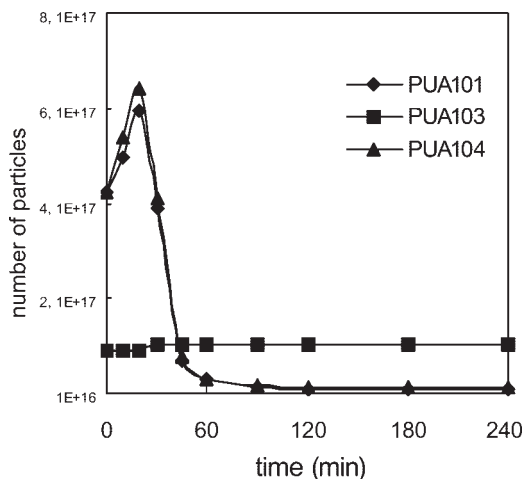
Figure 8 The influence of different polymerization methods on the number of particles while employing a 100/100 PU/monomer weight ratio.

Morphologies studied by TEM

The TEM images of latexes from miniemulsion polymerizations do not show any sign of phase separation inside the particles, as expected. By contrast, the particle size distribution is quite broad. In the case of seeded polymerizations, it depends on the route followed. Using route I, an inverted core–shell morphology is observed, as shown in Figure 15(a). Here, the PU seed is working more as a surfactant than as a seed. The copolymer produced during the second step emulsion polymerization can be vizualised as the core of the black particles, whereas the clearer PU is obviously at their surface.

Following route II leads to a quite different morphology as observed from Figure 15(b). Here, the particle seems to be an assembly of black and white domains, where somewhat more white PU domains are seen near the external part of the whole particle. The main difference between route I and route II lies in the fact that rather large amounts of SDS are used in the second step polymerization; then, in the added emulsion the SDS concentration is larger than the critical micelle concentration and there is micellar nucleation in addition to the radical capture by the seed
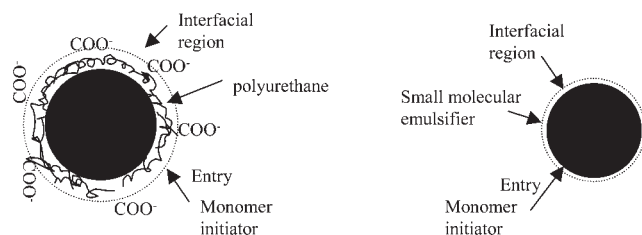

Figure 9 A schematic depiction of how the PU may increase the hindrance of the entry of the monomer and initiator.
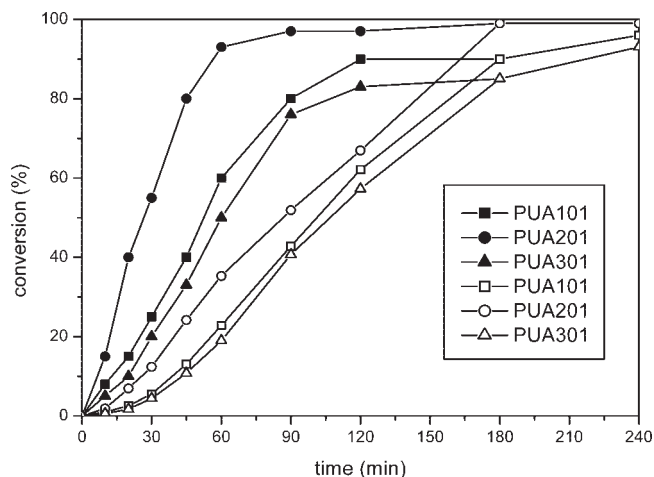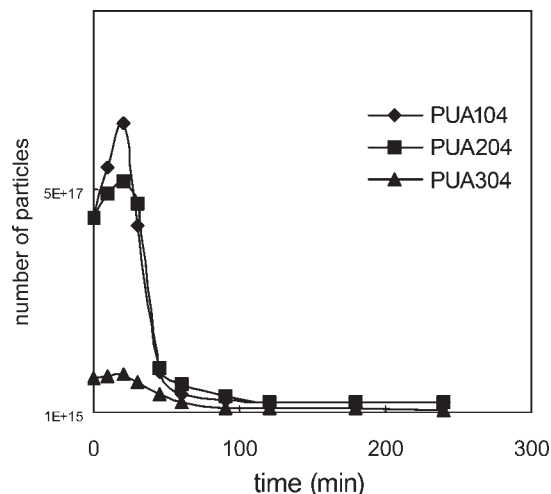

Figure 10 The influence of the DMPA content and PU/monomer weight ratio on the ($\square$, $\bigcirc$, $\triangle$) overall and ($\blacksquare$, $\bullet$, $\blacktriangle$) instantaneous conversion of PU as an emulsifier-type hybrid emulsion polymerization with AIBN as the initiator at 80°C.

particles. This micellar nucleation produces purely acrylic particles that agglomerate onto the seeded particles, without covalent links. Moreover, in route II the seed particles are not pure PU, but already contain acrylic copolymers in small amounts (7%)

In the case of route III, Figure 15(c) shows that the situation is not very different from route I. The procedures are close in terms of surfactant, the main difference being that the PU chain ends are now functionalized with acrylic reactive moieties. Thus, the latexes are more or less crosslinked and inside the particles the mobility of the chains is strongly reduced. The migration of the hydrophilic PU toward the particle surface is reduced, so that the amount of PU phase at the interface is less than for route I.
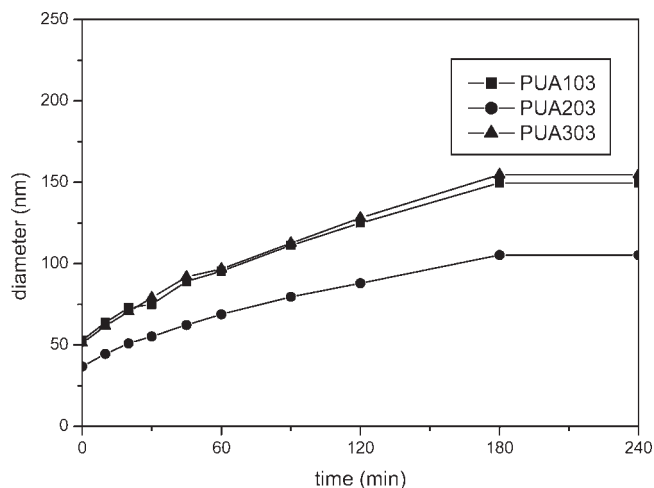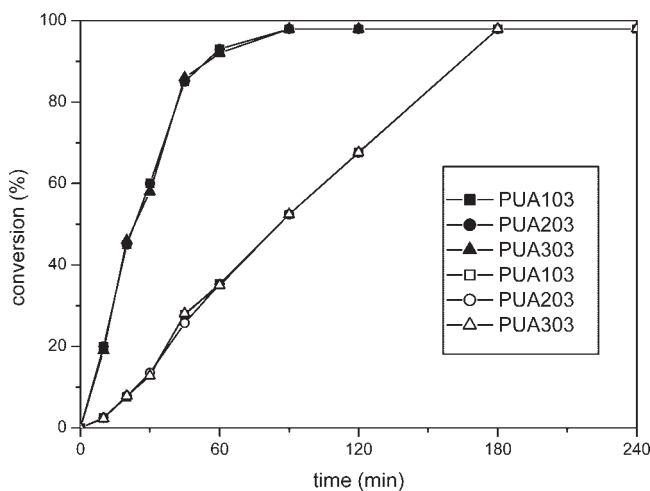

Figure 11 The influence of the DMPA content and PU/monomer weight ratio on the average diameter of PU as an emulsifier-type hybrid emulsion polymerization.
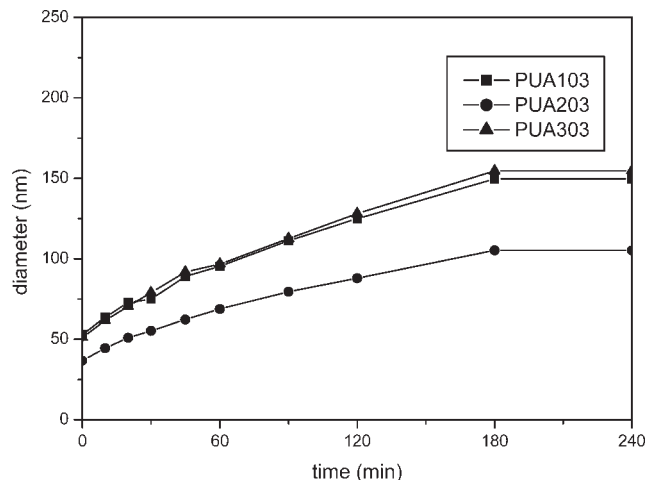
Figure 12 The influence of the DMPA content and PU/monomer weight ratio on the number of particles of PU–acrylic graft-type hybrid emulsion polymerization.
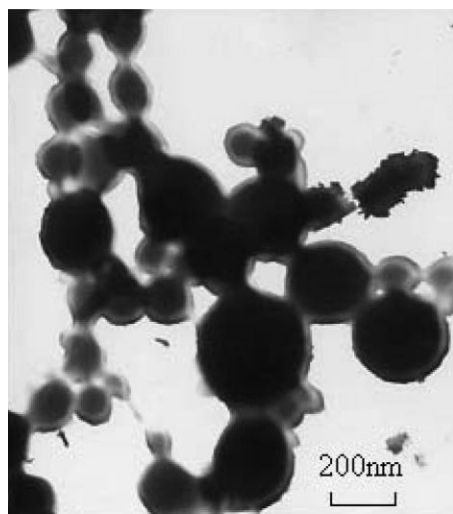

Figure 14 The influence of the DMPA content and PU/monomer weight ratio on the average diameter of the monomer as a solvent for prepolymer-type hybrid emulsion polymerization.

The TEM images corresponding to films from hybrid latex PUAs 101, 103, and 104 are shown in Figure 16(a–c). As expected from Figure 14, the most important degree of phase separation is observed for PUA 103 from route II, whereas the most homogeneous surface corresponds to PUA 104 containing crosslinks due to the functional PU chain ends in route III.

XPS analyses of the film surfaces were carried out to confirm these features. The corresponding data are reported in Table VI. The table compares the composition of the surface layer of the films to the compositions of the bulk materials an its PU component. An important difference can be observed between the materials from the miniemulsion polymerization (PUAs 89 and 96) and those from the seeded emulsion poly-

merization (PUAs 101, 103, and 104), at least in terms of nitrogen contents.
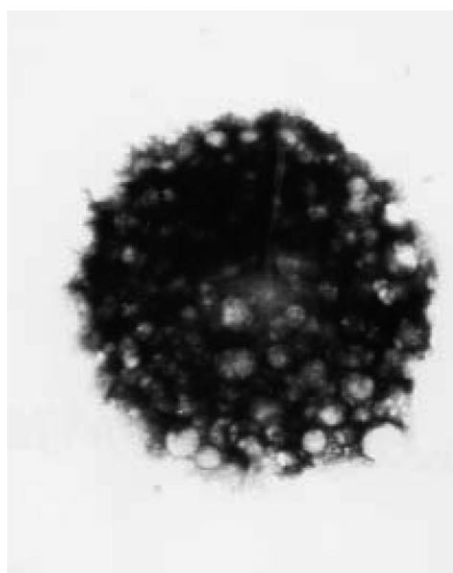
For seeded emulsion polymerization the composition is close to that of the PU, whereas in the case of miniemulsion polymerization it is closer to that of the bulk material. This means that the PU component is preferentially located near the surface of the film coming from the seeded emulsion polymerization, and this conclusion agrees with that deduced from the microscopic analysis. There is an exception to this statement for PUA 88 from miniemulsion polymerization. In this product, the excess of NCO groups, after chain extension with BD, is reacted with water. Such a reaction causes not only further chain extension, as already discussed, but also hydrophilic amine chain ends, which tend to locate the PU materials, which are poorly grafted onto the acrylic copolymer near the particle surface.
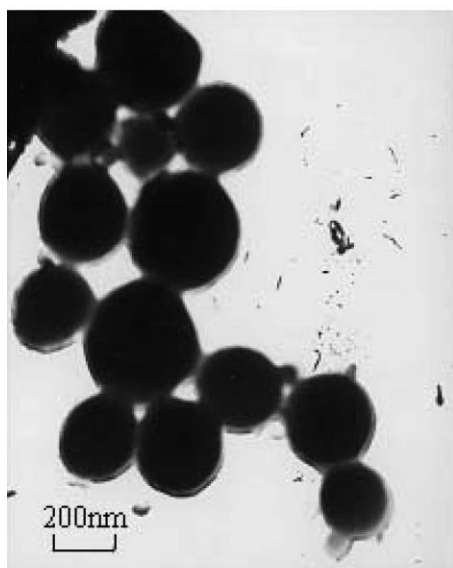
Comparison of mechanical properties

This comparison was done on the basis of the stress–strain properties. It was not straightforward, because the copolymer compositions were not identical. In films from latexes prepared using miniemulsion polymerization, there were binary copolymers containing 60 parts MMA and 40 parts BA. In the seeded emulsion polymerization there were ternary copolymers containing 30 parts St, 30 parts MMA, and 40 parts BA. However, because the glass-transition temperature (T_g) of PMMA is close to the T_g of polystyrene, it may be expected that these copolymers have similar mechanical properties, provided their molecular weight distributions are not too different. Another significant difference resides in their PU contents, which is 60

Figure 13 The influence of the DMPA content and PU/monomer weight ratio on the (□, ○, △) overall and (■, ●, ▲) instantaneous conversion of monomer as solvent for prepolymer-type hybrid emulsion polymerization.

(a)

(b)

(c)

parts PU for 100 parts binary copolymer in the miniemulsion polymerization (PUAs 88, 89, and 96) and 100 parts PU for 100 parts ternary copolymer in the seeded emulsion polymerization (PUAs 101, 103, and 104). Furthermore, the compositions of the PUs are also obviously different.

A comparison was carried out for those materials having the closest composition for the miniemulsion polymerization (PUs 88, 89, and 96) and for the seeded emulsion polymerization (PUAs 101, 103, and 104.

Figure 17 displays the stress–strain curves of PUA 101 for the seeded emulsion polymerization process and of PUA 88 and PUA 96 for the miniemulsion process. Elastomeric behavior is observed in the latter case, with what may be called a yield stress and some hardening upon elongation, the elongation at break being limited, especially for PUA 96, which is a crosslinked material. In the former case (seeded emulsion polymerization), a more regular decrease of the modulus is observed, as well as a much higher elongation.

In the case of miniemulsion polymerization, we previously reported[16] on a parametric study of the influence of structural features of the hybrid latexes on the mechanical properties of their films. We showed the effects of the nature of the PU chain ends (reactive or nonreactive in the polymerization process), as well as the PU molecular weight of the PU contents and the copolymer composition. Here, we report the effect of the structural parameters on the seeded emulsion polymerization. Figures 18 and 19 show the effects of the PU/copolymer ratio and the DMPA contents of the PU, respectively.

When the ratio between the PU and copolymer is decreased (Fig. 18), the initial modulus is much higher, a clear yield stress is apparent (PUA 103), upon elongation some hardening takes place, and the elongation at break is slightly smaller. In contrast, when the DMPA contents of the PU is lower (Fig. 19), the mechanical properties are decreased (smaller modulus and smaller elongation at break.

Finally, the route followed to prepare the hybrid latexes has important consequences on the mechanical properties of the films. In route II the seed particles are already hybrid latexes, containing 7% acrylic copolymer. Figure 20 compares the stress–strain curves for routes I and II with the same DMPA contents but two different PU/copolymer ratios, namely, 1/1 for PUA 101 (route I) and PUA 201 (route II) and 3/1 for PUA 103 (route I) and PUA 203 (route II).

The differences observed for the two materials prepared following route I almost disappear when route

Figure 15 TEM images of hybrid latex particles of seeded emulsion polymerization following (a) route I for PUA 101, (b) route II for PUA 103, and (c) route III for PUA 104.
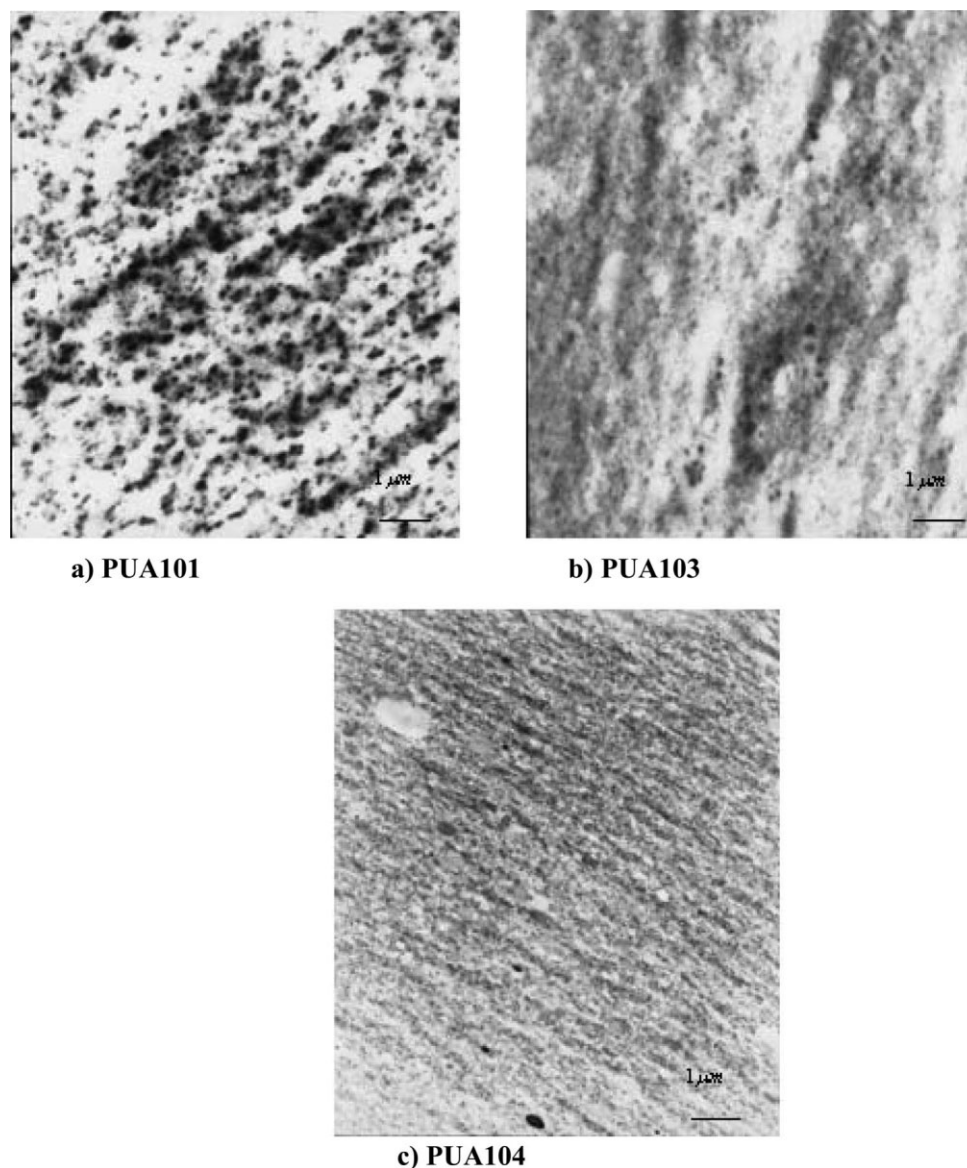
Figure 16 TEM images of the surface of films obtained from hybrid seeded emulsion polymerization following (a) route I for PUA 101, (b) route II for PUA 103, and (c) route III for PUA 104.

II is followed Only some difference of elongation at break remains. It is likely that the hybrid seed allows the production of much more homogeneous materials.

Figure 21 shows the curves obtained in the cases where the PU chain ends involve an acrylic reactive moiety. Upon polymerization in the presence of

TABLE VI
XPS Analysis of Composition of Surface of Films

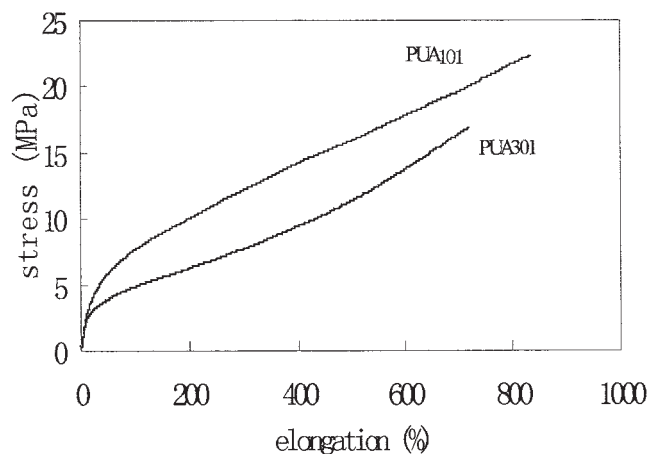| Material	C (%)			O (%)			N (%)		
	Surface	Bulk	PU	Surface	Bulk	PU	Surface	Bulk	PU
PUA 88	71.1	74.1	73.8	24.8	24.1	22.2	2.9	1.8	4.4
PUA 89	73.5	73.8	73.8	24.5	24.6	21.4	2.0	1.7	4.7
PUA 96	71.2	73.8	73.3	25.9	24.4	22.2	2.9	4.8	4.5
PUA 101	68.6	77.9	72.6	24.3	18.0	19.0	7.1	4.1	8.4
PUA 103	72.0	78.2	73.2	22.6	18.2	19.4	5.4	3.6	7.4
PUA 104	71.5	77.8	72.5	23.0	18.7	20.5	5.5	3.4	6.9
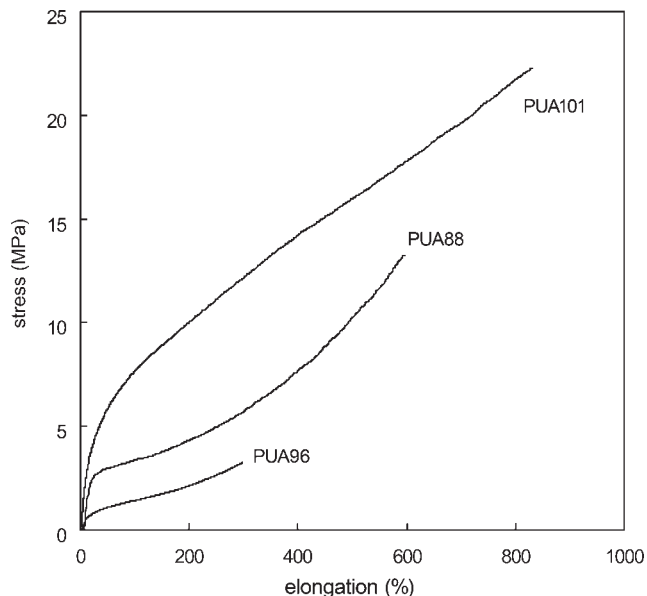
Figure 17 Stress–strain curves comparing the process for seeded emulsion polymerization (PUA 101) and miniemulsion polymerization (PUAs 88 and 96).

acrylic monomers, these hybrid materials are expected to be crosslinked. Such crosslinking causes an important decrease of the elongation at break in the case of miniemulsion polymerization (compare PUA 88 and PUA 96, Fig. 17). As shown in Figure 21, the same effect is observed upon following route III instead of route I. However, the crosslinking effect in route III is causing an important increase of the modulus, yield stress, and some hardening upon elongation. In contrast, Figure 22 shows the same effects of the structural parameters for route III as for the other routes.
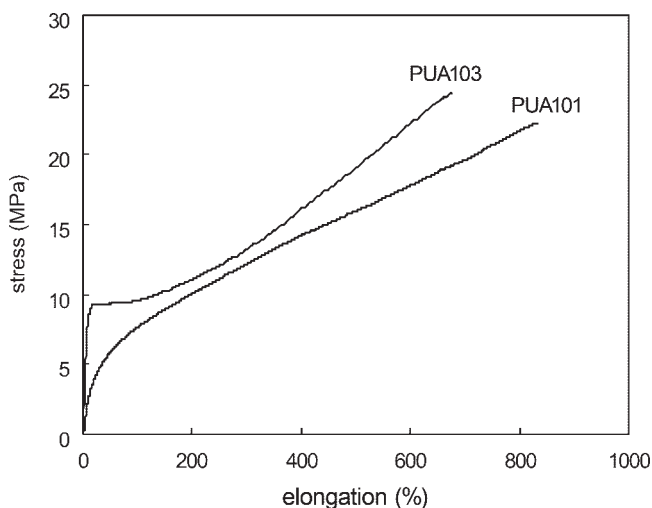

Figure 18 Stress–strain curves for materials from seeded emulsion polymerization with PU/copolymer ratios of 1/1 for PUA 101 and 3/1 for PUA 103.

Figure 19 Stress–strain curves for materials from seeded emulsion polymerization with 6.2% DMPA in PUA 101 and 4.2% DMPA in PUA 301.

CONCLUSION

Two main routes can be followed for the preparation of hybrid latexes containing both an acrylic polymer and a PU. These two routes are miniemulsion polymerization, in which a PU is dissolved in a mixture of acrylic monomers before dispersion and then polymerization, and a seeded emulsion polymerization of the acrylic monomers, using a PU latex as a seed.
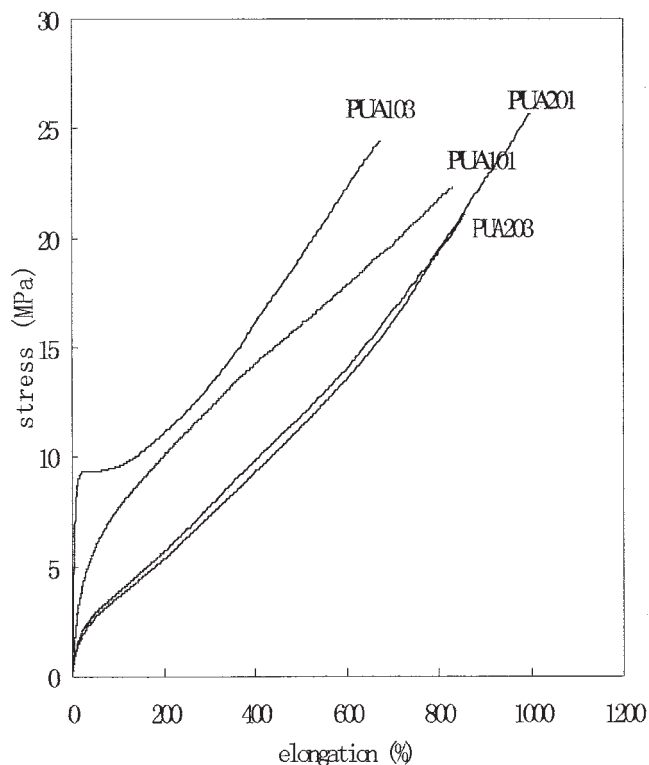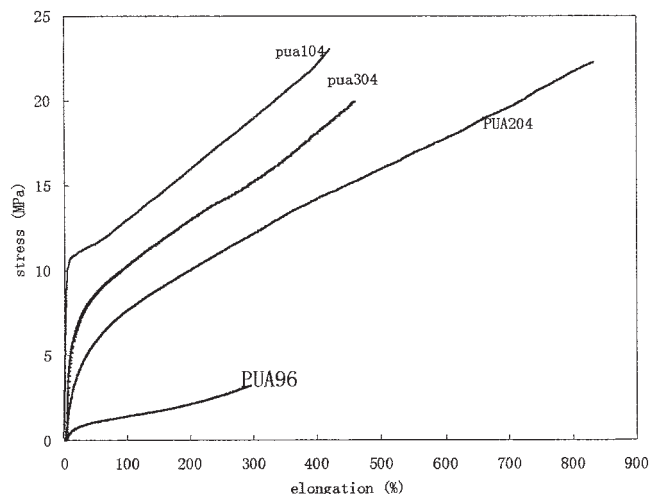

Figure 20 Stress–strain curves of films prepared using hybrid latexes following routes I (PUAs 101 and 103) and II (PUAs 201 and 203).
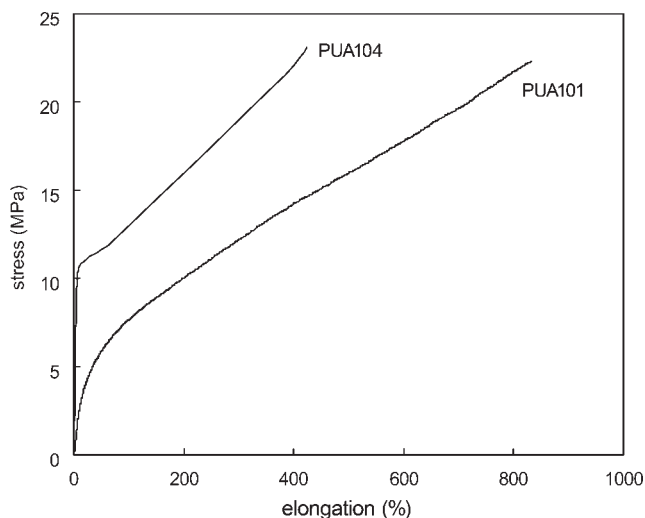
We followed the first route in our previous articles.[15–17] Here, we compared these two routes. The PU from the condensation of IPDI and PPG was modified by including DMPA in the recipe after polycondensation and chain extension using dimethyl amine and (or) BD (instead of BD only). The acid groups of DMPA were finally neutralized with stoichiometric amounts of TEA, so that, upon precipitation in water, the modified PU could be stabilized as a latex with small particles. These particles were then used as seed particles in the emulsion polymerization of a mixture of acrylic monomers. The composition of the mixture was chosen so that the final latex was film forming at room temperature. A comparison of these two routes was done concerning the polymerization kinetics, the development of the particle sizes, the morphology of the latexes, and the film morphology and their mechanical properties.

There were no important differences in the polymerization kinetics, because the polymerizations of the acrylic monomers were easily completed. Of course, differences were observed in the particle sizes because, in the miniemulsion route, the particle sizes of the initial droplets were always close to those of the final polymer particles, whereas the sizes of the seeded polymerizations did follow the characteristic changes of a classical emulsion polymerization, depending strongly on the nature and the amount of the emulsifiers used in the recipe.

In both cases, the hybrids were rather homogeneous materials, especially when they were crosslinked. However, because of differences in the composition of the PUs used in the two routes, it was quite difficult to compare the mechanical properties of the films. In addition to the differences in their composition, in the case of the seeded latexes, a reinforcing ionomer effect may exist, even if the cations are quaternary ammonium, instead of metal cations. In order to obtain a better comparison, some work is now in progress in

Figure 22 Stress–strain curves of two films using latexes prepared following routes I (PUA 101) and III (PUA 104).

our laboratories to produce acrylic–PU hybrids from miniemulsions using a DMPA containing PU.

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Figure 21 Stress–strain curves for films from hybrid latexes with acrylic PU chain ends.