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High Molecular Weight Polyurethane and Polymer Hybrid Particles in Aqueous Miniemulsion

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ABSTRACT: The polycondensation of isophorone diisocyanate (IPDI) with dodecanediol has been performed in aqueous miniemulsion in order to obtain hydrophobic polyurethane dispersions. The influence of several factors, such as temperature, surfactant, and catalyst, on the molecular weight has been studied in detail. It has been found that the use of hydrophobic organo-tin catalysts, a solvent of the polyaddition medium, or an off-stoichiometric ratio of the isocyanate and the diol component permits to considerably increase the molecular weight of the polymer. It is also shown that hybrid polymer nanoparticles based on polystyrene/polyurethane (PS/PU) or poly(butyl acrylate)/polyurethane (PBA/PU) can been synthesized using a one-pot procedure.

Introduction

Aqueous polyurethane (PU) dispersions are widely used for applications such as adhesives and coatings of various materials, e.g., textiles, metals, plastics, and wood.[1] Their films show an excellent elasticity and abrasion resistance and a superior low-temperature impact resistance.

Since isocyanate compounds are sensible to water, it is easier to synthesize polyurethanes in an organic system. Therefore, in the literature, polyurethane aqueous dispersions are almost exclusively obtained in a two-step procedure. In the first step, a polyurethane prepolymer is prepared in a nonaqueous system, which is then in a second step dispersed in water.[2] Recently, it was shown that hydrophobic polyurethane dispersions could be synthesized in water in a one-step procedure using the miniemulsion process.[3] Miniemulsions consist of stable small droplets which are obtained by intense shearing of a system containing a hydrophobic dispersing phase (the monomer), water, a surfactant, and a hydrophobe, a component which suppresses the mass exchange between the different oil droplets, the Ostwald ripening, by osmotic forces.[4,5] Polymerization of these stable monomeric droplets leads to particles which ideally keep their size.[6] For the preparation of polyurethane dispersions, a miniemulsion of hydrophobic diol and diisocyanate compounds is prepared and polymerized. During the polyaddition, the large amount of water surrounding each droplet can lead to reactions of the isocyanate with water, which disturbs the stoichiometry between the isocyanate and the hydroxyl component, resulting in a decrease of the molecular weight. To obtain polyurethane of high molecular weight, the reaction between isocyanate and hydroxyl (chain extension) and the reaction between isocyanate and water (foaming reaction) have to be well controlled.

The achievement of particles with high molecular weight polyurethane is obviously a first prerequisite for further applications. However, to improve the properties, such as mechanical stability, solvent and chemical resistance, and toughness, of an individual polyurethane system even more and to reduce costs, mixtures with polyacrylic system can be used. Blending a polyacrylic dispersion and a PU dispersion often leads to films of lower quality, which is attributed to a low compatibility of both components. Therefore, the formation of hybrid particles where each particle contains both polymers leads to a better mixing of both components.[7] The synthesis of such hybrid emulsions can help to solve the problem of homogeneity by thus allowing to combine suitably the properties of both polymers.

There are several examples of syntheses for polyacrylic−polyurethane hybrid dispersions,[8−11] but in all cases the polyurethane part was prepared in organic solvents and was later emulsified with an acrylic monomer. Moreover, for a better dispersion of the polyurethane in water, this polymer often bears water-soluble moieties. Here, it is however desired to produce a hydrophobic polyurethane together with an acrylic or styrenic polymer in a one-pot procedure. The preparation of particles, where in one droplet/particle two different types of polymerizations were carried out (polyaddition and radical polymerization), has already been shown for anionic and radical polymerization for the synthesis of polysiloxane−polyacrylate hybrid particles.[12,13]

In this article, we will first show that the miniemulsion process allows the synthesis of high molecular weight hydrophobic polyurethane. The influence of reaction parameters, such as the temperature, the surfactant, and the addition of a catalyst on the molecular weight, will be examined. The molecular weight will be analyzed by GPC, and the ratio of urethane to urea will be evaluated by IR spectroscopy.

Then, by combining polyaddition and radical polymerization in a one-pot procedure, the synthesis of well-defined hybrid particles will be performed.

Experimental Part

Chemicals. Isophorone diisocyanate (IPDI), dodecanediol, hydroxybutyl acrylate (HBA), dimethyldodecylamine (DMDA), dimethyltin diacetate (DMTDA), dibutyltin dibutyrate (DBTDB), dibutyltin bis(2-ethylhexanoate) (DBTDH), dibutyltin dilaurate (DBTDL), hexadecane (HD), perfluoromethyldecalin (PFD), potassium persulfate (KPS), and sodium dodecyl sulfate (SDS) were purchased from Aldrich and used as received.

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Styrene (Aldrich) and *n*-butyl acrylate (BA, Aldrich) were freshly distilled and stored at −10 °C. Dioctyltin dilaurate (DOTDL) from ABCR was used as received. The nonionic surfactants Lutensol AT50 (LuAT50, a hexadecyl-modified poly(ethylene glycol) ($C_{16}H_{33}$)($(EO)_{50}$) and BASF193 (BA193, a hydrophobically end-capped polyurethane) were obtained from BASF.

Polyurethane Latex Preparation. As a typical recipe, 3.141 g of IPDI (14.1 mmol), 2.859 g of finely divided dodecanediol (14.1 mmol), 200 mg of hexadecane, 200 mg of sodium dodecyl sulfate, and 24 g of water were stirred together for 1 h at room temperature. The miniemulsion was prepared by ultrasonicating the mixture for 120 s at 90% amplitude (Branson sonifier W450 digital) at 10 °C in order to prevent the polyaddition reaction. For polyaddition, the temperature was increased to 60 °C and, if indicated, a catalyst was then added. Completion of the reaction was observed after 4 h, as checked by GPC and IR analyses.

Hybrid Latex Preparation. As a typical recipe, 1.570 g of IPDI (7.06 mmol), 1.430 g of dodecanediol (7.06 mmol), 3 g of vinylic monomer(s), 200 mg of hexadecane, 200 mg of sodium dodecyl sulfate, and 24 g of water were stirred together for 1 h at room temperature. The miniemulsion was prepared by ultrasonicating the mixture during 120 s at 90% amplitude (Branson sonifier W450 digital) at 10 °C in order to prevent the polymerization. First, the polyaddition was conducted. The temperature was increased to 60 °C and, if indicated, a catalyst was then added. Completion of the polyaddition was observed after 4 h, as checked by GPC and IR analyses. No polystyrene was found at this stage. Second, for radical polymerization, the temperature was increased to 72 °C and 100 mg of potassium persulfate was added. Completion of the reaction was observed after 6 h, as checked by NMR by the absence of vinylic protons.

Analysis. The polymer molecular weights were determined by GPC analysis performed on a P1000 pump with UV1000 detector ($\lambda = 260$ nm) (both from Thermo Separation Products) and RI detector (Shodex RI-71), with 5 μm 8 × 300 mm SDV columns with 10^6, 10^5, and 10^3 Å (from Polymer Standard Service) in THF with a flow rate of 1 mL min^{-1} at 30 °C. The molecular weights were calculated with a calibration relative to polystyrene standards.

The particle sizes were measured by dynamic light scattering at low concentration, using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°.

Electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400 mesh carbon-coated copper grid and left to dry; no further contrasting was applied.

Scanning force microscopy (AFM) was performed with a NanoScope IIIa microscope (Digital Instruments, Santa Barbara, CA) operating in tapping mode. The instrument was equipped with a 10 × 10 μm E-Scanner and commercial silicon tips (model TSEP; the force constant was 50 N/m, the resonance frequency was 300 kHz, and the tip radius smaller than 20 nm). The samples were prepared by letting droplets of diluted aqueous solution (0.05 wt %) dry on freshly cleaved muscovite mica surfaces at room temperature.

Infrared spectroscopy was performed on a Biorad FTS 600 spectrometer in the absorbance setup. The samples were measured as pure products with an ATR accessory.

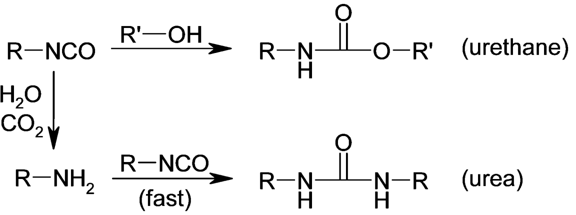
Liquid ^{1}H NMR spectra were recorded with a Bruker DPX400 using deuterated THF as solvent.

Results and Discussion

1. Influence of Some Parameters on the Polyaddition Reaction and More Specifically on the Molecular Weight of the Polyurethane in Order To Understand the Mechanism Involved.

During the miniemulsion polyaddition of IPDI with dodecanediol, two main reactions compete (see Scheme 1). The first one is the expected reaction of the isocyanate group with the alcohol (chain extension reaction), leading to the formation of the urethane. The second one is the side reaction of isocyanate with water (foaming reaction), leading to the formation of urea with release of CO_2.

Scheme 1



This latter reaction is responsible for the loss of stoichiometry, since for each reacting molecule of water, two isocyanate groups are consumed. To obtain a well-defined polyurethane of high molecular weight, it is then of high importance to reduce this side reaction.

As a reference for this study we chose the system defined in the previous article from Tiarks et al.,[3] entry A2 in Table 1. To compare the experiments, the molecular weight of the polyurethane was determined by GPC; the higher the molecular weight is, in principle the lower the proportion of side reaction with water was during the reaction.

To prove this assumption, polyurethanes of different molecular weights obtained by polyaddition in miniemulsion were analyzed using FT-IR spectroscopy and were compared to model polyurethane and polyurea. In the range between 1600 and 1770 cm^{-1}, peaks assigned to urethane (ca. 1700 cm^{-1}) and to urea (ca. 1630 cm^{-1}) can be observed in Figure 1.

As expected, the peak corresponding to urethane increases whereas the one corresponding to urea decreases as the molecular weight of the polyurethane increases. By this mean, we could confirm that the reaction with water was responsible for the decrease of the molecular weight and that GPC analysis could be used to compare properly the experiments.

The influence of several parameters on the molecular weight of the polyurethane and on the miniemulsion properties was studied (see Tables 1−3).

(a) Influence of the Temperature. It is a current mean to vary the temperature in order to differentiate the rate of two reactions. Indeed, by decreasing the temperature from 80 to 50 °C, entry A2 to A5, the molecular weight of the polyurethane increases. One possible explanation is the difference of the activation energy of the two main reactions. If the reaction with water has a higher activation energy than the reaction with the alcohol, it is then possible to favor the formation of urethane at lower temperature. This result could also be related to the concentration of water in the organic phase. With decreasing temperature, the solubility of water in the particles should decrease, which would favor the isocyanate−alcohol reaction. Such an effect has already been observed in a study on silanol polycondensation in emulsion by Saam et Huebner.[14]

(b) Influence of the Interface Nature. Owing to the different localization of the reactants (water and monomers), the reaction with water should take place near the interface. Therefore, the nature of the interface may have an influence on the kinetic of the reaction with water. To investigate this hypothesis, several surfactants have been tested (entries A2, A6, and A7). By changing the nature of the surfactant, it is only

Table 1. Bulk and Miniemulsion Polyaddition Results Carried out without Vinylic Monomer

	reaction conditions[a]								results		
exp group	entry	T (°C)	surfactant	m_S (g)	hydrophobe	m_H (g)	catalyst	m_C (mg)	part. size[b]	M_w[c]	PI[d]
bulk[e]	A1	60	SDS	0.2	HD	0.2				7.62	2.1
reference	A2	60	SDS	0.2	HD	0.2			175	3.75	1.8
temp influence	A3	80	SDS	0.2	HD	0.2			170	2.69	1.6
	A4	70	SDS	0.2	HD	0.2			195	2.82	1.6
	A5	50	SDS	0.2	HD	0.2			160	5.78	1.9
interface influence	A6	60	BA193	0.3	HD	0.2			220	4.25	1.7
	A7	60	LuAT50	0.5	HD	0.2			250	3.76	1.7
	A8	60	SDS	0.3	HD	0.2			180	3.77	1.6
	A9	60	SDS	0.4	HD	0.2			170	4.18	1.7
hydrophobe influence	A10	60	SDS	0.2	HD	0.12			180	4.28	1.8
	A11	60	SDS	0.2					490	4.28	1.8
	A12	60	SDS	0.2	PFD	0.2			650	4.96	1.8
catalyst influence	A13	60	SDS	0.2	HD	0.2	DMDA	25	175	3.71	1.8
	A14	60	SDS	0.2	HD	0.2	DMTDA	25	165	4.05	1.8
	A15	60	SDS	0.2	HD	0.2	DBTDB	25	175	3.81	1.8
	A16	60	SDS	0.2	HD	0.2	DBTDH	25	165	9.05	2.1
	A17	60	SDS	0.2	HD	0.2	DBTDL	25	170	7.28	2.1
	A18	60	SDS	0.2	HD	0.2	DOTDL	25[f]	170	8.24	2.1
	A19	60	SDS	0.2	HD	0.2	DMDA/DBTDL	25/25	160	7.19	2.2

[a] Unless otherwise stated, all experiments were carried out in miniemulsion using 6 g of an equimolar mixture of dodecanediol and IPDI and 24 g of water. [b] In nm, determined by dynamic light scattering at low concentration. [c] In kg mol^{-1}, determined by GPC vs polystyrene standards uncorrected. [d] Polydispersity index M_w/M_n. [e] Experiment carried out in bulk without water. [f] Added just before sonication.

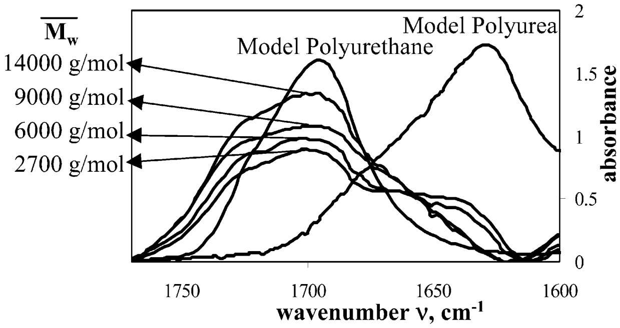


Figure 1. IR spectra of polyurethanes obtained by polyaddition in aqueous miniemulsion and compared to model polyurethane and polyurea.

possible to change slightly the molecular weight of the polyurethane. A better shielding of the interface is also expected by loading the droplets after miniemulsification with more surfactant molecules. This process does not lead to any change of the droplet size. In samples A8 and A9, SDS has been additionally added, leading to a slight increase of the molecular weight.

It has to be noted that the use of cationic surfactants like quaternary ammonium salts is not possible as those compounds are catalysts of the polyaddition. Therefore, the polymerization starts before the preparation of the miniemulsion.

(c) Influence of the Hydrophobe. Entries A10–A12 emphasize the importance of using an appropriate hydrophobe to obtain well-defined miniemulsions. Without any hydrophobe the particle size increases from 180 nm (with HD) to 490 nm. Even worse is the effect of using perfluoromethyldecalin (PFD) as hydrophobe. In fact, this fluorinated compound is not compatible with the two monomers, which increases the instability of the emulsion and leads to a particle size of 650 nm. The nature or the amount of hydrophobe has only a slight influence on the molecular weight. It will be shown below that the molecular weight is more probably influenced by the particle size than by the hydrophobe.

(d) Influence of the Catalyst Nature. In urethane chemistry, the functions of catalysts employed generally lie in bringing about faster reaction rates and establishing a proper balance between the chain extension and foaming reaction.[15] To increase the molecular weight of the polyurethane, several well-known catalysts of this polyaddition reaction have been tested in miniemulsion (entries A13–A19). The use of tertiary amines, like DMDA (entry A13), does not permit to increase the molecular weight. In fact, it is known that tertiary amines are catalysts for the isocyanate–hydroxyl as well as the isocyanate–water reaction. If both reactions are equally catalyzed, it is then not possible to increase the molecular weight with such compounds.

On the other hand, the use of tin catalysts gives very interesting results. The catalysts with a high hydrophilicity, DMTDA and DBTDB (entries A14 and A15), are not better than the tertiary amines. However with DBTDH, DBTDL, and DOTDL (entries A16–A18), it is possible to almost triple the molecular weight. In fact, it is also known that organo-tin compounds are very effective for the catalysis of the isocyanate–hydroxyl reaction. It is then possible to favor this reaction in comparison to the reaction with water, leading to higher molecular weight. To understand the differences observed between the tin compounds, the nature of the reaction medium has to be taken into account. To catalyze properly the isocyanate–hydroxyl reaction, the catalyst must be located in the droplets. With compounds that are too hydrophilic, like DMTDA or DBTDB, no increase of the molecular weight is observed, the catalyst being presumably mainly located in the water phase. Conversely, the most hydrophobic catalysts, DBTDH, DBTDL, and DOTDL, give the best results. For DOTDL, which is clearly the most hydrophobic of the tin catalysts used, the process has to be modified. This compound, unlike DBTDL or DBTDH, does not seem to diffuse fast enough toward the monomer droplets when added after sonication. In fact, the reverse effect seems to happen; the monomers seem to diffuse toward the catalyst macrodroplets, leading to a very high amount of flocculation (>80%). Simply by adding DOTDL before sonication, the catalyst is then directly localized in the monomer droplets, and the flocculation is reduced to less than 3%.

The combination of tertiary amine and organo-tin compounds, like stated in the literature, permits to considerably increase the catalyst activity. In the miniemulsion system, however, it does not lead to an increase of the molecular weight. Other good catalysts of the isocyanate−hydroxyl reaction have also been tested: stannous octoate, triphenylbismuth, or ferric acetylacetonate.[16] None of them permitted to increase the molecular weight.

(e) Effect of Styrene or Butyl Acrylate. As the final goal of this study is to synthesize polystyrene−polyurethane or poly(butyl acrylate)/polyurethane hybrid particles (see part 2), it is of interest to look at the influence of the presence of styrene and butyl acrylate on the polyaddition product and on the miniemulsion characteristics. For this purpose, the experiment A18 is repeated, replacing half of the organic phase by styrene or butyl acrylate (entries B1 and B2). This monomer acts then as a solvent for the polyurethane synthesis. The presence of the vinylic monomer leads to a strong decrease of the particle size and to a slight increase of the molecular weight. This increase can partly be explained by the dilution of the polyaddition medium and the decrease of its viscosity. Indeed, the decrease of viscosity favors reactions that are kinetically limited by the diffusion of the reactants. Therefore, by adding styrene or butyl acrylate, the reaction between two chain ends (hydroxyl−isocyanate reaction) is favored compared to the reaction between a chain end and water (water−isocyanate reaction). But viscosity is not the only parameter influencing the molecular weight. Indeed, even if the result does not account for it, the strong decrease of the particle size has a negative effect on the molecular weight, as shown in the next paragraph.

(f) Influence of SDS Concentration. There is almost no effect of adding an extra amount of SDS *after* sonication (entries A2, A8, and A9). Please note that in this case the droplet size does not change, but only the coverage of the droplet by surfactant is influenced. On the contrary, by increasing the amount of SDS *before* sonication, it is possible to reduce the particle size as well as the molecular weight (entries B3−B6). Indeed, by decreasing the particle size, the interfacial area increases, which favors the reaction with water at the interface and leads to lower molecular weights. A similar effect has been observed in a recent article on esterification in aqueous emulsion.[17] The authors could show that hydrolysis was favored when decreasing the particle size.

(g) Influence of the DBTDL Concentration. As expected, by increasing amount of tin catalyst (entries B7−B12), the molecular weight of the polymer increases significantly up to 25 mg of DBTDL (0.4 wt % relative to polymer). Above this concentration, the stabilization of molecular weight may be due either to the saturation of the organic phase in catalyst or to the limitation of the DBTDL catalytic effect.

(h) Influence of IPDI Excess. As the relatively low molecular weight of the polyurethane is mainly due the reaction of isocyanate with water conducting to a loss of stoichiometry, it is easy to compensate it by adding an excess of IPDI. Indeed, by increasing the excess of diisocyanate relative to dodecanediol (entries B13−B19), the molecular weight of the polymer dramatically increases, reaching 70 000 g mol^{-1} for 50% molar excess of IPDI. If we suppose that for such a molecular weight the stoichiometry between the reactive groups is obtained, this would mean that 17% of isocyanate groups have reacted with water.

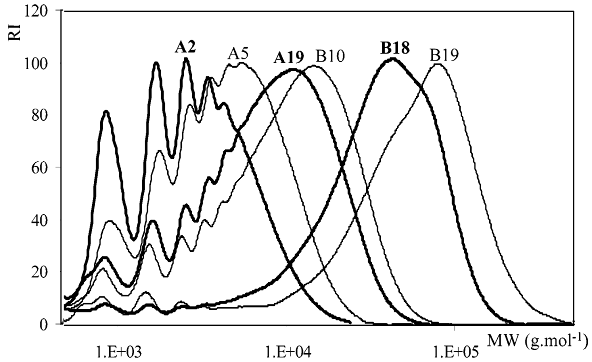


Figure 2. GPC traces of several polyurethanes obtained by miniemulsion polyaddition.

(i) Influence of the Addition of Dodecanediol or IPDI after Sonication. The addition of variable amounts of dodecanediol after sonication leads to a sensible increase of the polyurethane molecular weight (entries C1−C3 compared to entry A17). With only 17% of dodecanediol added after sonication, the molecular weight increases from 7200 to 13 100 g mol^{-1}. Globally, this result could be explained as follows. The fraction of dodecanediol added after sonication diffuses toward the nanodroplets containing IPDI and catalyst and adsorbs at the surface. Because of this diffusion process, the concentration of dodecanediol at the interface of the nanodroplets is artificially higher (compared to the experiment A17). This may then decrease the rate of the isocyanate−water reaction which takes place at the interface and lead to higher molecular weight. In practice, this process is difficult to control. Several parameters have to be known, in particular the diffusion rate of dodecanediol in water and the polyaddition rate. If the diffusion of dodecanediol is too slow compared to the polyaddition, the isocyanate−water reaction will be favored. The same is true if the amount of dodecanediol added after sonication is too high; the lack of alcohol in the droplets at the beginning of the polyaddition will favor the reaction with water, as shown by the decrease of the molecular weight (entries C1−C3).

The last experiment (entry C4) shows that it is even possible to add the whole IPDI amount after sonication and let it diffuse toward the miniemulsion nanodroplets. We chose for this experiment the most hydrophobic tin catalyst DOTDL in order to prevent the inverse diffusion of dodecanediol and catalyst toward IPDI macrodroplets, which could lead to a high amount of flocculation. Surprisingly, the diffusion of IPDI in water does not seem to favor extensively the reaction with water, as the molecular weight of the polyurethane is relatively high. Moreover, compared to experiments with the same amount of surfactant, a sensible decrease of the particle size is observed.

From this study (some of the GPC graphs are shown in Figure 2), it can be seen that several parameters permit to considerably increase the molecular weight of the polyurethane. An optimization of the reaction conditions, combining those parameters, should allow to obtain polyurethanes of much higher molecular weight.

2. Synthesis of Hybrid PS/PU or PBA/PU Particles. The procedure for the formation of hybrid

Scheme 2

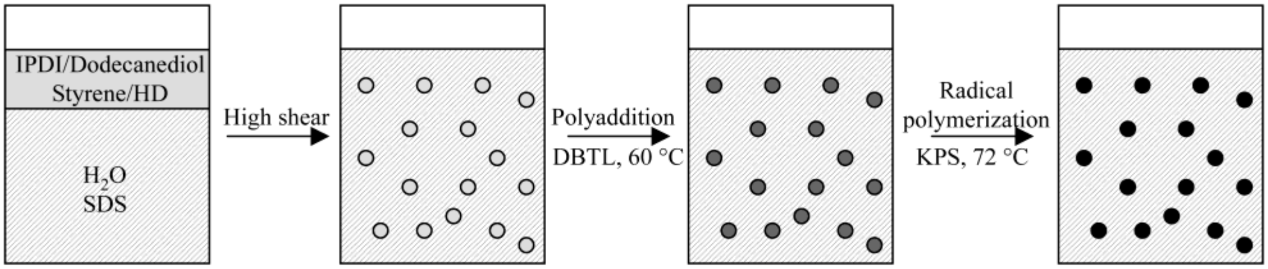


Table 2. Miniemulsion Polyaddition Results Carried out in the Presence of a Vinylic Monomer

	reaction conditions[a]						results		
exp group	entry	vinylic monomer	IPDI excess (mol %)[b]	SDS (g)	catalyst	m_C (mg)	part. size[c]	M_w[d]	PI[e]
vinylic monomer influence	B1	styrene	0	0.2	DMDA/ DBTDL	25/25	103	11.9	2.5
	B2	BA	0	0.2	DMDA/ DBTDL	25/25	105	8.83	2.1
SDS concn influence	B3	styrene	0	0.1			127	4.89	1.9
	B4	styrene	0	0.15			106	4.49	1.9
	B5	styrene	0	0.2			102	3.78	1.8
	B6	styrene	0	0.4			77	3.47	1.7
catalyst concn influence	B7	styrene	0	0.2	DBTDL	1.5		6.04	2.0
	B8	styrene	0	0.2	DBTDL	4.5		9.01	2.2
	B9	styrene	0	0.2	DBTDL	10		11.1	2.4
	B10	styrene	0	0.2	DBTDL	25	105	13.4	2.5
	B11	styrene	0	0.2	DBTDL	50	107	14.9	3.1
	B12	styrene	0	0.2	DBTDL	200	107	14.3	3.0
IPDI excess influence	B13	styrene	4.2	0.2	DMDA/ DBTDL	25/25	135	13.8	2.3
	B14	styrene	12.1	0.2	DMDA/ DBTDL	25/25		16.9	3.0
	B15	styrene	19.4	0.2	DMDA/ DBTDL	25/25		20.2	2.6
	B16	styrene	28.6	0.2	DMDA/ DBTDL	25/25	145	27.3	2.8
	B17	styrene	33.6	0.2	DMDA/ DBTDL	25/25	130	36.0	4.0
	B18	styrene	38.6	0.2	DMDA/ DBTDL	25/25	108	43.1	3.2
	B19	styrene	49.6	0.2	DMDA/ DBTDL	25/25	118	69.5	5.2

[a] All experiments were carried out using 3 g of a mixture of dodecanediol and IPDI, 3 g of a vinylic monomer, 0.2 g of hexadecane, and 24 g of water. [b] Excess relative to dodecanediol. [c] In nm, determined by dynamic light scattering at low concentration. [d] In kg mol^{-1}, determined by GPC vs polystyrene standards uncorrected. [e] Polydispersity index M_w/M_n.

Table 3. Miniemulsion Polyaddition Results Obtained in Case of Addition of All or Part of One of the Polyaddition Monomer after Sonication

	reaction conditions[a]					results		
entry	vinylic monomer	catalyst	m_C (mg)	polyaddition monomer added after sonication	amount added after sonication (%)[b]	part. size[c]	M_w[d]	PI[e]
C1		DBTDL	25	dodecanediol	17[f]	160	13.1	2.3
C2		DBTDL	25	dodecanediol	35[f]	180	11.8	2.1
C3		DBTDL	25	dodecanediol	52[f]	170	8.2	2.1
C4[g]	styrene	DOTDL	25	IPDI	100[h]	88	11.3	3.0

[a] Unless otherwise stated, all experiments were carried out using 6 g of an equimolar mixture of dodecanediol and IPDI, 0.2 g of hexadecane, 0.2 g of SDS, and 24 g of water. [b] Relative to the total amount of the monomer considered. [c] In nm, determined by dynamic light scattering at low concentration. [d] In kg mol^{-1}, determined by GPC vs polystyrene standards uncorrected. [e] Polydispersity index M_w/M_n. [f] Added all at once. [g] Experiment carried out using 3 g of an equimolar mixture of dodecanediol and IPDI, 3 g of a styrene, 0.2 g of hexadecane, 0.2 g of SDS, and 24 g of water. [h] Poured dropwise for 90 min.

particles consisting of polyurethane and polystyrene or poly(butyl acrylate) is shown in Scheme 2. The components IPDI, dodecanediol, styrene, and hexadecane are mixed and miniemulsified in water using SDS as surfactant. By increasing the temperature to 60 °C and adding DBTDL as catalyst, the polyurethane is formed. To start the radical polymerization of either styrene or butyl acrylate, the temperature was then increased to 72 °C and KPS as initiator was added. The reaction parameters and the characteristics of the polymer particles are summarized in Table 4.

It could be confirmed by NMR that, within the first step, the vinylic monomer did not undergo any reaction and that the entire vinylic monomer was consumed during the second step. The GPC traces after completing the polymerizations show two peaks as expected; one peak represents the molecular weight of the polyurethane (which is not UV-active and therefore just detected by the RI detector), and the other represents the

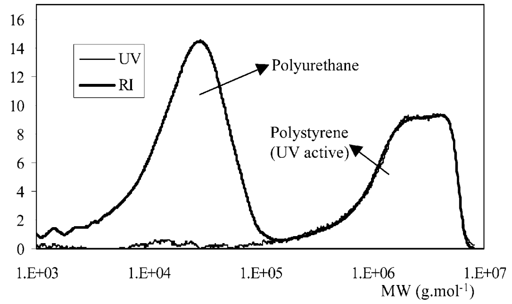


Figure 3. GPC traces of polyurethane and polystyrene obtained by the same one-pot procedure (entry D4).

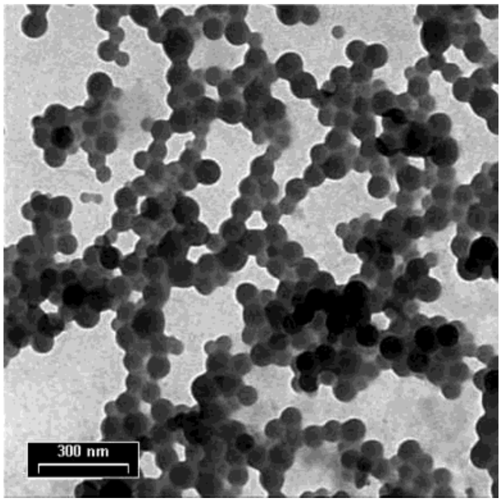


Figure 4. TEM picture of polystyrene/polyurethane hybrid particles.

high molecular weight polystyrene (which is detected by both detectors) (see Figure 3). Hydroxybutyl acrylate can also be added to the miniemulsion (entries D7 and D8). In that case, the hybrid particles are reticulated, as shown by the insolubility of the polymer. Actually, HBA plays the role of a cross-linking agent, being active for both the polyaddition and the radical polymerization: the OH group reacts with the isocyanate, allowing the coupling to the polyurethane, and the vinylic group is radically built in the polyacrylic or polystyrenic part.

The TEM (Figure 4) shows particles with a homogeneous morphology. Neither TEM nor ultracentrifuge measurements could detect two species of particles which could have been formed by phase separation.

Figure 5 shows the dried films of the latex particles before and after annealing at 60 °C, a temperature in between the T_G of the two polymers. Before annealing, a close packing of the particles is detected; after annealing, the particles are flattened and interdiffusion can be observed. From this observation, we can speculate that all particles indeed contain both polymers. Otherwise, some particles would flow (those containing only polyurethane) and some would stay perfectly round (containing only polystyrene), which is not observed.

Conclusion

In a first part, the synthesis of a hydrophobic polyurethane in aqueous miniemulsion was studied. It was confirmed that the isocyanate−water reaction was responsible for the lowering of the molecular weight.

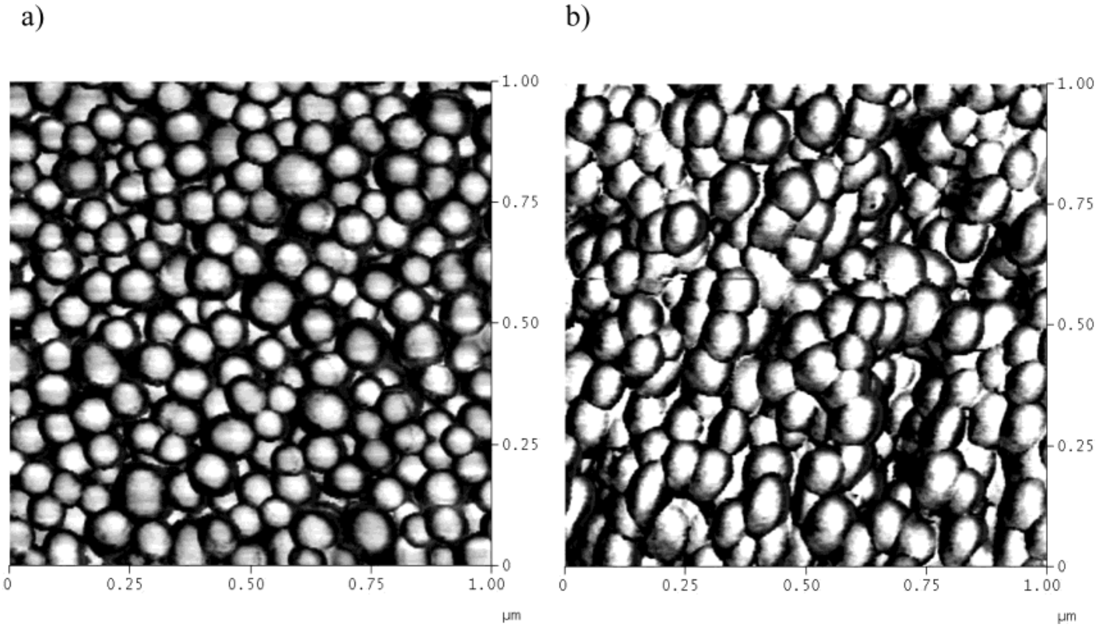


Figure 5. AFM picture of hybrid polystyrene/polyurethane particles (a) before and (b) after annealing (60 °C).

Table 4. Synthesis of PS/PU or PBA/PU Hybrid Particles

	reaction conditions[a]							
		polyaddition			results			
entry	vinylic monomer	T (°C)	catalyst	m_C (mg)	floc (wt %)[b]	part. size[c]	M_w (PS or PBa)[d]	PI[e]
D1	styrene	60			<1	92		
D2	styrene	50	DMDA/DBTDL	25/25	23	120	450	4.1
D3	BA	50	DMDA/DBTDL	25/25	9.2	135	800	2.7
D4	styrene	60	DMDA/DBTDL	25/25	15	103	600	4.0
D5	BA	60	DMDA/DBTDL	25/25	6.7	105	600	2.4
D6[f]	styrene	60	DOTDL	25[g]	5	88		
D7	BA/HBA[h]	60			10	130		
D8	styrene/ HBA[h]	60			9.2	105		

[a] Unless otherwise stated, all experiments were carried out using 3 g of an equimolar mixture of dodecanediol and IPDI, 3 g of a vinylic monomer, 0.2 g of hexadecane, 0.2 g of SDS, and 24 g of water. [b] Relative to the total amount of organic phase. [c] In nm, determined by dynamic light scattering at low concentration. [d] In kg mol^{-1}, determined by GPC vs polystyrene standards uncorrected. [e] Polydispersity index M_w/M_n. [f] IPDI poured dropwise for 90 min after sonication. [g] Added just before sonication. [h] Mixture of 0.185 g of hydroxybutyl acrylate and 2.815 g of styrene or butyl acrylate.

Nevertheless, numerous parameters permitted to decrease the proportion of this side reaction. Among them, the use of organo-tin compounds allowed to almost triple the polyurethane molecular weight. Also, the knowledge of the localization of the reaction has been used for this purpose. For example, by increasing the particle size, the isocyanate−water reaction, which is favored at the oil/water interface, was reduced compared to the isocyanate−hydroxyl reaction, which is favored in the core of the particles. Also, by increasing the amount of dodecanediol located at the interface, the reaction with water decreased and the molecular weight increased. Without any extensive optimization, a molecular weight in the range of 70 000 g mol^{-1} could be obtained, which is very promising regarding the potential of the system for applications.

In a second part, polyaddition and radical polymerization are combined using a one-pot procedure in order to synthesize hybrid PU/PS or PU/PBA particle. Small particle size (90−130 nm) and high molecular weight of the two polymers could be successfully achieved.

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