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ORIGINAL CONTRIBUTION

Preparation of high molecular weight polyurethane particles by nonaqueous emulsion polyaddition

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Abstract A versatile nonaqueous emulsion polyaddition process for the one-step fabrication of spherical polyurethane nanoparticles is presented. Three different emulsion systems were used consisting of *N*,*N*′-dimethylformamide (DMF) dispersed in *n*-hexane, acetonitrile dispersed in cyclohexane, and acetonitrile dispersed in tetradecane. After successful stabilization of the emulsion systems by using a poly(isoprene)-poly(methylmethacrylate) block copolymer, the fabrication of the polyurethanes was carried out within the dispersed polar phase. The polyurethane particles showed average diameters as small as 35 nm. Additionally, infrared (IR) characterization revealed that the formation of any urea, which decreases the mechanical properties of the polyurethanes, was prevented during the polyaddition. This was attributed to the anhydrous reaction conditions. Gel permeation chromatography (GPC) analysis demonstrated the average molecular weights (M_n) of the polyurethanes to be as high as 16,500 g/mol, corresponding to conversions of 0.98. Comparable molecular weights and conversions have not previously been achieved without the formation of urea.

Keywords Polyaddition · Polyurethane · Nanoparticles · Nonaqueous emulsion · Emulsion polymerization

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Introduction

The application of polyurethane particles has increased dramatically within the last decades, as they have been used as materials in various fields of application, including industrial adhesives and coatings for metals, wood, and textiles [1]. Of special significance are polyurethane powder and coil coatings, as they show good adhesion to metallic surfaces, high mechanical performance, and good resistance against chemicals and corrosion.[2] Those coatings that are, for example, applied for preventing corrosion on steel surfaces typically show film thicknesses of 10 to 60 μm [3]. Especially for this application, the shape and the size of the particles play a major role in determining the morphology of the films. Small spherical particles are required to obtain high fluidity and smooth thin coatings.

Because isocyanate compounds are sensitive to water, polyurethane nanoparticles with the size and shape of traditional polymer latex particles, e.g., polystyrene, cannot be fabricated without the formation of urea by the well-established emulsion, mini-emulsion, and suspension polymerization methods. Thus, alternative approaches have been developed over the last decades [4–6]. Today, polyurethane nanoparticles are almost exclusively obtained by two preparation methods: The first one involves the preparation of the nanoparticles in a two-step procedure. In the first step, the polyaddition reaction of diisocyanates and diols is carried out at high temperatures in bulk or in a nonaqueous solvent. For particle formation, the obtained polyurethanes are subsequently sprayed or mixed, either as a solution or a melt, into a second auxiliary agent, e.g., compressed CO_2 or another inert organic solvent [5–7]. By applying this multi-step process, polyurethane nanoparticles in a micrometer size range are obtained.

The second preparation method is based on the direct mini-emulsion polyaddition of diisocyanates and diols in water catalyzed by amines or organotin compounds, e.g., dibutyltin dilaureate [8–10]. Unfortunately, the excess of water causes a side-reaction of the isocyanate, leading to the formation of urea, which decreases the mechanical properties of the polyurethanes [11]. Additionally, as the correct stoichiometry during the reaction is no longer maintained, average molecular weights (M_n) of up to only 13,000 g/mol, with dispersities up to 5.2, have been reported [8, 9]. In this cases, polyurethane nanoparticles with mean diameters ranging from 80 to 250 nm are obtained.

To circumvent these serious drawbacks, a versatile method for the preparation of small polyurethane nanoparticles under mild and nonaqueous conditions is needed. Recently, we reported the preparation of conjugated polymers and polyester nanoparticles in various nonaqueous emulsions [12, 13]. These emulsions consisted of a polar organic solvent, e.g., acetonitrile or DMF, which was dispersed in a second, nonpolar organic solvent such as cyclohexane or *n*-hexane. Stabilization of these emulsions was achieved by using poly(isoprene)-block-poly(methylmethacrylate) (PI-b-PMMA) copolymers as stabilizers. To obtain polymer nanoparticles, the polyreactions were conducted directly in the dispersed phase that afforded polymer nanoparticles as small as 23 nm (standard deviation 6 nm). In the present article, the nonaqueous process of particle formation is extended to polyaddition reactions. This polymerization technique allows the formation of spherical polyurethane nanoparticles at moderate temperatures without the formation of urea and, at the same time, with high molecular weights.

Experimental

Reagents and solvents

4,4′-Methylenebis(cyclohexyl isocyanate) (HMDI) 95% purity; 4,4′-methylenebis(phenyl isocyanate) (MDI) 98% purity; 1,4-bis(hydroxymethyl)cyclohexane (BHC) 99% purity; anhydrous ethylene glycol (EG) 99% purity; dibutyltin diacetate (DBDA); and dibutyltin-2-ethylhexanoate (DBEH) were purchased from Sigma-Aldrich and used as received. Cyclohexane, *N*,*N*′-dimethylformamide (DMF), *n*-hexane, and acetonitrile were obtained from Acros Organics and dried over molecular sieves (4 Å). Tetradecane was purchased from Merck KGaA, Darmstadt (Germany) and dried in vacuo. Polyisoprene-block-polymethylmethacrylate (PI-b-PMMA) copolymer was prepared using a sequential anionic polymerization technique described elsewhere [14, 15].

Preparation of polyurethane nanoparticles

PI-b-PMMA copolymer (0.210 g) was stirred magnetically in cyclohexane (12.0 g, 140 mmol) at room temperature. BHC (0.231 g, 1.60 mmol) and DBDA (0.050 g, 0.14 mmol) were dissolved in acetonitrile (1.5 g, 35 mmol) and added dropwise to the cyclohexane/copolymer solution. The emulsion was formed at room temperature by stirring the mixture for 2 h and ultrasonication of the solution for 10 min using a Bandelin Sonorex RK255H ultrasonic bath, operating at 640 W. Subsequently, 4,4′-methylenebis(cyclohexyl isocyanate) (0.420 g, 1.60 mmol) was added dropwise to the emulsion. The polyaddition reaction proceeded under stirring for 8 h at 45 °C. The reaction product was placed in a separating funnel and an excess of acetonitrile was added to remove residual emulsifier. The precipitated particles were separated and washed twice with acetonitrile to give 0.6 g of a colorless solid that was either dried under vacuum overnight or directly redispersed in *n*-hexane.

Characterization methods

Gel permeation chromatography (GPC) vs poly(styrene) standard was carried out at 60 °C using MZ-Gel SDplus 10E6, 10E4, and 500 columns, an ERC RI-101 differential refractometer detector, and DMF as the eluent. Prior to chromatography, the samples were filtered through a 0.2-μm Teflon filter (Millipore) to remove the insoluble impurities.

Composition of the PI-b-PMMA copolymer was determined in $CDCl_3$ as solvent by ^{1}H-NMR spectroscopy using a Bruker Avance spectrometer operating at 500 MHz. ^{1}H-NMR characterization of the polyurethane nanoparticles was performed in DMF using a Bruker Avance spectrometer operating at 250 MHz. Profilometric characterizations of the polyurethane coatings were carried out on a Tencor P-10 step profiler. Fourier transform infrared (FTIR) spectra were obtained by a Nicolet 730 FTIR spectrometer using a thermo electron endurance attenuated total reflection (ATR) single-reflection ATR crystal. SEM images were taken by a Zeiss Gemini 912 microscope. For SEM sample preparation, the nanoparticles were dispersed in *n*-hexane and drop cast on silica wafers. Dynamic light scattering (DLS) measurements were carried out at scattering angles of 30, 60, 90, and 120° using an ALV 5000 correlator operating with a He/Ne laser at 632.8 nm.

Results and discussion

Polyaddition reactions were performed in three different nonaqueous emulsions consisting of DMF dispersed in

Table 1 Polyaddition reactions performed in nonaqueous emulsions—experimental conditions and results

Experiment	Diisocyanate	$n_{\text{diisocyanate}}$ (mmol)	Diol	n_{diol} (mmol)	Catalyst	m_{catalyst} (mg)	Diameter (nm)[a]	M_n (g/mol)[b]	D (M_w/M_n)[c]	Conversion[d]
A-2	HMDI	1.6	CHDM	1.6	DBDA	50	95	14,000	2.2	0.97
A-4	HMDI	1.6	EG	1.6	DBDA	60	65	6,000	2.9	0.95
B-9	HMDI	1.6	CHDM	1.6	DBDA	50	55	13,000	2.3	0.97
B-10[e]	HMDI	1.7	CHDM	1.6	DBDA	50	45	16,000	2.1	0.98
B-11	MDI	1.6	CHDM	1.6	DBDA	50	95	16,500	2.9	0.98
B-12[e]	HMDI	1.7	EG	1.6	DBDA	50	40	9,500	2.0	0.97
B-13[e]	HMDI	1.7	CHDM	1.6	DBEH	50	35	6,500	2.0	0.94
C-1	HMDI	1.6	CHDM	1.6	DBDA	50	35	13,000	2.3	0.97
C-2[e]	HMDI	1.7	CHDM	1.6	DBDA	50	60	15,000	1.8	0.97

The applied emulsion in experiments A was acetonitrile dispersed in tetradecane; in B, acetonitrile dispersed in cyclohexane; and in C, DMF dispersed in *n*-hexane. Stabilization was achieved by using 0.21 g PI-b-PMMA as an emulsifier

[a] Determined by DLS by number, scattering angle 90°, particles redispersed in *n*-hexane

[b] Determined by GPC in DMF vs polystyrene standards

[c] Dispersity of the polymer, determined by GPC

[d] Conversion calculated by Carothers equation

[e] Dropwise addition of the diisocyanate component (monomer starved conditions; 1.7 mmol/30 min)

n-hexane, acetonitrile dispersed in cyclohexane, and acetonitrile dispersed in tetradecane (Table 1). For stabilization of the emulsions, a PI-b-PMMA copolymer having an average molecular weight (M_n) of 24,500 g/mol (dispersity, 1.1) and a block composition of 71% PI and 29% PMMA was used (DP_{PI}=235, DP_{PMMA}=95). In all nonaqueous emulsion systems investigated, the PI-block, which is only soluble in the nonpolar continuous phase (cyclohexane or tetradecane), acts as the stabilizing moiety and the PMMA-block as the anchor moiety for the dispersed, polar organic droplets (acetonitrile or DMF).

As aliphatic diols, BHC and ethylene glycol (EG) were chosen. 4,4′-Methylenebis(cyclohexyl isocyanate) (HMDI) and MDI were used as diisocyanates. For promoting the polyaddition reaction and achieving high molecular weights, DBDA and DBEH were applied as catalysts [16].

To obtain polyurethane particles, the diol was dissolved together with the catalyst in the polar phase (acetonitrile or DMF) and emulsified in the nonpolar organic solvent (tetradecane, cyclohexane, or *n*-hexane). The characterization of both phases by nuclear magnetic resonance (NMR) spectroscopy revealed that the used diols were exclusively soluble in the polar phases. Upon addition of the diisocyanate, the polyaddition reaction was started by the diffusion of the diisocyanate from the continuous into the dispersed phase. Because the diol components, as well as the

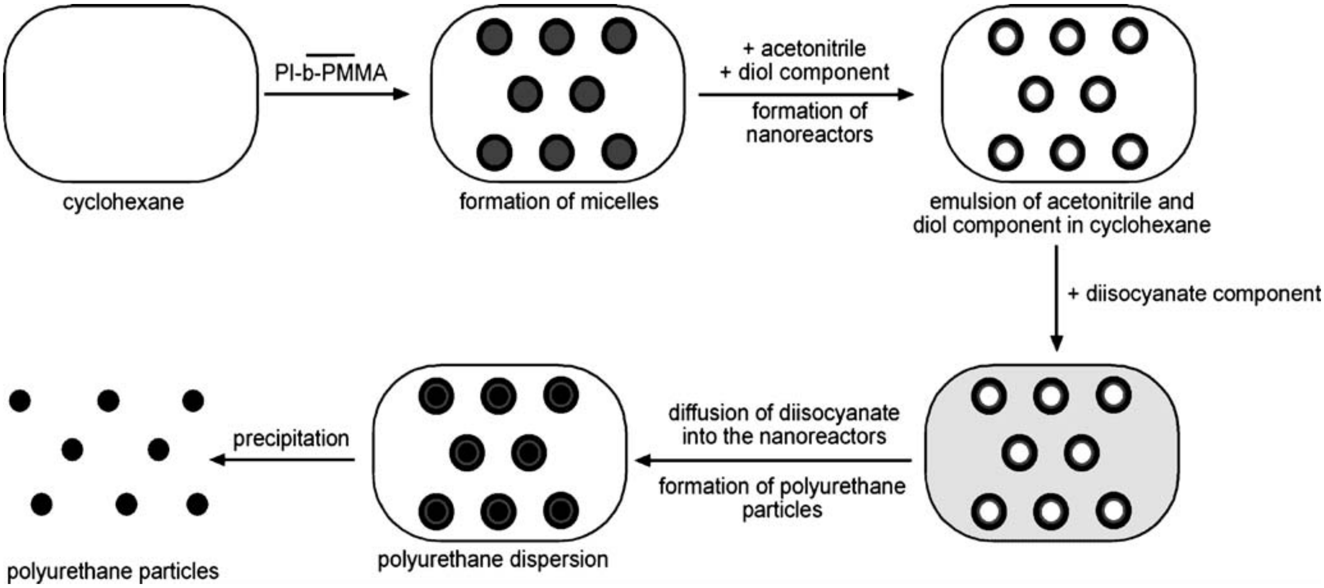

Fig. 1 Preparation of polyurethane nanoparticles in non-aqueous emulsions

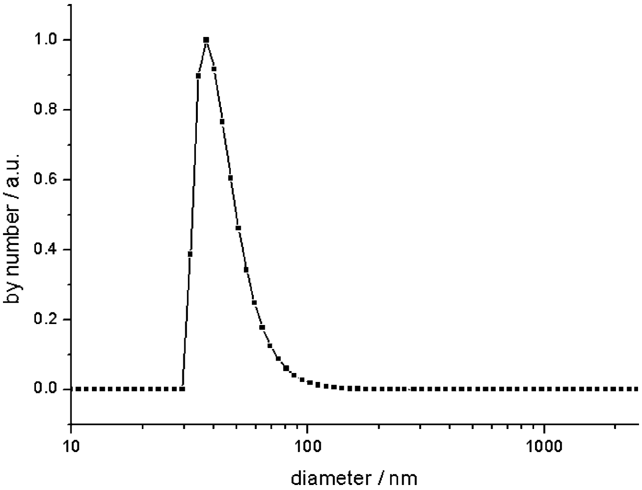

Fig. 2 Typical particle size distribution of the polyurethane particles (by DLS, sample B–10)

catalysts, were only soluble in this phase, one can safely assume that the polyaddition only occurred within the dispersed droplets (Fig. 1).

After the polyaddition reaction was complete, the precipitated nanoparticles were characterized by FTIR spectroscopy. The amide vibrations at 3,320 and 1,525 cm^{-1}, as well as the carbonyl signal at 1,690 cm^{-1} are strong evidence for the formation of a polyurethane. This was additionally confirmed by the disappearance of the isocyanate vibration at 2,260 cm^{-1} after the polyaddition reaction. It is worth mentioning that no additional carbonyl vibration around 1,650 cm^{-1}, which would be indicative of the formation of urea, was observed. Thus, it can be concluded that the polyurethane was successfully fabricated and that no side reactions with water leading to the formation of urea occurred.

The polyurethanes obtained in this study were also characterized by GPC, which revealed an average molecular weight as high as 16,500 g/mol (Table 1, entry B-11). In all cases, the molecular weights are higher than those reported for polyurethanes obtained from aqueous miniemulsion in the literature (M_n<13,000 g/mol) [8, 9, 17]. This is especially remarkable considering that these reported molecular weights could only be achieved if ca. 17% of the isocyanate groups had reacted with water.

According to the Carothers equation [18], the conversions of the step-growth reactions were calculated to be as high as 0.98. It is assumed that two factors are mainly responsible for the high molecular weights and conversions: (1) the absence of water during the emulsion polyaddition reaction, which eliminates the occurrence of side-reactions and, thus, maintains a balanced stoichiometry, and (2) the nearly diffusion-controlled polymerization conditions at the interfaces of the continuous and the dispersed phase (Schotten–Baumann conditions) [19]. As the diols were only soluble in the dispersed droplets, it can be assumed that the stoichiometry of the reaction was mainly controlled by the diffusion of the diisocyanate component into the dispersed droplets. However, as the diisocyanate components were also soluble in the dispersed phase, the polymerizations not only took place at the interface, but also inside the dispersed droplets. Hence, solid polyurethane nanoparticles, as demonstrated below, and not hollow particles, as expected from perfect Schotten–Baumann conditions, were formed.

Dropwise addition (monomer starved conditions) of the diisocyanate component did not significantly increase the molecular weights and the conversions (Table 1, entries B-10, B-12, B-13, C-2). This can be explained by the fact that the concentration of the diisocyanate component at the interface and inside the droplets is mainly controlled by the diffusion of the diisocyanate through the continuous phase and not by the rate of monomer addition to the emulsion.

The use of an aromatic diisocyanate, which is generally more reactive than analogous aliphatic systems, instead of an aliphatic one led to molecular weights and conversions in almost the same range (Table 1, entry B-11). However, high molecular weights were only observed in those cases where dibutyltin–diacetate was used as the catalyst (Table 1, entries A-2 to B-12, C-1, C–2). A reason for this might be the fact that dibutyltin–diacetate was only soluble in the dispersed polar droplets, whereas DBEH was also soluble in the nonpolar continuous phase. Hence, dibutyltin–diacetate was much more enriched in the dispersed phase and, as such, could better catalyze the polyaddition reaction.

The emulsion system used for the fabrication of the polyurethane nanoparticles had no significant influence on the molecular weight of the polyurethanes. Thus, all solvent systems investigated are suitable for the preparation of nonaqueous emulsions. However, using tetradecane as the continuous phase offers the possibility of removing the

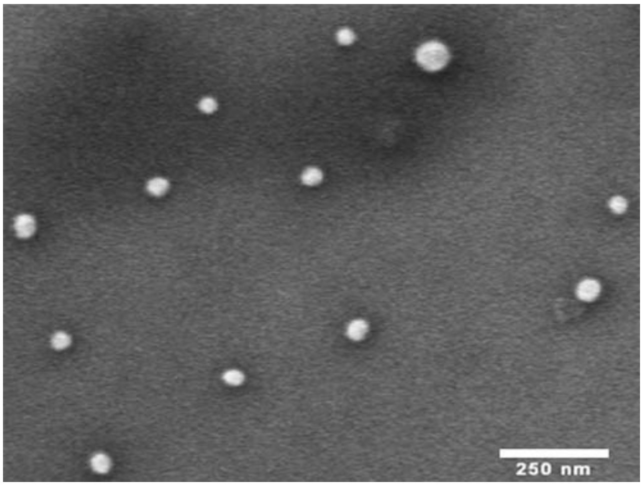

Fig. 3 Typical SEM image of polyurethane particles (sample C–2)

dispersed acetonitrile easily by evaporation immediately after nanoparticle formation. Hence, a stable polyurethane dispersion can be obtained directly in tetradecane.

NMR characterization of the nanoparticles demonstrated that the particles still had a coating of residual PI-b-PMMA emulsifier. Additionally, NMR experiments permitted to derive the ratio of emulsifier to polyurethane by comparing the PI signal of the emulsifier to the CH_2-O signal of the polyurethane. For all samples, a weight content of residual emulsifier of less than 10% with respect to polyurethane was found. Due to the presence of the residual emulsifier, the particles could be redispersed in *n*-hexane to form nonaqueous polyurethane dispersions.

For determination of the mean particle sizes, the dispersions were characterized by DLS (Table 1 and Fig. 2). For all samples, the average particle sizes were found to be in a range of 35 to 95 nm. These findings were additionally verified by scanning electron microscopy (SEM). A typical SEM image is shown in Fig. 3. The particles showed a spherical shape and a narrow particle size distribution. Additionally, there was no sign of porosity, which would have originated from the release of CO_2 generated in the side reaction with water.

Finally, the well-defined, spherical, nonporous polyurethane nanoparticles were applied for the coating of metal surfaces. A *n*-hexane dispersion of polyurethane nanoparticles (B9) was drop cast onto a steel plate. The solvent was then evaporated, and the particles were sintered at 140 °C for 30 min. FTIR and surface-profilometric characterizations of the resulting film demonstrated that a transparent 2-μm thin polyurethane coating was obtained. Compared to the literature [3], the layer thickness was more than five times smaller. This can be attributed to the smaller particle sizes that allow the fabrication of thin polyurethane coatings. Treating of the steel plate with dilute hydrochloric acid (0.1 N) for 24 h revealed that areas having no polyurethane coating showed high metal corrosion, whereas the coated areas showed none. Thus, based on these preliminary results, it can be assumed that the particles can be used as coatings for creating very thin polyurethane coatings on metal surfaces, suitable to prevent corrosion.

Conclusions

Spherical polyurethane latex particles with average diameters as small as 35 nm were obtained by nonaqueous emulsion polyaddition. In contrast to the methods described in the literature, this process allows the fabrication of polyurethane nanoparticles in one step and circumvents the formation of urea during the polyaddition reaction. This is of importance because the formation of urea is, in most cases, detrimental to polymer performance [3]. The average molecular weights (M_n) of the polyurethanes were found to be as high as 16,500 g/mol (dispersity, 2.9); this corresponds to conversions as high as 0.98. Additionally, preliminary experiments revealed that these polyurethane nanoparticles can be used for the fabrication of thin coatings for metallic surfaces, suitable to prevent corrosion using only 25% of the material traditionally applied for this application.

Up to now, including this work, it has been demonstrated that nonaqueous emulsions offer a versatile way for the fabrication of polymer nanoparticles by applying different polymerization mechanisms, including catalytic and oxidative polymerizations, polycondensations, as well as polyadditions [12, 13]. Currently, ongoing work focuses on the combination of the various polymerization techniques within the nonaqueous emulsions. This will offer a versatile access to novel core/shell morphologies in polymer nanoparticles, e.g., by combination of polyaddition/polymerization reactions.

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