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Oil-in-Oil Emulsions: A Unique Tool for the Formation of Polymer Nanoparticles

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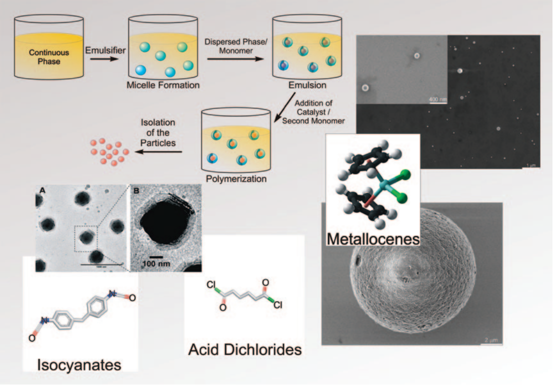

Polymer latex particles are nanofunctional materials with widespread applications including electronics, pharmaceuticals, photonics, cosmetics, and coatings. These materials are typically prepared using waterborne heterogeneous systems such as emulsion, miniemulsion, and suspension polymerization. However, all of these processes are limited to water-stable catalysts and monomers mainly polymerizable via radical polymerization. In this Account, we describe a method to overcome this limitation: nonaqueous emulsions can serve as a versatile tool for the synthesis of new types of polymer nanoparticles.

To form these emulsions, we first needed to find two nonmiscible nonpolar/polar aprotic organic solvents. We used solvent mixtures of either DMF or acetonitrile in alkanes and carefully designed amphiphilic block and statistical copolymers, such as polyisoprene-*b*-poly(methyl methacrylate) (PI-*b*-PMMA), as additives to stabilize these emulsions. Unlike aqueous emulsions, these new emulsion systems allowed the use of water-sensitive monomers and catalysts. Although polyaddition and polycondensation reactions usually lead to a large number of side products and only to oligomers in the aqueous phase, these new conditions resulted in high-molecular-weight, defect-free polymers. Furthermore, conducting nanoparticles were produced by the iron(III)-induced synthesis of poly(ethylenedioxythiophene) (PEDOT) in an emulsion of acetonitrile in cyclohexane.

Because metallocenes are sensitive to nitrile and carbonyl groups, the acetonitrile and DMF emulsions were not suitable for carrying out metallocene-catalyzed olefin polymerization. Instead, we developed a second system, which consists of alkanes dispersed in perfluoroalkanes. In this case, we designed a new amphipolar polymeric emulsifier with fluorous and aliphatic side chains to stabilize the emulsions. Such heterogeneous mixtures facilitated the catalytic polymerization of ethylene or propylene to give spherical nanoparticles of high molecular weight polyolefins.

These nonaqueous systems also allow for the combination of different polymerization techniques to obtain complex architectures such as core–shell structures. Previously, such structures primarily used vinylic monomers, which greatly limited the number of polymer combinations.

We have demonstrated how nonaqueous emulsions allow the use of a broad variety of hydrolyzable monomers and sensitive catalysts to yield polyester, polyurethane, polyamide, conducting polymers, and polyolefin latex particles in one step under ambient reaction conditions. This nonpolar emulsion strategy dramatically increases the chemical palette of polymers that can form nanoparticles via emulsion polymerization.

Introduction

Nanofunctional materials, such as polymer latex particles, have widespread applications ranging from electronics,[1,2] pharmaceutics, and photonics to cosmetics, coatings,[3] and catalysis.[4] This is due to their well-defined morphology, size, and surface, as well as to their unique physical and chemical properties.[5] Latex particles in particular

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are applied since they are easily accessible by waterborne heterogeneous systems.[5,6] Synthetic methods such as emulsion, mini-emulsion, and suspension polymerization are well-established for the preparation of nanoparticles in different size domains ranging from a few nanometers up to several hundred micrometers. However, all of these processes are limited to water-stable monomers, mainly polymerizable via radical polymerization.[7−9] The formation of such particles utilizing water-sensitive monomers (e.g., acid dichlorides) or moisture-sensitive reactions (e.g., catalyzed polymerization of olefins in the presence of metallocenes or postmetallocenes) continues to be a challenge. There are always side reactions, for example, the hydrolysis of reactive acid chlorides or isocyanates, resulting in a loss of stoichiometry in the polycondensation or polyaddition process and in the formation of ureas instead of polyurethane. Sensitive catalysts, such as metallocenes, used for olefin polymerization are decomposed; thus one of the remaining challenges in emulsion polymerization is the development of new biphasic organic solvent systems tolerating the above-mentioned examples. Some nonaqueous emulsions have already been described in the literature.[10−12] However, in these cases, water is replaced mainly by alcohol, which is in fact not a solution for the above-mentioned problems, because there are similar side reactions to those observed in the presence of water. Therefore immiscible nonpolar/polar aprotic organic solvents able to form nonaqueous emulsions (i.e., oil-in-oil) are required.

Developing a process that enables not only the catalytic polymerization of monomers but also the polycondensation or polyaddition in emulsion requires more than one system. Finding nonmiscible organic solvents and synthesizing suitable stabilizers are decisive factors. For example, polyesters and polyurethanes require a relatively polar dispersed phase, while an olefin polymerization process needs a nonpolar solvent as well as the absence of functional groups in both the solvent and the stabilizer due to the solubility of the polymer and the sensitivity of the catalyst. We present different types of versatile nonaqueous emulsion processes suitable for the synthesis of polymer lattices. Their suitability for performing water-sensitive catalytic and oxidative polymerizations, polycondensations, and polyadditions is demonstrated. It is also shown that such systems can dramatically increase the number of polymers accessible via emulsion polymerization.

Results and Discussion

For nonaqueous emulsions, combinations of nonmiscible organic solvents have to be identified. In the literature, combinations of alcohols, such as methanol, ethanol, or glycol, as nonaqueous emulsions have been described.[5,6,12,13] Such systems, however, cannot avoid the central problem of side reactions with reactive monomers. The goal here is the development of emulsion systems that do not contain solvents with reactive groups such as hydroxy or amino functions.

Oil-in-Oil Emulsions for Polycondensation and Polyaddition Reactions. The first approach focuses on the development of emulsions suitable for the polymerization of more polar polymers such as polyesters or polyurethanes. Polar aprotic solvents, therefore, have to be dispersed. Suitable solvent couples are DMF dispersed in *n*-hexane or acetonitrile in cyclohexane or tetradecane. Riess et al.[14] described emulsions based on mixtures of acetonitrile and hexane. However, only hexane was dispersed in the polar acetonitrile. This remains unsatisfactory because most of the monomers and polymers are much more soluble in the polar continuous phase than in the emulsified alkane. Obviously, this does not lead to polymerization inside the droplets but in the continuous phase, and particles are thus not accessible.

Emulsifier Design and Emulsion Properties. The failure to obtain applicable emulsions was mainly due to the lack of suitable emulsifiers. It can be expected that low molecular weight surfactants in mixtures of organic solvents will not possess a sufficiently different polarity to stabilize droplets. Most of the emulsifiers are slightly soluble in both phases and stable micelles are therefore not observed. However, amphipolar polymers should be able to overcome this problem. It is already known from aqueous emulsion systems that copolymers, especially block copolymers, are very effective as emulsifiers.[6,9] In comparison to low molecular weight surfactants, such as sodium dodecylsulfonate (SDS), much lower concentrations of an amphiphilic block copolymer are required to form stable micelles.[15] To find suitable combinations of block copolymers and to avoid a systematic screening, the so-called Hansen parameters were applied.[16] These parameters, calculated for manifold systems, allow the interaction of a polymer with a given solvent to be predicted. A polymer is perfectly soluble in a solvent if both show the same parameter δ.

DMF and acetonitrile are known to be ideal solvents for polyurethane and polyester formation. As shown in Figure 1, poly(methyl methacrylate) (PMMA) has a Hansen parameter similar to both DMF and acetonitrile; therefore, it should be a good candidate to stabilize the polar phase, while on the other hand polyisoprene (PI) matches the values of aliphatic solvents. Consequently, we expected a PI-*b*-PMMA to be able to stabilize emulsions of DMF in hexane. This polymer, with var-

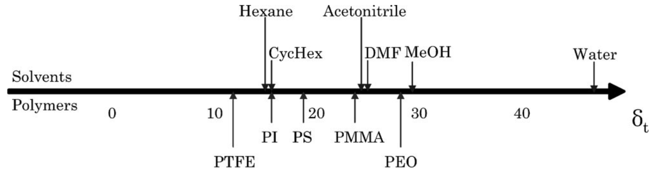


FIGURE 1. Hansen parameter values for common organic solvents.

ied average molecular weights and block ratios, was accessible by sequential anionic polymerization using standard procedures. Emulsions of DMF or acetonitrile in hexane in the presence of these polymers were prepared and characterized by dynamic light scattering (DLS). In all cases, stable nonaqueous oil-in-oil emulsions, with droplet diameters ranging from 20 to 100 nm, were observed (Table 1). The size of these "nanoreactors" was controlled by varying the PI-*b*-PMMA emulsifier concentration. It can be assumed that 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).

Nonaqueous Emulsion Polycondensation. It has so far not been possible to directly produce polyester nanoparticles with the size and shape of traditional polymer latex particles, for example, polystyrene. Reaction conditions involve temperatures of up to 250 °C and highly reduced pressures that hinder the application of well-established methods of latex preparation. Three attempts toward polyester particles using multistep procedures have already been described in the literature. The first one involves direct emulsion polycondensation of dicarboxylic acids and dioles in water in the presence of surfactants such as *p*-dodecylbenzenesulfonic acid or scandium tris(dodecyl sulfate).[18] However, the water present results in hydrolysis of the components and additionally shifts the equilibrium of the esterification toward the diacid and dihydroxy compound. Therefore, only number-average molecular weights of up to 1500 g/mol were reported for the polyesters in the nanoparticles with average particle diameters ranging from 100 to 500 nm.[19] The second concept is based on the spraying of polyester or polymer melts from supercritical solution, forming particles ranging from 0.5 to 2 μm with nonspherical shapes. In the third concept, a dispersion polymerization of polyester oligomers at temperatures of up to 200 °C was performed.[20] Drawbacks of this method were the use of silicon oil, which is difficult to remove, and a multistep procedure requiring the synthesis of oligomers, which were then transformed to high molecular weight polymers at high temperatures.

All of these difficulties are simply overcome by using the newly developed nonaqueous emulsions based on oil-in-oil dispersed mixtures.[21] The reactions were performed under mild conditions in emulsions of acetonitrile in cyclohexane and DMF in *n*-hexane, using pyridine or triethylamine as base. The emulsions were stabilized by PI-*b*-PMMA. Bis(hydroxymethyl)cyclohexane (BHC) (mixture of cis and trans isomers) **2** and ethylene glycol **4** were chosen as diols; adipoyl dichloride **1** and terephthaloyl dichloride were used as acid dichlorides (Scheme 1, Table 2). The diol was dissolved in the polar phase and emulsified in the nonpolar organic solvent. Upon addition of the dichloride to the base, the polycondensation reaction was started by diffusion of the dichloride from the continuous into the dispersed phase. Since the diol components as well as the catalysts are only soluble in this phase (as proven by ^{1}H NMR spectroscopy, measuring the concentration of the components separately in the different solvents), it

TABLE 1. Characterization of PI-*b*-PMMA Block Copolymers and Obtained Droplet Sizes[17a]

copolymer	M_n PI (g/mol)[b]	M_n PMMA (g/mol)[b]	PI/PMMA ratio	M_n total (g/mol)[b]	dispersity[b]	mean droplet size[c] (nm)
PI-*b*-PMMA I	5 500	2 500	2/1	8 000	1.2	37
PI-*b*-PMMA II	15 500	7 000	2/1	22 500	1.2	42
PI-*b*-PMMA III	23 000	7 000	3/1	30 000	1.3	95

[a] Hexane (12 g) was mixed with the PI-*b*-PMMA (0.2 g) and DMF (1.5 g) and then emulsified by stirring and ultrasonication. [b] By gel permeation chromatography (GPC) vs poly(isoprene) standard in THF. [c] By dynamic light scattering.

SCHEME 1. Polyester Formation of Different Diols and Diacid Dichlorides

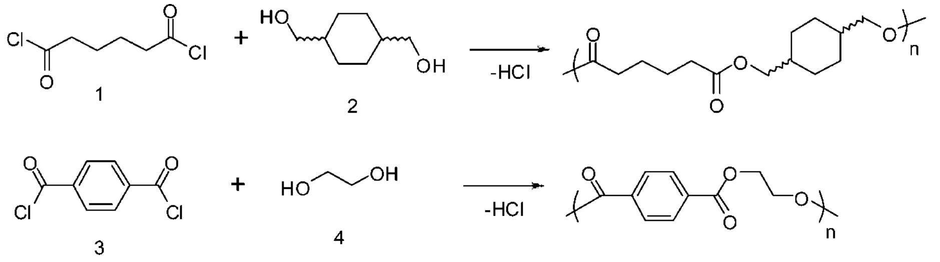


TABLE 2. Polyesterification Reactions Performed in Nonaqueous Emulsions: Experimental Conditions and Results

expt	dichloride	$n_{\text{dichloride}}$ (mmol)	diole	n_{diole} (mmol)	base	n_{base} (mmol)	diameter[a] (nm)	M_w[b] (g mol^{-1})	D[c]
1	ADCl	6.6	BHC	6	pyridine	8	60	22 000	1.7
2	ADCl	6.6	BHC	6	pyridine	8	60	20 000	2.2
3	ADCl	6.6	BHC	6	pyridine	13	58	16 000	2.7

[a] Determined by dynamic light scattering; particles redispersed in hexane at low concentration. [b] Determined by GPC in THF versus polystyrene standards. [c] Dispersity of the polymer, determined by GPC.

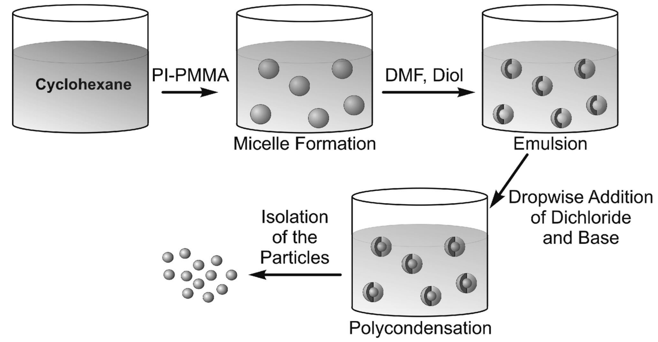


FIGURE 2. Synthesis of polyester particles in nonaqueous emulsion.

can be safely assumed that the polycondensation only occurred within the dispersed droplets (Figure 2). In all cases, narrowly distributed spherical polyester latex particles with average diameters as small as 60 nm (measured by scanning electron microscopy (SEM) and DLS) were obtained (Table 2, Figure 3).

In contrast to methods described in the literature, this process allows for the fabrication of small spherical particles in one single step.[22] The molecular weights (M_w) of the polyesters were found to be up to 22 000 g/mol, which was more than 12 times higher than the surfactant- catalyzed direct emulsion condensation method described in the literature.

Due to their residual emulsifier shell, the particles were redispersable in *n*-hexane after purification, and the dispersions showed a long period of stability (>4 weeks).

This is the first method that synthesizes spherical, high molecular weight polyester nanoparticles in one step at ambient temperatures.[21] It can be applied to all activated diacids and diols. The only requirement is that at least one component is exclusively soluble in the dispersed phase.

Polyaddition in Nonaqueous Emulsion. Because isocyanate compounds are sensitive to water, polyurethane nanoparticles cannot be produced by aqueous emulsion, miniemulsion, or suspension polymerization methods without the formation of side products. For example, the direct mini-emulsion polyaddition of diisocyanates and diols in water, catalyzed by amines or organotin compounds, such as dibutyltin dilaureate, results in decomposition of the isocyanate. This leads to the formation of amines and urea, proven by IR spectroscopy.[10,11,23] In addition, the control of the stoichiometry is no longer guaranteed, causing a decrease in the molecular weights. As a result, average molecular weights (M_n) of up to only 13 000 g/mol with dispersities as high as 5.2 are reported. In this case, polyurethane nanoparticles with mean diameters ranging from 80 to 250 nm are obtained. Another

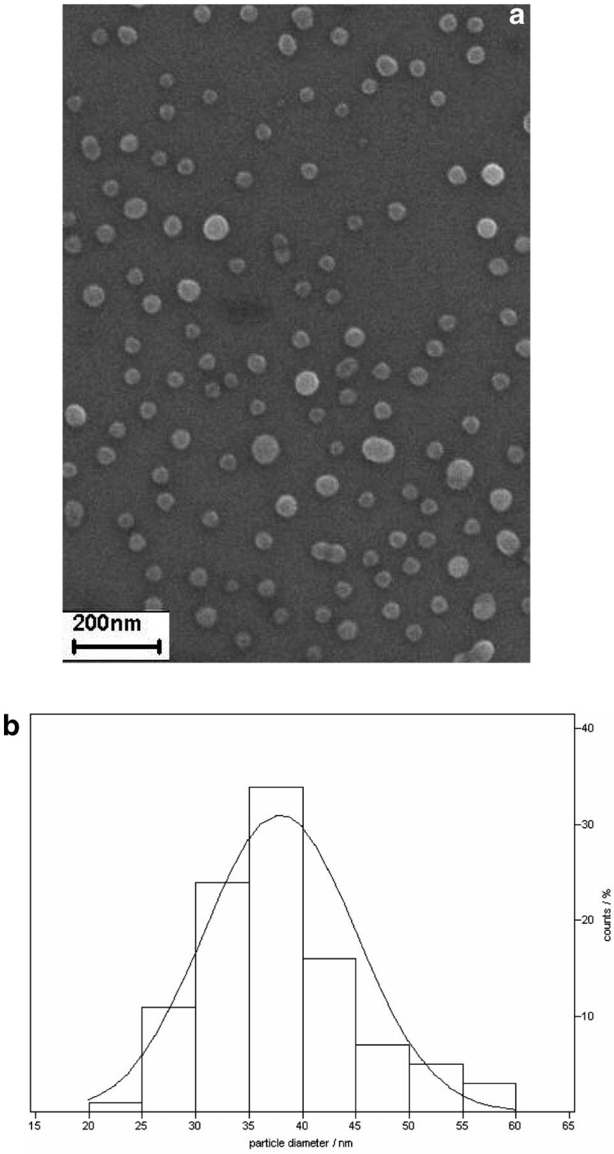


FIGURE 3. (a) SEM images and (b) particle size distribution of polyester nanoparticles (expt 4). Mean particle size = 38 nm (SD ± 7 nm) determined by SEM (based on 100 particles).

TABLE 3. Experimental Conditions[a] and Results of the Preparation of PU/Polymethacrylate Core–Shell Particles in Nonaqueous Emulsion

sample	HMDI (core) [mmol]	BHC (core) [mmol]	M_n[b] (core) [g/mol]	D[c] (core)	avg diam[c] ± SD[d] (core) [nm]	methacrylate (shell) [mmol]	avg diam[c] ± SD[d] (core–shell) [nm]
1	1.6	1.5	6 800	2.06	110 ± 40	5 (MMA)	150 ± 140
2	1.6	1.5	13 900	1.60	120 ± 90	5 (MMA)	420 ± 120
3	1.6	1.5	10 100	1.69	70 ± 30	3.5 (tBMA)	240 ± 110
4	1.6	1.5	14 800	1.55	90 ± 30	3.5 (tBMA)	130 ± 90
5	1.6	1.5	8 600	1.31	120 ± 100	3.8 (HEMA)	330 ± 80
6	1.28	1.2	8 100	1.66	500 ± 80	3.1 (HEMA)	600 ± 130

[a] In 12 g of *n*-hexane, 210 mg of PI-*b*-PMMA, and 1.2 g of DMF, after 10 min ultrasonication at 40 °C. [b] Determined by SEC in DMF versus PS standard. [c] Determined by SEM by measuring the diameter of 100 particles. [d] $\pm\sigma = (\sum(x - \bar{x}/(n - 1))^{0.5}$.

typical example describes the preparation of nanoparticles in a complex two-step procedure.[5] In the first step, the polyaddition reaction of diisocyanates and diols is performed at high temperatures in bulk or in a nonaqueous solvent. To form particles, the obtained polyurethanes are subsequently sprayed or mixed, as either a solution or a melt, into a second auxiliary agent, for example, compressed CO_2 or another inert organic solvent. To circumvent these serious drawbacks, a versatile method for the preparation of small polyurethane nanoparticles under mild and nonaqueous conditions is needed. In an approach similar to that presented for polycondensation, the developed nonaqueous emulsion systems may be applied for polyaddition reactions.[24] These emulsions again consist of a polar organic solvent, for example, acetonitrile or DMF dispersed in cyclohexane or *n*-hexane.

In contrast to the methods described in the literature, these systems allow the fabrication of polyurethane nanoparticles in one step without the formation of urea. The average molecular weights (M_n) of the polyurethanes were found to be as high as 40 000 g/mol (dispersity 2.0), which corresponds to conversions as high as 0.99. It is assumed that two main factors are responsible for the high molecular weights and conversions: (i) the absence of water during the reaction, which decreases the amount of side reactions and thus results in an unbalanced stoichiometry, and (ii) the fulfilled Schotten–Baumann conditions, which means that the 1:1 stoichiometry necessary for the polyaddition at the interface is controlled by the diffusion of the monomers at the interface of the continuous and the dispersed phase. Because the diols were only soluble in the dispersed droplets, the stoichiometry of the reaction was controlled by the diffusion of the diisocyanate component.[24] Preliminary experiments also revealed that these polyurethane (PU) nanoparticles may be applied as thin coatings on metallic surfaces for the prevention of corrosion, using only 25% of the material traditionally applied for this application.

Core–Shell Structures Formed in Oil-in-Oil Emulsions. Due to their excellent film-forming properties, one main application for latex particles obtained from emulsion polymerization is in coatings and paints.[3] However, this is only achieved when core–shell structures consisting of a core with a polymer of a high T_g is combined with the shell of a polymer with a low T_g. While the stiff core is responsible for the stability of the particles, the flexible shell is required for the film formation after casting on surfaces. Prominent examples are polystyrene-*b*-polybutylacrylate or polystyrene-*b*-polybutadiene. Such polymer structures are mainly accessible by using vinylic monomers, which drastically limits the potential number of combinations. Previously only radical polymerizations have been used for the construction of core–shell structures. Oil-in-oil emulsions now enable the combination of polycondensates or polymers obtained from polyadditions with radically formed polymers in such core–shell structures.

To build up a nonaqueous emulsion, DMF once again served as the dispersed phase and *n*-hexane was used as the continuous phase. These solvents were selected to ensure that the reaction took place exclusively in the dispersed phase (DMF), due to the solubility of all monomers therein and the insolubility of the diol (for polyaddition) and the initiator (for radical polymerization) in the continuous phase. A PI-*b*-PMMA was used as an emulsifier (Table 1, PI-*b*-PMMA IV).

The aliphatic diol (BHC) and the aliphatic diisocyanate 4,4′-methylenebis(cyclohexylisocyanate) (HMDI) were used for the synthesis of the PU core particles, as shown in Table 3. MMA, *tert*-butyl methacrylate (*t*BMA) and hydroxyethyl methacrylate (HEMA) were used to prepare the shell structures. BHC was dissolved in DMF with 2.5 mol % catalyst and added to the *n*-hexane/copolymer dispersion. The emulsion was formed by ultrasonication of this mixture. The polyaddition was started by the dropwise addition of HMDI to the emulsion. Dibutyltin diacetate (DBDA) was applied as the catalyst for promoting the polyaddition and obtaining high molecular weights (Figure 4).

Remarkably, the highest molecular weight was not achieved by mixing both components in an equimolar ratio but by adding HMDI slowly to the emulsion. This slow addition of HMDI, as used in industrial polycondensations or poly-

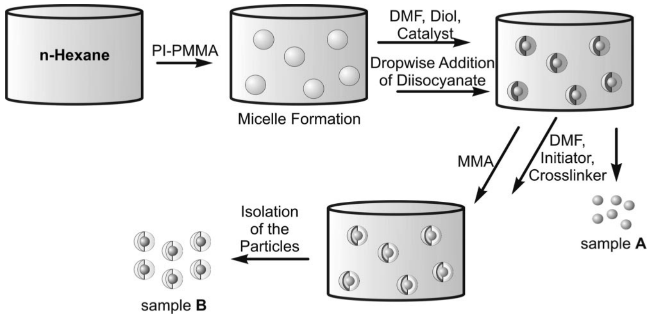


FIGURE 4. Preparation of PU/poly(methyl methacrylate) core−shell type particles in nonaqueous emulsion.

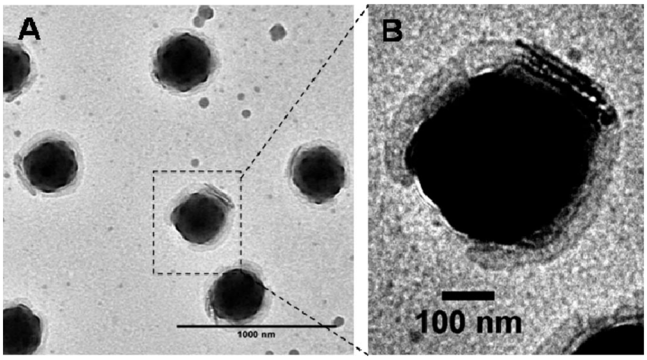


FIGURE 5. TEM images of sample 1B, 200 kV operating voltage, dropcast from solution.

addition reactions,[25] ensured that the exact equimolar ratio of the two reactants necessary to achieve high molecular weights was finally reached. To further prepare the shell structures, an extra amount of DMF containing the radical initiator and a cross-linking agent was added, followed by the methacrylate after ultrasonication. Since the initiator is insoluble in the *n*-hexane phase, polymerization around the PU cores started with the diffusion of methacrylate into the droplets and a temperature increase to 30 °C.

To exclude the possibility that pure PMMA particles and pure PU particles might coexist after the polymerization, the particle size before and after the shell formation was investigated by light scattering, transmission electron microscopy (TEM), and SEM. A clear increase in the particle size was observed (Table 3). An average value was calculated by evaluating the diameter of 100 particles obtained from the SEM images. In all cases, monomodal curves were observed, and the values measured by both methods were comparable. For example, the particle size of sample 1A (PU core particles) was about 110 nm, while the diameter of sample 1B (PU/PMMA core−shell particles) was about 150 nm. This indicated the formation of a shell structure around the cores.

In addition, the core−shell particles were visualized by TEM. Figure 5 presents a particle before and after the shell formation. The area of high contrast (black), caused by the polyurethane due to the urea groups, is surrounded by a ring of low contrast. This can be attributed to the acrylate shell since this polymer has a lower contrast in TEM. In addition, the TEM images reveal that some shells were partially discontinuous. A similar effect is observed when silica particles are surrounded by a polymer shell in emulsion. It can be assumed that the PU core particles were not located in the center of the micelles when MMA was added and therefore the shell was not equally thick around the core.

In addition, the molecular weights of the PU core particles as determined by means of SEC (DMF, polystyrene standard; Table 3) are up to 14 800 g/mol (M_n). These remarkably high molecular weights can be attributed to the absence of water. This leads to higher conversions for polyadditions due to the suppression of urea formation, which always causes deviations from the ideal stoichiometry of the diol and the diisocyanate. The preparation of high molecular weight cores allowed for the generation of particles with very rigid cores and soft shells. In comparison to the literature, where PU cores show molecular weights (M_n) not higher than 13 500 g/mol with a high content of urea structures, the described method provides higher molecular weights, at the same time avoiding multipot syntheses or the use of prepolymers. Apart from the high molecular weight, another improvement was the quantitative conversion of the isocyanate groups with the hydroxy groups. There was no side reaction with water, which normally results in a loss of educts and formation of urea derivatives, leading to an altering of the properties of the PU core.

Due to the detected increase of the particle size after the radical polymerization in combination with the observed shell around the dark PU cores in the TEM images, it can be safely assumed that the preparation of core−shell particles by water-sensitive monomers in nonaqueous emulsion was successful. Because this process is not restricted in principle to the preparation of polymers by polyaddition, this is a promising tool for generating new core−shell structures by applying synthetic procedures other than radical polymerization.

Oil-in-Oil Emulsions for Conducting Particles. While polycondensation and polyaddition reactions were discussed in the first section, this section describes catalytic reactions yielding conducting organic particles using the same solvent pairs and emulsifiers.

Nonaqueous Emulsion Polymerization of Acetylene. The high electrical conductivity of doped poly(acetylene), the simplest of all conjugated polymers, has attracted much attention.[26] However, due to its insolubility and inherent instability in both the pristine and doped state under ambient conditions, it has still to find a successful application. Produc-

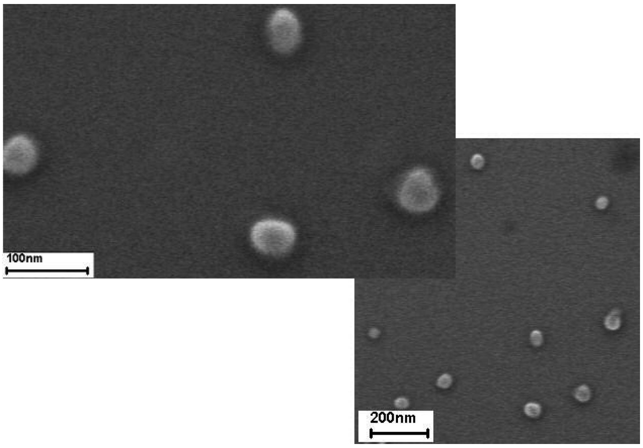


FIGURE 6. SEM image of poly(acetylene) nanoparticles.

ing poly(acetylene) latex nanoparticles would not only offer novel processing pathways but also allow the utilization of these particles as pigment materials and antistatic additives in various inert polymer matrices. In this approach, acetylene was polymerized in acetonitrile/hexane mixtures using a Luttinger catalyst.[17] The Luttinger catalyst was chosen because poly(acetylene) prepared by this method exhibits a higher stability toward oxygen than poly(acetylene) prepared by the original Shirakawa method.[26] The cobalt(II) nitrate and sodium borohydride based Luttinger catalyst was enclosed in the dispersed acetonitrile droplets. Polymerization was achieved at room temperature upon a flow of acetylene gas through the stirred emulsion. The average diameter of the particles was found to be 43 ± 10 nm (Figure 6).[17]

Conductivity was measured to be 0.30 S/cm at room temperature. It can thus be concluded that high conductivities can be obtained and that sufficient percolation pathways through the prepared nanoparticle film are present. Furthermore, these particles were printable by a standard ink-jet printer. Conjugated polymer nanoparticles prepared according to this route are expected to find many applications, such as antistatic pigments, materials for radio frequency identification technologies, and novel immunodiagnostic devices.

Nonaqueous Emulsion Polymerization of PEDOT. As a second example of a conjugated polymer, ethylenedioxythiophene (EDOT) was polymerized in the presence of Fe^{3+} salts in a nonaqueous emulsion system consisting of acetonitrile in cyclohexane. EDOT shows good solubility in cyclohexane as well as in acetonitrile. Due to the presence of its nitrile groups, acetonitrile is suitable to complex iron(III) ions, which are insoluble in cyclohexane. It can be safely assumed that polymerization only occurs in the dispersed acetonitrile phase (stabilized by PI-*b*-PMMA) because the monomer and the oxidant are only both present in these "nanoreactors" (Table 4, Figure 7). The obtained nanoparticles could be precipitated upon addition of excess methanol/acetonitrile.[27,28] Because both blocks of the PI-*b*-PMMA were completely soluble in THF, it was possible to obtain pure PEDOT nanoparticles upon washing the precipitate with THF. FT-IR spectra of the pure nanoparticles displayed no carbonyl bands, indicating the absence of residual PI-*b*-PMMA. The commonly observed drawback of dispersion polymerization for obtaining conducting polymer nanoparticles is the difficult removal of the polymeric stabilizer from the surface after polymerization. The residual block copolymer shell keeps the obtained nanoparticles apart and interrupts charge carrier percolation pathways between the particles.

TABLE 4. Characteristics of EDOT Polymerizations in Nonaqueous Acetonitrile/Cyclohexane Emulsion[a]

sample	emulsifier (wt %)[b]	EDOT (mmol)	$Fe(Cl)_3$ (mol % per EDOT)	mean particle diameter[c] (nm)
1	1.5	3.4	197	30 ± 13
2	2.2	3.7	186	23 ± 6
3	1.9	3.7	186	23 ± 7

[a] Polymerizations performed in 24 g of cyclohexane and 3 g of acetonitrile. [b] Cyclohexane wt %. [c] By SEM.

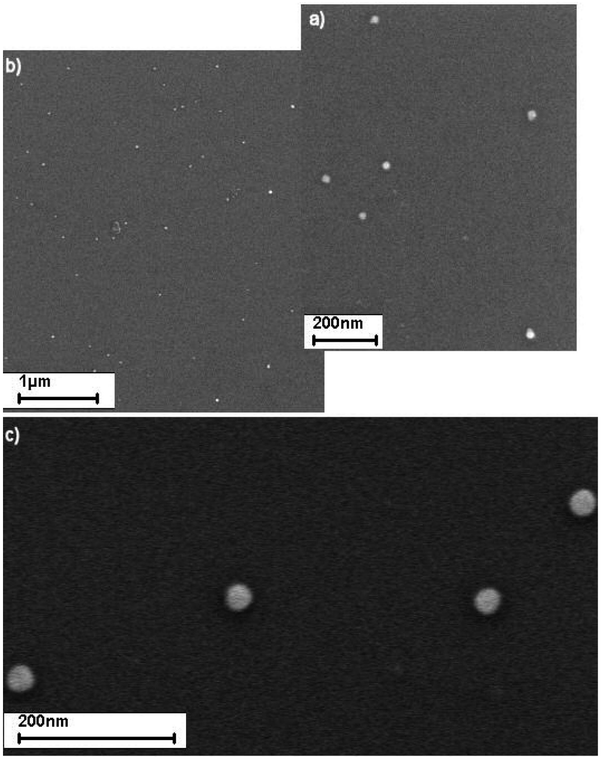
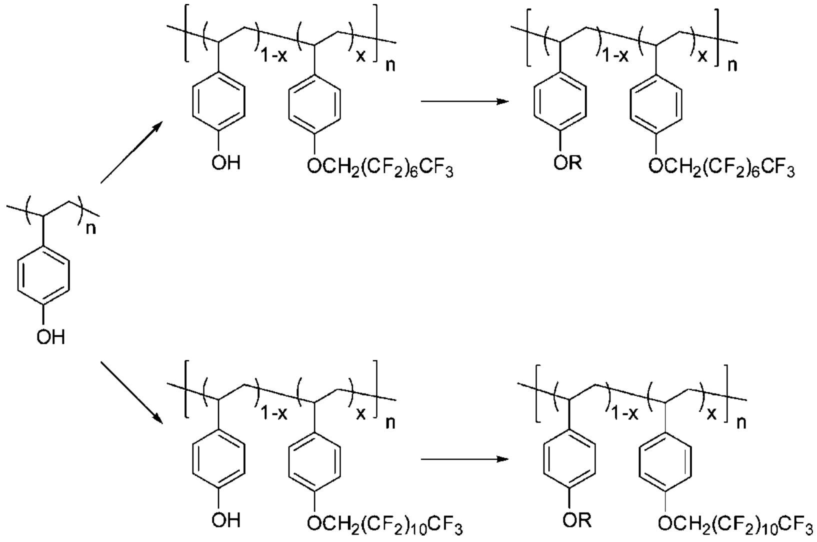


FIGURE 7. SEM images of PEDOT nanoparticles: (a) sample 1; (b) sample 2; (c) sample 3 (Table 4).

The obtained printable PEDOT particles were absolutely water-free in contrast to the commercially available PEDOT polystyrene sulfonate suspension. These particles could be printed by a standard ink-jet printer of the redispersed PEDOT using standard cartridges.

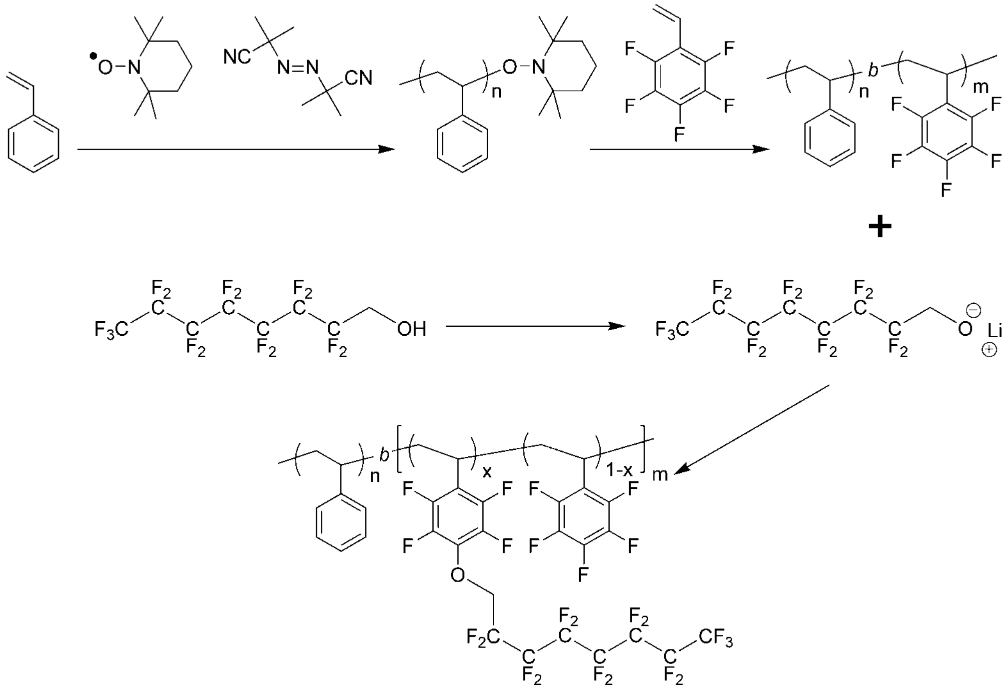
Oil-in-Oil Emulsions for Polyolefin Formation in Nonaqueous Fluorous Emulsions. While PI-*b*-PMMA is able to stabilize emulsions with DMF, which is an excellent solvent for polyesters and polyurethanes, such an emulsion system is not suitable for the metallocene-catalyzed[29,30] polymerization of olefins. DMF does not serve as a good solvent for polyolefins nor do metallocenes tolerate the applied emulsifiers. The development of an emulsion process applicable for polyolefins is very attractive because these polymers play a crucial role in contemporary life, indicated by a consumption of more than 100 million tons per year.[31−34] Most metallocenes possess excellent activities with respect to olefin polymerization and in addition allow control over the tacticity while yielding high molecular weights.[33,35] Unfortunately, most of these systems are highly moisture- and air-sensitive. In homogeneous polymerization, the size and shape of the obtained particles cannot always be properly controlled. Furthermore, reactor fouling occurs due to local overheating.

SCHEME 2. Synthesis of Statistical Fluorous Biphasic Stabilizers[a]



[a] The emulsifying properties are tuned by the substitution rate.

SCHEME 3. Synthesis of Biphasic Block Copolymers Bearing Fluorous Chains and Alkyl Chains



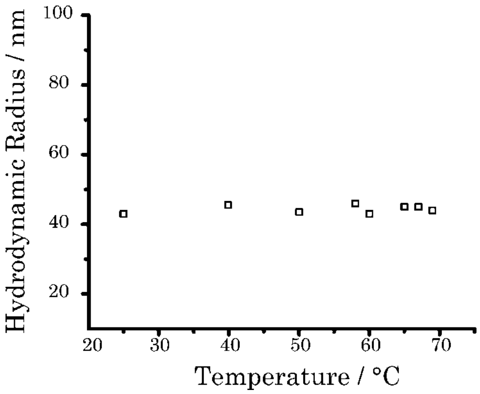


FIGURE 8. Dynamic light scattering of a fluorous/toluene emulsion (10 vol % toluene; 10 wt % block copolymer as emulsifier) showing temperature dependence of the hydrodynamic radius.

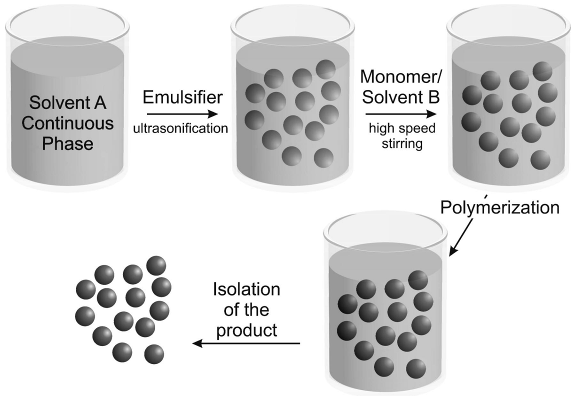


FIGURE 9. The emulsion polymerization of olefins in a perfluoralkane/alkane mixture.

TABLE 5. Polymerization Results of Ethylene and Propylene in Fluorous/Hydrocarbon Emulsions

run	pressure (bar)	time (min)	M_w (g/mol)[a]	activity (kg PP/ (mol Zr h bar) or kg PE/ (mol Zr h bar))	particle size[b]
1	30 (ethylene)	60	850 000	1400	1−20 μm
2	25 (ethylene)	30	1 400 000	650	1−20 μm
3	1 (propylene)	5	700 000	400	30 nm
4[c]	2 (propylene)	12	80 000	200	120 nm
5[d]	10 (propylene)	60	180 000	400	200 nm

[a] Measured by GPC (*o*-dichlorobenzene, 135 °C, polystyrene standard). [b] By SEM. [c] Gas phase propylene polymerization. [d] Liquid propylene dispersed in perfluoromethylcyclohexane.

This can be overcome by supporting the catalyst on magnesium chloride, silica particles, clays, or polymers.[36] Another approach to solve these problems is the use of water-based emulsions. Even though it is a rapidly developing field of research, most industrial catalyst systems do not tolerate water and thus still have no alternative.[37] Concepts for the use of the highly active metallocenes and postmetallocenes in an emulsion are still a challenge.

The emulsions described above are not applicable to the synthesis of polyolefins, due to the sensitivity of the metallocenes to nitrile and carbonyl groups. Therefore the utilization of a nonaqueous, fluorous/organic emulsion (alkane in perfluoromethyl cyclohexane) is proposed as a solvent mixture for olefin polymerization in emulsion. We opted for alkanes such as isobutene or hexane, typically used in slurry polymerizations of ethylene or propylene. Perfluoroalkanes were chosen as the continuous phase because they do not interact with the catalyst due to the lack of any functional groups and to their immiscibility with hydrocarbon solvents.

Emulsifier Design and Emulsion Properties. As in the systems mentioned above, the stabilization of the emulsions is also crucial here. While the application of perfluoro systems in aqueous phases and the necessary amphiphilic surfactants are widely described in the literature,[38,39] reports on emulsions in organic phases are lacking. In order to find suitable conditions for such an emulsion in fluorous media, new semifluorinated biphasic emulsifiers had to be developed. Statistical and block copolymers, containing both fluorous and aliphatic side chains, were proposed as emulsifiers. It was shown that both types of polymers were able to stabilize aqueous emulsions, and the same was expected for organic/fluorous emulsions. In the first approach polyhydroxystyrene was etherified in two steps, first with a perfluoroalkyl chain and subsequently with a hydrocarbon. The choice of the polymer was prompted in part by its low polarity, enabling its use with metallocene catalysts. On the other hand, the styrene backbone provided sufficient flexibility of the polymer side chains to reorganize on the surface of the droplet and suppress aggregation. An amphipolar statistical copolymer was obtained, which acted as a stabilizer in fluorous/organic solvent mixtures (Scheme 2).

A disadvantage in this approach is the poor solubility of the final emulsifiers in single organic solvents (alkanes, THF, DMF, etc., and also in pure fluorinated solvents) due to their amphiphilicity, as well as the difficulty in achieving the full substitution of the hydroxy groups. The second approach used nitroxide-mediated radical polymerization to copolymerize styrene and 1,2,3,4,5-pentafluorostyrene to achieve amphiphilic block copolymers acting as emulsifiers in fluorous/organic solvent mixtures. By insertion of perfluorinated alkyl chains, improvement of the emulsifying properties was expected, because the fluorous content was significantly increased (Scheme 3).

In order to investigate the properties of the emulsifiers, emulsions consisting of differing ratios of toluene and perfluoromethylcyclohexane (PFMCH) and emulsifier were prepared, and their properties were evaluated. Experiments were performed in a sealed scattering cell, allowing DLS measurements

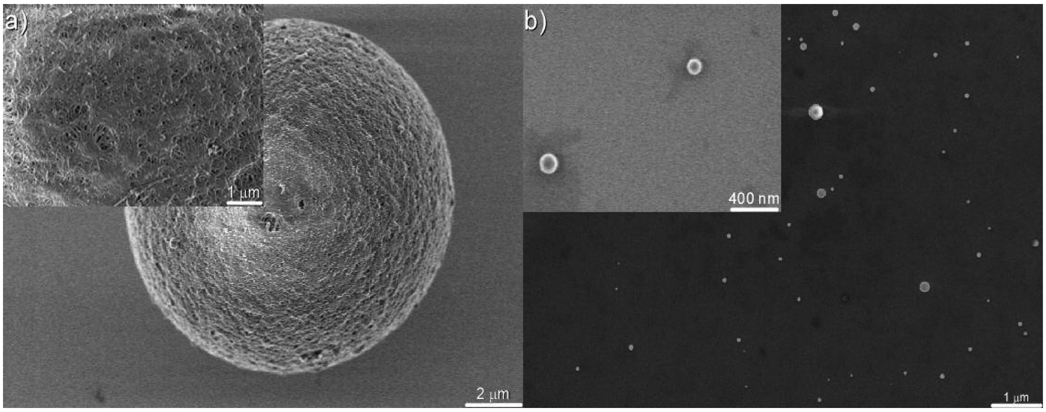


FIGURE 10. SEM images of the resulting polypropylene particles: (a) run 1; (b) run 3.

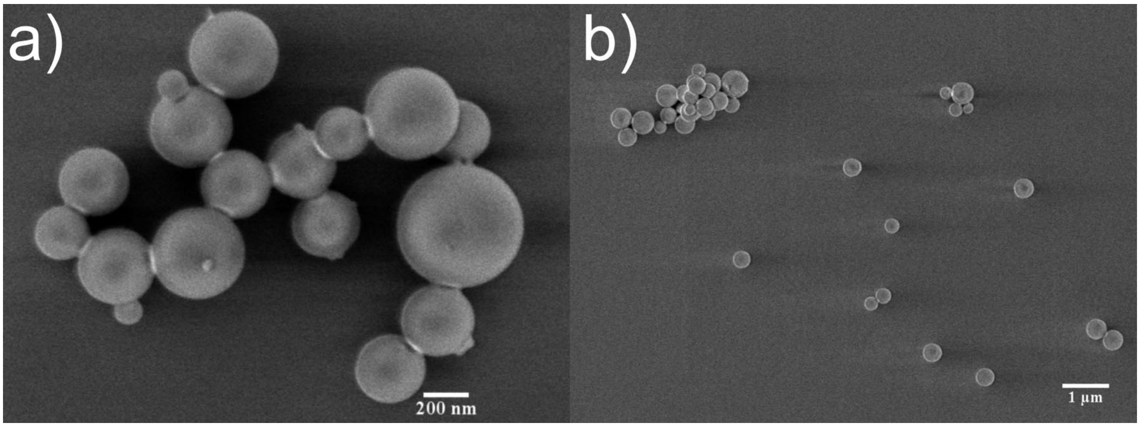


FIGURE 11. SEM images of the polypropylene particles resulting from liquid propylene emulsion polymerization (Table 5, run 5).

above the boiling point of the solvent while preventing evaporation. The measurements showed no change in the mean droplet size in the range between 25 and 70 °C. In the case of the fluorous oil-in-oil emulsion system, it was shown that the temperature does not influence the droplet size, even above the boiling point (Figure 8).

Olefin Polymerization. The water-free emulsion was tested as a reaction medium for metallocene-catalyzed olefin polymerization. Because neither the monomer nor the catalyst is soluble in the fluorous phase, the whole process takes place inside the confined geometry of the droplets (Figure 9).[40]

The resulting polymer was obtained as well-defined spherical particles with very high molecular weight (polyethylene M_w 1 400 000) (Table 5, run 2). Upon decrease of the polymerization time as well as the pressure, both polyethylene and polypropylene particle sizes decreased into the nanometer region (Table 5, runs 1 and 2 versus 3 and 4; Figure 10). This is typical for a classical emulsion polymerization and indicates the diffusion of the monomer as the limiting factor for the catalyst activity.

Polymerization of liquid propylene in a perfluorinated continuous phase was the logical extension. Perfectly shaped particles were formed inside the emulsion, a prerequisite for a very processable product (Table 5, run 5; Figure 11). In addition, the activities inside the emulsion were very high in comparison to run 4.[41]

While latex particle-based supports generate polyolefin particles in the millimeter range,[36] suitable for extrusion processing, the much smaller particles formed in an emulsion are highly attractive for cosmetics, paints, and adhesives and also as precursors for coatings. The better control obtained inside the emulsion allows liquid propylene to be used as dispersed phase and directly polymerized. Furthermore, varieties of core—shell structures are accessible in this water-free emulsion system, which broadens the application possibilities considerably.

Conclusions

Until now the synthesis of latex particles has been very much focused on waterborne systems, which severely restricts the type of polymers accessible by emulsion polymerizations. Typically, only vinylic polymers have been polymerizable to high molecular weights and without side reactions. Water-sensitive monomers have been applied but resulted typically in polymers either with low molecular weights or with defect structures or unwanted side products. Due to the development of nonaqueous conditions, the emulsion systems described allow the use of water-sensitive monomers and catalysts. This method is expected to permit the formation of new types of polymer nanoparticles.[15] Decisive in this new process was the right development of suitable emulsifiers able to stabilize two immiscible organic solvents, such as DMF in alkanes or alkanes in perfluoroalkane. A broad variety of hydrolyzable monomers and sensitive catalysts can be applied within this system to yield polyester, polyurethane, polyamide, and polyolefin latex particles in one step under ambient reaction conditions. Because this process can also be used for the subsequent polymerization of different monomers in emulsion, new core–shell structures based on combinations of polymers obtained from polycondensation, polyaddition, or catalytic processes are now accessible. Restrictions due to the use of systems based on acrylates or styryl derivatives are overcome. Because attributes such as film-forming and mechanical properties can now be adjusted and optimized by a larger number of polymers, a dramatic impact in colloid and polymer sciences is expected. The use of such particles as supports in catalysis or in medical applications, for example, for drug delivery or when labeled with dyes in diagnostics, are just a few examples worth mentioning. The incorporation of new types of nanoparticles results in improved impact, and modified materials can be considered for bulk applications. Because a pure organic system is created in this case, fewer compatibility problems can be expected.

Setting aside the unprecedented chances for new particle formation, an oil-in-water emulsion might seem ecologically more appealing than an oil-in-oil emulsion. Although water is considered as an environmentally benign solvent, when it is contaminated even with traces of organic compounds or solvents, it can complicate the processes of particle formation and processing. The easy removal and recycling of organic solvents might therefore be a further practicle advantage of the present protocol. The potential of this technology is already evident from these few considerations, and we can confidently propose it as a major breakthrough in polymer and colloid sciences.

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BIOGRAPHICAL INFORMATION

Dr. Markus Klapper was born in 1960 and got his Ph.D. degree from the University in Mainz (Prof. R. C. Schulz) in 1990. Since then he has been project leader of the subgroup *Polymer Synthesis* in the Organic Synthesis Department of Prof. Dr. Klaus Müllen at the Max-Planck-Institute for Polymer Research in Mainz. His research focuses in the area of catalysis, emulsion polymerization, and organic/inorganic nanoparticle formation. Other topics are membrane materials for fuel cells and polymer-analogous modifications.

Svetlin Nenov was born in 1979 in Sofia, Bulgaria. He received his Master of Science in the University of Sofia under the supervision of Prof. Dr. T. Deligeorgiev in 2004 for his work on synthesis of cyanine dyes for nucleic acid detection. He is now finishing his Ph.D. in the Max-Planck-Institute for Polymer Research under the supervision of Prof. Müllen. The topic of his research is "Nonaqueous Fluorous Emulsions".

Robert Haschick, born 1983 in Lauchhammer, Germany, studied Chemical Engineering at the Lausitz University of Applied Sciences and finished his Diploma Thesis on synthesis of core–shell nanoparticles in the group of Prof. Müllen at the Max Planck Institute for Polymer Research. He continues his work as a Ph.D. student in the same group since October 2007.

Dr. Kevin Müller (born 1980 in Wiesbaden, Germany) studied chemistry at the Fresenius University of Applied Sciences in Idstein and at the University of Mainz. After finishing his diploma thesis at Procter & Gamble on superabsorbent polymers, he joined the group of Prof. Klaus Müllen at the Max Planck Institute for Polymer Research, where he achieved his Ph.D. in 2008 for his work on nonaqueous emulsion polymerization. In January 2008, he moved to the polymer research laboratories of BASF SE in Ludwigshafen, Germany. For his research on superabsorbent polymers, Dr. Müller received the Max-Buchner-Award for technical chemistry in 2004. His research interests are centered on macromolecular chemistry and colloid science.

Prof. Dr. Klaus Müllen (born 1947 in Cologne, Germany) studied Chemistry at the University of Cologne. After finishing his Diploma Thesis with Prof. Vogel in 1969, he moved to the University of Basel, Switzerland, where he achieved his Ph.D. in 1972 for his work on EPR and NMR spectroscopy on bridged annulenes with Prof. Gersson. He obtained his habilitation in 1977 after postdoctoral research at ETH Zurich, working on NMR-spectroscopy and electrochemistry with Prof. J. F. M. Oth. In 1979, he became Professor in Organic Chemistry at the University of Cologne, and in 1983, he accepted the chair in Organic Chemistry at the University of Mainz. In 1989, Klaus Müllen became a scientific member of the Max Planck Society and was appointed director of the Synthetic Chemistry Department at Max Planck Institute for Polymer Research. He was appointed to a two year term as president of the German Chemical Society (GDCh) in January of 2008. His scientific focus lies on synthetic macromolecular chemistry, supramolecular chemistry, and materials science.

FOOTNOTES

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