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Polymer 46 (2005) 9892–9898

polymer

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Polydimethylsiloxane latexes and copolymers by polymerization and polyaddition in miniemulsion

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Received 24 January 2005; received in revised form 27 May 2005; accepted 27 July 2005
Available online 15 August 2005

Abstract

Different synthetic pathways have been explored to synthesize polysiloxane–acrylate and polysiloxane–urethane latexes with small and narrowly distributed particle sizes, using the specific advantages of the miniemulsion approach. Besides cross-linked latexes with high siloxane content, also hybrid particles were generated.

Keywords: Miniemulsion polymerization; Polysiloxane–acrylate; Polysiloxane–urethane

1. Introduction

Polydimethylsiloxane (PDMS) latexes are interesting for a number of purposes: Besides the very low glass transition of PDMS of 146 K [1] which allows thermoplasticity or toughening of bulk polymers even under extreme conditions, siloxane latexes are interesting to reduce the tack of rubbers [2], as carriers of actives [3] (and references cited therein) or for non-polluting, ultra-hydrophobic coatings [4]. As PDMS has only a low mechanical performance by itself, the PDMS is usually blocked or grafted with polyacrylates/polystyrene, giving core-shell latexes [5–7]. Polyurethane–polydimethylsiloxane particles of diameters in the range 500 nm up to 5 μm, have been also recently synthesized by step-growth polymerization in cyclohexaneor supercritical carbon dioxide [8]. For the generation of the PDMS from the monomer, both dispersion polycondensation of alkoxysilanes [5,9,10] as well as ring opening emulsion polymerization of the tetramer [7] have been employed. In the present context, it is important to note that the last reaction was also already performed in miniemulsions [11].

The classical pathways for the fabrication of the hybrid latex have to start from preformed polysiloxane particles; as standard emulsion polymerization with the very non-hydrophilic or oligomeric siloxane precursor it is practically impossible, due to the non- (or extremly slow) occurring transport of the siloxane through the aqueous phase. This is why the employment of miniemulsions is a promising alternative to broaden the range of accessible PDMS structures in dispersion. This was recently first evidenced by Stumbe et al. [12] and will be analyzed in the present paper in a broader context.

Miniemulsion polymerization is a powerful technique to produce a whole variety of new polymer latexes [13]. Nanodroplets with a diameter of 50–500 nm are formed by applying high shear already from the beginning of the reaction, and are stabilized throughout the polymerization by the simultaneous application of a surfactant and an osmotic stabilizer compound which is highly insoluble in the continuous phase [14–16]. The surfactant stabilizes the droplets against collisions; mass exchange (Ostwald ripening) between the droplets is suppressed by the use of the osmotic agent [17]. Each droplet then behaves like a nanoreactor, and the polymer particles produced have ideally the same size as the monomer droplets [18]. Because of that, the miniemulsion process can be applied in a much broader range than only radical polymerization [19–22],

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doi:10.1016/j.polymer.2005.07.080

especially also for polyaddition reactions of epoxides [21] and urethanes [22,23].

In this paper, we want to explore two different varieties of the miniemulsion polymerization to synthesize PDMS-containing polymer latexes with academic and industrial relevance:

- Telechelic PDMS macromonomers wearing two terminal acrylate units are directly polymerized by radical initiators to highly cross-linked PDMS microgels. These monomers are also copolymerized with standard monomers to generate interpenetrating hybrid microgels with hydrophobic and ultrahydrophobic subphases.
- Telechelic PDMS macromonomers wearing two terminal hydroxy groups are transferred into linear PDMS-polyurethanes by polyaddition in miniemulsion.

The obtained polymers and latexes are analyzed by dynamic light scattering, nuclear magnetic resonance (NMR) spectroscopy, surface tension measurements, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). Technical details about the procedure are found in our previous publications.

2. Experimental part

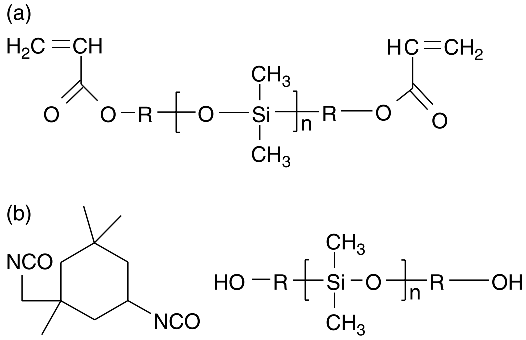
2.1. Chemicals

Styrene and butylacrylate were provided by Aldrich and distilled under reduced pressure prior to use. Potassium peroxodisulfate (KPS), sodium dodecyl sulfate (SDS) and isophoron diisocyanate (IPDI) from Fluka were used as received. Styrene and butyl acrylate (Fluka) were distilled before use. Lutensol AT50 (C_{16}/C_{18}-EO_{50}) was kindly provided by BASF AG. The initiator V59 (2, 2′-azobis(2-methyl-butyronitrile)) was a gift from Wako.

Telechelic polydimethylsiloxanes of different molecular weight were provided by TEGO Co.; there are two samples with two terminal acrylate groups (Scheme 1): TegoRad 2500 has a molecular weight of about 2000 g mol^{-1}, whereas TegoRad 2700 has a larger molecular weight of 6500 g mol^{-1}. Two other samples are terminated with two hydroxy-groups and have degrees of polymerisation of $n=10$ (Tegomer 2111) and $n=30$ (Tegomer 2311).

2.2. Synthesis via radical polymerization

A mixture of 6 g of the siloxane acrylate, 250 mg of hexadecane as hydrophobe and 100 mg of V59 as hydrophobic initiator were added to an aqueous solution consisting of 24 g water and the surfactant (type and amount see Table 1). After stirring rigorously for 1 h, the miniemulsion was obtained by ultrasonicating the mixture for 2 min at 90% amplitude (Branson sonifier W450, 1/2″ tip) under ice cooling in order to prevent polymerization. The miniemulsion was then heated to 60 °C and kept at that temperature for 14 h.



Scheme 1. Structures of the used monomers: (a) Polysiloxane with terminal end groups (b) isophoron diisocyanate (IPDI) and polysiloxane terminated with hydroxy groups ($n=10$ (Tegomer 2111) and $n=30$ (Tegomer 2311)).

2.3. Synthesis via polyaddition/urethane formation

Six grams of the monomer mixture (see Tables) and 200 mg hexadecane were added to a solution of 200 mg sodium dodecylsulfate and 24 g water. After vigorously stirring for 1 h, 50 mg of dioctyltindilaurate (DOTDL) were added. The miniemulsion was obtained by ultrasonicating the mixture for 2 min at 90% amplitude (Branson sonifier W450, 1/2″ tip) under ice cooling. The miniemulsion was then heated to 60 °C and kept at that temperature for 4 h. If vinylic monomers for radical polymerization were present in the minidroplets, the temperature was then increased to 72 °C and 12 mg potassium persulfate (KPS) per 1 g styrene was added. Full conversion was observed after 4 h as detected by NMR.

2.4. Analytical methods

The particle sizes were measured using a Nicomp particle sizer (Model 370, PSS Santa Barbara, USA) at a fixed scattering angle of 90°. The data were processed using the cumulants method.

Transmission electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted samples were mounted on 400-mesh carbon coated copper grids and left to dry. Contrasting was not applied.

3. Results

3.1. Radical polymerization

Stable miniemulsions even at high siloxane diacrylate contents were obtained with both siloxane chain lengths

Table 1
Characteristics of the nanoparticles obtained from siloxane acrylate

Sample	Siloxane acrylate	Surfactant	Surfactant concentration (%)	Particle size (nm)	Solid content (%)	Surface tension (mN/m)
2500 g	Rad-2500	SDS	1.2	195	13.82	37.4
2500 h	Rad-2500	SDS	2.4	197	19.09	39.9
2500 f	Rad-2500	SDS	3.3	189	20.45	39.0
2500 b	Rad-2500	SDS	6.0	179	21.01	40.2
2500 c	Rad-2500	Lutensol	3.3	365	20.80	36.2
2500 d	Rad-2500	Lutensol	8.3	285	21.04	35.9
2500 e	Rad-2500	Lutensol	13.3	264	21.10	38.9
2700 a	Rad-2700	SDS	1.2	253	20.37	38.7
2700 e	Rad-2700	SDS	2.4	249	17.96	36.8
2700 f	Rad-2700	SDS	4.8	205	18.89	33.8
2700 b	Rad-2700	SDS	6.0	408	16.26	34.7
2700 c	Rad-2700	Lutensol	3.3	2100	18.50	28.6
2700 d	Rad-2700	Lutensol	13.3	1090	21.39	29.8

Coagulated.

already at small amounts of surfactant. A polymerization of the monomers inside the droplets can only be obtained by hydrophobic initiators, which are soluble in the organic phase. Due to the absence of any monomeric species in the water phase, oligo-radicals that could enter the droplets cannot be formed in the water phase and therefore water-soluble initiators like KPS are not suited. The hydrophobic initiator V59 was used at a reaction temperature of 72 °C. The resulting data are summarized in Table 1.

Whereas for the monomer miniemulsion itself only small amounts of surfactant (e.g. 1.2 wt% sodium dodecyl sulfate (SDS) with respect to the monomer phase) is required, the amount had to be increased to obtain sufficient stability after polymerization, too. This speaks for an increase of hydrophobicity throughout polymerization and a weak adherence of the hydrocarbon surfactant SDS onto the bare siloxane particles. For the short chain siloxane (TegoRad2500) 2.4% of the surfactant sodium dodecyl sulfate was minimal to obtain a coagulum-free latex. The particle size of about 200 nm as determined by dynamic light scattering is the same before and after polymerization, which is a clear indication of a true miniemulsion polymerization process. This size is larger than in the case of styrene, in accordance with the high hydrophobicity of the monomer. Similar particle sizes were observed for the very hydrophobic lauryl methacrylate [24]. The surface tension of the latex is with 40 mN m^{-1} comparably low for a miniemulsion, indicating that the surfactant is not effectively adhered. This follows observations made below and is a result of the expected low compatibility between PDMS and SDS. Related to that, the particle size can only be slightly decreased with increasing SDS concentration. More efficient stabilization would rely on siloxane-based stabilizers, which were, however, out of the scope of the present contribution. Much larger particles were obtained when using the non-ionic surfactant Lutensol AT50; an amount of 3.3 wt% Lutensol AT50 led to particles of 365 nm, an increase to 13.3 wt% reduced the particle size to 264 nm.

Stable miniemulsions and latexes could also been made with a siloxane diacrylate of longer siloxane chain, TegoRad2700. With as low as 1.2 wt% SDS compared to the monomer phase, stable miniemulsions and after polymerization also stable dispersions with particle diameters of 250 nm were obtained. For the larger particle size (as compared to TegoRad2500) and connected lower surface tension, two possible explanations can be given: (1) The increased hydrophobicity due to the higher siloxane content; and (2) the increased viscosity of the monomer which influences the miniemulsification by mechanical energy. Increasing the SDS concentration to 4.8 wt% decreases the particle size, a further increase results in larger particles due to the fact that all additional surfactant ends up in the serum (the continuous phase), but does not contribute to stability. The use of Lutensol as surfactant only leads to particles in the micrometer range. In spite of the large size, the dispersions show nevertheless a high stability. TEM measurements of the soft particles of sample Rad-2500f still detects particles, which are, however, deformed and adhered due to the very low T_g of the siloxanes (Fig. 1(a)). Lowering the cross-linking density by using larger prepolymers in the case of Rad-2700 leads to softer particles as seen in Fig. 1(b). Due to a flattening of the particles, the diameter appears larger than detected by DLS measurements.

After drying the dispersion, deuterated chloroform can be added to the polymer in order to swell the polymer microgels to an extent that analysis of the conversion of the double bond by ^{1}H NMR is possible. For both telechelic macromonomers, the intensity of the vinyl protons was under the detection limit. This underlines the specific advantages of the miniemulsion approach, as full conversion of macromonomers is most easily obtained in a bulk-like polymerization.

In order to obtain hybrid nanoparticles, vinylic hydrocarbon monomers were added to form common droplets with the siloxane acrylates. Whereas prior to polymerization

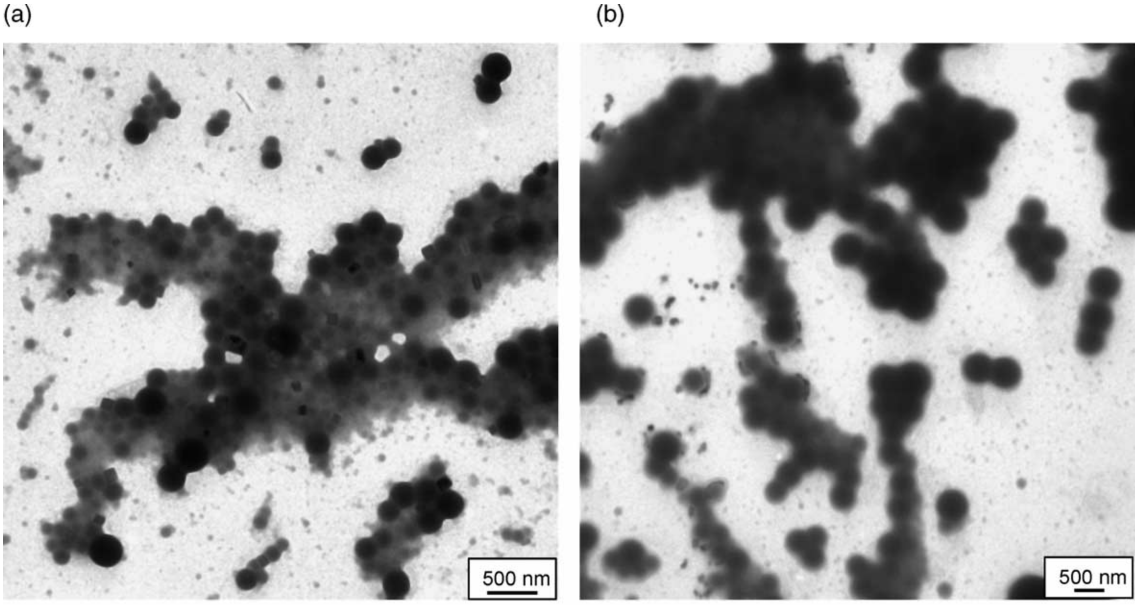


Fig. 1. TEM photographs of particles of samples (a) Rad-2500f and (b) Rad-2700e.

the monomers are miscible, the polymers are not. In bulk polymerization, this leads to phase separation on the scale of many micrometers, causing inefficient copolymerization. Inside the droplets, the phase separation is limited to the size of the particles, improving copolymerization. This is the main driver to perform such reactions in as small droplets as possible.

As seen in Table 2, with increasing the vinylic monomer content of butyl acrylate or styrene, those monomers replace the PDMS monomers from the interface, and the mixed particle size reduces remarkably to 80 nm in diameter. The polymers are still highly crosslinked and only swell, but do not dissolve in organic solvents. A linear vinylic polymer is not detected by GPC. This clearly indicates that the confinement of the droplets reduces the phase separation and favors efficient copolymerization of components of lower compatibility.

The copolymerization with styrene leads to harder particles which can also easily be detected in TEM measurements (Fig. 2).

Table 2
Characteristics of the nanoparticles obtained from PDMS-diacrylate and vinylic monomers

Sample	Siloxane acrylate	Amount (g)	Vinylic monomer	Amount (g)	Particle size (nm)	Solid content (%)	Surface tension (mN m^{-1})
UP-30	Rad-2500	5	BA	1	343	21.01	33.0
UP-29	Rad-2500	4	BA	2	134	17.50	40.5
UP-28	Rad-2500	3	BA	3	114	18.99	38.9
UP-27	Rad-2500	2	BA	4	99	19.77	34.9
UP-26	Rad-2500	1	BA	5	88	24.77	37.9
UP-35	Rad-2500	5	Sty	1	369	18.29	33.0
UP-34	Rad-2500	4	Sty	2	227	17.59	37.1
UP-33	Rad-2500	3	Sty	3	342	20.20	30.2
UP-32	Rad-2500	2	Sty	4	77	22.95	43.0
UP-31	Rad-2500	1	Sty	5	80	23.08	33.7
UP-40	Rad-2700	5	BA	1	254	19.44	32.7
UP-39	Rad-2700	4	BA	2	199	17.50	36.5
UP-38	Rad-2700	3	BA	3	170	20.25	40.0
UP-37	Rad-2700	2	BA	4	133	19.96	39.0
UP-36	Rad-2700	1	BA	5	106	21.74	38.1
UP-45	Rad-2700	5	Sty	1	301	23.16	36.8
UP-44	Rad-2700	4	Sty	2	200	14.95	39.9
UP-43	Rad-2700	3	Sty	3	150	13.38	45.9
UP-42	Rad-2700	2	Sty	4	100	20.46	50.5
UP-41	Rad-2700	1	Sty	5	81	20.07	52.0

The SDS concentration was kept content at 3.3 wt% compared to the monomer. Twenty-four grams water was used for the synthesis.

We were carefully checking the TEM pictures for chemical heterogeneities (indicated by different shades of greyness) or a potential inner structure of the latexes, but did not find any specific pattern. Also these experiments indicate the extraordinarily high homogeneity of the dispersion. Such particles might find direct use as high impact filler particles for polystyrene materials as they are already compatibilized by a polystyrene layer.

3.2. Polyaddition reactions

It was shown in previous work that even polyaddition reactions with isocyanates can be carried out in aqueous heterophase situations. Here, the water-sensitive diisocyanate is incorporated together with the diol in the droplets and builds the hydrophobic polyurethane in dispersion. Up to now, hydrocarbon diols were used, but the formation of siloxanes-based polyurethanes was not explored.

Stable miniemulsions are obtained using an equimolar 1:1 mixture of IPDI and siloxanes. As catalyst, dioctyltindilaurate (DOTDL) was added prior to miniemulsification. The characteristics of the resulting particles are summarized in Table 3. After increasing the temperature, the reaction took place resulting in a stable dispersion with particles of about 200 nm. The molecular weight of the polymer was determined by GPC to be 51,000 g mol^{-1} (relative to polystyrene), which is unusually high for a polyaddition reaction and also underlines the absence of perturbing demixing effects.

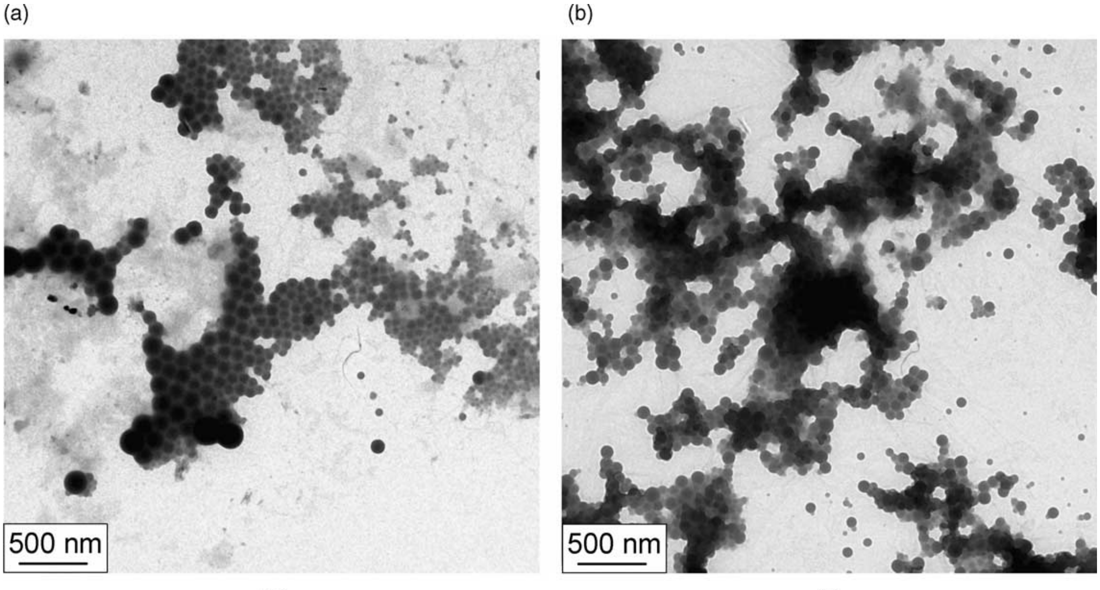
It is seen that the surface tensions of the resulting latexes are extremely low and even well below the saturation values of the surfactant. This means that a minor fraction of the urethane–siloxane chains is surface active, e.g. a single PDMS-diol with isocyanate-based headgroup (the low molar mass tail in the GPC experiments could be a hint). This is a negative and unwanted side-product of this reaction, but explains partly the very high stability and small particle size of such latexes.

A modulation of the hydrophobic contrast along the polyurethane chains can be obtained by substituting parts of the siloxane with dodecanediol. It is expected that the siloxane and the dodecandiol units are statistically incorporated in the polymer chain. The characteristics of those particles are also listed in Table 3. It is seen that dodecandiol has a negative influence on the latex stability already at smaller amounts. Due to the lower interface area in these systems, also the side reaction towards the surface active siloxane species is suppressed.

The siloxane acts as a super-low T_g soft segment in the polyurethane. As it can be detected by DSC measurements, one T_g is detected at about −50 °C. Additionally, two melting points are found, one T_m at 88 °C which can be attributed to the polyurethane and a second T_m between 1 and 6 °C.

In order to obtain hybrid particles composed of polyaddition and radical polymerization polymers, the components IPDI, siloxane (and other diols), styrene and hexadecane were mixed and then miniemulsified in water using SDS as surfactant. Prior to miniemulsification, DOTDL as catalyst was added. By increasing the temperature to 60 °C, the polyurethane is formed. To start the radical polymerization of styrene (50% compared to the PU phase), the temperature was then increased to 72 °C and KPS as initiator was added. The characteristics of the latexes are summarized in Table 4.

In good agreement with the previous experiments described above, addition of a hydrocarbon component lowers the droplet size and reveals very fine latexes with a



(a) (b)

Fig. 2. TEM photographs of (a) UP-33 (50% styrene, 50% Rad-2500) and (b) UP-31 (83.3, 16.7% Rad-2500).

Table 3
Characteristics of siloxane-PU particles

Sample	IPDI (mol ratio)	Siloxane (mol ratio)		Dodecandiol (mol ratio)	Solid content (%)	Particle size (nm)	Surface tension of the latex (mN/m)	M_w (kg/mol)	M_w/M_n
Siloxane–PUs from different siloxanes									
UP-10	1	Tegomer-2111	1	0	19.96	198	28.9	27.3	2.23
UP-1	1	Tegomer-2311	1	0	19.00	194	26.3	51.3	1.86
Siloxane–PUs consisting of siloxane and different amounts of dodecanediol									
UP-12	1	Tegomer-2111	0.5	0.5	20.98	116	43.6	29.1	1.91
UP-4	1	Tegomer-2311	0.75	0.25	19.86	222	33.9	51.2	1.78
UP-8	1	Tegomer-2311	0.5	0.5	18.15	680	39.3	46.7	1.90
UP-5	1	Tegomer-2311	0.25	0.75	17.50	1540	48.8	60.2	2.17

diameter smaller than 90 nm, as obtained for the simultaneous dispersion of styrene and the siloxane-diol in a 50:50 ratio (see UP-3 and UP-11). This small droplet size again diminishes the influence of a potential macrophase demixing structure onto the blocking efficiency, as found in the bulk. The analysis of the reaction mixture by GPC reveals two peaks: The polyurethane with a molecular weight of about 30,000–55,000 $\mathrm{g\,mol^{-1}}$, and the polystyrene has a high molecular weight of more than 400,000 $\mathrm{g\,mol^{-1}}$.

In this case, the chains were not interlinked by purpose, and phase separation would appear during film formation. A linkage of the two different polymer chains can be obtained by using 1–10 wt% of hydroxymethyl methacrylate as a comonomer. In this case, the OH group provides the possibility to a urethane linkage, while the vinyl group enables the copolymerization with the vinylic monomer. Due to the high crosslinking degree, the entire polymer is insoluble in organic solvent and only swells which makes it impossible to measure the molecular weight of the final polymer.

4. Conclusion

Polysiloxane–acrylate and polysiloxane–urethane latexes with small and narrowly distributed particle sizes have been synthesized using different synthetic pathways in miniemulsions. The polysiloxane acrylate latexes were obtained in a radical polymerization process; here a

Table 4
Characteristics of polyurethane/polystyrene hybrid particles

Sample	IPDI (mol ratio)	Siloxane (mol ratio)		Dodecan-diol (mol ratio)	Solid content (%)	PU:PS	Particle size (nm)	M_w (kg/mol)
UP-11	1	Tegomer-2111	1	0	24.31	50:50	43	PU: 36.7; PS: 423
UP-13	1	Tegomer-2111	0.5	0.5	21.29	50:50	44	PU: 32.5; PS: 465
UP-3	1	Tegomer-2311	1	0	18.37	50:50	85	PU: 55.6; PS: 513
UP-4	1	Tegomer-2311	0.75	0.25	21.22	50:50	84	PU: 54.9; PS: 705
UP-8	1	Tegomer-2311	0.5	0.5	17.36	50:50	83	PU: 42.4; PS: 485
UP-5	1	Tegomer-2311	0.25	0.75	19.90	50:50	90	PU: 34.2; PS: 647
UP-14	1	Tegomer-2311	0.5	0.5	23.45	96:4	331	PU: 53.3; PS: 541
UP-16	1	Tegomer-2311	0.5	0.5	19.67	84:16	152	PU: 52.3; PS: 481
UP-17	1	Tegomer-2311	0.5	0.5	16.93	75:25	150	PU: 39.9; PS: 421
UP-18	1	Tegomer-2311	0.5	0.5	19.42	67:33	126	PU: 63.6; PS: 484

copolymerization with other vinylic monomers is easily possible leading to highly crosslinked copolymer particles. Due to the confinement of the reaction within the minidroplets, the monomers are forced to copolymerize on the length scale of the droplets and the phase separation is limited on the size of the particles.

Polysiloxane–urethanes can be obtained in a polyaddition process using a diisocyanate and silanediols. Replacing parts of the low T_g siloxanediol segments by alkyldiols allows one to introduce crystalline parts with higher melting points in the material. These alkyldiols, however, have to be sufficiently hydrophobic that they do not interfere with the miniemulsion process. Hybrid particles can be obtained on the base of those systems, too, by using additionally styrene or an acrylate in the miniemulsification process. Although performed in a one pot reaction after the miniemulsification step, the two polymer reactions take place consecutively. In the first reaction step the polysiloxane–urethane forms, whereas the radical polymerization of the vinyl monomer takes place afterwards. By using hydroxy methyl methacrylate as a coupler, the two different polymers can be efficiently linked, and hybrid graft copolymers are formed.

Acknowledgements

We are indebted to Dr Sascha Oestreich/TEGO for providing the siloxane monomers and precursor structures as well as for the discussions. Financial support by the Max Planck Society and the Fonds der chemischen Industrie is gratefully acknowledged. A special thank is given to Prof Dr H.W. Spiess (MPI Mainz) for the very close cooperation in this project.

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