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A facile synthesis of poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) surfactant by click reaction and its use in the synthesis of polyhydroxyethyl methacrylate nanoparticles containing Disperse Red 1

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A synthetic path to poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide), a substitute for the "KLE" surfactant was developed. For this purpose, mono hydroxyl end-functionalized poly(ethylene-*co*-butylene) (~3800 g/mol) was modified with a triple bond at its hydroxyl group, while two samples of mono hydroxyl end-functionalized poly(ethylene oxide) (~2000 g/mol and 5000 g/mol) were modified with an azide group. The two blocks were bound together by click chemistry and the products characterized by ^{1}H NMR spectroscopy, EA and GPC. The ability of these new block copolymers to stabilize nanodroplets in inverse miniemulsion polymerization of 2-hydroxyethyl methacrylate (HEMA) was investigated. It was found that the molecular weight of the poly(ethylene oxide) block strongly influences the stability of the miniemulsions; only the copolymer with the short oligoethylene block gave satisfactory results. The possibility of encapsulating Disperse Red 1 (DR1) dye in polyhydroxyethyl methacrylate (PHEMA) was also investigated and the miniemulsions were optimized such as to prepare particles with a maximum DR1 loading of approximately 21 wt%. To avoid dye agglomeration and phase separation during polymerization, DR1 was equipped with a polymerizable group. The resulting particles were characterized by DLS, SEM, TGA, UV-vis and DSC. These particles are of importance as fillers in polydimethylsiloxane composites that are used as electrostrictive materials.

Introduction

The aim of this work was to establish a route to polable polar, high glass transition temperature (T_g) PHEMA nanoparticles (NPs) with DR1 dye molecule encapsulated to be used as filler in silicone elastomer composites. The proposed combination of elastomer and polable NPs has never been explored before and might lead to interesting materials for actuators, sensors or non-linear optical applications. The poling of polymers containing dipolar molecules is a well-established method and has been used to create polar non-centrosymmetric materials for non-linear optics. The alignment of the dipoles is done in a high electric field at a temperature above the polymer's T_g followed by freezing-in the oriented dipole by cooling below T_g while the electric field is maintained.[1]

Because of the large dipole moment of DR1 of 11.8 D, NPs loaded with this dye are attractive as fillers in chemically cross-linked silicone elastomers to increase their polarity as well as their mechanical and, in particular, dielectric properties.[2] The DR1 molecules in PHEMA NPs adopt a random orientation, where the dipoles cancel each other. Therefore the PHEMA NPs loaded with DR1 molecules have a low overall dipole moment and thus a low permittivity. However, when the DR1 molecules adopt an anisotropic orientation, NPs with increased permittivity should form. This manuscript is dealing with the preparation of such NP. For their preparation, miniemulsion polymerization of HEMA in the presence of DR1 was investigated. Miniemulsion polymerization is an effective tool used for the encapsulation of large quantities of guest molecules, pigments, and particles of small size.[3] In addition to this, it is a rather easy to perform method and allows for up scaling. There are some reports on inverse miniemulsion polymerization of HEMA[4] as well as hybrid PHEMA particles that contain some guest compounds. For example, PHEMA NPs containing tetrafluoroborate salts of different metals were prepared by inverse miniemulsion and the influence of salt content on the particle size distribution was extensively investigated.[5] Atom transfer radical polymerization of HEMA in miniemulsions was also investigated and polymers with a narrow weight distribution were prepared.[6] An overview of the miniemulsion polymerization of some polar monomers is given by Capek.[7] Also, reports exist regarding the encapsulation of dyes in polymeric NPs.[8] The encapsulation of dyes within polymeric NPs is a powerful way to overcome problems associated with dye aggregation in different phases, instability and poor processability. Dye loaded NPs found application as colorants in textiles, inks and coatings, or as fillers in laser, optical and semiconductor devices.

A common feature of the above chemistry is the use of the same surfactant, namely a poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) (PEB-PEO) known also under the name KLE. This is a powerful surfactant which however is not commercially available anymore.[9] This necessitates to first establish access to KLE or a close congener of it if chemistry in this direction is to be developed further.

We first describe the synthesis of two KLE-type block copolymers which, for conveniences sake, rests upon the two commercially available mono hydroxyl end-functionalized PEO blocks (M_n = 2000 g/mol and M_n = 5000 g/mol). These block lengths are the closest to the one used in KLE (M_n = 11500 g/mol). Both PEO blocks were connected to the PEB block via “click”-chemistry and the resulting block copolymers fully analyzed. Next, both of these polymers were employed in inverse miniemulsion polymerizations of HEMA as well as the encapsulation of acrylate functionalized (DR1-MA) or un-functionalized DR1 molecule into PHEMA NPs. It turned out that the block copolymer with the shorter PEO block is a perfect replacement for KLE while the one with the longer PEO block does not exhibit useful stabilization.

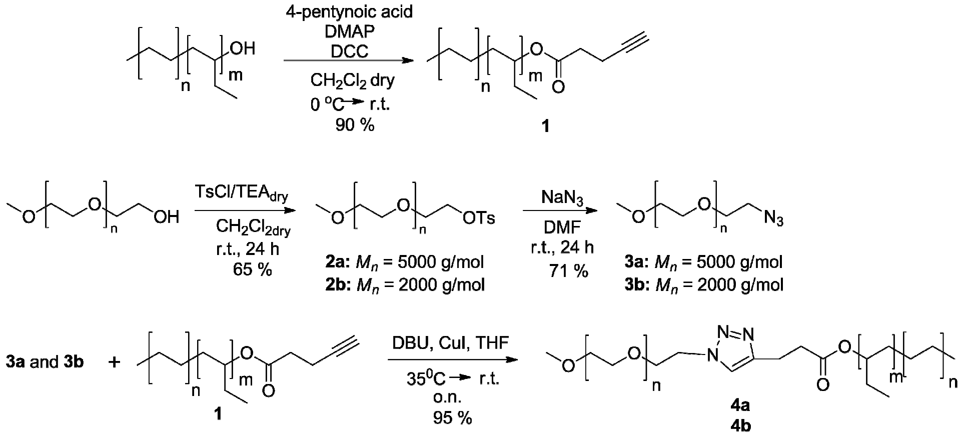
Experimental section

Materials

Kraton liquid L-1203 (M_n = 3800 g/mol) has a mole fraction of butylene units of 0.33 as determined by ^{1}H NMR and a terminal hydroxyl group on one end. KLE is a block copolymer poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) with M_n = 11500 g/mol (measured in our lab). It has about 41 wt % of ethylene oxide.[6] Kraton and KLE were kindly provided by Dr. H. Schlaad from MPI-KG, Potsdam, Germany. DR1 was functionalized with a methacrylate polymerizable group using a reported procedure.[10] All other chemicals were purchased from Aldrich and used as received. Solvents were purified and dried by standard procedures. Column chromatography was carried out on silica gel 60 (Macherey–Nagel, 0.04–0.063 mm/230–400 mesh) as the stationary phase. Reactions were monitored by thin layer chromatography (TLC) with TLC silica gel-coated aluminium plates (60 UV254, Macherey–Nagel) and visualized by ultraviolet light (λ = 254 nm and λ = 366 nm).

Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (^{1}H: 400 MHz and ^{13}C: 100 MHz at room temperature). Gel permeation chromatography (GPC) measurements were done with an Agilent 1100/PSS WinGPC 8.1 system in tetrahydrofurane calibrated with polystyrene standards (Polymer Standards Service). Two columns (100, 1000 Å pore size SDV-Gel) and a flow rate of 1 ml/min were used. Signals were detected with a UV and RI detector. GPC measurements of the polymeric nanoparticles were done on a GPCv2000 from Waters using a solution of 0.1% LiCl in dimethylformamide (DMF) at a flow rate of 0.6 ml/min at 60 °C using three columns (Styragel HR4 Column, 5 µm, 4.6 x 300 mm, Styragel HR2 Column, 5 µm, 4.6 x 300 mm, and Styragel HR0.5 Column, 5 µm, 4.6 x 300 mm) and polymethylmethacrylate standards. Signals were detected with a RI detector. The thermogravimetric analysis (TGA) was conducted with a Perkin Elmer TGA7 at a heating rate of 20 °C min^{-1} under a nitrogen gas flow up until 800°C. The NPs were observed by scanning electron microscope (SEM) on a FEI NovaNanoSEM 230 in secondary electron mode using either an Everhart Thornley Detector or a Through Lens Detector at 10-



Scheme 1. Alternative synthesis of a KLE-like block copolymer which avoids the use of gaseous ethylene oxide.

15 kV acceleration voltage. SEM particle size was determined by measuring the diameter of 50 neighboring particles in a representative area. UV-vis absorption spectra were recorded on a Cary 50 spectrophotometer and dynamic light scattering (DLS) was done with a Malvern Zetasized Nano ZS, where the results were averaged from 3 separate measurements. FT-IR spectra were taken on a Bio-Rad FTS 6000 spectrometer. Differential scanning calorimetry (DSC) measurements were done on a Perkin Elmer DSC 8000. The DSC cycle consisted of two heating steps from 20 °C to 200 °C and a cooling step from 200 °C to 20 °C at a rate of 20 °C/min.

Alkyne functionalized poly(ethylene-*co*-butylene) (PEB) (1):

Poly(ethylene-*co*-butylene) (Kraton liquid, 3.8 g), 4-pentynoic acid (0.196 g, 2 mmol), dimethylaminopyridine (0.24 g, 2 mmol) were dissolved in dried dichloromethane (20 ml). To this solution dicyclohexylcarbodiimide (DCCD) (0.41 g, 2 mmol) was added at 0 °C. The reaction mixture was let to warm up to RT and stirred for 2 days under argon. It was then washed with water and the organic phase was dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography on silica gel using hexane:ethyl acetate 9.5:0.5 as eluent to give a colourless viscous liquid (3.5 g, 91% yield). Visualization of the TLC plate was done by I_2.

^{1}H NMR ($CDCl_3$) δ = 4.11 (m, 1.8 H, -CH_2-O), 2.45-2.55 (m, 4 H, CH_2-CH_2-≡-H), 1.94 (s, 1 H, ≡-*H*), 1-1.5 (br m, CH, CH_2), 0.81 (br m, CH_3); EA: calcd. C 85.62%, H 14.37%; found C 84.77%, H 14.44%; M_n = 6700 g/mol, M_w = 6910 g/mol, M_w/M_n = 1.03.

Tosylated poly(ethylene glycol) methyl ether (2):

Synthesized according to the literature with some small modifications.[11] Poly(ethylene glycol)methyl ether M_n = 5000 g/mol (5 g, 1 mmol) was dissolved in dry dichloromethane (25 ml) and triethylamine (1.5 ml, 10.8 mmol). To this solution toluene-4-sulphonyl chloride (1.91 g, 10.0 mmol) was added at once. The reaction mixture was stirred at room temperature for 2 days under argon. It was thereafter washed with water two times and the organic phase was dried over $MgSO_4$. The solvent was removed and the remaining oil (or white solid) was dissolved in minimum amount of dichloromethane. To this solution diethyl ether was added to precipitate the product. This purification step was repeated twice in order to obtain pure product. Alternatively the purification can be done by column chromatography on silica gel using dichloromethane : methanol (9:1) as eluent. The products were obtained as white powders (**2a**: 4.5 g, 90% yield and **2b**: 3.26 g, 65.2%)

^{1}H NMR ($CDCl_3$) δ = 7.75 (d, 2H, J = 8, arom. *H*), 7.3 (d, 2H, J = 8, arom. *H*), 4.12 (m, 2H, CH_2-CH_2-OTs), 3.6 (s, O-(CH_2)$_2$-O), 3.50 (m, 2H, CH_2-CH_2-OTs), 3.37 (s, 3H, H_3C-O), 2.44 (s, 3H, H_3C-aryl); ^{13}C NMR ($CDCl_3$) δ = 145.5, 133.8, 130.6, 128.7, 71.5, 71.3, 69.3, 59.8, 22.4;

2a: EA: calcd. C 54.53%, H 9.15%; found C 54.00%, H 8.8%; M_n = 6400 g/mol, M_w = 6540 g/mol, M_w/M_n = 1.02.

2b: The same reaction was done on poly(ethylene glycol)methyl ether M_n = 2000 g/mol; EA: calcd. C 54.53%, H 9.15%, O 36.32; found C 53.67, H 8.84%, O 36.2%; M_n = 2350 g/mol, M_w = 2370 g/mol, M_w/M_n = 1.01.

Azide functionalized poly(ethylene glycol) methyl ether (3):

According to Opsteen *et al*. with small modifications.[11]

3a: Tosylated poly(ethylene glycol) methyl ether **2a** (2.5 g, 0.5 mmol) was dissolved in 40 ml dimethylformamide. To this solution, NaN_3 (325 mg, 5 mmol) was added at once and the reaction mixture was stirred at room temperature for 2 days. Then water and dichloromethane were added. The phases were separated and the aqueous phase was extracted once more. The organic phases were combined and washed three times with water and the organic phase was dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography or by precipitation with diethyl ether of a concentrated solution in dichloromethane.

3b: The same reaction was done on tosylated poly(ethylene glycol) methyl ether **2b**. White powders were obtained (**3a**: 2.1 g, 83% and **3b**: 1.78 g, 71.5%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.61 (s, O-(CH_2)$_2$-O), 3.51 (m, 2H, CH_2-CH_2-N_3), 3.36 (m, 2H, CH_2-CH_2-N_3), 3.34 (s, 3H, H_3C-O); ^{13}C NMR ($CDCl_3$) δ = 72.7, 71.3, 70.8, 59.8, 51.4.

3a: EA: calcd. C 54.53%, H 9.15%; found C 54.26%, H 9.07%.

3b: EA: calcd. C 54.53%, H 9.15%; found C 53.66%, H 8.86%; M_n = 2480 g/mol, M_w = 2520 g/mol, M_w/M_n = 1.02.

Cycloaddition reactions (typical procedure) (4):

4a: Alkyne functionalized poly(ethylene-*co*-butylene) **1** (0.93 g, 0.245 mmol), azide functionalized poly(ethylene glycol) methyl ether **3a** (1.22 g, 0.245 mmol), THF (20 ml) and DBU (0.59 g, 3.86 mmol) were placed in a Schlenk and degassed. To this, CuI (25 mg, 0.1 mmol) was added and the reaction mixture degassed again. It was stirred thereafter at 35 °C overnight. The solvent was removed, and the residue was purified by column chromatography on silica gel using dichloromethane:methanol 9:1 ($R_f = 0.5$).

To improve the yield it is recommended to use a small excess of alkyne functionalized PEB. This excess is easy to remove by column chromatography.

^{1}H NMR ($CDCl_3$) δ = 7.51 (s, 1H, *H*-triazole), 4,49 (t, J = 5, 2H, O-CH_2), 4.09 (t, J = 6.68, 2H CH_2-PEO), 3.85 (t, J = 5, 2H, CH_2-triazole), 3.61 (s, CH_2-O), 3.38 (s, 3H, CH_3), 3.02 (t, J = 7.6, 2H, CH_2-CH_2-COO), 2.72 (t, J = 7.6, 2H, CH_2-COO), 1-1.33 (br m, CH, CH_2), 0.78 (br m, CH_3);

4b: The same reaction was done with azide functionalized poly(ethylene glycol) methyl ether **3b** (95% yield).

4a: EA: calcd. C 73.78%, H 13.93%; found C 71.72%, H 12.16%; M_n = 14500 g/mol, M_w = 15100 g/mol, M_w/M_n = 1.04.

4b: EA: calcd. C 73.78%, H 13.93%; found C 72.15%, H 12.01%; M_n = 11200 g/mol, M_w = 11500 g/mol, M_w/M_n = 1.03.

The deviations of the data from combustion analysis with the calculated ones is likely due to residual water.

Inverse miniemulsion polymerization of HEMA

The surfactant and α,α'-azobisisobutyronitrile (AIBN) were dissolved in cyclohexane (CH) while DR1 or DR1-MA was dissolved in HEMA with or without the use of co-solvent. For the quantities used, please see Table 1. The two solutions were mixed together and stirred at room temperature to obtain a homogenous macroemulsion. A miniemulsion was produced by subjecting it to high shear forces using a Sonics Vibra-cellTM VCX 750 ultrasonicator at 40% power output (300 watt) for 5 min while being immersed in an iced water bath. The emulsion was bubbled through with Ar, and stirred under inert atmosphere in a preheated bath at 72 °C. After 24 h, the resulting suspension was cooled to RT.

Results and discussion

Synthesis of the KLE-like surfactant

As mentioned in the introduction, PEB-PEO also known under the name KLE, is an ideal surfactant for stabilization of monomer nanodroplets in inverse miniemulsions.[12] It is commonly synthesized using ω-hydroxy PEB (Kraton liquid) as macroinitiator in ethylene oxide polymerization.[13] The molecular weight given by the provider was about M_n = 3800 g/mol. The mole fraction of butylene units was determined by ^{1}H NMR spectroscopy to be 0.33. Although the PEO chain length can be precisely controlled by using the above approach, it has the disadvantage of involving gaseous ethylene oxide, which makes small scale experimentation demanding. Herein an alternative route to KLE is presented (Scheme 1).

In the first step PEB was esterified with 4-pentynoic acid by using active ester chemistry to give **1** (by GPC: M_w = 6910 g/mol, M_n = 6700 g/mol, M_w/M_n = 1.03), which represents the lipophilic part of the aimed at surfactant **4**. The hydrophilic part of this surfactant was obtained by using two commercial hydroxyl end-functionalized PEOs (M_n = 5000 g/mol and M_n = 2000 g/mol) that were chemically modified. They were first tosylated with tosyl chloride to give **2a** and **2b**. Tosylation followed by tosyl/azide exchange gave **3a** and **3b**.[14] The two building blocks **1** and **3a** and **3b** were covalently coupled together by so-called click chemistry under established conditions to give the block copolymers **4a** and **4b**, respectively.[15]

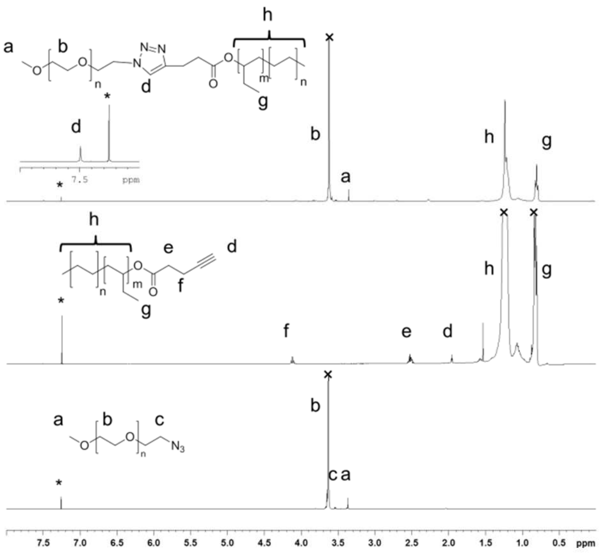


Figure 1. ^{1}H NMR spectra of the newly synthesized KLE analog **4a** by click chemistry (top) and of building blocks **1** (center) and **3a** (bottom). The insert shows a magnification of the aromatic part of the surfactant **4a**. Solvent signals are marked (*).

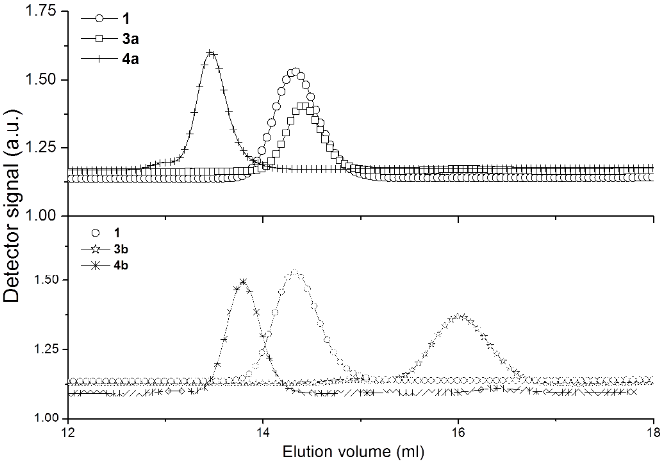


Figure 2. GPC elugrams of **1**, **3a** and of the surfactant **4a** (top), as well as of **1**, **3b** and of the surfactant **4b** (bottom) in tetrahydrofurane.

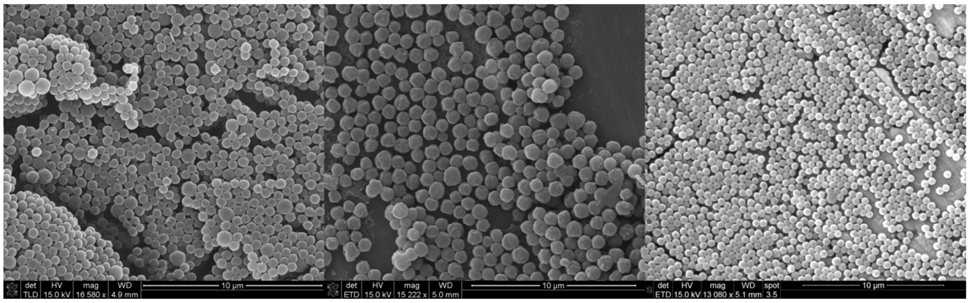


Figure 3. SEM images of PHEMA particles where KLE (NP 1, left) and **4b** was used as surfactant at the same conditions (NP 2, middle), and when **4b** was used with more CH (NP 3, right).

Table 1. Preparation and characterization of HEMA latexes.

Sample	HEMA	Dye		Dye/ HEMA	NMP	CH	**4b**	AIBN	Particle diameter		M_n	M_w	PDI
	[g]	type	[mg]	[wt%]	[g]	[g]	[mg]	[mg]	SEM [nm]	DLS [nm]	kg/mol	kg/mol	-
NP 1	1.5	-	-	-	-	6	50[a]	100	570 ± 80	680 ± 150	95	198	2.1
NP 2	1.5	-	-	-	-	6	50	100	840 ± 90	1320 ± 250	-[b]	-	-
NP 3	3.75	-	-	-	-	30	125	125	480 ± 30	560 ± 110	-[b]	-	-
NP 4	1.5	DR1	20	1.3	-	6	50	100	480 ± 40	510 ± 200	193	813	4.2
NP 5	0.5	DR1	66	11.8	0.5	8	36	66	820 ± 110	540 ± 170	92	191	2.1
NP 6	0.5	DR1	100	16.6	0.5	8	36	66	N/A	N/A	-	-	-
NP 7	1.5	DR1MA	20	1.3	-	6	50	100	480 ± 50	560 ± 180	186	744	4.0
NP 8	0.75	DR1MA	50	6.3	-	6	25	50	550 ± 100	520 ± 90	105	596	5.7
NP 9	0.75	DR1MA	100	11.8	-	6	25	50	570 ± 70	660 ± 130	96	531	5.5
NP 10	0.5	DR1MA	133	21.0	0.25	6	50	25	750 ± 90	560 ± 100	69	578	8.4
NP 11	0.5	DR1MA	150	30	0.5	8	50	33	N/A	N/A	-	-	-

[a] KLE was used as surfactant; [b]not soluble in DMF (0.1% LiCl).

The purification of the products was done by column chromatography. A slight excess of **1** makes the purification easier. When a slight excess of **3** was used as was the case for **4b**, the purification was tedious and even after precipitation and column chromatography a small rest of **3b** was still present (see Figure 2, bottom). Figure 1 shows the ^{1}H NMR spectra of the starting monofunctionalized polymers **1** and **3a** as well as of the prepared copolymer surfactant **4a**.

The disappearance of the acetylene-H signal of **1** at δ = 1.94 ppm and the appearance of the new signal in the spectrum of **4** at δ = 7.51 ppm characteristic for the triazol ring are clear evidences for the successful coupling. Typical elugrams of **1**, **3a** and **4a** as well as of **1**, **3b** and **4b** are shown in Figure 2. The block copolymers are shifted to smaller elution volumes compared to the respective blocks, **1** and **3a**/**3b**, from which they were synthesized while retaining narrow molecular weight distributions. It should be mentioned here that the two commercial PEO polymers used contained a small fraction (< 6%) of a higher M_w polymer that was carried through the synthesis. The newly prepared surfactants **4a** (M_w = 15100 g/mol, M_n = 14500 g/mol, M_w/M_n = 1.04) and **4b** ((M_w = 11500 g/mol, M_n = 11200 g/mol, M_w/M_n = 1.03) were tested in miniemulsion polymerizations (see below). For comparison the GPC of KLE surfactant were also done (M_w = 11700 g/mol, M_n = 11500 g/mol, M_w/M_n = 1.02). By comparing the GPC data, the molecular weight of **4b** is closer to that of KLE surfactant. The ability of surfactants **4a** and **4b** to replace KLE in inverse miniemulsion polymerization of HEMA is described below.

Inverse miniemulsions

The second aim of this work was to establish a route to polar, high T_g PHEMA NPs with DR1 dye molecules encapsulated. In order to prevent unwanted contamination with ions, non-ionic surfactants were preferred. Ionic surfactants are often employed in similar experiments, however, they are likely to result in ion conductivity when NPs are used as fillers in silicon composites.

Ion conductivity decreases the breakdown field of a composite when used in electrostrictive devices and is thus to be avoided. A variety of surfactants were tried including the commercially available Igepal® CO 210, CO 520, Span® 20, 40, 60, 65, 80, 85, Brij® 98, 30, Borchi Gen® 0451, 0755, Disponil® AFX 1080, Disponil® A 3065, and Tween® 80. Also KLE was employed. Of all these surfactants only KLE ensured sufficient stabilization of the emulsion for at least 1 hour, a time span that was required for the polymerization. The conditions reported in the experimental section were applied. Additionally, the two synthesized surfactants **4a** and **4b** were also tried under the same conditions.[6] As expected, the molecular weight of the PEO block played an important role. Only the surfactant **4b** with the short PEO block resulted in sufficiently stable miniemulsions. Its molecular weight is approximately the same as the one of the KLE surfactant. An overview of the prepared particles and the amounts of reagents used is given in Table 1. The dried latexes were investigated by SEM to determine the particle structure and homogeneity. Figure 3 shows the SEM images of the prepared particles when KLE and **4b** were used as surfactants. As can be seen, the average size and the shape of the polymeric latexes stabilized by these surfactants are about 500-600 nm when KLE was used (NP 1) and 800-900 nm for particles produced with **4b** (NP 2). By using more CH, while keeping the relative concentration of the other educts constant, the particle size using **4b** can be reduced (NP 3).

For the encapsulation, DR1 dye was selected due to its large dipole moment and availability. The aim was to encapsulate as much DR1 as possible, while avoiding agglomeration of the dye within the PHEMA particles. To overcome the low solubility of DR1 in HEMA (1.3 wt%), *N*-methyl-2-pyrrolidone (NMP) co-solvent was used. This allowed the dissolution of a maximum of 11.6 wt% of DR1 (Table 1) in the dispersed phase. It was assumed that all the dye is incorporated in the formed particles. This is supported by the insolubility of the dye in the continuous phase.

The SEM images and the DLS measurements of the particles are shown in Figure 4 and 5. It was found that spherical particles were obtained when encapsulating DR1 without NMP. In contrast, the particles produced with NMP co-solvent, while still roughly spherical, have a less uniform shape and are flattened against the substrate in the SEM image. This makes them seem larger (820 nm) then compared to the particles produced without co-solvent (480 nm), but DLS shows that they are of roughly the same size when in solution.

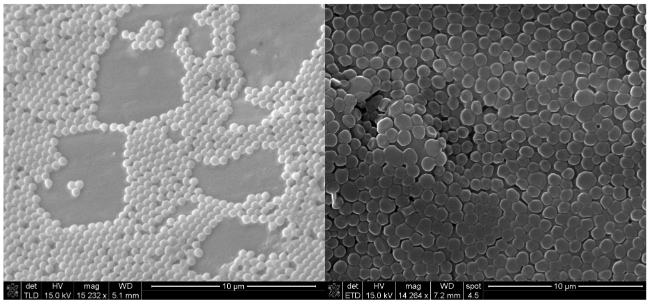


Figure 4. SEM images of particles that contain DR1: NP 4 (left) and NP 5 (right).

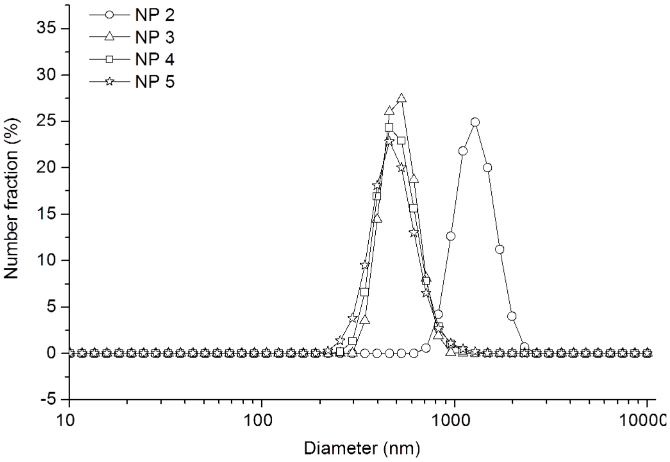


Figure 5. DLS measurements of NP 2, NP 3, NP 4 and NP 5.

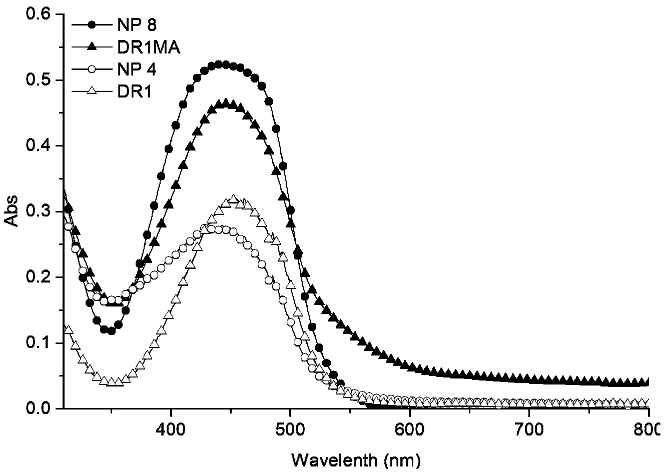


Figure 6. UV-vis spectra of DR1, DR1-MA and of the PHEMA particles with DR1 (NP 4) or DR1-MA dyes encapsulated (NP 8).

UV-vis spectroscopy was used to investigate the aggregation behavior of the dye. As aggregation is known to be associated with dipole moment compensation, this has to be avoided. Aggregation of DR1 results in a hypsochromic shift of the λ_{max} absorption while otherwise the signal stays constant.[16] UV-vis spectra of NPs with low and high load of DR1, were recorded by dispersing them into CH. They all show a $\lambda_{\max}$ = 442 nm. This is hypsochromocally shifted with respect to pure DR1 which absorbs at 456 nm. We therefore had to conclude that the encapsulation did not prevent the dye from aggregation. Gratifyingly, when the dye was functionalized with a methacrylate group (DR1-MA), the aggregation could be prevented. Thus, if polymerization is performed with the dye carrying a methacrylate unit, the UV-vis spectrum of the resulting NPs exhibits $\lambda_{\max}$ = 456 nm (Figure 6).

The functionalization also increased the solubility of DR1-MA in HEMA which allowed the encapsulation of more dye (11.8 wt%). Table 1 shows the miniemulsions prepared with functionalized DR1-MA. The DR1-MA concentration was gradually increased from 1.3 to 11.8 wt%. SEM images show that homogenous spherical particles were obtained and together with DLS show that the particle sizes remain constant with increasing amount of DR1-MA in the droplet (Figure 7 and 8). Miniemulsions with DR1-MA loading higher than 11.8 wt% resulted in polymer flakes in the suspension that are visible by eye. Again by using NMP co-solvent, it was possible to obtain loadings as high as 21 wt% in the nanodroplet. Attempts to further increase the concentration of DR1-MA were however not successful.

For samples NP1-4 and NP7-9 for which no NMP was used, the conversion was found to be higher than 95 %. However, for the experiments with NMP as dispersant the conversions were lower throughout: NP5 (40%) and NP10 (63%). Therefore, the amount of dye encapsulated for NP5 and NP10 was slightly higher than expected (NP5: 25 % and NP10: 30 %).

A systematic study on the influence of the presence of dye molecules on the molar mass was not conducted. Table 1 however contains all molar masses obtained and the GPC elugrams were included in ESI. As can be seen, the molar masses tend to increase in the presence of dye molecules, however, no direct correlation with the molecular weight can be done because other factors were also modified. We note that for the application of these particles as polable fillers, their absolute molar masses were not the critical factor but rather the fact whether the T_g was not dependent on the mass anymore. This was the case here. The samples NP1-NP3 are the only cases in which both surfactants were used (NP1: KLE; NP2,3: **4b**) and no dye molecules were present. Unfortunately, samples NP2 and NP3 were not soluble in DMF (0.1% LiCl). They could therefore not be analysed beyond particle size and a direct comparison of the influence of surfactants on the molecular weight could not be done.

The thermal stability of the DR1-MA samples was investigated by TGA (Table 2). Besides the initial stage of mass loss at between 80 and 140 °C, which can be attributed to evaporating water or residual solvent, the samples were all stable until at least 290 °C.

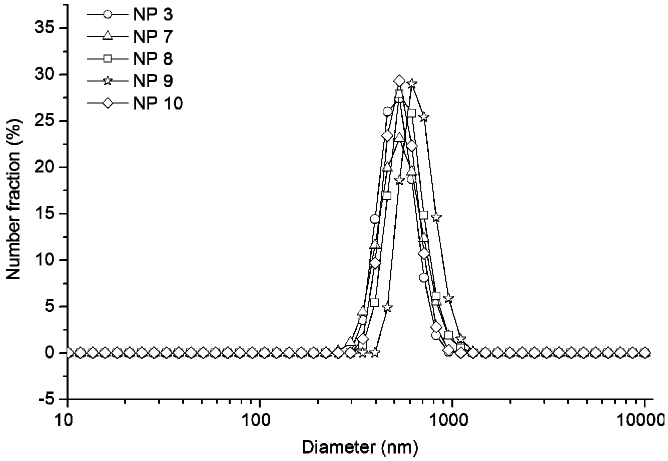


Figure 8. DLS measurements of NP 3 and NP 7 – NP 10.

Table 2. Thermal transitions and decomposition temperatures as measured with in DSC and TGA.

Sample	T_g [°C]	^aT_d [°C]
NP 2	96	415
NP 3	90	375
NP 7	93	380
NP 8	96	350
NP 9	92	335
NP 10	65	290

^{a}Decomposition temperature (T_d)

DSC was also used to determine the influence the dye on T_g of the particles (Table 2). These measurements were done well below the thermal decomposition temperature of the nanoparticles. It is known that the second heating curve can be quite different from the first one due to residual solvent and water as well as surface-pinning effects. The T_g of some selected samples are given in Table 2. As can be seen a maximum T_g is observed at a dye loading of 6.3 wt% and while most particles have a T_g between 90 and 96 °C the particles produced with NMP co-solvent have a sharply declined T_g of 65°C.

Conclusions

Two poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) surfactants with M_n of 14500 and 11200 g/mol were prepared by click chemistry of appropriate functionalized blocks. The prepared surfactants were used in the stabilization of nanodroplets in inverse miniemulsion polymerization. It was found that the surfactant which has the short poly(ethylene oxide) block functions well in stabilization of HEMA NPs and allows preparation of particles with narrow molecular weight dispersity. PHEMA nanoparticles with DR1 molecule encapsulated were prepared and the process was optimized to achieve a high dye loading in the NPs. Aggregation of the dye during polymerization was avoided when the dye was functionalized with a methacrylate group. The nanoparticles loaded with 11.8 wt% DR1-MA are stable up to 200 °C and have a Tg above 90 °C. The possibility of using these nanoparticles as polable filler in chemically cross-linked polydimethylsiloxane to be used as dielectricum in electrostrictive devices is under investigation.

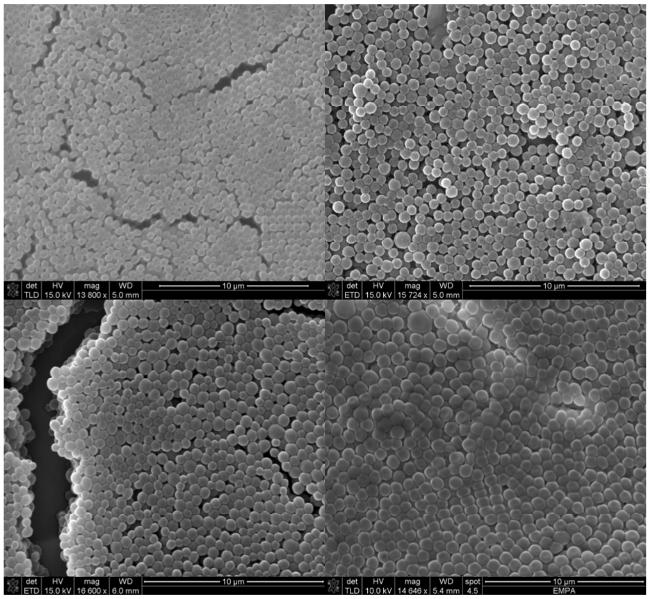


Figure 7. SEM images of particles that contain DR1MA: NP 7 (top left), NP 8 (bottom left), NP 9 (top right) and NP 10 (bottom right).

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Notes and references

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A new poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) surfactant was synthesized and used in inverse miniemulsion polymerization of 2-hydroxyethyl methacrylate with Disperse Red 1 encapsulated.