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Functionalization of Polymer Nanoparticles by Thiol−Ene Addition

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ABSTRACT: Syndiotactic 1,2-polybutadiene nanoparticles (volume average diameter 13 nm) were functionalized in aqueous dispersion by free radical mercaptan addition. By appropriate choice of both water-soluble radical initiator and mercaptan concentration, nanoparticles with a degree of functionalization of up to 85% were prepared using 3-mercaptopropionic acid methyl ester and 3-mercaptopropionic acid. Only a minor portion of double bonds formed cycles instead of the desired thiol−ene addition products. The composition and structure of the nanoparticles were elucidated by combination of elemental analysis, NMR, IR, DLS, and TEM. Highly hydrophilic mercaptans (3-mercaptopropanesulfonic acid sodium salts), in contrast, only reacted with surface accessible double bonds to afford stable and redispersible nanoparticles solely stabilized with covalently bound moieties on their surface. Analogous grafting of the tripeptide glutathione was demonstrated.

Introduction

Polymer nanoparticles are of broad practical and fundamental significance. Examples of relevant issues are the introduction or transport of guest molecules such as poorly soluble drugs, utilization as carriers in aqueous multiphase catalysis, or the homogeneous incorporation of functional molecules in solid matrices or as building blocks for ultrathin films.[1] Here, nanoparticles dispersed in water are essential. Also, a particle size lower than ca. 30 nm is desirable in many cases. Free-radical[2] or catalytic[3] microemulsion-polymerization techniques are suited in principle for the generation of such nanoparticles. Both techniques are largely complementary in terms of deployable monomers. An attractive feature of catalytic polymerization is the possible control of polymer microstructures. However, catalytic polymerizations in aqueous systems are largely limited to apolar hydrocarbon monomers.[4]

Postpolymerization modification is an alternative approach to functional polymer nanoparticles. Polybutadienes are well suited for postpolymerization reactions due to the terminal or internal double bond of every repeat unit. Moreover, the variety of microstructures (1,2-, 1,4-*cis*; 1,4-*trans*) enables variation of crystallinity and thermal properties over a large range.[5] Consequently, a large variety of functionalization reactions of polybutadiene have been reported, e.g., hydroformylation, aminomethylation, hydrosilylation, oxidation, epoxidation, or hydroboration.[6] Most of these modifications were studied in solution in organic solvents, but hydrogenation and hydroformylation of aqueous dispersions of polybutadiene nanoparticles have also been demonstrated.[7]

The well-known addition of thiols to olefins,[8,9] recently termed "thiol-click" reaction, has lately found widespread consideration as a coupling method.[10,11] The functionalization of polybutadienes in solution via thiol addition was studied by Schlaad et al. and Kornfield and co-workers.[12−15] Although the reaction is accompanied by some side reactions, namely ring closing reactions (Scheme 1), it can be used to introduce a wide range of different functional groups on the polymer chain. The mercaptyl radical, formed by abstraction of the hydrogen atom by a radical initiator or by an intermediately generated polymeryl radical, adds to the double bond in an anti-Markownikoff fashion. As a side reaction, the intermediately generated polymeryl radical can react with an adjacent double bond, which results in cycle formation (Scheme 1).

Regarding the postpolymerization modification of nanoparticles by high-yielding reactions, in addition to established coupling methods of carboxylic acid derivatives, Huisgen azide alkyne cycloaddition on small entities such as gold, silica, or also polymer nanoparticles for modification of their surface is well documented.[16] The thiol−ene reaction appears a useful extension of the methods available for the postpolymerization reaction of polymer nanoparticles in that it can be applied to and is compatible with other reactive groups, and in some cases the absence of added metal catalysts employed for promoting the alkyne−azide addition can be advantageous. Notably, the thiol−ene reaction has recently been employed for surface grafting of poly(divinylbenzene) microparticles with short-chain, thiol-end-capped polymers[17] and of poly(divinylbenzene) particles of 100 nm size with embedded smaller inorganic particles.[18]

In modification reactions of polymer nanoparticles, their efficiency and colloidal stability of the product nanoparticles are obviously central issues. Among others, conversion efficiency will depend on the miscibility of the polymer phase with the reagents employed and the accessibility of surface reactive groups. Complete conversion of non-cross-linked polymer particles can result in soluble polymers. We report a detailed study of the modification of aqueous polymer dispersions by thiol−ene reactions (Scheme 2).

Results and Discussion

As a starting material for thiol−ene postpolymerization modification (Scheme 2), an aqueous dispersion of nanoparticles of semicrystalline syndiotactic 1,2-polybutadiene was employed (97% 1,2- and 3% 1,4-*cis* as determined by IR spectroscopy; 13 nm average volume size as determined by DLS; M_w 3.4×10^4 g mol^{-1}; M_w/M_n: 2.1).[3]

For the postpolymerization modification of polymeric nanoparticles, solubility and partitioning of the reactants between the

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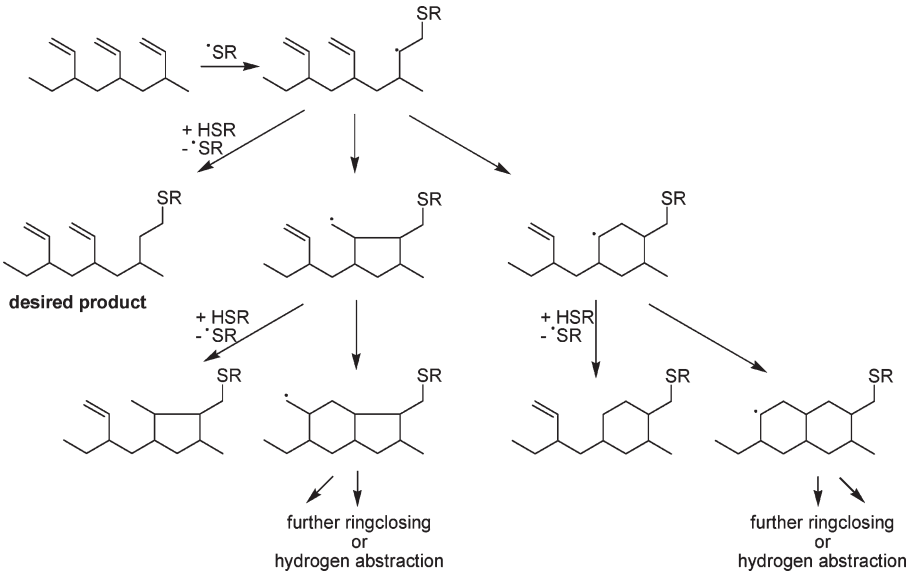
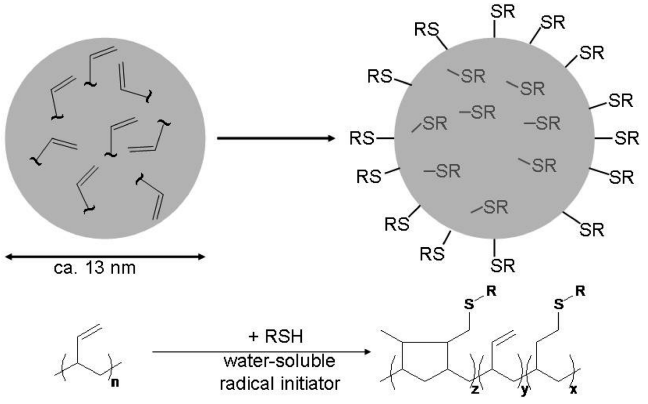
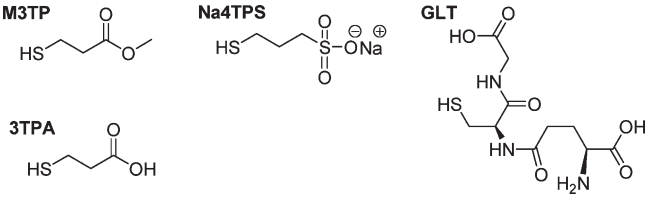
Scheme 1. Mechanism of Free Radical Mercaptan Addition to 1,2-Polybutadiene Including Ring-Closing Reactions According to Schlaad[13] and Kornfield[15]



Scheme 2. Radical Mercaptan Addition on 1,2-Polybutadiene Nanoparticles (Surfactant Omitted for Clarity)



Scheme 3. Mercaptans Employed



aqueous and apolar polyolefin phase are relevant. Both the radical initiator and the mercaptan must dissolve sufficiently in the aqueous phase of the polymer dispersion in order to access the particles. However, the mercaptyl radical formed should also react to a sufficient extent with the apolar hydrophobic polyolefin. A range of functionalized thiols with functional groups of variable polarity were studied (Scheme 3). Elevated temperatures can affect the colloidal stability of the latex. The water-soluble radical initiator VA-057 (2,2′-azobis[*N*-(2-carboxyethyl)-2-methylpropionamidine] hydrate) was chosen due to its low 10 h half-life decomposition temperature of 57 °C in order to perform the reaction at ambient temperature.

Blank Experiments. Blank experiments were carried out to evaluate the influence of radicals on polybutadiene particles. As outlined, intramolecular ring closures are a known side reaction of the radical mercaptan addition in dilute organic solution. In polymer dispersions, intermolecular reactions could be promoted by the high concentration of double bonds in a given particle. Polymer samples (Table 1, entries 2−4) isolated by precipitation with methanol from dispersions treated with different amounts of VA-057 for 20 h at 50 °C are insoluble in any solvent studied (tetrachloroethane, trichlorobenzene, chloroform, dichloromethane, toluene, tetrahydrofuran). This contrasts to the syndiotactic 1,2-polybutadiene starting material, which is soluble in tetrachloroethane at elevated temperatures. The alteration of the polymer on free-radical treatment is also reflected in its thermal properties, as observed by differential scanning calorimetry (DSC). Syndiotactic 1,2-polybutadiene prepared in microemulsion is semicrystalline with a melting point of 154 °C. Treatment with 0.025 equiv of radical initiator resulted in a reduction of the peak melting point by ca. 30 °C (entry 2). A material exhibiting no observable thermal transition indicative of crystallinity[19] was obtained when higher concentrations of radical initiator (0.1 and 0.4 equiv, entries 3 and 4, Table 1) were employed. IR spectroscopic analysis revealed no significant difference toward the starting material (cf. Supporting Information, Figure S1). This suggests that the above observations result from intra- and intermolecular cross-linking by conversion of a minor portion of the vinyl groups present. The colloidal stability of the dispersions is affected neither upon addition of the radical initiator nor by the cross-linking as evidenced by DLS data which show no significant increase in size.

3-Mercaptopropionic Acid Methyl Ester (M3TP). As a method for determination of the degree of functionalization of the vinyl groups by mercaptan addition, which is applicable also to samples insoluble in organic solvents, elemental analysis was employed. Degrees of functionalization were determined from the observed S/C ratio (cf. Supporting Information (eq S1)).

Polybutadiene dispersions were treated with variable amounts of M3TP and VA-057 at 50 °C for 20 h (Table 1, entries 5−7). The colloidal stability of the latex was not affected even upon reaction with 10 equiv (24.6 mL) of M3TP (entry 7) as proven by DLS after dialysis. All polymers

Table 1. Modification of 1,2-Polybutadiene Nanoparticles by Mercaptan Addition[a]

entry	mercaptan	$[C{=}C]_0$:[VA-057]$_0$:[HSR]$_0$[b]	degree of functionalization[c] (%)	size[d] (nm)	PDI[d]	T_m/T_g of bulk[e] (°C)
1	n.a.	n.a.	n.a.	13	0.39	154/n.o.
2	n.a.	1:0.025:0	n.a	15	0.15	125/n.o.
3	n.a.	1:0.1:0	n.a	15	0.48	n.o.
4	n.a.	1:0.4:0	n.a	15	0.19	n.o.
5	M3TP	1:0.0125:0.5	14 ± 1	16	0.23	101/−33
6	M3TP	1:0.02:1	18 ± 1	24	0.35	107/−30
7	M3TP	1:0.1:10	84 ± 3	18	0.26	n.o./−48
8	3TPA	1:0.05:0.75	26 ± 1	13	0.77	95/31
9	3TPA	1:0.025:1.5	17 ± 1	17	0.72	105/20
10	3TPA	1:0.05:1.5	29 ± 1	40	0.38	90/29
11	3TPA	1:0.1:3	35 ± 1	coag	n. o.	101/7
12	3TPA	1:0.333:5	85 ± 3	coag	n. o.	n.o./2
13	Na4TPS	1:0.0167:0.25	n.d.	15	0.23	n.o./−16
14	Na4TPS	1:0.0333:0.5	n.d.	16	0.34	n.o.
15	Na4TPS	1:0.1:1.5	5 ± 1[f]	15	0.30	n.o.
16	Na4TPS	1:0.1:3	9 ± 1[f]	16	0.34	n.o.
17	GLT	1:0.0333:0.5	8 ± 1	59	0.14	n.o.
18	GLT	1:0.1:1.5	11 ± 1	104	0.11	n.o.
19	GLT	1:0.1:10	15 ± 1	73	0.16	n.o.

[a] Reaction conditions: 2 wt % polybutadiene dispersion, addition of mercaptan and VA-057, 50 °C, 20 h, 5 days of dialysis; see Experimental Section for details. [b] Given as molar equivalents (equiv), i.e., double bonds present in the starting polymer (= repeat units) to radical initiator to mercaptan. [c] Determined by elemental analysis; see Supporting Information for details (Table S1). Experimental error estimated assuming a relative error of 1% in determination of the content of an element. [d] Volume average size and polydispersity determined by DLS. [e] Determined by DSC from second heating cycles. [f] Determined on freeze-dried samples.

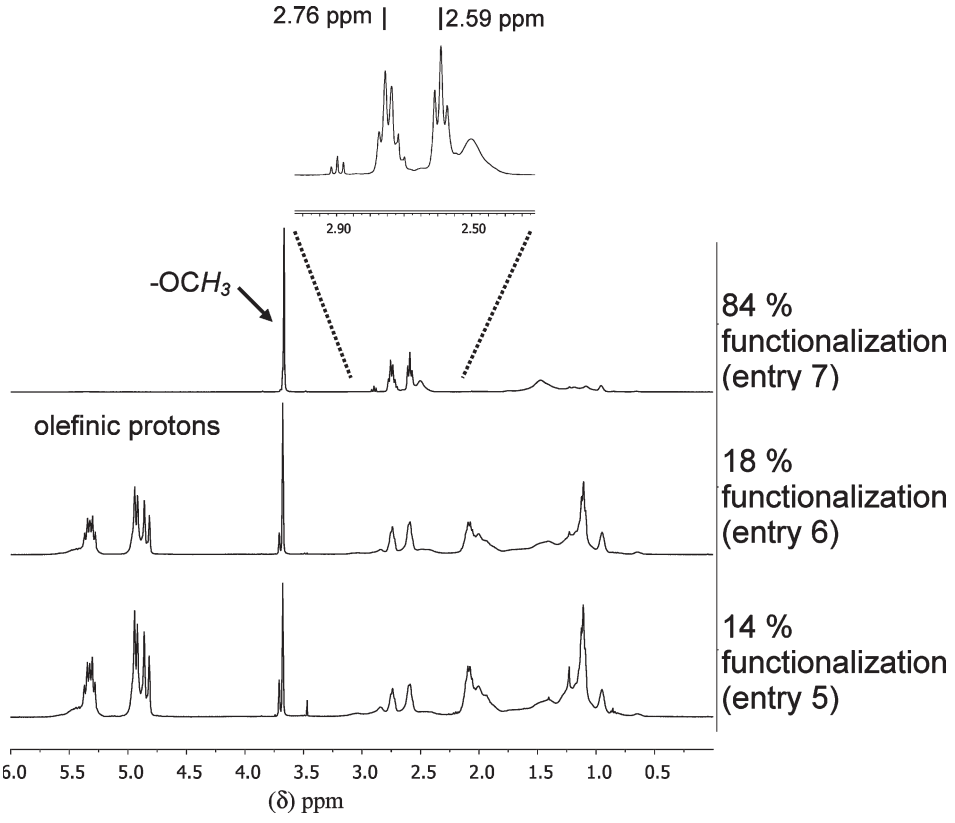


Figure 1. ^{1}H NMR spectra of ester-modified polymer samples using M3TP (entries 5−7, Table 1); $CDCl_3$, 25 °C.

modified with M3TP and precipitated with methanol are soluble in $CDCl_3$; no light scattering is observed, indicating that the polymers dissolve molecularly and not in the form of particles in this solvent. This allows for comprehensive NMR spectroscopic analysis (Figure 1).

A new singlet resonance at 3.6 ppm can be assigned to the methyl group of the ester. NMR spectra show that even at low mercaptan concentrations a significant portion of the double bonds was functionalized. The resonances of the olefinic protons between 4.7 and 5.7 ppm are reduced in intensity compared to the starting material (entries 5 and 6) or virtually absent (entry 7). 2D NMR spectra of the polymer from entry 7 provide further insights into the relative abundance of five- and six-membered rings originating from free radical side reactions (see Supporting Information Figure S2 for complete NMR spectra). Triplets at 2.76 and 2.59 ppm were assigned to methylene protons in α- and β-position to the sulfur atom, $-S^{\alpha}CH_2{}^{\beta}CH_2COOMe$, by ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HMBC (multiple bond correlation to carbonyl carbon nucleus; see Supporting Information, Figure S2)

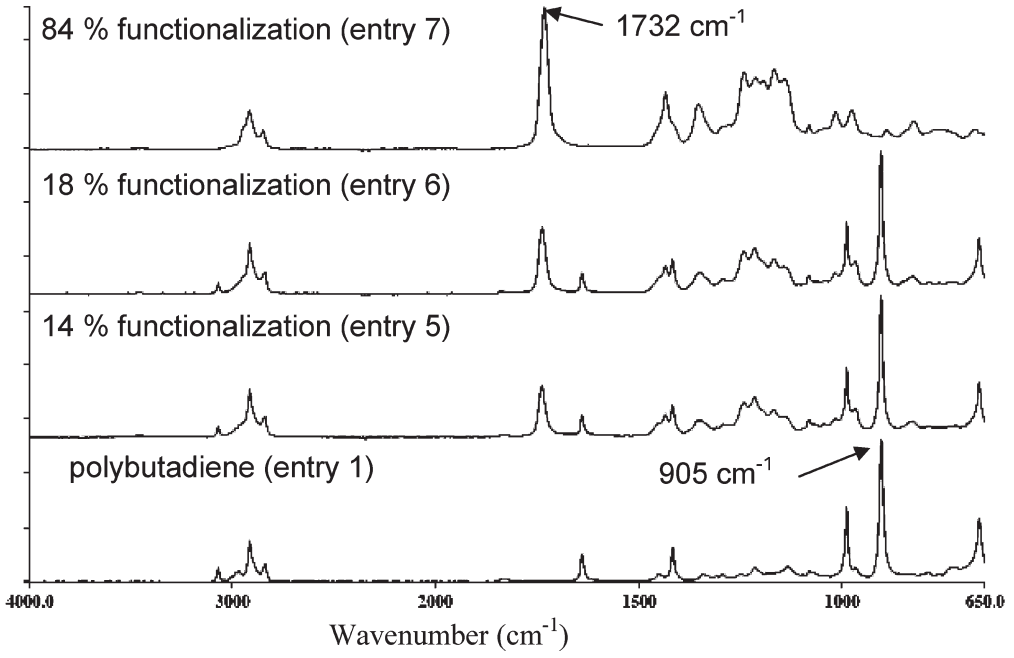


Figure 2. IR spectra of 1,2-polybutadiene (bottom) and polymers modified with variable amounts of M3TP.

spectroscopy. A second set of small signals at lower field is thought to arise from incorporation of an analogous group with different chemical environment, e.g., from reaction with a 1,4-polybutadiene unit (present in ca. 3% in the starting material) or more likely a neighboring cycle. An unstructured broad signal at 2.5 ppm corresponds to P−CH_2−SR (P = polymeric backbone), as indicated by phase-sensitive ^{1}H, ^{13}C-HSQC NMR spectra (see Supporting Information Figure S2). Phase-sensitive ^{1}H, ^{13}C-HSQC spectra clearly show a nonsplit cross-peak at 0.9/18 ppm, assigned to a methyl group of a five-membered ring. The relative amount of functionalization X_{func}, cyclization X_{cyc}, and unreacted repeating units $X_{unreact}$ can be estimated from ^{1}H NMR data by relative integration of −SCH_2R, =CH_2, and the aliphatic signal upfield of 2.2 ppm according to ref 15. For the polymer from entry 7, $X_{func} \sim 82\%$, $X_{cyc} \sim 17\%$, and $X_{unreact} \sim 1\%$ were determined. Even though six-membered rings cannot be excluded, it seems unlikely that they exist to a significant extent. The strong signal of the methyl group of a five-membered ring can fully account for the cyclized moieties (around 17%). For the polymers obtained by reaction with 0.5 and 1 equiv of M3TP (Table 1, entries 5 and 6) $X_{func} \sim 11\%$, $X_{cyc} \sim 32\%$, $X_{unreact} \sim 57\%$ and $X_{func} \sim 15\%$, $X_{cyc} \sim 25\%$, $X_{unreact} \sim 60\%$, respectively, were found. These NMR data are in good agreement with the degree of functionalization of 14%, 18%, and 84% for samples 5, 6, and 7 determined by elemental analysis (for details, see Supporting Information, Table S1). These data correspond to a grafting of 10^3−10^4 thiol moieties per starting polymer particle.

This degree of functionalization is comparable to previous studies in organic solution,[13] for which elemental analysis revealed a S/C ratio of 0.286, which corresponds to a maximum degree of functionalization of ∼75%[20] using 40 equiv of mercaptan. Concurrently, complete disappearance of double bonds was observed by NMR; that is, ∼25% of ring-closing reactions occurred.

Conversion of the vinyl group and functionalization of the polymer nanoparticles are also evident from IR spectra of the isolated polymers (Figure 2). The band at 905 cm^{-1}, which corresponds to a characteristic deformation band of the vinyl group, is reduced and finally disappears. Also,

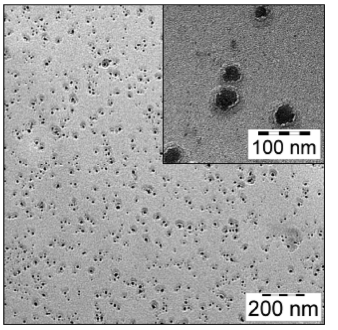


Figure 3. TEM image of completely M3TP-functionalized dispersion (entry 7, Table 1).

the stretching bands ν(C=C) at 1643 cm^{-1} and ν(=CH_2) at >3000 cm^{-1} vanish. Concurrently, a strong band at 1732 cm^{-1} characteristic for a carbonyl stretching vibration mode emerges.

As anticipated, the thermal properties are completely altered upon functionalization with the polar mercaptan. The melting point decreases and ultimately vanishes at high degrees of functionalization. In contrast to both the starting material and the polymer from blank experiments in the presence of radical initiator only, a glass transition is unambiguously observed by DSC between −30 and −50 °C. Accordingly, the isolated bulk material is very sticky. By TEM (Figure 3) particles of around 20 nm in size are observed, which is in reasonable agreement with DLS data.

The question arises to which extent SDS surfactant, introduced with the starting 1,2-polybutadiene dispersion, is still responsible for the stabilization of the product dispersion after dialysis. Comparing the polymer solids content (by precipitation) with overall solids content (by freeze-drying) of dialyzed dispersion from entry 7 revealed that 97% of the solid present in the dispersion is polymer, which indicated that this dispersion is depleted of surfactant. This result is also supported by elemental analysis. The freeze-dried sample has almost the same elemental composition and only a slightly higher sulfur content (cf. Supporting Information, Table S1), indicating the presence of only traces of SDS after

dialysis. Dispersions with lower degrees of functionalization appear to be costabilized by SDS as the ratio of polymer solids content to overall solids content is 80% and 87% for dispersions 5 and 6, respectively.[21]

Mercaptopropionic Acid (3TPA). Addition of high amounts of mercaptopropionic acid 3TPA reagent has an adverse impact on the colloidal stability of the polybutadiene dispersion. In most cases agglomeration occurred upon or shortly after addition of 3TPA. This could be due to an increase in ionic strength (or also change of pH). More than 3 equiv of 3TPA resulted in complete precipitation of the polymer. However, the radical addition of 3TPA still proceeds. Elemental analyses show that the degrees of functionalization are slightly lower than in the case of M3TP (compare e.g. entries 6 and 9). A high degree of conversion is also evidenced by IR spectroscopic measurements, which reveal the absence of double bonds for this sample and for sample 12 (5 equiv of M3TP; f = 85% according to S/C value).

Both mercaptan and radical initiator concentration influence the yield in functionalized double bonds. Comparing entry 9 (C═C:VA-057:HSR = 1:0.025:1.5) with entry 10 (C═C:VA-057:HSR = 1:0.05:1.5), it can be noted that doubling the initiator concentration leads to a significant increase in functionalization from 17% to 29% according to the S/C ratios. At low initiator concentration the influence of the mercaptan concentration is minor. For entry 8 (C═C:VA-057:HSR = 1:0.05:0.75) the degree of functionalization (26%) is only slightly lower than for entry 10 (C═C:VA-057:HSR = 1:0.05:1.5; degree of functionalization 29%).

The solubility behavior of the highly acid modified polymers (entry 12, 85% functionalization) clearly demonstrates the hydrophilic properties of these polymers. The material dissolves partially in methanol, diluted sodium hydroxide solution, or THF and completely in DMSO but is insoluble in apolar solvents like toluene or chloroform. By DLS, no signal was observed for DMSO solutions, indicating that the polymers dissolve molecularly. Both ^{1}H and ^{13}C NMR analyses (in DMSO-d_6; see Supporting Information, Figure S3) confirm the absence of a significant number of double bonds and the incorporation of the acid functionality; carbonyl resonances are observed at δ = 173.1 and 172.8 ppm.[22]

Functionalization with 3TPA reduces the crystallinity of the polymers. The polymer with the highest degree of acid modification (85%) is amorphous with a glass transition temperature of 2 °C. The reduction of crystallinity is also reflected by the particle shapes, as observed by TEM. At a degree of functionalization of roughly one-sixth (17%), the dispersion remains stable and particles are still nonspherical (Table 1, entry 9; see Figure 4, left). This is consistent with a partial remaining crystallinity as underlined also by the clear melting transition observed at 105 °C in DSC. At a higher conversion (Table 1, entry 10, 29%) only a weakly exothermic melt transition at 90 °C is observed, and the particles, which agglomerated to 40 nm in size, appear round and smooth in TEM measurements (Figure 4, right).

3-Mercaptopropanesulfonic Acid Sodium Salt (Na4TPS). Particles stabilized by ionic groups covalently attached to the particle surface were obtained by modification with Na4TPS. This results in an efficient stabilization; the Na4TPS-modified dispersions could not be be precipitated well by neither addition of excess methanol nor brine. Freeze-drying of the dialyzed dispersion yields a powdery product, which clearly varies from the starting material. The most significant difference is the dispersibility behavior. On addition of neat water, the polymers modified with the two highest mercaptan concentrations (entries 15 and 16, Table 1) readily redisperse. By comparison, 1,2-polybutadiene particles of the starting material form a nondispersible polymer bulk once water is removed. DLS of sample 16 indicates that the particle character is retained, and virtually no difference can be observed between the dispersion before and after freeze-drying (Figure 5). This is an indication of covalently bound stabilizing groups at the particle surface.

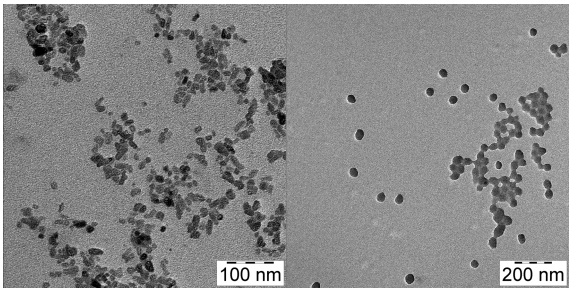


Figure 4. TEM images of partially 3TPA-modified dispersions (entries 9 and 10).

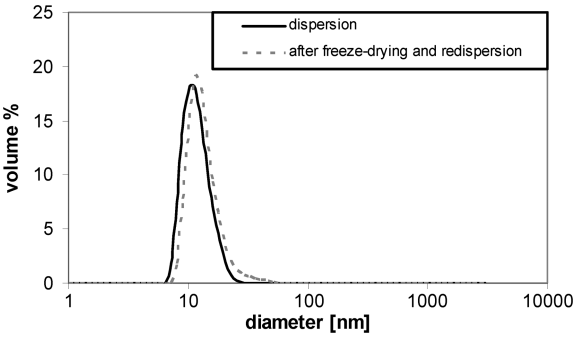


Figure 5. DLS of dialyzed Na4TPS-modified dispersion as prepared (entry 16) and after freeze-drying and redispersion.

To prove that only covalently bound groups are responsible for the stabilization and that no SDS is present after dialysis, the freeze-dried samples were dissolved in D_2O for NMR spectroscopic analysis. Because of their small size, nanoparticles do not disturb the measurement itself, and the solid material does not contribute to any significant signal under usual solution NMR conditions. For comparison, for a polybutadiene dispersion[23] containing absorbed SDS on the particle surface, NMR measurements yielded observable SDS resonances. Despite prolonged acquisition times,[24] hardly any NMR signal was detected for the Na4TPS-modified sample (Table 1, entry 16), which confirms the particulate nature of the sample and supports the absence of free SDS.

Elemental analysis conducted on the freeze-dried samples accounts for 9% of functionalization for entry 16 and 5% for entry 15.[25] In comparison to the modification with M3TP and 3TPA the degree of functionalization is much lower with Na4TPS. This behavior can be rationalized by the different solubilities of the mercaptans. In order to convert the majority of the double bonds, the mercaptan must penetrate the particle, which requires certain miscibility with the apolar polymer. Preliminary studies showed that M3TP is miscible with both water and hexane, which indicates that the mercaptyl radical should also be able to penetrate an apolar polybutadiene particle. The miscibility with hexane of 3TPA is lower vs M3TP, leading to a slightly lower degree of functionalization. In contrast, with highly hydrophilic, hexane-insoluble Na4TPS only the double bonds on the surface of the particle can react. Thus, it can be assumed that the grafting occurs on the surface leaving the core unaffected.

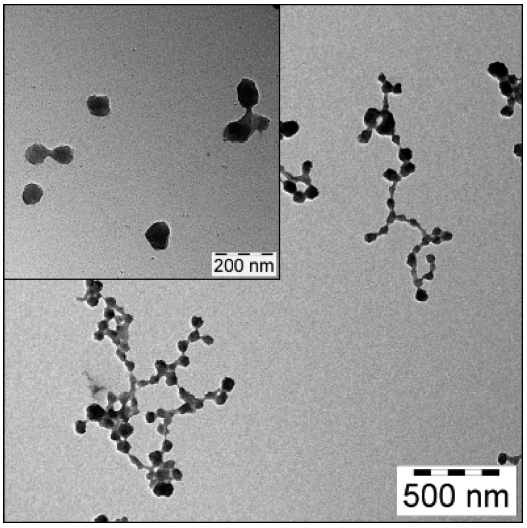


Figure 6. TEM image of GLT-functionalized particles (Table 1, entry 18).

This is also supported by IR spectroscopic measurements. Sharp and unaltered signals corresponding to 1,2-polybutadiene remain.

Glutathione (GLT). Mercaptan moieties are omnipresent in biological molecules, mainly in the form of cysteine. Glutathione (GLT), a tripeptide composed of glutamate, cysteine, and glycine, is present in most cells in high concentration and acts as an antioxidant and cysteine reservoir. Because of their hydrophilic groups, surface-grafted peptides could stabilize nanoparticles. More important, the biological uptake of nanoparticles could be dramatically changed by, e.g., peptide grafting. Glutathione was employed in radical mercaptan addition on polybutadiene dispersions with double bond to mercaptan ratios between 0.5 and 10 (Table 1, entries 17−19). According to elemental analysis (S/C ratios of 0.0458 and 0.0718), incorporations between 8 and 15% are achieved. Similar to the observation with Na4TPS, the degree of functionalization remains low (15%) even when 10 equiv of GLT is employed (entry 19). Analogous to Na4TPS, the glutathione as a hydrophilic mercaptan probably can only react with double bonds accessible at the surface.

The dispersions retain their colloidal stability under the reaction conditions. However, agglomeration to particles of ~100 nm occurred during removal of SDS surfactant by dialysis[26] as observed by DLS and TEM (Figure 6 and Figure S5). Apparently, the rather short tripeptide (note that the cysteine is the central amino acid) does not sufficiently stabilize the nanoparticles.

Covalent incorporation of glutathione is also evidenced by IR spectroscopy (Figure 7). In glutathione the SH stretching is observed at 2525 cm^{-1}. This vibration is not present in the modified polymer. A broad peak around 3300 cm^{-1}, which should correspond to the NH_2 moieties, and several new vibration bands in the carbonyl region are observed.[27]

Film Properties. Particle functionalization was also evidenced independently by water contact angles of films prepared from the dispersions.[28]

Films prepared from the apolar 1,2-polybutadiene dispersion (Table 1, entry 1) or from the "blank" samples (Table 1, entry 2) exhibit a large contact angle of almost 90°[29] after rinsing of the surface of the nascent films in order to remove surfactant.[30] Films prepared from the two dispersions with the highest degree of sulfonate modification dissolve too readily in water for these studies. A film prepared from a dispersion of a lower degree of functionalization (Table 1, entry 14) is highly wettable as exemplified by a small contact angle of ~20°. For this film prepared rinsing with water has no effect on their wetability. This behavior confirms the presence of covalently attached surface active agents.

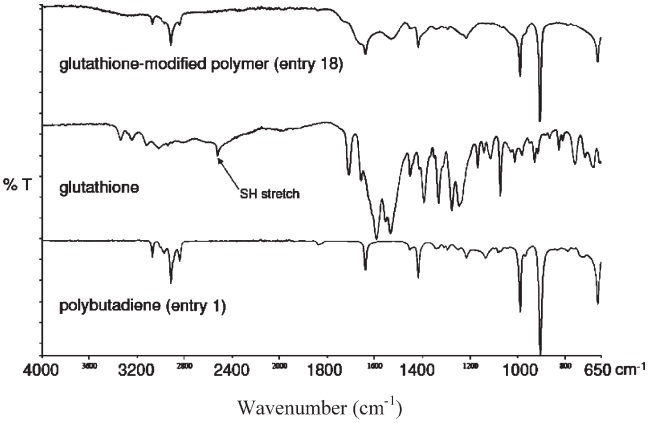


Figure 7. IR spectra of 1,2-polybutadiene, glutathione, and a glutathione-modified polymer (Table 1, entries 1 and 18).

Summary and Conclusions

The protocol described here allows for the modification of 1,2-polybutadiene nanoparticles with polar groups via thiol−ene addition. Colloidally stable dispersions are obtained with the appropriate combinations of reagents. The amount of cyclic units formed is negligible. Consequently, the largest portion of the vinyl groups of the starting material is available for substitution. By employing comparatively less polar mercaptans (esters or acids), complete conversion of the double bonds can be achieved, resulting in polar polymer nanoparticles. NMR studies provide detailed information on the polymer composition. With highly polar mercaptans, grafting of hydrophilic molecules to the surface of hydrophobic particles occurs. The resulting particles, stabilized by covalently bound mercaptan-based polar moieties bound to their surface, can be redispersed subsequent to complete drying. The approach pursued was also demonstrated for the tripeptide glutathione. Beyond the aspect of nanoparticle modification, the approach demonstrated allows for postpolymerization modification of syndiotactic 1,2-polybutadiene to otherwise inaccessible polymers. The crystallinity and low solubility of the starting material in organic solvents prohibit reactions in organic solutions. The findings reported underline that thiol−ene additions are a potentially useful method for polymer nanoparticle modification, also compatible with aqueous dispersions.

Experimental Section

General Methods and Materials. NMR spectra were recorded on a Bruker Avance 400 spectrometer. ^1H and ^{13}C NMR shifts were referenced to residual proton and naturally abundant ^{13}C resonances of the deuterated solvent. DSC was carried out on a Netzsch F1 instrument at a heating/cooling rate of 10 K min^{-1} on ~5 mg of polymer (T_m and T_g given are from the second heating cycles, unless otherwise noted). The molecular weight of 1,2-polybutadiene starting material was determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 160 °C on a Polymer Laboratories 220 instrument equipped with Mixed Bed PL-columns vs universal calibration (BHT was added as a stabilizer). TEM was carried out on a Zeiss Libra 120 instrument operated at 120 kV acceleration voltage. Samples were prepared from polymer dispersions of ca. 0.02 wt % by drop application to a carbon-coated grid and evaporation of water. Dynamic light scattering (DLS) was performed on a Malvern NanoZS ZEN 3600 particle size (173° backscattering)

on diluted dispersions. The autocorrelation function was analyzed using the Malvern dispersion technology software 5.1 algorithm to obtain volume-weighted particle size distributions and polydispersities. IR spectra of the isolated polymer were recorded on a Perkin-Elmer Spectrum 100 with an ATR sampling accessory. Elemental analysis was conducted on an Elemental vario MICRO CUBE. For static contact angle measurements a drop of dispersion (300 μL) was applied to the substrate and photographed. Glass substrates were cleaned with 7:3 mixture of 96% H_2SO_4 and 30% H_2O_2 prior to sample preparation.

All mercaptans were purchased from Aldrich and used as received. VA-057 is a generous gift of Wako Pure Chemical Industries, Ltd. 1,2-Polybutadiene dispersions were prepared according to ref 3.

Radical Mercaptan Addition in Dispersions. 1,2-Polybutadiene dispersions of 2.0 wt % polymer solids content were deoxygenated by carefully applying vacuum and flushing with argon several times. The respective amount of mercaptan and VA-057 initiator were added to 60 mL of the polybutadiene dispersion. In the case of glutathione, the scale was reduced to 1/5. For entry 19 (Table 1), the addition of another 30 mL of water was necessary to dissolve GLT. An overpressure release was installed, and the dispersion was heated under stirring to 50 °C. After 20 h the dispersion was transferred into a dialysis membrane (Spectra/Por Dialysis Membrane with a MWCO 6−8000) and dialyzed against neat water for 5 days; water was changed on regular basis. The dispersion was reconcentrated to around 1 wt % polymer solids content and filtered through a 20 μm nylon tissue. BHT was added as a stabilizer.

For analyses of the bulk polymer and determination of the polymer solids content, an aliquot was precipitated by addition to excess methanol or brine, filtered, washed with water and methanol, and dried in vacuum. For determination of the overall solids content, an aliquot was freeze-dried with a Christ Alpha 2-4 Ldplus freeze-dryer.

Key NMR Data of Completely M3TP-Modified Polybutadiene (Table 1, Entry 7). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ 3.67 (s, OCH_3), 2.76 (t, $^3J_{HH} = 7$ Hz, $S^{\alpha}CH_2^{\beta}CH_2$), 2.59 (t, $^3J_{HH} = 7$ Hz, $S^{\alpha}CH_2^{\beta}CH_2$), 2.50 (b, PCH_2S), 2−0.6 (m, aliphatic protons). ^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz): δ 172.6 (*C*O), 52.0 (OCH_3), 34.9 ($S^{\alpha}CH_2^{\beta}CH_2$), 29.7 ($PCH_2S$), 27.2 ($S^{\alpha}CH_2^{\beta}CH_2$), 18.3 ($CH_3$).

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Supporting Information Available: Additional polymerization data, NMR and IR spectra of polymers, TEM image, and DLS trace. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Electron diffraction on films prepared from this dispersion yielded only unstructured halos, arising from amorphous material.

(20) Calculated via eq S1 (cf. Supporting Information).

(21) Surface tensions of all these dispersion are between 53 and 59 mN m^{-1}.

(22) Complete NMR assignment is hampered by inclusion of impurities due to precipitation during the reaction. Minor amounts of SDS are detected, and a characteristic smell of free mercaptan of the bulk polymer is observed.

(23) Polybutadiene dispersion from entry 1, Table 1, dialyzed for at least 3 days, concentrated/diluted to a polymer solid content of 1.9 g L^{-1}, yielding a surface tension above 60 mN m^{-1}.

(24) For ^{13}C NMR > 12 000 scans.

(25) For samples of lower degrees of functionalization, elemental analysis was not determined as the absence of SDS cannot be assured with sufficient accuracy by the method.
(26) Comparison between polymer solids content and overall solids content of these dialyzed dispersions reveal that for all GLT-modified dispersions less than 20% of the solids is SDS.
(27) NMR characterization for analysis of the degree of cyclization was not possible due to insolubility.
(28) The dialyzed dispersions were spincoated on glass substrates, and the nascent films were rinsed with water to remove SDS from the film surface. A drop of water was applied on the films, and static contact angles were determined.
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