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# New Functional Diblock Copolymers Through Radical Addition of Mercaptans

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**Summary:** 1,2-Polybutadiene-*block*-poly(ethylene oxide)s were prepared by anionic polymerization and were subsequently modified by radical addition of ω-functional mercaptans (functional groups: carboxylic acid, amine, ethylene glycol, and fluorocarbon). The degree of functionalization of the products at full conversion of double bonds is 60–80%, and the molecular weight distribution is as narrow as that of the precursor polymer. The modified block copolymers are amphiphilic in nature and form complex aggregates in dilute aqueous solution.

**Keywords:** aggregates; anionic polymerization; free-radical addition; mercaptan; polybutadiene

## Introduction

The generation of self-organized colloidal structures with amphiphilic block copolymers, that are polymers with two or more incompatible block segments, is subject of continuous interest. The size and the shape of superstructures can be controlled via the chemical composition of polymer chains and the over-all number of repeating units, as long as structure formation is solely driven by the counterbalance of thermodynamic demixing and chain elasticity.[1,2] The aggregates most commonly observed in solution are spherical and cylindrical micelles and vesicles. The diversity and complexity of structures increases, like in biological or supramolecular systems,[3] when additional energy contributions from non-covalent interactions (electrostatic, hydrogen bonding interactions, etc.) come into play – some examples of complex aggregates have been described in the litereature.[4–10]

Searching for new interesting morphologies is indispensable connected with the synthesis of new, well-defined and appropriately functionalized block copolymers by controlled polymerization techniques.[11–14] Living anionic polymerization, the method of choice in our laboratory, can provide block copolymer materials of highest quality, but the number of polymerizable functional monomers is rather limited.[15] Its applicability can be extended by polymer-analogue reactions. Ideally, the modification reaction proceeds in a quantitative yield without altering the narrow molecular weight distribution of the precursor polymer.

A convenient tool for a one-step modification of polydienes appears to be the free-radical addition of ω-functional mercaptans[16–30] or of alkyl iodides.[31] These reactions are tolerant to many different functional groups (e.g. hydroxyl, amine, carboxylate, phosphonate), but the conversion of double bonds may not be complete and also cyclic units may be formed. An intermolecular cross-linking of chains, however, does not happen. Hence, modified polymers exhibit chemical defects but have the same narrow molecular weight distribution as the precursor.

In this contribution, we report on our results concerning the modification of 1,2-polybutadiene-*block*-poly(ethylene oxide)s (1,2-$PB_x$-*b*-$PEO_y$; subscripts denote average numbers of repeating units) with ω-functional mercaptans (see the list in Table 1;

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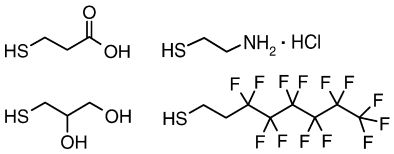
**Table 1.**
List of 1,2-PB-*b*-PEO copolymers and of ω-functional mercaptans.

| 1,2-PB$_x$-*b*-PEO$_y$ samples | ω-Functional mercaptans |
|---|---|
| **A**: $x = 25$, $y = 75$, PDI = 1.05 |  |
| **B**: $x = 40$, $y = 132$, PDI = 1.08 | |
| **C**: $x = 40$, $y = 273$, PDI = 1.06 | |

PDI = polydispersity index),[30] and show first results on the aggregation behavior of the products in dilute aqueous solution.

## Experimental Part

### Materials

All chemicals were purchased from Sigma-Aldrich, Fluka or Acros Organics (Germany) with the highest purity grade available (≥98%) and were used as received. 2-Mercapto-1,2-propanediol was available as a 90% solution in water. 1-Mercapto-1H,1H,2H,2H-perfluorooctane was provided by Fluorochem Limited (UK).

### Polymerization

Monomers and solvents were purified using conventional methods reported elsewhere in the literature.[32,33] All reactions were performed under a dry argon atmosphere. 1,2-PB(OH) was synthesized by anionic polymerization of buta-1,3-diene in tetrahydrofuran (THF) solution at −78 °C using *sec*-butyllithium (sBuLi) as the initiator. After one day, ethylene oxide was added, and the solution was stirred for three days at room temperature. The polymer was precipitated into methanol and dried under vacuum. 1,2-PB-*b*-PEO was prepared by anionic polymerization of ethylene oxide using 1,2-PB(OH)/phosphazene base *t*-BuP$_4$ as the initiator in THF. The solution was stirred at +50 °C for two days and then quenched with acetic acid. The polymer was precipitated into cold acetone, redissolved in water, and freeze-dried.

### Free-Radical Addition Reactions

Mercaptan (RSH) and 2,2-azoisobutyronitrile (AIBN) were added to a ~3 wt % solution of polymer in dry THF so that $[RSH]_0/[C{=}C]_0/[AIBN]_0 = 10{:}1{:}0.33$. The reaction mixture was degassed and heated to reflux for 24 hours under an argon atmosphere. Products were (*i*) precipitated several times in cold hexane, filtered, redissolved in water, dialyzed against water, and freeze-dried or (*ii*) precipitated twice in methanol, washed with water, and dried under vacuum to constant weight.

### Characterization of Polymers

C/H/N/S-specific elemental analysis (EA) was done with a Vario EL elemental analyzer. $^1$H NMR spectra were recorded at room temperature with a Bruker DPX-400 spectrometer operating at 400.1 MHz. Size exclusion chromatography (SEC) with simultaneous UV and RI detection was performed (*i*) in THF at 25 °C using a column set of three 300 × 8 mm MZ-SD*plus* (spherical polystyrene particles with an average diameter of 5 μm) columns with pore sizes of $10^3$, $10^5$, $10^6$ Å or (*ii*) in *N*-methyl-2-pyrrolidone (NMP + 0.5 wt % LiBr) at +70 °C using a column set of two 300 × 8 mm PSS-GRAM (spherical polyester particles with an average diameter of 7 μm) columns with pore sizes of $10^2$ and $10^3$ Å, respectively. Calibration was done with 1,2-PB and PEO standards.

### Characterization of Aggregates

Dynamic light scattering (DLS) measurements were done at +25 °C on a commercial spectrometer from ALV GmbH (Langen, Germany) consisting of a goniometer and an ALV 5000 multi-tau correlator. Measured diffusion coefficients were transformed into hydrodynamic radii via the Stokes-Einstein equation. Scanning force microscopy (SFM) was performed on a Nano-Scope IIIa microscope (Digital instruments, USA) using a $10 \times 10$ μm cantilever (Model TESP; force constant: 42 N/m). Surfaces were scanned in the tapping mode at a resonance frequency of 300 kHz. Cryogenic transmission electron microscopy (cryo-TEM) was done with a Zeiss EM 910, operating at 100 kV, with the aid of a cyro-transfer holder at $-120\,^{\circ}$C. Aqueous polymer solutions on Pioloform®-coated copper grids were shock-frozen in a Vitrobot™ (Fei, The Netherlands).

## Results and Discussion

### Synthesis

1,2-PB-*block*-PEO copolymers were prepared in two steps: First, butadiene was polymerized in THF at $-78\,^{\circ}$C using sBuLi as the initiator; the reaction was quenched by the addition of ethylene oxide. The isolated ω-hydroxy-polybutadienes (1,2-$PB_xOH$, $x = 25$ and 40) contained about 95% 1,2-units ($^1$H NMR) and had a narrow molecular weight distribution (PDI = 1.1; SEC). Second, ethylene oxide was polymerized in THF at $+50\,^{\circ}$C with 1,2-$PB_xOH$/*t*-$BuP_4$ as macroinitiator. The polymerizations were quenched with acetic acid, and the products were isolated by precipitation into cold acetone and freeze-drying. The main molecular characteristics of the block copolymers are summarized in Table 1 (characterization by $^1$H NMR and SEC). It is noteworthy that 1,2-$PB_xOH$ can also be used to initiate the polymerization of other heterocyclic monomers like lactones or 2-alkyl-$\Delta^2$-oxazolines.

***Table 2.***
List of the modified 1,2-PB-*b*-PEO copolymers.

| Sample | Precursor | Functionality | *f* |
|---|---|---|---|
| **1** | **A** | $-COOH$ | 0.78 |
| **2** | **B** | $-COOH$ | 0.70 |
| **3** | **A** | $-NH_2$ | 0.82 |
| **4** | **B** | $-NH_2$ | 0.77 |
| **5** | **B** | $-CH(OH)CH_2CH_2OH$ | 0.65 |
| **6** | **C** | $-CH(OH)CH_2CH_2OH$ | 0.58 |
| **7** | **C** | $-(CF_2)_5CF_3$ | 0.55 |

Modifications of the block copolymers were done in refluxing THF using a ten-fold excess of the mercaptan with respect to double bonds; AIBN served as the radical source. The degrees of functionalization, *f*, of the final products (samples **1**–**7**, Table 2) were calculated from the sulfur content (S/C) determined by EA. Values of *f* were found to be in the range of 60-80%, which means that the mercaptan was not added to every butadiene unit (see below). According to $^1$H NMR analysis, the copolymers do not contain residual double bonds (lack of resonances at $\delta = 4.8$–5.6 ppm), except for the one being modified with fluorocarbon

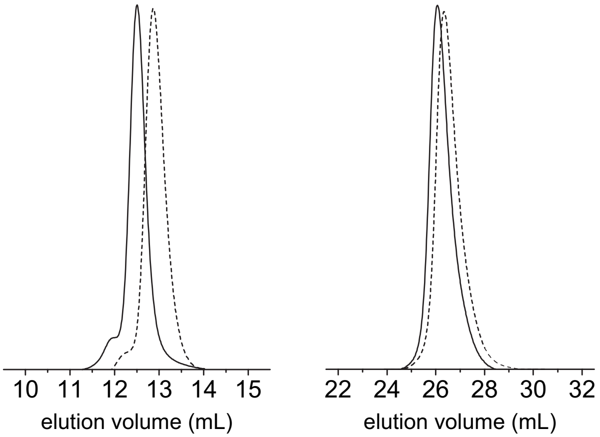


***Figure 1.***
SEC chromatograms of the modified 1,2-PB-*b*-PEO copolymers **5** (left; eluent: NMP) and **7** (right; eluent: THF) (see Table 2); dashed lines: 1,2-PB-*b*-PEO precursors.

chains (~11% residual double bonds). The two signals of methylene protons next to the sulfur atom usually display at $\delta = 2.4$–3.0 ppm. SEC analysis could only be done for the non-ionic block copolymer samples; chromatograms of samples **5** and **7** are shown in Figure 1. The samples exhibit a larger hydrodynamic volume and virtually the same narrow molecular weight distribution as the corresponding precursor polymer (see Figure 1).

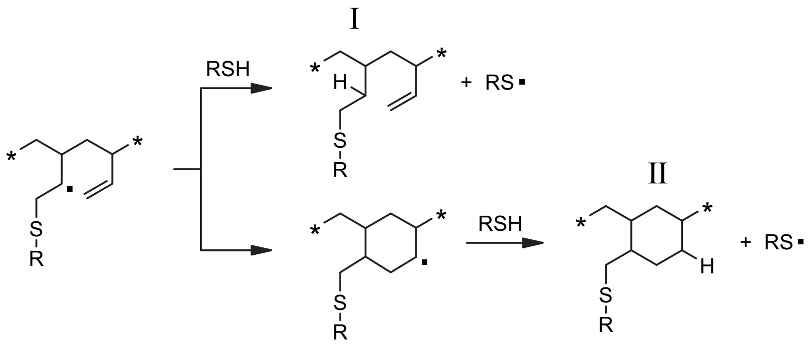
The reason for the less than quantitative degree of functionalization of the 1,2-PB segment at full conversion of double bonds is a side reaction of the intermediate radical species; see Scheme 1. The desired route is that the radical formed by the addition of RS• onto the vinyl double bond abstracts a hydrogen atom from another RSH molecule (→ unit I). Prior to hydrogen transfer, the radical may add to another double bond in its vicinity, leading to the formation of a six-member cyclic unit (→ unit II). The modified 1,2-PB chains have therefore to be considered as a random copolymers made of units I and II.[30]

## Aggregation Behavior

Due to the high amount of hydrophilic units, the 1,2-PB-*b*-PEO precursors are expected to form small micelles in dilute aqueous solution. Indeed, DLS analysis of a ~0.1 wt % solution of **B** in water indicates the presence of spherical micelles with a hydrodynamic radius of $R_h = 26$ nm. The modified block copolymers **1**–**7**, on the other hand, show a completely different aggregation behavior – cryo-TEM and SFM images of the aggregates formed by **2**, **4**, **5**, and **7** in aqueous solution are shown in Figures 2 and 3.

Samples **2** (–COOH) and **4** (–$NH_2$) were prepared in a phosphate buffer solution at pH 7.2, that is when the pendant electrolyte units should be fully ionized. In the case of the anionic block copolymer **2**, one observes no discrete objects but a cluster or network of spherical micelles (Figure 2, left). In DLS, these clusters appear to be large aggregates with a radius of about 200 nm. The cationic system **4**, however, self-assembles into cylindrical micelles with a diameter of ~30 nm (Figure 2, right). Sample **5** with pendant ethylene glycol units also assembles into cylindrical micelles in water; cross-section of the micelles is about 20 nm (Figure 3, left). Since modified copolymers are more hydrophilic than the precursors, the appearance of cylindrical micelles is counterintuitive. We believe that the aggregation behavior of the modified copolymers is very much controlled by electrostatic (**2** and **4**) and hydrogen-bonding interactions (**5**) – this is currently being investigated in more detail.

Whereas the former samples could be directly dissolved in water, this was not possible for fluorocarbon-containing copolymer **7**. In order to prepare an aqueous solution of **7**, the copolymer was first dissolved in a mixture of THF and water, and then the sample was left to stir until



***Scheme 1.***
Possible reactions of the intermediate radical species formed by the addition of RS• onto 1,2-PB.

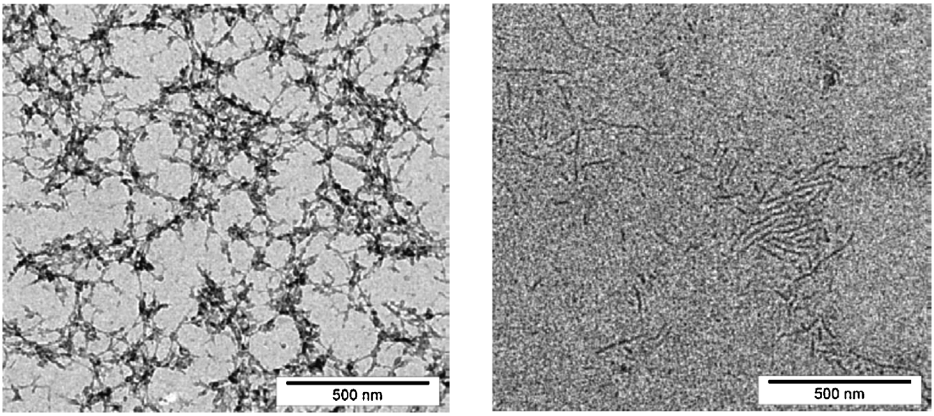


***Figure 2.***
Cryo-TEM images of aggregates formed by **2** (left) and **4** (right) in an aqueous phosphate buffer at pH 7.2 (polymer concentration: ~1 wt %).

THF has completely been evoporated. Analysis of the solution by SFM showed the presence of spherical objects with a diameter of about 50–100 nm (Figure 3, right) (DLS: $R_h \sim 30$ nm). In the phase image shown, domains formed by the fluorinated chains appear as a bright dot (also recognized in the height image). Interestingly, objects contain up to three distinct dots and may therefore be classified as multicompartment micelles.[34]

## Conclusion

The free-radical addition of ω-functional mercaptans onto double bonds is a versatile tool for the modification of 1,2-PB-based

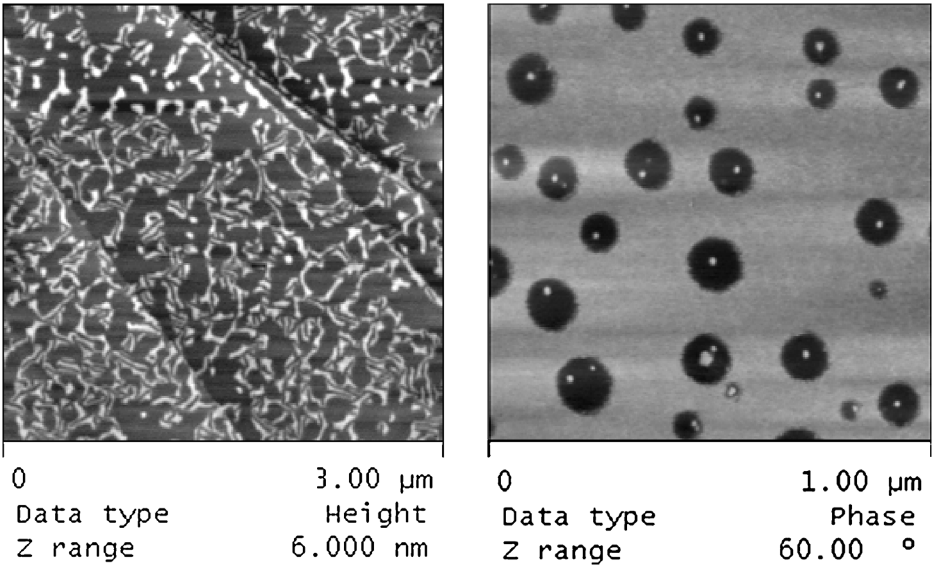


***Figure 3.***
SFM images of the aggregates formed by **5** (left) and **7** (right) in aqueous solution (~0.1 wt % polymer solution spin-coated on graphite).

block copolymers. The degree of functionalization of the products at full conversion of double bonds is 60–80%, and the molecular weight distribution is as narrow as that of the precursor polymer (1,2-PB-*b*-PEO, PDI $< 1.09$). The lower than theoretical number of functional groups is the result of an intramolecular side reaction of the intermediate radical species, which produces six-member cyclic units along the polymer backbone.

Thus obtained hydrophilically modified copolymers are amphiphilic in nature and can assemble into clusters of micelles (functional group = carboxylic acid) or cylindrical micelles (amine and ethylene glycol) in dilute aqueous solution. The copolymer modified with fluorocarbon chains seems to form micelles with a compartimentalized core.

The strategy described thus allows the preparation of a toolbox of well-defined functional block copolymers and complex assemblies.

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