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Toward a toolbox of functional block copolymers via free-radical addition of mercaptans

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Abstract

This work demonstrates the applicability of the free-radical addition of ω-functional mercaptans onto 1,2-polybutadienes as a modular synthetic pathway toward a toolbox of diverse functional block copolymers. Functional groups included, for instance electrolytes (carboxylic acid and amine), L-amino acid, and fluorocarbon. The number of functional groups attached to the polymer was lower than that of double bonds reacted (degree of functionalization = 50–85%, typically 70–80%) due to cyclization of two neighboring units, but the narrow molecular-weight distribution of the parent (co)polymer was always maintained.

Keywords: Modification; Block copolymer; Mercaptan

1. Introduction

Polymers containing covalently attached reactive functionalities have generated much interest for making materials with tailored properties [1–3]. The synthetic methods allowing the rational design of polymers with respect to molecular weight, molecular weight-distribution, composition, architecture, and functionality include living/controlled ionic [4,5], radical [6], and transition metal-catalyzed polymerization techniques [7].

Living anionic polymerization, the method of choice in our laboratory, can provide block copolymer materials of highest quality, but it also suffers from some experimental drawbacks. It demands high-purity and inert reaction conditions as well as protection of functional groups in monomers [8,9]. Also, for most anionic systems, sequential polymerization must follow a strict order in monomer addition so that the relative reactivity of anionic sites (as estimated by the pK_a value of the conjugate acid) is steadily decreasing, thus limiting the number of accessible block copolymers. Asymmetric block copolymers with a short second functional block, like for instance block ionomers, however, might be difficult to purify and separate from homopolymer impurities.

The applicability of anionic polymerization can be extended by modification reactions. Ideally, a modification of polymers proceeds in quantitative yield and without major side reactions (including preservation of the narrow molecular weight distribution), like for instance the hydrogenation or the hydroboration/oxidation of polybutadiene (PB) [1]. Epoxidation of 1,2-PB and subsequent treatment with a nucleophile, as introduced by Antonietti et al. [10], is a convenient way to make a variety of functional block copolymers via a modular approach.

Another efficient tool for a one-step modification of polymer precursors is the free-radical addition of ω-functional mercaptans [11–24] or alkyl iodides [25] onto vinyl double bonds. The former reaction has also been used for an end-functionalization of polymers [26,27]. The groups attached to PB homopolymers and eventually to random or block copolymers included alkane [11], perfluoroalkane [16,17,25], alkoxy silane [18], alcohol [13,14,22], amine [14,15,21], carboxylic acid [12,20,23], and phosphonate [19]. The addition of mercaptans was found to occur on the vinyl double bonds (1,2-units), mainly in an anti-Markownikoff fashion, as well as on the in-chain double bonds (1,4-units) of PB (see Scheme 1). An intramolecular cyclization of two neighboring monomer units, which is evident in the radical addition of alkyl iodides onto 1,2-PB [25], or a recombination of polymer chains could not be observed. Although the mercaptan was used in excess, the conversion of double bonds and thus the degree of functionalization of PB were usually less than quantitative.

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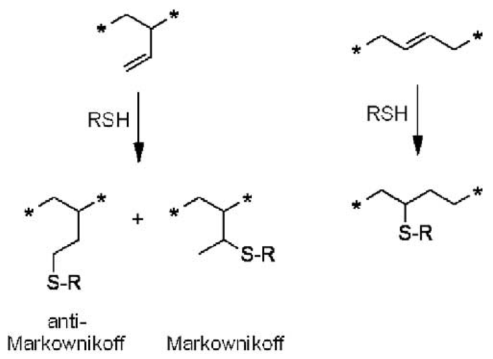


Scheme 1. Chemical structures of possible products obtained by the radical addition of mercaptans onto vinyl and in-chain double bonds of PB.

The present work demonstrates the applicability of free-radical addition of ω-functional mercaptans in the modular synthesis of a toolbox of well-defined functional homopolymers and block copolymers (see Table 1). In the first part, the course of the addition of mercaptans onto 1,2-PB is revisited. Against an earlier report [24] (see also Boutevin et al. [17]), however, the addition reaction is accompanied by an intramolecular cyclization, as evidenced by MALDI-TOF mass spectrometry. This side reaction has a noticeable impact on the degree of functionalization but not on the molecular-weight distribution of polymers. In the second part, the results obtained for the modifications of 1,2-PB-*b*-PEO (PEO = poly(ethylene oxide)) and 1,2-PB-*b*-PS (PS = polystyrene) with various ω-functional mercaptans (see Fig. 1) are presented. Products were characterized by elemental analysis (EA), ^{1}H NMR and FT-IR spectroscopy, and size-exclusion chromatography (SEC).

2. Experimental section

2.1. Materials

All chemicals were purchased from Sigma–Aldrich, Fluka, or Acros Organics (Germany) with the highest purity grade available and were used as received. 1-Mercapto-1H,1H,2H,2H-perfluorooctane was purchased from Flurochem Limited (United Kingdom). 1,4-PB (99% 1,4-units, molecular weight: 3.0 kg mol^{-1}) was provided by Sigma–Aldrich.

Table 1
Characteristics of 1,2-PB-based homopolymers and block copolymers

Sample	PB 1,2-units (%)[a]	Average number of repeating units[b]		Polydispersity index[c]
		x	*y*	
1,2-PB$_x$				
A	97	25	–	1.10
B	93	40	–	1.10
C	92	65	–	1.08
1,2-PB$_x$-*b*-PEO$_y$				
D	97	25	75	1.05
E	93	40	132	1.08
F	93	40	273	1.06
G	92	65	212	1.10
1,2-PB$_x$-*b*-PS$_y$				
H	97	85	351	1.15

[a] Determined by ^{1}H NMR according to Ref. [32].
[b] Determined by SEC (eluent: THF) using 1,2-PB calibration (*x*) and SEC/^{1}H NMR (*y*).
[c] Determined by SEC.

2.2. Polymerizations

Monomers and solvents were purified using conventional methods reported elsewhere in the literature [28,29]. All reactions were performed under a dry argon atmosphere. 1,2-PB(OH) was synthesized by anionic polymerization of 1,3-butadiene in tetrahydrofuran (THF) solution at −78 °C using sec-butyllithium (*s*BuLi) as the initiator. After 1 day, ethylene oxide was added, and the solution was stirred for 3 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)/phosphaszene base *t*-BuP$_4$ as the initiator in THF. The solution was stirred at +50 °C for 2 days and then quenched with acetic acid. The polymer was precipitated into cold acetone, redissolved in water, and freeze-dried. 1,2-PB-*b*-PS was prepared by sequential anionic polymerization of 1,3-butadiene and styrene in THF at −78 °C using *s*BuLi as the initiator: 1,3-Butadiene was condensed into a reactor containing a mixture of dry THF and *s*BuLi, and the solution was stirred overnight at −78 °C. After withdrawal of an aliquot from the reactor, styrene was condensed into the reactor and polymerized for 1 h at −78 °C. The reaction was quenched with degassed methanol, and the polymer was precipitated in methanol and dried under vacuum at +40 °C. The characteristics of all polymers prepared are summarized in Table 1.

2.3. Radical addition of mercaptan—general procedure

To a ∼3 wt% solution of polymer in dry THF was added the mercaptan and AIBN so that $[RSH]_0/[C{=}C]_0/[AIBN]_0 = 5\ldots40:1:0.33$. The solution was degassed and heated to about +70 °C for 24 h under a dry argon atmosphere. Depending on solubility, the crude product was either (i) precipitated several

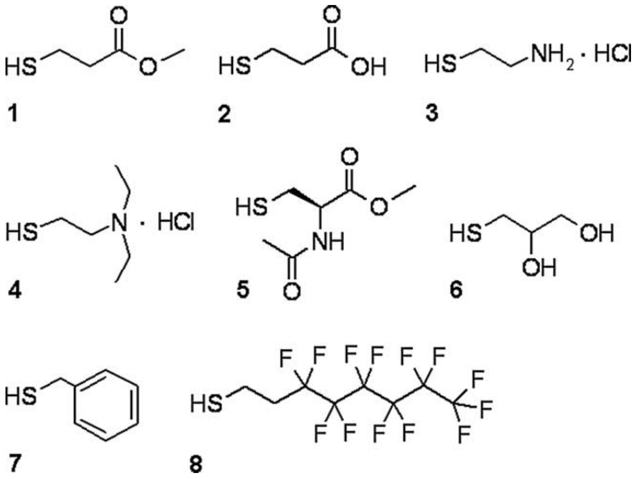


Fig. 1. Chemical structures of ω-functional mercaptans.

times into cold hexane, filtered, re-dissolved in water, dialyzed against bi-distilled water (molecular weight cut-off: 1 kDa), and freeze-dried or (ii) precipitated twice into methanol, washed with water, and dried under vacuum to constant weight.

2.4. Analytical methods and instrumentation

Gas chromatography (GC) was performed on a Hewlett Packard HP 6890 Series GC System. 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. Fourier-transform infrared (FT-IR) spectroscopy was done at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a single reflection diamond ATR. Circular dichroism (CD) spectroscopy was done at room temperature on a JASCO J 715. Contact angles were measured on a Krüss G10 contact angle goniometer using water as the test liquid. MALDI-TOF mass spectrometry was carried out on a Bruker Reflex II equipped with a nitrogen laser source operating at $\lambda=337$ nm; the set-up was calibrated with bovine insuline. The measurement was done in the reflectron mode using 2,5-dihydroxy benzoic acid as the matrix. 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-SDplus (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, PEO, or PS standards.

3. Results and discussion

All free-radical modification reactions of 1,2-PB-based polymers (Table 1) with ω-functional mercaptans (Fig. 1) were done as described above unless otherwise noted. Precipitated/dialyzed products did not contain detectable amounts of mercaptan, as indicated by SEC, GC, FT-IR spectroscopy, and lack of odor. Gravimetric yields were usually in the order of 70–90% (assuming quantitative addition of mercaptan).

3.1. Mechanistic study: radical addition of mercaptans onto PB homopolymers

For an examination of the course of the reaction, the free-radical addition of methyl-3-mercaptopropionate (mercaptan **1** in Fig. 1) was first performed with two PB homopolymer samples having different microstructures, namely 1,2-PB (**B**, 93% 1,2 + 7% *trans*-1,4) (see the ^{1}H NMR spectrum in Fig. 2) and 1,4-PB (99% 1,4). Reactions were carried out for 24 h in refluxing THF solution under inert argon atmosphere. 2,2′-Azoisobutyronitrile (AIBN) was chosen as the radical source and a 10-fold excess of the mercaptan with respect to PB double bonds was applied. The first mixture containing 1,2-PB maintained its low viscosity throughout the whole reaction time, and the product (**B1**) could afterwards be dissolved in common organic solvents. In the second case, however, gelation occurred after 1 h. Seemingly, experimental conditions (especially the high polymer concentration of about 3 wt%) were as such that 1,4-PB chains underwent a radical cross-linking, thus producing an insoluble material.

As indicated by SEC (not shown), sample **B1** exhibited a larger hydrodynamic volume but the same molecular weight distribution as the precursor polymer **B**. Any recombination products were not detected. FT-IR spectroscopy showed the presence of the ester carbonyl units ($\tilde{\nu}=1737\ \mathrm{cm}^{-1}$) and the absence of $>$C=C$<$ units ($\tilde{\nu}=1640\ \mathrm{cm}^{-1}$, **B**) in the product. The quantitative conversion of both the vinyl as well as the in-chain double bonds was confirmed by ^{1}H NMR by the complete lack of resonances at $\delta=4.8$–5.6 ppm (see Fig. 2). Signals from protons next to the sulfur atom of the newly formed thioether linkage display at $\delta=2.6$–2.8 ppm. The signal at $\delta=2.60$ ppm is split into three lines and can therefore be assigned to the methylene protons 4 of the anti-Markownikoff product (see the chemical structure in Fig. 2). Characteristic signals of –SCH$<$ methine protons of the adduct to the in-chain double bonds or of the Markownikoff product (cf. Boileau et al. [21]) could not be identified.

Elemental analysis revealed a ratio of S/C in the modified product of 0.272, which is 82% the theoretical value assuming quantitative addition of mercaptan onto the double bonds (S/C = 0.334). MALDI-TOF mass spectrometry (see the spectrum in Fig. 3) further revealed that the number-average molecular weight of the sample is $M_n \sim 5480$ Da (estimated from the position of the maximum of the frequency distribution) instead of 6900 Da (number of repeating units, $x=40$). Hence, there must be a fraction of monomer units to which no mercaptan was added. The most reasonable reaction pathway is given in Scheme 2 showing the regular addition of the mercaptan (→unit I) and the formation of a cyclic structure (→unit II, two isomers). Considering the different stability of

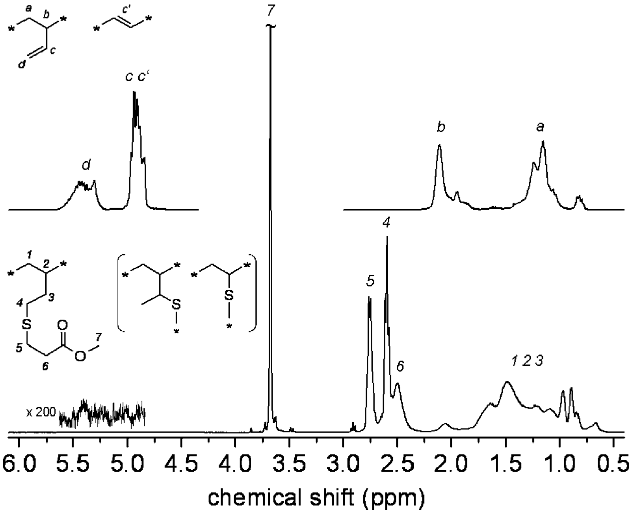


Fig. 2. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) of **B** (top) and **B1** obtained by radical addition of **1** onto **B** at 10-fold excess with respect to double bonds (bottom).

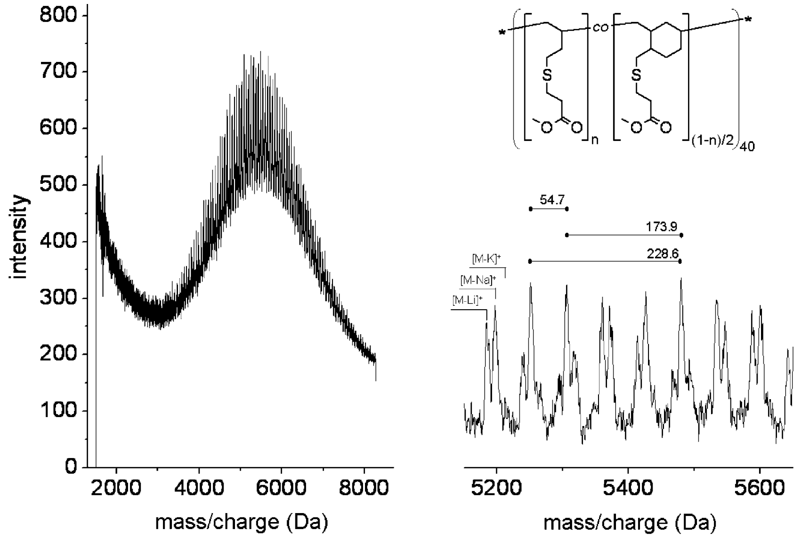


Fig. 3. MALDI-TOF mass spectrum and chemical structure of **B1** obtained by radical addition of **1** onto **B** at 10-fold excess with respect to double bonds.

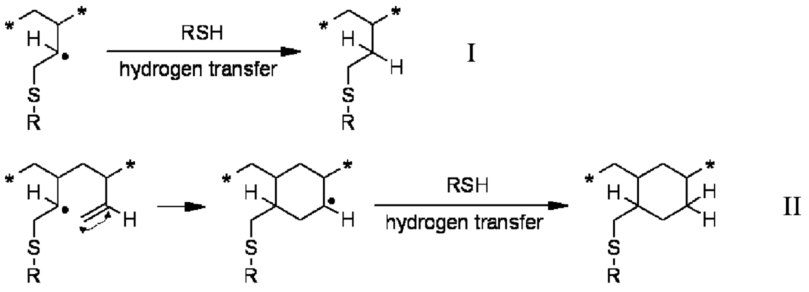
secondary and primary radical intermediates, the formation of a six-member cycle (anti-Markownikoff) should be preferred over that of a five-member one (Markownikoff) [17]. Polycyclic structures should not be produced. A likely random copolymer structure of **B1** is supported by MALDI-TOF MS, the spectrum displaying a series of peaks with $\Delta m \sim 54$ Da corresponding to the mass difference between the units I (174.1 Da) and II (228.2 Da). Given the (simplified) chemical structure shown in Fig. 3 and a degree of functionalization of $f=0.82$, the average composition of **B1** is I:II = 24.8:7.6 ($\mathrm{I}+2\mathrm{II}=x$, $\mathrm{I}+\mathrm{II}=fx$) and thus $M_\mathrm{n} \sim 6050$ Da.

The composition of the product should be determined by the rates of intermolecular hydrogen transfer and of intramolecular cyclization. The rate of transfer is linearly proportional to $[\mathrm{RSH}]_0$ and, in a first approximation, remains constant during the reaction due to the high excess of mercaptan used. The rate of cyclization does not depend on $[\mathrm{RSH}]_0$ but it will, as a matter of statistics, decrease with increasing conversion of the double bonds. Accordingly, the fraction of structural unit I in the product was found to be larger the higher the concentration of mercaptan (see Table 2). However, changes in composition were marginal at $[\mathrm{RSH}]_0/[\mathrm{C{=}C}]_0 \geq 10$, and the addition of the mercaptan reached a limit at a conversion of ~85% of butadiene units—supposedly due to steric reasons [30]. Results may be different when the PB chain contains higher amounts of 1,4 units that cannot take part in a cyclization reaction [17]. It is further noteworthy that the degree of functionalization was always much greater than 50%, thus excluding the presence of polycyclic units in the products.

Modification of **B** with the mercaptans **2** and **3** gave similar results, i.e. $f=0.7$–0.8, see Table 2. Although the degree of functionalization of the products **B2** and **B3** was somewhat lower as for **B1**, the chemical nature of the mercaptan does not seem to have a pronounced impact on the pathway of the reaction. Also, the results obtained for the modification of polymers **A**–**C** ($x=25$, 40, 65) with the mercaptans **2** and **3** do not reveal a dependence of the degree of functionalization on the length of the PB chain (see Table 3).

3.2. Modification of 1,2-PB-based block copolymers

The list of all modification reactions performed with 1,2-PB-based block copolymers **D**–**H** and mercaptans **1**–**8** is provided in Table 4. All reactions were done using a 10-fold excess of the mercaptan with respect to PB double bonds, unless otherwise noted. As will be seen, conversion of double bonds was usually complete, and the degree of



Scheme 2. Possible reaction pathways of the radical addition of mercaptans onto the vinyl double bonds of 1,2-PB.

Table 2
Chemical composition of products obtained by modification of 1,2-PB$_x$ sample **B** ($x=40$) with mercaptans **1**–**3**

RSH	$[RSH]_0/[C{=}C]_0$	C=C[a]	S/C[b]	f[c]	I:II[d]
1	5	None	0.257	0.77	22.6: 8.2
	10	None	0.272	0.82	24.8: 7.6
	20	None	0.278	0.83	26.4: 6.8
	40	None	0.286	0.86	28.8: 5.6
2	10	None	0.266	0.70	16.0:12.0
	20	None	0.279	0.73	18.4:10.8
3	10	None	0.352	0.79	23.2: 8.4
	20	None	0.324	0.73	18.4:10.8

[a] Determined by ^{1}H NMR.
[b] Determined by EA.
[c] Degree of functionalization.
[d] Ratio of structural units I and II (see Scheme 2).

Table 3
Chemical composition of products obtained by modification of 1,2-PB$_x$ samples **A**–**C** ($x=25$, 40, 65) with mercaptans **2** and **3** ($[RSH]_0/[C{=}C]_0=10$)

RSH	1,2-PB	C=C[a]	S/C[b]	f[c]	I:II[d]
2	**A**	None	0.259	0.68	9.0: 8.0
	B	None	0.266	0.70	16.0:12.0
	C	None	0.265	0.69	24.6:20.4
3	**A**	None	0.342	0.77	13.4. 5.8
	B	None	0.352	0.79	23.2: 8.4
	C	None	0.332	0.75	32.4:16.3

[a] Determined by ^{1}H NMR.
[b] Determined by EA.
[c] Degree of functionalization.
[d] Ratio of structural units I and II (see Scheme 2).

Table 4
Modification reactions performed with the 1,2-PB-based block copolymers **D**–**H** and mercaptans **1**–**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
D	**D1**	**D2**	**D3**	**D4**	**D5**	–	**D7**	–
E	**E1**	**E2**	**E3**	–	**E5**	**E6**	**E7**	–
F	–	**F2**	**F3**	–	–	**F6**	–	**F8**
G	–	**G2**	**G3**	–	–	–	–	–
H	**H1**	–	–	–	–	–	–	–

functionalization of the block copolymers was in the range of 60–80%. It is assumed that the reaction pathway is the same as for the modification of 1,2-PB homopolymers, thus the functional segments should be composed of the units I and II (see Scheme 2). Note that the fraction of I is higher than that of II if $f>2/3$ and vice versa if $f<2/3$.

(i) RSH = methyl-3-mercaptopropionate, **1**. Samples **D1** and **E1** contained virtually no residual double bonds as indicated by ^{1}H NMR ($CDCl_3$). Signals of the newly formed thioether linkage displayed at $\delta=2.6$ and 2.8 ppm while that of the ester methoxy groups was buried under the signal of PEO at $\delta=3.5$–3.7 ppm. FT-IR spectroscopy showed the presence of the characteristic valence vibration of ester carbonyl units at $\tilde{\nu}\sim1735\ \mathrm{cm}^{-1}$ and the absence of the bands of vinyl double bonds at $\tilde{\nu}=1640$ (valence vibration, ν(C=C)), 993 and 906 cm^{-1} (out-of-plane bending vibration, γ(C–H)). The degree of functionalization of **D1** and **E1** is, as derived from the S/C ratios determined by EA, about 70%: $f=0.70$ and 0.65 (0.72, $[RSH]_0/[C{=}C]_0=20$), respectively. Values are thus similar to the ones obtained for 1,2-PB homopolymers ($f\sim0.8$, cf. Table 2). SEC indicated that the samples have a slightly larger hydrodynamic volume but the same narrow molecular-weight distribution as the corresponding parent block copolymers (PDI < 1.1). High-molecular weight side products were not detected [24].

The ^{1}H NMR spectrum of sample **H1** showed the complete absence of double bonds and the presence of characteristic signals of the functional monomer units (see Fig. 4). From the signals of the ester methoxy groups ($\delta=3.6$ ppm, 7) and of the phenyl protons of PS ($\delta=6.4$–7.3 ppm), the degree of functionalization was calculated to be about 70%; this value was confirmed by EA: $f=0.74$. The SEC trace of **H1** (see Fig. 4) was found to be virtually identical to that of the parent copolymer.

(ii) RSH = 3-mercaptopropionic acid, **2**. Samples **D2**–**G2** did not contain double bonds according to ^{1}H NMR (DMSO-d_6). The signals of methylene protons of the thioether displayed at $\delta=2.4$–2.7 ppm. Exemplarily for **E2**, the FT-IR spectrum showed the valence vibration band of the carboxylic acid at $\tilde{\nu}=1720\ \mathrm{cm}^{-1}$; after neutralization with NaOH, anti-symmetric and symmetric valence vibrations of carboxylate showed at $\tilde{\nu}=1570$ and $1400\ \mathrm{cm}^{-1}$, respectively. According to EA, the samples have a degree of functionalization of about 70%, i.e. $f=0.78$ (**D2**), 0.70 (**E2**), 0.68 (**F2**), and 0.72 (**G2**), similar to that of carboxylic acid-modified 1,2-PB homopolymers ($f\sim0.7$, cf. Table 3). A characterization of the samples by SEC could, however, not be achieved.

(iii) RSH = 2-mercaptoethylamine hydrochloride, **3**. For the samples **D3**–**G3**, ^{1}H NMR (D_2O) confirmed the absence of double bonds and the presence of functional units, $\delta=3.00$, 2.55 ($-CH_2SCH_2-$), and 2.70 ppm $\left(-CH_2-NH_3^+\right)$. Further evidence for the presence of amino-functional groups was provided by FT-IR ($\delta\left(NH_3^+\right)$ at $\tilde{\nu}\sim1580\ \mathrm{cm}^{-1}$ (broad)) and EA. According to EA, the degree of functionalization is close to 80%, i.e. $f=0.82$ (**D3**), 0.77 (**E3**), 0.76 (**F3**), and 0.75 (**G3**) (cf. Table 3). A characterization of the samples by SEC was not possible.

(iv) RSH = 2-mercaptoethyl-diethylamine hydrochloride, **4**. The ^{1}H NMR ($CDCl_3$) analysis of **D4** showed no signals of double bonds; the signals of the methylene protons next to sulfur and nitrogen displayed at $\delta=2.35$–2.65 ppm. The presence of amino-functional groups was further indicated by the nitrogen content of the sample of 2.65%. By EA, the degree of functionalization was determined to be $f=0.59$. **D4** thus contains a higher amount of cyclic units II (I:II = 4.4:10.3) as compared to **D3** (I:II = 16.0:4.5), which is supposedly due to the increased bulkiness of the functional group.

(v) RSH = *N*-acetyl-L-cysteine methyl ester, **5**. ^{1}H NMR ($CDCl_3$) suggested that **D5** contained virtually no double bonds whereas in **E5** 11% of the double bonds remained. The successful attachment of the protected cysteine units onto the polymer backbone is supported by ^{1}H NMR, see the exemplary spectrum of **D5** in Fig. 5. In FT-IR, the characteristic valence vibrations of the ester could be observed at $\tilde{\nu}=1736\ \mathrm{cm}^{-1}$ and

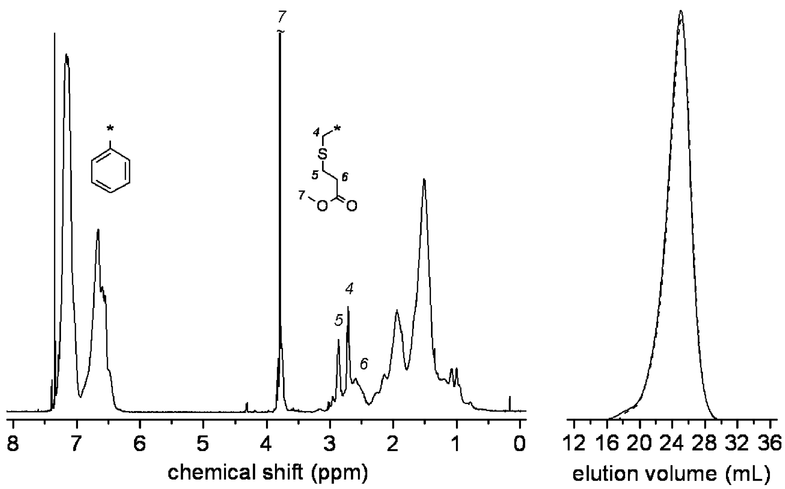


Fig. 4. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) and SEC chromatogram (THF) of **H1** obtained by radical addition of **1** onto 1,2-PB-*b*-PS sample **H** (SEC, dashed line: **H**).

that of amide I at 1657 cm^{-1}. The absorptions of the N–H stretching and bending (amide II) displayed at ~3280 and 1531 cm^{-1}, respectively. CD spectroscopic analysis of an aqueous solution of **D5** revealed strong positive Cotton effects due to the presence of chiral carbon centers. The degree of functionalization, as determined from the NMR signals of α-CH of the cysteine units (6, $\delta=4.8$ ppm) and of the PEO chain ($\delta=3.4$–3.7 ppm), is $f=0.70$ (**D5**) and $f\sim 0.5$ (0.52, EA) (**E5**). Hence, in addition to residual double bonds, sample **E5** exhibits a much higher fraction of cyclic units II (I:II = 6.0:14.8) than **D5** (I:II = 10.0:7.5). It is supposed that the preferential formation of II is due to steric restrictions caused by the branching in the β-position to sulfur (cf. structure in Fig. 5). SEC showed a narrow molecular-weight distribution for **D5** similar to that of the parent copolymer.

(vi) RSH = 3-mercapto-1,2-propanediol, **6**. ^{1}H NMR (CD_3OD or DMSO-d_6) evidenced the presence of traces of residual double bonds in the samples **E6** and **F6**. The functional units could be seen by ^{1}H NMR ($\delta=3.70$ (>C*H*–OH), 2.63 and 2.53 ppm ($-CH_2SCH_2-$)) and FT-IR (ν(O–H) at $\tilde{\nu}\sim 3350\ \mathrm{cm}^{-1}$). According to EA, the degree of functionalization is the order of 60%, i.e. $f=0.65$ (**E6**) and 0.58 (**F6**). The fraction of unit II is thus higher than that of unit I. SEC (eluent: THF or NMP) showed that both samples exhibit a larger hydrodynamic volume but the same narrow distribution as the corresponding parent copolymer.

(vii) RSH = benzyl mercaptan, **7**. ^{1}H NMR ($CDCl_3$ or acetone-d_6) showed that the samples **D7** and **E7** contain about 5% of unreacted double bonds. The signals of $-CH_2SCH_2(C_6H_5)$ protons displayed at $\delta=2.4$–2.5 and 7.2–7.4 ppm, respectively; the signal of methylene protons between sulfur and the phenyl ring was buried under that of PEO at $\delta=3.5$–3.7 ppm. According to EA, the degree of functionalization is ~70%, i.e. $f=0.72$ (**D7**) and 0.68 (**E7**). SEC indicated for

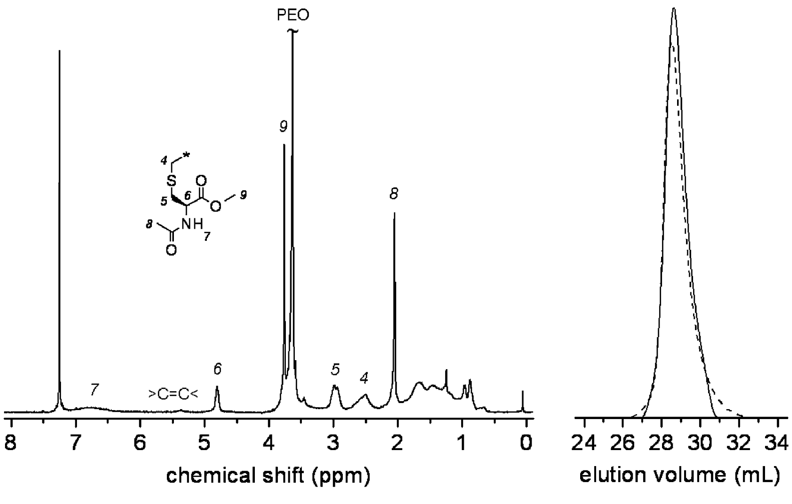


Fig. 5. ^{1}H NMR spectrum (400.1 MHz, $CDCl_3$) and SEC chromatogram (THF) of **D5** obtained by radical addition of **5** onto 1,2-PB-*b*-PEO sample **D** (SEC, dashed line: **D**).

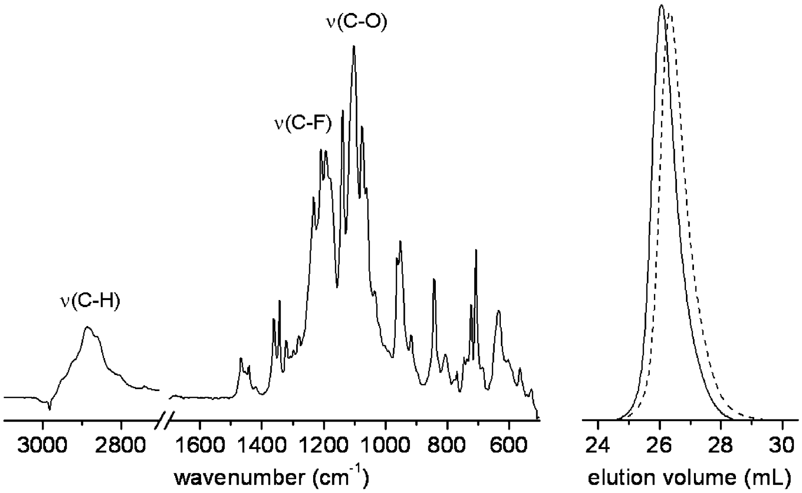


Fig. 6. FT-IR spectrum and SEC chromatogram (THF) of **F8** obtained by radical addition of **8** onto 1,2-PB-*b*-PEO sample **F** (SEC, dashed line: **F**).

either sample a narrow molecular-weight distribution, which is shifted to a higher molecular weight as compared to the parent copolymer.

(viii) RSH = 1-mercapto-1H,1H,2H,2H-perfluorooctane, **8**. According to ^{1}H NMR ($CDCl_3$), sample **F8** contained 11% of unreacted double bonds. Here, the reaction was performed for 48 h with the addition of a second portion of AIBN at half-time (after 24 h, the conversion of double bonds was 84%). The presence of C–F bonds in the product could be confirmed by FT-IR spectroscopy, the characteristic valence vibrations showing at $\tilde{\nu} \sim 1200$ cm^{-1} (see Fig. 4), and by measurement of the contact angle of a drop of water on a **F8** film. The value of the contact angle (100.4°) translates into a surface tension of $\gamma = 22.5$ mN m^{-1}, which is close to the 16.2 mN m^{-1} obtained for a Teflon FEP (fluorinated ethylene propylene) [31]. EA indicated a degree of functionalization of **F8** of 55%. As shown by SEC (see Fig. 6), **F8** exhibits the same narrow distribution as the parent copolymer.

Finally, for an overview, the main characteristics of all the functional block copolymers described in (i)–(viii) are collected in Table 5.

Table 5
Characteristics of functional block copolymers prepared ($[RSH]_0/[C{=}C]_0 = 10$, reaction time: 24 h)

Sample	Functionality	C=C[a]	f[b]	I:II[c]
D1	–$COOCH_3$	None	0.70	10.0: 7.5
E1[d]		None	0.72	17.6:11.2
H1		None	0.74	63.0:11.0
D2	–COOH	None	0.78	14.0: 5.5
E2		None	0.70	16.0:12.0
F2		None	0.68	14.4:12.8
G2		None	0.72	28.6:18.2
D3	–NH_2	None	0.82	16.0: 4.5
E3		None	0.77	21.6: 9.2
F3		None	0.76	20.8: 9.6
G3		None	0.75	32.4:16.3
D4	–$N(C_2H_5)_2$	None	0.59	4.4:10.3
D5	L-Amino acid	None	0.70	10.0: 7.5
E5		~11%	0.52	6.0:14.8
E6	Ethylene glycol	< 2%	0.65	12.8:13.2
F6		< 2%	0.58	7.2:16.0
D7	–C_6H_5	~6%	0.72	12.5: 5.5
E7		~3%	0.68	15.6:11.6
F8[e]	–$(CF_2)_5CF_3$	~11%	0.55	8.4:13.6

[a] Determined by ^{1}H HMR.
[b] Degree of functionalization, determined by EA (**D5**: ^{1}H NMR).
[c] Ratio of structural units I and II (see Scheme 2).
[d] $[RSH]_0/[C{=}C]_0 = 20$.
[e] Reaction time: 48 h, second addition of AIBN after 24 h.

4. Summary

In this work, the modular synthesis of functional polymers by radical addition of ω-functional mercaptans onto 1,2-PB-based homopolymers and block copolymers is demonstrated. Due to the commercial availability of a large number of different mercaptans, this method can be used for the generation of a toolbox of polymers with diverse functionalities including electrolytes or fluorocarbons as well as chiral amino acids and so on. Polymer samples become available which cannot or can hardly be made by any other synthetic method.

Modified polymer samples were usually free of double bonds, thus giving good thermal stability, but the degree of functionalization was always less than quantitative, i.e. 50–85% (typically 70–80%). The deviation between the number of converted double bonds and that of functional groups is due to a side reaction of radicals involving the formation of cyclic units. The amount of cyclic units is seemingly higher in polymers carrying bulky functional groups. Importantly, the cyclization reaction does not alter the molecular-weight distribution of the polymer backbone.

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