

Synthesis of multisegmented polymers by RAFT using linear polytrithiocarbonates

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Two types of polytrithiocarbonates were synthesized by step-growth polymerization. Method A was based on S_N2 reaction between di(trithiocarbonate) anions and α,α' -dibromidoesters, and method B was based on Huisgen 1,3-dipolar cycloaddition between dialkyne-terminated trithiocarbonate and diazide. These multifunctional chain transfer agents (mCTA) were employed in reversible addition-fragmentation chain transfer polymerization of 2-hydroxyethyl acrylate and styrene giving multisegmented homopolymers and multiblock copolymers multi-(polystyrene-*b*-poly(4-vinylbenzyl chloride)). mCTA prepared by the method A controls well polymerization of styrene, while mCTA prepared by the method B more suits for polymerization of 2-hydroxyethyl acrylate. Multisegmented polymers and multiblock copolymers were analyzed by size exclusion chromatography with triple detection, 1H nuclear magnetic resonance and differential scanning calorimetry. Dispersity of multisegmented poly(2-hydroxyethyl acrylate) was high, varying from 4 to 7, while dispersity of its hydrolyzed product (one block of poly(2-hydroxyethyl acrylate)) was narrow and equal to 1.2. It was demonstrated that multisegmented and multiblock polymers could be synthesized by the use of RAFT chain transfer agent with multiple trithiocarbonate moieties, and dispersity of the products was dependent on dispersity of the used mCTA.

Key words: RAFT, polytrithiocarbonate, multisegmented polymer, multiblock polymer, styrene, 4-vinylbenzyl chloride, 2-hydroxyethyl acrylate

INTRODUCTION

The nanoscale self-ordering of polymers into lamellar, cylindrical, bicontinuous, and spherical morphologies can be achieved by joining chemically distinct polymer chains (A and B) in a block copolymer (AB). Adjusting the length / relative volume fraction of A and B blocks, materials with defined physical properties can be obtained [1, 2]. While AB block copolymers are widely used industrially, it is advantageous increasing the number of blocks toward $(AB)_n$ multisegmented copolymers. Segmented block copolymers (or multiblock copolymers) consist of alternating homogeneous segments of two different monomeric units which are attached covalently to each other [3]. The increased number of chain junction with long alternating hard and soft segments leads to unique material properties as thermoplastic elastomers [1, 4–7] or demonstrates eventual mechanical properties [8]. Other industrial uses of multisegmented copolymers include the utilization as compatibilizers for blends of otherwise immiscible homopolymers [9–11],

and pressure-sensitive adhesives [1, 10, 12]. Stimuli-responsive multisegmented copolymers have potential applications in drug delivery, tissue engineering, and as sensors [2, 13, 14].

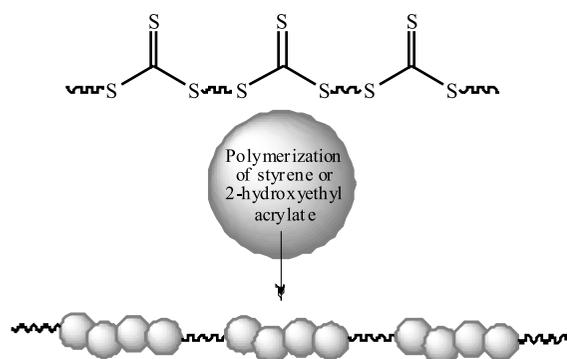
In order to synthesize multisegmented copolymers, several paths are employed. The most conventional method is the preparation of end group functionalized narrowly distributed prepolymers that are then joined together by coupling reaction. However, this method has some limitations. Because the concentration of reactive end groups is low, the reaction will stop as soon as a few copolymer blocks are coupled together. Furthermore, no molecules with long segments or with high numbers of alternating segments can be synthesized [3, 15]. Theoretically multisegmented copolymers can also be prepared by alternatively adding different types of monomers into a living polymerization system. However, in the experiment, each addition of new monomer introduces impurities, resulting in termination of living sites. Moreover, only certain pairs of monomers can be used [10, 16].

Among all techniques of Reversible Deactivation Radical Polymerization (RDRP), RAFT (Reversible Addition-Fragmentation Chain Transfer) polymerization [17, 18] seems to be the

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most promising method suitable for the synthesis of multisegmented copolymers. Using polytrithiocarbonates as multifunctional chain transfer agents (mCTA), well-defined (AB)_n multisegmented copolymers with narrow distribution of blocks were synthesized [3, 19, 20–24]. mCTA can be prepared either by ring-opening in situ polymerization of a cyclic trithiocarbonate [22, 23, 25, 26] or by step-growth polymerization of difunctional RAFT CTA with a desired chain extender [3, 21, 27–33].

The main task of the present study was the synthesis of multisegmented polymers characterized by relatively high molecular weight and relatively low dispersity (Scheme 1). For implementation of this task, two novel multifunctional RAFT CTA polytrithiocarbonates (mCTA) were synthesized and used to control polymerization of styrene, 2-hydroxyethyl acrylate and 4-vinylbenzyl chloride. Multisegmented homopolymers and multiblock copolymers containing several trithiocarbonate groups on the mainchain were synthesized and studied.



Scheme 1. General strategy for the synthesis of multisegmented polymers based on linear polytrithiocarbonates as RAFT mCTA

EXPERIMENTAL

Materials

1,2-Bis(bromoisobutyryloxy)ethane (BBE) [34], 1,3-diazidopropan-2-ol (DAP) [35] and bis(2-((butylsulfanyl)carbothioyl)sulfanyl)propanoic acid (BSPA) [36] were synthesized according to previously reported procedures with slight modifications. To remove inhibitor, styrene (St, 99.0%, Aldrich) and

4-vinylbenzyl chloride (VBC, 90.0%, Aldrich) were passed through a column of basic and neutral alumina, respectively. 2-Hydroxyethyl acrylate (HEA, 96%, Aldrich) was distilled under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN, Reachim) was recrystallized from methanol twice and dried under vacuum before use. *N,N*-Dimethylformamide (DMF, Aldrich) was dried with calcium hydride, then distilled fractionally under reduced pressure before use. Dichloromethane (DCM, p. a., Eurochemicals) was dried with calcium hydride, then distilled and stored over 4A molecular sieves. Carbon disulfide (CS₂, Riedel-de-Haën), triethylamine (TEA, ≥99.0%, Aldrich), 1,4-butanedithiol (97.0%, Aldrich), *L*-ascorbic acid (AscA, 99.0%, Aldrich), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, ≥98.0%, Fluka), copper (II) sulfate pentahydrate (99.999%, Aldrich), hydrazine monohydrate (≥98.0%, Fluka), propargyl alcohol (99.0%, Aldrich), 4-(dimethylamino) pyridine (DMAP, ≥99.0%, Aldrich), *N*-ethyl-*N*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, ≥98.0%, Fluka), 4-azobis(4-cyanopentanoic acid) (ACVA, ≥98.0%, Fluka), deuterated chloroform (CDCl₃, 99.8%D, Aldrich) and deuterated dimethyl sulfoxide (DMSO-d₆, 99.8%D, Merck) were used as received. All solvents were used without further purification unless specified otherwise.

Synthesis of polytrithiocarbonates

mCTA synthesized by nucleophilic substitution (Method A)

To the mixture of TEA (1.24 g, 123 mmol) and 1,4-butanedithiol (0.49 g, 40 mmol) in DCM (10 mL), carbon disulfide (1.23 g, 162 mmol) was added dropwise at room temperature. The solution changed to yellow-orange. After 2 h of stirring, BBE (1.33 g, 37 mmol) in 10 mL of DCM was added. Trying to synthesize mCTA with different molecular weight, time of the reaction was prolonged from 5 to 24 h (for the individual conditions, see Table 1). The reaction mixture was then diluted with DCM, washed with water (15 mL × 8) and 2 M HCl (15 mL × 7), dried over MgSO₄ for 24 h, filtered, and the solvent was evaporated. The obtained viscous orange oil was dried under vacuum at RT.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.39 (s, 4H, -OCH₂-CH₂O-), 3.44 (t, 4H, -SCH₂CH₂-), 1.89 (s, 12H, -SC(CH₃)₂-), 1.75 (t, 4H, -SCH₂(CH₂)₂CH₂S-).

Table 1. Molecular characteristics of polytrithiocarbonates

Method A	[di(trithiocarbonate) anions]/[BBE]	t, h	M _n · 10 ⁻³	\bar{D}	DP
mCTA1	1/0.9	5	0.6	1.38	1.3
mCTA2	1/0.9	21	1.3	1.69	2.8
mCTA3	1/0.15	20	12.5	1.60	26
mCTA4	1/1.5	24	2.3	1.66	4.9
Method B	[diPropargyl]:[DAP]:[Cu ²⁺]:[PMDETA]:[AscA]	t, min	M _n · 10 ⁻³	\bar{D}	DP
mCTA5	1:1:0.01:0.01:0.5	120	Destruction of trithiocarbonate		
mCTA6	1:1:0.01:0.01:0.05	25	2.6	1.16	4.0
mCTA7	1:1:0.01:0.01:0.5	25	1.6	1.20	2.5
mCTA8	1:1:0.01:0.01:1	25	1.3	1.60	2.0

mCtA synthesized by Huisgen 1,3-cycloaddition (Method B) [36]

BSPA (0.21 g, 0.52 mmol) and propargyl alcohol (0.14 g, 2.43 mmol) were dissolved in DMF (11 mL). The mixture was then cooled to 0 °C and kept for 10 min. DMAP (0.13 g, 1.04 mmol) and EDC (0.30 g, 1.56 mmol) in DMF (10 mL) were added slowly to the above solution. The solution changed to yellow-orange. The reaction mixture was then stirred for additional 42 h at RT. The reaction was monitored by tin layer chromatography (TLC). The reaction mixture was then diluted with DMF, washed with water (15 mL × 3) and 0.1 M HCl (15 mL × 3), dried over MgSO₄ for 12 h, filtered, and the solvent was evaporated. The obtained viscous yellow-orange oil was purified by flash chromatography using a mixture of ethyl acetate and hexane (1/2, v/v) as an eluent giving (1,4-bis((prop-2-ynyl sulfanylthiocarbonyl) sulfanyl)-butane) (PSSB).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.85 (q, 2H, -C(CH₃)H-), 4.73 (s, 2H, -CH₂CCH), 3.39 (t, 4H, -CH₂CH₂-), 2.50 (t, 4H, -CH₂CCH), 1.82 (t, 4H, -SCH₂(CH₂)₂CH₂S-), 1.61 (d, 6H, -SC(CH₃)-).

DAP (0.0456 g, 0.32 mmol) and PSSB (0.15 g, 0.32 mmol) containing terminal alkyne groups at both ends were dissolved in 0.54 g of DMF. A complex between copper (II) sulfate pentahydrate (0.8 g, 3.2 μmol) and PMDETA (0.55 mg, 3.2 μmol) was prepared in DMF (0.50 g) and added to the above solution. The solution was bubbled with N₂ for 30 min. The click reaction was initiated by adding AscA (0.028 g, 0.16 mmol) in 0.5 g of DMF. The reaction mixture was kept at RT monitoring the course of the reaction by TLC. The product of the click reaction was dissolved in THF, and the solution was passed through a column of neutral alumina for removal of the Cu²⁺ salt. Trying to synthesize mCtA with different molecular weight, the initial ratio of the reagents was changed (for the individual conditions, see Table 1). mCtA was precipitated by pouring the reaction mixture into diethyl ether, reprecipitated from diethyl ether, and dried in vacuum at 25 °C for 30 min.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.78 (s, 1H, in triazole ring), 5.27 (d, 2H, -CO₂CH₂-), 4.80 (q, 2H, -SC(CH₃)H-), 4.2–4.6 (m, 5H, -NCH₂C(OH)HCH₂N-), 3.32 (t, 4H, -SCH₂CH₂-), 1.66 (p, 4H, -SCH₂(CH₂)₂CH₂S-), 1.60 (d, 6H, -SC(CH₃)-).

Polymerization of styrene

St (0.5 g, 4.8 mmol), mCtA1 (0.02 g, 0.03 mmol) and AIBN (1.9 mg, 0.01 mmol) were added to a 25 ml round bottom flask equipped with a magnetic stirrer. The initial molar ratio of St, mCtA1 and AIBN was 400/2/1, respectively. The polymerization mixture was sealed with silicone septum and thoroughly degassed by bubbling with argon for 20 min. The flask was then placed into a thermostat maintaining the temperature at 60 °C. Aliquots were taken after 7 and 20 h. The polymerization was stopped by cooling the flask, and the polymer was precipitated by pouring the reaction mixture

to methanol, reprecipitated from methanol twice and dried under vacuum at 25 °C for 36 h. Monomer conversion was determined gravimetrically. Theoretical molecular weight of pSt was calculated by the equation:

$$M_{n, \text{calculated}} = \frac{[\text{monomer}]}{[\text{mCtA}]} \times M_{\text{monomer}} \times q + M_{\text{mCtA}},$$

where [monomer] and [mCtA] are initial concentrations of the monomer and mCtA, respectively, M_{monomer} and M_{mCtA} are molecular weights of these materials, and q is the conversion of St.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.89–7.12 (CH in aromatics), 6.32–6.88 (CH in aromatics), 1.2–2.0 (-CH₂-CH-).

Polymerization of 2-hydroxyethyl acrylate

RAFT polymerization of HEA initiated by ACVA was carried out in DMF solution containing mCtA7. HEA (3.45 g, 29.8 mmol), mCtA7 (0.182 g, 0.30 mmol), ACVA (0.083 g, 0.30 mmol), and DMF (8.05 g) were added to a round bottomed 25 ml flask equipped with a magnetic stirrer. The reaction mixture was bubbled for 15 min with nitrogen. Polymerization was carried out at 60 °C under magnetic stirring. The reaction was stopped after 4 h by cooling the flask. The crude yellow polymer was precipitated by pouring the reaction mixture to diethyl ether, and dried in vacuum at 35 °C for 48 h.

¹H NMR (400 MHz, DMSO-d₆) δ (ppm): 3.8–4.2 (-C(O)O-CH₂-CH₂-OH), 3.4–3.6 (-C(O)O-CH₂-CH₂-OH), 2.2–2.5 (-CH₂-CH-), 1.2–2.0 (-CH₂-CH-).

Synthesis of multiblock copolymers

multi(polystyrene-*block*-poly(4-vinylbenzyl chloride))

In a 25 ml round bottom flask equipped with a magnetic stirrer, mpSt (7 mg, 7.5 · 10⁻⁴ mmol) was dissolved in toluene (0.5 mL), and the solution was mixed with VBC (0.5 ml, 3.5 mmol). 0.5 mL solution of AIBN (0.08 mg, 5 · 10⁻⁴ mmol) in toluene was added to the reaction mixture. The initial molar ratio of VBC, mpSt and AIBN was 7 000/1.5/1, respectively. The solution was sealed with silicone septum and thoroughly degassed by bubbling with argon for 20 min. The flask was then placed into a thermostat maintaining the temperature at 60 °C. After 20 h the polymerization was stopped by cooling the flask, and the copolymer was precipitated by pouring the mixture to methanol, reprecipitated from methanol and dried under vacuum at 25 °C for 36 h. Monomer conversion was determined gravimetrically.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.89–7.22 (CH in aromatics), 6.23–6.81 (CH in aromatics), 4.36–4.66 (-CH₂-Cl), 1.2–2.0 (-CH₂-CH-).

Aminolysis of multisegmented pHEA [37]

Multisegmented polymer (1.00 g, 0.149 mmol of repeated units of mCtA7) was dissolved in 3.0 ml of water. 1 ml

50% aqueous solution of hydrazine monohydrate (75.0 mg, 1.49 mmol) was subsequently added dropwise. The initially yellow solution became colorless gradually. Aminolysis was conducted in water at 25 °C for 30 min. The reaction mixture was neutralized with 0.5 M HCl, and the hydrolyzed polymer was precipitated by pouring the mixture into a mixture of THF and methanol, and dried under vacuum at 35 °C for 24 h.

Characterization of polymers

Molecular weight and molecular weight distribution of polytrithiocarbonates and multisegmented polymers were determined by size exclusion chromatography (SEC). Viscotek TD-Max system composed of a triple-detection array (TDA305) consisting of a refractive index detector, right-angle (90°) and low-angle (7°) light scattering detectors, and viscosity detector plus a Viscotek UV detector 2500 (set at 265 nm for the samples of m(pSt/pSt-b-pVBC) and at 310 nm for the samples of mCTA and mpHEA) was used. A column was from Viscotek, Visco-Gel II-MBMMW-3078, eluent tetrahydrofuran (THF) for polytrithiocarbonates prepared by the method A and for the polymers m(pSt/pSt-b-pVBC), and CHCl₃ for polytrithiocarbonates prepared by the method B. Flow rate of the eluent was 0.5 mL min⁻¹, temperature 35 °C. For analysis of mpHEA, a column was from Viscotek, A6000M, 300 × 8.0 mm, general mixed for aqueous solutions, eluent 0.3 M NaNO₃ solution in the mixture of water and MeOH (75:25%, v/v).

¹H NMR measurements in CDCl₃ and DMSO-*d*₆ were performed on a Bruker 400 Ascend™ NMR spectrometer (400 MHz).

Differential scanning calorimetry (DSC) was carried out on a DSC 8000 (Perkin Elmer). DSC analyses were done under N₂ atmosphere (flow rate 40 mL min⁻¹). Samples of 2.5–5.9 mg were heated from -52 °C to 130 °C and cooled down to -52 °C. The heating and cooling rates were 10 °C min⁻¹. *T*_g values were determined from the second heating scan curves as the midpoint temperature of the shift of baseline.

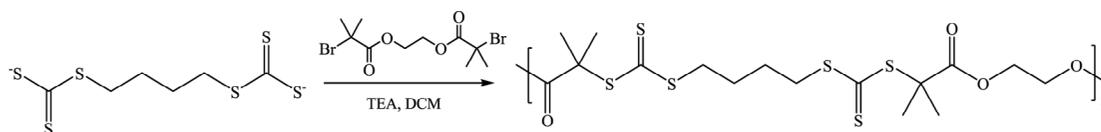
FT-IR spectra of polymers were recorded using a Perkin Elmer Frontier spectrometer.

RESULTS AND DISCUSSION

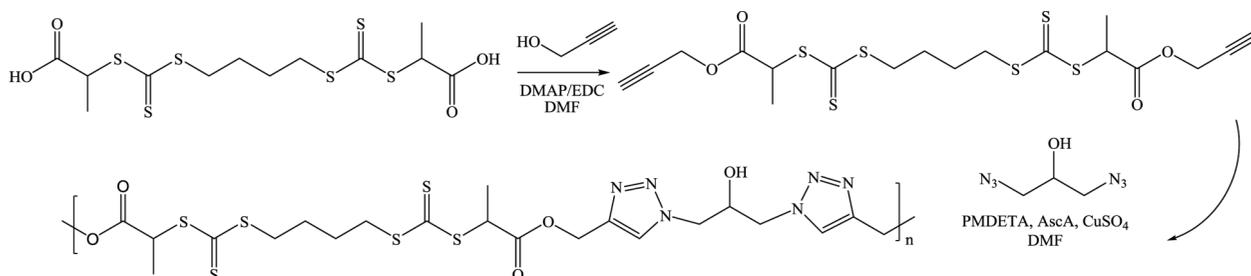
Synthesis and study of polytrithiocarbonates

Polytrithiocarbonates were prepared by step-growth polymerization between di(trithiocarbonate) anions and 1,2-bis(bromoisobutyryloxy)ethane (BBE), as shown in Scheme 2 (Method A). Number of trithiocarbonate groups in the multifunctional chain transfer agent (mCTA) was controlled changing the initial molar ratio of the reagents and varying extent of the reaction. Using the method A, four mCTA (mCTA1–mCTA4) were synthesized. Polytrithiocarbonates mCTA5–mCTA8 were prepared by the method B, i. e. step-growth polymerization between dialkyne-terminated trithiocarbonate and diazide, as shown in Scheme 3. Molecular characteristics of the prepared mCTA were examined by size exclusion chromatography (SEC) with triple detection. ¹H nuclear magnetic resonance (¹H NMR) spectra of polytrithiocarbonates are presented in Fig. 2. The reaction conditions and molecular characteristics of mCTA are listed in Table 1. It was planned to receive from 3 to 6 trithiocarbonate groups per molecule. Average number of trithiocarbonate groups per molecule was estimated being equal to the degree of step-growth polymerization (DP) and reached 2–5 groups per chain for mCTA prepared by the method A, and 2–4 groups per chain for mCTA prepared by the method B.

Molecular weight of polytrithiocarbonates prepared by the method A slightly depends on the duration of polymerization. Faster growth of the molecular weight of mCTA during polymerization was observed when the initial molar ratio of the reagents was non-equivalent. NMR spectra showed signals characteristic of mCTA. H₁ and H₂ signals were shifted to stronger magnetic field (1.94→1.89 ppm and 4.43→4.39 ppm, respectively) compared to those in BBE [34]. In contrast, H₃ signal



Scheme 2. Synthesis of polytrithiocarbonates by the method A



Scheme 3. Synthesis of polytrithiocarbonates by the method B

was shifted to weaker magnetic field (to 3.36–3.37 ppm in low molecular weight CTA and 3.44 ppm in mCTA) [36].

Bimodal molecular weight distribution is characteristic of mCTA with high molecular weight (Fig. 1A, curve 3). Moreover, non-soluble gels were obtained when the duration of polymerization was longer than 24 h. Thus, because of the side reaction, the synthesis of mCTA with high molecular weight is problematic.

During the synthesis of polytrithiocarbonates by the method B, ascorbic acid (AscA) was used in the click reaction as a reducing agent reacting with oxygen and producing hydrogen peroxide which, at long reaction time, can lead to destruction of trithiocarbonate groups [38]. To avoid side reactions, the reaction time was reduced from 120 min to

25 min. NMR spectra showed the signals characteristic of mCTA. Thus, the signal H_1 , characteristic of triazole proton, appeared at 7.78 ppm as a sharp singlet [39]. The signal H_2 was shifted from 4.74 ppm to 5.27 ppm, compared to that of 1,4-bis((prop-2-ynyl sulfanylthiocarbonyl) sulfanyl)-butane (PSSB). No signal was at 2.50 ppm which could be assigned to alkyne proton in PSSB.

The synthesis of mCTA6-mCTA8 was more controllable than the synthesis of mCTA1-mCTA4. Dispersity of mCTA6-mCTA8 was in the range of 1.2–1.6 compared to 1.4–1.7 for mCTA1-mCTA4. mCTA with 2–3 trithiocarbonate groups and rather low dispersity was chosen as appropriate mCTA for the synthesis of multisegmented polymers. mCTA1 and mCTA2 were used for RAFT polymerization of styrene, and mCTA7 for RAFT polymerization of HEA. Polytrithiocarbonates prepared by the method A were not suitable to control polymerization of 2-hydroxyethyl acrylate (HEA), since the polymerization proceeded in a complicated manner and resulted in non-soluble gels.

Synthesis of multisegmented polystyrene and poly(2-hydroxyethyl acrylate), and multiblock copolymers multi(polystyrene-*block*-poly(4-vinylbenzyl chloride))

For polymerization of styrene (St), polytrithiocarbonates prepared by the method A were selected due to the suitable leaving group R in the mCTA chain [18, 20]. Styrene was polymerized in bulk under inert atmosphere, using mCTA1 and mCTA2, as shown in Scheme 4. The reaction temperature was chosen to be low in order to minimize possible decomposition of trithiocarbonate groups [40]. Lower temperature is favourable also in

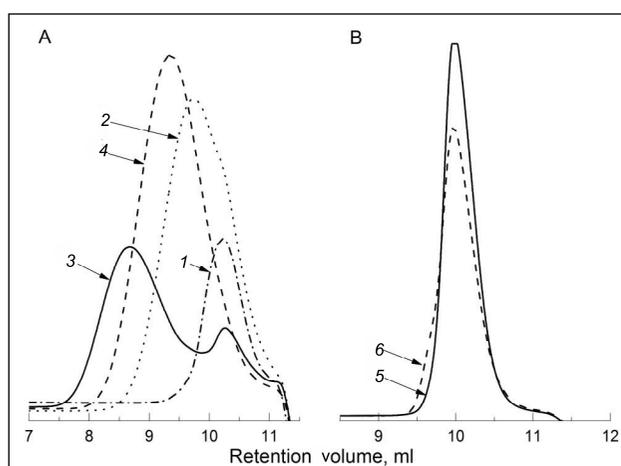


Fig. 1. SEC traces of polytrithiocarbonates prepared by the methods A and B: 1 – mCTA1, 2 – mCTA2, 3 – mCTA3, 4 – mCTA4; 5 – mCTA7, 6 – mCTA6

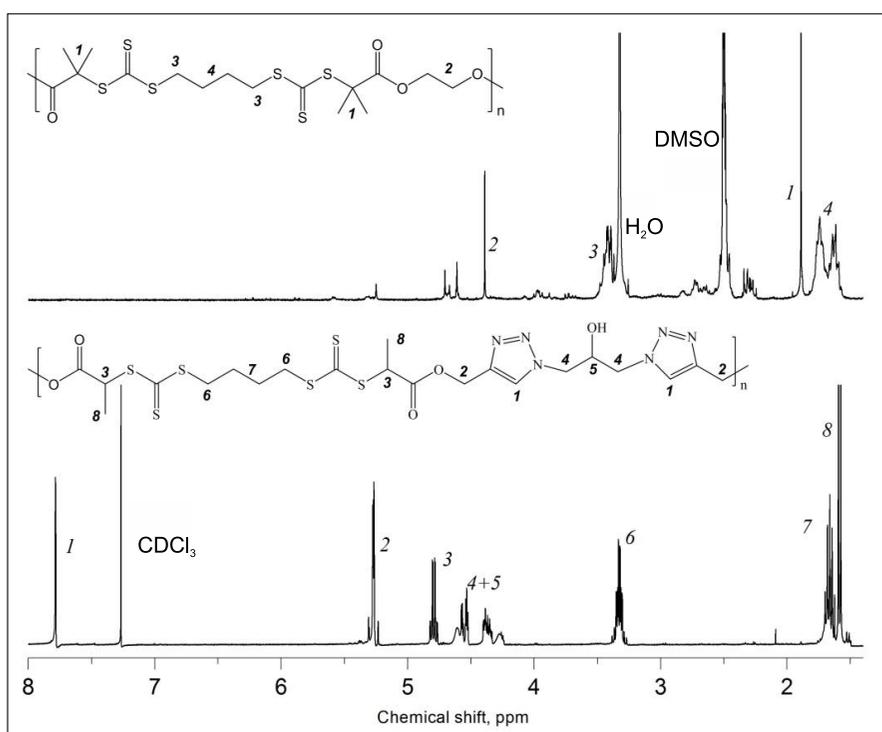
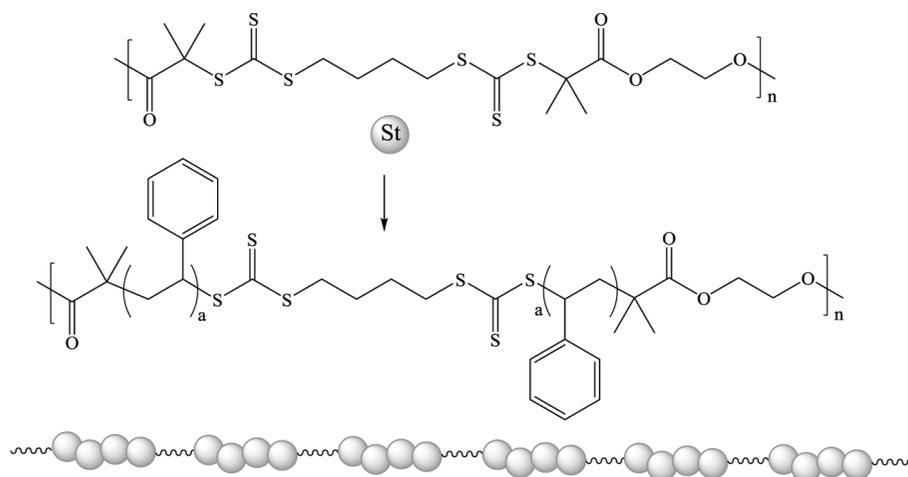


Fig. 2. ^1H NMR spectra of mCTA1 (top) and mCTA7 (bottom)



Scheme 4. Synthesis of multisegmented polystyrene

minimizing the amount of “dead” chains. Unfortunately, lower temperature is accompanied by lower polymerization rate. During polymerization, the molecular weight of the polymers was increasing with time, which was evidenced by a shift of the SEC signal to smaller retention volume (Fig. 3). The peak at the retention volume 8–9 ml in SEC chromatograms is assigned to multisegmented polymer containing multiple trithiocarbonate groups. The second peak at larger retention volume most likely belongs to the products with lower molecular weight produced by biradical coupling reactions [20]. The signal of the UV detector recorded at larger retention volumes indicates the presence of aromatics [41]. No RALS/LALS signal is observed at this retention volume, which indicates that the molecular weight of the “dead” chains is less than 1 kg mol^{-1} ($DP < 10$). It is known [20] that MWD of the “dead” chains should transform from a narrow peak to low-molecular shoulder of the main peak during polymerization. Such a trend was not observed during polymerization of St in the presence of mCTA. Theoretically, a fraction of the “dead” polymer is proportional to the concentration of the initiator and does not exceed 10% [42].

Molecular characteristics of multisegmented polystyrene are listed in Table 2. Number average molecular weight M_n of

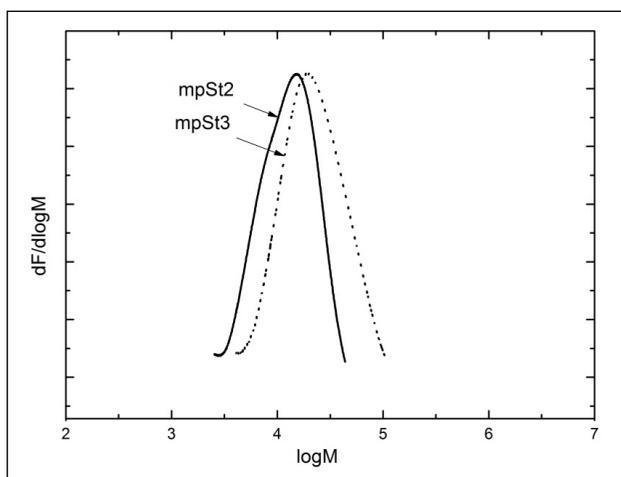


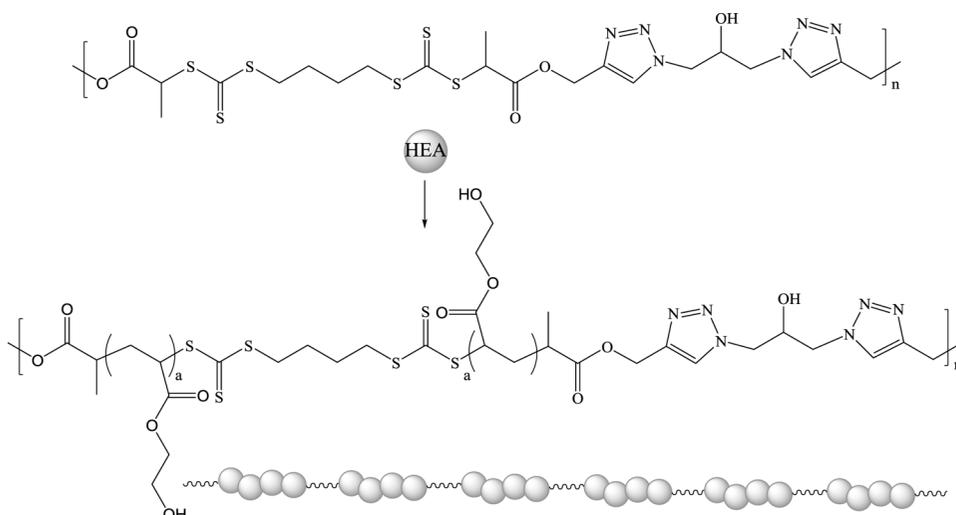
Fig. 3. MWD of multisegmented polystyrene mpSt2 and mpSt3

multisegmented polystyrene (mpSt) determined experimentally is 2–2.5 times larger than that calculated theoretically. This correlates well with the number of trithiocarbonate groups per initial mCTA (1.3–2.8), which indicates that several trithiocarbonate groups take part in controlling polymerization of styrene. Each block of mpSt consists of about 30–70 styrene units. It was noticed that the use of mCTA with higher molecular weight (more trithiocarbonate groups) led to shorter blocks of pSt. For example, mpSt1 synthesized in the presence of mCTA1 (1.3 trithiogroups) contained 67 St units per block, in comparison to 55 St units per block in mpSt3 synthesized in the presence of mCTA2 (2.8 trithiogroups). Dispersity of mpSt is similar to that of initial mCTA. Dispersity slightly increases during polymerization which indicates partial loss of livingness of the system during polymerization.

Table 2. Characteristics of multisegmented polystyrene

Abbr.	mCTA	τ, h	$q, \%$	$M_n^{\text{th}} \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	\bar{D}	DP _{block}	$T_g, ^\circ\text{C}$
mpSt1	mCTA1	20	19.7	4.7	9.7	1.57	67	–
mpSt2	mCTA2	7	18.5	5.2	9.9	1.66	30	61.1
mpSt3	mCTA2	20	25.2	6.6	17.5	1.71	55	60.0

RAFT polymerization of HEA was carried out in the presence of polytrithiocarbonate mCTA7 synthesized by the method B as shown in Scheme 5. Molecular characteristics of multisegmented mpHEA and products of its hydrolysis are listed in Table 3. An average number of pHEA blocks in multisegmented polymers can be estimated by the ratio of the molecular weights of mpHEA and its hydrolyzed product ($M_{n(\text{mpHEA})}/M_{n(\text{pHEA-hyd})}$). This ratio ranged from 2 to 3 and was close to the number of trithiocarbonate groups per chain (2.5) in mCTA7. The length of pHEA blocks varied from 40 to 70 units of HEA being maximal at the equimolar ratio of mCTA and the initiator. This tendency is in accord with the mechanism of RAFT polymerization predicting higher molecular weights at lower concentrations of CTA



Scheme 5. Synthesis of multi-segmented polymer mpHEA

Table 3. Characteristics of multisegmented polymer mpHEA and products of its aminolysis

Abbr.	mCTA	[M]/[mCTA]/[I]	$M_{n(\text{mpHEA})} \cdot 10^{-3}$	\bar{D}	DP_{block}	After aminolysis		
						$M_{n(\text{mpHEA-amin})} \cdot 10^{-3}$	\bar{D}	$M_{n(\text{mpHEA})}/M_{n(\text{mpHEA-hyd})}$
mpHEA1	mCTA7	100/1/1	15.9	3.8	55	11.2	1.2	1.4
mpHEA2		100/2/1	11.4	6.7	40	6.0		1.9
mpHEA3		100/1/1	20.0	5.4	70	7.0		2.9
mpHEA4		100/2/1	13.9	4.4	50	4.9		2.8

[17, 18]. SEC measurements evidenced that the dispersity of multisegmented mpHEA varied from 4 to 7, while the dispersity of the hydrolyzed mpHEA (pHEA block in multisegmented polymer) was narrow and equal to 1.2. Low dispersity of the hydrolysed pHEA means that the polymerization of HEA was efficiently controlled by mCTA7. High dispersity of multisegmented mpHEA is related, possibly, not only to a certain dispersity of mCTA7 but also to inter-chain transfer reactions occurring in the presence of chain transfer agents with multiple trithiocarbonate groups. Similar trend was observed before studying synthesis of multisegmented polystyrene [20]. MWD of mCTA7, mpHEA1 and its hydrolyzed product are presented in Fig. 4.

Multiblock copolymers polystyrene-*b*-poly(4-vinylbenzyl chloride) m(pSt-*b*-pVBC) were prepared using multisegmented polymers mpSt1 and mpSt3 as RAFT mCTA as shown in Scheme 6. Fourier transform infrared (FT-IR) spectroscopy and size exclusion chromatography were used to confirm the formation of multiblock copolymers m(pSt-*b*-pVBC). The FT-IR spectrum of multisegmented polystyrene (Fig. 5, 1) contained an absorption band characteristic of C-H in aromatics at 3 029 cm^{-1} , the absorption bands associated with stretching asymmetric and symmetric vibrational modes of the methylene group at 2 924 cm^{-1} and 2 848 cm^{-1} , respectively, and the adsorption band at 1 453 cm^{-1} associated with deformation vibrations of CH_2 in accord with double bonds of the aromatic ring [43]. The FT-IR spectrum of the multiblock copolymer m(pSt-*b*-pVBC) (Fig. 5, 2) contained additionally the absorp-

tion bands at 1 263 cm^{-1} , 827 cm^{-1} and 673 cm^{-1} which were attributed to the vibrations of C-Cl group [44–46].

Molecular characteristics of the block copolymers are presented in Table 4. Conversion of the second monomer was low reaching 5–15 mol% only, which means that only 3–4 monomeric units of VBC formed the second block. Slow polymerization rate can be explained by low polymerization temperature and partial loss of the control. The second block had no effect on the T_g (glass transition temperature) of multisegmented mpSt (Tables 2 and 4).

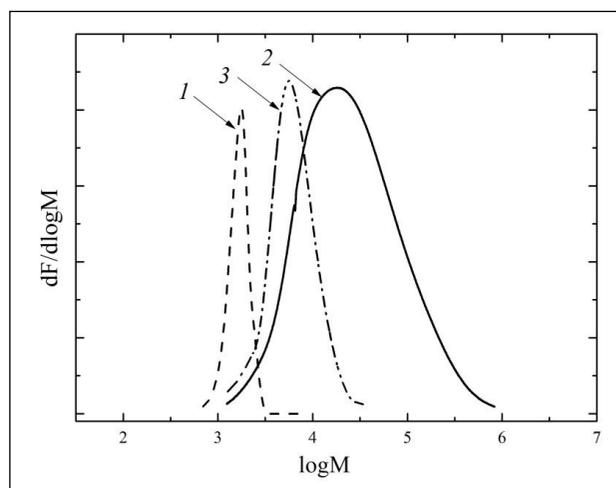


Fig. 4. MWD of mCTA7 (1), mpHEA1 (2) and its hydrolyzed product (3)

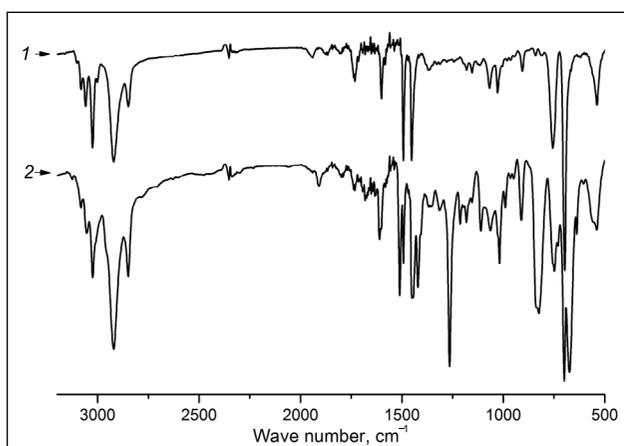
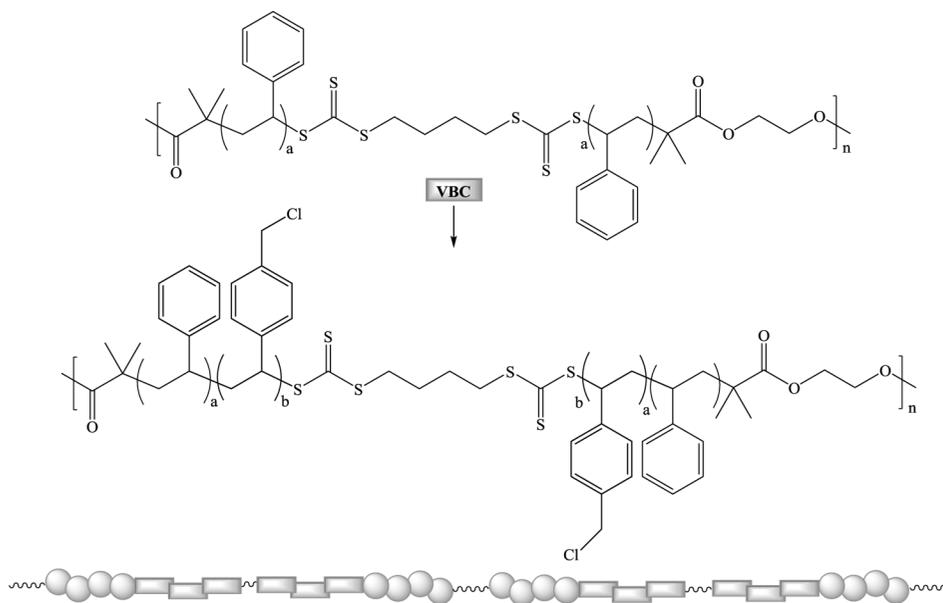


Fig. 5. FT-IR spectra of mpSt (1) and m(pSt-*b*-pVBC) (2)

Table 4. Characteristics of multiblock copolymers m(pSt-*b*-pVBC)

Abbr.	pSt	q^* , %	$M_n \cdot 10^{-3}$	\bar{D}	DP _{block} (St):DP _{block} (VBC)	T_g , °C
m(pSt- <i>b</i> -pVBC)1	pSt1	5.7	10.3	1.92	67:3	60.6
m(pSt- <i>b</i> -pVBC)2	pSt3	14	19.1	1.81	55:4	–

* Conversion of VBC.

CONCLUSIONS

Multifunctional RAFT chain transfer agents (mCTA) polytrithiocarbonates were synthesized either by step-growth polymerization of di(trithiocarbonate) anions and α, α' -dibromidoesters or by Huisgen 1,3-cycloaddition between

dialkyne-terminated trithiocarbonates and diazides. The RAFT polymerization of styrene or 2-hydroxyethyl acrylate in the presence of polytrithiocarbonates produced multi-segmented polymers with multiple trithiocarbonate groups per chain, and the number of segments (blocks) was close to the number of trithiocarbonate groups in polytrithiocarbonate. The RAFT polymerization of vinyl benzyl chloride in the presence of multisegmented pSt resulted in multiblock copolymers m(pSt-*b*-pVBC) in which the second block was short. The dispersity of multisegmented polymer mpHEA was high, varying from 4 to 7, while the dispersity of its hydrolyzed product (one block of pHEA) was narrow and equal to 1.2. Thus, polytrithiocarbonates can be used for the synthesis of multisegmented (multiblock) polymers which are rather polydisperse by the number of segments (blocks).

ACKNOWLEDGEMENTS

Financial support from the Research Council of Lithuania under Project MIP-51/2012 is gratefully acknowledged.

Received 28 November 2014

Accepted 23 December 2014

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MULTIBLOKINIŲ POLIMERŲ SINTEZĖ RAFT METODU NAUDOJANT LINIJINIUS POLITRITIOKARBONATUS

Santrauka

Linijiniai multifunkciniai RAFT grandinės perdavos agentai (mGPA) buvo susintetinti dviem būdais: vykdant nukleofilinio pakeitimo (S_N2) reakciją tarp dibromido esterio ir ditritiokarbonato anijonų (A metodas) bei Huisgeno 1,3-dipolinio ciklo prijungimo reakciją tarp dipropargilo ir diazido (B metodas). Šie mGPA buvo panaudoti multiblokinių stireno (St) ir 2-hidroksietilakrilato (HEA) homopolimerų bei stireno ir vinilbenzilchlorido multiblokinių kopolimerų m(pSt-*b*-pVBC) sintezei. Pirmojo tipo (A metodas) linijiniai mGPA yra tinkamesni St RAFT polimerizacijai, antrojo (B metodas) – HEA polimerizacijai. Molekulinių sietų chromatografijos (SEC) metodu nustatyta, kad mpHEA dispersiškumas siekia 4–7, tačiau atskiri pHEA blokai yra vienodo ilgio (dispersiškumas 1,2), t. y. multiblokinių polimerų dispersiškumas priklauso nuo sintezei naudojamo mGPA dispersiškumo.