

# Synthesis of anionic amphiphilic molecular brushes by conventional free-radical and RAFT terpolymerizations

Tatjana Krivorotova,

Romualdas Grigelis,

Jūratė Jonikaitė,

Ričardas Makuška\*

*Department of Polymer Chemistry,  
Vilnius University,  
Naugarduko 24,  
LT-03225 Vilnius,  
Lithuania*

Molecular bottle-brushes consisting of statistical terpolymers of poly(ethylene oxide) monomethyl ether methacrylate (PEOMEMA), lauryl methacrylate (LMA) and methacrylic acid (MAA) were synthesized by conventional free-radical and RAFT terpolymerizations. To perform RAFT terpolymerization, two chain transfer agents, *S*-(2-cyano-2-propyl)-*S*-dodecyltrithiocarbonate (CTA<sub>1</sub>) and 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (CTA<sub>2</sub>), were used. It was determined that the relatively hydrophilic CTA<sub>2</sub> controls PEOMEMA, LMA and MAA terpolymerization better than CTA<sub>1</sub> does. Terpolymers synthesized in the presence of CTA<sub>1</sub> were characterized by bimodal MWD and moderate polydispersity (up to  $M_w / M_n = 1.5$ ), while terpolymers synthesized in the presence of CTA<sub>2</sub> were monodisperse. RAFT terpolymerization of PEOMEMA, LMA and MAA enabled to synthesize brush terpolymers with low composition distribution and a more homogeneous distribution of PEO side chains along the mainchain.

**Key words:** RAFT, molecular brush, macromonomer, terpolymerization, composition

## INTRODUCTION

Bottle-brush polymers are regularly branched macromolecules which, due to their specific architecture, assume a well-defined shape with a characteristic intramolecular density distribution. They present a wide range of interesting properties, which are designed in a flexible way through selection of polymer backbone and side chains. The properties depend on a variety of parameters including the polymerization degree of main and side chains, graft density, main chain topology, and chemical composition.

Controlled radical polymerization techniques such as atom transfer radical polymerization (ATRP) [1–3], nitroxide mediated polymerization (NMP) [4] and reversible addition–fragmentation chain transfer polymerization (RAFT) [5, 6] are very convenient methods to prepare well-defined polymeric structures. RAFT polymerization is hereby a very versatile route that allows the synthesis of star-, comb- or block-copolymers with a good control over molecular

weight. This polymerization technique is applicable to a whole range of monomers and can be carried out at different temperatures including ambient temperature. Control over molecular weight and its distribution can be achieved using thiogroup-containing compounds such as thioesters [7], thiocarbonates [8, 9], dithiocarbamates [10] or xanthates [11]. The detailed mechanism of the RAFT process can be found elsewhere [12].

Although conventional free-radical copolymerization of macromonomers has been studied in a fairly large scope, studies on the kinetics of RAFT copolymerization of macromonomers are scarce [13–24]. Controlled/living radical copolymerization can result in a copolymer of a vastly different microstructure as compared with its conventional radical copolymerization counterpart. In a conventional system, the composition of polymeric chains varies with conversion due to the different relative rates of monomer consumption. In controlled copolymerization, all chains have the same overall monomer composition but with a composition gradient along the chains governed by the relative monomer consumption rates. Controlled radical copolymerization of a macromono-

\* Corresponding author. E-mail: ricardas.makuska@chf.vu.lt

mer thus gives a novel class of branched copolymers with a peculiar (gradient) microstructure.

The joining-up of amphiphilic macromolecules into complex structures is analogous to that of small surfactants such as soaps and lipids. Amphiphilic block copolymers are already important for a wide range of modern products ranging from medicine and pharmaceutical products to water-based paints and inks. Amphiphilic copolymers can spontaneously self-organize into supramolecular highly ordered core-shell nanoparticles characterized by a hydrophobic core and a hydrophilic outer surface. This special arrangement makes them suitable as long-circulating drug nanocontainers able to deliver drugs to different body compartments. Being loaded in the hydrophobic core of the micelles, the drug is well protected from inactivation under the effect of biological surroundings and is distributed according to the pharmacokinetics of the carrier system [24–26].

Poly(ethylene oxide) is widely used for biomedical applications due to its good biocompatibility [27]. Copolymers of methacrylic acid with the side chains of poly(ethylene oxide) can form intramolecular hydrogen-bonded complexes which exhibit reversible precipitation in water. Intramolecular complexes allow for a stable collapsed colloidal copolymer at acidic pH, which exhibits late-like viscosity. The complexes can be disrupted by increasing pH to give a viscous solution. This pH-dependent viscosity is desired so that the copolymer can be handled easily during formulation and then thickened by increasing the pH.

Here, we report the results of conventional and RAFT terpolymerizations of the macromonomer poly(ethylene oxide) monomethyl ether methacrylate (PEOMEMA) with low-molecular monomers, lauryl methacrylate (LMA) and methacrylic acid (MAA). The main goal of the present study was to compare the results of RAFT terpolymerization with those obtained for the same systems under conventional free-radical terpolymerization, and to find out conditions for the synthesis of charge-containing amphiphilic terpolymers with a low composition distribution.

## EXPERIMENTAL

### Materials

Poly(ethylene oxide) monomethyl ether methacrylate ( $M_n$  2080) (PEOMEMA) was purchased from “Aldrich” as a 50% aqueous solution and freeze-dried to recover an anhydrous monomer. Methacrylic acid (MAA) from “Fluka” was distilled under reduced pressure before use. Lauryl methacrylate (LMA) from “Fluka” was used as received. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. 1,4-Dioxane (DO) was distilled from metallic Na. Isopropanol and anisole were used as received. RAFT chain transfer agents *S*-(2-cyano-2-propyl)-*S*-dodecyltrithiocarbonate (CTA<sub>1</sub>) and 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanyl pentanoic acid (CTA<sub>2</sub>) were purchased from Strem Chemicals, Inc.

### RAFT terpolymerization of PEOMEMA, LMA and MAA

PEOMEMA (1.086 g, 0.522 mmol), LMA (0.089 g, 0.348 mmol), MAA (0.025 g, 0.29 mmol) and the chain transfer agent CTA<sub>1</sub> (5.0 mg,  $1.45 \cdot 10^{-2}$  mmol) were dissolved in a mixture of D<sub>2</sub>O (0.96 g) and DO (3.81 g), and anisole (42 mg, 0.39 mmol) as an internal standard was added. The solution containing 15% of the monomers was dosed into eight NMR tubes, and every filled tube was bubbled with nitrogen for 20 min. The <sup>1</sup>H NMR spectrum of the reaction mixture in one of the tubes was recorded, and the tubes sealed with septa were placed into a thermostat maintaining the temperature at 80 °C. The tubes were withdrawn periodically from the thermostat at 0.5–2 h intervals and cooled to –20 °C. Subsequently, the content of a tube was diluted twice by a mixture of D<sub>2</sub>O and DO (20/80, w/w) and neutralized by adding sodium carbonate (1.7 mg, 0.016 mmol) into each tube. <sup>1</sup>H NMR spectra of the reaction mixture at certain conversions of the monomers were recorded at 29 °C on a UNITY INOVA VARIAN spectrometer operating at 300 MHz.

### Conventional free-radical copolymerization of PEOMEMA, LMA and MAA

The procedure was identical to that of RAFT terpolymerization described above, except that instead of CTA<sub>1</sub> isopropanol (1.43 g, 23.8 mmol) as an irreversible chain transfer agent was used. The reaction was carried out at 60 °C.

### Calculation of terpolymerization parameters

Overall conversion of the monomers  $q_{\Sigma}$  (mol%) was calculated by the equation

$$q_{\Sigma} = \left[ 1 - \left( \frac{H_a + H_b + H_c}{H_s} \right)_i \cdot \left( \frac{H_s}{H_a + H_b + H_c} \right)_0 \right] \cdot 100,$$

where  $H_a$ ,  $H_b$ ,  $H_c$  and  $H_s$  are integrals of the signals in <sup>1</sup>H NMR spectra of terpolymerization mixtures, attributed to vinyl protons in PEOMEMA, vinyl protons in LMA, vinyl protons in MAA and aryl protons in internal standard anisole, respectively (Fig. 1); indices 0 and  $i$  denote initial and current values, respectively.

The instantaneous concentration of PEOMEMA  $c_1^i$ , LMA  $c_2^i$  and MAA  $c_3^i$  in the reaction mixture during terpolymerization was calculated by the equations

$$c_1^i = \frac{c_1^0 \cdot (H_a / H_s)^i}{(H_a / H_s)^0},$$

$$c_2^i = \frac{c_2^0 \cdot (H_b / H_s)^i}{(H_b / H_s)^0},$$

$$c_3^i = \frac{c_3^0 \cdot (H_c / H_s)^i}{(H_c / H_s)^0}.$$

The instantaneous composition of the monomer feed during terpolymerization  $f_1^i$  and instantaneous terpolymer composition  $F_1^i$  (PEOMEMA, mol%) were calculated as follows:

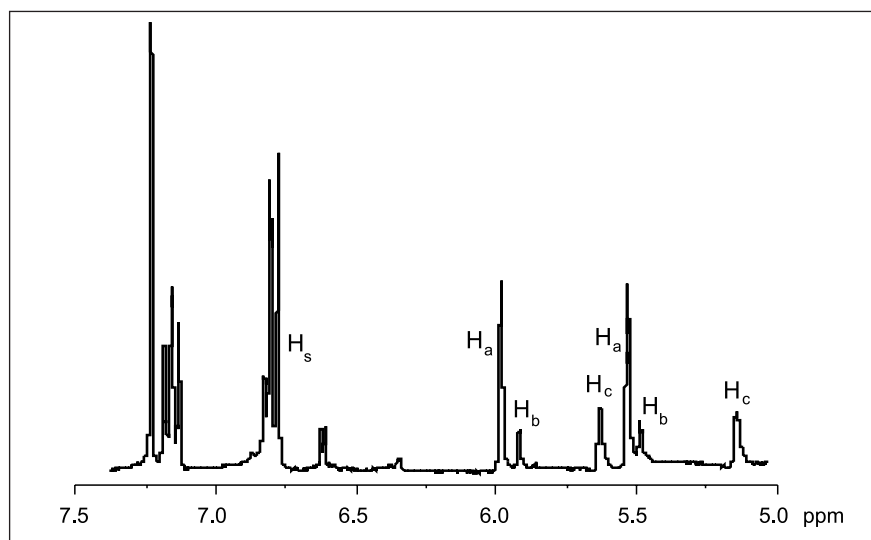


Fig. 1. Fragment of  $^1\text{H}$  NMR spectrum of the reaction mixture recorded before RAFT terpolymerization of PEOMEMA, LMA and MAA (75 / 15 / 10 mol%)

$$f_1^i = \frac{c_1^i}{c_1^i + c_2^i + c_3^i} \cdot 100,$$

$$F_1^i = \frac{c_1^{i-1} - c_1^i}{(c_1^{i-1} - c_1^i) + (c_2^{i-1} - c_2^i) + (c_3^{i-1} - c_3^i)} \cdot 100,$$

where  $c_n^i$  and  $c_n^{i-1}$  ( $n = 1, 2, 3$ ) are the current and the previous monomer concentrations, respectively.

#### Size exclusion chromatography

The molecular weight distribution (MWD) of the terpolymers was determined by SEC in THF using two columns PL gel MIXED-B LS (10  $\mu\text{m}$ ) and triple viscosity/concentration / light-scattering detection. The detection system consisted of a light-scattering DAWN DSP-F photometer (Wyatt Technology Corp.), measuring at 18 angles of observation, a modified differential Viscotek viscometer model TDA 301 (without internal light scattering and concentration detectors) and a Shodex RI 71 differential refractometer. The injection-loop volume was 0.1 ml and the mobile phase flow rate 0.5  $\text{ml min}^{-1}$ . The data were accumulated and processed using the Astra and triSEC software.

Elution curves in aqueous solutions were recorded using a Tosoh GMPWXL column and a Waters 410 differential refractive index detector. The mobile phase flow rate was 0.8  $\text{ml min}^{-1}$ .

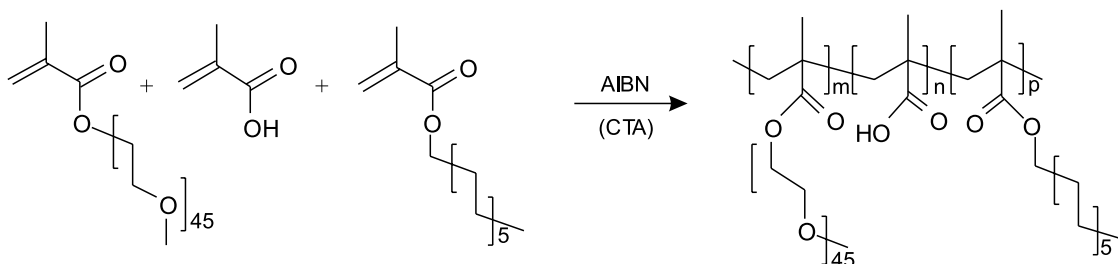
## RESULTS AND DISCUSSION

### Terpolymerization of PEOMEMA, LMA and MAA

The terpolymers AT-1, AT-2 and AT-3 (Table) were synthesized by the RAFT method using three monomers, PEOMEMA, LMA, and MAA (Scheme), at the molar ratio 75 : 15 : 10 mol%. Terpolymerizations were carried out in a dioxane and  $\text{D}_2\text{O}$  mixture. The use of dioxane is essential since LMA and RAFT agents were soluble in organic solvents only; on the other hand, aqueous solutions are preferable for hydrophilic PEOMEMA and MAA.

Figure 2 presents SEC eluograms of the AT-1 terpolymer in water (A) and in THF (B). Apparently, the chromatograms of terpolymers obtained at various conversions are bimodal. The form of eluograms of the AT-1 terpolymer in water and THF differs, but they still remain bimodal. The persistent bimodality of the SEC elution curves, despite the use of different columns and eluents, allowed concluding that the bimodality of the elution curves of the terpolymers synthesized using the RAFT chain transfer agent  $\text{CTA}_1$  reflected two chain growth mechanisms. The presence of two fractions with a different molecular weight evidenced that two parallel processes – RAFT and conventional free-radical polymerization – took part in parallel.

The bimodal elution curves induced us to increase the  $[\text{CTA}_1] / [\text{AIBN}]$  ratio. At the higher ratio, RAFT polymeriza-



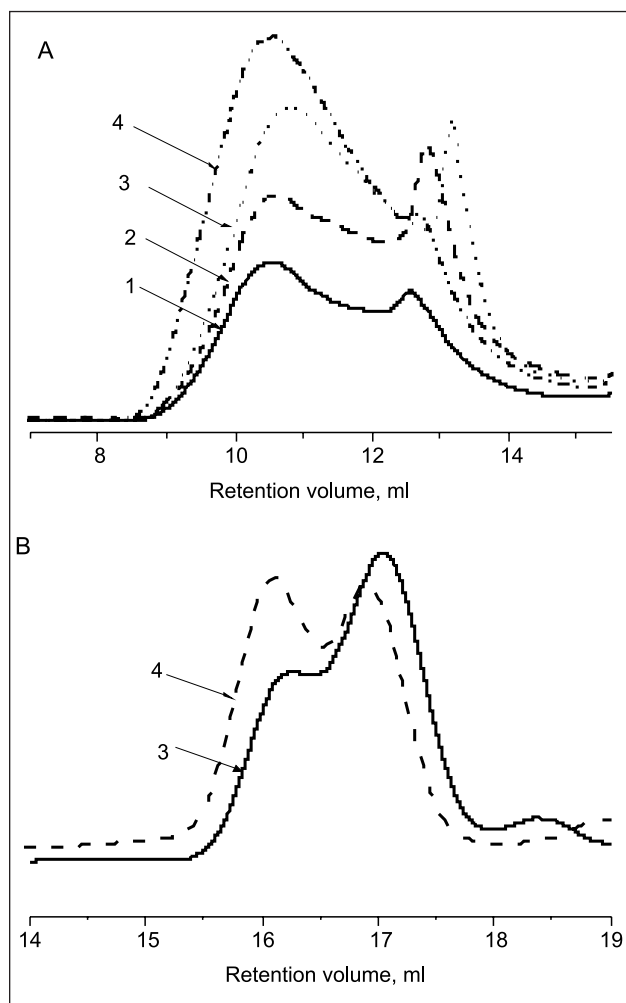
Scheme 1. Terpolymerization of PEOMEMA, LMA and MAA

tion was slower and gave a lower yield of terpolymers (AT-2). Unfortunately, this did not help to avoid the bimodality of the SEC elution curves. All the terpolymers synthesized from the monomer feeds rich in PEOMEMA and using CTA<sub>1</sub> had bimodal SEC elution curves and the likely bimodal MWD. The bimodal character of the MWD of the copolymers displaying an amphiphilic behaviour and synthesized by the RAFT process has been reported earlier [17, 28–30]. Such a hybrid behaviour could be due to a low chain transfer rate constant as compared with the propagation rate constant, or it could be caused by termination reactions which lead to fewer active chains.

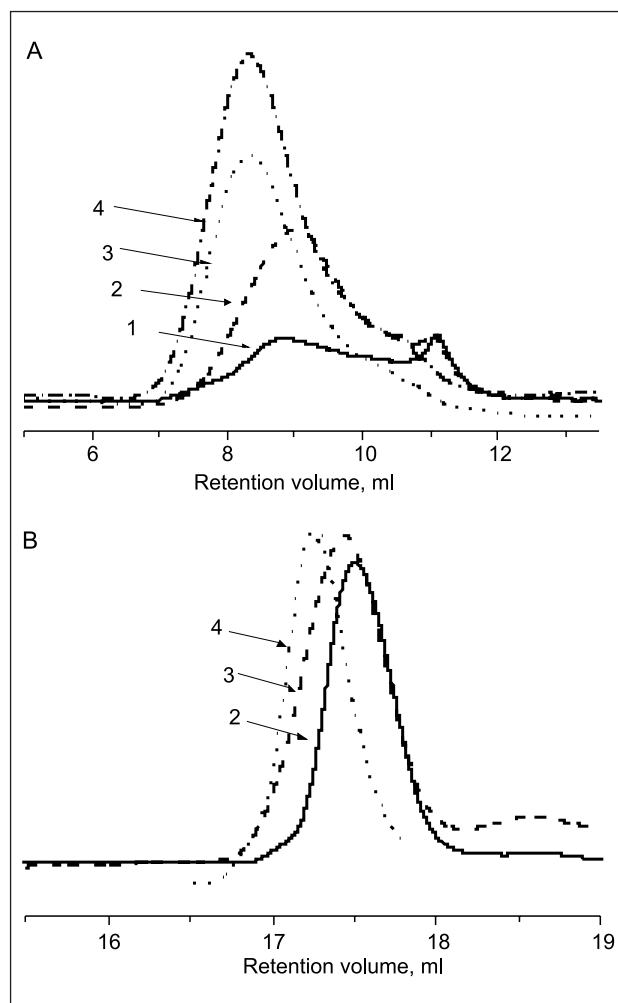
In order to ascertain the effect of CTA type on polydispersity of the terpolymers, terpolymerization was carried out in the presence of CTA<sub>2</sub> which was more hydrophilic than CTA<sub>1</sub> [31]. It is evident (Fig. 3) that CTA<sub>2</sub> controls the terpolymerization of PEOMEMA, LMA and MAA better than CTA<sub>1</sub> does. The SEC elution curves of the terpolymers synthesized in the presence of CTA<sub>2</sub> became unimodal at higher conversions of

the monomers, irrespective of the eluent and column. Nevertheless, to calculate the molecular weight and MWD of the terpolymers, SEC elution curves in THF were used, because SEC elution curves in water contained a sharp peak at higher retention volumes which could be attributed to a certain interaction between the amphiphilic terpolymer and the stationary phase of the column.

Terpolymers AT-4 and AT-5 (Table) were synthesized from the monomer feeds with a lower content of PEOMEMA (45 mol%). The control of terpolymerization was rather good in this case, giving almost unimodal SEC elution curves (Fig. 4). Apparently this was related to lower viscosity of the reaction mixture containing a lower amount of the macromonomer, and to the diminished diffusion control effect [21, 32–34]. Like in the case of AT-1 and AT-2, terpolymerization control was worse at the beginning and became satisfactory at higher conversions. The large excess of the RAFT chain transfer agent over the initiator ( $[CTA_1] / [AIBN] = 5$ ) had a retarding effect which resulted in a low conversion of the



**Fig. 2.** SEC eluograms in water (A) and in THF (B) of the random terpolymer AT-1 synthesized by RAFT terpolymerization using CTA<sub>1</sub>. Initial monomer feed [PEOMEMA] / [LMA] / [MAA] = 75 / 15 / 10 mol%, overall monomer conversion  $q_2 = 22$  mol% (1), 30 mol% (2), 45 mol% (3) and 67 mol% (4)



**Fig. 3.** SEC eluograms in water (A) and in THF (B) of the random terpolymer AT-3 synthesized by RAFT terpolymerization using CTA<sub>2</sub>. Initial monomer feed [PEOMEMA] / [LMA] / [MAA] = 75 / 15 / 10 mol%, overall monomer conversion  $q_2 = 5$  mol% (1), 34 mol% (2), 36 mol% (3) and 45 mol% (4)

Table. Results of RAFT terpolymerization (AT-1 – AT-5) and conventional free-radical terpolymerization (AT-6) of PEOMEMA, LMA and MAA

	Monomer feed composition			[CTAx]/[AIBN]	$q_{2,r}$ mol%	Terpolymer composition			$M_n \cdot 10^{-3}$	$M_w/M_n$
	PEOMEMA, mol%	LMA, mol%	MAA, mol%			PEOMEMA, mol%	LMA, mol%	MAA, mol%		
AT-1	75	15	10	2, CTA <sub>1</sub>	60	57	13	30	56.8	1.47
AT-2	75	15	10	5, CTA <sub>1</sub>	46	62	10	28	–	–
AT-3	75	15	10	2, CTA <sub>2</sub>	47	64	8	28	13.6	1.12
AT-4	45	30	25	5, CTA <sub>1</sub>	33	49	10	41	–	–
AT-5	45	30	25	3, CTA <sub>1</sub>	72	47	12	41	52.0	1.35
AT-6	45	30	25	–	93	43	29	28	–	–

monomers. The right [CTA<sub>1</sub>] / [AIBN] ratio was found to be about 3, which enabled a rather fast terpolymerization and a high conversion of the monomers, giving terpolymers with reasonable polydispersity (AT-5).

#### Composition of PEOMEMA, LMA and MAA terpolymers

The composition of PEOMEMA, MAA and LMA terpolymers was evaluated by analysing residual monomers in the reaction mixture by <sup>1</sup>H BMR spectroscopy according to the method described elsewhere [23]. Figure 5 presents changes in feed composition (A) and instantaneous terpolymer composition (B) during conventional free-radical and RAFT terpolymerizations. It is evident that during conventional free-radical terpolymerization the monomer feed composition shifts distinctly towards a high excess of PEOMEMA. MAA is the most reactive monomer under conventional free-radical terpolymerization. Because of the high reactivity of MAA, this monomer is almost completely consumed at a 60% overall conversion. Another unexpected feature of the conventional free-radical terpolymerization is a large variation of the content of LMA units in terpolymers with conversion. At the initial stages of terpolymerization, the

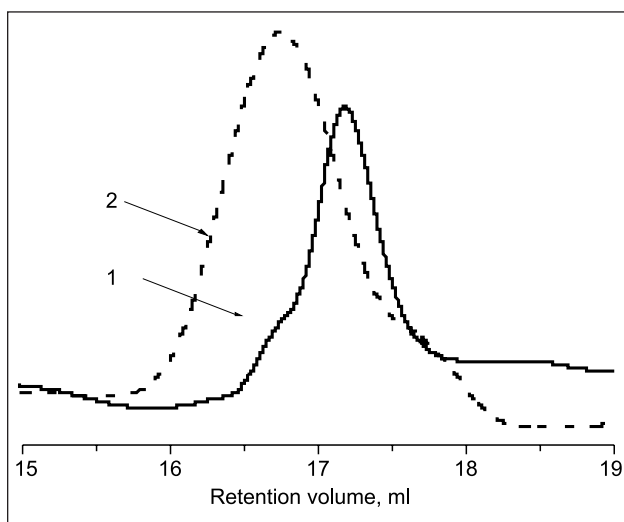


Fig. 4. SEC eluograms in THF of the random terpolymer AT-5 synthesized by RAFT terpolymerization using CTA<sub>1</sub>. Initial monomer feed [PEOMEMA] / [LMA] / [MAA] = 45 / 30 / 25 mol%, overall monomer conversion  $q_{2s} = 24$  mol% (1) and 72 mol% (2)

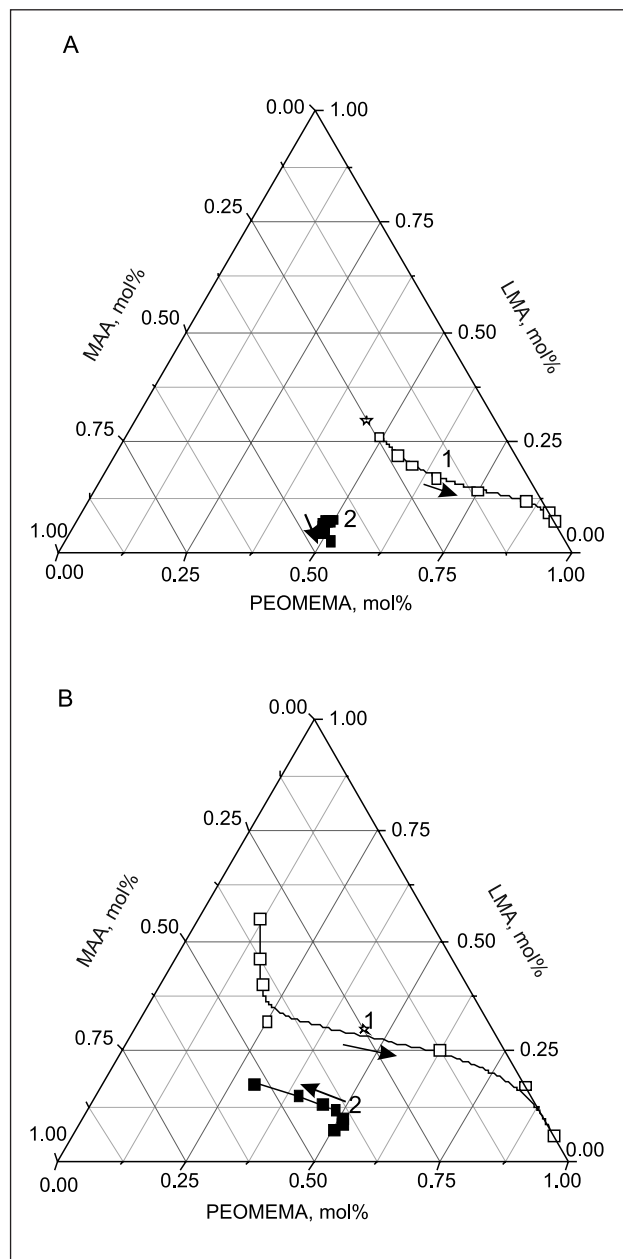


Fig. 5. Slocombe plots of the PEOMEMA / MAA / LMA system in conventional (1) and RAFT (2) terpolymerizations: A – feed composition, B – instantaneous terpolymer composition against overall conversion of the monomers ( $q_{2s} = 10, 20, 30, 40, 50, 60,$  and  $70$  mol%). The initial feed composition [PEOMEMA] / [LMA] / [MAA] = 45 / 30 / 25 mol% is marked with a star

terpolymers are rich in LMA units, while at 60–70 mol% conversions the LMA units constitute only 10 to 20 mol%. Because of the low reactivity ratio of the macromonomer, the terpolymer generated at the early stages of terpolymerization contains a small number of macromonomer units (10–20 mol%). At relatively high conversions (60–70 mol%), when the macromonomer dominates in the residual monomer feed, densely branched polymer chains containing 80–90 mol% of PEOMEMA units are produced. Thus, conventional free-radical terpolymerization of the monomer mixtures containing a macromonomer leads to the products with a large composition distribution as well as with a large distribution of branched structures.

Changes in monomer feed composition during RAFT terpolymerization are negligible (Fig. 5). Naturally, the variation in terpolymer composition during RAFT terpolymerization is significantly lower as compared with the conventional free-radical terpolymerization. Moreover, terpolymer composition changes in the opposite direction during the RAFT process as compared with the conventional free-radical terpolymerization; e. g., terpolymers formed at 10–30 mol% conversions contain about 50 mol% of PEOMEMA units, whereas those formed at 70 mol% conversions contain only 30 mol% of PEOMEMA units. This opens possibilities to synthesize slightly gradient terpolymers in which one end of polymer chains is preferably brush-type (more PEOMEMA units) and the other is preferably charge-containing (more MAA units). Surprisingly, according to variation in instantaneous terpolymer composition, the reactivity of PEOMAMA in the RAFT process is high, exceeding even the reactivity of LMA and MAA.

One major factor of the low reactivity of PEOMEMA in conventional free-radical terpolymerization is the diffusion control effect associated with the large size of the macromonomer. The reactivity of the macromonomer is increased by using the RAFT process in which the viscosity of the reaction mixture increases gradually during terpolymerization, in contrast to conventional free-radical terpolymerization when the viscosity of the reaction mixture increases rapidly. The diffusion control effect is less important during the RAFT process, since the time interval till monomer addition to a polymer chain becomes much larger (seconds or minutes) than that in a conventional free-radical system (milliseconds).

## CONCLUSIONS

1. The relatively hydrophilic 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanyl pentanoic acid (CTA<sub>2</sub>) controls the terpolymerization of PEOMEMA, LMA and MAA better than S-(2-cyano-2-propyl)-S-dodecyltrithiocarbonate (CTA<sub>1</sub>) does. Terpolymers synthesized in the presence of CTA<sub>1</sub> were characterized by a relatively high or even bimodal MWD and a moderate polydispersity (up to  $M_w / M_n = 1.5$ ), while terpolymers synthesized in the presence of CTA<sub>2</sub> were monodisperse ( $M_w / M_n = 1.12$ ).

2. Due to the low reactivity of the macromonomer, the conventional terpolymerization of PEOMEMA, LMA and MAA gave terpolymers with a large composition distribution and a large distribution of the branched structures. In the RAFT process, the variation in terpolymer composition was significantly lower, and slightly gradient terpolymers with the domination of charged units in one end and brush-type units in the other end of polymer chains were synthesized.

## ACKNOWLEDGEMENT

The authors are grateful to the Research Council of Lithuania for the financial support of the project MIP 50/2010.

Received 20 October 2011

Accepted 10 November 2011

## References

1. K. Matyjaszewski, N. V. Tsarevsky, *Nat. Chem.*, **1**, 276 (2009).
2. W. A. Braunecker, K. Matyjaszewski, *Prog. Polym. Sci.*, **32**, 93 (2007).
3. K. Matyjaszewski, J. Xia, *Chem. Rev.*, **101**, 2921 (2001).
4. D. Bertin, D. Gigmes, S. R. A. M. Tordo, P. Tordo, *Chem. Soc. Rev.*, **40**, 2189 (2011).
5. M. A. Harvison, A. B. Lowe, *Macromol. Rapid Commun.*, **32**, 779 (2011).
6. M. Semsarilar, S. Perrier, *Nat. Chem.*, **2**, 811 (2010).
7. J.-F. Baussard, J.-L. Habib-Jiwan, A. Laschewsky, M. Mertoglu, J. Storsberg, *Polymer*, **45**, 3615 (2004).
8. A. Postma, T. P. Davis, R. A. Evans, G. Li, G. Moad, M. S. O'Shea, *Macromolecules*, **39**, 5293 (2006).
9. O. I. Strube, L. Nothdurft, M. Drache, G. Schmidt-Naake, *Macromol. Chem. Phys.*, **212**, 574 (2011).
10. V. K. Patel, A. K. Mishra, N. K. Vishwakarma, C. S. Biswas, B. Ray, *Polym. Bull.*, **65**, 97 (2010).
11. A. K. Mishra, V. K. Patel, N. K. Vishwakarma, C. S. Biswas, M. Raula, A. Misra, T. K. Mandal, B. Ray, *Macromolecules*, **44**, 2465 (2011).
12. Ch. Barner-Kowollik, *Handbook of RAFT Polymerization*, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim (2008).
13. T. S. C. Pai, Ch. Barner-Kowollik, Th. P. Davis, M. H. Stenzel, *Polymer*, **45**, 4383 (2004).
14. Q. Yu, S. Xu, H. Zhang, Y. Ding, S. Zhu, *Polymer*, **50**, 3488 (2009).
15. E. Khouzakoun, J.-F. Gohy, R. Jérôme, *Polymer*, **45**, 8303 (2004).
16. H. Shinoda, K. Matyjaszewski, L. Okrasa, M. Mierzwa, T. Pakula, *Macromolecules*, **36**, 4772 (2003).
17. C. Pietsch, M. W. M. Fijten, H. M. L. Lambermont-Thijs, R. Hoogenboom, U. S. Schubert, *J. Polymer Sci. Polymer Chem.*, **47**, 2811 (2009).
18. E. Sprong, D. de Wet-Roos, M. Tonge, R. Sanderson, *J. Polym. Sci.: P B: Polym. Phys.*, **42**, 2502 (2004).
19. J.-F. Lutz, N. Jahed, K. Matyjaszewski, *J. Polymer Sci. Polymer Chem.*, **42**, 1939 (2004).

20. D. Rinaldi, T. Hamaide, C. Graillat, F. D'agosto, R. Spitz, S. Georges, M. Mosquet, P. Maitrasse, *J. Polymer Sci. Polymer Chem.*, **47**, 3045 (2009).
21. H. Shinoda, K. Matyjaszewski, *Macromol. Rapid Commun.*, **22**, 1176 (2001).
22. D.-H. Han, C.-Y. Pan, *Macromol. Chem. Phys.*, **207**, 836 (2006).
23. T. Krivorotova, A. Vareikis, D. Gromadzki, M. Netopilík, R. Makuška, *Eur. Polym. J.*, **46**, 546 (2010).
24. B. Hazer, *Intern. J. Polym. Sci.*, **2010**, 8 (2010).
25. L. Y. Qiu, Y. H. Bae, *Pharm. Res.*, **23**, 1 (2006).
26. W. B. Liechty, D. R. Kryscio, B. V. Slaughter, N. A. Peppas, *An. Rev. Chem. Biomol. Eng.*, **1**, 149 (2010).
27. E. Chiellini, R. M. Ottenbrite, *Polymers in Medicine: Biomedical and Pharmaceutical Applications*, CRC Press (1992).
28. S. Perrier, P. Takolpuckdee, J. Westwood, D. M. Lewis, *Macromolecules*, **37**, 2709 (2004).
29. C. Barner-Kowollik, J. F. Quinn, T. L. U. Nguyen, J. P. A. Heuts, T. P. Davis, *Macromolecules*, **34**, 7849 (2001).
30. S. Garnier, A. Laschewsky, *Macromolecules*, **38**, 7580 (2005).
31. E. Rizzardo, M. Chen, B. Chong, G. Moad, M. Skidmore, S. H. Thang, *Macromol. Symp.*, **248**, 104 (2007).
32. Y. Xia, B. D. Olsen, J. A. Kornfield, R. H. Grubbs, *J. Am. Chem. Soc.*, **131**, 18525 (2009).
33. S. Nguyen, R. H. Marchessault, *Macromolecules*, **38**, 290 (2005).
34. H. Shinoda, P. J. Miller, K. Matyjaszewski, *Macromolecules*, **34**, 3186 (2001).

Tatjana Krivorotova, Romualdas Grigelis, Jūratė Jonikaitė,  
Ričardas Makuška

#### ANIJONINIŲ AMFIFILINIŲ ŠEPETINIŲ TERPOLIMERŲ SINTEZĖ VYKDANT ĮPRASTĄ RADIKALINĘ IR RAFT TERPOLIMERIZACIJĄ

##### *S a n t r a u k a*

Cilindriniai šepetiniai terpolimerai, kurių makromolekules sudaro polietilenoksido monometiletermetakrilato (PEOMEMA), laurilmetakrilato (LMA) ir metakrilo rūgšties (MAR) grandys, buvo susintetinti vykdant įprastą radikaline ir RAFT statistinę terpolimerizaciją. RAFT terpolimerizacija buvo vykdoma, naudojant grandinės perdavos agentus S-(2-ciano-2-propil)-S-dodeciltritiokarbonatą (CTA<sub>1</sub>) ir 4-ciano-4-(dodecilsulfaniltiokarbonil)sulfanilpentano rūgštį (CTA<sub>2</sub>). Terpolimerams, susintetintiems naudojant CTA<sub>1</sub>, būdingas bimodalinis MMP ir vidutinis polidispersiškumas (iki  $M_w / M_n = 1,5$ ); terpolimerai, susintetinti naudojant CTA<sub>2</sub>, yra monodispersiniai. RAFT terpolimerizacija pasiteisino, kadangi taikant šį metodą susintetinti šepetiniai PEOMEMA, LMA ir MAA terpolimerai, kuriems būdinga maža sudėties sklaida ir pakankamai tolygi PEO šoninių grandinių sklaida išilgai pagrindinės grandinės.