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Conventional free-radical and RAFT copolymerization of poly(ethylene oxide) containing macromonomers

Tatjana Krivorotova [a], Aušvydas Vareikis [a], Daniel Gromadzki [a,b], Miloš Netopilík [b], Ričardas Makuška [a,*]

[a] Department of Polymer Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania
[b] Department of Supramolecular Polymer Systems, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

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ABSTRACT

Conventional free-radical and RAFT copolymerization of poly(ethylene oxide) substituent containing methacrylate macromonomers, PEO_5MEMA and $PEO_{45}MEMA$, was studied by the use of ^1H NMR spectroscopy for an analysis of residual monomers. From the monomer consumption curves, several parameters including monomer conversion, instantaneous copolymer composition and reactivity ratios of the monomers were evaluated. Reactivity ratios of PEO_5MEMA and MAA estimated by non-linear approach of error-in-variables model and presented as joint confidence regions were constant during conventional free-radical and RAFT copolymerizations of the above monomers but were slightly affected by the RAFT process. Reactivity ratio of $PEO_{45}MEMA$ was found to be lower than that of PEO_5MEMA and varied during copolymerization: increased with conversion in conventional free-radical copolymerization and slightly (without confidence) decreased in the RAFT process. RAFT copolymerization of $PEO_{45}MEMA$ and MAA enabled to synthesize comb copolymers with low composition distribution and more homogeneous distribution of PEO side chains along the mainchain. Under copolymerization with MAA, $PEO_{45}MEMA$ behaved like typical macromonomer with appropriate steric hindrance while the behavior of PEO_5MEMA was similar to that of a low-molecular methacrylate.

1. Introduction

One of the most useful ways to design and synthesize well-defined graft copolymers is the macromonomer method [1,2]. The macromonomer method is based on copolymerization of macromonomers – monomers containing oligomeric or polymeric substituent. The macromonomer method, however, is still deficient in controlling spacing of the side chains [2–5]. Subject to the method of the synthesis, side chains can be distributed homogeneously or heterogeneously; in the latter case the side chain density along macromolecule can be rather different. The spacing distribution in brush copolymers synthesized by the macromonomer method is predetermined by composition of the monomer feed and reactivity ratios of comonomers. The reactivity ratio of a macromonomer is affected by many factors including: (1) the inherent reactivity of a macromonomer predetermined by its chemical structure, (2) diffusion control of the macromonomer concentration in a close vicinity to the propagating radical associated with its large size, and (3) potential incompatibility of the macromonomer and propagating chain constituted mainly by a comonomer units due to thermodynamic repulsive interactions.

Controlled radical polymerization techniques such as atom transfer radical polymerization (ATRP) [6], nitroxide mediated polymerization (NMP) [7] and reversible

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* Corresponding author. Tel.: +370 52193227; fax: +370 52330987.
E-mail address: ricardas.makuska@chf.vu.lt (R. Makuška).

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addition–fragmentation transfer polymerization (RAFT) [8–10] 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 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 molecular weight distribution can be achieved using thio-containing compounds such as thioesters [11], thiocarbonates [12], dithiocarbamates [13] or xanthates [14]. The detailed mechanism of the RAFT process can be found elsewhere [9,10].

Although conventional free-radical copolymerization of macromonomers has been studied in fairly large scope, studies on kinetics of RAFT copolymerization of macromonomers are scarce [3,5,15–17]. Controlled/living radical copolymerization can result in a copolymer of vastly different microstructure compared to its conventional radical copolymerization counterpart. In a conventional system, the composition of the 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 macromonomer thus makes novel class of branched copolymers with peculiar (gradient) microstructure.

Reactivity ratios of macromonomers in radical copolymerization are often different compared to the low molecular monomers of the same structure at polymerizable end [18]. One of the most studied macromonomer is poly(ethylene oxide) monomethyl ether methacrylate (PEO_nMEMA, n – number of EO units). In fact, PEO_nMEMA represents not one substance but a series of macromonomers differing in molecular weight (length of EO side chains). The polymers with PEO side chains have potential applications in biomedical materials [19], as compatibilizers in polymer blending [20], as surfactants [21] and in high energy density lithium batteries [22]. The reactivity ratios of PEO_3MEMA or PEO_5MEMA and methacrylic acid (MAA) were reported to be 1.02 and 0.71 in DMSO [23], 1.02 and 1.03 in water, and 3.6 and 2.0 in water/ethanol (50/50, w/w), respectively [24]. The final composition of the copolymers of PEO_5MEMA and MAA synthesized in THF was found was differing not more than by 1–2 mol% from the composition of the corresponding monomer feeds [25]. Surprisingly, reactivity ratios of $PEO_{20}MEMA$ and MAA in THF were reported to be 0.6–0.9 and 0, respectively [26]. Reactivity ratios of $PEO_{45}MEMA$ and acrylic acid (AA) in RAFT copolymerization were found to be 2.02 and 0.49, respectively, while those of $PEO_{11}MEMA$ and AA – 2.81 and 0.36, respectively [27]. One should pay attention, however, that the values of reactivity ratios presented above should be qualified with caution since they were determined under non-identical conditions. For comparison, reactivity ratios of methyl methacrylate (MMA, low molecular analogue of PEO_nMEMA) and MAA in dioxane/water (50/50 v/v) mixture were reported to be 2.05 ± 0.63 and 0.70 ± 0.10, respectively, while those of MA and AA 0.31 ± 0.12 and 2.52 ± 0.26, respectively [28].

The present work deals with copolymerization of the macromonomers PEO_5MEMA or $PEO_{45}MEMA$ and MAA studied by the use of ^1H NMR spectroscopy. The main goal of the present study was to provide deeper understanding of the macromonomer copolymerization via the RAFT process and to compare the results with those obtained for the same systems under conventional free-radical copolymerization.

2. Experimental

2.1. Materials

Poly(ethylene oxide) monomethyl ether methacrylate (M_n 300) (PEO_5MEMA) from *Aldrich* was used as received. Poly(ethylene oxide) monomethyl ether methacrylate (M_n 2080) ($PEO_{45}MEMA$) was purchased from *Aldrich* as a 50% aqueous solution and freeze-dried to recover anhydrous monomer. Methacrylic acid (MAA) from *Fluka* was distilled under reduced pressure before use. 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 agent (CTA) S-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) was synthesized by the method described elsewhere [29].

2.2. RAFT copolymerization of PEO_5MEMA or $PEO_{45}MEMA$ and MAA

$PEO_{45}MEMA$ (2.40 g, 1.15 mmol), MAA (99 mg, 1.15 mmol), chain transfer agent MCPDB (5.8 mg, 1.9×10^{-2} mmol) and initiator AIBN (0.63 mg, 3.8×10^{-3} mmol) were dissolved in a mixture of D_2O (4.29 g) and DO (9.90 g), and anisole (84 mg, 0.78 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. ^1H NMR spectrum of the reaction mixture in one of the tubes was recorded, and the tubes sealed with septa were placed into thermostat maintaining the temperature at 80 °C. The tubes were withdrawn periodically from the thermostat in intervals 0.5–2 h and cooled to −20 °C. Subsequently the content of a tube was diluted twice by a mixture of D_2O and DO (30/70, w/w) and neutralized by adding sodium carbonate (14 mg, 0.13 mmol). ^1H NMR spectra of the reaction mixture at certain conversions of the monomers were recorded at ambient temperature on a UNITY INOVA VARIAN spectrometer operating at 300 MHz.

2.3. Conventional free-radical copolymerization of PEO_5MEMA or $PEO_{45}MEMA$ and MAA

The procedure was identical to the RAFT copolymerization described above except that instead of MCPDB isopropanol (1.43 g, 23.8 mmol) as an irreversible chain transfer agent was used. The reaction was carried out at 60 °C.

2.4. Calculation of the parameters of copolymerization

Overall conversion of the monomers q_Σ (mol%) was calculated by the equation:

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

where H_a, H_d and H_s are integrals of the signals in ^{1}H NMR spectra of copolymerization mixtures attributed to vinyl protons in PEO$_n$MEMA, vinyl protons in MAA and aryl protons in internal standard anisole, respectively (Fig. 1); indices 0 and i denote initial and current values, respectively.

Instantaneous concentration of PEO$_n$MEMA C_1^i and MAA C_2^i in the reaction mixture during copolymerization was calculated by the equations:

$$C_1^i = \frac{C_1^0 \cdot (H_a/H_s)^i}{(H_a/H_s)^0}, \quad C_2^i = \frac{C_2^0 \cdot (H_d/H_s)^i}{(H_d/H_s)^0},$$

where C_1^0 and C_2^0 are initial concentration (mmol) of PEO$_n$MEMA and MAA, respectively.

Instantaneous composition of the monomer feed during copolymerization f_1^i and instantaneous copolymer composition F_1^i (PEO$_n$MEMA, mol%) were calculated as follows:

$$f_1^i = \frac{C_1^i}{C_1^i + C_2^i} \cdot 100, \quad F_1^i = \frac{C_1^{i-1} - C_1^i}{(C_1^{i-1} - C_1^i) + (C_2^{i-1} - C_2^i)} \cdot 100,$$

where C^i and C^{i-1} are current and previous monomer concentrations, respectively.

Comonomer reactivity ratios r_1 and r_2 and the errors of these parameters were obtained using the RREVM software which is based on a non-linear Error in Variable Method (EVM) [30,31]. Both the composition of the feed and the instantaneous copolymer composition at a certain conversion were determined using ^{1}H NMR spectroscopy, and the error in this measurement was taken to be 5%.

2.5. Size exclusion chromatography

Polymer molecular weights were estimated using SEC instrument: Deltachrom pump (Watrex Comp.), autosampler Midas (Spark Instruments, The Netherlands), two columns with PL gel MIXED-B LS (10 μm), separating in the range of molecular weights approximately 400–1×10^7 g mol^{-1}. Acetate buffer was used as a mobile phase at flow-rate 0.75 cm^3/min. The injection-loop volume was 0.1 cm^3. Measurements were performed with triple viscosity/concentration/light-scattering detection. The set was connected to a light-scattering photometer DAWN DSP-F (Wyatt Technology Corp.), measuring at 18 angles of observation, a modified differential viscometer Viscotek model TDA 301 (without internal light scattering and concentration detectors) and a differential refractometer Shodex RI 71. The data were accumulated and processed using the Astra and triSEC software. The evaluation of the triple-detection data is described elsewhere [32].

3. Results and discussion

Conventional free-radical copolymerization and RAFT copolymerization of PEO$_5$MEMA or PEO$_{45}$MEMA and MAA (Scheme 1) was done in parallel in order to compare these methods and provide deeper understanding of the macromonomer copolymerization via the RAFT process. PEO$_{45}$MEMA is a typical methacrylate-terminated PEO macromonomer with relatively high molecular weight (M_n = 2080) and long PEO substitute (approx. 45 units of ethylene oxide). PEO$_5$MEMA has the same structure as PEO$_{45}$MEMA but significantly lower molecular weight (M_n = 300) and shorter PEO substitute (approx. 5 units of ethylene oxide).

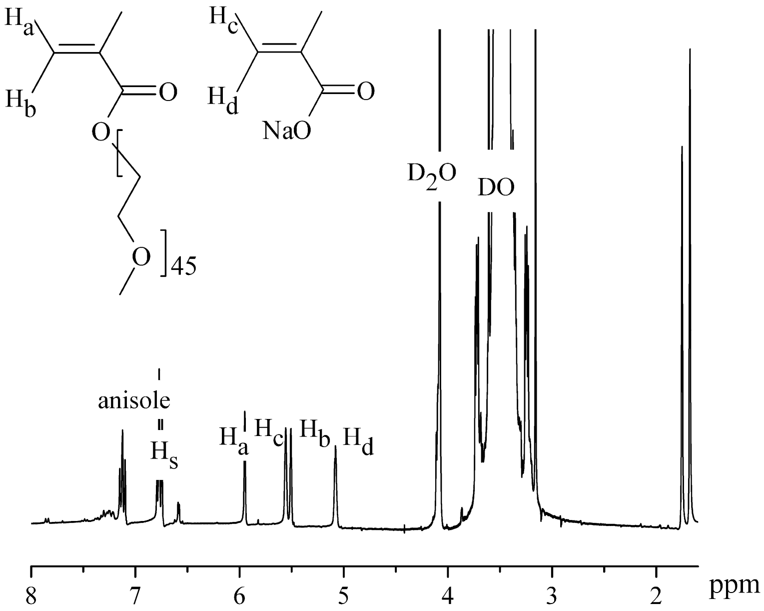
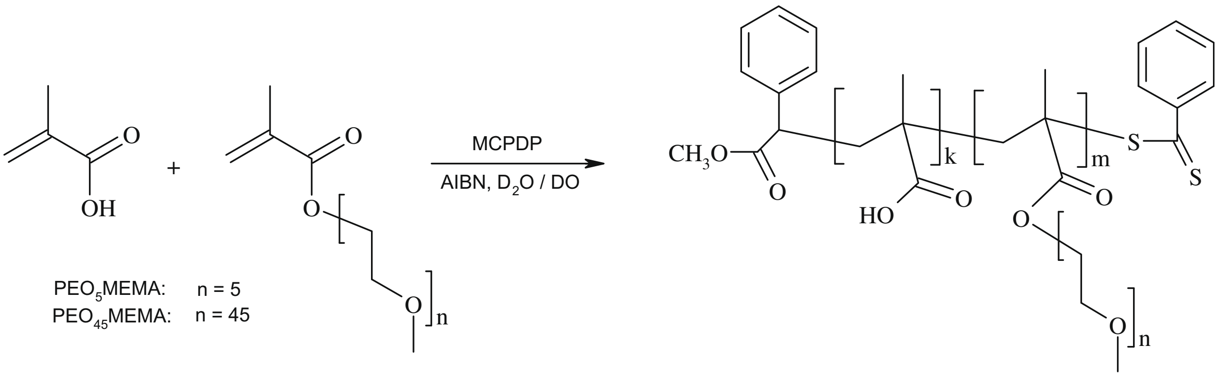


Fig. 1. ^{1}H NMR spectrum of the reaction mixture recorded before RAFT copolymerization of PEO$_{45}$MEMA and MAA (50/50 mol%).



Scheme 1. Synthesis of random copolymers of PEO$_n$MEMA and MAA via the RAFT process.

Copolymerization of PEO$_n$MEMA and MAA was studied at three different initial monomer feeds, namely, 80:20, 50:50 and 20:80, mol%. The use of ^{1}H NMR spectroscopy for an analysis of residual monomers enabled to follow, besides others, copolymerization of the macromonomer-rich monomer feeds, which is often impossible by gravimetric and even chromatographic techniques [33].

Fig. 1 represents ^{1}H NMR spectrum of the reaction mixture before RAFT copolymerization of PEO$_{45}$MEMA and MAA. The signals at 5.95 and 5.52 ppm were attributed to the vinyl protons in PEO$_{45}$MEMA (H_a, H_b), while the signals at 5.60 and 5.10 ppm to the vinyl protons in sodium methacrylate (H_c, H_d). Neutralization of the units of MAA enabled to shift the signals of H_c and H_d from 5.96 and 5.53 ppm to 5.60 and 5.10 ppm, respectively, thus avoiding overlapping with the signals H_a, H_b. Monomer consumption was determined by comparing the signals of the vinyl protons of the monomers with the signal of anisole (6.80 ppm, H_s) used as an internal standard.

Kinetic curves of consumption of PEO$_n$MEMA and MAA during copolymerization were obtained by non-linear fitting of the experimental data using a CurveExpert 1.3 program for Windows. From the monomer consumption curves, several secondary parameters were calculated, such as monomer conversion, instantaneous monomer feed composition, instantaneous copolymer composition, reactivity ratios of the monomers, etc. For the calculation of the reactivity ratios, two different instantaneous copolymer compositions and two different respective instantaneous monomer feeds in close vicinity to certain conversions were evaluated.

3.1. Kinetics of RAFT copolymerization of PEO macromonomers

Copolymers of PEO$_5$MEMA or PEO$_{45}$MEMA and MAA were synthesized in the mixed solvent of D$_2$O and DO (30/70, w/w) at 80 °C, the molar ratio [M]/[AIBN] being at 200, and the molar ratio [MCPDP]/[AIBN] at 5. It was found that the stoichiometry of the monomers to the initiator and of the RAFT chain transfer agent to the initiator was sufficient to maintain steady-state concentration of the radicals during copolymerization. Steady-state concentration of the radicals was proved by low polydispersity indices and linear kinetic plots in semilogarithmic coordinates (see below). A linear relationship between $\ln([M]_0/[M]_t)$ and the reaction time was reported for many RAFT polymerizations including the polymerization of MMA mediated by the same chain transfer agent MCPDB [29].

Semilogarithmic kinetic plots (A) and conversion curves (B) for the copolymerization of PEO$_5$MEMA and MAA are presented in Fig. 2. $[M]_0$ and $[M]_t$ in logarithmic ordinate denote initial and current overall concentration of the

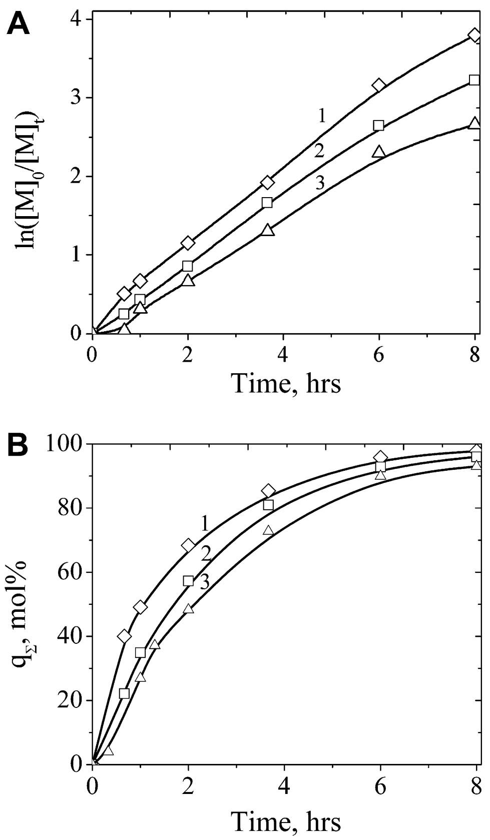


Fig. 2. Semilogarithmic kinetic plots (A) and conversion curves (B) for the copolymerization of PEO$_5$MEMA and MAA. Initial monomer feed, mol%, [PEO$_5$MEMA]/[MAA] = 80/20 (1, 4), 50/50 (2, 5) and 20/80 (3, 6).

monomers in the feed, respectively. Linear plots of $\ln([M]_0/[M]_t)$ vs time were obtained indicating that the number of propagating species were constant during copolymerization. A comparison of semilogarithmic kinetic plots with conversion curves demonstrated that concentration of propagating radicals remained constant up to nearly full consumption of the monomers (up to monomer conversion 95%). Rate of copolymerization (an increase in conversion) slightly depended on monomer feed being the highest for the MAA-rich monomer feed.

Kinetic plots in semilogarithmic coordinates for the copolymerization of PEO_{45}MEMA and MAA were rather different from those discussed above (Fig. 3). Pseudo-first-order plots stopped to be linear after around 6 h corresponding to the loss of the steady-state conditions when termination reactions were no longer balanced by the production of radicals from AIBN. The radical concentration began to decrease at monomer conversion ca 55 mol% for the PEO_{45}MEMA-rich monomer feed, and ca 80 mol% for the MAA-rich monomer feed.

A decrease in radical concentration can be related to an increase in the rate of termination reactions which more or less are accompanying RAFT polymerization. Similar behavior has been described for different meth(acrylates) [34,35]. Matyjaszewski reported [3] that the controlled nature of polymerization, especially, in the case of RAFT, can be suppressed by the diffusion control of macromonomer concentration. The role of diffusion control increases at high conversions when viscosity of the reaction mixture becomes high. In the RAFT polymerization system, the addition–fragmentation chain transfer reaction plays an essential role. Since the exchange reaction is a polymeric bimolecular reaction, when a macromonomer is polymerized, the reaction between the thiocarbonylthio-terminated polymer (dormant chain) and the growing polymer (active species) adjacent or close to the macromonomer unit may be hindered. If the exchange reaction rate becomes very low, the control of the radical polymerization may be lost, and the RAFT polymerization will resemble to the conventional radical polymerization.

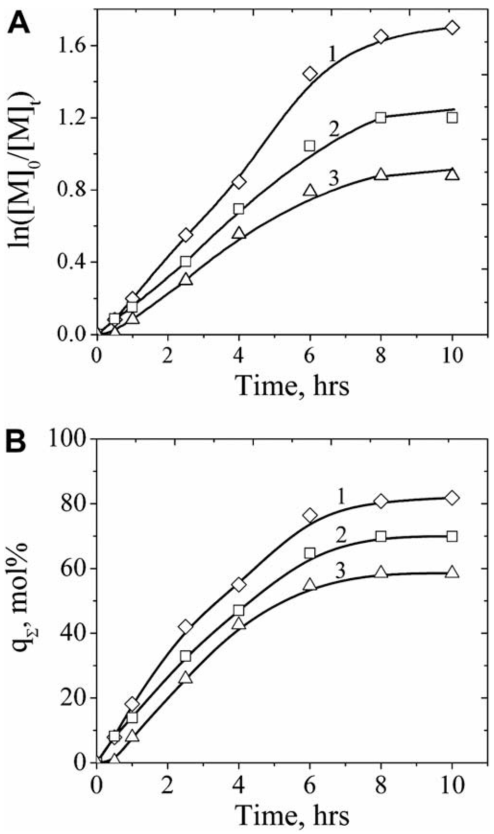


Fig. 3. Semilogarithmic kinetic plots (A) and conversion curves (B) for the copolymerization of PEO_{45}MEMA and MAA. Initial monomer feed, mol%, $[PEO_{45}MEMA]/[MAA]$ = 80/20 (1, 4), 50/50 (2, 5) and 20/80 (3, 6).

The role of termination reactions in copolymerization of PEO_{45}MEMA was manifested by leveling-off the conversion curves (Fig. 3B). In fact, after significant reduction in concentration of propagating radicals the copolymerization stopped. Maximal conversion of the monomers was obviously affected by the relative amount of the macromonomer reaching the lowest value (about 60 mol%) for the monomer feed containing 80 mol% of PEO_{45}MEMA.

3.2. MWD of the copolymers synthesized from PEO macromonomer by the RAFT process

SEC measurements of two RAFT and one conventional copolymers synthesized from the same monomer feed were done in order to ascertain whether RAFT copolymerization of PEO macromonomer is consistent with the mechanism of the RAFT process and give copolymers with low polydispersity and predetermined molecular weight. MWD curves of these copolymers are shown in Fig. 4. MWD of the RAFT copolymers is unimodal and narrow, and do not contain a high molecular fraction which can be present in the case of two parallel processes – RAFT and conventional polymerization [29,36,37]. These results prove that radical copolymerization of PEO_{45}MEMA and

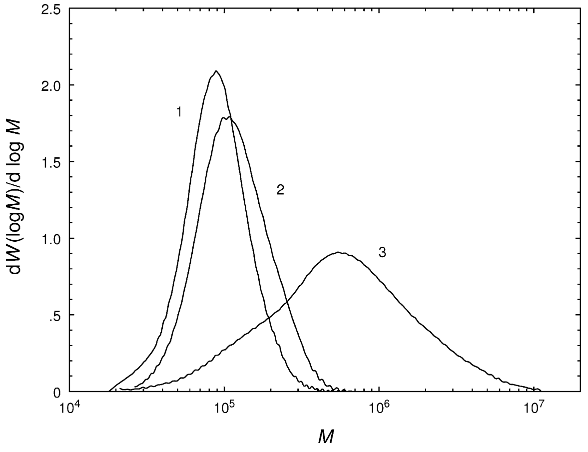


Fig. 4. MWD of random copolymers PEO_{45}MEMA – MAA synthesized by RAFT (1, 2) and conventional free-radical (3) processes. Initial monomer feed $[PEO_{45}MEMA]/[MAA]$ = 50/50 mol%, overall monomer conversion q_Σ 47 mol% (1), 69 mol% (2) and 68 mol% (3).

MAA is well controlled by the RAFT chain transfer agent MCPDB.

The values of absolute number-average molecular weight M_n, weight-average molecular weight M_w, polydispersity index M_w/M_n, degree of polymerization DP, intrinsic viscosity $[\eta]$ and radius of gyration R_g of the copolymers, obtained by triSEC measurements, are listed in Table 1. M_n of the copolymers synthesized by the RAFT process is fairly consistent with the ratio of the monomers to MCPDB and monomer conversion. Degree of polymerization of the RAFT copolymers is moderately high enabling to expect that kinetics of copolymerization is predetermined by regularities of statistics. Polydispersity indices of the RAFT copolymers are noticeably below the theoretical limiting value of 1.5 for conventional free-radical mechanism and more than twice lower compared to that of the copolymer synthesized by the conventional process. M_w/M_n of the RAFT copolymers is comparable with polydispersity of poly(methyl methacrylate) synthesized by the RAFT process using the same RAFT CTA [29,38]. Small increase in polydispersity with conversion can be explained by increasing role of termination reactions because of diffusion control of the macromonomer concentration. Intrinsic viscosity of the copolymers is rather low which is in accordance with brush structure of the copolymers [39].

3.3. Variation of instantaneous composition of the copolymers with conversion

Composition of the copolymers synthesized from the same monomer feed by conventional free-radical and RAFT copolymerization may be different [35,40,41]. The presence of a control (chain transfer) agent may modify the concentration balance between the different propagating radicals in comparison with conventional copolymerization, i.e. the formation of intermediate radicals in the RAFT process can favour preferential production of one type of propagating radicals. Considering the main RAFT equilibrium only, the copolymerization of A and B monomers gives rise to three different intermediate radicals IR_{AA}, IR_{BB} and IR_{AB} (Scheme 2), where the letters in the subscripts denote monomeric units through which the growing chains are attached to dithioester compound [42]. The selectivity of the fragmentation of these intermediate radicals is relative to the nature of A and B. The release of the macroradical $A^\cdot$ is favoured if $A^\cdot$ is more sterically hindered and stabilized than $B^\cdot$. For instance, in the case of MMA/styrene copolymerization, PMMA radical is released 100 times faster from IR_{AB} than the PS radical [43]. Than the $[A^\cdot]/[B^\cdot]$ ratio may be higher in the RAFT copolymerization than in a conventional one, thus influencing the relative rates of consumption of the comonomers. In fact, the variation of the $[A^\cdot]/[B^\cdot]$ ratio is more complex and does not only depend on the fragmentation selectivity but also on the selectivity of the addition reaction. The simulations [40] supported the experimental findings of an amplified incorporation of the monomer, which is preferred in conventional copolymerizations, through the RAFT process. It was shown also that the rate coefficients for the initiation reaction and the pre-equilibrium of the RAFT process play an important role in determining the copolymer composition [40].

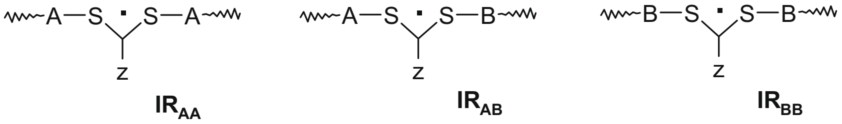
In our case, variation in instantaneous copolymer compositions with conversion under conventional and RAFT copolymerization of PEO_5MEMA and MAA is very similar (Fig. 5). Composition of the copolymers remains almost constant up to 80 mol% conversion for PEO_5MEMA-rich monomer feeds, and changes slightly towards lower content of PEO_5MEMA for MAA-rich monomer feeds. Small differences in composition of conventional and RAFT copolymers may be attributed to experimental errors which can reach 5% using NMR analysis.

In contrast to the above system, variation in instantaneous copolymer compositions with conversion between conventional and RAFT copolymerization of $PEO_{45}MEMA$ macromonomer differ substantially (Fig. 6). Instantaneous copolymer composition in conventional radical copolymerization changes with conversion leading to copolymers with considerable composition distribution. Contrarily, composition of the copolymers synthesized by the RAFT method and isolated at various monomer conversions is al-

Table 1
Results of random copolymerization of $PEO_{45}MEMA$ (M_1) and MAA. Initial monomer feed $[PEO_{45}MEMA]/[MAA] = 50/50$ mol%.

Sample No.	Process	Time (h)	q (%)	F_1 (mol%)	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	M_w/M_n	DP	$[\eta]$ (dL/g)	R_g (nm)
1	RAFT[a]	4	47	47	74.1	95.2	1.28	72	0.148	7.75
2	RAFT[a]	8	69	49	93.2	126	1.35	88	0.154	8.56
3	Conv.[b]	4	68	48	330	937	2.84	316	0.345	20.7

[a] $[\Sigma M] = 2.30$ mmol, $[AIBN] = 3.8 \times 10^{-3}$ mmol, $[MCPDB] = 1.9 \times 10^{-2}$ mmol.
[b] $[\Sigma M] = 2.30$ mmol, $[AIBN] = 3.3 \times 10^{-2}$ mmol.



Scheme 2. Various intermediate radicals formed during the RAFT copolymerization of monomers A and B [43].

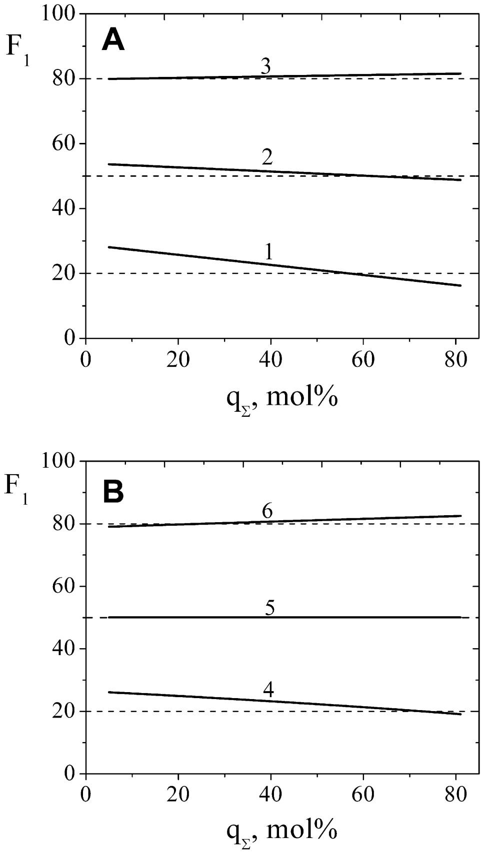


Fig. 5. Variation of instantaneous copolymer composition F_1 (PEO_5MEMA, mol%) with conversion of the monomers q_Σ under conventional (A) and RAFT (B) copolymerization. Initial monomer feeds, mol%, PEO_5MEMA/MAA = 20/80 (1, 4), 50/50 (2, 5) and 80/20 (3, 6) are indicated by dotted lines.

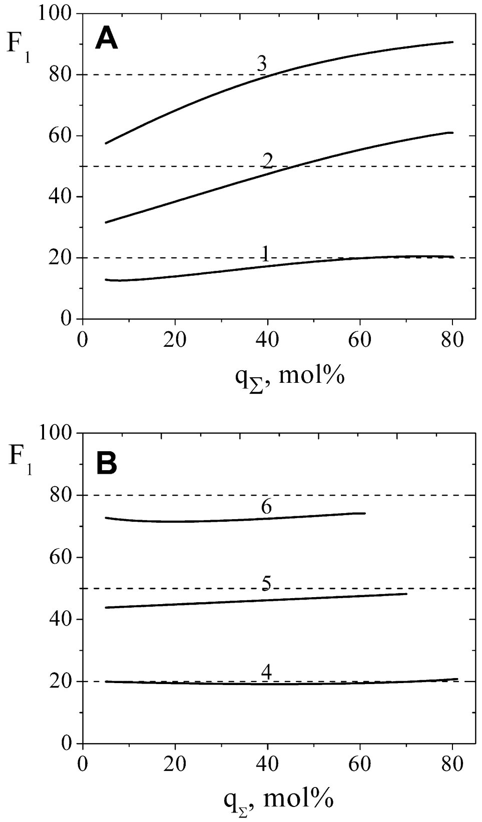


Fig. 6. Variation of instantaneous copolymer composition F_1 ($PEO_{45}MEMA$, mol%) with conversion of the monomers q_Σ under conventional (A) and RAFT (B) copolymerization. Initial monomer feeds, mol%, $PEO_{45}MEMA$/MAA = 20/80 (1, 4), 50/50 (2, 5) and 80/20 (3, 6) are indicated by dotted lines.

most constant. Copolymers synthesized by conventional copolymerization and isolated at low conversions contain considerably lower content of $PEO_{45}MEMA$ units compared to the initial monomer feeds which evidences lower reactivity ratio of the macromonomer. Similar tendency is observed in the RAFT process for the macromonomer-rich monomer feeds but in a lower extent.

3.4. Reactivity ratios of PEO_5MEMA and MAA in conventional and RAFT copolymerization

Reactivity ratios of PEO_5MEMA or $PEO_{45}MEMA$ (M_1) and MAA (M_2) were estimated by non-linear approach of error-in-variables model (EVM) [30,31]. An example of the 95% confidence regions for the reactivity ratios in conventional free-radical and RAFT copolymerizations of PEO_5MEMA and MAA is shown in Fig. 7. The solid line is the joint confidence region of linear approximation, the dashed line is the joint confidence region of exact shape and approximate probability, and the star is the point estimate. From the similarity of the two joint confidence regions, both for conventional and RAFT processes, one can conclude that for these systems the linear approximation is adequate for correct evaluation of the reactivity ratios. Similar observations were made regarding the non-linearity of the parameters in confidence regions for the both systems PEO_5MEMA – MAA and $PEO_{45}MEMA$ – MAA, for the both processes – conventional and RAFT, and for various conversions of the monomers.

Determination of the content of residual monomers during copolymerization enabled us to calculate reactivity ratios of the monomers at various conversions. The 95% joint confidence regions for the reactivity ratios depicted in Fig. 8 from the data sets collected at different conversions during conventional free-radical copolymerization of PEO_5MEMA and MAA clearly overlap. It means that changes of reactivity ratios during copolymerization are negligible, i.e. reactivity ratios of these monomers should be considered constant up to monomer conversions 60%. Similar tendency is characteristic for the RAFT copolymerization of the same monomers (Fig. 8). However, 95% joint confidence regions for the reactivity ratios from the data obtained by RAFT copolymerization are apparently offset from the ellipsoids for conventional free-radical copolymerization. Nevertheless, the differences in the reactivity ratios of PEO_5MEMA and MAA deduced from the confidence regions in conventional free-radical and RAFT copo-

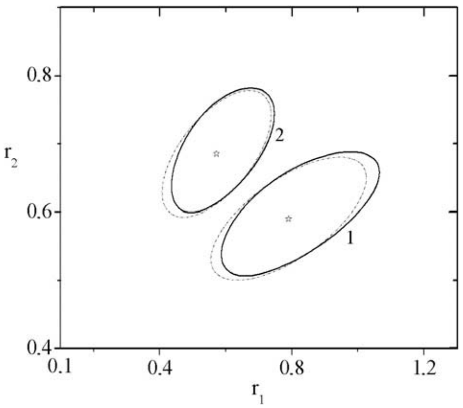


Fig. 7. The point estimate and 95% confidence regions for the reactivity ratios in conventional free-radical (1) and RAFT (2) copolymerizations of PEO_5MEMA – MAA using data sets collected at 20% conversion of the monomers. The solid line is the linear approximation, the dashed line is the exact shape, and the star is the point estimate.

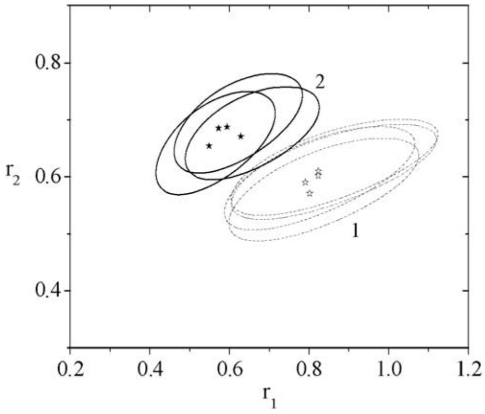


Fig. 8. The point estimate and 95% joint confidence regions (exact shape) for the reactivity ratios in conventional free-radical (1) and RAFT (2) copolymerizations of PEO_5MEMA – MAA. The joint confidence regions are depicted for the data sets collected at 10%, 20%, 40% and 60% conversions of the monomers.

lymerizations are minor and close to the experimental uncertainty. The analysis of the data presented in Fig. 8 and Table 2 suggests a small influence of the RAFT process on the composition of the copolymers of PEO_5MEMA and MAA.

Table 2
Reactivity ratios of PEO_xMEMA (M_1) and MAA (M_2) in conventional and RAFT copolymerizations.

Macromonomer	Method	r_1	r_2	f_1[b]
PEO_5MEMA	Conventional free-radical	0.81	0.60	0.68
	RAFT	0.59	0.68	0.44
$PEO_{45}MEMA$	Conventional free-radical	0.31[a]	1.83[a]	–
	RAFT	0.40	0.87	0.18

[a] At q = 10%.
[b] Azeotropic composition.

Reactivity ratios of both PEO_5MEMA and MAA in conventional free-radical copolymerization in D_2O/DO = 30/70 (w/w) were found to be lower than 1, and the reactivity of PEO_5MEMA was slightly higher than that of MAA (Table 2). This is in fairly good agreement with the data published earlier where copolymerization of the same monomers in DMSO and in water gave $r_1 = 1.02$, $r_2 = 0.71$ and $r_1 = 1.02$, $r_2 = 1.03$, respectively [23,24]. The differences between reactivity ratios determined in the present study and before can be easily explained by the solvent effect which is known to play significant role in copolymerization of ionogenic monomers [28]. Referring to the values of r_1 and r_2 for conventional free-radical copolymerization of PEO_5MEMA and MAA (Table 2), azeotropic point of the monomer feed is at 68 mol% of PEO_5MEMA which explains relatively small variation in instantaneous composition of copolymers synthesized from the monomer feeds PEO_5MEMA:MAA = 80:20 mol% and PEO_5MEMA:MAA = 50:50 mol% (Fig. 5).

In the RAFT copolymerization the reactivity ratio of PEO_5MEMA slightly decreased while reactivity ratio of MAA scarcely increased compared to conventional free-radical copolymerization of the same monomers (Fig. 8, Table 2). Apparent reactivity ratios of PEO_5MEMA and MAA in RAFT copolymerization shift azeotropic point of the monomer feed to 44 mol% of PEO_5MEMA making the monomer feed PEO_5MEMA:MAA = 50:50 mol% very suitable for the synthesis of copolymers with low chemical polydispersity (Fig. 5).

3.5. Reactivity ratios of $PEO_{45}MEMA$ and MAA in conventional and RAFT copolymerization

Fig. 9 shows joint confidence regions for the reactivity ratios in conventional free-radical and RAFT-mediated copolymerizations of $PEO_{45}MEMA$ and MAA using data sets collected at different conversions of the monomers. Joint confidence regions for the reactivity ratios in conventional free-radical copolymerizations are evidently shifted to-

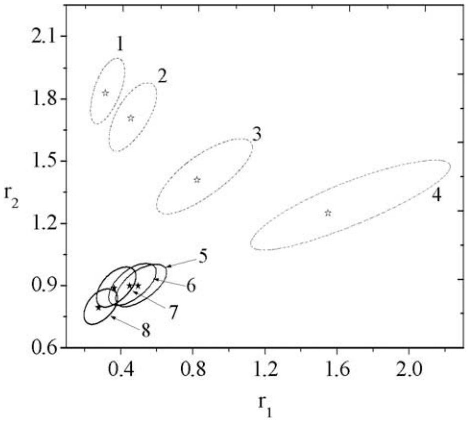


Fig. 9. The point estimate and 95% joint confidence regions (exact shape) for the reactivity ratios in conventional free-radical (1–4) and RAFT (5–8) copolymerizations of $PEO_{45}MEMA$ – MAA. The joint confidence regions are depicted for the data sets collected at 10% (1, 5), 20% (2, 6), 40% (3, 7) and 60% (4, 8) conversions of the monomers.

wards higher values of r_1 and lower values of r_2 at higher conversion of the monomers. The joint confidence regions from the data sets collected at different conversions are not overlapping and in sufficient distance from each other proving with the confidence that reactivity ratios of $PEO_{45}MEMA$ and MAA are changing during conventional free-radical copolymerization. Changes in reactivity ratio of the macromonomer $PEO_{45}MEMA$ are very large (from $r_1 = 0.31$ at 10% conversion to $r_1 = 1.55$ at 60% conversion) while changes in r_2 are less but also significant (from $r_1 = 1.83$ at 10% conversion to $r_1 = 1.25$ at 60% conversion).

Inspection of the joint confidence regions for the reactivity ratios in the RAFT copolymerizations of the same monomers shows only small differences among the data sets collected at different conversions (Fig. 9). The joint confidence regions are overlapped in this case, with a small trend towards lower values of r_1 at higher conversions. Thus, alteration of the reactivity ratio of the macromonomer $PEO_{45}MEMA$ with conversion is entirely opposite for conventional and RAFT copolymerizations but the effect is difficult to quantify with confidence in the RAFT process.

In spite of copolymerization technique (conventional or RAFT), the reactivity ratio of $PEO_{45}MEMA$ was found to be lower than that of MAA, except at high conversion (60%) in conventional copolymerization (Table 2). Obviously, it is also lower than the reactivity ratio of the macromonomer PEO_5MEMA. Low reactivity ratios of the methacrylate macromonomers are in contrast to the copolymerization of methyl methacrylate (MMA) with MAA (M_2) where the values $r_1 = 2.05$ and $r_2 = 0.70$ were reported [28]. Lower activity of the macromonomers PEO_nMEMA under copolymerization with MAA compared to the low-molecular methacrylate MMA might be expected because of steric hindrance when PEO_5MEMA or $PEO_{45}MEMA$ approaches to the growing radical and, especially, to the macromonomer end-capped radical.

According to the values of r_1 and r_2 for the RAFT copolymerization of $PEO_{45}MEMA$ and MAA, the azeotropic composition of the monomer feed is between 15 and 22 mol% of $PEO_{45}MEMA$. Vicinity to azeotropic point explains invariability of the copolymer composition with conversion under copolymerization of the monomer feed $PEO_{45}MEMA$:MAA = 20:80 mol%. Narrow composition distribution of the comb copolymers synthesized from the macromonomer-rich monomer feeds is predetermined by two opposite effects which compensate each other: (1) faster consumption of more active MAA which results in a drift in the copolymer composition with conversion toward higher content of $PEO_{45}MEMA$; (2) decreased reactivity ratio of the macromonomer at higher conversion which results in a drift in the copolymer composition toward lower content of $PEO_{45}MEMA$.

One should notice that the graft copolymers of $PEO_{45}MEMA$ and MAA prepared by free-radical process are heterogeneously branched. Because of lower reactivity ratio of $PEO_{45}MEMA$ compared to that of MAA (Table 2) and faster consumption of the latter, the copolymer generated at the early stage of the copolymerization has apparently lower density of PEO side chains than that generated at the later stage. In the RAFT process, where all chains propagate simultaneously, every polymer chain has similar branching structure. Because of lesser difference in reactivity ratios of the monomers (Table 2) and, especially, "compensating" effect related to alteration in reactivity ratio of the macromonomer with conversion, the distribution of branch spacing in the RAFT copolymers of $PEO_{45}MEMA$ and MAA is almost homogeneous. The above statement is evidently demonstrated by negligible variation in instantaneous copolymer composition with conversion regardless composition of the initial monomer feed (Fig. 6 B).

A difference in reactivity ratios of $PEO_{45}MEMA$ and MAA in conventional and RAFT copolymerization could be explained by different mechanisms of these polymerization processes. In conventional free-radical copolymerization, the polymer chains begin continually, and the chain growth is irreversibly interrupted because of termination reactions. Permanently increasing concentration of the copolymer affects viscosity of the reaction medium which increases fast with conversion changing mobility of the macromonomer. As it is addressed by Tsukahara et al. [44], a PEO macromonomer in viscous media has a tendency to intertwine with the propagating graft copolymer backbone, and that drifts reactivity ratios of the monomers to become similar. Data of Fig. 9 confirm the above considerations: r_1 increases and r_2 decreases with conversion becoming much closer to each other.

Under RAFT copolymerization, polymer chains grow slowly during all the process, and the viscosity remains relatively low until high degree of conversion. Thus the effect related to intertwining of grafted and free PEO chains could be negligible.

Usually, reactivity ratio of a low molecular comonomer in controlled radical copolymerization with a macromonomer is lower compared to the conventional free-radical copolymerization since in ATRP or RAFT processes the frequency of the monomer addition to a polymer chain is small enough, and the diffusion control effect on a macromonomer becomes less important [2,3]. This tendency was confirmed by copolymerization of $PEO_{45}MEMA$ and MAA where reactivity ratio of MAA in the RAFT process was indeed lower (Table 2). In contrast, reactivity ratio of MAA in the RAFT copolymerization with PEO_5MEMA was higher compared to the conventional free-radical copolymerization. Small influence of the RAFT process on reactivity ratios of PEO_5MEMA and MAA indicate that behavior of PEO_5MEMA in copolymerization is similar to that of low-molecular methacrylates and differ from typical macromonomers.

4. Conclusions

Differences in kinetics of conventional free-radical and RAFT-mediated copolymerizations of the poly(ethylene oxide) substituent containing macromonomers, PEO_5MEMA and $PEO_{45}MEMA$, with methacrylic acid (MAA) were evaluated by the use of ^1H NMR spectroscopy for the analysis of residual monomers. Reactivity ratios of PEO_5MEMA and MAA estimated by non-linear approach of error-in-variables model and presented as joint confidence regions were constant during conventional free-radical and RAFT copolymerizations of the above monomers but were slightly affected by the RAFT process. Reactivity ratio of $PEO_{45}MEMA$ was lower than that of PEO_5MEMA and varied during copolymerization: obviously increased with conversion in conventional free-radical copolymerization and slightly (without confidence) decreased in the RAFT process. RAFT copolymerization of $PEO_{45}MEMA$ and MAA enabled to synthesize comb copolymers with low composition distribution and more homogeneous distribution of PEO side chains along the mainchain. Under copolymerization with MAA, $PEO_{45}MEMA$ behaved like typical macromonomer with appropriate steric hindrance while the behavior of PEO_5MEMA was similar to that of a low-molecular methacrylate.

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