VILNIUS UNIVERSITY

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SYNTHESIS OF POLYELECTROLYTES CONTAINING POLY(ETHYLENE OXIDE) SIDE CHAINS BY LIVING RADICAL POLYMERIZATION

Summary of doctoral dissertation

Physical Sciences, Chemistry (03P)

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The scientific work was carried out in 2005-2009 at Vilnius University, Faculty of Chemistry, Department of Polymer Chemistry.

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VILNIAUS UNIVERSITETAS

Tatjana Krivorotova

POLIETILENOKSIDO ŠONINES GRANDINES TURINČIŲ POLIELEKTROLITŲ SINTEZĖ GYVYBINGOSIOS RADIKALINĖS POLIMERIZACIJOS METODAIS

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1. INTRODUCTION

Relevance of the work. The development in polymer technology is an indispensable building stone to cope with the technological challenges of the near future in all fields of science and technology, from domestic/food/personal care/ agriculture applications to microelectronics, automobile industry, and biomedical sciences. Depending on particular needs for a given application, new polymeric materials have to satisfy certain requirements in terms of processability, resistance to environment, cost, and specific performance aspects, such as mechanical, optical, surface, electrical, and thermal properties. Therefore, more and more demanding new technologies have boosted in the last decades the efforts of researchers to develop polymerization tools in order to obtain advanced polymeric structures and architectures. Particularly, the ability to control the macromolecular architecture becomes increasingly important. This includes, e.g., the control of molecular masses, polydispersities, tacticities, and terminal functional groups. A second crucial step is a deep understanding of the structure – properties relationships, in order to design tailor-made macromolecules with precise properties and performances.

Although the controlled/living polymerization (CRP) processes were realized in just the last 15 years, these techniques are already finding application in the commercial production of many new materials. A few examples of such materials already in production are acrylic copolymers with low PDI which allow preparing high-solid industrial coatings (Ciba), moisture-curable telechelic polyacrylates (Kaneka), although it is anticipated that many more specialty products will become available in the relatively near future. Thus, CRP has a very bright future, and it is anticipated that many new products will be introduced to the market within the next several years. The annual value of materials made by CRP was recently projected to reach as high as $20 billion, corresponding to ~10 % of all materials prepared by conventional radical polymerization

The tolerance that CRP processes show toward functional groups allows for the prolific production of a vast array of statistical, segmented (blocks and graft), periodic (mostly alternating), and gradient copolymers. In addition to materials prepared by one specific CRP technique, many are prepared by a combination of radical polymerization and other techniques.

The CRP of macromonomers is one of the most useful ways to prepare graft copolymers. It allows control over the molecular weight of a backbone and side chains, as well as over the average number of side chains. However, with the macromonomer method, the distribution of the spacing of the side chains cannot be entirely controlled. The spacing distribution of branches is determined by the reactivity ratios of the macromonomer and the low molecular weight comonomer.

The main aim of this work was to synthesize and study polyelectrolyte brushes containing charged poly(meth)acrylate backbone and poly(ethylene oxide) (PEO) side chains by living radical polymerization.

The objectives of the research are the following:

1. to study statistical copolymerization of PEO macromonomers differing in PEO chain length, with methacrylic (MAA) acid by conventional free-radical and RAFT methods;
2. to synthesize amphiphilic block copolymers by successive RAFT polymerization of lauryl methacrylate (LMA) and poly(ethylene oxide) monomethyl ether methacrylates (PEO_nMEMA) (n = 5, 45) or MAA and study their properties;
3. to synthesize and study cationic brush-on-brush polyelectrolytes with very high density of PEO side chains;
4. to study adsorption of cationic brush-on-brush polyelectrolytes on silica surfaces.

Scientific novelty and practical value of the work. A method to study copolymerization of PEO macromonomers was developed based on an analysis of residual monomers in the reaction mixture during copolymerization by the use of ^{1}H NMR spectroscopy *in situ*. Statistical copolymerization of methacrylic acid with PEO substituent containing macromonomers differing in PEO chain length was studied by conventional free-radical and RAFT methods for the first time. Amphiphilic non-ionic block copolymers of poly(lauryl methacrylate) and $PPEO_nMEMA$, and amphiphilic anionic block copolymers of poly(lauryl methacrylate) and poly(methacrylic acid) were prepared by the RAFT method, and their aggregation in aqueous and THF solutions were studied. Cationic brush-on-brush polyelectrolytes with very high density of PEO side chains were synthesized for the first time by ATRP, and their adsorption on negatively charged silica surfaces was studied. The novel brush-on-brush polyelectrolytes are promising candidates for applications requiring good colloidal stability and they also are promising as lubricants in aqueous solutions.

The results presented in the dissertation enable to defend the following most important ***statements***:

- ✓ RAFT copolymerization of PEO methacrylates results in brush copolymers with narrow MWD and almost homogenous distribution of side chains.
- ✓ Cationic brush-on-brush polyelectrolytes with very high density of PEO side chains adsorb forming highly hydrated layers and drastically decrease friction forces between coated surfaces.

Approbation of the research results. The results of the research were presented in 13 scientific publications including 3 papers in the journals from the ISI Web of Science list. The results of the work have also been reported in 8 international conferences.

Structure of the dissertation. The dissertation consists of introduction, three chapters, conclusions, list of references (204 entries) and the list of original scientific publications. The material of the dissertation is presented in 137 pages, including 17 schemes, 34 figures and 15 tables.

2. EXPERIMENTAL

Main materials. Poly(ethylene oxide) monomethyl ether methacrylate (M_n 300) (PEO_5MEMA), lauryl methacrylate (LMA) and cupper (I) chloride from Aldrich were 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`-Bipyridyl (Bpy) and 1,1,4,7,10,10-*N,N′,N″,N‴*-hexamethyltriethylenetetramine (HMTETA) were obtained from Aldrich. Synthesis of 2-(2-bromopropionyloxy)ethyl acrylate (BPEA), tris(2-(dimethylamino)ethyl)amine (Me_6TREN) and S-methoxycarbonylphenylmethyl dithiobenzoate (MDB) was carried out by known methods in our laboratory.

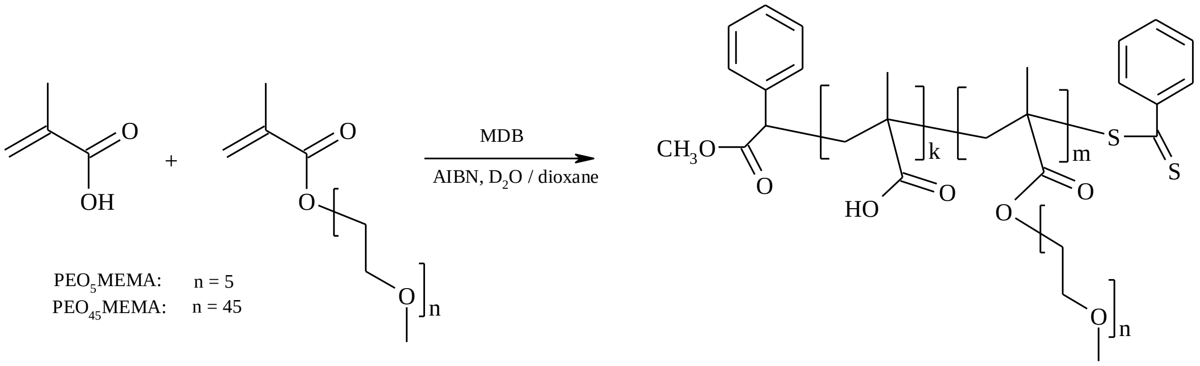
Methods. (Co)polymerization kinetics was examined using ^{1}H NMR spectroscopy. The NMR spectra were acquired on UNITY INOVA VARIAN spectrometer at 300 MHz and 29ºC. Solution properties of diblock copolymers have been studied by dynamic (DLS) and static (SLS) light scattering using an ALV instrument equipped with a 22 mW He–Ne laser. 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 ml), separating in the range of molecular weights approximately 400–1 10^7 g mol^{-1}. 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. Acetate buffer was used as a mobile phase at flow-rate 0.75 cm^3/min for statistical copolymers, and THF with the flow rate 0.5 ml/min was the mobile phase for PLMA and block copolymers. The data were accumulated and processed using the Astra and triSEC software.

3. RESULTS AND DISCUSSION

3.1. Conventional free-radical and RAFT copolymerization of PEO macromonomers with MAA

Conventional free-radical and RAFT copolymerization of PEO_5MEMA 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. Kinetics of copolymerization was studied by the use of ^{1}H NMR spectroscopy for an analysis of residual monomers which enabled to follow, besides others, copolymerization of the macromonomer-rich monomer feeds. 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 (Fig.1).

Kinetic curves of consumption of PEO_nMEMA and MAA during copolymerization were obtained by nonlinear 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.



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

Copolymers of PEO$_5$MEMA or PEO$_{45}$MEMA and MAA were synthesized in the mixture of D_2O and dioxane (30/70, wt/wt) at 80ºC, the molar ratio [M]/[AIBN] being at 200, and the molar ratio [MDB]/[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.

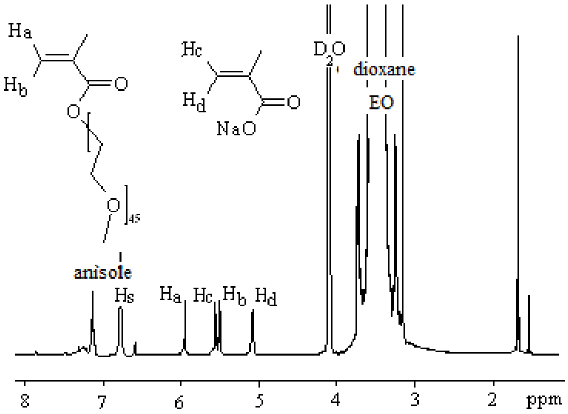


Fig. 1. ^{1}H NMR spectrum of the reaction mixture recorded before RAFT copolymerization of PEO$_{45}$MEMA and MAA (50/50, mol%)

A comparison of semilogarithmic kinetic plots for the RAFT copolymerization of PEO$_5$MEMA and MAA 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. Pseudo-first-order plots for the copolymerization of PEO$_{45}$MEMA and MAA stopped to be linear after around 6 hrs (Fig. 2) 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. The role of termination reactions in copolymerization of $PEO_{45}MEMA$ was manifested by leveling-off the conversion curves (Fig. 2B).

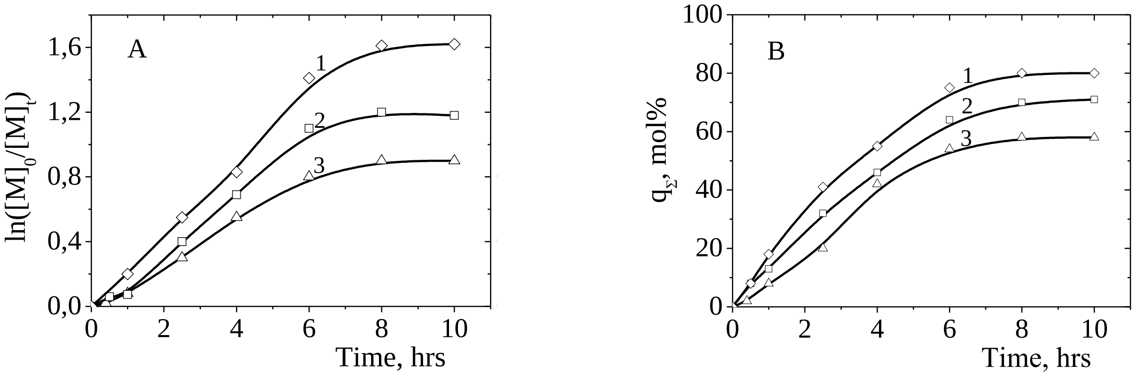


Fig. 2. Semilogarithmic kinetic plots (A) and conversion curves (B) for the RAFT copolymerization of $PEO_{45}MEMA$ and MAA. Initial monomer feed, mol%, $[PEO_{45}MEMA]/ [MAA]$ = 80/20 (1, 4), 50/50 (2, 5) and 20/80 (3, 6)

MWD curves of $PEO_{45}MEMA$ and MAA copolymers synthesized by conventional free-radical and RAFT methods are shown in Fig. 3. 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. 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.

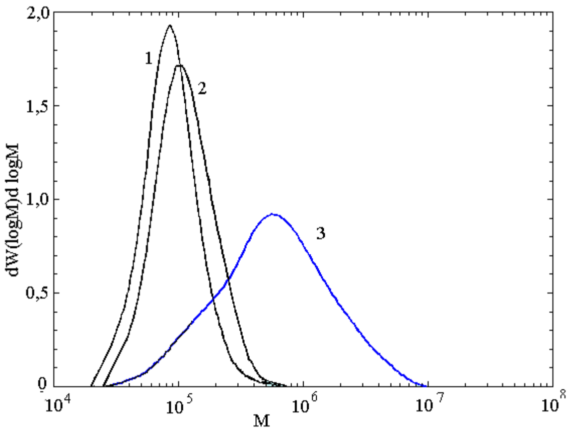


Fig. 3. MWD of random copolymers $PEO_{45}MEMA$ – MAA synthesized by RAFT (1, 2) and conventional free-radical (3) processes. Initial monomer feed $[PEO_{45}MEMA]/[MAA]$ = 50/50 mol%, overall monomer conversion q_{Σ} 47 mol% (1), 69 mol% (2) and 68 mol% (3)

Variation in instantaneous copolymer compositions with conversion under conventional and RAFT copolymerization of PEO_5MEMA and MAA is small and similar. 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.

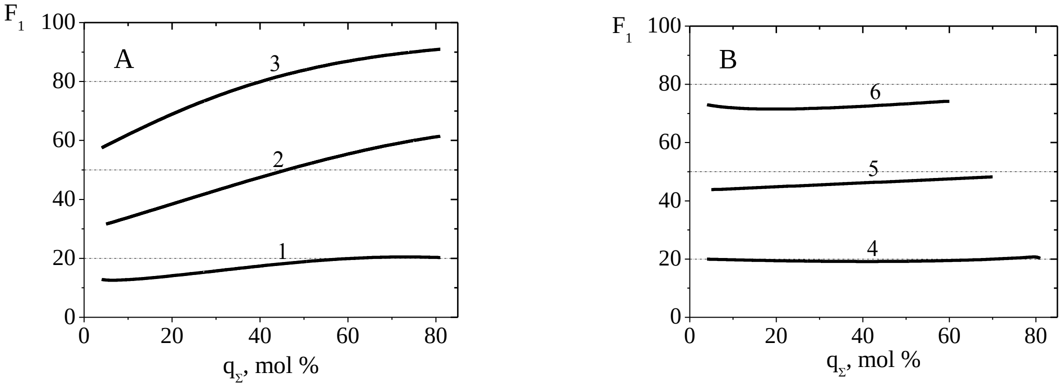


Fig. 4. Variation of instantaneous copolymer composition F_1 ($PEO_{45}MEMA$, mol%) with conversion of the monomers q_Σ under conventional (A) and RAFT (B) copolymerization. Initial monomer feeds, mol%, $PEO_{45}MEMA/MAA$ = 20/80 (1, 4), 50/50 (2, 5) and 80/20 (3, 6) are indicated by dotted lines.

In contrast, variation in instantaneous copolymer compositions with conversion between conventional and RAFT copolymerization of $PEO_{45}MEMA$ macromonomer differ substantially (Fig. 4). Instantaneous copolymer composition in conventional free-radical copolymerization changes with conversion leading to copolymers with considerable composition distribution (Fig. 4). Contrarily, composition of the copolymers synthesized by the RAFT method and isolated at various monomer conversions is almost 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.

Determination of the content of residual monomers during copolymerization enabled to calculate reactivity ratios of the monomers at various conversions. 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. The joint confidence regions for the reactivity ratios in conventional free-radical and RAFT copolymerizations of PEO_5MEMA (n = 5, 45) and MAA are shown in Fig. 5.

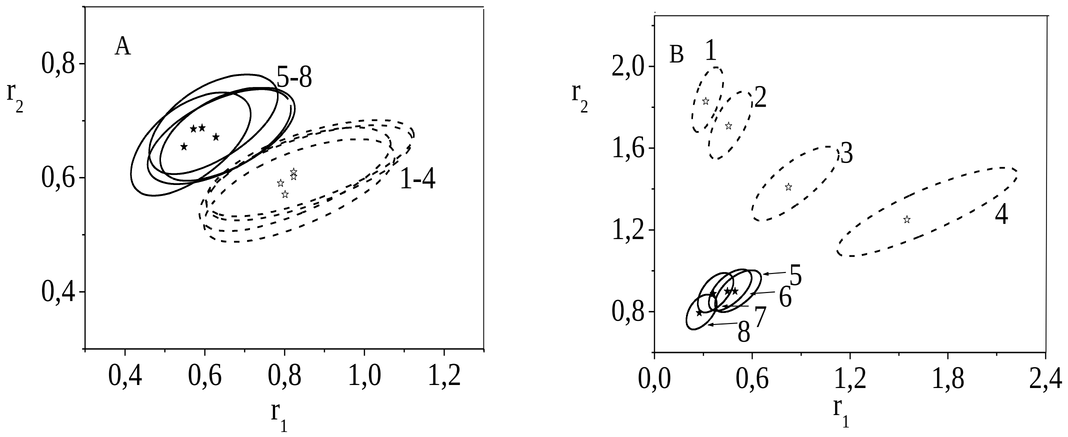


Fig. 5. The point estimate and 95% joint confidence regions (exact shape) for the reactivity ratios in conventional free-radical (1-4) and RAFT (5-8) copolymerizations of PEO_5MEMA – MAA (A) and $PEO_{45}MEMA$ – MAA (B). The joint confidence regions are depicted for the data sets collected at 10% (1, 5), 20% (2, 6), 40% (3, 7) and 60% (4, 8) conversions of the monomers

The 95% joint confidence regions for the reactivity ratios 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%.

Reactivity ratios of both PEO_5MEMA and MAA in conventional free-radical copolymerization in D_2O/dioxane = 30/70 (wt/wt) were found to be lower than 1, and the reactivity of PEO_5MEMA was slightly higher than that of MAA (Table 1).

Table 1. Reactivity ratios of PEO_nMEMA (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.

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. 5, Table 1). 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.

Joint confidence regions for the reactivity ratios in conventional free-radical copolymerizations of $PEO_{45}MEMA$ and MAA are evidently shifted towards higher values of r_1 and lower values of r_2 at higher conversion of the monomers (Fig. 5 B). 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. 5). 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.

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 – faster consumption of more active MAA and decreased reactivity ratio of the macromonomer at higher conversions.

3.2. Synthesis of amphiphilic diblock copolymer brushes by successive RAFT polymerization

Synthesis of amphiphilic diblock copolymers was started by RAFT polymerization of lauryl methacrylate (LMA), and the synthesized PLMA served as a macro chain transfer agent (CTA) for the RAFT polymerization of other monomers.

In order to ascertain control of polymerization and get PLMA with desirable chain length, RAFT polymerization of LMA was done at different ratios of the monomer, initiator AIBN and MDB as a RAFT CTA. Kinetics of the RAFT polymerization of LMA was followed by the use of ^{1}H NMR spectroscopy *in situ*. The signals of aromatic protons of MDB at 7.2–7.9 ppm present in the spectra of PLMA unambiguously evidenced that the process proceeded through the RAFT mechanism, and allowed calculation of molecular weight of PLMA. RAFT polymerization of LMA was rather fast giving over 60% monomer conversion within 1 hr at [CTA]/[AIBN] = 2.5, and within 4 hrs at [CTA]/[AIBN] = 4 (Fig. 8, B). At 4-fold excess of MDB over AIBN, kinetic plot in semilogarithmic coordinates was linear (Fig. 8, A) demonstrating steady-state radical concentration under RAFT polymerization of LMA. Significantly higher rate of polymerization at 2.5-fold excess of MDB compared to 4-fold excess may suggest that conventional free-radical polymerization operates in parallel with the RAFT process in this case. This hypothesis was confirmed by SEC measurements.

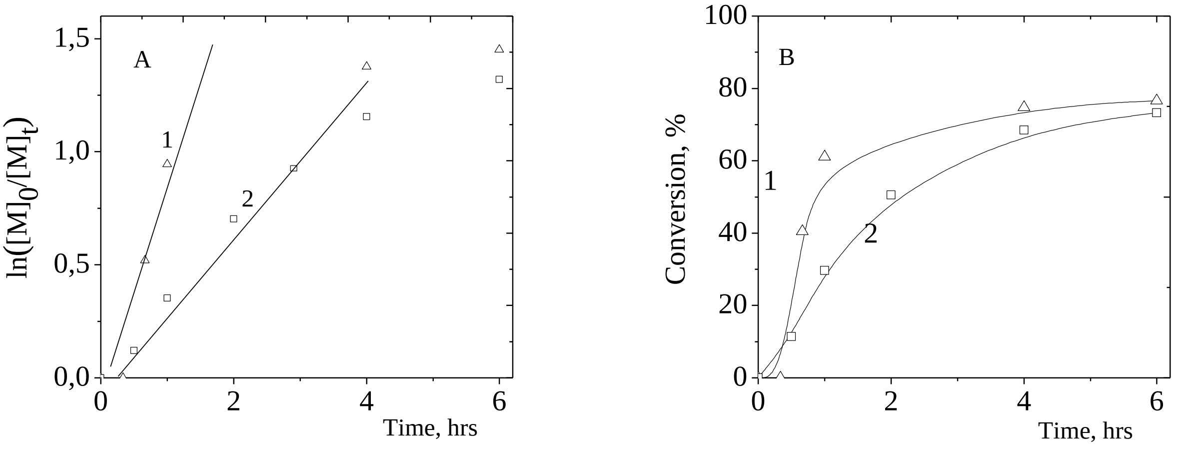


Fig 6. Semilogarithmic kinetic plots (A) and conversion curves (B) for polymerization of LMA in dioxane at 80ºC in the presence of MDB. $[LMA]_0$ = 1.7 mol/l, $[LMA]_0/[AIBN]_0$ = 300, $[CTA]_0/[AIBN]_0$ = 2.5 (1) and 4 (2)

PLMA synthesized at [CTA]/[AIBN] = 4 was characterized by unimodal and sharp elution curve which was consistent with excellent control of the process. In contrast, the elution curve of PLMA synthesized at [CTA]/[AIBN] = 2.5 was bimodal with the second peak at low elution volume. The presence of high molecular fraction in the last-mentioned polymer evidenced that two parallel processes – RAFT and conventional free-radical polymerization – took part in parallel. Obviously, radical polymerization of LMA is well controlled by the RAFT chain transfer agent MDB if the ratio of CTA to AIBN approaches 4. Furthermore, it was determined by varying concentration of the initiator that the optimal ratio [MDB]/[AIBN] depended on the ratio [LMA]/[AIBN] being lower at lower concentration of the initiator.

RAFT polymerization of LMA in bulk and in dioxane was done at the same conditions. Rate of polymerization in bulk was rather high giving over 75% conversion of the monomer within 1 hr. Control of the process was sufficient up to monomer conversion ca 90% (during 2 hrs). Rate of the RAFT polymerization in dioxane was apparently lower, and linearity in semilogarithmic coordinates showed good control over the process up to monomer conversion 70% (during 7 hrs). SEC measurements confirmed effectiveness of the RAFT polymerization of LMA both in bulk and dioxane (Table 2).

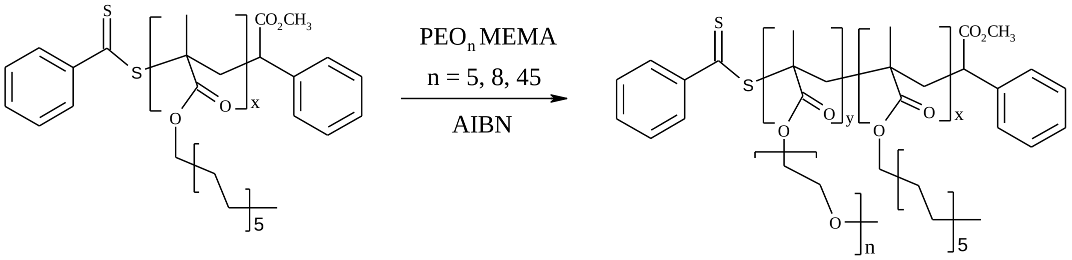
Three samples of PLMA which characteristics are given in Table 2 were used as macro-CTA in the synthesis of diblock copolymers PLMA-*b*-PPEO$_5$MEMA.

Table 2. RAFT polymerization of LMA at different ratios of the monomer, initiator and MDB. [M] = 1.7 mol/l, T = 80ºC, t = 7 hrs

No	$[LMA]_0$/ $[AIBN]_0$	$[CTA]_0$/ $[AIBN]_0$	q, %	$M_n \cdot 10^{-3}$				M_w/M_n	DP (NMR)
				SEC	UV	NMR	Theor*		
1	300	4	78	15.0	9.3	15.2	10.2	1.08	60
2	600	2.5	55	25.5	28.2	31.1	34.0	1.19	122
3**	600	2.5	95	49.2	62.6	66.0	58.0	1.08	260

* $M_n(theor) = \frac{[LMA]_0}{[MDB]_0} \cdot q \cdot M_{LMA} + M_{MDB}$;

** in bulk.



Scheme 2. Synthesis of amphiphilic diblock copolymers via the RAFT process

Several well-defined diblock copolymers PLMA-*b*-PPEO$_5$MEMA were successfully prepared and characterized in the present work (Scheme 2, Table 3). The length of the second block was well predetermined by the ratio of the macromonomer to macro-CTA if the first block was short (P(LMA)$_{60}$, Table 3, run 2). The use of longer block of PLMA (P(LMA)$_{122}$, Table 3, runs 3, 4) resulted in 1,5 – 2 times longer block of P(PEO$_5$MEMA)$_y$ than expected. Longer chains formed during controlled radical polymerization compared to calculated values give a message that the ratio of the macromonomer to macro-CTA is changed, i.e. PLMA as a macro-CTA is partly inactivated. The longest PLMA used as a macro-CTA ((PLMA)$_{260}$) showed good livingness, and the length of the block of PPEO$_5$MEMA was close to the expected value (at low ratio of the macromonomer to macro-CTA, Table 3, run 5) or shorter (at high ratio of the macromonomer to macro-CTA, Table 3, run 6).

Table 3. Characteristics of diblock copolymers P(LMA)$_x$-b-P(PEO$_x$MEMA)$_y$ synthesized from macro-CTA PLMA. [PEO$_x$MEMA] = 18% (in toluene), T = 80ºC, t = 6 hr

[PEO$_x$MEMA] / [AIBN]		[PLMA] / [AIBN]	[AIBN]·10^6, mol	q, mol%	$M_n \cdot 10^{-3}$		M_w/M_n	Block copolymer
					SEC	NMR		
1*	300	3	9.7	gel	-	-	-	P(LMA)$_{60}$-*b*-P(PEO$_5$MEMA)$_x$
2	300	3	9.7	82	31.1	36.3	1.10	P(LMA)$_{60}$-*b*-P(PEO$_5$MEMA)$_{67}$
3	1800	2	45	53	308	324	1.20	P(LMA)$_{122}$-*b*-P(PEO$_5$MEMA)$_{970}$
4	2500	4	1.4	74	245	263	1.19	P(LMA)$_{122}$-*b*-P(PEO$_5$MEMA)$_{776}$
5	200	2	9.5	88	88	89	1.29	P(LMA)$_{260}$-*b*-P(PEO$_5$MEMA)$_{77}$
6	2000	2	9.5	95	144	142	1.28	P(LMA)$_{260}$-*b*-P(PEO$_5$MEMA)$_{254}$
7	300	4	1.6	41	62	68	1.14	P(LMA)$_{260}$**

* [PEO$_x$MEMA] = 26 % in toluene; ** polymerization of PEO$_{45}$MEMA

An attempt was made to synthesize well defined diblock copolymers containing longer PEO side chains at hydrophilic block. For that, PEO$_{45}$MEMA was used instead of PEO$_5$MEMA for the construction of the second block (Table 3, run 8). An attempt to prepare diblock copolymers P(LMA)-*b*-P(PEO$_{45}$-MEMA) was unsuccessful. SEC traces of the reaction mixture containing PLMA as a macro-CTA, PEO$_{45}$MEMA and AIBN remained identical after 2 and 4 hours showing the peaks attributed to PLMA and PEO$_{45}$MEMA only, even at relatively high AIBN concentration. One of the two major factors affecting low reactivity of PEO$_{45}$MEMA is the diffusion control associated with the large size of the macromonomer. The other is related to phase separation occurring in the polimerization mixture containing PEO$_{45}$MEMA and PLMA.

A series of P(LMA)$_x$-*b*-P(MAA)$_z$ diblock copolymers was synthesized by RAFT polymerization of MAA from macro-CTA PLMA (Table 4). RAFT polymerization of MAA was dependent on molar ratio [PLMA]/[AIBN] being optimal at the ratio from 2 to 3. A loss of molecular weight control was observed at high ratio [MAA]/[AIBN] (Table 4, run 4). In the case, when significant part of the macro-CTA was dead, bimodal SEC traces were obtained, and the PDI values were much higher even at low conversion (Table 4, 5 run). High ratio [MAA]/[AIBN] or high molecular weight of macro-CTA lead to an increase in viscosity, especially at high conversions, which resulted in partial loss of polymerization control.

Table 4. Characteristics of diblock copolymers P(LMA)$_x$-b-P(MAA)$_z$ synthesized from macro-CTA P(LMA)$_x$. [P(LMA)$_x$+MAA] = 20%, T = 80°C, t = 6 hrs

No	[MAR]$_0$/ [AIBN]$_0$	[PLMA]$_0$/ [AIBN]$_0$	[AIBN]$_0$ 10^6, mol	q, mol%	$M_n \cdot 10^{-3}$		M_w/M_n	Block copolymer
					SEC	PT ***		
1	300	3	11.3	73	35.0	36.0	1.23	P(LMA)$_{122}$-*b*-P(MAR)$_{57}$
2	350	3	11.3	97	24.9	24.4	1.15	P(LMA)$_{60}$-*b*-P(MAR)$_{107}$
3	400	3	11.3	90	24.8	25.0	1.10	P(LMA)$_{60}$-*b*-P(MAR)$_{113}$
4	600	3	11.3	83	27.7	28.6	1.62	P(LMA)$_{60}$-*b*-P(MAR)$_{151}$
5	100	2	36.2	81	36.0	71.5	1.38	P(LMA)$_{260}$-*b*-P(MAR)$_{63}$

* – polymerization time 12 hrs; ** – polymerization time 24 hrs; *** potentiometric titration

Aggregation of amphiphilic diblock copolymers in aqueous and THF solutions was studied by DLS and SLS. Although solutions of P(LMA)$_{60}$-*b*-P(PEO$_5$MEMA)$_{67}$ and P(LMA)$_{260}$-*b*-P(PEO$_5$MEMA)$_{77}$ in THF were clear and transparent, DLS revealed the presence, alongside with individual macromolecules, micellar aggregates with hydrodynamic radius in the range 50 to 125 nm (Fig. 7). Aqueous solutions of these copolymers were opalescent and characterized by bimodal particles size distributions associated with small micelles (R_h = 50-60 nm) and large aggregates (R_h = 120-150 nm). Apparently, in aqueous solutions micelle-type aggregates are formed in which inner part (core) is composed of PLMA chains, and outer part (shell) of PPEO$_n$MEMA chains. THF is good (or satisfactory) solvent for both PLMA and PPEO$_n$MEMA chains which leads to less aggregation and allows the presence of both type chains alongside. The block copolymers P(LMA)$_x$-*b*-P(MAA)$_z$ also formed aggregates in water with similar hydrodynamic volumes to those of P(LMA)$_x$-*b*-P(PEO$_5$MEMA)$_y$. One characteristic feature of the last aggregates: if hydrophobic block is large (PLMA$_{260}$), their size doesn't depend on the length of the hydrophilic (ionogenic) block.

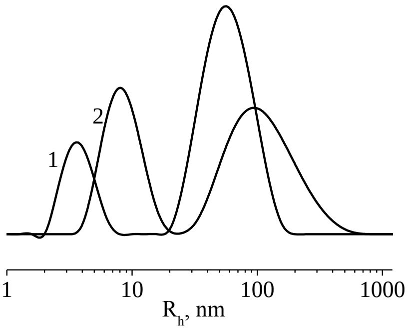


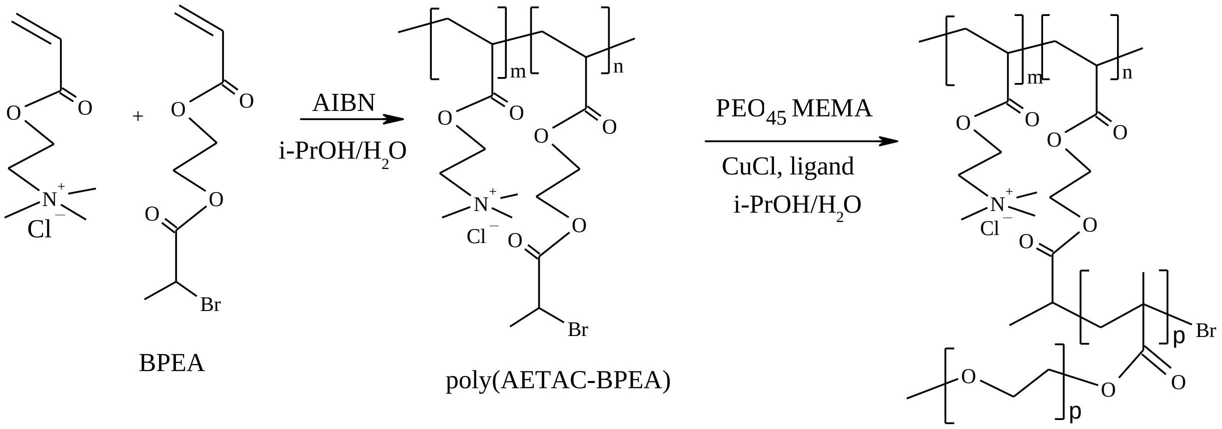
Fig. 7. Intensity average size distribution of the aggregates formed of diblock copolymers P(LMA)$_{60}$-b-P(PEO$_5$MEMA)$_{67}$ (1) and P(LMA)$_{260}$-b-P(PEO$_5$MEMA)$_{77}$ (2) in THF

The second virial coefficients determined by SLS of diblock copolymers in aqueous and THF solutions were small in most cases (except a series P(LMA)$_x$-*b*-P(MAA)$_z$ in THF) evidencing weak interaction of the segments of these copolymers with the solvents, i.e. the solvents hardly penetrated into core part of the aggregates. The ratio R_g/R_h and characteristic curvature of Zimm plots indicated that the aggregates of the diblock copolymers had the form of ellipsoids.

3.3. Synthesis and interfacial properties of novel cationic polyelectrolytes with brush-on-brush structure of PEO side chains

Cationic polyelectrolytes with brush-on-brush structure of PEO side chains were synthesized following a two-step strategy. First, conventional free-radical copolymerization of 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) and acryloxyethyl trimethylammonium chloride (AETAC) was carried out in the presence of AIBN. The obtained copolymer containing labile bromine in the BPEA units served as a macroinitiator for ATRP polymerization of another monomer. In the second step, PEO_{45}MEMA was grafted from the macroinitiator by an aqueous ATRP process resulting in brush-on-brush copolymers with very high density of PEO side chains (Scheme 3).

Free-radical copolymerization of BPEA and AETAC was carried out in a mixed water/isopropanol solvent where isopropanol served as both a co-solvent and a chain-transfer agent. The ^{1}H NMR spectrum of poly(AETAC–BPEA) is presented in Fig. 8. The ratio of the intensity of the signal at 3.7 ppm (I_1), which belongs to *N*-methylene protons in AETAC, to the intensity of the signals at 4.0-4.6 ppm (I_2) attributed to the sum of the protons of oxymethylene groups of BPEA and of AETAC gave the content of AETAC units in the copolymer, which, for this particular polymer, was equal to 86 mol%.



Scheme 3. Synthesis of cationic polyelectrolytes with very high content of PEO side chains by free-radical copolymerization of AETAC and BPEA followed by ATRP ''grafting from'' polymerization of PEO_{45}*MEMA*

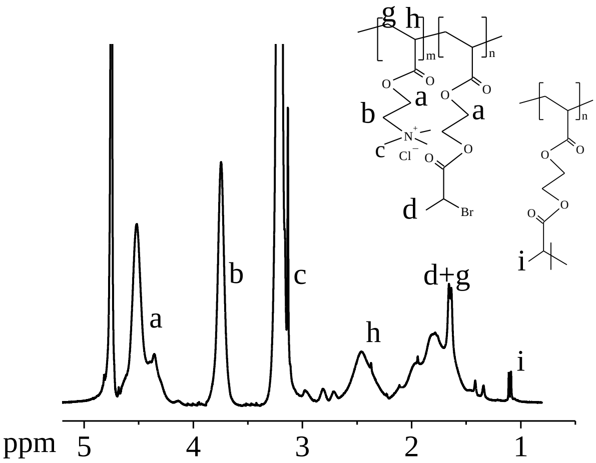


Fig. 8. ^{1}H NMR spectrum of the macroinitiator poly(AETAC–BPEA) containing 14 mol% of BPEA units

The signal from the methyl protons in geminal position relative to the bromine on pendent BPEA residues at 1.6 ppm is a direct evidence of the presence of labile bromine capable of initiating ATRP polymerization. The presence of the signal at 1.1 ppm assigned to protons in methyl groups that are pendent at a carbon–carbon chain means that a fraction of the bromine atoms is removed by a side reaction, e.g. chain transfer to monomer or polymer through abruption of bromine. Calculations based on the intensity of the signal at 1.1 ppm revealed that about 1/8 of the BPEA units in the copolymers did not contain bromine. Thus, the macroinitiator is a slightly branched copolymer of AETAC and BPEA in which initiating sites for ATRP polymerization is separated on average by 7 backbone units. Molecular weights of poly(AETAC–BPEA) determined by SEC are as follow: M_n = 19 200, M_w = 51 600 (Fig 9). Simple calculations based on number average molecular weight and copolymer composition gives a certain image of the macroinitiator: in average it contains nearly 100 monomeric units 12 of which are those carrying initiating sites.

Table 5 presents the results of ATRP polymerization of PEO_{45}MEMA using three different ligands for grafting from poly(AETAC–BPEA). The yield for the graft copolymers was high except for AETAC-50-*graft*-P(PEO_{45}MEMA) where the reaction time was apparently insufficient. It is obvious that ATRP polymerization using the ligand *Bpy* was slow but finally it resulted in grafts with the predicted length (see the sample AETAC-27-graft-P(PEO_{45}MEMA), compare the ratio [M]/[I] and DP). Similarly, the DP of the grafts coincides well with the molar ratio of PEO_{45}MEMA to the initiating sites of the macroinitiator under polymerization in the presence of HMTETA. The initiation system containing HMTETA is the most attractive one for grafting ATRP from the macroinitiator poly(AETAC–BPEA) in aqueous medium, since the reaction proceeds relatively fast even at room temperature. Grafting of PEO_{45}MEMA in the presence of Me_6TREN was less successful since it resulted in lower DP than predicted. Further, the solution obtained a russet colour due to disproportionation of the copper (I) complex with Me_6TREN, which often takes place in aqueous solutions.

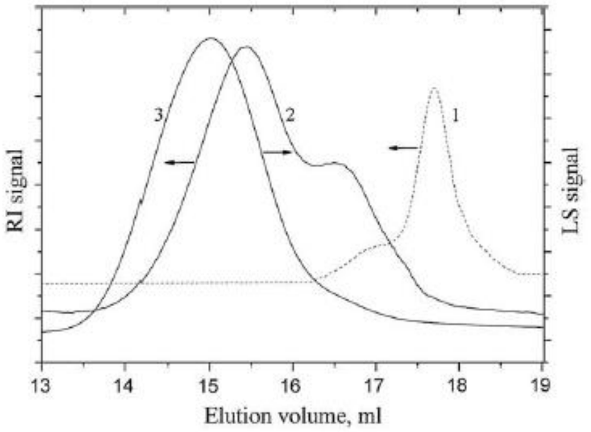


Fig. 9. SEC eluograms of poly(AETAC-BPEA) (1) and AETAC-27-graft-P(PEO_{45}MEMA) (2, 3) presented as RI (1, 2) and LS 90° (3) responses

Table 5. Synthesis of cationic polyelectrolytes with very high content of PEO side chains by aqueous ATRP of PEO_{45}MEMA under conditions of grafting from poly(AETAC-BPEA)

Abbreviation	$[M^a]_0/[I^b]_0$	$[CuCl]_0/[I^b]_0$	Ligand[c], $[L]_0/[I^b]_0$	T, °C	t, hrs	Yield %	AETAC, mol%	DP
AETAC-50-*graf*-P(PEO_{45}MEMA)	14	1.4	1; 2.8[d]	60	42	41	50	6
AETAC-27-*graf*-P(PEO_{45}MEMA)	16	1.4	1; 2.8[d]	60	168	94	27	16
AETAC-8-*graf*-P(PEO_{45}MEMA)	70	1.4	2; 1.4[d]	20	12	85	8	67
AETAC-17-*graf*-P(PEO_{45}MEMA)	42	1.4	3; 1.4[d]	40	48	77	17	31

[a] *Monomer PEO_{45}MEMA;*

[b] *Macroinitiator P(AETAC-BPEA), concentration of the initiating sites [I] = 0,07 mmol;*

[c] *Ligand: 1 – Bpy; 2 – HMTETA; 3 – Me_6TREN;*

[d] *Ratio of a ligand to the initiating sites of the macroinitiator.*

SLS measurements of AETAC-27-*graft*-P(PEO_{45}MEMA) gave M_w = 600 000 and the radius of gyration 24 nm. Molecular weights of the same copolymer determined by SEC are as follow: M_n = 490 000, M_w = 895 000. Although SEC gave nearly 1.5 times higher value of M_w compared to SLS, agreement between these two methods is fair, especially, keeping in mind brush structure of the copolymers and possible aggregation.

The adsorption of the AETAC-X-*graft*-P(PEO_{45}MEMA) (X = 8, 27) copolymers on silica was explored by QCM-D measurements. The low adsorption of AETAC-8-*graft*-P(PEO_{45}MEMA) on silica is likely due to the aggregation of this polymer in solution and the entropic penalty of confining the highly branched polymer at the interface. Contrarily, brush over brush with less PEO side chains and relatively higher content of charged segments AETAC-27-*graft*-P(PEO_{45}MEMA) has higher surface affinity than conventional random copolymer PEO_{45}MEMA-*st*-METAC-25. AETAC-27-*graft*-P(PEO_{45}MEMA) adsorbs on the silica surface from a 50 ppm solution, and the sensed mass is as high as 20 mg/m^2; for comparison, adsorption of PEO_{45}MEMA-*st*-METAC-25 on the silica surface from a 100 ppm solution resulted in a sensed mass of 12 mg/m^2. It was determined that adsorption of the copolymer AETAC-27-*graft*-P(PEO_{45}MEMA) formed a less rigid surface layer.

AETAC-27-*graft*-P(PEO_{45}MEMA) layers on silica showed favourable lubrication properties which was proved by studies using AFM colloidal technique. Adsorption of the polymer AETAC-27-*graft*-P(PEO_{45}MEMA) resulted in a complete suppression of the repulsive double-layer force, demonstrating that the charges within the layer fully compensated the silica surface charge. For comparison, the steric force observed for PEO_{45}MEMA:METAC-25 was more long-ranged and increased less strongly with decreasing surface separation than that obtained with AETAC-27-*graft*-P(PEO_{45}MEMA.

It was shown by direct force measurements that protective surface layers formed by AETAC-27-*graft*-PEO_{45}MEMA generated strongly repulsive steric forces, thus providing an effective barrier against flocculation. It was also shown that the adsorbed layer was sufficiently robust to withstand sliding experiments under a pressure up to 35 MPa. The friction force was very low, and the lubrication was characterized by a friction coefficient in the range of 0.02-0.06. Thus, the novel brush-on-brush polyelectrolytes are promising candidates for applications requiring good colloidal stability and they also are promising as lubricants in aqueous solutions.

CONCLUSIONS

1. Conventional free-radical and RAFT copolymerization of methacrylic acid (MAA) with poly(ethylene oxide) substituent containing methacrylate macromonomers, PEO_5MEMA and $PEO_{45}MEMA$, was studied for the first time. A method to study copolymerization of PEO macromonomers was developed based on an analysis of residual monomers in the reaction mixture during copolymerization by the use of ^1H NMR spectroscopy *in situ*.
2. During RAFT copolymerization of PEO_5MEMA and MAA, concentration of propagating radicals remained constant up to nearly full consumption of the monomers. Under RAFT copolymerization of $PEO_{45}MEMA$ and MAA carried out at an excess of the macromonomer, livingness of the system was lost at the monomer conversion ca 55 mol%. RAFT copolymerization of $PEO_{45}MEMA$ and MAA enabled to synthesize brush copolymers with low polydispersity (M_w/M_n <1,4), narrow composition distribution and more homogeneous distribution of PEO side chains.
3. Reactivity ratios of PEO_nMEMA and MAA in conventional free-radical and RAFT copolymerizations were estimated by non-linear approach of error-in-variables model. Reactivity ratios r_1 and r_2 calculated at various conversions of the monomers and presented in the form of joint confidence regions allowed estimating changes in reactivity of the macromonomers during copolymerization. Reactivity ratio of PEO_5MEMA was nearly constant during conventional free-radical and RAFT copolymerization but was 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 the conventional free-radical copolymerization and slightly (without confidence) decreased in the RAFT process.
4. RAFT polymerization of lauryl methacrylate (LMA) in the presence of *S*-methoxycarbonylphenylmethyl dithiobenzoate (MDB) as a RAFT CTA was studied in detail. It was shown that the ratio [MDB]:[AIBN] = 4 was optimal for livingness of the system but this ratio could be even lower at low concentration of the initiator. PLMA with low polydispersity (M_w/M_n = 1.08–1.19) and degree of polymerization DP 60 and 122 contained dormant dithiobenzene end groups and was useful as macro-

CTA. Livingness of some chains of PLMA with high molecular weight (M_n around 60 000, DP 260) was lost.

5. Two series of amphiphilic diblock copolymers PLMA-*b*-PPEO$_5$MEMA and PLMA-*b*-PMAA differing in molecular weight and length of hydrophobic and hydrophilic blocks were synthesized by the RAFT method using PLMA as a macro-CTA. If the ratio of the monomer to the initiator was not very high ([M]:[I] < 500), the length of the second block (molecular weight) was well predetermined by the ratio of the monomer to the macro-CTA, and polydispersity of the copolymers was low ($M_w/M_n < 1.3$). RAFT polymerization of PEO$_{45}$MEMA from PLMA as a macro-CTA failed.
6. Studies of amphiphilic diblock copolymers in aqueous and THF solutions by DLS and SLS revealed aggregation phenomena. Block copolymers PLMA-*b*-PPEO$_5$MEMA in THF exist in two forms: as individual macromolecules with hydrodynamic radius R_h 4–8 nm, and ellipsoid aggregates with hydrodynamic radius R_h 50–125 nm. In aqueous solutions, these copolymers form spherical aggregates associating 100–250 macromolecules; size distribution of these aggregates is bimodal and associated with small (R_h 50-60 nm) and large (R_h 120-150 nm) micelles. Block copolymers PLMA-*b*-PMAA formed aggregates in both water and THF, and the size of aggregates was independent on the length of the PMAA block when hydrophobic block was large.
7. Novel cationic copolymers with a brush-on-brush structure and very high density of PEO side chains were synthesized in which the PEO chains were located a distance away from the charged units of the backbone. These copolymers were prepared by ATRP polymerization of PEO containing macromonomer from cationic ATRP macroinitiator. High molecular weight copolymers (M_n over 500 000) with charge density from 8 to 50 mol% were synthesized.
8. Cationic brush-on-brush copolymers adsorbed to negatively charged surfaces in very thick layers (20 mg/m^2) containing over 80% of water. The adsorbed surface layers generated strongly repulsive steric forces and were sufficiently robust to withstand sliding experiments under a pressure up to 35 MPa. The friction force between two plates coated with the adsorbed layers was very low, and the lubrication was characterized by a friction coefficient in the range of 0.02-0.06. The novel brush-on-brush copolymers are promising candidates for applications requiring good colloidal stability and they also are promising as lubricants in aqueous solutions.

LIST OF ORIGINAL PUBLICATIONS

Papers in the journals from the ISI Master Journal list:

1. T. Krivorotova, R. Makuska, A. Naderi, P. M. Claesson, A. Dedinaite. Synthesis and interfacial properties of novel cationic polyelectrolytes with brush-on-brush structure of poly(ethylene oxide) side chains. *Eur. Polym. J.*, 2010, 46, 171–180.
2. T. Krivorotova, A. Vareikis, D. Gromadzki, M. Netopilík, R. Makuška. Conventional free-radical and RAFT copolymerization of poly(ethylene oxide) containing macromonomers. *Eur. Polym. J.,* 2010, 46, 546–556.
3. T. Krivorotova, E. Udrėnaitė, D. Gromadzki, R. Makuška. Synthesis of amphiphilic diblock copolymer brushes by successive RAFT polymerization of lauryl methacrylate and PEO-containing macromonomer. *Chemija*, 2010, 21, 63.

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1. T. Krivorotova, A. Vareikis, R. Makuška. Synthesis of ionogenic amphiphilic methacrylate terpolymers containing dodecyl- and poly(ethylene glycol) side chains. *Programme and Proceedings of Baltic Polymer Symposium*. Birini, Latvia, 2006, p. 36.
2. T. Krivorotova, A. Vareikis, R. Stupak, D. Mažeika, R. Makuška. Conventional free-radical and RAFT copolymerization of PEO containing macromonomer. *Polymer Chemistry and Technology: Proceedings of Scientific Conference Chemistry and Chemical Technology*. Kaunas, Lithuania, 2009, p. 88.
3. T. Krivorotova, J. Dumbaitė, D. Gromadzki, A. Vareikis, E. Udrėnaitė, R. Makuška. Synthesis of amphiphilic diblock copolymers by RAFT polymerization. *Baltic Polymer Symposium* 2009*: Programme and Proceedings of Baltic Polymer Symposium 2009.* Ventspils, Latvia, p. 72.

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1. T. Krivorotova, T. Kazlaitė, A. Vareikis, E. Udrėnaitė, R. Makuška. Synthesis of comb polyelectrolytes using RAFT polymerization technique. *Baltic Polymer Symposium: Programme and Book of Abstracts*. Druskininkai, Lithuania, 2007, p. 61.

2. T. Krivorotova, A. Vareikis, R. Makuška. Reactivity ratio of PEG macromonomer in conventional and RAFT terpolymerizations. *Baltic Polymer Symposium* 2008*: Programme and Book of Abstracts*. 2008, Otepaa, Estonia, p 53.
3. T. Krivorotova, A. Vareikis, R. Makuška. Synthesis of cationic polyelectrolytes containing poly(ethylene oxide) chains by aqueous ATRP. *International Conference ”Polyelectrolytes 2008”. Book of Abstracts*. Coimbra, Portugal, 2008, p. 201.
4. T. Krivorotova, A. Vareikis, R. Makuška. Synthesis of cationic polyelectrolytes containing poly(ethylene oxide) chains by aqueous ATRP. *VI Open Ukrainian Conference of Young Scientists on Polymer Science, Book of Abstracts*. 2008, Kyiv, Ukraine, p. 80.
5. R. Makuska, T. Krivorotova, A. Vareikis, D. Gromadzki. RAFT (co)polymerization of PEO macromonomers yielding random and block copolymers with bottles-brush structure. *11-th Pacific polymer conference*. Cairns, Australia, 2009, p. 1.

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POLIETILENOKSIDO ŠONINES GRANDINES TURINČIŲ POLIELEKTROLITŲ SINTEZĖ GYVYBINGOSIOS RADIKALINĖS POLIMERIZACIJOS METODAIS

Santrauka

Vienas iš šiuolaikinės polimerų chemijos uždavinių – gauti numatytos molekulinės masės ir architektūros polimerines medžiagas. Neseniai buvo sukurti nauji radikalinės polimerizacijos metodai, kurie priskiriami gyvybingajai (valdomai) polimerizacijai (GRP). Makromonomerų (MM) gyvybingoji radikalinė polimerizacija yra efektyvus būdas gauti šepetinius (cilindrinius) polimerus). Šepetiniai polimerai – tai makromolekulės, kuriose prie pagrindinės polimerinės grandinės prijungta daug šoninių mažesnės molekulinės masės polimerinių (oligomerinių) grandinių. Dėl tarp šoninių grandinių esančių erdvinės stūmos jėgų tokios makromolekulės įgauna neįprastų savybių, pvz., standumą, cilindrinę formą, didelį segmentų tankį.

Pagrindinis šio darbo tikslas buvo susintetinti norimos sudėties šepetinius polielektrolitinius polimerus, sudarytus iš krūvį turinčios poli(met)akrilato pagrindinės grandinės ir šoninių polietilenoksido grandinių, ir ištirti jų savybes.

Svarbiausieji šio darbo rezultatai, atspindintys jo naujumą, originalumą ir svarbą:

Pirmą kartą nuodugniai ištirta metakrilo rūgšties (MAR) ir dviejų skirtingų molekulinių masių polietilenoksido metakrilatų PEO_nMEMA ($n = 5, 45$) kopolimerizacija įprastiniu radikaliniu ir RAFT metodais. Sukurta metodika PEO makromonomerų kopolimerizacijos kinetikai tirti, užrašant ^1H BMR spektrus *in situ* ir įvertinant likutinę monomerų koncentraciją reakcijos mišinyje bei momentinę kopolimero sudėtį iki gilių konversijų. Netiesiniu kintamųjų paklaidų metodu apskaičiuoti monomerų PEO_nMEMA ir MAR santykiniai aktyvumai įprastinėje ir RAFT kopolimerizacijoje, esant įvairioms konversijoms. Santykinius monomerų aktyvumus r_1 ir r_2 pateikus elipsoidinių pasikliovimo sričių formoje, įvertintas jų kitimas makromonomerų kopolimerizacijos metu. Nustatyta, kad santykinis PEO_5MEMA aktyvumas įprastinėje ir RAFT kopolimerizacijose yra beveik pastovus ir nepriklauso nuo monomerų konversijos. $PEO_{45}MEMA$ santykinis aktyvumas kopolimerizacijoje yra mažesnis negu PEO_5MEMA ir kinta kopolimerizacijos metu – didėja įprastinėje radikalinėje kopolimerizacijoje ir mažėja RAFT kopolimerizacijoje.

Ištirta laurilmetakrilato (LMA) RAFT polimerizacija, gandinės perdavos agentu naudojant *S*-metoksikarbonilfenilmetilditiobenzoatą (MDB). Nustatyta, kad gyvybingos PLMA grandinės augimo sąlygos yra esant [MDB]:[AIBN] = 4, tačiau šis santykis gali būti ir mažesnis, jei iniciatoriaus koncentracija labai maža. Susintetinti mažo polidispersiškumo (M_w/M_n = 1,08-1,19) PLMA, kurių polimerizacijos laipsnis (PL) 60 ir 122, buvo pilnai gyvybingi ir tinkami polimeriniai grandinės perdavos agentai (makroGPA) blokinių kopolimerų sintezei. Dalis didelės molekulinės masės (M_n apie 60 000, PL 260) PLMA grandinių gyvybingumą buvo praradusios. Ištirta blokinių amfifilinių kopolimerų sintezė RAFT metodu kaip makroGPA naudojant PLMA. Susintetintos blokinių amfifilinių kopolimerų PLMA-*b*-$PPEO_5MEMA$ ir PLMA-*b*-PMAR serijos, kuriose kopolimerai skiriasi hidrofobinio ir hidrofilinio blokų ilgiu bei molekuline mase. Nustatyta, kad antrojo bloko ilgis (molekulinė masė) gerai nuspėjamas, skaičiuojant monomero ir makroGPA santykį, o kopolimerų polidispersiškumas mažas ($M_w/M_n < 1,3$), jeigu monomero ir iniciatoriaus santykis nėra labai didelis ([M]:[I] < 500). $PPEO_{45}MEMA$ RAFT polimerizacija nuo PLMA nevyko. Ištirta amfifilinių blokinių PLMA-*b*-$PPEO_5MEMA$ bei PLMA-*b*-PMAR kopolimerų agregacija tirpaluose.

Pirmą kartą susintetinti katijoniniai “šepečiai ant šepečių” struktūros kopolimerai, kuriuose labai didelis PEO grandinių tankis, be to, PEO grandinės yra nutolusios nuo krūvį turinčios pagrindinės grandinės. Katijoniniai “šepečiai ant šepečių” struktūros kopolimerai gerai sorbuojasi ant neigiamą krūvį turinčio paviršiaus labai storu sluoksniu (20 mg/m^2), sudarydami stipriai hidratuotus (turinčius daugiau kaip 80 % vandens) sluoksnius. Adsorbuotas sluoksnis yra pakankamai stiprus, atlaikantis 35 MPa šlyties įtempį, o jo paviršiuje dėl tankaus PEO grandinių „šepečio“ veikia stiprios erdvinės stūmos jėgos. Trinties jėga tarp adsorbuotais sluoksniais padengtų plokštelių yra labai maža, trinties koeficiento vertė siekia tik 0,02-0,06. „Šepečiai ant šepečių“ struktūros kopolimerai yra perspektyvios neigiamą krūvį turinčius paviršius modifikuojančios medžiagos, pasižyminčios antiflokuliacinėmis ir drėgmę sulaikančiomis savybėmis.