

VILNIUS UNIVERSITY  
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

JŪRATĖ JONIKAITĖ-ŠVĖGŽDIENĖ

**ANIONIC MOLECULAR BRUSHES: SYNTHESIS BY RAFT  
POLYMERIZATION AND *CLICK* CHEMISTRY AND INVESTIGATION**

*Summary of doctoral dissertation*

Physical Sciences, Chemistry (03P)

Vilnius, 2017

The scientific work was carried out in 2011–2016 at Vilnius University.

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The official defence of the doctoral dissertation will be held at the open meeting of the Defence Council at 12:00 p.m. on September 29, 2017, in the Auditorium of Inorganic Chemistry (room No. 141) of the Faculty of Chemistry and Geosciences of Vilnius University. Address: Naugarduko 24, LT-03225, Vilnius, Lithuania.

The Summary of doctoral dissertation was mailed out on 29 August, 2016. The doctoral dissertation is available at the Libraries of Vilnius University and Institute of Chemistry of the Center for Physical Sciences and Technology, and on VU website: [www.vu.lt/lt/naujienos/ivykiu-kalendorius](http://www.vu.lt/lt/naujienos/ivykiu-kalendorius).

VILNIAUS UNIVERSITETAS  
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

JŪRATĖ JONIKAITĖ-ŠVĖGŽDIENĖ

**ANIJONINIŲ ŠEPETINIŲ POLIMERŲ SINTEZĖ RAFT  
POLIMERIZACIJOS IR *KLIK* CHEMIJOS METODAIS IR JŲ TYRIMAS**

Daktaro disertacijos santrauka

Fiziniai mokslai, Chemija (03 P)

Vilnius, 2017

Disertacija rengta 2011–2016 metais Vilniaus universitete.

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Disertacija bus ginama viešame Gynimo tarybos posėdyje 2017 m. rugsėjo 29 d. 12 val. Vilniaus universiteto Chemijos ir geomokslų fakulteto Neorganinės chemijos auditorijoje (141 kambarys).

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Disertacijos santrauka išsiųsta 2017 m. rugpjūčio 29 d.

Su disertacija galima susipažinti Vilniaus universiteto ir Fizinių ir Technologijos mokslų centro Chemijos instituto bibliotekose bei VU interneto svetainėje adresu: [www.vu.lt/lt/naujienos/ivykiu-kalendorius](http://www.vu.lt/lt/naujienos/ivykiu-kalendorius).

## 1. INTRODUCTION

**Relevance of the work.** The interest in synthesis and investigation of precisely constructed ionic molecular brushes (brush polyelectrolytes) of various topologies is increasing. Due to the specific geometry and ionisable groups, they possess unique physicochemical properties and can be applied in various fields of science, medicine or industry as drug nanocarriers, dispersants, surfactants, emulsifiers, nano-reactors, materials for tissue engineering, stimuli-responsive coatings, biosensors, in photonics or lithographic patterning (smart surfaces). Subject to the nature of the monomers and macromolecular structure, these polymers respond to different external stimuli, such as pH, solvent, temperature, electric/magnetic field or ionic strength. Usually, such polymers are called as stimuli responsive and can be used to mimic natural biomacromolecules (for example, proteoglycans). Among all fascinating characteristics the most attractive is brush copolymers ability to self-assemble into various nano-scaled morphologies, including spherical micelle, cylinder, vesicle, and lamellae. To understand behaviour and interactions of complex biolubricating systems, synthetic molecular brushes mimicking biolubricants are being investigated. Thus, ionic molecular brushes are interesting from both practical and fundamental points of view.

The synthesis of complex polyelectrolytes with well-defined molecular characteristics such as desirable functionality, narrow molecular weight distribution and predetermined molecular weights requires new polymerization techniques, such as reversible addition-fragmentation chain transfer polymerization (RAFT). Due to facile experimental setup and tolerance to most vinyl monomers, RAFT is one of the most versatile methods of reversible deactivation radical polymerization (RDRP). The synthesis of molecular brushes with desired architecture and well-defined molecular characteristics is not trivial and often requires combination of several methods or development of new synthesis strategies. For example, for the synthesis of molecular brushes RAFT technique is often combined with other techniques of RDRP and coupling reactions, including *click* chemistry. The goal is to make the synthesis of these ionic brushes simpler, faster and easier.

**The aim of the present work** was to synthesize and study anionic molecular brushes of various architecture with poly(meth)acrylate or polystyrene-based backbone and poly((meth)acrylic acid) (p(M)AA) side chains.

**The objectives** of the research were the following:

- ✓ To synthesize several types of RAFT chain transfer agents (CTA) with a particular functional group (carboxyl or alkyne) possessing one, two or several trithiogroups and a certain position of R-group suitable for RAFT polymerization of (meth)acrylates and styrenic monomers.
- ✓ To synthesize anionic molecular brushes with polyacrylate or polystyrene-based backbone and poly(acrylic acid) (pAA) side chains via RAFT *grafting from* method. To synthesize random, diblock and two-type triblock (*coil-brush-coil* and *brush-coil-brush*) anionic brush copolymers.
- ✓ To synthesize anionic molecular brushes with poly(meth)acrylate backbone and p(M)AA side chains via azide-alkyne and epoxy-thiol *click* reactions.
- ✓ To study properties of the anionic molecular brushes including thermostability and thermal transitions, wettability, ionization behaviour, micellization and aggregation in mixed solvents.

### **Scientific novelty and practical value of the dissertation**

Four types of trithiocarbonates differing by functional groups, position of R-group and number of trithiogroups were synthesized and used as RAFT CTA for the RAFT polymerization of various monomers (styrene (St), vinylbenzyl chloride (VBC), acrylic acid (AA), *tert*-butyl methacrylate (*tert*-BMA)) for the first time.

Anionic molecular brushes with polyacrylate backbone and pAA side chains were synthesized via RAFT *grafting from* method and molecular brushes with polymethacrylate backbone and poly(*tert*-butyl methacrylate) (p(*tert*-BMA)) side chains were synthesized via epoxy-thiol *click* reaction for the first time.

Anionic molecular brushes with polystyrene-based backbone and pAA side chains of *coil-brush-coil* and *brush-coil-brush* architecture were synthesized by RAFT polymerization and the micellization/aggregation behaviour of these brush copolymers was studied and compared.

Anionic molecular brushes can be potentially used as carriers of hydrophobic drugs or surface modifiers. Anionic polystyrene-based triblock copolymers of *coil-brush-coil* and *brush-coil-brush* architecture are of interest as model systems to study surface forces and properties of the adsorbed layers.

**Defensive statements:**

- ✓ RAFT *grafting from* method is the most suitable for the synthesis of anionic molecular brushes.
- ✓ Synthesis of anionic molecular brushes by *grafting to* via *click* reactions is not viable.
- ✓ Anionic polyacrylate-based molecular brushes are weaker polyacids compared with linear pAA and their size is pH-dependent.
- ✓ The micellization and aggregation behaviour of polystyrene-based anionic molecular brushes in dioxane/water mixtures depends on the polymer architecture and the length of pAA side chains.

**Approbation of the research results.** Results of the research were presented in 2 scientific papers in the journals included into the database of *Clarivate Analytics Web of Science*. Results were also reported in 8 international conferences.

**Structure of the doctoral dissertation.** The doctoral dissertation is written in Lithuanian and contains the following chapters: Introduction with the motivation of the research objectives, Literature Survey, Experimental Part, Results and Discussion, Conclusions, List of References (280 entries) and List of Scientific Publications. Material of the dissertation is laid out in 186 pages, including 30 schemes, 36 figures and 16 tables.

## 2. MATERIALS AND METHODS

**Main materials.** 2-Hydroxyethyl acrylate (HEA, 96%) and acrylic acid (AA, 99%) were distilled under reduced pressure before use. Glycidyl methacrylate (GMA, 97%), butyl methacrylate (BMA, 99%), *tert*-butyl methacrylate (*tert*-BMA, 98%), styrene (St, 99%) and vinylbenzyl chloride (VBC, 90%) were purified by percolation over a column of either basic or neutral aluminium oxide. 2,2'-Azobis(isobutyronitrile) (AIBN) was

recrystallized from methanol twice, 4,4'-azobis(4-cyanovaleric acid) (ACVA, 98%) was used as received. Prior to use, the solvent dichloromethane (DCM, 99 %), *N,N*-dimethylformamide (DMF, 99%), 1,4-dioxane (DO, 99%), methanol (MeOH, 99%) and *N*-methyl-2-pyrrolidone (NMP, 99%) were purified according to standard procedures. Other reagents were of analytical grade and used without purification.

**Synthesis of anionic molecular brushes. Polyacrylate-based anionic molecular brushes.** A solution of AA, poly(hydroxyethyl acrylate) decorated by trithiocarbonate groups (pHEA-TTC), and azobis(4-cyanovaleric acid) (ACVA) in dry distilled DO was purged 30 min. with argon and then the flask was sealed with rubber septum. RAFT polymerization of AA from pHEA-TTC was carried out at 60 °C, taking the samples with a syringe for an analysis every 30 min. At the end of polymerization, the reaction mixture was diluted with acetone and the anionic brush polymer (pHEA-*graft*-pAA) was precipitated by pouring the solution to diethyl ether and dried in vacuum at room temperature for 24 h.

**Polymethacrylate-based anionic molecular brushes.** Random copolymer of glycidyl methacrylate and butyl methacrylate (p(GMA-*st*-BMA)), and thiol-group terminated p(*tert*-BMA) were dissolved in 17 ml NMP, the solution was purged with nitrogen for 30 min then the flask was sealed with rubber septum. Triethylamine was then introduced to the flask and the epoxy-thiol *click* reaction was carried out at 80 °C for 48 h. The polymer was precipitated by pouring the solution to deionized water and dried in a vacuum at 30 °C for 24 h. The hydrolysis of *tert*-BMA units of the polymer by HCl was carried out at 40 °C for 48 h. The anionic brush copolymer p(GMA-*st*-BMA)-*graft*-pMAA was obtained by pouring the solution to diethyl ether and dried in vacuum at 30 °C for 24 h.

**Polystyrene-based anionic molecular brushes.** A random, (diblock or triblock) copolymer of St and VBC bearing multiple TTC groups p(St-*co*-VBC-TTC) was dissolved in dry distilled DO. AA and ACVA were added to the solution which was purged with argon for 30 min, then the flask was sealed with rubber septum. RAFT polymerization of AA from p(St-*co*-VBC-TTC) was carried out at 60 °C for 3 h. At the end of the polymerization the reaction mixture was diluted with acetone and the copolymer p(St-*co*-VBC)-*graft*-pAA precipitated by pouring the solution into a large

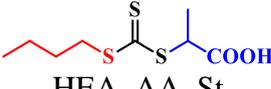
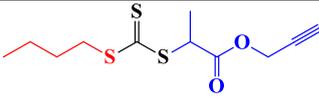
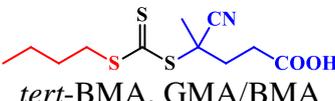
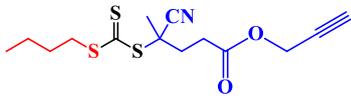
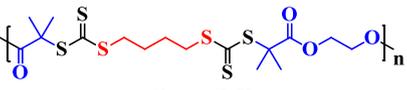
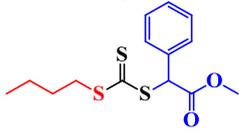
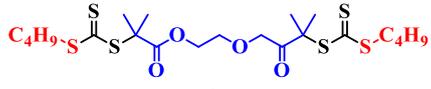
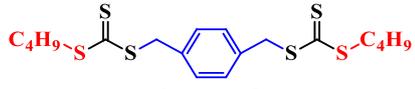
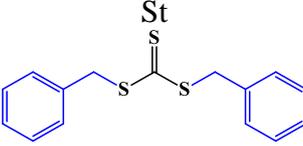
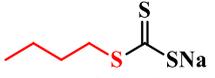
amount of diethyl ether and left stirring for an additional 2–3 hours. The procedure was repeated twice. The polymer was dried under vacuum at room temperature for 24 h.

**Characterization of polymers.** The composition, molecular weight ( $M_n$ ) and dispersity index ( $\mathcal{D}$ ) of polymers were determined by FTIR and NMR spectroscopy, SEC. Thermal stability and glass transition temperature ( $T_g$ ) of polymer were investigated by TGA and DSC methods. Wetting properties of polymer films were investigated by WCA measurements. The ionization behaviour of anionic brush pHEA-*graft*-pAA in water and micellization/aggregation of diblock and triblock anionic brushes p(St-*co*-VBC)-*graft*-pAA in dioxane/water mixture were studied by potentiometric titration, DLS and TEM.

### 3. RESULTS AND DISCUSSION

In the present work, anionic molecular brushes with poly(meth)acrylic acid (p(M)AA) side chains were synthesized combining RAFT polymerization and *click* reactions. Variety of anionic molecular brushes was prepared by the use of random, diblock and triblock backbone of poly(meth)acrylate or polystyrene-based type. Different RAFT CTA's were employed (Table 1).

Table 1. RAFT CTA's used in this work

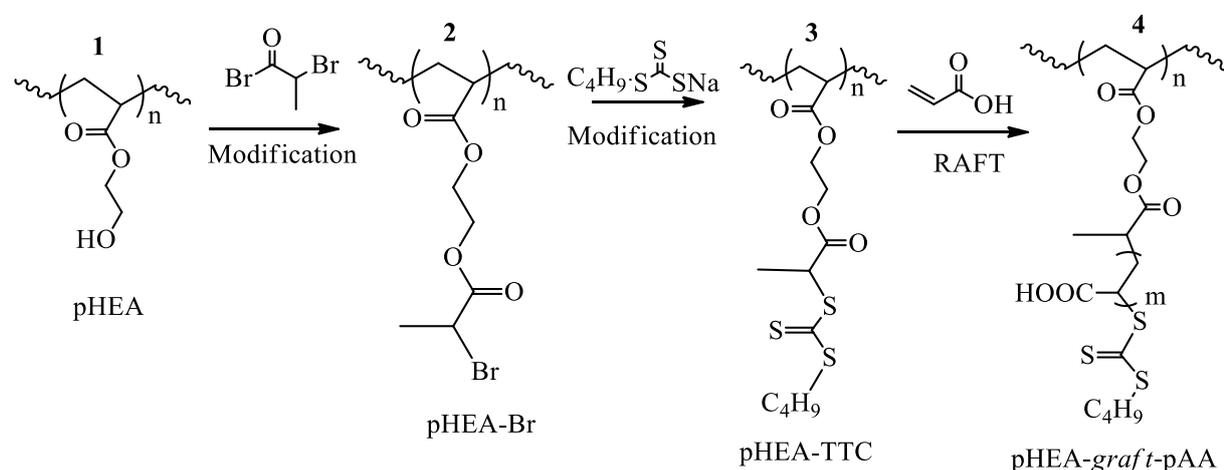
No.	CTA and use	No.	CTA and use
CTA1	 HEA, AA, St	CTA2	 AA (azide-alkyne <i>click</i> chemistry)
CTA3	 <i>tert</i> -BMA, GMA/BMA	CTA4	 <i>tert</i> -BMA (azide-alkyne <i>click</i> chemistry)
CTA5	 St/VBC	CTA6	 St
CTA7	 St, VBC	CTA8	 St, VBC
CTA9	 St, VBC	CTA10	 AA (modification of pHEA-Br and pVBC units)

CTA Z-group is marked blue and R-group is marked red. CTA1 and CTA4–CTA9 control RAFT polymerization of acrylates and styrene, meanwhile CTA3 and CTA4 control the polymerization of methacrylates.

### 3.1 Polyacrylate-based anionic molecular brushes via RAFT *grafting from*

#### 3.1.1 Synthesis of intermediate polymers and molecular brushes

Poly(2-hydroxyethyl acrylate) (pHEA) is a widely used biocompatible polymer, which hydroxyl groups can be modified easily to access various new structures. In order to synthesize polyacrylate-based anionic molecular brushes bearing pAA side chains via RAFT *grafting from* method, previously synthesized pHEA was modified in two steps to give multiCTA with multiple trithiocarbonate (TTC) groups (pHEA-TTC) (Scheme 1).



Scheme 1. Synthesis of polyacrylate-based anionic molecular brushes via RAFT *grafting from* method.

First, RAFT polymerization of 2-hydroxyethyl acrylate (HEA) was carried out in the presence of CTA1 and AIBN as initiator. The aim was to synthesize pHEA backbone with degree of polymerization (DP) at about 100. The best results were achieved when the initial molar ratio [HEA]/[CTA1]/[AIBN] in polymerization mixture was 200/1/1, the polymerization was carried out in DO for 8 hours at 60 °C. The synthesized pHEA was characterized by SEC giving  $M_n$  10500 (DP 90) and  $\bar{D}$  1.32. pHEA was then esterified with 2-bromopropanoyl bromide, resulting in pHEA-Br. Multiple RAFT CTA attached to polyacrylate-based backbone (pHEA-TTC) was synthesized by nucleophilic reaction of CTA10 with pHEA-Br acting as alkylating agent. Analysis of pHEA-TTC

( $M_n$  28500,  $\bar{D}$  1,24, 80 TTC groups) by  $^1\text{H}$  NMR spectroscopy revealed that bromine atoms were almost completely replaced by TTC groups. The results of RAFT polymerization of AA in the presence of well-defined pHEA-TTC are given in Table 2.

At two-fold excess of TTC over the initiator RAFT polymerization of AA was fast with 80–90% monomer conversion in 1–2 h. It was determined that two-fold excess of TTC groups over the initiator was optimal enabling to synthesize graft copolymers with rather low dispersity ( $\bar{D}$  1.23–1.36) and reasonably high DP of pAA side chains (up to 26). Molecular weight of the anionic molecular brushes (pHEA-*graft*-pAA) was increasing in time but usually differed fairly from the theoretically calculated molecular weight (Table 2). Likely, lower than expected molecular weight of the polymers synthesized at  $[\text{AA}]/[\text{TTC}]/[\text{ACVA}] = 25/2/1$  could be explained by parallel formation of pAA oligomers which were removed during purification of the molecular brushes. The longest pAA side chains (DP 20–26) were synthesized when the initial molar ratio  $[\text{AA}]/[\text{TTC}]/[\text{ACVA}]$  in the polymerization mixture was 50/2/1.

Table 2. Results of AA RAFT polymerization in the presence of pHEA-TTC (DO, 60 °C)

pHEA- <i>graft</i> -pAA	$[\text{AA}]/[\text{TTC}]/[\text{ACVA}]$	$\tau$ , h	q, %	$M_n^t$ , g·mol <sup>-1</sup>	$M_n$ , g·mol <sup>-1</sup>	DP <sub>pAA</sub>	$\bar{D}$
1		1	56	79500	32000	0.8	1.32
2	25/2/1	1.5	69	91700	47000	2.8	1.36
3		2	86	108000	65600	5.4	1.25
4	50/2/1	0.5	64	147000	174000	20	1.23
5		1	89	194000	223000	26	1.29
6	200/5/1	1.5	23	96100	47800	2.9	1.18
7		2	27	108000	62000	4.9	1.18
8	200/10/1*	1.5	8	38900	39400	1.8	1.29
9		2	33	76500	206000	24	1.71

\* Polymerization was carried out in DMSO.

The increase in  $[\text{TTC}]/[\text{ACVA}]$  ratio to 10/1 gave molecular brushes with broad molecular weight distribution (Fig. 1, 9). Likely, high-molecular weight shoulder of MWD curve is related to radical–radical coupling reactions taking place during RAFT

polymerization from pHEA-TTC backbone bearing multiple TTC groups where growing chains are very close one to another. RAFT polymerization of AA in the presence of pHEA-TTC is different from the RAFT polymerization of AA controlled by low-molecular CTA. During RAFT polymerization of AA from pHEA-TTC, TTC groups are always located at the end of the growing chains (Scheme 1). Due to the close vicinity of the growing chains, the main complication arising during AA RAFT polymerization is higher tendency of various inter- or intramolecular reactions between active centres of the growing chains.

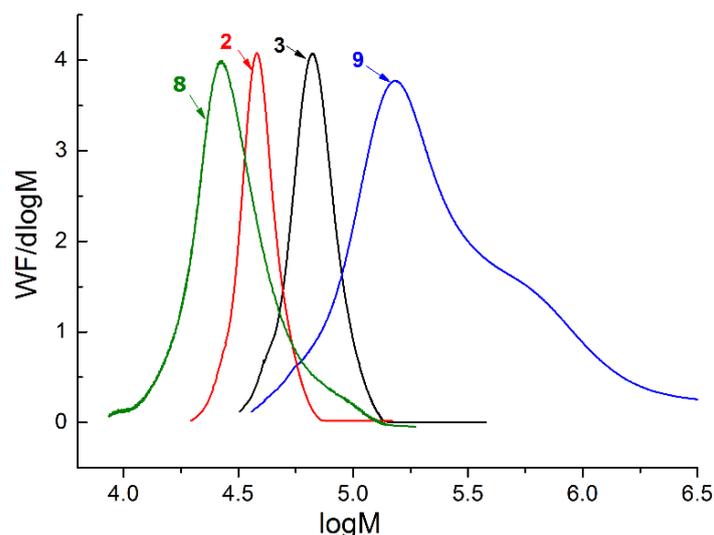


Fig. 1. Molecular weight distribution (MWD) curves of anionic polymer brushes pHEA-*graft*-pAA (see Table 2 for entries).

Nevertheless, RAFT *grafting from* method using pHEA-TTC enabled to synthesize rather monodisperse well-defined anionic molecular brushes pHEA-*graft*-pAA with short (DP about 5) and medium (DP 20–25) length pAA side chains.

The synthesis of polyacrylate-based anionic molecular brushes via azide-alkyne *click* reaction between pHEA backbone previously modified with azide groups (pHEA-N<sub>3</sub>) and alkyne terminated pAA side chains, synthesized in the presence of CTA2, was catalyzed by Cu(I) ions (CuAAC, *copper-catalyzed [3+2] Huisgen cycloaddition reaction*). This *grafting to* strategy to synthesize anionic molecular brushes was unsuccessful, probably, due to several reasons. Firstly, high-molecular-weight pAA ( $M_n$  4000–5000 g/mol) is difficult to graft to the backbone because of high steric hindrance

alongside the backbone. Secondly, carboxyl groups of pAA tend to form complexes with Cu(I) ions leading to inactivation of the catalyst of the azide-alkyne *click* reaction.

### 3.1.2 Properties of polyacrylate-based anionic molecular brushes

The thermal behaviour of anionic molecular brushes pHEA-*graft*-pAA was compared with that of linear pAA ( $M_n$  15500, DP 160). Glass transition temperature ( $T_g$ ) of anionic molecular brushes depends on the length of the pAA side chains. Molecular brush with short pAA chains had  $T_g$  at 90 °C, which is close to the value of linear pAA ( $T_g$  102 °C), while  $T_g$  of the molecular brush with medium-length pAA side chains was lower (63 °C). The thermal stability of linear pAA and anionic molecular brushes is similar.

The degree of ionization of weak polyelectrolytes depends on the degree of neutralization,  $\alpha$ , and therefore on the pH. To compare the ionization behavior of linear pAA and brush polymer pHEA-*graft*-pAA, diluted solutions of these polyelectrolytes were titrated potentiometrically. From the data of titration  $pK(\alpha)$  values at various degrees of neutralization of carboxylic groups were calculated.  $pK(\alpha)$  dependences of linear and brush pAA are different. High density of the carboxylic groups in the molecular brush makes ionization more difficult, which is evident from the rather flat slope (Fig. 2, left, 2 and 4 curves). Apparent  $pK_\alpha$  values in water of linear pAA and molecular brush pHEA-*graft*-pAA established using Henderson–Hasselbalch plots are respectively  $K_\alpha = 6.48$  and 7.20. An increase of ionic strength of the solution by addition of 0.1 M NaCl decreased  $pK_\alpha$  values to 5.10 and 6.19, respectively. Thus, acidic properties of the brush polymer pHEA-*graft*-pAA remained weaker compared to linear pAA even in salt solution.

Fig. 2 (right) represents intensity-average hydrodynamic diameters ( $D_h$ ) of anionic molecular brush pHEA-*graft*-pAA (A) and partly crosslinked derivatives/aggregates (B) as a function of solution pH. In acidic medium (at pH ~5) most AA groups are protonated, so repulsion between side chains is minimal and pAA brush is in coil conformation. Upon increase of pH from 4.6 to 6.5 the size of molecular brushes is increasing from ca 13 nm to 22–25 nm. Thus, polymers can be called pH-sensitive. Later on, when pH increases from 6.5 to 11, hydrodynamic diameter is almost constant. Likely, considerable increase in hydrodynamic diameter of the brush molecules during

neutralization of pHEA-*graft*-pAA is related to the length of the side chains: relatively short side chains of pAA (ca 26) can be unstretched and partially coiled even at high density of the side chains.

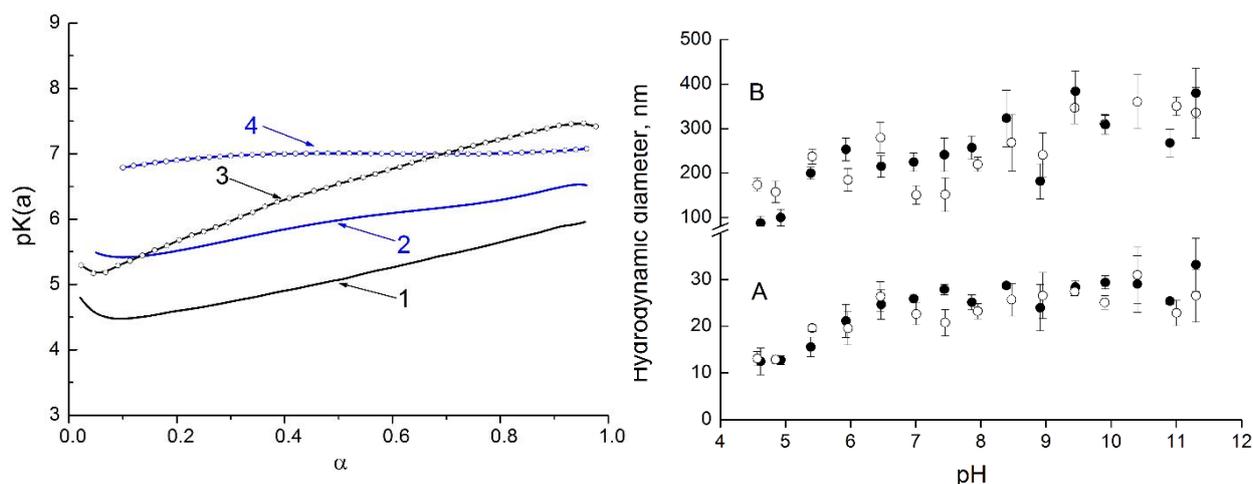


Fig. 2. The dependence of  $pK(\alpha)$  of linear pAA (1, 3) and molecular brush pHEA-*graft*-pAA (Table 1, no 5) (2, 4) on degree of neutralization in water (3, 4) and 0.1 M NaCl solution (1, 2) (left) and hydrodynamic diameters of molecular brush pHEA-*graft*-pAA (Table 1, no 5) as a function of solution pH (right). The initial polymer concentration 0.02 wt% (●) and 0.04 wt% (○). Error bars represent the standard deviation ( $N = 3$ ).

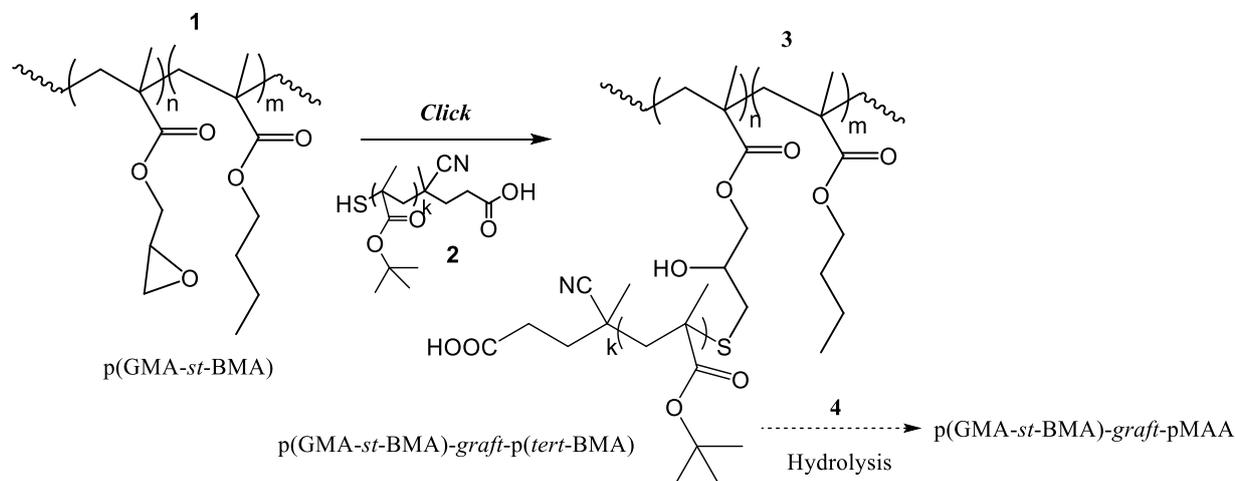
### 3.2 Polymethacrylate-based anionic molecular brushes via *click reactions*

Glycidyl methacrylate (GMA) is cheap and versatile monomer suitable for RAFT polymerization and post-polymerization modification. Copolymers based on pGMA can be biocompatible. Synthesis of polymethacrylate-based anionic molecular brush p(GMA-*st*-pBMA)-*graft*-pMAA bearing pMAA side chains via epoxy-thiol *click* reaction is given in Scheme 2.

First, random copolymers of glycidyl methacrylate (GMA) and butyl methacrylate (BMA) were synthesized via RAFT polymerization. The aim was to synthesize polymethacrylate-based backbone, in which GMA fragment with active epoxy group will be located every second monomeric unit, thus facilitating the further grafting of side chains. The RAFT polymerization of GMA and BMA was carried out in presence of CTA3 and AIBN as initiator. The best results were achieved when the initial molar ratio  $[GMA+BMA]/[CTA3]/[AIBN]$  in the polymerization mixture was 250/5/1, the

polymerization was carried out in NMP for 15 hours at 65 °C. The synthesized p(GMA-*st*-BMA) (52 mol% of GMA units) was characterized by SEC giving  $M_n$  8400 and  $\bar{D}$  1.15. Well-defined random copolymer p(GMA-*st*-BMA) was used for further epoxy-thiol *click* reactions.

Second, p(*tert*-BMA) side chains were synthesized separately by RAFT polymerization using the same CTA3. The aim was to synthesize well-defined polymers with low degree of polymerization (DP up to 20). The best results were achieved when the initial molar ratio [*tert*-BMA]/[CTA3]/[AIBN] in the polymerization mixture was 100/5/1, the polymerization was carried out in NMP for 8 hours at 65 °C. The synthesized p(*tert*-BMA) was characterized by SEC giving  $M_n$  2300 (DP 14) and  $\bar{D}$  1.19. In order to implement epoxy-thiol *click* reaction, the TTC end group of p(*tert*-BMA) was reduced to thiol groups by nucleophilic reduction reaction using hydrazine monohydrate. The aminolysis reaction was monitored by UV spectroscopy (UV absorbtion at 310 nm, C=S bond). The  $M_n$  and  $\bar{D}$  of p(*tert*-BMA) before and after aminolysis remained almost constant. This shows that no side reactions like disulphide formation were observed. Well-defined p(*tert*-BMA) was used for further epoxy-thiol *click* reaction.



Scheme 2. Synthesis of polymethacrylate-based anionic molecular brushes via epoxy-thiol *click* reaction

The polymethacrylate-based backbone p(GMA-*st*-BMA) and p(*tert*-BMA) side chains were joint together via trimethylamine catalysed epoxy-thiol *click* reaction. In typical  $^1\text{H}$  NMR spectrum of p(GMA-*st*-BMA)-graft-p(*tert*-BMA) the signals of epoxy ring at 4.28, 3.82, 3.22, 2.84 and 2.64 ppm disappeared (Fig.3, A) and new signals at

4.14 and 3.65 ppm attributed to new bonds between GMA units and *p*(*tert*-BMA) chains appeared (Fig. 3, B).

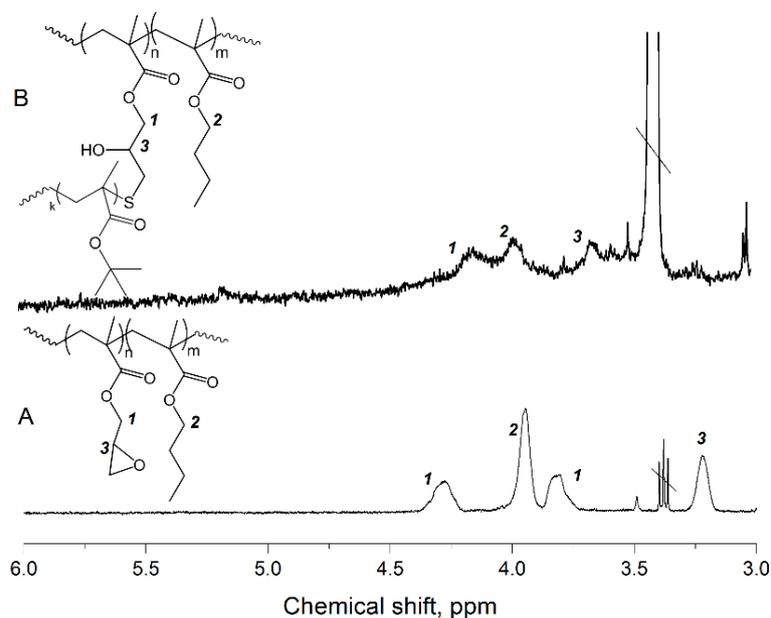


Fig. 3.  $^1\text{H}$  NMR spectra of *p*(GMA-*st*-BMA) (A) and *p*(GMA-*st*-BMA)-*graft-p*(*tert*-BMA) (B)

*tert*-BMA units in the brush copolymer *p*(GMA-*st*-BMA)-*graft-p*(*tert*-BMA) were hydrolysed to methacrylic acid (MAA) units using HCl. The successful hydrolysis was confirmed by FT-IR spectroscopy – new broad absorption band at  $3400\text{ cm}^{-1}$  attributed to hydroxyl group and a sharp absorption band of carboxyl group at  $1700\text{ cm}^{-1}$  appeared.

The synthesis of polymethacrylate-based anionic molecular brushes via azide-alkyne *click* reaction between *p*(GMA-*st*-BMA) backbone previously modified with azide groups (*p*(GMA- $\text{N}_3$ -*st*-BMA)) and alkyne terminated *p*(*tert*-BMA) side chains synthesized with CTA4 was catalyzed by Cu(I) ions. Synthesis of brush copolymers *p*(GMA-*st*-BMA)-*graft-p*(*tert*-BMA) via *grafting to* strategy was unsuccessful. This could be related to the stiffness of the polymethacrylate chain making its approach to the polymer backbone difficult.

Glass transition temperature ( $T_g$ ) of *p*(*tert*-BMA) is low ( $50\text{ }^\circ\text{C}$ ) compared with theoretical value ( $118\text{ }^\circ\text{C}$ ) probably due to the low molecular weight.  $T_g$  of *p*(GMA-*st*-BMA) was  $28\text{ }^\circ\text{C}$ , in between  $T_g$  of *p*GMA and *p*BMA homopolymers. One value of  $T_g$  of the brush copolymers *p*(GMA-*st*-BMA)-*graft-p*(*tert*-BMA) at  $31\text{--}37\text{ }^\circ\text{C}$  shows that both backbone and side chains are compatible: the chains have similar flexibility and the

rearrangement of the chains during heating is similar. Due to the high  $T_g$  of pMAA, DSC investigation of the brush copolymers p(GMA-*st*-BMA)-*graft*-pMAA is complicated because of partial destruction of TTK groups. TGA analysis of p(GMA-*st*-BMA), p(*tert*-BMA), p(GMA-*st*-BMA)-*graft*-p(*tert*-BMA) and p(GMA-*st*-BMA)-*graft*-pMAA revealed that brush copolymers and anionic brush copolymers are more thermally stable than the backbone and the side chains separately (Fig. 4).

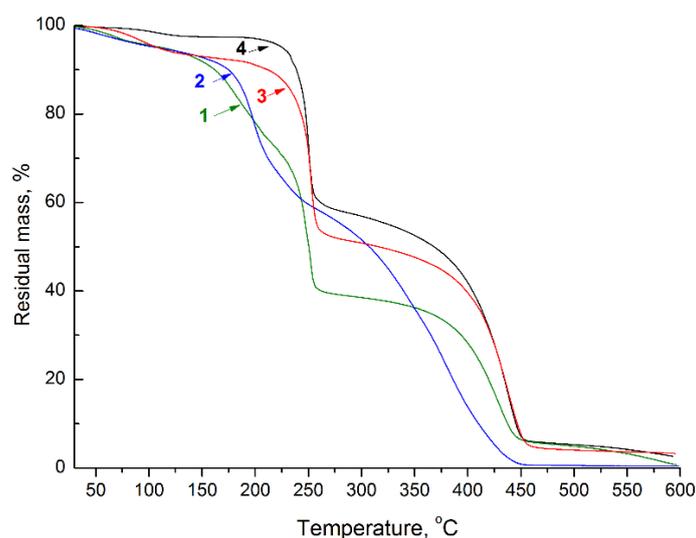


Fig. 4. TGA curves of p(*tert*-BMA) (1), p(GMA-*st*-BMA) (2), p(GMA-*st*-BMA)-*graft*-p(*tert*-BMA) (3) and p(GMA-*st*-BMA)-*graft*-pMAA (4)

### 3.3 Polystyrene-based anionic molecular brushes via RAFT *grafting from*

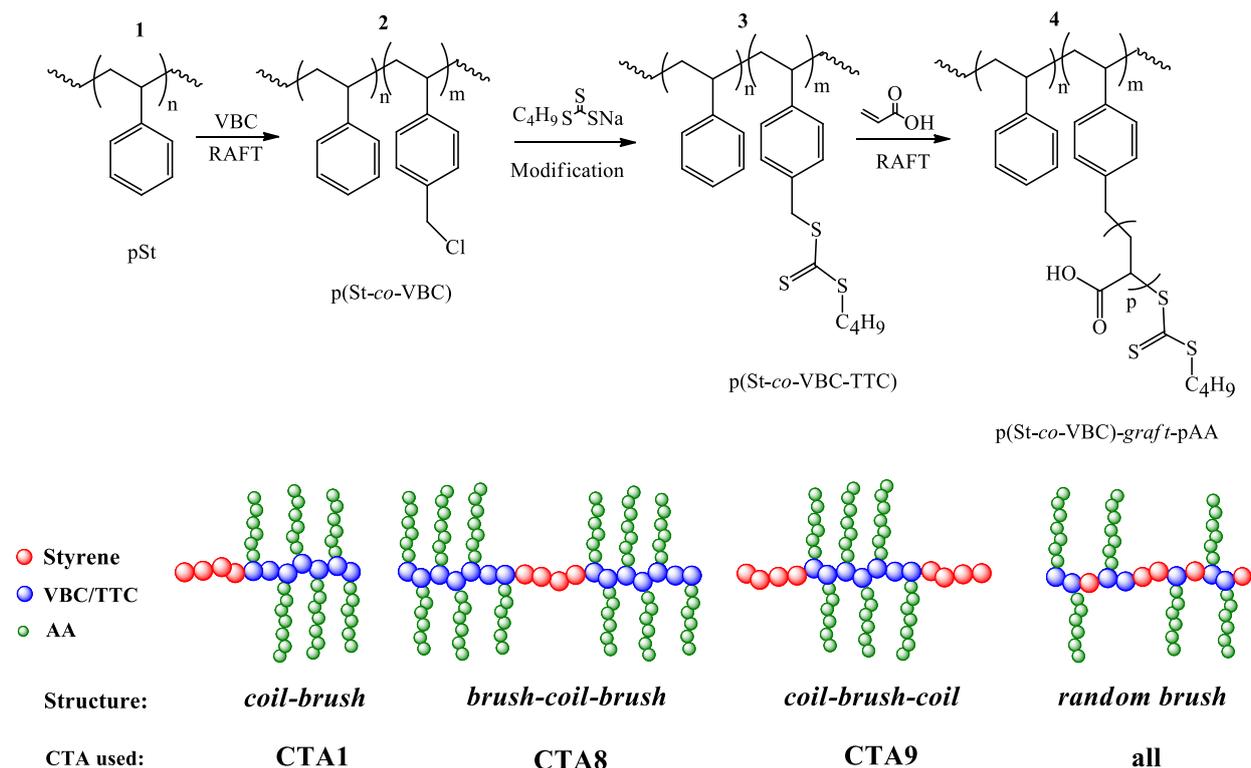
#### 3.3.1 Synthesis of intermediate polymers and molecular brushes

Polystyrenic (pSt) backbone has an advantage over poly(meth)acrylate backbone since it is non-susceptible to hydrolysis. Moreover, it is preferable in those cases when certain hydrophobicity of the polymer is an advantage. Amphiphilic copolymers with pSt block tend to form micelles of various topology and other nano-scaled structures.

In order to synthesize polystyrene-based anionic molecular brushes bearing pAA side chains via RAFT *grafting from* method, previously synthesized random, diblock and triblock poly(styrene-*co*-vinyl benzyl chloride) copolymers (pSt-*co*-pVBC) were modified to give multiCTA with multiple TTC groups (pSt-*co*-pVBC-TTC) (Scheme 3).

First, pSt was synthesized by thermally initiated bulk RAFT polymerization of St mediated by three different CTA's (see Scheme 3) The initial molar ratio [St]/[CTA] ranged from 300/1 to 1000/1. In all the cases, RAFT polymerization proceeded in a

controlled manner and the polymers with low dispersity index ( $\mathcal{D}$  1.10 to 1.18) and reasonably high degree of polymerization (DP, up to 135) were obtained. In the second step, previously synthesized pSt was used as macroCTA to mediate RAFT polymerization of vinylbenzyl chloride (VBC) to yield diblock (AB) and triblock (ABA and BAB) as well as random brush copolymers. Molecular weight distribution (MWD) curves of the copolymers were symmetric and unimodal which indicated controlled character of the chain extension and complete consumption of the macroCTA.



Scheme 3. Synthesis of polystyrene-based anionic molecular brushes via RAFT *grafting from* method and the structure of *coil-brush* copolymers

Starting from pSt1 and pSt2, synthesized with CTA1 as macroCTA, the diblock copolymers (AB) with approximately the same length of both pSt and pVBC blocks (DP 70) were synthesized (pSt<sub>70</sub>-*b*-pVB<sub>70</sub>). During the chain extension dispersity index  $\mathcal{D}$  of copolymers slightly increased and the  $M_n$  increased from ~7700 to ~18000 g/mol.

Using pSt3-St5 as macroCTA, synthesized with CTA8, triblock copolymers (BAB) pVBC<sub>33</sub>-*b*-pSt<sub>60</sub>-*b*-pVBC<sub>33</sub> and pVBC<sub>27</sub>-*b*-pSt<sub>100</sub>-*b*-pVBC<sub>27</sub> were synthesized. The chains of pSt2 and pSt3 were extended to two directions giving two pVBC blocks of the same length separated by middle pSt block. Chain extension of pSt3-pSt5 by the blocks of

pVBC led to the formation of copolymers of higher  $M_n$  (17000–19500 g/mol) with slightly higher dispersity ( $\bar{D}$  1.20–1.30).

Triblock copolymer (ABA) of the following structure and composition was synthesized in the presence of CTA9: pSt<sub>45</sub>-*b*-pVBC<sub>25</sub>-*b*-pSt<sub>45</sub>. In this case, pSt chain was split into two blocks which were separated by newly formed block of pVBC.

Random copolymers of St and VBC were synthesized using the same CTA1, CTA8 and CTA9. In all the cases, molecular weight was higher than theoretically calculated molecular weight. Moreover, dispersity index  $\bar{D}$  of the random copolymers was considerably higher (about 1.45) compared to that of block copolymers. Composition of the random copolymers was close to the composition of the initial monomer mixture. Random copolymer p(St-*st*-VBC) containing 76 mol% VBC units was used for further modification.

All synthesized copolymers were decorated with TTC groups by nucleophilic substitution of chlorine atom in VBC units. Degree of modification of the diblock copolymers and triblock copolymers BAB was 60–70%, and that of the triblock copolymers ABA 50% as well of random copolymers – 45–75%.

In order to synthesize more complex polystyrene-based multiblock anionic molecular brushes, linear multifunctional CTA's with 4 to 10 TTC groups were utilized in St and VBC RAFT block copolymerization. Due to the low conversion of second (VBC) monomer, which is crucial in further grafting process of pAA side chains, this method was unsuccessful.

The results of RAFT polymerization of AA in the presence of well-defined copolymers p(St-*co*-VBC-TTC) are listed in Table 3. RAFT polymerization of AA in the presence of the diblock copolymer with 34 TTC groups giving *coil-brush* anionic diblock copolymers was smooth and proceeded to high conversions (73–86%). MWD curves of the diblock brush copolymers were unimodal and narrow (Fig. 5, 2), with  $\bar{D}$  value about 1.1.

RAFT polymerization of AA in the presence of the triblock copolymers with 57 or 39 TTC groups gave *brush-coil-brush* anionic copolymers with low ( $\bar{D}$  1.1-1.2) or moderate ( $\bar{D}$  about 1.4) dispersity. Conversion of the monomer was rather high, giving DP of pAA side chains close to 50 (at the initial ratio  $[AA]/[TTC] = 50$ ) or to 25 (at the initial ratio  $[AA]/[TTC] = 25$ ).

Table 3. Results of AA RAFT polymerization in the presence of p(St-co-VBC-TTC) (DO, 60 °C)

p(St-co-VBC)-graft-pAA*	n(TTC)	[AA]/[TTC]	q, %	$M_n^t$ , g mol <sup>-1</sup>	$M_n$ , g mol <sup>-1</sup>	DP <sub>pAA</sub>	Đ	R <sub>h</sub> nm
CB1	34	25/1	86	82000	106000	30	1.13	6.8
CB2		50/1	73	114000	115000	35	1.07	7.1
BCB1	57	25/1	94	128000	135900	26	1.10	8.1
BCB2		50/1	66	166000	236300	50	1.20	8.5
BCB3	39	25/1	88	81600	79100	18	1.43	8.6
BCB4		50/1	74	125800	145200	41	1.42	8.7
CBC1	12	25/1	79	32000	24800	6	1.73	4.2
RB1	54	25/1	74	90200	85400	15	1.83	7.5
RB2		50/1	85	184000	215300	48	1.10	9.6

\* CB – coil-brush, BCB – brush-coil-brush, CBC – coil-brush-coil, RB – random brush.

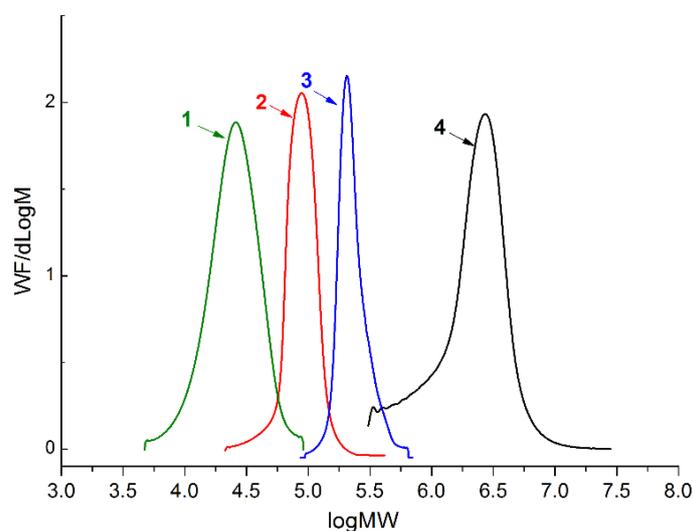


Fig. 5. MWD curves of polystyrene-based anionic brushes: CBC1 (1), CB2 (2), RB2 (3) and BCB2 (4)

RAFT polymerization of AA in the presence of the triblock copolymer with 12 TTC groups gave *coil-brush-coil* anionic copolymers. In this case, DP of pAA side chains was rather low – about 6, and dispersity index rather high – Đ about 1.7 (Fig. 5, 1). In this case TTC groups are shielded by two pSt blocks which hinder the

macroradical to access the TTC groups. Thus, the RAFT polymerization of AA is complicated. RAFT polymerization of AA in the presence of the random copolymer with 54 TTC groups gave brush copolymers with narrow MWD (Fig. 5, 3) and the length of pAA side chains close to predicted.

These results demonstrate that RAFT polymerization of AA in the presence of polystyrene-based copolymers decorated by TTC groups was efficient, and the target random, diblock (*coil-brush*) and triblock (*brush-coil-brush* and *coil-brush-coil*) anionic copolymers with relatively short and rather long pAA side chains were synthesized.

### 3.3.2 Properties of polystyrene-based anionic molecular brushes

The wettability (static water contact angle (WCA)) of the films of polystyrene-based anionic brush copolymers are listed in Table 4. Compared with the films of p(*St-co-VBC-TTC*) (WCA 78° to 92°), polystyrene-based anionic brush copolymers exhibit significantly lower WCA values, which shows an increased hydrophilicity of the films. The most hydrophilic are the films of *coil-brush* (CB1) and *brush-coil-brush* (BCB1-BCB4) copolymers (Table 4).

Table 4. Static water contact angle (WCA) and hydrodynamic diameter  $D_h$  of polystyrene-based anionic brush copolymers in DO/H<sub>2</sub>O at 30 °C.

Polymer	WCA, °	$D_{h,DLS}$ (nm) (DO)	$D_{h,DLS}$ (nm) (DO/H <sub>2</sub> O = 50/50)
CB1	28±2.9	16.3	84 and 830
BCB1	35±2.2	14.1	86 and 910
BCB2	25±1.7	14.6	22 and 1010
BCB3	45±2.4	18.8	1060
BCB4	31±1.4	19.2	34 and 330
CBC1	54±1.6	10.2	18 and 780
RB1	43±1.8	15.6	70 and 715
RB2	15±1.1	24.8	620

The lowest WCA values (25–31°) are characteristic for the films of the brush copolymers with long pAA side chains. Obviously, polystyrene-based anionic brush copolymers with one or two brush segments and one hydrophobic coil segment are more hydrophilic compared to the CBC copolymers with short brush block and two

hydrophobic coil segments. The copolymer RB1 of random brush structure demonstrated similar WCA value to that of BCB-type brush copolymers, while the same copolymer with longer pAA chains was characterized by very low WCA value (15°). The latter value is close to that of linear pAA (14°). WCA measurements revealed that both structure of the polystyrene-based brush copolymers and the length of pAA side chains have considerable effect on wettability of the polymer films.

TGA analysis revealed that polystyrene-based anionic copolymers were less thermally stable than p(St-co-VBC-TTC) but were similar by thermal stability to linear pAA.

As it is well known, amphiphilic block copolymers dissolved in appropriate solvents can self-assemble into micelles. DLS measurements of the anionic brush copolymers in DO and its mixtures with H<sub>2</sub>O were done at 30 °C (Table 4). Addition of 2% of water slightly decreased hydrodynamic diameter ( $D_h$ ) of anionic copolymers, which can be attributed to a shrinkage of hydrophobic pSt block. At water content 10%, DLS curve showed noticeable shift of the peak to the side of larger  $D_h$  particles (micelles) (25–100 nm). At water content 20%, particle size distribution curve in most cases became bimodal. Finally, at water content 30–50%, the micellar aggregates with  $D_h$  of 300–1000 nm are dominant.

Typical DLS curves of BCB-type copolymers in DO/water solutions are presented in Fig. 6. Solution behaviour of *brush-coil-brush* copolymers in the mixtures of DO/water depends on the length of pAA side chains. At water content 20% and more, BCB with short pAA chains tends to form large micellar aggregates (up to 500–1000 nm), while BCB with longer pAA side chains forms micelles with  $D_h$  of 30–60 nm.

A difference in aggregation behaviour of the BCB copolymers with short and long pAA side chains can be explained by a different ratio of hydrophobic and hydrophilic segments (different ratio of weight fraction of pAA to pSt-co-pVBC) in these copolymers. BCB copolymers with longer pAA side chains (large hydrophilic brush segments) tend to form stable micelles. Stabilization of the micelles formed by the same copolymers with shorter pAA side chains (smaller hydrophilic segments) is insufficient, which leads to formation of large micellar aggregates.

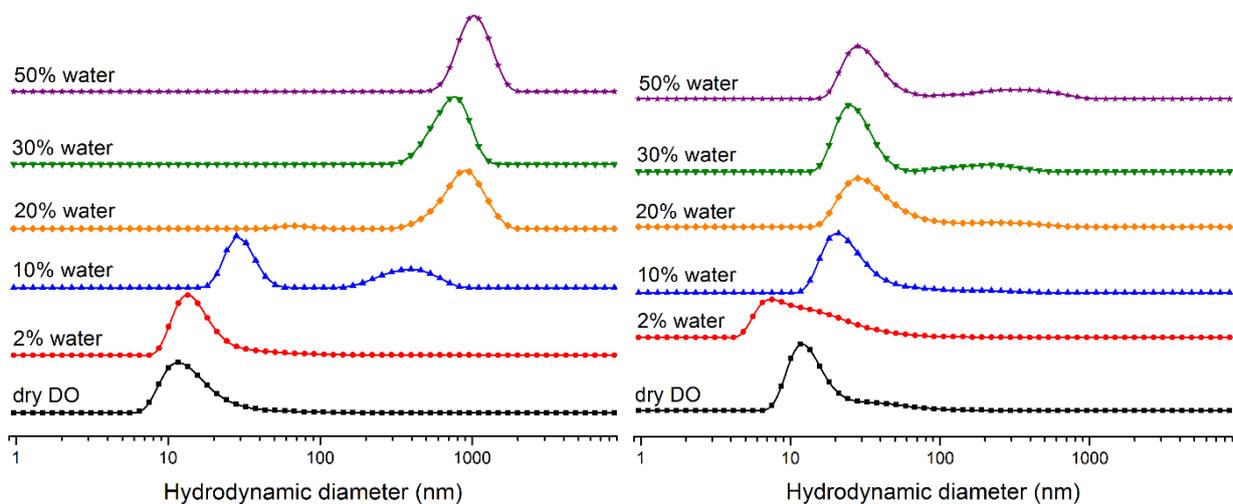


Fig. 6. Volume-based hydrodynamic diameter of the particles formed by the copolymers BCB3 (left) and BCB4 (right) in DO and its mixtures with water at 30 °C

Behaviour of the *coil-brush-coil* copolymer CBC1 in DO/water mixtures is different from that of BCB copolymers. At water content 20–50%, the copolymer CBC formed micelles which size (about 25 nm) was almost independent on water content. Irrespective of the pAA side chain length, self-assembly of the copolymers RB1 and RB2 is similar. At larger water content (20% and more), large unstable micellar aggregates with the diameter of 40–70 nm and 500–700 nm are observed.

Fig. 7 shows TEM images of polystyrene-based anionic brush copolymers of various structure. TEM images demonstrate that irrespective of copolymer structure, the micelles have spherical or near spherical shape and tend to form large aggregates. The size of micelles, formed by *coil-brush* copolymers is about 45 nm, by *brush-coil-brush* – 65 nm, by *coil-brush-coil* – 30 nm, and by random brush – 20–25 nm. These results correlate with DLS measurements data.

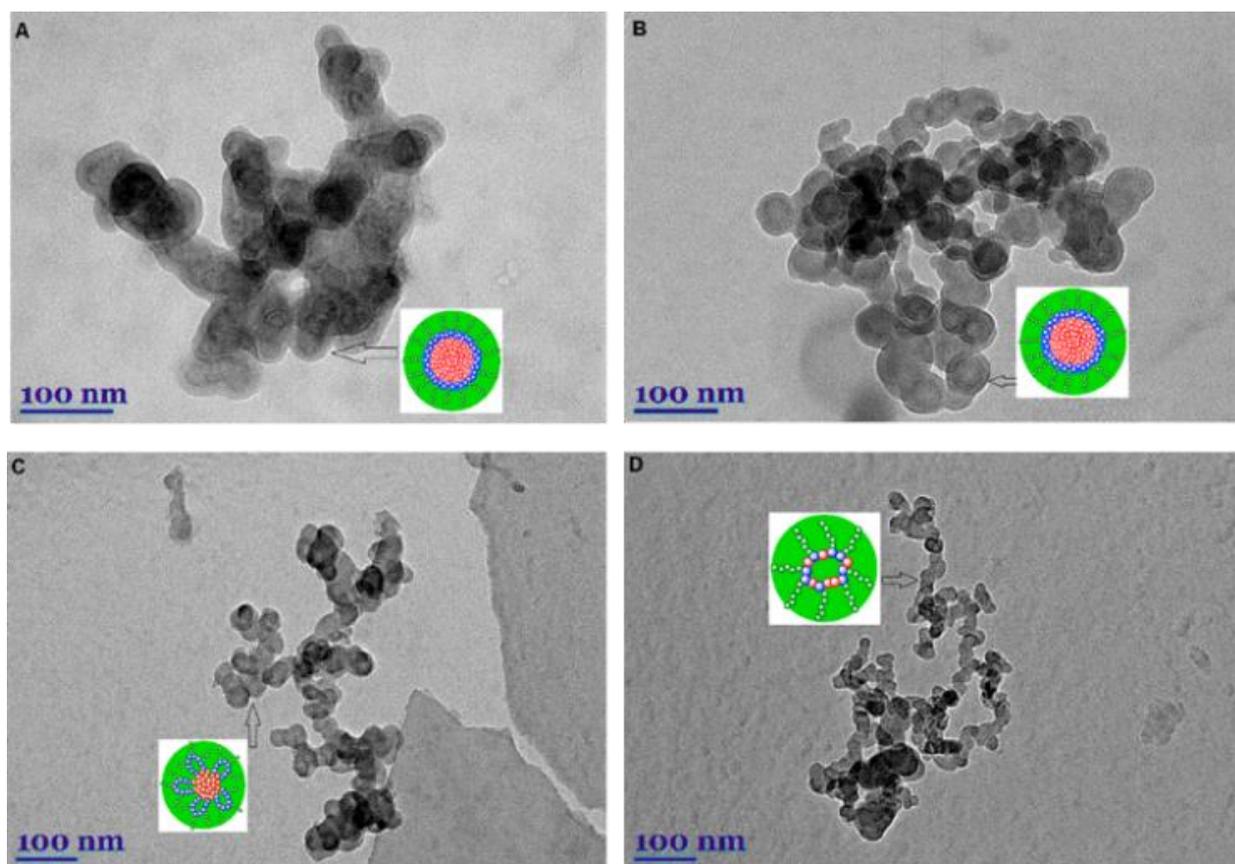


Fig. 7. TEM images of polystyrene-based *coil-brush* copolymers: *coil-brush* copolymer CB1 (A), *brush-coil-brush* copolymer BCB1 (B), *coil-brush-coil* copolymer CBC1 (C), and random brush copolymer RB2 (D). Inserts show possible structure of micelles.

## CONCLUSIONS

1. Anionic molecular brushes with polyacrylate or polystyrene-based backbone and poly((meth)acrylic acid) side chains were synthesized via RAFT *grafting from* method. This strategy is well suitable for the synthesis of densely grafted anionic brush copolymers with short (DP 5–10) or medium-length (DP 25–50) pAA side chains and narrow molecular weight distribution ( $\bar{D}$  1.2–1.5).
2. A possibility to use *click* reactions for the synthesis of anionic molecular brushes was evaluated. The Cu(I)-catalysed azide-alkyne *click* reaction between poly(meth)acrylate-based backbone bearing azide groups and alkyne terminated chains of pAA or p(*tert*-BMA) was negligible and complicated. The epoxy-thiol *click* reaction between p(GMA-*st*-BMA) backbone and thiol-group terminated p(*tert*-BMA) chains proceeded at high temperature (80 °C) only. The use of *click* reactions in the synthesis of anionic molecular brush is not viable.
3. Using mono- and difunctional RAFT CTA of various structures, random, diblock and two-type triblock copolymers of styrene and VBC were synthesized. After decoration of these copolymers by TTC groups and RAFT graft polymerization of AA, random brush, *coil-brush*, *brush-coil-brush* and *coil-brush-coil* copolymers with low dispersity ( $\bar{D}$  1.1–1.4) were synthesized.
4. Linear multifunctional CTA (multiCTA) with 4 to 10 TTC groups per molecule were synthesized. The use of multiCTA for the synthesis of the multiblock copolymers pSt-*b*-pVBC failed since extension of the pSt chain by VBC units was negligible. Furthermore, the synthesis and purification of linear multiCTA are rather complicated.
5. The  $pK_a$  values of anionic molecular brushes pHEA-*graft*-pAA are higher compared with that of linear pAA, so they are weaker acids. The size of anionic molecular brushes is pH-dependent with its minimal value at pH lower than 4.5. In the pH range 4.5 to 6.5, the anionic molecular brushes undergo the coil-rod transition, and their size increases. The thermal behaviour of pHEA-*graft*-pAA is similar to that of linear pAA.
6. The films of polystyrene-based anionic brush copolymers are more hydrophilic than those of p(St-*co*-VBC-TTC), with water contact angle between 15° and 45°.

The best wettability is characteristic for the films of *brush-coil-brush* copolymers with long pAA side chains.

7. The micellization and aggregation behaviour of polystyrene-based *coil-brush* copolymers in DO/water mixtures depends on structure of the copolymers and the length of pAA side chains. *Coil-brush* and *brush-coil-brush* copolymers tend to form spherical micelles ( $D_h = 20\text{--}100$  nm) and micellar aggregates ( $D_h = 300\text{--}1000$  nm), especially, when pAA side chains are short.

## LIST OF SCIENTIFIC PUBLICATIONS ON THE THEME OF DISSERTATION

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1. Krivorotova T., Jonikaite-Svegziene J., Radzevicius P., Makuska R. Synthesis by RAFT polymerization and properties of anionic cylindrical molecular brushes bearing poly(acrylic acid) side chains, *Reactive and Functional Polymers*, 2014, 76, P. 32-40.
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2. Krivorotova T., Jonikaitė-Švėgždienė J., Radzevičius P., Makuška R., RAFT polymerization of 2-hydroxyethyl (meth)acrylate. *Programme and Proceedings of International Conference of Lithuanian Chemical Society „Chemistry and Chemical Technology 2014“*, Kaunas, Lithuania, 2014, P. 342.
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4. Jonikaitė-Švėgždienė J., Merkytė V., Krivorotova T., Makuška R., Synthesis of anionic molecular brushes by „RAFT grafting from” approach. *Programme and Proceedings of International Conference of Lithuanian Chemical Society „Chemistry and Chemical Technology 2015“*, Vilnius, Lithuania, 2015, P. 296.
5. Jonikaitė-Švėgždienė J., Paukštis Š., Kudrešova A., Makuška R., Synthesis by RAFT and properties study of random and diblock bottle-brush polyelectrolytes. *Programme and Proceedings of Baltic Polymer Symposium 2016*, Klaipėda, Lithuania, 2016, P. 59.

6. Jonikaitė-Švėgždienė J., Kudrešova A., Paukštis Š., Makuška R., Synthesis and properties of polystyrene-based coil-brush copolymers. *There is no future without the past. Science on the interface of XIX – XXI centuries, the international conference dedicated to the 215-th birth anniversary of Ignacy Domeyko*. Vilnius, Lithuania, 2017, P. 104.

#### **Abstracts of international scientific conferences**

1. Jonikaitė-Švėgždienė J., Krivorotova, T. Joskaudas, T. Makuška R., Synthesis of multiblock copolymers by RAFT using linear multifunctional chain transfer agents. *Baltic Polymer Symposium 2013: Programme and Book of Abstracts*. 2013, Trakai, Lithuania, P. 85.
2. Jonikaitė-Švėgždienė J., Merkytė V., Krivorotova T., Makuška, R., Successive RAFT polymerization of styrene and 4-chloromethyl styrene yielding block copolymers. *Baltic Polymer Symposium 2014: Programme and Book of Abstracts*. 2014, Laulasmaa, Estonia, P. 88.

#### **ACKNOWLEDGEMENTS**

I'd like to express my appreciation to my supervisor Prof. Dr. Ričardas Makuška for the knowledge, all given advices and taking care of me during the years of PhD studies. I'd like to thank all the colleagues at the Department of Polymer Chemistry of Vilnius University, especially, Prof. Dr. Saulutė Budrienė, Doc. Dr. Aušvydas Vareikis, Doc. Dr. Tatjana Kochanė, Doc. Dr. Kostas Radzevičius, Dr. Tatjana Krivorotova, Dr. Alma Bočkuvienė, Dr. Virginija Pamedytytė, Dr. Daina Ragauskienė, Genė Umbrasienė, Irina Gerasimčik, Sandra Mačiulytė, Gediminas Čiuta, Vaidas Klimkevičius, Česlav Višnevskij and Medeina Steponavičiūtė for warmth of our relationship and practical advices. I acknowledge my students Vakarė Merkytė, Tadas Joskaudas, Šarūnas Paukštis, Alina Kudrešova, Matas Batutis and Povilas Radzevičius for their readiness and skill in the practical work.

I express my special thanks to all my family and friends for their big love, boundless care and patience.

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# ANIJONINIŲ ŠEPETINIŲ POLIMERŲ SINTEZĖ RAFT POLIMERIZACIJOS IR *KLIK* CHEMIJOS METODAIS IR JŲ TYRIMAS

## SANTRAUKA

Dėl itin plataus pritaikymo galimybių šiuo metu intensyviai tyrinėjami sudėtingos architektūros (šepetiniai, žvaigždiniai ir pan.) siauro molekulinų masių pasiskirstymo kopolimerai, galintys atrankiai reaguoti į aplinkos veiksnius (pH, tirpiklį, temperatūrą). Dėl fundamentinių ir praktinių priežasčių mokslininkus itin domina šių polimerų tirpaluose ir ant įvairių paviršių formuojamos sudėtingos struktūros – micelės, vezikulės, agregatai, klasteriai ir pan. Norint ateityje šepetinius polimerus sėkmingai pritaikyti biomedicinos ar panašiose srityse, reikia pasiekti, kad jie pasižymėtų tokiais pat ar net geresnėmis savybėmis nei imituojamos biomakromolekulės, pvz., proteoglikanai. Nuolat ieškoma naujų sintezės metodų ir strategijų šiems polimerams sintetinti. Vienas universaliausių metodų – RAFT (grįžtamojo prijungimo-fragmentacijos grandinės perdavos) polimerizacija. Derinant šį metodą su cheminio modifikavimo ir *klik* chemijos reakcijomis, galima išplėsti gaunamų kopolimerų sudėties ir struktūros ribas, neprarandant galimybės kontroliuoti jų molekulinų parametų. Šepetinių norimos struktūros kopolimerų sintezės metodikų kūrimas ir šių polimerų tirpalų savybių tyrimas – itin svarbi šiuolaikinės polimerų chemijos dalis.

Pagrindinis šio darbo tikslas – susintetinti ir ištirti įvairios struktūros anijoninius šepetinius polimerus, turinčius šonines poli((met)akrilo rūgšties) grandines. Svarbiausi šio darbo rezultatai, atspindintys naujumą, originalumą ir svarbą:

Pirmą kartą susintetinti ir išbandyti RAFT polimerizacijoje 4 tipų tritiokarbonatiniai grandinės perdavos agentai (GPA), tinkami įvairių monomerų (stireno, vinilbenzilchlorido, akrilo rūgšties, *tert*-butilmetakrilato) polimerizacijai kontroliuoti ir įvairios struktūros (ko)polimerams sintetinti.

Nustatyta, kad anijoninių šepetinių kopolimerų sintezei tinkamesnis RAFT *skiepijimo nuo* metodas, kai pagrindinė grandinė modifikuojama įvedant tritiokarbonato (TTK) grupes ir vykdoma skiepijamoji AR RAFT polimerizacija.

Pirmą kartą RAFT *skiepijimo nuo* metodu susintetinti tankūs anijoniniai šepetiniai kopolimerai, turintys pagrindinę poliakrilatinę grandinę ir trumpas ar vidutinio ilgio šonines poli(akrilo rūgšties) (pAR) grandines, kuriems būdingas siauras molekulinų

masių pasiskirstymas ( $\bar{M}_w/\bar{M}_n$  1,2–1,5). Anijoniniai šepetiniai kopolimerai pasižymi silpnesnėmis rūgštinėmis savybėmis nei linijinės struktūros pAR, jų  $pK_a$  vertės didesnės. Šių kopolimerų makromolekulių matmenys priklauso nuo pH – yra maži rūgštinėje terpėje ir ženkliai padidėja AR grandžių jonizacijos metu, kai pH yra nuo 4,6 iki 6,5.

Susintetinti linijiniai multifunkciniai GPA, kurių molekulėje yra nuo 4 iki 10 TTK grupių, ir ištirta jų panaudojimo galimybė, sintetinant multiblokinius St ir VBC kopolimerus. Multiblokinių kopolimerų  $m(pSt-b-pVBC)$  sintezė naudojant multifunkcinius GPA nepavyko, kadangi pratęsiant pSt grandinę VBC konversija buvo labai maža. Be to, linijinių multifunkcinių GPA sintezė ir gryninimas sudėtingi, jų  $\bar{M}_w/\bar{M}_n$  didelis ( $\bar{M}_w/\bar{M}_n > 1,7$ ), TTK grupės sunkiai prieinamos.

Pirmą kartą RAFT *skiepijimo nuo* metodu, specialiai parinkus vien- ir difunkcinius RAFT GPA, susintetinti *šepetukas-gyvatukas-šepetukas* ir *gyvatukas-šepetukas-gyvatukas* struktūros anijoniniai šepetiniai kopolimerai. TTK grupėmis modifikuotų St ir VBC kopolimerų dangų paviršius yra hidrofobinis, anijoninių šepetinių kopolimerų dangos yra hidrofilinės, jų vilgymo kampas yra 15–45°. Geriausiu vilgumu pasižymi statistinių ir triblokinių *šepetukas-gyvatukas-šepetukas* struktūros kopolimerų, turinčių ilgesnes pAR grandines, dangos. Nustatyta, kad anijoninių šepetinių polistireninių kopolimerų agregacija DO/H<sub>2</sub>O mišiniuose priklauso nuo kopolimero architektūros ir pAR šoninių grandinių ilgio. Diblokiniai ir triblokiniai *šepetukas-gyvatukas-šepetukas* struktūros kopolimerai linkę sudaryti įvairaus dydžio mices ( $D_h = 20–100$  nm), o triblokiniai *gyvatukas-šepetukas-gyvatukas* struktūros kopolimerai – mažiau struktūruotas mices. Micelės yra linkusios sudaryti micelių agregatus ( $D_h = 300–1000$  nm); šis polinkis didesnis, kai pAR šoninės grandinės yra trumpos.

Pirmą kartą anijoniniai šepetiniai kopolimerai susintetinti panaudojus epoksi-tiolis *klik* reakciją tarp epoksigrupes turinčios p(GMA-*st*-BMA) grandinės ir galinę merkaptogrupę turinčio poli(*tert*-butilmetakrilato). Šepetinių kopolimerų sintezė *skiepijimo į* metodu, vykdant *klik* reakcijas, nėra itin perspektyvi, nes jos vyksta sunkiai dėl didelės abiejų komponentų molekulinės masės, erdvinių trukdžių pagrindinėje grandinėje, o kai kuriais atvejais ir katalizines sistemas ardančių funkcinių grupių.