

VILNIUS UNIVERSITY
CENTRE OF PHYSICAL SCIENCES AND TECHNOLOGY

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**SYNTHESIS OF CATIONIC RANDOM AND DIBLOCK BRUSH
COPOLYMERS AND THEIR APPLICATION FOR STABILIZATION OF
TITANIA NANOPARTICLE DISPERSIONS**

Summary of doctoral dissertation
Physical Sciences, Chemistry (03P)

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The scientific work was carried out in 2012-2016 at Vilnius University.

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The doctoral dissertation is available at the Libraries of Vilnius University and Institute of Chemistry of the Centre for Physical Sciences and Technology, and on VU website:

<http://www.vu.lt/lt/naujienos/ivykiu-kalendorius>.

VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

VAIDAS KLIMKEVIČIUS

**KATIJONINIŲ ŠEPETINIŲ STATISTINIŲ IR DIBLOKINIŲ KOPOLIMERŲ
SINTEZĖ IR JŲ PANAUDOJIMAS TITANO DIOKSIDO NANODALELIŲ
DISPERSIJOMS STABILIZUOTI**

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INTRODUCTION

Relevance of the work. Titania nanoparticles are between the most important nanomaterials globally used due to their unique size dependent properties such as mechanical, chemical and optical stability, nontoxicity, low cost, and corrosion resistance. Titania nanoparticles are widely used not only in paint, papermaking, plastics, cosmetics, but also applied in many special research fields such as antibacterial, anticorrosion, antifogging, biomedical, fluid transportation, liquid separation, offset printing and liquid reprography, self-cleaning, site-selective functional patterning and water condensation. Physical and chemical properties of nanoparticles are affected not only by molecular structure, but also by their size, shape, organization, and surface properties. Due to their large surface area, titania nanoparticles have high tendency to adhesion and aggregation, therefore, the use of dispersants for the stabilization of titania nanodispersions is essential.

There is an increasing demand to use comb-type polyelectrolytes for steric stabilization of metal oxide nanoparticles, because of their ability to electrostatically bind to oppositely charged surfaces. The chains of such polyelectrolytes become solvated in polar media creating an effective steric barrier that prevents the other particles from approaching too close. Such kinds of dispersants are able to stabilize metal oxide dispersions in a broad pH range under high ionic strength and temperature. There are very few publications at the present describing stabilization of metal oxide dispersions, including TiO_2 , by the use of anionic comb polyelectrolytes. To our knowledge, there is only one publication related to stabilization of silica nanoparticles by the use of cationic comb polyelectrolytes, and no post about stabilization of titania nanoparticles.

The preparation of brush copolymers of complex architecture is extremely challenging since the block- or comb-type polyelectrolytes cannot be synthesized by using conventional free radical polymerization. Only the use of contemporary methods of reversible deactivation radical polymerization (RDRP) can meet the requirements. RAFT polymerization is one of the most popular methods of RDRP which has proved to be a robust and versatile process that is applicable to the majority of monomers subject to radical polymerization. The successful outcome in RAFT polymerization depends on

the selection of the RAFT chain transfer agent (CTA) for the specific monomers and reaction conditions, and it is the main limitation of this method. Because of narrow selection of commercially available products, most RAFT CTA must be synthesized *in house* using contemporary methods of organic chemistry. Thus, the synthesis of efficient CTA and their application in the RAFT polymerization allowed us to get the brush-type polyelectrolytes of complex structure called as “superdispersants” for the stabilization of aqueous titania nanoparticle dispersions.

The aim of the present work was to synthesize and study monodisperse brush copolymers of various composition and architecture, and use them for the stabilization of aqueous dispersions of titania nanoparticles.

The objectives of the research were the following:

- ✓ To prepare several RAFT CTA suitable for the RAFT polymerization of methacrylates, and evaluate their efficiency in control of the RAFT process.
- ✓ To study and compare RAFT polymerization of methacrylate macromonomers PEO_xMEMA differing by the length of PEO substitutes (x = 5, 9, 19, 43).
- ✓ To study RAFT copolymerization of PEO_xMEMA and cationic monomer METAC, and to synthesize well-defined cationic comb copolymers p(PEO_xMEMA-METAC) differing in both architecture and composition.
- ✓ To evaluate possibilities of the synthesis of brush block copolymers by the RAFT polymerization, and to synthesize double brush or cationic brush copolymers by successive RAFT polymerization of PEO_xMEMA macromonomers with different length of PEO substitutes, or METAC and PEO_xMEMA, respectively.
- ✓ To use cationic brush copolymers for the stabilization of aqueous dispersions of titania nanoparticles, and to evaluate the effects of structure and composition of the brush copolymers on stability and rheological behaviour of the dispersions.

Scientific novelty and practical value of the dissertation. In order to realize good control of the RAFT polymerization of methacrylate-type macromonomers, several novel RAFT CTA were prepared and used for the synthesis of random and diblock brush

copolymers. Kinetics of the RAFT polymerization of PEO methacrylates (PEO_xMEMA) with different length of PEO substitutes was studied and compared for the first time. Cationic random comb copolymers of low dispersity, desirable molecular weight (degree of polymerization) and composition were synthesized via RAFT polymerization. The optimal conditions for the synthesis of diblock brush copolymers by the RAFT were determined, and diblock brush copolymers with the blocks differing in the length of PEO side chains were synthesized for the first time. Cationic random and diblock brush copolymers were applied for the stabilization of concentrated aqueous dispersions of titania nanoparticles for the first time. The effect of the copolymer structure (charge density, length of PEO side chains) on stability of titania nanodispersions was evaluated. The stabilized dispersions of titania nanoparticles containing acrylic binders have high application potential for the preparation of scratch resistant nanocomposite coatings.

Defensive statements:

- ✓ RAFT polymerization is suitable method for the synthesis of cationic random and diblock brush copolymers of various architecture or composition.
- ✓ Dispersity of cationic diblock brush copolymers can be reduced by the use of „one-pot“ RAFT polymerization.
- ✓ Highly charged cationic comb copolymers with long PEO side chains are very efficient “superdispersants” for the stabilization of concentrated aqueous dispersions of titania nanoparticles.
- ✓ Cationic diblock brush copolymers are inappropriate for the stabilization of titania nanodispersions, since they act as efficient flocculants.

Approbation of the research results. The results of the research are presented in 10 scientific publications, 3 of them are the articles published in the journals included into the database of Clarivate Analytics Web of Science.

Structure of the doctoral dissertation. The doctoral dissertation is written in Lithuanian and consists of an introduction, 3 chapters, conclusions, a list of references (271 positions) and a list of scientific publications of the Author. The material of the doctoral dissertation is presented in 177 pages featuring 36 schemes, 44 figures, and 9 tables.

CONTENT OF THE DISSERTATION

Introduction presents the problem and relevance of the study, defines the aim and the research tasks, outlines the defensive statements, and discusses the scientific novelty as well as the practical value of the doctoral dissertation.

Chapter I introduces the literature review of the recent publications related to the topic of the doctoral dissertation.

Chapter II presents characteristics of the materials, the methods used for the synthesis of polymers and intermediate substances, and the methods of sample preparation and investigation.

Materials. Poly(ethylene oxide) monomethylether methacrylate (PEO_xMEMA, Aldrich, M_r 300, 475, 950, 2000, (x = 5, 9, 19, 43)) and [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC, Aldrich, M_r 207.70) were purified through column filled with basic Al₂O₃.

Titania (TiO₂) nanoparticles were from *Evonic* (P-25, M_r 79.87, n²⁰ 2.488-2.609, d₄²⁵ 4.84), diameter 25 nm, specific surface area 49 m²/g.

Polymer synthesis and characterization. The polymers used in this research were synthesized via RAFT polymerization. The number average molecular weight (M_n) and dispersity (Đ = M_w/M_n) of cationic random and diblock brush copolymers were determined by size-exclusion chromatography (SEC) using Viscotek TDAmx system equipped with triple detection array (TDA305) consisting of a refractive index detector, right-angle (90°) and low-angle (7°) light scattering detectors, and four-capillary bridge viscosity detector plus a Viscotek UV detector 2500.

Preparation and investigation of titania nanoparticle dispersions. Colloidal 5–30 wt % dispersions were prepared by dispersing TiO₂ nanoparticles in aqueous solutions under magnetic stirring. The dispersions were treated by cationic comb p(PEO_xMEMA-METAC) or diblock pMETAC-*b*-p(PEO_xMEMA) (x = 5, 9, 19, 43) copolymers with an appropriate amount up to 2 mg/m². Dispersions were stirred for 10 min and ball-milled using zirconia milling balls with a diameter of 0.4 mm for 20

minutes to several hours using *Retsch PM400* apparatus at the constant rate of 400 rpm. Maximal adsorption of the brush copolymers on TiO₂ nanoparticles was evaluated by thermogravimetric analysis using Mettler-Toledo TGA/DTA 851 equipment. The surface potential of TiO₂ nanoparticles covered by cationic polyelectrolytes was evaluated by measuring the zeta potential. The determination of the zeta potential was carried out using a Zetaprobe analyzer (Colloidal Dynamics). Dispersion stability and particle size distribution (PSD) of polymer-coated TiO₂ nanoparticles were evaluated by laser diffraction using Beckman Coulter LS230 equipped with a 4 mW laser at a wavelength of 750 nm and polarization intensity differential scattering (PIDS). Dynamic light scattering (DLS) measurements were done using ZetaSizer Nano ZS (Malvern Instruments) equipped with a 4 mW He-Ne laser at a wavelength of 633 nm. Rheological measurements of the aqueous dispersions of titania nanoparticles were performed using a modular compact rheometer MCR302 (Anton Paar) with two measuring systems of different geometry: a coaxial cylinder CC27 which was used for viscous dispersions and a double gap cylinder DG26.7/Q1 which was used for thin dispersions ($\dot{\gamma} < 200$ mPa·s).

Chapter III presents the results of experimental investigations. The experimental results cover preparation of RAFT CTA with different R-groups, synthesis of well-defined cationic comb and diblock brush copolymers of various architecture and composition by RAFT polymerization, and the use of the brush copolymers for the stabilization of titania nanoparticle dispersions.

Synthesis of RAFT CTA and evaluation of their efficiency. During the present study, six RAFT CTA were synthesised (Fig. 1) using two different methods of organic chemistry: 1) nucleophilic substitution (S_N2) reaction of a carbodithioate salt with an alkylating agent (1–4 compounds); 2) radical substitution of a bis(thioacyl) disulphide (5, 6 compounds). It is worth to note that the synthesized CTA are trithiocarbonates containing the same Z-group (butylthio- (BuS-)); thus the control of the RAFT polymerization depends on the structure of R-group of a CTA only.

The effect of R-group of CTA on RAFT polymerization was evaluated by comparing the dispersity (\bar{D}) of p(PEO₄₃MEMA) synthesized in the presence of various CTA (Fig. 2).

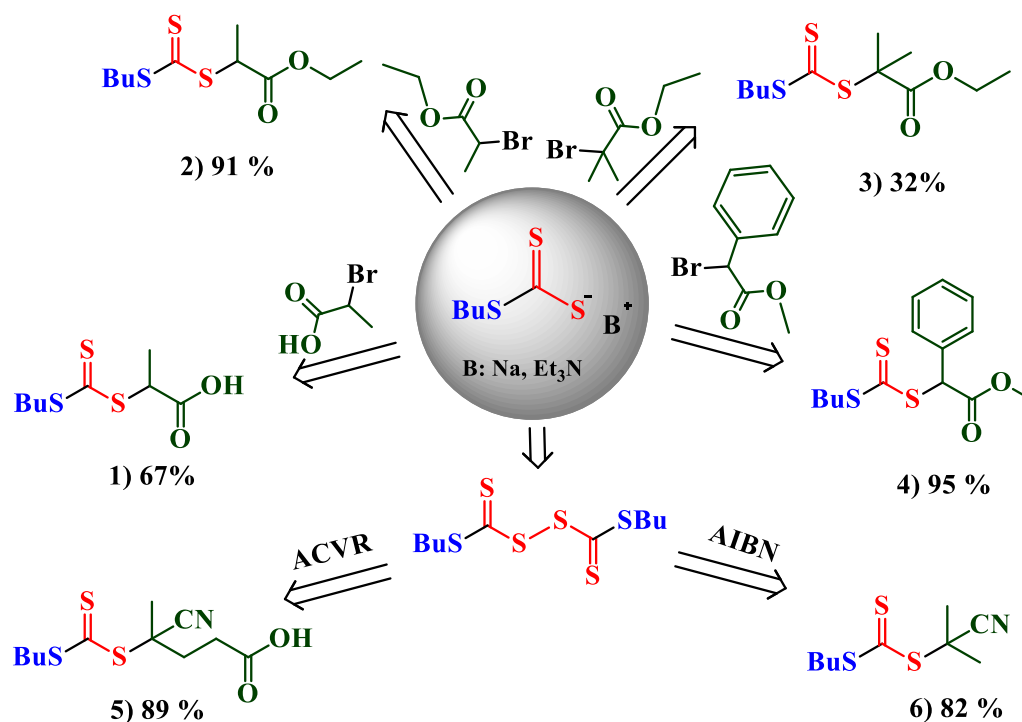


Fig 1. Structure and yield of the RAFT CTA prepared in the present study: 1) 2-(((butylthio)carbonothioyl)thio) propanoic acid (BCPA); 2) ethyl 2-(((butylthio)carbonothioyl)thio) propanoate (EBCP); 3) ethyl 2-(((butylthio)carbonothioyl)thio)-2-methylpropanoate (EBCMP); 4) methyl 2-(((butylthio)carbonothioyl)thio)-2-phenylacetate (MBCFA); 5) 4-(((butylthio)carbonothioyl)thio)-4-cyanopentanoic acid (BCVA); 6) butyl (2-cyanopropan-2-yl) carbonotrithioate (BCPCT).

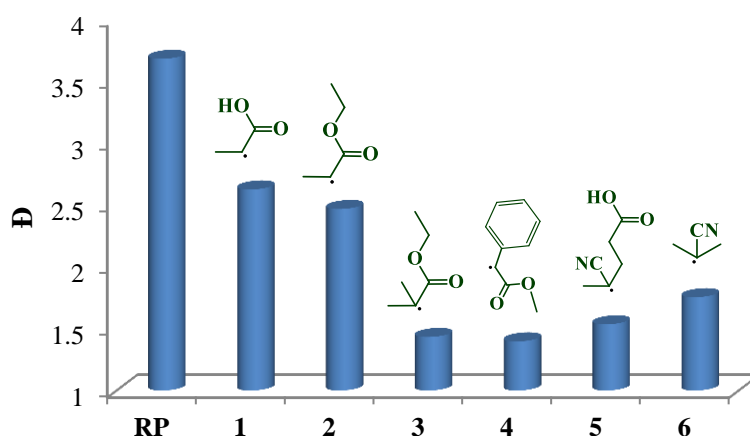


Fig. 2. The effect of R-group of CTA on dispersity of p(PEO₄₃MEMA) synthesized in the presence of various CTA. The number on x-axis meets the number of CTA in Fig. 1, RP refers to the polymer synthesized via conventional free radical polymerization.

The CTA according to the activity of the expelled radical (R^\bullet) could be divided into two groups: 1) with secondary R-group (1, 2 and 4 compounds) and 2) with tertiary R-group (3, 5 and 6 compounds). It is obvious that CTA with tertiary R-group control RAFT polymerization of PEO₄₃MEMA better than CTA with secondary R-group, except CTA 4 (MBCFA); effectiveness of CTA 4 is explained by an extra stabilization of the expelled radical by conjugation with phenyl group. Referring to the results presented in Fig. 2, to control RAFT polymerization of methacrylates with various substitutes, three RAFT CTA from the above presented were chosen, namely, CTA 4, CTA 5, and CTA 6. CTA 3, despite good control of the RAFT polymerization of PEO₄₃MEMA, was abandoned due to complicated synthesis and purification procedures, and low product yield.

RAFT polymerization of methacrylate macromonomers with different length of PEO substitutes. In the present study, RAFT polymerization of PEO_xMEMA with molecular weights M_n 300, 475, 950 and 2000, which correspond to the degree of polymerization (PL) in PEO substitutes approx. $x = 5, 9, 19$ and 43, respectively, was studied and compared. Schematic illustration of the RAFT polymerization of PEO_xMEMA using three different CTA is presented in Fig. 3.

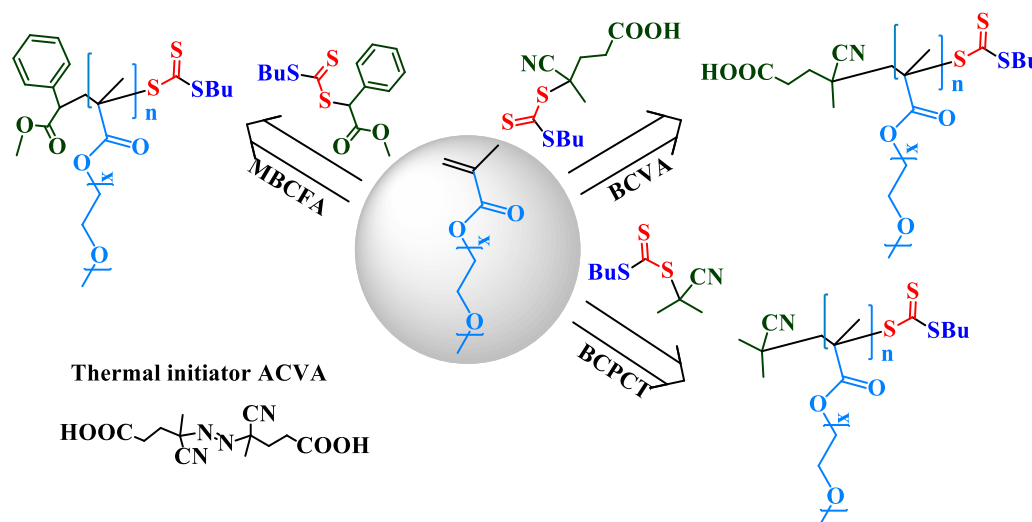


Fig. 3. Schematic illustration of the RAFT polymerization of PEO_xMEMA in the presence of MBCFA, BCVA and BCPCT as RAFT CTA and ACVA as thermal initiator

An increase of the molar ratio $[CTA]_0/[ACVA]_0$ from 1 to 10 leads to drastic reduction of dispersity of the polymers (Fig. 4). Obviously, the polymers synthesized

using BCVA as RAFT CTA exhibited the lowest dispersity at a certain ratio of $[CTA]_0$ to $[ACVA]_0$. For the most polymers, molar ratio $[BCVA]_0/[ACVA]_0 = 3/1$ was sufficient to get very low (nearly minimal) dispersity ($\mathcal{D} < 1.12$). Only dispersity of $p(\text{PEO}_{43}\text{MEMA})$ was higher ($\mathcal{D} = 1.22$) which could be explained by screening of the double bond of the macromonomer by long PEO chains. At low ratio $[CTA]_0$ to $[ACVA]_0$ (less than 2), dispersity of $p(\text{PEO}_{43}\text{MEM})$ was very high showing uncontrolled polymerization manner. At high ratio $[BCVA]_0$ to $[ACVA]_0$ (over 5), the control of PEO_xMEMA polymerization, even with long PEO chains, was excellent.

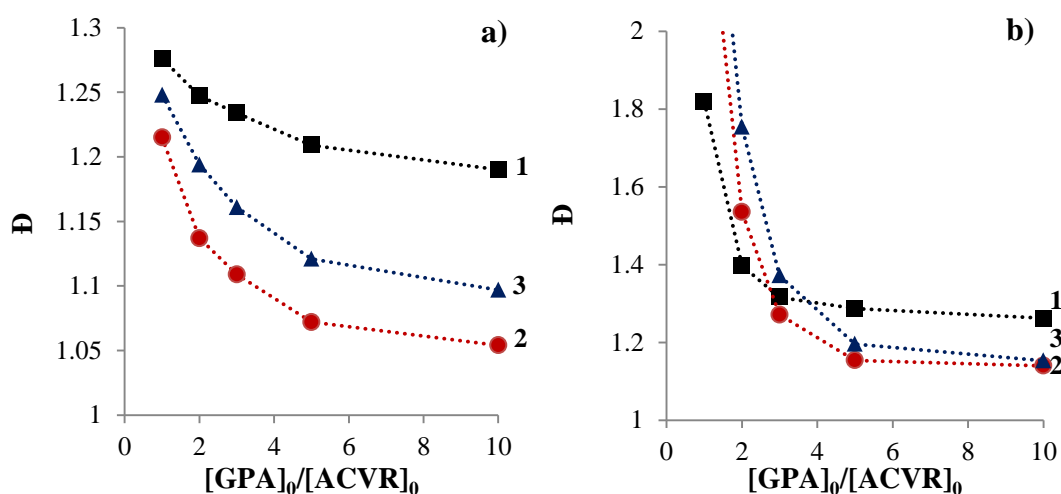


Fig. 4. Dispersity \mathcal{D} of $p(\text{PEO}_x\text{MEMA})$ vs molar ratio $[CTA]_0/[ACVA]_0$ used during RAFT polymerization of PEO_5MEMA (a) and $\text{PEO}_{43}\text{MEMA}$ (b) in presence of three different CTA: MBCFA (1), BCVA (2) and BCPCT (3). ($[M]_0/[ACVA]_0 = [100]/[1.5]$).

SEC results confirmed that molecular weight of the polymers got maximal values after 6 hours of polymerization and did not change during subsequent time. Conversion of the monomers with relatively short PEO chains ($x = 5$ or 9) after 6 hours of polymerization was very high (over 90 % at $[BCVA]_0/[ACVA]_0 = 10$, and over 97 % at $[BCVA]_0/[ACVA]_0 = 3$). Conversion of the monomers with longer PEO chains ($x = 19$ or 43) was lower; for example, conversion of $\text{PEO}_{43}\text{MEMA}$ at the molar ratio $[BCVA]_0/[ACVA]_0 = 10$ was only 70 %.

The correlation between molecular weight and monomer conversion showed linear trend (Fig. 6) which is usual relationship for controlled radical polymerization.

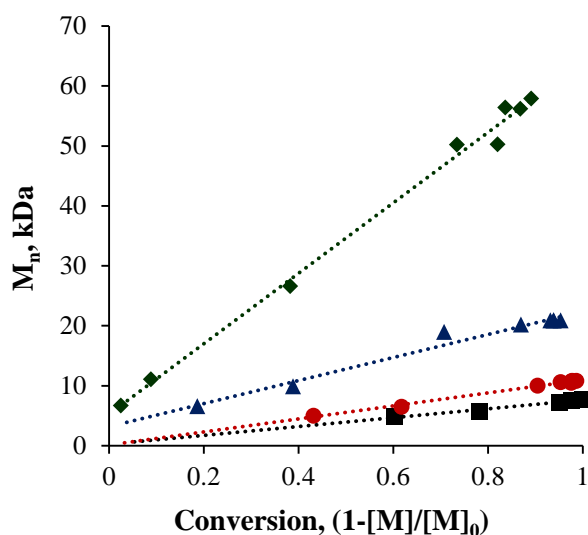


Fig. 6. Dependence of molecular weight of p(PEO_xMEMA) on conversion during RAFT polymerization of PEO₅MEMA (●), PEO₉MEMA (■), PEO₁₉MEMA (▲), and PEO₄₃MEMA (◆).

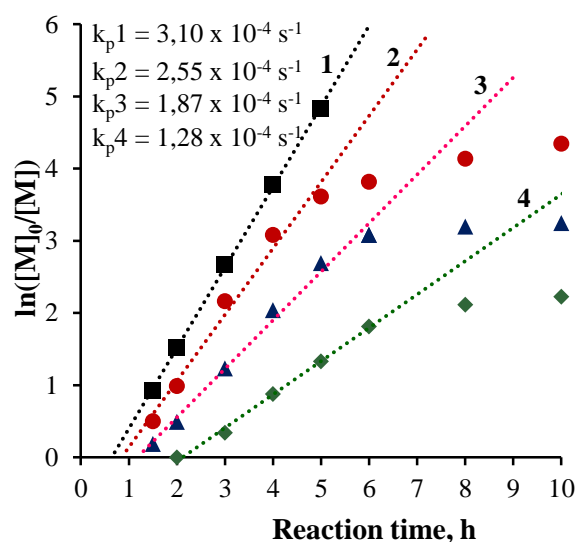


Fig. 7. Pseudo-first order kinetic plots for the RAFT polymerization of PEO₅MEMA (1), PEO₉MEMA (2), PEO₁₉MEMA (3), and PEO₄₃MEMA (4). [CTA]₀: [ACVA]₀ = 3.

Kinetic plots for the RAFT polymerization of PEO_xMEMA with various lengths of PEO chains under the same conditions are presented in Fig. 7. Polymerization of all the monomers, irrespective of the length of PEO chains, follows the pseudo-first reaction order. From the linear parts of the kinetic plots, the reaction rate constants k_p were calculated. The values of k_p show that the rate of the RAFT polymerization of PEO methacrylates contrariwise depends on the length of PEO side chains but the difference between the rates of polymerizations of PEO_xMEMA with the shortest and the longest PEO chains is not large, less than 2.5 times. Induction periods of 40, 50, 80 and 120 minutes were observed for the RAFT polymerization of PEO₅MEMA, PEO₉MEMA, PEO₁₉MEMA and PEO₄₃MEMA, respectively.

Synthesis and study of cationic comb copolymers p(PEO_xMEMA-METAC). A series of cationic comb copolymers of various charge density and length of PEO side chains, represented as p(PEO_xMEMA-METAC), were synthesized by RAFT copolymerization of METAC and PEO_xMEMA. Synthesis scheme and structure of the synthesized copolymers are shown in Fig. 8.

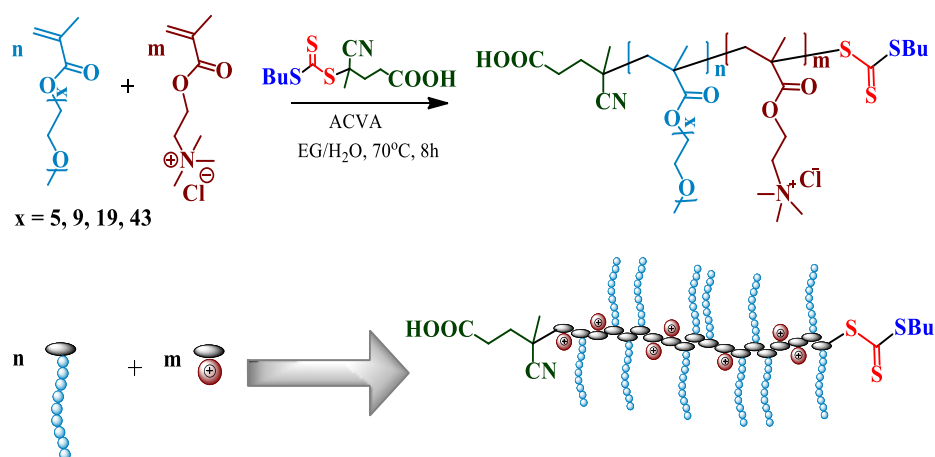


Fig. 8. Schematic illustration of the synthesis via RAFT polymerization and structure of cationic comb copolymers $p(\text{PEO}_x\text{MEMA-METAC})$.

Fig. 9 represents the dependences of degree of polymerization (DP) and dispersity \mathcal{D} of the cationic comb copolymers on the initial monomer feed ratio $[\text{PEO}_x\text{MEMA}]_0/[\text{METAC}]_0$ at a constant ratio of CTA to the initiator ($[\text{CTA}]_0/[\text{I}]_0 = 3$). RAFT copolymerization of PEO_xMEMA and METAC was well controllable resulting in the copolymers with low values of dispersity ($\mathcal{D} < 1.15$) (Fig. 9b). Only the copolymers containing long PEO side chains ($x = 43$) were characterized by higher dispersity (\mathcal{D} about 1.3). The degrees of polymerization of the synthesized comb polyelectrolytes were close to those theoretically calculated.

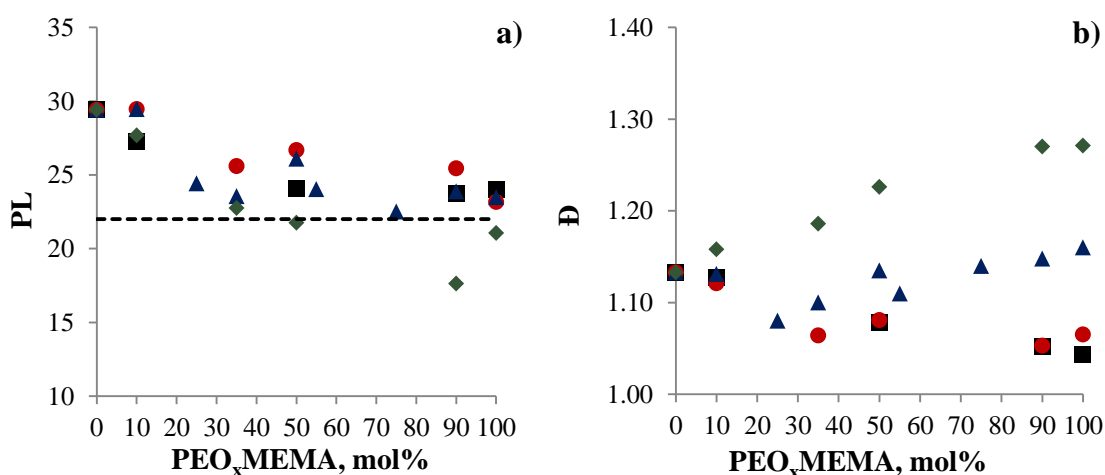


Fig. 9. Dependences of the degree of polymerization DP (a) and dispersity \mathcal{D} (b) of $p(\text{PEO}_x\text{MEMA-METAC})$ on initial monomer feed (mol %) during RAFT polymerization of PEO_5MEMA (\bullet), PEO_9MEMA (\blacksquare), $\text{PEO}_{19}\text{MEMA}$ (\blacktriangle), and $\text{PEO}_{43}\text{MEMA}$ (\blacklozenge). Reaction temperature 70°C , $[\text{CTA}]_0/[\text{ACVA}]_0 = 3$.

Synthesis and study of cationic diblock brush copolymers. p(PEO_xMEMA) synthesized by RAFT polymerization and containing terminal trithiocarbonate group (Fig. 3) was marked as p(PEO_xMEMA)-CTA. Diblock copolymers in which the both blocks are brush-type but contain PEO side chains of different length were synthesized by chain extension of p(PEO_xMEMA)-CTA by PEO_yMEMA units. For practical application of the diblock copolymers, PEO_xMEMA was used also for the chain extension of pMETAC-CTA.

Dispersity of the diblock copolymers synthesized by the chain extension of p(PEO_xMEMA)-CTA and pMETAC-CTA is presented in Fig. 10. Obviously, the diblock copolymers with low dispersity were synthesized in that case when the second block was of pMETAC or p(PEO_xMEMA) with short PEO chains (x = 5, 9). Dispersity of the diblock copolymers in which the first block was with short PEO chains (x = 5, 9) and the second block with long PEO chains (x = 19, 43) was moderate ($\mathcal{D} = 1.2\text{--}1.4$). And finally, dispersity of the diblock copolymers in which the both blocks were with long PEO chains (x = 19, 43) was large ($\mathcal{D} > 1.5$). An analysis of the data presented in Fig. 10 reveals the best way to synthesize diblock brush copolymers containing PEO side chains by RAFT: a monomer with shorter PEO chains should be polymerized first.

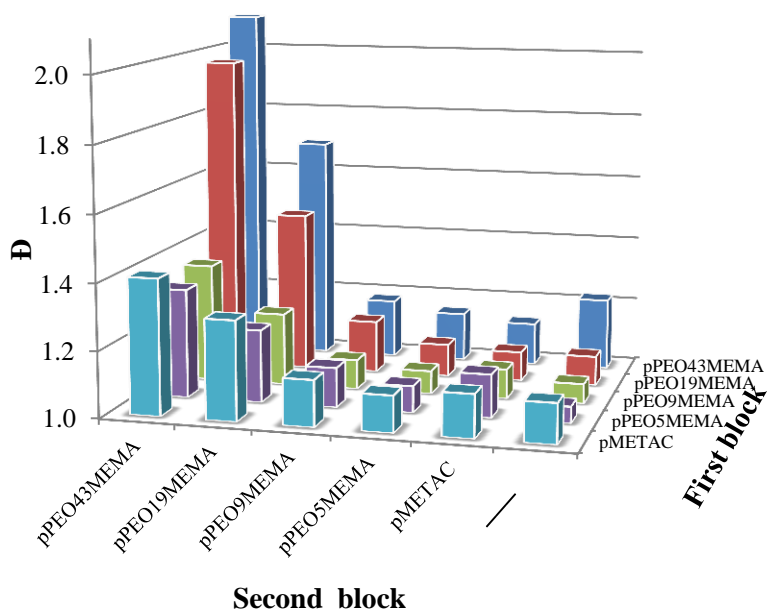


Fig. 10. Dispersity \mathcal{D} of the diblock copolymers containing the blocks of p(PEO_xMEMA) with PEO chains of various length and/or pMETAC and synthesized from various macro-CTA.

Table 1. Characteristics of the diblock copolymers p(PEO_xMEMA)-*b*-p(PEO_yMEMA) synthesized by RAFT polymerization with isolation of macro-CTA (A), and by “one-pot” RAFT technique (B)

No	Polymer	Yield, %		M _n , kDa		Đ	
		A	B	A	B	A	B
1	P(PEO ₁₉ MEMA)-CTA	93	93	20.4	22.1	1.09	1.10
2	P(PEO ₁₉ MEMA)- <i>b</i> -p(PEO ₁₉ MEMA)	94	94	40.3	43.8	1.49	1.29
3	P(PEO ₁₉ MEMA)- <i>b</i> -p(PEO ₄₃ MEMA)	94	91	55.0	56.2	1.97	1.72
4	P(PEO ₄₃ MEMA)-CTA	86	82	35.2	42.8	1.22	1.19
5	P(PEO ₄₃ MEMA)- <i>b</i> -p(PEO ₁₉ MEMA)	89	92	59.9	61.4	1.69	1.33
6	P(PEO ₄₃ MEMA)- <i>b</i> -p(PEO ₄₃ MEMA)	88	88	74.5	104.6	2.10	1.83

The effect of isolation of macro-CTA on the chain extension was evaluated by comparing characteristics of the diblock copolymers p(PEO_xMEMA)-*b*-p(PEO_yMEMA) synthesized by two methods – RAFT polymerization with isolation of macro-CTA and “one-pot” RAFT polymerization (Table 1). “One-pot” synthesis of diblock copolymers by the RAFT process means that the first block (macro-CTA) was neither isolated nor purified, and the chains were extended in the same reaction vessel just by addition of another monomer and an appropriate amount of an initiator. Only one parameter was obviously related to the method of the synthesis: dispersity Đ of the diblock copolymers synthesized by “one pot” technique was apparently lower. Chain extension by PEO₁₉MEMA using “one pot” technique gave diblock copolymers with reasonably low dispersity (Đ about 1.3). Contrarily, chain extension by PEO₄₃MEMA using “one pot” technique resulted in diblock copolymers with much higher dispersity, Đ about 1.7–1.8.

Stabilization of titania nanoparticle dispersions by cationic brush copolymers.

Two series of brush polymers with various charge densities, length of PEO side chains and structure (Fig. 11) designed for the stabilization of titania nanoparticle dispersions are presented in Tables 2 and 3.

TGA analysis revealed that maximal adsorption of cationic polymers on negatively charged surface of titania nanoparticles was dependent on charge density and side chain length of the polymers, and varied between 0.4 and 4.3 wt % (for neutral or random copolymers), and between 3.4 and 6.7 wt % (for diblock copolymers) of the

coated particle weight. Composition (METAC units in copolymer, mol %) of the diblock copolymers pMETAC-*b*-p(PEO_xMEMA) was similar (51–66 mol %), thus the adsorbed amount of the diblock copolymers depended on the length of PEO side chains only. The adsorbed amount of the cationic comb copolymers depended on their charge density (composition, METAC units in the copolymers, mol %) and was maximal when the copolymers contained 29–33 mol % of the charged units. The adsorbed amount decreased with increasing charge density of the cationic comb copolymers.

Table 2. Characteristics of the diblock brush copolymers pMETAC-*b*-p(PEO_xMEMA)

Polymer	METAC, mol %	M _n , kDa	Đ	DP _(n+m) (pMETAC+p(PEO _x MEMA))
pMETAC- <i>b</i> -p(PEO ₅ MEMA)	51	32.9	1.17	132 (67 + 65)
pMETAC- <i>b</i> -p(PEO ₉ MEMA)	56	37.5	1.16	120 (67 + 53)
pMETAC- <i>b</i> -p(PEO ₁₉ MEMA)	65	70.4	1.37	137 (89 + 48)
pMETAC- <i>b</i> -p(PEO ₄₃ MEMA)	66	113.1	1.57	135 (89 + 46)

Table 3. Characteristics of cationic comb copolymers p(PEO_xMEMA-METAC)

Polymer	METAC ₀ , mol %*	q, %	METAC, mol %**	M _n , kDa	Đ	DP
p(PEO ₅ MEMA-METAC)	25	83	33	22.8	1.48	85
p(PEO ₅ MEMA-METAC)	45	79	52	27.9	1.56	111
p(PEO ₅ MEMA-METAC)	65	80	70	50.7	1.32	215
p(PEO ₉ MEMA-METAC)	25	86	30	29.8	1.34	76
p(PEO ₉ MEMA-METAC)	45	86	54	29.1	1.43	88
p(PEO ₉ MEMA-METAC)	65	79	65	22.8	1.48	76
p(PEO ₁₉ MEMA-METAC)	25	94	29	61.1	1.34	70
p(PEO ₁₉ MEMA-METAC)	45	95	55	46.4	1.34	76
p(PEO ₁₉ MEMA-METAC)	65	85	69	43.5	1.29	99
p(PEO ₄₃ MEMA-METAC)	25	92	30	129	1.61	86
p(PEO ₄₃ MEMA-METAC)	45	94	57	107	1.60	105
p(PEO ₄₃ MEMA-METAC)	65	80	70	63.8	1.53	83
p(PEO ₁₉ MEMA)	0	85	0	77.4	1.30	70
pMETAC	100	95	100	14	1.30	68

* METAC in monomer feed

** METAC in copolymer (polymer charge density)

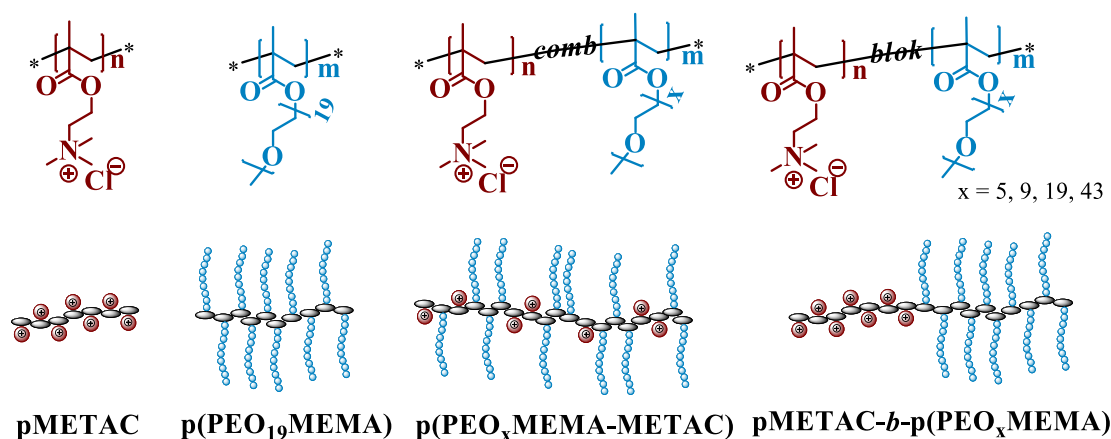


Fig. 11. Schematic structure of the polymers used for the stabilization of titania nanoparticle dispersions

Zeta potential of titania nanoparticles treated with cationic comb copolymers p(PEO_xMEMA-METAC) and cationic diblock brush copolymers pMETAC-*b*-p(PEO_xMEMA) is presented in Fig. 12. It is obvious, that changes in zeta potential are dependent on the length of PEO side chains. The maximal change in surface potential of titania nanoparticles followed with surface charge inversion into positive was observed using both cationic comb and diblock brush copolymers containing short PEO side chains ($x = 5, 9$). Thus, the surface potential of titania nanoparticles treated with the diblok copolymer pMETAC-*b*-p(PEO₄₃MEMA) was close to 0, and it remained negative (-5.81 mV) using the comb copolymer p(PEO₄₃MEMA-METAC).

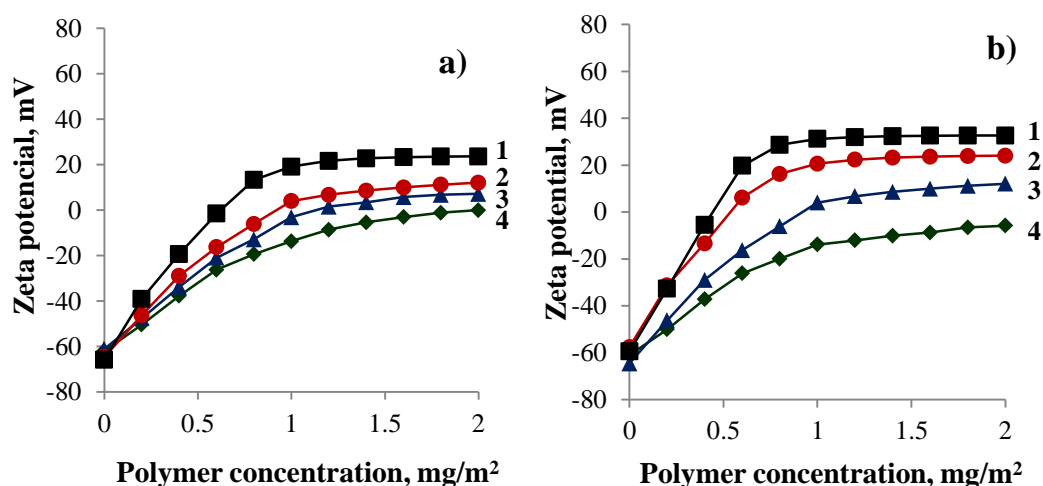


Fig. 12. Zeta potential of titania nanoparticles in aqueous dispersions (pH 10) versus concentration of the dispersants: a) cationic diblock brush copolymer pMETAC-*b*-p(PEO_xMEMA); b) cationic comb copolymer p(PEO_xMEMA-METAC) with charge density 51–66 mol %. Length of PEO chains, $x = 5$ (1); 9 (2); 19 (3), and 43 (4).

Aqueous dispersions of bare titania nanoparticles are unstable at both neutral (pH 6.5) and alkaline (pH 10) conditions. The use of the neutral brush polymer p(PEO₁₉MEMA) for stabilization of titania nanoparticles has little effect, since such dispersions contain agglomerates. Cationic polymer pMETAC does not stop flocculation at neutral conditions (pH 6.5) since the nanoparticles have no charge, and pMETAC cannot be adsorbed. At alkaline condition (pH 10.0), the dispersions stabilized by pMETAC show reasonable stability created by electrostatic discharge due to the charge inversion occurred during adsorption of pMETAC.

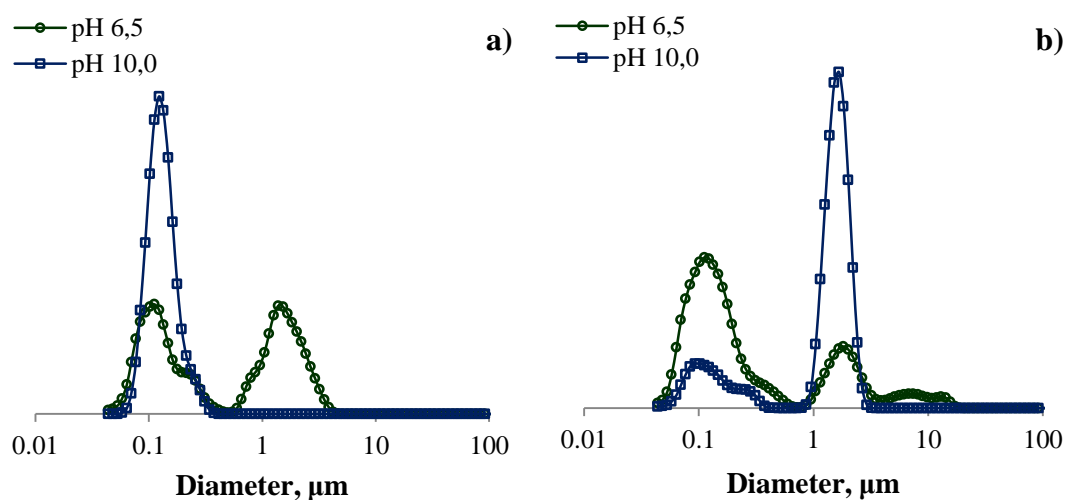


Fig. 13. PSD of titania nanoparticles treated with cationic comb copolymer p(PEO₁₉MEMA-METAC) (a) and cationic diblock brush copolymer pMETAC-*b*-p(PEO₁₉MEMA) (b).

PSD of titania nanoparticle dispersions treated by cationic polyelectrolytes comb copolymer p(PEO₁₉MEMA-METAC) and diblock brush copolymer pMETAC-*b*-p(PEO₁₉MEMA) at conditions close to neutral (pH 6.5) indicate instability of the dispersions (Fig. 13). It is worth to note, that the comb copolymers p(PEO_xMEMA-METAC) are acting as flocculants for titania nanoparticles at neutral conditions. Flocculating effect is confirmed by the absence of the small particles (diameter about 0.1 μm) in the dispersions stabilized by the cationic comb copolymers (Fig. 13). The same cationic comb polyelectrolytes at alkaline conditions (pH 10) act as efficient dispersants of titania nanoparticles, preventing agglomeration (Fig 13a). Due to cationic groups (METAC units in the copolymer) which are randomly distributed over the copolymer

main chain, p(PEO_xMEMA-METAC) could strongly adsorb onto oppositely charged surface of titania nanoparticles. The solvated PEO side chains of the polyelectrolyte are extended away from the surface providing steric stabilization (Fig. 14). Meanwhile, the diblock polyelectrolytes pMETAC-*b*-p(PEO₁₉MEMA) have completely different effect – they act as flocculants. Diblock copolymers pMETAC-*b*-p(PEO₁₉MEMA) adsorb on the surface of titania nanoparticles only by the cationic block of pMETAC, and the block of p(PEO₁₉MEMA) is extended from the surface. Due to very high density of PEO side chains, the brush blocks are stiff with interpenetrated PEO side chains forming networks including several (many) nanoparticles, which results in a flocculation process (Fig 14).

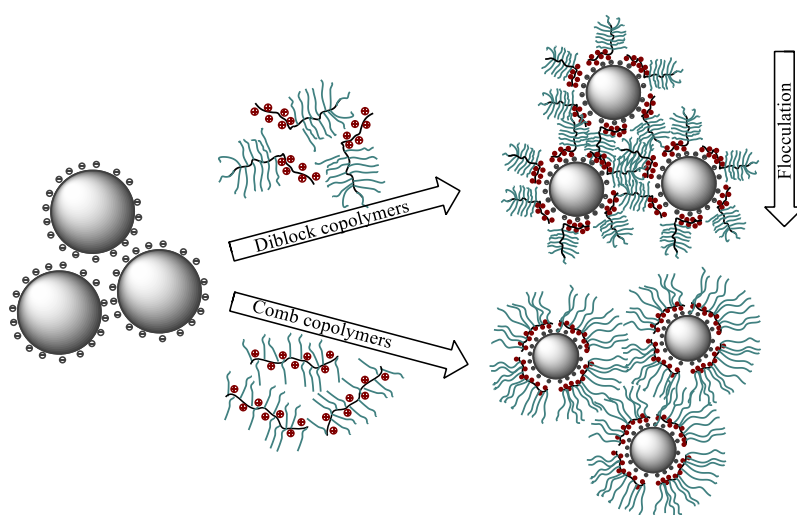


Fig. 14. Illustration of titania nanoparticles treated by cationic comb and diblock brush polyelectrolytes.

Thus, very efficient stabilization of titania nanoparticle dispersions is realized by the use of cationic comb copolymers, which can electrostatically adsorb on the particle surface providing steric effect by PEO side chains.

Rheology of titania nanoparticle dispersions stabilized by cationic comb copolymers. Viscosity of the concentrated dispersions of the bare titania was strongly dependent on the solid loading. At low titania concentration, 5 wt %, the dispersion exhibited *Newtonian* behaviour over a wide range of the shear rates ($\dot{\gamma} = 10\text{--}1000\text{ s}^{-1}$). At higher solid loading, 15–25 wt %, the dispersions exhibited strong shear-thinning behaviour. At low shear rates, the dispersions were very viscous; obviously, a high viscosity was invoked by agglomeration of the particles.

The dependences of viscosity of the titania dispersions, treated with various polymers, on shear rate are presented in Fig. 15. The highest viscosity is characteristic for the bare titania dispersions, irrespective of the solid loading. An increase in shear rate reduces viscosity of these dispersions, i.e. the bare titania dispersions exhibit shear-thinning flow behaviour. High viscosity of the dispersions and shear-thinning flow behaviour are predetermined by agglomeration of the nanoparticles and fragmentation of the agglomerates into smaller flow units at increased shear rates, respectively. The linear cationic polymer pMETAC did not prevent agglomeration of the titania nanoparticles in alkaline conditions (pH 10.0), it just diminished the extent of the agglomeration.

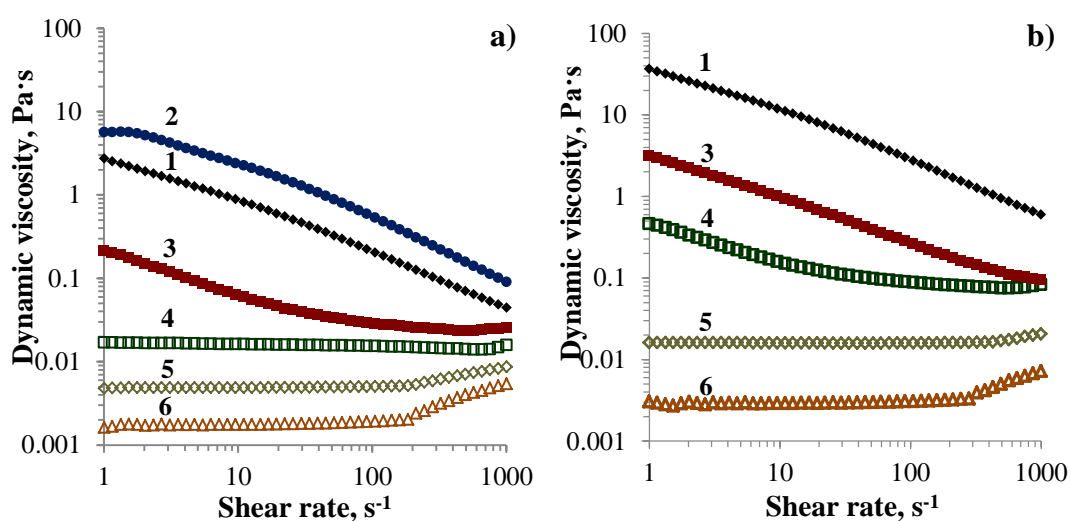


Fig. 15. Effect of the polymers at concentration 2 mg/m^2 on viscosity of the titania nanoparticle dispersions (pH 10.0) with the solid loading 15 wt % (a) and 25 wt. % (b). The plots represent viscosity vs. shear rate of the bare titania dispersion (1), and the titania dispersions treated with p(PEO₁₉MEMA) (2), p(METAC) (3) and cationic comb copolymers p(PEO₁₉MEMA-METAC) with different charge density (METAC units in copolymer): 29 mol % (4), 55 mol % (5) and 69 mol % (6).

Titania dispersions treated with cationic comb copolymers were very thin, and viscosity of the dispersions depended on charge density of the copolymers (or, the same, density of PEO side chains) (Fig. 15). The lowest viscosity (1.9 mPa·s) was characteristic for the dispersions treated with the comb copolymers of high charge density (69 mol %). The comb copolymers of high charge density reduced viscosity of the alkaline titania nanoparticle dispersions by about 100 times, compared to the

viscosity of the dispersions treated by the linear cationic polymer pMETAC, and by about 1000 times compared to the viscosity of the bare titania dispersions.

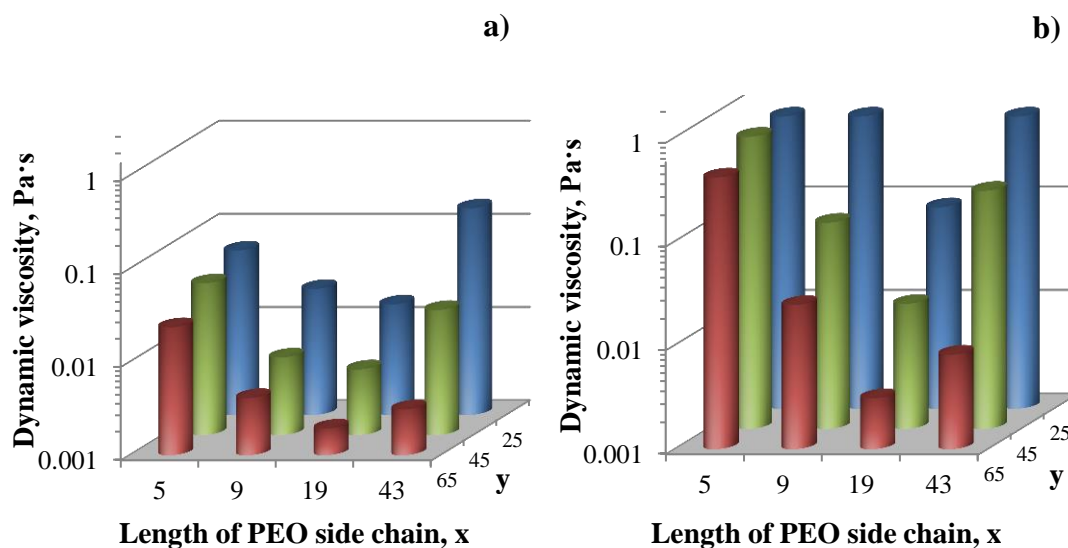


Fig. 16. Rheological behaviour of 15 wt % (a) and 25 wt % (b) titania nano-sized dispersions treated with the cationic comb copolymers p(PEO_xMEMA-METAC) differing in charge density (y, mol % of METAC units) and the length of PEO side chains (x, number of the repeating units of ethylene oxide).

In order to evaluate steric factor in stabilization of titania nanoparticle dispersions, the dispersions (pH 10.0) were treated with the cationic comb copolymers p(PEO_xMEMA-METAC) containing PEO side-chains of various length (x = 5, 9, 19, 43). Viscosity of the stabilized dispersions is presented in the form of three-dimensional diagrams (Fig. 16). Viscosity of the treated dispersions was decreasing when charge density of the copolymers was increasing, irrespective of the length of the side chains. It is worth to note, that viscosity of the treated dispersions was decreasing when the length of the side chains of the comb copolymers was increasing from x = 5 to x = 19 but increased back to higher values when the length of the side chains was x = 43, irrespective of the charge density of the copolymers. Thus, minimal values of the viscosity (1.9 and 3.1 mPa·s for the dispersions with the solid loading 15 wt % and 25 wt %, respectively) are characteristic for the titania nanoparticle dispersions treated with the highly charged (69 mol %) cationic comb copolymer p(PEO₁₉MEMA-METAC).

CONCLUSIONS

- Six RAFT chain transfer agents (CTA) (three of them novel) with the same Z-group but different R-groups were synthesized, and the effect of the structure of R-group on RAFT polymerization of methacrylates was evaluated. The best control of the RAFT polymerization was obtained by the use of the CTA with tertiary R-groups or with secondary R-group containing phenyl substituent. RAFT polymerization of methacrylate macromonomers PEO_xMEMA with PEO substitutes of various length ($x = 5, 9, 19, 43$) was thoroughly studied for the first time. It was determined that irrespective of the length of PEO substitute, the RAFT polymerization of PEO_xMEMA was well-controlled, and growing polymeric chains were „living“ if ($[CTA]_0/[I]_0 \geq 3$).
- Kinetics of the RAFT polymerization of PEO_xMEMA follows the pseudo-first reaction order, and the polymerization rate is inversely proportional to the length of PEO substitutes. Rather long induction periods (40 to 120 minutes) are characteristic for the RAFT polymerization of PEO_xMEMA, and duration of those periods is in correlation with the length of PEO substitutes.
- Cationic comb copolymers differing in both charge density and length of PEO side chains were synthesized by RAFT copolymerization of PEO_xMEMA ($x = 5, 9, 19, 43$) and a cationic monomer – [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride (METAC). The copolymerization was well-controlled, and the dispersity of the most copolymers was low ($\mathcal{D} < 1.15$) or moderate ($\mathcal{D} = \sim 1.3$, for the copolymers containing large amount of PEO₄₃MEMA units). The degree of polymerization of the comb copolymers was rather low (DP 25–30) and close to that theoretically calculated.
- The diblock copolymers pMETAC-*b*-p(PEO_xMEMA) and p(PEO_xMEMA)-*b*-p(PEO_yMEMA) were synthesized by chain extension in the solutions of “dormant” polymers p(PEO_xMEMA) or pMETAC containing terminal trithiocarbonate moieties. Conversion of the second monomer and the parameters of the cationic diblock brush copolymers are strongly dependent on the strategy of the polymerization. In order to get diblock brush copolymers with low dispersity by RAFT, PEO_xMEMA with short PEO substitutes or METAC should be polymerized first. Dispersity of the diblock

brush copolymers containing long PEO side chains is relatively high ($\zeta > 1.4$); it can be reduced if RAFT polymerization is carried out by “one-pot” technique.

- Cationic comb copolymers p(PEO_xMEMA-METAC) and diblock brush copolymers pMETAC-*b*-p(PEO_xMEMA) containing PEO side chains of various length ($x = 5, 9, 19, 43$) were applied for the stabilization of aqueous alkaline (pH 10.0) dispersions of titania nanoparticles. The highest adsorption (67.4 mg/g or 1.38 mg/m²) on the surface of the nanoparticles is characteristic for the diblock brush copolymers pMETAC-*b*-p(PEO_xMEMA) with the longest PEO side chains. Unfortunately, these copolymers are not suitable for the stabilization of the nanodispersions since they form interpenetrating networks binding titania nanoparticles and invoking flocculation. Cationic comb copolymers p(PEO_xMEMA-METAC) are the best stabilizers of colloidal titania dispersions since they can electrostatically adsorb onto oppositely charged surface of the nanoparticles and provide steric barrier to prevent particles from approaching to close (electrosteric stabilization).
- Dynamic viscosity of the concentrated (15–25 wt %) alkaline (pH 10.0) dispersions titania nanoparticles treated by cationic comb copolymers p(PEO_xMEMA-METAC) is reduced drastically (up to 1000 times) to very low values < 5 mPa·s; flow behavior of the stabilized dispersions turns to *Newtonian*. The lowest viscosity is characteristic for the dispersions stabilized by cationic comb copolymers with high charge density (69 mol % of METAC units) and relatively long PEO side chains ($x = 19$). The use of such dispersants enabled to stabilize very concentrated dispersions of titania nanoparticles with solid loading up to 35 wt %.

LIST OF SCIENTIFIC PUBLICATIONS

Articles in the journals included into the database of Clarivate Analytics Web of Science:

1. Klimkevičius, V., Graule, T., Makuška, R. Effect of structure of cationic comb copolymers on their adsorption and stabilization of titania nanoparticles. *Langmuir*, **2015**, *31* (7), 2074–2083.
2. Klimkevičius, V., Makuška, R., Graule, T. Rheological behaviour of concentrated aqueous dispersions of titania nanoparticles stabilized by cationic comb copolymers. *Appl. Rheol.* **2016**, *26* (1), 15199.
3. Klimkevičius, V., Makuška, R. Successive RAFT polymerization of poly(ethylene oxide) methyl ether methacrylates with different length of PEO chains giving diblock brush copolymers. *Eur. Polym. J.* **2017**, *86*, 94–105.

Theses and proceedings of international scientific conferences:

1. Klimkevičius, V., Makuška, R. RAFT copolymerization of PEO macromonomers in the presence of thithiocompounds. *Baltic Polymer Symposium 2013: Programme and Abstracts*. Trakai, Lithuania, **2013**, p. 89.
2. Klimkevičius, V., Graule, T., Makuška, R. Cationic random and diblock brush copolymers for stabilization of nanoceramic suspensions. *Programme and Proceedings of International Conference of Lithuanian Chemical Society “Chemistry and Chemical Technology 2014”*. Kaunas, Lithuania, **2014**, p. 238.
3. Klimkevičius, V., Graule, T., Makuška, R. Cationic random and diblock brush copolymers for stabilization of nanoceramic suspensions. *Annual Meeting of the Division of Polymers, Colloids and Interfaces “POLYCOLL 2014”*: Programme and Abstracts. Duebendorf, Switzerland, **2014**, p. 24.
4. Klimkevičius, V., Graule, T., Makuška, R. Cationic polyelectrolytes for stabilization of inorganic nanopowders. *Baltic Polymer Symposium 2014: Programme and Abstracts*. Laulasmaa, Estonia, **2014**, p. 26.
5. Klimkevičius, V., Graule, T., Makuška, R. Cationic brush polyelectrolytes for dispersion of titania nanopowders. *EMPA PhD Students' Symposium 2014 “Look Closer”*: Programme and Abstracts. St. Gallen, Switzerland, **2014**, p. 48.

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7. Klimkevičius, V., Laukžemis, V., Makuška, R. Synthesis of well-defined brush polymer blocks via RAFT technique. *Baltic Polymer Symposium 2016: Programme and Abstracts*. Klaipėda, Lithuania, **2016**, p. 75.

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2015 04 07 – Participation in the project of the scientist groups MIP-054/2015 “Multiblock polymers and their brush derivatives” funded by Research Council of Lithuania..

KATIJONINIŲ ŠEPETINIŲ STATISTINIŲ IR DIBLOKINIŲ KOPOLIMERŲ SINTEZĖ IR JŲ PANAUDOJIMAS TITANO DIOKSIDO NANODALELIŲ DISPERSIJOMS STABILIZUOTI

SANTRAUKA

Nanotechnologija – sparčiausiai besivystanti mokslinių tyrimų sritis, jau dabar turinti platų pritaikymą ir geras ateities perspektyvas. Siekiant praplėsti ir pagerinti polimerkeraminių dangų ir kompozitų savybes, kaip užpildas naudojamos nanodalelės. Mechaninės, cheminės ir optinės nanodalelių savybės lemia ne tik naudojamų medžiagų molekulinė sudėtis ar kristalografinė forma, bet ir dalelių dydis, pasiskirstymas bei savitasis paviršiaus plotas. Būtent dėl labai didelio paviršiaus ploto nanodalelės yra linkusios sulipti ir aglomeruotis, todėl siekiant pagerinti tikslinių iš nanodalelių gaunamų produktų savybes, dispersijas būtina stabilizuoti.

Stabilios dispersijos gaunamos tik naudojant priedus (stabilizatorius), todėl vis daugiau dėmesio skiriama medžiagų, kurios galėtų efektyviai stabilizuoti nanodalelių dispersijas, kūrimui. Yra nustatyta, kad efektyviausiai nanodalelių dispersijas stabilizuoja sudėtingos struktūros ir funkcionalumo medžiagos, dažniausiai, šepetinės struktūros polielektrolitai.

Pagrindinis šio darbo tikslas buvo susintetinti ir ištirti įvairios sudėties ir architektūros mažo dispersiškumo katijoninius šepetinius kopolimerus ir juos panaudoti titano dioksido nanodalelių vandeninėms dispersijoms stabilizuoti.

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

Susintetinti 6 tritiokarbonatiniai RAFT grandinės perdavos agentai (GPA) (3 iš jų pirmą kartą), turintys tą pačią butiltio- Z-grupę ir skirtingas R-grupes, tinkantys metakrilatų polimerizacijai kontroliuoti. Geriausiai radikalinę polimerizaciją kontroliuoja tretinės R-grupes arba fenilgrupe stabilizuotą antrinę R-grupę turintys GPA. Nepriklausomai nuo PEO pakaitų ilgio, PEO metakrilatų (PEO_xMEMA) polimerizacija kontroliuojama gerai ir augančios grandinės išlieka gyvybingos, kai $[GPA]_0/[I]_0 \geq 3$.

Nustatyta, kad PEO_xMEMA RAFT polimerizacijos kinetika aprašoma pseudopirmojo laipsnio kinetine lygtimi, o polimerizacijos greičio konstantų vertės yra atvirkščiai proporcingos PEO pakaito ilgiui. PEO makromonomerų polimerizacijai būdingas gana ilgas (nuo 40 iki 120 min) indukcinis periodas, kurio trukmė koreliuoja su

PEO pakaito ilgiu. Vykdamt PEO_xMEMA (x = 5, 9, 19, 43) ir katijoninio monomero [2-(metakriloiloksi)etil]trimetilamonio chlorido (METAC) RAFT kopolimerizaciją, susintetinti katijoniniai statistiniai šepetiniai kopolimerai, besiskiriantys šoninių PEO grandinių ilgiu bei krūvio tankiu. Kopolimerizacija buvo gerai kontroliuojama, daugumos kopolimerų dispersiškumo rodiklis mažas ($\bar{D} < 1,15$), o polimerizacijos laipsnis (PL) nedidelis (25–30) ir artimas numatytam.

Vykdamt RAFT polimerizaciją gyvybingų p(PEO_xMEMA) arba pMETAC tirpale, susintetinti diblokiniai šepetiniai kopolimerai pMETAC-*b*-p(PEO_xMEMA) ir p(PEO_xMEMA)-*b*-p(PEO_yMEMA). Antrojo monomero konversija ir diblokinių katijoninių šepetinių kopolimerų rodikliai labai priklauso nuo pasirinktos sintezės strategijos. Norint susintetinti mažo dispersiškumo diblokinius kopolimerus, kurių antrasis blokas turėtų ilgas PEO atšakas, pirmiau turi būti vykdoma METAC ar PEO_xMEMA su trumpais PEO pakaitais RAFT polimerizacija, o po to gautasis polimeras naudojamas kaip makro-GPA antrojo bloko „priauginimui“. Diblokinių katijoninių šepetinių kopolimerų dispersiškumą galima sumažinti, RAFT polimerizaciją vykdamt „vieno indo“ principu.

Statistiniai p(PEO_xMEMA-METAC) ir diblokiniai pMETAC-*b*-p(PEO_xMEMA) katijoniniai šepetiniai kopolimerai su skirtingo ilgio PEO šoninėmis grandinėmis (x = 5, 9, 19, 43) buvo panaudoti TiO₂ nanodalelių vandeninėms šarminėms (pH 10) dispersijoms stabilizuoti. Didžiausia adsorbcija nanodalelių paviršiuje (67,4 mg/g arba 1,38 mg/m²) pasižymi diblokiniai šepetiniai kopolimerai pMETAC-*b*-p(PEO_xMEMA), tačiau jie netinka dispersijoms stabilizuoti, nes veikia kaip flokuliantai. Dispersijas geriausiai stabilizuoja statistiniai katijoniniai šepetiniai kopolimerai p(PEO_xMEMA-METAC), kurie gali elektrostatiškai sorbuotis ant priešingą krūvį turinčių dalelių paviršiaus, suteikdami sterinį barjerą dalelių suartėjimui ir aglomeracijai.

Koncentruotas (15–25 %) TiO₂ nanodalelių vandeninės šarminės (pH 10,0) dispersijas stabilizuojant katijoniniais šepetiniais kopolimerais p(PEO_xMEMA-METAC), dispersijų dinaminė klampa sumažėja beveik 1000 kartų ir tampa mažesnė negu 5 mPa·s, o jų tėkmės pobūdis tampa panašus į *Niutoninių* skysčių. Mažiausia klampa būdinga dispersijoms, kurioms stabilizuoti buvo naudojami didelio krūvio tankio (69 mol % METAC grandžių) statistiniai šepetiniai katijoniniai kopolimerai, turintys gana ilgus (x = 19), bet ne ilgiausius PEO pakaitus.