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Synthesis of pH-responsive brush copolymers by RAFT polymerisation and *click* chemistry reactions

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In this study, anionic brush copolymers were synthesised by grafting onto strategy, combining radical addition fragmentation chain transfer (RAFT) polymerisation and two *click* chemistry reactions, namely, epoxy–thiol and azide–alkyne. The backbone of the prospective brush copolymers with multiple epoxy groups and the nearly equimolar composition of the monomeric units was synthesised by RAFT copolymerisation of butyl methacrylate (BMA) and glycidyl methacrylate (GMA). Poly(*tert*-butyl methacrylate) (p(*t*-BMA) as a precursor for the side chains was synthesised by RAFT polymerisation and, subject to the structure of the chain transfer agent, contained terminal thiol or alkyne groups. The course of the *click* reactions was monitored by DLS. Anionic brush copolymers containing carboxyl groups were obtained via acidic hydrolysis of *t*-BMA units.

Aqueous solutions of the anionic brush copolymers were studied by potentiometric and turbidimetric titration, and by DLS. Both anionic brush copolymers, irrespective of the type of *click* chemistry reaction, were weak polyacids. Anionic brush copolymers, synthesised by the epoxy–thiol *click* reaction, form rather compact aggregates, whereas those, synthesised by the azide–alkyne *click* reaction, assemble into larger microgel-like aggregates. In the synthesis of brush copolymers, the method of epoxy–thiol *click* chemistry has some advantages because of simpler experimental procedures and higher grafting density in the products.

Keywords: RAFT polymerisation, azide–alkyne, epoxy–thiol, *click* chemistry, pH-responsive anionic brush copolymers

INTRODUCTION

An increasing interest for 'smartness' in biomedical and engineering materials has gain a growing interest for synthetic polymers that exhibit an environmentally responsive behaviour [1]. pH-responsive polymers are a group of stimuli-responsive polymers that can respond to solution pH by undergoing structural and property changes such as chain conformation, solubility, or aggregation. These unique properties make pH-responsive polymers useful in various applications such as drug/gene delivery, modification of surfaces, sensors and membranes, and chromatography [2, 3]. One of the methods to synthesise such brush polymers is grafting-onto strategy. Using this method, side chains are grafted onto a pre-established backbone with multiple reactive groups by various coupling reactions, including *click* chemistry [4].

The synthesis of well-defined smart brush copolymers, including polyelectrolytes, relies on advanced techniques like reversible addition-fragmentation chain transfer (RAFT) polymerisation [5–7]. Known for its simple setup and broad monomer tolerance, RAFT is a highly versatile

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reversible deactivation radical polymerisation (RDRP) method. However, synthesising precise architecture molecular brushes remains challenging, often requiring the integration of RAFT with other RDRP techniques or *click* chemistry [6, 8, 9]. When designing a synthetic strategy for brush copolymers, the appropriate selection of monomers and the polymerisation method is of crucial importance. In this work, the RAFT method was chosen due to its versatility and straightforward implementation, utilising glycidyl methacrylate (GMA) as one of the monomers for the synthesis of the polymer brush backbone. GMA is a cheap versatile monomer [3], which meets the requirements for epoxy–thiol *click* chemistry and can be successfully polymerised via the RAFT method. Moreover, epoxy groups can serve as excellent precursors for introducing the azide groups required for subsequent azide–alkyne *click* reactions [10–12]. Additionally, copolymers based on pGMA can be biocompatible [13–15].

Huisgen cycloaddition (copper(I)-catalysed azide–alkyne cycloaddition (CuAAC)) is a highly efficient reaction, yielding 1,2,3-triazole linkages [16]. Due to their large dipole moments, these five-membered aromatic heterocycles act as versatile metal ligands and hydrogen-bonding facilitators. Consequently, incorporating 1,2,3-triazole units into polymers yields promising functional materials. Notably, the azide–alkyne *click* chemistry is extensively utilised for the synthesis of advanced macromolecular architectures and is widely regarded as the gold standard for the grafting-onto strategy [16, 17].

The base-catalysed ring-opening reaction between thiols and epoxides [18], widely recognised as the thiol–epoxy *click* reaction, has become an important synthetic tool for constructing thioether linkages in polymer chemistry, including both polymer preparation and post-polymerisation functionalisation [19–21]. A key feature of this reaction is its ability to simultaneously generate thioether and hydroxyl groups within the polymer structure, providing versatile functional sites for subsequent chemical modification and the fabrication of more complex macromolecular architectures. Moreover, the thiol–epoxy reaction exhibits the defining attributes of *click* chemistry, including a high efficiency, near-quantitative conversions, a minimal side-product formation, a metal-free product and compatibility with mild reaction conditions, while maintaining an excellent tolerance toward oxygen and moisture [22].

The main task of the present study was to demonstrate the possibilities to synthesise anionic brush copolymers with negative charges in the side chains by combining the methods of RAFT polymerisation and *click* chemistry. Yet another task was to compare two methods of *click* chemistry, namely, azide–alkyne and epoxy–thiol, for the attachment of the side chains to a linear copolymer, forming an anionic brush copolymer (Fig. 1).

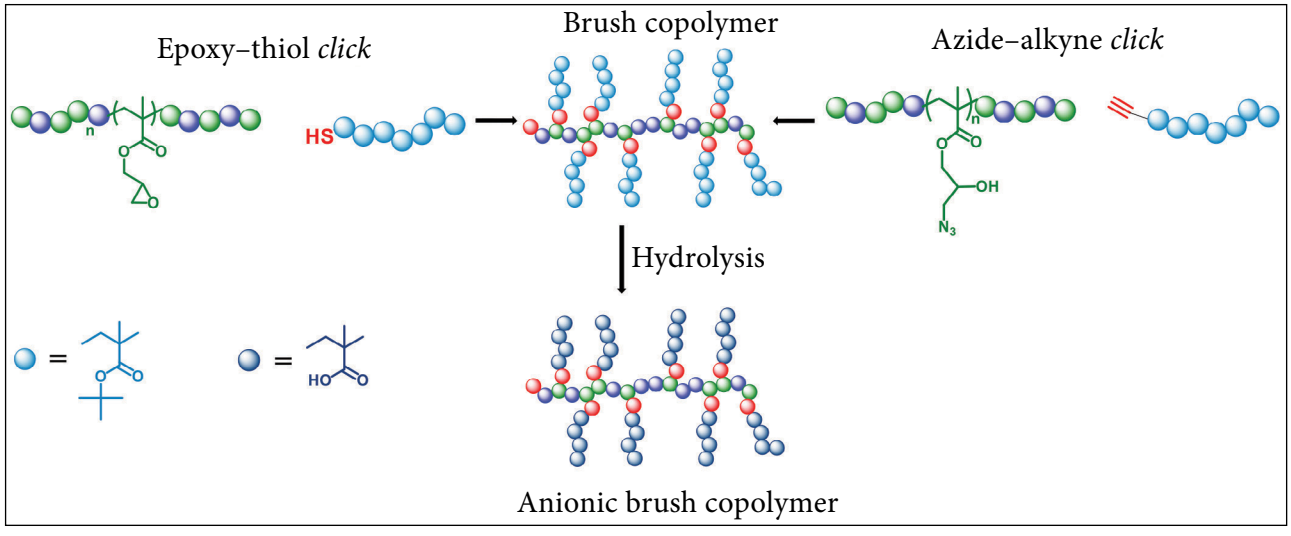

Fig. 1. General scheme for the synthesis of anionic brush copolymers via a grafting-onto approach combining RAFT polymerisation with epoxy–thiol and azide–alkyne *click* reactions

EXPERIMENTAL

Materials

All chemical reagents used were of analytical reagent grade. All organic solvents and compounds employed in CTA synthesis, chemical modification of polymers, and click chemistry reactions were dried and distilled, where possible, prior to use. Butyl methacrylate (BMA, Acros Organics, 99%), glycidyl methacrylate (GMA, Sigma-Aldrich, ≥97%) and *tert*-butyl methacrylate (*t*-BMA, Sigma-Aldrich, 98%) were purified to remove inhibitors by percolation over a column packed with basic Al_2O_3. RAFT Chains transfer agents 4-(butylthiocarbonylthioylthio)-4-cyanopentanoic acid (CTA1) and ethynyl 4-(((butylthio)carbonthioyl)thio)-4-cyanopentanoate (CTA2) (Fig. 2) were synthesised according to the methods described elsewhere with slight modifications [23, 24]. Initiator 2,2'-azobis(isobutyronitrile) (AIBN, Reachim) was recrystallised twice from methanol, and the initiator 4,4'azobis(4-cyanovaleric acid) (ACVA, Fluka, 98%) was used as received. Deuterated solvents $CDCl_3$ and D_2O (Carl-Roth, 99.8 atom% D) were used as received.

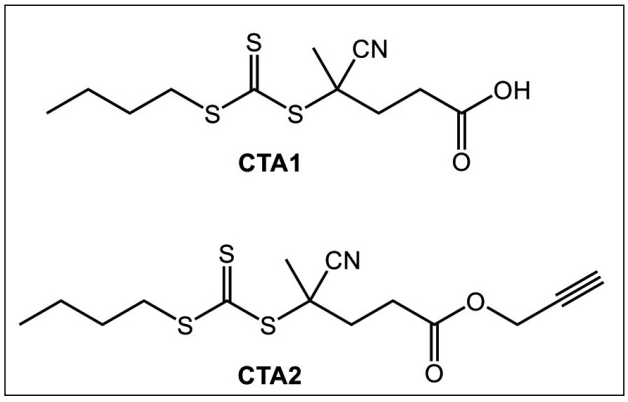

Fig. 2. Formulas of CTA1 and CTA2

Synthesis of statistical copolymers p(GMA-*st*-BMA) and p(AHPMA-*st*-BMA)

Into a 100 mL round-bottom flask equipped with a magnetic stirrer, CTA1 (0.48 g, 1.16 mmol), AIBN (0.038 g, 0.23 mmol), butyl methacrylate (BMA, 5.00 g, 35 mmol), glycidyl methacrylate (GMA, 5.00 g, 35 mmol) and 1-methyl-2-pyrrolidone (NMP, 40 mL) were added. The initial molar ratio of the monomers, CTA and AIBN was 300/5/1. The stirred solution was purged with nitrogen for 30 min, then the flask was sealed and placed in an oven. The RAFT polymerisation was carried out for 15 h at 65°C. After this time, the polymer was precipitated by pouring the reaction mixture into 100 mL of a MeOH/H_2O mixture (3:2, v/v). The polymer was collected by filtration through a glass filter and dried for 24 h at 35°C in a drying oven, followed by 24 h at room temperature under vacuum. Yellow powder was obtained. The p(GMA-*st*-BMA) copolymer was stored in a sealed container at –20°C. Polymer yield determined gravimetrically was 9.5 g (90.5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.26 and 3.79 (2H, -CHC**H**$_2$O-, in GMA), 3.95 (2H, -OC**H**$_2$CH$_2$CH$_2$CH$_3$, BMA), 3.23, 2.85, and 2.64 (3H, -CH$_2$C**H**(C**H**$_2$)O-, oxirane ring in GMA), 2.1–1.8 (2H, -CC**H**$_2$C-, backbone), 1.59 (2H, -CH$_2$C**H**$_2$CH$_2$CH$_3$, BMA), 1.39 (2H, -CH$_2$CH$_2$C**H**$_2$CH$_3$, BMA), 1.05–0.96 (3H, -C**H**$_3$, meta and 3H, -CH$_2$CH$_2$C**H**$_3$, BMA).

The theoretical molecular weight of p(GMA-*st*-BMA) copolymer was calculated by the equation

$$M_n^{theor.} = \left(\frac{[M_{GMA}]}{[CTA1]} \times M_{GMA} \times F_{GMA} + \frac{[M_{BMA}]}{[CTA1]} \times \right.$$
$$\left. \times M_{BMA} \times F_{BMA} \right) \times q + M_{CTA1}, \quad (1)$$

where [CTA1], [M_{GMA}] and [M_{BMA}] are initial concentrations of CTA1 and the monomers GMA and BMA, respectively. M_{GMA}, M_{BMA} and M_{CTA1} are the molecular weights of the corresponding materials, and *q* is the conversion of the monomers, determined gravimetrically. F_{GMA} and F_{BMA} are the molar parts of GMA and BMA units in the synthesised copolymer, respectively, determined by ^{1}H NMR spectroscopy and calculated by the equations

$$F_{GMA} = \frac{I_{4.26} + I_{3.79}}{I_{4.26} + I_{3.79} + I_{3.95}}, \quad (2)$$

$$F_{BMA} = 1 - F_{GMA}, \quad (3)$$

where $I_{4.26}$ and $I_{3.79}$ are the integrals of the signals of methylene proton adjacent to the epoxy group at 4.26 and 3.79 ppm, respectively, while $I_{3.95}$ is the integral of the signal of the methylene proton adjacent to the oxygen atom in the BMA units at 3.95 ppm.

Statistical copolymers p(AHPMA-*st*-BMA) containing monomeric units of 3-azido-2-hydroxy

propyl methacrylate (AHPMA) with an azide group were synthesised implementing the reaction between the epoxy group of p(GMA-*st*-BMA) and sodium azide. A reaction flask, equipped with a magnetic stirrer, was charged with a p(GMA-*st*-BMA) copolymer (1.00 g, 0.13 mmol, M_n^t = 8000 g/mol), and the solvent tetrahydrofuran (THF, 10 mL) was added. After copolymer dissolution, sodium azide (NaN_3, 1.04 g, 16.02 mmol) and ammonium chloride (NH_4Cl, 1.04 g, 19.50 mmol) were added, followed by the dropwise addition of dimethylformamide (DMF, 5 mL). The mixture was purged with nitrogen for 30 min and then placed in an oven at 50°C, where it was stirred for 48 h. The resulting solution was filtered and precipitated by pouring into 70 mL of a MeOH/H_2O mixture (3:2, v/v). The polymer was collected by filtration through a glass filter and dried for 24 h at 35°C in a drying oven, followed by 24 h at room temperature under vacuum. Orange crystals of p(AHPMA-*st*-BMA) were obtained. Polymer yield determined gravimetrically was 0.43 g (43%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.26 and 3.79 (2H, -CHC**H**$_2$O-, in GMA), 4.2–3.95 (2H, -OC**H**$_2$CH$_2$CH$_2$CH$_3$, BMA; 2H, $N_3CH_2CH(CH_2$-)-), and 1H, N_3CH_2CH-, GMA-N_3), 3.44 (2H, N_3CH_2-), 1.8–2.1 (2H, -CC**H**$_2$C-, backbone), 1.59 (2H, -CH$_2$C**H**$_2$CH$_2$CH$_3$, BMA), 1.41 (2H, -CH$_2$CH$_2$ C**H**$_2$CH$_3$, BMA), 1.05–0.96 (3H, -C**H**$_3$, meta, and 3H, -CH$_2$CH$_2$C**H**$_3$, BMA).

Synthesis of p(*t*-BMA) and its subsequent modification introducing terminal thiol groups

A 100 mL round-bottom flask was charged with CTA1 (0.84 g, 2.70 mmol) or CTA2 (0.89 g, 2.70 mmol) and AIBN (0.09 g, 0.54 mmol), followed by the addition of *tert*-butyl methacrylate (*t*-BMA, 7.68 g, 54 mmol) and NMP (28 mL). The initial molar ratio of the monomer, CTA, and AIBN was 100/5/1. The resulting solution was stirred using a magnetic stirrer and purged with N_2 for 30 min, then placed in an oven preheated to 65°C. After 6 h, the polymer was precipitated by pouring the reaction mixture into 100 mL of a MeOH/H_2O mixture (3:2, v/v). The polymer was collected by filtration through a glass filter and dried for 24 h at 35°C in a drying oven, followed by 24 h at room temperature under vacuum. Yellow powder was obtained. Polymer yield determined gravimetrically was 6.6 g (86.1%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.42 (t, 2H, -CH$_2$C**H**$_2$S-, from CTA), 2.55 (t, 2H, -CH$_2$C**H**$_2$ COOH, from CTA), 1.95–1.76 (2H, -CC**H**$_2$C-, backbone), 1.55–1.30 (9H, **(CH$_3$)$_3$**CO-), 1.1-0.90 (3H, **CH$_3$**C(CH$_2$)-).

The theoretical molecular weight of p(*t*-BMA) polymer was calculated by the equation

$$M_n^{theor.} = \left(\frac{[M_{t\text{–}BMA}]}{[CTA1 \text{ or } CTA2]} \times M_{t\text{–}BMA} \right) \times \times q + M_{CTA1 \text{ or } CTA2}, \quad (4)$$

where [CTA1 or CTA2] and [$M_{t\text{-}BMA}$] are the initial concentrations of CTA1 or CTA2, and the monomer t-BMA, respectively. $M_{t\text{-}BMA}$ and $M_{CTA1 \text{ or } CTA2}$ are the molecular weights of the corresponding materials, *q* is the conversion of the monomer, determined gravimetrically.

The degree of polymerisation (DP) and hence the number-average molecular weight (M_n^{NMR}) of p(*t*-BMA) was calculated from ^{1}H NMR spectra by the equations

$$DP_{p(t\text{–}BMA)} = \left(\frac{(I_{1.95\text{–}1.76})}{I_{2.55}} + \frac{(I_{1.55\text{–}1.35})}{9 \cdot I_{2.55}} + \frac{(I_{1.20\text{–}0.95}) \cdot 2}{3 \cdot I_{2.55}} \right) : 3, \quad (5)$$

$$M_n^{NMR} = PL_{p(t\text{–}BMA)} \cdot 142.2, \quad (6)$$

where $I_{1.95\text{–}1.76}$ corresponds to the integral of the main-chain methylene group protons at 1.95–1.76 ppm, $I_{2.55}$ corresponds to the integral of the methylene group protons from the CTA1 fragment (-CH$_2$C**H**$_2$ COOH) or methylene group protons from the CTA2 fragment (-CH$_2$C**H**$_2$COOCH$_2$C≡CH). $I_{1.55\div1.35}$ is the integral of the methyl(tert-butyl-) group protons at 1.95–1.76 ppm, and $I_{1.20\div0.95}$ is the integral of the methyl group protons at 1.2–0.95 ppm. 9 and 3 are the number of protons in the methyl(tert-butyl-) and methyl groups, respectively. 142.2 is the molecular weight of *t*-BMA.

Terminal thiol groups were introduced into p(*t*-BMA) polymers by aminolysis of terminal trithiocarbonate (TTC) groups. A reaction flask was charged with p(*t*-BMA) (4.56 g, 2.05 mmol, M_n = 2300 g/mol), and NMP (17 mL) was added. The mixture was thoroughly stirred until complete dissolution of the polymer, after which hydrazine monohydrate (0.5 mL, 10.23 mmol) was added dropwise using a syringe. The reaction was carried out at room temperature for 6 h. The modification was monitored

by UV spectroscopy in NMP. The product was precipitated from the reaction mixture by pouring it into water. The polymer was collected by filtration through a glass filter and dried for 24 h at 35°C in a drying oven, followed by 24 h at room temperature under vacuum. White powder was obtained. Polymer yield determined gravimetrically was 2.73 g (60.6%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.59 (t, 2H, -$CH_2C\mathbf{H}_2$COOH, from CTA), 1.76–1.95 (2H, -$CC\mathbf{H}_2$ C-, backbone), 1.35–1.55 (9H, $\mathbf{(CH_3)_3}$CO-), 1.05 (3H, $\mathbf{CH_3}C(CH_2)$-).

Synthesis of brush copolymers p(GMA-*st*-BMA)-*graft*-p(*t*-BMA) by epoxy–thiol click reaction

The copolymer p(GMA-*st*-BMA) (0.10 g, 0.01 mmol, M_n = 8400 g/mol) and p(*t*-BMA) with terminal thiol groups (1.05 g, 0.34 mmol, M_n = 2300 g/mol) were placed in a reaction flask, followed by the addition of NMP (6 mL). The mixture was thoroughly stirred and purged with N_2 for 30 min. Subsequently, a base – either triethylamine (TEA, 0.05 mL, 0.33 mmol) or 4-dimethylaminopyridine (DMAP, 0.04 g, 0.33 mmol) – was added via a syringe, and the mixture was further purged with N_2 for 10 min. The solution was then heated at different temperatures and the reaction kinetic was monitored by DLS. After 48 h, the product was precipitated from the reaction mixture by pouring it into deionised water. The copolymer was collected by filtration through a glass filter and dried for 24 h at 35°C in a drying oven, followed by 24 h at room temperature under vacuum. White powder was obtained. Polymer yield determined gravimetrically was 0.47 g (40.8%).

^{1}H BMR ($CDCl_3$) δ (ppm): 4.15 and 3.96 (3H, -OC$\mathbf{H_2CH}(CH_2$-)OH, from GMA; 2H, -C$\mathbf{H}_2CH_2CH_2CH_3$, BMA), 3.56 (2H, -CH$\mathbf{CH}_2$S-), 1,84 (2H, -C$\mathbf{CH}_2$C-, backbone), 1.59 (2H, -$CH_2C\mathbf{H}_2CH_2CH_3$, BMA), 1.40–1.43 (9H, $\mathbf{(CH_3)_3}$CO-, *t*-BMA), 1.01 (3H, $\mathbf{CH_3}C(CH_2)$-).

Synthesis of brush copolymers p(AHPMA-*st*-BMA)-*graft*-p(*t*-BMA) by azide–alkyne click reaction

Azide-functionalised statistical copolymer p(AHPMA-*st*-BMA) (0.10 g, 0.01 mmol, M_n = 8000 g/mol, 0.34 mmol azide groups) and alkyne-terminated p(*t*-BMA) (1.00 g, 0.34 mmol, M^t_n = 2500 g/mol, 6.31 mmol alkyne groups) were dissolved in 5 mL of DMF and degassed with N_2. In a separate flask, CuBr (0.04 g, 0.29 mmol) and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (0.18 mL, 0.86 mmol) were dissolved in 5 mL of DMF and purged with N_2 for 20 min. The polymer solution was added dropwise to the catalyst solution under N_2, and the mixture was further purged for 20 min. The reaction was carried out at room temperature for 24 h. The product was precipitated into deionized H_2O, collected by filtration, and dried at 35°C for 24 h, followed by 24 h under vacuum at room temperature. Polymer yield determined gravimetrically was 0.6 g (54.5%).

^{1}H BMR ($CDCl_3$) δ (ppm): 7.98 (1H, -C$\mathbf{CH}$N- (triazole ring), 3.94 (2H, -N$\mathbf{CH}_2CH(CH_2$-)OH), 1.84 (2H, -C$\mathbf{CH}_2$C-, backbone), 1.60 (2H, -$CH_2C\mathbf{H}_2$ CH_2CH_3), 1.41–1.44 (9H, $\mathbf{(CH_3)_3}$CO-), 1.03 (3H, $\mathbf{CH_3}C(CH_2)CH_2$).

Synthesis of anionic brush copolymers p(GMA-*st*-BMA)-*graft*-p(MAA) and p(AHPMA-*st*-BMA)-*graft*-p(MAA) by hydrolysis of *t*-BMA units

In a reaction flask, 0.33 g of a graft copolymer (1.57 mmol *t*-BMA units) was dissolved in 6 mL of CH_2Cl_2. After complete dissolution, 3 mL of trifluoroacetic acid (TFA, 28.75 mmol) was added dropwise. The reaction was allowed to proceed at room temperature for 24 h. The solution was purged with N_2 until the solvent evaporated. The polymer was repeatedly dissolved in CH_2Cl_2 and subjected to N_2 purging until the residual acid was removed, as confirmed by wet litmus paper. During evaporation of CH_2Cl_2, the anionic brush copolymer precipitated and was collected by filtration. It was insoluble in CH_2Cl_2 and other organic solvents, but highly soluble in an aqueous NaOH solution. An anionic brush copolymer solution was dialysed against 5% NaOH for one week using dialysis tubing with a molecular weight cutoff of 3.5 kDa. After dialysis, the copolymer solution was freeze-dried for one week at –30°C using an Alpha 2–4 LSCplus lyophilizer. The resulting polymer was white powder. Polymer yield determined gravimetrically was 0.26 g (78.8%).

^{1}H BMR (D_2O) δ (ppm): 1.6–1.84 (2H, -C$\mathbf{CH}_2$C-, backbone of pMAA), 1.0 (3H, $\mathbf{CH_3}C(CH_2)$- of pMAA).

Analysis and characterisation of the copolymers

FTIR spectroscopic analysis was performed using a Perkin Elmer Frontier spectrometer in a range of 650–4000 cm^{-1}.

^1H NMR measurements in $CDCl_3$ and D_2O were performed on a Brucker 400 Ascend™ NMR spectrometer (400 MHz).

UV spectra of p(*t*-BMA) in NMP were recorded on a Perkin Elmer UV/Vis Lambda 35 spectrometer. The absorption of trithiocarbonate (TTC) groups was measured at a wavelength of 310 nm [25].

The hydrodynamic radius (R_h) of the polymers was determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS equipped with a 4 mW He–Ne laser (λ = 633 nm). Scattered light intensity measurements were performed at 25°C and a scattering angle of 173°. Prior to analysis, samples were filtered through 0.22 μm polytetrafluoroethylene (PTFE) syringe filters. The pH-responsive behaviour of the anionic brush copolymers was monitored by DLS. Polymers were dissolved in 10 mL of 0.01 M NaOH, filtered through a polyethersulfone (PES) filter and titrated with 0.1 M HCl from pH 12 to pH 2. At each pH value, the R_h of anionic brush copolymers was measured. pH of the solutions was measured with a pH/ORP meter (HJ221, Hanna Instruments).

To evaluate the degree of ionisation and an apparent ionisation constant of the polyelectrolytes, potentiometric titration of the polymer solutions was performed. A sample of 12 mg of brush-like anionic polymer was dissolved overnight in 20 mL of 0.01 M NaOH. The solution was then potentiometrically titrated with 0.1 M HCl, adding 0.1 mL increments each time. After each addition, the solution was stirred for approximately 30 min, and then pH value was recorded. Titration continued until the pH reached 2. From the potentiometric titration curve, the equivalence point was determined, corresponding to the amount of ionisable groups per unit mass of the polyelectrolyte. Once the equivalence point was established, the degree of ionisation (α) was calculated for each titration point. The data were then plotted as pH versus log(α/(1–α)), corresponding to the Henderson–Hasselbalch coordinates. The resulting plot was fitted to a linear equation

$$\mathrm{pH} = \mathrm{pK}_{\alpha}^{\mathrm{app}} + n \times \lg\left(\frac{\alpha}{1-\alpha}\right), \quad (7)$$

where pK_{α}^{app} is an apparent ionisation constant of the polyelectrolyte, *n* is a coefficient related to the polymer structure, and α is the fraction of the ionized functional groups. In the linear fit, pK_{α}^{app} corresponds to the pH at which log(α/*(1*–α*)*) = 0 (i.e. the intercept), and n corresponds to the slope of the line.

To evaluate pH-induced changes in polymer solubility and aggregation, reflecting pH-responsive behaviour, turbidity measurements of the polymer solutions were performed. A sample of 12 mg of the anionic brush copolymer was dissolved overnight in 20 mL of 0.01 M NaOH. The solution was filtered through a glass filter and transferred into a cuvette, where it was titrated with 0.2 M HCl. After stabilisation of the pH value (approximately 15 min), the cuvette was placed into a turbidimeter Turb 430 IR/T, and the light scattering (optical absorbance, turbidity) of the solution was recorded. The titration was performed over a pH range from 12 to 2.

RESULTS

Synthesis of the linear statistical copolymers p(GMA-*st*-BMA) and p(AHPMA-*st*-BMA)

Random copolymers of GMA and BMA were synthesised via the RAFT polymerisation technique using CTA1 (Table 1, Fig. 3). The task was set to synthesise polymethacrylate-based backbone, in which a GMA fragment with an active epoxy group will be in every second monomeric unit, enabling the attachment of p(*t*-BMA) side chains. Reactivity ratios of the monomers GMA and BMA in radical copolymerisation are close to each other (r_{GMA} = 0.94, r_{BMA} = 0.85) [26], therefore, and it is expected that random copolymers of the desired composition should be synthesised. BMA was chosen as the comonomer due to its good solubility in solvents that dissolve GMA, *t*-BMA, and their corresponding polymers. Similar values of the Hansen solubility parameters for these monomers (17.8 $MPa^{0.5}$ for *t*-BMA, 18.5 $MPa^{0.5}$ for BMA and 20.5 $MPa^{0.5}$ for GMA) demonstrate a strong structural affinity that translates to their respective polymer segments, ensuring their homogeneous co-solubility in common organic solvents like NMP (22.96 $MPa^{0.5}$) [26, 27]. During the copolymerisation, the molar ratio of both monomers to CTA1 varied from 40/1 to 160/1.

The best results – the lowest dispersity index (Đ) and desirable molecular weight – were achieved when the initial molar ratio [GMA+BMA] to [CTA1] in the polymerisation mixture was 50/1 to 60/1.

Table 1. **Results of the RAFT polymerisation of GMA and BMA; [CTA1]/[AIBN] = 5/1, NMP, τ = 15 h, 65°C**

Polymer	[GMA+BMA]/[CTA1]	q, %	$M_n^{theor.}$	M_n^{SEC}	GMA, mol%	Đ
p(GMA-st-BMA)1	40/1	91	5500	5300	52.0	1.15
p(GMA-st-BMA)2	50/1	86	6400	8400	52.2	1.15
p(GMA-st-BMA)3	60/1	83	7400	7300	52.3	1.19
p(GMA-st-BMA)4	160/1	94	21700	23700	53.0	1.74

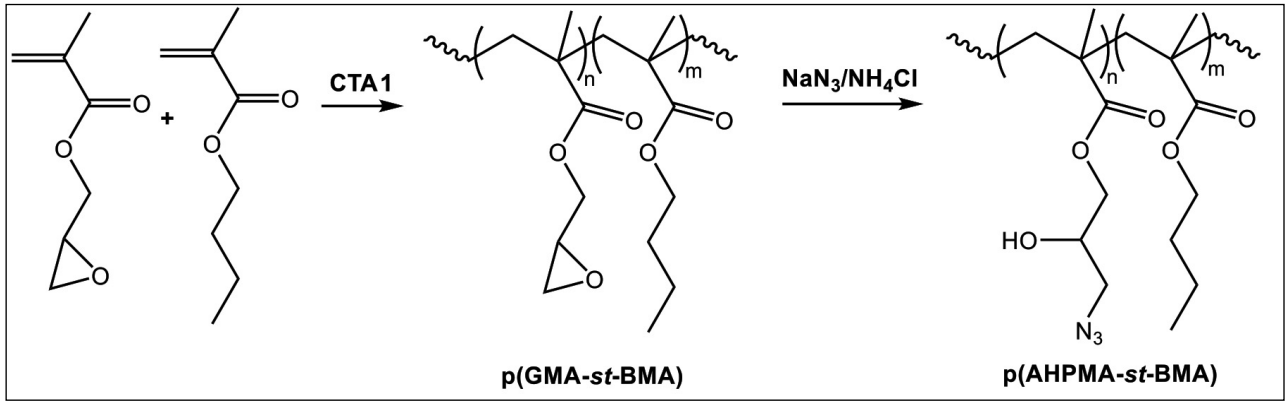

Fig. 3. General scheme of the synthesis of statistical linear copolymers p(GMA-*st*-BMA) and p(AHPMA-*st*-BMA)

The synthesised copolymer p(GMA-*st*-BMA), containing 52 mol% of GMA units, was characterised by molecular weight of approximately 7000–8000. Well-defined random copolymer p(GMA-*st*-BMA) was used for epoxy–thiol *click* reactions.

To make suitable for azide–alkyne *click* chemistry reactions, GMA units of the copolymer p(GMA-*st*-BMA) were reacted with sodium azide, which enabled to change epoxy groups to azide groups (Fig. 3).

Nearly quantitative conversion of GMA units to the units of 3-azido-2-hydroxy propyl methacrylate (AHPMA) was confirmed by ^{1}H NMR and FTIR spectroscopy. In the ^{1}H NMR spectrum of the p(AHPMA-*st*-BMA) (Fig. 4b), characteristic

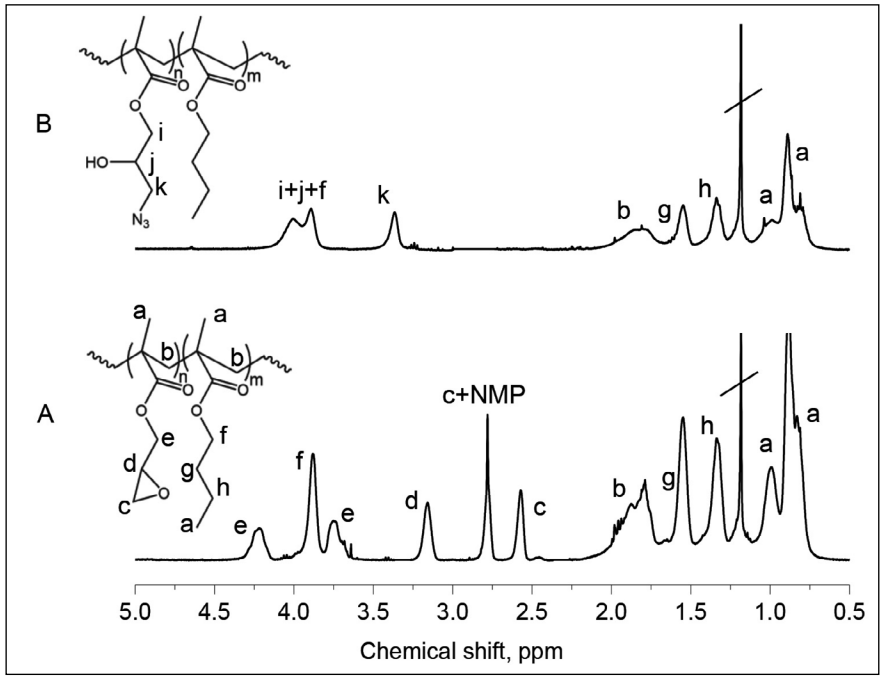

Fig. 4. ^{1}H NMR spectra of p(GMA-*st*-BMA) (A) and p(AHPMA-*st*-BMA) (B) in $CDCl_3$

chemical shifts of the epoxy group protons at 3.23, 2.85 and 2.64 ppm [10, 11] (Fig. 4a) were no longer observed.

Instead, new chemical shifts appeared at 3.45 and 4.09 ppm, which were assigned to the methylene protons adjacent to the azide group and to the –CH and $–CH_2$ protons located further away from the azide functionality, respectively [10, 11]. The latter chemical shifts overlap with the chemical shifts of the protons of the BMA units.

Synthesis of thiol or alkyne terminated p(*t*-BMA)

Poly(*tert*-butyl methacrylate) (p(*t*-BMA)) as a precursor of the side chains of brush copolymers was synthesised by RAFT polymerisation of *t*-BMA in the presence of CTA1 or CTA2 (Fig. 5). An attempt was made to synthesise well-defined polymers with a low degree of polymerisation (DP up to 15). Previous studies have shown [28–30] that grafting of long, sterically hindered and conformationally restricted polymer chains is challenging. Monomeric units of p(*t*-BMA) contain bulky *tert*-butyl substituents that significantly reduce chain flexibility and increase steric hindrance, particularly, for longer chain lengths. This structural feature can hinder grafting reactions. Thus, short p(*t*-BMA) chains (DP ≤ 15) and backbone incorporating BMA spacers between the reactive GMA units were chosen to minimise steric hindrance during the grafting onto the approach [29].

The best results were achieved when the initial molar ratio [*t*-BMA]/[CTA]/[AIBN] in the polymerisation mixture was 100/5/1, and the polymerisation was carried out in NMP for 6 h at 65°C (Table 2). These conditions were optimal for the polymerisation in the presence of both CTA1 and CTA2. The number-average molecular weight (M_n) and degree of polymerisation (DP) of the resulting polymers were 2000–2500. Alkyne terminated p(*t*-BMA4) and p(*t*-BMA5) synthesised in the presence of CTA2 were used for azide–alkyne *click* reactions. In the ^{1}H NMR spectrum of p(*t*-BMA) (Fig. 6), characteristic intensive chemical shifts of methyl group protons in the *tert*-butyl group are observed at 1.55–1.30 ppm [31].

To implement the epoxy–thiol *click* reaction, the terminal trithiocarbonate (TTC) groups of p(*t*-BMA) synthesised in the presence of CTA1 were reduced to thiol groups by the nucleophilic reduction reaction using hydrazine monohydrate. The aminolysis reaction was monitored by UV spectroscopy following the disappearance of the absorbance at 310 nm characteristic of the trithiocarbonate group [25]. Well-defined p(*t*-BMA)1, p(*t*-BMA)2 and p(*t*-BMA)3 with terminal thiol groups and a slightly decreased molecular weight due to the loss of the CTA1 fragment were used for subsequent epoxy–thiol *click* reactions.

Synthesis of the brush copolymers by *click* chemistry reactions

Statistical copolymers containing epoxy or azide groups and p(*t*-BMA) with terminal alkyne or thiol groups were coupled into brush polymers

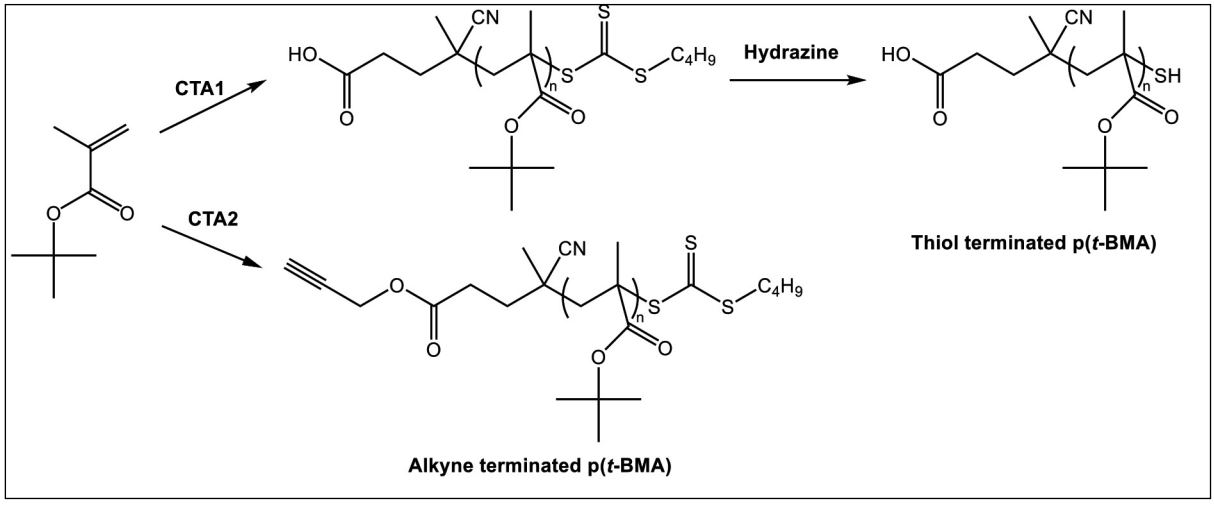

Fig. 5. General scheme of the synthesis of thiol or alkyne terminated p(*t*-BMA)

Table 2. **Results of the RAFT polymerisation of *t*-BMA; [*t*-BMA]/[CTA]/[AIBN] = 100/5/1, NMP, τ = 6 h, 65°C**

Polymer	CTA	q, %	$M_n^{theor.}$	M_n^{NMR}	DP (NMR)
p(*t*-BMA)1	CTA1	77	2500	1900	10
p(*t*-BMA)2	CTA1	86	2700	2300	14
p(*t*-BMA)3	CTA1	82	2600	1800	10
p(*t*-BMA)4	CTA2	81	2450	2000	12
p(*t*-BMA)5	CTA2	87	2800	2500	15

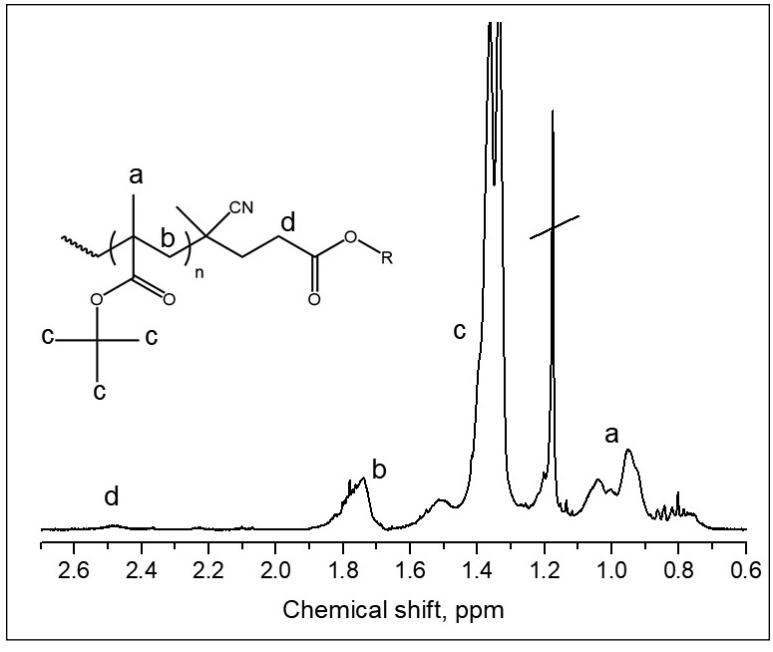

Fig. 6. ^{1}H NMR spectrum of p(*t*-BMA) in $CDCl_3$

via epoxy–thiol or azide–alkyne *click* reactions (Fig. 7). Anionic brush copolymers with functional carboxyl groups were obtained via the acidic hydrolysis of p(*t*-BMA) *tert*-butyl groups by trifluoroacetic acid (TFA) in CH_2Cl_2. After the hydrolysis, the polymer precipitated from CH_2Cl_2 but was soluble in water. The quantitative conversion of tert-butyl groups was confirmed by FTIR (Fig. 9) and ^{1}H NMR spectroscopy. No residual chemical shifts of the *tert*-butyl group were observed in the ^{1}H NMR spectra.

The progress of the *click* reactions was monitored by dynamic light scattering (DLS) (Fig. 8). The epoxy–thiol *click* reactions were carried out using two different alkaline catalysts: triethylamine (TEA) and 4-dimethylaminopyridine (DMAP), at temperatures of 70 and 80°C. At 70°C, the hydrodynamic radius (R_h) of the polymers in the TEA-catalysed system reached 5.95 nm after 24 h.

In contrast, the DMAP-catalysed reaction was slower giving the R_h value of 5.80 nm after 48 h. However, at 80°C, the TEA-catalysed process was significantly retarded, yielding a maximal R_h of the particles of only ~2 nm. The retardation is likely attributable to the volatility of TEA (b.p. ~90°C), the evaporation of which at elevated temperatures decreases the effective catalyst concentration, thereby retarding the reaction. Conversely, the DMAP-catalysed reaction proceeded more efficiently at 80°C, with the R_h of 4.35 nm after just 8 h. Furthermore, the alkyne–azide *click* reaction at room temperature demonstrated R_h value of 3.76 nm within 6 h with a slight increase up to 4.36 nm after 24 h.

Comparable hydrodynamic radiuses of the brush polymer particles suggest that both coupling strategies utilising the epoxy–thiol and azide–alkyne *click* reactions are effective for producing brush polymers. Nevertheless, the epoxy–

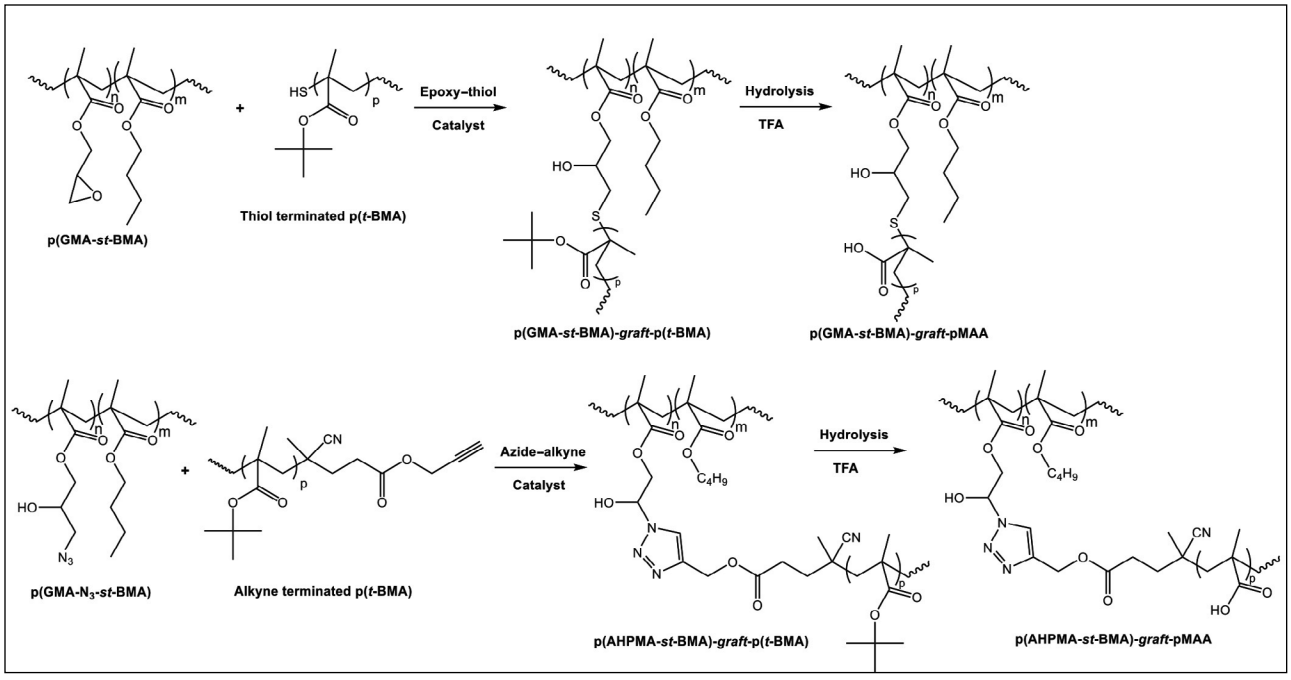

Fig. 7. General scheme of the synthesis of the brush copolymers carrying pMAA side chains by epoxy–thiol and azide–alkyne *click* reactions

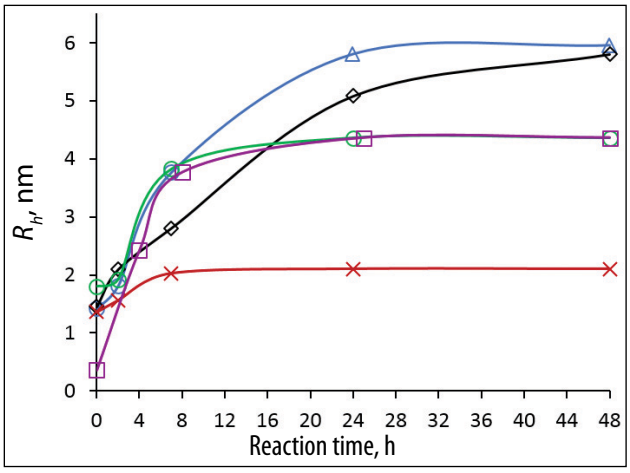

Fig. 8. Hydrodynamic radius R_h of the brush copolymers vs reaction time during the epoxy–thiol *click* reaction using different catalysts: TEA at 70°C (—Δ—), TEA at 80°C (—x—), DMAP at 70°C (—◊—), DMAP at 80°C (—○—) and azide–alkyne *click* reaction (—□—)

thiol *click* reaction demonstrates an even higher efficiency at 70°C, giving larger polymer particles.

Figure 9 presents the FTIR spectra of p(GMA-*st*-BMA) and p(AHPMA-*st*-BMA) as the mainchains, the p(*t*-BMA) as the side chains, and the resulting neutral and anionic brush copolymers. The successful introduction of azido units was confirmed via FTIR spectroscopy. The absorption bands at 908 and 845 cm^{-1} characteristic of the epoxide ring of p(GMA-*st*-BMA) (Fig. 9, left) completely disappeared. Simultaneously, a new strong absorption band emerged at ~2100 cm^{-1} (Fig. 9, right), which is assigned to the asymmetric stretching vibrations of the azido groups in the resulting p(AHPMA-*st*-BMA) [11]. The FTIR spectra of p(*t*-BMA) exhibit a characteristic doublet at 1396 and 1367 cm^{-1}, which is attributed to the symmetric bending vibrations of the *gem*-dimethyl groups within the *tert*-butyl fragment [32]. The FTIR spectra of the brush copolymers exhibit characteristic absorption bands of both the backbone and the side chains, alongside new absorption bands corresponding to the newly formed bonds. Most notably, a broad band appears at 3400 cm^{-1}, which is assigned to the stretching vibrations of the secondary hydroxyl (–OH) groups generated during the epoxy ring-opening process (Fig. 9, left). It is noteworthy that the FTIR spectrum of the brush copolymer synthesised by the azide–alkyne *click* reaction reveals a faint residual band at 2100 cm^{-1} attributed to the azide groups. This suggests an incomplete conversion of the azide groups, which likely leads to a lower grafting density of the brush copolymer compared to the epoxy–thiol system, where the characteristic bands of the epoxy groups are completely absent.

After dialysis from an alkaline solution and subsequent freeze-drying, the anionic brush polymers predominantly exist in the carboxylate ($–COO^-$) form.

This is evidenced by strong asymmetric and symmetric $–COO^-$ stretching bands at ~1534 and

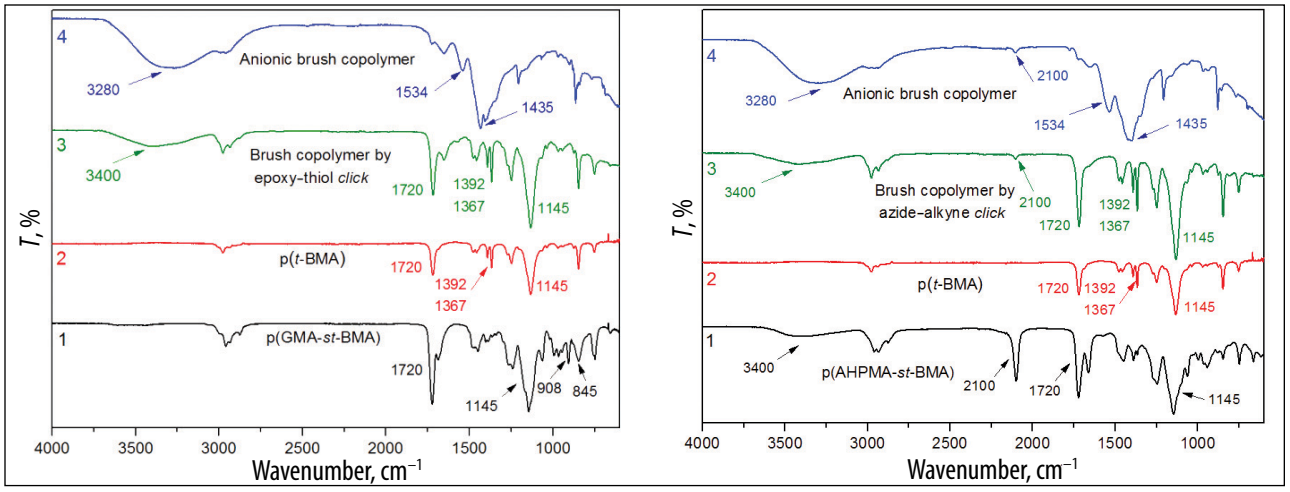

Fig. 9. FTIR spectra of the statistical copolymeric, p(*t*-BMA) and brush copolymers before and after acidic hydrolysis synthesised by epoxy–thiol (left) and azide–alkyne (right) *click* reactions

~1435 cm^{-1}, respectively [33], while the C=O stretching band of protonated carboxylic acid at ~1720 cm^{-1} is significantly reduced. The absorption band observed at 1145 cm^{-1} is attributed to the ester C–O–C stretching vibrations originating from the BMA, GMA and *t*-BMA segments. Following the acidic hydrolysis of the brush copolymers, the *tert*-butyl groups are cleaved, thereby eliminating their dominant contribution to the spectrum. Furthermore, the polymer backbone becomes spectrally and sterically shielded, rendering its residual absorption difficult to detect. After hydrolysis, the acid functionality is clearly visible in both *click* systems as the broad absorption from around 3000 to 3500 cm^{-1}.

Solution properties of anionic brush copolymers

Solution properties of the anionic brush copolymers were investigated by potentiometric/turbidimetric titrations (Fig. 10) and DLS (Fig. 11). Given that the dialysed brush copolymers are dissolved in the alkaline medium, they are in the form of polyanions with Na^+ counterions at pH 12.

During the HCl titration down to pH 2, the titration curve exhibits two distinct potentiometric inflection points: the first, at pH 8–9, corresponds to the neutralisation of free NaOH [34], while the second, between pH 6 and pH 3, is attributed to the protonation of the polyanion. As the carboxyl groups become undissociated, the polymer loses its charge, eliminating the electrostatic repulsions between the pMAA side chains. The resulting hydrophobisation of the brush structure promotes the formation of intermolecular hydrogen bonds and subsequent polymer aggregation. The protonation and aggregation process is confirmed by a sudden and drastic increase in solutions turbidity within a narrow pH range. At pH 6.3–6.5, the solution of the anionic brush copolymer synthesised by the epoxy–thiol

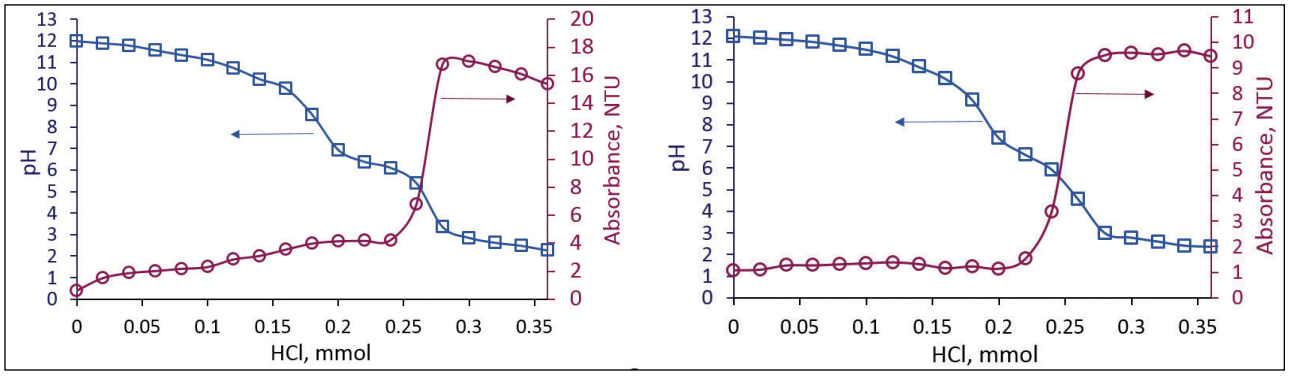

Fig. 10. Potentiometric (—□—) and turbidimetric (—○—) titration curves of the anionic brush copolymers, synthesised by epoxy–thiol (left) and azide–alkyne (right) *click* reactions

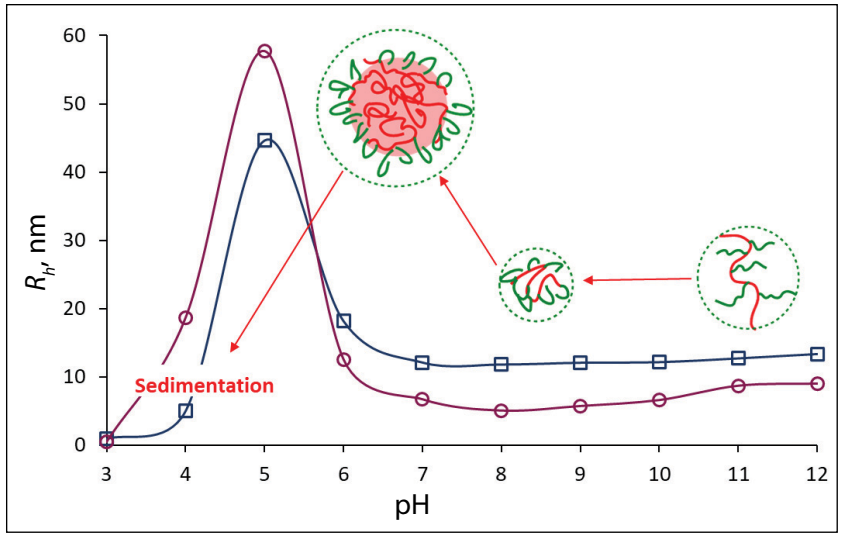

Fig. 11. Hydrodynamic radius R_h of anionic brush copolymers vs solution pH: —○— synthesised by azide–alkyne *click* reaction, —□— synthesised by epoxy–thiol *click* reaction

click reaction reached a turbidity of approximately 17 NTU (nephelometric turbidity units), whereas the anionic brush copolymer synthesised by the azide–alkyne *click* reaction exhibited a turbidity of about 9 NTU.

Such a difference in turbidity among similar anionic brush copolymer solutions of the same concentrations is a remarkable phenomenon requiring further elucidation via DLS measurements. DLS analysis revealed (Fig. 11) that at high pH values (10–12) anionic brush copolymers are individually solubilised forming a rather large volume (R_h ~ 7–12 nm) because of an extended, stretched conformation due to the negative charge repulsion. In near-neutral solutions (pH 6–8), the pMAA side chains become partially protonated, which decreases their solubility and induces the compactisation of the chains. As the pH drops to ~5, a significant degree of protonation is reached, driving the self-assembly into medium-sized micelles or aggregates (R_h ~ 45–60 nm). In acidic solutions (pH < 4), large micellar aggregates are formed, which are unstable and prone to sedimentation.

Although it is generally accepted [35] that solutions containing larger particles, namely aggregates, scatter light more intensely, leading to higher turbidity, our study demonstrates the opposite effect: solutions containing smaller aggregates exhibit higher turbidity. DLS measurements demonstrate that the epoxy–thiol anionic brush copolymer at pH 5 forms aggregates with R_h of 45 nm, whereas the azide–alkyne anionic brush copolymer tends to form larger aggregates with R_h of 60 nm.

Larger particles scatter light more intensely than smaller ones only when their densities are similar. We suggest that the aggregates formed by the epoxy–thiol and azide–alkyne brush polymers possess distinctly different internal architectures and densities. Drawing upon similar studies [36, 37], it can be suggested that the epoxy–thiol brushes assemble into smaller aggregates with a higher density, which accounts for the higher turbidity of their solutions. Conversely, the azide–alkyne copolymers tend to form larger, fuzzier, microgel-like aggregates containing a substantial amount of bound water. Consequently, their density is lower, resulting in a reduced solution turbidity.

Lower density of the azide–alkyne brush copolymer particles can be predetermined by two reasons: lower graft density and structural characteristics of the linker generated during the *click* reaction. Lower graft density of the azide–alkyne copolymers was confirmed by the FTIR spectrum (Fig. 9, right, spectrum 3) revealing residual azide ($-N_3$) vibrations in the copolymer. In contrast to the compact thioether linkage formed in the epoxy–thiol system, the 1,2,3-triazole ring formed via the azide–alkyne *click* reaction (see Fig. 7), together with its adjacent functional groups, constitutes a considerably longer and bulkier spacer. This extended linker increases the effective distance between the polymer

backbone and the grafted side chains, forcing the latter to adopt a more radially extended conformation and reducing their ability to pack densely around the backbone [38]. As a result, the azide–alkyne conjugates exhibit a more expanded macromolecular architecture.

Despite this steric expansion, the triazole ring remains a highly active supramolecular motif. Owing to its aromatic character and substantial dipole moment, triazole units promote an intermolecular association through a combination of π–π stacking and dipole–dipole interactions, facilitating the assembly of the expanded polymer chains into larger supramolecular aggregates, as reflected by the increased hydrodynamic radius (R_h = 60 nm). At the same time, the triazole ring is highly polar and can participate in extensive hydrogen–bonding interactions with surrounding water molecules. Consequently, the aggregation process is governed by a delicate balance between triazole–triazole association and triazole–water interactions [17, 39, 40].

From the potentiometric titration data, *Henderson-Hasselbalch* plots were obtained (Fig. 12). It was determined that the brush copolymers, irrespective of the type of *click* chemistry reaction used for the attachment of the side chains, were weaker polyacids (pK_α^{app} 6.5–6.7) compared to linear poly(methacrylic acid) (pMAA pK_α^{app} 4.2).

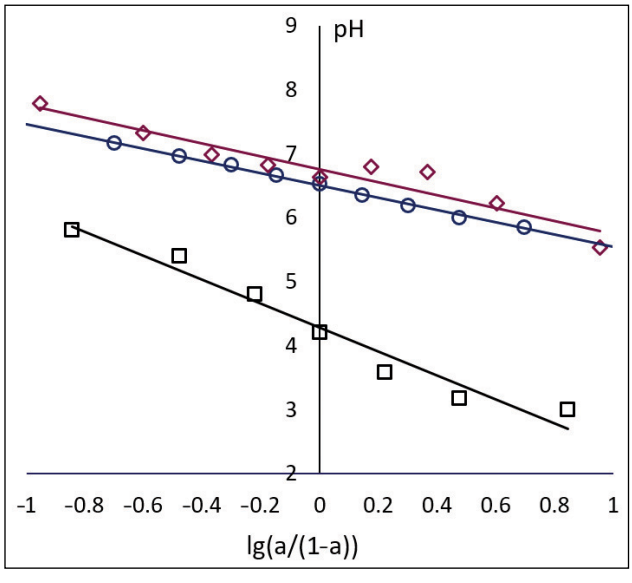

Fig. 12. Henderson–Hasselbalch plots of anionic brush copolymers: —◊— synthesised by azide–alkyne *click* chemistry, —○— synthesised by epoxy–thiol *click* reaction; and —□— pMAA

Such a shift toward higher pK_α^{app} values is characteristic of the brush polyelectrolytes. Since pMAA segments are attached to the mainchain, substantial steric hindrance restricts their conformational freedom and makes the deprotonation process more difficult compared to free linear chains [41].

CONCLUSIONS

Statistical copolymers of glycidyl methacrylate and butyl methacrylate as precursors for the backbone and poly(*tert*-butyl methacrylate) as a precursor for the side chains were successfully synthesised by RAFT polymerisation. Statistical copolymers were characterised by a predetermined molecular weight, a low dispersity index, and a nearly equimolar composition. p(*t*-BMA) was of a low molecular weight and contained thiol or alkyne groups. Anionic brush copolymers with negative charges in the side chains were prepared by two different *click* chemistry methods, namely, azide–alkyne and epoxy–thiol, with a successive acidic hydrolysis of *t*-BMA units. The progress of the *click* reactions was monitored by DLS enabling us to conclude that both coupling strategies were effective for producing brush copolymers. Nevertheless, it was determined that the method of epoxy–thiol *click* chemistry has some advantages over the alkyne–azide method despite the latter's popularity because of simpler experimental procedures and a higher grafting density in the products.

It was determined that anionic brush copolymers are weaker polyacids compared to linear poly(methacrylic acid) and tend to aggregate at pH lower than 6.3. Despite a larger hydrodynamic radius of the aggregates of anionic brush copolymers synthesised by alkyne–azide *click* chemistry, the turbidity of the solutions of such copolymers at pH 3–5 was lower. This behaviour was explained by more compact aggregates of the copolymers synthesised via the epoxy–thiol *click* reaction compared to those prepared using the azide–alkyne approach.

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pH JAUTRIŲ ŠEPETINIŲ KOPOLIMERŲ SINTEZĖ TAIKANT RAFT POLIMERIZACIJĄ IR „KLIK“ CHEMIJOS REAKCIJAS

S a n t r a u k a

Anijoniniai šepetiniai kopolimerai buvo susintetinti taikant „skiepijimo į“ strategiją, derinant grįžtamojo jungimosi–fragmentacijos grandinės perdavos (RAFT) polimerizaciją ir dvi „klik“ chemijos reakcijas: epoksido–tiolio ir azido–alkino. Šių dviejų tipų „klik“ reakcijų eiga ir efektyvumas buvo palyginti siekiant nustatyti tinkamesnį metodą šepetinių kopolimerų sintezei. Numatomų šepetinių kopolimerų pagrindinė grandinė su daugybe epoksidinių grupių ir beveik ekvimoline monomerinių grandžių sudėtimi buvo susintetinta vykdant butilmetakrilato (BMA) ir glicidilmetakrilato (GMA) RAFT kopolimerizaciją. Poli(*tret*-butilmetakrilatas) (p(*t*-BMA)) kaip šoninių grandinių pirmtakas buvo susintetintas vykdant RAFT polimerizaciją ir, priklausomai nuo grandinės pernašos agento struktūros, turėjo galines tiolio arba alkino grupes. „Klik“ reakcijų eiga buvo sekama dinaminės šviesos sklaidos metodu (DLS), registruojant šepetinių kopolimerų hidrodinaminio spindulio (R_h) didėjimą. Anijoniniai šepetiniai kopolimerai, turintys karboksigrupes, buvo gauti rūgštinės *t*-BMA grandžių hidrolizės būdu.

Anijoninių šepetinių kopolimerų vandeniniai tirpalai buvo tirti potenciometrinio ir turbidimetrinio titravimo bei DLS metodais. Nustatyta, kad abu anijoniniai šepetiniai kopolimerai, nepriklausomai nuo taikytos „klik“ chemijos reakcijos tipo, yra silpnos polirūgštys. Šepetiniai kopolimerai, gauti epoksido–tiolio „klik“ reakcija, sudaro gana kompaktiškus agregatus, o šepetiniai kopolimerai, gauti azido–alkino „klik“ reakcijos būdu – didesnius, mažesnio tankio mikrogelio tipo agregatus. Sintetinant šepetinius kopolimerus, epoksido–tiolio „klik“ chemijos metodas turi tam tikrų pranašumų prieš alkino–azido metodą, nepaisant pastarojo populiarumo, nes leidžia paprasčiau atlikti eksperimentines procedūras ir sudaro galimybę pasiekti didesnį šepetinių kopolimerų skiepijimo tankį.