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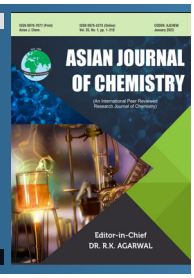

Synthesis of New Degradable AB-Type Polyesters with 1,2,3-Triazole Rings in the Backbone *via* "Click" Step-Growth Polymerization

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A series of new aliphatic AB-type polyesters (PEs) and co-polyesters (*co*-PEs) with 1,2,3-triazole rings in the backbone were successfully synthesized *via* Cu(I)-catalyzed click step-growth polymerization (SGP) following the efficient one pot/two step synthetic strategy. The structure of the click polymers was confirmed by FT-IR and NMR spectroscopy and the new materials were characterized in terms of yield, solubility, film-forming properties, molecular weights and molecular weight distribution by gel permeation chromatography (GPC) and degradation ability by total organic carbon (TOC) technique. The obtained hydrolytically degradable AB-type polyesters and co-polyesters with a rather high degree of polymerization, film-forming properties and solubility behaviour increase a library of available degradable click polymers promising for wide range of biomedical applications and also confirm the suitability of the present synthetic strategy for designing different types of triazole main chain degradable click polymers.

Keywords: Polyester, Copper(I) catalyzed azide-alkyne cycloaddition, Step-growth polymerization, 1,2,3-Triazole ring, Degradation.

INTRODUCTION

Copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) is one of the most powerful tools among "click" reactions finding its widespread application in various domains of contemporary polymer and material science [1,2]. Owing to its remarkable features, such as high reaction rate and efficiency, precise regioselectivity, tolerance towards "foreign" functional groups and mild reaction conditions, the CuAAC click reaction has been widely used for the synthesis of block-copolymers, cyclic polymers, dendrimers, hyper-branched macromolecules, star-shaped polymers, crosslinked polymeric networks, *etc.* and for functionalization/surface modification of polymeric materials [3-9].

Attracted by the prospect, synthetic polymer chemists tried to exploit the CuAAC to synthesize polytriazoles by step-growth polymerization (SGP) since year 2004 [10-13]. Although a impressive progress has been made, the area is still developing, with many challenges and obstacles yet [12,13]. There are quite limited reports on the synthesis of aliphatic main-chain triazole degradable polymers by CuAAC based click SGP. Nagao & Takasu [14] reported on the first successful synthesis of degradable polyesters. Galbis *et al.* [15] also obtained click polyesters based on erythritol bearing free hydroxyl groups. Click polymerization has been utilized for the synthesis of some other biomedical materials as well [16-22].

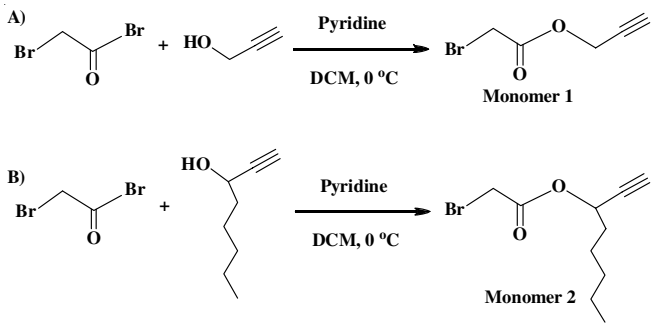
It should be underlined that click polymers bearing 1,2,3-tiazole rings in the main chain have some important advantages. Firstly, the triazole rings are known to be low-toxic moieties [23,24] with high level of mimicry of the amide bond of native peptides, moreover 1,2,3-triazole unit is structurally similar to the amide bond of proteins in terms of configuration, distance and planarity [25]. So, the incorporation of the triazole rings in the polymeric backbone is expected to improve the biocompatibility of the materials. Secondly, the presence of rigid triazole rings in the main chain can substantially improves the thermal properties of the polymers [26].

Moreover, one of the important merits of the click polymers is that 1,2,3-triazole rings are quaternizable moieties [27,28].

This, in turn, enables to perform post-polymerization functionalization of the polymers. The quaternization of the triazole rings using various quaternizing agents like halo-alkyls and polyethylene glycol (PEG) derivatives opens a way to cationic systems with 1,2,3-triazolium moieties in the backbone either cationic polymers or amphiphilic surfactants (*e.g.* PEG-bromides as quaternizing agents) and crosslinked hydrogels (when using bifunctional quaternizing agents like dibromo-PEGs) that are promising materials for numerous biomedical applications.

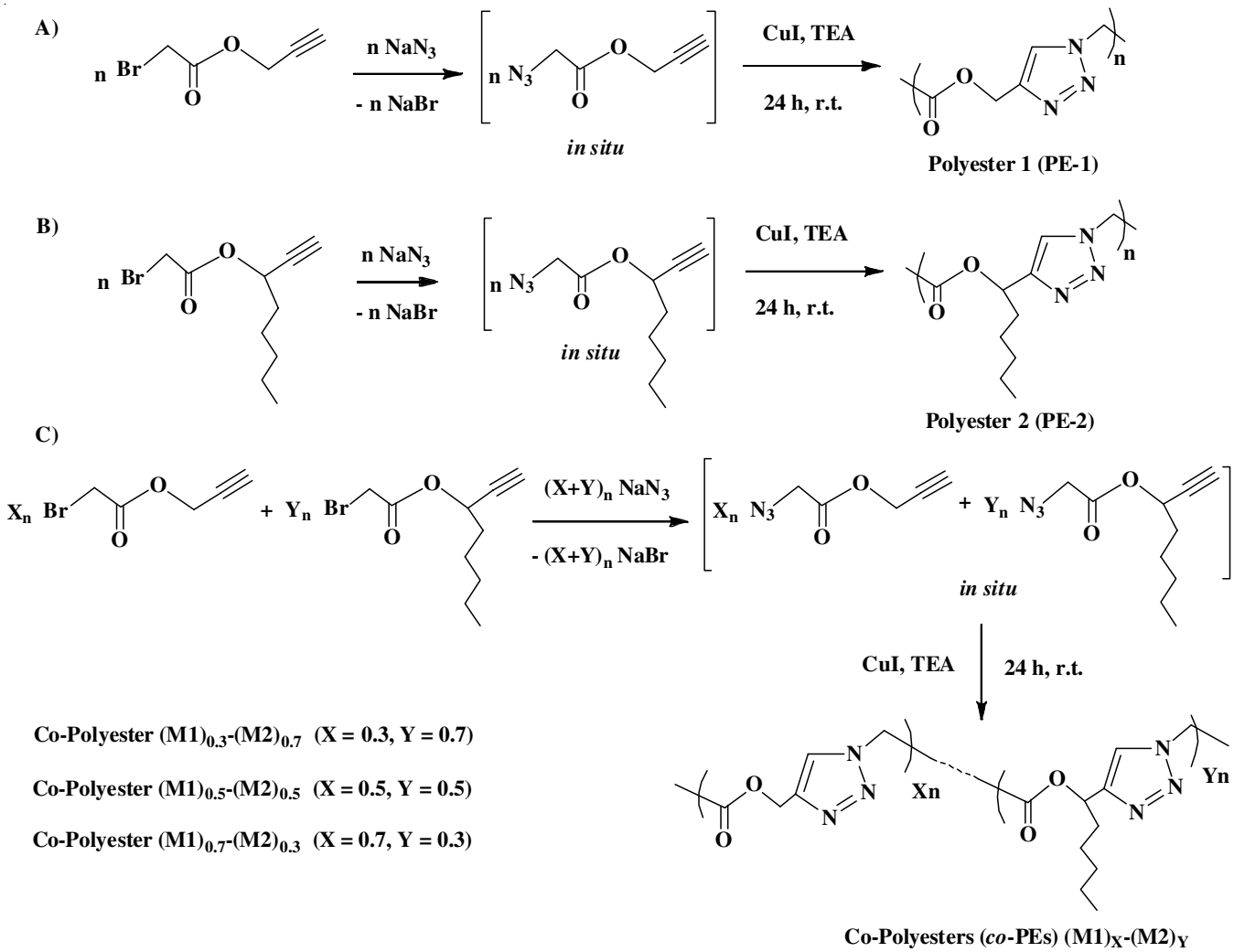
For obtaining new high molecular weight 1,2,3-triazole containing degradable polymers, a new synthetic strategy of CuAAC based click SGP have already been elaborated [26]. Present approach could be considered as more versatile compared to the existing strategies and allows to synthesize different types of (AB and AA-BB) and classes (polyesters, poly(ester amide)s, poly(ester urea)s, their co-polymers, *etc.*) of linear hetero-chain triazole-backbone click polymers without using potentially explosive organic azides *via* safe and facile one pot/two step procedures.

In present work, a successful synthesis of new linear AB-type click polyesters and co-polyesters *via* efficient synthetic strategy is reported. The key AB-type hetero-bifunctional monomers were synthesized by the interaction of bromoacetyl bromide with functionalized acetylenic derivatives (**Scheme-I**). In this synthetic strategy, the target click polymers bearing triazole rings in the backbone was performed by one-pot/two step SGP of the hetero-bifunctional monomers in the presence of sodium azide using copper(I) iodide/triethylamine (CuI/TEA) as catalytic system (**Scheme-II**).



Scheme-I: Synthesis of key hetero-bifunctional monomers

The structure of the synthesized monomers and polymers were confirmed by FT-IR and NMR spectroscopies. The synth-



Scheme-II: Synthesis of AB-type click polyesters (PEs) and Co-polyesters (*co*-PEs)

esized polymers were also characterized in terms of yield, solubility in organic solvents, film-forming properties, molecular weights and molecular weight distribution by GPC method and the degradation ability by total organic carbon (TOC) technique. The new AB-type polyesters increase a library of available degradable click polymers for wide range of biomedical applications.

EXPERIMENTAL

All the starting materials, chemicals and solvents purchased from the commercial sources were used without further purification. Bromoacetyl bromide, propargyl alcohol, 1-octyn-3-ol, pyridine, sodium azide, anhydrous sodium sulfate, copper(I) iodide, lithium bromide, aluminum oxide (alumina) (activated, basic, Brockmann I), acetone, ethanol, methanol, hexane, ethyl acetate, dichloromethane (DCM), *N,N*-dimethylformamide (DMF), *N,N*-dimetyl-acetamide (DMA) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) were purchased from Sigma-Aldrich (Germany). *N*-Methylpyrrolidone (NMP) were purchased from Carl Roth, Karlsruhe (Germany), while triethylamine (TEA) was purchased from Lancaster (U.K.). The phosphate-buffered saline (pH = 7.4) was obtained from Santa Cruz Biotechnology, Inc. (USA).

Characterization: The synthesized polyesters (PEs) were characterized by Fourier-transform infrared spectroscopy (FT-IR), ^{1}H & ^{13}C nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The polymer degradation was studied by measuring the total organic carbon concentrations (TOC) in aqueous solutions produced after hydrolytic degradation of polyesters.

The IR analysis of samples was performed on Thermo Nicolet Avatar 370 FT-IR spectrophotometer coupled with EZ OMNIC software measuring between wavelength range of 4000 and 400 cm^{-1}. The FT-IR spectra of the monomers were recorded using Avatar Multi-Bounce Flat Plate 45 degree Ge. Insoluble polymer (**PE-1**, powder) was grinded with mineral oil (nujol) and the obtained mull was applied on a KBr plate to acquire the FT-IR spectrum. To obtain the spectra of other polymers, the thin films were cast from HFIP solution on KBr plates, the solvent was evaporated at room temperature and films were dried in a vacuum at 40 ºC to a constant weight. The ^{1}H & ^{13}C NMR spectra were recorded at 300 K on a JEOL ECP 500 NMR spectrometer operating at 500 MHz. The $CDCl_3$ (for monomers) and DMSO-d_6 (for polymers) were used as solvents and internal standards.

The weight-average (M_w), number-average (M_n) molecular weights and molecular weight distribution (dispersity, Đ) of the polymers were determined on a customized GPC system (PSS Polymer Standard Service GmbH, Mainz, Germany), operating with DMF at 50 ºC and comprising two PSS SDV linear M 5 µm particle size columns (5 cm and 30 cm) connected in series to a PSS SECcurity RI differential refractometer detector. HPLC-grade DMF with 10 mmol lithium bromide was used as eluent. Injected volume 50 µL, flow rate 1.0 mL min^{-1}. The columns were calibrated with poly(methyl methacrylate) standards (M_n = 600-1600000 g mol^{-1}). A polymer sample solutions with concentration 1.5 mg mL^{-1} were prepared in the GPC eluent and filtered with PTFE filters (450 µm) prior to injection. Chromatograms were processed using the PSS WinGPC UniChrom software.

In vitro hydrolytic degradation of polymer was studied by direct total organic carbon (TOC) method using Hach Company (USA) equipment: Spectrophotometer DR 3900 with detection range 100-700 mg L^{-1}, Thermostat DRB200 and TOC Reagent Set, HR. A 0.5 g of selected polymer sample (thin film of co-polymer $[(M1)_{0.5}$-$(M2)_{0.5}]$ was immersed into 10 mL of phosphate-buffered saline (PBS, pH = 7.4) and stored at room tempertature for four weeks. The aliquots from the buffer were taken weekly and analyzed for TOC content.

Synthesis of monomer: The key hetero-bifunctional monomers were synthesized by interaction of bromoacetyl bromide with functionalized acetylenic derivatives (propargyl alcohol and 1-octyn-3-ol) in the presence of pyridine as base (**Scheme-I**). The detailed synthetic protocol is almost similar to the method as described by Mo *et al*. [29]. In brief for monomer **1**, bromoacetyl bromide (2.61 mL, 30.0 mmol) was added dropwise to a solution of propargyl alcohol (1.73 mL, 30 mmol) and pyridine (2.4 mL, 30 mmol) in DCM (40 mL) at 0 ºC to form a white suspension, which was stirred for 20 min at 0 ºC and again for additional 30 min at 25 ºC. Afterwards, 50 mL of water was added to the reaction mixture and the organic layer was separated. The aqueous layer was then extracted with DCM (20 mL × 2). The combined organic layers were washed with water (50 mL) and dried over anhydrous Na_2SO_4 and filtered off. The filtrate was concentrated resulting in brownish liquid. The product was then purified by column chromatography. Different solvent mixtures with various volume ratio (DCM/methanol, hexane/ethyl acetate) were tested as mobile phase for the column chromatography and then hexane/ethyl acetate [7/3 (v/v)] was selected as an optimal eluent for the purification of monomer. After column chromatography, the target monomer **1** was obtained as transparent colourless liquid. The monomer **2** was also synthesized following the same synthetic procedure.

Monomer 1: Yield: 89%. FTIR (ν_{max}, cm^{-1}): 3288 (≡C–H), 2953 (CH_2), 2120 (C≡C), 1744 (-CO- ester), 1151 (C-O-C ester). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 2.53 (1H, t, -C≡CH), 3.87 (2H, s, CH_2Br), 4.77 (2H, d, CH_2O). ^{13}C NMR (126 MHz, $CDCl_3$, δ ppm): 25.26 (CH_2Br), 53.71 (CH_2O), 76.91 (-C≡<u>C</u>H), 77.41 (-<u>C</u>≡CH), 166.60 (C=O).

Monomer 2: Yield: 87%. FTIR (ν_{max}, cm^{-1}): 3293 (≡C–H), 2929-2864 (CH_2), 2120 (C≡C), 1744 (-CO- ester), 1151 (C-O-C ester). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 0.89 (3H, t, CH_2-C<u>H</u>$_3$), 1.31 (4H, m, C<u>H</u>$_2$-C<u>H</u>$_2$-CH_2-CH_3), 1.46 (2H, m, CH_2-C<u>H</u>$_2$-CH_3), 1.82 (2H, m, C<u>H</u>$_2$-CH_2-CH_2-CH_2-CH_3), 2.50 (1H, d, -C≡CH), 3.85 (2H, s, CH_2Br), 5.39 (1H, td, O-CH). ^{13}C NMR (126 MHz, $CDCl_3$, δ ppm): 14.05 (CH_3), 22.55 (<u>C</u>H_2-CH_3), 24.55 (<u>C</u>H_2-CH_2-CH_2-CH_3), 25.71 (CH_2Br), 31.29 (<u>C</u>H_2-CH_2-CH_3), 34.51 (<u>C</u>H_2-CH_2-CH_2-CH_2-CH_3), 65.96 (CH-O), 76.91 (-C≡<u>C</u>H), 77.41 (-<u>C</u>≡CH), 166.37 (C=O).

Synthesis of polymers: The target PEs and *co*-PEs were synthesized according to the reported synthetic strategy [28]. The synthetic procedure is virtually same as for the AA-BB type click PEs that was reported previously [26], but in this

case the one-pot two-step reaction (**Scheme-II**) conditions were slightly changed and fit to new AB-type PEs.

PE-2: Monomer **2** (2.362 g, 9.558 mmol) and a slight excess of sodium azide (0.683 g, 10.51 mmol) were dissolved in 6.3 mL of NMP and stirred for 3 h at room temperature. followed by the addition of catalyst CuI (54.6 mg, 0.286 mmol) and TEA (0.199 mL, 1.43 mmol) in the ratio of 1/5 to the reaction solution. The reaction solution was stirred again at room temperature for 24 h. After completion of reaction, the solution was diluted with 7 mL of NMP and the copper catalyst was removed by passing the crude polymer solution through a small column of activated basic alumina. The obtained polymer solution was precipitated in water, filtered, thoroughly washed with water and dried under vacuum at room temperature. Then, the polymer was twice precipitated from acetone solution to water, filtered and dried under vacuum at room temperature to a constant weight. All the other polymers were synthesized following the same synthetic procedure, except for **PE-1**, to which the copper removal step of purification was not applied owing to poor solubility of polymer in organic solvents.

PE-1: Yield = 77.8%. FTIR (ν_{max}, cm^{-1}): 3150 (C=C-H of the 1,2,3-triazole moiety), 1736 (-CO- ester), 1213 (C-O-C ester). Due to the insolubility of **PE-1** in organic solvents, it was impossible to characterize by NMR spectroscopy.

PE-2: Yield = 83.4%. FTIR (ν_{max}, cm^{-1}): 3141 (C=C-H of the 1,2,3-triazole moiety), 2941-2855 (CH_2), 1752 (-CO- ester), 1213 (C-O-C ester). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 0.84 (3H, CH_2-C<u>H</u>$_3$), 1.25 (6H, C<u>H</u>$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH_3), 1.95 (2H, C<u>H</u>$_2$-CH_2-CH_2-CH_2-CH_3), 5.45 (2H, N-C<u>H</u>$_2$-CO), 5.94 (1H, O-C<u>H</u>), 8.16 (1H, -C=C<u>H</u>). ^{13}C NMR (126 MHz, DMSO-d_6, δ ppm): 13.78 (CH_2-<u>C</u>H_3), 21.85 (<u>C</u>H_2-CH_3), 24.20 (<u>C</u>H_2-CH_2-CH_3), 30.74 (<u>C</u>H_2-CH_2-CH_2-CH_3), 33.10 (<u>C</u>H_2-CH_2-CH_2-CH_2-CH_3), 50.31 (N-<u>C</u>H_2), 69.61 (O-<u>C</u>H), 125.06 (-C=<u>C</u>H), 145.09 (-<u>C</u>=CH), 166.57 (<u>C</u>=O).

***co*-PE (M1)$_{0.3}$-(M2)$_{0.7}$:** Yield = 84.8%. FTIR (ν_{max}, cm^{-1}): 3150 (C=C-H of the 1,2,3-triazole moiety), 2949-2868 (CH_2), 1748 (-CO- ester), 1200 (C-O-C ester). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 0.83 (CH_2-C<u>H</u>$_3$), 1.25 (C<u>H</u>$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH_3), 1.96 (C<u>H</u>$_2$-CH_2-CH_2-CH_2-CH_3), 5.28 (O-C<u>H</u>$_2$), 5.43 (N-C<u>H</u>$_2$), 5.93 (O-C<u>H</u>), 8.20 (C=C<u>H</u>).

***co*-PE (M1)$_{0.5}$-(M2)$_{0.5}$:** Yield = 83.4%. FTIR (ν_{max}, cm^{-1}): 3141 (C=C-H of the 1,2,3-triazole moiety), 2958-2859 (CH_2), 1752 (-CO- ester), 1204 (C-O-C ester). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 0.84 (3H, CH_2-C<u>H</u>$_3$), 1.25 (6H, C<u>H</u>$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH_3), 1.96 (2H, C<u>H</u>$_2$-CH_2-CH_2-CH_2-CH_3), 5.28 (2H, O-C<u>H</u>$_2$), 5.45 (4H, N-C<u>H</u>$_2$), 5.96 (1H, O-C<u>H</u>), 8.21 (2H, C=C<u>H</u>).

***co*-PE (M1)$_{0.7}$-(M2)$_{0.3}$:** Yield = 81.1%. FTIR (ν_{max}, cm^{-1}): 3145 (C=C-H of the 1,2,3-triazole moiety), 2945-2864 (CH_2), 1752 (-CO- ester), 1204 (C-O-C ester). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 0.84 (CH_2-C<u>H</u>$_3$), 1.25 (C<u>H</u>$_2$-C<u>H</u>$_2$-C<u>H</u>$_2$-CH_3), 1.96 (C<u>H</u>$_2$-CH_2-CH_2-CH_2-CH_3), 5.29 (O-C<u>H</u>$_2$), 5.47 (N-C<u>H</u>$_2$), 5.95 (O-C<u>H</u>), 8.21 (C=C<u>H</u>).

RESULTS AND DISCUSSION

In this work, the hetero-bifunctional AB-type monomers were synthesized by the interaction of bromoacetyl bromide with functionalized acetylenic derivatives (propargyl alcohol in case of monomer **1** and 1-octyn-3-ol in case of monomer **2**) in the presence of pyridine as HBr acceptor (**Scheme-I**). The yields of the obtained monomer **1** and monomer **2** were 89 and 87%, respectively.

Following the synthesis of mononers, a series of new click polymers *viz*. PEs and *co*-PEs were synthesized according to the reported one-pot/two-step synthetic strategies [26]. The synthetic procedure is virtually the same as for linear AA-BB type click PEs, but in this case the click SGP reaction conditions were slightly modified and fit to new AB-type PEs (**Scheme-II**). Due to the perfect stoichiometric balance between "clickable" functional groups in hetero-bifunctional monomers, the AB-type click SGP has considerable advantage over the previously reported AA-BB-type polymerization.This allowed us to optimize the synthetic procedure slightly for the one pot reaction without compromising the material qualities of the target polymers. Firstly, both steps of the one pot reaction (*i.e.* azidation and SGP itself) were conducted at room temperature in contrast to the previously reported procedure where the second step proceeded at 0 ºC. Secondly, the quantity of catalyst CuI was decreased as much as possible (from 20 mol% to 3 mol%) to facilitate the copper catalyst removal in the final stage. After the completion of reaction, the crude polymer solution was diluted with solvent and the copper catalyst was removed by passage of the polymer solution through a small column of activated basic alumina [30-32]. The synthesized polymers were obtained in good yields (77.8-84.8%). The molecular weight characteristics of the new click polymers (soluble in DMF ones) such as weight-average (M_w), number-average (M_n) molecular weights and molecular weight distribution (Đ) were determined using GPC with PMMA standards and are given in Table-1. Owing to the insolubility of **PE-1** in DMF (and other organic solvents, Table-2) its characterization by GPC turned out to be impossible.

TABLE-1
CHARACTERISTICS OF THE OBTAINED CLICK PE-2 AND *co*-PEs

Polymer	M_w (g mol^{-1})	M_n (g mol^{-1})	Đ	DP
PE-2	11,500	7,200	1.57	34
co-PE (M1)$_{0.3}$-(M2)$_{0.7}$	14,600	6,300	2.29	33
co-PE (M1)$_{0.5}$-(M2)$_{0.5}$	15,000	6,800	2.22	39
co-PE (M1)$_{0.7}$-(M2)$_{0.3}$	21,500	8,500	2.50	53

Đ - Dispersity (M_w/M_n); DP - Degree of polymerization.

According to the results, the average molecular weight of the novel click polymers is in the range of 11,500-21,500 g mol^{-1} and their molecular weight distribution is relatively wide (Đ = 1.57-2.50). The degree of polymerization (DP = 33-53) of the polymers is also quite satisfactory for step-growth polymers. To investigate film-forming abilities of the new click polymers, the thin films were cast from hexafluoroisopropanol (HFIP) solutions on polytetrafluoroethylene dishes, the solvent was allowed to evaporate and the films were finally dried in a vacuum at room temperature to a constant weight. All the obtained polymers showed an elastic film-forming properties (except **PE-1**, Table-2).

TABLE-2
SOLUBILITY OF THE CLICK PEs AND *co*-PEs (10 mg OF POLYMER IN 1 mL SOLVENT)

Polymer	DMSO	NMP	DMF	DMA	HFIP	DCM	Acetone	Water
PE-1	–	–	–	–	–	–	–	–
PE-2	+	+	+	+	+	+	+	–
co-PE $(M1)_{0.3}$-$(M2)_{0.7}$	+	+	+	+	+	+t	+	–
co-PE $(M1)_{0.5}$-$(M2)_{0.5}$	+	+	+	+	+	-	+	–
co-PE $(M1)_{0.7}$-$(M2)_{0.3}$	+	+	+	+	+	–	–	–

+ = Soluble at room temperature; +t = Soluble upon heating; – = Insoluble

Spectral studies: The structure of novel click PEs and *co*-PEs were studied using the FT-IR and NMR spectroscopy. The FT-IR study proved the presence of all key functional moieties of the synthesized polymers at 3150-3141 cm^{-1} correspond to C=C–H of the 1,2,3-triazole ring; 2958-2855 cm^{-1} is attributed to methylene moieties; 1752-1748 cm^{-1} is due to the presence of ester C=O and a peak at 1213-1200 cm^{-1} is due to the C-O-C moiety. A strong regioselectivity of Cu(I) catalyzed AB-type click SGP is supported by extensive ^{1}H NMR study of the sample **PE-2**. In brief, a signal of 1,2,3-triazole proton (C=C–H) at δ 8.16 ppm in the ^{1}H NMR spectrum and a single signal of C5 carbon at δ 125.06 ppm in the ^{13}C NMR spectrum confirmed the presence of exclusively 1,4-disubstituted 1,2,3-triazole rings in the backbone. Furthermore, the ^{1}H NMR spectroscopy was also used to study the detailed structure of the obtained *co*-PEs. The ratio of monomer residues in the co-polymers calculated according to ^{1}H NMR analysis well coincided with the feed ratio (Table-3). This results underline the suitability of the reported one pot/two step synthetic strategy for designing click co-polymers with tunable composition.

TABLE-3
FEED RATIO OF MONOMER RESIDUES IN *co*-PEs *vs.* CALCULATED RATIO ACCORDING TO ^{1}H NMR ANALYSIS

Co-Polymer	Feed ratio	Calculated ratio
co-PE $(M1)_{0.3}$-$(M2)_{0.7}$	$(M1)_{0.30}$-$(M2)_{0.70}$	$(M1)_{0.31}$-$(M2)_{0.69}$
co-PE $(M1)_{0.5}$-$(M2)_{0.5}$	$(M1)_{0.50}$-$(M2)_{0.50}$	$(M1)_{0.52}$-$(M2)_{0.48}$
co-PE $(M1)_{0.7}$-$(M2)_{0.3}$	$(M1)_{0.70}$-$(M2)_{0.30}$	$(M1)_{0.71}$-$(M2)_{0.29}$

Solubility studies: The solubility of the synthesized new click PEs and *co*-PEs in common organic solvents and water (10.0 mg in 1.0 mL) is presented in Table-2. All the polymers were insoluble in water. The **PE-1** was insoluble in all the tested organic solvents presumably owing to the absence lateral substituents (polymer contains only two methylene fragments per monomeric unit) along with the presence of rigid 1,2,3-triazlole rings, which stipulate strong intermolecular forces and a high rigidity of the polymer backbone.

The best solubility was demonstrated by **PE-2**, which readily dissolved at room temperature in all the tested common organic solvents. Apparently, the presence of lateral pentyl groups in the elemental unit significantly weakens intermolecular forces and increases flexibility of the macromolecules thereby alleviating the solubility of polymer. Expectedly, an increase of the lateral pentyl groups content in the *co*-PEs improves their solubility in organic solvents. The co-polymer *co*-PE $(M1)_{0.3}$-$(M2)_{0.7}$ containing 70 mol.% of monomer **2** revealed better solubility as compared to *co*-PEs $(M1)_{0.5}$-$(M2)_{0.5}$ and $(M1)_{0.7}$-$(M2)_{0.3}$, which were insoluble in both DCM and acetone even upon heating (Table-2). The results proved that the solubility behaviour of the *co*-PEs can be tuned by simple adjustment of ratio of the monomeric residues in the polymer architecture.

Degradation studies: The total organic carbon (TOC) method was exploited to investigate *in vitro* hydrolytic degradation of the new click polymers. The study was performed on the example of co-polymer *co*-PE $(M1)_{0.5}$-$(M2)_{0.5}$. The thin film of the selected sample was immersed into phosphate-buffered saline (PBS, pH = 7.4) and kept at room temperature for four weeks. The aliquots from the buffer were examined weekly for TOC content. The results of the experiments are displayed in Fig. 1 as TOC value (mg mL^{-1}) upon hydrolytic degradation *vs*. exposure time in PBS. Overall, the TOC concentration in buffer was steadily increasing over the observed period. At the end of first week, the TOC value was approximately 1.56 mg mL^{-1} indicating that approx. 6% of the TOC of polymer was released as a result of hydrolytic degradation (in case of complete degradation of the sample the TOC value would be 25.7 mg mL^{-1}). According to the obtained data, around 19% of the TOC of sample was released in four weeks of polymer degradation (the approximate TOC value was 4.91 mg mL^{-1}). The results demonstrate that the click polymer was indeed degraded by chemical hydrolysis. So, the experiments prove that the incorporation of rigid 1,2,3-triazole rings into polymer backbone does not suppress the hydrolytic degradation of the click polyesters and thus the polymer retain the anticipated degradability.

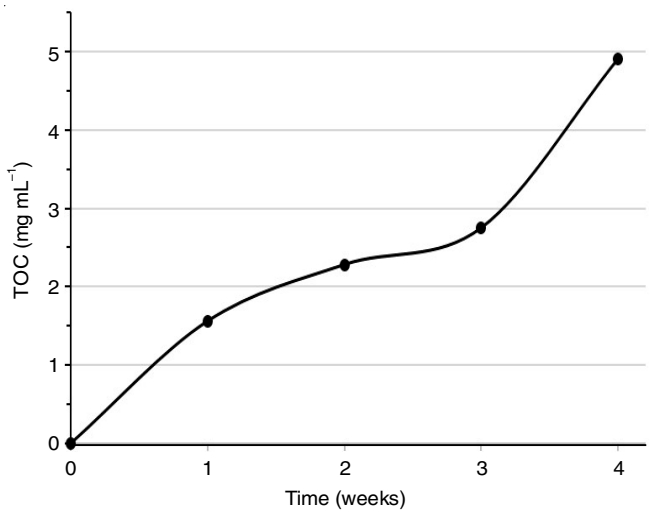


Fig. 3. TOC values *versus* exposure time to hydrolytic degradation in PBS at room temperature for co-polymer [*co*-PE $(M1)_{0.5}$-$(M2)_{0.5}$]

Conclusion

Two new aliphatic AB-type polyesters (PEs) and three co-polyesters (*co*-PEs) bearing 1,4-disubstituted 1,2,3-triazole rings in the main chain were successfully synthesized *via* Cu(I)-catalyzed click step-growth polymerization (SGP) using hetero-bifunctional monomers according to one pot two step synthetic strategy. The structure of the synthesized click polymers was confirmed by FT-IR and NMR analysis. According to GPC, the obtained PEs and *co*-PEs had average molecular weights (M_w) within 11,500-21,500 g mol^{-1}. These MWs correspond to rather high degree of polymerization (DP = 33-53), which is quite enough to give elastic films. The obtained polyesters are also prone to hydrolytic degradability that was proved by measuring total organic carbon (TOC) concentration obtained after the hydrolysis of co-polyester $(M1)_{0.5}$-$(M2)_{0.5}$ in PBS at room temperature.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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