Synthesis and characterization of ring-type and branched polymers including polyethylene glycols by “click” chemistry

Temel Öztürk¹ · Ergül Meyvacı¹ · Hakan Bektaş¹ · Emre Menteşe²

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Abstract

Synthesis of ring-type (or branched) polymers including polyethylene glycols was archived via “click” chemistry of 5,6-diazido-2-benzyl-1*H*-benzimidazole (Di-N₃) [or triazidoacetohydrazide derivative (Tri-N₃)] and terminally dipropargyl polyethylene glycols (PEG-dipropargyl) with different molecular weights. Di-N₃ was obtained by reaction of 5,6-dichloro-2-benzyl-1*H*-benzimidazole (Di-Cl) and sodium azide. 2-(2-benzyl-5,6-dichloro-1*H*-benzimidazol-1-yl)-*N*'-(4-chlorobenzylidene)acetohydrazide (Tri-Cl) was synthesized by using Di-Cl. Synthesis of Tri-N₃ was archived by means of reaction of Tri-Cl and sodium azide. PEG-dipropargyl was synthesized by using reaction of PEGs with different molecular weights and propargyl chloride. By using Di-N₃ (or Tri-N₃) and PEG-dipropargyl, ring-type (or branched) polymers including polyethylene glycols were synthesized. The polymers were relatively acquired in high yields and low dispersities. The primary parameters for example concentration and time were assessed. The characterization of products was accomplished by using multi instruments such as ¹H-NMR, FT-IR, GPC, TGA, DSC, and elemental analysis techniques. The multi instruments studies of the obtained polymers show that the ring-type and branched polymers easily formed as a result of “click” chemistry.

Keywords “Click” chemistry · Ring-type polymers · Branched polymers · Polyethylene glycol · Benzimidazole

1 Introduction

Sharpless et al. [1] were introduced “click” chemistry technique in literature. “Click” chemistry applications have been available until now [2–15]. Macromolecules are used in technological applications and theoretical studies [16–21]. Polymers based on polyethylene glycol (PEG) are attractive materials for biomedical, industrial, and chemicals applications, as PEG has unparalleled characters such as superior ion absorbability, flexibility, hydrophilicity, and biocompatibility [22–31]. PEG units are helpful for hydrophobic polymers to gain hydrophilicity [32–34]. Benzimidazoles are an important group of heterocyclic compounds in various areas of chemistry and are important intermediates in organic reactions [35, 36]. They are contained in agrochemicals,

dyestuffs, and high-temperature polymer products, and they have interesting biological and pharmaceutical activities [36–40]. Also, some drugs containing benzimidazole nucleus such as albendazole, fenbendazole, oxfenbendazole and thiabendazole, mebendazole are in medical use [41, 42]. Besides, benzimidazole derivatives can also act as ligands to transition metals for modeling biological systems [43, 44]. Recently, some metallophthalocyanines (Zn, Ni, Co, and Cu) containing benzimidazole ring have been reported with their antibacterial activity [45].

This paper demonstrates synthesis of ring-type and branched polymers including polyethylene glycols using “click” chemistry. In our previous works, we synthesized terminally dipropargyl polyethylene glycol (PEG-dipropargyl) [12],

✉ Temel Öztürk, temel.ozturk@giresun.edu.tr | ¹Department of Chemistry, Giresun University, 28200 Giresun, Turkey. ²Department of Chemistry, Recep Tayyip Erdoğan University, 53100 Rize, Turkey.

Scheme 1 Reaction pathways in the synthesis of Di-N₃

5,6-dichloro-2-benzyl-1*H*-benzimidazole (Di-Cl) [46, 47]. In this study, firstly, 2-(2-benzyl-5,6-dichloro-1*H*-benzimidazol-1-yl)-*N*'-(4-chlorobenzylidene)acetohydrazide (Tri-Cl) was obtained by using Di-Cl. 5,6-Diazido-2-benzyl-1*H*-benzimidazole (Di-N₃) was synthesized by chemical reaction of Di-Cl with NaN₃. In the same way, triazidoacetohydrazide derivative (Tri-N₃) was obtained by chemical interaction of Tri-Cl and with NaN₃. Lastly, PEG-dipropargyl and Di-N₃ (or Tri-N₃) were used to obtain the ring-type (or branched) polymers by “click” chemistry. Product characterization is fulfilled in detail.

2 Experimental

2.1 Materials

N,N-dimethylformamide (DMF), copper(I) bromide (CuBr), NaN₃, *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), aluminum oxide, and chloroform were supplied by Sigma-Aldrich. Diethyl ether was bought from Carlo Erba Reagent. 4,5-Dichloro-*o*-phenylenediamine, benzylcyanide and other chemicals were supplied from Merck (Darmstadt, Germany), Aldrich and Fluka (Buchs SG, Switzerland).

Scheme 2 Reaction pathways in the synthesis of Tri-Cl

Table 1 Synthesis of ring-type polymers including polyethylene glycols by “click” chemistry

Code	Di-N ₃ (10 ³ mol)	PEG-dipropargyl (10 ³ mol)	CuBr (10 ³ mol)	PMDETA (10 ³ mol)	CHCl ₃ (mL)	Time (h)	Yield (g)	Conversion (wt%)	Mw, GPC (g·mol ⁻¹)	Mw/Mn
EH-2	0.45	1.26 (synthesized using PEG with 1000 Da)	1.26	1.44	30	142	1.13	81.56	1200	1.23
EH-3	0.55	0.85 (synthesized using PEG with 1500 Da)	0.84	0.82	30	142	1.27	88.33	1781	1.23
EH-4	0.72	0.11 (synthesized using PEG with 3000 Da)	0.07	0.01	40	24	0.15	28.24	3115	1.36
EH-5	0.59	15.0 (synthesized using PEG with 400 Da)	0.14	1.44	40	24	0.25	32.17	–	–
EH-6	0.69	0.07 (synthesized using PEG with 1000 Da)	0.07	0.62	40	168	0.53	62.31	1276	1.16

Reaction temperature: 35 °C

2.2 Instrumentation

Mn, Mw, and dispersities were examined with HPLC/GPC-Shimadzu RID-10A GPC instrument with tetrahydrofuran mobile phase as the solvent 40 °C using refractive index detector (RID-10A). A calibration curve was generated with polystyrene standards: 1490 Da (Mw), 2500 Da (Mw), 5480 Da (Mw), 9500 Da (Mw), 20,800 Da (Mw), and 53,500 Da (Mw) of low polydispersity. NMR spectra were detected using Bruker Ultra Shield Plus, ultra-long hold time 400 NMR spectrometers. FT-IR spectra were detected using Jasco FT/IR 6600 FT-IR. TGA measurements were conducted using a Seiko II Exstar 6000 model instrument. The sample was heated at a rate of 10 °C/min from 25 °C to 900 °C under N₂. DSC measurements were conducted using a Hitachi DSC 7000 series thermal analysis system. Dried sample was heated at a rate of 10 °C/min from – 80 to 150 °C under N₂. The elemental analyses of the products were performed by a Costech ECS 4010. PEG-dipropargyl [12] and Di-Cl [47] were obtained by literatures.

2.3 Synthesis of 5,6-Diazo-2-benzyl-1H-benzimidazole (Di-N₃)

1.204 g (4.58 mmol) of Di-Cl, 2.925 g (44.98 mmol) of NaN₃, and 40 mL of DMF (as solvent) were put inside a 100 mL flask ([Cl]/[N₃] = 1/5, mol/mol). The flask was dip in an oil bath fixed at 70 °C on hot plate. The reaction was performed under N₂. After a fixed time, the contents were filtered. DMF was evaporated. The residue was drained into excess diethyl ether to separate Di-N₃. Di-N₃ was dried at 25 °C for 48 h in vacuum oven. Di-N₃ yield was determined gravimetrically. Scheme 1 includes the reaction pathway for the synthesis of Di-N₃.

2.4 Synthesis of 2-(2-Benzyl-5,6-dichloro-1H-benzimidazol-1-yl)-N'-(4-chlorobenzylidene)acetohydrazide (Tri-Cl)

A mixture of compound Di-Cl (0.010 mol), ethylbromoacetate (0.010 mol) and K₂CO₃ (0.025 mol) in acetone (25 mL) was stirred for 10 h at room temperature. After the completion of the reaction (monitored by TLC), the mixture was poured into water. The precipitate was collected by filtration and recrystallized from acetone–water (1:2) to give pure compound 1 in Scheme 2. To a solution of compound 1 (0.010 mol) in ethanol (20 mL), hydrazine monohydrate (0.025 mol) was added and was refluxed for 7 h. Then, the mixture was cooled to room temperature. The precipitate was filtered off and washed with ethanol to give pure compound 2 in Scheme 2. 4-Chlorobenzaldehyde (0.01 mol) was added to the solution of

Table 2 Synthesis of branched polymers including polyethylene glycols by “click” chemistry

Code	Tri-N ₃ (10 ³ mol)	PEG-dipropargyl (10 ³ mol)	PMDTA (10 ³ mol)	Yield (g)	Conversion (wt%)	Mw, GPC (g·mol ⁻¹)	Mw/Mn
HAT-1	0.59	2.53 (synthesized using PEG with 400 Da)	1.92	0.66	50.34	–	–
HAT-2	0.51	1.98 (synthesized using PEG with 600 Da)	1.44	0.59	40.71	–	–
HAT-3	0.53	1.01 (synthesized using PEG with 1000 Da)	1.92	0.95	74.71	1036	1.32
HAT-4	0.49	0.63 (synthesized using PEG with 1500 Da)	1.92	0.93	77.86	1942	1.11
HAT-5	0.49	0.80 (synthesized using PEG with 2000 Da)	1.92	0.99	53.46	2194	1.18
HAT-6	0.51	0.55 (synthesized using PEG with 3000 Da)	1.92	1.13	59.25	3145	1.26

Reaction temperature: 35 °C, CHCl₃ = 8 mL, CuBr = 0.07 × 10⁻³ mol, reaction time: 93 h

compound **2** (0.01 mol) in ethanol (20 mL) containing 0.5 mL of acetic acid and the mixture was refluxed for 7 h. After cooling the mixture to room temperature, a white solid appeared. This crude product was filtrated, dried and recrystallized from ethanol to obtain the pure product Tri-Cl.

2.5 Synthesis of triazidoacetohydrazide derivative (Tri-N₃)

1.352 g (3.23 mmol) of Tri-Cl, 3.150 g (48.46 mmol) of NaN₃, and 40 mL of DMF were put inside a 50 mL flask ([Cl]/[N₃] = 1/5, mol/mol). The flask was dip in an oil bath fixed at 70 °C on hot plate. The reaction was performed under N₂. After 8 h, the contents were filtered. DMF was evaporated. The residue was drained into excess diethyl ether to separate Tri-N₃. Tri-N₃ was dried at 25 °C for 48 h in vacuum oven. Tri-N₃ yield was determined gravimetrically.

2.6 Synthesis of ring-type and branched polymers including polyethylene glycols via “click” chemistry

The amounts of chemicals used in the polymerization are shown in Tables 1 and 2. Specified amounts of PEG-dipropargyl, Di-N₃, CuBr, PMDETA, and chloroform were put separately into a 250 mL flask followed by injecting N₂ for 2 min. The flask was put on a magnetic stirrer at 35 °C. After specific times, the flask contents were filtered. The mixture was drained into diethyl ether to separate precipitated ring-type polymers including polyethylene glycols. Small alumina column was used to remove remaining CuBr catalyst from copolymer. The polymer was dried at 25 °C for 48 h in vacuum oven. The same procedure was fulfilled by using Tri-N₃ instead of Di-N₃ to synthesize the branched polymers. The polymer yield was detected gravimetrically.

3 Results and discussion

3.1 Synthesis of Di-N₃

Di-N₃ was synthesized starting from Di-Cl. The conversion was 74.10 wt%. The results of elemental analysis of Di-N₃ show 42.69 wt% C, 2.83 wt% H, and 24.74 wt% N. The results of elemental analysis agreed with the theoretical values. The ¹H-NMR spectrum of Di-N₃ shown in Fig. 1a displayed peaks at 12.6 ppm for aromatic –NH, 7.8 ppm and 7.3 ppm for aromatic –CH, 4.2 ppm for –CH₂ linked aromatic groups. The FT-IR spectrum of Di-N₃ shown in Fig. 2a indicates signals at 3100 cm⁻¹ for –NH, 2770 cm⁻¹ for aliphatic –CH₂, 2352 cm⁻¹ for –CN, 2109 cm⁻¹ for –N₃. The observed peak at 2109 cm⁻¹ for –N₃ in the FT-IR spectrum of Di-N₃ was further evidence that Di-N₃ was obtained.

3.2 Synthesis of Tri-Cl

Tri-Cl was synthesized starting from Di-Cl. Scheme 2 includes the reaction outline for the synthesis of Tri-Cl. The conversion was 85.13 wt%. The ¹H-NM spectrum of Tri-Cl shown in Fig. 1b displayed at 11.8 ppm for –NH, 8.2 ppm and 8.0 ppm for –N=CH, 7.9–7.3 ppm for aromatic –CH, 5.5 ppm and 5.1 ppm for –CH₂C=O, 4.2 ppm for –CH₂ linked aromatic group. The FT-IR spectrum of Tri-Cl shown in Fig. 2b indicates signals at 3174 cm⁻¹ for –NH, 2954 cm⁻¹ for aliphatic –CH₂, 2352 cm⁻¹ for –CN, 1674 cm⁻¹ for –C=O.

3.3 Synthesis of Tri-N₃

Tri-N₃ was obtained from Tri-Cl. Scheme 3 includes the reaction pathway for the synthesis of Tri-N₃. The conversion was 88.42 wt%. The ¹H-NMR spectrum of Tri-N₃ displayed at 12.1 ppm for –NH, 8.2 ppm and 8.1 ppm for –N=CH, 8.0–7.2 ppm for aromatic –CH, 5.5 ppm and 5.1 ppm for –CH₂C=O, 4.3 ppm for –CH₂ linked aromatic group. The FT-IR spectrum of Tri-N₃ shown in Fig. 2c indicates signals at 3201 cm⁻¹ for –NH, 2900 cm⁻¹ for aliphatic

Fig. 1 ¹H-NMR spectrum of **a** Di-N₃; **b** Tri-Cl; **c** ring-type polymers including polyethylene glycol (EH-4 in Table 1)

–CH₂, 2352 cm^{−1} for –CN, 2102 cm^{−1} for –N₃, 1650 cm^{−1} for –C=O.

3.4 Synthesis of ring-type and branched polymers including polyethylene glycols via “click” chemistry

Ring-type polymers including polyethylene glycols were synthesized at 35 °C via the “click” chemistry of Di-N₃ and PEG-dipropargyl (Table 1). The syntheses were carried

out at 24, 142 and 168 h. The gravimetric conversion was between 28.24 and 88.33 wt%. The maximum yield of the polymer was acquired using PEG-dipropargyl synthesized using PEG with 1500 g coded EH-3. The minimum yield of the polymer was acquired using PEG-dipropargyl synthesized using PEG with 3000 g coded EH-4. Scheme 4 shows the reaction pathway for the ring-type polymer synthesis.

The ¹H-NMR spectrum of the ring-type polymers (EH-4 in Table 1) shown in Fig. 1c displayed peaks at 8.0 ppm for –NH, 7.7 ppm for aromatic –CH of triazole, 7.5 ppm for aromatic –CH, 3.5 ppm for –OCH₂ of PEG, 2.5 ppm for –CH₂ linked aromatic groups. The peak at 8.0 ppm for aromatic –CH proton of triazole was evidence that the ring-type polymer was synthesized. The FT-IR spectrum of the ring-type polymers (EH-4 in Table 1) shown in Fig. 2d indicates signals at 3394 cm^{−1} for –NH, 2873 cm^{−1} for aliphatic –CH₂, 2352 cm^{−1} for –CN, 1662 cm^{−1} and 1457 cm^{−1} for triazole units, 1099 cm^{−1} for –OC. The peaks at 1662 cm^{−1} and 1457 cm^{−1} for triazole units was evidence that the ring-type polymers was obtained. Figure 3 indicates the GPC curves of the polymers (EH-2 in Table 1, EH-3 in Table 1, EH-4 in Table 1, EH-6 in Table 1). Mw values of the polymers were between 1200 and 3115 g·mol^{−1}. Dispersity values of the polymers are between 1.16 and 1.36. Dispersity values of the polymers were relatively narrow as requested. Increases in the molecular weights of the polymers as compared with these of reactants is consistent with the formation of the polymer.

Thermal analysis of the polymers was carried out by DSC and TGA curves. The ring-type polymers has one main individual Td (Fig. 4). TGA has showed interesting properties of the ring-type polymers indicating continuous weight loss starting from 280 °C to nearly 390 °C with a derivative at 355 °C (Fig. 4a). Tg value of the ring-type polymer (EH-6 in Table 1) was 13 °C. Tg values were reported in the literature for homo PEG as −60 °C [48].

The branched polymers including polyethylene glycols were synthesized at 35 °C via the “click” chemistry of Tri-N₃ and PEG-dipropargyl (Table 2). Scheme 5 shows possible chemical structure of the branched polymer synthesis. The ¹H-NMR spectrum of the branched polymers (HAT-1 in Table 2) shown in Fig. 5 displayed peaks at 7.9 ppm for –NH, 7.3 ppm for aromatic –CH of triazole, 4.7 ppm for –N=CH, 4.0 ppm for –NCH₂, 3.5 ppm for –OCH₂ of PEG unit, 1.3 ppm aliphatic –CH₂. The syntheses were carried out at 93 h. The gravimetric conversion was between 40.71 and 77.86 wt%. The maximum yield of the polymer was acquired using PEG-dipropargyl synthesized using PEG with 1500 g coded HAT-4. The minimum yield of the polymer was acquired using PEG-dipropargyl synthesized using PEG with 600 g coded HAT-2. Mw values of the polymers were between 1036 and 3145 g·mol^{−1}. Dispersity values of the polymers are between 1.11 and 1.32. The

Fig. 2 FT-IR spectrum of **a** Di- N_3 ; **b** Tri-Cl; **c** Tri- N_3 ; **d** ring-type polymers including polyethylene glycol (EH-4 in Table 1)

Scheme 3 Reaction pathways in the synthesis of Tri- N_3

Scheme 4 Reaction outline for synthesis of ring-type polymers including polyethylene glycols

Fig. 3 GPC curves of the ring-type polymers: **a** EH-2 in Table 1; **b** EH-3 in Table 1; **c** EH-4 in Table 1; **d** EH-6 in Table 1

Fig. 4 TGA curves of the polymers: **a** EH-2 in Table 1; **b** EH-3 in Table 1; **c** EH-4 in Table 1; **d** HAT-5 in Table 2

branched polymers have one main individual T_d (Fig. 4d). TGA has showed interesting properties of the branched polymers indicating continuous weight loss starting from 300°C to nearly 400°C with a derivative at 363°C (Fig. 4d).

One main individual T_d of the polymers can be attributed to the high miscibility of the polymerizable propargyl groups of PEG-dipropargyl with moieties of Di-N_3 and Tri-N_3 .

Scheme 5 Chemical structure of the branched polymer including polyethylene glycols

Fig. 5 ^1H -NMR spectrum of the branched polymers including polyethylene glycol (HAT-1 in Table 2)

4 Conclusions

The “click” chemistry synthesis of ring-type and branched polymers including polyethylene glycols was acquired. The polymers were obtained in high yield and low dispersities. This method for synthesis of polymer including benzimidazole ring is simple and efficient. Products characterization was done using multi instruments. This study can provide new, well-characterized materials with wide biomedical application potential through the polymers including PEG and benzimidazole rings.

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Compliance with ethical standards

Conflict of interest The authors declare that they no competing interests.

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