

# Synthesis of Polymers Including Both Triazole and Tetrazole by Click Reaction

Jung-Ah Shin, Yeong-Gweon Lim,\* and Kyung-Hee Lee

5-4-5, Agency for Defense Development, Yuseong P.O. Box 35-5, Daejeon 305-600, Korea

\*E-mail: lim\_yg@yahoo.co.kr

Received May 4, 2010, Accepted December 6, 2010

Azido contained polymers were treated with various substituted N-propargyl tetrazoles in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O at room temperature by Cu-catalyzed [2+3] cycloaddition to afford high yields of the corresponding polymers, possessing both triazole and tetrazole moiety.

**Key Words:** Triazole, Tetrazole, Polymer, Cu-catalyst, Click reaction

## Introduction

The functionalization of polymers is one of the important fields in polymer chemistry. In several methods, the grafting using click chemistry is very useful way to make the original polymer more valuable materials.<sup>1</sup>

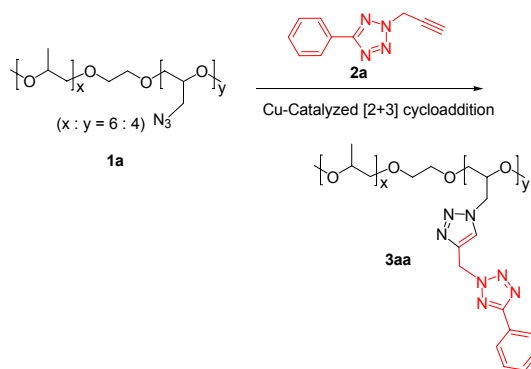
In the course of studies in energetic materials, we needed a new type of an energetic polymer instead of GAP (glycidyl azido polymer) as a binder in propellant formulation. With this point of view, we recently reported energetic polymers containing triazole groups prepared by click reaction from GAP with several alkyne compounds.<sup>2</sup>

Triazole and tetrazole compounds have received wide attention by many chemists as energetic materials,<sup>3</sup> pharmaceutical and material sciences.<sup>4</sup> Especially, these compounds are high energetic and high nitrogen contained materials. The heat of formation ( $\Delta_f H^\circ$ ) of 1,2,4-triazole is +109.0 KJ/mol, those of 1*H*-1,2,3-triazole and tetrazole are +272 KJ/mol and +237.2 KJ/mol, respectively.<sup>5</sup>

Recently, the demand of low vulnerable and eco-friendly energetic materials is on the increase greatly. Introduction of energetic materials into polymers makes it more insensitive. Polymeric energetic materials such as GAPs are much safer than molecular organic azido compounds.

Polymers containing triazole or tetrazole, respectively are well known as energetic materials.<sup>6</sup> While polymers containing triazoles made by click reaction are found easily, polymers containing tetrazole groups such as polyvinyltetrazole are very rare and begin to grab the attention as energetic polymers, recently.<sup>7</sup> However, they have limitation for application to energetic binder due to their low solubility in organic solvent. To improve their solubility, many efforts are in progress. Moreover, polymers containing both triazole and tetrazole are not published to date to the best of our knowledge. The non-polymeric compounds containing both triazole and tetrazole are also very rare.<sup>8</sup> Besides, their yields were moderate under simple reflux conditions in toluene.

Herein, we report syntheses of new polymers containing both triazole and tetrazole moiety using click-reaction for the first time. These polymers are expected to be good candidates for green and high energetic materials.



**Scheme 1.** Cu-catalyzed [2+3] cycloaddition of polymer **1a** with alkyne **2a**

## Results and Discussion

According to the synthetic approach described in Scheme 1, we studied that copolymer **3aa** having triazole and tetrazole group could be easily obtained at room temperature by Cu-catalyzed [2+3] cycloaddition from GAP-propylene oxide copolymer **1a**<sup>9</sup> with propargyl tetrazole **2a**.

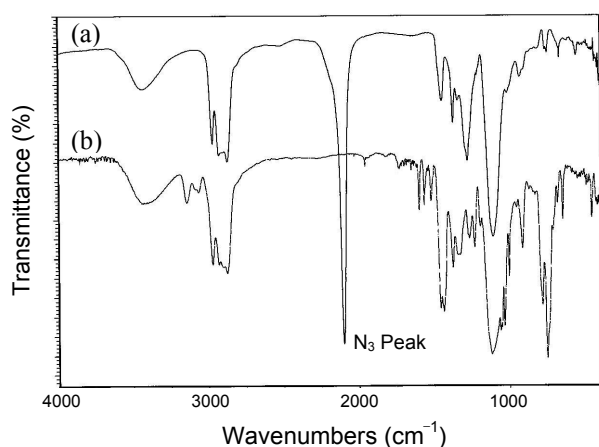
First of all, to find optimum solvent condition, various co-solvent systems<sup>10</sup> were applied as shown Table 1.

Tracking of this reaction was verified by FT-IR spectroscopy (Fig. 1). For all GAP polymers, a strong absorption is observed at 2100 cm<sup>-1</sup> due to asymmetric N<sub>3</sub> stretching vibration (Fig.

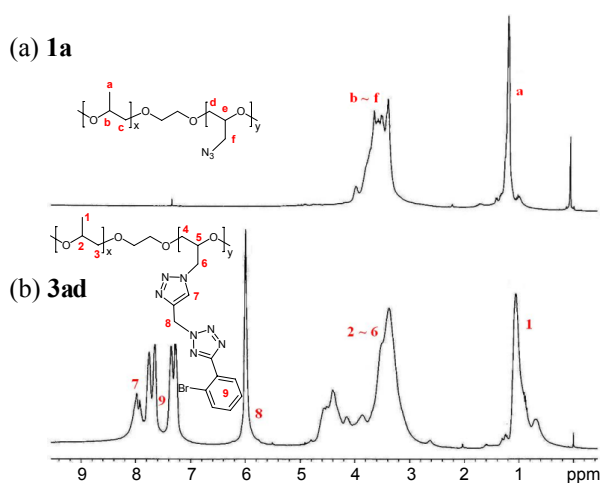
**Table 1.** Conversion of **1a** into **3aa**, having both triazole and tetrazole group, in the presence of **2a** (1.2 equiv.), sodium ascorbate (0.15 equiv.) and copper sulfate (0.05 equiv.) in various solvent systems

Entry	Solvent	Conversion (%) <sup>d</sup>
1 <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub> : H <sub>2</sub> O = 1 : 1	100
2 <sup>b</sup>	THF : H <sub>2</sub> O = 1 : 1	100
3 <sup>c</sup>	<sup>t</sup> BuOH : H <sub>2</sub> O = 1 : 1	97
4 <sup>d</sup>	DMSO : H <sub>2</sub> O = 1 : 1	88

<sup>a</sup>Conversion was based on IR spectroscopy. <sup>b</sup>The reaction was totally completed in 4.5 h. <sup>c</sup>The reaction was completed after 8.5 h. <sup>d</sup>After 20 h, conversion was 97%.



**Figure 1.** FT-IR spectra: (a) GAP-Propylene oxide copolymer **1a**, (b) Glycidyl tetrazolyl triazole copolymer **3ad**.



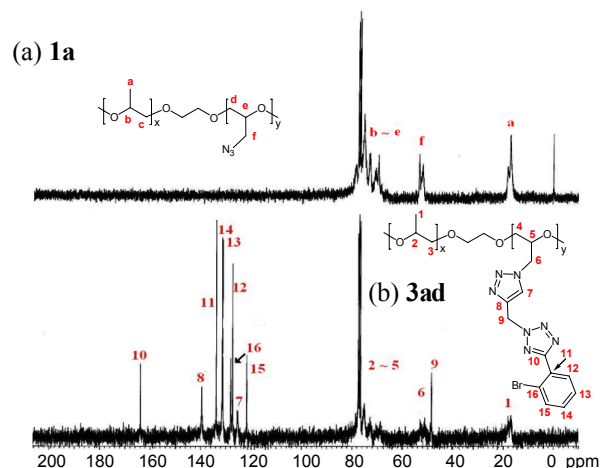
**Figure 2.** <sup>1</sup>H-NMR spectra: (a) GAP-Propylene oxide copolymer **1a**, (b) Glycidyl tetrazolyl triazole copolymer **3ad**.

1(a)). This peak becomes weaker and finally disappears with increasing reaction time, indicating the change azido group into triazole group (Fig. 1(b)).

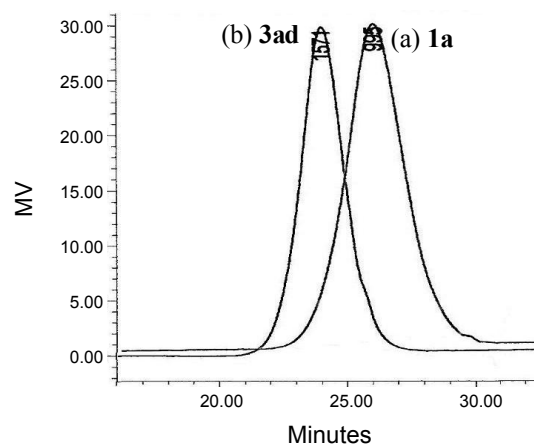
As depicted in Table 1, when it was run in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O or THF/H<sub>2</sub>O, the reaction was completed in 4.5 h (Entries 1-2). However, when the same reaction was also performed in *tert*-BuOH/H<sub>2</sub>O, one of the most popular solvent systems used for click reaction, conversion yield was 97% and further stirring for 4 h should be required until completion to copolymer **3aa** (Entry 3). In the case of DMSO/H<sub>2</sub>O co-solvent system, desired product **3aa** was just obtained 88% and the reaction was not completed until next day, because of low solubility of polymer **1a** in this system (Entry 4). Thus, of these solvent systems, we chose CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O as the best solvent for facility of workup.

Using this optimum solvent condition, Cu-catalyzed reactions were carried out in the presence of CuSO<sub>4</sub>·5H<sub>2</sub>O (5 mol %) and sodium ascorbate (15 mol %) in a 1:1 mixture of H<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> at room temperature to generate the desired compounds (**3aa-3af**) having triazole and tetrazole moiety as described in Table 2.

We explored click reaction of GAP-propylene oxide copoly-



**Figure 3.** <sup>13</sup>C-NMR spectra: (a) GAP-Propylene oxide copolymer **1a**, (b) Glycidyl tetrazolyl triazole copolymer **3ad**.

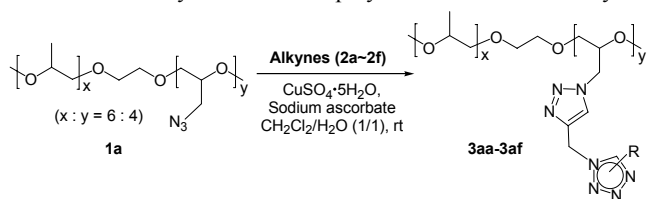


**Figure 4.** GPC spectra: (a) GAP-Propylene oxide copolymer **1a** ( $M_n = 851$ , PDI = 1.30), (b) Glycidyl tetrazolyl triazole copolymer **3ad** ( $M_n = 1412$ , PDI = 1.17).

mer **1a** with various propargyl tetrazoles (**2a-2f**). For these reactions, substituted *N*-propargyl tetrazoles (**2a-2f**) were prepared by treatment of substituted 1*H*-tetrazoles with propargyl bromide, and triethylamine in acetone<sup>11</sup> (or DMF<sup>12</sup>). The reactions gave a mixture of isomeric propargyl tetrazoles, 1,5-isomer and 2,5-isomer. The isomers could be separated successfully by column chromatography on silica gel.

All reactions proceeded to completion in less than 5.5 h, afforded new polymers containing both triazole and tetrazole group with excellent isolated yields.

Interestingly, some specific features were observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of all products (Figures 2 and 3). In <sup>1</sup>H NMR, in going from GAP polymer to the corresponding adducts, the proton signal of triazole ring appears at 7.7 - 8.1 ppm. Also, the chemical shifts of protons in the bridging methylene group between triazole and tetrazole are located at 5.6 - 5.9 ppm. In <sup>13</sup>C NMR, the signals of carbon atom of tetrazoles were observed in downfield extremely. While chemical shifts of products obtained from 2,5-isomer alkynes are found at 162 - 167 ppm, in the cases of 1,5-isomer alkynes are observed at 152 -

**Table 2.** Cu-Catalyzed reaction of polymer **1a** with various alkynes<sup>a</sup>

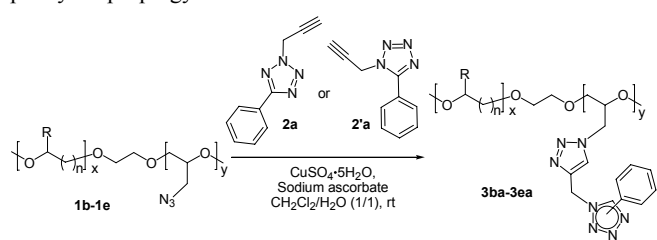
Entry	Alkyne	Product	Time (h)	Isolated yield (%)	M <sub>n</sub> (PDI)
1		<b>3aa</b>	4.5	96	1338 (1.18)
2		<b>3aa'</b>	5.5	88	1311 (1.18)
3		<b>3ab</b>	4.2	94	1318 (1.19)
4		<b>3ac</b>	2.8	91	1513 (1.18)
5		<b>3ad</b>	4.0	89	1412 (1.17)
6		<b>3ad'</b>	5.5	89	1392 (1.11)
7		<b>3ae</b>	4.5	93	1180 (1.21)
8		<b>3af</b>	4.3	90	1610 (1.33)

<sup>a</sup>Reactions of polymer **1a** (M<sub>n</sub> = 851, PDI = 1.30) with alkynes (1.2 equiv.), copper sulfate pentahydrate (0.05 equiv.) and sodium ascorbate (0.15 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O at room temperature gave compounds **3aa-3af**.

154 ppm. Besides, clearly carbon atom signals of 4- and 5-position of 1,2,3-triazoles are observed at 139 - 141 ppm for 4-position and 115 - 125 ppm for 5-position, respectively.

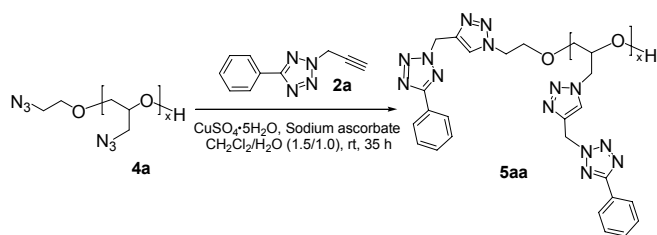
The number-average molecular weight (M<sub>n</sub>) of polymer **1a** changes from 851 to 1412 for being product **3ad** as time goes by without any degradation (Figure 4).

As described in Table 2, functional groups such as F, Br and EtO<sub>2</sub>C- are tolerated under reaction conditions (Entries 3-6). In this reaction, substrates **2b** (CH<sub>3</sub>), **2c** (F), **2d** (Br) reacted similarly to provide the corresponding adducts implying little effect of electronic substitution on benzotriazole (Entries 4-6, 8). As expected, the reaction rate of 1,5-isomer was slower than that of 2,5-isomer due to steric hinderance (Entries 1 and 2, 5 and 6). In addition to aromatic substitution on tetrazoles, alkyl substituted tetrazoles such as **2e** and **2f** worked well under the same reaction conditions (Entries 7-8).

**Table 3.** The [2+3] cycloaddition of several GAP polymers<sup>a</sup> with phenyl N-propargyl tetrazole

Entry	Polymer	Alkyne	Product	Time (h)	Isolated yield (%)	M <sub>n</sub> (PDI)
1		<b>2a</b>	<b>3ba</b>	10.7	95	1633 (1.14)
2	<b>1b</b>	<b>2'a</b>	<b>3ba'</b>	12.5	91	1580 (1.14)
3		<b>2a</b>	<b>3ca</b>	1.7	89	1410 (1.15)
4		<b>2a</b>	<b>3da</b>	5.5	87	1866 (1.28)
5		<b>2a</b>	<b>3ea</b>	12.3	92	1890 (1.14)

<sup>a</sup>M<sub>n</sub> (PDI) values - **1b**: 1012 (1.23), **1c**: 923 (1.13), **1d**: 1425 (1.23), **1e**: 1101 (1.14).

**Scheme 2.** The reaction of GAP polymer **4a** with alkyne **2a**

Next, we chose several polymers possessing a wide range of azido groups (**1b-1e**) to demonstrate the scope and the generality of Cu-catalyzed reaction for corresponding adducts (**3ba-3ea**) and the results are summarized in Table 3. As expected, all polymers used worked well under optimized conditions to give corresponding products in high yields.

Finally, we applied this reaction to a GAP polymer (**4a**<sup>9</sup>). Polymer **4a** reacted with **2a** under the reaction conditions above mentioned. The reaction proceeded slowly due to low solubility in CH<sub>2</sub>Cl<sub>2</sub> (50 h, 98% conversion). So, increased amount of CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O, 1.5/1.0) was used for the solvent system, the reaction was completed in 35 h as shown in Scheme 2.

Fortunately, unlike polyvinyltetrazoles, product **5aa** having triazole and tetrazole group at all units in polymer has good solubility in organic solvents.

## Conclusion

For the first time, we found that polymers containing azido groups converted easily to glycidyl tetrazolyl triazole polymers by the click chemistry. These polymers were obtained from various propargyl tetrazoles in good to high isolated yields. These polymers have good solubility in organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and THF. We believe that these polymers are good candidates for high energetic materials, pharmaceutical and material sciences.

## Experimental Section

IR spectra of all compounds were reported from Nicolet magna-IR<sup>TM</sup> Spectrometer 550. <sup>1</sup>H-NMR (300 MHz) and <sup>13</sup>C-NMR (75 MHz) spectra were recorded on a Varian Mercury NMR spectrometer system. Chemical shifts were reported in  $\delta$  units, parts per million (ppm) relative to the singlet as 7.24 ppm for chloroform-d. Mn and PDI values were measured by Waters Alliance gel permeation chromatography (GPC) which is composed of 2690 separation module, Styragel<sup>TM</sup> HR1, 2, 4 columns and 2410 RI detector.

**General Procedure for Conversion of GAP Polymer to Glycidyl Tetrazolyl Triazole Polymer Using Click Reaction.** To a stirred solution of **1a** (120 mg, 0.64 mmol), 5-phenyl-2-propargyl tetrazole **2a** (148 mg, 1.2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (2.4 mL) were added copper(II) sulfate pentahydrate (8.4 mg, 0.05 equiv.) and sodium ascorbate (20 mg, 0.15 equiv.) dissolved in H<sub>2</sub>O (2.4 mL) at room temperature. The reaction mixture was stirred for 4.5 h at room temperature. The resulting was poured into CH<sub>2</sub>Cl<sub>2</sub> (3 mL), washed with H<sub>2</sub>O (3 mL) and the organic layer was separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 mL  $\times$  3). Combined organic layer was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluted with Hexane/EtOAc (1/1) and CH<sub>2</sub>Cl<sub>2</sub>/MeOH (9/1) to afford 230 mg of **3aa** in 96% yield.

**Glycidyl-{4-[(5-phenyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3aa):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.12-7.78 (brs, Hs of Ar and H of triazole), 7.42-7.21 (Hs of Ar), 5.93 (brs,  $\alpha$ -Hs of tetrazole), 4.68-3.00 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.40-0.52 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.99, 139.84, 130.19, 128.63, 126.90, 126.56, 125.19, 75.30, 72.76, 70.54, 68.81, 52.96, 51.18, 48.33, 16.63; FT-IR (KBr, cm<sup>-1</sup>) 3441(br, -OH), 3142(w), 3073(w), 2920(m), 1610(w), 1465(vs), 1449(vs), 1140(s), 1073(s), 1045(s), 789(vs), 733(vs), 694(vs); Mn = 1338, PDI = 1.18.

**Glycidyl-{4-[(5-phenyl-1H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3aa):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.04-7.72 (Hs of Ar and H of triazole), 7.62-7.32 (Hs of Ar), 5.68 (brs,  $\alpha$ -Hs of tetrazole), 4.70-3.12 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.40-0.52 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  154.24, 140.43, 131.23, 129.08, 128.98, 125.51, 123.04, 75.19, 73.03, 71.32, 68.69, 53.21, 51.37, 43.23, 16.98; FT-IR (KBr, cm<sup>-1</sup>) 3416(br, -OH), 3143(w), 3077(w), 2971(m), 2874(m), 1609(w), 1473(vs), 1375(w), 1227(w), 1141(vs), 1052(s), 912(vs), 777(vs), 732(vs), 698(vs), 647(s); Mn = 1311, PDI = 1.18.

**Glycidyl-{4-[(5-tolyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ab):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (brs, Hs of Ar and H of triazole), 7.21 (brs, Hs of Ar), 5.92 (brs,  $\alpha$ -Hs of tetrazole), 4.60-2.92 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 2.50-1.98 (Hs of tolyl CH<sub>3</sub>), 1.42-0.64 (Hs of propylene oxide CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  165.13, 140.35, 129.37, 127.25, 126.54, 125.22, 124.18, 75.21, 72.67, 70.23, 68.91, 52.48, 51.26, 48.32, 21.50, 16.65; FT-IR (KBr, cm<sup>-1</sup>) 3471(br, -OH), 3137(w), 2968(m), 2916(m), 1617(w), 1463(s), 1275(m), 1108(vs), 1076(vs), 749(vs); Mn = 1318, PDI = 1.19.

**Glycidyl-{4-[(5-(para-fluorophenyl)-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ac):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (brs, Hs of Ar and H of triazole), 7.04 (brs, Hs of Ar), 5.89 (brs,  $\alpha$ -Hs of tetrazole), 4.66-2.54 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.28-0.48 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  165.31, 164.12, 161.99, 139.63, 128.62, 125.22, 123.05, 115.91, 75.27, 72.69, 70.49, 68.75, 53.00, 51.28, 48.27, 16.77; FT-IR (KBr, cm<sup>-1</sup>) 3446(br, -OH), 3145(w), 3079(w), 2916(m), 1608(w), 1464(vs), 1428(s), 1228(s), 1141(s), 1095(s), 1042(s), 846(s), 762(vs), 749(s); Mn = 1513, PDI = 1.18.

**Glycidyl-{4-[(5-(ortho-bromophenyl)-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ad):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.15-7.85 (H of Ar and H of triazole), 7.83-7.52 (Hs of Ar), 7.41-7.18 (Hs of Ar), 6.00 (brs,  $\alpha$ -Hs of tetrazole), 4.72-2.95 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.40-0.62 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.93, 139.56, 133.73, 131.39, 127.98, 127.21, 125.43, 121.64, 75.14, 72.74, 70.59, 68.45, 52.97, 51.11, 48.46, 18.11; FT-IR (KBr, cm<sup>-1</sup>) 3430(br, -OH), 3143(w), 3063(w), 2970(m), 2783(m), 1599(w), 1565(w), 1520(w), 1456(vs), 1436(vs), 1328(s), 1118(vs), 1059(vs), 780(s), 749(vs); Mn = 1412, PDI = 1.17.

**Glycidyl-{4-[(5-(ortho-bromophenyl)-1H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ad):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (brs, H of triazole), 7.79-7.70 (H of Ar), 7.58-7.14 (Hs of Ar), 5.53 (brs,  $\alpha$ -Hs of tetrazole), 4.62-2.95 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.40-0.62 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.45, 139.58, 133.01, 132.68, 132.03, 127.73, 125.09, 122.93, 75.09, 72.79, 70.44, 68.79, 51.14, 49.52, 43.24, 16.84; FT-IR (KBr, cm<sup>-1</sup>) 3399(br, -OH), 3141(w), 3085(w), 2971(m), 2874(m), 1600(s), 1566(w), 1456(vs), 1406(s), 1375(s), 1341(s), 1107(vs), 913(vs), 776(s), 732(vs), 646(s); Mn = 1392, PDI = 1.11.

**Glycidyl-{4-[(5-methyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ae):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.07-7.89 (H of triazole), 5.86 (brs,  $\alpha$ -Hs of tetrazole), 4.74-3.02 (Hs of CH, Hs of CH<sub>2</sub> and  $\alpha$ -Hs of triazole), 2.65-2.21 (Hs of CH<sub>3</sub>), 1.32-0.58 (Hs of propylene oxide CH<sub>3</sub>); <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>)  $\delta$  162.84, 139.72, 125.07, 75.25, 74.52, 72.77, 70.64, 68.62, 52.68, 51.05, 47.87, 16.74, 10.78; FT-IR (KBr, cm<sup>-1</sup>) 3452(br, -OH), 3140(w), 2970(m), 2875(m), 1504(m), 1456(s), 1374(m), 1260(m), 1107(vs), 1076(vs), 792(s), 764(s), 749(s); Mn = 1180, PDI = 1.21.

**Glycidyl-{4-[(5-(ethylacetate)-1H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3af):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (brs, H of triazole), 5.91 (brs,  $\alpha$ -Hs of tetrazole), 4.68-4.32 (Hs of CH), 4.20-4.05 (Hs of CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>),

4.02-3.91 (Hs of CH<sub>2</sub>CO<sub>2</sub>Et), 3.89-3.06 (Hs of CH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.38-1.24 (Hs of CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.22-0.98 (Hs of propylene oxide CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  167.95, 160.10, 139.55, 125.24, 75.19, 72.79, 70.25, 68.88, 61.48, 53.01, 51.57, 48.27, 31.70, 17.04, 14.04; FT-IR (KBr, cm<sup>-1</sup>) 3445(br, -OH), 3142(w), 2977(m), 2933(m), 1739(vs), 1505(m), 1456(vs), 1329(s), 1194(s), 1113(s), 1029(s), 793(w); Mn = 1610, PDI = 1.33.

**Glycidyl-4-[(5-phenyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ba):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.08-7.60 (brs, Hs of Ar and H of triazole), 7.45-7.01 (Hs of Ar), 5.88 (brs,  $\alpha$ -Hs of tetrazole), 4.58-2.82 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.30-0.46 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.88, 139.77, 130.22, 128.65, 126.69, 126.47, 125.26, 75.13, 72.76, 70.52, 68.59, 52.96, 50.97, 48.26, 16.83; FT-IR (KBr, cm<sup>-1</sup>) 3433(br, -OH), 3140(w), 3073(w), 2877(m), 1610(w), 1465(vs), 1449(vs), 1336(m), 1266(m), 1230(m), 1140(s), 1073(s), 1047(s), 789(s), 733(vs), 695(s); Mn = 1633, PDI = 1.14.

**Glycidyl-4-[(5-phenyl-1H-tetrazolyl)methyl]-1H-1,2,3-triazole}-propylene Oxide Copolymer (3ba')**: <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.18-7.73 (brs, Hs of Ar and H of triazole), 7.62-7.21 (Hs of Ar), 5.66 (brs,  $\alpha$ -Hs of tetrazole), 4.64-2.89 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.37-0.46 (Hs of CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  154.27, 140.51, 131.23, 129.08, 128.94, 125.57, 123.05, 75.14, 72.77, 68.74, 53.42, 51.04, 43.18, 21.02; FT-IR (KBr, cm<sup>-1</sup>) 3440(br, -OH), 3140(w), 3057(w), 2876(m), 1610(w), 1461(vs), 1436(s), 1404(m), 1227(m), 1111(vs), 1076(s), 1050(s), 777(vs), 734(vs), 698(vs); Mn = 1580, PDI = 1.14.

**Glycidyl-4-[(5-phenyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-tetrahydrofuran Copolymer (3ca):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.20-7.82 (Hs of Ar and H of triazole), 7.43 (brs, Hs of Ar), 5.94 (brs,  $\alpha$ -Hs of tetrazole), 4.64-3.07 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.66-1.23 (Hs of CH<sub>2</sub>); <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>)  $\delta$  164.78, 139.53, 130.00, 128.45, 126.68, 126.39, 124.76, 71.40, 71.07, 70.26, 70.12, 69.72, 68.65, 53.12, 51.73, 48.13, 26.25; FT-IR (KBr, cm<sup>-1</sup>) 3445(br, -OH), 3144(w), 3073(w), 2917(s), 2864(s), 1449(vs), 1465(vs), 1355(w), 1275(w), 1112(vs), 1074(s), 749(s), 733(vs), 694(s); Mn = 1410, PDI = 1.15.

**Glycidyl-4-[(5-phenyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-tetrahydrofuran Copolymer (3da):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.20-7.62 (Hs of Ar and H of triazole), 7.33 (brs, Hs of Ar), 5.88 (brs,  $\alpha$ -Hs of tetrazole), 4.60-2.58 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.62-0.68 (Hs of CH<sub>2</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.83, 139.61, 130.08, 128.52, 126.67, 126.42, 124.84, 71.47, 70.21, 69.78, 68.75, 53.10, 51.73, 48.22, 26.18; FT-IR (KBr, cm<sup>-1</sup>) 3442(br, -OH), 3142(w), 3073(w), 2944(m), 2868(m), 1449(vs), 1465(vs), 1363(w), 1226(w), 1116(vs), 1074(s), 1046(vs), 789(s), 734(vs), 695(s); Mn = 1866, PDI = 1.28.

**Glycidyl-4-[(5-phenyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-tetrahydrofuran Copolymer (3ea):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.03-7.64 (Hs of Ar and H of triazole), 7.33 (brs, Hs of Ar), 5.86 (brs,  $\alpha$ -Hs of tetrazole), 4.57-2.72 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole), 1.23-0.48 (Hs of CH<sub>2</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.77, 139.80, 130.23,

128.64, 126.60, 126.41, 125.26, 70.12, 68.57, 53.25, 50.78, 48.18; FT-IR (KBr, cm<sup>-1</sup>) 3431(br, -OH), 3141(w), 3072(w), 2875(m), 1449(vs), 1465(vs), 1334(m), 1266(m), 1230 (m), 1140(vs), 1073 (s), 1046(vs), 788(vs), 733(vs), 694(vs); Mn = 1890, PDI = 1.14.

**Hydroxyl Terminated Glycidyl-4-[(5-phenyl-2H-tetrazolyl)methyl]-1H-1,2,3-triazole}-polymer (5aa):** <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (brs, Hs of Ar and triazole), 7.32 (brs, Hs of Ar), 5.85 (brs,  $\alpha$ -Hs of tetrazole), 4.45-3.05 (Hs of OCH, Hs of OCH<sub>2</sub> and  $\alpha$ -Hs of triazole); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  164.77, 139.78, 130.24, 128.65, 126.58, 126.40, 125.18, 70.12, 68.55, 53.25, 50.73, 48.14; FT-IR (KBr, cm<sup>-1</sup>) 3445(br, -OH), 3141 (w), 3073(w), 3006(w), 2919(w), 1710(s), 1465(s), 1449(vs), 1362(s), 1225(s), 1141(s), 1046(vs), 913(m), 789(vs), 733(vs), 694(vs); Mn = 1421, PDI = 1.13.

## References

1. Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, 1369-1380. (b) Moses, J. E.; Moorhouse, A. D. *Chem. Soc. Rev.* **2007**, 36, 1249-1262. (c) Gil, M. V.; Arévalo, M. J.; López, Ó. *Synthesis* **2007**, 1589-1620. (d) Lutz, J.-F. *Angew. Chem. Int. Ed.* **2007**, 46, 1018-1025. (e) Meldal, M.; Tornøe, C. W. *Chem. Rev.* **2008**, 108, 2952-3015. (f) Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2008**, 29, 952-981.
2. Jung, J.-H.; Lim, Y.-G.; Lee, K.-H.; Koo, B. T. *Tetrahedron Lett.* **2007**, 48, 6442-6448.
3. (a) Licht, H. H.; Ritter, H. *J. Energ. Mater.* **1994**, 12, 223. (b) Licht, H. H.; Ritter, H. *Propell. Explos. Pyrotech.* **1997**, 22, 333. (c) Ostrovskii, V. A.; Pevzner, M. S.; Kofmna, T. P.; Shcherbinin, M. B.; Tselinskii, I. V. *Targets Heterocycl. Syst.* **1999**, 3, 467. (d) Hiskey, M.; Chavez, D. E.; Naud, D. L.; Son, S. F.; Berghout, H. L.; Bome, C. A. *Proc. Int. Pyrotech. Semin.* **2000**, 27, 3. (e) Kofman, T. P. *Russ. J. Org. Chem.* **2002**, 38, 1231-1243. (f) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. *Angew. Chem. Int. Ed.* **2006**, 45, 3584-3601. (g) Klapötke, T. M. *Structure and Bonding: High Energy Density Compounds*; Springer: Berlin/Heidelberg, 2007; Vol. 125.
4. (a) Singh, H.; Chawla, A. S.; Kapoor, V. K.; Paul, D.; Malhotra, R. K. *Prog. Med. Chem.* **1980**, 17, 151. (b) Alvarez, R.; Velazquez, S.; San-Felix, A.; Aquaro, S.; DeClercq, E.; Perno, C. F.; Karlsson, A.; Balzarini, J.; Camarasa, M. J. *J. Med. Chem.* **1994**, 37, 4194. (c) Chem, X. M.; Li, Z. J.; Ren, Z. X.; Huang, Z. T. *Carbohydr. Res.* **1999**, 315, 262. (d) Brockunier, L.; Parmee, E. R.; Ok, H. O.; Candelore, M. R.; Cascieri, M. A.; Colwell, L. F.; Deng, L.; Fee-ney, W. P.; Forrest, M. J.; Hom, G. J.; MacIntyre, D. E.; Tota, L.; Wywrat, M. J.; Fisher, M. H.; Weber, A. E. *Bioorg. Med. Chem. Lett.* **2000**, 10, 2111.
5. (a) Ostrovskii, V. A.; Pevzner, M. S.; Kofman, T. P.; Tselinskii, I. V. *Targets Heterocyclic syst.* **1999**, 3, 467. (b) Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; Mckay, M. *Propell. Explos. Pyrotech.* **2003**, 28, 174.
6. (a) Tsarevsky, N. V.; Bernaerts, K. V.; Dufour, B.; Du Prez, F. E.; Matyjaszewski, K.; *Macromolecules* **2004**, 37, 9308-9313. (b) Petrova, T. L.; Kizhnyayev, V. N.; Tsykina, N. A.; Vereshchagin, L. I.; Smirnov, A. I. Russian Pat. 2261873, 2005. (c) Miller, C. G.; Williams, G. K. U. S. Pat. US 2007/0040167 A1, 2007. (d) Kizhnyayev, V. N.; Pokatilov, F. A.; Vereshchagin, L. I. *Polym. Sci. Ser. A* **2007**, 49, 28-34. (e) Reddy, T. S.; Satpute, R. S.; Nair, J. K.; Gore, G. M.; Sikder, A. K. *J. Polym. Mater.* **2008**, 25, 557-562. (f) Tian, J.; Wan, L.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *Polym. Bull.* **2008**, 60, 457-465. (g) Gromadzki, D.; Lokaj, J.; Cernoch, P.; Diat, O.; Nallet, F.; Štěpánek, P. *Eur. Polym. J.* **2008**, 44, 189-199. (h) Kizhnyayev, V. N.; Pokatilov, F. A.; Vereshchagin, L. I.; Verkhovzina, O. N.; Petrova, T. L.; Prodaikov, A. G.; Ratovskii, G. V.;

- Tyukalova, O. V. *Russ. J. Appl. Chem.* **2009**, *82*, 1769-1775. (i) Klapötke, T. M.; Sproll, S. M. *J. Polym. Sci.: Part A: Polym. Chem.* **2010**, *48*, 122-127. (j) Klapötke, T. M.; Sproll, S. M. *Eur. J. Org. Chem.* **2010**, 1169-1175.
7. Govokov, A. T.; Fomina, M. P.; Bannova, E. A. *High Energy Chem.* **1990**, *24*, 439.
8. (a) Verkhozina, O. N.; Kizhnyayev, V. N.; Vereshchagin, L. I.; Rokhin, A. V.; Smirnov, A. I. *Russ. J. Org. Chem.* **2003**, *39*, 1792-1796. (b) Ye, C.; Gard, G. L.; Winter, R. W.; Syvret, R. G.; Twamley, B.; Shreeve, J. M. *Org. Lett.* **2007**, *9*, 3841-3844.
9. Preparation of **1a**; To a stirred ethylene glycol (1.15 g, 18.4 mmol) was added boron trifluoride etherate (1.30 g, 9.2 mmol) under N<sub>2</sub> atmosphere. The mixture was stirred for 30 min at room temperature and concentrated in vacuo. The resulting mixture was dissolved in dichloromethane (25 mL) under N<sub>2</sub> atmosphere. Epichlorohydrin (14.3 g, 8.4 mmol) and propylene oxide (13.4 g, 12.6 mmol) which were premixed in additional funnel were added dropwise to the resulting solution at 40 °C for 1 h. The reaction mixture was stirred at room temperature for 1 h and poured into aqueous Na<sub>2</sub>CO<sub>3</sub> solution. The organic solution was extracted with dichloromethane (50 mL × 3 times) and concentrated in vacuo to afford 28 g of poly(epichlorohydrin-*co*-propylene oxide) in 96.8% yield. To a solution of poly(epichlorohydrin-*co*-propylene oxide) (20 g, 111.7 mmol) in DMSO (60 mL) was added NaN<sub>3</sub> (8.72 g, 134.1 mmol) and stirred at 100 °C for 9 h. The reaction mixture was cooled to room temperature and poured into H<sub>2</sub>O (50 mL). The resulting was extracted with dichloromethane (50 mL × 3 times). The extracts were washed with aqueous 10% MeOH solution and concentrated in vacuo to afford 20 g of **1a** in 96.2% yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 3.94-3.26 (Hs of OCH, Hs of OCH<sub>2</sub>, CH<sub>2</sub>-N<sub>3</sub>), 1.35-0.88 (CH<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 78.57, 75.22, 73.21, 72.85, 71.11, 70.65, 69.43, 53.21, 51.85, 18.20, 17.06; FT-IR (KBr, cm<sup>-1</sup>) 3403(br, -OH), 2972(m), 2873(m), 2100(vs, -N<sub>3</sub>), 1455(w), 1374(w), 1280(m) 1109(s), 934(w); Mn = 851, PDI = 1.30.
- Preparation of **4a**; To a stirred 2-chloroethanol (8 g, 99.3 mmol) was added boron trifluoride etherate (0.7 g, 4.9 mmol) under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 30 min and concentrated in vacuo. The resulting mixture was dissolved in dichloromethane (60 mL) under N<sub>2</sub> atmosphere. Epichlorohydrin (81.3 g, 873.8 mmol) was added dropwise to the resulting solution at 40 °C for 1 h. The resulting was stirred for 1 h at room temperature and poured into aqueous Na<sub>2</sub>CO<sub>3</sub> solution. The resulting organic layer was extracted with dichloromethane (120 mL × 3 times) and concentrated in vacuo to afford 88 g of epichlorohydrin polymer in 98.5% yield. To a solution of epichlorohydrin polymer (10 g, 108 mmol) in DMSO (100 mL) was added NaN<sub>3</sub> (8.58 g, 129.7 mmol) and stirred at 100 °C for 7 h. The reaction mixture was cooled to room temperature and poured into H<sub>2</sub>O (50 mL). The resulting was extracted with dichloromethane (50 mL × 3 times). The extracts were washed with aqueous 10% MeOH solution and concentrated in vacuo to afford 9.64 g of **4a** in 88.5% yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 3.94-3.31 (Hs of OCH, Hs of OCH<sub>2</sub>), 3.03-2.93 (CH<sub>2</sub>-N<sub>3</sub>); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 79.01, 78.59, 76.57, 71.99, 71.87, 71.73, 71.21, 70.53, 70.34, 69.97, 69.65, 69.46, 53.14, 52.98, 51.65, 50.57; FT-IR (KBr, cm<sup>-1</sup>) 3461(br, -OH), 2925(m), 2873(m), 2100(vs, -N<sub>3</sub>), 1443(w), 1282(m) 1127(m), 935(w); Mn = 639, PDI = 1.13.
10. (a) Helms, B.; Mynar, J. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020-15021. (b) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem. Int. Ed.* **2004**, *43*, 3928-3932. (c) Rodionov, V. O.; Fokin, V. V.; Finn, M. G. *Angew. Chem. Int. Ed.* **2005**, *44*, 2210-2215. (d) Lee, B. Y.; Park, S. R.; Jeon, H. B.; Kim, K. S. *Tetrahedron Lett.* **2006**, *47*, 5105-5109.
11. Verkhozina, O. N.; Kizhnyayev, V. N.; Vereshchagin, L. I.; Rokhin, A. V.; Smirnov, A. I. *Russ. J. Org. Chem.* **2003**, *39*, 1792-1796.
12. Koyama, M.; Ohtani, N.; Kai, F.; Moriguchi, I.; Inouye, S. *J. Med. Chem.* **1987**, *30*, 552-562.