

## Research Article

# Synthesis of Polyethers Containing Triazole Units in the Backbone by Click Chemistry in a Tricomponent Reaction

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A series of linear aromatic polyethers containing triazole units were synthesized via the direct click reaction of dibromide and bisethynyl compounds in the presence of sodium azide as one pot reaction. The structures of polymers were approved by using IR and  $^1\text{H}$  NMR techniques. The solubility experiments showed that polymers have good solubility in polar aprotic solvents such as DMSO, DMF, and NMP at higher temperatures. Thermal stability of the polymers was measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) which indicated that they possessed good thermal stability ( $T_{50}$  up to  $558^\circ\text{C}$ ) and high  $T_g$  ( $191.7\text{--}260^\circ\text{C}$ ) under  $\text{N}_2$  atmosphere. All the polymers were amorphous according to the DSC and X-ray diffraction. These polymers exhibited strong UV-vis absorption maxima near to 400 nm and up to 500 nm in DMSO solution.

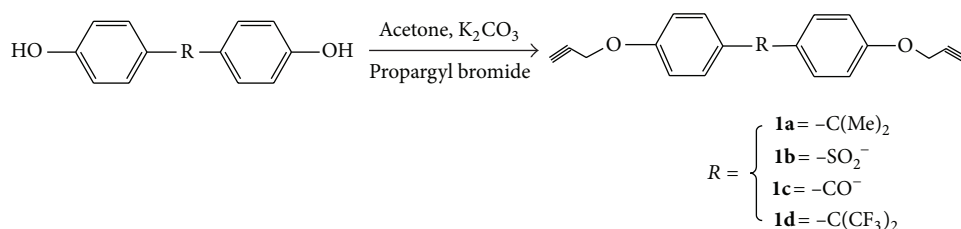
## 1. Introduction

Poly(arylene ether)s (PAEs) are known as an important class of the high-performance polymeric materials which consist of aromatic rings and ether linkages [1]. So far, one of the most common and effective methods for the formation of aromatic ether linkages in polyether synthesis was nucleophilic aromatic substitution ( $\text{S}_{\text{N}}\text{Ar}$ ) reaction. Different poly(aryl ether)s including poly(ether sulfone)s, poly(ether ketone)s, and poly(ether imide)s have been prepared using the  $\text{S}_{\text{N}}\text{Ar}$  reaction and commercialized [2]. However, this method suffers from some serious limitations such as high temperature and harsh conditions. In addition, only appropriate monomers having electron-withdrawing groups at the ortho position to the leaving group could be polymerized.

Recent innovations in synthetic methodology have improved polymer synthesis, enabling the custom design of a large variety of macromolecular architectures under incorporation of desired functional units [3, 4]. To find an outstanding polymerization reaction, polymer chemists and biotechnologists have increasingly turned towards advanced synthetic organic concepts. In this respect, the most interesting one is click chemistry well documented in the past decade.

The applications of click reactions are wide in scope. The click reactions give excellent yields and generate inoffensive by-products that can be removed by convenient methods. The required process characteristics include simple reaction conditions, readily available reactants, solvent free reactions or using a solvent that is benign or easily removed, and simple product isolation [5].

To date, the most popular reaction that satisfied these features is the 1,3-dipolar cycloaddition, also known as Huisgen cycloaddition, between an azide and a terminal alkyne which affords the triazole moiety [6]. The applicability of this reaction is very high, since alkyne and azide components can be incorporated into a wide range of substituents [7]. Unfortunately, this reaction suffers from a lack of selectivity yielding a mixture of the 1,4- and the 1,5-regioisomers. Furthermore, this transformation requires heating and long reaction times to go to completion, and the mixtures of regioisomers are at times laborious to separate using classical chromatographic procedures [7]. Recently, it has been reported that copper(I) salts accelerate the reaction rate enormously. Surprisingly, the copper catalyst produces only the 1,4-regioisomer at room temperature in moderate heating [8, 9].



SCHEME 1: Synthesis of bis propargyl ethers.

Although, the applications of click reaction in materials science are especially interesting, most of them were focused on the preparation of dendronized polymers [10, 11] and conjugated polymers [12] or limited to incorporation of 1,2,3-triazole rings into polymers by graft polymerization [13–15]. According to our literature survey, it is found that the 1,2,3-triazole ring was rarely incorporated into the backbone of linear poly(arylene ether)s [16–19].

In this paper, we wish to describe the synthesis and characterization of a novel class of linear aromatic and aliphatic polyethers such as poly(ether ketone)s, poly(ether sulfone)s, and fluorinated poly ether containing triazole units in the backbone via the in situ click reaction of bisethynyl and dibromide compounds in the presence of sodium azide as a tricomponents reaction.

## 2. Materials and Methods

Acetone was dried over  $\text{CaH}_2$  and distilled before use. Other reagents or materials were used as received. The chemicals used in this experiment were purchased from Merck (Germany).

**2.1. Characterization.** Melting points were measured by an Electrothermal 9100 apparatus.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX-400. IR spectra were recorded on a Perkin Elmer FT-IR- 1710 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were recorded on a thermal science PLSTA 1500 system under nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . Inherent viscosity at a concentration of 0.5 g/dL was measured with an Ubbelohde suspended-level viscometer at  $25^\circ\text{C}$  in DMSO solution. X-ray diffraction (XRD) patterns were obtained at room temperature on a Rigaku D/Max-2550 powder diffractometer with a scanning speed of  $5^\circ \text{min}^{-1}$ , and the patterns were recorded in the  $2\theta$  range of  $5\text{--}50^\circ$ . Relative molecular weights and distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index (RI) detector, a Waters 2487 dual wavelength  $\lambda$  absorbance detector, and a set of Waters Styragel columns (HR3, HR4, and HR5,  $7.8 \text{ mm} \times 300 \text{ mm}$ ). GPC measurements were carried out at  $35^\circ\text{C}$  using DMF as eluent at a flow rate of 1.0 mL/min. Ultraviolet-visible spectra were recorded on a Cecil 5503 (Cecil Instruments,

Cambridge, UK) spectrophotometers using a dilute polymer solution (0.20 g/dL) in DMSO.

**2.2. Synthesis of Bis Propargyl Ether of Bisphenol.** Bisphenol (0.05 mol), potassium carbonate (0.15 mol), dry acetone (50 mL), and propargyl bromide (0.125 mol) were mixed in a round bottom flask equipped with a condenser and a heater stirrer. Then the mixture was kept at  $80^\circ\text{C}$  overnight. On completion of the reaction, the solvent was evaporated and the product was washed with 5%  $\text{K}_2\text{CO}_3$  aq. and deionized water several times. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate (4 : 1) as eluent to give **1a–d**. Then, it was recrystallized from ethanol twice to obtain crystalline monomers. Synthesis of bis propargyl ethers of bisphenols is shown in Scheme 1.

**1a:** Yield: 90%. m.p.  $80\text{--}82^\circ\text{C}$  [20].

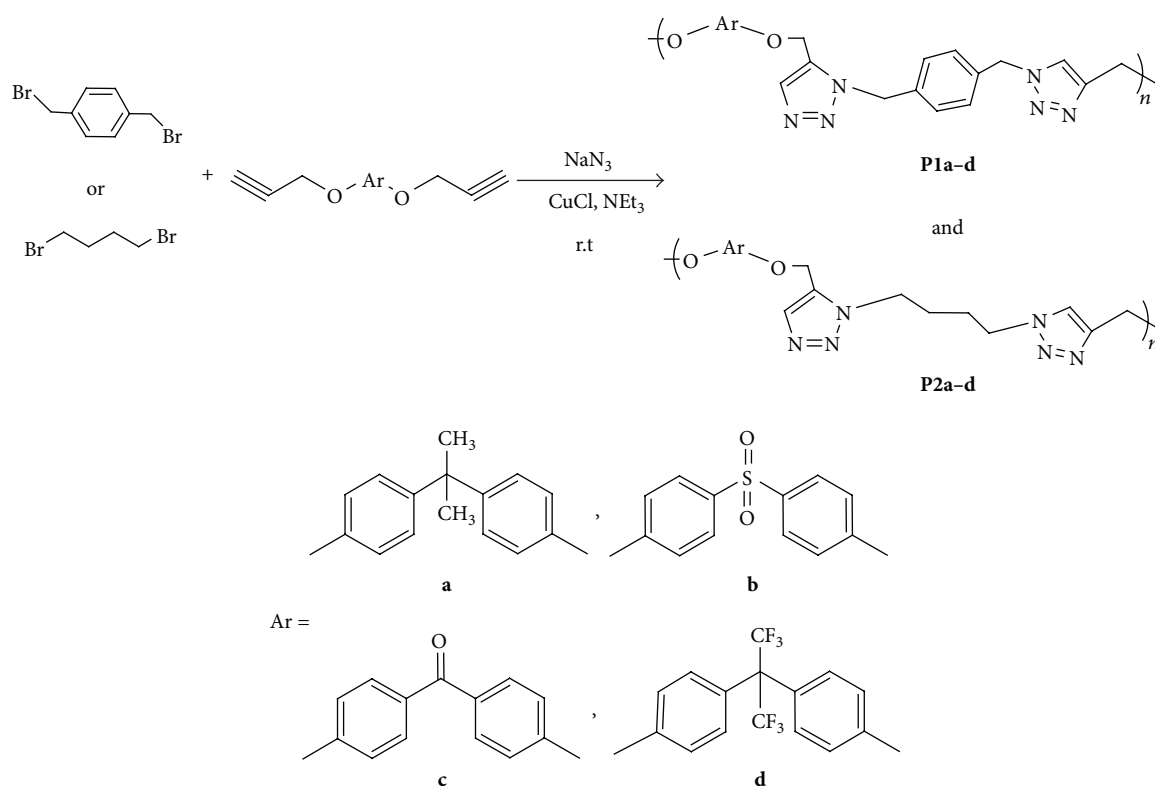
**1b:** Yield: 85%. m.p.  $180\text{--}182^\circ\text{C}$  [20].

**1c:** Yield: 88%. m.p.  $89\text{--}90^\circ\text{C}$  [20].

**1d:** Yield: 89%. Oil; IR (KBr,  $\text{cm}^{-1}$ ): 3299 ( $\equiv\text{CH}$ ), 2127 ( $\text{C}\equiv\text{C}$ ); 1247 (Ar–O); 1189 (O– $\text{CH}_2$ ); 827 ( $-\text{CF}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.59 (tr,  $J = 2.4 \text{ Hz}$ , 2H,  $\equiv\text{CH}$ ), 4.79 (d,  $J = 2.4 \text{ Hz}$ , 4H,  $-\text{CH}_2$ ), 7.06 (d,  $J = 9.2 \text{ Hz}$ , 4H,  $-\text{O}-\text{Ar}-\text{H}$ ), 7.82 (d,  $J = 9.2 \text{ Hz}$ , 4H,  $-\text{C}-\text{Ar}-\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.8, 66.3, 76.1, 77.8, 114.3, 131.3, 132.1, 160.7, 194.3. MS  $m/z$  (relative intensity) 412.

**2.3. Synthesis of Polymer 1a–d and 2a–d from Bis Propargyl Aryl Ethers and Dibromides.** In a 25 mL flask, to a solution of bisethynyl compounds (0.50 mmol), dibromide (146 mg, 0.50 mmol) and sodium azide (71.5 mg, 1.1 mmol) in DMF (10 mL), was added a suspension of CuCl (9.85 mg, 20 mol %) in  $\text{H}_2\text{O}$  (2 mL) in dropwise. Then  $\text{NEt}_3$  was added gradually until color of mixture changes from brown to light green. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted by water (20 mL) and then concentrated ammonia (5 mL) was added and stirred for another 1 h. The mixture was filtered and the resulting solid material was washed with  $\text{H}_2\text{O}$ , methanol, and THF. Finally, the obtained polymer was further purified using continuous extraction by soxhlet in THF.

**1a:** 90% yield. IR (KBr,  $\text{cm}^{-1}$ ): 3180, 3085, 2929, 1650, 1604, 1508, 1430, 1307, 1226, 1180, 1018, 829, 688.  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz, ppm)  $\delta$ : 8.11 (s, 2H, CH of triazole ring), 7.63 (br, 4H, phenyl), 7.11 (br, 4H, phenyl), 6.91 (br, 4H, phenyl), 4.71 (br, 4H,  $\text{CH}_2\text{--O}$ ), 4.25 (br, 4H,  $\text{CH}_2\text{--N}$ ), 1.68 (s,



SCHEME 2: Synthesis of poly(triazole ether)s.

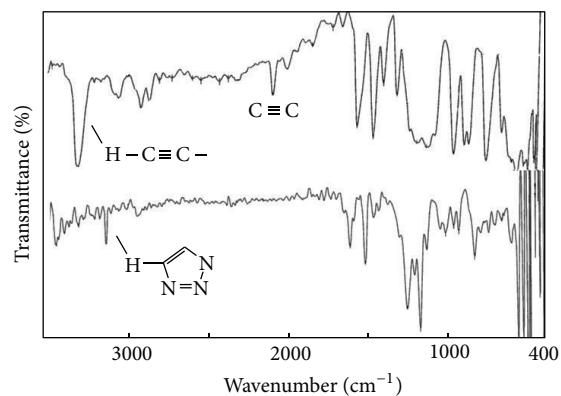
6H, CH<sub>3</sub>). Anal. Calc. for (C<sub>29</sub>H<sub>28</sub>N<sub>6</sub>O<sub>2</sub>)<sub>n</sub>: C 70.73, H 5.69, N 17.07. Found: C 71.25, H 5.56, N 17.81%.

**P1b**: 93% yield. IR (KBr, cm<sup>-1</sup>): 3140, 3058, 2920, 1592, 1494, 1459, 1294, 1253, 1177, 1149, 1106, 1050, 998. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.19 (s, 2H, CH of triazole ring), 7.83 (br, 4H, phenyl), 7.51 (br, 4H, phenyl), 6.95 (br, 4H, phenyl), 4.83 (br, 4H, CH<sub>2</sub>-O), 4.05 (br, 4H, CH<sub>2</sub>-N). Anal. Calc. for (C<sub>26</sub>H<sub>22</sub>N<sub>6</sub>O<sub>4</sub>S)<sub>n</sub>: C 60.7, H 4.28, N 16.34. Found: C 61.23, H 5.1, N 16.93%.

**P1c**: 89% yield. IR (KBr, cm<sup>-1</sup>): 3255, 3056, 2948, 1644, 1598, 1508, 1455, 1423, 1311, 1247, 1166, 998, 927. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.01 (s, 2H, CH of triazole ring), 7.52 (br, 4H, phenyl), 7.21 (br, 4H, phenyl), 7.01 (br, 4H, phenyl), 4.64 (br, 4H, CH<sub>2</sub>-O), 4.44 (br, 4H, CH<sub>2</sub>-N). Anal. Calc. for (C<sub>27</sub>H<sub>22</sub>N<sub>6</sub>O<sub>3</sub>)<sub>n</sub>: C 67.78, H 4.6, N 17.57. Found: C 68.34, H 4.86, N 18.01%.

**P1d**: 83% yield. IR (KBr, cm<sup>-1</sup>): 3139, 3045, 2958, 2875, 1614, 1515, 1461, 1427, 1249, 1170, 1051, 962, 825. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.16 (s, 2H, CH of triazole ring), 7.43 (br, 4H, phenyl), 7.25 (br, 4H, phenyl), 7.08 (br, 4H, phenyl), 4.75 (br, 4H, CH<sub>2</sub>-O), 4.25 (br, 4H, CH<sub>2</sub>-N). Anal. Calc. for (C<sub>29</sub>H<sub>22</sub>N<sub>6</sub>O<sub>2</sub>F<sub>6</sub>)<sub>n</sub>: C 56.49, H 3.57, N 13.63. Found: C 55.63, H 4.03, N 14.05%.

**P2a**: 91% yield. IR (KBr, cm<sup>-1</sup>): 3180, 3042, 2962, 1606, 1508, 1459, 1363, 1297, 1242, 1182, 1011, 830. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.31 (s, 2H, CH of triazole ring), 7.78 (br, 4H, phenyl), 7.08 (br, 4H, phenyl), 5.15 (br, 4H, CH<sub>2</sub>-O),

FIGURE 1: IR of **1d** (up) and **P2d** (down) using the KBr tablets.

4.16 (br, 4H, CH<sub>2</sub>-N), 1.72 (s, 6H, CH<sub>3</sub>), 1.54 (br, 4H, CH<sub>2</sub>-CH<sub>2</sub>). Anal. Calc. for (C<sub>25</sub>H<sub>28</sub>N<sub>6</sub>O<sub>2</sub>)<sub>n</sub>: C 67.56, H 6.3, N 18.91. Found: C 68.22, H 6.43, N 19.01%.

**P2b**: 90% yield. IR (KBr, cm<sup>-1</sup>): 3125, 3051, 2960, 1602, 1494, 1457, 1295, 1248, 1180, 1138, 1106, 1050, 998. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.21 (s, 2H, CH of triazole ring), 7.82 (br, 4H, phenyl), 7.18 (br, 4H, phenyl), 5.20 (br, 4H, CH<sub>2</sub>-O), 4.36 (br, 4H, CH<sub>2</sub>-N), 1.74 (br, 4H, CH<sub>2</sub>-CH<sub>2</sub>). Anal. Calc. for (C<sub>22</sub>H<sub>22</sub>N<sub>6</sub>O<sub>4</sub>S)<sub>n</sub>: C 56.65, H 4.72, N 18.02. Found: C 57.71, H 4.85, N 18.51%.

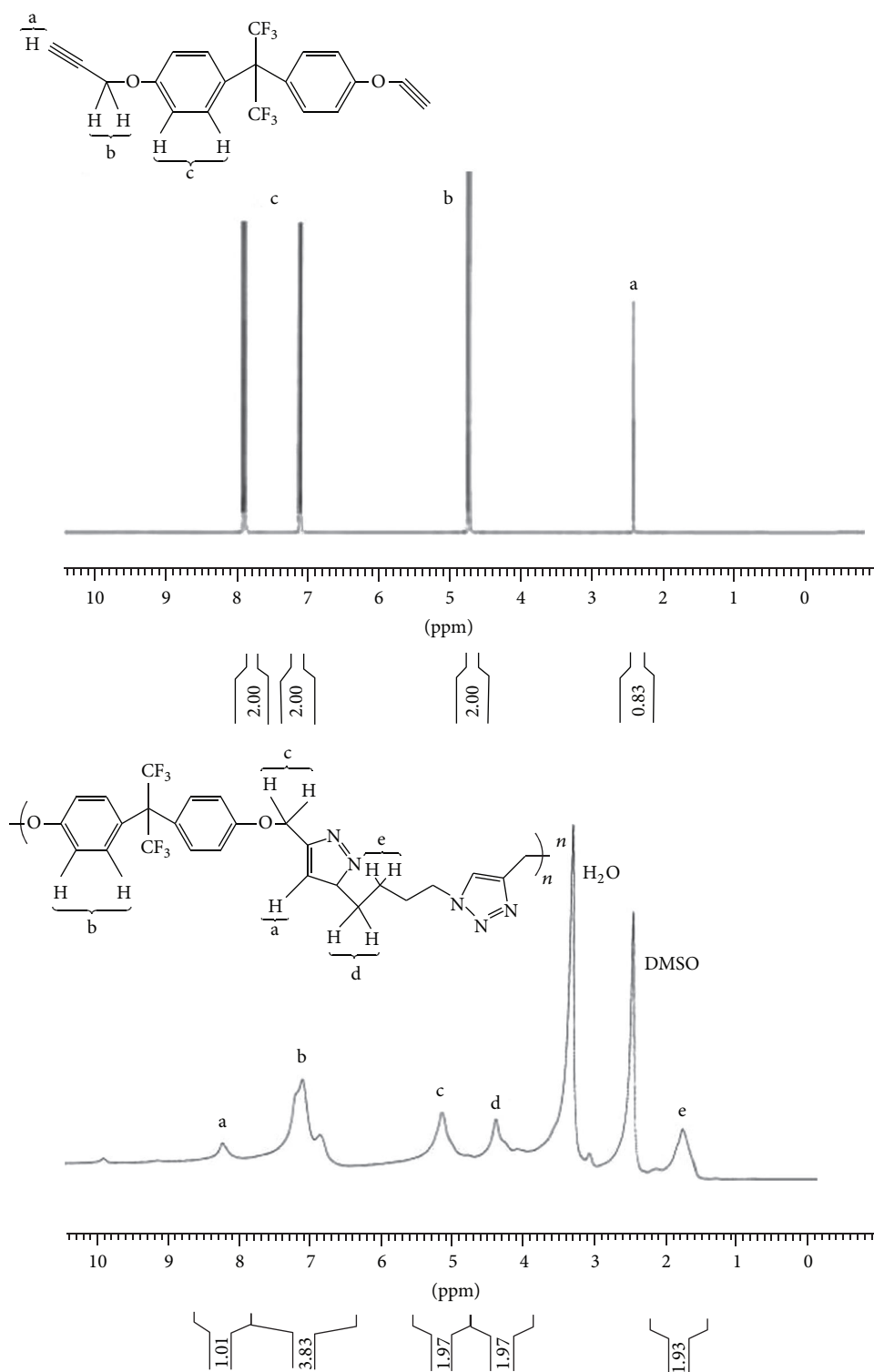


FIGURE 2: 400 MHz <sup>1</sup>H NMR of **1d** in CDCl<sub>3</sub> and **P2d** in DMSO-d<sub>6</sub>.

**P2c**: 89% yield. IR (KBr, cm<sup>-1</sup>): 3155, 3051, 2958, 1644, 1588, 1501, 1453, 1423, 1289, 1242, 1156, 988. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.08 (s, 2H, CH of triazole ring), 7.63 (br, 4H, phenyl), 7.01 (br, 4H, phenyl), 5.31 (br, 4H, CH<sub>2</sub>-O), 4.19 (br, 4H, CH<sub>2</sub>-N), 1.65 (br, 4H, CH<sub>2</sub>-CH<sub>2</sub>). Anal. Calc.

for (C<sub>23</sub>H<sub>22</sub>N<sub>6</sub>O<sub>3</sub>)<sub>n</sub> C 64.18, H 5.11, N 19.53. Found: C 65.11, H 5.61, N 19.27%.

**P2d**: 85% yield. IR (KBr, cm<sup>-1</sup>): 3129, 3055, 2978, 1624, 1505, 1451, 1407, 1239, 1159, 1045, 980, 827. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm) δ: 8.23 (s, 2H, CH of triazole ring), 7.12

(br, 4H, phenyl), 6.87 (br, 4H, phenyl), 5.15 (br, 4H, CH<sub>2</sub>-O), 4.39 (br, 4H, CH<sub>2</sub>-N), 1.78 (br, 4H, CH<sub>2</sub>-CH<sub>2</sub>). Anal. Calc. for (C<sub>25</sub>H<sub>22</sub>N<sub>6</sub>O<sub>2</sub>F<sub>6</sub>)<sub>n</sub> C 54.34, H 3.98, N 15.21. Found: C 55.69, H 4.09, N 15.61%.

### 3. Results and Discussion

**3.1. Synthesis and Characterization of Polymers.** Since triazole ring is chemically inert toward oxidation, reduction, and hydrolysis conditions and has an intermediate polarity [21], incorporation of such stable structural unit in polyethers can enhance their thermophysical properties. Traditionally, 1,2,3-triazoles were prepared from click reaction of azides and alkynes under Cu(I) catalysis which has been comprehensively reviewed [22]. However, low molecular weight organic azides may be unstable and should be handled with caution. Azides with a C/N ratio greater than one and no more than 3 can be synthesized and isolated but should be stored below room temperature at no more than 1 M concentration. Organic azides with C/N < 1 should never be isolated and practically they were used without further purification [19]. Therefore, to avoid the use of azides, the polymers containing triazole unites, poly(triazole ether)s (**P1a-d** and **P2a-d**), were obtained from direct click reaction of corresponding dibromides with bisethynyl compounds **1a-d** in the presence of sodium azide (Scheme 2). The reactions were carried out in a 10:2 solvent ratio of DMF:H<sub>2</sub>O and using 20 mol% CuCl with NEt<sub>3</sub> as base and stabilizing agent [23, 24] at room temperature. It is found that the reaction in dry DMF and/or in the absence of NEt<sub>3</sub> gives polymers in low yield. It can be seen from the infrared spectra of **P1a-d** and **P2a-d** the strong absorption peaks about 3,300 and 2,100 cm<sup>-1</sup> assigned to stretching vibrations of C≡C-H and -C≡C, respectively, disappeared, while new strong absorption peaks at 3042–3085 cm<sup>-1</sup> corresponding to stretching vibration of C=C-H of the 1,2,3-triazole moiety appeared (Figure 1). Representative <sup>1</sup>H NMR spectrum of monomer **1d** and its aliphatic polymer **P2d** is shown in Figure 2. It is clear that the 1,2,3-triazole rings of the polymer were characterized by signals near 8.2 ppm corresponding to triazole protons. As seen in <sup>1</sup>H NMR spectrum of the polymer **P2d**, it confirmed that the resulting polymers contain triazole units corresponding to IR analysis. These data indicate that direct polymerization between dibromide with bisethynyl compounds **1a-d** in the presence of sodium azide via the click reaction was successful. In comparison with previous works for synthesis of these types of polymers [25], our method is novel, convenient, and in best agreement with click chemistry requirements (benign solvents, room temperature, simple isolation, ...) and the most important feature of this method is the one pot synthesis that prevents from further purification and use of dangerous diazide compounds.

**3.2. Consideration of Molecular Weights and Distributions of Polymers.** The corresponding data of GPC analysis in DMF for polymers were showed in Table 1. The results show that the polymerization via click chemistry produced polymers with adequately high molecular weights and narrow distributions.

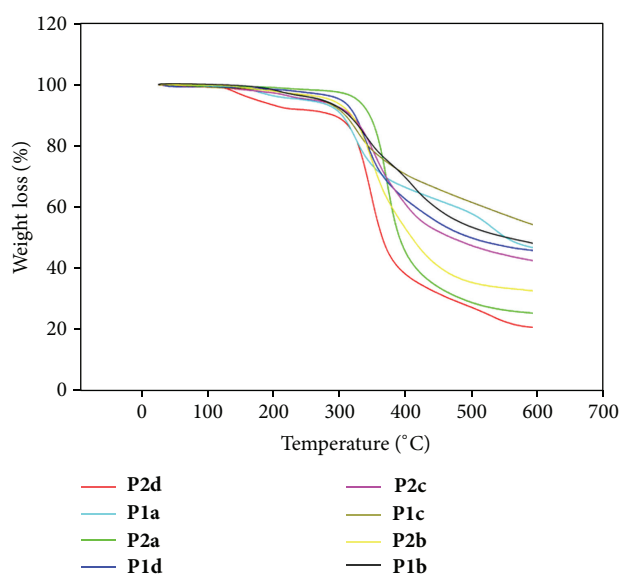


FIGURE 3: Thermogravimetric analysis under N<sub>2</sub> atmosphere and heating rate of 10° C/min.

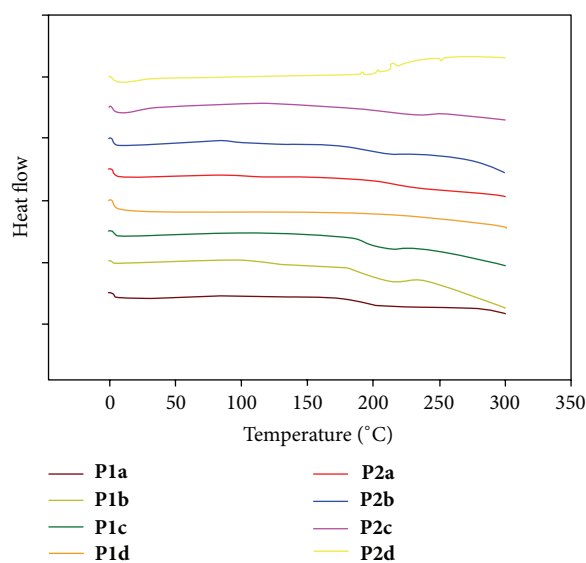


FIGURE 4: Differential scanning calorimetric under N<sub>2</sub> gas with heating rate of 10° C/min.

The number average molecular weights of them are between 17,300 and 24,800 and the distributions range is from 1.09 to 1.68. All polydispersities of polymers are less than 1.68 which is standard for polymerization reaction [26]. According to the high molecular weight and narrow distribution, it is found that the click chemistry is an effective route for polymerization.

**3.3. Solubility Behavior of Polymers.** The solubility of polymers was quantitatively determined in common organic solvents by dissolving 5.0 mg of solid polymers in 1.0 mL of solvents. In the solubility experiments, it was found that these polymers were completely insoluble in MeOH, THF, EtOAc,



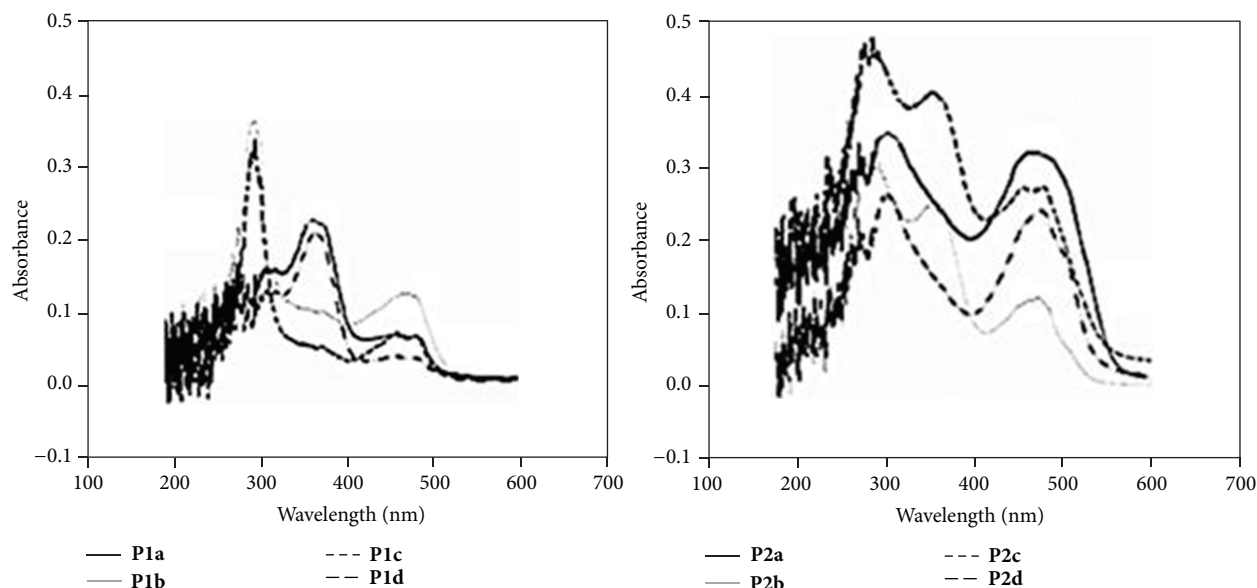


FIGURE 5: UV-vis absorption spectra of **P1a–d** and **P2a–d** were recorded using a dilute polymer solution (0.20 g/dL) in DMSO.

TABLE 1: Molecular weights and distributions of polymers.

Polymers	$M_n^a$	$M_w^a$	$(M_w/M_n)^a$	$\eta_{inh}$ (dl/g)
<b>P1a</b>	23,100	29,800	1.29	0.62
<b>P1b</b>	21,000	32,200	1.53	0.58
<b>P1c</b>	21,300	32,800	1.54	0.55
<b>P1d</b>	24,800	27,000	1.09	0.63
<b>P2a</b>	19,100	30,900	1.62	0.45
<b>P2b</b>	17,300	29,100	1.68	0.42
<b>P2c</b>	20,500	27,500	1.34	0.49
<b>P2d</b>	22,400	27,300	1.22	0.58

<sup>a</sup>GPC in DMF versus polystyrene in flow rate of 1.0 mL/min at 35°C.

TABLE 2: Thermal properties of polymers.

Polymers	$T_5$ (°C)	$T_{10}$ (°C)	$T_{50}$ (°C)	Char yield (%)	$T_g$ (°C)
<b>P1a</b>	249.6	321.4	499.5	46	210
<b>P1b</b>	274.2	313.8	556.7	48.3	260
<b>P1c</b>	271.3	309	—	54.46	220
<b>P1d</b>	302.2	310.9	558.8	44.3	212.5
<b>P2a</b>	327.1	345.6	390.9	25.6	191.7
<b>P2b</b>	287.4	319.1	410.2	32.9	196.7
<b>P2c</b>	261.7	316.05	469.64	42.7	208.3
<b>P2d</b>	175.2	297.5	370.8	18.7	196.8

and toluene at room and high temperatures. But polymers showed low solubility in DMSO, DMF, and NMP at room temperature and good solubility at higher temperatures.

**3.4. Thermal Properties of Polymers.** Thermal stabilities of **P1a–d** and **P2a–d** were evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC). The resulting data are summarized in Table 2. The

resulting polymers exhibited high resistance to thermal decomposition up to 558°C under nitrogen gas and decompose gradually above that temperature which is probably attributed to chain scission of ether linkage. It was seen from Figure 3 that rates of weight loss of aliphatic polymers were greater than aromatic polymers due to the decomposition of methylene groups. The glass transition temperature ( $T_g$ ) of polymers, determined by DSC, ranged between 191.7 and 260°C and increased with the increase of conformational rigidity (Table 2). As was expected, since **P1b** has rigid sulfone groups in the polymer, backbone which restricts molecular rotation  $T_g$  of **P1b** is the highest. **P2a** was the lowest owing to higher flexibility of the methyl groups. The data reveal that  $T_g$  decreases with the nature of the aliphatic chain spacer. Absence of crystallization temperature in DSC curves (Figure 4) also shows the amorphous nature of the polymers, which was confirmed by X-ray diffraction studies. Inherent viscosity ( $(\eta)_{inh} = \ln \eta_{rel}/c$ ) at a concentration of 0.5 g/dL was measured with an Ubbelohde suspended-level viscometer at 25°C in DMSO solution. Viscometry studies exhibited that polymers have moderate molecular weight (Table 1).

**3.5. UV-Vis Properties of the Polymers.** The photophysical properties of the **P1a–d** and **P2a–d** were investigated by UV-visible spectroscopy in DMSO solution. There are similar pair curves as can be seen in UV-vis diagrams (Figure 5) which exhibited strong absorption at 283 nm and 465 nm corresponding to phenyl and triazole rings of the polymer backbones, respectively. The presence of extra conjugation of  $-\text{SO}_2$  and  $-\text{CO}$  groups in the backbone of the polymer caused some blue shift. This effect has not been seen for the polymers bearing  $-(\text{CH}_3)_2-$  and  $-(\text{CF}_3)_2-$  spacer due to conjugation loss. Indeed, owing to the existence of different aromatic rings with different linkage between them, three characteristic absorption peaks could be seen in **P2b** and **P2c**. The peaks

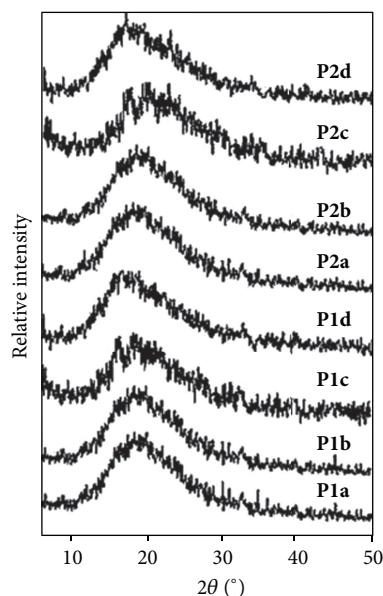


FIGURE 6: X-ray diffraction (XRD) patterns at room temperature on a powder diffractometer.

about 280 and 354 and about 480 nm are corresponding to arylenes and triazole rings, respectively [27, 28].

**3.6. X-Ray Diffraction Studies of Polymer P1a–d and P2a–d.** In order to further consider the crystallinity of these series of polymers, all polyether triazoles were characterized by X-ray diffractograms. The X-ray diffractogram curves of polymers were shown in Figure 6. XRD of all polymers demonstrates broad halo at about  $2\theta$  at  $15\text{--}30^\circ$  in the wide angle region exhibiting that the polymers **P1a–d** and **P2a–d** are amorphous in nature which is in agreement with the DSC analysis. This result could be explained that the etheric linkage caused the flexibility of the polymer chain which restricted the ordered arrangement of polymer chains.

## 4. Conclusion

In this work, convenient tricomponent click polymerizations of dialkynes containing ether linkages and dibromides were achieved in the presence of sodium azide to synthesize various polyethers (**P1a–d** and **P2a–d**). This polymerization accompanied the formation of triazoles in the polyether main chain by a Cu(I) catalyst in excellent yields. It is found that triazole ring formation in the polyether main chain leads to improved thermal properties. This work is a report of convenient synthesis of polymers that the triazoles rings inserted into backbone of the polymers under mild conditions. These fundamental results provide a new guideline to synthesize frontier polyether-based materials.

## Acknowledgment

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