

## SYNTHESIS AND CHARACTERIZATION OF TRIAZOLE CONTAINING LIQUID CRYSTALLINE POLYMERS THROUGH 1,3-DIPOLAR CYCLOADDITION POLYMERIZATION

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**Abstract** Liquid crystalline polymers containing 1,2,3-triazole units as linking groups have been synthesized from the monomers containing triad ester diazide and flexible dialkyne ester by 1,3-cycloaddition reaction and were characterized. Click reaction of azide and alkyne functionals catalyzed by Cu(I) yielded target polyesters with 1,2,3-triazole groups. The structure of the polymer was confirmed by spectral techniques. GPC analysis reveals that the polymers have moderate molecular weight with narrow distribution. Hot stage optical polarizing microscopic investigation confirms the liquid crystalline nature of the polymers with lengthy flexible spacers, while the short chain containing polymers does not show the mesomorphic properties. Differential scanning calorimetric analysis confirms the formation of mesophase in some of the polymers, and it is in accordance with the microscopic results. Thermal stabilities of the polymers were analyzed by thermogravimetric analysis.

**Keywords:** Triazole; Click chemistry; Main chain polymers; Azide-alkyne cycloaddition; Liquid crystalline polymers.

### INTRODUCTION

The studies of mesomorphic properties of liquid crystalline polymers have gained tremendous impetus owing to their applications in hi-tech areas. Several reports have appeared in the literature on *para*-linked aromatic liquid crystalline polymers with aliphatic methylene spacers<sup>[1, 2]</sup>. The effects of methylene spacers and various substituents in the aromatic moiety of the main chain liquid crystalline polymers with respect to physical properties have been well documented. The effect of introduction of lateral substitution in the spacer group in both conformational characteristics and transition temperatures has been studied<sup>[3–6]</sup>. Any alteration in the length of the methylene spacer and incorporation of any polar group seriously affect the molecular parameter. Several reports have appeared on the spacer containing hetero atoms like Si, P, O and N along with or without methylene chain<sup>[7–10]</sup>.

To date, the coupling reaction was found to be achievable through the emerging field of “click reactions”. The term “click chemistry” was coined by Sharpless *et al.* in the synthetic chemistry which is a 1,3-dipolar cycloaddition reaction of organoazides and alkynes to provide heterocyclic five membered rings. Huisgen *et al.*<sup>[11]</sup> investigated the 1,3-dipolar cycloaddition of alkynes with azides in the presence of catalytic amount of Cu(I) yielding 1,2,3-triazoles. This has sought much attention because of the synthetic importance of the aromatic and non-aromatic five-membered heterocycles, the quantitative yields, low susceptibility to side reactions, easily applicable reaction conditions, moderate temperature and tolerance to oxygen and moisture. This click chemistry has found many applications in organic chemistry, drug discovery, bioconjugations, *etc.*, some click reactions have already been successfully used in polymers and in materials chemistry such as in the

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efficient preparation of well-defined polymeric tetrazoles or dendrimers, amphiphilic block copolymers, cross-linked block copolymer vesicles, adhesives for metals, *etc.* In general, polymers have to be synthesized in moisture free solvent, the presence of which may terminate the polymerization process in many cases *viz.*, metathesis, gas transfer radical polymerization, free radical addition polymerization and atom transfer radical polymerization. But in the case of copper catalyzed 1,3-cycloaddition, the process was not affected by the presence of water and in fact, it promotes the solubility of the catalyst and hence enhances the catalytic activity.

The applications in materials science are especially interesting. However, most of them were focused on the preparation of dendronized polymers<sup>[12, 13]</sup> and conjugated polymers<sup>[14]</sup> or in the incorporation of 1,2,3-triazole rings into polymers by graft polymerization<sup>[15–17]</sup>. The 1,2,3-triazole ring was seldom incorporated into the backbone of linear polymers<sup>[18–20]</sup>, as the stable 1,4-disubstituted 1,2,3-triazoles could be formed as part of the polymer<sup>[21–23]</sup>. In this investigation, our aim is to utilize the click reaction to synthesize polymers from monomers having diazide and dialkyne end groups. Here, we have synthesized a diazide compound and have coupled it with several dialkynes to get a series of polymers with liquid crystalline properties.

## EXPERIMENTAL

### Materials

The solvents such as benzene, methanol, ethanol, dichloromethane and acetone were purified as per reported procedure<sup>[24]</sup>. HBr 47% (SRL), 1,6-hexanediol (Merck), potassium hydroxide, sodium hydroxide, potassium carbonate, hydrochloric acid (SD fine & Merck Mumbai), 4-hydroxybenzoic acid, *N,N*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP) and hydroquinone were used as received.

### Measurements

The chemical structure of the intermediates and target materials were analyzed by infrared spectrophotometer (Nicolet 380 FT-IR) using KBr pellets and nuclear magnetic resonance spectrophotometer (Joel EX-400 FTNMR) in CDCl<sub>3</sub> with TMS as an internal standard. Thin layer chromatography was performed with Merck pre-coated TLC sheets GF<sub>254</sub>, and the spots were detected by UV irradiation or by spraying 50% alcoholic H<sub>2</sub>SO<sub>4</sub> and visualizing after heat treatment in the hot air oven. Thermal properties, phase transition temperatures and enthalpies were determined by differential scanning calorimeter (Perkin-Elmer DSC-7) at a heating rate of 5 K/min. The liquid crystalline properties of all the compounds were studied by using a Euromax polarizing microscope equipped with a Linkem HFS91 heating stage and a TP93 temperature programmer. Small quantities of the samples were sandwiched between two thin cover slips and placed on a heating stage interfaced with programmer. The anisotropic properties of the samples were investigated through microscope with controlled heating/cooling at the rate of 5 K/min. The photographs were taken with a Nikon FM10 camera, exposed on a Konica film. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) equipped with Styrogel columns. GPC measurements were carried out using THF as eluent with a 1.0 mL/min flow rate. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer model TGA Pyris 1 system at a heating rate of 20 K/min in N<sub>2</sub> atmosphere.

### Synthesis of Precursors and Monomers

#### Synthesis of 1,6-dibromohexane (**1**)

A 500 mL three necked round-bottom flask fitted with a Dean and Stark apparatus and a reflux condenser was charged with 1,6-hexane diol (0.12 mol) and benzene (250 mL) and heated to reflux. Then HBr 47% (0.2 mol) was added to it drop wise for half an hour. The heating was then continued until the water removal ceased through Dean and Stark apparatus. Then the benzene layer was washed with 150 mL of 6 mol/L sodium hydroxide solutions, followed by 150 mL of 1 mol/L hydrochloric acid solution. The organic layer was dried over anhydrous sodium sulphate, the solvent was removed and the oil was purified by chromatography over silicagel with hexane to give the targeted compound **1** as colorless oil. Yield 80%.

IR (KBr):  $\nu = 2936, 644 \text{ cm}^{-1}$ . <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 3.39$  (t, 4H, Br—CH<sub>2</sub>),

1.90 (m, 4H, CH<sub>2</sub>), 1.39 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 33.94, 31.49, 27.20.

#### Synthesis of methyl 4-hydroxy benzoate (2)

4-Hydroxy benzoic acid (0.1 mol) was placed in a 500 mL round bottom flask. To this, 100 mL of methanol and 3 mL of concentrated sulphuric acid were added. The reaction mixture was refluxed for 12 h, cooled to room temperature and was poured in ice cooled water. Precipitated solid was washed several times with water to remove the traces of acid and was crystallized using aqueous alcohol. Yield 78%.

IR (KBr):  $\nu$  = 3638 (—OH), 3128 (—C—H), 1735 (C=O), 1474 (C=C), 1110 cm<sup>-1</sup> (—C—O). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 7.82 (d, 2H, Ar), 6.86 (d, 2H, Ar), 5.09 (s, 1H, OH), 3.82 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.09, 163.01, 133.92, 122.98, 116.05, 51.92.

#### Synthesis of methyl 4-[(6-bromohexyl)oxy] benzoate (3)

Methyl 4-hydroxy benzoate (0.01 mol) was dissolved in acetone (100 mL). To this finely powdered anhydrous potassium carbonate (0.3 mol) and potassium iodide (100 mg) were added, and the mixture was refluxed. After half an hour, 1,6-dibromohexane (0.1 mol) was added drop wise to the refluxing mixture over a period of 30 min. It was refluxed for 3 days and was filtered. The precipitated solid was washed with acetone, and the washings were added to the filtrate. The solvent was removed under vacuum, and the solids obtained were purified by column chromatography using chloroform as eluent. Yield 56%.

IR (KBr):  $\nu$  = 2939 (—C—H), 1733 (—C=O), 1608 (C=C), 1191 (C—O—C), 699 cm<sup>-1</sup> (C—Br). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 7.84 (d, 2H, Ar), 6.85 (d, 2H, Ar), 3.98 (t, 2H, O—CH<sub>2</sub>), 3.81 (s, 3H, —COOCH<sub>3</sub>), 3.58 (t, 2H, Br—CH<sub>2</sub>—), <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.05, 161.01, 130.98, 119.95, 115.12, 69.25, 51.94, 34.18, 32.60, 29.67, 27.89, 25.01

#### Synthesis of methyl 4-[(6-azidohexyl)oxy]benzoate (4)

Methyl 4-[(6-bromohexyl)oxy]benzoate (0.015 mol) was dissolved in dimethylsulphoxide in a 250 mL round bottom flask equipped with a stirrer and a thermometer. To this, sodium azide (0.06 mol) was added, and stirring was continued for 12 h at 50°C. The reaction mixture was poured in water and was extracted with dichloromethane. The organic layer was washed several times with water to remove DMSO traces. It was then dried over anhydrous sodium sulphate, filtered and the solvent was removed under reduced pressure. The product was purified with column chromatography using dichloromethane as eluent.

IR (KBr):  $\nu$  = 2948 (—C—H), 2107 (N<sub>3</sub>), 1736 (—C=O), 1602 (C=C), 1259 (Aromatic O—CH<sub>2</sub>), 1154 cm<sup>-1</sup> (C—O—C). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 7.81 (d, 2H, Ar), 6.83 (d, 2H, Ar), 4.1 (t, 2H, N<sub>3</sub>—CH<sub>2</sub>), 3.68 (s, 3H, COOCH<sub>3</sub>), 3.89 (t, 2H, O—CH<sub>2</sub>), 1.83–1.21 (m, 10H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.05, 161.03, 130.97, 119.96, 115.14, 69.27, 51.69, 51.24, 30.62, 26.64, 25.09, 24.09.

#### Synthesis of 4-[(6-azidohexyl)oxy]benzoic acid (5)

Methyl 4-[(6-azidohexyl)oxy]benzoate (0.1 mol) was placed in a one-liter single necked round bottom flask equipped with a condenser. Ethanol (150 mL) and sodium hydroxide (0.24 mol) dissolved in distilled water (150 mL) were added to the flask. The solution was refluxed for 6 h, and excess alcohol was removed under reduced pressure. It was then neutralized with 1 mol/L hydrochloric acid. The precipitated solids were crystallized with alcohol. Yield 73%.

IR (KBr):  $\nu$  = 3324 (—OH), 2097 (N<sub>3</sub>), 1713 (—C=O), 1255 (Aromatic O—CH<sub>2</sub>), 1108 (C—O—C), 1607 cm<sup>-1</sup> (C=C). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 11.02 (s, 1H), 8.15 (d, 2H), 7.01 (d, 2H), 3.98 (t, 2H), 1.84–1.86 (m, 2H), 1.26–1.30 (m, 8H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.55, 163.11, 130.91, 122.91, 115.23, 69.36, 51.99, 30.75, 28.69, 25.98, 24.56.

#### Synthesis of 1,4-bis[(6-azidohexyloxy)-4-carbonyloxy]benzene (6)

4-[(6-Azidohexyl)oxy]benzoic acid (0.0045 mol), hydroquinone (0.002 mol) and 4-(dimethylamino)pyridine (DMAP) (0.001 mol) were dissolved in dry dichloromethane (25 mL). To this solution, dicyclohexylcarbodiimide (DCC) (0.005 mol) was added, and the resulting mixture was stirred at room temperature for 5 h under N<sub>2</sub> atmosphere. The precipitated urea was removed by filtration, and the filtrate was washed with 5%

acetic acid (3 × 50 mL) and saturated NaCl (3 × 50 mL) followed by water. The organic layer was dried over anhydrous sodium sulphate, and the solvent was removed under reduced pressure. The solid obtained was purified by column chromatography using chloroform as eluent, and recrystallised from ethanol to give a white crystalline solid. Yield 90%.

IR (KBr):  $\nu$  = 2097 (N<sub>3</sub>), 2934 (—CH), 1713 (—C=O), 1604 (C=C), 1255 (C—O), 1106 cm<sup>-1</sup> (C—O—C). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 8.08(d, 4H), 7.17 (d, 4H), 6.93 (d, 4H), 3.96 (t, 4H), 1.80–1.82 (m, 4H), 1.29–1.33 (m, 16H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.75, 163.06, 139.88, 129.69, 121.23, 115.55, 69.16, 51.58, 30.44, 28.45, 24.39.

#### Synthesis of diprop-2-ynyl succinate (**8a**)

Succinoyl chloride (0.01 mol) was dissolved in 50 mL of dry tetrahydrofuran, and the mixture was cooled to 10°C. Propargyl alcohol (0.025 mol) dissolved in 50 mL of dry tetrahydrofuran was added to the mixture drop wise in such a way that the temperature of the reaction mixture was maintained at around 10–15°C, followed by dry triethylamine (TEA) (0.025 mol). The mixture was slowly brought to room temperature and stirred for further 12 h under nitrogen atmosphere. Precipitated TEA-hydrochloride was filtered, and the solvent was completely removed. The reaction mixture was filtered to remove the precipitated triethylamine hydrochloride and was washed with THF, and the washings were collected. The solvent was removed by vacuum, and the crude product was dissolved in minimum amount of chloroform and was chromatographed over silica-gel with chloroform as eluent. Yield 85%. All the homologous compounds (**8b–8e**) were prepared using other acid chlorides (ClCO(CH<sub>2</sub>)<sub>n</sub>COCl, *n* = 4, 6, 8, 10).

Compound **8a**: IR (KBr): 3292 (HC≡CH), 2920 (—CH<sub>2</sub>—), 1739 (—C=O), 1252 cm<sup>-1</sup> (—C—O). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 2.53 (t, 4H), 1.86 (s, 2H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.65, 72.60, 46.44, 27.36.

Compound **8b**: IR (KBr): 3294 (HC≡CH), 2952 (—CH<sub>2</sub>—), 1741 (—C=O), 1257 cm<sup>-1</sup> (—C—O). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 2.24 (t, 4H), 1.86 (s, 2H), 1.58 (m, 4H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.65, 72.60, 46.44, 32.87, 23.95.

Compound **8c**: IR (KBr): 3299 (HC≡CH), 2948 (—CH<sub>2</sub>—), 1727 (—C=O), 1240 cm<sup>-1</sup> (—C—O). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 2.24 (t, 4H), 1.85 (s, 2H), 1.57–1.58 (m, 6H), 1.30–1.32 (m, 4H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.65, 72.61, 46.44, 32.86, 28.96, 24.91.

Compound **8d**: IR (KBr): 3290 (HC≡CH), 2962 (—CH<sub>2</sub>—), 1749 (—C=O), 1223 cm<sup>-1</sup> (—C—O). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 2.24 (t, 4H), 1.86 (s, 2H), 1.57–1.58 (m, 4H), 1.30–1.32 (m, 2H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.65, 72.61, 46.43, 32.85, 28.96, 24.92.

Compound **8e**: IR (KBr): 3295 (HC≡CH), 2948 (—CH<sub>2</sub>—), 1755 (—C=O), 1288 cm<sup>-1</sup> (—C—O). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 2.25 (t, 4H), 1.86 (s, 2H), 1.57–1.58 (m, 4H), 1.30–1.32 (m, 4H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.66, 72.61, 46.43, 32.85, 28.95, 24.91.

#### Synthesis of polymers (**9**)

To a 50 mL three-necked round-bottom flask equipped with a magnetic stirrer and a thermometer, compounds **6** (0.001 mol), **8a** (0.001 mol), and 25 mL of tertiary butanol:THF (1:5 V/V) mixture were added. To the solution, CuI (20 wt%) was added with stirring. The resulting mixture was stirred at room temperature for 10–12 h. The precipitate formed was dissolved by adding another 2–5 mL of THF and was stirred overnight. The mixture was heated to 50°C over a water bath with stirring for another one day. The precipitate formed was filtered and dissolved in chloroform, and the organic layer was washed with water and liquid ammonia and was filtered. The filtrate was concentrated to syrupy mass and precipitated using methanol. The polymer thus obtained was purified by repeated precipitation using chloroform and methanol. The precipitate was dried in vacuum oven. The similar procedure was used to prepare other polymers in the homologous series using corresponding dialkynes (**8a–8e**) and the compound **6**. Yield 85%–90%.

Polymer **9a**: IR (KBr): 3138 (=C—H), 2948 (—CH<sub>2</sub>—), 1755 (—C=O), 1604 (C=C), 1288 (—C—O), 1106 cm<sup>-1</sup> (C—O—C). <sup>1</sup>H-NMR (CDCl<sub>3</sub> 400 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta$  = 8.08 (d, 4H), 7.18 (d, 1H), 7.17 (d,

4H), 6.91 (d, 4H), 5.35 (s, 4H), 3.97–4.00 (m, 4H), 3.21–3.24 (m, 4H), 1.20–2.08 (m, 24H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.9, 164.7, 163.4, 148.3, 142.8, 132.3, 122.6, 121.4, 120.5, 114.2, 68.0, 63.2, 51.3, 49.4, 34.0, 33.5, 29.0, 26.4, 25.5, 25.4, 24.5.

Polymer **9b**: IR (KBr): 3130 ( $=\text{C}-\text{H}$ ), 2944 ( $-\text{CH}_2-$ ), 1743 ( $-\text{C}=\text{O}$ ), 1609 ( $\text{C}=\text{C}$ ), 1295 ( $-\text{C}-\text{O}$ ),  $1124\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$  400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 8.06 (d, 4H), 7.18 (d, 1H), 7.17 (d, 4H), 6.91 (d, 4H), 5.35 (s, 4H), 3.97–4.00 (m, 4H), 3.21–3.24 (m, 4H), 1.20–2.11 (m, 284H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.9, 164.6, 163.4, 148.23, 142.8, 132.13, 122.56, 121.6, 120.5, 114.2, 68.1, 63.2, 51.3, 49.4, 34.1, 33.5, 29.0, 26.3, 25.5, 25.4, 24.2

Polymer **9c**: IR (KBr): 3138 ( $=\text{C}-\text{H}$ ), 2948 ( $-\text{CH}_2-$ ), 1756 ( $-\text{C}=\text{O}$ ), 1604 ( $\text{C}=\text{C}$ ), 1279 ( $-\text{C}-\text{O}$ ),  $1106\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$  400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 8.08 (d, 4H), 7.17 (d, 1H), 7.17 (d, 4H), 6.91 (d, 4H), 5.35 (s, 4H), 3.97–4.00 (m, 4H), 3.21–3.24 (m, 4H), 1.20–2.13 (m, 32H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.9, 164.7, 163.4, 148.3, 142.7, 132.3, 122.6, 121.4, 120.4, 114.3, 68.0, 63.1, 51.3, 49.4, 34.0, 33.5, 29.0, 26.4, 25.5, 25.3, 24.5.

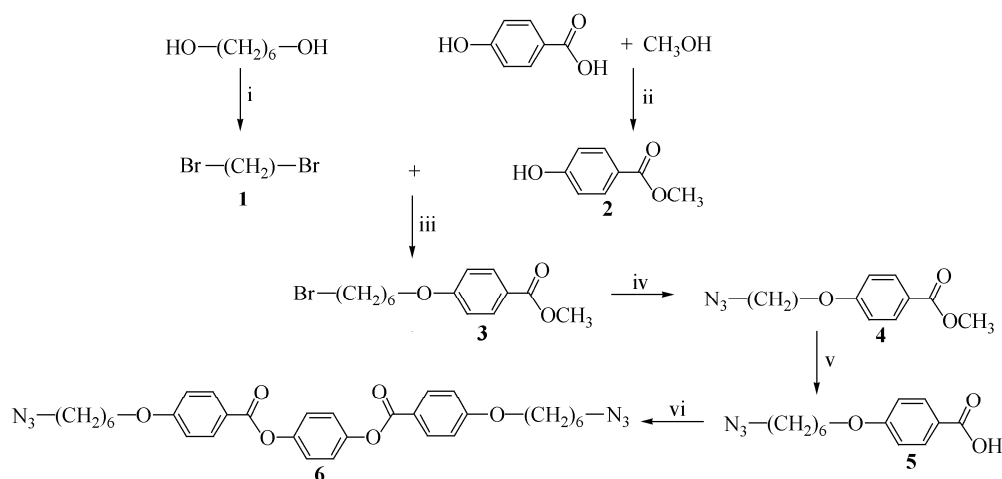
Polymer **9d**: IR (KBr): 3138 ( $=\text{C}-\text{H}$ ), 2948 ( $-\text{CH}_2-$ ), 1755 ( $-\text{C}=\text{O}$ ), 1604 ( $\text{C}=\text{C}$ ), 1287 ( $-\text{C}-\text{O}$ ),  $1106\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$  400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 8.07 (d, 4H), 7.18 (d, 1H), 7.17 (d, 4H), 6.91 (d, 4H), 5.35 (s, 4H), 3.97–4.00 (m, 4H), 3.21–3.24 (m, 4H), 1.20–2.14 (m, 36H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.9, 164.7, 163.5, 148.3, 142.7, 132.3, 122.5, 121.4, 120.5, 114.2, 68.0, 63.2, 51.3, 49.4, 34.2, 33.5, 28.9, 26.4, 25.5, 25.6, 24.5.

Polymer **9e**: IR (KBr): 3138 ( $=\text{C}-\text{H}$ ), 2948 ( $-\text{CH}_2-$ ), 1755 ( $-\text{C}=\text{O}$ ), 1604 ( $\text{C}=\text{C}$ ), 1287 ( $-\text{C}-\text{O}$ ),  $1106\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$  400 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , TMS):  $\delta$  = 8.06 (d, 4H), 7.16 (d, 1H), 7.17 (d, 4H), 6.91 (d, 4H), 5.35 (s, 4H), 3.97–4.00 (m, 4H), 3.21–3.24 (m, 4H), 1.20–2.14 (m, 40H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.9, 164.8, 163.4, 148.3, 142.7, 132.4, 122.6, 121.4, 120.2, 114.2, 68.0, 63.1, 51.3, 49.2, 34.0, 33.5, 29.0, 26.4, 25.3, 25.4, 24.5.

## RESULTS AND DISCUSSION

### Synthesis

The general strategy applied for the synthesis of the novel functionalized azide monomer **1**, 4-bis[(6-azidoheptyl)oxy]-4-carboxybenzoate (**6**) is shown in Scheme 1. 1,6-Dibromohexane (**1**) was prepared from hexanediol by halogen displacement reaction. The subsequent *O*-alkylation of 4-hydroxymethylbenzoate (**2**) with 1,6-dibromohexane was used to give methyl 4-[(6-bromohexyl)oxy]benzoate (**3**). Methyl 4-[(6-azidoheptyl)oxy]-

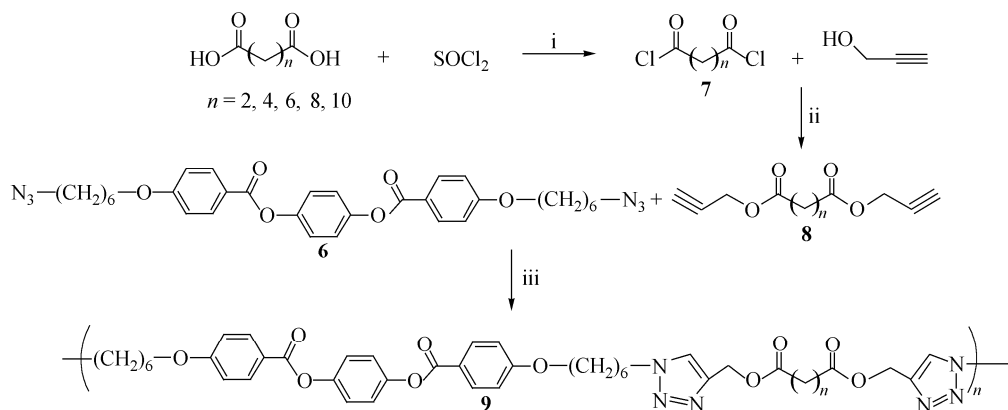


**Scheme 1** Synthesis of diazide monomer

Reagents: i) HBr, benzene; ii)  $\text{H}^+$ ; iii)  $\text{K}_2\text{CO}_3/\text{KI}$ , acetone; iv)  $\text{NaN}_3$ , DMSO; v) KOH/Ethanol; vi) Hydroquinone, DCC, DMAP

benzoate (**4**) was prepared from compound **3** by reacting  $\text{NaN}_3$  at room temperature. Then the deprotection of methyl group of **4** was achieved by alkaline hydrolysis to give 4-[(6-azidohexyl)oxy]benzoic acid (**5**). The monomer **6** was synthesized by the esterification of compound **5** and quinol as shown in Scheme 1.

$\alpha,\omega$ -Dipropargylic succinate (**8**) was prepared from propargyl alcohol and acid chloride in the presence of TEA and THF as shown in Scheme 2. The linear main chain polymers containing 1,2,3-triazole rings were synthesized from monomers **6** and **8a–8e** respectively. Polymerization reactions were carried out through ‘click reaction’ at room temperature. All the triazole based polymers (**9a–9e**) were synthesized (Scheme 2) by addition polymerization *via* Huisgen [3 + 2] cycloaddition with good yield.



**Scheme 2** Synthesis of polymers

Reagents: i) Benzene, DMF (1 drop); ii) THF, TEA; iii)  $\text{CuI}$ , *t*-butanol/water

## Characterization

### Spectral characterization

All the monomers and polymers were characterized by various spectral techniques confirming the molecular structure of the precursors, monomers and polymers. The formation of diazido compound (**6**) was confirmed by the appearance of strong absorption at  $2097\text{ cm}^{-1}$  in IR spectroscopy ascribed to azide function. Further it was confirmed by a downfield shift of methylene proton ( $\delta$  3.96) attached near to azido group than that of methylene proton attached to ether linkage of the compound **6** in NMR spectroscopy. The alkyne group of other monomer (compound **8a–8e**) was confirmed by absorption of a band at  $3926\text{ cm}^{-1}$  in IR spectroscopy and appearance of acetylenic proton in NMR spectroscopy at  $\delta = 2.53$ . The polymerization reaction was confirmed by the formation of 1,2,3-triazole rings in the chain. It was identified by observing strong stretching absorption at  $3137\text{ cm}^{-1}$  due to triazole ring C–H stretching and disappearance of  $3292\text{--}3295\text{ cm}^{-1}$  and  $2097\text{ cm}^{-1}$  ascribed to propargyl and azide functionality in FT-IR spectroscopy as shown in Fig. 1. Further, it was confirmed by the resonance signals at  $\delta = 7.18$  and at  $\delta = 148.3, 132.2$  of triazole carbons in the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra respectively (Fig. 2). The yield of the polymers were nearly quantitative and are soluble in THF,  $\text{CHCl}_3$ , DMF and DMSO and insoluble in organic solvents like methanol, ethanol and other non-polar/hydrocarbon solvents.

### Molecular weight

GPC analyses showed that the number-average molecular weight of the polymers was in the range of 25000–28000. It reveals that the degree of polymerization is moderate, and the average repeating unit of the monomers in the chain amounts to 20–25. In order to improve the molecular weight of the polymer, the polymerization experiment was conducted at  $50\text{--}60^\circ\text{C}$  and  $60\text{--}70^\circ\text{C}$  to enhance the solubility of the polymers. The GPC analysis showed no marked improvement in molecular weight, and this may be due to the precipitation of the polymer and the insolubility in presence of even small amounts of alcoholic solvents. The experiment was carried out in other polar solvents in neat form (THF, isopropyl ether, dibutyl ether) as well as in the mixed form

with a small amount of highly polar aprotic solvents (DMF), and both ended with the same result. The polydispersity index (PDI) of the samples was in the range of 1.2–1.5, indicating the selectivity of the azide alkyne coupling reaction.

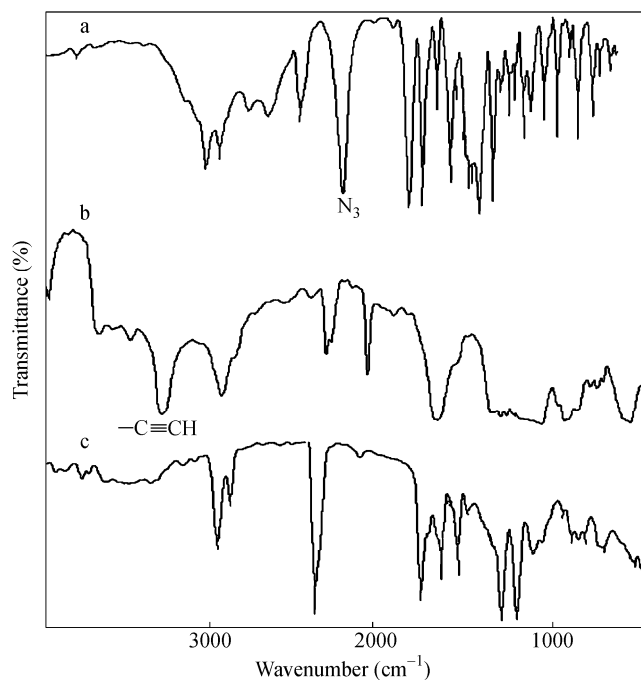


**Fig. 1** IR spectra of (a) azide monomer, (b) alkyne monomer and (c) polymer **9a**

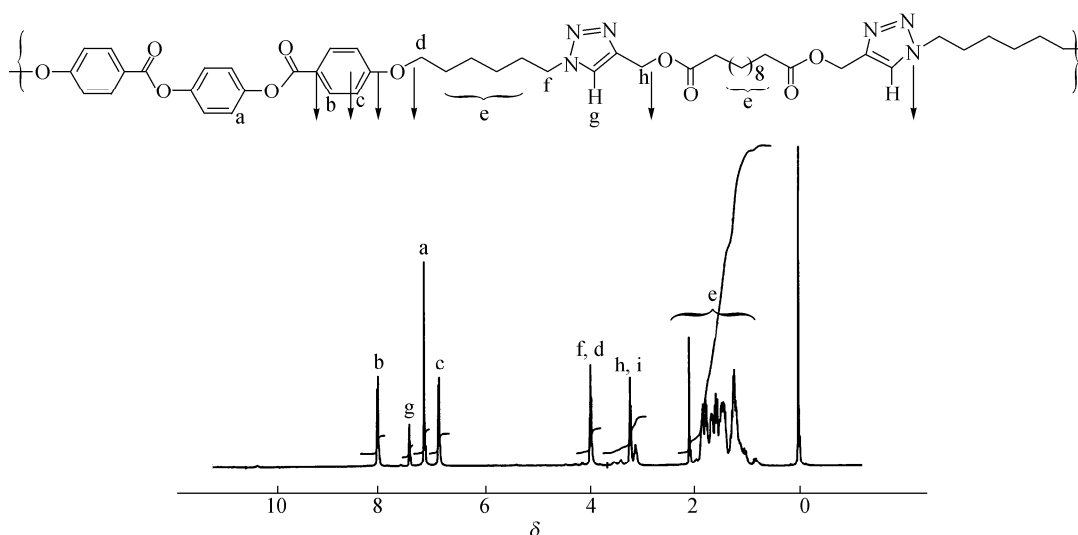


**Fig. 2**  $^1\text{H}$ -NMR spectroscopy of polymer **9e**

#### Thermal stability

Thermogravimetric (TGA) traces of the polymers obtained in nitrogen atmosphere are furnished in Fig. 3. The temperature corresponding to 10% and 50% weight loss as well as the char residue at 600°C is summarized in

Table 1. The data reveal that the polymers were stable up to 291–328°C, and 50% weight loss was taking place at around 363–425°C. All the polymers undergo single stage decomposition. The char yield at 600°C was in the range of 10%–17%. Among these polymers, polymer **9a** showed maximum thermal stability than all others. Also, the thermal stability decreases with increase in the methylene chain in monomer (**8a–8e**) due to added aliphatic carbon which enhances the thermal oxidation. The results of the thermal analysis demonstrated that the resulting poly(alkyl aryl) esters had good thermal stability and melting fluidity which would be suitable for application and processing.

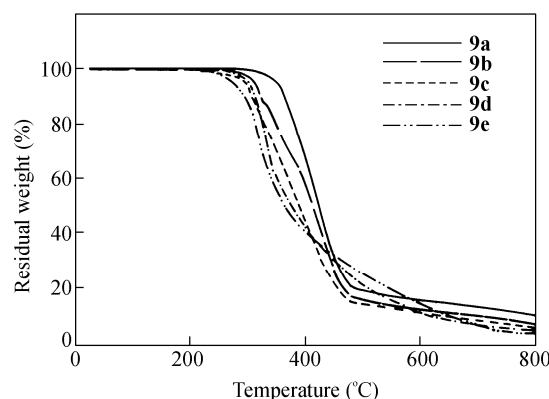


Fig. 3 TGA traces of polymers **9a–9e**

Table 1. Thermogravimetric analysis of polymers **9a–9e**

| Polyme<br>r | $M_n^a$ | 10% weight<br>loss<br>(°C) | 50% weight<br>loss<br>(°C) | Char yield at 800°C |
|-------------|---------|----------------------------|----------------------------|---------------------|
| <b>9a</b>   | 28781   | 328                        | 425                        | 10.7                |
| <b>9b</b>   | 27562   | 320                        | 417                        | 8.6                 |
| <b>9c</b>   | 26693   | 313                        | 390                        | 6.8                 |
| <b>9d</b>   | 26146   | 302                        | 375                        | 5.5                 |
| <b>9e</b>   | 25551   | 219                        | 363                        | 4.7                 |

<sup>a</sup> GPC in THF versus polystyrene at 35°C

#### Liquid crystalline properties

Liquid crystalline properties of the monomers and polymers were investigated using a hot stage polarizing microscope (HOPM). Monomer **6** shows simple melting at 280°C which does not show any mesomorphic characteristics. It may be due to the permanent dipole of the azide group at both ends of the compound which produces ionic interaction between the molecules that increases the crystallinity of the molecules. But after polymerization, the ionic end groups were converted to triazole rings leading to the loss of high polar aggregations. Microscopic investigation during heating of the polymers **9c–9e** showed two thermal transitions, one was at melting and the other one at isotropic transition. On cooling from isotropic melt it forms grainy liquid crystalline mesophase which is presented in the Fig. 4. The grain size of the liquid crystalline texture did not improve much, which could be due to the viscosity of the sample and the non-mesogenic triazole ring present in the spacer segment. Polymers **9a** and **9b** showed only the melting transition and failed to exhibit the mesomorphic behavior which may be due to the short spacer between two adjacent triazole rings in the polymer. The polar and electronic interaction generated by three nitrogen atoms of triazole rings could be the major reason for mesophase extinction.

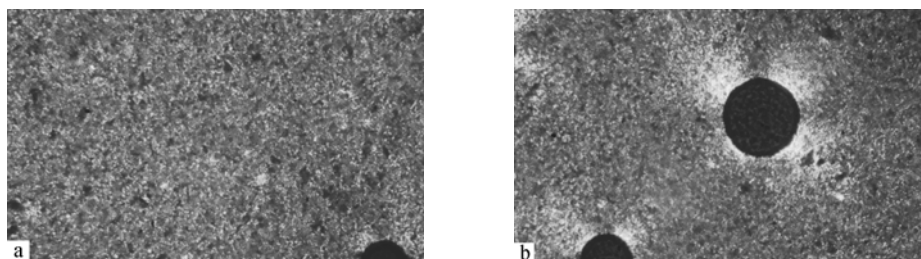


**Fig. 4** Polarizing microscopic pictures of (a) polymer **9d** and (b) polymer **9e** on cooling from isotropic melt

DSC thermal analysis was performed in nitrogen atmosphere at a heating rate of 10 K/min, the results are summarized in Table 2, and the traces of thermograms are shown in Fig. 5. Polymers **9c–9e** showed two endothermic peaks corresponding to melting transition ( $T_m$ ) and isotropic transition temperature ( $T_i$ ), respectively, which confirms the liquid crystalline nature of the sample. The data reveal that the  $T_m$  decreases with increase in the spacer length. But the mesophase stability increases with increase in spacer length. It is also noted that, even a reduction of a single carbon in the methylene chain affects the mesophase stability considerably by around 30–40°C.

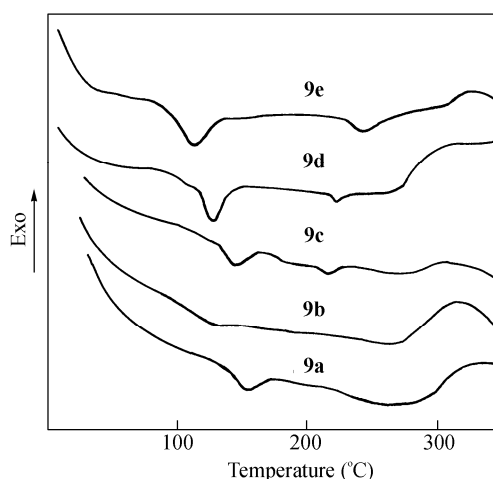


**Fig. 5** DSC traces of polymers **9a–9e**

**Table 2.** DSC analysis of polymers **9a–9e**

| Polymer   | $T_m$ (°C) | $T_i$ (°C) | $\Delta T$ (°C) |
|-----------|------------|------------|-----------------|
| <b>9a</b> | 160        | —          | —               |
| <b>9b</b> | 130        | —          | —               |
| <b>9c</b> | 150        | 220        | 70              |
| <b>9d</b> | 130        | 240        | 110             |
| <b>9e</b> | 110        | 250        | 140             |

## CONCLUSIONS

A series of 1,2,3-triazole ring containing polyesters with different spacer lengths ( $n = 2, 4, 6, 8$  and  $10$ ) were synthesized using ‘click reaction’. The structures of polyesters were confirmed by usual spectroscopic techniques. The average molecular weights of these polymers were moderate as evidenced by GPC. It was also noted that the molecular weight of the polymers were not improved by usual techniques such as change of solvent, increase in temperature and modification of polarity. TGA analysis clearly exhibits the thermal stability and showed that the  $T_m$  and  $T_i$  of the polymers increased with a decrease in the methylene chain. Among these

five polymers, only three polymers exhibited liquid crystalline characters, and the remaining two showed only simple melting characteristics. The mesophase formation was further confirmed by differential scanning calorimetric analysis.

## REFERENCES

- 1 Demus, D., Goodby, J., Gray, G.W., Speices, H.W. and Vill, V., "Hand Book of Liquid Crystals", Vol. 3, New York, Wiley-VCH, 1998, p.26
- 2 Donald, A.M. and Windle, A.H., "Liquid Crystalline Polymers", Cambridge University Press, Cambridge, London, 1995, Chapter 2
- 3 Meurisse, P., Noel, C., Monner, L. and Fayolle, B., Br. Polym. J., 1980, 13: 55
- 4 Jin, J.L., Autoun, S., Ober, C.K. and Lenz, R.W., Br. Polym. J., 1980, 12: 132
- 5 Chiellini, E., Galli, G., Carrozzino, S. and Gallot, B., Macromolecules, 1990, 23: 2106
- 6 Craig, A.A. and Imrie, C.T., Macromolecules, 1995, 28: 3617
- 7 Aharoni, S.M., Macromolecules, 1988, 21: 1941
- 8 Aquilera, C., Bartulin, J., Hisgen, B. and Ringsdorf, H., Makromol. Chem., 1983, 184: 253
- 9 Galli, G., Laus, M., Chiellini, E., Ober, C.K. and Lenz, R.W., Makromol. Chem., 1982, 183: 2963
- 10 Angeloni, A.S., Caretti, D., Laus, M., and Chiellini, E., Polym. J., 1988, 20: 1157
- 11 Huisgen, R., Angew. Chem. Int. Ed. Engl., 1963, 2: 565
- 12 Scheel, A.J., Komber, H. and Viot, B.I., Macromol. Rapid Commun., 2004, 25: 1175
- 13 Wu, P., Feldman, A.K., Nugent, A.K., Hawker, C.J., Scheel, A. and Voit, B., Angew. Chem. Int. Ed., 2004, 43: 3928
- 14 van Steenis, D.J.V.C., David, O.R.P., van Strijdonck, G.P.F., van Maarseveen, J.H. and Reek, J.N.H., Chem. Commun., 2005, 34: 4333
- 15 Helms, B., Mynar, J.L., Hawker, C.J. and Fréchet, J.M.J., J. Am. Chem. Soc., 2004, 126: 15020
- 16 Parrish, B., Breitenkamp, R.B. and Emrick, T., J. Am. Chem. Soc., 2005, 127: 7404
- 17 Carroll, J.B., Jordan, B.J., Xu, H., Erdogan, B., Lee, L. and Cheng, L., Org. Lett., 2005, 7: 2551
- 18 Opsteen, J.A. and van Hest, J.C.M., Chem. Commun., 2005, 1: 57
- 19 Díaz, D.D., Punna, S., Holzer, P., Mc Pherson, A.K., Sharpless, K.B. and Fokin, V.V., J. Polym. Sci. Part A: Polym. Chem., 2004, 42: 4392
- 20 Ossipov, D.A. and Hilborn, J., Macromolecules, 2006, 39: 1709
- 21 Wang, Z.X. and Qin, H.L., Chem. Commun., 2003, 19: 2450
- 22 Rostovtsev, V.V., Green, L.G., Fokin, V.V. and Sharpless, K.B., Angew. Chem. Int. Ed., 2002, 41: 2596
- 23 Tornøe, C.W., Christensen, C. and Meldal, M., J. Org. Chem., 2002, 67: 3057
- 24 Perrin, D.D. and Armarego, W.L.F., "Purification of Laboratory Chemicals", 3<sup>rd</sup> ed., Pergamon Press, New York, 2003