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Preparation and characterization of novel main-chain azobenzene polymers via step-growth polymerization based on click chemistry

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ABSTRACT

A novel α-azide and ω-alkyne A–B type azobenzene monomer, 3′-ethynylphenyl[4-(4-azidobutoxy)-phenyl]azobenzene (EAPA), was synthesized and used to generate a novel polymer via step-growth polymerization using 1,3-dipolar cycloaddition reaction under the catalysis of $CuSO_4 \cdot 5H_2O$/sodium ascorbate/H_2O ("Click" chemistry). The structure of the resultant main-chain azobenzene polymer, PEAPA, was characterized by GPC, ^{13}C NMR, UV–vis and FT-IR spectra. Thermal stability and crystallinity of PEAPA powder were studied by TGA and WAXD. The photo-induced *trans–cis* isomerization of PEAPA and EAPA in *N,N′*-dimethyl formamide (DMF) solution was investigated. Furthermore, the thermal *cis–trans* isomerizations of PEAPA and EAPA were also observed at 60 °C in dark. Thermal stability and *trans–cis–trans* isomerization behavior of PEAPA was compared with its non-triazole analog, PDHA.

1. Introduction

In recent years, polymeric materials containing azobenzene chromophore, e.g. azobenzene polymers, have gained a great deal of attention due to their unique optical *trans–cis–trans* isomerization [1]. These azobenzene polymers can be potentially applied in fascinating photo-responsive variations, such as optical data storage [2], liquid crystal displays [3], optical switching [4], holographic surface relief gratings (SRGs) [5] and so on. A large amount of papers about the designing and synthesizing azobenzene polymers have been reported in the last few years. The azobenzene chromophore can be incorporated into polymers and become side chains [6] or parts of the polymer main chains [7] via chemical reaction. It can also be introduced into polymer matrices via doping technique [8]. As compared with the side-chain approach, main-chain azobenzene polymers showed good thermal stability (high glass-transition temperature (T_g) and thermal decomposition temperature (T_d) [9]), which is one of the important factors responsible for their unique properties, such as nonlinear optical properties [10] and surface profile gratings [11]. However, few papers involved the synthesis of main-chain azobenzene polymers. The synthetic methods such as the conventional polycondensation [12], step-growth polymerization [13] and coupling polymerization [14] were used in preparing main-chain azobenzene polymers. Domenico Acierno et al. [12] reported the synthesis of main-chain azobenzene polymers by polycondensation reaction of dihydroxy azobenzenes and dichlorides in solution and also studied the liquid crystalline properties of the polymers. Xiaogong Wang et al. [15] developed a new synthetic method through two-stage azo-coupling reactions based on a novel AB_2 monomer. The obtained hyperbranched main-chain azobenzene polymers were used to prepare SRGs.

In 2001, Sharpless and his co-workers successfully optimized the reaction of azide and terminal alkyne leading to 1,2,3-triazole via copper(I) catalysis, subsequently named as one of "click" chemistry [16]. This concept of popular reaction has drawn widespread attention due to its high efficiency, quantitative yields and selectivity under mild reaction conditions. These advantages have been particularly useful in the area of polymer chemistry. Polymers with different topologic structures, including linear, block, star polymers and dendrimers, have been reported [17]. This technique has also been widely used in materials science, such as bioconjugates and versatile functional polymers [17]. In very recent years, click reactions have also been used for the synthesis of linear main-chain polytriazoles by the step-growth polymerization. Fokin et al. [18] successfully synthesized a series of dialkyne and diazide monomers, by which linear polymers were prepared via the step-growth click polymerization, and the obtained polytriazoles were found to be insoluble in most solvents. Meudtner and Hecht [19] reported the preparation of alternating triazole–pyridine/benzene copolymers based on AA + BB step-growth polymerization process via click chemistry and a polymer of low molecular weight ($M_n = 2000$ g/mol) was obtained. Drockenmuller and his co-workers [20] reported the click polymerization of A–B type

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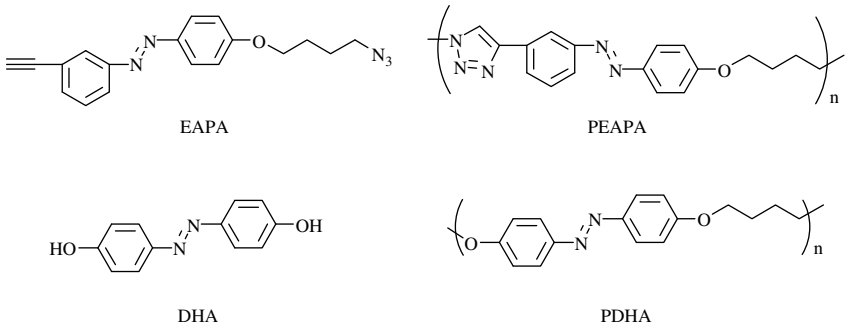


Scheme 1. Chemical structures of monomer 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA), polymer PEAPA, monomer 4,4′-dihydroxyazobenzene and polymer PDHA.

monomers with copper(I) catalysis, yielding polymers with M_n values of 13 000 g/mol. During preparation of this paper, we noticed a paper just published by Takasu et al. They synthesized polyesters with different structures through click reaction [21]. The obtained polyesters with molecular weight varying from 10 000 to 70 000 g/mol showed improved thermal properties.

To the best of our knowledge, there have been few accounts of main-chain azobenzene polymers prepared by step-growth polymerization using "click" chemistry in the literature [22]. Herein, we reported on the synthesis of a novel A–B type azobenzene monomer containing α-azide and ω-alkyne groups, 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA) (Scheme 1). Then, poly(EAPA) (PEAPAs) were successfully prepared by one-pot step-growth polymerization via click chemistry. Thermal properties and photo-induced *trans–cis–trans* isomerization of PEAPAs were investigated against with non-triazole analog, PDHA (Scheme 1).

2. Experimental section

2.1. Materials

3-Ethynylaniline (≥98%; Aldrich), phenol (analytical reagent; Shanghai Chemical Reagent Co. Ltd, Shanghai, China), 2-bromoisobutyryl bromide (98%; Aldrich), 1,4-dibromobutane (analytical reagent; Shanghai Chemical Reagent Co. Ltd, Shanghai, China), and sodium azide (≥99.5%; Aldrich) were used as received. Dimethyl formamide (DMF; analytical reagent; Shanghai Chemical Reagent Co. Ltd, Shanghai, China) was purified by vacuum distillation over anhydrous calcium hydroxide (CaH_2) before use. Other reagents were purified using standard procedure before use.

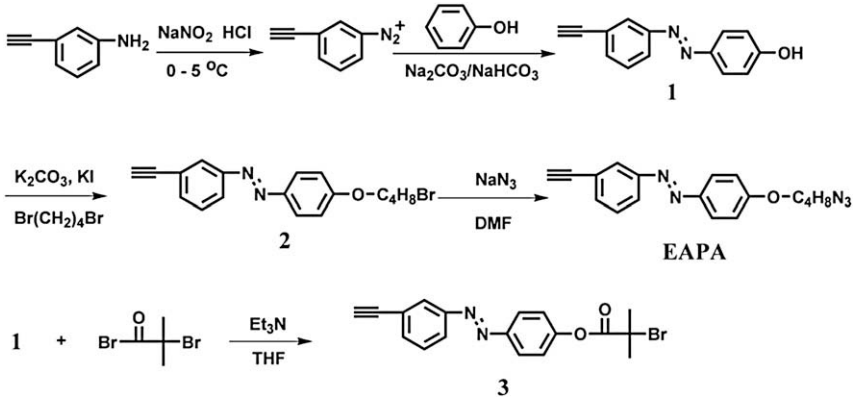
2.2. Synthesis of 3′-ethynylphenyl[4-(4-azidobutoxy)-phenyl]azobenzene (EAPA)

As demonstrated in Scheme 2, the monomer EAPA was prepared through sequential diazonium, azo-coupling reaction, bromoalkylation and azidation procedures. Detailed synthetic procedures and characterization data were followed. Compound **3** was synthesized accordingly with a similar procedure. Compound **3** was used as mono-functionalized monomer to control polymer's molecular weight.

2.2.1. 3′-Ethynylphenyl(4-hydroxy)azobenzene (**1**)

3-Ethynylaniline (5.85 g, 50 mmol) was added dropwise to a solution of concentrated HCl (37%, 15 mL) in deionized water (30 mL). The mixture was stirred in an ice bath to keep the reaction temperature at 0–5 °C. Then a water solution (10 mL) of sodium nitrite (3.50 g, 50.7 mmol) was added slowly for 10 min. The mixture was stirred at 0–5 °C for further 60 min. A yellow transparent diazonium salt solution was obtained. A coupling solution was prepared as follows: phenol (8 g, 85 mmol), NaOH (4 g, 100 mmol) and $NaHCO_3$ (4.2 g, 50 mmol) was dissolved in 250 mL of water under vigorous stirring at 0–5 °C. Then the diazonium salt solution was added dropwise to the coupling solution with the temperature of 0–5 °C. The final mixture was kept being stirred at 5 °C for 3 h. The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. The crude product was purified by recrystallization from ethanol. Compound **1** was then obtained as red-orange crystal (10.0 g, yield: 90.0%).

The characteristic analytical data involved are as follows: ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.04–7.97 (s, 1H, ArH), 7.94–7.83 (m, 3H, ArH), 7.62–7.52 (d, 1H, ArH), 7.50–7.42 (m, 1H, ArH),



Scheme 2. The synthetic routes of 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA) and compound **3**.

7.00–6.91 (d, 2H, ArH), 5.36–5.27 (s, 1H, ArOH), 3.17–3.10 (s, 1H, ArC≡CH); Elemental analysis: Calculated (%): C 75.66, H 4.54, N 12.60; Found (%): C 75.31, H 4.34, N 13.11.

2.2.2. 3′-Ethynylphenyl[4-(4-bromobutoxy)phenyl]-azobenzene (**2**)

A solution of compound **1** (5.0 g, 22.5 mmol), 1,4-dibromobutane (21.5 g, 100.0 mmol), potassium carbonate (3.1 g, 22.5 mmol), catalytic amount of potassium iodide and 100 mL of DMF was prepared in a 500 mL round bottom flask under vigorous stirring. The solution was stirred under reflux at 110 °C for 5 h. After cooling to room temperature, the mixture was poured into 300 mL water under vigorous stirring. The resultant mixture was extracted with ethyl acetate (3 × 100 mL). The organic layer was dried with anhydrous $MgSO_4$ overnight, filtered and evaporated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10) to yield compound **2** as yellow solid (6.9 g, 86.0%).

The characteristic analytical data involved are as follows: ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.06–7.97 (s, 1H, ArH), 7.97–7.90 (d, 2H, ArH), 7.90–7.83 (d, 1H, ArH), 7.60–7.53 (d, 1H, ArH), 7.52–7.42 (m, 1H, ArH), 7.07–6.96 (d, 2H, ArH), 4.18–4.03 (m, 2H, $ArOCH_2$), 3.60–3.46 (m, 2H, $-CH_2Br$), 3.16–3.12 (s, 1H, ArC≡CH), 2.19–1.91 (m, 4H, $-CH_2CH_2-$); Elemental analysis: Calculated (%): C 60.52, H 4.80, N 7.84; Found (%): C 60.51, H 4.42, N 7.92.

2.2.3. 3′-Ethynylphenyl[4-(4-azidobutoxy)phenyl]-azobenzene (EAPA)

To a 500 mL round-bottomed flask equipped with a stir bar and a condenser were added compound **2** (6 g, 16.8 mmol), DMF (200 mL), sodium azide (1.6 g, 25 mmol) and deionized water (10 mL). The mixture was vigorously stirred under reflux at 80 °C for 24 h and then cooled to room temperature. Then water (300 mL) was added. The mixture was extracted with ethyl acetate (3 × 100 mL). The organic layer obtained was dried with anhydrous $MgSO_4$ overnight, filtered and evaporated in a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10) to yield EAPA as yellow solid (4.8 g, 89.5%).

The characteristic analytical data involved are as follows: ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.08–7.98 (s, 1H, ArH), 7.98–7.90 (d, 2H, ArH), 7.90–7.84 (d, 1H, ArH), 7.62–7.53 (d, 1H, ArH), 7.52–7.43 (m, 1H, ArH), 7.08–6.96 (d, 2H, ArH), 4.17–4.04 (m, 2H, $ArOCH_2$), 3.51–3.33 (m, 2H, $-CH_2N_3$), 3.21–3.08 (s, 1H, ArC≡CH), 2.03–1.75 (m, 4H, $-CH_2CH_2-$); Elemental analysis: Calculated (%): C 67.70, H 5.37, N 21.93; Found (%): C 67.42, H 5.35, N 21.50; FT-IR (KBr, see Fig. 3 (EAPA)) γ_{max}/cm^{-1} 3280, 2925, 2855, 2148, 2109, 1601, 1581, 1499 and 1248.

The ^{1}H NMR spectrum of EAPA is shown in Fig. 1.

2.3. Synthesis of 2-bromo-2-methyl-propionic acid 4-(3-ethynyl-phenylazo)-phenyl ester (**3**) (Scheme 2)

Compound **1** (2.22 g, 10 mmol), freshly distilled THF (50 mL) and dry triethylamine (2.02 g, 20 mmol) were added to a three-necked flask of 250 mL. The solution was stirred in an ice bath. A solution of 2-bromoisobutyryl bromide (3.45 g, 15 mmol) in dry THF (10 mL) was added dropwise to the mixture with the temperature at 0–5 °C. The reaction mixture was vigorously stirred for another 3 h at 0–5 °C, and then at room temperature for overnight. After filtration, the filtrate was evaporated under vacuum. The remaining yellow mixture was dissolved in dichloromethane and washed with 5% Na_2CO_3 aqueous solution and deionized water for three times. After drying with anhydrous $MgSO_4$ overnight, dichloromethane was evaporated under a reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5) to yield compound **3** as saffron solid (1.32 g, 62.1%).

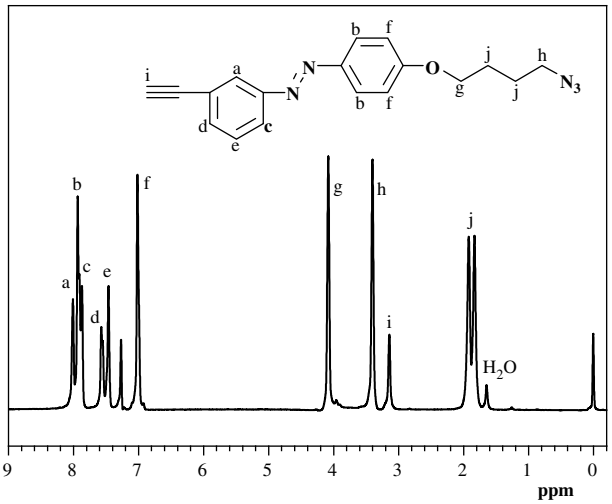
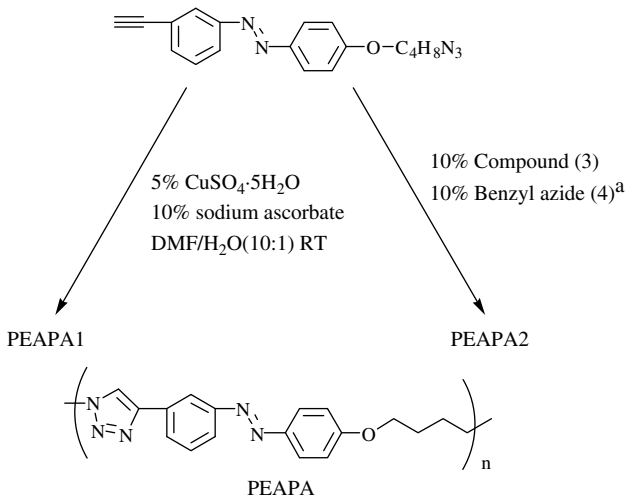


Fig. 1. ^{1}H NMR spectrum of the monomer EAPA in $CDCl_3$.

The characteristic analytical data involved are as follows: ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.07–8.03 (s, 1H, ArH), 8.02–7.97 (d, 2H, ArH), 7.93–7.88 (d, 1H, ArH), 7.63–7.57 (d, 1H, ArH), 7.52–7.44 (m, 1H, ArH), 7.35–7.28 (d, 2H, ArH), 3.17–3.13 (s, 1H, ArC≡CH), 2.12–2.08 (s, 6H, $-CH_3$); Elemental analysis: Calculated (%): C 58.04, H 4.07, N 7.55; Found (%): C 57.82, H 4.33, N 7.83.

2.4. Preparation of PEAPA1 (Scheme 3)

EAPA (0.638 g, 20 mmol) and $CuSO_4 \cdot 5H_2O$ (0.005 g, 1 mmol) were dissolved in 10 mL DMF. Then, sodium ascorbate (0.393 g, 2 mmol) dissolved in deionized water (1 mL) was added dropwise to the mixture under vigorous stirring at room temperature. Several seconds later, a large amount of precipitate was observed. The mixture was poured into 250 mL methanol. Precipitate (PEAPA1) was collected by filtration, washed sequentially with the dilute hydrochloric acid solution, THF and deionized water several



a) benzyl bromide, DMF, NaN_3, 80 °C [23]

Scheme 3. The synthetic routes of polymers PEAPA1 and PEAPA2.

times, and dried under vacuum (0.588 g, yield: 92.2%). The obtained polymer PEAPA1 was insoluble in common solvents such as chloroform, THF and DMF.

2.5. Preparation of PEAPA2 (Scheme 3)

In a 25 mL single-necked flask, EAPA (0.638 g, 20 mmol), compound **3** (0.074 g, 2 mmol), benzyl azide (**4**, 0.023 g, 2 mmol) and $CuSO_4 \cdot 5H_2O$ (0.005 g, 1 mmol) were dissolved in 10 mL of DMF. Sodium ascorbate (0.393 g, 2 mmol) dissolved in deionized water (1 mL) was added dropwise to the mixture stirred at room temperature. After stirring for 4 h, the mixture was diluted with hot DMF (5 mL) and precipitated into 250 mL methanol. The precipitate (PEAPA2) was obtained by filtration, washed sequentially with the dilute hydrochloric acid solution, THF and deionized water several times, and dried to a constant weight at room temperature in vacuum (0.570 g, yield: 89.3%).

The characteristic analytical data involved are as follows: GPC (DMF): $M_n = 7200$ g/mol, PDI (M_w/M_n) = 1.52. UV–vis (DMF): $\lambda = 354.5$ nm; FT-IR (KBr, see Fig. 3 (PEAPA2)) γ_{max}/cm^{-1}: 2928, 2869, 1597, 1500, 1467, 1385, 1250, 1147 and 686.

2.6. Synthesis of 4,4′-dihydroxyazobenzene DHA (Scheme 1)

A mixture of potassium hydroxide (20 g, 304 mmol), *p*-nitrophenol (5 g, 36 mmol) was fabricated with mortar, then added to a 250 mL three-necked flask. Deionized water (5 mL) was added dropwise to the mixture. The mixture was stirred at room temperature for 30 min then heated to 120 °C followed by standing for 1 h. The temperature was slowly elevated to about 200 °C. The reaction vigorously started to give brown viscous liquid with a large number of bubbles developing. After reaction finished (no bubble release), the product was dissolved in 500 mL water to afford a dark-red solution. The solution was acidified to pH 3 with concentrated hydrochloride and then was extracted with ether. The organic layer was dried by anhydrous magnesium sulfate overnight. Then, the ether was removed under reduced pressure. The final crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:4) to yield DHA as yellow solid (1.8 g, 49.6%).

The characteristic analytical data involved are as follows: ^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 10.10 (s, 2H, OH); 7.71 (d, 4H, ArH); 6.90 (d, 4H, ArH). Elemental analysis: Calculated (%): C 67.28, H 4.71,N 13.08; Found (%): C 66.66, H 4.99, N 12.33.

2.7. Preparation of polymer PDHA1 and PDHA2

DHA (0.214 g, 1.0 mmol), 1,4-dibromobutane (0.215 g, 1.0 mmol), potassium carbonate (0.276 g, 2.0 mmol) and catalytic amount of potassium iodide were dissolved in 10 mL of DMF. The solution was stirred under reflux at 110 °C for 6 h. After cooling to room temperature, the mixture was poured into 100 mL water. The obtained crude polymer was collected by filtration, washed sequentially with deionized water several times, and dried to a constant weight at room temperature in vacuum. The polymer PDHA1 was obtained by Soxhlet extraction using methanol as solvent (0.256 g, yield: 94.4%).

The polymer PDHA2 was prepared by adding 10% mono-functionalized compound 4-hydroxyazobenzene accompanying with monomer DHA to adjust the molecular weight of the polymer. The treatment and condition of the polymerization were the same as those of polymer PDHA1. A yellow solid PDHA2 was obtained (0.206 g). Yield: 73.4%. $M_{n(GPC)} = 7600$ g/mol, PDI = 1.72. γ_{max}/cm^{-1}: 2950, 2870, 1580, 1500, 1470, 1400, 1320,1250, 1150, 1010 and 837. $\lambda_{max} = 361.5$ nm.

2.8. Analysis and characterizations

^{1}H NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using $CDCl_3$ and DMSO-d_6 as a solvent, tetramethyl-silane (TMS) as the internal standard. A solid ^{13}C NMR spectrum of the polymer was recorded on a BRUKER 300 MHz NMR instrument (DSX 300). The number average molecular weights (M_ns) and molecular weight distributions (M_w/M_ns) of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with a refractive index detector, using HR1, HR3, and HR4 column with a molecular weight range of 100–500 000 calibrated with PS standard samples. DMF and THF were used as the eluent at a flow rate of 1.0 mL/min operated at 30 °C. Elemental analysis of C, H and N were conducted with an EA1110 CHNO–S instrument. The UV–vis spectra were determined on a Shimadzu-RF540 spectrophotometer at room temperature. Thermal analysis was performed by differential scanning calorimetry (DSC) using a TA instruments DSC2010 with a heating/cooling rate of 10 °C/min under a continuous nitrogen flow. FT-IR spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer. The XRD analysis was performed with a Rigaku D/max-γ rotation anode X-ray diffractometer, using graphite-monochromatized Cu K_α radiation sources ($\lambda = 1.5406$ Å). A scanning rate of 0.005°/s was applied in the 2θ range of 0–60°.

3. Results and discussions

3.1. Synthesis of EAPA

The A–B type α-azide and ω-alkyne azobenzene monomer, 3′-ethynylphenyl[4-(4-azidobutoxy)phenyl]azobenzene (EAPA), was synthesized according to Scheme 2. The monomer (EAPA) was obtained from sequential diazonium, azo-coupling reaction, bromo-alkylation and azidation procedures. The structure of EAPA was characterized by elemental analysis, IR spectroscopy, ^{1}H NMR and ^{13}C NMR spectra. The monomer EAPA is stable in the absence of Cu(I) catalyst, and could not be exploded in room temperature ($(n_C + n_O)/n_N > 3$) [24], where n_C, n_O and n_N were the number of carbon, oxygen and nitrogen atoms.

3.2. Synthesis of polymers PEAPA1 and PEAPA2

Click chemistry technology has drawn widespread attention due to its high efficiency, quantitative yields and selectivity under mild reaction conditions in different reaction media [16]. The use of Cu(I) catalyst accelerates the reaction rate up to 10^7 while retaining high quantitative yields [25]. Click chemistry has been also introduced into polymer synthesizing [18–20]. Therefore, we describe the synthesis of PEAPAs by their efficient step-growth click coupling in the presence of Cu(I) catalytic system. Monomer EAPA was polymerized in DMF using 5% $CuSO_4 \cdot 5H_2O$ and 10% sodium ascorbate as a catalyst. The reaction was completed in a few minutes. However, the formed polymer, PEAPA1, was insoluble in a common organic solvent. The poor solubility may be caused by the high molecular weight of the obtained polymer. The molecular weight of polymers prepared via step condensation polymerization can be controlled by adding mono-functionalized compound accompanying with monomer [19]. Thus, two mono functional compounds (10% compound **3** and 10% compound **4** based on the monomer in molar ratio) were introduced into polymerization reaction to adjust the molecular weight of the polymer. Under this condition, PEAPA2 was obtained, which was soluble in DMF. Thus, the solubility of PEAPA2 was improved as expected.

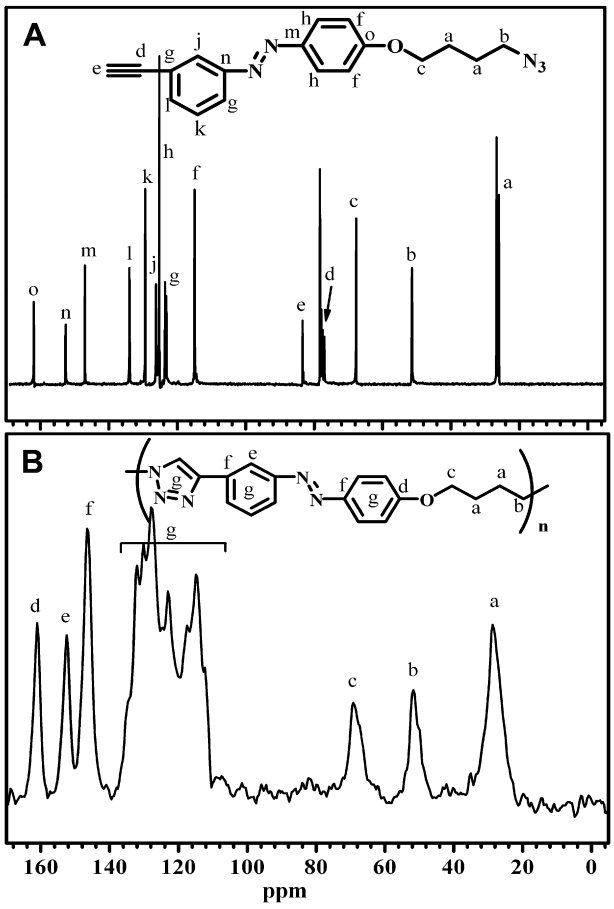


Fig. 2. (A) ^{13}C NMR spectrum of monomer EAPA in $CDCl_3$. (B) Solid ^{13}C NMR spectrum of polymer PEAPA2 ($M_n = 7200$ g/mol, PDI (M_w/M_n) = 1.52).

3.3. Structural characterization of the polymers

To confirm the structure of PEAPA2, ^{13}C NMR spectra of EAPA and PEAPA2 were investigated and shown in Fig. 2. The chemical shift of the alkyne group at around 83.4 and 77.5 ppm in EAPA (assigned as: "d" and "e" in Fig. 2A) disappeared in the spectrum of

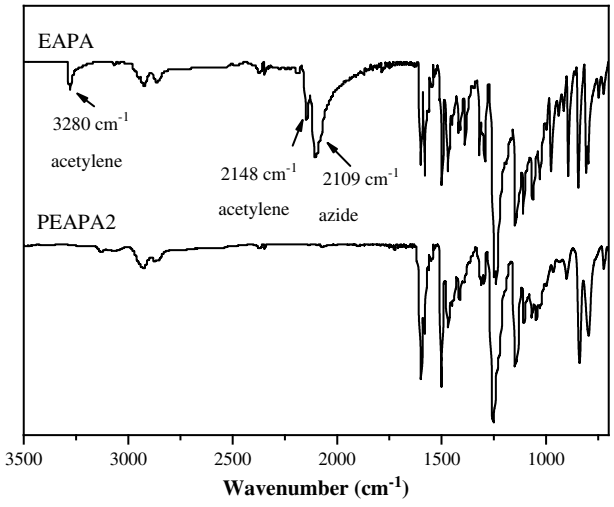


Fig. 3. FT-IR spectra of monomer EAPA and polytrazole PEAPA2.

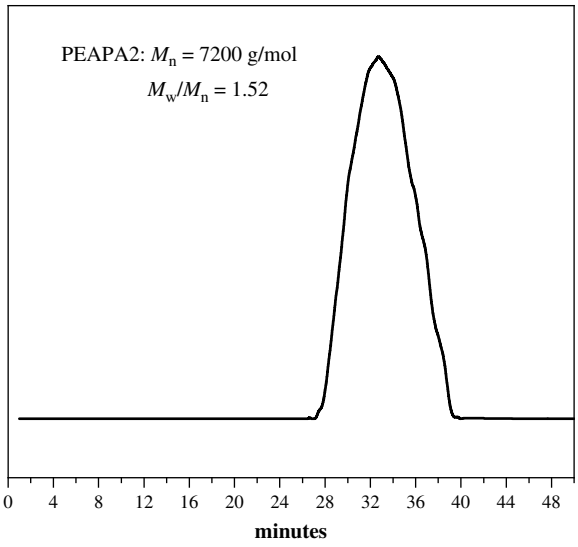


Fig. 4. GPC curve of polytrazole PEAPA2.

PEAPA2 (Fig. 2B) after click polyaddition. The new signal of triazole rings in PEAPA2 appeared between 110.1 ppm and 138.3 ppm. The FT-IR spectra (Fig. 3) further confirmed the formation of triazole ring. The signals at 3280, 2148 and 2109 cm^{-1} (Fig. 3, EPAP) assigned to the alkyne and azide groups in EAPA disappeared after the reaction. The FT-IR spectra indicated the high efficiency of the click reaction of EAPA. These results indicated that the alkyne and azide groups in EAPA successfully formed the triazole ring in PEAPA2 after this step-growth polymerization via click chemistry.

To confirm it was a polymer, PEAPA2 was characterized by gel permeation chromatographer (GPC) using DMF as the eluent. The result showed that PEAPA2 has M_n and PDI values of 7200 g/mol and 1.52, respectively, according to the polystyrene standards. A GPC curve of PEAPA2 is shown in Fig. 4, where a peak at the elution time of 27.1–39.5 min with a normal distribution was observed. This indicates that the click reaction is a useful tool to prepare main-chain azobenzene polymers containing triazole groups in the same time.

3.4. Thermal characterization

Thermal and crystallinity properties of the main-chain azobenzene polymers were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and wide-angle X-ray diffraction (WAXD), respectively. To avoid thermal decomposition, the polymers were heated or cooled with a heating/cooling rate of 10 °C/min under a continuous nitrogen flow. The thermal properties of PEAPAs are summarized in Table 1. The glass-transition temperature (T_g) of PEAPA2 ($M_n = 7200$, PDI = 1.52) was 123 °C. PEAPA1 showed the T_g at 134 °C, which was much higher than that of PEAPA2. This result confirmed that the molecular

Table 1
Characteristics of polytriazoles PEAPA1, PEAPA2 and polymers PDHA1, PDHA2.

Sample	M_n (g/mol)	T_g(I) (°C)	T_d (°C)	T_m (°C)	ΔH_f (J/g)	Solubility
PEAPA1	–	134	357	214	28.99	–
PEAPA2	7200[a]	123	334	173	25.32	DMF and hot DMSO
PDHA1	–	109	278	–	–	–
PDHA2	7600[b]	105	224	–	–	DMF and THF

[a] Obtain by GPC in DMF according to polystyrene standards.
[b] Obtain by GPC in THF according to polystyrene standards.

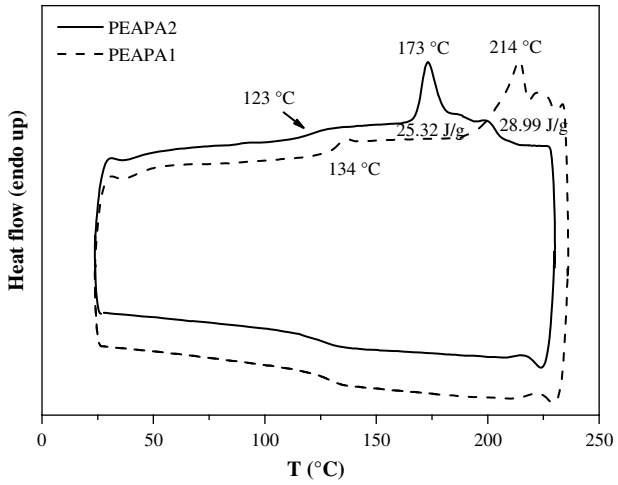


Fig. 5. Second DSC heating and cooling curves of polytrazoles PEAPA1 and PEAPA2.

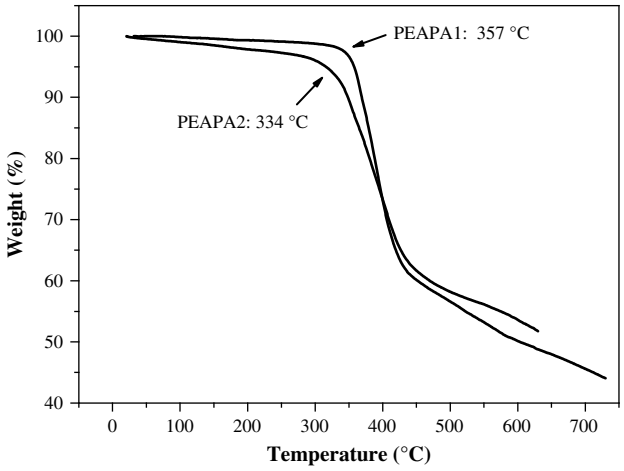


Fig. 7. Thermogravimetric analysis (TGA) of polytrazoles PEAPA1 and PEAPA2.

weight of PEAPA1 should be higher than that of PEAPA2. Moreover, from Table 1, the T_gs of PEAPAs were much higher than those of PDHA1 (109 °C). The introduction of triazole ring in the main chain of polymer can improve its T_g significantly. The DSC curves are shown in Fig. 5. It should be stated that no obviously heat absorption peak can be found in DSC curves of PDHA polymers. While, a melting peak was observed in PEAPA2 with $T_m = 173$ °C, which indicated that the polymer had crystalline states besides the glassy state. The high transition enthalpy ΔH_f of polymer PEAPA2 was 25.32 J/g. No liquid crystalline phase of polymer PEAPA2 could be observed in the polarization microscope, even though there was a strong mesophase transition on the second DSC heating curve. Certainly, PEAPA1 also exhibited a higher melting transition at 214 °C ($\Delta H_f = 28.99$ J/g). The WAXD spectrum of PEAPA2 (Fig. 6) further confirmed the existence of crystalline states in the polymer as the appearing of a broad peak with small sharp peaks at $2\theta = 18.43°$, 20.67° and 21.97°.

The thermogravimetric analysis (TGA) results of polymer under a continuous nitrogen flow are shown in Fig. 7. PEAPA2 was thermally stable up to 334 °C (at about 5% weight loss) under nitrogen atmosphere and lost 40% of its weight at the temperature of 469 °C which can be attributed to the presence of aliphatic segment in the backbone structure. Similarly, PEAPA1 has 5% (weight) degradation temperature at 357 °C, which was higher than that of PEAPA2. The reason may be due to the increased polymerization degree. PDHA1 and PDHA2 showed much low decomposition temperature than its triazole analogs PEAPA1 and PEAPA2. These results confirmed the introduction of triazole ring can improve thermal stability of polymers. Hence, both PEAPA1 and PEAPA2 were quite thermally stable up to their T_ms and the introduction of triazole ring in the polymer backbone plays an additional favorable role in improving the thermal stability [14,20,26].

3.5. Photo- and thermal isomerization behaviors

Azobenzene compounds and their derivatives exhibit reversible *trans–cis–trans* isomerization behaviors. These compounds undergo conversion from *trans*- to *cis*-forms under irradiation of ultraviolet light (about 365 nm), and reverse *cis-to-trans* forms under thermal energy in the dark. The *trans–cis* photoisomerization and *cis–trans* thermal isomerization of EAPA and PEAPA2 in DMF solution were investigated. Firstly, both of the samples were irradiated under 365 nm ultraviolet light. The UV–vis absorption spectra were recorded at the different time intervals until photostationary state was reached. Secondly, the irradiated samples were kept in the dark at 60 °C until they reverted to their initial state as the *trans*-form is thermodynamically more stable [27] (Scheme 4).

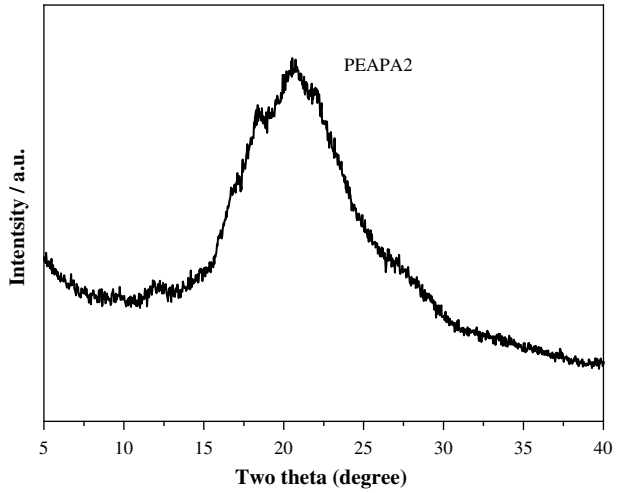
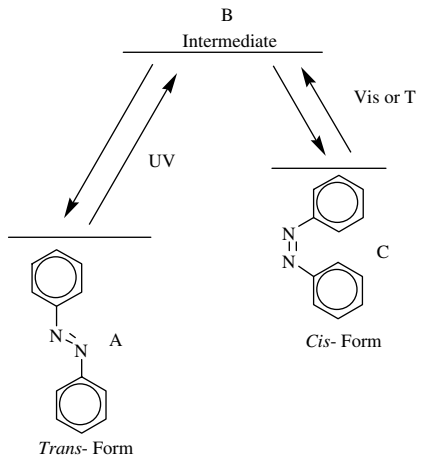


Fig. 6. WAXD spectrum of polytrazole PEAPA2 at room temperature.



Scheme 4. Illustration of the *trans–cis–trans* isomerization process of azobenzene.

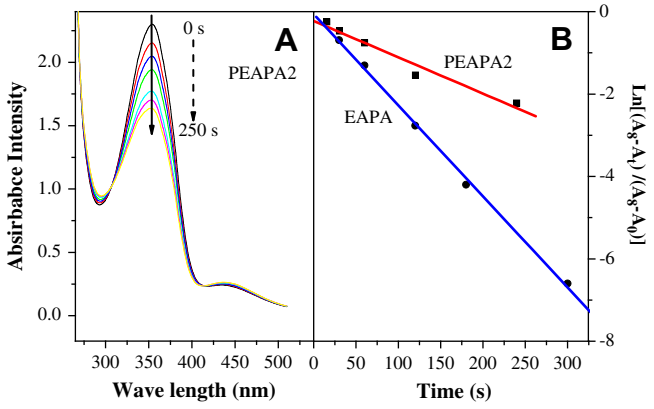


Fig. 8. (A) The UV–vis absorption changes of polytrazole PEAPA2. (B) First-order for *trans–cis* photoisomerization of monomer EAPA and polytrazole PEAPA2. The concentration of the solution is 5.0×10^{-6} M during the irradiation time with 365 nm UV light in DMF solution at room temperature.

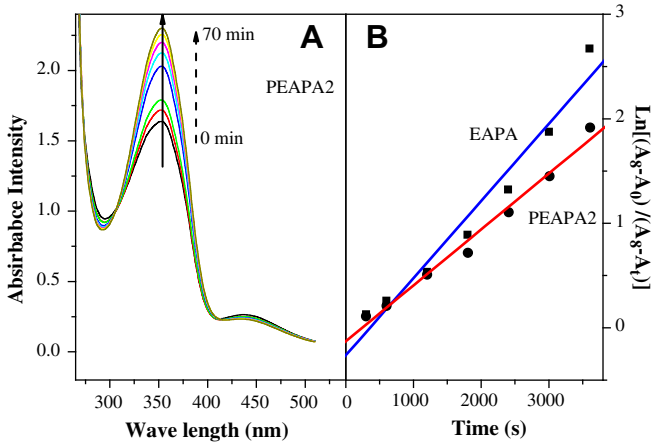


Fig. 9. (A) The UV–vis absorption changes of polytrazole PEAPA2. (B) First-order for *cis–trans* thermal isomerization of monomer EAPA and polytrazole PEAPA2. The concentration of the solution is 5.0×10^{-6} M in DMF solution under different time intervals at 60 °C in the dark room.

The UV–vis absorption changes of PEAPA2 are given in Fig. 8(A). The maximum absorption at 354.5 nm was the characteristic intense π–π^* transition of azobenzene (*trans*-form) before UV exposure. After irradiation with 365 nm UV light, the *trans*-form of azobenzene changed to the *cis*-form (weak n–π^* transition) at about 435 nm. The absorption (354.5 nm) of *trans*-form azobenzene rapidly decreased upon UV irradiation, whereas the intensity of the *cis*-form azobenzene (435 nm) slightly increased without any side reactions of photo-crosslinking and photodegradation, etc. However, after a prolonged UV irradiation, the *trans*-form of the azobenzene did not completely disappear, which indicated the incomplete photoisomerization (*trans*-form of azobenzene was still 70.7% as listed in Table 2) [28]. The similar characteristic of EAPA and PDHA2 was also observed. The maximum absorption of PDHA2 at 361.5 nm was the characteristic intense π–π^* transition of azobenzene (*trans*-form), and the absorption at about 435 nm corresponded to the *cis*-form (weak n–π^* transition) in Table 2.

The rate of *trans–cis* photoisomerization was analyzed from the absorption of 354.5 nm. The photoisomerization kinetics of EAPA and PEAPA2 were further studied and presented in Fig. 8(B). The first-order rate constants were determined by Equation (1):

$$\ln\left(\frac{A_\infty - A_t}{A_\infty - A_0}\right) = -k_e t \tag{1}$$

where A_∞, A_0 and A_t are the absorbances at 354.5 nm at time infinite, time zero and time t, respectively. The results confirmed the first-order kinetic plot for the *trans–cis* photoisomerization of both EAPA and PEAPA. It is interesting that the *trans–cis* rate of EAPA was 0.022 s^{-1} (Table 2) in DMF solution, which was about 2.5 times faster than that of PEAPA2 (0.0088 s^{-1} for PEAPA2). Moreover, PDHA2 without the triazole group showed the fastest transition of *trans–cis* photoisomerization, e.g. 0.0301 s^{-1}. The reason was considered due to sterically hindering effect of the main-chain configuration and the triazole group in PEAPA2.

Simultaneously, *cis–trans* thermal isomerizations of EAPA, PEAPA2 and PDHA2 in DMF solution were also investigated at 60 °C in a dark room. As illustrated in Fig. 9(A), the absorption at 354.4 nm was rapidly restored to the initial state of PEAPA2 before UV irradiation at 70 min. The intensity of the *cis*-form azobenzene (435 nm) was slightly decreased. The kinetics of the *cis–trans* thermal isomerizations of samples in a dark room were fitted satisfactorily to Equation (2):

$$\ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = k_H t \tag{2}$$

where A_∞, A_0 and A_t are the absorbances at 354.5 nm at time infinite, time zero and time t, respectively. The UV–vis absorption changes and the first-order *cis–trans* thermal isomerizations are shown in Fig. 9. The *cis–trans* rate constant (k_H) of EAPA was 5.4×10^{-4} s^{-1}, the k_H of PEAPA2 was 7.4×10^{-4} s^{-1}, and the k_H of PDHA2 was 4.5×10^{-4} s^{-1}. Same trend was observed here as in the case of *trans–cis* isomerization, that is the triazole ring in polymer main chain showed significant stereo hinder for photo-induced *trans–cis–trans* isomerization. Apart from the kinetic results, these results further confirmed that the isomerization of azobenzene in the polymer backbone is reversible by the photo- and thermo procedures.

Table 2
Kinetic parameters for the *trans–cis–trans* isomerization of EAPA, PEAPA2, DHA, and PDHA2.

Sample	λ_{max} (*trans*)[a] (nm)	λ_{max} (*cis*)[b] (nm)	k_e[c] $\times 10^3$ (s^{-1})	k_H[d] $\times 10^4$ (s^{-1})	[*trans*][e] (%)	[*cis*][f] (%)
EAPA	354.5	435	22.1	5.4	64.4	35.6
PEAPA2	354.5	435	8.8	7.4	70.7	29.3
PDHA2	361.5	451	30.1	4.5	53.7	46.3

[a] The maximum absorption of *trans*-form azobenzene.
[b] The maximum absorption of *cis*-form azobenzene.
[c] Rate constant of *trans–cis* photoisomerization.
[d] Rate constant of *cis–trans* thermal isomerization at 60 °C.
[e] *trans*-form concentration when photo-stationary state was reached.
[f] *cis*-form concentration when photo-stationary state was reached.

4. Conclusions

A novel main-chain azobenzene polymer, PEAPA, was successfully synthesized by a step-growth polymerization via 1,3-dipolar cycloaddition reactions ("Click" chemistry), under the catalysis system of $CuSO_4 \cdot 5H_2O$/sodium ascorbate/H_2O. This novel method provided a high efficiency way to prepare a main-chain azobenzene polymer. The obtained linear main-chain azobenzene polymer PEAPA containing 1,2,3-triazole group showed a good thermal stability and crystallinity, due to the introduction of the triazole ring in the polymer backbone. Furthermore, the *trans–cis–trans* isomerization of PEAPA and EAPA was also observed at DMF solution. Comparing the rate constant of *trans–cis* photoisomerization of monomer EAPA ($k_e = 0.022$ s^{-1}), the corresponding value of PEAPA was much slower ($k_e = 0.0088$ s^{-1}). However, the *cis–trans* thermal

isomerization behavior of PEAPA2 was similar to EAPA's. The introduction of triazole ring into polymer main chain showed hindering effect for the *trans–cis–trans* isomerization of azobenzene.

Acknowledgments

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