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Synthesis and Characterization of a Novel Polytriazole

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p-Xylylene diazide (XDA) and dipropargyl ether of bisphenol A (DPEBPA) were synthesized and then a novel polytriazole, poly(4,4′-(propane-2,2-diyl) diphenyl-oxy-methylene-1,5 (and 1,4)-(1,2,3-triazole)-p-xylene), was prepared from XDA and DPEBPA by 1,3-dipolar cycloaddition polymerization and characterized by FTIR, ^{1}H-NMR, GPC, DSC, WAXD, TGA, etc. The results show that the polytriazole with the number average molecular weight of 9.77×10^4 is a partially crystalline polymer. The tensile strength and tensile modulus of the polytriazole film are 72.9 MPa and 2.95 GPa, respectively. The glass transition temperature of the polymer is 93.6°C and thermal decomposition temperature arrives at 350°C.

Keywords: polytriazole; 1,3-dipolar cycloaddition reaction; *p*-xylylene diazide; dipropargyl ether of bisphenol A

1 Introduction

1,3-Dipolar cycloaddition reaction of azides and alkynes takes place at lower than 70°C to form 1,4-disubmitted and 1,5-disubmitted 1,2,3-triazole compounds with interesting biological properties (1–4), such as anti-allergic (5–7), anti-bacterial (8), and anti-HIV activity (9). In the 1960's, Jonsons et al. first reported the synthesis of linear polytriazoles by 1,3-dipolar cycloaddition reaction of monomers with both azide and alkyne groups (10, 11). However, the synthesized polytriazoles with aromatic structures were unsoluble and unmeltable in any organic solvent. Therefore, the further characterization of the structures and properties of the polytriazoles was unfeasible and the processability of the polytriazoles was unavailable. Recently, some research work has focused on the syntheses of block copolymers (12), graft copolymers (13) and dendrimers (14–18) by 1,3-dipolar cycloaddition of azides and alkynes groups. Our laboratory has been developing a new series of polytriazoles with a variety of structures, some of which possess not only excellent processability but also good mechanical properties and thermal stability (19–22). The polytriazole resins are expected to find wide application in advanced composites, coatings, and adhesives.

In this paper, a diazides and a dialkynes were synthesized, and then a novel polytriazole was prepared by 1,3-dipolar cycloaddition reaction of the groups -N=N=N and -C≡CH. The structure and properties of the polytriazole were characterized.

2 Experimental

2.1 Materials

p-Xylylene dichloride was recrystallized in methanol before used. Propargyl bromide was distilled before used. Dimethylformamide (Analytical Reagent Grade), benzene (Analytical Reagent Grade), sodium azide (Chemical Purity), sodium hydroxide (Analytical Reagent Grade), magnesium sulfate (anhydrous, Analytical Reagent Grade), bisphenol A (Chemical Purity). tetrabutylammonium bromide(Analytical Reagent Grade), and chloroform (Analytical Reagent Grade) were used as purchased.

2.2 Intrumentation

Sample powder of the obtained polytriazole was pressed into a pellet with KBr. Its infrared spectrum was obtained on the Nicolet 550 spectrometer. ^{1}H-NMR spectrum was recorded on a Bruker Avance 500 (500 MHz). $CDCl_3$ was used as a solvent and chemical shifts were reported in ppm. Differential scanning calorimetry (DSC) analyses were performed on a Universal V2.3 TA Instruments 2910 modulated system with the heating rate of 20°C/min. Wide angle X-ray diffraction (WAXD) analysis was performed on a Digaku D/max

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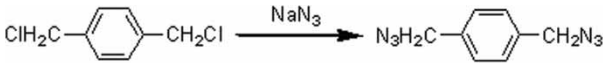
2550 VB/PC X-Ray diffractomter. Dynamic mechanical analysis (DMA) was carried out on a Rheogel-E4000 analyzer operating in the tension mode from −75 to 150°C at the frequency of 11 Hz with a programmed heating rate of 3°C/min. Thermogravimetric analysis (TGA) was conducted on a METTLER TGA/SDTA 851 analyzer under nitrogen with a heating rate of 10°C/min. Inherent viscosities of a polytriazole were measured with an Ubbelohde viscometer at 30 ± 0.5, using chloroform as a solvent. Weight average and number average molecular weights were determined on a Perkin-Elmer Series 2000 gel permeation chromatogragh (GPC) using dimethylformamide as the solvent. The tensile properties were measured according to ASTM 638 on a Shimadzu AG-50kNE universal tester. A standard dumbbell specimen with a $30 \times 5 \times 0.5\,\mathrm{mm}^3$ neck was made of polymer film prepared by pressing the powder of the polytriazole at 120°C on a press machine.

2.3 The Preparation of Monomers

2.3.1 Synthesis of p-Xylylene Diazide(XDA) (23)

4.38 g (0.0250 mol) *p*-xylylene dichloride, 6.50 g (0.100 mol) sodium azide, 20 ml dimethylformamide, and 20 ml benzene were added into a three-necked round bottom flask (250 ml) with a magnetic stirrer and a reflux condenser. The reaction mixture was slowly heated to 75.0°C and kept at this temperature for 6 h. Then, it was poured into a beaker with 200 ml deionized water. The organic layer was separated and the aqueous layer was extracted three times with 20 ml benzene. All organic benzene layers were combined and dried with anhydrous magnesium sulfate overnight. The benzene was then distilled out and a light yellow solid product of 3.93 g was obtained. Yield: 83.6%, mp: 27.5–29.0°C. FT-IR: 2098 cm^{-1} (azide). ^{1}H-NMR ($CDCl_3$, TMS): δ 7.33 (d, 4H, Ar-H, $J_{HH} = 7.86$), 4.35 (s, 4H, Ar-CH_2N_3). The synthesis reaction was shown in Scheme 1.



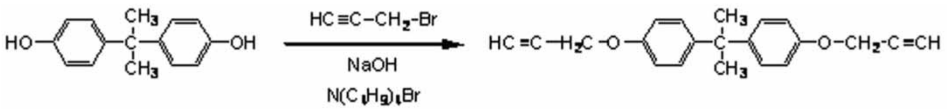
Scheme 1. Synthesis of *p*-xylylene diazide.

2.3.2. Synthesis of Dipropargyl Ether of Bisphenol A (DPEBPA) (24)

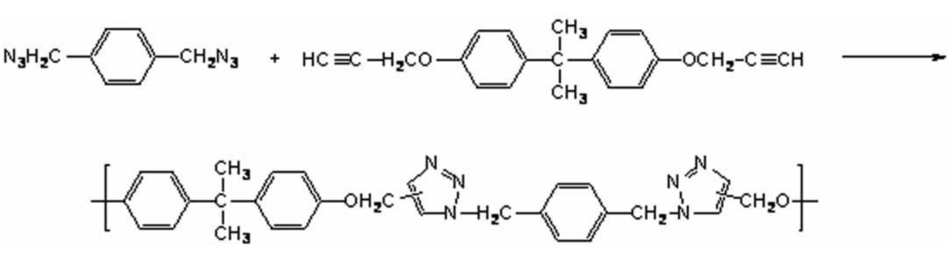
11.4 g (0.0500 mol) bisphenol A, 6.00 g (1.50 mol) sodium hydroxide, 30 ml deionized water, and 0.20 g tetrabutylammonium bromide were added into a 250 ml three-necked round bottom flask with a magnetic stirrer, a reflux condenser and a nitrogen gas inlet tube. 14.9 g (0.125 mol) propargyl bromide was then added dropwise into the flask at 80°C for 3 h under stirring, and then the mixture was remained at the same temperature for 6 h. Thereafter, the reaction product was washed several times with deionized water to remove the catalyst tetrabutylammonium bromide and the salt formed in the reaction. The crude product was recrystallized in methanol twice. 12.9 g yellow solid of dipropargyl ether of bisphenol A was obtained. Yield: 85.0%, m. p. 77.0–78.0°C. ^{1}H-NMR ($CDCl_3$, TMS) δ 1.62 (s, 6H, -CH_3), 2.50 (s, 2H, $\equiv$CH), 4.65 (s, 4H, -CH_2), 6.86 (d, 4H, -O-Ar-H, $J_{HH} = 8.73$), 7.15 (d, 4H, -C-Ar-H, $J_{HH} = 7.99$). FT-IR: (KBr) 3286 cm^{-1} (characteristic of $\equiv$C—H), 2110cm^{-1} (characteristic of C$\equiv$C). The reaction was shown in Scheme 2.

2.4 Polymerization of XDA and DPEBPA

7.60 g (0.0250 mol) DPEBPA and 4.70 (0.0250 mol) g XDA were charged into a 100 ml three-necked flask and the flask and heated to 70°C and kept at this temperature until the mixture became homogeneous. Then, the mixture was continuously stirred at 70°C for 24 h, in which the polymers were sampled for viscosity measurement every 4 h. Thereafter, the temperature was elevated to 150°C and the reaction mixture was kept at 150°C for 4 h. The polymerization of DPEBPA and XDA was described in Scheme 3.



Scheme 2. Synthesis of dipropargyl ether of bisphenol A.



Scheme 3. Polymerization of XDA and DPEBPA.

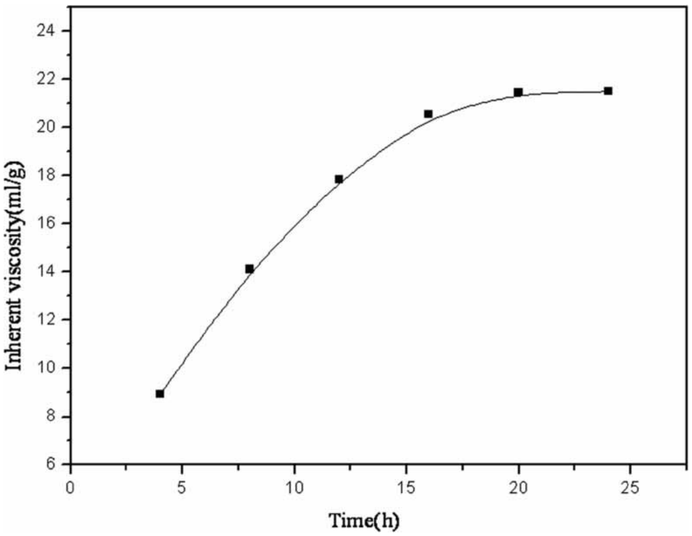


Fig. 1. The function of inherent viscosity of the polytriazole as the polymerization time at 70°C.

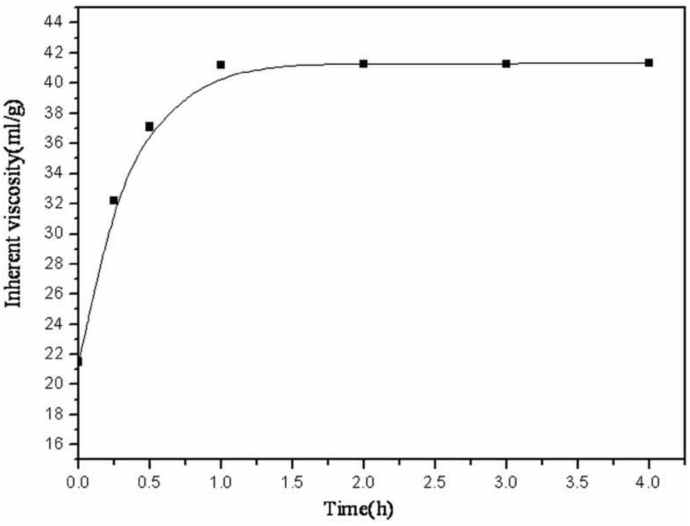


Fig. 2. The function of inherent viscosity of the polytriazole as the time at 150°C after polymerization at 70°C for 24 h.

3 Results and Discussion

3.1 The Polymerization of XDA and DPEBPA

The polymerization of XDA and DPEBPA was traced by viscosity measurements. The variation of the inherent viscosity of the polytriazole obtained with time at a constant temperature of 70°C is shown in Figure 1. As shown in the figure, the inherent viscosity of the polymer increases with the polymerization time and reaches a constant value after 20 h at 70°C. Such behavior may be attributed to the limitation of polymer chain mobility with the increase in the molecular weight. In order

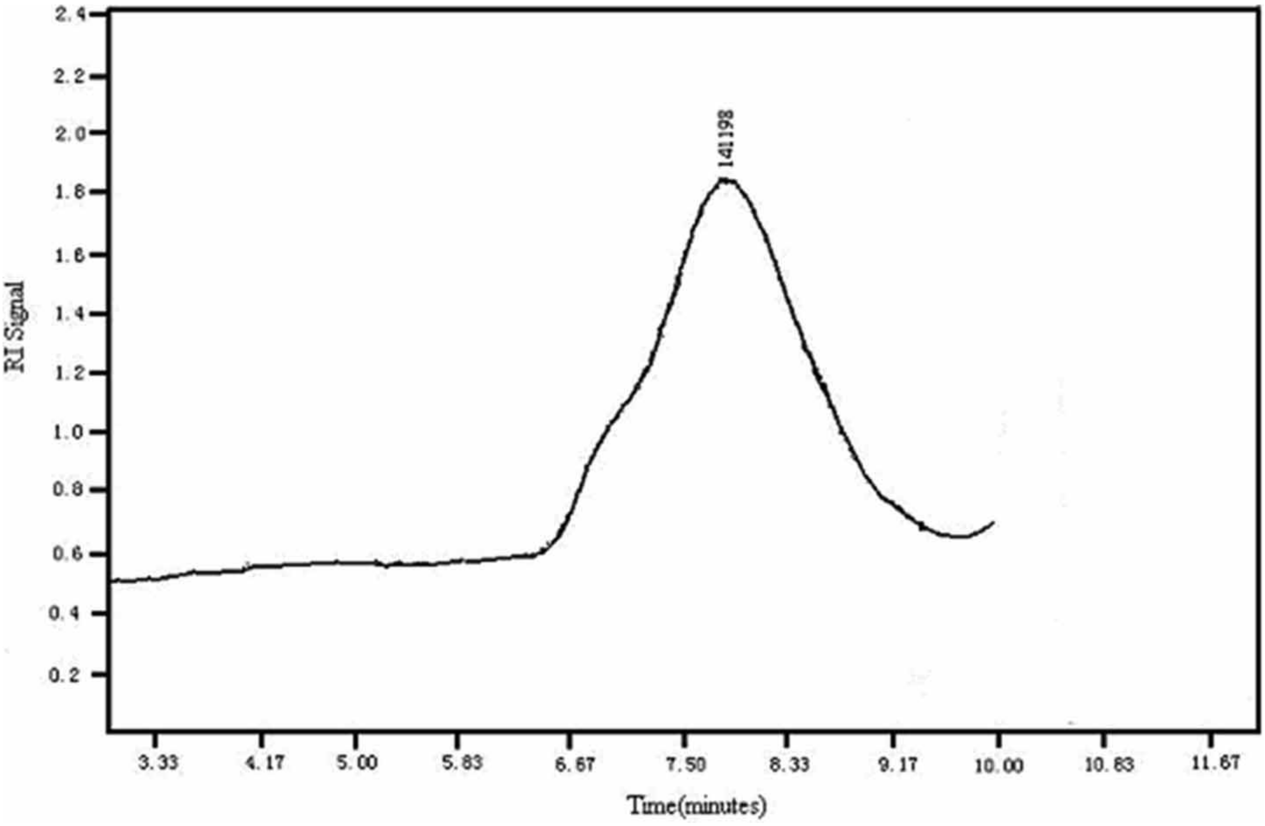


Fig. 3. GPC trace of the polytriazole (mobile phase: DMF).

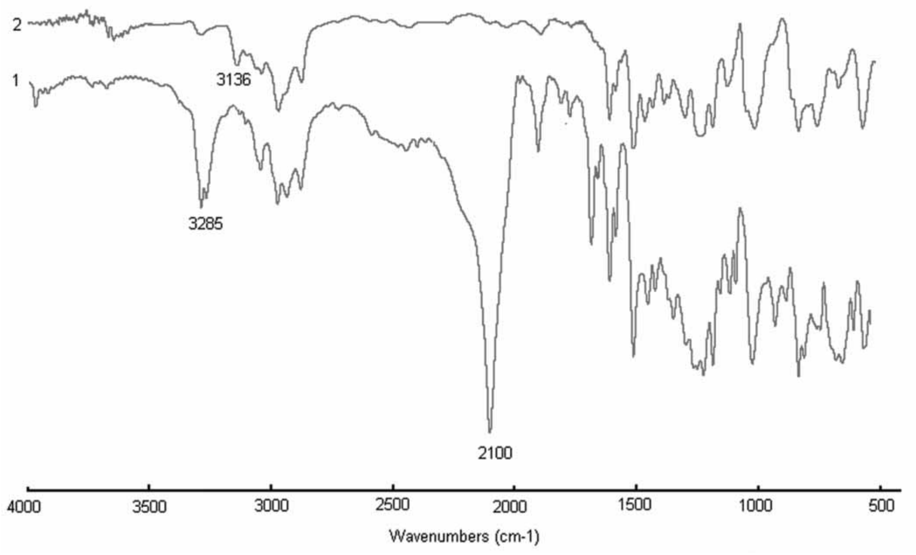


Fig. 4. IR spectra of the mixture of XDA and DPEBPA (1) and the polytriazole (2).

to make the polytriazole with higher molecular weight, the polymerization temperature was elevated to 150°C and kept at this temperature for 4 h. As shown in Figure 2, a marked increase of viscosity of the polymer is observed. However, the viscosity of the polymer does not increase after 2 h.

3.2 The Structure and Properties of the Polytriazole

3.2.1 The Molecular Weight of the Polymer

Figure 3 shows GPC analysis results of the obtained polytriazole. The weight average molecular weight and the number average molecular weight of the polytriazole are 2.16×10^5 and 9.77×10^4, respectively. The molecular weight distribution index DI was 2.21. It illustrates that the polytriazole has a wide molecular distribution.

3.2.2 The Molecular Structure of the Polymer

Figure 4 shows FT-IR spectra of the mixture of monomers and the obtained polymer. The absorption at 3285 cm^{-1} is due to the stretching vibration of ≡C-H and the absorption at 2100cm^{-1} is due to the stretching vibration of $-N_3$ and C≡C. As shown in the figure, the peak at 2100 cm^{-1} on the spectrum of the polymer disappears. A new peak at 3136 cm^{-1} occurs for the polymer, which is attributed to the vibration absorption of C-H of triazole ring. This indicates that the triazole ring in polymer chains has formed.

Figure 5 shows ^{1}H-NMR spectra for the polytriazole. The research showed that the chemical shift of the triazole proton for 1,4-substituted triazole appears downfield as compared to that of 1, 5-substituted triazole (25). Therefore, the peaks at chemical shift 7.7 and 7.6 ppm belong to the characteristic resonance of H on the rings of 1, 4-disubstituted-1,2,3-triazole (a) and 1,5-disubstituted-1,2,3-triazole (a'), respectively. The peaks at 5.6 and 5.4 ppm are the characteristic resonance of H of the group $-CH_2-O-$ connected to 1,4-disubstituted-1,2,3-triazole (b) and 1, 5-disubstituted-1, 2, 3-triazole (b'), respectively. The peaks at 4.9 and 5.1 ppm are the characteristic resonance of H of the group $-CH_2-Ar-$ connected to 1,4-disubstituted-1,2,3-triazole (c) and 1, 5-disubstituted-1,2,3-triazole (c'), respectively. The ratios of intensity of the peak at 7.7 ppm to that at 7.6 ppm, 5.6 ppm to 5.4 ppm, and 4.9 ppm to 5.1 ppm were all equal to 1.0:1.6, which corresponds to the ratio of two isomeric triazole structures in the polymer chain. The result illustrates

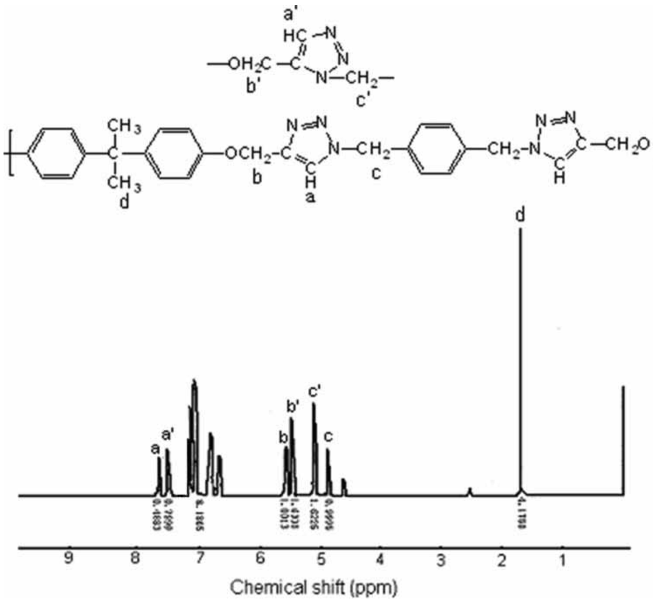


Fig. 5. ^{1}H-NMR spectrum of the polytriazole.

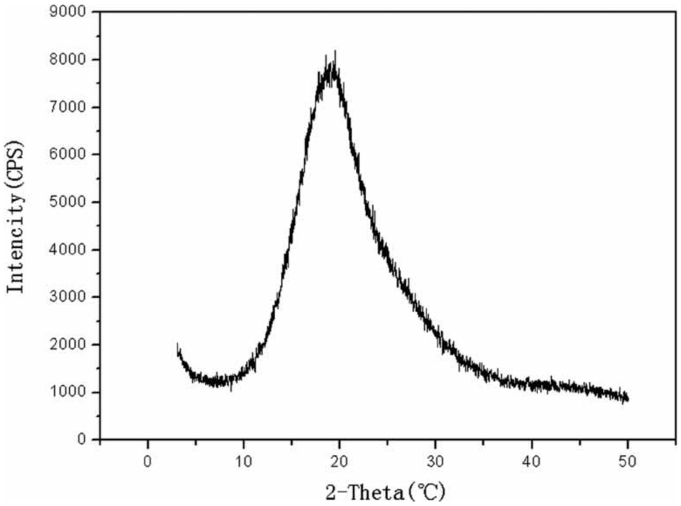


Fig. 6. WAXD diagram of the polytriazole.

that the ratio of 1,4-disubstituted-1,2,3-triazole to 1,5-disubstituted-1,2,3-triazole in the polymer chain is 1.0:1.6. The peak at 1.7 ppm was attributed to H (d) resonance of -CH_3. The peaks at 6.7–7.2 ppm were characteristic of H (e) resonance of benzene ring. The ratio of the intensities at a and a', b and b', c and c', d, and e is 2:4:4:6:12, which corresponds with the polymer structure. The small peaks at 4.7 ppm and 2.5 ppm are for H resonance of -CH_2- and -CH, respectively, of a propargyl group unreacted (end group of the polymer).

3.2.3 The Morphology of the Polymer

Figure 6 shows a diagram of wide angle X-ray diffraction (WAXD) analysis for the obtained polymer. An extraordinary peak at 20°of 2θ, which is different from both the typical pinnacle of a crystalline material and the blunt peak of an amorphous material, is observed. The phenomenon demonstrates that the polytriazole is a partially crystalline polymer.

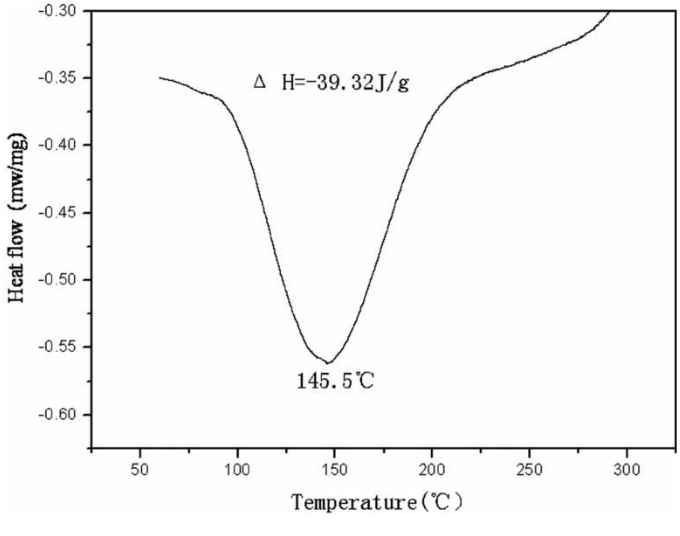


Fig. 7. DSC curve of the polytriazole (heating rate: 20°C/min, N_2).

Table 1. Solubility of the polytriazole (+: soluble ×: unsoluble)

Solvent	Solubility	Solvent	Solubility
Tetrahydrofuran	×	Toluene	×
Ethyl acetate	×	Chloroform	+
Petroleum ether	×	Dichloromethane	+
Ethanol	×	1,2-Dichloroethane	+
Acetone	×	Dimethylacetamide	+
Methyl Ethyl Ketone	×	Dimethyl sulfoxide	+
Ethy1 Ether	×	Dimethylformamide	+

The differential scanning calorimetry (DSC) analysis of the polytriazole is shown in Figure 7. There is a broad endothermal peak at 145.5°C and the heat is 39.3 J/g. The endothermal peak contributes to the melting of the polymer. This means the melting temperature of the polymer is 145.5°C. This result also illustrates that the polytriazole is a partially crystalline polymer, which corresponds with that on the WAXD analysis.

3.2.4 The Properties of the Polytriazole

The Solubility of the Polytrizaole. The solubility of the obtained polytriazole in various solvents is tabulated in Table 1. As shown in the table, the polytriazole is soluble in chlorinated hydrocarbon solvents such as chloroform, dichloroethane and strong polar aprotic solvents such as DMF, DMSO, but unsoluble in nonpolar solvents or weak polar solvents.

3.2.5 The Mechanical Properties of the Polytriazole. Tensile property of the polytriazole film was measured. The results are tabulated in Table 2. As shown in the table, the tensile strength and tensile modulus of polytriazole film are 72.9 MPa and 2.95 GPa, respectively. The elongation at break is 4.36%.

3.2.6 The Thermal Properties of the Polytriazole. Dynamic Mechanical Analysis (DMA) for the polytriazole was carried out at a heating rate of 3°C/min. The result is shown in Figure 8. As shown in the figure, the glass transition temperature T_g of the polytriazole is 93.6°C.

Thermal stability of the polytriazole was evaluated through thermogravimetry analysis. The TGA curve is

Table 2. Tensile proterties of the polytriazole film

Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
72.9	2.95	4.36

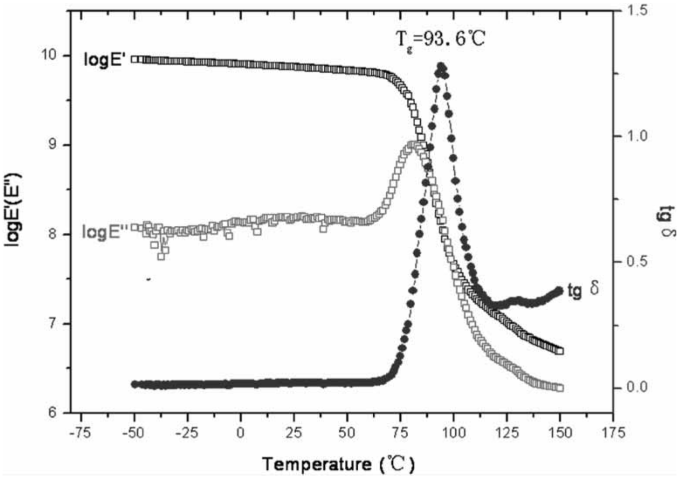


Fig. 8. DMA diagram of the polytriazole (heating rate: 3°C/min, frequency:11 Hz).

shown in Figure 9. As shown in the figure, the initial thermal decomposition temperature of the polytriazole arrives at 350°C.

4 Conclusions

A novel polytriazole was synthesized from p-xylylene diazide and dipropargyl ether of bisphenol A. The 1, 3-dipolar addition polymerization can take place at 70°C. The structures and properties of the polytriazole are characterized by FT-IR, ^{1}H-NMR, WAXD, DSC, DMA, and TGA techniques. The results show that the number molecular weight of polytriazole reaches 9.77 × 10^4. There are two different isomers of the triazole in the polymer chains due to triazole ring connection and the ratio of 1,4-disubmitted-1,2,3-triazole to 1,5-disubmitted-1,2,3-triazole is 1.0:1.6. The polytriazole is a partially crystalline polymer and soluble in some common solvents, and exhibits good mechanical properties and thermal properties. The tensile strength and modulus of the polytriazole film are, respectively, 72.9 MPa and 2.95 GPa. The glass transition temperature and thermal decomposition temperature of the polymer are 93.6°C and 350°C, respectively.

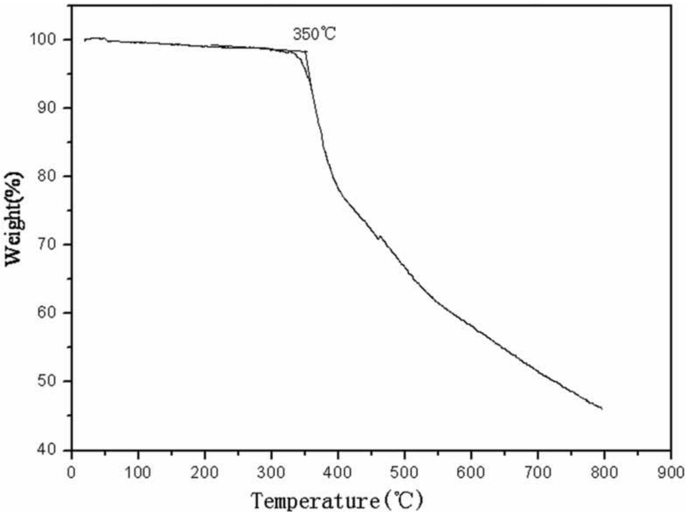


Fig. 9. TGA diagram of the polytriazole (heating rate: 10°C/min, N_2).

5 Acknowledgements

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