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Polyether-based main-chain-type polytriazole elastomer with benzoxazine via a 1,3-dipolar cycloaddition reaction

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ABSTRACT: A novel functional polyether-based elastomer with a benzoxazine structure in its main chain was successfully synthesized via a 1,3-dipolar cycloaddition reaction. Benefitting from a facile one-pot synthesis strategy, the elastomer was prepared at low temperature (80°C) and was characterized clearly afterward. The azide-terminated polyether and acetylene-terminated benzoxazine were used as the soft and hard segments, respectively, in the polymer chain. Because the triazole rings served as stable linkage between the soft and hard segments, the elastomer possessed good thermal stability (the 5% weight loss temperature could exceed 350°C) compared to traditional elastomers, such as polyurethane. The rigid benzoxazine rings provided the product with good mechanical properties (the tensile strength of the elastomer could exceed 30 MPa). Furthermore, the ring-opening polymerization of oxazine rings in the structure gifted the elastomer with possibility of thermally induced structural transformation. The thermally induced structural transformation could conveniently realize the conversion of the elastomer to a thermosetting resin. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42820.

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INTRODUCTION

The synthesis of benzoxaine with a primary amine, a phenolic derivative, and formaldehyde was reported by Holly and Cape[1] first in 1944. After the fundamental investigation of benzoxazine chemistry was done by Burke and coworkers,[2–4] benzoxazine resin was proven to be a novel functional material with high performance. Furthermore Burke and coworkers studied the fundamental benzoxazine chemistry extensively. The cationic ring-opening polymerization procedure for obtaining polybenzoxazine was first reported by Ning and Ishida[5] in 1994. The facile synthesis strategy and polymerization of benzoxazine resin offered the flexibility for structural design by various raw materials. According to the reported study, benzoxazine was announced as a precursor of a high-performance polymer that possessed superior mechanical properties and good thermal stability. Thanks to the high performance of benzoxazine resin, it had been used in many different fields.[6–10]

However, applications in the synthesis of elastomers with benzoxazine structures have rarely been reported. The distinguished features of the 1,3-dipolar cycloaddition reaction, such as its high yields and mild reaction conditions, were revealed by Sharpless *et al.*[11] and Medal *et al.*[12] Since then, the reaction has become a popular synthesis strategy in the functional polymer design and preparation field.[13–15] Since acetylene-terminated benzoxazine (BA-apa)[16] was successfully synthesized and characterized, studies of anchoring benzoxazine with various polymer chains via a 1,3-dipolar cycloaddition reaction have rapidly sprouted up.[17–21] According to the studies mentioned previously, a 1,3-dipolar cycloaddition reaction has turned out to be a facile and reliable strategy for attaching functional groups to the main chain or side chain of benzoxazine. Moreover, on the basis of our previous research, the 1,3-dipolar cycloaddition reaction was proven to be a powerful method for preparing novel elastomers.[22]

In this article, we report a facile one-pot synthesis of a polyether-based main-chain-type benzoxazine elastomer via a metal-free 1,3-dipolar cycloaddition reaction. The elastomer was synthesized with an azide-terminated polyether (ATPEG), BA-apa, and a diazide monomer. Triazole rings introduced by a 1,3-dipolar cycloaddition reaction between azide and alkyne groups served as linkers in the structure of the elastomer. The thermal and mechanical properties of the elastomer were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile testing. Moreover, the thermal properties of the structurally transformed polyether-based main-chain type benzoxazine elastomer (PBE) after post thermal treated were also revealed in this study.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (number-average molecular weight = 2000 g/mol, Chemical Purity), thionyl chloride [$SOCl_2$; analytical reagent (AR)], bisphenol A (AR), 4,4′-bis(chloromethyl)-1,1′-biphenyl (Chemical Purity), paraformaldehyde (AR), anhydrous magnesium sulfate (CP), sodium hydroxide (Chemical Purity), anhydrous sodium sulfate (Chemical Purity), and sodium azide (NaN_3; Chemical Purity) were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used as received. The solvents benzene, *N,N*-dimethylformamide (DMF; AR), and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd., and were dried over 4A activated molecular sieves before use.

Characterization

^{1}H-NMR spectroscopy characterizations were recorded on a Bruker Avance 500 (500-MHz) spectrometer. Fourier transform infrared (FTIR) spectra of the product were obtained on a Nicolet 6700 spectrometer equipped with a smart ITR accessory. The DSC analysis results were obtained from a TA Q2000 differential scanning calorimeter with a heating rate of 20°C/min in a 50 mL^3/min nitrogen atmosphere. Elemental analyses were conducted with an Elementar Analysensysteme GmbH vario EL III. TGA was conducted on a TA SDT Q600 analyzer. The sample was heated from room temperature to 800°C at a heating rate of 10°C/min in a nitrogen atmosphere. The tensile properties of PBE were obtained on a universal mechanical test machine (Shenzhen SANS testing machine, CMT4204, Shenzhen, China) according to the widely accepted standard ASTM D 638. The tensile rate and temperature were 100 mm/min and 25°C, respectively.

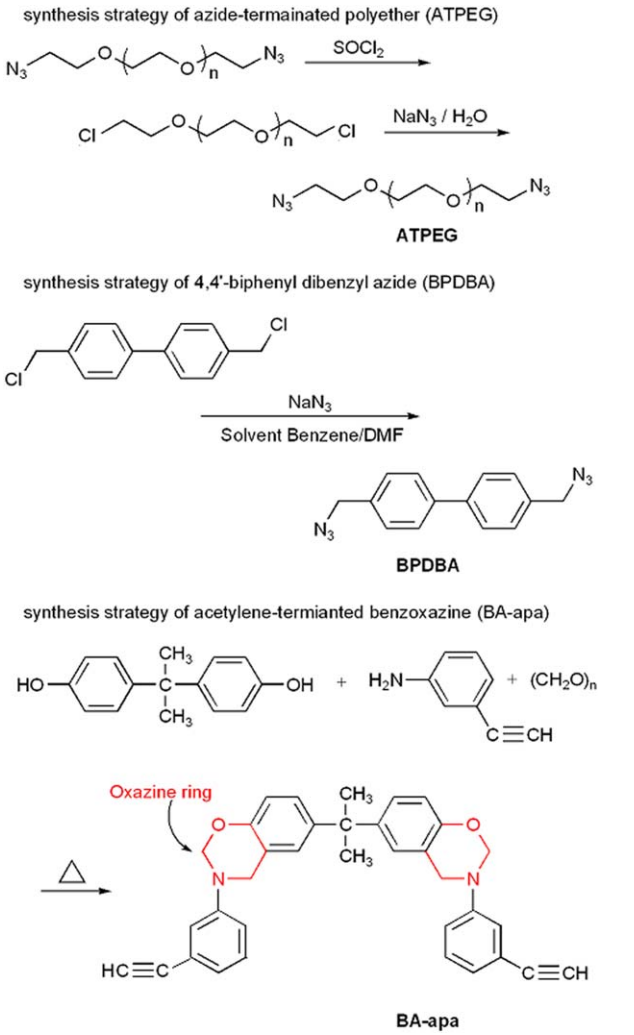
Synthesis of ATPEG

ATPEG was synthesized according to a method from a previous report.[23] The detailed synthesis procedure is described as follows. Poly(ethylene glycol) (64 g, 0.032 mol) was added to a 250-mL, round-bottomed flask equipped with a magnetic stirrer. After the dropwise addition of 100 mL of $SOCl_2$, the chlorination procedure was conducted at 65°C for 72 h. The sodium bicarbonate and deionized water were used to adjust the pH value of the mixture to neutral after the evaporation of the excess $SOCl_2$. The mixture was extracted with 60 mL of chloroform after filtration and then dried by anhydrous magnesium sulfate for 24 h. After filtration and solvent evaporation, the white chlorinated polyether was obtained. The substitute reaction was carried out in a 250-mL, round-bottomed flask with NaN_3 (26 g, 0.4 mol) and deionized water (150 mL). After it was stirred at 100°C for 100 h, the mixture was then extracted with chloroform (60 mL) and washed with deionized water. Then, the organic phase was dried with anhydrous magnesium sulfate for 24 h. The white ATPEG was obtained after filtration and solvent evaporation *in vacuo*. The molecular weight of ATPEG was 1913.8 g/mol according to the calculated elementary analysis result (Scheme 1).

mp = 58–60°C. ^{1}H-NMR ($CDCl^3$, δ): 3.62–3.70 (m, —CH_2—), 3.53–3.57 (m, 2H), 3.37 (t, 2H, —CH_2—N_3). ANAL. Found: C, 52.1%; H, 8.98%; N, 4.39%.

Synthesis of 4,4′-Biphenyl Dibenzyl Azide (BPDBA)

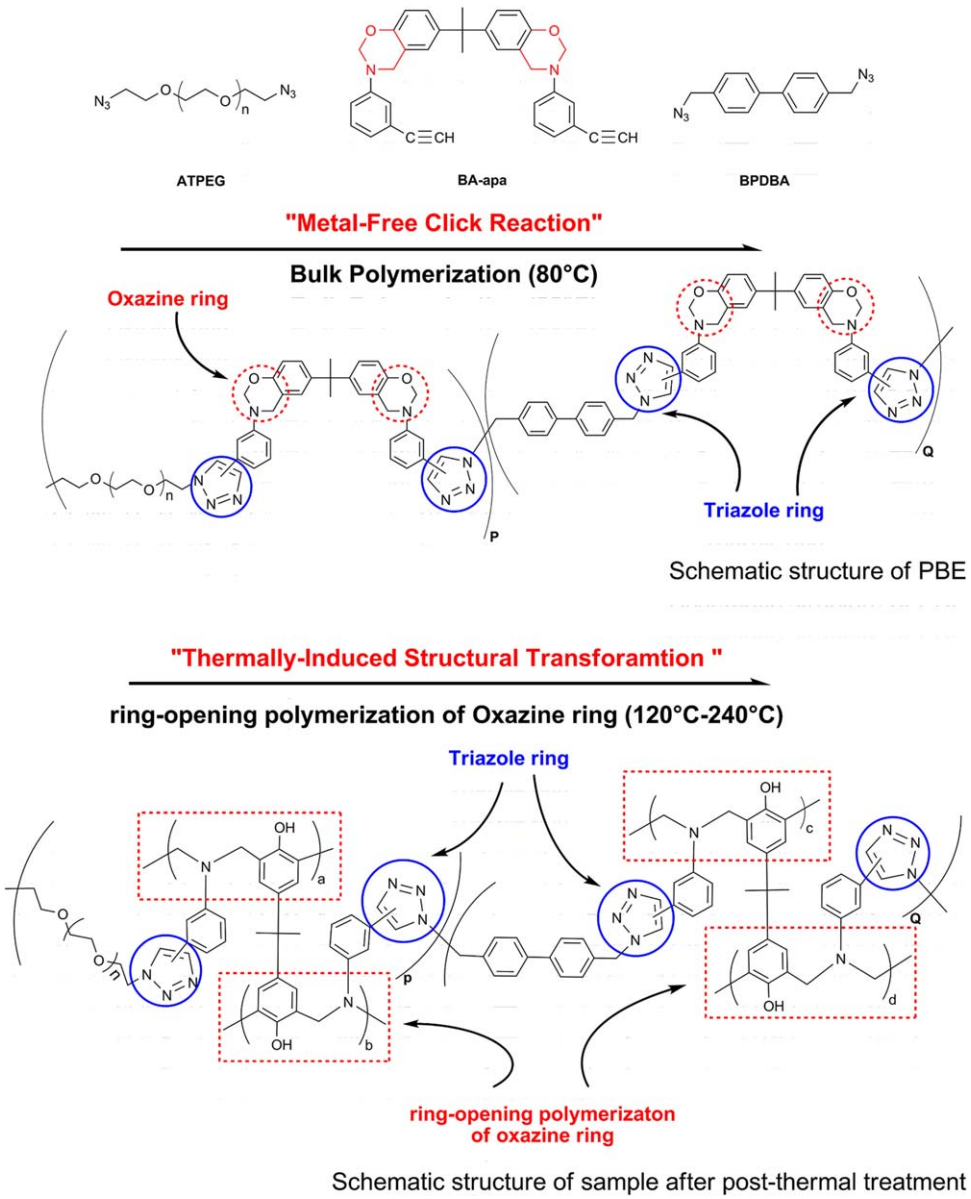
BPDBA was synthesized according to the literature.[24] Here, we give a short description of this synthesis procedure. Into a 100-mL, three-necked, round-bottomed flask, 4,4′-bis(chloromethyl)-1,1′-biphenyl (6.28 g 0.025 mol) and NaN_3 (3.25 g 0.05 mol) were added. The solvents used in the reaction were benzene (20 mL) and DMF (20 mL). The reaction was conducted at 75°C for 3 h. Then, the mixture was poured into deionized water (200 mL) to yield a white solid. The white solid powder product was obtained after filtration, washing with deionized water, and drying *in vacuo*. The characterization results of BPDBA were consistent with a previous report.mp = 70–71°C (reported value = 69–72°C). ^{1}H-NMR ($CDCl_3$, δ): 4.40 (s, 4H, Ar—CH_2—N_3), 7.39–7.42 (d, 4H, Ar—H), 7.60–7.26 (d, 4H, Ar—H).



Scheme 1. Synthesis strategies and structures of the monomers used for the preparation of PBE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis of BA-apa

BA-apa was synthesized basically according to a method reported by Ishida *et al.*[16] The detailed synthesis procedure, which had some differences compared to Ishida's method, is described later. Bisphenol A (22.8 g 0.1 mol), paraformaldehyde (12.0 g 0.4 mol), and 3-aminophenylacetylene (23.4 g 0.2 mol) were added to a 100-mL, three-necked flask equipped with an agitator and a condenser. The reaction was conducted at 100°C



Scheme 2. Synthesis strategy and schematic illustration of the structures of PBE and the structural transformation of PBE after the postthermal treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for 20 min. The mixture was dissolved in toluene and washed with a 3*N* sodium hydroxide solution. Then, the mixture was washed to neutral by deionized water. The toluene layer was dried by anhydrous sodium sulfate. After the evaporation of the solvent, BA-apa was obtained. The characterization results of the product were consistent with the previous report.[16]

^{1}H-NMR ($CDCl_3$, δ): 4.58 (s, Ar—CH_2—N), 5.30 (s, O—CH_2—N), 3.03 (s, C≡C—H), 6.70–7.22 (m, Ar—H).

Synthesis of a Polyether-Based Main-Chain-Type Benzoxazine Elastomer via a 1,3-Dipolar Cycloaddition Reaction (PBE)

The synthesis of PBE is shown in Scheme 2. ATPEG, BPDBA, and BA-apa were added to a three-necked flask equipped with an agitator according to calculated molar ratios. After 10 mL of acetone was added, the reaction was conducted at 60°C for 1 h to yield a homogeneous and clarified mixture. Then, the mixture was poured into a dumbbell-shaped mold before the mold was shifted to a vacuum oven (70°C) to remove residual solvents and bubbles for 2 h and prevent their damaging effects on the mechanical properties. A metal-free click reaction between the azide monomers and acetylene monomer was achieved at 80°C over the following 24 h. The sample we obtained so far could be classified as an elastomer by its appearance. The amount of raw materials used to prepare the PBE and the molar ratios of ATPEG to BPDBA are shown in Table I.

The sample could be transformed into a thermosetting material by the thermally induced ring-opening polymerization of the oxazine ring in its structure. The postthermal treatment was

Table I. Amounts of Raw Materials Used for the Preparation of PBE and Molar Ratios of ATPEG to BPDBA

Sample	Amount of raw material used in reaction (mmol)			Molar ratio of ATPEG to BPDBA
	ATPEG[a]	BPDBA[b]	BA-apa[c]	
PBE-1	2.0	6.0	8.0	1/3
PBE-2	2.0	4.0	6.0	1/2
PBE-3	2.0	2.0	4.0	1/2

[a] Number-average molecular weight = 1913 g/mol.
[b] Number-average molecular weight = 264 g/mol.
[c] Number-average molecular weight = 510 g/mol.

carried out at 120, 150, 180, and 240°C for 2, 2, 2, and 1 h, respectively. Photos of the elastomer and sample obtained after PBE went through postthermal treatment are given in Figure 1.

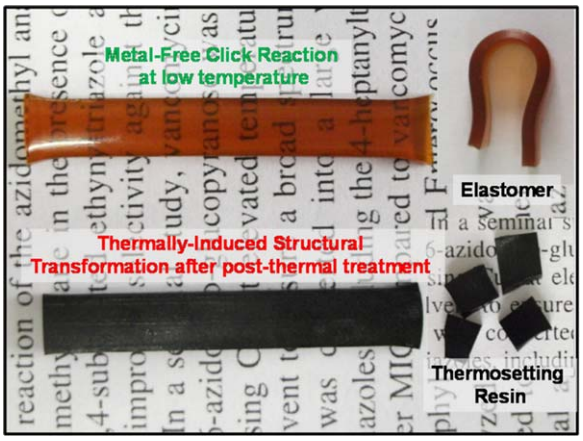


Figure 1. Photograph of the PBE and samples obtained after the thermally induced ring-opening polymerization of PBE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of the PBE before and after Postthermal Treatment

The characterization results of the monomers were consistent with values from previous studies. Because the reaction rate of the Cu(I)-catalyzed 1,3-dipolar addition reaction is very fast at 80°C, which was the melting temperature of the mixture of the monomers, if we used the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction to prepare the polytriazole elastomer, an explosive polymerization would occur. So, we used a metal-free 1,3-dipolar addition reaction to prepare the polytriazole elastomer. The synthesis strategy of PBE was conducted with bulk polymerization according to our initial idea for the convenience of preparing samples for mechanical testing. The ambient reaction temperature, which ensured the complete conduction of the 1,3-dipolar cycloaddition reaction, should have been insufficient for the ring-opening polymerization of the oxazine ring according to our best understanding. However, the obtained elastomer unexpectedly had poor insolubility in all solvents. The poor solubility of PBE was possibly caused by the low solvating power of solvent to the resulting PBE,

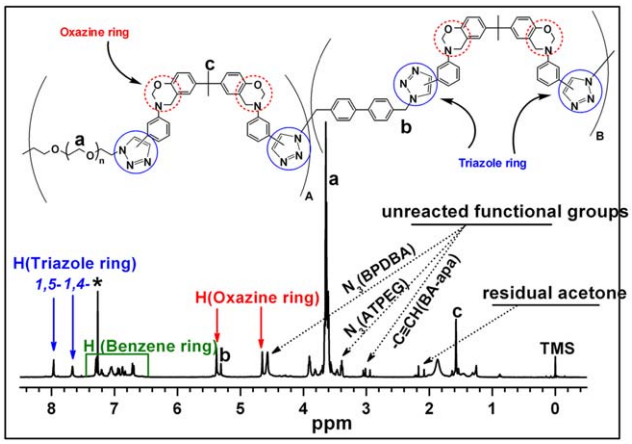


Figure 2. ^{1}H-NMR spectra of the PBE precursor synthesized at 60°C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and the nitrogen-rich heteroatom rings in the structure also resulted in the insolubility of the product, according to an explanation by Tang.[25] The insolubility of the PBE caused trouble in the characterization of its structure with the ^{1}H-NMR method and gel permeation chromatography. Also, the solution polymerization of PBE led to difficultly in the formation of the sample for the mechanical tests because of its high viscosity after several hours of reaction. Therefore, after the reaction was conducted in solvent at 60°C for 1 h, the mixture with a low viscosity was poured into the mold for further bulk polymerization. The mixture, after being heated at 60°C for 1 h, was considered a precursor of PBE. Then, the precursor was characterized by ^{1}H-NMR to confirm its structure to some extent. The ^{1}H-NMR spectrum is shown in Figure 2, and the main characteristic peaks are labeled. The peaks appeared at 7.67 and 7.97 ppm, which represented the hydrogens of the 1,4- and 1,5-substitute of triazole rings and revealed the occurrence of the click reaction. Other peaks were also observed in their appropriate positions according to Figure 2 and previous reports.[16,26,27] The ^{1}H-NMR results show that the 1,3-dipolar cycloaddition reaction was a facile synthesis strategy for the design and synthesis of PBE with a benzoxazine ring in its structure.

PBE: ^{1}H-NMR ($CDCl_3$, δ): 3.62–3.70 (m, —CH_2—), 3.53–3.57 (m, —CH_2—), 3.37 (t, 2H,—CH_2—N_3), 4.40 (s, 4H, Ar—CH_2—N_3), 4.58 (s, O—CH2—N), 5.30 (s, Ar—CH_2—N), 3.03 (s, ≡CC—H), 6.70–7.4 (m, Ar—H), 7.67 (s, —CH=C—N), 7.67 (s, —CH=C—N), 2.05–2.2 (m, —CH_3—CO—CH_3).

FTIR characterization was used to verify the synthesis of the PBE obtained after bulk polymerization at 80°C and its structural transformation from linear to crosslinked after postthermal treatment. PBE-1 was used as a typical sample for the characterization of the successful synthesis of PBE.

According to Figure 3 and previous reports,[24,25,27] the appearance of similar characteristic absorption peaks convinced us of the achievement of the 1,3-dipolar cycloaddition reaction. The absorption peaks observed at 3134, 1605, 1451, and 1042 cm^{-1} were attributed to the stretching vibrations of =C—H, —C=C—, —N=N—, and —C—N— in the triazole rings

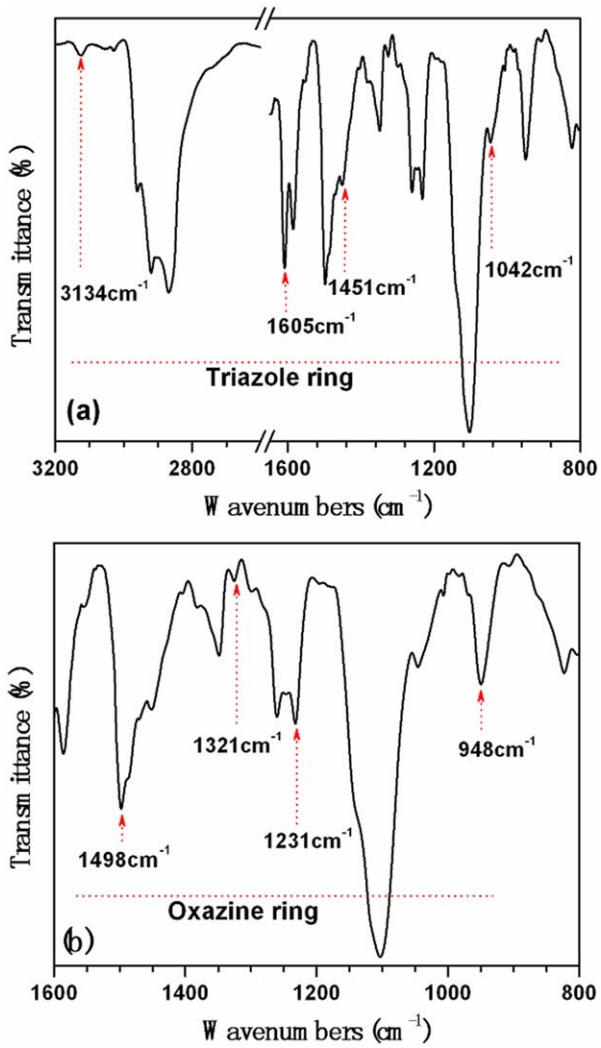


Figure 3. FTIR spectrum of PBE-1: (a) peaks assigned to the triazole ring and (b) peaks assigned to the benzoxazine ring. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

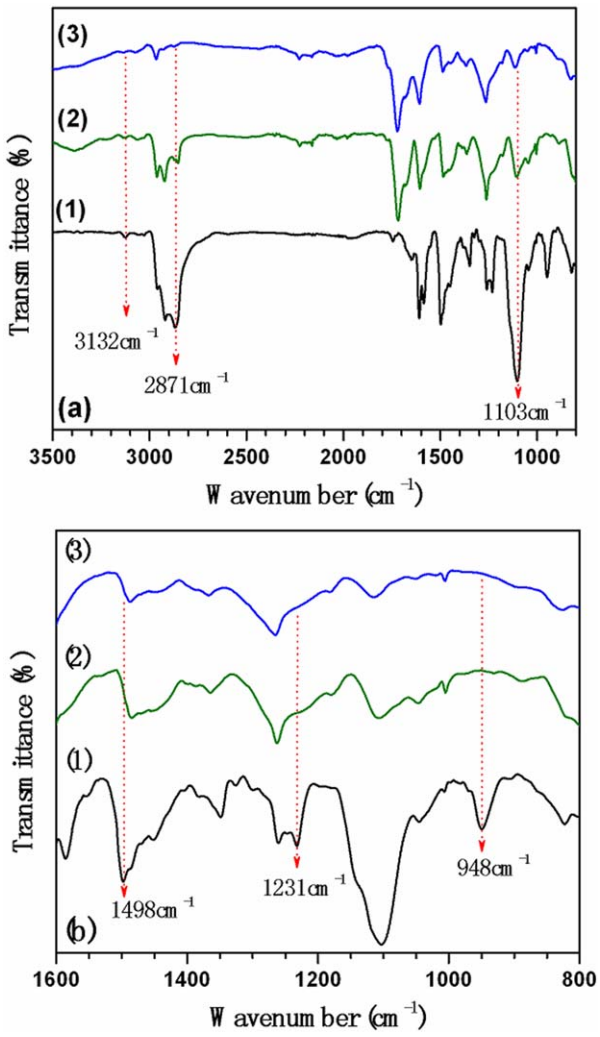


Figure 4. FTIR spectrum of the PBE-1 and samples obtained after PBE-1 was treated at different temperatures: (a) peaks assigned to the triazole ring and (b) peaks assigned to benzoxazine ring [(1) PBE prepared at 80°C, (2) a sample after treatment at 180°C for 2 h, and (3) a sample after treatment at 240°C for 1 h]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Figure 3(a)], respectively. In addition, the strong absorption band at 2871 cm^{-1} was caused by the CH_2 antisymmetric stretching mode of the polyether chain presented in the PBE. The absorption peak at 1109 cm^{-1} was assigned to the antisymmetric C—O—C stretching vibrations of the polyether chain. Carbon–carbon stretching vibrations determined from the 1, 2, 4-substitution of a benzene ring of the benzoxazine molecule appeared at about 1498 cm^{-1}. Another characteristic peak of BA-apa was the antisymmetric C—O—C stretching at 1231 cm^{-1}, whereas the bending vibrations of C—H appeared at 948 cm^{-1} [Figure 3(b)]. The structural transformation of PBE from a linear polymer to a crosslinking polymer induced by the ring-opening polymerization of oxazine rings at an elevating temperature was also investigated by FTIR characterization (Figure 4). We observed that the absorption peaks at 1498, 1321, 1231, and 948 cm^{-1} caused by benzoxazine almost disappeared after they were thermally treated [Figure 4(b)]. We inferred from Figure 4 that the ring-opening polymerization of the oxazine ring occurred and was conducted completely after thermal treatment at 240°C for 1 h.

Mechanical Properties

The tensile properties of the PBEs prepared with various molar ratios of ATPEG to BPDBA are presented in Table II and Figure 5, respectively.

Table II. Strain–Stress Test Results for PBEs Prepared with Various Molar Ratios of ATPEG to BPDBA

Sample	Molar ratio of ATPEG to BPDB	Stress (MPa)	Elongation at break (%)	Modulus (MPa)
PBE-1	1:3	37.6	515	303.4
PBE-2	1:2	18.9	760	1.3
PBE-3	1:1	0.9	546	0.2

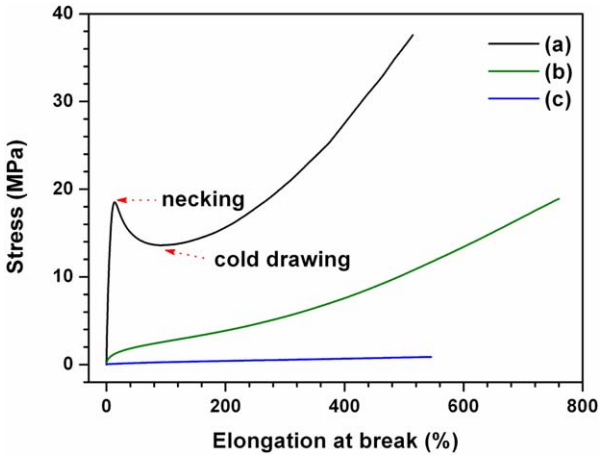


Figure 5. Stress–strain curves of the PBEs prepared with different molar ratios of ATPEG to BPDBA: (a) 1:3, (b) 1:2, and (c) 1:1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

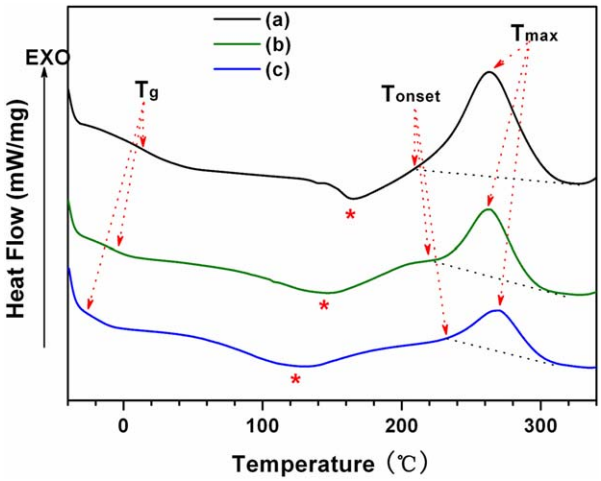


Figure 6. DSC curves of the PBEs prepared with various molar ratios of ATPEG to BPDBA: (a) 1:3, (b) 1:2, and (c) 1:1. The asterisk shows the melting peak. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the mechanical tests, the mechanical behaviors of all of the samples conformed with those of typical elastomers. The molar ratios of ATPEG to BPDBA had obvious influence on the mechanical properties of PBE according to the obtained tensile test results. The stress–strain curve of PBE-1 indicated that it had gone through the cold-drawing and necking procedure during the test. The unique stages reflected in the stress–strain curve suggested that PBE-1 had some plastic characteristics. This phenomenon could be attributed to the steric hindrance effect because of the high benzene content in its structure. The high tensile strength (37.6 MPa) and elongation at break (515%) compared to some popular polyurethane elastomers interested us because of the potential engineering applications. The mechanical properties of PBE-3 were counterintuitive according to the test results. According to our understanding, this abnormal phenomenon was due to the poor compatibility of the soft and hard segments, which was caused by the excess amount of ATPEG. Hence, the molar ratio of ATPEG to BPDBA should be controlled within a certain range (1 : 3–1:2) during the synthesis of PBE to ensure its elasticity and strength. The elastomer could be considered as a promising polymer because of the mechanical properties mentioned previously.

Table III. DSC Analysis Results of PBEs Prepared with Various Molar Ratios of ATPEG to BPDBA

Sample	T_g (°C)	T_{onset} (°C)[a]	T_{max} (°C)	ΔH (J/g)[b]
PBE-1	13	209	262	151.4
PBE-2	−13	220	263	82.73
PBE-3	−23	232	269	58.39

[a] T_{onset} of the ring-opening polymerization of oxazine ring.
[b] ΔH of the exothermic peak.

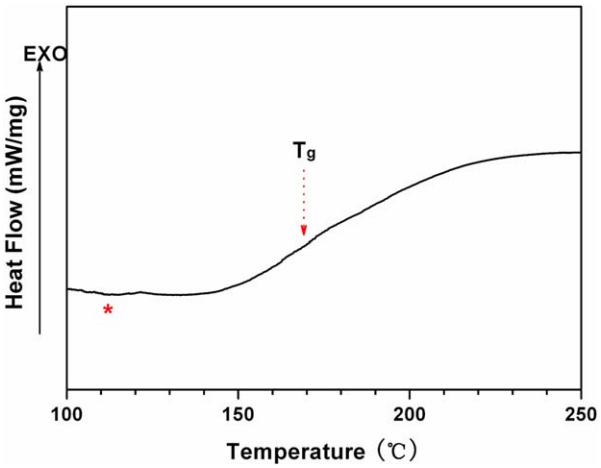


Figure 7. DSC curve of a sample obtained after PBE-1 was treated at 240°C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

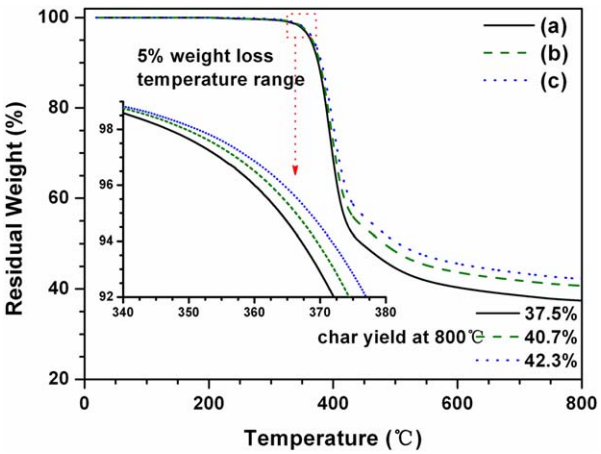


Figure 8. TGA curves of PBEs prepared with different molar ratios of ATPEG to BPDBA: (a) 1:3, (b) 1:2, and (c) 1:1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. TGA Results of PBEs Prepared with Different Molar Ratios and Treated at Different Temperatures

	PBEs prepared with different molar ratios				Samples after postthermal treatment at different temperatures		
Sample	T_{d5} (°C)	T_{d10} (°C)	Y_{800} (%)	Sample	T_{d5} (°C)	T_{d10} (°C)	Y_{800} (%)
PBE-1	364	376	37.5	PBE-1[a]	364	376	37.5
PBE-2	365	378	31.9	PBE-1[b]	366	378	40.7
PBE-3	369	380	26.1	PBE-1[c]	368	381	42.3

T_{d10}, 10% weight loss thermal decomposition temperature; Y_{800}, char yield at 800°C.
[a] Prepared at 80°C.
[b] After thermal treatment at 180°C for 2 h.
[c] After thermal treatment at 240°C for 1 h.

DSC Characterization of PBE before and after the Postthermal Treatment

The thermal properties of the PBEs prepared with various molar ratios of ATPEG to BPDBA were revealed by DSC (Figure 6). The detailed values are listed in Table III.

According to the data obtained from the DSC curves, the glass-transition temperatures (T_g's) of PBEs were all lower than room temperature. The low T_g benefited from the introduction of flexible polyether groups; meanwhile, it ensured that the PBE was a kind of elastomer at room temperature. Also, T_g decreased with increasing ATPEG content, according to classical polymer theory. The onset temperatures (T_{onset}'s) of all of the PBE crosslinking were higher than those of the original BA-apa used in the synthesis procedure and the temperatures of the exothermic peaks (T_{max}'s). The increased polymerization temperatures were a simple dilution effect of the oxazine ring content by the other inert components, such as ethylene glycol units. Meanwhile the total enthalpy (ΔH) of PBE decreased with the lower mass ratio of the oxazine ring in the structure. According to Figure 7, we found that the T_g of the postthermally treated PBE-1 increased (151°C). However, the T_g value of the cured PBE-1 was lower than that of the original polybenzoxazine[28] because flexible polyether groups existed in its structure.

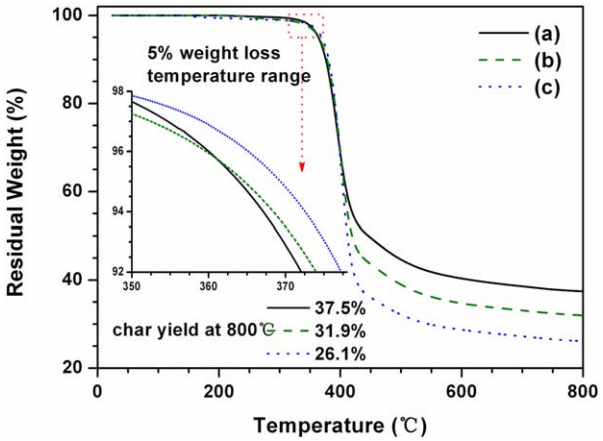


Figure 9. TGA curves of samples obtained after PBE-1 was treated at different temperatures: (a) PBE prepared at 80°C, (b) PBE-1 treated at 180°C for 2 h, and (c) PBE-1 treated at 240°C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA of PBE before and after the Postthermal Treatment

TGA was used to characterize the thermal stabilities of the PBEs prepared with different molar ratios of ATPEG to BPDBA and samples transformed after the postthermal treatment of PBE-1 at various temperatures. The TGA curves are shown in Figures 8 and 9. In addition, Table IV tabulates the detailed values acquired through the TGA characterization. According to the curves shown in Figures 8 and 9, we found that all of the thermogravimetric decomposition behaviors of the samples followed a similar pattern. According to the detailed values given in Table IV, the 5% weight loss temperatures (T_{d5}'s) of all of the samples exceeded 360°C. Hence, PBE could be considered a kind of thermally stable elastomer. Also, PBE is expected to have applications in some high-temperature demanding areas.

CONCLUSIONS

In summary, we synthesized and characterized a novel polyether-based main-chain-type benzoxazine elastomer (PBE) via a metal-free click reaction. The metal-free click reaction offered a facile one-pot synthesis strategy for preparing the novel elastomer via a combination of the benzoxazine ring and triazole ring. PBE could be classified as a kind of thermal stable elastomer with satisfactory mechanical properties. Thanks to the ring-opening polymerization characteristics of the oxazine ring in the benzoxazine structure, the elastomer was endowed with the possibility of a thermally induced structural transformation. This unique property makes the conversion of the elastomer to a thermosetting resin possible only with thermal treatment. The prepared elastomer could be expected to be applied as a heat-resistant elastomer.

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