

Study on Preparation and Properties of Polyether Polytriazole Elastomers^{*}

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Abstract To explore the application of click chemistry in the field of elastomer materials, propargyl-terminated ethylene oxide-tetrahydrofuran copolymer (PTP(E-co-T)) was prepared from hydroxyl-terminated ethylene oxide-tetrahydrofuran copolymer (P(E-co-T)) by end-etherisation modification. FTIR and ¹³C-NMR results indicate that P(E-co-T)-terminated hydroxyl was etherified thoroughly, yielding the target product PTP(E-co-T), and the content of terminated alkynyl of PTP(E-co-T) was evaluated to be 0.428 mmol·g⁻¹. Using a polyazide compound as a cross-linker, polytriazole elastomers with various functional molar ratio (*R*) values were prepared from PTP(E-co-T) by virtue of the CuAAC reaction. Mechanical property tests indicate that with the increase in *R*, the modulus *E* and stress σ_b of the polytriazole elastomers first increase and subsequently decrease, whereas the strain first decreases and later increases. The mechanical properties of the polytriazole elastomers show a parabolic dependence on the *R* value. Near the stoichiometric ratio, *E* and σ_b show maxima and the strain ϵ_b shows a minimum. Swelling tests demonstrate that the apparent molecular weight of polytriazole elastomer strands also first decreases and subsequently increases. At the stoichiometric ratio, the network structure possesses strands with a minimum apparent molecular weight and a maximum apparent density. Dynamic mechanical analysis reveals that the polytriazole elastomers presented damping peaks at approximately -64 °C, corresponding to the glass transition of copolyether strands, and the elastomer exhibited the lowest dissipation factor $\tan\delta$ at the stoichiometric ratio. Thermal analysis suggests that the weight-loss process of the polytriazole elastomer is characteristic of one-step decomposition, and the elastomer begins to decompose from polyether strands, not triazole groups.

Keywords: Click chemistry; Polytriazole; Elastomers; PTP(E-co-T).

INTRODUCTION

A thermoset elastomer is a polymer material that exhibits large reversible deformabilities with a distinctly low elastic modulus and is widely utilised in many applications. The unique mechanical properties of the elastomers originate from the cross-link density in the network or, analogously at the molecular scale, the average molecular weight between junction points.

Conventional thermoset elastomers formed by random cross-linking methods possess very obscure structures with a broad network strand length distribution and an unknown number of dangling chains, and their properties cannot be accurately controlled^[1]. In contrast, well-characterised elastomers with unambiguous structural parameters can be prepared by end-linking reactions; thus, elastomers with desired properties can be easily obtained by controlling the distribution of the precursor chains and cross-linker functionality.

The study of end-linking elastomers has long focussed mainly on the isocyanate reaction^[2], hydrosilylation reaction^[3] and epoxy addition reaction^[4], among others^[5]. However, the aforementioned reactions are typically associated with shortcomings such as sensitivity to water or oxygen, low efficiency and stringent reaction conditions, causing the formation of defective network structures and adversely affecting mechanical properties.

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More recently, click chemistry, coined by Sharpless and his coworkers in 2001, has received tremendous attention because of its advantages of high efficiency, regioselectivity, mild reaction conditions, *etc*^[6–8]. The copper-catalysed azide-alkyne Huisgen [3 + 2] dipolar cycloaddition (CuAAC) reaction is the most appealing click chemistry reaction for generating 1,2,3-triazole compounds^[9] and has become a versatile synthetic tool with applications in the field of biomedicine. For example, Eduardo synthesised three generations of azido-terminated PEG-dendritic block copolymers and then introduced carbohydrate units into the block copolymer by click chemistry; the resultant compound can be applied in drug delivery^[10]. Grieshaber modified an alkyne-terminated peptide using click reaction and prepared elastin-mimetic hybrid polymers^[11]. Click chemistry has also been utilised in the field of polymer science^[12]. Wang first prepared azido-terminated and alkynyl-terminated triblock copolymers and then synthesised multiblock copolymers using click chemistry^[13]. By virtue of the specificity of click chemistry, Yao reported the simultaneous synthesis of interpenetrating polymer networks of poly(ethylene glycol) and poly(2-hydroxyethyl methacrylate) by click chemistry reaction and atom transfer radical polymerisation^[14]. Gonzaga synthesised diethynyl-terminated tetramethyldisiloxane and poly(azidopropylmethyl)-*co*-(dimethylsiloxane) and then prepared silicone elastomeric materials by random cross-linking *via* click chemistry^[15]. Yang synthesised alkyne-terminated perfluoropolyether and using a tripod azide organic small molecule as a curing agent prepared a fluorinated elastomer through click chemistry end-linking^[16].

A copolyether is non-toxic, high flexible, and can be utilized to manufacture low temperature elastomer^[17]. However, to date, few studies regarding the synthesis of copolyether elastomers end-linked by a click reaction have been reported. In this study, a polyazide compound and propargyl-terminated ethylene oxide-tetrahydrofuran copolymer (PTP(E-*co*-T)) were synthesised. *Via* the CuAAC reaction, polytriazole elastomers were prepared, and their properties were examined.

EXPERIMENTAL

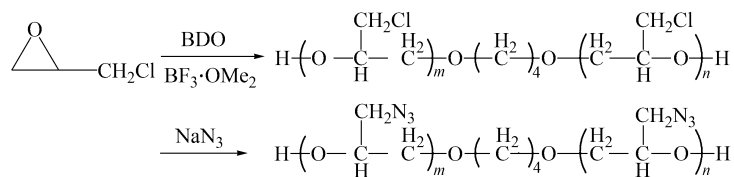
Materials

The prepolymer used was hydroxyl bi-functionalised ethylene oxide-tetrahydrofuran copolymer (P(E-*co*-T), hydroxyl value 0.435 mmol·g⁻¹, M_n 4038), and purchased from Liming Research Institute of Chemical Industry. All other agents were utilised as received.

Synthesis of Polyazide

Referring to Reference [18], to a three-neck flask fitted with a thermometer and nitrogen inlet, 1.50 g (0.0167 mol) of butanediol (BDO), 800 μ L BF₃-dimethyl ether complex and 75 mL anhydrous methylene chloride (CH₂Cl₂) were added. The reaction mixture was stirred at room temperature for an hour. After cooling the reaction mixture to 0 °C, 6.17 g (0.0667 mol) of epichlorohydrin (ECH) was slowly added dropwise. After the addition of ECH, the reaction was continued for another 12 h at room temperature, and then a small amount of NaHCO₃ solution was added to terminate the reaction. The resultant product was washed with H₂O until neutral, separated and evaporated under reduced pressure to recover approximately 5 g of PECH oligomer. The elemental analysis results calculated for the PECH oligomer were as follows: C, 41.74. H, 6.5; the results observed were as follows: C, 40.5. H, 6.25. The vapour pressure osmometer (VPO) analysis: $M = 460$; FTIR: ν (–OH) = 3458 cm⁻¹, ν (C–O–C) = 1100 cm⁻¹, ν (C–Cl) = 745 cm⁻¹.

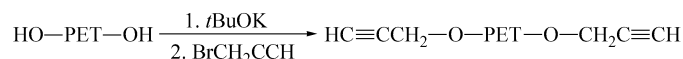
Five grams PECH oligomer, 30 mL dimethyl formamide (DMF) and 4 g sodium azide (NaN₃) were added to a three-necked flask fitted with a thermometer and condenser. The mixture was reacted for 24 h at 80 °C. Thereafter, 50 mL H₂O was added to the flask, followed by 50 mL CH₂Cl₂. The organic layer was separated, successively washed twice with 2 $\times$ 30 mL H₂O and evaporated under reduced pressure to obtain 4.5 g polyazide compound. The elemental analysis calculated for the polyazide compound were as follows: C, 39.51. H, 6.17. N, 34.57; the observed results were as follows: C, 38.86. H, 5.99. N, 32.3. The applied experimental conditions were as follows: FTIR: ν (–OH) = 3420 cm⁻¹, ν (C–O–C) = 1100 cm⁻¹, ν (–N₃) = 2088 cm⁻¹; vapour pressure osmometer (VPO) analysis: $M = 480$. The azido content of the polyazide was determined to be 7.69 mmol·g⁻¹, and average functionality 3.82. The synthesis route of the polyazide compound is shown in Scheme 1.



Scheme 1 Synthesis of polyazido compound

Preparation of PTP(E-co-T)

To a three-neck flask fitted with a thermometer, condenser and nitrogen inlet, 12.5 mmol potassium *t*-butoxide and 100 mL tetrahydrofuran (THF) were added. After stirring for 30 min at 0 °C, P(E-co-T) (21.9 g, 10 mmol hydroxyl) was added, and the reaction was continued for an hour. Then, 20 mmol propargyl bromide was added dropwise. After the addition of propargyl bromide, the resultant mixture was warmed to 30 °C and reacted for another 40 h. The mixture obtained was successively washed twice with 2 × 160 mL brine. The organic layer was separated and evaporated under reduced pressure to form propargyl terminated ethylene oxide-tetrahydrofuran copolymer (PTP(E-co-T)) at a yield of approximately 20 g (20 °C density 1.049 g·cm⁻³, light, golden liquid). The synthesis route for the polyazide compound is shown in Scheme 2.



Scheme 2 Preparation of propargyl terminated ethylene oxide-tetrahydrofuran copolymer (PTP(E-co-T))

Preparation of Elastomers

The elastomer compositions are listed in Table 1. All components were mixed uniformly, degassed under vacuum and cured at 50 °C for 7 days, and elastomers end-linked by a triazole group were obtained. In Table 1, *R* is the equivalent ratio of the cross-linker functional group to the prepolymer functional group; the catalyst used was a copper(I) hexafluoroacetylacetonate cyclooctadiene complex. Using the density bottle method, the density of the obtained elastomers was determined to be (1.071 ± 0.003) g·cm⁻³.

Table 1. Elastomer components in mass ratio

Example	<i>R</i>	Catalyst	Prepolymer PTP(E-co-T)	Cross-linker polyazide
S1	0.8	0.005	10	0.430
S2	0.9	0.005	10	0.484
S3	1.0	0.005	10	0.548
S4	1.1	0.005	10	0.591
S5	1.2	0.005	10	0.645
S6	1.3	0.005	10	0.699

Swelling Test

Swelling measurements were carried out in toluene at 20 °C, and the volume fractions of the elastomers were determined gravimetrically. Small pieces of the elastomers (approximately 0.15 g, 10 mm × 5 mm × 3 mm) were immersed in toluene, and the swollen gels were removed from solvent at different times, quickly blotted with dry filter paper and weighed till the mass change was less than 0.01 g over a period of 30 min. The volume swelling ratio of the elastomers (q_v) can be calculated by assuming the additivity of volumes using equation (1).

$$q_v = 1 + (w/w_0 - 1)\rho_2/\rho_1 \quad (1)$$

where w_0 is the weight of the specimen before swelling, w is the weight of the specimen after swelling and ρ_1 and ρ_2 are the densities of solvent and polymer, respectively.

Instrumentation

Infrared spectra were recorded on a Nicolet 6700 infrared spectrometer. Vapor pressure osmometry (VPO) measurements were performed with a Knauer K-7000 vapor pressure osmometer using solvent trichloromethane

at 20 °C. ^{13}C -NMR spectra were recorded on a Bruker 600 spectrometer (> 500 scans) using gated decoupling, a spectrum width of 20 kHz, a recycle delay of 25 s and a 90° pulse. Chemical shifts (δ) were reported, relative to tetramethylsilane (TMS). The molecular weight of the polymers was determined using a WATERS1515 gel permeation chromatograph (solvent tetrahydrofuran, solution concentration $0.1 \text{ mg}\cdot\text{mL}^{-1}$, three fat-soluble gel chromatography columns (HT3, HT4, HT5, respectively) connected in series, column temperature 40 °C, flux $1 \text{ mL}\cdot\text{min}^{-1}$, differential refractive index detector 2414). At room temperature, the mechanical properties of the elastomers (specification $100 \text{ mm} \times 20 \text{ mm} \times 5 \text{ mm}$) were measured on an Instron 6022 mechanical tester at a crosshead speed of $100 \text{ mm}\cdot\text{min}^{-1}$. Dynamic mechanical analysis (DMA) of the elastomers (specification $5 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$) was carried out using a METTLER instrument SDTA861e DMA at a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$ and a frequency of 1 Hz. Thermal gravimetric analysis (TGA) was performed on a Netzsch 209 F1 thermal analyser under nitrogen atmosphere at a heating rate of $20 \text{ K}\cdot\text{min}^{-1}$ from 40 °C to 800 °C. A 10 mg sample was used, and the gas flow rate was $60 \text{ mL}\cdot\text{min}^{-1}$.

RESULTS AND DISCUSSION

Structure of PEP(E-co-T)

The FTIR spectra for P(E-co-T) and PTP(E-co-T) are shown in Fig. 1. P(E-co-T) shows major characteristic vibrations, such as hydroxyl groups at 3408 cm^{-1} , ether groups at 1103 cm^{-1} and others, in good agreement with the report in Reference [19]. Compared with P(E-co-T), PTP(E-co-T) presents characteristic peaks of alkynyl groups at 3244 cm^{-1} and 664 cm^{-1} because of the terminated hydroxyl of P(E-co-T) having been etherified, in addition to other characteristic peaks. Correspondingly, the peak attributed to hydroxyl groups does not appear in the PTP(E-co-T) spectrum.

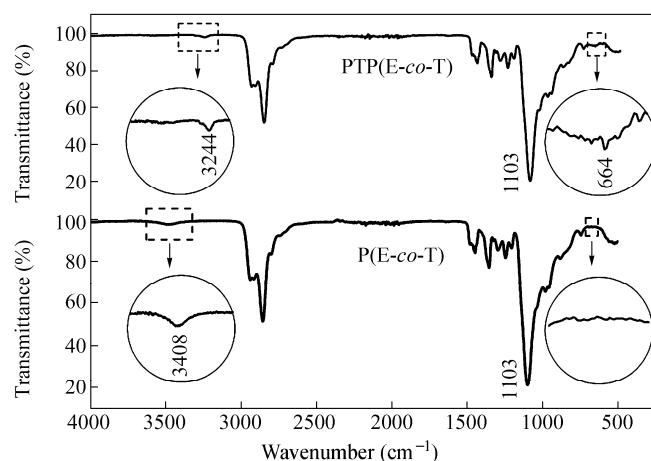


Fig. 1 FTIR spectra of P(E-co-T) and PTP(E-co-T)

The ^{13}C -NMR spectra for P(E-co-T) and PTP(E-co-T) are shown in Fig. 2. In the P(E-co-T) spectrum, it is clear that carbon atoms 1, 2 and 3 are attributed to the multiple peaks at approximately $\delta = 71$ and 26, and carbon atom 4 is assigned to the peak at $\delta = 72.5$, in good agreement with the spectral features reported in References [20] and [21]. It should be noted that the peak at $\delta = 61.6$ originates from primary carbon atoms 5 and 6 associated with the hydroxyl group^[22].

In the ^{13}C -NMR spectra of PTP(E-co-T), the typical peaks of P(E-co-T) attributed to carbon atoms 1, 2 and 3 persist at approximately $\delta = 71$ and 26. Due to P(E-co-T) terminal hydroxyl having been etherified by propargyl, the peaks at $\delta = 61.6$ attributed to the primary carbon atoms associated with the hydroxyl group thoroughly disappear. Instead, the peaks attributed to carbon atoms 7, 8 and 9 emerge at $\delta = 58.3, 74.5, 79.6$, respectively. In addition, other carbon atoms are clearly assigned. These indicate that the terminated hydroxyl of P(E-co-T) has been thoroughly etherified, yielding the target product PTP(E-co-T).

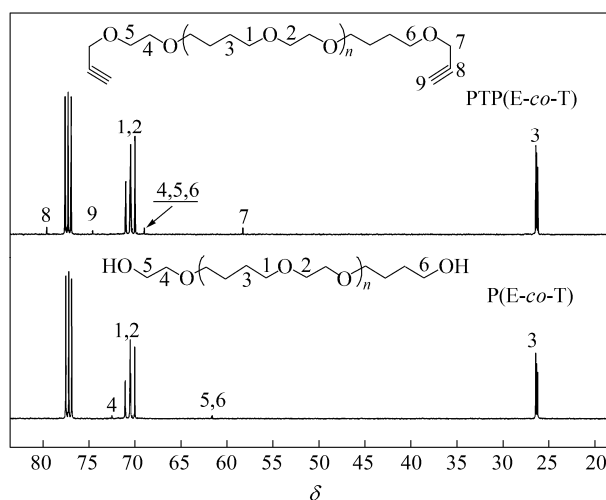


Fig. 2 ^{13}C -NMR spectra of P(E-co-T) and PTP(E-co-T)

According to GPC measurements, the number average molecular weights of P(E-co-T) and PTP(E-co-T) are $4.0 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ and $4.1 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$, respectively. And the weight-average molecular weight of P(E-co-T) and PTP(E-co-T) are $7.0 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$ and $7.1 \times 10^3 \text{ g}\cdot\text{mol}^{-1}$, respectively. PTP(E-co-T) molecular weights are merely slightly higher than those of P(E-co-T) because the terminated hydroxyl of P(E-co-T) has been etherified. Correspondingly, the polydispersity index of PTP(E-co-T) (1.73) is very close to that of P(E-co-T) (1.75). These results suggest that few chain extension and break reactions occurred and that P(E-co-T) was transformed into PTP(E-co-T) only through end-capping modification. Thus, according to the P(E-co-T) hydroxyl value given, the content of terminated alkynyl groups of PTP(E-co-T) was determined to be $0.428 \text{ mmol}\cdot\text{g}^{-1}$ (see Eq. 2), which was used to obtain the R value of the polytriazole elastomer (see Table 1).

$$c_{\text{alkynyl}} = c_{\text{hydroxyl}} / [1 + c_{\text{hydroxyl}} \times (M_{\text{propargyl}} - 1)] \quad (2)$$

where c_{alkynyl} is the content of alkynyl groups, $\text{mmol}\cdot\text{g}^{-1}$, c_{hydroxyl} is the content of hydroxyl groups, $\text{mmol}\cdot\text{g}^{-1}$, and $M_{\text{propargyl}}$ is the molecular weight of propargyl groups ($39 \text{ g}\cdot\text{mol}^{-1}$).

Mechanical Properties

The mechanical properties of polytriazole elastomers S1-S6 prepared from PTP(E-co-T) are listed in Table 2. It can be observed that the modulus E and stress σ_b first increase from (0.87 ± 0.05) and $(0.77 \pm 0.01) \text{ MPa}$ to (1.82 ± 0.17) and $(1.19 \pm 0.08) \text{ MPa}$ and then decrease to (1.28 ± 0.10) and $(1.01 \pm 0.08) \text{ MPa}$, respectively, with

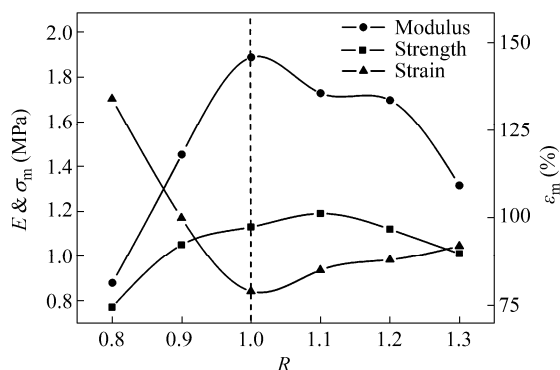


Fig. 3 Mechanical property curves of S1-S6

increasing R . In contrast, the strain ε_b first decreases from $(135 \pm 7)\%$ to $(79 \pm 4)\%$ and then increases to $(92 \pm 10)\%$. The maximum and minimum values simultaneously appear near the stoichiometric ratio ($R = 1.0$). As shown in Fig. 3, the dependence of the mechanical properties of the polytriazole elastomers on R is parabolic, but the values of the mechanical properties are not symmetrical about the peak values.

Table 2. Mechanical properties of elastomers S1–S6

Mechanical properties	Elastomer examples					
	S1	S2	S3	S4	S5	S6
Young's modulus, E (MPa)						
1	0.8	1.43	1.68	1.75	1.69	1.38
2	0.86	1.38	1.68	1.71	1.46	1.15
3	0.91	1.43	1.92	1.69	1.9	1.25
4	0.89	1.41	2.01	1.52	1.52	1.32
Average	0.87 ± 0.05	1.41 ± 0.02	1.82 ± 0.17	1.67 ± 0.10	1.64 ± 0.20	1.28 ± 0.10
Stress at break, σ_b (MPa)						
1	0.78	1.01	1.12	1.25	1.11	0.91
2	0.77	1.08	1.19	1.1	1.09	1.02
3	0.76	1.05	1.14	1.13	1.12	1.01
4	0.77	1.06	1.07	1.26	1.16	1.10
Average	0.77 ± 0.01	1.05 ± 0.03	1.13 ± 0.05	1.19 ± 0.08	1.12 ± 0.03	1.01 ± 0.08
Strain at break, ε_b (%)						
1	140	97	77	89	86	80
2	125	104	84	77	87	89
3	137	99	80	82	87	92
4	136	99	74	93	90	105
Average	135 ± 7	100 ± 3	79 ± 4	85 ± 7	88 ± 2	92 ± 10

Network Structure

The volume swelling curves of the polytriazole elastomers are shown in Fig. 4. It can be observed that the initial volume swelling rates of the elastomers gradually decrease for S1–S3 and then increase for S3–S6. Elastomer S3 has the lowest volume swelling rate. After 450 min, all volume swelling ratios (q_v) come to equilibrium, and elastomer S3 has the minimum equilibrium volume swelling ratio.

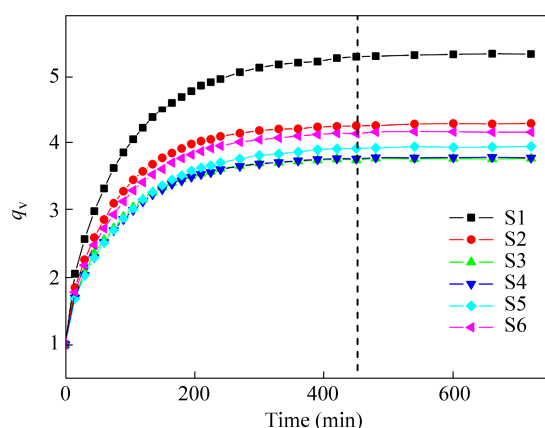


Fig. 4 Volume swelling curves of polytriazole elastomers

Based on the equilibrium volume swelling ratios (q_v) of the elastomers, the volume fractions (v_{2m}) of the polymers can be evaluated using the Bristow-Watson Equation (Eq. 3)^[23]. In addition, the Flory-Huggins interaction parameter between the polymer and the solvent (χ_1) can be evaluated using Eq. (4)^[24]. Thus, the apparent average molecular weights (M_s) of elastomer strands between junction points can be further calculated

according to Flory-Huggins theory (see Eq. 5)^[25]. Moreover, the apparent densities of elastomer strands (N_0 , the moles of the strands per cubic centimeter) can be determined using Eq. (6).

$$v_{2m} = 1/q_v \quad (3)$$

$$\chi_1 = 0.34 + \frac{V_s}{RT} (\delta_p - \delta_s)^2 \quad (4)$$

$$M_s = -V_s \rho (v_{2m}^{1/3} - v_{2m}/2) / [\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \quad (5)$$

$$N_0 = \rho / M_c \quad (6)$$

where V_s denotes the molar volume of the toluene solvent (106.4 mL·mol⁻¹), δ_p and δ_s denote the solubility parameter of the polymer and the solvent, which are determined to be 18.06 (J cm³)^{1/2} and 18.1 (J cm³)^{1/2}, respectively, according to the additivity of groups^[26], and ρ denotes the density of the elastomers.

The calculated structure parameters of the polytriazole elastomers are listed in Table 3. It can be observed that with the increase in R , M_s first decreases from $(6.67 \pm 0.06) \times 10^3$ g·mol⁻¹ to the minimum $(3.03 \pm 0.02) \times 10^3$ g·mol⁻¹ and then increases again to $(3.83 \pm 0.02) \times 10^3$ g·mol⁻¹. Correspondingly, N_0 increases from (0.160 ± 0.001) to the maximum (0.353 ± 0.002) mmol·cm⁻³ and then decreases to (0.280 ± 0.001) mmol·cm⁻³. Elastomer S3 exhibits the minimum apparent molecular weight and maximum apparent strand density.

Table 3. Structure parameters of polytriazole elastomers

Sample	R	χ_1	q_v	v_{2m}	M_s (g·mol ⁻¹)	N_0 (mmol·cm ⁻³)
S1	0.8	0.340	5.348 ± 0.004	0.1870 ± 0.0001	$(6.67 \pm 0.06) \times 10^3$	0.160 ± 0.001
S2	0.9	0.340	4.282 ± 0.004	0.2335 ± 0.0002	$(4.07 \pm 0.04) \times 10^3$	0.263 ± 0.003
S3	1.0	0.340	3.761 ± 0.004	0.2659 ± 0.0003	$(3.03 \pm 0.02) \times 10^3$	0.353 ± 0.002
S4	1.1	0.340	3.777 ± 0.004	0.2648 ± 0.0003	$(3.06 \pm 0.02) \times 10^3$	0.350 ± 0.002
S5	1.2	0.340	3.934 ± 0.005	0.2542 ± 0.0003	$(3.36 \pm 0.03) \times 10^3$	0.318 ± 0.003
S6	1.3	0.340	4.158 ± 0.005	0.2405 ± 0.0003	$(3.83 \pm 0.02) \times 10^3$	0.280 ± 0.001

Because the CuCCA reaction involves no side-reactions^[7], the elastomers' network structures can be conceived to be those schematically shown in Fig. 5. When $R < 1.0$, the terminated alkynyl content of PTP(E-co-T) is in excess and terminated alkynyl groups cannot be completely reacted with azide groups, causing the formation of many dangling strands in the elastomer network (Fig. 5a). Consequently, the elastomers exhibit higher M_s and lower N_0 . At the stoichiometric ratio, the terminated alkynyl content is equivalent to that of the azide groups, and terminated alkynyl groups are nearly reacted to completion with azide groups of the cross-linker. The resultant network structure approaches that of a integrated lattice, with few propargyle and azide groups in the elastomer (Fig. 5b); additionally, M_s is minimised and N_0 is maximised. When $R > 1.0$, the excess azido groups in the cross-linker molecules cannot be reacted with and are still appended at some cross-linking points, forming nonuniform meshes (Fig. 5c). Resultantly, M_s again increases and N_0 again decreases. These results are in accordance with the trends shown in Table 3. As a result, it can be concluded that the higher M_s and lower N_0 are the results of dangling strands when $R < 1.0$, whereas the higher M_s and lower N_0 originate from the nonuniform meshes caused by unreacted azide groups when $R > 1.0$. Combining Fig. 3, it can also be inferred that the asymmetrical mechanical properties on 1.0 (R value) should be originated from the topographical asymmetry of the elastomer networks. Regarding the finding that the value of M_s is less than that of the prepolymer PTP(E-co-T) in polytriazole elastomers S2–S6, the disparity is presumably caused by the formation of many physical entanglements among the strands.

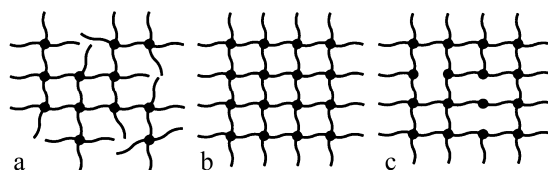


Fig. 5 Network structures of polytriazole elastomers

The stress and modulus of end-linking elastomers are proportional to the apparent density of network chains N_0 , and the strain is proportional to the apparent average molecular weight $M_s^{[27]}$. Thus, it can be inferred that the stress and modulus of the polytriazole elastomers should first increase to a maximum value and then decrease and the strain should first decrease to a minimum value and then increase with increasing R . These trends are in good agreement with the results obtained for the mechanical properties measured (Fig. 3). Moreover, because N_0 is inversely proportional to the migration rate of the solvent in the elastomers^[28], the volume swelling rates measured also first decrease and then increase (Fig. 4).

Damping Properties

The $\tan\delta$ responses of the polytriazole elastomers measured by DMA are shown in Fig. 6. It can be observed that all of the elastomers present damping peaks at approximately -64°C , corresponding to the glass transition of the copolyether strands^[29]. Furthermore, careful observation reveals that there exist shoulder peaks at approximately -40°C only for elastomers S1 and S2, which are simultaneously accompanied by plateau-raising peaks at approximately -10°C . Above the plateau-raising peak, the $\tan\delta$ curves gradually decrease for elastomers S1–S3, and the curve of elastomer S3 lies at the bottom. When $R > 1.0$, the $\tan\delta$ curves are again gradually elevated with the increasing R .

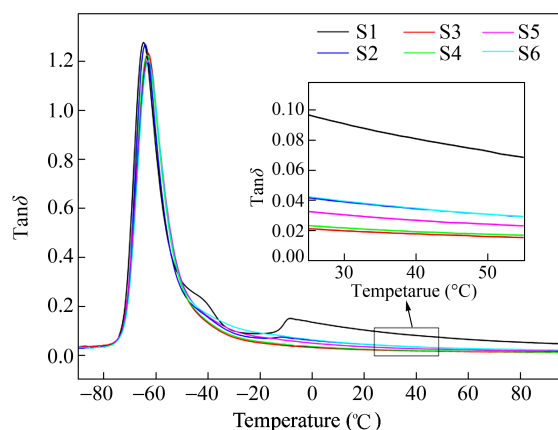


Fig. 6 Temperature dependence of loss tangent for polytriazole elastomers

Referring to the network structure, it is clear that there exist dangling strands in the networks of elastomers S1 and S2, whereas elastomers S3–S6 contain no dangling chains. The dangling strands could dissipate the applied work as heat energy by viscoelastic relaxation and decrease the amount of energy stored in the elastomer chains^[30]; thus, it can be inferred that the shoulder peaks of elastomers S1 and S2 should originate from the viscoelastic relaxation caused by dangling strands in the transition region between the glassy and viscoelastic states, and the accompanying plateau-raising peaks are due to the melting phase transition of dangling chains^[20]. Moreover, because elastomer S1 possesses more dangling strands than S2 and elastomer S3 possesses a perfect network structure, the $\tan\delta$ curves gradually decrease for elastomers S1–S3 above the melting temperature of the dangling chains. The $\tan\delta$ curves gradually increase again for elastomers S4–S6, which is presumably caused by the nonuniform meshes of the elastomers and should be studied further.

Thermal Properties

The TG and DTG curves of S3 are shown in Fig. 7. It can be observed that the weight loss of the elastomer begins at 364 °C and terminates at 426 °C. The DTG curve suggests that the process shows a one-step decomposition characteristic, and the thermal decomposition rate reaches a maximum at 406 °C. Because the thermal cleavage temperature of triazole groups (end-linking points) is approximately 570 °C^[31, 32], whereas that of the polyether strands falls in the range between 350 °C and 420 °C^[33–35], the weight-loss process of S3 should be solely attributed to the thermal degradation of polyether strands rather than that of end-linking triazole groups. As a result, the thermal stability of the polyether polytriazole elastomers depends on the polyether strands.

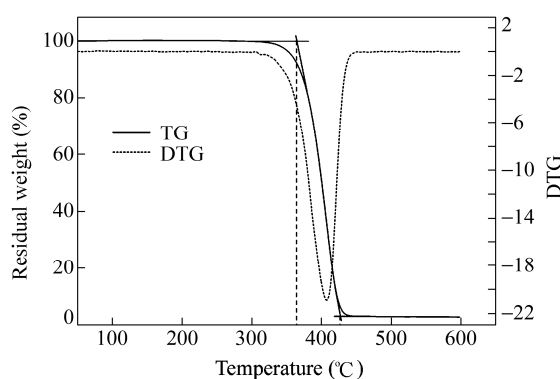


Fig. 7 TG and DTG curves of S3

CONCLUSIONS

Propargyl-terminated ethylene oxide-tetrahydrofuran copolymer (PTP(E-co-T)) was prepared from P(E-co-T) by end-capping modification. FTIR, ¹³C-NMR and GPC results indicate that PTP(E-co-T) was prepared from P(E-co-T) only through the end-capping modification, and the alkynyl content was determined to be 0.428 mmol·g⁻¹.

Because the CuCCA reaction involves no side-reactions, the dependence of the mechanical properties of the polytriazole elastomers on *R* was observed to be parabolic. Near the stoichiometric ratio, the network structures of the elastomers possess strands with a minimum apparent molecular weight and a maximum apparent density. The modulus *E* and stress σ_b exhibit maximum values and the strain ϵ_b a minimum value.

DMA analysis reveals that the glass transition temperature of the polytriazole elastomers is approximately -64 °C. At the stoichiometric ratio, the polytriazole elastomer exhibits the lowest dissipation factor $\tan\delta$, as helps to extend the preparation method of low damping materials. In addition, the thermal stability of the polyether polytriazole elastomers depends on the polyether strands, rather than on the end-linking triazole groups.

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