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Group interval-controlled polymers: an example of epoxy functional polymers *via* step-growth thiol–yne polymerization†

Yaochen Zheng,[a,b] Shengying Cai,[a] Li Peng,[a] Yu Jin,[a] Han Xu,[a] Zhulin Weng,[a] Zhengguo Gao,[a,b] Bo Zhao[a] and Chao Gao*[a]

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We have coined a new term, group interval-controlled polymers (GICPs), to describe the unique structure of macromolecules with a tunable functional group interval. The precise control of a polymer main chain structure itself is still a big challenge, let alone the purposeful control of group interval simultaneously. Here, we successfully synthesized a series of epoxy GICPs *via* one-step UV-triggered thiol–yne polymerization of commercial glycidyl propargyl ether and dithiols at 0 °C. Subsequently, α,ω-thiols of each epoxy GICP were capped by two allyl glycidyl ethers *via* a thiol–ene click reaction, affording a stable product. Their unique group interval-controlled chemical structures were confirmed by a combination of nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and pyrene-fluorescent probe tests. Moreover, the epoxy groups within the GICPs were highly reactive and could be further functionalized and turned into a diverse range of customized groups such as azide, tertiary amino, thioester, and hydroxyl, *etc*. Therefore, a series of GICPs with designed functional groups are readily achieved on a large scale. Our work presents a reliable synthetic methodology for GICPs, paving a new way for the precise structure control of artificial macromolecules.

Introduction

Over the past few decades, numerous efforts have been devoted to manipulating the architecture of synthetic macromolecules. To produce a well-defined polymer, various strategies, including living/control radical polymerization, iterative cycles, templates, and so on, have been identified.[1–14] Typically, using an iterative strategy, Merrifield synthesized sequence-defined polypeptides *via* a solid-phase synthesis technique, setting a precedent for sequence-controlled polymers.[4–8] Furthermore, several seminal works declared the successful structure control of man-made macromolecules by a nonenzymatic protocol, following a template polymerization mechanism.[15–25] Although solid-phase synthesis and template polymerization can offer precise sequences, they often have problems with scalable synthesis and/or structural diversity. In contrast, chemical synthesis methods have access to diverse sequences using a wide variety of monomers.[2] Besides, various ingenious protocols have been developed to control polymer structure *via* the chemical synthesis route. For example, a liquid-phase supporter or template was employed to control the reaction point, guaranteeing the formation of a regular architecutre.[26–29] Due to the deactivation of hydroxyl methyl to a terminal halogen , allyl alcohol only carried out propagation once during atom transfer radical polymerization (ATRP). As the hydroxyl group was oxidised to a carboxyl group, the single-monomer addition of allyl alcohol could be triggered again. Through the iterative cycle of single-monomer addition, structure-defined polymers were formed.[30] Lutz and Kamigaito *et al.* utilized cross chain propagation of electron-donor and electron-acceptor monomers for regular structure control.[31–36] Moreover, the combination of time-controlled additions of electron-acceptor monomers and a living polymerization technique could facilely tune the sequential structure of products.[31] Besides the aforementioned strategies, sequence-controlled polymers were synthesized *via* homo-polymerization of as-prepared monomers with a specific sequential structure to ensure the product possessed a perfect sequence.[37,38] Recently, Johnson and coworkers synthesized structure-controlled polymers on the 100–800 mg scale *via* solution-phase iterative exponential growth using α-epoxy-ω-*tert*-butyldi-

[a]*MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: chaogao@zju.edu.cn; Tel: +86-0571-87952088*
[b]*Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Yantai University, 30 Qingquan Road, Yantai 264005, P. R. China*

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methylsilyl protected alkyne monomers as feed materials.[39,40] Although numerous advances of the synthesis of well-defined polymers have been achieved, most of them are lacking in available functional groups.[41] Meanwhile, limited by synthetic strategy, the interval between two adjacent functional groups cannot be facilely tuned. Therefore, the precise synthesis of group interval-controlled polymers (GICPs) with a controlled group interval still remains a great challenge for polymer chemists.

In biological systems, the molecular group interval is crucial for biological functions. For instance, bisethylnorspermine (BENSPM) and its analogue bisethylhomospermine (BEHSPM) gave different results in the inhibition of mammalian cancer cells. As shown by cell growth and viability, IC_{50} values (decreasing the growth to half the maximal amine concentration needed) of BENSPM and BEHSPM were 0.40 and 0.22, respectively.[42] This result obviously illuminates that the structure difference (*i.e.*, amine interval) between the two analogues has an important effect on cell growth. Additionally, in organic photovoltaic or electronic applications, the bulk electron transport largely depends on the orbital couplings which are dominated by the interval of electron donors and acceptors. The conductance also depends on the thiophene-1,1-dioxide (TDO) interval.[43] With increasing chain length of TDO moieties, the lowest unoccupied molecular orbitals of these n-type molecules drops from 3.4 to 4.1 eV. Therefore, control of group interval events is conducive to revealing the mechanism at a molecular level, but still stays largely confusing, mainly suffering from the lack of a general synthesis method for GICPs.

Here, we designed and facilely synthesized a series of epoxy GICPs *via* one-step photo-initiated thiol–yne polymerization of commercial glycidyl propargyl ether and dithiols [$HS(CH_2)_kSH$, k = 2, 4, 6, 8 and 10]. Their chemical structures were confirmed by a combination of nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and pyrene-fluorescence probe measurements. By thiol–epoxy click reactions, the epoxy GICPs were fully functionalized to contain other groups, such as azide, tertiary amino, and hydroxyl, *etc.*, indicating that GICPs with desired functional groups can be readily available on the basis of the epoxy GICP platform.

Additionally, besides the precise control of group interval, the generated epoxy GICP itself is extremely significant. Firstly, the epoxy-containing polymer is a very useful precursor, which has been widely applied as a molecular platform for diverse modifications or functionalization. However, its synthesis is very difficult, due to the lack of suitable synthetic protocols. To our knowledge, poly(glycidyl methacrylate) (PGMA) is the sole analogue of our epoxy GICPs, which is sensitive to acid or alkali compounds because of its intramolecular ester bonds. Thus, without an ester bond involved, the resultant epoxy GICP should be more stable than PGMA in its chemical properties, making it more generally applicable. Secondly, the obtained epoxy GICPs possess a low glass transition temperature (T_g < −42.0 °C), so they have a promising potential application for flexible thermosetting materials. Incidentally, the epoxy GICPs can be produced on a large scale, since all of the employed feed materials in this work are commercially available. Therefore, we believe this efficient approach enables easy and scalable synthesis of epoxy GICPs, greatly promoting their use in real material applications.

Experimental section

Materials

Dithiol compounds including 1,2-ethanedithiol (98%), 1,3-propanedithiol (98%), 1,4-butanedithiol (97%), 1,5-pentanedithiol (98%), 1,6-hexanedithiol (95%), 1,8-ocatnedithiol (98%), and 1,10-decanedithiol (95%), were purchased from J & K Chemical Co. Glycidyl propargyl ether (95%) was obtained from Nanjing Datang Pharm Technology Ltd. Allyl glycidyl ether, 2,2-dimethoxy-2-phenylacetophenone (DMPA, 98%) and anhydrous tetrahydrofuran were purchased from Aldrich Co. 1-Pyrenebutyric acid (99%), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl, 99%), and 4-dimethylaminopyridine (DMAP, 99%) were obtained from Aladdin Industrial Co. Sodium azide (99%) was purchased from Xiya Reagent Co. Ltd. *N*,*N*′,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%) was purchased from TCI Co. Ammonium chloride and cuprous bromide (CuBr) were obtained from Sinopharm Chemical Reagent Co. Ltd. Before use, CuBr was purified by glacial acetic acid and washed by methanol repeatedly. Then, CuBr was dried under vacuum at room temperature for 24 h. Propargyl alcohol (95%) was redistilled prior to use. Dimethyl formamide (DMF) was dried over anhydrous magnesium sulfate. All organic solvents (>95%) and other reagents were used as received unless specifically mentioned.

Synthesis of epoxy group interval-controlled polymers

Epoxy group interval-controlled polymers (GICPs) were synthesized *via* free radical triggered thiol–yne polymerization of glycidyl propargyl ether and dithiols under UV-irradiation. Typically, glycidyl propargyl ether (0.518 g, 4.6 mmol), 1,2-ethanedithiol (0.453 g, 4.8 mmol), and 2,2-bimethoxy-2-phenylacetophenone (DMPA, 35.5 mg, 0.14 mmol) were dissolved in 2.0 mL of 1,4-dioxane. Subsequently, the mixture was added into a 10 mL round-bottom flask which was sealed by a rubber stopper. High-purity N_2 was bubbled through the solution for 30 min to fully remove O_2, and the polymerization was carried out under UV irradiation (λ = 365 nm) in an ice-water bath for 1.5 h. Then, allyl glycidyl ether (1.0 mL, 8.4 mmol) containing 2 wt% of DMPA was injected into the reaction system through a syringe. After additional irradiation for 1.5 h, the mixture was diluted with about 2.0 mL of THF and dropped into cold anhydrous ether (50 mL), affording a colorless viscous precipitate. This above-mentioned process was repeated three times. After drying under vacuum, the product (0.696 g) was obtained with a yield of 73.2%.

Synthesis of GICP with alternating azide groups

Azide-functionalized GICPs were synthesized *via* the azidation of sodium azide and epoxy GICP in dry DMF. According to pre-

vious literature,[44–46] either ammonium chloride or sodium bicarbonate can donate a proton to the epoxy group and therefore be used as a catalyst to promote ring-opening reactions of epoxy groups. Typically, **2** (0.418 g, 1.9 mmol) was dissolved in 15 mL of dry DMF. Sodium azide (0.370 g, 5.7 mmol) and ammonium chloride (0.305 g, 5.7 mmol) were added into the solution and stirred at 0 °C for 2.0 h. Then the mixture was gradually heated to 50 °C and stirred for 48 h. After removal of most of the solvent, the residual solution was precipitated into 50 mL of deionized water, centrifuged, separated, and dried under vacuum. A pale yellow viscous liquid (0.396 g) was obtained.

Synthesis of GICPs with alternating pyrene

Pyrene-containing GICPs were synthesized by Cu-catalyzed azide–alkyne cycloaddition (CuAAC) of azide-functionalized SCPs and propargyl-1-pyrenebutyrate. The propargyl-1-pyrenebutyrate was synthesized *via* esterification of 1-pyrenebutyric acid and propargyl alcohol, using EDC·HCl as a dehydrating agent and DMAP as a catalyst. Typically, in a 500 mL round bottom flask equipped with a magnetic stirrer, 1-pyrenebutyric acid (2.880 g, 10 mmol) and (0.841 g, 15 mmol) propargyl alcohol were dissolved in 250 mL of anhydrous THF. The mixture was immersed in an ice-water bath and DMAP (0.122 g, 1 mmol) was added into the reaction system. The mixture was kept under vigorous stirring for 24 h at room temperature. After filtration, the solvent of the filtrate was removed *via* rotary evaporator. Redissolving the remnant solid with 250 mL dichloromethane (DCM), the resultant solution was washed with 5 wt% sodium bicarbonate (50 mL × 3) and deionized water (100 mL × 3). The organic phase was dried over anhydrous $MgSO_4$ overnight. We filtrated and collected the organic phase, then removed the solvent on a rotary evaporator and dried under vacuum at 30 °C overnight, affording a light brown solid (3.069 g, 9.4 mmol).

Subsequently, azide-functionalized GICP (0.141 g, 0.64 mmol of azide groups), propargyl-1-pyrenebutyrate (0.314 g, 0.96 mmol), and PMDETA (30.5 μL) were dissolved in 6 mL of dry DMF. After being purged with high purity nitrogen for 30 min, CuBr (21 mg, 0.13 mmol) was introduced into the mixture to trigger the click reaction. The mixture was stirred for 48 h at room temperature. After dilution by 5 mL of THF, the mixture was passed through a column of neutral alumina using THF as an eluent. Removing most of the solvent on a rotary evaporator, the residue was precipitated into cold diethyl ether to remove residual monomers. The precipitate was dissolved in THF and repeatedly precipitated in a 10-fold excess of cold diethyl ether. After drying in a vacuum oven for 24 h at 30 °C, pyrene-functionalized SCPs were achieved as a light brown solid (0.128 g).

Structural characterization

^{1}H NMR spectra were measured on a Varian Mercury plus 400 NMR spectrometer (400 MHz) using $CDCl_3$ as solvent and tetra-methylsilane (TMS) as an internal reference. ^{13}C NMR and 2D ^{1}H–^{13}C HMQC spectra were recorded on an Avance III 500 NMR spectrometer (500 MHz). The molecular weight and molecular weight distribution of the resultant polymers were measured through gel permeation chromatography (GPC) using a Waters 1515 at 40 °C. THF with a flow rate of 1 mL min^{-1} and polystyrene were used as the eluent and standard, respectively. Fourier transform infrared (FTIR) measurements were carried out on a PE Paragon 1000 spectrometer (film or KBr disk). Fluorescence spectra were performed on a Shimadzu RF-5301PC fluorophotometer. A Varian Cary 300 Bio UV-Vis spectrometer was applied to record UV-Vis spectra.

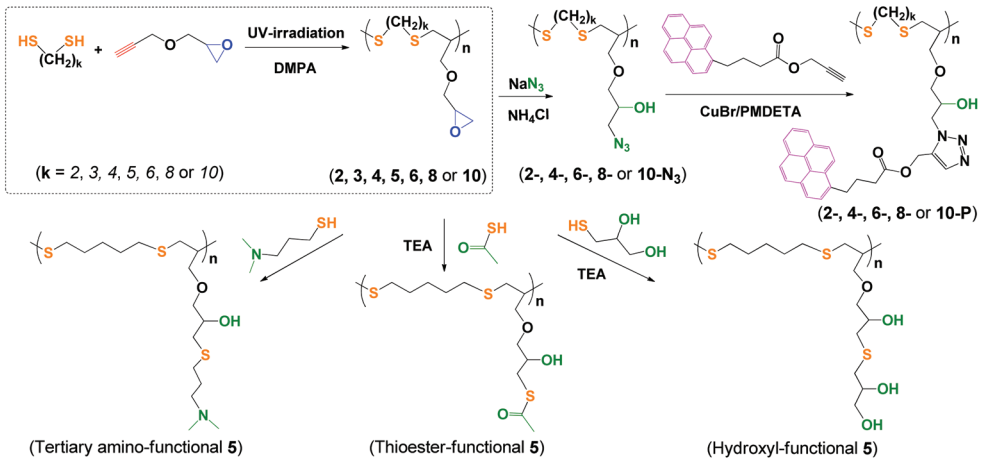
Results and discussion

Synthesis of epoxy GICPs

To achieve GICPs, the biggest challenge is ensuring that a regular sequence and intact functional groups with precise intervals are introduced into the molecular chain simultaneously. Here, we designed and selected step-growth thiol–yne polymerization to achieve this, as intrinsic cross propagation during the process of thiol–yne polymerization affords a regular sequence, which is the premise for specific group intervals.[41] Moreover, free radical initiation makes various groups able to access the product intactly, benefiting from the large chain transfer constant of thiol (up to 48). The group interval of products can be precisely adjusted by changing the type of commercial dithiols (the number of $-CH_2-$ unit, k, as shown in Scheme 1) used.

In our previous studies, sequence-controlled polymers with alternating hetero-functional groups (such as OH/alkyl, OH/COOH, OH/NH_2, OH/N_3, and so on) and diverse topologies have been successfully synthesized *via* step-growth thiol–yne polymerization.[41] However, under our reported conditions (such as thermal initiation at 70 °C or UV irradiation at room temperature), the thiol–yne polymerization of glycidyl propargyl ether and dithiols cannot generate an epoxy group sequence-controlled polymer. Undesirable additions between epoxy groups and thiols occur during propagation which would give rise to an irregular sequence and even gelation.

Due to large ring tension, the epoxy group is highly reactive. In the presence of nucleophiles, thiol is firstly transformed into the thiolate anion which attacks the epoxy group quickly, carrying out the thiol–epoxy addition.[47–50] This proton transfer process is thermodynamically driven. Reasonably, both heat and nucleophiles can accelerate proton transfer which further promotes the thiol–epoxy reaction. Therefore, at low temperatures and in the absence of a catalyst, such thiol-epoxy side reactions could be suppressed largely. Nevertheless, UV-initiated free radical polymerization could occur smoothly at low temperatures because of its small activation energy (E_a, generally <20 kJ mol^{-1}).[51] In contrast, the E_a of the thiol–epoxy reaction reached 75–85 kJ mol^{-1}, even in the presence of a tertiary amine catalyst.[52] The large E_a difference between the two types of reaction presented the possibility for successful synthesis of epoxy GICPs. In this work, we carried out UV-triggered thiol–yne polymerization of glycidyl propargyl ether and dithiols at 0 °C in chemically neutral media.



Scheme 1 Synthesis and functionalization of epoxy GICPs. The group interval of the polymers can be precisely tuned by *k*.

Besides the reaction temperature, here, we optimized other reaction conditions including solvent, monomer concentration, feed ratio, terminal thiol capping and product purification. To avoid chain transfer caused by solvents as much as possible, we chose an inert aprotic solvent, 1,4-dioxane or THF, as the medium. With a relatively low viscosity, the monomer concentration was kept at ~30 wt% to facilitate hydrogen abstraction and avoid the termination of coupling through two polythioether radicals.[53,54] Moreover, in our system, the molar ratio of dithiol and alkyne was about 1.05 : 1. Excess thiol ensured that the transfer from polythioether radical to thiol was 100% and eliminated the possible homopolymerization of alkynyl groups completely.[55–57]

Chemical structures of the GICPs were characterized by NMR spectroscopy. The chemical structure of **2**, synthesized by 1,2-ethanedithiol and glycidyl propargyl ether, is shown in Fig. 2 and S1.† Signals at 2.70–2.88 ppm in the ^{1}H NMR spectrum and 32.0, 33.4 and 34.9 ppm in the ^{13}C NMR spectrum were assigned to the thioether protons. No proton signals of vinyl sulfides emerged at 5.6 and 6.3 ppm, illustrating that two sequential additions of two thiols to one alkyne generated a regular sequence.[56,58] The proton signals appearing at 2.93, 3.16, and 3.36 ppm as well as the carbon signals at 44.2, 46.1 and 50.7 ppm in ^{1}H and ^{13}C NMR spectra were attributed to epoxy groups. Moreover, the ratio of the integration of the proton signals labeled with "b" to that of signals marked with "e" approaches 1 : 1, implying that the epoxy groups suspended on the backbone of **2** were intact (Fig. 1a).

As mentioned above, thiol–epoxy addition between thiol and epoxy groups can take place spontaneously. To entirely eliminate the possible thiol–epoxy addition, excess allyl glycidyl ether monomers were introduced to cap α,ω-thiol groups *via* photo-initiated thiol–ene addition at 0 °C. As displayed in Fig. 1a, the terminal thiol proton signals at 1.67 ppm completely disappeared, which meant that all the thiols of **2** were consumed during the terminal thiol capping.[58] Once it was modified, the product could be stored without gelation for a few weeks at room temperature.

Further verification with gel permeation chromatography (GPC) confirmed the sequential structure of **2** (Fig. 1c). The corresponding results of GPC tests are summarized in Table 1. The resultant **2** exhibited a higher molecular weight (3033 mol g^{-1}, degree of polymerization = 14.7) and lower dispersity (PDI = 1.38) than those synthesized by thermally initiated methods.[41] In addition, the GPC profile was unimodal, illustrating that both the coupling termination of polythiolether radicals and the thiol–epoxy side reaction had been mainly avoided under our optimized conditions. It was also observed that the polydispersity of **2** can be further narrowed by a repeated precipitation method, with THF as the solvent and a mixture of diethyl ether and hexane (1 : 1, v/v) as precipitant. The relatively narrow polydispersity (PDI = 1.29) and moderate molecular weight (~3100 g mol^{-1}) were achieved during polymer fractionation (Fig. S2†).

Scalable synthesis is a prerequisite for the use of GICPs in a real material application. Our protocol is highly efficient and can achieve scalable synthesis of GICPs. For instance, we could synthesize **2** with a number average molecular weight (M_n) of about 3000 g mol^{-1} on ~4.3 g scale in only 3 h (Fig. S3†). Besides scalable synthesis, our strategy possessed atom economy and has given access to a much more extensive range of chemical structures.

To check the reliability of the synthesis strategy, other dithiols with different alkyl lengths were employed to carry out thiol–yne polymerization. The chemical structures of the products (**3**, **4**, **5**, **6**, **8** and **10**) were characterized by a combination of NMR spectroscopy and GPC analyses (Fig. 1, S4–S10† and Table 1). As shown in the 2D ^{1}H–^{13}C HMQC spectra, no proton signals assigned to vinyl groups or thiols appeared, confirming the formation of a uniform sequence and full consumption of terminal thiols. Additionally, the chemical shifts and integration values of the epoxy proton signals in Fig. 1a, S4–S10† were the same as in the case of **2**, verifying that the epoxy groups were intact. Among their ^{1}H (or ^{13}C) NMR spectra, the main difference was in the proton signals at 1.0–2.0 ppm (about 30 ppm in ^{13}C NMR spectra) which belonged to the

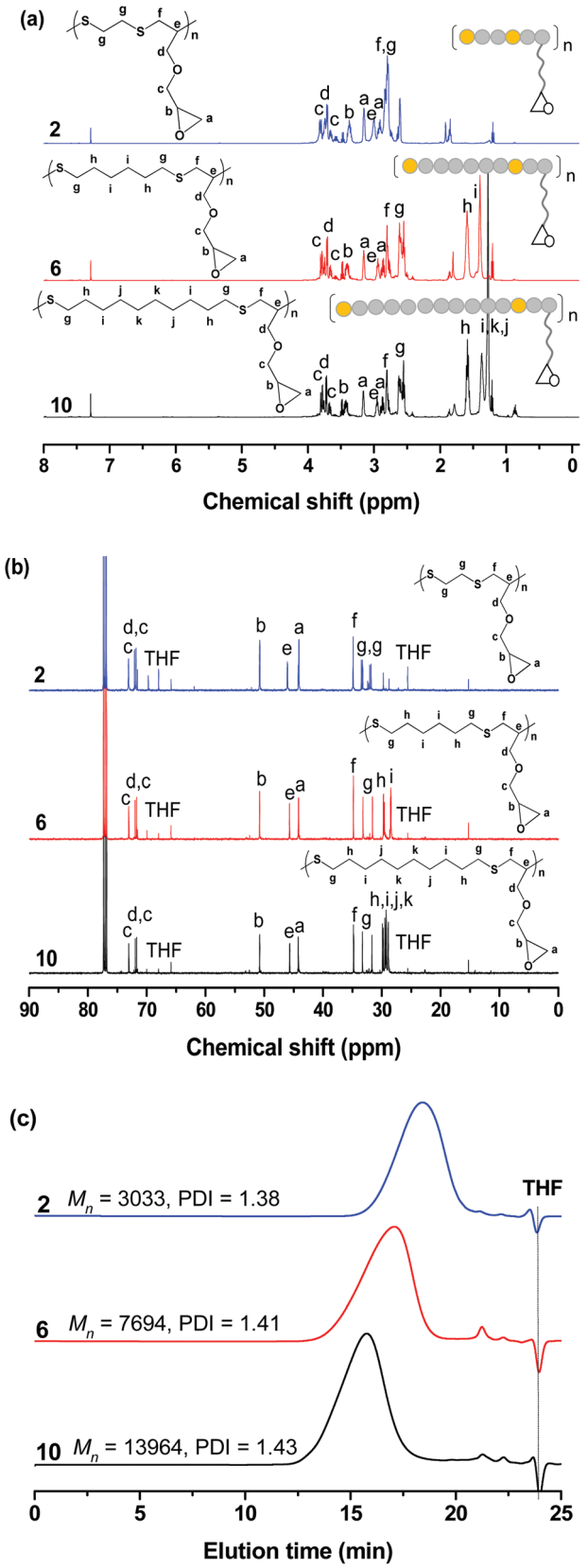


Fig. 1 ^{1}H and ^{13}C NMR spectra and GPC traces of **2**, **6** and **10**.

Table 1 Summarized test results for samples, **2–10**

Sample	Yield (%)	M_n (g mol^{-1})	PDI	D_p [a]
2	73.2	3033	1.38	14.7
2-N$_3$	79.6	3820	1.34	15.3
2-P	42.9	6161	1.36	10.2
4	75.6	4039	1.41	17.2
4-N$_3$	69.4	4913	1.43	17.7
4-P	41.1	7246	1.42	11.4
6	78.4	7694	1.43	29.3
6-N$_3$	74.2	8145	1.45	26.7
6-P	44.7	10 614	1.74	16.0
8	84.3	7822	1.46	27.0
8-N$_3$	73.0	9449	1.47	28.4
8-P	45.5	14 323	1.62	20.8
10	76.2	13 964	1.43	43.9
10-N$_3$	80.6	14 316	1.73	39.6
10-P	43.9	18 384	1.64	25.6

[a] D_p was calculated from M_n which was measured by GPC.

methylene group of the dithiols, indicating that the epoxy intervals of **4–10** were different and tunable. Therefore, group intervals can be facilely and precisely adjusted through altering the dithiols used.

Furthermore, the obtained epoxy GICPs were characterized by GPC measurements (in Fig. 1 and S11†). All the GPC curves of **2–10** exhibited a unimodal shape, implying that no thiol–epoxy side reaction occurred in the above reaction systems. With the increasing molecular weight of the dithiols used, the average molecular weights or degree of polymerization (D_p) of **2–10** increased, due to the gradual decrease in electrophilicity of the dithiols (Table 1).[57] Therefore, the results of NMR and GPC analyses proved that our synthesis strategy for epoxy GICPs is reliable and universal.

Functionalization of epoxy GICPs

To further verify that the introduced epoxy is intact and reactive, four kinds of nucleophilic compounds, including sodium azide, 3-(dimethylamino)-1-propanethiol, 3-mercapto-1,2-propanediol, and thiolacetic acid were selected as model modifiers (Scheme 1).

Inspired by the work of Matyjaszewski *et al.*, ring-opening of the epoxy groups of **2–10** with an excess of NaN_3 in the presence of ammonium chloride affords **2-N$_3$–10-N$_3$**.[44] According to previous reports, NH_4Cl can greatly accelerate ring-opening and efficiently eliminate side reactions, ensuring the complete transformation of epoxy to azide.[45,46] To obtain 100% group modification, the reaction was kept at 50 °C for 48 h.

Typical ^{1}H and ^{13}C NMR spectra, in this case of **2-N$_3$**, are shown in Fig. 2a and S12,† and all signals have been well-assigned based on its chemical structure. Compared with the ^{1}H NMR spectrum of **2** (Fig. 1a), resonance signals at 2.93, 3.16 ppm (labeled with "a") and 3.36 ppm (designated with "b") characteristic of epoxy groups entirely disappeared (Fig. 2a). Correspondingly, carbon signals at 44.0, 46.0 ppm (g) and 50.7 ppm (f) belonging to the epoxy also completely vanished (in Fig. 1b). The appearance of new peaks "a" (3.4 ppm) and "b" (4.0 ppm) can further verify that all epoxy groups were

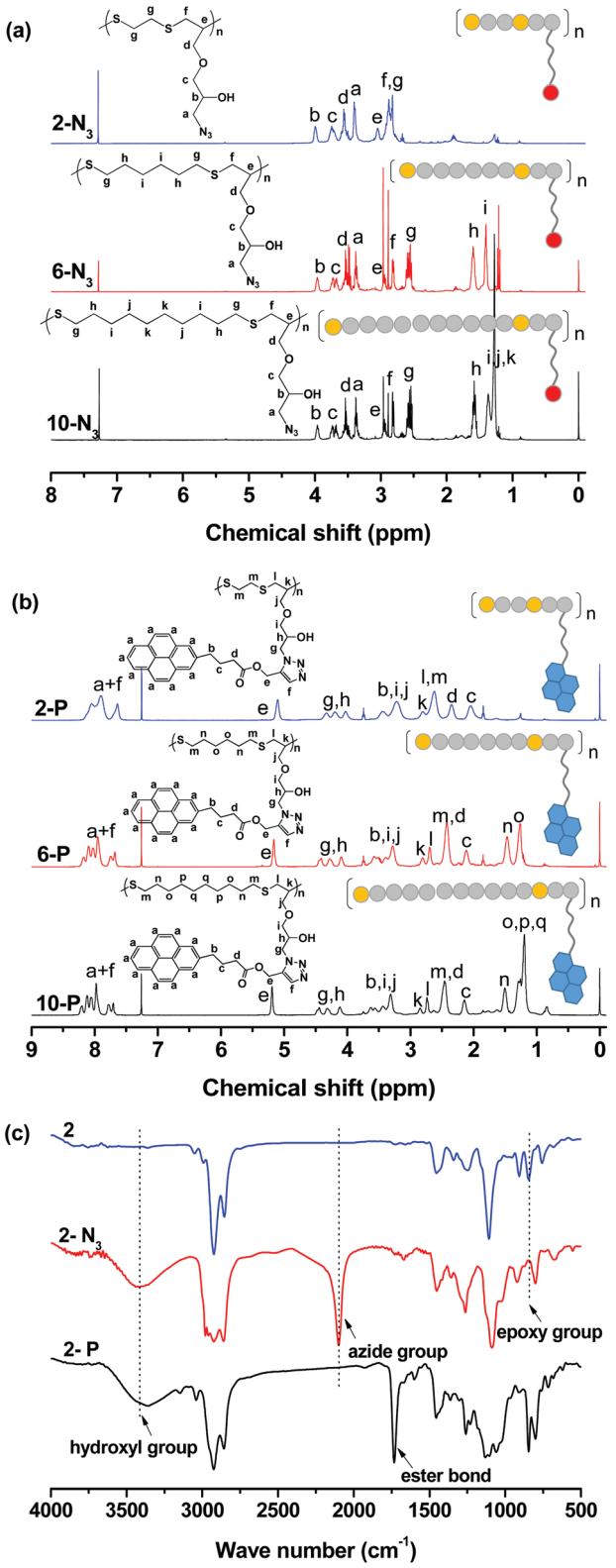


Fig. 2 ^{1}H NMR spectra of **2-N$_3$**, **6-N$_3$**, **10-N$_3$**, **2-P**, **6-P** and **10-P**, and FTIR spectra of **2**, **2-N$_3$** and **2-P**.

consumed during the ring-opening reaction (Fig. 2a). The integral ratio of peak "d" to that of peak "b" in the ^{1}H NMR spectra of **2-N$_3$**, **6-N$_3$** and **10-N$_3$** is nearly 2 : 1. All of these results illustrate that NaN_3 exclusively attacked the "f" carbon in the epoxy of **2**, **6** or **10** which was in good accordance with those reported in previous works.[44–46,58] By comparing the integral ratio of peaks "d" to that of "f", the degree of epoxy group functionalization was calculated to be close to 100%.

Subsequently, the click chemistry of **2-N$_3$**–**10-N$_3$** with propargyl-1-pyrenebutyrate was used to synthesize pyrene-containing GICPs (**2-P**–**10-P**).[45,46] Their chemical structures were characterized by NMR spectroscopy (Fig. 2a, b and S13–S17†). The chemical structure of **2-P** was confirmed by ^{1}H NMR analysis (Fig. 2a). The appearance of the aromatic ring ("a") and triazole ("f") signals of **2-P** verified the efficient generation of pyrene GICPs. The integration area ratio of peaks "a + f" (7.52–8.30 ppm) to those of peaks "g + h" (3.88–4.46 ppm) was determined to be 10 : 3, implying an almost quantitative functionalization. The resultant **2-P** possessed one pyrene and one hydroxyl on each repeated unit.

In the FTIR spectra of **2** (Fig. 2c), a strong absorbance peak at 846 cm^{-1} characteristic of an epoxy was clearly observed. After modification, the resultant azide and hydroxyl groups in **2-N$_3$** could be evidenced by the presence of characteristic absorbance peaks at 2097 and 3200–3600 cm^{-1}, respectively. In comparison with that of **2-N$_3$**, the peak at 2097 cm^{-1} ascribed to azide group entirely disappeared and a new peak appeared at 1734 cm^{-1} belonging to the ester bond of the propargyl-1-pyrenebutyrate moiety, illustrating that the azide groups of **2-N$_3$** were completely consumed during the process of click modification.

GPC traces of all products again revealed a monomodal elution peak (Fig. S18–S22† and Table 1), indicating that no branching or crosslinking occurred during the ring-opening reaction and subsequent click modification. Moreover, for every series of GICPs (such as **2**, **2-N$_3$** and **2-P**), the measured MWs exhibited gradually increased, confirming again that the functionalization was successful.

In addition to copper-catalyzed azide–alkyne cycloaddition, thiol–epoxy addition had been used to functionalize the resultant epoxy GICPs. The chemical structures of the resultant products were characterized by ^{1}H NMR and FTIR analyses (Fig. S23–S27†) and all signals have been well-assigned according to their chemical structures. As declared by Khan and coworkers, in the presence of base, thiol–epoxy addition occurs in a quantitative manner.[47–50] Since the modifier, 3-(dimethylamino)-1-propanethiol, contained a nucleophilic tertiary amine moiety in its structure, the autocatalytic modification of the epoxy GICP was performed smoothly without a catalyst. The dimethylamino-modified GICP had been verified to be a universal molecular platform for desired functionalization.[59] With regard to 3-mercapto-1,2-propanediol or thiolacetic acid, 5–10 wt% of triethylamine was needed as a catalyst to accelerate the modification, affording a water soluble GICP or a thioester-functionalized GICP (the precursor for a thiol compound).[60–62] All the aforementioned evidence illustrated

that functional GICPs were successfully synthesized, and that the epoxy group suspended in the GICPs was still highly reactive and could be further functionalized *via* various modifications for a diverse range of potentials.

Proof of pyrene-probe test for epoxy GICPs

Apart from ^{1}H NMR and GPC analyses, the epoxy group interval-controlled structures of **2–10** have also been confirmed by pyrene-probe measurements. As displayed in Fig. 3a–c, the peaks at 377 (M1) and 398 nm (M2) were ascribed to monomer emission, and the peak at 475 nm (E) was attributed to dynamic excimer emission. The intensity ratio of excimer to monomer, I_E/I_{M1}, in other words the degree of excimer emission enhancement, is greatly dependant on the interval of two adjacent pyrene units.[63–67] At the same pyrene concentration and with the increase of thiol molecular weights (**2** → **6** → **10**), the values of I_E/I_{M1} gradually decreased, implying that the pyrene-interval within **2-P–10-P** was correspondingly enhanced. According to the hypothetical structure, atom numbers of repeat units within **2-P–10-P** were 6, 10 and 14, respectively. That is, the pyrene-interval in **6-P** (ten repeated atoms) should be equal to about one-half of the pyrene-interval sum of **2-P** (six repeated atoms), leading to a prediction that the $I_E/I_{M1}$of **6-P** will appear at the location of the dotted line, one-half of the I_E/I_{M1} sum of **2-P** and **10-P** (Fig. 3d). As expected, the I_E/I_{M1} values from practical testing (red solid line) were in good accordance with those of the predicted values. This result again verified that the group intervals of **2–10** are controlled and tunable.

Notably, at an identical pyrene group concentration (such as at 1.0×10^{-4} M), the I_E, I_{M1} and I_E/I_{M1} values of **2-P–10-P** were different from each other, although they possessed the same AwzAB type of sequence (Fig. 3a–c). Therefore, group interval of polymers, rather than sequence, was the real determinant for some polymeric functions or properties.

Flexible thermosetting materials based on epoxy GICPs

Differential scanning calorimeter (DSC) tests and thermogravimetric analyses (TGA) were performed to evaluate the thermal properties of **2–10**. As revealed by Fig. S30,† the epoxy GICPs, **2–10**, exhibited low glass transition temperatures (T_gs) of −42.0, −47.8, −58.3, −56.0 and −55.4 °C, respectively, due to the regularly appearing flexible thioether bonds and alkyl chains. The result of the TGA indicated that **2**, **6** and **8** were stable up to about 295 °C which was in good agreement with that of a similar polymer reported in previous works (Fig. S31 and S32†).[47–49]

To further explore their potential applications, selected epoxy GICPs, **2** and **8**, were crosslinked by polyether amine D2000. The resultant thermosetting materials exhibited good transparency. The transmittance reached up to ~50% and ~70% when the thicknesses of cured **8** (**8-c**) were 0.307 and 0.113 mm, respectively (Fig. 4a).

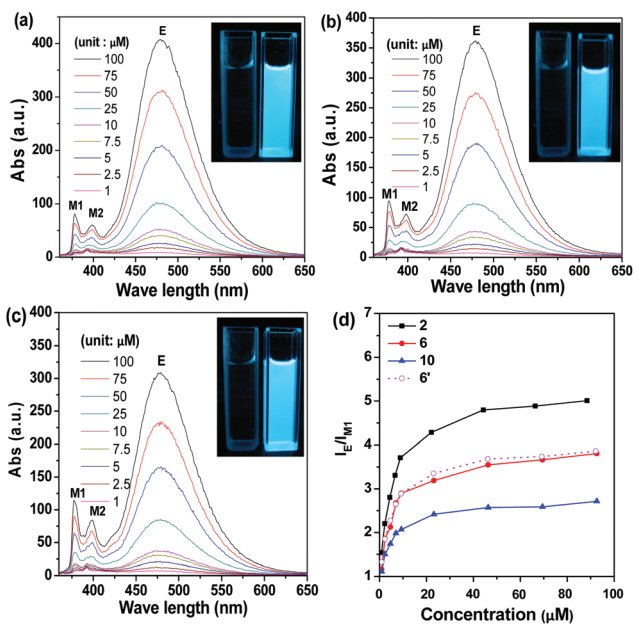


Fig. 3 Fluorescence emission spectra of **2-P** (a), **6-P** (b) and **10-P** (c) at a pyrene concentration from 1.0×10^{-6} to 1.0×10^{-4} M excited at 344 nm. E is the excimer emission peak and M1 and M2 are monomer emission peaks. Inset: Photographs of **2-P–10-P** solutions at 1.0×10^{-4} M before (left) and after (right) excitation at 365 nm. I_E/I_{M1} as a function of pyrene concentration (d).

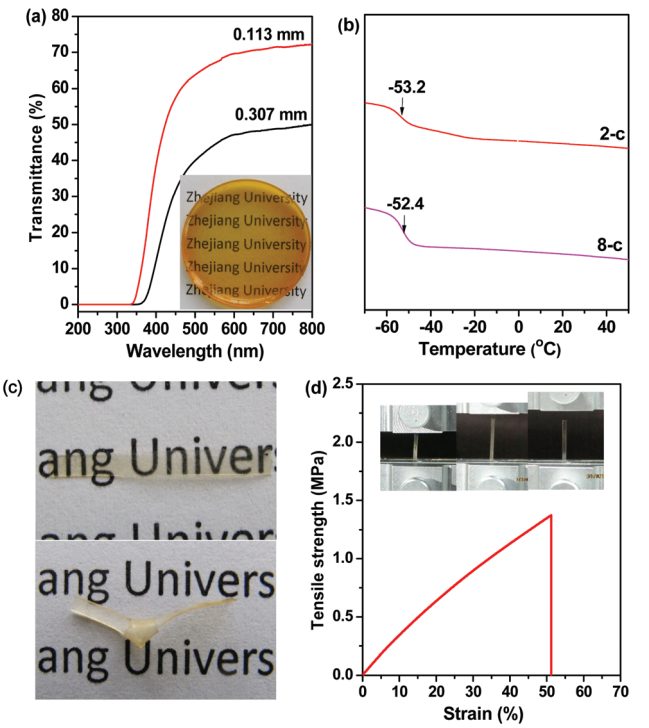


Fig. 4 Optical transmittance of **8-c** with different thicknesses (a), representative DSC curves of **2-c** and **8-c** (b), typical photograph images of **8-c** (upper) and knotted **8-c** (bottom) (c), and stress–strain curve of **8-c**. The inset in (a): a photograph of **8-c** (about 3.0 mm in thickness), the inset in (d): images demonstrating the course of tension, before (left) and after (right) tension.

The cured samples, **2-c** and **8-c**, showed T_gs of −53.2 and −52.4 °C which were attributed to the sufficient flexibility of the polythioether, alkyl, and polyether chains between two crosslinking points (Fig. 4b). Such a low T_g of the crosslinked epoxy GICPs endowed them with high flexibility. For instance, **8-c** can be knotted at room temperature (Fig. 4c). Details of **8-c**'s mechanical properties were further revealed by stress–strain tests. As displayed in Fig. 4d, a sample of **8-c** had a tensile strength (σ) of ~1.37 MPa at ultimate elongation (ε) of about 51.0%, showing that thermosetting materials based on epoxy GICPs possessed very high flexibility. Notably, our epoxy polymers have no degradable bonds such as esters, so the thermosetting materials would be highly stable in real applications.

Conclusions

We coined the term group interval-controlled polymers (GICPs) and synthesized them by UV-triggered thiol–yne addition of glycidyl propargyl ether and dithiols at 0 °C. The obtained epoxy GICPs possessed a precise and tunable epoxy group interval which was confirmed by NMR, GPC and pyrene probe tests. After being capped by excess allyl glycidyl ether, the resultant products became stable at room temperature. The epoxy group suspended on the main chain was intact and reactive, and was further functionalized into diverse available groups (such as azide, tertiary amino, hydroxyl, thioester and so on). Due to the backbone being composed of flexible thioether and alkyl moieties, these epoxy GICPs exhibited low T_gs (in the range of −42.0 to −58.3 °C). After being crosslinked by polyamine, the afforded thermosetting materials exhibited good transparencies (up to ~50% and ~70% at the thicknesses of 0.307 and 0.113 mm) and outstanding high flexibility (σ of 1.37 MPa and ε of 51.0%). We presented a facile synthetic strategy for the scalable synthesis of GICPs, making novel polymers with available functional groups possible for real applications.

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