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Copper-catalyzed multicomponent polymerization of elemental selenium for regioselective synthesis of poly(5-diselenide-triazole)s†

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Herein, a unique multicomponent polymerization of elemental selenium, alkynes and azides was developed to prepare poly(5-diselenide-triazole)s with high regioselectivities and atom economy under mild conditions. Such selenium-containing triazoly polymers featured well-defined structures, high molecular weights (M_n up to 71 300 g mol^{-1}) and yields (up to 90%), good solubility, high stability, and excellent redox-degradation properties.

Selenium-containing polymers possess unique advantages, such as reactive covalent Se–Se bonds,[1] redox responsiveness,[2] chemical degradation,[3] high affinity for heavy metal ions,[4] and anticancer activity,[5] and have recently attracted much attention and are widely utilized in controlled drug delivery systems,[2b,6] solar cells,[7] precious metal recovery,[4] biotherapy,[8] polymer recycling,[3] nanoparticle preparation,[9] and so on. However, the preparation of selenium-containing polymers remains rare and challenging. They are usually prepared from selenium-containing monomers such as diselenides, selenocyclic carbonates, selenophenols, and sodium selenide by ring-opening polymerization,[10] free radical polymerization,[11] and transition-metal-catalyzed polymerization reactions.[12] These selenium-containing monomers are generally toxic, expensive, and unstable, requiring multi-step preparations under harsh conditions and inert gas protection when handling sensitive reagents.

Compared to other selenium monomers, elemental selenium is a readily available, inexpensive, stable reagent with low toxicity,[13] which could be an ideal selenium source for the preparation of selenium-containing polymers. Multicomponent polymerization (MCP), as a recently emerged strategy for constructing complex polymers, has been rapidly developed due to its high efficiency, operational simplicity, high atom economy, environmental friendliness, and remarkable structural diversity. For example, Hu and Tang's group reported several elegant approaches to afford various selenium-containing heterocyclic polymers using elemental selenium by an MCP strategy.[14] Among all organic selenium compounds, selenium-containing triazolyl N-heterocycles with potential biological activity and functionality are widely utilized in pharmacology, materials science, bioconjugation and synthetic organic chemistry,[15] which can bring new properties and functions to selenium-containing polymers. However, there are few reports on the preparation of selenium-containing triazolyl N-heterocyclic polymers.[16] The main issues are both the lack of economical and reliable selenium-containing monomers and the lack of efficient and convenient synthetic methods. Therefore, it is still urgent and necessary to disclose novel polymer synthesis-oriented reaction customization on monomers and conditions for the synthesis of selenium-containing polymers.

In this paper, a unique MCP of elemental selenium, alkynes and azides was developed to prepare poly(5-diselenide-triazole)s with high regioselectivity and atom economy under mild conditions. Such selenium-containing triazoly polymers featured well-defined structures, high molecular weights (M_n up to 71 300 g mol^{-1}) and yields (up to 90%), good solubility, high stability, and excellent redox-degradation properties (Scheme 1).

To gain more micro-structure details and demonstrate that all the monomers participated in the MCP, the ^{1}H NMR and ^{13}C NMR spectra of **AK1**, **AZ1**, a small molecular model compound **M1** and the resulting polymer **P1** in DMSO are shown in Fig. 1. Comparing the ^{1}H NMR spectra of **AK1** and **AZ1** with **M1** and **P1**, the alkynyl peak at δ 4.38 ppm in **AK1** vanished in **M1** and **P1**. The peak of methylene at δ 4.45 ppm in **AZ1** shifted downfield in **M1** and **P1**. The above two changes indicated the successful transformation of alkyne and azide monomers to the polymer (Fig. 1A). In ^{13}C NMR spectra, the alkynyl carbons of **AK1** located at δ 83.30 and 83.39 ppm vanished after MCP, which remarkably demonstrated the complete consumption of **AK1**. For **AZ1**, the typical benzyl peak could be easily found in **M1** and **P1**. Compared to **AK1** and **AZ1**, a significant triazole

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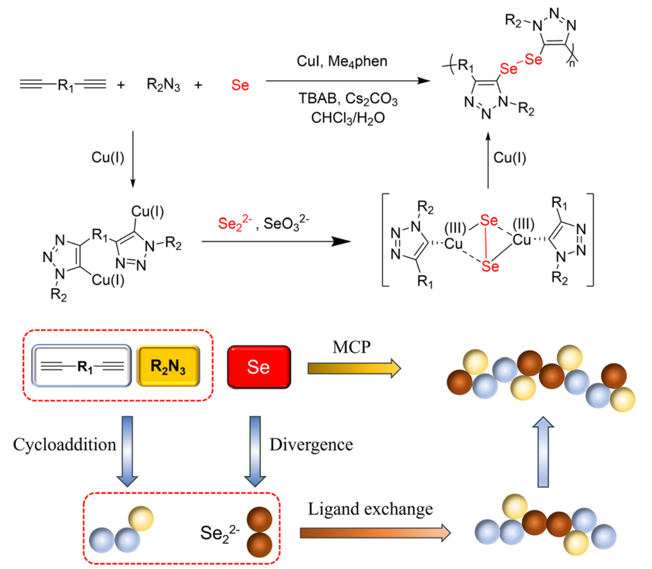

Scheme 1 MCPs of elemental selenium, alkynes and azides.

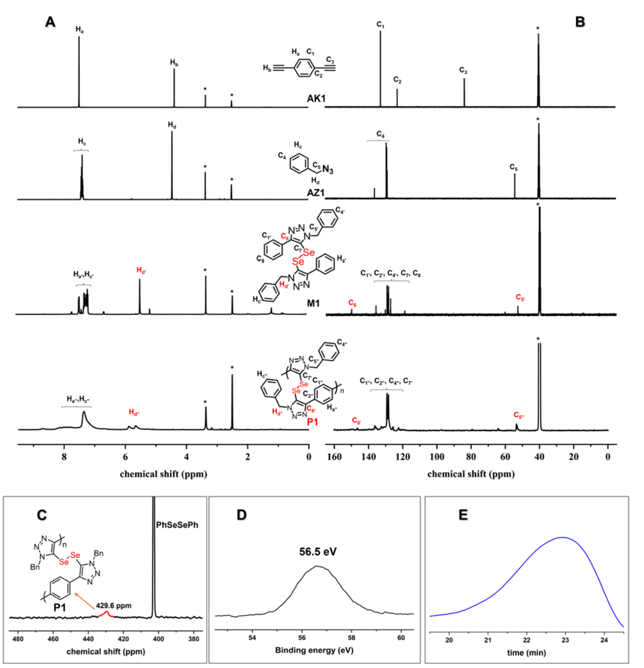

Fig. 1 (A) ^{1}H NMR spectra of **AK1**, **AZ1**, **M1** and **P1** in DMSO. (B) ^{13}C NMR spectra of **AK1**, **AZ1**, **M1** and **P1** in DMSO. (C) ^{77}Se NMR spectra of **P1** in $CDCl_3$ (PhSeSePh as an external standard). (D) XPS spectra of **P1**. (E) GPC curve of **P1**.

ring characteristic peak signal at δ 149.9 ppm was observed in **M1**, and a similar change was observed in **P1** (Fig. 1B). In addition, ^{77}Se NMR spectra were also used for the characterization of such selenium-containing polymers. It was obvious to find the peak of a diselenide bridge at δ 429.6 ppm in the ^{77}Se NMR spectra of **P1** (Fig. 1C). The structure of polymer **P1** was also confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. 1D). The Se 3d peak of **P1** was shown at 56.5 eV, which was very close to the peak of the diselenide (Se–Se bond) according to the XPS results. Both ^{77}Se NMR and XPS indicated that elemental selenium was involved in MCP with a diselenide bridge structure existing in the generated polymers. The polymer's M_n and $Đ$ were 41 700 g mol^{-1} and 1.16 as determined by gel permeation chromatography (GPC) (Fig. 1E).

In order to expand the substrate scope of the MCP, five diynes **AK1–AK5**, five azides **AZ1–AZ5**, two alkynes **AK6–AK7** and one diazide **AZ6** were used as monomers. All of them could smoothly participate in the MCP to generate eleven polymers **P1–P11** (Scheme 2). **AK1** could efficiently achieve the polymerization with **AZ1** and elemental selenium to afford **P1** with high yield (86%) and M_n (41 700 g mol^{-1}). Biphenyl diyne **AK2** and diphenyl ether diyne **AK3** could be well tolerated and give the desired polymers (**P2–P3**) in good M_ns albeit with slightly decreased yields. The 9,10-anthracyl diyne **AK4** could be utilized in the polymerization to obtain **P4** with an excellent yield (90%) and M_n (12 700 g mol^{-1}). If 2,6-naphthyl diyne **AK5** was used instead of **AK4**, the highest M_n (71 300 g mol^{-1}) of the polymer **P5** was acquired. Besides **AZ1**, a monomer with increased steric hindrance of the azide (**AZ2**) could also be polymerized with **AK1** and Se to generate polymer **P6** regardless of the decreasing M_n. An azide with the introduction of a methoxy group (**AZ3**) could be used as an electron-donor monomer to form **P7** in 85% yield and 32 200 g mol^{-1} M_n. Extending the σ-bond length of the azides (**AZ4** and **AZ5**) did not decrease the yields and M_ns for **P8** and **P9**. Using 1 equiv. diazide **AZ6** as a monomer, the MCP could also be accomplished with 6 equiv. alkynes **AK6–AK7** and elemental selenium. 3-Ethynylthiophene (**AK6**) as a heterocyclic monomer could supply **P10** in 88% yield and 8400 g mol^{-1} M_n. Other monoalkynes (**AK7**) could also be polymerized with diazide to give high yields for **P11** with slightly lower molecular weights due to the reduced reactivity.

The chemical characterizations have unambiguously confirmed the successful introduction of diselenide bridges into the polymer backbones for the synthesis of redox dual-responsive polymers **P1–P11**. The polymer **P1** could be degraded to small molecules by treatment with an oxidant (H_2O_2) or reducing agent dithiothreitol (DTT) (Scheme 3). Treatment of polymer **P1** (41 700 g mol^{-1} M_n) with H_2O_2 for 1 h at 37 °C resulted in degradation to diselenite acids as revealed by GPC and LC-MS with HRMS (m/z = 614.9803) (Fig. S3A and Fig. S4A, ESI†). In addition, adding DTT to the same polymer **P1** for 1 h at 37 °C, the polymer **P1** (41 700 g mol^{-1} M_n) was also degraded to diselenophenols, as evidenced by GPC and LC-MS (liquid chromatography-mass spectrometry) with HRMS (m/z = 551.0007) (Fig. S3B and S4B, ESI†). The above experimental results indicated that these diselenide-bridged polymers could be rapidly degraded in the presence of either oxidative or reductive reagents, which proved that redox-responsive degradable polymers containing Se–Se bonds could be efficiently synthesized by this unique MCP approach.

In conclusion, the copper-catalyzed cascade multicomponent polymerization using readily available and stable elemental selenium as a monomer for regioselective synthesis of poly(5-diselenide-triazole)s was disclosed. Such selenium-containing triazole polymers featured well-defined structures, high molecular weights (M_n up to 71 300 g mol^{-1}) and yields (up to 90%),

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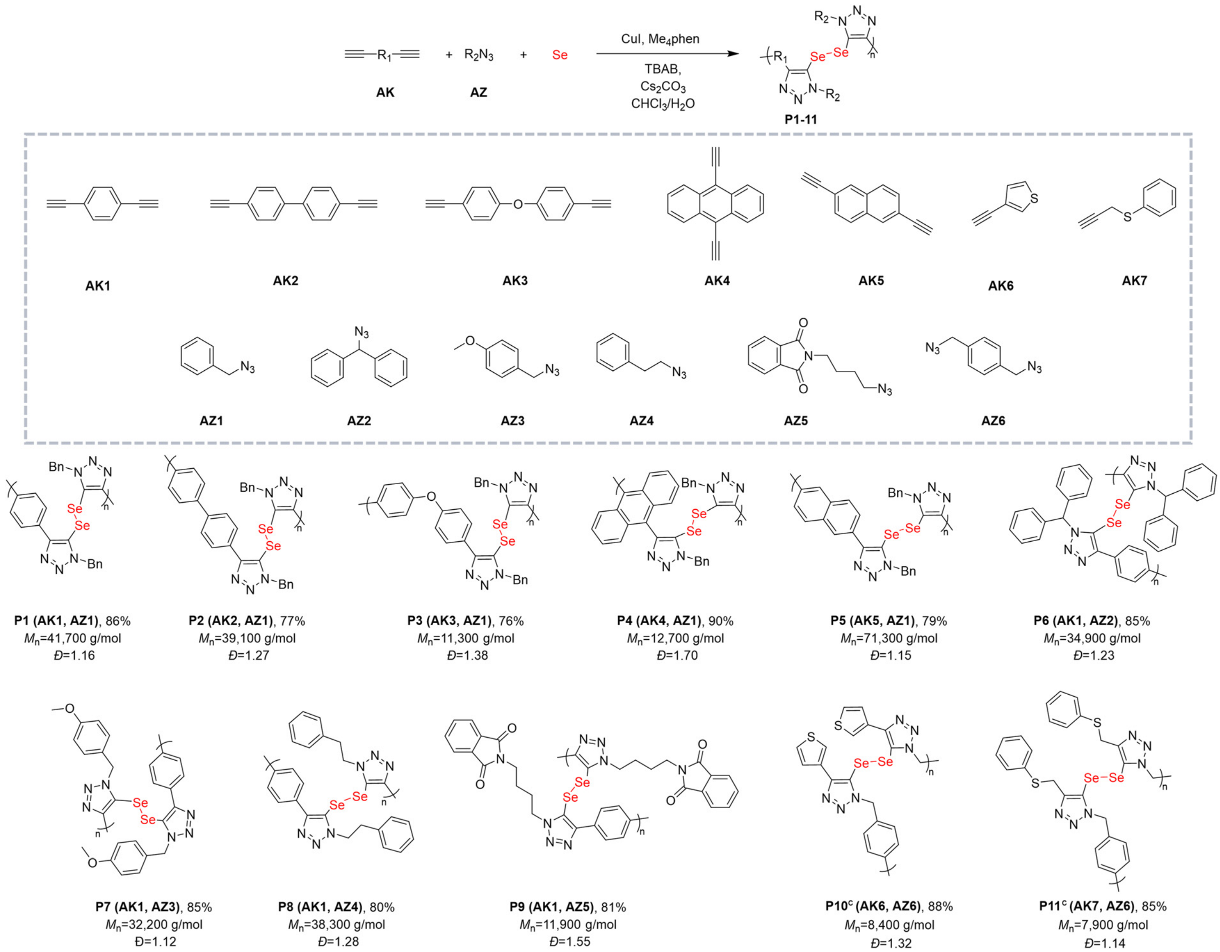
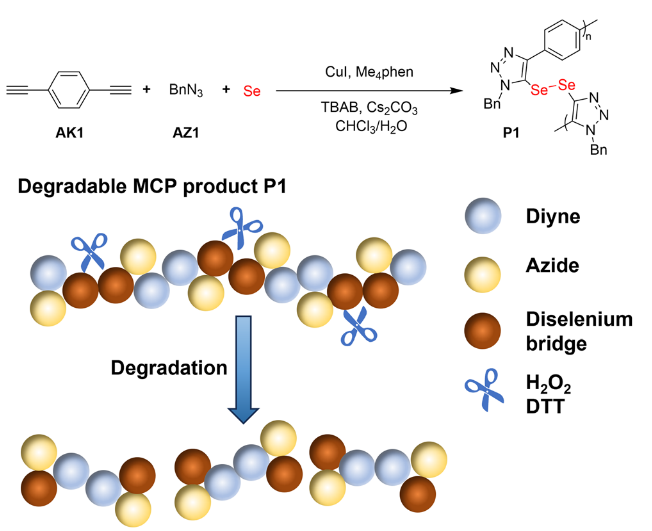


Scheme 2 The MCP scope of AKs (1–7), AZs (1–6), and elemental selenium.[a,b,c] [a] Reaction conditions: **AK** (0.1 mmol), **AZ** (6.0 equiv.), Se (12.0 equiv.), CuI (5 mol%), Me_4phen (6 mol%), Cs_2CO_3 (6.0 equiv.) and TBAB (1.0 equiv.) in $CHCl_3/H_2O$ (V : V = 1 : 1, 1.0 mL) at 50 °C for 12 h. [b] M_n, M_w and $Đ$ were determined by GPC in DMF with PS (polystyrene) standards. [c] **AZ** (0.1 mmol) and **AK** (6.0 equiv.) were used.



Scheme 3 The degradation of selenium-containing polymers responsive to H_2O_2 (5 mmol L^{-1}) or DTT (5 mmol L^{-1}).

good solubility and high stability. Remarkably, the unique diselenide structures as linkages enjoyed excellent redox degradation properties, which promoted the chemical recycling of selenium-containing polymers to small molecular selenides under either oxidative or reductive conditions.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare that they have no conflict of interest.

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