

One-Step Precise Synthesis of Sequence-Defined ABCB-Type Se-Containing Polymers with Tunable Properties

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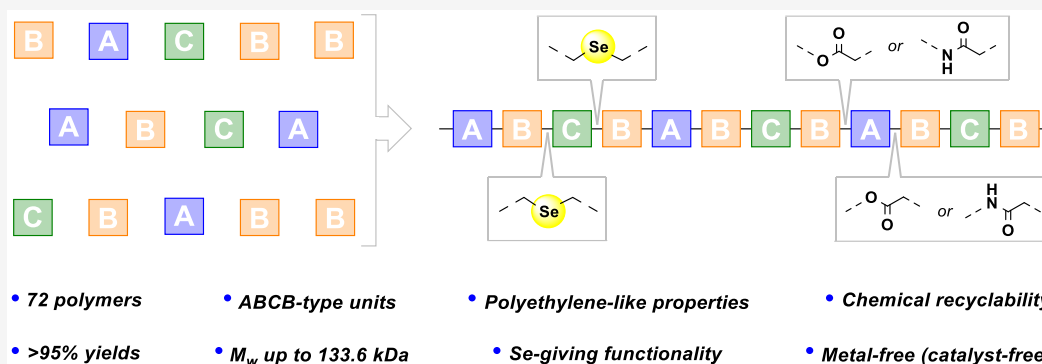
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ABSTRACT: The development of synthetic polymers with precisely tailored monomer sequences represents a critical yet challenging frontier in polymer science. In this study, we present a modular strategy for the synthesis of ABCB-type periodic polymers through the first reported step-polymerization of diols (or diamines), diacrylates, and a Se-containing lactone. This approach leverages exclusive chemoselectivity to achieve precise monomer placement within the polymer chain, enabling the incorporation of selenoether and ester (or amide) groups in well-defined repeating units. The method exhibits broad monomer compatibility, yielding 72 new polymers with precisely controlled sequences. The resulting polymer library demonstrates extensively tunable properties, including glass transition temperatures ranging from -69 to 21 °C, melting temperatures from 1 to 132 °C, polyethylene-like mechanical characteristics, chemical recyclability, and Se-donating functionality. Notably, the process is atom-economical, metal-free, and catalyst-free, utilizing readily available monomers to produce polymers with >95% yields and weight-average molecular weights up to 133.6 kDa. This work establishes a facile and versatile platform for the synthesis of sequence-controlled Se-containing polymers, offering new opportunities for advanced material design.

INTRODUCTION

The regularity of monomer sequences plays a pivotal role in determining the properties of polymeric materials.^{1,2} While nature excels in achieving precise sequence control in biopolymers such as nucleic acids and proteins,³ synthetic polymers often lack such precision in the sequential arrangement of multiple monomer units.^{4–7} Over the past few decades, several strategies have emerged to regulate monomer sequences in polymer synthesis (Figure 1a).^{8–30} For example, iterative single-unit monomer addition has proven effective for sequence control,^{31,32} as demonstrated in maleimide-based polymer synthesis,^{33–35} though it often requires significant time and effort to achieve high molecular weights (MWs). Alternatively, polymerization of presequenced monomers offers another route,^{36–38} yet the synthesis of such monomers is typically inefficient. Direct chain-growth or step-growth polymerization of multiple monomers in a single step represents a simpler approach,^{39,40} but achieving precise sequence control remains a formidable challenge.

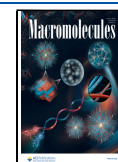
Step-growth polymerization of diols and diacrylates via oxo-Michael addition provides an atom-economical route to polyesters.^{41,42} However, the low nucleophilicity of oxygen anions limits the versatility and efficiency of this method, often resulting in polymers with low MWs and simple AB alternating sequences. In contrast, the Michael addition of selenols to activated alkenes is highly efficient and versatile due to the superior nucleophilicity of selenium (Se) anions.⁴³ This stark difference in nucleophilicity between O and Se anions inspired us to explore a bridging molecule capable of converting hydroxyl groups into selenides, which can then undergo in situ reactions with activated alkenes. This strategy is expected to

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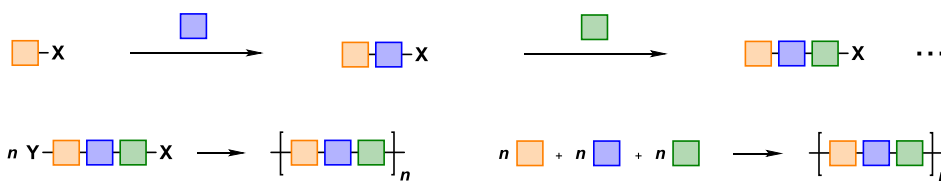
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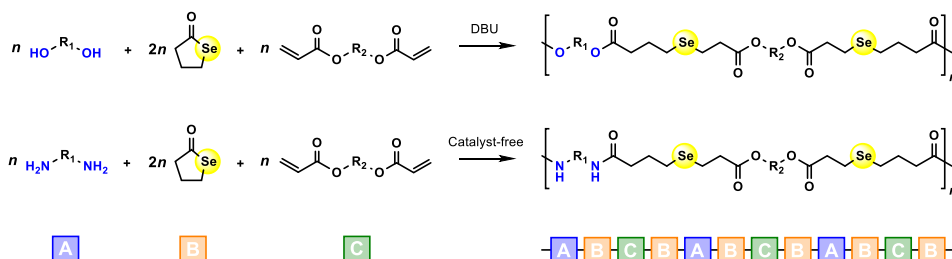
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(a) Methods for sequence-controlled polymer synthesis



(b) This work: One-step synthesis of sequence-controlled ABAC-type Se-containing polymers



- ◇ General protocol
- ◇ Sequence-controlled and easy-to-tune structure
- ◇ Metal-free (Catalyst-free)
- ◇ Chemically recyclable
- ◇ Polyethylene-like mechanical properties
- ◇ Atom-economical

Figure 1. (a) Previously reported synthesis of sequence-controlled polymers. (b) One-step synthesis of sequence-defined ABCB-type Se-containing polymers..

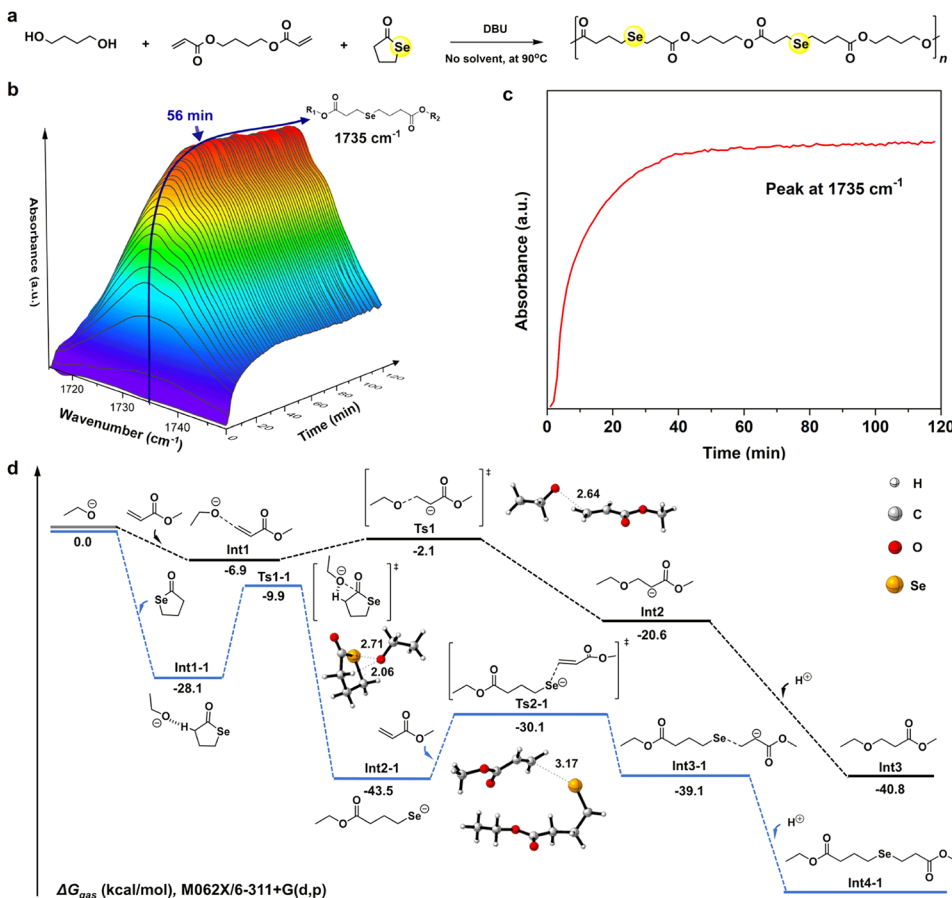


Figure 2. (a) One-step polymerization for the synthesis of P1. (b) Time-dependent 3D stack plot of the IR spectra. (c) Time-dependent peak intensity at 1735 cm^{-1} IR profile. (d) Free energies associated with the coupling reaction.

enable efficient polymerization and the formation of complex monomer sequences. However, the high susceptibility of

selenols to oxidation, compared to thiols, has limited the development of general methodologies for selenol syn-

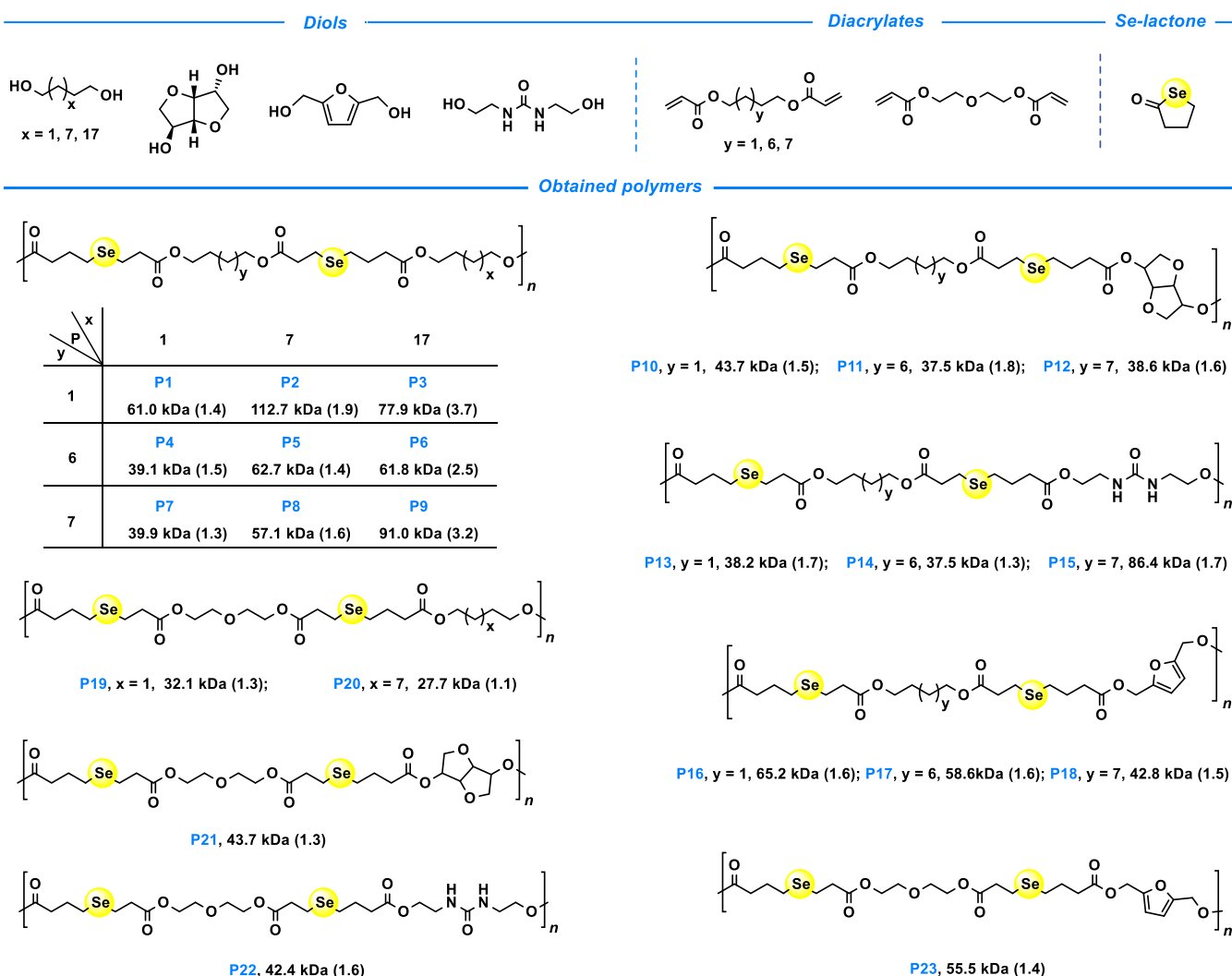


Figure 3. One-step synthesis of P1 to P23. Conditions: at 90 °C for 4 h, DBU as a catalyst, $[\text{diol}]_0/[\text{diacrylate}]_0/[\gamma\text{-SBL}]_0/[\text{DBU}] = 100:100:220:1$. M_w and \mathcal{D} values are determined by GPC (Figures S148–S153).

thesis.^{43,44} Consequently, the direct generation of Se anions from selenols for polymer synthesis is highly constrained. Instead, the in situ generation of Se anions from readily available precursors offers a more practical solution.

Se chemistry has garnered significant attention in modern materials science due to its unique properties.^{45,46} As an essential trace element in the human body,⁴⁷ the incorporation of Se into polymers can impart novel functionalities,^{48–51} making Se-containing polymers promising candidates for biomaterials,⁵² redox-responsive systems,⁵³ chemically recyclable materials,⁵⁴ and nanobiotechnology applications.⁵⁵ Despite recent advances, the precise incorporation of Se into polymers remains challenging,^{56–64} particularly in the context of polymers with tailor-made monomer sequences.

Here, we report a facile and versatile one-step synthesis of sequence-defined ABCB-type Se-containing polymers (Figure 1b). The monomers employed include diols (or diamines), diacrylates, and γ -selenobutyrolactone (γ -SBL). Diols, diamines, and diacrylates are industrially abundant and diverse, with many derived from renewable resources. The γ -SBL is synthesized through two steps from bioderived γ -butyrolactone and Se powder, a byproduct of metal refining (Figures S1 and S2, Supporting Information).^{65,66} This atom-economical and

metal-free polymerization method yields 72 new polymers, each featuring precisely arranged selenoether and ester (or amide) groups in their repeating units.

RESULTS AND DISCUSSION

We first investigated the base-catalyzed step-growth polymerization of diols, diacrylates, and γ -SBL. The diols employed included 1,4-butanediol, 1,10-decanediol, 1,20-eicosanediol, isosorbide, 2,5-furandimethanol, and 1,3-bis(2-hydroxyethyl)urea, while the diacrylates comprised 1,4-butanediol diacrylate, 1,9-nonanediol diacrylate, 1,10-decanediyl diacrylate, and diethylene glycol diacrylate. The organobase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was identified as an efficient catalyst for this reaction. All chemicals were used as received without further purification.

The polymerization process was monitored in situ using infrared (IR) spectroscopy, with 1,4-butanediol and 1,4-butanediol diacrylate selected as representative monomers (Figure 2a). Under optimized conditions ($[\text{diol}]_0/[\text{diacrylate}]_0/[\gamma\text{-SBL}]_0/[\text{DBU}] = 100:100:220:1$, 90 °C, solvent-free), the reaction proceeded smoothly, as evidenced by the appearance of a characteristic C=O peak at 1735 cm^{-1} in the IR spectrum of the resulting polymer (P1) (Figure S3).

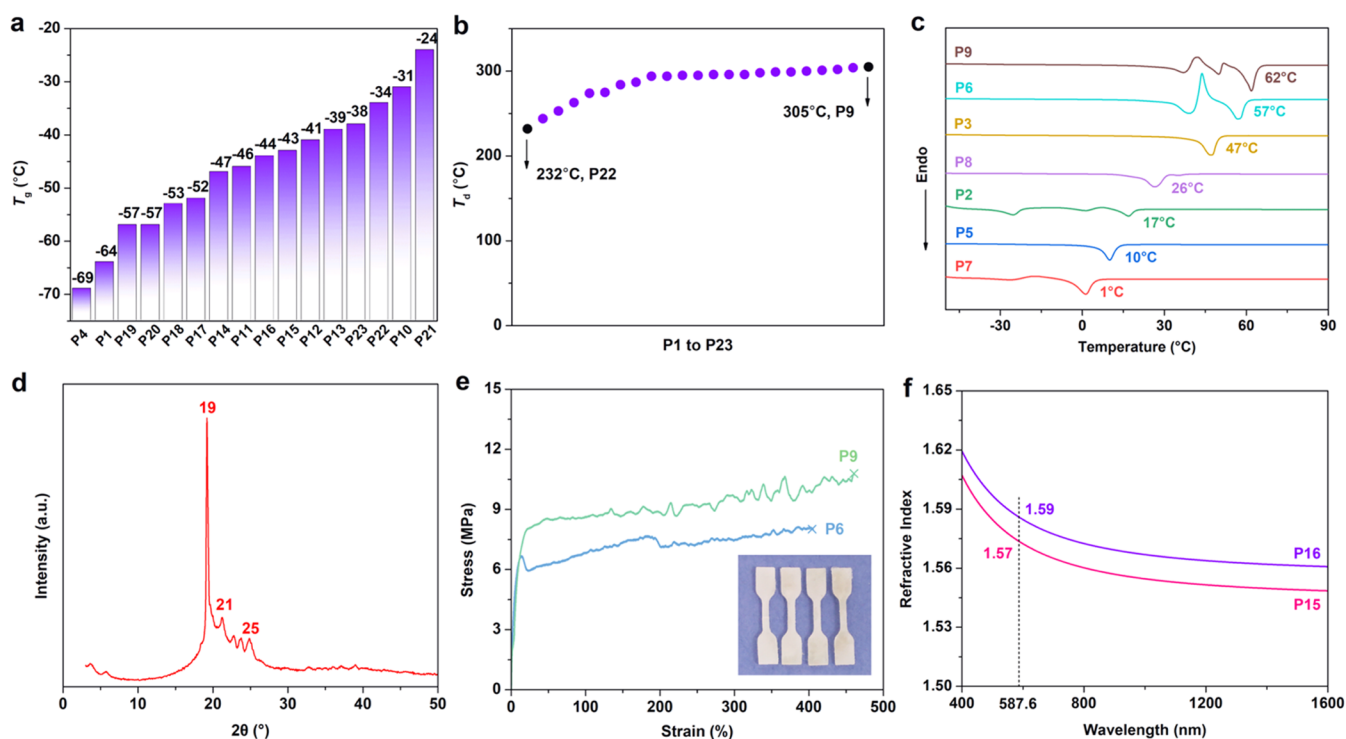


Figure 4. (a) T_d values as determined by TGA. (b) T_g values as determined by DSC. (c) DSC curves of semicrystalline polymers. (d) XRD curve of P9. (e) Stress–strain curves. (f) Refractive indices of P15 and P16.

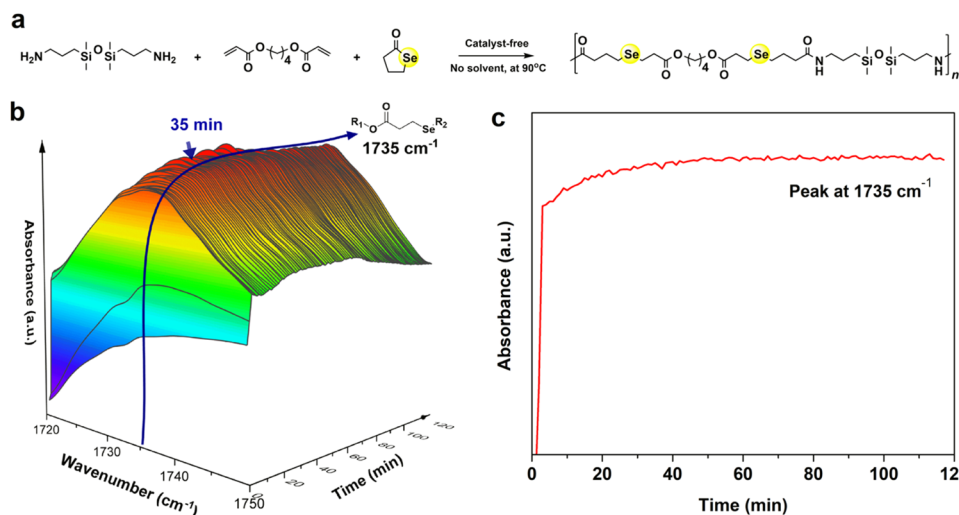


Figure 5. (a) Step-growth polymerization for the synthesis of P49. (b) Time-dependent 3D stack plot of the IR spectra of the polymerization. (c) Time-dependent peak intensity at 1735 cm^{-1} IR profile.

This peak, absent in the monomers, corresponds to the ester carbonyl group adjacent to the selenoether moiety. Real-time IR monitoring revealed rapid growth of the 1735 cm^{-1} peak, reaching equilibrium within 1 h (Figure 2b,c). After 120 min, P1 exhibited a weight-average molecular weight (M_w) of 54.1 kDa, as determined by gel permeation chromatography (GPC). NMR analysis confirmed the ABCB-type periodic structure of P1 (Figures S4 and S5). In contrast, the direct polymerization of 1,4-butanediol and 1,4-butanediol diacrylate under identical conditions yielded only low-MW oligomers ($M_w = 3.5$ kDa).

To elucidate the polymerization mechanism and chemoselectivity, density functional theory (DFT) calculations were

performed using ethanol, methyl acrylate, and γ -SBL as model reactants (Figure 2d and Supporting Information). The reaction proceeds through a cascade of Michael additions: (1) deprotonation of ethanol generates an oxygen anion, which attacks the carbonyl group of γ -SBL (barrier: -9.9 kcal mol^{-1}) to form a Se anion intermediate (Int2-1); (2) the selenium anion subsequently attacks the C=C bond of methyl acrylate (barrier: -30.1 kcal mol^{-1}), yielding a negatively charged intermediate (Int3-1); and (3) proton transfer completes the formation of the three-component adduct (Int4-1). The ring-opening of γ -SBL, with a barrier of -9.9 kcal mol^{-1} , was identified as the rate-determining step. In contrast, the direct addition of ethanol to methyl acrylate requires a higher barrier

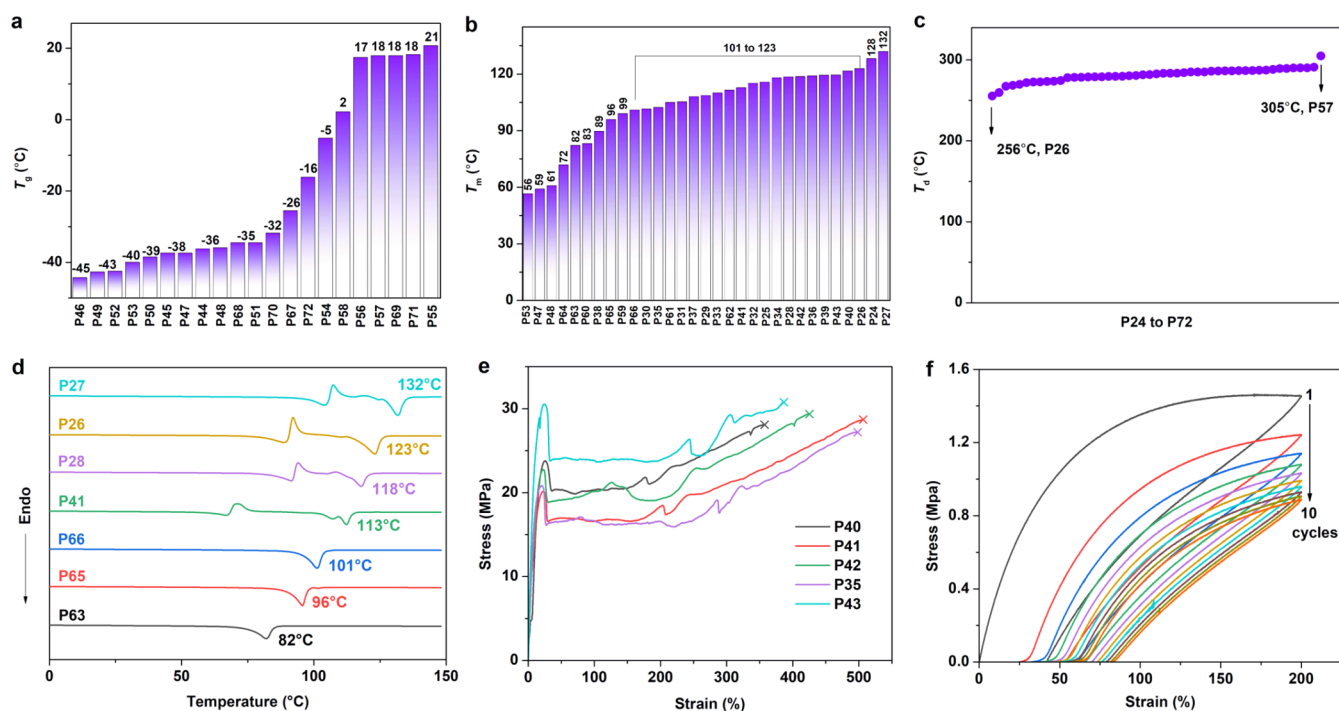


Figure 7. (a) T_d values as determined by TGA. (b) T_g values as determined by DSC. (c) T_m values as determined by DSC. (d) DSC curves. (e) Stress–strain curves. (f) Cyclic tensile testing without delay of P58.

common organic solvents (THF, CH_2Cl_2 , CHCl_3 , DMF). NMR analysis confirmed the ABCB-type structure and the presence of selenoether and ester groups in the repeating units (Figures S6–S49) (Figure 3).

The polymers exhibited tunable thermal and mechanical properties. Thermogravimetric analysis (TGA) revealed high thermal stability, with decomposition temperatures (T_d , 5% mass loss) ranging from 232 to 305 °C (Figures S161–S183). Polymers with short carbon chains or in-chain substituents (P1, P4, P10–P23) were amorphous, with glass-transition temperatures (T_g) ranging from -69 to -24 °C (Figures S233–S255). In contrast, polymers with long carbon chains (P2, P3, P5–P9) were semicrystalline, with melting temperatures (T_m) of 1–62 °C (Figure 4c). P9, with the lowest density of polar groups, exhibited the highest T_m (62 °C) and distinct diffraction peaks in wide-angle X-ray scattering (WAXD) patterns (Figure 4d). Tensile testing revealed low-density polyethylene (LDPE)-like mechanical properties,⁶⁷ with P6 and P9 showing ultimate tensile strengths (σ_B) of 8.1 and 10.2 MPa and elongations at break (ϵ_B) of 406 and 461%, respectively. Additionally, the incorporation of selenium imparted notable optical properties, with P15 and P16 exhibiting high refractive indices (n_d , 587.6 nm) of 1.57 and 1.59, suggesting potential optoelectronic applications (Figure 4f).

To further enhance mechanical and thermal properties, we explored the incorporation of amide groups via the polymerization of diamines, diacrylates, and γ -SBL. The strong nucleophilicity of primary amines enabled catalyst-free polymerization. Using 1,3-bis(3-aminopropyl)tetramethyl disiloxane and 1,4-butanediol diacrylate as representative monomers ($[\text{diamine}]_0/[\text{diacrylate}]_0/[\gamma\text{-SBL}]_0 = 1:1:2$, 90 °C, solvent-free), the reaction reached equilibrium within 35 min, as monitored by in situ IR spectroscopy (Figure 5b,c). The resulting polymer (P49) exhibited an M_w of 41.2 kDa and

the expected ABCB-type periodic structure (Figures S100 and S101). In contrast, direct polymerization of the diamine and diacrylate yielded an insoluble cross-linked polymer due to secondary amine formation and subsequent Michael addition.⁶⁸

Under optimized conditions ($[\text{diamine}]_0/[\text{diacrylate}]_0/[\gamma\text{-SBL}]_0 = 1:1:2$, 90 °C, DMF solvent), we synthesized 49 additional polymers (P24–P72) with M_w values of 25.6–133.6 kDa and \bar{D} values of 1.4–3.3 (Table S4, Figure 6). Broad \bar{D} values (>2.0) were attributed to heterogeneous polymerization systems caused by limited polymer solubility. NMR analysis confirmed the incorporation of selenoether, amide, and ester groups in the repeating units (Figures S50–S147). The amide-containing polymers exhibited high thermal stability ($T_d = 256$ –305 °C, Figure 7a) and enhanced mechanical properties. Amorphous polymers (P44–P58, P67–P72) displayed T_g values ranging from -45 to 21 °C, while semicrystalline polymers (P24–P43, P59–P66) exhibited T_m values of 72–132 °C (Figure 7b,c). Tensile testing revealed high-performance materials, with P29, P35, P36, P37, P40, P41, P42, and P43 showing σ_B values of 22.5–32.0 MPa and ϵ_B values of 358–603%, comparable to high-density polyethylene (HDPE, Figure 7d,e).⁶⁹ Additionally, polymers such as P57 and P58 exhibited thermoplastic elastomer behavior, with σ_B values of 1.2 and 0.9 MPa and ϵ_B values of 1297 and 832%, respectively (Figures S307 and S308). Cyclic tensile tests demonstrated excellent elastic recovery, with recovery rates of 78 and 79% after 10 cycles (Figures 7f and S309).

Finally, we demonstrated the chemical recyclability of these polymers via methanolysis and polycondensation (Figure 8a). Owing to the incorporation of massive in-chain ester groups, the polymers are easily degraded via the cleavage of ester bonds. For example, methanolysis of P8 (1 g) in the presence of Ti(IV) *n*-butoxide (0.042 mol %) at 120 °C for 24 h yielded a 98% recovery of 1,10-diol and selenium-containing dimethyl

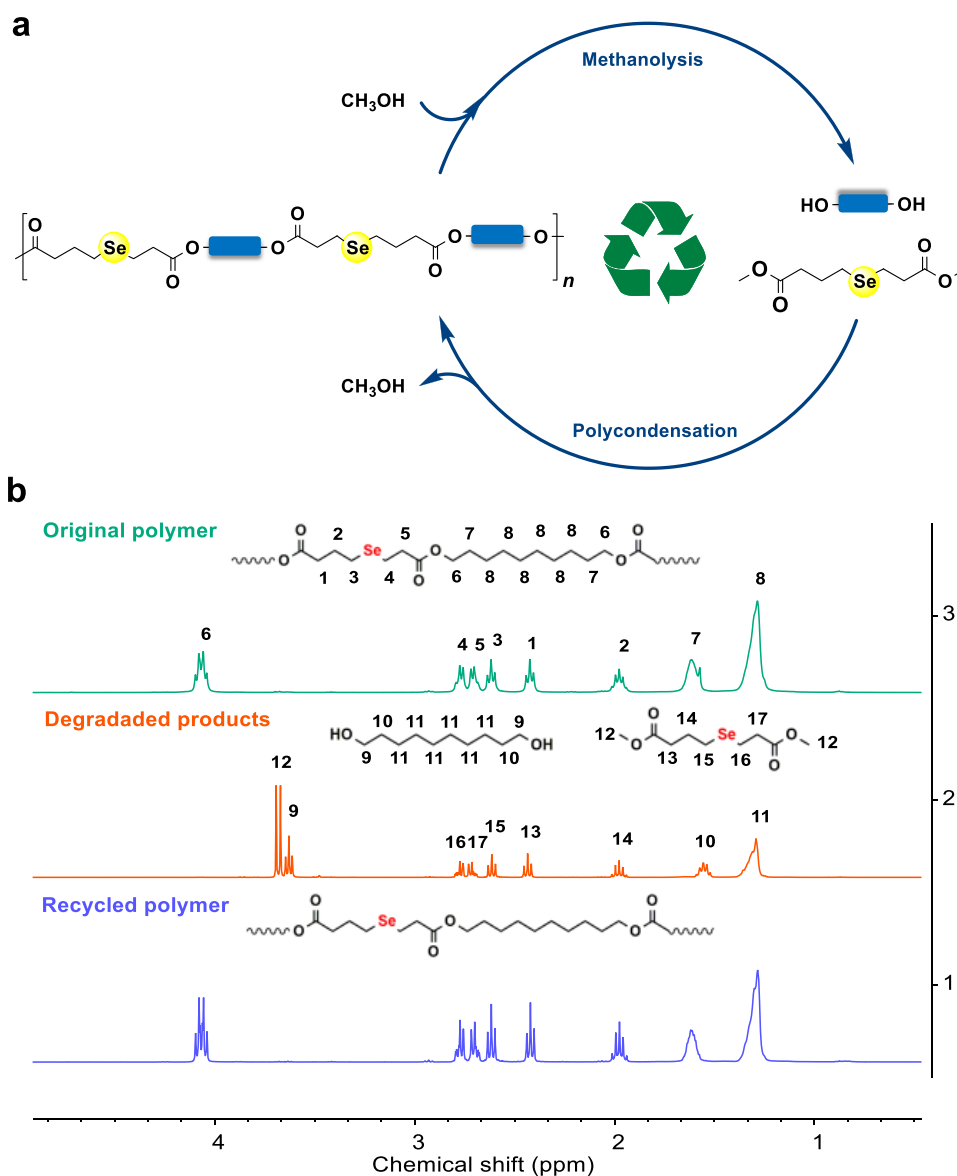


Figure 8. (a) Chemical recycling of the polymer. (b) ^1H NMR spectra of the polymers and degraded products.

ester (Figure 8b, Supporting Information). Conveniently, nonvolatile $\text{Ti}(\text{iv})$ *n*-butoxide also remained in the mixture, which can further catalyze the next polycondensation. Subsequent polycondensation of the recovered monomers regenerated **P8** with an M_w of 37.7 kDa ($\bar{D} = 1.5$), highlighting the potential for closed-loop recycling.

CONCLUSIONS

In summary, we have developed a modular strategy for the synthesis of ABCB-type periodic polymers through the step-growth polymerization of diols (or diamines), diacrylates, and a Se-containing lactone. The reaction proceeds via a cascade of nucleophilic additions, exhibiting exceptional regio- and chemoselectivity, which enables the precise placement of multiple monomers into the polymer backbone. Leveraging the diversity of commercially available monomers and the versatility of this method, we successfully synthesized 72 polymers featuring well-defined sequences of selenoether, ester, and amide groups within their repeating units.

This polymer library exhibits a broad range of tunable properties, including T_g from -69 to 21 $^\circ\text{C}$, T_m from 1 to 132 $^\circ\text{C}$, and mechanical properties comparable to LDPE and HDPE. The incorporation of Se further imparts unique functionality, such as redox responsiveness and notable optical properties. Notably, the in-chain ester groups serve as dynamic linkages, enabling closed-loop chemical recycling through methanolysis and polycondensation.

The method is atom-economical, metal-free, and catalyst-free, affording polymers in high yields ($>95\%$) with M_w up to 133.6 kDa. The structural and property tunability of these polymers offers significant potential for further optimization and application. This work provides a straightforward and versatile platform for the synthesis of sequence-defined, selenium-containing polymers, opening new avenues for the design of functional materials with tailored properties.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.5c00528>.

Additional experimental details, materials, and methods; NMR, IR, GPC, DSC, TGA, XRD, and tensile test data of the obtained polymers; computational details; Tables S1–S4 and Figures S1–S309 (PDF)

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Notes

The authors declare no competing financial interest.

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