

Preparation of Sequence-controlled Aliphatic Polysulfones by Group Transfer Radical Polymerization

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Abstract: The integration of sulfur atoms into polymer backbones to synthesize S-containing polymers, such as aliphatic polysulfones, renders many unique properties of the materials. Conventional methods are facing great challenges to achieve sequence-controlled aliphatic polysulfones with high molecular weight (MW), significantly restricting the use of these polymers. We devise a novel approach for the preparation of aliphatic polysulfones via sulfonyl radical-mediated group transfer radical polymerization (GTRP). The polymerization proceeds through a practical SO₂-free pathway, producing a series of ABC sequence-defined high-MW polymers (up to 199 kg/mol). DFT calculations are conducted, which support the radical Smiles rearrangement pathway involved in the GTRP process.

Introduction

The copolymerization of olefins with gaseous SO₂ presents an effective method for the direct preparation of aliphatic polysulfones (Fig. 1A). However, this copolymerization is constrained by the influence of ceiling temperature (T_c), above

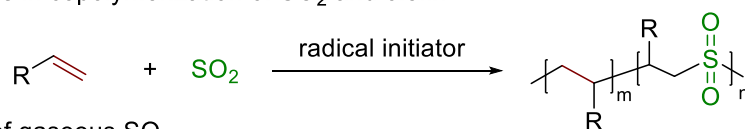
which depolymerization occurs, necessitating that reactions be conducted at low temperatures.^[1-5] The corrosive nature of SO₂ also places higher demands on polymerization equipment. Additionally, the impact of stereoelectronic effects of different olefins sometimes leads to the uncontrollable sequence structure of polymers in the copolymerization, such as styrene/SO₂ system.^[6-8] The lack of polar functionalities on aliphatic polysulfones may also cause the poor solubility in common solvents, which impedes chain propagation and ultimately generates a product with low molecular weight and wide distribution.^[7, 8] These reasons undoubtedly deteriorate the applications of aliphatic polysulfones.^[9]

Cyclic vinylsulfones (CVS) serve as a new monomer for constructing aliphatic polysulfones via a SO₂-free strategy (Fig. 1B), in which sulfonyl radical engages in chain-propagation during free radical-mediated ring-opening polymerization.^[10-13] However, due to the difficult incorporation of extra polar pendants in CVS monomers, aliphatic polysulfones are also obtained with poor solubility. Moreover, random ring-opening of CVS during the polymerization leads to uncontrollable sequence of polymers, and the newly formed C=C bond in backbone results in poor thermal resistance.^[14] Therefore, the facile preparation of sequence-controlled aliphatic polysulfones with high molecular weights still remains a formidable challenge.

Group transfer radical polymerization (GTRP) proves to be a robust strategy for radical polymerization, which has been applied to the construction of carbon-chain polyolefins.^[15-20] We conceive to explore a new polymerization pattern harnessing sulfonyl radical-mediated GTRP for the production of aliphatic polysulfones, where the strategically designed sulfone-substituted α -olefins are employed as monomers (Fig. 1C). Mechanistically, the alkyl radical (**a**) derived from the addition of an initiating radical to α -olefin triggers the intramolecular Smiles rearrangement via 1,4 or 1,5-cyclic transition state,^[21] generating a sulfonyl radical species (**c**) with the SO₂ unit retained in the structure. This electrophilic radical species rapidly adds to another olefinic monomer, enabling a kinetically favored propagation process. Herein, we report the proof-of-concept study, where a series of aliphatic polysulfones is produced

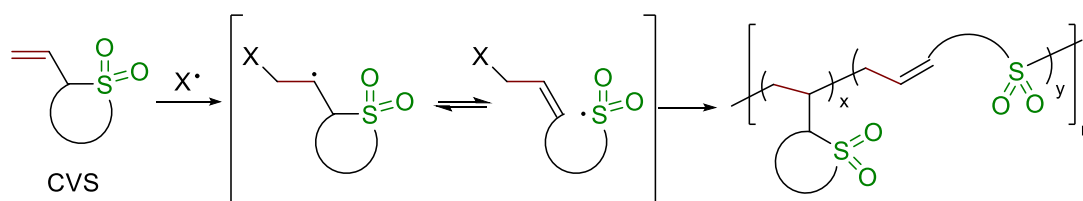
with high molecular weights (up to 199 kg/mol) and remarkable low distributions compared to existing methods. The GTRP proceeds via a SO₂-free process, giving rise to various ABC sequence-regulated polymers, analogous to the ternary copolymers from conjugate olefin, ethylene (or cyclopropane), and SO₂, otherwise highly difficult to prepare by other methods. Notably, this is the first example of applying Smiles rearrangement in radical polymerization.

(A) Challenges in copolymerization of SO₂ and olefin



1. use of gaseous SO₂
2. uncontrollable sequence
3. low molecular weight

(B) Synthesis of aliphatic polysulfones from cyclic vinylsulfones



1. uncontrollable sequence
2. poor solubility
3. limited thermal stability

(C) Group transfer radical polymerization via Smiles rearrangement (*this work*)

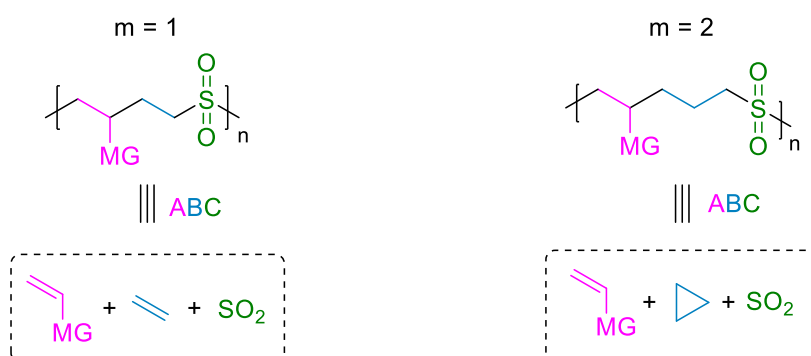
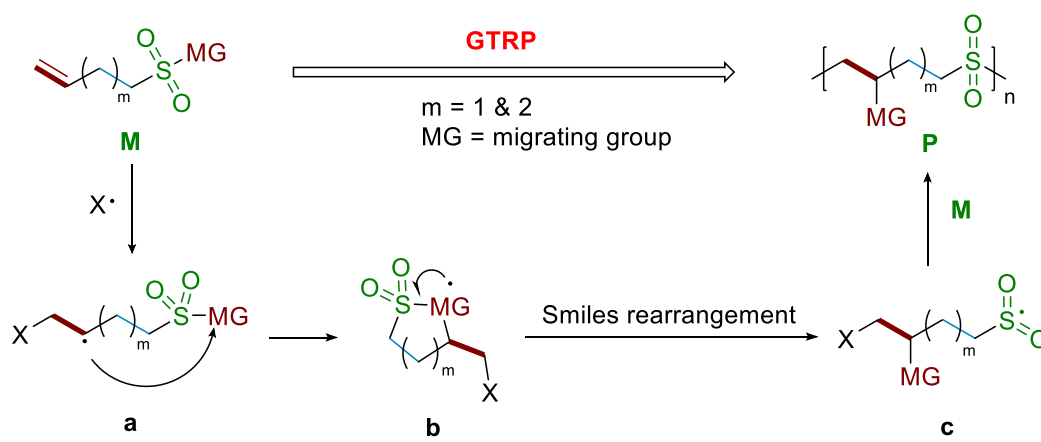


Fig 1. (A) Challenges in copolymerization of SO₂ and olefin; (B) Synthesis of aliphatic polysulfones from cyclic vinylsulfones; (C) Group transfer radical polymerization via Smiles rearrangement.

Results and discussion

Our investigation commenced with the exploration of optimal conditions for the homopolymerization of butenyl benzothiazolyl sulfone (**M1**) as monomer (Table S1). The polymerization of **M1** was initiated using A as the initiator across various solvents. The conversion of **M1** reached only 49%, with size exclusion chromatography (SEC) revealing a number-average molecular weight (M_n) of 36.4 kg/mol and distribution (D) of 1.26 (Table S1, entry 1). Both the conversion and M_n were elevated under identical conditions (Table S1, entries 2 and 3). An increased temperature of 180 °C resulted in a reduced conversion of **M1** to 47% (Table S1, entry 4). This decrease could potentially be attributed to the thermal desulfonation of sulfonyl radical intermediates, which interrupts chain propagation. Subsequently, initiation conditions utilizing B and C were examined. The polymer obtained exhibited a high M_n of 61.4 kg/mol, although the conversion was comparable to that achieved with the A system at 66% (Table S1, entry 5). Remarkably, the B system achieved nearly complete conversion of **M1**, producing a polymer with an increased M_n of 82.3 kg/mol (Table S1, Entry 6). With an elevation of temperature to 160 °C, the polymerization maintained high efficiency, but with a slight decrease in M_n and an increase in D to 2.00 (Table S1, Entry 7). Under the conditions of entry 6, kinetic studies showed that this GTPR process can generate a high M_n product at the beginning, and the M_n keeps at a high level when the conversion reaches 80% (Fig. S2), consistent with the characteristics of fast chain propagation in free radical polymerization.

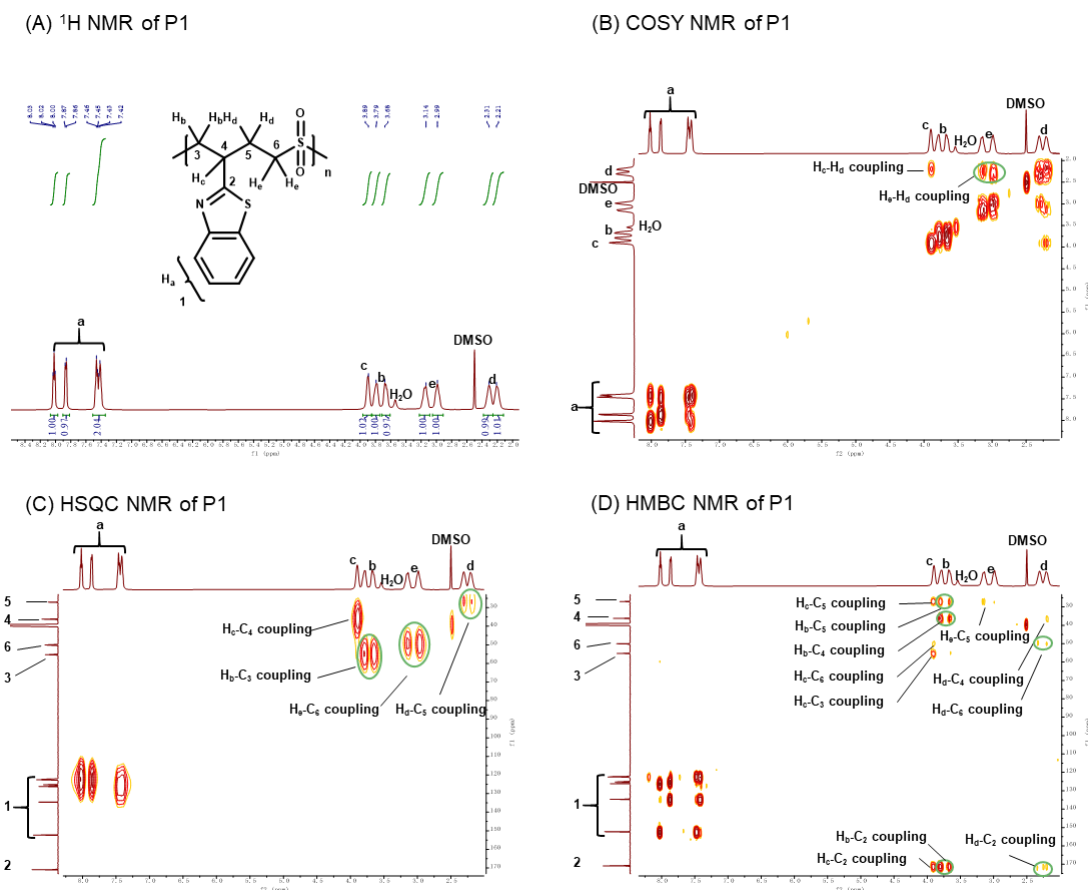


Fig 2. Chain structure characterization of polymer **P1**. (A-D) ^1H NMR, COSY, HSQC, and HMBC spectra of **P1**.

To verify whether **M1** undergoes the expected polymerization, nuclear magnetic resonance (NMR) spectroscopy was sought to obtain more information about the chain structure of polymer **P1**. As illustrated in Fig. 2A, alkyl hydrogens resonated in the low-field region (3.60-3.85 ppm), attributed to the electron-withdrawing effect, indicating that no desulfonation occurred during the polymerization. Moreover, the ^1H - ^1H correlation spectroscopy (COSY) and ^1H - ^{13}C heteronuclear single quantum coherence (HSQC) spectra revealed that H_c represents a single hydrogen atom, whereas H_b , H_e , and H_d are associated with methylene groups (Fig. 2B and 2C). This structural elucidation further confirmed that the migration of benzothiazole (Bt) to C_4 position by shifting H_c to the lower field. The ^1H - ^{13}C heteronuclear multiple bond correlation (HMBC) (Fig. 2D) provided coupling signals that support a precise alternating mechanism involving 1,4-group transfer and the addition of sulfonyl

radical to the C=C bonds.

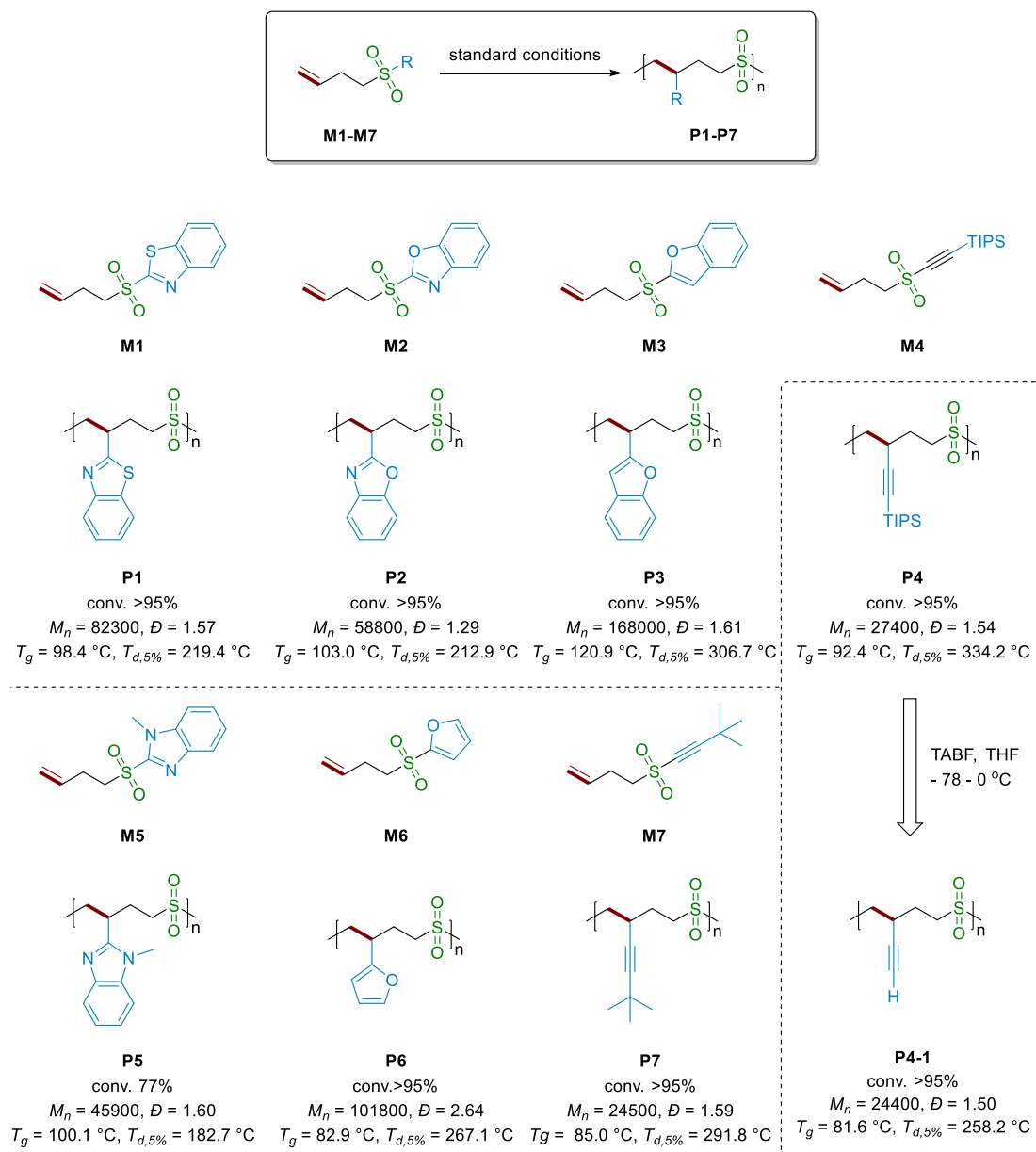


Fig 3. Radical polymerization via 1,4-group transfer.

Subsequently, a series of butenylsulfone monomers bearing different migrating groups were tested for 1,4-group transfer (Fig. 3). Beside **M1**, monomers with benzoxazole, benzofuran, and (triisopropylsilyl)acetylene (**M2-M4**) also exhibited good polymerization reactivity, achieving conversions above 95% under the standard conditions. The M_n of polymer **P3** reached 168 kg/mol, a high level challenging to attain with previous methods such as olefins/SO₂ copolymerization. While only

moderate conversions were given under the identical conditions (Table S2), the conversion of **M5** (with 1-methylbenzimidazole) was improved to 77%, and **M6** (with furan) and **M7** (with *tert*-butylacetylene) yielded the corresponding polymers (**P6** and **P7**) with complete conversions. The same backbone structure bearing various migrating groups exhibited distinct solubility of polymers (Figure S1). Generally, enhanced solubility facilitates sustained chain propagation, correlating with the higher M_n observed for **P3** and **P6**, compared to **P4** and **P7**. Notably, deprotection of **P4** with the treatment of tetrabutylammonium fluoride (TBAF) efficiently furnished polymer **P4-1** containing terminal alkynyl moiety, reserving avenues for post-functionalization via click reaction.^[22, 23] Thermal properties of the aliphatic polysulfones were characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Glass transition temperatures (T_g) of the aliphatic polysulfones varied from 82.9 °C to 120.9 °C, influenced by the polarity and steric hindrance of the pendant groups. The presence of C-S bond and the type of pendant group in the aliphatic polysulfones affected the thermal stability, with decomposition temperatures ($T_{d,5\%}$) ranging from 182.7 °C to 334.2 °C.^[24]

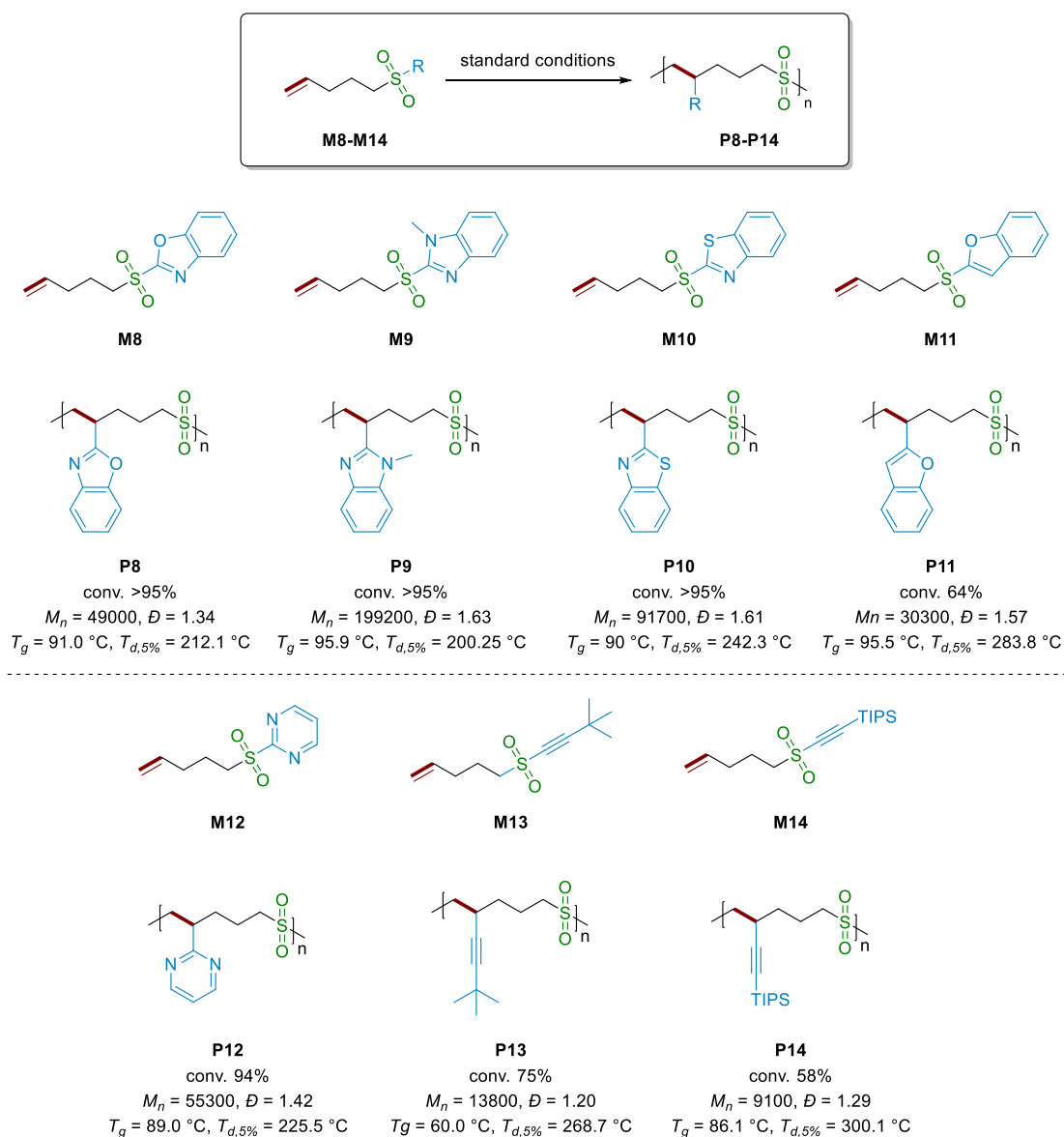


Fig 4. Radical polymerization via 1,5-group transfer.

To further enrich the chain structure of aliphatic polysulfones, a series of pentenylsulfone monomers were subjected to 1,5-group transfer (Fig. 4). Under the similar conditions, **M8** (with benzoxazole), **M9** (with 1-methylbenzimidazole), **M10** (with benzothiazole), and **M12** (with pyrimidine) were readily converted into the corresponding high-MW polymers with high conversions, through temperature control. Of note, **P9** even exhibited a higher M_n of 199 kg/mol. The conversion of **M11** (with benzofuran), **M13** and **M14** (with alkyne), which performed well in 1,4-group transfer, yet was not satisfactory in 1,5-group transfer process. The conversion of **M11** could only be increased to 64%, while these of **M13** and **M14** still remained low

(Table S2). ^1H and ^{13}C NMR spectra indicate that **P13** and **P14** also follow the 1,5-group transfer polymerization to obtain chain structures with well-defined sequences as other aliphatic polysulfones. The poor solubility of polymerized products led to lower M_n of **P13** and **P14**. Thermal property characterization of polymers (**P8-P14**) reveals that after adding one more methylene unit into the backbone, the range of T_g is reduced to 60.0-95.9 °C, probably due to the increased flexibility of the chains. However, extended carbon chain does not significantly change the thermal stability of polymers, which is consistent with the trend of pendant group impact in 1,4-group transfer polymerization.

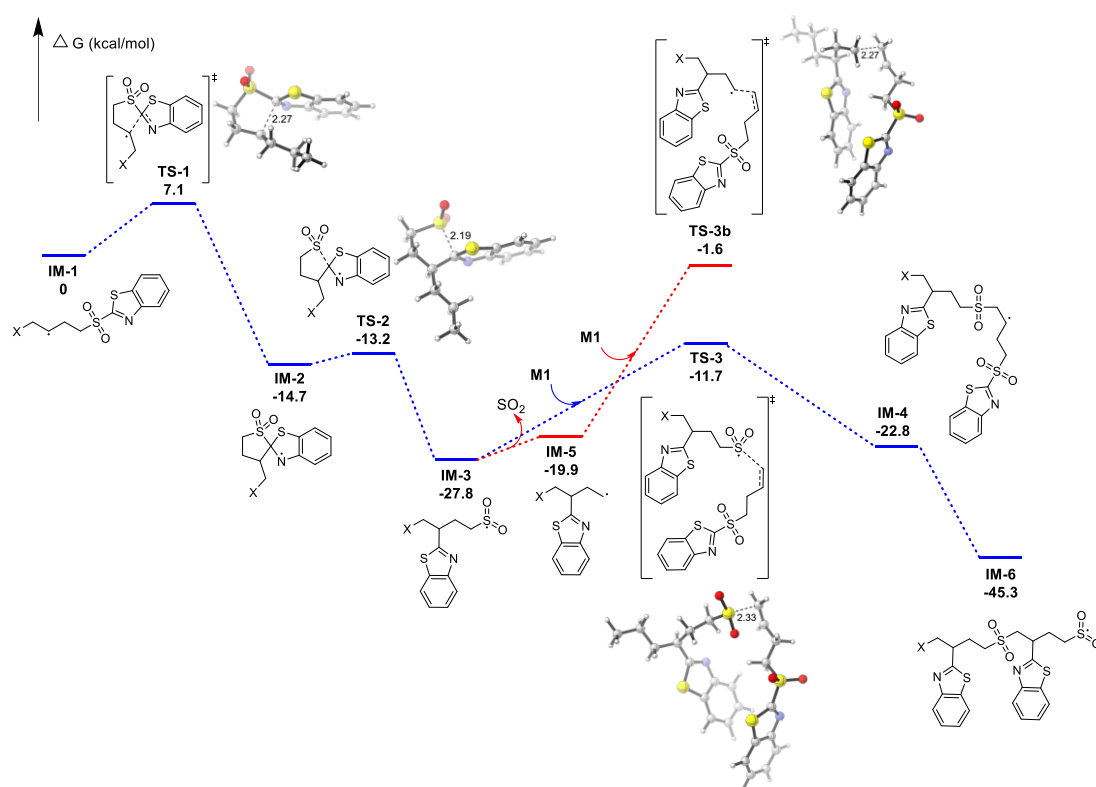


Fig 5. DFT studies for understanding the GTRP mechanism. Numbers in figures of optimized structures of transition states denote key bond lengths. Unit: Å. (see Supporting Information for calculation details).

To gain a deeper insight into the sulfonyl radical-mediated GTRP process, density functional theory (DFT) calculations was performed. As shown in Fig. 5, after chain initiation between **M-1** and an ethyl radical to form the alkyl radical **IM-1**, its

cyclization via **TS-1** to form **IM-2** requires an energy barrier of 7.1 kcal/mol. **IM-2** readily undergoes ring-opening via **TS-2** with a barrier of only 1.5 kcal/mol to form a relatively stable sulfone radical **IM-3**. The chain propagation process between **IM-3** and **M1** via **TS-3** to form **IM-4** requires a barrier of 16.1 kcal/mol. Another possible competing pathway involves the elimination of SO₂ from **IM-3** to form **IM-5**. According to relaxed potential energy surface scan results (Fig. S6), this elimination is barrierless. However, **IM-5** is thermodynamically unfavored over **IM-4** by 2.9 kcal/mol. Moreover, **IM-5** is a nucleophilic radical, and its addition to the vinyl group of monomer **M1** via **TS-3b** requires a barrier of 26.2 kcal/mol with respect to **IM-3** as the stable initial state. Such a substantial barrier related to **TS-3b** is 10.1 kcal/mol higher than that necessitated by **TS-3**, meaning the addition of sulfonyl radical **IM-3** to **M1** is kinetically favored over than that between **IM-5** and **M1**. On the other hand, **IM-4** can undergo further rearrangement to form a more stable electrophilic sulfonyl radical **IM-6**, which is energetically favorable by 22.5 kcal/mol. This rearrangement significantly promotes the continuous chain propagation process. Therefore, the proposed mechanism is feasible under the experimental conditions.

Conclusion

We have devised a practical approach for the synthesis of aliphatic polysulfones by the strategy of group transfer radical polymerization. This protocol employs new butenylsulfone and pentenylsulfone monomers, avoids the use of gaseous SO₂, generates a diverse array of ABC sequence-defined aliphatic polysulfones with high molecular weights and low distributions. DFT calculations have been performed and reveal that a radical Smiles rearrangement pathway is involved in the GTRP process.

Supporting Information

Experimental procedures, compound characterized data, copies of spectra including NMR, SEC, TG, DSC, and FT-IR were included.

Acknowledgements

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Keywords: radical polymerization, group transfer, aliphatic polysulfones, sequence-defined polymers

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