Radical Homopolymerization of α-Olefins to Synthesize Polysulfones – a "SO_2-free" Approach

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Abstract: Traditionally, α-olefins have been regarded as non-homopolymerizable substrates in textbook examples. However, they have the ability to copolymerize with sulfur dioxide, leading to the creation of alternating copolymers. These commodity poly(olefin sulfone)s exhibite a wide array of applications. Nevertheless, the synthesis process involving sulfur dioxide pose considerable hazards and practical difficulties. In this study, we report on the "SO_2-free" radical homopolymerization of sulfonyl α-olefin monomers, resulting in the production of ABC sequence-controlled poly(vinylbenzothiazole-olefin-sulfone)s. This unique radical polymerization process is enhanced by 1,4/1,5-aryl migration, facilitated by the sulfonyl radicals involved in propagation. This demonstrated aryl group migration radical polymerization opens up new possibilities for synthesizing polysulfones with unprecedented main chain sequences and structures, which hold great promise as candidates for innovative polymeric materials.

Radical polymerization has emerged as a powerful technique for synthesizing polymeric materials that are prevalent in our everyday lives. This flexible and economically viable process has been extensively utilized to produce a wide variety of products, spanning from food packaging to textiles and fibers. One of the persistent challenges in radical polymerization is the inability of non-activated olefins to undergo radical homopolymerization, which is hindered by degradative chain transfer side reactions.[1,2] This fact is well-documented in polymer chemistry and related textbooks. Despite this limitation, these olefins can copolymerize with sulfur dioxide (SO_2), another non-homopolymerizable monomer, to produce poly(olefin sulfone)s.[3,4] Poly(olefin sulfone)s are significant not only because they serve as a classic example of alternating radical copolymerization but also due to their widespread use, evidenced by numerous patents from the industry.[5-8] However, the typical polymerization process involving the use of corrosive SO_2, which requires low-temperature liquefaction within specialized glass or stainless steel pressure vessels, poses challenges due to its inherent hazards and practical limitations (Figure 1a).[9]

Radical rearrangements are advanced techniques for editing molecular structures, offering creative solutions to problems faced in radical polymerization.[10-12] Recently, radical smiles rearrangements have been well developped for achieving aryl migrations, which enable structural changes.[13-16] In these transformations, SO_2 serves as a non-permanent linker that connects two functional groups, a strategy

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also employed in radical ring-opening polymerization by the Niu group. [17-20] However, the spontaneous removal of SO_2 during polymerization, driven by entropic factors, prevents the synthesis of poly(olefin sulfone)s. In contrast, the Wang group has recently introduced a new method for smiles rearrangements that retains SO_2 within the molecular structures (Figure 1b). [21]

Our research group has been interested by the radical homopolymerization of functionalized α-olefins.[22,23] Inspired by Wang's seminal report, we envision that upon initiation, secondary carbon radicals are formed, subsequently trigging aryl migration to generate sulfonyl radicals. These electron-deficient sulfonyl radicals can then propagate the polymerization by adding to another α-olefin monomer. Through this radical relay mechanism, the radical homopolymerization of sulfonyl α-olefins can proceed with propagating sulfonyl radicals. Herein, we introduce a novel strategy for the radical homopolymerization of sulfonyl α-olefin monomers, yielding sequence-regulated poly(vinylbenzothiazole-olefin-sulfone)s for the first time. Notably, the production of ABC-sequence-regulated polymers remains relatively unexplored compared to the extensively studied AB alternating, ABA, and AAB sequences.[24-35] This unique polymerization process relies on 1,4-aryl migrations under radical conditions. Moreover, this unprecedented strategy can be extended to radical homopolymerization involving 1,5-aryl migrations, furnishing polysulfones with an additional methine unit within the main chains. In contrast to conventional polysulfone synthesis methods employed in academia and industry, which primarily adjust properties by altering olefin monomers, this "SO_2-free" approach offers a versatile means of tuning the chemical space by tailoring the sequence composition (Figure 1c).

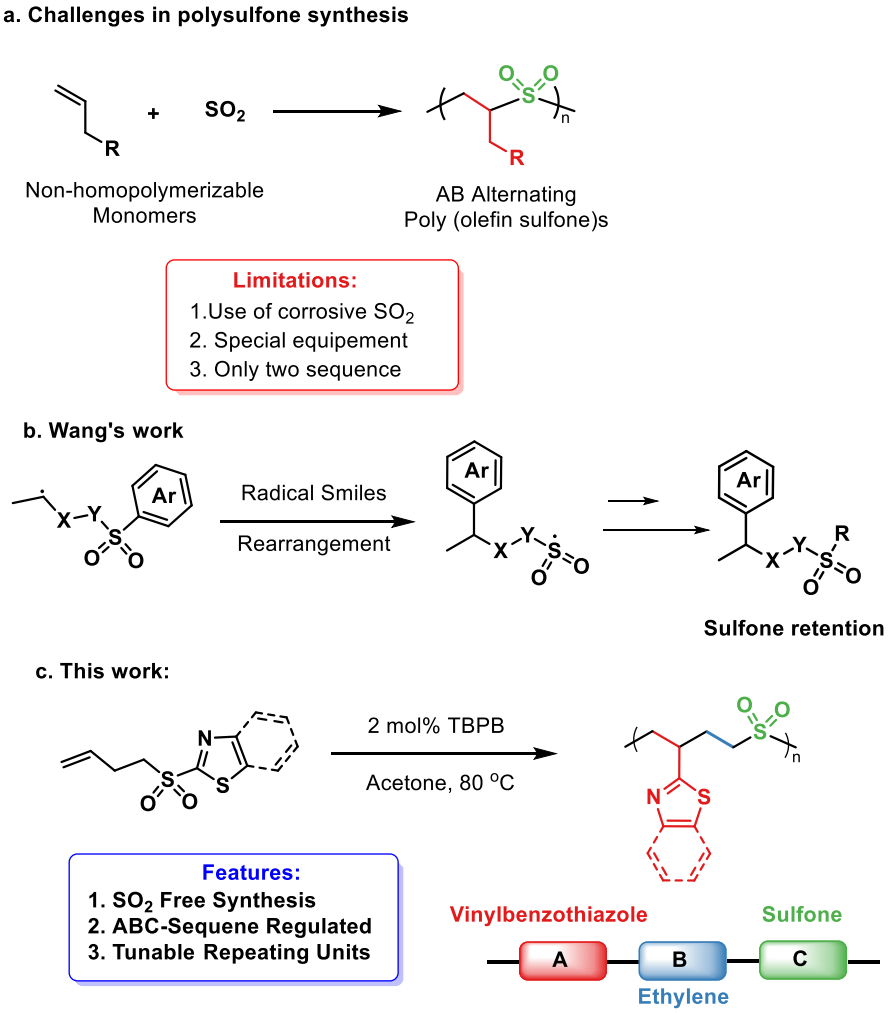

Figure 1: (a). Challenges in polysulfone synthesis. (b). Wang's inspiring work. (c) This work: ABC sequence-regulated polysulfones synthesis via a "SO_2-free" approach.

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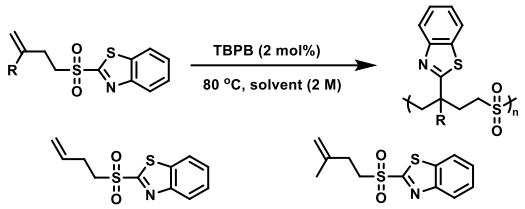
The sulfonyl monomers M1 can be readily obtained through the substitution of homo-allylic bromides with thiols, followed by oxidation (See SI for synthetic details). Initially, the radical homopolymerization of M1 was investigated using *tert*-butyl peroxybenzoate (TBPB) as an initiator in chlorobenzene (PhCl) at a concentration of 2 M and a temperature of 80 °C. After 24 hours, a light-yellow product precipitated from the reaction mixture. The polymeric products exhibited limited solubility in polar solvents such as *N*, *N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Analysis by size exclusion chromatography (SEC) revealed a number-averaged molecular weight (M_n) of 19.8 k and a dispersity ($Đ$) of 5.91 (Table 1, entry 1). Subsequently, the effect of solvents on polymerization was examined. Acetone was found to yield the polysulfones with highest conversion (Table 1, entries 2-5). Additionally, 1,1'-Azobis(cyclohexane-1-carbonitrile) (V-40) could also initiate polymerization, albeit with a reduced conversion (Table 1, entry 6). When the polymerization was conducted in a more diluted solution, the conversion decreased to 24% (Table 1, entry 7). The limited solubility of the obtained polymers only permitted the acquisition of the ^{1}H nuclear magnetic resonance (NMR) spectrum, which hindered the determination of the main chain structures. However, we were pleased to observe that the solubility of the polymers could be significantly enhanced by using a monomer (M2) with a methyl group introduced on the vinyl position. The polymerization proceeded with an 62% conversion, giving polymers with a M_n of 31.1k and a dispersity of 2.13 (Table 1, entry 8).

Table 1: Optimization of radical polymerization



Entry[a]	Monomer	Solvent	Conv.[b]	M_n[c]	$Đ$[c]
1	M1	PhCl	58%	19.8 k	5.91
2	M1	DMF	74%	7.7 k	1.71
3	M1	Dioxane	69%	11.2	2.26
4	M1	THF	47%	9.4 k	2.14
5	M1	Acetone	>95%	14.8 k	3.75
6[d]	M1	Acetone	55%	11.0 k	2.54
7[e]	M1	Acetone	24%	7.6 k	1.90
8	M2	Acetone	62%	31.1 k	2.13

a. Experimental conditions: monomer concentration [M] = 2 M, 80 °C for 24 h. b: The monomer conversion was determined by ^{1}H NMR spectroscopy using 1, 3, 5-trimethoxybenzene as internal standard. c: Molecular weight and dispersity were determined by DMF SEC analysis calibrated to linear poly(methyl methacrylate) (PMMA) standards. d. 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40) used as an initiator. e. [M] = 0.5 M. Conv.: conversion.

Since the sequence of the polymer main chain is unprecedented, the polymer chain structure (P2) was unambiguously characterized by ^{1}H & ^{13}C nuclear magnetic resonance (NMR) spectroscopy, ^{1}H-^{1}H correlation spectroscopy (COSY), ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC), and ^{1}H-^{13}C heteronuclear single quantum coherence (HSQC) (Figure 2a, 2b, 2c, 2d and 2e). The aliphatic peak observed between 3.81-3.32 ppm was attributed to H_b adjacent to the sulfones, while the aliphatic peak between 3.05-2.74 ppm was assigned to H_e, which exhibited couplings with H_d. Analysis of the ^{13}C NMR spectrum revealed that the C_6 position on the benzothiazole shifted from 165.7 ppm (M2, Figure S3) to 175.0 ppm (P2, Figure 2b), indicating a modification in the chemical environment due to aryl migration. In the HMBC spectrum, the C_6 clearly showed coupling with H_b, H_c, and H_d. These findings provide strong evidence for establishing the repetitive ABC (vinylbenzothiazole-olefin-sulfone) sequence.

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Additionally, kinetic studies confirmed the chain-growth free radical polymerization behavior, resulting in polymers with a high molecular weight even at low conversion.

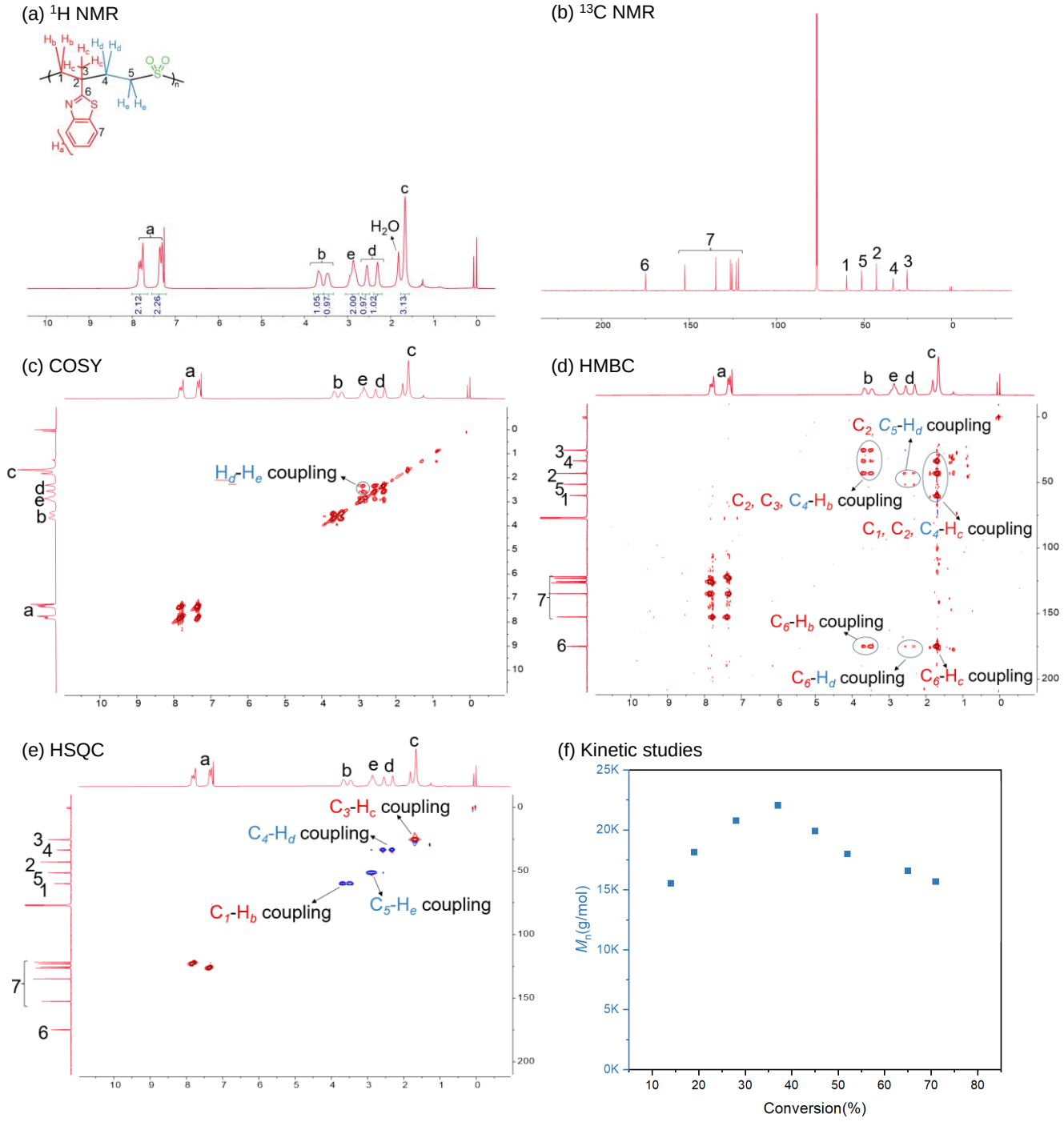

Figure 2. Polymer chain structure determination (a-e) ^{1}H NMR, ^{13}C NMR, COSY, HMBC, and HSQC spectra of P2 confirming the polymer chain sequence. (f) Kinetic studies.

Encouraged by these results, we then directed our efforts towards exploring the scope of these sequence-regulated polysulfones (Figure 3). If a pentyl group was attached adjacent to the benzothiazole sulfonyl group, the resulting polymer exhibited a sequence equivalent to poly(vinylbenzothiazole-heptene-sulfone) (P3). Monomers with thiazole as the migration group yielded insoluble polymers, which hindered our ability to characterize the products (P4). The solubility could be increased through methyl substitution on the vinyl positions. SEC analysis revealed that the polymers had a M_n of 32.7 k with a dispersity of 2.82 (P5). However, benzoxazole-sulfonyl monomers produced insoluble polymer products (P6). By

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incorporating an additional methine group, we observed the occurrence of 1,5-aryl group migration, allowing us to obtain polysulfones with varied lengths of repeating units—a feat that is particularly difficult to accomplish with existing chain-growth polymerization methods (P8). In contrast, 1,3 or 1,6-aryl migration did not take place when using monomers with modified alkyl spacers. Furthermore, using thiophene, pyridine, or pyrimidine as migration groups failed to yield any polymers.

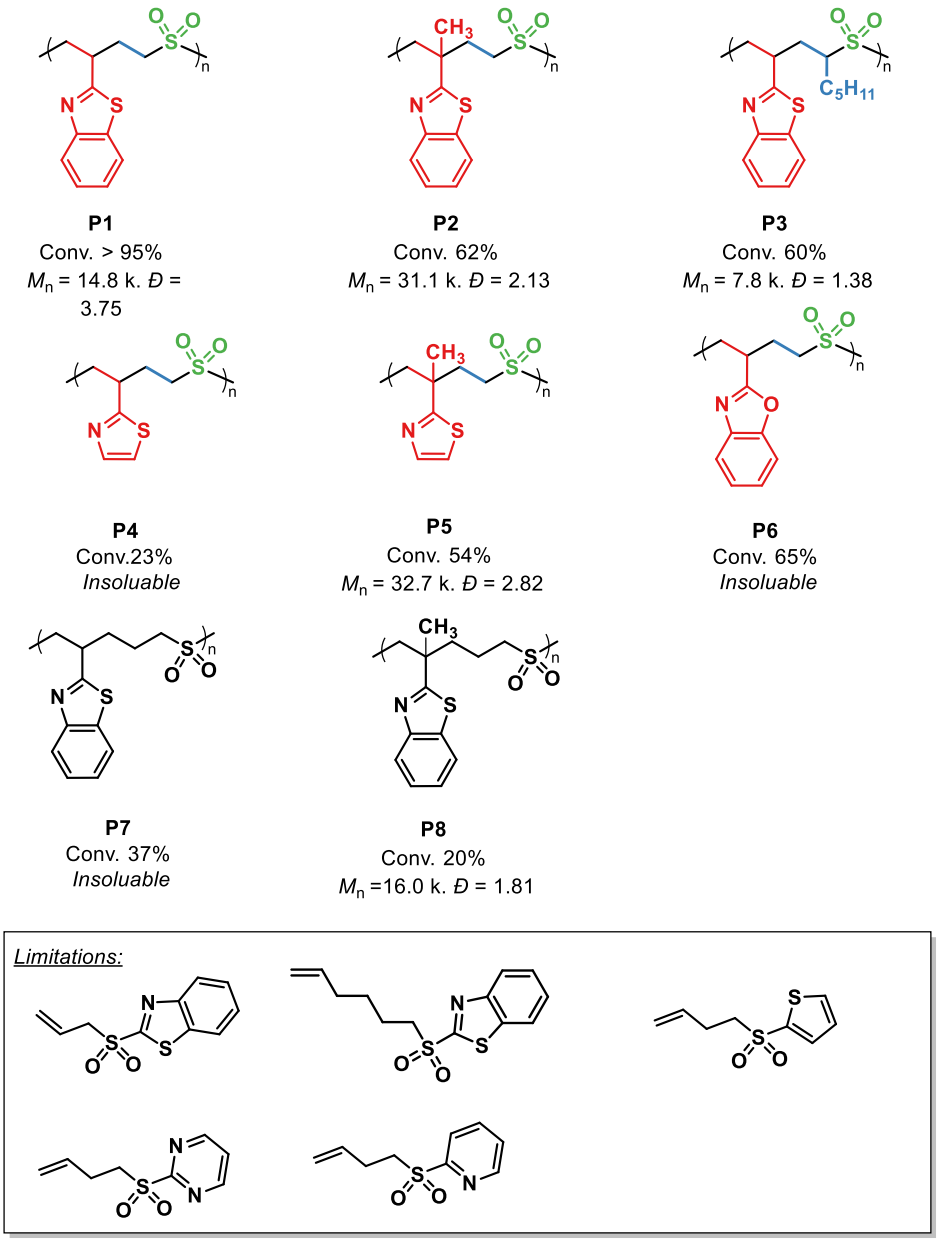

Figure 3. Polymer structure, conversion, molecule weight, dispersity.

In summary, we have successfully developed a novel free radical polymerization process for α-olefins involving aryl group migration. This unique approach enables the synthesis of a diverse range of ABC sequence-regulated polysulfones in a "SO_2-free" manner, surpassing the limitation of traditional polysulfones which can only achieve two alternating sequences. By extending this strategy to monomers with additional methine spacers, we can access polysulfones with varying main chain compositions. We firmly believe that our aryl group migration radical polymerization strategy will open up new possibilities

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for designing unprecedented α-olefin monomers, leading to the discovery of polymers with innovative sequences and functionalities. Currently, we are actively engaged in designing various types of α-olefin monomers, studying their (co)polymerization behavior, and collaborating with academic and industrial partners to explore their potential applications.

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Conflict of interest

Part of the results have been filed in patents in which B.A and Y. L. are the inventors.

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