Polymer
Chemistry

ROYAL SOCIETY
OF CHEMISTRY

REVIEW

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2022, **13**, 5282

Sulfur-containing polymers derived from SO_2: synthesis, properties, and applications

Xiao-Feng Zhu, Xin-Yu Lu, Huan Qi, Yuhui Wang and Guang-Peng Wu *

Received 27th May 2022,
Accepted 23rd August 2022

DOI: 10.1039/d2py00685e

rsc.li/polymers

Sulfur-containing polymers enjoy the merits of excellent optical performance, degradation, chemical recyclability, and adhesive abilities toward metal ions. Recently, increasing attention has been paid to the synthesis and applications of sulfur-containing polymers in both academia and industry. Compared to several sulfur-containing monomers that suffer from either restricted accessibility, low reactivity or tedious synthesis, sulfur dioxide, a well-known air pollutant, is a kind of easily obtained monomer with high reactivity and undergoes copolymerization with olefins and epoxides to produce degradable polysulfones and polysulfites. SO_2-based polymer materials are of intense industrial and theoretical interest in terms of the large quantities of available monomers, facile polymerization, unique mechanism, and high performance of the resultant copolymers. In this review, we summarize the progress achieved in the copolymerization of SO_2 with olefins and epoxides, mainly focusing on the monomer scope, mechanism, and properties of the resultant copolymers.

1. Introduction

Synthetic polymers dramatically shaped human modern life with an annual output of over 370 M tons. The popularity of polymers lies in their low costs, excellent formability, and immense chemical diversity, allowing for precise tailoring of material properties across a wide spectrum to fulfill the demands of diverse applications.[1] Nowadays, synthetic polymers are widely employed in a variety of applications, from commonplace items like clothes, packaging, and household goods to high-value-added products like microelectronics, bulletproof vests, and medication delivery systems.[2,3] The continuous development of society gives rise to the additional requirement of polymer functionality, driving the discovery of innovative multifunctional polymers.[4] The incorporation of functional groups or atoms into polymers has been shown to be a promising route in this regard. In the past decades, functional ester, amide, carbonate, and urethane groups have been successfully introduced into polymers, resulting in polymers with fascinating properties.[5] Additionally, introduction of sulfur atoms allows for feasible access to functional polymers with attractive features, including high refractive index,[6] adhesion to heavy metal ions,[7–9] and chemical recyclability.[10–12] Sulfur-containing polymers gained increasing attention in both academia and industry. For example, poly(phenylene sulfide) and its derivatives, known as super engineering plastics exhibiting outstanding thermal stability, superior toughness, inherent flame resistance, and excellent chemical resistance, are successful commercial sulfur-containing polymers.[13] However, applications of sulfur-containing polymers remain in their infancy. The limited accessibility of sulfur-containing monomers and the difficulty in their polymerization process are largely responsible for this situation.

Among various sulfur-containing monomers, episulfides enjoy the merits of massive structural diversity and high reactivity. Homopolymerization of episulfides can be carried out efficiently under mild conditions (room temperature, simple thiolate initiated, and even in water), yielding polythioethers with unique oxidation responsiveness and adsorption.[14] Hubbell and co-workers achieved the first oxidation-responsive polymeric vesicles using poly(ethylene glycol)-*b*-poly(propylene sulfide)-*b*-poly(ethylene glycol) triblocks,[15] and their potential applications as nanocontainers in drug delivery,[16] biosensing and biodetection[17] have been described. Additionally, episulfides can undergo copolymerization with elemental sulfur,[18] carbon disulfide,[19,20] isothiocyanates,[21,22] or cyclic thioanhydrides,[23] providing a facile route to a variety of functional sulfur-containing polymers. Despite such progress, the unpleasant smell and poor shelf life hinder the popularity of episulfide-involved (co)polymerizations.

Elemental sulfur is abundant and cheap with an annual output of over 60 M tons as a by-product of the petroleum industry.[24,25] Chemical conversions of elemental sulfur into sulfur-containing polymers can be achieved *via* copolymerization with alkenes, affording polysulfides.[26,27] Recently, sulfur-

---

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: gpwu@zju.edu.cn

based multicomponent polymerizations emerged as a novel and diverse strategy to target functional sulfur-containing polymers.[28–31] For instance, terpolymerization of sulfur, diols, and diisocyanides co-reported by Sun and Tang gave poly(*O*-thiocarbamate)s. Tetraphenylethene moieties with inherent aggregation-induced emission (AIE) can be installed onto the resultant sulfur-containing polymers, enabling the materials to be used as fluorescent sensors to detect the harmful metal cation Hg^{2+} with high sensitivity (limit of detection = 32 nM).[28] Even so, utilization of elemental sulfur suffers from severe back-biting side reactions and low reactivity.

Carbon disulfide is another sulfur-containing commodity chemical, and more than 0.6 M tons of carbon disulfide is produced annually in China.[32] Polythiocarbonates can be fabricated *via* the copolymerization of CS_2 with epoxides[33] or episulfides.[19,20] However, low reactivity remains a problem. The polymerization rate and production efficiency cannot fulfill the demands of industrial production. Moreover, copolymerization of CS_2 and epoxides is accompanied by severe oxygen/sulfur scrambling and backbiting side reactions,[34–36] making the control of the polymer structure and properties difficult. In a word, cheap and abundant sulfur-containing monomers which can be efficiently transformed into high value-added polymers are still highly desired.

Sulfur dioxide (SO_2), known as one of the major atmospheric pollutants, is a colorless, relatively stable, and incombustible gas with an irritating odor. Although SO_2 is not a greenhouse gas, its accumulation is responsible for acid rain, which adversely affects ecosystems and human buildings. In addition, SO_2 is also a detriment to human health, causing respiratory disease sometimes.[37] Naturally, volcanic eruptions and decay of plants or animals are supposed to release SO_2. Currently, more SO_2 is produced from metal smelting, oil production, and fossil fuel burning, leading to serious environmental problems (Fig. 1). Although many methods have been tried to reduce SO_2 release, its emissions remain at a relatively high level. Taking China as an example, industrial SO_2 emissions peaked at over 26 M tons in 2006 and have gradually decreased since then, but leveled off at around 22 M tons in the next 9 years. After 2016, industrial SO_2 emissions remained at around 6 M tons (ref. 38) (Fig. 2). It is conspicuous that the massive SO_2 emissions cannot be avoided until people get rid of petrochemicals. In this case, chemical transformation of SO_2 into functional sulfur-containing polymers would be of significant interest, not only to environmental governance and emission reduction, but also in providing an economical approach to functional sulfur-containing polymers.

The polymerizations of SO_2 were firstly described in the early 20th century and it was discovered that SO_2 copolymerized with olefins and epoxides efficiently to afford polysulfones and polysulfites, respectively. In the last nearly 100 years, great progress has been achieved in terms of the monomer scope, mechanism understanding, and polymer applications. In this review, we summarize the achievement in the copolymerizations of SO_2 with olefins and epoxides with an aim to enlighten future studies of this promising synthon and the derived polymer materials.

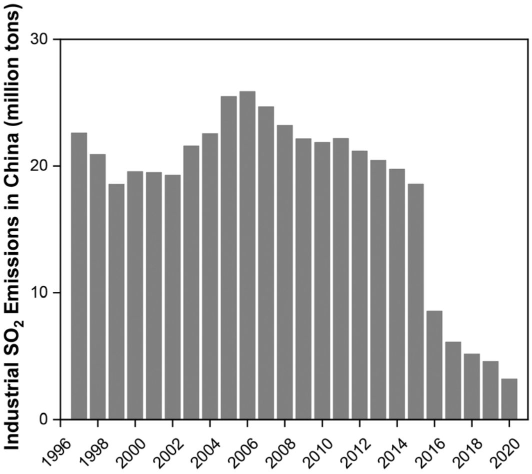


Fig. 2 Industrial SO_2 emissions in China (data taken from the Ministry of Ecology and Environment of the People's Republic of China).

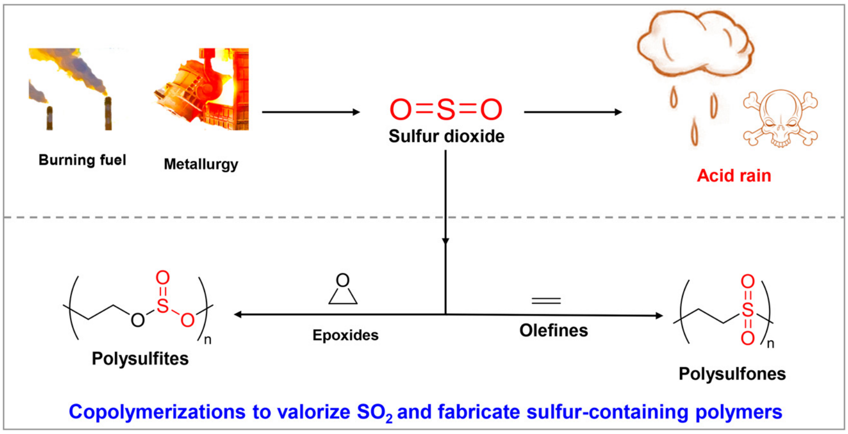


Fig. 1 Life of SO_2 in the atmosphere and methods to convert SO_2 into degradable polymers.

2. Copolymerization of SO_2 and olefins

The reaction of olefins and SO_2 can be traced back to 1898 when Solonina described the copolymerization of SO_2 with allyl alcohol and allyl ethers.[39] In the following decades, little attention was paid to this reaction and virtually nothing was published. Until the 1930s, several laboratories noticed the interesting reaction and a great deal of enthusiasm was devoted to the copolymerization. Copolymerization of olefins and SO_2 is of great industrial interest, since it provides a facile and mature method for degradable synthetic thermoplastics and even high value-added functional materials from inexpensive and abundant raw materials. In addition to the commercial aspects, the reaction itself displays unique chemical behavior in many cases, making its investigation of intense theoretical interest.[40] In this section, we summarize this reaction according to the structure of the monomers.

2.1 Monoolefins

Mechanism. The copolymerization of SO_2 and olefins proceeds in a free-radical manner and light or catalysts are necessary to trigger the reaction. In the absence of light and catalysts, Snow and Frey proved that no reaction took place even after storage for one year in any scenario. Although the copolymerization before the addition of catalysts was observed occasionally, an in-depth study disclosed that small amounts of impurities presented in the system were responsible for initiation.[39] Free radical initiators such as oxygen, various organic and inorganic peroxides, and 2,2-azobisisobutyronitrile (AIBN) are all effective catalysts for the polymerization. Of great interest, "ceiling temperatures" were observed in the course of copolymerization of olefins and SO_2, above which no polymerization took place. Accordingly, the reaction can be started or stopped repeatedly at will by lowering or raising the temperature in one or two-degree increments. In addition, each olefin exhibited a characteristic ceiling temperature independent of the catalytic agent.[41] For example, the ceiling temperatures of propylene, isobutylene, 1-butene, and 2-butene lied at 87–89 °C, 4–5 °C, 63–66 °C, and 43–45 °C, respectively. Subsequently, Ivin *et al.* rationalized the occurrence of ceiling temperature as the equilibrium between a depropagation reaction and a propagation step.[42] The afforded polysulfones can be chemically depropagated back to the original olefins and SO_2 during the copolymerization (Fig. 3), and the energy barrier for degradation is higher than that of propagation, therefore, ceiling temperatures occurred.[43] The authors pointed out that the ceiling temperature not only depends on the nature of olefins but also on the concentrations. Nowadays, the ceiling temperature is frequently observed in the ring-opening polymerization of chemically recyclable monomers.[44–48] The ceiling temperature in the copolymerization of SO_2 and olefines can be used to clarify the inhibition behavior of isobutylene,[39] where the addition of around 10% isobutene to 1-butene slowed down the copolymerization to about one-tenth of the normal rate at room temperature even if isobutene was not incorporated into polymers. Only when the reaction temperature was lower than the ceiling temperature of both olefins, terpolymerization of olefins and SO_2 could proceed smoothly. As the ceiling temperature of isobutylene is relatively low (4–5 °C), terpolymerization involving isobutylene was partially inhibited at room temperature or higher.

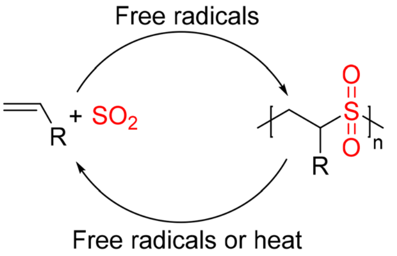


Fig. 3 Propagation of SO_2/olefins and depropagation of polysulfones.

Monoolefins. The copolymerization of SO_2 with monoolefins boasts impressive functional group tolerance and it is rather general and suitable for diverse unsaturated organic compounds (Fig. 4). Alcohol, carboxylic acid, ester, urethane and azide groups can be directly incorporated without tedious deprotection or postpolymerization modification. In addition to the facile preparation of functionalized polymers, a broad monomer scope enables the tuning of material properties. For example, polysulfones derived from olefins and SO_2 generally exhibit inferior heat stability resulting from their high tendency to degrade back to monomers as shown in Fig. 3. It was possible to obtain thermally stable polysulfones using norbornene or its derivatives as comonomers, which degraded at temperatures over 250 °C.[49] Moreover, reactions proceeded in an alternating manner for most monoolefins. Several olefins including styrene and vinyl chloride also copolymerized with SO_2, nevertheless, composition of the afforded polymers varied with the reaction conditions and they will be discussed below. Olefins with large steric hindrance, such as trimethylethylene and tetramethylethylene, failed to afford copolymers.

Styrene and its derivatives. The first publication that mentioned the reaction of SO_2 and styrene was communicated in 1935 by Staudinger and Ritzenthaler (Fig. 5A).[50] They noticed that the molar ratio of enchained styrene and SO_2 is around 2/1 and then they presented the resultant polymers as an inseparable mixture of polystyrene and poly(styrene sulfone) with a ratio of 1/1. Subsequently Glavis *et al.* described the preparation of an alternating copolymer from styrene and SO_2 catalyzed by 'old' (*i.e.* peroxide-containing) paraldehyde.[51] However, repeated experiments performed by Barb under similar conditions found that copolymers consisted of more styrene compared to SO_2 and 1 : 1 copolymers cannot be afforded.[50] An in-depth study into the polymerization of styrene and SO_2 in the presence of AIBN revealed that it was impossible to obtain a copolymer containing more than 1 mol of sulfur dioxide and 2 mol of styrene.[50,52] Based on these results and the previously reported 1 : 1 styrene/SO_2 charge-transfer molecular complex formation in the mixture of styrene and SO_2, Barb proposed that the copolymerization of

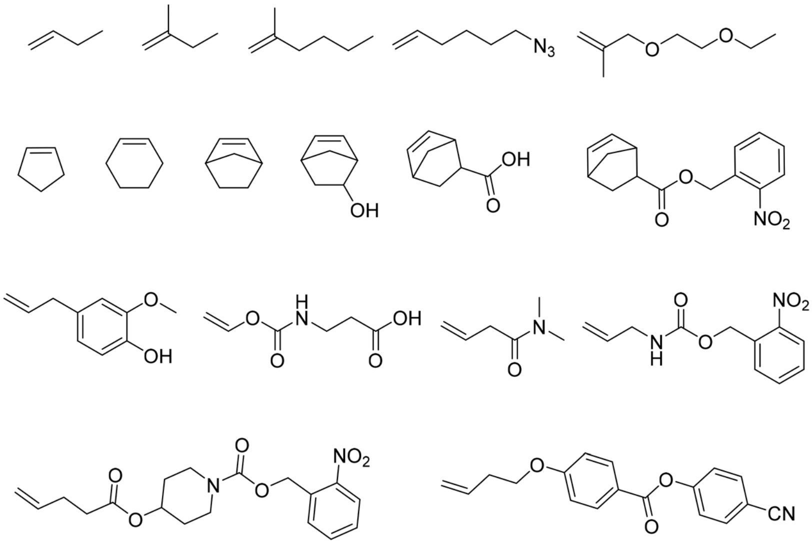


Fig. 4 Selected monoolefins for copolymerization with SO_2.

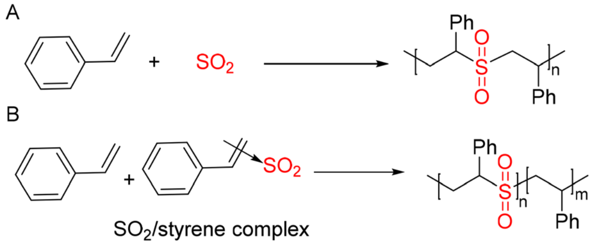


Fig. 5 (A) Copolymerization of styrene and SO_2. (B) Proposed mechanism involving the copolymerization of free styrene and the SO_2/styrene complex.

styrene and SO_2 proceeded in a radical copolymerization of a 1 : 1 SO_2/styrene monomer complex with free styrene (Fig. 5B), and the completely suppressed homopropagation of the complex rationalized the low probability of SO_2 incorporation.

Subsequently, a series of styrene derivatives were investigated. In liquid sulfur dioxide, apart from radical copolymerization, cationic homopolymerization of olefins occurred for the derivatives with electron-donating groups, such as *p*-methylstyrene[53] and *p*-isopropylstyrene,[54] which disturbed the composition analysis of the obtained copolymers. As for *p*-bromostyrene, no cationic homopolymerization was observed. Interestingly, α-methylstyrene with high steric hindrance and electron density can only undergo cationic homopolymerization and no polysulfone was afforded.[53] Additionally, the ratio of incorporated SO_2 and olefins for radical copolymerization is around 2/1 in each case. Masuda *et al.* investigated the copolymerization of *p*-nitrostyrene and *m*-bromostyrene bearing electron-withdrawing groups with SO_2 and found that the copolymer composition deviates from 2/1, with a higher proportion of *p*-nitrostyrene and *m*-bromostyrene in the produced copolymers.[55]

Matsuda and coworkers reinvestigated the copolymerization of styrene and SO_2 and found the following experimental behaviours: the composition of the copolymer was primarily affected by the total monomer concentration and temperature, independent of the feed composition; at a low temperature (0 °C), the composition was unaffected by the total monomer concentration, and the overall rate of copolymerization was barely affected by SO_2 concentration.[56] Accordingly, the unique 2/1 composition of styrene/SO_2 copolymerization didn't invoke the reaction of free styrene and the styrene/SO_2 complex as proposed by Barb.[53] Matsuda and coworkers showed that the composition of copolymers was determined by the concurrent depropagation and propagation during the reaction (Fig. 6).[56,57] In fact, all the polysulfones underwent degradation to the original olefins and SO_2 in the presence of free radicals, and the unique polymerization behavior of poly(styrene sulfone) lied in the fact that the homopolymerization

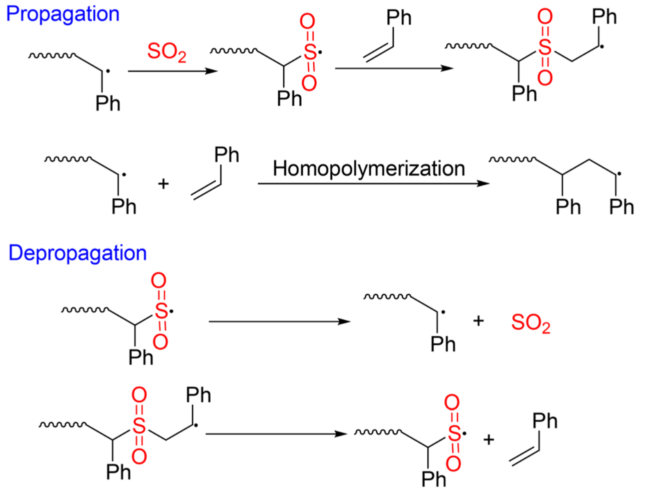


Fig. 6 Proposed mechanism for the copolymerization of styrene with SO_2 based on the propagation/depropagation equilibrium.

of styrene was able to take place while the homopolymerization of other common olefins was completely inhibited during the copolymerization. During the copolymerization of styrene and SO_2, both depropagation of the growing sulfonyl radicals and the elimination of an olefin molecule from $-SO_2CH_2CH(R)^•$ took place. Notably, the elimination of olefin molecules could trigger their isomerization. Monitoring the copolymerization of *cis*-β-deuteriostyrene with SO_2 evidenced the occurrence of *cis*–*trans* isomerization (Fig. 7), and provided solid evidence for the elimination of styrene molecules during the copolymerization.[58] Therefore, by altering the reaction temperature, the equilibrium of propagation and depropagation shifted and the copolymer composition changed. Based on this behavior, a series of styrene-based copolymers with varying styrene ratios have been synthesized and analyzed by Matsuda's group.[57,59,60]

Vinyl chloride and its derivatives. Marvel and coworkers first presented the copolymerization of vinyl chloride and vinyl bromide with SO_2 catalyzed by peracetic acid at 0 °C in 1938.[61] In both cases, polysulfones contained two vinyl halide units for each SO_2 unit on average,[62] indicating that they are rare examples that could copolymerize with SO_2 in a free radical mechanism to form nonalternant polysulfones (Fig. 8). The detailed mechanism study could not be found in their subsequent studies, but the authors suggest that the unique complexation between vinyl chloride and SO_2 where one SO_2 molecule apparently complexes asymmetrically with the double bond and another with the chlorine atom might be the reason.[61,63] Then, the effect of temperature and the feeding comonomer ratio on the composition of copolymers was investigated using γ-radiation for initiation. It was found that the composition of the produced copolymers is highly dependent on the temperature where the ratios of incorporated vinyl chloride and SO_2 are 1.5 and 2.0 at −75 °C and 25 °C, respectively. In contrast, the copolymer composition was independent of the feeding comonomer ratios from 0.10 to 0.84 (molar ratio of vinyl chloride).[64,65] On the basis of these discoveries, Matsuda and Thio proposed that the composition of poly(vinyl chloride sulfone) is governed by the depropagation and propagation in a mechanism similar to the styrene/SO_2 system.[66,67]

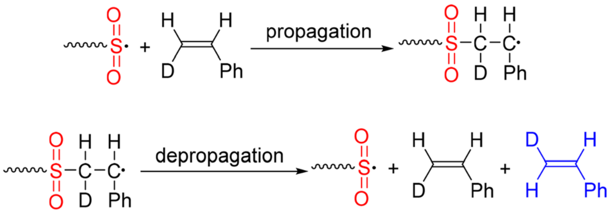


Fig. 7 Copolymerization of *cis*-β-deuteriostyrene with SO_2. During the reaction, *trans* β-deuteriostyrene appeared, evidencing the occurrence of elimination of styrene from growing styryl radicals.

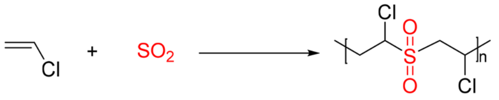


Fig. 8 Copolymerization of vinyl chloride and SO_2.

The composition of copolymers greatly affected their chemical and physical properties. Copolymers with a ratio of enchained vinyl chloride and SO_2 around 2/1 are white, amorphous, high-melting, and insoluble in most solvents.[61] Surprisingly, copolymers with other compositions are readily soluble in acetone and tetrahydrofuran. The discontinuous dissolution behavior reveals that 2/1 copolymers may have a regular molecular structure and nuclear magnetic resonance (NMR) analysis performed by Cais and Donnell proved this assumption. That is, the 2/1 copolymers mainly consisted of a highly regular SO_2–vinyl chloride–vinyl chloride–SO_2 structure (around 96%).[68,69] Additionally, copolymers underwent severe dehydrochlorination during ageing, heating, or upon their exposure to basic solvents, affording conjugated polyene structures with darkening color. Notably, dehydrochlorination took place preferentially from chloroethylene units between two sulfonyl units, and copolymers with a molar ratio of chloroethylene : sulfonyl of <2 showed enhanced hydrogen chloride elimination.[70]

Acrylates and vinyl ester monomers. Acrylates, such as methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and methyl methacrylate (MMA) are reluctant to copolymerize with SO_2, mainly resulting from the strong electron-accepting properties of both SO_2 and vinyl ester monomers. In this context, continuous enchainment of vinyl ester dominated during the radical copolymerization.[71] FlorjarIczyk's group reported the copolymerization of MA and SO_2 at a low temperature in 1988. Analysis of the resultant copolymers *via* elemental analyses indicated that the maximal incorporated SO_2 content was 30 mol% at −78 °C and decreased with the increasing temperature (Fig. 9).[72] Further research on expanding the scope of acrylates showed that the sequence distribution of the resultant polymers practically didn't depend on the character of aliphatic substituents. EA and BA exhibited similar polymerization behaviors to MA.[72] As for aromatic acrylates, the maximal incorporated SO_2 content was 10% for phenyl acrylate at −78 °C, which is much lower than that of aliphatic acrylates. The high homopolymerization reactivity of aromatic acrylates might be the reason.[73] Interestingly, when methyl methacrylate (MMA) was used as a monomer, no reaction was detected and neither a copolymer nor a homopolymer was identified.[72] To account for the non-alternating copolymerization, Florjadczyk and coworkers proposed that SO_2 can only be enchained into the macroradicals with terminal acrylates and the reaction is highly reversible even at −78 °C. In contrast, enchainment of acrylate monomers is irreversible.[74]

Vinyl ester showed a similar structure to acrylates except for the location of the vinyl group. However, copolymerization of vinyl ester and SO_2 proceeded mainly in a strictly alternating manner at low temperature. Frbchet's group systematically studied the radical copolymerization of SO_2 and vinyl ester in 1991. It is found that strictly alternating poly(vinyl acetate-*alt*-SO_2) was generated when copolymerization was conducted at

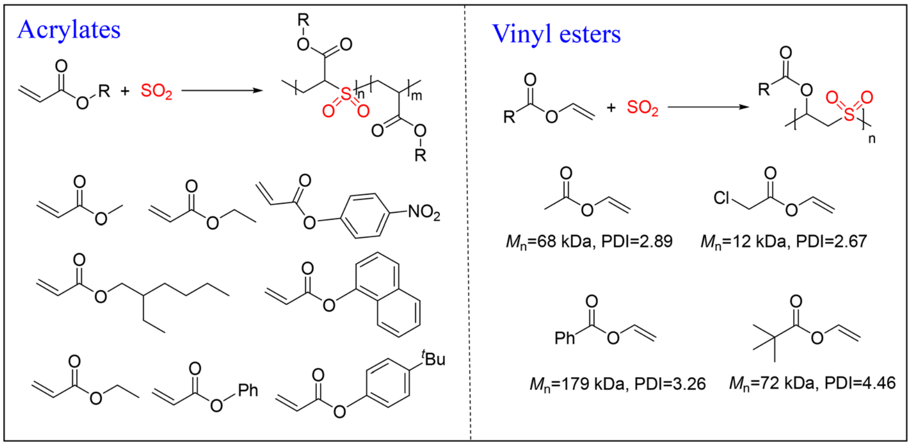


Fig. 9 Copolymerization of acrylates and vinyl esters with SO_2.

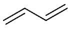
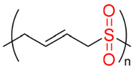
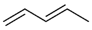
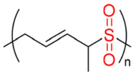
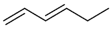
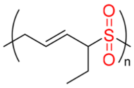
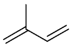
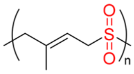
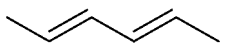
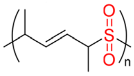
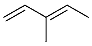
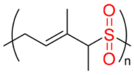
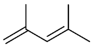
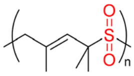
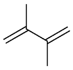
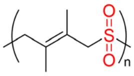
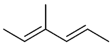
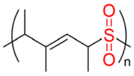
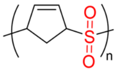
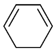
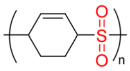
−60 °C to −70 °C with a feed SO_2/vinyl acetate ratio range of 20–40. Deviation in the polymerization conditions led to the formation of sulfur deficient copolymers. Additionally, a low ceiling temperature of −20 °C was observed, resulting from the fast degradation during the copolymerization.[75] In fact, easy decomposition is an important feature of poly(vinyl ester-*alt*-SO_2). Research done by Goodwin's group showed that poly(vinyl ester-*alt*-SO_2) is able to break down into their parent vinyl ester and SO_2 in response to radiation, ultrasonication, and various reactive oxygen species.[76] Moore's group synthesized a series of poly(vinyl-*alt*-SO_2)s with different substituents (Fig. 9) and characterized their degradation behavior in the presence of a base. It is observed that poly(vinyl ester-*alt*-SO_2)s were highly stable in aqueous environments; however, they degraded rapidly when exposed to a base both in bulk and in solution. The rate of degradation is highly dependent on the nature of vinyl ester, in that poly(vinyl chloroacetate-*alt*-SO_2) > poly(vinyl acetate-*alt*-SO_2) > poly(vinyl benzoate-*alt*-SO_2) > poly(vinyl pivalate-*alt*-SO_2).[77] The intriguing decomposition behavior enables poly(vinyl ester-*alt*-SO_2)s to be promising candidates in the field of drug delivery and resists.

2.2 Dienes

Conjugated dienes. Copolymerization of butadiene and sulfur dioxide was first described in the 1930s, where alternating copolymers were selectively afforded.[78] The alternating structures indicate that one double bond remains in each unit of the copolymers. However, the copolymers are resistant to oxidation and bromination, from which it has been speculated that they have an all-1,4 rather than a 1,2 or 3,4 structure.[79,80] In 2010, Matsumoto's studied the structures and properties of the copolymers produced from the copolymerization of SO_2 with conjugated dienes (Table 1).[81–83] In each case, alternating copolymers with exclusive conjugated dienes were detected. Investigation of the regioselective propagation by density functional theory (DFT) revealed that the reversible propagation steps are key for controlling the regioselectivity.[84] Due to the structural regularity and high crystallinity, copolymers exhibited poor solubility depending on the diene monomers. For example, poly(butadiene-*alt*-SO_2) is completely insoluble, poly(isoprene-*alt*-SO_2) is soluble only in dimethyl sulfoxide, while poly(2,4-hexadiene-*alt*-SO_2) can be dissolved in most of the organic solvents. Additionally, the poly(diene-*alt*-SO_2)s readily degraded upon heating due to the reversibility of the alternating copolymerization of dienes and SO_2. It was proved that hydrogenation of the double bond in the polymer main chain resulted in a drastic increase in thermal stability. Specifically, the 5% weight loss temperature of poly(2,4-hexadiene-*alt*-SO_2) increased from 135 to 317 °C after hydrogenation. Subsequently, the same group investigated the thermodynamics of the degradation reactions. It was found that significant depropagation occurred accompanied by polymerization and a relatively low ceiling temperature of 42 °C for 2,4-hexadiene was identified under the conditions of [2,4-hexadiene] = 2.0 mol L^{-1} and [SO_2] = 5.0 mol L^{-1}.[81] Recently, Jia's group described the copolymerization of naturally occurring monoterpene (β-myrcene) and SO_2 initiated by AIBN at 60 °C. 1,4-*cis* and 1,4-*trans*, minor 1,2-vinyl and 3,4-addition microstructures emerged during the copolymerization.[85]

Cyclocopolymerization. Cyclocopolymerization of olefins and SO_2 was initially described by Stille and Thomson in 1962.[86] It was proved that the copolymerization of a nonconjugated diene, 1,5-hexadiene, with sulfur dioxide delivered polysulfones with a cyclic structure on the backbone (Fig. 10A). Frazer and Neill discovered similar cyclopolymerization behavior for *cis*,*cis*-l,5-cyclooctadiene (Fig. 10B).[87] It is reported that copolymerization in bulk resulted in cross-linked insoluble copolymers, while cyclocopolymerization occurred when copolymerization was performed in the presence of a solvent. The copolymers displayed inferior crystallinity and could be dissolved in dimethyl sulfoxide and tetramethylene. Installation of cycle-structures on the backbone didn't improve the thermal stability. Degradation of these copolymers initiated at around 170 °C. However, unlike the abovementioned polysulfones whose degradation selectively delivered original olefins and SO_2, a certain amount of unidentified hydrocarbon was

Table 1 Thermal properties of copolymers derived from dienes and SO_2 before and after hydrogenation

				Thermal properties before hydrogenation		Thermal properties after hydrogenation	
Entry	Monomer	Polymer	M_n (PDI)	T_g (°C)	T_d (°C)	T_g (°C)	T_d (°C)
1			N. F.	—	233	—	291
2			N. F.	—	141	60.6	322
3			N. F.	—	138	35.3	288
4			N. F.	93.4	156	82.3	206
5			11.1 kDa (2.0)	—	135	81.7	283
6			N. F.	—	133	—	—
7			N. F.	—	130	—	—
8			N. F.	—	166	—	—
9			13.3 kDa (1.7)	—	164	—	202
10			N. F.	—	141	—	291
11			N. F.	—	156	—	274

M_n: molecular weight, N. F.: not found due to insolubility. T_g: glass transition temperature, T_d: 5% weight loss temperature, —: not found due to degradation initiated before T_g.

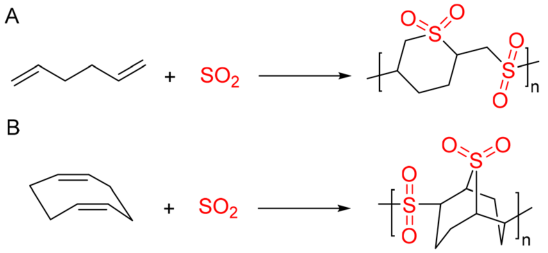


Fig. 10 Cyclopolymerization of 1,5-hexadiene (A) and 1,5-cyclooctadiene (B) with SO_2.

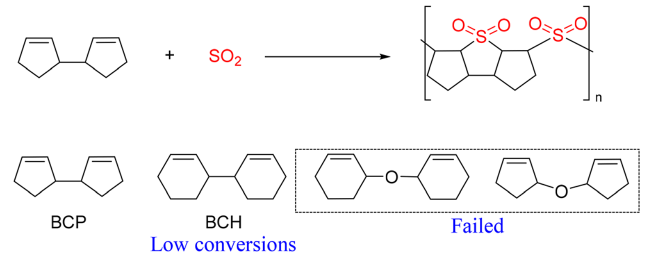


Fig. 11 Cyclopolymerization of dicyclic dienes and SO_2.

generated for the thermal degradation of 1,5-cyclooctadiene based polysulfones.[88,89]

Meyersen *et al.* attempted to synthesize fused three-ring polymers from dicyclic dienes and SO_2.[90] Copolymerization of 1,1′-bi-cyclopent-2,2′-ene (BCP) and SO_2 proceeded readily at a low temperature (<0 °C), and soluble fused three-ring copolymers were afforded as expected (Fig. 11). 1,1′-Bicyclohex-2,2′-ene (BCH) also underwent copolymerization with SO_2, but at a far slower rate and with low conversion. No polysulfones were afforded for the 1,6-diene systems, dicyclopentenyl and dicyclohexenyl ether, suggesting that the location of diene played a significant role in cyclopolymerization.

Harada *et al.* reported the cyclocopolymerization of SO_2 with diallylamine hydrochloride in 1966.[91] The reaction could be successfully carried out in solvents such as dimethyl sulfoxide, methanol, and acetone in the presence of various commercial free-radical initiators.[92] Unlike other cyclopolymerizations mentioned above, the obtained copolymers showed a 1/1 molar ratio of the monomeric units. Further study revealed that this protocol could be directly extended to unsubstituted 1,6-heptadiene derivatives[93–95] and a series of diallyl quaternary ammonium,[96–101] providing a facile route to functional cationic or zwitterionic copolymers (Fig. 12). These polymers have been proved to be efficient at the removal of heavy metal ions[102–105] and oil/water separation.[106]

2.3 Acetylenes

Alkynes are a kind of reactive monomer in copolymerization with SO_2. Copolymerization could be triggered by small amounts of organic hydroperoxide impurity originating from the long-term storage of olefins or solvents in open air.[107] Ryden and Marvel observed the copolymerization of 1-heptyne and SO_2 in 1935 during the screening of olefin's scope, and alternating copolymers were selectively afforded in each case.[108] Further study revealed that acetylene itself and disubstituted acetylenes, such as 2-butyne,2-hexyne, and methyl phenylacetylenes could not copolymerize with sulfur dioxide, while terminal aliphatic acetylenic and phenylacetylene could readily copolymerize with sulfur dioxide.[109,110] An investigation by Wazeer *et al.* in 1986 disclosed the structure of copolymers derived from terminal aliphatic acetylenic and SO_2. Strictly alternating copolymers with high *trans*-stereoselectivity were afforded when reactions were performed in the temperature range of −55 to −17 °C. Since terminal aliphatic acetylenic itself could not be homopolymerized under these conditions, it was speculated that SO_2 would complex with acetylenes and the generated complex was more susceptible towards free radicals, leading to the stereoselective *trans* addition (Fig. 13).[107] A thermodynamic study on the copolymerization of 1-alkynes found ceiling temperatures of 90.5 and 84.5 °C for 1-hexyne and 1-octyne, respectively. In addition, the energy barrier for the elimination of SO_2 is 26.7 kcal mol^{-1} (1-octyne), much higher than that of 1-butene (20.3 kcal mol^{-1}), indicative of less probability of degradation.[111]

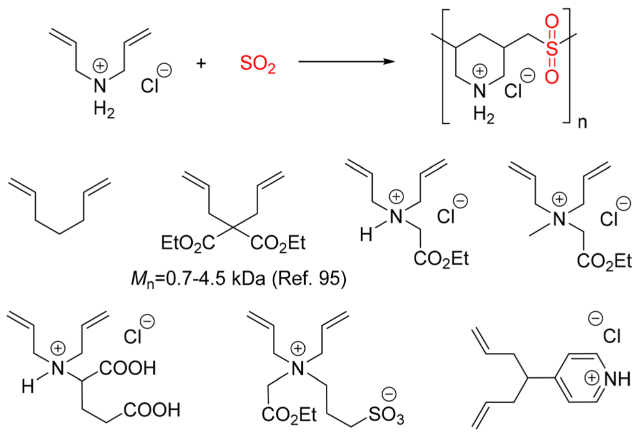


Fig. 12 Cyclopolymerization of diallyl compounds and SO_2 and some of the reported monomers.

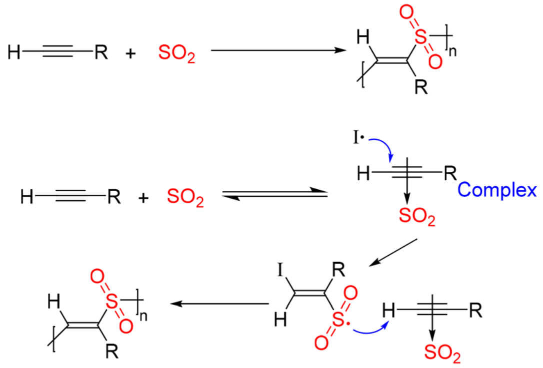


Fig. 13 Copolymerization of acetylenes and SO_2 and the proposed mechanism (R is the alkyl group).

In 1987, Hwang and Matsuda separately reported the copolymerization of phenylacetylene and SO_2 in the presence of AIBN as the initiator. However, quite different results were observed. Hwang *et al.* obtained strictly alternating copolymers at 50 °C,[112] while Matsuda *et al.* showed that the composition of copolymers varied with the temperature, feeding monomer ratios, and total monomer concentration at 60–80 °C.[113] All the authors accepted that the reactions consisted of depropagation and propagation steps, which governed the composition of the produced copolymers. However, the different results have not been explained, indicative of ample room left for further investigations.

2.4 Properties and applications

As summarized above, many polysulfones derived from copolymerization olefins and SO_2 show inferior thermal stability, and degradation initiates before softening during the heating. However, the structural diversity of available and polymerizable olefins enables fine tailoring of the performance of the copolymer over a broad range. For example, no glass transition temperatures before degradation were observed for copolymers derived from 2-pentene and 2-hexene, while 1-hexene and isopropylethylene based polysulfones softened at 100 and 200 °C, respectively. Poly(1-heptene-*alt*-SO_2) and poly(1-decene-*alt*-SO_2) were soft and rubbery even at room temperature. Additionally, some progress has been achieved in the synthesis of stable polysulfones by copolymerization of conjugated dienes with SO_2 and subsequent hydrogenation[81] or using special comonomers.[114] Therefore, in terms of the enormous quantities and low-cost of both olefins and SO_2, we believe that copolymerization of olefins and SO_2 holds great promise in producing synthetic thermoplastics. The thermal and chemical instabilities of polysulfones[76,77,115] allow them to be degraded after being discarded or even recycled back to the original monomers, which is supposed to alleviate plastic pollution.[116]

Due to easy and complete degradation under diverse stimuli, polysulfones can be used as sensitive positive resists for electron beam lithography, which have similar behaviors to CO_2-based polycarbonates.[117] Bowden and Thompson found that polysulfones derived from different terminal olefins have similar degradation rates,[118] and the sensitivity was of the order of 1–2 × 10^{-6} coulomb per cm^2 at 5 kV, determined in solution development. Interestingly, it was reported that polysulfones could also be etched in a vapor development process. Copolymerization in the presence of free radicals was reversible and the radicals generated during electron irradiation could also trigger their degradation to volatile olefins and SO_2, which could be continuously removed by vacuum. Therefore, equilibrium will not be attained and the polysulfones can be completely degraded.[119–121] Then, Himics and Ross examined the application of poly(5-hexene-2-one sulfone) as a resist and a mechanism for the photodegradation process was proposed with the help of IR spectroscopy, revealing two major discoveries including random scission of carbon–sulfur linkages in the backbone and rapid depolymerization ('unzipping' reaction) during irradiation (Fig. 14). Furthermore, in order to improve the reactive-ion etch resistance, some silicon-bearing groups[122–124] were directly installed into polysulfones as the oxygen plasma treatment of silicon-containing groups would result in a layer of SiO_x (x = 1 or 2), which could protect the underlying layer from oxidative degradation.

In addition to electron beam lithography, polysulfones could also be used as positive photoresists for ultraviolet (UV) lithography. Lawrie *et al.* disclosed that polysulfones spontaneously degraded into the original olefins and SO_2 under extreme ultraviolet (EUV) exposure and therefore they can be directly used as positive resists for EUV lithography. However, the concurrent reduction of SO_2 to sulfide occurred leading to the presence of insoluble residues after exposure.[125] Chang's group showed that the addition of small amounts of triphenylsulfonium hexafluoroarsenate can trigger the backbone scission of poly(olefin sulfones) under 254 nm deep UV exposure and concurrent baking at 80 °C. In this case, UV inert poly (butene-1 sulfone) could be used as a positive resist for UV lithography once mixed with triphenylsulfonium hexafluoroarsenate.[126] Thompson *et al.* described the utilization of poly (*tert*-butoxycarbonyl styrene sulfone) as a high-performance chemically amplified resist. When mixed with either 2.6-dinitrobenzyl tosylate, or triarylsulfonium salt acid precursors, cleavage of the *tert*-butoxycarbonyl group took place under irradiation and the change of hydrophilicity enabled the efficient removal of the irradiated polymers by choosing a suitable developer (Fig. 15).[127] A polysulfone resist formulation exhibits a sensitivity of 26 mJ cm^{-2} and a contrast of over 20.

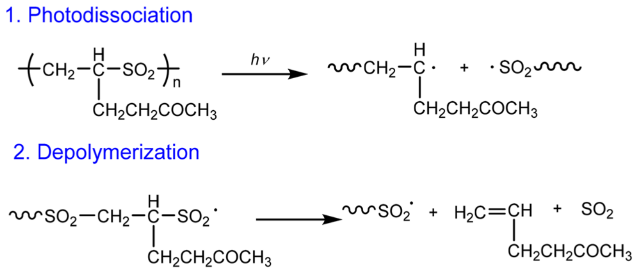


Fig. 14 Proposed mechanism for the etching of poly(5-hexene-2-one sulfone).

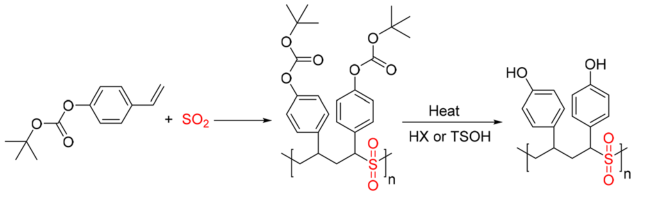


Fig. 15 Synthesis of poly(*tert*-butoxycarbonyl styrene sulfone) and its application as a chemically amplified resist.

Sasaki's group performed UV lithography by installment of photobase generating groups onto the polysulfones in terms of the rapid chain scission of polysulfones in the presence of a base (Fig. 16). UV irradiation produced a base, which extracted protons from the backbone of the poly(olefin sulfone) and thus triggered chain scission.[128,129] It was estimated that 95% polysulfones could be removed *via* this method.

Apart from positive resists, the excellent degradation behavior of polysulfones allows them to be also used for slow release.[130] For example, mixing fertilizers with poly(eugenol sulfone) resulted in an excellent slow release performance, which obeyed the Ritger–Peppas equation the best. Investigation on the influence of molecular weight revealed that the higher the molecular weight, the better the slow-release performance as expected. The greatest advantages of poly(eugenol sulfone) is that it underwent degradation when buried in the soil and this methodology provides a now route to the sulfur cycle.[131]

3. Copolymerization of SO_2 and epoxides to polysulfites

3.1 Cationic ring-opening copolymerization

Schaefer and co-workers first disclosed the ring-opening polymerization of propylene oxide (PO) and SO_2 catalyzed by $SnCl_4$, $SbCl_5$ or $ZnEt_2$ in 1968.[132,133] It was discovered that apart from sulfite linkages derived from alternating copolymerization, a mass of ether motifs stemmed from the homopolymerization of PO existing in the resultant copolymers. Based on the gas–liquid partition chromatographic analysis results of the copolymers hydrolyzed with NaOH, Schafer proposed that monomer distribution in the copolymers obeyed or disobeyed the Markovian statistics depending on the nature of a given catalyst.[128] Similar results were provided by Matsuda *et al.*[134] who investigated the copolymerization of cyclohexene oxide (CHO) and SO_2 mediated by similar catalysts, such as $SnCl_4$, $FeCl_3$, $SbCl_5$, and $TiCl_4$. The resultant copolymers consisted of only around 20 mol% sulfite linkages, suggesting the lower reactivity of SO_2 compared with epoxides. Subsequently, Florjańczyk systematically investigated $SbCl_5$ mediated copolymerization of SO_2 and a series of epoxides.[40] They found that more epoxides are enchained than SO_2 in each case and the

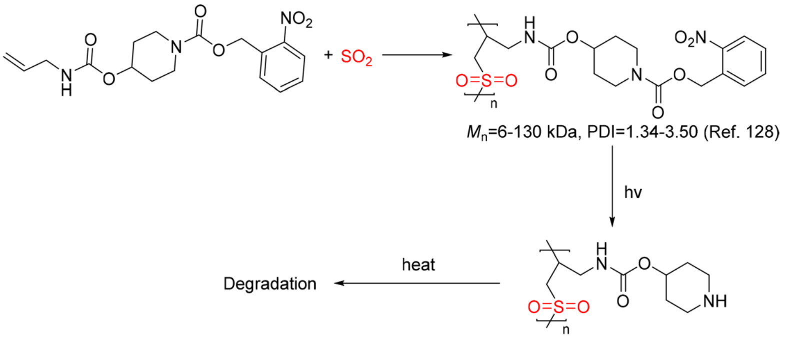
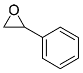
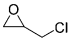


Fig. 16 Synthesis of polysulfones bearing a photobase and the involved lithography process.

relative reactivity of SO_2 decreased with the increasing steric effects of epoxides (Table 2).

The mechanism of PO/SO_2 copolymerization was not explored by Schafer's group.[132,133] Matsuda and coworkers revealed that the copolymerization of epoxides and SO_2 in the presence of $SnCl_4$ or $SbCl_5$ proceeded in a cationic manner. Oxonium was initially formed in the presence of catalysts, then attacking the methylene of the growing end by the oxygen atoms of SO_2, inducing the ring-opening of epoxides, led to the generation of oxosulfonio species (Fig. 17). However, oxygen in epoxide monomers boasts higher nucleophilicity than that in SO_2. Therefore, homopolymers of epoxides emerge.[134]

Table 2 Content of SO_2 monomeric units in copolymers catalyzed by $SbCl_5$

Comonomer	SO_2 content in a copolymer (mol%)
	31.5
	19.5
	16.7
	14.4

Conditions: SO_2/epoxides/$SbCl_5$ = 200/20/1, 25 °C.

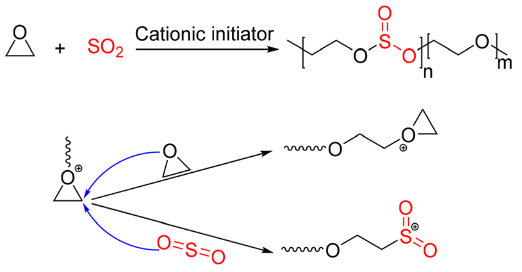


Fig. 17 Copolymerization of epoxides and SO_2 in the presence of cationic initiators and the corresponding mechanism.

3.2 Anionic ring-opening polymerization

Anionic ring-opening copolymerization of epoxides/SO_2 can be traced back to 1977 when Soga and co-workers reported the amine-initiated copolymerization of ethylene oxide (EO) and SO_2.[135] They discovered that aromatic tertiary amines such as quinoline and pyridine displayed the highest reactivity and selectivity among various amines. Of great interest, reactions proceeded in an almost alternating manner and the molar content of incorporated SO_2 within the resultant copolymers was within the range of 41% to 49%. When CHO was used as the monomer, polymerization behaved similarly. Small amounts of polyethers were afforded and pyridine gave the highest selectivity where the highest molar content of SO_2 in copolymers was 49.3%.[136]

Based on these results, an anionic polymerization mechanism was proposed. Initiation involves the formation of a zwitterion *via* the equimolar reaction of epoxide, SO_2, and pyridine, whose anionic sites served as initiators for propagation. The formed zwitterion was relatively stable and it was isolated and characterized by Zbigniew's group,[137] providing solid evidence for the proposed mechanism. During the propagation, the electropositive sulfur atom within SO_2 could activate the epoxide *via* the interaction between sulfur and the oxygen atom of epoxide (Fig. 18). Density functional theory (DFT) calculations done by Lu and co-workers revealed that the energy barrier for the ring-opening of CHO goes down from 32.8 kcal mol^{-1} to 13.1 kcal mol^{-1} as a result of SO_2/CHO interaction.[138] In this context, active anionic species attacks the epoxide/SO_2 pairs and both monomers are enchained in almost equal proportions. Additionally, back-biting reactions also occurred in some cases, resulting in the generation of some cyclic sulfites (ratio: 0–40%

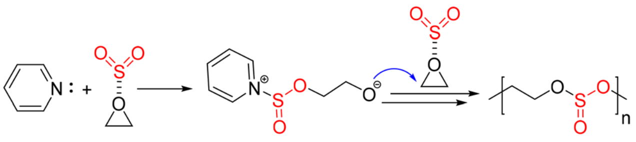


Fig. 18 Mechanism for the pyridine-initiated copolymerization of epoxides and SO_2.

for the copolymerization of EO/SO_2 mediated by various Lewis bases, depending on the initiators and reaction conditions[139]).

Later, Florjańczyk *et al.* systematically studied the pyridine-initiated copolymerization of SO_2 and a series of cyclic ethers.[140] It was found that this protocol can be extended to epichlorohydrin (ECH), styrene oxide (SO), butyl glycidyl ether (BGE), oxetane and so on, paving the route to diverse functional polysulfites. Due to the presence of electron-withdrawing groups, however, lots of cyclic sulfites are generated for the copolymerizations of SO_2 with SO or ECG (selectivity for polymers < 60%). The relative reactivity of epoxides in competitive addition to sulfite anions was compared based on terpolymerization systems and marked as CHO > EO > phenyl glycidyl ether > PO > oxiran-2-ylmethyl acetate > ECH. SO was an exception since side reactions such as homopolymerization of both epoxides occurred in ternary systems, which disturbed the comparison of its reactivity.

Further attempts in expanding the scope of initiators revealed that various Lewis bases such as dimethyl sulfoxide, acetonitrile, *N*,*N*-dimethylformamide, and poly(4-vinylpyridine) were able to initiate the copolymerization of epoxides and SO_2,[140] and the initiation rates were highly related to the difficulty of formation of zwitterions. Recently, a kind of porous organic material named SNW-KUST1 containing a mass of amines was employed as a heterogeneous catalyst for the copolymerization of epoxides and SO_2 by Zhi and Shan.[141] The catalyst exhibited excellent efficiency and selectivity for the copolymerization of a series of epoxides (CHO, SO, PO, EO, and 1,2-butene oxide) and SO_2 with the production of cyclic sulfides limited to less than 27%.

Direct addition of salts as anionic initiators can also initiate the anionic copolymerization of epoxides and SO_2. Florjariczyk *et al.* first achieved the copolymerization of EO and SO_2 using organic or inorganic salts.[142] Salts containing I^-, Br^-, Cl^-, F^-, $CH_2{=}C(CH_2)COO^-$, p-$CH_3C_6H_4SO_3^-$, CO_3^-, and PO_4^{3-} anions were proved to be active components of the initiating system. Counterions of the salts also played an important role in the copolymerization. It was found that the larger the counterion bulk, the higher the activity of the growth center and the faster the polymerization rate. Therefore, the addition of crown ether to complex the counterions benefited the polymerization for inorganic salts. In this regard, organic ammonium salts ensured higher monomer conversions over inorganic salts due to the bulkiness of quaternary ammonium ions. Lithium salts appeared to be completely inactive in copolymerization. In-depth research disclosed that the insertion of one EO activated by SO_2 into lithium salts occurred, however, the generated sulfite anion with a lithium counterion could not enchain the remaining epoxides.[142]

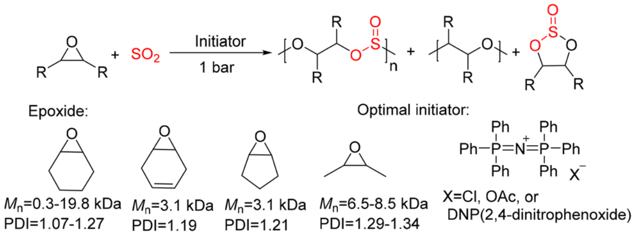


Fig. 19 Copolymerization of epoxides and SO_2 initiated by organic ammonium salts. Adapted with permission from ref. 138. Copyright 2020, American Chemical Society.

Recently, Lu's group reported the copolymerization of a series of internal epoxides including CHO, 1,2-epoxy-4-cyclohexene (CEO), cyclopentane oxide (CPO), and *cis*-2,3-epoxybutane (CBO) with SO_2 in the presence of organic ammonium salts consisting of a bulky bis(triphenylphosphine)iminium cation and a nucleophilic anion (Fig. 19).[138] It was discovered that copolymerization proceeded efficiently under ambient conditions (25–50 °C, 1 bar of SO_2, and a turnover frequency (TOF) up to 1116 h^{-1}). Side reactions including consecutive insertion of epoxides and backbiting occurred, however, only small amounts of byproducts are detected (less than 12%). Under optimal conditions, perfectly alternating copolymers can be acquired, which was proved by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF). The resultant polysulfites displayed a narrow polymer dispersity index (PDI) less than 1.35 and the measured molecular weights (M_n) were significantly lower than the theoretical values. These results suggest that a chain transfer reaction occurred due to the presence of a trace amount of water in the system. MALDI-TOF results confirmed the chain transfer reaction where two polymer distributions ascribed to the initiation of organic ammonium salts and water could be clearly observed, and the chain transfer reaction is a common phenomenon observed in the ring-opening (co)polymerization of epoxides.[143–146] Subsequently, Ren and coworkers described the organic ammonium salt-mediated copolymerization of PO and SO_2. Formation of polyether segments, five-membered cyclic sulfite molecules, and cyclic polymers was significantly suppressed. A linear polysulfide with sulfite linkages up to 96% was synthesized. Furthermore, it is observed that PPNCl mediated PO/SO_2 copolymerization proceeded in a living polymerization manner, and it is thus easy to prepare polysulfides with tunable molecular weights (4.4 kDa to 42.2 kDa) and low PDIs of 1.08–1.28. Stereochemical studies of polysulfides derived from the copolymerization of optically pure PO and SO_2 disclosed that the copolymerization shows a poor regioselectivity control. Ring-opening of PO preferred a 72% attack at the methene carbon and a 28% attack at the methine carbon.[147]

3.3 Coordination polymerization

Homopolymerization of epoxides[148,149] or copolymerizations with other oxa-monomers[150–154] (such as anhydrides or carbon dioxide) in the presence of coordination catalysts proceeded smoothly with high reactivity and polymer selectivity. The improved polymerization behavior could be ascribed to the coordination interaction between the catalysts and the oxygen atom in epoxides that greatly reduces the energy barrier for the ring-opening. Although the weak interaction between SO_2 and epoxides is able to reduce the energy barrier of epoxide ring-opening, the use of coordination catalysts is expected to greatly accelerate the copolymerization. Ree and coworkers investigated the copolymerization of PO and SO_2 in the presence of zinc glutarate.[155] It was found that poly(propylene sulfite) with a molecular weight up to 42 kg mol^{-1} can be synthesized. Due to the activation of PO by both SO_2 and zinc glutarate, homopolymerization of PO occurred and the resultant copolymers contained 10–20% ether linkages. In 2016, Jia *et al.* reported the Salen CrCl-mediated copolymerization of CHO and SO_2.[156] Due to overactivation of CHO by Salen CrCl and SO_2, the resultant polysulfite consisted of around 25% polyether (Fig. 20).

Based on the catalytic performance of Salen CrCl, Shan and Jia fabricated reusable heterogeneous Salen CrCl catalysts *via* a multistep chemical modification of cellulose (Fig. 21A).[157] The resultant catalysts displayed a high efficiency towards the copolymerization of CHO and SO_2. Additionally, they could be separated from the product *via* simple filtration and reused several times without any detectable deterioration of the catalytic performance. However, 15–50% cyclic sulfite and 5–25% ether linkages are simultaneously generated. Recently, the same group loaded the Salen Cr catalyst onto cellulose *via* the reaction of Salen $CrClO_4$ with amine-functionalized cellulose (Fig. 21B)[158] and the obtained Salen Cr-based heterogeneous catalysts displayed similar catalytic performance and recyclability.

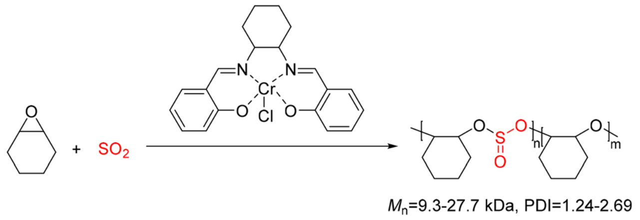


Fig. 20 Salen CrCl-catalyzed copolymerization of CHO and SO_2.

3.4 Properties and applications

The synthesized polysulfites exhibit inferior thermal properties compared to their polycarbonate analogues. For example, the T_g of poly(PO-*alt*-SO_2) and poly(CHO-*alt*-SO_2) with a few polyether linkages are 14 °C (ref. 155) and 45 °C,[138] respectively, while the T_g of poly(PO-*alt*-CO_2) and poly(CHO-*alt*-CO_2) are around 38 °C and 120 °C, respectively. Due to the inherently low thermal stability of the sulfite group, degradation of poly(PO-*alt*-SO_2) and poly(CHO-*alt*-SO_2) initiates at 160 °C (ref. 155) and 217 °C,[138] respectively.

Research studies related to the application of polysulfites are still rare. One example is their utilization in solid-state electrolytes as reported by Florjanczyk *et al.*[159] Since the amount of SO_2 inserted into the copolymers in the cationic ring-opening polymerization of EO and SO_2 is limited and random, the afforded copolymers are amorphous with only one T_g signal located at around 100 °C on a DSC curve. Additionally, random copolymers exhibit an excellent ionic conductivity, outperforming commercially used polyethylene oxide (PEO) (4.9×10^{-6} S cm^{-1} for copolymers and 6.1×10^{-7} S cm^{-1} for PEO at room temperature). Therefore, polysulfites can be used as electrolytes, avoiding the serious crystallization problem of commercial PEO in solid electrolytes. When mixed with PEO, polysulfites could function as a very effective crystallization inhibitor for PEO and only a small melting peak at 120 °C was found (weight ratio of 3/7). In this context, an extremely high ionic conductivity of 1.4×10^{-5} S cm^{-1} was detected for the mixture.

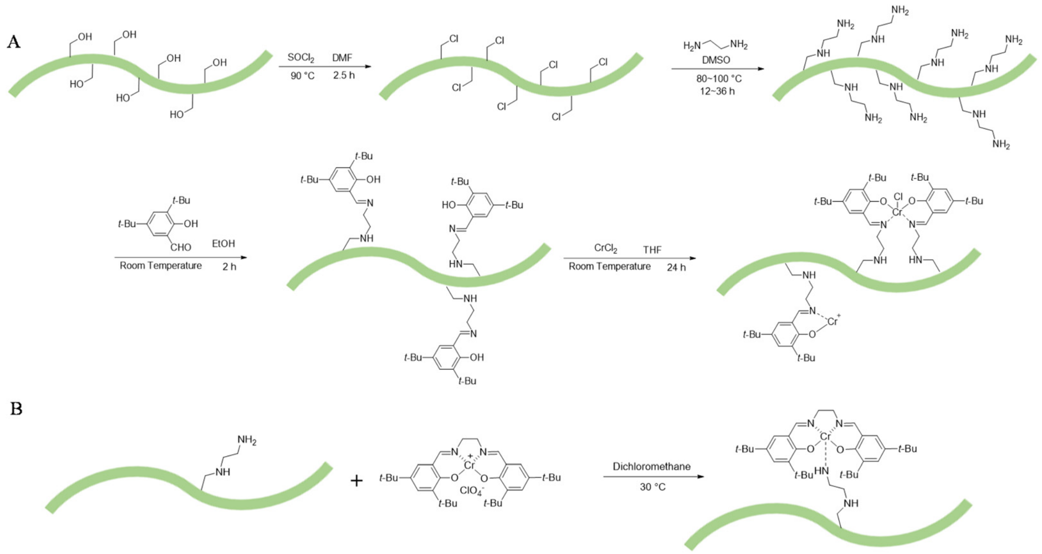


Fig. 21 Synthesis of Salen Cr-based heterogeneous catalysts by multi-step reactions (A) and direct coupling of Salen Cr with amine-functionalized cellulose (B) (backbone: cellulose).

4. Conclusion and outlook

We highlight the progress achieved in the synthesis of degradable polysulfones and polysulfites *via* the copolymerization of SO_2 with olefins or epoxides. These two transformations enjoy the following merits: (1) all the monomers involved are inexpensive and commercially available in large quantities, and the structural diversity of olefins and epoxides provides a facile route to tailor the performance of the resultant copolymers. (2) Due of the high reactivity of SO_2, both reactions can be carried out under mild conditions, and neither complex catalysts nor harsh conditions are necessary. Notably, these two copolymerizations can be initiated by metal-free initiators and special purifications of the resultant polymers are avoided. (3) The resultant copolymers exhibit intriguing properties. The thermal properties of hydrogenated polysulfones derived from conjugated dienes and SO_2 (T_g: ~100 °C and T_d: ~300 °C) are more competitive than those of commercial thermoplastics. Additionally, most of them degrade readily upon heating or chemical stimulation, which potentially meets the requirement to reduce plastic pollution and their degradability is a great advantage in some functional applications such as slow release and drug delivery. Therefore, we reason that SO_2-based copolymers might hold great promise in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Zhejiang Provincial Natural Science Foundation of China (LR21B040001) and the National Natural Science Foundation of China (Grants 91956123, 51973186, and 22101253).

References

1 D. J. Walsh, M. G. Hyatt, S. A. Miller and D. Guironnet, Recent Trends in Catalytic Polymerizations, *ACS Catal.*, 2019, **9**, 11153–11188.

2 T. J. Yue, L. Y. Wang and W. M. Ren, The Synthesis of Degradable Sulfur-Containing Polymers: Precise Control of Structure and Stereochemistry, *Polym. Chem.*, 2021, **12**, 6650–6666.

3 A. J. Plajer and C. K. Williams, Heterocycle/Heteroallene Ring-Opening Copolymerization: Selective Catalysis Delivering Alternating Copolymers, *Angew. Chem., Int. Ed.*, 2022, **61**, e202104495.

4 A. S. Abd-El-Aziz, M. Antonietti, C. Barner-Kowollik, W. H. Binder, A. Böker, C. Boyer, M. R. Buchmeiser, S. Z. D. Cheng, F. D'Agosto, G. Floudas, H. Frey, G. Galli, J. Genzer, L. Hartmann, R. Hoogenboom, T. Ishizone, D. L. Kaplan, M. Leclerc, A. Lendlein, B. Liu, T. E. Long, S. Ludwigs, J. F. Lutz, K. Matyjaszewski, M. A. R. Meier, K. Müllen, M. Müllner, B. Rieger, T. P. Russell, D. A. Savin, A. D. Schlüter, U. S. Schubert, S. Seiffert, K. Severing, J. B. P. Soares, M. Staffilani, B. S. Sumerlin, Y. Sun, B. Z. Tang, C. Tang, P. Théato, N. Tirelli, O. K. C. Tsui, M. M. Unterlass, P. Vana, B. Voit, S. Vyazovkin, C. Weder, U. Wiesner, W. Y. Wong, C. Wu, Y. Yagci, J. Yuan and G. Zhang, The Next 100 Years of Polymer Science, *Macromol. Chem. Phys.*, 2020, **221**, 2000216.

5 C. Williams and M. Hillmyer, Polymers from Renewable Resources: A Perspective for a Special Issue of Polymer Reviews, *Polym. Rev.*, 2008, **48**, 1–10.

6 T. J. Yue, B. H. Ren, W. J. Zhang, X. B. Lu, W. M. Ren and D. J. Darensbourg, Randomly Distributed Sulfur Atoms in the Main Chains of CO_2-Based Polycarbonates: Enhanced Optical Properties, *Angew. Chem., Int. Ed.*, 2021, **60**, 4315–4321.

7 S. Wu, M. Luo, D. J. Darensbourg, D. Zeng, Y. Yao, X. Zuo, X. Hu and D. Tan, Non-Isocyanate and Catalyst-Free Synthesis of a Recyclable Polythiourethane with Cyclic Structure, *ACS Sustainable Chem. Eng.*, 2020, **8**, 5693–5703.

8 D. W. Tan, X. Hu, Z. Cao, M. Luo and D. J. Darensbourg, Zwitterionic Alternating Polymerization to Generate Semicrystalline and Recyclable Cyclic Polythiourethanes, *ACS Macro Lett.*, 2020, **9**, 866–871.

9 S. Wu, M. Luo, D. J. Darensbourg and X. B. Zuo, Catalyst-Free Construction of Versatile and Functional CS_2-Based Polythioureas: Characteristics from Self-Healing to Heavy Metal Absorption, *Macromolecules*, 2019, **52**, 8596–8603.

10 J. Yuan, W. Xiong, X. Zhou, Y. Zhang, D. Shi, Z. Li and H. Lu, 4-Hydroxyproline-Derived Sustainable Polythioesters: Controlled Ring-Opening Polymerization, Complete Recyclability, and Facile Functionalization, *J. Am. Chem. Soc.*, 2019, **141**, 4928–4935.

11 C. Shi, M. L. McGraw, Z.-C. Li, L. Cavallo, L. Falivene and E. Y. X. Chen, High-Performance Pan-tactic Polythioesters with Intrinsic Crystallinity and Chemical Recyclability, *Sci. Adv.*, 2020, **6**, eabc0495.

12 Y. Wang, M. Li, J. Chen, Y. Tao and X. Wang, O-to-S Substitution Enables Dovetailing Conflicting Cyclizability, Polymerizability, and Recyclability: Dithiolactone vs. Dilactone, *Angew. Chem., Int. Ed.*, 2021, **60**, 22547–22553.

13 A. S. Rahate, K. R. Nemade and S. A. Waghuley, Polyphenylene Sulfide (PPS): state of the art and Applications, *Rev. Chem. Eng.*, 2013, **29**, 471–489.

14 C. D. Vo, G. Kilcher and N. Tirelli, Polymers and Sulfur: what are Organic Polysulfides Good For? Preparative Strategies and Biological Applications, *Macromol. Rapid Commun.*, 2009, **30**, 299–315.

15 A. Napoli, M. Valentini, N. Tirelli, M. Muller and J. A. Hubbell, Oxidation-Responsive Polymeric Vesicles, *Nat. Mater.*, 2004, **3**, 183–189.

16 A. E. Vasdekis, E. A. Scott, C. P. O'Neil, D. Psaltis and J. A. Hubbell, Precision Intracellular Delivery Based on

Optofluidic Polymersome Rupture, *ACS Nano*, 2012, **6**, 7850–7857.

17 C. C. Song, F. S. Du and Z. C. Li, Oxidation-Responsive Polymers for Biomedical Applications, *J. Mater. Chem. B*, 2014, **2**, 3413–3426.

18 J. Y. Chao, T. J. Yue, B. H. Ren, G. G. Gu, X. B. Lu and W. M. Ren, Controlled Disassembly of Elemental Sulfur: An Approach to the Precise Synthesis of Polydisulfides, *Angew. Chem., Int. Ed.*, 2022, **61**, e202115950.

19 S. Silvano, C. F. Carrozza, A. R. de Angelis, I. Tritto, L. Boggioni and S. Losio, Synthesis of Sulfur-rich Polymers: Copolymerization of Cyclohexene Sulfide and Carbon Disulfide Using Chromium Complexes, *Macromolecules*, 2020, **53**, 8837–8846.

20 K. Nakano, G. Tatsumi and K. Nozaki, Synthesis of Sulfur-Rich Polymers: Copolymerization of Episulfide with Carbon Disulfide by Using [PPN]Cl/(salph)Cr(III)Cl System, *J. Am. Chem. Soc.*, 2007, **129**, 15116–15117.

21 X. F. Zhu, R. Xie, G. W. Yang, X. Y. Lu and G. P. Wu, Precisely Alternating Copolymerization of Episulfides and Isothiocyanates: A Practical Route to Construct Sulfur-Rich Polymers, *ACS Macro Lett.*, 2021, **10**, 135–140.

22 X. F. Zhu, G. W. Yang, R. Xie and G. P. Wu, One-Pot Construction of Sulfur-Rich Thermoplastic Elastomers Enabled by Metal-Free Self-Switchable Catalysis and Air-Assisted Coupling, *Angew. Chem., Int. Ed.*, 2022, **61**, e202115189.

23 T. J. Yue, M. C. Zhang, G. G. Gu, L. Y. Wang, W. M. Ren and X. B. Lu, Precise Synthesis of Poly(thioester)s with Diverse Structures by Copolymerization of Cyclic Thioanhydrides and Episulfides Mediated by Organic Ammonium Salts, *Angew. Chem., Int. Ed.*, 2019, **58**, 618–623.

24 M. J. H. Worthington, R. L. Kucera and J. M. Chalker, Green Chemistry and Polymers Made from Sulfur, *Green Chem.*, 2017, **19**, 2748–2761.

25 J. Lim, J. Pyun and K. Char, Recent Approaches for the Direct Use of Elemental Sulfur in the Synthesis and Processing of Advanced Materials, *Angew. Chem., Int. Ed.*, 2015, **54**, 3249–3258.

26 J. M. Catala and M. Clauss, Anionic Synthesis of Polysulfide Oligomers from Elemental Sulfur and Methacrylic Esters, *Macromolecules*, 1991, **24**, 2663–2667.

27 D. H. Kim, W. Jang, K. Choi, J. S. Choi, J. Pyun, J. Lim, K. Char and S. G. Im, One-Step Vapor-Phase Synthesis of Transparent High Refractive Index Sulfur-Containing Polymers, *Sci. Adv.*, 2020, **6**, 5320.

28 J. Zhang, Q. Zang, F. Yang, H. Zhang, J. Z. Sun and B. Z. Tang, Sulfur Conversion to Multifunctional Poly(O-thiocarbamate)s through Multicomponent Polymerizations of Sulfur, Diols, and Diisocyanides, *J. Am. Chem. Soc.*, 2021, **143**, 3944–3950.

29 T. Tian, R. Hu and B. Z. Tang, Room Temperature One-Step Conversion from Elemental Sulfur to Functional Polythioureas through Catalyst-Free Multicomponent Polymerizations, *J. Am. Chem. Soc.*, 2018, **140**, 6156–6163.

30 W. Cao, F. Dai, R. Hu and B. Z. Tang, Economic Sulfur Conversion to Functional Polythioamides through Catalyst-Free Multicomponent Polymerizations of Sulfur, Acids, and Amines, *J. Am. Chem. Soc.*, 2020, **142**, 978–986.

31 W. Li, X. Wu, Z. Zhao, A. Qin, R. Hu and B. Z. Tang, Catalyst-Free, Atom-Economic, Multicomponent Polymerizations of Aromatic Diynes, Elemental Sulfur, and Aliphatic Diamines toward Luminescent Polythioamides, *Macromolecules*, 2015, **48**, 7747–7754.

32 C. J. Zhang and X. H. Zhang, Chemoselective Coupling of CS_2 and Epoxides for Producing Poly(thioether)s and COS via Oxygen/Sulfur Atom Exchange, *Macromolecules*, 2019, **53**, 233–239.

33 N. Adachi, Y. Kida and K. Shikata, Copolymerization of Propylene Oxide and Carbon Disulfide with Diethylzinc–Electron-Donor Catalyst, *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 937–944.

34 J. L. Yang, L. F. Hu, X. H. Cao, Y. Wang and X. H. Zhang, An Investigation on the Production of Random Copolymer with Monothiocarbonate and Trithiocarbonate Units over Cyclic Thiocarbonate via Metal-free Catalysis, *Chin. J. Chem.*, 2020, **38**, 269–274.

35 M. Luo, X. H. Zhang and D. J. Darensbourg, An Investigation of the Pathways for Oxygen/Sulfur Scramblings during the Copolymerization of Carbon Disulfide and Oxetane, *Macromolecules*, 2015, **48**, 5526–5532.

36 J. Diebler, H. Komber, L. Häußler, A. Lederer and T. Werner, Alkoxide-Initiated Regioselective Coupling of Carbon Disulfide and Terminal Epoxides for the Synthesis of Strongly Alternating Copolymers, *Macromolecules*, 2016, **49**, 4723–4731.

37 S. J. Smith, J. V. Aardenne, Z. Klimont, R. J. Andres, A. Volke and S. D. Arias, Anthropogenic Sulfur Dioxide Emissions: 1850–2005, *Atmos. Chem. Phys.*, 2011, **11**, 1101–1116.

38 Date source: **https://www.mee.gov.cn/hjzl/sthjzk/**.

39 R. D. Snow and F. E. Frey, Reaction of Sulfur Dioxide with Olefins, *Ind. Eng. Chem.*, 1938, **30**, 176–182.

40 Z. Florjańczyk, On the Reactivity of Sulfur Dioxide in Chain Polymerization Reactions, *Prog. Polym. Sci.*, 1991, **16**, 509–560.

41 R. D. Snow and F. E. Frey, The Reaction of Sulfur Dioxide with Olefins: the Ceiling Temperature Phenomenon, *J. Am. Chem. Soc.*, 1943, **65**, 2417–2418.

42 F. S. Dainton and K. J. Ivin, Reversibility of the Propagation Reaction In Polymerization Processes and Its Manifestation in the Phenomenon of a Ceiling Temperature, *Nature*, 1948, **162**, 705–707.

43 R. E. Cook, F. S. Dainton and K. J. Ivin, Effect of Olefin Structure on the Ceiling Temperature for Olefin Polysulfone formation, *J. Polym. Sci.*, 1957, **26**, 351–364.

44 M. Hong and E. Y. Chen, Completely Recyclable Biopolymers with Linear and Cyclic Topologies via Ring-Opening Polymerization of Gamma-Butyrolactone, *Nat. Chem.*, 2016, **8**, 42–49.

45 J. B. Zhu, E. M. Watson, J. Tang and E. Y. Chen, A Synthetic Polymer System with Repeatable Chemical Recyclability, *Science*, 2018, **360**, 398–403.

46 G. W. Coates and Y. D. Y. L. Getzler, Chemical Recycling to Monomer for an Ideal, Circular Polymer Economy, *Nat. Rev. Mater.*, 2020, **5**, 501–516.

47 X. B. Lu, Y. Liu and H. Zhou, Learning Nature: Recyclable Monomers and Polymers, *Chem. – Eur. J.*, 2018, **24**, 11255–11266.

48 X. Tang and E. Y. X. Chen, Toward Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters, *Chem*, 2019, **5**, 284–312.

49 X. Liu, Y. Zhi, S. Shan, H. Su and Q. Jia, Tunable Thermal Degradation and Refractive Index of Poly(norbornene sulfone)s via Two Different Polymerization Methods, *J. Appl. Polym. Sci.*, 2017, **134**, 44534.

50 W. G. Barb, The Copolymerization of Styrene and Sulphur Dioxide - I. Properties and Composition of the Copolymer, and Evidence for the Existence of a Styrene/Sulphur Dioxide Complex, *Proc. R. Soc. London, Ser. A*, 1952, **212**, 66–80.

51 F. J. Glavis, L. L. Ryden and C. S. Marvel, The Reaction between Sulfur Dioxide and Olefins. V.1 The Structure of the Polysulfones from Olefins of the Type RCH=CH2, *J. Am. Chem. Soc.*, 1937, **59**, 707–711.

52 W. G. Barb, The Copolymerization of Styrene and Sulphur Dioxide II. The Kinetics of Polymerization, *Proc. R. Soc. London, Ser. A*, 1952, **212**, 177–192.

53 N. Tokura, M. Matsuda and Y. Ogawa, Polymerization in liquid sulfur dioxide. Part XIII. Polymerization of styrene derivatives in liquid sulfur dioxide, *J. Polym. Sci., Part A: Gen. Pap.*, 1963, **1**, 2965–2976.

54 N. Tokura, M. Matsuda and K. Arakawa, Polymerization in liquid sulfur dioxide. Part XVIII. Polymerization of p-isopropylstyrene and its copolymerization with styrene in liquid sulfur dioxide, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 3355–3363.

55 M. Iino, T. Masuda and N. Tokura, Radical Copolymerization ofm-Bromostyrene with Liquid Sulfur Dioxide, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 752–753.

56 M. Matsuda, M. Iino, T. Hirayama and T. Miyashita, Radical Copolymerization of Sulfur Dioxide and Styrene, *Macromolecules*, 1972, **5**, 240–246.

57 M. Iino, K. Katagiri and M. Matsuda, Radical Copolymerization of Sulfur Dioxide and Styrene. II. Sequence Distribution in Poly(styrene sulfone), *Macromolecules*, 1973, **7**, 439–443.

58 M. Iino, H. H. Thoi, S. Shioya and M. Matsuda, Radical Copolymerization of Sulfur Dioxide and Styrene. 3. Evidence for the Occurrence of the Depropagation of Growing Styryl Radicals, *Macromolecules*, 1979, **12**, 160–161.

59 R. E. Cais, J. H. O'Donnell and F. A. Bovey, Copolymerization of Styrene with Sulfur Dioxide. Determination of the Monomer Sequence Distribution by Carbon-13 NMR, *Macromolecules*, 1977, **10**, 254–260.

60 H. J. Bae, T. Miyashita, M. Iino and M. Matsuda, Radical Copolymerization of Sulfur Dioxide and Styrene. 5. The Styrene Sequence Distribution of Poly(styrene sulfones), *Macromolecules*, 1988, **21**, 26–30.

61 C. S. Marvel and F. J. Glavis, Vinyl Halide Polysulfones. Peracetic Acid as a Catalyst for the Reaction between Sulfur Dioxide and Olefins, *J. Am. Chem. Soc.*, 1938, **60**, 2622–2626.

62 C. S. Marvel and L. H. Dunlap, Vinyl Chloride Polysulfone, *J. Am. Chem. Soc.*, 1939, **61**, 2709–2710.

63 R. E. Cais and J. H. O'Donnell, Copolymerization of Vinyl Chloride with Sulphur Dioxide—I Molecular Association between Vinyl Chloride and Sulphur Dioxide, *Eur. Polym. J.*, 1975, **11**, 749–754.

64 C. Schneider, J. Denaxas and D. Hummel, Strahlenchemische Darstellung von Polysulfonen bei Verschiedenen Temperaturen, *J. Polym. Sci., Part C: Polym. Symp.*, 1967, **16**, 2203–2213.

65 R. E. Cais and J. H. O'Donnell, Variable-Composition Polysulfones by Free-Radical Copolymerization of Vinyl Chloride with Sulfur Dioxide, *J. Polym. Sci., Polym. Symp.*, 1976, **55**, 75–85.

66 M. Matsuda and H. H. Thoi, Propagation Mechanism of Radical Copolymerization of Sulfur Dioxide and Vinyl Chloride, *J. Macromol. Sci., Chem.*, 1977, **11**, 1423–1437.

67 R. E. Cais, D. J. T. Hill and J. H. O'Donnell, Copolymerization of Vinyl Chloride and Sulfur Dioxide. III. Evaluation of the Copolymerization Mechanism, *J. Macromol. Sci., Chem.*, 1982, **17**, 1437–1467.

68 R. E. Cais and J. H. O'Donnell, Monomer and Configurational Sequence Regularity in the 2 : 1 Copolymer of Vinyl Chloride with Sulfur Dioxide, *J. Polym. Sci., Polym. Lett. Ed.*, 1976, **14**, 263–272.

69 R. E. Cais and J. H. O'Donnell, NMR Determination of the Microstructure of Poly(vinyl chloride sulfone). I. 1H Spectra, *Macromolecules*, 1976, **9**, 279–289.

70 R. E. Cais and J. H. O'Donnell, Dehydrochlorination of Poly(sulfony1-co-2-chloroethylene), *Makromol. Chem.*, 1975, **176**, 3517–3535.

71 M. Iino, K. Seki and M. Riatsuda, Radical Terpolymerization of Sulfur Dioxide, Hexene-l, and Methyl Acrylate or Methyl Methacrylate, *J. Polym. Sci., Polym. Chem. Ed.*, 1972, **10**, 2993–3001.

72 Z. FlorjarIczyk, T. Floriariczyk and E. Zygadio, Copolymers of Acrylates with Sulfur Dioxide: Synthesis and Structural Studies by ^{13}C NMR Spectroscopy, *Makromol. Chem.*, 1988, **189**, 2719–2730.

73 Z. Florjahczyk and E. Zygadto, On the Reactivity of Aromatic Acrylates in Free-Radical Copolymerization with SO2 and Terpolymerization with S02 and 1-Heptene, *Polymer*, 1991, **32**, 2853–2855.

74 Z. Florjadczyk, E. Zygadro and D. Raducha, On the Kinetic Model for the Radical Copolymerization of Methyl Acrylate and Sulfur Dioxide, *Macromolecules*, 1990, **23**, 2901–2903.

75 Y. Jiang and J. M. J. Frbchet, Design and Synthesis of Thermally Labile Polymers for Microelectronics. Poly(vinyl tert-butyl carbonate-sulfone), *Macromolecules*, 1991, **24**, 3528–3532.

76 K. Kumar and A. P. Goodwin, Alternating Sulfone Copolymers Depolymerize in Response to Both Chemical and Mechanical Stimuli, *ACS Macro Lett.*, 2015, **4**, 907–911.

77 C. M. Possanza Casey and J. S. Moore, Base-Triggered Degradation of Poly(vinyl ester sulfone)s with Tunable Sensitivity, *ACS Macro Lett.*, 2016, **5**, 1257–1260.

78 R. S. Bauer, H. E. Lunk and E. A. Youngman, Diene Polysulfones. I. Structure of the Butadiene–Sulfur Dioxide Copolymer, *J. Polym. Sci., Part A-1: Polym. Chem.*, 1970, **8**, 1915–1920.

79 K. J. Ivin and N. A. Walker, Structure of the Polysulfones of Some Conjugated Dienes, *J. Polym. Sci., Part B: Polym. Lett.*, 1971, **9**, 901–906.

80 M. Delamar, P. C. Lacaze, B. Lemiere, J. Y. Dumousseau and J. E. DuBois, A New Method for Preparing Polysulfones: Electrochemically Induced Copolymerization of Sulfur Dioxide and Conjugated Dienes in Liquid SO_2, *J. Polym. Sci., Part A: Polym. Chem.*, 1982, **20**, 245–248.

81 T. Kitamura, N. Tanaka, A. Mihashi and A. Matsumoto, Soluble and Thermally Stable Polysulfones Prepared by the Regiospecific and Alternating Radical Copolymerization of 2,4-Hexadiene with Sulfur Dioxide, *Macromolecules*, 2010, **43**, 1800–1806.

82 N. Tanaka, E. Sato and A. Matsumoto, Thermally Stable Polysulfones Obtained by Regiospecific Radical Copolymerization of Various Acyclic and Cyclic 1,3-Diene Monomers with Sulfur Dioxide and Subsequent Hydrogenation, *Macromolecules*, 2011, **44**, 9125–9137.

83 A. Matsumoto, S. Lee and H. Okamura, Molecular design of diene monomers containing an ester functional group for the synthesis of poly(diene sulfone)s by radical alternating copolymerization with sulfur dioxide, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1000–1009.

84 N. Tanaka, E. Sato and A. Matsumoto, Highly-Controlled Regiospecific Free-Radical Copolymerization of 1,3-Diene Monomers with Sulfur Dioxide, *Org. Biomol. Chem.*, 2011, **9**, 3753–3758.

85 X. Guo, X. Liu, S. Shan, W. Zhao, H. Su and Q. Jia, Green Approach toward Sustainable Adhesive: Synthesis and Characterization of Poly(myrcene sulfone), *J. Taiwan Inst. Chem. Eng.*, 2019, **95**, 208–216.

86 J. K. Stille and D. W. Thomson, The Cyclocopolymerization of 1,5-Hexadiene and Sulfur Dioxide, *J. Polym. Sci.*, 1962, **62**, S118–S120.

87 A. H. Frazer and W. P. O'Neill, Bicyclo-Copolymerization of Sulfur Dioxide and *cis*,*cis*-1,5-Cyclooctadiene, *J. Am. Chem. Soc.*, 1963, **85**, 2613–2616.

88 A. H. Frazer, Thermal Stability of the Copolymer of Sulfur Dioxide and *cis*,*cis*-1,5-Cyclooctadiene, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 4031–4038.

89 F. L. Ramp, *cis*,*trans*-1,5-Cyclodecadiene—Sulfur Dioxide Copolymer, *J. Macromol. Sci., Chem.*, 1967, **1**, 603–615.

90 K. Meyersen and J. Y. C. Wang, Cyclocopolymerization of Bicyclopentene and Other Dicyclic Dienes with Sulfur Dioxide to Fused Ring Systems, *J. Polym. Sci., Part A-1: Polym. Chem.*, 1967, **5**, 1827–1844.

91 S. Harada and M. Katayama, The Cyclo-copolymerization of Diallyl Compound and Sulfur Dioxide, *Makromol. Chem.*, 1966, **90**, 177–186.

92 R. M. Ottenbrite and W. S. Ryan, Cyclopolymerization of N,N-Dialkyldiallylammonium Halides. A Review and Use Analysis, *Ind. Eng. Chem. Prod. Res. Dev.*, 1980, **19**, 528–532.

93 Y. Amemiya, M. Katayama and S. Harada, The Cyclo-Copolymerization of Diallyl Compounds and Sulfur Dioxide, 6. 1,6-Heptadiene and Sulfur Dioxide, *Makromol. Chem.*, 1977, **178**, 2499–2505.

94 Y. Amemiya, M. Katayama and S. Harada, The Cyclo-Copolymerization of Diallyl Compounds and Sulfur Dioxide, (5*) Copolymerization of Some 4-Substituted 1,6-Heptadiene Derivatives with Sulfur Dioxide, *Makromol. Chem.*, 1977, **178**, 289–315.

95 J. Y. Tsai and P. B. Shevlin, Structure of the Products of the Cyclooligomerization of Sulfur Dioxide with Diethyl Diallylmalonate, *J. Org. Chem.*, 1998, **63**, 3230–3234.

96 S. Harada and K. Arai, The Cyclo-Copolymerization of Diallyl Compounds and Sulfur Dioxide 11. Diallyldimethylammoniurn Chloride and Sulfur Dioxide, *Makromol. Chem.*, 1967, **107**, 64–77.

97 T. Ueda and S. Harada, Effect of the Structure of Cationic Polysulfone on the Flocculation of Kaolinite, *J. Appl. Polym. Sci.*, 1968, **12**, 2383–2393.

98 Y. Amemiya, M. Katayama and S. Harada, The Cyclo-Copolymerization of Diallyl Compounds and Sulfur Dioxide, (4*) 4-(4-Pyridy1)-1,6-heptadiene Hydrochloride and Sulfur Dioxide, *Makromol. Chem.*, 1975, **176**, 1289–1305.

99 S. A. Ali and A. Rasheed, Synthesis and Solution Properties of a Betaine-Sulfur Dioxide Polyampholyte, *Polymer*, 1999, **40**, 6849–6857.

100 S. A. Ali, H. A. Al-Muallem and M. I. M. Wazeer, Synthesis of a New Amino Acid/Sulfur Dioxide Copolymer and its Use in Aqueous Two-Phase Polymer Systems, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 2464–2477.

101 Z. A. Jamiu and S. A. Ali, Alternate Cyclopolymer of Diallylglutamic Acid and Sulfur Dioxide, *RSC Adv.*, 2016, **6**, 31019–31030.

102 T. A. Saleh, I. B. Rachman and S. A. Ali, Tailoring Hydrophobic Branch in Polyzwitterionic Resin for Simultaneous Capturing of Hg(II) and Methylene Blue with Response Surface Optimization, *Sci. Rep.*, 2017, **7**, 4573.

103 Z. A. Jamiu, T. A. Saleh and S. A. Ali, Biogenic Glutamic Acid-Based Resin: Its Synthesis and Application in the Removal of Cobalt(II), *J. Hazard. Mater.*, 2017, **327**, 44–54.

104 Z. A. Jamiu, T. A. Saleh and S. A. Ali, Synthesis of a Unique Cross-Linked Polyzwitterion/Anion with an Aspartic Acid Residue and its Use for Pb^{2+} Removal from Aqueous Solution, *RSC Adv.*, 2015, **5**, 42222–42232.

105 T. A. Saleh, A. M. Musa and S. A. Ali, Synthesis of Hydrophobic Cross-Linked Polyzwitterionic Acid for Simultaneous Sorption of Eriochrome Black T and Chromium Ions from Binary Hazardous Waters, *J. Colloid Interface Sci.*, 2016, **468**, 324–333.

106 N. Baig, Z. Arshad and S. A. Ali, Synthesis of a Biomimetic Zwitterionic Pentapolymer to Fabricate High-Performance PVDF Membranes for Efficient Separation of Oil-in-Water Nano-Emulsions, *Sci. Rep.*, 2022, **12**, 5028.

107 C. P. Tsonis, S. A. Ali and M. I. M. Wazeer, Stereoselective Alternating Copolymerization of Aliphatic Acetylenes with Sulphur Dioxide, *Polymer*, 1986, **27**, 1991–1998.

108 L. L. Ryden and C. S. Marvel, The Reaction between Sulfur Dioxide and Olefins. III.1 Higher Olefins and Some Limitations of the Reaction, *J. Am. Chem. Soc.*, 1935, **57**, 2311–2314.

109 L. L. Ryden and C. S. Marvel, Polysulfones from Acetylenes and Sulfur Dioxide1, *J. Am. Chem. Soc.*, 1936, **58**, 2047–2050.

110 C. S. Marvel and W. W. Williams, Acetylene Polysulfones. XI.1 The Compound $C_{10}H_{16}SO_2$ from 1-Pentynepolysulfone and Some Experiments on Other Acetylenepolysulfones, *J. Am. Chem. Soc.*, 1939, **61**, 2710–2714.

111 S.-J. Kim and M. Matsuda, Free Radical Copolymerization of Sulfur Dioxide with 1-Alkynes, *J. Polym. Sci., Part A: Polym. Chem.*, 1989, **27**, 2305–2311.

112 C. P. Tsonis, S. A. Ali and J. S. Hwang, Studies on the Copolymer Composition of Sulphur Dioxide and Phenylacetylene, *Polymer*, 1987, **28**, 2139–2144.

113 S.-J. Kim, F. Akiyama and M. Matsuda, Free Radical Copolymerization of Sulfur Dioxide with Phenylacetylene, *J. Polym. Sci., Part A: Polym. Chem.*, 1987, **25**, 1641–1651.

114 E. H. Hill and J. R. Caldwell, Polysulfones of Norbornene and Derivatives, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 1251–1255.

115 O. P. Lee, H. Lopez Hernandez and J. S. Moore, Tunable Thermal Degradation of Poly(vinyl butyl carbonate sulfone)s via Side-Chain Branching, *ACS Macro Lett.*, 2015, **4**, 665–668.

116 M. Hong and E. Y. X. Chen, Chemically Recyclable Polymers: A Circular Economy Approach to Sustainability, *Green Chem.*, 2017, **19**, 3692–3706.

117 X. Y. Lu, H. Luo, K. Wang, Y. Y. Zhang, X. F. Zhu, D. Li, B. Ma, S. Xiong, P. F. Nealey, Q. Li and G. P. Wu, CO_2-Based Dual-Tone Resists for Electron Beam Lithography, *Adv. Funct. Mater.*, 2020, **31**, 2007417.

118 L. F. Thompson and M. J. Bowden, A New Family of Positive Electron Beam Resists—Poly(Olefin Sulfones), *J. Electrochem. Soc.*, 1973, **120**, 1722.

119 M. J. Bowden and L. F. Thompson, Electron Irradiation of Poly(olefin sulfones). Application to Electron Beam Resists, *J. Appl. Polym. Sci.*, 1973, **17**, 3211–3221.

120 M. J. Bowden and L. F. Thompson, Poly(Styrene Sulfone) —A Sensitive lon-Millable Positive Electron Beam Resist, *J. Electrochem. Soc.*, 1974, **121**, 1620.

121 M. J. Bowden and L. F. Thompson, Effect of Olefin Structure on the Vapor-Development of Poly (olefin sulfones) under Electron Irradiation, *Polym. Eng. Sci.*, 1977, **17**, 269–273.

122 M. J. Bowden, A. S. Gozdz, J. M. DeSimone, J. E. McGrath, S. Ito and M. Matsuda, Reactive-Ion Etch Resistant Polysulfones for Microlithography, *Makromol. Chem., Macromol. Symp.*, 1992, **53**, 125–137.

123 A. Watanabe, T. Sakakibara, S. Ito, H. Ono, Y. Yoshida, S. Tagawa and M. Matsuda, Photodegradation and Electron-Beam-Induced Degradation of Poly[(pentamethyldisilyl)styrene sulfones], *Macromolecules*, 1992, **25**, 692–697.

124 J. M. DeSimone, G. A. York, J. E. McGrath, A. S. Gozdz and M. J. Bowden, Synthesis, Bulk, Surface and Microlithographic Characterization of Poly(1-butene sulfone)-g-Poly(dimethylsiloxane), *Macromolecules*, 1991, **24**, 5330–5339.

125 K. Lawrie, I. Blakey, J. Blinco, R. Gronheid, K. Jack, I. Pollentier, M. J. Leeson, T. R. Younkin and A. K. Whittaker, Extreme Ultraviolet (EUV) Degradation of Poly(olefin sulfone)s: Towards Applications as EUV Photoresists, *Radiat. Phys. Chem.*, 2011, **80**, 236–241.

126 W. A. Loong and H. W. Chang, Photoacid Catalyzed Main Chain Scission of Poly(butene-1 sulfone) as a Deep UV Positive Resist, *Microelectron. Eng.*, 1991, **14**, 101–108.

127 R. G. Tarascon, E. Reichmanis, F. M. Houlihan, A. Shugard and L. F. Thompson, Poly(*t*-BOC-styrene sulfone)-Based Chemically Amplified Resists for Deep-UV Lithography, *Polym. Eng. Sci.*, 1989, **29**, 850–855.

128 H. Yaguchi and T. Sasaki, Photoinduced Depolymerization of Poly(olefin sulfone)s Possessing Photobase Generating Groups in the Side Chain, *Macromolecules*, 2007, **40**, 9332–9338.

129 T. Sasaki and H. Yaguchi, Photoinduced Unzipping Depolymerization of Poly(olefin sulfone)s Possessing Photobase Generator and Base Amplifier, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 602–613.

130 K. Kumar, E. J. Castano, A. R. Weidner, A. Yildirim and A. P. Goodwin, Depolymerizable Poly(O-vinyl carbamate-alt-sulfones) as Customizable Macromolecular Scaffolds for Mucosal Drug Delivery, *ACS Macro Lett.*, 2016, **5**, 636–640.

131 L. Liu, Y. Ni, Y. Zhi, W. Zhao, M. Pudukudy, Q. Jia, S. Shan, K. Zhang and X. Li, Sustainable and Biodegradable Copolymers from SO2 and Renewable Eugenol: A Novel Urea Fertilizer Coating Material with Superio Slow Release Performance, *Macromolecules*, 2020, **53**, 936–945.

132 J. Schaefer, R. J. Kern and R. J. Katnik, The Monomer Distributions of Propylene Oxide-Sulfur Dioxide Copolymers, *Macromolecules*, 1968, **1**, 107–111.

133 J. Schaefer, Equilibrium of Catalytic States in the Copolymerization of Propylene Oxide and Sulfur Dioxide, *Macromolecules*, 1968, **1**, 111–116.

134 M. Matsuda, F. Akiyama and Y. Hara, Ring-opining Cationic Copolymerization of Liqud SO2 with Cyclohexene Oxide, *Kobunshi Ronbunshu*, 1975, **32**, 660–664.

135 K. Soga, I. Hattori, J. Kinoshita and S. Ikeda, Alternating Copolymerization of Ethylene Oxide and Sulfur Dioxide, *J. Polym. Sci., Polym. Chem. Ed.*, 1977, **15**, 745–753.

136 K. Soga, K. Kiyohara, I. Hattori and S. Ikeda, Alternating Copolymerization of Cyclohexene Oxide and Sulfur Dioxide, *Makromol. Chem.*, 1980, **181**, 2151–2159.

137 Z. Florjańczyk and D. Raducha, On the Initiation Mechanism of the SO_2 Copolymerization with Ethylene Oxide in the Presence of Pyridine, *Makromol. Chem., Rapid Commun.*, 1991, **12**, 393–397.

138 B. H. Ren, W. M. Ren and X. B. Lu, Alternating Copolymerization of SO_2 with Epoxides Mediated by Simple Organic Ammonium Salts, *Macromolecules*, 2020, **53**, 9901–9905.

139 Z. Florjańczyk and D. Raducha, Copolymerizationof Ethylene Oxide and Sulfur Dioxide Initiated by Lewis Bases, *Makromol. Chem.*, 1993, **194**, 2605–2613.

140 Z. Florjańczyk, D. Raducha and A. Kozera-Szałkowska, On the Ionic Species Formed in Reactions of Sulfur Dioxide with Cyclic Ethers and Propylene Sulfide, *Macromolecules*, 1996, **29**, 826–834.

141 Z. Li, Y. Zhi, Y. Ni, H. Su, Y. Miao and S. Shan, Novel Melamine-Based Porous Organic Materials as Metal-Free Catalysts for Copolymerization of SO_2 with Epoxide, *Polymer*, 2021, **217**, 123434.

142 Z. Florjanczyk and D. Raducha, Copolymerization Of Ethylene Oxide And Sulfur-Dioxide Initiated by Salts, *Makromol. Chem., Rapid Commun.*, 1993, **14**, 207–211.

143 Y. Y. Zhang, G. W. Yang and G. P. Wu, Construction of Polylactide-block-Polystyrene Copolymer by Orthogonal ROP and O-ATRP via Bifunctional β-Diiminate Zinc Catalyst, *Acta Polym. Sin.*, 2021, **52**, 467–476.

144 J. Ren, X. Shu, Y. Wang, D. Wang, G. Wu, X. Zhang, Q. Jin, J. Liu, Z. Wu, Z. Xu, C. Z. Li and H. Li, Key Progresses of MOE Key Laboratory of Macromolecular Synthesis and Functionalization in 2020, *Chin. Chem. Lett.*, 2022, **33**, 1650–1658.

145 G. P. Wu and D. J. Darensbourg, Mechanistic Insights into Water-Mediated Tandem Catalysis of Metal-Coordination CO_2/Epoxide Copolymerization and Organocatalytic Ring-Opening Polymerization: One-Pot, Two Steps, and Three Catalysis Cycles for Triblock Copolymers Synthesis, *Macromolecules*, 2016, **49**, 807–814.

146 Y. Y. Zhang, G. W. Yang, Y. Wang, X. Y. Lu, G. P. Wu, Z. S. Zhang, K. Wang, R. Y. Zhang, P. F. Nealey, D. J. Darensbourg and Z. K. Xu, Synthesis of CO_2-Based Block Copolymers via Chain Transfer Polymerization Using Macroinitiators: Activity, Blocking Efficiency, and Nanostructure, *Macromolecules*, 2018, **51**, 791–800.

147 X. C. Jin, B. H. Ren, G. G. Gu, T. J. Yue and W. M. Ren, The Copolymerization of SO_2 with Propylene Oxide Mediated by Organic Ammonium Salts: A Comprehensive Study of the Main-Chain Structure, Living Polymerization Character and Regioselectivity, *Polym. Chem.*, 2022, **13**, 3136.

148 G. W. Yang, Y. Y. Zhang, R. Xie and G. P. Wu, High-Activity Organocatalysts for Polyether Synthesis via Intramolecular Ammonium Cation Assisted SN2 Ring-Opening Polymerization, *Angew. Chem., Int. Ed.*, 2020, **59**, 16910–16917.

149 G. W. Yang, Y. Y. Zhang, R. Xie and G. P. Wu, Scalable Bifunctional Organoboron Catalysts for Copolymerization of CO_2 and Epoxides with Unprecedented Efficiency, *J. Am. Chem. Soc.*, 2020, **142**, 12245–12255.

150 Y. Y. Zhang, L. Yang, R. Xie, G. W. Yang and G. P. Wu, Perfectly Alternating Copolymerization of CO and Epoxides to Aliphatic Polyester Oligomers via Cooperative Organoboron–Cobalt Complexes, *Macromolecules*, 2021, **54**, 9427–9436.

151 G. W. Yang, Y. Y. Zhang and G. P. Wu, Modular Organoboron Catalysts Enable Transformations with Unprecedented Reactivity, *Acc. Chem. Res.*, 2021, **54**, 4434–4448.

152 G. W. Yang, C. K. Xu, R. Xie, Y. Y. Zhang, X. F. Zhu and G. P. Wu, Pinwheel-Shaped Tetranuclear Organoboron Catalysts for Perfectly Alternating Copolymerization of CO_2 and Epichlorohydrin, *J. Am. Chem. Soc.*, 2021, **143**, 3455–3465.

153 R. Xie, Y. Y. Zhang, G. W. Yang, X. F. Zhu, B. Li and G. P. Wu, Record Productivity and Unprecedented Molecular Weight for Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides Enabled by Organoboron Catalysts, *Angew. Chem., Int. Ed.*, 2021, **60**, 19253–19261.

154 Y.-Y. Zhang, G.-P. Wu and D. J. Darensbourg, CO_2-Based Block Copolymers: Present and Future Designs, *Trends Chem.*, 2020, **2**, 750–763.

155 B. Lee, J. H. Jung and M. Ree, Synthesis and Characterization of Poly(propylene sulfite) from Sulfur Dioxide and Propylene Oxide Using Zinc Derivatives as Catalysts, *Macromol. Chem. Phys.*, 2000, **201**, 831–839.

156 Y. Zhi, J. Wu, A. Ma, N. Tian, S. Shan, Q. Jia and H. Su, Efficient Alternating Copolymerization of Sulfur Dioxide with Cyclohexene Oxide and a Mechanistic Understanding, *RSC Adv.*, 2016, **6**, 32881–32886.

157 Y. Zhi, X. Deng, Y. Ni, W. Zhao, Q. Jia and S. Shan, Cellulosic Cr(salen) Complex as an Efficient and Recyclable Catalyst for Copolymerization of SO_2 with Epoxide, *Carbohydr. Polym.*, 2018, **194**, 170–176.

158 Y. Liu, Y. Chen, Y. Zhi, X. Yu, P. Wang, S. Wang and S. Shan, SalenCr Catalyst Immobilized on Amino-Functionalized Cellulose for the Copolymerization of SO2 with Cyclohexene Oxide, *Catal. Lett.*, 2022, DOI: **10.1007/s10562-022-03940-5**.

159 Z. Florjanczyk, E. Zygadlo-Monikowska, D. Raducha, K. Such and W. Wieczorek, Polymeric Electrolytes Based on Sulfur Dioxide Copolymers, *Electrochim. Acta*, 1992, **37**, 1555–1558.