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REVIEW

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Depolymerization and Functionalization of Super Engineering Plastics

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Abstract Chemical recycling/upcycling of plastics has emerged as one of the most promising strategies for the plastic circular economy, enabling the depolymerization and functionalization of plastics into valuable monomers and chemicals. However, studies on the depolymerization and functionalization of challenging super engineering plastics have remained in early stage and underexplored. In this review, we would like to discuss the representative accomplishments and mechanism insights on chemical protocols achieved in depolymerization of super engineering plastics, especially for poly(phenylene sulfide) (PPS), poly(aryl ether)s including poly(ether ether ketone) (PEEK), polysulfone (PSU), polyphenylsulfone (PPSU) and polyethersulfone (PES). We anticipate that this review will provide an overall perspective on the current status and future trends of this emerging field.

Keywords Super engineering plastics; Chemical recycling/upcycling; Depolymerization; Functionalization

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INTRODUCTION

Due to their low cost, excellent performance, and ease of versatile molding and processing, polymers have played an indispensable role in modern life and the global economy.[1−3] In polymer science, general plastics are typically categorized based on their thermal property into three classes: general-purpose plastics (GPPs) with glass transition temperature T_g<100 °C, engineering plastics (EPs) with T_g between 100–150 °C, and super engineering plastics (SEPs) with T_g>150 °C (Fig. 1).[4] Particularly, super engineering plastics in the pyramid tip such as poly(phenylene sulfide) (PPS) and poly(aryl ether)s—including polyether ether ketone (PEEK), polysulfone (PSU), polyphenylsulfone (PPSU), polyethersulfone (PES), polyimide (PI) and polyetherimide (PEI)—have been extensively utilized in high-end applications ranging from aerospace and automotive industries to electronics and medical devices, owing to their high thermal stability and chemical resistance.[5] However, the non-biodegradability of these plastics has resulted in a substantial accumulation of waste, posing a severe environmental challenge.[6,7]

Over the past decades, significant contributions have been made to develop new chemical protocols for depolymerization of plastic waste, which are among the most promising and sustainable solutions for the circular plastic economy to decrease the amount of disposed plastics contaminating the environment and reduce the greenhouse gas emissions

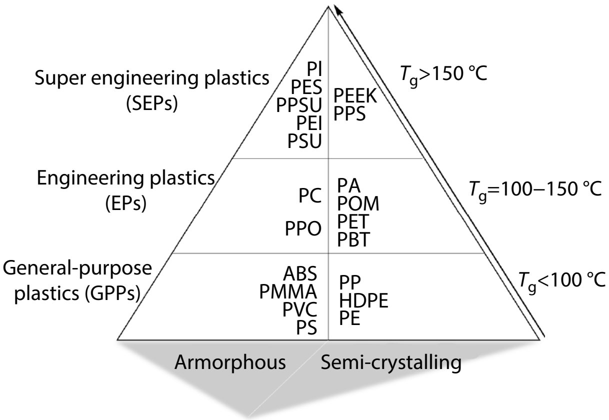

Fig. 1 Plastic pyramid in polymer science. General-purpose plastics: polyethene (PE), high density polyethylene (HDPE) polypropene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), acrylonitrile butadiene styrene copolymer (ABS), and poly(methyl methacrylate) (PMMA). Representative engineering plastics (EPs): polycarbonate (PC), poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), polyoxymethylene (POM), poly(phenylene oxide) (PPO), and polyamides (PAs).

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caused by the manufacturing of virgin plastics.[8−10] Because of the high bond-dissociation energies for specific aromatic carbon-carbon and carbon-heteroatom bonds, as well as the robust rigidity of polymer chains, the chemical recycling/upcycling of SEPs are of great challenge. While there have been efforts to explore possible chemical recycling methods, the examples remain limited, though those that exist are considered decisive in advancing the field.

In this review, we would like to discuss the representative accomplishments and mechanism insights on chemical protocols achieved in depolymerization and functionalization of super engineering plastics into monomers or oligomers, especially for polyphenylene sulfide (PPS), poly(aryl ether)s including polyether ether ketone (PEEK), polysulfone (PSU), polyphenylsulfone (PPSU) and polyethersulfone (PES). The "depolymerization" step primarily refers to the cleavages of chemical bonds or scissions of polymer main chains, while the "functionalization" step involves the installations of new functional groups or formations of new chemical bonds after "depolymerization" step. We anticipate that this review will provide an overall perspective on the current status and future trends of this emerging field.

DEPOLYMERIZATION INTO VALUABLE CHEMICALS

Depolymerization and Functionalization of PPS

PPS consists of alternating benzene rings and sulfur atoms, which was first produced by Phillips petroleum company in the 1960s.[11] PPS represents one of the most widely used high-performance thermoplastic resins due to its excellent heat resistance, flame retardancy, insulation properties, high strength and hardness. In 2022, the global PPS market attained a volume of 3631.95 hundred tonnes experiencing a growth of 6.6% (2019–2022), expected to reach \$2.5 billion by 2030.[12] The significant rigidity and regularity of PPS chains makes it difficult to deform under extreme high-temperature and high-humidity conditions and allow it to exhibit excellent resistance to solvents and chemical corrosion, thus posing great challenges for its depolymerization.

In the 1990s, Yu and co-workers discovered that high molecular weight PPS could react with 50% amount of sodium sulfide (Na_2S) in the assistance of NaOH (33 mol%) in hexamethylphosphoramide (HMPA), yielding PPS-oligomers at temperatures above 220 °C for 4 h under atmospheric pressure. The number-average molecular weight (M_n) of PPS decreased from *ca*. 9328 g/mol to 367 g/mol. This depolymerization process was an efficient route for the preparation of thiol-terminated PPS oligomers (Fig. 2).[13]

Later, Meng's group developed a modified nucleophilic substitution method for PPS with Na_2S (Fig. 3).[14] When treated with one equivalent of Na_2S in the presence of potassium carbonate (K_2CO_3, 28 mol%) in 1-methylpyrrolidone (NMP) at 170–175 °C for 48 h, PPS was depolymerized into mixtures of aromatic dithiols or corresponding oligomers, offering a direct way to prepare thiol-terminated aromatic dithiols. Notably, these obtained aromatic dithiols can undergo copper-catalyzed oxidative head-to-end cyclization with oxygen to form macrocyclic disulfide oligomers, which were further transferred into high-molecular weight polydisulfides through ring-opening polymerizations.

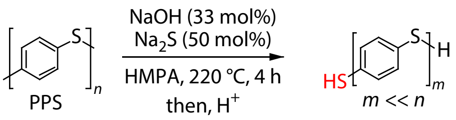


Fig. 2 Depolymerization of PPS into oligomers.

Metathesis reactions that involve the interchange of two functional groups between two reactants, are one the most powerful molecular transformations in synthetic organic chemistry. In 2017, Morandi and co-workers developed a palladium-catalyzed carbon-sulfur bond metathesis reaction between aryl thioethers and alkyl thiols (Fig. 4).[15] The use of a Pd-NHC (NHC = *N*-heterocyclic carbene) catalyst with LiHMDS (HMDS = hexamethyldisilazane) as the base in toluene facilitated the proposed carbon-sulfur oxidative addition, rapid thiolate ligand exchange and reductive elimination processes kinetically accessible. Various readily available aryl methyl thioethers successfully reacted with alkyl thiols under the optimal conditions to access alkyl aryl thioethers with moderate to high yields. This reaction exhibited broad functional group tolerance. In addition, this catalytic system could cleave various unprotected thiophenols in *o*-xylene. The Pd-catalyzed carbon-sulfur bond metathesis was then applied to the depolymerization of PPS. Compared to the previous depolymerizations of PPS, which generally formed complex mixtures of sulfur containing compounds. In contrast, the gram-scale reaction of PPS (weight average molecular weight, M_w=~10000 g/mol) with four equivalents of cyclopentanethiol was conducted in the presence of 0.8 mol% of Pd-catalyst and 7.8 equiv. of LiHMDS in *o*-xylene at 140 °C for 12 h, providing the single product 1,4-bis(cyclopentylthio)benzene in 85% yield. The *para*-substituted benzene-1,4-dithioether is a promising synthetic precursor for constructing organic light-emitting diodes (OLEDs).

Recently, Yamaguchi, Yatabe and co-workers developed a $Pd(OAc)_2/PCy_3$ catalyzed direct cross-metathesis of diaryl

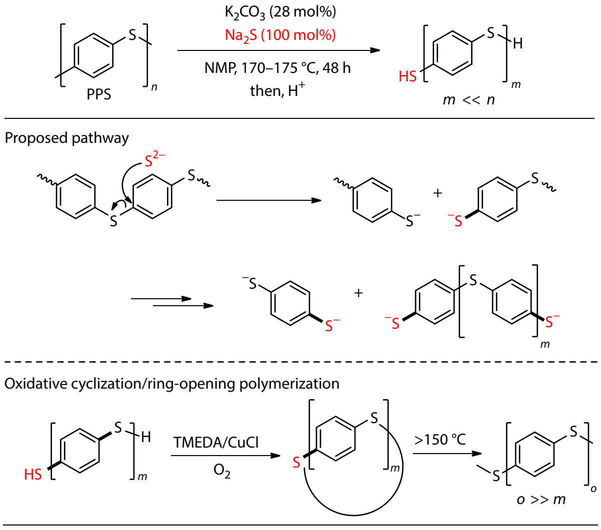


Fig. 3 Depolymerization and repolymerization of PPS.

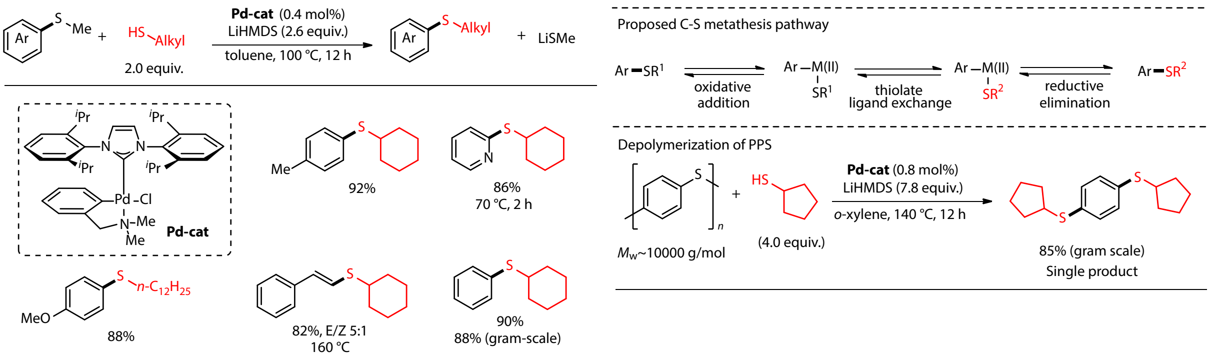


Fig. 4 Palladium-catalyzed depolymerization of PPS *via* carbon-sulfur bond metathesis reaction with alkyl thiols.

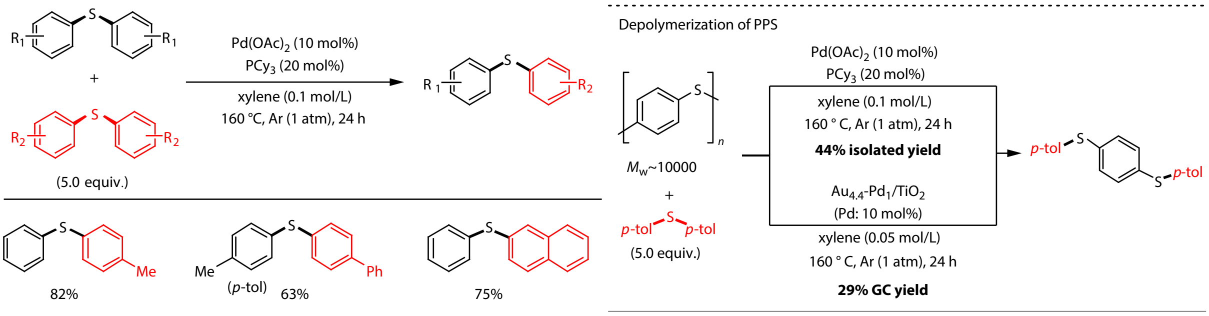


Fig. 5 Palladium-catalyzed depolymerization of PPS *via* carbon-sulfur bond metathesis reaction with aryl thioethers.

thioethers without the use of free thiols and basic additives, enabling the formations of unsymmetric diaryl thioethers bearing base-sensitive or electrophilic functionalities (Fig. 5).[16] Notably, in the presence of 10 mol% of Pd(OAc)$_2$ and 20 mol% of PCy$_3$, the reaction of PPS with 5 equiv. of di-*p*-tolylsulfane was conducted in xylene (0.1 mol/L) at 160 °C under Ar (1 atm) for 24 h, providing 1,4-bis(*p*-tolylthio)benzene in 44% isolated yield. Further characterization and control experiments indicated that the *in situ* formed homogeneous Pd(0) nanocluster species with multiple active surface sites, served as the active species for these diary thioether transformations.

Very recently, the same group achieved similar diaryl thioethers metathesis reaction catalyzed by a heterogeneous Au$_{4.4}$-Pd$_1$/TiO$_2$ alloy nanoparticle catalyst (Fig. 5).[17] When the Pd ensembles were diluted by Au alloying, the changed adsorption mode of thioethers on the nanoparticles lowered the adsorption/desorption energy and enabled aryl C—S bond metathesis, which was proved by catalyst characterization and density functional theory (DFT) calculations. Moreover, the intermediates generated from the oxidative addition of sulfides onto Pd species could be transferred to Au species without the formation of highly stable structures thereby allowing direct thioether metathesis with a broad substrate scope and functional group tolerance. Under the optimal conditions, the depolymerization of PPS afforded the desired product with a 29% GC yield. The catalyst could be regenerated through calcination in air followed by reduction with NaBH$_4$, yet with much decreased catalytic efficiency after two cycles.

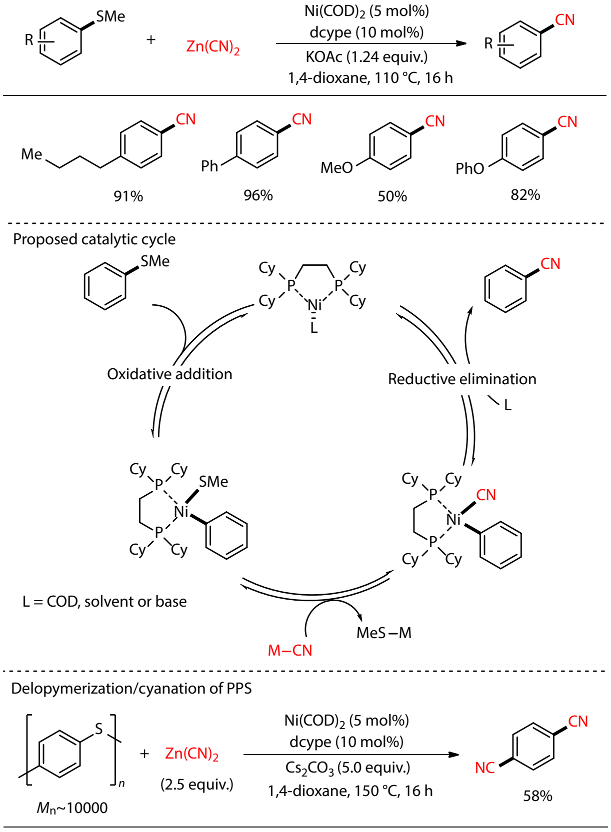


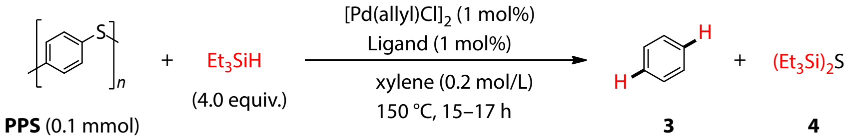
Fig. 6 Nickel-catalyzed delopymerization/cyanation of PPS.

Transition metal-catalyzed direct C—S bond functionalization of thioethers offered a new and rapid platform for carbon-carbon and carbon-heteroatom bond formations. In 2021, the Morandi group reported an efficient nickel-catalyzed cyanation of aryl thioethers (Fig. 6).[18] In the presence of 5 mol% of low-valent Ni(COD)$_2$, 10 mol% of 1,2-bis(dicyclohexylphosphanyl)ethane) (dcype) and 1.24 equiv. of potassium acetate (KOAc), the reactions of various aryl thioethers with $Zn(CN)_2$ were performed in 1,4-dioxane (0.5 mol/L) at 150 °C for 16 h to access aryl nitriles with high efficiency. In the proposed catalytic cycle, the reaction of generated active Ni(I)-species with thioethers *via* oxidative addition formed Ar—Ni(II)—SR intermediates, which reacted with $Zn(CN)_2$ through transmetalation to afford the complex Ar—Ni(II)—CN with the release of $(RS)_2Zn$ salt. Finally, directed reductive elimination occurred to give aryl nitriles and regenerate active Ni(I)-species. Under a modified reaction conditions using $CsCO_3$ as the base at slightly higher temperature, the reaction of PPS with 2.5 equivalents of $Zn(CN)_2$ provided the corresponding terephthalonitrile in 58% yield.

In 2021, the Minami and Nakajima group disclosed a protocol for the hydrofunctionalization of PPS (Fig. 7).[19] Inspired by work developed by Morandi and co-workers, it was found that the singacycle-A1 palladium catalyst could facilitate the reaction of PPS with triethylsilane, forming benzene and 1,1,1,3,3,3-hexaethyldisilathiane in high yields (entry 1). When the reactions were performed with $Pd(allyl)Cl_2$ with a phosphine ligand, lower yields were obtained (entries 2 and 3). NHC ligand showed higher efficiency and the IcHex-HCl gave the best result (entries 4–9). This reaction could give competitive yields of the products when conducted at lower temperature for a longer time (entry 10). Under a modified condition, a 10 mmol scale reaction of PPS with triethylsilane in the presence of low loading of catalyst/ligand in concentrated solution afforded benzene in 72% NMR yield and 1,1,1,3,3,3-hexaethyldisilathiane in 77% isolated yield, respectively. In the proposed pathway, the C—S bond in PPS was firstly cleaved by triethylsilane assisted by the palladium catalyst to form an aryl–H bond and Si—S bond. Then, the other aryl-S bonds in PPS-residual were cleaved continuously to form aryl–H bonds, releasing the benzene product and 1,1,1,3,3,3-hexaethyldisilathiane as by-product.

Depolymerization and Functionalization of Sulfone-Containing Poly(arylene ether)s

Sulfone-containing poly(arylene ether)s, commonly known as polysulfones (PSFs), are typical amorphous thermoplastic resins consisting of inert aryl sulfonyl and aryl ether moieties in polymer backbones.[20] Commercially available PSFs materials based on different synthetic monomers, are divided into polysulfone (PSU), polyether sulfone (PES), polyphenylene sulfone (PPSU) and analogues (Fig. 8). These polymers with extremely high T_g exhibit high molecular stability, transparency, hydrolysis stability, chemical resistance, excellent mechanical properties and biocompatibility, which are widely used in a large number of end-user industries including food processing, automotive, aerospace, healthcare, and electronics. In 2020, the global mar-



Entry	Ligand	Yield [b] 3	Yield [b] 4
1	Singacycle-A1 (1 mol%)	78	96
2	PCy_3	24	28
3	$P(1\text{-}Ad)_3$	50	45
4	IMes-HCl/KO*t*Bu (1 mol%)	50	72
5	SIMes-HCl/KO*t*Bu (1mol%)	73	85
6	IPr	83	99
7	SIPr-HCl/KO*t*Bu (1 mol%)	2	34
8	IcHex-HCl/KO*t*Bu (1 mol%)	89	>99
9	IAd-HBF_4/KO*t*Bu (1 mol%)	53	58
10 [a]	**IcHex-HCl/KO*t*Bu (1 mol%)**	**77**	**83**

[a] 100 °C for 66 h; [b] NMR yield.

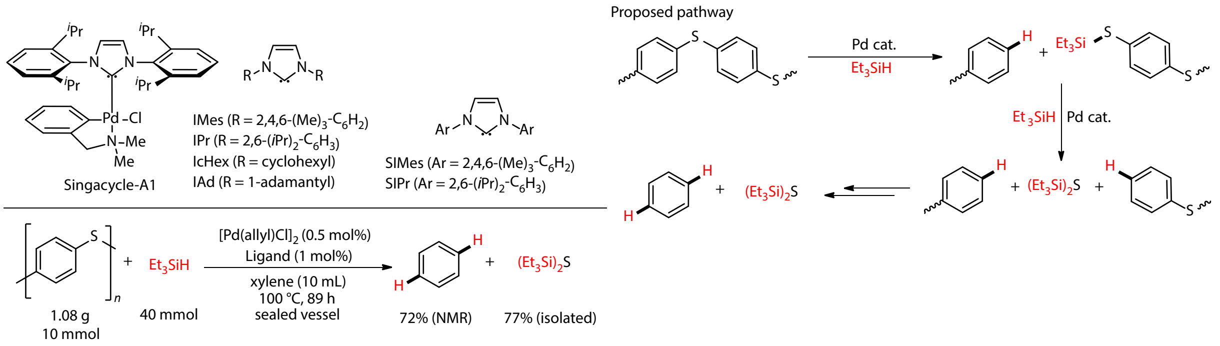


Fig. 7 Palladium-catalyzed reductive delopymerization of PPS.

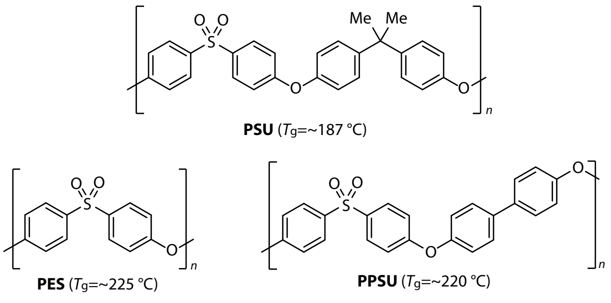


Fig. 8 Typical sulfone-containing poly(arylene ether)s.

ket size of sulfone polymers was valued at USD 1.66 billion in 2020 and was anticipated to grow at a CAGR of 4.9% from 2021 to 2027.[21] The increasing demand for sulfone-containing poly(arylene ether)s drives efforts to address the challenges of recycling and utilizing sulfone-containing poly(arylene ether)s plastics.

In 2013, a hydroxylation depolymerization of PES in subcritical water in the presence of sodium hydroxide at average 300 °C was developed by Yoshida and Fukunaka's group (Fig. 9). However, this protocol showed lower efficiency and poor selectivity, resulting in mixtures of functionalized diphenyl sulfones in much lower yields. This seminal nucleophilic substitution showed the possibility of the cleavages of carbon-oxygen bond within PES chains.

Ten years later, Minami and co-workers achieved the depolymerization of super engineering plastics by hydroxylating the oxy-phenylene main chain with alkaline nucleophiles *via* the selective cleavage of carbon-oxygen bonds (Fig. 10).[22] For the depolymerization of the PSU pellet (M_n=~16.0 kg/mol), four equivalents of cesium hydroxide monohydrate ($CsOH·H_2O$) as the hydroxyl source and 4 equiv. of calcium hydride (CaH_2) as the dehydrating agent in 1,3-dimethyl-2-imidazolidinone (DMI) were employed at 150 °C for 17 h, giving monomers including bisphenol S (BPS) and bisphenol A (BPA) in high yields after quenching by HCl, respectively. The uses of other hydroxides such as NaOH and KOH, other dehydrating agents including molecular sieve 4 Å, $MgSO_4$, CaO and $CaCl_2$ showed poor efficiency. And other solvents such as NMP was proved to decompose under current conditions. When the reaction of PSU was conducted at 5 mmol scale, BPS and BPA were obtained in 72% yield and 58% yield, respectively. Control experiments and DFT calculations demonstrated that the *para*-aryloxyl/oxygen anion of the sulfonyl group significantly enhanced the reactivity of aryl—O bond cleavages and maintained aryl—SO_2 bonds, facilitating the selective carbon-oxygen bond cleavage of PSU chains. The generated BPS could be transferred into 4,4'-sulfonylbis(fluorobenzene) in two-steps in moderate yield, which is the synthetic monomer for sulfone-containing poly(arylene ether)s with corresponding bisphenols.

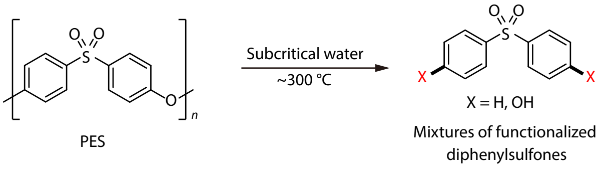


Fig. 9 Delopymerization of PES in subcritical water.

The depolymerization/hydroxylation method was well compatible with other super engineering plastics (Fig. 11).[22] For example, in the presence of three equivalents of $CsOH·H_2O$, the reaction of PES pellets conducted at 150 °C for 4 hours, BPS was obtained in 92% yield without the addition of CaH_2. Under the optimal conditions, the depolymerization/hydroxylation of PPSU powder successfully gave BPS and 4,4'-dihydroxybiphenyl in 87% yield and 80% yield, respectively. Notably, PPSU pellets cut from commercial baby bottles were also investigated, smoothly giving BPS and 4,4'-dihydroxybiphenyl in 64% yield and 77% yield, respectively. In addition, when polyetherethersulfone（PEES）was subjected to the optimal conditions, mixtures of BPS products, 1,4-hydroquinone and 4-((4-(4-hydroxyphenoxy)phenyl)sulfonyl)phenol (BPS-HQ-type dimer) were obtained in yields of 55%, 27% and 27%, respectively. Interestingly, when replacing $CsOH·H_2O$ with KOH, the BPS-HQ-type dimer was isolated in

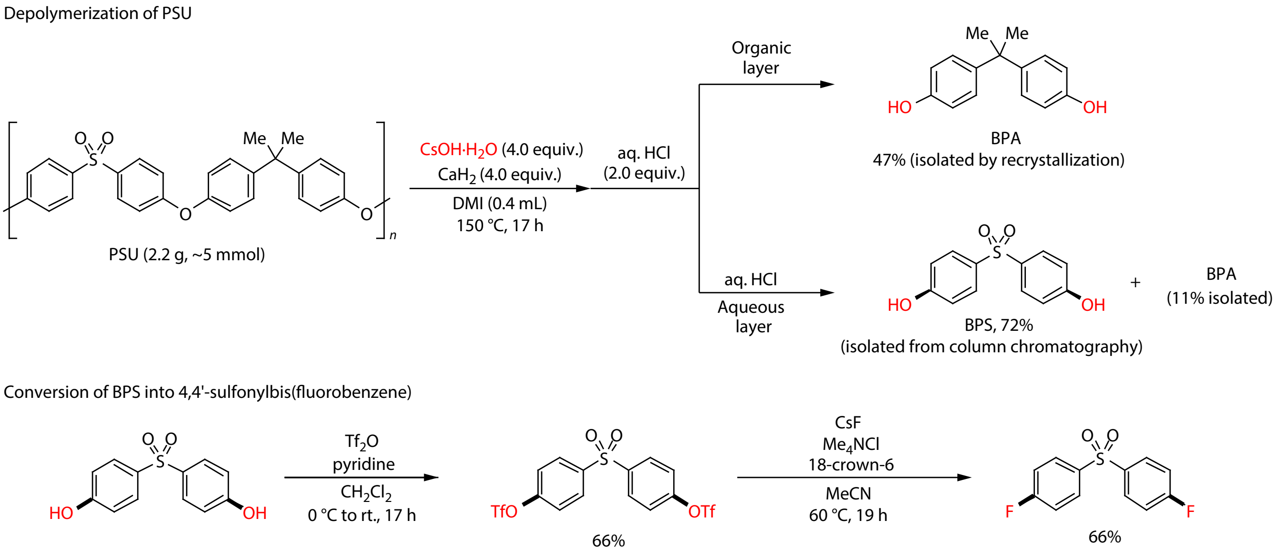


Fig. 10 Delopymerization/hydroxylation of PSU and further transformation.

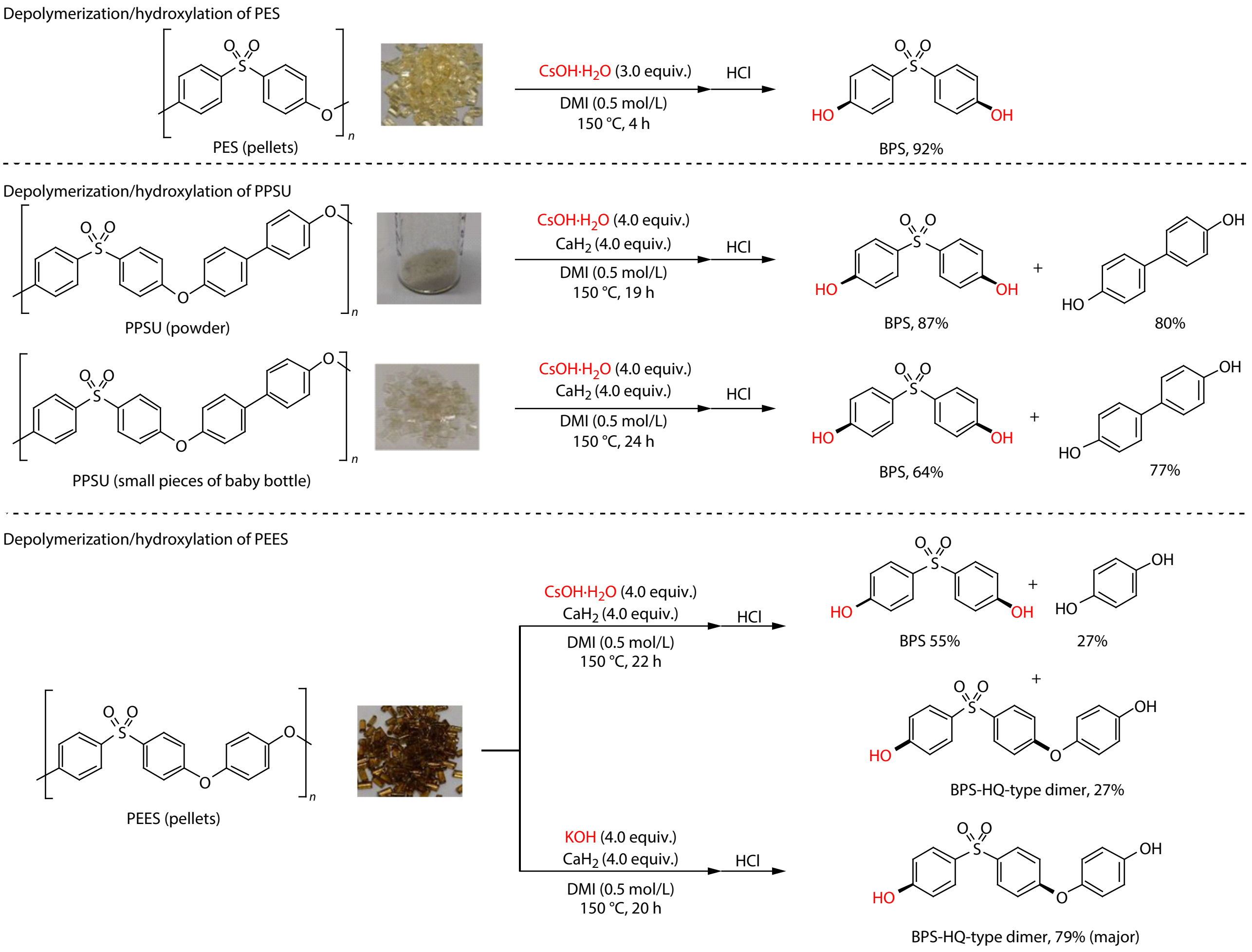


Fig. 11 Depolymerization/hydroxylation of PPSU, PSU and PEES.

79% yield as a major product.

Photocatalysis facilitates reactivity up-conversions by harnessing the energy of visible light. Over the past decades, photocatalysis has emerged as a sustainable strategy in organic synthesis.[23] Building on continuous studies of photoinduced functionalization of aromatics and chemical upcycling of plastics,[24] the Jiang group recently achieved a photoinduced $UO_2(NO_3)_2{\cdot}H_2O/ZnBr_2$ co-catalyzed depolymerization and hydroxylation of PES resin with water as oxygen source (Fig. 12).[25] In the presence of 5 mol% of $UO_2(NO_3)_2{\cdot}H_2O$, 10 mol% of $ZnBr_2$ and one equivalent of Cl_3COOH, the reaction of PES in mixed dichloromethane/acetone (10/1) under the irradiation of blue LEDs (460 nm, 9 W) was conducted to give BPS in an average 25% yield through the cleavage of carbon-oxygen bond. The O^{18}-labeling experiment indicated that the oxygen atom of BPS originally came from H_2O. In the proposed catalytic cycle, fact, the excited uranyl salts oxidize to form peroxide uranyl dimers with H_2O. Under light irradiation, the excited $*UO_2^{2+}$ underwent a single-electron transfer (SET) process assisted by $ZnBr_2$ with PES to generate UO_2^{+} species and radical cations, which reacted with uranyl peroxide dimer through oxygen-atom transfer (OAT) process to afford phenol cationic free radicals and release phenols. The repeated SET and OAT processes finally resulted the depolymerization of PES. This photoinduced strategy offered a new route for the chemical upcycling of PES under room temperature, avoiding the addition of strong bases and the use of high-temperature.

Despite the depolymerization/hydroxylation reactions, Minami and co-workers then discovered that alcoholysis reactions of super engineering plastics occurred selectively under mild conditions (Fig. 13).[26] By treating model PSU with methanol in DMI, and promoting the reaction with 2.2 equivalents of sodium hydroxide at 80 °C, bis(4-methoxyphenyl) sulfone (BPS-Me_2) and BPA could be easily formed in 92% and 97% yields, respectively. A gram-scale depolymerization/methanolysis reaction of PSU in the presence of 30 mmol of MeOH, 5.6 equiv. of NaOH in DMI (5.0 mL) proceeded smoothly at 80 °C for 28 h, yielding di(4-methoxyphenyl) sulfone and BPA in 61% yield and 66% yield, respectively.

Other alcohols were also tested under the optimal conditions. When replacing MeOH with 6 equiv. of EtOH or *i*-PrOH, the corresponding reaction of PSU heated at 100 °C also furnished the desired depolymerization products, di(4-ethoxyphenyl) sulfone and BPA, with yields of 54% and 83%, respectively. Similarly, bis(4-isopropoxyphenyl) sulfone and BPA were obtained in yields of 49% and 51%, respectively, from the reaction performed with 6 equiv. of *i*-PrOH instead

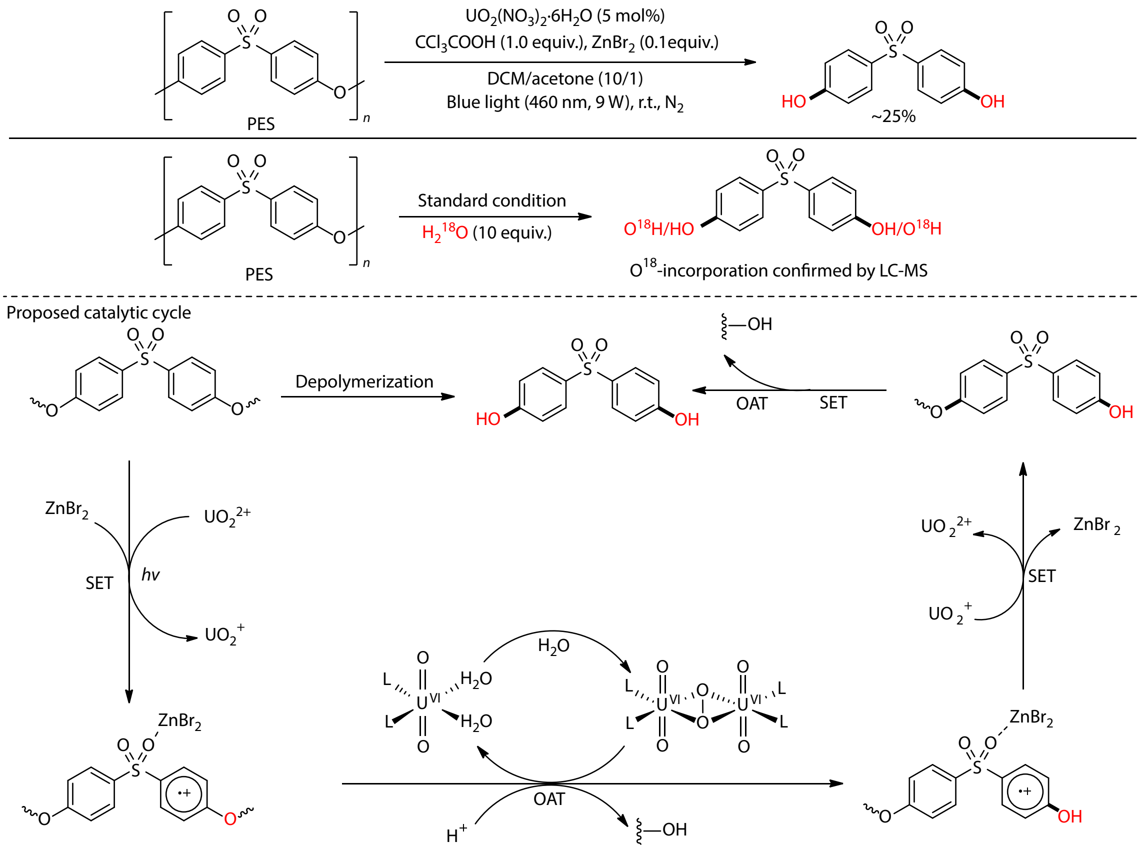
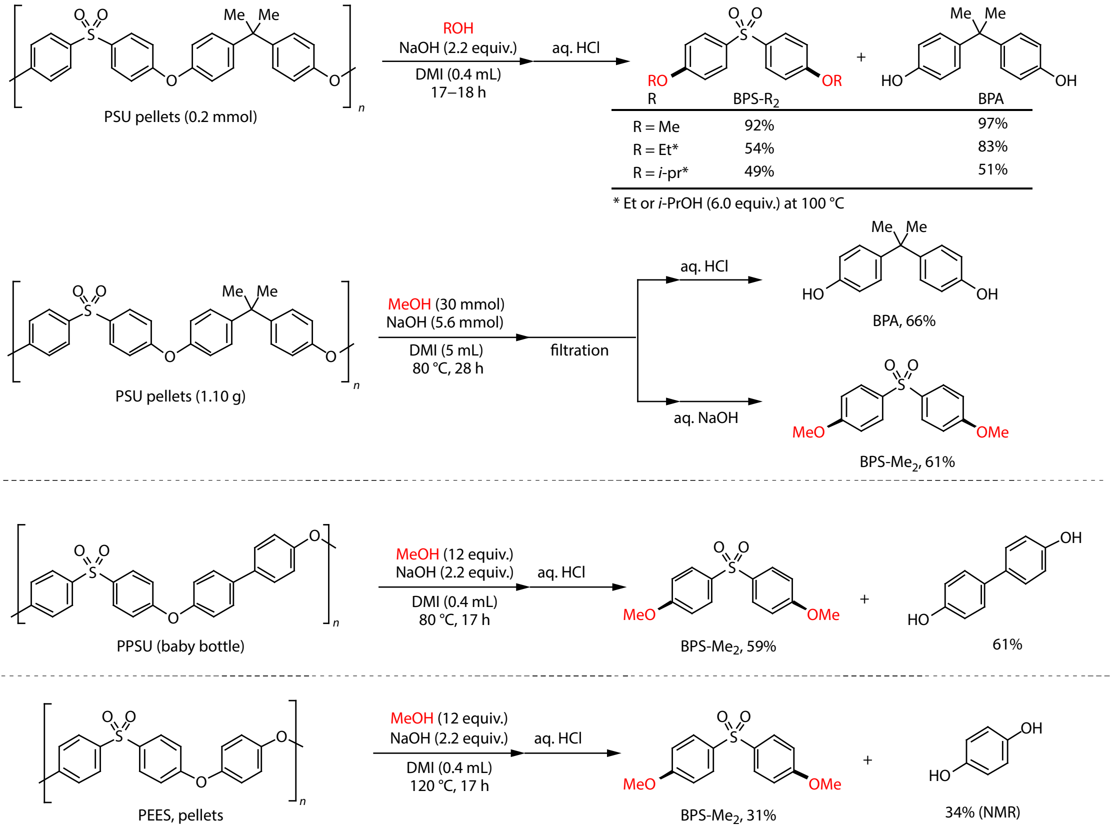


Fig. 12 Photoinduced uranium-catalyzed depolymerization/hydroxylation of PES.



R	$BPS-R_2$	BPA
R = Me	92%	97%
R = Et*	54%	83%
R = *i*-pr*	49%	51%

* Et or *i*-PrOH (6.0 equiv.) at 100 °C

Fig. 13 Depolymerization/alcoholysis of sulfone-containing poly(arylene ether)s.

of MeOH. Moreover, the protocol was then applied for the depolymerization/methanolysis reaction of other PSU analogues. A PPSU pellets cut from postconsumer baby bottles could smoothly give BPS-Me_2 and 4,4'-dihydroxybiphenyl in 59% and 61% yields, respectively. PEES could also undergo depolymerization/methanolysis reaction at 120 °C, forming the corresponding products with satisfactory yields. These results indicated that the depolymerization reactivity could be attributed to the structure of the main chain and the nucleophilicity of the alcohol. In this protocol, the role of NaOH as an activator was proposed to accelerate the reaction by excluding one product from the reaction system and facilitated product separation by simple filtration.

The depolymerization of sulfone-containing poly(arylene ether)s to form carbon-nitrogen bond has also been achieved by Zhu and co-workers (Fig. 14).[27] Studied on an aminolytic depolymerization reaction of PSU and PES with organic amines were conducted and analyzed by NMR spectra and GPC. The reactions were proposed to undergo a S_N2-type mechanism, where the aryl carbon-oxygen bond carbon in the aryl ring with a *para*-sulfonyl substituent was attacked by a free amine, yielding the new polymers with less than 5 mol% of amino groups. This method offered a feasible approach for material modification, especially surface functionalization by introducing active amino and hydroxyl groups to the end of the polymer chain.

Thiols represent a typical class of nucleophile in organic synthesis. Recently, depolymerization/thiolation reaction of sulfone-containing polymers with thiols enabled by P_4-*t*Bu catalyst was developed (Fig. 15).[28] This reaction showed

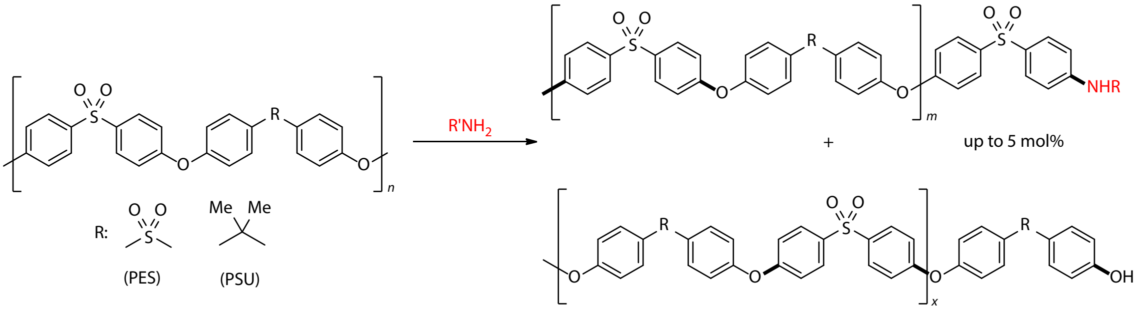


Fig. 14 Aminolytic depolymerization reaction of PSU and PES.

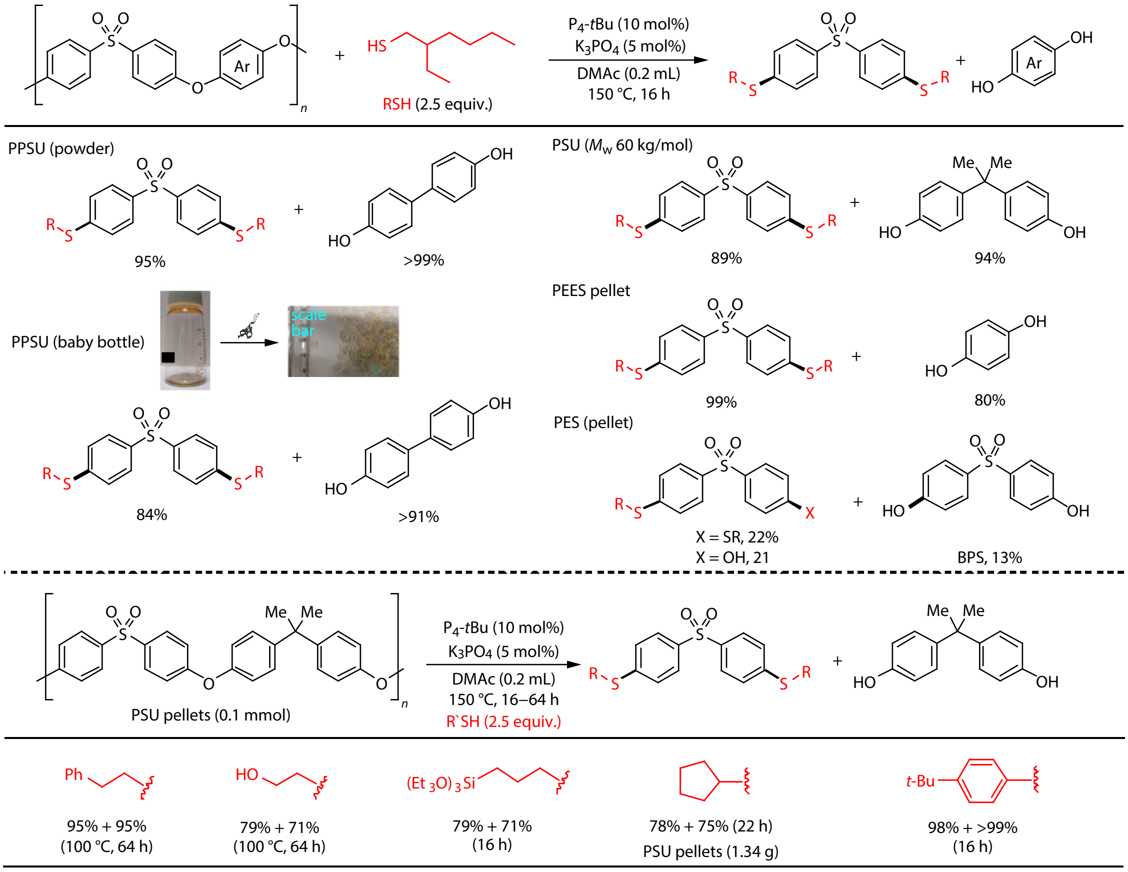
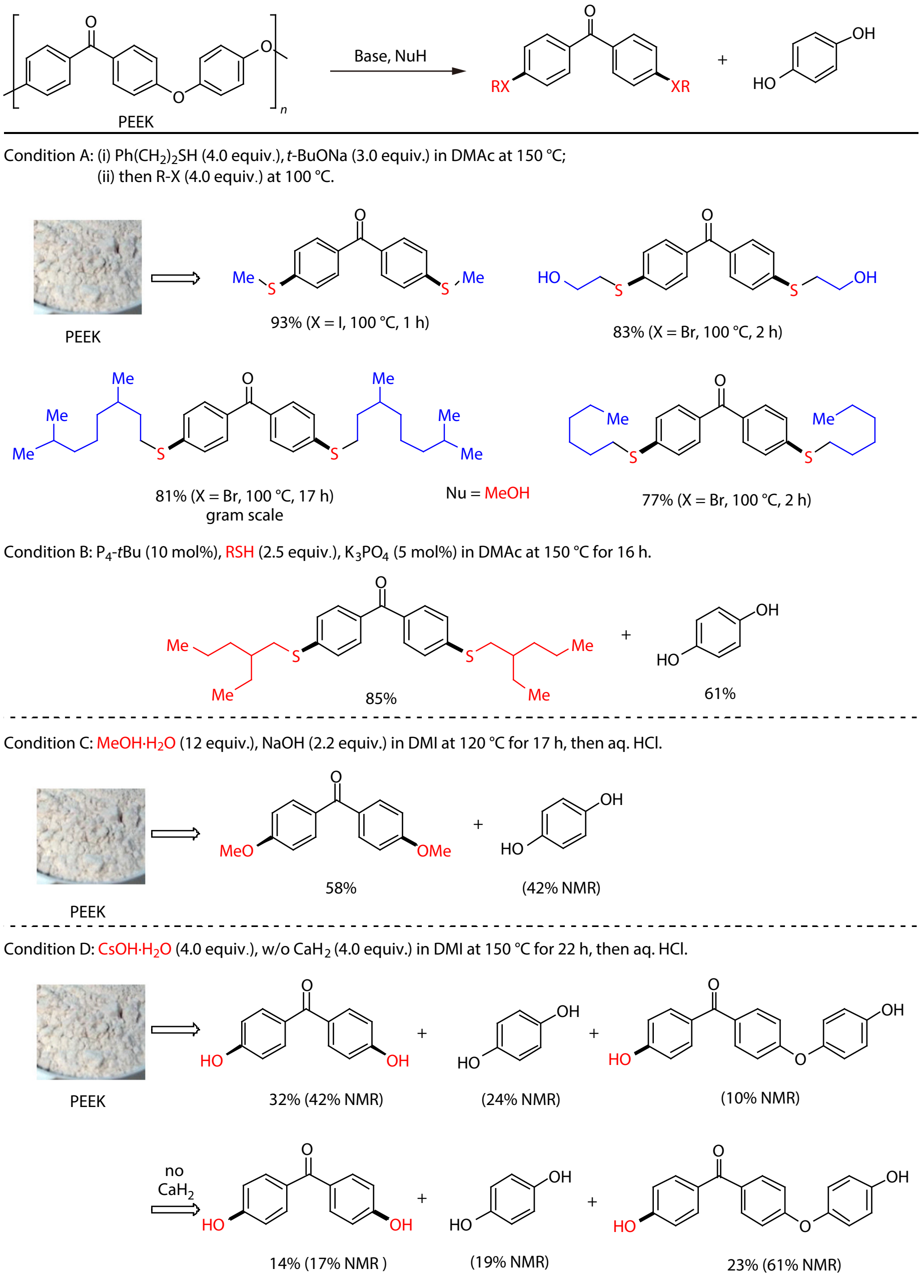


Fig. 15 P_4-*t*Bu-catalyzed depolymerization/thiolation reaction of PSFs.

same chemo- and regio-selectivities with previous depolymerization/alcoholysis of sulfone-containing poly(arylene ether)s. By the usages of P_4-*t*Bu (10 mol%) and K_3PO_4 (5 mol%), the depolymerization/thiolation reaction of PSU (M_w ~60 kg/mol) with 2-ethylhexane-1-thiol (2.5 equiv.) in dimethylacetamide (DMAc) heated at 150 °C for 16 h, yielding the desired aryl thioether and phenol in 89% and 94% yields, respectively. PEES, PPSU resins and plastic from baby bottles were well tolerated, providing the corresponding products in high yields. When PES was examined under the standard conditions, however, mono-/di-thioether and BPS were generated, yet with lower yields. A variety of primary and secondary alkyl thioethers and aryl thioethers reacted smoothly with PSU pellets under the optimal conditions, accessing the desired products in excellent yields. To demonstrate the scalability of the depolymerization protocol, a gram-scale reaction of PSU (1.34 g) with cyclopentanethiol in the presence of 5 mol% P_4*t*Bu and K_3PO_4, could provide the thiothers in 78% and BPA in 75% yields, respectively.

Depolymerization and Functionalization of PEEK

PEEK is a semi-crystalline thermoplastic consisting of repeating aromatic rings, ketone, and ether moieties, with the melting point reaching 334 °C, making it suitable for high performance engineering applications.[29] PEEK can generally maintain high wear resistance and low friction coefficient at a high tempera-



Condition A: (i) $Ph(CH_2)_2SH$ (4.0 equiv.), *t*-BuONa (3.0 equiv.) in DMAc at 150 °C;
(ii) then R-X (4.0 equiv.) at 100 °C.

Condition B: P_4-*t*Bu (10 mol%), RSH (2.5 equiv.), K_3PO_4 (5 mol%) in DMAc at 150 °C for 16 h.

Condition C: $MeOH{\cdot}H_2O$ (12 equiv.), NaOH (2.2 equiv.) in DMI at 120 °C for 17 h, then aq. HCl.

Condition D: $CsOH{\cdot}H_2O$ (4.0 equiv.), w/o CaH_2 (4.0 equiv.) in DMI at 150 °C for 22 h, then aq. HCl.

Fig. 16 Depolymerization/nucleophilic substitution of PEEK.

ture of 250 °C, with a tensile strength of up to 100 MPa. It is widely used in the transportation industry, accounting for about 40.2%. In recent years, several chemical protocols that enable the depolymerization of PEEK have been developed.

By taking advantages of the strong nucleophilicity of thiols, Minami and co-workers developed a depolymerization/functionalization of PEEK resins (Fig. 16).[30] In the presence of three equivalents of sodium *tert*-butoxide (*t*-BuONa) as the base, 4 equiv. of phenylethyl thiol as the nucleophile, the reaction of a PEEK powder (M_w~2.08×10^4) in DMI was heated at 150 °C for 20 h, and then quenched with methyl iodide at 100 °C for 1 h, proceeding to give the desired monomer product, 4,4′-dimethylthiobenzophenone in 93% isolated yield. Under the standard conditions, various electrophilic reagents such as alkyl halides and acyl chlorides were investigated, yielding the corresponding dithiofunctionalized benzophenones and thioesters in moderate to high yields. Functional groups including vinyl, ether, free hydroxyl and ester groups were well tolerated. It was worth noting that a gram scale reaction was also achieved in high efficiency. Particularly, the method was highly compatible with PEEK materials containing 30 wt% carbon fiber or glass fiber reinforcement. Using the catalyst combination of P_4-*t*Bu (10 mol%) and K_3PO_4 (5 mol%), the reaction of a PEEK powder (M_w ~2.08×10^4) with 2-ethyl-1-hexanethiol (2.5 equiv.) was conducted in 1,3-dimethyl-2-imidazolidinone (0.5 mol/L) at 150 °C for 16 h. This process yielded the desired dithiofunctionalized benzophenone in 85% yield and hydroquinone in 61% yield, respectively. Additionally, the resulting disulfide-functionalized aromatics can be converted into sulfonium cations through further fluorination or arylation reactions, offering new routes for the conversion of PEEK into new chemicals.[28]

Moreover, the two aforementioned methods that employed highly oxygen-nucleophilic reagents for the depolymerization of sulfone-containing poly(arylene ether)s, were also utilized to explore the potential for PEEK depolymerization. Using alkoxides as the nucleophiles, PEEK reacted smoothly to furnish the desired bis(4-methoxyphenyl)methanone in 58% yield and hydroquinone in 42% NMR yield, respectively. However, in the presence of $CsOH\cdot H_2O$ and CaH_2, the reaction of PEEK conducted in DMI at 150 °C for 22 h, afforded 4,4'-dihydroxybenzophenone, hydroquinone and (4-(4-hydroxyphenoxy)phenyl)(4-hydroxyphenyl)methanone in lower yields. In the absence of CaH_2, 4,4'-dihydroxybenzophenone and (4-(4-hydroxyphenoxy)-phenyl)(4-hydroxyphenyl)methanone coud be isolated in 14% and 23% yields, respectively.[22]

CONCLUSIONS AND PERSPERCTIVES

In summary, we have showcased the latest advancements in the depolymerization and functionalization of super engineering plastics into valuable monomers *via* chemical protocols, particularly for PPS, sulfone-containing poly(arylene ether)s, and PEEK. Although research on the depolymerization reactions of these materials is still in its early stage, several aspects should be stressed in future studies. Firstly, the scope of reactions remains limited. For PPS depolymerization, only a few low-valent Pd-/Ni-catalyzed carbon-sulfur functionalization reactions have been developed. For sulfone-containing poly(arylene ether)s and PEEK, research has predominantly concentrated on classical nucleophilic substitutions with highly active reagents. Secondly, these achievements typically require high catalyst loadings or harsh conditions, such as the use of excess or catalytic amounts of strong bases or elevated temperatures (generally exceeding 100 °C, even at 150 °C). Although the preliminary attempts have been made using emerging photocatalysis strategy, the efficiency remains suboptimal under milder conditions. Therefore, expanding the reaction scope, designing and developing highly efficient and innovative chemical protocols that enabled the depolymerization/functionalization of super engineering plastics under milder conditions will be essential for advancing a sustainable plastic circular economy.

BIOGRAPHIES

Yinsong Zhao is a professor (Zijiang Young Researcher) at East China Normal University since 2022. He received his BS degree in 2013 and PhD degree in 2018 from Sichuan University under the guidance of Professor Ge Gao and Jingsong You. From 2018 to 2021, he worked as a research fellow at National University of Singapore. He then worked as a research assistant/associate professor in the research group of Professor Dawei Ma at Southern University of Science and Technology from 2021 to 2022. His current research interests are focused on transition-metal-catalyzed and/or photoinduced inert C–H/C–X bond functionalization of small molecules and polymers.

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Conflict of Interests

The authors declare no interest conflict.

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