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Controlled degradation of chemically stable poly(aryl ethers) via directing group-assisted catalysis†

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To establish a sustainable society, the development of polymer materials capable of reverting into monomers on demand is crucial. Traditional methods rely on breaking labile bonds such as esters in the main chain, which limits applicability to polymers that consist of robust covalent bonds. We found that the integration of directing groups allowed the engineering of resilient polymers with built-in recyclability. Our study showcases phenylene ether-based polymers fortified with directing groups, which can be selectively disassembled under nickel catalysts via selective cleavage of carbon–oxygen bonds. Notably, these polymers exhibit exceptional chemical stability towards acids, bases, and oxidizing agents, while being degradable to well-defined, repolymerizable molecules in the presence of a catalyst. Our findings allow for the development of next-generation polymer materials that are chemically recyclable by design.

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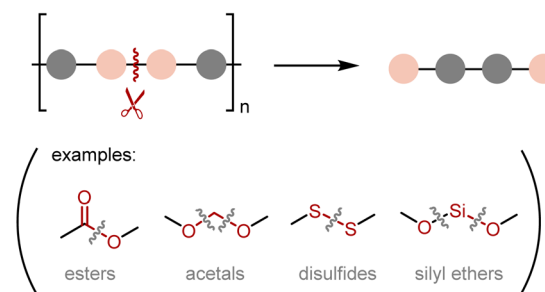
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Introduction

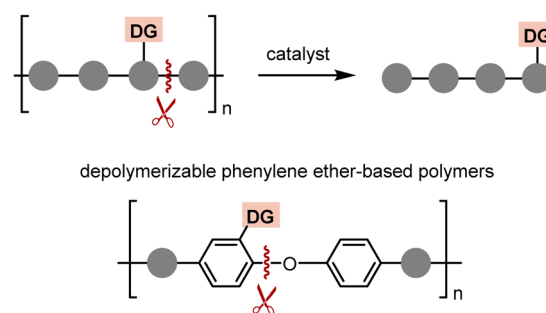
Serious concerns about the long-term environmental impact caused by plastic pollution are prompting us to transition away from single-use plastics toward a more sustainable and circular polymer economy.¹ To this end, mechanical recycling has been implemented on an industrial scale. However, the physical properties of the recycled materials are frequently compromised compared to the original ones, and mechanical recycling cannot be universally applied to all plastics.² A more ideal approach is chemical recycling, wherein polymers are transformed back into monomers or other well-defined small molecules that could subsequently be repolymerized.³ Although this approach is appealing in principle, successful examples have primarily been limited to the polymers that contain chemically labile bonds in their main chains encompassing esters,⁴ acetals,⁵ disulfides,⁶ and silyl ethers⁷ (Fig. 1a). Polymers that consist of strong covalent bonds, such as C–C or C(aryl)–O bonds, often exhibit high robustness, which in turn makes depolymerization into monomers a challenge due to the lack of mild methods that could be used to cleave these bonds. Therefore, only a limited array of techniques has been documented for depolymerizing such polymers. For instance,

polyolefins may be depolymerized by heating above the ceiling temperature (T_{ceiling}), which is defined as the temperature at which the rates of polymerization and depolymerization of

(a) Chemically labile bonds in main chain (common)



(b) Introduction of directing groups (This Work)



DG (directing group) facilitates the cleavage of strong bonds.

Fig. 1 Strategies for the design of depolymerizable polymers.

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these polymers are equal. However, the T_{ceiling} for common robust polyolefins exceeds 400 °C,⁸ which poses difficulties in controlling degradation into well-defined monomers. Alternatively, multi-step post-polymerization modifications⁹ such as C–H oxidation¹⁰ and dehydrogenation¹¹ have been employed to promote the cleavage of C–C bonds in polymer backbones. These methods, however, also tend to yield a mixture of products that are unsuitable for repolymerization.

Herein, we introduce a directing group (DG) that serves as a design principle for depolymerizable polymers devoid of labile chemical bonds in their main chain (Fig. 1b). DG is a heteroatom-containing functional group that coordinates to a transition metal catalyst to facilitate the cleavage of strong covalent bonds by forming a stable metallacyclic intermediate.¹² DGs are strategically used to develop catalytic reactions that involve the activation of strong σ -bonds in low molecular weight compounds.¹³ Surprisingly, however, the DG strategy has not been exploited for the cleavage of the main chain of polymeric materials. It is noteworthy that a DG does not fundamentally alter the thermal and chemical stability of neighboring covalent bonds but rather promotes their cleavage only in the presence of a suitable catalyst. Therefore, the robust nature of parent polymers is anticipated to be preserved with the introduction of DGs.

As a proof-of-concept study, our investigation focuses on assessing the impact of a DG on the depolymerization of polymers containing a phenylene ether unit, because our group demonstrated that the cleavage of a C(aryl)–O bond can be accelerated by a DG in a nickel-catalyzed process.¹⁴ Phenylene ethers serve as crucial structural motifs in several durable polymers, notably, poly(phenylene ether)s (PPEs) and poly(ether ether ketone)s (PEEKs). While previous studies have reported the direct depolymerization of these materials using heterogeneous catalysts,¹⁵ chemical oxidation,¹⁶ or nucleophilic aromatic substitution methods,¹⁷ the resultant degraded products were obtained in forms that were unsuitable for straightforward repolymerization into the parent phenylene ether-based polymers. Herein, we demonstrate that a DG strategy enables the development of phenylene ether-based polymers capable of undergoing degradation to yield well-defined low-molecular-weight compounds, which can subsequently be repolymerized into the parent polymers.

Results and discussion

Preparation of DG-installed polymers

We initiated our studies by investigating the effect of DGs on the efficiency of the catalytic cleavage of a C(aryl)–O bond in model monomeric substrates **1** (Fig. S1†). Building upon our previous studies,^{14a} diphenyl ether derivatives **1a–d** were reacted with HSiMe(OMe)₂ (reductant) in the presence of Ni(cod)₂ (a catalyst precursor) and PCy₃ (a ligand) in toluene at 80 °C for 18 h. Although the reaction did not occur when a substrate had no DG (Entry 1), the introduction of 2-pyridyl (Entry 2), ester (Entry 3) and amide (Entry 4) groups facilitated the reductive cleavage of C(aryl)–O bonds to form **2**, with a 2-pyridyl group being the most effective. Therefore, we decided to employ a 2-pyridyl group as the DG for the development of depolymerizable polymers.

A PPE-based polymer bearing a 2-pyridyl group (**DG-PPE**) was synthesized by polycondensation *via* nucleophilic aromatic substitution (S_NAr) using an initiator (Fig. 2a).¹⁸ Thus, the reaction of 4-fluorophenol derivative **3** in the presence of KH (1.0 equiv., base) and 4,4'-difluorobenzophenone (0.63 mol%, initiator) in NMP at 200 °C for 4 h afforded the desired **DG-PPE** in a 62% isolated yield upon reprecipitation from CHCl₃/MeOH. The relatively high dispersity of **DG-PPE** ($D = 3.01$) compared with the value reported in Yokozawa's work ($D = 1.1$) can be attributed to the higher polymerization temperature used in our study, which induced undesired main-chain cleavage as a side reaction (see the ESI† for details). A PEEK-based polymer bearing a 2-pyridyl group (**DG-PEEK1**) was also synthesized using a similar method of polycondensation between hydroquinone derivative **4** and 4,4'-difluorobenzophenone derivative **5** in the presence of a catalytic amount of Cs₂CO₃ in NMP at 150–180 °C (Fig. 2b).¹⁹ The polycondensation of bis(phenol) derivative **6** and difluoride **5** afforded a PEEK derivative that possesses fewer 2-pyridyl groups (one pyridine ring per two ether moieties for **DG-PEEK2** vs. one pyridine per one ether for **DG-PEEK1**, Fig. 2c). All DG-installed polymers were characterized by ¹H and ¹³C NMR and MALDI-TOF MS (see the ESI†).

Properties of DG-installed polymers

The physical properties of DG-installed polymers are summarized in Table 1. All DG-installed polymers exhibited notable thermal stability with high decomposition temperatures at 5% weight loss ($T_{d5} = 399$ –465 °C). The T_{d5} values measured under

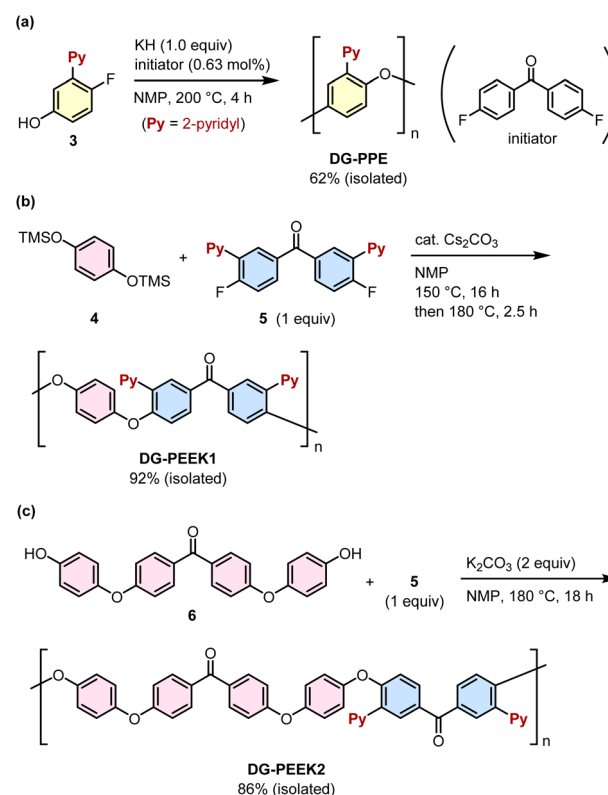


Fig. 2 Synthesis of (a) DG-PPE, (b) DG-PEEK1, and (c) DG-PEEK2.

Table 1 Properties of DG-PPE, DG-PEEK1 and DG-PEEK2

Entry	Polymer	M_w^a [kDa]	D^a	T_g^b [°C]	T_{d5}^c [°C]
1	DG-PPE	4.98	3.01	143	399 (419)
2	DG-PEEK1	27.2	1.81	182	465 (473)
3	DG-PEEK2	59.0	2.21	172	437 (451)
4	PPE ^d	— ^e	— ^e	83	(390) ^f
5	PEEK ^g	— ^e	— ^e	143	576

^a Weight average molecular weights and dispersities were determined by size-exclusion chromatography in CHCl_3 by comparison with low dispersity polystyrene standards. ^b Glass transition temperature as determined by DSC thermogram (*exo* up, 10 °C min^{-1} , second run). ^c Decomposition temperature at 5% weight loss as determined by TGA thermogram (10 °C min^{-1} under nitrogen gas flow). The values in parentheses refer to those measured under air, unless otherwise noted. ^d Values for poly(*p*-phenylene oxide), which are cited from ref. 20. ^e Not determined due to insolubility in organic solvents at room temperature. ^f Decomposition temperature at 2% weight loss that was reported in ref. 20. ^g Values for a sample purchased from Aldrich (Cat. No. 456640).

air are comparable to those measured under nitrogen. DG-PPE displayed the transition temperature (T_g) of 143 °C, which is significantly higher than that reported for a parent PPE (83 °C).²⁰ Similarly, DG-PEEK1 exhibited a markedly higher T_g value of 182 °C, showcasing that the introduction of DGs does not compromise the exceptional heat resistance of PEEK (T_g = 143 °C). DG-PEEK2 also exhibited a comparable T_g value (172 °C), indicating that the feed ratio of DGs has minimal impact on thermal properties. None of the DG-installed polymers synthesized in this study exhibited discernible T_m values. This departure from the behavior of the parent PPE (T_m = 290 °C) and that of PEEK (T_m = 344 °C) underscores the significant influence of the DG incorporation on polymer crystallinity.

The chemical stabilities of DG-PPE and DG-PEEK1 were investigated through immersion in five distinct solutions for 24 h: aqueous HCl (12 M), aqueous NaOH (10 M), aqueous H_2O_2 (30%), AcOH and boiling water. SEC analysis of the recovered polymeric materials after neutralization revealed no change in molecular weight after these treatments (Fig. 3a for DG-PPE; Fig. 3b for DG-PEEK1). Additionally, minimal differences were observed in the FT-IR spectra before and after exposure to the solutions (Fig. 3c for DG-PPE; Fig. 3d for DG-PEEK1), indicating the stability of these polymers towards strong acids, bases, and oxidants.

Controlled degradation of DG-installed polymers

Having confirmed the thermal and chemical stability of DG-introduced polymers DG-PPE, DG-PEEK1 and DG-PEEK2, we next investigated their catalytic degradation. On the basis of model studies (Fig. S1†), nickel-catalyzed reductive degradation of these polymers with hydrosilane was investigated. The reaction of DG-PPE with $\text{HSiMe}(\text{OME})_2$ (2 equiv. per monomer unit) in the presence of a $\text{Ni}(\text{cod})_2/\text{PCy}_3$ catalyst in toluene at 80 °C for 18 h afforded phenol **7** in an isolated yield of 64% (Fig. 4a). These nickel-catalyzed conditions were successfully applied to disassemble DG-PEEK1, selectively yielding hydroquinone

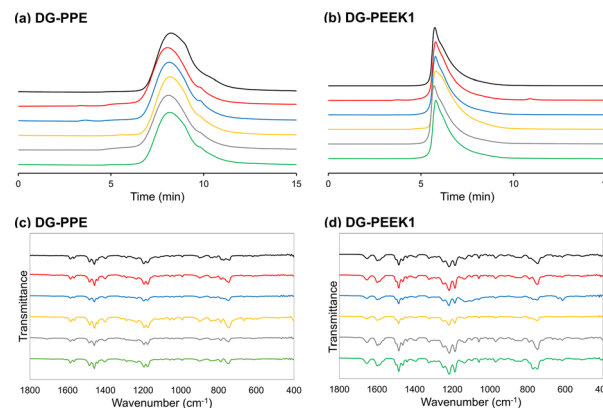


Fig. 3 Chemical stability of DG-PPE and DG-PEEK1. ^a SEC (a and b) and FT-IR (c and d) analysis measured after neutralization for polymer samples treated with the following solutions at rt for 24 h: black, none; red, HCl (12 M); blue, NaOH (10 M); orange, H_2O_2 (30%); gray, AcOH; green, boiling water.

component **8** and benzophenone component **9** in isolated yields of 78 and 87%, respectively (Fig. 4b). Similarly, DG-PEEK2 underwent degradation to afford **9** (80%) and **10** (68%) under analogous conditions (Fig. 4c). Notably, the site-selective cleavage of C(aryl)–O bonds positioned *ortho* to the directing group occurred, while other C(aryl)–O bonds remained intact. The resultant structurally well-defined degraded products were converted back into the parent polymers in a few chemical steps (Fig. 4d). For instance, phenol **7** was *ortho*-fluorinated to form **3** by palladium catalysis,²¹ which enabled its use in the polymerization of DG-PPE. Compound **9**, which was generated from the degradation of DG-PEEK1 and DG-PEEK2, was transformed into fluorinated benzophenone **5** through oxidation and *ortho*-fluorination. Consequently, the straightforward recycling of DG-PEEK1 was feasible by reacting **5** with a degraded product **8**. Similarly, DG-PEEK2 was chemically recycled by oxidizing degraded product **10** into ketone **6**, which was followed by condensation with **5** (see the ESI†). Of particular significance is the pivotal role played by the directing group in the *ortho*-fluorination step, as well as its contribution to the depolymerization process. This underscores the advantageous utilization of directing groups in the strategic design of recyclable polymers.

The method for depolymerizing DG-installed polymers exhibits remarkable specificity, and diverges from conventional approaches used for polymers containing labile chemical bonds, such as simple acids or bases. For example, polyethylene terephthalate (PET) undergoes efficient depolymerization under basic conditions (condition A, Fig. 4e),²² whereas DG-PEEK1 remains entirely stable under these circumstances. Conversely, the nickel-catalyzed conditions utilized for DG-PEEK1 degradation (condition B, Fig. 4e) exhibit no impact on PET, underscoring the selectivity of this catalyst system toward substrates featuring DGs. This orthogonal behavior bears significant advantages for the design of chemical recycling protocols, particularly when addressing polymer mixtures.



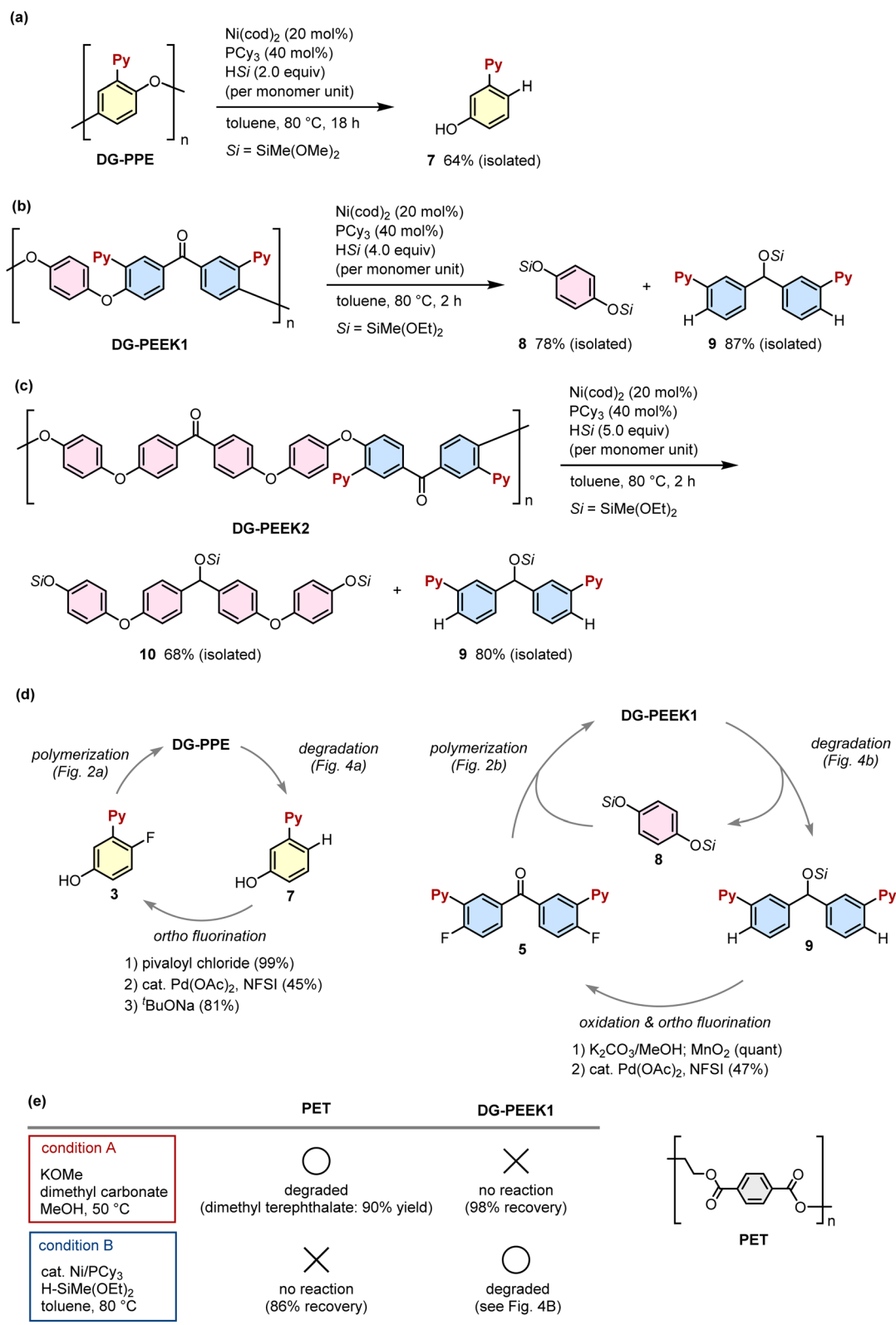


Fig. 4 (a) Controlled degradation of DG-PPE. (b) Controlled degradation of DG-PEEK1. (c) Controlled degradation of DG-PEEK2. (d) Chemical recycling of DG-PPE and DG-PEEK1. (e) Orthogonal degradation of PET and DG-PEEK1.



Conclusions

While the demand for polymer materials that could be depolymerized into monomers is on the rise, current design strategies are limited mostly to the incorporation of labile covalent bonds, such as esters, into their main chains. Our work presented herein showcases a novel approach: polymers composed of strong covalent bonds can be selectively degraded into well-defined monomers by integrating the concept of a directing group. This directing group facilitates the cleavage of robust chemical bonds within the polymer's main chain through the formation of stable metallacyclic intermediates with transition metal catalysts. It is important to note that the introduction of pyridine directing groups did not compromise the chemical stability of the polymers in the absence of a catalyst, which shows promise as a potent strategy for designing robust polymers that are chemically recyclable. We are currently exploring the application of this strategy to other resilient polymers in our laboratory, which should open new avenues for the design and recycling of sustainable materials.

Data availability

All data are available in the main text or the ESI.†

Author contributions

UH and MT conceived of the work. All authors designed the experiments. SO and HM performed the experiments. All authors prepared the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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