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Recyclable and malleable thermosets enabled by activating dormant dynamic linkages

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Chemical recycling of polymers is critical for improving the circular economy of plastics and environmental sustainability. Traditional thermoset polymers have generally been considered permanently crosslinked materials that are difficult or impossible to recycle. Herein, we demonstrate that by activating 'dormant' covalent bonds, traditional polycyanurate thermosets can be recycled into the original monomers, which can be circularly reused for their original purpose. Through retrosynthetic analysis, we redirected the synthetic route from forming conventional C–N bonds via irreversible cyanate trimerization to forming the C–O bonds through reversible nucleophilic aromatic substitution of alkoxy-substituted triazine derivatives by alcohol nucleophiles. The new reversible synthetic route enabled the synthesis of previously inaccessible alkyl-polycyanurate thermosets, which exhibit excellent film properties with high chemical resistance, closed-loop recyclability and reprocessing capability. These results show that 'apparently dormant' dynamic linkages can be activated and utilized to construct fully recyclable thermoset polymers with a broader monomer scope and increased sustainability.

Plastics have become an indispensable part of our daily life. Properties of most plastics, such as being lightweight, being durable, having excellent barrier properties and being low cost, have brought tremendous social benefits and technological advances. However, the ever-increasing demand for plastics, the negative environmental impact of their disposal and the challenges in recycling them have raised concerns over their detrimental long-term effects on the environment and human health[1,2]. Realizing the recyclability of polymeric materials to achieve a circular economy and environmental sustainability has attracted great attention[3–8]. Chemical recycling has shown great potential due to its capability to degrade polymers to their precursors and building blocks, which could be used as feedstocks similar to petroleum-based chemicals[9–14]. Thermosets with monomers permanently crosslinked by strong covalent bonds are usually produced as by-design non-processable and non-recyclable plastics. To solve their recyclability problem, many new thermosetting polymers have been created, via introducing cleavable[15] or dynamic covalent bonds[16] into monomers or as crosslinkers[17–21]. Various chemistries such as dynamic imine bonds[22], transesterification[23], boronic ester bonds[24,25], urethane[26,27] and silyl ether bonds[28] have been explored as cleavable units to prepare those materials. However, research that focuses on achieving the recyclability and malleability of existing thermosets to achieve a circular economy remains scarce[29]. Although it is important to develop new polymers as 'green' replacements, revisiting traditional materials with new features added is crucial and can generate critical knowledge guiding the development of sustainable materials.

Retrosynthetic analysis has long been the norm for synthetic chemists to evaluate the possible disconnection choices of target

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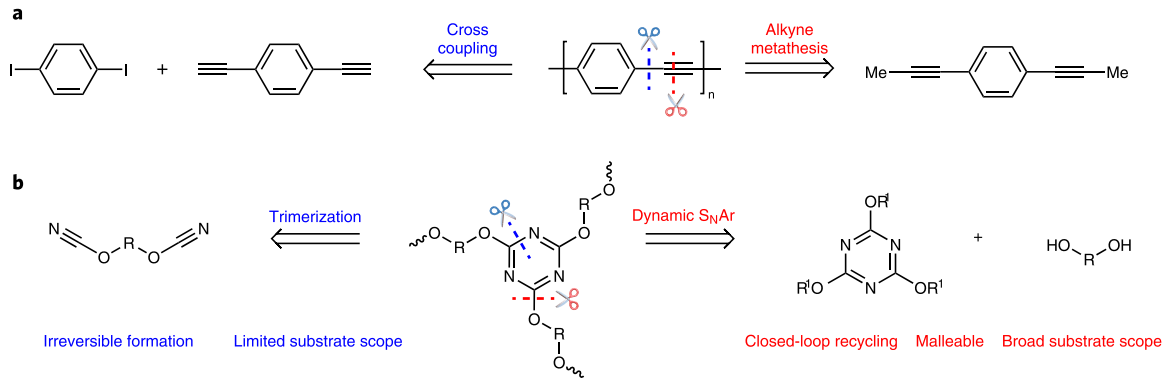

Fig. 1 | Synthetic strategies of polymers. a, PPEs can be prepared through either cross-coupling between aryl halide and terminal alkynes (blue) or alkyne metathesis polymerization (red). **b**, PCNs can be prepared through [2 + 2 + 2] cyclotrimerization of cyanate esters (blue) or dynamic S_NAr reaction between alkoxyl triazine and alcohol (red). The [2 + 2 + 2] cyclotrimerization is an irreversible reaction, and the method is limited to the synthesis of aryl PCNs. By contrast, the reversibility in the S_NAr reaction can be activated under certain conditions, thus enabling the malleability and recyclability of PCNs. Both aryl PCNs and alkyl PCNs are accessible through the S_NAr reaction.

structures and find the most efficient synthetic route. However, the importance of retrosynthetic analysis in polymer synthesis is often overlooked because polymers are made of simple repeating units with limited possible connectivity. By searching backward, alternative synthetic pathways can be found for polymers, which could offer unexpected benefits. For example, poly(phenyleneethynylene)s (PPEs) were typically synthesized through cross-coupling reactions, which generally provide PPEs with relatively low molecular weight and diyne defects (Fig. 1a). However, by forming C≡C bonds instead of C–C bonds through alkyne metathesis, defect-free PPEs with high molecular weight can be obtained[30]. More importantly, by employing dynamic alkyne metathesis, depolymerization of PPEs into small molecules[31] and their potential closed-loop recycling could be possible. Recent studies on chemically recyclable polymers[9–14,21] and covalent adaptable networks[17] show that the activation of reversibility for bond connections in polymers could be the key driver of the recyclability and malleability of thermosetting polymers. Therefore, we sought to uncover potentially reversible bonds through retrosynthetic analysis in traditional thermosetting polymers.

As a proof of concept, we chose cyanate ester resins as the model system to demonstrate our strategy of achieving recyclability and malleability by activating dormant dynamic linkages of traditional thermosets. Polycyanurate networks (PCNs) have been widely employed in the aerospace and microelectronics industries, and their market is expected to reach US$338 million in 2022 (ref. [32]). Cyanate ester resins are traditionally cured through [2 + 2 + 2] cyclotrimerization of three aromatic cyanate groups (Fig. 1b) to form PCNs, which exhibit unique properties such as good flame retardancy, high thermal stability, low moisture absorption, low dielectric constant dissipation factors, excellent compatibility with carbon fibres and adherence to metals[33,34]. Recycling such crosslinked thermosets is challenging. Previously, PCNs were degraded into triazine-based structures and phenols by treatment with various nucleophiles. The resulting products were obtained as mixtures, which can be further used in polyurethane synthesis[35–37]. However, the closed-loop recycling of PCNs into clean and reusable building blocks (for example, triazine-based monomers for repolymerization) has yet to be achieved. In addition, synthesis of alkyl PCNs remains challenging due to the isomerization of alkyl O–C≡N monomers at high temperature[38]. By performing retrosynthetic analysis and rethinking the possible alternative routes, we envision that PCNs can also be constructed by forming the single bond between triazine carbon and oxygen through nucleophilic aromatic substitution (S_NAr). Here, we demonstrate that by adopting reversible S_NAr chemistry instead of irreversible cyclotrimerization, the dormant dynamic linkage in PCNs can be activated. Therefore, recyclable and malleable PCNs can be prepared from two simple building blocks, and upcycling traditional aryl PCNs to reusable monomers for alkyl-PCN synthesis is possible. Through this new synthetic route, the monomer scope of

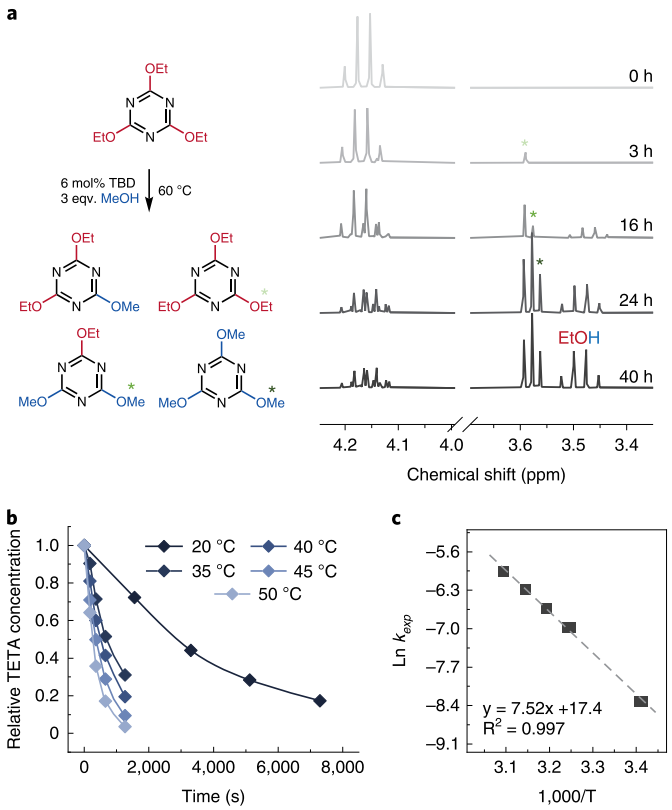

Fig. 2 | S_NAr in cyanurate exchange reactions. a, When 6 mol% of TBD was added, the exchange reaction between TETA and methanol occurred and reached equilibrium within 40 hours at 60 °C (evidenced by ^{1}H-NMR spectra). Three new types of triazines, which are substituted with one, two or three methoxy groups, were formed. **b**, Kinetic profiles of the S_NAr reaction at different temperatures were obtained by plotting the relative concentrationof TETA (percent of remaining TETA) versus time. **c**, Arrhenius plot of experimental rate constant (k_{exp}) and temperature (T) and its linear fitting of the small-molecule analogue reaction. The activation energy is determined to be 62.5 kJ mol^{-1} (R^2 denotes the coefficient of determination).

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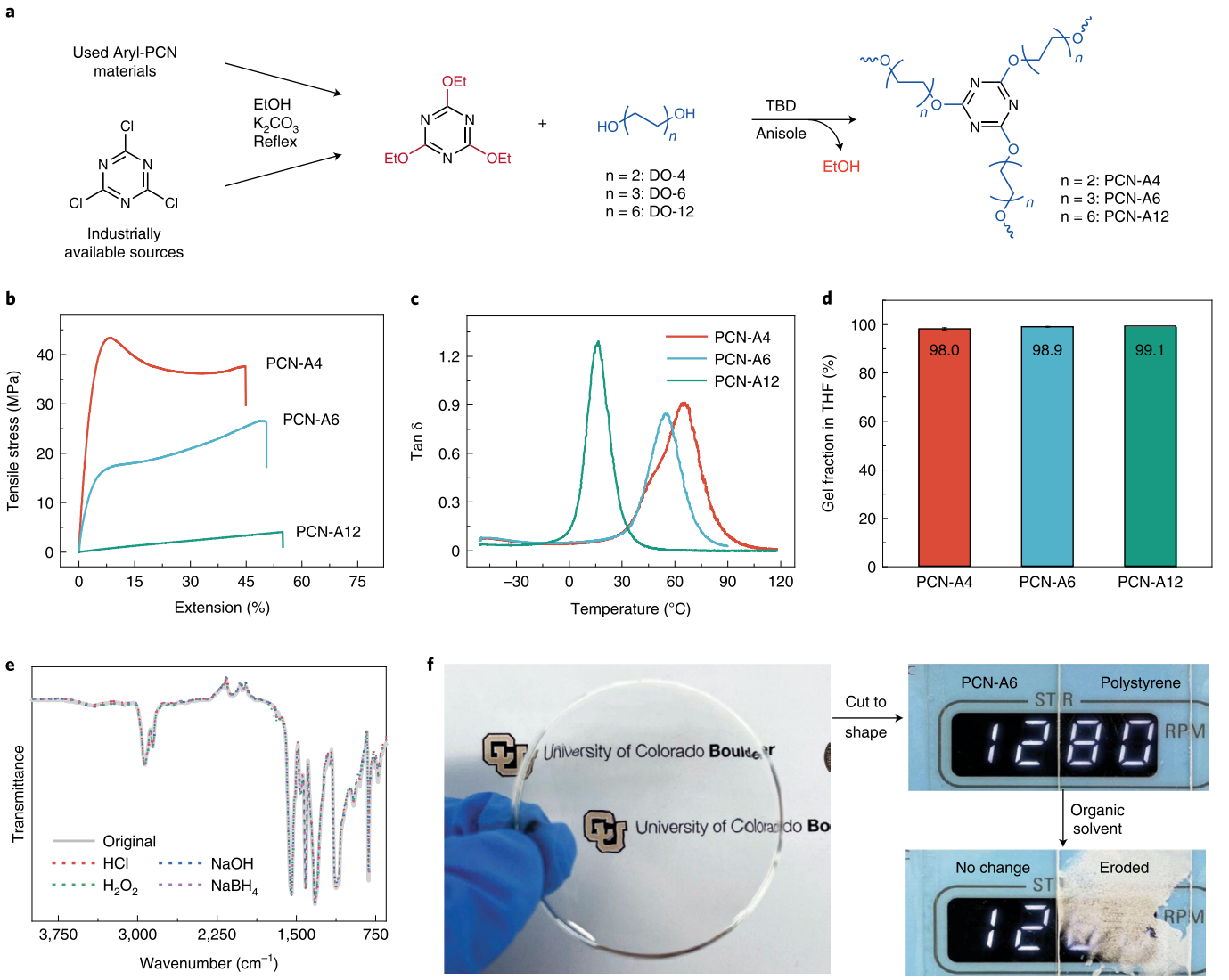

Fig. 3 | Preparation and characterization of PCNs. a, TETA monomer can be either obtained from the depolymerization of used aryl PCN prepared via the conventional trimerization or synthesized from commercially available cyanuric chloride. The alkyl PCNs were synthesized through S_NAr reaction between TETA and various diols in anisole. DO-4, 1,4-butandiol; DO-6, 1,6-hexandiol; DO-12, 1,12-dodecanediol. **b**, Representative stress–strain curves of the PCNs. **c**, The loss ratio (tan δ)-temperature curves obtained through dynamic mechanical analysis of the PCNs. **d**, Gel fraction test of the PCNs. THF, tetrahydrofuran. Error bars correspond to standard deviation. **e**, Comparison of FTIR spectra of PCN-A6 after different solution treatments for 48 hours. **f**, The transparent film of PCN-A6 can be used as a chemically resistant film. After treatment with different solvents (acetone, dichloromethane and ethanol), PCN-A6 retained the same transparency while polystyrene was severely damaged.

PCNs can be expanded to alkyl linkers, offering unprecedented tunability in PCN properties, which has proven technically challenging when the traditional cyclotrimerization approach is used. The alkyl PCNs show excellent film properties, chemical resistance and recyclability. End-of-life PCNs in the mixed plastic waste stream could be selectively degraded to the starting monomers, which could be separated and directly reused in the next production cycle, achieving closed-loop polymer-to-polymer recycling.

Results and discussion

Dynamic S_NAr in small model compounds

S_NAr reactions on heterocyclic substrates such as pyridines, pyrimidines and triazines have been widely performed in medicinal chemistry[39]. However, the application of such reactions in polymer synthesis has been explored much less[40,41]. Although the reaction between phenols and monoaryloxy-substituted triazines has been explored previously[39], the dynamic nature of such a S_NAr reaction has yet to be determined. In this context, at first, we used 2,4,6-triethoxy-1,3,5-triazine (TETA) and methanol as the model compounds to study the reversibility of S_NAr between alkyl cyanurates and alcohols. We first demonstrated the thermodynamic equilibrium of cyanurate exchange reactions (Fig. 2a). In the absence of any catalyst, there is no exchange reaction between TETA and methanol at 60 °C (Extended Data Fig. 1). By contrast, when a catalytic amount of triazabicyclodecene (TBD) was added, the exchange of ethoxy with methoxy groups occurred immediately, indicating the reversibility of such a S_NAr reaction. A diluted solution of TETA and methanol in a 1:3 molar ratio provided four types of triazines in an approximately 1:3:3:1 molar ratio after heating at 60 °C for 40 hours, where up to three ethoxy groups were replaced by methoxy groups. Such a result indicates that all three ethoxy groups are reactive and the exchange reaction has reached an equilibrium. The kinetics of the cyanurate exchange were investigated at various reaction temperatures (Fig. 2b). The reaction progress was monitored by measuring the decrease in intensity of TETA proton signals in ^{1}H NMR spectra over

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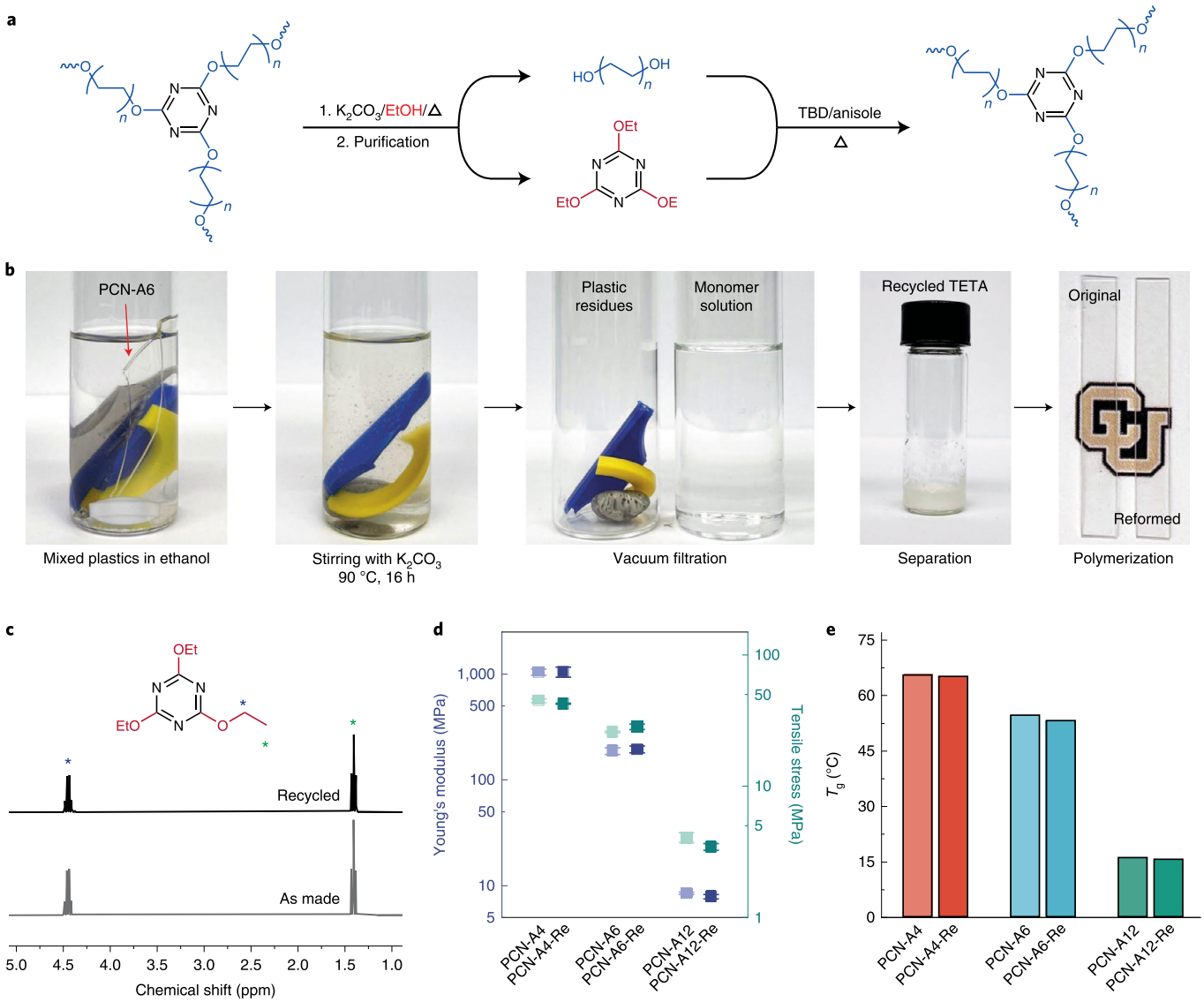


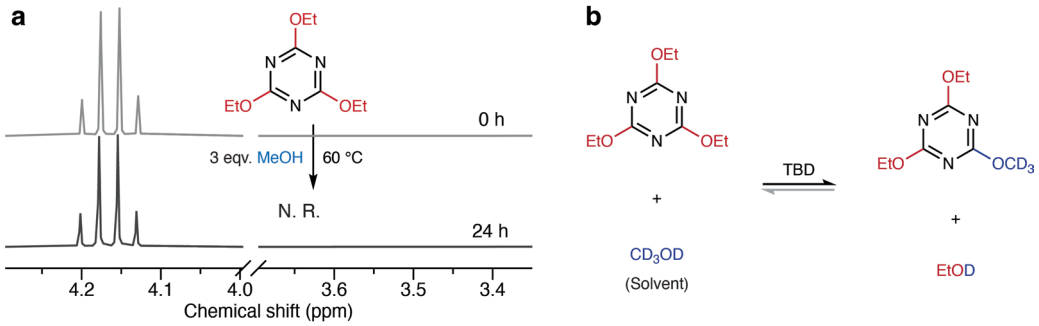
Fig. 4 | Chemical recycling of PCNs. a, Closed-loop recycling of PCNs. The PCNs can be depolymerized into monomers, which can be repolymerized to form recycled PCNs with nearly identical chemical, thermal and mechanical properties. The reversible S_NAr reaction thus enables a closed-loop polymer–polymer recycling of PCNs. **b**, Photographs showing selective recycling procedures of PCN-A6 from plastic waste containing high-density polyethylene, polypropylene and polystyrene. PCN-A6 was cleanly converted to soluble monomers, while other plastics remained as solids. The recycled TETA was reused to form PCN-A6. **c**, Comparison of the ^{1}H NMR spectra of recycled and freshly made TETA. Recycled TETA shows identical NMR proton signals as the freshly synthesized TETA. **d**, The mechanical properties of the virgin PCNs (light data points) and recycled PCNs (dark data points) are highly comparable. Error bars correspond to standard deviation. **e**, Recycled PCNs exhibit nearly identical glass transition temperatures as the virgin PCNs.

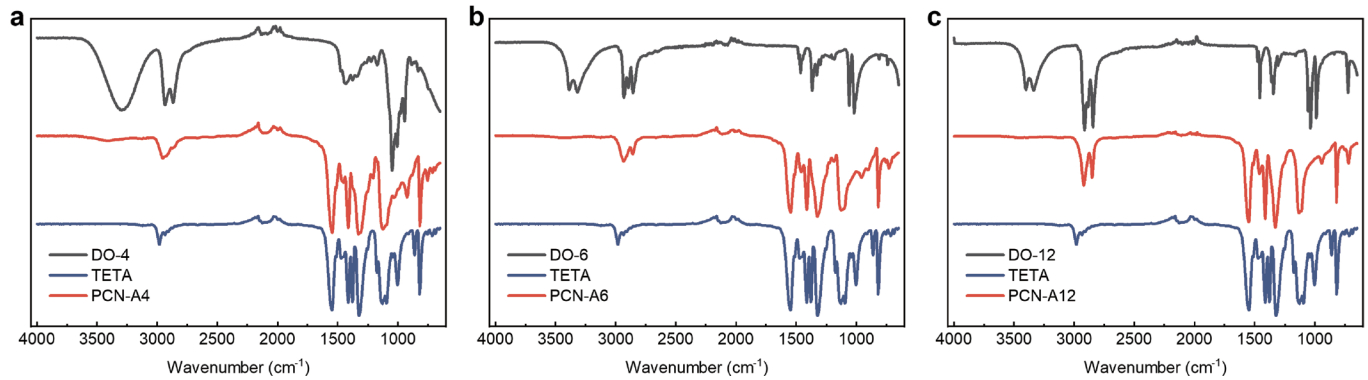
time. The S_NAr reactions on a 1,3,5-triazine core in phenolysis or aminolysis have been studied, and a concerted second-order substitution mechanism was proposed[39]. Considering a large excess of methanol and fast proton transfer between the alcohol and TBD, we assumed the reaction is an irreversible pseudo-first-order reaction and calculated the experimental rate constants based on the TETA concentration decrease (Fig. 2b and Supplementary Table 1). Using the reaction rate constants measured at different temperatures, the activation energy of the exchange reaction was calculated to be 62.5 kJ mol^{-1} from the Arrhenius plot and its linear fitting (Fig. 2c).

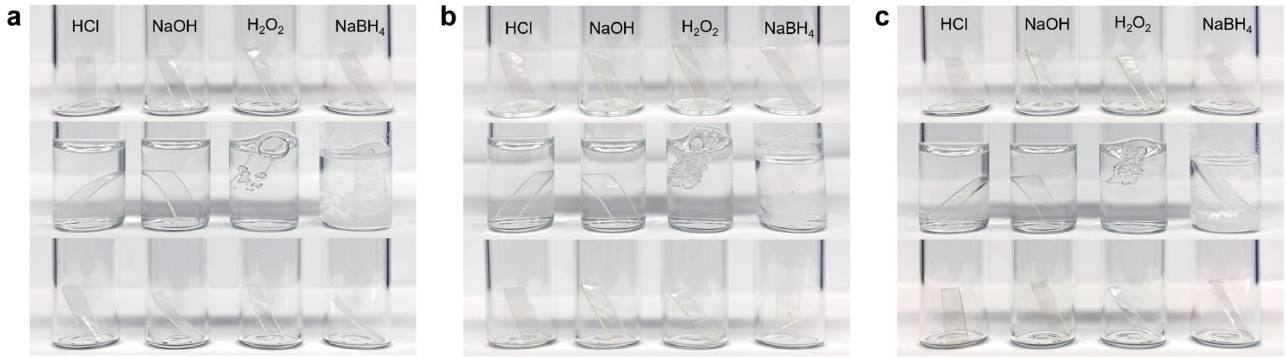
PCN synthesis and characterization

Unlike well-known aryl PCNs, alkyl PCNs have been inaccessible because alkyl cyanate monomers undergo undesired isomerization to isocyanates under the conventional [2 + 2 + 2] trimerization conditions[34]. There has been no viable synthetic approach for alkyl PCNs, which could have a high impact toughness compared to conventional aryl PCNs. We envisioned that our approach could provide alkyl PCNs with various thermal and mechanical properties that have been challenging to achieve using the traditional cyclotrimerization approach.

Thus, we explored the synthesis of alkyl PCNs using a dynamic S_NAr reaction of triazine with various diols. Various alkyl PCNs (PCN-A4, A6 and A12) were prepared using 1,4-butanediol, 1,6-hexanediol and 1,12-dodecanediol as the linkers through S_NAr reaction (Fig. 3a). TBD (2 mol% to the cyanurate group) was added as the catalyst. Fourier-transform infrared (FTIR) spectra of the PCNs show the existence of a C–O–C stretching band at 1,130 cm^{-1} and triazine bands at 815 cm^{-1} and 1,550 cm^{-1}, and the disappearance of the methyl rocking band at 1,379 cm^{-1} (Extended Data Fig. 2), supporting the cyanurate structure with the ethoxy group replaced by alkyl diols. Solid-state cross polarization magic angle spinning NMR spectra show that only a small amount (4–10 mol%) of ethoxy groups remained unreacted.


a
OEt
N
N
EtO
N
OEt
0 h
3 eqv. MeOH
60 °C
N. R.
24 h
4.2
4.1
4.0
3.6
3.5
3.4
Chemical shift (ppm)
b
OEt
EtO
OEt
+
CD3OD
(Solvent)
TBD
OEt
EtO
OCD3
+
EtOD


a
DO-4
TETA
PCN-A4
4000 3500 3000 2500 2000 1500 1000
Wavenumber (cm-1)
b
DO-6
TETA
PCN-A6
4000 3500 3000 2500 2000 1500 1000
Wavenumber (cm-1)
c
DO-12
TETA
PCN-A12
4000 3500 3000 2500 2000 1500 1000
Wavenumber (cm-1)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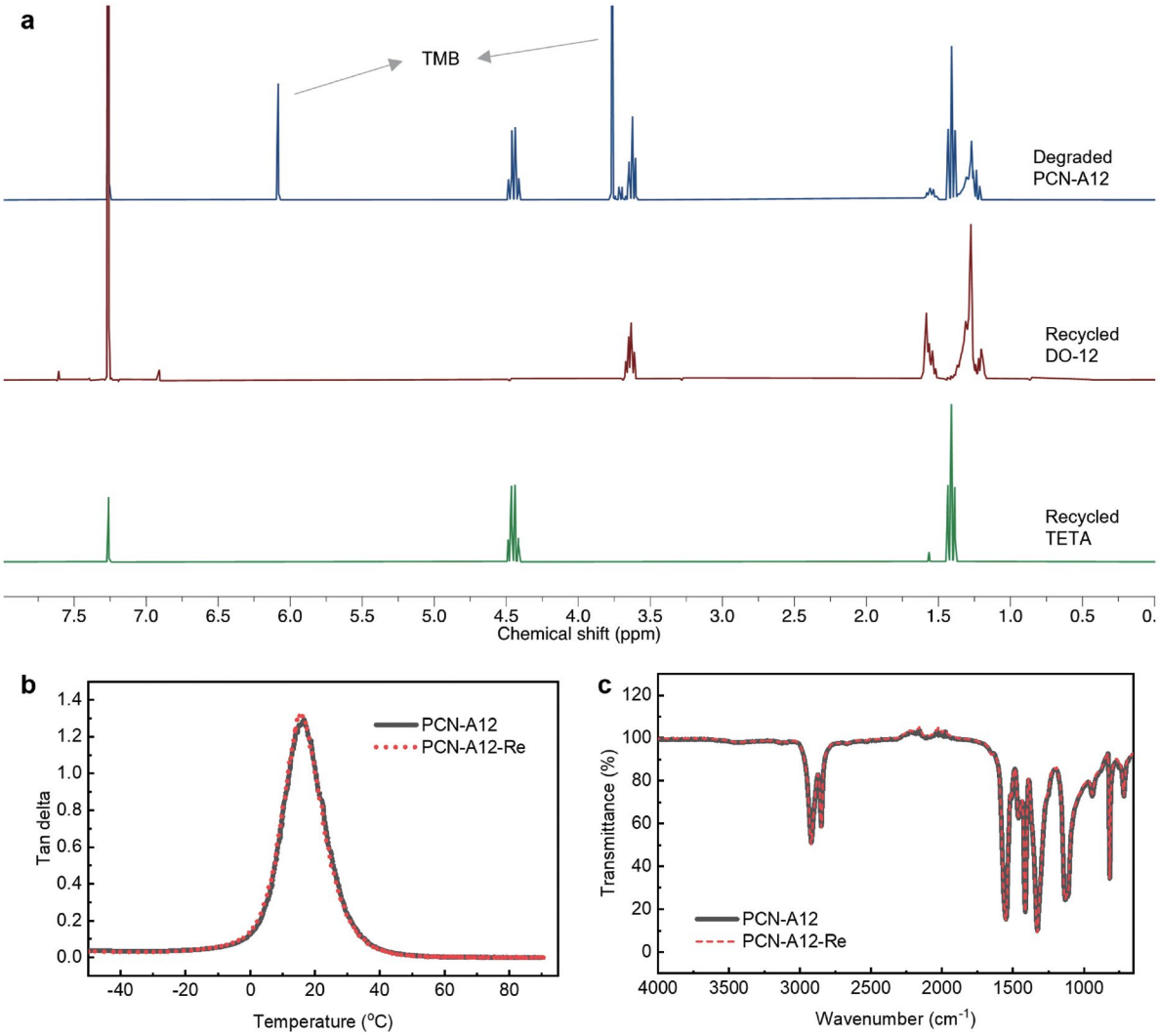
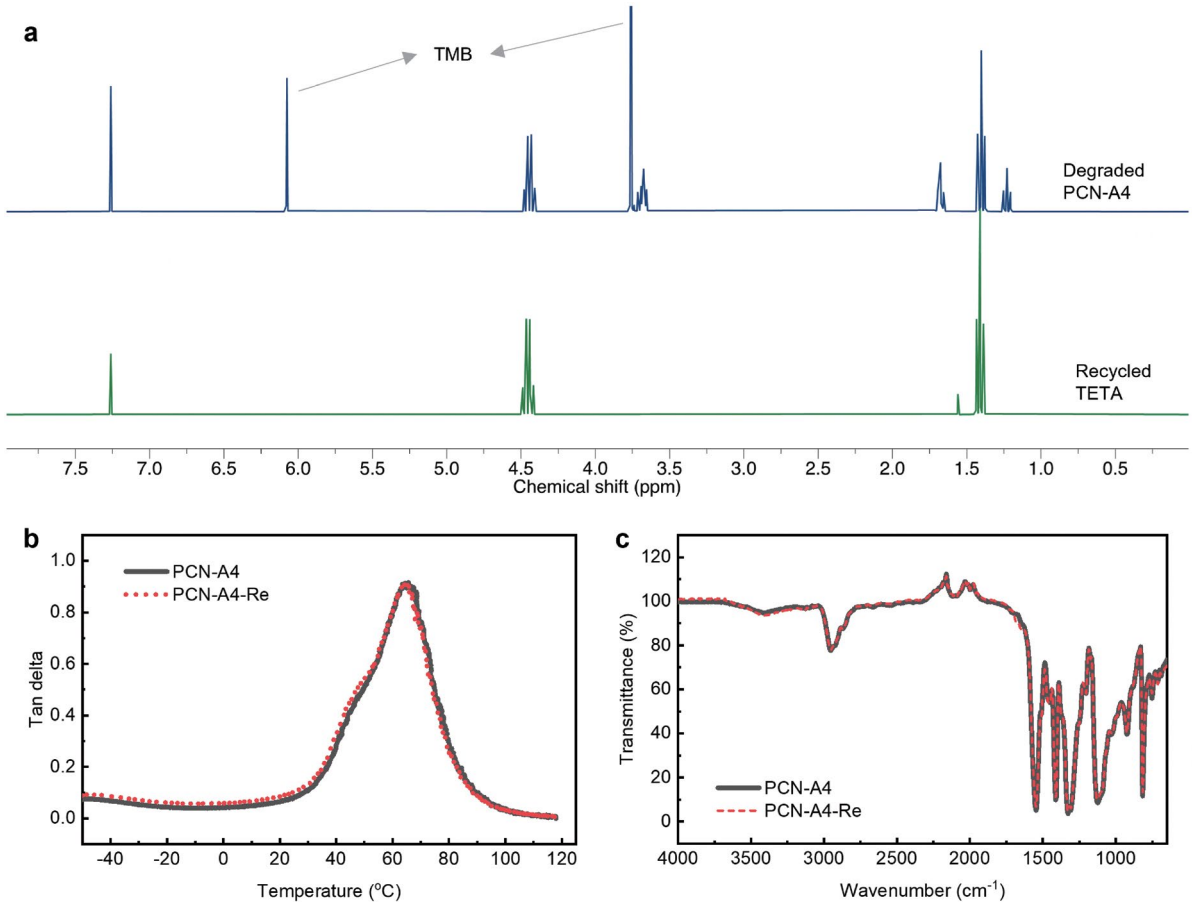
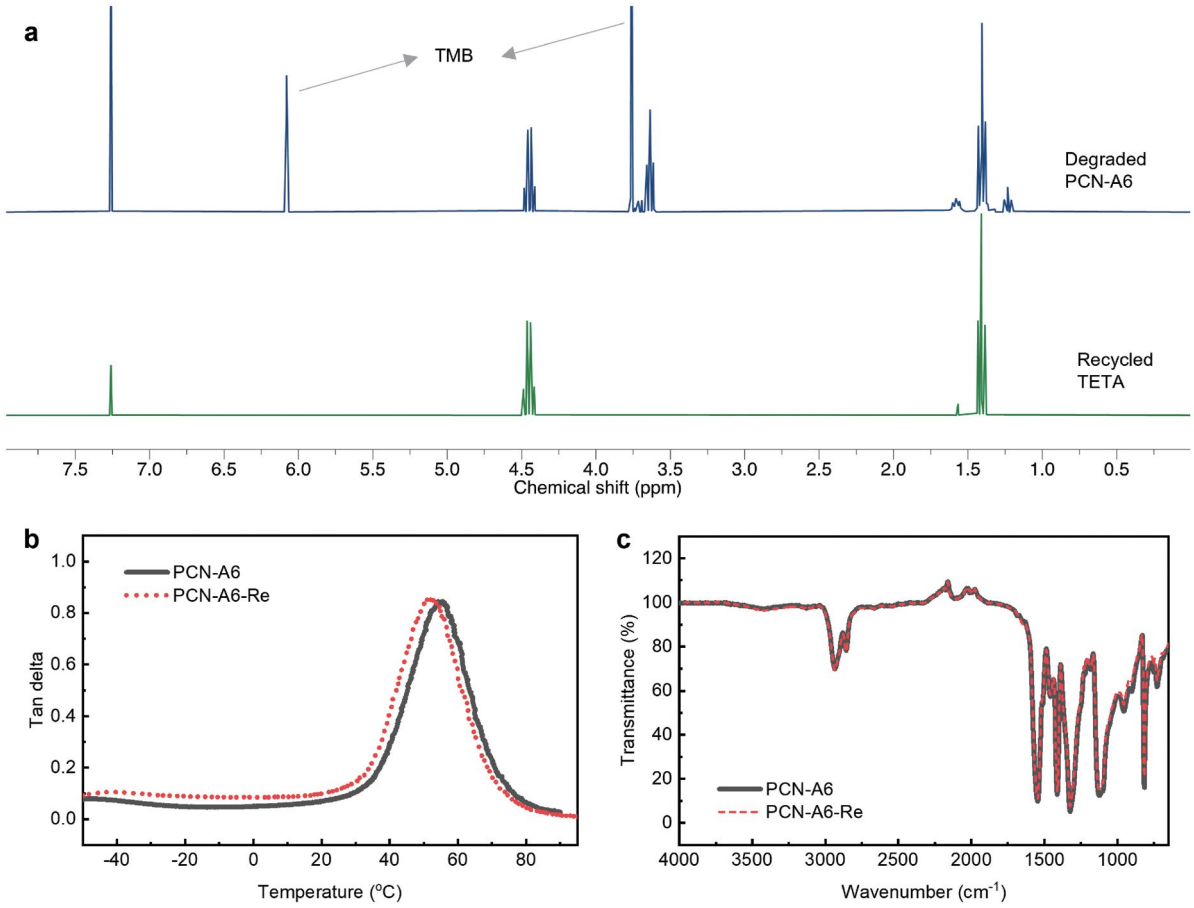
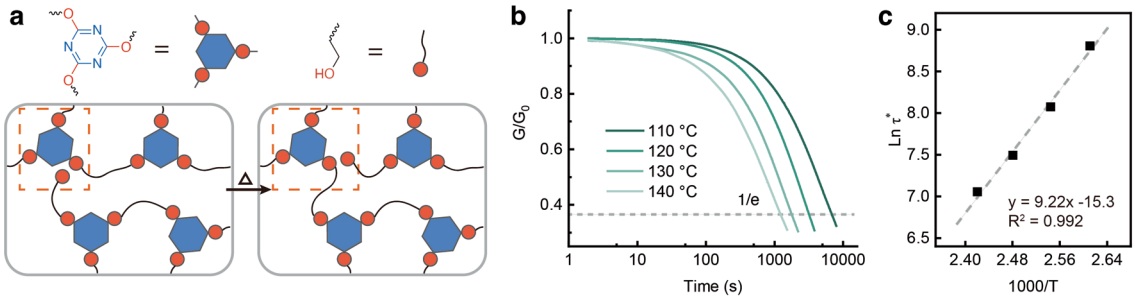
HCl
NaOH
H_2O_2
$NaBH_4$
b
HCl
NaOH
H_2O_2
$NaBH_4$
c
HCl
NaOH
H_2O_2
$NaBH_4$


a
TMB
Degraded
PCN-A12
Recycled
DO-12
Recycled
TETA
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
Chemical shift (ppm)
b
Tan delta
1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
PCN-A12
PCN-A12-Re
-40 -20 0 20 40 60 80
Temperature (°C)
c
Transmittance (%)
120 100 80 60 40 20 0
PCN-A12
PCN-A12-Re
4000 3500 3000 2500 2000 1500 1000
Wavenumber (cm-1)


a
TMB
Degraded
PCN-A4
Recycled
TETA
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical shift (ppm)
b
PCN-A4
PCN-A4-Re
Tan delta
1.0 0.8 0.6 0.4 0.2 0.0
-40 -20 0 20 40 60 80 100 120
Temperature (°C)
c
Transmittance (%)
120 100 80 60 40 20 0
PCN-A4
PCN-A4-Re
4000 3500 3000 2500 2000 1500 1000
Wavenumber (cm-1)


a
TMB
Degraded
PCN-A6
Recycled
TETA
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical shift (ppm)
b
PCN-A6
PCN-A6-Re
Tan delta
1.0
0.8
0.6
0.4
0.2
0.0
-40
-20
0
20
40
60
80
Temperature (°C)
c
Transmittance (%)
120
100
80
60
40
20
0
PCN-A6
PCN-A6-Re
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)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Δ
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130 °C
140 °C
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1
10
100
1000
10000
Time (s)
c
9.0
8.5
8.0
7.5
7.0
6.5
Ln τ*
y = 9.22x -15.3
R² = 0.992
2.40
2.48
2.56
2.64
1000/T