Cleavable comonomers enable degradable, recyclable thermoset plastics

Thermosets—polymeric materials that adopt a permanent shape upon curing—have a key role in the modern plastics and rubber industries, comprising about 20 per cent of polymeric materials manufactured today, with a worldwide annual production of about 65 million tons. The high density of crosslinks that gives thermosets their useful properties (for example, chemical and thermal resistance and tensile strength) comes at the expense of degradability and recyclability. Here, using the industrial thermoset polydicyclopentadiene as a model system, we show that when a small number of cleavable bonds are selectively installed within the strands of thermosets using a comonomer additive in otherwise traditional curing workflows, the resulting materials can display the same mechanical properties as the native material, but they can undergo triggered, mild degradation to yield soluble, recyclable products of controlled size and functionality. By contrast, installation of cleavable crosslinks, even at much higher loadings, does not produce degradable materials. These findings reveal that optimization of the cleavable bond location can be used as a design principle to achieve controlled thermoset degradation. Moreover, we introduce a class of recyclable thermosets poised for rapid deployment.

Existing strategies to create reprocessable thermosets have focused on dynamic covalent bond exchange, thermomechanical degradation or wholesale replacement of network components with degradable versions. We hypothesized that optimizing the location of cleavable bonds within thermosets may provide a complementary approach, enabling the mild, chemically triggered degradation and recycling of thermosets at low cleavable bond loadings using existing manufacturing workflows. Here, leveraging polydicyclopentadiene and recent advances in ring-opening metathesis polymerization (ROMP) comonomer design, we establish that the introduction of cleavable bonds within the strands of covalently crosslinked thermoset plastics can impart degradability and potential recyclability at low co-monomer loadings, whereas the analogous addition of cleavable crosslinks cannot. This design principle may apply to other materials formed via crosslinking of reactive polymers, including acrylics, styrene-divinylbenzene, vulcanized rubber and silicones, and could enable searches for novel cleavable comonomers and potentially contribute to the design of sustainable plastics and elastomers.

Theoretical framework

To estimate the amount of cleavable comonomer required to degrade networks of strands with crosslinkable functional groups and crosslinks into soluble products, we derived a reverse gel-point model based on the Miller–Macsisko and Flory–Stockmayer theories (Fig. 1b, Extended Data Fig. 1; see Methods):

\[ x > \frac{c(2f - 1) - f}{c + f} \]

From this relationship, we observe that when \( f \approx c \), degradation into soluble products is expected when \( x \) is greater than \(-2c\). If we instead assume that \( f = c \), then degradation to soluble products is expected when:

\[ x > c - 1. \]

Thus, the model predicts what is also intuitive: degradation of thermosets to soluble products can be achieved when the number of cleavable bonds in strands is similar in magnitude to the number of crosslinks. We note that this model assumes that the cleavable bonds are randomly distributed along strands, that equivalent functional groups have equal and independent reactivity and that there are no intramolecular reactions. Therefore, the model provides only an estimate of \( x \); the presence of loops may further lower the number of degradable bonds needed to achieve degradation.

Cleavable bond location controls degradability

To test the validity of this model, we used recently reported silyl ether monomers that copolymerize with norbornene derivatives by ROMP to produce degradable statistical copolymers. Here, DCPD was mixed with different amounts of the silyl ether monomer iPrSi.
(0, 5, 10 or 15 vol% or approximately one equivalent of iPrSi per 31, 15 and 9 equivalents of DCPD, respectively; Fig. 1c). The mixtures were cured at 120 °C for 30 min in the presence of Grubbs second-generation catalyst (total DCPD and iPrSi monomer/catalyst ratio of ~2,500:1).

Although this curing protocol was not further optimized, the resulting materials displayed Young’s moduli in the gigapascal range, as expected for pDCPD thermosets. In the initial stage of pDCPD curing, the norbornene component of DCPD copolymerizes with iPrSi to form linear polymer strands with cyclopentene sidechains as potential crosslinking sites and x cleavable silyl ether linkages (Fig. 1c). Cyclopentene sidechain metathesis leads to iPrSi-doped pDCPD with c crosslinks. Silyl ether cleavage is expected to generate fragments with on average \((c/(x + 1))\) crosslinks per strand; thus, as \(x\) approaches \(c\), lower-mass products should be produced. We note that this approach stands in contrast to the indiscriminate degradation of thermosets, which produces products of uncontrolled size and chemical composition that typically have much lower value; the comonomer strategy provides a way to trigger thermoset degradation at low comonomer loadings and control degradation product size and composition. Lastly, we note that a preliminary techno-economic analysis suggested that iPrSi can be manufactured inexpensively, making it potentially feasible for large-scale use, especially if used as an additive to existing pDCPD workflows (Supplementary Fig. 1, Supplementary Table 1).

Fig. 1 | Conceptual basis of this work.

To compare iPrSi-doped pDCPD to analogues with cleavable crosslinks, pDCPD samples were prepared in the presence of up to 80 vol% of a bis-cyclooctene crosslinker featuring a silyl ether linkage (SiXL; Fig. 1d, Supplementary Information Figs. 2, 3). In this case, the addition of \(y\) cleavable crosslinks (from SiXL) is expected to yield thermosets with \(c + y\) crosslinks; cleavage of the \(y\) linkages leaves a network with \(c\) crosslinks, precluding the formation of soluble products for all \(y\) values other than those much greater than \(c\) (Fig. 1d). We note that in thermosetting materials with mostly cleavable crosslinks, theoretically it is possible—although often difficult in practice—to achieve material degradation once nearly all of the crosslinks are cleaved.

For thermosets that lack naturally cleavable crosslinks, however, the addition of a small number of cleavable crosslinks is not expected to produce degradable materials.

To test this hypothesis, samples of iPrSi-doped, SiXL-doped and native pDCPD (Fig. 2a, Extended Data Fig. 2) were exposed to an excess of tetrabutylammonium fluoride (TBAF), a fluoride reagent that selectively cleaves silyl ethers and is often used to etch silicone elastomers, at room temperature. After ~4 h, the native pDCPD remained fully intact (Fig. 2b); by contrast, samples with 7.5 vol%, 10 vol% or 15 vol% iPrSi dissolved (Fig. 2a, b). Although the 5% iPrSi-doped sample remained intact, it was noticeably swollen, suggesting a decrease in crosslink density, which was further confirmed by analysis of the Si content using inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Supplementary Information Fig. 4). In each case, degradation of the iPrSi-doped samples occurred over the course of ~4 h, presumably limited by fluoride diffusion into the materials (Supplementary Information Fig. 5). Meanwhile, SiXL-doped materials did not degrade into soluble products, even at 80% SiXL loading (Fig. 2b, Extended Data Fig. 2, Supplementary Information Figs. 6, 7). The rate of SiXL cleavage by fluoride was observed to be similar to that of iPrSi (Supplementary Information Fig. 8), suggesting that this difference in the extent of degradation is due to the cleavable bond location and not the silyl ether structure.
To further compare the roles of cleavable strands versus crosslinks in these materials, samples of 5 vol% and 10 vol% iPrSi and 20 vol% SiXL-doped pDCPD were swollen to equilibrium in tetrahydrofuran (THF) and characterized by oscillatory rheology (Fig. 2c, Extended Data Fig. 3, Supplementary Information Fig. 9). Strikingly, treatment of the iPrSi-doped samples with TBAF led to large decreases in storage modulus (~100-fold for 5% iPrSi-doped pDCPD), whereas the modulus of the 20 vol% SiXL-doped sample decreased by only ~5-fold.

Functional evaluation of degradable pDCPD

Next, we studied the functional performance of iPrSi-doped pDCPD for comparison to the native material. In tensile tests, the 10% and 20% iPrSi-doped samples showed nearly identical moduli and elongations at break compared to pDCPD (Fig. 3a–c, Supplementary Information Figs. 12, 13). Thermal graviometric analysis revealed that films of 10% iPrSi-doped material stopped projectile impact (Fig. 3h), indicating indistinguishable high-strain-rate responses.

We next sought to probe the degradation of these materials in more detail. In addition to TBAF, which is convenient for laboratory-scale reactions, hydrofluoric acid, which is used to etch silicon on a large scale in the semiconductor industry, readily dissolved our iPrSi-doped pDCPD at room temperature (Supplementary Information Fig. 18). Silyl ethers are also susceptible to cleavage under acidic or basic conditions30; however, owing to their hydrophobic nature, iPrSi-doped pDCPD samples displayed sluggish hydrolysis in aqueous acidic (pH = 0) or basic (pH = 14) conditions, although they did show evidence of surface etching following exposure to aqueous sodium hydroxide for 30 min (Supplementary Information Figs. 19, 20). To demonstrate tuning of the degradation of these materials, we prepared samples doped with 10 vol% EtSi, a comonomer considerably more susceptible to hydrolysis32. These materials displayed enhanced degradation under mixed aqueous/organic acidic conditions (Extended Data Fig. 5). We envision that through the use of a wider range of comonomers, it may be possible to generate thermosets with variable degradation rates and mechanisms (for example, photochemical and enzymatic)33.

Finally, given concerns over the accidental release of plastic waste into the natural environment32, we studied the degradation of iPrSi- and EtSi-doped pDCPD exposed to synthetic seawater and ultraviolet light for 16 d (Fig. 3i, Extended Data Fig. 6, Supplementary Information Tables 4, 5). We observed sizable increases (up to ~2–3 fold) in the extent of degradation relative to native pDCPD. Transmission electron microscopy (TEM) revealed the presence of sub-5-nm particles following degradation (Supplementary Information Fig. 21). Although the generation of microplastics (typically micrometre–millimetre-range particles) may be a concern33, nanoscale plastics could be important intermediates that enhance the total degradation rate of bulk plastics. Notably, optimization of the size and composition of pDCPD degradation products can be achieved by tuning the silyl ether monomer substituents and loading, which is challenging for less selective degradation processes.

Characterization and reprocessing of iPrSi-doped pDCPD degradation products

The degradation products of iPrSi-doped pDCPD are hydroxylated polymers bearing cyclopentene functionalities that could be used to
Fig. 3 | Functional evaluation of doped pDCPD. a, iPrSi-doped pDCPD shows no significant difference in Young's modulus (measured at room temperature) between 0% and 10% iPrSi. The 33% and 50% iPrSi-doped samples are closer to or above their Tg value at room temperature (46 ± 7 °C and 14 ± 2 °C, respectively), which explains their different tensile behaviours compared to that of native pDCPD. b, iPrSi-doped pDCPD shows no significant difference in strain at break at low iPrSi loadings. c, Stress–strain curves obtained at room temperature for iPrSi-doped pDCPD samples and native pDCPD, highlighting the similarity between the 10% iPrSi-doped sample and native pDCPD, as well as the ability to control stress–strain behaviour with comonomer loading. d, iPrSi-doped pDCPD samples show comparable reduced moduli to native pDCPD, as assessed by nanoindentation. e, iPrSi-doped pDCPD shows no statistically significant difference in modulus compared to pDCPD at low iPrSi loadings, as determined by DMA. f, iPrSi-doped pDCPD shows similar decomposition temperatures as native pDCPD. g, Representative image sequences of impact and rebound for 0% and 10% iPrSi-doped pDCPD impacted by steel microparticles. h, Coefficient of restitution plots for 0% and 10% iPrSi-doped pDCPD. Positive, zero and negative coefficients of restitution correspond to particle rebound, embedment and film perforation, respectively. i, iPrSi and EtSi doping allows tuning of the degradation in synthetic seawater, as assessed by analysis of dissolved carbon. These results suggest that the comonomer approach could enable optimization of degradation for applications of interest. NS, not significant, *P < 0.05; **P < 0.01. Statistical significance determined through a Student’s t-test. Centre values denote average. Error bars denote s.e.m. n = 3 for the 0% and 10% samples, n = 4 for the 20% sample, n = 2 for the 33% sample and n = 1 for the 50% sample used for tensile testing, n = 46–49 for the nanoindentation measurements, n = 3 for DMA and n = 3 for weathering experiments.
Fig. 4 | Soluble pDCPD fragments enable high-resolution characterization of pDCPD and can be recycled into new materials. a, Dried pDCPD fragments from 10% iPrSi-doped material. These soluble, processable fragments have a large number of cyclopentene functional groups and exchangeable alkene-containing crosslinks available for further crosslinking. b, Comparison of 13C NMR spectra of pDCPD derived from CP-MAS (traditional approach for thermoset characterization) or from solution analysis of degradation products from the 10% iPrSi-doped sample. The soluble products display improved spectral resolution, enabling assignment and characterization of the structure of iPrSi-doped pDCPD. c, GPC traces of fragments derived from the dissolution of iPrSi-doped pDCPD. As expected, increased iPrSi loading leads to smaller degradation products, as evidenced by increases in retention time. d, TEM images of fragments (stained with RuO₄) derived from 10 vol% iPrSi-doped pDCPD, showing an average particle size of ~4 nm. e, Images of representative recycled and new pDCPD samples. Discolouration of the recycled sample is attributed to residual Ru from the first crosslinking and degradation process. f, Stress–strain curves from dogbone-shaped samples of new and recycled pDCPD, showing comparable stress–strain curves with increased strain at break for the recycled samples. g, Elastic moduli of native and recycled pDCPD, as assessed by DMA and tensile testing. h, Carbon fibre recovery from 10% iPrSi-doped pDCPD composites. Costly carbon fibre filler is often unrecoverable from thermoset composites. The degradable comonomer approach allows its recovery under mild conditions. i, Raman spectra of pristine and recovered carbon fibres, suggesting no chemical damage to the carbon fibre material. Centre values denote average. Error bars denote s.e.m.; n = 3 for all conditions. a.u., arbitrary units.

gain insights into the structure of pDCPD or for recycling or repurposing (Fig. 4a). To demonstrate the former concept, samples of 10%, 20%, 33% and 50% iPrSi-doped pDCPD were prepared and subjected to degradation using TBAF (Supplementary Information Fig. 22). The resulting soluble products were characterized by one- and two-dimensional solution-state NMR, including 1H, 13C, 1H–1H correlation spectroscopy (COSY), heteronuclear single quantum coherence spectroscopy (HSQC), heteronuclear multiple bond correlation spectroscopy.
(HMBC), and nuclear Overhauser effect spectroscopy (NOESY) (Supplementary Information Figs. 23–29) with greatly improved resolution compared to cross-polarization magic-angle spinning (CP-MAS) $^{13}$C NMR (Fig. 4b). To enable comparison of the NMR spectra, a sample of linear, non-crosslinked pDCPD was independently prepared (Supplementary Information Figs. 30, 31). From the combination of these studies, a 3:2 ratio of aliphatic to olefinic carbons could be assigned in the $^{13}$C NMR spectrum of the $\text{PrSi}$ doped pDCPD degradation products, indicating that ~15% of the cyclopentenes of the polynorbornene strands had reacted (Fig. 4b). On the basis of our model (Fig. 1b), a material with 15% effective crosslinks would require >15% cleavable bonds to degrade into soluble products; thus, we estimate that a large fraction of the reacted cyclopentene groups in pDCPD are consumed through intramolecular reactions (loops). This insight into the structure of pDCPD, uniquely enabled by the cleavable comonomer approach, lends clear and quantitative support to the model of pDCPD as being crosslinked by secondary metathesis reactions of cyclopentene substituents.

To examine the effect of $\text{PrSi}$ loading on the size of the degradation products, the soluble samples described above were analysed by gel-permeation chromatography (GPC) (Fig. 4c) and diffusion-ordered spectroscopy (DOSY) (Supplementary Information Figs. 32–35), both of which showed an inverse relationship between $\text{PrSi}$ loading and degradation product size. From GPC, the weight-average molar masses of these samples were 2–8 kDa (Supplementary Information Table 6), whereas DOSY allowed us to estimate that the average diameter of the degradation products of the 10% $\text{PrSi}$-doped material was ~4 nm, which is on the length scale of individual polymer strands. This result was further corroborated by TEM imaging (Fig. 4d, Supplementary Information Fig. 36).

Given that these degradation products possess many unreacted cyclopentene substituents and exchangeable alkene-containing crosslinks (Fig. 4a,b), we reasoned that they could be reprocessed into new pDCPD materials. Indeed, mixing the degradation products of our 10% $\text{PrSi}$-doped material (25 wt%); we note that the degradation products are soluble in DCPD up to ~40 wt% with DCPD and curing following the same procedure used for native pDCPD produced recycled samples with comparable stress–strain behaviour and elastic moduli (Fig. 4e,f, Supplementary Information Figs. 37–48). Moreover, the recycled samples displayed similar ballistic impact resistance to native pDCPD (see Supplementary Information). Finally, carbon fibre composites of pDCPD have been explored for high-performance applications, but the costly embedded carbon fibre typically cannot be recovered from such materials. When carbon fibre fabrics were embedded into 10% $\text{PrSi}$-doped pDCPD, they could be quantitatively recovered (Fig. 4i). Raman spectra for pristine versus recovered carbon fibre were very similar, suggesting that the mild pDCPD degradation process has no impact on the fibre composition (Fig. 4j). These results hint at potential opportunities for thermoset composite recycling.

**Online content**

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Methods

A general theoretical framework for degradable thermosets via copolymerization

Here, we describe the theoretical model for network degradation in further detail. We utilize the following variables, which are consistent with the terminology defined in Fig. 1, and we introduce an additional variable for the dispersity of the degradation fragments. 

\[ f, \text{ number-average degrees of polymerization of non-degradable, functional (crosslinkable) monomer (for example, DCPD)}; \]

\[ c, \text{ number-average crosslinks per strand (that is, the number of } f \text{ groups that have reacted to form crosslinks)}; \]

\[ x, \text{ number-average degrees of polymerization of degradable comonomer (for example, iPrSi)}; \]

\[ D, \text{ dispersity of linear fragments obtained after strand degradation in reverse gel-point model}. \]

To begin, we assume that the network structure formed by the crosslinking of linear copolymer strands followed by cleavage of degradable bonds in those strands (as is done experimentally in our study) is identical to the network formed by first cleaving the linear copolymer strands and then crosslinking the resulting 'fragments', as shown in Extended Data Fig. 1. Then, we use the classical Flory–Stockmayer and Miller–Macosko theories to determine what values of } x \text{ would inhibit gelation for given values of } f \text{ and } c. \text{ As is the case for these classical gelation theories, our model assumes that all functional groups of the same type have equal reactivity, that all functional groups react independently of each other and that there are no intramolecular reactions. Moreover, we assume that degradable comonomers } x \text{ are randomly distributed along the strand backbone.}

We estimate the number-average degrees of polymerization (DP) of the linear fragments generated after degradable monomer cleavage as:

\[ \text{DP} = \frac{f}{x+1}. \]

To provide an estimate of } D \text{ for these fragments, we apply a Monte Carlo analysis in which } x \text{ degradable comonomers are randomly incorporated into a linear polymer of } \text{DP}=f, \text{ and calculate the fragment DP after degradation. We repeat this process } 10^6 \text{ times to arrive, as expected, when } f \gg x \gg 1, \text{ to a fragment dispersity of about 2.}

Based on the Miller–Macosko theory, we define the critical extent of reaction required for gelation during crosslinking of a disperse mixture of polymer strands with a single crosslinking functionality as \( p_c \):

\[ p_c = \frac{1}{f_w-1}. \]

where \( f_w \) is the weight-average crosslink functionality of the fragments, which is defined as:

\[ f_w = \frac{Df}{x+1}. \]

We also note that for crosslinked networks below the gel point:

\[ \frac{c}{f} \leq p_c. \]

By combining equations (2), (3) and (4), we obtain:

\[ \frac{c}{f} \leq \left( \frac{p_w}{x+1} \right) - 1. \]

Solving for \( x \) provides the following relationship:

\[ x > \frac{c(Bf-1) - f}{c + f}. \]

Assuming } B = 2 \text{ gives the expression provided in the main text and plotted in Fig. 1b for } f = 3,000:

\[ x > \frac{c(2f-1) - f}{c + f}. \]

Whereas our model can account for any } f \text{ value, in practice many materials can be approximated by either of two limiting cases: } f \gg c \text{ or } f \ll c. \text{ The limiting case of } f \gg c \text{ represents materials in which the number of crosslinks is low relative to the number of potential crosslinkable functionalities. Such is the case for vulcanized thermosets. By contrast, the limiting case of } f \ll c \text{ corresponds to materials in which nearly every crosslinkable functionality is involved in a crosslink, as is found, for example, in many epoxy thermosets.}

pDCPD resin precursor preparation

DCPD and iPrSi were mixed in the desired ratio. Next, finely powdered Grubbs second-generation catalyst was dissolved into this mixture at a concentration of 2 mg ml\(^{-1}\). The finely powdered initiator was generated by dissolving the commercially obtained Grubbs second-generation catalyst in dichloromethane in a glass vial, evaporation of the solvent under vacuum and scraping the residue from the side of the vial with a spatula. This process enables the rapid and full dissolution of the catalyst in DCPD–iPrSi mixtures. The solutions remained liquid at room temperature at silyl ether concentrations of 10% or higher, whereas solidification occurred at 5% or lower concentrations. In these cases, the solidified monomer mixture was melted by gentle heating in a water bath (~40 °C). The homogenous pink solutions were used within 5 min to prepare resins of the desired geometry.

pDCPD pellet curing

200 μl of the solutions described above were added to 2 ml flat-bottom screw-thread glass vials (VWR, part No. 46610-772, 12 x 32 mm). The vials were heated to 120 °C in an oven for 15 min, during which the pink solution turned into a yellow solid as it polymerized and crosslinked to form pDCPD. The vials were then removed from the oven, cooled to room temperature and broken with a hammer to release the sample. The collected pDCPD samples were cured for another 30 min at 120 °C and then stored at room temperature until further use.

Laser-induced projectile impact testing of iPrSi-doped pDCPD

Laser-induced projectile impact testing (LIPIT) serves as a platform for studying the high-strain-rate impact response of materials\(^{29}\). LIPIT has been used previously to study the impact responses of gels, metals, ceramics and a range of other materials\(^{30,31,32} \). In brief, a high-energy laser pulse (Nd:YAG, 532 nm, 10 ns) is focused onto a glass substrate (210 μm) coated with an ablative gold layer (60 nm) and a polyurea film (40 μm); this glass–gold–polyurea configuration will hereafter be referred to as the ‘launch pad’. The launch pad is coated with microparticles, and after ablation of the gold layer by a high-energy laser pulse, a particle is propelled at high speeds ranging from tens of metres per second up to 2 km s\(^{-1}\), with the characteristic strain rate defined as the impact velocity divided by the particle diameter. The projectile speed is varied by adjusting the laser pulse energy. The particle trajectory and impact are captured by an ultrahigh-speed camera (SIMX16, Specialized Imaging) with 16 independently triggered charge-coupled devices, illuminated by a second pulsed laser (640 nm, 30 μs). This configuration provides 16 frames with a minimum exposure time of 5 ns and varied interframe time. The particle pre-impact velocity \( \omega_p \) and post-impact velocity \( \omega_f \) are extracted from the image sequences. All particle diameters are measured before impact,
and film thicknesses are measured with confocal microscopy after impact.

In this experiment, steel microparticles (12.8 ± 0.4 µm diameter) were launched with speeds ranging from 150 ± 3 m s⁻¹ to 950 ± 19 m s⁻¹ at film samples with thicknesses of 23.0 ± 1.7 µm. Three regimes of impact response were observed: particle rebound, particle embedment and film perforation. The coefficient of restitution, the ratio of pre- and post-impact velocities (−vᵢ/vᵣ), was calculated and plotted to compare the impact responses of the two films. Positive, zero and negative coefficients of restitution correspond to particle rebound, embedment and film perforation, respectively.

Weathering experiments
To assess pDCPD degradability under a marine environment, we exposed pDCPD materials to a synthetic seawater matrix both in the dark and under simulated solar irradiation. We hypothesized that photooxidation of tPrSi-doped pDCPD would further enhance its aqueous wettability by introducing oxygen functional groups, assisting the hydrolysis of silyl ether groups. A polymer pellet of approximately 100 mg was submerged in 60 ml of a synthetic seawater matrix in a clear vial sealed with a polytetrafluoroethylene-lined cap. The synthetic seawater composition was: 420 mM NaCl, 0.8 mM NaBr, 29 mM Na₂SO₄, 54 mM MgCl₂·6H₂O, 11 mM CaCl₂·2H₂O, 10 mM KCl, 0.35 mM H₃BO₃, 1.8 mM NaHCO₃, 0.26 mM Na₂CO₃ and 5 mM FeCl₃.

The vial was then placed inside a Rayonet photoreactor with Hg lamps and with the output spectrum shown in Extended Data Fig. 6a, b (measured by an OceanInsight FLAME-S-XRI-ES spectroradiometer) for 16 d. We note that glass containers were used to filter sub-300-nm light to more closely emulate the solar distribution (represented by ASTM 177 reference spectra). In both the light and dark experiments the temperature was 45–46 °C; the temperature inside the Rayonet reactor was monitored, and the dark experiments were performed in an oven maintained at 45–46 °C.

We calculated degradation as the mass of carbon released in the seawater solution over the mass of carbon in the original material. The total organic carbon was measured as non-purgable organic carbon using a Shimazu TOC-5000 total organic carbon analyser. Prior to analysis, the sample was acidified with 50% HCl to pH < 3 and sparged with N₂ for 8 min to remove inorganic carbon from the seawater matrix. The total organic carbon in the virgin polymer was inferred from the chemical formulas and mass fractions of tPrSi or EtSi co-monomers. A paired t-test was performed to determine whether the content of tPrSi or light exposure has an impact on degradability.

Recycling of pDCPD fragments
pDCPD fragments derived from 10% tPrSi-doped pDCPD were prepared following the standard workflow described above. 500 mg of the fragments were dissolved in 1.5 g of DCPD, forming a viscous brown liquid, to which 8 mg of finely powdered Grubbs’ second-generation catalyst were added. The material was poured into vials (to form disks) and silicone moulds (for tensile and DMA measurements) and cured at 120 °C for 30 min.

Data availability
All data supporting the findings of this study are available within this Article and its Supplementary Information and from the corresponding author upon reasonable request. Source data are provided with this paper.

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Author contributions
P.S. and J.A.J. conceived of the idea. P.S., W.Z. and K.E.L.H. synthesized the materials. P.S., W.Z., S.L.K. and K.E.L.H. characterized the materials. D.J.L., P.S. and J.A.J. developed the theoretical framework. B.X. and D.L.P. conducted accelerated weathering experiments. P.S. and J.A.J. performed techno-economic analyses. J.L., D.V., Y.S. and K.A.N. designed and conducted microparticle impact experiments. P.S. and J.A.J. wrote the manuscript. All authors read and revised the manuscript.

Competing interests
P.S., W.Z., K.E.L.H. and J.A.J. are named inventors on patent applications (US Patent Application 16/542,824 and US Provisional Application 62/935,799) filed by the Massachusetts Institute of Technology on the copolymers described in this work.

Additional information
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Extended Data Fig. 1 | The reverse gel-point concept used to derive the model of degradable thermosets shown in Fig. 1b. **a**, A thermoset network containing $f$ potential crosslinking sites per strand, $c$ actual crosslinks per strand and $x$ cleavable bonds within each strand may or may not be degraded into soluble fragments after bond cleavage. A model that determines whether the material will dissolve can be described as a function of $f$, $c$ and $x$ (Fig. 1b). **b**, The reverse gel-point concept enables this model by assuming that the minimum $x$ required to enable thermoset degradation for given $c$ and $f$ values corresponds to the value that will inhibit the gelation of degradation fragments derived from strands with $f$ potential crosslinking sites and $x$ cleavable bonds. We use existing gelation theories (Miller–Macosko and Flory–Stockmayer) to solve for $x$, given $f$ and $c$. Key to the reverse gel-point concept is the assumption that the network structure formed by the crosslinking of linear copolymer strands followed by cleavage of degradable bonds in those strands is identical to the network formed by first cleaving the linear copolymer strands and then crosslinking the resulting degradation products.
Extended Data Fig. 2 | Characterization of pDCPD. a, Images of pDCPD with various amounts of iPrSi and without iPrSi. b, Images of pDCPD with and without 20 vol% SiXL. c, pDCPD doped with up to 80 vol% SiXL remains intact after 12 h of TBAF treatment.
Extended Data Fig. 3 | Further quantification of the impact of silyl ether incorporation into pDCPD strands.  

**a**, Samples containing different amounts of iPrSi (0, 2.5, 5, 7.5 and 10 vol%) were incubated in 0.5 M TBAF in THF overnight, showing iPrSi-dependent degradation. **b**, Loss moduli for native pDCPD and 2.5% and 5% iPrSi-doped samples before and after TBAF treatment, as measured by oscillatory rheology. The storage moduli are presented in Fig. 2c. **c**, THF swelling ratios (THF swollen mass divided by dry mass) for native pDCPD and 2.5% and 5% iPrSi-doped samples following TBAF treatment. Centre values denote average. Error bars denote s.e.m. n = 3 for all samples.
Extended Data Fig. 4 | Characterization of mechanical and thermal properties of iPrSi-doped pDCPD by DMA. a, Loss factor (tan(delta)) plots of pDCPD samples as a function of iPrSi incorporation. b, Storage moduli collected at \( T_g - 60 \) °C for all samples. Centre values denote average. Error bars denote s.e.m. \( n = 3 \), except for the 33% sample, for which \( n = 5 \).
Extended Data Fig. 5 | Synthesis and degradation of EtSi- and iPrSi-doped pDCPD. a, Structure of EtSi, which differs from iPrSi in terms of the alkyl substituents on the silyl ether group. The less sterically hindered ethyl groups render this monomer more susceptible to cleavage. b, Images of 10% EtSi- or iPrSi-doped pDCPD. c, 10% EtSi dissolves in 0.5 M TBAF in THF after 12 h. d, Images of 10% EtSi-doped (left) and iPrSi-doped (right) pDCPD exposed to THF containing 15% concentrated aqueous HCl (12.1 N). The EtSi sample shows noticeably more rapid degradation under these conditions as compared to the iPrSi sample. Both samples are largely degraded within 12 h. In this case, acidic hydrolysis is facilitated by the presence of organic solvent to swell the network.
Extended Data Fig. 6 | Weathering studies. a, The weathering setup. Samples were kept inside glass vials over the course of the weathering experiments. b, Measured irradiance for samples during the weathering experiments and comparison to solar reference spectra (ASTM G177). c, Ultraviolet-visible spectra for the 0%, 10% iPrSi- and 10% EtSi-doped pDCPD samples. The sample thickness was 1 mm. d, Images of samples before and after the weathering studies.