CHEMISTRY

Coordination-induced polymerization of P=C bonds leads to regular (P—C)$_n$ polycarbophosphanes

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The replacement of carbon in (C—C)$_n$ chains of polyolefins by phosphorus leads to polycarbophosphanes (P—C)$_n$, which may possess unique chemical and physical properties. However, macromolecules with a regular (P—C)$_n$ chain have never been unambiguously identified. Here, we demonstrate that addition polymerization, a general concept to polymerize olefins, can be extended to P=C double bonds. The polymerization of monomeric 2-phosphanaphthalenes is mediated by copper(I) halides and leads to polycarbophosphanes with an M_n of 14 to 34 kDa. Each phosphorus is coordinated to Cu(I), which can be easily removed. Unlike long-term durable polyolefins, the metal-free polymers depolymerize rapidly back to monomers under sunlight or ultraviolet irradiation at λ = 365 nm. The monomers can be recycled for repolymerization, demonstrating a cradle-to-cradle life cycle for polycarbophosphanes.

INTRODUCTION

The polymerization of olefins was discovered in 1839 (1). Today, hundred million tons of polyolefins are produced every year using sophisticated processes that allow the controlled polymerizations of the C=C double bonds in alkenes (2). The incorporation of noncarbon elements into the polymer chains gives access to previously unidentified materials with unique physical and chemical properties (3, 4). Many monomers with a C=E bond, for example, E=N (5), O (6, 7), S (8), and Se (9), can be polymerized in a head-to-tail pattern (addition polymerization), usually with an initiator. This process, schematically shown in Fig. 1A, necessitates monomers (A=B), which are sufficiently kinetically inert to allow isolation and purification. However, many doubly bonded species of noncarbon elements as potential monomers are highly reactive and short-lived. They require steric protection or electronic stabilization, for example, incorporation into a conjugated π system to make them stable and manageable, which, in turn, makes them reluctant to polymerize. Thus, many inorganic polymers such as polysiloxanes [—R$_2$Si—O—]$_n$, polyphosphazenes [—R$_2$P=N—]$_n$, or polyphosphates [—(RO)P(O)—O—]$_n$ are prepared by different methods such as polycondensation or ring opening polymerization, which do not require monomers of multiple bonds (3, 4, 10). The head-to-tail polymerization of phosphaalkenes, R$_2$C=PR′, would allow the preparation of a polymer with a regular (P—C)$_n$ backbone but early attempts only led to ill-defined materials of "polymeric nature" (11). Later, in particular, Gates et al. (3, 12, 13) intensively investigated possibilities to polymerize phosphaalkenes. Several sterically stabilized phosphaalkenes (Fig. 1B) with mesityl (Mes) substituent at P and variable substituents R on carbon (R = phenyl, 9-phenanthryl, 4-methoxyphenyl, 1-naphthyl, ferrocenyl, pyrenyl, and oxazoline-derived groups) were polymerized or copolymerized. The initial assumption that these polymers contain a regular (P—C)$_n$ backbone had to be corrected (14, 15). Instead, a complex polymerization process that involves isomeri-

zation takes place, leading to polymers with an irregular microstructure as shown in Fig. 1C.

The stability of hydrocarbon polymers and their massive and still increasing use causes severe environmental problems (2). A simple solution would be to mechanically recycle plastics, which, however, is not without problems (2, 16). Another strategy consists in chemically breaking down a polymer into its monomer units for reuse (17). Some poly(phthalaldehyde)s, polyesters, polycarbonates, polyurethanes, polythioesters, poly(enol ether)s, and polymers based on covalent diketoenamine bonds follow this "cradle-to-cradle" design (18–26). Their degradation/depolymerization relies on thermolysis, catalytic ring-closing depolymerization, or bond exchange reactions that require the use of quantitative amounts of additional reagents. Polymers that unzip exclusively back to the monomers at low temperature or triggered by physical stimuli remain of great interest (27). Specifically, depolymerization under irradiation with light has great potential to tackle the problem of plastic pollution (28), which is an even more sustainable approach compared to the photodegradation of polymers (29).

Here, we report the successful polymerization of P=C bonds in 2-phosphanaphthalenes to regular (P—C)$_n$ chains promoted by copper(I) halides. Removal of Cu(I) allows the isolation of the free polymers that are stable as a solid. In solution, the polymers depolymerize exclusively to the monomers. This process is very slow at
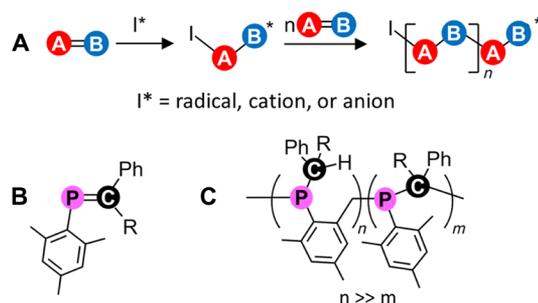
Fig. 1. Polymerization of double bonds. (A) Schematic presentation of an addition polymerization of doubly bonded species A=B using an initiator I*. (B) Previously used phosphaalkenes for polymerization. (C) Observed microstructure resulting from the polymerization of phosphaalkenes shown in (B).

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room temperature, but becomes faster at elevated temperatures, and is very fast under irradiation with sunlight or at $\lambda = 365$ nm. The obtained monomers can be fully reverted to polymers simply by adding copper(I) halides again without any further purification.

RESULTS AND DISCUSSION
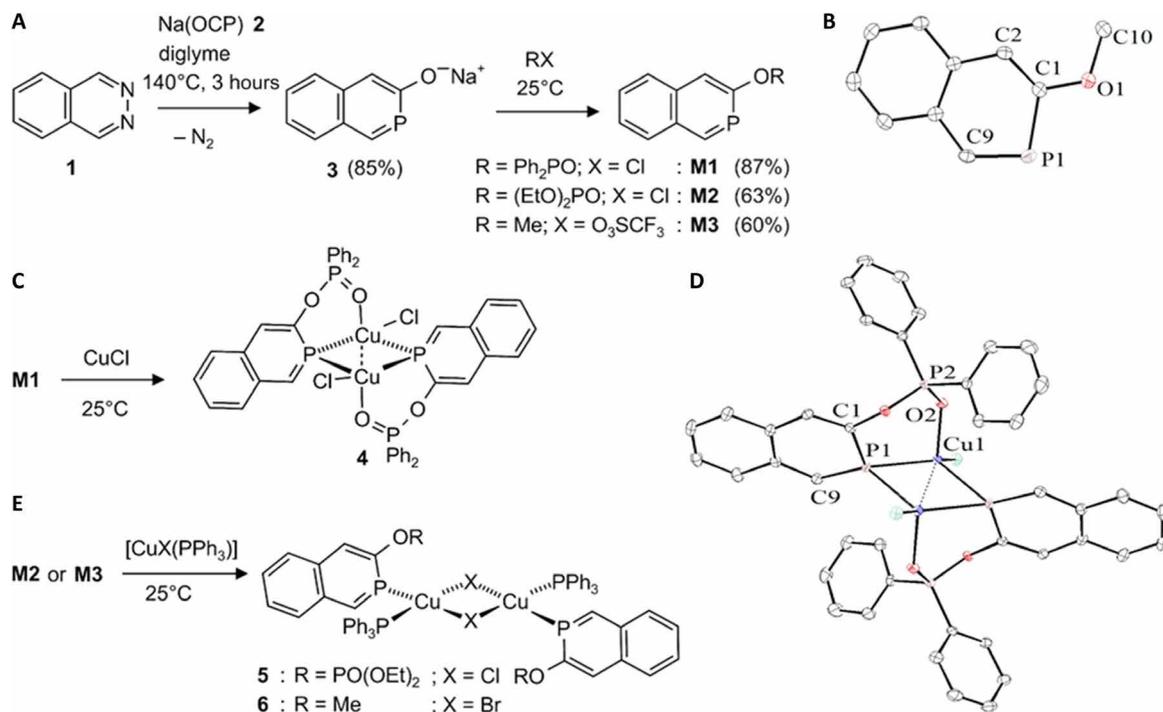
2-Phosphanaphthalenes

Sodium phosphaethynolate, Na(OCP) 2, became a versatile synthon (30) and can be used to synthesize sodium 2-phosphanaphthalene-3-olate 3 from commercially available phthalazine 1 (31). Upon reaction with various electrophiles, the neutral 2-phosphanaphthalenes M1 to M3 are produced in good yields (Fig. 2A).

The ^{31}P chemical shift of the λ^3-P_{ring} nucleus in the ring is at relatively high frequency [M1: $\delta(^{31}P) = 172.8$ parts per million (ppm); M2: $\delta(^{31}P) = 171.3$ ppm; M3: $\delta(^{31}P) = 158.9$ ppm], which is typical for 2-phosphanaphathalenes (32). Phosphanaphthalene M3 was further characterized by single-crystal x-ray diffraction, and its crystal structure is shown in Fig. 2B. The P1—C9 bond length [1.70(2) Å] in M3 is in the typical range of P=C double bonds [$\sum r_{cov}(C=P) = 1.69$ Å] (33) and much shorter than the P1—C1 bond [1.78(1) Å]. This and all other structural features are comparable to the previously described ones for M1 (31). Calculations indicate that both the PC_5 and C_6 ring in M1 are aromatic (31).

Phosphanaphthalene M1 was reacted with CuCl in methylene chloride as a solvent to give a single product 4 (Fig. 2C), which is sparingly soluble and precipitated as a bright yellow powder from the reaction mixture (92% isolated yield). The structure of 4 was determined by single-crystal x-ray diffraction (Fig. 2D). In the solid state, complex 4, $(M1^{CuCl})_2$, contains a $Cu_2(\mu^2\text{-P})_2$ core, where each

phosphanaphthalene ligand bridges two copper centers. The structural parameters of the coordinated phosphanaphthalene are almost identical to the ones in free M1 (table S1). Each P=O unit of the phosphoryl substituents coordinates via the oxygen center O2 to a copper center, which, as a result, resides in a distorted tetrahedral coordination sphere. Overall, the core of complex 4 consists of a tricyclic structure in a zigzag confirmation. The reaction of M2 or M3 with CuCl initially gives Cu phosphanaphthalene complexes as indicated by the ^{31}P nuclear magnetic resonance (NMR) spectra, but they rapidly react further (vide infra). However, the Cu triphenyl phosphane precursors [CuX(PPh$_3$)] (X = Cl, Br) lead to stable dinuclear copper complexes 5 and 6 with M2 and M3 as terminal η^1-binding ligands, respectively (Fig. 2E). The halogen centers (X = Cl, Br) take μ^2-bridging positions (figs. S122 to S123). Again, the structure metrics of the coordinated phosphanaphthalene rings are almost identical to the unbound ones (table S1).

The coordination shift [$\Delta^{coord} = \delta(^{31}P_{ring})^{complex} - \delta(^{31}P_{ring})^{unbound}$] allows differentiating between the terminal η^1-binding and bridging μ^2-binding mode of a phosphinine ligand. It also helps to decide whether the solid-state structure of a complex is retained when dissolved in solution (34). A large negative Δ^{coord} indicates a bridging phosphinine, and a small negative Δ^{coord} manifests a terminal one. The solid-state ^{31}P MAS NMR of 4 shows a resonance at $\delta = 104$ ppm for the λ^3-P_{ring} nucleus ($\Delta^{coord} = -68$ ppm), which is very different from the one in solution [$\delta(^{31}P_{ring}) = 141.6$ ppm; $\Delta^{coord} = -32$ ppm]. This suggests that in solution, 4 converts to a species with a η^1-phosphanaphthalene as seen in 5 or 6. The solid-state ^{31}P MAS NMR spectrum of 5 shows a signal at 143 ppm ($\Delta^{coord} = -28$ ppm), while in solution, the ^{31}P$_{ring}$ nuclei is detected at 162.1 ppm ($\Delta^{coord} = -9$ ppm). The small Δ^{coord} indicates η^1-bound

Fig. 2. Synthesis and structures of monomers and their metal complexes. (**A**) Synthesis of 2-phosphanaphthalenes M1 to M3. (**B** and **D**) Crystal structures of M3 and 4. (**C** and **E**) Synthesis of copper complexes 4 to 6.

phosphanaphthalene in both the solid and solution, but the different ^{31}P chemical shifts infer that the solid-state structure of **5** is likely not retained either when dissolved. The hydrodynamic volume of **5** in solution was determined to be 268 Å^3 in CD$_2$Cl$_2$ and 333 Å^3 in CDCl$_3$ by diffusion ordered NMR spectroscopy. This corresponds roughly to the half of the volume of **5** in the solid state (1013 Å^3), which indicates that **5** dissociates into a mononuclear complex in solution. Typically, the resonances of the $^{31}P_{ring}$ nuclei are broadened by quadrupolar coupling to the directly bound $^{63}Cu/^{65}Cu$ nuclei (half-widths $v_{1/2}$ of 123 to 637 Hz; table S2).

Polymerization

Mixing phosphanaphthalene **M2** or **M3** with copper halides CuX (X = Cl, Br) in dichloromethane (DCM) or *N,N'*-dimethylformamide at room temperature rapidly gives yellow solutions, which show broadened $^{31}P_{ring}$ NMR signals [**M2**^{CuCl} $\delta(^{31}P_{ring})$ = 166.5 ppm, Δ^{coord} = −5 ppm; **M2**^{CuBr} $\delta(^{31}P_{ring})$ = 169.2 ppm, Δ^{coord} = −2 ppm; **M3**^{CuCl} $\delta(^{31}P_{ring})$ = 142.6 ppm, Δ^{coord} = −16 ppm], indicating the formation of η^1-phosphanaphthalene Cu complexes. The intensity of these signals decreases with time while simultaneously broad signals at significantly lower frequencies increase in intensity indicating the conversion of the P=C unit in **M2** or **M3** to P—C single bonds and the formation of polymers **P2**^{CuCl} [$\delta(^{31}P_{ring})$ = −30.9 ppm, $v_{1/2}$ = 714 Hz], **P2**^{CuBr} [$\delta(^{31}P_{ring})$ = −31.6 ppm, $v_{1/2}$ = 514 Hz], and **P3**^{CuCl} [$\delta(^{31}P_{ring})$ = −26.0 ppm, $v_{1/2}$ = 823 Hz]. Concomitantly, the ^1H and ^{13}C NMR signals of the relevant P,C units (table S3) are shifted to significantly lower frequencies likewise indicating the conversion of the double bonds to P—C single bonds. Full conversion is reached after some hours at room temperature and evaporation of the solvent. As an example, Fig. 3A displays the ^{31}P NMR spectra of the phosphoryl substituted phosphanaphthalene **M2** (top), the reaction mixture of **M2** with a slight excess of CuCl (middle), and the pure product **P2**^{CuCl} (bottom). The products **P2**^{CuCl}, **P2**^{CuBr}, and **P3**^{CuCl} were obtained as brittle yellow solids in good yields (60 to 85%). Slow evaporation of a DCM solution of **P2**^{CuCl} yielded a brittle yellow film.

That **M2** and **M3** undergo a coordination-induced polymerization is verified by gel permeation chromatography (GPC, figs. S102 to S105) and high-mass matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) (figs. S106 to S110) of the resulting polymers. Figure 3B shows, as an example, the high-mass MALDI-MS spectrum of the polymer **P2**^{CuCl}. The number average molecular weight (M_n) of **P2**^{CuCl} (M_n = 26.8 kDa), **P2**^{CuBr} (M_n = 14.4 kDa), and **P3**^{CuCl} (M_n = 34.2 kDa) indicates medium-size polymers with a size distribution in the range of Đ = 1.88 (**P2**^{CuBr}) to 2.41 (**P3**^{CuCl}) (Đ = polydispersity index). Two-dimensional (2D) NMR spectra allow us to unequivocally determine the alternating sequence of carbon and phosphorus nuclei (see the Supplementary Materials for details). Elemental analysis data indicate that the phosphorus of each repeating unit binds to one CuX unit.

The initial difficulty in achieving reproducible kinetic data led to the discovery that traces of water influence the rate of the polymerization. The deliberate addition of small amounts of water to a DCM solution of the copper complex **M2**^{CuCl} significantly accelerates the polymerization and the conversion reaches 100% in 5 min at ambient temperature. GPC analysis of this polymer **P2**^{CuCl} gave M_n = 29.0 kDa with Đ of 1.84, which is comparable to previously obtained data. The polymerization of a 0.2 M solution of **M2**^{CuCl} in DCM was followed by ^{31}P NMR, showing an apparent rate constant of k_{ap} = 5.2 × 10^{-4} s^{-1} (see the Supplementary Materials for details).

Ionic substances like HBF$_4$(OEt$_2$) or [Ph$_4$P]$^+$Cl$^-$ were found to retard the polymerization. The use of Ag(O$_3$SCF$_3$) leads to a stable colorless coordination polymer [Ag(O$_3$SCF$_3$)(**M2**)]$_\infty$ (see the Supplementary Materials for details). [AuCl(SMe$_2$)] promotes the polymerization of **M2** but a less defined material is obtained. Metal salts like MnBr$_2$(THF)$_2$, Fe$_2$Cl$_4$(THF)$_3$, CoCl$_2$, NiCl$_2$(DME), or ZnCl$_2$ do not boost the polymerization.

The coordinated copper can be easily removed from **P2**^{CuCl}, **P2**^{CuBr}, and **P3**^{CuCl} by adding an excess of phosphanes under the conditions indicated in Fig. 4. These conditions were optimized such that the polymers can be easily obtained in pure form as insoluble white solids while the by-products remain in solution. Alternatively, aqueous NaCN can be used to displace the Cu$^+$ ions. The loss of copper is indicated by a substantial narrowing of the ^{31}P NMR signals due to the absence of coupling to the quadrupolar Cu nuclei. Furthermore, the $^{31}P_{ring}$ resonance is shifted to significantly lower
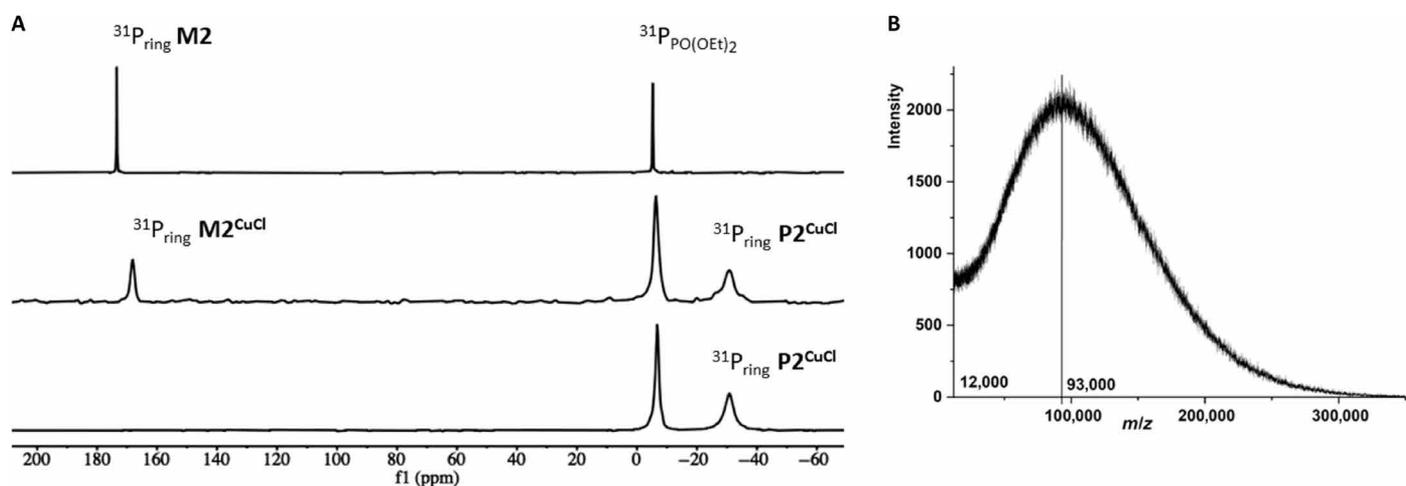
Fig. 3. NMR spectra and mass analysis by matrix-assisted laser desorption/ionization (MALDI). (**A**) ^{31}P NMR spectra of **M2** (top), the reaction mixture of **M2** with CuCl in DCM (middle), and the pure **P2**^{CuCl} (bottom). [The ^{31}P NMR resonance for the PO(OEt)$_2$ group is not significantly affected by complexation or polymerization.] (**B**) High-mass MALDI-MS spectrum of **P2**^{CuCl}. *m/z*, mass/charge ratio.
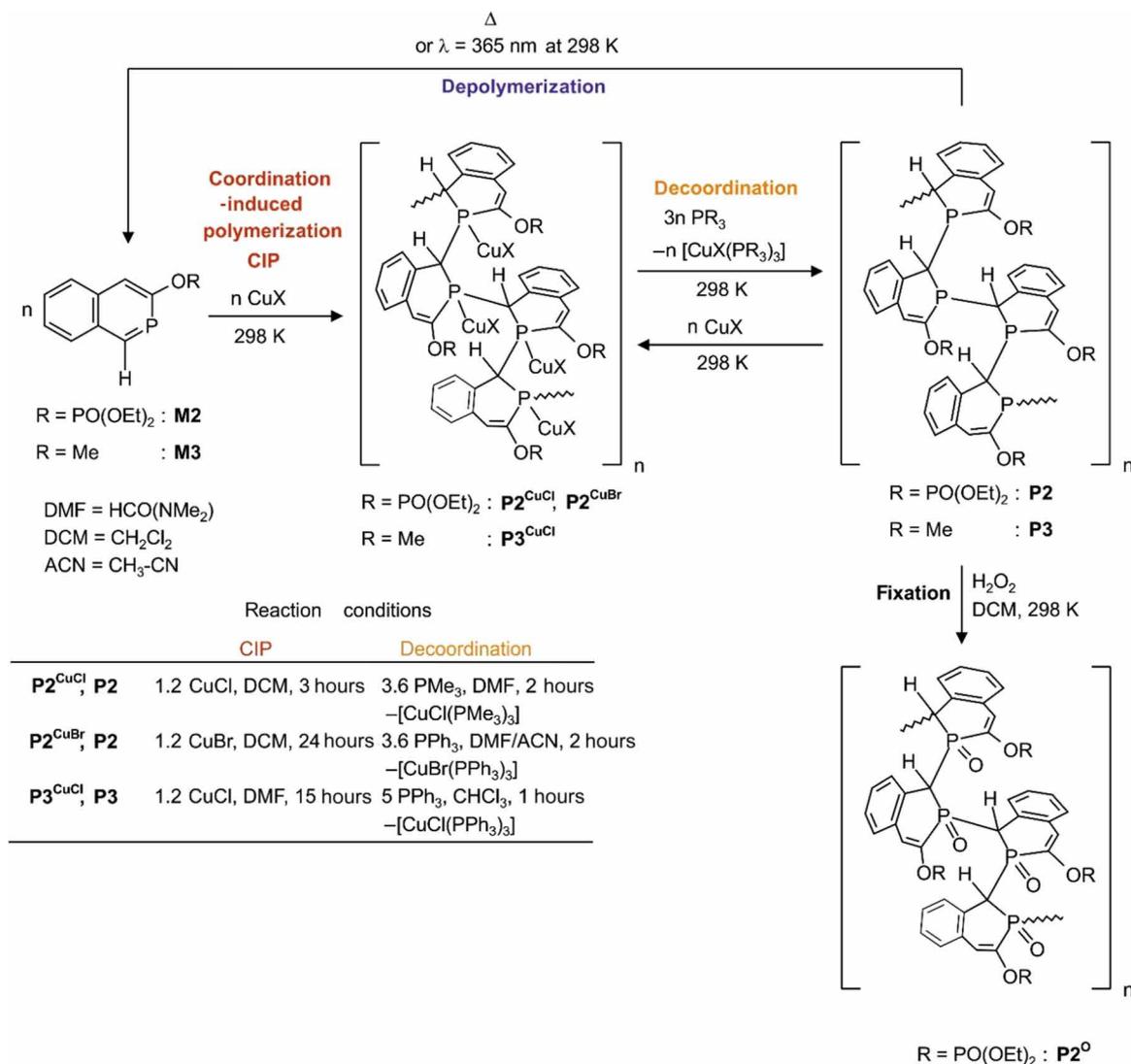
Fig. 4. Synthesis of polymers P2^{CuCl}, P2^{CuBr}, and P3^{CuCl} by coordination-induced polymerization (CIP), their decoordination to give the metalfree polymers P2 and P3, the depolymerization and oxidation.

frequencies in **P2** [δ(^{31}P$_{ring}$) = −47.4 ppm; ν½ = 40 Hz] and **P3** (−46.1 ppm; ν½ = 136 Hz). The regular (P—C)$_n$ sequence in **P2** and **P3** was again proven by 1D (^{1}H, ^{13}C, and ^{31}P) and 2D NMR (heteronuclear single-quantum coherence, heteronuclear multiple-bond correlation, and correlation spectroscopy) (figs. S71 to S79 for **P2** and figs. S84 to S93 for **P3**). We were not able to obtain satisfactory GPC data of **P2** or **P3**. However, the reaction of **P2** with CuCl quantitatively gives **P2^{CuCl}** and the oxidation of **P2** using aqueous hydrogen peroxide gives polymer **P2^O**, which could be characterized by GPC and high-mass MALDI-MS experiments.

The NMR spectra for **P2** show only one relatively narrow peak for the ^{13}C and ^{31}P nuclei in the (P—C)$_n$ backbone. This strongly suggests that **P2** shows remarkable stereoregularity (vide infra). On the contrary, polymer **P3** consists of atactic (P—C)$_n$ backbones, which show several ^{13}C and ^{31}P resonances.

In the solid state, polymers **P2** and **P3** are stable for several months at room temperature in the absence of ultraviolet light, monitored by Fourier transform infrared spectroscopy. A very slow

depolymerization of **P2** and **P3** to the monomers **M2** and **M3** was observed at room temperature in solution. The full conversion of **P3** takes 2 months but quantitatively leads to analytically pure **M3**. The even slower depolymerization of **P2** was followed by ^{31}P and ^{1}H NMR spectroscopy in 1,1,2,2-tetrachloroethane-d$_2$ at four different temperatures (353, 373, 393, and 410 K) (see the Supplementary Materials for details). The depolymerization reaction follows first-order kinetics, and Arrhenius plots allow us to determine the activation energy E_a to be 32.9 ± 5.3 kJ mol^{-1} ($\Delta G^{\#}_{298K}$ = 104.9 ± 9.3 kJ mol^{-1}) and 39.8 ± 7.9 kJ mol^{-1} ($\Delta G^{\#}_{298K}$ = 106.1 ± 14.3 kJ mol^{-1}) based on ^{1}H and ^{31}P NMR, respectively ($\Delta G^{\#}$ = Gibbs energy of activation). Note that the E_a for the depolymerization of polyolefins is much larger (200 to 300 kJ mol^{-1}) (35). Under the irradiation with light of λ = 365 nm or simply sunlight, quantitative conversion of **P2** and **P3** to **M2** and **M3** is achieved at room temperature within 10 min. When CuCl is added to these reaction mixtures, the quantitative reconstitution of the polymers **P2^{CuCl}** and **P3^{CuCl}** is observed.

Mechanism and DFT calculations

It is well known that coordination to a metal center renders the P=C bonds of phosphinines more susceptible to addition of nucleophiles such as water (36, 37). When $(\mathbf{M1^{CuCl}})_2$ **4**, which does not polymerize, is reacted with water, complex **7** is obtained in high yield (Fig. 5A). When the polymerization of $\mathbf{M2^{CuCl}}$ with the addition of water was retarded by $[\mathrm{Ph_4P}]^+\mathrm{Cl}^-$, the formation of an analog of **7** was observed (see the Supplementary Materials for details).

According to these experimental observations, further supported by end group analysis by MALDI-TOF (time-of-flight) study of **P2** (see the Supplementary Materials for details), we therefore assume that hydroxide ions initiate the polymerization. A possible mechanism, which is bolstered by density functional theory (DFT) calculations [M06-2X/6-31G(d,p)], is depicted in Fig. 5B. The addition of OH⁻ to the phosphorus center of $\mathbf{M3^{CuCl}}$ is exergonic ($\Delta G = -60.7$ kcal mol⁻¹) and leads first to intermediate **I1**, which rearranges to its more stable tautomer **I2** ($\Delta G = -11.4$ kcal mol⁻¹). This can either be protonated to give **7′** or react with monomer $\mathbf{M3^{CuCl}}$, which is in large excess at the beginning of the reaction, to give intermediate **I3** in an exergonic reaction ($\Delta G = -29.0$ kcal mol⁻¹). Note that a related water-promoted dimerization of a coordinated phosphinine has been recently reported (38). Chain propagation starts from **I3** at the nucleophilic carbon center. Protonation terminates the active chain ends. According to the calculations, each chain propagation step is exergonic by about −23 kcal mol⁻¹ (figs. S131 to S132). DFT calculations on a pentamer of $\mathbf{P3^{CuCl}}$ (Fig. 5C) indicate that the isotactic polymer is slightly more stable than the syndiotactic or atactic one. This may explain why polymer **P2** carrying the bulkier PO(OEt)₂ substituent shows remarkable stereoregularity as indicated by a single and only slightly broadened ³¹P NMR resonance. DFT calculations also predict that the metal-free polymer **P3** is thermodynamically unstable and that each depolymerization step is exergonic by about −4 kcal mol⁻¹ (figs. S133 to S134).

In conclusion, the P=C bonds in 2-phosphanaphthalenes can be polymerized in the presence of Cu(I) halides to give, as a first example, a family of polymers with a regular $(\mathrm{P-C})_n$ backbone of three-valent phosphorus. Under irradiation with light, the quantitative depolymerization of the metal-free polymers is triggered. In solution, both polymerization and depolymerization proceed under very mild conditions at room temperature and can be repeatedly performed. However, in the solid state, these stimulus-responsive polymers remain stable, which may allow for potential applications in the course of their lifetime. For example, because they contain
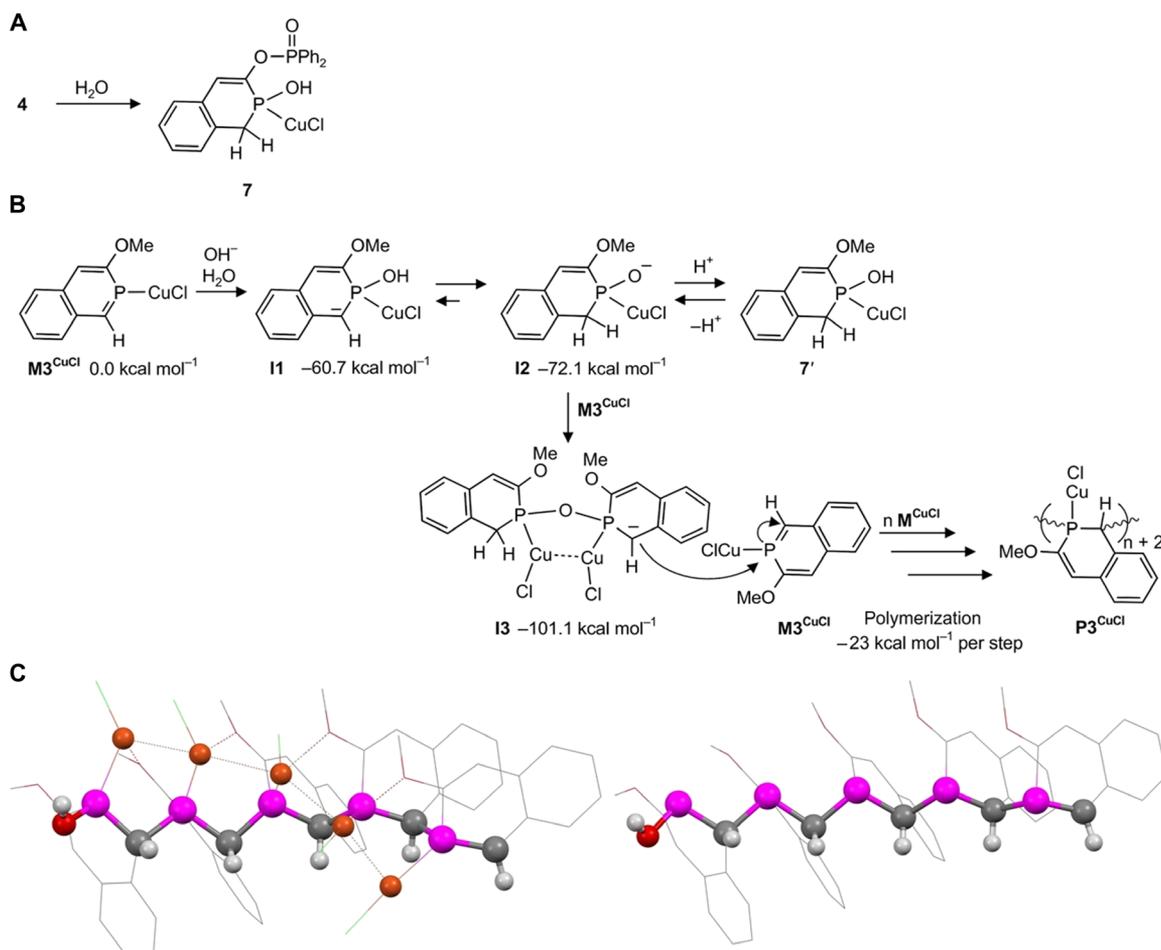
Fig. 5. Proposed simplified mechanism of the polymerization. (**A**) Addition of water to the C=P bond in **4**. (**B**) Possible mechanism for the polymerization of the phosphanaphthalene copper complexes $\mathbf{M^{CuX}}$, represented by $\mathbf{M_3^{CuCl}}$. (**C**) Calculated isotactic pentamer of $\mathbf{P3^{CuCl}}$ (left) and **P3** (right).

coordination sites for metals, various metallopolymers with tunable properties are potentially accessible, which can be used for different applications such as immobilized catalysts or optoelectronic materials (39). At the end of their lifetime, these polymers can be easily unzipped in solution and the monomers can be fully recycled. Although the general nature of these observations remains open to further investigation, the results described here do show that monomers can be found to prepare fully recyclable polymers under mild conditions exemplifying the concept of cradle-to-cradle processes in polymer science.

MATERIALS AND METHODS
Because of the lengthy description of the experimental methods, synthesis, and characterization of all the compounds, these details can be found in the Supplementary Materials.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/11/eabf4272/DC1

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