

# Poly(carbyne)s via reductive C1 polymerization

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## Abstract

C1 polymerizations enable the synthesis of densely functionalized, persubstituted polymers that are challenging to access using conventional methods. One class of C1 polymers are the poly(carbyne)s, which are unique in that they can adopt branched or linear structures, or combinations thereof. Herein, we report the synthesis of new poly(carbyne)s, including those that feature side chains with carbonyl-containing functional groups. The polymers were obtained by exposing solutions of monomers outfitted with trihalomethyl or trimethyl orthoformate groups to metallic lithium, and reaction performance was improved when electron transfer agents (e.g. naphthalene) were included. The mechanisms of the polymerizations were also deconvoluted and found to depend on the monomer employed.

Supporting information may be found in the online version of this article.

**Keywords:** C1 Polymerization; Chain growth polymerization; Poly(carbyne); Polymer architecture; Step growth polymerization

## INTRODUCTION

A C1 polymerization is a reaction that grows polymer chains in single carbon increments.<sup>1</sup> Such a process deviates from the more common polymerization reactions that extend polymer backbones by two or more carbon atoms during each propagation step. Beyond the fundamental distinction, C1 polymerizations offer access to highly substituted polymers which often exhibit unique<sup>2</sup> or enhanced<sup>3,4</sup> physicochemical properties compared to less substituted analogues. Diazo compounds,<sup>1,5–7</sup> ylides,<sup>5,6,8,9</sup> isocyanides<sup>1,10</sup> and geminal dihalides<sup>11</sup> are typically used as monomers in C1 polymerizations because they are capable of generating carbenoid-like intermediates that can condense in a repeating fashion (Scheme 1(a)). Catalysts are often required to activate the monomer and some offer controlled<sup>12</sup> or living characteristics.<sup>13–17</sup>

A relatively less studied class of C1 polymers are the poly(carbyne)s. Carbyne additions can result in different polymer architectures that depend on the bonding configuration of the repeating unit (Scheme 1(b)). While branched networks or linear polymers represent two of the limiting structures, mixtures are also possible. To date, only geminal trihalides have been utilized as carbyne precursors in C1 polymerizations. Kryazhev *et al.* reported (1969, 1979) that treatment of  $\alpha,\alpha,\alpha$ -trichlorotoluene (**1**) with an excess of lithium, magnesium or zinc leads to the formation of a linear, unsaturated polymer.<sup>18,19</sup> Bianconi and colleagues later found that exposing **1** to a sodium potassium amalgam afforded branched polymers that consisted primarily of sp<sup>3</sup>-hybridized carbons in the backbones.<sup>20,21</sup> Likewise, poly(carbyne)s derived from bromoform, chloroform and 1,1,1-trichloroethane have also been characterized as branched.<sup>21–23</sup>

Inspired by these early reports, a number of potential monomers were envisioned and explored in reductive C1 polymerizations. Herein we report the first synthesis of poly(carbyne)s that contain ester or ketone groups as well as the first poly(carbyne)s synthesized from halogen-free monomers. The carbonyl-containing monomers were found to polymerize primarily in a step growth manner and afforded linear polymers. In contrast, the reductive C1 polymerization of arylated monomers afforded branched polymers and proceeded in a manner that was consistent with a chain growth process. It was also discovered that adding electron transfer agents (e.g. naphthalene) to the reactions increased the polymerization rates as well as the yields of the polymer products.

## RESULTS AND DISCUSSION

A library of monomers that were envisioned to afford poly(carbyne)s via a reductive C1 polymerization are shown in Scheme 2 and include various geminal trichlorides (**2–5**) and arylated

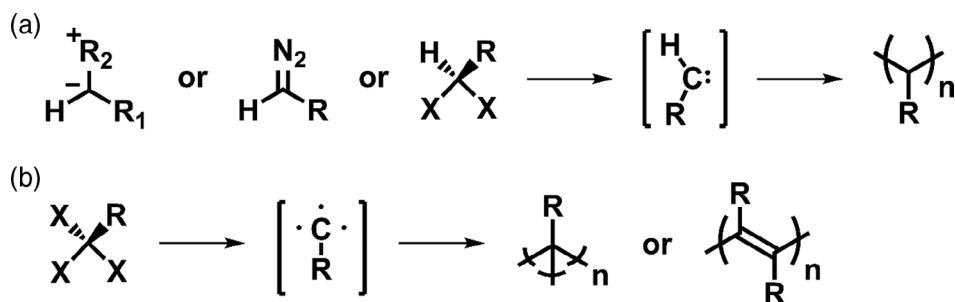
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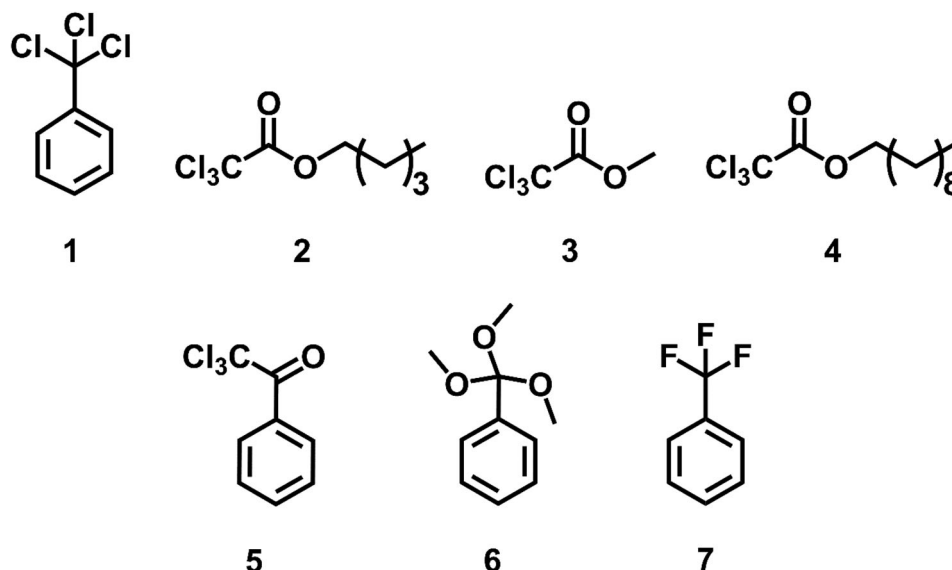
The authors declare no competing financial interests.

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**Scheme 1.** C1 polymerizations of (a) carbenes and (b) carbynes.



**Scheme 2.** Structures of selected monomers.

compounds (**6**, **7**). A common trait of the series is that they feature carbon atoms in the +3 oxidation state and thus are capable of forming carbynes upon reduction. A preliminary set of polymerization reactions was performed with *n*-pentyl 2,2,2-trichloroacetate (**2**). A 1.0 mol L<sup>-1</sup> tetrahydrofuran (THF) solution of the monomer was charged with 3.2 equivalents of Li at room temperature. After 24 h, the reaction mixture was quenched with methanol, extracted and then added dropwise into *n*-hexane to induce precipitation. Collection of the precipitated solids afforded the corresponding polymer in 21% yield, which was subsequently increased to 31% by repeating the reaction at 70 °C. Performing the reaction at 70 °C with six equivalents of Li further increased polymer yield to 39% after 12 h.

Electron transfer agents have been reported to facilitate the activation of carbon–halogen bonds by alkali metals.<sup>24,25</sup> As such, it was reasoned that the addition of an electron transfer agent to the reaction may improve the performance of the polymerization. Naphthalene was selected because it readily forms lithium naphthalenide, a radical anion, upon exposure to lithium. The addition of naphthalene (0.25 equiv. with respect to monomer) to the optimized reaction parameters described above ([**2**]<sub>0</sub> = 1.0 mol L<sup>-1</sup>, [Li]<sub>0</sub>/[**2**]<sub>0</sub> = 6, THF, 70 °C, 12 h) increased the yield of polymer to 50%. The use of relatively more or less naphthalene was observed to have detrimental effects (Appendix S1, Table S4). As such, the conditions were deemed optimal and

applied toward the polymerization of the other monomers shown in Scheme 2; see Table 1 for a summary.

A series of spectroscopic measurements indicated that the monomers utilized in the aforementioned reactions were converted into polymeric derivatives. For example, the infrared spectrum recorded for the polymer obtained from **2** exhibited relatively broad signals compared to that of its monomer (Fig. 1). Moreover, the characteristic  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C=O}}$  and  $\nu_{\text{C-O}}$  signals of **2** were retained while the salient  $\nu_{\text{C-Cl}}$  signals (880, 824 and 680 cm<sup>-1</sup>) were absent. A new signal at 1619 cm<sup>-1</sup>, consistent with an alkene stretching frequency and indicative of an unsaturated polymer backbone, was also observed. Similar signals (1628–1598 cm<sup>-1</sup>) were identified in the infrared spectra recorded for the polymers derived from **3–5** (Appendix S1, Figs S30–S32). The spectroscopic data collected for the polymers obtained from **1**, **6** and **7** (Figs S33–S35) agreed with those reported for poly(phenyl carbyne)<sup>21</sup> and thus their structures were assigned as branched.

NMR spectroscopy was utilized to further elucidate the structures of the poly(carbyne)s. While the solution-state <sup>1</sup>H and <sup>13</sup>C NMR spectra recorded for the polymers synthesized from **2–7** were consistent with their structures, the signals were found to be broad which challenged refinement. For example, the <sup>13</sup>C NMR signal assigned to the carbonyl group in **4** can be observed at 162 ppm; however, the corresponding signal was suppressed upon analysis of the corresponding polymer along with other

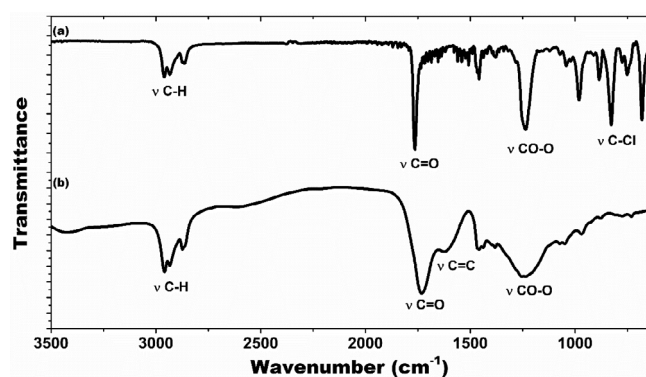
**Table 1.** Polymerization of various monomers<sup>a</sup>

Monomer	$M_n$ (kDa) <sup>b</sup>	PDI	Yield (%)
<i>n</i> -Pentyl trichloroacetate ( <b>2</b> )	1.64	4.5	50
Methyl trichloroacetate ( <b>3</b> )	0.72	2.9	78
<i>n</i> -Decyl trichloroacetate ( <b>4</b> )	1.92	6.1	34
2,2,2-Trichloroacetophenone ( <b>5</b> )	2.28	5.7	48
Trimethyl orthobenzoate ( <b>6</b> )	1.21	2.0	30
$\alpha,\alpha,\alpha$ -Trifluorotoluene ( <b>7</b> )	2.31	2.7	29
$\alpha,\alpha,\alpha$ -Trichlorotoluene ( <b>1</b> )	2.45	2.7	37
$\alpha,\alpha,\alpha$ -Trichlorotoluene ( <b>1</b> ) <sup>c</sup>	2.48	2.8	86

<sup>a</sup> Conditions: [monomer]<sub>0</sub> = 1.0 mol L<sup>-1</sup>, [Li]<sub>0</sub>/[monomer]<sub>0</sub> = 6, [naphthalene]<sub>0</sub> = 0.25 mol L<sup>-1</sup>, THF, 70 °C, 12 h.

<sup>b</sup> Determined by SEC versus a polystyrene standard in THF.

<sup>c</sup> Conditions: [monomer]<sub>0</sub> = 1.0 mol L<sup>-1</sup>, [Li]<sub>0</sub>/[monomer]<sub>0</sub> = 6, THF, 70 °C, 12 h (no added naphthalene).

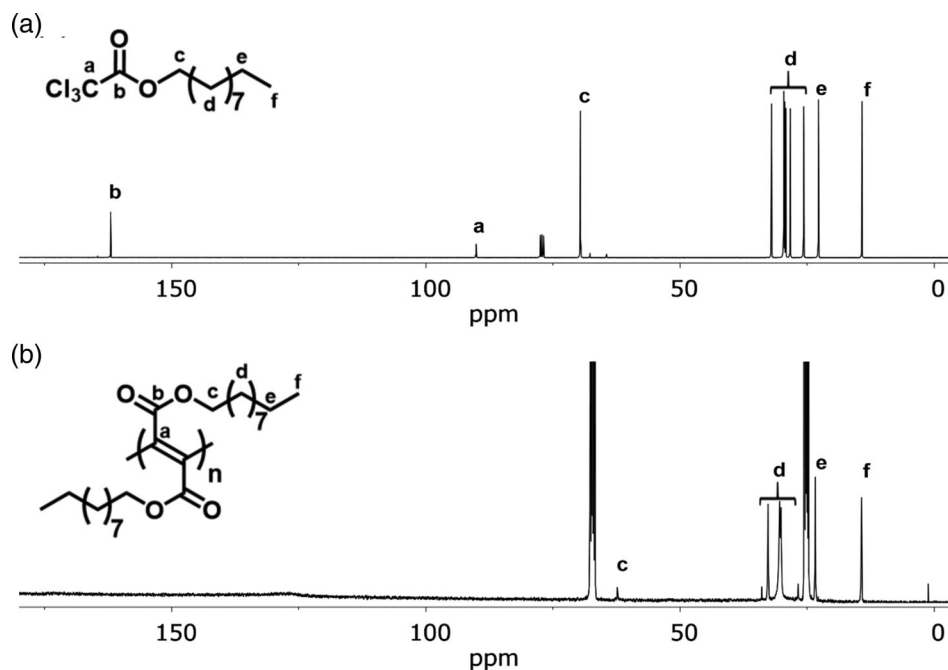


**Figure 1.** Infrared spectra recorded for (a) monomer **2** and (b) its polymeric derivative.

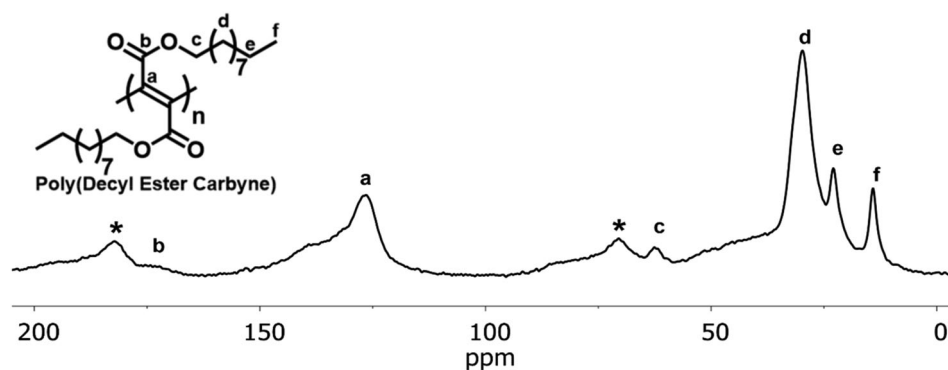
salient signals (Fig. 2). The suppression was effectively managed using <sup>1</sup>H-<sup>13</sup>C cross-polarization magic-angle spinning (CP MAS)

NMR spectroscopy, where the <sup>13</sup>C NMR signal of the carbonyl group in the polymer was observed at 173 ppm (Fig. 3). A <sup>13</sup>C NMR signal was also recorded at 126 ppm and attributed to alkene groups, consistent with the Fourier transform infrared (FTIR) data. Similar data were recorded for the polymers that were synthesized from **2–5** (Figs S21–S24). The <sup>1</sup>H-<sup>13</sup>C CP MAS NMR spectra of the polymers obtained from **1**, **6** and **7** (Figs S20, S25 and S26) exhibited broad signals at 51 ppm, which have been attributed to the quaternary carbons of a branched network.<sup>21</sup>

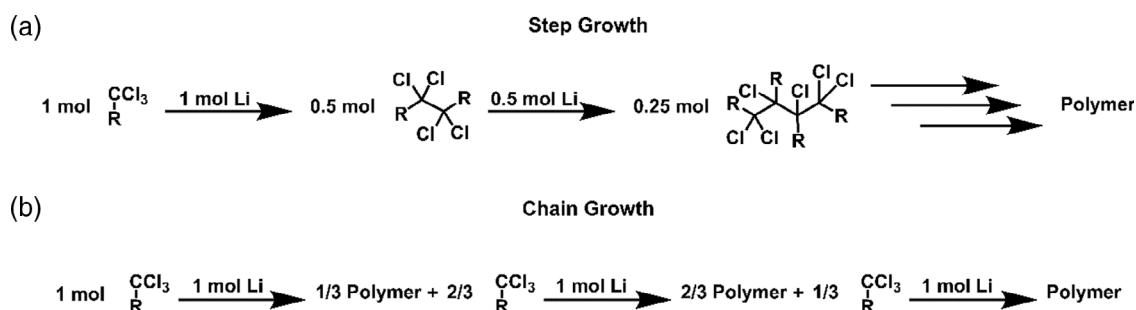
It was reasoned that the NMR signal suppression effects may be due to the presence of polymer-based radicals in part because poly(phenyl carbyne)s have been previously reported to contain unpaired electrons.<sup>18–20</sup> Electron paramagnetic resonance (EPR) spectroscopy revealed that the polymers described above exhibited sharp signals at  $g = 2.002$ – $2.003$  with a separation of 8–10 G, consistent with carbon-centered radicals. The corresponding spin densities were calculated to be of the order of  $10^{17}$ – $10^{18}$  spins g<sup>-1</sup> (Appendix S1, Table S5).



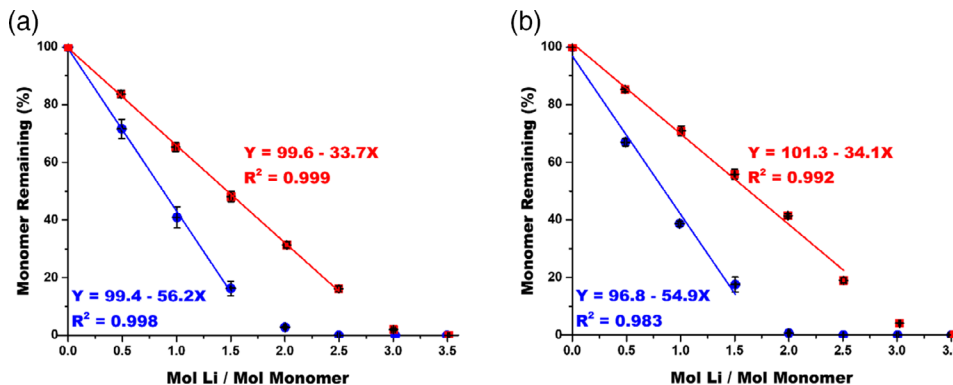
**Figure 2.** <sup>13</sup>C NMR spectra recorded for **4** before (a) CDCl<sub>3</sub> and after (b) THF-*d*<sub>8</sub> polymerization.



**Figure 3.**  $^1\text{H}$ - $^{13}\text{C}$  CP MAS NMR spectrum recorded for the polymer obtained from **3**. Conditions: MAS = 7 kHz,  $t_{\text{CP}}$  = 2 ms, relaxation delay = 10 s; \* denotes spinning sidebands.



**Scheme 3.** A comparison of polymerization mechanisms.



**Figure 4.** (a) Monomer (**1**, red squares or **2**, blue circles) remaining as a function of equivalents of Li added. (b) Monomer (**1**, red squares or **2**, blue circles) remaining as a function of equivalents of Li added and in the presence of naphthalene.

The observed differences in bonding along the polymer backbone may reflect a variation in the mechanism by which the polymers are formed. Polymerization reactions typically proceed through step or chain growth pathways. If the former were operative (Scheme 3(a)), then the majority of the monomer should be consumed during an early stage of the reaction. Alternatively, if the polymer were to grow in a chain-like manner, then the monomer should be consumed at a steady rate (Scheme 3(b)). To test which mechanism was operative, solutions of either **1** or **2** were charged with varying quantities of Li (0.5–3.5 equiv. relative to monomer) in THF and the consumption of the monomer was ascertained by gas chromatography (GC). The percentage of monomer remaining ( $([M]/[M]_0) \times 100$ ) versus the equivalents of Li added ( $[Li]_0/[M]_0$ ) was then plotted. As shown in Fig. 4(a), **1**

(red squares) was detected in solution even after several equivalents of Li were added. Linear regression of the data showed that approximately 34% of monomer was consumed for each equivalent of Li added, a result that agreed with the value (33%) expected for an ideal chain growth polymerization. In contrast, linear regression of the data recorded for analogous experiments performed with **2** (Fig. 4(a), blue circles) indicated that approximately 56% of the monomer was consumed per equivalent of Li added, in good agreement with an ideal step growth polymerization. Further support for these conclusions were obtained by plotting the fraction of monomer remaining ( $[M]/[M]_0$ ) against the extent of the reaction ( $p$ ) (see Fig. S1).

The potential effects of the added electron transfer agent on the polymerization mechanisms were also investigated by repeating

the monomer consumption experiments with added naphthalene (0.25 equiv.); key results are shown in Fig. 4(b). In the presence of naphthalene, the amount of monomer consumed per equivalent of Li added was calculated to be approximately 34% and 55% for **1** and **2**, respectively (red squares and blue circles, respectively). Kinetics data were also recorded and revealed that the monomers were consumed relatively rapidly when naphthalene was added. For example, the amount of **1** consumed after 1 h was determined to be 28% in the presence of naphthalene and 16% in the absence. Likewise, conversions of 76% and 34%, respectively, were measured for experiments that involved **2**. Collectively, these data indicate that higher reaction rates were observed when **2** was polymerized in comparison to **1** and that the charge transfer agent accelerated the polymerization without affecting the underlying mechanism.

The differential polymerization rates and mechanisms may be attributed to multiple factors. For example, the steric bulk of the phenyl group in **1** may render coupling less favorable in comparison to the ester group in **2**.<sup>26</sup> Alternatively, the benzyl radicals formed upon dechlorination of **1** may be more stable than the acetyl radicals formed from **2** and result in a lower rate of reaction.<sup>27,28</sup> Because the termini of the growing polymer chains feature functional groups that differ from those found in their respective monomers, reactivity differences and other types of change-of-substituent effects<sup>29</sup> may also be operative.

## CONCLUSIONS

New poly(carbyne)s were synthesized, including the first examples to contain polar carbonyl-containing side chains, using C1 polymerization methodology. A series of spectroscopic techniques indicated that the poly(carbyne)s derived from arylated derivatives **1**, **6** and **7** featured branched structures whereas those prepared from carbonyl-containing carbyne precursors (**2–5**) were linear. The underlying polymerization mechanism also appeared to depend on the monomer: the polymerization of **1** appeared to follow a chain growth pathway whereas **2** proceeded in a step growth manner. Finally, it was demonstrated that the addition of naphthalene enhanced the rates of the reactions without altering the underlying polymerization mechanisms.

## EXPERIMENTAL

### General considerations

All solvents were dried using a Vac Atmospheres solvent purification system. Monomer syntheses were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Since lithium nitride can form when lithium is exposed to nitrogen, the polymerization reactions were set up under an atmosphere of argon and run in sealed vials. All reagents were purchased from commercial sources and used as received unless otherwise noted.  $\alpha,\alpha,\alpha$ -Trichlorotoluene and 2,2,2-trichloroacetophenone were purchased from Alfa Aesar (Incheon, South Korea). Methyl 2,2,2-trichloroacetate and  $\alpha,\alpha,\alpha$ -trifluorotoluene were purchased from TCI Chemicals (Tokyo, Japan). Methyl orthobenzoate was purchased from Sigma Aldrich (Seoul, South Korea). Solution-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature on a Bruker Avance III HD spectrometer operating at 400 MHz for  $^1\text{H}$ , in  $\text{CDCl}_3$  (internal standard: 7.26 ppm,  $^1\text{H}$ ; 77.16 ppm,  $^{13}\text{C}$ ),  $\text{CD}_2\text{Cl}_2$  (internal standard: 5.32 ppm,  $^1\text{H}$ ; 53.84 ppm,  $^{13}\text{C}$ ) or  $\text{THF}-d_8$  (internal standard: 3.58 ppm,  $^1\text{H}$ ; 67.21 ppm,  $^{13}\text{C}$ ). Splitting patterns are denoted as follows: br,

broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Solid-state  $^1\text{H}$ - $^{13}\text{C}$  CP MAS NMR spectra were recorded at room temperature using a Bruker Avance III HD 11.7 T wide-bore spectrometer operating at a  $^1\text{H}$  NMR frequency of 500.31 MHz and a  $^{13}\text{C}$  NMR frequency of 125.81 MHz. For all measurements, a Bruker triple-resonance MAS NMR probe (MASDVT500W2 BL3.2) was used with 3.2 mm diameter rotors consisting of  $\text{ZrO}_2$  barrels and Vespel® end caps. The magic angle was set using the  $^{79}\text{Br}$  resonance of KBr. The  $^{13}\text{C}$  chemical shifts were externally referenced to the  $-\text{COOH}$  signal of  $\alpha$ -glycine ( $\delta = 176.03$  ppm relative to tetramethylsilane). The CP MAS measurements started with a 2.25 ms,  $90^\circ$   $^1\text{H}$  pulse. During the contact time, the  $^{13}\text{C}$  spin lock field strength was held constant while the  $^1\text{H}$  spin lock field was ramped linearly (ramped amplitude CP) down to 50% of the initial value.<sup>30</sup>  $^1\text{H}$  decoupling was carried out with a SPINAL-64 sequence.<sup>31</sup> Samples were run at various spin rates using a 2 ms cross-polarization time and a relaxation delay of 10 s. Size exclusion chromatography was performed on a Malvern Viscotek 305 TDA system equipped with a refractive index detector using THF as an eluent at  $0.8\text{ mL min}^{-1}$ . Infrared spectra were collected either by attenuated total reflectance (ATR) on an Agilent Cary-630 spectrometer using a germanium crystal for liquid samples or via transmission through a KBr pellet on a Perkin-Elmer Frontier spectrometer for solid samples. GC was performed on an Agilent Technologies 6850 system fitted with a flame ionization detector using *n*-dodecane as an internal reference. Method details: 30 m, 0.32 mm ID, 0.25  $\mu\text{m}$  coating HP-1 column, 100:1 split ratio,  $1.5\text{ mL min}^{-1}$  flow of He,  $100^\circ\text{C}$  for 1.5 min, ramp to  $200^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$ . EPR spectra were collected at 295 K with an X-band microwave frequency of 9.393 GHz, a modulation frequency of 100 kHz, a modulation amplitude of 10 G, a microwave power of 0.633 mW, a time constant of 5.12 ms and a sweep time of 30 s.

### *n*-Pentyl trichloroacetate (**2**)

A dry 250 mL flask was charged with 100 mL of anhydrous  $\text{CH}_2\text{Cl}_2$  and 4.176 g (47.4 mmol) of 1-pentanol. The flask was cooled to  $0^\circ\text{C}$  and then charged with 10.306 g (54.7 mmol) of trichloroacetyl chloride. After adding 4 mL of pyridine in a dropwise manner to the flask, the resulting mixture was slowly warmed to room temperature and stirred overnight. The mixture was then washed with 100 mL of an aqueous solution of HCl (10%) followed by 100 mL of brine before being dried over  $\text{MgSO}_4$ . After filtration, the solvent was evaporated to afford 10.096 g (91% yield) of the desired compound as a straw-colored liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.32 (t, 2H), 1.73 (m, 2H), 1.34 (m, 4H), 0.88 (t, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.86, 90.00, 69.43, 27.84, 27.67, 22.10, 13.80. FTIR (Ge-ATR): 2960, 2932, 2863, 1763, 1457, 1379, 1236, 1042, 980, 885, 827, 751, 680  $\text{cm}^{-1}$ .

### *n*-Decyl trichloroacetate (**4**)

A dry 250 mL flask was charged with 100 mL of anhydrous  $\text{CH}_2\text{Cl}_2$  and 7.622 g (48.15 mmol) of 1-decanol. The flask was cooled to  $0^\circ\text{C}$  and then charged with 10.129 g (55.7 mmol) of trichloroacetyl chloride. After adding 4 mL of pyridine in a dropwise manner to the flask, the resulting mixture was slowly warmed to room temperature and stirred overnight. The mixture was then washed with 100 mL of an aqueous solution of HCl (10%) followed by 100 mL of brine before being dried over  $\text{MgSO}_4$ . After filtration, the solvent was evaporated to afford 14.216 g (97% yield) of the desired compound as a straw-colored liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.34 (t, 2H), 1.74 (m, 2H), 1.25 (m, 14H), 0.86 (t, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.14, 90.16, 69.68, 32.01, 29.60, 29.55,



29.40, 29.19, 28.33, 25.70, 22.80, 14.22. FTIR (Ge-ATR): 2956, 2924, 2854, 1765, 1457, 1379, 1239, 1042, 984, 878, 827, 751, 680  $\text{cm}^{-1}$ .

### General procedure A: synthesis of poly(carbyne)s

Under an atmosphere of argon, a 20 mL glass vial equipped with a glass-coated stir bar was charged with 5 mmol of monomer and 5 mL of anhydrous THF. While stirring the solution, Li granules were added to the vial over the course of 30 min. The vial was then sealed, immersed in a heating bath that was pre-heated to a predetermined temperature, and stirred overnight. To quench the reaction, methanol was added until solid lithium was no longer observed. The mixture was then added dropwise to 500 mL of methanol to precipitate the polymer and filtered through a medium pore size frit. The precipitate was collected, dissolved in a minimal volume of THF, and added dropwise to 500 mL of toluene. The precipitated solids were collected, dissolved in a minimal volume of THF and added dropwise to 500 mL of *n*-hexane. The precipitated solids were collected by filtration and dried under vacuum at 70 °C. Note that, similar to data reported for other poly(carbyne)s,<sup>18,21</sup> signals consistent with the incorporation of THF into the polymer were observed in some cases as minor side-products.

### General procedure B: synthesis of poly(carbyne)s in the presence of naphthalene

Under an atmosphere of argon, 5 mL of anhydrous THF, 160.2 mg (1.25 mmol) of naphthalene and 208.2 mg (30 mmol) of lithium were added to a 30 mL vial equipped with a glass-coated stir bar. The vial was sealed and then charged with 5 mmol of monomer in a dropwise manner via syringe before heating the mixture to 70 °C overnight. The reaction mixture was then cooled to room temperature. To quench the reaction, methanol was added until solid lithium was no longer observed. The solvent was then evaporated, and the solid residue was washed with 50 mL of an aqueous solution of HCl (10%) and then dissolved in 100 mL of ethyl acetate. The organic phase was washed with 50 mL of an aqueous solution of HCl (10%) followed by 100 mL of brine. The organic phase was then dried over  $\text{MgSO}_4$ , filtered, and the solvent was removed under vacuum. The product was dissolved in a minimal volume of THF, added dropwise to an excess of *n*-hexane, collected via filtration, and dried under vacuum at 70 °C. Note that, similar to data reported for other poly(carbyne)s,<sup>18,21</sup> signals consistent with the incorporation of THF into the polymer were observed in some cases as minor side-products.

### Poly(phenyl carbyne)

Using general procedure A, monomer **1** and 30 mmol of Li afforded 381 mg (86% yield) of poly(phenyl carbene) as a brown powder. Using general procedure B, monomers **1**, **6** and **7** afforded 165 mg (37% yield), 133 mg (30% yield) and 129 mg (29% yield), respectively, of poly(phenyl carbyne) as a brown powder.  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ ):  $\delta$  7.21 (br), 2.12 (s), 1.67 (br), 1.26 (s), 0.86 (m).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF}-d_8$ ):  $\delta$  128.84, 67.42, 32.00, 27.33, 23.08, 14.35.  $^{13}\text{C}$  CP MAS NMR (15.5 kHz):  $\delta$  140.34, 127.51, 49.22. FTIR (KBr): 3432, 3055, 3024, 2929, 2870, 1598, 1492, 1444, 1179, 1157, 1073, 1029, 913, 863, 757, 697  $\text{cm}^{-1}$ .

### Poly(pentyl ester carbyne)

Using general procedure B and monomer **2** afforded 317.9 mg (50% yield) of a dark brown polymer.  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ ):  $\delta$  4.17 (br), 1.36 (br), 0.94 (br).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF}-d_8$ ):  $\delta$  28.08, 22.20, 13.36.  $^{13}\text{C}$  CP MAS NMR (18 kHz):  $\delta$  172.36, 126.48,

62.43, 30.76, 22.82, 13.94. FTIR (KBr): 3422, 2959, 2933, 2871, 1733, 1619, 1462, 1233  $\text{cm}^{-1}$ .

### Poly(methyl ester carbyne)

Using general procedure B and monomer **3** afforded 252.3 mg (78% yield) of a dark brown polymer.  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ ):  $\delta$  3.80 (br), 3.66 (m), 1.82 (m), 1.33 (m), 0.93 (t).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF}-d_8$ ):  $\delta$  31.54, 22.53, 13.4.  $^{13}\text{C}$  CP MAS NMR (18 kHz):  $\delta$  173.22, 125.05, 62.22, 31.79, 22.84, 14.12. FTIR (KBr): 3376, 2955, 1738, 1628, 1444, 1222  $\text{cm}^{-1}$ .

### Poly(decyl ester carbyne)

Using general procedure B and monomer **4** afforded 355.4 mg (34% yield) of a dark brown polymer.  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ ):  $\delta$  2.08 (m), 1.33 (br), 0.91 (br).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF}-d_8$ ):  $\delta$  62.34, 33.90, 32.68, 30.39, 30.12, 26.75, 23.39, 14.29, 1.17.  $^{13}\text{C}$  CP MAS NMR (7 kHz):  $\delta$  173.32, 130.16, 126.48, 61.89, 29.76, 22.91, 14.13. FTIR (KBr): 3394, 2955, 2931, 2870, 1714, 1615, 1455, 1374, 1242, 1182, 1036, 757  $\text{cm}^{-1}$ .

### Poly(benzoyl carbyne)

Using general procedure B and monomer **5** afforded 281.1 mg (48% yield) of a dark brown polymer.  $^1\text{H}$  NMR (400 MHz,  $\text{THF}-d_8$ ):  $\delta$  7.16 (br), 2.52 (s), 1.33 (s), 0.93 (t), 0.14 (s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF}-d_8$ ):  $\delta$  128.81.  $^{13}\text{C}$  CP MAS NMR (10 kHz):  $\delta$  170.5, 138.18, 67.48, 31.53, 22.50, 22.50, 22.77, 14.12. FTIR (KBr): 3443, 3058, 3028, 2931, 2874, 1718, 1598, 1494, 1447, 1247, 1076, 1030, 759, 700  $\text{cm}^{-1}$ .

### Monomer consumption analyses

A total of eight 30 mL vials equipped with glass-coated stir bars were each charged with 4 mmol of monomer, 4 mmol of *n*-dodecane, 4 mL of anhydrous THF and in some cases 1 mmol of naphthalene. Seven of the vials were charged with 13 mg (2 mmol) of lithium. After 5 min, additional lithium (13 mg) was added to six of the vials. This process was repeated every 5 min until samples were created with lithium to monomer molar ratios of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5. Other reaction conditions and work-up procedures are described above. Aliquots (50  $\mu\text{L}$ ) were withdrawn from the vials, diluted with a 4:1 (v/v) mixture of THF and methanol (1 mL) and then analyzed by GC. Monomer consumption was determined by comparing the area of the GC signal assigned to the monomer to that of an internal standard (*n*-dodecane). Each analysis was performed in triplicate.

### Kinetics analyses

Under an atmosphere of argon, 5 mL of anhydrous THF, 5 mmol of *n*-dodecane and 208.2 mg (30 mmol) of lithium were added to a 30 mL vial equipped with a glass-coated stir bar. In some cases, 160.2 mg (1.25 mmol) of naphthalene was added. The vial was sealed and 5 mmol of monomer was added dropwise via syringe before heating the resulting mixture to 70 °C. After 1 h, an aliquot (50  $\mu\text{L}$ ) was withdrawn from the reaction mixture, diluted with a 4:1 (v/v) mixture of THF and methanol (1 mL) and then analyzed by GC as described above.

## ACKNOWLEDGEMENTS

The Institute for Basic Science (IBS-R019-D1) is acknowledged for support. We thank Professor Jan-Uwe Rohde and Jungha Lee for their assistance with the EPR measurements.

## SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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