Articles

Repetitive sp^3-sp^3 Carbon−Carbon Bond-Forming Copolymerizations of Primary and Tertiary Ylides. Synthesis of Substituted Carbon Backbone Polymers: Poly(cyclopropylidine-*co*-methylidine)

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ABSTRACT: We report a repetitive sp^3-sp^3 carbon−carbon bond-forming polymerization for the controlled synthesis of cyclopropyl containing carbon backbone polymers with tailored end groups and molecular weight. Poly(cyclopropylidine-*co*-methylidine) copolymers (**10**) were synthesized via copolymerization of (dimethylamino)-tolyloxosulfonium cyclopropylide (**11**) with dimethylsulfonium methylide (**8**). The polymer was synthesized in M_n ranges from 1800 to 6714. The cyclopropyl:methyl incorporation ratios varied from 1:12 and 1:18. The composition of the poly(cyclopropylidine-*co*-methylidine) polymer (**10**) was established by NMR and IR. GPC revealed a monomodal distribution with PDI between 1.06 and 1.28. The cyclopropyl groups extend the range of functionality that can be incorporated into carbon backbone polymers and illustrate for the first time the use of *tertiary* ylides as monomers for the polymerization reaction. Direct control of the amount of cyclopropyl groups in the carbon backbone has potential for selective modification of the polymer by, for example, radical ring-opening reactions to create new topologies and cross-linking opportunities.

Introduction

Functional groups on a hydrocarbon polymer backbone are used to tailor properties such as adhesion, barrier performance, and solvent resistance.[1] The cyclopropyl group can provide a conformational constraint in the polymer backbone and is available for further chemical modification that may facilitate degradation, copolymer formation, or the introduction of other functional groups that modify solubility.[1−7] The utility of the cyclopropyl group prompts the design of new methods for the incorporation of this group in synthetic carbon backbone polymers. Direct control of the amount of cyclopropyl groups in the polymer is important to fine-tune polymer properties.

Previous reports of cyclopropyl-containing polymers include synthesis via ring-opening metathesis of spiro(bicyclo[2.2.l]hept-2-ene-7,1-cyclopropane), a reaction that introduces the spiro cyclopropyl group,[8] or by the nickel[9−11] or zirconium[12] catalyzed homopolymerization of methylenecyclopropane derivatives, a reaction that introduces a cyclopropylidene group in the polymer chain.

The polyhomologation reaction offers the potential for synthesis of polymers with substituents and substitution patterns that are not readily available by olefin polymerization. Trialkylboranes are used as both initiator and catalyst for the polymerization.[13,14] The monomers in polyhomologation reactions are ylides or ylide-like monomers.[13,14] The mechanism of boron initiation and polymer chain growth is illustrated in Scheme 1.[13,14] The monomer, a sulfur-based ylide or diazo compound (**1**), contains a nucleophilic carbon and three substituents (X, Y, L), one of which is a good leaving group such as the sulfonium or N_2 group (L), which can also stabilize the anionic site. The remaining substituents X and Y can be hydrogen, alkyl, or aryl groups.

The key reaction in polyhomologation is the repetitive elongation of the polymer chain *one carbon at a time*. The nucleophilic ylide monomer attacks a trialkylborane (BR_3) (**2**) to form a borate intermediate **3**. Subsequently, one of the three alkyl groups in borate **3** undergoes 1,2 migration to form homologated borane **4**. The rate of this migration is dependent on the substitution pattern of the ylide. Unsubstituted ylides react faster than monosubstituted or disubstituted ylides.[15] The 1,2 migration elongates one of the branches by one carbon, and in all cases studied, all three polymer branches grow with equal probability.[14] The reaction continues until the ylide is consumed. In the presence of excess ylide, repetitive homologation occurs so that a three-armed organoborane star polymer **5** is obtained.

Following consumption of the monomer, the terminal carbon−boron bond can be cleaved by a number of reactions. These include, but are not limited to, oxidative cleavage to an alcohol using H_2O_2 and NaOH or trimethylamine *N*-oxide (TAO). The reaction results in an ω-functionalized polymer **6**.

Le Gall and Mioskowski et al. reported an analogous reaction that uses allylic triphenylarsonium ylides.[16−18] In this reaction the polymers are synthesized three carbons at a time. The PDI of the resulting high molecular weight polymers varied between 1.21 and 1.71.[16,18] The reaction produces arsenic byproducts that may limit some of the polymer applications.

The propagation step in the polyhomologation reaction differs from conventional olefin polymerization. Therefore, potential exists for the synthesis of *substituted* carbon backbone polymers that are not readily available by traditional olefin polymerzations.

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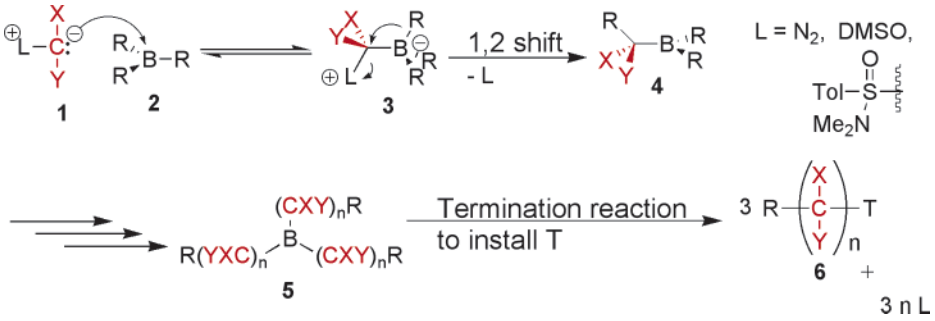
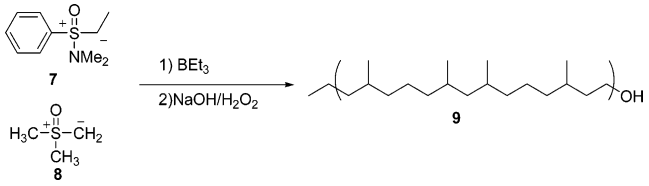
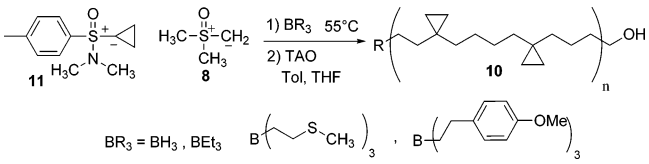
Scheme 1. Polyhomologation Mechanism[13,14]



Scheme 2. Co-polymerization of Secondary Ylide 7 and Methyl Ylide 8



Scheme 3. Copolymerization of Tertiary Ylide 11 and Primary Ylide 8



The first example of this was the copolymerization of primary and secondary ylides by trialkylboranes (Scheme 2).[15] (Dimethylamino)phenyloxosulfonium ethylide (**7**) served as a source of the ethylidene group ($CHCH_3$). This monomer was copolymerized with methylide **8** to give a random copolymer poly(ethylidene-*co*-methylidene) (**9**), a polymer with the same chemical composition as an ethylene−propylene copolymer.[15]

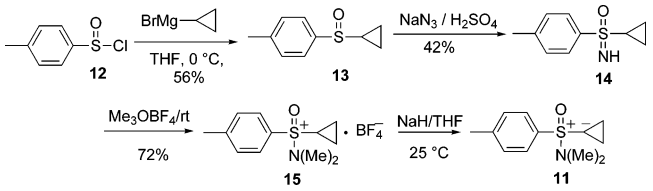
Herein we demonstrate for the first time reaction with a *tertiary* ylide. Polymerization results in the synthesis of cyclopropyl-containing polymers with tailored end groups and MW. The cyclopropyl group extends the range of functionality that can be incorporated into carbon backbone polymers and illustrates the use of tertiary ylides as monomers for the polyhomologation reaction.

Results and Discussion

Poly(cyclopropylidine-*co*-methylidine) polymers (**10**) were prepared by the copolymerization of (dimethylamino)-*p*-tolyloxosulfonium cyclopropylide (**11**) and dimethylsulfonium methylide (**8**) monomers (Scheme 3). The two monomers supply the cyclopropylidene and methylene groups to the growing polymer chain. The dimethylsulfoxonium methylide (**8**) was synthesized via a two-step reaction as described previously.[13]

The synthesis of (dimethylamino)-*p*-tolyloxosulfonium cyclopropylide (**11**) was modified from published[19,20] procedures (Scheme 4). Toluenesulfinyl chloride (**12**) was synthesized from *p*-toluenesulfinic acid sodium salt and thionyl chloride.[16] Addition of **12** to a cyclopropyl Grignard reagent resulted in an improved overall yield of sulfoxide **13**. Furthermore, a rapid addition of H_2SO_4 was found to maximize the yield of sulfoximine **14**. The trifloroborate salt **15** was recrystallized from 2-propanol. The cyclopropyl ylide **11** was freshly prepared in situ by reaction of **15** with NaH before each polymerization. This process was adapted due to a competing unimolecular

Scheme 4. Synthesis of Ylide 11



decomposition of the ylide. In contrast, methyl ylide **8** was stable for several months when stored at 0 °C.

The homopolymerization of cyclopropyl ylide **11** (DP 20) was attempted using $BH_3{\cdot}Me_2S$ as the initiator/catalyst. 2 equiv of methyl ylide **8** was added prior to the 20 equiv of cyclopropyl ylide **11** to generate the trialkylborane in situ. However, no polymer was observed after 12 h at 60 °C. Examination of molecular models of the products resulting from insertion of 2 or 3 equiv of ylide **11** provided an explanation for the result. The short C−B bond distance compounds the steric bulk of three cyclopropyl groups on the borane and renders the borane atom inaccessible to attack by the nucleophilic ylide **11**. This will prevent subsequent addition of ylide **11** and prevent homopolymerization (Figure 1).

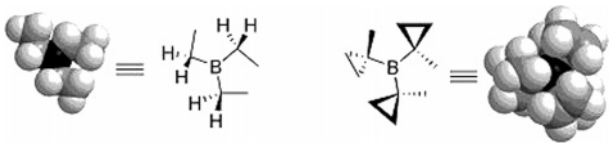


Figure 1. Comparison of space-filling models of triethylborane (left) and tri(1-methylcyclopropyl)borane (right) (MM2 minimized Chem 3D ultra). The central boron atom is dark shaded.

Despite the failure to homopolymerize monomer **11**, conditions were developed for the copolymerization with methyl ylide **8** (Scheme 3). The initiators either were commercially available in ~1 M solutions in THF or CH_2Cl_2 or were synthesized via hydroboration of the corresponding alkene. The copolymerization was carried out by alternative addition of monomers **11** and **8** using a programmable addition apparatus. The aliquots were adjusted to enable each polymer chain to sequentially incorporate, on average, one cyclopropylide group followed by a larger number of methylene groups. An aliquot of dimethylsulfoxonium methylide (**8**) was added first and last in the reaction. The first addition of **8** was used to introduce a polymethylene spacer from the end group. The last addition of **8** was to ensure that the terminus of the polymer chain did not contain a cyclopropyl group. Oxidative cleavage would generate a cyclopropanol that is expected to be unstable under the reaction conditions.[21,22] Following the above protocol, the products of the polyhomologation and oxidative cleavage were either white powders at high MW or waxes at low MW.

The copolymer produced from monomers **11** and **8** were analyzed by ^1H NMR and IR. The peaks, centered at 0.31 and

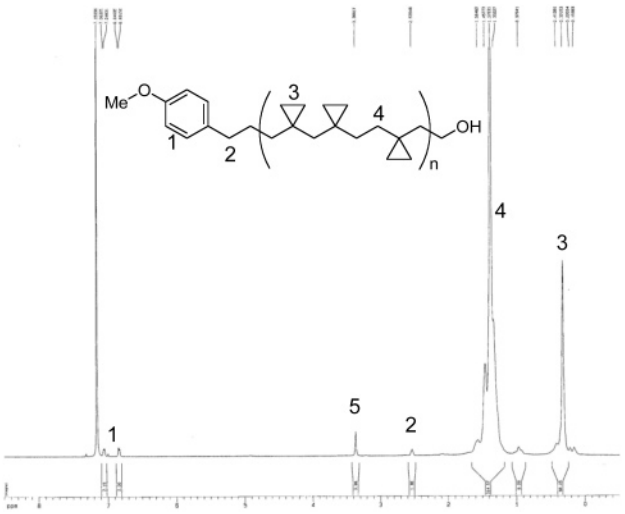


Figure 2. ^{1}H NMR of poly(cyclopropylidine-*co*-methylidine) polymer in d_6-benzene.

Table 1. Polymer Summary

sample	initiator	theoretical copolymer composition[a]	actual copolymer composition[b]	$M_{w,n}$	yield (%)
1	$(MeOPhEt)_3B$	1:5	1:12	3212[c]	30
2	$(MeSEt)_3B$	1:3	1:16	6714[d]	52
3	Et_3B	1:3	1:18	1808[e]	54

[a] Based on stoichiometry [cyclopropyl:methyl]. [b] Ratio based on ^{1}H NMR methylene peak centered at 1.36 ppm to cyclopropyl peak centered at 0.31 ppm. [c] Based on ^{1}H NMR. [d] PS standardized GPC. [e] PE standardized GPC.

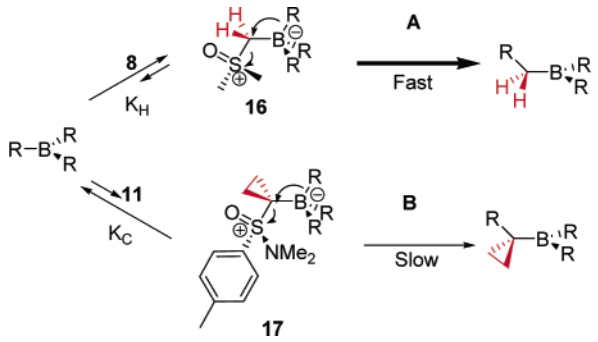
1.36 ppm in the ^{1}H NMR spectra (Figure 2), are diagnostic for methyl and cyclopropyl groups of poly(cyclopropylidine-*co*-methylidine) polymer, respectively.[8,9] The IR bands at 3068 and 2993 cm^{-1} are assigned to the cyclopropyl carbon hydrogen stretch.[23] The bands at 2924 and 2851 cm^{-1} are attributed to the methyl carbon hydrogen stretch.[23] In the ^{1}H NMR spectrum the cyclopropyl protons correspond to the peak centered at 0.31 ppm, and methylene protons appear as broad peaks centered at 1.36 ppm (Figure 2). [8,9] The ^{1}H NMR was used to determine the relative ratios of incorporated groups in the polymers by integrating the corresponding peaks.

A number of boron initiators were studied for this reaction (Table 1). In all cases, the resulting copolymers were found to incorporate the cyclopropyl group. The polymers were ether white solids or waxes depending on the molecular weight. Simple alkylboranes such as Et_3B made the quantification of the extent of cyclopropyl group incorporation difficult by ^{1}H NMR end-group analyses. Tris(4-methoxyphenylethyl)borane was used to simplify this problem. GPC analysis revealed that the polymers were monomodal. The PDI of the polymers varied from 1.06 (sample 3) to 1.28 (sample 2).

The amount of cyclopropyl groups incorporated was always lower than that calculated from stoichiometric ratios of monomers (Table 1). There are two explanations to account for the this: competing decomposition of the cyclopropyl ylide (**11**) monomer under the polymerization conditions and the higher activation energy of the 1,2-migration for the cyclopropyl monomer borate complex.

The principal cause of the low cyclopropyl ylide **11** incorporation is the competing decomposition of the ylide. Similar ylides such as **(**dimethylamino)phenylsulfoxonium cyclopropyl ylide are known to decompose readily by α-elimination to (dimethylamino)-*p*-phenyl sulfoxide at room temperature.[20] We

Scheme 5. Two Possible Reaction Paths



believe that ylide **11** decomposes in a similar manner, but at a somewhat slower rate. However, since the polymerization reaction was carried out at 60 °C, the competing decomposition of **11** would proceed at a faster rate than it would at room temperature.[20] It was observed that when the cyclopropyl monomer **11** was added in portions, the amount of cyclopropyl groups incorporated increased. Small aliquots of the monomer **11** minimized the amount of decomposition prior to incorporation into the hydrocarbon chain at high temperature.

Low incorporation of the cyclopropyl groups in the copolymerization is also explained by the higher activation energy for migration of the cyclopropyl monomer. In support of this, when cyclopropyl ylide **11** and methyl ylide **8** were added simultaneously at 50 °C, the cyclopropyl group did not incorporate into the polymer product to any appreciable extent. In the polyhomologation reaction, the rate-limiting step is the 1,2 migration.[13] The coordination of each ylide is reversible under the polymerization conditions (Scheme 5),[13] but due to the increased steric bulk of ylide **11** compared to **8**, $K_H > K_C$. The lower activation energy for path A would result in the methyl ylide **8** being incorporated faster into the polymer. This would be expected to result in methylene incorporation, outcompeting the cyclopropyl path B (Scheme 5), which has a higher E_a energy. The result is consistent with the order of reactivity of nucleophilic displacement reactions at primary and tertiary carbons.

Conclusions

Polymerization conditions have been developed for the controlled incorporation of cyclopropyl groups in carbon backbone polymers. Poly(cyclopropylidine-*co*-methylidine) copolymers (**10**) were synthesized via co-polyhomologation of (dimethylamino)tolyloxosulfonium cyclopropylide (**11**) with dimethylsulfonium methylide (**8**).

The co-polyhomologation of ylide **11** and **8** was developed to introduce cyclopropyl groups into a polymer carbon backbone. Polymers were synthesized in molecular weight ranges from 1000 to 7000. The cyclopropyl:methyl incorporation ratios were varied between 1:12 and 1:18. ^{1}H NMR and IR analysis were used for polymer characterization and to establish the composition of the poly(cyclopropylidine-*co*-methylidine) polymers (**10**). GPC established the polymers as monomodal with PDI between 1.06 and 1.28.

The successful incorporation of sterically hindered functional groups into hydrocarbon chains marks an important step in providing access to a range of materials with tailored composition. This study demonstrates that, by changing the alkyl groups in (dimethylamino)phenyloxosulfonium alkylide, it is possible to synthesize a variety of substituted carbon backbone polymers by the polyhomologation reaction.

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Experimental Section

General. ^{1}H NMR spectra were recorded on a General Electric GN-500 (500 MHz) or Bruker Omega 500 (500 MHz). The chemical shifts were reported in ppm using deuterated solvent peaks as the internal references. Coupling constants (*J*) were reported in hertz, and the splitting abbreviations used are as follows: s, single; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet; br, broad. ^{13}C NMR spectra were obtained using the same instruments operating at 125.8 MHz. ^{11}B NMR spectra were also obtained using the same instruments operating at 160.4 MHz. Infrared spectra were obtained using an FTIR spectrometer. GPC chromatography solvent was filtered and sonicated prior to use. The samples were run using *o*-xylene as an eluent with a flow rate of 1.0 mL/min at 100 °C. The samples for chromatography were prepared as 0.50−0.60% solutions in *o*-xylene. Four PLgel (5 μm particle size) columns were used in series: 500 Å × 2; 100 Å × 2. The molecular weight analysis from GPC was reported as M_w and polydispersity index (PDI). The GPC calibration curves were made with polyethylene standards from Polymer Laboratories and from Scientific Polymer Products. The calibration curve has an $R^2 = 0.999$. NMR spectra of the copolymer were performed on a Bruker Omega 500 (500 MHz) NMR at 70−100 °C. All solvents were distilled from drying agents (CaH_2) or filtered through alumina beds prior to use. Commercially available starting materials were acquired from Aldrich or Acros and were used as received. Tris(3-methylsulfanylpropyl)borane was generously provided by Xian-Zhi Zhou.

Cyclopropyl *p*-Tolyl Sulfoxide (13). To a dry, N_2-purged flask equipped with a stir bar and a condenser were added magnesium (2.59 g, 0.1036 mol, 1.81 equiv) and THF (38 mL). At 0 °C, cyclopropyl bromide (10.51 g, 7.02 mL, 0.0876 mol, 1.53 equiv) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 3 h. The Grignard reagent was formed and diluted with additional THF (38 mL) for use. *p*-Toluenesulfinyl chloride (**12**)[19] (10.07 g, 0.0577 mol, 1.00 equiv) in dry THF (110 mL) was added to the above Grignard reagent solution. After the mixture was stirred for 12 h at room temperature, the solution was quenched with saturated NH_4Cl solution and extracted three times with CH_2Cl_2. The organic layers were combined, dried with Na_2SO_4, and concentrated in vacuo to give crude product as yellow oil. The crude product was purified by flash column chromatography using 1:1 hexanes and ethyl acetate as eluant. Cyclopropyl-*p*-tolyl sulfoxide (**13**) (5.73 g, 56%, $R_f = 0.20$) was obtained as light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, $J = 8.0$ Hz, 2H,), 7.32 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 3H), 2.24 (tt, $J = 7.9$, 4.8 Hz, 1H), 1.22 (m, 1H), 0.99 (m, 1H), 0.93 (m, 2H) ^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 141.6, 141.3, 129.8, 124.0, 33.8, 21.4, 3.3, 2.7. HRMS (CI) calcd for $C_{10}H_{12}OS$ ($M + H^+$): 181.0687; observed: 181.0669.

***S*-Cyclopropyl-*S*-(*p*-tolyl)sulfoximine (14).** A dry, N_2-purged flask equipped with an addition funnel, a condenser, and a stir bar was charged with $CHCl_3$ (45 mL), cyclopropyl-*p*-tolyl sulfoxide (**13**) (4.17 g, 0.0231 mol, 1.0 equiv), and sodium azide (3.03 g, 0.0467 mol, 2.0 equiv). Concentrated H_2SO_4 (5.85 mL) was quickly added to the mixture at 0 °C. The reaction mixture was heated at 50 °C for 12 h. The mixture was cooled to room temperature before ice water (30 mL) was added. The unreacted starting material (**13**) was extracted from the solution with $CHCl_3$ to be recycled at a later time. The aqueous layer was made basic (pH 10) with NaOH (1 N) and reextracted with $CHCl_3$. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to give *S*-cyclopropyl-*S*-(*p*-tolyl)sulfoximine (**14**) (1.94 g, 43%) as a dark yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.3$ Hz, 2H), 2.65 (br, 1H), 2.51 (tt, $J = 7.9$, 4.7 Hz, 1H), 2.47 (s, 3H), 1.37 (m, 1H), 1.17 (m, 1H), 1.03 (m, 1H), 0.89 (m, 1H) ^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 143.7, 140.3, 129.9, 128.1, 34.5, 21.7, 6.1, 5.7. HRMS (CI) calcd for $C_{10}H_{13}OSN$ ($M + H^+$): 196.0796; observed: 196.0797.

(Dimethylamino)cyclopropyl-*p*-tolylsulfoxonium Tetrafluoroborate (15). A dry, N_2-purged flask equipped with a stir bar was charged with $CHCl_3$ (41 mL) and *S*-cyclopropyl-*S*-(*p*-tolyl)-sulfoximine (**14**) (6.00 g, 0.0307 mol, 1.00 equiv). Trimethyloxonium tetrafluoroborate (5.15 g, 0.0349 mol, 1.13 equiv) was added to the above reaction mixture at 0 °C. The Meerwein's salt was synthesized as described by Curphey.[24] Stirring at room temperature for 2 h, and the excess Meerwein's salt was filtered off. The filtrate was made basic (pH 9) with NaOH and extracted with $CHCl_3$ (3 × 25 mL). The organic portion was dried with Na_2SO_4. The product was concentrated in vacuo, and subsequently, the methylating process was repeated two more times to improve the yield. Finally, the product (**15**) was recrystallized twice in EtOH and once in 2-propanol to afford the (dimethylamino)cyclopropyl-*p*-tolylsulfoxonium tetrafluoroborate (**15**) (6.00 g, 63%) as white needles that were powdered and stored in a vacuum oven (60 °C, 15 mmHg) overnight. ^{1}H NMR (500 MHz, d-DMSO) δ: 8.05 (d, $J = 8.5$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 3.97 (tt, $J = 7.6$ Hz, 4.5 Hz, 1H), 3.09 (s, 6H), 2.51 (s, 3H), 1.76 (m, 2H), 1.39 (m, 1H), 1.18 (m, 1H), ^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 149.6, 132.2, 129.4, 125.94, 38.3, 28.7, 22.2, 8.9, 6.9. HRMS (FAB) calcd for $C_{12}H_{18}OSN$ (M^+): 224.1109; observed: 224.1113.

(Dimethylamino)-*p*-tolylsulfoxonium Cyclopropyl Ylide (11). A dry, N_2-purged flask equipped with a condenser and a stir bar was charged with NaH (60% dispersion in mineral oil, 0.385 g, 0.0096 mol, 3.0 equiv), which was washed with hexanes (3 × 25 mL) and dried under N_2. (Dimethylamino)cyclopropyl-*p*-tolylsulfoxonium tetrafluoroborate (**15**) (1.00 g, 0.00321 mol, 1.0 equiv) and dry THF (3 mL) was added to the sodium hydride. Evolution of H_2 and a color change were observed. The resulting mixture was stirred for 3 h at room temperature until H_2 stopped evolving. The mixture was filtered through a Schlenk filter containing Celite 545 to remove $NaBF_4$ salt. The filtrate was a yellow solution. Titration, using phenolphthalein as an indicator, of an aliquot (0.2 mL), in 10 mL of H_2O, of the yellow solution was performed using HCl (0.1 N) to determine the concentration of ylide (**11**) (0.750 M). The ylide (**11**) was made in small quantities because of its short shelf life even at −20 °C.

Poly(cyclopropylidine-*co*-methylidine) (10): Copolymerization of Cyclopropylide (11) and Methylide (8). A dry, N_2-purged flask equipped with a condenser and a stir bar was charged first with an aliquot of methyl ylide (**8**) (0.625 mL/aliquot, 0.64 M in toluene). The borane initiator (Table 1), for example $(MeOPhCH_2CH_2)_3B$ (0.14 mL, 0.19 M in THF, 0.026 mmol, 1 equiv), was added at room temperature. The mixture was stirred for 4 min, and then the temperature was raised to 50 °C. To the above mixture was added first aliquot of cyclopropyl ylide (**11**) (0.20 mL/aliquot, 0.40 M in THF). After the mixture was stirred for 6 min, addition of a second aliquot of methyl ylide (**8**) (0.625 mL/aliquot, 0.64 M) was performed. The alternating additions of methylide (**8**) (0.625 mL/aliquot, 6.25 mL total, 0.40 M, 1.33 mmol, 50 equiv) and cyclopropylide (**11**) (0.200 mL/aliquot, 2.00 mL total, 0.40 M, 0.26 mmol, 10 equiv) were repeated at 4 and 6 min intervals, respectively, until the monomers were used up (∼3 h). There was a pause between additions, which was intended to enable the monomers to incorporate in the growing carbon chain. After the additions were completed, trimethylamine *N*-oxide (0.014 g, 0.186 mmol, 7 equiv) was added to oxidatively cleave the carbon−boron bonds. After the reaction mixture was heated at reflux for 12 h. The solvent was removed in vacuo, and CH_3CN or MeOH was added to the residue to precipitate the polymer **10**. The resulting suspension was filtered and dried (25 °C, 1 mmHg, 24 h) to afford the product as white powder (27.1 mg, 30%). ^{1}H NMR (500 MHz, d-Tol) δ: 7.05 (d, $J = 7.32$ Hz, 2H), 6.84 (d, $J = 8.01$ Hz, 2H), 3.98 (s, 4H), 2.53 (t, $J = 7.4$ Hz, 2H), 1.7−1.2 (br, 315H), 0.94−0.90 (br, 6H), 0.26−0.23 (m, 66H). ^{13}C NMR (125.8 MHz, d-benzene) δ: 129.9, 126.0, 114.52, 55.14, 36.9, 36.8, 33.6, 30.9, 30.6, 30.2, 27.5, 27.5, 23.5, 20.0, 14.7, 13.1, 12.9, 10.23, 1.75. IR (neat): 3068, 2993, 2924, 2851, 1453, 1329 cm^{-1}.

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CDV

Supporting Information Available: IR spectra of poly(cyclopropylidine-*co*-methylidine) polymer and ^{13}C and ^{1}H NMR of poly(cyclopropylidine-*co*-methylidine) polymer in d_6-benzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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