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Ersatz Ethylene−Propylene Copolymers: The Synthesis of Linear Carbon Backbone Copolymers One Carbon Atom at a Time

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The simplest hydrocarbon polymer is comprised of a string of methylene (CH_2) groups. In principle, the carbon chain can be broken into any number of repeat units (Figure 1). The analysis reveals that the linear hydrocarbon polymer can be synthesized not only from C2 (ethylene) subunits, but also from C1, C3, C4, or larger building blocks. A similar analysis of polypropylene reveals the "traditional" monomer and nonstandard combinations of building blocks that can serve as precursors to this familiar polymer structure (Figure 1).

The increasing demand for high-performance polymers creates a need for greater control of factors that influence their physical properties.[1] Our studies have concentrated on developing new polymerization reactions that utilize nontraditional monomers as the carbon source.[2] Non-olefin approaches to carbon backbone polymers can provide access to new topologies, architectures,[3] and copolymers[4] of these important materials. In addition, since many olefins do not readily polymerize, these synthetic methods can serve as an entry to completely new substances.

The examples to date have employed dimethylsulfoxonium methylide **1** (Figure 2), an *unsubstituted* ylide which can be efficiently polymerized by alkyl boranes to produce linear polymethylene.[5] Trialkyl boranes function as the initiator/catalyst in this polymerization. All three alkyl groups on boron are extended by repetitive insertions of the ylide derived methylene group (CH_2) into the carbon−boron bond in a polymerization referred to as *polyhomologation*[6] (Figure 3). The ylide precursor, trimethyloxosulfonium chloride, is prepared by S-methylation of dimethyl sulfoxide. Unfortunately, S-alkylation of sulfoxides is not a general reaction and cannot serve as a source of substituted derivatives of this ylide.[7] This limits sulfoxonium ylides to the CH_2 group and synthesis of polymethylene derivatives. In addition, few ylides possess sufficient thermal stability to survive the reaction conditions.[8]

In an effort to extend this reaction to the synthesis of *substituted* carbon backbones, we have found that (dimethylamino)phenyloxosulfonium ylides **2** and **3** possess a convenient balance of properties for successful employment as a polymerizable monomer. Their reactivity closely parallels dimethylsulfoxonium methylide **1**. Furthermore, the ylides, which are derived from (dimethylamino)phenyloxosulfonium salts, are available with extensive structural variation.[7]

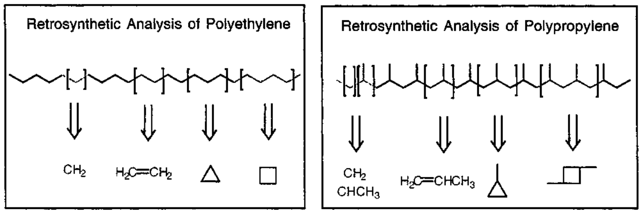


Figure 1. Retrosynthetic analysis of simple hydrocarbon polymers, illustrating possible disconnections into different carbon building blocks.

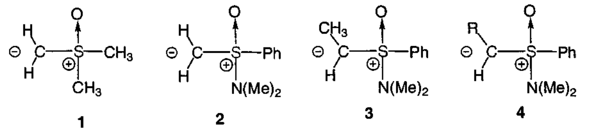


Figure 2. Structures and numbering scheme for ylides described in this paper.

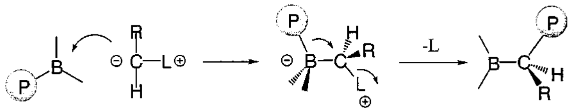
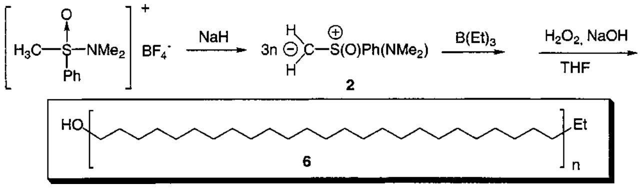


Figure 3. Generalized mechanism of the polyhomologation reaction. P refers to one of three polymer chains attached to boron.

Scheme 1



The utility of ylides **2** and **3** was established first with the *unsubstituted* derivative, (dimethylamino)phenyloxosulfonium methylide **2**. The ylide could be polymerized by triethylborane to produce, after oxidative cleavage of the boron−carbon bond, polymethylene **6** (Scheme 1).

The resultant polymer, a hydroxyl-terminated polymethylene **6**, was analyzed by both solution NMR and size exclusion chromatography (SEC). The results, summarized in Table 1, reveal both molecular weight control and low polydispersity consistent with a controlled, living polymerization. The ylide was found to be stable at elevated temperatures, and the reaction byproduct, (dimethylamino)phenylsulfoxide, does not interfere with the polymerization reaction.

For the synthesis of a representative *substituted* carbon chain, we examined (dimethylamino)phenyloxosulfonium ethylide **3**, an ylide that serves as a source of the ethylidene group ($CHCH_3$). This monomer was copolymerized with dimethylsulfoxonium methylide **1** (Scheme 2).

The polymerization is achieved by slow addition of a solution of ylide **1** to a solution of ylide **3** containing triethylborane. The molar ratio of ylides **1**/**3** were varied from 6:1 to 2:1. Following consumption of monomers, the star organoborane was oxidatively cleaved with basic H_2O_2. The reaction product, a hydroxyl-terminated poly[ethylidene-*co*-methylidene] **7**, has the same chemical composition as an ethylene−propylene copolymer. Relativity low molecular weight oligomers were prepared for these studies to simplify analysis.

Comparison of the theoretical molecular weight, based on the calculated ratio of total ylide to triethylborane, with the experi-

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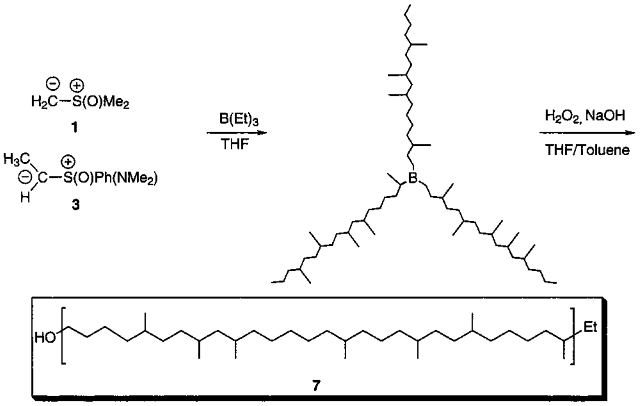
Table 1. Summary of Analysis of Polymers **6** and **7**

	6			7		
sample	1	2	3	4	5	6
M_n (calcd from feed ratio)[a]	326	746	1166	886	1008	1166
M_n (^{1}H NMR)	438	816	1418			
M_n (SEC)[b]	426	927	*c*	866	1298	1609
PDI	1.11	1.02	*c*	1.09	1.15	1.13
[M]/[E](calcd from feed ratio)[d]				6.0	4.0	2.0
[M]/[E](^{1}H NMR)				6.1	4.4	2.1
[M]/[E](^{13}C NMR)[e]				6.1	4.2	2.0
yield(%)		71		82	78	72

[a] M_n = (mol methylide × 14 + mol ethylide × 28)/(mol borane × 3) + 46. [b] SEC analyses were performed at 100 °C in *o*-xylene. Narrow molecular weight polyethylene standards were used for calibration.[c] In THF when the degree of polymerization from the feed ratio is greater than 50, precipitation of the growing polymer chains during polymerization result in a broadened distribution. [d] [M]/[E] = (mol methylidene)/(mol ethylidene). [e] Quantitative ^{13}C NMR was obtained under the same conditions as described in the caption of Figure 4.

Scheme 2



mental values from SEC analysis (Table 1), shows good molecular weight control. Furthermore, the polymers have narrow molecular weight distributions with low PDI values. Both results are consistent with a controlled, living polymerization reaction.

Polymer composition, that is, the relative amounts of methylidene (CH_2) to ethylidene ($CH(CH_3)$) groups in the polymer, was established by a combination of ^{1}H- and ^{13}C NMR spectra. Spectral assignments were made on the basis of computed chemical shifts and literature assignments.[9-11] A representative ^{13}C NMR (sample 5) with partial annotation is shown in Figure 4.[12]

DEPT experiments were performed to distinguish methylene from the methyl and methine carbons. These data, in conjunction with both calculated and experimental chemical shifts, permitted assignment of the ^{13}C chemical shifts of the methyl groups to the region between 10−22 ppm. This region is distinct from the methine and methylene groups which fall between 23−50 ppm.

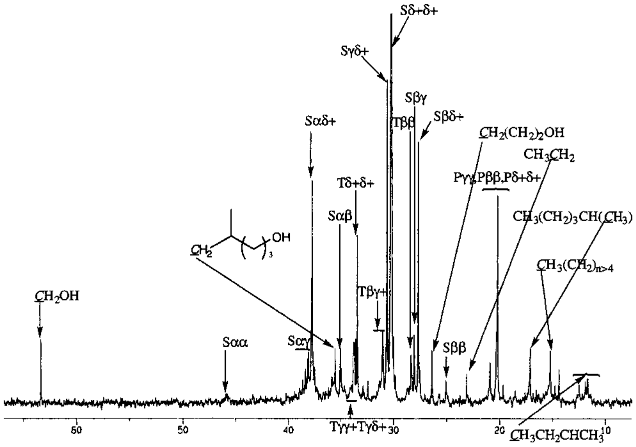


Figure 4. Full ^{13}C NMR spectrum of poly(ethylidene-*co*-methylidene). ^{13}C NMR spectra for the copolymer was performed with inverse-gated decoupling at 500 MHz NMR on a solution of polymer (50−100 mg) in a mixture of trichlorobenzene with 10% 1,1,2,2-tetrachloroethane-d_2 (0.5 mL) at 100 °C. The interpulse relaxation delay was 10 s, the pulse width was 3 μs (46° flip-angle). 32K time domain data points were acquired with a sweep width of 31446 Hz. Exponential multiplication was applied before FT with line-broadening factor of 1 Hz.

The compositional ratio can be expressed by eq 1.

$$[M]/[E] = \{[CH_2 + CH] - [CH_3]\}/[CH_3] \qquad (1)$$

The results are also summarized in Table 1. The ratio of methylidene [M] to ethylidene [E] from NMR analysis is very close to that estimated from the reaction feed ratio **1**/**3** indicating excellent control of polymer composition.

The incidence of the $-CH(CH_3)-CH(CH_3)-$ group in the polymer is low. This observation can be understood in terms of the mechanism of formation of the polymer. The introduction of an ethylidene group at boron (a secondary carbon that corresponds to a branch point) increases steric crowding at the boron center and decreases reactivity toward addition of the next *ethylidene* monomer **3**. This is supported by the fact that monomer **3** does not homopolymerize in the presence of triethylborane. Tri-*sec*-butyl borane does however react with an excess of the sterically less demanding methylide **1**, to produce a polymethylene star organoborane that is end capped with *sec*-butyl groups. These findings suggest that following ethylidene addition, there is a strong tendency to add a methylene group. A very slow rate of addition of **1** during the copolymerization produces an ethylidene rich monomer pool that can result in the accumulation of more highly branched carbon chains at boron. The reaction will slow and eventually stop until more monomer **1** is added.

The polymer formed from this living copolymerization has the same chemical composition as an ethylene-propylene copolymer. However, in this case *the carbon backbone is constructed one carbon at a time from CH_2 and $CHCH_3$ fragments.* The ylides used as monomers for this reaction,that is, **4**, may accommodate a number of substituents including both linear and branched alkyl groups as well as heteroatom containing functionality. The method, therefore, permits one to specify functionality on the main chain as well as at either end of the polymer chain. This new synthesis of substituted polymer chains marks an important step in the ability to prepare “designer” materials for establishing structure−property relationships or reference materials.

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(12) Here we use the nomenclature proposed by Carman (ref 10) in which Greek letters are used to designate the proximity of each of the methine carbons relative to their backbone methylene carbons of interest. Thus αβ denotes the methylene group that is one carbon away form the first branch point and two carbons away from the second branch point. A carbon that is located four or more carbons from a branch point is identified as δ+. P, S, and T are used as prefixes to these Greek letters to designate whether the carbon of interest is primary, secondary, or tertiary, respectively.