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Communications to the Editor

Acyclic Diene Metathesis (ADMET) Depolymerization. Synthesis of Mass-Exact Telechelic Polybutadiene Oligomers

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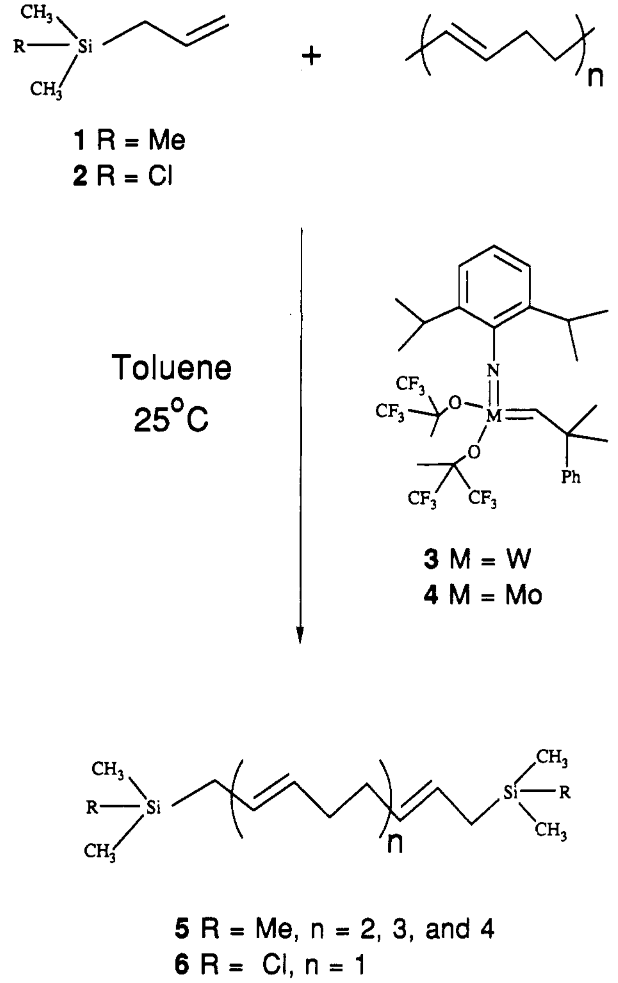
We report the synthesis of mass-exact telechelic polybutadiene by the metathesis depolymerization of 1,4-polybutadiene using allylsilane monoenes and Lewis acid-free alkylidenes. The chemistry is displayed in Figure 1.

Telechelic molecules have been a goal for chemists for many years,[1,2] where one approach has involved metathesis chemistry. For example, olefin metathesis degradation has been explored by Ivin,[3] Hummel,[4] Harwood,[5] and others,[6-9] wherein unsaturated polymers are degraded under a variety of conditions to produce a wide mixture of products. More recently, Chung and Chasmawala have degraded 1,4-polybutadiene with 1,10-bis(9-BBN)dec-5-ene to telechelic oligomers with reported functionality between 0.1 and approximately 2.0.[10] This chemistry employs the use of Lewis acid catalysts such as $WCl_6/Sn(CH_3)_4$ which lead to side reactions.[3-8,10]

Our recent discovery that Lewis acid-free metathesis catalysis yields only one reaction product[11] stimulated us to investigate the synthesis of perfectly difunctional telechelic oligomers. Thus far, we have shown that ethylene successfully depolymerizes polybutadiene, polyisoprene, poly(styrene-*b*-butadiene) (Kraton), polyoctenamer, and polynorbornene.[12] These depolymerizations are clean and afford well-defined vinyl-terminated oligomers.

While these divinyl oligomers are interesting, we also are seeking disilanes, diamines, diols, and diacids via ADMET depolymerization. In our first example, allyltrimethylsilane (**1**) is dimerized and in situ reacted with 1,4-polybutadiene.[13] Mass-exact α,ω-bis(trimethylsilyl)-1,4-polybutadiene (**5**) is the result, where *n* is 2, 3, and 4 (Figure 1). These perfectly functionalized oligomers can further be reacted with common electrophiles to form other telechelics.[14]

This depolymerization chemistry occurs by reacting 10 equiv of allyltrimethylsilane/repeat unit of 1,4-polybutadiene. Dry allyltrimethylsilane[15] was placed in a reaction flask containing purified polybutadiene[16] and catalyst **3**[17] (polybutadiene repeat unit/catalyst ratio 500:1). Ethylene instantly evolved when allyltrimethylsilane was transferred into the reaction flask, which was the result of allyltrimethylsilane dimerization. The ethylene was removed, and 25 mL of purified toluene[18] was added to produce a homogeneous solution. The reaction proceeded for 48 h and was terminated by exposure to the atmosphere. The volatiles, which were composed of toluene and allyltrimethylsilane dimer, were removed from the reaction flask, yielding mass-exact α,ω-bis(trimethylsilyl)-1,4-polybutadiene (**5**).[19]



1 R = Me
2 R = Cl

3 M = W
4 M = Mo

5 R = Me, n = 2, 3, and 4
6 R = Cl, n = 1

Figure 1. Acyclic diene metathesis (ADMET) depolymerization.

Evidence for perfect difunctionality is found in Figures 2–4. Figure 2 shows the ^1H NMR spectrum for allyltrimethylsilane, the monoene which depolymerized 1,4-polybutadiene to produce three mass-exact telechelic oligomers. The ^1H NMR spectrum of the oligomers exhibited four peaks corresponding to the vinylic hydrogens (5.35 ppm), the polybutadiene methylenes (2.00 ppm), the allylic protons (1.35 ppm), and the trimethylsilyl protons (0.00 ppm). Incorporation of trimethylsilyl end groups into the oligomers is demonstrated by the loss of its terminal vinylic proton (6.00 ppm) and the appearance of allylic protons (1.35 ppm).

Gel permeation chromatography (GPC) data (Figure 3) clearly demonstrate the clean depolymerization of high molecular weight 1,4-polybutadiene (M_n = 87 000) to perfectly difunctional oligomers of polybutadiene. Three gas chromatography/mass spectral (GC/MS) traces (Figure 4) unequivocally show that mass-exact telechelic oligomers have been synthesized by this chemistry. Note that the peaks in Figure 4 are GC peaks with mass-exact labels attached to each of them. The top GC trace displays a mass-exact 308 oligomer which corresponds to α,ω-bis-

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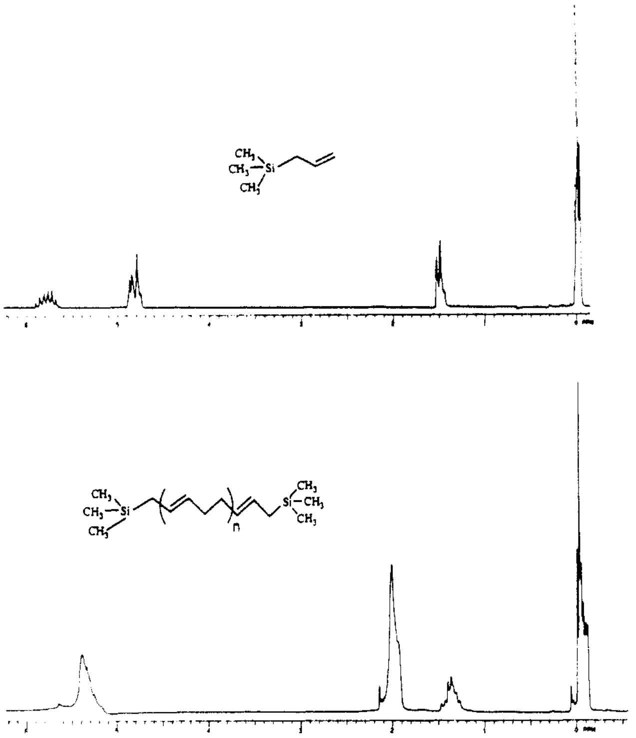

Figure 2. 200-MHz ^{1}H NMR spectra of monoene 1 (top) and the resulting α,ω-bis(trimethylsilyl)-1,4-polybutadiene (5).

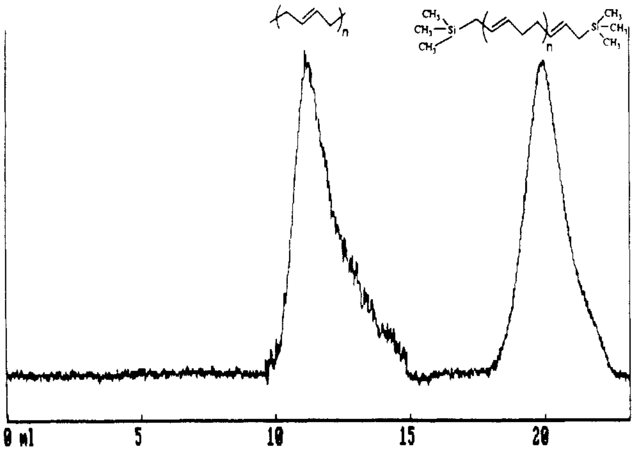

Figure 3. Gel permeation chromatography of 1,4-polybutadiene and the resulting α,ω-bis(trimethylsilyl)-1,4-polybutadiene (5).

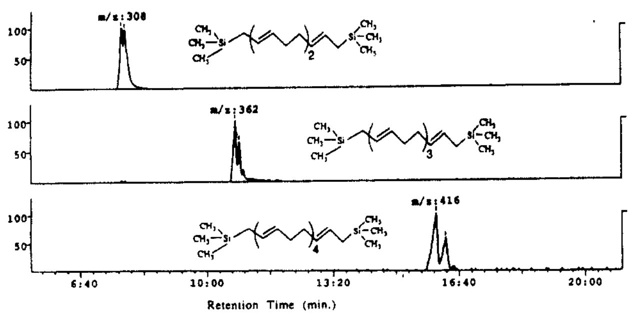

Figure 4. Gas chromatograph with mass-exact labels obtained from mass spectra of α,ω-bis(trimethylsilyl)-1,4-polybutadiene (5) where n = 2, 3, and 4.

(trimethylsilyl)-1,4-polybutadiene (5), n= 2. The following two GC traces are mass-exact for n = 3 (m/e 362) and n = 4 (m/e 416), respectively. No other products are present in this reaction mixture. Each of the three traces show more than one peak present, which reflects the presence of isomers for each mass-exact oligomer. Most likely, these are geometric isomers of polybutadiene.

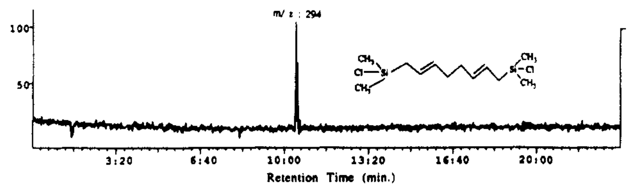

Figure 5. Gas chromatograph with mass-exact labels obtained from the mass spectrum of α,ω-bis(chlorodimethylsilyl)octa-2,6-diene (6).

Another functionalized monoene, allylchlorodimethylsilane (2), also depolymerized 1,4-polybutadiene, in this case using the molybdenum catalyst[20] 4. The result is quantitative conversion of the polymer to difunctionalized monomer 6 (m/e 294). The GC/MS trace unequivocally shows that α,ω-bis(chlorodimethylsilyl)octa-2,6-diene (6) is the sole product of this reaction (Figure 5).

We believe this depolymerization will become important in recycling of polymers while also becoming a powerful tool for the synthesis of a wide variety of perfectly difunctionalized telechelics.

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(13) 1,4-Polybutadiene was synthesized anionically by the DeSimone Group at the University of North Carolina at Chapel Hill. The polydispersity was 1.04, and the microstructure was 96% 1,4.
(14) Examples of allylsilanes reacting with carbon electrophiles can be found in: Fleming, I.; Paterson, I. *Synthesis* **1979**, 445.
(15) Allyltrimethylsilane was dried over calcium hydride under vacuum.
(16) 1,4-Polybutadiene was precipitated in methanol and degassed.
(17) The most effective ADMET catalyst has been Schrock's Lewis acid-free alkylidene, first described in: Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.
(18) Toluene was purified by washing with cold sulfuric acid, followed by washing with basic potassium permanganate, and then distilled from potassium benzophenone ketyl under argon.
(19) α,ω-Bis(trimethylsilyl)-1,4-polybutadiene (5) was further purified via column chromatography to remove the catalyst.
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