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Notes

Conjugated Monomers in Acyclic Diene Metathesis (ADMET) Polymerization

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Introduction

Acyclic diene metathesis (ADMET) polymerization is a step condensation reaction which has proven to be a viable synthetic route to high molecular weight unsaturated polymers and copolymers (Figure 1).[1-6]

Until recently, only nonconjugated monomers have been used in ADMET polymerization, where a spacer group (R in Figure 1) has been present between two terminal olefins. This paper describes the reactivity of conjugated ADMET monomers, 2,4-hexadiene and 2,4,6-octatriene, in acyclic diene metathesis polymerization using Schrock's molybdenum catalyst, Mo[CHC(C_6H_5)(CH_3)$_2$](N-2,6-C_6H_3-*i*-Pr_2)[OCCH$_3$(CF_3)$_2$]$_2$.[7] The polymerizations appear to occur much faster than for nonconjugated monomers, and well defined polyenes were obtained (Figure 2).

Since polyenes are the key structures to the study of the properties of polyacetylenes[8-10] and are important components in natural products,[11-14] such as carotenoids, polyene research has become an attractive area. Unsubstituted polyenes obtained from different synthesis methods have been reported.[15-22] For example, Schrock *et al.*[15] have reported *tert*-butyl capped polyenes containing up to 15 double bonds through the ring-opening metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]deca-3,7,9-triene and aldehyde capping reagents. Dimethylpolyenes have also been made by Spangler *et al.* through the coupling of the 2,4-hexadienal with various bis-Wittig dienyl salts.[16] The conjugated ene units numbered from 7 to 10.

We report here the synthesis of methyl terminated polyenes containing up to 20 double bonds which have been obtained directly from the metathesis polymerization of conjugated acyclic diene or trienes. The reactions are clean, and high yields are obtained.

The polymerizability of conjugated dienes with methyl groups at each end of the molecule may offer a method to obtain telechelic polyacetylene, which could be used in the synthesis of segmented polyacetylene multiphase copolymers. This polymerization method may also be potentially useful in synthesizing carotenoid-like products.

Results and Discussion

According to the general ADMET polymerization mechanism, the reaction cycle of the polymerization of 2,4-hexadiene can be described as in Figure 3. One double bond of 2,4-hexadiene reacts with the initial metal alkylidene to form a metallacyclobutane (Figure 3, step 1), which then rearranges to form a second alkylidene and a neophyl alkene (step 2). This alkylidene then reacts with the olefin moiety of another monomer to form a second metallacyclobutane which then rearranges to a dimer and a third metal alkylidene (steps 3 and 4). The reaction process is continued as a cycle (steps 3–6) to obtain longer chain molecules and to release 2-butene.

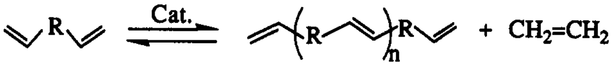

Figure 1. Acyclic diene metathesis (ADMET) polymerization.

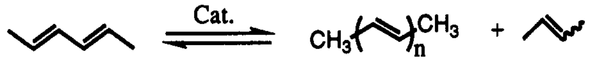

Figure 2. Methyl terminated polyene obtained through ADMET polymerization of conjugated 2,4-hexadiene.

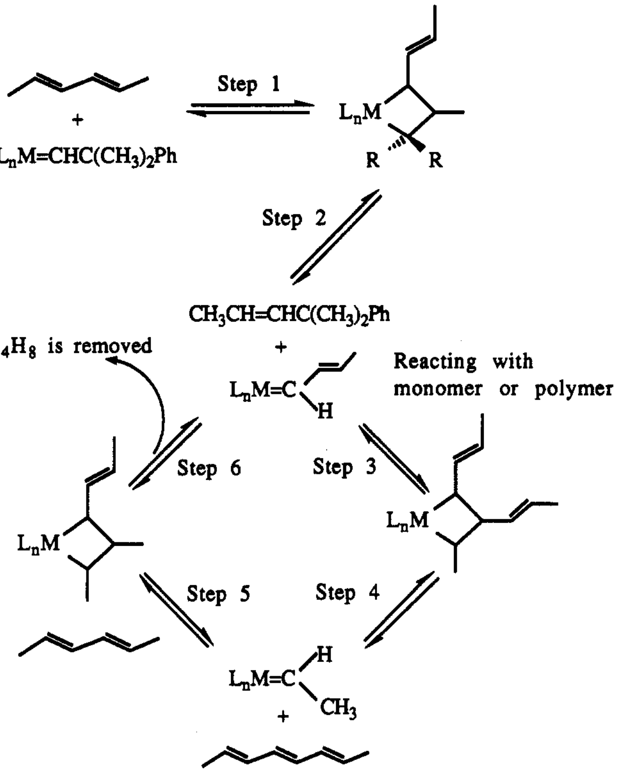

Figure 3. ADMET polymerization cycle of 2,4-hexadiene.

In the bulk ADMET polymerization of 2,4-hexadiene, the side product, 2-butene, was collected as a 4:1 mixture of the *trans* and *cis* isomers, respectively, as determined by NMR spectroscopy. The polyenes were characterized by NMR spectroscopy using chloroform-*d* as solvent. The polyenes are partially soluble in $CDCl_3$, and their NMR spectra (Figure 4) clearly show that methyl groups are present at both ends of the polyene chain. The protons of the terminal methyl groups are at 1.8 ppm, and the protons of the conjugated double bonds are found mainly between 6.0 and 6.4 ppm. The peak near 5.7 ppm is assigned to the protons of the conjugated double bonds at the ends of the polyene chain. Solid state ^{13}C NMR spectroscopy confirmed the polyene structure.

According to the ^1H NMR integration values, polyenes from the bulk polymerization of 2,4-hexadiene were an average of 6–10 repeat units. Since higher molecular weight polyene is partially soluble in $CDCl_3$, the actual

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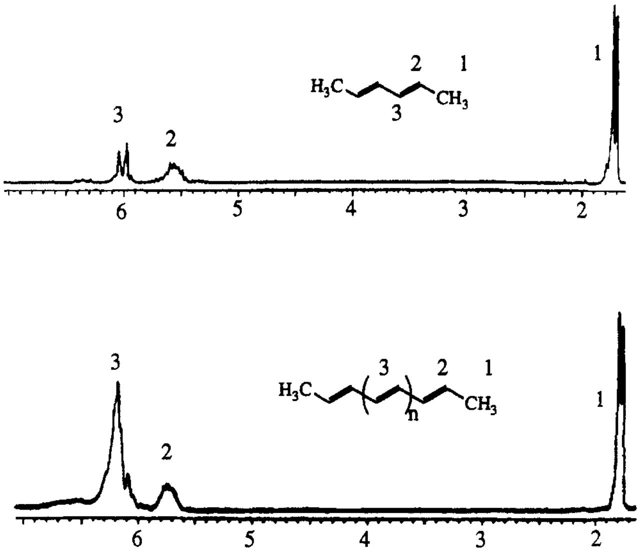

Figure 4. ^{1}H NMR of 2,4-hexadiene and its resultant polyene.

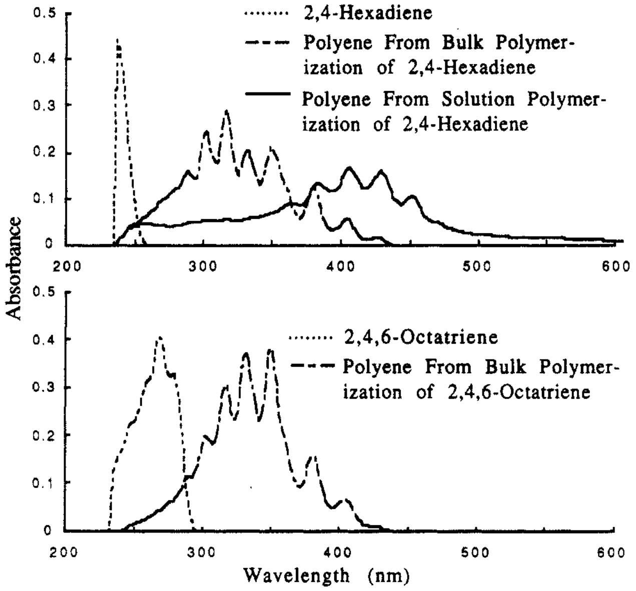

Figure 5. UV spectra of 2,4-hexadiene, 2,4,6-octatriene, and their polyenes.

average molecular weight of the entire sample could be higher than that calculated from the NMR spectra. Mass spectrometry (MS) showed that the highest detectable length for the polyenes from 2,4-hexadiene in 20 repeat units, and gel permeation chromatography (GPC) vs polybutadiene standards shows an average of 15 repeat units. Only polyene oligomers were produced in this step condensation, equilibrium polymerization because the methyl terminated polyenes have high melting points[18] (4-ene, mp 115 °C; 5-ene, mp 150 °C) and solidify at low degrees of polymerization. In this manner, the terminal olefins of the polyene oligomers are restricted from further metathesis condensation.

To extend the degree of polymerization, the reaction was also run in solution. When 2,4-hexadiene was dissolved in toluene, followed by addition of catalyst, the polyene oligomers remained soluble for approximately 10 min before precipitating. In this manner, polyenes with an average of 10–15 repeat units were prepared as determined by NMR spectroscopy (GPC, 20 average repeat units; MS, 21 maximum repeat units).

The UV spectra of 2,4-hexadiene and the soluble portion of its bulk and solution polymers are shown in Figure 5 (upper). According to the work of Spangler,[16] methyl terminated polyenes containing 7 or more double bonds show three main absorbances. Compared with the UV spectra of individual polyenes (7-ene to 10-ene) in Spangler's paper, the multiple UV absorption of the polyenes here can be attributed to the different polyene chain lengths. The highest absorption of the methyl terminated polyene from bulk polymerization is at 426 nm, which could be from the polyene containing 8 conjugated repeat units. The middle length polyene has an absorption at 349 nm, which can be assigned to the 5-ene. The chain length exhibited by this UV spectrum is consistent with that from the NMR spectrum for the same sample. The solution polymerization polyenes have slightly longer lengths than bulk polymerization polyenes. The highest absorption wavelength at 470 nm represents a polyene length higher than 10 repeat units.

The reactivity of 2,4,6-octatriene was compared to 2,4-hexadiene for the bulk ADMET polymerization. Under nearly identical reaction conditions, polyenes with similar lengths and physical properties were prepared. For example, the UV spectrum of the polyenes generated from the bulk polymerization of 2,4,6-octatriene (Figure 5, lower) is similar to that of the polyenes obtained from 2,4-hexadiene, except for the different distributions of the two samples.

Experimental Section

Monomer and Catalyst Synthesis and Purification. 2,4-Hexadiene was purchased from Aldrich Chemical Co. 2,4,6-Octatriene was synthesized by the method described in the literature.[18] Reagent grade toluene was distilled from Na–K ketyl under argon prior to use. Monomers were purified by drying over calcium hydride for 24 h and degassed by four freeze–thaw–vacuum cycles. In order to ensure absolute dryness and the absence of oxygen, the monomers were vacuum transferred to a sodium mirrored flask for 4 h and then transferred to and stored in a vacuum flask equipped with a Teflon stopcock. The monomers were then ready for use in the polymerization reaction.

Schrock's molybdenum catalyst $Mo[CHC(C_6H_5)(CH_3)_2](N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$ used in the polymerizations was synthesized by the method described in the literature.[7]

Polymerization. Bulk Polymerization. In an argon drybox, 1.0 g of the purified diene (or triene) and Schrock's catalyst were weighed (mole ratio of monomer to catalyst, 500:1) and mixed in a high vacuum flask containing a magnetic stirring bar. The reaction mixture was stirred, sealed, and then moved to a vacuum system. The polymerization was continued at room temperature with stirring. *cis* and *trans*-2-butene generated from the reaction were removed by intermittent application of high vacuum ($<10^{-4}$ mmHg) to drive the equilibrium reaction forward. Polyene solids started to form in 5 min. The reaction was continued for 12 h and quenched by exposure to air. The polymer was added to chloroform (swelling and partially soluble), precipitated (brown solids) in methanol, and then filtered and dried.

Solution Polymerizations. Solution polymerizations were conducted in a procedure similar to that of bulk polymerizations. Identical mole ratios of monomer to catalyst (500:1) were used, and the reactions were conducted in toluene solution (1.0 M). After dissolution of monomer in solvent, catalyst was added in the normal manner. Polyene formation was observed by precipitation after 10 min. The reaction was continued for 12 h and quenched by exposure to air.

Characterization. ^{1}H NMR 200-MHz and ^{13}C NMR 50-MHz spectra were obtained with a Varian XL 200 spectrometer. A Perkin-Elmer Lambda 9 UV/vis spectrophotometer was used to obtain UV/vis spectra ($CHCl_3$ as solvent). Mass spectra were obtained with a Finnigan MAT 95 Q mass spectrometer using a mixture of dithiothreitol and dithioerythritol as solvent. Gel permeation chromatography (GPC) data (vs polybutadiene standards) were collected using a Waters Associates liquid chromatography apparatus equipped with a refractive index detector and two Phenogel columns (100 and 500 Å). The eluting solvent was HPLC-grade THF supplied at a flow rate of 1.0 mL/min.

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