Acyclic Diene Metathesis Copolymerization of 1,5-Hexadiene and 1,9-Decadiene

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Introduction

The recent success in the development of a new polymerization scheme utilizing the metathesis reaction with acyclic dienes as monomers[1,2] prompted the research reported in this paper. Acyclic diene metathesis (ADMET) polymerization, a new equilibrium step propagation, condensation-type polymerization, provides the opportunity to expand metathesis polymerizations beyond the well-known ring-opening metathesis polymerization.[3-8] The successful employment of acyclic dienes as monomers provides the opportunity to investigate the synthesis of copolymers (Figure 1) via ADMET polymerization techniques. The synthesis of new copolymers broadens the scope and further illustrates the feasibility of acyclic diene metathesis polymerization.

We first reported on acyclic diene metathesis polymerization using a tungsten hexachloride–ethylaluminum dichloride catalyst system and found that metathesis polymerization was limited by the competing vinyl addition chemistry.[9] We have demonstrated, with model compound studies, that by employment of a Lewis acid free catalyst system the metathesis reaction is quantitative; the competing vinyl addition chemistry is completely eliminated.[10] With the successful homopolymerization of 1,9-decadiene and 1,5-hexadiene to perfectly linear highly trans polyoctenamer and polybutadiene, respectively, ADMET polymerization became a reality. We subsequently focused our efforts on the formation of copolymers by ADMET techniques. Here we report the synthesis of new perfectly random linear polybutadiene–polyoctenamer copolymers using 1,5-hexadiene and 1,9-decadiene as monomers via ADMET polymerization (Figure 1).

Experimental Section

Polymerizations. The procedure described herein was used to synthesize three copolymers possessing differing mole percentages of 1,5-hexadiene and 1,9-decadiene. The monomers, 1,5-hexadiene and 1,9-decadiene, were purified separately. These monomers, 25 mL of each, were dried over calcium hydride and then subjected to four freeze–thaw–vacuum cycles to remove dissolved gases. In order to ensure absolute dryness, the monomers were vacuum transferred to a flask containing a potassium mirror, where they were stirred for approximately 1 h. The dried monomers were vacuum transferred to a reaction flask where they were exposed to catalyst ($[(CF_3)_2CH_3CO]_2(NAr)W{=}CHC(CH_3)_3$)[11] (20 mg, 0.025 mmol) for 0.5 h and then transferred under vacuum to storage flasks and stored under vacuum in a freezer. Monomer mixtures of varying ratios were prepared in a drybox; these comonomer feeds were stored in evacuated breakseal ampules. Three different monomer ratios were employed, 1,9-decadiene/1,5-hexadiene molar ratios of 50/50, 75/25, and 95/5. The monomer feeds were prepared as follows: 50/50 monomer feed, 1.22 mL (6.62 mmol) of 1,9-decadiene was added to 0.78 mL (6.60 mmol) of 1,5-hexadiene; 75/25 monomer feed, 1.65 mL (8.95 mmol) was added to 0.35 mL (2.95 mmol) of 1,5-hexadiene; 95/5 monomer feed, 1.94 mL (10.5 mmol) of 1,9-decadiene was added to 0.35 mL (0.56 mmol) of 1,5-hexadiene.

Polymerizations were conducted on a vacuum line by first transferring the catalyst solution (20 mg/2 mL of pentane), from a breakseal ampule to the evacuated reaction vessel, followed by removal of the solvent. A solid deposit of catalyst residue remained to which the premixed monomer feeds (2 mL) were introduced directly to the reaction vessel via breakseal ampules. Additionally, a fourth copolymerization was performed. Instead of using a comonomer feed, we synthesized[2] the homopolymer of 1,5-hexadiene (1.56 mL; 13.2 mmol/20 mg of catalyst) to which an equimolar amount of 1,9-decadiene (2.44 mL, 13.2 mmol) was added.

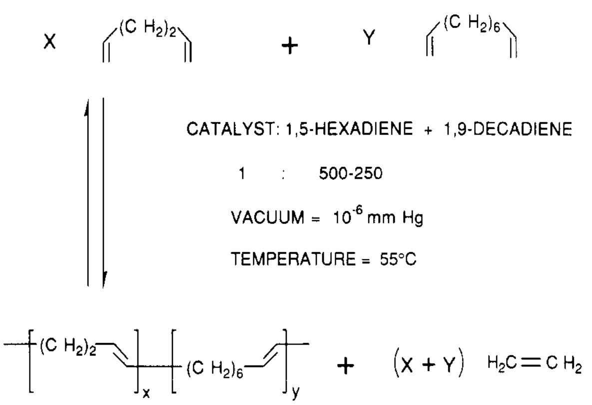

Figure 1. Acyclic diene metathesis (ADMET) copolymerization.

Reactions were conducted by utilizing bulk polymerization techniques. These reactions were stirred continuously at 55 °C with intermittent applications of vacuum. A second addition of catalyst (20 mg/2 mL of pentane) during each polymerization was made when deemed necessary. Reactions were terminated once the polymer's viscosity had increased to the point where they could no longer be stirred by magnetic agitation. The new copolymers were dissolved in benzene and precipitated in methanol. The weight percent yield for these copolymerizations with monomer feeds of 50/50, 75/25, and 95/5, and polybutadiene/1,9-hexadiene (50/50) are 71%, 75%, 77%, and 70%, respectively.

Copolymers of similar composition were prepared by the transmetathesis polymerization of already formed homopolymer with either monomer. In a typical example, 3.5 g of polyoctenamer was transferred to a reaction vessel, which was placed on the vacuum line. Three freeze–thaw cycles were done, followed by introduction of the catalyst (20 mg, 0.025 mmol in pentane) from a breakseal ampule. The solvent was removed under vacuum, followed by the addition of 3.5 g of 1,5-hexadiene, which resulted in a viscous solution. The copolymerization was terminated once the copolymer's viscosity increased to the point where it no longer could be stirred by agitation. Structure determination was done as before, showing that a 50/50 random copolymer had been formed.

Characterization. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) were obtained with a Varian XL Series NMR superconducting spectrometer system. Elemental analyses were performed by Atlantic Microlab. Size-exclusion chromatography data were obtained in toluene by using a Waters Associates liquid chromatography apparatus equipped with an RI detector. Intrinsic viscosities were determined by using an Oswaltd dilution viscometer at 25 °C with toluene as the solvent. Vapor pressure osmometry analyses were performed by utilizing a Wescan Model 233 molecular weight apparatus at 50 °C in toluene.

Results and Discussion

The scope of acyclic diene metathesis polymerization has been expanded to the synthesis of random, hydrocarbon-based copolymers. The monomers, 1,9-decadiene[1] and 1,5-hexadiene,[2] have each been homopolymerized previously by ADMET techniques yielding 1,4-polybutadiene and polyoctenamer, respectively. These monomers have been copolymerized via ADMET techniques by using different feed ratios, as well as by the introduction of one monomer to the homopolymer of the other monomer, to produce a series of poly(1,4-butadiene-

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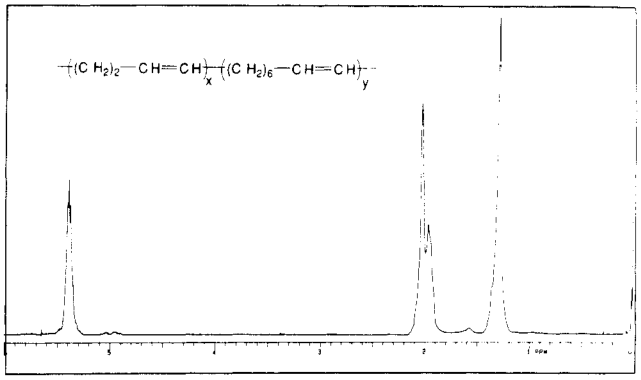

Figure 2. ^{1}H NMR spectrum of 50/50 poly(1,4-butadiene-*co*-octenamer) formed via ADMET polymerization techniques.

Table I
Copolymer Composition by NMR

monomer feed 1,9-decadiene/ 1,5-hexadiene ratio	^{1}H NMR data (found): methylene protons^a	^{13}C NMR data (found)	
		methylene^b	alkene^c
50/50	48/52	51/49	49/51
75/25	72/28	75/25	75/25
95/5	95/5	92/8	92/8

^{a} Determined by integration of methylene protons (1.8–2.0 ppm). ^{b} Determined by integration of methylene carbons (26–34 ppm). ^{c} Determined by integration of alkene carbons (129–131 ppm).

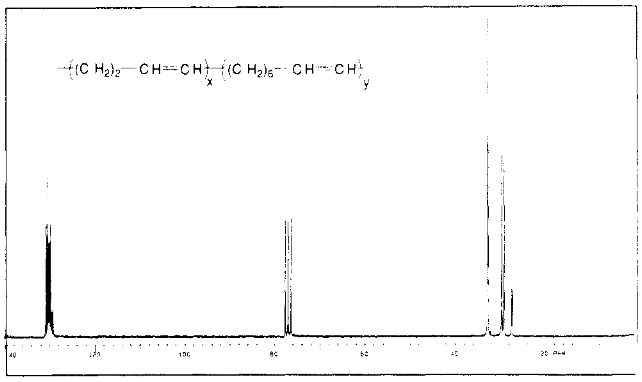

Figure 3. ^{13}C NMR of 50/50 poly(1,4-butadiene-*co*-octenamer).

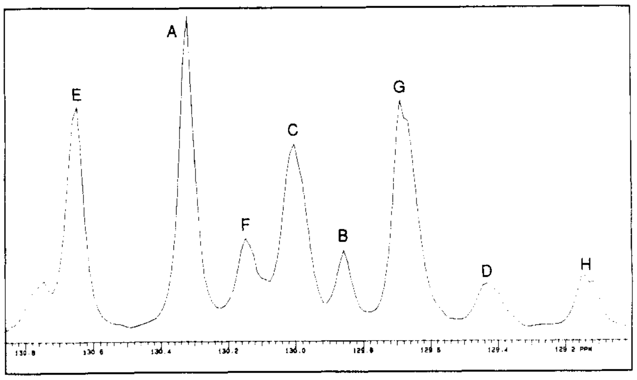

Figure 4. Expanded ^{13}C NMR of 50/50 poly(1,4-butadiene-*co*-octenamer).

Table II
NMR Analysis of Random Nature of Copolymer

monomer unit		linkages between repeat units	relative no. of linkages	
peak	ppm		obsd by carbon NMR	statistical
A	130.32	trans 1,9–1,9 link		
B	129.86	cis 1,9–1,9 link	1.00	1.00
C	130.00	trans 1,5–1,5 link		
D	129.44	cis 1,5–1,5 link	0.87	1.00
E	130.64	trans 1,9–1,5 link		
F	130.14	cis 1,9–1,5 link	1.05	1.00
G	129.68	trans 1,5–1,9 link		
H	129.14	cis 1,5–1,9 link	1.00	1.00

co-octenamer) copolymers. The polymerization scheme (Figure 1) shows that only two products result from this reaction, poly(1,4-butadiene-*co*-octenamer) and ethylene. The ethylene produced, identified by GC/MS, was removed to drive this equilibrium reaction.

Integration of the methylene peaks[12,13] at 1.3 and 2.0 ppm in the ^{1}H NMR spectrum (Figure 2) shows that the ratios of octenamer to butadiene units in these copolymers is dictated by the monomer feed ratios (Table I). This result is consistent with any equilibrium step polymerization and is confirming evidence for the nature of this polymerization scheme. Elemental analysis data agree with copolymers consisting of varying ratios of butadiene and octenamer repeat units as provided by the monomer feed. For example, the elemental analysis of the 75/25 1,9-decadiene/1,5-hexadiene copolymer yield the following: % carbon calculated, 87.68; percent found, 87.43; % hydrogen calculated, 12.32; % hydrogen found, 12.50.

This series of copolymer structures was previously unknown, and further structural evidence lies in a detailed analysis of its ^{1}H NMR spectrum, which is additive for the homopolymer, and for its ^{13}C NMR spectrum (Figure 3). The sp^2 region (129–131 ppm) clearly confirms the formation of random copolymers. While the ^{13}C NMR spectrum for each homopolymer possesses only two signals (cis and trans stereochemistry),[14,16] the spectra for the series of copolymers exhibits eight signals (Figure 4).

These eight signals are due to the presence of additional linkages in the copolymer (see Table II). The intensity for each type of link is statistically known, and the experimental intensities agree well with these statistical values. Peaks labeled E–H were assigned by comparison of the ^{13}C NMR spectra for the three copolymer compositions that were synthesized; changes in signal intensity permitted unequivocal assignment.

It should be noted that these polybutadiene-*co*-polyoctenamer copolymers can be prepared via transmetathesis reactions as well. 1,5-Hexadiene can be combined with an equal weight of polyoctenamer to give a perfectly random 50/50 copolymer, and vice versa. Copolymers made in this fashion exhibit spectra identical with those prepared directly from the comonomers. Transmetathesis is expected under equilibrium conditions, and these results lend additional evidence to the step nature of the chemistry at hand. On the basis of these results, it would appear that any metathesis copolymer, block or otherwise, would scramble under equilibrium conditions to a perfectly random copolymer if the olefin reactivity in each comonomer were the same.

Molecular weights and distributions were determined by VPO and SEC. Since the Mark–Houwink constants used to describe the viscosity molecular weight relationship are unknown for these novel copolymers, absolute number-average molecular weights were obtained via VPO measurements. Excellent agreement between these values and the relative molecular weights obtained from polybutadiene calibrated SEC was found (Table III). These data are roughly $^1/_2$ the values for polyoctenamer and polybutadiene homopolymers prepared previously.[1,2] largely because of inefficient (magnetic bar) stirring during the reaction. It appears that high-torque stirring is needed to achieve maximum molecular weights, since reaction kinetics are dictated by the removal of ethylene, which becomes diffusion limited. The higher catalyst concen-

Table III
Molecular Weight Comparison for Poly(1,4-Butadiene-*co*-octenamer) Samples Prepared by ADMET Polymerizations (Polystyrene Standards)

no.	ratio of 1,9 to 1,5 monomers	viscosity $[\eta]$, dL/g	GPC $\bar{M}_w$	GPC $\bar{M}_n$	GPC $\bar{M}_w/\bar{M}_n$	VPO: $\bar{M}_n$
1	50/50	0.30	15 600	8100	1.93	7980
2	75/25	0.35	25 000	12700	1.98	12400
3	95/5	0.28	15 000	7800	1.94	7960

tration used in these copolymerization studies also restricts the ultimate molecular weights that can be achieved.

Molecular weight distributions approaching 2.0 indicate that these copolymers were formed by an equilibrium step propagation method. A single peak was observed in the SEC, which illustrates the product is a copolymer and not a blend of homopolymers.

These copolymerizations demonstrate how easily known homopolymers such as polybutadiene can be altered in structure via ADMET copolymerization techniques. In the examples above, three different "polybutadienes" were prepared, and it should prove possible to alter the structure of any unsaturated homopolymer in this manner, provided the homopolymer itself does not poison the ADMET metathesis catalyst.

Clearly, the scope of metathesis copolymerization has been extended in this chemistry, thereby complementing the ring-opening metathesis reactions. In the future, we aim to further broaden the scope of ADMET copolymerization, to prepare a variety of copolymers based on known unsaturated homopolymer structures, and to examine thepossibility of copolymerizing dienes possessing olefins of unequal reactivity.

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Registry No. Poly(1,4-butadiene-*co*-octenamer) (copolymer), 129457-74-5; ethylene, 74-85-1.