

## Acyclic diene metathesis depolymerization of elastomers

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(Date of receipt: January 31, 1991)

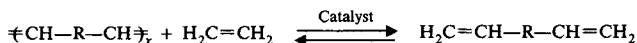
### Introduction

The advent of acyclic diene metathesis (ADMET) polymerization as a viable synthetic route to high-molecular-weight linear polymers<sup>1-2)</sup> and copolymers<sup>3)</sup> has provoked a unique and currently important examination of metathesis chemistry. Whereas ring-opening metathesis polymerization<sup>4)</sup> (ROMP) is a chain growth, addition type polymerization driven by the alleviation of ring strain, acyclic diene metathesis is a step growth, equilibrium condensation type polymerization and thus provides the opportunity to shift the equilibrium between monomer and polymer, depending upon reaction conditions.

We have found that a highly active Lewis acid free tungsten alkylidene catalyst<sup>1,5,6)</sup> of the type  $((CF_3)_2CH_3CO)_2(NAr)-W=CHC(CH_3)_3$ , in combination with ethylene, depolymerizes unsaturated polymers, yielding low-molecular-weight oligomers and  $\alpha,\omega$ -alkadienes. In this paper we report the facile reversibility of acyclic diene metathesis (ADMET) polymerization and its potential applicability to other polymer systems.

By driving this equilibrium, condensation type polymerization toward monomer with an excess of ethylene, polymers synthesized by ADMET and commercially available unsaturated elastomers can be depolymerized successfully as depicted in *Scheme 1*.

*Scheme 1:*



### Experimental part

Poly(1-octenylene) (polyoctenamer, weight-average molecular weight  $\bar{M}_w = 108\,000$  by GPC) was prepared by the ADMET polymerization of 1,9-decadiene as described previously<sup>1)</sup>. Polybutadiene ( $\bar{M}_w = 200\,000$ , ratio of weight-to number-average molecular weights,  $\bar{M}_w/\bar{M}_n = 2,1$ , 55% *trans*, 42% *cis*, 8% vinyl) and poly-*trans*-isoprene ( $\bar{M}_w = 2,5 \cdot 10^5$ , GPC versus polystyrene standards) were purchased from Polysciences Inc. The Kraton<sup>TM\*</sup> sample ( $\bar{M}_w = 86\,000$ , 17% polystyrene block,  $\bar{M}_w = 14\,600$ , 40% 1,2-linkages in polybutadiene block) was generously donated by SHELL. Polynorbornene was prepared with the same catalyst as that used for depolymerization according to published methods<sup>6)</sup>. Ethylene (Polymer Grade 99,9%) was obtained from Matheson Gas Products. The catalyst  $((CF_3)_2CH_3CO)_2(NAr)-W=CHC(CH_3)_3$  was

\* Kraton<sup>TM</sup>: polybutadiene/polystyrene diblock copolymer.

prepared by published methods<sup>6</sup>). In general, a mole ratio repeating unit/catalyst of 20:1 was used unless otherwise stated. The polymer samples were purified prior to use by several precipitations with different solvents in methanol and dried under high vacuum for several days. All solvents were distilled from potassium and stirred over potassium-mirrors.

**Depolymerization:** The polyoctenamer experiment was carried out by adding the polymer to a custom ADMET reaction vessel equipped with magnetic stirrer, and a breakseal ampule containing catalyst in the repeating unit/catalyst mole ratio of 43:1. Toluene was introduced to dissolve the polymer, and the solution was subjected to four freeze/thaw vacuum cycles. The catalyst was added, followed by the addition of excess ethylene with a pressure of 3,5 atm. Depolymerization was carried out for 48 h at room temperature, after which the volatile reaction products were vacuum-transferred and analyzed by GC/MS.

The reactions at atmospheric pressure were performed in a 100 mL reaction flask equipped with a gas bubbler and breakseal containing catalyst. The flask was flame-dried under high vacuum, and the polymer was added under an argon flow after which a high vacuum ( $10^{-6}$  mmHg) was applied for several hours. Toluene was vacuum-transferred in the flask after which the catalyst was washed down. Ethylene was bubbled through the solution at a slow consistent rate. In the case of the depolymerization of polynorbornene at atmospheric pressure, the polynorbornene sample was made in situ (under argon) after which the sample was exposed to an additional amount of catalyst and ethylene.

The high pressure reactions were performed in a thickwall glass pressure bottle fitted with a metalcap with valve. The reaction mixture was prepared and added under argon after which the vessel was closed and pressurized to 4–6 atm. After several days, the reaction was stopped by exposing the mixture to air and separating the volatiles from the non-volatile oligomers by vacuum transfer.

**Characterization:** <sup>1</sup>H NMR 200 MHz and <sup>13</sup>C NMR 50 MHz spectra were obtained with a Varian XL-Series NMR superconducting spectrometer system. Size-exclusion chromatography data were obtained using a Waters Associates liquid chromatograph apparatus equipped with a RI detector and Phenogel columns (polybutadiene standards were used for the polybutadiene samples, in the other cases polystyrene standards were used). GC/MS data were obtained with a Finnegan 4500 gas chromatograph/mass spectrometer. Identification of products were confirmed by comparison with an authentic sample. GC data were obtained with a Hewlett Packard 5880a gas chromatograph equipped with a HP 5% phenylmethylsilicone column.

## Results and discussion

Acyclic diene metathesis depolymerization chemistry is distinguished from metathesis degradation chemistry. Although polymer degradation by metathesis is known and has been investigated<sup>4</sup>), problems due to difficult product control and loss of unsaturation are common. The term “degradation” and not “depolymerization” is appropriately used in this prior work in that the products of these degradation reactions are seldom of any effective use. Notable exceptions include the work of Harwood<sup>7</sup>), Hummel<sup>8</sup>) and Calderon<sup>9</sup>). Harwood determined sequence length distribution of styrene-butadiene copolymers by metathesis degradation with 2-butene. Hummel demonstrated metathesis degradation with octenes, and Calderon illustrated the commercial usefulness of degrading various polyalkenamers.

Most recently, Alimuniar<sup>10</sup>) et al. have reported the intramolecular metathesis degradation of natural rubber with  $WCl_6/C_2H_5AlCl_2$ , yet it is not clear how the degradation occurs. Although loss in molecular weight is reported, loss in unsaturation is also observed. Problems such as these are anticipated when traditional metathesis catalysts systems<sup>4</sup>) are used which typically contain Lewis acid cocatalysts as in Alimuniar's work. We have found that the use of a Lewis acid free metathesis catalyst

solves these degradation problems, since the forward and reverse mechanisms of ADMET mutually enjoy a clean and well-defined path and the chemistry is void of any competing reactions. Under these conditions, the reverse reaction of acyclic diene metathesis is depolymerization, not degradation.

Polymers we have depolymerized by this method include polyoctenamer, polynorbornene and three commercially obtained elastomers: polybutadiene, polyisoprene and a Kraton™ sample (polystyrene/polybutadiene diblock copolymer). Kraton™ was studied with the intent of producing functionalized prepolymers from commercially available thermoplastic elastomers, since only the unsaturated blocks would be affected. The depolymerization results are summarized in Tab. 1.

Tab. 1. Depolymerization results

Polymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Method	MW of products	Detected monomer
Polyoctenamer	108 000 <sup>a)</sup>	(1,9)	A	1 000 <sup>c)</sup>	1,9-Decadiene <sup>f)</sup>
Polybutadiene	200 000 <sup>b)</sup>	(2,1)	B, C	2 000 <sup>d)</sup>	1,5-Hexadiene <sup>f, g)</sup>
	200 000 <sup>b)</sup>	(2,1)	C(THF)	1 000 <sup>e)</sup>	1,5-Hexadiene <sup>f, g)</sup>
Polyisoprene	2,5 · 10 <sup>5</sup> <sup>b)</sup>	(1,0)	C	1 000 <sup>e)</sup>	2-Methyl- -1,5-hexadiene <sup>f, g)</sup>
Kraton™ (17 mol-% PS)	86 000 <sup>b)</sup>		C	15 400 <sup>e)</sup>	Polystyrene <sup>h)</sup> and
				1 000 <sup>e)</sup>	1,5-Hexadiene <sup>f)</sup>
Polynorbornene	94 430 <sup>e)</sup>	(2,2)	C	19 850 <sup>e)</sup>	—
	130 770 <sup>e)</sup>	(1,7)	B	50 600 <sup>e)</sup>	—

a)  $\bar{M}_w$  determined by gel-permeation chromatography (GPC) (versus polystyrene standards).

b) From supplier.

c)  $\bar{M}_n$  determined by quantitative <sup>13</sup>C NMR.

d)  $\bar{M}_w$  from GPC (versus polybutadiene standards).

e)  $\bar{M}_w$  from GPC (versus polystyrene standards).

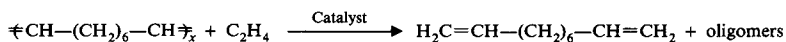
f) Detected by gas chromatography/mass spectroscopy (GC/MS).

g) Detected by GC.

h) Characterized by NMR. Method A: In acyclic diene metathesis (ADMET) polymerization flask with ethylene pressure of 3,5 atm in toluene. Method B: Bubbled ethylene at atmospheric pressure in toluene. Method C: High ethylene pressure of 4–6 atm in toluene.

In order to construct a complete proof of reversibility for this reaction, a well-characterized ADMET polymer was depolymerized to the original monomer. A clean and well-defined sample of polyoctenamer was synthesized by the ADMET polymerization of 1,9-decadiene, as described previously<sup>1)</sup>. The polymer was dissolved in toluene, then depolymerized by exposure to catalyst under an ethylene pressure of 3,5 atm as shown in *Scheme 2*.

Scheme 2:



A large decrease in molecular weight was observed (Tab. 1) and 1,9-decadiene was detected by GC/MS. The oligomers exhibit an increase in average *trans*-olefin content from 88% to 96% as measured by quantitative  $^{13}\text{C}$  NMR. This increase probably originates from the known higher reactivity of *cis*-olefins or a polymer-polymer interchange<sup>4)</sup> (transmetathesis). The  $^{13}\text{C}$  NMR data of the starting material and unpurified oligomers obtained exemplifies the very clean depolymerization pathway. The  $^{13}\text{C}$  NMR spectra are shown in Fig. 1.

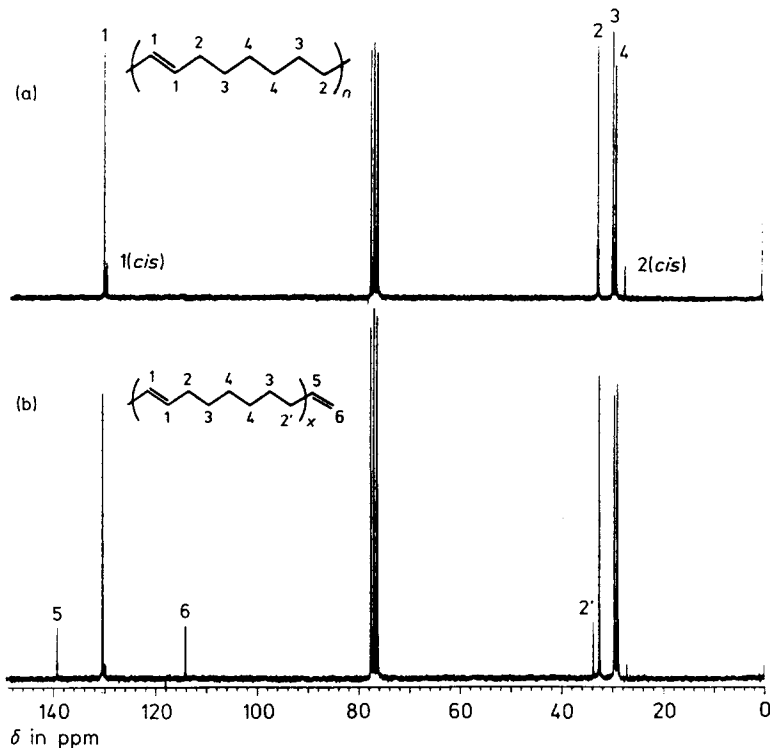


Fig. 1.  $^{13}\text{C}$  NMR of (a) polyoctenamer starting material and (b) octenamer oligomers after depolymerization

With this information in hand, a commercial sample of polybutadiene was depolymerized with ethylene simply by bubbling the gas through a solution of polybutadiene and catalyst in toluene at atmospheric pressure. The products obtained were polybutadiene oligomers and 1,5-hexadiene (Tab. 1), which is the monomer used to prepare polybutadiene by ADMET polymerization<sup>1)</sup>. Similar results were obtained when using THF as solvent, indicating catalyst tolerance towards ethers. The depolymerization of polybutadiene is shown in *Scheme 3*.

Scheme 3:

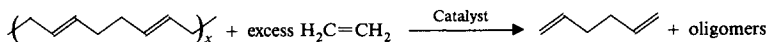
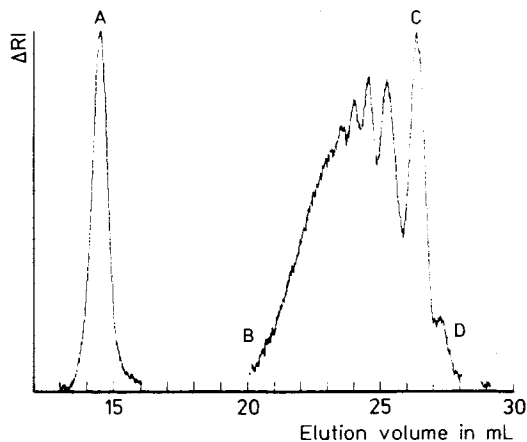


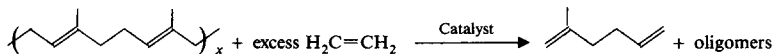
Fig. 2 shows the gel-permeation trace of several oligomeric products. The end groups of these oligomers are also evident in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the reaction mixture. The complexity of the product mixture arises primarily from the presence of 1,2-addition linkages in the starting material.

Fig. 2. Gel-permeation chromatography (GPC) trace of starting material and residue from the depolymerization of polybutadiene. Peak A: Starting material ( $\bar{M}_w = 200\,000$ ,  $\bar{M}_w/\bar{M}_n = 2,1$ ); peak B:  $\bar{M}_w = 2\,000$ ; peak C: catalyst; peak D:  $\bar{M}_w = 60$  (molecular weights relative to polybutadiene standards)



In a third depolymerization, polyisoprene depolymerizes to 2-methyl-1,5-hexadiene and oligomers, shown in Scheme 4.

Scheme 4:

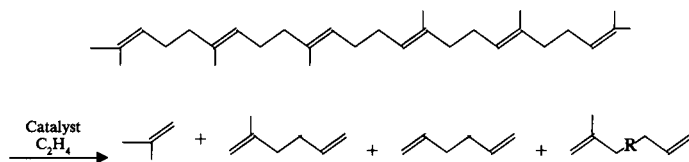


This reaction is only successful when carried out under an increased ethylene pressure of 5–6 atm and at 50 °C. These more stringent conditions are required due to the reduced reactivity of substituted olefins toward metathesis<sup>4</sup>. Apparently, the equilibrium is sufficiently shifted to depolymerization by elevated temperature and pressure, whereas concurrent results in our labs indicate that ADMET polymerization (the forward reaction) of 1,1-disubstituted olefins does not occur<sup>11</sup>.

In order to prove once more that the depolymerization reaction proceeds along a well-defined and clean pathway, a sample of squalene was depolymerized under the same conditions as the polyisoprene depolymerization. This reaction is shown in Scheme 5.

After the reaction, 2-methylpropene, 1,5-hexadiene, and 2-methyl-1,5-hexadiene were identified by GC and/or GC/MS (Tab. 1). The  $^{13}\text{C}$  NMR spectrum of the non-volatile residue shows only signals from the starting material and unsubstituted and methyl-substituted vinyl end groups. No loss of unsaturation was observed.

Scheme 5:



Depolymerization of Kraton™ (polybutadiene/polystyrene diblock copolymer) yields two polymeric fractions (Tab. 1) as depicted in Scheme 6.

Scheme 6:



The high-molecular-weight peak ( $\bar{M}_w = 15\,400$ ), shown in Fig. 3, is the polystyrene block which, within experimental error, agrees well with the molecular weight of polystyrene blocks reported for the starting material ( $\bar{M}_w = 14\,600$ ). The  $^1\text{H}$  NMR of the product (purified by precipitation in pentane) shows the ratio styrene/butadiene units to be approximately 35:1. The low-molecular-weight fraction consists of polybutadiene oligomers.

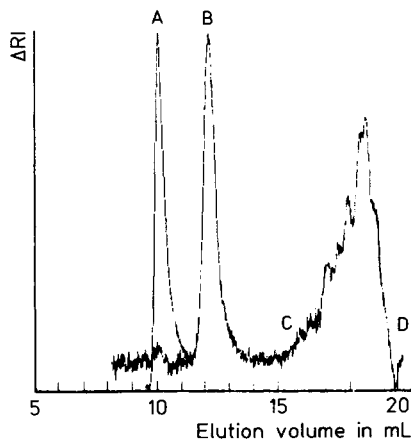
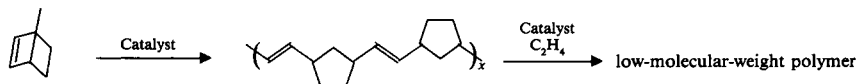


Fig. 3. Gel-permeation chromatography (GPC) trace of starting material and residue from the depolymerization of Kraton™. Peak A: starting material ( $\bar{M}_w = 86\,000$  17% PS); peak B:  $\bar{M}_w = 15\,400$ ,  $\bar{M}_w/\bar{M}_n = 1,01$ ; peak C:  $\bar{M}_w = 1\,000$ ; peak D:  $\bar{M}_w = 80$  (molecular weights relative to polystyrene standards)

Polynorbornene has also been subjected to the depolymerization process as shown in Scheme 7.

Scheme 7:



A significant decrease in the polymer's molecular weight is observed (Tab. 1). The structure of the polymeric product is the same as the starting material according to NMR spectroscopy. We have not yet been able to show with GC/MS the presence of the expected monomer, 1,3-divinylcyclopentane.

Without question, acyclic diene metathesis polymerization (ADMET) is a true equilibrium process. Products at any extent of conversion can be isolated and subjected to further polymerization, or depolymerization, by shifting the concentration of the condensed olefin. This process is further applicable to a variety of unsaturated polymers, and this result constitutes a meaningful opportunity to generate useful chemicals from waste polymers. The synthesis of vinyl functionalized prepolymeric products and pure dienes represent but two examples of numerous possibilities resulting from ADMET depolymerization, which may offer a unique incentive to recycling. Further research will concentrate on quantitation of the depolymerization reaction and the tolerance of this catalyst toward impurities and functionalities, as well as investigations involving new catalyst systems.

We thank the *National Science Foundation* (DMR-8912026) for their support of this work. We also thank Dr. *J. G. Nel* for his pioneering efforts in this area, the *SHELL Development Company* for providing the Kraton<sup>TM</sup> sample, Dr. *J. M. Boncella* and Dr. *A. S. Gamble* for catalyst synthesis, the *University Research Initiative Program* (Grant #NOOO14-86-G-0224) as conducted by *DARPA* and the *Naval Research Office*.

- 1) K. B. Wagener, J. M. Boncella, J. G. Nel, R. P. Duttweiler, M. A. Hillmeyer, *Makromol. Chem.* **191**, 365–374 (1990)
- 2) For polymers containing silane, ester, ether, and aromatic functionalities prepared by ADMET, see Wagener et al., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **32**(1) (1991) (in press); K. B. Wagener, J. G. Nel, R. P. Duttweiler, M. A. Hillmeyer, J. M. Boncella, J. Konzelman, D. W. Smith Jr., R. Puts, L. Willoughby, *Rubber Chemistry and Technology*, **64**(1), 83 (1991)
- 3) K. B. Wagener, J. G. Nel, J. Konzelman, J. M. Boncella, *Macromolecules* **23**, 5155 (1990)
- 4) K. J. Ivin, "Olefin Metathesis", Academic press, New York 1982
- 5) M. Lindmark-Hamberg, K. B. Wagener, *Macromolecules* **20**, 2949 (1987)
- 6) R. R. Schrock et al., *Organometallics* **9**, 2262–2275 (1990); R. R. Schrock, J. Feldman, L. F. Cannizzo, *Macromolecules* **20**, 1169 (1987)
- 7) L. Michailov, H. J. Harwood, in "Polymer Characterization: Interdisciplinary Approaches", ed. by C. D. Craver, Plenum press, New York 1971, p. 221
- 8) K. Hummel, G. Raithofer, *Angew. Makromol. Chem.* **50**, 183 (1976)
- 9) CA 1 095 646 (1981), Goodyear Tire & Rubber Co., inv.: N. Calderon; *Chem. Abstr.* **95**: 8034w
- 10) A. Alimuniar, M. A. Yarmo, M. Z. Ab. Rahman, S. Kohjija, Y. Ikeda, S. Yamashita, *Polym. Bull. (Berlin)* **23**, 119–126 (1990)
- 11) J. Konzelman, K. B. Wagener, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **31**(1) (1991), in press