Macromolecules **2001,** *34,* 7929−7931

Highly Efficient Acyclic Diene Metathesis Depolymerization Using a Ruthenium Catalyst Containing a N-Heterocyclic Carbene Ligand

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Received July 9, 2001
Revised Manuscript Received September 18, 2001

A recent series of reports have compared the metathetical activity of the alkoxy−imido molybdenum complex (**1**)[1] and $RuCl_2(=CHPh)(PCy_3)_2$ (**3**)[2] with newly developed ruthenium complexes bearing N-heterocyclic carbene ligands such as **4**[3,4] (see Figure 1). While **3** has demonstrated greater functional group tolerance than **1**, the latter is generally of greater activity. Complex **4** is more active than complex **3** in ring-closing metathesis (RCM),[4c,d,5] cross-metathesis (CM),[5,6] and ring-opening metathesis polymerization (ROMP),[7] while maintaining the latter's functional group tolerance. In the case of sterically hindered or electronically deactivated substrates, which are frequently inert to **3**, the activity of **4** has often met or surpassed that of **1**.[5,7a] Herein we report that the activity of **4** in acyclic diene metathesis (ADMET) depolymerization is greater than that of both **1** and **3** for polybutadiene. Moreover, that unlike **1** and **3**, **4** is capable of the depolymerization of the sterically hindered unsaturations of polyisoprene at mild temperature and pressure. The ability of **4** to depolymerize samples of cross-linked polyisoprene, of importance for the analysis and recycling of these materials, is also demonstrated.

The metathetical degradation of unsaturated polymers has been investigated for over 30 years.[8] Initially, these efforts applied CM with small symmetric olefins to the investigation of linear polymer microstructure. For example, the distribution of 1,2 and 1,4 repeat units in polybutadiene was correlated to the quantities of cyclic olefins produced by CM of this polymer with 3-hexene and subsequent RCM between adjacent repeat units.[9] While these methods were somewhat successful, the cost of symmetric olefins has limited their widespread application. Subsequent efforts have focused on the utility of reverse ADMET reactions, that is, cross-metathesis with ethylene, to the study of polymer degradation.[10] This promises two important advantages over CM with symmetric olefins: the much lower cost of ethylene and the synthetic utility of the α,ω-diolefin products. Wagener and co-workers investigated the ADMET depolymerization of elastomers using the tungsten catalyst **2**. While 3−5 atm of ethylene at room temperature was found to be sufficient to reduce the molecular weight of polymers containing disubstituted unsaturations, such as polybutadiene and polynorbornene, by 2 orders of magnitude in 48 h, a similar depolymerization of the trisubstituted unsaturations in polyisoprene was possible only at 50 °C and greater than 5 atm of ethylene pressure.[10f] A subsequent study employed the more robust and functional group tolerant ruthenium alkylidene catalyst **3**.[10e] Where the depolymerization of 1,4-polybutadiene with **2** had required an unsaturation-to-catalyst ratio of 20:1 in order to synthesize even trace amounts of 1,5-hexadiene, **3** achieved between 40% and 80% conversion at a ratio of 400:1.

In this study, the rate of reverse ADMET depolymerization of styrene−butadiene and styrene−isoprene ABA triblock copolymers with complexes **1**, **3**, and **4** was measured. Following depolymerization at 4 psig of ethylene at 20 °C, the styrene-containing fragments were isolated, and the number of remaining attached butadiene or isoprene repeat units was determined by ^{1}H NMR using the metathesis-inert styrene block as an internal standard.[11] Due to the known propensity of depolymerization reactions to form large numbers of macrocyclic products during the initial reaction period,[10a−c,12] this method is expected to give a more precise estimate of depolymerization progress than gel permeation chromatography against linear molecular weight standards or gas/liquid chromatography of small molecule products.

Interestingly, although the overall rate of **4** in many metathesis reactions in known to be much greater than that of **3**, comparison of their polybutadiene depolymerization rates in Table 1 shows that cleavage of polybutadiene with **3** initially progressed more rapidly than with **4**. This is in keeping with recent measurements of the initiation rates of these complexes which reveal that **3** initiates CM with vinyl ethyl ether significantly faster than **4**: $k_{\mathrm{init}} = 1.0 \times 10^{-3}$ and 4.6×10^{-4} s^{-1}, respectively. The methylidene analogues of **3** and **4**, produced by reaction of these complexes with ethylene, which are the principal active catalytic species in the reverse ADMET reaction, show a similar trend.[13]

In Table 1 it can also be seen that both the degree of depolymerization at the end of the reaction and the reaction rate varied greatly from one complex to another. Complex **1** reduced the molecular weight of the polybutadiene block by an order of magnitude over a 72 h period. This is consistent with the aforementioned high-pressure depolymerization of polybutadiene with the tungsten complex **2**.[10f] While an earlier report of the depolymerization of polybutadiene with complex **3** was allowed to react for 48 h, our data show that this reaction is complete in only 2 h.[10e] This short reaction time may be related to the rapid decomposition of the methylidene derivative of **3**. This species is known to have a half-life of only 40 min at 55 °C in benzene, whereas the more stable methylidene analogue of **4** was still detectable in a ring-closing metathesis reaction after 4 h at 55 °C.[14] Indeed, the stability of the methylidene derivative of **4** may account for the essentially complete degradation of the polybutadiene block by **4**.

As expected, degradation of the trisubstituted unsaturations of polyisoprene with **4** progressed more slowly, and to a lesser degree, than that of the disubstituted unsaturations of polybutadiene. Following an initial induction period, the number of repeat units attached to polystyrene was found to follow a pseudo-first-order

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10.1021/ma011188p CCC: $20.00

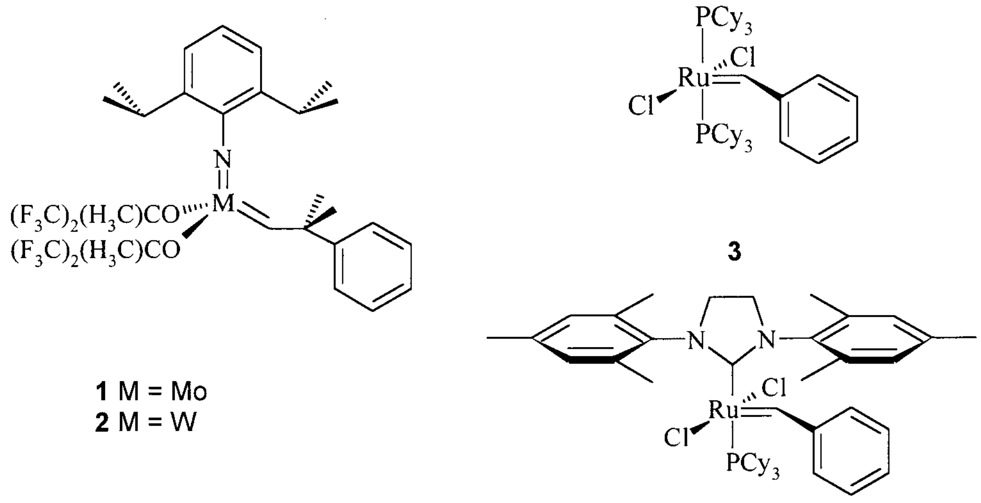

Figure 1. Catalysts used in this study.

Table 1. Average Number of Polyisoprene and Polybutadiene Repeat Units Attached to Polystyrene

	catalyst polymer			
rxn time (h)	**4**/SIS[a] repeat units polyisoprene	**4**/SBS[b] repeat units polybutadiene	**3**/SBS repeat units polybutadiene	**1**/SBS repeat units polybutadiene
0	1000	550	550	550
1	136	29	9	391
2	133	5	7	359
3	116	3	14	297
4	93	2	9	223
6	74	1	8	196
8	62	*c*	8	169
20	20	1	8	118
48	20			93
72				63
96				64

[a] SIS = styrene−isoprene ABA block copolymer. [b] SBS = styrene−butadiene ABA block copolymer. [c] Not determined.

rate in agreement with the theoretical model developed by Hummel.[15] These initial deviations have been ascribed to the high reactivity of macrocyclic species formed by backbiting reactions competing with the polymeric substrate.

No direct correlation of ethylene pressure to polymer degradation progress was observed for a similar set of experiments run at elevated pressures. This is consistent with results for the depolymerization of polybutadiene with **3**, which suggest that as ethylene pressure was increased, the rate of nonproductive CM with ethylene increased in competition with depolymerization.[10e]

Investigation of the oligomeric polybutadiene byproducts of reactions with complexes **3** and **4** by GC-MS determined that the majority of the material was tetrameric or smaller. No evidence of fragments larger than a hexamer was found. This is in agreement with the relative integration of terminal and internal unsaturations in the ^{1}H NMR spectra of this material. Analysis of the oligomeric polyisoprene residue found a similar number of repeat units per fragment. Such controlled ADMET depolymerization of polybutadienes with difunctional olefins has shown promise as a route to telechelic oligomers,[16] a method analogous to the use of difunctional chain transfer agents in ROMP.[7a,17] The activity of **4** in the depolymerization of trisubstituted unsaturations therefore suggests a convenient metathetical route to telechelic polyisoprenes.

The utility of metathesis for the analysis of cross-linking structure and additive distribution in cross-linked polymers such as polybutadiene and its copolymers has been investigated by a number of groups.[8b,15,18] However, these methods have not been applicable to cross-linked polyisoprene due to the low reactivity of its trisubstituted double bonds. In addition, methods for the recycling of these materials require extremes of pressure and temperature: 25 MPa and 200 °C.[19] We now report that at only 4 psig of ethylene **4** can depolymerize cross-linked polyisoprene to form soluble oligomeric products in as few as 4 h at room temperature. These depolymerizations were performed heterogeneously on samples of sulfur cross-linked *cis*-1,4-polyisoprene swollen in a toluene solution of **4**. Assuming a linear product, comparison of the end group and internal double bond integrations indicated a M_n of 720 g/mol or approximately 10 repeat units. This is consistent with the average number of repeat units still attached to polystyrene in the linear block copolymer experiments. However, calculation of the molecular weight by GPC against linear polystyrene standards indicated that the M_n of the product was 1800 g/mol. Since linear calibration standards are expected to underestimate the molecular weight of branched polymers, it may therefore be concluded that the true molecular weight is even higher and that there are a number of intact cross-links per molecule. A measure of cross-linking density in the original material may thus be derived from the ratio of molecular weights calculated by these two complementary methods, providing a convenient method for the investigation of cross-linking density.

In conclusion, the 1,3-dimesitylimidazolidine-2-ylidene ruthenium alkylidene complex **4** demonstrates more efficient ADMET depolymerization of polybutadiene than the well-known metathesis catalysts $RuCl_2(=CHPh)(PCy_3)_2$ (**3**) and the alkoxy−imido molybdenum alkylidene (**1**). Unlike both **1** and **3**, complex **4** is capable of the rapid depolymerization of the trisubstituted unsaturations in linear and cross-linked polyisoprene under very mild conditions. Potential applications of this chemistry include the synthesis of telechelic polyisoprenes and the analysis of cross-linked materials. Its functional group tolerance and mild conditions hold promise for the application of ADMET depolymerization to the recycling of real world materials.

Acknowledgment. Financial support was provided by the University of Massachusetts, Amherst, and the NSF sponsored Materials Research Science and Engineering Center (MRSEC) at UMass.

Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; Dimare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886. (b) Bazan, G. C.; Oskam, J. H.; Cho, H. N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899−6907. (c) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378−8387.

(2) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (c) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001−4003.

(3) While it is common practice to refer to the saturated N-heterocyclic carbene ligand of complex **4** as 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (for example, in refs 4b,c and 5), it is actually correctly termed either 1,3-dimesityl-2,3,4,5-tetrahydro-1*H*-imidazol-2-ylidene or 1,3-dimesitylimidazolidine-2-ylidene. An analogous problem exists for the monounsaturated N-heterocyclic carbene ligands in ref 4a. For a discussion of the nomenclature of these species, see: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162−2187.

(4) (a) Huang, J. K.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674−2678. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247−2250. (c) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956. (d) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787−4790.

(5) Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783−3784.

(6) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751−1753.

(7) (a) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906. (b) Frenzel, U.; Weskamp, T.; Kohl, F. J.; Schattenman, W. C.; Nuyken, O.; Herrmann, W. A. *J. Organomet. Chem.* **1999**, *586*, 263−265.

(8) For reviews of metathesis depolymerization, see: (a) Ivin, K.; Mol, J. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997. (b) Hummel, K. In *Olefin Metathesis and Polymerization Catalysts: Synthesis, Mechanism and Utilization*; Imamoflu, Y., Zümreoglu-Karan, B., Amass, A. J., Eds.; Kluwer Academic Publishers: Boston, 1990; Vol. 326, pp 209−232.

(9) (a) Abendroth, H.; Canji, E. *Makromol. Chem.* **1975**, *176*, 775−779. (b) Thorn-Csanyi, E.; Perner, H. *Makromol. Chem.* **1979**, *180*, 919−928.

(10) (a) Thorn-Csanyi, E.; Ruhland, K. *Macromol. Chem. Phys.* **1999**, *200*, 2606−2611. (b) Thorn-Csanyi, E.; Ruhland, K. *Macromol. Chem. Phys.* **1999**, *200*, 2245−2249. (c) Thorn-Csanyi, E.; Ruhland, K. *Macromol. Chem. Phys.* **1999**, *200*, 1662−1671. (d) Viswanathan, T.; Gomez, F. J.; Wagener, K. B. *J. Polym. Sci., Polym. Chem.* **1994**, *32*, 2469−2477. (e) Watson, M. D.; Wagener, K. B. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 1857−1861. (f) Wagener, K. B.; Puts, R. D.; Smith Jr., D. W. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 419−425.

(11) Experimental details and analysis are included in the Supporting Information.

(12) Hummel, K.; Stelzer, F.; Heiling, P.; Wedam, O. A.; Griesser, H. *J. Mol. Catal.* **1980**, *8*, 253−262.

(13) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.

(14) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202−7207.

(15) Hummel, K. *Pure Appl. Chem.* **1982**, *54*, 351−364.

(16) (a) Viswanathan, T.; Gomez, F.; Wagener, K. B. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2469−2477. (b) Marmo, J. C.; Wagener, K. B. *Macromolecules* **1995**, *28*, 2602−2606.

(17) (a) Bielawski, C. W.; Scherman, O. A.; Grubbs, R. H. *Polymer* **2001**, *42*, 4939−4945. (b) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718−721.

(18) (a) Ast, W.; Hummel, K. *Naturwissenschaften* **1970**, *57*, 545−557. (b) Griesser, H.; Hummel, K. *Colloid Polym. Sci.* **1980**, *258*, 467−468.

(19) Morin, J. E.; Farris, R. J. *Polym. Mater. Sci. Eng. Prepr.* **2001**, *84*, 1063−1064.

MA011188P