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Acyclic Metathesis Polymerization. The Olefin Metathesis Reaction of 1,5-Hexadiene and 1,9-Decadiene

Since the appearance of Natta and Dall'Asta's report of the polymerization of cyclopentene with a catalyst/cocatalyst metal pair,[1] countless publications have probed the subject of olefin metathesis over the past 20 years.[2] Elegant mechanistic studies have shown that metallocarbenes are the reactive intermediates responsible for this disproportionation reaction,[3] that the reaction is general, and that the reaction has commercial value for the polymerization of strained cyclolefins.[4] These ring opening polymerizations, which are depicted in Figure 1, are thought to be driven by a release of ring strain,[5] and indeed high molecular weight polymers are formed very rapidly by this technique. The polymerization of cyclopentene,[6] norbornene,[7] and cyclooctene[8] have received the most attention during this 20-year period, and the metathesis polymerization of strained rings remains an active field.[9]

In this present paper, we report our efforts to employ olefin metathesis in a step polymerization, condensation-type reaction scheme, as shown in Figure 2, wherein an equilibrium is established such that a volatile compound can be removed to drive the polymerization.[10] Such a reaction would provide a significant opportunity to create a wide variety of new polymer structures, if indeed the metathesis reaction can be precisely controlled. The identity of substituent "R_1" in Figure 2 would be restricted only by factors that govern intramolecular vs. intermolecular metathesis chemistry, since the intent is for intermolecular reactions to predominate. Though the suggestion of doing polycondensation metathesis chemistry is not new,[11] virtually no results have been reported to determine the viability of the approach.

Our first reactions have been done with 1,9-decadiene and 1,5-hexadiene (structures 1 and 2 in Figure 2). These monomers were chosen since their self-metathesis would release an easily identifiable gas (ethylene, R_2 = H) and would yield well-characterized polymers (polyoctenamer and polybutadiene, respectively). Thus, the polymerization technique and not the polymers themselves become the principal object of the study. The 1,5-hexadiene polymerization appeared particularly challenging, since it has been stated that self metathesis does not occur at all for this monomer.[12]

All reactions were carried out under an argon atmosphere, either in bulk or with chlorobenzene as a solvent, and we chose the $WCl_6/EtAlCl_2$ catalyst system (monomer/tungsten 100:1 and tungsten/aluminum 1:4) for our initial experiments. Tungsten hexachloride was stored under argon, and $EtAlCl_2$ was used as received (1 M solution in hexane). In a representative polymerization the monomer and WCl_6 were combined and cooled to −78 °C, followed by the addition of the cocatalyst. The homogeneous reaction mixture was then permitted to warm to 25 °C, and after 30 min the reaction was terminated with a few drops of methanol. In some cases a slight vacuum was applied to the reaction system to remove the gases formed. Gas samples were collected during the reaction and analyzed by gas chromatography.[13]

In the 1,9-decadiene reaction, a large volume of gas was released instantly when the cocatalyst was added to the reaction flask, and GC analysis showed the major com-

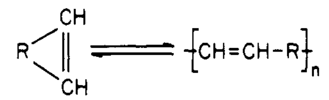

Figure 1. Ring-opening polymerization of strained cycloolefins.

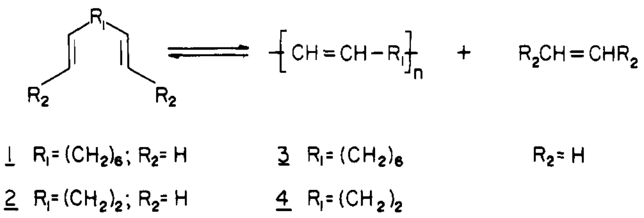

Figure 2. Step propagation, condensation type polymerization of acyclic dienes.

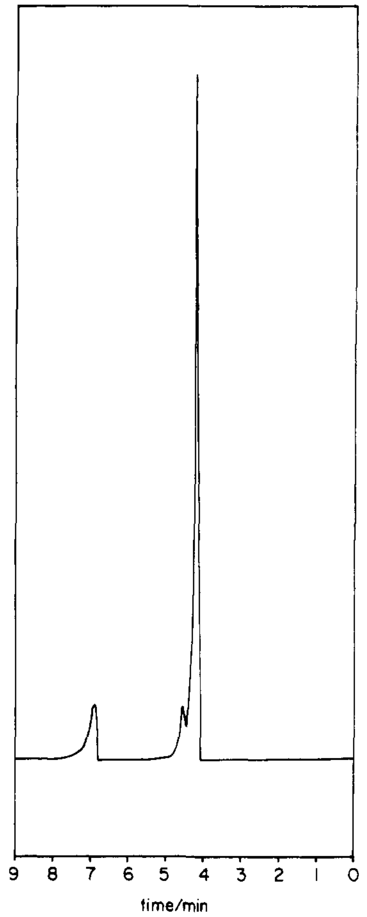

Figure 3. GC chromatogram of the gases released during the 1,9-decadiene reaction. The large peak at 4 min is identified as ethylene by comparison with an authentic sample. Identical results were observed for 1,5-hexadiene.

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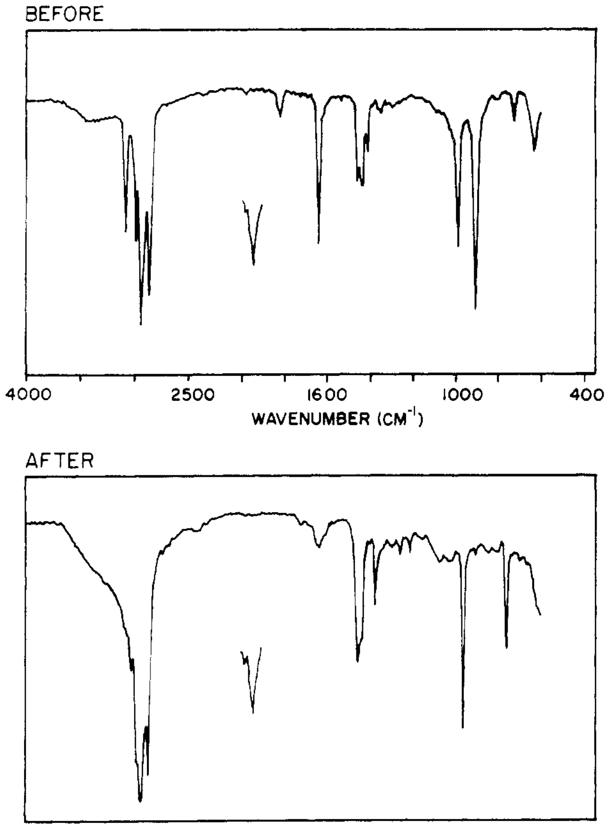

Figure 4. IR spectra before and after the polymerization of 1,9-decadiene. The characteristic olefin stretch at 1640 cm^{-1} is absent in the product of the reaction.

ponent to be ethylene (Figure 3). The reaction was extremely fast, in spite of the fact that terminal olefins experience degenerate metathesis 10 to 100 times more often than productive metathesis.[14] Both a soluble, highly viscous oil and an intractable solid resulted. A comparison of the IR spectra (Figure 4) of the monomer and the oil shows the virtual disappearance of the monomer's terminal olefin absorption at 1640 cm^{-1}. Carbon-13 spectral comparisons (Figure 5) show the loss of the monomer's terminal carbon resonance at 114 ppm with the appearance of a complex multiplet at 130 ppm for the internal olefin carbons. These observations strongly suggest that acyclic olefin metathesis is the predominant reaction, though apparently not the only one, since a detectable amount of two other gases is released and since roughly 30% of the reaction product is insoluble.

The oil was further purified by dissolution in hexane and precipitation in THF. The proton NMR spectrum (resonances at 5.4, 2.0 and 1.3 ppm) and the IR spectra of the product are as expected for polyoctenamer;[15] however, the number-average molecular weight of the soluble fraction as determined by vapor pressure osmometry is low, less than 5000.[16]

1,5-Hexadiene behaves somewhat differently under these reaction conditions. At first the reaction is very slow; however, when a slight vacuum is applied a gas is evolved instantly (mostly ethylene, as before), resulting in a soluble, highly viscous oil and an insoluble fraction. As in the case for 1,9-decadiene, spectral comparisons of the monomer and the product show the loss of the terminal olefin groups of the monomer with the retention of internal olefin bond character in the product. Purification of the product was done as for polyoctenamer, and the product's spectral features are identical with those of polybutadiene,[17] though the molecular weight of the soluble fraction is low (less than 5000).

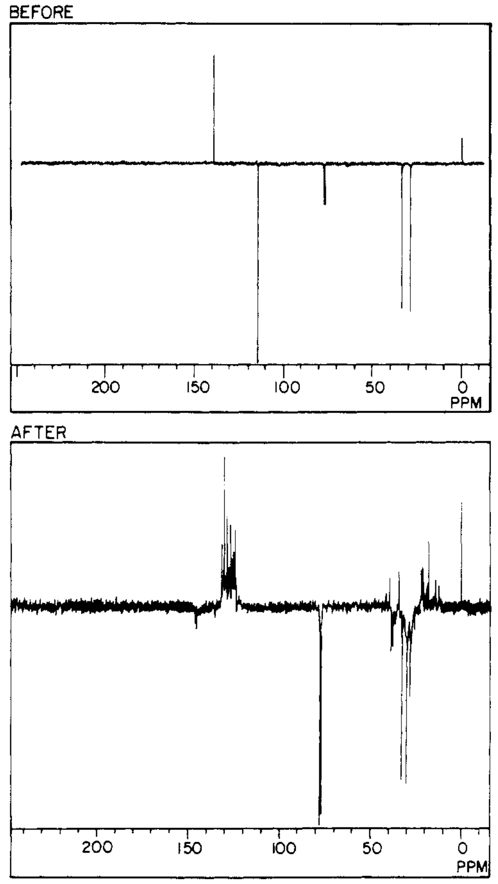

Figure 5. ^{13}C NMR spectra before and after the polymerization of 1,9-decadiene. The terminal carbon signal at 114 ppm is missing in the product of the reaction.

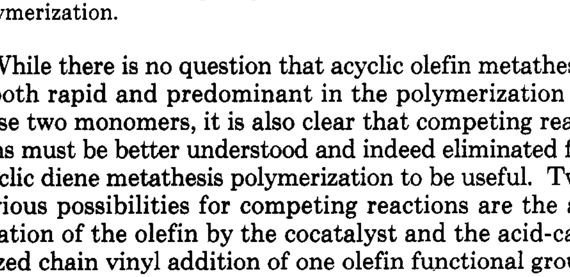

Figure 6. Potential competing side reactions in acyclic metathesis polymerization.

While there is no question that acyclic olefin metathesis is both rapid and predominant in the polymerization of these two monomers, it is also clear that competing reactions must be better understood and indeed eliminated for acyclic diene metathesis polymerization to be useful. Two obvious possibilities for competing reactions are the alkylation of the olefin by the cocatalyst and the acid-catalyzed chain vinyl addition of one olefin functional group to another, as shown in Figure 6. A third and less likely possibility would be a Ziegler–Natta polymerization of olefin functional groups leading to insoluble polymer. Of the two former possibilities, the vinyl addition reaction is probably more important. For example, the intractable fraction found in the above polymerizations could be the result of vinyl addition.[18] In order to examine these competing reactions, we performed model studies with styrene (Figure 7), which would yield either stilbene if metathesis predominates or polystyrene if vinyl addition predominates. In fact, polystyrene is the only product of the reaction, and no ethylene is evolved at all. Most likely we are observing a cationic polymerization initiated by EtAlCl$_2$. Polystyrene is found when tetramethyltin is used

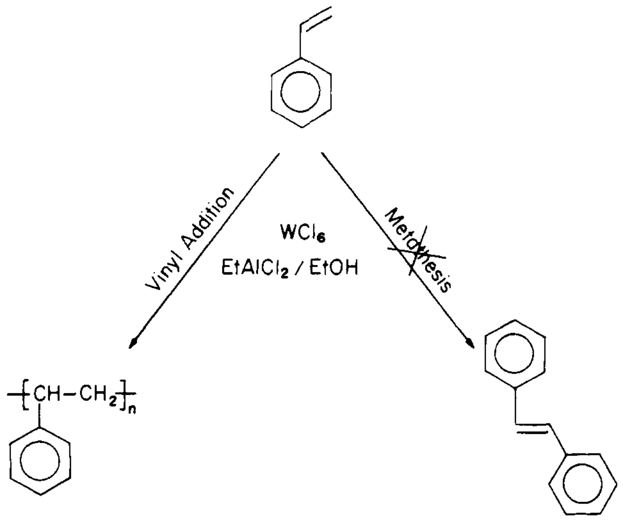

Figure 7. Styrene model compound reactions.

as a cocatalyst and even when tungsten hexachloride is used with no cocatalyst at all. Vinyl addition reactions are important "side" reactions, which indeed become the only reaction when the monomer favors cationic polymerization.

Obviously catalyst selection is important, and our research has turned to the synthesis of metathesis catalysts based on molybdenum and tungsten wherein no Lewis acid cocatalyst are present.[19] Our work on acyclic diene metathesis polymerization will continue since we feel the potential for this polymerization scheme is significant.

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Registry No. 1 (homopolymer), 108793-14-2; 2 (homopolymer), 25067-96-3; 3, 28702-45-6; 4, 25038-44-2; WCl_6, 13283-01-7; $EtAlCl_2$, 563-43-9; $C_6H_5CH{=}CH_2$, 100-42-5.

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(3) Olefin metathesis remains a subject of active mechanistic research. See: Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318.
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(10) Step polymerization, condensation type reactions are viable only for reactions that essentially can be driven to quantitative completion. This factor, of course, is the key element in this research.
(11) See: Doyle, G. *J. Catal.* **1973**, *30*, 118. Dall'Asta, G.; Stigliani, G.; Greco, A.; Matta, L. *Chim. Ind.* **1973**, *55*, 142. Korshak, Y. V.; Tienkpoatchev, M. A.; Dologoplosk, B. A.; Avdeikina, E. G.; Kutepov, D. F. *J. Mol. Catal.* **1982**, *15*, 207.
(12) See Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983; p 143. Self-metathesis was thought not to be possible "...presumably because the degenerate reaction is strongly favored". The author does note that cross metathesis of 1,5-hexadiene and cycloocta-1,5-diene has been observed (Pinazzi, C. P.; Campistron, I.; Reyx, D. *Revl. Trav. Chim. Pays-Bas* **1977**, *96*, M59). Other 1,5-hexadiene cross-metathesis reactions have been reported as well.
(13) The gas chromatograph used was an Aerograph Model 600-D, equipped with a 30-ft × $^1/_8$-in. column packed with 20% SE-30 on chromosorb P. The infrared spectrometer was a Perkin-Elmer Model 281. NMR spectra were obtained on a Nicolet NT-300 spectrometer operating at a field of 7 T.
(14) Degenerate metathesis of terminal olefins exchanges carbons and simply recreates the reactant, whereas productive metathesis produces a coupled product plus—in this case—ethylene. See: Tanaka, K.; Tanaka, K.; Miyahara, K. *J. Chem. Soc., Chem. Commun.* **1979**, 314.
(15) Polyoctenamer NMR and other data can be found in: Sato, H.; Okimoto, K.; Tanaka, Y. *J. Macromol. Sci.—Chem.* **1977**, *A11*, 767.
(16) To a certain extent this low number is not unexpected, since we used 98% pure 1,9-decadiene in these experiments. Assuming a stoichiometric imbalance ratio of 0.98 and 99% metathesis of the monomer in this step polymerization, calculations predict a number-average degree of polymerization of only 50, or a number-average molecular weight of 5500. Also, the monomer/catalyst ratio is also rather low in this work.
(17) Comparisons were made with the spectra of an authentic sample of polybutadiene obtained from Aldrich.
(18) In fact, if the polymerization is not terminated with methanol, the oil becomes insoluble in hexane after standing over a period of weeks, suggesting that slow vinyl addition reactions are continuing.
(19) At least one homogeneous metathesis catalyst free of Lewis Acids has been made. See: Schaverian, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

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Photochromic and Fluorescent Probe Studies in Glassy Polymer Matrices. 2. Isomerizable Planar Probe Molecules Lacking an Inversion Center of Symmetry

The extent of conversion of certain photochromic molecules which undergo trans–cis photoisomerization has been shown to be nearly always less in a rigid matrix such as a polymer glass (without significant sub-T_g relaxation taking place) than in nonviscous solutions.[1-5] This is consistent with the presence of two molecular environments in the rigid matrix: one which allows trans–cis isomerizations at rates comparable with those in solution, and another which blocks the isomerization. The blocking environment has been hypothesized to arise from insufficient local free volume to allow the isomerization at a molecular level.[2-5] In paper 1 of this series,[2] minimum local free volumes required by various trans–cis photochromic molecules to isomerize were calculated[2] based on van der Waals molecular volumes and known isomerization pathways. It was found that as the local free volume required for photoisomerization increases, the extent of isomerization at photoequilibrium achieved in polystyrene glass, divided by that achieved in toluene, decreases. This correlation amounts to a quantitative measurement of the distribution of local free volume in the polystyrene glass,[2] slightly increased by the local free volume added by the presence of small probe molecules.

In contrast with our previous findings for unattached photoisomerizable probe molecules,[2] and those of Sung et al.[4] for polymers having covalently attached azobenzene labels, Priest and Sifain[1] found that 4-ethoxyazobenzene had the same extent of isomerization at photoequilibrium

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