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Polymerization of Dicyclopentadiene: A Tale of Two Mechanisms

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Introduction

The homopolymerization of dicyclopentadiene (DCPD) has been studied using various metathesis catalyst systems which are typically composed of a transition metal halide and a non-transition metal cocatalyst.[1−6] The structure of the resulting polymer depends upon the identity of both catalyst components, ranging from a highly cross-linked, insoluble polymer to one that is linear and completely soluble. The formation of poly(dicyclopentadiene) (poly-DCPD) is thought to occur as illustrated in Figure 1, through the ring-opening metathesis polymerization (ROMP) of the strained norbornene ring. The olefin present in the cyclopentene ring is also assumed to undergo a ROMP reaction leading to cross-linked polymer.[7−9] This reasonable assumption has been accepted for more than 25 years, primarily due to the difficulty associated with characterizing cross-linked polymers. However, our work shows that a second mechanism—olefin addition—contributes to cross-linking. Thus, two polymerization mechanisms are operating simultaneously to form poly-DCPD.

We have synthesized soluble linear "model" polymers to gain a better understanding of the mechanisms responsible for the formation of poly-DCPD. We chose two "model" monomers (Figure 2) for these polymerizations: 8,9-dihydrodicyclopentadiene (**A**) and 5,6-dihydrodicyclopentadiene (**B**), since each monomer possesses only one of the olefins present in dicyclopentadiene. The polymerization behavior of these compounds was examined first with a classical $WCl_6/(C_2H_5)_2AlCl$ system, which is similar to catalyst systems used industrially[10] and is known to generate entirely cross-linked poly-DCPD samples.[2] The polymerization of these monomers was also studied with a well-defined metathesis catalyst, Schrock's molybdenum alkylidene, $Mo(CH\text{-}CMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$. Classical catalyst systems are capable of initiating both olefin addition and metathesis polymerization, while the well-defined Schrock catalyst exclusively promotes metathesis chemistry.[11]

Experimental Section

Tungsten hexachloride (Aldrich), diethylaluminum chloride (Aldrich; 1.8 M in toluene), and *endo*-8,9-dihydrodicyclopentadiene (**A**) (2,3,3a,4,7,7a-hexahydro-4,7-methano-*H*-indene; Wiley Organics) were used as received. Dicyclopentadiene (Aldrich; predominantly *endo*) was purified as described in the literature[10] prior to use. *endo*-5,6-Dihydrodicyclopentadiene (**B**) (3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-indene) was purchased from TCI America and sublimed prior to use. The molybdenum-based Schrock's catalyst, $Mo(CH\text{-}CMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$, was synthesized as described in the literature.[12] All polymerizations were carried out under an argon atmosphere at 25 °C for at least 8 h using toluene (distilled from NaK) as the solvent. Classical polymerizations of **A** were conducted by dissolving 10 mmol of monomer and 0.1 mmol of tungsten hexachloride in 1 mmol of toluene and then adding 0.4 mmol of diethylaluminum chloride via syringe. Monomer **B** was treated with the classical catalyst system in both the presence and absence of 1 μL of methanol. Solution polymerizations utilizing Schrock's catalyst employed 10 mmol of monomer and 0.01 mmol of catalyst dissolved in 100 mmol of toluene. Bulk polymerizations of dicyclopentadiene were conducted by adding 0.01 mmol of Schrock's catalyst to 10 mmol of dicyclopentadiene and 1 mmol of toluene (to solubilize catalyst). All soluble polymers were precipitated from methanol and dried under vacuum prior to characterization.

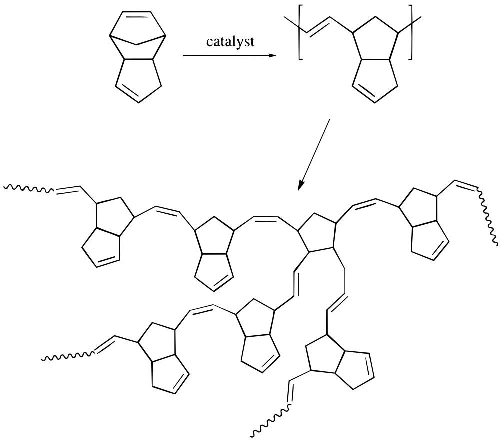

Figure 1. Currently accepted mechanism for the polymerization of dicyclopentadiene (DCPD).

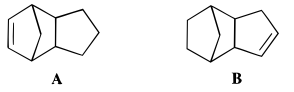

Figure 2. "Model" monomers 8,9-dihydrodicyclopentadiene (**A**) and 5,6-dihydrodicyclopentadiene (**B**) used in reactivity model study.

Results and Discussion

In our initial reactivity studies, treatment of 8,9-dihydrodicyclopentadiene (**A**) with the classical catalyst system (WCl_6/Et_2AlCl) gave ring-opening metathesis polymerization, consistent with the results of Oshika.[1] Polymerization was rapid and exothermic, with the reaction being complete in <1 min. For a pure ROMP polymerization of this monomer, the integration of the olefinic region of the ^{1}H NMR spectrum relative to the aliphatic region should be 2:12, respectively. ^{1}H NMR analysis of the resulting polymer showed a slight decrease in the intensity of the olefinic signals (2:20 olefinic:aliphatic), indicating that a small amount of olefin addition had taken place. However, the ring-opening metathesis of the strained bicyclic ring is the fundamental reaction which leads to the formation of polymer in this case. These results are as expected and support the assumption that ROMP of the strained bicyclic ring is the primary step in the polymerization of dicyclopentadiene.

The polymerization of 5,6-dihydrodicyclopentadiene (**B**) was studied using both the WCl_6/Et_2AlCl catalyst system and Schrock's molybdenum catalyst. Monomer **B** in the presence of the WCl_6/Et_2AlCl system with trace amounts of methanol yielded oligomers **II** with M_n of ca. 3000 and M_w/M_n of 1.22 (determined by GPC vs polystyrene standards). These results differ from those of Ofstead and Calderon,[13] who studied the polymerization of several cyclic olefins with a $WCl_6/EtAlCl_2$ catalyst system and reported that **B** resisted attempts

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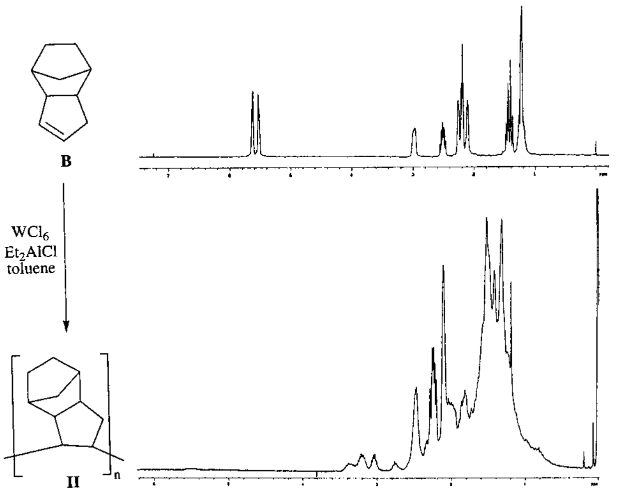

Figure 3. ^{1}H NMR spectra illustrating the polymerization of **B** in the presence of $WCl_6/(C_2H_5)_2AlCl$.

at polymerization. We previously attempted the polymerization of B in the absence of methanol and also saw no polymerization. However, providing a proton source by the addition of methanol allowed polymerization to occur.

NMR analysis (Figure 3) of oligomer **II** unequivocally defines the nature of this polymerization system. Olefinic signals are no longer present in the ^{1}H NMR spectra of oligomer **II**, which rules out ring-opening metathesis as a reaction pathway and indicates that oligomer **II** forms via an olefin addition reaction. This result is important, as it provides new insight into the mechanism of the cross-linking reaction that occurs in DCPD polymerization under classical conditions. These findings differ from the generally accepted speculation that DCPD cross-linking occurs through ROMP chemistry.

There is a substantial precedence for this type of olefin addition chemistry, for the addition and cationic polymerization of DCPD and its derivatives have been extensively studied.[14] Exposing *endo*- and *exo*-dicyclopentadiene to a Pd(II) catalyst has been shown to generate linear, non-cross-linked addition polymers with the unsaturation in the pendant ring remaining intact.[15] Linear oligomers of DCPD have also been synthesized by Cesca and co-workers,[16] who studied the polymerization of DCPD and its derivatives. Their results are consistent with the fact that oligomers are generated from **B**.

In order to further prove the point, model monomer **B** was exposed to Schrock's metathesis catalyst under identical reaction conditions to see if ROMP was feasible, since this catalyst system only initiates metathesis chemistry.[11] All attempts to polymerize **B** using Schrock's catalyst resulted in the recovery of only monomer. No ring-opening metathesis polymerization occurred, indicating that **B** is completely inert to metathesis polymerization under these conditions.

These results with **B** suggest that polymerization of DCPD initiated by Schrock's catalyst should form linear, soluble polymer through the ring-opening metathesis polymerization of the strained norbornene ring, and this is what we observe. The polymerization of DCPD was carried out in solution,[17] and after 24 h of stirring under argon, the polymer remained completely soluble. Polymer **III** (Figure 4) was precipitated in cold methanol and dried under vacuum prior to GPC and NMR analysis. GPC analysis of polymer **III** (in chloroform vs polystyrene standards) shows $M_n = 52\,000$ and $M_w/M_n = 2.2$.[18] NMR analysis of polymer **III** confirms that only the strained norbornene olefin undergoes metathesis during the polymerization, while the olefin in the pendant five-membered ring remains intact. This result is further supported by the fact that polymer **III** remained completely soluble during the polymerization and was readily soluble in chloroform. These observations of this system eliminate the possibility of cross-linking by metathesis through the less strained double bond.

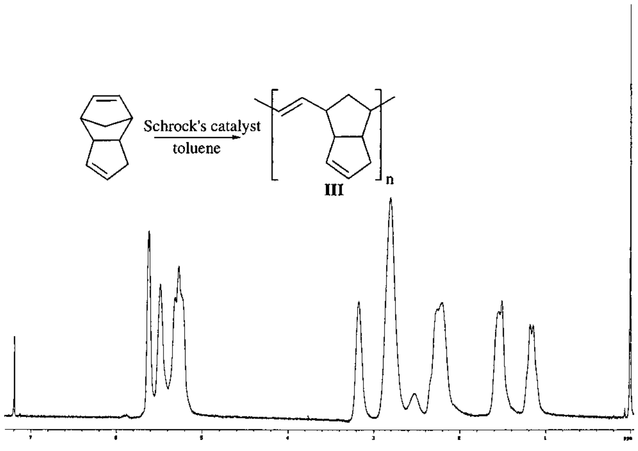

Figure 4. ^{1}H NMR spectrum of linear DCPD polymer made with Schrock's catalyst.[19]

As noted previously by Fisher and Grubbs,[9] high concentrations of DCPD produce insoluble material using Schrock's catalyst which, in keeping with the conventionally accepted cross-linking reaction, they attribute to an equilibrium metathesis reaction of the cyclopentene ring of DCPD. We have also observed the formation of insoluble polymer in the bulk polymerization of DCPD with Schrock's catalyst. However, since the pendant cyclopentene ring is inert to metathesis polymerization (see our model study of monomer **B**), we attribute the formation of insoluble polymer in bulk DCPD polymerizations with Schrock's catalyst to an addition reaction induced by the large amount of localized heat released during the highly exothermic ROMP of the strained norbornene olefin. When the polymerization is conducted in a less concentrated solution, heat is dissipated to the solvent. In this way, the higher activation energy olefin addition process is obviated, and cross-linking does not occur. In order to demonstrate that the cross-linking reaction can be thermally induced, we conducted a control experiment[20] in which 5,6-dihydrodicyclopentadiene (**B**) was heated in the absence of catalyst. ^{1}H NMR analysis of the products shows a dramatic decrease in the olefinic peak integration, while GC–MS analysis indicates the formation of dimers and trimers. These results lend evidence to support a thermally induced olefin addition reaction. We have also observed that most of the DCPD polymer made under bulk polymerization conditions can be solubilized when warmed in common organic solvents such as toluene, xylene, and trichlorobenzene. Thus, the polymer obtained is only lightly cross-linked, indicating a limited degree of olefin addition.

Conclusions

The olefin in the strained bicyclic ring of DCPD, isolated as 8,9-dihydrodicyclopentadiene, polymerizes through a metathesis mechanism in the presence of

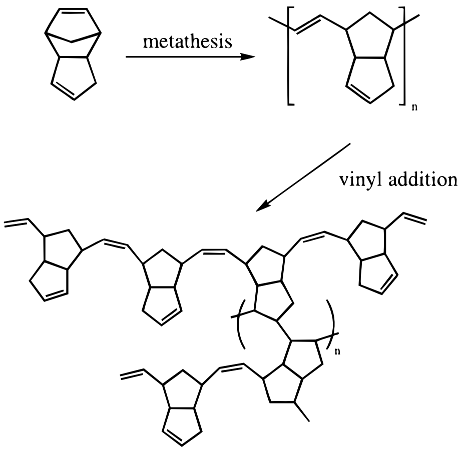

Figure 5. Polymerization of DCPD: a tale of two mechanisms.

either a classical catalyst system or Schrock's alkylidene. The olefin in the pendant five-membered ring, illustrated by 5,6-dihydrodicyclopentadiene, however, is inert to metathesis polymerization but undergoes olefin addition to form polymer. We conclude, on the basis of the use of classical and well-defined catalyst systems, that olefin addition contributes to the formation of cross-linked poly-DCPD (Figure 5).

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(17) Conditions of polymerization: 10:1 ratio of toluene to monomer, 1000:1 ratio of monomer to catalyst, 25 °C under argon for 24 h.
(18) Broad molecular weight distribution is due to transmetathesis reactions which occur during the prolonged reaction time.
(19) Integration of olefinic region to aliphatic region is 4:8, respectively.
(20) Reaction conditions: 5,6-dihydrodicyclopentadiene (1 g) and toluene (0.5 mL) sealed under argon and heated at 160 °C for 4 days.

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