The polymerization of dicyclopentadiene: an investigation of mechanism

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Abstract

This contribution presents further information about the mechanism of the cross-linking reaction which occurs during the polymerization of dicyclopentadiene with the classical catalyst, WCl_6/Et_2AlCl (**1**), and the well-defined preformed alkylidene, $Mo(N-2,6-C_6H_3-i-Pr)(CHC(CH_3)_2Ph)(OCCH_3(CF_3)_2)_2$ (**2**). When the classical system **1** was used as a catalyst, insoluble polymer was formed in all cases. However, when molybdenum catalyst **2** is employed, solution concentration determines whether soluble or insoluble polymer will form. The formation of insoluble material is attributed to an olefin addition process catalyzed by the heat released upon ring-opening metathesis polymerization of the norbornene subunit of the monomer. If the heat is removed from the polymerization system through dilution or by cooling the solution, soluble linear polymer is formed. These results suggest that an olefin addition process is at least partly responsible for the cross-linking reaction that occurs during the polymerization of dicyclopentadiene. All attempts to cross-link oligomers of linear polydicyclopentadiene with the well-defined molybdenum alkylidene **2** resulted in only the recovery of soluble polymer. With the classical catalyst system **1**, insoluble material was obtained, which was assumed to be cross-linked through olefin addition. These results disprove the idea that metathesis cross-linking can be induced by a critical chain length or concentration of polydicyclopentadiene. On the contrary, no indication of metathesis cross-linking was observed whatsoever for these polymerization systems. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past 50 years, the field of polymer science has given chemists an opportunity to expand their scientific creativity through a new world of compounds which has become accessible. It is now possible to tailor-make new substances and materials with specific structures and properties, utilizing well-defined systems to obtain the desired product. Understanding the mechanisms responsible for the formation of these materials is integral to expanding the knowledge base which allows advances in technology. Although many polymerization methods are well understood, there are still some processes which are more difficult to examine, especially in the case of cross-linked polymers.

This contribution seeks to provide insight into the polymerization of dicyclopentadiene, the only industrially important polymer made

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today via metathesis chemistry. For more than 25 years, the accepted mechanism for the formation of this cross-linked polymer has been one of exclusively ring-opening metathesis [1]. Polymerization of the strained norbornene ring is assumed to occur first, followed by the subsequent metathesis of the cyclopentene unit, as depicted in Fig. 1. This is a reasonable assumption, yet due to the difficulty associated with characterizing cross-linked polymers, it is nearly impossible to ascertain the mode of polymerization.

We chose to examine the polymerization of dicyclopentadiene with both a classical catalyst system (**1**) and a well-defined preformed alkylidene (**2**), as shown in Fig. 2. Classical, multicomponent systems are often used industrially for their reactivity and cost effectiveness. However, due to the presence of a Lewis acid cocatalyst in the system, side reactions often compete with metathesis polymerization. Conversely, well-defined, preformed alkylidenes are known for exclusively catalyzing metathesis chemistry without the competing side reactions associated with classical systems [2], since they do not require a Lewis acid cocatalyst to be metathesis active. The most commonly utilized complexes
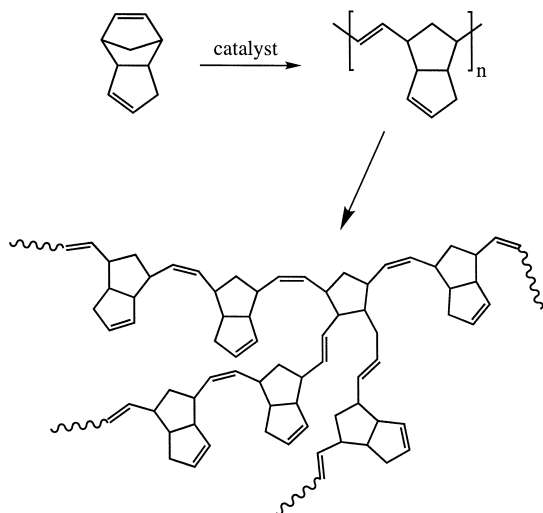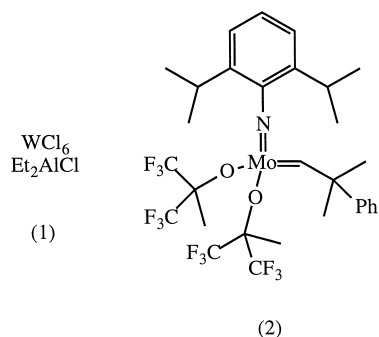

Fig. 2. Classical catalyst **1** and Schrock's molybdenum alkylidene **2**.

of this type include tungsten and molybdenum alkylidenes developed by Schrock et al. [3,4], Bazan et al. [5,6], Fox and Schrock [7], Feldman et al. [8] and Oskam and Schrock [9], and the ruthenium based alkylidenes of Nguyen et al. [10] and Schwab et al. [11,12].

The nature of the material formed during the polymerization of dicyclopentadiene, including double bond geometry and cross-link density, is ultimately determined by the catalyst systems which are utilized. Many catalyst systems have been studied for their reactivity in the polymerization of dicyclopentadiene, and it seems that the formation of a linear, soluble polymer is highly dependent upon the choice of transition metal halide, as well as on the Lewis acidity of the cocatalyst. In general, the more active the transition metal is towards metathesis, and the more Lewis acidic the cocatalyst, the more likely it is that the catalyst will form an insoluble polymer [13].

There have been a few studies in the past which seek to explain the mechanism responsible for the formation of cross-linked polydicyclopentadiene [14,15]. Although these investigations have presented some support for a metathesis cross-linking mechanism, there is no definitive way to determine how cross-links were formed in an insoluble polymer. In order to help provide some understanding of what occurs during the polymerization of dicyclopentadiene, we conducted a model study in which

Fig. 1. Currently accepted structure of cross-linked polydicyclopentadiene.

linear, soluble polymers were synthesized from compounds containing only one site of unsaturation. From these results, we have previously demonstrated that olefin addition process is a viable process contributing to the formation of insoluble, cross-linked polydicyclopentadiene [16]. This contribution addresses the information we have gained from studying the polymerization of dicyclopentadiene with the well-defined Schrock alkylidene, $Mo(N-2,6-C_6H_3-i-Pr)(CHC(CH_3)_2Ph)(OCCH_3(CF_3)_2)_2$ (**2**).

2. Experimental

2.1. Materials and techniques

A mixture of tungsten hexachloride (WCl_6, Aldrich, 99.9 + %) and diethylaluminum chloride (Et_2AlCl, Aldrich, 1.8 M in toluene) (**1**) was used as a classical metathesis catalyst system. The preformed metathesis alkylidene employed in this research was previously developed in the laboratories of Schrock and coworkers. The molybdenum version of Schrock's alkylidene, $Mo(CHR')(NAr)(OR)_2$ (**2**) where Ar $= 2,6(i-Pr)_2-C_6H_3$, R' $= C(CH_3)_2Ph$, and R $= CCH_3(CF_3)_2$, was synthesized according to published literature methods [4–9].

8,9-Dihydrodicyclopentadiene (**3**) was purchased from Wiley Organics (99%) and used as received. 5,6-Dihydrodicyclopentadiene (**4**) was purchased from TCI (95 + %) and sublimed prior to use. Dicyclopentadiene (**5**) was purchased from Aldrich (95% minimum, 90/10 *endolexo*) and further purified as described in the literature [17] prior to polymerization. Norbornene (Acros, 99%) was vacuum transferred to a Schlenk tube prior to use. 1,9-Decadiene (Aldrich, 98%) was dried over CaH_2, followed by vacuum transfer from a potassium mirror prior to use. All monomers were stored under argon in high vacuum storage flasks equipped with Teflon™ valves or in Teflon™ capped vials in the dry box.

2.2. General polymerization procedure

All monomer and catalyst manipulations were conducted either in an argon glove box or under standard Schlenk conditions. Toluene used in polymerizations was freshly distilled from NaK and stored under argon in a round bottom flask equipped with a high vacuum Teflon™ valve. Metathesis polymerizations were conducted in Teflon™ capped vials containing a magnetic stir bar in an argon dry box. All monomers (0.1–2.0 g) were added to the vials in the dry box where the appropriate amount of solvent (0–20 g) was added. Stirring was initiated, and catalyst (2–20 mg) was introduced. Polymerizations initiated by the classical catalyst system were quenched by exposure to air. Polymers formed from the Schrock alkylidene initiator were terminated by the addition of purified benzaldehyde [18]. Polymers were isolated by precipitation from toluene/methanol or chloroform/methanol prior to characterization.

3. Results and discussion

3.1. Model polymerization studies

Although a mechanism of purely metathesis is assumed for the formation of polydicyclopentadiene, some doubt remains due to the presence of ill-defined Lewis acid cocatalysts traditionally found in industrial polymerization systems. There is little question that metathesis polymerization occurs when highly strained monomers are exposed to these catalysts. However, Lewis acidic catalyst systems have been known to initiate cationic and addition processes, especially in the case of less strained rings [14].

Dicyclopentadiene can be classified as a monomer possessing two sites of functionality, each one capable of reacting during polymerization, leading to a cross-linked network polymer. We have previously described a model study
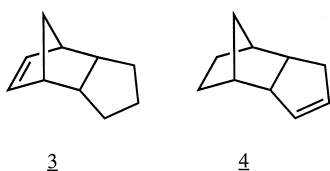
Fig. 3. **3** and **4** used in model study of olefin reactivity.

which isolated the reactive olefins present in dicyclopentadiene [16]. Two monofunctional compounds were chosen for this model study of olefin metathesis activity, as shown in Fig. 3. The first compound, 8,9-dihydrodicyclopentadiene (**3**) (tricyclo[5.2.1.0^{2,6}]dec-8-ene), was found to undergo ring-opening metathesis polymerization with each of the catalyst systems studied. The analogous compound, 5,6-dihydrodicyclopentadiene (**4**) (tricyclo[5.2.1.0^{2,6}]dec-3-ene), was found to be inert to metathesis polymerization, but instead underwent olefin addition with the classical catalyst system (**1**). Polymerization of 5,6-dihydrodicyclopentadiene in the presence of **2** has also been attempted at $-40°C$ and $100°C$, but in each case, no polymer or metathesis product was formed.

Several copolymerizations were attempted to determine if an actively metathesizing alkylidene could initiate the polymerization of **4**. Monomer **4** was exposed to molybdenum catalyst **2** at room temperature in the presence of 1,9-decadiene, norbornene, and **3**, as illustrated

in Fig. 4. In each of these cases, only homopolymer of the known reactive monomers was obtained, with absolutely no indication by either ^{1}H or ^{13}C NMR that **4** had been incorporated into the polymer. This demonstrated that even in the presence of an actively metathesizing alkylidene, the olefin present in monomer **4** is not reactive to metathesis polymerization.

The results from these copolymerization studies are important because they lend support to the conclusion that disubstituted cyclopentenes, including **4**, are inert to metathesis chemistry. The only successful polymerization chemistry that has been observed with compound **4** was the limited olefin addition initiated by the classical Lewis acid cocatalyst system (**1**). No reaction was observed for **4** with either a well-defined metathesis initiator or an actively metathesizing polymer chain end.

3.2. Cross-linking studies of dicyclopentadiene

The results from our model polymerization study with **3** and **4** begin a natural progression to the polymerization of **5**. These results suggest that polymerization of dicyclopentadiene by these initiators should form linear, soluble polymer through the ring-opening metathesis polymerization of only the strained norbornene ring. It is proposed here that an alternative polymerization mechanism, olefin addition, is also
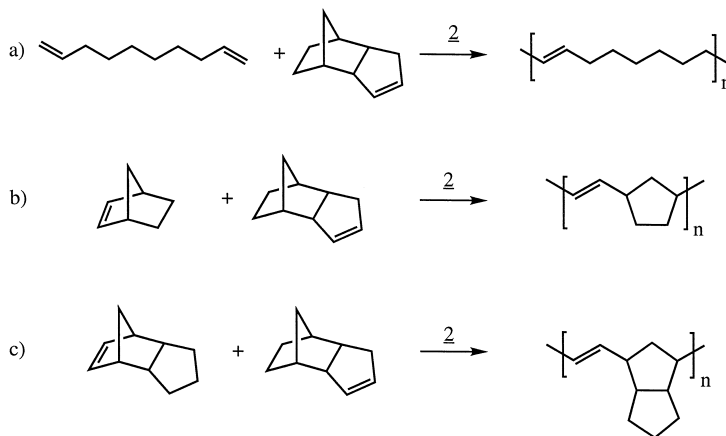

Fig. 4. Attempted copolymerization of monomer **4** with various monomers: (a) 1,9-decadiene, (b) norbornene and (c) **3**.

occurring when classical catalysts are employed, and may be responsible for the formation of insoluble, cross-linked polymer.

When the polymerization of dicyclopentadiene with Schrock's molybdenum alkylidene (**2**) is conducted in dilute solution, linear, soluble polymer is formed (Fig. 5). When the concentration of the solution is increased, the formation of insoluble polymer is evident. Fisher and Grubbs have conducted similar studies of the solution polymerization of dicyclopentadiene [15]. Their results show that high concentrations of dicyclopentadiene produce an insoluble material using Schrock's hexafluoro molybdenum catalyst (**2**). In keeping with the conventionally accepted theories, Fisher and Grubbs speculate that the formation of cross-linked polydicyclopentadiene is similar to the equilibrium ring-opening metathesis polymerization of cyclopentene. Perhaps when the concentration of the pendant cyclopentene units is high enough, ring-opening metathesis polymerization would be possible. This reaction could be responsible for the formation of cross-links in the final polydicyclopentadiene.

Although this assumption is feasible from an equilibrium concentration standpoint, inconsistencies are evident when the results of our model study are considered [16]. As discussed previously, model polymerization studies with **4** have indicated that even at high monomer concentrations and low temperatures, no metathesis is observed for this compound with molybdenum alkylidene **2**. Additionally, the reactivity of bicyclo[3.3.0]oct-2-ene, a structure identical to the repeat unit found in linear polydicyclopenta-

Fig. 5. Solution polymerization of monomer **5** with molybdenum catalyst **2**.

diene, has been previously examined [19], and this compound was also found to be inert to metathesis polymerization.

We attribute the formation of insoluble polymer during the polymerization of dicyclopentadiene with Schrock's molybdenum alkylidene **2** to the large amount of heat released during bulk polymerization. The ring-opening polymerization of the norbornene moiety is highly exothermic, as this unit possesses a ring strain of 27.2 kcal/mol [20]. When the polymerization of dicyclopentadiene is conducted in a less concentrated solution, the solvent could potentially act as a heat sink, obviating the higher activation energy required for the olefin addition process. Therefore, cross-linking does not occur when polymerization is conducted in dilute solution.

We have previously shown that dimers and trimers of the model compound, 5,6-dihydrodicyclopentadiene, can be generated through heating under inert conditions in the absence of any catalyst [16]. A similar reaction might occur during the exotherm of the dicyclopentadiene polymerization when monomer concentration is high and heat is not easily dissipated. If the cross-linking of polydicyclopentadiene is thermally induced, prevention of the reaction exotherm should allow for the formation of linear, soluble polymer.

The polymerization of dicyclopentadiene at low temperature was conducted in a 2.28 M toluene solution, a concentration which is known to yield an insoluble product at room temperature. By carrying out the polymerization at this concentration, it can be reasonably assumed that temperature would be the only variable to determine whether soluble or insoluble polymer would form. The toluene solution of **5** was cooled to −78°C in a dry ice/isopropanol bath, and the molybdenum catalyst **2**, dissolved in a minimum amount of toluene, was transferred to the flask via cannula. The reaction mixture was allowed to warm slowly to room temperature, during which time the polymer remained entirely soluble, as illustrated in Fig. 6. After precipitation from methanol, the polymer (M_n
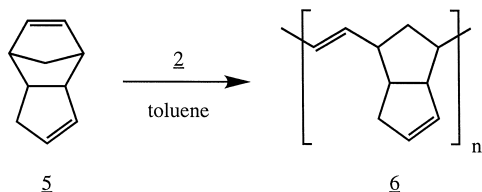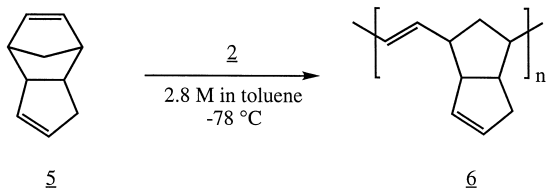
Fig. 6. Polymerization of **5** in toluene (2.28 M) at −78°C with molybdenum catalyst **2**.

= 28 000 g/mol by GPC) was readily soluble in common organic solvents.

This finding is significant. If equilibrium ring-opening metathesis of the pendant cyclopentene were responsible for cross-linking, it would be expected that this reaction would be subject to a ceiling temperature restriction, below which cross-linking occurs. For a solution of dicyclopentadiene in toluene with an initial monomer concentration of 2.28 M, the ceiling temperature must clearly be above 25°C, since cross-linked product was formed under these conditions. If the mechanism for cross-linking were truly metathesis, one would expect an insoluble product to form below room temperature as well, since reaction conditions would still be below the ceiling temperature. From this standpoint, the formation of a cross-linked polymer cannot be attributed to the metathesis of the pendant cyclopentene. Another source, namely the heat generated from the opening of the norbornene ring, must be responsible for the generation of insoluble products.

The results described earlier suggest that cross-linking does not occur exclusively by metathesis in the production of polydicyclopentadiene, but by an alternative mechanism that is thermally induced. These conclusions stem from the assumption that the reaction of the pendant cyclopentene through ring-opening metathesis is thermodynamically unfavorable. Ring-opening metathesis is an equilibrium polymerization that is typically driven by the release of ring strain. If a molecule does not possess sufficient ring strain, in comparison to the linear ring-opened polymer, the equilibrium will lie in favor of the reactants, usually resulting in a positive ΔG for

the reaction. In cases where ΔH is zero or just slightly negative, high concentrations of monomer are necessary to shift the equilibrium in favor of products. These requirements are imposed on the reaction due to the inherent loss of entropy that is typically associated with polymerization. Further studies were conducted to determine the effects of chain length and concentration on the cross-linking reaction.

If a critical concentration of growing polymer chain ends is required for metathesis cross-linking to occur in polydicyclopentadiene, then solutions which are above this concentration should yield insoluble polymer. This theory was tested by generating linear, soluble polydicyclopentadiene in solution under inert conditions, then gradually concentrating the solution under vacuum, as described in Fig. 7. Since the catalyst should remain active during the concentration of the solution, metathesis cross-linking could be feasible once the critical concentration of growing chains was reached. The solution was slowly evaporated to the point of dryness, then exposed to air, which rendered the catalyst inactive for further metathesis. Toluene was
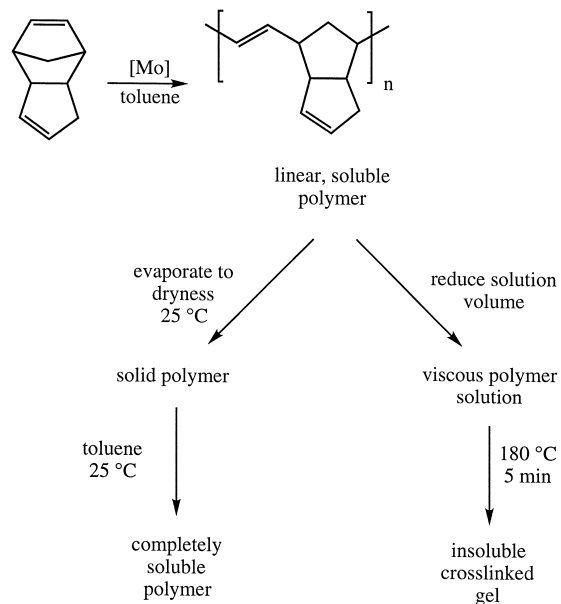

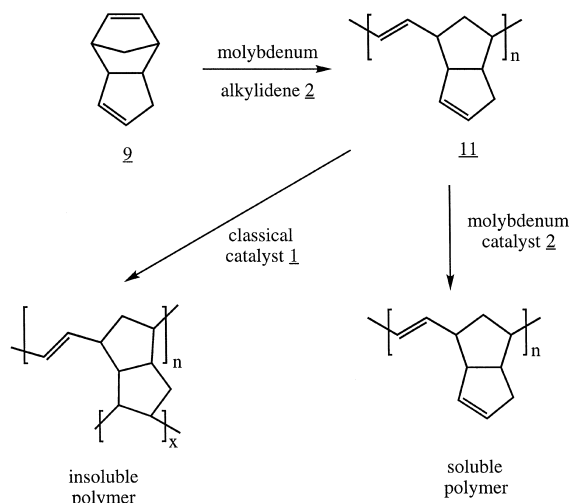Fig. 7. Results of gradual concentration of growing polydicyclopentadiene.

Fig. 8. Delayed cross-linking of polydicyclopentadiene.

added to the flask, and the polymer that had formed dissolved in a matter of minutes, indicating that cross-linking had not occurred. The toluene solution was poured into methanol, and the linear dicyclopentadiene was isolated as a white stringy precipitate.

In a second experiment designed to simulate the heat generated during the exotherm of a dicyclopentadiene polymerization, a solution of dicyclopentadiene and molybdenum catalyst **2** in toluene was prepared under inert conditions and gradually concentrated until the solution volume was decreased to about one third of its original value. At that time, the flask was plunged into an oil bath at 180°C, and immediate formation of an insoluble gel was observed. Even with warming the polymer in both toluene and 1,2,4-trichlorobenzene, no appreciable dissolution of the polymer was observed.

The results of this study revealed interesting aspects of the formation of polydicyclopentadiene. The gradual concentration of the reaction mixture effectively mimics a series of incremental concentrations, during which time a critical concentration of repeat units and chain ends would have been obtained. At some point during the evaporation of solvent, the concentration of this solution would be equal to the necessary concentration for cross-linking. However, during these experiments, the polymer remained entirely soluble, indicating that even at the maximum concentration of growing chain ends and repeat units, metathesis cross-linking did not occur. Further, if the volume of the solution of growing polymer chains is reduced and this concentrated solution is heated, an insoluble gel forms instantly. These findings support the argument that heat released during the polymerization is responsible for the formation of cross-linked polydicyclopentadiene with the well-defined molybdenum catalyst, rather than an equilibrium concentration metathesis reaction.

Linear, soluble polydicyclopentadiene was also generated and isolated, then exposed independently to the classical catalyst system **1** and the Schrock molybdenum alkylidene **2** to determine if delayed cross-linking was possible. Samples of linear, soluble polydicyclopentadiene were made using Schrock's molybdenum alkylidene **2** in a solution of toluene and end-capped with benzaldehyde. After precipitation and drying of the polymer, the samples were redissolved in various amounts of dry toluene under inert conditions, and the classical catalyst

Table 1
Delayed cross-linking of dicyclopentadiene oligomers by classical catalyst **1** and molybdenum alkylidene **2**

X_n of oligomer[a]	Concentration[b]	Final polymer with **1**	Final polymer with **2**
45	1 M	insoluble	completely soluble
45	5 M	insoluble	completely soluble
180	1 M	insoluble	completely soluble
180	5 M	insoluble	completely soluble
1800	1 M	insoluble	completely soluble

[a] Degree of polymerization calculated from monomer/catalyst ratio.
[b] Concentration based on repeat units/liter of solution.

system **1** and Schrock's molybdenum alkylidene **2** were added independently, as illustrated in Fig. 8. The polymer formed from the classical catalyst was insoluble in warm toluene, *o*-xylene, and 1,2,4-trichlorobenzene, indicating that a cross-linked network may have formed. Since the model compound 5,6-dihydrodicyclopentadiene did not undergo metathesis when exposed to the classical catalyst **1**, the mode of cross-linking for this dicyclopentadiene system is also assumed to be an olefin addition process. Conversely, no further reaction was observed with the molybdenum catalyst **2**, and the polymer remained completely soluble (Table 1).

4. Summary

Linear polydicyclopentadiene (**6**) can be generated in solution with the well-defined molybdenum catalyst **2**. However, at higher concentrations of monomer, insoluble material is formed. It is believed that the formation of this material is due to either an olefin addition process or a rearrangement catalyzed by the heat released upon the ROMP of the norbornene subunit of the monomer. An olefin addition process has also been observed with 5,6-dihydrodicyclopentadiene, which contains a fused cyclopentene by thermal exposure without a catalyst present. If the heat is removed from the polymerization of dicyclopentadiene through dilution or by cooling the solution, soluble linear polymer is formed. These results suggest that a thermally catalyzed process is at least partly responsible for the cross-linking reaction that occurs during the polymerization of dicyclopentadiene.

All attempts to cross-link oligomers of linear polydicyclopentadiene with the well-defined molybdenum alkylidene **2** resulted in only the recovery of soluble polymer. With the classical catalyst system **1**, insoluble material was obtained, which was assumed to be cross-linked through olefin addition. These results disprove the idea that metathesis cross-linking can be induced by a critical chain length or concentration of polydicyclopentadiene. On the contrary, no indication of metathesis cross-linking was observed whatsoever for these polymerization systems.

Acknowledgements

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