

Ring-opening metathesis polymerization of dicyclopentadiene by tungsten catalysts supported on polystyrene¹

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Abstract

Ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) was conducted by using catalyst systems WCl_6-Et_2AlCl , $(WCl_6-PhCOMe)-Et_2AlCl$ and their polystyrene supported counterparts. Experimental results indicate that the acetophenone modified catalyst system shows better catalytic properties than the unmodified system does and that supporting the catalysts on a polystyrene can improve further the catalyst systems' catalytic properties. As a result, the polymer yield of the ROMP increased, the mechanical properties of NIS (notched impact strength), TS (tensile strength) of synthesized polydicyclopentadiene (PDCPD) enhanced. The mechanism in which supporting improves the properties of the catalyst systems is discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ring-opening metathesis polymerization; Dicyclopentadiene; Tungsten; Supported catalyst

1. Introduction

In recent years, the achievements of ring-opening metathesis polymerization (ROMP) in synthesizing polymeric materials with excellent properties and in tailoring polymers with novel structures are spectacular [1–8]. ROMP of DCPD is a subject relating to the reasonable utilization of C_5 fraction, a by-product from the process of ethelene production in petrochemical industry, which contains a fairly large amount of DCPD (ca. 15–17%). Hence, it attracted interest and efforts of quite a number of scientists engaged in polymer synthesis. During the past decade, several papers dealing with ROMP of DCPD were published [9–14]. None of them, however, tried polymer-supported catalysts. Recently, we found that the catalytic behaviour of catalyst system based on WCl_6-Et_2AlCl could be greatly improved when being supported on some polymer supports [15,16]. In this paper, we report our recent work on ROMP of DCPD catalyzed by catalyst systems WCl_6-Et_2AlCl , $(WCl_6-PhCOMe)-Et_2AlCl$ and their polystyrene supported counterparts.

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2. Experimental

2.1. Reagents

DCPD (98.95%, Yanshan Petrochemical Corp., Beijing, China) was rectified under reduced pressure before use. Tungsten hexachloride was prepared according to Ref. [17] and was purified by sublimation under nitrogen right before use. Diethyl aluminum chloride (C1% = 30.36, C1/A1 = 1.07, Tianjin No. 2 Petrochemical plant, China) was used as available without any further purification. Polystyrene ($\overline{M}_w = 1.6 \times 10^5$, Jindai Chemical Works, Tianjin, China). THF and toluene were dried by refluxing over sodium under UHP nitrogen, distilled out and degassed immediately before use. Acetophenone was a reagent of analytically pure. All manipulations were performed under UHP nitrogen using a vacuum line and standard Schlenk techniques.

2.2. Polymerization and mechanical property measurement of product polymer

Polymerization was performed according to the procedures described in Ref. [15]. After polymerization, the polymer samples were cut to long narrow pieces of size set by the State Standard of China. Notched impact strength (NIS) indices of the samples were measured with a Charpy impact tester of type XCT-500 at 23°C. Tensile strength (TS) and breaking elongation ratio (BER) indices of the samples were measured at 23°C with an electronic tensile machine of type WD-10E. The flexural strength (FS) indices of the samples were measured at 23°C with an electronic universal press of type WD-10E.

2.3. Ageing experiments of catalyst systems

The ageing experiments of the catalytic systems were performed as follows: To a Schlenk flask connected to a vacuum line a certain amount of WCl_6 , polystyrene (or no) was added. The flask was immediately deoxygenated. Then, degassed toluene was added. After the solid was completely dissolved, Et_2AlCl was added to the solution. The mixture was stirred continuously under UHP nitrogen for a time. Then the aged catalyst mixture was introduced to another Schlenk flask containing a certain amount of DCPD and THF. After polymerization the product polymer was Soxhlet extracted with toluene under nitrogen at refluxing temperature for 24 h and was then vacuum-dried at 100°C.

3. Results and discussion

3.1. Comparison of behaviour of catalyst system WCl_6-Et_2AlCl and its acetophenone-modified counterpart

Ligand modifying is a commonly adopted method for improving a homogeneous catalyst's properties. Using acetophenone as a modifying ligand for the catalyst system WCl_6-Et_2AlCl , we carried out ROMP of DCPD. Experimental results obtained by using the two catalyst systems are listed in Tables 1 and 2.

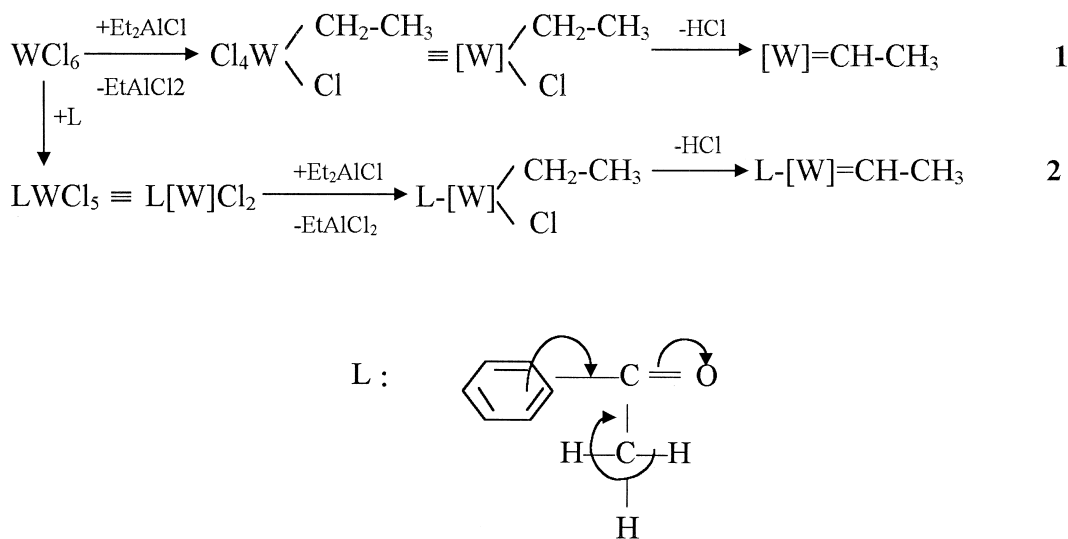
Table 1
Influence of catalyst systems over ROMP of DCPD

No.	Catalyst system	Gelation time (s)	Polymer yield (%)
1	WCl ₆ -Et ₂ AlCl	55	94.5
2	(WCl ₆ -PhCOMe)-Et ₂ AlCl	110	97.1

^aReaction conditions: DCPD:WCl₆:PhCOMe = 10 000:1:1 (molar ratio), polymerization temperature 80°C.

The experimental results indicate that the acetophenone-modified catalyst system (WCl₆-PhCOMe)-Et₂AlCl, as compared with the catalyst system WCl₆-Et₂AlCl, not only leads to the increase of polymer yield of ROMP of DCPD (94.5–97.1%), but also to the distinct enhancement of mechanical properties of NIS and TS of synthesized polydicyclopentadiene (PDCPD), which are the two most important mechanical property indices when PDCPD is used as an impact resistant plastics.

According to a well-accepted viewpoint, the actual catalytic active species in ROMP is a metallocarbene, tungstenocarbene in this case, which is a highly electron-deficient species by its very nature. When acetophenone (L), an electron-rich ligand, is added to the catalyst system WCl₆-Et₂AlCl, the coordination of it with the tungsten atom increases the electron density of coordination center of the catalytic active tungsten-carbene complex (2) formed hereafter.



And thus, it stands to reason that the stability of tungstenocarbene complex **2** is higher than that of complex **1**. The properly increase of stability of the very labile metallocarbene species initiating

Table 2
Influence of catalyst systems over mechanical properties of synthesized PDCPD

No.	NIS (kJ/m ²)	TS (MPa)	BER ^a (%)	FS ^b (MPa)
1	64	32	1.5 × 10 ²	47
2	74	35	1.4 × 10 ²	44

^aBreaking elongation ratio.

^bFlexural strength.

Table 3
Influence of supporting of homogeneous catalysts over ROMP of DCPD^a

No.	Catalyst system	Gelation time (s)	Polymer yield (%)
1	WCl ₆ -Et ₂ AlCl	55	94.5
3	WCl ₆ /PS-Et ₂ AlCl	52	97.7
2	(WCl ₆ -PhCOMe)-Et ₂ AlCl	110	97.1
4	(WCl ₆ -PhCOMe)/PS-Et ₂ AlCl	100	98.1

^aReaction conditions are the same as shown in Table 1.

ROMP of DCPD is good for the propagation reaction, that is to say, good for the polymerization to go to completion. As a result, the polymer yield of the ROMP increases (Table 1). On the other hand, the properly increase of stability of initiation species increases undoubtedly the lifetime of the propagating macromolecular metallocarbene species, and it avoids or at least reduces undesirable chain-transfer reaction. The size and crosslinking density of formed polymer network could thus, increase too, and as a result, it leads to the increase of NIS and TS of synthesized PDCPD (Table 2).

3.2. Support effect—*influence of catalyst supporting over ROMP of DCPD and the mechanical properties of synthesized PDCPD*

To obtain a supported catalyst, which retains the high catalytic activity of a homogeneous complex catalyst, has been a subject attracting the interest and efforts of scientists engaged in catalysis. For the catalyst systems WCl₆-Et₂AlCl and (WCl₆-PhCOMe)-Et₂AlCl, mentioned above, we surprisingly found that when the catalysts were supported on a polystyrene support, not only did the polymer yield of ROMP increase obviously (Table 3), at the same time the NIS and TS of synthesized PDCPD enhanced sharply (Table 4).

In order to find out further the influence of supporting over the lifetime of tungstenocarbene species initiating the ROMP, we carried out ageing experiments of the catalyst system WCl₆-Et₂AlCl and its polymer supported counterpart. Experimental results are listed in Table 5.

It is clear from Table 5 that ageing firstly the catalyst system WCl₆-Et₂AlCl for 60 min and then introducing it into DCPD the polymer yield of the ROMP is 0.36%. In case of the polymer supported catalyst system WCl₆/PS-Et₂AlCl things are quite different. Introducing the catalyst mixture being aged for as long as 120 min into DCPD, the polymer yield of the ROMP can still reach as high as 0.38%. We can reasonably deduct, from this fact, that when the catalyst system WCl₆-Et₂AlCl is supported on the polymer support, the lifetime of catalytic active tungstenocarbene species initiating ROMP of DCPD increases by two times.

The mechanism in which supporting can increase the lifetime of tungstenocarbene species initiating the ROMP of DCPD is still not very clear. One possible explanation is that the weak π -coordination

Table 4
Influence of supporting of homogeneous catalysts over mechanical properties of synthesized PDCPD

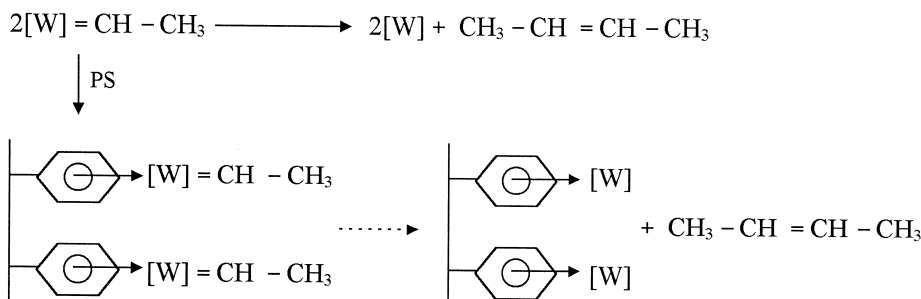
No.	NIS (kJ/m ²)	TS (MPa)	BER (%)	FS (MPa)
1	64	32	1.5 × 10 ²	47
3	89	40	1.4 × 10 ²	45
2	74	35	1.4 × 10 ²	44
4	84	36	1.5 × 10 ²	47

Table 5
Ageing time of the catalyst systems over the polymer yield of ROMP of DCPD^a

Catalyst system	Ageing time (min)	Polymer yield (%)
WCl ₆ -Et ₂ AlCl	30	0.49
	60	0.36
WCl ₆ /PS-Et ₂ AlCl	60	0.48
	90	0.45
	120	0.38

^aPolymerization conditions are the same as shown in Table 1.

binding between the benzene ring on polystyrene chains and tungsten atom in the tungsten-carbene complex causes, to some extent, the site separation of active metallocarbene species bound on the polymer chains, and as to reduce greatly the possibility of the highly labile metallocarbene species' bimolecular disproportionation termination which is unnegligible without support [18]:



4. Conclusions

As a modifying ligand acetophenone, an electron-rich ligand, can distinctly improve the catalytic behaviour of catalyst system WCl₆-Et₂AlCl for ROMP of DCPD—the polymer yield of the polymerization is increased, the mechanical properties of NIS and TS of synthesized PDCPD are distinctly enhanced. Supporting the catalyst systems WCl₆-Et₂AlCl and (WCl₆-PhCOMe)-EtAlCl on a polystyrene support, their catalytic behaviour is improved further. The ageing experiments of the catalyst systems demonstrate that the lifetime of catalytic active species for ROMP of DCPD increases by two times in the case of supported catalysis.

Acknowledgements

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