

Macroligand effect of tungsten catalyst for ring opening metathesis polymerization of dicyclopentadiene[☆]

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Abstract

The macroligand effect of the catalytic system WCl_6-Et_2AlCl for ring opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) was investigated. The experimental results show that macroligand effect varies with the structure of the ligands. The macroligands bearing benzene group and steric hindered phenolic unit not only can obviously increase the yield of synthesized polydicyclopentadiene (PDCPD) but also improve the synthesized polymer's mechanical properties. The mechanism of macroligand effect is discussed. The synthesized PDCPD was characterized by methods of scanning electron microscopy (SEM) and X-ray diffraction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ring opening metathesis polymerization; Polydicyclopentadiene; Macroligand effect

1. Introduction

Developing new and efficient homogeneous and heterogeneous catalysts for ring opening metathesis polymerization (ROMP) has attracted widespread interest over the past decade [1–5]. We first reported ROMP of dicyclopentadiene (DCPD) by polymer supported tungsten catalytic system [6–8]. This paper reports our recent work on ROMP of DCPD by catalytic system WCl_6-Et_2AlCl supported on different polymer supports and discusses the macroligand effect of the catalyst system.

2. Experimental

2.1. Reagents

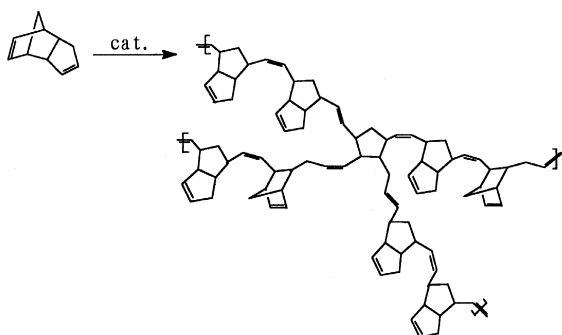
Tungsten, 99.8% (Shanghai No. 2 Smeltery, China); Diethylaluminumchloride: $Cl/Al = 1.07$, $Cl\% = 30.36$ (Tianjin No. 2 Petrochemical Plant, China); DCPD, 98% (Yanshan Petrochemical, China), was rectified under reduced pressure before use. Tungsten hexachloride was prepared according to Ref. [9], and was purified by sublimation under nitrogen before use. All other reagents are of A.R. grade.

Linear phenol formaldehyde resin ($\bar{M}_w = 1 \times 10^5$, Jinan Chemical plant, China); polystyrene ($\bar{M}_w = 1.6 \times 10^5$, Jindai Chemical Works, Tianjin, China)

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Scheme 1. ROMP of DCPD.

2.2. Preparation of macroligand poly-*p*-acetylstyrene (PAS)[10,11]

PAS was prepared according to Refs. [10,11]. The product was refined by reprecipitation method (toluene–water and methanol) and dried under vacuum at 50°C overnight. The IR spectrum of the purified product shows an absorption peak at 1683 cm⁻¹ indicating the presence of the acetyl group in polystyrene.

2.3. Polymerization and mechanical property measurement of the synthesized polymer

Polymerization reaction of DCPD (Scheme 1) and the determination of the synthesized polydicyclopentadiene's (PDCPD) mechanical properties were carried out according to Refs. [6,12].

2.4. Characterization of the synthesized PDCPD

Wide angle X-ray diffraction analysis of the PDCPD sample was performed with a RIGAKUD/MAX-rA [target: CuK_α, voltage: 40 kV; electric current: 100 mA; DS/SS = 1°/1°; RS = 0.3 mm; scanning rate: 5/min; scanning scope: 10°/50°(2θ)]. The notched impact fracture morphology of the synthesized PDCPD was performed using a scanning electron microscope of (HITACHI) X-650.

3. Results and discussion

3.1. Comparison of different ligand effects of the catalyst system WCl₆–Et₂AlCl

For the homogeneous complex catalysts, altering kinds and structures of ligands coordinated with the active central metal atoms is an effective and commonly adopted method for the modification of the catalyst's properties. Our previous investigation on ROMP of DCPD indicated that modifying the catalyst system WCl₆–Et₂AlCl with suitable ligands results in not only the increase of the monomer conversion of polymerization, but also the improvement of the synthesized polymer's mechanical properties. In order to have an understanding of the mechanism of macroligand effect, we carried out the ROMP of DCPD using different macroligands to modify the catalyst system. Experimental results are listed in Table 1 and Table 2.

The results listed in Table 1 and Table 2 show that the ligand: 2,6-di-*tert*-butyl-cresylol (DTBC), as compared with the others, has an obvious effect for the improvement of mechanical properties of the synthesized PDCPD. This might be due to the reason that DTBC could coordinate with tungsten carbene species initiat-

Table 1
Influence of supporting homogeneous catalysts over the ROMP of DCPD^a

No.	Ligand	Gelation time(s)	Polymer yield(%)
1		55	94.5
2		110	97.1
3		80	96.7

^aReaction conditions: DCPD/cat. = 10000:1 (molar ratio); cat./cocat. = 1:20 (molar ratio); and polymerization temperature: 80°C.

Table 2

Influence of supported catalyst systems over the mechanical properties of synthesized PDCPD^a

No.	NIS (kJ/m ²)	TS (Mpa)	BER (%)	FS (Mpa)
1	64.3	32.8	1.5 × 10 ²	47.4
2	73.7	35.3	1.4 × 10 ²	43.9
3	85.7	39.4	1.6 × 10 ²	47.6

^aNIS: notched impact strength; TS: tensile strength; BE: breaking elongation; FS: flexural strength.

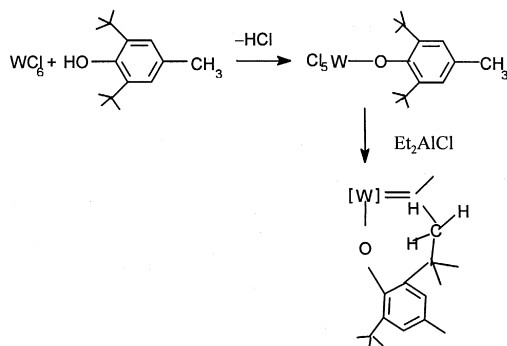
ing polymerization in the following way (Scheme 2).

An intramolecular cyclometalation via hydrogen transfer from a tertial butyl group to the carbene atom may occur [6]. Such an intramolecular cyclometalation increases to some extent the stability of metallocarbene species initiating the polymerization of DCPD, delays the gelation of the reaction system (55 s → 80 s), and so as to cause the increase of the monomer conversion and the mechanical properties of the synthesized PDCPD.

For the acetophenone-modified catalyst system, (WCl₆-PhCOMe)-Et₂AlCl, a possible explanation is given in Ref. [13].

3.2. Macroligand effect of the catalyst system WCl₆-Et₂AlCl

It is clear, from our previous work, that the activity and the stability of the tungsten cat-



Scheme 2. The possible coordination of DTBC with tungsten carbene complex.

Table 3

Macroligand effect of catalytic system for the ROMP of DCPD^a

No.	Ligand	Gelation time(s)	Polymer yield(%)
1		55	94.5
4		55	98.1
2		110	97.1
5		100	98.1
6		65	98.2
3		80	96.7
7		60	98.3
8		60	98.1

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

alytic system for the ROMP of DCPD would increase when being supported on polystyrene. Since the mechanism of supporting effect is still not very clear, we made further investigations by using the polymers having analogous structures of the modified ligand as supports. The

Table 4

Macroligand effect of supported catalyst system over the mechanical properties of synthesized PDCPD

No.	NIS (kJ/m ²)	TS (Mpa)	BER (%)	FS (Mpa)
1	64.3	32.8	1.5 × 10 ²	47.4
4	86.1	39.8	1.5 × 10 ²	42.9
2	73.7	35.3	1.4 × 10 ²	43.9
5	84.1	35.3	1.5 × 10 ²	47.5
6	80.3	34	1.4 × 10 ²	41.1
3	85.7	39.4	1.7 × 10 ²	47.6
7	88.5	46	1.7 × 10 ²	47.5
8	80.8	44.3	1.7 × 10 ²	49.3

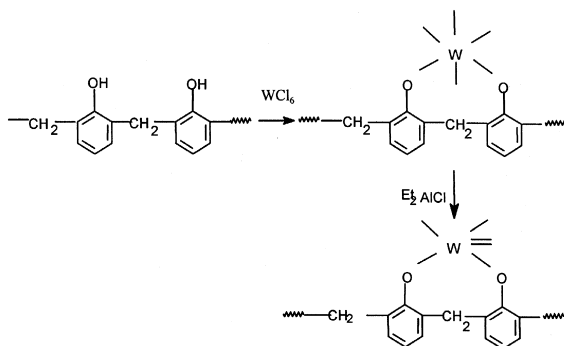
experimental results are listed in Table 3 and Table 4.

The experimental results show that acetophenone-modified catalyst system supported on polystyrene (WCl_6 -PhCOMe)/PS- Et_2AlCl has higher activity, as compared with the catalyst system supported on PAS WCl_6 -PAS- Et_2AlCl , which leads to the increase of mechanical properties of the synthesized PDCPD. Similar results are obtained with the catalyst system WCl_6 -LPF- Et_2AlCl .

Although the mechanism of macroligand effect is not very clear, it seems that the weak π -coordination binding between the benzene ring and the tungsten atom in the tungsten-carbene complex can increase the stability of the labile metallocarbene species, and that polystyrene might have the synchronous effect of this weak coordination and the site separation of the active metallocarbene species on the polymer backbones, which reduces the possibility of the highly labile metallocarbene species' bimolecular disproportionation termination [13].

The linear phenol formaldehyde (LPF) is actually a steric hindered polymeric phenol and can form an aryloxy complex with the tungsten catalyst in the following way (Scheme 3).

The π -coordination existing between phenolic ring and tungsten through oxygen atom causes the increase of stability of the active initiation species to some extent, which finally leads to the results mentioned above.



Scheme 3. The possible coordination of LPF with tungsten carbene complex.

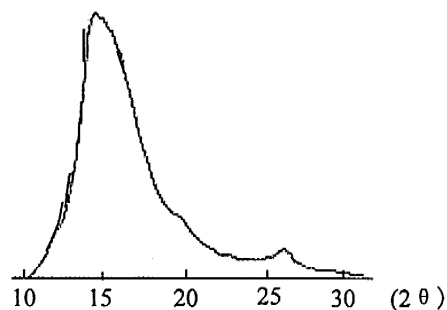


Fig. 1. X-ray diffraction of the synthesized PDCPD.

3.3. The physical character of the synthesized PDCPD

PDCPD made by ROMP possesses both high tensile strength and flexural modulus. Up to now though, published papers dealing with the catalyst systems and reaction conditions are few. However, these papers made mention of the morphology analysis of the polymer. In our laboratory, the morphology of the impact fracture and the way of fracture of the synthesized PDCPD samples with notch were investigated by scanning electron microscopy (SEM). The X-ray diffraction analysis of the synthesized PDCPD was also conducted. The results are shown in Fig. 1 and Fig. 2.

There is a strong peak at 15.9 (2θ) in Fig. 1, indicating the synthesized PDCPD possesses crystallization degree to a certain extent. Fig. 2 shows the SEM of the PDCPD sample with notch. Coarse surface has been noted illustrating that the synthesized PDCPD has high impact

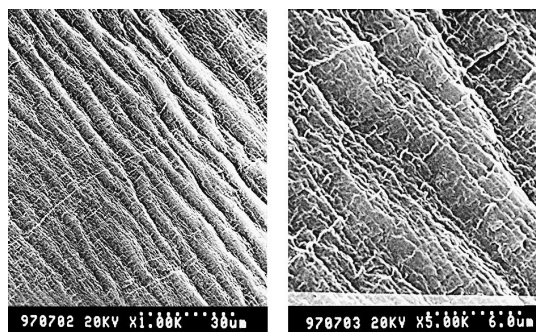


Fig. 2. SEM analysis of notched impact fracture morphology.

strength. This is attributable in part, to a combination of relatively high order in the crystalline regions and high disorder in the amorphous regions. That is, synthesized PDCPD has high impact strength and high flexural modulus because of the presence of the chain stiffening unit



backbone of PDCPD, and some flexibility provided by the single bond in the chain.

4. Conclusion

The macroligand effect of the catalytic system WCl_6-Et_2AlCl has a positive influence on the ROMP of DCPD. The macroligands having phenyl group and the steric hindered substituent on the phenolic ring can increase both the yield of the synthesized PDCPD and the mechanical properties of PDCPD. This might be due to the synchronous effect of the weak coordination between the ligands and catalytic active metal and the site separation of the labile metal carbene species on the polymer chains. SEM and X-ray diffraction of the synthesized PDCPD show that synthesized PDCPD is a semicrystalline polymer, possessing high impact strength and high flexural modulus because of the combination of the amorphous regions and the crystalline regions.

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