

The ring-opening metathesis polymerization of dicyclopentadiene with titanocene complexes

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Received 26 February 1998; accepted 27 August 1998

Abstract

The ring-opening metathesis polymerization of dicyclopentadiene with dimethyltitanocene and in situ prepared substituted dimethyltitanocenes was studied. The results showed that at low concentration dimethyltitanocene catalyzed the polymerization of dicyclopentadiene to give linear polymer at 70–90°C and that the introduction of oxygen-containing substituents on cyclopentadienyl rings decreased catalytic activity due to a steric effect. © 1999 Elsevier Science B.V. All rights reserved.

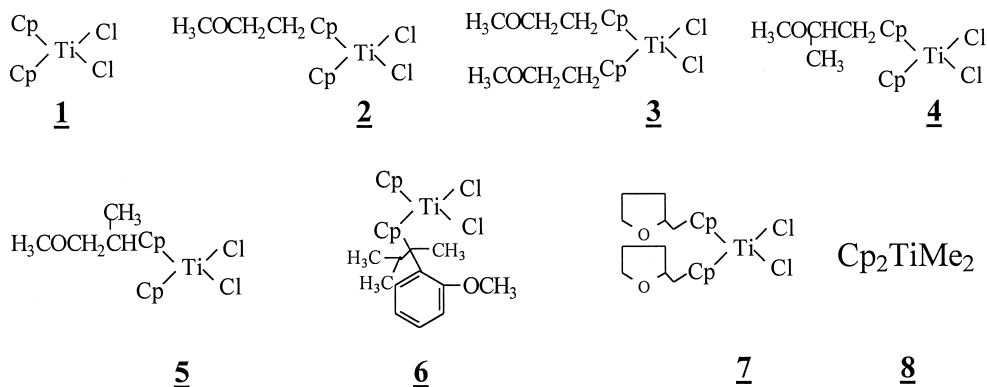
Keywords: Ring-opening metathesis polymerization; Dicyclopentadiene; Titanocene

1. Introduction

Polydicyclopentadiene, or poly(DCPD), featured by its important property of stiffness and toughness, is a new commercial polymer prepared by ring-opening metathesis polymerization (ROMP). The catalysts used for the ROMP of dicyclopentadiene were Ziegler–Natta type catalysts such as WCl_6 , $MoCl_5$, $ReCl_5$, $OsCl_3$, and $WCl_{6-x}(OAr)_x$ combined with Me_4Sn , $AlEt_2Cl$, $AlEtCl_2$ [1–3]. A recent development in ROMP of dicyclopentadiene was the use of $W(NAr)Cl_{4-x}(OAr)_xL$, $W(NAr)Cl_{4-x}(OR)_x$ [4,5] and Tebbe reagents [6,7] as catalysts. To investigate the substituent effect in titanium carbene initiators, we have synthesized a series of substituted titanocene dichlorides (**1–7**) and used the in situ prepared dimethyl titanocene (**8**) for the ROMP of dicyclopentadiene.

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2. Experimental

DCPD (85%) was purified by vacuum distillation, pyrolysis, dimerization, and vacuum distillation. **1–3**, [8] **4**, **5** [9], **6** [10], **7** [11] and **8** [12] were prepared according to the literature.

Polymerization was carried out in ampules which were baked under vacuum and flushed with Ar several times. Thus 0.1875 mmol of a titanocene dichloride, 0.5 ml of toluene and 0.375 mmol of MeLi were introduced into the ampules under Ar at -20°C , and aged for 1.5 h. Then 4 ml of DCPD in toluene ($v/v = 1$) was injected, and the ampules were placed in an oil bath at a given temperature. The polymerization was terminated after 24 h with 100 ml 5% HCl in acetone.

GPC analysis was performed on Waters-244 spectrometer, with polystyrene as a standard. The intrinsic viscosity was measured at 30°C in THF by Ubbelohde viscometer.

3. Results and discussion

The ROMP of DCPD by titanium catalysts was first reported in 1986 by Grubbs and Gilliom [6], who used titanacyclobutanes and Tebbe's reagent as catalysts. In 1993, Petasis and Fu [7] reported the ROMP of norbornene with titanium alkylidenes generated by thermolysis of dimethyltitanocene and related cyclopentadienyltitanium derivatives. To study the substituent effect on cyclopentadienyl ring in the ROMP of DCPD, we first used dimethyl titanocene as the catalyst for the ROMP of DCPD.

Table 1 shows the effect of catalyst concentration on the polymerization. The higher the [Ti], the higher the conversion and molecular weight of polymer. When $[\text{Ti}] = 5.4 \times 10^{-2} \text{ M}$, the conversion

Table 1
The influence of catalyst concentration on the polymerization

[Ti] (10^{-2} M)	Conversion (%)	M_n (10^4)	M_w / M_n	Solubility
5.4	96			insoluble
3.6	79	2.24	1.50	soluble
2.7	46	1.16	1.58	soluble
1.8	31	1.01	1.61	soluble
1.4	15	0.90	1.70	soluble

[DCPD] = 2.7 M, PhMe, 80°C , 24 h.

Table 2
The influence of temperature and time on polymerization

Parameter	Temp. ^a (°C)				Time ^b (h)			
	70	80	90	100	15	20	24	30
Conv. (%)	7	80	97	100	19	74	79	80
[η] (ml/g)	11.3	19.0	20.3		31.0	48.0	20.0	19.0

[DCPD] = 3.2 M, [Ti] = 4.3×10^{-2} M, PhMe.

^a24 h.

^b80°C.

reaches 96%, but the polymer is insoluble in common organic solvents, indicating that high [Ti] may cause cross-linking of the polymer. It seems that molecular weight distribution is not affected by [Ti], while at lower [Ti], a soluble poly(DCPD), which dissolves in common organic solvents such as tetrahydrofuran, toluene, benzene, chloroform, and dichloromethane, is obtained, indicating a linear structure of the polymer.

Table 2 summarized the influence of temperature and time on the polymerization. As can be seen, temperature has a pronounced effect on the conversion. Below 70°C, very little polymerization occurs, while at 80°C the conversion is 80%. The reason for this great change is that dimethyltitanocene decomposes to form $\text{Cp}_2\text{Ti}=\text{CH}_2$ very slowly at 70°C, while very fast at 80°C. In fact, a brown red color, which is the color of dimethyltitanocene in toluene, persisted throughout the polymerization at 70°C. However, dark color developed as the polymerization proceeded at 80°C. Above 90°C, insoluble cross-linked polymer is formed. Polymerization time has also a great effect. When the reaction time is less than 15 h, little polymer is precipitated from acetone. However, after 20 h, the yield of polymer is sharply increased and the maximum intrinsic viscosity of polymer is obtained, indicating that the polymerization proceeds via an oligomerization reaction following by the formation of polymers [13]. A further increase in polymerization time results in a decrease of intrinsic viscosity presumably due to the metathesis reaction within a propagating chain ('back-biting'). When the polymerization time exceeds 40 h, insoluble polymer is formed, indicating that cross-linking takes place.

The dimethyltitanocene produced in situ by reaction of titanocene dichloride and MeLi has an activity comparable with that of isolated dimethyl titanocene for the ROMP of dicyclopentadiene. To learn more about the influence of substituents on the polymerization, a series of substituted titanocene dichlorides in combination with MeLi are used for the ROMP of dicyclopentadiene (Table 3).

Table 3
The influence of substituents

Catalysts	Conv. (%)	M_n (10^4)	M_w/M_n
1/MeLi	81	2.33	2.23
2/MeLi	54	1.45	1.87
3/MeLi	43	1.53	1.58
4/MeLi	54	2.61	2.73
5/MeLi	48	1.64	1.86
6/MeLi ^a	14	1.63	1.63
7/MeLi	27	1.13	2.21

[DCPD] = 3.5 M, [Ti] = 4.2×10^{-2} M, PhMe, 80°C, 24 h.

^a48 h.

Results showed that catalytic activities were lowered by increasing the bulkiness of substituents on the Cp rings. As shown in Table 3, the introduction of a methoxyethyl substituent on the cyclopentadienyl ring greatly lowered the polymer yield (from 81 to 54%); two substituents made the polymer yield even lower (43%). The more bulky the substituents, the lower is the polymer yield. It is generally accepted that titanacyclobutane and titanium carbene are true initiators in ROMP of cycloolefins. Thus large substituents are unfavorable to the formation of titanacyclobutane from titanium carbene and sterically hindered monomer, dicyclopentadiene. Further more, the oxygen in substituents may also coordinate to titanium, which competes with the monomer and thus results in the drop of activity. In most cases the introduction of substituents lead to a drop in molecular weight and polydispersity.

Acknowledgements

We acknowledge the financial support from the National Natural Science Foundation of China(29734145), scholarship from 3M, and State Key Laboratory of Coordination Chemistry, Nanjing University.

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