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Preparation of polynorbornene with β-diketonate titanium / MAO catalysts

Xia Mi[1], Demin Xu[1], Weidong Yan[2], Cunyue Guo[1], Yucai Ke[1], Youliang Hu[1] (✉)

[1] State Key Lab of Engineering Plastics, Center for Molecular Science, Beijing Laboratory of Catalysis, CNPC Key Laboratory of Catalysis, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China
[2] Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, China
e-mail: huyl@infoc3.icas.ac.cn, Tel.: +86-10-6256 2815, Fax: +86-10-6256 9564

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Summary

Polynorbornene was synthesized by β-diketonate titanium / MAO (methylaluminoxane) catalysts. The polymerization activity was up to 8 x 10^3 g polymer/(mol Ti h). FT-IR, ^{1}H NMR, ^{13}C NMR and WAXD analyses showed that the polynorbornenes contained both ring-opening metathesis (trans and cis) and addition polymer chain structures and they are amorphous. The portions of trans- and cis- double bonds decreased when the polymerization temperature and Al/Ti molar ratio decreased. In addition, using 1,2-dichlorobenzene, instead of toluene, as the polymerization solvent increased the activity and produced the polymer containing more cis-double bonds. The glass transition temperature of the elastic polymers ranged from 330°C ~ 400°C.

Introduction

The polymerization of norbornene (bicyclo [2.2.1] heptene-2) has been investigated since the 1950s [1-8]. Due to the high thermal stability, low water absorption and excellent optical properties, the resulting polymers and their copolymers have attracted considerable attention. So far, three modes of reaction have been shown for the polymerization of norbornene: ring-opening olefin metathesis polymerization (ROMP), 2,7- and 2,3- addition polymerization, as summarized in Figure 1.

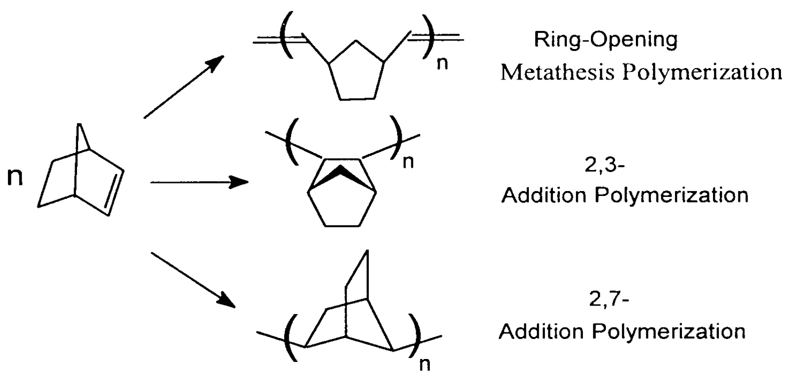


Figure 1. Three modes for polymerization of norbornene

In addition to Cr-, Mo-, W-, Ru-, Os- and Ir-based catalytic systems [4], the traditional heterogeneous Ti-based Ziegler-Natta catalysts usually caused the ring-opening polymerization, yielding polymers with cyclopentane rings and cis and / or trans unsaturation [1,3]. The addition polymerization of norbornene, which formed saturated polymers, was first realized when Al/Ti ratio was reduced to 0.5 in the Ti-based catalyst system [2]. Subsequent studies showed that catalysts such as Zr-based metallocene, half-metallocene and Ni or Pd-based late transition metal catalysts caused the addition polymerization of norbornene [5].

Recently, some nonmetallocene complexes have been used as catalysts for olefin polymerization. The homogeneous β-diketonate zirconium complexes / MAO (methylaluminoxane) were used for ethylene polymerization [6]. Several kinds of β-diketonate titanium analogues, including $\mathrm{Ti(acetylacetonato)_2Cl_2}$ $\mathrm{[(acac)_2TiCl_2]}$, $\mathrm{Ti(acetylacetonato)_2(OPh)_2}$ $\mathrm{[(acac)_2Ti(OPh)_2]}$ and $\mathrm{Ti(dibenzoylmethanato)_2(OPh)_2}$ $\mathrm{[(dbm)_2Ti(OPh)_2]}$, have been used for ethylene homopolymerization, ethylene/styrene copolymerization and especially styrene syndiospecific polymerization with fairly high activity and high syndioacticity [6]. Easier synthesis, lower costs, weaker air or moisture sensibility of the catalysts make these complexes attractive. To date, the preparation of polynorbornene by these catalysts hasn't yet been reported.

In this paper, polymerization of norbornene was catalyzed with several β-diketonate titanium complexes combined with MAO. The effects of catalyst structure, Al/Ti molar ratio, monomer concentration, polymerization temperature and polymerization solvents on polymerization activity are discussed. The structures of the resulting polymers were characterized by FT-IR and NMR spectra.

Experimental

All operations were performed under argon using standard Schlenk techniques.

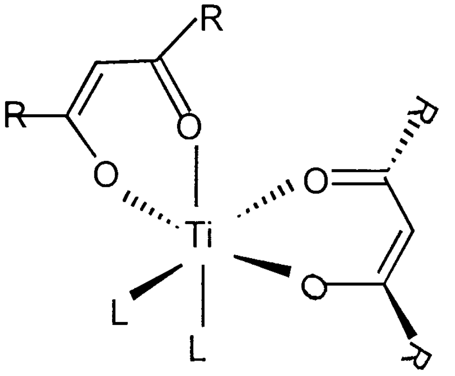
Materials

Norbornene (from Acros) was distilled from sodium and then dissolved in dried toluene to give a 0.4g/ml solution. 1,2-Dichlorobenzene was dried with calcium dihydride (CaH_2) and then vacuum distilled. Toluene (from Beijing Chemical Co. Ltd.) was refluxed with sodium and freshly distilled before use.

Methylaluminoxane (MAO) (purchased from Albemarle Co., 1.4 M in toluene) was used as received.

Preparation of the catalysts

The catalysts, $(acac)_2TiCl_2$, $(acac)_2Ti(OPh)_2$ and $(dbm)_2Ti(OPh)_2$, were prepared according to the literature [6]. The structures of these complexes are shown in Figure 2.



R = Me, L = Cl : $(acac)_2TiCl_2$

R = Me, L = OPh : $(acac)_2Ti(OPh)_2$

R = Ph, L = OPh : $(dbm)_2Ti(OPh)_2$

Figure 2. The structures of the β-diketonate titanium complexes

Polymerization and analytical procedures

To a 50 ml thermostatted flask were added 28.3 mg $(dbm)_2Ti(OPh)_2$, 10 ml of norbornene solution (0.4g/ml in toluene) and toluene to predetermined volume. The mixture was stirred until the $(dbm)_2Ti(OPh)_2$ dissolved and then MAO was added. After about an hour, the reaction was quenched with ethanolic hydrochloric acid. The insoluble polymer was kept in excess of 10 vol.-% ethanolic hydrochloric acid solution overnight and washed in turn with ethanol and water in a Büchner tunnel, separated and dried under vacuum at 80 °C.

The glass transition temperatures of the polymers were determined by DSC with a Perkin Elmer DSC-7 at a heating rate of 10 °C/min. FT-IR spectra were recorded on a Perkin- Elmer 2000 spectrometer at a scanning speed of 0.2 cm^{-1}/s. The ^1H NMR spectrum was recorded on a Bruker DMX-300 NMR spectrometer using TMS as an internal standard. The ^{13}C NMR spectrum was obtained with a Bruker DMX-300 NMR spectrometer (chloroform-d as the solvent). WAXD(wide angle X-ray diffraction) curves of the polymer powder was obtained using a RINT-2400 X-ray Diffractometer, with monochromatic radiation at a wavelength of 1.54Å. Scanning was performed with 2θ ranging from 3° to 60°.

Results and Discussion

The relationships between polymerization activity and polymerization conditions, such as Al/Ti molar ratio, polymerization temperature and solvents as well as catalyst composition are summarized in Table 1. It is clear that $(dbm)_2Ti(OPh)_2$ system possesses a higher activity than the other two catalysts and the highest activity is realized at 80°C. Moreover, the activity increases slightly with increasing Al/Ti ratio and monomer concentration. It should be noted that polymers precipitate rapidly in toluene, while in 1,2-dichlorobenzene they form a gel. The activity in 1,2-dichlorobenzene is higher than that in toluene.

Table 1. Results of norbornene polymerization [a)]

Catalyst	Temperature (°C)	[Ti] (10^{-3} mol • L^{-1})	Al/Ti (mol/mol)	Monomer concentration (mol • L^{-1})	Solvent	t (h)	Activity (kgPolymer/molTi • h)
1	90	2.083	100	2.128	toluene	2.083	2.746
2	90	2.083	100	2.128	toluene	2.083	3.200
3	90	2.083	100	2.128	toluene	2.083	3.400
3	80	0.83	500	0.851	toluene	2.083	1.413
3	80	0.83	100	0.851	toluene	2.083	1.125
3	80	0.83	40	0.851	toluene	2.083	1.089
3	80	2.083	100	2.128	toluene	2.083	3.642
3	80	2.083	100	2.128	C)	1[b)]	8.414
3	70	2.083	100	2.128	toluene	2.083	3.232
3	50	2.083	100	2.128	toluene	2.083	2.173
3	0	2.083	100	2.128	toluene	2.083	0.068

a). Catalysts: 1, $(acac)_2TiCl_2$; 2, $(acac)_2Ti(OPh)_2$; 3, $(dbm)_2Ti(OPh)_2$.

b). System gelification appeared after an hour, so the polymerization was stopped.

c). 1,2-dichlorobenzene

Selective extraction studies indicate that the polynorbornenes are almost insoluble in acetone, but partially soluble in toluene, 1,2-dichlorobenzene and chloroform. To determine the structures of the polymers, ^{1}H NMR, ^{13}C NMR and FT-IR analyses are carried out.

The polymer was separated to two fractions, soluble (66.6%)and insoluble fractions(33.4%) in chloroform before the analyses. The chloroform soluble fraction was characterized by ^{1}H NMR and ^{13}C NMR spectra. The proton spectrum (Figure 3) peaks from 5.21 to 5.34 ppm indicate the presence of some unsaturated structures, which we believe arise from ring-opening polymerization chains. The resonances from 1 to 2.5 ppm much stronger than those from 5.21 to 5.34 show the presence of another structures resulting from 2,3-addition polymerization. Ring-opening polymerization are further confirmed by the ^{13}C NMR spectrum which contains peaks from 132 to 133 ppm, as shown in Figure 4. The peaks at 47, 38, 30 and 29 ppm are attributed to the backbone carbon, bridgehead carbon, one and two carbon bridges, respectively, according to addition polymer structures of norbornene [7]. The chloroform soluble fraction was inferred to contain the chain mixture of ring-opening (x=0.15) and addition (y=0.85) polymers.

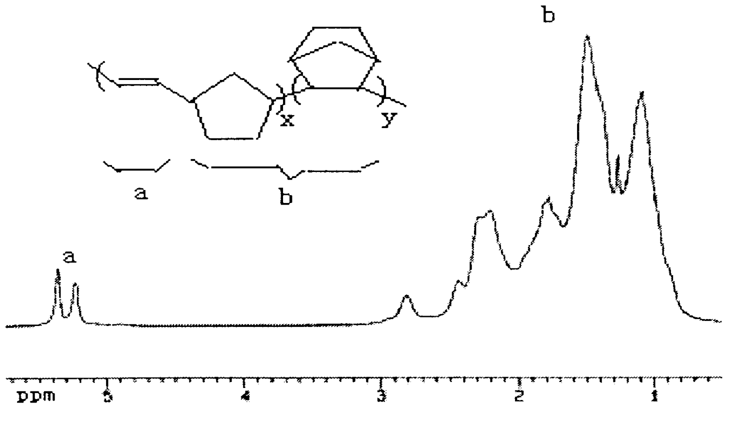


Figure 3. The ^{1}H NMR spectrum of the chloroform soluble fraction of polynorbornene

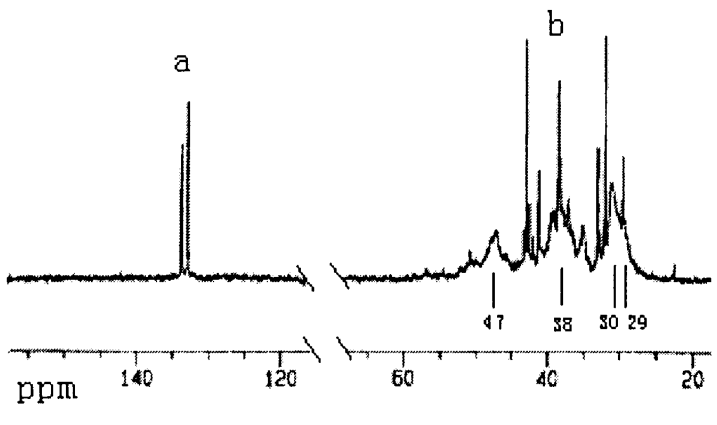


Figure 4. The ^{13}C NMR spectrum of the chloroform soluble fraction of polynorbornene

The FT-IR analysis was used to further characterize the polymer. The FT-IR spectra exhibit absorption bands at 730cm^{-1} and 960cm^{-1} which have been assigned to cis and trans double bonds, respectively, in vinylcyclopentane units resulting from ring-opening polymerization[3]. As shown in Figure 5, the fractions soluble and insoluble in chloroform both show the absorption near 960cm^{-1} and the absorption of the insoluble portion is slightly stronger than that of the soluble portion. Ring-opening polymer structures are included in both fractions and the insoluble fraction has more trans ring-opened structures and less or no addition structures comparing to the soluble fraction.

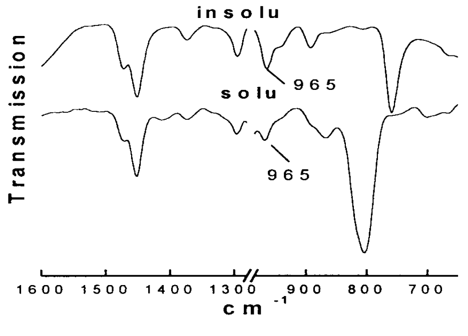


Figure 5. The FT-IR spectra of soluble and insoluble fractions in chloroform

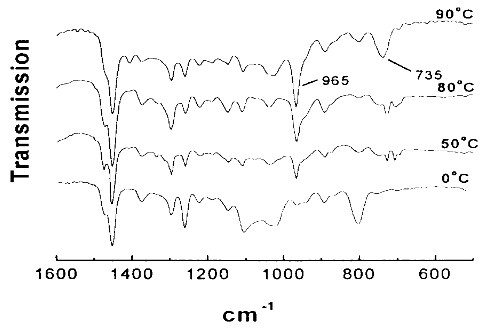


Figure 6. Influence of polymerization temperature on the polymer structures

The FT-IR analyses further indicate that the polymerization conditions influence the polymer structures, as seen from Fig 6~ 8. As the polymerization temperature decreases, the intensity of the two bands at 730cm^{-1} and 960cm^{-1} both become weaker (Figure 6), implying that ring-opening polymerization is less favorable at lower temperatures. A similar trend is noted when Al/Ti ratio is decreased (Figure 7). It is interesting to note that the polymer structures obtained in different solvents differ. As can be seen in Figure 8, the polymer prepared in toluene contains more trans-double bonds and the one obtained in 1,2-dichlorobenzene contains more cis-double bonds.

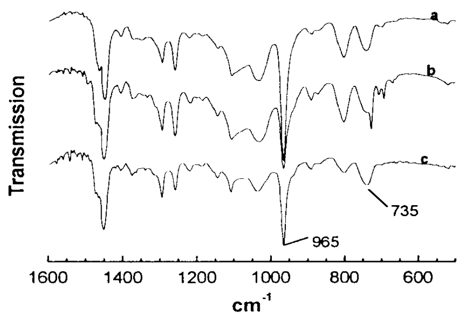


Figure 7. Influence of Al/Ti on the polymer structures

Al/Ti molar ratio : a. 500; b. 100; c. 40

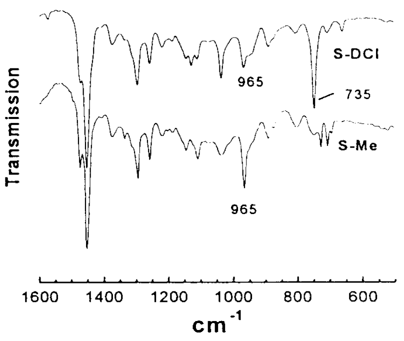


Figure 8 Influence of solvents on the polymer structures

S-DCl: 1,2-diclorobenzene as the solvent

S-Me: toluene as the solvent

The X-ray wide angle diagram (Figure 9) reveals the presence of two partially overlapped broad halo in the wide angle regime that can be attributed to a short range order and the polynorbornene is amorphous[8]. The DSC analysis shows that the polynorbornene exhibits the glass transition temperatures (Tg) in range of 330~400 °C, and decomposes without melting (Figure 10). Tg rises slightly with decreasing Al/Ti molar ratio, which may be attributed to increased content of saturated structures.

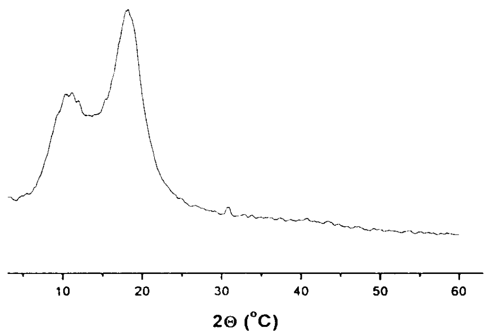


Figure 9 WAXD diagram of the polynorbornene

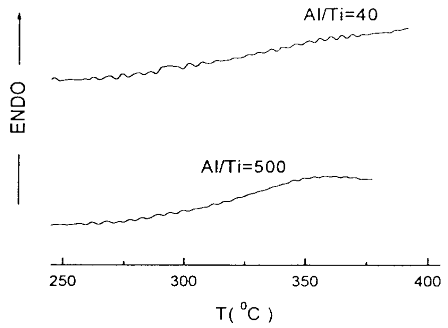


Figure 10. The glass transition temperatures of the polynorbornene

In conclusion, norbornene has been polymerized by β -diketonate titanium / MAO. NMR spectra and FT-IR spectra indicate that the resulting polynorbornene is confirmed to contain both addition and ring-opening (trans and cis) polymer chain structures. It is noted that lower polymerization temperatures and lower Al/Ti molar ratios are favorable to addition polymer structures. 1,2-Dichlorobenzene instead of toluene used as the polymerization solvent increases the activity and induces the polymer containing more cis-double bonds.

Acknowledgement

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