

Copolymerization of Tetracyclododecene or Norbornene with Styrene in the Presence of Ni(II) Complex/MAO Catalytic System: First Example for Transition Metal Catalyzed Copolymerization of Tetracyclododecene with Styrene

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ABSTRACT: The first example for transition metal catalyzed copolymerization of tetracyclododecene (TD) with styrene as well as of norbornene (NB) with styrene was achieved by the use of nickel(II) complex in the presence of MAO. High cyclic olefin contents of these copolymers were showed by ^1H NMR measurements. Their GPC curves are all unimodal and M_w/M_n ratio of both homo- and copolymer samples are rather narrow value. These results show that these homo- and copolymerization take place at a

single active site. The cyclic olefin content in these copolymers could be changed by changing the comonomer feed ratio. TD/styrene copolymers showed higher T_g value than that for NB/styrene copolymers and the T_g value were increases with an increase of TD content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1562–1565, 2008

Key words: copolymerization; metal-organic catalysts/organometallic; synthesis; polyolefins

INTRODUCTION

Cyclic olefin copolymers (COCs), have attracted much attention in the field of material chemistry because of its high glass transition temperature, high optical transparency, low moisture absorption, and low birefringence.^{1–4} Many examples for copolymerization of norbornene with α -olefin were reported so far,^{5–8} while other kinds of cyclic olefin were also used for the synthesis of copolymers to modify their physical properties.^{9–20} Tetracyclododecene (TD), which skeleton is rigid and bulky, is a potential monomer for novel copolymers with improved properties (Fig. 1). A copolymer of TD with styrene is expected to show higher T_g value than norbornene/styrene copolymer because the rotation of the polymer main chain is restricted due to their bulky structure of TD unit. However, reports for the synthesis of TD/ α -olefin copolymers are limited in number.^{21,22} Moreover, a transition metal catalyzed copolymerization of TD with styrene has not been reported in any literature, although various transition metal catalytic systems were utilized for the copolymerization of cyclic olefins with α -olefins.

In this article, we report effective copolymerizations of TD with styrene as well as of norbornene with styrene in the presence of nickel(II) complex bearing acyl hydrazone ligands and MAO. The nickel(II) complex was reported recently to show high catalytic activity for the homopolymerization of norbornene.²³

EXPERIMENTAL

General procedures

All manipulations were carried out under nitrogen atmosphere. All solvents were distilled over appropriate drying agents prior to use. Norbornene and styrene were distilled over CaH_2 and NaOH prior to use, respectively. TD was obtained from Mitsui Chemical Co. and was dried over activated aluminum oxide and degassed by N_2 bubbling before use. Other reagents employed in this research were used without further purification.

^1H NMR spectra were recorded on a JEOL AL-400 spectrometer at 25 or 110°C. Polymers for the NMR measurements were dissolved in 1,1,2,2-tetrachloroethane- d_2 or chloroform- d . The T_g values were recorded on a RIGAKU Thermo plus DSC 8260 and RIGAKU Thermo plus TG8120. Gel permeation chromatography was recorded on JEOL RI-2031 Plus Intelligent RI detector eluted with chloroform at 40°C using monodispersed polystyrene as the stand-

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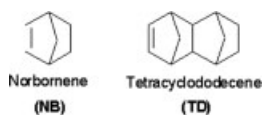


Figure 1 Norbornene and tetracyclododecene.

ard. High-temperature GPC analyses were carried out using a Waters Alliance GPC 2000 eluted with *o*-dichlorobenzene at 140°C using monodispersed polystyrene as the standard.

Synthesis of bis[*N*-(pyridine-2-carboxaldehyde)benzoylhydrazon]nickel(II) dibromide

Bis[*N*-(pyridine-2-carboxaldehyde)benzoylhydrazon]nickel(II) dibromide was prepared according to literature methods.²³ Bis[*N*-(pyridine-2-carboxaldehyde)benzoylhydrazon] (1290 mg, 6.2 mmol) was dissolved in CH₂Cl₂ (20 mL). A CH₂Cl₂ solution (30 mL) of NiBr₂(DME) (959 mg, 3.1 mmol) was added drop-wise. The mixture was stirred for 16 h at room temperature and nickel complex was precipitated. The precipitate was filtered, washed with CH₂Cl₂ and dried under reduced pressure. The nickel complex was obtained as yellow-green solid (1190 mg, 53%). ¹H NMR (DMSO-*d*⁶) δ 7.5–8.2 (m, 18H), 8.88 (s, 2H), 15.56 (s, 2H, NH).

Typical procedure for the homopolymerization and copolymerization catalyzed by Ni(II)/MAO system

Monomers were placed in a 100 mL of flask containing a magnetic stirrer bar, and then chlorobenzene was added. Chlorobenzene solution of nickel complex and MAO was added to this mixture and the reaction was carried out at 25°C. After the time indicated in the Table I, the solution was poured into

acidic methanol, filtered to collect the polymer. In case of homopolymerization of styrene, and copolymerization of norbornene/styrene and TD/styrene, solvent fractionation was carried out by the use of diethyl ether. Then, obtained white solid dried *in vacuo* at 60°C for 6 h to yield the polymer.

Formula used for the calculation of the cyclic olefin content in the copolymers

Norbornene content (mol %) in norbornene/styrene copolymer

$$\begin{cases} I_{\text{St}} = \frac{I_1}{5} \\ 3I_{\text{St}} + 10I_{\text{NB}} = I_0 \end{cases}$$

$$\text{NB content (mol \%)} = \left(1 - \frac{I_{\text{St}}}{I_{\text{St}} + I_{\text{NB}}}\right) \times 100$$

$$= \left(1 - \frac{I_{\text{St}}}{\frac{3I_1}{5} + \frac{(I_0 - 3I_1)}{10}}\right) \times 100$$

where *I*₁, integration value in phenyl region of styrene units; *I*₀, total of integration value in methylene protons of styrene units, and C–H, C–H₂ protons of norbornene units.

TD content (mol %) in TD/styrene copolymer

$$\begin{cases} I_{\text{St}} = \frac{I_1}{5} \\ 3I_{\text{St}} + 16I_{\text{TD}} = I_0 \end{cases}$$

$$\text{TD content (mol \%)} = \left(1 - \frac{I_{\text{St}}}{I_{\text{St}} + I_{\text{TD}}}\right) \times 100$$

$$= \left(1 - \frac{\frac{I_1}{5}}{\frac{3I_1}{5} + \frac{(I_0 - 3I_1)}{16}}\right) \times 100$$

TABLE I
Copolymerization of Tetracyclododecene or Norbornene with Styrene by Ni Complex/MAO^a

Entry	Cycloolefin	Monomer in feed		Time (h)	Yield (%)	Activity ^b	CO content ^c (mol %)	<i>M_n</i> ^d (10 ⁻⁴)	<i>M_w</i> / <i>M_n</i> ^d	<i>T_g</i> ^e (°C)
		CO (mol/L)	St (mol/L)							
1	–	0	1	1	46.7	144	–	1.9	1.9	100
2	NB	1	0	5 min	62.3	1400	100	11	3.9	n.d. ^f
3	NB	0.1	0.9	4	8.7	5.40	85.6	0.42	2.0	361
4	NB	0.5	0.5	4	22.7	15.0	90.1	0.76	2.5	336
5	TD	1	0	1	3.5	11.3	100	2.5	2.2	n.d. ^f
6	TD	0.1	0.9	24	4.7	0.342	64.4	0.28	1.6	356
7	TD	0.3	0.7	24	14.9	1.16	88.6	0.52	2.1	360 ^g
8	TD	0.5	0.5	24	29.7	2.47	93.2	0.81	2.9	388 ^g

^a Polymerization conditions: total volume = 25 mL, solvent = chlorobenzene, Ni = 12.5 μmol, Al/Ni = 500, Temperature = room temperature.

^b Activity = kg_(poly)mol_(Ni)⁻¹h⁻¹.

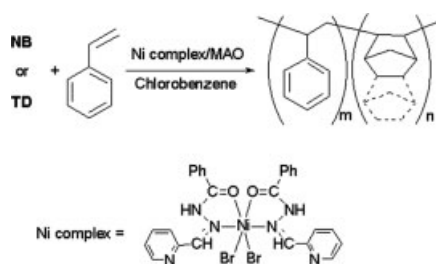
^c Determined by ¹H NMR.

^d Determined by GPC.

^e Determined by DSC.

^f Not detected.

^g Determined by TG-DTA.



Scheme 1 Copolymerization of cycloolefin with styrene.

where I_1 , integration value in phenyl region of styrene units; I_0 , total of integration value in methylene protons of styrene units, and C—H, C—H₂ protons of TD units.

RESULTS AND DISCUSSION

Copolymerization of norbornene with styrene

The copolymerization of norbornene with styrene was conducted using nickel(II) complex bearing acyl hydrazone ligands (bis[*N*-(pyridine-2-carboxaldehyde)benzoylhydrazone]nickel(II) dibromide) in the presence of MAO (Scheme 1). The results and polymerization conditions are summarized in Table I.

In case of styrene homopolymerization, high catalytic activity was observed at room temperature for 1 h (144 kg_(poly)mol⁻¹(Ni)⁻¹h⁻¹) (entry 1). Homopolymerization of norbornene result in the formation of polynorbornene with high catalytic activity than in case of homopolymerization of styrene (activity for homopolymerization of norbornene: 1400 kg_(poly)mol⁻¹(Ni)⁻¹h⁻¹) (entry 2). On the reaction conditions of norbornene and styrene feed ratio 0.1 : 0.9 in the presence of nickel(II) complex and MAO, the copolymerization of norbornene and styrene proceeded (entry 3). High norbornene content of the copolymer (85.6%) was showed by ¹H NMR spectroscopic measurement (Fig. 2). In case of norbornene and styrene feed ratio 0.5 : 0.5, the norbornene content of the obtained copolymer reached 90.1% (entry 4). M_w/M_n of norbornene/styrene copolymers showed rather narrow value (2.0 (entry 3); 2.5 (entry 4)). As shown in Table I, the activities of copolymers are lower than that of homopolymer of styrene or norbornene and decrease with an increase in the styrene feed content (entries 3 and 4). Moreover, molecular weight (M_n) of the copolymers are low and dependent on styrene feed content. These results suggest that the styrene monomer play a significant role in the chain termination reaction.²⁴ These experimental results are similar to the results reported in the literature.^{15–20} T_g values increases with an increase of norbornene content from measurement of DSC (nor-

bornene content 85.6% (entry 3): 261 °C; norbornene content 90.1% (entry 4): 336°C).

Copolymerization of TD with styrene

Next, the copolymerization of TD with styrene in the presence of the nickel(II) complex/MAO catalytic system was investigated. The results and polymerization conditions are also summarized in Table I (entry 5–8). The nickel(II) complex showed high catalytic activity for the homopolymerization of TD and polytetracyclododecene was obtained as white powder (activity: 11.3 kg_(poly)mol⁻¹(Ni)⁻¹h⁻¹) (entry 5). The ¹H NMR spectrum of polytetracyclododecene in 1,1,2,2-tetrachloroethane-d₂ at 110°C displayed broad signals at 0.5–3.0 ppm that were assignable to the protons on the cyclic unit. The nickel(II) catalyst system also exhibits catalytic activity for the copolymerization of TD with styrene. On the copolymerization of TD with styrene in various monomer feed ratio (TD/styrene = 0.1 : 0.9–0.5 : 0.5), copolymers with different TD contents were obtained (entry 6–8). In ¹H NMR measurements of these copolymers, broad signals that are assignable to the phenyl protons of styrene unit were observed at 6.2–7.5 ppm in addition to signals derived from TD (Fig. 3). The TD content in the copolymers could be changed by changing the comonomer feed ratio (64.4–93.2 mol % (entry 6–8)). Their GPC curves are all unimodal and M_w/M_n ratio of both homo- and copolymer samples are rather narrow value (1.6–2.9 (entry 5–8)). These results show that homopolymerization of tetracyclododecene and copolymerization of TD with styrene take place at a single active site.^{15–20} The relation among styrene feed ratio, activity and molecular weight of TD/styrene copolymer are similar to the result of copolymerization between TD with styrene. T_g value in the copolymers (356–388°C)

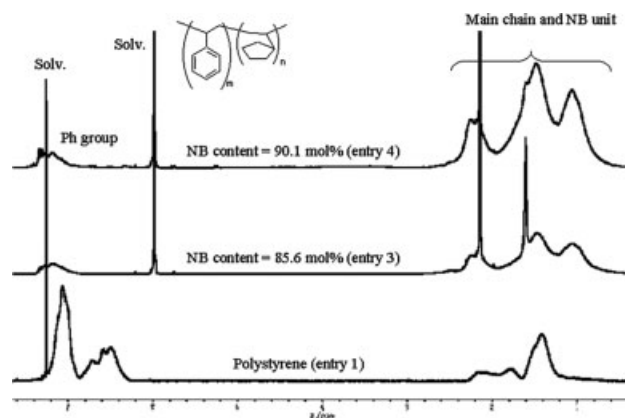


Figure 2 ¹H NMR spectra of norbornene/styrene copolymers.

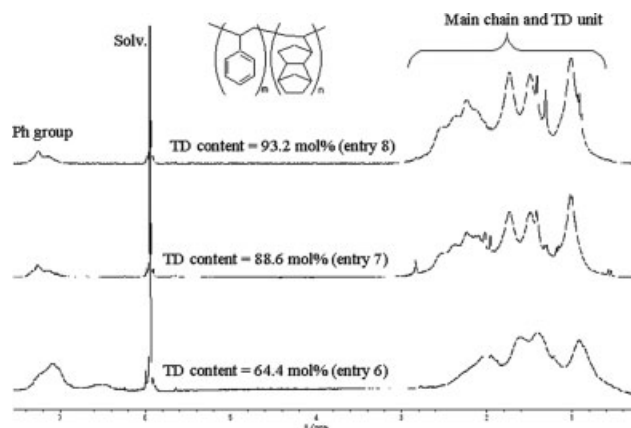


Figure 3 ^1H NMR spectra of tetracyclododecene/styrene copolymers.

were higher than that for norbornene/styrene copolymers and increases with an increase of TD content.

The $\text{Ni}(\text{acac})_2/\text{MAO}$ system is effective for the copolymerization of norbornene with styrene.²⁵ However, attempt for copolymerization of TD with styrene by the use of $\text{Ni}(\text{acac})_2/\text{MAO}$ system result in the formation of trace amounts polymer. The result indicate that the nickel(II) acyl hydrazone complex/MAO system is suitable nickel(II) catalyst for homopolymerization of TD and for copolymerization of TD with styrene.

CONCLUSIONS

In summary, we have demonstrated that the copolymerization of TD with styrene as well as norbornene with styrene by the use of nickel(II) acyl hydrazone complex. First example for transition metal catalyzed homopolymerization of TD and copolymerization of TD with styrene were achieved. TD/styrene copolymers showed higher T_g value than norbornene/styrene copolymers. These results demonstrate that TD is of potentials as useful monomer for synthesis of novel copolymers in the field of material chemistry.

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