Ring-Opening Metathesis Polymerization and Hydrogenation of
Ethyl-substituted Tetracyclododecene

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Ring-opening metathesis polymerization (ROMP) of an ethyl-substituted tetracyclododecene (8-ethyl-tetracyclo[4.4.0.1^2,5.1^7,10] dodec-3-ene, Et-TCD) was carried out in the presence of a ternary catalyst system consisting of WCl_6, triisobutyl aluminium (iso-Bu_3Al), and ethanol. The optimal molar ratio of Et-TCD/WCl_6/iso-Bu_3Al/ethanol was found as 500/1/3/2 at which the yield of ring-opened polymer was 100%. 1-Hexene was shown to be an effective molecular weight controlling agent for ROMP reaction of Et-TCD. The hydrogenation of the ring opened polymer (p-Et-TCD) was conducted successfully using Pd(5 wt %)/γ-Al_2O_3 at 80 °C for 1 h. Chemical structures of p-Et-TCD and its hydrogenated product(H_2-p-Et-TCD) were characterized using 2D NMR techniques (^1H-^1H COSY and ^1H-^13C HSQC). The changes of physical properties such as thermal stability, glass transition temperature and light transmittance after the hydrogenation were also investigated using TGA, DSC, and UV.

Key Words : Ring-opening metathesis polymerization (ROMP), Hydrogenation, 2D NMR technique, Tetra-cyclododecene

Introduction

Cycloolefin polymers (COPs) have found wide variety applications in the areas of optical lenses, pharmaceutical packaging films, semiconductors, and liquid crystal displays (LCDs), due to their many excellent physical properties such as outstanding transparency, low birefringence, high heat resistance, and low water absorptivity.1-4

Currently, COPs are being produced industrially from a two-step process involving ring opening metathesis polymerization (ROMP) of cycloolefins, Diels-Alder products between olefins and cyclopentadiene (CPD), and consequent hydrogenation (Scheme 1 & Scheme 2).5,6 The hydrogenation of ROMP polymers is required, because the presence of double bonds in the polymer backbone deteriorates the thermal, light, and oxidation stability.

Since the first discovery of the ROMP process in the 1960s, extensive effort has been devoted to developing efficient catalysts for this unique polymerization process and to understanding the underlying mechanism. Accordingly, a number of papers have been published on the catalysts and mechanisms for various ROMP processes including W, Ti, Mo, and Ru complexes.7-9 On the other hand, the hydrogenation of ROMP polymers has rarely been investigated in detail, despite that it is an essential process for the practical application of ROMP polymers.

Ru complexes such as RuHCO(Cl)(PPh)_3, RuCl_2(PPh)_3, RuCl_2(PPh)_4 and third-generation Grubbs catalyst were reported as homogeneous catalysts for the hydrogenation of ROMP polymers.4,10-12 In spite of high activity of these catalysts, Ru-catalyzed hydrogenation has a serious drawback in terms of product purification due to contamination by hard-to-remove Ru complexes and low molecular weight side products formed from the polymer chain scission reaction.13 For instance, it was known that the transparency and adhesion property of the COPs are significantly deteriorated by small amounts of catalyst residues in the hydrogenated COPs.14

To circumvent the problems associated with homogeneous catalysis, the use of Ni- and Pd-based heterogeneous catalysts were reported for the hydrogenation of ring-opened poly cyclo-olifins.15-18 However their hydrogenation catalytic activities were too low for industrial uses. For example, Register et al. reported the hydrogenation of ring-opened polynorborene using a Pd(5 wt %)/support and showed that the reaction completely proceeded at reaction condition of...
H isobutylaluminum (γ-Al₂O₃) were purchased from Aldrich Chemicals Co. ethanol (anhydrous), 1-hexene (anhydrous), and cyclohexane traces of water present. Ni/2/1.
tetracyclododecene (8-ethyl-tetracyclo[4.4.0.1\(-2,5\).1\(-7,10\)]dodec-3-ene (Et-TCD)).

100 °C for 48 h with a polymer/catalyst weight ratio of 1/1-2/1.17,18

Although the use of a sacrificial hydrogenation reagent such as p-toluene sulphonic acid has been studied for the hydrogenation of a ring-opened polymer of norbornene, its application in industrial areas is basically impractical.19-20

With the hope of gaining insight into directions for the development of high performance heterogeneous catalysts ROMP polymers, we carried out a detailed investigation of various factors affecting the hydrogenation reactions of the ROMP polymer (p-Et-TCD) obtained from ethyl-substituted tetracyclododecene (8-ethyl-tetracyclo[4.4.0.1\(-2,5\).1\(-7,10\)]dodec-3-ene (Et-TCD)) (Fig. 1).

Herein, we report in detail on the synthesis of p-Et-TCD and its hydrogenated polymer, H₂-p-Et-TCD as well as characterization of both products.

**Experimental**

All reagents including tungsten hexachloride (WCl₆), triisobutylaluminium (iso-But₃Al, 1 M solution in hexane), ethanol (anhydrous), 1-hexene (anhydrous), and cyclohexane (anhydrous) were purchased from Aldrich Chemicals Co. and used as received without further purification. Ru/C, Ru/γ-Al₂O₃, and Raney nickel were obtained from Aldrich Chemicals Co. and dried under vacuum at 120 °C to remove traces of water present. Ni/γ-Al₂O₃ (65% Ni) was purchased from Degussa. Et-TCD (purity > 98%) was donated from Kolon Industry and distilled over Na/K alloy before use.

**Ring Opening Metathesis Polymerization of Et-TCD.** ROMP of Et-TCD was conducted in similar manner to that reported previously.21 Inside a glove box (O₂ < 1 ppm and H₂O < 1 ppm), 1.88 g of purified Et-TCD (10 mmol) and 40 mL of anhydrous cyclohexane was added to a 100 mL round bottomed flask. Next, 1-hexene (0.1 mmol), iso-But₃Al (0.06 mmol), ethanol (0.06 mmol), and WCl₆ (0.02 mmol) were successively added to the monomer solution with a vigorous stirring. After the reaction was conducted at room temperature for 1 h, the resulting viscous solution was poured into a 500 mL beaker containing an excess amount of isopropl alcohol (200 mL) to isolate p-Et-TCD. White precipitates were collected and dried under vacuum (1.84 g, 98%).

**Hydrogenation of ROMP Polymer.** Romp polymer of Et-TCD, p-ET-TCD (1 g), cyclohexane (40 mL) as a hydrogenation solvent and an appropriate catalyst were charged into a 100 mL Parr reactor equipped with a magnet driven stirrer and an electrical heater. The reactor was flushed with nitrogen three times and pressurized with hydrogen to about 3.4 MPa. The reactor was then heated with agitation to a specified reaction temperature. The pressure inside the reactor was maintained at 3.4 MPa by means of H₂ reservoir equipped with a high pressure regulator. After the reaction was completed, the reactor was cooled to room temperature and vented, and the product mixture was filtered to remove the catalyst. The resulting filtrate was poured into a beaker containing isopropanol (200 mL) to precipitate H₂-p-Et-TCD as white solid. The degree of hydrogenation of the resulting polymer was calculated based on the 1H NMR spectra recorded on a Varian Unityplus (300 MHz).

**Characterization of p-Et-TCD and H₂-p-Et-TCD.** Chemical structures and cyclic monomer contents of polymers were characterized using NMR spectroscopy. All of these NMR spectra of p-Et-TCD, 13C-DEPT of p-Et-TCD and H₂-p-Et-TCD were measured on a Bruker Avance 600 (600 MHz). The polymers were dissolved in deuterated chloroform (CDCl₃), which was used as a lock as a reference chemical shift versus tetramethylsilane, TMS. Two dimensional homonuclear correlation spectroscopy (2D 1H-1H COSY), two-dimensional heteronuclear single quantum coherence (2D 1H-13C HSQC), and 13C distortionless enhancement by polarization transfer (DEPT) NMR experiments were carried out to assign NMR peaks and to characterize the polymer structure.

The molecular weight and molecular weight distribution were measured on an Younglin gel permeation chromatography (GPC) equipped with a detector (RI-750F), pump (SP930D), and an oven (CTS30). For the analysis of the polymer, three Styragel HR4 columns (Waters, 7.8 mm × 300 mm) were connected and toluene was used as an eluent. The operating temperature and the flow rate of eluent were set at 35 °C and 1.0 L/min, respectively. Monodisperse polystyrene standards (Mw 1,000-200,000) were used to make a calibration curve.

Differential scanning calorimeter (DSC) measurement were performed using a Q10 DSC equipped with a refrigerated cooling system (RCS90), manufactured by TA Instruments (New Castle, DE). The glass transition temperatures (Tg) of the polymer samples were determined during the 1st and 2nd scan at a 10 °C/min heating rate.

Thermogravimetric analysis (TGA) was performed using TGA 2050 of TA instruments from room temperature to 600 °C at a scan rate of 5 °C/min under nitrogen.

For the measurement of light transmittance of the polymer, polymer film was prepared by dissolving 0.5 g polymer powder in 4.5 mL cyclohexane, and the solution was poured on a 10 cm ID petri dish. Slow solvent evaporation left a transparent film with a thickness was 60 ± 5 μm. Light transmittance of the polymer film was measured using UV (Cary 5000, Varian) at the range of 200-600 nm.

**Results and Discussion**

**ROMP of Et-TCD.** In a previous paper, we reported on a catalytic system consisting of WCl₆, iso-But₃Al, and EtOH, and showed that it was highly effective for the ROMP polymerization of tetracyclo[4.4.0.1\(-2,5\).1\(-7,10\)]dodec-3-ene (TCD). The yield of the ROMP polymer and the degree of gel formation were significantly affected by the concent-
The same catalytic system was also employed for the ROMP polymerization of Et-TCD and the catalyst composition was optimized. The molar ratio of Et-TCD/WCl<sub>6</sub> was fixed at 500. As shown in Table 1, the yield of p-Et-TCD reached 100% when the molar ratio of WCl<sub>6</sub>/iso-Bu<sub>3</sub>Al/EtOH/1-hexene was 1/3/2/5. Any variation of the catalyst composition resulted in a reduction of p-Et-TCD yield or caused gelation. For instance, the yield of p-Et-TCD was decreased significantly by an increase of the amount of ethanol from 2 to 3 equivalents with respect to WCl<sub>6</sub>. By contrast, a decrease of the molar ratio of EtOH/WCl<sub>6</sub> from 2 to 1 resulted in the gel formation. A similar phenomenon was also observed when iso-Bu<sub>3</sub>Al/WCl<sub>6</sub> was varied while fixing the molar ratio of Et-TCD/WCl<sub>6</sub>/EtOH/1-hexene at 500/1/2/5. When the amount of iso-Bu<sub>3</sub>Al was increased from 3 to 4 eq., with respect to WCl<sub>6</sub>, complete gelation was observed. On the contrary, a decrease of the amount of iso-Bu<sub>3</sub>Al to 1 eq. resulted in poor p-Et-TCD yield. Taken together, it is concluded that the molar ratio of Et-TCD/WCl<sub>6</sub>/iso-Bu<sub>3</sub>Al/EtOH of 500/1/3/2 is the optimal catalyst composition for the synthesis of p-Et-TCD.

The effect of 1-hexene on the molecular weight and the glass transition temperature (Tg) of p-Et-TCD was also examined. As shown in Table 2, the weight-average molecular weight (Mw) and Tg were greatly affected by the molar ratio of Et-TCD/1-hexene. The largest Mw (5.3 × 10<sup>4</sup>) and the highest Tg (189.2 °C) were attained when the molar ratio of 1-hexene/Et-TCD was 0.005. Upon further increase of the molar ratio to 0.04, Mw and Tg of p-Et-TCD decreased to 1.4 × 10<sup>4</sup> and 168.0 °C, respectively. Polydispersity (Mw/Mn) of the resulting p-Et-TCD was found in the range 2.7-2.4, irrespective of the amount of 1-hexene used. It is worth to note that the Tg values of 168-189 °C measured for p-Et-TCD are 40-50 °C lower than those of 180-210 °C for the ROMP polymer prepared from TCD. This decrease in the Tg values of p-Et-TCD can be largely attributed to an increase of the free volume exerted by the substitution of an ethyl group on the tetracyclododecene unit.

### Table 1. ROMP reaction of Et-TCD using WCl<sub>6</sub>/iso-Bu<sub>3</sub>Al/EtOH catalyst system<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer/ WCl&lt;sub&gt;6&lt;/sub&gt;</th>
<th>iso-Bu&lt;sub&gt;3&lt;/sub&gt;Al/ WCl&lt;sub&gt;6&lt;/sub&gt;</th>
<th>EtOH/ WCl&lt;sub&gt;6&lt;/sub&gt;</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Gel content (%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>2</td>
<td>2</td>
<td>100</td>
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<td>500</td>
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</tr>
<tr>
<td>6</td>
<td>500</td>
<td>3</td>
<td>1</td>
<td>100</td>
<td>48.6</td>
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<sup>a</sup>Reaction condition: Et-TCD 10 mmol, WCl<sub>6</sub> 0.02 mmol, 1-hexene 0.1 mmol, cyclohexane 40 mL, room temp., 1 h. <sup>b</sup>Polymerization yield. <sup>c</sup>Gel content was obtained from the weight ratio of insoluble polymer in solvent to the synthesized polymer.

### Table 2. Effect of 1-hexene on ROMP reaction of Et-TCD<sup>d</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>WCl&lt;sub&gt;6&lt;/sub&gt;/iso-Bu&lt;sub&gt;3&lt;/sub&gt;Al/EtOH (molar ratio)</th>
<th>1-hexene/ monomer (molar ratio)</th>
<th>Mw (*10&lt;sup&gt;4&lt;/sup&gt;)</th>
<th>MWD</th>
<th>Tg (°C)</th>
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<tr>
<td>1</td>
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<td>0.005</td>
<td>5.35</td>
<td>2.7</td>
<td>189.2</td>
</tr>
<tr>
<td>2</td>
<td>1/3/2</td>
<td>0.01</td>
<td>3.79</td>
<td>2.4</td>
<td>182.6</td>
</tr>
<tr>
<td>3</td>
<td>1/3/2</td>
<td>0.02</td>
<td>2.11</td>
<td>2.6</td>
<td>173.5</td>
</tr>
<tr>
<td>4</td>
<td>1/3/2</td>
<td>0.04</td>
<td>1.41</td>
<td>2.5</td>
<td>168.0</td>
</tr>
</tbody>
</table>

<sup>d</sup>Reaction condition: Et-TCD 10 mmol, WCl<sub>6</sub> 0.02 mmol, cyclohexane 40 mL, room temp., 1 h.

**Figure 2.** Hydrogenation of p-Et-TCD using various catalysts. Metal content: Pd and Ru on support were 5 wt %. Ni on γ-Al<sub>2</sub>O<sub>3</sub> was 65 wt %. Reaction condition: Poly(Et-TCD) 1 g, cyclohexane 40 ml, catalyst 0.1 g, 500 psig, 80°C, 1 h. For Ni/γ-Al<sub>2</sub>O<sub>3</sub> and Raney nickel, hydrogenation was conducted at 160°C for 5 h.
polar solvent might enhance the hydrogenation activities of Pd/C and Pd/Al₂O₃. As shown in Table 3, the yield of H₂-p-Et-TCD was found to increase with increasing content of ethanol in cyclohexane up to 10 vol %, at which almost complete hydrogenation was achieved. Upon further increase of ethanol content to 20 vol %, however, the hydrogenation yield was drastically reduced to 48.5%, possibly due to the decreased solubility of p-Et-TCD in this solvent. The use of 10 vol % of EA, THF, or isopropanol as a co-solvent was also effective for improving the yield of H₂-p-Et-TCD up to around 90%. These results strongly indicate that both the solvent polarity and the solubility of p-Et-TCD are important factors in determining the activity of Pd/Al₂O₃.

**Pd Content and Reaction Time.** Effects of Pd content and reaction time on the hydrogenation were also examined at 80 °C and 3.4 MPa. The loading of Pd/γ-Al₂O₃ with respect to p-Et-TCD was fixed at 1 wt %. As listed in Table IV, the hydrogenation yield decreased with decreasing Pd content, whereas the yield of H₂-p-Et-TCD increased with an increase of the reaction time. The yields of H₂-p-Et-TCD were found as 37.6% for 0.5 wt % Pd/γ-Al₂O₃ and 67.2% for 1 wt % Pd/γ-Al₂O₃, respectively, which were considerably lower than that obtained with 5 wt % Pd/γ-Al₂O₃.

**Characterization of p-Et-TCD and H₂-p-Et-TCD.** The structures of p-Et-TCD and H₂-p-Et-TCD were elucidated using ¹H-¹³C HSQC, ¹H-¹H COSY, and ¹³C-DEPT NMR technique (Fig. 3, Fig. 4, and Supporting Information). The ¹H-¹H COSY spectrum in Figure 3(b) shows that the vinyl protons appeared at 5.5 ppm are correlated with the signals at 3.0 ppm and 2.7 ppm. These signals could be assigned to methine proton labeled as “4” and “5”. Through an analysis of the coupling between the protons in the ¹H-¹H COSY spectrum, all the proton signals are analyzed.

In the ¹H-¹³C HSQC spectrum of p-Et-TCD (Fig. 3(a)), the resonances at δ = 131.2 and 130.5 ppm could be assigned to the vinyl group and the peaks at δ = 12.5-29.2 ppm could be assigned to the ethyl group, “a” and “b”. ¹³C-DEPT (Supporting Information) shows that the peaks detected at 33.0, 37.2, 37.6, 38.1, 42.8, and 43.6 could be assigned to the methylene carbon and the peaks detected at the region of δ = 38-53 except the peaks of 42.8 and 43.6 ppm, which could be assigned to methyl carbon in the tricyclic ring unit.

H₂-p-Et-TCD was also analyzed using one and two dimensional NMR spectroscopy. ¹H and ¹³C NMR (Supporting Information) showed the vinyl carbon and proton which were detected at 131.3, 130.5 (¹³C) and 5.5 (¹H) ppm, disappeared completely with the appearance of new peaks at 30.5 (¹³C) and 1.39 (¹H) ppm after hydrogenation. Based on ¹³C-DEPT and ¹H-¹³C HSQC NMR spectra, carbon peaks appeared at 52.1, 51.0, 44.6, 43.6-42.4, 39.8, 39.7 and 37.9 ppm.
could be assigned to methine carbon and the peaks appeared at 25.3, 29.2, 29.7, 33.4, 37.3, 38.2, and 30.5 are methylene carbon. On the other hands, the signal at 12.7, 13.2, 25.3, and 29.2 ppm in the $^{13}$C spectra are assigned to the ethyl group substituted in the tricyclododecene ring.

Through an analysis of the coupling between the protons in the $^1$H-$^1$H COSY spectra, all the $^1$H NMR signals could also be unambiguously assigned to p-Et-TCD and H$_2$-p-Et-TCD. From the assignment of the proton signal, $^{13}$C-DEPT, and the correlation in the $^1$H-$^{13}$C HSQC spectra, the carbon signals are also unambiguously assigned as shown in Figs. 3 and 4.

Glass transition temperatures (Tg) of representative p-Et-TCD and H$_2$-p-Et-TCD samples were measured by DSC (Fig. 5). As mentioned earlier, the Tg of p-Et-TCD is reduced significantly upon hydrogenation to H$_2$-p-Et-TCD from 183.6°C to 132°C. The much higher Tg of p-Et-TCD than that of H$_2$-p-Et-TCD is ascribed to the restriction of chain mobility and rotation caused by the presence of double bonds. No melting endotherm was observed in the DSC thermograms of both polymers, indicating that p-Et-TCD and H$_2$-p-Et-TCD are amorphous.

The hydrogenation was also found to increase the thermal stability of the ROMP polymer, p-Et-TCD. TGA curves of p-Et-TCD and H$_2$-p-Et-TCD show that H$_2$-p-Et-TCD is thermally stable up to 420°C, whereas p-Et-TCD decomposes rapidly below 400°C (see Fig. 6).
Light transmittance is also enhanced by the hydrogenation. As shown in Fig. 7, the hydrogenated ROMP polymer, H$_2$-p-Et-TCD, showed higher transmittance than the ROMP polymer, p-Et-TCD, especially at wavelength shorter than 400 nm.

**Conclusion**

The proposed catalytic system, WCl$_6$/iso-Bu$_3$Al/EtOH, was highly effective for ROMP polymerization of Et-TCD and the optimal composition was found as Et-TCD/WCl$_6$/(iso-Bu)$_3$Al/EtOH of 500/1/3/2 in molar ratio. At this composition, the yield of p-Et-TCD reaches 100% and no gel formation is observed.

Hydrogenation p-Et-TCD was efficiently carried out in cyclohexane using Pd/C and Pd/$\gamma$-Al$_2$O$_3$ as catalysts. The catalytic activities of Pd/C and Pd/$\gamma$-Al$_2$O$_3$ were further increased when the hydrogenation was conducted in a mixed solvent of cyclohexane and ethanol. High quantitative yield of H$_2$-p-Et-TCD was attained when hydrogenation was conducted at 80 °C and 3.4 MPa of H$_2$ for 1 h with 5 wt % Pd/$\gamma$-Al$_2$O$_3$ in a mixed solvent consisting of 90% cyclohexane and 10% ethanol in volume ratio.

Instrumental analyses showed that the thermal stability and light transmittance of p-Et-TCD was greatly enhanced by the hydrogenation.

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**References**


