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

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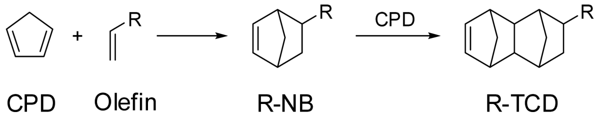
Ring-opening metathesis polymerization (ROMP) of an ethyl-substituted tetracyclododecene (8-ethyl-tetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$] dodec-3-ene, Et-TCD) was carried out in the presence of a ternary catalyst system consisting of WCl_6, triisobutyl aluminium (*iso*-Bu_3Al), and ethanol. The optimal molar ratio of Et-TCD/WCl_3/*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-^{13}C 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, Tetracyclododecene

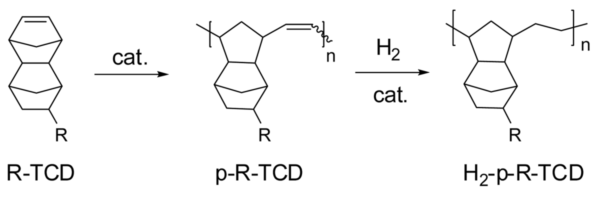
Introduction

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.



Scheme 1. Synthesis of alkyl-substituted tetracyclododecene *via* consecutive Diels-Alder reaction.



Scheme 2. ROMP polymerization and hydrogenation of alkyl-substituted tetracyclododecene.

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 $RuHCO(Cl)(PPh)_3$, $RuCl_2(PPh_3)_3$, $RuCl_2(PPh_3)_4$ 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 the 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-olfins.[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

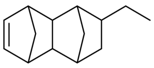


Figure 1. Structure of 8-ethyl-tetracyclo[4.4.0.$1^{2,5}$.$1^{7,10}$] dodec-3-ene (Et-TCD).

100 ºC 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*-toluenesulphonhydrazide 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, H_2-p-Et-TCD as well as characterization of both products.

Experimental

All reagents including tungsten hexachloride (WCl_6), tri-isobutylamluminum (*iso*-Bu_3Al, 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-Al_2O_3, and Raney nickel were obtained from Aldrich Chemicals Co. and dried under vacuum at 120 ºC to remove traces of water present. Ni/γ-Al_2O_3 (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 (O_2 < 1 ppm and H_2O < 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*-Bu_3Al (0.06 mmol), ethanol (0.06 mmol), and WCl_6 (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 isopropyl alcohol (200 mL) to isolate p-Et-TCD. White precipitates were collected and dried under vacuum (1.84 g, 98.0%).

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 H_2 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 H_2-p-Et-TCD as white solid. The degree of hydrogenation of the resulting polymer was calculated based on the ^{1}H NMR spectra recorded on a Varian Unityplus (300 MHz).

Characterization of p-Et-TCD and H_2-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, ^{13}C-DEPT of p-Et-TCD and H_2-p-Et-TCD were measured on a Bruker Avance 600 (600 MHz). The polymers were dissolved in deuterated chloroform ($CDCl_3$), which was used as a lock and as reference chemical shift versus tetramethylsilane, TMS. Two dimensional homonuclear correlation spectroscopy (2D ^{1}H-^{1}H COSY), two-dimensional heteronuclear single quantum coherence (2D ^{1}H-^{13}C HSQC), and ^{13}C 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 ºC/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 WCl_6, *iso*-Bu_3Al, 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-

Table 1. ROMP reaction of Et-TCD using WCl_6/*iso*-Bu_3Al/EtOH catalyst system[a]

Entry	Monomer/ WCl_6	*iso*-Bu_3Al/ WCl_6	EtOH/ WCl_6	Yield (%)[b]	Gel content (%)[c]
1	500	4	2	100	100
2	500	3	2	100	0
3	500	2	2	46.5	0
4	500	3	4	28.9	0
5	500	3	3	56.3	0
6	500	3	1	100	48.6

[a]Reaction condition: Et-TCD 10 mmol, WCl6 0.02 mmol, 1-hexene 0.1 mmol, cyclohexane 40 mL, room temp., 1 h. [b]Polymerization yield. [c]Gel content was obtained from the weight ratio of insoluble polymer in solvent to the synthesized polymer.

ration of each component.[21]

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_6 was fixed at 500. As shown in Table 1, the yield of p-Et-TCD reached 100% when the molar ratio of WCl_6/*iso*-Bu_3Al/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_6. By contrast, a decrease of the molar ratio of EtOH/WCl_6 from 2 to 1 resulted in the gel formation. A similar phenomenon was also observed when *iso*-Bu_3Al/WCl_6 was varied while fixing the molar ratio of Et-TCD/WCl_6/EtOH/1-hexene at 500/1/2/5. When the amount of *iso*-Bu_3Al was increased from 3 to 4 eq. with respect to WCl_6, complete gelation was observed. On the contrary, a decrease of the amount of *iso*-Bu_3Al to 1 eq. resulted in poor p-Et-TCD yield. Taken together, it is concluded that the molar ratio of Et-TCD/ WCl_6/*iso*-Bu_3Al /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 × 10^4) 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 × 10^4 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 2. Effect of 1-hexene on ROMP reaction of Et-TCD[a]

Entry	WCl_6/*iso*-Bu_3Al/EtOH (molar ratio)	1-hexene/ monomer (molar ratio)	Mw (× 10^4)	MWD	Tg (°C)
1	1/3/2	0.005	5.35	2.7	189.2
2	1/3/2	0.01	3.79	2.4	182.6
3	1/3/2	0.02	2.11	2.6	173.5
4	1/3/2	0.04	1.41	2.5	168.0

[a]Reaction condition: Et-TCD 10 mmol, WCl_6 0.02 mmol, cyclohexane 40 mL, room temp., 1 h.

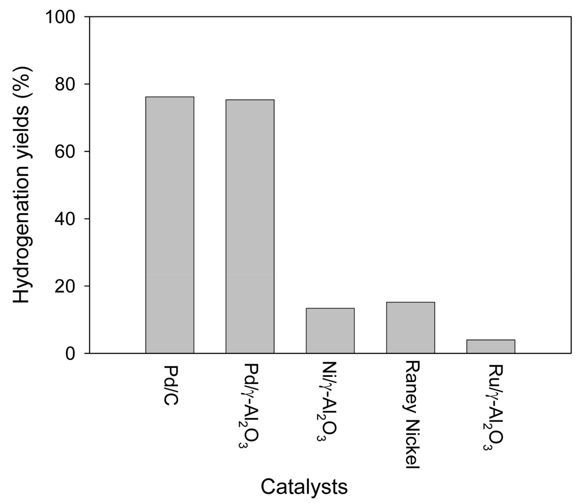


Figure 2. Hydrogenation of p-Et-TCD using various catalysts. Metal content: Pd and Ru on support were 5 wt %. Ni on γ-Al_2O_3 was 65 wt %. Reaction condition: Poly(Et-TCD) 1 g, cyclohexane 40 ml, catalyst 0.1 g, 500 psig, 80°C, 1 h. For Ni/γ-Al_2O_3 and Raney nickel, hydrogenation was conducted at 160°C for 5 h.

Hydrogenation of ROMP Polymer. Hydrogenation of p-Et-TCD was investigated using various commercially available hydrogenation catalysts (Fig. 2). The starting material, p-Et-TCD, was prepared from Et-TCD at the optimal condition of Et-TCD/WCl_6/*iso*-Bu_3Al/EtOH/1-hexene at 500/1/3/ 2/0.5. Hydrogenation was conducted at 80 °C for 1 h using cyclohexane as a solvent and the weight ratio of p-Et-TCD/ catalyst was set at 10. Among the catalysts tested, Pd/C and Pd/Al_2O_3 exhibited similarly high activities, producing H_2-p-Et-TCD in yields of 76.2 and 75.3%, respectively. By contrast, Ru/γ-Al_2O_3 produced H_2-p-Et-TCD in only 4.3% yield. Ni/γ-Al_2O_3 and Raney nickel produced H_2-p-Et-TCD in much lower yields of 13.4% and 15.2%, respectively, even at elevated temperature of 160 °C and longer reaction time of 5 h.

Effects of Solvent. The hydrogenation of an olefin using a supported Pd catalyst is commonly carried out in a polar solvent such as alcohol or a medium polar solvent such as tetrahydrofuran (THF) and ethyl acetate (EA).[22,23] However, in the case of hydrogenation of p-Et-TCD, polar and medium polar solvent cannot be used because of the extremely poor solubility of p-Et-TCD in these solvents. Although Pd/C or Pd/Al_2O_3 showed relatively high activities for the hydrogenation of p-Et-TCD in a cyclohexane solvent, their activities still need to be substantially improved. It is anticipated that the use of cyclohexane together with a polar or a medium

Table 3. Effect of polar solvent on the hydrogenation of p-Et-TCD[a]

Entry	Polar solvent	Polar solvent/ cyclohexane (vol%)	Hydrogenation Yields (%)
1	-	0	74.3
2	Ethanol	10	> 99
3	Ethanol	20	48.5
4	Ethanol	7.5	83.8
5	Ethanol	5	78.8
6	Ethyl acetate	10	90.0
7	Isopropanol	10	91.2
8	$CHCl_3$	10	33.1

[a]Reaction condition: poly (Et-TCD) 1 g, Pd(5 wt %)/γ-Al_2O_3 0.1 g, solvent 40 mL, 80 °C, 500 psig, 1 h.

polar solvent might enhance the hydrogenation activities of Pd/C and Pd/Al_2O_3. As shown in Table 3, the yield of H_2-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 H_2-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/Al_2O_3.

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-Al_2O_3 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 H_2-p-Et-TCD increased with an increase of the reaction time. The yields of H_2-p-Et-TCD were found as 37.6% for 0.5 wt % Pd/γ-Al_2O_3 and 67.2% for 1 wt % Pd/γ-Al_2O_3 respectively, which were considerably lower than that obtained with 5 wt % Pd/γ-Al_2O_3.

Characterization of p-Et-TCD and H_2-p-Et-TCD. The structures of p-Et-TCD and H_2-p-Et-TCD were elucidated using ^{1}H-^{13}C HSQC, ^{1}H-^{1}H COSY, and ^{13}C-DEPT NMR technique (Fig. 3, Fig. 4, and Supporting Information). The ^{1}H-^{1}H 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 ^{1}H-^{1}H COSY spectrum, all the proton signals are analyzed.

Table 4. Effect of catalyst amount and reaction time on the hydrogenation of p-Et-TCD[a]

Entry	Pd content on γ-Al_2O_3 (wt %)	Catalyst/ polymer (wt/wt)	Reaction time (min)	Hydrogenation Yield (%)
1	0.5	0.1	60	37.6
2	1	0.1	60	67.2
3	1	0.1	180	> 99
4	5	0.1	15	70.3
5	5	0.1	30	82.5
6	5	0.1	60	> 99
7	5	0.05	60	52.4

[a]Reaction condition: poly (Et-TCD) 1 g, solvent 40 mL, 80 °C, 500 psig, 1 h.

In the ^{1}H-^{13}C 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". ^{13}C-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 methine carbon in the tricyclic ring unit.

H_2-p-Et-TCD was also analyzed using one and two dimensional NMR spectroscopy. ^{1}H and ^{13}C NMR (Supporting Information) showed the vinyl carbon and proton which were detected at 131.3, 130.5 (^{13}C) and 5.5 (^{1}H) ppm, disappeared completely with the appearance of new peaks at 30.5 (^{13}C) and 1.39 (^{1}H) ppm after hydrogenation. Based on ^{13}C-DEPT and ^{1}H-^{13}C HSQC NMR spectra, carbon peaks appeared at 52.1, 51.0, 44.6, 43.6-42.4, 39.8, 39.7 and 37.9

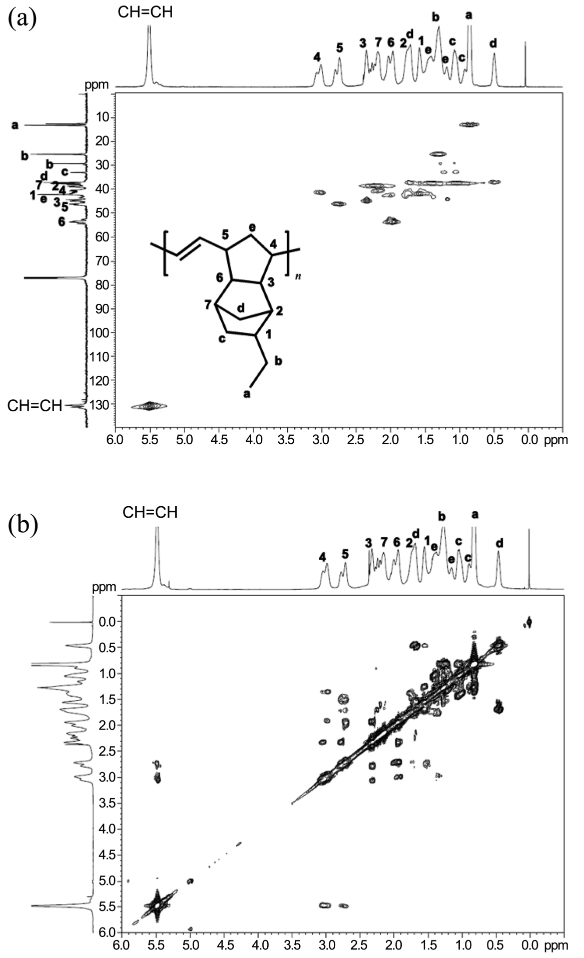


Figure 3. (a) ^{1}H-^{13}C HSQC and (b) ^{1}H-^{1}H COSY spectra of p-Et-TCD.

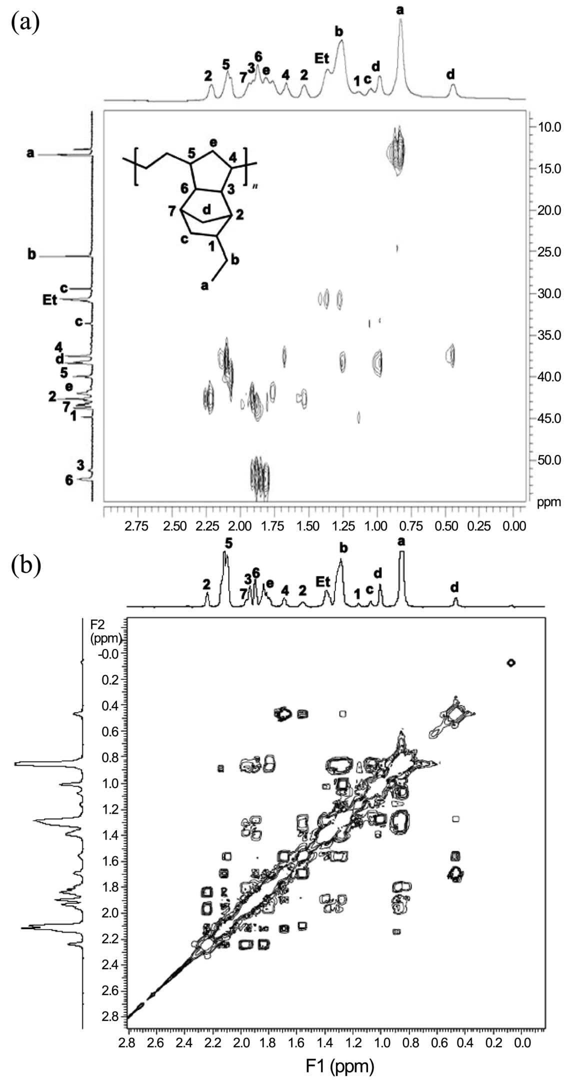


Figure 4. (a) ^{1}H-^{13}C HSQC and (b) ^{1}H-^{1}H COSY spectra of H_2-p-Et-TCD.

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-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.

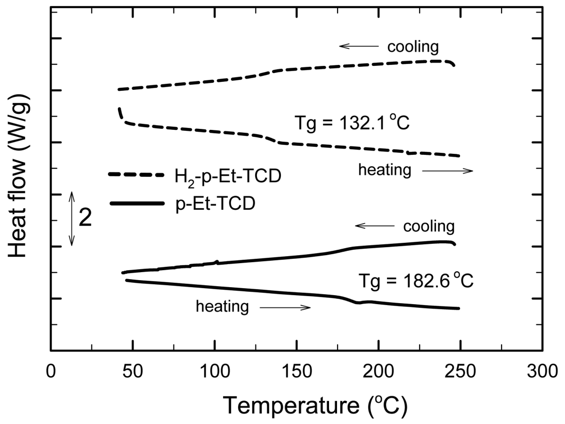


Figure 5. DSC thermogram of p-Et-TCD and H_2-p-Et-TCD.

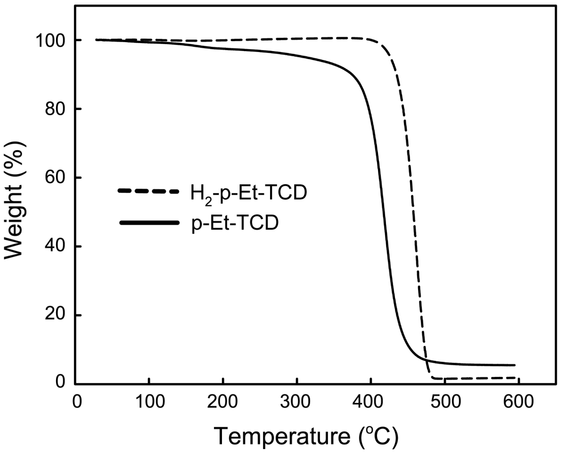


Figure 6. Thermogravimetric analyses of p-Et-TCD and H_2-p-Et-TCD.

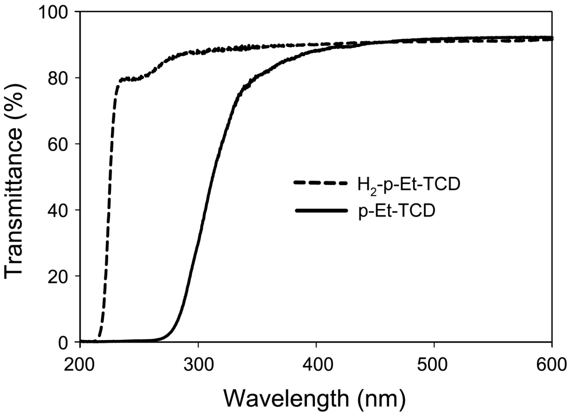


Figure 7. Light transmittance of p-Et-TCD and H_2-p-Et-TCD.

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_3Al/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/γ-Al_2O_3 as catalysts. The catalytic activities of Pd/C and Pd/γ-Al_2O_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/γ-Al_2O_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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