

# Synthesis of cyclic olefin polymers with high glass transition temperature and high transparency using tungsten-based catalyst system

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## ABSTRACT

Novel cyclic olefin polymers (COPs) derived from bulky cyclic olefins, tricyclodipentadiene (TCPD) and tricyclo[6.4.0.19,12]-tridec-10-ene (TTE), with high glass transition temperature ( $T_g$ ), excellent thermal stability, and high transparency, have been synthesized by ring-opening metathesis polymerization (ROMP) and subsequent hydrogenation. ROMP of TCPD and TTE was carried out successfully without gel formation using a  $WCl_6/i-Bu_3Al/Et-OH$ /hexene catalyst system at room temperature. By changing the TCPD/TTE molar ratio, the optimized catalyst component ratio for the polymerization varied. Chemical structures of the unsaturated and hydrogenated polymers were characterized by  $^1H$  NMR technique. Thermal properties of these newly synthesized polymers were determined using TGA and DSC measurements. The degradation temperatures ( $T_d$ ) were all above 420°C in  $N_2$ , indicating that all these copolymers had excellent thermal stability. After hydrogenation,  $T_g$  of ROMP polymers was decreased by 30–60°C. The  $T_g$  of h-pTCPD reached as high as about 230°C. The light transmittances of these polymer films were also analyzed using UV-Vis absorption spectroscopy. A high light transmittance of up to 92% was found by UV-Vis absorption spectra for these polymer films. **Polyolefins J (2018) 5: 15-22**

**Keywords:** Ring-opening metathesis polymerization; cyclic olefin polymer; norbornene derivatives; tungsten; glass transition temperature.

## INTRODUCTION

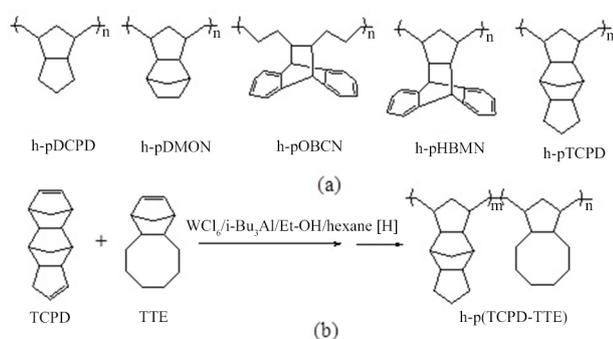
Cyclic olefin polymers (COPs), a kind of high performance thermoplastic engineering plastics, are synthesized through ring-opening metathesis polymerization (ROMP) of norbornene derivatives and subsequent hydrogenation [1-3]. COPs have received great attention primarily because they possess attractive properties such as excellent transparency, low birefrin-

gence, low density, high thermal stability, low shrinkage and low moisture absorption [4]. Considering these advantages, COPs have been extensively used in plastic lenses, optical storage media, drug packaging, prefilled syringes, and so on [2]. Among various performance parameters of COPs, a high  $T_g$  is the most critical one as it influences the thermal stability of COPs and determines their end-uses [5]. To achieve high  $T_g$ , a monomer with large steric hindrance is necessary.

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The most common monomer is dicyclopentadiene (DCPD, Scheme 1). However, the  $T_g$  of its hydrogenated polymer is only about 95°C [4,6]. 1,4,5,8-Dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (DMON) which has been used for synthesizing COPs with high  $T_g$  of 173°C, is commercialized by ZEON corporation with brand name of ZEONEX [6]. Recently, Endo group reported a monomer based on cyclooctene skeleton, (5R,5aS,12R,Z)-5,5a,6,7,10,11,11a,12-octahydro-5,12-[1,2] benzenocycloocta[b]naphthalene (OBCN) [7]. This monomer was synthesized from cyclooctadiene and anthracene. While bulky structure was involved in the polymer backbone, the corresponding COP (h-pOBCN, Scheme 1) showed a relatively low  $T_g$  value of 112°C. This was because of the low content of cyclic structure mole fraction of 25 mol%. In most cases, the  $T_g$  of COPs is often below 180°C. Novel COPs with higher  $T_g$  are scarce. Recently, we have found a very useful monomer, exo-1,4,4a,9,9a,10-hexahydro-9,10(1',2')-benzeno-1,4-methanoanthracene (HBMN), which could be easily synthesized on a large scale from norbornadiene and anthracene [8]. The  $T_g$  of h-pHBMN was as high as ca. 220°C (Scheme 1) [9,10]. To the best of our knowledge, this value was the highest one among all the COPs previously reported.

Tricyclopentadiene (TCPD) is also a bulky monomer with five rings, which can be easily available by heating DCPD under reflux [11,12]. In present work, the homopolymerization (ROMP) of TCPD was first achieved using tungsten-based catalyst system. Compared with ruthenium (Ru)-based Grubbs catalysts, the commercially available tungsten-based catalyst system comprised of  $WCl_6/i-Bu_3Al$ /ethanol/1-hexene is



**Scheme 1.** (a) Typical polymeric structures of reported COPs; (b) Synthesis procedure of h-p(TCPD-TTE) in this research.

cheaper and more suitable for industrial applications. After hydrogenation, a novel COP with a very high  $T_g$  of 230°C was achieved. Moreover, to adjust the  $T_g$ , copolymerizations of TCPD and tricyclo[6.4.0.19,12]-tridec-10-ene (TTE) with various molar ratios were conducted. Under optimum conditions, all the polymerizations were performed successfully and no gel formation was observed.

## EXPERIMENTAL

### Materials

All work involving air and/or moisture sensitivity was carried out in an Mbraun glovebox or using the standard Schlenk technique. Anhydrous solvents used in this study were purified by a solvent purification system which was purchased from Mbraun. Chlorobenzene was dried by  $CaH_2$  before use. Dicyclopentadiene (97%) and cyclooctene (99%) were purchased from Aldrich and used without further purification. Norbornene (98%) and 1-hexene (98%) were also purchased from Aldrich and dried by  $CaH_2$  before use. Tripropylamine (TPA, 98%) and  $WCl_6$  (99%) were used as received from Alfa Aesar. Triisobutylaluminum ( $i-Bu_3Al$ , 99%) was purchased from Akzo Nobel Chemical Inc., and used without further purification. 4-Methylbenzenesulfonylhydrazide (TSH, 97%) was purchased from Acros.

### Characterizations

All  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Varian Unity-400 MHz spectrometer (400.0 MHz for  $^1H$ , 100.0 MHz for  $^{13}C$ ). The molecular weights (MWs) and molecular weight distributions (MWDs) of the polymer samples were determined at 150°C by a PL-GPC 220 type high-temperature gel permeation chromatography (GPC). 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min, and the calibration was made by polystyrene standard Easi-Cal PS-1 (PL Ltd.). Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Pyris 1 DSC instrument under a nitrogen atmosphere. The samples were heated and cooled down at a rate of 20°C/min. The glass transition temperature ( $T_g$ ) was taken from the

second heating run and was read as the midpoint of change in heat capacity. Thermogravimetric analyses (TGA) were performed with a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 20°C/min in nitrogen. The transparency of copolymer film was recorded on a Shimadzu UV-3600 spectrophotometer.

### Synthesis of tricyclopentadiene (TCPD)

Synthesis of TCPD was according to previous reports [11,13] with some modification. Dicyclopentadiene (320 g, 2.4 mol) and cyclopentadiene (160 g, 2.4 mol) were mixed in a bomb reactor and heated at 150°C under N<sub>2</sub> pressure of 20 bar for 12 h. Unreacted reactants were removed (380 g) through vacuum distillation. Then the residue was added into 1 L ethanol, and insoluble oligomeric compounds were filtered off. After the filtrate was stored in freezer for 3 h, the precipitate solid was collected by filtration (84 g). The collected solid was crystallized one more time using ethanol (840 mL) to give a pure compound (67 g, 67%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 5.98 (m, 2H), 5.68 (m, 1H), 5.52 (m, 1H), 3.00 (m, 1H), 2.76 (m, 2H), 2.42 (m, 1H), 2.36-2.22 (m, 2H), 2.21-2.10 (m, 2H), 2.08-1.92 (m, 3H), 1.32-1.20 (m, 1H), 1.18-1.12 (m, 1H), 0.84-0.72 (m, 1H). <sup>13</sup>C-NMR (100.4 MHz, CDCl<sub>3</sub>, δ): 136.45, 135.89, 132.12, 131.35, 56.04, 53.36, 47.24, 46.89, 44.84, 44.38, 42.78, 41.37, 40.45, 38.00, 31.46.

### Synthesis of tricyclo[6.4.0.19,12]-tridec-10-ene (TTE)

TTE was also synthesized according to previous report [14] with some modification. Dicyclopentadiene (155 g, 1.2 mol) and cis-cyclooctene (310 g, 2.8 mol) were mixed in a bomb reactor and heated at 200°C for 6 h. Unreacted cyclooctene was distilled first at about 140°C and then TTE was distilled to give about 144 g of a colorless liquid under reduced pressure. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 6.08 (s, 2H), 2.70(s, 2H), 2.35(s, 1H), 1.94 (m, 3H), 1.05-1.60 (m, 14H). <sup>13</sup>C-NMR (100.4 MHz, CDCl<sub>3</sub>, δ): 135.25, 51.50, 44.01, 31.10, 27.19, 26.72.

### Typical polymerization procedure

ROMP reaction was conducted in a glove box (O<sub>2</sub> < 1 ppm and H<sub>2</sub>O < 1 ppm) as reported [6,15,16]. A desired amount of TCPD and TTE (total: 6 mmol) was

mixed with 40 mL of anhydrous toluene in a 100 mL round bottomed flask. 0.06 mmol of 1-hexene (0.12 M in toluene), 0.03 mmol of *i*-Bu<sub>3</sub>Al (0.06 M in toluene), 0.024 mmol of Et-OH (0.2 M in toluene), and 0.012 mmol of WCl<sub>6</sub> (0.01 M in toluene) were added successively into this solution. The solution was stirred for 2 h at room temperature until a dark yellow viscous solution was formed. Then the polymer solution was diluted and poured into a large amount of ethanol. Finally, white precipitates were separated by filtration. The solid was dried under vacuum overnight below 30°C. The yields of isolated polymers were 100%.

### Typical hydrogenation procedure

The polymer (double bond: 6 mmol) and TSH (30 mmol) were weighed and transferred into a 100 mL round bottom flask. Toluene (30 mL) and TPA (35 mmol) were added together to obtain a heterogeneous mixture. The mixture was stirred and heated at 110°C under N<sub>2</sub>. After 16 h, the reaction was stopped upon cooling to room temperature. The mixture was poured into ethanol to obtain a white solid. After filtration, the solid was immersed into distilled water for 3 h, and then the polymer was washed with ethanol. The obtained white polymer was dried under vacuum at 50°C for 24 h. The yields of saturated polymers were over 95%.

### Typical procedure for film preparation

The saturated polymer was dissolved into chlorobenzene (10 wt%) in a 50 mL round-bottom flask, then the mixture was heated at 50°C for at least 10 h. After the complete dissolution, a thick and clear solution was filtered and spread on a glass plate in an oven with nitrogen atmosphere. The solvent in the spread film was carefully evaporated at 50°C for 12 h. Then the film was further dried in a vacuum oven at 80°C for another 12 h. After the evaporation, the thickness of obtained film was measured to be about 90-120 μm.

## RESULTS AND DISCUSSION

### Ring-opening metathesis polymerization and hydrogenation

WCl<sub>6</sub>/*i*-Bu<sub>3</sub>Al/Et-OH/hexene catalyst system is an ill-

defined catalyst system [17,18].  $WCl_6$ , as the central metal compound, is extremely sensitive to oxygen and moisture. However, the reactivity of this catalyst system is very high. Moreover, the activity can be tuned in a wide range by adjusting the feed ratio of  $WCl_6/i-Bu_3Al/Et-OH$ . Hexene acts as the chain transfer agent to tune the polymer's molecular weight. Compared with the traditional ruthenium-based catalyst, the  $WCl_6$ -based catalyst system is cheaper. The merits of commercial accessibility and economic advantages have made this catalyst system a feasible catalyst for industrial production of COPs. Thus, the  $WCl_6$ -based catalyst system was used in this research.

TCPD and TTE were prepared easily through Diels-Alder reaction. Note that TCPD has two types of double bond, one in the norbornene ring and the other in the five-membered ring. The norbornene-type double bond is more reactive than cyclopentene-type double bond because of its larger ring strain [19]. However, the cyclopentene-type double bond could also participate in polymerization by using the  $WCl_6$ -based catalyst system, resulting in crosslinking. To avoid gel formation, an optimized catalyst formula was needed. The comonomer TTE had been synthesized and used in our previous work [14]. Compared with DCPD, TTE has only one double bond. This would de-

crease the trend for crosslinking. Moreover, the bulky cyclooctene structure could increase the  $T_g$  of COP.

In this work, the molar ratio of monomers to  $WCl_6$  was fixed at 500. Ratio of monomer to 1-hexene was fixed at 100. All the polymerizations were terminated after 2 h. To achieve quantitative conversion and to avoid gel formation, the  $i-Bu_3Al/WCl_6$  and  $Et-OH/WCl_6$  ratios were changed to tune the catalyst activity.

For the homopolymerization of TCPD, when the ratio of  $WCl_6/i-Bu_3Al/Et-OH/hexene$  was 1/3/2/5, a polymer with about 45% gel content was obtained (entry 1, Table 1). Increasing the molar ratio of  $WCl_6/i-Bu_3Al$  from 1/3 to 1/2.5 could avoid the crosslinking (entry 2, Table 1). However, the yield was only 80% within 2 h. It was found that 100% monomer conversion and no gel formation could be achieved by decreasing the molar ratio of  $WCl_6/Et-OH$  from 1/2 to 1/3 (entry 3, Table 1). For the copolymerization of TCPD and TTE, when the feed ratio of TCPD/TTE was 3/1 (entry 4, Table 1), the  $WCl_6/i-Bu_3Al/Et-OH/hexene$  catalyst system with molar ratio of 1/2.5/2/5 was effective to achieve quantitative conversion and to avoid gel formation. For the copolymerization of TCPD and TTE with feed ratio of 1/1, we started the polymerization with  $WCl_6/i-Bu_3Al/Et-OH/hexene$  ratio of 1/1/1/5 (entry 5, Table 1). However, only

**Table 1.** ROMP Using  $WCl_6/i-Bu_3Al/Et-OH/hexene$  catalyst system <sup>(a)</sup>.

Entry	TCPD/TTE <sup>(b)</sup>	$WCl_6/i-Bu_3Al/Et-OH/hexene$ <sup>(b)</sup>	Yield (%) <sup>(c)</sup>	Gel content (%) <sup>(d)</sup>	Polymer code
1	100/0	1/3/2/5	100	45	pTCPD-1
2	100/0	1/2.5/2/5	80	0	pTCPD-2
3	100/0	1/3/3/5	100	0	pTCPD-3
4	75/25	1/2.5/2/5	100	0	p(TCPD <sub>3</sub> -TTE <sub>1</sub> )-1
5	50/50	1/1/1/5	Trace	0	p(TCPD <sub>1</sub> -TTE <sub>1</sub> )-1
6	50/50	1/1.5/1/5	100	90	p(TCPD <sub>1</sub> -TTE <sub>1</sub> )-2
7	50/50	1/2.5/2/5	100	10	p(TCPD <sub>1</sub> -TTE <sub>1</sub> )-3
8	50/50	1/2/2/5	100	0	p(TCPD <sub>1</sub> -TTE <sub>1</sub> )-4
9	25/75	1/2/2/5	100	0	p(TCPD <sub>1</sub> -TTE <sub>3</sub> )-1
10	0/100	1/2/2/5	63	0	pTTE-1
11	0/100	1/2/1.5/5	100	0	pTTE-2

<sup>(a)</sup> Reaction condition: room temperature, TCPD + TTE = 6 mmol, [monomers]/[ $WCl_6$ ] = 1000, [monomers]/[1-hexene] = 100, toluene = 40 mL, time = 2 h;

<sup>(b)</sup> Molar ratio;

<sup>(c)</sup> Polymer yield, precipitated from ethanol;

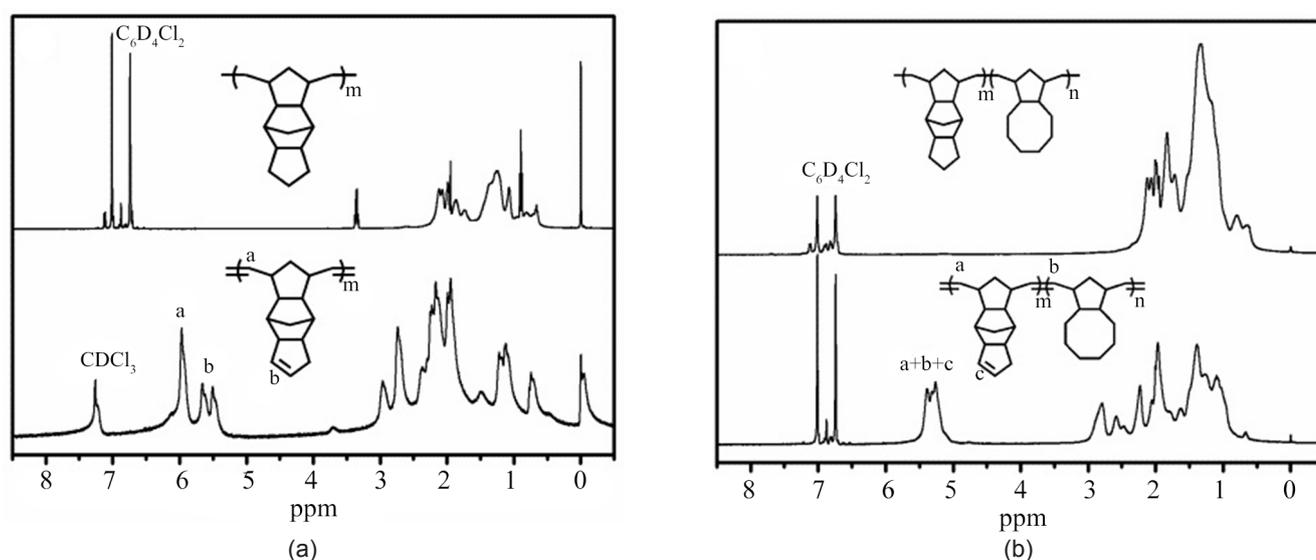
<sup>(d)</sup> Gel content was obtained from the weight ratio of insoluble polymer in solvent to the synthesized polymer.

a trace of polymer was attained. 100% yield was achieved by decreasing the molar ratio of  $WCl_6/i-Bu_3Al$  from 1/1 to 1/1.5 (entry 6, Table 1). Nevertheless, a serious gel formation of about 90% was found. To suppress gelation, the  $WCl_6/i-Bu_3Al/Et-OH/hexene$  ratio of 1/2.5/2/5, which was successful for the copolymerization of TCPD and TTE with a feed ratio of 3/1, was used again (entry 7, Table 1). Gelation was indeed restrained. Nonetheless, 10% gel content still existed. To suppress gelation completely, we further adjusted the catalyst component by decreasing the feeding of  $i-Bu_3Al$ . When the  $WCl_6/i-Bu_3Al/Et-OH/hexene$  ratio was 1/2/2/5, no gelation was observed, and the polymerization completed within two hours (entry 8, Table 1). Fortunately, the same catalyst component was also successfully applied to copolymerize of TCPD and TTE with a feed ratio of 1/3 (entry 9, Table 1). For the homopolymerization of TTE, the same catalyst component was applied again. While no gelation was found, the polymerization yield was only 63% (entry 10, Table 1). To increase the polymerization yield to 100%, the  $WCl_6/Et-OH$  ratio was increased from 1/2 to 1/1.5. Efficaciously, complete conversion was achieved. By elaborately adjusting the proportions of  $i-Bu_3Al$  and  $Et-OH$  in the polymerization process, a series of non-hydrogenated COPs with 100% yield and with no gel formation were synthesized. The codes of these polymers are also listed in Table 1. The copolymers were written in the form of

$p(TCPD_x-TTE_y)_n$ , where  $x$  and  $y$  indicated their feed molar ratio values of TCPD and TTE, respectively, and the  $n$  was corresponded to the serial number of one type polymer.

These novel polymers were characterized by  $^1H$  NMR. The  $^1H$  NMR spectra of pTCPD-3,  $p(TCPD_1-TTE_1)_4$ , and pTTE-2 are shown in Figure 1 and Figure S1. The peaks of the polymers became broader relative to those of monomers, and the peaks of double bonds overlapped with each other. The content of each monomer in the copolymer was difficult to be calculated due to the overlap of characteristic peaks. However, since the yield was 100%, the ratio of TCPD and TTE should be the same as the initial feed ratio. The molecular weights (MWs) and molecular weight distributions (MWDs) of these polymers were measured by GPC analysis. The GPC data of selected polymers are listed in Table 2. The molecular weights of these polymers were between  $2.6-5.6 \times 10^4$  Dalton, which were very close to the values of commercial samples. Their molecular weight distributions were relatively broad and their PDI values were between 2.69 and 3.83, which are typical for this W-based catalyst system.

Because of the presence of double bonds in the polymers, the hydrogenation reaction should be carried out immediately. Hydrogenation of the double bonds of ROMP products was generally carried out for the improvement of chemical and mechanical



**Figure 1.**  $^1H$  NMR spectra of unsaturated (bottom) and hydrogenated (top) polymers of (a) pTCPD-3 and (b)  $p(TCPD_1-TTE_1)_4$ .

**Table 2.** GPC and DSC data of selected polymers.

Entry	Polymer code	$M_n$ ( $\times 10^4$ ) <sup>(a)</sup>	PDI <sup>(a)</sup>	$M_{n,h}$ ( $\times 10^4$ ) <sup>(a)</sup>	PDI <sub>h</sub> <sup>(a)</sup>	$T_g$ (°C) <sup>(b)</sup>	$T_{g,h}$ (°C) <sup>(c)</sup>
1	pTCPD-3	/ <sup>(d)</sup>	/ <sup>(d)</sup>	3.5	2.73	286.9	229.8
2	p(TCPD <sub>3</sub> -TTE <sub>1</sub> )-1	/ <sup>(d)</sup>	/ <sup>(d)</sup>	5.0	3.83	252.1	190.8
3	p(TCPD <sub>1</sub> -TTE <sub>1</sub> )-4	4.2	2.92	5.6	3.14	223.4	175.3
4	p(TCPD <sub>1</sub> -TTE <sub>3</sub> )-1	2.6	2.69	3.3	2.73	191.1	155.6
5	pTTE-2	4.1	2.64	5.6	2.87	163.1	127.3

<sup>(a)</sup> Number-average molecular weight ( $M_n$ ) and PDI of the resultant polymer determined by GPC at 150 °C in  $C_6H_3Cl_3$  vs. narrow polystyrene standards;  $M_{n,h}$  and PDI<sub>h</sub> represent the GPC data of hydrogenated polymers; <sup>(b)</sup> Determined by DSC. <sup>(c)</sup>  $T_g$  of hydrogenated polymers (COPs); <sup>(d)</sup> not obtained due to serious crosslinking during solvation.

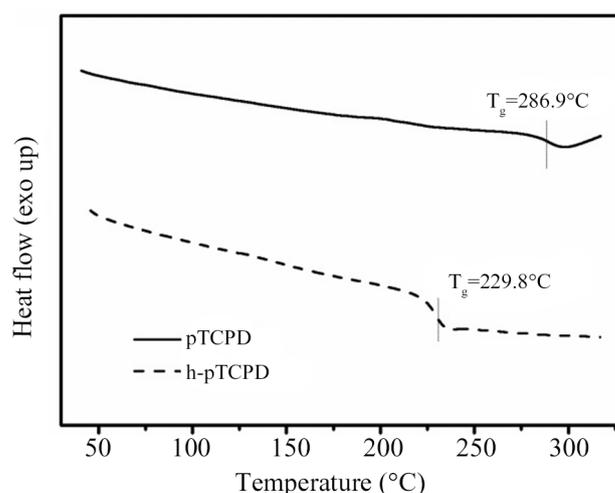
resistance and tolerance toward heat and light. Metal catalysts were usually used to hydrogenate the double bond in the main chain and the cyclic double bond in polymers, for example  $Ni(acac)_2$ ,  $(PCy_3)_2Ru(CO)(H)$  [20,21]. These metal catalysts are able to cause efficient hydrogenation. However, they often act at high temperature (> 150°C) and high  $H_2$  pressure leading to gelation under these conditions. For polymer hydrogenation in this work, we used TSH-based chemical hydrogenation instead of the traditional metal catalyst. The reaction was refluxed in toluene for about 16 h with a yield more than 95% and no gelation. This method greatly improved the safety and efficiency of the hydrogenation degree of polymers. The  $^1H$  NMR spectra of these hydrogenated polymers (COPs) are also shown in Figure 1a-b and Figure S1. Complete hydrogenation could be confirmed by the disappearance of the vinyl signals at 5.5-6.0 ppm in the  $^1H$  NMR spectra of the hydrogenated polymers. Their MWs and MWDs (Table 2) were also measured by GPC. Compared with their corresponding unsaturated polymers, their MWs increased a little and their PDI had no obvious change, indicating the successful hydrogenation. Similar to the representation of unsaturated polymers, the COPs were written in the form of h-p(TCPD<sub>x</sub>-TTE<sub>y</sub>)-n.

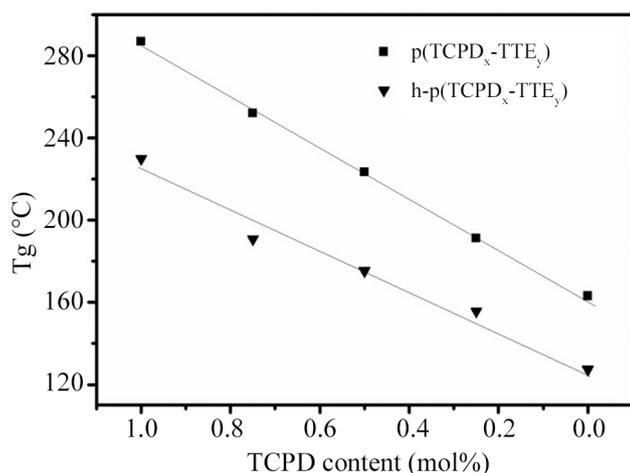
### Thermal properties and transmittance

A high  $T_g$  was very crucial for achieving high heat-resistance COPs. The newly COPs in this research were synthesized from highly sterically hindered monomers. Thus, a very high  $T_g$  was expected, especially for the copolymers with high TCPD content. The  $T_g$ s obtained by DSC measurements are listed in Table 2. As we could see from Figure 2, the  $T_g$  of

h-p(TCPD) was as high as 229.8°C, which was even higher than that of h-pHBMN (ca. 220°C). To the best of our knowledge, this value was the highest among the COPs prepared by ROMP approach.

The dependence of  $T_g$  value of polymers on TCPD content in the copolymers is shown in Figure 3. The  $T_g$  values of unsaturated polymers were about 30-60°C higher than those of corresponding hydrogenated polymers (COPs). As shown in Figure 3, a linear relationship was observed if  $T_g$  values were plotted against the TCPD content. The  $T_g$ s of both unsaturated and hydrogenated copolymers decreased with the reduction of TCPD content in the copolymers. This result indicated that various grades of heat-resistant COPs could be obtained predictably by deliberately varying the composition ratios of copolymers. With varying TCPD contents from 75 to 25 mol% for h-p(TCPD-TTE)s, the  $T_g$  value could be controlled in the range of 155-190°C.

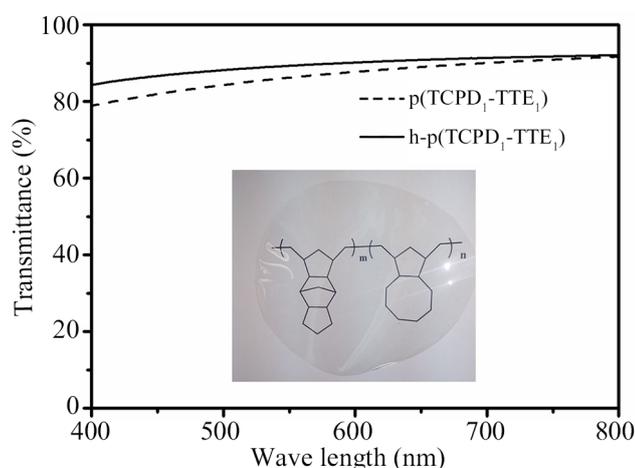
**Figure 2.** DSC curves (second heating) of pTCPD and h-pTCPD.



**Figure 3.** The relationship between TCPD content and  $T_g$ s for the unsaturated and hydrogenated copolymers.

The thermal stability of the COPs obtained was investigated by TGA. The typical TGA curves are shown in Figure S2. The onset degradation temperatures ( $T_d$ ) were defined by the temperatures of 10% weight loss in TGA curves. The  $T_d$  values were all above 420°C in  $N_2$ , indicating that all these copolymers have excellent thermal stability. The  $T_d$  values of these COPs were much higher than their  $T_g$  values, which indicated that these materials were very favorable for melting processing.

The transparency of the COPs was investigated by UV-Vis absorption spectra. The prepared films of COPs were very transparent. The representative curves of the unsaturated (p(TCPD<sub>1</sub>-TTE<sub>1</sub>)) and hydrogenated (h-p(TCPD<sub>1</sub>-TTE<sub>1</sub>)) polymers scanned from 400 to 800 nm are shown in Figure 4. For both



**Figure 4.** Transmittance of selected copolymer films and image of the transparent film of h-p(TCPD<sub>1</sub>-TTE<sub>1</sub>); the sample is expressed in the words.

the polymer films, the transmittance was higher than 80%. Very high transmittance up to 92% was reached at high wavelengths. Moreover, the transmittance of COP was higher than that of its corresponding unsaturated polymer film. The image of the transparent thin film of h-p(TCPD<sub>1</sub>-TTE<sub>1</sub>) is also shown in Figure 4, and the transparent COPs' film through which the text was clearly visible. Thus, the COPs presented here should be a type of highly potential optical materials with an outstanding heat resistance.

## CONCLUSION

By adjusting the proportions of *i*-Bu<sub>3</sub>Al and Et-OH in a WCl<sub>6</sub>-based catalyst system, a series of ring-opened polymers derived from bulky norbornene derivatives have been synthesized successfully with 100% yield and no gel formation. Corresponding COPs were obtained by complete reduction of double bond in the main chain using a chemical method, which was confirmed by <sup>1</sup>H NMR spectra. The DSC results showed that the  $T_g$  of h-pTCPD was as high as 229.8°C. To the best of our knowledge, this value is the highest  $T_g$  value reported for the cyclic olefin copolymers, indicating that the COP possesses outstanding heat-resistance properties. The  $T_g$  could be adjusted from 130 to 230°C by changing the feed ratios of TCPD and TTE. Furthermore, the copolymers exhibited desirable properties such as excellent transparency, high thermal stability and good film-forming ability.

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