

# Ring-Opening Metathesis Polymerization of Tetracyclododecene Using Various Catalyst Systems

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**ABSTRACT:** Ring-opening metathesis polymerization (ROMP) of a polycyclic olefin monomer (tetracyclododecene, TCD) was carried out using various catalyst systems. The catalysts included titanium-based ternary system (titanium tetrachloride,  $\text{TiCl}_4$ /triethylaluminum,  $\text{Et}_3\text{Al}$ /triethylamine,  $\text{Et}_3\text{N}$ ), tungsten-based ternary system (tungsten hexachloride,  $\text{WCl}_6$ /triisobutyl aluminum,  $(i\text{-Bu})_3\text{Al}$ /ethanol), and a ruthenium benzylidene catalyst (Grubbs 1st catalyst). The Grubbs 1st catalyst was most active in ROMP of TCD. The tungsten-based catalyst was found to be more active than the titanium-based catalyst. In contrast to the titanium-based and the Grubbs 1st catalysts, ROMP of TCD with the tungsten-based catalyst was very sensitive to gelation in the course of reaction. The effects of ethanol,  $\text{WCl}_6$  concentration, TCD/ $\text{WCl}_6$  ratio, and 1-hexane on the polymerization yield

and the polymer gel formation were investigated in detail, and optimized ROMP conditions were determined. Chemical structure of synthesized polymer was characterized using one- and two-dimensional 150 MHz  $^{13}\text{C}$  and 600 MHz  $^1\text{H}$  nuclear magnetic resonance spectroscopy, molecular weights were measured using gel-permeation chromatography, and thermal properties were characterized using differential scanning calorimetry. Number-average molecular weights ( $M_n$ ) of the polymer were in the range of  $1.5\text{--}4.7 \times 10^4$  g/mol, and glass transition temperatures were in the range of 185–220°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 479–485, 2010

**Key words:** ROMP; cyclic olefin polymer; organometallic catalysts; tetracyclododecene; tungsten hexachloride

## INTRODUCTION

Cyclic olefin polymers (COPs) are widely used thermoplastic engineering materials. Unique optical, electrical, thermal, and mechanical properties of COP make them utilized in a variety of areas including optical parts for digital cameras and laser beam printers, optical recordings, medical products, and electrical insulation applications.<sup>1–4</sup> A wide variety of cycloolefins including monocyclic, bicyclic, and polycyclic olefins have been used as monomers.<sup>1,4</sup> Commercially, the COPs are synthesized by ring-opening metathesis polymerization (ROMP) of the polycyclic olefins followed by hydrogenation of double bonds to provide thermal stability and weatherability, as shown in Scheme 1, for tetracyclododecene (TCD) species.

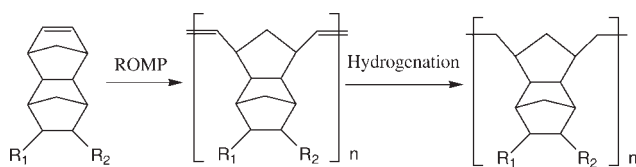
Typical ROMP catalysts include three-component systems of metal halides, organometallic com-

pounds, and amine or alcohol additives such as titanium tetrachloride ( $\text{TiCl}_4$ )/triethylaluminum ( $\text{Et}_3\text{Al}$ )/triethyl amine ( $\text{Et}_3\text{N}$ ) and tungsten hexachloride ( $\text{WCl}_6$ )/triisobutyl aluminum ( $(i\text{-Bu})_3\text{Al}$ )/ethanol. Amine is used to activate  $\text{TiCl}_4$  catalyst. Alcohol species are used to activate  $\text{WCl}_6$  catalyst through formation of W–O bond<sup>5</sup> and to retard gelation during polymerization. The organo-aluminums are typically used as cocatalysts. These catalyst systems are known to be extremely sensitive to the presence of oxygen and moisture and to substituted functional groups in the cyclic olefin monomers ( $\text{R}_1$  and  $\text{R}_2$  in Scheme 1).<sup>6</sup> Generally, tungsten halides are more active than titanium halides in the ROMP of the cyclic olefin monomers. However, the tungsten halide catalysts often cause gelation in the course of polymerization, resulting in low-molecular-weight polymers and organic solvent-insoluble polymer fractions (or polymer gels).<sup>7</sup> Thus, several attempts have been made to alleviate gelation and to synthesis high-molecular-weight COPs with the tungsten halide catalyst systems.<sup>7–9</sup> The drawbacks of the titanium halide and the tungsten halide catalysts have been overcome by developing ruthenium benzylidene species such as benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs 1st catalyst) and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-

Additional Supporting Information may be found in the online version of this article.

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**Scheme 1** The synthesis of COP.

2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Grubbs 2nd catalyst). The Grubbs catalysts exhibit high stability toward moisture and oxygen and retain high activity/high polymerization yields in the ROMP of cyclic olefin monomers.<sup>6,10–14</sup>

Polycyclic olefin polymers were commercialized under the trade names of Zeonex<sup>®</sup> at 1991 and of Arton<sup>®</sup> at 1997, and many synthesis works have been published in open literatures and patents. Most of the published works dealt with ROMP of functional group-substituted TCD. Yoshida et al.<sup>15</sup> reported that ROMP of ester- or cyano-substituted TCD monomers ( $R_1$  = methyl or hydrogen,  $R_2$  = methyl ester, ethyl ester, butyl ester, or cyano in Scheme 1) with  $WCl_6/(Et)_2AlCl$ . They showed that the polymerization yields were highly dependent on the chemical nature of the substituted groups ( $R_1$  and  $R_2$ ). Later, Otsuki et al.<sup>16</sup> reported that ROMP of ester-substituted TCD monomers ( $R_1$  = methyl,  $R_2$  = methyl ester in Scheme 1) with various catalysts including  $WCl_6/(Et)_2AlCl$ ,  $WOCl_5/(Et)_2AlCl$ , and  $MoCl_5/(Et)_2AlCl$ . High polymerization yields (>99%) resulted with small amount of catalysts (monomer/W or monomer/Mo ratio = 5000). In a patent of Kohara et al.,<sup>17</sup> methyl dimethanooctahydronaphthalene (MTD,  $R_1$  = hydrogen,  $R_2$  = methyl in Scheme 1) or ethyl dimethanooctahydronaphthalene (ETD,  $R_1$  = hydrogen,  $R_2$  = ethyl in Scheme 1) was ring-opening polymerized with  $TiCl_4/Et_3Al/Et_3N$  as the ROMP catalyst. Relatively, large amount of catalysts was required (monomer/Ti ratio = 100–50) to result in polymerization yield of  $\sim 70\%$ . In a patent of Kodemura et al.,<sup>7</sup> MTD was polymerized by ROMP with catalyst systems comprised of metal halide, organoaluminum compound, and alcohol such as  $WCl_6/Et_3Al/i$ -butyl alcohol and  $MoCl_5/(i-Bu)_3Al/i$ -butyl alcohol. High polymerization yields ( $\sim 100\%$ ) without formation of polymer gels resulted when two-step polymerization was used; in the first step, a certain amount of the monomer was polymerized, and in the second step, last amount of the monomer and catalyst solutions were added dropwise to the mixtures that were prepared in the first step.

In contrast to ROMP of functional group-substituted TCD, only few ROMP studies of nonfunctional groups-substituted TCD ( $R_1$  = hydrogen,  $R_2$  = hydrogen in Scheme 1) were reported. Nishi et al.<sup>18</sup> reported that TCD was ring-opened polymerized

with  $TiCl_4/Et_3Al/Et_3N$  as the ROMP catalyst. TCD/Ti ratio was 180, and the polymerization yield was 63%. Ogata et al.<sup>19</sup> reported that cationic polymerization of TCD with a nickel complex (bis[*N*-(pyridine-2-carboxaldehyde)benzoylhydrazone]nickel(II)dibromide)/methylaluminoxane (MAO) as a catalyst. TCD/Ni ratio was 2000, and the polymerization yield was low (3.5%). Although it has been shown that TCD can be ROMP'd with the titanium halide catalyst, systematic studies on ROMP behavior using the tungsten-based catalysts and ROMP result comparison using various catalyst systems have not been explored. Herein, we carried out a systematic study of TCD ROMP with various catalyst systems including  $TiCl_4/Et_3Al/Et_3N$ ,  $WCl_6/(i-Bu)_3Al/ethanol$ , and the Grubbs 1st catalyst to compare polymerization yields and polymer properties from the different catalyst systems and to obtain optimal polymerization condition. We use commercially available TCD as a model compound in an effort to understand ROMP behavior using the various catalyst systems. It is noted that commercial COP materials are known to be produced by ROMP of ester-substituted TCD or ethyl-substituted TCD.<sup>20</sup> It will be demonstrated that polymers with high molecular weights with no gels can be obtained at high yield by controlling ethanol and/or by controlling  $WCl_6$  solution concentration when the tungsten halide-based catalyst was used. The sections that follow describe the effects of catalyst types, catalyst concentration, amount of ethanol, and amount of 1-hexane on polymerization yields, polymer gelation, and molecular weights. Structural analysis of the synthesized polymers was performed using one- and two-dimensional 150 MHz <sup>13</sup>C and 600 MHz <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy. The molecular weights were determined by gel-permeation chromatography (GPC), and the glass transition temperatures were determined using scanning electron microscopy.

## EXPERIMENTAL SECTION

### Materials

Tetracyclododecene (TCD, >95%) was purchased from Tokyo Chemical Industry (Japan). Titanium tetrachloride ( $TiCl_4$ , >99.9%), tungsten hexachloride ( $WCl_6$ , >99.9%), benzylidene-bis(tricyclohexylphosphine) dichlororuthenium (Grubbs 1st catalyst), triethylaluminum ( $Et_3Al$ , 25 wt % in toluene), triisobutyl aluminum ((*i*-Bu)<sub>3</sub>Al, 25 wt % in toluene), triethylamine ( $Et_3N$ , >99%), anhydrous toluene (>99.8%), and methanol (HPLC grade) were purchased from Sigma-Aldrich (St. Louis, MO). Toluene and TCD were purified using distillation with Na/K alloy

before use. The other reagents were used without further purification.

### Polymerization procedure

#### TiCl<sub>4</sub> catalysts

All polymerization reaction was carried out in a glove box. In a 50-mL flask, 6 mmol of TCD was dissolved in 3 g of toluene. In this solution, experimentally desired amount of Et<sub>3</sub>Al (25 wt % toluene solution), Et<sub>3</sub>N (15 wt % solution), and TiCl<sub>4</sub> (20 wt % toluene solution) were added. The mixture was stirred at 30°C for 2 h. The resulted viscous polymer solutions were poured into a large amount of methanol with vigorous stirring to precipitate the polymers. White polymer solids were filtered and dried under vacuum at 40°C overnight.

#### WCl<sub>6</sub> catalysts

In a 50-mL flask, 6 mmol of TCD was dissolved in 3 g of toluene. In this solution, a desired amount of 1-hexane (1 wt % in toluene) was added, followed by addition of 0.03 mmol of (*i*-bu)<sub>3</sub>Al (25 wt % in toluene) and a desired amount of ethanol (5 wt % in toluene). Then, WCl<sub>6</sub> (0.1–1 wt % in toluene) was introduced dropwise to the monomer mixture. After 2-h reaction at 30°C, white polymer solids were obtained as described previously.

#### Grubbs 1st catalysts

In a 50-mL flask, 6 mmol of TCD was dissolved in 3–39 g of toluene. In this solution, a desired amount of the Grubbs 1st catalyst was added (0.1 wt % in toluene). After 2-h reaction at 30°C, white polymer solids were obtained as previously described.

### Analytical methods

Chemical structure of the polymer was characterized using a VARIAN UNITY INOVA 600 MHz Spectrometer equipped with an Oxford narrow bore magnet, RedHat Linux 1.1 Dell host workstation, and VNMR J software (version; 2.1B). The NMR samples were prepared by dissolving the polymer sample in deuterated chloroform (CDCl<sub>3</sub>). Two-dimensional homonuclear correlation spectroscopy (2D COSY) (<sup>1</sup>H–<sup>1</sup>H), two-dimensional heteronuclear multiple quantum coherence (HMQC) (2D <sup>1</sup>H–<sup>13</sup>C one bond), and <sup>13</sup>C distortionless enhancement by polarization transfer (DEPT) NMR experiments were carried out to assign NMR peaks and to characterize the polymer structure.

Molecular weights of the polymers were measured using GPC with toluene as a mobile phase. The GPC system equipped with a 20 μL injector loop, a high-

pressure pump (series 200, PerkinElmer, Waltham, MA), three Styragel® 4.6 × 300 mm<sup>2</sup> columns (models HR3, HR4, and HR4E, Waters Corporation, Milford, MA) for the polymer separation, and a refractive index detector (series 200a, Perkin Elmer). Number-average molecular weight (*M<sub>n</sub>*) and weight-average molecular weight (*M<sub>w</sub>*) relative to polystyrene standard were determined.

The thermal properties of the polymers were measured using a Q10 differential scanning calorimeter (DSC) equipped with a refrigerated cooling system (RCS90), manufactured by TA Instruments (New Castle, DE). The glass transition temperature (*T<sub>g</sub>*) of the samples was determined during the 1st and 2nd scan using a 10°C/min heating rate.

To measure gel content in the polymers, a known amount of polymers was dissolved in toluene (10 g) with stirring for 2 h. The mixture was then filtered using a 0.45-μm pore size filter paper. The nonsoluble polymer fraction on the filter was dried in vacuum at 80°C for 1 day and weighed. The gel content was determined by

$$\text{Gel content} = \frac{\text{weight of nonsoluble polymer fraction}}{\text{total weight of polymer}}$$

The polymerization yield was estimated by

$$\% \text{ Yield} = \frac{\text{weight of dried polymer}}{\text{weight of monomer}} \times 100.$$

## RESULTS AND DISCUSSION

First, WCl<sub>6</sub>/(*i*-bu)<sub>3</sub>Al/ethanol catalyst system was used as the ROMP catalyst. The effect of WCl<sub>6</sub> concentration in toluene on the ROMP of TCD was examined, and the results are listed in Table I. When 1 wt % WCl<sub>6</sub> in toluene was used, the formation of polymer gels was observed with dropwise introduction of 0.001 mmol WCl<sub>6</sub> into the monomer solution (P38). A total of 0.011 mmol of WCl<sub>6</sub> (TCD/W = 500) was further injected into the reaction mixture and the polymerization proceeded for 2 h. Although high polymerization yield resulted (100%), the gel content, as defined in the Analytical section, was also high (18%). When the WCl<sub>6</sub> concentration decreased to 0.5 wt %, the gel content decreased to 7% (P40). This indicates gel formation during the polymerization was somewhat alleviated at the lower WCl<sub>6</sub> concentration. When the WCl<sub>6</sub> concentration was further decreased to 0.1 wt %, gel formation during the dropwise injection of the WCl<sub>6</sub> catalyst solution was not observed (P56). The polymerization yield was almost complete (99%), and the gel content in the polymer was zero. Thus, as decreasing

TABLE I  
Effect of  $WCl_6$  Concentration and TCD/W Ratio on ROMP of TCD<sup>a</sup>

Entry	$WCl_6$ conc. (wt %)	TCD/W (mol/mol)	Yield (%)	Gel content (%)	$M_n$ (g/mol)	MWD	$T_g^b$ (°C)
P38	1	500	100	18	N.D. <sup>c</sup>	N.D. <sup>c</sup>	210.2
P40	0.5	500	98	7	N.D. <sup>c</sup>	N.D. <sup>c</sup>	203.8
P56	0.1	500	99	0	$3.9 \times 10^4$	2.89	213.8
P49	0.1	1000	54	0	$2.5 \times 10^4$	2.89	187.9
P45	0.1	2000	15.4	0	$1.5 \times 10^4$	2.85	182.8

<sup>a</sup> Amount of 1-hexane was fixed to 0.06 mmol; TCD concentration in toluene was 25 wt %; amount of (i-Bu)<sub>3</sub>Al was fixed to 0.03 mmol; EtOH/TCD ratio was fixed to  $1.67 \times 10^{-2}$ .

<sup>b</sup> Determined by DSC.

<sup>c</sup> Not detectable. The polymer solubility in toluene was very low, and the GPC system did not work properly.

the catalyst solution concentration, polymers with no gels can be obtained. The number-average molecular weight ( $M_n$ ) with the 0.1 wt %  $WCl_6$  concentration was measured to be  $3.9 \times 10^4$  g/mol. This molecular weight is comparable to those of the well-known commercial COP ( $2.3\text{--}4.3 \times 10^4$  g/mol).<sup>20</sup>

The effect of monomer/catalysts ratio was examined, and the results are listed in Table I. A total of 0.1 wt %  $WCl_6$  in toluene was used as the catalyst. As the TCD/W ratio increased slightly from 500 to 1000, the polymerization yield decreased significantly from 100 to 54% (P56 and P49). When the TCD/W ratio further increased to 2000, the polymerization yield decreased to 15.4% (P45). In addition,  $M_n$  and  $T_g$  of the polymers synthesized with the TCD/W ratios of 1000 and 2000 were smaller than those of the polymers synthesized with the TCD/W ratio of 500, indicating the polymerization degree decreased when higher TCD/W ratio was used.

Figure 1 shows the thermal properties of the ring-opened poly(TCD) that was characterized using DSC. It can be seen that poly(TCD) synthesized using the  $WCl_6$  catalyst retain only glass transition temperature ( $T_g$ ) at 213.8°C during 1st heating and 2nd heating scan of DSC. The high  $T_g$  of poly(TCD) can result from bulky nature of the polycyclic groups and the presence of double bonds in the main chain, which can lead to sluggish polymer chain mobility and hindered chain rotation. No melting endotherms were observed in the DSC thermogram, indicating that poly(TCD) is an amorphous polymer.

The effect of ethanol on ROMP of TCD was examined, and the results are listed in Table II. In the absence of ethanol, polymer gel particles formed with the dropwise introduction of extremely small amount of the catalyst (TCD/W = 9670 or  $6.1 \times 10^{-4}$  mmol of  $WCl_6$ ) in the monomer solution (P46). When the formation of polymer gels was observed, the charge of the catalyst to the reaction mixture was stopped and polymerization reaction proceeded for 2 h. The polymerization yield was 31%, and the gel content was 19%. In the presence of a small

amount of ethanol (EtOH/TCD =  $8.33 \times 10^{-3}$ ), the formation of polymer gels was observed when  $1.1 \times 10^{-3}$  mmol of  $WCl_6$  (TCD/W ratio of 5276) was introduced in the reaction mixture (P48). Gel formation was observed at higher  $WCl_6$  concentration of  $3.5 \times 10^{-3}$  mmol (TCD/W ratio of 1690) when larger amount of ethanol was used (EtOH/TCD =  $1.25 \times 10^{-2}$ ) (P67). This indicates that ethanol acts as gel retarding agent in the ROMP of TCD. Polymer with no gels was obtained as the EtOH/TCD ratio increased to  $1.67 \times 10^{-2}$ . Therefore, gelation can be alleviated by controlling the amount of ethanol in ROMP of TCD with the  $WCl_6$  catalyst. When the EtOH/TCD ratio further increased to  $2.5 \times 10^{-2}$  or above, no polymerization of TCD resulted. This indicates that excess amount of ethanol has a detrimental effect on the ROMP reaction. Thus, amount of ethanol should be controlled carefully to alleviate the gelation and to obtain high polymerization yield. It is noted that the optimal EtOH/TCD ratio can be different when different amount of 1-hexane in the reaction mixture is used, as will be discussed in the next section.

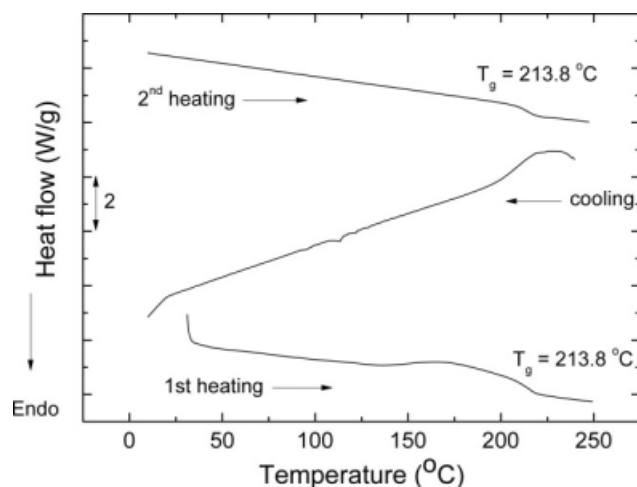


Figure 1 DSC thermogram of poly(TCD) synthesized with the  $WCl_6$ /(i-bu)<sub>3</sub>Al/ethanol catalyst system. ROMP condition is listed in Table I (Entry P56).



TABLE II  
Effect of Ethanol Concentration on ROMP of TCD<sup>a</sup>

Entry	TCD/W (mol/mol)	EtOH/TCD (mol/mol)	Yield (%)	Gel content (%)	$M_n$ (g/mol)	MWD	$T_g^b$ (°C)
P46	9670	0	31	19	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>d</sup>
P48	5276	$8.33 \times 10^{-3}$	16	15.6	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>d</sup>
P67	1690	$1.25 \times 10^{-2}$	11	9.6	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>d</sup>
P56	500	$1.67 \times 10^{-2}$	99	0	$3.9 \times 10^4$	2.89	213.8
P66	500	$2.50 \times 10^{-2}$	No polymerization	N.A. <sup>e</sup>	N.A. <sup>e</sup>	N.A. <sup>e</sup>	N.A. <sup>e</sup>
P39	500	$6.51 \times 10^{-2}$	No polymerization	N.A. <sup>e</sup>	N.A. <sup>e</sup>	N.A. <sup>e</sup>	N.A. <sup>e</sup>

<sup>a</sup> Amount of 1-hexane was fixed to 0.06 mmol; TCD concentration in toluene was 25 wt %; amount of (i-Bu)<sub>3</sub>Al was fixed to 0.03 mmol; WCl<sub>6</sub> concentration in toluene was fixed to 0.1 wt %.

<sup>b</sup> Determined by DSC.

<sup>c</sup> Not detectable. The polymer solubility in toluene was very low, and the GPC system did not work properly.

<sup>d</sup> Not detectable. Glass transition was not observed in the DSC thermogram.

<sup>e</sup> Not available.

The effect of 1-hexane on ROMP of TCD was examined, and the results are listed in Table III. In the absence of 1-hexane, polymer gels formed when a small amount of the catalyst (TCD/W = 1750) was injected into the monomer solution (P54). The polymerization yield was 41% and the gel content was 39.2%, indicating most of the synthesized polymer in the absence of 1-hexane was polymer gels that did not dissolve in toluene. When 1-hexane/TCD ratio of 0.01 was used, gelation was not observed during the addition of the catalysts and the 2-h polymerization reaction period (P56). This suggests that gelation of the polymer in the course of ROMP is sensitive to the presence of 1-hexane. As the 1-hexane/TCD ratio increased to 0.015 and 0.02, molecular weights decreased from  $3.9 \times 10^4$  to  $3.0 \times 10^4$  and  $2.5 \times 10^4$  g/mol, respectively, indicating that higher concentration of 1-hexane lead to decrease molecular weight (P58 and P57). The decrease of molecular weight with an increase in 1-hexane agrees well with the previous reports. The molecular weights of the polymer ROMP'd from ester-substituted TCD (8-methyl-8 methoxy carbonyl tetracyclo[4.4.0.12,5.17,10]dodec-3-ene; R<sub>1</sub> = methyl, R<sub>2</sub> = methyl ester in Scheme 1) and the polymer ROMP'd from ester-substituted bicycloheptene (4-methyl-4-

methoxycarbonylbicyclo[2.2.1]hept-1-ene) decreased with an increment in 1-hexane concentration.<sup>15,16</sup> However, the polymerization yield at higher 1-hexane/TCD ratio (P57 and P58) was low (32–48%) compared with the yield of the lower 1-hexane/TCD ratio of 0.01 sample (P56). With an effort to increase polymerization yield at higher 1-hexane concentration, larger amount of WCl<sub>6</sub> was used. As listed in Table III, when the TCD/W ratio decreased from 500 to 300, the polymerization yield increased from 48 to 97–98% (P57-1 and P58-1). The molecular weight of the 1-hexane/TCD ratio of 0.015 is smaller than that of the 1-hexane/TCD ratio of 0.02, indicating again that larger amount of 1-hexane leads to decrease the molecular weights. The presence of 1-hexane in the polymerization mixture not only controlled the molecular weights but also affected the polymerization yield. Thus, when it needs to adjust molecular weight by controlling the amount of 1-hexane, monomer/catalyst ratio should also be taken into account to obtain high polymerization yield.

The polymer synthesized using WCl<sub>6</sub>/(i-Bu)<sub>3</sub>Al/ethanol was fully characterized through the analysis of one- and two-dimensional NMR spectra. Figure 2 shows two-dimensional HMQC (2D <sup>1</sup>H–<sup>13</sup>C one bond) and two-dimensional homonuclear correlation

TABLE III  
Effect of 1-Hexane Concentration on ROMP of TCD<sup>a</sup>

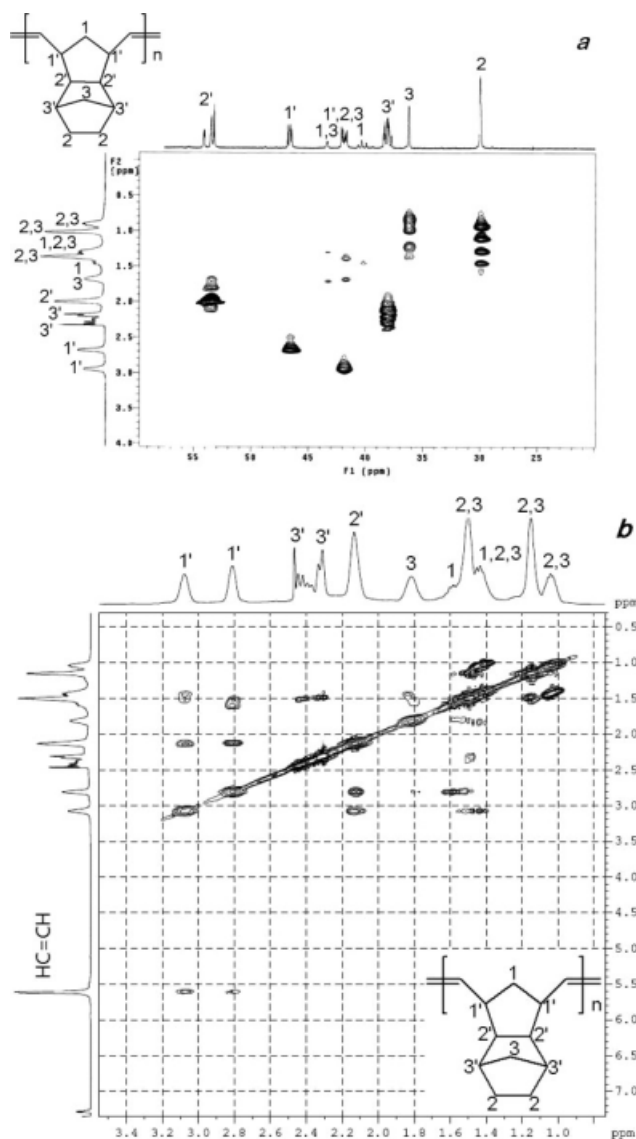
Entry	TCD/W (mol/mol)	1-Hexane/TCD (mol/mol)	Yield (%)	Gel content (%)	$M_n$ (g/mol)	MWD	$T_g^b$ (°C)
P54	1750	0	41	39.2	N.D. <sup>c</sup>	N.D. <sup>c</sup>	N.D. <sup>d</sup>
P56	500	0.01	99	0	$3.9 \times 10^4$	2.89	213.8
P58	500	0.015	48	0	$2.8 \times 10^4$	2.45	210.5
P57	500	0.02	32	0	$2.0 \times 10^4$	2.24	207.4
P58-1	300	0.015	98	0	$2.7 \times 10^4$	2.28	203.0
P57-1	300	0.02	97	0	$1.8 \times 10^4$	2.95	193.9

<sup>a</sup> TCD concentration in toluene was 25 wt %; WCl<sub>6</sub> concentration in toluene was fixed to 0.1 wt %; amount of (i-Bu)<sub>3</sub>Al was fixed to 0.03 mmol; EtOH/TCD ratio was fixed to  $1.67 \times 10^{-2}$ .

<sup>b</sup> Determined by DSC.

<sup>c</sup> Not detectable. The polymer solubility in toluene was very low, and the GPC system did not work properly.

<sup>d</sup> Not detectable. Glass transition was not observed in the DSC thermogram.



**Figure 2** (a) Two-dimensional heteronuclear multiple quantum coherence (HMQC) ( $2D$   $^1\text{H}$ – $^{13}\text{C}$  one bond) spectrum of poly(TCD) and (b) two-dimensional homonuclear correlation spectroscopy ( $2D$  COSY) ( $^1\text{H}$ – $^1\text{H}$ ) of poly(TCD).

spectroscopy ( $2D$  COSY) ( $^1\text{H}$ – $^1\text{H}$ ). Because of the double bond in the polymer backbone, the  $^1\text{H}$ -NMR spectrum mainly showed two set of signals. A broad peak at 5.51 ppm in the  $^1\text{H}$ -NMR spectrum and multiple peaks at 130.31–131.76 ppm in the  $^{13}\text{C}$ -NMR spectrum correspond to the double-bond region of poly(TCD). The methine and methylene protons and carbons were analyzed using the  $^1\text{H}$ – $^{13}\text{C}$  HSQC,  $^1\text{H}$ – $^1\text{H}$  COSY,  $^{13}\text{C}$ -DEPT NMR spectra. In the  $^{13}\text{C}$ -DEPT NMR spectra, sharp singlets at 29.66, 35.38 and multiple signals at 39.61–40.40, 41.33–41.73, and 43.07 ppm correspond to methylene carbons. The other multiple signals at 35.38–38.16, 41.45–41.81, 46.17–46.53, and 52.40–53.87 ppm correspond to methane carbons (see Supporting Information). In

the  $^1\text{H}$ – $^{13}\text{C}$  HSQC spectrum [Fig. 2(a)], the signals above 1.9 ppm in the  $^1\text{H}$ -NMR spectrum are assigned as methine protons, and all the signals below 1.9 ppm are assigned to methylene protons. All the  $^1\text{H}$ -NMR peaks were assigned using the  $^1\text{H}$ – $^1\text{H}$  COSY spectrum [Fig. 2(b)]. The  $^{13}\text{C}$ -NMR signals were confirmed using the correlation data between the carbon and proton signals obtained from  $^1\text{H}$ – $^{13}\text{C}$  HMQC spectrum. The NMR peak assignments are shown in Figure 2.

Table IV shows the effects of the various catalysts on ROMP of TCD. When  $\text{TiCl}_4/\text{Et}_3\text{Al}/\text{Et}_3\text{N}$  was used, a large amount of  $\text{TiCl}_4$  (TCD/Ti ratio of 100) was required to have polymerization yield of 70% (P12). This polymerization yield agrees well with the previous results (68%).<sup>18</sup> Formation of polymer gels during the polymerization was observed with the  $\text{TiCl}_4$ -based catalysts. When  $\text{WCl}_6/(\text{i-bu})_3\text{Al}/\text{ethanol}$  was used, almost complete polymerization yield resulted with relatively small amount of catalyst (TCD/W ratio of 500) (P56). As discussed previously, polymer gelation can be controlled by adjusting the amount of ethanol and the  $\text{WCl}_6$  concentration. It has been demonstrated that Grubbs 1st catalyst is very effective in ROMP of various cyclic olefin monomers.<sup>6,10–14,21</sup> The Grubbs 1st catalyst is relatively stable to oxygen and air compared with the  $\text{TiCl}_4$  and the  $\text{WCl}_6$  catalysts. In addition, typically a very small amount of the Grubbs 1st catalyst (monomer/Grubbs 1st catalyst ratio of 10,000–40,000) is enough to result in high polymerization yield. In the case of ROMP of TCD, polymerization yield of 99% resulted with the use of small amount of the Grubbs 1st catalyst (TCD/catalyst ratio of 40,000). It is noted that low monomer concentrations need to be used to polymerize TCD without gelation when the Grubbs 1st catalyst was used. With the monomer concentration of 10–25 wt %, gelation during the polymerization was observed, while when 2.5 wt % TCD in toluene was used, polymers with no gels were obtained. As in the case of poly(TCD) synthesized using the  $\text{WCl}_6$  catalyst, no melting endotherms were observed in DSC thermograms of poly(TCD) synthesized using the  $\text{TiCl}_4$  catalyst and the Grubbs 1st catalyst, indicating that the polymers are amorphous. Although the Grubbs 1st catalyst was found to be a most active and stable catalyst in the ROMP of TCD, the Grubbs 1st catalyst is expensive, and it is not an easy task to separate the catalyst that chemically attached to the polymer chain end and to reuse the catalyst. This can make it difficult to use the Grubbs 1st catalyst in a commercial, full-scale production of the polymer. However, the  $\text{WCl}_6$  catalyst, separated from the polymer solution in the methanol precipitation step, can be recovered and recycled. Thus, relatively cheap  $\text{WCl}_6$  can be an attractive catalyst in a commercial point of view.

TABLE IV  
ROMP of TCD by Various Catalysts Systems

Entry	Catalysts	TCD/Ti, W, Grubbs (mol/mol)	Al/Ti, W (mol/mol)	1-Hexane (mmol)	Yield (%)	$M_n$ (g/mol)	MWD	$T_g^a$ (°C)
<sup>b</sup> P12	TiCl <sub>4</sub> /Et <sub>3</sub> Al/Et <sub>3</sub> N	100	1.3	0.06	76	$4.7 \times 10^4$	1.92	220.2
<sup>c</sup> P56	WCl <sub>6</sub> /(i-bu) <sub>3</sub> Al/EtOH	500	2.63	0.06	99	$3.9 \times 10^4$	2.89	213.8
<sup>d</sup> P34	Grubbs 1st	40,000	–	0.06	99	$4.5 \times 10^4$	2.1	218.9

<sup>a</sup> Determined by DSC.

<sup>b</sup> TCD concentration in toluene was 20 wt %; TiCl<sub>4</sub> concentration in toluene was 20 wt %; Et<sub>3</sub>N/Ti ratio was 4.5.

<sup>c</sup> TCD concentration in toluene was 25 wt %; WCl<sub>6</sub> concentration in toluene was 0.1 wt %; EtOH/TCD ratio was  $1.67 \times 10^{-2}$ .

<sup>d</sup> TCD concentration in toluene was 1 wt %; Grubbs 1st catalyst concentration in toluene was 0.1 wt %.

## CONCLUSIONS

ROMP of TCD was carried out using three different catalyst systems of TiCl<sub>4</sub>/Et<sub>3</sub>Al/Et<sub>3</sub>N, WCl<sub>6</sub>/(i-Bu)<sub>3</sub>Al/ethanol, and Grubbs 1st catalyst. The WCl<sub>6</sub>/(i-Bu)<sub>3</sub>Al/ethanol catalyst system was very sensitive to gelation in the course of polymerization. It was necessary to carefully control the amount of ethanol, 1-hexane, and WCl<sub>6</sub> concentration to obtain high polymerization yield with no polymer gels. The optimal polymerization condition was found to be the WCl<sub>6</sub> concentration in toluene of 0.1 wt %, the TCD/W ratio of 500, the Al/W ratio of 2.63, the EtOH/TCD ratio of  $1.67 \times 10^{-4}$ , and the 1-hexane/TCD ratio of 0.01. At these conditions, almost complete polymerization (99%) and polymer with high  $M_n$  of  $3.9 \times 10^4$  g/mol were obtained. With the TiCl<sub>4</sub>/Et<sub>3</sub>Al/Et<sub>3</sub>N catalyst, a relatively large amount of TiCl<sub>4</sub> (TCD/Ti ratio of 100) was needed to obtain 70% polymerization yield, whereas with the Grubbs 1st catalyst small amount of the catalyst (TCD/Grubbs 1st ratio of 40,000) was enough to obtain 100% polymerization yield. Chemical structure of poly(TCD) was characterized using one- and two-dimensional <sup>13</sup>C- and <sup>1</sup>H-NMR spectroscopy.  $M_n$  of the poly(TCD) was in the range of  $1.5\text{--}4.7 \times 10^4$  g/mol, and  $T_g$  was in the range of 185–220°C, depending on the catalyst systems and the polymerization conditions.

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