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Preparation of a Bulky Cycloolefin/Ethylene Copolymer and Its Tensile Properties

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ABSTRACT: Regioselective partial hydrogenation of tricyclopentadiene (TCPD) was achieved with a high turnover number of 10 000 by catalysis with a N-heterocyclic carbene−palladium complex. Copolymerization of ethylene and the partially hydrogenated product, dihydrotricyclopentadiene (HTCPD), was realized using a catalytic system of $[8\text{-}(\eta^5\text{-}C_5Me_4)\text{-}2\text{-}Me(C_9H_8N)\text{-}\kappa N]TiMe_2$ ($C_9H_{10}NH$ = 1,2,3,4-tetrahydroquinoline) activated with $(Ph_3C)^+[B(C_6F_5)_4]^-$. The copolymer was unambiguously characterized through the analysis of one- and two-dimensional NMR spectra. The monomer reactivity ratios, r_{ethylene} and r_{HTCPD}, determined through the Fineman−Ross plot, were 2.8 and 0.025, respectively, indicating negligible successive insertion of two HTCPD. A nearly alternating copolymer with a HTCPD content of 45 mol % was obtained with a satisfactory activity (4.7×10^6 g/(mol Ti h)), of which T_g was 177 °C, significantly higher than that of norbornene/ethylene copolymer at the same cycloolefin content. Tensile stress−strain curves indicated that the brittleness observed for a high-T_g norbornene/ethylene copolymer was relieved to show some ductile property for the HTCPD/ethylene copolymer of the same level of high T_g.

Introduction

Cycloolefin copolymer (COC), a kind of polyolefin prepared through copolymerization of cycloolefin and ethylene, is an attractive resin for a number of applications.[1,2] COC's of norbornene derivatives containing polar groups have also been realized with nickel catalysts.[3] These highly transparent amorphous resins have a low birefringence. Other advantages are a low density and good barrier properties compared with competitive transparent resins such as polycarbonate (PC) and poly(methyl methacrylate) (PMMA).[4] These properties may allow potential applications as a novel substrate for high-density data storage devices, packaging, and optical/biomedical applications. COC is commercialized under the trade names APEL by Mitsui and Topas by Ticona.[5] A typical COC is a norbornene/ethylene copolymer (**1** in Chart). Norbornene is a Diels−Alder adduct of ethylene and cyclopentadiene, a major constituent in the C5-stream of naphtha cracking. Up to now, most C5-streams have not been used as a source of chemical but have instead been incinerated as energy.

The glass transition temperature (T_g) of COC can be modulated through tuning of the norbornene content in the polymer chains. For example, we can prepare a resin of which T_g is that of PC (150 °C) by controlling the norbornene content to ~54 mol %. At such a high norbornene content, polymer chains are so rigid that chain entanglement density is low, which is responsible for brittleness of the high T_g norbornene/ethylene copolymer. Brittleness hampers COC utility in areas such as an optical film. One approach to overcome this brittleness problem may be to employ a bulkier cycloolefin monomer than norbornene. With less incorporation of the bulkier cycloolefin, the same level of high T_g can be attained. Because the polymer chains contain a flexible ethylene unit in a higher amount, a higher chain entanglement density and consequently some ductile property can be expected. To this end, the bulkier cycloolefin 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphtalene (DMON) was introduced in the preparation of COC (**2** in Chart). However, metallocene catalysts showed significantly low activities in DMON/ethylene copolymerization ((0.0004−0.94) × 10^6 g/(mol Zr h)).[6] The DMON/ethylene copolymer of a high DMON content (44 mol %) was reported not to be amorphous but semicrystalline, showing a melting point at 380 °C.

Recently, we disclosed a new COC, 5,6-dihydrodicyclopentadiene (HDCPD)/ethylene copolymer (**3** in Chart).[7] HDCPD can be prepared inexpensively from dicyclopentadiene (DCPD) through regioselective partial hydrogenation. The HDCPD/ethylene copolymerization had not hitherto been realized due to a low reactivity of the remaining 2,3-double bond in HDCPD. Even the constrained geometry catalyst (CGC), $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$,[8] which has a reputation to be excellent in incorporating a bulky monomer, failed in copolymerizing HDCPD and ethylene.[9] A key to the success in the preparation of HDCPD/ethylene copolymers is development of catalyst **6** that is better than CGC in terms of comonomer incorporation and activity.[10] We developed a series of *o*-phenylene-bridged analogues of CGC.[11] HDCPD/ethylene copolymer is attractive because the polymer structure of the alternating copolymer resembles that of polymer **4** that is obtained through the ROMP of DMON and subsequent hydrogenation. Such polymers are called cycloolefin polymers (COPs) and are commercialized by Zeon. Zeon's DMON-derived COP is reportedly not as brittle as norbornene-derived COC.[12] However, we failed to equal the high T_g (162 °C) of Zeon's DMON-derived resin using the HDCPD/ethylene copolymers. The highest T_g attained was 114 °C with a HDCPD content of 44 mol %.

In this work, we report a new COC (**5** in Chart) prepared from a bulky dihydrotricyclopentadiene (HTCPD) monomer, which attained a maximum T_g of 177 °C. The HTCPD-derived COC was not as highly brittle as the norbornene-derived COC.

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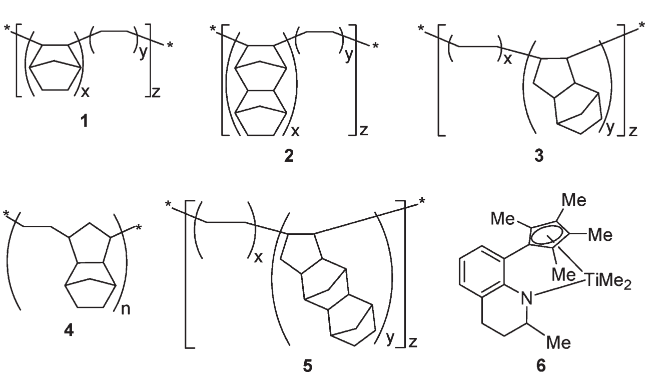
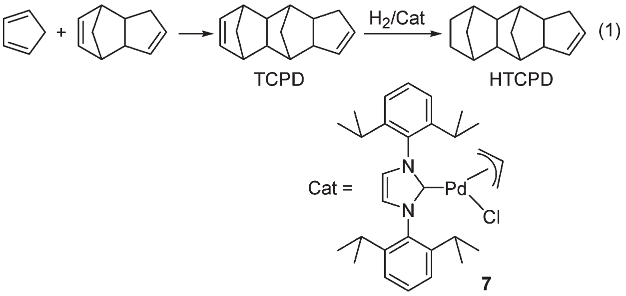
Chart 1. Molecular Structures of COCs (1−3, and 5), COP (4), and a Catalyst (6)



Results and Discussion

Preparation of HTCPD Monomer. Tricyclopentadiene (TCPD) was prepared through the Diels−Alder reaction of cyclopentadiene (CPD) and dicyclopentadiene (DCPD) (eq 1). Further successive Diels−Alder reactions over TCPD occurred, and formation of oligocyclopentadienes inducing tetracyclopentadiene and pentacyclopentadiene was inevitable. In fact, products of this thermal oligomerization are light colored resins commercially used in the production of inks, varnishes, adhesives, waxes, and protective layers.[13] However, 50%−60% conversion of DCPD to TCPD was realized under well-controlled conditions in either a batch-type reactor or a continuous pilot-plant reactor.[13,14] TCPD could be easily fractionated through vacuum distillation from the side products and the unreacted reactants. Several stereoisomers are conceptually possible in TCPD, but only two isomers were detected in a rough ratio of 4:1.[14] The major isomer could be isolated in pure form from the minor isomer by crystallization in ethanol in 70 g laboratory scale.



DCPD contains two kinds of double bonds: a norbornene type and a cyclopentene type. Typically, the norbornene type of double bond is much more reactive than the cyclopentene type. Hence, regioselective hydrogenation of the norbornene-type double bond in DCPD is possible while the cyclopentene-type double bond is untouched.[15] It is also possible either to polymerize DCPD through ROMP[16] or to copolymerize it with ethylene regioselectively using the norbornene-type double bond, while the less reactive cyclopentene-type double bond remains intact.[17] The reactivity of the cyclopentene-type double bond on HDCPD was determined to be about one-tenth of the norbornene-type double bond in copolymerization studies carried out using **6**.[7] TCPD also contains the norbornene and cyclopentene types of double bonds, and the regioselective hydrogenation of the norbornene-type double bond has been reported.[18] In that report, the catalyst was nickel particles prepared in situ through the reduction of nickel acetate tetrahydrate with $NaBH_4$. A fairly high amount of nickel was used; 0.36 mg of $Ni(OAc)_2 \cdot 4H_2O$ was used for reduction of 1.5 g of TCPD. Furthermore, an equimolar amount of H_2 gas was necessary to prevent overreduction. We failed in the regioselective hydrogenation of TCPD employing conventional hydrogenation catalysts such as Pd/C, Pd/alumina, or Rh/alumina, which was effective in regioselective hydrogenation of DCPD once an equimolar amount of H_2 gas was fed. The fully hydrogenated compound was concomitant even at the early stage of the TCPD hydrogenation reaction.

The desired regioselective hydrogenation was achieved by employing a Pd complex of a bulky N-heterocyclic carbene (eq 1). Preparation and utilization of N-heterocyclic carbene (NHC) transition metal complexes are a current hot issue in organometallic chemistry.[19] Recently, transfer hydrogenation of alkynes to alkenes using (NHC)Pd(0) complex and hydrogenation of alkenes using $(NHC)(PCy_3)Pd(0)$ were reported.[20] A carbene Pd complex (**7** in eq 1) is a very effective hydrogenation catalyst that can discriminate the two types of double bonds in TCPD. Even though we kept the reaction pot under H_2 pressure for some time after H_2 consumption ceased, the cyclopentene-type double bond was intact to provide selectively HTCPD. In ^1H and ^{13}C NMR spectra of the product, only a set of HTCPD signals was observed, and the signals of fully hydrogenated compound were negligibly detected (Supporting Information). The catalyst was not sensitive to the reaction conditions, and consistent results were obtained under the variations of H_2 pressure (1−20 bar) and solvents (methylene chloride, toluene, methanol, or acetonitrile). The catalyst was so effective and robust that we could attain full conversion of TCPD to HTCPD by running the hydrogenation reaction at a condition of [TCPD]/[Cat.] = 10000, representing a turnover number (TON) of 10 000.

Copolymerization Reactions. Complex **6** activated with $(Ph_3C)^+[B(C_6F_5)_4]^-$ in the presence of excess $Al(iBu)_3$ was able to copolymerize HTCPD and ethylene (Table 1). Typically, 1−3 g of polymer was isolated by copolymerization for 5−9 min with 4.0 μmol of catalyst in 30 mL of toluene solution, which corresponded to activities of $(2-5) \times 10^6$ g/(mol Ti h)and a HTCPD conversion below 20%. The activity was almost in the same range as that attained in HDCPD/ethylene copolymerization with **6**. The activities were higher compared with those attained with metallocene catalysts for DMON/ethylene copolymerization $((0.0004-0.94) \times 10^6$ g/(mol Zr h)).[6]

The copolymers were soluble in chloroform at room temperature, and NMR studies were fully carried out for a sample (entry 9). ^1H and ^{13}C NMR signals were unambiguously assigned through the analysis of ^{13}C DEFT (distortionless enhancement of polarization transfer), $^1H-^{13}C$ HMQC (heteronuclear multiple-quantum coherence), and $^1H-^1H$ COSY NMR spectra. Figure 1 shows the two-dimensional NMR spectra along with the assignment. In the ^1H NMR spectrum, the signal could be clearly divided into a 2.4−1.7 ppm region and a 1.7−0.8 ppm region. All the methine protons except one labeled as "2" were assigned to the 2.4−1.7 region, while all the methylene protons except a proton labeled as "b" were assigned to the 1.7−0.8 region. On the basis of this assignment, the HTCPD content could be calculated by the relationship of $(A/10)/[(A/10) + (B - 10)/4]$, where A and B are the integration values of 2.4−1.7 and 1.7−0.8 ppm regions, respectively.

Lowering the ethylene pressure gradually from 60 psig to 10 psig while fixing the HTCPD concentration at a constant value (1.40 M) achieved the gradual increase of the HTCPD content in the copolymer from 20 to 41 mol % (entries 1−5). Because the activity at a pressure of 10 psig was significantly

Table 1. Ethylene/HTCPD Copolymerization Results by 6[a]

entry	[HTCPD]	$P_{C_2H_4}$ (psig)	$[C_2H_4]^b$	T (°C)	time (min)	A^c	HTCPD incorp[d] (mol %)	T_g (°C)	$M_n{}^e \times 10^{-3}$	$M_w/M_n{}^e$
1	1.40	60	1.90	70	8.0	4.1	20	64	22	1.7
2	1.40	40	1.30	70	5.0	5.3	21	76	30	1.7
3	1.40	30	0.95	70	6.0	3.8	26	101	23	1.5
4	1.40	20	0.63	70	6.0	3.9	31	126	25	1.6
5	1.40	10	0.32	70	9.0	1.8	41	165	20	1.6
6	1.80	20	0.63	70	8.0	4.3	33	135	48	1.1
7	2.10	20	0.63	70	6.0	3.3	40	156	21	1.5
8	2.80	20	0.63	70	7.0	3.0	44	174	24	1.6
9	3.20	20	0.63	70	7.0	4.7	45	177	41	1.6
10[f]	2.30	20		25	90	1.5	37	154	100	1.9

[a] Polymerization conditions: toluene solution of HTCPD (30 mL), catalyst = **6** (4.0 μmol) + $(Ph_3C)^+[B(C_6F_5)_4]^-$ (16.0 μmol) in the presence of $Al(iBu)_3$ (800 μmol). [b] Ethylene concentration measured with an ethylene flow meter. [c] Activities in units of $\times 10^6$ g/(mol Ti h). [d] 5,6-Dihydrotricyclopentadiene content in the copolymer determined by ^1H NMR spectroscopy. [e] Determined on GPC using the polystyrene standard. [f] Large-scale polymerization using 100 mL of toluene solution to get ~30 g of polymer.

lower (1.8×10^6 g/(mol Ti h)) than other values ($(3.8-5.3) \times 10^6$ g/(mol Ti h)), we fixed the ethylene pressure at 20 psig and increased the HTCPD concentration gradually from 1.40 to 3.20 M to increase the HTCPD content further (entries 6−9). At 20 psig ethylene and 3.20 M [HTCPD] (18.2 g of HTCPD in 30 mL of toluene), a copolymer of 45 mol % HTCPD content was reached, which exhibited a glass transition temperature of 177 °C (entry 9).

With increases in HTCPD content, the glass transition temperature, T_g, increased linearly (Figure 2). For norbornene/ethylene and HDCPD/ethylene copolymers, T_g also increased linearly with increases of the cycloolefin content (Figure 2).[21] The HTCPD/ethylene copolymer exhibited significantly higher T_g at the same mol % cycloolefin content than norbornene/ethylene and HDCPD/ethylene copolymers. For example, T_g was ~60 °C higher at a 45 mol % cycloolefin content. Interestingly, the slope was also higher for HTCPD/ethylene copolymers (53 °C increase per 10 mol % increase) than those observed for norbornene/ethylene and HDCPD/ethylene copolymers (36−37 °C per 10 mol % increase). The T_g of DMON/ethylene copolymer at 44 mol % DMON has been reported to be 143 °C,[6] which is a lower value than that of HTCPD/ethylene copolymer of the same HTCPD content (174 °C, entry 8). The DMON/ethylene copolymer was reported to be semicrystalline showing melting point at 380 °C,[6] but presently the HTCPD/ethylene copolymer was amorphous and did not exhibit any melting point.

The polymerization data set carried out at 70 °C (entries 2−8) fitted well to the Fineman−Ross plot ($R^2 = 0.996$), and the monomer reactivity ratios, r_{ethylene} and r_{HTCPD}, were determined to be 2.8 and 0.025, respectively, representing almost same values obtained for ethylene/HDCPD copolymerizations ($r_{\mathrm{ethylene}} = 2.3$ and $r_{\mathrm{HDCPD}} = 0.008$). The low r_{HTCPD} value of 0.025 implies that successive incorporation of two HTCPDs is negligibly allowed. Because of the low value of r_{HTCPD}, we could not obtain a copolymer whose HTCPD content was over 50 mol %, and the copolymer of 45 mol % (entries 8 and 9) could be assigned to a nearly alternating copolymer. A similar alternating copolymerization of cyclopentene and ethylene was also realized with a catalytic system of $[Me_2Si(Ind)(N\textit{t}Bu)]TiCl_2$ or bis(phenoxyimine)titanium catalyst.[22]

Tensile Properties. In order to compare tensile properties of a HTCPD/ethylene copolymer with those of a commercial norbornene-derived COC (T_g, 146 °C; M_n, 100 000; M_w, 180 000), a HTCPD/ethylene copolymer was prepared in 30 g scale, of which T_g was slightly higher (154 °C) than that of the commercial norbornene-derived COC (entry 10). We ran the copolymerization for a longer time, 90 min, to obtain substantial amount of polymers (~30 g). A gradual increase of viscosity was observed during the polymerization time, and the average activity was not markedly lowered (1.5×10^6 g/(mol Ti h)) compared with those attained in batches at the small scale and short polymerization time ($(2-5) \times 10^6$ g/(mol Ti h)). This result indicates that the catalyst is robust and negligibly deactivated during the 90 min polymerization time. Because the molecular weights of the copolymers prepared at 70 °C were unsatisfactorily low (M_n, 20 000−48 000, entries 1−9), we ran the copolymerization at a low temperature of 25 °C; almost same molecular weight observed for the commercial norbornene−COC was attained ($M_n = 100\,000$; $M_w = 190\,000$).

Casting films were prepared with a thickness of 110 μm using an micrometer adjustable film applicator from a solution in $CHCl_3$ (15 wt %). A homogeneous transparent film was obtained after solvent evaporation from HTCPD/ethylene copolymer, whereas some bubbles were formed during the evaporation in case of norbornene/ethylene copolymer. Five test bars were cut avoiding bubbles with a size of 110 mm × 15 mm, and the stress−strain behaviors were measured by the standard method. Figure 3 shows the tensile stress−strain curve of HTCPD/ethylene copolymer compared with that of nobornene/ethylene copolymer. An noticeable difference between the two samples was a plateau for the HTCPD/ethylene copolymer, which is indicative of some ductile property of the copolymer and, hence, an improvement of brittleness (Figure 3). In the case of a highly brittle norbornene/ethylene copolymer, the polymer was broken without displaying that plateau. Because of the presence of the plateau, strain at breakage increased from 2.1% to 2.8% (Table 2). Typically, the brittleness of COC was more severe for a polymer of higher T_g. The T_g of the HTCPD/ethylene copolymer was higher than that of the norbornene/ethylene copolymer (154 vs 146 °C), but the HTCPD/ethylene copolymer showed some ductile property while the norbornene/ethylene copolymer did not. Polymer chains of the HTCPD/ethylene copolymer contained more flexible ethylene unit than norbornene/ethylene copolymer at the same level of T_g. Hence, chain entanglement is more facile in HTCPD/ethylene copolymer, which possibly results in some ductile property. The average of five measurements of stresses at yield and break were slightly higher for the HTCPD/ethylene copolymer, and the tensile modulus was also higher for the HTCPD/ethylene copolymer (Table 2).

Summary and Conclusions

Tricyclopentadiene is a bulky compound that can be cheaply prepared in a bulk scale from cyclopentadiene, a major constituent in the C5 stream of naphtha cracking. Between the norbornene-type and the cyclopentene-type double bonds that

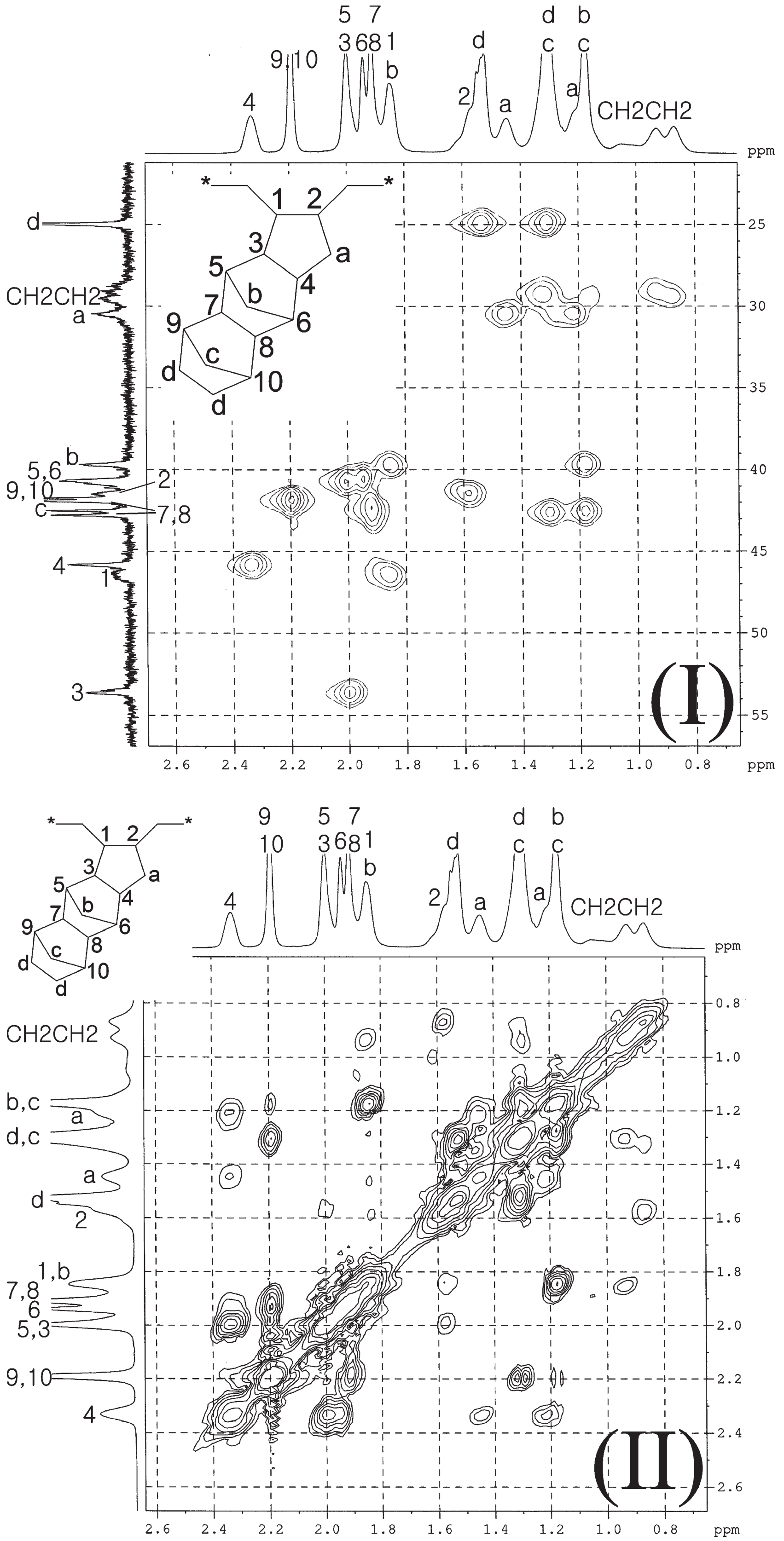


Figure 1. $^1H-^{13}C$ HMQC (**I**) and $^1H-^1H$ COSY (**II**) spectra of an HTCPD/ethylene copolymer.

tricyclopentadiene contains, the norbornene type could be regioselectively hydrogenated by employing an N-heterocyclic carbene–palladium complex as a catalyst with a high TON up to 10 000. Copolymerizations of ethylene and the partially hydrogenated product, HTCPD, were realized using a catalytic system of $[8-(\eta^5-C_5Me_4)-2-Me(C_9H_8N)-\kappa N]TiMe_2$ ($C_9H_{10}NH$ = 1,2,3,4-tetrahydroquinoline) activated with $(Ph_3C)^+[B(C_6F_5)_4]^-$ with satisfactory activities ($(2-5) \times 10^6$ g/(mol Ti h)). Copolymers of HTCPD contents of 20−45 mol % were obtained through variation of ethylene and HTCPD feeding concentrations. As the HTCPD content increased, T_g linearly increased according to the equation T_g (°C) = 5.3 × (HTCPD mol %) − 46. The slope was higher than those observed for norbornene/ethylene and HDCPD/ethylene copolymers (3.6−3.7), while the intercepting points on the T_g axis were almost invariable at −43 to −50 °C for all three copolymers. The attained highest T_g was 177 °C at a HTCPD content of 45 mol %, which was almost 60 °C higher than those of norbornene/ethylene and HDCPD/ethylene copolymers at the same cycloolefin content. The monomer reactivity ratios, r_{ethylene} and r_{HTCPD}, determined through the Fineman−Ross plot, were 2.8 and 0.025, respectively, indicating successive insertion of two HTCPD was negligibly allowed, which supports the view that the copolymer of HTCPD content of 45 mol % is a nearly alternating copolymer. A HTCPD/ethylene copolymer (T_g = 154 °C; M_n = 100 000) was prepared in 30 g scale, and its tensile properties were measured compared with the commercial norbornene/ethylene copolymer whose T_g and M_n are almost same with those of HTCPD/ethylene copolymer (T_g = 145 °C; M_n = 100 000). Tensile stress−strain curves indicated that the brittleness observed for the norbornene/ethylene copolymer was relieved to show some ductile property for HTCPD/ethylene copolymer, which might result from more chain entanglement in HTCPD/ethylene copolymer. At the same T_g, the HTCPD/ethylene copolymer contains flexible ethylene units in higher amount; hence, chain entanglement may be more facile in the HTCPD/ethylene copolymer.

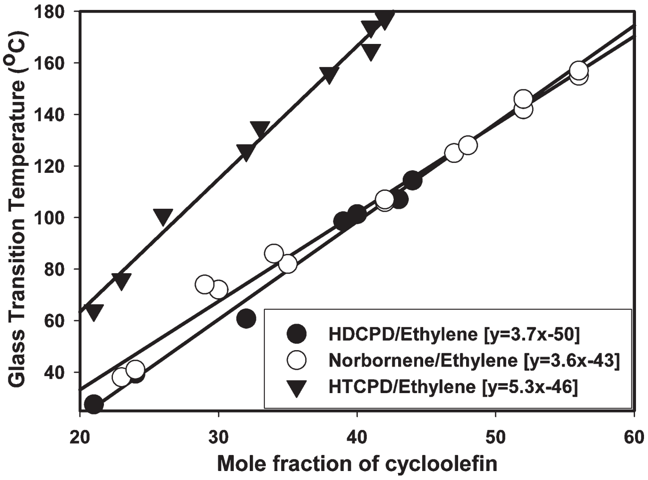


Figure 2. Relationship between T_g's and cycloolefin contents.

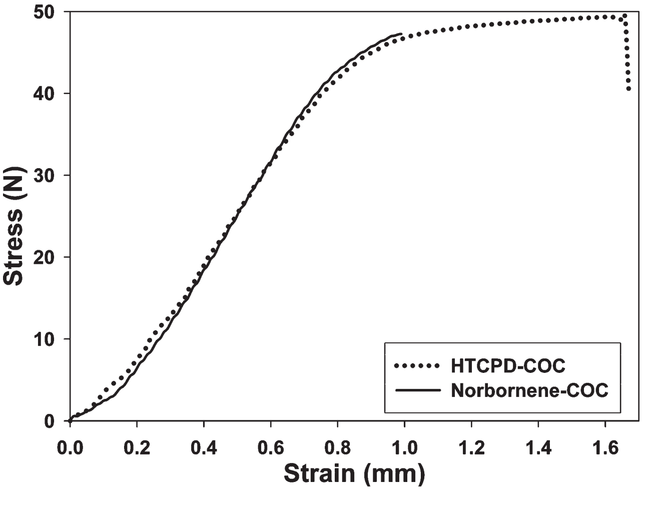


Figure 3. Tensile stress−strain curves for HTCPD/ethylene and norbornene/ethylene copolymers.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene (anhydrous grade, Aldrich) and HTCPD were distilled over Na/K alloy. Ethylene (99.0%) was purchased from Conley Gas and purified by contact with molecular sieves and copper for several days under 200 psig pressure. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of the copolymers were recorded on a Bruker Advance 600 at 25 °C. Gel permeation chromatograms (GPC) were obtained at 30 °C in $CHCl_3$ on Waters model 150-C+ GPC apparatus, and the data were analyzed using a polystyrene analyzing curve. Differential scanning calorimetry (DSC) was performed on a Thermal Analysis Q10. Glass transition temperatures (T_g) were determined with DSC on a second heating at a heating rate of 15 °C/min.

Tricyclopentadiene (TCPD). Dicyclopentadiene (320 g) and cyclopentadiene (160 g) were mixed in a bomb reactor, and it was heated at 150 °C under N_2 pressure of 20 bar for 12 h. Unreacted reactants were recovered (380 g) through vacuum distillation (70 °C/0.3 mmHg). To a flask containing the residue was added ethanol (1.0 L), and insoluble oligomeric compounds were filtered off. When the filtrate was stored in a freezer for 3 h, solid precipitated which was collected by filtration (84 g). The collected solid was crystallized one more time using ethanol (840 mL) to give pure compound (67 g). ^{1}H NMR ($CDCl_3$): 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) ppm. ^{13}C {^{1}H} NMR ($CDCl_3$): 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 ppm.

Dihydrotricyclopentadiene (HTCPD). Tricyclopentadiene (63 g, 320 mmol) dissolved in CH_2Cl_2 (200 mL) and (IPr)(η^3-C_3H_5)PdCl (**7**, 18 mg, 0.032 mmol) were charged into a bomb reactor. After the reactor was cooled with a dry ice acetone bath, it was evacuated for 20 min. The evacuated reactor was charged with H_2 gas under 20 bar pressure. The solution was stirred overnight. A pressure drop of 10 bar was observed. The remaining H_2 gas was vented off, and the solution was filtered over a short pad of silica gel to remove catalyst. Evaporation of solvent gave a product which was stirred over Na/K alloy at 40 °C. The compound was transferred to a reservoir by vacuum distillation and stored inside a glovebox. ^{1}H NMR (C_6D_6): δ 5.58 (m, 1H), 5.45 (m, 1H), 3.06 (m, 1H), 2.45 (m, 1H), 2.28−2.06 (m, 5H), 2.00 (m, 1H), 1.88−1.72 (m, 3H), 1.64−1.48 (m, 2H), 1.36−1.24 (m, 3H), 1.18−1.12 (m, 2H) ppm. ^{13}C {^{1}H} NMR (C_6D_6): δ 132.48, 131.23, 55.63, 45.49, 44.20, 42.66, 42.06, 41.63, 41.58, 41.38, 39.93, 38.44, 32.34, 25.59, 24.84 ppm.

Ethylene/HTCPD Copolymerization (Small Scale). In a glovebox, 28 mL of a toluene solution of HTCPD was added to a

Table 2. Tensile Properties of Norbornene−COC and HTCPD−COC Films[a]

sample	T_g	M_n	M_w	stress at yield (MPa)[b]	stress at break (MPa)[b]	strain at break (%)[b]	tensile modulus (MPa)[b]
NB−COC	146	100 000	180 000	28(0.9)	29(0.8)	2.1(0.2)	1700(140)
HTCPD/ethylene copolymer (entry 10)	154	100 000	190 000	30(1.4)	31(1.6)	2.8(0.5)	2100(190)

[a] Casting films of 110 μm thickness. [b] Average values for five measurements, and the values in parentheses are the standard deviations.

dried 60 mL glass reactor with a magnetic bar. The reactor was assembled and brought out from the glovebox. The reactor was then heated to 70 °C with a mantle. After an activated catalyst, which was prepared by mixing **6** (4.0 μmol), $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (16.0 μmol), and $Al(iBu)_3$ (800 μmol) in 2.0 mL of toluene, was added via a syringe, the ethylene gas was fed immediately under pressure (Table 1). After polymerization was conducted for a given time (Table 1), the ethylene gas was vented off. The viscous polymerized solution was transferred into a one-neck flask. After toluene was removed under vacuum, unreacted HTCPD was recovered by vacuum distillation (80 °C/0.3 mmHg). The residue was dissolved in chloroform, and the resulting solution was filtered over a short pad of Celite. Methanol was added to the solution to yield a white precipitate, which was collected by filtration. The precipitate was dried under vacuum above its T_g. The copolymer (5 mg) was dissolved in $CDCl_3$, and the NMR spectra were recorded at 25 °C.

Ethylene/HTCPD Copolymerization (Large Scale). A toluene solution of HTCPD (90 mL) was transferred into a dried bomb reactor under a N_2 atmosphere. After an activated catalyst, which was prepared by mixing the catalyst (15.4 μmol), $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (61.7 μmol), and $Al(iBu)_3$ (3.1 mmol) in 10 mL of toluene, was added via a syringe, the ethylene gas was charged immediately under 20 psig pressure. After polymerization was conducted for 90 min, the ethylene gas was vented off. The viscous polymerized solution was treated as described above to the filtration step.

Preparation of Film. Polymer was dissolved in $CHCl_3$ to obtain a thick viscous solution (15 wt %), which was filtered using a 0.45 μm GD/X PVDF syringe filter. The viscous solution was spread on a glass plate (25 cm × 40 cm) with a thickness (750 μm) determined using an micrometer adjustable film applicator. The solvent in the spread film was carefully evaporated at room temperature for 1.0 h in an inert condition and then at 100 °C for 1.0 h. After evaporation, the film thickness was 110 μm. In case of norbornene/ethylene copolymer, some bubbles were formed during the evaporation (Supporting Information).

Measurement of Tensile Properties. The tensile test bars (110 mm × 15 mm) were cut from the films avoiding bubbles. The tensile tests were performed according to the ASTM D 638 on UTM (WL2100). The drawing rate was 5 mm/min.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of HTCPD and the ^{13}C-DEPT NMR spectra of a copolymer. The material is available free of charge via the Internet at http://pubs.acs.org

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