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Notes

Copolymerization of 5,6-Dihydrodicyclopentadiene and Ethylene

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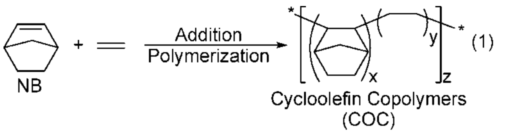
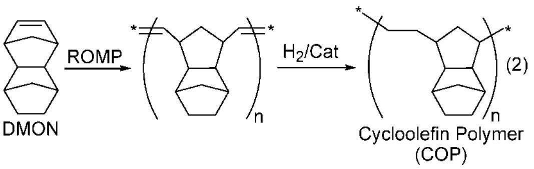
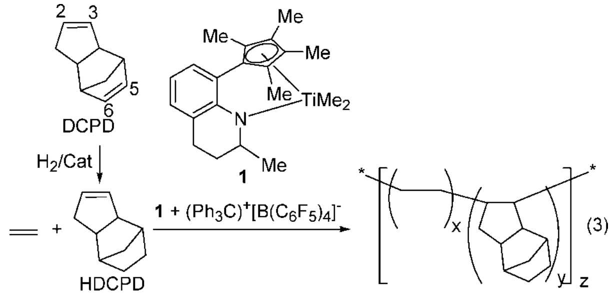
Introduction

Cyclopentadiene or its spontaneous Diels−Alder adduct, dicyclopentadiene, is a major constituent in the C5 stream of naphtha cracking.[1] Up to now, however, most C5 streams have not been used as a source of chemicals but have instead been incinerated as an energy source. An approach to add value to cyclopentadiene is the production of Diels−Alder adducts of cyclopentadiene with olefins and their use for production of valuable polymers. Two approaches have been developed to polymerize Diels−Alder adduct (cycloolefin). One is vinyl addition copolymerization with ethylene (eq 1).[2] The copolymer obtained through this method is called cycloolefin copolymer (COC) and is commercialized under the trade names APEL by Mitsui and Topas by Ticona.[3] The other approach is ring-opening metathesis (ROMP) of cycloolefin and subsequent hydrogenation of the resulting polymer (eq 2). This is called cycloolefin polymer (COP) and is also commercialized under the trade names Zeonex and Zeoner by Zeon.[4] The former approach is more attractive not only because the properties of the resin can be varied by changing the cycloolefin content in the copolymer but also because the hydrogenation process, which is necessary in the latter approach, is not required. The saturation of all the double bonds present in the polymer backbone by hydrogenation is not an easy task.





5,6-Dihydrodicyclopentadiene (HDCPD) is an attractive cycloolefin monomer. It can be prepared inexpensively from dicyclopentadiene (DCPD) through regioselective hydrogenation of DCPD (eq 3).[5] The 5,6-double bond in DCPD is more reactive than the 2,3-double bond, and hence the addition of an equimolar amount of hydrogen gas to DCPD in the presence of a catalyst affords mainly HDCPD. Because of reactivity difference of the two double bonds in DCPD, it is also possible either to polymerize DCPD through ROMP[6] or to copolymerize it with ethylene[7] with the less reactive 2,3-double bond intact, consequently not providing a cross-linked polymer. Because of the lower reactivity of the 2,3-double bond, the copolymerization of HDCPD and ethylene has not been realized yet. Even CGC (constrained geometry catalyst, $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$),[8] which has a reputation to be excellent in incorporating a bulky monomer, fails in copolymerizing HDCPD and ethylene.[9] When copolymerization is attempted with CGC, only pure polyethylene not containing any HDCPD unit is obtained. The homopolymerization of HDCPD was reported with a metathesis catalyst, WCl_5/Et_2AlCl, but a low-molecular-weight oligomer ($M_n = 3000$) was obtained.[10] Recently, we reported the preparation and polymerization reactivity of a series of *o*-phenylene-bridged analogues of CGC.[11] One of them, complex **1** as shown in eq 3, shows better comonomer incorporation and activity than CGC ($[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$) in ethylene/1-octene copolymerization.[12] In this work, we report successful HDCPD/ethylene copolymerization employing complex **1** as catalyst precursor (eq 3). Once the alternating copolymerization is realized, the obtained polymer structure is close to that of Zeon's resin obtained through the ROMP of 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (DMON), as shown in eq 2. Preparation of DMON is much more difficult than that of HDCPD, and furthermore, the hydrogenation process is not necessary in eq 3.



Results and Discussion

Complex **1** activated with $(Ph_3C)^+[B(C_6F_5)_4]^-$ in the presence of excess $Al(iBu)_3$ is able to copolymerize HDCPD and ethylene (Table 1). In similar conditions, CGC, $[Me_2Si(\eta^5\text{-}Me_4C_5)(N^tBu)]TiCl_2$ provides pure polyethylene only, that is, not incorporating any HDCPD. The activity is reasonably good ($(2.0-18) \times 10^6$ g/(mol Ti h)). By lowering ethylene pressure while the HDCPD concentration is fixed at 1.40 M, the activity decreases (entries 1−4). The molecular weight also decreases by lowering the pressure. The molecular weight distribution is narrow (M_w/M_n, 1.3−1.7), indicating a single active site.

The copolymer is fairly soluble in chloroform at room temperature. The copolymer of 32 mol % HDCPD content (entry 3) is fully characterized through the analysis of one and two-

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Table 1. Ethylene/HDCPD Copolymerization Results by 1[a]

entry	[HDCPD]	$P_{C_2H_4}$ (psig)	time (min)	$[C_2H_4]$[b]	activity × 10^{-6} g/(mol Ti h)	HDCPD incorporation[c] (mol %)	T_g (°C)	M_n[d] × 10^{-3}	M_w/M_n[d]
1	1.40	60	3.0	1.90	18	21	27.5	54	1.70
2	1.40	40	7.0	1.30	7.3	24	39.4	47	1.60
3	1.40	20	8.0	0.63	7.3	32	60.8	44	1.46
4	1.40	10	6.0	0.32	2.0	40	101.3	33	1.46
5	2.80	20	8.0	0.63	7.0	39	98.5	72	1.72
6	3.50	20	6.0	0.63	6.7	43	107.1	64	1.27
7	4.20	20	6.0	0.63	5.8	44	114.4	70	1.34
8	4.20	10			*e*				

[a] Polymerization conditions: toluene solution of HDCPD (30 mL), catalyst = **1** (2.0 μmol) + $(Ph_3C)^+[B(C_6F_5)_4]^-$ (8.0 μmol) in the presence of $Al(iBu)_3$ (800 μmol), 70 °C. [b] Ethylene concentration measured with a ethylene flow meter. [c] 5,6-Dihydrodicyclopentadiene content in the copolymer determined by ^1H NMR spectroscopy. [d] Determined on GPC using the polystyrene standard. [e] Negligible.

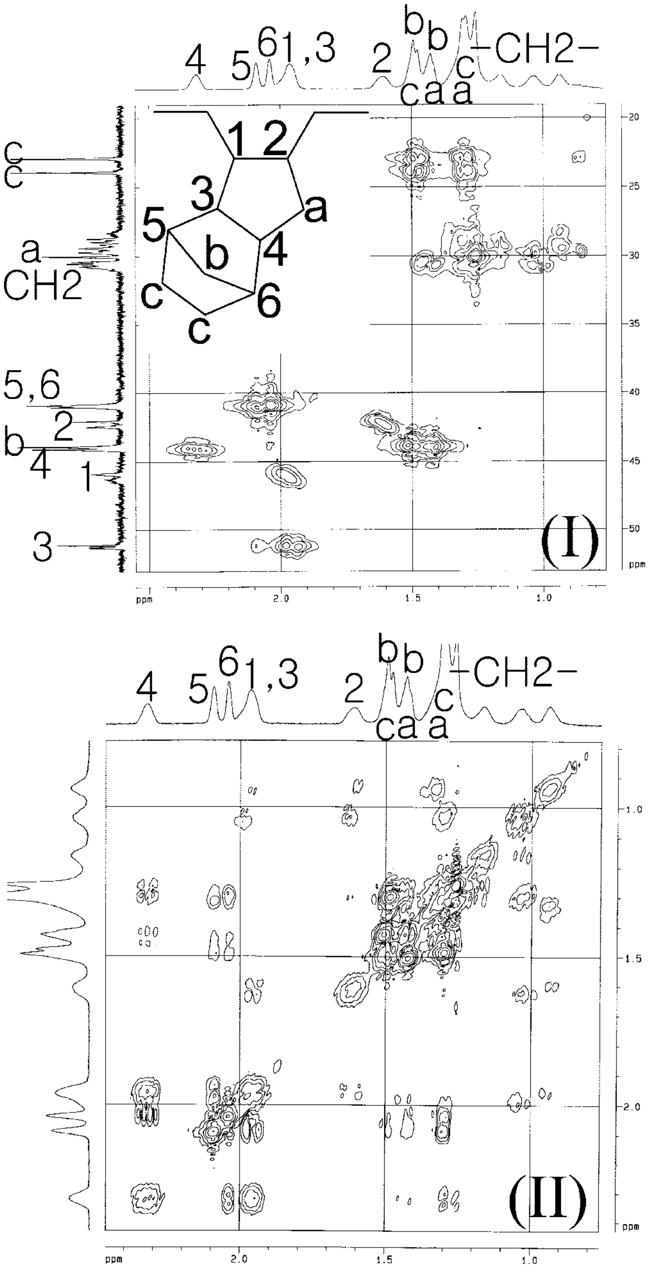


Figure 1. $^1H-^{13}C$ HMQC (**I**) and $^1H-^1H$ COSY (**II**) spectra of an HDCPD/ethylene copolymer.

dimensional NMR spectra (Figure 1). As shown in the label scheme of the copolymer inside the $^1H-^{13}C$ HMQC (heteronuclear multiple-quantum coherence) spectrum in Figure 1, there are three kinds of methylene carbon or hydrogen in the skeleton derived from HDCPD monomer, which are labeled as "a", "b", and "c"; then there are six kinds of methine carbon or hydrogen, which are labeled using Arabic numbers. Through the ^{13}C-DEPT NMR study, sharp singlet signals at 22.9, 23.9, and 43.9 ppm as well as multiple signals at 28−31 ppm are assigned to methylene carbons, while the other signals at 51, 46, 44, 42, and 41 ppm are assigned to methine carbons. From the $^1H-^{13}C$ HMQC spectrum, the six signals above 1.55 ppm in the ^1H NMR spectrum are assigned to methine protons, while all the signals below 1.55 ppm are assigned to methylene protons. Through an analysis of the coupling between the protons in the $^1H-^1H$ COSY spectrum, all the ^1H NMR signals are unambiguously assigned. From the assignment of the proton signals and from the correlation data between the carbon and proton signals obtained in the $^1H-^{13}C$ HMQC spectrum, the carbon signals are also unambiguously assigned. The assignment is shown in Figure 1.

The data set of mole fraction of ethylene in the copolymers and the mole fraction of ethylene in the feeding are well fitted to the Fineman−Ross plot ($R^2 = 0.98$), and the monomer reactivity ratios, $r_{ethylene}$ and r_{HDCPE}, are determined to be 2.3 and 0.008, respectively. The low r_{HDCPE} value of 0.008 implies that successive incorporation of two HDCPDs is strongly disfavored. If successive incorporation of two HDCPDs is not allowed, the attainable HDCPD content in the copolymer is limited below 50 mol %. At the condition of [HDCPD] of 1.40 M, the HDCPD incorporation up to 40 mol % is achieved by applying a low ethylene pressure of 10 psig, but both the activity and the molecular weight of the obtained copolymer are unsatisfactorily low (entry 4). By doubling simultaneously both ethylene pressure and [HDCPD], both the activity and the molecular weight of the resulting copolymer favorably increase more than doubly while the HDCPD incorporation is preserved at 39 mol % (entry 5). When [HDCPD] is further increased to 3.50 and 4.20 M while the ethylene pressure is fixed at 20 psig, HDCPD content increases 43 and 44 mol %, respectively. When the ethylene pressure is lowered to 10 psig at the condition of [HDCPD] = 4.20 M in an attempt to increase HDCPD content further, negligible amount of polymer is obtained. Not only the low r_{HDCPE} value of 0.008 determined on the Fineman−Ross plot but also the failure to obtain a copolymer whose HDCPD content is over 50 mol % indicates that the copolymer of 44 mol % HDCPD content is a nearly alternating copolymer. In the ^{13}C NMR spectrum of the nearly alternating copolymer, most of signals are singlets (see the Supporting Information), but the signals assigned to methine carbon "1" and $-CH_2-CH_2-$ are still a multiplet, which might be ascribed to a regio-irregular insertion of HDCPD. A similar alternating copolymerization of cyclopentene and ethylene was also realized with a catalytic system of $[Me_2Si(Ind)(NtBu)]TiCl_2$ or bis(phenoxyimine)titanium catalyst.[13]

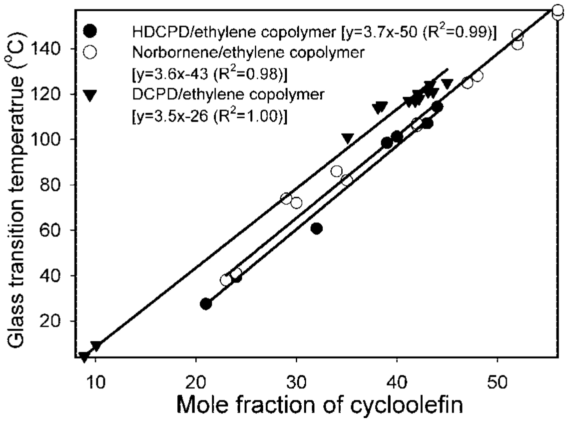
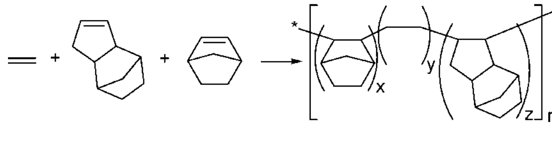


Figure 2. Relationship between T_g's and cycloolefin contents.

With increases in HDCPD content, the glass transition temperature, T_g, increases linearly (Figure 2), and the highest T_g value attained in this study is 114 °C observed for the copolymer of 44 mol % HDCPD content. For ethylene/norbornene and ethylene/dicyclopentadiene copolymerizations, the T_g also increases linearly with increases of the cycloolefin content (Figure 2).[14] Interestingly, the slope is almost same for all three copolymerizations (35−37 °C per 10 mol % increase), and the ethylene/HDCPD copolymer shows the lowest T_g among the three copolymers at the same mole content of cycloolefin. The fittings of the data sets indicate the T_g of ethylene/HDCPD copolymer is ∼24 °C lower than that of ethylene/dicyclopentadiene copolymer at the same mole content of cycloolefin. The lower T_g in ethylene/HDCPD copolymer might be attributed to the more flexibility of the cyclopentane unit through which the polymer backbone is enchained. Some conformational change is possible in the cyclopentane unit, but such conformational motion is prohibited in norbornene unit in ethylene/norbornene and ethylene/dicyclopentadiene copolymers by the rigidity of the bicyclic system.

The catalyst is also active for the terpolymerization of HDCPD, norbornene, and ethylene. When the terpolymerization is carried out at the conditions of same [HDCPD] and [norbornene] (0.70 M, respectively) and 40 psig ethylene gas, a terpolymer is obtained in 7.7×10^6 g/(mol Ti h) activity. The glass transition temperature (T_g) of the terpolymer is 100.4 °C, and the M_w and M_w/M_n values are 96 000 and 1.47, respectively. The analysis of the ^{1}H NMR spectrum reveals that the ratio of the three monomers in the terpolymer is ethylene:norbornene:HDCPD = 14:8.6:1.0, implying that the reactivity of the double bond on HDCPD is about one-tenth of that of norbornene. By increasing the [HDCPD]/[norbornene] ratio in the feeding from 1.0 to 5.0 while the sum of [HDCPD] and [norbornene] is fixed at 1.40 M, a terpolymer of higher HDCPD content is obtained (ethylene:norbornene:HDCPD = 9.5:1.0:2.3) with almost same activity (7.1×10^6 g/(mol Ti h)).



(4)

In summary, copolymerization of ethylene and 5,6-dihydrodicyclopentadiene, which is easily prepared through regioselective hydrogenation of dicyclopentadiene, is 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 is unambiguously characterized through analysis of one- and two-dimensional NMR spectra. The monomer reactivity ratios, $r_{ethylene}$ and r_{HDCPC}, determined through the Fineman−Ross plot, are 2.3 and 0.008, indicating successive insertion of two HDCPD is strongly disfavored. A nearly alternating HDCPD/ethylene copolymer is obtained at a high [HDCPD]/[ethylene] feeding. The T_g of HDCPD/ethylene copolymer is lower than those of dicyclopentadiene/ethylene and norbornene/ethylene copolymers at the same mole content of cycloolefin.

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Supporting Information Available: Polymerization details, ^{1}H and ^{13}C NMR spectra, and GPC and DSC curves of the copolymers. The material is available free of charge via the Internet at http://pubs.acs.org.

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