

Selective synthesis of highly soluble cyclic olefin copolymers with pendant vinyl groups using 1,5-hexadiene as a comonomer



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ABSTRACT

Copolymerization of norbornene (NB) and 1,5-hexadiene (HD) was performed using a fluorenylamido-ligated titanium catalyst which conducts copolymerization of NB and 1-alkene. The obtained copolymers possessed pendant vinyl groups, of which content was varied from 0 to 9.4% by the initial feed ratio of the monomers. The copolymers were soluble in various solvents even at high conversion (>85%), showing that the crosslinking of pendant vinyl groups was negligible. The glass transition temperature of the copolymer was changed from 79 °C to over 300 °C, depending on the comonomer composition. Post-functionalization of the pendant vinyl groups with 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene via ruthenium-catalyzed metathesis reaction was also performed and fluoroalkyl-functionalized cyclic olefin copolymer was successfully obtained. The fluorinated copolymer film showed higher contact angle than the unfunctionalized copolymer.

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1. Introduction

Cyclic olefin copolymers (COC), which contains alicyclic hydrocarbon skeleton, is one of the most attractive candidates of optical materials for its high heat-deflection temperature, transparency, hardness and resistance to various chemicals. COCs are usually synthesized by coordination-insertion polymerization of norbornene (NB) and its derivatives [1–5].

Some properties such as adhesion, compatibility, and mechanical strength can be improved by the introduction of functional groups to polyolefins and copolymerization of NB with other olefins. Direct copolymerizations of NB and polar functional monomers such as butyl methacrylate and functionalized norbornenes have mainly been achieved by using group 10 metal catalysts [6–13]. In early transition metal chemistry, copolymerizations of norbornene and functionalized monomer protected by alkylaluminums [14–16] or group 13-alkenyl comonomers have been reported [17–19]. Incorporated these comonomers can be converted to polar functional groups via deprotection with acid or further transformation such as oxidation and carboxylation.

The carbon-carbon double bond in polymer can be a good precursor of polar or non-polar functional groups. Some research

groups including us reported on the incorporation of C=C double bond into polynorbornene main chain by copolymerizing norbornene and conjugated dienes [20–23]. On the other hand, C=C double bond at side chain can be incorporated by the copolymerization of non-conjugated dienes such as dicyclopentadiene, vinyl- or vinylidene substituted norbornenes, and α , ω -dienes [24–29]. In the copolymerization of α , ω -dienes, the amount of pendant vinyl groups can be controlled with a suitable catalyst system and polymerization conditions, but the possibility of cyclopolymerization and crosslinking tends to increase with conversion because the incorporated vinyl groups can react competitively with its own propagation center and the other propagation chain [30–35]. For example, Nomura and coworkers conducted terpolymerization of norbornene, 1-octene and 1,7-octadiene by half-titanocene catalysts to obtain COC with pendant vinyl groups, but their conversions were kept low probably for preventing crosslinking [36].

Here, we investigated copolymerization of NB and 1,5-hexadiene (HD) using titanium complex **1** (Fig. 1), which is very effective for the copolymerization of NB and various α -olefins [37–39], and found to give highly soluble copolymers with pendant vinyl groups even at high conversion. Furthermore, we performed functionalization of the obtained NB/HD copolymer via olefin metathesis to give fluorine-containing COC.

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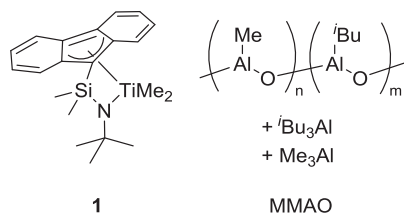


Fig. 1. Structure of titanium complex **1** and MMAO.

2. Experimental section

2.1. General

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk line techniques. Modified methylaluminoxane (MMAO, 6.5 wt% Al in toluene) was generously donated by Tosoh-Finechem Co. (Japan). Dry toluene was purchased from Kanto Chemical Co. Inc., and distilled over sodium metal. 2,6-Di-*tert*-butyl-4-methylphenol (BHT) was used as a 0.30 M stock solution in toluene. Norbornene (NB), 1,5-hexadiene (HD) and 1,7-octadiene were distilled from CaH₂ prior to use. Titanium complex **1** was synthesized by previously reported procedure [40]. Other materials were used without further purifications. ¹H, ¹⁹F and ¹³C NMR spectra were recorded in tetrachloroethane-*d*₂ or chloroform-*d* on a JEOL Lambda 500 NMR spectrometer. The obtained spectra were referenced to the signal of a residual trace of the partially protonated solvents [¹H: $\delta = 5.91$ ppm (C₂HDCl₄), $\delta = 7.26$ ppm (CHCl₃)], solvents [¹³C:

$\delta = 73.8$ ppm (C₂D₂Cl₄), $\delta = 77.1$ ppm (CDCl₃)] or external standard [¹⁹F: $\delta = -63.7$ ppm (CF₃C₆H₅)]. Molecular weights of polymers were determined by GPC on a Viscotec HT-GPC350 chromatograph (*T* = 150 °C; eluent, *o*-dichlorobenzene) or a Tosoh HLC-8320 chromatograph (*T* = 40 °C; eluent, THF) calibrated with polystyrene standard. The concentration of polymers in the injecting solutions was approximately 2–3 mg/mL and the injection volume was 0.2 mL.

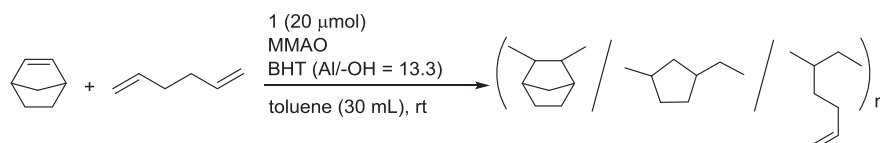
2.2. Copolymerization of NB and HD

To a 100 mL two-necked flask, MMAO (6.5 wt% Al in toluene, 1.8 mL, 4.0 mmol), NB (5.0 M in toluene, 21 mmol, 4.2 mL), HD (1.3 mL, 10.5 mmol) and toluene (18 mL) were charged under nitrogen. BHT (0.50 M in toluene, 0.60 mmol, 1.2 mL) was added to the solution and stirred for 30 min. The polymerization reaction was started by the addition of a solution of titanium catalyst **1** (7.4 mg, 20 μ mol) in toluene (1.0 mL). After stirring 5 min at room temperature, the reaction mixture was poured into 200 mL of MeOH containing 4 mL of concentrated HCl and the precipitated polymer was collected by filtration. The obtained polymer was dried for 6 h under vacuum at 60 °C to the constant weight to give 830 mg of colorless copolymer.

2.3. Post-functionalization of NB/HD copolymer

To a 100-mL two-necked flask, NB/HD copolymer (500 mg, *M*_n = 22000, PDI = 1.7, vinyl content = 1.4%) was dissolved into a mixture of toluene (20 mL) and 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (1.0 mL). Then a solution of Grubbs 2nd generation

Table 1
Copolymerization of NB and HD using **1**–MMAO/BHT system.



Run	NB/HD (mmol)	Time (min)	Al/Ti	Yield (g)	Conv. ^a (%)	<i>M</i> _n ^b (10 ⁴)	PDI ^b	<i>N</i> ^c (μ mol)	<i>T</i> _g ^d (°C)	C=C ^e (mol%)
1	21/21	5	400	0.68	18	1.5	1.5	45	236	2.2
2	21/10.5	5	400	0.83	29	1.5	1.6	55	251	1.6
3	21/5.3	5	400	0.94	39	3.2	1.8	29	n.d. ^f	0.7
4	21/2.6	5	400	1.03	47	8.3	1.8	12	n.d. ^f	n.d. ^g
5	5.3/21	5	400	0.21	9	1.1	1.7	19	96	8.3
6	2.6/21	5	400	0.57	29	2.0	2.6	29	n.d. ^f	9.4
7	3.5/3.5	15	400	0.32	52	0.6	1.7	49	197	2.1
8	21/10.5	60	800	2.48	87	1.2	2.0	206	239	1.9
9	21/10.5	60	400	2.00	71	1.5	1.8	133	234	1.9
10	21/10.5	60	200	0.88	31	1.4	1.7	63	253	1.5
11	5.3/21	60	400	1.41	64	1.7	4.1	83	79	8.5
12 ^h	21/5.3	5	400	1.29	43	6.5	1.6	20	256	- ⁱ
13	0/5	5	400	0.32	78	1.5 ^j	4.1 ^j	21	23 ^k	n.d. ^g
14 ^l	21/21	5	400	2.05	48	12 ^j	2.3 ^j	17	151	- ^j

^a Yield per total feed of monomer.

^b Measured by GPC calibrated with polystyrene standards.

^c Number of polymer chain calculated from yield and *M*_n.

^d Determined by DSC.

^e Determined by ¹H NMR.

^f Not detected between 0 and 300 °C.

^g Not detected by ¹H NMR.

^h 5.3 mmol of 1-octene was added.

ⁱ Not determined.

^j Only partly soluble in THF and *o*-dichlorobenzene.

^k A melting point was detected at 95 °C besides *T*_g.

^l 1,7-Octadiene was used in place of HD.

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