Synthesis and Properties of Hydrogenated Ring-Opening Polymers of Endo/Exo-Dicyclopentadiene

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(Received December 21, 1994)

ABSTRACT: Cyclic olefin polymers were obtained by ring-opening metathesis polymerization (ROMP) of endo- and exo-dicyclopentadiene (DCP) followed by the complete hydrogenation of double bonds. The cyclic olefin polymers are amorphous and transparent. Cyclic olefin polymers of endo- and exo-DCP have glass transition temperatures (T_g) of 97 and 66°C, respectively. The cyclic olefin polymer of endo-DCP shows extremely low water vapor permeability of $0.09\,\mathrm{g \cdot mm\,m^{-2} \cdot 24\,h}$ which is lower than those of crystalline polyolefins such as polyethylene (PE) or polypropylene (PP).
            KEY WORDS   Dicyclopentadiene / Endo and Exo Isomers / Ring-Opening Metathesis Polymerization / Hydrogenation / Water Vapor Permeability /

A number of studies on water vapor permeability of crystalline polyolefin films, for example, polyethylene (PE) or polypropylene (PP), have been reported.[1-3] Particularly, the relation between water vapor permeability constants, polymer densities, and polymer crystallinity have been studied. Water vapor permeability constants of polyolefins usually decrease as polymer density increases. This is caused by volume dilution of amorphous factions by a relatively impermeable crystalline phase.

Polymer films with low water vapor permeabilities are useful for pharmaceutical packaging materials such as strip package and a press through package (PTP). Poly(vinyl chloride) (PVC) films have been widely used for PTP. Recently, however, PVC films have been replaced by PP films, which have lower water vapor permeabilities, because of environmental concern related to the PVC waste. The resistance of a PP film to water vapor permeation (water vapor permeability constant $P_c = 0.27\,\mathrm{g \cdot mm\,m^{-2} \cdot 24\,h}$) is superior to that of a PVC film ($P_c = 0.90\,\mathrm{g \cdot mm\,m^{-2} \cdot 24\,h}$).

However, laminated films of PP and poly-(chloro-tri-fluoroethylene) are still needed to achieve higher resistance to water vapor permeation.

We investigated the synthesis and physical properties of hydrogenated ring-opening polymers of norbornene derivatives for optical uses.[4] Hydrogenated ring-opening polymers are amorphous and have good transparency. In our recent studies, it was found that hydrogenated ring-opening polymers show relatively lower water vapor permeation properties than crystalline polyolefins such as PE or PP.

Among norbornene derivatives, dicyclopentadiene (DCP) is the most easily available monomer. DCP has an endo or exo isomeric structure. We studied water vapor permeation and other properties of hydrogenated ring-opening polymers and copolymers of endo- and exo-DCP. The synthesis and properties of these polymers are described in this paper.

EXPERIMENTAL

Materials

Endo-DCP (from Nippon Zeon Co., Ltd.) was dried over CaH_2 and distilled under reduced pressure. The purity determined by GC analysis was more than 99%.

Exo-DCP was obtained from endo-DCP according to the method by Nelson et al.[5] Obtained DCP consisted of 95% exo-DCP and 5% endo-DCP.

Toluene and cyclohexane were dried over CaH_2 and distilled before use. 1-Hexene was dried over molecular sieves. WCl_6, Me_4Sn, and $RhCl(PPh_3)_3$ from Aldrich Chemical Co., Ltd. were used without further purification.

Hydrogenated Ring-Opening Polymer of Endo-DCP Polymerization

Polymerizations of endo-DCP were performed according to the method described previously,[6] using a catalyst consisting of WCl_6, and $(CH_3)_4Sn$, and 1-hexene as a molecular weight modifier in toluene under nitrogen atmosphere.

50.2 g (0.38 mol) of endo-DCP were dissolved in 950 ml of toluene and 0.32 g (0.0038 mol) of 1-hexene was added. To this solution were added 10.4 g of 10 wt% $(CH_3)_4Sn$ (0.0058 mol)/toluene solution and 57.5 g of 2 wt% WCl_6 (0.0029 mol)/toluene solution and ring-opening metathesis polymerization was started at 70°C. After 2 hours, DCP was no more observed in the reaction mixture by GC analysis. 2 g of 2-propanol were added to stop the reaction. The reaction mixture was poured into 3 liters acetone–2-propanol (1 : 1) to precipitate the polymer, followed by filtration. It was dried under vacuum for 24 hours at 40°C. Yield was 47.7 g (95%).

Hydrogenation

40 g of the ring-opening polymer of endo-DCP were dissolved in 400 ml cyclohexane. After adding 4 g of $RhCl(PPh_3)_3$ as a hydrogenation catalyst, the mixture was charg-

ed into an 1 liter autoclave equipped with an agitator. The contents were kept for 3 hours under a hydrogen pressure of $30\,kg\,cm^{-2}$ at 100°C with stirring. After the reaction, the resulting hydrogenated polymer solution was poured into 2-propanol (2 liters) and the precipitate was collected by filtration. It was then dried under vacuum for 48 hours at 50°C. The yield was 36.7 g (92%).

Hydrogenated Ring-Opening Copolymers of Endo- and Exo-DCP

Hydrogenated ring-opening copolymers of endo/exo mixtures with four compositions (endo/exo molar ratio of 75/25, 50/50, 25/75, and 5/95) were obtained in the same manner as above.

Analysis

Molecular weights (M_n and M_w) of the polymers were determined by gel permeation chromatography (GPC) in toluene as the eluent at 60°C on a Tosoh HLC-803D instrument equipped with gel packed columns (TSKgel G5000, G4000 and G2000-HXL) and a differential refractometer. Molecular weights were calibrated using standard polystyrenes. Glass transition temperatures were measured by differential scanning calorimetry at a heating rate of $10°C\,min^{-1}$ on a Seiko DSC220 instrument. Thermal decomposition temperature at 5% weight loss was measured by thermogravimetric analysis in nitrogen atmosphere at a heating rate of $10°C\,min^{-1}$ on a Seiko TGA instrument. ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ were measured with a JOEL JNM-EX400WB operating at 400 MHz and 25.1 MHz, respectively. Water vapor permeabilities of polymer films with a thickness of $300\,\mu m$ were measured according to JIS Z 0208 (condition B). Films were prepared by the compression molding method at 150°C. Crystallinities of the polymers were estimated by small-angle X-ray scattering intensity distribution, operating at 40 kV and 100 mA on a Rigaku Rotaflex RU-200B. Specific gravity

was measured according to JIS K 7112 (method A). Refractive indexes were measured by Abbe's refractometer at 30°C.

RESULTS AND DISCUSSION

Hydrogenated Ring-Opening Polymer of Endo-DCP

DCP has two reactive double bonds. The double bond of the norbornene ring is more reactive than that of the cyclopentene ring. Therefore, selective ring-opening metathesis polymerization is required to obtain a linear polymer of DCP. According to Hamilton *et al.*[6] and Pacreau *et al.*,[7] the soluble linear polymer **2** (as shown by eq 1) of endo-DCP was obtained by the selective metathesis reaction of the double bond of the norbornene ring.

$$\text{(1)}$$
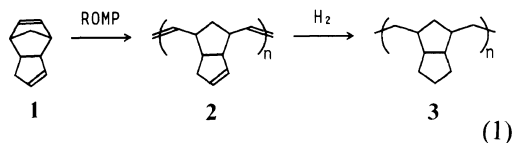
The linear polymer of endo-DCP with well controlled molecular weight was prepared using 1-hexene as shown in Table I.

The saturated polymer **3** was prepared under mild conditions by complete hydrogenation of double bonds of the main chain and the side chain of the polymer **2** using Wilkinson complex as a catalyst.

The IR spectrum of polymer **2** shows a weak

absorption at $965\,\mathrm{cm^{-1}}$ and relative strong absorption at $755\,\mathrm{cm^{-1}}$ corresponding to trans and cis double bonds, respectively. The $^1\mathrm{H}$ NMR spectrum of polymer **2** shows two blocks of signals in the region from 0.6 to 3.4 ppm and from 5.2 to 5.8 ppm assigned to protons attached to saturated carbons and olefinic protons, respectively. The ratio of integrated area of two blocks of signals is $H_{(\mathrm{sat.})}/H_{(\mathrm{olefinic})} = 2.0$. The results of IR and $^1\mathrm{H}$ NMR spectra showed that the polymer has a ring-opening structure.

In the IR spectrum of polymer **3**, absorption bands at 965 and $755\,\mathrm{cm^{-1}}$ were no more observed, and in the $^1\mathrm{H}$ NMR spectrum, signals of olefinic protons also completely disappeared in the region from 5.2 to 5.8 ppm. The hydrogenation rate was accurately determined with $^1\mathrm{H}$ NMR, showing that more than 99% of double bonds were hydrogenated (Table II).

Polymer **2** has poor heat stability and is degraded easily by air-oxidation, owing to the unsaturated character. On the other hand, polymer **3** shows high heat resistance and good stability against air-oxidation. Weight loss curves of them are shown in Figure 1. Thermal decomposition temperature of polymer **3** is more than 430°C and more than 30°C higher than that of polymer **2**.

Glass transition temperatures of polymers **2** and **3** are 138 and 97°C, respectively. The higher T_g of the former is attributed to more

Table I. Ring-opening polymerization of endo-DCP and endo/exo-DCP[a]

Endo/exo ratio of DCP monomer	Conversion %	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n
100/ 0	100	1.12	2.39	2.13
75/25	100	1.47	2.94	2.00
50/50	100	0.89	1.98	2.22
25/75	100	1.60	3.72	2.32
5/95	100	1.21	2.83	2.34

[a] $[\mathrm{DCPD}] = 0.38\,\mathrm{M}$, $[\mathrm{WCl_6}] = 2.9 \times 10^{-3}\,\mathrm{M}$, $[\mathrm{Me_4Sn}]/[\mathrm{WCl_6}] = 2$, $[1\text{-Hexene}]/[\mathrm{DCPD}] = 0.01$.

Table II. Hydrogenation of ring-opening polymers of endo-DCP, and exo/endo-DCP

Endo/exo ratio of DCP monomer	Endo/exo ratio[a] in the hydrogenated polymer	Hydrogenation rate[b] %
100/ 0	99/ 1	>99
75/25	73/27	>99
50/50	55/45	>99
25/75	19/81	>99
5/95	5/95	>99

[a] Calculated from $^{13}\mathrm{C}$ NMR spectra. [b] Calculated from $^1\mathrm{H}$ NMR spectra.
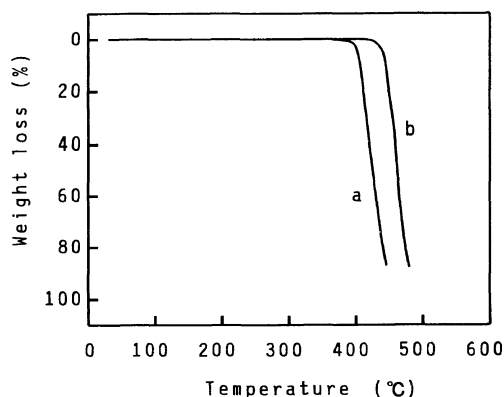
Figure 1. Thermogravimetric analysis of ring-opening polymer **2** and hydrogenated ring-opening polymer **3** of endo-DCP under N_2. Heating rate, $10°C \, min^{-1}$; a, polymer **2**; b, polymer **3**.

Figure 2. Dependence of the glass transition temperature of hydrogenated ring-opening polymers of DCP on endo percentage.

rigid structure of the main chain consisting of double bonds.

Hydrogenated Ring-Opening Copolymers of Endo/Exo-DCP

To compare properties of the hydrogenated ring-opening polymer of exo-DCP isomer with those of endo isomer, exo-DCP was synthesized and copolymerized with the endo isomer. Hydrogenated ring-opening copolymers were prepared in four exo/endo ratios using the same method as homopolymer.

Results of the polymerization of endo/exo-DCP are shown in Table I. Polymers obtained were all soluble in toluene, suggesting that they are linear polymers without any cross linking. Using GPC, the number-average molecular weight ($\bar{M}_n$) and polydispersity (d) were determined: $\bar{M}_n$ was in the range of 8900 to 16000 and d was 2.00 to 2.34. The molecular weight and distribution were also controled by adding 1-hexene.

Hydrogenation of these polymers were similarly carried out with more than 99% hydrogenation rates (Table II).

Structure of Hydrogenated Ring-Opening Homo- and Copolymers
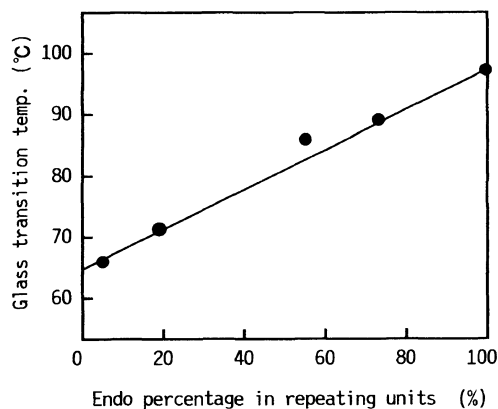
Both hydrogenated ring-opening homo-polymers derived from endo- and exo-DCP showed ^{13}C NMR spectra similar to those reported by Hamilton et al.[6] In the ^{13}C NMR spectra of hydrogenated ring-opening copolymers, signals of the repeating units derived from endo- and exo-DCP can be readily identified. The endo/exo ratio of the repeating unit was calculated by the intensity of signals in the ^{13}C NMR spectra and the results are shown in Table II. Endo/exo ratios of the repeating units in the hydrogenated ring-opening copolymers were found approximately the same as those of the endo/exo-DCP monomers used, which suggests that the structural feature of the monomers is maintained in the polymer.

The Relation between Polymer Structure and T_g

T_g of the hydrogenated ring-opening polymer of endo-DCP is 97°C and that of exo-DCP is surprisingly low 66°C.

The relation between the ratio of repeating units from endo/exo-DCP and T_g of copolymers is shown in Figure 2. A linear correlation was observed which demonstrates the additive property of T_g.

The difference of T_g between the hydrogenated ring-opening polymers of endo- and exo-DCP is attributed to stiffness or flexibility

of the main chain. The 5-membered ring substituent attached to the cyclopentane ring in endo-DCP polymer main chain is considered geometrically closer to the main chain than that of exo-DCP polymer. Therefore, the steric hindrance around main chain of the polymer from endo isomer is larger than that of the exo isomer, resulting in higher T_g.

The Relation between the Polymer Structure and the Water Vapor Permeability

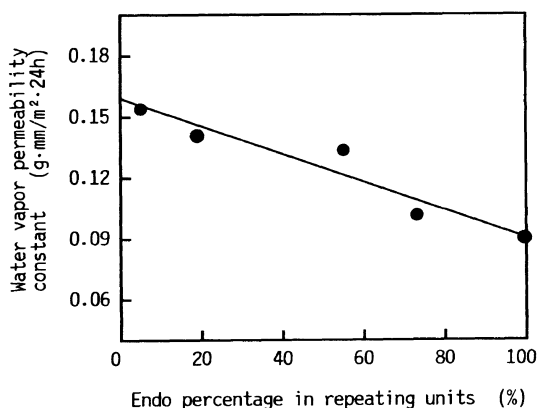Transparent sheets of hydrogenated ring-opening polymers of DCP of 300 μm thickness

Figure 3. Water vapor permeability constants of films prepared from hydrogenated ring-opening polymers of endo/exo-DCP.

Table III. Water vapor permeabilities, specific gravities and refractive indexes of hydrogenated ring-opening polymers of DCP and other polyolefins

Endo/exo ratio in the hydrogenated polymer	Water vapor permeability constant[a] $g \cdot mm \, m^{-2} \cdot 24\,h$	Specific gravity $g\,cm^{-3}$	Refractive index
99/ 1	0.09	0.986	1.5234
55/45	0.135	0.980	1.5291
5/95	0.15	0.975	1.5248
PE	0.13	0.955	1.52
PP	0.27	0.910	1.49

[a] Permeability constants were calculated from data of films of 300 μm thickness.

were prepared by compression molding at 150°C. Water vapor permeability of the sheets was measured at 40°C, as shown in Figure 3. Water vapor permeabilities also depend on the ratio of repeating units of polymers derived from endo- and exo-DCP.

The water vapor permeability of the polymer sheet is generally influenced by several factors such as the intermolecular space (free volume fraction), the attractive force between polymer molecules, the crystallinity of a polymer, the chemical interaction between polymer and water molecules, and others. The intermolecular space mainly contributes to the dependence of the water vapor permeability on the ratio of repeating units derived from endo- and exo-DCP. Chemical interactions between endo and exo isomeric polymers and water molecules are expected to be the same. Both endo- and exo-DCP polymers are amorphous from the results of X-ray analysis. Intermolecular spaces are expected to be closely related to specific gravity of molded articles of isomeric polymers. Water vapor permeabilities and specific gravities of polymers of endo- and exo-DCP are shown in Table III. The fact that larger specific gravity leads to the lower water vapor permeability suggests that the intermolecular space of the polymer of endo-DCP is smaller than that of exo-DCP. Moreover, specific gravity is correlated to refractive indices as shown in Table III. The polymer of endo-DCP with the higher specific gravity has a higher refractive index.

The amorphous polymer of endo-DCP was found to show lower water vapor permeability than crystalline polyolefins such as PE and PP (Table III). Higher crystallinity contributes to high specific gravity and low water vapor permeability. It is expected that the water vapor permeability of a film of the amorphous DCP polymer can be further lowered by stretching the film for molecular orientation.

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