Hydrogenation of Poly(1,3-cyclohexadiene)

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ABSTRACT: The hydrogenation of poly(1,3-cyclohexadiene)s (PCHDs) with various homogeneous catalysts are reported. The initial screening for hydrogenation catalysts was carried out using cyclohexene as a model compound for the monomeric unit in the polymer chain. High conversion for both cyclohexene and 1,4-linked PCHD were found with carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) [RuHCl(CO)(PPh₃)₃]. The existence of units formed by 1,2-addition (the 1,2-CHD unit) in the polymer chain strongly influenced the extent of hydrogenation of PCHD. Complete hydrogenation of PCHD (polycyclohexane: PCHE) containing 1,2-CHD units was found with the cobalt(III)acetylacetonate[Co(acac)₃] / triisobutylaluminium[(*i*-C₄H₉)₃Al] system. The PCHE obtained was composed of cyclohexane rings directly connected in the main chain, and had excellent thermal stability.

KEY WORDS Polycyclohexane / Hydrogenation / Homogeneous Catalyst / Steric Hindrance / Poly(1,3-cyclohexadiene) /

There has been considerable interest in the synthesis of cyclic olefin polymers with narrow molecular weight distribution and well-defined polymer chain structure in recent years. In particular, cyclic olefin polymers having directly connected alicyclic structures within the main chain are very interesting (*e.g.*, polycyclopentene, polycyclopentane, polycyclohexene, polycyclohexane), since a dramatic improvement in thermal stability, chemical stability, mechanical strength, and optical and electrical properties are expected for such polymers compared to the conventional polyolefins (*e.g.*, polyethylene, polypropylene, polystyrene).

Although polycyclohexane (PCHE), one of the typical polymers in the area, is expected to be of particular interest in this respect, the synthesis of PCHE has been reported to be difficult. Several synthetic procedures have been reported, including anionic polymerization of 1,3-cyclohexadiene (1,3-CHD) with *n*-butyllithium (*n*-BuLi) followed by the hydrogenation of poly(1,3-cyclohexadiene) (PCHD) with diimide formed by the thermal decomposition of *p*-toluenesulfonylhydrazide (TSH). The polymers obtained were of low molecular weight and of broad molecular weight distribution. The catalytic hydrogenation of PCHD has not been attempted before this paper.^{1,2}

In previous papers,^{3–5} we reported the first successful living anionic polymerization of 1,3-CHD with the *n*-BuLi/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) system as an initiator, and showed examples of the synthesis of homopolymers and block copolymers with a narrow molecular weight distribution and controlled molecular weight. Furthermore, we prepared PCHE with various molecular weights and their block copolymers by the hydrogenation of PCHD homopolymer and

Scheme 1. Hydrogenation of Poly(1,3-cyclohexadiene).

block copolymers with heterogeneous catalysts.⁶ The properties and potential applications of PCHEs as industrial materials were also reported.^{6–8}

In this paper, we report the hydrogenation of PCHD with homogeneous catalysts (Scheme 1). The relationship between the microstructure of the polymer chain and the activity of the hydrogenation catalysts is also discussed.

EXPERIMENTAL

Materials

n-Butyllithium(*n*-BuLi; 1.44 M in *n*-hexane), triisobutylaluminium[(*i*-C₄H₉)₃Al; 1.0 M in cyclohexane], 1,2,4-trichlorobenzene (TCBz), 1,2-bis(2-methoxyethoxy)ethane (triglyme; TG), cyclohexene, toluene, decalin, benzene, ethanol (EtOH), methanol (MeOH), and acetone were used without further purification. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), 1,3-cyclohexadiene (1,3-CHD), and cyclohexane were refluxed over calcium hydride and then distilled under an argon atmosphere. Chlorotris(triphenylphosphine)rhodium(I) [RhCl(PPh₃)₃], dichlorobis(triphenylphosphine)palladium(II) [PdCl₂(PPh₃)₂], carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) [RuHCl(CO)(PPh₃)₃], cobalt(III) acetylacetonate [Co(acac)₃], and titanocene dichloride

[TiCl₂(Cp)₂] were dried under reduced pressure under an argon atmosphere.

*Synthesis of 1,4-Linked PCHD (Anionic Polymerization of 1,3-CHD with *n*-BuLi)*

A well-dried 100 mL Schlenk tube was purged with dry argon, and toluene (25.8 g) and 1,3-CHD (24.1 g; 0.3 mol) were supplied by hypodermic syringe at room temperature. *n*-BuLi (6.06 mmol) was added to this solution and the polymerization was carried out under dry argon atmosphere at 50 °C for 8 h. After polymerization, an equimolar amount of dried methanol was added to the reaction mixture to terminate the reaction. Then the polymerization mixture was poured into a large amount of acetone (1000 mL) to precipitate the polymer, which was separated by filtration. The product was dried in a vacuum for 8 h at 50 °C, to give a white powdery 1,4-linked PCHD ($M_n = 12500$; $M_w/M_n = 2.05$; 1,2-CHD units/1,4-CHD units = 2/98).

*Synthesis of PCHD with High Content of 1,2-CHD Units (Living Anionic Polymerization of 1,3-CHD with the *n*-BuLi/TMEDA System)*

A well-dried 100 mL Schlenk tube was purged with dry argon, and cyclohexane (27 g) and *n*-BuLi (0.3 mmol) were added by hypodermic syringe. To this solution were then added TMEDA (0.375 mmol) and 1,3-CHD (3.0 g; 37.4 mmol) by hypodermic syringe, and the reaction mixture was kept stirring magnetically in an argon atmosphere at 40 °C for 4 h. After polymerization, an equimolar amount of dried methanol was added to the reaction mixture to terminate the reaction. The polymerization mixture was poured into a large amount of acetone (1000 mL) to precipitate the polymer, which was separated by filtration. The product was dried in a vacuum for 8 h at 50 °C, to give a white powdery PCHD with high content of 1,2-CHD units ($M_n = 12600$; $M_w/M_n = 1.08$; 1,2-CHD units/1,4-CHD units = 50/50).

Hydrogenation of Cyclohexene

A prescribed amount of hydrogen catalyst was placed in a stainless steel autoclave equipped with an electromagnetic induction stirrer, and the autoclave was purged with dry nitrogen. Organic solvent and cyclohexene were supplied by hypodermic syringe at room temperature, and the solution was stirred for 10 min at room temperature.

The autoclave was filled with hydrogen gas, and the solution was warmed up to the reaction temperature. The reaction was conducted under a designed hydrogen pressure for a stated reaction time. The extent of hydrogenation of cyclohexene (conversion of cyclohex-

ane from cyclohexene) was estimated by gas chromatographic analysis (GC).

Hydrogenation of PCHD

PCHD was placed in a stainless steel autoclave equipped with an electromagnetic induction stirrer and then dried under reduced pressure. The autoclave was alternately evacuated and filled with dry nitrogen several times. Organic solvent was added by hypodermic syringe under dry nitrogen atmosphere, and the solution was stirred for 30 min at room temperature to dissolve the polymer. To this solution was then added a prescribed amount of the catalyst solution which was prepared by mixing the homogeneous hydrogen catalyst and organic solvent by hypodermic syringe.

The autoclave was filled with hydrogen in place of nitrogen, and the solution was warmed up to the reaction temperature. The reaction was conducted under a designed hydrogen pressure for a stated reaction time. After hydrogenation, the resulting solution was poured into a large amount of MeOH to precipitate the product, which was separated by filtration. The product was dried in a vacuum for 8 h at 50 °C, to give a white powdery polymer. The extent of hydrogenation of PCHD (conversion of cyclohexane units from cyclohexene units in the polymer chain) was estimated by the loss of olefinic signals as measured by proton nuclear magnetic resonance (¹H NMR).

Measurements

¹H NMR spectra of the polymer were measured with a 1.0 wt% solution in deuterated *o*-dichlorobenzene (DCBz) at 135 °C, using a JEOL Type α -400 spectrophotometer operating at 400 MHz using added cyclohexane as a reference (1.4 ppm). The average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Polymer Laboratory Type PL-GPC 210 column. The eluent was DCBz, and flow rate was 1.0 mL min⁻¹. A molecular weight calibration curve was obtained by using polystyrene standards. Gas chromatographic analysis (GC) was carried out using a Shimadzu Type 14A gas chromatograph using ethylbenzene as an internal standard. Thermogravimetric analysis (TGA) was carried out using a Shimadzu Type TGA-50 under an air atmosphere (air flow: 200 mL min⁻¹, heating rate: 10 °C min⁻¹).

RESULTS AND DISCUSSION

Hydrogenation of Cyclohexene as a Model Compound

As shown in Scheme 1, PCHD has a structure of a main chain consisting of units formed by 1,2-addition

Table I. Hydrogenation of cyclohexene as a model compound^a

No.	Catalyst (mg; mmol)	Hydrogen pressure (MPa)	Temp. (°C)	Reaction time (h)	Conversion (%) ^b
1	RhCl(PPh ₃) ₃ (10.0; 8.19 × 10 ⁻³)	3.9	80	5	35.8
2	RhCl(PPh ₃) ₃ (10.0; 8.19 × 10 ⁻³)	3.9	180	8	42.4
3	PdCl ₂ (PPh ₃) ₂ (10.0; 14.25 × 10 ⁻³)	3.9	80	5	3.35
4	RuHCl(CO)(PPh ₃) ₃ (10.0; 10.00 × 10 ⁻³)	3.9	165	4	94.5

^aHydrogenation was carried out in 1,2,4-trichlorobenzene (TCBz) as a solvent. [Cyclohexene]/[Solvent] = 1 g/50 mL. ^bEstimated by GC.

Table II. Hydrogenation of cyclohexene with RuHCl(CO)(PPh₃)₃^a

No.	RuHCl(CO)(PPh ₃) ₃ (mg) (mmol)		Solvent	Hydrogen pressure (MPa)	Conversion (%) ^b
1	10.0	10.0 × 10 ⁻³	TCBz ^c	3.9	72.0 (94.5) ^d
2	10.0	10.0 × 10 ⁻³	TCBz	7.8	96.2
3	10.0	10.0 × 10 ⁻³	TCBz/TG ^e (9/1)	3.9	59.0
4	10.0	10.0 × 10 ⁻³	Toluene	3.9	95.2
5	10.0	10.0 × 10 ⁻³	Decalin	3.9	99.0
6	1.00	1.00 × 10 ⁻³	Decalin	3.9	97.9
7	0.10	0.10 × 10 ⁻³	Decalin	3.9	94.7

^a[Cyclohexene]/[Solvent] = 20.0 g/100 mL, Reaction temperature: 165°C, Reaction time: 4 h. ^bEstimated by GC. ^c1,2,4-Trichlorobenzene. ^d[Cyclohexene]/[Solvent] = 1 g/50 mL (Table I, No.4). ^eTriglyme [=1,2-Bis(2-methoxyethoxy)ethane.]

(the 1,2-CHD unit) and 1,4-addition (the 1,4-CHD unit). The 1,2-CHD units/1,4-CHD units molar ratio can be determined by two dimensional NMR.^{5,6} The 1,2- and 1,4-CHD units can be regarded as the derivatives of cyclohexene. Therefore, the result of hydrogenation of cyclohexene (which is the most simple model compound for the 1,2- and 1,4-CHD units) seemed a good model for the initial screening of homogeneous catalysts for the hydrogenation of PCHD. In addition, it is well-known that the extent of hydrogenation of polymer by homogeneous catalysts can be strongly affected by the solubility of the reactants in the reaction solvent. Thus the selection of solvent was also considered to be very important factor for the screening of homogeneous catalysts for the hydrogenation of PCHD.

Since TCBz was one of the best solvents for PCHD, the hydrogenation of cyclohexene was conducted with three types of homogeneous catalysts in TCBz. The obtained results are shown in Table I.

Among the three types of catalysts used, RhCl(PPh₃)₃ and PdCl₂(PPh₃)₂ gave poor conversions. On the other hand, RuHCl(CO)(PPh₃)₃ gave a 95% conversion in TCBz at 165°C under hydrogen pressure of 3.9 MPa. The order of activity of each catalyst for the hydrogenation of cyclohexene in TCBz was RuHCl(CO)(PPh₃)₃ > RhCl(PPh₃)₃ > PdCl₂(PPh₃)₂.

Hydrogenation of Cyclohexene with RuHCl(CO)-(PPh₃)₃

In order to determine the optimum reaction conditions using RuHCl(CO)(PPh₃)₃ as a catalyst, the hydrogenation of cyclohexene was conducted with various organic solvents. As shown in Table II, strong solvent effects for the hydrogenation of cyclohexene with RuHCl(CO)(PPh₃)₃ were observed. The hydrocarbon solvents (*e.g.*, Toluene, decalin) gave over 90% conversion under a hydrogen pressure of 3.9 MPa at 165°C for 4 h. The best conversion was 99% (Table II; No.5) in the case of decalin as a solvent. The halogenated solvent (TCBz) gave a 72% conversion. The activity of the catalyst was slightly reduced by TG (a polar solvent). The order of solvent effects on the hydrogenation of cyclohexene using RuHCl(CO)(PPh₃)₃ were Decalin > Toluene > TCBz > TG. Under a high hydrogen pressure (7.8 MPa), TCBz gave a 96% conversion (Table II; No.2).

Hydrogenation of 1,4-Linked PCHD

The results in Table I and II suggested that RuHCl(CO)(PPh₃)₃ was a good hydrogenation catalyst for PCHD. The hydrogenation of 1,4-linked PCHD (*M_n* = 12500; *M_w*/*M_n* = 2.05; 1,2-CHD units/1,4-CHD units = 2/98) was conducted with two types of homogeneous catalysts for 5 h. As shown in Table III,

Table III. Hydrogenation of 1,4-linked poly(1,3-cyclohexadiene)^a

Polymer No.	Catalyst (mg; mmol)	Solvent ^b	Hydrogen pressure (MPa)	Temp. (°C)	Reaction time (h)	Conversion (%) ^c
1	RhCl(PPh ₃) ₃ (10.0; 8.19 × 10 ⁻³)	Cyclohexane	3.9	80	5	46
2	RhCl(PPh ₃) ₃ (90.0; 73.7 × 10 ⁻³)	Benzen/EtOH(9/1)	0.98	100	5	29
3	RhCl ₂ (PPh ₃) ₂ (10.0; 8.19 × 10 ⁻³)	TCBz ^d	3.9	180	5	22
4	RuHCl(CO)(PPh ₃) ₃ (10.0; 10.0 × 10 ⁻³)	TCBz	3.9	165	5	100

^a $M_n = 12500$, $M_w/M_n = 2.05$. ^b[Polymer]/[Solvent] = 1 g/50 mL. ^cEstimated by ¹H NMR. ^d1,2,4-Trichlorobenzene.

Table IV. Effect of 1,2-CHD units on hydrogenation of poly(1,3-cyclohexadiene)^a

Polymer No.	M_n	M_w/M_n	T_g (°C) ^b	1,2-CHD units/1,4-CHD units (%) ^c	Conversion (%) ^c
4	12500	2.05	89	2/98	100
5	12600	1.08	148	50/50	50

^aCatalyst: RuHCl(CO)(PPh₃)₃ (10.0 mg; 10.0 × 10⁻³ mmol), Solvent: 1,2,4-Trichlorobenzene, [Polymer]/[Solvent] = 1 g/50 mL, Hydrogen pressure: 3.9 MPa, Reaction temperature: 165 °C, Reaction time: 5 h. ^bMeasured by DSC. ^cEstimated by ¹H NMR.

RhCl(PPh₃)₃ gave less than 46% conversion while RuHCl(CO)(PPh₃)₃ gave a 100% conversion of the CHD units to the CHE units in TCBz (Polymer 4). This completely hydrogenated 1,4-linked PCHD can be considered as a 1,4-linked polycyclohexane (PCHE) with 1,4-CHE units.

Effect of 1,2-CHD Units on Hydrogenation of PCHD

To reveal the relationship between the microstructure of polymer chain and the activity of the hydrogenation catalysts, PCHDs having different 1,2-CHD units/1,4-CHD units ratios with the number average molecular weights of about 12500 were compared. The hydrogenation of PCHD was conducted with RuHCl(CO)(PPh₃)₃ in TCBz under a hydrogen pressure of 3.9 MPa at 165 °C for 4 h.

As shown in Table IV, the conversion of the 1,2-CHD units (Polymer 5) was only 50%. Compared with "Polymer 4", the existence of 1,2-CHD units in "Polymer 5" appears to be the primary factor for the difficulty of the hydrogenation of double bonds in the polymer chain.

For PCHD polymer chains, the insertion of 1,2-CHD units seems to prevent the movement of polymer chain by producing large steric hindrance effects. Actually the T_g of PCHD increases with an increase in the ratio of 1,2-CHD units to 1,4-CHD units.^{6,7} Thus the steric hindrance effects of molecular structure in PCHD should be considered to explain these tabulated results.

The possible molecular models of a polymer chain consisting of PCHD are shown in Figure 1 (a: all 1,2-CHD units, b: alternating 1,2-CHD and 1,4-CHD units,

Figure 1. Schematic representation of several polymer chain structures of poly(1,3-cyclohexadiene): (a) all 1,2-CHD units sequence; (b) an alternating 1,2-CHD units and 1,4-CHD units sequence; (c) all 1,4-CHD units sequence.

c: all 1,4-CHD units). Inspection of molecular models, shows (Figure 1), clearly the large steric hindrance effects by the insertion of 1,2-CHD units into the polymer chain of PCHD. A long sequence of 1,2-CHD units would be prohibitively crowded [Figure 1a]. The intermediate of 1,2-CHD and 1,4-CHD units is also crowded [Figure 1b]. On the other hand, steric hindrance effects of a long sequence of 1,4-CHD units seems to be not so severe [Figure 1c]. From these reasons, the hydrogen catalyst [e.g., RuHCl(CO)(PPh₃)₃] appears to be easily approached the double bonds in 1,4-linked PCHD, while it is relatively hard in the case of PCHD containing the high molar ratios of 1,2-CHD units in the polymer chain.

Solvent Effect for PCHD Containing 1,2-CHD Units

The molecular model of PCHD (Figure 1) suggested

that the completely hydrogenated PCHD (polycyclohexane: PCHE) containing 1,2-CHE units has excellent thermal stability, chemical stability, and mechanical strength due to a very rigid polymer chain structure with no double bonds. To improve the extent of hydrogenation of PCHD containing 1,2-CHD units, the solvent effects for hydrogenation were examined, carefully. The hydrogenation of PCHD was conducted with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ as a catalyst.

As shown in Table V, the conversions were around 50% for each organic solvent (TCBz, cyclohexane, decaline, and decaline/toluene). Thus there were no solvent effects with $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ during the hydrogenation of PCHD containing 1,2-CHD units. Therefore, the maximum conversion of CHE units from CHD units under the above-mentioned reaction condition seem to represent a limit imposed by steric factors between the polymer chain structure of PCHD containing 1,2-CHD units and the size of the catalyst, $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$.

Table V. Solvent effect on hydrogenation^a of poly(1,3-cyclohexadiene)^b with the *n*-BuLi/TMEDA system

Polymer No.	Solvent	Conversion (%) ^c
6	1,2,4-Trichlorobenzene	51
7	Cyclohexane	56
8	Decaline	53
9	Decaline/Toluene (9/1)	48

^aCatalyst: $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (10.0 mg; 10.0×10^{-3}), [Polymer]/[Solvent] = 1 g/100 mL, Hydrogen pressure: 3.9 MPa, Reaction temperature: 165 °C, Reaction time: 4 h. ^b $M_n = 12600$, $M_w/M_n = 1.08$, 1,2-CHD units/1,4-CHD units = 50/50. ^cEstimated by ¹H NMR.

Synthesis of PCHE Containing 1,2-CHE Units

In order to obtain the completely hydrogenated PCHD (polycyclohexane: PCHE) containing 1,2-CHE units, hydrogenations were conducted with several homogeneous catalysts under high hydrogen pressure (8.3 MPa) in cyclohexane at 180 °C for 4 h. The results are shown in Table VI (Polymers 10–12).

As shown in the table, $\text{Co}(\text{acac})_3$ combined with $(i\text{-C}_4\text{H}_9)_3\text{Al}$ gave a 100% conversion of CHE units from CHD units in PCHD containing 1,2-CHD units (1,2-CHD units/1,4-CHD units = 50/50). The ¹H NMR spectra of PCHD ($M_n = 12600$; $M_w/M_n = 1.08$; 1,2-CHD units/1,4-CHD units = 50/50) and its completely hydrogenated product (Polymer 10) are shown in Figure 2. As can be seen, the olefinic peaks perfectly disappear in “Polymer 10”. This successfully hydrogenated PCHD can be considered as a PCHE formed with equimolar amounts of 1,2-CHE and 1,4-CHE units. $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{TiCl}_2(\text{Cp})_2/(i\text{-C}_4\text{H}_9)_3\text{Al}$ system gave about 90% conversion. Thus in this investigation the most active catalyst for PCHD containing 1,2-CHD units appeared to be $\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ system.

To determine the optimum reaction conditions, the hydrogenations of PCHD with the $\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ system were conducted with various hydrogenation pressures and concentrations of PCHD in cyclohexane. The results are shown in Table VI (Polymers 13–15).

Although the hydrogen pressures were relatively low (1.0–2.9 MPa), $\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ system gave over 99% conversion. Therefore, the steric hindrance effects seems to be reduced between the polymer chain of PCHD containing 1,2-CHD units and the

Table VI. Hydrogenation^a of poly(1,3-cyclohexadiene)^b with the *n*-BuLi/TMEDA system

Polymer No.	Catalyst	Hydrogen pressure MPa	Conversion (%) ^c
10	$\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ (1/6)	8.3	100
11	$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	8.3	92
12	$\text{TiCl}_2(\text{Cp})_2/(i\text{-C}_4\text{H}_9)_3\text{Al}$ (1/6)	8.3	90
13	$\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ (1/6)	1.5	100
14 ^d	$\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ (1/6)	1.0	≥ 99
15 ^e	$\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ (1/6)	2.9	≥ 99

^aCatalyst = 0.30 mmol, Solvent: Cyclohexane, [Polymer]/[Solvent] = 1 g/100 mL, Reaction temperature: 180 °C, Reaction time: 4 h. ^b $M_n = 12600$, $M_w/M_n = 1.08$, 1,2-CHD units/1,4-CHD units = 50/50. ^cEstimated by ¹H NMR. ^d[Polymer]/[Solvent] = 10 g/100 mL. ^e[Polymer]/[Solvent] = 200 g/2500 mL, Reaction time: 6 h.

Figure 2. ^1H NMR spectra of poly(1,3-cyclohexadiene) and polycyclohexane in 1.0 wt% solution of *o*-dichlorobenzene- d_4 at 135 °C.

$\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ system.

Thermal Stability of PCHE

Polycyclohexane (PCHE) has a special structure where the main chain is formed by directly connected cyclohexane units (which is composed of the stable C–C single-bonded six-membered ring).

Since an improvement of thermal stability was expected for such saturated hydrocarbon rings and polymer chain structure, the thermogravimetries of PCHD and PCHE were contrasted. The results are shown in Figure 3. PCHE showed the excellent thermal stability compared to PCHD's. For PCHD, the weight loss of polymer was observed from around 250 °C. When the temperature was over 350 °C, the decomposition of PCHD was accelerated. On the other hand, PCHE was found to be very stable up to 400 °C. Therefore, the cyclohexane structure of PCHE is considered to have good influence on its thermal stability.

CONCLUSIONS

PCHE can be synthesized by (living) anionic polymerization of 1,3-CHD and complete hydrogenation of PCHD with homogeneous catalysts. 1,4-linked PCHD was hydrogenated by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ with high conversion. Compared with 1,4-linked PCHD, the hy-

Figure 3. Thermal stabilities of poly(1,3-cyclohexadiene) and polycyclohexane under an air atmosphere.

drogenation of PCHD containing 1,2-CHD units was relatively hard. PCHE containing 1,2-CHE units were successfully obtained by the hydrogenation of PCHD with the $\text{Co}(\text{acac})_3/(i\text{-C}_4\text{H}_9)_3\text{Al}$ system as a catalyst. Completely hydrogenated PCHD (PCHE) was composed of cyclohexane rings directly connected in the main chain, and had excellent thermal stability. The information obtained concerning the hydrogenation of PCHD should accelerate the developing of new industrial materials containing cyclohexane rings as a key structure.

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