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Cyclopolymerization of 1,6-Heptadiyne by Molybdenum and Tungsten-Based Catalysts

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Abstract: The polymerization of 1,6-heptadiyne was carried out by molybdenum and tungsten-based transition metal catalysts. This polymerization by $MoCl_5$ alone proceeded well to give a quantitative yield of polymer. The effect of monomer to catalyst mole ratio (M/C), initial monomer concentration ($[M]_0$), and the polymerization temperature for the cyclopolymerization of 1,6-heptadiyne was studied and discussed. The polymerization solution exhibited red color even after 30 min of polymerization time. The resulting polymers were mostly brown powders and mostly insoluble in any organic solvents although the polymerization proceeded in homogeneous manner in some cases. The polymer structure was characterized by various instrumental methods to have the conjugated polymer backbone structure carrying cyclic recurring unit. The thermal and morphological properties of the resulting poly(1,6-heptadiyne) were also discussed.

Introduction

Conjugated polymer systems obtained from acetylene derivatives have been studied as organic semiconductors,[1-3] as membranes for gas separation and for liquid-mixture separation,[4-10] as materials for enantioseparation for racemates by high performance liquid chromatograpy,[11,12] as a side-chain liquid crystal,[13-16] as materials for chemical sensors,[17,18] and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties.[19-24]

Cyclopolymerization (ring-forming polymerization) is any type of chain-growth addition polymerization leading to the introduction of cyclic structure into the polymer main chain via an alternating intramolecular-intermolecular chain propagation.[25-27] Cyclopolymerizations of nonconjugated diynes were extensively investigated in an attempt to prepare polymers containing alternating double and single bonds along the polymer main chain with a cyclic recurring unit.[2,28-30]

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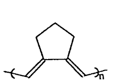
Stille and Frey first reported the study on the polymrization of nonconjugated diynes, especially 1,6-heptadiyne (HD) with Ziegler-Natta catalysts.[31] Poly(HD)s obtained were dark red or black, which indicate a high order of conjugation in the polymer. Even though a head-to-tail internal propargation would be expected, there are three possible cyclic recurring units (**1-3**) and structure **4**, which can be written to account for a soluble polymer with alternating double and single bonds along the polymer backbone.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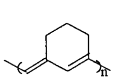
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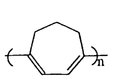
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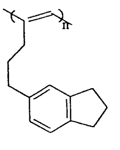
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Meriwether *et al.* obtained oligomers and polymers from the alkadiynes of $HC\equiv C(CH_2)_nC\equiv CH$ on dicarbonylbis(triphenylphosphine)nickel $[Ni(CO)_2(Ph_3P)_2]$,[32] and the polycyclized structure (4) deduced by them was in agreement with the results on Ziegler catalysts ($TiCl_4/AlEt_3$) by Hubert and Dale.[33]

Gibson *et al.* reported the insoluble, free-standing films with metallic luster by the polymerization of HD on the surfaces of concentrated solutions of "Shirakawa catalyst", a homogeneous catalyst derived from $Ti(OR)_4$ (R: n-C_4H_9, i-C_3H_7, n-(C_9H_{19})/AlR_3 (R: C_2H_5, CH_3, i-C_4H_9), using a specifically designed reactor.[34,35]

The attempted polymerization of HD with $NbCl_5$ and $TaCl_5$ yielded a mixture of cyclotrimer (15%) and polymer (25% for $NbCl_5$ and 20% for $TaCl_5$), having a relatively low conversion (40% for $NbCl_5$, 35% for $TaCl_5$).[36]

However, there have been no report on the study for the polymerization of HD by Mo- and W-based transition metal catalysts, which had been widely used for the polymerization of substituted acetylenes.[37-41] It may be very interesting to study the polymerization behaviors by Mo- and W- based catalysts of HD and the properties of resulting poly(HD)s.

Experimental

Materials. HD (Farchan Laboratories) was dried with calcium hydride and fractionally distilled. $MoCl_5$ (Aldrich Chemicals, 99.9+%), $MoCl_4$ (Aldrich Chemicals, contains 10% or more $MoCl_5$), Cp_2MoCl_2 (Aldrich Chemicals., 98%), WCl_6 (Aldrich Chemicals., 99.9+%) were used without further purification. Et_3Al, Et_2AlCl, and $EtAlCl_2$ (Aldrich Chemicals, 25 wt% (1.8 M) solution in toluene) and Me_4Sn (Aldrich Chemicals, 95%) were used as received. Ph_4Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. The polymerization solvent, chlorobenzene, was dried with CaH_2 and fractionally distilled.

Polymerization of HD by $MoCl_5$. In a 20 mL ampule equipped with rubber septum, 0.54 mL (0.054 mmol, M/C: 100) of 0.1 M $MoCl_5$ chlorobenzene solution, chlorobenzene (4.36 mL, $[M]_0$ = 1.0 M), and 0.5 g (5.43 mmol) of HD were added in that order given. And the polymerization was carried out at 30 °C for 24 hrs under nitrogen atmosphere. The polymerization proceeded in the homogeneous manner at the early polymerization time. After 24 hrs, 10 mL of chloroform was added to the polymerization solution in order to dilute the polymerization solution. The polymer solution was prepicipitated into an excess of methanol, filtered from the solution, and then dried under vacuum at 40 °C for 24 hrs. The polymer yield was 52%.

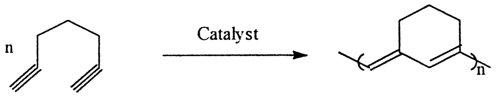
Polymerization of HD by $MoCl_5$-$EtAlCl_2$. In a 20 mL ampule equipped with rubber septum, chlorobenzene (8.71 mL, $[M]_0$ = 0.5 M), 1.08 mL (0.109 mmol, M/C: 50) of 0.1 M chlorobenzene solution of $MoCl_5$, and 0.54 mL (0.218 mmol) of 0.4 M chlorobenzene solution of $EtAlCl_2$ were added in that order given. After shaking the catalyst solution at 30 °C for 15 min, 0.5 g HD (5.43 mmol) was injected. The polymerization proceeded in some heterogeneous manner. After 24 hrs, 10 mL of chloroform was added to the polymerization solution. The polymer solution was poured into an excess of methanol, filtered from the solution, and then dried under vacuum at 40 °C for 24 hrs. The polymer yield was 56%.

Polymerization of HD by WCl_6-$EtAlCl_2$. The polymerization procedure is the same as that of $MoCl_5$-$EtAlCl_2$ catalyst. The polymer yield was 27%.

Instruments and Measurement. IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Solid-state ^{13}C-NMR spectra of insoluble polymer were also recorded on a Bruker AM-200 spectrometer (5-s repetition time, 3.5-ms cross polarization mixing time, 8-W decoupler power, and 3.8-KHz spinning) and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. Elemental analyses were performed with FISONS EA1110 Elemental Analyzer. UV-visible spectra of polymer solid film and solution were taken on a JASCO V-530 spectrophotometer. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min up to 800 °C with a DuPont 2200 thermogravimetric analyzer. X-ray diffractograms were measured with a PHILIPS X-ray diffractometer (Model: XPert-APD).

Results and Discussion

The cyclopolymerization of HD, a typical cyclopolymerizable monomer, was attempted out by Mo- and W-based transition metal catalysts (Scheme I).



Scheme I. Cyclopolymerization of 1,6-Heptadiyne.

Table I shows a typical result for the polymerization of HD by molybdenum-based catalysts. $MoCl_5$ alone polymerized HD monomer very effectively. The polymer yield was quantitative when the monomer to catalyst mole ratio (M/C) and the initial monomer concentration ($[M]_0$) were 50 and 1.0 M, respectively. This polymerization (exp. No. 1) proceeded very vigorously at the initial several minutes and was accompanied by the strong exothermic reaction. However, at the low initial monomer concentration ($[M]_0$: 0.5), the polymerization proceeded in some mild and homogeneous manner. In the cyclopolymerization of dipropargyl

Table I. Polymerization of 1,6-Heptadiyne by Molybdenum-Based Catalysts[a]

Exp. No	Catalyst System[b]	M/C[c]	$[M]_0$[d]	Temp. (°C)	P. Y.(%)[e]
1	$MoCl_5$	50	1.0	30	100
2	$MoCl_5$	100	1.0	30	52
3	$MoCl_5$	250	1.0	30	18
4	$MoCl_5$	500	1.0	30	trace
5	$MoCl_5$	50	0.2	30	40
6	$MoCl_5$	50	0.5	30	69
7	$MoCl_5$	50	2.0	30	100
8	$MoCl_5$	50	1.0	0	56
9	$MoCl_5$	50	1.0	60	100
10	$MoCl_5$	50	1.0	90	100
11	$MoCl_5/EtAlCl_2$ (1:2)	50	1.0	30	56
12	$MoCl_5/Et_2AlCl$ (1:2)	50	1.0	30	48
13	$MoCl_5/Et_3Al$ (1:2)	50	0.5	30	42
14	$MoCl_5/Ph_4Sn$ (1:2)	50	0.5	30	64
15	$MoCl_5/Me_4Sn$ (1:2)	50	0.5	30	58
16	$MoCl_4$	50	0.5	30	73
17	$MoCl_4$	50	1.0	30	95
18	$MoCl_4/EtAlCl_2$ (1:2)	50	1.0	30	57
19	$Cp_2MoCl_2/EtAlCl_2$ (1:2)	50	1.0	30	41

[a] Polymerization was carried out for 24 hrs in chlorobenzene.
[b] Mixture of catalyst and cocatalyst solution was aged for 15 min at 30 °C before use.
[c] Monomer to catalyst mole ratio. [d] Initial monomer concentration. [e] Polymer yield.

ether,[42] a similar derivative of HD, there has been a retardation time (about 5 min), in which the color of catalyst solution was disappeared after injection of dipropargyl ether into the $MoCl_5$-catalyst solution. However in the present polymerization, the polymerization instantaneously proceeded without the retardation time after the injection of HD into the catalyst solution.

The effect of initial monomer concentration ($[M]_0$) for this cyclopolymerization was tested (exp. No: 3-7). At the low initial monomer concentration ($[M]_0$: 0.2), the polymerization proceed more mildly in homogeneous manner. On the other hand, the polymerization proceeded vigorously at the high initial monomer concentration ($[M]_0$: 2.0) to give a quantitative yield of polymer.

It has been known that the addition of a small amount of reducing agents such as Ph_4Sn and n-Bu_4Sn increases the polymer yield and molecular weight in the $MoCl_5$-catalyzed polymerization of 2-ethynylthiophene[43] and 1-butyl-2-trimethylsilylacetylene,[44] and also the organoaluminum compounds such as $EtAlCl_2$ and Et_2AlCl were very effective cocatalyst in the polymerization of 1-ethynylcyclohexene[45] and 4-ethynyltoluene.[46] However the organotin and organoaluminum compounds did not exhibit any cocatalytic activity in this Mo-catalyzed polymerization of HD. The $MoCl_4$ itself also shows a similar catalytic activity to that of $MoCl_5$ (exp. no. 16-18). Such metallocene catalyst as Cp_2MoCl_2-$EtAlCl_2$catalyst system, which has been found to be effective catalysts for the polymerization of phenylacetylene[40,41] was also found to be effective for this cyclopolymerization of HD.

The polymerization at 0 °C proceeded in very mild manner and the methanol-insoluble polymer yield was very low ($\leq$ 12%). However above 30 °C, the polymer yields were mostly quantitative (exp. No: 1,9,10).

Table II shows the polymerization results for the polymerization of HD by W-based catalysts. In general, the WCl_6-based catalysts showed lower catalytic activity in this polymerization. The polymer yields were slightly increased when such cocatalysts as $EtAlCl_2$ and Ph_4Sn are used. It has been known that the catalytic activity of Mo-based catalysts was more effective than those of W-based catalysts in the cyclopolymerization of 1,6-heptadiynes such as diphenyldipropargylmethane,[37] diethyldipropargylmalonate,[38,39] and 4,4-bis((*tert*-butyldimethylsiloxy)-methyl))-1,6-heptadiyne.[47]

Table II. Polymerization of 1,6-Heptadiyne by Tungsten-Based Catalysts[a]

Exp. No.	Catalyst System[b] (mole ratio)	M/C[c]	$[M]_0$[d]	P. Y. (%)[e]
1	WCl_6	50	1.0	11
2	WCl_6	100	1.0	5
3	WCl_6	100	0.5	trace
4	$WCl_6/EtAlCl_2$ (1:2)	50	1.0	27
5	WCl_6/Ph_4Sn (1:2)	50	1.0	18

[a] Polymerization was carried out at 30 °C for 24 hrs in chlorobenzene.

[b] Mixture of catalyst and cocatalyst solution was aged for 15 min at 30 °C before use.

[c] Monomer to catalyst mole ratio.

[d] Initial monomer concentration (*M*).

[e] Polymer yield.

Figure 1 shows the time dependence curve of polymer yield for the polymerization of HD by $MoCl_5$ and $MoCl_5$-$EtAlCl_2$ in chlorobenzene. As shown in this figure, when initial monomer concentration ($[M]_0$) and the monomer to catalyst mole ratio (M/C) were 1.0 M and 50, the polymerization proceeded very rapidly at initial polymer-

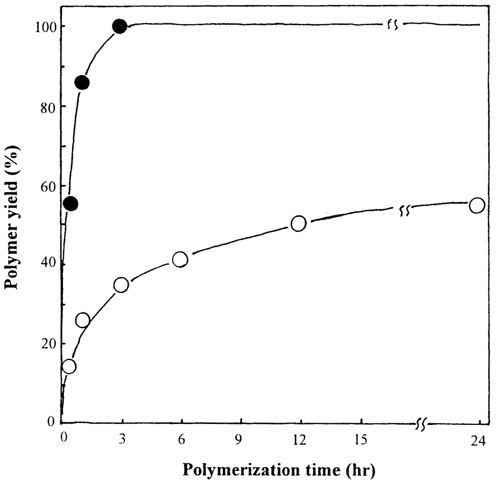


Figure 1. The time dependence curves of polymer yield for the polymerization of HD by $MoCl_5$ (●) and $MoCl_5$-$EtAlCl_2$ (O)catalyst systems.

ization time, the polymer yield nearly quantitative even after 1 hr. On the other hand, the polymerization of HD by $MoCl_5$-$EtAlCl_2$ catalyst system proceeded more slowly.

Polymer Structure. It was very difficult to identify the exact polymer structure in solution state because of the insolubility of the resulting poly(HD). The polymer structure of poly(HD) was characterized by various instrumental methods such as solid-state ^{13}C-NMR, IR, UV-visible spectroscopies and elemental analysis.

Figure 2 shows the IR spectra of HD, poly(HD), and poly(HD) after exposing to air for 3 days. The IR spectrum of poly(HD) did not show the acetylenic C ≡ C bond stretching frequency at 2118 cm^{-1} and the acetylenic =C-H stretching frequency at about 3294 cm^{-1}. Instead, the C=C double bond stretching frequency peak of conjugated polymer backbone at 1604 cm^{-1} was newly observed. A small peak at 3032 cm^{-1}, which is absent at the IR spectrum of HD, is originated by the vinylic =C-H stretching frequency of the conjugated polymer backbone.

Figure 3 shows the solid-state ^{13}C-NMR spectrum of poly(HD). This spectrum did not show any acetylenic carbon peaks, which was seen at 68.84 and 82.61 ppm in the ^{13}C-NMR spectrum of HD. Instead it exhibited the new vinyl carbon peaks of conjugated polymer backbone of poly (HD) at 110-150 ppm, which did not observed in the ^{13}C-NMR spectrum of monomer (HD). It also showed two broad peaks due to the methylene carbons adjacent to conjugated double bonds and the methylene protons of 4-position at 50-95 ppm and 10-43 ppm, respectively.

Figure 4 shows the UV-visible spectra of poly (HD) [thin solid film and chloroform solution]. The UV-visible spectra of poly(HD) showed the characteristic broad absorption peak at the visible region, which is originated from the $\pi \rightarrow \pi^*$ conjugation band transition of the polyene main chain, which had not been observed at the UV-visible spectrum of monomer, HD. The absorption peak of poly(HD) film tailed upto 700 nm.

The elemental analysis data of poly(HD) agreed with the theoretical value though it has a slight

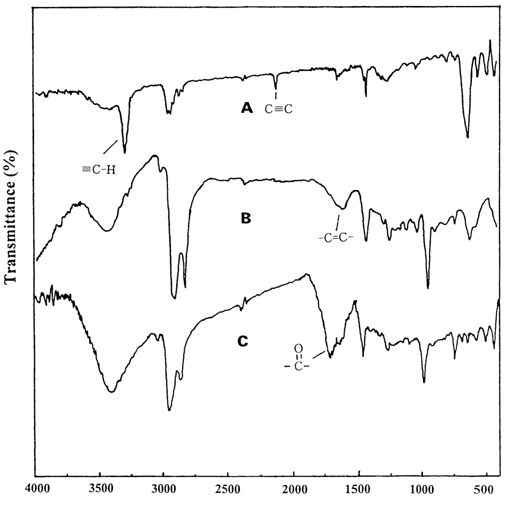


Figure 2. FT-IR spectrum of HD (A), poly(HD) (B)prepared by $MoCl_5$, and poly(HD) after exposing to air for 3 days (C).

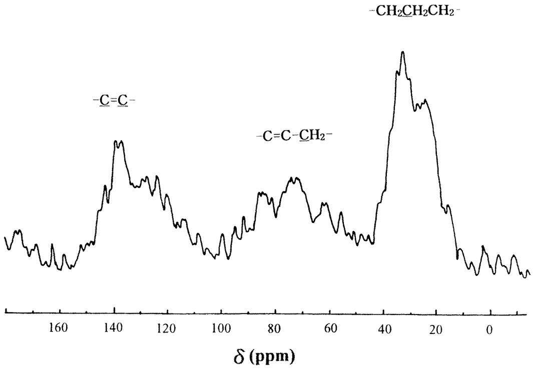


Figure 3. Solid-state ^{13}C-NMR spectrum of poly(HD) sample prepared by $MoCl_5$ (exp. no. 1).

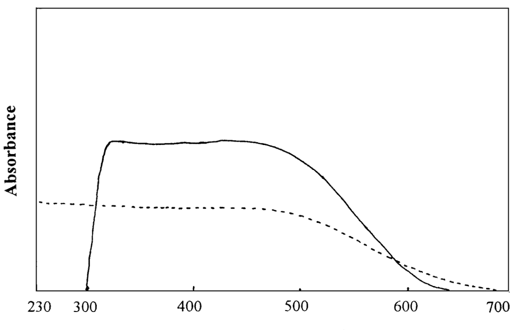


Figure 4. UV-visible spectra of poly(HD) [thin solid film (----) and chloroform solution (—)].

deviation: Calcd for $(C_7H_8)_n$: C, 91.25%; H, 8.75%, Found: C, 89.25%; H, 8.70%. Inspite of exhaustive washing procedures, ash due to the catalyst residues was always present because its insolubility to the purification solvents. It was found that the Mo-catalyst residues and oxygen atom due to the air oxidation during the process were contained in this polymer sample to the extent of 2%. Both Mo and Al were detceted by energy dispersive X-ray analysis.

It has been also reported that the conjugated cyclic polymers obtained by both a classical metathesis catalyst and a well-defined alkylidene initiator produced five- and six-membered rings of a certain ratio, which depended on the polymerization conditions and kinds of catalysts used.[29,48] The effect of size and type of substituents upon the fine and conformational structure for this potentially interesting class of cyclic polyenes was systematically performed.[49] The ratio between five-membered and six-membered rings increased with the size and number of substituents at the 4-position. In particular it was reported that the five-membered polymer was only produced when an extermely bulky substituent such as the tert-butyldiphenylsiloxymethyl group was introduced at the 4-position of 1,6-heptadiyne.[49] $MoCl_5$ catalyst is sterically very small compared to the well-defined alkylidene complexes. Of th possible structures, structure **2** was judged to be the most favorable one in the viewpoint of its stability and probability associated with the transition state in the cyclopolymerization.[26,50]

Polymer Properties. The resulting Poly(HD)s were generally dark-brown or black powders. The final poly(HD)s were generally insoluble in any organic solvents regardless of the catalysts and the polymerization methods, which is originate from the chain rigidity of poly(HD) and/or the cross-linking reaction of the labile allylic hydrogen atoms. The final polymers were insoluble although the polymerization solution seemed to be homogeneous and it was solution castable into thin polymer film.

If the polymer **4** was formed majorly in the early polymerization time, the polymer precipitated after early polymerization time (30 min or 1 hr) must be soluble in organic solvent because the polymer **4** is simple polyacetylene having substituent, which may be expected to be soluble in common organic solvents. However the obtained poly(HD)s were insoluble in any organic solvents regardless of the catalyst and polymerization conditions although the polymer solution in the early polymerization time was homogeneous. This indicate that the present poly(HD) structure isnt structure **4** but structure **1**, **2**, and **3**, a conjugated polyenes having cyclic recurring unit are more favorable ones. Similar homologues such as poly (dipropargyl ether)[41] and poly(dipropargyl sulfide)[51] were also found to be insoluble in any organic solvents. This means that this poly(1,6-heptadiyne) itself is structurally very regid form as like with that of polyacetylene.

The homogeneous polymerization solutions at the early polymerization time were casted into a thin homogeneous polymer film with orange-red color. However the resulting polymer films were too brittle to measure the mechanical properties such as tensile strenth, modulus, and failure strain.

The resulting poly(HD) were also found to be very unstable to air oxidation, regardless of the polymer films and polymer powder. Even after 3 days, the IR spectrum of poly(HD) shows a strong carbonyl carbon absorption peak at 1710 cm^{-1}, which did not seen in the IR spectrum of the initial polymer sample (Figure 2).

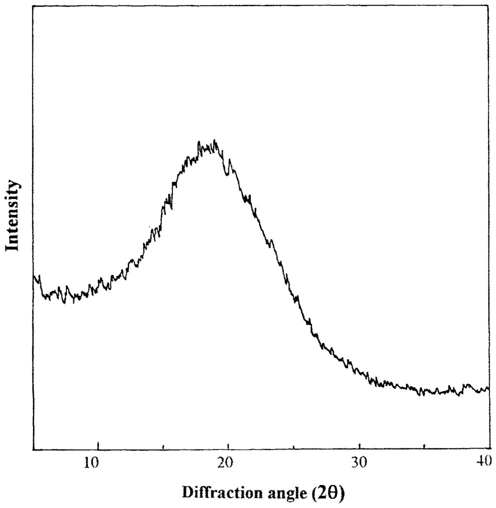


Figure 5. X-ray diffractogram of poly(HD) prepared by $MoCl_5$ (exp. no. 1).

The TG thermogram of poly(HD) showed that the polymer retains 99% of its original weight at 100 °C, 90% at 210 °C, 80% at 300 °C, 60% at 452 °C, 45% at 700 °C. The char yield after heating upto 1000 °C was 31%.

The morphology of poly(HD) was also investigated by X-ray diffraction analysis (Figure 5) and the peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35,[52] the present poly(HD)s are amorphous.

Conclusions

The cyclopolymerization of HD, a simlpest dipropargyl derivative, proceeded well to give conjugated polyene polymer with Mo- and W-based transition metal catalyst systems. The catalytic activity of $MoCl_5$-based catalysts were found to be greater than those of WCl_6-based catalyst system. The polymerization behaviors were found to be depended on the catalysts and polymerization conditions. The resulting poly(HD) were insoluble in any organic solvents regardless of the catalyst and the reaction conditions, which is originate from the chain rigidity of poly(HD) and/or the cross-linking reaction of the labile allylic hydrogen atoms. The polymer structure was characterized by various instrumental methods to have conjugated polymer backbone structure with cyclic recurring units. The X-ray diffraction data indicated that the present poly(HD)s are mostly amorphous.

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