



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US95/00746 <b>(22) International Filing Date:</b> 19 January 1995 (19.01.95) <b>(30) Priority Data:</b> 08/189,988 1 February 1994 (01.02.94) US <b>(71) Applicant:</b> NORTHWESTERN UNIVERSITY [US/US]; 633 N. Clark Street, Evanston, IL 60208 (US). <b>(72) Inventors:</b> YANG, Xinmin; 800 Hinman Avenue, Evanston, IL 60202 (US). MARKS, Tobin, J.; 2300 Central Park Avenue, Evanston, IL 60201 (US). SEYOM, Afif, M.; 1915 Maple #119, Evanston, IL 60201 (US). <b>(74) Agents:</b> SHEKLETON, Gerald, T. et al.; Welsh & Katz, Ltd., 135 S. LaSalle Street, Suite 1625, Chicago, IL 60603 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> RARE EARTH HOMOGENEOUS CATALYSTS FOR RING-OPENING (CO)POLYMERIZATION OF STRAINED-RING OLEFINS  <b>(57) Abstract</b>  The organolanthanide hydrides (Cp' <sub>2</sub> LnH) <sub>2</sub> (Cp' = $\eta^5$ -Me <sub>5</sub> C <sub>5</sub> ; Ln = Sm, Lu) rapidly catalyze the copolymerization of methylenecyclopropane and ethylene to cleanly yield high molecular weight polyolefins of microstructure {[CH <sub>2</sub> CH <sub>2</sub> ] <sub>x</sub> [CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> ] <sub>y</sub> } <sub>n</sub> via sequential olefin insertion and ring-opening/ $\beta$ -alkyl shift processes. Homopolymerization of methylenecyclopropane likewise cleanly yields polymers of the structure [CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> ] <sub>n</sub> .		

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**"RARE EARTH HOMOGENEOUS CATALYSTS FOR RING-OPENING  
(CO)POLYMERIZATION OF STRAINED-RING OLEFINS"**

Background of the Invention

5 This invention was made with Government support under  
The National Science Foundation (Grant CHE9104112). The  
Government has certain rights under this contract.

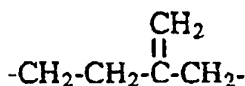
This application is a continuation-in-part of  
application Serial No. 962,390, filed October 16, 1992.

10 This application relates to catalysts and more  
particularly to homogeneous catalysts for use in polymerization  
via the ring opening of strained ring systems.

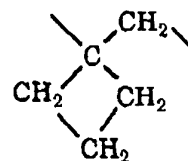
In the presence of Ziegler-Natta catalysts, such as  
AlEt<sub>2</sub>Cl-Cr(acac)<sub>3</sub> and Al(i-AlBu)<sub>3</sub>-TiCl<sub>4</sub>ARA, it is known that  
15 methylenecyclobutane (A) can be polymerized into a polymer  
consisting of a mixture of structure units B and C, through a  
ring-opening mechanism and a simple vinyl type insertion  
mechanism, respectively. Structure B is particularly interesting  
in that it imparts



A



B



C

useful functionalities into polyolefins. However, the activity of these catalysts are extremely sluggish.

In U.S. Application Serial No. 962,390 a new class of homogeneous group 4 metal-based catalysts was disclosed to catalyze the ring-opening polymerization of A into B with both much higher activity and selectivity. Furthermore, these homogeneous catalysts can also effectively copolymerize A and simple olefins such as ethylene and propylene to form copolymers containing a broad range of exomethylene functionalities, with a general formula  $\{-(CH_2CHR)_x-[CH_2CH_2CH_2C(CH_2)]_y\}_n$ . These catalysts can be generally represented as  $L_1L_2MR^+X^-$ , where  $L_1$  and  $L_2$  are cyclopentadienyl or substituted cyclopentadienyl ligands; M is a metal selected from Ti, Zr and Hf; R is a hydrogen or a alkyl radical with 1-20 carbon atoms;  $X^-$  is a charge-compensating anion selected from  $R'B(C_6F_5)_3^-$ ,  $B(C_6F_5)_4^-$ , or methylalumoxane. The homo- and co-polymers formed using the homogeneous catalysts have been characterized by  $^1H/^{13}C$  NMR spectroscopy and GPC analysis.

Lanthanide complexes of the types  $(C_5Me_5)_2LnR$  and  $(Me_2Si)(C_5Me_4)_2LnR$ , where Ln is a metal chosen from the lanthanide series in The Periodic Table, or Sc and Y; R is hydrogen or an alkyl radical, are a unique class of complexes and have been shown to be efficient catalysts for a variety of chemical transformations including the polymerization of simple olefins such as ethylene and propylene.

#### Summary of the Invention

Therefore, an object of the subject invention is a novel catalyst for polymerizations having high activity.

A further object of the subject invention is a catalyst for olefin polymerization which operates via a ring-opening mechanism.

A still further object of the subject invention is a catalyst by which electrophilic lanthanide catalysts catalyze the facile regioselective ring-opening homopolymerization of exomethylene substituted cyclic organic compounds and the

copolymerization of such compounds with olefins such as ethylene, propylene and styrene via a  $\beta$ -alkyl shift mechanism.

Rare earth homogeneous complexes of the type  $(\text{Cp}'_2\text{LnH})_2$  ( $\text{Ln} = \text{Sm}, \text{Lu}$ ;  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ ) can efficiently catalyze the copolymerization of simple olefins and methylenecyclopropane to form exomethylene functionalized polyolefins with the general structure  $\{-(\text{CH}_2\text{CHR})_x-[\text{CH}_2\text{CH}_2\text{C}(\text{CH}_2)]_y-\}$ , where R is H,  $\text{CH}_3$  or Ph when the olefin is ethylene, propylene or styrene, respectively. The Lu catalysts also effect the homopolymerization of methylenecyclopropane to form  $[-\text{CH}_2\text{CH}_2\text{C}(\text{CH}_2)-]_n$ . The key step in these polymerization processes is a lanthanide-mediated  $\beta$ -alkyl shift ring-opening process. Such a ring-opening polymerization process should be applicable to the polymerization of a variety of strained ring monomers having exocyclic unsaturation.

These and other objects of the subject invention are more apparent from the following detailed description when taken in conjunction with the accompanying drawings wherein:

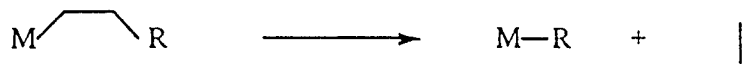
Fig. 1 is the  $^1\text{H}$  NMR spectrum (400 MHz, toluene- $d_8$ ) of the ethylene-methylenecyclopropane copolymer from entry 4, Table I.

Fig. 2(a) is the  $^1\text{H}$  NMR spectra (400 MHz, benzene- $d_6$ ) of a  $(\text{Cp}'_2\text{LuH})_2$  catalyzed methylenecyclopropane homopolymer.

Fig. 2(b) is the  $^{13}\text{C}$  NMR spectra (100 MHz, benzene- $d_6$ ) of  $(\text{Cp}'_2\text{LuH})_2$  catalyzed methylenecyclopropane homopolymer.

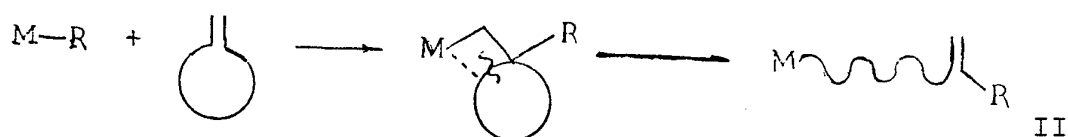
#### Detailed Description of the Invention

Facile  $\beta$ -alkyl transpositions are a distinctive feature of electrophilic  $d^0$  hydrocarbyl chemistry (e.g., equation (I)) and

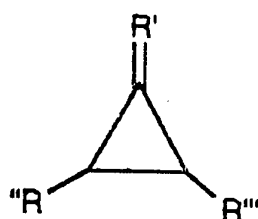


I

represent an important chain transfer channel in certain olefin polymerization processes. In principle, such transpositions might also provide an unusual pathway to functionalized polyolefins by coupling olefin insertion and strained monomer ring-opening sequences (equation (II)).



The exo-methylene cyclic organic compounds may be represented by the general formulas D:



D

where  $R^I$ ,  $R^{II}$ , and  $R^{III}$  are hydrogen, aryl or alkyl groups (C=1-10) which may also include O, N, S or P. Preferably, the monomer is methylenecyclopropane.

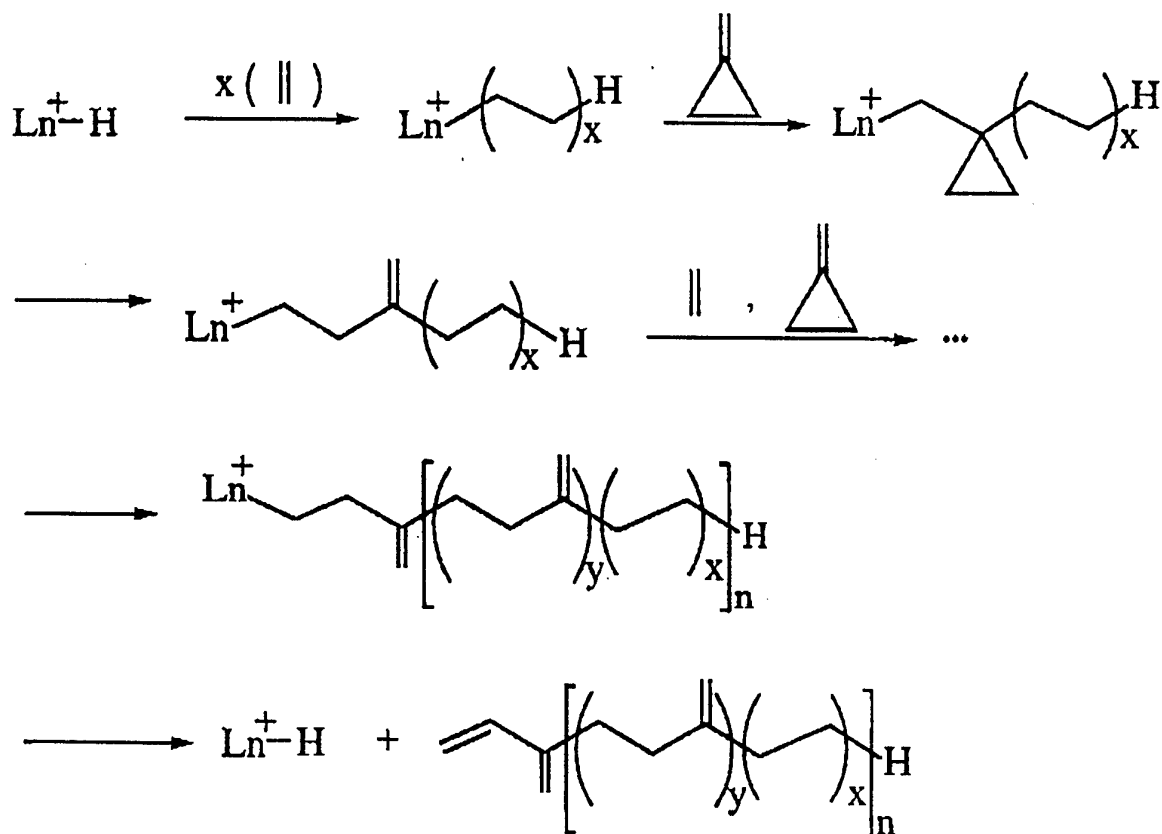
The simple olefin used in the copolymerization can be ethylene or other  $\alpha$ -olefins such as propylene, 1-hexene or styrene.

The lanthanide catalysts used can be represented as  $[\eta^5-R^1R^2R^3R^4R^5C_5]_2LnR^6$ , where  $R^{1-6}$  = an alkyl (1-20 carbons), aryl, or hydride group; one of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , can be an organic or organometallic group which bridges the two cyclopentadienyl-type rings (e.g.;  $Me_2Si$ ); Ln is a metal chosen from the lanthanide series in The Periodic Table, Sc, and Y.

Copolymerization of D with olefins such as ethylene, propylene and styrene, etc. can be readily effected by stirring D neat or in a diluent such as toluene, or other hydrocarbon in the presence of the co-monomer at a temperature from 0-100°C.  $^1H$  and  $^{13}C$  NMR spectroscopy indicates that the derived copolymers have ring-opened microstructure D exclusively and that the x and

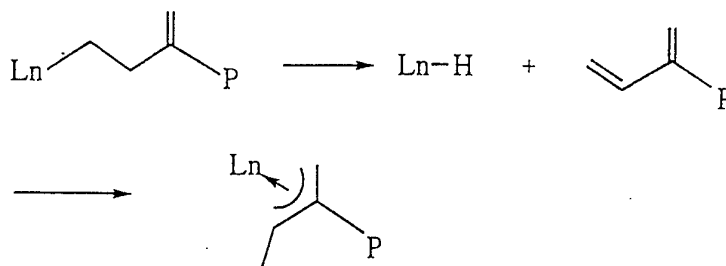
y proportions can be controlled via the reaction stoichiometry.

The proposed reaction mechanism for the copolymerization is shown below:



The homopolymerization of methylenecyclopropane by the lanthanide catalysts according to the subject invention, shows some very unusual behavior. For instance,  $(\text{Cp}'_2\text{LuH})_2$  can homopolymerize methylenecyclopropane very selectively through a ring-opening mechanism. The structure of the resulting polymer has been confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Figure 2). However, the yield of the polymer per unit amount of catalyst is very low compared to the analogous polymerization of methylenecyclobutane by the zirconium catalysts. The polymerization stops even though there is still a large amount of monomer left. However, this is not a result of

poisoning by any impurity in the reaction media. This phenomenon could be demonstrated by the observation that when ethylene is added to such a reaction system, very fast copolymerization then occurs. From the reaction chemistry of such lanthanide catalysts it is believed that some kind of metal allyl species like Reaction Sequence III is formed during the homopolymerization process.



III

Such an allylic complex cannot react further with the bulky methylenecyclopropane but can react with the smaller ethylene.

### Examples

All operations were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware in a dual manifold Schlenk line or interfaced to a high vacuum ( $10^{-5}$  torr) system, or in a nitrogen or argon filled glovebox with a high capacity atmosphere recirculator. Argon, ethylene and propylene were purified by passage through a supported MnO oxygen removal column and a molecular sieve column. Aliphatic hydrocarbon solvents were pretreated with concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$  solution,  $\text{MgSO}_4$  and Na, 4Å molecular sieves. All reaction solvents were distilled from Na/K/benzophenone under nitrogen and were condensed and stored in vacuo in bulbs on the vacuum line containing a small amount of  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}]_2\text{ZnCl}_2$  as indicator. Methylenecyclopropane was additionally dried over Na/K.



Catalyst Syntheses

In general  $\text{Cp}_2'\text{MCHTMS}_2$  complexes may be prepared by mixing approximately equimolar amounts of the corresponding  $\text{Cp}'_2\text{LnCl}_2\text{Li(ether)}_2$  complex and  $\text{LiCHTMS}_2$  as appropriate, in toluene for 8-16 hours (preferably 12 hours) at  $-10^\circ\text{C}$ . to  $25^\circ\text{C}$ . (preferably  $0^\circ\text{C}$ .). The solvent is then removed and the residue extracted with another solvent, preferably pentane. The extract is cooled to recrystallize the  $\text{Cp}_2'\text{MCHTMS}_2$  complex.

EXAMPLE 1 $\text{Cp}_2'\text{LuCHTMS}_2$ 

The aforementioned procedure set forth above was carried out with 3.1 g  $\text{Cp}'_2\text{LuCl}_2\text{Li(ether)}_2$  and 0.79 g  $\text{LiCHTMS}_2$  in 150 mL of toluene. The standard workup and pentane recrystallization yielded 1.8 g (64%) of  $\text{Cp}_2'\text{LuCHTMS}_2$ .

$(\text{Cp}_2'\text{MH})_2$  compounds may be prepared by stirring  $\text{Cp}_2'\text{MCHTMS}_2$ /pentane under a hydrogen atmosphere for 0.1-2.5 hours, preferably 2 hours) at a temperature of  $-10^\circ\text{C}$ . to  $10^\circ\text{C}$ . (preferably  $0^\circ\text{C}$ .). The resulting precipitate may be isolated by filtration, washing and the like.

EXAMPLE 2 $(\text{Cp}_2'\text{LuH})_2$ 

$\text{Cp}_2'\text{LuCHTMS}_2$  (1.0 g) was stirred under and  $\text{H}_2$  atmosphere in 50 mL of pentane for 2 hours at  $0^\circ\text{C}$ . The resulting colorless precipitate was isolated by filtration, washed with 2X3 mL pentane, and dried in vacuo to yield 0.72 g (98%)  $(\text{Cp}_2'\text{LuH})_2$  as a microcrystalline solid.

EXAMPLE 3 $(\text{Cp}_2'\text{SmH})_2$ 

$\text{Cp}_2'\text{SmCHTMS}_2$  (1.0 g) was stirred under and  $\text{H}_2$  atmosphere in 50 mL of pentane for 2 hours at  $0^\circ\text{C}$ . The resulting colorless precipitate was isolated by filtration,

washed with 2X3 mL pentane, and dried in vacuo to yield 0.65 g (90%)  $(Cp_2'SmH)_2$  as a pink powder.

#### EXAMPLE 4

#### Copolymerization of ethylene and methylenecyclopropane.

In a typical copolymerization experiment, 15 mg of the catalyst  $(Cp_2'LnH)_2$  was loaded into a 50 mL flask in the glove box. On the vacuum line, 20 mL of toluene and a measured amount of methylenecyclopropane were then condensed into the flask. The reaction mixture was exposed to 1 atm of ethylene and stirred at room temperature with a constant bubbling of ethylene. The reaction was quenched by the addition of a small amount of methanol. The polymer was collected by suction filtration, washed with acetone three times, dried under vacuum for 12 h. The polymer product was characterized by  $^1H$  NMR spectroscopy and GPC. Different ratios of methylenecyclopropane with ethylene result in the data of Table I.

Table 1. Copolymerization of Methylenecyclopropane with Ethylene Using  $(Cp_2'LnH)_2$  ( $Ln=Sm, Lu$ ) Catalyst

Entry	Catalyst Amount ( $\mu$ mol)	Methylene-cyclopropane (mL)	Ethylene Pressure (atm)	Reaction Time (h)	Yield of Polymer (g)	Activity (g polymer/Mol Ln h)	Number of <i>exo</i> -methylenes per 1000-CH <sub>2</sub> -Unit	$M_n(M_w)^c$ x1000
1	21.4 (Sm)	0.25	1.0	0.10	0.42	$2.0 \times 10^5$	4.2	13(7)
2	21.4 (Sm)	0.50	1.0	0.17	0.45	$1.2 \times 10^5$	6.7	184(42)
3	33.6 (Lu)	0.50	1.0	0.10	0.60	$1.8 \times 10^5$	40	92(26)
4	33.6 (Lu)	2.50	1.0	0.10	0.47	$1.4 \times 10^5$	91	3(2)

<sup>a</sup>Monomer conversion by  $^1H$  NMR.

<sup>b</sup>Ratio of methylenecyclopropane and ethylene (per 1000 CH unit) incorporated into the copolymer as determined by  $^1H$  NMR.

<sup>c</sup>By GPC versus polystyrene.

EXAMPLE 5Homopolymerization of methylenecyclopropane by  $(Cp^*_2LuH)_2$ .

To a J-Young NMR tube, 10 mg. of the catalyst was loaded in the glove box. Then deuterated solvent ( $C_6D_6$  or toluene- $d_8$ ) and a suitable amount of methylenecyclopropane were condensed into the NMR tube. It was allowed to react at room temperature. The resulting polymer was characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy.

From Table 1 both the samarium and lutetium catalysts are shown to be highly active for the copolymerization of ethylene and methylenecyclopropane to give high molecular weight polymers. The fairly high molecular weight also suggests that it is not significantly affected by the incorporation of such a monomer. The molecular weight distribution of about 2 is typical of homogeneous catalysts having similar active centers. Most importantly, the incorporation of exo-methylene functional groups in the copolymers is confirmed by the presence of a sharp signal at  $\delta=4.8$  ppm in the  $^1H$  NMR spectrum (Figure 1). The lack of any peaks in the region of 0.1-0.5 ppm in the above spectrum suggests that there is no "ring-unopened" unit (cyclopropane) in the copolymer. In addition, since a relatively high concentration of methylenecyclopropane was used in the copolymerization process (Entry 4, Table 3), peaks can be seen in the NMR spectrum that result from two (or more) ring-opened methylenecyclopropane monomers neighboring to each other.

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not

5       be limited to the particular embodiment disclosed as the  
best mode contemplated for carrying out this invention, but  
that the invention will include all embodiments and  
equivalents falling within the scope of the appended  
claims.

          Various features of the invention are set forth  
in the following claims.

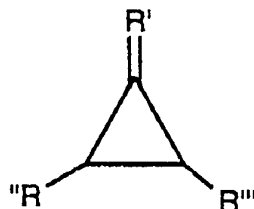
## WE CLAIM:

1. A process for the ring-opening polymerization of exomethylene-containing cyclic hydrocarbons comprising: (a) providing a rare earth catalyst; (b) contacting said catalyst with said exomethylene-containing cyclic olefin in a solvent and stirring at 0-100°C, quenching the reaction with an alcohol and collecting the polymeric product.

2. The process of Claim 1, where said catalyst is  $[\eta^5\text{-R}^1\text{R}^2\text{R}^3\text{R}^4\text{R}^5\text{C}_5]_2\text{LnR}^6$ , where  $\text{R}^{1-6}$  = an alkyl (1-20 carbon), aryl, hydride group; one of  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ , can be an organic or organometallic group which bridges the two  $\text{C}_p$  rings; Ln is a metal chosen from the group consisting of the lanthanide series of The Periodic Table, Sc and Y.

3. The process of Claim 2, where said solvent is a hydrocarbon.

4. The process of Claim 3, where said exomethylene-containing cyclic hydrocarbon is:



Where  $\text{R}'$ ,  $\text{R}''$  and  $\text{R}'''$  may be selected from the group consisting of H, hydrocarbyl (1-20 carbons), and substituted hydrocarbons and heteroatom (O, S, N, P)-containing groups.

5. The method of Claim 1 wherein one of  $\text{R}^1\text{-R}^6$  may be  $\text{Me}_2\text{Si}$ .

6. The process of Claim 4, where said catalyst is  $(\text{Cp}'_2\text{LnH})_2$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ ; Ln = Sm, Lu).

7. The process of Claim 4, where said solvent is toluene.

8. The process of Claim 4, where said exomethylene-containing cyclic olefin is methylenecyclopropane.

9. A process for the copolymerization of olefins with an exomethylene-containing cyclic olefin comprising the steps of:

(a) providing a rare earth catalyst.

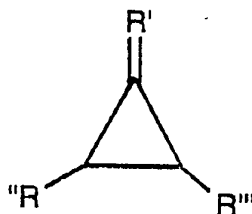
(b) contacting said catalyst with an exomethylene-containing cyclic olefin in a diluent, and stirring at 0-100°C in the presence of a olefin, quenching the reaction with an alcohol and collecting the polymeric product.

10. The process of Claim 9, where the said catalyst is  $[\eta^5-R^1R^2R^3R^4R^5C_5]_2LnR^6$ , where  $R^6$  = an alkyl (1-20 carbons), aryl, or hydride group; one of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ , can be an organic or organometallic group which bridges the two  $C_p$  rings; Ln is a metal chosen from the group consisting of the lanthanide series; Sc, and Y.

11. The process of Claim 9, where said olefin is  $CHR'=CR''R'''$ , where  $R'$ ,  $R''$  and  $R'''$  is selected from the group consisting of H, or alkyl (1-20 carbons) or aryl.

12. The process of Claim 11, where said diluent is a hydrocarbon solvent.

13. The process of Claim 11, where said exomethylene-containing cyclic olefin is:



Where  $R'$ ,  $R''$  and  $R'''$  may be selected from the group consisting of H, hydrocarbyl (1-20 carbons), or substituted hydrocarbyl, or heteroatom (O, S, N, P)-containing groups.

14. The process of Claim 13, where said catalyst is  $(\text{Cp}'_2\text{LnH})_2$  ( $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$ ;  $\text{Ln} = \text{Sm}, \text{Lu}$ ).

15. The process of Claim 12, where said diluent is toluene.

16. The process of Claim 13, where said exomethylene-containing cyclic olefin is methylenecyclopropane.

17. The process of Claim 12, where said olefin is ethylene.

18. The process of Claim 9 wherein said organic or organometallic group is  $\text{Me}_2\text{Si}$ .

19. A method for the polymerization of olefins comprising the steps of adding toluene and methylenecyclopropane at a temperature of about  $-78^\circ\text{C}$  to a flask containing a catalyst of the formula  $(\text{Cp}'_2\text{MH})_2$ , stirring at  $20^\circ\text{C}$ , quenching with methanol and recovering the polymerized product, where  $\text{Cp}' =$  a cyclopentadienyl-containing ligand and  $\text{M} = \text{Lu}$  or  $\text{Sm}$ .

20. A method for the copolymerization of olefins comprising the steps of adding a solvent and methylenecyclopropane at a temperature of about  $-78^\circ\text{C}$  to a flask containing a catalyst, said catalyst including an electrophilic metal, adding an  $\alpha$ -olefin, stirring, quenching and recovering the polymer product.

21. The method of Claim 20 wherein said solvent is a nonpolar organic solvent.

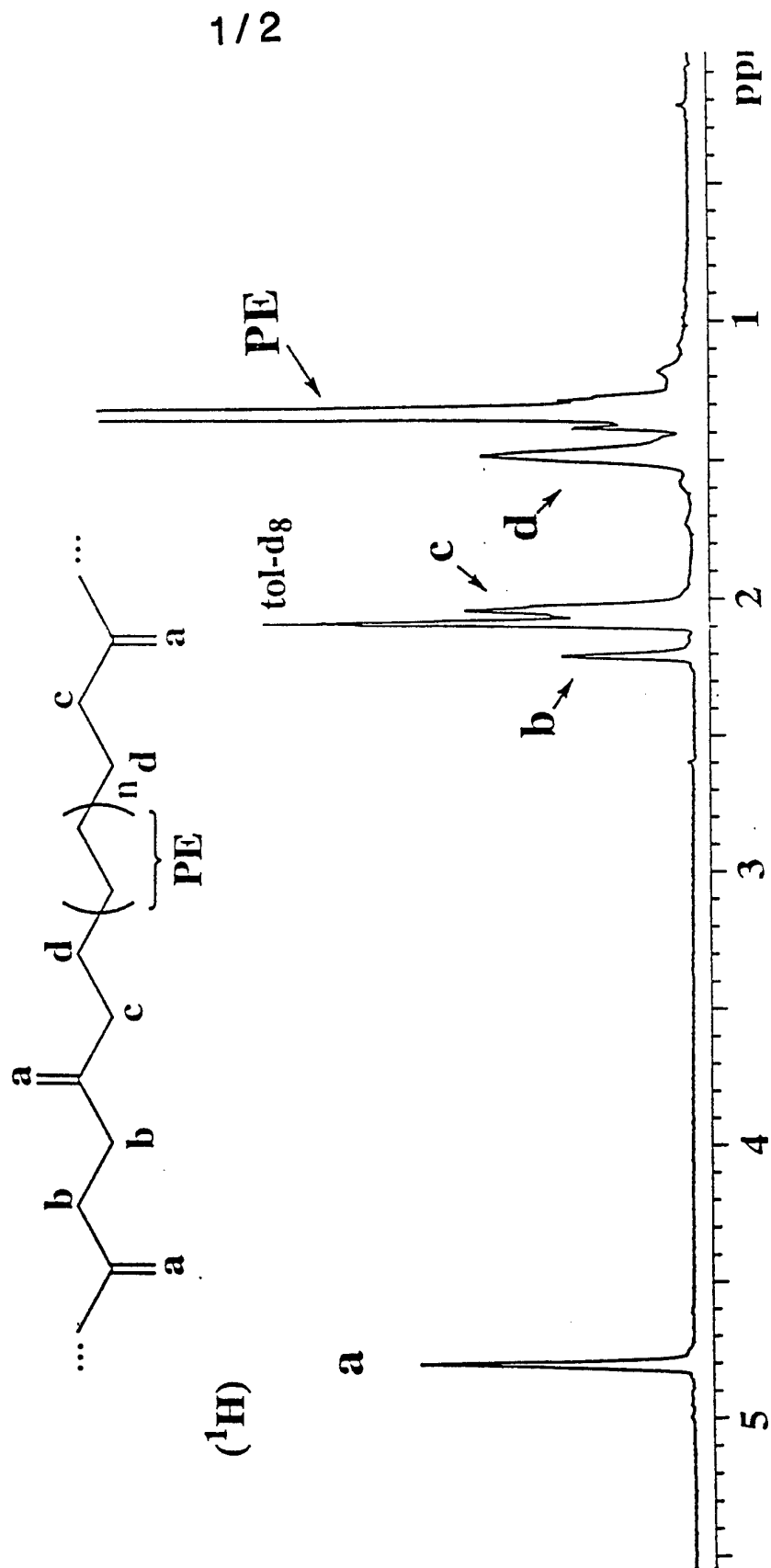
22. The method of Claim 21 wherein said solvent is selected from the group consisting of aliphatic and aromatic hydrocarbons and others.

23. The method of Claim 22 wherein said solvent is toluene.

24. The method of Claim 21 wherein said catalyst comprises  $(\text{Cp}'_2\text{MH})_2$ , where  $\text{Cp}' =$  a cyclopentadienyl-containing ligand,  $\text{M} = \text{Lu}, \text{Sm}$ .

25. The method of Claim 21 wherein said  $\alpha$ -olefin is ethylene, propylene, butylene or styrene.

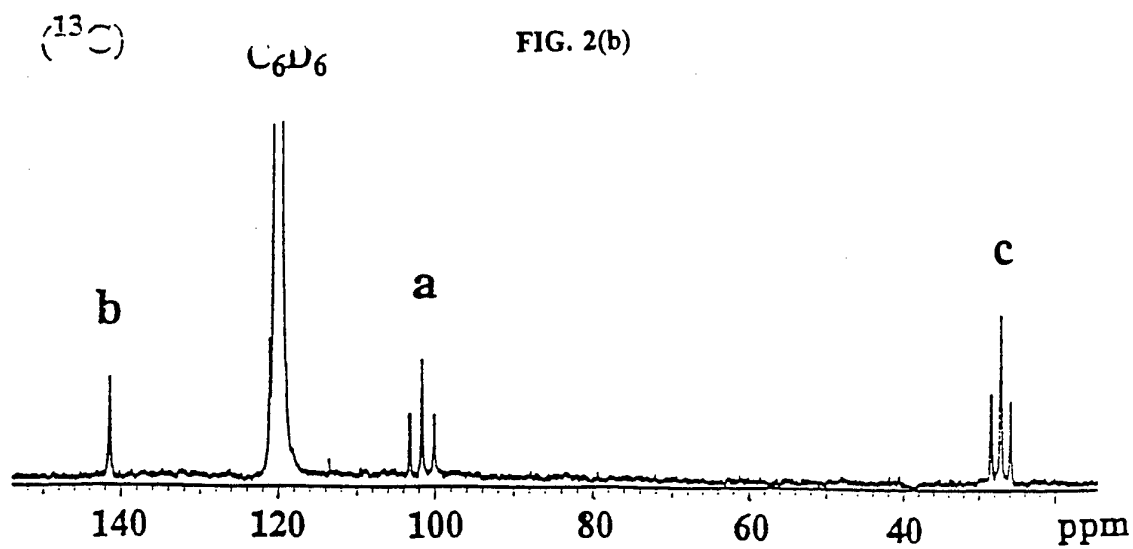
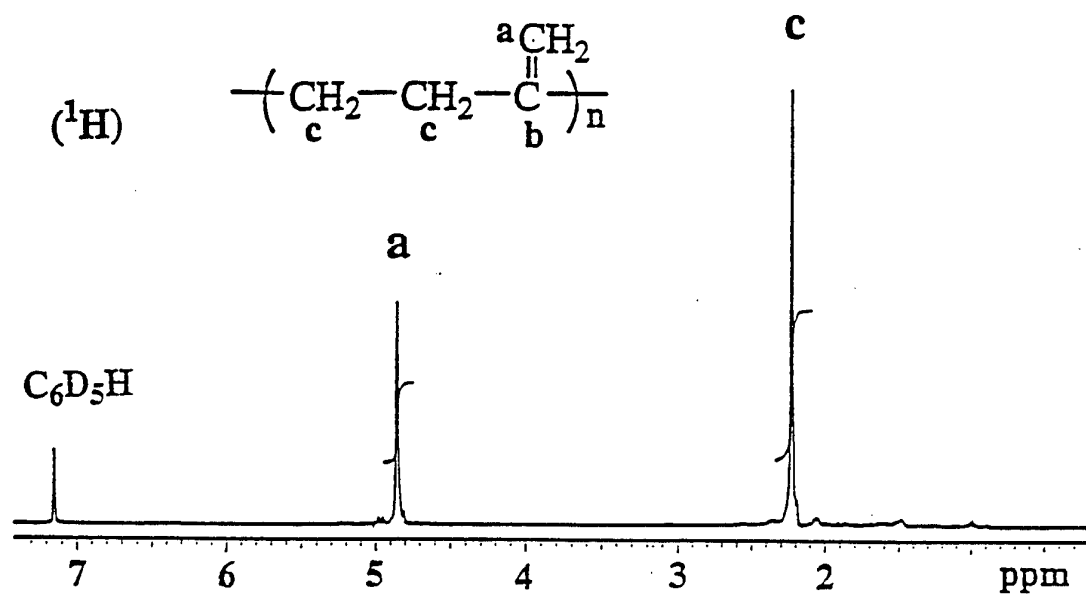
FIG. 1





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FIG. 2(a)



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/00746

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C08F 4/52; C08G 61/06

US CL : 526/126, 170, 308

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/126, 170, 308

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,801,666 (MARKS ET AL.) 31 January 1989, column 2, lines 35-36; column 5, lines 44-46; column 6, lines 1-14.	1-25
A,P	US, A, 5,312,881 (MARKS ET AL.) 17 May 1994.	1-25
A	US, A, 5,066,739 (PETTIJOHN ET AL.) 19 November 1991.	1-25
A	US, A, 3,919,227 (ANDREADES ET AL.) 11 November 1975.	1-25

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

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