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EDIFICIO SISKI

CARRERA 4 No. 72 -

BOGOTA 8, COLOMBIA

SUPERINDUSTRIA Y COMERCIO

Radicacion : 00051051 00000002

Fecha (ACID): 2000-10-04 16:48:41

Tramite : 002 PATENTES D 1 REGISTRO/ 329 COMPLEMEN

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Folios: 83

611

995

Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
E. S. D.

Referencia : Expediente No. 00.051.051

Solicitante : THE DOW CHEMICAL COMPANY

Asunto : Solicitud de patente para: "POLIMERIZACION DE
OXIDOS DE ALQUILENO USANDO CATALIZADORES DE
CIANURO DE METAL Y COMPUESTOS INICIADORES
INSATURADOS"

Fecha de solicitud : 7 de julio de 2000

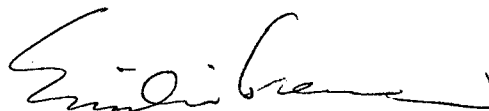
TRAMITE 002 EVENTO 001 ACTUACION 329

1. Yo, Emilio FERRERO, obrando como apoderado de la solicitud en referencia, atentamente, presento con este escrito las copias certificadas de las solicitudes de patente Estadounidenses No. 60/143,075, No. 60/143,078, No. 60/143,079, No. 60/143,081, No. 60/143,082, del 9 de julio de 1999, y la número 60/205,772 del 19 de mayo de 2000, de las cuales se reclama prioridad en esta solicitud de patente.

2. Ruego a la Señora Jefe se sirva aceptar este escrito con sus anexos, y se continúe con el trámite de la solicitud.

Bogotá, -4 OCT. 2000

Señora Jefe;



EMILIO FERRERO

T.P.A. No. 31.929

WCS COLO 00286-801-117-8
WJC-ID-1528

00065
58

PA 289107

THE UNITED STATES OF AMERICA

~~TO ALL TO WHOM THESE PRESENTS SHALL COME:~~

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 14, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,075

FILING DATE: July 09, 1999



By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

H. L. Jackson

H. L. JACKSON

Certifying Officer



3553 U.S. P.T.O.

11/11/99
PTO XXXX

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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c)

Docket Number		60068	Type a plus sign (+) inside this box	+
INVENTOR(s)/APPLICANT(s)				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
Clement	Katherine	S.	115 Poinciana, Lake Jackson, Texas 77566, United States of America	
Walker	Louis	L.	246 Barbara Drive, Clute, Texas 77531, United States of America	
Wehmeyer	Richard	M.	205 Zinnia, Lake Jackson, Texas 77566, United States of America	
Whitmarsh	Robert	H.	55 North Calla Lilly Court, Lake Jackson, Texas 77566, United States of America	
☐ Additional inventors are being named on separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
PROCESS FOR POLYOXIDES INITIATED WITH ACETYLENIC ALCOHOLS				
CORRESPONDENCE ADDRESS				
Gene L. Tyler THE DOW CHEMICAL COMPANY Patent Department 2301 N. Brazosport Blvd., B-1211 Freeport, Texas 77541 U.S.A.			Telephone: 409-238-7239 Fax: 409-238-0878	
ENCLOSED APPLICATION PARTS (check all that apply)				
☒ Specification		Number of Pages	4	☐ Small Entity Statement
☐ Drawing(s)		Number of Sheets	_____	☐ Other (specify)
METHOD OF PAYMENT (check one)				
☐ A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT	\$150.00
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 04-1512				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government				
☒ No				
☐ Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,

Gene L. Tyler
Registration No.: 35,395
Phone No.: 409-238-7239

EXPRESS MAIL MAILING NO.: EL026307204US
DATE OF DEPOSIT: July 9, 1999

GLT/jka

PROVISIONAL APPLICATION FILING ONLY

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

00067

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Approval of Department Head
Object No.:

Please fill out carefully. The requested information is needed for proper preparation of a patent application.

You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DO NOT WRITE IN THIS SPACE	
Disclosure No. 60068 S	
Assigned to:	Date

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Polyoxides initiated with acetylenic alcohols

Persons submitting this Disclosure of Invention:

Name (Please type or print):			
First	Katherine	Middle	S. Last Clement
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State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	Chemist		
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Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-297-2295	Master No.	144988

Signature

I. Name (Please type or print)			
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State	Texas	Zip Code	77566
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Occupation/Profession	chemist		
Division	Texas	Bldg.	B-1215
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Phone	409-238-9895	Master No.	093721

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Occupation/Profession	Technologist		
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State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	B-4810
Department	Polyglycols R&D	Lab Code	1054
Phone	409-238-4613	Master No.	143727

Signature

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party? ☐ YES ☒ NO

If YES, please identify the party and the contract _____

Witness:

I have read and understood this Disclosure and attachments.
My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness

Signature

Date

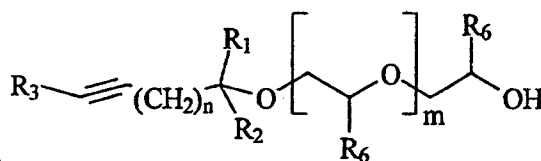
DESCRIPTION OF THE INVENTION

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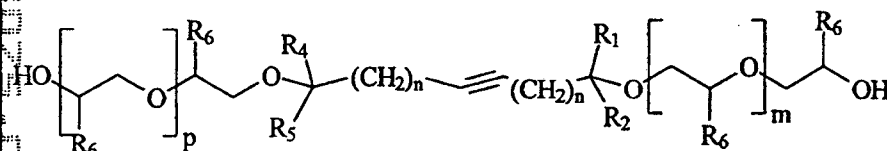
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Give a summary/abstract of the Invention: Alkyne functionalized polyoxides were previously unavailable because the alkyne group is base sensitive. Therefore, these acetylenic polyols cannot be made using conventional base catalysis due to rearrangement or migration of the alkyne functionality and/or decomposition of the initiator. The alkyne initiators which are prepared via a reaction of acetylide and a reactive carbonyl compound such as acetone, formaldehyde, acetaldehyde, etc. are particularly unsuited for conventional base catalysis since under base catalysis acetylene is produced by decomposition of the initiator, presenting a reactive chemical hazard. Linear primary alcohols such as 3-butyn-1-ol do not produce acetylene under basic reaction conditions, but are also unsuited for conventional base catalysis due to migration of the alkyne to an internal position and reaction of alkoxide species onto the alkyne. Although acetylenic alcohols have been ethoxylated previously by Lewis acid catalyzed reaction with ethylene oxide, this method cannot be used to make the desired alkyne functionalized polyols due to the production of large amounts of cyclic by-products and difunctionalized products resulting from the reaction of the initiator in a capping reaction with the polymer chain end. In the present invention using double metal cyanide catalysts, the alkyne functionalized polyethers are produced cleanly, with only trace amounts of cyclic by-products and no difunctionalized species. By using double metal cyanide catalysts such as zinc hexacyanocobaltate prepared with glyme or t-butanol the acetylene containing alcohols may be converted to polyols without rearrangement, side reactions onto the alkyne, or decomposition of the initiators. These alkyne functionalized polyethers, especially polyethylene, polypropylene, and polybutylene glycols are prepared by polymerizing an oxide or mixture of oxides, especially ethylene oxide, propylene oxide, and butylene oxide onto an acetylenic alcohol initiator using a double metal cyanide catalyst. Examples of acetylenic alcohols useful as initiators include 2-methyl-3-butyn-2-ol; 3-butyn-1-ol; propargyl alcohol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like.



The products correspond to the formula:

$R_1, R_2, R_3 = \text{H, or alkyl}; R_6 = \text{H, alkyl}; n = 0-12; m > 1$ and the formula:



where $R_1, R_2, R_4, R_5, R_6 = \text{H, or alkyl}; n = 0-12; m, p > 1$

The reactions are carried out by adding the catalyst to the initiator in a stirred pressure vessel, adding up to 10% of the theoretical amount of oxide and heating the mixture at temperatures of 90-100°C until a decrease in pressure is observed, indicating that the reaction has initiated. The remaining oxide is then fed in at such a rate that the temperature is controlled at 90 to 100°C.

The invention relates to: (Check as many as seem applicable):

☐ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

We Claim:

A process for preparing a polyether from an acetylenic initiator comprising alkoxylation in the presence of a double metal cyanide catalyst.

2	List any literature (including patents) of which you are aware relating to the invention.
	1. Croxall, W. J.; Dawson, N.D. US 3,021,341 (1962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-butyn-2-ol using ethylene oxide with $\text{BF}_3\text{Et}_2\text{O}$ as the catalyst. The mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization. 2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared]. 3. Reppe et al.; Justus Liebigs Ann. Chem.; 596; 1955; 1,75 Preparation of diethoxylate of propargyl alcohol using aqueous NaOH 4. Additional preparations of monoethoxylated propargyl alcohol by various methods: (1) Bottini, A.T., et al. J. Org. Chem.; 30; 1965; 2988-2994; (2) Pola, J. et al.; Collect. Czech. Chem. Commun.; 43; 1978; 760-768 ; (3) Bovicello, P.; Mincione, E.; Patamia, M.; Synth. Commun.; 21; 7; 1991; 907-913; (4) Hernandez, E.; Galan, a.; Rovira, C.; Veciana, J.; Synthesis; 11; 1992; 1164-1169; (5) Takahashi; Matsumoto; Nippon Kagaku Zasshi; 84; 1963; 145, 147; (6) US 3048598 (1962) Miles Laboratories; (7) Kuznetsov; Krasavtsev; Sov. Prog. Chem. (Engl. Transl.); 45; 2; 1979; 61,62; (8) Shikhiyev et al.; J. Gen. Chem. USSR (Engl. Transl.); 46; 1976; 2509; (9) Shikhiyev et al.; Izv. Vyssh. Uchen. Zaved. Khim. Khim. Tekhnol.; 15; 1972; 534; (10) Karaew et al.; Uch. Zap. Azerb. Inst. Nefti Knim. Ser. 9; 9; 1973; 2-62, 63-66; (11) Faure; Descotes, C.R. Hebd. Seances Acad. Sci.; 261; 1965; 1327; (12) BASF DE 2241157; 1972 CA80: 145400 (13) BASF DE 2241155; 1972 CA80: 145406 (14) BASF DE 2241156; CA80: 145399 (15) Rsaewa et al.; Azeerb. Khim. Zh.; 5-6; 1971; 89,91; (16) Black et al.; J. Chem. Soc. C; 1967; 2260
3	State the nature and extent of your literature search. Scifinder search of " alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" Beilstein search of ethoxylate structures of propargyl and 2-methyl-3-butyn-2-ol.
4	How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. The acetylene functionality is sensitive to base. Using base catalysis causes side reactions, rearrangements and sometimes dangerous decomposition of the initiator, especially when the initiator contains a terminal acetylene group. Attempted polymerization onto 2-methyl-3-butyn-2-ol resulted in dangerous decomposition to acetylene and acetone prior to the oxide feed. Attempted polymerization onto 3-butyn-1-ol resulted in significant rearrangement of the terminal alkyne functionality to an internal position and produced a polyol with very dark color. Although, some polymerizations onto acetylenic glycols are performed with amine catalysts, these acetylenic glycols possess structures which are not easily rearranged. Terminal acetylenic functionalized species known to date have very low degrees of polymerization (1 to 2). Ethoxylation of acetylenic alcohols using BF_3 has only been used to produce the mono- ethoxylate and required a large excess of the acetylenic alcohols. An attempt to ethoxylate both propargyl alcohol and 2-methyl-3-butyn-2-ol to a DP (degree of polymerization) of seven resulted in products with broad polydispersity containing a significant amount of cyclic byproducts and products terminated on both ends with the acetylenic initiator. These by-products are not easily removed, if removable at all. The process using double metal cyanide catalyst to polymerize oxides onto acetylenic initiators results in product with narrow polydispersity and good color. Furthermore, the products made using tertiary acetylenic initiators have unusually narrow polydispersities compared with polyols made using KOH catalysis from similar but nonacetylenic tertiary alcohols. . Polydispersity can be an important variable in a number of end-uses. In the specific case of ethoxylates with a targeted degree of polymerization of 6 to 12 EO units, products made using KOH have a broad polydispersity resulting in a solid product at room temperature. The product made using DMC catalysis is liquid and the small amount of high molecular weight fraction may be easily removed by solvent fractionation and filtration, resulting in a clear liquid product.

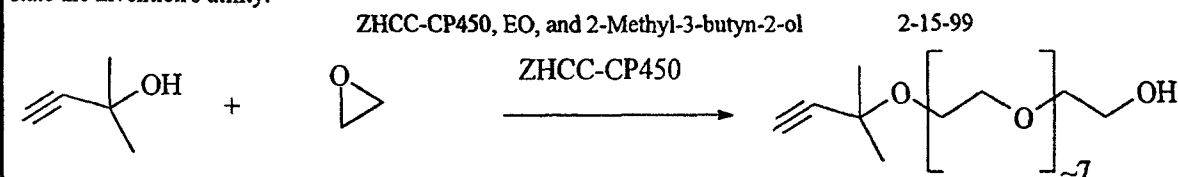
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DESCRIPTION OF THE INVENTION

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Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.



g	230.7	1024	6.8 = 5422 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	2.74	23.24	
ratio	1	8.48	

2-methyl-3-butyn-2-ol : Aldrich, dried over 3Å sieves
Catalyst used was prepared on 1-22-99

The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Mark Warny). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 20 minutes after addition. A total of thirty minutes after the initial addition, an additional 50 g of EO was added and the reactor pressure was watched carefully. The pressure dropped more rapidly and the rest of the EO was fed automatically. As the reaction progressed a vigorous exotherm developed, reaching a differential of almost 30°C from wall to reaction. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~50°C and was pale yellow in color. As the material cooled, it became opaque, but remained liquid. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 560 Mn, PDI of 1.63.

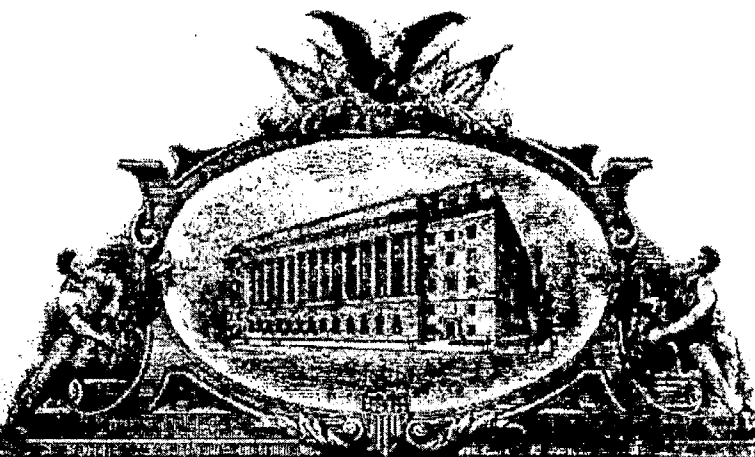
Fractionation of t-Butynol Polyol:

A sample of the polyol of Run 1 (t-butynol initiated [199800896-12]~660 g) along with the retains from samples previously fractionated and tested for residual catalyst was slurried with 1980 g of isopropyl alcohol and hexane (~2:1 by weight, recovered from the stripping operation of Run 3) in a 6 L flask. The mixture was stirred and chilled in an ice bath for about 1 hour. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 653 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g of CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through #1 Whatman paper (some product loss through filter). The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 5 minutes and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 20 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then recentrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 8.17 g

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LOS ESTADOS UNIDOS DE AMERICA

**A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS**

Oficina de Patentes y Marcas de los Estados Unidos

14 de agosto de 2000

**LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL
DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS
UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS
ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORQUE UNA FECHA
DE PRIORIDAD BAJO 35 USC 111..**

SOLICITUD NUMERO: 60/143,075

FECHA DE PRESENTACION: 9 de julio de 1999



**Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS**

Firmado por

H.L. JACKSON

Funcionario Certificador

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65

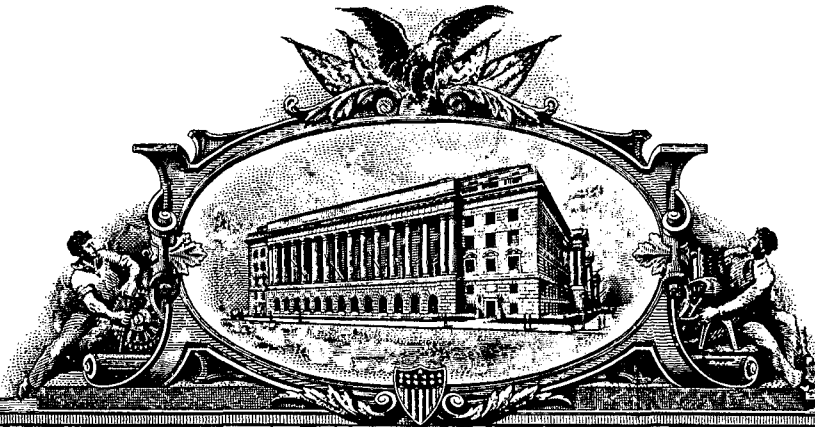
REIVINDICACIONES

1. Un proceso para la preparación un poliéter de un iniciador acetilénico que comprende la alcoxilación en presencia de un catalizador de cianuro metálico doble.

COLO 00286-801-117-8
JJC-ID-1519

00074
66

PA 289114



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 11, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,078

FILING DATE: July 09, 1999



By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

P. SWAIN

Certifying Officer

07/09/99
JCS53 U.S. PTO

Approval for use through OMB 0651-00XX
Patent and Trademark Office, U S DEPARTMENT OF COMMERCE

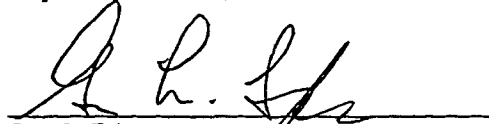
12/1/99
PTO XXXX
00075
67

PROVISIONAL APPLICATION COVER SHEET

a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number		60071	Type a plus sign (+) inside this box	+
INVENTOR(s)/APPLICANT(s)				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
Clement	Katherine	S.	115 Poinciana, Lake Jackson, Texas 77566 United States of America	
Walker	Louis	L.	246 Barbara Drive, Clute, Texas 77531 United States of America	
Wehmeyer	Richard	M.	205 Zinnia, Lake Jackson, Texas 77566 United States of America	
Whitmarsh	Robert	H.	55 North Calla Lilly Ct, Lake Jackson, Texas 77566 United States of America	
☐ Additional inventors are being named on separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
POLYETHERS INITIATED WITH ACETYLENIC ALCOHOLS				
CORRESPONDENCE ADDRESS				
Gene L. Tyler THE DOW CHEMICAL COMPANY Patent Department 2301 Brazosport Blvd. B-1211 Freeport, Texas 77541 U.S.A.			Telephone: 409-238-7239 Fax: 409-238-0878	
ENCLOSED APPLICATION PARTS (check all that apply)				
☒ Specification		Number of Pages	4	☐ Small Entity Statement
☐ Drawing(s)		Number of Sheets	_____	☐ Other (specify)
METHOD OF PAYMENT (check one)				
☐ A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT	\$150.00
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 04-1512				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government				
☒ No				
☐ Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,



Gene L. Tyler
Registration No.: 35,395
Phone No.: 409-238-7239

EXPRESS MAIL MAILING NO.: EL026307204US
DATE OF DEPOSIT: July 9, 1999

GLT/II

PROVISIONAL APPLICATION FILING ONLY

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

00076
68

Approval of Department Head

Project No.:

Please fill out carefully. The requested information is needed for proper preparation of a patent application.

You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DO NOT WRITE IN THIS SPACE	
Disclosure No.	60071 S
Assigned to	
Date	

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Polyethers initiated with acetylenic alcohols

Persons submitting this Disclosure of Invention:

I. Name (Please type or print):
First Katherine Middle S. Last Clement
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State Texas Zip Code 77566
Citizenship USA
Occupation/Profession Chemist
Division Texas Bldg. B-1215
Department Materials Research & Lab
Synthesis Code 1260
Phone 409-297-2295 Master No. 144988
Signature

II. Name (Please type or print):
First Louis Middle L. Last Walker
Home Address 246 Barbara Drive
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State Texas Zip Code 77531
Citizenship USA
Occupation/Profession Technologist
Division Texas Bldg. B-1215
Department Materials Research & Lab
Synthesis Code 1260
Phone 409-238-9815 Master No. 139939
Signature

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party?
If YES, please identify the party and the contract

YES NO

Witness:

I have read and understood this Disclosure and attachments.

My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness

Signature

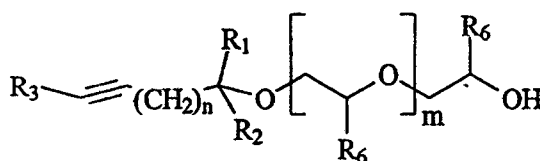
Date

DESCRIPTION OF THE INVENTION

00077

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1 Give a summary/abstract of the Invention: Alkyne functionalized polyethers were previously unavailable because the alkyne group is base sensitive. Therefore, these acetylenic polyols cannot be made using conventional base catalysis due to rearrangement or migration of the alkyne functionality and/or decomposition of the initiator. The alkyne initiators which are prepared via a reaction of acetylide and a reactive carbonyl compound such as acetone, formaldehyde, acetaldehyde, etc. are particularly unsuited for conventional base catalysis since under base catalysis acetylene is produced by decomposition of the initiator, presenting a reactive chemical hazard. Linear primary alcohols such as 3-buten-1-ol do not produce acetylene under basic reaction conditions, but are also unsuited for conventional base catalysis due to migration of the alkyne to an internal position and reaction of alkoxide species onto the alkyne. Although acetylenic alcohols have been ethoxylated previously by Lewis acid catalyzed reaction with ethylene oxide, this method cannot be used to make the desired alkyne functionalized polyols due to the production of large amounts of cyclic by-products, and difunctionalized products resulting from the reaction of the initiator in a capping reaction with the polymer chain end. In the present invention using double metal cyanide catalysts, the alkyne functionalized polyethers are produced cleanly, with only trace amounts of cyclic by-products and no difunctionalized species. By using double metal cyanide catalysts such as zinc hexacyanocobaltate prepared with glyme or t-butanol the acetylene containing alcohols may be converted to polyols without rearrangement, side reactions onto the alkyne, or decomposition of the initiators. These alkyne functionalized polyethers, especially polyethylene, polypropylene, and polybutylene glycols are prepared by polymerizing an oxide or mixture of oxides, especially ethylene oxide, propylene oxide, and/or butylene oxide onto an acetylenic alcohol initiator using a double metal cyanide catalyst. Examples of acetylenic alcohols useful as initiators include 2-methyl-3-buten-2-ol; 3-buten-1-ol; propargyl alcohol; and the like.



The new compositions correspond to the formula:

$\text{R}_1, \text{R}_2, \text{R}_3 = \text{H}, \text{ or alkyl}; \text{R}_6 = \text{H}, \text{ or alkyl}; n = 0-12; m > 1$

The reactions are carried out by adding the catalyst to the initiator in a stirred pressure vessel, adding up to 10% of the theoretical amount of oxide and heating the mixture at temperatures of 90-100°C until a decrease in pressure is observed, indicating that the reaction has initiated. The remaining oxide is then fed in at such a rate that the temperature is controlled at 90 to 100°C.

The invention relates to: (Check as many as seem applicable):

- ☒ A composition of matter (compounds, alloy, plastic, mixture, etc.)
☐ A process (production, fabrication, use, treatment, etc.)
☐ A machine or article (tool, apparatus, package or other "thing")

We claim: a composition of matter
 comprising a ~~polyether~~ polyether having a terminal
 acetylenic group.

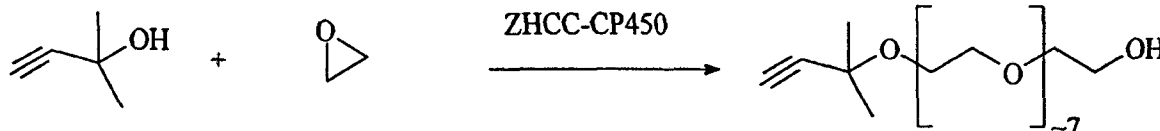
2	List any literature (including patents) of which you are aware relating to the invention. 1. Croxall, W. J.; Dawson, N.D. US 3,021,341 (1962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-butyn-2-ol using ethylene oxide with $\text{BF}_3\text{Et}_2\text{O}$ as the catalyst. The mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization. 2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared]. 3. Reppe et al.; Justus Liebigs Ann. Chem.; 596; 1955; 1,75 Preparation of diethoxylate of propargyl alcohol using aqueous NaOH 4. Additional preparations of monoethoxylated propargyl alcohol by various methods: (1) Bottini, A.T., et al. J. Org. Chem.; 30; 1965; 2988-2994; (2) Pola, J. et al.; Collect. Czech. Chem. Commun.; 43; 1978; 760-768 ; (3) Bovicello, P.; Mincione, E.; Patamia, M.; Synth. Commun.; 21; 7; 1991; 907-913; (4) Hernandez, E.; Galan, a.; Rovira, C.; Veciana, J.; Synthesis; 11; 1992; 1164-1169; (5) Takahashi; Matsumoto; Nippon Kagaku Zasshi; 84; 1963; 145, 147; (6) US 3048598 (1962) Miles Laboratories; (7) Kuznetsov; Krasavtsev; Sov. Prog. Chem. (Engl. Transl.); 45; 2; 1979; 61,62; (8) Shikhiev et al.; J. Gen. Chem. USSR (Engl. Transl.); 46; 1976; 2509; (9) Shikhiev et al.; Izv. Vyssh. Uchen. Zaved. Khim. Khim. Tekhnol.; 15; 1972; 534; (10) Karaew et al.; Uch. Zap. Azerb. Inst. Nefti Knim. Ser. 9; 9; 1973; 2-62, 63-66; (11) Faure; Descotes; C.R. Hebd. Seances Acad. Sci.; 261; 1965; 1327; (12) BASF DE 2241157; 1972 CA80: 145400 (13) BASF DE 2241155; 1972 CA80: 145406 (14) BASF DE 2241156; CA80: 145399 (15) Rsaewa et al.; Azeerb. Khim. Zh.; 5-6; 1971; 89,91; (16) Black et al.; J. Chem. Soc. C; 1967; 2260
3	State the nature and extent of your literature search. Scifinder search of " alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" Beilstein search of ethoxylate structures of propargyl and 2-methyl-3-butyn-2-ol.
4	How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. Acetylenic functionalized species known to date have very low degrees of polymerization (1 to 2) and are unsuitable for conversion to the desired surfactants. Ethoxylation of acetylenic alcohols using BF_3 has only been used to produce the mono- ethoxylate and requires a large excess of the acetylenic alcohols. If the large excess of alcohol is not used, the product produced contains large amounts of by-products which are not easily removed, if at all. Using base catalysis causes side reactions, rearrangements and sometimes dangerous decomposition of the initiator, especially when the initiator contains a terminal acetylene group. Furthermore, the products made using tertiary acetylenic initiators have unusually narrow polydispersities compared with polyols made using KOH catalysis from similar but nonacetylenic tertiary alcohols. Polydispersity can be an important variable in a number of end-uses. In the specific case of ethoxylates with a targeted degree of polymerization of 6 to 12 EO units, products made using KOH have a broad polydispersity resulting in a solid product at room temperature. The product made using DMC catalysis is liquid and the small amount of high molecular weight fraction may be easily removed by solvent fractionation and filtration, resulting in a clear liquid product.

DESCRIPTION OF THE INVENTION

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5 Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol 2-15-99



g	230.7	1024	6.8 = 5422 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	2.74	23.24	
ratio	1	8.48	

2-methyl-3-butyn-2-ol: Aldrich, dried over 3Å sieves
Catalyst used was prepared on 1-22-99

The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Mark Warny). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 20 minutes after addition. A total of thirty minutes after the initial addition, an additional 50 g of EO was added and the reactor pressure was watched carefully. The pressure dropped more rapidly and the rest of the EO was fed automatically. As the reaction progressed a vigorous exotherm developed, reaching a differential of almost 30°C from wall to reaction. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~50°C and was pale yellow in color. As the material cooled, it became opaque, but remained liquid. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of $\equiv\text{C}$ from 89 ppm to 85 ppm]. GPC analysis showed 560 Mn, PDI of 1.63.

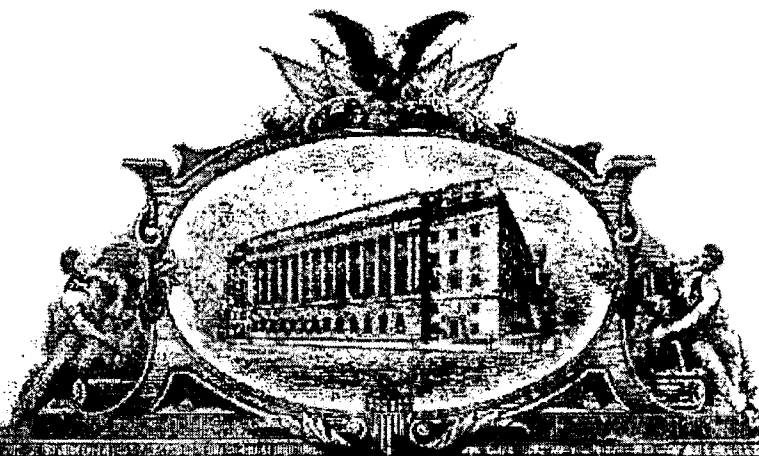
Fractionation of t-Butynol Polyol:

A sample of the polyol of Run 1 (t-butynol initiated [199800896-12]~660 g) along with the retains from samples previously fractionated and tested for residual catalyst was slurried with 1980 g of isopropyl alcohol and hexane (~2:1 by weight, recovered from the stripping operation of Run 3) in a 6 L flask. The mixture was stirred and chilled in an ice bath for about 1 hour. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse). The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 653 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g of CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through #1 Whatman paper (some product loss through filter). The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 5 minutes and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 20 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then recentrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 8.17 g

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PA 115442

LOS ESTADOS UNIDOS DE AMERICA

**A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS**

Oficina de Patentes y Marcas de los Estados Unidos

11 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORQUE UNA FECHA DE PRIORIDAD BAJO 35 USC 111..

SOLICITUD NUMERO: 60/143,078

FECHA DE PRESENTACION: 9 de julio de 1999



Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS

Firmado por
P. SWAIN

Funcionario Certificador

REIVINDICACIONES

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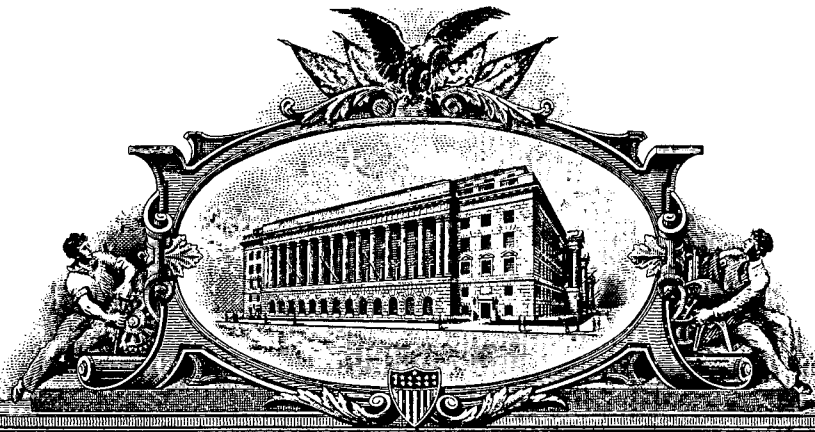
1. Una composición de material que comprende un poliéter que posee un grupo acetilénico terminal.

COLO 00286-801-117-8
JJC-ID-1520

PA 289118

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THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 14, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,079

FILING DATE: July 09, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

**P. R. GRANT
Certifying Officer**

3553 U.S. PTO

Approval for use through OMB 0651-00XX
 Patent and Trademark Office, U.S. DEPARTMENT OF COMMERCE

PTO XXXX

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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number

60072

Type a plus sign (+)
inside this box

-

INVENTOR(s)/APPLICANT(s)

LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)
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Walker	Louis	L.	246 Barbara Drive, Clute, Texas 77531 United States of America
Rauscher	Wanda	W.	709 Noreda, Angleton, Texas 77515 United States of America
Whitmarsh	Robert	H.	55 North Calla Lilly Ct., Lake Jackson, Texas 77566 United States of America

☐ Additional inventors are being named on separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

PROCESS FOR PREPARING POLYETHERS WITH REACTIVE SUBSTITUENTS

CORRESPONDENCE ADDRESS

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 THE DOW CHEMICAL COMPANY
 Patent Department
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 Freeport, Texas 77541
 U.S.A.

Telephone: 409-238-7239

Fax: 409-238-0878

ENCLOSED APPLICATION PARTS (check all that apply)

- ☒ Specification Number of Pages 4 ☐ Small Entity Statement
- ☐ Drawing(s) Number of Sheets ☐ Other (specify)

METHOD OF PAYMENT (check one)

☐ A check or money order is enclosed to cover the Provisional filing fees

☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number:

04-1512

PROVISIONAL
FILING FEE
AMOUNT

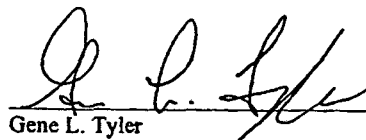
\$150.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government

☒ No

☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,



Gene L. Tyler
 Registration No.: 35,395
 Phone No.: 409-238-7239

EXPRESS MAIL MAILING NO.: EL026307204US
 DATE OF DEPOSIT: July 9, 1999

GLT/ll

PROVISIONAL APPLICATION FILING ONLY

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

00087

26

Approval of Department Head
Project No.:

Please fill out carefully. The requested information is needed for proper preparation of a patent application.
You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

DO NOT WRITE IN THIS SPACE	
Disclosure No.	60072 S
Assigned to:	Date

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Preparing Polyethers with reactive substituents
--

Persons submitting this Disclosure of Invention:

I. Name (Please type or print):			
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State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	Chemist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-297-2295	Master No.	144988
Signature			

II. Name (Please type or print):			
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Home Address	246 Barbara Drive		
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State	Texas	Zip Code	77531
Citizenship	USA		
Occupation/Profession	Technologist		
Division	Texas	Bldg.	B-1215
Department	Materials Research & Synthesis	Lab Code	1260
Phone	409-238-9815	Master No.	139939
Signature			

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Home Address	709 Noreda		
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Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	
Department	Polyglycols TS&D	Lab Code	1054
Phone	409-238-3873	Master No.	140999
Signature			

IV. Name (Please type or print):			
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City	Lake Jackson	County/Parish	Brazoria
State	Texas	Zip Code	77566
Citizenship	USA		
Occupation/Profession	chemist		
Division	Texas	Bldg.	B-4810
Department	Polyglycols R&D	Lab Code	1054
Phone	409-238-4613	Master No.	143727
Signature			

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party? YES NO
If YES, please identify the party and the contract

Witness:		
I have read and understood this Disclosure and attachments.		
My initials and date are included on all pages attached to this disclosure.		
Type or print name of Witness	Signature	Date

DESCRIPTION OF THE INVENTION

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Give a summary/abstract of the Invention: The polyoxide polymerization process using KOH as the catalyst cannot be used with initiators which contain base sensitive functionality such as alkyne, halogen, ester, ketones, aldehydes, alkynes, lactones and acids. Normal acid catalysis allow for the use of base sensitive functionalities but acid catalyzed polyol processes are generally disadvantaged in that the products have broader polydispersities and cyclic by-products are produced. In this invention, double metal cyanide catalysts are used for polymerizing oxides onto initiators containing base sensitive groups such as halogen, ester, ketone, aldehyde, alkyne, lactone and acid. The resulting functionalized polyoxide can be used as is or converted to other products by functional group manipulation. For example, polymerization of ethylene oxide onto 2-chloroethanol will produce a chloro-terminated polyol. This polyol can be reacted with an amine to produce a polyol with amine functionality on one terminus and a hydroxy group on the other.

The invention relates to: (Check as many as seem applicable):

☒ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

2

List any literature (including patents) of which you are aware relating to the invention.

1. Croxall, W. J.; Dawson, N.D. US 3,021,341 (1962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-butyn-2-ol using ethylene oxide with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the catalyst. The mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization.
2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared].

3	State the nature and extent of your literature search. Scifinder search of "alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" Beilstein search of ethoxylate structure of 2-methyl-3-butyn-2-ol. Derwent search of polyethylene glycol of 2-methyl-3-buten-2-ol.
4	How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. : Base catalysis cannot be used to prepare polyethers from initiators having base sensitive groups. In the case of acetylenic groups, rearrangement or decomposition can result from treatment with base. However, acid catalysis of oxide polymerizations, while allowing for the use of initiators with base sensitive groups typically produce products having broader polydispersities. In addition, under acid catalysis cyclic by-products are also a problem. Also, under acid catalysis, initiators which can form stable carbonium ions can produce an additional type of byproduct by reacting with the hydroxy end-groups of the polyol, thus "capping" the chain. In the present invention using double metal cyanide catalysts, the polyoxides produced exhibit narrow polydispersity. No "capped" products are produced. Only a trace quantity of any other by-products are seen. The use of double metal cyanide catalyst allows the initiator to contain functional groups sensitive to base, such as halo, alkyne, ester, etc.

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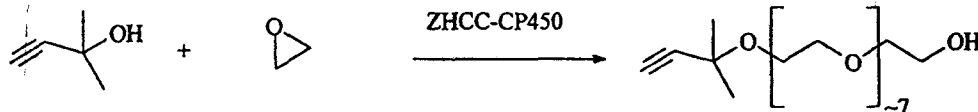
DESCRIPTION OF THE INVENTION

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Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol 4-20-99



g	265.51	~1050	6. = 4560 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	3.156	23.83	
ratio	1	7.55	

2-methyl-3-butyn-2-ol : Air Products, dried over 3Å sieves
Catalyst used was Batch D prepared on p. 7

The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-3808 (Vicki Harrington). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (~50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 40 minutes after addition. A hour after the initial addition, an additional ~50 g of EO was added and the reactor pressure was watched. The pressure dropped more rapidly and the feed rate was put in automatic mode. This caused the feed rate to go above 10 g/min. As the reaction progressed a vigorous exotherm developed, reaching a differential of over 30°C from wall to reaction. This caused the system to become destabilized with wide swings in the jacket temperature causing wide swings in the reactor temperature from <80°C to more than 106°C for brief periods. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~20°C after stirring overnight in the reactor and was pale amber in color. The material was opaque, but remained liquid. Some settling was observed. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 380 Mn, PDI of 1.82.

Fractionation of Run 3 t-Butynol Polyol : 5-13-99

The polyol (Run 3 of t-butynol initiated [199900896-12]~1205 g) was slurried with 2410 g of isopropyl alcohol in a 6 L flask. The material was stirred and 1205 g of hexane was added. The mixture was stirred and chilled in an ice bath for several hours. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 1078 g. The weight of the air dried wax was 109.09 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through 2 sheets of #1 Whatman paper (no product loss through filter), rinsing with about 20 mL of DI water. The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 3 minutes in a centrifuge bottle and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 25 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then centrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 12.00 g

U.S. DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

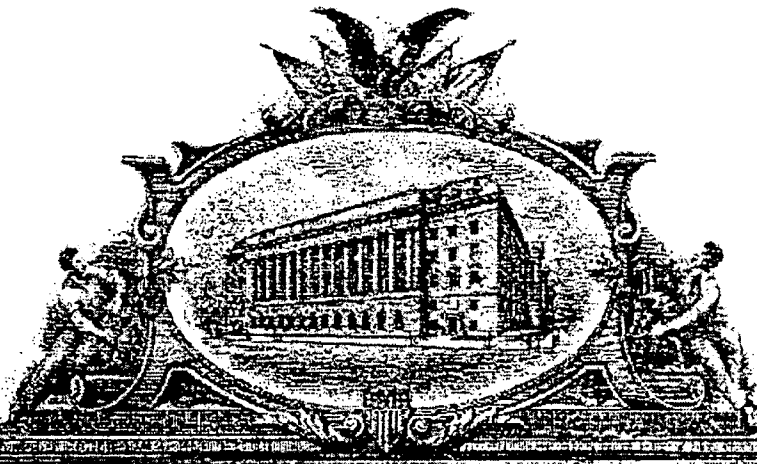
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***THIS IS TO CERTIFY that page (s) 4 is
missing from the U.S. Patent and Trademark Office Scanned
Image or Microform Records.***

P. A. Hunt
Certifying Officer

AUG 14 2000
Date

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LOS ESTADOS UNIDOS DE AMERICA

**A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS**

Oficina de Patentes y Marcas de los Estados Unidos

14 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORGUE UNA FECHA DE PRIORIDAD BAJO 35 USC 111..

SOLICITUD NUMERO: 60/143,079

FECHA DE PRESENTACION: 9 de julio de 1999



Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS

Firmado por
P.R. GRANT

Funcionario Certificador

DESCRIPCIÓN DE LA INVENCION

1. Dar un resumen de la invención: El proceso de polimerización de polióxido usando KOH como el catalizador no pueden ser usados con iniciadores los cuales contienen funcionalidad de base sensible como alquino, halógeno, éster, cetonas, aldehídos, alquinos lactonas y ácidos. La catálisis de ácido normal permite el uso de funcionalidades sensibles de base pero los procesos poliol catalizados ácidos son generalmente desventajosos en que los productos tienen amplias polidispersiones y se producen subproductos cíclicos. En esta invención, los catalizadores de cianuro de metal doble son usados para la polimerización de óxidos en iniciadores que contienen grupos de base sensibles como, halógeno, éster, cetona, aldehído, alquino, lactona y ácido. El polioxido funcionalizado resultante puede ser usado como es o convertirlo a otros productos por manipulación funcional de grupo, por ejemplo, la polimerización del óxido de etileno en 2-cloroetanol producirá un poliol terminado en cloro. Este poliol puede reaccionado con una amina para producir un poliol con funcionalidad amina en un término y un grupo hidroxil en el otro.

La invención está referida a

X una composición de materia (compuestos , aleación, plástico, mezcla, etc).

X Un proceso (producción, fabricación, uso, tratamiento, etc.)

2. Liste alguna literatura de la cual usted está seguro esté relacionada con la invención.

1. Croxall, W. J. ; Dawson, N. D. US 3,021,341 (1962) [Miles laboratories] describe la etoxilación del 2-metil-3-butin-2-ol usando óxido de etileno con $\text{BF}_3\text{Et}_2\text{O}$ como el catalizador. El compuesto mono-etoxilado fue aislado por destilación por conversión a metilendioxano por ciclización.

2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.;21; 1951;1247, 1248,1251; engl. Aussg. S.1361, 1362, 1364 Etoxilación de 2 metil-3-butin-2-ol con óxido de etileno usando N,N-dimetilanilina a 150 °C. [Bajo esas condiciones hubo ciertamente alguna presencia de degradación del alquino. Los productos estaban mono y dietoxilados].

3. Estado de la naturaleza y extensión de la búsqueda de la literatura. Búsqueda Scifinder de "Polioles funcionalizados en alquino o acetileno conteniendo polietilen glicoles o propilenglicoles". Búsqueda beilstein de la estructura del etoxilato de 2-metil-3-butin-2-ol. Búsqueda Derwent de polietilen glicol de 2-metil-3-buten-2-ol.

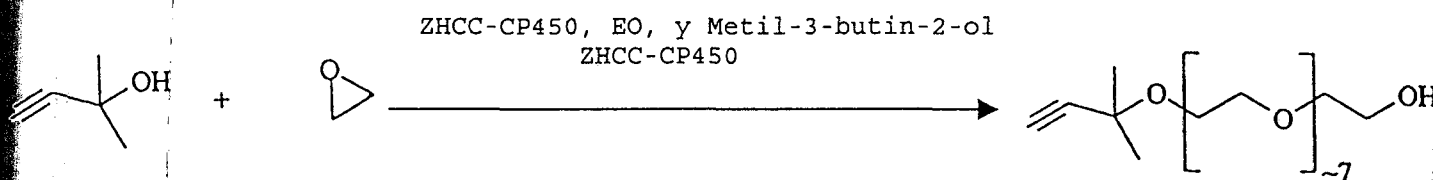
4. En que manera esta invención difiere de, y liste las ventajas sobre, la literatura conocida por usted como también de las alternativas, si las hay actualmente empleadas: Las catálisis de base no pueden ser usadas para preparar poliéteres de iniciadores que tienen

grupos de base sensibles. En el caso de los grupos acetilénicos, el reagrupamiento o la descomposición puede resultar de el tratamiento con una base. Sin embargo, catálisis ácida de polimerizaciones de óxido, mientras permitan el uso de iniciadores con grupos de base sensibles típicamente produce productos teniendo amplias polidispersiones. Además, bajo catálisis ácida los subproductos cíclicos son también un problema. También, bajo catálisis ácida, los iniciadores los cuales pueden formar iones carbonio estables pueden producir un tipo adicional de subproducto reaccionando con los grupos que terminan en hidroxil del poliol, por lo tanto "coronando" la cadena.

En la presente invención usando los catalizadores de cianuro de metal doble, los polioxidos producidos exhiben una escasa polidispersidad. No se producen productos "coronados". Solamente se han visto una cantidad traza de cualquiera de otros subproductos. El uso de un catalizador de cianuro de metal doble permite al iniciador contener los grupos funcionales sensibles a la base, tales como halo, alquino, éster, etc.

5. coloque al menos un ejemplo demostrando la invención con detalle suficiente de forma que otros puedan repetirlo y describa la manera preferida de realizar la invención. En su descripción incluya, -si se aplica- datos, propiedades químicas y resultados de pruebas analíticas. Si es conveniente use fórmulas químicas. Favor incluir el rango de proporciones de ingredientes, temperatura, tiempo, presión y otras variables las cuales usted considere pueden ser usadas para realizar la invención. Además, señale que material equivalentes pueden ser útiles en la invención. Use el sistema internacional de unidades en la descripción. Si no es lo suficiente claro explique la utilidad de la invención.

4-20-99



g	265.51	~1050	
MW	84.12	44.05	6.=4560 ppm
d=	.868	d=.882	
mol	3.156	23.83	
tasa	1	7.55	

2-metil-3-butin-2-ol: Productos de aire, secado en mallas encima de 3Å
El catalizador utilizado fue un el bache D preparado en la página 7.

El catalizador fue pesado en una botella de 4 OZ de boca ancha y se peso 2-metil-3-butin-2-ol seco en una botella de 500 ml de boca angosta. La botella del catalizador fue llenada con un porción de la cantidad de t-butinol pesada y transferida a un reactor en B-4808 (Vicki Harrington). La botella del catalizador fue luego lavada varias veces con t-butinol, transferidos los enjuagues al reactor, seguido por un remanente de t-butinol. El reactor fue posteriormente sellado y manualmente se eliminó/

purgó siete veces con nitrógeno (no se permitió que la presión bajara por debajo de la atmosférica para prevenir la pérdida del iniciador). La mezcla fue agitada y calentada a 90°C. La línea EO hacia el reactor fue ventilada con nitrógeno para llenar la línea con EO. Una porción de EO (~50 g) fue agregada y la mezcla fue calentada y agitada mientras se monitoreaba la presión de el reactor para detectar cuando la reacción había iniciado. Una pequeña cantidad de presión fue observada comenzando los 40 minutos después de la adición. Una hora después de la adición inicial, ~50 g de EO adicional fue agregado y se observó la presión del reactor. La presión cayó más rápido y la tasa de alimentación se colocó en el modo automático.. Esto causó que la tasa de alimentación se fuera por encima de 10g/min. A medida que la reacción progresó se desarrolló una exotérmica vigorosa, llegando a un diferencial por encima de 30° C desde la pared a la reacción. Esto causó que el sistema se desestabilizara con amplios movimientos en la chaqueta, la temperatura causó amplios movimientos en la temperatura del reactor de <80°C a más de 106°C por períodos breves. El EO alimentó rápidamente y la reacción fue digerida rápidamente. El material fue embotellado -20°C después de haberse agitado toda la noche en el reactor y tenía un color ámbar pálido. El material era opaco, pero permaneció líquido. Se observó algún asentamiento. El análisis NMR claramente mostró que t-butinol había comenzado la polimerización [cambio de =C de 89 ppm a 85 ppm]. El análisis GPC mostró 380 Mn, PDI de 1.82.

Fraccionamiento de la corrida 3 t-butinol poliol: 5-13-99

El poliol (Corrida de t-butinol iniciado [199900896-12]~1205g) fue suspendido con 2410 g de alcohol de isopropilo en un frasco de 6l. El material fue agitado y se agregó 1205 g de hexano. La mezcla fue agitada y enfriada en un baño en hielo por algunas horas. La mezcla fue filtrada al vacío a través de un paño de media pulgada con ayuda de un filtro de aire en un embudo de vidrio de 3 l. La corriente líquida fue adicionada en un papel filtro para facilitar la transferencia sin lavar el filtro. La solución limpia fue concentrada por evaporación rotatoria que dio un color amarillo pálido. El peso de el poliol bajo Mn fue de 1078 g. El peso de la cera secada en aire fue de 109.9 g.

Preparación del catalizador:

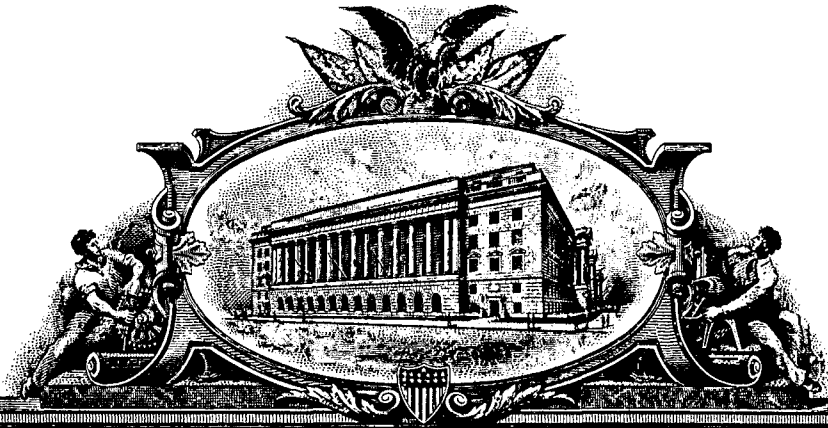
Hexacianocobaltato de potasio (8 g) disuelto en 140 ml en agua desionizada (grado HPLC) [solución 1] fue agregada en una licuadora comercial de una velocidad (modelo Waring 33BL79). La licuadora se encendió y se le agregó cloruro de zinc (25 g) disuelto en 40 ml de agua [solución 2 fue agregado rápidamente. Una mezcla de 100 ml de agua y 100 ml de t-BuOH [solución 3] fue agregada inmediatamente y la mezcla fue licuada por 10 minutos (la mezcla comenzó a calentarse). La mezcla luego fue lavada en una botella de 1 l con solución A [2g CP-450 en 200 mL de agua] y agitada por cerca de 5 minutos, permitiendo que la mezcla se enfriara de alguna manera. La mezcla fue luego filtrada al vacío a través de 2 hojas de papel Whatman #1 (no se perdió producto a través del filtro), se lavó con 20ml de DI agua. La costra húmeda, fue ablandada con solución B [2g de CP-450 en 140ml de agua y 60 ml de t-BuOH] por tres minutos en una botella centrífuga y luego centrifugada en la centrífuga Mistral 3000E por 25 minutos. El líquido sobrenadante fue decantado y la mezcla fue resuspendida en una solución C [1 g de CP-450 en 200 ml de t-BuOH] por varios minutos y luego centrifugados. El líquido sobrenadante fue decantado y el sólido fue secado por la noche

00094
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a 75°C bajo vacío (30 pulgadas). Los sólidos secos fueron luego molidos en un mortero y triturado y transferido en un disco de cristal para un posterior secado a peso constante. Obtenido 12.00 g.

COLO 00286-801-117-8
JJC-ID-1521

PA 289145

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86



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 11, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,081

FILING DATE: July 09, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

P. SWAIN

Certifying Officer

07/09/99
JCS53 U.S. PTO
00096

PROVISIONAL APPLICATION COVER SHEET

request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number	60073	Type a plus sign (+) inside this box	+
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Whitmarsh	Robert	H.	55 North Calla Lilly Ct, Lake Jackson, Texas 77566 United States of America

☐ Additional inventors are being named on separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

PROCESS FOR PREPARING POLYETHYLENE GLYCOLS FROM PRIMARY, SECONDARY, AND TERTIARY ALCOHOL
INITIATORS USING A DOUBLE METAL CYANIDE CATALYST

CORRESPONDENCE ADDRESS

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ENCLOSED APPLICATION PARTS (check all that apply)

☒ Specification Number of Pages 4 ☐ Small Entity Statement
☐ Drawing(s) Number of Sheets _____ ☐ Other (specify)

METHOD OF PAYMENT (check one)

☐ A check or money order is enclosed to cover the Provisional filing fees

☒ The Commissioner is hereby authorized to charge
filing fees and credit Deposit Account Number:

04-1512

PROVISIONAL
FILING FEE
AMOUNT

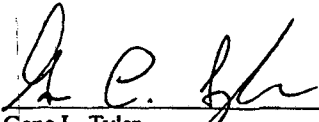
\$150.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government

☒ No

☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,


Gene L. Tyler
Registration No.: 35,395
Phone No.: 409-238-7239

EXPRESS MAIL MAILING NO.: EL026307204US
DATE OF DEPOSIT: July 9, 1999

GLT/II

PROVISIONAL APPLICATION FILING ONLY

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

00097 88

Approval of Department Head _____

Project No.: _____

Please fill out carefully. The requested information is needed for proper preparation of a patent application.

You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DO NOT WRITE IN THIS SPACE

Disclosure No. _____

Assigned to _____ Date _____

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Preparing Polyethylene glycols from Primary, Secondary and Tertiary Alcohol Initiators Using a Double Metal Cyanide Catalyst

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Signature _____

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party? YES NO

If YES, please identify the party and the contract _____

Witness:

I have read and understood this Disclosure and attachments.

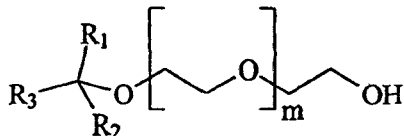
My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness _____ Signature _____ Date _____

DESCRIPTION OF THE INVENTION

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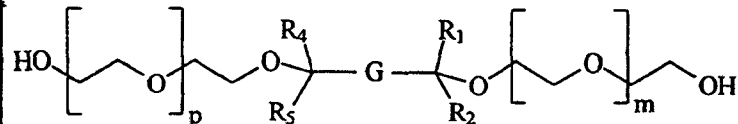
Give a summary/abstract of the invention: Double metal cyanide catalysts have been used in the past to prepare polypropylene oxides from primary, secondary and tertiary alcohol initiators. However, the conventional wisdom from the teachings and the literature was that DMC catalysts could not be used to cap polypropylene glycols with ethylene oxide. It was an accepted fact that DMC complex catalysts would not polymerize ethylene oxide onto secondary or tertiary alcohols without forming large amounts of homopolymer (polyethyleneoxide diol). For example, in US patent 4,877,906 (Harper, S.D. to Arco Chemical Technology, Inc.) *Purification of Polyols prepared using Double Metal Cyanide Complex Catalysts* (1989) line 48 column 3 states "Direct ethylene oxide end-capping of propylene oxide polyols using double metal cyanide complex catalysis is not feasible due to the high reactivity of ethylene oxide and the consequent tendency to form highly ethoxylated by-products which are inhomogeneous with the remainder of the polyol." Also, due to the same fear of producing homopolymer, there do not appear to be any instances of using DMC catalysts to form ethoxylates of primary alcohols as well. Surprisingly, we have found that double metal cyanide catalysts will very efficiently polymerize ethylene oxide onto primary, secondary and tertiary alcohol initiators without forming large amounts of polyethylene diols.



The products correspond to the formula:

$R_1, R_2, R_3 = H$, or alkyl, optionally substituted with groups such as alkyne, alkene, $m > 1$

Other base sensitive groups such as ester, acid, halogen, etc. can be substituted onto the initiator. Other possible products correspond to the formula:



where $R_1, R_2, R_4, R_5 = H$, or alkyl; $G =$ alkyl, alkenyl, aryl, alkynyl, optionally substituted with groups such as ester, halo, etc.; $m, p > 1$

The reactions are carried out by adding the catalyst to the initiator in a stirred pressure vessel, adding up to 10% of the theoretical amount of ethylene oxide and heating the mixture at temperatures of 90-100°C until a decrease in pressure is observed, indicating that the reaction has initiated. The remaining ethylene oxide is then fed in at such a rate that the temperature is controlled at 90 to 100°C. Catalyst is used at levels from 30 ppm to 10,000 ppm.

The invention relates to: (Check as many as seem applicable):

☒ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

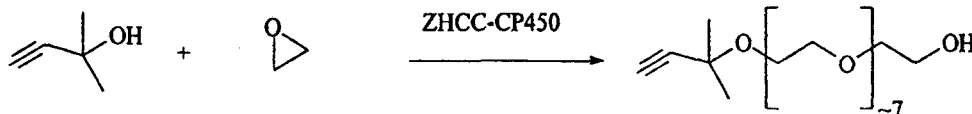
2	List any literature (including patents) of which you are aware relating to the invention. 1. Jorgenson, M.W.; Budnik, R.; Miller, G.A. to Osi Specialties, Inc. US 5,856,369 Polyethers and Polysiloxane Copolymers Manufactured with Double Metal Cyanide Catalysts. Polyols are made by polymerizing a blend of PO and EO onto allyl alcohol or a tripropoxylate of allyl alcohol using DMC catalysts, specifically Zinc Hexacyanocobaltate catalyst. The examples specify that the catalyst (a glyme complex) must be activated with PO prior to the start of the PO and EO cofeed. 2. CRI 888124 Laycock, D.E.; Gobbi, G.C.; Sheehan, R.J. Zinc Hexacyanocobaltate Catalysis: Ethylene Oxide Capping of Homo-propylene Oxide Polyether Polyols. CP 700 and CP3000 were both reacted with EO at 125°C in the presence of Zinc Hexacyanocobaltate. (DEL 891 and 893) Conclusion made that EO would not react without forming polyethyleneoxide. 3. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared]. 4. Herold, R.J.; Bingham, R.E., Brevet D'Invention No. 81 18520 General Tire and Rubber, Co., (1981) on preferred method for removal of ZHCC catalyst residues from homo-PO polyol, also recommends this procedure as a means of capping the homo-PO polyol with EO, implying that ZHCC causes EO to homopolymerize. 5. Harper, S.D. to Arco Chemical Technology, Inc., US 4,877,906 Purification of Polyols prepared using Double Metal Cyanide Complex Catalysts (1989) line 48 column 3 "Direct ethylene oxide end-capping of propylene oxide polyols using double metal cyanide complex catalysis is not feasible due to the high reactivity of ethylene oxide and the consequent tendency to form highly ethoxylated by-products which are inhomogeneous with the remainder of the polyol." 6. Numerous other Arco and General Tire patents also teach that EO cannot be polymerized onto the secondary hydroxyl groups of PO polyols with double metal cyanide complex catalysis due to the formation of large amounts of polyethylene oxide. 7. CRI 1339 Bergeron, S., Badhwar, A.; Facca, M.; Laycock, D.E.; Rudolf, P. Review and Evaluation of Competitive Technology for Synthesis and Use of DMC Catalysts and Recent Modifications by Dow. (Aug. 1998) and references contained within.
3	State the nature and extent of your literature search. Scifinder search of "alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" and "double metal cyanide" Beilstein search of ethoxylate structure of 2-methyl-3-butyn-2-ol. Derwent search of polyethylene glycol of 2-methyl-3-buten-2-ol.
4	How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. : Use of DMC catalysts to react EO onto secondary and tertiary alcohol groups has not been reported in the literature. We have also not found reference to DMC having been used as the catalyst to ethoxylate primary alcohol initiators. The polyethers prepared from tertiary alcohols using DMC have narrower polydispersities than the polyethers prepared from tertiary alcohol initiators using KOH as the catalyst. For example, even a low molecular weight polyethylene glycol (500 MW) product prepared from 2-methyl-3-buten-2-ol was a solid at room temperature. Acid catalysis of oxide polymerizations onto tertiary alcohols also produce products having broad polydispersities. In addition, under acid catalysis cyclic by-products are also a problem. Also, under acid catalysis, tertiary alcohols can form stable carbonium ions which can produce an additional type of byproduct by reacting with the hydroxy end-groups of the polyol, thus "capping" the chain. In the present invention using double metal cyanide catalysts, the polyethers produced using tertiary alcohol initiators exhibit narrow polydispersity. No "capped" products are produced. Only a trace quantity of any other by-products are seen. The molecular weight distribution is bimodal, with the major portion exhibiting the desired molecular weight target with a polydispersity typically of less than 1.6. A small amount of high molecular weight by-product is produced, also having a narrow polydispersity. Because of the narrow polydispersity, and the low level of high molecular weight fraction, the low molecular weight products remain liquid at room temperature. In the case of polyethylene glycols with DP of < 12, the minor high molecular weight component crystallizes from the mixture and can be separated using a solvent fractionation. Examples of alcohols useful as initiators include 2-methyl-3-butyn-2-ol; 2-methyl-3-buten-2-ol; t-butanol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like. The catalyst also allows the presence of functional groups sensitive to base, such as halo, alkyne, ester, etc.

DESCRIPTION OF THE INVENTION

5

Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol 4-20-99



g	265.51	~1050	6. = 4560 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	3.156	23.83	
ratio	1	7.55	

00100

2-methyl-3-butyn-2-ol : Air Products, dried over 3Å sieves
Catalyst used was Batch D prepared on p. 7

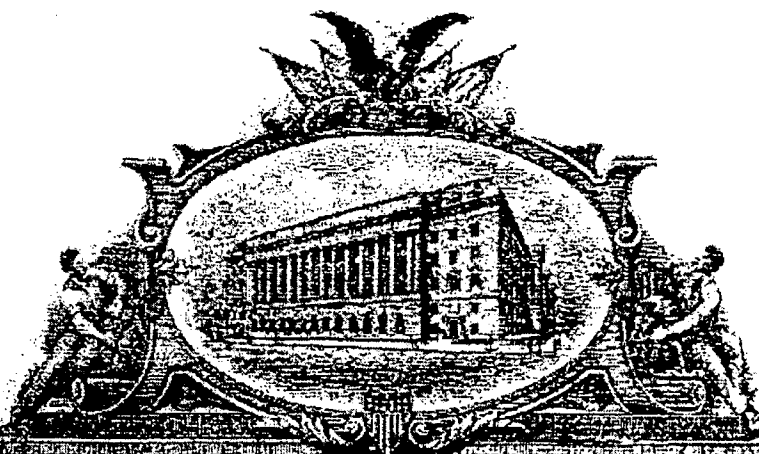
The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Vicki Harrington). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (~50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 40 minutes after addition. A hour after the initial addition, an additional ~50 g of EO was added and the reactor pressure was watched. The pressure dropped more rapidly and the feed rate was put in automatic mode. This caused the feed rate to go above 10 g/min. As the reaction progressed a vigorous exotherm developed, reaching a differential of over 30°C from wall to reaction. This caused the system to become destabilized with wide swings in the jacket temperature causing wide swings in the reactor temperature from <80°C to more than 106°C for brief periods. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~20°C after stirring overnight in the reactor and was pale amber in color. The material was opaque, but remained liquid. Some settling was observed. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 380 Mn, PDI of 1.82.

Fractionation of Run 3 t-Butynol Polyol : 5-13-99

The polyol (Run 3 of t-butynol initiated [199900896-12]~1205 g) was slurried with 2410 g of isopropyl alcohol in a 6 L flask. The material was stirred and 1205 g of hexane was added. The mixture was stirred and chilled in an ice bath for several hours. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 1078 g. The weight of the air dried wax was 109.09 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through 2 sheets of #1 Whatman paper (no product loss through filter), rinsing with about 20 mL of DI water. The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 3 minutes in a centrifuge bottle and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 25 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then centrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 12.00 g



LOS ESTADOS UNIDOS DE AMERICA

A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

Oficina de Patentes y Marcas de los Estados Unidos

11 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORGUE UNA FECHA DE PRIORIDAD BAJO 35 USC 111..

SOLICITUD NUMERO: 60/143,081

FECHA DE PRESENTACION: *julio 9 de 1999*

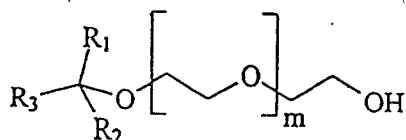


Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS

Firmado por
P. SWAIN

Funcionario Certificador

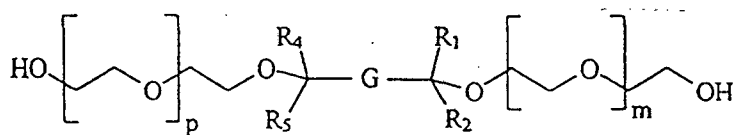
1. Dar un resumen de la invención: Los catalizadores de cianuro de metal doble han sido usados en el pasado para prepara óxidos de polipropileno de alcoholes iniciadores primarios, secundarios y terciarios. Sin embargo, el conocimiento de las enseñanzas y la literatura era que los catalizadores DMC no podían ser usados para "coronar " polipropilén glicoles con óxido de etileno. Se aceptaba como un hecho que los catalizadores complejos DMC no podían polimerizar óxidos de etileno en alcoholes secundarios y terciarios sin formar grandes cantidades de homopolímero (diol de polietilénóxido). Por ejemplo la patente estadounidense 4,877,906 (Harper, S.D. de Arco Chemical Technology, Inc.) purificación de polioles preparados usando catalizadores de complejo de cianuro de metal doble (1989) línea 48 columna 3 dice " "coronamiento" final directo en óxido de etileno de polioles de óxido de polipropileno, usando catálisis de complejos de cianuro de metal doble no es factible debido a la alta reactividad del óxido de etileno y la consecuente tendencia a formar gran cantidad de subproductos etoxilados los cuales no son homogéneos con el poliol sobrante." También debido a ese miedo de la producción de homopolímeros, estos no aparecen ser alguna instancia para el uso de catalizadores CMD para formar etoxilatos de alcoholes primarios. Sorprendentemente, nosotros encontramos que catalizadores de cianuro de metal doble podrán polimerizar óxido de etileno a alcoholes primarios, secundarios y terciarios muy eficientemente sin formar grandes cantidades de dioles de polietileno.



Los productos corresponden a la fórmula:

R1, R2, R3=H, o alquilo, opcionalmente substituido con grupos como alquino, alqueno, m>1

Otros grupos sensibles a las bases tales como éster, ácido, halógeno, etc, pueden ser substituidos a el iniciador. Otros productos posibles corresponden a la fórmula:



Donde R1, R2, R4, R5=H, o alquilo; G = alquilo, alqueno, opcionalmente substituidos con grupos como éster, halo, etc.; m, p>1

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Las reacciones son llevadas a cabo adicionando el catalizador al iniciador en un recipiente de presión agitado, adicionando hasta el 10 % de la cantidad teórica del óxido de etileno y el calentamiento de la mezcla a temperaturas de 90- 100°C hasta que una disminución en presión es observada, indicando que la reacción ha comenzado. El óxido de etileno restante es alimentado en una tasa tal que la temperatura es controlada entre 90 a 100°C. El catalizador es usado a niveles desde 30 ppm hasta 10,000 ppm.

2. Liste alguna literatura de la cual usted está seguro esté relacionada con la invención.

1. Jorgenson, M.W., Budnik, R. ; Miller, G.A. to Osi Specialties, Inc. US 5,856,369 Polyethers and Polysiloxane Copolymers manufactured with double metal cyanide catalysts. Polyols are made by polymerizing a blend of PO and EO onto allyl alcohol or a tripropoxilate of allyl alcohol using DMC catalysts, specifically Zinc Hexacyanocobaltate catalyst. The examples specify that the catalyst (a glyme complex) must be activated with PO prior to the start of the PO and EO cofeed.
2. CRI 888124 Laycock, D.E.; Gobbi, G.C.; Sheehan, R.J. Zinc Hexacyanocobaltate catalysis: Ethylene oxide capping of homo-propylene. Oxide polyether polyols. CP 700 and CP3000 were both reacted with EO at 125°C in the presence of zinc Hexacyanocobaltate (DEL 891 and 893) conclusion made that EO would not react without forming polyethyleneoxide.
3. Petrow; Lagutschewa; ZOKHA4; Zh.Obshch Khim.; 21; 1951 1247, 1248, 1251; engl. Ausg. S.1361, 1362, 1364 Ethoxilation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alquinoxil occurring. Both mono- and diethoxylated products are prepared].
4. Herold, R. J. , Bingham , R. E., Brevet D'Invention No. 81 18520 General Tire and Rubber, Co., (1981) on preferred method for removal of zhcc catalyst residues from homo-PO polyol, also recommends this procedure as a means of capping the homo-PO polyol with EO, implying that ZHCC causes EO to homopolymerize.
5. Harper, S.D. to Arco Chemical Technology, Inc., US 4, 877,906 purification of polyols prepared using double Metal Cyanide Complex Catalysts (1989) line 48 column 3 "Direct ethylene oxide end-capping of propylene oxide polyols using double metal cyanide complex catalysis is not feasible due to the high reactivity of ethylene oxide and the consequent tendency to form highly ethoxylated by-products which are inhomogenous with the remainder of the polyol."
6. Numerous other Arco and General Tire patents also teach that EO cannot be polymerized onto the secondary hydroxyl groups of PO polyols with double metal cyanide complex catalysis due to the formation of large amounts of polyethylene oxide.
7. CRI 1339 Bergeron, S. Badhwar, A.; Facca, M.; Laycock, D.E.; Rudolf, P. Review and evaluation of competitive technology for

synthesis and use of DMC catalysts and recent modifications, by Dow (Aug.1998) and references contained within.

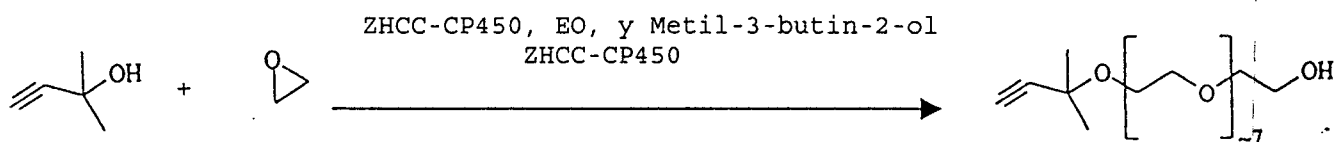
3. Estado de la naturaleza y extensión de la búsqueda de la literatura. Búsqueda Scifinder de "Polioles funcionalizados en alquino o acetileno conteniendo polietilen glicoles o propilenglicoles" y "cianuro de metal doble" Búsqueda Beilstein de la estructura del etoxilato de 2-metil-3-butin-2-ol. Búsqueda Derwent de polietilen glicol de 2-metil-3-buten-2-ol.

4. En que manera esta invención difiere de, y liste las ventajas sobre, la literatura conocida por usted como también de las alternativas, si las hay actualmente empleadas: El uso de catalizadores de CMD para reaccionar con EO en alcoholes de grupo secundario y terciario no han sido reportados en la literatura. Nosotros no hemos encontrado referencia donde el CMD haya sido usado como catalizador del iniciador de alcoholes primarios de etoxilato. Los poliéteres preparados de alcoholes terciarios usando CMD tienen escasas polidispersiones que los poliéteres preparados de iniciadores de alcoholes terciarios usando KOH como catalizador. Por ejemplo, aun el producto de polyetilen glicol de bajo peso molecular (MW) preparado de 2-metil-3-buten-2-ol fue sólido a temperatura ambiente. Catálisis ácida de polimerizaciones de óxido en alcoholes terciarios también produce productos que tienen amplias polidispersiones. Además, la presencia de subproductos de catálisis ácida cíclica son un problema. También, bajo catálisis ácida, los alcoholes terciarios pueden formar iones carbonio estables pueden producir un tipo adicional de subproducto reaccionando con los grupos que terminan en hidroxilo del poliol, por lo tanto "coronando" la cadena. En la presente invención usando los catalizadores de cianuro de metal doble, los polióxidos producidos exhiben una escasa polidispersidad. No se producen productos "coronados". Solamente se han visto una cantidad traza de cualquiera de otros subproductos. La distribución del peso molecular es bimodal, con la mayor porción exhibiendo el peso molecular deseado como blanco con una polidispersión típicamente menor a 1.6. Una pequeña cantidad de subproducto de alto peso molecular es producido, también teniendo una escasa polidispersión. Debido a la escasa polidispersión, y el bajo nivel de fracción en peso de alto peso molecular, los productos de bajo peso molecular permanecen líquidos a temperatura ambiente. En el caso de los polietilen glicoles con DP de <12, el componente menor de alto peso molecular se cristaliza de la mezcla y puede ser separado usando un solvente para el fraccionamiento. Ejemplos de alcoholes útiles como iniciadores incluyen el 2-metil-3-butin-2-ol, 2-metil-3-buten-2-ol; t-butanol; 2,5-dimetil-3hexyn-2,5-diol, 2,4,7,9 tetrametil-5-decino-4,7 diol y sus similares. El catalizador también permite la presencia de grupos funcionales sensibles a base tales como halo, alquino, éster, etc.

5. Coloque al menos un ejemplo demostrando la invención con detalle suficiente de forma que otros puedan repetirlo y describa la manera preferida de realizar la invención. En su descripción incluya, -si se aplica- datos, propiedades químicas y resultados de pruebas analíticas. Si es conveniente use fórmulas químicas. Favor incluir el rango de proporciones de ingredientes, temperatura, tiempo, presión y otras variables las cuales usted considere pueden ser usadas para realizar la

invención. Además, señale que material equivalentes pueden ser útiles en la invención. Use el sistema internacional de unidades en la descripción. Si no es lo suficiente claro explique la utilidad de la invención.

4-20-99



g	265.51	~1050	6.=4560 ppm
MW	84.12	44.05	
d=	.868	d=.882	
mol	3.156	23.83	
tasa	1	7.55	

2-metil-3-butin-2-ol: Productos de aire, secado en mallas encima de 3Å
El catalizador utilizado fue un el bache D preparado en la página 7.

El catalizador fue pesado en una botella de 4 OZ de boca ancha y se peso 2-metil-3-butin-2-ol seco en una botella de 500 ml de boca angosta. La botella del catalizador fue llenada con un porción de la cantidad de t-butinol pesada y transferida a un reactor en B-4808 (Vicki Harrington). La botella del catalizador fue luego lavada varias veces con t-butinol, transferidos los enjuagues al reactor, seguido por un remanente de t-butinol. El reactor fue posteriormente sellado y manualmente se eliminó/purgó siete veces con nitrógeno (no se permitió que la presión bajara por debajo de la atmosférica para prevenir la pérdida del iniciador). La mezcla fue agitada y calentada a 90°C. La línea EO hacia el reactor fue ventilada con nitrógeno para llenar la línea con EO. Una porción de EO (~50 g) fue agregada y la mezcla fue calentada y agitada mientras se monitoreaba la presión de el reactor para detectar cuando la reacción había iniciado. Una pequeña cantidad de presión fue observada comenzando los 40 minutos después de la adición. Una hora después de la adición inicial, ~50 g de EO adicional fue agregado y se observó la presión del reactor. La presión cayo más rápido y la tasa de alimentación se colocó en el modo automático.. Esto causó que la tasa de alimentación se fuera por encima de 10g/min. A medida que la reacción progresó se desarrolló una exotérmica vigorosa, llegando a un diferencial por encima de 30° C desde la pared a la reacción. Esto causó que el sistema se desestabilizara con amplios movimientos en la chaqueta, la temperatura causó amplios movimientos en la temperatura del reactor de <80°C a más de 106°C por períodos breves. El EO alimentó rápidamente y la reacción fue digerida rápidamente. El material fue embotellado ~20°C después de haberse agitado toda la noche en el reactor y tenía un color ámbar pálido. El material era opaco, pero permaneció líquido. Se observó algún asentamiento. El análisis NMR claramente mostró que t-butinol había comenzado la polimerización [cambio de =C de 89 ppm a 85 ppm]. El análisis GPC mostró 380 Mn, PDI de 1.82.

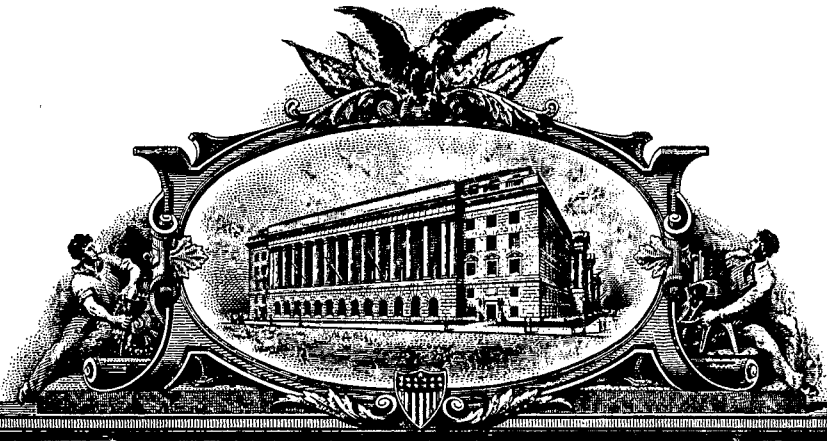
Fraccionamiento de la corrida 3 t-butinol poliol: 5-13-99

El poliol (Corrida de t-butinol iniciado [199900896-12]-1205g) fue suspendido con 2410 g de alcohol de isopropilo en un frasco de 6l. El material fue agitado y se agregó 1205 g de hexano. La mezcla fue agitada y enfriada en un baño en hielo por algunas horas. La mezcla fue filtrada al vacío a través de un paño de media pulgada con ayuda de un filtro de aire en un embudo de vidrio de 3 l. La corriente líquida fue adicionada en un papel filtro para facilitar la transferencia sin lavar el filtro. La solución limpia fue concentrada por evaporación rotatoria que dio un color amarillo pálido. El peso de el poliol bajo Mn fue de 1078 g. El peso de la cera secada en aire fue de 109.9 g.

Preparación del catalizador:

Hexacianocobaltato de potasio (8 g) disuelto en 140 ml en agua desionizada (grado HPLC) [solución 1] fue agregada en una licuadora comercial de una velocidad (modelo Waring 33BL79). La licuadora se encendió y se le agregó cloruro de zinc (25 g) disuelto en 40 ml de agua [solución 2 fue agregado rápidamente. Una mezcla de 100 ml de agua y 100 ml de t-BuOH [solución 3] fue agregada inmediatamente y la mezcla fue licuada por 10 minutos (la mezcla comenzó a calentarse). La mezcla luego fue lavada en una botella de 1 l con solución A [2g CP-450 en 200 mL de agua] y agitada por cerca de 5 minutos, permitiendo que la mezcla se enfriara de alguna manera. La mezcla fue luego filtrada al vacío a través de 2 hojas de papel Whatman #1 (no se perdió producto a través del filtro), se lavó con 20ml de DI agua. La costra húmeda, fue ablandada con solución B [2g de CP-450 en 140ml de agua y 60 ml de t-BuOH] por tres minutos en una botella centrífuga y luego centrifugada en la centrífuga Mistral 3000E por 25 minutos. El líquido sobrenadante fue decantado y la mezcla fue resuspendida en una solución C [1 g de CP-450 en 200 ml de t-BuOH] por varios minutos y luego centrifugados. El líquido sobrenadante fue decantado y el sólido fue secado por la noche a 75°C bajo vacío (30 pulgadas). Los sólidos secos fueron luego molidos en un mortero y triturado y transferido en un disco de cristal para un posterior secado a peso constante. Obtenido 12.00 g.

COLO 00286-801-117-8
JJC-ID-1526



0.8

THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 14, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: 60/143,082

FILING DATE: July 09, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

H. L. Jackson

H. L. JACKSON

Certifying Officer

1553 U.S. PTO
07/09/00

Approval for use through OMB 0651-00XX
Patent and Trademark Office, U S DEPARTMENT OF COMMERCE

PROVISIONAL APPLICATION COVER SHEET

00108

PTO XXXX

99

request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number		60070	Type a plus sign (+) inside this box	+
INVENTOR(s)/APPLICANT(s)				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
Clement	Katherine	S.	115 Poinciana, Lake Jackson, Texas 77566 United States of America	
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Wehmeyer	Richard	M.	205 Zinnia, Lake Jackson, Texas 77566 United States of America	
Whitmarsh	Robert	H.	55 North Calla Lilly Ct, Lake Jackson, Texas 77566 United States of America	
☐ Additional inventors are being named on separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
PROCESS FOR PREPARING NARROW POLYDISPERSITY POLYOXIDES FROM TERTIARY INITIATORS				
CORRESPONDENCE ADDRESS				
Gene L. Tyler THE DOW CHEMICAL COMPANY Patent Department 2301 Brazosport Blvd. B-1211 Freeport, Texas 77541 U.S.A.			Telephone: 409-238-7239 Fax: 409-238-0878	
ENCLOSED APPLICATION PARTS (check all that apply)				
☒ Specification		Number of Pages 4		☐ Small Entity Statement
☐ Drawing(s)		Number of Sheets _____		☐ Other (specify)
METHOD OF PAYMENT (check one)				
☐ A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT	\$150.00
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 04-1512				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government				
☒ No				
☐ Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,

Gene L. Tyler
Registration No.: 35,395
Phone No.: 409-238-7239

GLT/II

EXPRESS MAIL MAILING NO.: EL026307204US
DATE OF DEPOSIT: July 9, 1999

PROVISIONAL APPLICATION FILING ONLY

100
00109

DISCLOSURE OF INVENTION TO PATENT DEPARTMENT
THE DOW CHEMICAL COMPANY

Approval of Department Head

Object No.:

Please fill out carefully. The requested information is needed for proper preparation of a patent application.

You are requested to use only the space provided to describe your invention and to attach additional pages only if necessary.

However, please attach any report which might prove beneficial in describing or understanding your invention. Call your Patent Department if you have a question.

DO NOT WRITE IN THIS SPACE	
Disclosure No.	60070
Assigned to	Date

DOW
CONFIDENTIAL

TITLE OF INVENTION OR DISCOVERY: Process for Preparing Narrow Polydispersity Polyoxides from tertiary initiators

Persons submitting this Disclosure of Invention:

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Signature

Was this invention made or completed in the course of work under a contract with any governmental agency or other outside party?

YES x NO

If YES, please identify the party and the contract

Witness:

I have read and understood this Disclosure and attachments.

My initials and date are included on all pages attached to this disclosure.

Type or print name of Witness

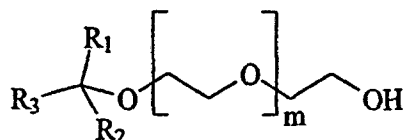
Signature

Date

DESCRIPTION OF THE INVENTION

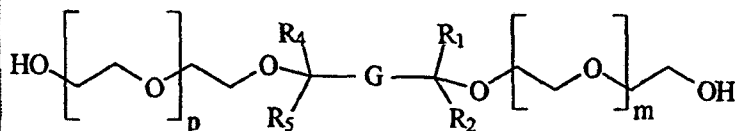
1

Give a summary/abstract of the Invention: Polyoxides prepared from tertiary alcohol initiators using KOH or NaOH as the catalyst typically exhibit broad polydispersities. For example, using standard base catalysis even a low target molecular weight polyethylene glycol (500 MW) product prepared from 2-methyl-3-buten-2-ol is a solid at room temperature. Product produced from primary alcohols with a target molecular weight of 500 using standard base catalysis are liquids at room temperature. In the present invention using double metal cyanide catalysts, the polyoxides produced using tertiary alcohol initiators exhibit narrow polydispersity. The molecular weight distribution is bimodal, with the major portion exhibiting the desired molecular weight target with a polydispersity of less than 1.5. A small amount of high molecular weight by-product is produced, also having a narrow polydispersity. Because of the narrow polydispersity, the low molecular weight products remain liquid at room temperature. In the case of polyethylene glycols, the minor high molecular weight component crystallizes from the mixture and can be separated using a solvent fractionation. Examples of alcohols useful as initiators include 2-methyl-3-buten-2-ol; 2-methyl-3-buten-2-ol; t-butanol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like.



The products correspond to the formula:

$R_1, R_2, R_3 = H$, or alkyl, optionally substituted with groups such as ester, halo, etc.; $m > 1$ and the formula:



where $R_1, R_2, R_4, R_5 = H$, or alkyl; $G =$ alkyl, alkenyl, aryl, alkynyl, optionally substituted with groups such as ester, halo, etc.; $m, p > 1$

The reactions are carried out by adding the catalyst to the initiator in a stirred pressure vessel, adding up to 10% of the theoretical amount of oxide and heating the mixture at temperatures of 90-100°C until a decrease in pressure is observed, indicating that the reaction has initiated. The remaining oxide is then fed in at such a rate that the temperature is controlled at 90 to 100°C. Catalyst is used at levels from 30 ppm to 10,000 ppm.

The invention relates to: (Check as many as seem applicable):

☐ A composition of matter (compounds, alloy, plastic, mixture, etc.)

☒ A process (production, fabrication, use, treatment, etc.)

☐ A machine or article (tool, apparatus, package or other "thing")

2

List any literature (including patents) of which you are aware relating to the invention. 1. Croxall, W. J.; Dawson, N.D. US 3,021,341 (1962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-buten-2-ol using ethylene oxide with $BF_3 \cdot Et_2O$ as the catalyst. The mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization.

2. Petrow; Lagutschewa; ZOKHA4; Zh. Obshch. Khim.; 21; 1951; 1247, 1248, 1251; engl. Ausg.S. 1361, 1362, 1364 Ethoxylation of 2-methyl-3-buten-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alkynol occurring. Both mono- and diethoxylated products are prepared].

3.

3

State the nature and extent of your literature search. Scifinder search of "alkyne functionalized polyols or acetylene containing polyethylene glycols or polypropylene glycols" Beilstein search of ethoxylate structure of 2-methyl-3-buten-2-ol. Derwent search of polyethylene glycol of 2-methyl-3-buten-2-ol.

4

How does this invention differ from, and list its advantages over, the literature known to you as well as the alternatives, if any, currently being employed. : Polyethers prepared from tertiary alcohol initiators using KOH as the catalyst typically exhibit broad polydispersities. Polydispersity can be an important variable in a number of end-uses. In the specific case of ethoxylates with a targeted degree of polymerization of 6 to 12 EO units, products made using KOH have a broad polydispersity resulting in a solid product at room temperature. Acid catalysis of oxide polymerizations onto tertiary alcohols also produce products having broad polydispersities. In addition, under acid catalysis cyclic by-products are also a problem. Also, under acid catalysis, tertiary alcohols can form stable carbonium ions which can produce an additional type of by-product by reacting with the hydroxy end-groups of the polyol, thus "capping" the chain.

In the present invention using double metal cyanide catalysts, the polyethers produced using tertiary alcohol initiators exhibit narrow polydispersity. No "capped" products are produced. Only trace quantities of any other by-products are seen. The molecular weight distribution is bimodal, with the major portion exhibiting the desired molecular weight target with a polydispersity typically of less than 1.6. A small amount of high molecular weight by-product is produced, also having a narrow polydispersity. Again, in the specific case of ethoxylates with a targeted degree of polymerization of 6 to 12 EO units, the minor high molecular weight component crystallizes from the mixture and can be separated using a solvent fractionation.

Examples of alcohols useful as initiators include 2-methyl-3-butyn-2-ol; 2-methyl-3-buten-2-ol; t-butanol; 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and the like. The catalyst also allows the presence of functional groups sensitive to base, such as halo, alkyne, ester, etc.

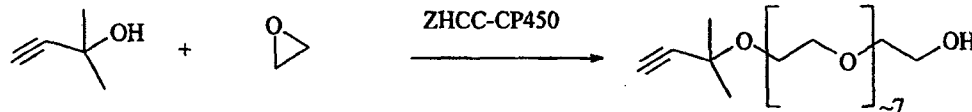
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DESCRIPTION OF THE INVENTION

5

Set forth at least one working example demonstrating the invention in sufficient detail that others could repeat it and describe the preferred manner of practicing the invention. In your description, include--if applicable--performance data, chemical properties and analytical test results. If appropriate, use chemical formulas. Please include the range of proportions of the ingredients, temperature, time, pressure and other variables which you consider can be used in practicing the invention. In addition, state what equivalent materials might be useful in the invention. Use SI (metric) units in the description. If not otherwise apparent, state the invention's utility.

ZHCC-CP450, EO, and 2-Methyl-3-butyn-2-ol 4-20-99



00112

g	265.51	~1050	6. = 4560 ppm
MW	84.12	44.05	
	d=.868	d=.882	
mol	3.156	23.83	
ratio	1	7.55	

2-methyl-3-butyn-2-ol : Air Products, dried over 3Å sieves
Catalyst used was Batch D prepared on p. 7

The catalyst was weighed into a 4 oz wide mouth bottle and dry 2-methyl-3-butyn-2-ol was weighed into a 500 mL narrow mouth bottle. The catalyst bottle was filled with a portion of the weighed amount of t-butynol and transferred into a reactor at B-4808 (Vicki Harrington). The catalyst bottle was then rinsed several times with t-butynol, transferring the washes into the reactor, followed by the remainder of the t-butynol. The reactor was then sealed and manually degassed/purged seven times with nitrogen (pressure not allowed to drop below atmospheric to prevent loss of initiator). The mixture was stirred and heated to 90°C. The EO line to the reactor was vented of nitrogen to fill the line with EO. A portion of EO (~50 g) was added and the mixture was heated and stirred while monitoring the pressure of the reactor to detect when the reaction had initiated. A small pressure drop was observed starting about 40 minutes after addition. A hour after the initial addition, an additional ~50 g of EO was added and the reactor pressure was watched. The pressure dropped more rapidly and the feed rate was put in automatic mode. This caused the feed rate to go above 10 g/min. As the reaction progressed a vigorous exotherm developed, reaching a differential of over 30°C from wall to reaction. This caused the system to become destabilized with wide swings in the jacket temperature causing wide swings in the reactor temperature from <80°C to more than 106°C for brief periods. The EO fed out rapidly and the reaction was digested quickly. The material was bottled out at ~20°C after stirring overnight in the reactor and was pale amber in color. The material was opaque, but remained liquid. Some settling was observed. NMR analysis clearly showed that the t-butynol had initiated the polymerization [shift of =C from 89 ppm to 85 ppm]. GPC analysis showed 380 Mn, PDI of 1.82.

Fractionation of Run 3 t-Butynol Polyol : 5-13-99

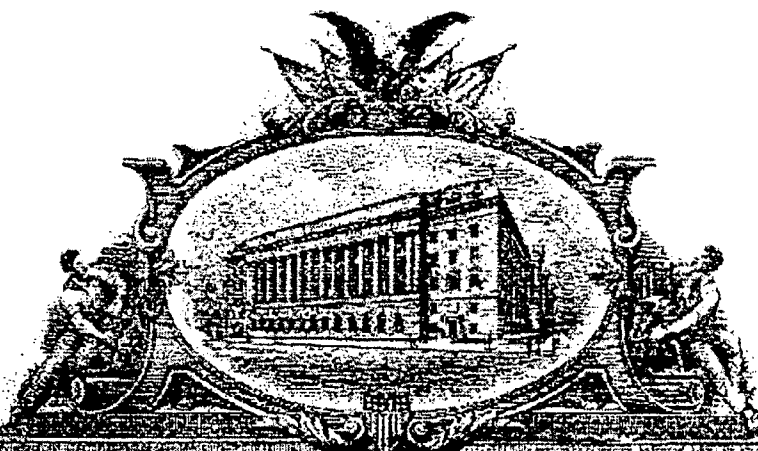
The polyol (Run 3 of t-butynol initiated [199900896-12]~1205 g) was slurried with 2410 g of isopropyl alcohol in a 6 L flask. The material was stirred and 1205 g of hexane was added. The mixture was stirred and chilled in an ice bath for several hours. The mixture was then vacuum filtered through a half inch pad of filter aid in a 3 L fritted glass funnel (coarse) The liquid stream was poured onto a paper filter to facilitate transfer without washing out the filter aid. The clear solution was concentrated by rotary evaporation to give a pale yellow liquid. The weight of the recovered low Mn polyol was 1078 g. The weight of the air dried wax was 109.09 g.

Catalyst preparation:

Potassium hexacyanocobaltate (8 g) dissolved in 140 mL of deionized water (HPLC grade) [Solution 1] was added to a commercial one speed blender (Waring model 33BL79). The blender was turned on and zinc chloride (25 g) dissolved in 40 mL of water [Solution 2] was added rapidly. A mixture of 100 mL of water and 100 mL of t-BuOH [Solution 3] was added immediately and the mixture was blended for 10 minutes (mixture became warm). The mixture was then rinsed into a 1 liter flask with Solution A [2 g CP-450 in 200 mL of water] and stirred for about 5 minutes, allowing the mixture to cool somewhat. The mixture was then vacuum filtered through 2 sheets of #1 Whatman paper (no product loss through filter), rinsing with about 20 mL of DI water. The wet cake was reblended with Solution B [2 g of CP-450 in 140 mL of water and 60 mL of t-BuOH] for 3 minutes in a centrifuge bottle and then centrifuged at 3000 rpm in the Mistral 3000E centrifuge for 25 minutes. The supernatant liquid was decanted and the mixture was reslurried in Solution C [1 g of CP-450 in 200 mL of t-BuOH] for several minutes and then centrifuged. The supernatant liquid was decanted and the solid was dried overnight at 75°C under vacuum (30 in.). The dried solids were ground in a mortar and pestle and transferred to a crystallizing dish for further drying to constant weight. Yield 12.00 g

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LOS ESTADOS UNIDOS DE AMERICA

**A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS**

Oficina de Patentes y Marcas de los Estados Unidos

14 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORGUE UNA FECHA DE PRIORIDAD BAJO 35 USC 111..

SOLICITUD NUMERO: 60/143,082

FECHA DE PRESENTACION: 9 de julio de 1999



Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS

Firmado por

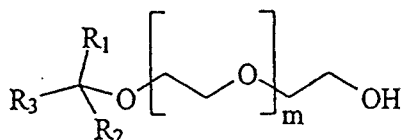
H.L. JACKSON

Funcionario Certificador

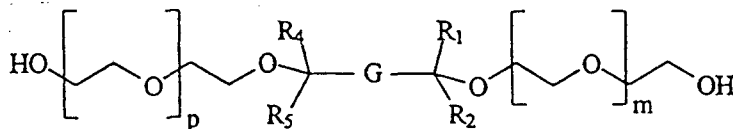
DESCRIPCIÓN DE LA INVENCIÓN

1. Dar un resumen de la invención: polióxidos preparados de iniciadores de alcoholes terciarios usando KOH o NaOH como catalizador típicamente exhibe amplias polidispersiones. Por ejemplo, usando una catálisis base estándar el producto polietilen glicol de bajos blanco de peso molecular preparado del 2-metil-3-buten-2-ol, es un sólido a temperatura ambiente. El producto producido de alcoholes primarios con un blanco de peso molecular de 500 empleando una catálisis de base estándar son líquidos a temperatura ambiente. En la presente invención usando catalizadores de cianuro de metal doble, los polióxidos producidos usando iniciadores de alcohol terciarios exhiben escasa polidispersidad. La distribución del peso molecular es bimodal, con la mayor porción exhibiendo el blanco del peso molecular deseado con una polidispersión de menos de 1.5. Una pequeña cantidad de subproductos de alto peso molecular es producido, también teniendo una escasa polidispersión. Debido a la escasa polidispersión, los productos de bajo peso molecular permanecen líquidos a temperatura ambiente. En el caso de polietilen glicoles, el componente menor de alto peso molecular se cristaliza de la mezcla y puede ser separado usando un solvente para el fraccionamiento. Ejemplos de alcoholes útiles como iniciadores incluyen el 2-metil-3-buten-2-ol, 2-metil-3-buten-2-ol; t-butanol; 2,5-dimetil-3-hexyn-2,5-diol, 2,4,7,9-tetrametil-5-decino-4,7 diol y sus similares.

Los productos corresponden a la fórmula



$R_1, R_2, R_3 = H$, o alquilo, opcionalmente substituido con grupos tales como éster, halo, etc.; $m > 1$ y la fórmula:



Donde $R_1, R_2, R_4, R_5 = H$, o alquilo; $G =$ alquilo, alqueno, opcionalmente substituidos con grupos como éster, halo, etc.; $m, p > 1$

Las reacciones son llevadas a cabo adicionando el catalizador al iniciador en un recipiente de presión agitado, adicionando hasta el 10 % de la cantidad teórica del óxido de etileno y el calentamiento de la mezcla a temperaturas de 90 a 100°C hasta que una disminución en

presión es observada, indicando que la reacción ha comenzado. El óxido de etileno restante es alimentado en una tasa tal que la temperatura es controlada entre 90 a 100°C. El catalizador es usado a niveles desde 30 ppm hasta 10,000 ppm.

La invención está relacionada a

Un proceso (producción, fabricación, uso, tratamiento, etc)

2. Liste alguna literatura de la cual usted está seguro esté relacionada con la invención.

1.. Croxall, W.J.; Dawson, N. D.US 3,021341 81962) [Miles Laboratories] describes the ethoxylation of 2-methyl-3-butyn-2-ol using ethylene oxide with BF_3Et_2 as the catalyst. The Mono-ethoxylated compound was isolated by distillation for conversion to methylenedioxane by cyclization.

2. Petrow; Lagutschewa; ZOKHA4; Zh.Obshch Khim.; 21;1951 1247,1248, 1251; engl. Ausg. S.1361,1362,1364 Ethoxilation of 2-methyl-3-butyn-2-ol with ethylene oxide using N,N-dimethylaniline at 150°C. [Under these conditions there was almost certainly some degradation of the alquino occurring. Both mono- and diethoxylated products are prepared].

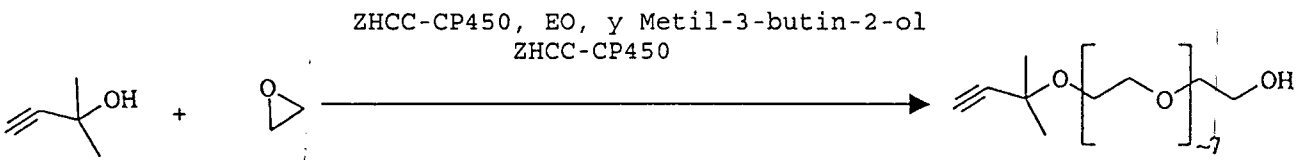
3. Estado de la naturaleza y extensión de la búsqueda de la literatura. Búsqueda Scifinder de "Polioles funcionalizados en alquino o acetileno conteniendo polietilen glicoles o propilenglicoles" Búsqueda Beilstein de la estructura del etoxilato de 2-metil-3-butyn-2-ol. Búsqueda Derwent de polietilen glicol de 2-metil-3-buten-2-ol.

4. En que manera esta invención difiere de, y liste las ventajas sobre, la literatura conocida por usted como también de las alternativas, si las hay actualmente empleadas: poliéteres preparados de iniciadores de alcohol terciario usando KOH como catalizador típicamente exhibe amplias polidispersiones. La polidispersión puede ser una variable importante en número y en usos finales. En el caso específico de los etoxilatos con un grado deseado de polimerización de 6 a 12 EO unidades, los productos hechos usando KOH tienen una amplia polidispersión resultando en un producto sólido a temperatura ambiente. Las catálisis ácidas de polimerizaciones de óxido en alcoholes terciarios también producen productos teniendo amplias polidispersiones. Además, bajo catálisis ácida subproductos cíclicos son también un problema. También bajo catálisis ácida, los alcoholes terciarios pueden formar iones carbonium los cuales pueden producir un tipo adicional de subproducto reaccionando con los grupos finalizados en hidroxilo de el poliol, por lo tanto "coronando" la cadena. En la presente invención usando los catalizadores de cianuro de metal doble, los polióxidos producidos exhiben una escasa polidispersidad. No se producen productos "coronados". Solamente se han visto una cantidad traza de cualquiera de otros subproductos. La distribución del peso molecular es bimodal, con la mayor porción exhibiendo el peso molecular

deseado como blanco con una polidispersión típicamente menor a 1.6. Una pequeña cantidad de subproducto de alto peso molecular es producido, también teniendo una escasa polidispersión. Debido a la escasa polidispersión, y el bajo nivel de fracción en peso de alto peso molecular, los productos de bajo peso molecular permanecen líquidos a temperatura ambiente. En el caso de los polietilen glicoles con DP de <12, el componente menor de alto peso molecular se cristaliza de la mezcla y puede ser separado usando un solvente para el fraccionamiento. Ejemplos de alcoholes útiles como iniciadores incluyen el 2-metil-3-butin-2-ol, 2-metil-3-buten-2-ol; t-butanol; 2,5-dimetil-3hexyn-2,5-diol, 2,4,7,9 tetrametil-5-decino-4,7 diol y sus similares. El catalizador también permite la presencia de grupos funcionales sensibles a base tales como halo, alquino, éster, etc.

5.coloque al menos un ejemplo demostrando la invención con detalle suficiente de forma que otros puedan repetirlo y describa la manera preferida de realizar la invención. En su descripción incluya , -si se aplica- datos, propiedades químicas y resultados de pruebas analíticas. Si es conveniente use fórmulas químicas. Favor incluir el rango de proporciones de ingredientes, temperatura, tiempo, presión y otras variables las cuales usted considere pueden ser usadas para realizar la invención. Además, señale que material equivalentes pueden ser útiles en la invención. Use el sistema internacional de unidades en la descripción. Si no es lo suficiente claro explique la utilidad de la invención.

4-20-99



g 265.51	~1050	6.=4560 ppm
MW 84.12	44.05	
d=.868	d=.882	
mol 3.156	23.83	
tasa 1	7.55	

2-metil-3-butin-2-ol: Productos de aire, secado en mallas encima de 3Å
El catalizador utilizado fue un el bache D preparado en la página 7.

El catalizador fue pesado en una botella de 4 oz de boca ancha y se peso 2-metil-3-butin-2-ol seco en una botella de 500 ml de boca angosta. La botella del catalizador fue llenada con un porción de la cantidad de t-butinol pesada y transferida a un reactor en B-4808 (Vicki Harrington). La botella del catalizador fue luego lavada varias veces con t-butinol, transferidos los enjuagues al reactor, seguido por un remanente de t-butinol. El reactor fue posteriormente sellado y manualmente se eliminó/ purgó siete veces con nitrógeno (no se permitió que la presión bajara por debajo de la atmosférica para prevenir la pérdida del iniciador). La

mezcla fue agitada y calentada a 90°C. La línea EO hacia el reactor fue ventilada con nitrógeno para llenar la línea con EO. Una porción de EO (~50 g) fue agregada y la mezcla fue calentada y agitada mientras se monitoreaba la presión de el reactor para detectar cuando la reacción había iniciado. Una pequeña cantidad de presión fue observada comenzando los 40 minutos después de la adición. Una hora después de la adición inicial, ~50 g de EO adicional fue agregado y se observó la presión del reactor. La presión cayo más rápido y la tasa de alimentación se colocó en el modo automático.. Esto causó que la tasa de alimentación se fuera por encima de 10g/min. A medida que la reacción progresó se desarrolló una exotérmica vigorosa, llegando a un diferencial por encima de 30° C desde la pared a la reacción. Esto causó que el sistema se desestabilizara con amplios movimientos en la chaqueta, la temperatura causó amplios movimientos en la temperatura del reactor de <80°C a más de 106°C por períodos breves. El EO alimentó rápidamente y la reacción fue digerida rápidamente. El material fue embotellado ~20°C después de haberse agitado toda la noche en el reactor y tenía un color ámbar pálido. El material era opaco, pero permaneció líquido. Se observó algún asentamiento. El análisis NMR claramente mostró que t-butinol había comenzado la polimerización [cambio de δ C de 89 ppm a 85 ppm]. El análisis GPC mostró 380 Mn, PDI de 1.82.

Fraccionamiento de la corrida 3 t-butinol poliol: 5-13-99

El poliol (Corrida de t-butinol iniciado [199900896-12]-1205g) fue suspendido con 2410 g de alcohol de isopropilo en un frasco de 6l. El material fue agitado y se agregó 1205 g de hexano. La mezcla fue agitada y enfriada en un baño en hielo por algunas horas. La mezcla fue filtrada al vacío a través de un paño de media pulgada con ayuda de un filtro de aire en un embudo de vidrio de 3 l. La corriente líquida fue adicionada en un papel filtro para facilitar la transferencia sin lavar el filtro. La solución limpia fue concentrada por evaporación rotatoria que dio un color amarillo pálido. El peso de el poliol bajo Mn fue de 1078 g. El peso de la cera secada en aire fue de 109.9 g.

Preparación del catalizador:

Hexacianocobaltato de potasio (8 g) disuelto en 140 ml en agua desionizada (grado HPLC) [solución 1] fue agregada en una licuadora comercial de una velocidad (modelo Waring 33BL79). La licuadora se encendió y se le agregó cloruro de zinc (25 g) disuelto en 40 ml de agua [solución 2 fue agregado rápidamente. Una mezcla de 100 ml de agua y 100 ml de t-BuOH [solución 3] fue agregada inmediatamente y la mezcla fue licuada por 10 minutos (la mezcla comenzó a calentarse). La mezcla luego fue lavada en una botella de 1 l con solución A [2g CP-450 en 200 mL de agua] y agitada por cerca de 5 minutos, permitiendo que la mezcla se enfriara de alguna manera. La mezcla fue luego filtrada al vacío a través de 2 hojas de papel Whatman #1 (no se perdió producto a través del filtro), se lavó con 20ml de DI agua. La costra húmeda, fue ablandada con solución B [2g de CP-450 en 140ml de agua y 60 ml de t-BuOH] por tres minutos en una botella centrífuga y luego centrifugada en la centrífuga Mistral 3000E por 25 minutos. El líquido sobrenadante fue decantado y la mezcla fue resuspendida en una solución C [1 g de CP-450 en 200 ml de t-BuOH] por varios minutos y luego centrifugados. El líquido sobrenadante fue decantado y el sólido fue secado por la noche a 75°C bajo vacío (30 pulgadas). Los sólidos secos fueron luego molidos

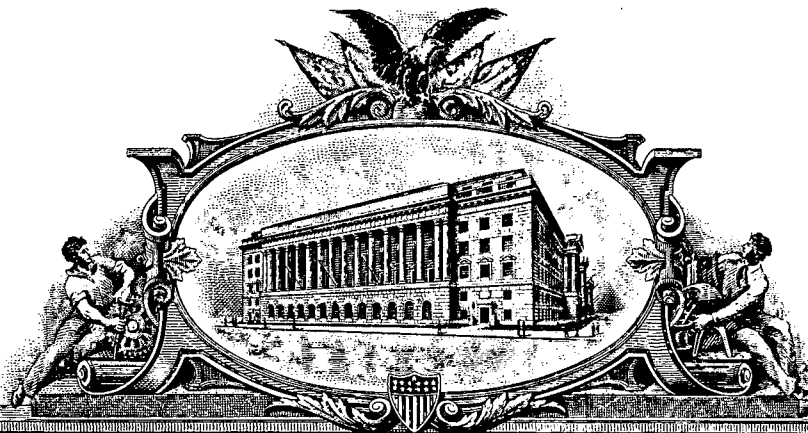
103
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en un mortero y triturado y transferido en un disco de cristal para un
posterior secado a peso constante. Obtenido 12.00 g.

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PA 289121



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 14, 2000

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 60/205,772

FILING DATE: May 19, 2000



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

P. R. Grant

P. R. GRANT

Certifying Officer

05/19/00
36777 U.S. PTO

05-22-00

A/PROV

111
90121

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

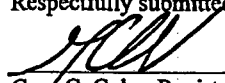
This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

JCS41 U.S. PTO
60/205772
05/19/00

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☐ Additional inventors are named on the attached hereto.	
TITLE OF THE INVENTION (280 characters max) POLYMERIZATION OF ALKYLENE OXIDES USING METAL CYANIDE CATALYSTS AND UNSATURATED INITIATOR COMPOUNDS	
CORRESPONDENCE ADDRESS	
Direct all correspondence to: Gary C. Cohn GARY C. COHN PLLC 4010 Lake Washington Boulevard NE, Suite 105, Kirkland, WA 98033 (425) 576-1656 Fax: (425) 576-1756	
ENCLOSED APPLICATION PARTS	
☒ Specification, 25 pages	☐ Small entity statement
☐ Drawings, sheets	☐ Other
METHOD OF PAYMENT	
☐ A check or money order is enclosed to cover the filing fees.	
☒ The commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account No. 04-1512	
FILING FEE AMOUNT: \$150	
☐ This invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. The name of the U. S. Government agency and the Government contract number are:	

Respectfully submitted,

Express Mail EJ740959925US



Gary C. Cohn, Registration No. 30,456
(425) 576-1656
Date: May 19, 2000
Attorney Docket No. 60068

POLYMERIZATION OF ALKYLENE OXIDES USING METAL CYANIDE
CATALYSTS AND UNSATURATED INITIATOR COMPOUNDS

5 BACKGROUND OF THE INVENTION

This invention relates to processes for preparing poly(oxyalkylene) polymers and to methods for preparing same.

Polyethers made from alkylene oxides are well known and useful in a number of applications such as detergent and cleaner compositions, oil well drilling fluids, inks, metal working fluids, lubricants in paper coating compositions, ceramics manufacturing, chemical intermediates for nonionic surfactants which in turn are used in cosmetics, textiles and chemical processing, polyurethanes which are used as flexible foams and elastomers, chemical intermediates for esters which are used in textile spin finishes, cosmetic agents, and as foam control agents for a wide variety of processes.. These polymers may have no more than one oxyalkylene group in succession, or be a higher molecular weight polymer containing one or more long chains of consecutive oxyalkylene groups.

Polyethers of this type are commonly made through an anionic polymerization process, whereby the alkylene oxide is combined with an initiator compound and a strongly basic catalyst such as potassium hydroxide or certain organic amines. The initiator compound contains one or more oxyalkylatable groups such as hydroxyl, thiol, carboxylic acid and the like. The initiator compound determines the functionality (i.e., number of hydroxyl groups/molecule of product) and in some cases may introduce some desired functional group into the product.

There are some disadvantages of polymerizing alkylene oxides using these strongly basic catalysts. One problem is that the strongly basic catalysts do not produce a low polydispersity product when a tertiary alcohol initiator compound is used. In addition, the basic catalyst usually must be removed from the product before it is used, which increases manufacturing costs.

In addition, some kinds of initiator compounds cannot be alkoxylated using strongly basic catalysts, because they contain base-sensitive functional groups. For example, initiators containing certain types alkenyl or alkynyl groups undergo a side reaction in which the alkenyl or alkynyl group will "migrate" along the molecular

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chain, so that the unsaturation in the polyether is at a different place than it was on the initiator. This is of particular concern when terminal unsaturation is desired. Often, unsaturation that is in a terminal position on the initiator migrates to a non-terminal position during the alkoxylation reaction.

5 Unsaturated compounds in which the unsaturation is adjacent to a hydroxyl-substituted tertiary carbon atom are prone to decomposing during the alkoxylation reaction. Many compounds of this type are reaction products of acetylene with a ketone such as acetone. Alkali metal or alkaline earth bases can cause these initiators to decompose to regenerate acetylene. Acetylene is an explosion hazard.

10 In order to try to avoid these problems, Lewis acids such as boron trifluoride-diethyl etherate and organic amines such as triethylamine have been tried. However, some of these catalysts tend to promote the formation of large amounts of by-products, especially when it is attempted to add three or more moles of alkylene oxide per equivalent of initiator compound. The Lewis acid catalysts tend to catalyze "back-biting" reactions where the growing polymer chain reacts with itself. The reactions
15 form cyclic ethers such as dioxane, dimethyldioxane and various crown ethers. These cannot be removed easily from the desired product, and so the product cannot be used in many applications.

 Thus, it would be desirable to provide a method whereby polyethers made
20 using certain unsaturated initiator compounds could be produced in good yield with low levels of by-products.

SUMMARY OF THE INVENTION

 In one aspect, this invention is a process for preparing a polyether, comprising
25 forming a mixture of an initiator compound having one or one oxyalkylatable groups, at least one alkylene oxide and a metal cyanide catalyst complex, and subjecting the mixture to conditions sufficient to activate the catalyst complex and to alkoxylation the oxyalkylatable groups of the initiator,
 wherein the initiator compound contains nonconjugated carbon-carbon unsaturation
30 that is (a) migratable, as defined below, (b) adjacent to a hydroxyl-substituted tertiary carbon atom, or both (a) and (b).

 In a second aspect, this invention is a poly(alkylene oxide) polymer containing the residue of an initiator compound having nonconjugated carbon-carbon

unsaturation that is (a) migratable, as defined below, (b) adjacent to a hydroxyl-substituted tertiary carbon atom, or both (a) and (b), the polymer having an average alkoxy degree of polymerization of at least three moles of alkylene oxide per equivalent of initiator compound.

5 This invention permits the ready formation of polymers of unsaturated initiators containing certain types of carbon-carbon unsaturation that tend to engage in side-reactions during previous alkoxylation processes. Even before any clean-up, the product polymers contain desired, predetermined types of carbon-carbon unsaturation that are predictable from the selection of the initiator compound.

10

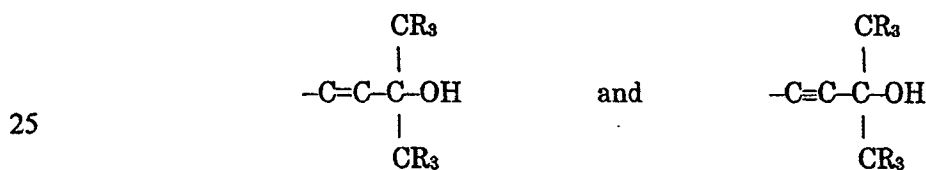
DETAILED DESCRIPTION OF THE INVENTION

In this invention, certain initiator compounds are alkoxyated by reaction with one or more alkylene oxides in the presence of a catalytically effective amount of a metal cyanide catalyst. The alkoxylation is conducted by combining the initiator, 15 metal cyanide catalyst and alkylene oxide. The catalyst is then allowed to become activated in the presence of the alkylene oxide. Once the catalyst has become activated, the mixture is subjected to conditions sufficient to polymerize the alkylene oxide. In this manner, the initiator compound becomes alkoxyated until poly(oxyalkylene) chains of a desired length are introduced. As discussed below, once 20 polymerization has begun, other types of monomers that are copolymerizable with alkylene oxides can be polymerized as well.

The initiator compound used in the process contains carbon-carbon unsaturation, i.e., a carbon-carbon double bond (i.e., an alkenyl group) and/or a carbon-carbon triple bond (i.e., an alkynyl group). The carbon-carbon unsaturation is 25 not conjugated, i.e., is not part of a sequence of two or more double or triple bonds that alternate with single bonds. Thus, the carbon-carbon unsaturation is not part of an aliphatic hydrocarbyl conjugated structure (such as $-\text{CH}=\text{CH}-(\text{CH}=\text{CH}-)_x$), part of an aromatic group, nor part of a conjugated structure including carbonyl groups (such as a $-\text{CR}=\text{CR}-\text{C}(\text{O})-$ grouping, as is present, for example, in acrylic or methacrylic 30 compounds, maleic acid, fumaric acid, and the like). In the foregoing structure, each R independently represents hydrogen or an unsubstituted or inertly substituted group hydrocarbon that is attached to the indicated carbon atom through a carbon-carbon single bond. By "inertly substituted", it is meant a group that does not react under

the conditions of the alkoxylation process of the invention.

In addition, the carbon-carbon unsaturation is either migratable, adjacent to a hydroxyl-substituted tertiary carbon atom, or both. In the case of a carbon-carbon double bond, y "migratable", means that the unsaturation is adjacent to a-CHR⁶- group that is not substituted with any heteroatom, where R⁶ is hydrogen or an unsubstituted or inertly substituted alkyl group. Thus, a migratable alkenyl group would have the structure -CR=CR-CHR⁶-R¹OH, where R is as defined above and R¹ is either a single bond or an unsubstituted or inertly substituted alkyl group]. A migratable alkynyl group is adjacent to a methylene group and would have the structure -C≡C-CH₂-R¹OH, where R¹ is as defined above. Unsaturation of this type can "migrate" to the adjacent -CHR⁶- or -CH₂- group under basic conditions. Thus, for example, the migratable alkenyl group shown above can isomerize to form a -CHR-CR=CR⁶-R¹OH group under basic conditions. In the same way, the migratable alkynyl group shown above can isomerize to form a -CH₂-C≡C-R¹OH group. Among the initiators of this type, those in which the carbon-carbon unsaturation occupies a terminal position (i.e. those of the general structure H₂C=C-CHR⁶-R¹-OH or H₂C≡C-CH₂-R¹-OH are of particular interest. Among the initiators of this type are 3-butyne-1-ol, 3-butene-1-ol, allyl alcohol, 3-buten-2-ol, cyclohex-2-ene-1-ol and the like. Carbon-carbon unsaturation adjacent to a hydroxyl-substituted tertiary carbon atom can be represented by the structures



where R is as defined above. These compounds are of particular interest because they form products having broad polydispersities under standard alkoxylation conditions with alkali or alkaline earth catalysis. Furthermore alkyne unsaturation adjacent to a hydroxyl-substituted carbon atom tends to decompose under basic conditions forming acetylene in some cases and creating an explosion hazard. Among the initiators of this type are 2-methyl-3-butyne-2-ol, 2-methyl-3-butene-2-ol, 3,5-dimethyl-1-hexyn-3-ol, 3,6-dimethyl-4-octyne-3,6-diol, 2,5-dimethyl-3-hexyn-2,5-diol, 2,4,7,9-

tetramethyl-5-decyne-4,7-diol, and the like, as well as other alkynyl tertiary alcohols that are formed in the reaction of acetylene and a ketone such as acetone in various proportions.

5 The alkoxylation is performed by first mixing the initiator, catalyst and an alkylene oxide and allowing the mixture to sit for a period of time at room or an elevated temperature. When these materials are mixed, a so-called induction period occurs, during which the oxyalkylene reaction occurs very slowly. The induction period may range from a few minutes to several hours, depending on the particular catalyst that is used and the temperature. During this induction period, the catalyst
10 becomes activated, and rapid polymerization of the alkylene oxide then commences.

The starting mixture of catalyst, initiator compound and alkylene oxide is conveniently made by combining the catalyst and initiator compound in a pressure reactor (or by forming the catalyst in the initiator), and then pressurizing the reactor with an initial quantity of alkylene oxide. The induction period follows, as indicated
15 by a nearly constant or slowly decreasing pressure in the reactor. The onset of rapid polymerization that follows the induction period is evidenced by a drop in pressure as the alkylene oxide is consumed.

The starting mixture of catalyst, initiator compound and alkylene oxide may be brought to any convenient temperature, such as from about 20°C, preferably from
20 about 50°C, more preferably from about 70°C, even more preferably from about 80°C to about 150°C, most preferably to about 130°C. These temperatures are also suitable for conducting the polymerization once the catalyst is activated.

Depending on the desired degree of alkoxylation, all the necessary alkylene oxide may be added to the reactor at the outset. It is usually preferred to add more
25 alkylene oxide to the reactor once the catalyst has become activated, especially when making higher molecular weight polyethers. A convenient way of adding the alkylene oxide is to pressurize the reactor with alkylene oxide and allow alkylene oxide to feed to the reactor on demand, maintaining a more or less constant pressure inside the reactor. Alternatively, any additional alkylene oxide may be fed in one or more
30 discrete increments.

The total amount of alkylene oxide that is fed will depend on the desired equivalent weight of the product. As few as one mole of alkylene oxide per equivalent

of initiator compound can be added. This invention is particularly suited for polymerizing at least about 3 moles of alkylene oxide per equivalent of initiator compound. Sufficient alkylene oxide can be added to make any desirable molecular weight polyether, such as one having a weight average molecular weight of 200,000
5 daltons or more. However, in most cases the intended end-use of the product will dictate its molecular or equivalent weight. Thus, for example, for making polyols for polyurethane applications, polyether equivalent weights of from about 75-500 are of particular interest for rigid polyurethane foams, equivalent weights of from about 300-1300 are of particular interest for making molded foams and high resiliency
10 slabstock foams, and equivalent weights of from about 800-3000 are of particular interest for making conventional slabstock foam and reaction injection molded elastomers. For surfactant applications, molecular weights of from about 350 to about 6000 are of particular interest. In most applications, it is desirable that the product be a liquid. Poly(oxyethylene) homopolymers tend to form solids when their weight
15 average molecular weights exceed about 1000 daltons. Thus, when a poly(ethylene oxide) homopolymer is made in accordance with the invention, preferred molecular weights are about 1000 or below. All weights reported above are number average molecular weights.

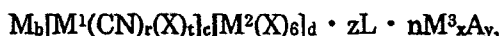
Similarly, the selection of alkylene oxide will depend to a large extent on the
20 intended end-use of the product. Among the alkylene oxides that can be polymerized with the catalyst complex of the invention are ethylene oxide, propylene oxide, 1,2-butylene oxide, styrene oxide, and mixtures thereof. Mixtures of these can be used, and two or more of them can be polymerized sequentially to make block copolymers. For polyurethanes applications, preferred alkylene oxides are propylene oxide alone,
25 mixtures of at least 50 weight % propylene oxide and up to about 50 weight % ethylene oxide (to form a random copolymer), and propylene oxide followed by ethylene oxide, so as to form terminal poly(oxyethylene) chains constituting up to about 30% of the total weight of the product. For other applications, ethylene oxide alone, 1,2-butylene oxide, ethylene oxide/1,2-butylene oxide mixtures, ethylene oxide
30 followed by propylene oxide or butylene oxide, butylene oxide followed by ethylene and/or propylene oxide, propylene oxide alone, mixtures of propylene oxide and ethylene and/or butylene oxide, and propylene oxide followed by ethylene and/or butylene oxide are preferred alkylene oxides.

In addition, monomers that will copolymerize with the alkylene oxide in the presence of the catalyst complex can be used to prepare modified polyether polyols, after the catalyst has become activated. Such comonomers include oxetanes as described in U. S. Patent Nos. 3,278,457 and 3,404,109 and anhydrides as described in U. S. Patent Nos. 5,145,883 and 3,538,043, which yield polyethers and polyester or polyetherester polyols, respectively. Hydroxyalkanoates such as lactic acid, 3-hydroxybutyrate, 3-hydroxyvalerate (and their dimers), lactones as described in U. S. Patent No. 5,525,702 and carbon dioxide are examples of other suitable monomers that can be polymerized with the catalyst of the invention.

10 The polymerization reaction may be performed continuously or batchwise. In such continuous processes, the activated initiator/catalyst mixture is continuously fed into a continuous reactor such as a continuously stirred tank reactor (CSTR) or a tubular reactor. A feed of alkylene oxide is introduced into the reactor and the product continuously removed.

15 The concentration of the catalyst is selected to polymerize the alkylene oxide at a desired rate or within a desired period of time. Generally, a suitable amount of catalyst is from about 5 to about 10,000 parts by weight metal cyanide catalyst complex per million parts of the product. For determining the amount of catalyst complex to use, the weight of the product is generally considered to equal the combined weight of alkylene oxide and initiator, plus any comonomers that may be used. More preferred catalyst complex levels are from about 10, especially from about 20 25, to about 5000, more preferably about 3000 ppm, on the same basis.

The metal cyanide catalyst can be represented by the general formula:



25 wherein M is a metal ion that forms an insoluble precipitate with the $M^1(CN)_r(X)_t$ group and which has at least one water soluble salt;

M^1 and M^2 are transition metal ions that may be the same or different;

each X independently represents a group other than cyanide that coordinates with an M^1 or M^2 ion;

30 L represents an organic complexing agent;

M^3A_y represents a water-soluble salt of metal ion M^3 and anion A, wherein M^3 is the same as or different than M;

b and c are positive numbers that, together with d, reflect an electrostatically neutral

complex;

d is zero or a positive number;

x and y are numbers that reflect an electrostatically neutral salt;

r is from 4 to 6; t is from 0 to 2;

- 5 z is zero or a positive number and n is a positive number indicating the relative quantities of the complexing agent and M_xA_y , respectively. z and n may be fractions.

The X groups in any $M^2(X)_6$ do not have to be all the same. The molar ratio of c:d is advantageously from about 100:0 to about 20:80, more preferably from about 100:0 to about 50:50, and even more preferably from about 100:0 to about 80:20.

- 10 Similarly, the catalyst may contain two or more types of $M^1(CN)_r(X)_t$ groups and two or more types of $M^2(X)_6$ groups.

- M and M^3 are preferably metal ions selected from the group consisting of Zn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , Mo^{+4} , Mo^{+6} , Al^{+3} , V^{+4} , V^{+5} , Sr^{+2} , W^{+4} , W^{+6} , Mn^{+2} , Sn^{+2} , Sn^{+4} , Pb^{+2} , Cu^{+2} , La^{+3} and Cr^{+3} . M and M^3 are more preferably Zn^{+2} , Fe^{+2} , Co^{+2} , Ni^{+2} , La^{+3} and Cr^{+3} . M
15 is most preferably Zn^{+2} .

Suitable anions A include halides such as chloride and bromide, nitrate, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, perchlorate, isothiocyanate, and a C_{1-4} carboxylate. Chloride ion is especially preferred.

- M^1 and M^2 are preferably Fe^{+3} , Fe^{+2} , Co^{+3} , Co^{+2} , Cr^{+2} , Cr^{+3} , Mn^{+2} , Mn^{+3} , Ir^{+3} ,
20 Ni^{+2} , Rh^{+3} , Ru^{+2} , V^{+4} and V^{+5} . Among the foregoing, those in the plus-three oxidation state are more preferred. Co^{+3} and Fe^{+3} are even more preferred and Co^{+3} is most preferred.

- Preferred groups X include anions such as halide (especially chloride), hydroxide, sulfate, C_{1-4} carbonate, oxalate, thiocyanate, isocyanate, isothiocyanate,
25 C_{1-4} carboxylate and nitrite (NO_2^-), and uncharged species such as CO, H_2O and NO. Particularly preferred groups X are NO, NO_2^- and CO.

- The catalyst is usually complexed with an organic complexing agent. A great number of complexing agents are potentially useful, although catalyst activity may vary according to the selection of a particular complexing agent. Examples of such
30 complexing agents include alcohols, aldehydes, ketones, ethers, amides, nitriles, sulfides, and the like.

Suitable alcohols include monoalcohols and polyalcohols. Suitable monoalcohols include methanol, ethanol, n-propanol, isopropanol, n-butanol,

isobutanol, t-butanol, octanol, octadecanol, 3-butyne-1-ol, 3-butene-1-ol, propargyl alcohol, 2-methyl-2-propanol, 2-methyl-3-butyne-2-ol, 2-methyl-3-butene-2-ol, 3-butyne-1-ol, 3-butene-1-ol, 1-t-butoxy-2-propanol and the like. Suitable monoalcohols also include halogenated alcohols such as 2-chloroethanol, 2-bromoethanol, 2-chloro-1-propanol, 3-chloro-1-propanol, 3-bromo-1-propanol, 1,3-dichloro-2-propanol, 1-chloro-2-methyl-2-propanol as well as nitroalcohols, keto-alcohols, ester-alcohols, cyanoalcohols, and other inertly substituted alcohols.

Suitable polyalcohols include ethylene glycol, propylene glycol, glycerine, 1,1,1-trimethylol propane, 1,1,1-trimethylol ethane, 1,2,3-trihydroxybutane, pentaerythritol, xylitol, arabitol, mannitol, 2,5-dimethyl-3-hexyne-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, sucrose, sorbitol, alkyl glucosides such as methyl glucoside and ethyl glucoside, and the like. Low molecular weight polyether polyols, particular those having an equivalent weight of about 350 or less, more preferably about 125-250, are also useful complexing agents.

Suitable aldehydes include formaldehyde, acetaldehyde, butyraldehyde, valeric aldehyde, glyoxal, benzaldehyde, toluic aldehyde and the like. Suitable ketones include acetone, methyl ethyl ketone, 3-pentanone, 2-hexanone and the like.

Suitable ethers include cyclic ethers such as dioxane, trioxymethylene and paraformaldehyde as well as acyclic ethers such as diethyl ether, 1-ethoxy pentane, bis(betachloro ethyl) ether, methyl propyl ether, diethoxy methane, dialkyl ethers of alkylene or polyalkylene glycols (such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether and octaethylene glycol dimethyl ether), and the like.

Amides such as formamide, acetamide, propionamide, butyramide and valeramide are useful complexing agents. Esters such as amyl formate, ethyl formate, hexyl formate, propyl formate, ethyl acetate, methyl acetate, triethylene glycol diacetate and the like can be used as well. Suitable nitriles include acetonitrile, propionitrile and the like. Suitable sulfides include dimethyl sulfide, diethyl sulfide, dibutyl sulfide, diamyl sulfide and the like.

Preferred complexing agents are t-butanol, 1-t-butoxy-2-propanol; polyether polyols having an equivalent weight of about 75-350 and dialkyl ethers of alkylene and polyalkylene glycols. Especially preferred complexing agents are t-butanol, 1-t-butoxy-2-propanol, polyether polyols having an equivalent weight of 125-250 and a

dimethyl ether of mono-, di- or triethylene glycol. t-Butanol and glyme (1,2-dimethoxy ethane) are especially preferred.

A silane-functional complexing agent, as described in the copending application of Wehmeyer entitled Method for Preparing Metal Cyanide Catalysts using Silane-functional Ligands, filed on even date herewith, may be used instead of or in addition to the aforementioned complexing agents. As described therein, the silane-functional complexing agent may be polymerized to form a film or polymer, optionally on a support, or may function as a coupling agent to attach the catalyst complex to a support material.

In addition, the catalyst complex often contains a quantity of water that is bound into the crystalline lattice of the complex. Although the amount of bound water is difficult to determine, it is believed that this amount is typically from about 0.25 to about 3 moles of water per mole of M^1 and M^2 ions.

Exemplary catalysts include:

- 15 Zinc hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nZnCl_2$;
 $Zn[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nZnCl_2$;
 $Zn_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nZnCl_2$ (o, p = positive numbers, $s=1.5o + p$);
 $Zn_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nZnCl_2$ (o, p, q = positive numbers, $s=1.5(o+p)+q$);
20 Zinc hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nLaCl_3$;
 $Zn[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nLaCl_3$;
 $Zn[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nLaCl_3$ (o, p = positive numbers, $s=1.5o + p$);
 $Zn_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nLaCl_3$ (o, p, q = positive numbers, $s=1.5(o+p)+q$);
25 Zinc hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nCrCl_3$;
 $Zn[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nCrCl_3$;
 $Zn_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nCrCl_3$ (o, p = positive numbers, $s=1.5o + p$);
30 $Zn_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nCrCl_3$ (o, p, q = positive numbers, $s=1.5(o+p)+q$);
Magnesium hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nZnCl_2$;
 $Mg[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nZnCl_2$;

$Mg_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nZnCl_2$ (o, p = positive numbers, $s=1.5o + p$);

$Mg_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nZnCl_2$ (o, p, q = positive numbers, $s=1.5(o+p)+q$);

5 Magnesium hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nLaCl_3$;

$Mg[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nLaCl_3$;

$Mg_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nLaCl_3$ (o, p = positive numbers, $s=1.5o + p$);

10 $Mg_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nLaCl_3$ (o, p, q = positive numbers, $s=1.5(o+p)+q$);

Magnesium hexacyanocobaltate $\cdot zL \cdot aH_2O \cdot nCrCl_3$;

$Mg[Co(CN)_5NO] \cdot zL \cdot aH_2O \cdot nCrCl_3$;

$Mg_s[Co(CN)_6]_o[Fe(CN)_5NO]_p \cdot zL \cdot aH_2O \cdot nCrCl_3$ (o, p = positive numbers, $s=1.5o + p$);

15 $Mg_s[Co(CN)_6]_o[Co(NO_2)_6]_p[Fe(CN)_5NO]_q \cdot zL \cdot aH_2O \cdot nCrCl_3$ (o, p, q = positive numbers, $s=1.5(o+p)+q$);

as well as the various complexes such as are described at column 3 of U. S. Patent No. 3,404,109, incorporated herein by reference.

The catalyst complex may be supported. One method of making a supported
20 catalyst is by precipitating the catalyst in the presence of a polycarboxyl or polycarboxylate compound, as described in copending application of Wehmeyer entitled Method for Preparing Metal Cyanide Catalysts using Polycarboxylic Acids filed on even date herewith. Supported catalysts as described in WO 99/44379 are also useful. In addition, supported catalysts can be prepared as described in the
25 copending application of Wehmeyer entitled Method for Preparing Metal Cyanide Catalysts Using Silane-Functional Ligands, filed on even date herewith.

The catalyst complex is conveniently made using standard precipitation methods as are described, for example, in U. S. Patent Nos. 3,278,457, 3,278,458, 3,278,459, 3,404,109, 3,427,256, 3,427,334, 3,427,335, 5,470,813, 5,482,908, 5,536,883,
- 30 5,589,431, 5,627,120, 5,627,122, 5,639,705, 5,714,428, 5,731,407, 5,780,584, 5,783,513, all incorporated herein by reference. In addition, the catalyst may be formed directly as a dispersion in an initiator compound, as described in copending application of Wehmeyer, entitled Method for Preparing Metal Cyanide Catalyst/Polyol Initiator

Slurries filed on even date herewith, or through an incipient wetness technique as described in the copending application of Molzahn et al, entitled Incipient Wetness Method for Making Metal-Containing Cyanide Catalysts, filed on even date herewith.

5 The product polyether contains one or more chains of oxyalkylene groups that are bonded to the initiator compound through a heteroatom. The heteroatom is preferably oxygen and the linkage is most preferably an ether linkage.

10 The product polyether is typically prepared in good yield with only small amounts of undesired by-products. In some instances, the product may contain a high molecular weight "tail" that has a weight average molecular weight of 2X or more of that of the desired product. Typically, when this "tail" is present, it constitutes about 20% or less, more typically less than about 10% of the total weight of the product.

15 Other than the high molecular weight "tail", the process of the invention permits the alkoxylation of a wide range of initiator compounds with the formation of few by-products. By-products other than unreacted starting materials and the high molecular weight "tail" typically constitute less than about 10% by weight of the product, more typically less than about 5 weight percent and even more typically less than about 2 weight percent.

20 In particular, the product is characterized in that the unsaturation from the initiator compound is to a very large degree unaffected by the polymerization process. Migratable carbon-carbon unsaturation tends not to migrate under the conditions of the polymerization reaction. Hydroxyl-substituted tertiary carbon atoms adjacent to carbon-carbon unsaturation tend to be unaffected by the process, and in particular these tertiary carbons do not cleave from the adjacent unsaturated group to form by-products such as acetylene. Thus, the product of this invention typically contains no
25 more than about 10 weight percent, preferably less than about 5 weight percent and even preferably less than about 2 weight percent of by-products, other than unreacted starting materials and the high molecular weight "tail", based on the total weight of the product, prior to any clean-up or purification.

30 The product polyether is generally characterized by having a good polydispersity, typically less than about 2.0, more typically less than about 1.6 and preferably less than about 1.2, as crude products before purification to remove high molecular weight species. These polydispersities can be obtained even when the initiator contains secondary or tertiary oxyalkylatable groups.

The following examples are provided to illustrate the invention, but are not intended to limit its scope. All parts and percentages are by weight unless otherwise indicated.

5 **Example 1**

 A zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex (6.8 g) and 229.86 g of 2-methyl-3-butyn-2-ol are charged to a 2 gallon reactor, taking care to transfer all of the catalyst complex into the reactor. The reactor is sealed and degassed/purged several times with nitrogen, with the pressure
10 being maintained above atmospheric pressure at all times to prevent loss of initiator. The mixture is stirred and heated to 90°C. A portion of ethylene oxide (50 g) is added. The mixture is heated and stirred. A small pressure drop is observed after about 20 minutes. Thirty minutes after the initial addition of ethylene oxide, an additional 50 g of ethylene oxide is added. Another 950 g of ethylene oxide are then fed upon
15 demand. As the reaction progresses, a vigorous exotherm develops. The EO feeds out rapidly and is digested quickly. The product is a pale yellow liquid that becomes opaque but remains liquid as it cools to room temperature. The M_n of the product is 560, and the polydispersity is 1.63. NMR analysis shows that the ethylene oxide has added onto the initiator.

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Example 2

 2-methyl-3-butyn-2-ol (233.84 g), 4.26 g of the catalyst complex described in Example 1 and 950 grams of ethylene oxide are polymerized in the same manner as described in Example 1, except that the initial charge of ethylene oxide weighs about
25 75-100 g. The reaction proceeds more slowly than that of Example 1. A brown product of 370 M_n and 2.03 polydispersity is obtained. NMR analysis clearly shows that the t-butynol has initiated the polymerization.

Example 3

30 A zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex (6.0 g) and 271.87 g of 2-methyl-3-butyn-2-ol are charged to a 2 gallon reactor, taking care to transfer all of the catalyst complex into the reactor. The reactor is sealed and degassed/purged several times with nitrogen, with the pressure

being maintained above atmospheric pressure at all times to prevent loss of initiator. The mixture is stirred and heated to 90°C. A portion of ethylene oxide (135 g) is added. After thirty minutes, an additional 50 g of ethylene oxide is added. After another 90 minutes, another 50 g of ethylene oxide is added. About two hours after that, an ethylene oxide feed to the reactor is begun, starting at 1g/min and gradually increasing to 4 g/min and then decreasing to 3.5 g/min, until a total of 1105 g ethylene oxide has been added. The yield is 1260 g of a very light colored liquid which becomes opaque upon standing overnight but remains fluid. GPC analysis shows the product to have a M_n of 380, with a main fraction at M_n 360 (polydispersity of 1.31) and a small fraction at M_n 1560 (polydispersity of 1.03). Overall polydispersity is 1.37. C^{13} NMR analysis showed that some starting material remains in the product.

Example 4

A zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex (0.53 g) and 235.05 g of 2-methyl-3-buten-2-ol are homogenized and charged under nitrogen to a 2 gallon reactor, taking care to transfer all of the catalyst complex into the reactor. The reactor is sealed and degassed/purged several times with nitrogen, with the pressure being maintained above atmospheric pressure at all times to prevent loss of initiator. The mixture is stirred and heated to 90°C. A portion of ethylene oxide (about 50–150 g) is added. When the pressure in the reactor drops, indicating the start of polymerization, a feed of ethylene oxide is begun. The feed rate is varied until a constant reactor pressure is obtained. A total of 2165 g of ethylene oxide is added. As the reaction progresses, a vigorous exotherm develops. The product has a M_n of 940 and a polydispersity of approximately 1.0.

Example 5

A. Preparation of Supported Metal Cyanide Catalyst

A mixture of 600 mL water and 5 g (about 0.0454 eq. $-COO^-$) of small (99% <1000 microns) lightly crosslinked poly(acrylic acid) potassium salt beads (Aldrich catalog #43,532-5) is prepared. The beads swell when added to the water. To the mixture is added a solution of 4.0 g (0.036 eq.) $K_3Co(CN)_6$ in 100 mL of water. With mixing, a solution of 19.35 g (0.284 eq.) zinc chloride in 50 mL water is added to the bead mixture over about 1 minute. As soon as the zinc chloride addition is complete,

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100 mL t-butanol is added. The resulting mixture is stirred for 10 minutes, then filtered through Whatman® #4 filter paper. The collected solids are reslurried in a solution of 6.45 g (0.094 eq.) zinc chloride in 140 mL t-butanol and 60 mL water, stirred for 10 minutes and filtered again. The solids are again reslurried in 200 mL t-butanol, stirred for 10 minutes and filtered as before. A white, powdery filtrate is obtained, which is dried overnight in a vacuum over (30 mm Hg, 50°C). The mass of the dried catalyst complex is 8.85 g.

B. Ethoxylation of 2-methyl-3-butyn-2-ol

2-methyl-3-butyn-2-ol (259.24 g) is ethoxylated with 1050 g ethylene oxide according to the general method described in Example 1, using 16.6 g of the supported catalyst from part A. The product has an M_n of 380 and a polydispersity of about 1.66.

Example 6

A. Preparation of Supported Metal Cyanide Catalyst

89.65 g of a 3.66 wt% solution of $H_3Co(CN)_6$ in methanol (15.05 mmol $H_3Co(CN)_6$) is added over 15 minutes to a stirred mixture of $ZnCl_2$ (6.15 g, 45.2 mmol), 25.0 g of an 8000 molecular weight bis(dimethoxymethylsilyl)-terminated poly(propylene oxide) (Aldrich catalog #45,041-3) and 15 g tetraethyl orthosilicate (15.0 g) in 150 mL methanol. A slurry forms immediately. After stirring the slurry for 15 minutes, water (5.2 g) is added and the mixture stirred for 5 minutes. The slurry is then added in small batches over about 110 minutes to 150 g silica gel (60-200 mesh particles, 150A pore size, Aldrich catalog #24,3998-1) while the flask is occasionally swirled and shaken to allow the silica to be uniformly wetted. The silica is stripped on a rotoevaporator at 70-75°C bath temp and 25 inches Hg vacuum once during the coating process, after approximately two-thirds of the total slurry is added. After the slurry is added the silica is further dried on the rotoevaporator at 70-75°C bath temp and 25 inches Hg vacuum, then finally at 70-75°C bath temp (>30 inches Hg vacuum) for approximately 10-15 min. The product is further dried in a vacuum oven at full pump vacuum (90-95°C/>30 in Hg vacuum) for 14 hours. The resultant product contains approximately 4.2% catalyst.

B. Ethoxylation of 2-methyl-3-butyn-2-ol

2-methyl-3-butyn-2-ol (257.61 g) is ethoxylated with 1005 g ethylene oxide

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according the general method described in Example 1, using 16.6 g of the supported catalyst from part A. The product has a polydispersity of about 1.4.

Example 7

- 5 Allyl alcohol (284.37 g) is ethoxylated with 1615 g ethylene oxide in the presence of 2.86 g of a zinc hexacyanocobaltate/t-butanol/450 MW poly(propylene oxide) triol catalyst complex, according the general method described in Example 1. C^{13} NMR confirms that the ethoxylate of allyl alcohol has been formed. The unsaturation in allyl alcohol starting material appears at 115 ppm and 137 ppm and
- 10 the product unsaturation appears at 117 ppm and 135 ppm. The M_n of the primary product is 380. The high molecular weight wax constitutes 3.4 wt % of the total product and has a M_n of 3300. Polydispersity is 1.06 by GPC.

Example 8

- 15 The ability of several catalysts to ethoxylate various initiator compounds is evaluated by placing a quantity of the initiator, a catalyst and ethylene oxide into a dried Wheaton vial fitted with a stir bar. The vial is sealed with a septum cap and purged with nitrogen. About 0.5 g of ethylene oxide are added by syringe and the septum cap is replaced with a solid cap under nitrogen. The vial is heated at 90°C for
- 20 14 hours. Table 1 identifies certain other reaction parameters, as well as characteristics of the resulting polymer.

In all cases, C^{13} NMR confirms that the initiator compound is consumed in the alkoxylation reaction.

The initiators are:

- 25 A. 3-butyne-1-ol
 B. 3,5-dimethyl-1-hexyne-3-ol
 C. 3-methyl-1-pentyne-3-ol
 D. 2-methyl-1-butyne-3-ol
 E. 2-methyl-3-buten-2-ol

30 The catalysts are:

- A. Zinc hexacyanocobaltate complexed with t-butanol and treated with a 450 molecular weight poly(propylene oxide) triol.
 B. Zinc hexacyanocobaltate complexed with glyme.

- 5 C. A supported catalyst made as follows: A mixture of 600 mL water and 5 g (about 0.0454 eq. $-\text{COO}^-$) of small (99% <1000 microns) lightly crosslinked poly(acrylic acid) potassium salt beads (Aldrich catalog #43,532-5) is prepared. To the mixture is added a solution of 4.0 g (0.036 eq.) $\text{K}_3\text{Co}(\text{CN})_6$ in 100 mL of water. With mixing, a solution of 19.35 g (0.284 eq.) zinc chloride in 50 mL water is added to the bead mixture over about 1 minute. As soon as the zinc chloride addition is complete, 100 mL t-butanol is added. The resulting mixture is stirred for 10 minutes, then filtered through Whatman® #4 filter paper. The collected solids are reslurried in a solution of 6.45 g (0.094 eq.) zinc chloride in 140 mL t-butanol and 60 mL water, stirred for 10 minutes and filtered again. The solids are again reslurried in 200 mL t-butanol, stirred for 10 minutes and filtered as before. A white, powdery filtrate is obtained, which is dried overnight in a vacuum over (30 mm Hg, 50°C).
- 10 D. A supported catalyst made as follows: A mixture of 50 mL water and 5 g of a 45% solution of poly(acrylic acid) sodium salt in water (Aldrich catalog #41,601-0, about 0.053 mol Na^+) is prepared. To the mixture is added a solution of 4.0 g (0.036 eq.) $\text{K}_3\text{Co}(\text{CN})_6$ in 70 mL of water. With mixing, a solution of 19.35 g (0.142 mol) zinc chloride in 40 mL water is added over about 1 minute. A white precipitate forms immediately. A mixture of 50 mL t-butanol and 50 mL water is added, and the mixture is stirred for 10 minutes and filtered through Whatman® #4 filter paper. The collected solids are reslurried in a solution of 6.45 g zinc chloride in 140 mL t-butanol and 60 mL water, stirred for 10 minutes and filtered again. The collected solids are then reslurried in 200 mL t-butanol, stirred as before and filtered again. A white filtrate is obtained, which is dried overnight in a vacuum oven (30 mm Hg, 50°C).
- 20 E. A supported catalyst made as follows: A solution of potassium hydroxide in water (0.053 moles KOH in 50 mL water is added to solid 1,3,5-benzene tricarboxylic acid (BTA) (3.71 g, 0.177 mmol), and diluted to a volume of 300 mL with additional water. An additional 0.26 g of solid 85% KOH and a small quantity of potassium bicarbonate are added to form a clear, colorless solution. Solid $\text{K}_3\text{Co}(\text{CN})_6$ (4.0 g, 0.012 mol) is added with stirring. Then, a solution of 19.35 g (0.142 mol) zinc chloride in 40 mL of water is added with continued stirring. A
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white flocculent forms as the zinc chloride solution is added. A solution of 50 mL water and 50 mL of t-butanol is immediately added. The mixture is stirred for 10 minutes and filtered through Whatman® #41 filter paper. The filtered solid is reslurried in a solution of zinc chloride (6.45 g, 0.047 mol) in 140 mL t-butanol and 60 mL water, stirred 10 minutes and filtered again. The filtered solids are then reslurried in 200 mL t-butanol, stirred 10 minutes, filtered and dried in a vacuum oven overnight at 50°C. The mass of the final product is 10.16 g.

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F. A supported catalyst made as follows: 30.72 g of the $\text{H}_3\text{Co}(\text{CN})_6$ solution (6.02 mmol $\text{H}_3\text{Co}(\text{CN})_6$) is stirred into a mixture of zinc chloride (2.461 g, 18.1 mmol), 8 g of an 8000 molecular weight bis(dimethoxymethylsilyl)-terminated poly(propylene oxide) (Aldrich catalogue #45,041-3), tetraethyl orthosilicate (1.0 g, 4.8 mmol), and 30 mL of methanol. A slurry forms, which is stirred for about 10 minutes before 0.36 g of water is added. The slurry is then stirred for an additional 5-10 minutes prior to addition to the various supports. The resultant methanolic slurry contains approximately 4.53 wt% of metal cyanide catalyst. Part (22.9 g) of the slurry is added in one portion to 10 g (undried weight) of Grade 62, 60-200 mesh silica gel particles. The solvent is then removed using a rotoevaporator, initially at 70-75°C/25 inches Hg vacuum, followed by a few minutes at 30 inches Hg vacuum on the rotoevaporator. The product is further dried overnight in a vacuum oven at 50°C/<30 inches Hg vacuum. The product is estimated to contain 7.7 wt. % metal cyanide catalyst (as $\text{Zn}_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{ZnCl}_2$, ignoring any associated water and complexing agent).

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G. A supported catalyst made as follows: 30.72 g of a $\text{H}_3\text{Co}(\text{CN})_6$ solution (6.02 mmol $\text{H}_3\text{Co}(\text{CN})_6$) is stirred into a mixture of zinc chloride (2.461 g, 18.1 mmol), 8 g of an 8000 molecular weight bis(dimethoxymethylsilyl)-terminated poly(propylene oxide) (Aldrich catalogue #45,041-3), tetraethyl orthosilicate (1.0 g, 4.8 mmol), and 30 mL of methanol. A slurry forms, which is stirred for about 10 minutes before 0.36 g of water is added. The slurry is then stirred for an additional 5-10 minutes prior to addition to the various supports. The resultant methanolic slurry contains approximately 4.53 wt% of metal cyanide catalyst. 20.0 g of the resulting slurry is added in batches to 25 g (undried weight, including about 13% water) of 6-16 mesh, irregularly shaped silica gel chips, with periodic removal of solvent during

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the additions using a rotoevaporator. After the addition of the slurry is complete, the product is further stripped on the rotoevaporator at 70-75°C/25 inches Hg vacuum. This is followed by a few minutes at 30 inches Hg vacuum on the rotoevaporator. The product is further dried overnight in a vacuum oven at 50°C/<30 inches Hg vacuum. The product is estimated to contain 3.5 wt. % metal cyanide catalyst.

H. A supported catalyst made as follows: 30.72 g of a $\text{H}_3\text{Co}(\text{CN})_6$ solution (6.02 mmol $\text{H}_3\text{Co}(\text{CN})_6$) is stirred into a mixture of zinc chloride (2.461 g, 18.1 mmol), 8 g of an 8000 molecular weight bis(dimethoxymethylsilyl)-terminated poly(propylene oxide) (Aldrich catalogue #45,041-3), tetraethyl orthosilicate (1.0 g, 4.8 mmol), and 30 mL of methanol. A slurry forms, which is stirred for about 10 minutes before 0.36 g of water is added. The slurry is then stirred for an additional 5-10 minutes prior to addition to the various supports. The resultant methanolic slurry contains approximately 4.53 wt% of metal cyanide catalyst. 20.0 g of the slurry is added in batches to 25 g porous 7/32" diameter alumina spheres, with periodic removal of solvent during the additions using a rotoevaporator. After the addition of the slurry is complete, the product is further stripped on the rotoevaporator at 70-75°C/25 inches Hg vacuum. This is followed by a few minutes at 30 inches Hg vacuum on the rotoevaporator. The product is further dried overnight in a vacuum oven at 50°C/<30 inches Hg vacuum. The product is estimated to contain 3.3 wt. % metal cyanide catalyst.

I. A supported catalyst made as follows: About 15.36 g of a $\text{H}_3\text{Co}(\text{CN})_6$ solution (3.01 mmol $\text{H}_3\text{Co}(\text{CN})_6$) is stirred into a mixture of zinc chloride (1.026 g), 2 g of an 8000 molecular weight bis(dimethoxymethylsilyl)-terminated poly(propylene oxide) (Aldrich catalog #45,041-3), and 20 mL of methanol. A slurry forms, which is stirred for about 10 minutes before 0.25 g of tetraethyl orthosilicate is added. After stirring another 10 minutes, the resulting slurry is added in batches to 10 g of Grade 62, 60-200 mesh silica gel particles, with periodic removal of solvent during the additions using a rotoevaporator (70-75°C/25 inches Hg vacuum). After the addition of the slurry is complete, the product is further stripped on the rotoevaporator at 70-75°C/25 inches Hg vacuum. This is followed by a few minutes at 30 inches Hg vacuum. Further drying overnight at 50°C, the product contains

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approximately 10.2 wt% metal cyanide catalyst.

J. A supported catalyst is made as follows: 89.65 g of a 3.66 wt% solution of $H_3Co(CN)_6$ in methanol (15.05 mmol $H_3Co(CN)_6$) is added over 15 minutes to a stirred mixture of $ZnCl_2$ (6.15 g), 25.0 g of an 8000 molecular weight bis(dimethoxymethylsilyl)-terminated poly(propylene oxide) (Aldrich catalog #45,041-3) and 15 g tetraethyl orthosilicate in 150 mL methanol. After stirring the slurry for 15 minutes, water (5.2 g) is added and the mixture stirred for 5 minutes. The slurry is then added in small batches over about 110 minutes to 150 g silica gel (60-200 mesh particles, 150A pore size, Aldrich catalog #24,3998-1) while the flask is occasionally swirled and shaken to allow the silica to be uniformly wetted. The silica is stripped on a rotoevaporator at 70-75°C bath temp and 25 inches Hg vacuum once during the coating process, after approximately two-thirds of the total slurry is added. After the slurry is added the silica is further dried on the rotoevaporator at 70-75°C bath temp and 25 inches Hg vacuum, then finally at 70-75°C bath temp (>30 inches Hg vacuum) for approximately 10-15 min. The product is further dried in a vacuum oven at full pump vacuum (90-95 °C / >30 in Hg vacuum) for 14 hours. The resultant product contains approximately 4.2% catalyst.

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Table 1

Sample Letter	Initiator		Catalyst		EO, Grams	Product	
	Type	mg	Type	mg		M _n	PDI
A	A	115.3	A	6.1	.5	300	1.4
B	B	190.4	A	.12	.5	420	2.62
C	A	102.9	A	1.8	.5	460	1.24
D	C	146.7	A	1.37	.5	520	1.77
E	D	133.5	B	6.7	.5	470	2.13
F	A	115.3	B	6.1	.5	390	1.77
G	D	137.2	C	18.1	.5	240	2.17
H	D	164.3	D	32.9	.5	300	1.67
I	D	137.7	E	28.6	.5	310	2.06
J	D	125.1	F	8.03	.5	460	1.65

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K	D	131.9	G	6.38	.5	320	1.63
L	D	136.2	H	23	.5	460	1.3
M	D	131.3	I	16	.5	450	1.38
N	E	130.4	J	35.5	.5	390	1.72

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WHAT IS CLAIMED IS:

1. A process for preparing a polyether, comprising forming a mixture of an initiator compound having one or one oxyalkylatable groups, at least one alkylene
5 oxide and a metal cyanide catalyst complex, and subjecting the mixture to conditions sufficient to activate the catalyst complex and to alkoxylate the oxyalkylatable groups of the initiator,
wherein the initiator compound contains nonconjugated, carbon-carbon unsaturation that is (a) migratable, as defined below, (b) adjacent to a hydroxyl-substituted tertiary
10 carbon atom, or (c) both (a) and (b).
2. The process of claim 1 wherein the carbon-carbon unsaturation is a migratable double bond.
- 15 3. The process of claim 2 wherein the alkylene oxide is ethylene oxide.
4. The process of claim 2 wherein the alkylene oxide is propylene oxide or 1,2-butylene oxide.
- 20 5. The process of claim 2 wherein the initiator compound contains at least one secondary or tertiary hydroxyl group, at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.
- 25 6. The process of claim 5 wherein the initiator compound is 3-butene-1-ol, allyl alcohol, 3-buten-2-ol or cyclohex-2-ene-1-ol.
7. The process of claim 1 wherein the carbon-carbon unsaturation is a migratable triple bond.
- 30 8. The process of claim 7 wherein the alkylene oxide is ethylene oxide.

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9. The process of claim 7 wherein the alkylene oxide is propylene oxide or 1,2-butylene oxide.
10. The process of claim 7 wherein the initiator compound contains at least one secondary or tertiary hydroxyl group, at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.
11. The process of claim 10 wherein the initiator compound is 3-butyn-1-ol.
12. The process of claim 1 wherein the initiator contains an alkynyl group adjacent to a hydroxyl-substituted tertiary carbon atom.
13. The process of claim 12 wherein the alkylene oxide is ethylene oxide.
14. The process of claim 12 wherein the initiator compound contains at least one secondary or tertiary hydroxyl group, at least three moles of alkylene oxide are added per equivalent of initiator, and the polydispersity of the product is less than about 1.25.
15. The process of claim 14 wherein the initiator compound is 2-methyl-3-butyn-2-ol, 2-methyl-3-butene-2-ol, 3,5-dimethyl-1-hexyn-3-ol, 3,6-dimethyl-4-octyne-3,6-diol, 2,5-dimethyl-3-hexyn-2,5-diol or 2,4,7,9-tetramethyl-5-decyne-4,7-diol.
16. An initiated poly(alkylene oxide) polymer containing the residue of an initiator compound having nonconjugated carbon-carbon unsaturation that is (a) migratable, as defined below, (b) adjacent to a hydroxyl-substituted tertiary carbon atom, or (c) both (a) and (b), the polymer having an average alkoxy degree of polymerization of at least three moles of alkylene oxide per equivalent of initiator compound.
17. The initiated poly(alkylene oxide) polymer of claim 16 wherein the alkylene oxide is ethylene oxide or propylene oxide.

18. The initiated poly(alkylene oxide) polymer of claim 17 wherein the alkylene oxide is ethylene oxide and the number average molecular weight of the polymer is up to about 1000.

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19. The initiated poly(alkylene oxide) polymer of claim 18 wherein the carbon-carbon unsaturation is terminal, migratable alkynyl unsaturation.

20. The initiated poly(alkylene oxide) polymer of claim 19 wherein the carbon-carbon unsaturation is an alkynyl group adjacent to a hydroxyl-substituted tertiary carbon atom.

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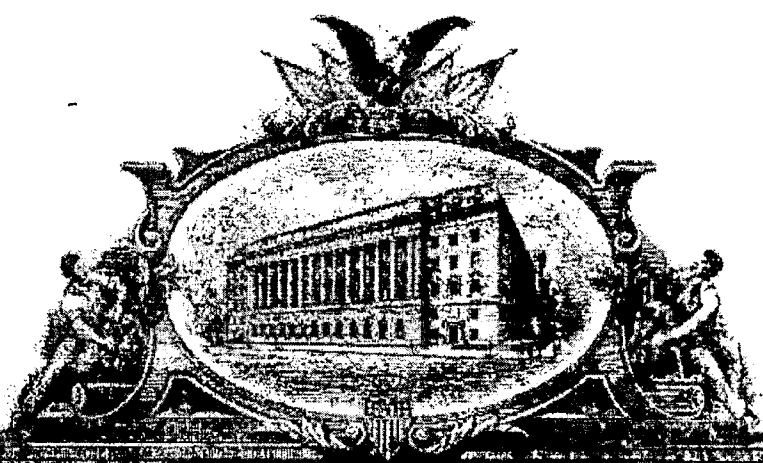
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ABSTRACT OF THE DISCLOSURE

Certain alcohol initiators containing unconjugated carbon-carbon double bonds
can be alkoxyated with excellent efficiency and low production of by-products using
5 an metal cyanide catalyst.

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**A TODOS AQUELLOS A QUIENES LA PRESENTE CONCIERNE:
DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS**

Oficina de Patentes y Marcas de los Estados Unidos

14 de agosto de 2000

LA PRESENTE ES PARA CERTIFICAR QUE LA ANEXA A ESTA ES UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA SOLICITUD DE PATENTE IDENTIFICADA MAS ADELANTE QUE SATISFACEN LOS REQUISITOS PARA QUE SE OTORGUE UNA FECHA DE PRIORIDAD BAJO 35 USC 111..

SOLICITUD NUMERO: 60/205,772

FECHA DE PRESENTACION: 19 de mayo de 2000



**Por la Autoridad del
COMISIONADO DE PATENTES Y MARCAS**

**Firmado por
P.R. GRANT**

Funcionario Certificador

REIVINDICACIONES

1. Un proceso para preparar un poliéter, que comprende formar una mezcla de un compuesto iniciador teniendo uno o más grupos oxialquilables, al menos un óxido de alquileo y un complejo de catalizador de cianuro de metal, y someter la mezcla a condiciones suficientes para activar el complejo de catalizador y alcoxilar los grupos oxialquilables del iniciador,
5 en donde el compuesto iniciador contiene una insaturación de carbono-carbono, no conjugada, que es (a) capaz de migrar, (b) adyacente a un átomo de carbono terciario substituido con hidroxilo, o (c) tanto (a) como (b).
2. El proceso de la reivindicación 1, en donde la insaturación de carbono-carbono es un doble enlace capaz de migrar.
- 15 3. El proceso de la reivindicación 2, en donde el óxido de alquileo es óxido de etileno.
4. El proceso de la reivindicación 2, en donde el óxido de alquileo es óxido de propileno o óxido de 1,2-butileno.
5. El proceso de la reivindicación 2, en donde el compuesto iniciador
20 contiene al menos un grupo hidroxilo secundario o terciario, se adicionan al menos tres moles de óxido de alquileo por equivalente de iniciador y la polidispersidad del producto es menor que aproximadamente 1.25.
6. El proceso de la reivindicación 5, en donde el compuesto iniciador es 3-buten-1-ol Alcohol alilo o ciclohex-2-eno-1-ol.

7. El proceso de la reivindicación 1, en donde la insaturación de carbono-carbono es un triple enlace capaz de migrar.
8. El proceso de la reivindicación 7, en donde el óxido de alquileno es óxido de etileno.
- 5 9. El proceso de la reivindicación 7, en donde el óxido de alquileno es óxido de propileno o óxido de 1,2-butileno.
- 10 10. El proceso de la reivindicación 7, en donde el compuesto iniciador contiene al menos un grupo hidroxilo secundario o terciario, se adicionan al menos tres moles de óxido de alquileno por equivalente de iniciador y la polidispersidad del producto es menor que aproximadamente 1.25.
11. El proceso de la reivindicación 10, en donde el compuesto iniciador es 3-butin-1-ol.
12. El proceso de la reivindicación 1, en donde el iniciador contiene un grupo alquínico adyacente a un átomo de carbono terciario substituido con hidroxilo.
- 15 13. El proceso de la reivindicación 12, en donde el óxido de alquileno es óxido de etileno.
14. El proceso de la reivindicación 12, en donde el compuesto iniciador contiene al menos un grupo hidroxilo secundario o terciario, se adicionan al menos tres moles de óxido de alquileno por equivalente de iniciador y la polidispersidad del producto es menor que aproximadamente 1.25.
- 20 15. El proceso de la reivindicación 14, en donde el compuesto iniciador es 2-metil-3-butin-2-ol, 2-metil-3-buten-2-ol, 3-5-dimetil-1-hexin-3-ol, 3,6-dimetil-4-octino-3,6-diol, 2,5-dimetil-3-hexin-2,5-diol o 2,4,7,9-tetrametil-5-decino-4,7-diol.
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16. Un polímero de poli(oxialquileno) iniciado conteniendo el residuo de un compuesto iniciador que tiene una insaturación de carbono-carbono no conjugada, que es (a) capaz de migrar, como se define más adelante, (b) adyacente a un átomo de carbono terciario substituido con hidroxilo, o (c) tanto (a) como (b), teniendo el polímero un grado de polimerización de alcoxí promedio de al menos tres moles de óxido de alquileno por equivalente de compuesto iniciador.
17. El polímero de poli(oxialquileno) iniciado de la reivindicación 16, en donde el óxido de alquileno es óxido de etileno u óxido de propileno.
18. El polímero de poli(oxialquileno) iniciado de la reivindicación 17, en donde el óxido de alquileno es óxido de etileno y el peso molecular promedio de número del polímero es hasta aproximadamente 1000.
19. El polímero de poli(oxialquileno) iniciado de la reivindicación 18, en donde la insaturación de carbono-carbono es una insaturación de alquínilo, capaz de migrar, terminal.
20. El polímero de poli(oxialquileno) iniciado de la reivindicación 19, en donde la insaturación de carbono-carbono es un grupo alquínilo adyacente a un átomo de carbono terciario substituido con hidroxilo.

RESUMEN

Ciertos iniciadores de alcohol conteniendo dobles enlaces de carbono-carbono, no conjugados, pueden ser alcoxilados con excelente eficiencia y baja producción de subproductos usando un catalizador de cianuro de metal.