

# New Heterogeneous Catalysis for the Synthesis of Poly(ether polyols)

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**ABSTRACT:** Novel double-metal cyanide (DMC) complex catalysts were prepared with various precursors of cobalt or nickel and zinc with potassium cyanide. In the presence of an alcohol initiator, but in the absence of an organic-binding ligand, the catalysts were highly active for the polymerization of alkyl- or alkenyl-substituted epoxides to produce poly(ether polyols). The polymer obtained from propylene oxide showed a more isotactic structure than did the polymer made from nonselective conventional catalysts. The

influence of different reaction variables were examined, including the ratio of the initiator to the substrate, the presence of a protonic agent, the temperature, as well as the concentration of the catalyst and the solvent. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1553–1557, 2002

**Key words:** catalysis; polyethers; ring-opening polymerization

## INTRODUCTION

Poly(ether polyols) are important industrial compounds used in the production of polyurethanes, sealants, elastomers, adhesives, and coatings.<sup>1</sup> Generally, poly(ether polyol)s are prepared by the catalytic addition of an alkyl epoxide or a mixture of alkyl epoxides, either simultaneously or sequentially, to an alcohol usually referred to as an initiator. Although the alkoxylation catalyst may be alkaline, neutral, or acid, an alkaline catalyst such as an alkali metal hydroxide is most often used.<sup>2</sup> However, this type of catalyst has a number of drawbacks. Paramount among these are the neutralization and filtration of the catalyst employed after the completion of the reaction. Therefore, it would be an advantage to develop a catalyst which can overcome this deficiency and also can produce poly(ether polyol)s that have narrow polydispersity, good stereoregularity, and a specific concentration of hydroxyl groups.

A highly active amorphous double-metal cyanide (DMC) complex catalyst has been described, made from zinc chloride and potassium hexacyanocobaltate with an organic complexing agent such as *t*-butanol.<sup>3,4</sup> Compared to conventional catalysts, this catalyst showed excellent activity with a very low level of unsaturation.<sup>5</sup>

We now report on the preparation and reactivities of some new DMC catalysts, made from various precursors

of nickel or cobalt and zinc with potassium cyanide. These new DMC complex catalysts were very active, without a binding ligand, for the polymerization of epoxides with an alcohol initiator. We used GPA700 (a 700 molecular weight glycerin and propylene oxide adduct) as an alcohol initiator, because GPA700 is widely employed in industry as an initiator for the synthesis of poly(ether polyol)s from alkyl epoxides.

## EXPERIMENTAL

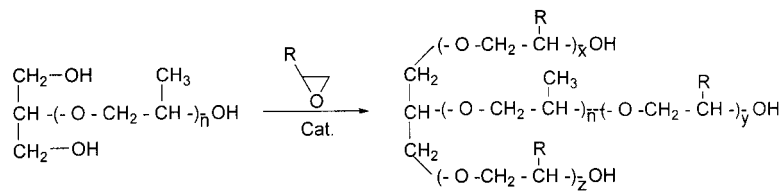
### Materials and instruments

Solvents and reagents were reagent grade and used as received from the suppliers. IR spectra were recorded using a Bomem MB100-C15 instrument. <sup>1</sup>H- and <sup>13</sup>C-NMR spectral determinations were made on a Varian Gemini 200-MHz spectrometer using TMS as the internal reference in CDCl<sub>3</sub> at 25°C. Molecular weights and molecular weight distributions were measured at 45°C by gel permeation chromatography (GPC) using a Waters 510 pump with three consecutive  $\mu$ Styragel HT columns with the effective molecular weight range of 500–4 × 10<sup>6</sup> and a Waters 410 differential refractometer detector. Polystyrene standards were used for the calibration. HPLC-grade tetrahydrofuran was used as an eluant at a flow rate of 1 mL/min, and a sample concentration of 1 mg/mL was used. All polymerization reactions were carried out in a 45-mL stainless-steel autoclave with a glass liner.

### Catalyst preparation: synthesis of the NiCl<sub>2</sub>—KCN—Zn(ACO)<sub>2</sub> (1:6:6) complex

Nickel(II) chloride, 5 mmol (0.648 g) (Sigma, Milwaukee, WI; 98%) was dissolved in 100 mL of distilled

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Scheme 1

water. After the solution turned transparent green, 30 mmol (1.954 g) of potassium cyanide (Aldrich, 97%) was added followed by 30 mmol (6.585 g) of zinc acetate dihydrate (Aldrich, Milwaukee, WI; 98%). The reaction mixture was stirred overnight and the formed solid was filtered. The obtained solid was washed with water several times and then dried in a vacuum oven (30 mmHg) at 50°C for 18 h, to give 1.79 g of the catalyst as a white solid. Other catalysts were prepared by similar methods.

### Polymerization

A typical experiment was performed as follows (Table II, run 1): 0.05 g of the  $\text{CoCl}_2\text{—KCN—ZnCl}_2$  catalyst, 70 mmol (5 mL) of propylene oxide, 0.7 mmol (0.5 g) of GPA700, and 10 mL of *n*-hexane were placed in the glass liner. The autoclave was purged three times with  $\text{N}_2$  and heated with stirring at 110°C for 24 h. After the reaction, the catalyst was removed by simple filtration of the product. Another way to remove the catalyst was to dilute the product with a solvent such as THF, reduce the viscosity, and then filter the mixture.

## RESULTS AND DISCUSSION

To first confirm the catalytic activity of the amorphous DMC catalyst (zinc hexacyanocobaltate/*t*-butanol) for the synthesis of a poly(ether triol) with GPA700 as the alcohol initiator, we prepared the catalyst according to the patent method.<sup>3,4</sup> (see Scheme 1). The results of the polymerization of propylene oxide with GPA700 in the presence of this catalyst are summarized in Table I.

When the reaction was carried out at 110°C for 24 h using *n*-hexane as the solvent, almost a quantitative

amount of the corresponding poly(ether triol) was obtained with a molecular weight of 7070 and a polydispersity of 1.55 (run 1, Table I). The ratio of propylene oxide and GPA700 was 100:1 and the weight ratio of propylene oxide and the catalyst was 200:1. The catalyst prepared without a binding ligand, or prepared with potassium *t*-butoxide instead of *t*-BuOH, was inactive for the polymerization (runs 2 and 3, Table I). Because of the apparent need of a ligand, we were interested in developing the use of other ligands and found that DMSO or sulfolane could be used as a ligand instead of *t*-BuOH (runs 4 and 5, Table I). Indeed, the polydispersity was better using DMSO than *t*-BuOH (run 4, Table I).

We then tried to prepare a DMC catalyst using different precursors of cobalt or using other metals such as nickel. The catalysts were prepared by the reaction of aqueous solutions of metal chlorides and potassium cyanide instead of zinc chloride and potassium hexacyanocobaltate. We prepared the catalysts using various ratios of zinc to cobalt or nickel and to cyanide (e.g., 1–6:1:6–12), and the catalyst prepared using the 6:1:6 ratio showed the best result. So, the ratio of zinc to cobalt or nickel and to cyanide was maintained at 6:1:6 (Table II). The reactivities of the  $\text{CoCl}_2\text{—KCN—ZnCl}_2$  and  $\text{NiCl}_2\text{—KCN—ZnCl}_2$  catalysts, with *t*-BuOH as a binding ligand in the polymerization of propylene oxide, under the same reactions as described in the patent literature (run 1, Table I), were lower than those of the amorphous DMC catalyst. Also, a higher concentration of the catalyst was required here (weight ratio of propylene oxide and the catalyst was 80:1). Furthermore, the polydispersities (GPC) of the corresponding poly(ether triols) were broader and showed unsymmetrical tailings in the

TABLE I  
Polymerization of Propylene Oxide by Zinc Hexacyanocobaltate Prepared with Zinc Chloride and Potassium Hexacyanocobaltate

Run	Catalyst	$M_w$	Polydispersity	Yield (%)
1	$\text{K}_3[\text{Co}(\text{CN})_6]\text{—ZnCl}_2/t\text{-butanol}$	7070	1.55	>99
2	$\text{K}_3[\text{Co}(\text{CN})_6]\text{—ZnCl}_2^a$	—	—	0
3	$\text{K}_3[\text{Co}(\text{CN})_6]\text{—ZnCl}_2/\text{K}(t\text{-BuO})$	—	—	0
4	$\text{K}_3[\text{Co}(\text{CN})_6]\text{—ZnCl}_2/\text{DMSO}$	7750	1.26	95
5	$\text{K}_3[\text{Co}(\text{CN})_6]\text{—ZnCl}_2/\text{sulfolane}$	5890	1.80	80

Reaction conditions: 0.02 g catalyst (Co:Zn = 1:6), 70 mmol propylene oxide, 0.7 mmol GPA700, 10 mL *n*-hexane for 24 h at 110°C.

<sup>a</sup> No binding ligand.

TABLE II  
Polymerization of Propylene Oxide by DMC Complexes Prepared with Metal Chlorides and Potassium Cyanide

Run	Catalyst	$M_w$	Polydispersity <sup>a</sup>	Yield (%)
1	CoCl <sub>2</sub> —KCN—ZnCl <sub>2</sub> <sup>b</sup>	14100	2.96	82
2	CoCl <sub>2</sub> —KCN—ZnCl <sub>2</sub>	8520	2.34	87
3	NiCl <sub>2</sub> —KCN—ZnCl <sub>2</sub> <sup>b</sup>	25260	4.29	80
4	NiCl <sub>2</sub> —KCN—ZnCl <sub>2</sub>	34710	4.89	79
5	NiCl <sub>2</sub> —KCN—ZnCl <sub>2</sub> <sup>c</sup>	147700	3.92	polyether

Reaction conditions: 0.05 g catalyst [Co (or Ni):CN:Zn = 1:6:6], 70 mmol propylene oxide, 0.7 mmol GPA700, 10 mL *n*-hexane for 24 h at 110°C.

<sup>a</sup> The GPC peak showed unsymmetrical tailing in the high molecular weight region.

<sup>b</sup> The catalyst was washed with *t*-butanol after its precipitation.

<sup>c</sup> Without GPA700.

high molecular weight region. These results might be due to the aggregation of the catalyst or to the presence of different active sites in the catalyst (runs 2 and 4, Table II).<sup>6</sup>

To develop a catalyst which can produce the poly(ether triol) with narrow polydispersity and without tailing in the high molecular weight region, we prepared the catalyst using different precursors including cobalt acetate, nickel acetate, nickel cyanide, and zinc acetate instead of metal chlorides. All these DMC catalysts showed high reactivities for the polymerization of propylene oxide with GPA700 as an alcohol initiator and without a binding ligand. The shape of the GPC peaks were quite symmetrical (Table III). Among the catalysts prepared, the Ni(AcO)<sub>2</sub>—KCN—ZnCl<sub>2</sub> catalyst system produced the corresponding polymer with a molecular weight of 8630 and a polydispersity of 1.92, which is comparable to the polymer formed by the previously described catalyst (run 2, Table III, and run 1, Table I).

Previous investigations reported the formation and use of active catalysts such as Zn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> · *x*ZnCl<sub>2</sub> · *y*H<sub>2</sub>O · *z*(glyme),<sup>7</sup> Zn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> · *x*ZnCl<sub>2</sub> · *y*H<sub>2</sub>O · *z*(*t*-butanol),<sup>8</sup> Zn<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> · *x*ZnCl<sub>2</sub> · *y*(polyol) · *z*(*t*-butanol),<sup>9</sup> all of which contain both zinc chloride and a ligand. However, the catalyst used in run 3 (Table III) produced a polymer with a molecular weight of 10,930 and a polydispersity of 2.12, although it does not have zinc chloride in the complex. The catalysts

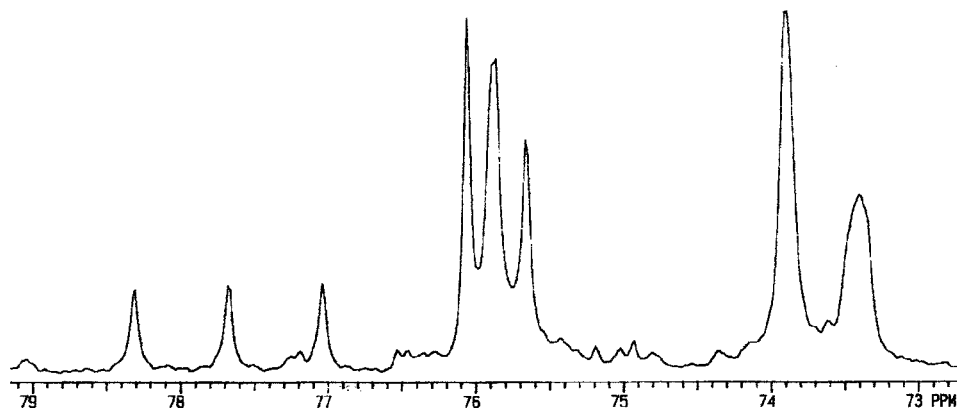
prepared from the metal acetates or metal cyanide were also active without zinc chloride and a ligand (runs 4 and 5, Table III). The structure, active site, and role of each metal of these newly synthesized catalysts are not clear at present, but it is conceivable that zinc can be complexed with the oxygen atom of the epoxide ring and can promote the ring opening of the epoxides. The polymer obtained by the DMC complex in the absence of a ligand showed a more isotactic structure (Fig. 1), compared to a nonselective catalyst such as KOH, which affords atactic polymers in the ratio of 1:2:1 for isotactic, heterotactic, and syndiotactic structures, respectively.<sup>10</sup> First, we analyzed the alcohol initiator, GPA700, to determine the number of hydroxyl groups of the synthesized polymer. As GPA700 is an adduct of glycerin and propylene oxide, it can have three terminal hydroxyl groups. This was supported by <sup>13</sup>C-NMR spectroscopy (the three carbons containing hydroxyl groups displayed signals at 66.1, 67.7, and 72.0 ppm). We believe that the polymer obtained from GPA700 and propylene oxide may have a structure similar to that of GPA700. Indeed, the <sup>13</sup>C-NMR spectrum of the polymer was almost identical with the spectrum of GPA700 (carbon signals for hydroxyl-bearing carbons occurred between 66 and 73 ppm: 66.2, 67.8, and 72.1 ppm, but the ratios of the isotactic, heterotactic, and syndiotactic structures were different). Also, the <sup>13</sup>C-NMR spectrum of the poly-

TABLE III  
Polymerization of Propylene Oxide by DMC Complexes Prepared with Different Precursors

Run	Catalyst	$M_w$	Polydispersity	Yield (%)
1	Ni(AcO) <sub>2</sub> —KCN—ZnCl <sub>2</sub>	8630	1.92	>99
2	Co(AcO) <sub>2</sub> —KCN—ZnCl <sub>2</sub>	10,600	2.82	78
3	NiCl <sub>2</sub> —KCN—Zn(AcO) <sub>2</sub>	10,930	2.12	>99
4	Ni(AcO) <sub>2</sub> —KCN—Zn(AcO) <sub>2</sub>	19,530	3.61	97
5	Ni(CN) <sub>2</sub> —KCN—Zn(AcO) <sub>2</sub> <sup>a</sup>	8810	2.64	53

Reaction conditions: 0.05 g catalyst [Co (or Ni):CN:Zn = 1:6:6], 70 mmol propylene oxide, 0.7 mmol GPA700, 10 mL *n*-hexane for 24 h at 110°C.

<sup>a</sup> Ni:CN:Zn = 1:8:6.



**Figure 1**  $^{13}\text{C}$ -NMR of poly(ether polyol) prepared by  $\text{Ni}(\text{AcO})_2\text{-KCN-Zn}(\text{AcO})_2$  catalyst (Table III, run 4). The spectrum shows the region to CH ( $\delta = 76.064$ , isotactic triad RRR or SSS;  $\delta = 75.872$ , heterotactic triad RRS or SSR;  $\delta = 75.667$ , syndiotactic triad RSR or SRS) and  $\text{CH}_2$  ( $\delta = 73.899$ , isotactic dyad RR or SS;  $\delta = 73.407$ , syndiotactic dyad RS). Integration area ratios: isotactic triad:heterotactic triad:syndiotactic triad = 0.36:0.42:0.22 and isotactic dyad:syndiotactic dyad = 0.58:0.42.

mer showed no unsaturated carbons and, thus, the degree of unsaturation is very low.

To reduce the rather wide polydispersity, the ratio of the initiator to propylene oxide was varied, and methanol was added to the system (Table IV). When the amount of the initiator was increased, the molecular weight and the polydispersity were slightly decreased (runs 1–3, Table IV). When methanol was added in small quantities, the molecular weight of the polymer was reduced and the polydispersity was narrowed (run 4, Table IV). Methanol could assist in the termination step because a protonic reagent is usually necessary for the termination of the anionic polymerization of epoxides.<sup>11</sup> However, the reaction rate and yield were reduced by the addition of methanol (run 5, Table IV).

The influence of the temperature, catalyst, and solvent on the reaction was examined, and the results are presented in Table V. When the reaction temperature was increased from 80 to 150°C, the molecular weights of the polymer increased as well as the polydispersity (runs 1–3, Table V). However, the number-average molecular weights were very similar. Since the DMC

complexes are more expensive than is a conventional basic catalyst such as KOH, and the separation of the catalyst costs more, it is important to use less catalyst. Also, if the amount of the catalyst in the poly(ether triol) is very low, it does not necessarily have to be removed from the product. In run 5, the amount of the catalyst was decreased to 20%, but the reaction was not completed after 24 h. However, when the concentration of propylene oxide was increased without any solvent, the polymerization was much faster (run 6, Table V). Note that polymerization did not take place when THF was used as a solvent with this DMC complex (run 5, Table V).

Using the new DMC catalyst prepared from  $\text{NiCl}_2\text{-KCN-Zn}(\text{AcO})_2$  ( $\text{Ni}:\text{CN}:\text{Zn} = 1:6:6$ ), we examined the polymerization of several other alkyl- or alkenyl-substituted epoxides in the presence of GPA700 as an alcohol initiator and the results are summarized in Table VI. In general, the longer alkyl or alkenyl chain-substituted epoxides required higher reaction temperatures and longer reaction times compared to pro-

**TABLE IV**  
Effect of GPA700 and Methanol in the Polymerization of Propylene Oxide

Run	GPA700–Methanol	$M_w$	Polydispersity	Yield (%)
1	1.0 mmol	13,690	3.71	97
2	1.4 mmol	11,830	3.04	>99
3	2.1 mmol	5920	2.11	90
4	0.7 mmol–30 $\mu\text{L}$	6720	2.00	>99
5	1.0 mmol–30 $\mu\text{L}$	4960	1.88	84
6	1.4 mmol–30 $\mu\text{L}^a$	4360	1.72	92

Reaction conditions: 0.05 g  $\text{Ni}(\text{AcO})_2\text{-KCN-Zn}(\text{AcO})_2$  (1:6:6) catalyst, 70 mmol propylene oxide, 10 mL *n*-hexane for 24 h at 110°C.

<sup>a</sup> Reaction time, 48 h.

**TABLE V**  
Effect of Some Reaction Variables in the Polymerization of Propylene Oxide

Run	Variable	$M_w$	Polydispersity	Yield (%)
1	Temperature, 80°C	5950	1.81	87
2	Temperature, 130°C	7490	2.52	>99
3	Temperature, 150°C	13,650	3.89	>99
4	Catalyst, 0.01 g <sup>a</sup>	7900	2.48	76
5	Solvent, THF <sup>b</sup>	—	—	0
6	Without solvent <sup>c</sup>	22,940	4.53	>99

Reaction conditions: 0.05 g  $\text{Ni}(\text{AcO})_2\text{-KCN-Zn}(\text{AcO})_2$  (1:6:6) catalyst, 70 mmol substrate, 0.7 mmol GPA700, 30  $\mu\text{L}$  methanol, 10 mL *n*-hexane for 24 h.

<sup>a</sup> Temperature, 110°C.

<sup>b</sup> Run 5 using THF as solvent.

<sup>c</sup> 210 mmol substrate and 2.1 mmol GPA700.

TABLE VI  
Polymerization of 1,2-Alkylene Oxides Catalyzed by NiCl<sub>2</sub>—KCN—Zn(AcO)<sub>2</sub> (1:6:6)

Run	1,2-Alkylene oxide	<i>M<sub>w</sub></i>	Polydispersity	Yield (%)
1	1,2-Epoxyhexane <sup>a</sup>	10,555	2.54	73
2	1,2-Epoxyhexane <sup>b</sup>	9809	2.32	99
3	1,2-Epoxy-5-hexene	18,926	3.12	77
4	1,2-Epoxy-5-hexene <sup>b</sup>	26,901	4.90	89
5	1,2-Epoxyoctane	9771	2.77	71
6	1,2-Epoxyoctane <sup>b</sup>	9825	2.21	93
7	1,2-Epoxy-7-octene	9260	2.45	80
8	Cyclopentene oxide	5290	1.95	>99
9	Cyclopentene oxide <sup>b</sup>	2719	1.05	>99
10	Cyclohexene oxide <sup>c</sup>	1576	1.02	85
11	Cyclohexene oxide <sup>b,c</sup>	1869	1.03	>99
12	<i>cis</i> -2,3-Epoxybutane <sup>d</sup>	2526	1.15	72
13	<i>cis</i> -2,3-Epoxybutane <sup>b,d</sup>	>1200	—	91
14	Styrene oxide <sup>e</sup>	10,284	2.07	>99
15	Styrene oxide <sup>b,e</sup>	>1200	—	>99

Reaction conditions: 0.0125 g catalyst, 17 mmol substrate, 0.18 mmol GPA700, 5 mL *n*-hexane for 64 h at 220°C.

<sup>a</sup> 34 mmol substrate, 1.5 mL *n*-hexane, for 47 h at 210°C.

<sup>b</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>]-ZnCl<sub>2</sub>/*t*-butanol catalyst.

<sup>c</sup> 0.36 mmol GPA700, 1.5 mL *n*-hexane.

<sup>d</sup> 8.5 mmol substrate, 0.02 mmol GPA700, without solvent.

<sup>e</sup> 5 mmol substrate, 0.02 mmol GPA700, 0.75 mL *n*-hexane.

pylene oxide. In the case of alkyl-substituted epoxides, 1,2-epoxyhexane and 1,2-epoxyoctane, the NiCl<sub>2</sub>—KCN—Zn(AcO)<sub>2</sub> catalyst and the amorphous DMC {ZnCl<sub>2</sub>—K<sub>3</sub>[Co(CN)<sub>6</sub>]/*t*-BuOH} catalyst gave similar results (runs 1, 2, 5, and 6, Table VI). But in the case of an alkenyl-substituted epoxide, 1,2-epoxy-5-hexene, the NiCl<sub>2</sub>—KCN—Zn(AcO)<sub>2</sub> catalyst produced the corresponding poly(ether triol) with a lower molecular weight but also with narrower polydispersity, compared to the previously described catalyst (runs 3 and 4, Table VI). In the case of cyclopentene oxide and cyclohexene oxide, both catalysts produced low molecular weight polymers with very low polydispersities (runs 8, 9, 10, and 11, Table VI). Interestingly, the NiCl<sub>2</sub>—KCN—Zn(AcO)<sub>2</sub> system catalyzed the polymerization of *cis*-2,3-epoxybutane and styrene oxide, giving similar results to that of cycloalkenyl oxides and alkyl-substituted epoxides, respectively (runs 12 and 14, Table VI), while the polymerization with the amorphous DMC catalyst did not proceed under the same reaction conditions (runs 13 and 14, Table VI).

## CONCLUSIONS

New DMC complex catalysts were prepared from various precursors of cobalt or nickel and zinc with potassium cyanide. These catalysts show high activity

for the polymerization of epoxides in the presence of an alcohol initiator (GPA700) without a binding ligand. The catalyst made using Ni(AcO)<sub>2</sub>—KCN—ZnCl<sub>2</sub> (Ni:CN:Zn = 1:6:6) is promising for the polymerization of propylene oxide.

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