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Double metal cyano catalyst for ring opening polymerization of propylene oxide

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Abstract A double metal cyano (DMC) catalyst is very effective for ring opening polymerization of propylene oxide (PO). The characteristics of the DMC complex were studied by Fourier transform infrared spectroscopy (FTIR) and thermogravimetry (TG). DMC complex generally result in a significant reduction of monols in the polyol production process. DMC catalyst is characterized by an approximately 1000 times higher activity compared to the conventional KOH catalyst. Disadvantages of the conventional KOH process are long reaction times, costly work-up procedures to remove the base catalyst and the formation of undesired unsaturated by-products (so called "monols") especially in the preparation of long chain polyether polyols.

Keywords Double metal · Cyano catalyst · Propylene oxide · Polymerization · Polyether polyol · TG · FTIR

Introduction

Polyether polyols together with polyisocyanates are essential components in the manufacture of polyurethanes. The commercial production of polyether polyols is conducted by ring opening polymerization of epoxides (propylene oxide (PO), ethylene oxide) with polyfunctional starter compounds. In the conventional production process, this reaction is catalyzed by strong bases (KOH). The coordinative polymerization of epoxides with double metal cyano (DMC) complex catalysts has been known for more than 40 years [1].

The best DMC catalyst is based on zinc hexacyanocobaltate [2–6]. The DMC catalyst is obtained by the reaction of an aqueous solution of potassium hexacyanocobaltate $K_3[Co(CN)_6]_2$ with an aqueous solution of $ZnCl_2$. DMC catalysts have the following general formula:

$$Zn_3\left[Co(CN)_6\right]_2 \cdot xZnCl_2 \cdot yH_2O \cdot zL \cdot wT$$

where L is functional polymer and T is organic alcohol.

Instead of Co^{3+}, very active catalysts were obtained with cyanocobaltate complexes of Fe, Cr, Pt, Ir [2–6]. These catalysts have a very high efficiency for PO polymerization, initiated by hydroxyl groups, leading to high molecular weight polyether polyols with very low unsaturation.

DMC catalysts are considered to be the ones that perform best at this time for PO polymerization initiated by hydroxyl groups. BAYER developed the first continuous process, with a very high productivity, for the synthesis of polyether polyols with DMC catalysts (IMPACT Catalyst Technology). In a short and simple production cycle, a large variety of polyether diols of very low unsaturation for elastomers, sealants, coatings and low monol content polyether triols destined for flexible polyurethane foams

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are obtained. This is one of the best developments in the last few years in the field of polyether polyols synthesis.

Thermal analysis and spectral studies are very useful techniques for materials characterization. Therefore, it is not surprising that many authors have used these techniques for the investigation of various materials [7–27]. The present paper describes TG and FTIR spectral data of prepared DMC complex.

Experimental

The experiments were performed in a 2 L PARR reactor. The experiments in Part A were based on a constant weight of both catalyst and starter and different temperature. The starter was a polyoxypropylene triol with OH number = 150 mg KOH/g. The catalyst concentrations in final polyol were generally 200 ppm. The theoretical OH number of final polyether polyol was calculated on 28 mg KOH/g.

The experiments in Part B were based on a constant reaction temperature and constant weight of starter and different concentration of catalyst. Reaction temperature was constant 140 °C.

Measurements

Thermal decomposition of the $Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yH_2O \cdot zL \cdot wT$ was performed on a NETZSCH TG 209 F1 in the temperature range 25–1000 °C in nitrogen atmosphere at a heating rate of 10 °C/min.

The FTIR spectra of investigated powder sample were recorded on a FTIR spectrometer Tensor 27 in the region 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

Results and discussion

A series of polyether polyols with DMC catalyst were prepared by two different methods using different temperature of reaction and different concentration of catalysts. The data in Table 1 are based on different reaction temperature. The data in Table 2 are based on different concentration of catalyst.

The polyether polyols were obtained and analysed. The first common characteristic of polyols for polyurethanes is the presence of terminal hydroxyl groups. The hydroxyl number is defined as the quantitative value of the amount of hydroxyl groups available for the reaction with isocyanates. The hydroxyl number is expressed as milligrams of potassium hydroxide equivalent for 1 g of the sample (mg KOH/g).

Another characterization of polyether polyols is unsaturation. Unsaturation (standard test methods ASTM D4671 [28] and ISO 17710 [29] represents the amount of terminal double bonds in polyether polyols. Unsaturation is expressed in meqv/g of sample.

The effect of different reaction temperature on final parameters of polyether polyol is presented in Table 3. The effect of different concentrations of catalyst on final parameters of polyether polyol is given in Table 4.

Table 1 Effect of temperature on polymerization rate

Sample No.	Temperature/°C	Consumption of PO/g	Time of polymerization/min	Rate of polymerization/g PO/min
1	90	827	300	2.76
2	100	827	265	3.12
3	110	827	255	3.24
4	120	827	260	3.18
5	130	827	190	4.35

PO propylene oxide

Table 2 Effect of concentration of catalyst on polymerization rate

Sample No.	Concentration of DMCC/ppm	Consumption of PO/g	Time of polymerization/min	Rate of polymerization/g PO/min
6	100	726	227	3.20
7	200	827	195	4.24
8	300	827	180	4.59
9	400	827	165	5.01
10	500	827	175	4.73

Table 3 Effect of reaction temperature on final parameters of polyether polyol

Sample No.	Temperature/ °C	OH number/ mg KOH/g	Unsaturation/ meqv/g	MWD
1	90	28.66	0.002	1.18
2	100	30.90	0.004	–
3	110	31.30	0.004	–
4	120	31.60	0.005	–
5	130	30.20	0.004	1.13

MWD molecular weight distribution (polydispersity)

Table 4 Effect of different concentration of catalyst on final parameters of polyether polyol

Sample No.	Concentration of DMCC/ppm	OH number/ mg KOH/g	Unsaturation/ meqv/g	MWD
6	100	31.70	0.007	–
7	200	28.10	0.008	1.13
8	300	31.00	0.006	–
9	400	30.80	0.006	1.13
10	500	29.30	0.004	–

MWD molecular weight distribution (polydispersity)

It was found that if the temperature of polymerization reaction is increased, the rate of polymerization is increased too (Fig. 1).

The concentration of DMC catalyst directly proportionally influences the rate of polymerization reaction at constant temperature (Fig. 2).

TG analysis

The studied compound is consists of cyano complex, molecules of zinc chloride, water, functional polymer, and organic alcohol. Therefore, the TG curve is complicated.

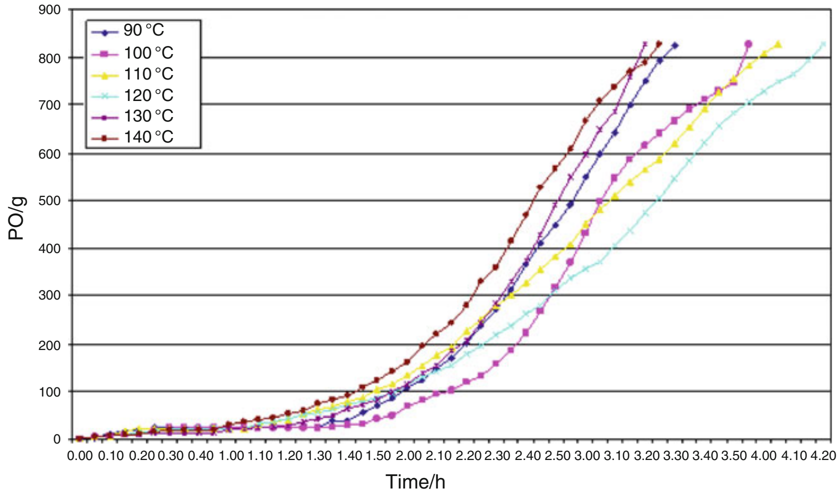
The TG curve of the prepared powder complex of $Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yH_2O \cdot zL \cdot wT$ is shown in Fig. 3. For the studied cyano complex, three main mass loss steps are observed at 90–900 °C. The thermal decomposition of studied complex starts with the emission of water molecules and/or organic components at 90–250 °C accompanied with 10.49% mass loss. The second decomposition step took place at 250–425 °C is accompanied with 24.13% mass loss and the third decomposition step took place at 425–900 °C with17.11% mass loss. These decomposition steps are related with decomposition of complicated complex, from the mass loss of water molecules, organic compounds, and the mass loss of other simple volatile compounds gradually. Residual mass 40.38% include simple inorganic metal compounds.

FTIR spectroscopy

The FTIR spectral analysis of the studied cyano compex has been carried out between 400 and 4000 cm^{-1} and the spectrum is shown in Fig. 4. The FTIR spectrum of the studied compound showed a broad band at around 3486 cm^{-1}. This frequency corresponds to the asymmetric and symmetric OH stretching. This broad band confirm the presence of crystal water in this compound. The weak band at around 3100 cm^{-1} and the sharp band at around 1617 cm^{-1} are assigned to H_2O stretching vibrations. The absorption band within the range of 2976–2900 cm^{-1} can be assigned to stretching vibrations of C–H groups from organic alcohol or functional polymer. The sharp band around 2194 cm^{-1} assigned stretching vibrations of CN group.

Upon coordination to a metal, the v(CN) shift to higher frequencies. The CN^- ion acts as a σ-donor by donating electrons to the metal and also as a π-acceptor by accepting electrons from the metal [30]. In addition to v(CN), the studied cyano complex also exhibits v(MC) and δ(MCN).

Fig. 1 Effect of different temperature on rate of polymerization reaction



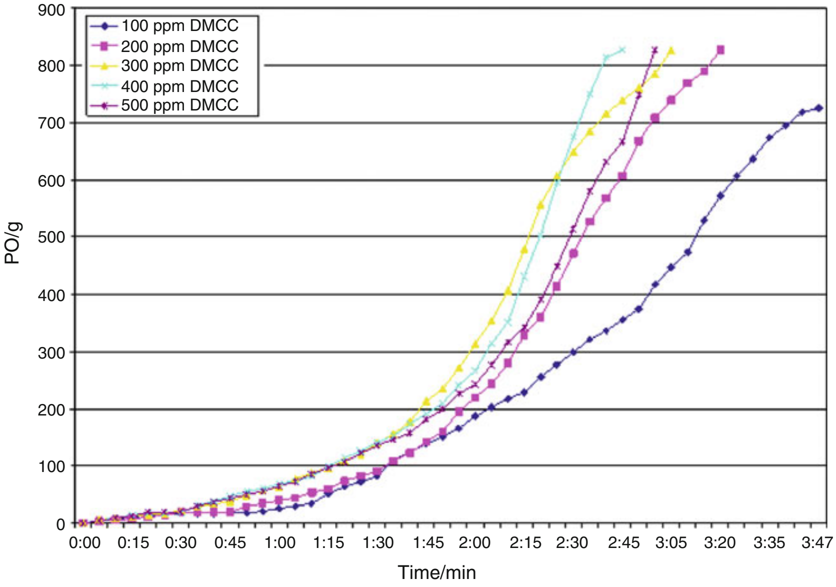


Fig. 2 Effect of different concentration of catalyst on rate of polymerization reaction at constant temperature

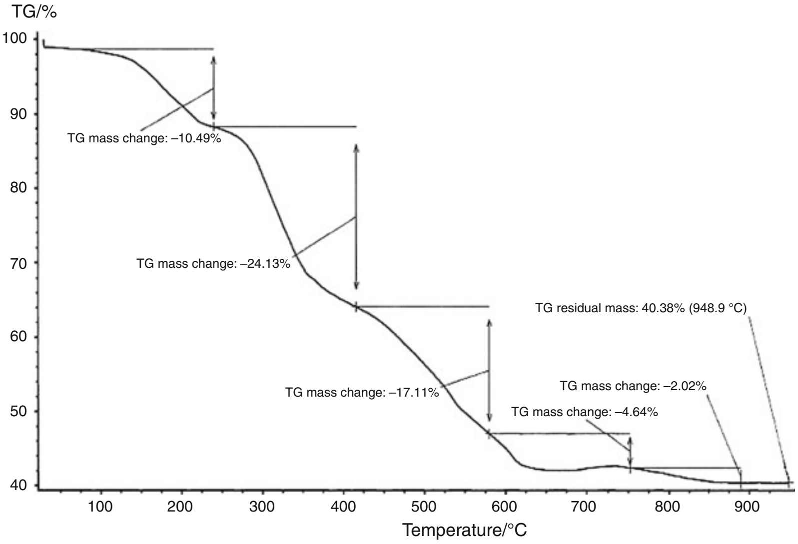


Fig. 3 TG curve of the prepared cyano complex $Zn_3[Co(CN)_6]_2\cdot xZnCl_2\cdot yH_2O\cdot zL\cdot wT$

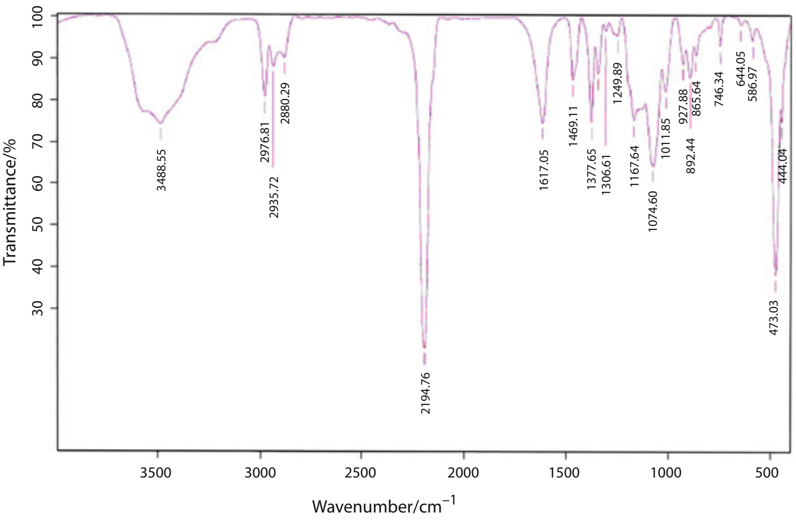


Fig. 4 FTIR analysis of the prepared cyano complex $Zn_3[Co(CN)_6]_2\cdot xZnCl_2\cdot yH_2O\cdot zL\cdot wT$

Conclusions

The preparation routes and conditions such as temperature and the concentration of DMC catalyst have significant effect on the quality of final polyether polyol. The results of the present work demonstrate that catalytic activity values were strongly dependent on reaction temperature and different concentration of DMC catalyst.

DMC catalyst has excellent activity for the ring opening polymerization of PO and gives polyether polyols with a narrow molecular weight distribution (M_w/M_n) and very low unsaturation.

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