

Communications

Modified Montmorillonite as a Tuner of Propylene Oxide Polymerization Behavior Catalyzed by Double Metal Cyanide Compound

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Introduction

Double metal cyanide (DMC) complexes based upon $Zn_3[Co(CN)_6]_2$ framework are well-known catalyst for the polymerization of propylene oxide (PO) to produce poly(propylene oxide) polyol (PPG), one of the main raw materials in a wide range of polyurethane applications.¹

Recent improvements have made DMC catalysts much more attractive for commercial manufacture of polyether polyols since they give high-quality PPG products that have low unsaturation level (UL) resulting in monols, narrow molecular weight distribution (MWD) and low viscosity, especially compared to conventional base catalysts such as KOH.¹ While DMC catalysts offer attractive advantages over most widely used base catalysts, they must be activated for a long time before the polymerization starts.^{1,2} This long induction period (IP), e.g. several hour, increases cycle time and therefore undercuts the economic advantage of DMC catalysts. In addition, heating the catalyst for a prolonged period at high polymerization temperature above 100 °C can reduce its activity or deactivate it completely.²

In this communication, we show our preliminary results how to tune polyol properties as well as activity and IP of DMC-catalyzed PO polymerizations by combining DMC catalyst with modified montmorillonite (m-MMT) as a simple external additive.

Results and Discussion

Typical DMC catalyst using tert-butanol (t-BuOH) as a complexing agent has been prepared according to the litera-

ture procedures.¹¹ Elemental analyses confirmed the DMC compound has a molecular formula, $Zn_{2.3}Cl_{1.0}[Co(CN)_6]_{1.0} \cdot 2.0 t\text{-BuOH} \cdot 1.0 H_2O$. In highly crystalline Prussian blue analogue, $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$, prepared in the absence of t-BuOH, charge balance with the Zn^{2+} ions leads to vacancies at one-third of the $[Co(CN)_6]^{3-}$ sites in the framework.² The water molecules fill the resulting cavities as Zn^{2+} -bound and solvate.³ If complexing agents such as t-BuOH are used, they also be able to interact with the open coordination sites on the Zn^{2+} ions arising upon substitution of the bound water molecules.

The complexation of t-BuOH may result in framework collapse.^{2,3} PO polymerization runs with the crystalline $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ compound showed no activity, demonstrating the complexing agent and the crystal structure of the compound play important roles in the polymerization. Detailed characterizations of DMC catalyst including IR, x-ray photoelectron spectroscopy, and x-ray powder diffraction were reported elsewhere.²

The performance of the DMC catalyst for PO polymerization was tested by semi-batch runs carried out at 115 °C by using difunctional PPG (MW = 700) as a starter. As illustrated in Figure 1(a), the DMC catalysts show high activity (maximum rate of polymerization $R_{p,max} = 2,587$ g-polymer/

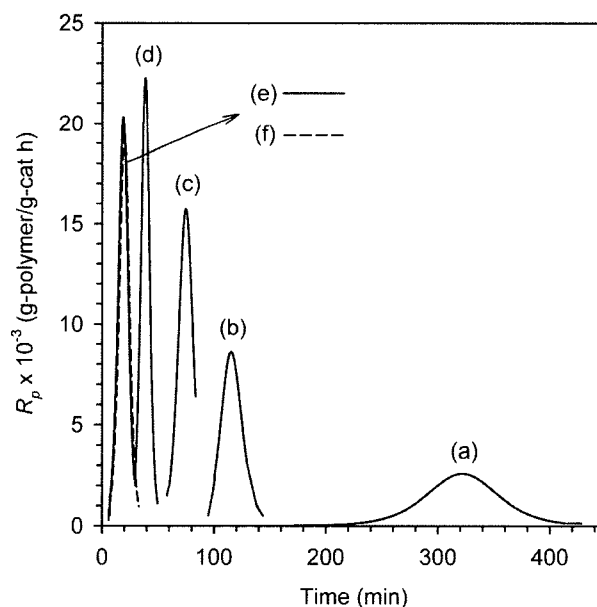
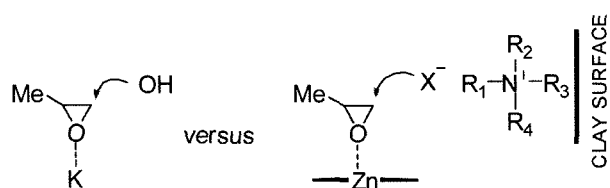


Figure 1. Polymerization rate profile obtained by DMC catalyst at 115 °C (a) and those by DMC catalyst combined with various mMMTs modified by (b) $[M_2(EH)_2(HT)_1N]^+(MSO_4)^-$, (c) $[(HE)_2M_1T_1N]^+Cl^-$, (d) $[M_2B_1(HT)_1N]^+Cl^-$, (e) $[M_1(HT)_2NH]^+(HSO_4)^-$, and (f) $[M_2(HT)_2N]^+Cl^-$. Polymerization conditions: temperature = 115 °C, PPG starter = 70 g, catalyst = 0.1 g, and MMT = 0.5 meq modifier ($[modifier]/[Zn] = 1.25$).

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Scheme I. Comparison of activation of KOH catalyzed PO polymerization with that of DMC catalyzed polymerization combined with m-MMTs.

g-cat h) once it is activated. Taking a careful look at the rate profiles, it is evident that it needs a long IP before polymerization starts. The time to reach $R_{p,max}$ is 321 min. In spite of numerous trials to solve this shortcoming of DMC catalysts by controlling preparation parameters as well as by screening of their compositions, successful results haven't been reported.¹

In order to overcome these problems we revisit the mechanism of PO polymerization initiated KOH catalyst, where no induction period observes (Scheme I). Assuming potassium atom is corresponding to zinc atom, we propose an idea to speed up the activation. As the OH anions make nucleophilic attack to make the PO monomer ring opened, the addition of the second anionic species together with the DMC catalyst may help fast activation. This was tested by using m-MMT. There are a number of commercially available m-MMTs (Southern Clay Products) modified with quaternary ammonium compounds with different chain length and anion. The m-MMTs used were modified with $[M_2(HT)_2N]^+Cl^-$ ($d_{100} = 31.5 \text{ \AA}$), $[M_1(HT)_2NH]^+(HSO_4)^-$ (23.6 \AA), $[M_2B_1(HT)_1N]^+Cl^-$ (19.2 \AA), $[M_2(EH)_2(HT)_1N]^+(MSO_4)^-$ (18.6 \AA), and $[(HE)_2M_1T_1N]^+Cl^-$ (18.5 \AA), where M = methyl, T = tallow, HT = hydrogenated tallow, B = benzyl, EH = 2-ethylhexyl, and HE: 2-hydroxyethyl.

Figure 1 shows rate profiles of PO polymerizations obtained by DMC/m-MMT binary catalysts. It is evident that binary catalyst systems combining DMC catalyst with m-MMT are a simple and efficient way of tuning IP as well as activity. The IP as a time to $R_{p,max}$ becomes short from 321 min for DMC alone to 19 min for DMC/ $[M_2(HT)_2N]^+Cl^-$ m-MMT binary catalyst (Table I). In addition, the catalytic activity increases remarkably by simply combining small amount of m-MMT. For example, the $R_{p,max}$ value reaches to 22,260 g-polymer/g-cat h for DMC/ $[M_2B_1(HT)_1N]^+Cl^-$ m-MMT catalyst. In general, considering both IP and activity, m-MMTs with larger d_{100} values give better results, most probably due to relatively facile delamination during the early period of polymerization. Control polymerization tests with only m-MMTs in the absence of DMC catalyst gave no activities, indicating m-MMT alone cannot initiate PO polymerization.

Investigation on the effect of m-MMT amount on poly-

Table I. Results of PO Polymerizations Catalyzed by DMC Catalyst and DMC/m-MMT Binary Catalysts^a

Modifier	$R_{p,max}^b / t_{max}^c$	M_n^d	MWD ^e	Unsat. ^e (meq/g)	Vis. ^f (cP)
Not added	2,587/321	3,700	1.43	0.017	1,790
$M_2(EH)_2(HT)_1N$	8,617/115	7,100	1.24	0.010	1,130
$(HE)_2M_1T_1N$	1,5729/74	6,900	1.38	0.010	1,170
$M_2B_1(HT)_1N$	2,2260/38	6,600	1.33	0.011	1,250
$M_1(HT)_2NH$	1,9312/20	6,900	1.36	0.007	1,300
$M_2(HT)_2N$	2,0347/19	6,400	1.43	0.008	1,380

^aConditions are given in Figure 1. ^bIn g-polymer/g-cat h. ^cTime (min) to reach $R_{p,max}$. ^dMeasured by GPC at 25°C in THF. ^eUnsaturation level of polyols measured by ASTM D2847. ^fViscosity measured by a Brookfield viscometer model DV III (Brookfield Instruments), with a spindle no. 21.

merization was made by changing the amount of m-MMT modified with $[M_2(HT)_2N]^+Cl^-$ from 0.024 g (corresponding to 0.03 meq of modifier; $[modifier]/[Zn] = 0.075$) to 0.8 g (1.0 meq of modifier; $[modifier]/[Zn] = 2.5$) at the similar conditions employed in Figure 1. The catalytic activity (as $R_{p,max}$) increases remarkably from 2,587 with DMC alone to 15,722 g-polymer/g-cat h by combining with very small amount of m-MMT (0.024 g). It increases monotonously to 17,246, 18,611, and 19,561 g-polymer/g-cat h when the amount of m-MMT is 0.06, 0.12, and 0.3 g, respectively, and the highest activity (20,797 g-polymer/g-cat h) was recorded at around 0.32 g of m-MMT ($[modifier]/[Zn] \approx 1$) and then reached to asymptotic values at larger amount of m-MMT (e.g. 19,845 g-polymer/g-cat h at 0.8 g of m-MMT), suggesting a typical Langmuir-type dependence of the activity on $[m-MMT]$.

m-MMT also improved important polymer properties (Table I) such as MW, viscosity and UL. The UL of polyol produced by DMC (0.017 meq/g) decreases remarkably by combining with m-MMT. For example, DMC/ $[M_1(HT)_2NH]^+(HSO_4)^-$ m-MMT produces polyol with ultra low UL, 0.007 meq/g. The MW value of polyols increases from $M_n = 3,700$ to larger than 6,000 by combining with m-MMT. All polyols are featured by narrow MWD, from 1.24 to 1.43. The viscosity of polymer also decreases by combining with m-MMTs.

In summary, we showed that DMC-catalyzed PO polymerization behavior is tunable by combining with various m-MMTs as external additives. Thus, (1) they make the zinc-monomer bond faster activated during the initial stage of polymerization, (2) they make the zinc-monomer bond more active, (3) they stabilize the polymerization centers and prevent their decomposition, and (4) they improve important polymer properties such as molecular weight, viscosity and UL.

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