Polyester polyol synthesis by alternating copolymerization of propylene oxide with cyclic acid anhydrides by using double metal cyanide catalyst

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ABSTRACT

Ring-opening copolymerizations of propylene oxide (PO) with cyclic acid anhydrides, succinic anhydride (SA), maleic anhydride (MA) and phthalic anhydride (PA) were carried out in the presence of a double metal cyanide (DMC) catalyst of molecular formula Zn2.3Cl1.0[Co(CN)6]1.0·2.0BuOH·1.0H2O as a means of developing functional polyols bearing ester backbones. Uniform alternating copolymers are produced when [PO]([anhydride]) in the copolymer approaches unity. All resulting copolymers have moderate molecular weights (Mn = 2300–10,600) and a narrow polydispersity index (1.02–1.49). The apparent reactivity ratio of PO is 0.34, 0.28, and 0.26 for PO/SA, PO/MA, and PO/PA copolymerizations, respectively, assuming that the reactivity ratio of the anhydrides is zero. The DMC-catalyzed PO copolymerizations with anhydrides are an efficient way to produce polyester polyols, expanding the versatility of conventional polyols.

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1. Introduction

Polyurethane (PU) elastomers have excellent abrasion resistance and exhibit properties of both rubber and plastics. It has been well known that conventional PUs produced by using polyester polyol exhibit excellent physical properties, such as impact, low temperature, and weather resilience. However, they are inferior in the tensile strength, abrasion resistance, and heat resistance to PUs obtained from polyester polyols [1–5]. Accordingly, much effort has been made for many years to improve the strength and heat resistance of PUs while maintaining their good physical properties based on the polyester polyols.

Efforts have been made to employ a modified polyester polyol obtained by esterification of a usual polyester polyol, or to employ a polyol mixture obtained by mixing a polyester polyol and a specific polyester polyol [6–7]. However, the physical properties of PUs produced by utilizing these polyols are not satisfactory. Furthermore, it is very difficult to synthesize polyester polyols with esterified terminals using the same catalyst and conventional techniques [8]. Namely, if one uses a strong base catalyst for terminal esterification, one obtains a polyol with a very wide molecular weight distribution and a substantial amount of byproducts containing short chain polyester components due to the ester exchange reaction, which substantially reduces the impact resilience, compression permanent set, etc. of the flexible PU foam obtainable from such polyols [6–8].

The copolymerization of cyclic anhydride (AA) with a cyclic ether was an easy and economic candidate to overcome these drawbacks and was thus tested by Inoue et al. in 1969 with diethyl zinc as a catalyst [9]. Ring-opening copolymerization of propylene oxide (PO) with maleic anhydride (MA) was also reported by several research groups who used simple organometallic complexes based on zinc [10], aluminum [11], magnesium [12], and iron [13]. Recently, Coates and coworkers demonstrated a highly active catalyst for the alternating copolymerization of a range of epoxides and cyclic anhydrides [14]. However, all of these catalytic systems showed only moderate activities or required tedious synthesis procedures that might not be commercially acceptable.

Double metal cyanide (DMC) complexes, which are the reaction products of a water-soluble metal salt and a water-soluble metal cyanide salt, are well-known catalyst for the polymerization of epoxides and for the synthesis of propylene oxide (PO)-based polyester polyols, which are used in a wide range of PU applications [15]. Recent improvements have made DMC catalysts much more attractive for the commercial manufacture of polyester polyols since they give high-quality poly(propylene glycol) (PPG) products with a low level of unsaturation, high molecular weight (MW) narrow polydispersity and low viscosity, especially compared to those produced by conventional base catalysts [16]. The ring-opening copolymerization of maleic anhydride (MA) with propylene oxide PO was successfully carried out by using the DMC catalyst, which yielded uniform alternating copolymers [17]. However, no starters...
(or initiators) generating chain-end hydroxyl group and controlling the functionality of the resulting polyols were utilized in this study.

In this article, three kinds of cyclic acid anhydrides, MA, succinic anhydride (SA) and phthalic anhydride (PA), were selected for ring-opening copolymerizations with PO, resulting in both ether and ester units in the macromolecular backbone. Although there are a number of possible DMC formulations, we chose a Zn–Co DMC complex because of its catalytic activity and anhydride reactivity. The kinetics of the copolymerizations were presented and discussed. The structure of the copolymers was characterized by spectroscopy, and the MW and polydispersity of the copolymers were measured by gel permeation chromatography (GPC).

2. Experimental

2.1. Materials

The DMC complex of the molecular formula Zn$_{2.3}$Cl$_{1.0}$[Co(CN)$_6$]$_{1.0}$·2.0BuOH·1.0H$_2$O was prepared and characterized according to our previously reported method [18]. All materials, such as MA, PA and SA, are analytically pure grade reagents purchased from Aldrich that were purified by recrystallization from benzene. Glutaric anhydride (GA) was purified by recrystallization from acetic anhydride. PPG (MW = 700; PPG-700) was used as an initiator (or starter), and the polymerization grade of PO was donated by Kumho Petrochem. Co. (Korea).

2.2. Bulk copolymerization of PO with acid anhydrides

Semi-batch bulk copolymerizations of PO with cyclic acid anhydrides were carried out in a 1-L autoclave (Parr). The reactor was charged with 70 g of bifunctional PPG-700 as a starter and 50 mg DMC catalyst and then purged several times with nitrogen. The mixture was heated to 100 ºC and evacuated for 6 h with vigorous agitation to remove traces of moisture from the reaction mixture. Then, 10 g of PO/AA mixture of predetermined composition was introduced into the reactor at 110 ºC. When the pressure drop in the reactor accelerated, indicating the activation of the catalyst, suitable amounts of the PO/AA mixture were continuously introduced into the reactor, keeping the reactor pressure constant. The polymerizations were stopped when there were no pressure changes in the reactor or when the total amount of added monomer reached 400 g. The copolymer product was obtained after the removal of unreacted PO and AA monomers under vacuum and by extraction, respectively. The composition of PO and AA in the copolymer was calculated by the quantitative integration of OCH (ester; 5.12–5.25 ppm), OCH$_2$ (ester; 4.15–4.25 ppm) and OCH$_3$ (ether; 3.42–3.55 ppm) protons from the $^1$H NMR spectrum.

Homopolymerizations of PO were also performed in similar procedures in the absence of AA comonomers.

2.3. Characterizations

Infrared (IR) spectra were recorded for film samples cast on KBr disks from THF solution on a Shimadzu IR Prestige-21 spectrophotometer with 32 scans per experiment at a resolution of 1 cm$^{-1}$. $^1$H NMR spectra of the copolymers were obtained by a Varian Gemini 2000 & HPSP with CDCl$_3$ as solvent. MW and polydispersity index (PDI) were measured using a Waters 150 instrument operated at 25 ºC, with 10$, 10^2$, and 500 Å columns in THF. Poly(ethylene glycol) standards with low polydispersity were used to generate a calibration curve.

3. Results and discussion

The DMC compounds are prepared from a water-soluble metal salt and a water-soluble metal cyanide salt in the presence of suitable complexing agents. The water-soluble metal salts have the general formula $\text{MX}_n$, in which $M$ is selected from Zn$^{II}$, Fe$^{II}$, Co$^{II}$, and Ni$^{II}$. $X$ is typically a halide, hydroxide, sulfate, carbonate, cyanide, or oxalate anion [16]. The water-soluble metal cyanide salts usually have the general formula $\text{K}_m\text{M}^+\text{CN}_n$ in which $\text{M}^+$ is $\text{Co}^{II}$, $\text{Co}^{III}$, $\text{Fe}^{II}$, $\text{Fe}^{III}$, $\text{Cr}^{III}$, $\text{Ir}^{III}$, or $\text{Ni}^{II}$. The water-soluble metal cyanide salt can contain one or more of these metals. Both $a$ and $b$ are integers greater than or equal to 1, balancing the charge of $M$. The resulting DMC compounds possess structures based on a simple cubic $\text{M}^{n+}\text{CN}_m$ framework in which octahedral $[\text{M}^{n+}\text{CN}_m]^n$ complexes are linked via octahedrally coordinated, nitrogen-bound $\text{M}^{n+}$ ions in the $\text{M}^{n+}$–CN–M–complexing agent (CA) [16]. Generally, organic CAS such as alcohols and ethers are complexed to the catalyst matrix to enhance catalytic activity. Although there are many possible catalyst formulations using different $M$ and $M’$, DMC catalysts comprised of Zn as $M$ and Co as $M’$ are known to be the most active and economic, and thus have been widely studied [16,18,19]. Accordingly, we chose the same system for the investigation of PO/AA copolymerizations.

The DMC catalyst of molecular formula Zn$_{2.3}$Cl$_{1.0}$[Co(CN)$_6$]$_{1.0}$·2.0BuOH·1.0H$_2$O, prepared from the reaction of zinc(II) chloride (ZnCl$_2$) and potassium hexacyanocobaltate(III) $(\text{K}_3[\text{Co(CN)}_6]_2)$ in the presence of BuOH as a complexing reagent showed high activity in semi-batch homopolymerizations of PO at the temperature above 70 ºC (Fig. 1). The properties of the resulting polyether polyols are summarized in Table 1. Upon investigation of the rate profiles of PO polymerizations and the results of the polymer analyses, the DMC catalyst is characterized by (1) a long induction period that increases as the temperature increases, (2) very high activity once it is activated, (3) ultra-low unsaturation levels (0.0018–0.0022 meq/g), (4) high MW and a polydispersity index (PDI) that slightly decrease as the temperature increases, and (5) very low viscosity that is favorable for the handling of the product. Note that this type of polyether polyol featured by high
MW and ultra-low unsaturation is not achievable with conventional base catalysts, which is one of the reasons behind our investigation of the PO/AA copolymerizations. Although the insolubility of the DMC catalyst made intensive investigations on the characteristics of active sites difficult, especially using spectroscopic methods, we gathered some evidence that the DMC-catalyzed polymerizations present both cationic and coordinative characteristics of active sites difficult, especially using spectroscopic approaches superimposed on the thermodynamic factor. The approach of propagating active sites to a monomer molecule is sterically hindered. The propagation step is extremely slow because of steric interaction between the β-substituent of the propagating sites and the two substituents of the incoming 1,2-disubstituted monomers.

The copolymerizations of PO with MA, SA and PA were performed at 110 °C by employing similar procedures used for the homopolymerizations. The results of the copolymerizations are summarized in Table 2. As a control, the copolymerization of PO with GA with six-membered ring was also carried out (run no. 20). Compared to AAs with five-membered ring, it shows much lower activity, probably due to the structural stability that makes the ring-opening reactions difficult. The DMC catalyst showed only negligible copolymerization activity when the molar feed ratio of monomer is above 0.1.

Copolymerization between monomers containing different functional groups is usually selective. One of the cross-propagation steps in a contemplated copolymerization may be highly unfavorable because of the wide variations in the types of propagating centers involved and because of the energies of the bonds being broken during propagation. Copolymerization between certain types of monomers does not occur and that between others is difficult to achieve, while some copolymerizations occur with relative ease. Thus, the combination of a lactam with any other type of monomer, such as a lactone, epoxide, or alkene, is incompatible because of differences in their propagation mechanisms. For example, the anionic copolymerization of a lactam with an epoxide does not occur because the anion derived from the epoxide terminates by proton abstraction from the lactam monomer.

Epoxides readily undergo anionic copolymerization with lactones and cyclic anhydrides because the propagation centers are similar—alkoxide and carboxylate [20–24]. Most of the polymerizations show alternating behavior with the formation of polyester, but the mechanism for alternation is unclear. There are few reports of cationic copolymerizations of lactones and cyclic ethers other than the copolymerizations of β-propiolactone.

Table 1
Analytical results of polyether polyols produced with double metal cyanide catalysts. Conditions: catalyst = 50 mg, poly(propylene glycol) (Mn = 700) starter = 70 g, and no solvent.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>GPC Mn (g/mol)</th>
<th>PDI</th>
<th>Unsat. level (meq/g)</th>
<th>OH value (mg KOH/g)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>5900</td>
<td>1.12</td>
<td>0.0022</td>
<td>19.1</td>
<td>5874</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>6100</td>
<td>1.25</td>
<td>0.0022</td>
<td>18.8</td>
<td>5967</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>6200</td>
<td>1.18</td>
<td>0.0019</td>
<td>18.5</td>
<td>6063</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>6500</td>
<td>1.31</td>
<td>0.0018</td>
<td>17.7</td>
<td>6339</td>
</tr>
</tbody>
</table>

Table 2
Results of copolymerizations of propylene oxide with cyclic acid anhydrides (AAs) using double metal cyanide catalyst at 110 °C. Conditions: catalyst = 50 mg, poly(propylene glycol) (Mn = 700) starter = 70 g, and no solvent.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Temp. (°C)</th>
<th>Molar feed ratio (PO/AA)</th>
<th>Reaction time (min)</th>
<th>Yield (%)</th>
<th>GPC Mn (g/mol)</th>
<th>PDI</th>
<th>Copolymer composition (PO/AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>110</td>
<td>10.0/0.0</td>
<td>422</td>
<td>99.0</td>
<td>5900</td>
<td>1.12</td>
<td>100.0/0.0</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>90.0/10.0</td>
<td>373</td>
<td>88.0</td>
<td>7000</td>
<td>1.42</td>
<td>80.6/19.4</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>80.0/20.0</td>
<td>201</td>
<td>75.8</td>
<td>6900</td>
<td>1.38</td>
<td>69.6/30.4</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>70.0/30.0</td>
<td>183</td>
<td>79.0</td>
<td>6900</td>
<td>1.26</td>
<td>64.5/35.5</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>60.0/40.0</td>
<td>125</td>
<td>65.8</td>
<td>4300</td>
<td>1.16</td>
<td>60.1/39.1</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>50.0/50.0</td>
<td>122</td>
<td>35.9</td>
<td>3500</td>
<td>1.17</td>
<td>57.3/42.7</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>40.0/60.0</td>
<td>89</td>
<td>23.3</td>
<td>2700</td>
<td>1.07</td>
<td>55.3/44.7</td>
</tr>
<tr>
<td>8</td>
<td>90</td>
<td>90.0/10.0</td>
<td>354</td>
<td>85.7</td>
<td>7100</td>
<td>1.49</td>
<td>86.5/13.5</td>
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<tr>
<td>9</td>
<td>80</td>
<td>80.0/20.0</td>
<td>315</td>
<td>82.7</td>
<td>5400</td>
<td>1.33</td>
<td>73.2/26.8</td>
</tr>
<tr>
<td>10</td>
<td>70</td>
<td>70.0/30.0</td>
<td>228</td>
<td>77.5</td>
<td>4900</td>
<td>1.31</td>
<td>61.2/38.8</td>
</tr>
<tr>
<td>11</td>
<td>60</td>
<td>60.0/40.0</td>
<td>166</td>
<td>73.9</td>
<td>4700</td>
<td>1.26</td>
<td>57.4/42.6</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>50.0/50.0</td>
<td>118</td>
<td>34.5</td>
<td>3200</td>
<td>1.10</td>
<td>56.0/44.0</td>
</tr>
<tr>
<td>13</td>
<td>40</td>
<td>40.0/60.0</td>
<td>72</td>
<td>29.6</td>
<td>3100</td>
<td>1.10</td>
<td>51.3/48.7</td>
</tr>
<tr>
<td>14</td>
<td>90</td>
<td>90.0/10.0</td>
<td>252</td>
<td>92.3</td>
<td>6700</td>
<td>1.35</td>
<td>85.7/14.3</td>
</tr>
<tr>
<td>15</td>
<td>80</td>
<td>80.0/20.0</td>
<td>155</td>
<td>90.2</td>
<td>6200</td>
<td>1.32</td>
<td>73.8/26.2</td>
</tr>
<tr>
<td>16</td>
<td>70</td>
<td>70.0/30.0</td>
<td>148</td>
<td>76.5</td>
<td>5400</td>
<td>1.24</td>
<td>57.8/42.2</td>
</tr>
<tr>
<td>17</td>
<td>60</td>
<td>60.0/40.0</td>
<td>123</td>
<td>60.0</td>
<td>4200</td>
<td>1.21</td>
<td>60.8/39.2</td>
</tr>
<tr>
<td>18</td>
<td>50</td>
<td>50.0/50.0</td>
<td>85</td>
<td>41.5</td>
<td>4200</td>
<td>1.19</td>
<td>56.5/43.5</td>
</tr>
<tr>
<td>19</td>
<td>40</td>
<td>40.0/60.0</td>
<td>67</td>
<td>29.2</td>
<td>2200</td>
<td>1.03</td>
<td>51.4/48.6</td>
</tr>
<tr>
<td>20</td>
<td>95</td>
<td>95.0/5.0</td>
<td>61</td>
<td>26.5</td>
<td>6400</td>
<td>1.51</td>
<td>84.3/15.7</td>
</tr>
</tbody>
</table>

*a* Duration of copolymerization recorded when the polymerization was stopped, since there was no pressure change in the reaction mixture.

*b* Weight ratio of reactants introduced to product obtained.

*c* Obtained by gel permeation chromatography.

*d* Calculated by $^1$H NMR spectroscopy.
with tetrahydrofuran and 3,3-bis(chloromethyl)oxetane, probably indicative of the difference in propagating centers (dioxocarboxylation and oxonium ion, respectively) [25,26]. The copolymerizations tend toward ideal behavior with the product containing large amounts of the cyclic ether.

Since the DMC catalyst was first activated in the presence of PPG starter, the general scheme of the copolymerizations to yield polyetherester (PEE) polyols consisting of both ether and ester backbones can be summarized as shown in Fig. 2. Considering the homopolymerizations of AAs are impossible with the DMC catalyst, alternating copolymers with ester backbones are intrinsically formed as major products; however, a large proportion of ether linkages is also expected, especially when the amount of PO chains is larger than the number of anhydride chains due to the homopolymer units of PO. To gain insight on the structure of the copolymer, IR spectra of the copolymers were recorded. Fig. 3 shows the IR spectra of the copolymers. All copolymers show some characteristic absorptions exhibiting the existence of an ester backbone: i.e., saturated, unsaturated or aromatic polyester at 1730 cm\(^{-1}\) \([\text{ester}]\), 1213 and 1164 cm\(^{-1}\) \([\text{ester}]\), which are not observed in the IR spectrum of the PO homopolymer. The alkenyl C–C stretching absorption of poly(PO-co-MA) and the aromatic C=C bending absorption of poly(PO-co-PA) are observed at 1640 and 1600 cm\(^{-1}\) respectively. The characteristic absorptions exhibiting the existence of ether backbones [i.e., 1082 and 1113 cm\(^{-1}\) \([\text{ether}]\)] are also observed not only in PO homopolymer, but in all copolymers. It is interesting to note that the no characteristic absorptions of polyanhydride at around 1810 cm\(^{-1}\) appear in the IR spectra of any of the copolymers, indicating no existence of AA homopolymer units. All polymers show broad absorptions at around 3500 cm\(^{-1}\) assigned to alcoholic OH, demonstrating that they are all \(\alpha,\omega\)-hydroxylated polymers. Since a bifunctional PPG starter was used for the polymerizations, all resulting polymers are assumed to be bifunctional polyols that are applicable as raw materials of PU elastomer.

All of the above structural features of the copolymer are also identified by \(^1\)H NMR spectra. Fig. 4 shows the \(^1\)H NMR spectra of poly(PO-co-SA) (run no. 4 in Table 2), poly(PO-co-MA) (run no. 10), and poly(PO-co-PA) (run no. 16). All suitable assignments are marked in Fig. 4. As an example, the characteristic peaks for poly(PO-co-MA) appear at 6.23–6.29 ppm \([\text{CH}=\text{CH}]\), 5.12–5.25 ppm \([\text{OCH (ester)}]\), 4.15–4.25 ppm \([\text{OCH}_2 (\text{ester})]\), 3.42–3.55 ppm \([\text{OCHCH}_2 (\text{ether})]\), 1.29–1.33 ppm \([\text{–CH}_3 (\text{ester})]\), and 1.12–1.18 ppm \([\text{–CH}_3 (\text{ether})]\). Considering these spectroscopic assignments and the fact that no homopolymerizations are possible with cyclic anhydrides, the polyester backbones are composed of cyclic AA–PO alternating segments and partial PO self-propagation segments generating polyether backbone segments. Accordingly, as the ratio of cyclic anhydride/PO approaches to unity, the alternating characteristics of the copolymers are expected to become more perfect.

The MW values of the resulting polyester polyols are higher than those of PO homopolymer (polyether polyol; run no. 1 in Table 2) when the amount of AA unit in the copolymer is small; however, they decrease monotonously with a large amount of AA.

---

**Fig. 2.** Proposed structures of polyetherester polyols produced by the copolymerizations of propylene oxide with cyclic acid anhydrides in the presence of poly(propylene glycol) starter.
unit. All copolymers are characterized by narrow PDI, ranging from 1.02 to 1.49. The PDI values increases slightly as the MW increases in a same series of copolymerizations. The small PDI value of the homo- and copolymers can generally be achieved by controlled ionic polymerization in a living mode. In this sense, it is interesting to note a mechanistic pathway of DMC catalysis resulting in such a narrow PDI. Since we used a large excess of initiator (0.1 mol) in comparison to catalyst (50 mg), initiator-to-catalyst molar ratios over 10^3 were reached. Accordingly, it is impossible to assume that all chains were grown in a living mode like controlled anionic polymerization. It is therefore reasonable to assume that rapid exchange reactions between the dormant and active sites account for the control of the MW and the narrowing of PDI. As a result of the exchange reactions, the dormant sites and transient dead-polymer chains that can be rapidly reactivated are generated. If the exchange reaction is faster than the propagation reaction, the number of growing polymer chains stays constant depending on the initial amount of initiator, resulting in polymers of small PDI values.

The identification of copolymer composition is an important factor in the evaluation of utility [27,28]. The theory of radical copolymerization leads to the conclusion that the copolymer composition and its distribution are dependent on the monomer reactivity ratios. Reactivity ratios may be evaluated by linear procedures, nonlinear procedures, and other copolymer composition equations. The Kelen–Tüdös method has been widely used [29]. The monomer reactivity ratios for the copolymerizations of PO with cyclic AAs were determined from the monomer feed ratios and the copolymer compositions that are measured by NMR analysis. The apparent reactivity ratio of PO \( r_{\text{PO}} \) was calculated by the Kelen–Tüdös method from Eq. (1), assuming the reactivity ratio of acid anhydride \( r_{\text{AA}} \) is zero:

\[
\frac{x(y - 1)}{2y + x^2} = \frac{r_{\text{PO}}x^2}{2y + x^2} = \frac{r_{\text{PO}}x^2}{2y + x^2} \quad (1)
\]

where \( x = M_{\text{PO}}/M_{\text{AA}} \) (mol/mol), the ratio of molar fractions of PO and AA in the feed, \( y = dM_{\text{PO}}/dM_{\text{AA}} \) (mol/mol), the ratio of molar fractions of PO and AA in the copolymer, and \( x \) is an equation parameter that is calculated according to Eq. (2).

\[
x = \sqrt{\frac{x_{\min} \cdot x_{\max}}{y_{\min} \cdot y_{\max}}} \quad (2)
\]

where \( x_{\min} \) and \( x_{\max} \) are minimal and maximal molar fractions in the feed, respectively; \( y_{\min} \) and \( y_{\max} \) are minimal and maximal molar fractions in the copolymer. Transform Eq. (1) into the form:

\[
x = \sqrt{\frac{x_{\min} \cdot x_{\max}}{y_{\min} \cdot y_{\max}}} = \frac{x^2}{2y + x^2} = \frac{x^2}{2y + x^2}
\]

Fig. 3. Infrared spectra of polyether polyols produced by propylene oxide (PO) polymerization (a), PO/succinic anhydride (b), PO/maleic anhydride (c), and PO/phthalic anhydride (d) copolymerizations.

Fig. 4. ^1H NMR spectra of polyether polyol (d) produced by propylene oxide (PO) polymerization and polyetherester polyols produced by PO/succinic anhydride (a), PO/maleic anhydride (b), and PO/phthalic anhydride (c) copolymerizations.
The plot of $s$ versus $n$ gives a straight line, and the extrapolation of the line to $n = 1$ or the slope of the line gives $r_{PO}$. The apparent monomer reactivity ratios for PO are 0.34, 0.28, and 0.26 for PO/SA, PO/MA, and PO/PA copolymerizations, respectively (Fig. 5).

Considering the reactivity ratios of PO and AA, well-defined alternating copolymers are produced when $x < 1$, since $y$ approaches unity.

4. Conclusions

The DMC catalyst bearing $t$BuOH as a complexing agent showed very high activity in the copolymerizations of PO with cyclic AAs, such as SA, MA and PA, as well as in the homopolymerizations of PO. Well-defined alternating copolymers, poly(PO-alt-SA), poly(PO-alt-MA) and poly(PO-alt-PA), are produced when $M_{PO}/M_{AA}$ in the feed is less than unity, since $dM_{PO}/dM_{AA}$ in the copolymer become almost unity, demonstrating that copolymerizations of PO with cyclic AA are an easy and economic process to produce various polyols containing a polyester backbone structure. The versatility of polyols as functional raw materials for PU could be effectively expanded by these copolymerizations. All copolymers are characterized by moderate MW and narrow PDI. The reactivity ratios of PO in PO/SA, PO/MA and PO/PA copolymerizations, estimated by the extended Kelen–Tüdös equation, were 0.34, 0.28, and 0.26, respectively, assuming the reactivity ratios of AA are zero since AAs could not be homopolymerized by using the DMC catalyst.

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