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Novel ring-expansion reaction between cyclic formal and ethylene oxide

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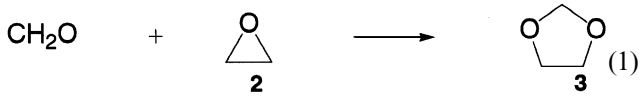
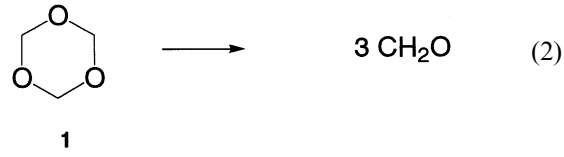
Abstract—Novel direct reactions between trioxane and ethylene oxide were discovered, and three novel cyclic formals were isolated and identified. These novel cyclic compounds clarified the initiation mechanism of the copolymerization of trioxane and ethylene oxide. This type of direct reaction is not only limited to the reaction between trioxane and ethylene oxide, but it was also found to be generalized to the reaction between the cyclic formal and ethylene oxide. © 2000 Elsevier Science Ltd. All rights reserved.

Polyacetal resin is an industrially useful and important engineering thermoplastic. The annual worldwide demand of polyacetal resin is over 400,000 tons. Polyacetal resin is produced by the polymerization of formaldehyde or copolymerization of trioxane **1** and ethylene oxide **2**. For the copolymerization of **1** and **2**, it is known that there exists an induction period before the rapid polymerization of **1** into the solid crystalline polyoxymethylene.[1,2] For the induction period, Weissermel et al.[3,4] of the Hoechst group proposed the reaction of formaldehyde with **2** to form 1,3-dioxolane **3** as the initiation mechanism of the copolymerization of **1** and **2** (Eq. (1)). The formation of formaldehyde by the decomposition of **1** was already confirmed by Kern et al. during the induction period of the polymerization of **1** (Eq. (2)).[1] Collins et al.[5] of the Celanease group proposed that **2** was converted to **3** and then 1,3,5-trioxepane **4** was formed. They stated that the direct reaction of **2** with **1** was not possible due to the weak basicity of **1**.

Weissermel et al.[3,4] and Collins et al.[5] proposed the formation mechanism of **3** from **2** as shown in Eqs. (1) and (2) and this was long thought to be the plausible initiation mechanism of the copolymerization of **1** and **2**.

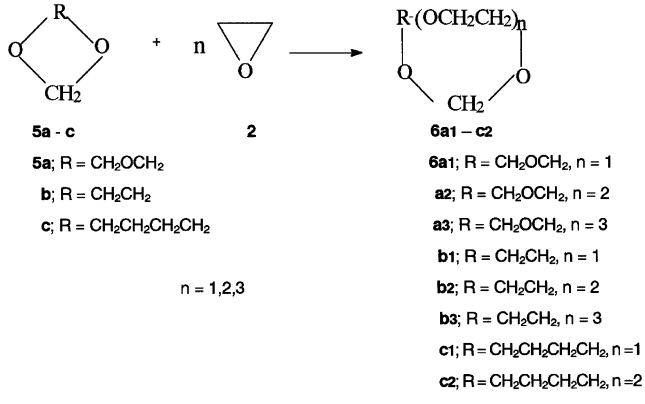


(1)



(2)

Recently, we have found a novel direct reaction between **1** and **2**, and isolated various novel cyclic compounds **6** (Scheme 1). From one of these novel cyclic compounds, **4** was formed and then **3** was also generated. This reaction gives us a plausible initiation mechanism of the copolymerization of **1** and **2**. Furthermore, this type of reaction was found to be generalized to the direct reaction between the cyclic formal and **2**.



Scheme 1. Reaction between cyclic formal **5** and ethylene oxide **2**.

Keywords: cyclic formals; ethylene oxide; ring-expansion reaction.
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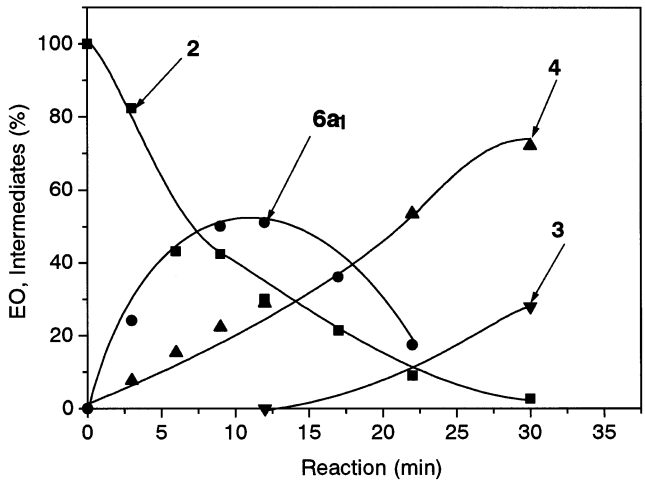
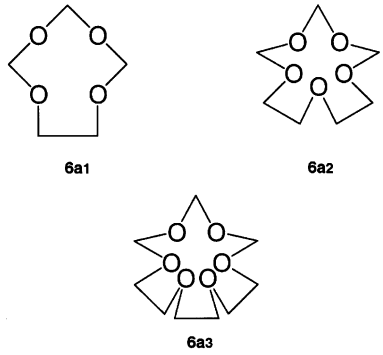


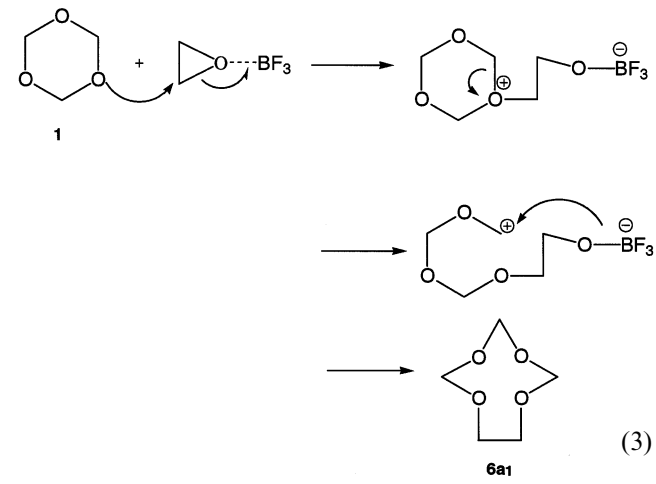
Figure 1. Reaction between trioxane **1** (**5a**) and ethylene oxide **2**. $[2]_0$: 0.95 mol% to **1**, $BF_3{\cdot}OBu_2$: 8.4×10^{-5} mol/mol-**1**, reaction temperature: 70°C.

Purified trioxane **1** was melted under an N_2 atmosphere in a glass vessel immersed in an oil bath and controlled at 70°C. Gaseous ethylene oxide **2** was introduced into the molten **1** which was stirred with a magnetic mixer. A cyclohexane solution of boron trifluoride dibutyl ether was introduced through the cap of the glass vessel with a microsyringe into the mixture. The mixture was stirred using a magnetic mixer in an oil bath to control the reaction temperature at 70°C. During the induction period, the reaction mixture is a homogenous liquid. The reaction mixture was sampled with a syringe and then poured into *n*-propanol containing a small amount of NaOH. The reaction mixture was analyzed by gas chromatography. The reaction mixture was separated by micro distillation and finally separated and collected by gas chromatography.

Three novel cyclic compounds were separated from the reaction mixture in the reaction of **5a** with **2**. They were 1,3,5,7-tetraoxacyclononane **6a1**, 1,3,5,7,10-pentaoxacyclododecane **6a2** and 1,3,5,7,10,13-hexaoxacyclopentadecane **6a3**. The structure of **6a1**–**3** were unambiguously determined by ^1H, ^{13}C NMR, EI-MS, and elemental analysis.

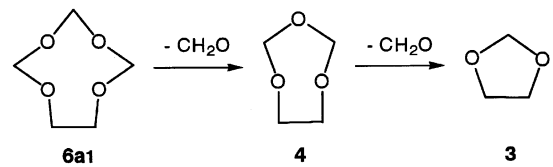


The experimental results are shown in Fig. 1. Under the conditions similar to the commercial production of the acetal copolymer from **1** and **2**, bulk copolymerization of **1** and **2** was carried out. Initial concentration of **2** was 0.95 mol% to **1**. At first, with the decrease of the concentration of **2**, **6a1** and 1,3,5-trioxepane **4** simultaneously appeared. The highest concentration of **6a1** was obtained around 10 min, but that of **4** increased constantly until the reaction time reached to 30 min. After the appearance of **4**, a little later, **3** appeared. Based on these results, it can be concluded that the formation of **6a1** comes from the direct reaction of 1 mole of trioxane **1** with 1 mole of ethylene oxide **2** (**6a1**, Eq. (3)).



(3)

As **6a1** is a nine-membered compound with high ring strain energy, thus, the formation of **4**, which is a seven-membered ring compound with less ring strain energy, may come from the elimination of formaldehyde from **6a1**, and the formation of **3** may come from the elimination of formaldehyde from the resulting **4** (Eq. (4)). As the ring strain energy of **4** of a seven-membered ring compound and **3** of a five-membered ring compound is the same level, there should be chemical equilibrium between **4** and **3**.



(4)

It is remarkable to say that the existence of **6a1** is observed under the condition of the presence of ethylene oxide. This may be due to the high ring strain energy of nine-membered ring **6a1**; thus, energetically unstable **6a1** is easily turned to **4**, which is a seven-membered ring compound, and **3**, which is a five-membered ring compound, in the absence of ethylene oxide. Former studies, made by Weissermel et al.[3,4] and Collins et al.[5], could not find the existence of **6a1**, because in the presence of Lewis acid **6a1** is stable only in the coexistence of ethylene oxide, and under the condition of consumption of ethylene oxide, **6a1** changed to **4** and **3**. Thus, they stated that direct reaction of ethylene oxide **2** with **1** was impossible due to the weak basicity of **1**.[5]

We studied the effect of the ethylene oxide concentration on the reaction between **1** and ethylene oxide **2**. When the initial concentration of **2** was low (0.95–2.2 mol% of **1**), only the formation of **6a1** was observed.

When the initial concentration of **2** was slightly increased (3.3 mol% of **1**), the formation of **6a1** and **6a2** was observed. When the concentration of **2** was further increased (3.9 mol% of **1**, and this concentration is similar to the commercial production of the acetal copolymer), the formation of **6a1**, **6a2** and **6a3** was observed. The highest concentration of **6a1** was obtained around 25 min, but that of **6a2** and **6a3** was observed around 15 min and that of **4** increased constantly until the reaction time reached to 40 min. After the appearance of **6a1**, a little later, **4** appeared and **3** appeared around 25 min. The yield of **6a1** was 50% to the initial ethylene oxide, and that of **6a2** was 20%, and that of **6a3** was 15%. Apparently, a critical concentration of **2** is involved for the formation of **6a2** and **6a3**. Just before the consumption of **2**, **6a2** and **6a3** were consumed and, after the consumption of **2** in the reaction mixture, polymerization immediately started to form a solid crystalline polymer.

Thus, considering the studies made by Price et al.,[2] Weissermel et al.,[3,4] and Collins et al.,[5] the following initiation mechanism for the copolymerization of **1** and **2** may be plausible. The first point is the consumption of **2** to form **6a1**, **6a2** and **6a3**. The second point is the formation of **4** and **3** from **6a1**. The third point may be the copolymerization of **1** with **4**, **3**, **6a2** and **6a3**.

For another ring-expansion reaction, a novel direct reaction between 1,3-dioxolane and **2** was found. (Scheme 1; $R = CH_2CH_2$, **5b**) The reaction procedure was similar to that of **5a** (**1**). The reaction product was presumed to be diethylene glycol formal **6b1**, triethylene glycol formal **6b2** and tetraethylene glycol formal **6b3**, respectively.

Fig. 2 shows the reaction of **5b** and **2**. When the ethylene oxide concentration in the reaction mixture is low (1 mol% of **5b**), the formation of **6b1**, which is the direct reaction product of one mole of **5b** and one mole of **2**, is predominant (selectivity is nearly 99%.). However, with the increase in ethylene oxide concentration

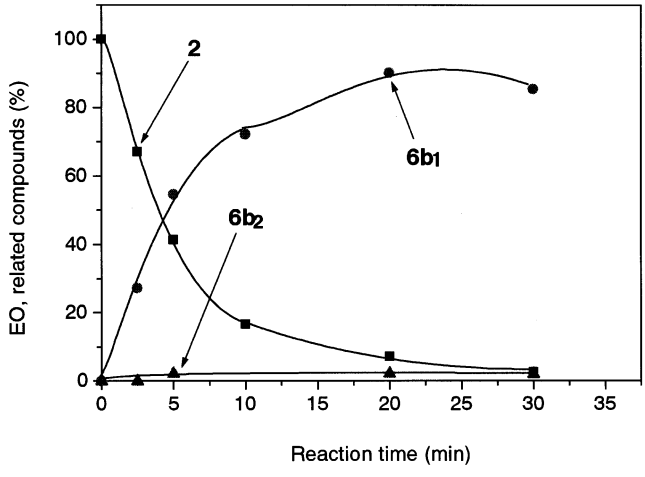


Figure 2. Reaction between 1,3-dioxolane **5b** and ethylene oxide **2**. $[2]_0$: 1.0 mol% to **5b**, $BF_3{\cdot}OBu_2$: 3.6×10^{-5} mol/mol-**5b**, reaction temperature: 30°C.

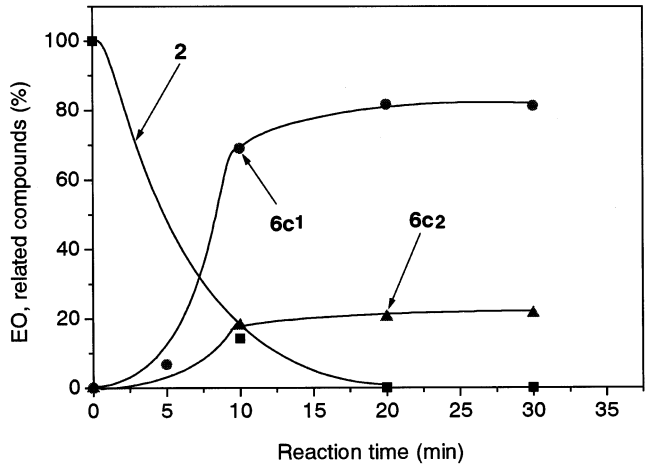


Figure 3. Reaction between 1,3-dioxacycloheptane **5c** and ethylene oxide **2**. $[2]_0$: 0.55 mol% to **5c**, $BF_3{\cdot}OBu_2$: 9.6×10^{-5} mol/mol-**5c**, reaction temperature: 30°C.

(5 mol% of **5b**, the formation of **6b2** and **6b3**, which are the direct reaction products of one mole of **5b** and two moles of **2**, and one mole of **5b** and three moles of **2**, respectively, was observed. The concentration of **6b1**, **6b2**, and **6b3** increased constantly until the reaction time reached to 60 min. For the consumption of 90% of **2**, final yield of **6b1** was 80% to the initial ethylene oxide, and that of **6b2** was 10% and that of **6b3** was 2%, respectively. The reaction product was confirmed by gas chromatography and mass spectroscopy. For the formation of the **6b2**, there seemed to exist a critical concentration of **2**. For the formation of **6b3**, there also seemed to exist some critical concentration of **2**.

For another ring-expansion reaction, a novel direct reaction between 1,3-dioxacycloheptane (1,4-butanediol formal) and ethylene oxide was found. (Scheme 1; $R = CH_2CH_2CH_2CH_2$, **5c**) The reaction procedure was similar to that of **5a**. The reaction product was presumed to be 1,3,6-trioxacyclodecane **6c1** and 1,3,6,9-tetraoxacyclotridecane **6c2**, respectively. Fig. 3 shows the results of the reaction between **5c** and **2**. The formation of **6c1** and **6c2**, which are the direct reaction product of one mole of **5c** and one mole of **2** and one mole of **5c** and two moles of **2**, respectively, was observed. The concentration of **6c1** and **6c2** increased constantly until the reaction time reached to 20 min. For the 100% consumption of **2**, final yield of **6c1** was 82% to initial ethylene oxide and that of **6c2** was 19%, respectively. The reaction product was confirmed by mass spectroscopy.

Based on the observed three novel direct reactions, the generalization of the reaction between cyclic formals and ethylene oxide **2** for the ring expansion is thought to be valid. This new reaction may provide us the possibility of a new route for synthesizing a new type of crown ether. We are now determining whether this ring-expansion reaction is limited only to the reaction between cyclic formals and ethylene oxide, and how this reaction can be generalized for other systems.

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