A novel cyclic formal, 1,3,5,7-tetraoxacyclononane, from the direct reaction of 1,3,5-trioxane and ethylene oxide

J. Masamoto,*[a]† N. Yamasaki,[a] W. Sakai,[a] T. Itoh,[a] N. Tsutsumi[a] and H. Nagahara[b]

[a] *Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan*
[b] *Asahi Chemical Industry Co., Ltd. Kojimashionasu, Kurashiki 711-8510, Japan*

A new reaction between 1,3,5-trioxane and ethylene oxide has been observed and a novel cyclic formal, which is the reaction product of 1 equiv. of 1,3,5-trioxane and 1 equiv. of ethylene oxide, has been isolated and identified.

Weissermel and co-workers[1,2] proposed the reaction of formaldehyde with ethylene oxide to form 1,3-dioxolane as the initiation mechanism of the copolymerization of 1,3,5-trioxane and ethylene oxide. Collins *et al.*[3] confirmed that ethylene oxide was converted to 1,3-dioxolane and then from 1,3-dioxolane, 1,3,5-trioxepane was formed. They stated that the direct reaction of ethylene oxide with 1,3,5-trioxane was impossible because of the weak basicity of 1,3,5-trioxane. Weissermel and co-workers[1,2] and Collins *et al.*[3] proposed the formation mechanism of 1,3-dioxolane from ethylene oxide and formaldehyde, and for a long time this was thought plausible for the initiation mechanism of copolymerization of trioxane and ethylene oxide.

We have performed the direct reaction of ethylene oxide with 1,3,5-trioxane, which was thought impossible for a long time, and isolated a novel cyclic formal. From this novel cyclic formal, 1,3,5-trioxepane was formed and then 1,3-dioxolane was also generated. This reaction identified the precise initiation mechanism of the copolymerization of 1,3,5-trioxane and ethylene oxide.

Purified 1,3,5-trioxane (30 g) was melted under an N_2 atmosphere in a glass vessel immersed in an oil bath and held at 70 °C. Gaseous ethylene oxide (4.5 mol% with respect to 1,3,5-trioxane) was introduced into the molten 1,3,5-trioxane which was stirred with a magnetic mixer. A cyclohexane solution of $BF_3{\cdot}OBu_2$ (7×10^{-3} mol% with respect to 1,3,5-trioxane) was introduced into the molten mixture of 1,3,5-trioxane and ethylene oxide through the cap of the glass vessel with a microsyringe. The mixture was stirred using a magnetic mixer in an oil bath to maintain the reaction temperature at 70 °C. The reaction mixture was sampled with a syringe and then poured into PrOH containing a small amount of KOH. The reaction mixture was analyzed by gas chromatography. This showed a 33% yield of the novel compound based on the initial amount of ethylene oxide.

The novel compound was separated using a micro-distillation apparatus (bp 180 °C at 1 atm; mp 8.4 °C and bp 95 °C at 25 torr). Its chemical structure was confirmed using ^1H NMR, ^{13}C NMR and mass spectral and elemental analysis.

Fig. 1 shows the ^1H NMR pattern of the new compound. The ratio of H^a (proton of formal linkage, δ 5.05) to H^b (proton of formal linkage, δ 4.93) and H^c (proton of ether linkage, δ 3.85) is 1:2:2. Fig. 2 shows the ^{13}C NMR pattern of the new compound, and shows three different types of carbon: C^a (formal carbon, δ 96.9), C^b (formal carbon, δ 97.1) and C^c (ether carbon, δ 70.5). Fig. 3 shows the EI mass spectrum of the new compound, which shows the molecular weight of 134 and composition formula of $C_5H_{10}O_4$, which is in accordance with the molecular weight and composition formula of 1,3,5,7-tetraoxacyclononane (TOCN). The observed elemental analyses are in accordance with the theoretical values (Found: C, 44.76; H, 7.75. Calc.: C, 44.78; H, 7.50%).

The reaction concentration profile is shown in Fig. 4. The profile begins when the initiator (a cyclohexane solution of $BF_3{\cdot}OBu_2$) is injected into the molten mixture of 1,3,5-trioxane and ethylene oxide. At first, as the ethylene oxide concentration (4.5 mol% with respect to 1,3,5-trioxane) decreases, the TOCN concentration increases proportionally. Later, as the TOCN

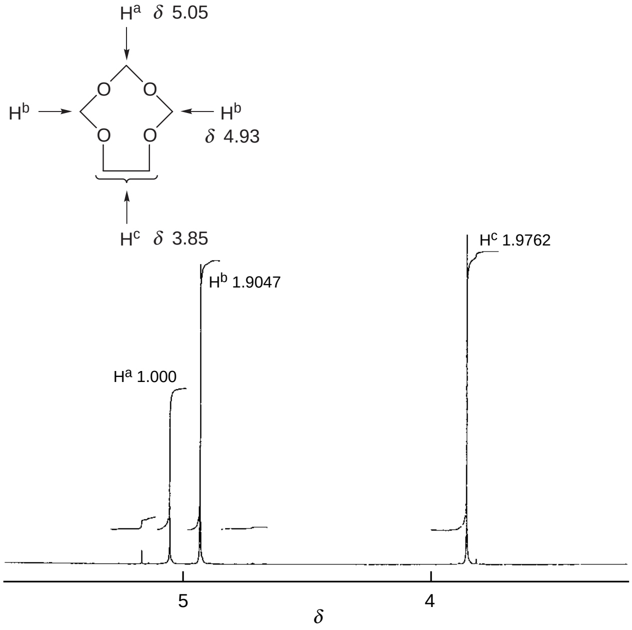


Fig. 1 ^1H NMR spectrum of the new compound

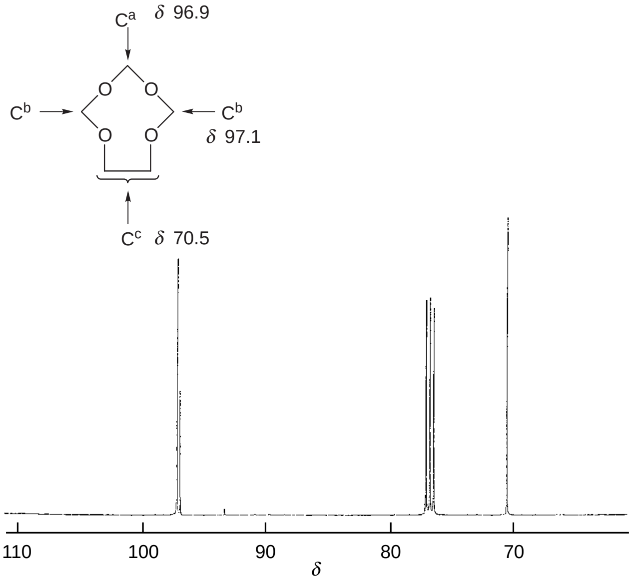


Fig. 2 ^{13}C NMR spectrum of the new compound

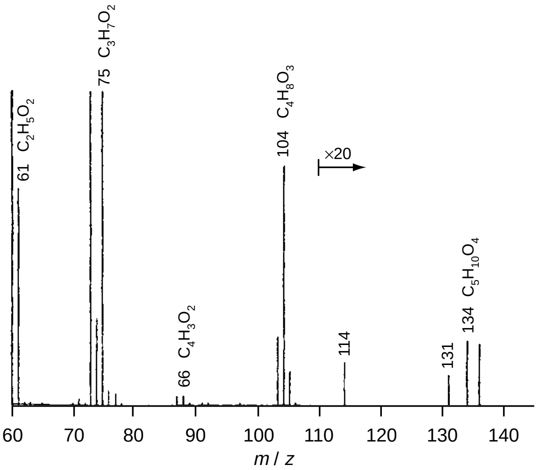


Fig. 3 EI mass spectrum of the new compound

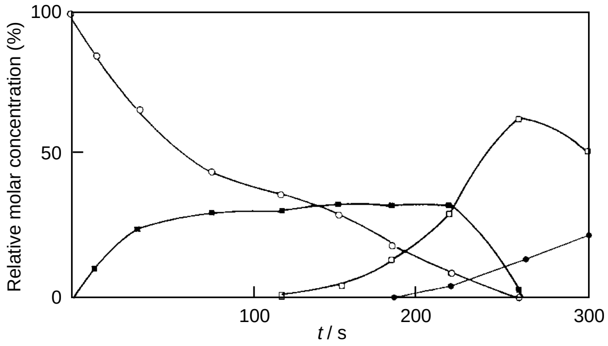
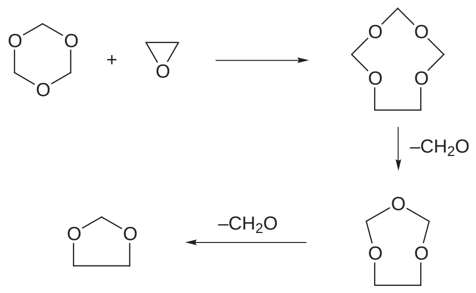


Fig. 4 Profile of reaction of 1,3,5-trioxane and ethylene oxide: (○) ethylene oxide, (■) 1,3,5,7-tetraoxacyclononane, (□) 1,3,5-trioxepane, (●) 1,3-dioxolane. $[EO]_0$ = 4.5 mol% with respect to 1,3,5-trioxane. t = 0 indicates the time at which the initiator is injected into the molten mixture of 1,3,5-trioxane and ethylene oxide. Percentage on the vertical axis indicates the relative molar concentration of ethylene oxide or related compounds to the initial concentration of ethylene oxide.

concentration decreases again, the concentration of 1,3,5-trioxepane increases. Soon after the appearance of 1,3,5-trioxepane, 1,3-dioxolane appeares, and with the decrease in concentration of 1,3,5-trioxepane, the concentration of 1,3-dioxolane increases.

Although the equilibrium concentration of 1,3,5-trioxepane and 1,3-dioxolane exist, there is no equilibrium concentration of TOCN. This might be attributed to the higher ring strain energy of the nine-membered ring compound of TOCN compared to those of the seven- and five-membered ring compounds. In the case of the cycloalkane, the ring strain energy of the nine-membered ring compound is 27 kJ mol^{-1} higher compared to those of the seven- and five-membered ring compounds.[4]



Scheme 1

The newly isolated intermediate, the novel cyclic compound TOCN, identifies a new direct reaction between 1,3,5-trioxane and ethylene oxide, as well as the precise initiation mechanism of the copolymerization of 1,3,5-trioxane and ethylene oxide. First, ethylene oxide directly reacts with 1,3,5-trioxane to produce TOCN (Scheme 1). The 1,3,5-trioxepane is then formed from TOCN, and 1,3-dioxolane is formed from 1,3,5-trioxepane.

Using gas chromatography, we observed compounds of higher molecular weights than TOCN as minor components, which were presumed to be the addition product of ethylene oxide and TOCN. Confirmation of this point will be discussed in the near future.

Notes and References

† E-mail: masamoto@ipc.kit.ac.jp

1 K. Weissermel, E. Fischer, K. Gutweiler and H. D. Hermann, *Kunststoffe*, 1964, **54**, 410.

2 K. Weissermel, E. Fischer, K. Gutweiler, H. D. Hermann and H. Cherdron, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 526.

3 G. L. Collins, R. K. Green, F. M. Beradinelle and W. H. Ray, *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 1579.

4 P. Kubisa, in *Cationic Polymerization: Mechanism, Synthesis, and Applications*, ed. K. Matyjaszewski, Dekker, New York, 1995, pp. 437–553.

Received in Cambridge, UK, 27th February 1998; 8/01653D