# NMR Spectra of Cyclic Formals Formed During the Early Stage of the Copolymerization of Trioxane and Ethylene Oxide

## NAOAKI YAMASAKI, JUNZO MASAMOTO,\* and KENJI KANAORI

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585 Japan (J.M., K.K.); and Functional Additives Technology Department One, Asahi Chemical Industry Co., Ltd. 6-2700, Asahi-machi, Nobeoka 882-0847 Japan (N.Y.)

During the early stage of the copolymerization of trioxane and ethylene oxide, we found the formation of three novel cyclic compounds: 1,3,5,7-tetraoxacyclononane (TOCN), 1,3,5,7,10-pentaoxacyclododecane (POCD), and 1,3,5,7,10,13-hexaoxacyclopentadecane (HOCP). These novel cyclic compounds were new direct reaction products of 1 mole of trioxane and 1 mole of ethylene oxide, 1 mole of trioxane and 2 moles of ethylene oxide, and 1 mole of trioxane and 3 moles of ethylene oxide, respectively. We compared the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of each cyclic compound and precisely assigned the signals of each spectrum using NOESY (nuclear Overhauser enhancement spectroscopy) and HETCOR (heteronuclear correlated spectroscopy). We also compared the <sup>1</sup>H-NMR spectra of POCD and HOCP with the corresponding cyclic formals with one oxymethylene unit, diethylene glycol formal (DEGF) and triethylene glycol formal (TEGF). Interestingly, we found that DEGF and TEGF, which have only one oxymethylene unit, showed no proton splitting of the oxyethylene units, while POCD and HOCP, which have three consecutive oxymethylene units, have split signals for the oxyethylene units.

Index Headings: <sup>1</sup>H-NMR spectra; <sup>13</sup>C-NMR spectra; Cyclic formals.

## INTRODUCTION

Polyacetal resin, which is a representative engineering plastic, is produced by the polymerization of formaldehyde (acetal homopolymer) or the copolymerization of trioxane with a cyclic ether such as ethylene oxide (acetal copolymer). There are few reports on the polymerization of formaldehyde;<sup>1–7</sup> on the other hand, there have been numerous reports on the polymerization of trioxane. However, these studies academically deal mainly with the copolymerization of trioxane with 1,3-dioxolane. In spite of the importance of the copolymerization of trioxane with ethylene oxide, which is presently produced on an industrial basis, the number of reports are relatively few.<sup>8–13</sup>

We found a direct reaction between trioxane and ethylene oxide, which was reported to be impossible by several authors,<sup>9,13</sup> during our studies on the copolymerization of trioxane and ethylene oxide, and we found several novel compounds. We then determined each compound to be 1,3,5,7-tetraoxacyclononane (TOCN) (reaction 1), 1,3,5,7,10-pentaoxacyclododecane (POCD) (reaction 2) and 1,3,5,7,10,13-hexacyclopentadecane (HOCP) (reaction 3), respectively (see Scheme I). We also determined that from TOCN, 1,3,5-trioxepane was formed (reaction 1), and from 1,3,5-trioxepane, 1,3-dioxolane was formed (reaction 1).

It is already known that the commercial acetal copolymer from trioxane and ethylene oxide has a certain kind of ethylene oxide sequence, that is, one ethylene oxide sequence, two consecutive ethylene oxide sequences, and three consecutive ethylene oxide sequences. It was postulated that one ethylene oxide sequence will come from the copolymerization of trioxane with 1,3-dioxolane and 1.3-trioxepane, two consecutive ethylene oxide sequences will come from the copolymerization of trioxane with POCD, and three consecutive ethylene oxide sequences will come from the copolymerization of trioxane with HOCP. We then compared the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of these three novel cyclic formals (TOCN, POCD, and HOCP), which were obtained as the reaction products of the copolymerization of trioxane and ethylene oxide, and precisely assigned each spectrum using NOESY (nuclear Overhauser and enhancement spectroscopy) and HETCOR (heteronuclear correlated spectroscopy).

TOCN, POCD, and HOCP have three consecutive oxymethylene units, while diethylene glycol formal (DEGF) and triethylene glycol formal (TEGF) have only one oxymethylene unit (see Fig. 1). We compared the NMR spectra of these compounds and found an interesting phenomenon with respect to differences in the splitting of the oxyethylene unit.

### EXPERIMENTAL

Material. Each material-TOCN, POCD, and HOCP—was obtained as the reaction product of trioxane and ethylene oxide. The reaction was done as follows. In a 100 mL glass flask, 65 g (0.72 mol) of trioxane was melted at 70 °C under an N2 atmosphere and stirred with a magnetic stirrer. Gaseous ethylene oxide (3.9 mol % to trioxane) was absorbed by trioxane, and the cyclohexane solution of  $BF_3 \cdot OBu_2$  (3.9  $\times$  10<sup>-5</sup> mol/mol-trioxane; BF<sub>3</sub>·OBu<sub>2</sub> was diluted 50 times by cyclohexane) was injected into the reaction mixture with a microsyringe, and then the reaction proceeded at 70 °C. The reaction mixture was in a homogeneous state before the beginning of the polymerization. The reaction mixture with a homogeneous state was withdrawn (20 g) by a syringe at definite times (15 min, 20 min, and 25 min after the injection of  $BF_3 OBu_2$ ), poured into an *n*-PrOH solution of NaOH (0.1 wt % NaOH in *n*-propanol, 50 mL), and the reaction was stopped. The formation yield of each material for the

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<sup>\*</sup> Author to whom correspondence should be sent. Present address: Dept. of Management Science, Fukui University of Technology, 3-6-1, Gakuen, Fukui-shi, 910-8505 Japan.



SCHEME I. Reaction scheme.

initial ethylene oxide was as follows: TOCN, 48%; POCD, 20%; HOCP, 15%. The reaction products were first separated by microdistillation (TOCN showed a boiling point of 180 °C at 760 torr, while POCD showed a boiling point of 182 °C at 4 torr, and HOCP showed a boiling point of 212 °C at 4 torr), and finally separated and collected by preparative gas chromatography using a packed column (4.0 mm diameter, 2 m length, packing agent: Chromosorb W containing 10% liquid silicone OV-17) at a column temperature of 150 °C.

For the confirmation of each cyclic formal, the mass spectra were checked. The electron impact mass spectrometry (El MS) of TOCN showed a molecular ion peak of 134 and composition formula of  $C_5H_{10}O_4$ , which is in accordance with the molecular weight and composition formula of TOCN. The El MS of POCD showed a molecular ion peak of 177 and the composition formula of  $C_7H_{14}O_5$ , which is in accordance with the compound of a one-proton elimination of POCD (molecular weight: 178; composition formula:  $C_7H_{15}O_5$ ). The chemical ionization mass spectrometry (Cl MS) of HOCP showed a molecular ion peak of 223, which is in accordance with the compound of a one-proton attachment of HOCP (molecular weight: 222).

The observed elemental analyses of each formal are in accordance with the theoretical values: TOCN (Found: C, 44.76; H, 7.75. Calc.: C, 44.78; H, 7.50%), POCD (Found: C, 47.25; H, 8.06. Calc.: C, 47.19; H, 7.87%), HOCP (Found: C, 48.35; H, 8.00. Calc.: C, 48.65; H, 8.11%).

DEGF was synthesized from diethylene glycol (0.2 mol) and paraformaldehyde (0.2 mol) catalyzed by 0.5 wt % pyrophosphoric acid in the presence of heptane (boiling point 98.4 °C 20 wt % of the reactant) immersed in an oil bath controlled at 130 °C with refluxing heptane in the reaction zone, while the generated water was withdrawn. After generation of the water stopped, DEGF was distilled under the reduced pressure of 30 torr at 60 °C (yield: 81% of the initial diethylene glycol). DEGF was redistilled for purification. A similar procedure was done for the synthesis of TEGF (yield: 63% of initial triethylene glycol), and purified TEGF was obtained (30 torr, 78 °C)

Analysis. A 400 MHz NMR (JEOL JNM-AL 400 FT NMR system spectrometer) was used for the <sup>1</sup>H-NMR



Fig. 1. Notation of each proton and carbon of TOCN, POCD, HOCP, DEGF, and TEGF.

and <sup>13</sup>C-NMR measurements, and CDCl<sub>3</sub> was used for the solvent. About 20 mg of each sample was dissolved in 0.7 mL CDCl<sub>3</sub>. The NOESY and HETCOR spectra were measured for the precise assignment of each signal. The spectrometer settings were as follows: For the NOESY measurement, pulse width, 11.5  $\mu$ s; delays, 1.134 s; spectral widths, 700 Hz for both dimensions; number of time domain points, 256 (td 2) × 128 (td 1); mixing time, 200 ms; data size, 512 (f2) × 512 (f1); window function, sine bell. For the HETCOR measurement, pulse widths, 11.6  $\mu$ s for <sup>13</sup>C and 11.0  $\mu$ s for <sup>1</sup>H; delays, 1.170 s; spectral widths, 3100.7 Hz for <sup>13</sup>C and 700 Hz for <sup>1</sup>H; number of time domain points, 1024 (td 2) × 256 (td 1); data size: 1024 (f2) × 512 (f1); window function, sine bell.

#### **RESULTS AND DISCUSSION**

To make the discussion clear, the notation of each proton and carbon atom of TOCN, POCD, and HOCP is shown in Fig. 1 as  $H^a$ ,  $H^b$ ,  $H^c$ ,  $H^d$ , and  $H^e$  for each proton, and  $C^a$ ,  $C^b$ ,  $C^c$ ,  $C^d$  and  $C^e$  for each carbon.

**NMR Spectra of TOCN.** The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of TOCN are summarized in Tables I and II, respectively. In the <sup>1</sup>H-NMR spectrum, three singlets were observed at 5.05, 4.93, and 3.85 ppm, and its area ratio was 1:2:2. From the signal strength, 5.05 ppm was attributed to H<sup>a</sup>, 4.93 ppm was attributed to H<sup>b</sup>, and 3.85 ppm was attributed to H<sup>c</sup>. From the viewpoint of chemical bonding, the carbon atom, which is connected to H<sup>a</sup>, is surrounded

TABLE I. <sup>1</sup>H-NMR chemical shift assignment of TOCN, POCD, HOCP, DEGF, and TEGF.<sup>a</sup>

	Hª	Нь	H°	$\mathbf{H}^{d}$	He
TOCN	5.05	4.93	3.85		
	s, 2H	s, 4H	s, 4H		
POCD	5.05,	4.90	3.83-3.85,	3.73-3.75,	
	s, 2H	s, 4H	m, 4H	m, 4H	
HOCP	5.08,	4.92,	3.75-3.79,	3.68-3.73,	3.66,
	s, 2H	s, 4H	m, 4H	m, 4H	s, 4H
DEGF	4.90	3.81,			
	s, 2H	s, 8H			
TEGF	4.79	3.83,	3.69		
	s, 2H	s, 8H	s, 4H		

<sup>a</sup> Unit is ppm. Characters s and m indicate singlet and multiplet signals, respectively.

with two -OCH<sub>2</sub>O units, and the carbon atom, which is connected to  $H^{b}$ , is connected to one side by  $-OCH_{2}$ , and to the other side by  $-OCH_2CH_2$ . Thus, considering the electron attractivity of the oxygen atom, the electron density of H<sup>a</sup> was thought to be lower than that of H<sup>b</sup>, and this order was in accordance with that of the chemical shift. On the other hand, with respect to the <sup>13</sup>C-NMR, two formal carbon signals were observed at 96.9 and 97.1 ppm, and their height ratio was 1:2. For assignment of the <sup>13</sup>C signals, the <sup>13</sup>C-<sup>1</sup>H COSY (HETCOR) was measured, and the result is shown in Fig. 2. From the result of the HETCOR, C<sup>a</sup> was assigned to 96.9 ppm, and C<sup>b</sup> was assigned to 97.1 ppm. We first expected that C<sup>a</sup> shifted to a lower magnetic field than C<sup>b</sup>, because C<sup>a</sup> is surrounded by two -OCH<sub>2</sub>O units, while C<sup>b</sup> is surrounded on one side by -OCH<sub>2</sub>O and on other side by -OCH<sub>2</sub>CH<sub>2</sub>. However, the result showed that C<sup>a</sup> shifted to a high magnetic field. From these observations, it was suggested from the result of the chemical shift of the <sup>13</sup>C-NMR that in the formal unit of three consecutive formals, the electron density on C<sup>b</sup> may be higher than that on C<sup>a</sup>.

Next, we compared the <sup>1</sup>H-NMR spectrum of TOCN with that of 1,3-dioxolane and 1,3-trioxepane. For 1,3dioxolane the chemical shift of the formal was 4.91 ppm, and for 1,3-trioxepane the chemical shift of the formal was 4.92 ppm.<sup>14</sup> Comparing the chemical shift of the formal of TOCN, H<sup>a</sup> was 5.05 ppm, and H<sup>b</sup> was 4.93 ppm. Among the formal chemical shifts, H<sup>a</sup> of TOCN is shifted to the lowest magnetic field, and this result was deduced to be due to both sides being surrounded with a formal unit. Among the formals connected to oxyethylene, the H<sup>b</sup> of TOCN, the formal of 1,3-trioxepane, and the formal of 1,3-dioxolane shifted to the low magnetic field in this order; however, the difference was very small (0.01 ppm).

**NMR Spectra of POCD and DEGF.** The <sup>1</sup>H-NMR spectrum of POCD is also shown in Table I. The area strength of each spectrum is 1:2:2:2 in the order from the low magnetic field. As for the formals, a similar situation was observed for POCD;  $H^a$  was assigned to 5.00 ppm and  $H^b$  was assigned to 4.90 ppm from the order of the low magnetic field.

As for the oxyethylene, as shown in Fig. 3 each signal was split, centered at 3.79 ppm, to two symmetrical signals with five splits on the left side (3.83–3.85 ppm) and right side (3.73–3.75 ppm) because of spin–spin coupling.

To assign H<sup>c</sup> and H<sup>d</sup>, we measured the HETCOR. The

TABLE II. <sup>13</sup>C-NMR chemical shift assignment (ppm) of TOCN, POCD, and HOCP.<sup>a</sup>

	$C^a$	$C^{b}$	C°	$\mathbf{C}^{d}$	Ce
TOCN	96.9	97.1	70.5		
POCD	95.1	95.9	68.7	70.6	
НОСР	91.3	93.2	66.5	70.7	70.4

<sup>a</sup> Unit is ppm.

result is shown in Fig. 4. Carbon atoms of the formal were assigned similarly to that of TOCN; a signal of 95.1 ppm was assigned to C<sup>a</sup>, and that of 95.9 ppm was assigned to C<sup>b</sup>. As for the oxyethylene, the signal of 70.6 ppm of <sup>13</sup>C makes the cross peak of the proton of oxyethylene occur at high magnetic field (3.73-3.75 ppm), and the signal of 68.7 ppm makes the cross peak of the proton occur at low magnetic field (3.83-3.85 ppm). Thus the symmetrical multiplet signals of <sup>1</sup>H of oxyethylene were found to be connected to the different carbon atoms.

To assign the H<sup>c</sup> and H<sup>d</sup>, that is to say, to confirm which <sup>1</sup>H nucleus is sterically nearer to the <sup>1</sup>H nucleus of H<sup>b</sup>, we measured the NOESY (Fig. 5). The one-dimensional <sup>1</sup>H-NMR spectrum of POCD is shown on the vertical axis and horizontal axes. The stronger the cross peak of NOESY, the stronger the interaction of the dipole between the protons, and the results showed that the distance was closer. With respect to the cross peak of the proton of H<sup>b</sup> (4.90 ppm), a strong cross peak was observed between the multiplet (3.83–3.85 ppm) at the low magnetic field; only a weak cross peak was observed for the multiplet (3.73-3.75 ppm) at the high magnetic field. From this observation, the signal of a proton at 3.83-3.85 ppm was assigned to H<sup>c</sup>, which is near to H<sup>b</sup>, and the signal at 3.73-3.75 ppm was assigned to H<sup>d</sup>. Thus, each signal in the 1H-NMR spectrum was confirmed to be in accordance with H<sup>a</sup>, H<sup>b</sup>, H<sup>c</sup>, and H<sup>d</sup>, which is shown in the chemical structure of Fig. 1. In Table II, a precise assignment of the <sup>13</sup>C-NMR spectrum of POCD is shown. On the basis of the chemical shift of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of POCD, H<sup>c</sup>, which is surrounded with -OCH<sub>2</sub>O and -OCH<sub>2</sub>CH<sub>2</sub>, shifted to a low magnetic field, while



FIG. 2. HETCOR spectrum of TOCN.



FIG. 3.  $~^{1}\!H\text{-}NMR$  spectra of  $H^{c}$  and  $H^{d}$  of POCD (A), and  $H^{c},$   $H^{d},$  and  $H^{c}$  of HOCP (B).

H<sup>d</sup>, which is surrounded with  $-CH_2OCH_2$  and  $-OCH_2CH_2$ , shifted to a high magnetic field. On the other hand, C<sup>c</sup> shifted to a magnetic field higher than C<sup>d</sup>; thus, the electron density of C<sup>d</sup> may be higher than that of C<sup>c</sup>.

DEGF is the cyclic formal whose chemical structure corresponds to POCD and has only one formal. In Table I, the <sup>1</sup>H-NMR spectrum of DEGF is shown, and its assignment is also shown. In the spectrum, two signals were observed whose strengths were 1:4, and these signals were assigned to the protons of the formal and oxyethylene, respectively. The chemical shift of the formal, H<sup>a</sup>, was 4.90 ppm, the same value of the chemical shift as H<sup>b</sup> of POCD. It was remarkable that in POCD, H<sup>c</sup> and H<sup>d</sup> of the oxyethylene were observed at different chemical shifts, while in DEGF, the proton of oxyethylene is observed at the same value, and spin–spin coupling disappeared, thus showing one signal. That is to say, a nonequivalence of the proton of the oxyethylene was ob-



FIG. 4. HETCOR spectrum of POCD.

served in the compound with three consecutive formals in one molecule, although this nonequivalence of the proton of oxyethylene was not observed for the compound with one formal in one molecule. For the compound with one formal, the movement of the ring may not be restricted; thus mobility of each methylene proton in the oxyethylene unit may be significant. Thus, each methylene proton in the oxyethylene unit may be equivalently observed, while for the compound with three formals, the ring size is large; thus the movement of the ring may be restricted. Thus, the chemical shift of each methylene proton in the oxyethylene unit may be separated.

**NMR Spectra of HOCP and TEGF.** The <sup>1</sup>H-NMR spectrum of HOCP is also shown in Table I. The area strength of each spectrum is 1:2:2:2:2 in the order from the low magnetic field. As for the formals, a similar situation was observed for HOCP; H<sup>a</sup> and H<sup>b</sup> were assigned from the order of the low magnetic field.

As for the oxyethylene, as shown in Fig. 3, each signal



FIG. 5. NOESY spectrum of POCD.



FIG. 6. NOESY spectrum of HOCP.

was split, centering at 3.74 ppm, two symmetrical signals with six splits to the left side (3.75–3.79 ppm) and right side (3.68–3.73 ppm) because of spin–spin coupling, and one single signal was observed at 3.66 ppm.

To precisely assign the H<sup>c</sup>, H<sup>d</sup>, and H<sup>e</sup> of the oxyethylene, as with POCD, we measured the NOESY (Fig. 6) and HETCOR (Fig. 7). As for the <sup>1</sup>H signals, H<sup>a</sup>, H<sup>b</sup>, H<sup>c</sup>, H<sup>d</sup>, and H<sup>e</sup> were assigned from the order of the lower magnetic field, and the NOE cross peak between H<sup>b</sup> and H<sup>c</sup> was strong, while the cross peaks between H<sup>b</sup> and H<sup>d</sup>, and between H<sup>b</sup> and H<sup>e</sup>, were weak. As for the <sup>13</sup>C signals, the signal at 91.3 ppm was assigned to C<sup>a</sup>, and the one at 93.2 ppm was assigned to C<sup>b</sup>. In the oxyethylene signals, the signal at 66.5 ppm was assigned to C<sup>c</sup>, the one at 70.7 ppm was assigned to C<sup>e</sup>, and the one at 70.4 ppm was assigned to C<sup>d</sup>.

As in the case of HOCP, the chemical shift of the carbon atom was in the order of C<sup>d</sup>, C<sup>e</sup>, and C<sup>c</sup> from the low magnetic field, and the electron density may be high in this order. In Table II, the precise assignment of the <sup>13</sup>C-NMR spectrum of HOCP is shown.

TEGF is the cyclic formal whose chemical structure corresponds to HOCP, and has only one formal. In Table I, the <sup>1</sup>H-NMR spectrum of TEGF is shown, and its assignment is also shown. In the spectrum, three signals were observed at a strength of 1:4:2.

The chemical shift of formal H<sup>a</sup> was 4.79 ppm. This signal shifted 0.13 ppm to a higher magnetic field compared to the H<sup>b</sup> of HOCP. In the case of HOCP, the oxyethylene signals, H<sup>c</sup>, H<sup>d</sup>, and H<sup>e</sup>, were independently observed, while in the case of the TEGF, H<sup>b</sup> of the oxyethylene signal (3.83 ppm) was observed at the single signals, similar to the case of DEGF. However, H<sup>b</sup> is rather broad. Perhaps there is a small unresolved coupling, suggesting that all four of the H<sup>b</sup> protons are not quite equivalent.

The spin-spin coupling, which was observed in the case of POCD and HOCP, was not observed for DEGF and TEGF, which both belonged to the same family.

It is a remarkable fact that the proton in the oxyethylene, which is connected to three consecutive formals,



FIG. 7. HETCOR spectrum of HOCP.

was in nonequivalence, and spin-spin coupling was observed, while the proton of the oxyethylene, which is connected to one formal, is in the equivalent magnetic field environment, and no spin-spin coupling was observed.

#### CONCLUSION

Comparing the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra for the three novel cyclic formals—TOCN, POCD, and HOCP— which were obtained during the early stage of the copolymerization of trioxane and ethylene oxide, and assigning each signal on the basis of NOESY and <sup>13</sup>C-<sup>1</sup>H COSY (HETCOR), we obtained the following results:

- 1. The chemical structure of each compound was identified, and each signal of the NMR spectra was precisely assigned.
- 2. The signal of the oxyethylene of POCD and HOCP, which have three consecutive formal units, was independently observed, and spin-spin coupling was observed. The signal of the oxyethylene of DEGF and TEGF, which correspond to the former compound, and have only one consecutive formal unit, showed only one signal and showed no spin-spin coupling. Increasing the formal from one to three units, the oxyethylene became nonequivalent, and spin-spin coupling phenomena were observed. There is some possibility that, with an increase in the formal unit, the chemical structure of oxyethylene will be fixed.
- 3. The chemical shift of the TOCN, POCD, and HOCP <sup>13</sup>C-NMR spectra showed the possibility that the electron density of carbon (C<sup>b</sup>) of the formal adjacent to the oxyethylene unit is higher than that of the center carbon (C<sup>a</sup>) of the formal.
- 4. The chemical shift of the <sup>13</sup>C-NMR spectrum of the compound having two and three consecutive oxyethylene units showed the possibility that the electron density on the oxyethylene carbon is the highest for the carbon (C<sup>d</sup>) next to the carbon adjacent to the formal.

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