

Proton-NMR Studies of Polyacetal Copolymers

TOSHIO OGAWA, *Department of Mechanical Systems Engineering, Faculty of Engineering, Kanazawa Institute of Technology, 7-1, Ohgigaoka, Nonoichi, Ishikawa 921, Japan*, and WATARU ISHITOBI and KAZUYA JINTA, *Hirakata Laboratory, Corporate Research and Development, Ube Industries, Ltd., Hirakata, Osaka 573, Japan*

Synopsis

Sequence length of ethylene oxide and the amount of end groups in polyacetal copolymers were determined using proton NMR. Peaks from ethylene oxide usually appear in the region from 3.5 to 3.8 ppm, when tetramethylsilane was used as the internal standard. These peaks were divided into three triad sequences, i.e., MEM, MEE, EEE (E = ethylene oxide, M = methylene oxide) by referring to several polymers of similar structure. The sequence length in a copolymer prepared from ethylene oxide was 1.37 and that from trioxocane was 2.00. Small peaks from end groups usually appear in the region higher than 3.5 ppm. The peaks from methoxy and ethoxy groups were easily detected and determined quantitatively. The peak from hydroxy group was detected after acetylation of a copolymer, because the original sample did not give a distinct peak corresponding to that group. The number-average molecular weight of the copolymer prepared from trioxocane was estimated from the content of methoxy, ethoxy, and hydroxy groups. The value thus obtained was consistent with that obtained by gel permeation chromatography.

INTRODUCTION

Polyacetal is prepared from formaldehyde which is, in turn, made from methanol. Ethylene oxide, butylene oxide, and trioxocane can be used as comonomers. Comonomer content and sequence length of these comonomer units play a more important role in determining the properties of copolymers than identification of the above comonomers. Two methods of determining comonomer content have been presented by various investigators; one is by gas chromatography^{1,2} and the other by NMR spectroscopy.³⁻⁷ Concerning comonomer content, both methods are satisfactory except for the case in which very exact values are required. However, the sequence length is obtainable only by NMR. The sequence length was estimated from the peaks of methylene oxide unit appearing at 4.5 ppm in proton NMR by Yamashita et al.³ However, this is an indirect method requiring some assumptions. Carbon-13-NMR may be applicable for this purpose with the addition of a lanthanide shift reagent.⁵ We tried this technique at 135°C, but no change was observed in the spectrum. This method may be only useful at room temperature or relatively low temperature. Polyacetal copolymers are generally crystalline because of low comonomer content. No good solvent has been found yet to dissolve these copolymers at room temperature.

Various kinds of end groups will be present depending on the extent of polymerization. However, all polyacetals commercially available have been stabilized. After this process, only limited amounts of end groups such as hydroxy, methoxy, ethoxy, and acetyl groups may be present in these copoly-

mer chains with sufficient stability. All of these groups are not always present in a polymer sample. The kind of end groups depends on the process adopted for production and stabilization of polyacetals. It was impossible previously to identify end groups with NMR, because the contents of end groups were extremely small and the resolution to the spectra was not satisfactory. Recently very high resolution NMR spectrometers have become available. Using such high resolution instruments, the end groups, especially for the polymer prepared from trioxocane as the comonomer, were identified and evaluated quantitatively in this paper.

EXPERIMENTAL

NMR

Proton NMR spectra were obtained for a 3% polymer solution in *o*-dichlorobenzene at 150°C using a JEOL JNM-GX-270 spectrometer at 270 MHz. One hundred and twenty-eight scans were accumulated at a repetition rate of 10 s to obtain the spectra. Tetramethylsilane [Si(CH₃)₄] was used as the internal standard.

Polymers

Polyethylene glycol having number-average molecular weight of 6000 was purchased from Kishida Chemical Co., Osaka, Japan. Poly(1,3-dioxolane) (PDOL) was prepared in toluene from 1,3-dioxolane, C₃H₆O₂, with BF₃ · OEt₂ as catalyst. After stopping the polymerization by the addition of a small amount of aqueous ammonia, the polymer was precipitated with petroleum ether, followed by drying. Polytrioxocane (PTOC) was prepared from trioxocane (C₅H₁₀O₃) in the same way as for poly(1,3-dioxolane).

Copolymer A was prepared from formaldehyde and trioxocane, the content of which is 1.6 mol %. Copolymer B was prepared from formaldehyde and ethylene oxide in the same manner as for copolymer A. The comonomer content of this copolymer is 1.9 mol %. Polymerization of these copolymers was carried out in a manner similar to poly(1,3-dioxolane). After polymerization, the precipitated polymers were washed many times with acetone, followed by drying.

Acetylation

The mixture of 20 g of polyacetal, 140 ml dimethylformamide, 70 ml of acetic anhydride, and 5 ml of triethylamine was refluxed for 1 h with stirring. The polymer was precipitated by cooling the reaction mixture to room temperature. The polymer was filtered off, washed with excess methanol, and dried under vacuum. The yield of this acetylation is expected to be almost 100%, since an excess amount of the reagent was added.

RESULTS AND DISCUSSION

Sequence Length of Ethylene Oxide Unit

Peaks from ethylene oxide unit appear from 3.5 to 3.8 ppm, and these peaks will be used to discuss the chain microstructure. In this paper, ethylene

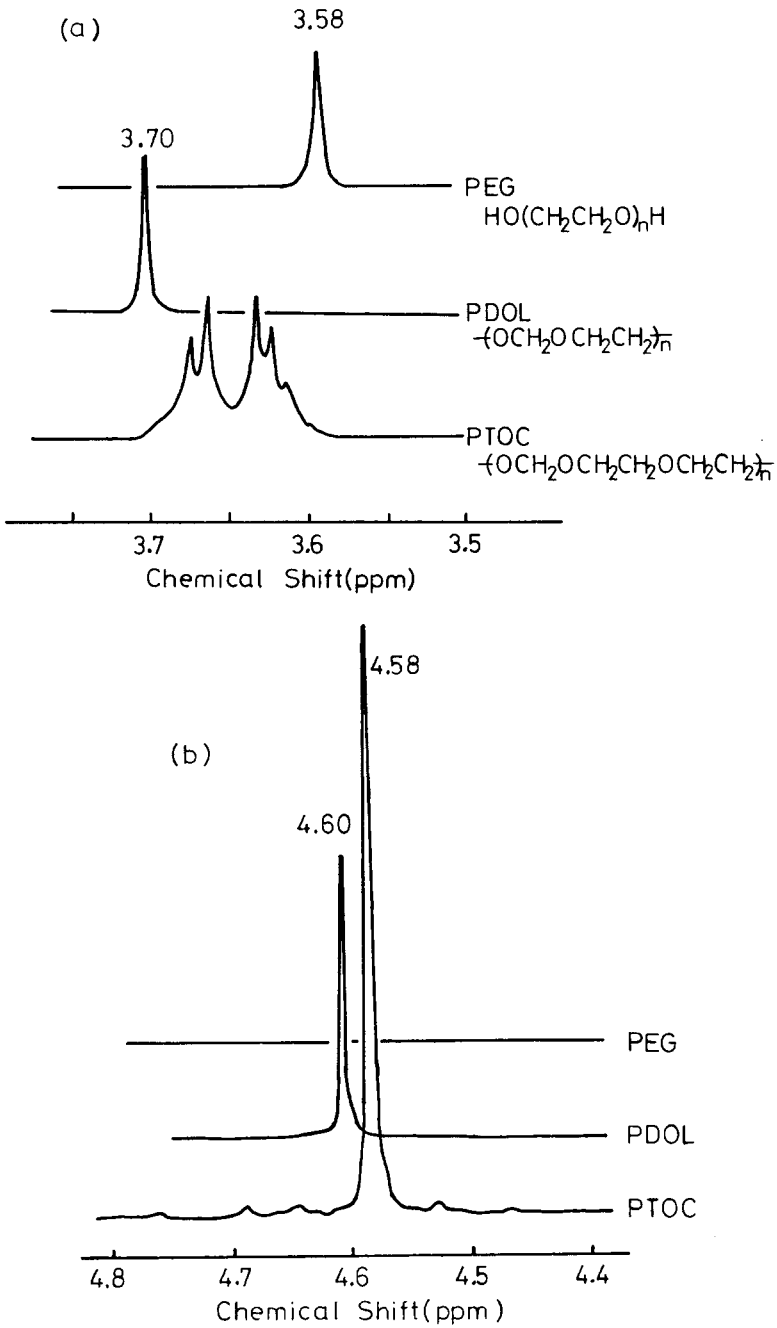


Fig. 1. NMR spectra of reference polymers, PEG, PDOL, and PTOC: (a) ethylene oxide region; (b) methylene oxide region.

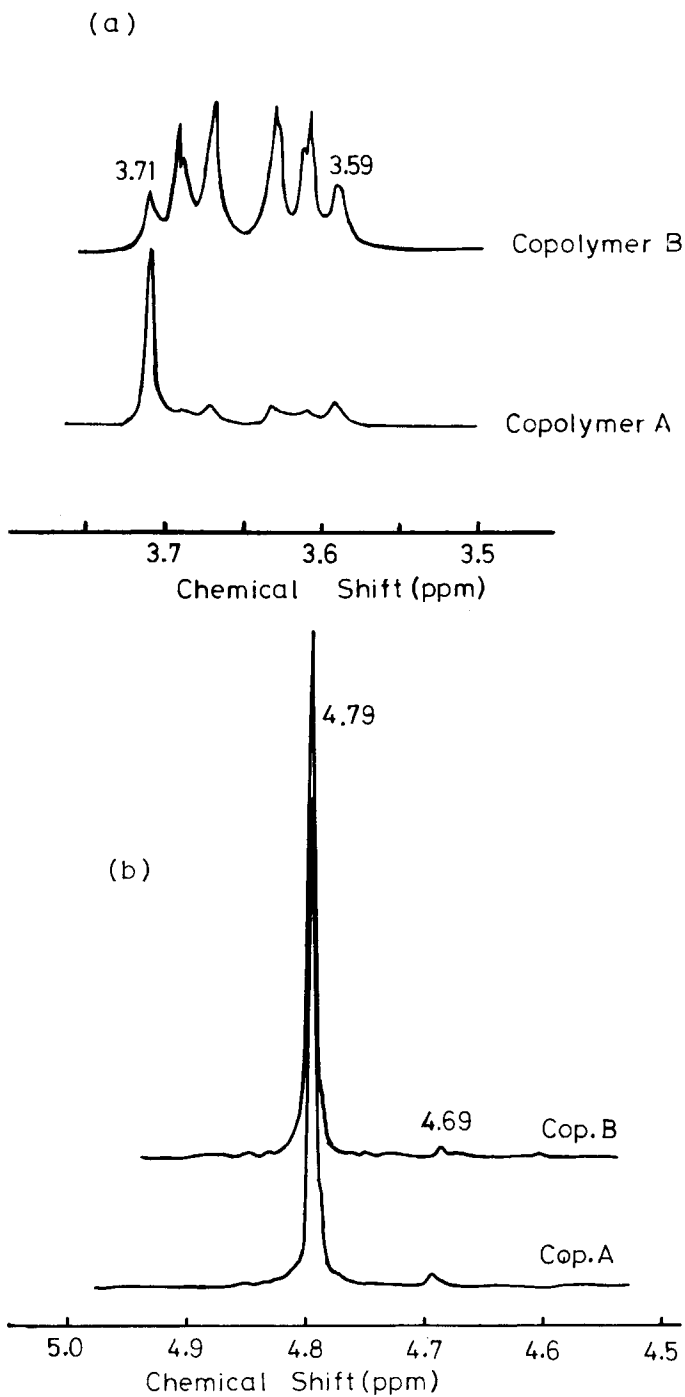
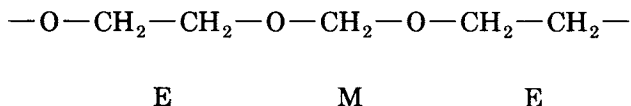
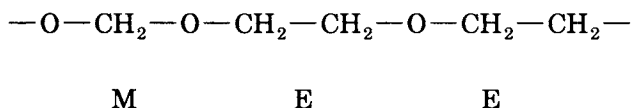


Fig. 2. NMR spectra of copolymers A and B: (a) ethylene oxide region; (b) methylene ox region.

oxide ($-\text{O}-\text{CH}_2-\text{CH}_2-$) will be denoted by E and methylene oxide ($-\text{O}-\text{CH}_2-$) by M. The chain structure of PDOL would be expressed by MEM, if the polymer were propagated in head-to-tail linkages. Figure 1 shows only one strong peak at 3.7 ppm for PDOL, proving that the above reaction linkage is the major structure. The spectrum of PTOC will be more complicated, since the following two different units are expected to be present:



and



As shown in Figure 1, the NMR spectrum of PTOC has many peaks in the range of 3.6–3.7 ppm. However, almost all the chain structure of this polymer will be MEE, because there is no peak completely coinciding with those of E due to PDOL and poly(ethylene glycol) (PEG). The spectra from ethylene oxide in copolymers are shown in Figure 2. Most of the ethylene oxide is present as the MEM unit, because the chemical shift of the main peak is very close to that of PDOL (3.7 ppm). The slight discrepancy of the chemical shift between the two polymers may be due to the difference of E-centered pentad sequence. Thus, PDOL has the sequence EMEME and copolymer A has mainly the sequence MMEMM, when we observe the ethylene oxide unit only. In contrast, copolymer B has a very complicated spectrum. Figure 2 suggests that this copolymer has all kinds of triad sequences, i.e., MEM, MEE, and EEE, because the two peaks from ethylene oxide unit coincide with those of PDOL and PEG. Unfortunately, the other four peaks do not exactly correspond to those of PTOC. However, both the polymers have four main peaks, and in this sense, copolymer B is close to PTOC. All these assignments are summarized in Table I. The last column in Table I indicates the recommended

TABLE I
Assignment of Peaks Due to Ethylene Oxide Unit

Triad sequence	Pentad sequence	Observed (ppm)	Recommended region for triad structure (ppm)
MEM	MEMM	Copolymer B	3.70
	EMEME	PDOL	
	EMEMM		
EEE	EEEE	PEG	3.60
	EEEEM		
	MEEEM		
MEE	EMEEM	PTOC	3.60
	MMEEM		
	MMEEE		3.62
	EMEEE		3.67

TABLE II
 Number-Average Sequence Length of Ethylene Oxide Unit^a

Sample	Triad Content			Sequence length N_e
	MEM	MEE	EEE	
Copolymer A	56.0	33.8	10.1	1.37
Copolymer B	11.3	77.3	11.3	2.00

^aThese values were calculated according to the equation $N_e = (\text{MEM} + \text{MEE} + \text{EEE}) / (\text{MEM} + 1/2\text{MEE})$.

region for calculating the sequence distribution of the ethylene oxide unit. Table II shows the calculated sequence length. Most of commercial polymers prepared with ethylene oxide showed values similar to that of copolymer A. The value of 2.00 in copolymer B is entirely incidental. As is clear from Figure 2, the chain microstructure of this copolymer actually consists of long, medium, and short sequence lengths of ethylene oxide.

End Groups

The chemical shifts of some organic compounds were examined under similar experimental conditions. The values shown in Table III are not different from those measured under more standard conditions, e.g., tetrahydrofuran as solvent and room temperature. Figure 3 shows the enlarged spectra of copolymer B for the region in which peaks from the end groups are expected to appear. The peaks for methyl unit in methoxy and ethoxy groups appear at 3.29 and 1.14 ppm triplet, respectively, and were assigned by referring to the values shown in Table III. Additionally, it was proved from the spectrum of triethylene glycol monoethyl ether that the peak for methylene unit of ethoxy groups overlapped with that for ethylene oxide. These two peaks are reproducible for the acetylated polymer. In the spectrum of the original (nonacetylated) sample, the peak from hydroxy group is not obvious in the region of 1.9–2.5 ppm. This fact may be due to very rapid exchange reaction of the hydrogen atom in hydroxy group with itself or a trace amount of other components having hydroxy groups because of high temperature. The

 TABLE III
 Chemical Shift of Some End Group Reference Compounds at Room Temperature

Compound	Chemical shift (ppm)		
	—OH	—OCH ₃	—OCH ₂ CH ₃
CH ₃ (OCH ₂ CH ₂) ₂ OCH ₃		3.25	
C ₂ H ₅ O(CH ₂ CH ₂ O) ₂ H	1.91		1.11 (triplet)
CH ₃ OCH ₂ OCH ₃		3.24	
CH ₃ O(CH ₂ CH ₂ O) ₂ H	1.94	3.25	
C ₂ H ₅ OCH ₂ CH ₂ OH	1.68		1.11 (triplet)
HO(CH ₂ CH ₂ O) ₄ H	2.35		
CH ₃ O(CH ₂ CH ₂ O) ₃ H	2.03	3.25	
HO(CH ₂ CH ₂ O) ₃ H	2.29		
C ₂ H ₅ O(CH ₂ CH ₂ O) ₃ H	2.03		1.12 (triplet)

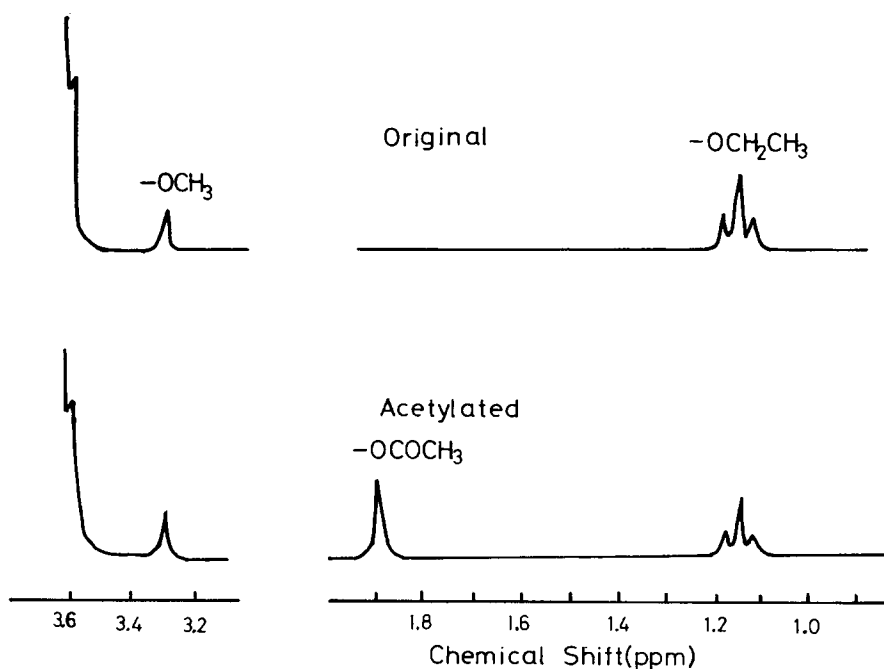


Fig. 3. Peaks due to acetyl, methoxy, and ethoxy groups.

peak from acetyl group is clearly and reproducibly observed at 1.89 ppm in the sample obtained by acetylation of the original sample. This peak can be used as indication of hydroxy group. Even if the original polymer contains acetyl group, the content of the original acetyl and hydroxy groups will be easily determined from the change in the areas under peak after acetylation.

We conclude that methoxy, ethoxy, and hydroxy end groups can be separately detected with proton NMR. The content of these end groups was determined for copolymer B together with that of methylene oxide and ethylene oxide units. As shown in Table IV, the mole fraction of all the end groups noticed in this study is 0.235 mol %, and that of the ethoxy group is the largest among them. Generally two end groups should be present for one

TABLE IV
Content of End Groups and Estimated Value of Number-Average Molecular Weight of Copolymer

Group	Mole ratio	Mole fraction	Molecular weight ^a
—OCH ₂ O—	819.0	95.99	24570
—OCH ₂ CH ₂ O—	32.2	3.77	1417
—OCH ₃	0.3740		12
—OH	0.7222	0.235	12
—OCH ₂ CH ₃	0.9029		41

$$\bar{M}_n = 26052$$

^aOne oxygen atom only was counted for each methylene oxide or ethylene oxide unit, because oxygen atom links up with two groups in a molecular chain.

molecular chain, if the polymer was completely linear. With this assumption, the number-average molecular weight was calculated from the relative mole ratio of all groups present in a chain. As shown in Table IV, the calculated number-average molecular weight is 26,052 g/mol and is close to that (29,500 g/mol) from gel permeation chromatography.⁸ This proves that the end-group analysis employed in this study is in general agreement. In other words, end groups other than those described above or chain branching is negligible in copolymer B.

References

1. M. Droscher, G. Lieser, H. Rieman, and G. Wegner, *Polymer*, **16**, 497 (1975).
2. M. Droscher, K. Hertwig, H. Rieman, and G. Wegner, *Makromol. Chem.*, **177**, 1695 (1976).
3. Y. Yamashita, T. Asakura, M. Okada, and K. Ito, *Makromol. Chem.*, **129**, 1 (1969).
4. I. Ishigaki, A. Ito, T. Iwai, and K. Hayashi, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 1883 (1972).
5. D. Fleischer and R. C. Schulz, *Makromol. Chem.*, **162**, 103 (1972).
6. D. Fleischer and R. C. Schulz, *Makromol. Chem.*, **176**, 677 (1975).
7. C. S. H. Chen and A. Diedward, *J. Macromol. Sci. Chem. Part A*, **4**, 349 (1970).
8. T. Ogawa and T. Oka, unpublished data, presented at The 46th Symposium of Analytical Chemistry, Japan, 1985, p. 83 (*J. Polym. Sci., Polym. Chem. Ed.*, submitted).

Received May 26, 1987

Accepted July 8, 1988