

# Fractionation and Characterization of Polyacetal Copolymers by Column Elution Method

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## Synopsis

Sufficient fractionation was attained for polyacetal copolymers by the column elution method. The characteristics of molecular weight, composition, and sequence length of the original copolymers were evaluated through the analyses of fractions by  $^1\text{H-NMR}$ , GPC, and DSC. Comonomer content in polymer fractions decreased with the increase of molecular weight in any samples, and the copolymer prepared by gas-phase polymerization showed broad compositional distribution as compared with that by solution polymerization.

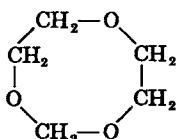
## INTRODUCTION

Polyacetal is well known as one of the most common engineering plastics. Moulded articles of polyacetal are being used in almost all industries. Slight differences in chemical structure, such as molecular weight, comonomer content, and sequence length, influence greatly mechanical and thermal properties. For this reason, the molecular characterization of polyacetal is very significant. Especially, the polyacetal copolymer is composed of various molecular species having different chemical structures. The copolymer must be inevitably separated into individual molecular species by applying some fractionation techniques. However, this technique is not complete yet for this polymer, although several papers have been already published concerning this subject.<sup>1-4</sup> We found good fractionation conditions for the column elution method. Several polyacetal copolymers prepared by different polymerization processes were fractionated. The fractions obtained thus were analyzed using GPC, NMR, and DSC.

## EXPERIMENTAL

### Polyacetal

Three different copolymers were subjected to the fractionation experiments; sample I was prepared by gas-phase polymerization and samples II and III by solution polymerization. The comonomer of samples I and II is trioxocane, i.e.,



and that of sample III is ethylene oxide. The characteristics of these samples are shown in Table I.

### Fractionation

The column elution method was adopted for fractionation. A small size of fractionation column was designed ( $27 \Phi \times 750$  mm) and is shown in Figure 1. Dedeposition of the polymer onto a support (Celite 545, a kind of diatomaceous earth) from solution was followed by ordinary steps.<sup>5</sup> Fractionation experiments were carried out by changing the solvent power stepwise at the beginning and continuously at a given temperature. Dimethylformamide (DMF) or tetralin was used as solvent and tetralin or decalin as nonsolvent. Decalin is not miscible with DMF, and tetralin is not complete as a nonsolvent for polyacetal copolymer. Therefore, the mixture of decalin with tetralin was used as eluent at the beginning of fractionation, where tetralin worked as solvent. When the tetralin content reached 100%, the mixture of tetralin with DMF was supplied, where tetralin was performed as nonsolvent. Final eluent composition was set up from a cloud point curve as shown in Figure 2. For example, the final eluent contains DMF of 18%, when we adopted 161°C as fractionation temperature. Details on fractionation temperature will be discussed later. Eluted solution was cut for each 500 mL and polymer fraction was recovered from eluted fractions by use of ultracentrifuge (15,000 rpm, 30 min). This condition on the centrifuge was chosen through recovering experiments for a polymer solution known in concentration.

### NMR Measurement

<sup>1</sup>H-NMR spectra of fractions were obtained from 4% solution in 1,2,4-trichlorobenzene at 160°C using a JEOL JNM-GX270 spectrometer operated at 270 MHz. The samples of only 10–30 mg were supplied for NMR measurement. The comonomer contents of fractions were determined from the areas of signals due to oxymethylene (4.5 ~ 4.9 ppm) and oxyethylene (3.5 ~ 3.8 ppm) groups

TABLE I  
Characteristics of Three Samples

| Sample | Comonomer content <sup>a</sup><br>(mol %) | Sequence length <sup>b,f</sup><br>( $n_E$ ) | Intrinsic viscosity <sup>c</sup><br>(dL/g) | Melting point <sup>d</sup><br>(°C) | MFR <sup>e</sup><br>(g/10 min) |
|--------|---|---|--|------------------------------------|--------------------------------|
| I      | 1.82                                      | 2.15  | 1.81                                       | 164.8                              | 7.6                            |
| II     | 1.87                                      | 2.12  | 1.62                                       | 163.1                              | 9.9                            |
| III    | 1.90                                      | 1.38  | 1.60                                       | 162.8                              | 9.9                            |

<sup>a</sup> As oxyethylene group.

<sup>b</sup> Average sequence length of oxyethylene group.

<sup>c</sup> Determined in *p*-chlorophenol at 60°C.

<sup>d</sup> Determined by DSC at heating rate of 10°C/min.

<sup>e</sup> Determined at 190°C under the load of 2160 g.

<sup>f</sup> Trioxocane is used as the comonomer for samples I and II. Average sequence length should have the value of around 2, judging from the structure of the comonomer.

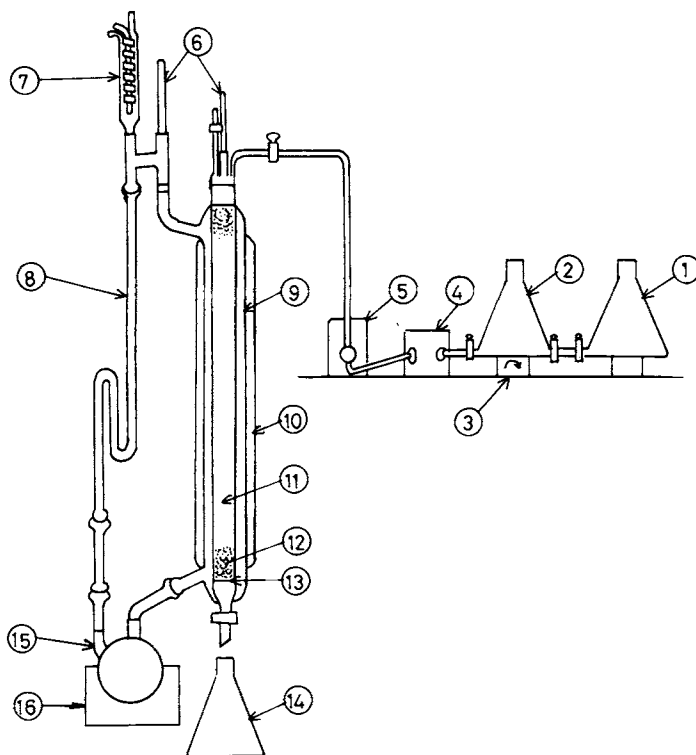


Fig. 1. Fractionation apparatus. (1 and 2) eluent container; (3) magnetic stirrer; (4) degasser; (5) pump; (6) thermometer; (7) condenser; (8) glass tube for heating medium; (9) fractionation column; (10) heating mantle; (11) support coated with polymer (Celite); (12) glass wool; (13) sintered glass; (14) flask for collecting eluted fraction; (15) flask for heating medium; (16) heating mantle.

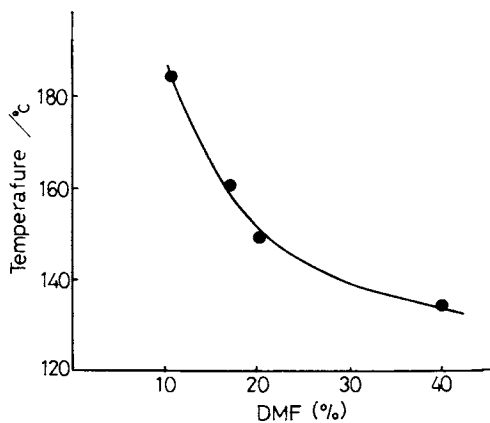


Fig. 2. GPC chromatogram of original polyacetals: (—) sample I; (---) sample II; (- - -) sample III.

were determined in  $^1\text{H-NMR}$  spectra.<sup>7</sup> For the copolymers prepared from trioxocane, comonomer content  $x$  is expressed as eq. (1) by taking into account the number of hydrogen atoms.

$$x = S_b/4S_a \quad (1)$$

where  $S_a$  represents the peak area due to oxyethylene group and  $S_b$  that due to oxymethylene group. For the copolymer prepared from ethyleneoxide,  $x$  is expressed as

$$x = S_b/(2S_a + S_b) \quad (2)$$

The sequence lengths of oxyethylene group were determined by assigning the signal to triad structure.

### GPC Measurement

The chromatograms were measured in DMF at 135°C using a Waters Model 150-C ALC/GPC with RI detector. The flow rate was 1.0 mL/min. Antioxidant of about 0.3 wt % (BHT) was added into solvent. Two columns packed with crosslinked polystyrene gel Shodex AD-80M/S were employed, which had separation performance ranging from  $10^2$  to  $10^7$  in molecular weight of polystyrene. The chromatograms of the original samples are shown in Figure 3. In this study, the absolute molecular weights are not obtained for these polyacetals.

### DSC Measurement

The thermal history of samples was removed by raising the temperature to 190°C twice. The melting points were determined with samples of 4 mg at a heating rate of 10°C/min using a Perkin-Elmer Model DSC-2C. These values were corrected with the melting point of indium metal.

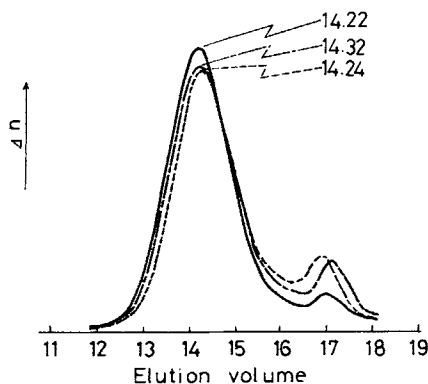


Fig. 3. Cloud point curve for 0.1% solution of polyacetal in DMF/tetralin system.

## RESULTS AND DISCUSSION

## Effect of Fractionation Temperature

It is preferable for fractionation to be essentially carried out in liquid-liquid phase equilibrium. One polyacetal copolymer was fractionated at 149.5 and 161°C by use of *n*-nonane and cyclohexanol as a heating medium, respectively. However, the quantity of polymer contained in each eluent did not vary steeply at 161°C as compared with that at 149.5°C, as shown in Figure 4. Therefore, the temperature of 161°C was adopted for fractionations in this study. The fractionation should be principally attained according to molecular weight because comonomers hardly influence the solubility of the polymer due to very low content. Figure 5 reveals that fractionation is mainly carried out according to molecular weight as expected. At the same time, compositional fractionation is also expected, if the composition of sample varies with molecular weight. Therefore, distributions of composition and sequence length of the original polymer can be estimated by analysis of fractionation results.

## Distributions of Composition and Sequence Length

An example of fractionation results is shown in Table II. From this result, it is shown that that fractionation is carried out not only according to molecular weight but also composition. Compositional distribution curves were evaluated for three different copolymers from the comonomer contents of fractions. The results are shown in Figure 6. These results are expressed in the form of cumulative weight distributions. It appears that a copolymer by gas-phase polymerization (sample I) is broader than the others, although the molecular weight distributions are very similar to each other, as shown in Figure 3. At the same time, it also means that comonomer content of these copolymers increases with

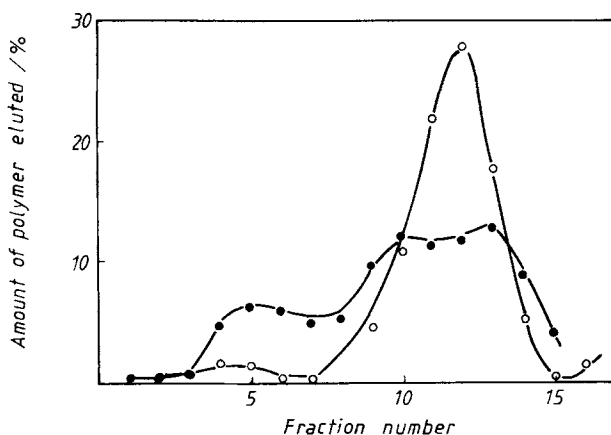


Fig. 4. Quantity of each polymer fraction expressed as a function of elution number, where fractionations were carried out at different temperatures: (○) 149.5°C; (●) 161°C. Elution number indicates the amount of eluent run out, e.g., in the case of elution number 5, 2500 mL ( $5 \times 500$  mL) is eluted.

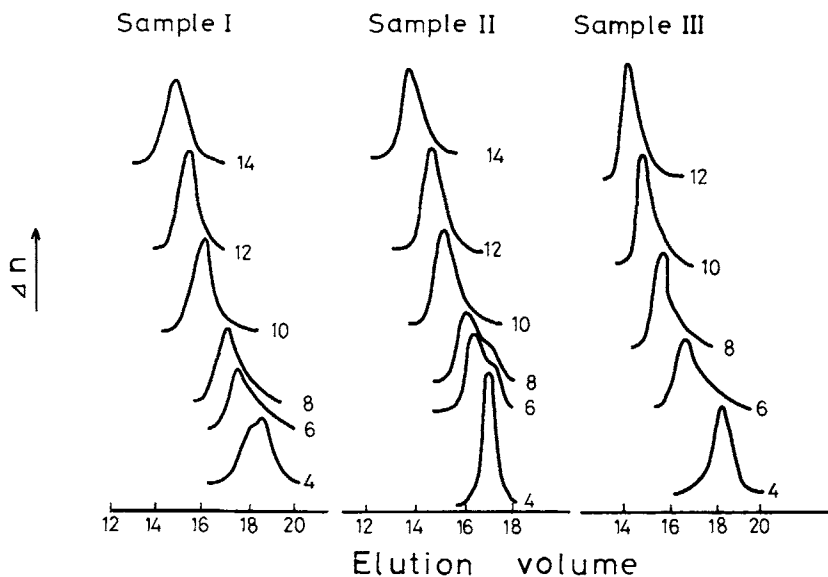


Fig. 5. GPC chromatograms of fractions for three samples. Numbers represent fraction numbers.

molecular weight, when we take into account the GPC chromatograms of fractions.

The average sequence length  $n_E$  of the ethylene group was calculated by the following equation<sup>6</sup>

$$n_E = (\text{FEF} + \text{FEE} + \text{EEE}) / (\text{FEF} + 1/2 \cdot \text{FEE})$$

TABLE II  
Fractionation Results of Sample I

| Fractionation number | Weight fraction (%) | Comonomer content <sup>a</sup> (mol %) | GPC peak (mL) |
|----------------------|---------------------|--|---------------|
| 2                    | 0.55                | —                                      | —             |
| 3                    | 0.64                | —                                      | —             |
| 4                    | 4.74                | 3.60                                   | 18.55         |
| 5                    | 4.26                | 4.00                                   | 17.67         |
| 6                    | 4.59                | 3.56                                   | 17.27         |
| 7                    | 3.62                | 3.15                                   | 17.07         |
| 8                    | 5.44                | 2.83                                   | 16.80         |
| 9                    | 14.05               | 2.15                                   | 16.35         |
| 10                   | 11.51               | 1.94                                   | 15.85         |
| 11                   | 10.10               | 1.81                                   | 15.62         |
| 12                   | 17.37               | 1.61                                   | 15.27         |
| 13                   | 18.32               | 1.31                                   | 14.90         |
| 14                   | 4.81                | 0.94                                   | 14.65         |

<sup>a</sup> As oxyethylene group.

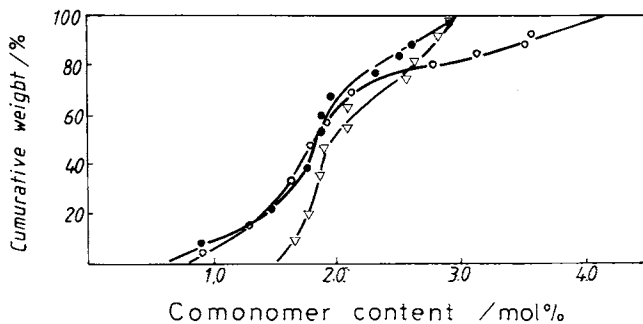


Fig. 6. Compositional distribution curves expressed by cumulative weight percent: (O) sample I; (●) sample II; (▽) sample III.

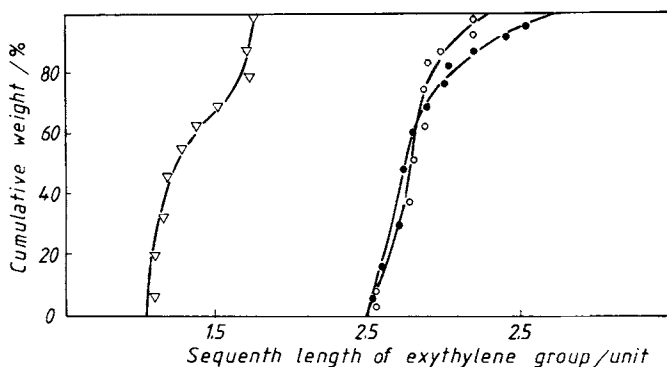


Fig. 7. Sequence length distribution curves for three samples: (O) sample I; (●) sample II; (▽) sample III.

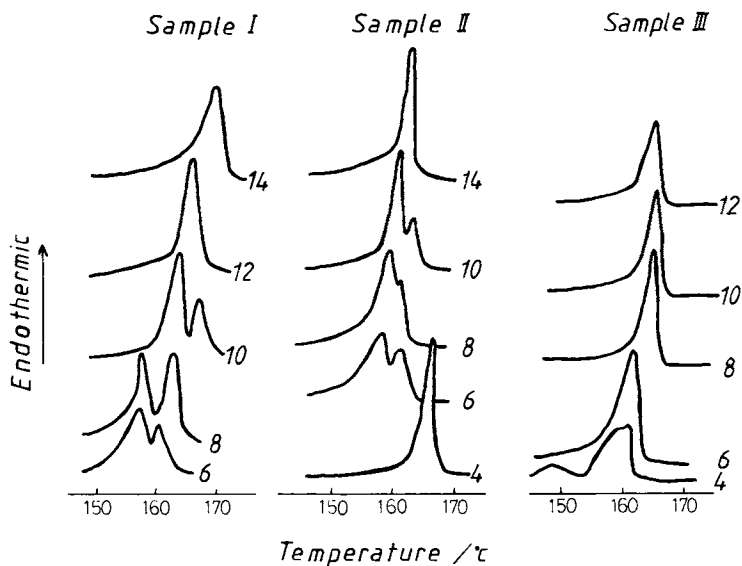


Fig. 8. DSC thermograms of fractions for three samples. Numbers represent order of fractions.

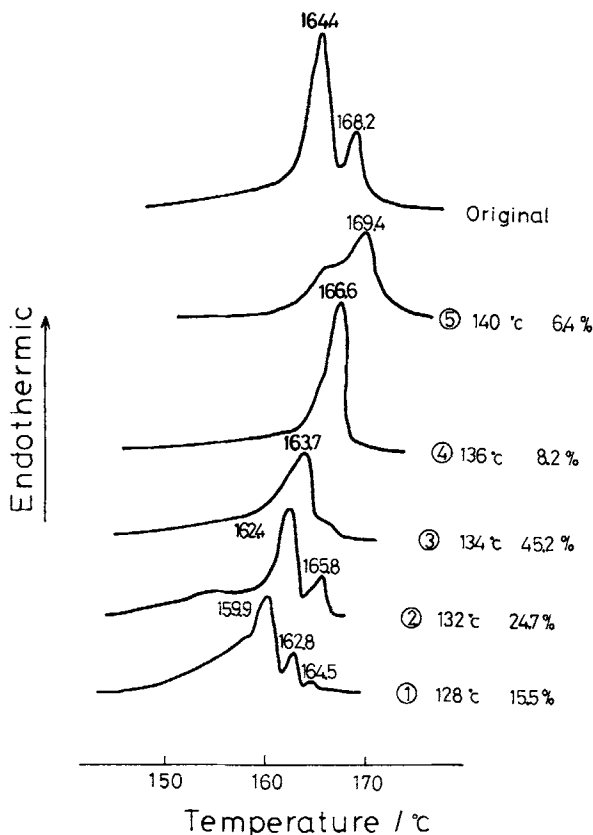


Fig. 9. DSC thermograms of refracted samples (original fraction is no. 10 in sample I). Numbers on peaks represent melting points and temperatures on the right indicate the rising temperature method.

where F represents an oxymethylene group and E an oxyethylene group. The partition of peak area to triad structure was carried out according to a previous study.<sup>7</sup> The sequence length distribution curves were obtained by calculating  $n_E$  for all fractions, as shown in Figure 7. However, any difference is not recognized among the samples. Additionally, the location of the distribution curve in sample III is different from others because ethylene oxide is used instead of trioxocane as comonomer.

### Thermal Behavior

The thermal behavior was examined by DSC. Figure 8 shows the DSC thermograms for some of fractions. Most of DSC thermograms in samples I and II have two peaks. For example, fraction 8 in sample I shows 5.3°C in temperature difference between them. Fraction 10 still has two peaks in spite of the fact that the GPC chromatogram is very narrow. Accordingly, it suggests that these fractions are composed of different polymer species, for example, the mixture of high molecular weight and high comonomer content polymer species and low molecular weight and low comonomer content polymer species, judging



from solubility of the copolymer. As another possibility, two peaks are caused by the existence of block copolymers. To clarify these possibilities, one fraction was refractionated by the rising temperature method. DSC thermograms for the fractions are shown in Figure 9. Many peaks appeared according to fractionation temperature, and some showed only one peak. Thus, the former case is more possible, i.e., the mixture of different polymer species.

## CONCLUSIONS

Fractionation was tried with polyacetal copolymers composed of the comonomers containing oxyethylene group. DMF or tetralin was used as solvent and tetralin or decalin as nonsolvent depending upon the fractionation steps. This experiment was sufficiently performed at a temperature of 161°C by the column elution method. Polymer fractions were analyzed by <sup>1</sup>H-NMR, GPC, and DSC. Comonomer content in polymer fractions decreased with increase of molecular weight. The copolymer prepared by gas-phase polymerization showed broad compositional distribution as compared with that by solution polymerization.

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Received March 9, 1989

Accepted October 2, 1989