Sequence Distributions of Polyacetals Studied by Reactive Pyrolysis–Gas Chromatography in the Presence of Cobalt Sulfate

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ABSTRACT: Reactive pyrolysis of copolymer type polyacetals in the presence of cobalt sulfate incorporated into pyrolysis–gas chromatography equipped with a high-resolution capillary separation column was applied to the study of sequence distributions. The ethylene oxide (E) contents and the distributions of E sequences up to E_7 in the polymer chain were evaluated on the basis of peak intensities of cyclic ethers containing E units on the pyrogram. These vlaues were in good agreement with those obtained by hydrolysis.

Introduction

Polyacetals which are mainly comprised of oxymethylene ($-OCH_2-$) (F) units are among the most popular engineering plastics. In industry the thermal stability of polyacetals is improved by acetylation of terminal OH groups or by copolymerization with a small amount of ethylene oxide ($-OCH_2CH_2-$) (E) because the oxymethylene homopolymer is subject to thermal depolymerization to formaldehyde at relatively low temperatures, even below 170 °C. In the copolymer polyacetals, it is important to estimate the E content and the distributions of E units, since these affect various properties of the polymer. A structural investigation of polyacetals, however, is quite difficult, even by spectroscopic methods, because of their insolubility in most solvents at room temperature. So far only a few studies to characterize polyacetal copolymers by means of NMR have been reported.[1–4]

Yamashita et al.[1] estimated the sequence length of F and E units in copolymers of 1,3-dioxolane and 1,3,5-trioxane by ^{1}H-NMR at 60 MHz using their chloroform solutions at 60 °C. Later, Fleischer et al.[2] applied ^{13}C-NMR at 25.2 MHz using a lanthanide shift reagent in chloroform solution to study the sequence distribution of such copolymers. In these reports, however, only polyacetal samples containing relatively large amounts (more than 3.5 mol %) of E units were studied because of their solubility in the used solvent. On the other hand, Ogawa et al. evaluated the end groups and the sequence distributions of a copolyacetal with a smaller E content (1.6 mol %) by ^{1}H-NMR at 270 MHz using *o*-dichlorobenzene as a solvent at 150 °C.[3] However, dissolving the polymer in *o*-dichlorobenzene at such an elevated temperature might cause degradation of oxymethylene sequences in the polymer chain depending on the copolymer composition. Recently, Wada et al.[3] reported the determination of end groups in polyacetal copolymers by ^{1}H-NMR at 270 MHz using hexafluoro-2-propanol (HFIP) as a solvent at room temperature.

Pyrolysis–gas chromatography (Py–GC) is known to be a powerful technique for studying the chemical structures of even intractable polymers. However, the ordinary Py–GC method has not been applied successfully to the characterization of copolyacetals because of their depolymerization mostly to formaldehyde with very low yields of the products reflecting the minor E sequences in the copolymers.

On the other hand, more than a quarter century ago, Burg et al.[5] reported that the pyrolysis of copolyacetals in the presence of inorganic salts such as cobalt sulfate preferentially yielded various cyclic ethers containing the E units rather than depolymerized and/or thermally cleaved linear products. In that report, the E content in copolymers of trioxane with ethylene oxide was evaluated for the relative yields of the cyclic ethers obtained by reactive Py–GC. Later, Yoshikawa et al. applied this technique to the determination of trioxocane units in the copolymerized acetals.[6] In these studies, however, the satisfactory separation of characteristic peaks on the pyrograms was not attained because of the poor resolving power of the conventional packed separation columns utilized. Furthermore, the distributions of E units could not be estimated accurately because cyclic ethers containing more than three E units were not eluted by the packed columns.

In the present work, the reactive pyrolysis of copolymer polyacetals in the presence of cobalt sulfate incorporated into Py–GC equipped with a high-resolution capillary separation column was successfully applied to study their sequence distributions. The E contents and the distributions of E sequences up to E_7 in polymers were evaluated on the basis of peak intensities of cyclic ethers containing E units on the pyrogram.

Experimental Section

Polymer Samples. Two series of polyacetal samples ([A] and [B]) studied in this work are listed in Table 1. Series A consisted of three polyacetal copolymer samples designated POM–EO (ethylene oxide) copolymer that contained various lengths of E sequences. The E contents (mol %) and sequence distributions (mol %) provided in the table were estimated by hydrolysis followed by GC measurement. Series B consisted of three model polyacetal samples, each of which contained one kind of E sequence. These were used as reference polymers: the poly(oxymethylene) (POM) homopolymer contained no E units; the POM–1,3-dioxolane (DO) copolymer and the POM–1,3,6-trioxocane (TOC) copolymer contained only isolated E units and EE dyads, respectively.

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Table 1. Polyacetal Samples Used in This Study

[A] Ethylene Oxide Copolymers

	E unit contents (mol %)[a]	sequence distributions (mol %)[a] FEF/FE$_2$F/FE$_3$F/FE$_4$F/FE$_5$F
POM−EO-1	1.39	79.3/17.2/3.5
POM−EO-2	4.69	59.0/31.6/8.7/0.7
POM−EO-3	8.87	47.1/32.2/14.9/4.9/0.9

[B] Model Polymers

	E units contents (mol %)	sequence length of E units
poly(oxymethylene) (POM) homopolymer $-(CH_2O)_n-$		
POM−dioxolane (DO) copolymer $-(CH_2O)_n(CH_2CH_2OCH_2O)_m-$	5.38	1
POM−trioxocane (TOC) copolymer $-(CH_2O)_n(CH_2CH_2OCH_2CH_2OCH_2O)_m-$	7.40	2

[a] mol % for E unit determined by hydrolysis followed by GC measurement.

Cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$) supplied by Wako Chemical was used as the catalyst for the reactive pyrolysis. Mixtures of polyacetal samples (200 mg) and cobalt sulfate (0−10 mg) were cryomilled into a fine powder by a freezer mill (SPEX 6700) at liquid nitrogen temperature prior to Py−GC measurement in order to attain homogeneous samples.

Condition for Py−GC. A vertical microfurance-type pyrolyzer (Yanaco GP1018) was directly attached to a gas chromatograph (Shimadzu GC-7A) equipped with a flame ionization detector (FID). About 0.1 mg of the milled sample was placed in a platinum sample cup and then pyrolyzed under the flow of helium carrier gas. A fused silica capillary column (50 m × 0.25 mm i.d.) coated with poly(methylphenylsiloxane) (0.25 μm thick) supplied by Quadrex was used. The 50 mL/min carrier gas flow rate at the pyrolyzer was reduced to 1.0 mL/min at the capillary column by means of a splitter. The column temperature was initially set at 50 °C and then programmed up to 300 °C at a rate of 5 °C/min. Identification of the peaks on the pyrograms was mainly carried out using a GC−MS system (Shimadzu QP-1000) with an electron impact ionizer (70 eV) to which the pyrolyzer was directly attached.

Hydrolysis Method. Three milliliters of concentrated HCl and 15 mL of methanol were added to ca. 3 g of a polyacetal sample taken in a 50 mL flask, and this mixture was refluxed at 65 °C for 1.5 h. After fractional distillation of low-boiling compounds at 65 °C, the remaining solution was neutralized by sodium methylate, and subjected to GC measurement. The GC instrument (Hitachi 663-30) was equipped with a FID and a 1 m × 3 mm (i.d.) glass column of 5% PEG 20M on Celite 545 DMCS. The injection temperature was set at 250 °C, and the flow rate of the carrier gas (nitrogen) was regulated at 40 mL/min. The column temperature was programmed as follows: first held at 130 °C for 3 min, secondly increased up to 160 °C at a rate of 60 °C/min and held for 2.5 min, then increased up to 210 °C at a rate of 60 °C/min and held for 3 min, and finally increased up to 220 °C at a rate of 60 °C/min. The E content and the sequence distributions up to the E pentads were determined on the basis of the peak intensities of mono-, bis-, tris-, tetrakis-, and pentakis(ethylene glycol) on the resulting chromatogram.

Results and Discussion

Pyrolysis in the Presence of Cobalt Sulfate. Figure 1 shows typical pyrograms obtained from the POM−EO-3 sample at 400 °C (a) without adding cobalt sulfate and (b) in the presence of 5 wt % of cobalt sulfate. In the pyrogram of (a) a strong peak due to formaldehyde formed from the main component of the polyacetal is observed at the early retention time even though it shows a very weak FID response. However, it is very difficult to obtain effective information about the sequence distributions of the polymer chain on the basis of this pyrogram because the characteristic peaks reflecting E sequences are too weak even for semiquantitative estimations. On the other hand, the pyrolysis in the presence of cobalt sulfate gives a drastically different pyrogram, as shown in (b). The main characteristic peaks identified by Py−GC−MS are summarized in Table 2 together with their structures. As was expected from former reports,[5,6] cyclic ethers containing E and F units are predominant. In this case, much larger cyclic ethers are observed up to E$_7$F and (E$_2$F)$_3$ by using a capillary column. Here, the peaks of E$_2$F and F$_4$ overlapped completely when using a nonpolar column such as poly(dimethylsiloxane). However, by using mildly polar poly(methylphenylsiloxane), they were sufficiently resolved. The distributions of E units as well as the E contents of the polymers can be determined from the intensities of peaks due to these cyclic ethers obtained if the peaks on the pyrogram reflect the chemical structures in the original polymer chain.

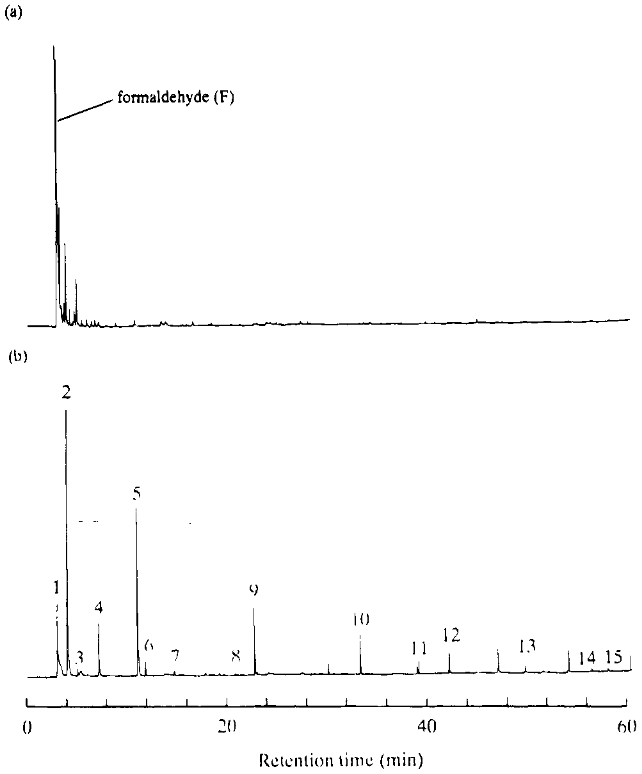
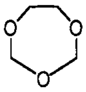
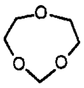
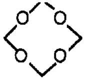
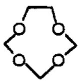


Figure 1. Pyrograms of POM−EO-3 at 400 °C: (a) without $CoSO_4$; (b) in the presence of 5 wt % $CoSO_4$. Peaks 1−15 are assigned in Table 2.

Py−GC Measurements of Model Polymers. The three model polymers were subjected to Py−GC analysis in the presence of cobalt sulfate in order to confirm whether the sequence distributions estimated by the cyclic ethers on the pyrograms reflect those in the original polymer chain. Figure 2 shows the pyrograms of (a) POM homopolymer, (b) POM−1,3-dioxolane (DO) copolymer, and (c) POM−1,3,6-trioxocane (TOC) copolymer at 400 °C in the presence of 5 wt % cobalt sulfate.

As would be expected from the polymer structure, in the pyrogram of the POM homopolymer (a), formaldehyde (F) and cyclic compounds comprising only F units are observed while no cyclic ether containing E unit(s) is observed. This result suggests that the formation of E unit(s) from oxymethylene sequences does not occur during the reactive pyrolysis of the POM homopolymer

Table 2. GC–MS Peak Assignment of the POM–EO-3 Pyrolysates in the Presence of Cobalt Sulfate

Peak No.[a]	representation by E and F unit[b]	structure (name)	Peak No.[a]	representation by E and F unit[b]
1	F	CH_2O (formaldehyde)	8	$\ulcorner F_5 \urcorner$
2	$\ulcorner EF \urcorner$	 (1,3-dioxolane)	9	$\ulcorner E_3F \urcorner$
			10	$\ulcorner E_4F \urcorner$
3	$\ulcorner F_3 \urcorner$	 (1,3,5-trioxane)	11	$\ulcorner (E_2F)_2 \urcorner$
			12	$\ulcorner E_5F \urcorner$
4	$\ulcorner EF_2 \urcorner$		13	$\ulcorner E_6F \urcorner$
5	$\ulcorner E_2F \urcorner$	 (1,3,6-trioxocane)	14	$\ulcorner E_7F \urcorner$
			15	$\ulcorner (E_2F)_3 \urcorner$
6	$\ulcorner F_4 \urcorner$			
7	$\ulcorner EF_3 \urcorner$			

[a] Peak no. corresponds to that in Figures 1–3. [b] E = ethylene oxide, F = oxymethylene.

sample. Similarly, in the pyrogram of POM–DO copolymer (b), only cyclic ethers reflecting isolated E units such as EF, EF_2, and EF_3 are observed in addition to the cyclic ethers formed from the F sequences. Furthermore, in the pyrogram of the POM–TOC copolymer (c), cyclic ethers reflecting EE dyads such as E_2F, $(E_2F)_2$, and $(E_2F)_3$ are characteristically observed. Here, the fact that a small peak of EF is observed suggests that the degradation of the EE dyad in the polymer chain to form EF occurs to some extent. However, since the peak intensity of EF is much smaller than those of cyclic ethers reflecting EE dyads such as E_2F, $(E_2F)_2$, and $(E_2F)_2$, the contribution of the degraded EE dyad could be negligible. These results observed for the model polymers indicate that the sequence distributions of E units in the original polymer chain are almost quantitatively reflected in the cyclic ethers formed through the reactive pyrolysis in the presence of cobalt sulfate.

Effect of Pyrolysis Temperature. In order to study the effect of the pyrolysis temperature on the reactive pyrolysis, three pyrograms of the POM–EO-1 sample weighing about 100 μg were measured in the presence of 5 wt % cobalt sulfate at different temperatures. Since pyrolysis temperatures lower than 300 °C caused serious tailing of the characteristic peaks, three different temperatures, 400, 500, and 600 °C, were examined. The variations of the observed intensities per unit sample weight of the main peaks on the pyrograms are summarized in Table 3. Here, the intensities of the characteristic peaks on the pyrogram obtained at 400 °C are set at 100. The intensity of formaldehyde slightly increases while those of cyclic compounds comprising only F units drastically decreased at higher pyrolysis temperatures. This tendency suggests that depolymerization of F sequences through ordinary pyrolysis is favored at elevated pyrolysis temperatures. Similarly, the peak intensities of cyclic ethers containing E unit(s) considerably decrease when the pyrolysis temperature is increased, which also suggests that the contribution of ordinary pyrolysis rather than catalytic pyrolysis is favored at elevated temperatures. These results suggest that cyclic ethers are most effectively formed through the reactive pyrolysis in the presence of cobalt sulfate at 400 °C. Therefore, the following determination was exclusively carried out at 400 °C.

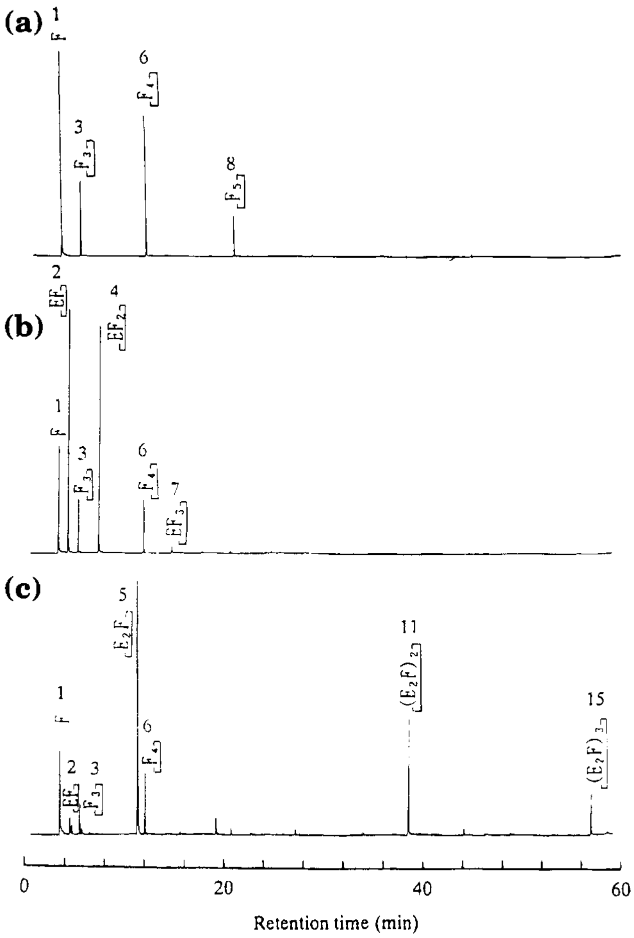


Figure 2. Pyrograms of model polymers at 400 °C in the presence of 5 wt % $CoSO_4$: (a) POM homopolymer; (b) POM–DO copolymer; (c) POM–TOC copolymer. Peaks 1–15 are assigned in Table 2.

Table 3. Effect of Pyrolysis Temperature on Intensities of Characteristic Peaks in the Pyrogram of POM–EO-1 Observed in the Presence of 5 wt % $CoSO_4$

pyrolysis temp (°C)	peak intensities/unit sample weight[a]								
	F	$\ulcorner EF \urcorner$	$\ulcorner F_3 \urcorner$	$\ulcorner EF_2 \urcorner$	$\ulcorner E_2F \urcorner$	$\ulcorner F_4 \urcorner$	$\ulcorner EF_3 \urcorner$	$\ulcorner F_5 \urcorner$	$\ulcorner E_3F \urcorner$
400	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>
500	105	100	17	91	98	57	71	48	86
600	105	90	6	79	84	3	82	53	60

[a] Peak intensities obtained at 400 °C were used as the reference values.

Effect of the Amount of Cobalt Sulfate. Polyacetal samples were pyrolyzed in the presence of different amounts of cobalt sulfate between 0.5 and 5 wt % at 400 °C. When cobalt sulfate was added in the range 0.5–1 wt %, the sequence distributions by Py–GC estimated for the POM–EO-1 sample with the

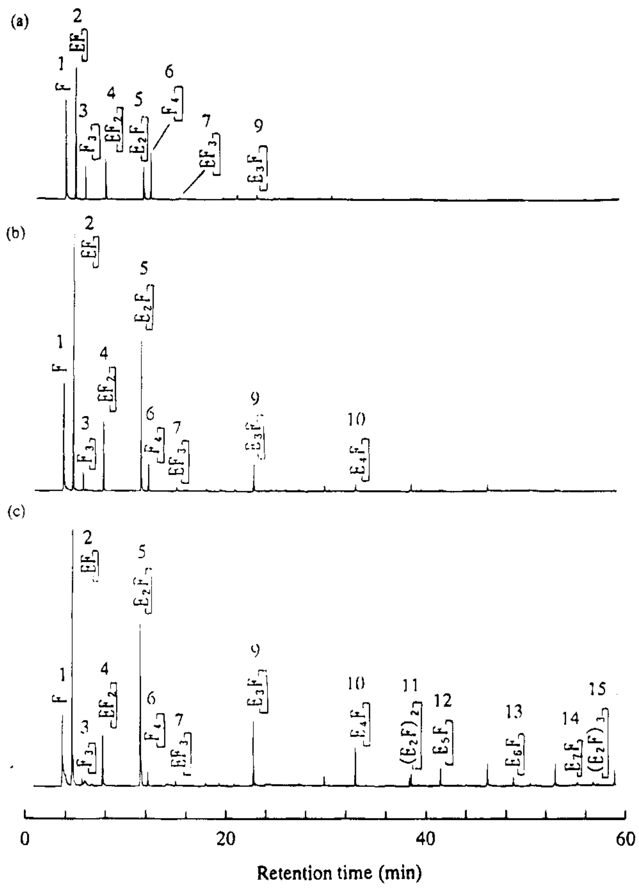


Figure 3. Pyrograms of POM copolymers at 400 °C in the presence of 5% cobalt sulfate: (a) POM−EO-1 (F/E = 98.6/1.4); (b) POM−EO-2 (F/E = 95.3/4.7); (c) POM−EO-3 (F/E = 91.3/8.9). Peaks 1−15 are assigned in Table 2.

lowest E content (1.39 mol %) agreed most closely with results obtained by hydrolysis followed by GC measurement. However, reactive pyrolysis for POM−EO-2 and POM−EO-3 which had higher E contents in the presence of 0.5−1 wt % of cobalt sulfate resulted in serious tailing of the characteristic peak on the pyrograms mainly because of the slow pyrolysis. However, when the pyrolysis was carried out in the presence of 5 wt % catalyst, the tailing almost disappeared. This indicates that addition of cobalt sulfate between 0.5 and 1 wt % is insufficient to cause the quantitative cyclization of polyacetals containing larger amounts of the E unit. Therefore, the reactive pyrolysis in the following determinations were carried out in the presence of 5 wt % cobalt sulfate.

Determination of the EO Contents and the Distributions of EO Units in the Polymer Chain. Determination of the E contents and the sequence distributions of the E units(s) in the polymer chain were carried out for the three POM−EO copolymer samples. Figure 3 shows the pyrograms of (a) POM−EO-1, (b) POM−EO-2, and (c) POM−EO-3 at 400 °C in the presence of 5 wt % cobalt sulfate. In the pyrogram of POM−EO-1 (a), cyclic ethers containing up to three E units are observed. This fact suggests that the original polymer chain contains at least isolated E units, EE dyads, and EEE triads. On the other hand, in the pyrograms of POM−EO-2 and POM−EO-3, cyclic ethers containing up to four and seven E units are observed, respectively, which indicates that E sequences in the polymer chain become longer for the copolymers with higher E contents.

Compositional analysis was carried out on the basis of the total molar yield of E units, *M*(total), evaluated from peak intensities of cyclic ethers containing E units on the pyrograms shown in Figure 3. *M*(total) is calculated as follows.

First, the observed peak intensity, $I_{E_iF_j}$ (counts), of a cyclic ether having i unit(s) of E and j units(s) of F is converted into the corrected peak intensity, $C_{E_iF_j}$, that is, relative molar peak intensity of the corresponding cyclic ether normalized by sample weight, w (μg) as follows:

$$C_{E_iF_j} = I_{E_iF_j}/w(1.1i + 0.16j) \qquad (1)$$

Here, 1.1 and 0.16 are the effective carbon numbers (ECNs) of an E ($-CH_2-CH_2-O-$) and an F ($-CH_2-O-$) unit, respectively, which correspond to the respective molar sensitivities for FID. Thus, the value ($1.1i + 0.16j$) corresponds to the molar sensitivity for the cyclic ether (E_iF_j). The ECNs (1.1 and 0.16) are empirically determined from the GC data for a known amount of toluene (ECN = 7) solution of 1,3,5-trioxane (FFF) and 1,4-dioxane (EE). For example, when $I_{E_iF_j}$ is observed to be 16 200 (counts) by use of a polyacetal sample weighing 100 μg, the value of $C_{E_iF_j}$ for the E_2F is calculated as follows:

$$\begin{aligned} C_{E_2F} &= I_{E_2F}/w(1.1i + 0.16j) \\ &= 16200/100(1.1 \times 2 + 0.16 \times 1) = 68.6 \end{aligned}$$

Furthermore, the value of $C_{E_iF_j}$ multiplied by the number of E unit(s) involved in the cyclic ether (i), $iC_{E_iF_j}$, should be directly proportional to the molar yield of E unit(s) contained in the cyclic ether. Therefore, *M*(total), which can be used as a measure of the E content in the polyacetal, is expressed as the summation of the products as follows:

$$M(\text{total}) = \sum_{i=1}^{7}\sum_{j=1}^{3} iC_{E_iF_j} \qquad (2)$$

For example, as for POM−EO-2 weighing 100 μg, of which observed peak intensities ($I_{E_iF_j}$ (counts)) for EF, EF_2, E_2F, EF_3, E_3F, E_4F, and $(E_2F)_2$ are 25 400, 6860, 16 200, 509, 2720, 663, and 292, respectively, *M*(total) is calculated as follows:

$$\begin{aligned} M(\text{total}) &= \sum_{i=1}^{7}\sum_{j=1}^{3} iC_{E_iF_j} \\ &= 25400/100(1.1 \times 1 + 0.16 \times 1) + \\ &\quad 6860/100(1.1 \times 1 + 0.16 \times 2) + \\ &\quad 2 \times 16200/100(1.1 \times 2 + 0.16 \times 1) + \\ &\quad 509/100(1.1 \times 1 + 0.16 \times 3) + \\ &\quad 3 \times 2720/100(1.1 \times 3 + 0.16 \times 1) + \\ &\quad 4 \times 663/100(1.1 \times 4 + 0.16 \times 1) + \\ &\quad 4 \times 292/100(1.1 \times 4 + 0.16 \times 2) \\ &\doteqdot 422 \end{aligned}$$

Figure 4 shows the relationship between the percentages of the E unit contained in the three polyacetal samples and the values of *M*(total) calculated by eq 2. Since an almost linear relationship is observed for the three polyacetal samples, the E content of an unknown sample can be determined from the intensities of the characteristic peaks on the pyrogram using such a calibration curve.

Table 4. Sequence Distributions of Polyacetal Copolymers Estimated by Py–GC

	POM–EO-1 [98.6/1.4]		POM–EO-2 [95.3/4.7]		POM–EO-3 [91.1/8.9]	
	Py–GC[a]	hydrolysis[b]	Py–GC[a]	hydrolysis[b]	Py–GC[a]	hydrolysis[b]
–FEF–	70.1 (74.5)	79.3	60.0	59.0	44.3	47.1
$-FE_2F-$	25.5 (22.3)	17.2	33.0	31.6	37.1	32.2
$-FE_3F-$	4.4 (3.2)	3.5	5.6	8.7	9.5	14.9
$-FE_4F-$			1.4	0.7	5.2	4.9
$-FE_5E-$					2.7	0.9
$-FE_6E-$					0.9	
$-FE_7F-$					0.3	
total	100.0	100.0	100.0	100.0	100.0	100.0

[a] Sequence distribution obtained by Py–GC through the reactive pyrolysis at 400 °C in the presence of 5 wt % cobalt sulfate. The values in parentheses are obtained in the presence of 1 wt % cobalt sulfate. [b] Sequence distribution obtained from hydrolysis followed by gas chromatography.

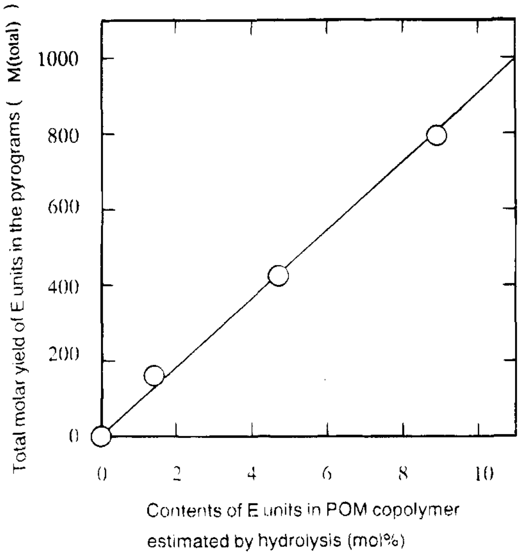


Figure 4. Relationship between total molar yield of the E units estimated by Py–GC and contents of E units in POM–EO copolymer estimated by hydrolysis.

Finally, the distributions of the E_x-unit sequence in the polymer chain [$D(-FE_xF-)$] were calculatd by the following equations:

$x = 1$

$$D(-\mathrm{FEF}-)\ (\mathrm{mol}\ \%) = \frac{\sum_{j=1}^{3} C_{\mathrm{EF}_j}}{M(\mathrm{total})} 100 \qquad (3)$$

$x = 2$

$$D(-\mathrm{FE_2F}-)\ (\mathrm{mol}\ \%) = \frac{2\sum_{n=1}^{3} nC_{(\mathrm{E_2F})_n}}{M(\mathrm{total})} 100 \qquad (4)$$

$x \geq 3$

$$D(-\mathrm{FE}_x\mathrm{F}-)\ (\mathrm{mol}\ \%) = \frac{xC_{\mathrm{E}_x\mathrm{F}}}{M(\mathrm{total})} 100 \qquad (5)$$

The symbols in eqs 3–5 are basically the same as those for eqs 1 and 2. The number n (1–3) in eq 4 corresponds to the repeating number of $-(E_2F)-$ units for peaks 4, 11, and 15 shown in Table 2. The summation of $C_{E_xF_j}$ multiplied by x corresponds to the total molar yield of E units in the E_x-unit sequence. Therefore, the distributions of E_x-unit sequence can be determined from the total molar yield of E units in the E_x-unit sequence against M(total).

The sequence distributions of polyacetal samples estimated by reactive Py–GC are summarized in Table 4 together with those obtained by hydrolysis followed by GC measurement. Generally, fairly good agreement is observed for the values obtained by the two procedures. As for the POM–EO-3 sample having the highest E content (8.9 mol %), the distributions including longer E sequences up to the EEEEEEE heptads can be determined by Py–GC. Here, the biggest discrepancies between the data of Py–GC and hydrolysis are observed for the POM–EO-1 sample with the lowest E content mainly because of the excess amount of cobalt sulfate (5 wt %) employed. As shown in the data in parentheses in Table 4, when the amount of the catalyst is decreased to 1 wt %, the discrepancies are much smaller. These data suggest that for accurate determination of the sequence distributions in copolyacetals containing E units, the optimum amount of the catalyst should be changed depending on the E content. The reproducibility evaluated for the distributions of isolated E units is about 1.5% based upon the relative standard deviation for three repeated runs using the POM–EO-1 sample.

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