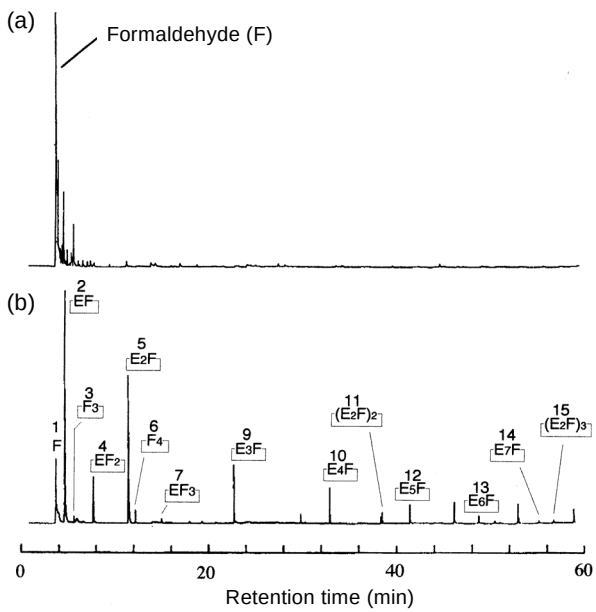
Analysis of Sequence Distribution of Polyacetal Copolymers by Reactive Py-GC in the Presence of Cobalt Sulfate

[Background] Reactive Py-GC in the presence of a solid acid catalyst, such as cobalt sulfate ($CoSO_4$), has been successfully used to characterization polymers having ether-bonds, such as polyacetal (PA) and cellulose. Specifically, it has been reported that the pyrolysis of polyacetal copolymers in the presence of cobalt sulfate leads to the preferential formation of various cyclic ethers containing the comonomer units. The comonomer reflects the sequence distribution in the original polymer chains. This note describes the analysis of the chemical composition and sequence distribution of polyacetal copolymers by means of reactive Py-GC in the presence of cobalt sulfate.

[Experimental] A series of PA samples, comprised of oxymethylene [($-OCH_2-$) (F)] units as a main component and small amounts (1-9 mol%) of ethylene oxide [($-OCH_2CH_2-$) (E)] units, are examined. Mixtures of the PA samples (200 mg) and $CoSO_4 \cdot 7H_2O$ (10 mg) were cryo-milled into a fine powder using a freezer mill at liquid nitrogen temperature. Approximately 100 µg of the milled sample is subjected to reactive Py-GC at 400ºC.



[Results] Figure 1 shows a typical pyrogram obtained from the pyrolysis of a PA sample, containing *ca*. 9 mol% of E units, at 400ºC. The top pyrogram (a) was obtained without cobalt sulfate present and the bottom pyrogram (b) was obtained in the presence of 5 wt % of cobalt sulfate. Pyrogram (a), contains a large formaldehyde peak. However, it was almost impossible to obtain additional information on the sequence distribution of the polymer sample from this pyrogram because the characteristic peaks reflecting E sequences are too weak. On the other hand, the second pyrogram (b) obtained in the presence of cobalt sulfate exhibits cyclic ethers comprised of E and F units, which reflect the chemical structures in the original polymer chain. Based on the peak intensities of these cyclic ethers, the distributions of E units as well as the E contents of the copolymer samples can be determined accurately and precisely.

Figure 1. Pyrograms of copolyacetal sample obtained at 400ºC:
(a) without addition cobalt sulfate ; (b) in the presence of 5 wt% cobalt sulfate.

Pyrolysis temp. : 400ºC, GC oven temp. : 50ºC- (5 ºC/min)-300ºC, Carrier gas flow : 50 ml/min
Separation column : Poly(methylphenylsiloxane), Length 50mm, 0.25mm i.d., Film thickness 0.25µm, Column flow : 1.0 ml/min

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