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Thermal degradation of aromatic polyformals derived from bisphenol A and bisphenol AF¹

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Abstract

Thermal degradation of fluorine-containing Polyformal II from bisphenol AF and dichloromethane was studied by TG-DTA/ FTIR, Pyr-GC/MS and Pyr-GC and compared with that of Polyformal I without fluorine atoms, which was derived from bisphenol A and dichloromethane. The thermal degradation of Polyformal II occurs in two stages, whereas that of Polyformal I occurs in a single stage. The major products of thermal decomposition of Polyformal I are α -methylstyrene, phenol, 4-hydroxy- α -methylstyrene, isopropyl phenol, and 4-isopropenyl anisole, whereas those of Polyformal II are pentafluoroisopropenyl benzene and pentafluoroisopropenyl anisole. The two-step decrease in weight of Polyformal II by thermal degradation is not caused by the different reactions, but results from the different vapor pressures, that is, the different rates of vaporization between the decomposition products, more volatile pentafluoroisopropenyl benzene and less volatile pentafluoroisopropenyl anisole.

Keywords: Thermal degradation; Aromatic polyformal; Fluorine-containing polymer

1. Introduction

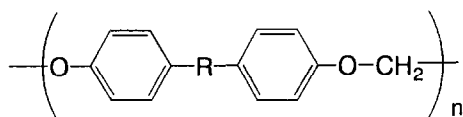
Recently, various fluorine-containing polymers have been prepared, because they have excellent properties, such as thermal stability, resistance to chemicals, are water and oil repellent and have a low friction coefficient.

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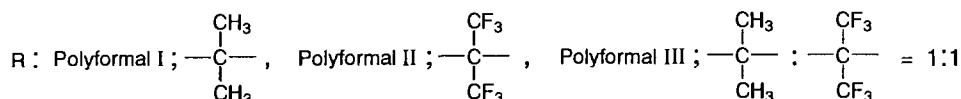
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Previously, one of authors reported on the preparation and characterization of fluorine-containing polyformals from bisphenol AF (2,2-bis(*p*-hydroxyphenyl)hexafluoropropane) [1]. Among various properties, fluorine-containing polyformal exhibits improved thermal stability compared to polyformal derived from bisphenol A (2,2-bis(*p*-hydroxyphenyl)propane).

In the present study, we intend to clarify the effect of fluorine-substitution in the isopropylidene moiety on the thermal degradation of polyformal by thermogravimetry-differential thermal analysis/Fourier transformation infrared spectroscopy (TG-DTA/FTIR), pyrolysis gas chromatography/mass spectrometry (Pyr-GC/MS), pyrolysis gas chromatography (Pyr-GC). The mechanism of thermal decomposition of polyformals is also proposed.



Polyformal



2. Experimental

Polyformals were prepared according to the method reported previously [1].

TG-DTA/FTIR was carried out with a Seiko TG-DTA 220 and a Nicolet Valor III at a heating rate of 20°C min⁻¹ and a gas capture temperature of 280°C. Peak products of pyrograms were identified using a tandem combination of a Shimadzu PYR pyrolyzer, a Varian 1440 gas chromatograph and a NEVA TE-500 mass spectrometer (pyr-GC/MS). The amounts of evolved gases were determined with a Shimadzu GC-6A gas chromatograph with a Shimadzu PYR-2A furnace-type pyrolyzer (Pyr-GC). This procedure was used because the data on Pyr-GC/MS are less accurate than those on Pyr-GC due to the suction of the GC column from the ion chamber of the mass spectrometer in the Pyr-GC/MS apparatus.

The mass spectra of peak products were compared with those of reference materials thermally decomposed under the same conditions [2–4].

3. Results and discussion

3.1. TG-DTA/FTIR

The results of TG-DTA/FTIR are shown in Figs. 1 and 2.

In the TG curves, the onset temperatures of weight loss shift to higher temperatures with increasing fluorine content as reported previously [1]. The weight loss of Polyfor-

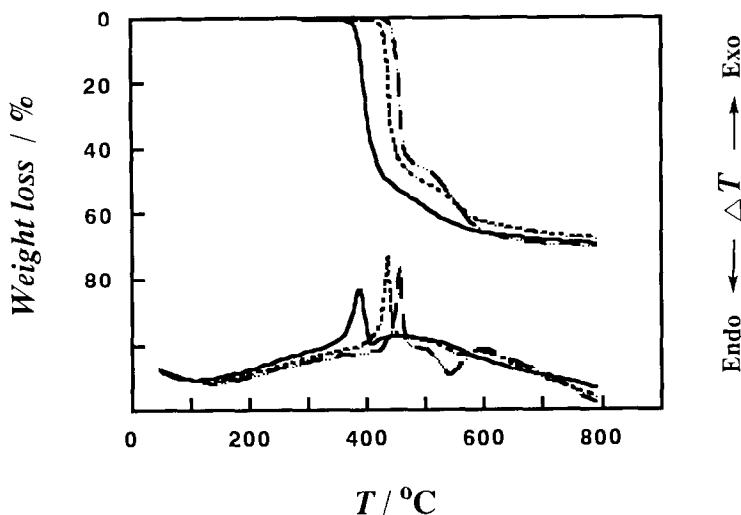


Fig. 1. TG-DTA curves of polyformals I (—), II (---), and III (-·-·-).

mal I occurs in a single stage, whereas the weight of fluorine-containing polyformals decreases in two stages and the inflection at about 500°C appears more definite for polyformal II with higher fluorine content. The first stage of the degradation is exothermic and the second is endothermic in the DTA curve.

As seen from Fig. 2, the IR spectra of gas mixtures evolved in thermal decomposition of Polyformal II at various decomposition temperatures suggest the existence of benzene rings and C–O–C bonds, because the absorption bands in the 1500–1600 cm^{-1} region and those in the 1200–1300 cm^{-1} region are associated with a benzene ring vibration and a C–O–C stretching vibration, respectively. Moreover, an absorption band due to a C=C stretching vibration is observed at about 2200 cm^{-1} , indicating that the formation of the

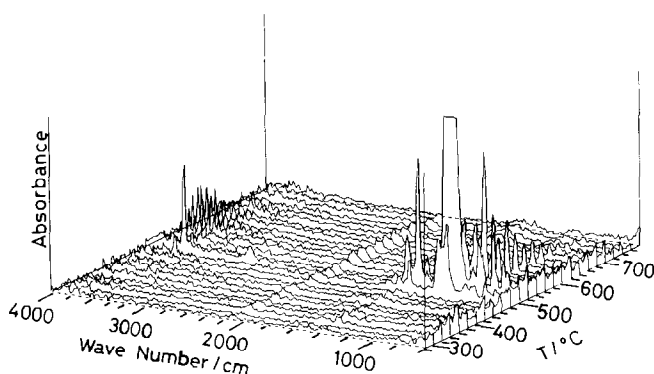


Fig. 2. FTIR spectra of evolved gas mixtures in decomposition of polyformal II at various temperatures (raised at 20°C min^{-1}).

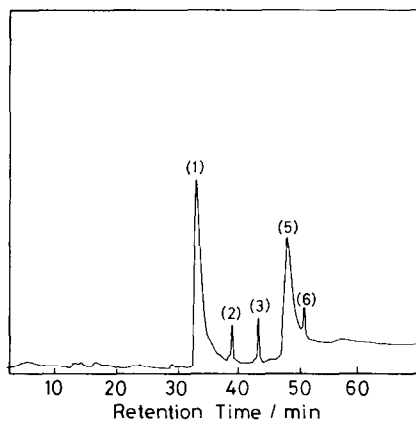


Fig. 3. A pyrogram of bisphenol A: decomposition temperature, 500°C.

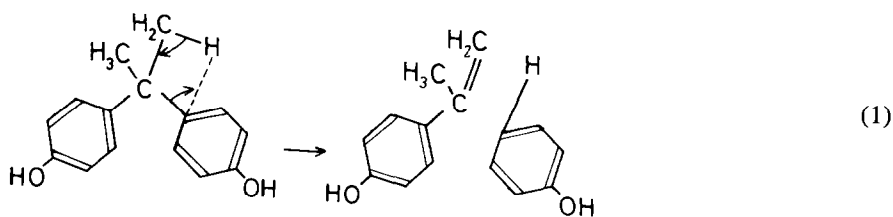
compound with C=C bonds is associated with the exothermic nature of the first stage of degradation. The absorption due to a C–O–C bond diminishes gradually with a rise in decomposition temperature. In the IR spectra of the decomposition products of Polyformal II, a band due to C–F is also observed at 3800 cm^{-1} .

3.2. Pyr-GC/MS and Pyr-GC

Fig. 3 shows a pyrogram of Pyr-GC of bisphenol-A, thermally decomposed at 500°C. The major peak products, 1, 2, 3, 5 and 6 are identified as α -methylstyrene, phenol, *p*-cresol, 4-hydroxy- α -methylstyrene, and isopropyl phenol, respectively, by Pyr-GC/MS.

The amount of products evolved from bisphenol A is remarkably dependent on the decomposition temperature as shown in Table 1. The sum of evolved products 1 and 5 is about 94% and about 86% at 300°C and at 500°C, respectively. At 700°C, product 1 increases to about 45%, but product 5 is scarcely observed and light gases increase. Generally, the chemical structure of thermal decomposition products reflects the mechanism of the decomposition reaction [5].

The formation of α -methylstyrene and 4-hydroxy- α -methylstyrene suggests that the following cleavage reaction occurs:



The amount of phenol evolved is much smaller than that expected from the reaction (1), probably because of the formation of products with high boiling temperature, such as

Table 1

Peak areas of major products in pyrograms of bisphenol A at various decomposition temperatures

Product	Reaction time/min	Peak area/%				
		300°C	400°C	500°C	600°C	700°C
Light gas	4	–	–	–	11.1	21.0
1	33	80.4	37.9	43.7	62.8	44.9
2	39	0.6	2.9	2.1	1.7	6.2
3	44	1.5	4.9	2.9	2.3	2.0
5	49	13.7	37.4	42.6	0.0	0.0
6	51	2.8	13.3	7.8	9.1	0.3

diphenyl ether, by the secondary reaction of phenol. However, the evolution of α -methylstyrene and 4-hydroxy- α -methylstyrene does not decrease because the depolymerization occurs for the products (polymers) formed by the secondary reaction.

Fig. 4 shows a pyrogram of Polyformal I decomposed at 300°C. The peak products 1, 2, 5 and 6 are identified as α -methylstyrene, phenol, 4-hydroxy- α -methylstyrene, and isopropanol, respectively. The products 1, 2, 5 and 6 are identical with the degradation products from bisphenol A. However, the mass spectrum of the peak product 4 is different from that of the peak product 3 in the pyrogram of bisphenol A. The apparent parent peak appears at m/z 148 and the major fragment peaks are observed at m/z 31, 41, 76, 107, and 117. Therefore, product 4 is identified as 4-isopropenyl anisole produced by the reaction (1).

The predominant reaction in the thermal degradation of polycarbonate derived from bisphenol A has been reported to be a rearrangement of carbonyldioxy groups and not a cleavage resulting in propane-2-ylidene groups by reaction (1) [5,6]. The predominance of reaction (1) in the thermal degradation of polyformal I is explained in terms of the high thermal stability of methylenedioxy groups.

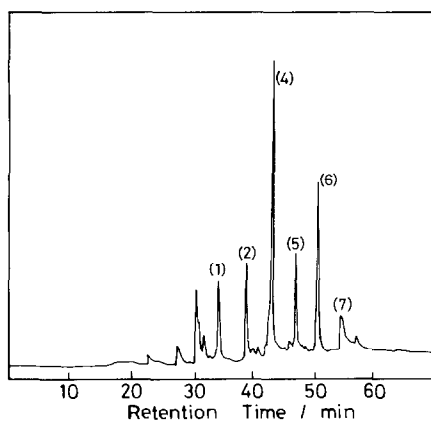


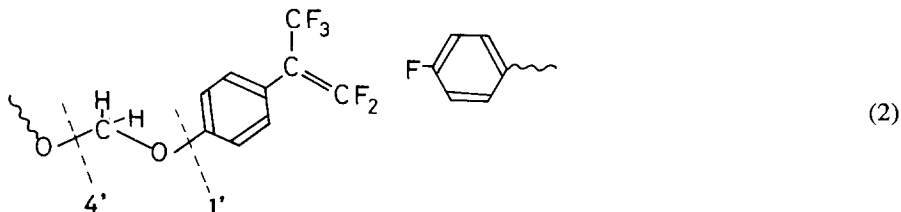
Fig. 4. A pyrogram of Polyformal I: decomposition temperature, 300°C.

Table 2

Peak areas of major products in pyrograms of Polyformals I and II

Product	Reaction time/min	Peak area/%			
		Polyformal I		Polyformal II	
		300°C	500°C	400°C	600°C
Light gas	–	1.1	1.3	–	–
1	34	7.3	17.7	–	–
1'	35	–	–	75.1	65.4
2	39	8.0	2.2	–	–
4	43	23.5	19.1	–	–
4'	45	–	–	24.9	34.6
5	48	9.6	12.6	–	–
6	51	14.8	14.5	–	–
7	54	7.8	2.4	–	–

Table 2 shows the major products evolved from Polyformals I and II thermally decomposed at various temperatures. They are identified by Pyr-GC/MS measurements. The major peak products in the pyrograms of Polyformal II are only two species, the products 1' (pentafluoroisopropenyl benzene) and 4' (pentafluoroisopropenyl anisole), corresponding to α -methylstyrene and 4-hydroxy- α -methylstyrene from Polyformal I, respectively. The products 1' and 4' are produced by the cleavage of phenylene-oxy bonds and oxy-methylene bonds by reaction (2).



The bond dissociation energy of phenylene-oxy bonds is not so much different from that of oxy-methylene bonds. Therefore, the two step decrease in weight of Polyformal II is not caused by the different reactions, but it results from the different vapor pressures, that is, the different rates of vaporization between the product 1' and the product 4' itself or polymerized products. Namely, product 4' is produced by reaction (1) and the cleavage of oxy-methylene bonds, and then product 1' is formed by the secondary degradation of product 4'. The more volatile 1' is evaporated in the first stage and then the less volatile 4' in the second stage.

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