Pyrolysis-Gas Chromatographic Studies of Ionically-chlorinated Poly-α-methylstyrenes

Tadaoki Okumoto* and Tsugio Takeuchi**

* *Engineering Department, Nagoya Rubber Co., Ltd., Haruhi-mura, Nishikasugai-gun, Aichi 452*

** *Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464*

(Received October 7, 1972)

The microstructure of ionically-chlorinated poly-α-methylstyrene with or without a catalyst and the distribution of chlorine in the aromatic nucleus of the polymers were studied by means of pyrolysis-gas chromatography. The degradation products, such as α-methylstyrene, *p*-chloro-α-methylstyrene, and 3,4-dichloro-α-methylstyrene, gave good information about substitution reactions on the aromatic nucleus in original poly-α-methylstyrene. The differences between two series of ionically-chlorinated poly-α-methylstyrene were also discussed on the basis of yield of α-methylstyrene and *p*-chloro-α-methylstyrene.

Chlorinated polystyrenes and poly-α-methylstyrenes have been synthesized by both ionic and radical mechanisms. The chlorination of polystyrene has been the subject of a number of investigations.[1-4] However, only one study of the chlorinated poly-α-methylstyrene (CPMS) has been reported.[4]

Jenkins *et al.*[1] have examined the radically-chlorinated polystyrene by the use of an IR spectrometer, etc. They reported the determination of the change in the infrared spectrum, the glass transition temperatures, and the molecular weight of the polymers.

In our previous work[2] we have studied the distribution of chlorine atoms as a function of the degree of chlorination in the chlorinated polystyrene formed by radical chlorination by means of pyrolysis-gas chromatography(PGC).

Teyssie *et al.*[3] have investigated the structure of ionically-chlorinated polystyrene by both chemical and infrared spectrometric analyses and concluded that the chlorine is preferentially oriented in the para, and secondarily in the ortho, position, and that, with the further introduction of chlorine, 3,4-, 2,5- and, to a lesser extent, 2,4-dichloro-substituted phenyl groups are formed.

Bachman *et al.*[4] elucidated the depolymerization of ionically-chlorinated polystyrene and poly-α-methylstyrene and identified halogenated styrene and α-methylstyrenes, such as *p*-chlorostyrene, 3,4-dichlorostyrene and 3,4-dichloro-α-methylstyrene, after the fractional distillation of the depolymerized mixture.

In the present work, we have studied a pyrolysis-gas chromatographic method for elucidating the microstructure of ionically-chlorinated poly-α-methylstyrene, especially the distribution of chlorine in the aromatic nucleus of the polymers.

Experimental

Materials. The poly-α-methylstyrene was dissolved in chloroform and then purified. Chlorine gas was introduced into the polymer solution with constant stirring. Two series of ionically-chlorinated poly-α-methylstyrenes were prepared by the following methods of chlorination. The first method was a catalytic method where CPMS was synthesized by the chlorination of poly-α-methylstyrene in the iron powder, which acted as a catalyst in the dark. The second method was a direct method, where poly-α-methylstyrene was chlorinated in the absence of a catalyst. The samples were purified by the same procedure as that described in our previous work.[2] The polymers formed by the catalytic and direct methods will be abbreviated as "CPMS–Cat" and "CPMS–Direct" respectively. The chlorine content of the chlorinated polymers was chemically determined.

The degree of chlorination (DC) of the samples is defined as the number of chlorine atoms contained per monomer unit in the polymer as follows:

$$\mathrm{DC} = \frac{118.19 \times \mathrm{Cl\ wt\%}}{3545 - 34.4 \times \mathrm{Cl\ wt\%}}$$

Pyrolysis-Gas Chromatographic Conditions. The pyrolysis of the polymer was carried out by means of a furnace-type pyrolyzer (Hitachi Model KP–1) which was directly attached to the inlet port of a gas chromatograph equipped with dual flame-ionization detectors. At the optimum pyrolysis temperature, 550 °C, reproducible and characteristic pyrograms were obtained.

The gas-chromatographic conditions were the same as those described in our previous work.[2] Separation columns (3 mm i. d. × 2 m) packed with Diasolid L (80—100 mesh) and coated with PEG–6000 (10 wt% to the support) were used at programmed temperatures ranging from 100 to 210°C at a rate of 5 °C/min. The peaks on the pyrograms were identified by the use of PGC–MS and Hitachi–RMS–4 apparatuses and by means of the retention data of the pure substances.

Infrared Spectrometry. The infrared absorbance curves were obtained on Hitachi Model EPI–S_2 spectrometer. The various chlorinated poly-α-methylstyrene samples were examined by the KBr disc method.

Results and Discussion

In the following discussion, α-methylstyrene, *p*-chloro-α-methylstyrene, and 3,4-dichloro-α-methylstyrene are briefly denoted by MS, *p*-CMS, and 3,4-CMS respectively.

Figure 1 shows typical pyrograms of poly-α-methylstyrene and CPMS–Cat at the pyrolysis temperature of 550 °C. Raw poly-α-methylstyrene yields, nearly quantitatively, the α-methylstyrene monomer, while, with the rise in the degree of chlorination, chlorinated

---

[1] R. K. Jenkins, N. R. Byrd, and J. L. Lister, *J. Appl. Polym. Sci.*, **12**, 2059 (1968).

[2] S. Tsuge, H. Ito and T. Takeuchi, This Bulletin, **43**, 3341 (1970).

[3] Ph. Teyssie, M. C. Wilde, and G. Smets, *J. Polym. Sci.*, **16**, 429 (1955).

[4] G. B. Bachman, H. Hellman, K. R. Robinson, R. W. Finholt, E. J. Kahlar, L. J. Filar, L. L. Levis, and D. D. Micucci, *J. Org. Chem.*, **12**, 108 (1947).

Table 1. Realtive yields of pyrolysis products in CPMS-Cat (mol%)

Sample (No.)	Chlorine content (wt%)	Degree of chlorination (DC)[a]	α-methyl-styrene	*p*-chloro-α-methylstyrene	3,4-dichloro-α-methylstyrene
1	3.5	0.12	92.8	7.2	—
2	8.6	0.31	76.0	18.0	6.0
3	12.5	0.47	65.5	25.4	9.1
4	17.5	0.70	48.3	38.2	13.5
5	22.4	0.95	35.6	48.1	16.3
6	24.0	1.04	23.3	55.1	21.6
7	26.3	1.18	16.8	59.5	23.7
8	28.9	1.34	11.2	62.7	26.1
9	29.4	1.37	9.3	66.4	24.3
10	31.8	1.53	5.4	68.9	25.7

a) Calculated from the chemical analysis.

Table 2. Relative yields of pyrolysis products in CPMS-direct (mol%)

Sample (No.)	Chlorine content (wt%)	Degree of chlorination (DC)[a]	α-methyl-styrene	*p*-chloro-α-methylstyrene	3,4-dichloro-α-methylstyrene
1	6.2	0.22	87.0	10.6	2.4
2	12.9	0.49	67.4	23.7	8.9
3	17.8	0.71	47.8	38.2	14.0
4	20.4	0.85	39.4	43.4	17.2
5	23.3	1.03	33.4	47.6	18.7
6	26.1	1.17	29.4	49.4	21.2
7	29.4	1.37	23.2	53.8	23.0
8	34.8	1.75	19.2	52.2	28.6

a) Calculated from the chemical analysis.

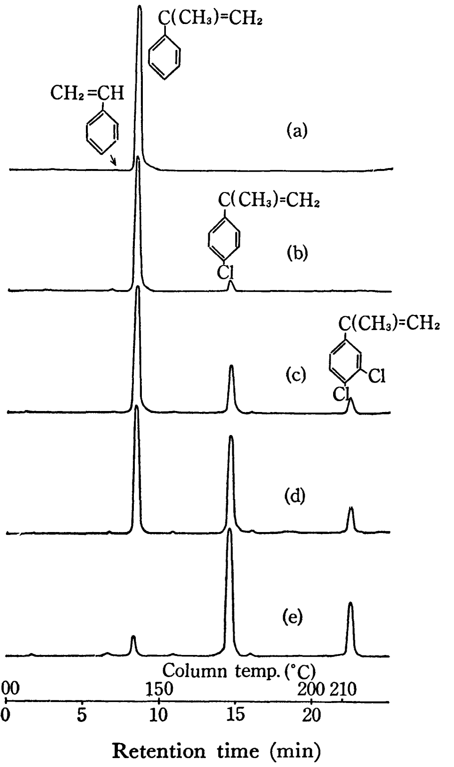


Fig. 1. Typical pyrograms of CPMS-Cat at 550 °C.
(a): PMS,, (b)—(d): CPMS; (b): DC=0.12, (c): DC=0.47, (d): DC=0.95, (e): DC=1.53

poly-α-methylstyrene yields two kinds of chlorine-substituted α-methylstyrene, such as *p*-CMS and 3,4-CMS. The relative yields of α-methylstyrene derivatives from the CPMS-Cat and -Direct methods are summarized in Tables I and II, where a small amount of styrene is added to the yield of α-methylstyrene. These values are calculated from the relative peak areas appearing on the pyrograms, considering the relative sensitivities of compounds for the flame-ionization detectors.

Figure 2 shows the relationships between the DC and the yields of the degradation products of the ionically CPMS-Cat and -Direct methods. The two series of CPMS differ generally from one another, especially in the yields of MS and *p*-CMS, as is shown in Fig. 2. It is apparent from the above observations that a chlorination reaction is taking place, mainly on the aromatic nucleus. The chlorine is nearly oriented in the para position and with the further introduction of chlorine, 3,4-dichloro-substituted phenyl group is formed.

Figure 3 shows the infrared spectrum of chlorinated poly-α-methylstyrene with various DC. The disappearance of the absorption bands at 700, 750, and 1030 cm^{-1} is indicative of chlorine substitution on the aromatic nucleus. On the other hand, sharp bands of 825 and 1010 cm^{-1} which are related to the position of the substitution in the nucleus appear on the spectrum with the rise in DC. These results are in

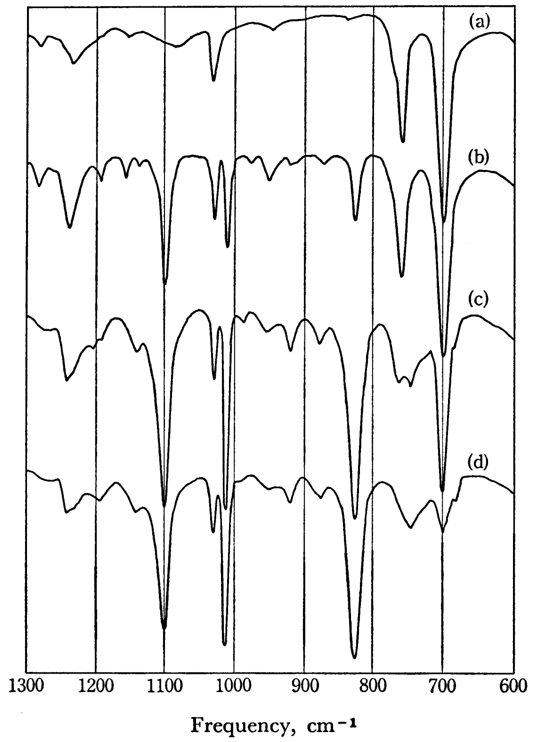


Fig. 3. Infrared spectra of CPMS-Cat.
(a): PMS, (b)—(d): CPMS; (b): DC=0.47, (C): DC=1.18, (d): DC=1.53

fairly good agreement with those of polystyrene reported by Teyssie et al.[3]

At a small degree of chlorination with or without a catalyst, only the yield of *p*-CMS through monochloro-substituted α-methyl styrene appeared on the pyrograms, while the yield of isomers did not appear. This is different from the case with chlorinated polystyrene. This is mainly due to the steric hindrance of methyl group in the polymer. This is also supported by the fact the yield of dichloro-substituted α-methylstyrene is almost 3,4-CMS.

The ionic chlorination of poly-α-methylstyrene mainly proceeds by means of the direct substitution of the aromatic nucleus under these conditions. At the beginning of chlorination, a substitution reaction takes place in nearly the para position. The second chlorine atom is preferentially directed into the phenyl ring in the 3 positions for the para chloro-α-methyl styrene unit before all the phenyl ring is substituted. It is also thus apparent that the formation of *p*-CMS is locally competitive with the formation of 3,4-CMS. Consequently, *p*-CMS is formed by the following mechanisms;

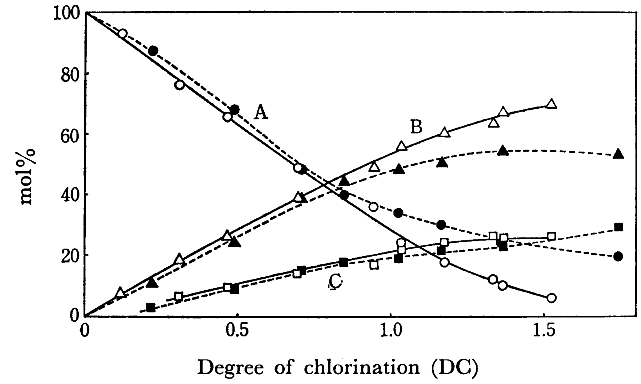
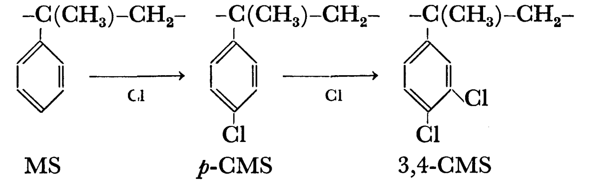


Fig. 2. Relationships between the degree of chlorination (DC) and relative yields of the degradation products of CPMS.
—— Solid line: CPMS-Cat
---- Broken line: CPMS-Direct
A: α-methylstyrene, B: *p*-chloro-α-methylstyrene
C: 3,4-dichloro-α-methylstyrene.



The two series of CPMS differ from one another, especially in the yields of α-methylstyrene and *p*-chloro-α-methylstyrene, as is illustrated in Fig. 2.

No appreciable differences are observed between the two series of CPMS with respect to the yields of dichloro-α-methylstyrene. However, the yields of MS and *p*-CMS change in different ways as a function of DC. The ratio of *p*-CMS to 3,4-CMS of CPMS-Cat is also larger than that of CPMS-Direct. These results suggest that the distribution of the chlorine introduced to the phenyl ring of CPMS-Cat is more homogeneous than that of CPMS-Direct.