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Pyrolysis-Gas Chromatographic Investigation of Chlorinated Polystyrenes

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The distribution of chlorine atoms in radically chlorinated polystyrenes was studied by means of pyrolysis gas chromatography. Degradation products such as styrene, benzene, toluene and chlorobenzenes are related to different structures of the chlorinated polymers. The sequence distribution of each structure was discussed over a wide range of degree of chlorination. Chlorine atoms are first substituted with α- then β-hydrogen in the main chain of polystyrene. The first ring substitution of chlorine occurs competitively at *p*-position even before both α- and β-hydrogens are substituted.

Many types of chlorinated polymers have been synthesized in a search for improved thermal characteristics such as flammability, heat-distortion temperature and thermal stability. Thermal properties are closely associated with the microstructres of polymers, especially with the distribution of chlorine atoms.

Chlorinated polystyrenes have been synthesized by both ionic and radical mechanisms and their structures have been studied by various methods.[1-3]

Bachmann *et al.*[1] reported on the depolymerization of some ionically chlorinated polystyrenes to clucidate their structures. They identified halogenated styrenes such as *p*-chlorostyrene and 3,4-dichlorostyrene after fractional distillation of the depolymerized mixture.

Teyssie *et al.*[2] also carried out an ionic chlori-

1) G. B. Bachman, H. Hellman, K. R. Robinson, R. W. Finholt, E. J. Kahler, L. J. Filar, L. L. Lewis and D. D. Micucci, *J. Org. Chem.*, **12**, 108 (1947).

2) Ph. Teyssie, M. C. de Wilde and G. Smets, *J. Polym. Sci.*, **16**, 429 (1955).

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

nation of polystyrene and characterized the resulting structure by chemical and infrared spectrometric analysis. The chlorination reaction takes place concurrently on the aromatic nucleus and on the main chain. The chlorine, which is substituted on the aromatic nucleus, is preferentially bonded to the para position and secondarily to the ortho position. The second chlorine is then introduced mainly in 3 position with respect to *p*-chlorostyrene unit and in 5 position with respect to *o*-chlorostyrene unit to form 3,4- and 2,5-dichlorostyrene units, respectively.

Jenkins *et al.*[3] prepared chlorinated polystyrenes by means of the radical method using ultraviolet radiation and determined the changes in the infrared spectrum, glass transition temperature and molecular weight of the polymers. In contrast to the ionic reaction, the radical chlorination reaction proceed mainly by substitution at the α-hydrogen position in the main chain. Main chain scission also took place as the chlorination reaction proceeded.

In our previous work, we characterized chlorine containing polymers such as vinyl chloride-vinylidene chloride copolymers,[4] chlorinated polyethyrenes[5] and chlorinated polyvinylchlorides[6] by means of pyrolysis-gas chromatography (PGC).

The purpose of the present work is to characterize the distribution of chlorine atoms in radically chlorinated polystyrenes with the use of PGC. Degradation products of the polymers at 455°C were separated chromatographically and identified to be styrene monomer, benzene, toluene, chlorobenzenes. Benzene and toluene, which are related with the structures produced by substituting the main chain, are observed concurrently with chlorobenzenes which are originated from the structures of substituted aromatic rings. The sequence distribution of each structure was discussed as a function of degree of chlorination.

Experimental

Chlorination. Polystyrene (PSt) was dissolved in chloroform and filtered. The polymer was chlorinated by slowly passing Cl_2 gas into the solution (55 g/*l*) under the illumination of a mercury lamp. Samples of the solution (30 m*l*) were removed from the reaction flask, neutralized and precipitated in sodium hydroxide-methanol solution. The samples were dried in a vacuum oven.

Pyrolysis-Chromatography. The gas chromatograph was a GCG-550F with flame ionization detectors and the pyrolysis apparatus a GP-1000, both supplied by Yanagimoto Co., Ltd. The sample holder and the precut portion of the pyrolysis apparatus were modified to increase the precision of the data and to trap hydrogenchloride gas evolved at the pyrolysis, respectively.[4,5] Operating conditions were as follows.

Column: 3 mm×2 m copper column packed with Diasolid L(80—100 mesh) coated with PEG 6000 (10 wt% to the support)

Carrier gas: nitrogen gas flowing at the rate of 20 cc/min

Pyrolysis temperature: 455°C

Infrared Spectrometry. Infrared spectra were obtained on a Nihon Bunko IR-S by the KBr disc methoed.

The chlorine content of the polymers were chemically determined. In the following, the degree of chlorination D is defined as the number of chlorine atoms per styrene monomer unit.

Results and Discussion

The pyrograms of the polymers with various *D* are shown in Fig. 1. Raw PSt yields nearly quantitatively styrene monomer. As the chlorine content increases, peaks for benzene, toluene and

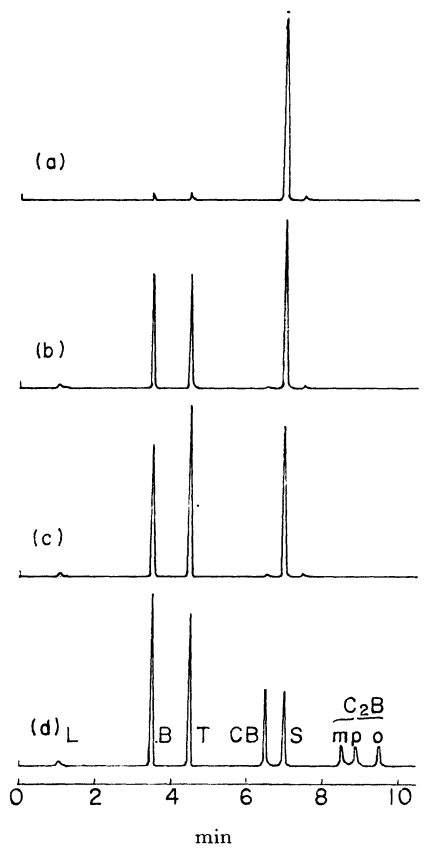


Fig. 1. Typical programs of PSt and chlorinated PSt at 455°C.
(a): PSt, (b)—(d): chlorinated PSt; (b): D=0.57, (c): D=1.50, (d): D=2.25, where D is the degree of chlorination (the number of chlorine atoms per monomer unit).

4) S. Tsuge, T. Okumoto and T. Takeuchi, *Makromol. Chem.*, **123**, 123 (1969).

5) S.Tsuge, T. Okumoto and T. Takeuchi, *Macromol.*, **2**, 200 (1969).

6) S. Tsuge, T. Okumoto and T. Takeuchi, *ibid.*, **2**, 277 (1969).

chlorobenzenes appear on the pyrograms, while the yield of styrene monomer decreases.

The relationships between the relative yields among the aromatic products and D are shown in Fig. 2, where a small amount of low boiling point products appearing in the earliest retention time is neglected for the sake of simplicity.

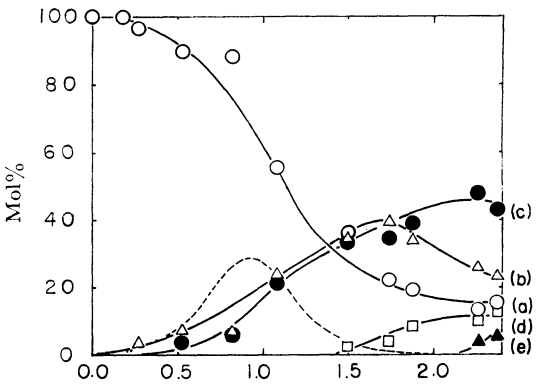


Fig. 2. Relationships between the degree of chlorination (D) and the yield of the degradation products from chlorinated PSt.
A: styrene monomer, B: toluene, C: benzene, D: chlorobenzene, E: dichlorobenzenes.
Dotted curve is calculated from Eq. (2) for $n=3$.

The yield of styrene monomer decreases monotonously as a function of D. The yield of toluene is first observed at $D=0.27$ and shows a maximum (40 mol%) at $D=1.74$. On the other hand, benzene, which first appears at $D=0.53$, increases monotonously up to $D=2.26$. The appearance of chlorobenzene starts at $D=1.50$. Dichlorobenzenes are observed above $D=2.26$.

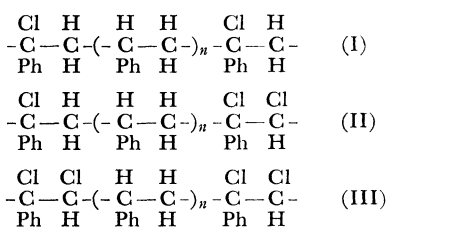
Each characteristic product is closely related to the structure of the polymers as follows:

Styrene Monomer. PSt with molecular weight higher than ten thousand was depolymerized nearly completely to monomer.[7] PSt with lower molecular weight, however, yielded such additional products as toluene and benzene. Thus the relative yield of styrene monomer decreases with the decrease of molecular weight.

In the case of chlorination of PSt, we must consider competitive reactions such as substitution of the hydrogen atoms in the main chain of PSt or in the aromatic ring of PSt and simple scission of the main chains. Each reaction causes shorter sequences of styrene unit than that of the raw PSt and accordingly is responsible for the reduction of the yield of styrene monomer.

Toluene. The chlorination reaction of PSt proceeds mainly by substituting at the α-hydrogen in the main chain.[3] For chlorinated PSt with D above 1.0, some monomer units have two chlorine atoms at both α- and β-positions, since no ring protons are substituted until $D=1.5$ as described below.

The relative yield of toluene in the pyrolysis products of PSt increases rapidly with the decrease of its degree of polymerization.[7] Thus we consider the apparent reduction of the sequence of unsubstituted styrene unit in chlorinated PSt as follows.



For the sake of simplicity, it is assumed that chlorination reaction takes place almost at rondom at α- or β-hydrogen, but that of α-substitution occurs in preference to β-one.[3] The substitution of ring protons is not taken into consideration.

Sequences (I), (II) and (III) are formed with the probabilities of ac^na, ac^nb+bc^na and bc^nb, respectively, where a and b are the probabilities of substitution of only α- and both α- and β-hydrogens, respectively, and c is that of non-substitution and n is sequence number of styrene unit. Consequently, the following equation is expected to hold for the total number of the unstubstituted styrene units.

$$N=\sum_{k=1}^{n} Pc^k(a^2+2ab+b^2)$$

where P is the degree of polymerization of PSt and $a+b+c=1$. The number of the hydrogen atoms that can be substituted is $2P$, provided that the substitution reactions take place at α-hydrogen and one of β-hydrogens. On the other hand, the number of chlorine atoms contained in chlorinated PSt is $D\times P$. When we assume random substitution, the probability of introduction of one chlorine atom is $D\times P/2P=D/2$ and that of non-substitution is $\{1-(D/2)\}$. Consequently, we have $a=2(D/2)\{1-(D/2)\}$, $b=(D/2)^2$ and $c=\{1-(D/2)\}^2$.

Thus, N can be shown as a function of D, where we have only to consider relatively small n value (at most $n=10$).

$$N=\sum_{k=1}^{n} P\{1-(D/2)\}^{2k}[4(D/2)^2\{1-(D/2)\}^2 +4(D/2)^3\{1-(D/2)\}+(D/2)^4] \quad (2)$$

As shown in Fig. 2 with a dotted curve, the function always passes through a maximum between $D=0$ and 2.0. The observed yield of toluene shows a maximum value between $D=0$ and 2.0 ($D\sim1.6$).

7) S. Tsuge, T. Okumoto and T. Takeuchi, *J. Chromatogr. Sci.*, **7**, 250 (1969).

The results suggest that toluene may be closely associated with the short sequences mentioned above. However, the fact that the theoretical curve deviates at high D may be attributed to the rough assumptions, where the substitution of ring protons and reduction of molecular weight during chlorination are neglected. Strictly speaking, reduction of molecular weight of PSt during chlorination also leads to the yield of toluene. However, if this had been predominant, the yield of toluene should have had a monotonously increasing inclination as the rise of D.

Benzene. The yield of benzene, which is very small even in PSt with low molecular weight,[7] increases almost monotonously up to $D=2.25$ as the rise of D. This suggests that the mole fraction of both α- and β-disubstituted styrene unit increases as chlorination proceeds. However, the fact that the yield exhibits a decreasing tendency above $D=2.26$ implies that a substitution of the hydrogen atoms considerably participates in the aromatic ring of PSt.

Chlorobenzenes. Chlorobenzene is first observed at $D=1.50$. The infrared spectrum of chlorinated PSt with $D=1.50$ has an absorption band near 1080 cm^{-1}, which is characteristic for p-substituted styrene unit.[2] It is very interesting that the substitution of ring protons begins at $D=1.50$, where α- and β-hydrogens in the main chain are not completely substituted. The first ring substitution occurs at p-position, but the second one seems to proceed at random since o-, m- and p-dichlorobenzenesappear almost at the same time above $D=2.25$.

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