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Determination of cross-linking reagent, divinylbenzene in polystyrene-type ion exchange resin precursors with chloromethyl substituents by pyrolysis-gas chromatography in aiding preliminary reduction of chlorine atoms in the samples

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Cross-linking reagents, divinylbenzene (DVB) in polystyrene-type ion exchange resin precursors with chloromethyl substituents were determined by pyrolysis-gas chromatography (PY-GC) in aiding preliminary reduction of chlorine atoms in the samples. The characteristic peaks of DVB or its derivatives were completely separated on the pyrograms of the reduced precursors. The relative peak intensities ($I_{\rm rel}$) of DVB or its derivatives were calculated from their peak area, and interpreted in terms of the amounts of cross-linking reagents introduced into the resin precursors synthesized by different synthetic pathways. © 1997 Elsevier Science Ltd.

(Keywords: cross-linked polystyrene; divinylbenzene; pyrolysis-gas chromatography)

INTRODUCTION

Cross-linked styrene (ST)-divinylbenzene (DVB) copolymers with chloromethyl substituents ($-CH_2Cl$) have a wide range of applications in the preparation of ion-exchange resins, and the supports for catalyst, gel permeation, gas and liquid chromatography and others because they contain reactive functional groups ($-CH_2Cl$). The physical and chemical properties of the cross-linking copolymers are significantly affected by, for example, preparation conditions. Therefore, various studies on characterizing the networks had been carried out by many researchers. In particular, analytical pyrolysis techniques proved to be suitable in characterizing such insoluble cross-linked polymers[1–4]. Nakagawa *et al.* determined chlorine in the chloromethyl-substituted ST-DVB cross-linked copolymers by pyrolysis-gas chromatography (PY-GC), and studied their thermal degradation behaviour by thermogravimety (TG)[1]. Boinon *et al.* studied the kinetics and mechanism of the thermal degradation of poly-*p*-chloromethylstyrene by PY-GC-mass spectroscopy (MS), and isothermal and dynamic TG[2]. Oehme *et al.* qualitatively analysed para-chloromethyl substituted ST-DVB copolymers by PY-GC and i.r.[3]. Nicolaides *et al.* studied the amounts of cross-linking reagents introduced into the ST-DVB cross-linked copolymers and the degree of chloromethylation by MS at 300–370°C, where they used the intensity ratio of fragments at $m/z = 132$ and 208 to estimate the percentage of DVB in the copolymers, and that of fragments at $m/z = 117$ and 104 to the degree of $-CH_2Cl$ substitution[4]. Although the amounts of cross-linking reagents introduced into the ST-DVB cross-linked copolymers had been studied by PY-GC[5–7], up to now no reports have published results estimating the amounts of cross-linking reagents introduced into ST-DVB copolymers with chloromethyl substituents through the use of PY-GC.

In this work, a new method to determine the cross-linking reagents in ion exchange resin precursors with $-CH_2Cl$ was developed using high-resolution PY-GC with the aid of preliminary reduction of the cross-linked copolymer samples. The reduction of the chloromethyl groups of the resin precursors were carried out before pyrolysis in order to avoid a complex side-reaction of dehydrochlorination when they were pyrolyzed. The cross-linking reagents in resin precursors were able to be determined directly from the relative peak intensity ($I_{\rm rel}$) of DVB or its derivatives observed in the resulting pyrograms.

EXPERIMENTAL

Sample preparation

Two types of the precursor samples, a series of cross-linked copolymers of poly [chloromethylstyrene (Cl-MST)-co-DVB], and another series of chloromethylated poly

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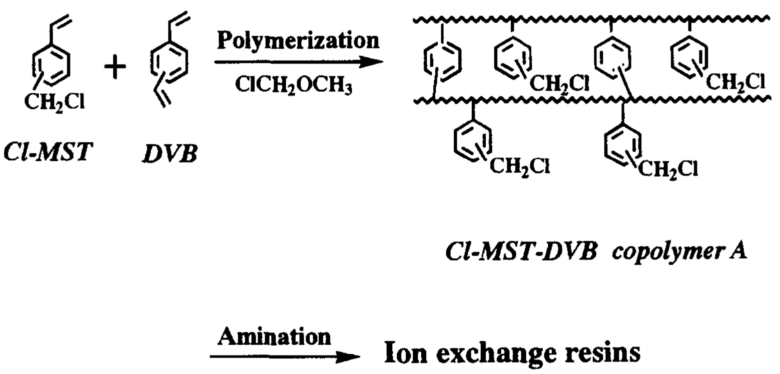
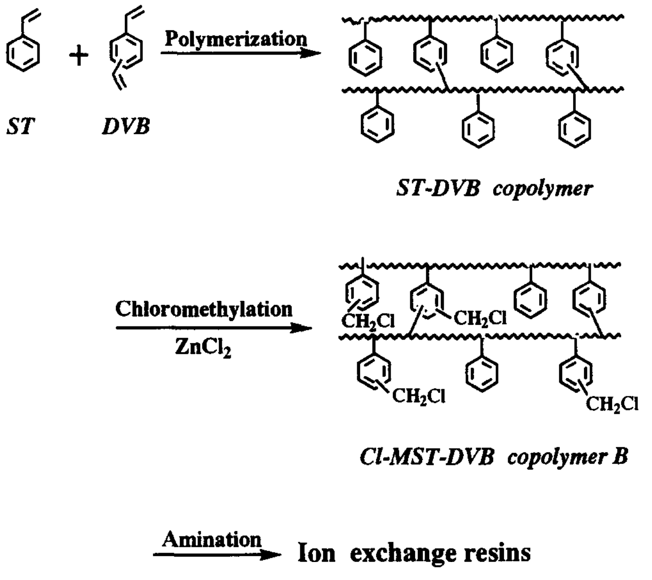


Scheme 1

Table 1 Cl-MST-DVB copolymer samples

Sample number	Cl-MST (g)	Cross-linking agent[a] (g) (DVB mol%)	AMVN[b] (g)	Cl[c] (wt%)	
				Theoretical	Observed
A-1	95.1	4.9 (3.3)	1.0	22.1	22.3
A-2	89.9	10.1 (6.6)	1.0	20.9	20.9
A-3	84.5	15.5 (10.1)	1.0	19.7	19.8

[a] DVB content: 56.5 wt%, the remainder is ethylstyrene. Values in parentheses are net DVB molar content in the copolymers.
[b] AMVN: 2,2'-azobis (2,4-dimethylvaleronitorile) as initiator.
[c] Cl (wt%). Theoretical: calculated values from the monomer feed ratio. Observed: observed values by elemental analysis.



Scheme 2

(ST-co-DVB) samples were prepared as shown in *Scheme 1* and *Scheme 2*, respectively.

Synthesis of chloromethylstyrene-DVB cross-linked copolymer samples (A series). A 1000 ml four-neck flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet adapter and a thermocouple for the thermostatical control was charged with 500 ml of water. Chloromethylstyrene and the cross-linking reagent, which is the mixture of DVB (56.5%) and ethylstyrene (43.5%), were added to the flask along with the initiator, 2, 2'-azobis(2,4-dimethylvaleronitorile) (AMVN), under a nitrogen atmosphere, and were dispersed in water by agitation of 180 rpm at 20°C, then stabilized for 1 h. Then temperature was raised to 65°C and maintained for 8 h under similar agitation. After completing the suspension polymerization, the copolymer was filtrated, washed by a large amount of water, dried under a vacuum at 50°C for 8 h, and then crushed under freezing. Finally, the product was further dried a under vacuum at 40°C for 3 h to obtain a Cl-MST-DVB cross-linked copolymer. Further details of the synthetic conditions and the chemical composition of the formed Cl-MST-DVB copolymers are summarized in *Table 1*.

Synthesis of chloromethylated ST-DVB cross-linked copolymer samples (B series). ST-DVB cross-linked copolymer samples were first synthesized by basically the same way as for the preparation of the A series copolymer samples. Styrene and DVB were added to the flask used above together with the benzoyl peroxide as the initiator under a nitrogen atmosphere, were also dispersed in water by agitation of 180 rpm at 20°C, and then stabilized for 2 h. Then the temperature was raised to 80°C and maintained for 8 h under similar agitation. After completing the suspension polymerization, the ST-DVB cross-linked copolymer was filtrated, washed by a large amount of water, and dried by the same way mentioned previously.

Then about 30 g of the ST-DVB cross-linked copolymer was put into the flask. After the copolymer was significantly swelled by ethylenedichloride, 240 g of chloromethyl methyl ether (CME) and 12 g of zinc chloride ($ZnCl_2$) were added to the flask and maintained at 50°C for 8 h. After completing the chloromethylation, the product was washed by methanol, dried under a vacuum at 50°C for 5 h, and then was crushed under freezing. Finally, the product was further dried under a vacuum at 50°C for 3 h. Further details of the synthetic conditions and the composition of the chloromethylated ST-DVB copolymer samples are summarized in *Table 2*.

Reagents for reduction

Azobisisobutyronitrile (AIBN), *o*-xylene, tetrahydrofunan (THF) and methanol were supplied from WAKO Pure

Table 2 Chloromethylated ST-DVB copolymer samples

	ST-DVB copolymerzation			
Sample number	ST (g)	Cross-linking agent[a] (g) (DVB mol%)	BPO[b] (g)	Cl content[c] (wt%)
B-1	66.3	3.7 (2.4)	0.47	22.9
B-2	63.8	6.2 (4.1)	0.47	21.7
B-3	60.1	9.9 (6.6)	0.47	20.5

[a] DVB content: 56.5 wt%, the remainder is ethylstyrene. Values in parentheses are the DVB molar content in the original ST-DVB copolymers.
[b] BPO: benzoyl peroxide.
[c] Cl (wt%) observed by elemental analysis.

Table 3 Reduction ratios of Cl-MST-DVB copolymers

		Cl (wt%)		
Sample number	DVB (mol%)	Before reduction	After reduction	Reduction ratios (%)
A-1	3.3	22.3	6.2	72.2
A-2	6.6	20.9	0.3	98.6
A-3	10.1	19.8	2.6	86.9

Table 4 Reduction ratios of chloromethylated ST-DVB copolymers

		Cl (wt%)		
Sample number	DVB (mol%)	Before reduction	After reduction	Reduction ratios (%)
B-1	2.4	21.6	0.8	96.4
B-2	4.1	14.1	0.4	98.6
B-3	6.6	22.9	0.3	97.0

Chemical Ind., and tributyltin hydride (Bu_3SnH) was from Aldrich Chem. Co. All reagents were used as received.

Reduction of cross-linked copolymer samples

Reduction of the resin precursors with $-CH_2Cl$ was carried out by basically the same way reported by Hjertberg and Wendel, where they reduced poly(vinyl chloride) (PVC) in the presence of Bu_3SnH using a mixture solvent of THF and xylene[8].

A resin precursor sample weighing about 0.1 g was put into a 500 ml three-necked round-bottomed flask that was immersed in a thermostatically controlled oil bath. The flask was equipped with an inlet tube for nitrogen, dropping funnel, reflux condenser and Teflon-coated magnetic stirring bar. In order to swell the sample with network, after adding 3 ml of *o*-xylene and 9 ml of THF, the temperature was raised to 50°C and held for about 30 min. Then, after adding 12 ml of *o*-xylene the temperature was raised to 80°C, and 1.5 ml of BU, SnH and 18 mg of AIBN dissolved in 6 ml of *o*-xylene were added in order to carry out preliminary reduction. After preliminary reduction was carried out about 2 h, the reflux condenser was removed and THF was allowed to evaporate off. Then, 0.3 ml of Bu_3SnH and 9 mg of AIBN dissolved in 3 ml of *o*-xylene were added to the flask and the temperature was raised to 90°C and maintained for 15.5 h to attain complete reduction. Immediately after stopping the reaction, the reactant solution was slowly poured into 100 ml of methanol with vigorous agitation to precipitate the reduced resin precursor sample. The precipitate was recovered by suction filtration with a 3G3 glass filter and washed with methanol. Finally, the product was dried under a vacuum at 50°C for 3 h. The degree of reduction for the samples was determined by elemental analysis. The reduction ratio (*RR*) was calculated by equation (1):

$$RR\ (\%) = [1 - \{\text{chlorine in reduced copolymer } (\%)/\text{chlorine in copolymer } (\%)\}] \times 100 \qquad (1)$$

The observed reduction ratios for the A and B series samples are shown in *Table 3–Table 4*, respectively.

PY-GC conditions

A furnace pyrolyzer (PY-2010 SL from Frontier Lab.) was directly attached to a gas chromatograph (HP 5890 SERIES II equipped with a flame ionization detector (FID) and a fused-silica capillary column (50 m × 0.2 mm i.d.) coated with immobilized methyl silicone gum (0.33 μm film thickness) supplied by Hewlett-Packard (Ultra 1). The column temperature was initially set at 50°C, then programmed to 280°C at a rate of 4°C min^{-1} and finally held at 280°C. A weighed sample of 50 μg was pyrolyzed either at 500 or 600°C under a flow of helium carrier gas (50 ml min^{-1}). The optimum pyrolysis temperature of 600°C for the A series samples and 500°C for the B series samples were empirically determined to obtain the best separation of the characteristic products on the resulting pyrograms with higher sensitivity. The pyrolysis products introduced into the separation column were split with a split ratio of 55:1. The peak identification was mostly carried out using a gas chromatograph-mass spectrometer system (JEOL Automass system) to which the same pyrolyzer was also attached.

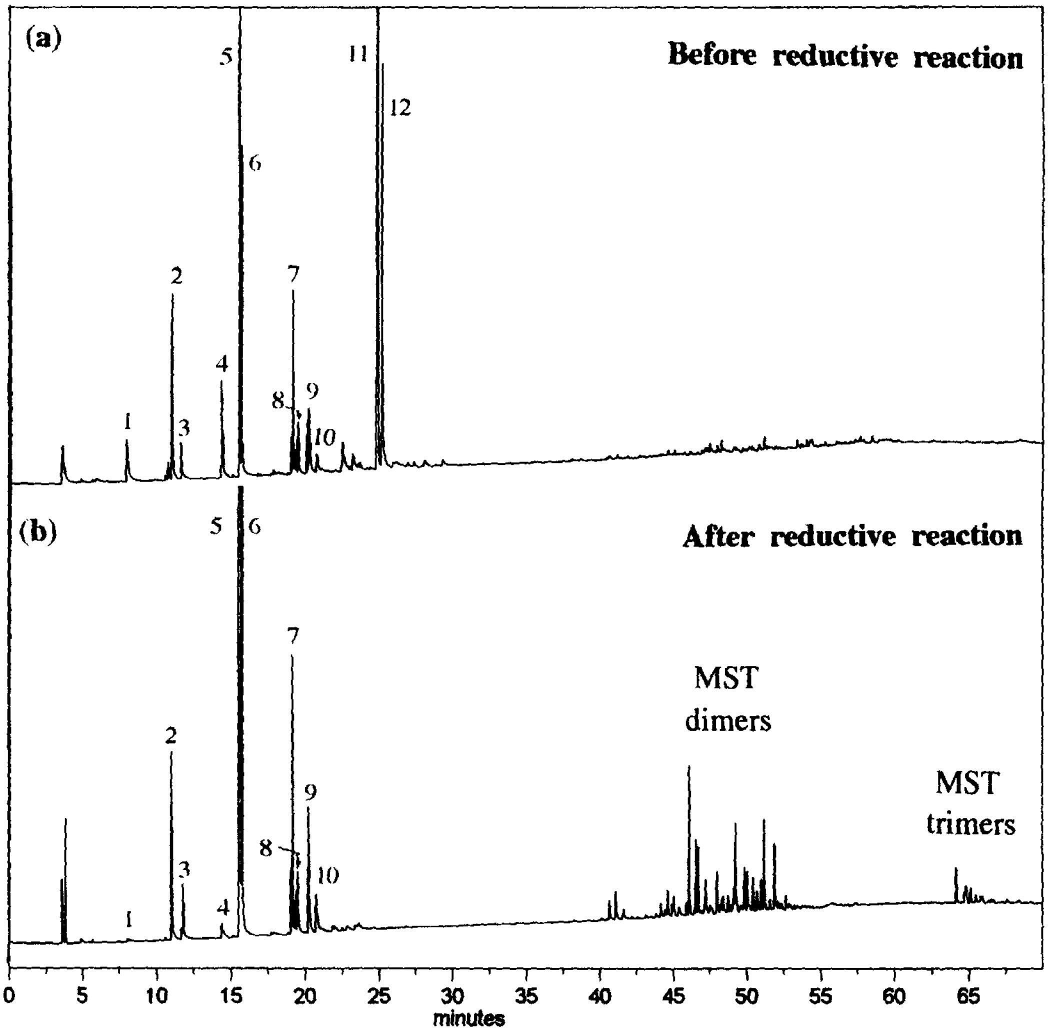


Figure 1 Pyrograms of Cl-MST-DVB cross-linked copolymer before (a) and after (b) reductive reaction. Sample: A-2. Pyrolysis temperature: 600°C. Peak numbers correspond to those in *Table 5*.

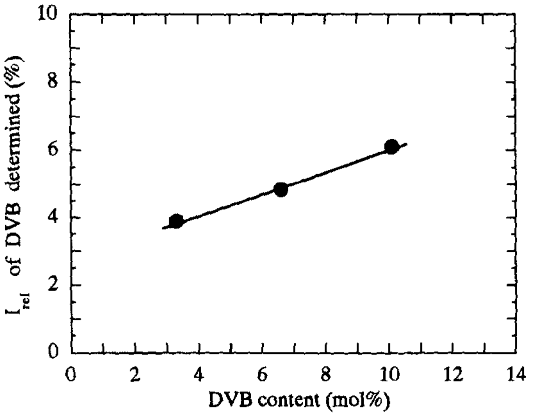


Figure 2 Relationship between DVB content in the Cl-MST-DVB copolymers (A-series) and relative peak intensities of DVB to total components observed on the programs.

RESULTS AND DISCUSSION

CL-MST-DVB cross-linked copolymers

Figure 1(a) shows a typical pyrogram of a Cl-MST-DVB cross-linked copolymer (A-2) at 600°C, whose peak assignment is shown in *Table 5*. Chloromethylated or methylated components related to the Cl-MST units in the polymer, for example, *m,p*-xylenes, *m,p*-ethyltoluenes, *m,p*-methylstyrenes, *m,p*-chloromethylstyrenes, etc., were observed besides the components observed in the ST-DVB copolymer [7]. In addition, *m*- and *p*-DVB were also observed as a clearly separated peak, and their peak intensities increased with the amounts of DVB introduced into the copolymers. Thus, by fundamentally the same method used in Ref. [7], the relative peak intensity (I_{rel}) of DVB was calculated as follows. Firstly, the corrected peak intensity (I_{corr}) is obtained from its observed peak intensity (I_{obs}), and divided by its effective carbon number (*ECN*) for FID, which can be empirically calculated[9]:

$$I_{\mathrm{corr}} = I_{\mathrm{obs}}/ECN \tag{2}$$

$$\begin{aligned} I_{\mathrm{rel}}(\mathrm{DVB}) = [&I_{\mathrm{corr}}(\mathrm{DVB})/\{I_{\mathrm{corr}}(\mathrm{TO}) + I_{\mathrm{corr}}(\mathrm{XY}) + I_{\mathrm{corr}}(\mathrm{ST}) \\ &+ I_{\mathrm{corr}}(\mathrm{ETO}) + I_{\mathrm{corr}}(\mathrm{MST}) + I_{\mathrm{corr}}(\mathrm{EST}) + I_{\mathrm{corr}}(\mathrm{DVB}) \\ &+ I_{\mathrm{corr}}(\mathrm{Cl-MST})\}] \times 100 \end{aligned} \tag{3}$$

where TO, XY, ST, ETO, MST, EST, DVB and Cl-MST are toluene, xylenes, styrenes, ethyltoluene, methylstyrenes, ethylstyrenes, divinylbenzenes and chloromethylstyrenes, respectively.

Figure 2 shows the relationship between the DVB content in Cl-MST-DVB copolymers and the observed I_{rel} values. Although a fairly good straight line was obtained, it did not pass through the origin, contrary to the case for the ST-DVB cross-linked copolymers without chloromethyl substituents[7]

Table 5 Peak assignments on the pyrograms of cross-linked copolymers before and after the reductive reaction

Peak number	Product	Structure
1	Toluene	C–Ph
2	p-Xylene	C–Ph–C
3	Styrene	C=C–Ph
3′	α-Methylstyrene	Ph–C(C)=C
4	p-Ethyltoluene	C–Ph–C–C
5	m-Methylstyrene	C–Ph–C=C
6	p-Methylstyrene	C–Ph–C=C
7	m-Ethylstyrene	C–C–Ph–C=C
8	p-Ethylstyrene	C–C–Ph–C=C
9	m-Divinylbenzene	C=C–Ph–C=C
10	p-Divinylbenzene	C=C–Ph–C=C
11	m-Chloromethylstyrene	CCl–Ph–C=C
12	p-Chloromethylstyrene	CCl–Ph–C=C
13	Isopropylstyrene	C–C(C)–Ph–C=C
14	Methyl-m-ethylstyrene	C–C–(C)–Ph–C=C
15	Methyl-m-divinylbenzene	C=C–(C)–Ph–C=C
16	p-Isopropylmethylstyrene	C–C(C)–Ph(C)–C=C
17	1,2-Diphenylethane	C(Ph)–C–Ph
18	Styrene dimer	C=C(Ph)–C–C–Ph
19	2,4-Diphenylpentene-1	C=C(Ph)–C–C(Ph)–C
20	2,5-Diphenylhexadiene-1,5	C=C(Ph)–C–C–C(Ph)=C
21	Styrene trimer	C=C(Ph)–C–C(Ph)–C–C–Ph
22	1-Tolyl-2-ethylphenylethane	CPh–C–C–Ph(C–C)
23	Methylstyrene dimer	C=C(Ph–C)C–C–Ph–C
24	2,4-Ditolylpenta-1,5-diene	C=C(Ph–C)C–C(Ph–C)=C
25	Methylstyrene trimer	C=C(Ph–C)C–C(Ph–C)C–CPh–C

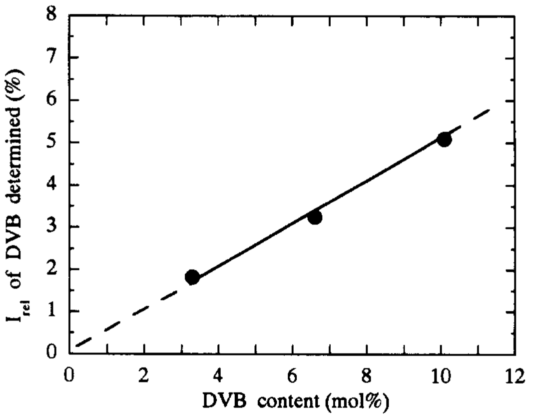


Figure 3 Relationship between DVB content in Cl-MST-DVB copolymers (A-series) and relative peak intensities of DVB to total components observed on the pyrograms after reductive reaction.

This observation might be attributed to the effect of chlorine atoms in chloromethyl groups of the Cl-MST-DVB copolymers, which do not exist in the ST-DVB copolymers. Chlorine atoms of the chloromethyl groups may cause complex side-reactions such as dehydrochlorination, causing further intermolecular cross-linking during pyrolysis. Actually, fairly significant amounts of non-volatile residues were observed in the sample holder after the pyrolysis of the sample because of less complete pyrolysis of the cross-linked copolymers with Cl-MST units. This phenomenon was also supported by the fact that methylated components were mainly observed in the resulting pyrograms rather than the chloromethylated ones. On the other hand, the effect of chlorine atoms to lower the recovery of DVB units also became more serious for the cross-linked copolymers with higher DVB content. As a consequence, the calibration curve with a certain gradient of inclination shown in *Figure 2* did not pass the origin.

In order to remove the effect of chlorine atoms, a reductive reaction, by which chloromethyl groups were reduced into methyl groups, was carried out for Cl-MST-DVB copolymers. The reductive reaction was followed according to the reduction method proposed for PVC[8].

A pyrogram of reduced Cl-MST-DVB copolymer is also shown in *Figure 1*(b). Compared with that before reduction, chloromethylstyrene was not observed because chloromethyl groups were reduced to methyl groups. Total peak intensifies were increased approximately by a factor of four because the reduced Cl-MST-DVB copolymer was pyrolyzed almost completely.

Thus, the I_{rel} of DVB was calculated again by equation (3). The results were shown in *Figure 3*. A good linear relation passing through the origin was obtained between the I_{rel} of DVB and DVB content for reduced Cl-MST-DVB copolymers, as shown in *Figure 3*. Hence, cross-linking reagents of Cl-MST-DVB copolymers could be determined by PY-GC.

Chloromethylated ST-DVB cross-linked copolymers

Figure 4 shows the pyrograms of ST-DVB cross-linked copolymer before and after chloromethylation. After chloromethylation, methylstyrene and chloromethylstyrene were mainly observed in the pyrogram instead of styrene, which was observed mainly before chloromethylation.

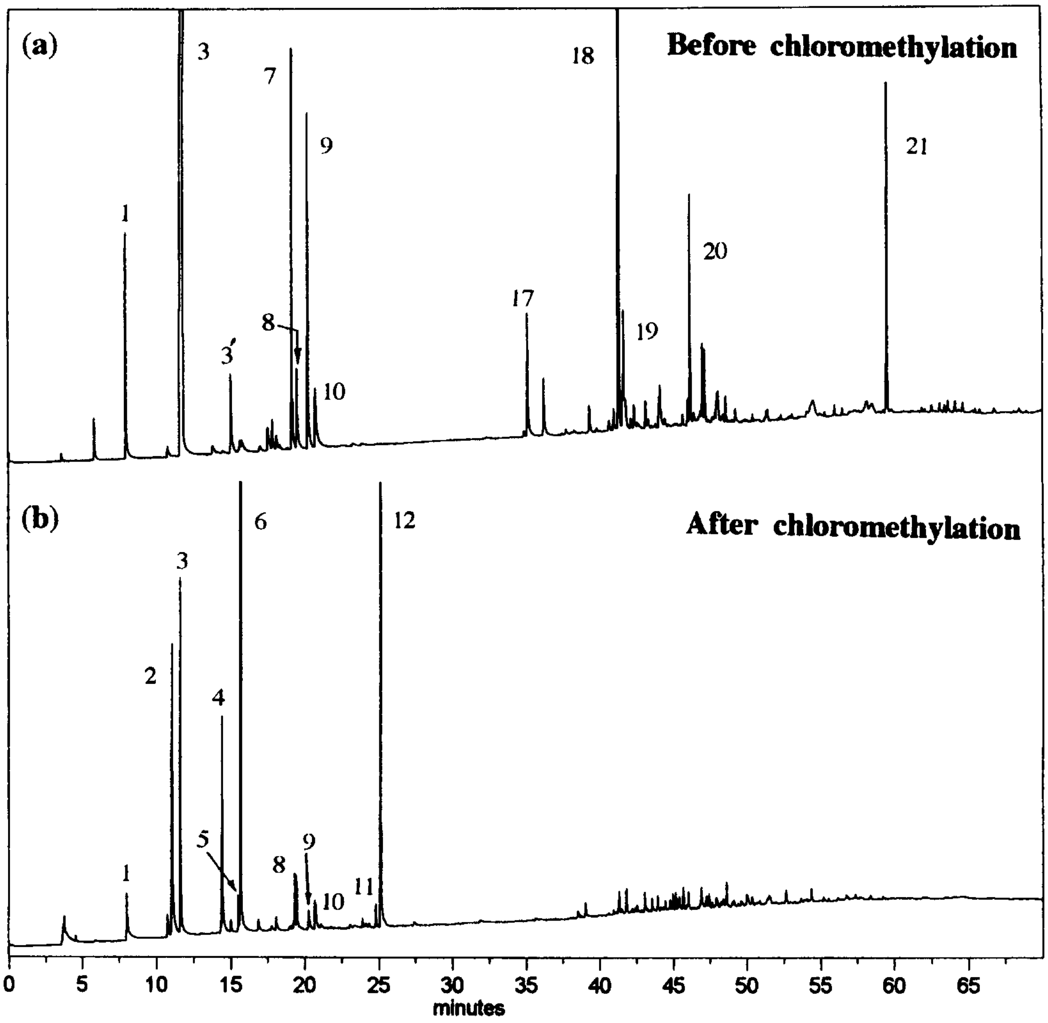


Figure 4 Pyrograms of ST-DVB cross-linked copolymer before (a) and after (b) chloromethylation. Sample: B-2. Pyrolysis temperature: 500°C. Peak numnbers correspond to those in *Table 5*.

Although pyrolysis products related to the cross-linking agent, DVB and ethylstyrene, which were clearly observed before chloromethylation, were also observed on the pyrogram of the chloromethylated ST-DVB copolymer, the shape and the relative intensity of the characteristic peaks changed after chloromethylation. In particular, the peaks of *m*-isomer of the cross-linking agent almost disappeared. Moreover, the observed peak intensity of *p*-DVB did not correlate with the content of the cross-linking agent at all.

In this polymer systems, chloromethylation could take place not only in the unit of styrene, but also in that of DVB. Chlorine atoms existing here were a primary factor in causing a complex side-reaction during pyrolysis as mentioned above. Hence, the chlorine atom had to be reduced to a hydrogen atom in order to remove this effect. Thus, similar to those of the Cl-MST-DVB copolymers, a reductive reaction was also carried out for chloromethylated ST-DVB copolymers.

Figure 5 shows typical pyrograms of the chloromethylated ST-DVB copolymer (B-2) before (a) and after (b) the reductive reaction. Although the peak of *p*-DVB was intensified, that of *m*-DVB was hardly observed even after reduction. Additional new characteristic peaks, such as methyl *m*-divinylbenzene (MDVB, peak 15) etc., were also observed in the pyrogram of the reduced copolymer, and the total peak intensifies increased approximately by a factor of five because the pyrolysis efficiency of the reduced copolymer much more increased than that before reduction. It is interesting to note that the peak intensity of MDVB increased with a rise in DVB content, whereas that of *p*-DVB was independent of the DVB content even after reduction. A possible route to yield MDVB from the moiety of chloromethylated *m*-DVB in the copolymer structure through reduction followed by pyrolysis is shown in the *Scheme 3*. Moreover, observed results suggest that the degree of chloromethylation of the *m*-DVB units was almost quantitative, while that of the *p*-DVB units was less so.

By the same method used above, I_{rel} of MDVB to total area of all the assigned pyrolysis products was also calculated from the peak intensities of characteristic peaks on high-resolution pyrograms. The results are shown in *Figure 6*. It was evident that there was a good linear relation passing through the origin between the I_{rel} of MDVB and the amounts of DVB introduced into the copolymers. Therefore, cross-linking reagents of chloromethylated ST-DVB copolymers could also be determined by PY-GC.

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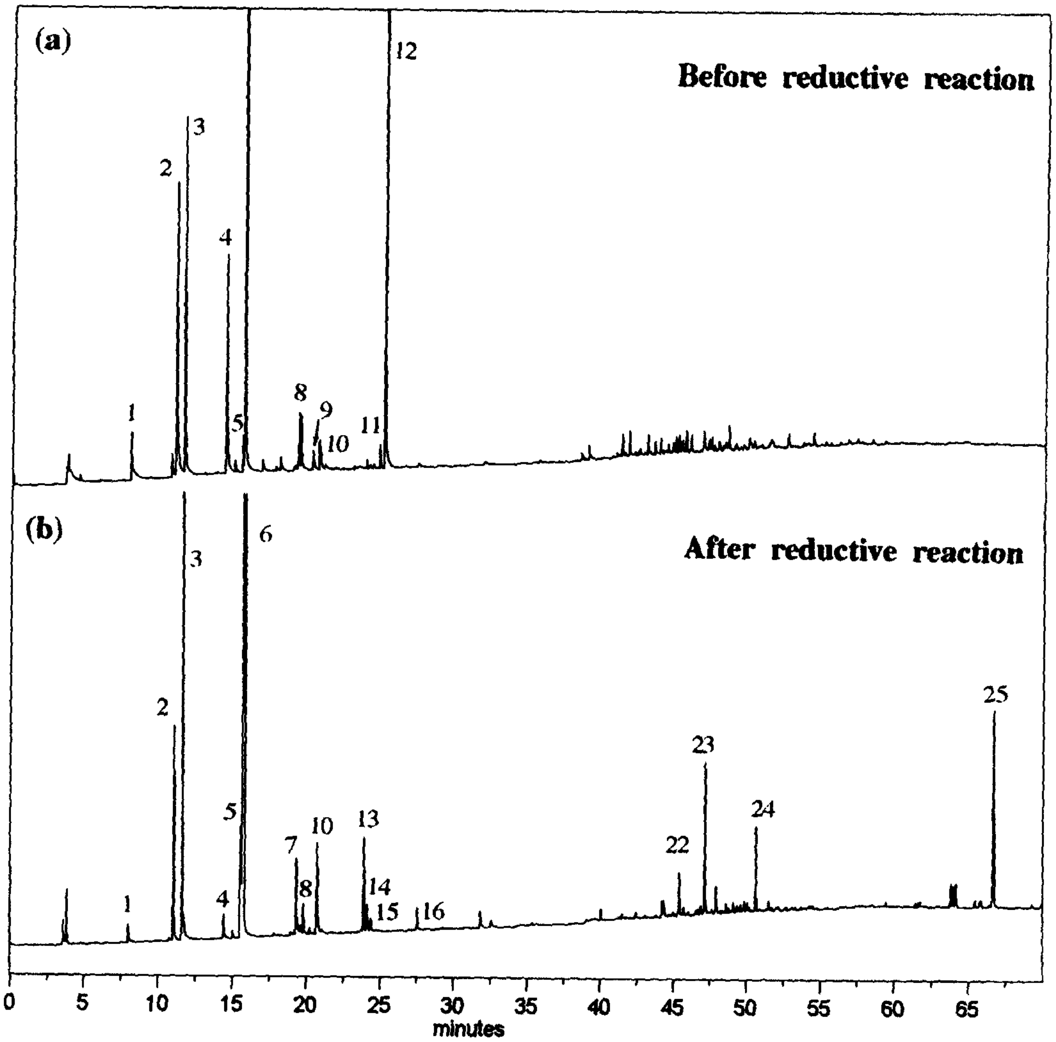
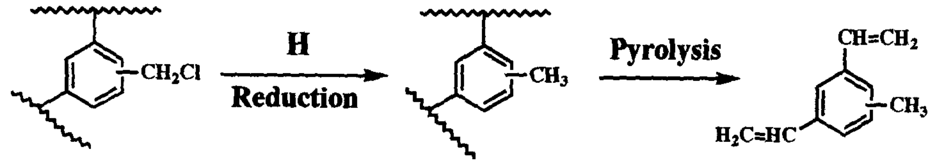


Figure 5 Pyrograms of chloromethylated ST-DVB cross-linked copolymer (B-2) before (a) and after (b) reductive reaction. Pyrolysis temperature: 500°C. Peak numnbers correspond to those in *Table 5*.



Scheme 3

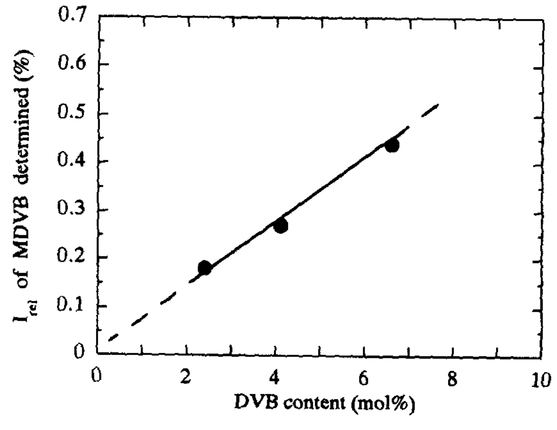


Figure 6 Relationship between DVB content in chloromethylated ST-DVB copolymers (B-series) and relative peak intensities of MDVB observed on the pyrograms after reductive reaction.

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