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Characterization of Chloromethyl-Substituted Polystyrene Networks by High-Resolution Pyrolysis–Gas Chromatography

H. Nakagawa and S. Tsuge*

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

S. Mohanraj and Warren T. Ford

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078.

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ABSTRACT: Three types of chloromethyl-substituted polystyrene networks prepared by different methods are studied by high-resolution pyrolysis–gas chromatography. The methods of introduction of chloromethyl groups are readily identified from the pyrolyzates characteristic of each copolymer. The degree of chloromethyl substitution is also estimated from the changes in the peak intensities of the characteristic pyrolyzates. Additionally, the thermal degradation behavior of these polystyrene networks is studied by thermogravimetric analysis. The pyrolysis–gas chromatography results can be used as a method of quantitative analysis of the amount of chlorine in these chloromethyl-substituted polystyrenes.

Chloromethyl-substituted polystyrene gels usually cross-linked with divinylbenzene (DVB) are widely used as key intermediates for ion-exchange resins, supports for solid-phase peptide synthesis and polymer-bound organic synthesis. Chloromethyl groups have been introduced into the gel polymers most often by Friedel–Crafts alkylation with chloromethyl methyl ether. Alternatively, chloromethyl groups can be introduced by copolymerization of styrene (ST), (chloromethyl)styrene (Cl-MST), and DVB. Also, chloromethyl groups can be conveniently introduced by radical chlorination of *p*-methylstyrene–DVB (*p*-MST–DVB) copolymers by using laundry or swimming pool bleach.[1] The properties of the resulting copolymers vary depending on the methods of introduction of the chloromethyl groups as well as the degree of chloromethyl substitution. Therefore, reliable analytical methods to obtain structural information on these chloromethyl-substituted polystyrenes are needed. However, analysis of their chemical structures, especially by spectrometric methods such as IR and NMR, has been restricted because of their insoluble network structures.

Previously, chloromethylated ST–DVB and ST–Cl-MST–DVB copolymers were characterized by high-resolution ^{13}C NMR spectroscopy of swelled samples. Chloromethylated ST–DVB and ST–Cl-MST–DVB copolymers were differentiated by the line widths of the backbone methine and chloromethyl carbon peaks.[2] Dependence of the line widths and detected peak areas on DVB content and isomeric distribution of the chloromethyl groups has been discussed.[3,4]

On the other hand, analytical techniques based on pyrolysis, such as pyrolysis–gas chromatography (PyGC) and pyrolysis–mass spectrometry (PyMS) are advantageous for obtaining information on the chemical structures of insoluble polystyrene networks.[5-9] Particularly, high-resolution PyGC is a powerful technique for characterization of copolymers with cross-linked structures.[8,9] These reports include analysis of the compositions of ST–DVB copolymers prepared by conventional radical copolymerization and also the average molecular weights of ST sequences between the network junctions by using linear polystyrene standards.[8] Structural differences between anionically and radically prepared ST–DVB copolymers were studied on the basis of the high-resolution pyrograms.[9]

In the present work, various chloromethyl-substituted copolymers prepared by different methods are studied by high-resolution PyGC. The methods of introduction of chloromethyl groups, which greatly affects the properties of the resulting copolymers, are readily identified from the pyrolyzates characteristic of each copolymer system. The degrees of chloromethyl substitution are also estimated from the changes in the peak intensities of the pyrolyzates characteristic of unsubstituted moieties. Thermal degradation behavior of these copolymers are also studied by thermogravimetric analysis (TGA) and discussed in connection with dehydrochlorination reaction occurring during pyrolysis.

Table I
Chloromethyl-Substituted Polystyrene Samples

sample	Cl content, wt %[a] CH$_2$Cl	Cl content, wt %[a] CHCl$_2$
Chloromethylated ST–DVB Copolymers		
A	0	0
B	2.5	0
C	4.6	0
D	5.7	0
ST–Cl-MST–DVB Copolymers		
E	0.2	0
F	1.5	0
G	6.0	0
Chlorinated *p*-MST–DVB Copolymers		
H	0	0
I	6.0	0.6
J	10.6	0.9
K	15.0	2.2
L	16.8	5.4

[a] From ^{13}C NMR analysis for the chlorinated *p*-MST–DVB copolymers.

Experimental Section

Materials. Chlorine content of the three types of chloromethyl-substituted polystyrene samples utilized is listed in Table I. Samples A–D were prepared by Friedel–Crafts alkylation of ST–DVB copolymers (1 wt % DVB cross-linked) by using chloromethyl methyl ether.[4] Samples E–G were prepared by copolymerization of ST, Cl-MST (7/3 meta-para mixture) and DVB (2 wt %).[3] Samples H–L were prepared by radical chlorination of p-MST–DVB copolymers (1 wt % DVB cross-linked) by using laundry or swimming pool bleach.[1] Chlorine content of the chlorinated *p*-MST–DVB copolymers was calculated from the ^{13}C-NMR peak areas.[1] The methods of introduction of a chloromethyl group are summarized in Figure 1.

Conditions for PyGC. A vertical microfurnace-type pyrolyzer (Yanagimoto GP-1018) was directly attached to a gas chromatograph (Yanagimoto G3800) with a high-resolution fused-silica capillary column (0.2 mm i.d. × 25 m long) coated with immo-

Table II
Peak Intensities of the Major Pyrolyzates on the Pyrograms of Chloromethyl-Substituted Polystyrenes

	peak intensity, count/μg^a										
sample	ST	ST dimer	ST trimer	*m*-MST	*p*-MST	*p*-MST dimer	*p*-MST trimer	*m*-Cl-MST	*p*-Cl-MST	DVB + EST	recovery on pyrogram, %^{b}
					Chloromethylated ST–DVB Copolymers						
A	3950	334	268							40.2	87.7
B	3240	176	138		15.0	104				20.7	74.8
C	2630	105	67.7		35.5	123				16.0	64.7
D	2190	74	44.9		33.4	127				13.6	56.4
					ST–Cl-MST–DVB Copolymers						
E	3950	303	221			8.5				88.8	86.9
F	3550	249	174	13.6	5.9	9.9		40.4	6.6	82.3	79.8
G	2560	71.9	68.8	64.6	30.1	21.2		109	22.6	80.1	64.3
					Chlorinated *p*-MST–DVB Copolymers						
H				3900	229	183					87.3
I					2940	110	86.2		95.6		69.8
J					1500	34.5	27.5		130		41.6
K					665	6.3			165		25.0
L					237				247		15.3

[a] Peak area/hydrocarbon net weight. [b] Total peak area/hydrocarbon net weight when the value for poly(α-methylstyrene) is regarded as 100%.

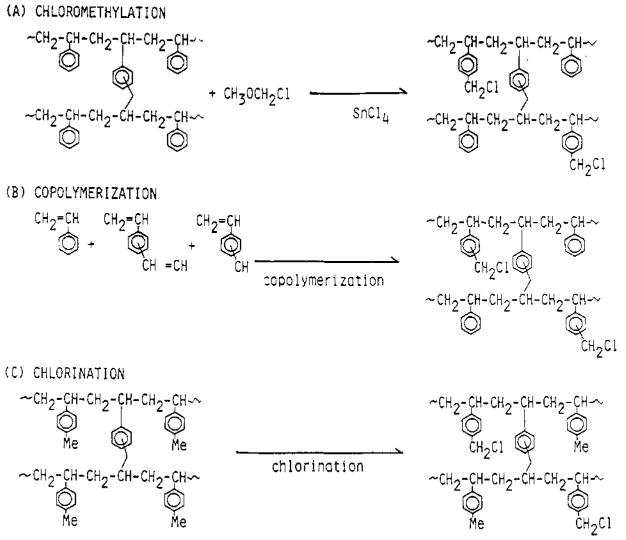

Figure 1. Methods of introduction of chloromethyl groups.

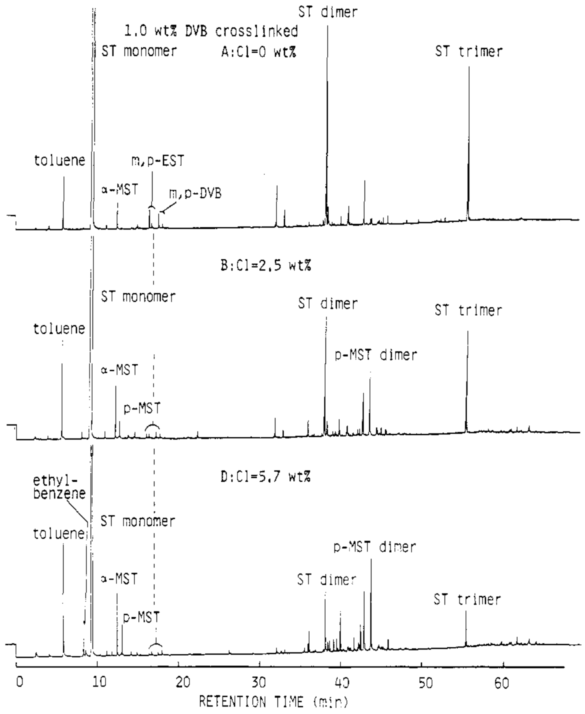

Figure 2. High-resolution pyrograms of chloromethylated ST–DVB copolymers.

bilized methylphenylsilicone (5% phenyl) supplied from Hewlett-Packard. The column was used in a temperature programming mode from 50 to 280 °C at a rate of 4 °C/min. Weighed samples of about 0.15 mg were pyrolyzed at 600 °C under a flow of nitrogen carrier gas (30 mL/min) which was reduced to 0.4 mL/min at the capillary column through a splitter. The peak identification was primarily carried out by a GC–MS system (JEOL JSM-DX300) attached to the pyrolyzer.

Conditions for TGA. TGA measurements were made on a Rigaku Denki thermobalance with about 6 mg of the sample weighed in a platinum disk from room temperature to about 700 °C at a rate of 10 °C/min under nitrogen atmosphere.

Results and Discussion

Typical pyrograms of chloromethylated ST–DVB, ST–Cl-MST–DVB and chlorinated *p*-MST–DVB copolymers are shown in Figures 2, 3, and 4, respectively. Peak intensities of major pyrolyzates on the pyrograms and the recovery rate (%) on the pyrograms are summarized in Table II. In this case, peak intensities are defined as the observed peak areas normalized by the amount of hydrocarbon (μg) in the sample, since the flame ionization detector (FID) responds only to the combustible hydrocarbon in the sample. Similarly, the recovery rate (%) is defined as the total peak area on the pyrogram normalized by the amount of hydrocarbon (μg) when the value for poly(α-methylstyrene), which decomposes quantitatively into the monomer around 600 °C, is regarded as 100%.

In the pyrograms of chloromethylated ST–DVB copolymers (Figure 2), ST monomer, dimer, and trimer characteristics of ST sequences are commonly observed, and their peak intensities decrease as the chlorine content increases. Additionally, decreases in the peak intensities of the meta and para isomers of DVB and ethylstyrene (EST) as a function of chlorine content indicate that Friedel–Crafts chloromethylation also occurs on the DVB and EST moieties in the copolymer. The greater decreases in the peak intensities of the meta isomers than those of the para isomers suggest that the Friedel–Crafts chloromethylation occurs more selectively on the meta isomers of DVB and EST units. *p*-MST and its dimer characteristic of chloromethylated ST units are observed in the

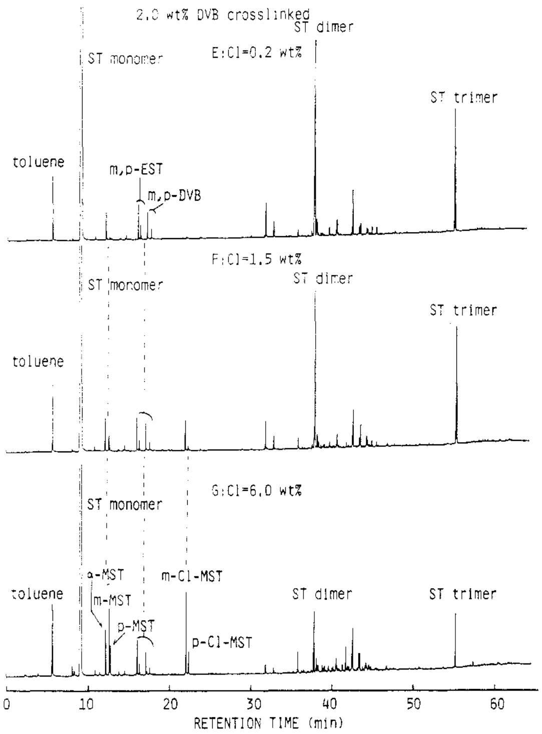

Figure 3. High-resolution pyrograms of ST–Cl-MSt–DVB copolymers.

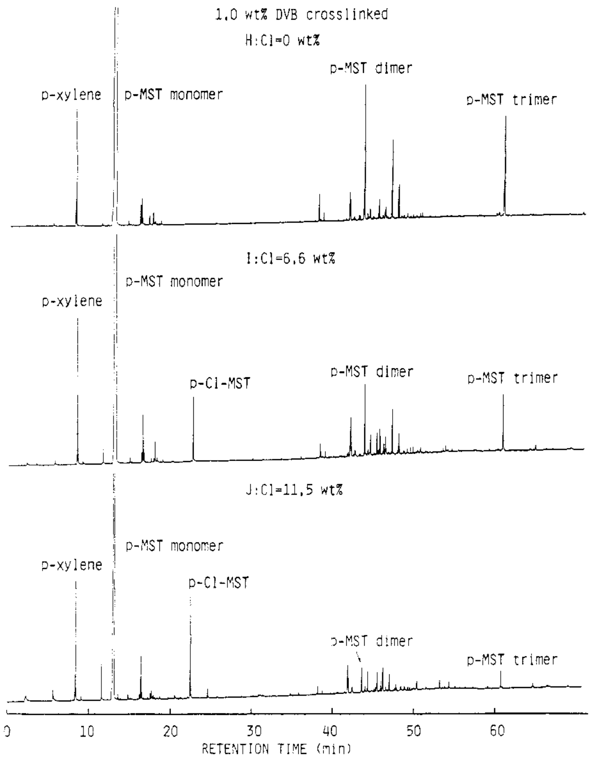

Figure 4. High-resolution pyrograms of chlorinated *p*-MST–DVB copolymers.

pyrograms of chloromethylated samples since the Friedel–Crafts chloromethylation occurs mostly on the para position of the ST units.[4]

Similarly, ST monomer, dimer, and trimer peaks and peaks related to EST and DVB isomers are observed in the pyrograms of ST–Cl-MST–DVB copolymers (Figure 3). Although the intensities of ST monomer, dimer, and trimer decrease as the chlorine content rises, the peak intensities of EST and DVB isomers remain almost constant regardless of the chlorine content, since constant amounts of DVB and EST are introduced by copolymerization. Here meta and para isomers are observed for MST and Cl-MST, since these isomers are contained in the Cl-MST used for the copolymerization and their intensities increase as a function of chlorine content. Therefore, the chloromethylated ST-DVB copolymers and ST-Cl-MST–DVB copolymers could readily be distinguished by comparing their pyrograms.

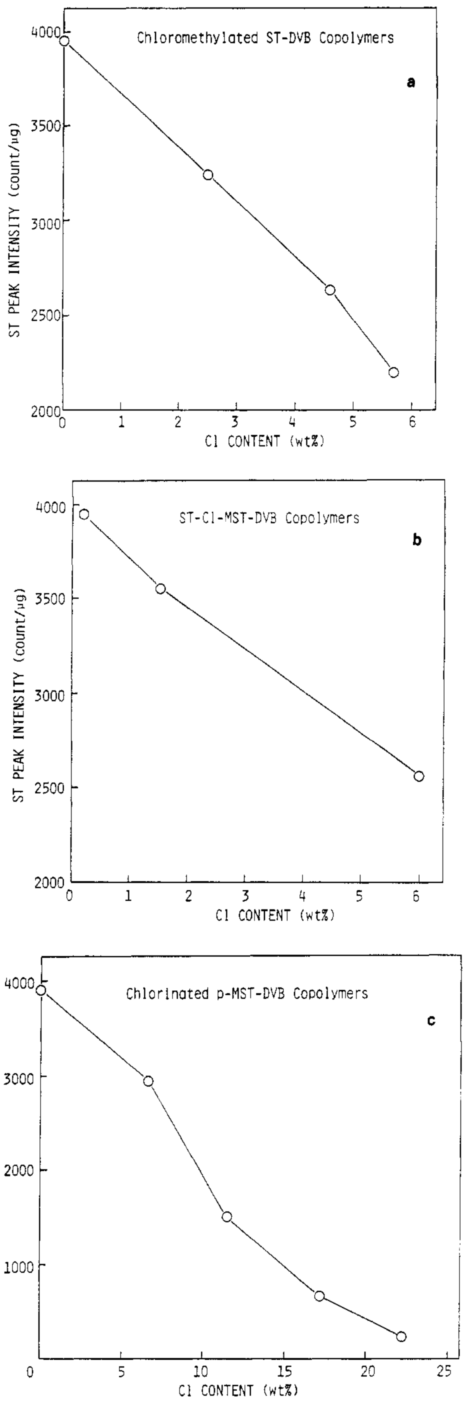

Figure 5. Relationships between chlorine content and peak intensities of the characteristic pyrolyzates for the three types of chloromethyl-substituted polystyrenes. ST–DVB copolymers.

In the pyrograms of chlorinated *p*-MST–DVB copolymers (Figure 4), peak intensities due to *p*-MST monomer, dimer, and trimer decrease as the chlorine content increases. As expected, the intensities of *p*-Cl-MST peaks, characteristic of chlorinated *p*-MST units, increase as the degree of chlorination increases. Consequently, chlorinated *p*-MST–DVB copolymers can readily be distinguished

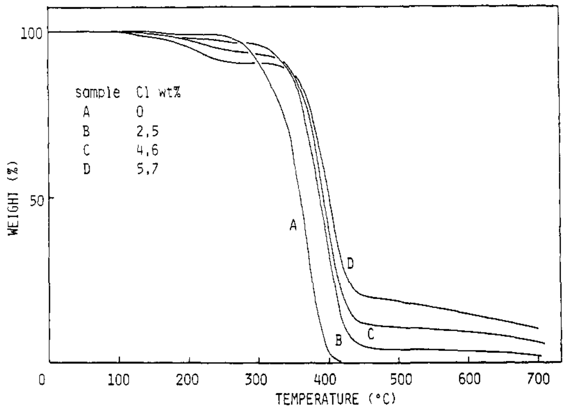

Figure 6. TGA weight loss curves of chloromethylated ST–DVB copolymers.

from the other two types of chloromethyl-substituted polystyrenes.

Relationships between chlorine content and peak intensities of the characteristic pyrolyzates for the chloromethylated ST–DVB copolymers derived from Table II are shown in Figures 5a–c. As shown in Figure 5a, peak intensities of ST monomer decrease almost linearly with the rise in the chlorine content for the chloromethylated ST–DVB copolymers. Generally, similar relationships are observed between chlorine content and peak intensities of the characteristic products for the other copolymers. Consequently, these relationships could be used as calibration curves for determining the degree of chloromethyl substitution for corresponding copolymer systems.

The Cl-MST peaks observed for both ST–Cl-MST–DVB and chlorinated *p*-MST–DVB copolymers are not observed for chloromethylated ST–DVB copolymers. This phenomenon might be closely related to the methylene cross-linking formed during the Friedel–Crafts chloromethylation.[4] In connection with this phenomenon, the total peak intensities of ST monomer, dimer, and trimer for the chloromethylated ST–DVB copolymers are smaller than those of the ST–Cl-MST–DVB copolymers of corresponding chlorine content for the samples with larger chlorine content (Table II).

Typical TGA weight loss curves of the chloromethylated ST–DVB copolymers are shown in Figure 6. Generally, the weight loss occurs stepwise. The first weight loss, occurring around 200 °C, increases as the degree of chloromethylation increases. The main degradation, occurring around 400 °C, shifts to higher temperature, and the amounts of residue increase as the decrease of chloromethylation increases, even though the degree of DVB cross-linking, which primarily affects the thermal stability of the network, is essentially the same. These phenomena suggest that dehydrochlorination occurs around 200 °C, and the residue with a methylene cross-linked structure undergoes further degradation around 400 °C. In connection with this, chlorine-containing pyrolyzates observed by PyGC for either copolymer system are relatively small, considering the chlorine contents of the original copolymers and the recovery rates in PyGC shown in Table II decreased as the chlorine content increased.

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Registry No. (ST)(*p*-Cl-MST)(*m*-Cl-MST)(DVB) (copolymer), 80531-81-3.

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Direct NMR Observation of Model and Macromolecular Esters in Polymerization of Styrene by Perchloric Acid

Krzysztof Matyjaszewski

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, Pennsylvania 15213. *Received June 11, 1987*

ABSTRACT: 1-Phenylethyl perchlorate (1) was prepared from 1-phenylethyl bromide and $AgClO_4$ directly CD_2Cl_2–C_6D_6 (2:1) solvent mixture and observed directly by ^1H NMR at −78 °C. 1 decomposes at temperatures above −40 °C via Friedel–Crafts alkylation. It reacts with water at −78 °C to form bis(1-phenylethyl) ethers. In the reaction with styrene 1 is converted to macromolecular ester. The ^1H NMR absorption of the macromolecular perchlorate is shifted upfield in comparison with 1 because of the diamagnetic shielding by adjacent aromatic rings.

Introduction

The term "pseudocationic" polymerization was introduced more than 20 years ago to describe propagation via covalent esters in the polymerization of styrene initiated by perchloric acid,[1] but up to now neither macromolecular ester nor its low molecular weight analogue, 1-phenylethyl perchlorate, has been observed directly.

Recently several new well-defined polymers were prepared from monomers which are known to polymerize exclusively through ionic mechanisms by using initiators with counterions forming covalent bonds with active centers.[2] These polymers (polyacrylates or poly(vinyl ethers))

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