Notes

Pyrolysis Gas Chromatographic Study on Sequence Distribution of Dyads in Styrene–*m*-Chlorostyrene and Styrene–*p*-Chlorostyrene Copolymers

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Copolymerization can lead to a variety of copolymers differing in composition and in the arrangement of two different monomer units. Knowledge of the detailed structure of a copolymer is necessary for the investigation of copolymerization mechanisms and the characterization of properties.

The nmr and ir spectra provide some information with respect to the sequence distribution in styrene copolymers such as styrene–methyl acrylate,[2a,b] styrene–butadiene,[3] and styrene–maleic anhydride.[4] Those spectra of styrene–*m*- and *p*-chlorostyrene (St/*m*-CSt and *p*-CSt) copolymer, however, are not sufficiently characteristic to allow quantitative interpretation of the microstructures.

Wall[5] has proposed that the yield of the regenerated and hybrid monomers through thermal decomposition of copolymers can be expressed in terms of the copolymer composition and the fraction of internal bonds broken during the pyrolysis of the copolymers. Shibasaki[6,7] has suggested a method for quantitative evaluation of the boundary effect of constituting monomers during thermal decomposition of copolymers by using pyrolysis gas chromatography (pgc). The resulting hybrid monomers from the copolymers provide valuable information about the monomer distribution.

In previous work,[8,9] the dyad concentrations in acrylonitrile–methyl acrylate and acrylonitrile–styrene copolymers have been discussed on the basis of yield of the dimer peaks by means of pgc. In the present work, we have studied the sequence distribution of dyads in the St–*m*-CSt and St–*p*-CSt copolymers by utilizing the cluster of dimer peaks appearing on the pyrograms. The observed dyad concentrations are in excellent agreement with those calculated from copolymerization theory over a wide range of the compositions.

Experimental Section

Materials. St–*m*-CSt and St–*p*-CSt copolymers were prepared by bulk polymerization at 70° in the presence of α,α'-azoisobutyronitrile. When a weight conversion of 2–7% was reached, the polymer was precipitated with methanol and purified by reprecipitation with methanol from the toluene solution, and then dried under vacuum at 60° for 48 hr.

The composition of copolymers was determined by elemental analyses. The results of these analyses are listed in Table I. Assuming pure radical copolymerization, the monomer reactivity ratios for both copolymer systems were experimentally determined by the Fineman–Ross method; the results are shown in Table II.

Pyrogram Measurement. A heated furnace-type pyrolyzer, Hitachi KP-1, was used to decompose the samples. The pyrolyzer was directly attached to the inlet port of the Hitachi Model 063 gas chromatograph equipped with dual flame ionization detectors. The operating conditions are as follows: separating column: 2-m stainless-steel tubing (3-mm i.d.) packed with Diasolid L (80–100 mesh) coated with Apiezon Grease L (10 wt %); column temperature, programmed for 100–300° at a rate of 10°; pyrolysis temperature, 550°; sample size, 0.1–0.3 mg.

Identification of the pyrolysis products appearing on the pyrograms was performed by combination of the pyrolysis gas chromatograph with a mass spectrometer, Hitachi RMS-4. The exact position of the double bond could not be determined in some dimer molecules. However, this introduced no difficulties in the calculation of dyad concentrations, since isomers differing only in double-bond position should have almost the same sensitivity toward the flame ionization detectors.[10]

Results and Discussion

Pyrolysis Products and Sequence Distribution. When moderately high temperatures are used for rapid thermal degradation of polymers, chain scission reactions take place along the polymer molecules to yield macromolecular radicals which subsequently unzip into the associated monomers, dimers, and other molecules.[8,9] If the macromolecular radicals depolymerize into products with an even number of carbon atoms (C_2 and C_4) along the polymer chain, the following pyrolysis products will be formed

Macromolecular radicals		Monomer	Dimer
——A–A·	⟶	A	A–A
——A–B· ——B–A·	⟶	A, B	A–B
——B–B·	⟶	B	B–B

A and B denote the two kinds of monomer unit. Trimer (C_6) and larger degradation products, if any, cannot be eluted under the gas chromatographic conditions used, and they are therefore neglected here. In the following discussion, the relative yields of the dimers are considered with respect to dyad distributions in the copolymers. Provided that the observed yields of the dimers are proportional to the concentrations of the corresponding dyads in the copolymers, the following relationships can be expected to hold true.

$$k_1 P_2(\text{A–A}) = Y(\text{A–A}) \qquad (1)$$

$$k_2\{P_2(\text{A–B}) + P_2(\text{B–A})\} = Y(\text{A–B}) \qquad (2)$$

$$k_3 P_2(\text{B–B}) = Y(\text{B–B}) \qquad (3)$$

Here, $P_2(\cdots)$ represents the dyad concentration in the copolymers, k_1, k_2, and k_3 are the formation constants of the dimers from the corresponding dyad structures in the copolymers, and Y(A–A), Y(A–B), and Y(B–B) are the observed relative yields between the dimers (Y(A–A) + Y(A–B) + Y(B–B) = 1).

Generally, k_1, k_2, and k_3 are not the same. However, when considering a given copolymer system, the formation constants will become mutually comparable if the fol-

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Table I
Composition of the Prepared Copolymer Samples

Sample No.	St in Feed Mole Fraction	St in Copolymer[a] Mole Fraction
	St-*m*-CSt Copolymers	
1	0.129	0.097
2	0.157	0.141
3	0.309	0.258
4	0.433	0.326
5	0.596	0.501
6	0.741	0.635
7	0.903	0.856
	St-*p*-CSt Copolymer	
a	0.116	0.087
b	0.194	0.170
c	0.305	0.272
d	0.490	0.465
e	0.610	0.509
f	0.726	0.672
g	0.823	0.780
h	0.919	0.891

[a] Calculated from chlorine content (elemental analysis).

Table II
Copolymerization Reactivity Ratios and Dimer Yields from Homopolymers

Copolymer	Reactivity Ratio[a]	Rel Yield of Dimers[b] Polymer	Dimer Yield (mol %)
St-*m*-CSt	$r_s = 0.79, r_m = 1.10$	PSt	14.8
St-*p*-CSt	$r_s' = 0.62, r_p = 1.35$	P-*m*-CSt	13.2
		P-*p*-CSt	12.2

[a] $r_s(r_s')$, r_m and r_p denote the monomer reactivity ratios for styrene, *m*-chlorostyrene, and *p*-chlorostyrene, respectively. [b] Relative yield of dimers is defined as follows: $[\Sigma Y_{\text{dimer}}/(\Sigma Y_{\text{monomer}} + \Sigma Y_{\text{dimer}})] \times 100$, where Y_{monomer} and Y_{dimer} denote yield of monomers and dimers at 550°, respectively.

Table III
Observed and Theoretical Concentration of Dyads in St-*m*-CSt Copolymers

Sample No.	P_2(St-St)		P_2(St-CSt) + P_2(CSt-St)		P_2(CSt-CSt)	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
1	0.008	0.000	0.178	0.184	0.814	0.816
2	0.012	0.008	0.214	0.218	0.774	0.774
3	0.052	0.042	0.378	0.392	0.570	0.566
4	0.111	0.104	0.472	0.487	0.417	0.409
5	0.239	0.235	0.522	0.521	0.239	0.244
6	0.418	0.407	0.471	0.475	0.111	0.118
7	0.729	0.716	0.253	0.250	0.018	0.034

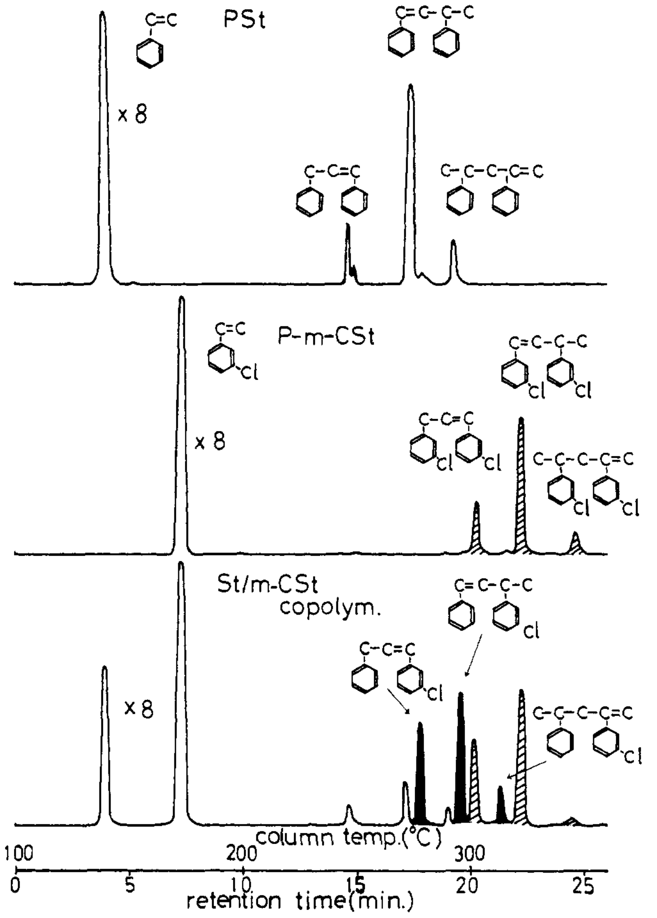


Figure 1. Typical pyrograms of PSt, P-*m*-CSt, and St-*m*-CSt copolymers (sample 4).

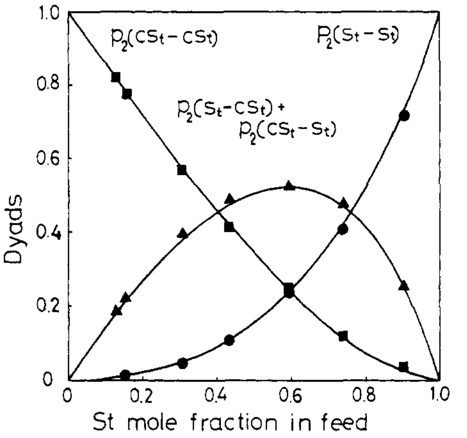


Figure 2. The concentration of dyads in the St-*m*-CSt copolymers: solid line, theoretical curves calculated from eq 4-6.

lowing conditions are met: (1) the corresponding two homopolymers have similar thermal characteristics, especially for the depolymerization process into monomers and dimers, and (2) the comonomers' reactivity ratios are not widely different. Table II summarizes the copolymerization reactivity ratios and dimer yields of homopolymers, polystyrene (PSt), poly(*m*-chlorostyrene) (P-*m*-CSt), and poly(*p*-chlorostyrene) (P-*p*-CSt).

The data suggest that the formation constants, k_1, k_2, and k_3 for the St-*m*-CSt and St-*p*-CSt copolymers should be very similar. Accordingly, in the following calculation, the observed relative yields between the dimers were directly correlated to the dyad concentrations in the copolymers.

Copolymerization theory (terminal model) gives the following relationships 4-6 corresponding to eq 1-3, respectively.

$$P_2(\text{A-A}) = P_1(\text{A})P_{\text{AA}} = r_{\text{A}}z/(2 + r_{\text{A}}z + r_{\text{B}}/z) \quad (4)$$

$$P_2(\text{A-B}) + P_2(\text{B-A}) = P_1(\text{A})P_{\text{AB}} + P_1(\text{B})P_{\text{BA}} = 2/(2 + r_{\text{A}}z + r_{\text{B}}/z) \quad (5)$$

$$P_2(\text{B-B}) = P_1(\text{B})P_{\text{BB}} = r_{\text{B}}/z/(2 + r_{\text{A}}z + r_{\text{B}}/z) \quad (6)$$

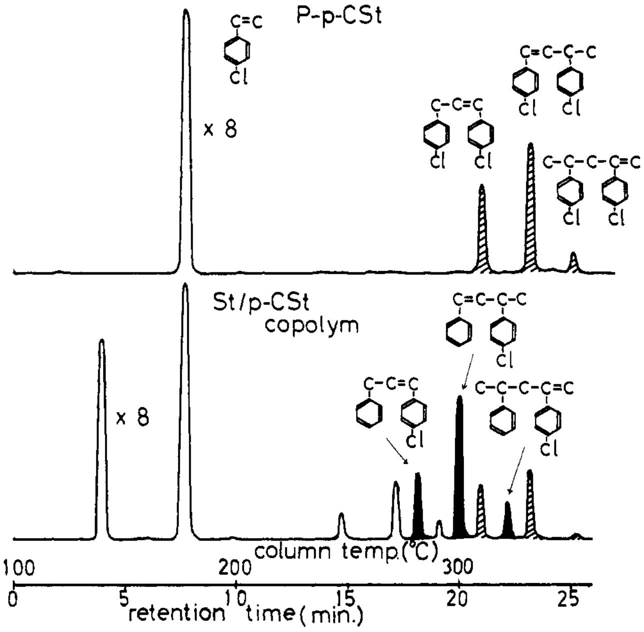
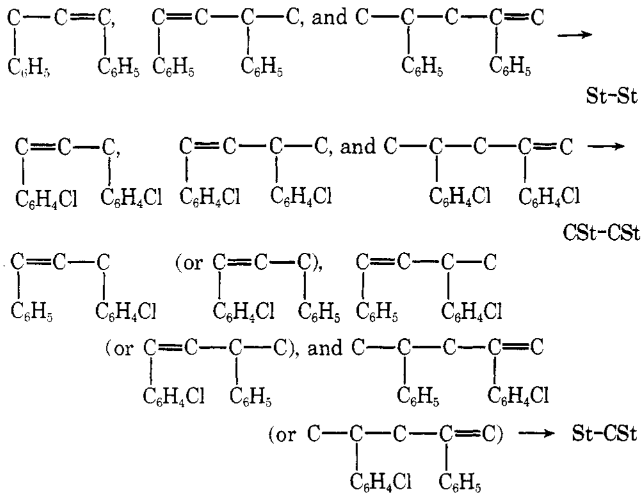


Figure 3. Typical pyrograms of P-*p*-CSt and St-*p*-CSt copolymer (sample d).

where r_A and r_B represent the monomer reactivity ratios and z in eq 4-6 represents A/B feed ratios. $P_1(\cdots)$ represents the corresponding monomer concentration, and P_{AB}, for example, is the probability of an A unit followed by a B unit.

St-*m*-CSt Copolymers. Figure 1 illustrates typical pyrograms of PSt, P-*m*-CSt, and St-*m*-CSt copolymers at the pyrolysis temperature of 550°. The main degradation products of PSt and P-*m*-CSt are monomers and dimers. On the other hand, St-*m*-CSt copolymers yield characteristic hybrid dimers in addition to the above products.

As shown in Figure 1, the resulting dimers consist of various carbon skeletons. In the following calculation, all associating dimer peaks were assigned to one dyad. For example, three kinds of dimers which contain two -C-(C_6H_5)- units were assigned to the St-St dyad after making correction for the molar sensitivity of each component in the flame ionization detector.[10] Similarly, the other dimer peaks were assigned to other dyads as follows



$$\underset{C_6H_5}{C}{-}C{=}\underset{C_6H_5}{C},\quad \underset{C_6H_5}{C}{=}C{-}\underset{C_6H_5}{C}{-}C,\ \text{and}\ C{-}\underset{C_6H_5}{C}{-}C{-}\underset{C_6H_5}{C}{=}C \longrightarrow \text{St-St}$$

$$\underset{C_6H_4Cl}{C}{=}C{-}\underset{C_6H_4Cl}{C},\quad \underset{C_6H_4Cl}{C}{=}C{-}\underset{C_6H_4Cl}{C}{-}C,\ \text{and}\ C{-}\underset{C_6H_4Cl}{C}{-}C{-}\underset{C_6H_4Cl}{C}{=}C \longrightarrow \text{CSt-CSt}$$

$$\underset{C_6H_5}{C}{=}C{-}\underset{C_6H_4Cl}{C}\ \left(\text{or}\ \underset{C_6H_4Cl}{C}{=}C{-}\underset{C_6H_5}{C}\right),\quad \underset{C_6H_5}{C}{=}C{-}\underset{C_6H_4Cl}{C}{-}C$$
$$\left(\text{or}\ \underset{C_6H_4Cl}{C}{=}C{-}\underset{C_6H_5}{C}{-}C\right),\ \text{and}\ C{-}\underset{C_6H_5}{C}{-}C{-}\underset{C_6H_4Cl}{C}{=}C$$
$$\left(\text{or}\ C{-}\underset{C_6H_4Cl}{C}{-}C{-}\underset{C_6H_5}{C}{=}C\right) \longrightarrow \text{St-CSt}$$

The observed and calculated concentrations of dyads in the copolymer are presented in Table III.

Table IV
Observed and Theoretical Concentration of Dyads in St-*p*-CSt Copolymers

Sample No.	P_2(St-St) Calcd	P_2(St-St) Obsd	P_2(St-CSt) + P_2(CSt-St) Calcd	P_2(St-CSt) + P_2(CSt-St) Obsd	P_2(CSt-CSt) Calcd	P_2(CSt-CSt) Obsd
a	0.009	0.006	0.191	0.187	0.800	0.807
b	0.025	0.017	0.297	0.259	0.678	0.724
c	0.065	0.043	0.415	0.397	0.520	0.560
d	0.178	0.127	0.522	0.528	0.300	0.345
e	0.291	0.243	0.524	0.536	0.185	0.221
f	0.438	0.380	0.465	0.506	0.097	0.114
g	0.596	0.536	0.361	0.415	0.043	0.043
h	0.794	0.746	0.197	0.244	0.009	0.010

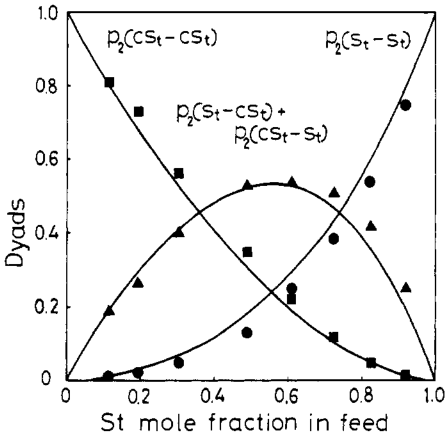


Figure 4. The concentration of dyads in the St-*p*-CSt copolymers: solid lines, theoretical curves calculated from eq 4-6.

In Figure 2, the observed dyad concentrations are plotted against the molar fraction of styrene in the starting monomer mixture [$F_{St}/(F_{St} + F_{m\text{-CSt}})$], together with the theoretical curves calculated from eq 4 to 6.

St-*p*-CSt Copolymers. Typical pyrograms of P-*p*-CSt and St-*p*-CSt copolymer are shown in Figure 3 at the same pyrolysis temperature of 550°. Since both St-*p*-CSt and St-*m*-CSt copolymers show basically an identical pyrogram pattern, the procedure mentioned above was adopted for the calculation of the dyad concentrations. The results obtained are summarized in Table IV and Figure 4.

As shown in Figures 2 and 4, the excellent agreement of the observed dyad concentrations with theoretical values supports the assumptions implicit in the characterization of these copolymer systems using pgc.

In this paper, a unique method for determining the distribution of dyads in St-*m*-CSt and St-*p*-CSt copolymers using pgc has been demonstrated. This technique for characterizing the microstructures of copolymers may also be applicable to other copolymer systems in which the thermal depolymerization processes to yield monomers and dimers resemble each other. If this is not so, the formation constants of dimers from the copolymer (k_1, k_2, and k_3 above) cannot be regarded as the same.

Although St-*o*-chlorostyrene (St-*o*-CSt) copolymers were also synthesized and efforts were made to determine the dyad concentrations using the same method, the resulting hybrid dimer peaks appeared on the pyrograms at retention times very close to the dimer peaks from the corresponding homopolymers. Further work on St-*o*-CSt and other copolymers is currently in progress.