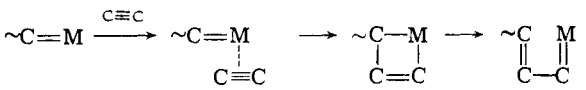
of cycloolefins.[24,25] It will be probable that the active species in the present polymerization is also a four-membered metallocycle, because the metathesis polymerization and the present polymerization exhibit many common features (for example, organotin compounds act as a good cocatalyst in both polymerizations[26,27]). If the active species in the present polymerization is a four-membered metallocycle, as shown in Scheme I, the polymer structure should be expressed in a more accurate form, $\{CH—C(Ph)\}_n$. This is a problem to be proved in a future investigation.

Scheme I



(M = W or Mo)

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Characterization of Sequence Distributions in Methyl Acrylate–Styrene Copolymers to High Conversion by Pyrolysis Gas Chromatography

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ABSTRACT: The sequence distributions in methyl acrylate–styrene copolymers over a wide range of composition and conversion were investigated by means of pyrolysis gas chromatography. Copolymer samples ranging from 0.2 to 0.5 mg were pyrolyzed under a flow of nitrogen at 510°C in a furnace type pyrolyzer directly attached to a gas chromatograph. Each cluster of dimer and trimer peaks appearing on the pyrogram was identified by means of mass spectrometry and was interpreted in terms of dyad and triad concentrations in the copolymer chain. Experimental results for the sequence distributions were fairly compatible with those predicted by the usual theories of copolymerization for low and high conversion.

Characterization of sequence distributions in copolymer chains has mostly been carried out by NMR and/or ir. Although these methods are most powerful for some types of copolymers, their effectiveness is sometimes limited because of inadequate resolution and intensity of the spectra and because of difficulty in finding suitable solvents for the copolymers. The sequence distributions in styrene (St) and methyl acrylate (MA) copolymers have been studied by NMR[1] and ir,[2] but such spectra do not afford quantitative information about sequence distributions.

On the other hand, pyrolysis gas chromatography (PGC) has recently been recognized as an effective tool in the field of polymer characterization. In our earlier work,[3] PGC was employed for the first time to determine triad distributions in vinylidene chloride–vinyl chloride copolymers, where specific degradation products such as benzene and chlorinated benzenes, formed through dehydrochlorination and subsequent cyclization reactions, were used. Basically, the same degradation mechanisms mentioned above were applied to elucidate the microstructures of chlorinated polyethylenes,[4] chlorinated poly(vinyl chlorides),[5,6] polypropylenes,[7] and ethylene–propylene copolymers.[8]

In previous PGC work, the dyad distributions in some vinyl-type copolymers of low conversion such as acryloni-

Table I
Composition and Conversion of St-MA Copolymer Samples

Sample no.	St in feed, mol fraction	St in copolymer,[a] mol fraction	Conversion, wt %
R-11	0.850	0.860	6.3
R-12	0.704	0.745	6.6
R-13	0.500	0.640	7.7
R-14	0.336	0.556	7.4
R-15	0.250	0.500	8.1
R-16	0.178	0.414	7.6
R-18	0.101	0.330	6.4
R-19	0.060	0.238	4.4
B-1	0.200	0.402	7.9
B-2	0.200	0.383	12.7
B-3	0.200	0.363	22.0
B-4	0.200	0.355	29.2
B-5	0.200	0.349	39.8
B-6	0.200	0.312	57.6
B-7	0.200	0.248	76.9
B-8	0.200	0.221	86.3
B-9	0.200	0.227	90.4

[a] From NMR for R series, and from elemental analysis for B series.

trile (AN)-MA,[9] AN-St,[10] and St-*m*-chlorostyrene (*m*-Cl-St) and St-*p*-Cl-St[11] copolymers were characterized using the specific peaks of linear dimers and hybrid dimers formed by thermal degradation of the copolymers. In our most recent paper,[12] a new theory was introduced for the PGC evaluation of the dyad distributions in vinyl-type copolymers. This theory uses new parameters, termed dimer formation probability constants, which account for the influence of boundary effect of monomer units on the formation of dimer during the degradation of the copolymers. The proposed method was successfully used to characterize dyad distributions in AN-*m*-Cl-St and AN-*p*-Cl-St copolymers of low conversion.

No PGC work, however, has ever appeared where sequence distributions in vinyl-type copolymers of high conversion are discussed. In this paper, dyad and triad distributions in St-MA copolymers of various composition and different conversions were studied using specific degradation products such as dimers and hybrid dimers for dyad characterization, and trimers and hybrid trimers for triad characterization.

Experimental Section

Materials. Samples of St-MA copolymer used are listed in Table I. Low conversion samples of different composition (R series in Table I) were kindly supplied by Dr. Y. Yamashita, Nagoya University. They were synthesized by free-radical copolymerization in benzene at 30°C in the presence of *n*-butyllithium.[1] Other samples of various conversions (B series) were prepared by free-radical copolymerization in benzene at 70°C using α,α'-azobis(isobutyronitrile) as an initiator. When a desired conversion was approximately reached, the polymer was precipitated with methanol and purified twice by reprecipitation with methanol from acetone solution and then dried under vacuum at 80°C for 50 hr. The compositions of the copolymers were determined by NMR and elemental analysis and are listed in Table I together with monomer feed and weight conversion data. The monomer reactivity ratios derived from these data are $r_s = 1.0 \pm 0.1$ and $r_m = 0.16 \pm 0.02$ for styrene and methyl acrylate, respectively. Previously reported reactivity ratios ($r_s = 0.75$ and $r_m = 0.20$) were used for B series copolymers.

Pyrolysis Gas Chromatographic Conditions. A Yanagimoto GP-1000 furnace-type pyrolyzer was used to decompose the polymers. It was directly attached to the inlet port of a Yanagimoto GCG-550F gas chromatograph with dual flame ionization detector (FID). The separating column, 2 m long copper tubing (3 mm i.d.) packed with 5% FFAP (free fatty acid) on 60–80 mesh Diasolid L, was programed between 100 and 260°C at a rate of 12°C/min. Samples ranging from 0.3 to 0.6 mg were pyrolyzed at 510°C using a small sample holder under a flow of carrier gas (N_2). The areas of the peaks appearing on the pyrogram were integrated by a Takeda Riken TR-2213 Digital Integrator. Identification of the pyrolysis products was mostly carried out by combination of the pyrolysis gas chromatograph with a Hitachi RMS-4 mass spectrometer. Some trimers, however, were assigned from their retention data. The exact position of the double bond in some of the pyrolysis products could not be determined. However, this did not introduce any difficulties in the calculation of their concentration, because isomers differing only in the double-bond position should have almost the same sensitivity for the FID (carbon detector).

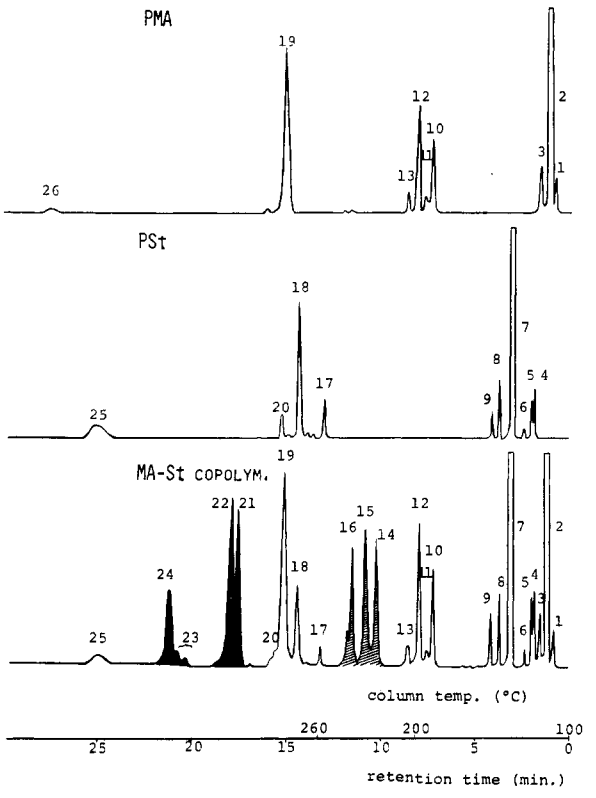


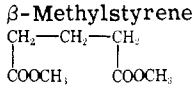
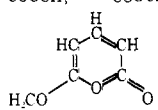
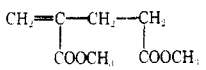
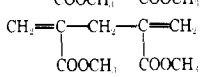
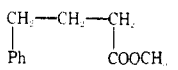
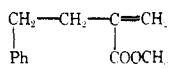
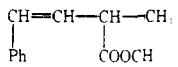
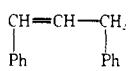
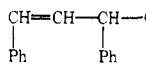
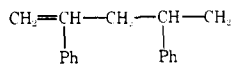
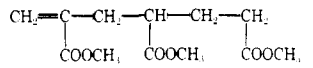
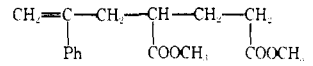
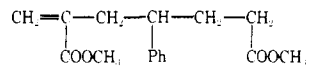
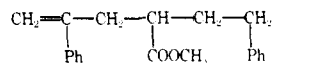
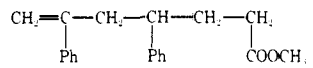
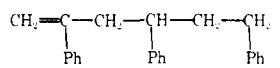
Figure 1. Typical pyrograms of PMA, PSt, and MA-St copolymer: sample, R-14 in Table I.

Results and Discussion

Pyrolysis Products (Pyroducts). Figure 1 illustrates the typical pyrograms of poly(methyl acrylate) (PMA), polystyrene (PSt), and a MA-St copolymer at the pyrolysis temperature of 510°C. The main products from PMA and PSt are monomers, dimers, and trimers, while the copolymer yields characteristic hybrid dimers (hatched peaks in Figure 1) and hybrid trimers (blackened peaks) in addition to the above pyroducts from the homopolymers. As summarized in Table II, each cluster of dimers and trimers appearing on the pyrograms was related to appropriate dyads and triads in the polymer chain.

As can be seen in Table II, except for peak 11 of MM which has a ring form, most of the dimers and trimers have linear structures. These characteristic products are mostly formed through a series of intramolecular free-radical transfer reactions. In a recent PGC report, Haken et al.[14] also reported the same linear dimers of MM as peaks 12, 13, and 14 from PMA. The formation of the cyclic product may support the degradation mechanisms of PMA-related

Table II
Assignment of Pyroducts

Peak no.	Assignment	
1	Methanol	
2	Methyl acrylate	
3	Methyl methacrylate	
4	Benzene	
5	Toluene	
6	Ethylbenzene	
7	Styrene	
8	α-Methylstyrene	
9	β-Methylstyrene	
10		MM dimers
11		
12		
13		
14		MS hybrid dimers
15		
16		
17		SS dimers
18		
20		
19		MMM trimer
21		MMS hybrid trimers
22		
23		MSS hybrid trimers
24		
25		SSS trimer
26	(MMMM tetramer)	

copolymers proposed by Cameron et al.[15] and Grassie et al.,[16] where the formation of some intermediate cyclic structures was postulated.

On the other hand, intermolecular free-radical reactions, which yield less characteristic pyroducts than intramolecular reactions do, must participate competitively in the degradation of PMA. This is supported by the facts that a small quantity of carbon residue is observed on the sample holder after the degradation and that the large amount of methanol observed on the pyrogram cannot be explained by intramolecular free-radical reactions alone. The amount of residue increased as the degradation temperature was lowered.

Dyad Distributions. As was described in previous papers,[9-12] there are some functionalities between the dyad concentration in a A-B copolymer ($P_2(\cdot\cdot)$) and the dimer yield observed on the pyrogram ($Y_2(\cdot\cdot)$):

$$Y_2(AA) = k_{d1}P_2(AA) \quad (1)$$

$$Y_2(AB) = k_{d2}\{P_2(AB) + P_2(BA)\} \quad (2)$$

$$Y_2(BB) = k_{d3}P_2(BB) \quad (3)$$

where k_{d1}, k_{d2}, and k_{d3} are dimer-formation parameters from the corresponding dyad in the copolymer. Generally, these parameters should vary depending on the dyad arrangement, the chemical and physical nature of the monomer units, and the pyrolysis conditions such as temperature, atmosphere, and sample size.[12] However, for some copolymer systems such as St-*m*-Cl-St and St-*p*-Cl-St, in which the corresponding homopolymers have similar degradation characteristics, the relative dimer yields are in excellent agreement with theoretical dyad concentrations.[11] In this case, the dimer-formation parameters can be regarded as equal to unity over the whole range of copolymer composition and the following simple equations can be used instead of eq 1, 2 and 3:

$$Y_2(AA) = P_2(AA) \quad (4)$$

$$Y_2(AB) = P_2(AB) \quad (5)$$

$$Y_2(BB) = P_2(BB) \quad (6)$$

As will be discussed below, this is almost the case for the relationships between the dyad concentrations and the yields of dimers derived from MA-St copolymers. In Figure 2, the experimentally determined dyads are plotted against the molar fraction in the monomer feed together with the theoretical curves for the low conversion samples of the R series. These results demonstrate fairly good agreement between the observed and the theoretical dyad concentrations over the whole range of the copolymer composition.

Triad Distributions in Copolymer Chain. Although the appearance of trimers on the pyrograms has been re-

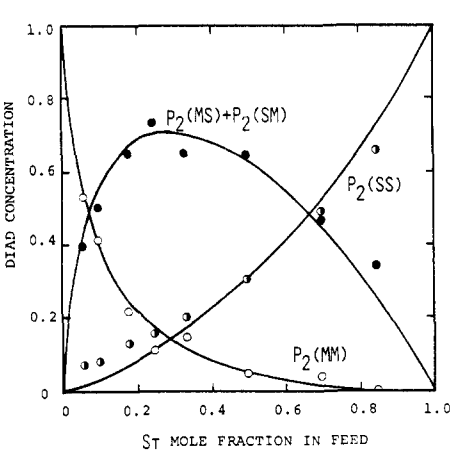


Figure 2. Dyad concentration vs. styrene molar fraction in feed in the low conversion MA-St copolymers (R series): (○, ●, ◑) observed Y_2 (··), and (—) copolymerization theory P_2 (··).

Table III
Observed and Theoretical Triad Concentrations

Sample no.	Y_3(MMM) obsd	P_3(MMM)	Y_3(MMS) obsd	P_3(MMS) + P_3(MSM)	Y_3(MSS) obsd	P_3(MSS) + P_3(SMS)	Y_3(SSS) obsd	P_3(SSS)
R-11	0.000	0.000	0.097	0.027	0.707	0.347	0.196	0.627
R-12	0.000	0.001	0.253	0.095	0.613	0.527	0.133	0.377
R-13	0.043	0.007	0.327	0.246	0.603	0.589	0.026	0.158
R-14	0.092	0.027	0.503	0.406	0.391	0.507	0.013	0.060
R-15	0.073	0.056	0.567	0.497	0.344	0.418	0.016	0.030
R-16	0.137	0.107	0.556	0.556	0.307	0.314	0.000	0.013
R-18	0.347	0.237	0.473	0.586	0.180	0.173	0.000	0.003
R-19	0.449	0.393	0.408	0.518	0.143	0.088	0.000	0.001

ported with polyacrylonitrile and its copolymers,[12] their relative yields have not been correlated quantitatively with triad distributions because of the lack of trimers from long sequences of the comonomers and/or volatility restrictions of the trimers for gas chromatographic separation. Fortunately, however, the trimers and the hybrid trimers from MA-St copolymers can be separated by chromatography using a polar column (low loading) such as FFAP, the temperature of which was programed from 100 to 260°C.

Basically the same type of relationships as discussed in the foregoing section could be applied between the trimers ($Y_3(\cdots)$) and the triads ($P_3(\cdots)$):

$$Y_3(\mathrm{AAA}) = k_{t1}P_3(\mathrm{AAA}) \tag{7}$$

$$Y_3(\mathrm{AAB}) = k_{t2}\{P_3(\mathrm{AAB}) + P_3(\mathrm{BAA})\} \tag{8}$$

$$Y_3(\mathrm{ABA}) = k_{t3}P_3(\mathrm{ABA}) \tag{9}$$

$$Y_3(\mathrm{BBA}) = k_{t4}\{P_3(\mathrm{BBA}) + P_3(\mathrm{ABB})\} \tag{10}$$

$$Y_3(\mathrm{BAB}) = k_{t5}P_3(\mathrm{BAB}) \tag{11}$$

$$Y_3(\mathrm{BBB}) = k_{t6}P_3(\mathrm{BBB}) \tag{12}$$

where $k_{t1} \sim k_{t6}$ represent trimer formation parameters. To simplify these relations, the optimum pyrolysis temperature to correlate the trimer yields with the triad concentrations was assumed to exist around 510°C, which was successfully used for the case of the dyad distribution. Accordingly, the following simple relationships were used providing $k_{t1} = k_{t2} = \ldots = k_{t6} = 1$:

$$Y_3(\mathrm{AAA}) = P_3(\mathrm{AAA}) \tag{13}$$

$$Y_3(\mathrm{ABA}) + Y_3(\mathrm{AAB}) = P_3(\mathrm{ABA}) + P_3(\mathrm{AAB}) + P_3(\mathrm{BAA}) \tag{14}$$

$$Y_3(\mathrm{BAB}) + Y_3(\mathrm{BBA}) = P_3(\mathrm{BAB}) + P_3(\mathrm{BBA}) + P_3(\mathrm{ABB}) \tag{15}$$

$$Y_3(\mathrm{BBB}) = P_3(\mathrm{BBB}) \tag{16}$$

In this simplification, eq 8 and 9 and eq 10 and 11 were combined into eq 14 and 15, respectively, since some of the trimer peaks could not be separated from each other. However, it was possible to calculate the individual triad distributions of MMS and MSM because their peaks (21 and 22 in Figure 1) were satisfactorily separated from each other.

The experimentally obtained relative trimer yields and the calculated trimer concentrations from the usual copolymerization theory[3] are listed in Table III.

The observed triad distributions for the copolymers with lower styrene content are generally in fair agreement with the theoretical. However, considerable deviation occurs in the case of the copolymers with high styrene contents. This is mostly attributed to the relatively low yields of SSS trimers from long sequences of styrene units. For comparison,

Table IV
Relative Yields of Monomer, Dimer, and Trimer from PSt and PMA at 510°C[a]

Sample	Relative yields		
	Monomer	Dimer	Trimer
PSt	58.1	36.3	5.6
PMA	29.0	32.0	39.0

[a] Relative yields are defined among monomers, dimers, and trimers.

Table IV summarizes the thermal conversion ratios of homopolymers (PSt and PMA) into the monomers, dimers, and trimers at 510°C. With regard to the dimer yields, PSt and PMA have almost comparable values around 35%. On the other hand, PSt yields only 5.6% of the trimers while PMA yields up to 39%, which reflects the discrepancy between the observed and the theoretical triad content of styrene-rich copolymers. Therefore, for more strict discussion of the triad distribution in MA-St copolymers with higher styrene contents, the boundary effect of monomer units[12] on the formation of the trimers should be taken into consideration. In other words, the assumption of the same trimer formation parameters ($k_{t1} = k_{t2} = \ldots = k_{t6}$) which was posturated to get the simplified eq 13 through 16 cannot always hold for this copolymer system, especially in the styrene-rich region.

Sequence Distributions in Copolymers Carried to High Conversion. Most copolymers in practical use are prepared in relatively high conversion. This generally results in heterogeneous sequence distributions, depending upon the extent of conversion, the ratio of monomer feeds, and the value of the monomer reactivity ratios. Average sequence distributions in several high-conversion copolymer systems have mostly been studied by NMR. In the following, PGC was applied to characterize the average dyad and triad concentrations in MA-St copolymers to high conversion.

At any instant during copolymerization, the composition and the sequence of the polymer formed change as a function of the instantaneous monomer composition when the associating monomer reactivity ratios are different from each other. Accordingly, the relationship of the average sequence concentration in the copolymer with the molar conversion, c, can be calculated by numerical or graphical integration of the corresponding instantaneous sequence concentration:[17,18]

$$P_n(\cdots) = \frac{1}{c}\int_0^c P_n(\cdots)dc \tag{17}$$

$$n = 1, 2, \ldots$$

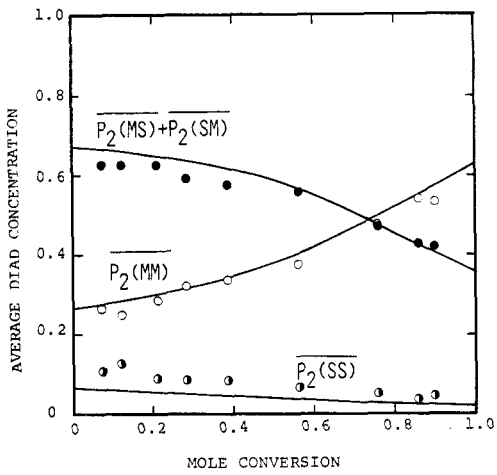


Figure 3. Average dyad concentration vs. molar conversion in the MA-St copolymers (B series): (○, ●, ◑) observed Y_2(··), and (—) copolymerization theory P_2(··).

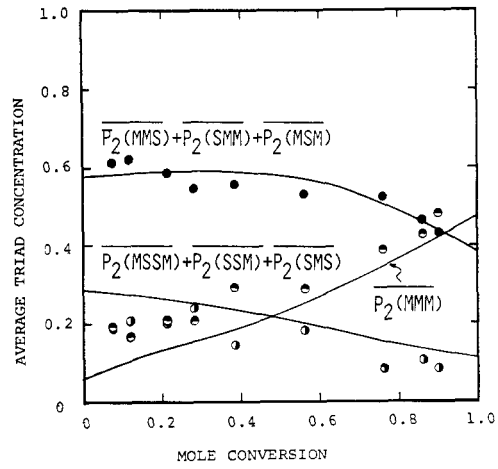


Figure 4. Average triad concentration vs. molar conversion in the MA-St copolymers (B series): (●, ◓, ◑) observed Y_3(···), and (—) copolymerization theory P_3(···).

The instantaneous sequence concentration can easily be calculated by the usual copolymerization theory,[3,11,12] once the associating instantaneous monomer composition, f_A or f_B, is determined by integrating Skeist's equation[19] as a function of c and the monomer reactivity ratios:

$$(1-c)^{1+r_Ar_B-r_A-r_B} = (f_A/f_{Ao})^{r_B-r_Ar_B}(f_B/f_{Bo})^{r_A-r_Ar_B} \times \{((1-r_B)f_{Bo}-(1-r_A)f_{Ao})/((1-r_B)f_B-(1-r_A)f_A)\}^{1-r_Ar_B} \quad (18)$$

where f_{Ao} and f_{Bo} are the initial monomer molar fraction of A and B, respectively.

The average dyad distribution in MA-St copolymers observed by PGC is plotted against the molar conversion together with the theoretical distribution curves in Figure 3, where the relations of eq 4 through 6 were used to get the observed average dyad concentration. These high-conversion copolymers were synthesized from the initial styrene molar feed of 0.2 (B series). The general trend of the observed distributions is fairly compatible with those predicted by the theory mentioned above. The slightly positive deviations of SS dyads from the theory could be explained by the small difference between the relative dimer yields from PMA and PSt (Table IV).

Similarly, Figure 4 shows the average triad distributions for B-series copolymers against the theoretical curves. In these copolymers, the SSS triad concentration is negligibly small throughout the entire range of conversion. The distribution trends of MMS and SSM triads are in fair agreement with the theoretical distributions. The significant positive deviation of MMM triad distributions could also be attributed to the remarkable difference in the ease of the associated trimer formation (Table IV).

In this work the PGC method was applied to elucidate the sequence distribution of MA-St copolymers which has not yet been characterized quantitatively by other spectroscopic methods. It has been proved that this method is also applicable to get average sequence distributions for high-conversion copolymers. Further work on characterization of other high-conversion copolymer systems is currently in progress where the boundary effect on the formation of the dimers and trimers has to be taken into consideration since the associating homopolymers have much different thermal characteristics.

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