

PYROLYSIS-GAS CHROMATOGRAPHY OF METHYL  
METHACRYLATE-STYRENE AND METHYL  
METHACRYLATE- $\alpha$ -METHYLSTYRENE COPOLYMERS

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SUMMARY

The pyrolysis-gas Chromatographic behaviour of methyl methacrylate copolymers with styrene or  $\alpha$ -methylstyrene was investigated with a Curie-point pyrolyzer. Monomer yield from each copolymer was very high as a result of the high probability of unzipping. Though only small quantities of dimers and/or trimers are formed on the pyrolysis of two copolymers, they reflect the sequence distribution of copolymers. Under some assumption, the run number of each copolymer is calculated using the amounts of dimer and/or trimer formed.

INTRODUCTION

Many polymers with unique primary structures have been produced and some show specific properties resulting from their primary structures. It is therefore important to investigate the latter. Pyrolysis-gas Chromatography (PyGC) is one of the most effective methods for this purpose. It has provided much useful information about polymers, including concentration of chain branches and crosslinks [1-3], mechanisms of thermal degradation [4-6], and structures of multipolymers [7].

In our previous work, the relationships between the pyrolyzates and the primary structures of five butadiene copolymers were reported [8]. In this work, we describe the PyGC investigation of methyl methacrylate-styrene and methyl methacrylate -  $\alpha$  methylstyrene copolymers.

EXPERIMENTAL

Alternating copolymers of methyl methacrylate (MMA) with styrene (St) [9] and  $\alpha$ -methylstyrene (MSt) [10] were synthesized by complexed copolymerization with ethylaluminium sesquichloride. Homopolymers and low-

TABLE 1

Composition of methyl methacrylate copolymers

A = alternating copolymer, R = random copolymer.

MMA-St	MMA (mole %)	MMA-MSt	MMA (mole %)
A	51.2	A	54.0
R <sub>1</sub>	21.1	R <sub>1</sub>	28.3
R <sub>2</sub>	28.6	R <sub>2</sub>	44.8
R <sub>3</sub>	36.1	R <sub>3</sub>	60.7
R <sub>4</sub>	43.3	R <sub>4</sub>	75.3
R <sub>5</sub>	47.0		
R <sub>6</sub>	52.5		
R <sub>7</sub>	54.5		
R <sub>8</sub>	60.9		

conversion random copolymers were prepared by radical polymerization with azobisisobutyronitrile as initiator.

Table 1 shows the copolymer compositions calculated using elemental analysis.

A Curie-point pyrolyzer (Japan Analytical Industry JHP-2) was coupled directly to a gas chromatograph (Shimadzu GC-6AM) equipped with a dual flame ionization detector. Samples of 40-80  $\mu$ g were pyrolyzed, and a stainless-steel column (2 m X 3 mm I.D.) packed with 10% SE-30 on 60-80 mesh Chromosorb W was used. In the case of MMA-St copolymers, the column temperature was maintained at 120°C for the first five minutes and controlled up to 250°C at a program rate of 10°C min<sup>-1</sup>. With MMA-MSt copolymers, the temperature was controlled between 140°C and 220°C at a program rate of 5°C min<sup>-1</sup>. The nitrogen flow-rate was 50 ml min<sup>-1</sup>, the hydrogen and air pressures were 0.5 kg cm<sup>-2</sup> and 1.0 kg cm<sup>-2</sup>, respectively. The peak areas were measured by an integrator (Shimadzu Chromatopac-E1A). Identification of the peaks was carried out by comparison with retention data of known substances and/or by a pyrolysis-gas chromatograph-mass spectrometer system (Shimadzu PYR-10A and GC-MS-7000).

## RESULTS AND DISCUSSION

### *Methyl methacrylate-styrene copolymers*

Fig. 1 shows the pyrograms of poly(methyl methacrylate), polystyrene and MMA-St copolymers at the pyrolysis temperature of 560°C. Similar to the monomer yields of two homopolymers, the yields of copolymers are high. It is therefore possible to determine the copolymer composition easily from the amounts of two monomers produced on pyrolysis [11]. The peaks of the two monomers were separated completely at the isothermal column temperature of 60°C (not shown in the figure). Including the alternating copolymer, the yield of St was plotted against the St content of the copoly-

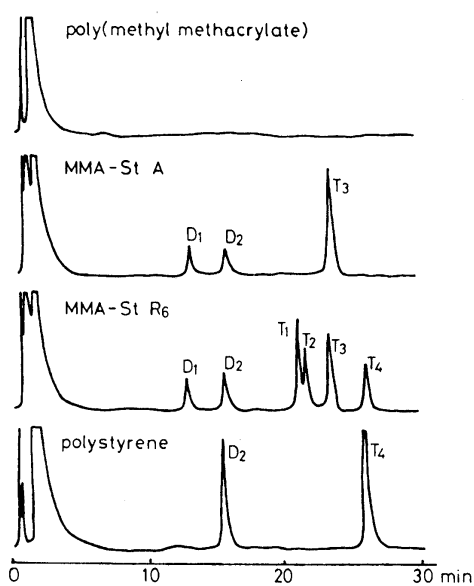


Fig. 1. Pyrograms of MMA and St homopolymers and MMA—St copolymers at 560°C.

mer, where the yield is taken as the St mole fraction in MMA and St of the pyrolyzates, i.e.  $St/(St + MMA)$ , and a very good linear relationship was obtained. From least squares regression analysis, the regression line of the St content of copolymer ( $y$ ) on the St yield ( $x$ ) was  $y = 0.991x + 0.60$ , and the error variance ( $V_{yx}$ ) was 1.64.

Information on the sequence distribution of copolymers can be obtained from investigation of the specific products which correspond to the dimer and trimer. On the pyrograms of copolymers, two peaks,  $D_1$  and  $D_2$ , are observed in the dimer region.  $D_2$  also appears on the pyrogram of polystyrene and is identified to be the St dimer (2,4-diphenyl-1-butene). On the other hand,  $D_1$  is concluded to be the St-MMA hybrid dimer from the mass spectrum ( $M^+ = 204$ ). In this hybrid dimer, the position of the double bond is not clear.

If the probability of dimer formation from the dyad which corresponds to each dimer is constant through its entire range of copolymer composition, peak areas of dimers,  $A(\text{dimer})$ , can be given as follows.

$$A(\text{St-MMA}) = k_1 N_D 2P(\text{St-MMA}) \quad (1)$$

$$A(\text{St-St}) = k_2 N_D P(\text{St-St}) \quad (2)$$

In these equations,  $N_D$  is the total number of dyads in the copolymer samples;  $P(\text{dyad})$  is the dyad concentration;  $k_1$  and  $k_2$  are constants containing the dimer formation probability of each dyad and the molar sensitivity to a flame ionization detector. The accurate value of  $N_D$  is not clear because it is difficult to measure the small sample size exactly. So,  $N_D$  is eliminated from

eqns. 1 and 2:

$$\frac{A(\text{St-MMA})}{A(\text{St-St})} = \frac{k_1 2P(\text{St-MMA})}{k_2 P(\text{St-St})} \quad (3)$$

This equation means that the ratios of peak areas are proportional to the ratios of dyad concentrations. The ratios of peak areas are estimated from the pyrograms, and those of dyad concentrations are calculated using the copolymerization theory [12]. Therefore, the value of  $k_1/k_2$  can be determined. Fig. 2 shows the values of the fraction of St-MMA peak area in the total peak area of dimers,  $A(\text{St-MMA})/[A(\text{St-MMA}) + A(\text{St-St})]$ , together with the theoretical values calculated as  $k_1/k_2 = 0.52$ . Using the run number,  $R$ , and St mole% of copolymer,  $X$ , eqn. 3 can be rewritten as follows:

$$\frac{A(\text{St-MMA})}{A(\text{St-St})} = \frac{k_1 2R/2}{k_2 (X - R/2)} \quad (4)$$

If  $k_1/k_2$  is known, the run number can be calculated from the values of  $X$  and  $A(\text{dimer})$  obtained on pyrolysis. The calculated run number of each copolymer,  $R_D$ , is shown in Table 2.

There are four peaks in the trimer region on the pyrograms of copolymers. Being identified from the mass spectra,  $T_1$  and  $T_2$  are the St-St-MMA hybrid trimers ( $M^+ = 308$ ),  $T_3$  is the St-MMA-St hybrid trimer, and  $T_4$  the St trimer (2,4,6-triphenyl-1-hexene). The difference between alternating and random copolymers is obviously seen in the trimer region on the pyrograms: the alternating copolymer hardly gives trimers other than  $T_3$ .

Applying an assumption similar to that made for dimers to the trimer formation, each Peak area of trimer can be described as follows:

$$A(\text{St-St-St}) = K_1 N_T P(\text{St-St-St}) \quad (5)$$

$$A(\text{St-MMA-St}) = K_2 N_T P(\text{St-MMA-St}) \quad (6)$$

$$A(\text{St-St-MMA}) = K_3 N_T 2P(\text{St-St-MMA}) \quad (7)$$

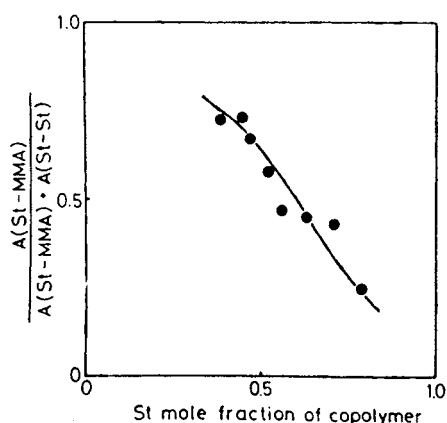


Fig. 2. Fraction of MMA-St dimer peak area for random copolymers. —, Theoretical curve ( $k_1/k_2 = 0.52$ ).

TABLE 2

Run numbers of methyl methacrylate-styrene copolymers

Copolymer	$R_D$ *	$R_T$ **
A	61	98
R <sub>1</sub>	39	36
R <sub>2</sub>	59	47
R <sub>3</sub>	57	55
R <sub>4</sub>	53	60
R <sub>5</sub>	62	63
R <sub>6</sub>	63	64
R <sub>7</sub>	66	63
R <sub>8</sub>	60	60

\* Run numbers calculated from dimers.

\*\* Run numbers calculated from trimers.

In these equations,  $N_T$  is the total number of the triad in copolymer samples;  $P(\text{triad})$  is the triad concentration.,  $K_1$ ,  $K_2$ , and  $K_3$  are the constants containing the trimer formation probability of each triad and the molar sensitivity of each trimer to the detector. From eqns. 5-7 the following two equations are obtained :

$$\frac{A(\text{St-St-St})}{A(\text{St-St-MMA})} = \frac{K_1 P(\text{St-St-St})}{K_3 2P(\text{St-St-MMA})} \quad (8)$$

$$\frac{A(\text{St-MMA-St})}{A(\text{St-St-MMA})} = \frac{K_2 P(\text{St-MMA-St})}{K_3 2P(\text{St-St-MMA})} \quad (9)$$

The values of  $K_1/K_3$  and  $K_2/K_3$  are determined by a method similar to that applied to dimers. Fig. 3 shows the observed values for the fraction of

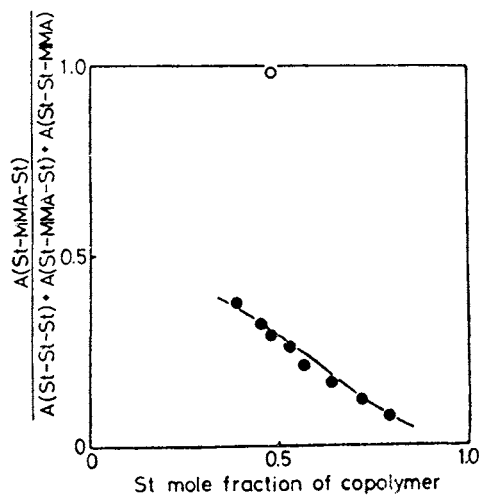


Fig. 3. Fraction of St-MMA-St trimer peak area. ●, Random copolymer; ○, alternating copolymer; —, theoretical curve ( $K_1/K_3 = 2.7$  and  $K_2/K_3 = 0.80$ ).

St-MMA-St peak area in the total peak area of trimers and the theoretical curve calculated as  $K_1/K_3 = 2.7$  and  $K_2/K_3 = 0.80$ . The fraction of St-MMA-St peak area,  $FA(\text{St-MMA-St}) = A(\text{St-MMA-St})/[A(\text{St-St-St}) + A(\text{St-MMA-St}) + A(\text{St-St-MMA})]$ , can be written as follows:

$$FA(\text{St-MMA-St}) = \frac{K_2 R^2 / 4 Y}{K_1 (X - R/2)^2 / X + K_2 R^2 / 4 Y + K_3 R (X - R/2) / X} \quad (10)$$

where R is the run number, X and Y are St mole% and MMA mole% of copolymer, respectively. Similarly to the case for dimers, the run number can be calculated from the values of X, Y, and  $FA(\text{St-MMA-St})$  if  $K_1/K_3$  and  $K_2/K_3$  are known. The run number of each copolymer thus obtained,  $R_T$ , is also shown in Table 2.

It is shown on the pyrogram that the alternating copolymer gives a small amount of the St dimer. The St trimer, however, is not observed on the pyrogram of this alternating copolymer. This leads to the following interpretation. The alternating structure of the copolymer synthesized with  $\text{Et}_{1.5}\text{AlCl}_{1.5}$  is not perfect: this copolymer has few St-St dyads besides the alternating units. Being calculated from the amount of dimers, the run number of the alternating copolymer is as small as that of the random copolymer. This is supposed to result from the predominant formation of St dimer from St-St dyads having MMA units on both sides. There are some deviations of the observed values (the filled circles) from the calculated line in Fig. 2, and the order of the run numbers for random copolymers is apparently abnormal, considering the composition of copolymers. On the other hand, the observed values of  $FA(\text{St-MMA-St})$  are in good agreement with the theoretical values; the run number calculated from the amounts of trimer shows a reasonable value for each copolymer.

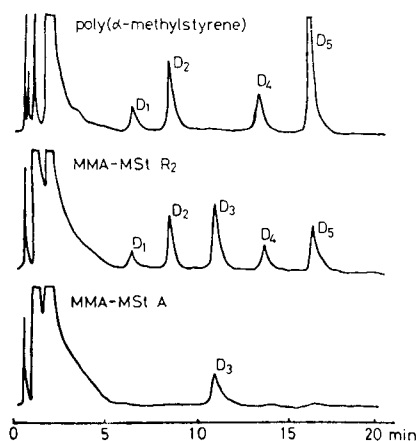


Fig. 4. Pyrograms of MSt homopolymer and MMA-MSt copolymers at 434°C.

### Methyl methacrylate- $\alpha$ -methylstyrene copolymers

Fig. 4 shows the pyrograms of poly( $\alpha$ -methylstyrene) and MMA-MSt copolymers at the pyrolysis temperature of 434°C. These copolymers have higher monomer yields than MMA-St copolymers. On the pyrograms no peaks with retention times longer than that of D<sub>5</sub> were observed under the GC condition at the column temperature of 260°C. The MSt yield, MSt mole fraction in two monomers, indicates the copolymer composition. The regression line of the MSt content of copolymer (y) on the MSt yield (x) was  $y = 0.946x + 4.17$  and  $V_{yx}$  was 5.63.

The difference between the alternating and random copolymers is obvious, as shown in Fig. 4. D<sub>1</sub> is a compound having one phenyl group; in the case of copolymers, D<sub>2</sub> is a mixture of the compound found in the pyrogram of poly( $\alpha$ -methylstyrene) and other unknown products from copolymers. D<sub>1</sub> and D<sub>2</sub> can not be identified from the mass spectrometric data. D<sub>3</sub> is the MMA-MSt hybrid dimer ( $M^+ = 232$ ), D<sub>4</sub> the MSt dimer ( $M^+ = 222$ , 2,4-diphenyl-1-pentene), and D<sub>5</sub> the MSt dimer ( $M^+ = 236$ , not 4-methyl-2,4-diphenyl-1-pentene). Using the same treatment for the MMA-St copolymers, the ratio of peak areas can be written as

$$\frac{A(\text{MSt-MMA})}{A(\text{MSt-MSt})} = \frac{k_1 2P(\text{MSt-MMA})}{k_2 P(\text{MSt-MSt})} \quad (11)$$

Fig. 5 shows the observed fraction of D<sub>3</sub> Peak area in the total peak area of three dimers (D<sub>3</sub>, D<sub>4</sub> and D<sub>5</sub>) and the theoretical curve calculated with  $k_1/k_2 = 0.30$ . By the method applied to MMA-St copolymers, the run number can be calculated from eqn. 4 and these values are shown in Table 3. It is reasonable that the alternating copolymer has a highly alternating structure, as shown by the high value of the run number in Table 3.

As described above, the monomer yield indicates the copolymer composi-

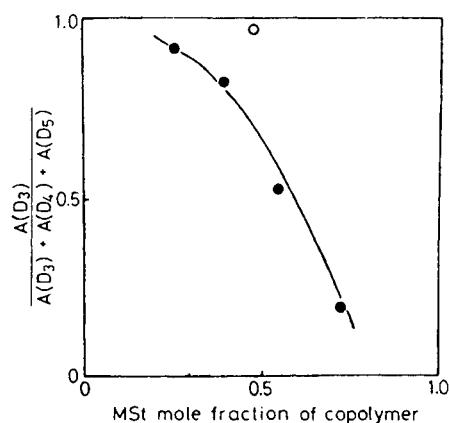


Fig. 5. Fraction of MMA-MSt dimer peak area. ●, Random copolymer; ○, alternating copolymer; —, theoretical curve ( $k_1/k_2 = 0.30$ ).

TABLE 3

Run numbers of methyl methacrylate- $\alpha$ -methylstyrene copolymers

Copolymer	R
A	92
R <sub>1</sub>	38
R <sub>2</sub>	70
R <sub>3</sub>	70
R <sub>4</sub>	47

tion satisfactorily in the case of these two copolymers. Although the amounts of dimer and/or trimer in the pyrolyzates are small, these dimers and/or trimers reflect the sequence distribution of copolymers. Hence, the discrimination of alternating from random copolymers can be achieved from the investigation on these pyrolyzates.

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#### REFERENCES

- 1 M. Seeger and E.M. Barrall II, *J. Polym. Sci. Part A-1*, 13 (1975) 1515.
- 2 D.H. Ahlstrom and S.A. Liebman, *J. Polym. Sci. Part A-1*, 14 (1976) 2479.
- 3 M. Seeger, R.J. Gritter, J.M. Tibbitt, M. Shen and A.T. Bell, *J. Polym. Sci. Part A-1*, 15 (1977) 1403.
- 4 K.J. Voorhees, F.D. Hileman, I.N. Einhorn and J.H. Futrell, *J. Polym. Sci. Part A-1*, 16 (1978) 213.
- 5 M. Seeger and R.J. Gritter, *J. Polym. Sci. Part A-1*, 15 (1977) 1393.
- 6 F. Hrabak, J. Mitera, V. Kubelka and M. Bezdek, *Eur. Polym. J.*, 14 (1978) 219.
- 7 H. Eustache, N. Robin, J.C. Daniel and M. Carrenga, *Eur. Polym. J.*, 14 (1978) 239.
- 8 T. Shimono, M. Tanaka and T. Shono, *Anal. Chim. Acta*, 96 (1978) 359.
- 9 M. Hirooka, H. Yabuuchi, J. Iseki and Y. Nakai, *J. Polym. Sci. Part A*, 6 (1968) 1381.
- 10 B.K. Patnaik and N.G. Gaylord, *J. Macromol. Sci. Chem.*, A7 (1973) 1247.
- 11 D.L. Evans, J.L. Weaver, A.K. Mukherji and C.L. Beatty, *Anal. Chem.*, 50 (1978) 857.
- 12 K. Ito and Y. Yamashita, *J. Polym. Sci. Part A*, 3 (1965) 2165.