European Polymer Journal, Vol. 14, pp. 625 to 630
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0014-3057/78/0901-0625$02.00/0

CALCULATION OF KINETIC PARAMETERS AND SEQUENCE DISTRIBUTION FROM PYROLYSIS GAS CHROMATOGRAPHIC DATA OF STYRENE–METHYL ACRYLATE COPOLYMERS

MARIANNE BLAZSÓ and GÁBOR VÁRHEGYI
Hungarian Academy of Sciences, Research Laboratory for Inorganic Chemistry, H-1112 Budapest, Budaörsi ut 45. Hungary

(*Received* 23 *January* 1978)

Abstract—Styrene–methyl acrylate copolymers have been investigated by pyrolysis gas chromatography. The pyrolysis product distribution, ranging from methyl acrylate monomer to styrene trimer, was measured and introduced into a mathematical model described previously. Applying this model, the sequence distribution and the rate constants of the degradation reactions were obtained. The results show that the sequential arrangement is important in the thermal decomposition of styrene–methyl acrylate copolymers. In most cases the rate constant of a product release reaction depends considerably on the nature and sequence of the monomer units in the product molecule, as well as on the nature of the monomer unit remaining on the macroradical end, from which the molecule was released.

INTRODUCTION

The thermal degradation of monosubstituted vinyl polymers can be properly understood with the theory of free decomposition mechanism of paraffin hydrocarbons [2–4], provided it does not affect the substituent groups. The same mechanism holds also for monosubstituted vinyl copolymers, and may explain the phenomenon called "boundary effect" [5–7] i.e. the differences between the degradation of a homopolymer mixture and the corresponding copolymer. According to this mechanism, macroradicals are formed during the degradation. The depolymerization of the macroradicals produces monomers; at the same time dimers and trimers are also produced through the combination of intramolecular radical transfer and beta scission. For copolymers, dimer and trimer may be composed of different monomers as well. A mathematical model has been suggested [1] to establish how the yields of the different products might depend on the sequence distribution of the copolymer and on the rate constants of the degradation reactions. The application of this model to styrene–methyl acrylate copolymers is now demonstrated using pyrolysis gas chromatographic data.

EXPERIMENTAL

Samples

The styrene–methyl acrylate copolymers were synthesized at 50° with azobis (isobutyronitrile) initiator in the Central Research Institute for Chemistry of the Hungarian Academy of Sciences. The conversions were less than 10%. The compositions of the samples, by elemental analysis, are given in Table 3.

Pyrolysis

Thermal degradation of the copolymers was carried out at 350° for 30 sec in argon, in a ribbon type pyrolyser, constructed in our laboratory and described earlier [8]. The sample weights were about 0.1 mg. The pyrolysis temperature was chosen as low as 350° because larger quantities of dimer and trimer are formed at this temperature than at higher and because side reactions are negligible below 500°. Varying the pyrolysis time up to 3 min, the distribution of reaction products does not change significantly. An example is shown in Table 1 to illustrate the reproducibility of pyrolysis at 350° in our pyrolyser. In the first column of the table, symbols are given for the product molecules. In these symbols 1 and 2 represent styrene and methyl acrylate monomer units respectively. The standard deviations have been calculated from seven parallel measurements.

The mixture of the homopolymers (PS and PMA) was also pyrolysed. In this case there was superposition of the corresponding homopolymer pyrograms; no hybrid product could be detected.

Gas chromatographic analysis

The pyrolyser was coupled with a Perkin–Elmer 900 gas chromatograph equipped with a flame ionization detector. The separation of the pyrolysis products was performed on a 3 m, 2 mm I.D. column packed with 80–100 mesh Chromosorb G coated with 5% OV-17 stationary phase. A temperature program from 40° to 280° at a rate of 8°/min was applied. The peak areas of the pyrolysis products were measured by a Perkin–Elmer D-26 electronic integrator. The gas chromatographic separation of the pyrolysis products of sample 6 is shown in Fig. 1. The trimer isomers are not separated totally on OV-17 packed column. The same analysis on capillary column of high separation power (20 m × 0.2 mm glass capillary coated with FFAP) established the presence of all possible trimer isomers (Fig. 2).

Qualitative analysis

The compositions of the pyrolysis products of styrene–methyl acrylate copolymers were determined by Tsuge *et al.* [9] by mass spectrometry. The identification of the isomeric structure of dimers and trimers is not possible by M.S. and so another method is needed. Since insufficient pyrolysis products were available for structure identification methods, we have deduced the

Table 1. Reproducibility of pyrolysis at 350° (sample 6)

Symbol	Product compound	Peak area % (mean value)	Standard deviation
2	CH$_2$—CH—Mc*	8.57	0.56
1	CH$_2$=CH—Ph*	61.24	0.88
22	CH$_2$=C(Mc)—CH$_2$—CH$_2$—Mc	0.10	0.05
21	CH$_2$=C(Mc)—CH$_2$—CH$_2$—Ph	1.71	0.03
12	CH$_2$=C(Ph)—CH$_2$—CH$_2$—Mc	1.73	0.04
222	CH$_2$=C(Mc)—CH$_2$—CH(Mc)—CH$_2$—CH$_2$—Mc	0.63	0.03
11	CH$_2$=C(Ph)—CH$_2$—CH$_2$—Ph	2.42	0.05
221	CH$_2$=C(Mc)—CH$_2$—CH(Mc)—CH$_2$—CH$_2$—Ph	5.72	0.14
212	CH$_2$=C(Mc)—CH$_2$—CH(Ph)—CH$_2$—CH$_2$—Mc		
122	CH$_2$=C(Ph)—CH$_2$—CH(Mc)—CH$_2$—CH$_2$—Mc	4.04	0.15
	CH$_2$=C(Mc)—CH$_2$—CH(Ph)—CH$_2$—CH$_2$—Ph		
	CH$_2$=C(Mc)—CH$_2$—CH(Ph)—CH$_2$—CH$_2$—Ph		
112	CH$_2$=C(Ph)—CH$_2$—CH(Ph)—CH$_2$—CH$_2$—Mc	7.02	0.39
111	CH$_2$=C(Ph)—CH$_2$—CH(Ph)—CH$_2$—CH$_2$—Ph	0.38	0.03

* Mc: —COOCH$_3$ (-methoxy-carbonyl).
Ph: —C$_6$H$_5$ (phenyl).

Table 2. Pyrolysis product yields

Product symbol	Yields from sample No. 2 Calc.	No. 2 Obs.	No. 5 Calc.	No. 5 Obs.	No. 8 Calc.	No. 8 Obs.
2	54	51	149	147	211	210
1	801	797	589	589	426	423
22	0	0	1	1	3	3
21	4	4	9	9	9	11
12	4	3	9	9	9	10
222	0	0	1	1	13	12
11	17	16	11	12	7	7
221	0	1	7	17	18	32
212	1		9		15	
122	0	0	9	9	27	28
211	3	12	6	16	4	7
121	5		10		7	
112	13	11	23	23	18	22
111	9	10	3	2	1	1

Table 3. Sequence distribution parameters in the investigated styrene–methyl acrylate copolymer samples

Sample No.	Copolymer composition (methyl acrylate mole fraction)	f_{12} depolymerization model	f_{12} copolymerization theory
1	0.042	0.042	0.042
2	0.085	0.085	0.084
3	0.165	0.156	0.159
4	0.213	0.193	0.202
5	0.260	0.222	0.241
6	0.324	0.248	0.289
7	0.363	0.272	0.314
8	0.421	0.264	0.342
9	0.466	0.269	0.345
10	0.609	0.199	0.328

isomeric structures of products from their gas chromatographic retention behaviour.*

The isomeric structures found for the hybrid dimers and trimers are shown in Table 1; pyrolysis products are listed in the same sequence as in the chromatograms of Figs 1 and 2.

Calculations

The gas chromatographic peak areas of the experiments have to be converted into molar amounts to obtain molar pyrolysis product yields for the calculations of the mathematical model. We have done the conversion with

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* Information about the deduction can be obtained from the authors.

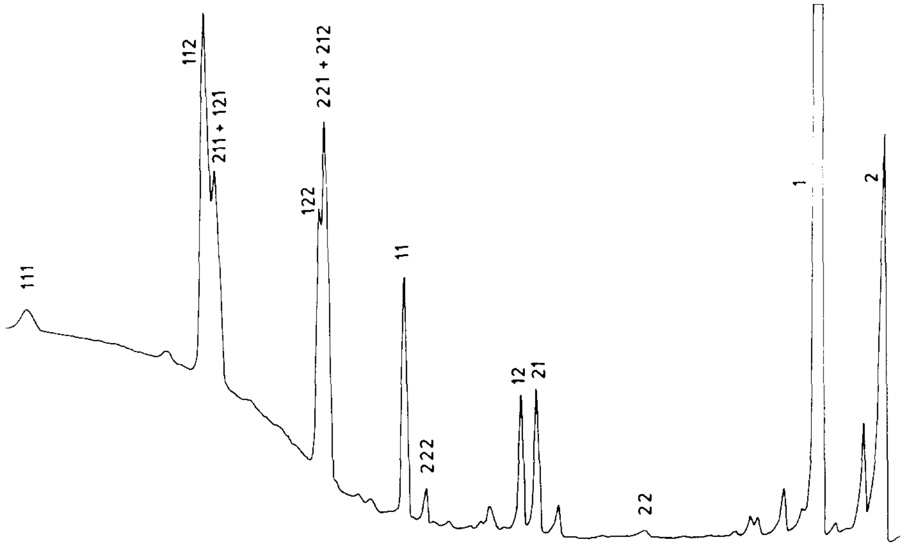

Fig. 1. Pyrogram of St-MA copolymer at 360°, on OV-17 column (1—styrene-unit, 2—methyl acrylate-unit).

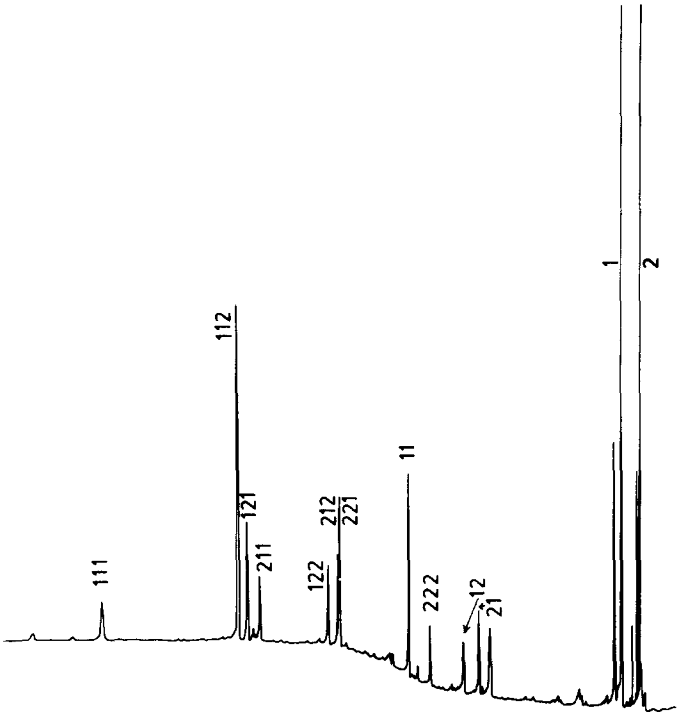

Fig. 2. Pyrogram of St-MA copolymer at 350°, an FFAP glass capillary column (1—styrene-unit, and 2—methyl acrilate-unit).

estimated response factors using published response data of the Flame Ionization Detector [10]. Because of the incomplete gas chromatographic separation of the 122–212 and 112–121 trimers, their yields were given as sums. Thus, we had ten pyrolysis product distributions, each containing twelve yield values, as experimental data. Figs 4, 5 and 6 show the monomer, dimer and trimer yields, respectively, against copolymer composition.

We handled the sequence distributions as unknown. According to the approximation given previously [1], we characterized the sequence distribution with parameter f_{12}. (f_{12} is the probability of finding a "$\underline{12}$ sequence", i.e. -styrene–methyl acrylate- sequence, in the copolymer chain.) The formation of 14 different products has been described with the help of 24 rate constants [1]. Thus we

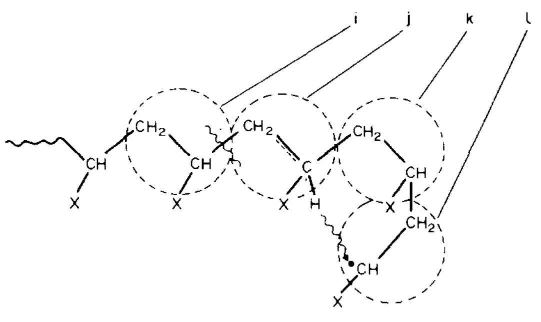

Fig. 3. Formation of a trimer from a macroradical (-X—phenyl or -methoxy-carbonyl).

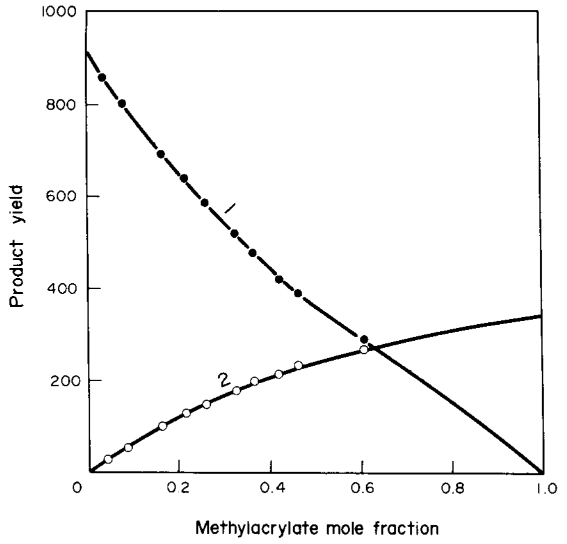

Fig. 4. Variation of monomer production with copolymer composition.

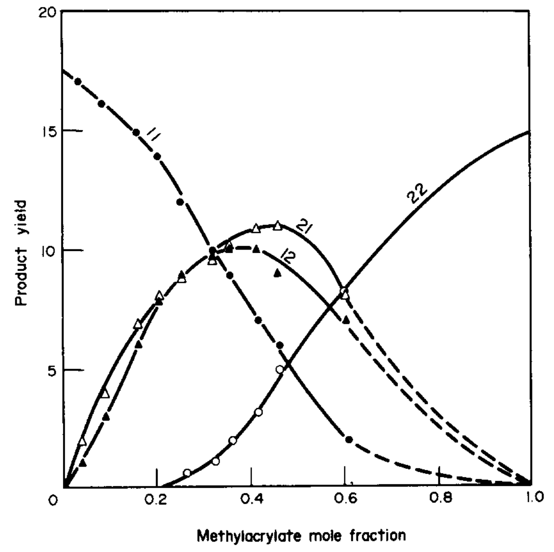

Fig. 5. Variation of dimer production with copolymer composition.

are faced with 34 unknown parameters, viz one sequence distribution parameter (f_{12}) for each copolymer sample with 24 rate constants. The method of least squares was used to find values for the unknown parameters. The difference between the calculated and experimental pyrolysis product yields was minimized simultaneously for all ten copolymer samples.

It emerged during the calculations that, besides the parameter set giving the best fit, several other parameter sets could also provide acceptable fit. To solve this problem, we introduced chemical assumptions concerning the rate constants.

According to the accepted mechanism [4], the formation of a dimer or a trimer is a combination of two reactions: intramolecular transfer of the degrading macroradical and beta scission (see Fig. 3). Concerning these reactions our assumption was:

1. Those monomer units which are involved directly neither in intramolecular transfer nor in beta scission (unit k of the macroradical end in Fig. 3) may have only a slight effect on the rate constant of the trimer formation.

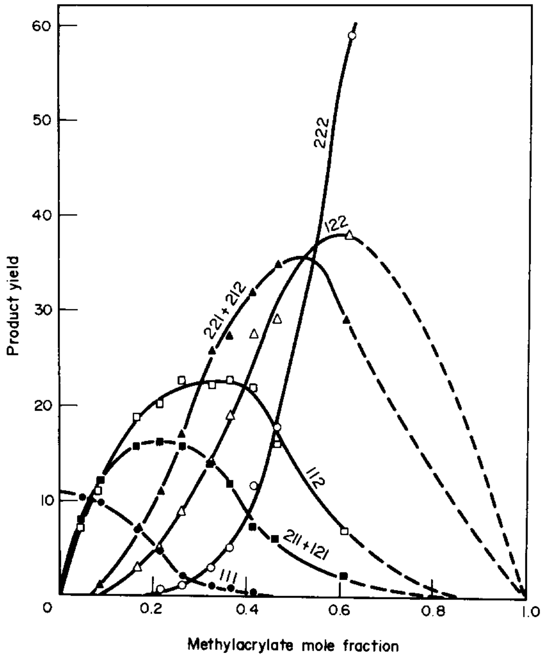

Fig. 6. Variation of trimer production with copolymer composition.

2. The monomer unit which can influence only the beta scission not being involved in the intramolecular transfer (unit i in Fig. 3) may have a less pronounced effect on the rate of the whole process than those which are involved in both reactions (j and l units in Fig. 3).

In the following discussion, we use the symbols defined previously [1]. i, j, k, l are variables representing either styrene (constituent 1) or methylacrylate (constituent 2) monomer unit. $k_{i;jkl}$, $k_{j;kl}$ and $k_{k;l}$ represent rate constants of the trimer, dimer and monomer release, respectively, from a macroradical end of $\sim ijkl^{\cdot}$ composition. Using these symbols we can formulate the above two assumptions:

1. $k_{i;j1l} \approx k_{i;j2l}$;

2. $k_{1;jkl}$ must have the same order of magnitude as $k_{2;jkl}$ and $k_{1;kl}$ as $k_{2;kl}$.

When these assumptions are introduced in the model, the calculations give a single solution. Results are shown in Tables 4 and 5.

Computation methods

The calculations were carried out on a CDC-3300 computer. In the minimization of the least-squares sum,

Table 4. Rate constants of the reactions of $\sim ijk1^{\cdot}$ macroradicals

$k_{1;1}$	100	$k_{1;11}$	2.3	$k_{1;111}$	1.5	$k_{1;121}$	1.1
$k_{2;1}$	12.9	$k_{2;11}$	3.5	$k_{2;111}$	0.4	$k_{2;121}$	0.3
		$k_{1;21}$	0.7	$k_{1;211}$	5.0	$k_{1;221}$	5.4
		$k_{2;21}$	0.5	$k_{2;211}$	1.3	$k_{2;221}$	1.4

Table 5. Rate constants of the reactions of $\sim ijk2^{\cdot}$ macroradicals

$k_{1;2}$	100	$k_{1;12}$	7.4	$k_{1;112}$	26.5	$k_{1;122}$	28.2
$k_{2;2}$	37.3	$k_{2;12}$	4.5	$k_{2;112}$	21.5	$k_{2;122}$	26.0
		$k_{1;22}$	1.8	$k_{1;212}$	19.8	$k_{1;222}$	13.9
		$k_{2;22}$	1.8	$k_{2;212}$	22.6	$k_{2;222}$	22.3

a direct search technique (the Hooke–Jeeves algorithm) was used. Assumption 1 was reached by adding "penalty functions" to the least square sum. These penalty functions had the following form:

$$C\left|\frac{k_{i;j1l}-k_{i;j2l}}{k_{i;j1l}+k_{i;j2l}}\right|^3 \qquad (1)$$

The constant C regulated the values of expression (1) that these should be small compared to the least-squares sum. In our calculations the values of expression (1) were lower than 3/1000 of the least squares sum. Similar penalty functions were applied to reach assumption 2. In this case the constant C was chosen about one third of that used for expression (1), because assumption 2 means less strict restriction than assumption 1. However, to avoid too much deviation from assumption 2, the ratios

$$\frac{k_{1;kl}}{k_{2;kl}} \quad \text{and} \quad \frac{k_{1;jkl}}{k_{2;jkl}}$$

were strictly limited to remain within a given interval. In the calculations, this interval could be chosen as close as $[\frac{1}{4}, 4]$ without increasing significantly the least-squares sum.

RESULTS AND DISCUSSION

The fit

The difference between the calculated and experimental product yields was within the limits of the experimental accuracy for all the 120 yield values. Table 2 shows the yields for three samples (No. 2, 5 and 8). The adequate fit proves that the assumptions are reasonable.

Sequence distribution

As outlined above, f_{12} values, characteristic for the sequence distribution of the examined samples, were also calculated together with the rate constants. These data, given in Table 3, may be useful to obtain information about the copolymerization processes. For comparison, f_{12} values calculated from published reactivity ratios [11] and copolymer compositions and applying the terminal copolymerization theory, are also given in Table 3. These data and our results are independent, since the main assumptions of the depolymerization model differ from those on which the copolymerization theories are based. The discussion of the obtained f_{12} data will be given in a later publication [12].

Rate constants

The mathematical model provides the relative ratios of the rate constants. If no special chemical assumption is introduced, four groups of relative rate constants are obtained. These groups represent the reactions of macroradicals $\sim ij11^{\cdot}$, $\sim ij21^{\cdot}$, $\sim ij12^{\cdot}$ and $\sim ij22^{\cdot}$. However, in the present calculations, assumption 1 correlates the trimer formation reactions of the first two and second two groups of macroradicals respectively. Thus we have evaluated two independent groups of relative rate constants, which represent the reactions of macroradicals $\sim ijk1^{\cdot}$ and $\sim ijk2^{\cdot}$ respectively. The first group is given in Table 4 and the second in Table 5. Since these values are relative, we selected 100 for $k_{1;1}$ and $k_{1;2}$ arbitrarily.

Consider the information obtained about the degradation reactions from the data of Tables 4 and 5. For the monomer producing reactions, we obtained:

$$k_{1;1} > k_{2;1} \quad \text{and} \quad k_{1;2} > k_{2;2}. \qquad (2)$$

This indicates that depolymerization leading to $\sim ijk1^{\cdot}$ macroradical is more favourable than that leading to $\sim ijk2^{\cdot}$ irrespective of the nature of the released monomer.

Interpretation of the results on the rate constants of the dimer and trimer producing reactions is more difficult. The release of dimer and trimer from a macroradical is not a simple C–C scission; it is preceded by an intramolecular radical transfer as illustrated in Fig. 3. For the dimer release reactions, we obtained:

$$k_{1;jk} \simeq k_{2;jk} \qquad (3)$$

and

$$k_{i;1k} > k_{i;2k}. \qquad (4)$$

So, in the dimer formation the rate constants are mainly influenced by the nature of the released dimer. The intramolecular transfer towards the j monomer unit seems to be easier when it is a styrene unit. Concerning the trimer formation from macroradicals $\sim ijk2^{\cdot}$, the $k_{i;jk2}$ rate constants are of the same magnitude as $k_{2;222}$. Contrary to this, in the case of trimer formation from macroradicals $\sim ijk1^{\cdot}$, the relative values of $k_{i;jk1}$ rate constants are significantly influenced by the nature of monomer units i and j, as follows:

$$k_{1;jk1} > k_{2;jk1} \qquad (5)$$

and

$$k_{i;1k1} < k_{i;2k1}. \qquad (6)$$

Accordingly, trimer release from the $\sim ijk2^{\cdot}$ macroradicals of a styrene–methyl acrylate copolymer scarcely differs from that of the PMA homopolymer. This fact may indicate that the intramolecular transfer of a $\sim ijk2^{\cdot}$ macroradical towards the fifth atom of the radical end (see Fig. 3) has a relatively high rate regardless of the nature of the other monomer units involved in the trimer release. On the other hand the trimer formation of a $\sim ijk1^{\cdot}$ copolymer macroradical has a relatively low rate as that of a PS macroradical. However, the rate constant may be 3–4 times higher than that in PS, when the j monomer unit towards which the radical is transferred is a methylacrylate unit. Apart from this the trimer release from a $\sim ijk1^{\cdot}$ macroradical leading to a new $\sim ijk1^{\cdot}$ macroradical seems to be more favourable than that leading to $\sim ijk2^{\cdot}$.

Acknowledgement—The authors thank Dr T. Földes-Berezsnich, Central Research Institute for Chemistry of the Hungarian Academy of Sciences, for generously providing the styrene–methyl acrylate copolymer samples.

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