Compositional analysis by g.l.c. of monomer feed in copolymerization – errors due to adsorption of monomer to copolymers

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It is shown that the relative errors in determining the monomer feed composition by gas–liquid chromatography (g.l.c.) are not always independent of the degree of conversion to copolymer. In view of the sensitivity of the integral copolymerization equation to errors of the magnitude likely to be associated with g.l.c. analysis, the determination of small changes in the value of copolymerization parameters by this method can be very unreliable. Data showing the extent of adsorption of monomers to copolymers are presented.

Keywords Copolymerization parameters determination; g.l.c.; monomer adsorption

INTRODUCTION

A large number of copolymerization reactivity ratios have been measured previously[1]. As shown by Tidwell and Mortimer, and others[2–9], however, much of the experimental data is inaccurate and has only a limited value.

Potentially the most accurate method for determining the copolymerization reactivity ratios is based on monitoring the monomer feed compositional analysis throughout the copolymerization reaction[10]. This approach has become possible with gas–liquid chromatographic analysis (g.l.c.)[11]. Employing the integrated form of the copolymerization equation, the experimental data are then evaluated using a regression analysis which preferably[8] takes into account the presence of errors in all variables.

In this communication we show that the assumption[10] that the relative errors in determining the monomer feed composition by g.l.c. are independent of the degree of conversion to copolymer, is not always valid. We also show that the integral copolymerization equation is sensitive enough to errors likely to be associated with g.l.c. analysis. In consequence, the determination of small changes in the value of copolymerization parameters can be very unreliable.

EXPERIMENTAL

G.l.c. analysis

Samples containing monomers and an inhibitor were made up to represent real polymerizing mixtures of a given degree of conversion. The samples contained: 1-vinylimidazole (M_1), styrene (M_2), toluene (internal standard), ethanol, 4-methyl-2,6-ditertiary-butylphenol (Topanol OC, ICI, inhibitor), and polymer [polystyrene, poly(1-vinylimidazole) or poly(styrene-co-1-vinylimidazole)]. The g.l.c. analysis was carried out using a Hewlett-Packard 5710 A Gas Chromatograph equipped with a flame-ionization detector. The following experimental conditions were employed: column—180 cm long, coiled glass tubing, 2 mm internal diameter; column packing—either Gaschrom R 80–100 mesh, coated with 28% (by wt) Pennwalt 223 and 4% KOH (Chrompack), or Chromosorb 103, 80–100 mesh, coated with 6% CP TM Wax 51 (Chrompack); carrier gas—nitrogen dried over 3–A molecular sieve (1/8″ pellets, Linde Air Products Company), flow rate—60 ml min^{-1}, (the nitrogen flow was controlled using the model 18714A flow controller (Hewlett-Packard)); hydrogen–flow rate 60 ml min^{-1}; air—flow rate 260 ml min^{-1}, dried over 5–A molecular sieve, 1/8″ pellets; the flow rates of air and hydrogen were controlled by reducing valves on the corresponding gas cylinders; column temperature—140°C for Pennwalt 223 and 180°C for Chromosorb 103; the temperature was maintained constant with an oven temperature controller of the proportional-integral action (the Hewlett-Packard specified stability better than 0.1% of the set temperature); detector–flame ionization type (Hewlett-Packard), temperature–200°C; injection—on-column, manually using a Hamilton 7101 1 μl syringe, heated injection port, 200°C. The sample size—0.3 ± 0.1 μl. A typical chromatogram is shown in *Figure 1*. The peak areas were measured by analysing the detector output using a Hewlett-Packard 3380A integrator.

Thermogravimetric analysis

The ease of desorption of the monomers from various substrates was examined by thermogravimetric analysis using a Stanton Redcroft TG 750 thermobalance. The samples (5–6 mg) were heated rapidly (within 2 min) to 140°C in air. The temperature was kept at 140°C and the loss of weight of the sample with time was recorded (cf. *Table 3* and *Figure 2*).

Simulated calculations

The integrated form of the Alfrey–Mayo copolymerization equation was used:

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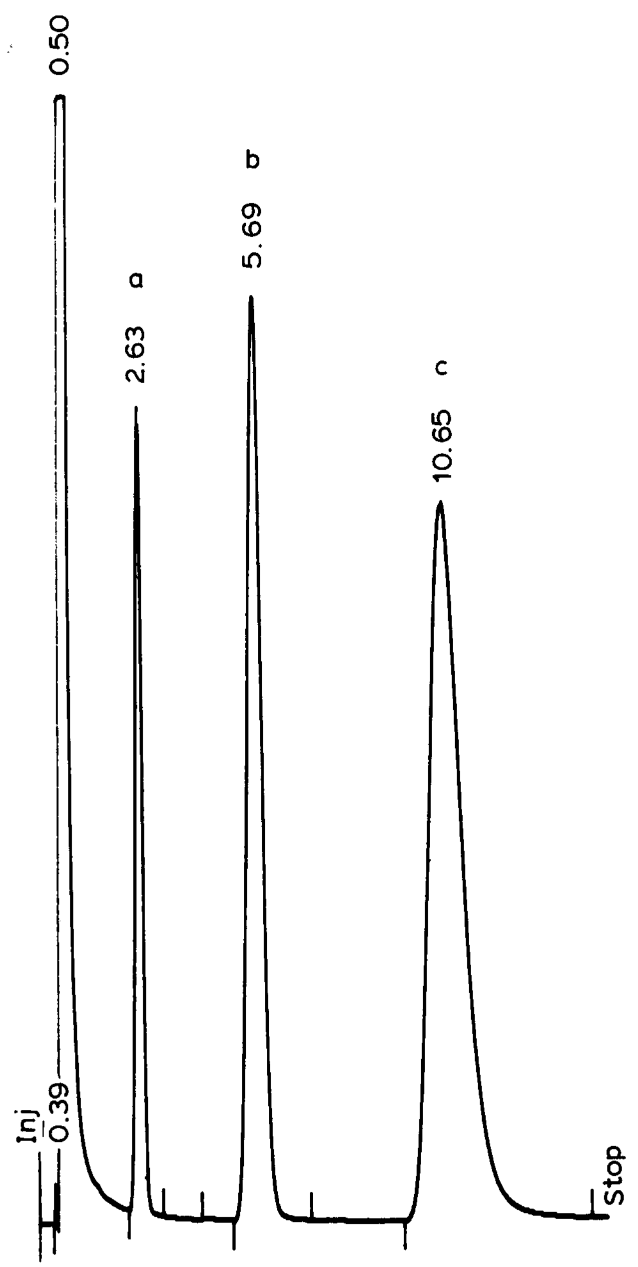

Figure 1 A typical g.l.c. trace. a, toluene, b, styrene, c, 1-vinylimidazole

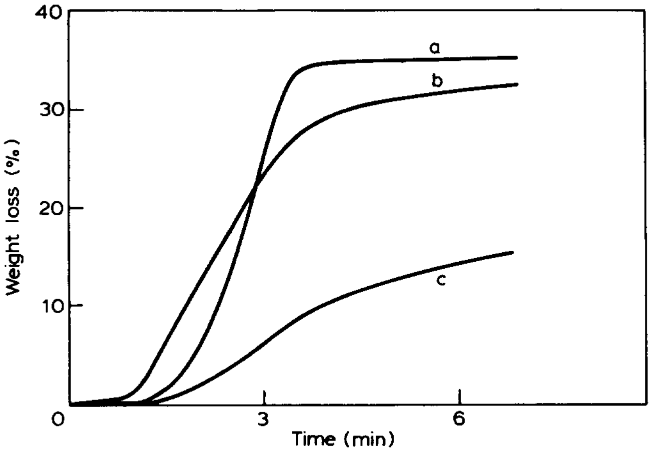

Figure 2 Some typical desorption curves (as determined by thermogravimetry). (a) 1-vinylimidazole and styrene on Chromosorb 103; (b) styrene on polystyrene; (c) 1-vinylimidazole on polystyrene

$$f_2 = 100\left[1 - \left(\frac{q}{q_0}\right)^{-x_2-1}\left(\frac{x_2 q - x_1}{x_2 q_0 - x_1}\right)^{x_1+x_2+1}\right] \qquad (1)$$

where f_2 is the degree of conversion of M_2, in %, q_0 is the starting ratio of the molar concentrations of monomers M_1 and M_2, M_1/M_2, q is the molar ratio of M_1 and M_2 at a given conversion; $x_1 = 1/(r_1 - 1)$ and $x_2 = 1/(r_2 - 1)$ where r_1 and r_2 are the monomer reactivity ratios as defined in the Alfrey–Mayo model.

The initial estimates of r_1 and r_2 were chosen arbitrarily to represent typical monomer pairs: $r_1 = 0.1$ and $r_2 = 10.0$; $r_1 = 1.5$ and $r_2 = 0.3$; $r_1 = 0.6$ and $r_2 = 0.3$. The simulated starting feed ratios (q_0) were chosen in accordance with the experiment design scheme of Tidwell and Mortimer[3]. First, the equation (1) was used to calculate f_2 using the chosen values of r_1, r_2, q_0 and q. Then, to each value of q was added an error, e. The $q+e$ values were used to calculate the new r_1 and r_2, using the Gauss–Newton non-linear regression procedure. The results are summarized in *Table 1*. In each calculation of the new parameters, 20 values of q covering the conversion f_2 range from about 5 to 95% were used.

RESULTS AND DISCUSSION

There are many experimental and data evaluation methods that can provide approximate values of the copolymerization parameters[12]. The importance of taking into account the error in all variables when evaluating the data has been demonstrated by O'Driscoll *et al.*[8] The limitations of the linear regression methods have been discussed by Watts *et al.*[13] For the linear regression methods to be reliable, the conversion of both monomers must be large enough compared with the measurement error. The use of an 'Error-in-Variables' approach requires additional information on the error variances and covariances[8]. In any case, the source of errors should be recognized and removed, or at least the errors should be quantified. This is particularly true for any bias in the experimental data[14,15]. In *Table 1* we show briefly the effect of positive bias on the values of r_1 and r_2 using simulated calculations.

The use of the experimental data for more than a semiquantitative estimate of the mutual reactivity of two comonomers requires that the overall accuracy of the determination is high. The g.l.c. analysis of the monomer feed composition during a copolymerization reaction is one of the best currently available techniques for studying the progress of such reactions. The overall accuracy of g.l.c. analysis will depend, however, on a combination of various factors that are not independent[16]. With most g.l.c. instruments, results with errors less than ±1% are difficult to achieve[17]. German and Heikens[11] studied the effect of sample size, column oven temperature, carrier gas flow, detector sensitivity and integration with an electronic integrator, using a custom-made, semiautomatic g.l.c. apparatus. For the two monomers used (vinyl acetate, M_1; vinyl propionate, M_2) the errors were reported[10] to be 1.0, 1.0 and 1.5% for M_1, M_2 and the solvent, respectively. Sampling from the gas phase was used. In the final calculations, the relative errors were supposed to be independent of the degree of conversion of monomers to copolymer.

The choice of comonomers, and the conditions of analysis as used in ref. 10 can be considered near ideal. When other monomer pairs are studied, and when more conventional g.l.c. analysis conditions are employed,

Table 1 The effect of bias in the data on the values of r_1 and r_2

Estimated r_1	Estimated r_2	q_0	$+e$ (%)	Calculated r_1	STD	r_2	STD	r_2/r_1
0.1	10.0	0.053	0.0	0.10	4.0×10^{-3}	10.0	5.6×10^{-3}	100
			0.1	0.25	8.8×10^{-2}	10.34	0.13	41
			0.5	0.75	0.30	11.52	0.46	15
			1.0	2.17	1.41	14.74	2.38	7
			3.0	10.45	11.56	36.04	25.59	3.5
0.1	10.0	0.205	0.1	0.08	0.013	9.97	0.05	125
			0.5	0.47	0.17	12.30	0.67	26
			1.0	1.09	0.50	16.11	2.28	14.8
1.5	0.3	0.137	0.1	1.49	8.6×10^{-3}	0.30	2.2×10^{-4}	0.20
			0.5	1.39	2.4×10^{-2}	0.29	6.2×10^{-4}	0.22
			1.0	1.26	4.0×10^{-2}	0.29	1.0×10^{-3}	0.24
			3.0	0.94	0.15	0.29	3.9×10^{-3}	0.31
			5.0	0.62	0.25	0.28	6.7×10^{-3}	0.47
1.5	0.3	1.460	0.1	1.50	1.4×10^{-3}	0.30	6.4×10^{-4}	0.20
			0.5	1.47	7.0×10^{-3}	0.29	3.2×10^{-3}	0.20
			1.0	1.45	1.4×10^{-2}	0.28	6.6×10^{-3}	0.19
			3.0	1.37	4.2×10^{-2}	0.26	2.0×10^{-2}	0.19
			5.0	1.29	7.1×10^{-2}	0.24	3.5×10^{-2}	0.18
0.6	0.3	0.298	0.1	0.60	3.4×10^{-4}	0.30	3.0×10^{-5}	0.50
			0.5	0.54	9.6×10^{-3}	0.29	8.8×10^{-4}	0.55
			1.0	0.48	3.2×10^{-2}	0.29	2.9×10^{-3}	0.61
			3.0	0.29	8.8×10^{-2}	0.28	8.4×10^{-3}	0.97
			5.0	0.10	0.16	0.27	1.5×10^{-2}	2.8
0.6	0.3	6.701	0.1	0.61	4.6×10^{-3}	0.44	5.1×10^{-2}	0.7
			0.5	0.66	2.5×10^{-2}	1.01	0.28	1.5
			1.0	0.72	5.3×10^{-2}	1.81	0.60	2.5
			3.0	1.00	1.2×10^{-2}	5.72	0.15	5.7
			5.0	1.41	0.60	11.80	8.03	8.4

STD = Standard Error of the Sample Mean = $\sigma/\sqrt{n}$, where σ – standard error of an individual observation, n – sample size; $+e$ – positive error added to the calculated q values

Table 2 The effect of added poly(1-vinylimidazole) on the reproducibility of g.l.c. analysis

Calculated % conversion of M_1	$\frac{[M_1]}{[\text{Toluene}]}$	σ	N	Error %	$\frac{[M_2]}{[\text{Toluene}]}$	σ	N	Error %
0	3.6575	0.0309	15	0.85	2.2485	6.865×10^{-3}	15	0.31
9.4	3.5677	0.0943	8	2.64	2.2356	0.0183	8	0.82
17.1	3.1719	0.0695	8	2.19	2.1960	0.0152	8	0.69
38.3	3.8538	0.1496	9	3.90	2.2394	0.0102	9	0.45
50.8	3.3082	0.1385	13	4.20	2.2147	8.304×10^{-3}	13	0.37
75.6	3.2062	0.1525	24	4.80	2.2208	0.0204	24	0.92
83.8	3.3412	0.1737	14	5.20	2.2433	0.0108	14	0.48

σ = Sample Standard Deviation

$$= \left[\frac{\Sigma X^2 - \frac{(\Sigma X)^2}{N}}{N-1}\right]^{1/2}$$

where X – observed value, N– the total number of data points entered

larger experimental errors can be expected. Kolinsky *et al.*[19], for example, achieved, for the entire experimental range used, the accuracy of determination of conversion ±3.0%. We have chosen two monomers that differ greatly in their relative chemical reactivity and physical properties: 1-vinylimidazole (M_1) and styrene (M_2). The previously reported copolymerization parameters are: $r_1 - 0.1$, $r_2 - 10.0$.[17] The g.l.c. analysis of a liquid phase mixture of the two monomers can be carried out quite well, giving the standard deviation of a quantitative determination of the two monomers in a non-polymerizing mixture as $\sigma M_1 = 0.85\%$ and $\sigma M_2 = 0.31\%$. The g.l.c. analysis, however, of the two monomers in the presence of a polymer is much less satisfactory. We analysed mixtures containing constant relative quantities of 1-vinylimidazole, styrene, toluene (internal standard) and different amounts of polymers, and tested the constancy of the M_1/toluene and M_2/toluene ratios. It can be seen in *Table 2* that the higher the relative amount of the polymer (poly-1-vinylimidazole) in the sample the less accurate the analysis becomes. In collating the data in *Table 2*, a total of 91 experimental points was considered. The overall standard deviation was 0.87% for M_2, but 7.1% for M_1. Similar results were obtained with polystyrene and poly(styrene-co-1-vinylimidazole).

The reason for the observed behaviour is likely to be associated with adsorption of the monomers. Using thermogravimetric analysis we examined the ease with

Table 3 Desorption of monomers from various substrates

Substrate	1-vinylimidazole	Styrene
Poly(styrene)-co-(1-vinylimidazole)	36[a]	30
Poly(1-vinylimidazole)	52	19
Poly(styrene)	47	18
Chromosorb 103	4	3
Pennwalt 223	3	3
Carbowax 20M	2.5	2.5
SE–30	3	3
FFAP	3	3

[a] Time (in min) required for 97% weight loss of monomers

which the two comonomers desorb from various g.l.c. column packing materials and also from the corresponding polymers. The results are given in *Figure 2* and *Table 3*. It can be seen that the desorption of monomers from polymers can be slow under the conditions of g.l.c. analysis. This can have a significant effect on the accuracy of a quantitative g.l.c. analysis.

The detection of even small changes in the value of copolymerization parameters is important in comparative studies such as in investigating the solvent or the temperature effect on the course of copolymerization[7]. In view of the sensitivity of the integral copolymerization equation to the experimental errors in the variables, the determination of the copolymerization parameters can be very unreliable. The currently available methods for studying copolymerization reactions, including g.l.c. analysis, are unlikely to provide sufficiently good data, nor should it be assumed that such experimental data have the same, independent random variation. Validity of conclusions based on such data is in question.

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