Determination of Monomer Reactivity Ratios in the Cross-Linking Copolymerization of Methyl Methacrylate with Ethylene Dimethacrylate

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ABSTRACT: Methyl methacrylate (MMA) has been copolymerized with ethylene dimethacrylate (EDMA) in bulk by γ-irradiation to various stages of fractional conversion C_w ($C_w = 0.001-0.901$). On addition of n-heptane the cross-linked copolymer was isolated and FTIR measurements on the resultant solutions of unreacted monomer mixture in n-heptane afforded the composition (w_1) of unreacted monomer mixture. Full details are reported of essential precautions and the appropriate calibration method. Although subsequent implementation of the data to calculate copolymer composition and thereby reactivity ratios is satisfactory in principle, this route was demonstrated to be inherently inaccurate in practice, especially at low values of C_w. Instead, C_w, w_1, and the initial monomer feed composition were employed to calculate the reactivity ratios by a specially devised nonlinear least squares program using a simplex algorithm, yielding $r_{MMA} = 0.674 \pm 0.045$ and $r_{EDMA} = 1.34 \pm 0.18$.

Introduction

Characterization of polymer networks is generally more difficult than that of soluble polymers and very often requires the use of an appropriate kinetic model to make theoretical predictions about the network structure. For networks produced by free radical copolymerization the monomer reactivity ratios are very important parameters for carrying out such theoretical predictions.

Ethylene dimethacrylate (EDMA) is a cross-linker widely used to make polymer networks. Very few reactivity ratio data involving EDMA with other monomers appear to have been reported in the literature. For example, in the third version of the *Polymer Handbook* (Wiley: New York, 1989), only one pair of reactivity ratios (EDMA–styrene) has been collected. The main reason for so few reactivity ratios being available is that copolymerization of EDMA with other monomers will cause cross-linking, and hence insolubility of the copolymer produced. The majority of analytical methods for measuring copolymer composition, such as IR, NMR, UV, etc., are carried out on solutions. If the copolymer is insoluble, then none of these methods can be used. For the copolymer of EDMA with methyl methacrylate (MMA), it is even more difficult to find an analytical method, because the EDMA unit is almost equivalent to two MMA units combined together. Hence elemental analysis, which does not require the solubility of sample, cannot be used either.

There are various kinetic models for copolymerizations involving divinyl monomers such as EDMA. The simplest model merely adopts the normal terminal model, neglecting possible terpolymerization effects owing to the pendant double bond.[1–4] Within this model, there are two different conventions regarding calculation of the concentration of divinyl monomer. In convention A, the divinyl monomer is treated completely the same as normal one-double-bond monomers.[1,2] Thus the copolymerization equation has the normal form:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1^A[M_1] + [M_2]}{r_2^A[M_2] + [M_1]}\right) \tag{1}$$

In convention B it is assumed that the two double bonds in the EDMA molecule always maintain the same reactivity and the copolymerization equation is modified by replacing the concentration of monomer with that of the double bond (D) on the right side of the equation, i.e.,

$$\frac{d[M_1]}{d[M_2]} = \frac{[D_1]}{[D_2]}\left(\frac{r_1^B[D_1] + [D_2]}{r_2^B[D_2] + [D_1]}\right) \tag{2}$$

In other words, when the monomer mixture is considered, the concentration of the divinyl monomer is doubled, but when the copolymer composition is considered, the concentration of the monomer unit of the divinyl monomer remains the same.[3,4] If we always index the divinyl monomer as M_2, the copolymerization equation (eq 2) is equivalent to

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{2[M_2]}\left(\frac{r_1^B[M_1] + 2[M_2]}{2r_2^B[M_2] + [M_1]}\right) \tag{2'}$$

which can be rewritten as

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{(r_1^B/2)[M_1] + [M_2]}{(2r_2^B)[M_2] + [M_1]}\right) \tag{3}$$

Comparison of eq 3 with eq 1 yields $r_1^A = 0.5r_1^B$ and $r_2^A = 2r_2^B$. This means that, although convention B seems more reasonable than convention A, both conventions are equivalent, when used to describe copolymerization behavior.

Other complex kinetic models take the pendant vinyl group into consideration. If one of the double bonds in the divinyl monomer is reacted, the other will become a pendant vinyl group, which not only may have a different reactivity but also may involve different consequent reactions, for example, with monomer (chain

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propagation), with another pendant vinyl group in the same macromolecular chain (cyclization), or with the pendant vinyl in a different macromolecular chain (cross-linking).[5,6]

Clearly from the copolymerization data usually obtained, i.e., the initial comonomer compositions and the compositions of the final produced copolymers, preferably plus the conversion data, it is only possible to derive reactivity ratios with the simplest model. If the reactivity ratios are to be derived from the more complex models, further information, at least the pendant vinyl concentration, must be obtainable. Dušek and Spěváček[7] have pointed out that, in spite of the strong cyclization and deviation in cross-linking copolymerization from the usual view, the copolymerization parameters determined with neglect of cyclization need not be too distorted. Thus many data reported in the literature[3,8-11] (derived from the simplest kinetic model) may be regarded, cautiously, as an approximate measure of the reactivity of vinyl groups.

The reactivity ratios of MMA (monomer 1) with EDMA (monomer 2) are particularly useful, because these comonomers are so widely used as components of polymer networks of both pure and industrial importance.[12] There are some biased reactivity ratio data, that have been reported for this monomer pair. Li et al.[2] used GC to analyze the unreacted monomer mixtures and obtained $r_1 = 0.67 \pm 0.07$ and $r_2 = 1.49 \pm 0.21$ (convention A). Landin and Macosko[5] used NMR to measure the soluble copolymers and found the polymer ratio of vinyl groups is the same as the monomer ratio, indicating equal reactivities of the vinyl groups and thus r_1 and r_2 were both set equal to 1 (convention B). In order to avoid cross-linking, they used only a very small amount of EDMA in the monomer mixture (the highest EDMA content was 1.70 mol %). Such feed compositions provide little information about reactivity ratios, because the feed composition–copolymer composition diagram is very insensitive to both reactivity ratios in this feed range.[13] Using NMR, Whitney and Burchard[14] also found the copolymer composition to be equal to the initial monomer composition (convention B), but in their paper, no reactivity ratios were reported. Tobita et al.[15] found that their experimental data over a wide range of conversion could be fitted well by means of values of $r_1 = 0.43$ and $r_2 = 2.0$ (convention A). However, the data related to only two very low contents of EDMA in the initial feed. Perhaps more critical is the fact that their system was an emulsion polymerization, in which the monomer concentrations may well be different in the two phases. It is apparent, therefore, that even with neglect of pendant vinyl group reactions, there remains a need to re-examine the MMA–EDMA system in order to either corroborate or refute the small number of reported reactivity ratios.

In this work, monomer reactivity ratios of MMA and EDMA are estimated from copolymerization data covering a wide range of initial monomer feed from the simplest kinetic model and with convention A. The composition of copolymer is not analyzed directly due to its insolubility. Instead, the composition of the unreacted monomer mixture is analyzed.

Experimental Section

Materials. MMA (Fisons) was dried with $MgSO_4$ and then distilled at 373–374 K. EDMA (Aldrich) was vacuum distilled at 349–350 K/0.3 mmHg. *n*-Heptane (Fisons) was used as received.

Table 1. Compositions of Calibration Standards for FTIR

series	monomer:heptane (wt:wt)	W_m
a	1:6	0.1429
b	1:8	0.1111
c	1:10	0.0909
d	1:12	0.0769
e	1:14	0.0667

Copolymerization. All copolymerizations were carried out in bulk at room temperature by γ-irradiation from a ^{60}Co source at Salford University, the doses ranging from 2 to 50 kGy. The feed mixture, containing an accurately known weight of each monomer, was placed in a tightly capped, tared glass vial, which was tightly sealed by parafilm and put in the γ-ray source room. After a certain period, the vial was removed and a 6–7-fold excess of the heptane was added. The vial was tightly sealed again and allowed to stand for several days for complete precipitation of the produced polymer and allow the unreacted monomers to mix fully with the heptane.

Preliminary tests verified that the weight loss of monomer during polymerization was negligible. Thus the weight of heptane added to the vial could be obtained from the total weight just before FTIR measurement.

Analysis of Monomer Mixture. The solution of monomer mixture in heptane mentioned above was analyzed by FTIR measurement, running at room temperature with a Perkin-Elmer 1710 infrared Fourier transform spectrometer, under conditions of eight scans, 2 cm^{-1} resolution, and interleaved mode. The same liquid cell was used for all measurements.

After FTIR measurement, the monomer mixture–heptane solution was carefully poured out and the precipitated polymer left in the vial was washed with heptane and dried in vacuum at 318 K for several days to constant weight. The conversion was calculated gravimetrically. From the conversion data, weight of monomers in the initial feed and the weight of heptane added, the weight fraction of total monomers in the monomer mixture–heptane solution, denoted by W_m, can also be calculated as

$$W_m = \frac{(g_1 + g_2)(1 - C_w)}{(g_1 + g_2)(1 - C_w) + g_h} \tag{4}$$

where g_1 and g_2 are the weights of MMA and EDMA, respectively, in the initial feed, g_h is the weight of the heptane added as precipitant, and C_w is the total conversion of monomers to polymer on a weight basis.

Results and Discussion

FTIR Measurement. In comparison with previous successful quantitative analysis of copolymer composition by FTIR[16,17] in which the copolymers are soluble, thus enabling all FTIR measurements to be carried out at the same polymer concentration, one disadvantageous factor in the present work is that it is impossible to always have the same total monomer concentration W_m when heptane is added into the reaction vial. This is because at the time of this addition, the conversion is still unknown. Previous experience has shown that keeping the concentration of a single or binary solute the same as that in calibration standards is a key point to obtain accurate results.[16] To overcome this problem, the calibrations in this work were carried out five times at five different W_m each time. These five series of standards are labeled as a, b, c, d, and e, and cover quite a wide range of W_m, as shown in Table 1.

Although the infrared spectra of MMA and EDMA appeared very similar, they do in fact possess several small differences, making the quantitative analysis possible. Figure 1 shows the infrared spectra of pure MMA and pure EDMA. It can be seen that MMA has

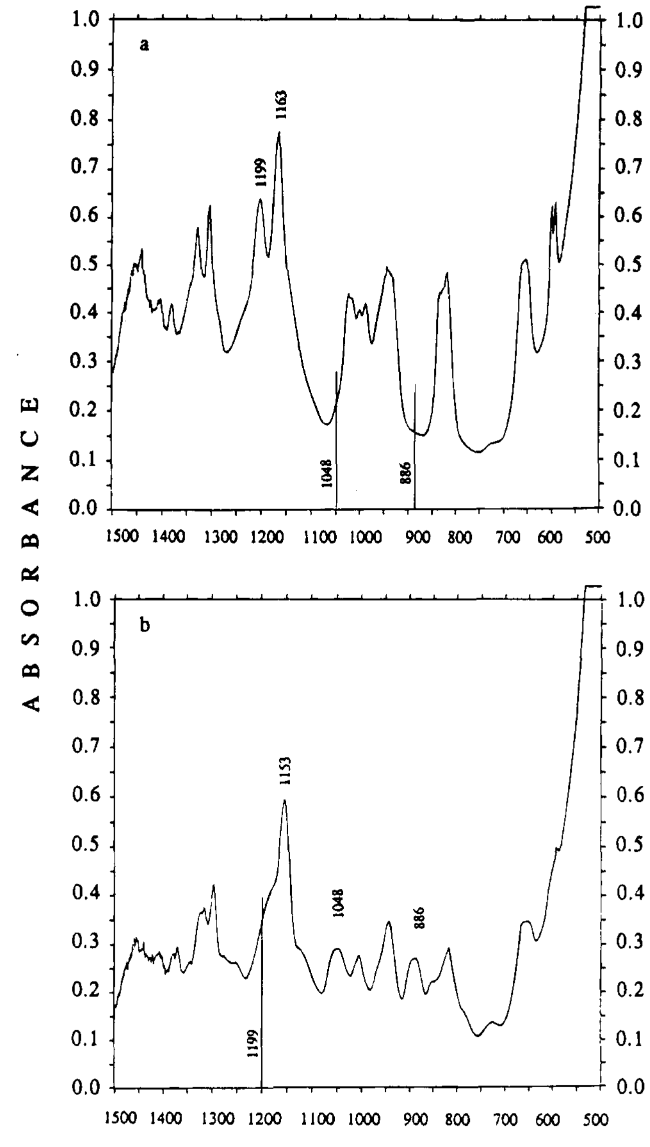

Figure 1. FTIR spectra of (a) pure MMA and (b) pure EDMA.

an absorption peak at 1199 cm^{-1} which EDMA does not, and EDMA has peaks at 1048 and 886 cm^{-1} which are not exhibited by MMA. From Figure 2 it is seen that n-heptane does not have strong absorptions at the peaks mentioned above. Moreover, this solvent does not have peaks within the range of 1600–1800 cm^{-1} so that it is suitable to select a common peak of MMA and EDMA as the reference peak inside this range. Thus the common absorbance of MMA and EDMA, 1640 cm^{-1}, has been selected as the reference peak.

Figure 3 is an example of the infrared spectrum of the calibration standard. The absorption peaks of monomers dissolved in heptane may have a small wavenumber shift (≤ 2 cm^{-1}) compared to those of pure monomers. Figure 4 is an example of the three possible calibration curves each obtained by using 14 different values of w_1: A_{1197}/A_{1640} vs w_1, A_{1048}/A_{1640} vs w_1, and A_{886}/A_{1640} vs w_1. Here w_1 is the weight fraction of MMA related to the total weight of MMA and EDMA and A is the absorbance at the wavenumber specified by its subscript. Examination of all calibration curves for all standards led to final selection of the absorbance ratio A_{1197}/A_{1640} as the most sensitive, since it undergoes the greatest change in magnitude with a change in w_1.

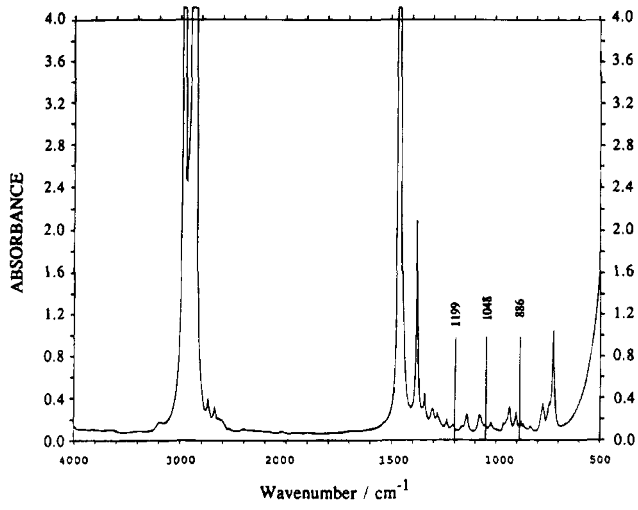

Figure 2. FTIR spectrum of pure heptane.

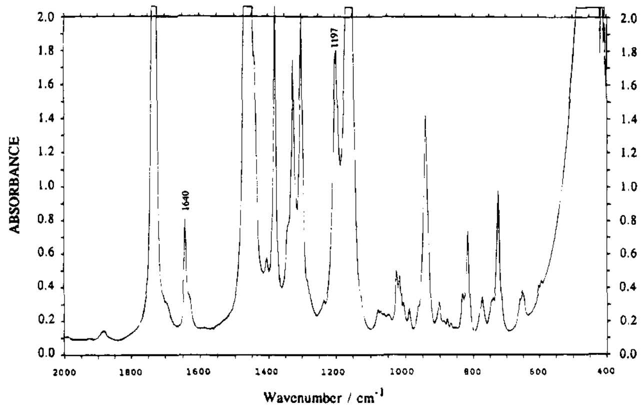

Figure 3. FTIR spectrum of a calibration standard in which $w_1 = 0.4570$ and $W_m = 0.1429$.

From the five series of standards, five linear calibration equations were obtained as

$$A_{1197}/A_{1640} = 0.9495 + 2.0051w_1 \tag{5a}$$

$$A_{1197}/A_{1640} = 0.9375 + 2.0408w_1 \tag{5b}$$

$$A_{1197}/A_{1640} = 0.9578 + 1.9774w_1 \tag{5c}$$

$$A_{1197}/A_{1640} = 0.9515 + 1.9676w_1 \tag{5d}$$

$$A_{1197}/A_{1640} = 0.9534 + 1.9470w_1 \tag{5e}$$

In eqs 5a–5e the total concentrations of monomer, W_m, are those indicated as a–e, respectively, in Table 1.

The composition of the unknown sample was calculated by linear insertion into the composition data obtained from the two calibration equations with nearest W_m. The calculation steps of the monomer mixture composition of sample no. 4 are given here as an example.

For sample no. 4, its $A_{1197}/A_{1640} = 1.1980$ and the value of W_m determined via eq 4 is 0.1061. Thus (refer to Table 1) calibration equations (5b) and (5c) were chosen. $w_1(c) = 0.1215$ was obtained from eq 5c, and $w_1(b) = 0.1276$, from eq 5b. The values of W_m are separated by small intervals and so the final value of w_1 for sample 4 may be calculated by linear interpolation, viz.

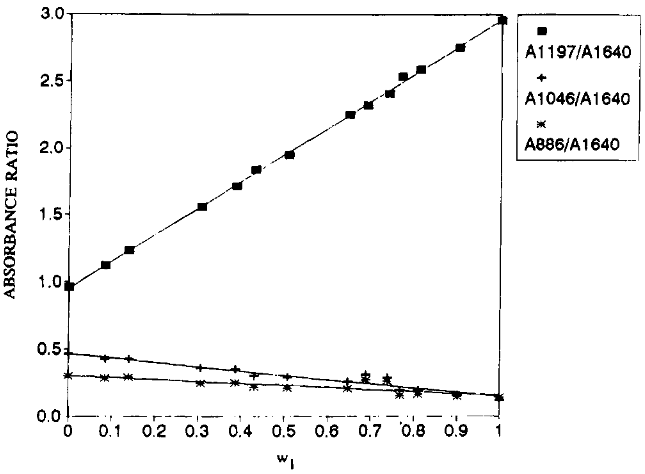

Figure 4. Calibration curves of series-a standards (W_m = 0.1429).

$$\begin{aligned} w_1 &= w_1(\mathrm{c}) + [w_1(\mathrm{b}) - w_1(\mathrm{c})]\left[\frac{W_m - W_m(\mathrm{c})}{W_m(\mathrm{b}) - W_m(\mathrm{c})}\right] \\ &= 0.1215 + (0.1276 - 0.1215)\frac{0.1061 - 0.0909}{0.1111 - 0.0909} \\ &= 0.1261 \end{aligned}$$

All composition data w_1 of the unreacted monomer mixtures were calculated similarly and are listed in Table 2, where the initial feed composition $w_1{}^0$ and the conversion C_w are also given.

Several copolymerizations, i.e., sample nos. 1, 6, 10, 14, 18, 21, 23, and 31 in Table 2, were run deliberately to very low conversion to check the reliability of the FTIR analysis results. It is well established that at very low conversion, the composition of the unreacted monomer mixture will be definitely very close to that of the initial feed. From Table 2 it can be seen that, for these very low conversion copolymerizations, the value of w_1 obtained from FTIR analysis is indeed almost equal to the corresponding $w_1{}^0$, thus confirming the reliability of the FTIR results.

Reactivity Ratios. Theoretically, the composition of the cumulative copolymer W_1 (weight fraction of MMA unit in copolymer) can be calculated from the composition of the initial feed and of the unreacted monomer mixture in conjunction with the conversion data. If all of these quantities are on a weight basis, it is readily shown that

$$W_1 = \frac{w_1^0 - w_1}{C_w} + w_1 \qquad (6)$$

However, when the data in Table 2 are converted into copolymer composition W_1 via eq 6 (values also listed in Table 2), the values of W_1 obtained for sample nos. 6, 10, 14, 18, 21, and 31 became negative or greater than 1, both findings being physically impossible.

The reason for these unreasonable W_1 data is that when eq 6 is used to convert w_1 to W_1, the error structure is transformed incorrectly. If C_w is small, a very small error in w_1 could cause a very big error in W_1. This is equally evident by examining the relative error in copolymer composition ($\mathrm{d}W_1/W_1$) in terms of the relative error in composition of unreacted monomer ($\mathrm{d}w_1/w_1$). On the assumption that there are essentially no errors in the quantities obtained simply by direct weighing $w_1{}^0$ and C_w, suitable treatment of eq 6 affords

Table 2. Experimentally Determined Copolymerization Parameters[a]

no.	$w_1{}^0$	C_w	w_1	W_1	$f_1{}^0$	f_1
1	0.1057	0.006	0.1022	0.7271	0.190	0.184
2	0.1057	0.148	0.1099	0.0818	0.190	0.196
3	0.1057	0.325	0.1076	0.1018	0.190	0.193
4	0.1057	0.331	0.1261	0.0646	0.190	0.222
5	0.1057	0.342	0.1097	0.0980	0.190	0.196
6	0.1540	0.006	0.1480	1.1784	0.265	0.256
7	0.1540	0.085	0.1450	0.2516	0.265	0.251
8	0.1540	0.345	0.1817	0.1015	0.265	0.305
9	0.1540	0.378	0.1768	0.1165	0.265	0.298
10	0.3383	0.004	0.3412	−0.4207	0.503	0.506
11	0.3383	0.109	0.3520	0.2260	0.503	0.518
12	0.3383	0.306	0.3553	0.2997	0.503	0.522
13	0.3383	0.382	0.3871	0.2592	0.503	0.556
14	0.4037	0.003	0.3982	2.2067	0.573	0.567
15	0.4037	0.098	0.4044	0.3973	0.573	0.573
16	0.4037	0.240	0.4220	0.3456	0.573	0.591
17	0.4037	0.450	0.4369	0.3631	0.573	0.606
18	0.5108	0.003	0.5056	2.5288	0.674	0.669
19	0.5108	0.041	0.5043	0.6646	0.674	0.668
20	0.5108	0.487	0.5770	0.4410	0.674	0.730
21	0.6026	0.001	0.5965	6.9318	0.750	0.745
22	0.6026	0.849	0.7493	0.5765	0.750	0.855
23	0.7016	0.001	0.7012	0.9882	0.823	0.823
24	0.7016	0.064	0.7141	0.5181	0.823	0.832
25	0.7016	0.693	0.8053	0.6556	0.823	0.891
26	0.7016	0.879	0.8576	0.6802	0.823	0.923
27	0.7016	0.901	0.8590	0.6816	0.823	0.923
28	0.8034	0.106	0.8081	0.7637	0.890	0.893
29	0.8034	0.397	0.8348	0.7556	0.890	0.909
30	0.8034	0.438	0.8582	0.7331	0.890	0.923
31	0.9002	0.001	0.8987	2.7606	0.947	0.946
32	0.9002	0.554	0.9184	0.8854	0.947	0.957

[a] Compositions of monomer mixture initially ($w_1{}^0$), composition measured (w_1) after various conversions (C_w), and copolymer composition (W_1) calculated from w_1 via eq 6. Also included are the mole fractions $f_1{}^0$ and f_1 (corresponding to $w_1{}^0$ and w_1, respectively), that are used to calculate the reactivity ratios.

$$\frac{\mathrm{d}W_1}{W_1} = \frac{\mathrm{d}w_1/w_1}{1 - (w_1^0/w_1)(1 - C_w)} \qquad (7)$$

At low conversion $(1 - C_w)$ tends to 1 and $(w_1{}^0/w_1)$ also tends to 1; thus eq 7 shows that $\mathrm{d}W_1/W_1$ tends to ∞ for any finite error in monomer composition.

Normally, the reactivity ratios are calculated from the initial feed and the cumulative copolymer composition data[18,19] and sometimes conversion data are also taken into consideration.[20-22] However, the discussion just given shows that, if the copolymer composition is not directly measured from experiment, but is converted from the compositions of the initial feed, unreacted monomer, and conversion, then the converted copolymer composition data may be quite unreliable. Thus it is essential to estimate reactivity ratios directly from the initial feed, unreacted monomer composition, and conversion data by an appropriate nonlinear least squares procedure developed here.

A computer program for calculating reactivity ratios from $f_1{}^0$, f_1, and C_w was developed. It uses a simplex algorithm to minimize the following object function Y:

$$Y \equiv G(\mathbf{R}) = \sum_{i=1}^{N}[f_1^{\mathrm{exptl}}(i) - f_1^{\mathrm{calcd}}(\mathbf{R};f_1^0(i),C_w(i))]^2 \quad (8)$$

where vector $\mathbf{R}$ represents a point in the r_1, r_2 plane; i.e., the coordinate of $\mathbf{R}$ is (r_1, r_2). $f_1{}^{\mathrm{exptl}}$ is the experimental measured composition of unreacted monomer on a mole fraction basis. $f_1{}^{\mathrm{calcd}}$ is the value of the corresponding quantity calculated theoretically from the corresponding f_1^0, C_w, and the searched r_1, r_2 values, by integrating the differential equation (1) or (2) numerically step-by-step.[21] The initial feed and the unreacted monomer compositions were converted to molar fractions and are included in Table 2.

The simplex algorithm searches points in infinite space; i.e. each variable is searched in the range $(-\infty, +\infty)$. Negative reactivity ratios have no physical meaning. Consequently, the computer search in our work must be limited within the range $0 \le r_1 < +\infty$ and $0 \le r_2 < +\infty$. This condition is achieved by the following variable transform:

$$r_1 = x_1^2 \quad \text{and} \quad r_2 = x_2^2$$

Instead of searching **R** directly, the computer program searches **X** in the infinite (x_1, x_2) plane. Thus, any searched (x_1, x_2) values can guarantee the corresponding (r_1, r_2) values in the meaningful range. When the best estimates $\hat{\mathbf{R}} = (\hat{r}_1, \hat{r}_2)$ were found, the 95% joint confidence interval was calculated by the curve satisfying the following equation:[23]

$$(\mathbf{R} - \hat{\mathbf{R}})'[\mathbf{P}'\mathbf{P}](\mathbf{R} - \hat{\mathbf{R}}) = \frac{2Y_{\min}}{N-2}F_{0.05}(2,N-2) \quad (9)$$

where $Y_{\min} = G(\hat{\mathbf{R}})$ is the residual sum of squares of eq 8, $F_{0.05}(2,N-2)$ is the F distribution having 2 and $N-2$ degrees of freedom, and $\mathbf{P}$ is a $N \times 2$ matrix with element P_{ij} in row i and column j as

$$P_{ij} = \left.\frac{\partial f_1^{\text{calcd}}(\mathbf{R};f_1^0(i),C_w(i))}{\partial r_j}\right|_{\mathbf{R}=\hat{\mathbf{R}}} \quad (10)$$

The 95% individual confidence intervals were calculated from[23]

$$\Delta r_j = \pm t_{0.025}(N-2)\sqrt{\frac{Y_{\min}}{N-2}C_{jj}} \quad (11)$$

where $t_{0.025}(N-2)$ is the Student's t distribution with $N-2$ degrees of freedom and with each tail area probability equaling 0.025, C_{jj} is the jth diagonal element of the $[\mathbf{P}'\mathbf{P}]^{-1}$ matrix. The flow chart of the computer program is shown in Figure 5.

The experimental data were fitted very well with eq 1 (see Figure 6), indicating the simplest model is reasonably good to describe the copolymerization behavior of the MMA–EDMA system. The result of best fitting is

$$r_1 = 0.674 \pm 0.045 \quad \text{and} \quad r_2 = 1.34 \pm 0.18$$

These reactivity ratio data are in good agreement with those obtained by Li et al.[2] The 95% joint confidence interval is shown in Figure 7.

Conclusions

1. Appropriately planned and calibrated FTIR measurement provides a sensitive method of quantitatively analyzing the composition of unreacted monomer mixture at any stage of conversion.

2. If the experimentally obtainable quantity is the composition of unreacted monomer mixture rather than copolymer composition, the monomer reactivity ratios should be calculated directly from the former data. One should not first convert it to copolymer composition and then use these indirectly measured data to calculate reactivity ratios.

3. The simplest kinetic model describes the copolymerization behavior of this system quite well. The reactivity ratios for the MMA (M_1)–EDMA (M_2) comonomer system are $r_1 = 0.674 \pm 0.045$ and $r_2 = 1.34 \pm 0.18$, thus indicating an approximately ideal copolymerization ($r_1r_2 = 0.90$).

4. Provided that the approximation embodied in the simple model adopted here is also applicable, then in principle there is no difference in procedure if EDMA is replaced by a monomer of higher functionality. Tetra- and penta-acrylates and methacrylates are sometimes employed in cross-linking copolymerizations, but are rarely available in a sufficiently pure form to allow accurate measurements to be made for the purpose of determining rates and/or reactivity ratios. An example of a very commonly used polyfunctional cross-linker to which this objection does not hold and to which the present procedure could be applied profitably is 1,1,1-trimethylolpropane trimethacrylate.

Further details of the computer program derived and utilized here are available from R. M. whose Email address is R.Mao@chemistry.salford.ac.uk.

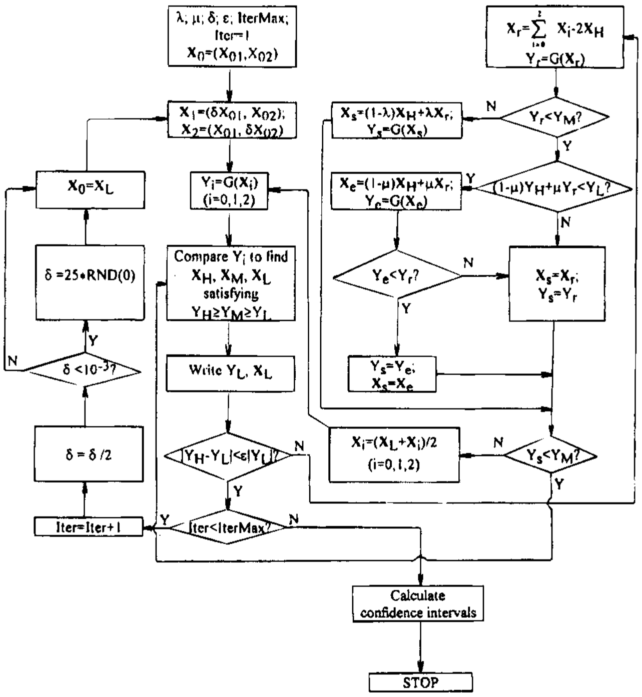

Figure 5. Flow chart of the computer program.

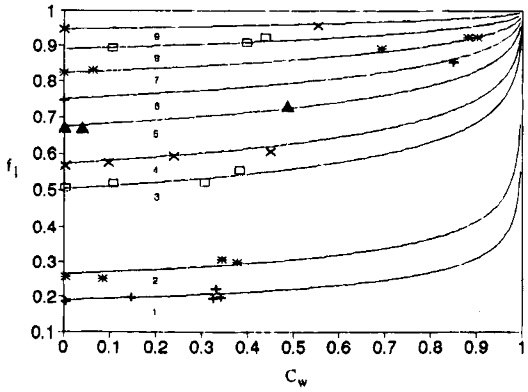

Figure 6. Best fit lines compared with experimental data with the following initial feed compositions: (1) $f_1^0 = 0.190$; (2) $f_1^0 = 0.265$; (3) $f_1^0 = 0.503$; (4) $f_1^0 = 0.573$; (5) $f_1^0 = 0.674$; (6) $f_1^0 = 0.750$; (7) $f_1^0 = 0.823$; (8) $f_1^0 = 0.890$; (9) $f_1^0 = 0.947$.

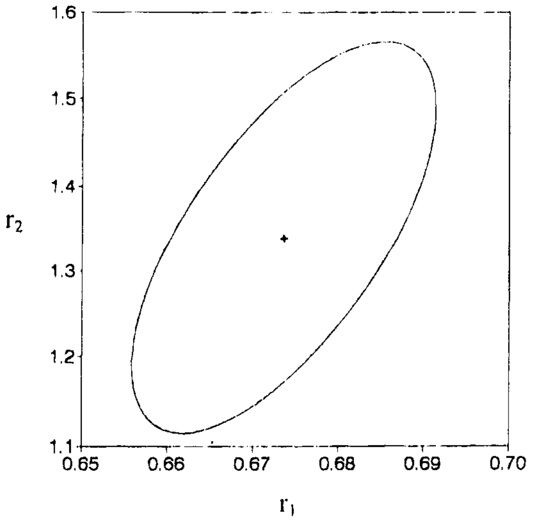

Figure 7. 95% joint confidence interval of the estimated reactivity ratios. Its equation is

$$0.3101(r_1 - 0.6736)^2 - 0.1047(r_1 - 0.6736)(r_2 - 1.3395) + 0.0199(r_2 - 1.3395)^2 = 5.642 \times 10^{-4}.$$

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