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Some aspects of the copolymerization of glyceryl methacrylate with methyl methacrylate

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Free radical polymerization of glyceryl methacrylate (GMA) has been conducted (i) in bulk, (ii) in moderately concentrated aqueous solution and (iii) in dilute aqueous solution. For (i) and (ii) the resultant poly(glyceryl methacrylate) (PGMA) was either insoluble or only swelled in a wide range of common solvents, whereas for (iii) solubility occurred in three polar liquids of which only one (2-methoxyethanol) was capable of dissolving poly[GMA-*co*-methyl methacrylate (MMA)] over the whole range of copolymer composition. The γ-ray initiated copolymerization of GMA with MMA in bulk has been effected to various conversions. On addition of di-isopropyl ether (DPE) the copolymer was isolated, and carefully calibrated Fourier transform infra-red measurements on the resultant solutions of unreacted monomer mixture in DPE afforded the composition of unreacted monomer mixture. This quantity, in conjunction with the initial feed composition and the value of the fractional conversion, was employed to calculate the monomer reactivity ratios by a specially devised non-linear least-squares program using simplex algorithm, yielding $r_{\mathrm{MMA}} = 0.53$ and $r_{\mathrm{GMA}} = 1.61$.

(Keywords: glyceryl methacrylate; methyl methacrylate; poly(glyceryl methacrylate-*co*-methyl methacrylate))

INTRODUCTION

2,3-Dihydroxypropyl methacrylate, henceforth to be referred to by its more common name glyceryl methacrylate (GMA), is a hydrophilic, water soluble monomer that readily undergoes free radical polymerization and copolymerization. Early studies on crosslinked networks based on GMA focused on the effects of crosslinking density and temperature on the swelling behaviour in water[1]. Later related studies were made on crosslinked hydrogels based on GMA with the somewhat less hydrophilic comonomer 2-hydroxyethyl methacrylate (HEMA)[2,3]. More recent investigations have been made of the permselectivity of poly(glyceryl methacrylate) (PGMA) membranes[4–6] and of the use of swollen PGMA, crosslinked to various extents, to assess the validity of scaling laws[7]. Although Macret and Hild[8] have given results of a kinetic investigation and the reactivity ratios for GMA–HEMA copolymerization, other published information on the fundamental characteristics of the polymerization and copolymerization of GMA appears to be very scant.

The present paper is concerned primarily with the copolymerization of GMA with its opposite extreme with regard to hydrophilicity, i.e. methyl methacrylate (MMA). Attention is focused on the monomer reactivity ratios, which are important not only for quantifying compositional heterogeneity through various stages of conversion, but also for modelling networks obtainable from the comonomers in the presence of a crosslinker. The solubility of relevant monomers, polymers and copolymers in common solvents is also addressed, since this information is not available elsewhere and the findings have a direct practical bearing on the procedure adopted to determine the reactivity ratios.

In addition to those already given, the following abbreviations are adopted: PMMA, poly(methyl methacrylate); PHEMA, poly(2-hydroxyethyl methacrylate); AIBN, 2,2-azobisisobutyronitrile; DMSO, dimethyl sulfoxide; DPE, di-isopropyl ether; MOE, 2-methoxyethanol; THF, tetrahydrofuran. In monomer mixtures and copolymers, subscript 1 is used to relate to MMA or the MMA unit, respectively.

EXPERIMENTAL

Materials

MMA (Fisons) was dried with $MgSO_4$ and then distilled before use. GMA, provided by Pilkington, had an estimated purity via gas chromatography of 99.9%. AIBN from Fluka was recrystallized from ethanol/toluene. Ammonium persulfate (G.P.R.) from Hopkin and Williams and DPE from Aldrich were used as received. Other liquids employed for solubility tests were used as received. Water and gaseous nitrogen used were deionized and oxygen-free, respectively.

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Polymerization of GMA

(a) In bulk. GMA in the presence of 0.2 wt% AIBN was outgassed with nitrogen for 10–15 min after which the sealed reaction tube was left for 8.5 h at 333 K. The resultant polymer was precipitated in acetone, washed several times with acetone and dried to constant weight in vacuum at 318 K.

(b) In solution. Here the procedure was similar to that adopted in (a) above except for the use of 1 wt% ammonium persulfate as initiator and the inclusion of water as solvent. For the two systems examined the concentrations of GMA were 4 and 10 wt%, the relevant reaction times being 8 and 6.5 h, respectively.

Copolymerization of GMA and MMA

(a) Chemically initiated copolymerization in solution. With AIBN as initiator, various proportions of GMA and MMA in MOE were outgassed for 10–15 min with nitrogen and reaction in the tightly sealed tubes was allowed to proceed at 343 K for 30 min. Copolymers, isolated by precipitation in diethyl ether, were dissolved in MOE, reprecipitated and dried to constant weight in vacuum at 313 K.

(b) In bulk via γ-irradiation. Various proportions of GMA and MMA in the absence of solvent and initiator were irradiated in tightly capped vials at ambient temperature (293 K) by γ-rays from a ^{60}Co source at Salford University for different doses within the range 3–60 kGy. Comparison of the total mass before and after irradiation showed that loss of monomer by evaporation was negligible. Addition of an excess of DPE precipitated the copolymer within the vial and the unreacted monomer mixture was allowed to mix completely with the DPE by leaving the capped vial for several days. *Fourier transform infra-red.* (*FT*i.r.) measurement was made directly on the liquid above the precipitated copolymer without removing the latter. Immediately prior to the *FT*i.r. measurement the total mass (m_t) of solution and copolymer was measured. Hence:

$$m_t = m_u + m_c + m_d \tag{1}$$

where m_u, m_c and m_d are the masses of unreacted monomer mixture, copolymer and DPE, respectively. After the *FT*i.r. measurement the solution was discarded and the precipitate was washed with DPE and dried to constant weight (m_c). If m_i is the known initial mass of monomer mixture, it follows that $m_u = m_i - m_c$. Hence m_d is obtainable via equation (1), thereby yielding the concentration (m_u/m_d) of unreacted monomer mixture in the solution used for *FT*i.r. and also affording the fractional conversion on a mass basis (θ) as $\theta = m_c/m_i$.

Solubility tests

The solubility of GMA, MMA, the homopolymers of GMA prepared under different conditions, a sample of PMMA and the copolymers of GMA with MMA prepared by solution copolymerization was assessed by visual inspection after adding ~1 ml of liquid to ~0.01 g of sample and leaving for several days at ambient temperature.

Infra-red measurements.

I.r. spectra of solutions in DPE of monomers, monomer blends and the unreacted monomer mixtures were recorded on a PE 1710 *FT*i.r. spectrometer. Measurements were made under conditions of eight scans, 2 cm^{-1} resolution and interleaved mode. The same liquid cell was used for all the measurements.

Table 1 Solubility[a] of GMA, MMA, and their homopolymers in common liquids of solubility parameter δ[b]

					PGMA prepared in		
Liquid	δ (MPa)$^{1/2}$	MMA	PMMA	GMA	4% GMA	10% GMA aq. solution	Bulk
DPE	14.5	s	i	s	i	i	i
Diethyl ether	15.1	s	i	s	i	i	i
n-Heptane	15.1	s	i	i	i	i	i
Di-n-butyl ether	16.0	s	i	i	i	i	i
Toluene	18.2	s	s	i	i	i	i
THF	18.6	s	s	s	i	i	i
Chloroform	19.0	s	s	s	sw	sw	sw
Acetone	20.3	s	s	s	i	i	i
Dioxan	20.5	s	s	s	i	i	i
2-n-Butoxy ethanol[c]	21.3	s	s	s	i	i	i
Pyridine	21.9	s	i	s	i	i	i
DMSO	24.6	s	sw	s	ps	sw	sw
MOE[c]	24.9	s	s	s	s	sw	sw
Ethanol	26.0	s	i	s	sw	sw	sw
Methanol	29.7	s	i	s	sw	sw	sw
Ethylene glycol	29.9	s	i	s	s	sw	sw
Water	47.9	i	i	s	s	i	i

[a] s, Soluble; i, insoluble; ps, partly soluble; sw, swollen

[b] δ is solubility parameter taken from a standard compilation[9]. For the two liquids indicated by [c], no literature values were available and δ was calculated via the density and group attraction constants according to Van Krevelen[10]

Table 2 Characteristics[a] of solution copolymerization producing copolymers C1–C10

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
w_1^0	0.933	0.894	0.792	0.708	0.623	0.501	0.405	0.311	0.197	0.102
θ	0.101	0.159	0.094	0.057	0.113	0.127	0.106	0.085	0.110	0.073
W_1	0.886	0.829	0.684	0.579	0.491	0.374	0.290	0.214	0.132	0.066

[a] W_1 is weight fraction of MMA units in copolymer produced to a fractional conversion on a mass basis of θ, from an initial feed mixture in which the weight fraction of MMA is w_1^0. Values of W_1 were calculated using the reactivity ratios derived in this study

Table 3 Solubility of poly(GMA-*co*-MMA) in common liquids (for compositions of copolymers C1–C10, refer to *Table 2*, and for meanings of s, i, ps and sw, refer to *Table 1*)

Liquid	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Di-n-butyl ether	sw	i	i	i	i	i	i	i	i	i
Toluene	sw	i	i	i	i	i	i	i	i	i
THF	sw	sw	i	i	i	i	i	i	i	i
Chloroform	s	ps	sw	sw	sw	sw	sw	sw	sw	sw
Acetone	ps	i	i	i	i	i	i	i	i	i
Dioxan	i	i	i	i	i	i	i	i	i	i
2-n-Butoxy ethanol	sw	i	i	i	i	i	i	i	i	i
Pyridine	i	i	i	i	i	i	i	i	i	i
MOE	s	s	s	s	s	s	s	s	s	s
Ethanol	i	s	s	s	s	s	s	s	s	s
Water	i	i	i	i	i	sw	sw	ps	s	s

RESULTS AND DISCUSSION

Solubility of monomers, homopolymers and copolymers

Results of qualitative solubility tests on GMA, MMA, PMMA and PGMA are shown in *Table 1*. The liquids used encompass a wide range of solubility parameter δ. The majority of the liquids acted as solvent for both GMA and MMA. Consistent with the known[9] solubility parameter $\delta = 18.4\text{–}19.4\ (\mathrm{MPa})^{1/2}$ for PMMA, this polymer is soluble only in the liquids within the medium range of δ. With regard to PGMA, none of the liquids acted as a solvent for polymer prepared in bulk or in moderate concentration. However, for PGMA prepared by polymerization in dilute solution, solubility occurred in the polar liquids, i.e. those of $\delta \geqslant 25\,(\mathrm{MPa})^{1/2}$. Although the solubility parameter of this polymer is not known the findings suggest that it is of the order of $\sim 30\ (\mathrm{MPa})^{1/2}$, which is similar to the value of $\delta = 29(\mathrm{MPa})^{1/2}$ known[11] for the related, slightly less hydrophilic polymer, PHEMA.

It is of interest that the two liquids (including water) which dissolve the PGMA prepared in dilute aqueous solution, do not dissolve the polymer prepared either in bulk or from 10 wt% GMA aqueous solution. For the latter two situations it is probable that insolubility arises from a form of intermolecular interaction (crosslinking during chain growth, which can only be suppressed at sufficient dilution of the polymerization medium. The findings are broadly similar to those of Refojo[1], who observed that the bulk polymerized sample swelled in water to a transparent hydrogel. If the concentration of GMA in water was reduced to <5 wt%, no gel was formed; instead, a water-soluble viscous polymer was obtained. *Table 1* indicated that MOE is the only liquid, of those examined, that dissolves both of the homopolymers.

A series of copolymers C1–C10 was prepared (see Experimental section) from feed mixtures having various initial weight fractions w_1^0 of MMA. The value of w_1^0 together with the relevant conversions are listed in *Table 2*, which also includes the weight fractions W_1 of MMA units in the copolymers calculated by means of the monomer reactivity ratios r_1 (for MMA) and r_2 for (GMA) derived in this study. Results of solubility tests on these copolymers are given in *Table 3*, which shows that, although the sample of very low GMA content dissolves in two of the liquids and samples of very high GMA content are soluble in three of the liquids, the only solvent for copolymers encompassing the whole range of composition is MOE.

Copolymer composition

Most methods for calculating reactivity ratios, whether by means of the linear[12,13] or non-linear least-squares[14,15] procedure, require experimentally measured cumulative copolymer compositions. In the first instance, consideration was paid to this possible route. For the GMA/MMA system direct analysis of copolymer composition is difficult: (a) the percentages of C, H and O in the two monomer units are not sufficiently dissimilar to allow the use of elemental analysis; (b) because the GMA unit contains two hydroxyl groups, determination of the latter by acetylation is suitable in principle. However, in practice the method is untenable, since it requires the use of pyridine as solvent and, as seen in *Table 3*, copolymers of all compositions are insoluble in this liquid; (c) the use of MOE (see *Table 3*) has some disadvantages as solvent for the copolymers. First, its deuterated form is not readily accessible as a solvent for nuclear magnetic resonance spectroscopy. Secondly, its i.r. spectrum is very complex and it is impossible to find useful absorption peaks due to groups in the copolymer

Table 4 Results obtained for copolymerization of GMA with MMA at four different mole fractions f_1^0 of MMA in initial feed. f_1 is the mole fraction of MMA in monomer mixture at a fractional conversion θ

No.	f_1^0	f_1	θ	m_u/m_d (w/w)	A_{3470}/A_{1730}
1	0.3341	0.3335	0.0928	1/24.94	0.4217
2		0.3414	0.1778	1/20.52	0.4048
3		0.3888	0.6011	1/43.47	0.4513
4		0.4556	0.6527	1/42.08	0.4168
5		0.4692	0.7001	1/36.33	0.3983
6	0.5343	0.5427	0.0054	1/25.51	0.3106
7		0.6782	0.6075	1/36.61	0.2710
8		0.6994	0.6371	1/36.02	0.2568
9		0.6583	0.6945	1/53.25	0.3482
10	0.6433	0.6468	0.0266	1/35.69	0.2887
11		0.6714	0.3098	1/41.82	0.2949
12		0.7493	0.4500	1/22.10	0.1884
13	0.8754	0.8928	0.2757	1/16.17	0.0924
14		0.8710	0.3735	1/21.52	0.1215
15		0.9164	0.5815	1/20.29	0.0969

within the region where MOE has no or little absorption. However, it is evident from *Tables 1* and *3* that there are several solvents for the two monomers and hence the route involving compositions of unreacted monomer mixture at different conversions was adopted as the most suitable procedure.

Determination of reactivity ratios via composition of unreacted monomer mixture: General consideration

This procedure, which is not utilized very frequently, requires careful attention to certain aspects. (1) There must be no loss of monomers other than by copolymerization; in particular, loss by evaporation should be minimized. For this reason copolymerization was conducted without heating, by γ-irradiation at ambient temperature. Moreover, degassing by passage of nitrogen was not employed as this could be another source of loss, especially of the more volatile monomer (MMA). Although failure to outgas may well have influenced the kinetics (with which we were not concerned), it did not prevent copolymerization occurring to high conversion. (2) The conversion θ should not be too low. In this connection it can be readily shown that:

$$W_1 = (w_1^0 - w_1)/\theta + w_1 \qquad (2)$$

Equation (2) shows that, if the fractional conversion θ is very small, even very small errors in w_1^0 (from weighing components in initial feed mixture) and w_1 (from i.r analysis of unreacted monomer mixture) can lead to significant errors in the calculated copolymer composition W_1. To obtain reasonable conversion data, copolymerizations were carried out in batches. Within each batch w_1^0 was fixed and different radiation doses yielded different values of θ. *FT* i.r. analysis then afforded the unreacted monomer mixture composition w_1. Results are listed in *Table 4*, where w_1^0 and w_1 have been converted to their more usual forms of mole fractions, f_1^0 and f_1 respectively.

FT i.r. procedures

Solvent and absorbance ratio. From the *FT* i.r. spectra of the monomers (*Figure 1*), it was found that they both have a strong peak at about 1730 cm^{-1} ($\nu_{C=O}$) and that GMA exhibits a reasonably strong peak at about 3470 cm^{-1} (ν_{O-H}) which is not given by MMA.Thus the absorbance (A) ratio of A_{3470}/A_{1730} can be used to measure the composition of GMA/MMA mixtures, i.e. that of unreacted monomer mixtures.

The liquid used as solvent must satisfy the requirements of (a) ability to dissolve both GMA and MMA and (b) absence of very strong i.r. absorption near the previously mentioned peaks due to groups in the monomers. Among common liquids only diethyl ether and DPE satisfy these requirements. The high volatility of diethyl ether imposes difficulty in maintaining the ratio of monomer mixture/solvent constant during dissolution and i.r. measurement. Hence DPE, the spectrum of which is given in *Figure 1*, was selected as solvent.

Calibration. Previous investigations[16,17] on the use of *FT* i.r. on solutions of copolymers and solutions of monomer mixtures have shown that accurate results necessitate that both the measurements for the unknown and those for the calibration be conducted at equal concentrations of solute. Here, calibration was effected at ratios by weight of mixed monomers/DPE having the following values: 1/20, 1/25, 1/35 and 1/43. For each of these systems the absorbance ratio was determined at 11 values of w_1. Excellent correlation with experimental results was obtained by fitting third-order polynomials, i.e.

$$A_{3470}/A_{1730} = a_0 + a_1 w_1 + a_2 w_1^2 + a_3 w_1^3 \qquad (3)$$

Figure 2 is an example of the third-order polynomial curve for the calibration in which mixed monomers/DPE = 1/25 (w/w). The relevant coefficients a_0, a_1, a_2 and a_3 for this particular system were found to be 0.565, −0.574, −0.181 and 0.272, respectively. The corresponding curves and values of the coefficients were obtained for the calibrations at the three other (monomer mixture/DPE) ratios, but are not reproduced here.

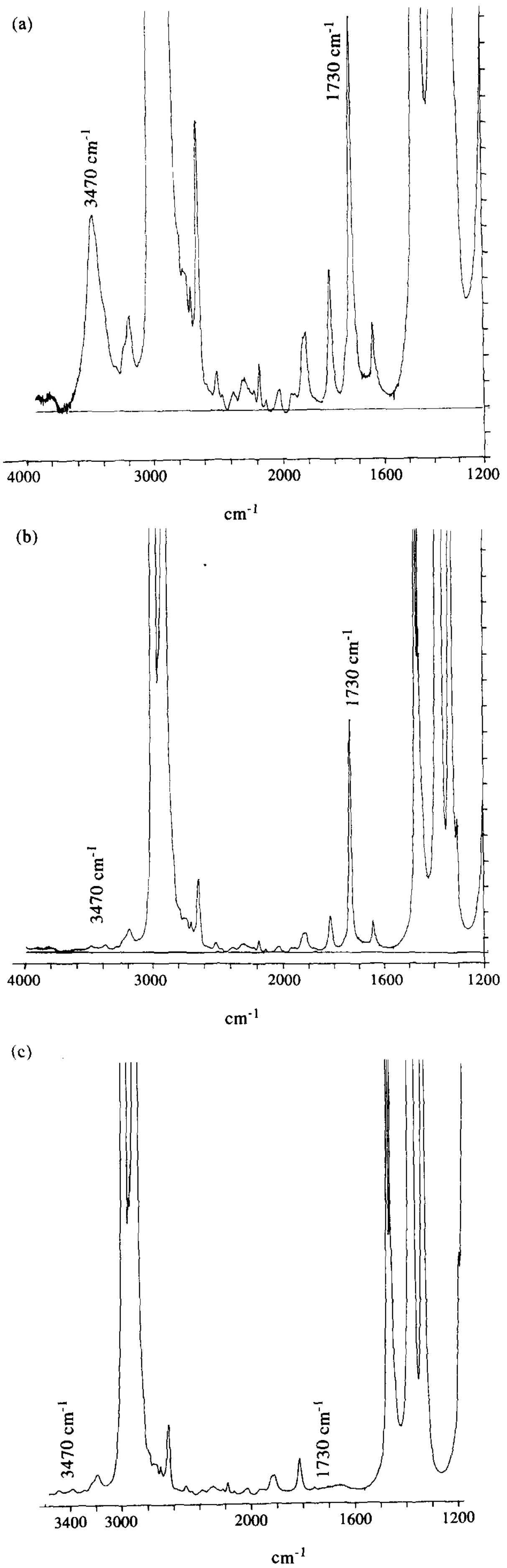

Figure 1 I.r. spectra of (a) GMA in DPE (GMA/DPE = 1/25), (b) MMA in DPE (MMA/DPE = 1/25) and (c) DPE

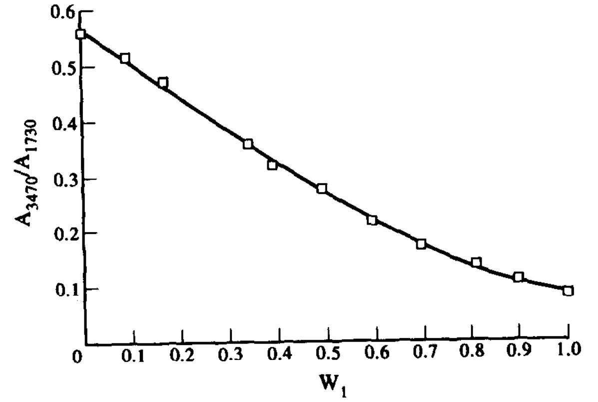

Figure 2 Absorbance ratio as a function of weight fraction of MMA in GMA/MMA mixture in solutions having composition (GMA/MMA mixture)/DPE = 1/25 (w/w)

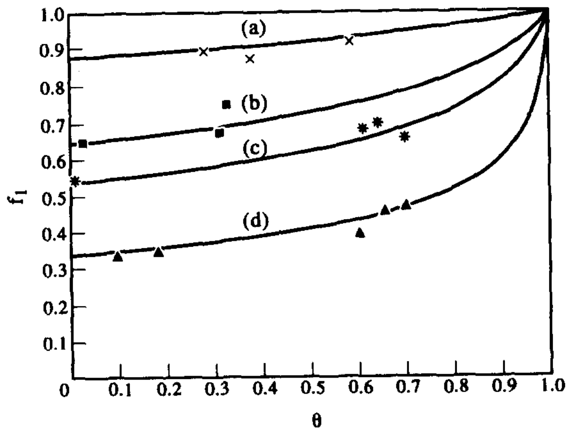

Figure 3 Composition of unreacted monomer mixture as a function of conversion. Curves are calculated using derived values of r_1 and r_2. Experimental compositions are indicated as data points. Initial compositions of feed mixtures f_1^0 are (a) 0.8754, (b) 0.6433, (c) 0.5343 and (d) 0.3341

Composition of unreacted monomer mixtures. The quantity corresponding to (monomer mixture/DPE) (w/w) in a calibration is the experimental ratio m_u/m_d in the actual copolymerizations (see Experimental section), the values of which and those of the absorbance ratios are included in *Table 4*. Two calibration curves having values of monomer mixture/DPE closest to the particular value of m_u/m_d were chosen. From each of them, a value of w_1 was obtained by solving equation (3) using the relevant calibration coefficients a_0, a_1, a_2 and a_3. Mathematically, solution of equation (3) for each set of coefficients can yield three values of w_1. However, only one of these is meaningful, i.e. complies with the necessary restriction $1 > w_1 > 0$. In this manner a value of w_1 was obtained by each of two close calibrations. The true value of w_1 for the sample was then calculated by a linear insertion procedure at the particular m_u/m_d in question. Resultant values of w_1, converted to the more common form of f_1 (i.e. mole fraction of MMA in unreacted monomer mixture), are included in *Table 4* together with other data referred to previously. It is seen that for copolymerizations 6 and 10, which were conducted to very low conversions, the composition of the unreacted monomer mixture is very close to that of the initial feed, thus confirming the reliability of the values of f_1 (or w_1) yielded by *FT*i.r. analysis.

Reactivity ratios

If the directly measured quantity is the composition of unreacted monomer, then it is possible in principle to obtain the copolymer composition by calculation and thereby determine the reactivity ratios. However, as indicated previously, calculated values of copolymer composition via equation (2) can be subject to considerable error for low conversion data (yielding in some instances copolymer compositions W_1 which are not meaningful, i.e. negative or >1). Hence the stage of calculating copolymer compositions was bypassed and the quantities of f_1^0, f_1 and θ utilized directly to estimate r_1 and r_2. For this purpose, a computer program* was developed using simplex algorithm to minimize the object function G:

$$G(r_1, r_2) = \Sigma[f_1^e - f_1^c(r_1, r_2)] \qquad (4)$$

where f_1^e is the experimentally determined composition of unreacted monomer mixture and f_1^c is the value calculated from the corresponding initial value (f_1^0) and the sought values of r_1 and r_2. Further details of the flow chart of the program have been given elsewhere[18]. From the normal terminal model of copolymerization the derived reactivity ratios are found to be $r_1 = 0.53$ and $r_2 = 1.61$, and this system is hence close to an ideal copolymerization ($r_1 \times r_2 = 0.85$).

Finally, the validity of these calculated values of r_1 and r_2 was examined by using them to calculate curves of f_1 versus θ for each of the four copolymerizations, i.e. for each f_1^0. The curves, given in *Figure 3*, show good accord with the experimentally determined compositions of unreacted monomer mixtures, indicated as data points.

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* Further details of the computer program derived and utilized here are available from R. M. (E-mail address: R.Mao@chemistry.salford.ac.uk)