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Reactivity ratios in copolymerizations involving allyl methacrylate

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The copolymerizations of allyl methacrylate (AMA) with methyl methacrylate (MMA) and of AMA with N-vinyl-2-pyrrolidone (VP) have been effected in bulk by γ-irradiation to various stages of fractional conversion θ extending over a wide span of θ. Addition of n-heptane isolated the crosslinked copolymer. *FT* i.r. analysis on the supernatant solution yielded the composition of unreacted monomer mixture, which was used in conjunction with θ and the composition of initial feed to determine the reactivity ratios (r) via an iterative procedure involving a simplex algorithm, yielding AMA(1)/MMA(2) $r_1 = 1.55 \pm 0.16$, $r_2 = 0.99 \pm 0.19$ and AMA(1)/VP(2) $r_1 = 1.408 \pm 0.074$, $r_2 = 0.401 \pm 0.044$. For the system AMA/VP, analysis of crosslinked copolymer (via nitrogen analysis) was also possible and manipulation of the data by three modern procedures afforded good agreement with the values of r_1 and r_2 obtained by analysis of monomer mixture alone. Copyright © 1996 Elsevier Science Ltd.

(Keywords: allyl methacrylate; methyl methacrylate; *N*-vinyl-2-pyrrolidone; reactivity ratio; copolymerization)

INTRODUCTION

Allyl methacrylate (AMA) is an asymmetric, tetrafunctional monomer, which has been used widely as an alternative crosslinker to ethylene glycol dimethacrylate (EDMA) in the preparation of coatings[1–3], resin foams[4–6] and materials of high water absorption[7], for example.

In their early studies on the radical copolymerization of AMA with methyl methacrylate (MMA), Rutovskii and Shur[8,9] did not take into account any possible cyclization. Later, Rätzsch and Stephan analysed the radical polymerization of a related allylic monomer, allyl acrylate, and noted that normal propagation proceeded *ca* 2.4 times more quickly than cyclization[10]. More recently, Heatley and coworkers[11] investigated by n.m.r. the free radical polymerization of AMA and copolymerization of it with several other monomers and found no evidence for any lactone rings which may have resulted from intramolecular cyclization. The signals in the n.m.r. spectra of PAMA were entirely consistent with normal polymerization at the methacrylic and allylic C=C bonds.

It is realized that copolymerizations involving tetrafunctional monomers such as EDMA and AMA are really terpolymerizations allowing, in principle, additional reactions of the pendant double bonds (e.g. crosslinking, cyclization) not consumed in straight chain propagation, thus requiring additional reactivity ratios. However, Dušek and Spěpácek[12] have pointed out that, despite cyclization and deviation in crosslinking copolymerization from the conventional mechanism, the copolymerization parameters determined with neglect of cyclization need not be very distorted. Thus many data in the literature that were derived from the simplest kinetic model may be regarded, approximately at least, as a measure of the reactivity of vinyl groups. On this basis the present authors have determined previously the reactivity ratios in the system EDMA–MMA[13].

The present work is concerned in part with the corresponding hydrophobic system in which EDMA is replaced by AMA. The only reported values for this system are $r_{\mathrm{AMA}} = 0.57 \pm 0.03$, $r_{\mathrm{MMA}} = 0.35 \pm 0.02$[14] for emulsion copolymerization and the widely different values of $r_{\mathrm{AMA}} = 0.91 \pm 0.10$, $r_{\mathrm{MMA}} = 0.67 \pm 0.07$[15] for radical copolymerization in solution. The hydrophilic system for AMA/VP is also investigated, but for this copolymerization, there do not appear to be any previously reported values of the reactivity ratios. Systems in which the products are crosslinked are, in general, not very amenable to direct analysis of copolymer composition and hence unreacted monomer mixture is analysed instead. However, for the system AMA/VP only, determination of copolymer composition is possible (by nitrogen analysis) and reactivity ratios are derived also via them as a basis for comparison.

EXPERIMENTAL

Materials

MMA (Fisons) was dried over anhydrous magnesium sulphate and distilled at normal pressure. VP (Aldrich) and AMA (Aldrich) were dried over anhydrous

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magnesium sulphate and distilled at reduced pressure (52–53°C/0.3–0.4 mmHg for VP and 38–40°C/11–12 mm Hg for AMA). n-Heptane (Aldrich) was used as received.

Copolymerization and analysis of monomer mixture

The procedures for copolymerization and analysis of the residual monomer mixture are the same as those for MMA–EDMA system[13]. Essentially for each of the two systems, monomer mixtures covering a wide span of initial weight fraction of AMA (w_1^0) were made up gravimetrically in capped, tared vials and subjected to γ-irradiation at dose rate 0.25 kGy h^{-1} from a 333 TBq ^{60}Co source at Salford University. Various doses were used to effect different extents of fractional conversion on a weight basis, θ.

For AMA/MMA, θ ranged from 6 to 60 kGy and for AMA/VP the range of θ was 1.7 to 30 kGy. An excess of n-heptane was added, the resultant vials were left for several days and the supernatant mixture of unreacted monomers in n-heptane was analysed by *FT* i.r. (after appropriate calibration) to yield the weight fraction of AMA (w_1^0) in unreacted monomer mixture at the particular stage of conversion θ. It was verified that the weight loss of monomers during copolymerization was negligible. Thus the weight of n-heptane added to the vial could be obtained from the total weight before *FT* i.r. measurement, allowing the dilution ratio h/m to be calculated (h and m are, respectively, the masses of n-heptane and of monomer mixture). The absorbance A depends not only on composition, but also to some extent on the overall concentration or its reciprocal h/m. After final washing, drying and weighing of crosslinked copolymer, θ was obtained.

Determination of composition of AMA/VP copolymers by nitrogen analysis

The nitrogen content of some AMA/VP copolymers was measured by a KJELTEC Auto 1030 Analyzer[16] and used to calculate the mole fraction F_2 of VP units in the copolymers. A very small correction factor was applied via the measured nitrogen content of a sample of pure poly-VP (theoretical: 12.60 wt% nitrogen). The mole fraction of AMA units, F_1, is $1 - F_2$.

RESULTS AND DISCUSSION

FT *i.r. calibration*

FT i.r. spectra of n-heptane and of separate solutions of AMA, VP and MMA in this solvent were run in order to locate suitable absorbance peaks for analysis of monomer mixtures in n-heptane. Maxima at 1640 cm^{-1} are exhibited by both AMA and MMA, whereas absorbance at 1197 cm^{-1} is shown by MMA but not AMA. Although other absorbance ratios were possible, that of A_{1197}/A_{1640} was selected for calibration, since (a) it exhibited a strong dependence on composition of monomer mixture, w_1, and (b) it did not have a very strong dependence on h/m. Calibrations were conducted at five different values of h/m ranging from 2 to 25, and for each of these the monomer mixture comprised 11 different values of w_1. These calibration data fitted well with a fifth-order polynomial, viz.

$$A_{1197}/A_{1640} = a_0 + a_1 w_1 + a_2 w_1^2 + a_3 w_1^3 + a_4 w_1^4 + a_5 w_1^5. \tag{1}$$

The value of the coefficients were derived for all the systems, but are reproduced here only for that in which $h/m = 5$, viz. $a_0 = 2.881$, $a_1 = -1.296$, $a_2 = -2.049$, $a_3 = 2.858$, $a_4 = -2.121$ and $a_5 = 0.586$.

A similar procedure was adopted for calibration of AMA/VP mixtures in n-heptane. Absorbance at 1627 cm^{-1} occurs for VP but not for AMA and absorbance at 1319 cm^{-1} is exhibited by AMA but not by VP. Fifth-order polynomials were fitted for the dependence of A_{1629}/A_{1319} on w_1. For example, the values of the coefficients for the system in which $h/m = 5$ were: $a_0 = 11.788$, $a_1 = -47.755$, $a_2 = 100.518$, $a_3 = -122.292$, $a_4 = 78.182$ and $a_5 = -20.309$. The values of h/m used ranged from 2 to 25. Although these calibrations were

Table 1 Copolymer parameters for system AMA(1)/MMA(2): f_1^0—mole fraction of AMA in initial feed mixture, f_1—mole fraction of AMA in unreacted monomer mixture at a fractional conversion on a weight basis θ, h/m—ratio of weight n-heptane to unreacted monomer mixture in solution analysed by *FT* i.r. to yield w_1 (and thereby f_1)

f_1^0	θ	h/m	f_1
0.0890	0.000	5.62	0.089
0.0890	0.002	5.44	0.080
0.0890	0.073	3.60	0.081
0.0890	0.218	3.49	0.070
0.0890	0.250	4.22	0.087
0.0890	0.258	3.49	0.058
0.1826	0.000	6.11	0.173
0.1826	0.002	7.43	0.182
0.1826	0.097	5.58	0.174
0.1826	0.188	4.53	0.183
0.1826	0.197	3.32	0.181
0.1826	0.273	5.03	0.161
0.2533	0.000	5.05	0.243
0.2533	0.001	6.79	0.247
0.2533	0.008	4.31	0.254
0.2533	0.079	3.52	0.242
0.2533	0.101	6.55	0.253
0.2533	0.125	13.38	0.251
0.4437	0.000	4.99	0.434
0.4437	0.000	5.11	0.443
0.4437	0.079	4.48	0.444
0.4437	0.356	4.90	0.442
0.4437	0.398	4.19	0.433
0.4437	0.462	3.83	0.430
0.5462	0.000	7.20	0.547
0.5462	0.000	9.90	0.529
0.5462	0.009	9.21	0.547
0.5462	0.090	3.83	0.524
0.5462	0.146	3.11	0.538
0.5462	0.387	2.82	0.517
0.6489	0.000	5.85	0.649
0.6489	0.001	5.66	0.634
0.6489	0.006	4.04	0.634
0.6489	0.108	3.24	0.649
0.6489	0.185	5.55	0.618
0.6489	0.520	12.57	0.642
0.7612	0.000	4.40	0.762
0.7612	0.013	3.56	0.753
0.7612	0.049	4.28	0.749
0.7612	0.064	31.81	0.756
0.7612	0.075	4.92	0.743
0.7612	0.928	3.32	0.583
0.8772	0.000	8.55	0.881
0.8772	0.022	5.09	0.872
0.8772	0.046	3.33	0.873
0.8772	0.065	3.21	0.879
0.8772	0.104	2.43	0.872
0.8772	0.144	3.62	0.882

satisfactory for the majority of systems, a few circumstances presented difficulties due to the absorbance peak at 1629 cm^{-1} being off scale ($A_{1629} > 4.578$). Specifically this occurred (a) for $w_1 < 0.3$ when $h/m > 5$ or (b) for $w_1 < 0.6$ when $h/m < 2$, both of which situations were sometimes encountered in some of the actual *FT* i.r. analyses of solutions of monomer mixtures from the copolymerizations. Under these circumstances, the problem was resolved by using the absorbance at 1265 cm^{-1} by VP (but not by AMA) to establish relevant additional calibrations, viz. polynomials of A_{1265}/A_{1319} as a function of w_1.

Reactivity ratios calculated from FT *i.r. analysis of monomer mixtures for AMA/MMA and AMA/VP systems*

For neither of the two groups of copolymerization studies was any outgassing or purging with nitrogen carried out on the initial feed mixtures prior to γ-irradiation. This was to ensure that no change from w_1^0 occurred due to volatilization. In this connection the use of ambient temperature was also helpful. No kinetic measurements were made, but it was observed that the induction period for AMA/MMA was considerably longer than that for AMA/VP. For both copolymerizations several different initial feed compositions were used and for each of these the reaction proceeded to different conversions, the composition of resultant, unreacted monomer mixture being determined by *FT* i.r. analysis. The relevant copolymerization data for AMA/MMA and AMA/VP are listed in *Tables 1* and *2*, respectively, where the weight fractions w_1^0 and w_1 have been converted to the more usual form of mole fractions f_1^0 and f_1, respectively. For reasons discussed elsewhere[13] it is inadvisable to convert the data to copolymer compositions and instead the reactivity ratios were derived according to the terminal model, adopting the convention that AMA can be treated in the same way as a normal monomer having one double bond. Data were treated by a non-linear least squares method, manipulation being effected by a specially designed computer programme. The results are given in *Table 3* and the calculated joint confidence intervals are shown in *Figure 1* for the systems AMA/MMA and AMA/VP. Using the derived reactivity ratios, calculated curves were

Table 2 Copolymerization parameters for system AMA(1)/VP(2): f_1^0—mole fraction of AMA in initial feed mixture, f_1—mole fraction of AMA in unreacted monomer mixture at a fractional conversion on a weight basis θ, h/m—ratio of weight of n-heptane to unreacted monomer mixture in solution analysed by FTIR to yield w_1 (and thereby f_1)

f_1^0	θ	h/m	f_1
0.1813	0.010	17.85	0.180
0.1813	0.180	15.53	0.134
0.1813	0.477	13.69	0.091
0.1813	0.592	15.79	0.029
0.1813	0.816	16.66	0.018
0.1813	0.867	6.70	0.019
0.2706	0.026	2.57	0.286
0.2706	0.146	3.60	0.234
0.2706	0.513	3.19	0.176
0.2706	0.757	8.30	0.119
0.2706	0.793	16.21	0.096
0.2706	0.830	3.81	0.061
0.3695	0.011	19.15	0.369
0.3695	0.097	14.72	0.369
0.3695	0.370	20.02	0.343
0.3695	0.586	12.99	0.287
0.3695	0.596	23.94	0.216
0.3695	0.905	26.67	0.020
0.4844	0.466	12.74	0.385
0.4844	0.951	4.70	0.040
0.4844	0.965	5.75	0.064
0.4844	0.974	2.58	0.067
0.4844	0.976	6.11	0.035
0.4844	0.986	8.08	0.009
0.6724	0.087	10.79	0.660
0.6724	0.103	4.85	0.659
0.6724	0.469	6.04	0.636
0.6724	0.587	4.27	0.622
0.6724	0.773	3.26	0.532
0.6724	0.945	3.79	0.365
0.7959	0.003	2.02	0.794
0.7959	0.012	23.84	0.797
0.7959	0.033	4.27	0.800
0.7959	0.956	5.91	0.538
0.7959	0.962	3.15	0.433
0.7959	0.970	3.73	0.414
0.8921	0.005	14.45	0.885
0.8921	0.009	21.34	0.892
0.8921	0.099	25.07	0.889
0.8921	0.173	4.19	0.885
0.8921	0.349	9.05	0.891
0.8921	0.969	9.55	0.735

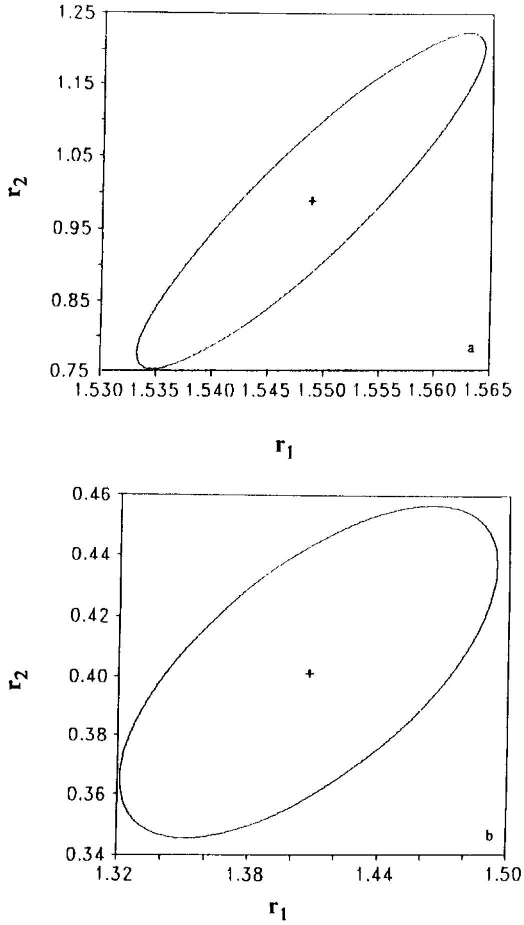

Figure 1 (a) 95% joint confidence interval of the estimated reactivity ratios of AMA(1)/MMA(2) from *FT* i.r. results. Its equation is: $0.0771(r_1 - 1.5488)^2 - 0.1192(r_1 - 1.5488)(r_2 - 0.9884) + 0.0558(r_2 - 0.9884)^2 = 5.424 \times 10^{-4}$. (b) 95% joint confidence interval of the estimated reactivity ratios of AMA(1)/VP(2) from *FT* i.r. results. Its equation is: $0.9338(r_1 - 1.4078)^2 - 2.0284(r_1 - 1.4078)(r_2 - 0.4011) + 2.6094(r_2 - 0.4011)^2 = 4.646 \times 10^{-3}$

Table 3 Reactivity ratios derived via different procedures

Procedure	r_{AMA}	r_{MMA}	r_{AMA}	r_{VP}
Analysis of monomer mixture + non-linear least squares	1.55 ± 0.16	0.99 ± 0.19	1.408 ± 0.074	0.401 ± 0.044
Analysis of copolymer + linear K–T			1.21 ± 0.26	0.55 ± 0.19
Analysis of copolymer + linear Ex.K–T			1.30 ± 0.23	0.50 ± 0.14
Analysis of copolymer + linear M–H			1.31 ± 0.17	0.49 ± 0.11

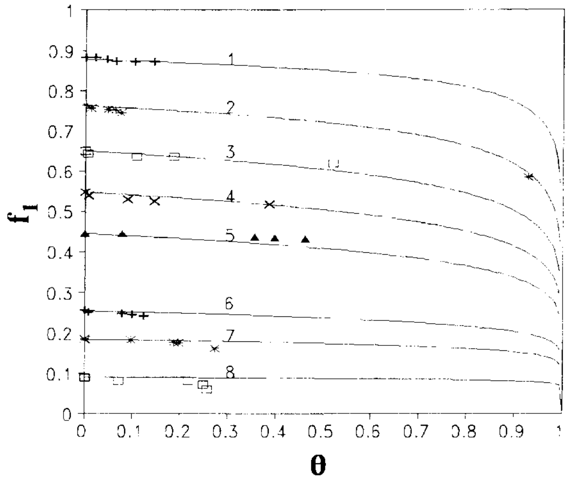

Figure 2 The best fitted lines compared with experimental data with initial feed composition for AMA(1)/MMA(2) system: (1) $f_1^0 = 0.8772$; (2) $f_1^0 = 0.7612$; (3) $f_1^0 = 0.6489$; (4) $f_1^0 = 0.5462$; (5) $f_1^0 = 0.4437$; (6) $f_1^0 = 0.2533$; (7) $f_1^0 = 0.1826$; (8) $f_1^0 = 0.0890$

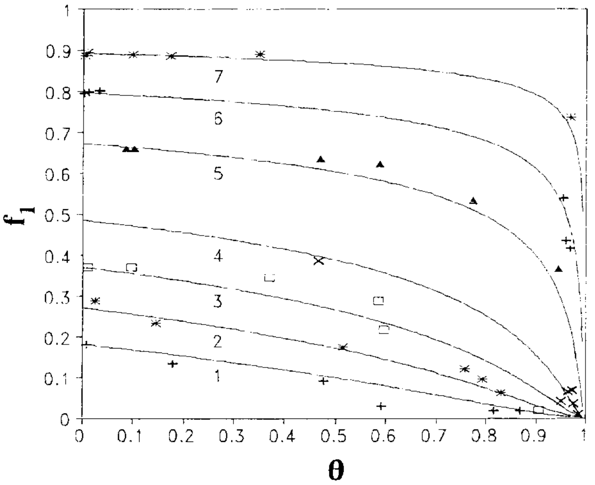

Figure 3 The best fitted lines compared with experimental data with initial feed composition for AMA(1)/VP(2) system: (1) $f_1^0 = 0.1813$; (2) $f_1^0 = 0.2706$; (3) $f_1^0 = 0.3695$; (4) $f_1^0 = 0.4844$; (5) $f_1^0 = 0.6724$; (6) $f_1^0 = 0.7959$; (7) $f_1^0 = 0.8921$

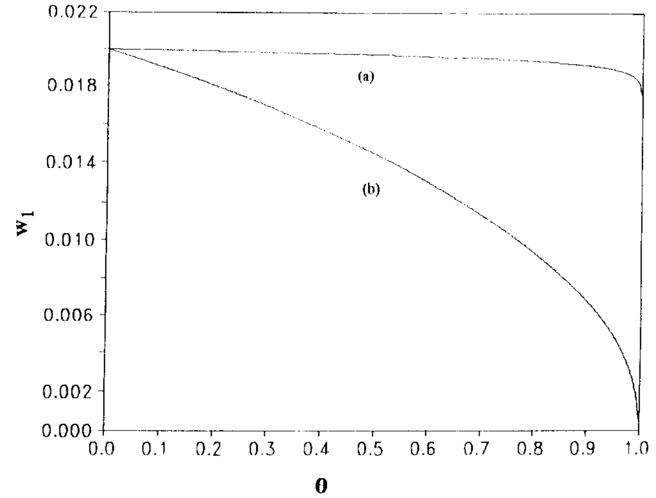

Figure 4 Curves computed from reactivity ratios for the weight fraction (w_1) of AMA or EDMA in unreacted monomer mixture at different fractional conversions on a weight basis θ for the copolymerizations (a) AMA/MMA and (b) EDMA/MMA. The initial value of w_1 is 0.02 for both (a) and (b)

Table 4 Nitrogen analysis results and the calculated compositions of some AMA-VP copolymer as well as their initial feed and conversion data

f_1^0	wt% N	F_1	θ
0.1813	8.54	0.296	0.180
0.3695	6.40	0.460	0.370
0.4844	5.23	0.554	0.466
0.2706	7.15	0.402	0.146
0.2706	8.23	0.319	0.513
0.6724	2.73	0.761	0.103
0.6724	3.14	0.726	0.469
0.6724	3.38	0.707	0.587
0.8921	0.93	0.917	0.349

Mole fractions (F_1) of AMA-units calculated from nitrogen analysis on AMA/VP copolymers prepared to fractional conversions on a weight basis θ from mixtures containing an initial mole fraction f_1^0 of AMA.

constructed for the variation in composition of unreacted monomer with conversion and given as *Figures 2* and *3* for the systems AMA/MMA and AMA/VP, respectively. It is seen that the actual experimentally determined compositions, also indicated in these figures, fall well on the calculated curves, thus according confidence in the reliability of the reactivity ratios.

Reactivity ratios calculated from nitrogen analysis of copolymers for AMA/VP system

Despite the crosslinked nature of poly(AMA-*co*-VP), its composition can be determined by nitrogen analysis. However, for copolymers prepared to very low conversion, there was insufficient sample for N-analysis. For copolymers prepared to very high conversions, the composition can provide very little information about reactivity ratios, because at 100% conversion, the copolymer composition is always equal to the initial feed composition regardless of the reactivity ratios. Thus only those copolymers with medium–high conversion were selected. *Table 4* gives the results of nitrogen analysis and the calculated copolymer composition of these selected AMA/VP copolymers. From these data, the monomer reactivity ratios were calculated by the Kelen–Tüdős (K–T)[17] and extended Kelen–Tüdős (Ex.K–T)[18] procedures, and the iterative procedure of Mao and Huglin (M–H)[19]. Reference should be made to the relevant papers for full details of these procedures. The derived reactivity ratios are included in *Table 3*. It is seen that the values via the Ex.K–T and M–H procedures are similar and the uncertainty limits are the smallest using the M–H method. The uncertainty limits are smaller still for the AMA/VP system when analysis of monomer mixture is used.

CONCLUSIONS

With the reservation that no allowance has been made for possible reactivity of pendant double bonds, reactivity ratios have been derived successfully by analysis of unreacted monomer mixture. The results are not restricted to low conversion copolymerization and the reactivity ratios obtained have been used to construct curves of composition of unreacted monomer mixture vs conversion; the actual measured compositions fall well on these curves. The values of the reactivity ratios for the system AMA/MMA differ from the two discordant sets of values in the literature. The values of reactivity ratios for the AMA/VP system, reported here for the first time, accord with the values obtained by analysis of composition of crosslinked copolymer, provided that the data are treated by the Ex.K–T or M–H methods.

Adopting the same assumptions, we have obtained previously values of $r_{\mathrm{EDMA}} = 1.34$, $r_{\mathrm{MMA}} = 0.67$ for the copolymerization of MMA with the more widely used crosslinker, EDMA[13]. As indicated in *Table 3*, the corresponding values for the copolymerization of MMA with AMA are rather different. It is instructive to compare these two systems on the basis of compositional homogeneity of unreacted monomer mixture (or equivalently, of copolymer) throughout the various stages of conversion. Although a wide range of initial feed compositions (w_1^0 or f_1^0) was employed here to derive the reactivity ratios, in common practice, crosslinking copolymerizations actually involve the use of only a small content of crosslinker ($\not>$ *ca* 5 wt%). Accordingly, an initial value of $w_1^0 = 0.02$ was taken for both the AMA/MMA and EDMA/MMA copolymerizations and the values of w_1 (weight fraction of AMA in unreacted monomer mixtures) were computed at all values of θ. The resultant curves in *Figure 4* demonstrate that w_1 undergoes a marked continuous decrease with θ when EDMA is the co-monomer. In contrast, the fall in AMA with conversion is very slight until the final stages of conversion, indicating a much more compositionally homogeneous system.

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