Free-radical copolymerization of methyl acrylate with methyl methacrylate in benzene solution

C. Arias
Departamento de Química-Física Farmaceutica, Facultad de Farmacia, Universidad Complutense, Ciudad Universitaria, E-28040 Madrid, Spain

and M. M. C. López-González, M. Fernández-García, J. M. Barrales-Rienda and E. L. Madruga*
Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain
(Received 18 June 1992; revised 15 October 1992)

Methyl acrylate and methyl methacrylate have been copolymerized using the initiator 2,2'-azobisisobutyronitrile over a wide composition and conversion range. Free-radical copolymerization has been carried out in benzene solution using 3 and 5 $\mathrm{mol\,l^{-1}}$ as the overall concentrations of monomers. Reactivity ratios do not, apparently, change by dilution. Cumulative copolymer composition was independent of total monomer concentration, being described satisfactorily by the integrated Mayo–Lewis equation. The overall copolymerization coefficients are not affected by total monomer concentration. They were analysed on the basis of a penultimate effect on the propagation reaction.

(Keywords: solution–radical copolymerization; high conversion; reactivity ratios; methyl acrylate–methyl methacrylate; overall copolymerization rate)

INTRODUCTION

In the last two decades many publications have referred to the effect of solvent on the reactivity ratios of a series of monomers copolymerized by a free-radical mechanism. The subject has been reviewed by Plochocka[1].

Changes in the reactivity ratios have been explained[2] in terms of: (i) electrostatic repulsion of charged monomers and radicals; (ii) changes in monomer polarity; (iii) participation of monomers in complexes; (iv) hydrogen bonding of monomer with solvent; and (v) solvent dielectric effects. However, a universal treatment has not been developed so far.

Recently, Harwood[2] has observed that copolymers having the same composition have the same microstructure, independent of the solvent used during their preparation. By considering this fact, Harwood[2] proposed that solvent effects in copolymerization are not manifested in the chain-end reactivity but rather in a solvent partitioning, whereby an equilibrium may exist in which monomers are distributed between free solvent, i.e. in the whole reaction medium, and domains in the neighbourhood of the growing chain-end radicals. This kind of effect has been called[2] the 'bootstrap effect'.

On the other hand, Kratochvíl *et al.*[3] have pointed out that the ratio between the local and analytical molar concentration of a component depends markedly on the volume in which the preferentially solvated component is dispersed. It is obvious that the largest relative differences between the local and analytical concentrations due to preferential solvation, and hence also the largest effect of preferential solvation on the kinetics, may be expected for low monomer concentrations.

Furthermore, in the free-radical copolymerization of acrylonitrile–styrene[4] and the free-radical copolymerization of 2-ethylacrylic acid–methacrylic acid[5], it has been observed that variations in overall concentration of monomers in *N,N'*-dimethylformamide produce changes in the value of reactivity ratios. The observed trends have been explained considering preferential solvation[5,6]. Variation in reactivity ratios with the overall concentration of monomers is also found in the free-radical copolymerization of vinyl acetate–methyl methacrylate when propanol, acetone or acetonitrile is used as a solvent[7].

Bearing in mind these facts, this investigation focuses on the dilution effect in the free-radical copolymerization of methyl acrylate–methyl methacrylate in benzene, considering composition data, and therefore reactivity ratios, as well as overall copolymerization rates.

EXPERIMENTAL

Materials

Monomers, methyl acrylate (MA) and methyl methacrylate (MMA), were purified by conventional methods[8].

2,2'-Azobisisobutyronitrile (AIBN) was purified by successive crystallizations from methanol. Benzene (Merck) for analysis was used without any further purification, disregarding generous head and tail fractions by distillation.

Copolymerization

Copolymerization reactions were conducted at 50 ± 0.1°C in Pyrex glass ampoules sealed under high vacuum. The calculated amount of AIBN dissolved in purified acetone to give $1.5\times10^{-2}\,\mathrm{mol\,l^{-1}}$ was run into the ampoules. For each feed composition the calculated amount of

---

* To whom correspondence should be addressed

0032-3861/93/081786-04

monomers was weighted and the required volume of benzene to give monomer concentrations of 3 or 5 mol l^{-1} was added. The mixture was degassed by successive freeze–pump–thaw cycles. The ampoules were kept frozen in liquid nitrogen until required. The resulting copolymers were isolated by pouring the contents of the glass ampoules into methanol. The precipitated materials were purified by reprecipitation from benzene–methanol system and then filtered and dried until constant weight was attained.

Copolymer analysis

^{1}H n.m.r. spectroscopy was used to determine copolymer compositions. Spectra were recorded at 50°C for all copolymers on about 8% solutions in deuterochloroform by using a Bruker AM-200 spectrometer operating at 200 MHz. Copolymer composition was determined following the method of Grassie *et al.*[9].

RESULTS AND DISCUSSION

Free-radical copolymerization of MA–MMA was carried out at 50°C in 3 or 5 mol l^{-1} benzene solution using 1.5×10^{-2} mol l^{-1} of AIBN as initiator concentration. Both reactivity ratios were obtained by preparing copolymers from monomer feed compositions as near as possible to those determined by the 'approximate design scheme' proposed by McFarlane *et al.*[10]. To obtain initial estimated reactivity ratios, arithmetic means of the values reported in the literature[9,11–14] were used; they are shown in *Table 1*.

Copolymer composition (F_{MA}) data are quoted in *Table 2*, together with monomer feed compositions (f_{MA}) obtained from the 'approximate design scheme', and others which widen the experimental range. It is observed that the copolymer compositions are independent of the global concentrations of monomers in the feed, and for a determined monomer feed the copolymers exhibit, within experimental error, similar molar fraction compositions. The reactivity ratios have been obtained by means of the Kelen and Tüdos linearization method[15] considering the results obtained with both overall concentrations of monomers. The Kelen–Tüdos plot is shown in *Figure 1*, the corresponding reactivity ratios being $r_{MA} = 0.42 \pm 0.08$ and $r_{MMA} = 2.36 \pm 0.32$. In order to ratify this finding, high-conversion copolymerization of MA–MMA has been carried out using several feed compositions of monomers. *Figure 2* shows the cumulative copolymer composition as a function of conversion. The solid lines were drawn according to the integrated copolymer

Table 1 Literature values for the reactivity ratios of methyl acrylate–methyl methacrylate copolymerization

r_{MA}	r_{MMA}	Ref.
0.34	1.69	11
0.35	1.80	9
0.36	2.23	12
0.45	2.30	12
0.50	2.30	13
0.47	2.30	14

Table 2 Analytical data for the copolymerization of MA with MMA at 50°C in benzene solution using AIBN as initiator

[MA]+[MMA] (mol l^{-1})	f_{MA}	Conversion (%)	F_{MA}
3.0	0.858	7.9	0.671
	0.825	7.8	0.699
	0.801	8.1	0.641
	0.700	3.8	0.498
	0.548	5.0	0.340
	0.504	8.2	0.311
	0.452	4.7	0.250
	0.300	5.6	0.130
5.0	0.823	3.0	0.671
	0.801	2.8	0.596
	0.698	2.9	0.521
	0.503	3.0	0.325
	0.451	2.6	0.265

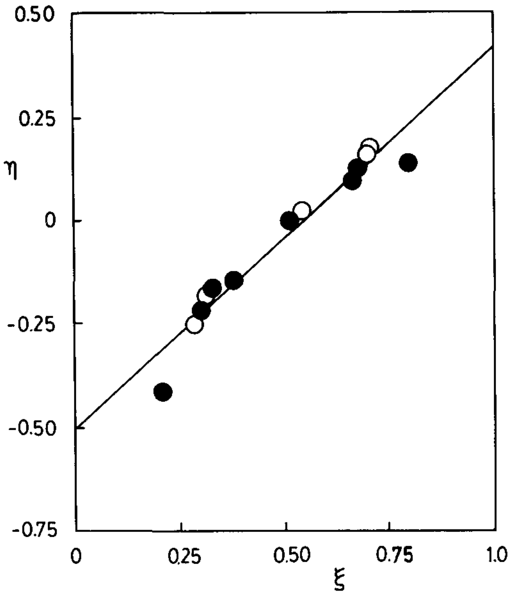

Figure 1 Data of the system methyl methacrylate (MMA)–methyl acrylate (MA)–benzene–AIBN at 50°C plotted according to the Kelen–Tüdos equation. Feed composition for [MA]+[MMA] = 5 mol l^{-1} (●) and = 3 mol l^{-1} (○)

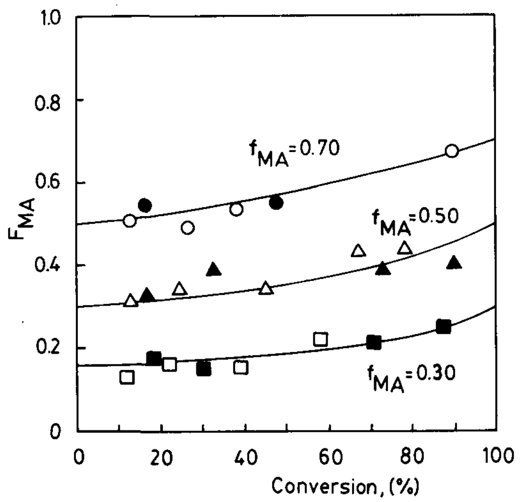

Figure 2 Cumulative copolymer composition F_{MA} as a function of the degree of conversion. The solid lines have been calculated from the terminal model integrated copolymer equation with reactivity ratios determined as $r_{MA} = 0.42 \pm 0.08$ and $r_{MMA} = 2.36 \pm 0.32$. Solid and open points represent copolymer composition obtained using 5 and 3 mol l^{-1} as the overall concentration of monomers, respectively

composition equation using the reactivity ratios given above. It is clear that the experimental data are consistent with the Mayo–Lewis terminal model, independent of the total monomer concentration. For this reason the propagation step is not apparently affected by dilution under the experimental conditions employed in the present work.

Free-radical copolymerization of MA with MMA has been followed up to moderate conversions using an overall concentration of monomers of 3 and 5 $\mathrm{mol\,l^{-1}}$ and changing the MMA molar feed composition from 0.3 to 0.8. *Figure 3* shows the experimental results. It can be seen that the overall concentration of monomers does not influence the copolymerization coefficient. However, as expected, the copolymerization rate hardly changes as a function of molar monomer feed compositions, being higher when MA molar fraction in the feed increases.

From the initial slope of the lines in *Figure 3*, the initiator concentration and rate coefficients, $(k_p/k_t^{1/2})(fk_d)^{1/2}$, for the MA–MMA–benzene system were estimated. In *Figure 4* the rate coefficients are plotted *versus* MMA molar composition in the feed. From a classical point of view, the shape of the curve shown in *Figure 4* would be attributed to changes in the termination reactions[16]. However, recent experimental evidence[17–19] using different techniques has shown a certain type of deviation from the profiles of the overall copolymerization propagation rate constant (k_p) *versus* monomer feed composition (f_i) calculated according to the Mayo–Lewis equation. Such deviations have been interpreted as a consequence of the penultimate effect on the propagation reaction. Considering the 'terminal model', the apparent propagation rate constant could be expressed thus[17]:

$$k_p=\frac{r_1f_1^2+2f_1f_2+r_2f_2^2}{(r_1f_1/k_{11})+(r_2f_2/k_{22})} \tag{1}$$

where $r_i=k_{ii}/k_{ij}$ $(i\neq j)$ is the reactivity ratio and k_{ij} is the rate constant for radical i adding j (i, $j=1$ or 2) and $f_i=(1-f_j)$, the mole fraction of monomer i in the feed. According to the penultimate model, and following the nomenclature of Fukuda *et al.*[20], k_p can be expressed by equation (1) with k_{11} and k_{22} replaced by the following functions:

$$k_{11}=k_{111}(r_1f_1+f_2)/(r_1f_1+s_1^{-1}f_2) \tag{2}$$

$$k_{22}=k_{222}(r_2f_2+f_1)/(r_2f_2+s_2^{-1}f_1) \tag{3}$$

$$s_1=k_{211}/k_{111} \quad \text{and} \quad s_2=k_{122}/k_{222} \tag{4}$$

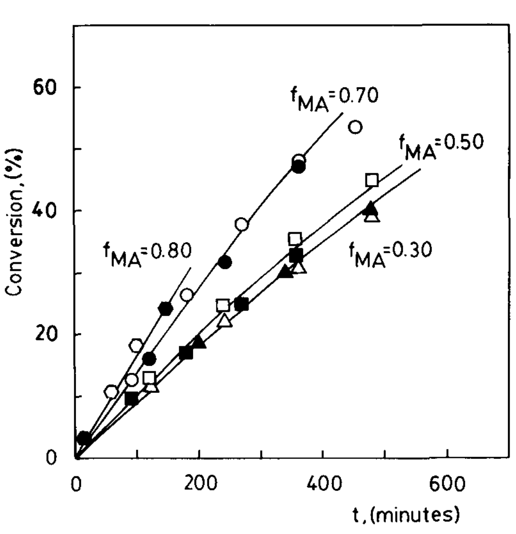

Figure 3 Plot of degree of conversion *versus* copolymerization time for the system methyl methacrylate (MMA)–methyl acrylate (MA)–benzene–AIBN at 50°C. Solid and open points represent conversion obtained using 5 and 3 $\mathrm{mol\,l^{-1}}$ as the overall concentration of monomers, respectively

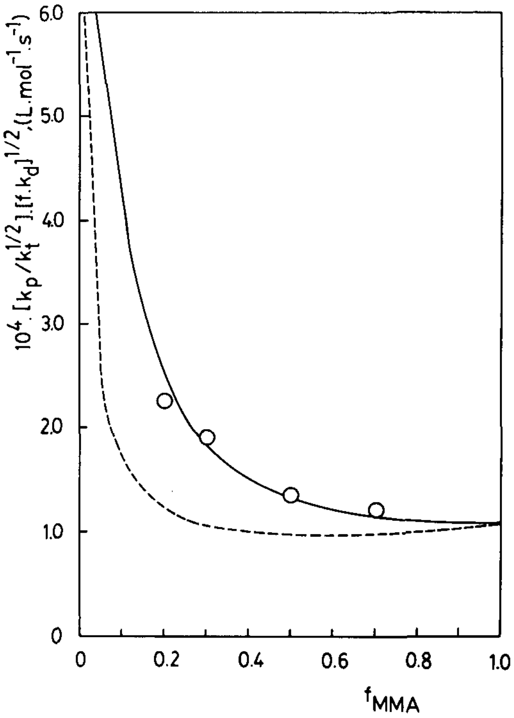

Figure 4 Plot of $[k_p/k_t^{1/2}][fk_d]^{1/2}$ *versus* f_{MMA} for the system methyl methacrylate (MMA)–methyl acrylate (MA)–benzene–AIBN at 50°C. The open circles are experimental data points estimated as indicated in the text. ---, calculated values for the penultimate model by considering $s_1=s_2=(r_1r_2)^{1/2}$; ———, s_1 and s_2 estimated from experimental results by a method of fitting for the best representation. r_1 and r_2 are the experimental reactivity ratios obtained at low conversions

where k_{ijm} is the rate constant for the terminal radical j with penultimate unit i, adding to monomer m and k_{111} and k_{222} refer to the homopolymerization of MA and MMA, respectively.

The penultimate influence is asserted through the parameters s_1 and s_2 which do not influence either composition or sequence distribution[21].

On the other hand, termination rate constant in copolymerization might be represented by a simple weighted average of the homotermination rate constants[17,22] for both homopolymers, according to the 'ideal termination model' of Atherton and North's theory[23]:

$$k_t=F_1k_{t11}+F_2k_{t22} \tag{5}$$

where F_1 and F_2 are the respective mole fractions of monomer units in the copolymer.

Furthermore the value of fk_d, where f is the efficiency factor for initiator decomposition in copolymerization and k_d is the initiator decomposition rate constant in copolymerization, is a function of the feed composition and its product varies linearly with monomer feed composition according to the following empirical relationship[22]:

$$fk_d=f_1(fk_d)_1+f_2(fk_d)_2 \tag{6}$$

Table 3 Homopolymerization rate constants for methyl methacrylate and methyl acrylate copolymerization at 50°C in benzene solution using AIBN as initiator

Monomer	k_p (l mol^{-1} s^{-1})	$k_t \times 10^{-7}$ (l mol^{-1} s^{-1})	$fk_d \times 10^6$ (s^{-1})
MA	4200	2.54	0.70
MMA	544.5	3.49	1.36

Homopolymerization rate constants for both MA and MMA monomers shown in *Table 3* were taken from previous studies[24,25]. For homopropagation rate constant of MA a value of 4200 l mol^{-1} s^{-1} was estimated, taking into account the value given by Davis *et al.*[26]. Homopolymerization rate constant, together with the reactivity ratio values mentioned above and the experimental rate coefficients of copolymerization, $(k_p/k_t^{1/2})(fk_d)^{1/2}$, allow s_1 and s_2 to be determined by a fitting procedure. The full curve, represented in *Figure 4*, was calculated with values of 0.8 and 10.0 for s_1 and s_2, respectively. It can be seen that experimental values are in qualitative agreement with calculated ones. At first sight, these values are unrealistic, since Fukuda *et al.*[20], using a model based on radical stabilization energies which varies according to the nature of the penultimate unit, have predicted that $r_1r_2 = s_1s_2$ with $s_1 = s_2$. However, by taking $s_1 = s_2 = (r_1r_2)^{1/2}$ the resulting value for $s_1 = s_2$ is 0.996. The theoretical curve for rate coefficient of copolymerization, $(k_p/k_t^{1/2})(fk_d)^{1/2}$, *versus* MMA monomer feed composition is shown in *Figure 4* as a dashed curve. It is observed that this curve is far from fitting the experimental data, but when values of $s_1 = 0.8$ and $s_2 = 10.0$ are used, the penultimate model provides a better fit for the experimental data.

The Mayo–Lewis terminal model, together with the reactivity ratios calculated at low conversions, has been used to calculate the changes in copolymer composition with increasing conversion. The experimental results compare very well with the estimated ones.

The Mayo–Lewis model does not describe copolymerization rate coefficient, $(k_p/k_t^{1/2})(fk_d)^{1/2}$, for the copolymerizations carried out in the present study. The penultimate model of Fukuda *et al.*[17], together with some other empirical relationships such as the Atherton–North model for the termination constant k_t and that of O'Driscoll–Huang for the initiator decomposition constant and its efficiency factor fk_d, has been used to fit the data. A best curve fitting calculation yields $s_1 = 0.8$ and $s_2 = 10.0$ as optimum values. The curve provides a very satisfactory description of the experimental results. It may indicate that, at least from a phenomenological point of view, the penultimate model can describe the experimental results without taking into account any adjustable parameter. However, because of all approximations made in deriving the equations we have employed, as well as the large uncertainties involved in the overall copolymerization rate constants used to calculate $(k_p/k_t^{1/2})(fk_d)^{1/2}$, our present analysis can be considered conclusive only from a qualitative point of view.

Free-radical copolymerization of MMA–MA in benzene solution using the Fukuda nomenclature[27] shows an implicit penultimate-unit effect, which means that the penultimate unit only influences the absolute value of the copolymerization rate propagation constant, but does not influence the reactivity ratio values.

ACKNOWLEDGEMENTS

This work was supported by the CICYT through grants PG 89-0069 and MAT 381/91.

REFERENCES

1 Plochocka, K. *J. Macromol. Sci.-Rev. Macromol. Chem.* 1981, **C-20**, 67

2 Harwood, H. J. *Makromol. Chem. Macromol. Symp.* 1987, **10/11**, 331

3 Kratochvíl, P., Straková, D., Stejskal, J. and Tuzar, Z. *Macromolecules* 1983, **16**, 1136

4 Pichot, C., Zaganiaris, E. and Guyot, A. *J. Polym. Sci. Symp.* 1975, **52**, 55

5 You, H. and Tirrell, D. A. *J. Polym. Sci., Part A, Polym. Chem.* 1990, **28**, 3155

6 Pichot, C., Guyot, A. and Strazielle, C. *J. Polym. Sci., Polym. Chem. Edn* 1969, **17**, 2269

7 Busfield, W. K. and Low, R. B. *Eur. Polym.* 1975, **11**, 309

8 Stickler, M. *Makromol. Chem. Macromol. Symp.* 1987, **10/11**, 17

9 Grassie, N., Torrance, B. J. D., Fortune, J. D. and Gemmell, J. D. *Polymer* 1965, **6**, 653

10 McFarlane, R. C., Reilly, P. M. and O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Edn* 1980, **18**, 251

11 Bevington, J. C., Harris, D. O. and Johnson, M. *Eur. Polym. J.* 1966, **1**, 235

12 Zubov, V. P., Valuev, L. I., Kabanov, V. A. and Kargin, V. A. *J. Polym. Sci. A-1* 1971, **9**, 833

13 Kotera, A., Shima, M., Akiyama, K., Kume, M. and Miyakawa, M. *Bull. Chem. Soc. Jpn* 1966, **39**, 758

14 Shima, M. and Kotera, A. *J. Polym. Sci., Part A* 1963, **1**, 1115

15 Kelen, T. and Tüdos, F. *J. Macromol. Sci.-Chem.* 1975, **A-9**, 1

16 Procházka, O. and Kratochvíl, P. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21**, 3269

17 Fukuda, T., Ma, Y.-D. and Inagaki, H. *Macromolecules* 1985, **18**, 17

18 Davis, T. P., O'Driscoll, K. F., Pitton, M. C. and Winnik, M. A. *J. Polym. Sci., Polym. Lett. Edn* 1989, **27**, 181

19 Olaj, O. F., Schnöll-Bitai, I. and Kremminger, P. *Eur. Polym. J.* 1989, **25**, 535

20 Fukuda, T., Ma, Y.D. and Inagaki, H. *Makromol. Chem. Rapid Commun.* 1987, **8**, 495

21 O'Driscoll, K. F. and Davis, T. P. *J. Polym. Sci., Part C, Polym. Lett.* 1989, **27**, 417

22 O'Driscoll, K. F. and Huang, J. *Eur. Polym. J.* 1989, **25**, 629

23 Atherton, J. N. and North, A. M. *Trans. Faraday Soc.* 1962, **58**, 2049

24 Madruga, E. L., San Román, J. and Del Puerto, M. A. *Anal. Quim.* 1979, **75**, 294

25 López Madruga, B. E., Barrales-Rienda, J. M. and Guzmán, G. M. International Symposium on Macromolecular Chemistry, IUPAC, Budapest, Preprints, 1969, Vol. III, pp. 5–10

26 Davis, T. P., O'Driscoll, K. F., Piton, M. C. and Winnik, M. A. *Polym. Int.* 1991, **24**, 65

27 Fukuda, T., Mae, Y. D., Kubo, K. and Inagaki, H. *Macromolecules* 1991, **24**, 370