ELSEVIER

Polymer Vol. 37 No. 2, pp. 263-268, 1996

0032-3861/96/$15.00 + 0.00

A kinetic study on the radical copolymerization of dimethyl itaconate and methyl methacrylate in benzene

M. Fernández-García and E. L. Madruga*
Instituto de Ciencia y Tecnologia de Polimeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

and R. Cuervo-Rodríguez
Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense, Ciudad Universitaria s/n, 28040 Madrid, Spain
(Received 15 March 1995; revised 30 June 1995)

The copolymerization of dimethyl itaconate and methyl methacrylate with 2,2′-azobisisobutyronitrile was investigated kinetically at 50°C in benzene. The copolymer composition conforms to the terminal model within experimental error, but the variation of the copolymerization rate shows a penultimate effect on the propagation reaction. Homopolymerization kinetic coefficients for dimethyl itaconate monomer were also determined.

(Keywords: radical copolymerization; reactivity ratios; kinetics)

INTRODUCTION

During the last few years, interest in the properties and applications of monoesters and diesters derived from itaconic acid has increased, not only because itaconic acid is obtained by a fermentation process but also as a consequence of the great variety of polymers that can be prepared owing to the existence of two lateral esterifiable groups in the monomer[1-3]. Dialkyl itaconate esters (DRIs) are radically polymerized at moderate rates to yield polymers of high molecular weight in spite of their two bulky substituents[3-9]. The overall rate of polymerization of DRI is reported to be proportional to the square root of initiation concentration, whereas the kinetic order with respect to monomer concentration is higher than unity[4-6,9,10]. The overall activation energy of the polymerization is lower than those observed for conventional monomers such as methyl methacrylate or styrene[4,5,7,10]. In order to explain such behaviour, individual kinetics coefficients for each step of free-radical homopolymerization have been determined[4,8,10-12]. DRIs have homopropagation and homotermination rate coefficients lower than those found for the usual vinyl monomers, which indicates that steric effects of the substitutents play an important role in both homopropagation and homotermination rate constants[4,5,10].

On the other hand, a slight variation of homopropagation rate coefficients is noted on changing the monomer concentration, but efficiency factor and termination rate coefficient decrease with an increase of the monomer concentration[4,5,10]; this has been ascribed to the increase of the medium viscosity and/or chain-length dependence. It is well known, that termination rate coefficient is dependent on the chain length and Sato *et al.*[9] found a slope of –0.65 in the plot of termination rate coefficients vs. chain length. This value is higher than those found for methyl methacrylate (–0.15) or for styrene[13,14] (–0.24). Thus the large chain-length dependence of the termination rate coefficient seems to originate mainly from the dependence of termination rate on the monomer concentration. Besides, the kinetics parameters are modified as a function of the carbon number of the ester alkyl group. Thus, propagation and termination rate coefficients are reduced with an increase of the carbon number of the alkyl substituents, but the decrease of termination rate coefficient is larger than that for the propagation rate coefficient, giving rise to an increase of the overall rate of polymerization when the length of alkyl substituents increase[7-9].

Although no kinetics mechanisms have been studied, copolymerization of some DRI with styrene (S) has shown that the apparent copolymerization rate increase with the increase of S concentration in the feed[3,8,9]. The structure of alkyl substituents in the itaconate esters does not change the values of the reactivity ratios significantly when S is used as a comonomer, and the observed *Q*/*e* values indicate that DRI is an electron-acceptor and conjugative monomer[3,8,9]. On the other hand, the relative reactivity of DRI towards polystyrene radical was found to decrease slightly by the introduction of electron-donor and sterically hindered alkyl groups[3-9].

Only a few and opposite reactivity ratio values for free-radical copolymerization of DRI with methyl methacrylate (MMA) have been reported[1,9] but unfortunately no

---

* To whom correspondence should be addressed

experimental detail is given in the papers. Recently our group has reported kinetics studies for free-radical copolymerization of di-n-butyl itaconate (DBI) with MMA. Cumulative copolymer composition in a whole range of conversions[15,16] as a function of molar composition in the feed is well explained by the Mayo–Lewis terminal model (MLTM) not only at low but throughout all conversions. Changes in experimental values of overall copolymerization rate with the molar composition in the feed cannot be explained using the MLTM but they can be fitted with the penultimate Fukuda model[17,18]. So, using the Fukuda nomenclature[19] free-radical copolymerization of DBI-MMA shows an implicit penultimate-unit effect (IPUE), 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.

In order to gain additional insight into DRI–MMA copolymerization it is desirable to investigate the behaviour in composition as well as in kinetic trend of DRI with different substituents. These studies may contribute to a better understanding of the influence of substituents on the kinetics copolymerization of DRI with MMA. Therefore, this investigation focuses on the kinetics copolymerization of dimethyl itaconate (DMI) with MMA in the terms expressed above.

EXPERIMENTAL

Materials

The monomers, methyl methacrylate (MMA, Merck) and dimethyl itaconate (DMI, ICN-Flow) were purified by conventional methods[20]. 2, 2′-Azobisisobutyronitrile (AIBN) was purified by crystallization from methanol and benzene (Merck) for analysis, and 2,2′-diphenyl-1-picrylhydrazyl (DPPH, Fluka) was used without any further purification.

Purification

All experiments were carried out in Pyrex glass ampoules sealed off at high vacuum. DMI was polymerized at 50°C in a thermostatic bath, regulated with a precision of ±0.1°C, using AIBM as an initiator and benzene as a solvent ($[M] = 3\,\mathrm{mol\,l^{-1}}$). After the desired time, the reaction mixture was transferred to a vessel with a large excess of methanol containing a small amount of water and the precipitated polymer was filtered off, washed and dried at reduced pressure until constant weight. The rate of initiation for DMI was studied from dilatometric experiments carried out in the presence of various concentrations of DPPH inhibitor by using the experimental conditions mentioned before.

Copolymers of DMI and MMA (monomers 1 and 2, respectively) were prepared by free-radical polymerization of mixtures of both monomers with different compositions in a $3\,\mathrm{mol\,l^{-1}}$ benzene solution at 50°C using AIBN as initiator. The copolymer samples were isolated after the desired polymerization time by pouring the reaction mixture into a large excess of methanol containing a small amount of water. The precipitated samples were filtered off, washed and dried at reduced pressure until constant weight.

Copolymer analysis

^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy was used to determine copolymer composition. Spectra were recorded at room temperature on about 8% solutions in deuterochloroform by using a Varian Geminis spectrometer operating at 200 MHz.

RESULTS AND DISCUSSION

Copolymerization of dimethyl itaconate with methyl methacrylate

Free-radical copolymerization of DMI–MMA was carried out at 50°C in a $3\,\mathrm{mol\,l^{-1}}$ benzene solution using AIBN as initiator. Conversions were measured gravimetrically. Some of the results obtained are shown in *Figure 1*. As observed in *Figure 1*, low conversions were obtained to satisfy the differential copolymerization equation.

Copolymers were prepared using DMI molar fraction in the feed as near as possible to those determinated by the 'approximate design scheme' proposed by McFarlane *et al.*[21]. As described by Tidwell and Mortimer[22] this scheme uses optimally designed experiments in which the values of molar fractions in the feed are given by the following expressions:

$$f' = 2/(2 + r_1)$$

$$f'' = r_2/(2 + r_2)$$

However, recognizing that the reactivity ratios cannot be known exactly in advance, McFarlane *et al.*[21] suggested taking values of reactivity ratios that differed from r_1 and r_2 by 20%. Preliminary reactivity ratios were calculated using Q/e. Q and e values were taken from the literature[3,23]. In addition, a lower DMI molar fraction in the feed (0.210) was used. The average molar fraction composition of copolymers was determined by ^{1}H n.m.r. spectroscopy by comparing the integrated intensities of the carboxymethyl and α-methyl resonance signals, corresponding the first to both MMA and DMI and the second to MMA.

The average molar fraction composition in the copolymer, F_{DMI}, together with molar fraction composition in the feed, f_{DMI}, are given in *Table 1*. As seen in *Table 1* the experiments have been carried out using two different initiator concentrations, so copolymers with different chain length are obtained. However, although Semichikov *et al.*[24] have noted an effect of chain length on copolymer composition, in our experimental conditions the copolymer molecular weight obtained does not apparently modify the composition. The application of all the data collected in *Table 1* to the Kelen–Tüdos linearization method[25] gave the diagram in *Figure 2*. From the slope and intercept of the straight line the value of r_{DMI} and r_{MMA} were calculated and are reported in *Table 2*. The reactivity ratios were also determined by application of the non-linear least-squares analysis suggested by Tidwell and Mortimer[22]; their values are also collected in *Table 2*, and are very close to those calculated by the Kelen–Tüdos linearization method. The dimensions of the elliptical diagrams (*Figure 3*) generated for the 95% confidence limits for the reactivity ratios quoted in *Table 2* are similar, which indicates that under well-designed experimental conditions the Kelen–Tüdos linearization method may be used with almost as

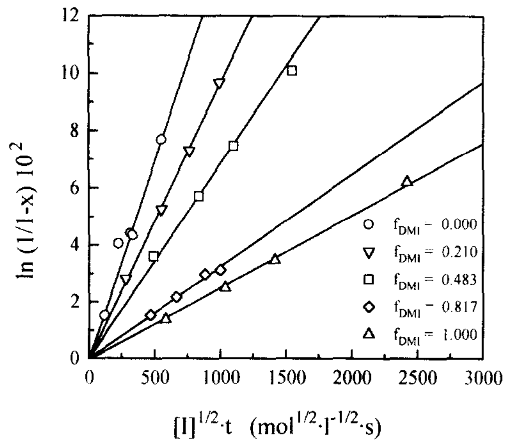

Figure 1 Radical copolymerization of DMI–MMA system in 3 mol l^{-1} benzene solution

Table 1 Analytical data for the copolymerization of dimethyl itaconate with methyl methacrylate at 50°C in a 3 mol l^{-1} benzene solution using AIBN as initiator

$[I]$ (10^3 mol l^{-1})	Time (min)	f_{DMI} (feed)	Conversion (%)	F_{DMI} (copolymer)
1.5	120	0.21_0	2.82	0.15_4
15	75	0.21_0	5.26	0.16_6
1.5	330	0.21_0	7.32	0.16_2
15	135	0.21_0	9.68	0.16_8
1.5	210	0.38_3	3.61	0.27_7
1.5	360	0.38_3	5.72	0.27_9
15	150	0.38_3	7.48	0.26_8
15	210	0.38_3	10.10	0.28_4
1.5	120	0.43_8	1.93	0.34_0
1.5	210	0.48_8	3.41	0.34_1
15	95	0.43_8	4.58	0.32_7
15	125	0.43_8	6.01	0.32_2
1.5	120	0.48_3	1.65	0.37_4
1.5	210	0.48_3	3.07	0.37_4
15	95	0.48_3	4.25	0.37_5
15	130	0.48_3	5.81	0.38_7
1.5	240	0.74_9	2.04	0.60_5
1.5	370	0.74_9	2.63	0.60_7
15	150	0.74_9	4.33	0.60_6
15	210	0.74_9	5.82	0.60_4
1.5	240	0.78_1	2.13	0.61_9
1.5	360	0.78_1	3.42	0.66_2
15	150	0.78_1	3.84	0.65_0
15	210	0.78_1	5.52	0.65_3
1.5	200	0.81_7	1.54	0.68_4
15	90	0.81_7	2.17	0.68_2
15	120	0.81_7	2.98	0.69_0
1.5	430	0.81_7	3.14	0.72_2

much confidence as a non-linear least-squares procedure, which has also been indicated by McFarlane *et al.*[21].

In order to have a semiquantitative estimation of the alkyl length effect on the reactivity of itaconic acid derivatives, the rate constant for cross-propagation can be evaluated from the combination of monomer reactivity ratios for M_1 (DRI) and M_2 (MMA) ($r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$) with k_ps of the respective monomers (k_{11} and k_{22}). The monomer reactivity ratios for DBI with MMA[15] are $r_{DBI} = 0.717$ and $r_{MMA} = 1.283$. The k_p value for MMA[26] is 602 l mol^{-1} s^{-1} at 50°C, while for DMI and DBI[7] the values are 10 and 5.9 l mol^{-1} s^{-1}, respectively. The values of k_{12} for addition of poly(DRI) radical to MMA and the k_{21} value for addition of poly(MMA) radical to DRI are calculated as in *Table 3*.

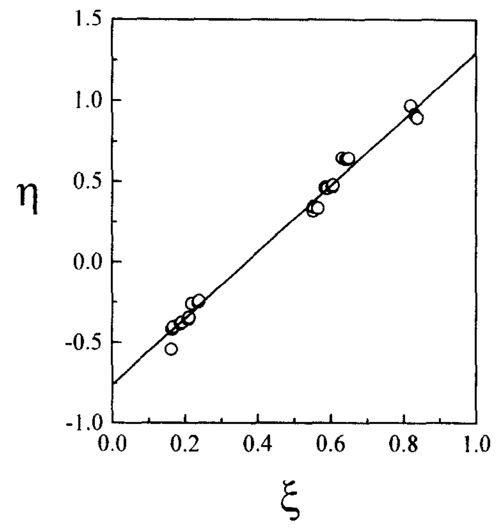

Figure 2 Data of DMI–MMA copolymerization system plotted according to the Kelen–Tüdos equation

Table 2 Monomer reactivity ratios for radical copolymerization of DMI with MMA at 50°C in a 3 mol l^{-1} benzene solution

Method	r_{DMI}	r_{MMA}
Kelen–Tüdos	0.417 ± 0.009	1.283 ± 0.015
Tidwell–Mortimer	0.419	1.297

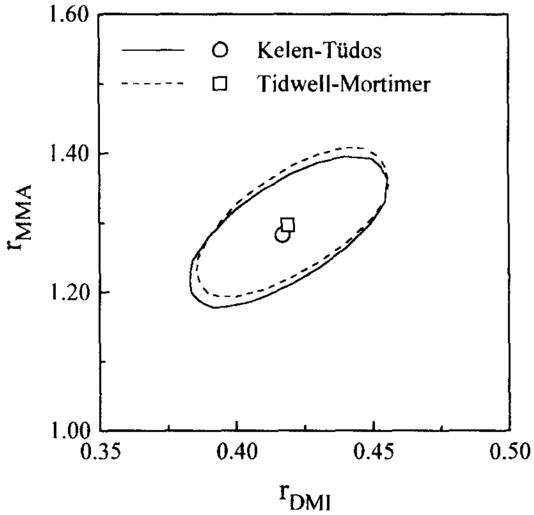

Figure 3 The 95% confidence regions for DMI–MMA reactivity ratios

Table 3 Rate constant for cross-propagation (k_{ij}) in copolymerization of DRI (M_1) with MMA (M_2) in benzene

Radical	Monomer	k_{ij} (l mol^{-1} s^{-1})
DMI	MMA	24
DBI	MMA	8
MMA	DMI	469
MMA	DBI	453

The reactivity of DBI monomer towards poly(MMA) radical is rather similar to that for DMI, but poly(DBI) radical is less reactive than poly(DMI) radical towards MMA monomer by a factor of three. Thus, the steric hindrance of the alkyl groups decreases the reactivity of DRI. A similar behaviour is found when copolymerization of DRI with S is considered[3,9].

Homopolymerization and copolymerization kinetics analysis

The rate of homopolymerization at low conversion can be expressed as:

$$\frac{dx}{dt} = \frac{k_p}{\sqrt{k_t}}(2f\,k_d[I])^{1/2}(1-x) \tag{1}$$

where x is the conversion defined as the weight fraction of monomer converted to polymer; k_d, k_p and k_t are the constants for initiation decomposition, propagation and termination reactions, respectively. [I] is the concentration of initiator and f is the efficiency of initiator. If the initiator has a half-life which is long compared to the time required to achieve a moderate conversion, this expression can be integrated to give

$$-\ln(1-x) = \frac{k_p}{\sqrt{k_t}}(2f\,k_d[I])^{1/2}t \tag{2}$$

A plot of $-\ln(1-x)$ vs. $[I]^{1/2}t$ for data at a single temperature is expected to yield one straight line for initiator concentration, the slope of which is the overall polymerization rate coefficient $K = k_p(2f\,k_d/k_t)^{1/2}$. The use of such a plot has been reported previously by Crosato-Arnaldi *et al.*[27] for suspension polymerization of vinyl chloride, by Cardenas and O'Driscol[28] for bulk and solution homopolymerization of ethyl methacrylate, and by Tulig and Tirrell[29] for bulk homopolymerization of methyl methacrylate.

The results for the homopolymerization of DMI and MMA at 50°C in a 3 mol l^{-1} benzene solution are plotted in the form of equation (2) in *Figure 1*. The overall polymerization rate coefficients were 2.53×10^{-5} and 13.96×10^{-5} l mol^{-1} s^{-1} for DMI and MMA, respectively.

The initiation rate R_i was determined by an inhibition method using DPPH as an inhibitor:

$$R_i = \frac{Z_0}{t_i} \tag{3}$$

where Z_0 and t_i are the concentration of inhibitor and the induction period, respectively. Values for R_i of DMI at 50°C were calculated from the slope of *Figure 4*, in which the concentration of DPPH against the induction period is presented. From the R_i value obtained and considering the initiator concentration used in our experiments (1.5×10^{-2} mol l^{-1}), the value of $2f\,k_d$ is 1.98×10^{-6} s^{-1}. A value of $2f\,k_d = 3.38 \times 10^{-6}$ s^{-1} has been obtained previously under the same experimental conditions for MMA homopolymerization[15].

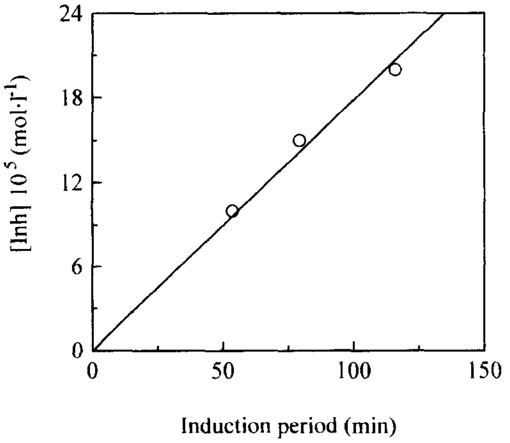

Figure 4 Determination of R_i in a 3 mol l^{-1} benzene solution at 50°C for DMI. [AIBN] = 1.5×10^{-2} mol l^{-1}

Table 4 Polymerization rates and kinetics coefficients for the system dimethyl itaconate–methyl methacrylate at 50°C in benzene solution

f_{DMI} (feed)	R_p (10^5 mol l^{-1} s^{-1})	$2fk_d$[a] (10^6 s^{-1})	$\bar{w}$ (10^2 l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$)
0.000	5.13	3.38	7.18
0.210	3.54	3.08	5.50
0.383	2.50	2.84	4.04
0.438	2.41	2.77	3.94
0.483	2.24	2.70	3.71
0.749	1.40	2.33	2.50
0.781	1.32	2.29	2.38
0.817	1.23	2.24	2.24
1.000	0.93	1.98	1.81

[a] Estimated from equation (6)

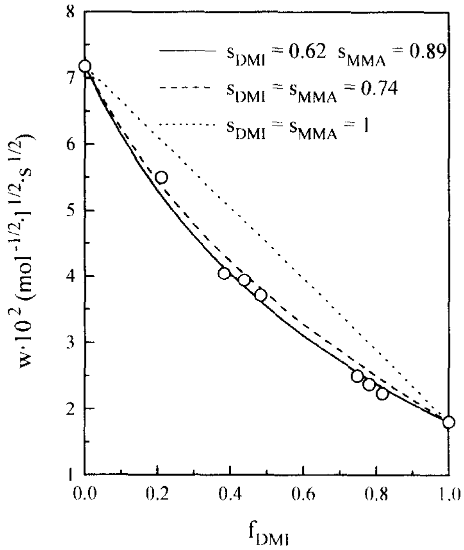

Figure 5 Plot of $\bar{w}$ *versus* f_{DBI} for the system DMI–MMA–benzene–AIBN at 50°C

Once the initiator rate was determined, the ratio $k_p/k_t^{1/2}$ was evaluated from

$$\frac{K}{(2f\,k_d)^{1/2}} = \frac{k_p}{\sqrt{k_t}} \tag{4}$$

Values of $k_p/k_t^{1/2}$ were calculated to be 0.018 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ and 0.072 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ for DMI and MMA, respectively. Values of $k_p/k_p^{1/2}$ for DMI[7] of 0.013 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ and for MMA[30] of 0.087 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ have been reported.

The rate of copolymerization can be expressed as analogous to that of homopolymerization, but using average, composition-dependent values for the rate parameters[31]. Thus

$$\frac{dx}{dt} = \frac{\bar{k}_p}{\sqrt{\bar{k}_t}}(2\bar{f}\bar{k}_d[I])^{1/2}(1-x) \tag{5}$$

in which composition-dependent parameters are denoted by an overbar. Therefore, in order to determine overall copolymerization coefficient $\bar{K}$, an equation similar to equation (2) can be used when the copolymerization time is short compared to the half-life of initiator. *Figure 1* shows the results of some kinetics measurements made in DMI–MMA copolymerization.

The rate coefficients of initiation in the copolymerization vary linearly with monomer feed composition ($f_i, i = 1$ or 2) according to the following empirical relationship[31]:

$$(2\overline{fk}_\mathrm{d}) = f_1(2fk_\mathrm{d})_1 + f_2(2fk_\mathrm{d})_2 \tag{6}$$

Overall copolymerization rate coefficient (R_p) extracted from *Figure 1*, the estimated rate of initiation coefficient, $2\overline{fk}_\mathrm{d}$, from equation (6), together with the $\bar{k}_\mathrm{p}/\bar{k}_\mathrm{t}^{1/2}$ ($= \bar{W}$) parameters are collected in *Table 4*.

The experimental values of $\bar{k}_\mathrm{p}/\bar{k}_\mathrm{t}^{1/2}$, which are higher when MMA in the feed increases, have been plotted in *Figure 5* as a function of DMI monomer feed composition.

Before the 1980s it was thought that variation of copolymerization rate as a function of molar fraction of the monomer feed was mainly due to changes in termination reactions[32]. However, in 1985 Fukuda *et al.*[17] showed that the copolymerization termination rate constant is a diffusion-controlled process, its average values being represented by a simple weighted average of the homotermination rate constants for both homopolymers, according to the ideal termination model proposed by Atherton and North[33]. Also, Fukuda *et al.*[17] noted that copolymerization termination constants are reasonably well described by the Walling model[34] with $\phi = 1$. Furthermore, Fukuda *et al.*[17] showed that the copolymerization propagation rate constant cannot be expressed, following the Mayo–Lewis terminal model, as a function of homopropagation rate constants (k_{ii}) and monomer reactivity ratios (r_i) weighted by the monomer feed composition, $[f_i = (1 - f_j)]$:

$$k_\mathrm{p} = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{(r_1 f_1/k_{11}) + (r_2 f_2/k_{22})} \tag{7}$$

The copolymerization propagation rate constant has been interpreted as a consequence of the penultimate effect on the propagation reaction[17,35–38].

According to the penultimate model and following the nomenclature of Fukuda *et al.*[17,37], k_p can be expressed by equation (7), where k_{11} and k_{22} represent the following functions:

$$\begin{aligned} k_{11} &= \frac{k_{111}(r_1 f_1 + f_2)}{(r_1 f_1 + f_2 s_1^{-1})} \\ k_{22} &= \frac{k_{222}(r_2 f_2 + f_1)}{(r_2 f_2 + f_1 s_2^{-1})} \end{aligned} \tag{8}$$

$$s_1 = \frac{k_{211}}{k_{111}} \quad \text{and} \quad s_2 = \frac{k_{122}}{k_{222}} \tag{9}$$

where k_{ijm} is the rate constant for the terminal radical j with penultimate unit i, adding to monomer m. The penultimate influence is asserted through the parameters s_1 and s_2 which do not influence either the composition or sequence distribution[39]. So, the 'terminal model' can therefore be seen as a special case of the penultimate model is $s_1 = s_2 = 1$.

A similar test of the penultimate model may be done using the overall copolymerization parameter $\bar{k}_\mathrm{p}/\bar{k}_\mathrm{t}^{1/2}$. Thus Fukuda *et al.*[18] proposed the following equation system:

$$\bar{w} = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{(r_1 f_1/\bar{w}_1) + (r_2 f_2/\bar{w}_2)} \tag{10}$$

where $\bar{w} = \bar{k}_\mathrm{p}/\bar{k}_\mathrm{t}^{1/2}$ and $\bar{w}_1$ and $\bar{w}_2$ are given by:

$$\bar{w}_i = \frac{w_i(r_i f_i + f_j)}{r_i f_i + f_j s_i^{-1}} \tag{11}$$

with $w_i = k_{iii}/k_{\mathrm{t}i}^{1/2}$ and $j \neq i = 1$ or 2.

Homopolymerization coefficients, w_i, together with the reactivity ratio values mentioned above and the experimental rate coefficients of copolymerization, $\bar{w}$, obtained using an overall monomer concentration of $3\,\mathrm{mol\,l^{-1}}$, allow s_1 and s_2 to be determined by a fitting procedure.

The theoretical curve of rate of copolymerization $\bar{w} = \bar{k}_\mathrm{p}/\bar{k}_\mathrm{t}^{1/2}$ vs. DMI monomer feed composition considering $s_1 = s_2 = 1$ is shown in *Figure 5* as a dotted curve. This curve shows that the 'terminal model' fails to predict rate coefficient $\bar{w}$ for the copolymerization of DMI with MMA.

Fukuda *et al.*[40], using a model based on radical stabilization energy which varies according to the nature of the penultimate unit, have suggested that $r_1 r_2 = s_1 s_2$ with $s_1 = s_2$. From this prediction the values found are $s_1 = s_2 = 0.74$ and the theoretical curve drawn with these data (dashed curve in *Figure 5*) seems to fit the experimental data. However, a best fit of data can be done if we do not apply the constraint $s_1 = s_2$. In this way, the solid curve represented in *Figure 5* has been calculated used equation (10) with $s_1 = 0.620$ and $s_2 = 0.890$, being $s_1 = r_1 r_2/s_2$. The standard deviations from the experimental and theoretical data are 18.4% for the terminal model, 6.59% for the penultimate model with $s_1 = s_2 = 0.74$, and 3.15% for the penultimate model with $s_1 = 0.620$ and $s_2 = 0.890$. Considering the standard deviations mentioned above, it seems that the penultimate model is useful at least as a phenomenological model.

In a previous work[15], the chain-end reactivity ratios for di-n-butyl itaconate ($\mathrm{M_1}$)–methyl methacrylate ($\mathrm{M_2}$) system copolymerized at 50°C in a $3\,\mathrm{mol\,l^{-1}}$ benzene solution were measured. Values found for chain-end reactivity ratios were $s_1 = 0.691$ and $s_2 = 1.379$. The values of s_1 for DMI–MMA and DBI–MMA are similar and less than unity. These results indicate that when the penultimate unit is MMA it has a similar effect on the propagation rate of both itaconate derivatives. However, when dimethyl itaconate or di-n-butyl itaconate is the penultimate unit it has a different influence on the rate. In this way the DBI–MMA radical seems to be more reactive towards MMA monomer than is the MMA–MMA radical, whereas in the case of the DMI–MMA radical the reverse might be true. However, considering the error inherent in the experimental procedure, no definitive statement can be made regarding the penultimate unit effect of itaconate derivatives.

ACKNOWLEDGEMENT

This work has been partially supported by CICYT through grant PB93–1250.

REFERENCES

1 Tate, B. E. in 'Vinyl and Diene Monomers' (Ed. E. C. Leonard), Wiley Interscience, New York, 1970, p. 205

2 Cowie, J. M. G. *Pure Appl. Chem.* 1979, **51**, 2331

3 Otsu, T., Watanabe, H., Yang, J. Z., Yoshioka, M. and Matsumoto, A. *Makromol. Chem. Macromol. Symp.* 1992, **63**, 87

4 Otsu, T. and Watanabe, H. *Eur. Polym. J.* 1993, **29**, 167

5 Otsu, T., Hirose, Y., Seno, M., Tanaka, H., Uchiumi, N. and Matsumoto, M. *Eur. Polym. J.* 1994, **30**, 347

6 Sato, T., Inui, S., Tanaka, H., Ota, T., Kamachi, M. and Tanaka, K. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 637

7 Sato, T., Morino, K., Tanaka, H. and Ota, T. *Makromol. Chem.* 1987, **188**, 2951

8 Sato, T., Morita, M., Tanaka, H. and Ota, T. *J. Polym. Sci., Polym. Chem. Edn* 1989, **27**, 2497

9 Sato, T., Takahashi, Y., Seno, M., Nakamura, H., Tanaka, H. and Ota, T. *Makromol. Chem.* 1991, **192**, 2909

10 Otsu, T., Yamagishi, K. and Yoshioka, M. *Macromolecules* 1992, **25**, 2713

11 Otsu, T., Yamagishi, K., Matsumoto, M., Yoshioka, M. and Watanabe, H. *Macromolecules* 1993, **26**, 3026

12 Sato, T., Schimizu, T., Seno, M., Tanaka, H. and Ota, T. *Makromol. Chem.* 1992, **193**, 1439

13 Mahabadi, H. K. *Makromol. Chem., Macromol. Symp.* 1987, **10/11**, 127

14 Mahabadi, H. K. *Macromolecules* 1985, **18**, 1319; 1991, **24**, 606

15 Madruga, E. L. and Fernández-García, M. *Polymer* 1994, **35**, 4437

16 Madruga, E. L. and Fernández-García, M. *Eur. Polym. J.* in press

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

18 Fukuda, T., Ma, Y. D., Kubo, K. and Tankada, A. *Polym. J.* 1989, **21**, 1003.

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

20 Stickler, M. *Makromol. Chem., Maromol. Symp.* 1987, **10/11**, 17

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

22 Tidwell, P. W. and Mortimer, G. A. *J. Polym. Sci. (Part A)* 1965, **3**, 369

23 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 3rd edn, Wiley Interscience, New York, 1989

24 Semchikov, J. D., Smirnova, L. A., Knyazeva, T. J., Bulgakova, S. A. and Sherstyanyskh, V. I. *Eur. Polym. J.* 1990, **26**, 883

25 Kelen, T. and Tüdos, F. *J. Macromol. Sci., Chem. (A)* 1975, **9**, 1

26 Hutchinson, R. A., Aroson, M. T. and Richards, J. R. *Macromolecules* 1993, **26**, 6410

27 Crosato-Arnaldi, A., Gasparini, P. and Talamini, G. *Makromol. Chem.* 1968, **117**, 140

28 Cardenas, J. N. and O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Edn* 1977, **15**, 2097

29 Tulig, T. and Tirrell, M. *Macromolecules* 1982, **15**, 459

30 Eastmond, G. C. *Makromol. Chem., Macromol. Symp.* 1987, **10/11**, 71

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

32 Russo, S. *Makromol. Chem., Macromol. Symp.* 1987, **10.11**, 395

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

34 Walling, C. *J. Am. Chem. Soc.* 1949, **71**, 1930

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

36 Davis, T. P., O'Driscoll, K. F., Pitton, M. C. and Winnik, M. A. *J. Polym. Sci., Polym. Lett. Edn* 1989, **27**, 1981

37 Fukuda, T., Kubo, K. and Ma, Y. D. *Prog. Polym. Sci.* 1992, **17**, 875

38 O'Driscoll, K. F. *Makromol. Chem., Macromol. Symp.* 1992, **53**, 53

39 O'Driscoll, K. F. and Davis, T. P. *J. Polym. Sci., Polym. Lett. Edn* 1989, **27**, 417

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