Free-radical homopolymerization and copolymerization of di-n-butyl itaconate

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Di-n-butyl itaconate (DBI) was polymerized at 50°C in a $3\,\mathrm{mol\,l^{-1}}$ benzene solution using 2,2′-azobisisobutyronitrile (AIBN) as a free-radical initiator. Kinetic constants for DBI were obtained as follows: $k_p/k_t^{1/2}=0.021\,\mathrm{mol^{-1/2}\,l^{1/2}\,s^{-1/2}}$, $2fk_d=3.62\times10^{-6}\,\mathrm{s^{-1}}$. Copolymerization reaction between DBI and methyl methacrylate (MMA), under the same experimental conditions, was carried out and the values of $r_{\mathrm{DBI}}=0.717\pm0.11$ and $r_{\mathrm{MMA}}=1.329\pm0.09$ were found for the reactivity ratios. Applying the Q–e scheme led to $Q=0.61$ and $e=0.62$ for DBI. Overall copolymerization rate coefficients have been analysed on the basis of terminal and penultimate effects on the propagation reaction. These parameters as well as the copolymer composition are not affected by total monomer concentration.

(Keywords: free-radical polymerization; di-n-butyl itaconate; kinetics)

INTRODUCTION

Recently keen attention has been paid to the dialkyl itaconate esters (DRI) since they are radically polymerized at moderate rates to yield polymers of high molecular weights in spite of their two bulky substituents[1–7]. The fundamental monomer, itaconic acid, is not an oil-based product, but is obtained commercially by a fermentation process[8]. Furthermore, one can regard poly(itaconic acid diesters) as poly(alkyl methacrylates) in which one hydrogen of the α-methyl group is replaced by a second ester group and, as might be expected, poly(di-n-alkyl itaconates) exhibit many of the properties associated with the poly(alkyl methacrylates)[9,10].

In the homopolymerization of DRI, overall rate of polymerization (R_p) is reported to be proportional to the square root of initiator concentration, indicating that bimolecular termination occurs in these polymerization systems. However, the orders with respect to the monomer are higher (between 1.6 and 2.0) than those observed for usual polymerization of vinyl monomers[1–3,7].

From R_p and initiation rate of polymerization (R_i) of some DRIs together with the concentration of propagating polymer radicals determined from e.s.r. spectroscopy, homopropagation (k_p) and homotermination (k_t) rate coefficients have been estimated[1,2,4,5]. Values found for both, k_p and k_t, are smaller than those for the usual vinyl monomers and Otsu *et al.*[5] indicate that the high reactivity of DRI may arise from the consequence that k_t are small enough to compensate for the low k_p.

On the other hand, copolymerization of some DRI with styrene (S) has been carried out, showing that the apparent copolymerization rate increases with the increase of S concentration in the feed[5–7]. The structure of the alkyl substituents in the itaconate esters does not change the values of the reactivity ratios significantly when S is used as a comonomer. From the observed Q/e values, all DRIs were found to be electron-accepting and conjugative monomers[5–7].

Only a few and opposite reactivity ratio values[8] for the free-radical copolymerization of DRI with methyl methacrylate (MMA) have been reported, the values obtained for Q and e parameters being very different from those obtained from the copolymerization with S. Furthermore, critical tests of terminal or other kinetic models for the overall copolymerization rate of DRI have not been examined. So this paper is focused on the kinetic copolymerization study of a DRI, di-n-butyl itaconate, with MMA. Besides the determination of the reactivity ratio values, the mechanism of the overall copolymerization rate will be examined.

EXPERIMENTAL

Materials

The monomers, methyl methacrylate (MMA; Merck) and di-n-butyl itaconate (DBI; ICN-Flow), were purified by conventional methods[11]. 2,2′-Azobisisobutyronitrile (AIBN) was purified by crystallization from methanol, and benzene (Merck) for analysis and 2,2′-diphenyl-1-picrylhydrazyl (DPPH) (Fluka) were used without any further purification.

Polymerization

All experiments were carried out in Pyrex glass dilatometers, sealed off at high vacuum. DBI and MMA were polymerized at 50°C in a thermostatic bath, regulated with a precision of ±0.1°C, using AIBN as an initiator ($[\mathrm{I}]=1.5\times10^{-2}\,\mathrm{mol\,l^{-1}}$) and benzene as a solvent ($[\mathrm{M}]=3\,\mathrm{mol\,l^{-1}}$). After the desired time, the

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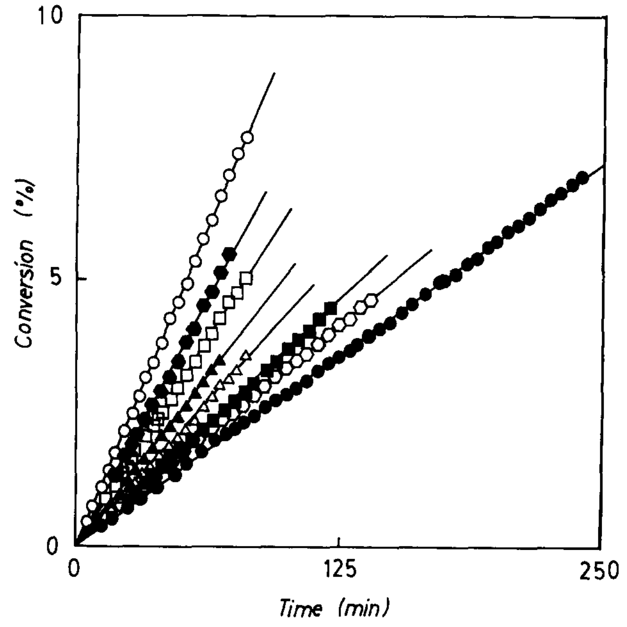

Figure 1 Radical copolymerization of DBI/MMA systems in 3 mol l^{-1} benzene solution. f_{DBI}: (●) 1.0, (○) 0.798, (■) 0.698, (△) 0.491, (▲) 0.449, (□) 0.301, (●) 0.199, (○) 0.0

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 rates of initiation of both DBI and MMA were studied from dilatometric experiments carried out in the presence of various concentrations of DPPH inhibitor by using the experimental conditions mentioned before.

Copolymers of DBI and MMA (monomers 1 and 2, respectively throughout the work) were prepared by free-radical polymerization of mixtures of both monomers with different compositions, in benzene at 50°C. The total concentration of monomers was 3 or 5 mol l^{-1} and the concentration of AIBN was 1.5×10^{-2} mol l^{-1}. The copolymer samples were isolated after the polymerization time desired, 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 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 methyl methacrylate with di-n-butyl itaconate

Free-radical copolymerization of MMA/DBI was carried out at 50°C in a 3 or 5 mol l^{-1} benzene solution using 1.5×10^{-2} mol l^{-1} of AIBN as initiator. Conversions were measured dilatometrically, and then tested by gravimetry. Some of the obtained results are shown in *Figure 1*. As can be observed in *Figure 1*, conversions lower than 8% were obtained to satisfy the differential copolymerization equation. Copolymers were prepared using DBI molar fraction in the feed ranging from 0.03 to 0.8.

The average molar fraction composition of copolymers was determined by ^{1}H n.m.r. spectroscopy, considering the carboxymethyl and the carboxymethylene resonance signals of the MMA and of the DBI, respectively. Spectra are shown in *Figure 2*, which also include those of poly(methyl methacrylate) and of poly(di-n-butyl itaconate). The average molar fraction composition of copolymers (F_{DBI}), together with molar fraction composition of monomer feed (f_{DBI}), are quoted in *Table 1*.

A Kelen–Tüdös plot[12] is shown in *Figure 3*, the corresponding reactivity ratios being $r_{DBI} = 0.717 \pm 0.11$ and $r_{MMA} = 1.329 \pm 0.09$. From these reactivity ratio values, predicted copolymer compositions are rather

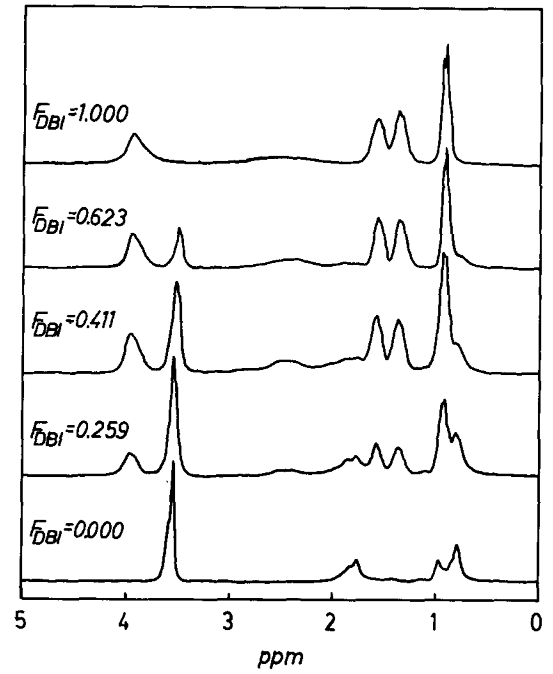

Figure 2 ^{1}H n.m.r. spectra of homopolymers and copolymer samples of DBI/MMA prepared by free-radical copolymerization at 50°C in 3 mol l^{-1} benzene solution. F_{DBI} correspond to the molar fraction of DBI in the copolymer samples

Table 1 Analytical data for the copolymerization of d-n-butyl itaconate with methyl methacrylate at 50°C in benzene solution using AIBN as initiator

[DBI] + [MMA] (mol l^{-1})	f_{DBI}	Conversion (%)	F_{DBI} Expt.	F_{DBI} Calc.
3.0	0.035	6.46	0.026	0.027
	0.064	6.04	0.043	0.049
	0.065	8.05	0.056	0.050
	0.199	5.34	0.165	0.157
	0.301	5.09	0.246	0.243
	0.301	5.97	0.259	0.243
	0.449	3.61	0.377	0.376
	0.453	8.77	0.382	0.380
	0.491	3.86	0.411	0.416
	0.547	4.18	0.459	0.470
	0.599	3.17	0.512	0.523
	0.698	4.47	0.623	0.628
	0.798	4.64	0.732	0.740
5.0	0.301	4.82	0.272	0.243
	0.492	4.05	0.416	0.417
	0.700	4.75	0.628	0.630

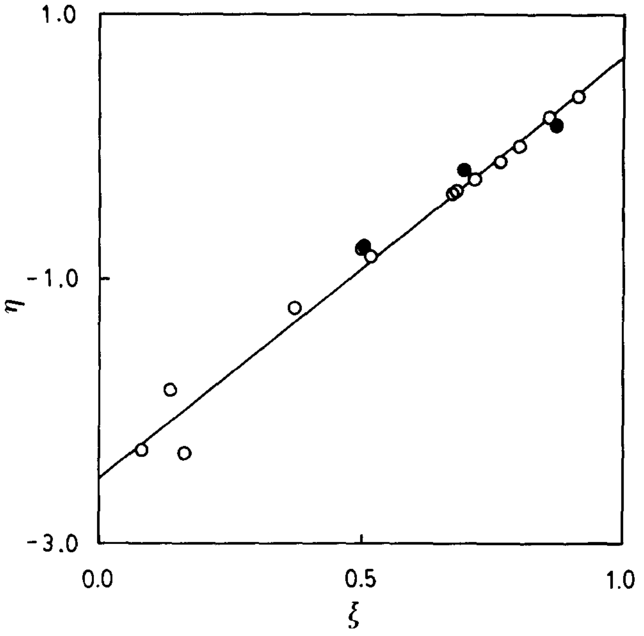

Figure 3 Data of DBI/MMA copolymerization system plotted according to the Kelen–Tüdös equation. Feed composition for [DBI] +[MMA] = 3 mol l^{-1} (○) and 5 mol l^{-1} (●)

Table 2 Copolymerization Q and e parameters

Q_{DBI}	e_{DBI}	Ref.
0.61	0.62	This work
0.47	0.77	3
0.49	0.73	7

close to experimental values, even when total monomer concentration in the feed is 5 mol l^{-1}. This fact seems to indicate that no changes in the reactivity ratio values can be expected with the dilution.

Q and e values for DBI were calculated from the reactivity ratios considering the corresponding Q and e values of MMA reported in the literature[13], and their values are shown in *Table 2* together with those reported using the reactivity ratios found in the free-radical copolymerization of styrene with di-n-butyl itaconate. As can be observed in *Table 2*, the Q and e values for di-n-butyl itaconate obtained from copolymerization of this monomer with methyl methacrylate are different from those obtained from the copolymerization of di-n-butyl itaconate with styrene. In order to assess these values, it is necessary to consider that spectroscopic data are related to the Q and e parameters. In this way, it has been reported by Ito *et al.*[14] that a linear relationship exists between $\log Q$ and the maximum absorption wavelength, λ_{max}, of the double bond in vinyl monomers, as follows:

$$\log Q = -10.88 + (5.175 \times 10^{-2})\lambda_{max} \qquad (1)$$

A value of 207 nm in methanol has been found for the absorption maximum wavelength of the di-n-butyl itaconate double bond. Using this λ_{max} value in equation (1), Q has been bound to be 0.68, which agrees well with 0.61 obtained from MMA copolymerization.

On the other hand, it has been recognized that there is a linear relationship between the relative reactivity of vinyl monomers and the chemical shift of the β-hydrogens in the ^{1}H n.m.r. or the β-carbon in the ^{13}C n.m.r. spectra, which is related to the electron density of the carbon–carbon double bond[15]. Therefore, the value of parameter e increases with increasing chemical shift of the β-carbon of the corresponding vinyl compound. Herman and Teyssie[15] have suggested that the parameter e for vinyl monomers may be estimated approximately from the chemical shift of the β-carbon according to the equation:

$$e = \frac{\delta_{C\beta}(\text{ppm/TMS}) - 113.5}{22} \qquad (2)$$

The application of equation (2) to the $\delta_{C\beta}$ of di-n-butyl itaconate (127.4 ppm) gives a value of $e = 0.63$, very close to that calculated from the reactivity ratios determined in this work. The qualitative agreement found between Q and e values obtained in this work with spectroscopic measured data seems to indicate that the obtained Q and e parameters of DBI when this monomer is copolymerized with MMA are more reliable than those obtained when DBI is copolymerized with styrene.

Homopolymerization of di-n-butyl itaconate and methyl methacrylate

Di-n-butyl itaconate was polymerized at 50°C in benzene solution, [DBI] = 3 mol l^{-1}, using AIBN as a free-radical initiator, [AIBN] = 1.5×10^{-2} mol l^{-1}. Methyl methacrylate was also polymerized under the same experimental conditions.

The overall rates of homopolymerization, determined dilatometrically, were 1.44×10^{-5} and 4.85×10^{-5} mol l^{-1} s^{-1} for DBI and MMA, respectively.

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

$$R_i = Z_0 / t_i \qquad (3)$$

where Z_0 and t_i are the concentration of inhibitor and the induction period, respectively. Values of R_i for both, DBI and MMA at 50°C, were calculated from the slopes of *Figure 4*, in which the concentration of DPPH against the induction period is represented.

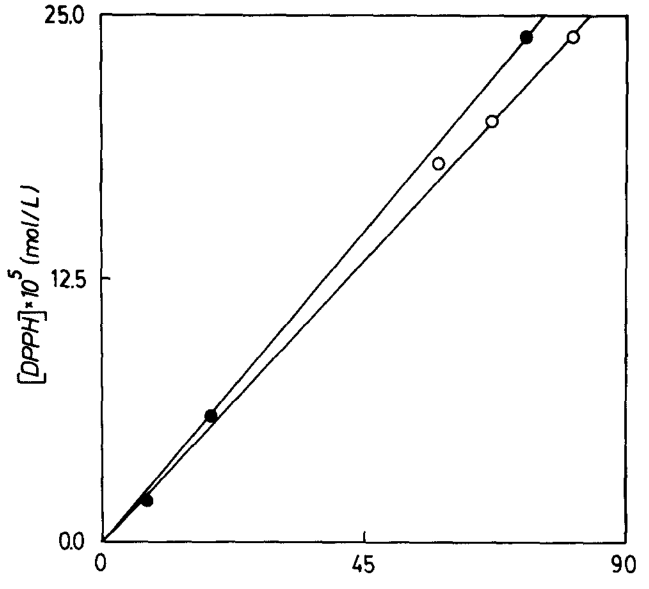

Figure 4 Determination of R_i in a 3 mol l^{-1} benzene solution at 50°C for MMA (○) and DBI (●). [AIBN] = 1.5×10^{-2} mol l^{-1}

Table 3 Polymerization rates and kinetics coefficients for the system di-n-butyl itaconate/methyl methacrylate at 50°C in benzene solution

[DBI]+[MMA] (mol l^{-1})	f_{DBI}	$R_p \times 10^5$ (mol l^{-1} s^{-1})	$(2fk_d) \times 10^6$ (s^{-1})^a	$\bar{w} \times 10^2$ (mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$)
3.0	0.000	4.85	3.38	7.18
	0.035	4.55	3.39	6.74
	0.064	4.14	3.40	6.13
	0.065	4.42	3.40	6.51
	0.199	3.61	3.43	5.29
	0.301	3.10	3.45	4.52
	0.301	3.20	3.45	4.68
	0.449	2.58	3.49	3.75
	0.453	2.55	3.49	3.69
	0.491	2.38	3.50	3.48
	0.547	2.11	3.51	3.04
	0.599	1.93	3.52	2.82
	0.698	1.83	3.55	2.65
	0.798	1.63	3.57	2.33
	1.000	1.44	3.62	2.05
5.00	0.301	4.90	3.45	4.31
	0.492	4.17	3.50	3.31
	0.700	3.24	3.55	2.81

^{a}Estimated from equation (8)

In the presence of initiator, the initiation rate is given by:

$$R_i = 2fk_d[I] \qquad (4)$$

where f, k_d and [I] are the initiator efficiency, the decomposition rate constant of the initiator and the concentration of initiator, respectively. From the R_i obtained and considering the initiator concentration used in our experiments (1.5×10^{-2} mol l^{-1}) the values of $2fk_d$ are 3.38×10^{-6} s^{-1} and 3.62×10^{-6} s^{-1} for MMA and DBI respectively.

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

$$k_p/k_t^{1/2} = k/(2fk_d[I])^{1/2} \qquad (5)$$

k being the slope of the dilatometric plot, i.e. the overall polymerization rate coefficient. Values of $k_p/k_t^{1/2}$ were calculated to be 0.072 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ and 0.021 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ for MMA and DBI, respectively. Values of $k_p/k_t^{1/2}$ for MMA of 0.087 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ (ref. 16) and for DBI of 0.026 mol$^{-1/2}$ l$^{1/2}$ s$^{-1/2}$ (ref. 4) have been reported.

Analysis of the copolymerization rate of methyl methacrylate/di-n-butyl itaconate system

Copolymerization rate of MMA/DBI was determined as a function of the monomer molar fraction in the feed. Experiments were carried out in benzene solution, at 50°C, by using an overall monomer concentration of 3 and 5 mol l^{-1} with AIBN as an initiator (1.5×10^{-2} mol l^{-1}). As can be observed in *Figure 1*, plots of conversion *versus* time, determined by dilatometric measures, afforded a good linearity. The rates of copolymerization were obtained from the slopes of the straight lines taking into account the overall monomer concentration in the feed. As shown in *Table 3*, the overall rate of copolymerization is higher when MMA in the feed increases.

The copolymerization rate of two monomers 1 and 2 in the presence or absence of solvent at low conversion may be expressed formally in a similar way as for homopolymerization:

$$R_p = \frac{\bar{k}_p}{\bar{k}_t^{1/2}}(2fk_d)^{1/2}[I]^{1/2}[M] \qquad (6)$$

where $\bar{k}_p$ and $\bar{k}_t$ are the overall copolymerization propagation and termination constants, $R_i = 2fk_d$, [I] is the rate of initiation for the copolymerization and $[M] = [M_1] + [M_2]$ is the overall monomer concentration in the feed.

From a classical point of view, variation of copolymerization rate as a function of the molar fraction of the monomer feed has been attributed to changes in termination reactions[17]. Changes in propagation coefficient and in rates of initiation may also be important, in addition to possible changes in termination. The termination step kinetics of free-radical copolymerization has been explained by three different mechanisms: the chemical-controlled mechanism[18,19], the diffusion-controlled mechanism[20] and the combined physical and chemical mechanism proposed by Russo and Munari[21]. However, recent experimental evidence[22–25] has shown that 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[20]:

$$k_t = F_1 k_{t11} + F_2 k_{t22} \qquad (7)$$

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

Furthermore, the rate coefficient of initiation ($2fk_d$) varies linearly with monomer feed composition (f_i, $i = 1$ or 2) according to the following empirical relationship[22]:

$$2fk_d = f_1(2fk_d)_1 + f_2(2fk_d)_2 \qquad (8)$$

The propagation rate constants of a number of copolymerization systems have been measured by use of

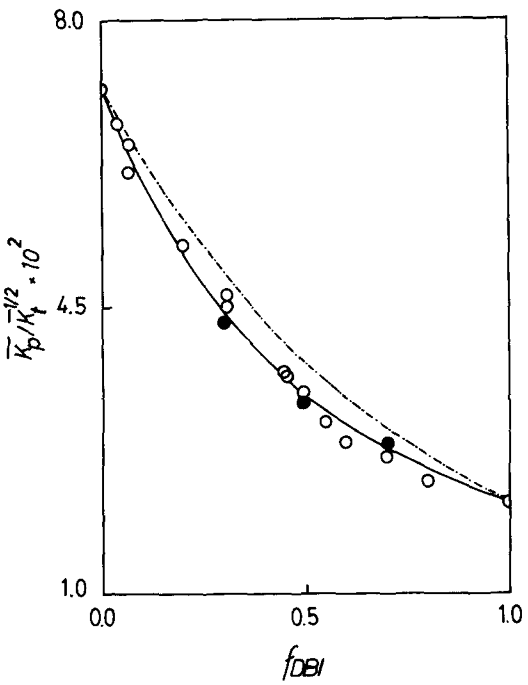

Figure 5 Plot of $\bar{w}$ *versus* f_{DBI} for the system DBI/MMA/benzene/AIBN at 50°C. The chain and full curves were calculated considering $s_1 = s_2 = 1$ and s_1 and s_2 estimated from experimental results, respectively

rotating sector method[26], the spatial intermittent polymerization technique[27] or pulsed laser polymerization experiments[28]. All experimental results[29,30] confirm the failure of the Mayo–Lewis terminal model and the data obtained have been interpreted as a consequence of the penultimate effect on the propagation reaction[26,28,29,31]. Considering the 'terminal model' the apparent propagation rate constant could be expressed thus:

$$k_p = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{(r_1 f_1/k_{11}) + (r_2 f_2/k_{22})} \tag{9}$$

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 to j $(i,j = 1$ or $2)$ and $f_i = (1 - f_j)$ is the mole fraction of monomer i in the feed. According to the penultimate model and following the nomenclature of Fukuda *et al.*[26,29], k_p can be expressed by equation (9) with k_{11} and k_{22} replaced by the following functions:

$$k_{11} = k_{111}(r_1 f_1 + f_2)/(r_1 f_1 + s_1^{-1} f_2) \tag{10}$$

$$k_{22} = k_{222}(r_2 f_2 + f_1)/(r_2 f_2 + s_2^{-1} f_1) \tag{11}$$

$$s_1 = k_{211}/k_{111} \qquad s_2 = k_{122}/k_{111} \tag{12}$$

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 composition or sequence distribution[32]. So, the 'terminal model' can therefore be seen as a special case of the penultimate model if $s_1 = s_2 = 1$.

A similar test of the penultimate model may be done using the overall copolymerization parameter $\bar{k}_p/\bar{k}_t^{1/2}$. Thus Fukuda *et al.*[33] proposed the following equation system:

$$\bar{w} = \frac{r_1 f_1^2 + r_2 f_2^2 + 2f_1 f_2}{(r_1 f_1/\bar{w}_1) + (r_2 f_2/\bar{w}_2)} \tag{13}$$

where $\bar{w} = \bar{k}_p/\bar{k}_t^{1/2}$ and $\bar{w}_1$ and $\bar{w}_2$ are given by:

$$\bar{w}_i = \frac{w_i(r_i f_i + f_j)}{r_i f_i + (f_j/s_i)} \tag{14}$$

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

The rate of initiation for each monomer feed composition in the MMA/DBI system can be estimated considering equation (8) and the values found for initiation rate coefficients, $(2fk_d)_i$, of both monomers, together with the initiator concentration. From the copolymerization rate and taking into account the initiation rate of copolymerization values and those of the overall monomer concentration, the parameter $\bar{w}$ has the values indicated in *Table 3*.

Homopolymerization coefficients, $\bar{w}_i$, 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 $\bar{w}$ *versus* DBI monomer feed composition considering $s_1 = s_2 = 1$ is shown in *Figure 5* as a chain curve. This curve shows that the 'terminal model' fails to predict rate coefficient $\bar{w}$ for the copolymerization of DBI with MMA.

Fukuda *et al.*[34], using a model based on radical stabilization energies 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 $s_1 = s_2 = 0.976$ and in practice the theoretical curve coincides with those obtained for the 'terminal model'. Unlike Fukuda *et al.*[34], we have not applied the constraint $s_1 = s_2$, but the full curve represented in *Figure 5* has been calculated using equation (13) with $s_2 = 1.38$ and $s_1 = 0.691$, being $s_1 = r_1 r_2/s_2$. Comparison of the theoretical values with the experimental ones shows that the Fukuda model, within the limits of experimental accuracy, fits the data well. The standard deviations from the experimental and theoretical data are 10.17% for the terminal model, 9.35% for the penultimate model with $s_1 = s_2 = 0.976$ and 4.38% for the penultimate model with $s_2 = 1.38$ and $s_1 = 0.691$. However, although no definitive statement can be made considering the standard deviations mentioned above and the error inherent in the experimental procedures, it seems that the penultimate model is useful at least as a phenomenological model.

On the other hand, as can be seen in *Figure 5*, the theoretical curve previously obtained fits the experimental results well when the overall monomer concentration is $5\,\mathrm{mol\,l^{-1}}$, so it must be concluded that overall monomer concentration has no significant effect on the copolymerization rate coefficient.

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