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

E. L. Madruga* and M. Fernández-Garcia
Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de a Cierva 3, 28006 Madrid, Spain
(Received 11 October 1993; revised 30 March 1994)

Di-n-butyl itaconate (DBI) was polymerized at 50°C in a 3 mol l⁻¹ benzene solution using 2,2'-azobisisobutyronitrile (AIBN) as a free-radical initiator. Kinetic constants for DBI were obtained as follows: kₚ/kₜ⁰.⁵ = 0.021 mol⁻¹¹²₁⁻¹² s⁻¹², 2/kₑ = 3.62 × 10⁻⁸ s⁻¹. Copolymerization reaction between DBI and methyl methacrylate (MMA), under the same experimental conditions, was carried out and the values of r_DB I = 0.717 ± 0.11 and r_MMA = 1.329 ± 0.09 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 substituents¹⁻⁷. The fundamental monomer, itaconic acid, is not an oil-based product, but is obtained commercially by a fermentation process⁸. Furthermore, one can regard poly(itaconic acid diesters) as poly(methacrylates) in which one hydrogen of the x-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(methacrylates)⁹⁻¹⁰.

In the homopolymerization of DRI, overall rate of polymerization (Rₚ) 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 monomers¹⁻³⁻⁷. From Rₚ and initiation rate of polymerization (Rᵢ) of some DRIs together with the concentration of propagating polymer radicals determined from e.s.r. spectroscopy, homopropagation (kₚ) and homotermination (kₜ) rate coefficients have been estimated¹⁻²⁻⁴⁻⁵. Values found for both, kₚ and kₜ, 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 kᵢ is small enough to compensate for the low kₚ.

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 feed⁵⁻⁷. 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 monomers⁵⁻⁷.

Only a few and opposite reactivity ratio values⁸ 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 methods¹¹. 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 ([I] = 1.5 × 10⁻² mol l⁻¹) and benzene as a solvent ([M] = 3 mol l⁻¹). After the desired time, the
Free-radical polymerization of di-n-butyl itaconate: E. L. Madruga and M. Fernández-García

Copolymerization of methyl methacrylate with di-n-butyl itaconate

Free-radical polymerization of DBI/MMA 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 ¹H 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–Túdós plot is shown in Figure 3, the corresponding reactivity ratios being r_{DBI}=0.717±0.11 and r_{MMA}=1.329±0.09. From these reactivity ratio values, predicted copolymer compositions are rather

Table 1

<table>
<thead>
<tr>
<th>[DBI] + [MMA] (mol L⁻¹)</th>
<th>f_{DBI}</th>
<th>Conversion (%)</th>
<th>F_{DBI}</th>
<th>Expt.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.035</td>
<td>6.46</td>
<td>0.026</td>
<td>0.027</td>
<td></td>
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<tr>
<td></td>
<td>0.064</td>
<td>8.05</td>
<td>0.056</td>
<td>0.050</td>
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<tr>
<td></td>
<td>0.199</td>
<td>5.34</td>
<td>0.165</td>
<td>0.157</td>
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</tr>
<tr>
<td></td>
<td>0.301</td>
<td>5.97</td>
<td>0.246</td>
<td>0.243</td>
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</tr>
<tr>
<td></td>
<td>0.301</td>
<td>5.97</td>
<td>0.259</td>
<td>0.243</td>
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<tr>
<td></td>
<td>0.449</td>
<td>3.61</td>
<td>0.377</td>
<td>0.376</td>
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<tr>
<td></td>
<td>0.453</td>
<td>8.77</td>
<td>0.382</td>
<td>0.380</td>
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<tr>
<td></td>
<td>0.491</td>
<td>3.86</td>
<td>0.411</td>
<td>0.416</td>
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<tr>
<td></td>
<td>0.547</td>
<td>4.18</td>
<td>0.459</td>
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<tr>
<td></td>
<td>0.599</td>
<td>3.17</td>
<td>0.512</td>
<td>0.523</td>
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<tr>
<td></td>
<td>0.698</td>
<td>4.47</td>
<td>0.623</td>
<td>0.628</td>
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<tr>
<td></td>
<td>0.798</td>
<td>4.64</td>
<td>0.732</td>
<td>0.740</td>
<td></td>
</tr>
</tbody>
</table>

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 1  Radical copolymerization of DBI/MMA systems in 3 mol L⁻¹ benzene solution. f_{ DBI } (O) 1.0, ( ) 0.798, ( ) 0.698, ( A ) 0.491, ( A ) 0.449, ( ) 0.301, ( ) 0.199, ( ) 0.0.

Figure 2  ¹H 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.
Free-radical polymerization of di-n-butyl itaconate: E. L. Madruga and M. Fernández-García

Figure 3 Data of DBI/MMA copolymerization system plotted according to the Kelen-Tiódos equation. Feed composition for [DBI] + [MMA] = 3 mol l⁻¹ (©) and 5 mol l⁻¹ (●).

Table 2 Copolymerization Q and e parameters

<table>
<thead>
<tr>
<th>Q_{DBI}</th>
<th>e_{DBI}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.61</td>
<td>0.62</td>
<td>This work</td>
</tr>
<tr>
<td>0.47</td>
<td>0.77</td>
<td>3</td>
</tr>
<tr>
<td>0.49</td>
<td>0.73</td>
<td>7</td>
</tr>
</tbody>
</table>

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 literature¹³, 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:

\[ \log Q = -10.88 + (5.175 \times 10^{-2}) \lambda_{\text{max}} \]  

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 \( \lambda_{\text{max}} \) value in equation (1), Q has been found 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 \(^{13}\)C n.m.r. spectra, which is related to the electron density of the carbon-carbon double bond¹⁵. Therefore, the value of parameter e increases with increasing chemical shift of the β-carbon of the corresponding vinyl compound. Herman and Teyssie¹³ 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:

\[ e = \frac{\delta_{\text{DBI}}(\text{ppm/TMS}) - 113.5}{22} \]  

(2)

The application of equation (2) to the \( \delta_{\text{DBI}} \) 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:

\[ R_i = \frac{Z_0}{t_i} \]  

(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.
Free-radical polymerization of di-n-butyl itaconate: E. L. Madruga and M. Fernández-García

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⁻¹) | \( f_{on} \) | \( R_p \times 10^5 \) (mol⁻¹ s⁻¹) | \( 2(2k_d) \times 10^6 \) (s⁻¹) | \( \bar{w} \times 10^2 \) (mol⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻¹⁻²⁻�
rotating sector method\textsuperscript{26}, the spatial intermittent polymerization technique\textsuperscript{27} or pulsed laser polymerization experiments\textsuperscript{28}. All experimental results\textsuperscript{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\textsuperscript{26,29,31,34}. Considering the ‘terminal model’ the apparent propagation rate constant could be expressed thus:

\[
{\overline{w}}_i = \frac{w_i(r_{fi} + fj)}{r_{fi} + (jf/s_i)}
\]

with \(w_i = k_{ii}/k_{11}^{1/2}\) and \(j \neq i = 1 \text{ or } 2\).

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, \((2f/k_i)_0\), 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 \(\overline{w}\) has the values indicated in Table 3.

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

The theoretical curve of rate of copolymerization \(\bar{\omega}\) 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 \(\omega\) for the copolymerization of DBI with MMA.

Fukuda \textit{et al.}\textsuperscript{34}, using a model based on radical stabilization energies which varies according to the nature of the penultimate unit, have suggested that \(r_j r_i = s_1 s_2\) with \(s_1 = s_2 = 0.976\) and in practice the theoretical curve coincides with those obtained for the ‘terminal model’. Unlike Fukuda \textit{et al.}\textsuperscript{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 \(s_1 = 1.38\) and \(s_2 = 0.691\), being \(s_1 = r_i r_j s_2/s_1\). 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 mol l\(^{-1}\), so it must be concluded that overall monomer concentration has no significant effect on the copolymerization rate coefficient.

ACKNOWLEDGEMENT

This work was supported by CICYT through Grant MAT 381/91.

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