Synthesis, polymerization and copolymerization of *N*-(2-acryloyloxyethyl)phthalimide

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The present paper reports the synthesis and free-radical polymerization of *N*-(2-acryloyloxyethyl)phthalimide (A) and its copolymerization with methyl methacrylate (M). This acrylic monomer was prepared in fairly good yield according to a synthetic scheme that includes two steps. The purified acrylic derivative was polymerized in dimethylformamide solution at 60°C, using azobisisobutyronitrile as free-radical initiator. The kinetic behaviour indicates that this monomer presents a rather high polymerization rate, with a value of $k_p/k_t^{1/2} = 1.36\ \mathrm{l}^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{s}^{-1/2}$. Copolymerization reactions were carried out in the same experimental conditions and the reactivity ratios were determined by the application of the Kelen–Tüdös and non-linear least-squares methods. The values of reactivity ratios calculated by the linearization method were $r_A = 0.29 \pm 0.02$ and $r_M = 3.02 \pm 0.32$, whereas the application of the non-linear least-squares method gave values of $r_A = 0.30$ and $r_M = 3.07$. From these values the corresponding Q and e parameters were calculated, giving values of $Q = 0.27$ and $e = 0.71$.

(Keywords: imide monomer; free-radical polymerization; copolymerization; acrylic monomer; characterization)

INTRODUCTION

The copolymerization of imide-containing monomers has been reported in many papers. For example, *N*-vinylsuccinimide[1–3] and *N*-vinylphthalimide[4–6] have been homopolymerized and copolymerized in different ways with common vinyl monomers such as styrene, methyl methacrylate, vinylidene chloride, vinyl acetate, etc.

Imide-containing acrylates and methacrylates have also been used as monomers and comonomers for free-radical-initiated polymerizations[7–9]. These works were mainly directed to the synthesis of new polymers and copolymers with improved properties (better thermal stability[7,8], crosslinking or photo-crosslinking ability[9]), and less attention has been given to the study of the polymerization reaction itself and to the kinetic parameters that govern the polymerization process. The work of Berger and Zweifel[10] can be considered as an exception to this rule, since they made a conscientious study of the homopolymerization and copolymerization reactions of *N*-vinylethylene dimethylmaleimide.

In the present work, an acrylic monomer containing the phthalimide residue *N*-(2-acryloyloxyethyl)phthalimide (A) has been prepared by a facile, high-yield synthetic route, and it has been homopolymerized and copolymerized with methyl methacrylate (M). An extensive characterization study has also been carried out, along with the evaluation of the polymerization reactivities and the kinetic parameters in the light of the polymerization and copolymerization theories.

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EXPERIMENTAL

Reagents

Phthalic anhydride (Scharlau) was used without further purification. Ethanolamine (Merck) was purified by distillation. Acrylic acid (Merck) was distilled under reduced pressure of N_2. Dimethylacetamide (DMA) and dimethylformamide (DMF) were distilled twice over P_2O_5 at reduced pressure of N_2, and stored in dark glass bottles over dried molecular sieves, 4 Å. Toluene was distilled and stored over clean sodium. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized twice in methanol (m.p. = 104 ± 1°C).

N-(*2-Hydroxyethyl*)*phthalimide*

Phthalic anhydride (14.8 g, 0.1 mol) and ethanolamine (6.10 g, 0.1 mol) were made to react in a mixture of DMA (100 ml) and toluene (50 ml) at 150°C for 3 h. The imidation water was separated by means of a Dean–Stark trap during the reaction. After cooling, the crude reaction solution was poured into excess water, filtered off and dried until constant weight; the yield was 85%. After crystallization from water the intermediate showed a m.p. = 132°C (literature value[11] 130–131°C).

N-(*2-Acryloyloxyethyl*)*phthalimide*

N-(2-Hydroxyethyl)phthalimide (10.00 g, 0.052 mol) was dissolved in 100 ml of dry toluene together with 0.5 g of an equimolar mixture of *p*- toluenesulphonic acid and boric acid. After the addition of a trace of hydroquinone to the reaction medium, the solution was refluxed and 4.32 g (0.060 mol) of purified acrylic acid were added slowly under nitrogen atmosphere. After 5 h of reaction, the crude product was isolated by precipitation into cool hexane. The precipitated product was filtered off and recrystallized with acetone/hexane; the yield was 80%; m.p. = 116°C.

Polymerization

The acrylate phthalimide derivative was polymerized at 60°C in a thermostatic bath regulated with a precision of 0.1°C, using AIBN as initiator at $[I] = 5.0 \times 10^{-3}$ $mol\,l^{-1}$ and DMF as solvent ($[M] = 1.0\,mol\,l^{-1}$). All experiments were carried out in a Pyrex glass dilatometer sealed off at high vacuum. After the desired time, the reaction mixture was transferred to a vessel with a large excess of methanol and the precipitated polymer was filtered off, washed with methanol and dried at reduced pressure until constant weight.

Copolymers of *N*-2-(acryloyloxyethyl)phthalimide (A) with methyl methacrylate (M) were prepared by the free-radical polymerization of mixtures of both monomers with different composition, in DMF at 60°C. As in the homopolymerization, the global monomer concentration was $1.0\,mol\,l^{-1}$ and the concentration of AIBN initiator was $[I] = 5.0 \times 10^{-3}\,mol\,l^{-1}$. The copolymer samples were isolated after the desired polymerization time, by pouring the reaction mixture into a large excess of cool methanol. The precipitated samples were filtered off, washed with cool methanol and dried at reduced pressure until constant weight.

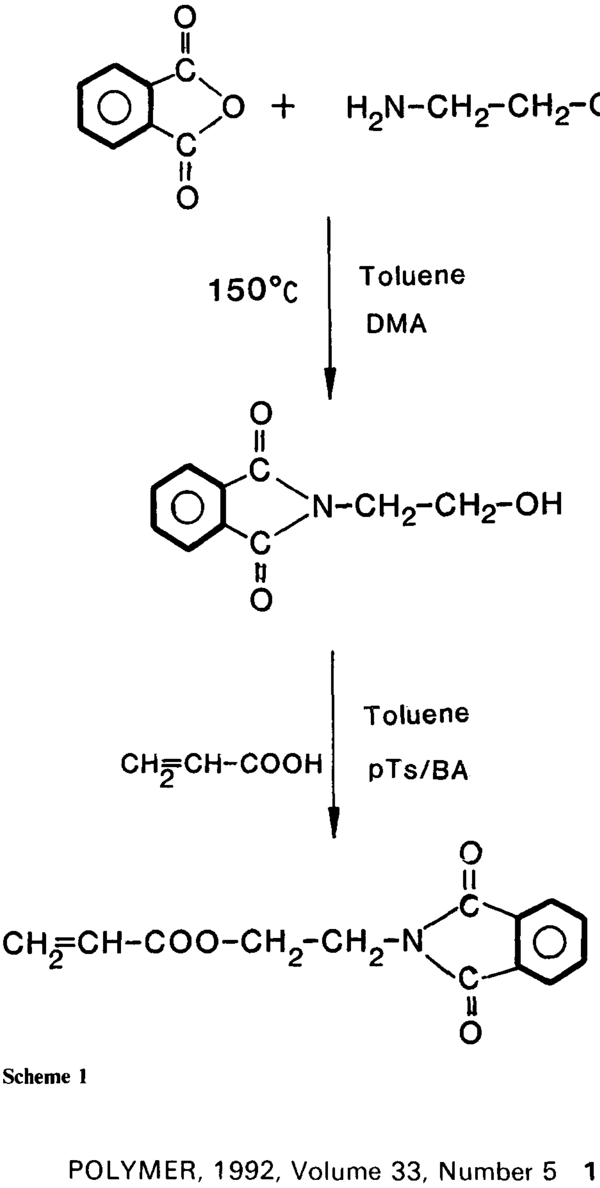
Characterization

All the products synthesized were characterized by i.r. and n.m.r. spectroscopies. Melting points and glass transition temperatures were determined by d.s.c. with a Perkin–Elmer DSC-4 equipment. I.r. spectra were recorded in KBr pellets on a Perkin–Elmer 457. ^1H n.m.r. and ^{13}C n.m.r. spectra of copolymers were recorded at 80°C in deuterated dimethylsulphoxide, 25% w/v (tetramethylsilane (TMS) as internal reference), on a Varian XL-300 spectrometer, operating at 300 MHz for ^1H and75.5 MHz for ^{13}C. The ^{13}C spectra were recorded using a flip angle of 80° (pulse width of 13 s), a relaxation delay of 4 s, an inverse gated decoupling during acquisition, a spectral width of 16 kHz and 16000 data points. These conditions assure the complete relaxation of all the ^{13}C nuclei analysed. The relative peak areas were measured by means of the electronic integrator or by triangulation and planimetry.

RESULTS AND DISCUSSION

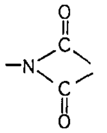
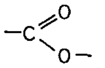
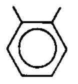
Pyriadi and Alasli[7] have recently published the synthesis and polymerization of *N*-(2-acryloyloxyethyl)phthalimide via the reaction of phthalimide with 2-bromoethanol or the treatment of phthalic anhydride with ethanolamine, according to a scheme involving two separate steps. They reported a melting point of 211–212°C for the *N*-(2-hydroxyethyl)phthalimide synthesized, whereas in an earlier publication Phillips[11] reported a m.p. = 130–131°C and we have found a value of 132 ± 1°C for this compound. Moreover, these authors[7] reported a m.p. = 102–103°C for the *N*-(2-acryloyloxyethyl)phthalimide, whereas we have found a value of 116 ± 1°C.

Recently Kim *et al.*[12] have described the synthesis of *N*-(2-hydroxyethyl)-1,8-naphthalimide by the direct condensation of 1,8-naphthalic anhydride with 2-aminoethanol in an aqueous medium at 100°C with good yield. Therefore, we considered the synthesis of *N*-(2-acryloylxyethyl)phthalimide according to *Scheme 1*, which involves two steps: The first one is a direct imidation reaction of the phthalic anhydride by ethanolamine under mild conditions, giving rise to *N*-(2-hydroxyethyl)phthalimide with good yield. The second step is the esterification of this intermediate with acrylic acid, using an equimolar mixture of *p*-toluenesulphonic acid (pTs) and boric acid (BA) as catalyst, and a little amount of hydroquinone in order to avoid the uncontrolled polymerization of the acrylic double bond. The monomer was isolated with a purity higher than 99%, as found by h.p.l.c. The main i.r. and ^1H n.m.r. signals of the acrylic monomer are collected in *Table 1*. The characteristic absorption signals of the phthalimide group at 1770, 1700 and 725 cm^{-1} can be clearly distinguished by i.r. as well as the strong absorption of the carbonyl ester group at 1710 cm^{-1}. The i.r. spectrum allowed one to distinguish also the absorption bands of the aromatic nuclei (1610 cm^{-1}) and the characteristic absorption of the acrylic double bond (1635 cm^{-1}). With respect to the ^1H n.m.r.



Scheme 1

Table 1 Spectroscopic characteristics of *N*-(2-acryloyloxyethyl) phthalimide

Functional group	I.r. (cm^{-1})	^1H n.m.r.[a] (ppm)
	1770 1700 725	–
	1710 1200	–
	1610	7.5–8.0 (m)
$CH_2{=}CH–$	1635	5.5–6.5 (m)
$–CH_2–N<$	1000–1100	4.01 (t)
$–CH_2–O–$	1150–1120	4.41 (t)

[a] Solvent, Cl_3CD; (m) multiplet, (t) triplet

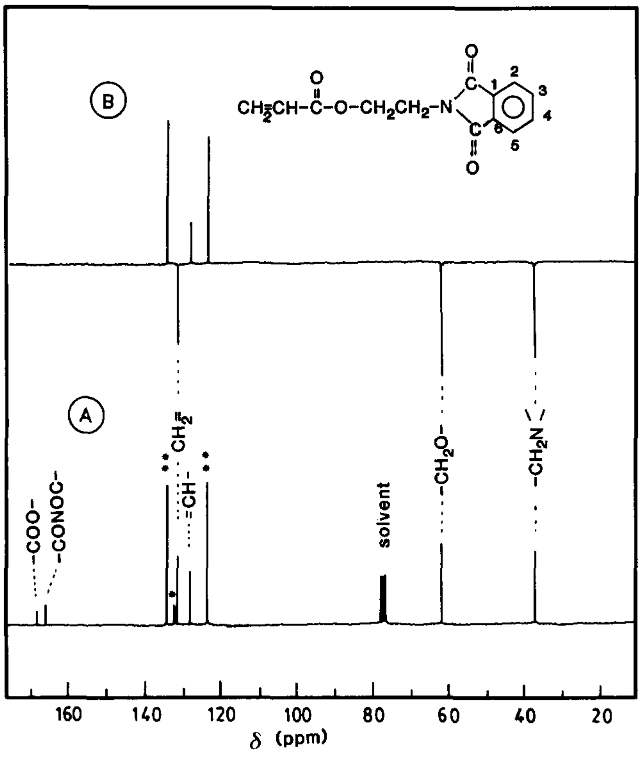


Figure 1 ^{13}C-n.m.r. spectra (75.5 MHz) of *N*-(2-acryloyloxyethyl) phthalimide recorded in Cl_3CD solution at room temperature: (A) proton-decoupled spectrum; (B) DEPT 135° spectrum; (∗) aromatic carbons 1 and 6; (∗∗) aromatic carbons 2 and 5

spectrum, apart from the resonance multiplets between 7.5 and 8.0 ppm from TMS, assigned to the aromatic protons, and between 5.5 and 6.5 ppm, characteristic of the protons of the acrylic double bond, the appearance of two well defined triplets at 4.01 and 4.41 ppm is noteworthy, which correspond to the $–CH_2–$ groups linked to the imide nitrogen and acrylic ester, respectively. Curiously, the protons of both methylene groups are magnetically equivalent for the intermediate product, *N*-(2-hydroxyethyl)phthalimide, giving only a sharp singlet at 3.84 ppm.

The chemical structure of the *N*-(2-acryloyloxyethyl) phthalimide has also been tested by ^{13}C n.m.r. *Figure 1A* shows the proton-decoupled ^{13}C n.m.r. spectrum of the acrylic compound, registered in deuterated chloroform at 40°C. The assignment of the resonance signals outlined in this figure has been carried out on the basis of the DEPT (distortionless enhancement by polarization transfer, 135°) spectrum drawn in *Figure 1B*. In this spectrum the methylene groups appear as negative signals, whereas the signals of the carbonyl groups, aromatic substituted carbons 1 and 6 (see the figure) and solvent are absent.

Homopolymerization of N-(*2-acryloyloxyethyl*) *phthalimide*

The acrylic monomer *N*-(2-acryloyloxyethyl)phthalimide (A) was polymerized in solution in DMF, $[M] = 1.0\ mol\ l^{-1}$, using AIBN as free-radical initiator, $[I] = 5.0 \times 10^{-3}\ mol\ l^{-1}$, at 60°C. Methyl methacrylate (M) was also polymerized under the same experimental conditions to provide comparative results.

Assuming that thermal polymerization is negligible, the rate of radical-initiated polymerization is given by:

$$-\frac{d[M]}{dt} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][I]^{1/2} \qquad (1)$$

where k_d, k_p and k_t are the rate constants for initiator decomposition, propagation and termination reactions, respectively. [M] and [I] are the instantaneous concentrations of monomer and initiator and f is the efficiency of the initiator[13]. If the decomposition of the initiator is assumed to be a first-order reaction:

$$[I] = [I_0]\exp(-k_d t) \qquad (2)$$

Equations (1) and (2) lead to:

$$-\frac{d[M]}{dt} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][I_0]^{1/2}\exp(-k_d t/2) \qquad (3)$$

Integration of equation (3) gives:

$$[M] = [M_0]\exp\left(-\frac{2k_p f^{1/2}}{k_t^{1/2}k_d^{1/2}}[I_0]^{1/2}[1-\exp(-k_d t/2)]\right)$$

Non-linear least-squares analysis of the dilatometric data yielded the values $k_p/k_t^{1/2} = 1.36\ l^{1/2}\ mol^{-1/2}\ s^{-1/2}$ and $k_d = 1.12 \times 10^{-5}\ s^{-1}$ for the acrylate monomer, and $k_p/k_t^{1/2} = 0.33\ l^{1/2}\ mol^{-1/2}\ s^{-1/2}$ and $k_d = 1.07 \times 10^{-5}\ s^{-1}$ for methyl methacrylate. The values of k_d are in very good agreement with that reported by Van Hook and Tobolsky[14] for the thermal decomposition of AIBN at 60°C ($0.91 \times 10^{-5}\ s^{-1}$). The ratio $k_p/k_t^{1/2}$ for the polymerization of the acrylic monomer A is higher than those reported for the free-radical polymerization of methyl acrylate (0.68 at 60°C) and ethyl acrylate (0.67 at 60°C)[15], which could indicate a lower termination rate constant for A than for methyl or ethyl acrylates, since, as has been pointed out by Mahabadi and O'Driscoll[16], the termination rate constant may be higher for the more flexible chains.

The decrease of k_t with respect to those of the alkyl acrylates considered may be due to the stiffness of polymer segments owing to the presence of the phthalimide side groups. In this sense, although traditionally the flexibility of polymer chains has been

Table 2 Average molar composition of A–M copolymers prepared in DMF solution at 60°C

Monomer feed		Copolymer chains					
		f_M			f_A		
F_M	F_A	^{1}H n.m.r.	^{13}C n.m.r.	Average	^{1}H n.m.r.	^{13}C n.m.r.	Average
0.11_1	0.88_9	0.30_0	0.31_0	0.30_5	0.70_0	0.69_0	0.69_5
0.13_6	0.86_4	0.36_0	0.34_0	0.35_0	0.64_0	0.66_0	0.65_0
0.15_9	0.84_1	0.39_0	0.35_0	0.37_0	0.61_0	0.65_0	0.63_0
0.20_0	0.80_0	0.42_0	0.44_0	0.43_0	0.58_0	0.56_0	0.57_0
0.37_6	0.62_4	0.64_4	0.66_0	0.65_5	0.35_5	0.34_0	0.34_5
0.40_0	0.60_0	0.70_0	0.66_0	0.68_0	0.30_0	0.34_0	0.32_0
0.41_9	0.58_1	0.72_5	0.68_0	0.70_0	0.27_5	0.32_0	0.30_0
0.47_6	0.52_4	0.71_0	0.75_0	0.73_0	0.29_0	0.25_0	0.27_0
0.60_0	0.40_0	0.85_0	0.83_0	0.84_0	0.15_0	0.17_0	0.16_0
0.80_0	0.20_0	0.90_5	0.94_0	0.92_0	0.09_5	0.06_0	0.08_0

expressed by the ratio of the mean-square end-to-end distance of a polymer chain to that of the freely jointed chain, a qualitative indication of this parameter is given by the value of the glass transition temperature. The T_g of poly[*N*-(2-acryloyloxyethyl)phthalimide] determined by d.s.c. is 84°C, somewhat higher than those of the mentioned alkyl acrylates, which is in agreement with the kinetic results reported. Moreover, the relatively higher value of T_g may also have a dipolar origin rather than be caused by steric hindrance. For example, poly(phenyl acrylates) with rigid aromatic rings directly linked to the acrylic ester group show a T_g about 50°C[17], more than 30°C lower than that of the phthalimide derivative.

Copolymerization

N-(2-Acryloyloxyethyl)phthalimide (A) was copolymerized with methyl methacrylate (M) in order to prepare copolymer systems with different monomeric sequences, by changing the composition of the monomer mixture with molar fractions of A ranging from 0.20 to 0.80. The copolymerization reactions were carried out in the same experimental conditions as for the homopolymerization. The reaction time was regulated to reach conversions lower than 5 wt%, in order to satisfy the differential copolymerization equation[18].

The average molar composition of copolymers was determined by ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopies. Although in general the ^{1}H n.m.r. spectra of polyacrylates do not present good resolution, for this copolymer system the molar fraction of monomeric species could be determined by comparison of the integrated intensities of well resolved peaks assigned to A and M units. In this sense, we have selected the resonance signal centred at 7.80 ppm from TMS of the aromatic protons of the phthalimide residue, to determine the molar fraction of A units in the copolymer chains, whereas the resonance signal centred at 0.85 ppm, assigned to the α-CH_3 protons, was used to determine the molar fraction of M units. The values obtained for the compositions studied have been quoted in *Table 2*.

Furthermore, the average composition could be determined with accuracy through the analysis of the very sharp resonance signals of the proton-decoupled ^{13}C n.m.r. spectra registered in the experimental conditions outlined above, which guarantee the complete magnetic relaxation of the nucleus of interest. *Figure 2* shows the ^{13}C n.m.r. spectra of three copolymer samples with different compositions. The signals could be easily identified taking into consideration the spectrum of the monomeric acrylate drawn in *Figure 1A* and that of poly(methyl methacrylate)[19,20]. On this basis we have considered the integrated intensities of the sharp peak at $\delta = 52$ ppm, assigned to the OCH_3 group of M units, and that of $\delta = 62$ ppm, assigned to the $-OCH_2-$ residue of A units, to determine the molar fraction of both monomeric species in the copolymer chains. The results obtained are quoted in *Table 2*. It is interesting to stress here that the ^{13}C n.m.r. spectra drawn from *Figure 2* also gave information about the distribution of monomeric sequences and the stereoregularity of copolymer segments, but the corresponding analysis is rather difficult as could be deduced from the complicated pattern of the carbonyl ester resonances at $\delta = 175$–179 ppm and that of the α-CH_3 group at $\delta = 18$–22 ppm.

The reactivity ratios of this system were determined by preparing copolymers from a monomer composition as near as possible to those determined by the 'approximate design scheme'. As described by Tidwell and Mortimer[21] this scheme uses the optimally designed experiment, 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.*[22] suggested taking values of reactivity ratios that differed from r_1 and r_2 by 20%. In this work we have estimated the approximate values of r_A and r_M by the application of the Fineman–Ross[23] linearization method to the composition data of four copolymer samples prepared with feed compositions of $F_A = 0.2$, 0.4, 0.6 and 0.8 (see *Table 2*). From the values of r_A and r_M obtained the best compositions were determined according to the 'approximate design scheme', which correspond to the data of compositions collected in *Table 2*.

The application of all these data to the known Kelen–Tüdös linearization method[24] gave the diagram drawn in *Figure 3*. From the slope and intercept of the straight line the values of r_M and r_A were calculated and are reported in *Table 3*. The reactivity ratios were also

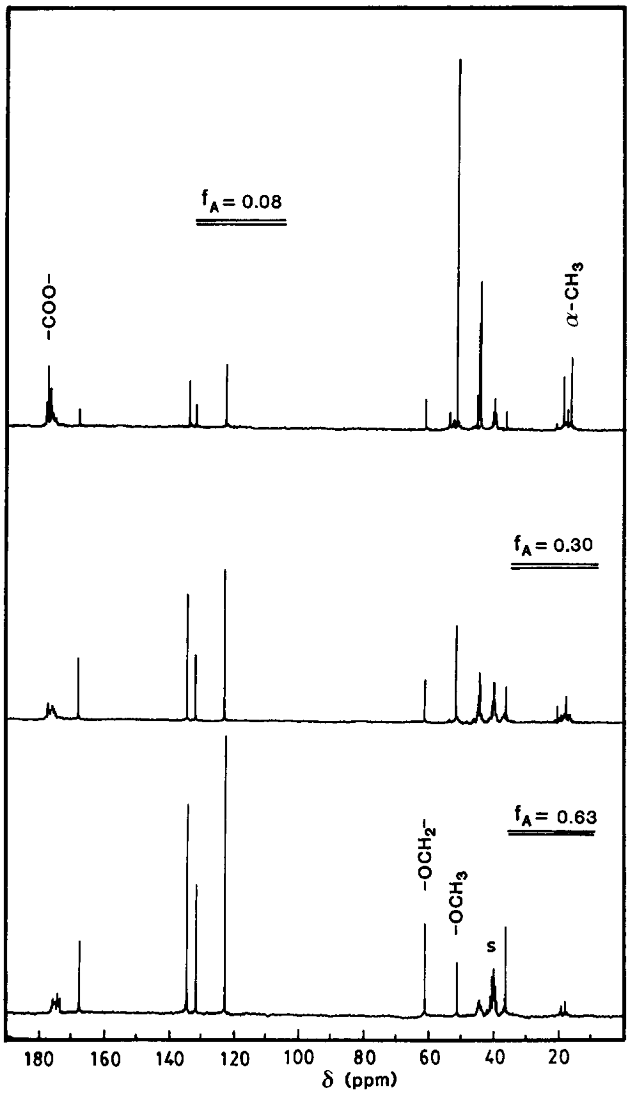


Figure 2 Proton-decoupled ^{13}C n.m.r. spectra (75.5 MHz) of copolymers prepared from *N*-(2-acryloyloxyethyl)phthalimide (A) and methyl methacrylate, recorded in deuterated dimethylsulphoxide (DMSO-d$_6$) solution at 80°C. f_A corresponds to the molar fraction of A in the copolymer samples; s = solvent

determined by the application of the non-linear least-squares analysis suggested ty Tidwell and Mortimer[21], and their values are collected in *Table 3*, being very close to those calculated by the Kelen–Tüdös linearization method. In this table are also quoted the values of the well known parameters *Q* and *e*, which were calculated considering the corresponding values for methyl methacrylate: $Q = 0.74$ and $e = 0.40$.

The 95% confidence limits give an idea of the magnitude of the experimental error and the goodness of experimental conditions used to generate the composition data[21]. If the experimental error is reasonably small and the data have been taken in the appropriate conditions, the approximation can be remarkably good, which is illustrated by the dimensions of the elliptical diagram generated by the application of the mathematical treatment suggested by Bechnken[25] and Tidwell and Mortimer[21].

The application of this treatment to the copolymerization data reported in *Table 2* and the reactivity ratios quoted in *Table 3* provides the 95% confidence limits defined by the area of the elliptical diagrams drawn in *Figure 4*. As expected, the non-linear least-squares

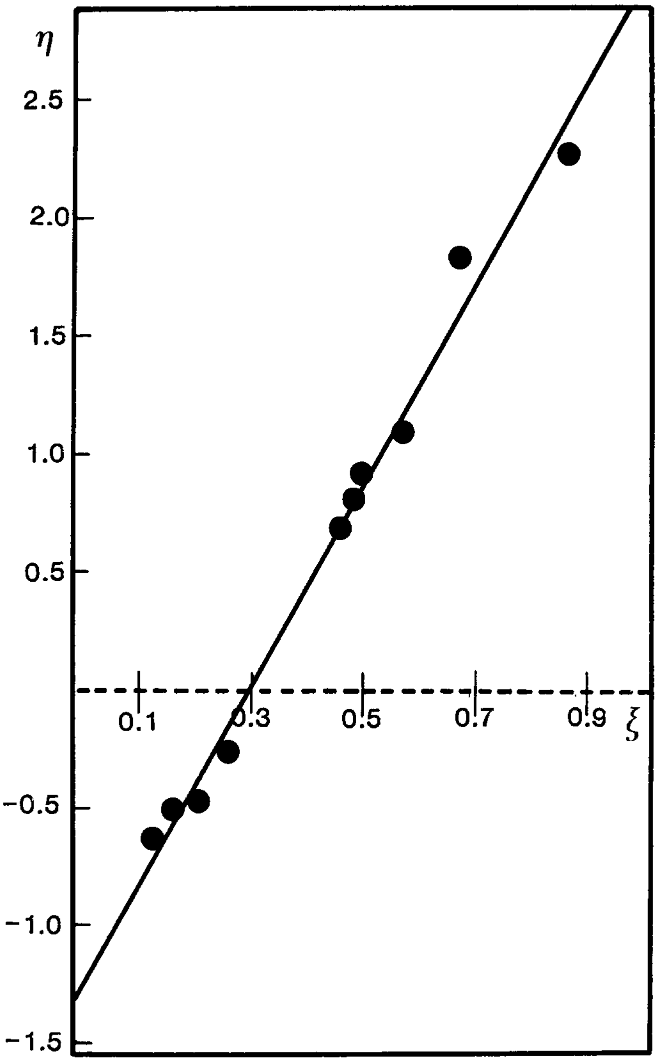


Figure 3 Kelen–Tüdös linearization diagram for the composition data of the A–M copolymerization system at 60°C in DMF solution

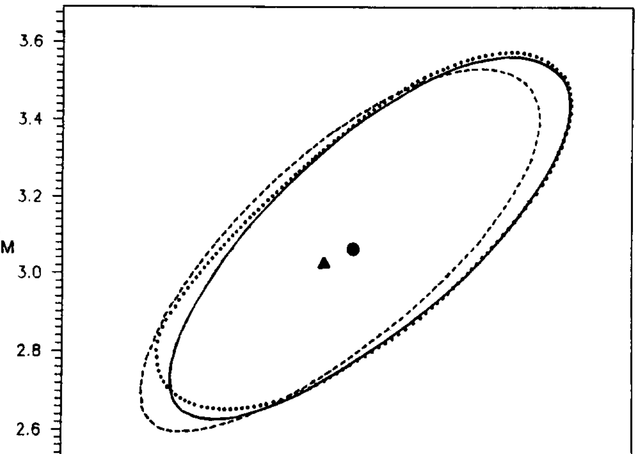


Figure 4 The 95% confidence limits for the copolymerization of A with M in DMF solution at 60°C: (----) Kelen–Tüdös data; (——) approximate; (·····) exact; (●) non-linear estimation; (▲) Kelen–Tüdös

Table 3 Copolymerization parameters for the free-radical polymerization of A with M in DMF solution at 60°C

Method	r_M	r_A	Q	e
Kelen–Tüdös	3.02 ± 0.32	0.29 ± 0.02	0.27	0.73
Tidwell–Mortimer	3.07	0.30	0.27	0.71

analysis gives the best estimation of r_A and r_M, although the application of the Kelen–Tüdös method also gives an excellent approximation to the real values. These results verify that, under well designed experimental conditions, the linearization method suggested by Kelen and Tüdös[24] may be used with almost as much confidence as a non-linear least-squares procedure, which has also been indicated in earlier papers by McFarlane[22].

On the other hand, the average value of the polar parameter e (0.72) of A is somewhat higher than those of methyl acrylate (0.60) or methyl methacrylate (0.40)[15], which indicates a higher polarity of the corresponding acrylic double bond. In this sense, 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[26]. Therefore, the value of parameter e increases with increasing chemical shift of the β-carbon of the corresponding vinyl or acrylic compound.

The chemical shift of the β-carbon of A (131.2 ppm) is higher than that of the same carbon of methyl methacrylate (125.1 ppm) or methyl acrylate (129.9 ppm), reflecting the lower electron density on the β-carbon of the acrylic double bond of monomer A, with respect to methyl acrylate or methyl methacrylate, and justifies the relatively high value of the parameter e of this acrylic monomer. Herman and Teyssie[26] have suggested that for vinyl monomers the parameter e may be estimated approximately from the chemical shift of the β-carbon, according to the equation:

$$e = \frac{\delta_{c\beta}(\mathrm{ppm/TMS}) - 113.5}{22}$$

The application of this equation to the $\delta_{c\beta}$ of monomer A gives a value of $e = 0.81$, very close to that calculated from the reactivity ratios determined in this work.

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