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Photoinitiated copolymerisation of furfuryl methacrylate and *N,N*-dimethyl acrylamide

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Copolymers of furfuryl methacrylate (**F**) and *N,N*-dimethyl acrylamide (**A**) were prepared by free radical photoinitiated polymerisation in bulk at 40°C, using 2,2-azobisisobutyronitrile (AIBN) as photoinitiator. The reactivity ratios of both monomers (r_F and r_A) were determined according to the general copolymer composition equation by applying the Tidwell and Mortimer non-linear least squares fit. To this end initial approximated values of r_F and r_A were obtained by means of the Fineman–Ross and Kelen–Tüdos linearisation methods. The reactivity ratios obtained were $r_F = 2.06$ and $r_A = 0.28$. Also, kinetic parameters such as reaction rate (R_p) and copolymerisation quantum yield (ϕ_m) were determined for the above system over a wide composition interval, with molar fraction of **F** ranging from 0. 1 to 0.9 in the monomer feed. The kinetics of photopolymerisation were followed using differential scanning photocalorimetry. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The preparation of N-substituted polyacrylamides has attracted the attention of a great number of researchers, due to the interesting physical behaviour of their swollen hydrogels which show, amongst other characteristics, a specific thermosensitive response near to the physiological temperature[1–10]. Ionic gels eventually come to an osmotic equilibrium with the surrounding electrolyte solutions. The density of charged groups fixed to the hydrogel determines the swelling behaviour at different pH values or even the volume transitions with changes in temperature[11,12]. In addition, the mechanical characteristics of highly hydrated hydrogels are determined not only by the chemical structure of the repeating units of the polymer chains, but also by the light cross-linking of the macromolecules, which thus provides a network structure[5,8].

The density of ionic groups in macromolecules can be controlled by the preparation of copolymers of the ionisable monomer (e.g. acrylamide derivatives) together with a second monomer which provides a suitable hydrophobic/hydrophilic balance and stiffness of the macromolecular chains in the swollen state. The presence of small amounts of a tetrafunctional monomer is recommended for the formation of the network structure of the system. In this way, we have studied the behaviour of copolymers prepared by the free radical copolymerisation of furfuryl–acrylic compounds with hydrophilic monomers such as vinyl pyrrolidone[13,14] or hydroxyethyl methacrylate[15]. The properties of the corresponding copolymers are controlled by the average composition of the system as well as by the distribution of monomeric units along the macromolecular chains, which in addition depend on the relative reactivity of the furfuryl–acrylic compounds and the hydrophilic monomers.

One interesting characteristic of furfuryl–acrylic compounds is their reactivity in free radical processes[16]. In fact, the polymerisation of furfuryl acrylate or furfuryl methacrylate, as well as their copolymerisation with vinyl and acrylic monomer, give rise to the formation of linear, soluble polymers when the reaction is carried out in solution or in bulk at low conversion. However, for a high degree of conversion, lightly crosslinked macromolecular systems are obtained[15,16].

The network structure is formed as a consequence of the relatively high reactivity of the hydrogen atom in the C5 position of the furan ring[17,18], which gives rise to branched and eventually crosslinked polymeric chains when the polymerisation is carried out in bulk at high or total conversion.

Therefore, furfuryl–acrylic monomers provide an excellent means of controlling the microstructure of copolymer chains, and eventually give a slightly crosslinked structure. In order to study the reactivity of furfuryl methacrylate in its free radical copolymerisation with *N,N*-dimethylacrylamide, we analyse in this paper the photoactivated free radical copolymerisation of these monomers in bulk, and at low conversion and temperature, with the aim of obtaining soluble non-crosslinked copolymers.

EXPERIMENTAL

Monomer preparation and purification of materials

Furfuryl methacrylate was prepared by transesterification of methyl methacrylate with furfuryl alcohol in the presence of sodium carbonate as catalyst, and ionol as inhibitor. The product was distilled, dissolved in chloroform and passed through a chromatographic column containing silica gel 60 (Macherey-Nagel, Germany). The eluent was analysed by thin layer chromatography using kieselgel 60 F 254 (Merck)

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as the stationary phase. The selected fraction was rotoevaporated to separate the solvent, and then distilled, stored in the dark at low temperature and distilled again just prior to use.

N,N-Dimethyl acrylamide supplied by Fluka was distilled under reduced pressure and used without further purification.

2,2-Azobisisobutyronitrile was purified by fractional crystallisation from methanol and stored in the dark at low temperature, m.p. 104°C.

Polymerisation

Photochemically initiated polymerisation reactions were carried out by direct irradiation of the sample placed in the holder sample of a differential scanning calorimeter. A standard Perkin-Elmer d.s.c.-4 calorimeter was adapted for measuring polymerisation rates of irradiated samples. The two ends of a two-branch u.v. light conducting fibre were inserted into the cover of the d.s.c.-4 aluminium block by drilling holes directly above the sample and reference holders. The two-branch flexible u.v. light guides were terminated with a ferrule connector. As such, the input fibre was plugged into the side of an aluminium cylinder assembly containing a manual shutter (to block the incident light on the input end of the light guide), a 365 nm interference filter (International Light NB-365), a solid i.r. filter (Schott KG-1), and neutral density filters. This assembly was mounted into the water-cooled housing of a Hanovia Uvitron irradiation system provided with a quartz lens and a 100 W high-pressure mercury lamp. The intensity of the transmitted light was controlled by adjusting the position of the internal cavity within the cylinder. With this arrangement it was possible to irradiate samples and to monitor exothermic reaction rates on the d.s.c. simultaneously. For irradiation under anaerobic conditions, a standard nitrogen flow of 20 cc min^{-1} was maintained into the d.s.c. chamber for at least 10 min before starting the irradiation. This delay allowed the oxygen dissolved in the sample to diffuse out, and also ensured that the samples had attained the selected equilibrium temperature.

D.s.c. calibration, data processing, incident light intensity determination, as well as complementary details, were performed as described elsewhere[19,20].

All polymerisation experiments were carried out in bulk at a temperature of 40°C. The photoinitiator, AIBN, was used at a concentration of 1.5×10^{-2} mol L^{-1} in order to ensure a total light absorption at 365 nm. By use of the above described photocalorimeter the preparation of polymers and copolymers at the required conversion was possible.

Copolymer characterisation

The copolymers prepared with different feed composition were analysed by ^{1}H n.m.r. spectroscopy using a Varian XL-300 spectrometer working at 300 MHz. The spectra were recorded in DMSO-d_6 solution (5% w/v) at 80°C. The copolymer composition was determined by comparison of the integrated intensities of resonance signals with chemical shifts, 5.0 δ being assigned to the $-O-CH_2$ protons of **F** units or the signals at 6.30 δ assigned to the H 3 and H 4 of the furan ring, with the $-N-CH_3$ protons (2.90 δ) of the **A** units (*Figure 1*).

RESULTS AND DISCUSSION

Prior to the copolymerisation study, the heat of polymerisation of the monomer **A** was determined photocalorimetrically. The photopolymerisation was carried out to total conversion under isothermal conditions (40°C). The heat of polymerisation obtained for **A** was 62.1 ± 2 kJ mol^{-1}. The validity of the procedure employed for determining the heat of polymerisation was established in a previous work[21] in which the heat of polymerisation of **F** was calculated to be 50.1 ± 1 kJ mol^{-1}.

From these values the evolution in real time of the % conversion of copolymer prepared from various monomer mixtures could be easily calculated by assuming that the contribution of both monomers to the total heat of polymerisation was proportional to their molar fraction in the feed.

The rates of polymerisation were calculated by linear least squares fit of the steady state region of the conversion *versus* time graphs, and the quantum yield of polymerisation was calculated as the ratio of the conversion degree (mol) to the amount of energy absorbed (einstein).

The results obtained, summarised in *Table 1*, show that

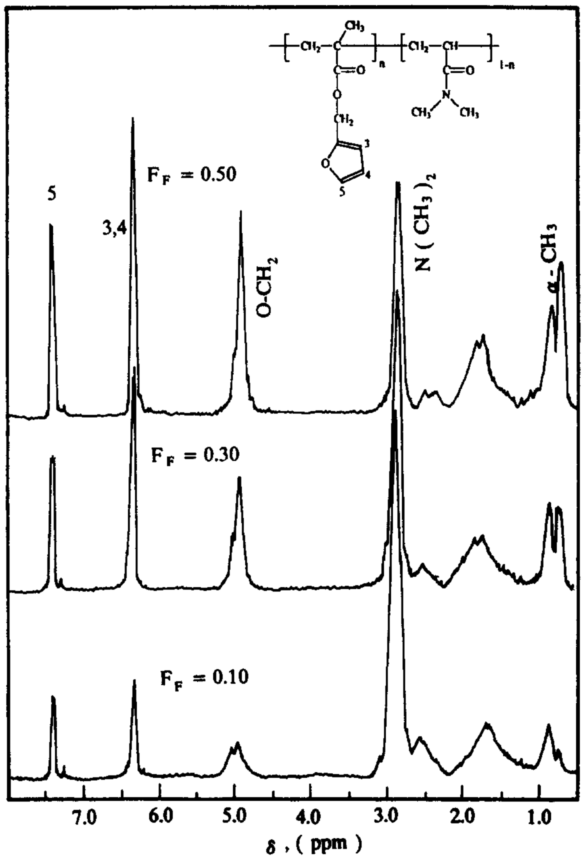

Figure 1 ^{1}H n.m.r. (300 MHz) spectra of furfuryl methacrylate–dimethyl acrylamide copolymers

Table 1 Experimental and calculated data of free radical photopolymerisations of **F** and **A** followed by photocalorimetry using 1.5×10^{-2} mol L^{-1} AIBN as photoinitiator

No.	F_F	$R_p \times 10^3$ (mol L^{-1} s^{-1})	$\phi_m \times 10^{-2}$
1	0.9	2.40	6.00
2	0.8	2.54	5.91
3	0.7	2.61	7.05
4	0.5	2.88	7.88
5	0.3	3.06	7.85
6	0.1	5.20	13.40

$I_0 = 0.3$ mcal s^{-1}, $T = 40$°C

the rate of polymerisation and the quantum yield increased as the molar fraction of **A** in the monomer feed increased.

Copolymer composition

For this study the same composition range of molar fractions of both monomers in the feed was used, at the reaction temperature of 40°C. The reaction time was initially adjusted to achieve conversions lower than 5 wt% to satisfy the differential copolymerisation equation[22]. The molar fraction of monomer units incorporated in the copolymer was determined from the ^{1}H n.m.r. spectra of copolymer samples prepared with different monomer feeds. The data of molar composition of the initial mixtures of comonomers used and of the resulting copolymers are given in *Table 2*.

Table 2 Composition data and R values of the photoinitiated free radical copolymerisations of **F** and **A** in bulk at 40°C

F_F^a	f_F^a	Conversion (wt%)	R
0.1	0.26	3.3	9.73
0.3	0.53	2.4	28.88
0.5	0.70	2.6	46.08
0.5	0.71	3.1	46.08
0.7	0.85	2.8	56.56
0.9	0.93	3.7	42.12

$^a F_F$ and f_F are the molar fractions of **F** in the monomer feed and in the copolymer samples, respectively
[AIBN] = 1.5×10^{-2}

The reactivity ratios of the monomers were determined according to the general copolymer composition equation by applying the Tidwell and Mortimer non-linear least squares analysis[23]. To this end approximate initial values of r_F and r_A were obtained by means of Fineman–Ross[24] and Kelen–Tüdos[25] linearisation methods. The results are shown in *Table 3*. It must be pointed out that although the r_F and r_A values obtained using the linearisation methods were somewhat different, the same values were obtained when the non-linear least squares method was used. We stress here that the r values determined by the application of the analysis suggested by Tidwell and Mortimer[23] are the most probable values for this system.

The 95% confidence limit gives an idea of the experimental error and the accuracy of the experimental conditions used to generate the composition data[23]. When the experimental error is reasonably small, and the data have been collected under appropriate conditions, the approximation can be remarkably good. This is illustrated by the dimensions of the elliptical graph generated by applying the mathematical treatment suggested by Behnken[26] and Tidwell and Mortimer[23]. The application of this treatment to the copolymerisation data reported in *Table 2* and the r values quoted in *Table 3* provides the 95% confidence limits defined by the area of the elliptical diagram in *Figure 2*. This diagram

Table 3 Copolymerisation parameters of the free radical copolymerisation of **F** and **A** at 40°C

Method	r_F	r_A	$r_F \times r_A$	$1/r_F$	$1/r_A$
Fineman–Ross	1.94 ± 0.2	0.27 ± 0.01	0.524	0.52	3.70
Kelen–Tüdos	1.70 ± 0.2	0.20 ± 0.3	0.340	0.59	5.0
Tidwell–Mortimer	2.06	0.28	0.577	0.49	3.57

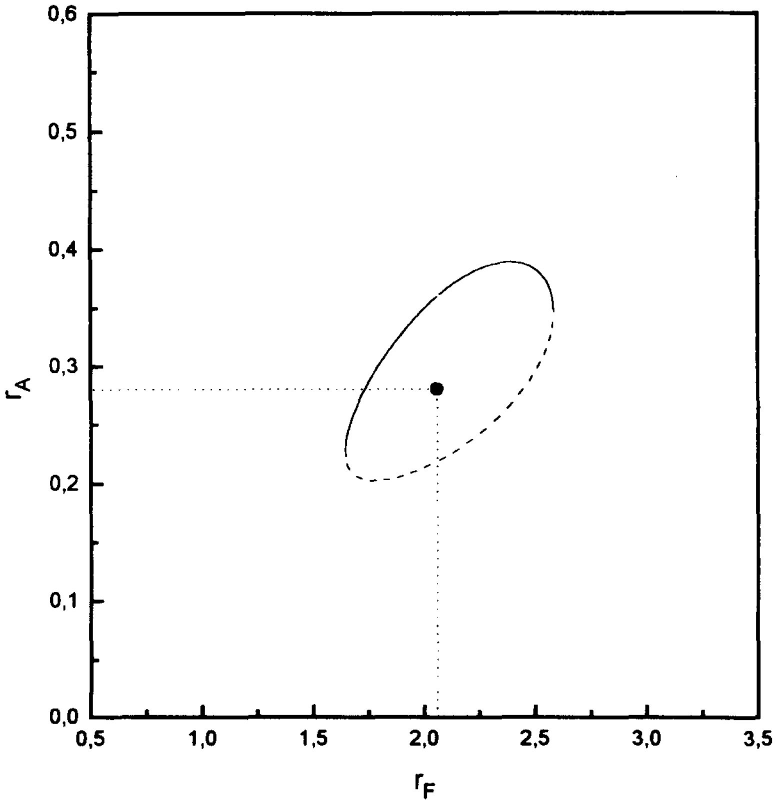

Figure 2 The 95% confidence interval for the reactivity ratios of **F** and **A**, r_F and r_A, determined by the non-linear least squares method suggested by Tidwell and Mortimer

confirms the excellent approximation of the r_F and r_A values as indicated by the reduced dimensions of the ellipse.

The average composition diagram shown in *Figure 3* was drawn with the Tidwell and Mortimer r_F and r_A values using the Lewis–Mayo classical copolymerisation equation. The experimental composition data adequately fit the theoretical diagram represented by the broken line. The reactivity of growing radicals with **F** ends, as measured by $1/r_F$ is somewhat higher towards **F** than **A** monomer molecules, whereas the reactivity of the growing radical with **A** ends is

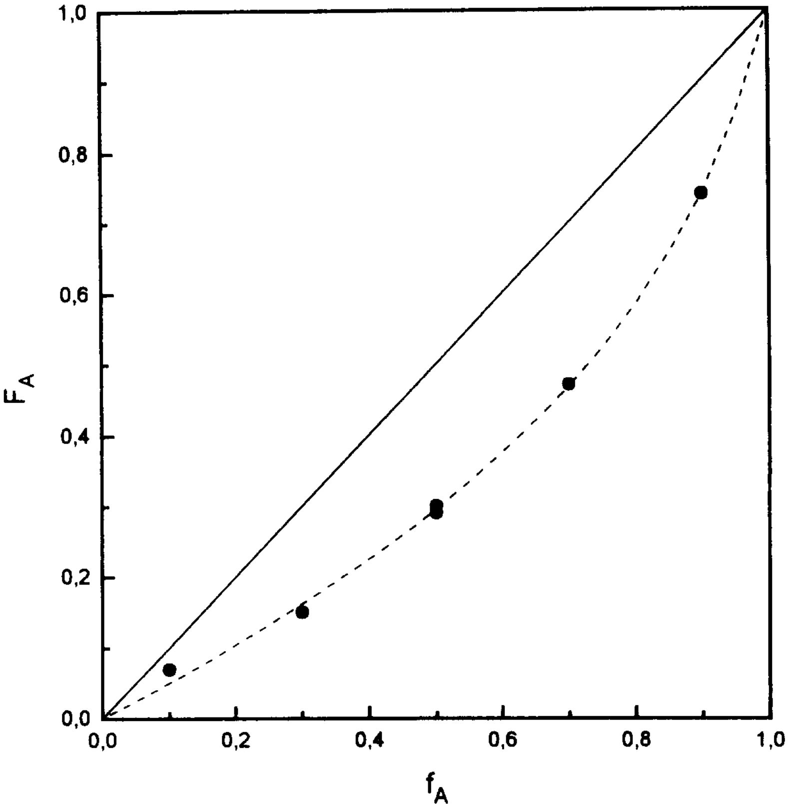

Figure 3 Experimental composition diagram of the **F–A** copolymer system. The broken line corresponds to the theoretical diagram deduced from the Tidwell–Mortimer *r* values given in *Table 2*

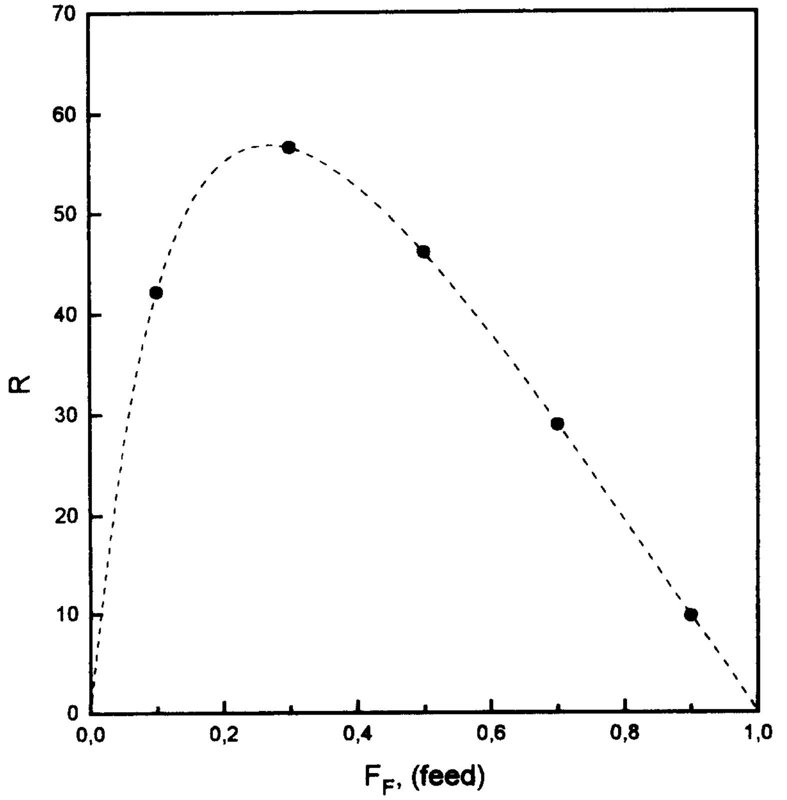

Figure 4 Variation of the 'run number' *R* with the feed composition F_F

much higher towards **F**, in such a way that it can be considered that the growing radicals ending in an acrylamide unit add preferentially an **F** molecule.

From the values of r_F and r_A given in *Table 3* and taking into account well known statistical relationships, we have determined the 'run number', R, defined by Harwood and Ritchey[27] as the average number of monomer alternations in a copolymer for sequences of 100 monomeric units. This parameter provides a useful picture of the sequence distribution in a copolymer chain and can be used to estimate the variation of the physical properties of copolymers with their composition. This parameter can be determined in terms of r values by the expression:

$$R = \frac{200}{2 + r_F - X + r_A/X} \qquad (1)$$

where $X = [\mathbf{F}]/[\mathbf{A}]$ is the ratio of the concentration of **F** and **A** in the monomer feed.

Figure 4 shows the variation of R with F_F. The maximum value of R (56.7) is reached for $F_F \sim 0.27$. This is the result of the preference of addition of **F** molecules by radicals ending in acrylamide.

The copolymer data obtained indicate the statistical character of this copolymerisation system. With these results it is possible to predict the distribution of the ionisable dimethylacrylamide units along the macromolecular chains. According to the reactivity ratio, for a relatively wide range of compositions, the dimethylacrylamide units have a noticeable tendency to be incorporated into the polymeric chains as single elements among sequences of furfuryl methacrylate units, which in addition provide a source of crosslinking when the copolymerisations are carried out in bulk at high conversion.

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