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Photoinitiated bulk polymerization of furfuryl methacrylate. Experimental and kinetic modelling results obtained at different temperatures

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A kinetic model has been proposed for the photopolymerization of furfuryl methacrylate taking into account degradative transfer by the furan ring. Solution of the ordinary differential equation system obtained through the proposed kinetic scheme and the Arrhenius correlation have allowed one set of kinetic constants to be chosen from several estimated sets at different temperatures. The Arrhenius parameter values calculated for each individual proposed step in the model were found to be in good agreement with experimental values for methyl methacrylate and furan compounds. The apparent calculated activation energy gave the value 3.1 kcal mol^{-1} which was close to the experimental value (3.4 kcal mol^{-1}) determined photocalorimetrically. In all steps where allylic radicals were involved, the activation energy values were found to be higher in comparison to those steps in which less-stabilized species operate. Statistical analysis of the adequacy of the model has shown excellent agreement between the experimental data and those determined theoretically at different temperatures using the best set of kinetic constants "estimated" by simulation. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: photopolymerization; experimental and kinetic modelling; photocalorimetry)

INTRODUCTION

Mathematical modelling and sensitivity analysis applied to physico-chemical process are powerful tools with which to gain a better insight into reaction mechanisms. By applying suitable computer programs that incorporate integration methods of Ordinary Differential Equation Systems (ODES), together with different parameter estimation routines, a better understanding and description of different systems present in nature has been made possible.

In the field of polymers, many researchers have been dedicated to the study of the radical polymerization in bulk of methyl methacrylate (MMA) through kinetic modelling[1-3]. However, to the authors' knowledge, this tool has never been applied to the polymerization of acryl-furanic monomers.

Furfuryl methacrylate (FM) is of particular interest in clinical applications as a biomaterial (bone cement) due to its low polymerization shrinkage and its lower than MMA heat of polymerization[4] (MMA is a traditional monomer employed in the preparation of various biomaterials). Over the past few years, several authors have studied the behaviour of hydrogels prepared by the free radical copolymerization of 2-hydroxyethyl methacrylate with small amounts (<30 wt%) of an acrylic derivative containing hydrophobic, but polar, side groups of biomedical interest[5]. More recently, the same authors have reported the swelling behaviour of *N*-vinyl pyrrolidone-furfuryl methacrylate copolymer systems prepared by free radical polymerization with acrylic monomer content lower than 30 wt%[6]. Due to their biocompatibility, these systems have shown possibilities as bio-active controlled dosification systems[7]. As a result, the characteristics of polymerization of furfuryl methacrylate have become of increasing interest.

The possibility of photochemically initiating such polymerizations using, for example, AIBN allows the polymerization process to be performed at lower temperatures. Furthermore, the process can be halted exactly at a preselected conversion degree simply by turning off the irradiating light. This then enables greater control to be exerted over the biomaterial preparation procedure.

The characteristics of the photopolymerization of FM initiated by AIBN are not currently well known. The individual reaction steps of the mechanism and its kinetic parameter values are still unknown. In this context, in the present paper, a mechanism for the photopolymerization of FM has been proposed and the energy parameters of the Arrhenius equation have been estimated for each individual step.

MECHANISTIC CHARACTERISTICS OF THE POLYMERIZATION

The polymerization in bulk of furfuryl methacrylate (FM) tends to lead to the formation of insoluble polymers even at moderate conversion due to the participation of the C-5 position of the furan ring (see *Figure 1*) as radical trapping[8].

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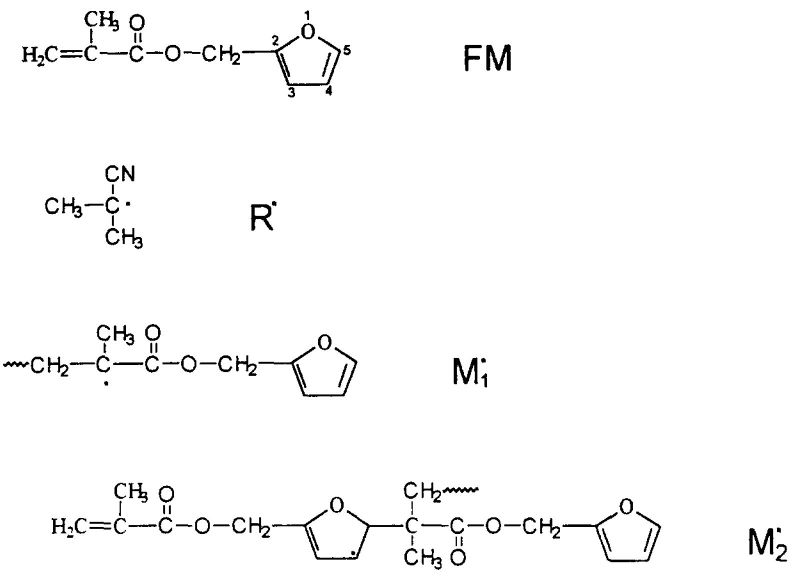

Figure 1 Molecular structure of the species that participate in the mechanism of the polymerization of furfuryl methacrylate

Mihajlov and Boudevska[9] studied FM and the carbomethoxifurfuryl methacrylate (CMFM) polymerization under the same conditions. The fact that the polymerization rate of CMFM was found to be greater than that of FM was explained through the formation of a more stable complex between the polymeric radicals and the furan ring. However, the interaction of radicals with the furan ring has been shown to occur through the addition of the radical to the C-5 position of the furan ring with the formation of a stabilized allylic-type radical[8]. This leads to a so-called degradative transfer process of the chain in the case of the polymerization of acryl-furanic compounds.

In proposing the kinetic scheme of the radical polymerization of MF, the results of the study of the retardant effect of simple furan compounds, such as 2-methyl furan, 2-furanic acid and furfuryl acetate in the radical polymerization of methyl methacrylate and vinyl acetate[4,10] were taken into account. In the case of vinyl acetate, the kinetic scheme of the process was reported, which included, in addition to the "ideal" polymerization steps (initiation, propagation and termination), the transfers with macro- and micro-radicals, and the corresponding crossed terminations[10]. In the case of MF, it is reasonable to suppose that its polymerization follows a similar mechanism, since this monomer possesses a furan ring in its structure.

However, the results of recent works[4,11], dedicated to the kinetic study of the radical polymerization of furfuryl methacrylate and acrylate were taken into account. The kinetic parameters obtained, and the observed cross-linking of the chains (in both cases insoluble polymers were produced, even at low conversions) provided evidence of the participation of the furan ring in the propagation steps.

Thus, the kinetic scheme for the photoinitiated free radical FM polymerization takes into account the possible reactions of the acrylic and furanic moiety. The mechanism contains eleven steps and five species:

$$\mathrm{I} \xrightarrow{\phi} 2\mathrm{R}^{\cdot}$$ photo induced primary radical production

$$\mathrm{R}^{\cdot} + \mathrm{FM} \xrightarrow{k_i} \mathrm{M}_1^{\cdot}$$ primary initiation

$$\mathrm{M}_1^{\cdot} + \mathrm{FM} \xrightarrow{k_p} \mathrm{M}_1^{\cdot}$$ acrylicm acroradical propagation

$$\mathrm{M}_1^{\cdot} + \mathrm{M}_1^{\cdot} \xrightarrow{k_t} \mathrm{P}$$ acrylic macroradical termination

$$\mathrm{M}_1^{\cdot} + \mathrm{FM} \xrightarrow{k_{trd1}} \mathrm{M}_2^{\cdot}$$ intermolecular degradative transfer

$$\mathrm{M}_2^{\cdot} + \mathrm{FM} \xrightarrow{k_{is}} \mathrm{M}_1^{\cdot}$$ re – initiation

$$\mathrm{M}_2^{\cdot} + \mathrm{M}_1^{\cdot} \xrightarrow{k_{tc}} \mathrm{P}$$ allylic – acrylic termination

$$\mathrm{M}_2^{\cdot} + \mathrm{R}^{\cdot} \xrightarrow{k_{tp2}} \mathrm{P}$$ allylic primary termination

$$\mathrm{M}_1^{\cdot} + \mathrm{R}^{\cdot} \xrightarrow{k_{tp1}} \mathrm{P}$$ acrylic primary termination

$$\mathrm{FM} + \mathrm{R}^{\cdot} \xrightarrow{k_{ptrd}} \mathrm{M}_2^{\cdot}$$ primary degradative transfer

$$\mathrm{M}_1^{\cdot} + \mathrm{FM} \xrightarrow{k_{trm}} \mathrm{M}_1^{\cdot} + \mathrm{P}$$ monomer transfer

where P represents polymers and the molecular structures of the species are shown in *Figure 1*. Mathematical treatment of the mechanistic model according to the mass action law gives the following set of non-lineal ordinary differential equations

$$\mathrm{d}[\mathrm{R}^{\cdot}]/\mathrm{d}t = 2\phi I_{\mathrm{a}} - k_{\mathrm{i}}[\mathrm{R}^{\cdot}][\mathrm{FM}] - k_{\mathrm{tp1}}[\mathrm{M}_1^{\cdot}][\mathrm{R}^{\cdot}] - k_{\mathrm{tp2}}[\mathrm{M}_2^{\cdot}][\mathrm{R}^{\cdot}] - k_{\mathrm{ptrd}}[\mathrm{FM}][\mathrm{R}^{\cdot}]$$

$$\mathrm{d}[\mathrm{M}_1^{\cdot}]/\mathrm{d}t = k_i[\mathrm{R}^{\cdot}][\mathrm{FM}] + k_{\mathrm{is}}[\mathrm{M}_2^{\cdot}][\mathrm{FM}] - 2k_{\mathrm{t}}[\mathrm{M}_1^{\cdot}]^2 - k_{\mathrm{tp1}}[\mathrm{M}_1^{\cdot}][\mathrm{R}] - k_{\mathrm{trd1}}[\mathrm{M}_1^{\cdot}][\mathrm{M}] - k_{\mathrm{tc}}[\mathrm{M}_2^{\cdot}][\mathrm{M}_1^{\cdot}]$$

$$\mathrm{d}[\mathrm{M}_2^{\cdot}]/\mathrm{d}t = k_{\mathrm{trd1}}[\mathrm{M}_1^{\cdot}][\mathrm{FM}] - k_{\mathrm{tp2}}[\mathrm{M}_2^{\cdot}][\mathrm{R}^{\cdot}] - k_{\mathrm{is}}[\mathrm{M}_2^{\cdot}][\mathrm{FM}] - k_{\mathrm{tc}}[\mathrm{M}_2^{\cdot}][\mathrm{M}_1^{\cdot}]$$

$$\mathrm{d}[\mathrm{FM}]/\mathrm{d}t = k_{\mathrm{i}}[\mathrm{R}^{\cdot}][\mathrm{FM}] - k_{\mathrm{p}}[\mathrm{M}_1^{\cdot}][\mathrm{FM}] - k_{\mathrm{trd1}}[\mathrm{M}_1^{\cdot}][\mathrm{FM}] - k_{\mathrm{ptrd}}[\mathrm{FM}][\mathrm{R}^{\cdot}] - k_{\mathrm{trm}}[\mathrm{M}_1^{\cdot}][\mathrm{FM}]$$

here:

$I_a = I_0(1 - \exp\{-\epsilon[1]l\}$
ϕ: initiation quantum yield.
I_a: intensity of light absorbed by photoinitiator AIBN (Einstein$\cdot$L$^{-1}\cdot$s^{-1}).
I_0: incident light intensity (Einstein$\cdot$L$^{-1}\cdot$s^{-1}).
ϵ: molar absorption coefficient of the photoinitiator AIBN (L$\cdot$mol$^{-1}\cdot$cm^{-1}).
[I]: photoinitiator concentration (mol$\cdot$L^{-1}).
l: optical path length (cm).

The following points have been taken into account when establishing the model:

- Termination between radicals $\mathrm{M}_2^{\cdot}$ was not included because these are stabilized and sterically hindered.
- The absorbed light I_a, was considered to be constant during the polymerization since the photoinitiator depletion rate is negligible.
- The extent of the reaction between radicals and pendant groups in the polymer were considered to be negligible as a result of the low conversion of polymerization. (Details of network formation are to be published separately.)
- All radicals $\mathrm{M}_2^{\cdot}$ were considered to have the same reactivity whether their formation was through primary or intermolecular degradative transfer. (The length has no influence on the $\mathrm{M}_2^{\cdot}$reactivity.)
- In this scheme it has been assumed that no cyclization occurs.

EXPERIMENTAL

The monomer FM was obtained, purified and characterized as described in reference[12].

The process of photopolymerization initiated by 2,2′-azo-bis-isobutyronitrile, AIBN (λ = 365 nm) was followed by measuring the heat evolved in the reaction as a function of the irradiation time using differential photocalorimetry.

Photochemically initiated polymerization reactions were carried out by direct irradiation of the sample placed in the sample holder of a differential scanning calorimeter. A standard Perkin-Elmer DSC-7 calorimeter was modified and adapted for measuring the polymerization rates of irradiated samples. The two ends of a two-branch UV-light conducting fibre were inserted into the cover of the DSC-4 aluminium block by drilling holes directly above the sample and reference holders. The two-branch flexible UV light guides were terminated with a ferrule connector. As such, the input fiber is 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), an interference 365 nm filter (International Light NB-365), a solid IR filter (Schott KG-1), and neutral density filters. This assembly was mounted onto 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 simultaneously monitor exothermic rates on the DSC. For irradiations under anaerobic conditions, a standard nitrogen flow of 20 cc min^{-1} was maintained in the DSC chamber for at least 10 min before starting the irradiation. This operation allowed the oxygen dissolved in the sample to diffuse out and also ensured that the samples attained the selected equilibrium temperature.

DSC calibration, data processing, incident light intensity determination, as well as complementary details, were performed as described elsewhere[13,14].

All the polymerization experiments were carried out in bulk. The photoinitiator AIBN was used at a concentration of 1.5×10^{-2} mol L^{-1} to ensure total light absorption at 365 nm. Sample quantities of 20 μl were accurately measured using a Hamilton microsyringe. The photocalorimeter described above facilitated the preparation of polymers at a selected temperature and with the required conversion.

The parameter optimization at different temperatures in the proposed kinetic model was carried out with the computer program (EASY-FIT)[15]. A 5th-order implicit Runge–Kutta routine with stiffness was used for the integration of ODES. In this software a routine by gradient searching (NLSFIT) for parameter estimation was used.

RESULTS AND DISCUSSION

Simulation of the polymerization mechanism was drawn up on the basis of data obtained from the kinetic study of the photopolymerization of MF at various temperatures.

All experimental conditions and data obtained, together with the calculated kinetic parameters, are shown in *Table 1*, where I_0 is the incident light intensity, R_p is the rate of polymerization obtained by least-squares calculation from the slope of the linear initial part of the kinetic curve, *r* is the correlation coefficient, and ϕ_m is the polymerization quantum yield (being the amount of monomer polymerized per photon absorbed).

In order to analyse the temperature dependence of the polymerization rate of the monomer, FM, an Arrhenius-type relationship was assumed. The slope of the plot of R_p against reciprocal temperature is proportional to the apparent activation energy, E_R for the polymerization. Assuming a mechanism with a bimolecular termination step and zero activation energy for the initiator, E_R is equal to (E_p − E_t/2). *Figure 2* shows the Arrhenius plot, which allows the corresponding apparent activation energy to be determined. Using a least-squares calculation of the slope, a value of 3.4 kcal mol^{-1} was obtained.

SIMULATION

The fitting was obtained using initial values of the parameters at intervals as shown in *Table 2*. It was possible to obtain several sets of kinetic constants, since these are statistically dependent. However, the sets for each temperature, as detailed in *Table 3*, were selected according to the expected values for this kind of polymerization system. Thus, when these values were used for modelling the variation of monomer concentration with irradiation time, a good correlation was achieved between experimental and calculated data (see *Figure 3*).

The sets of kinetic constants obtained by modelling were used to calculate the apparent activation energy of polymerization (E_R). The estimated value 3.1 kcal mol^{-1}

Table 1 Experimental and calculated data for FM bulk polymerization followed by photocalorimetry using 1.5×10^{-2} mol L^{-1} AIBN as photoinitiator at different temperatures

No.	I_0/mcal s^{-1}	T/°C	$R_p.10^4$/mol L^{-1} s^{-1}	r	$\phi_m 10^{-2}$
1	0.15	0	7.60	0.9999	2.52
2	"	"	7.29	0.9999	2.38
3	"	10	9.48	0.9999	3.59
4	"	"	9.17	0.9999	3.18
5	0.12	20	9.48	0.9999	4.11
6	"	"	10.00	0.9999	4.40
7	0.11	30	10.80	0.9999	5.91
8	"	"	11.50	0.9999	7.02
9	0.18	40	17.90	0.9996	6.85
10	"	"	17.81	0.9998	6.79

Table 2 Initial value intervals of each kinetic constant (L mol^{-1} s^{-1}) in the range of temperatures studied

	Intervals	
Kinetic constant Symbol	Lower limit	Upper limit
k_p	10	6050
k_i	10	1097
ϕ(adim.)	0.2	0.8
k_t	7×10^4	4×10^7
k_{tp1}	6×10^5	5×10^7
k_{trd1}	10	1445
k_{tp2}	1×10^4	9×10^5
k_{ptrd}	20	5455
k_{is}	2×10^{-2}	1.0
k_{tc}	1×10^4	9×10^4
k_{trm}	1×10^{-5}	7.06

Key: adim., adimensional

was in good agreement with the experimental value reported above (3.4 kcal mol^{-1}).

Furthermore, the simulated parameters enabled the activation energy and pre-exponential factor for each reaction step to be determined. This is in accordance with literature data (see below).

In *Table 4*, the concentrations of the species that participate in the mechanism as polymerization proceeds are assembled. As can be seen in this table, the concentration of $M_2^{\cdot}$ is the highest of all radicals since it is stabilized by an allylic resonating structure. Sensitivity analysis (see *Table 5*) also corroborated this result, showing that all steps in which $M_2^{\cdot}$ is involved are sensitive, except primary termination with $M_2^{\cdot}$ (K_{tp2}). Since R radical has the smallest concentration of all species, primary termination with any radical in this model is hence negligible.

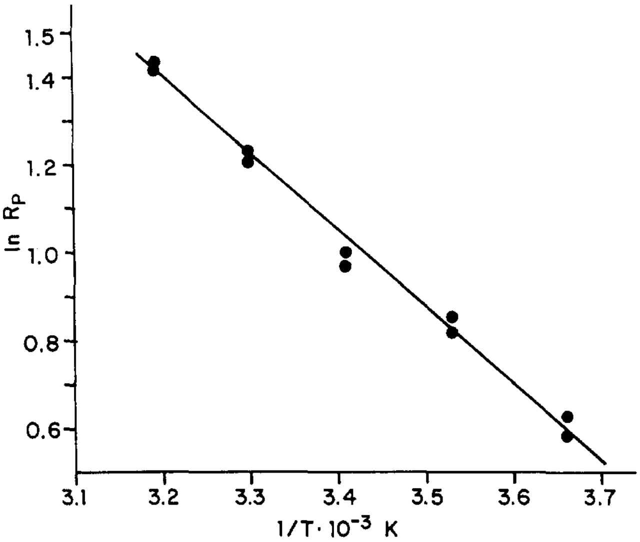

Figure 2 Arrhenius plot of the data obtained for free radical polymerization of FM in bulk photoinitiated by AIBN

ANALYSIS OF ADEQUACY OF THE MODEL.

A statistical test for suitability of the fit of the model[17] can be carried out by comparing adequacy variance of the model S_A^2 with pure error variances S_{pe}^2 using Fischer

Table 3 Kinetic constants (L mol^{-1} s^{-1}) "estimated" at different temperatures for the photopolymerization of furfuryl methacrylate/AIBN in bulk

Kinetic constant	T/°C			
	0	10	30	40
k_p	752.7	1915	2060	2837
k_i	802.6	841.6	946.3	995.1
ϕ(adim)	0.4868	0.1131	0.1097	0.3133
k_t	6×10^5	6.3×10^5	1.05×10^6	1.25×10^6
k_{tp1}	7×10^5	1.14×10^6	1.7×10^6	2.2×10^6
k_{trd1}	621.8	1132	1302	1991
k_{tp2}	1×10^4	2.36×10^4	7.73×10^4	1.4×10^5
k_{ptrd}	998.8	1781	5456	8970
k_{is}	3.97×10^{-2}	0.197	0.563	0.5825
k_{tc}	1.001×10^4	1.657×10^4	3.123×10^4	9.13×10^4
k_{trm}	1.00	9.00	9.298	12.71

Key: adim, adimensional.

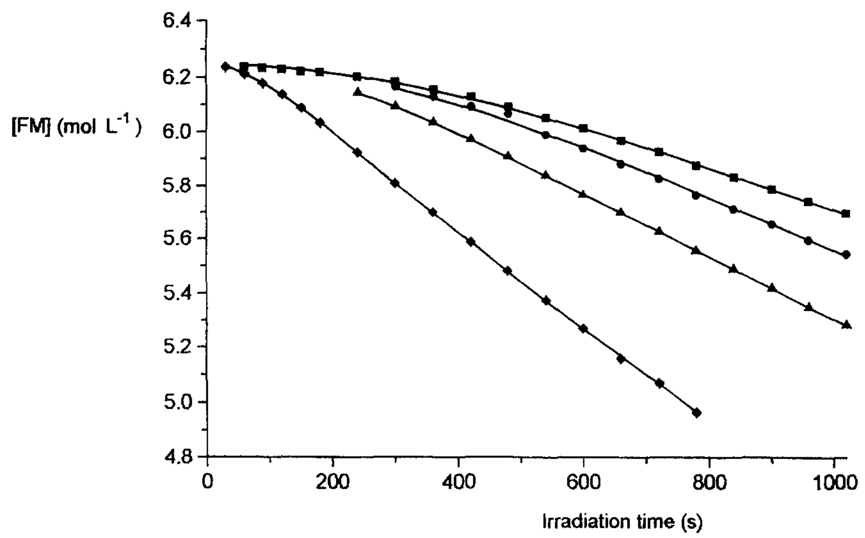

Figure 3 Evolution of the monomer concentration with the irradiation time in the photoinitiated bulk polymerization of furfuryl methacrylate at different absorbed light intensities (Einstein L^{-1}s^{-1}) and temperatures (°C): ■, 1.92 × 10^{-6} (0°C); ●, 1.91 × 10^{-6} (10°C); △, 1.41 × 10^{-6} (30°C); ◆, 2.29 × 10^{-6} (40°C). Continuous lines correspond to the model while the points correspond to experimental values

Table 4 Calculated concentrations (mol L^{-1}) by simulation at 0°C of all the involved species in the proposed reaction mechanism as polymerization time (*t*/s) elapses

t/s	$[R^{\cdot}] \times 10^{10}$	$[M_1^{\cdot}] \times 10^{8}$	$[M_2^{\cdot}] \times 10^{4}$	[FM]
60	1.652	0.732	1.112	6.247
120	1.654	1.43	2.205	6.239
180	1.658	2.104	3.261	6.226
240	1.662	2.744	4.265	6.208
300	1.668	3.344	5.205	6.185
360	1.675	3.896	6.072	6.158
420	1.684	4.400	6.862	6.127
480	1.693	4.852	7.573	6.093
540	1.703	5.255	8.205	6.056
600	1.714	5.609	8.763	6.017
660	1.726	5.919	9.250	5.975
720	1.739	6.187	9.672	5.932
780	1.752	6.419	10.04	5.887
840	1.765	6.617	10.35	5.842
900	1.78	6.786	10.61	5.795
960	1.794	6.930	10.84	5.747
1020	1.809	7.051	11.03	5.699

Snedecork critical values. S_A^2 can be readily calculated through the following equation

$$S_A^2 = \frac{2 \sum_{i=1}^{n} ([\mathrm{FM}]\mathrm{obs.}_i - [\mathrm{FM}]\mathrm{calc.}_i)^2}{n-L}$$

where

[FM]obs.$_i$[FM]calc.$_i$: experimental and calculated monomer concentration respectively.
n: number of experimental points.
L: number of parameters (rate constants).
n − *L*: number of degrees of freedom.

By repeating the experiments, the pure error variance could be obtained

$$S_{pe}^2 = \frac{\sum_{i=1}^{n} ([\mathrm{FM}]\mathrm{obs.1}_i - [\mathrm{FM}]\mathrm{obs.2}_i)^2}{2n}$$

where [FM]obs.1$_i$, [FM]obs.2$_i$ are two experimental monomer concentration values at a particular time.

Table 5 Sensitivity matrix for the photopolymerization of FM/AIBN in bulk at 0°C. The rows equal to 0.0 indicate non-sensitive steps according to Come's methodology[16]

	I	$R^{\cdot}$	$M_1^{\cdot}$	$M_2^{\cdot}$	FM
ϕ	−0.1	1.0	1.0	1.0	−0.1
K_i	0.0	−0.8	0.0	0.0	0.0
K_p	0.0	0.1	0.0	0.0	−0.1
K_t	0.0	0.0	0.0	0.0	0.0
K_{tp1}	0.0	0.0	0.0	0.0	0.0
K_{trd1}	0.0	−0.4	31.9	1.0	0.3
K_{tp2}	0.0	0.0	0.0	0.0	0.0
K_{ptrd}	0.0	−1.2	0.0	0.0	0.0
K_{is}	0.0	0.1	1.0	−1.1	−0.1
K_{tc}	0.0	−0.1	−1.1	−1.1	0.1
K_{trm}	0.0	0.0	0.0	0.0	0.0

An assessment of the adequacy of fit is obtained through the fulfilment of inequality equation (1). This is a sufficient condition for excellent fitting of the model to experimental data

$$\frac{S_A^2}{S_{pe}^2} \leq F(n-L, n, 0.01) \qquad (1)$$

From results shown in *Table 6*, it can be seen how adequately the model describes the experimental data at all temperatures.

COMPARISON OF THE KINETIC CONSTANTS WITH THE LITERATURE DATA

As already mentioned, in the literature there can be found no report of the kinetic constants at different temperatures for FM polymerization. However, it is possible to obtain an estimate of certain kinetic constants using data from the polymerization of monomers having similar acrylic structures, such as MMA, which itself has been thoroughly studied. The ratio k_p/k_t at 50°C for MMA is equal to 16.06 × 10^{-6}[18]. The same relation was calculated for FM from Arrhenius fitting, giving a result 11.9 × 10^{-6}.

In order to compare the value of calculated kinetic parameters with literature data of similar systems, the Arrhenius temperature dependence was used. In this way, the ratio k_{trd1}/k_p for the system furfuryl malonitrile/methyl methacrylate has been reported as being equal to 1.2 at

Table 6 Results obtained from the analysis of adequacy of the model at different temperatures T(°C). The model is adequate to describe experimental data when

$$\frac{S_A^2}{S_{pe}^2} < F(n, n-L, 0.01)$$

T	S_A^2	S_{pe}^2	$n - L$	n	$\frac{S_A^2}{S_{pe}^2}$	$F(n, n-L, 0.01)$
0	9.9×10^{-5}	1.5×10^{-4}	6	17	0.65	4.1
10	2.2×10^{-3}	4.9×10^{-4}	1	12	4.49	9.3
30	8.4×10^{-6}	1.3×10^{-2}	3	14	6.5×10^{-4}	5.56
40	4.2×10^{-5}	2.9×10^{-5}	2	13	1.41	6.7

Table 7 Arrhenius equation for each reaction step found by fitting of the kinetic constants reported in *Table 2* at different temperatures

Kinetic constant/L mol^{-1} s^{-1}	Found equation
k_p	$5.4 \times 10^6 e^{(-4.8\ \mathrm{kcal\ mol}-1/RT)}$
k_i	$4.4 \times 10^3 e^{(-0.9\ \mathrm{kcal\ mol}-1/RT)}$
k_t	$2.7 \times 10^8 e^{(-3.4\ \mathrm{kcal\ mol}-1/RT)}$
k_{tp1}	$5.4 \times 10^9 e^{(-4.8\ \mathrm{kcal\ mol}-1/RT)}$
k_{trd1}	$1.6 \times 10^6 e^{(-4.2\ \mathrm{kcal}-\mathrm{mol}-1/RT)}$
k_{tp2}	$6.7 \times 10^{12} e^{(-10.9\ \mathrm{kcal}-\mathrm{mol}-1/RT)}$
k_{ptrd}	$3.1 \times 10^{10} e^{(-9.3\ \mathrm{kcal\ mol}-1/RT)}$
k_{is}	$4.1 \times 10^7 e^{(-11.1\ \mathrm{kcal\ mol}-1/RT)}$
k_{tc}	$6.3 \times 10^{10} e^{(-8.54\ \mathrm{kcal\ mol}-1/RT)}$
k_{trm}	$2.4 \times 10^7 e^{(-8.9\ \mathrm{kcal\ mol}-1/RT)}$

44.1°C[19]. On the other hand, this ratio for the system vinyl acetate/furfuryl alcohol at 50°C was reported to be 0.25[10,20]. For FM at the above temperatures, these values were calculated as being 0.75 and 0.76, respectively. All these results demonstrated that the kinetic parameters obtained in the present study are consistent with systems of polymerization whenever the furan ring is involved.

ENERGY AND ENTROPY ANALYSIS OF CERTAIN INDIVIDUAL STEPS

The Arrhenius parameters for each reaction step as estimated are displayed in *Table 7*. The energy of activation for the propagation step E_p was estimated to be 4.8 kcal mol^{-1}. This value must be the same for the propagation of MMA. The activation energies reported for the propagation of MMA are rather scattered in the interval 4–6 kcal mol^{-1} (4.4, 5.5, 5.8, 6.31 kcal mol^{-1} in reference[18]). Thus, the value estimated by modelling is reasonable. The collisional factor for the propagation step of FM ($A_p = 5.4 \times 10^6$ L·mol^{-1}·S^{-1}) was found to be equal to that reported for MMA ($A_p = 5 \times 10^6$ L·mol^{-1}·S^{-1})[15]. The activation energy for the termination between acrylic macroradicals (k_t) was estimated as being E_t = 3.4 kcal mol^{-1}. The same values reported for MMA are 2.84 and 4.0 kcal mol^{-1} (in Ref. 18). Thus, the value obtained here for E_t is reasonably good.

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