ELSEVIER

European Polymer Journal 38 (2002) 281–286

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Kinetics of furfuryl alcohol polymerisation by iodine in methylene dichloride

Regino González [a,b,*], Jacques Rieumont [b], Juan M. Figueroa [a], Javier Siller [a], Hilda González [b]

[a] *Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del Instituto Politécnico Nacional (CICATA-IPN), Legaria 694, Col. Irrigación, D.F., C.P. 11500, Mexico*

[b] *Facultad de Química-IMRE, Universidad de la Habana, Habana 10400, Cuba*

Received 13 November 2000; accepted 1 March 2001

Abstract

The kinetic studies of furfuryl alcohol polymerisation by iodine in methylene dichloride showed a pseudo-first-order behaviour in monomer. The pseudo-first-order constant obtained varies linearly with the concentration of iodine. Our previous work on the system concluded for a pseudo-cationic polymerisation mechanism based on the admission of non-ionic propagating species. The good fitting among the experimental monomer concentration data and the one obtained from computer simulation justifies the mechanism proposed for the system. The set of estimated values of the rate parameters is also reported.

Keywords: Furfuryl alcohol; Iodine; Modelling; Pseudo-cationic polymerisation

1. Introduction

Polymerisation of furfuryl alcohol (FA) by Brönsted and Lewis acid has been previously studied using different experimental conditions [1–4] However little attention has been devoted to the study of the FA polymerisation by iodine. Nature of active species (ionic or covalent centres), influence of iodine as an initiator, which produces a counterion of high nucleophilicity (living polymers by iodine [5]) and oxidant character of iodine (''self-doping agent'' in semiconductors polymers), are aspects of interest and that should be investigated. Recently the polymerisation of FA initiated by iodine was studied by us using different experimental conditions such as the influence of air, iodine concentration and temperature. Chemical structures of polymers was established and a mechanism of polymerisation was offered [6]. The self-condensation kinetics of furanic carbinols is a subject that has not been thoroughly studied. With the exception of some data on the kinetics of FA with formaldehyde reaction [7,8] we do not know about any other serious report which deals with this subject. The main problems encountered in studying the kinetics of FA polymerisation is the difficulty of analysis of monomer in the presence of its resins, owing to which the extent of reaction of the FA cannot be directly determined. Polymerisation of furanic carbinol differs dramatically with respect to that of its benzenic homologous. The processes with FA and other carbinol furanics, present such a complexity that no analogy with the benzene analogue can be established, because the carbon C-5 position of the furan ring introduces side reactions that lead to branching, colour and the last step crosslinking [3].

This paper reports the kinetics of the polymerisation of FA initiated by iodine in methylene dichloride (MDC) solution. Also the paper reports a mathematical

* Corresponding author. Address: Faculty of Chemistry, University of the Havana, Zapata and G, C.P. 10400 Havana City, Cuba.

E-mail addresses: reginog@yahoo.es, reginog@imre.oc.uh.cu (R. González).

0014-3057/01/$ - see front matter
PII: S0014-3057(01)00091-X

model for the mechanism which permit to model experimental concentration versus time and know the trend of all reacting species.

2. Experimental part

All experiments were carried out taking particular care to insure the stringent requirements for reliability imposed by the good practice of kinetic investigation. Therefore, we thoroughly purified and dried all reagents.

FA (from Merck) was purified, dried and handled on a high vacuum system as reported previously [1]. The purity of FA was checked by HPLC to be greater than 99%. Iodine (Fluka), was purified by sublimation. MDC (from Merck) was fractionally distilled. The middle portion was collected over calcium hydride.

The kinetic study was performed using chromatographic determinations by HPLC in presence of air. HPLC investigations were carried out on a Varian 9012, injector RHEODYNE 7125; detector arrangement of diodes; Colum: Perkin Elmer NH/CN 250 × 5; injection volume 20 ul; mobile phase H_2O (Baker)/acetonitrile (Merck) 60/40; flow 0.5 ml.

A set of ordinary non-linear equations obtained from the polymerisation mechanism (see Appendix A) constitutes the mathematical model used to simulate the polymerisation under study. By solving the set of equations under different initial conditions is possible to obtain the concentration–time course of each chemical species of the polymerising system. A program to model the monomer concentration versus time, written in FORTRAN-77 was implemented on an IBM compatible microcomputer [9]. The simultaneous simulation of monomer concentration versus time for six kinetic runs with 68 experimental points was carried out using a Gear algorithm coupled with *s* steepest descend routine in order to minimise the error function $S = \sum(\mathrm{FA_{exp}} - \mathrm{FA_{cal}})^2$. Other reacting species were calculated.

The initial set of kinetic parameters was chosen in order to avoid local minima by analogy with similar furan system. The initial set of parameters chosen was the following:

$k_1 = 7.00\ \mathrm{l^2\,mol^{-2}\,min^{-1}}$,
$k_2 = 10\ \mathrm{l^2\,mol^{-2}\,min^{-1}}$,
$k_3 = 4.00\ \mathrm{l^2\,mol^{-2}\,min^{-1}}$,
$k_4 = 0.1\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_5 = 0.60\ \mathrm{l^2\,mol^{-2}\,min^{-1}}$,
$k_6 = 0.01\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_7 = 10\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_8 = 0.1\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_9 = 0.01\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_{10} = 0.01\ \mathrm{l^2\,mol^{-2}\,min^{-1}}$,
$k_{11} = 0.1\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_{12} = 0.1\ \mathrm{l\,mol^{-1}\,min^{-1}}$,
$k_{13} = 1.00\ \mathrm{l\,mol^{-1}\,min^{-1}}$.

The propagation kinetic parameters were assumed as for a pseudo-cationic polymerisation [10–13]. Transfer constants with monomer were taken in the range for a cationic polymerisation. Initiation parameters are in line with the results of Giusti et al. for styrene polymerisation by iodine [11]. Terminations with formation of allylic ions was taken from the system trichloroacetic acid with ciclopentadiene and furan monomers [14,15].

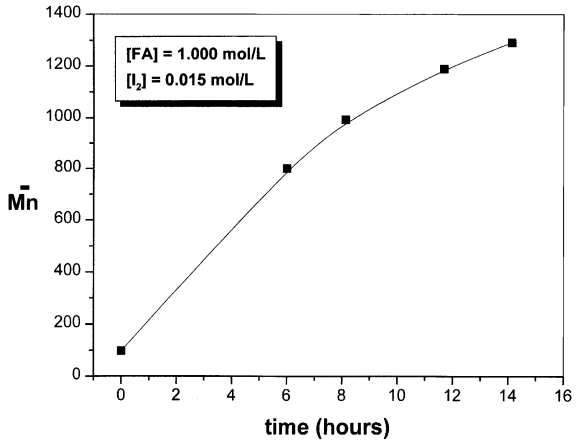


Fig. 1. Plot of the number-average molecular weight (M_n) versus time. $[\mathrm{FA}]_0 = 1.000\ \mathrm{mol\,l^{-1}}$; $[\mathrm{I_2}]_0 = 0.015\ \mathrm{mol\,l^{-1}}$; temperature = 25°C.

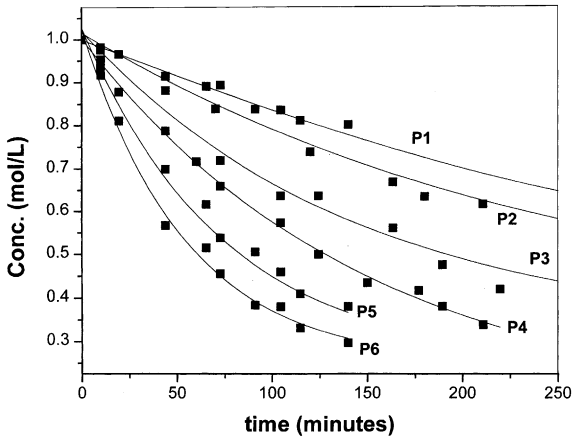


Fig. 2. Experimental (■) and theoretical (—) conversion–time curves for the FA polymerisation. Conditions experimental are shown in Table 1.

3. Results and discussion

The variation of M_n for FA polymerisation at different reaction times is shown in Fig. 1. Even though the M_n of resin grew as time elapses, this system could not be considered as a classical polycondensation, since the concentration of the monomer did not decreased suddenly after the reaction had started. On the contrary, its variation occurred smoothly as in a polyaddition system (see Fig. 2).

The results of the kinetic study for FA polymerisation by iodine are shown in Table 1. In all runs, the regression coefficient was greater than 0.9980. The monomer concentration decreasing with time is a pseudo-first-order reaction (see Fig. 3). The pseudo-first-order constant k' obtained from the data reported in Table 1 varies linearly with the concentration of iodine as is shown in Fig. 4. Their slopes gave second-order constants $k = 0.22\,\mathrm{l\,mol^{-1}\,min^{-1}}$. Therefore, the rate law for this reaction is $-\mathrm{dFA}/\mathrm{d}t = k[\mathrm{FA}][\mathrm{I_2}]$.

Table 1
FA polymerisation by iodine in MDC[a]

Polymer	$[FA]_0$ (mol l^{-1})	$[I_2]_0$ (mol l^{-1})	$k' \times 10^{3}$[b] (min^{-1})
P1	1.000	0.010	2.30
P2	1.000	0.015	2.53
P3	1.000	0.020	4.80
P4	1.000	0.025	5.57
P5	1.000	0.030	7.50
P6	1.000	0.035	9.51

Number-average molecular weight M_n was measured by vapour–pressure osmometry.

[a] All runs were carried out at 25°C for 24 h. $[FA]_0$, $[I_2]_0$ initial concentrations of FA and iodine respectively.

[b] k': specific pseudo-rate constant.

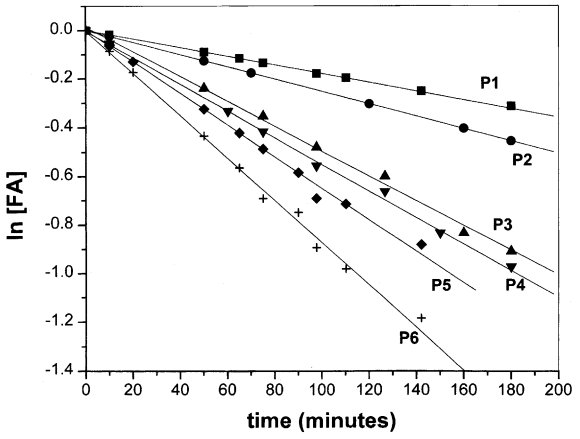


Fig. 3. Pseudo-first-order plots for FA polymerisation in MDC by iodine. Conditions experimental are shown in Table 1.

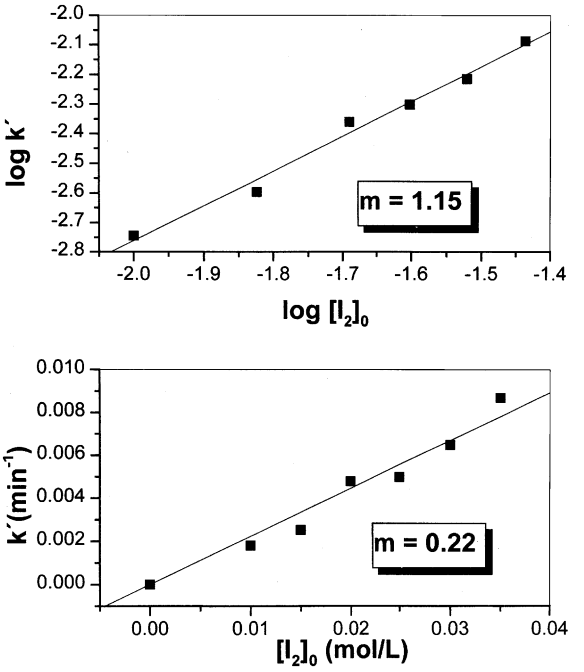


Fig. 4. Values of apparent rate constant (k') at different initial concentration of iodine ($[I_2]_0$) and plot of $\log(k')$ versus $\log[I_2]_0$.

In order to explain this kinetic behaviour we suggested the mechanism already proposed and explained by us [6] (see Appendix B).

4. Mathematical modelling

The proposed mechanism for the FA polymerisation by iodine was computational modelled using simultaneously data of different runs. Table 2 shows the experimental data and the fitting for the monomer concentration expressed as per cent mean error, for all experimental point of each run. Modelled monomer conversion–time curves were compared with the experimental curves. Fig. 5 shows the experimental and calculated values. The good fitting between the modelled and experimental curve suggests that the reaction mechanism is quite reliable taking into consideration the chemical complexity. In Fig. 5 are shown the modelled curves for $[I_2]$ and $[H_2O]$ from experiment P4. Initiator concentration actually decreases during the first 2 h of reaction up to 30%. Later its decreasing is lower. Iodine consumption during polymerisation is related to the formation of active centres and HI principally. An acid kidnapping is a feature that characterises the furan

Table 2
Simulation of the FA polymerisation in MDC by iodine

Polymer	$[FA]_0$ ($mol\,l^{-1}$)	$[I_2]_0$ ($mol\,l^{-1}$)	Experimental points	Mean error per run (%) in estimation of monomer concentration
P1	1.000	0.010	12	6.01
P2	1.000	0.015	14	2.34
P3	1.000	0.020	12	4.45
P4	1.000	0.025	10	2.88
P5	1.000	0.030	10	8.01
P6	1.000	0.035	10	9.15

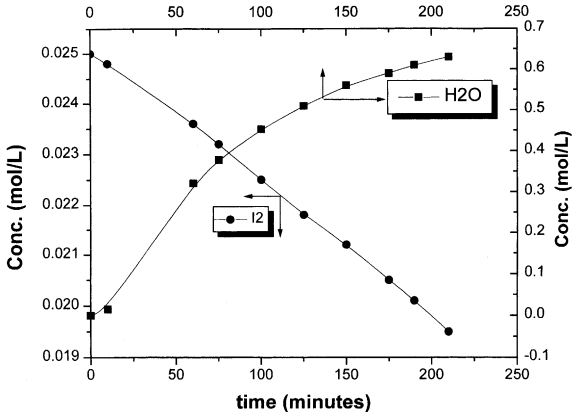


Fig. 5. Trend of the theoretical concentrations for the species I_2 and H_2O for the experiment P4.

carbinol polymerisation [4,10]. Water concentration increases during the polymerisation as is showed and confirmed in Fig. 5. One of the most complex aspects in the study of cationic polymerisation is the nature of active centres. If the reaction proceeds by ionic species then the polymerisation will be characterised by high rate and sensitivity to humidity. However, if the active centres are principally polarised centres, the rate will be much smaller, and usually water not interfere with the polymerisation reaction [16–18]. Our previous work on this system concluded for a pseudo cationic mechanism based on the admission of non-ionic propagating species [6].

The estimated values of the rate parameters for each mechanism step are the following:

$k_1 = 4.56 \times 10^{-4}\ l^2\,mol^{-2}\ min^{-1}$,
$k_2 = 6.29 \times 10^{-4}\ l^2\,mol^{-2}\ min^{-1}$,
$k_3 = 5.36 \times 10^{-1}\ l^2\,mol^{-2}\ min^{-1}$,
$k_4 = 4.60 \times 10^{1}\ l\,mol^{-1}\ min^{-1}$,
$k_5 = 4.86 \times 10^{1}\ l^2\,mol^{-2}\ min^{-1}$,
$k_6 = 6.74 \times 10^{-1}\ l\,mol^{-1}\ min^{-1}$,
$k_7 = 1.30 \times 10^{2}\ l\,mol^{-1}\ min^{-1}$,
$k_8 = 1.09 \times 10^{-1}\ l\,mol^{-1}\ min^{-1}$,
$k_9 = 1.28 \times 10^{-3}\ l^2\,mol^{-2}\ min^{-1}$,
$k_{10} = 2.13 \times 10^{-2}\ l\,mol^{-1}\ min^{-1}$,
$k_{11} = 1.61 \times 10^{-4}\ l^2\,mol^{-2}\ min^{-1}$,
$k_{12} = 4.72 \times 10^{-1}\ l\,mol^{-1}\ min^{-1}$,
$k_{13} = 1.28 \times 10^{-1}\ l\,mol^{-1}\ min^{-1}$.

k_7 values is same order of a propagation constant for a pseudo-cationic polymerisation [19]. k_9 constant value is lower than k_7 and by analogy with FA polymerisation catalysed with trifluoroacetic acid [1], its value is indicating that the formation of oligomers through the electrophilic substitution at the C-5 furan ring position prevails over the ether formation.

This is a very complex system, in which the experimental determination of each reaction constant is very difficult. The set of constants reported has only the purpose to give a series of parameters that permit to justify the conversion of the monomer appropriately in the time starting from the data obtained experimentally and also to confirm the modelled reaction mechanism proposed.

5. Conclusion

The FA polymerisation in MDC catalysed by iodine was followed kinetically. The monomer concentration decreases with time obeys a pseudo-first-order reaction. It showed several features typical of either polyaddition or polycondensation, all of which could be explained by the mechanism and modelling put forward.

Acknowledgements

The authors gratefully acknowledge the support of the sponsor of this research: Research Centre for Applied Science and Advanced Tecnology. National Polytechnic Institute (CICATA-IPN).

Appendix A

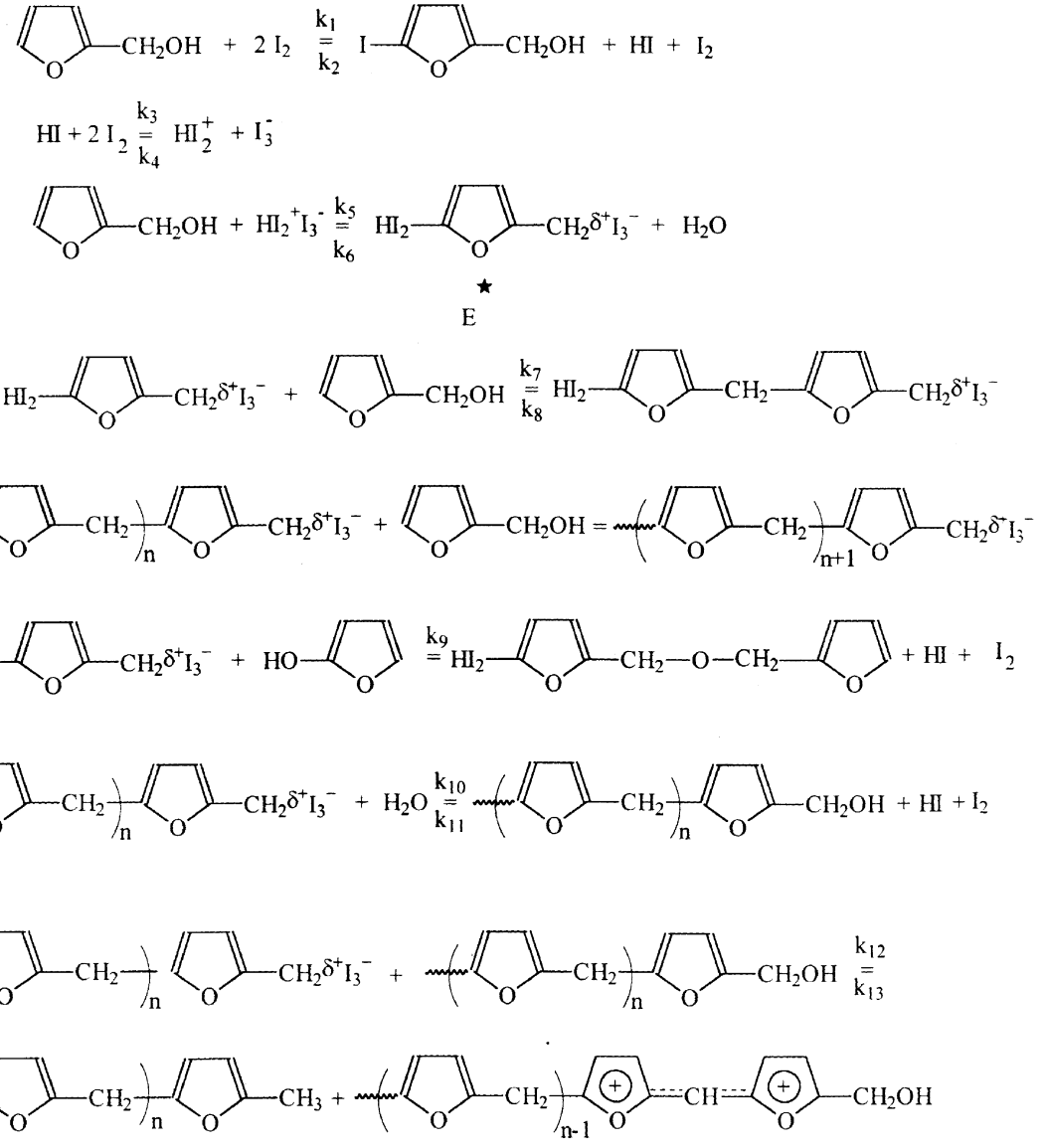
Rate equations for the mechanics of FA polymerisation by iodine and the species mass balance equations.

$V(1) = k_3[FA][I_2][I_2]$,

$V(2) = k_4[\text{I–FA}][\text{HI}][\text{I}_2]$,
$V(3) = k_5[\text{HI}][\text{I}_2][\text{I}_2]$,
$V(4) = k_6[\text{HI}_2^+][\text{I}^{3-}]$,
$V(5) = k_7[\text{FA}][\text{HI}_2^+][\text{I}_3^-]$,
$V(6) = k_8[\text{E}^*][\text{H}_2\text{O}]$,
$V(7) = k_9[\text{E}^*][\text{FA}]$,
$V(8) = k_{10}[\text{E}^*][\text{H}_2\text{O}]$,
$V(9) = k_{11}[\text{E}^*][\text{FA}]$,
$V(10) = k_{12}[\text{E}^*][\text{H}_2\text{O}]$,
$V(11) = k_{13}[\text{POH}][\text{HI}][\text{I}_2]$,
$V(12) = k_{14}[\text{E}^*][\text{POH}]$,
$V(13) = k_{15}[\text{Ps}][\text{Pv}]$.

Appendix B

Mechanistic scheme of FA polymerisation by iodine in MDC.



References

[1] González R, Martínez R, Ortíz P. Makromol Chem 1992;193:1.
[2] González R, Martínez R, Ortíz P. Makromol Chem Rapid Commun 1992;13:517.
[3] Choura M, Naceur M, Gandini A. Macromolecules 1996;29:3839.
[4] Principe M, Martínez R, Ortíz P. Polym Int 1999;48:637.
[5] Sawamoto M. Prog Polym Sci 1991;16:111.
[6] González R, Figueroa JM, González H. Eur Polym J 2002;38:287.
[7] Laszlo-Hedvig Z, Szestay M, Faix F, Tüdos F. Angew Makromol Chem 1982;107:61.
[8] Szestay M, Laszlo-Hedvig Z, Tüdos F. Angew Makromol Chem 1983;170:173.
[9] Paz JA, Rieumont J. Polymer 1995;36(12):2425.
[10] González E, González R, Ortiz P, Rieumont J. Polymer 2000;41:2491.
[11] Maschio G, Cerrai P, Giusti P. Polym Bull 1982;8:147.
[12] González R, Rieumont J. Macromol Theory Simul, in press.
[13] González R, Rieumont J, Ortiz P, Mendoza L, Radilla J. Macromol Chem Phys 2001;202(5):710.
[14] Upadlhyay J, Wallace G, Wasssermann A. Polymer 1966;7:465.
[15] Armour M, Davies A, Upadlhyay J, Wassermann A. J Polym Sci A-1 1967;5:1527.
[16] Gandini A, Cherddame H. Adv Polym Sci 1980;34/35:80.
[17] Plesch PH. Makromol Chem, Macromol Symp 1988;13/14:370.
[18] Plesch PH. Eur Polym J 1989;25(7/8):875.
[19] Galego G, Peniche C, Introductión a la Química Física de los Polímeros Edit. Rev., MES, Cuba, 1990. p. 159.