

The resinification of 2-ethenylfuran catalyzed by trifluoroacetic acid in water–chloroform mixtures

E. González, M. González, R. González, P. Ortiz, J. Rieumont*

Faculty of Chemistry-IMRE, University of Havana, Havana 10400, Cuba

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Abstract

The 2-ethenylfuran polymerization catalyzed by trifluoroacetic acid in a water–chloroform mixture yields oligomers at the beginning and products at higher reaction times. Some features of the polymerization resemble a polycondensation process such as molecular weight increasing with time. Polymers obtained were characterized and its structure did not differ from those obtained with 1 (2-furyl) 1-ethanol. Thus, a vinylic propagation can be ruled out. However, the monomer concentration decreased steadily during polymerization and the kinetic first order in monomer and catalyst could only be explained assuming a steady state for the polarized ester concentration, which is the active center that gives the corresponding carbinol. Both of these facts suggest a chain reaction. Computer simulation helped to confirm the envisaged mechanism for this system. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: 2-Ethenyl furan; Acid resinification mechanism; Modeling

1. Introduction

One of the most complex aspects in the study of cationic polymerization of vinylic monomers is the nature of active centers. If the reaction proceeds by ionic species then the polymerization will be characterized by high rate and sensitivity to humidity. However, if the active centers are principally polarized esters, the rate will be much smaller, and usually, water will not interfere with the polymerization reaction. This is known as pseudo-cationic polymerization [1–3].

In this context the cationic polymerization of 2-alkenylfurans present the same features with an additional complication due to the nucleophilic attack at the C-5 position of the furan ring [4–6]. Active centers of ionic and covalent nature are present during the polymerization of these monomers by trifluoroacetic acid (TFA) in methylene dichloride [7] (DCM). The predominance of one of them depends on the experimental conditions.

In the present work the polymerization of 2-ethenylfuran was studied in water–chloroform heterogeneous mixtures 1/45 (system A) and 50/50 (system B) in volume. In this condition, the possibility of ionic centers is practically

non-existent and the polymerization should therefore be induced by polarized esters.

2. Experimental

2.1. Materials

2-Ethenylfuran (VF) was obtained and purified as described in Ref. [5]. The purity of VF was checked by GLC to be greater than 99%. Trifluoroacetic acid (TFA) from Carlo Erba was purified and dried as previously reported [8], and chloroform from Merck was fractionally distilled.

2.2. Techniques

The polymerization of VF was carried out in a three-neck flask under reflux and stirring, the solution of TFA in CH_3Cl being added dropwise to give a colored resin.

Kinetic determinations were carried out by UV–Vis spectroscopy. First, the stirring was stopped and samples of the organic phase were removed with a pipette. Its content was added into a volumetric flask containing a solution of sodium hydroxide in ethanol. The flask was then brought to level with ethanol. The concentration of VF was calculated from the absorption at 264 nm ($\epsilon = 1.8 \times 10^4$), corresponding to the maximum of its $\pi-\pi^*$ band.

*Corresponding author. Universidade Estadual do Norte Fluminense, CCT.LAMAV, Ave. Alberto Lamego, Horto 2000 ampos Dos Goytacazes, RJ Brazil.

Table 1

2-ethenyl furan polymerization in heterogeneous mixture of water–chloroform (all runs were carried out at 30°C for 8 h. Exceptions are indicated in the table)

Exp.	[VF] ₀ mol l ^{-1a}	[TFA] ₀ mol l ⁻¹	V(H ₂ O/CHCl ₃) ^b	k × 10 ³ min ^{-1c}	Mn
P1	1.00	0.0125	1/45	2.30	d
P2	1.00	0.0225	1/45	3.60	d
P3	1.00	0.0350	1/45	6.04	d
P4	1.00	0.0450	1/45	7.60	d
P5	1.00	0.0530	1/45	8.00	3200
P6	1.00	0.0600	1/45	9.15	d
P7	1.00	0.1000	50/50	d	d
P8	1.00	0.1000	50/50	d	d
P9	1.00	0.2000	50/50	2.9	d
P10	1.00	0.5000	50/50	5.8	d
P11	1.00	1.0000	50/50	10.3	5115
p12	0.50	1.0000	50/50	d	2853
p13	0.50	1.0000	50/50	d	3308 ^e
P14	0.50	1.0000	50/50	d	9535 ^f
P15	0.50	0.5000	50/50	d	d
P16	0.50	0.2000	50/50	2.9	d

^a [VF]₀, [TFA]₀: initial concentrations of 2-ethenyl furan and trifluoroacetic acid, respectively.^b V(H₂O/CHCl₃): water–chloroform ratio.^c k': specific pseudo-rate constant.^d Not calculated.^e Reaction time: 12 h.^f Reaction time: 24 h.

2.3. Modeling

A program to model the monomer concentration versus time, written in Fortran 77 Ms, was implemented on an IBM compatible microcomputer [9]. The system of ordinary differential equations for the mechanism (See Appendix A) is solved using a Gear algorithm coupled with a steepest descend routine in order to minimize the error function: $S = \sum(M_{\text{exp}} - M_{\text{cal}})^2$. The initial set of rate parameters used was estimated by analogy with similar chemical systems [10].

2.4. Measurements

¹H and ¹³C NMR spectra of polymer solutions in CDCl₃ were obtained using a Bruker AC-250F working at 250 MHz (¹H) and 62.90 MHz (¹³C). IR and UV spectra were registered using a UNICAM PU-9512 and a UNICAM PU 8715, respectively. Number average molecular weights

(Mn) were determined by vapor pressure osmometry with a Knauer equipment.

3. Results and discussion

3.1. Resin structure

Experimental conditions for different reactions of VF with TFA exposed to air, in water–chloroform heterogeneous mixtures, are shown in Table 1. Chemical composition for the systems A and B were similar. The Mn did depend on the acid concentration and on the reaction time. Same results were obtained in the study of resinification of furfuryl alcohol (FA) with these initiators [11].

The composition of the water–chloroform mixture did not affect the nature of the products. Nevertheless, those obtained in water, separated spontaneously from the reaction mixture, although they were soluble in CH₂Cl₂ and CHCl₃. All these resins became insoluble in these organic

Table 2

Main absorption bands (cm⁻¹) in the IR spectra of resin P11, a resin from (2-furyl) 1-ethanol [14] (PFC) and a resin from furfuryl alcohol [11]

	γCH	γCH	ν ^S C–O	ν ^A C–O	δC–H	νC=C	νC=O	νC–H	νC=CH	νOH
P11	740	800	1020	1240	1460	1570	1720	2950	3150	3420
PFC	735	790	1010	1230	1430	1560	1700	2960	3125	3400
PFA	740	790	1010	1230	1435	1565	1710	2940	3125	3490

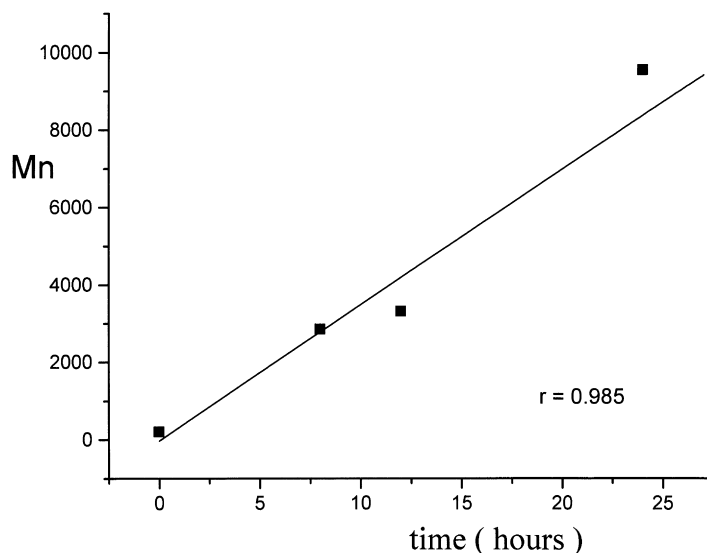
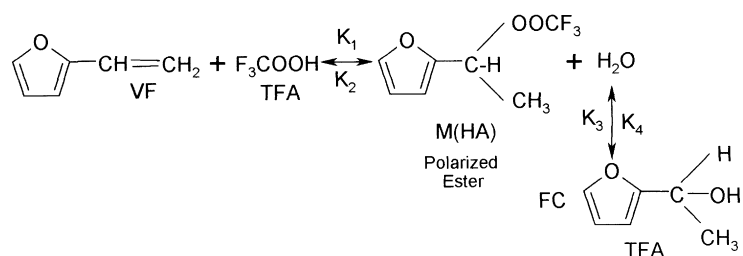


Fig. 1. Linear plot of the number average molecular weight versus time for experiments P12, P13, P14.

solvents when the reaction time was longer than 4 h. If the solvent is removed from these resins, they become insoluble

water due to the hydrolysis of the intermediary ester M(HA):



in less than 2 h. This behavior becomes more pronounced as Mn increases [11–13].

The P11 polymer was chosen as the reference in this work. The most important IR absorption bands of P11, of a poly(FA) synthesized in the same experimental conditions than P11, and of a resin from 1(2-furyl)1-ethanol(FC), obtained in DCM with SnCl₄ as initiator [14] are similar (see Table 2). The bands in the regions 735–740, 1020, 1150, 1510, 1560–1570 and 3125–3150 cm⁻¹ are attributed to monosubstituted furan rings according to the literature, while the bands appearing at 790–800 and 1560–1570 cm⁻¹ are, respectively, due to bending out of the plane of the CH linkage, and to the valence deformation of the –C=C– groups in the 2–5 disubstituted furanic rings. The band at 2950–2960 cm⁻¹ is due to symmetrical vibrations of aliphatic CH groups, whereas the 3400–3490 cm⁻¹ band is assigned to OH groups. The P11 resin was previously heated under vacuum at 110°C for 8 h, with the purpose of eliminating all traces of humidity. Its IR spectrum was recorded again and no change was noted. The presence of macromolecules with OH groups is attributed to the polymerization of FC and suggests that VF gives furyl carbinol (FC) in

In a way similar to that for FA and FC resins [11,12,14], the absorption band at 1720 cm⁻¹ is due to the carbonylic structures showing the hydrolysis of some furanic rings in aqueous acid media. Its contribution, however, is not significant thus the furan ring remains the predominant structure.

Spectroscopic evidences obtained by NMR indicate that all the above structures are similar. This is illustrated with P11 resin, as shown in Table 3. The assignments of the signals were made according to the ¹H NMR and ¹³C spectra of different model compounds [14].

In the system under study there is no evidence of vinyl polymerization through the double bond. It seems the VF reacts with TFA in order to produce a intermediary ester M(HA) which gives FC. This species selfcondense to give complex resins.

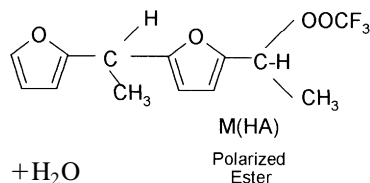
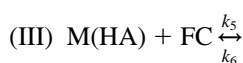
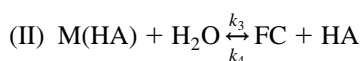
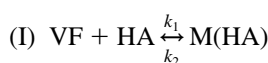
3.2. Kinetics

The linear variation of Mn for experiments P12, P13 and P14 (see Table 1) at different reaction times is shown in Fig. 1. This is a typical feature of polycondensation. However, this system could not be considered as classical polycon-

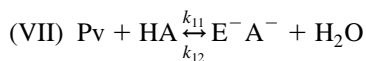
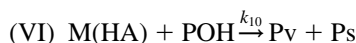
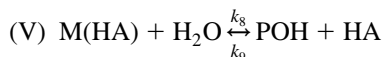
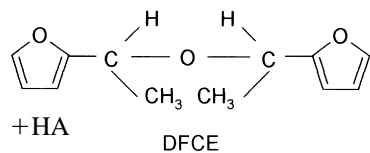
densation, since the concentration of the monomer did not decrease suddenly after the reaction had started. On the contrary, its variation occurred smoothly as in a vinyl poly-addition system (see Fig. 2).

The results of the kinetic study for the systems A and B are shown in Table 1. The monomer concentration decreases with time and obeys a pseudo-first-order reaction. Further, the pseudo-first-order constants (k') obtained (see Table 1) varies linearly with the concentration of TFA as is shown in Fig. 3.

Their slopes gave second-order constants, 0, 16 (for the system A) and 0.01 (for system B) $l \text{ mol}^{-1} \text{ min}^{-1}$. Therefore, the rate law for this reaction is $-d[\text{VF}]/dt = k[\text{TFA}][\text{VF}]$. In order to explain this kinetic behavior the following mechanism is proposed:



(dimeric)



VF reacts with a molecule of TFA giving 1(2-furyl)ethyl trifluoro-acetate (M(HA)), which is the active species for polymerization. Later its hydrolysis in acidic solution gives FC (step II). M(HA) reacts with FC by electrophilic substitution at the C-5 position of the furan ring resulting macromolecules of different degree of polymerization (step III) or forming ethereal structures (step IV) as has been published for the system FA/DCM/TFA [11]. For a lower

Table 3
RMN ^1H and ^{13}C signal assignation for the P11 resin

NMR values		Structure
^1H	^{13}C	
2.88	27	
1.53	19	
4.10	33	
4.70	60	
5.8–6.4	110	
7.30	140	
–	153	

ratio $[\text{VF}]_0/[\text{TFA}]_0$ step IV prevails over step III as shown for FA-DCM-TFA system [12].

In these systems, the reaction of FC giving the corresponding ether is not important and the predominant condensation steps giving dimers, trimers, etc. involve the electrophilic substitution at the C-5 position of the furan ring of the carbinol. FC behaves as an intermediate product (see Fig. 4) and its maximum concentration is never over $4.0 \times 10^{-1} \text{ mol l}^{-1}$, as indicated by the computer modeling.

The presence of chains with OH ending groups is due to step V which can be considered a termination reaction that stops the chain growing and producing small macromolecules.

The cause of the resin color is associate to the formation of conjugated macroions (Pv) as a result of the interaction between M(HA) and some methyne hydrogens between

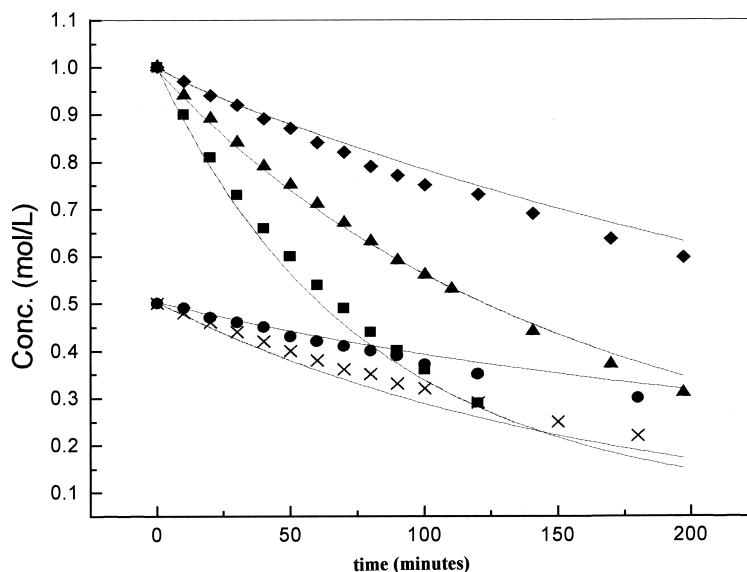


Fig. 2. Conversion–time curves for runs with different initial 2-ethenylfuran and trifluoroacetic acid concentrations (mol l^{-1}). Theoretical (—); Experimental (■); $[\text{VF}]_0 = 1.00$; $[\text{TFA}]_0 = 1.00$ (▲) $[\text{VF}]_0 = 1.00$; $[\text{TFA}]_0 = 0.50$; (◆) $[\text{VF}]_0 = 1.00$; $[\text{TFA}]_0 = 0.23$ (×) $[\text{VF}]_0 = 0.50$; $[\text{TFA}]_0 = 0.50$; (●) $[\text{VF}]_0 = 0.50$; $[\text{TFA}]_0 = 0.20$.

furan rings (step VI) on the chains. This explanation was used in the case of furfuryl acetate using boron trifluoride in acetonitrile [15] or in the FA/DCM/ SnCl_4 system [14].

These conjugated chains can react with TFA to give E^+A^- like species (step VII) that probably are macromolecules with ester type ending groups.

Acid removal occurs during this step and it is a feature that characterizes the furan carbinol polymerization. For example, during the polymerization of FA in DCM with *p*-toluene sulphonic acid (PTS) 40% of the acid is trapped due to the formation of esters and conjugated species [16]. The formation

of crosslinked structures during the second step could occur as in the case of the system FA/DCM/ SnCl_4 system [14].

The kinetic behavior observed seems to be related to step I as a controlling step (reaction step k_1) or to step II, however step III should lead to a second order in monomer concentration. The active center $\text{M}(\text{HA})$ does not strictly obey the steady state hypothesis at the beginning (see Fig. 5), but it is possible to apply this criteria after a period of time because the $\text{M}(\text{HA})$ concentration becomes practically constant: $[\text{M}(\text{HA})] = K_1[\text{VF}][\text{TFA}]/(K_2 + (K_3 + K_8)[\text{H}_2\text{O}])$ assuming step IV negligible in the present conditions. If

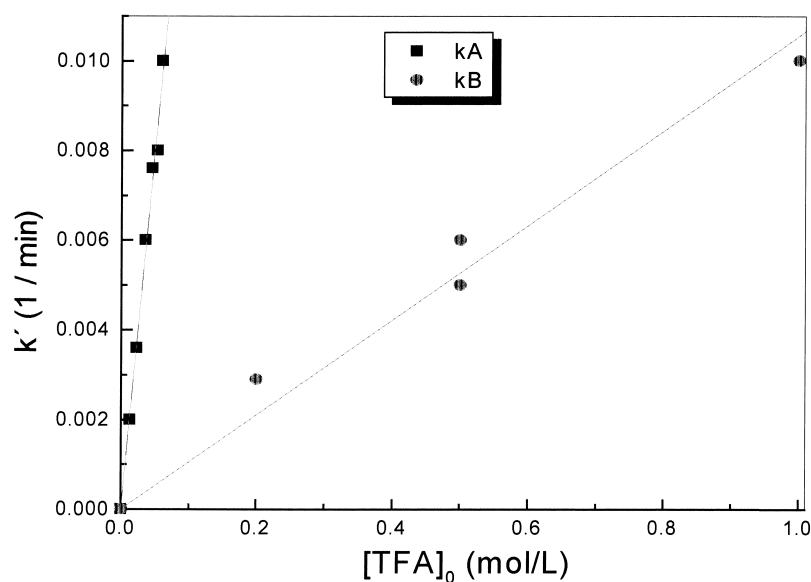


Fig. 3. Linear plot of the pseudo rate constants (k') versus initial concentration of trifluoroacetic acid. for systems A and B. Correlation coefficients 0.992 and 0.994.

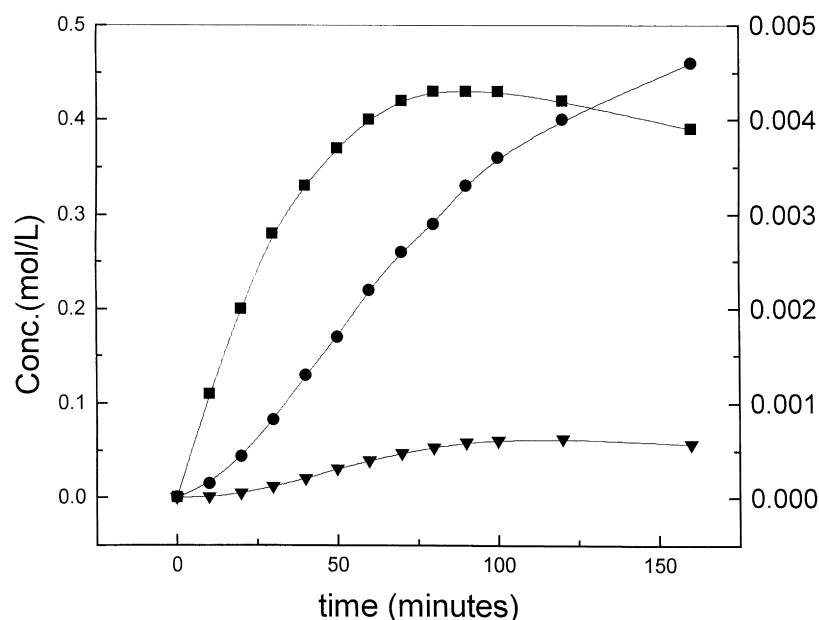


Fig. 4. Intermediary modeling for the species FC(■), POH(●) and DFCE species (▼) in P11 experiment.

$K2 < (K3 + K8)[H_2O]$ then $[M(HA)] = K1/K3 + K8[VF][TFA]$ and the step II rate would be second order.

3.3. Mathematical modeling

The proposed mechanism for the reaction was computationally modeled using all experimental data of different runs simultaneously for the system B. Table 4 shows the experimental data used and the fitting for the monomer concentration expressed as percent mean error, for all experimental points of each run.

Modeled monomer conversion–time curves were compared with the experimental ones. Fig. 2 shows the experimental and calculated values. The fitting is good taken into account this complex heterogeneous system and indicates the proposed mechanism is reliable at the beginning of the polymerization prior to branching and crosslinking.

Monomer conversion curves do not show an induction period in spite of the fact that a stationary concentration of M(HA) is attained after 60 min (Fig. 5) it implies a kinetic control by step I.

3.4. Acid consumption

TFA concentration decreases during polymerization (See Fig. 5). For the first hour of the reaction 96% of the acid is free, but when the reaction reaches 100% of monomer conversion there is only 61% of free acid. This result is very similar to that obtained in the FA/DCM/pTS system [16]. Acid trapping is due to the formation of the conjugated species Pv and the polymeric esters E^+A^- as discussed above.

3.5. Estimated rate parameters

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

$$K1 = 2.3 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K2 = 9.75 \times 10^{-3} \text{ min}^{-1}$$

$$K3 = 8.94 \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K4 = 1.18 \times 10^{-2} \text{ l mol}^{-1} \text{ min}^{-1}$$

Table 4

Simulation of the 2-ethenylfuran resinification catalyzed by trifluoroacetic acid in a water–chloroform mixture 50/50 in volume

	[VF] ₀ (mol/L)	[TFA] ₀ (mol/L)	Experimental points	Mean error per run (%) in estimation of monomer concentration
P1	1.000	1.000	13	4.16
P2	1.000	0.050	15	1.87
P3	1.000	0.020	15	2.85
P4	0.505	0.050	14	5.52
P5	0.500	0.020	15	3.61

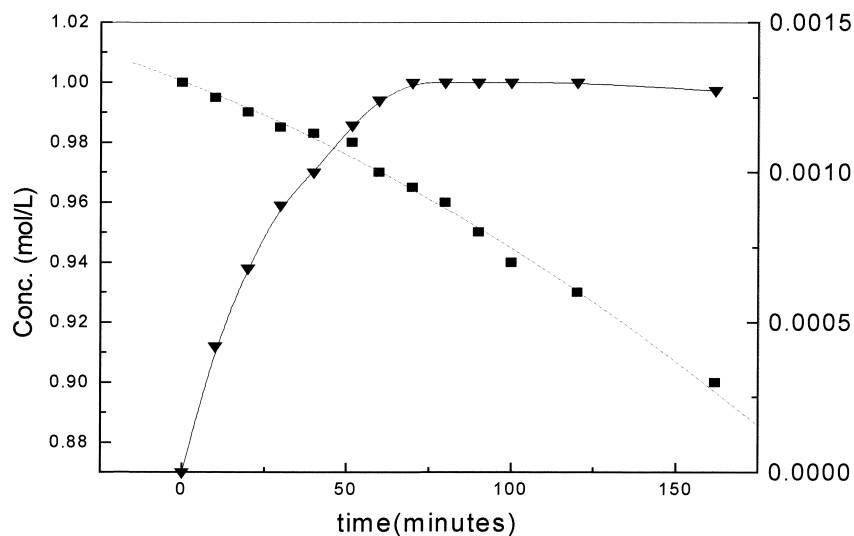


Fig. 5. Concentration modeling of the for the species TFA(■) and M(HA) species (▼) in P11 experiment.

$$K5 = 2.14 \times 10^{-1} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K6 = 9.87 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K7 = 8.87 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K8 = 3.38 \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K9 = 8.05 \times 10^{-3} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K10 = 9.46 \times 10^{-2} \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K11 = 1.00 \times 10^2 \text{ l mol}^{-1} \text{ min}^{-1}$$

$$K12 = 2.12 \times 10^{-4} \text{ l mol}^{-1} \text{ min}^{-1}$$

The $K4$ value ($2.14 \times 10^{-1} \text{ l mol min}^{-1}$) is of the same order as that of a propagation constant for a pseudocationic polymerization [17]. The $K6$ constant value ($9.87 \times 10^{-4} \text{ l mol min}^{-1}$) is lower than $K5$ and by analogy with the FA polymerization catalyzed with TFA [11], 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. The $K10$ value ($9.46 \times 10^{-2} \text{ l mol}^{-1} \text{ min}^{-1}$) is similar to k_5 , indicating the importance of the conjugated species that impart color to the resin. The $K11$ value ($1.0 \times 10^2 \text{ l mol}^{-1} \text{ min}^{-1}$) is similar to that obtained for the VF/DCM/TFA system in vacuum [18] and similar to that obtained for the system cyclopentadiene with trifluoroacetic acid [19] and to the furans adducts obtained with the same acid [20].

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 [21–22] we do not know about any

other serious reports which deals with this subject. This is the first report of a model of such reaction mechanism giving an estimation of rate constants for each of the proposed steps.

4. Conclusions

The 2-ethynylfuran polymerization in water–chloroform mixture catalyzed by trifluoroacetic acid was followed spectroscopically and kinetically studied. It showed several features typical of either polyaddition or polycondensation.

Taking into consideration the analysis of the spectra and the above kinetic discussion, it seems that the proposed mechanism has been successful to explain the phenomenological behavior of this non-typical polymerization. It can be summarized as follows:

- vinylic propagation can be ruled out;
- M_n increases with time as in a classical polycondensation;
- M_n are quite low and crosslinking is observed at higher times;
- the monomer concentration decreases steadily as in a chain process;
- the concentration of polarized ester M(HA) tends to a steady state (as in a chain reaction). M(HA) is not able to polymerize VF through its double bond but attacks the C-5 position of the furan ring of its carbinol by substitution.

All these features can be simultaneously explained by the kinetic scheme offered. Thus, the propagation steps (III) involve the disappearance of the active center M(HA) so a chain process cannot be switch on. Further, the concentration of VF decreases smoothly and does not participate in

the electrophilic attack of M(HA) because its ring is highly conjugated in comparison to the carbinols one.

Appendix A. Rate equations for the mechanics of cationic polymerization of 2-ethenylfuran and the species mass balance equations

$$V(1) = K1[VF][TFA]V(2) = K2[M(HA)]V(3) \\ = K(3)[M(HA)][H2O]$$

$$V(4) = K4[FC][TFA]V(5) = K5[M(HA)][FC]V(6) \\ = K6[M(HA)][FC]$$

$$V(7) = K7[DFCE][TFA]V(8) = K8[M(HA)]H2O]V(9) \\ = K9[TFA][POH]$$

$$V(10) = K10[POH][M(HA)]V(11) = K11[Pv][TFA]$$

$$V(12) = K12 \cdot [E^+ A^-] \cdot [H2O]$$

$$YPRIME(VF) = -V(1) + V(2)$$

$$YPRIME(TFA) = -V(1) + V(2) + V(3) - V(4) + V(6) \\ -V(7) + V(8) - V(9) - V(11) + V(12)$$

$$YPRIME(M(HA)) = V(1) - V(2) - V(3) + V(4) - V(6) \\ +V(7) - V(8) + V(9) - V(10)$$

$$YPRIME(H_2O) = -V(3) + V(4) + V(5) + -V(8) + V(9) \\ +V(11) - V(12)$$

$$YPRIME(FC) = +V(3) - V(4) - V(5) - V(6) + V(7)$$

$$YPRIME(DFCE) = V(6) - V(7)$$

$$YPRIME(POH) = +V(8) - V(9) - V(10)$$

$$YPRIME(Pv) = V(10) - V(11) + V(12)$$

$$YPRIME(E^+ A^-) = V(11) - V(12)$$

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