Kinetic and Structural Features of Furan Compounds as Inhibitors of the Radical Polymerization of Vinyl Acetate.

Rebeca Vega and Jacques Rieumont

Abstract: Some furan compounds bearing a double bond in the side group have been examined as inhibitors of the radical polymerization of vinyl acetate initiated by AIBN in ethyl acetate at 60 ^{o}C. The inhibition effect was found to follow the order: furfurylidenacetone > furylacrolein > furanacrylic acid > furylacrylmorpholinamide as a consequence of the greater stabilization of the radical formed. The site of radical attack can be considered either as the C-5 position of the furan ring or as the double bond of the side group. The compounds taken as models such as 5-methylfuranacrylic acid and furfurylidenbutanal indicate that both positions can participate in the inhibitory process.

Keywords: *Inhibited vinyl acetate polymerization; furan compounds; kinetic study.*

Introduction

Many furan compounds behave as retarders or inhibitors of the radical polymerization of common monomers[1]. Some features of their behaviour have been thoroughly discussed and in this context it has been suggested that the carbon in the C-5 position of the furan ring acts as a preferred site of addition for the macroradicals.

In 1983 Rieumont and co-workers began a systematic quantitative kinetic treatment of the retarded and inhibited polymerization of vinyl acetate in the presence of simple furan compounds[2,3,4,5]. This classical approach was complemented by a sensitivity analysis of the mechanism and estimation of the rate constants by modelling the experimental data.

At present, it is possible to compare the strengths as retarders of the following furan compounds: 2-furaldehyde > 2 acetylfuran > 2-furamide = 2-furoic acid > 2-furylamine > 2-furfurylalcohol > furan > 2-methylfuran.

Also, it has been recognized that the furan compounds can produce remarkable effects as inhibitors, when the furan moieity is conjugated with other groups, such as the case of 2-furanacrylic acid or that in which a strong acceptor group such as a nitro group is linked to the ring. Both compounds have been throughly studied as inhibitors[4] and their degradative transfer constants and stoichiometric coefficient have been estimated.

Following this quantitative approach, other conjugated furan compounds with other conjugated side groups were chosen for a through kinetic study of the inhibited vinyl acetate polymerization to reveal all the mechanistic features of these systems.

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Experimental Part

All polymerizations were carried out in ethyl acetate at 60 °C using 2,2'-azoisobutyronitrile (AIBN) as initiator. Vinyl acetate (BDH) was purified by prepolymerization and distilled twice. Ethyl acetate (BDH) and AIBN (REACHIM) were purified by standard techniques.

The furan inhibitors were synthetized by standard techniques already reported[6] and purified by recrystalization or distillation under low pressure. They were correctly identified by their physical constants and by their IR and 'H RMN spectra.

The technique of dilatometric determinations of the rates has been already reported[4].

Results and Discussion

The log M_0/M versus time curves determined by a dilatometric technique (where M_0 is the initial monomer concentration) obtained for the inhibited polymerization of vinyl acetate with furylacrolein (3-(2-furyl)-propenal) show that the inhibitor does not suppress the polymerization completely (Figure 1).

This effect allows the determination of the ratio for the degradative transfer and chain propagation (k_{trs}/k_p), according to the equation obtained by Bartlett and Kwart[7]

$$\ln M_o/M = k_p/k_{trs} \ln Z_o/Z \qquad \text{Eq. 1}$$

where Z_0 is the initial inhibitor concentration. For the calculation of Z_o/Z the following approach was used, valid for strong inhibitors[7]:

$$\frac{Z_0}{Z} = [1 - t/t(inh)]^{-1} \qquad \text{Eq. 2}$$

where t(inh) is the inhibition time, measured from the intercept of the straight lines with the abscissa in Figure 1.

In Figure 2 is shown a plot according to Eq.1. It was constructed using the data obtained for all curves log M_0/M vs t for a initial monomer concentration of 3,254 mol/L in the presence of different amounts of the inhibitor, during the induction period. The ratio k_{trs}/k_p obtained from the slope of this plot is 192 and the value of k_{trs} was estimated as 400000 dm^3/ (mol.s) using a

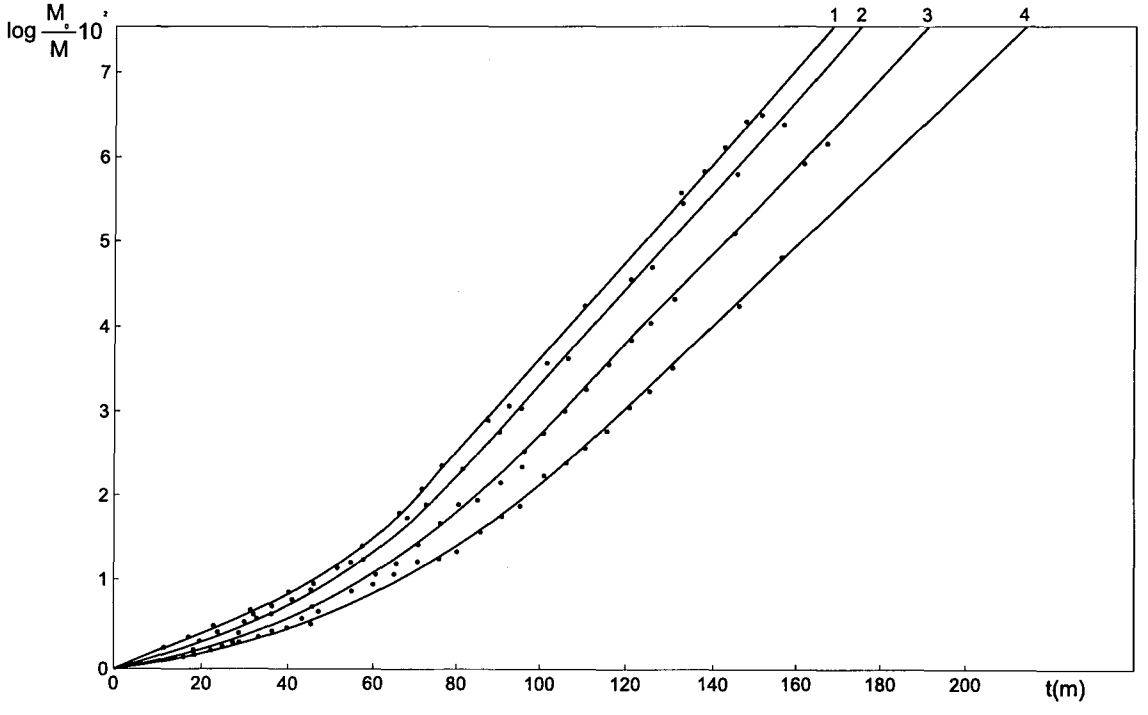


Figure 1. Log M_0/M vs t curves for the system vinyl acetate (3,254 mol/L), AIBN (0,002 mol/L), furylacrolein (Z)
1. c(Z) = 0,000005
2. c(Z) = 0,00001
3. c(Z) = 0,000015
4. c(Z) = 0,00002

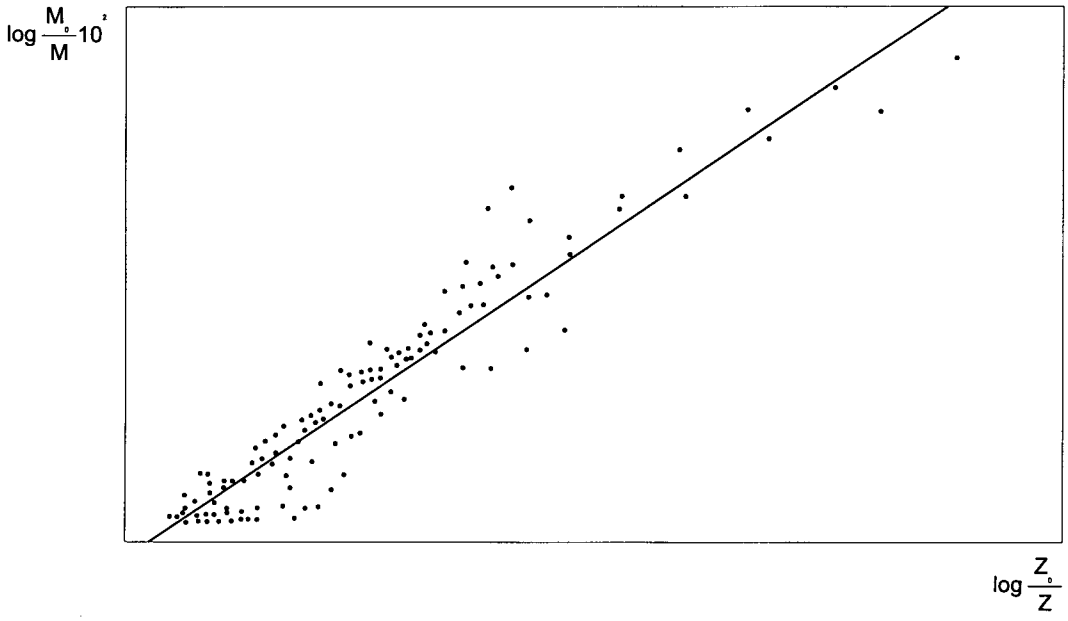


Figure 2. Log M_0/M vs Z_0/Z plot for the system vinyl acetate (3,254 mol/L), AIBN (0,002 mol/L), furylacrolein

value of k_p from the literature (2300 dm^3 / (mol.s))[8].

An apparent dependence of the ratio k_{trs}/k_p with the monomer concentration is observed in these experiments (see Table 1). This behaviour has been already reported by Tudös[9], who explained this anomaly by the hot radical theory.

However other authors argued[4] that this behaviour can be due to a kinetic complication. Equation 1 was obtained assuming that the consumption of the inhibitor (Z) only occurs by reaction with the macroradicals M* (reaction k_{trs}), but the mechanism of the inhibition could be more complex if the transfer reaction with primary radicals R* is operating (k'_{trs}). Thus, the kinetic scheme leading to Eq.1 is not entirely adequate in the present context because:

$$M^* + Z \rightarrow MZ^* \quad k_{trs}$$

$$R^* + Z \rightarrow RZ^* \quad k_{trs}$$

In order to calculate the stoichiometric coefficient of the inhibitor μ, the inhibition times were plotted versus Z_0/I according to equation 3

$$t(inh) = \frac{\mu}{2fk_d} Z_0/I \qquad \text{Eq. 3}$$

where f is the efficiency of the initiator, k_d is the initiation constant, and I is the mean initiator concentration during the inhibition period. These plots show a deviation from linearity, which means that the reinitiation reaction (k_{is}) could occur in this system:

$$MZ^* + M \rightarrow M^* \quad k_{is}$$

In the presence of reinitiation, it is possible to obtain the stoichiometric coefficient, if the data are corrected by the following equation[9]:

$$[Z_0/I\, t(inh)]^3 = [2fk_d\mu]\,[1 + 0{,}324c(Z_0/I)] \qquad \text{Eq. 4}$$

$$\text{where } c = \frac{4\mu M_0 k_{trs} k_i}{2fk_d k_{trs}}$$

Unfortunately in the case of furylacrolein the intercepts obtained are negative. Thus this system is

Table 1. Vinyl acetate polymerization initiated by AIBN (0,002 mol/L) in ethyl acetate at 60 °C in presence of furylacrolein

c(M) (mol/L)	c(Z).10^5 (mol/L)	t(inh) (m)	$k_{trs}\ k_p$	$k_{trs}\ 10^{-5}$ (dm^3/mol/s)*
3,254	0,5	37	192	4,0
	1,0	41		
	1,5	47		
	2,0	57		
5,376	2,0	52	51,5	1,2
	5,0	79		
	7,0	107		
	10,0	122		
7,529	2,0	39	52,6	1,2
	7,0	76		
	10,0	102		

*k_p = 2300 dm^3/mol.s [8]

Table 2. Vinyl acetate polymerization 3,254 mol/L initiated by AIBN (0,002 mol/L) in ethyl acetate at 60 °C in presence of furan compounds

Inhibitor	c(Z).10^5 (mol/L)	t(inh) (m)	k_{trs} k_p	k_{trs} 10^{-5} (dm^3/mol.s)*
furfurylidena-cetone	0,1	15	238	5,4
	0,3	24		
	0,5	42		
	1,0	84		
	2,0	180		
	3,0	255		
furylacrylmo-rfoline-amide	5,0	37	43,8	0,95
	7,0	45		
	13,0	65		
	16,0	97		
	20,0	117		

*k_p = 2300 dm^3/mol.s [8]

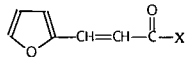
even more complicated or equation 4 fails because the linearization modifies the distribution of errors since the independent variable is mixed with the dependent one as has been observed in copolymerization systems[10]. Thus, it is not possible to calculate a value of the stoichiometric coefficient for this inhibitor.

Furthermore, the curves of log M_0/M vs t (Figure 1) for different initial furylacrolein concentrations are not parallel. It means that a secondary retardation reaction occurs with the polymer or with another product of the system.

Similar curves log M_0/M vs t are obtained when the furfurylidenacetone (4-(2-furyl)-3-buten-2-ona) is used as inhibitor in the vinyl acetate polymerization. The inhibition times and the estimated transfer rate constant (Table 2) in this case are larger than the values obtained for the furanacrylic acid (3-(2-furyl)-propenoic acid)[4] and furylacrolein. It means that the substituent (-COOH, -COH , COCH3) has a certain effect in the reactivity of the furan compound, because the radical formed is more stable. It is also observed in this case that there is a secondary retardation after the induction period. As for furylacrolein, it is impossible to obtain the stoichiometric coefficient, because of the non linearity of the plot t(inh) vs Z_0/I. Thus, the re-initiation reaction seems to be more important in these systems than in the case of furanacrylic acid.

Table 3. Substituent effect in the inhibitory strength of the furanacrylic acid ant its related compounds.

Side group	c(X) 10^5	t(inh)	k_{trs} 10^{-5}
-HC=CH-COOH	1	14	3
	5	44	
-HC=CH-CONRR'	5	37	1
-HC=CH-COH	1	41	4
-HC=CH-$COCH_3$	1	84	5,4



where NRR' is the morfoline group

In order to complete the study of the substituent effect in these furan compounds, 2-furylacrylmorpholinamide (3-(2-furyl)propen-tetrahydro-1,4-oxazinamide) was examined as inhibitor of the vinyl acetate polymerization (Table 2). The plot of the inhibition times versus Z_0/I gives in this case a straight line. It allows calculation of the stoichiometric coefficient for this inhibitor. The value μ= 0.98 is aproximately the same as obtained for furanacrylic acid[4], and it indicates that in these types of compounds only one macroradical is trapped by an inhibitor molecule. The results obtained with these four inhibitors indicate that the acid and the amide are weaker than the ketone and the aldehyde (Table 3).

These results can be explained by the greater stabilization of the radical MZ* formed on the furfurylidenacetone and furylacrolein. Nevertheless, the stabilization seems to be decreased when X is a donor group such as -NRR' or -OH.

Thus, the strength of these inhibitors is as follows: furfurylidenacetone > furylacrolein > 2-furanacrylic acid > 2-furylacrylmorfolinamide

In another paper[11], it was suggested that the lateral chain of the furan ring could participate in the reaction with the radicals. In order to clarify the site of the radical attack in this family of furan compounds, the vinyl acetate polymerization was studied in the

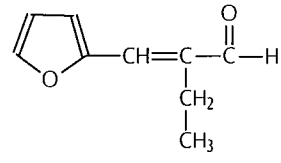


Figure 3. Furfurylidenbutanal

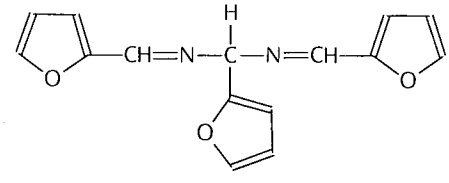


Figure 4. Hydrofuramide

Table 4. Initial rate of the vinyl acetate polymerization (3,254 mol/L) in the presence of some furan compound. (Concentration of the inhibitor 0,00005 mol/L)

Compound	Rp. 10^5 (mol/s.L)
furancrylic acid	1,75
5-methyl-furanacrylic acid	4,1
furfurylidenbutanal	13,6
hydrofuramide	4,5

presence of 5-methyl-furanacrylic acid (3-(2-(5-methyl)furyl)propenoic acid) and furfurylidenbutanal (2-ethyl,3-(2-furyl)propenal).

The polymerization with these compounds has a noticeable initial rate that cannot be neglected. On the other hand, the log Mo/M vs t curves are not parallel and their slopes decrease on increasing the concentration of the inhibitor. Thus, it is impossible to delimit the inhibition period but their initial reactions rates can be compared (Table 4)

The initial rate of the polymerization increases when the reaction takes place in the presence of 5-methyl-furanacrylic acid instead of furanacrylic acid. It can be explained by a steric hindrance at the C-5 position. Therefore this position could be involved in the transfer reaction with the radicals.

Another site of the radical attack could be the double bond in the side chain. The initial rate of the polymerization is also greater and no inhibition period detected when a steric factor is operating as in the case of furfurylidenbutanal (Fig 3) respect to the furylacrolein. This situation had been predicted theoretically by MNDO calculations in a previous comunication[11].

The last compound studied was hydrofuramide (N,N'-difurfuryliden-2-furanethane-diamine) (Fig 4). It behaves as a strong retarder in comparison with the inhibitor furancrylic acid. This effect is a consequence of the lesser extent of the conjugation because the methyne group does not participate as in the case of the aldehyde or ketone, as can be judged from its structure in spite of the three C-5 positions available.

Conclusions

A study was made of the inhibition effect of several furan compounds in the radical polymerization of vinyl acetate initiated by AIBN. Their strength as inhibitors can be compared by the inhibition times, the estimated value of the transfer reaction constant and the initial rates of polymerization. It can be concluded that the order of reactivity is:

furfurylidenacetone > furylacrolein > furanacrylic acid > furylacrylmorfolinamide > 5-methylfurancrylic acid > hydrofuramide > furfurylidenbutanal.

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