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KINETICS OF THE ADDITION OF ELECTROPHILIC VINYL REAGENTS ON PROTONATED TERTIARY AMINES SUPPORTED BY A POLYMERIC CHAIN

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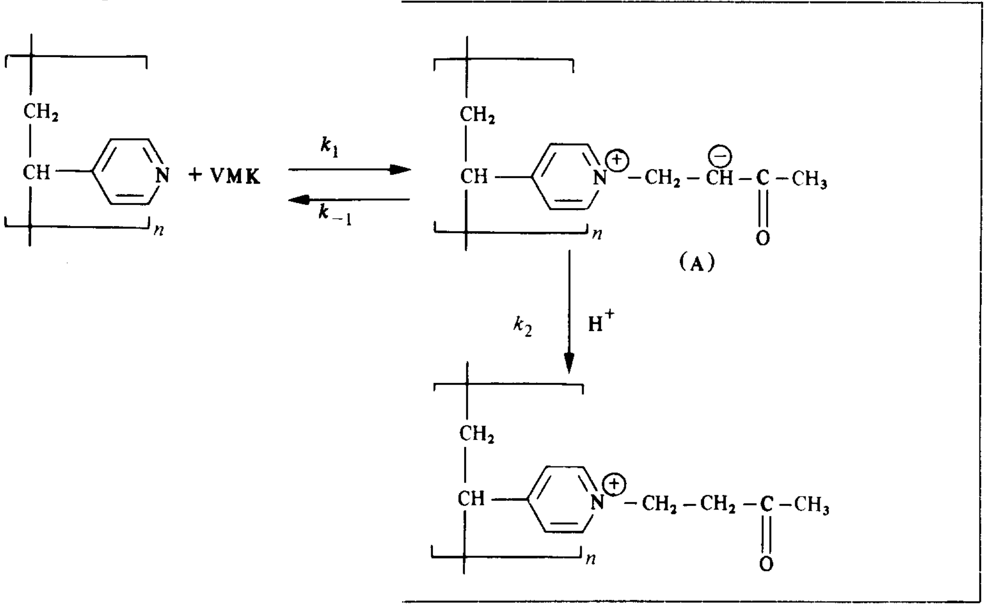
Abstract—Starting from the mechanism of the addition of vinyl methyl ketone to protonated tertiary polyamine, we examined the kinetics of addition of acrylic acid, acrylamide and methyl acrylate to P4VP in the presence of HBr. The reactivities depend on the electrophilic character of the double bond; the kinetics of addition of vinyl methyl ketone to poly(2-methyl-5-vinylpyridine), poly(2-vinylpyridine), poly(2-vinylquinoline) and poly(dimethylaminostyrene) in the presence of HBr depend essentially on the steric hindrance of the tertiary amine.

INTRODUCTION

It has been shown previously that a polymeric protonated tertiary amine can add some electrophilic vinyl compounds [1–4]. The mechanism of this reaction has been established [5] for the addition of vinyl methyl ketone (VMK) to poly(4-vinylpyridine) (P4VP) in the presence of HBr. Two steps have been indicated: the first is the addition of VMK to the tertiary amine; then protonation of the intermediate species (A) takes place according to the scheme:



where H^+ represents all the species able to give a proton (free H^+ and protonated tertiary amine). Since $k_2 \gg k_{-1}$ the velocity of the reaction can be written as $v = k_1[\mathrm{P4VP}][\mathrm{VMK}]$. This law is satisfied only if the ratio of the initial concentrations of HBr and P4VP is < 0.5 (it has been suggested that for $[\mathrm{HBr}]/[\mathrm{P4VP}] > 0.5$ the electrostatic field due to the neighbouring positive charges limits the accessibility to the unreacted pyridine units). The addition was supposed to obey a second order kinetic law and, if A_0 and B_0 represent the inital concentrations of P4VP and VMK respectively, we can write:

$$\frac{1}{B_0 - A_0} \ln \frac{A_0(B_0 - x)}{B_0(A_0 - x)} = k_1 t. \qquad (1)$$

If the reaction extent $\tau = x/A_0$ is introduced, Eqn (1) becomes:

$$\frac{1}{B_0 - A_0} \ln \frac{1 - \tau A_0/B_0}{1 - \tau} = F(\tau) = k_1 t \qquad (2)$$

$F(\tau)$ should be a linear function of time and the slope

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should give k_1. We assumed that the mechanism of addition of the electrophilic vinyl reagents to a tertiary amine supported by a polymeric chain in the presence of HBr does not depend on the nature of the tertiary amine and of the vinyl reagent (for [HBr]/[tertiary amine] < 0.5). The purpose of the present paper was to study on the one hand the kinetics of the addition of acrylic acid (AA), acrylamide (AM) and methyl acrylate (MA) to P4VP in the presence of HBr. On the other hand the kinetics of the addition of VMC to poly(2-methyl-5-vinylpyridine) (P2M5VP), poly(2-vinylpyridine) (P2VP), poly(2-vinylquinoline) (P2VQ) and poly(dimethylaminostyrene) (PDMAS) in the presence of HBr were investigated.

EXPERIMENTAL

The various polymers were obtained by conventional radical polymerization of the corresponding monomers except PDMAS which was a commercial product. All the monomers were commercial except for 2-vinylquinoline which was obtained by the method of Kagan *et al.* [6]. The reactions were carried out in a solvent for the protonated polymers at various temperatures. All the systems remain homogeneous. The rate of reaction was determined by following the monomer concentration vs time using a gas chromatographic technique (with an internal standard). The chromatograph was a GIRDEL 3000 instrument with a flame ionization detector. The polymers were blocked on glass wool in the injector. The columns used depended on the nature of the monomer, the solvent and the internal standard. LTT 4402 data integrator was connected to the gas chromatograph. The velocity constants k_1 were obtained from the slope of the linear graph $F(\tau) = k_1 t$.

RESULTS AND DISCUSSION

Addition of AA, AM and MA to P4VP

In these cases, the solvent was methanol. Figure 1 shows the plot of $F(\tau)$ vs time for the addition of AA and AM (278 K) and MA (330 K). The results are reported in Table 1. In order to compare the k_1 values, we determined the activation energy ΔE of the addition of MA by plotting ln k vs $1/T$. This value is $\Delta E = 10.8$ kcal mol^{-1} and we obtained $k_1 = 9 \cdot 10^{-5}$ l·mol^{-1} min^{-1} at 278 K. For addition of VMK to P4VP in the presence of HBr we have [5] at the same temperature $k_1 = 158 \cdot 10^{-3}$ l·mol^{-1} min^{-1}. We can arrange the reactivities of substances towards P4VP in the presence of HBr thus: VMK > AA > AM > MA. This order agrees with the decreasing electrophilic character of the double bond. We can note that the curves $F(\tau) = k_1 t$ are linear up to high value of τ. We do not observe any neighbouring effect (experimental conditions are such that this effect is reduced to a minimum).

Table 1. Velocity constants in the reaction of P4VP with various vinylic reagents; [HBr] and [P4VP] are respectively 0.07 and 0.14 mol·l^{-1}

Vinylic reagent	T (K)	Vinylic reagent (mol·l^{-1})	$k_1 \cdot 10^3$ (l·mol^{-1} min^{-1})
AA	278	0.138	13.2
AM	278	0.07	6.5
MA	320	0.464	1.12
	326	0.464	1.47
	330	0.464	1.91

Addition of VMK to some tertiary amines supported by a polymeric chain

For P2VP, P2VQ and PDMAS, dimethylformamide was used as solvent; for P2M5VP methanol was the solvent. Figure 2 shows the variation of $F(\tau)$ with time for P2VP and PDMAS at 317 K. Figure 3 shows the same function for P2M5VP and P2VQ at 278 K. The values of k_1 are reported in Table 2.

In order to compare the k_1 values, we determined the activation energies for the addition for P2VP and PDMAS. The plots of ln k vs $1/T$ are linear and we obtained for both these two additions $\Delta E = 10.8$ kcal mol^{-1}. We evaluated k_1 for P2VP and PDMAS at

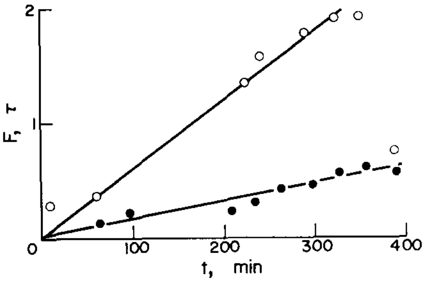

Fig. 2. $F(\tau)$ vs t for addition of VMK on PDMAS and P2VP at 317 K.

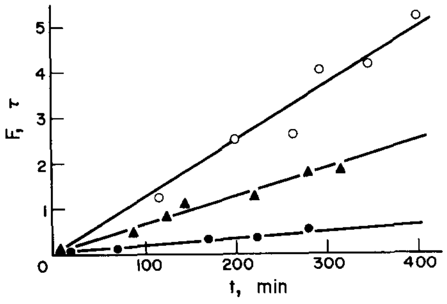

Fig. 1. $F(\tau)$ vs t for addition of AM ▲ and AA ○ on P4VP at 278 K and for addition of MA ● at 330 K.

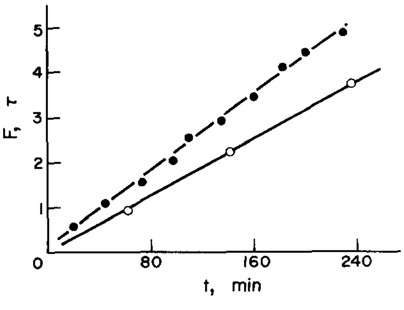

Fig. 3. $F(\tau)$ vs t for addition of VMK on P2VQ ● and P2M5VP ○ at 278 K.

Table 2. Velocity constants in the reaction of some tertiary amines, supported by a polymeric chain, with VMK in the presence of HBr

Polymer	Solvent	T (K)	[VMK] ($\mathrm{mol \cdot l^{-1}}$)	$k_1 \cdot 10^3$ ($\mathrm{l \cdot mol^{-1} \cdot min^{-1}}$)
P2M5VP	Methanol	278	0.07	20.5
P2VP	Dimethylformamide	317	0.28	1.34
		325	0.28	2.09
		336	0.28	3.46
P2VQ	Dimethylformamide	278	0.16	15.4
PDMAS	Dimethylformamide	316	0.07	5.72
		323	0.07	7.95
		326	0.07	9.03

[HBr] and [Polymer] are respectively 0.07 and 0.14 $\mathrm{mol \cdot l^{-1}}$.

278 K as $0.12 \cdot 10^{-3}$ and $0.53 \cdot 10^{-3}$ $\mathrm{l \cdot mol^{-1}\ min^{-1}}$ respectively. Thus the reactivities of the polymers tested can be arranged thus: P4VP > P2M5VP > P2VQ > PDMAS > P2VP This order agrees with the fact that this type of addition [7] is essentially governed by the steric hindrance of the tertiary amine.

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