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Quaternary Ammonium Polyelectrolytes. VI. Kinetic Studies on the Quaternization Reactions of Chloromethylated Polystyrene with 4,4'-Bipyridil and of Poly(4-Vinylpyridine) with Ethylchloroacetate

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QUATERNARY AMMONIUM POLYELECTROLYTES. VI. KINETIC STUDIES ON THE QUATERNIZATION REACTIONS OF CHLOROMETHYLATED POLYSTYRENE WITH 4,4'-BIPYRIDIL AND OF POLY(4-VINYLPYRIDINE) WITH ETHYLCHLOROACETATE

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ABSTRACT

Kinetic studies on the quaternization of chloromethylated polystyrene with 4,4'-bipyridil in dimethylsulfoxide and *N,N*-dimethylformamide, as well as on the quaternization of poly(4-vinylpyridine) with ethylchloroacetate in formamide, *N,N*-dimethylformamide, and methanol, were performed. For most solvents, kinetic studies of the reactions between model compounds, such as benzylchloride and 4-methylpyridine, with 4,4'-bipyridil and ethylchloroacetate, respectively, were also performed. Both the kinetic behaviors and the kinetic parameters were determined. Analytical and ¹H-NMR methods were used, the latter only for the reaction of poly(4-vinylpyridine) and 4-methylpyridine with ethylchloroacetate in deuterated methanol. In the case of polymers, different kinetic behaviors were observed for the same quaternization reaction, depending on the nature of the solvent. Thus, the reaction of chloromethylated polystyrene with 4,4'-bipyridil in dimethylsulfoxide followed a normal second-order kinetics, while in *N,N*-dimethylformamide the acceleration phenomenon appeared. The reactions of poly(4-vinylpyridine) with ethylchloroacetate in *N,N*-dimethylformamide and

methanol were accompanied by an acceleration phenomenon, but in formamide a slight deceleration occurred. These behaviors were assigned to polymer-solvent interactions and were observed to change during the reaction.

INTRODUCTION

The reaction between a halogenated compound and a tertiary amine, in which a partner is macromolecular, is the most frequently used method to obtain quaternary ammonium polymers.

From the kinetic point of view, the most studied reactions are quaternizations of chloromethylated polystyrene and polysulfone with different tertiary amines, as well as quaternizations of poly(4-vinylpyridine) with alkyl and arylalkyl halides.

In the case of chloromethylated polymers, normal second-order kinetics, along with a decreasing or increasing rate constant during the quaternization reactions, was observed [1-6].

In the case of poly(4-vinylpyridine), a decrease of the rate constant during the quaternization reaction is always observed. In such a situation the neighboring group model scheme is frequently used for the kinetic characterization [7-9]. Thus, three rate constants are required to quantify the system: k_0 , k_1 , and k_2 . Parameter k_0 represents the rate constant for the reaction of pyridil groups without already reacted neighbors, whereas k_1 and k_2 refer to groups with one and two already quaternized neighbors.

Recently, a simple kinetic model based on a second-order kinetic equation including a steric parameter was proposed [10]. The steric effect was considered as a global effect of the whole polymer molecule and not a local effect of the neighboring groups.

The present paper deals with kinetic studies of the quaternization reactions, namely the reaction of chloromethylated polystyrene with 4,4'-bipyridil and poly(4-vinylpyridine) with ethylchloroacetate in different solvents. Kinetic measurements were also carried out for the reaction of such model compounds as benzyl chloride and 4-methylpyridine with 4,4'-bipyridil and ethylchloroacetate, respectively.

The present contribution completes some previous kinetic studies of ours [3-5].

EXPERIMENTAL

Chloromethylated polystyrene (CMPS) was prepared according to methods given in the literature [11, 12] by using a polystyrene with $\bar{M}_v = 40,000$. A chlorine content of 21.60% was obtained, a value reflecting a molar transformation degree of 90%.

Poly(4-vinylpyridine) (P4VP) was obtained from freshly vacuum-distilled monomer by radical polymerization in methanol at 50°C with AIBN as initiator, under nitrogen, for 72 hours. The polymer was isolated by precipitation with ethyl ether, then dissolved in methanol and precipitated in ether. After two purification treat-

ments the polymer thus obtained was dried in vacuum at 50°C. A polymer with $\bar{M}_v = 240,000$ was used for kinetic determinations.

4,4'-Bipyridil (4,4'-Bpy), benzyl chloride (BC), 4-methylpyridine (4-MeP), and ethylchloroacetate (EtCA) were analytical grade agents. The first was purified by recrystallization, the others by vacuum distillation, before use.

N,N-Dimethylformamide (DMF), dimethylsulfoxide (DMSO), formamide (FA), and methanol were used as solvents. They were purified by conventional methods.

For kinetic measurements by the analytical method, the following technique was applied. Approximately 0.6 g polymer or its model was dissolved in 100 mL solvent. After thermostating, a quantity of 4,4'-Bpy or ethylchloroacetate corresponding to an amine:chloromethylated product molar ratio of 5:1 and an ethylchloroacetate:pyridinic compound molar ratio of 2:1 was added. The temperature of the reaction mixture was maintained within $\pm 0.2^\circ\text{C}$. The experiments were carried out in a reaction flask equipped with a stirrer and a condenser. At certain time intervals, 2 mL aliquots of the reaction mixture were removed, poured in bidistilled water, then immediately neutralized with 0.5 N nitric acid in order to stop the reaction, after which the amount of chlorine was potentiometrically determined with 0.02 N silver nitrate.

All reactions were carried out in air.

$^1\text{H-NMR}$ determinations were performed on a Jeol C-60 HL in 5 mm NMR tubes at 50°C. The following were employed: initial concentration of pyridinic compound, 0.5 mol/L; ethylchloroacetate:pyridinic compound molar ratio equal to 2; deuterated solvent volume of 0.5 mL.

Kinetic NMR measurements were made by determining the reaction mixture composition on the basis of the aromatic proton signals integrals at various reaction times. For example, the aromatic part of an instantaneous spectrum of the reaction mixture for P4VP and ethylchloroacetate in CD_3OD is shown in Fig. 1. Using the areas I_1 , I_2 , and I_3 for the signals denoted in the figure, the concentration of reacted pyridinic compound resulted from one of the following relations:

$$\beta = I_2 / (I_2 + I_3) = I_2 / I_1 \quad (1)$$

β represents the fraction of molecules (for the model compound) or of structural units (for polymers) where the nitrogen is positively charged.

RESULTS AND DISCUSSION

It is known that the reaction between a halogenated compound and a tertiary amine follows second-order kinetics. The integrated form of the rate expression is

$$f(x) = \frac{1}{a-b} \ln \frac{1-\alpha}{1-\beta} = kt \quad (2)$$

where $\alpha = x/a$ and $\beta = x/b$ (molar transformation degree), x is the concentration of halogen ions at time t in mol/L, and a and b are the initial concentrations of the reactants in mol/L.

For a reaction with normal second-order kinetics, the plot of $f(x)$ against time should be linear, with a slope equal to k .

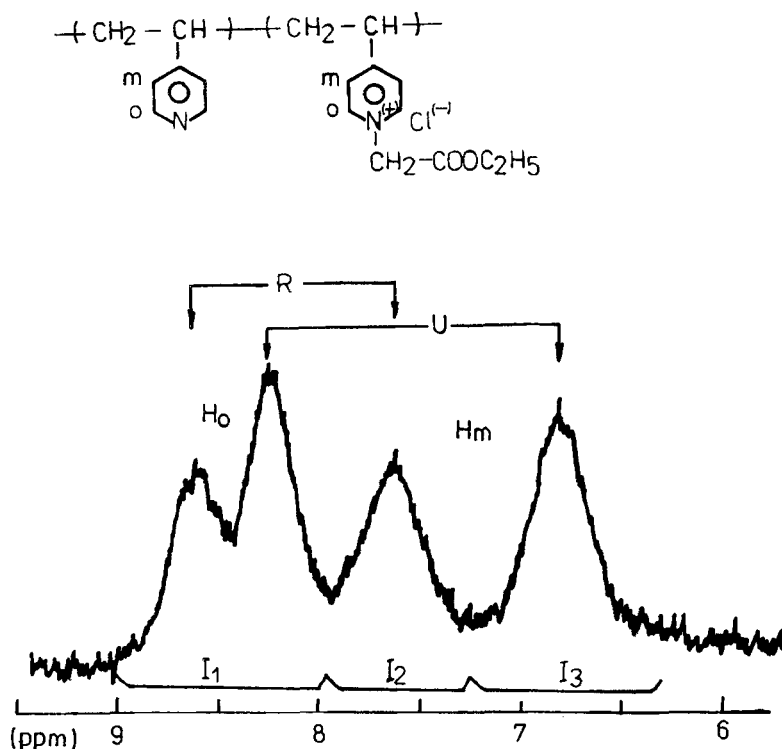


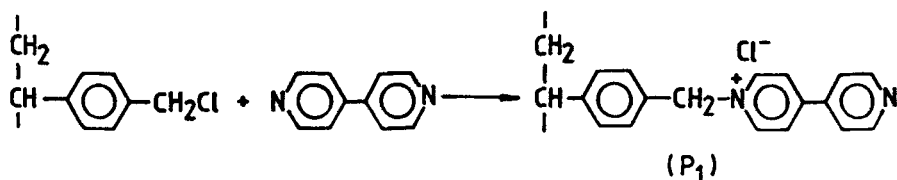
FIG. 1. Part of ¹H-NMR 60-MHz spectra of the reaction mixture of P4VP with ethylchloroacetate in CD₃OD at 50°C.

Quaternization of CMPS and of Its Model with 4,4'-Bipyridil

Since 4,4'-Bpy is a bifunctional compound, experiments with different molar ratios of CMPS:4,4'-Bpy were performed in order to obtain linear polymers, named P₁. Crosslinking does not occur for a CMPS:4,4'-Bpy molar ratio of 1:5.

The reaction takes place according to Scheme 1. Characterization of the P₁ polymer is presented in Table 1. From the data given in Table 1, it can be observed that the reaction of CMPS with 4,4'-Bpy, using a molar polymer:amine ratio of 1:5, yields a soluble polymer with a high nitrogen content.

Figures 2-4 show the kinetic behaviors of BC and CMPS reactions with 4,4'-Bpy. Figure 2 shows that the reaction of BC with 4,4'-Bpy follows second-order



SCHEME 1.

TABLE 1. Characterization of the P₁ Polymer^a

Chlorine content, %				Nitrogen content, %		Solubility
Calculated		Found		Calculated	Found	
Cl _t	Cl _i	Cl _t	Cl _i			
11.08	11.08	11.18	10.47	8.75	8.35	Methanol, ethanol, DMSO, DMF

^aCl_t = total chlorine, determined by the Schrodinger method and potentiometrically titrated with 0.02 N AgNO₃. Cl_i = ionic chlorine, determined by the potentiometric titration of a methanolic solution of polymer with 0.02 N aqueous AgNO₃. Reaction conditions: CMPS: 4,4'-Bpy molar ratio of 1:5, polymer concentration of 5% (w/v); DMF as solvent; 70°C; 24 hours.

kinetics. Figures 3 and 4 show that the kinetic behavior of the CMPS reaction depends on the nature of the solvent. Thus, in DMSO the reaction follows second-order kinetics while in DMF a positive deviation from linearity appears for a degree of transformation higher than 30%. Therefore, in the latter case, an acceleration phenomenon occurs.

Such situations are in good agreement with our former observation on the reaction of CMPS with *N,N*-dimethyl-2-hydroxyethylamine in DMSO and DMF

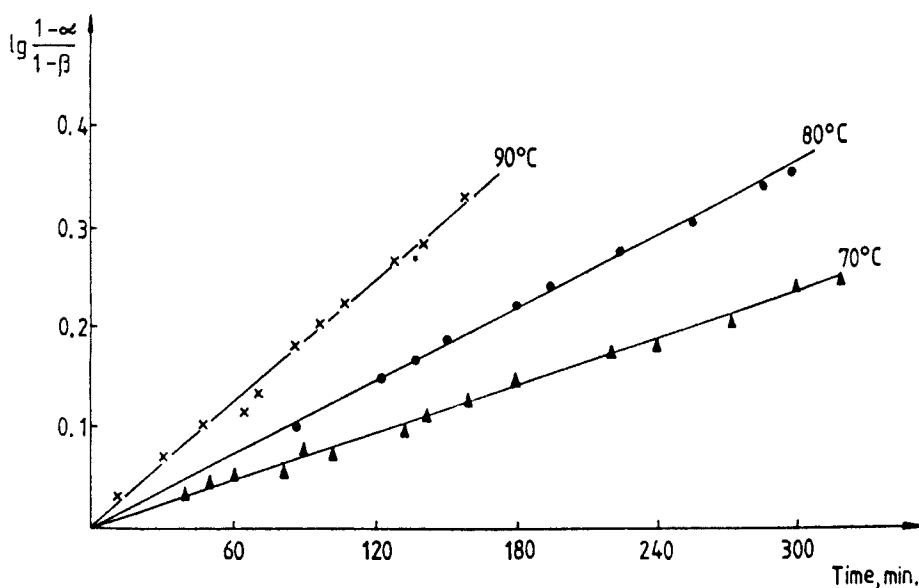


FIG. 2. Conventional second-order plot for the quaternization of BC with 4,4'-BPY in DMF.

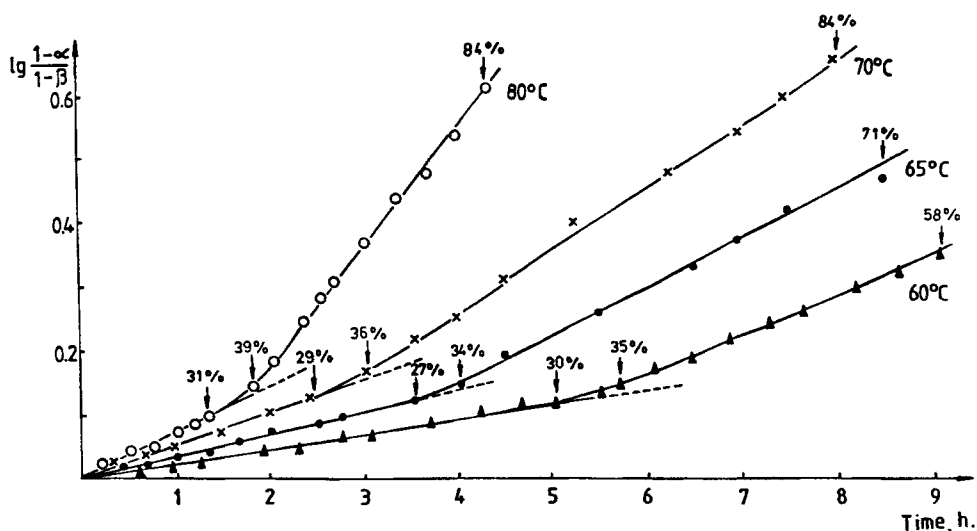


FIG. 3. Conventional second-order plot for the quaternization of CMPS with 4,4'-Bpy in DMF. The percentage values express the molar transformation degree (β).

[4]. Also, the literature data show acceleration for the reaction of CMPS with 4-methylpyridine [13].

Table 2 gives the values of the kinetic parameters rate constant (k), activation energy (E_a), and frequency factor (A) for the three above-mentioned quaternization cases. In the case of the CMPS polymer, only the initial rate constant was calculated.

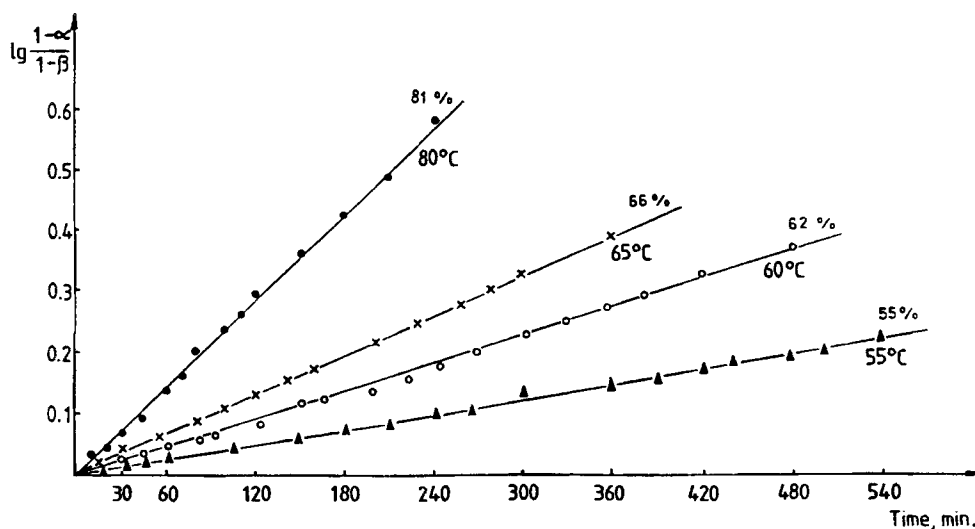


FIG. 4. Conventional second-order plot for the quaternization of CMPS with 4,4'-Bpy in DMSO.

TABLE 2. Quaternization of 4,4'-Bpy with BC and CMPS

Chloro- methylated compound	Initial reagent concentration, mol/L		Solvent	Temperature, °C	$K_i \times 10^3$ L/mol·min	Kinetic behavior
	4,4'-Bpy	Chlorine				
For quaternization in DMF with BC: $E_a = 46.91$ kJ/mol, $\log A = 5.20$						
BC	0.2370	0.0474	DMF	70	9.67	Normal
BC	0.2370	0.0474	DMF	80	15.49	Normal
BC	0.2370	0.0474	DMF	90	25.44	Normal
For quaternization in DMF with CMPS: $E_a = 63.40$ kJ/mol, $\log A = 7.85$						
CMPS	0.1829	0.0366	DMF	60	7.80	Acceleration
CMPS	0.1829	0.0366	DMF	65	9.43	Acceleration
CMPS	0.1829	0.0366	DMF	70	12.67	Acceleration
CMPS	0.1829	0.0366	DMF	80	25.63	Acceleration
For quaternization in DMSO with CMPS: $E_a = 56.16$ kJ/mol, $\log A = 12.95$						
CMPS	0.1829	0.0366	DMSO	55	6.61	Normal
CMPS	0.1829	0.0366	DMSO	60	11.86	Normal
CMPS	0.1829	0.0366	DMSO	65	17.73	Normal
CMPS	0.1829	0.0366	DMSO	80	37.75	Normal

The kinetic parameter values were calculated by using the following: the rate constants with Eq. (2), E_a from the slopes of lines in graphs of $\log k$ against $1/T$, and A with Eq. (3):

$$\log k = \log A - E_a/2.303RT \quad (3)$$

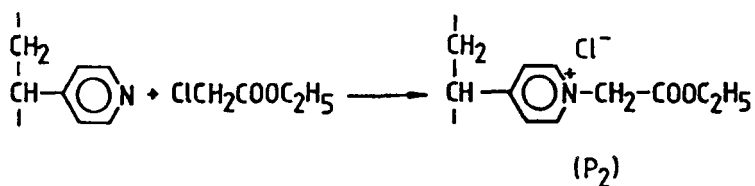
The results listed in Table 2 show that the reaction between BC and 4,4'-Bpy takes place with lower rate constants than that of CMPS with the same amine, which is in good agreement with the increasing A value in the reaction of the polymer. Also, as expected, the reaction is faster in DMSO.

Quaternization of P4VP and of Its Model with Ethylchloroacetate

The reaction takes place according to Scheme 2.

It is known that different colors are observed in the reaction medium during quaternization of P4VP with alkyl halides in DMF, nitromethane, nitrobenzene, and tetramethylene sulfone. This phenomenon is most often attributed to the presence of impurities or to side reactions with the solvent, although the NMR spectra of the polymers show neither degradation nor additional peaks.

Boucher and coworkers recently reviewed the observations and concluded that a charge-transfer phenomenon occurs: $RPy^+X^- \rightarrow RPy^{\cdot}X^{\cdot}$ [14].



SCHEME 2.

In the present study, FA, DMF, and methanol or methanol-*d*₄ were used as solvents for kinetic determinations, the last one in ¹H-NMR measurements.

It is known that alcohol must be avoided because of alcoholysis of halogenated compounds. In our kinetic determination by analytical and ¹H-NMR methods, quaternizations of 4-MeP, as a model for P4VP, with EtCA in methanol and CD₃OD, follow normal second-order kinetics (Figs. 5 and 6). In FA, the same behavior is observed (Fig. 7).

The following experiment was also performed. A solution of 0.5 mol/L EtCA in methanol was kept at 50°C for 72 hours. At the end of the experiment, this solution did not contain ionic chlorine.

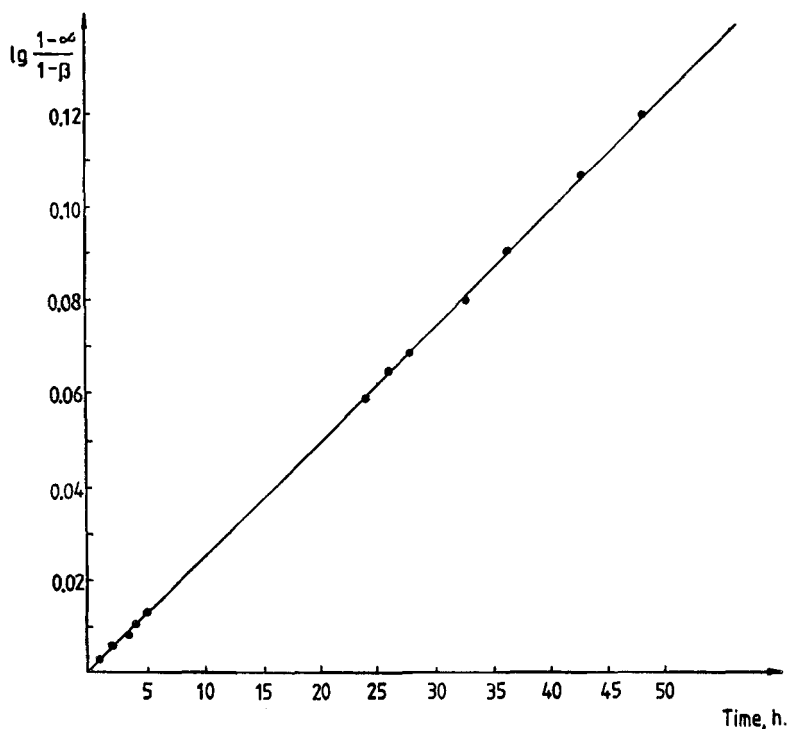


FIG. 5. Conventional second-order plot for the quaternization of 4-MeP with EtCA at 50°C in methanol.

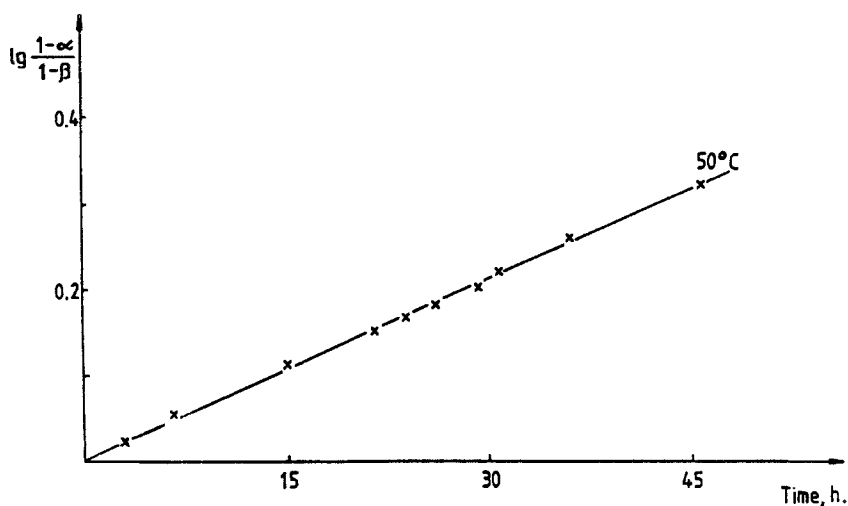


FIG. 6. Conventional second-order plot for the quaternization of 4-MeP with EtCA in CD_3OD at 50°C .

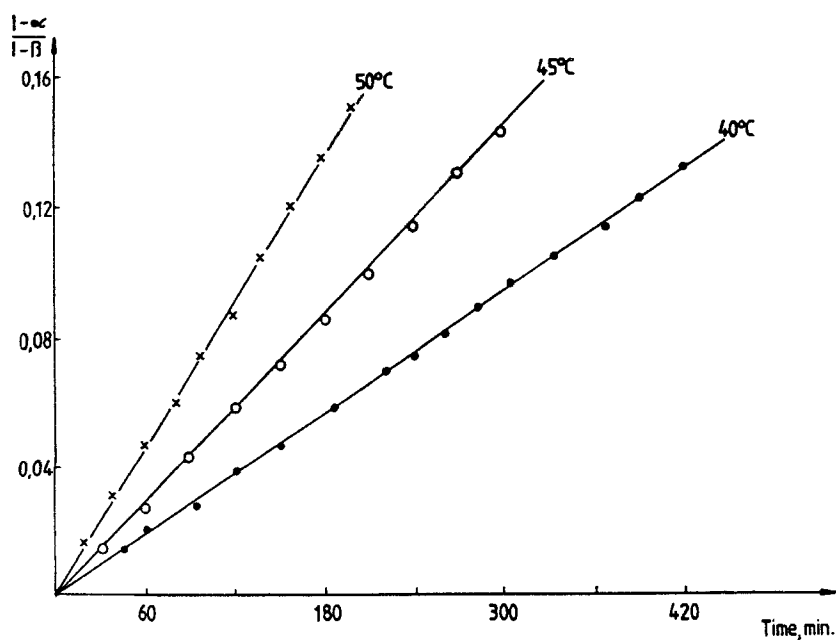


FIG. 7. Conventional second-order plot for the quaternization of 4-MeP with EtCA in FA.

The kinetic behaviors of P4VP quaternization with EtCA in different solvents are shown in Figs. 8-11. Figure 8 shows the kinetic behavior for the quaternization of P4VP with EtCA in DMF, and Fig. 9 shows the behavior in methanol. From these plots it can be seen that both quaternizations are undoubtedly accompanied by acceleration phenomena. Deviations from linearity appear at degrees of transformation of about 30% in the case of DMF and 50% in the case of methanol. Unlike DMF and methanol, in FA (Fig. 10) a deceleration phenomenon appears at very low values of the degree of transformation ($\sim 10\%$). The plot for the quaternization of P4VP in CD_3OD (Fig. 11) has a distinct aspect because the reaction starts with a certain rate constant but at about a 50% degree of transformation a positive deviation from linearity appears and at about a 75% degree of transformation a negative deviation occurs. However, it is noteworthy that kinetic determinations by analytical method were carried out for relative low degrees of transformation (about 50-60%) while by the 1H -NMR method they were continued up to the cessation of the reaction.

Tables 3 and 4 list the kinetic parameter values for the quaternization of 4-MeP and P4VP. As expected, the values in Tables 3 and 4 show that the rate constants increase with an increase in the dielectric constant of the solvent.

Quaternizations of P4VP in FA and methanol take place at a lower rate than those of its model compound.

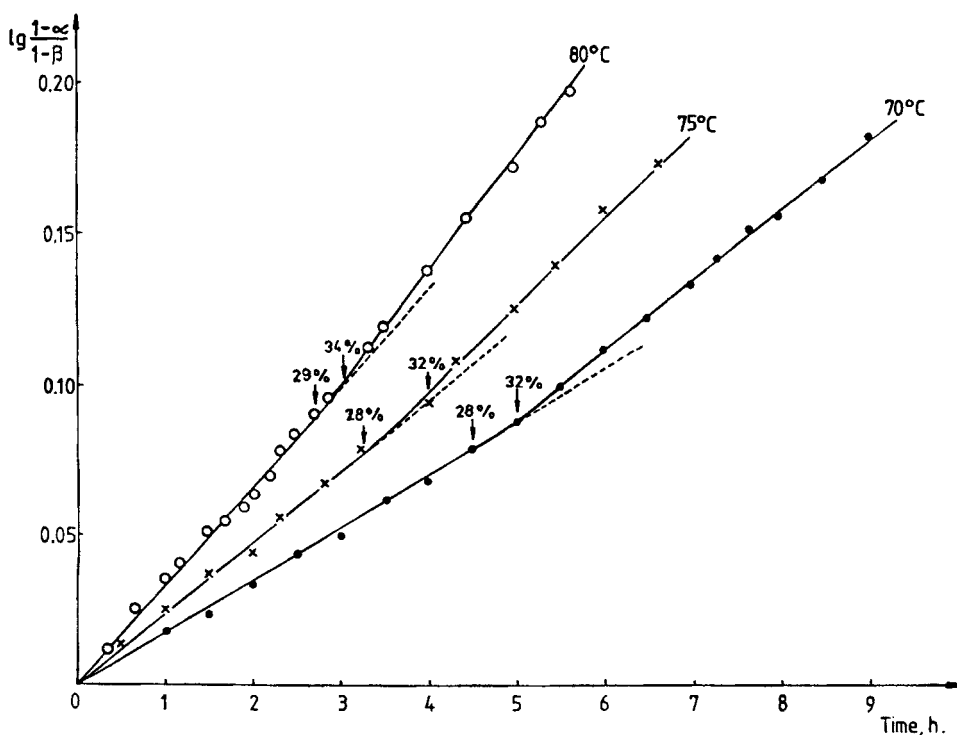


FIG. 8. Conventional second-order plot for the quaternization of P4VP with EtCA in DMF. The percentage values express the β values.

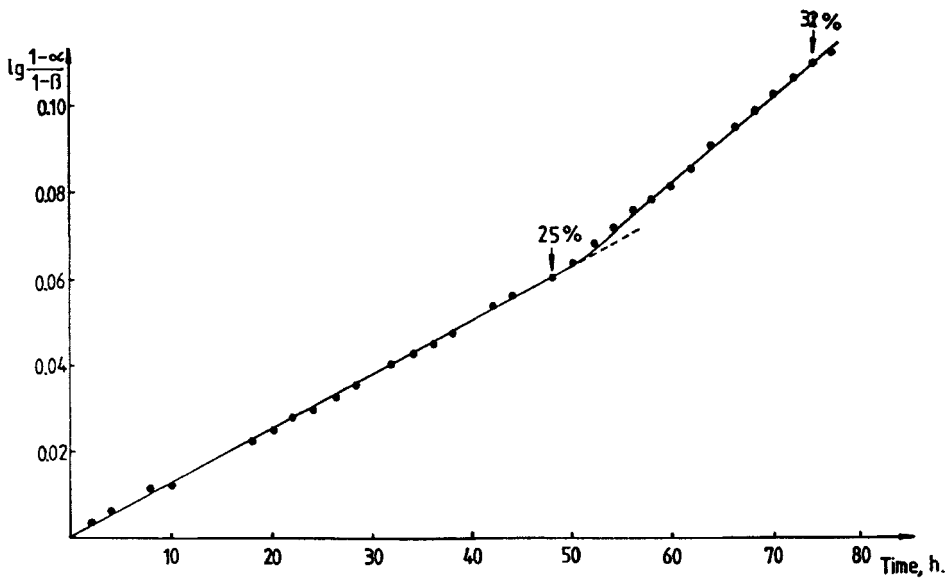


FIG. 9. Conventional second-order plot for the quaternization of P4VP with EtCA in methanol at 50°C.

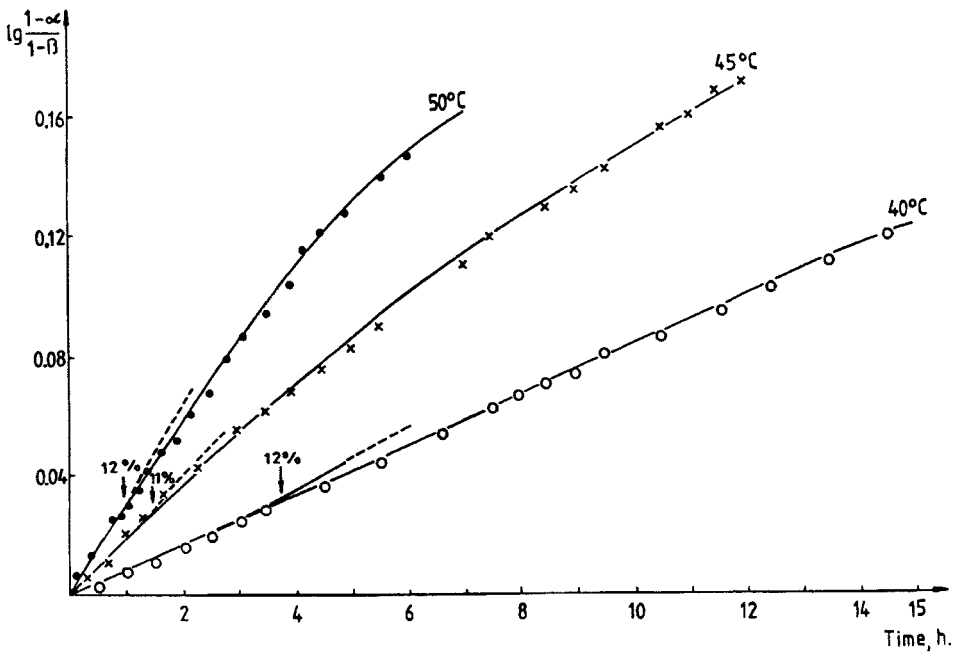


FIG. 10. Conventional second-order plot for the quaternization of P4VP with EtCA in FA.

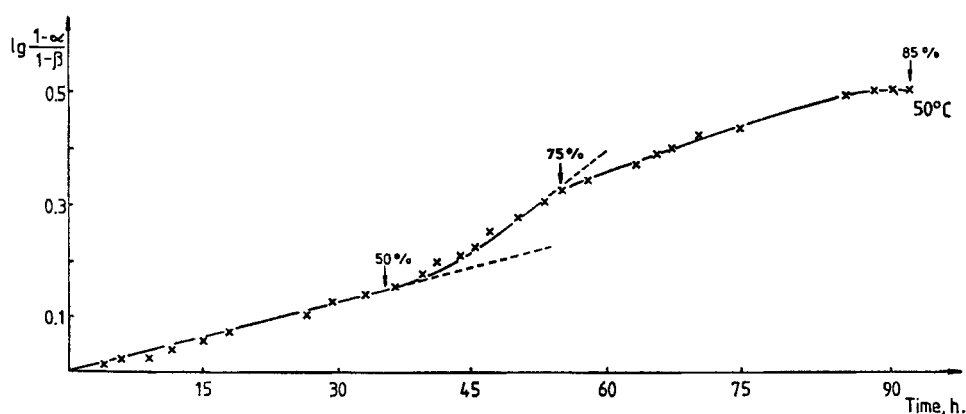


FIG. 11. Conventional second-order plot for the quaternization of P4VP with EtCA in CD_3OD at 50°C .

Comparison of the kinetic determinations made by analytical and $^1\text{H-NMR}$ methods leads to the conclusion that no significant differences exist between them.

Flory's principle asserts that the reactivity of the functional groups attached to a polymer chain is assumed to be equivalent to that of the model compounds [15]. However, in many instances the quaternization rates of reactions involving polymers are significantly different from those of the corresponding models. Moreover, distinct differences in the kinetic profile have often been observed for reactions on polymers [2-5, 16]. These aspects have also been observed for the reactions studied in the present paper.

We assume that the major factor influencing the kinetic profile of the quaternization reactions is represented by the polymer-solvent interactions which change

TABLE 3. Quaternization of 4-MeP with Ethylchloroacetate

Initial reagent concentration, mol/L		Solvent	Temperature, $^\circ\text{C}$	$K_i \times 10^3$ L/mol·min	Kinetic behavior
EtCA	4-MeP				
0.1718	0.0859	FA	40	8.64	Normal
0.1718	0.0859	FA	45	12.90	Normal
0.1718	0.0859	FA	50	20.10	Normal

For quaternization in FA: $E_a = 70.22$ kJ/mol, $\log A = 10.97$

0.3436	0.1718	Methanol	50	0.572	Normal
1.08	0.5	CD_3OD	50	0.598	Normal

TABLE 4. Quaternization of P4VP with Ethylchloroacetate

Initial reagent concentration, mol/L		Solvent	Temperature, °C	$K_i \times 10^3$ L/mol·min	Kinetic behavior
EtCA	Pyridine structure units				
0.1524	0.0762	DMF	70	8.88	Acceleration
0.1524	0.0762	DMF	75	12.36	Acceleration
0.1524	0.0762	DMF	80	16.98	Acceleration
For quaternization in DMF: $E_a = 63.27$ kJ/mol, $\log A = 10.20$					
0.1524	0.0762	FA	40	5.97	Deceleration
0.1524	0.0762	FA	45	10.18	Deceleration
0.1524	0.0762	FA	50	17.58	Deceleration
For quaternization in FA: $E_a = 89.05$ kJ/mol, $\log A = 18.76$					
1.20	0.5	CD ₃ OD	50	0.300	Acceleration
0.3048	0.1524	Methanol	50	0.342	Acceleration

during the reaction. These changes induce conformational modifications of the polymer backbone.

The modality in which conformational transformations can determine acceleration phenomena has been discussed for the quaternization of CMPS with *N,N*-dimethyl-2-hydroxypropylamine [17]. The same explanation can be given for the acceleration phenomena occurring during the reactions of the present study.

The influence of steric hindrances cannot explain the deceleration phenomena appearing at very low degrees of transformation (about 10%) for the quaternization of P4VP with EtCA in FA, but they probably determine the deceleration for the quaternization of P4VP with EtCA in methanol at about a 75% degree of transformation.

FA is a poor solvent for P4VP but a good solvent for the quaternary ammonium polymer. Thus, a shift from a packed coil to a swollen coil during the reaction, concurrently with the separation of the transformed groups toward the solvent, takes place. The quaternary ammonium groups prefer contact with solvent and, consequently, they are oriented outside the coil while the pyridine groups are oriented inside the coil. Therefore, access of the low molecular weight reagent to the reactive groups is more difficult.

Also, the favorable interactions between the quaternary ammonium polymer and the solvent may induce a more pronounced solvation of the polymer chain because of the accumulation of positive charges along the chain. Thus, the "solvent cage" created around the backbone reduces the accessibility of the reagent to reactive groups.

CONCLUSIONS

Comparative kinetic studies on the quaternization of CMPS and of its model with 4,4'-Bpy, as well as of P4VP and of its model with EtCA in different solvents, showed that the model compounds follow normal second-order kinetics, while normal second-order kinetics and acceleration and deceleration phenomena appear for polymers. The same reaction may have different kinetic behaviors, depending on the nature of the solvent.

Based on these observations, we consider that the major factor influencing the kinetic behavior of the reaction on the polymer is the polymer-solvent interaction, known to change during the reaction. These changes can induce both conformational modifications and various solvations of the polymer backbone, and may be either favorable or unfavorable for the reaction rates.

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