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New Aspects of Polymers Containing Quaternary Ammonium Groups

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ABSTRACT

It was established that linear polymers with quaternary ammonium groups are obtained by the reaction of chloromethylated polystyrene (CMPS) with hydroxyalkylic tertiary amines when the amines contain one or two hydroxyl groups, and that crosslinked polymers are obtained with aminoether groups when the amines have three hydroxyl groups, i.e., tris(2-hydroxyethyl)amine. The aminoether units appear by intramolecular rearrangement of quaternary ammonium structural units. Kinetic studies on the synthesis of polymers with quaternary ammonium groups from CMPS, poly(N,N-dimethylaminoethylmethacrylate), and poly(N,N-dimethylaminopropylacrylamide), were performed. The main factors which influence the kinetics of reactions are steric hindrance of near neighboring groups, hydrophilic effect for hydroxyalkylamines and polymer-solvent interaction.

INTRODUCTION

Polymers containing quaternary ammonium groups can be conveniently synthesized by two methods: 1) chemical modification of polymers by single or multiple step reactions, and 2) polymerization of monomers with quaternary ammonium groups. Radical, cyclopolymerization, or ionic techniques are used, especially cationic ring-opening

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polymerization or, in the case of ionenes, nucleophilic substitution (so-called "polyalkylation").

The development of research and applications in this field have evolved during the last 50 years. The first synthesis of polymers with ammonium groups in the main chain was accomplished by Marvel [1] in 1930, reconsidered by Kern [2] in 1941, and completed and extended by Rembaum [3] in 1968.

In 1947 McBurney [4] and then Pepper in 1953 [5] synthesized the first anion exchanger with vinylbenzyltrialkylammonium chloride units by the reaction of the chloromethylated copolymer of styrene-divinylbenzene with trialkylamine. In 1957 Jones [6] reported the synthesis of p-vinylbenzyltrimethylammonium chloride and its polymerization. In 1951 Butler [7] synthesized the monomeric N,N-dialkyldiallylammonium chloride and its polymers. Anthes [8] in 1951 and Barney [9] in 1954 claimed the syntheses of acrylamide and acrylic ester quaternary ammonium salts monomers. Fuoss and Strauss [10] reported in 1949 the synthesis of vinylpyridinium salt polymers.

A first attempt at literature surveys in this field were done by Hoover [11] in 1969 and by Hoover and Butler [12] in 1974. The results in this field are very diversified and are oriented toward practical applications (ion exchange, water treatment, antistatics, biomaterials, etc.). Most of them are covered by patents and are proprietary information. Scientific publications represent only a small part of the total. These publications have been appearing at a constant rate for many years.

The Ghent Symposium (September 1979) [13] was a milestone in the evolution of this field. Based on the conclusions of that meeting and the experience of the last years, the following trends are evident.

1. Syntheses of new monomers, studies concerning the mechanism of polymerization and copolymerization, and physicochemical properties of the polymers obtained.
2. Emphasis of studies on ring-opening cationic polymerization, mainly small rings N-heterocycles.
3. Finding new ways for quaternization reactions.
4. Developing more elaborate studies of the quaternization reaction kinetics.
5. Studies and applications of polyelectrolyte complexes containing quaternary polymers.

In our studies we have been particularly interested in the quaternization reactions of functional polymers containing $-CH_2Cl$ or tertiary amine groups. Our purpose has been both the preparation of new polymers and kinetic studies of the reactions. Studies concerning this specific topic are continuing.

RESULTS AND DISCUSSION

Ammonium quaternary polymers reported in the present paper have been obtained through substitution reactions of small molecular reagents on such macromolecular supports as chloromethylated polystyrene (CMPS), poly(N,N-dimethylaminoethylmethacrylate) (PDMAEM), and poly(N,N-dimethylaminopropylacrylamide) (PDMAPA).

Reactions on Chloromethylated Polystyrene

We have carried out amination reactions on this polymer with tertiary hydroxyalkylamines. These amines have been employed to bring about subsequent modifications at the OH groups on the ammonium quaternary polymers obtained. We also wanted to determine the role played by the number of OH groups in the secondary reactions (which occur in some situations) during the quaternization reaction. Table 1 shows the polymers obtained.

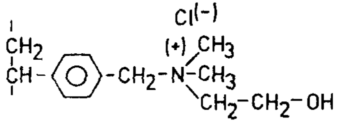
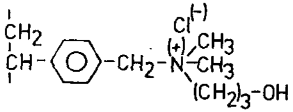
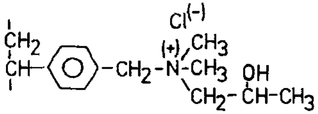
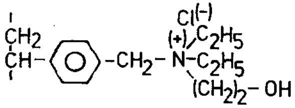
We have noticed that by using amines with only one –OH group, linear polymers are obtained [14]. As we expected, OH groups react easily with thionyl chloride, generating quaternary ammonium groups with a chloroalkyl substituent (Q_5-Q_8) [15]. The Q_5 polymer thus obtained is the macromolecular analogue of chlorcholine chloride (CCC) where a methyl group is replaced by a p-vinylbenzyl group [16]. CCC is well-known as a plant growth stimulating agent.

Analytical data of Q_1-Q_4 and Q_5-Q_8 polymers are listed in Tables 2 and 3.

The IR spectra further confirm the structure of the synthesized polymers; thus, the disappearance of the absorption band at 1260 cm^{-1}, characteristic to the chloromethyl group, and the appearance of the large band at 1000-1100 cm^{-1} for the OH group indicate that the desired quaternization reaction took place. In the case of the IR spectra of Q_5-Q_8 compounds, the absorption band at 1000-1100 cm^{-1} is missing.

The polyelectrolyte behavior of Q_1-Q_8 polymers is shown in Figs. 1 and 2. Figures 1 and 2 show that, in general, reduced viscosity values decrease with the growth of the hydrophobic character of the N^+ atom radicals. We can explain the appearance of distinctions among polyelectrolytes substituted with the 2-hydroxypropyl and 3-hydroxypropyl groups (the first having much higher viscosity values than the latter) by the greater degree of packing of the macromolecular chain which contains 3-hydroxypropyl group than that of the chain bearing the 2-hydroxypropyl branched group. One can also note that Q_1-Q_4 polyelectrolytes have higher values for reduced viscosities than the Q_5-Q_8

TABLE 1. Quaternary Ammonium Polymers Synthesized from Chloromethylated Polystyrene

Polymer	Substrate	Nucleophilic compound	Structural unit
Q_1	CMPS	N,N-Dimethyl-2-hydroxyethylamine (DMHEA)	
Q_2	CMPS	N,N-Dimethyl-3-hydroxypropylamine (DM3HPA)	
Q_3	CMPS	N,N-Dimethyl-2-hydroxypropylamine (DM2HPA)	
Q_4	CMPS	N,N-Diethyl-2-hydroxyethylamine (DEHEA)	

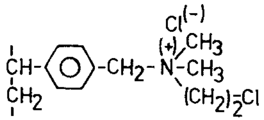
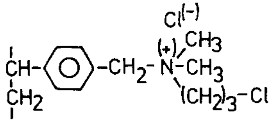
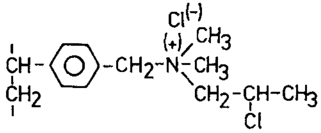
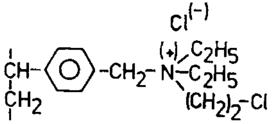
Q_5	Q_1	$SOCl_2$	
Q_6	Q_2	$SOCl_2$	
Q_7	Q_3	$SOCl_2$	
Q_8	Q_4	$SOCl_2$	
Q_9	CMPS	Tris(2-hydroxyethyl)amine (THEA)	Crosslinked product that contain quaternary ammonium and tertiary amine units.

TABLE 2. Chemical Characterization of Quaternary Ammonium Polyelectrolytes Q_1-Q_4[a]

	Cl, %				
Polymer	Cl_t found	Cl_i found (calc)	Cl_c found	N, % found (calc)	α, %
Q_1	15.12	14.13 (14.69)	0.99	5.47 (5.79)	94
Q_2	14.48	13.10 (13.89)	1.38	5.09 (5.48)	91
Q_3	14.55	12.92 (13.89)	1.63	5.08 (5.48)	89
Q_4	14.32	11.72 (13.17)	2.60	4.65 (5.19)	82

[a] Cl_t = total chlorine; Cl_i = ionic chlorine; Cl_c = (covalent chlorine) = Cl_t - Cl_i; α = molar transformation degree.

TABLE 3. Characterization of Quaternary Ammonium Polyelectrolytes Q_5-Q_8 by Chlorine and Nitrogen Contents

	Chlorine content, %						Nitrogen content, %	
	Cl_t		Cl_i		Cl_c			
Polymer	Calc	Found	Calc	Found	Calc	Found	Calc	Found
Q_5	27.16	26.96	13.16	13.42	14.00	13.24	5.19	5.22
Q_6	25.77	25.48	12.28	12.33	13.48	13.15	4.84	4.88
Q_7	25.74	24.07	12.12	12.30	13.62	11.77	4.78	4.92
Q_8	24.50	23.08	11.04	11.20	13.46	12.88	4.35	4.42

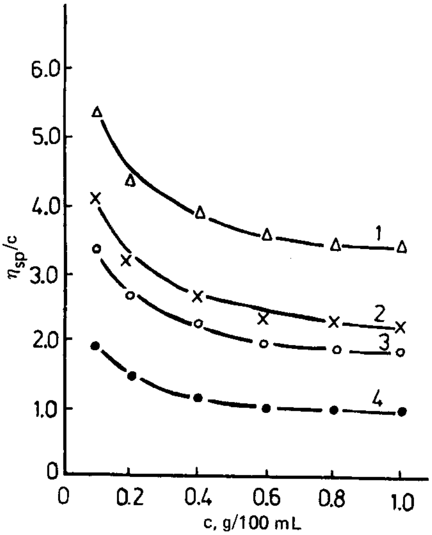


FIG. 1. The reduced viscosity variation versus the concentration of aqueous solutions of Q_1-Q_4 polymers, 25°C: (1) Q_3 polyelectrolyte, (2) Q_1 polyelectrolyte, (3) Q_2 polyelectrolyte, (4) Q_4 polyelectrolyte.

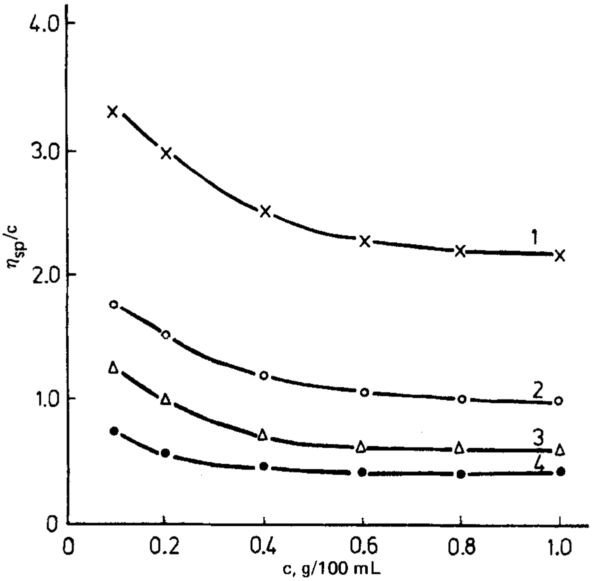
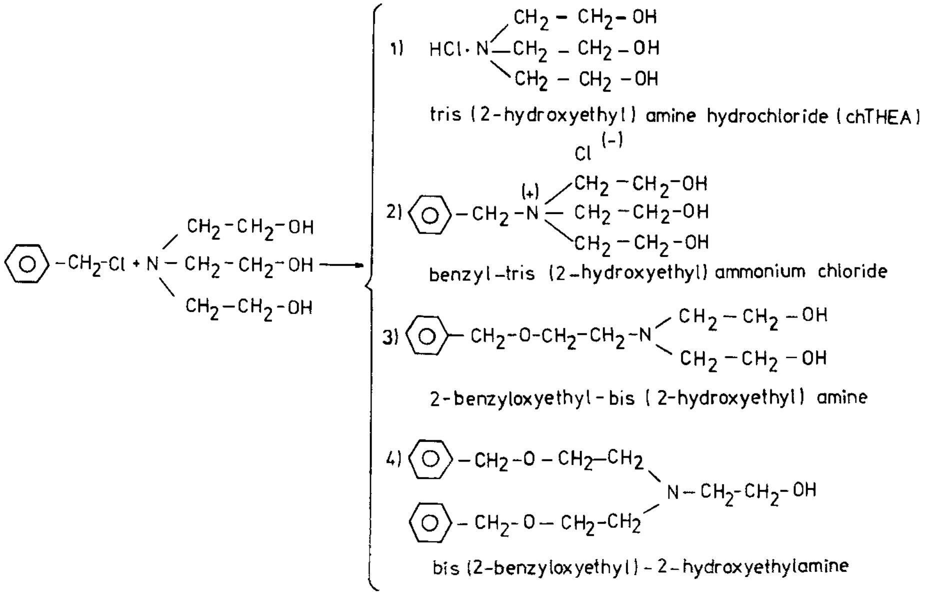


FIG. 2. The reduced viscosity variation versus the concentration of aqueous solutions of Q_5-Q_8 polymers, 25°C: (1) Q_7 polyelectrolyte, (2) Q_5 polyelectrolyte, (3) Q_6 polyelectrolyte, (4) Q_8 polyelectrolyte.



SCHEME 1. Compounds isolated from the synthesis of benzyl chloride with THEA.

polyelectrolytes. This behavior can be explained by the existence, in the first class, of hydrogen bondings which determine a higher degree of extension of the chain than in the case of Q_5-Q_8 polymers.

By using THEA in the quaternization reaction, crosslinking phenomena appear. In order to explain this process, we carried out the reaction between benzylchloride (BC) and THEA. The products presented in Scheme 1 have been isolated from this reaction [17].

The formation of aminoethers can be interpreted as resulting from an intramolecular rearrangement of the ammonium quaternary salt. This supposition is supported by a previous observation [18-21] which shows that the quaternary salt obtained from N,N-dimethyl-2-hydroxyethylamine with diphenylmethane chloride, when heated, suffers an intramolecular rearrangement in the corresponding aminoether.

The rearrangement reaction in the case of THEA with BC takes place even at room temperature.

If we employ small molar ratios of the reagents CMPS:THEA (1:1-1:3), we discover the following facts.

1. The presence of ChTHEA, resulting from amination, is established in the polymers. This is proved by the decrease in Cl and N content of the polymers after washing the samples with distilled water. We found a large amount of ChTHEA in the wash water.

2. By using the analytical technique for ion exchanger characterization, we found indirect evidence for both the presence of quaternary groups (by strong base exchange capacity) and amine groups (by weak base exchange capacity) in these polymers.

We have made experiments with varying molar ratios in order to obtain linear polymers (CMPS:THEA = 1:25) by this reaction. Under these conditions we found out that there were no crosslinkings. The linear polymer dissolved in water was dialyzed against distilled water. It was possible to separate and identify ChTHEA in the dialysates.

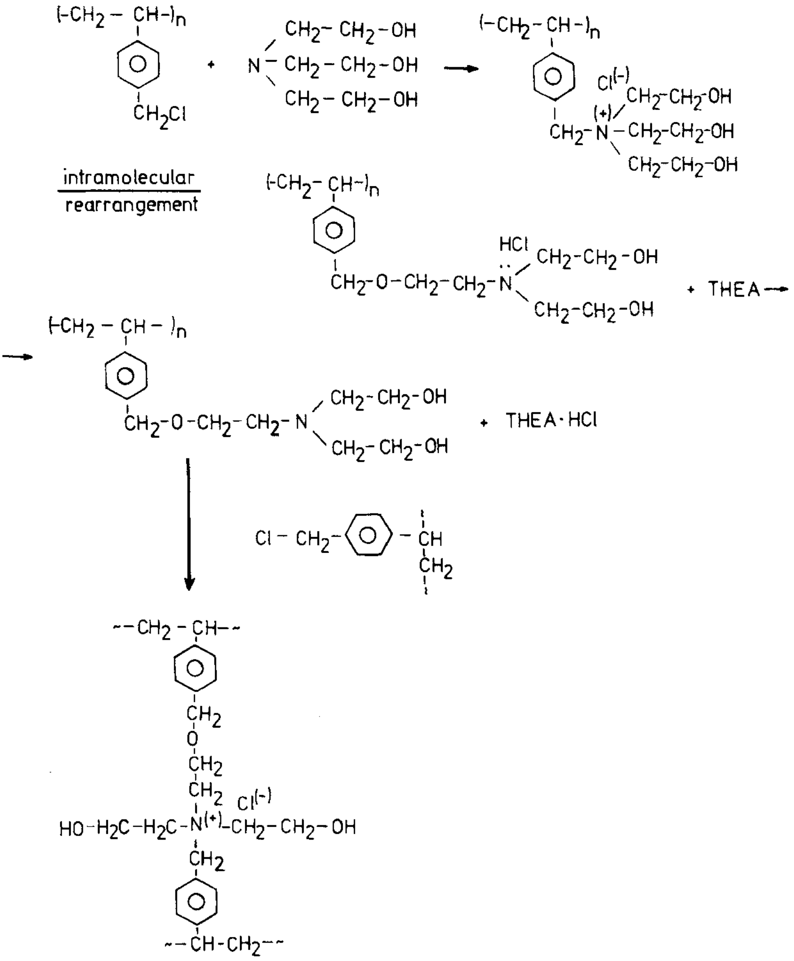
The polymer recovered by precipitation was analyzed by chemical and spectral methods. In this way it was proved that the polymer contains 10-30% quaternary ammonium salt units (untransposed units) and 90-70% aminoether units. The presence of tertiary amine units was also confirmed through their quaternization reaction with BC, which is an indirect proof of the interchain crosslinking reaction between the tertiary aminoethers and the $-CH_2Cl$ groups from CMPS [22]. Those reactions are illustrated in reaction Scheme 2.

Kinetical Aspects of CMPS Amination Reactions

Deviations from "normal" kinetics, specific for low molecular weight compounds, have often been made evident in kinetic studies of chemical reactions in functional macromolecular compounds. These deviations can be positive or negative, i.e., the reaction rate is subject to deceleration or acceleration as the reaction progresses.

Deceleration phenomena were noticed by Fuoss and co-workers in P4VP quaternization with n-butylbromide [23, 24]. Arcus and Hall studied P4VP quaternization with n-butylbromide in tetramethylene sulfone, dimethylformamide (DMF), and their mixtures; they found that in the case of tetramethylene sulfone the reaction rate decreases and in the case of pure DMF the reaction takes place with "normal" second-order kinetics. These authors noticed deceleration during the quaternization of poly(4-N,N-dimethylaminostyrene) with CH_3I in DMF [25, 26]. The deceleration of the P4VP quaternization rate with various alkyl halides was also reported by Boucher and coworkers [27-29]. This decrease of the rate is due, on the one hand, to the steric hindrances created by the already reacted neighboring groups and, on the other hand, to the interactions of polymer-solvent. Those interactions first cause an extension of the macromolecular chain and then a contraction of the chain when they become less favorable.

Kawabe and co-workers performed a detailed study on the kinetics of the CMPS amination reaction with primary, secondary, and tertiary amines, and they recorded both deceleration and acceleration phenomena [30-33]. In more recent studies they explain these phenomena as



SCHEME 2. Amination of CMPS with THEA.

follows: deceleration is attributed to the effects of steric hindrance, but acceleration, which is, in general, observed in the case of CMPS amination with amino alcohol, is attributed to the hydrogen bonds appearing in the transition state [34, 35]. Tsuchida and Irie [36] determined that P4VP quaternization with BC occurs with deceleration and that CMPS amination with pyridine takes place with acceleration. This behavior is explained by the role of the positive electrostatic potential of the macromolecules.

In quaternization studies on polycondensation chloromethylated polymers, Daly and co-workers [37, 38] arrived at the conclusion that the kinetics of those reactions depend on the steric hindrances created by the neighboring groups, on the "hydrophilic" effect of the OH group when hydroxyalkyl amines participate in the reaction, and on the nature of the macromolecular chain, i.e., on its flexibility or rigidity.

The aminations studied by us from the kinetic point of view [39-42] are presented in Table 4 where the values of the kinetic parameters determined are also presented. Besides the hydroxyalkyl tertiary amines, we also compared two n-alkyl tertiary amines–triethylamine (TEA) and N,N-dimethyloctylamine (DMOA).

The following facts are made evident by analysis of the data presented in Table 4.

1. The higher the first step, the greater the amine nucleophilicity. The reaction rate is also influenced by the amine basicity; this is made evident by the values of the rate constants of the first rate step in amination with DMHEA in DMF.
2. The higher the first step rate constants, the greater the solvent polarity (as expected).
3. All hydroxyalkyl amines show the acceleration phenomena in DMF and DMAc, with the acceleration value greater in DMF, although the two solvents have approximately equal dielectrical constants. We explain this by the differing influence of the solvent on the transition state.

From these facts we establish that the nature of both the amine and the solvent influence the kinetics of the amination reactions.

From the plots of Figs. 3-5 the influence of the nature of the solvent on the CMPS amination reaction is clearly seen.

Thus, amination with the same amine, in our case DMHEA, takes place differently as a function of the solvent used.

1. In DMSO with a single rate step.
2. In DMF with two rate steps; the acceleration takes place at a transformation degree of approximately 33%.
3. In DOX and DOX:DMF mixtures with three rate steps; the first acceleration takes place at a transformation degree of 10-15% and the second at 33-40%. The value of the first acceleration (K_2/K_1 ratio) decreases concomitantly with an increase of the amount of DMF in the mixture. As for the nature of the amine, all the aminations except the DMOA reaction take place with acceleration, with their values depending on both the nucleophilic character of the amine and the chemical nature of substitutes for the nitrogen atom.

TABLE 4. Kinetic Study of Chloromethylated Polystyrene[a]

Run	Solvent	T, °C	a, mol/L	b, mol/L	a/b	$k_1 \times 10^3$, L/mol·s	$k_2 \times 10^3$, L/mol·s	$k_3 \times 10^3$, L/mol·s	k_2/k_1	k_3/k_2
Amination with DMHEA										
1	DMF	30	0.1082	0.0541	2.0	1.00	5.30	-	5.30	-
2	DMF	40	0.1082	0.0541	2.0	1.60	8.60	-	5.37	-
3	DMF	50	0.1082	0.0541	2.0	2.60	13.60	-	5.23	-
			For (k_1), $E_a = 9.30$ kcal/mol; $A \times 10^{-3} = 5.71$ L/mol·s							
			For (k_2), $E_a = 9.30$ kcal/mol; $A \times 10^{-3} = 30.28$ L/mol·s							
4	DMSO	20	0.1082	0.0541	2.0	4.80	-	-	-	-
5	DMSO	25	0.1082	0.0541	2.0	5.90	-	-	-	-
6	DMSO	30	0.1082	0.0541	2.0	7.10	-	-	-	-
7	DMSO	35	0.1082	0.0541	2.0	8.80	-	-	-	-
			$E_a = 7.71$ kcal/mol; $A \times 10^{-3} = 2.923$ L/mol·s							
8	DOX	40	0.1082	0.0541	2.0	0.356	1.71	3.14	4.80	1.83
9	DMF:DOX (1:1, v/v)	40	0.1082	0.0541	2.0	1.42	2.95	6.85	2.07	2.32
10	DMF:DOX (3:1, v/v)	40	0.1082	0.0541	2.0	2.28	3.42	9.13	1.50	2.67

Amination with DM3HPA										
11	DMAc	40	0.1064	0.0532	2.0	1.53	2.89	-	1.89	-
12	DMAc	50	0.1062	0.0531	2.0	2.45	4.79	-	1.95	-
13	DMAc	60	0.1066	0.0532	2.0	4.46	8.60	-	1.92	-
14	DMF	40	0.0690	0.03479	1.98	1.856	3.382	-	1.77	-
			For (k_1), E_a = 10.83 kcal/mol; $A \times 10^{-4}$ = 6.306 L/mol·s (10.98) (8.045)							
	DMAc									
			For (k_2), E_a = 11.00 kcal/mol; $A \times 10^{-4}$ = 16.36 L/mol·s (11.20) (21.78)							
15	DMSO	25	0.08921	0.0437	2.04	5.052	-	-	-	-
16	DMSO	30	0.08921	0.04376	2.038	6.377	-	-	-	-
17	DMSO	35	0.08921	0.04376	2.038	7.681	-	-	-	-
18	DMSO	40	0.08921	0.04388	2.03	10.347	-	-	-	-
19	DMSO	50	0.09084	0.04365	2.08	17.068	-	-	-	-
			E_a = 9.32 kcal/mol; $A \times 10^{-4}$ = 3.517 L/mol·s (9.31) (3.566)							
Amination with DM2HPA										
20	DMAc	40	0.1070	0.0535	2.0	0.85	1.30	-	1.526	-
21	DMAc	50	0.1063	0.0532	2.0	1.49	2.495	-	1.675	-
22	DMAc	60	0.1069	0.0535	2.0	2.41	3.81	-	1.58	-
23	DMF	40	0.069	0.03395	2.03	1.084	2.151	-	1.98	-

(continued)

TABLE 4 (continued)

Run	Solvent	T, °C	a, mol/L	b, mol/L	a/b	$k_1 \times 10^3$, L/mol·s	$k_2 \times 10^3$, L/mol·s	$k_3 \times 10^3$, L/mol·s	k_2/k_1	k_3/k_2
	DMAc		For (k_1), E_a = 10.57 kcal/mol; $A \times 10^{-4}$ = 2.398 L/mol·s (10.72) (3.035) For (k_2), E_a = 10.67 kcal/mol; $A \times 10^{-4}$ = 4.147 L/mol·s (11.07) (8.427)							
24	DMSO	30	0.08948	0.04324	2.07	3.30	-	-	-	-
25	DMSO	35	0.08948	0.04322	2.07	4.33	-	-	-	-
26	DMSO	40	0.08948	0.04230	2.115	5.934	-	-	-	-
27	DMSO	45	0.0922	0.04310	2.139	7.170	-	-	-	-
28	DMSO	50	0.08948	0.04314	2.074	9.343	-	-	-	-
			E_a = 10.26 kcal/mol; $A \times 10^{-4}$ = 8.769 L/mol·s (9.987) (6.117)							
Amination with DEHEA										
29	DMF	60	0.1027	0.0515	1.99	0.119	0.264	-	2.21	-
30	DMF	65	0.1027	0.0515	1.99	0.187	0.390	-	2.08	-
31	DMF	70	0.1027	0.0515	1.99	0.295	0.637	-	2.15	-
32	DMF	75	0.1027	0.0515	1.99	0.437	0.913	-	2.08	-
			For (k_1), E_a = 13.26 kcal/mol; $A \times 10^{-3}$ = 38.79 L/mol·s For (k_2), E_a = 14.56 kcal/mol; $A \times 10^{-3}$ = 64.25 L/mol·s							

Amination with TEA									
33	DMF	50	0.1078	0.0541	1.99	0.128	0.153	-	1.19	-
34	DMF	60	0.1078	0.0541	1.99	0.223	0.282	-	1.26	-
35	DMF	70	0.1078	0.0541	1.99	0.398	0.534	-	1.34	-
			For (k_1), E_a = 11.57 kcal/mol; $A \times 10^{-3}$ = 9.97 L/mol·s							
			For (k_2), E_a = 12.47 kcal/mol; $A \times 10^{-3}$ = 54.62 L/mol·s							
Amination with DMOA										
36	DMF	30	0.1026	0.0515	1.99	1.46	1.04	-	0.71	-
37	DMF	35	0.1026	0.0515	1.99	1.93	1.41	-	0.73	-
38	DMF	40	0.1026	0.0515	1.99	2.45	1.84	-	0.75	-
39	DMF	50	0.1026	0.0515	1.99	4.26	3.22	-	0.75	-
			For (k_1), E_a = 10.46 kcal/mol; $A \times 10^{-3}$ = 53.76 L/mol·s							
			For (k_2), E_a = 11.34 kcal/mol; $A \times 10^{-3}$ = 174.80 L/mol·s							

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[a] a = the initial concentration of amine; b = the initial concentration of $-CH_2Cl$ groups. The reaction rate constant was calculated from the slopes of conventional second-order plots. E_a and A were calculated by means of the Arrhenius equation. Values in parentheses were calculated by the least square method. DOX = dioxane; DMAc = dimethylacetamide; DMSO = dimethylsulfoxide.

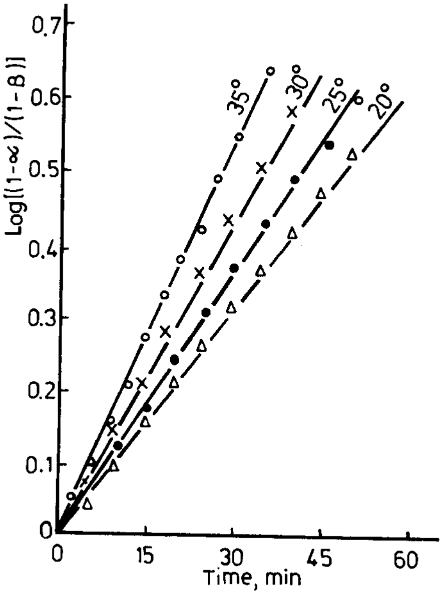

FIG. 3. Amination of CMPS with DMHEA in DMSO.

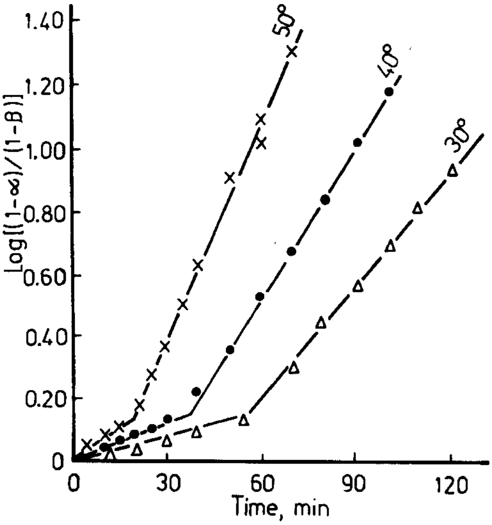

FIG. 4. Amination of CMPS with DMHEA in DMF.

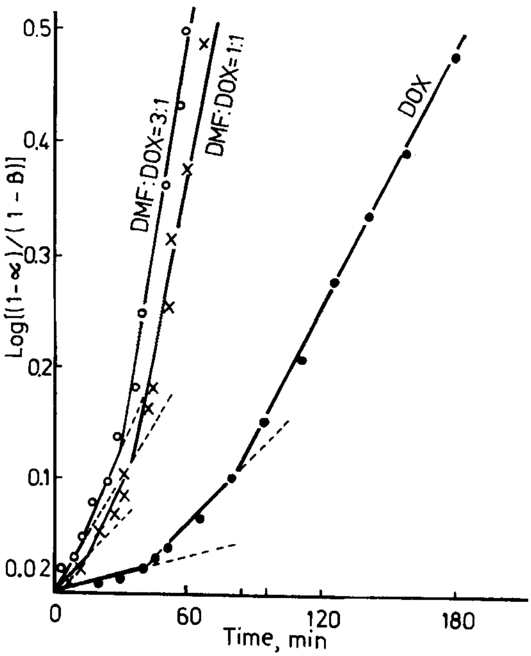

FIG. 5. Amination of CMPS with DMHEA in DOX and DMF:DOX mixture, 40°C.

Kinetic Aspects of PDMAEM and PDMAPA Quaternization Reactions

In order to draw more general conclusions, we compared the kinetics of the reactions between PDMAEM and PDMAPA with BC and allyl chloride (AC) in DMF, DMAc, and DMSO [41-43]. It has been established from plotting the logarithmic term of the reaction rate constant equation versus time that the quaternization reactions of both polymers in DMF and DMAc take place with two or three rate steps which depend on both the nature of the polymer and the solvent. Thus, PDMAPA quaternization with BC and AC in DMF takes place with two rate steps; when DMAc is used, the quaternization takes place with three rate steps as shown in Figs. 6 and 7.

PDMAEM quaternization takes place with three rate steps both in DMF and in DMAc.

Quaternization reactions with BC in DMSO are characterized by a single rate step for both polymers (Fig. 8).

Taking into account the results of kinetic studies on the three poly-

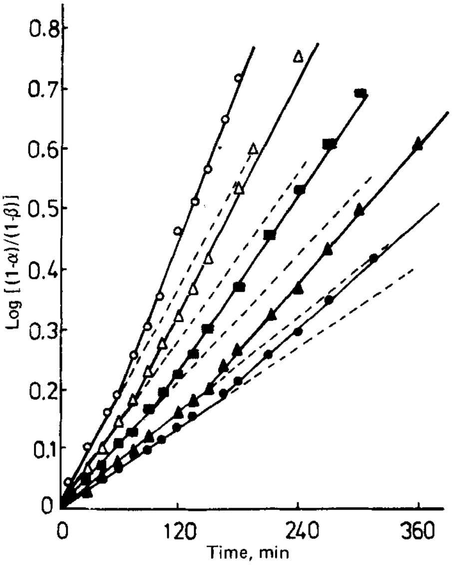

FIG. 6. Quaternization of PDMAPA with BC in DMF: (●) 35, (▲) 40, (■) 45, (△) 50, (○) 55°C.

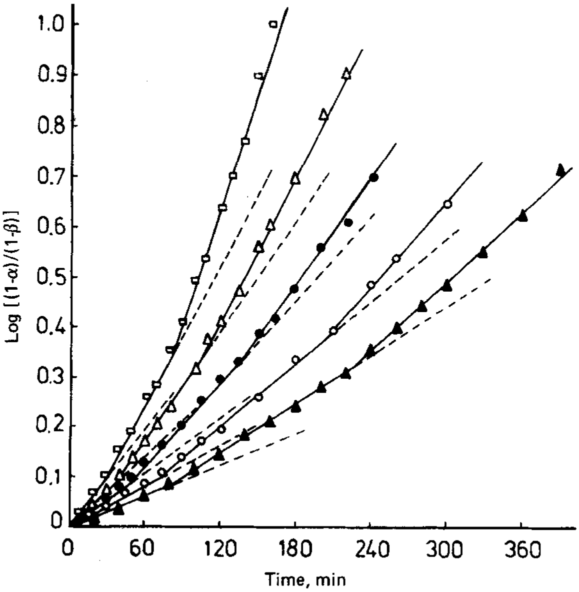

FIG. 7. Quaternization of PDMAPA with BC in DMAc: (▲) 45, (○) 50, (●) 55, (△) 60, (□) 65°C.

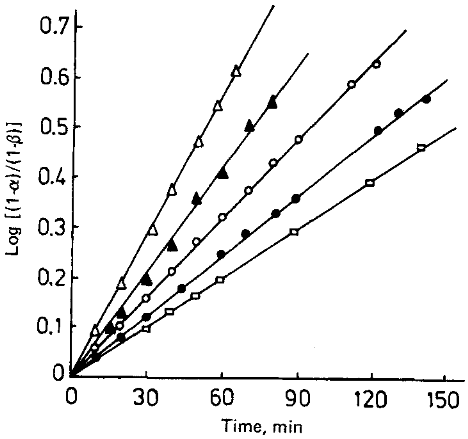

FIG. 8. Quaternization of PDMAPA with BC in DMSO: (□) 31, (●) 35, (○) 40, (▲) 45, (△) 50°C.

mers CMPS, PDMAEM, and PDMAPA, we consider that the significant factors which influence the kinetic aspect of the reactions are:

1. Steric hindrances at small distances created by the substituent of the already reacted neighboring groups
2. The "hydrophilic effect" when the amines contain hydroxyl groups
3. Polymer-solvent interactions

The steric hindrance effects can be noticed in the case of CMPS amination with DMOA. The bulky n-octyl substituent screens the unreacted neighboring $-CH_2Cl$ groups. Deceleration appears at a transformation degree of approximately 50% when the $-CH_2Cl$ group has two transformed neighboring groups.

Proof of the existence of the "hydrophilic effect" results from a comparison of the acceleration value (K_2/K_1 ratio) of the amination reaction with TEA and with DEHEA (Table 4). Although the second amine is bulkier, the acceleration is almost twice as great as in the case of the first amine.

By taking into account the kinetic studies performed on the three types of polymers in order to obtain quaternary ammonium polymers, we believe that the major fact which determines the kinetics of the reactions is polymer-solvent interaction. The role of this factor in the appearance of a positive kinetic deviation becomes preponderant, especially in the case of flexible polymers, i.e., the polymers studied by us.

The viscometric data on the reaction mixture of PDMAPA with BC

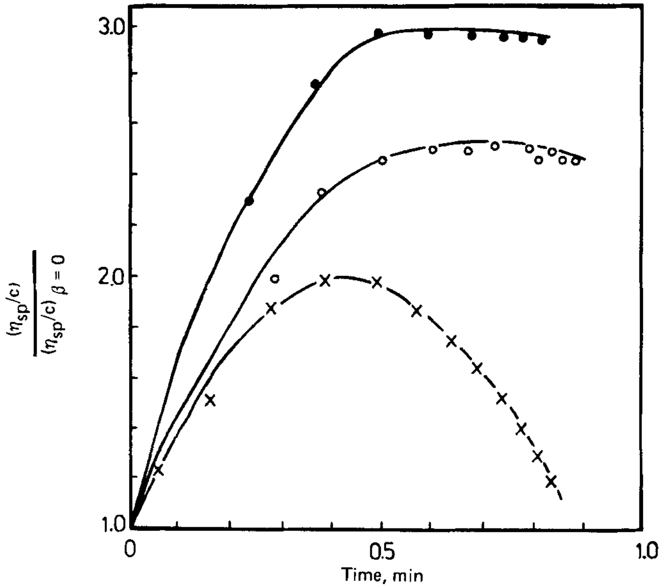

FIG. 9. The variation of ratio A = $(\eta_{sp}/c)/(\eta_{sp}/c)_{\beta=0}$ versus β for the quaternization reaction of PDMAPA: (×) with BC in DMF, (○) with BC in DMSO, (●) with AC in DMSO, 35°C.

and AC in DMF or DMSO, presented in Fig. 9, reinforce the supposition that the polymer-solvent interaction plays an important role.

We established that the variation of ratio A versus β in DMF increases up to 2.0, corresponding to $\beta = 0.5$, followed by a decrease to nearly 1.0.

Unlike DMF, the reaction in DMSO shows a rise of ratio A up to 2.5 with BC and up to 3.0 with AC, corresponding to $\beta \cong 0.5$, followed by a flattening of the curves which persists until the reaction stops.

We can say that DMF is a "bad" solvent for quaternary polymers; as a consequence, contraction of the macromolecular coil takes place after $\beta = 0.5$.

Orientation of the tertiary amine groups toward the solvent takes place concomitantly with orientation of the quaternary ammonium groups toward the interior of the macromolecular coil. This orientation supports continuation of the quaternization reaction and determines the appearance of the acceleration phenomenon.

As the curves in Fig. 9 show, the reaction in DMSO is not accompanied by conformational changes. This fact is also reflected in normal reaction kinetics (Fig. 8).

EXPERIMENTAL

Chloromethylated polystyrene (CMPS) was prepared according to the literature [44, 45] by using a polystyrene with $\overline{M}_v = 37{,}000$. A chlorine content of 22.70-24.00% was obtained.

Solvents were purified by conventional methods. Amines, BC, and AC were vacuum distilled before use.

Synthesis of polymers with quaternary ammonium groups by amination of CMPS with hydroxyalkylic tertiary amines and the chlorination of these polymers by means of $SOCl_2$ have been described in previous work [14, 15]. All the reaction products of BC and THEA were separated and characterized according to methods presented in previous work [17]. The methods for the separation of soluble polymers prepared from reaction of CMPS with THEA have been presented in detail [22].

Kinetic measurements were carried out according to a previously reported technique [39, 40, 43].

PDMAEM was obtained by the radical polymerization of the monomer with 0.9% AIBN in benzene as solvent [46].

Polymer PDMAPA was prepared by aminolysis-hydrolysis of the nitrile groups of poly(acrylonitrile) with N,N-dimethyl-1,3-diaminopropane [47].

Viscometric measurements were carried out using a Ubbelohde suspended level viscometer [14, 42].

Total chlorine (Cl_t) was determined by the Schöniger method and potentiometrically titrated with 0.02 N $AgNO_3$.

Ionic chlorine (Cl_i) was determined by potentiometric titration of polymer-water solutions with 0.02 N $AgNO_3$.

CONCLUSIONS

By CMPS reaction with hydroxyalkyl tertiary amines we can obtain polymers with ammonium quaternary groups; their nature depends on the number of hydroxyl groups in the amine molecule. Amines containing one or two OH groups lead to linear polymers. Under normal synthesis conditions, THEA yields crosslinked polymers; linear polymers with 70-90% aminoether units are obtained with a molar amine excess (CMPS:THEA ratio greater than 25:1).

From comparative kinetic studies performed on polymers and on model compounds, "normal" or deviated (positive or negative) kinetics have been ascertained for polymers.

Kinetic anomalies depend on 1) the nature of the solvent employed as a reaction medium. It determines the interactions of the solvent with the initial and transformed polymer. 2) The chemical nature of the nucleophilic reagent and of the substrates.

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