Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Quaternary Ammonium Polyelectrolytes. V. Amination Studies of Chloromethylated Polystyrene with *N,N*-Dimethylalkylamines

Cornelia Luca[a]; Ecaterina Avram[a]; I. Petrariu[a]
[a] "P. Poni" Institute of Macromolecular Chemistry, Jassy, Romania

To cite this Article Luca, Cornelia , Avram, Ecaterina and Petrariu, I.(1988) 'Quaternary Ammonium Polyelectrolytes. V. Amination Studies of Chloromethylated Polystyrene with *N,N*-Dimethylalkylamines', Journal of Macromolecular Science, Part A, 25: 4, 345 — 361

To link to this Article: DOI: 10.1080/00222338808053373

URL: http://dx.doi.org/10.1080/00222338808053373

J. MACROMOL. SCI.–CHEM., A25(4), pp. 345-361 (1988)

QUATERNARY AMMONIUM POLYELECTROLYTES. V. AMINATION STUDIES OF CHLOROMETHYLATED POLYSTYRENE WITH *N,N*-DIMETHYLALKYLAMINES

CORNELIA LUCA, ECATERINA AVRAM, and I. PETRARIU

"P. Poni" Institute of Macromolecular Chemistry
6600 Jassy, Romania

ABSTRACT

The amination reactions of chloromethylated polystyrene with *N,N*-dimethyldodecylamine, *N,N*-dimethyltetradecylamine, and *N,N*-dimethylhexadecylamine were studied. The physical properties, particularly the solubility properties of the resulting polymers, are influenced by the hydrophobic properties of the long alkyl chain on the N^+ atoms. The main factor that influences the kinetics of the reactions is the polymer-solvent interaction parameter.

INTRODUCTION

The reaction between a tertiary amine and a halogenated compound is known as a bimolecular nucleophilic substitution reaction with second-order kinetics. However, in many instances, if one of the reaction components is a polymer, the reactions do not follow the normal second-order kinetics observed for the corresponding low molecular weight analogs. In the amination of the chloromethylated polymers chloromethylated polystyrene and polysulfones, acceleration and deceleration or normal second-order kinetics are observed.

Lloyd and Durocher [1] first investigated the kinetics of the amination process between poly(vinylbenzyl chloride) crosslinked with 0.05-0.1% divinylbenzene and aqueous trimethylamine. They observed that the rate of amination decelerated markedly at about 50% conversion. Noda and Kagawa [2] carried out kinetic studies for the reaction of chloromethylated polystyrene with triethylamine in DMF and established that the amination followed a second-order kinetics scheme. Daly and coworkers [3, 4] studies the amination of various chloromethylated polysulfones with tertiary amines, such as 2-hydroxyethyldimethylamine, bis(2-hydroxyethyl)methylamine, tri(2-hydroxyethyl)-amine, triethylamine, and tri-*n*-butylamine in DMSO, DMSO:DOX, and DMSO: THF mixtures. Acceleration or deceleration of reaction rates as well as normal second-order kinetics were observed. The authors suggest that the flexibility of the polymer backbone plays the most important role in the rate profile.

In previous papers [5-7] we studied the kinetic aspects of the amination of chloromethylated polystyrene with tertiary amines, such as *N,N*-dimethyl-2-hydroxyethylamine (DMHEA), *N,N*-diethyl-2-hydroxyethylamine (DEHEA), *N,N*-dimethyl-2-hydroxypropylamine (DM2HPA), *N,N*-dimethyl-3-hydroxypropylamine (DM3HPA), triethylamine (TEA), and dimethyloctylamine (DMOA) in various solvents.

The present paper reports studies of the reaction of chloromethylated polystyrene (CMPS) with *N,N*-dimethyldodecylamine (DMDA), *N,N*-dimethyltetradecylamine (DMTA), and *N,N*-dimethylhexadecylamine (DMHA) as well as with the kinetic aspects of these reactions in various solvents.

EXPERIMENTAL

Chloromethylated polystyrene was prepared according to data in the literature [11, 12] using a polystyrene with $\bar{M}_v$ 37 000 and with a chlorine content of 22.70%. Solvents (for abbreviations, see Table 2) were purified by conventional methods. The amines were of reagent analytical grade.

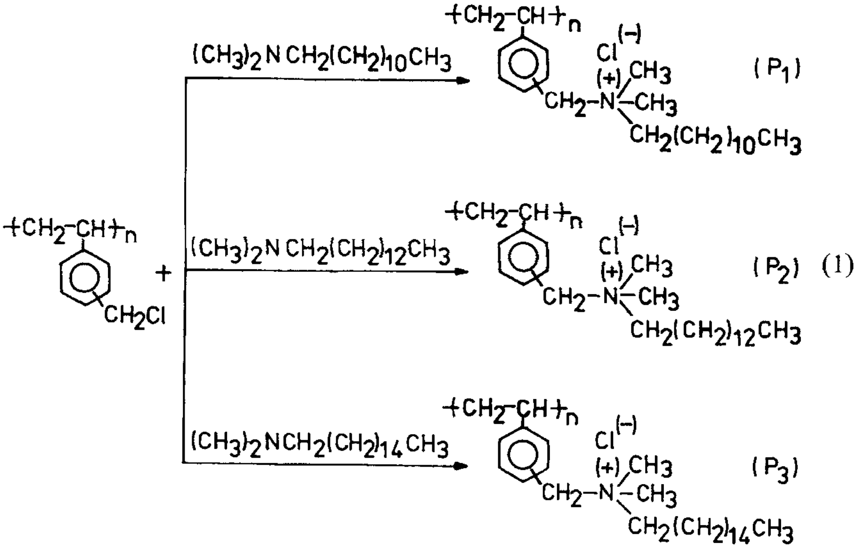
The kinetic measurements were carried out according to a previously reported technique [6]. In the cases where phase separation took place (the reaction mixture shifts to opalescent), the kinetic measurements were carried out in sealed tubes immersed in a thermostat. After the desired time, the sealed tubes were opened and the Cl^- ion concentration was measured.

The reduced viscosity in methanol at 25°C was determined by means of Ubbelohde suspended-level viscometers.

RESULTS AND DISCUSSION

Amination of Chloromethylated Polystyrene

The reactions of CMPS with the above-mentioned amines take place according to Scheme 1.



SCHEME 1.

Analytical data of the resulting P_1-P_3 polymers are listed in Table 1. The quaternized polymers are white powders. Their solubilities are shown in Table 2. The P_1-P_3 polymers have a solubility behavior different from the other quaternary polymers; they are insoluble in water and soluble in some halogenated compounds.

The dependence of the reduced viscosity on the dilution (Fig. 1) shows typical polyelectrolyte behavior. The P_3 polymer has the lowest reduced viscosity, while P_1 and P_2 and the quaternary ammonium compound obtained by the reaction of CMPS with *N,N*-dimethyloctylamine (P_0 polymer) have approximately the same reduced viscosities at concentrations above 1.2 g/100 mL. At lower concentrations, the reduced viscosities follow the order $P_0 > P_2 > P_1 \gg P_3$.

Generally speaking, the reduced viscosity values decrease with the magnitude of the hydrophobic character of the N^+ atom radicals because the packing of the macromolecular chain varies with the hydrophobic intramolecular interactions. But in our case the P_2 sample fell out of line, which is difficult to explain.

TABLE 1. Chemical Characterization of P_1-P_3 Polymers[a]

	Chlorine content, %		Nitrogen content, %		
Polymer	Calculated	Found	Calculated	Found	%[b]
P_1	9.70	10.28	3.83	3.65	89.39
P_2	9.00	9.39	3.56	3.50	95.91
P_3	8.41	8.69	3.32	3.20	90.48

[a] All amination reactions carried out on CMPS with a 22.70% chlorine content.

[b] Molar conversion calculated from nitrogen content.

Kinetic Aspects

It is well known that second-order kinetics follow

$$k = \frac{1}{(a-b)t} \ln \frac{b(a-x)}{a(b-x)} = \frac{2.303}{(a-b)t} \log \frac{1-\alpha}{1-\beta}, \tag{2}$$

where a is the initial concentration of amine, mol/L; b is the initial concentration of chloromethyl groups, mol/L; x is the concentration of halogen ions at time t; $\alpha = x/a$, the fraction of amine reacted at time t; and $\beta = x/b$, the fraction of chloromethyl groups reacted at time t (conversion).

The logarithmic terms in Eq. (2) are plotted versus time in order to determine the kinetic behavior, and the results are presented in Figs. 2-6.

From these graphs one can observe that:

1. The plots for aminations with all three amines in DMF, DMAc, and DMF:DOX mixtures are represented by two straight lines which intersect near $\beta = 0.50$. This shows that the reactions take place in two steps with different rate constants, k_1 and k_2. Since k_1 is higher than k_2, deceleration takes place.
2. The reaction between CMPS and DMTA in DMAc has a lower reaction rate than DMF although the two solvents have approximately the same dielectric constants. The higher rate constants in DMF are considered to be due to the better solvation of the transition state in this solvent.
3. The reaction rate is decreased by the introduction of DOX into DMF. This was expected because it is well known that, in bimolecular nucleophilic

TABLE 2. Solubility of Polymers at Room Temperature

Experiment	Solvent	Result[a]
1	Water	-
2	Methyl alcohol	+
3	Ethyl alcohol	+
4	Butyl alcohol	+
5	Acetone	-
6	Methylethylacetone	-
7	*N,N*-Dimethylformamide (DMF)	+ -
8	*N,N*-Dimethylacetamide (DMAc)	+ -
9	Dimethylsulfoxide (DMSO)	+ -
10	Dioxane (DOX)	-
11	Dioxane:DMF (1:1; v/v)	+ -
12	Dioxane:DMF (2:1; v/v)	-
13	Benzene	-
14	CH_2Cl_2	+
15	$CHCl_3$	+
16	CCl_4	-
17	$C_2H_4Cl_2$	-
18	$C_2H_2Cl_4$	+

[a] +, easily soluble; + –, difficulty soluble (but soluble above 35°C); –, insoluble.

substitutions, an increase of the dielectric constant of the aprotic solvent favors the reaction.

4. It is interesting to note that amination with DMTA in DOX is characterized by a slight acceleration.

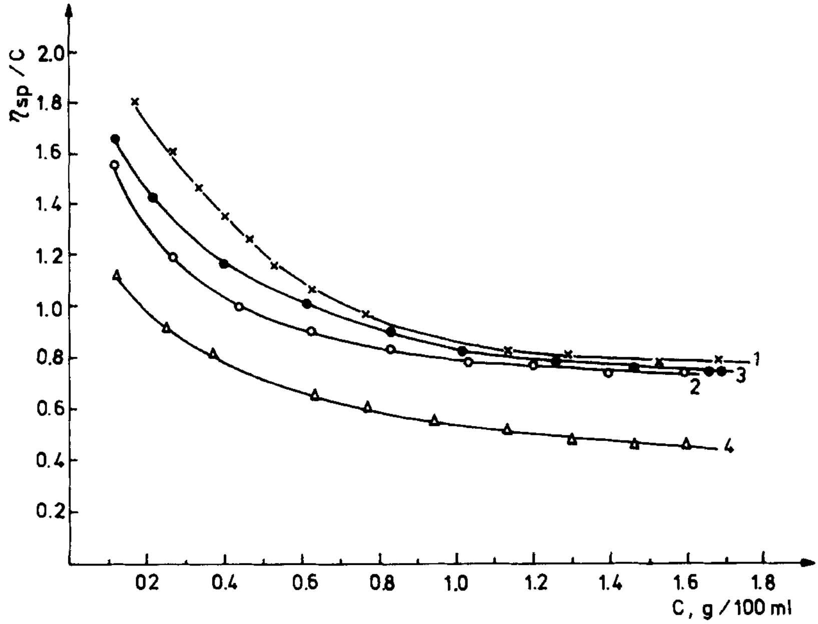


FIG. 1. Huggins plots of solutions in methanol at 25°C: (1) P_0 polymer, (2) P_1 polymer, (3) P_2 polymer, (4) P_3 polymer.

The rate constant of the first reaction stage (k_1) was calculated from the experimental data by Eq. (2). In order to compute the rate constant of the second reaction stage (k_2), the following relationship was used:

$$k = \frac{2.303}{(a - b)(t - \tau)} \left(\log \frac{1 - \alpha}{1 - \beta} - \log \frac{1 - \lambda/a}{1 - \lambda/b} \right), \tag{3}$$

where τ is the time (s) and λ is the concentration (mol/L) of Cl^- ions at the onset of the second stage.

Figure 7 shows that Arrhenius plots are linear, and this allows us to calculate the activation energy E_a and the frequency factor A by

$$\log k = \log A - E_a/2.303RT, \tag{4}$$

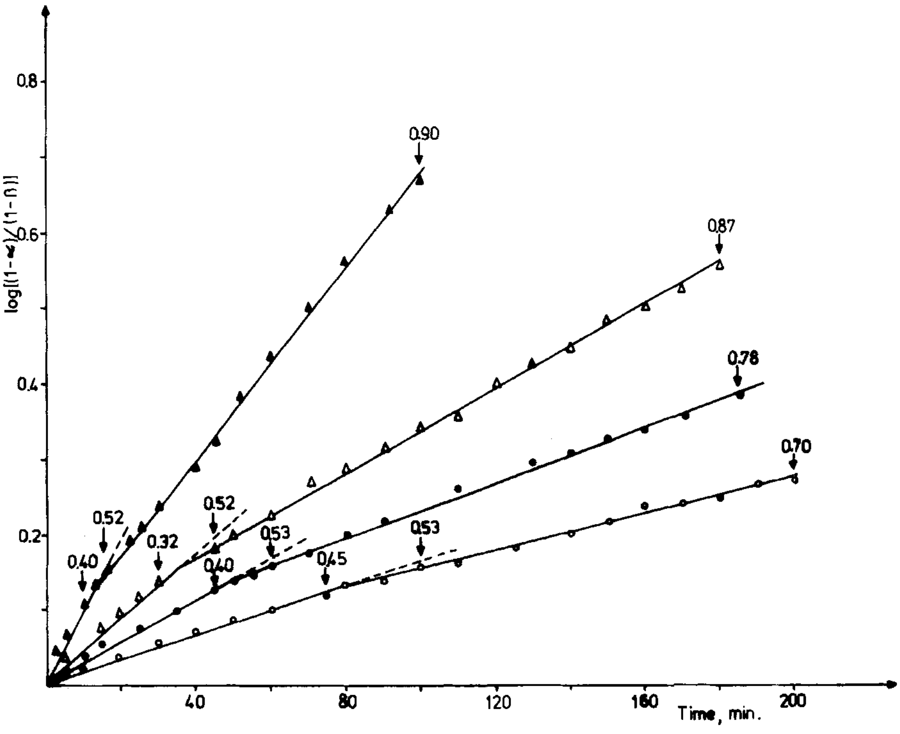


FIG. 2. Amination of chloromethylated polystyrene with *N,N*-dimethyldodecylamine (DMDA) in DMF: (○) 40°C, (●) 50°C, (△) 60°C, (▲) 70°C.

where R is the gas constant (1.97 cal/mol·K) and T is the absolute temperature. Table 3 gives the values of the rate constants, k, calculated by means of Eqs. (2) and (3), and the activation energies E_a and the frequency factors A computed by means of Eq. (4), as well as the deceleration or acceleration effects (represented by k_2/k_1 and k_3/k_2). The data in Table 3 show that the reactivities of the three amines in DMF are approximatively the same.

The extent of deceleration decreases with decreasing temperature (the k_2/k_1 ratio increases). This can probably be explained by the conformational transformations of the polymer backbone as the polymer-solvent interaction changes with temperature. It is well known that the intrinsic viscosity of polymer solutions can increase or decrease or even go through a maximum as

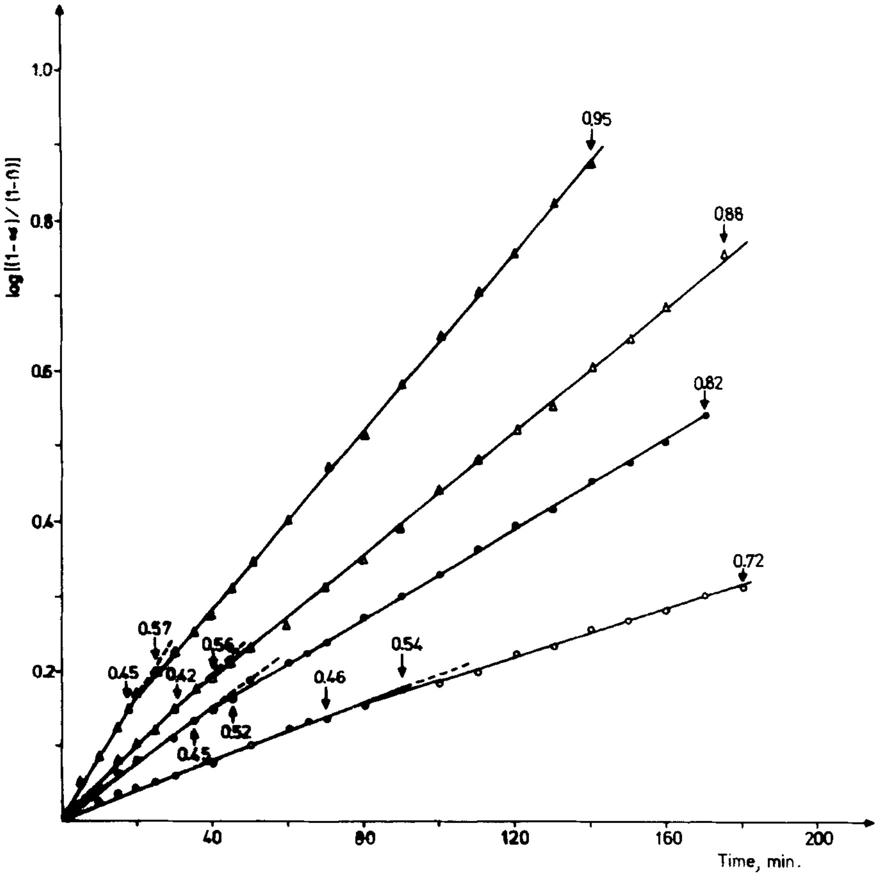


FIG. 3. Amination of chloromethylated polystyrene with *N,N*-dimethyltetradecylamine (DMTA) in DMF: (○) 40°C, (●) 50°C, (△) 60°C, (▲) 70°C.

a function of temperature. Theoretically, all polymer-solvent systems have a temperature at which the intrinsic viscosity is at a maximum.

Also, one observes that in DMF:DOX mixtures the extent of deceleration decreases as the proportion of DOX is increased until, in pure DOX, there are small accelerations at $\beta \simeq 0.16$ and 0.45. This is unexpected because one might assume that the reactions of CMPS with amines that contain a bulky substituent (as in our cases) are decelerated due to the steric hindrance of $-CH_2Cl$ groups by the quaternized neighboring groups.

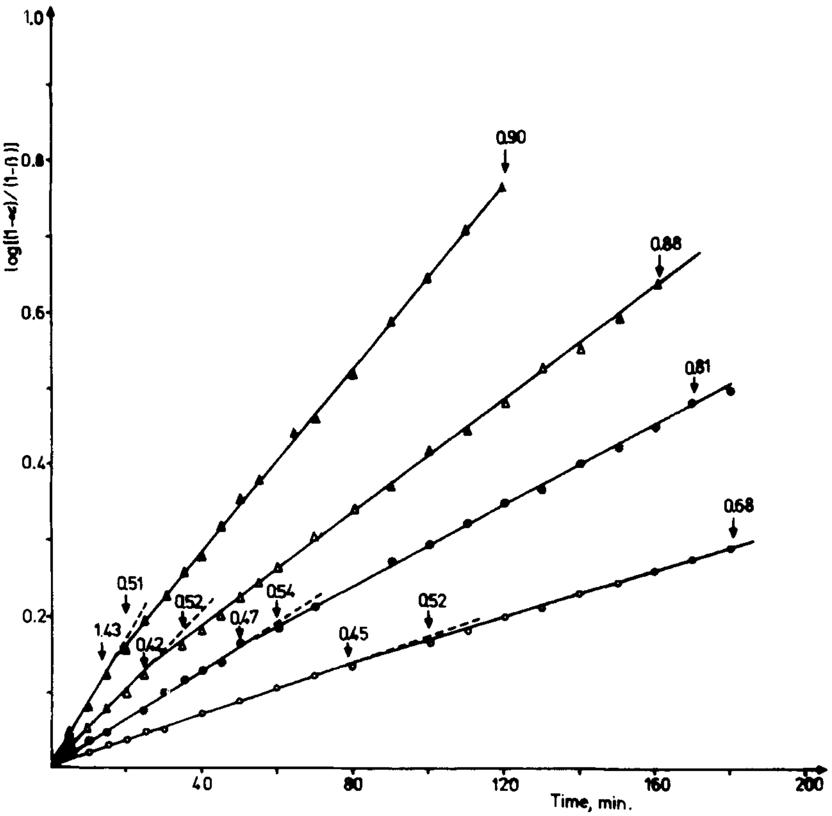


FIG. 4. Amination of chloromethylated polystyrene with *N,N*-dimethylhexadecylamine (DMHA) in DMF: (○) 40°C, (●) 50°C, (△) 60°C, (▲) 70°C.

The kinetic behavior of the amination reaction of CMPS with DMOA in DMSO was also investigated (Fig. 8). The same reaction in DMF was reported in a previous paper [7]. The deceleration phenomenon takes place in both DMSO and DMF.

For comparison, we show in Table 4 the kinetic behavior of reactions of CMPS with tertiary amines studied in the present and previous papers. The data in Table 4 show that the kinetics of the amination reactions of CMPS depend on the nature of the amine and the nature of the solvent.

We consider that the significant factors which influence the kinetic aspect of the reactions are: 1) the polymer-solvent interactions and 2) the steric

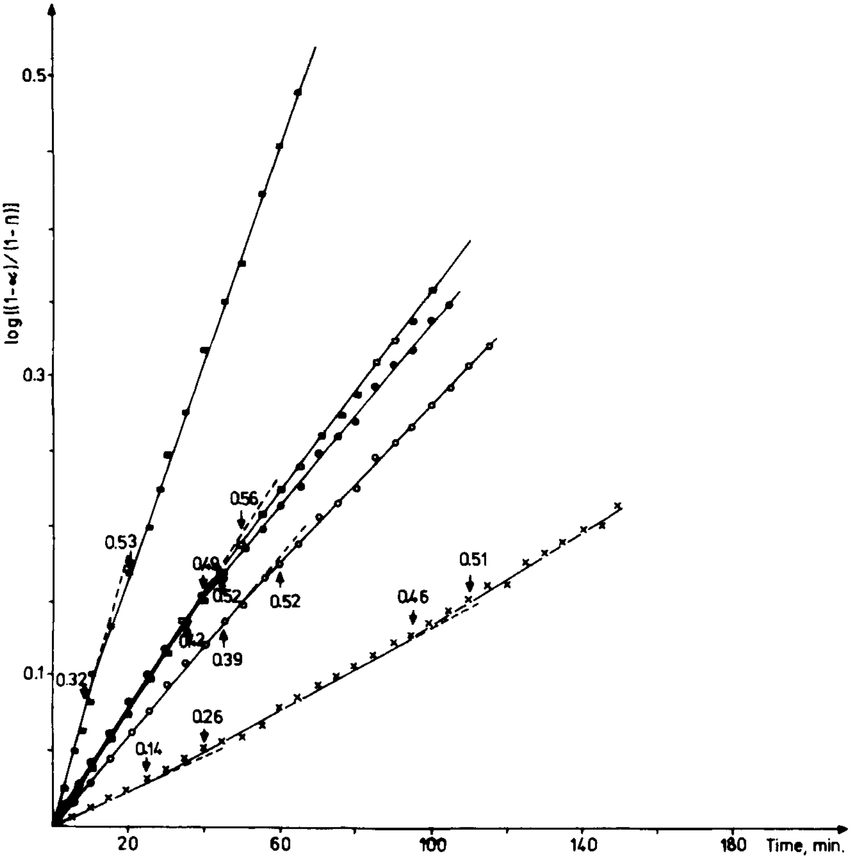


FIG. 5. Amination of chloromethylated polystyrene with *N,N*-dimethyltetradecylamine (DMTA) in various solvents at 70°C. (X) DOX; (○) DMF: DOX, (1:2, v/v); (●) DMAc; (□) DMF:DOX (1:1, v/v); (■) DMF.

hindrances at small distances resulting from the neighboring substituent groups.

We noted that the reaction mixture became opalescent in Runs 1-3, 5, 6, 15, 16, and 18. This is the first sign that the reaction medium is becoming a nonsolvent for the polymers produced and that, therefore, the polymer-solvent interaction changes. The above runs take place with acceleration (Runs 1-3, 5, 6, and 16) or with deceleration (Runs 15 and 18). Also,

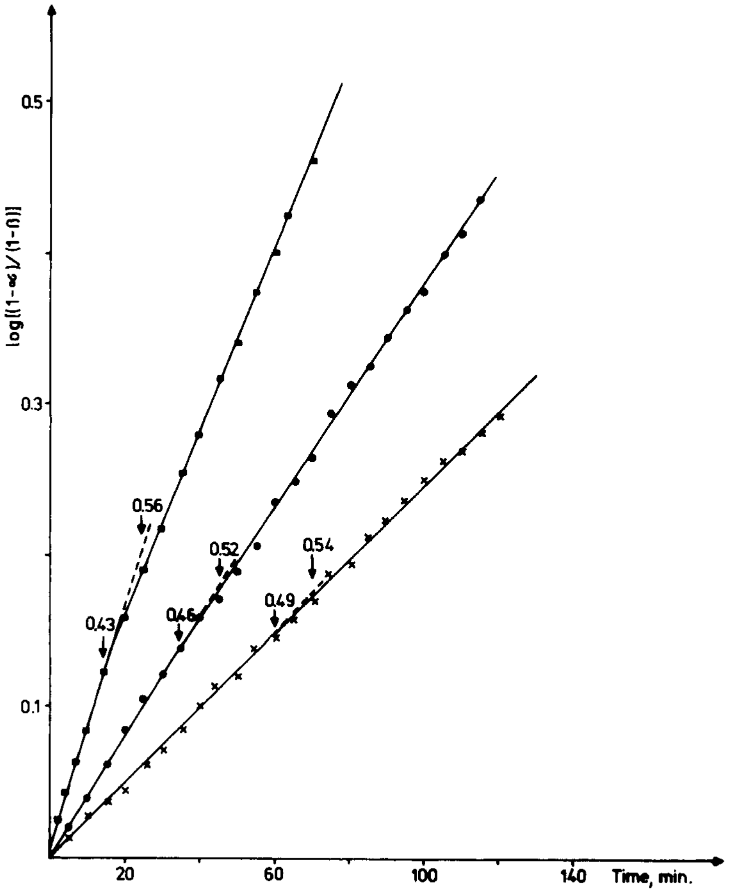


FIG. 6. Amination of polystyrene chloromethylated with *N*,*N*-dimethylhexadecylamine (DMHA) in various solvents at 70°C. (X) DMF:DOX (1:2, v/v); (●) DMF:DOX (1:1, v/v); (■) DMF.

acceleration takes place in Runs 8 and 9 when the reaction mixture does not become opalescent.

When the reactions between CMPS and triethylamine or *N*,*N*-diethyl-2-hydroxyethylamine were carried out in DMF at high polymer concentration (~10 wt%), the product ammonium quaternary compound separated from the solution after the conversion reached ~33%, but no phase separation is observed at a very low polymer concentration (~0.0500 mL/L).

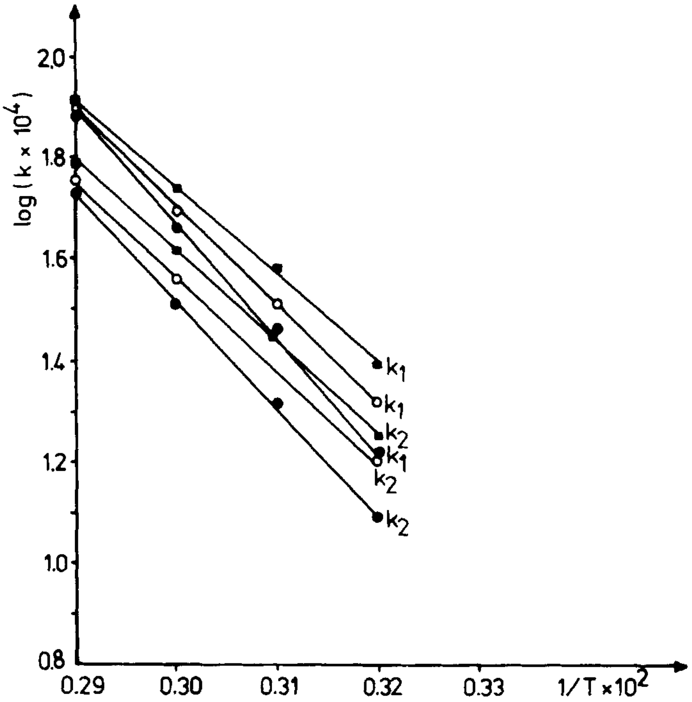


FIG. 7 Arrhenius plots for amination chloromethylated polystyrene in DMF: (■) DMDA, (○) DMTA, (●) DMHA.

These observations led us to assume that DMF, a solvent for CMPS, shifts to nonsolvent for the quaternary ammonium compounds formed by reaction of CMPS with triethylamine and *N,N*-diethyl-2-hydroxyethylamine.

Broadly speaking, acceleration took place when the amination reaction of CMPS was carried out in a nonsolvent for formed quaternary ammonium compound if there are no steric hindrances. In a solvent for the quaternary ammonium polymer, there was normal kinetic behavior, or deceleration when there was steric hindrance.

The "hydrophylic effect" can be seen by comparing the acceleration (k_2/k_1 ratio) of the reaction with triethylamine and with diethyl-2-hydroxyethylamine [7]. Although the latter is bulkier, the acceleration is almost twice that for the former. But this effect could come about because DMF is a strong-

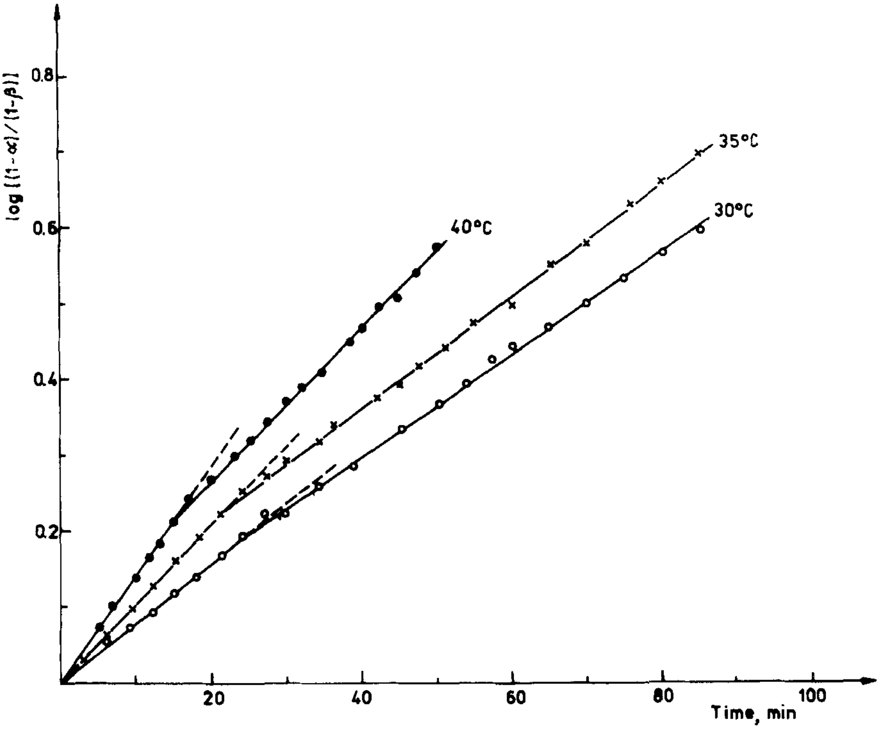


FIG. 8. Kinetic behavior of CMPS amination reaction with DMOA in DMSO.

er nonsolvent for the ammonium quaternary polymer from diethyl-2-hydroxyethylamine.

In conclusion, as also shown in previous papers, the conformational modifications of a polymer chain can take place during the formation of quaternary ammonium polymers [7-9]. These modifications appear because the polymer-solvent interactions change when a certain amount of quaternary ammonium groups is on a backbone; hence, at a certain conversion β. Conformational modifications take place in the flexible polymers, such as CMPS [10]. We suppose that conformational modifications are the major factors that influence the kinetics of CMPS aminations.

TABLE 3. Amination of Chloromethylated Polystyrene

Run	Solvent	T, °C	a, mol/L	b, mol/L	a/b	k_1, mL/(mol·s)	k_2, mL/(mol·s)	k_3, mL/(mol·s)	k_2/k_3	k_2/k_3
Amination with DMDA[a]										
1	DMF	40	0.0935	0.0570	1.64	2.05	1.75	–	0.85	–
2	DMF	50	0.0935	0.0570	1.64	2.84	2.16	–	0.76	–
3	DMF	60	0.0935	0.0570	1.64	3.06	2.32	–	0.75	–
4	DMF	70	0.0935	0.0570	1.64	6.42	4.67	–	0.73	–
Amination with DMTA[b]										
5	DMF	40	0.0930	0.0534	1.74	1.55	1.35	–	0.87	–
6	DMF	50	0.0930	0.0534	1.74	2.35	1.96	–	0.83	–
7	DMF	60	0.0930	0.0534	1.74	2.91	2.24	–	0.77	–
8	DMF	70	0.0930	0.0534	1.74	4.94	3.64	–	0.73	–
9	DMAc	70	0.0930	0.0534	1.74	3.75	2.64	–	0.70	–
10	DMF:DOX (1:1, v/v)	70	0.0930	0.0534	1.74	3.52	3.14	–	0.89	–
11	DMF:DOX (1:2, v/v)	70	0.0930	0.0534	1.74	2.75	2.53	–	0.92	–
12	DOX	70	0.0930	0.0534	1.74	1.07	1.29	1.47	1.20	1.14

Amination with DMHA[c]										
13	DMF	40	0.0992	0.0570	1.74	1.23	1.05	–	0.85	–
14	DMF	50	0.0992	0.0570	1.74	2.23	1.82	–	0.82	–
15	DMF	60	0.0992	0.0570	1.74	2.79	2.15	–	0.77	–
16	DMF	70	0.0992	0.0570	1.74	4.68	3.37	–	0.72	–
17	DMF:DOX (1:1, v/v)	70	0.0992	0.0570	1.74	3.43	3.09	–	0.90	–
18	DMF:DOX (1:2, v/v)	70	0.0992	0.0570	1.74	2.68	2.48	–	0.93	–

[a] For k_1, E_a = 10.3 kcal/mol, log A = 4.51; for k_2, E_a = 10.5 kcal/mol, log A = 4.52.

[b] For amination in DMF: for k_1, E_a = 11.4 kcal/mol, log A = 5.16; for k_2, E_a = 11.1 kcal/mol, log A = 4.88.

[c] For amination in DMF: for k_1, E_a = 13.4 kcal/mol, log A = 6.48; for k_2, E_a = 12.8 kcal/mol, log A = 5.97.

TABLE 4. Kinetic Behavior of Aminations of Chloromethylated Polystyrene with Tertiary Amines

Run	Amine	Solvent	Kinetic behavior
1	Dimethyl-2-hydroxyethyl	DMF	Acceleration
2		DOX	Acceleration
3		DMF:DOX mixtures	Acceleration
4		DMSO	Normal second-order
5	Dimethyl-3-hydroxypropyl	DMF	Acceleration
6		DMAc	Acceleration
7		DMSO	Normal second-order
8	Diethyl-2-hydroxyethyl	DMF	Acceleration
9	Triethyl	DMF	Acceleration
10	Dimethyloctyl	DMF	Deceleration
11		DMSO	Deceleration
12	Dimethyldodecyl	DMF	Deceleration
13	Dimethyltetradecyl	DMF	Deceleration
14		DMAc	Deceleration
15		DMF:DOX mixtures	Deceleration
16		DOX	Acceleration
17	Dimethylhexadecyl	DMF	Deceleration
18		DMF:DOX mixtures	Deceleration

CONCLUSIONS

In comparative kinetic studies of the reactions of CMPS with tertiary amines, acceleration or deceleration phenomena, as well as normal second-order kinetics, are observed.

We suppose that the major factor that influences the kinetics of these reactions is the polymer-reaction medium interactions which change during the course of the reaction. These changes determine the conformational modifications of the polymer backbone which are favorable or nonfavorable for the reaction rates. That the amination of CMPS with DMTA (bulky amine) in DOX takes place with a small acceleration supports our supposition.

REFERENCES

[1] W. G. Lloyd and T. E. Durocher, *J. Appl. Polym. Sci., 8,* 953 (1964).

[2] S. Noda and I. Kagawa, *Kogyo Kagaku Zasshi, 66,* 857 (1963).

[3] W. H. Daly, S. Chotiwana, and J. C. Lion, "Polymeric Amines and Ammonium Salts," in *Papers of the International Symposium, Ghent, Belgium, September 24-26, 1979,* Pergamon, Oxford, 1980, p. 37.

[4] W. H. Daly and S. J. Wu, in *Modification of Polymers* (B. U. Culbertson, ed.), American Chemical Society, Washington, D.C., 1983.

[5] S. Drăgan, I. Petrariu, and M. Dima, *J. Polym. Sci., Polym. Chem. Ed., 10,* 3077 (1972).

[6] C. Luca, I. Petrariu, and M. Dima, *Ibid., 17,* 3879 (1979).

[7] A. Carpov, C. Luca, S. Drăgan, and I. Petrariu, *J. Macromol. Sci.–Chem., A22,* 907 (1985).

[8] H. Kawabe, *Bull. Chem. Soc. Jpn., 47,* 2936 (1974).

[9] S. Drăgan, S. Ioan, I. Petrariu, and M. Dima, *J. Polym. Sci., Polym. Chem. Ed., 23,* 1267 (1985).

[10] S. Drăgan, S. Ioan, and M. Dima, *Polym. Bull., 7,* 473 (1982).

[11] G. D. Jones, *Ind. Eng. Chem., 44,* 2688 (1952).

[12] I. Petrariu and J. Stamberg, *Collect. Czech. Chem. Commun., 32,* 798 (1967).

Received November 7, 1985
Revision received September 28, 1987