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### Modification of Condensation Potymers

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## Modification of Condensation Polymers

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### ABSTRACT

Techniques for chloromethylation of polyarylether sulfones, polyphenylene oxide, phenolic resin, and a model compound for the polyarylether sulfone are described. The rates of quaternization of chloromethylated polyarylether sulfone, I, and the corresponding model compound, II, with triethylamine, tri-n-butylamine, and quinuclidine in either DMSO or DMSO/dioxane are reported. Second-order kinetics are observed in the quaternization of II for the entire range of substitution. In contrast, quaternization of I followed second-order kinetics during the initial 35-60% of reaction only; higher degrees of quaternization occurred at reduced rates. After evaluating the potential impact of steric hindrance, added electrolyte, and initial extent of chloromethylation, the decrease in quaternization rate at high degrees of substitution is attributed to steric effects imposed by restricted rotation of the polymer chain. Comparable retardations are not observed during the quaternization of chloromethylated polystyrene under identical conditions.

Although the preparation of quaternary-ammonium-containing resins from appropriately substituted vinyl monomers has been studied extensively [1], elaboration of condensation polymers has not received comparable attention. Condensation polymers cannot be prepared with sufficiently high molecular weights or satisfactory chemical stability for most applications involving flocculation or viscosity enhancement. However, the excellent mechanical properties exhibited by many aromatic condensation polymers suggest that specialty applications, in particular, permselective membranes, could be served by suitably modified resins. We have observed that polymers containing oxyphenylene repeat units are subject to facile electrophilic substitution including chloromethylation; the reactive derivatives can be cast into tough, flexible films [2].

Quaternary ammonium ion-exchange resins were produced initially by chloromethylating crosslinked polystyrene beads with chloromethyl methyl ether, followed by quaternization with tertiary amines [3]. We have circumvented exposure to the highly carcinogenic bis-(chloromethyl)ether, a common contaminant of commercial chloromethyl methyl ether, by employing 1,4-bis(chloromethoxy)butane or 1-chloromethoxy-4-chlorobutane and have produced chloromethylated poly(oxy-2,6-dimethyl-1,4-phenylene), polysulfone, and phenoxy resin\* [4]. Alternatively, chloromethyl methyl ether can be generated from acetyl chloride and methylal [5], and the reaction mixture, 4, utilized directly in chloromethylation of activated aromatic repeat units.

### CHLOROMETHYLATION OF CONDENSATION POLYMERS

Under suitable conditions chloromethylation of polysulfone yields a derivative with a maximum of two  $-\text{CH}_2\text{Cl}$  substituents per repeating unit; no substitution occurs on the aryl sulfone rings due to the powerful deactivating influence of the sulfone group. Since relatively high reaction temperatures are required, 1,1,2,2-tetrachloroethane was chosen as the solvent for the chloromethylation. Results obtained with 0.1 mol of  $\text{SnCl}_4$  and 1 mol of polysulfone are shown in Fig. 1. No crosslinking is observed up to 99% conversion if a 20-to-1 ratio of chloromethyl methyl ether to polysulfone is employed. At increased concentrations of polysulfone, i.e., 10 mol of ether to 1 mol of polysulfone, a gel-point is reached at about 75% conversion. The substitution is accompanied by a substantial broadening of the molecular weight distribution; a concomitant increase in the weight-average

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\*Correct IUPAC nomenclature: polysulfone, poly[oxy-1,4-phenylene-sulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene]; phenoxy resin, poly[oxy(2-hydroxytrimethylene)oxy-1,4-phenylene-(1-methylethylidene)-1,4-phenylene].

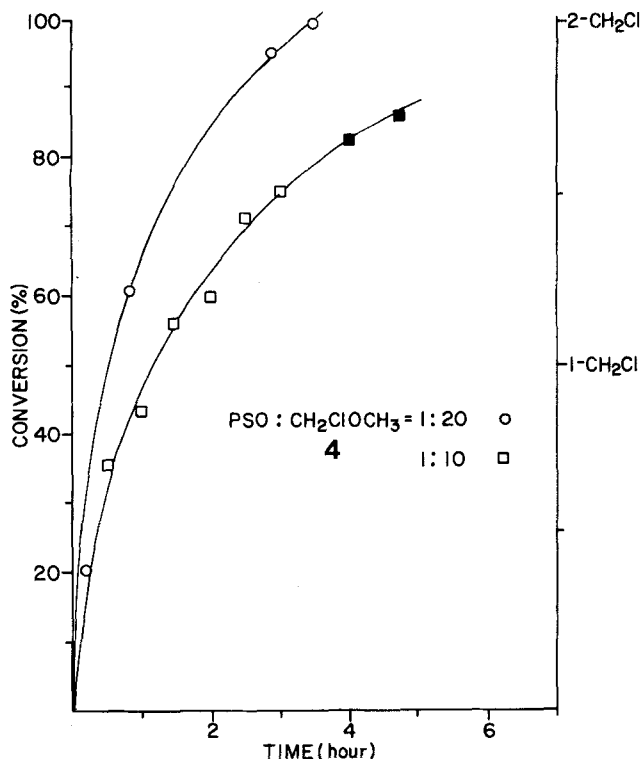


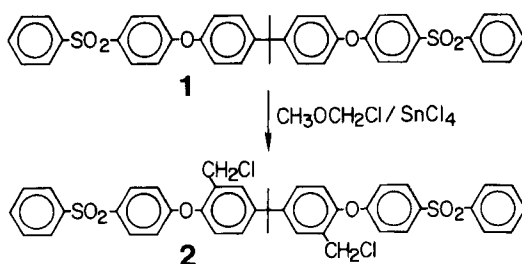
FIG. 1. Chloromethylation of polysulfone. (○) Polysulfone, 7 g; 4, 52.7 mL; SnCl<sub>4</sub>, 0.185 mL in 140 mL 1,1,2,2-tetrachlorethane at 96°C. (□) Polysulfone, 7 g; 4, 26.4 mL; SnCl<sub>4</sub>, 0.185 mL in 140 mL 1,1,2,2-tetrachlorethane at 113°C. (■) Gelled.

molecular weight suggests that both crosslinking and degradative side reactions are occurring. The side reactions can be minimized by using less active catalysts such as titanium tetrachloride. Chloromethylated polysulfone exhibits good mechanical properties, is soluble in chloroform and dimethylsulfoxide, and is subject to facile nucleophilic modification.

Reaction of phenoxy resin with a chloromethylating agent is accompanied by crosslinking, but up to 4.6 meq/g of active chloride can be introduced. Soluble derivatives can be synthesized by acetylating the resin before conducting the chloromethylation. Aromatic polycarbonates, polyethylene terephthalate, and polyurethanes derived from bis-(4-isocyanatophenyl)methane form very stable Lewis acid complexes

with the catalysts. Low degrees of substitution can be achieved if greater than equimolar catalyst:substrate ratios are employed, but extensive polymer degradation occurs under the reaction conditions necessary to introduce a chloromethyl substituent, so the final products have little utility.

Although benzyl chloride is usually selected as the model for chloromethylated polymers, we chose to synthesize a difunctional model that would be sensitive to neighboring group effects. Condensation of 4-chlorophenyl phenyl sulfone with the disodium salt of bis-phenol-A yielded an excellent model for the polysulfone segment, **1**. Quantitative chloromethylation of **1** with a chloromethyl methyl ether/methyl acetate mixture in the presence of stannic chloride afforded the corresponding bischloromethyl adduct, **2**.



### QUATERNIZATION OF CHLOROMETHYLATED POLYMERS

Since the quaternization of triethylamine with ethyl iodide was first studied by Menshutkin [6], extensive kinetic investigations have established the basic conditions governing an  $S_N2$  reaction between two neutral species forming a charged product. Quaternization is irreversible under normal experimental conditions, so only the kinetically favored products are obtained and the reaction affords a relatively sensitive probe into the influence of the polymer backbone on rates of polymer reactions. The formation of a charged transition state is favored by more polar solvents, which solvate the developing charge. Polymer backbones may be considered as part of the solvent matrix; thus, reactions on more polar condensation polymers should be more facile than those occurring in a hydrocarbon matrixlike polystyrene.

The kinetics of a chloromethylated polystyrene quaternization process were investigated first by Lloyd and Durocher [7]. The rate of quaternization of poly(vinylbenzyl chloride) latex, PVBC, composed of about 60% para- and 40% ortho-isomers, decelerated markedly at about 50% conversion. This deceleration was attributed to the different reactivities of o- and p- chloromethyl substituents on the aromatic rings. In order to ascertain the impact of positional isomers of the

"copolymer" rates, two "homopolymer" latexes were prepared from 99% p-vinylbenzyl chloride and 95% o-vinylbenzyl chloride, respectively. The p-PVBC reacted very fast, while the high ortho analogue, after an initial surge, reacted much more sluggishly. Furthermore, for p-PBVC, the rate constant at 20-50% conversion is significantly higher than that of the initial 0-20% conversion; deceleration was observed in the case of o-PVBC. The accelerating rate with increasing conversion of p-PVBC suggested that the quaternized group provided a more polar environment for unreacted neighboring sites; consequently, the formation of a charged transition state was favored. Charges introduced close to the polymer backbone in the ortho position were buried in a hydrocarbon matrix and failed to influence the environment of the residual chloromethyl groups. Thus the steric hindrance imposed by the backbone exerted the dominating influence on the quaternization rate. The rates of both "homopolymers" and the "copolymer" were retarded at very high conversions (> 90%) due to an electrostatic field effect.

In a systemic kinetic study of the reaction of various amines with chloromethylated polystyrene (CMPS), Kawabe and co-workers [8-10] found the rate profiles to be significantly influenced by the nature of the amine and the reaction media. They observed that some cases conformed to simple second-order reaction rate laws, but slight variations in the reaction conditions produced either deceleration or acceleration as quaternization proceeded. The deceleration was observed in the reactions of bulky amines, i.e., diethylamine or dibutylamine, in DMF, DMSO, and dioxane. This rate retardation could be attributed to the steric hindrance imposed by the quaternized neighboring group. The nature of the solvent also played an important role in the quaternization process; for instance, a normal second-order reaction was observed between triethylamine and CMPS in DMF. In DMSO, a deceleration attributed to an electrostatic effect was observed [10].

Accelerations occurred commonly when hydroxyethyl amines were allowed to react with CMPS in dioxane or dimethylacetamide, indicating that a hydrophilic effect or the formation of intramolecular hydrogen bonds may play an important role in promoting quaternization [11]. Autoacceleration occurred at about 33% conversion, suggesting that when a chloromethyl group has at least one quaternized neighboring group, the presence of hydroxyl in that quaternary group contributes to the solvation of adjacent transition states. Rate comparisons at different temperature regimes demonstrated that the hydrophilic effect was stronger in dioxane than in dimethylacetamide. Quaternizations of CMPS with triethylamine, N-(2-hydroxyethyl)dimethylamine, or N,N-bis-(2-hydroxyethyl)methylamine, conducted in DMF, also exhibited stepwise acceleration [12].

Quaternization of the polysulfone model, 2, proceeded to completion with no deviation from second-order kinetics. The kinetic data for the reaction of 2 with triethylamine and quinuclidine are summarized in Table 1. Note that the reaction of quinuclidine is two orders of magnitude faster than that of triethylamine even after the rate has been mod-

TABLE 1. Quaternization of the Polysulfone Model, 2

Run	T, °C	a, mmol/mL	b, meq/mL	a/b	$k \times 10^3$ , L·mol <sup>-1</sup> ·s <sup>-1</sup>	% Conversion
<u>With Triethylamine in DMSO</u>						
1	61	0.0530	0.0248	2.14	1.46	86.3
2	50	0.0530	0.0248	2.14	0.691	71.4
3	41	0.0510	0.0249	2.05	0.402	63.9
4	35	0.0500	0.0250	2.00	0.267	55.2
	$E_a = 13.5$ kcal/mol				$\log A = 5.99$	
<u>In DMSO/Dioxane</u>						
5	60	0.0535	0.0246	2.17	0.335	60
<u>With Quinuclidine in DMSO/Dioxane</u>						
6	35	0.0505	0.0254	1.99	101.	82.3
7	30	0.0520	0.0251	2.07	80.5	81.3
8	26	0.0520	0.0258	2.02	64.3	74.8
9	20	0.0535	0.0257	2.08	47.1	75.1
	$E_a = 9.6$ kcal/mol				$\log A = 5.8$	

erated by mixing dioxane with the DMSO. It is obvious that neither an electrostatic effect nor a steric effect can be detected in reactions involving the polysulfone model system. Apparently the chloromethyl sites in the model compound are shielded from each other by the relatively rigid isopropylidene bridge which restricts the rotation of the aryl units in the oxyphenylene structure.

Chloromethylated polysulfone containing an average of 1.9 chloromethyl groups per repeating unit, **3**, was treated with triethylamine in DMSO. We expected the isolation of active sites demonstrated with model **2** would prevail in the polysulfone system. This was not the case, as is evident in Fig. 2. The kinetic plots are concaved downward because the quaternization of the polysulfone proceeds less and less rapidly as the degree of conversion increases. The quaternization of **3** with TEA can be modeled by two reaction rate constants,  $k_0$  and  $k_2$ . Normally, three individual rate constants,  $k_0$ ,  $k_1$ , and  $k_2$ , are defined for polymer modification. These constants depend on the distribution of reacted sequences along the chain. In the initial stage of quaternization, the reaction is undoubtedly a random process along a given polymer chain, and the probability of quaternization of a site which has a reacted neighbor is small, but as the reaction proceeds beyond 1/3 conversion, a deviation should appear if  $k_0 \neq k_1$ . However, the kinetic behavior of the model compound indicated that the chemical reactivity of a given  $-\text{CH}_2\text{Cl}$  group is independent of whether its nearest neighbor has reacted or not. Therefore, it is reasonable to assume that for quaternization of **3**, the relation between these rate constants is  $k_0 = k_1 > k_2$ , where  $k_2$  pertains to reactions on an extended chain with a high charge density.

The values for  $k_0$  and  $k_2$  estimated from the slopes of conventional second-order plots are summarized in Table 2. The ratios  $k_0/k_2$  are also reported. These ratios remain quite constant for all runs except 14 and 15, in which the concentration ratio of amine: $-\text{CH}_2\text{Cl}$  is about 10. Note also that the rate constants for these two runs, 14 and 15, are slower than for Runs 11 and 12 where the concentration ratio of amine: $-\text{CH}_2\text{Cl}$  is 2. A similar observation was made by Kawabe in the amination of chloromethylated polystyrene with 2-aminobutanol in DMSO [8]. This abnormal phenomena is not fully understood, but the possibility of solvent polarity change due to the high concentration of amine required cannot be ruled out.



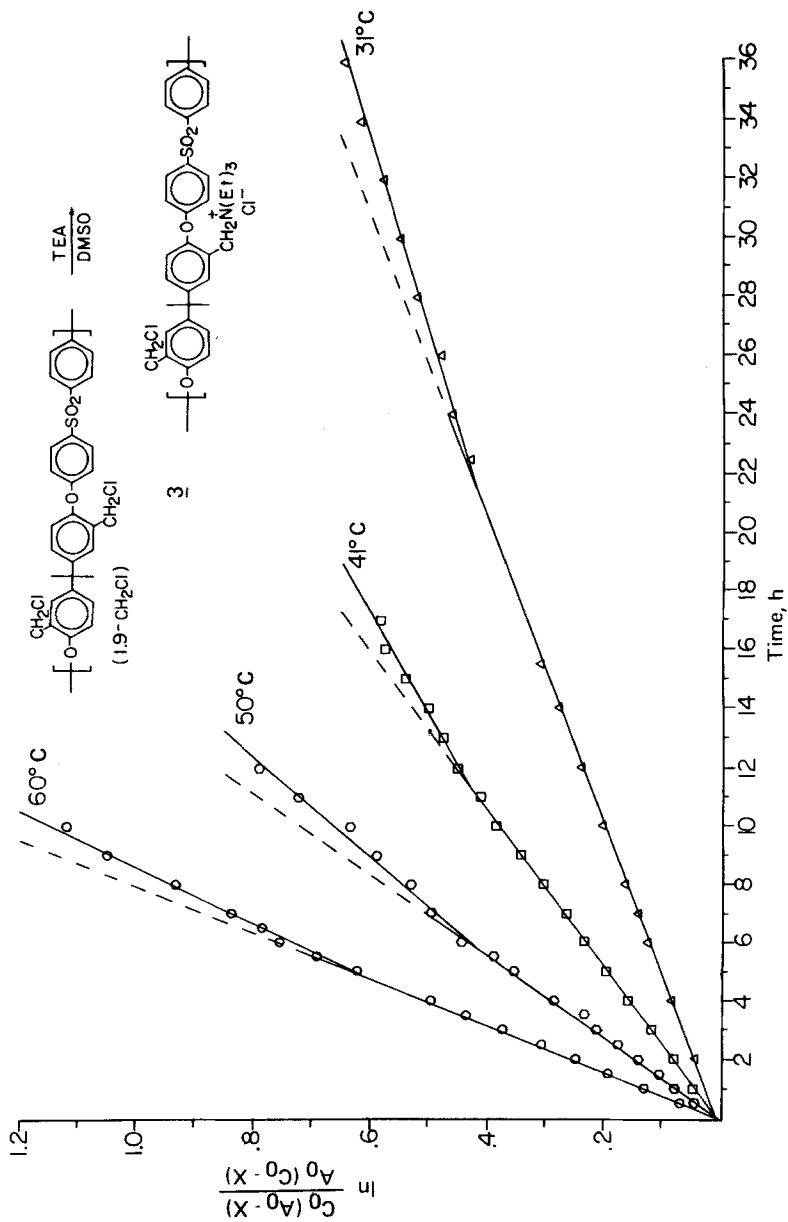


FIG. 2. Quaternization of 3 with triethylamine in DMSO;  $[-\text{CH}_2\text{Cl}]$ , 0.024 meq/mL;  $[\text{TEA}]$ , 0.053 mmol/mL.

TABLE 2. Quaternization of Chloromethylated Polysulfone

Run	T, °C	a, mmol/mL	b, meq/mL	a/b	$k_0 \times 10^3$ , L·mol <sup>-1</sup> ·s <sup>-1</sup>	$k_2 \times 10^3$ , L·mol <sup>-1</sup> ·s <sup>-1</sup>	$k_0/k_2$
Treatment of 3 with Triethylamine in DMSO							
10	60.5	0.0530	0.0252	2.11	1.22	1.03	1.18
11	50.5	0.0530	0.0248	2.14	0.709	0.585	1.21
12	41	0.0510	0.0250	2.04	0.393	0.311	1.26
13	31.2	0.0505	0.0238	2.12	0.196	0.169	1.16
		$E_a = 12.4$ kcal/mol		log A = 5.26			
14	51	0.249	0.0251	9.92	0.464	0.309	1.50
15	41	0.251	0.0249	10.1	0.263	0.173	1.52
In the Presence of 1% NH <sub>4</sub> NO <sub>3</sub>							
16	51	0.0510	0.0251	2.03	0.815	0.653	1.25
In DMSO/Dioxane							
17	60	0.0535	0.025	2.15	0.336		
Treatment of 4 with Triethylamine in DMSO							
18	60	0.0545	0.0250	2.18	1.23	1.13	1.09
19	50	0.0505	0.0250	2.02	0.703	0.565	1.24

(continued)

TABLE 2 (continued)

Run	T, °C	a, mmol/mL	b, meq/mL	a/b	$k_0 \times 10^3$ , L·mol <sup>-1</sup> ·x <sup>-1</sup>	$k_2 \times 10^3$ , L·mol <sup>-1</sup> ·s <sup>-1</sup>	$k_0/k_2$
Treatment of <u>4</u> with Triethylamine in DMSO (continued)							
20	41	0.0530	0.0250	2.12	0.375	0.341	1.10
21	31	0.0505	0.0243	2.08	0.195	0.173	1.13
		E <sub>a</sub> = 12.4 kcal/mol		log A = 5.37			
Treatment of <u>3</u> with Quinuclidine in DMSO/Dioxane							
22	31.5	0.0498	0.0247	2.02	8.70	58.9	1.48
23	26.2	0.0510	0.0255	2.00	6.60	45.5	1.45
24	20	0.0484	0.0249	1.94	4.91	32.9	1.49
		E <sub>a</sub> = 8.8 kcal/mol		log A = 5.2			
Treatment of <u>3</u> with Tri-N-butylamine in DMSO/Dioxane							
25	66	0.052	0.025	2.07	0.280		
26	61	0.052	0.025	2.08	0.210		
27	55	0.051	0.025	2.04	0.123		
		E <sub>a</sub> = 16.4 kcal/mol		log A = 7.05			

## IMPACT OF STERIC HINDRANCE

Most observations of rate retardation in polymer modifications have been attributed to steric hindrance. In order to estimate the steric influence of the relatively bulky triethylbenzylammonium substituent on an unreacted site during quaternization, bicyclic quaternary ammonium groups were introduced. It is well known that the nucleophilicity of quinuclidine in displacement reactions is greater than that of triethylamine, since bicyclic amines are less sterically hindered, and a comparable reduction in the steric bulk of the quaternary salt is expected. Preliminary experiments on the quaternization of chloromethylated polysulfone with quinuclidine in DMSO showed that the reaction velocity was too rapid to investigate using our experimental techniques, i.e., 85% conversion was obtained with 3 min. Therefore, we were forced to add a less polar solvent to DMSO in order to reduce the reaction rate. It was found that a 50:50 (v/v) mixture of dioxane and DMSO dissolved both chloromethylated and quaternized polysulfone so the rate could be measured in a homogeneous system. The introduction of a nonpolar solvent reduced the initial rate of triethylamine substitution fourfold (Table 2, Run 17).

The initial velocity of quinuclidine substitution is significantly faster than that of triethylamine at the same temperature (Table 2, Runs 21-23), even though the former was investigated in a mixed solvent. Similar results were found in the quaternization of the model compound. If a steric effect were considered to be the sole factor producing the decrease in  $k_2$  with respect to  $k_0$ , one would expect that: 1)  $k_0/k_2$  for quinuclidine substitution should be smaller than  $k_0/k_2$  for TEA substitution, and/or 2) the initial linearity in the second-order plot would extend beyond 52% conversion where deviation occurs in the triethylamine system. Experimental results refute these expectations. Rate retardation is enhanced in quinuclidine reactions; furthermore, the break point is almost the same for both cases.

We anticipated a more pronounced steric effect to appear in substitutions with tri-n-butylamine. Since this amine is not soluble in DMSO, we were forced to use the DMSO/dioxane mixture. The corresponding initial rate for tributylamine was slightly less (Runs 25-27) than the TEA rate, and no break point was detected. The rate reduction can be attributed to the reduced nucleophilicity of tributylamine and the nonpolar solvent character of long-chain aliphatic amines. The absence of a break point indicates that no significant neighboring group steric effect is contributing to the retardation. These observations led us to believe that a steric effect is not the sole factor responsible for the deceleration.

## IMPACT OF ADDED ELECTROLYTE

In order to investigate whether the conformational change of polymer during reaction influenced the kinetics of quaternization, Boucher and co-workers [13] measured the reduced viscosity during the quaternization of poly(4-vinylpyridine); these measurements were conducted in the presence or absence of an added electrolyte, N-ethyl pyridinium bromide. The reduced viscosity was found to increase to a maximum value at 15% conversion, and then gradually decrease. Upon addition of electrolyte, the reduced viscosity remained constant throughout the reaction. They found no significant effect of added salt on kinetic measurements except in runs which exhibited a cloud point as the reaction proceeded. The retardation in rate produced by added salt was proposed to be due to a global effect, i.e., a decrease in the overall dimension of the macromolecules as the cloud point was approached.

The influence of added salts on the polysulfone quaternization kinetics was determined by adding 1% ammonium nitrate (Run 16 in Table 2). Salt concentrations up to 1% could be employed before the chloromethylated polysulfone began to salt-out, and no interference in the titration process was detected. There was no appreciable alteration in the rate profile but the initial rate increased by 15%; this rate increase is consistent with the anticipated accelerative salt effect for reactions involving polar transition states. The reduced viscosities measured as the reaction progressed are shown in Fig. 3. A sharp increase in the viscosity was observed in the initial stage of reaction if no electrolyte was added. Upon addition of 1%  $\text{NH}_4\text{NO}_3$ , no significant change in the reduced viscosity was observed. These results imply that quaternized polysulfone tends to expand to maximum extension if no salt is present, but maintains an equilibrium dimension when electrolytes are present to shield the developing charges along the chain. However, no change is observed in the rate profile in the presence of added salts, so the chain expansion cannot be responsible for the rate retardation at high degrees of conversion.

## IMPACT OF CHAIN FLEXIBILITY

Chloromethylated polysulfone indeed exhibits different kinetic behavior in the quaternization with TEA than its corresponding model compound. From experimental results it is clear that the rate retardation is not due to steric hindrance, the degree of chloromethylation on the polymer chain, or a salt effect. Stereoisomeric effects are not a potential factor, since chloromethylated polysulfone consists of only one detectable isomer. In spite of these results, we knew that the polymer backbone must play an important role in this reaction. Under the same experimental conditions used to quaternize chloromethylated polysulfone, poly(vinylbenzyl chloride) exhibited normal second-order

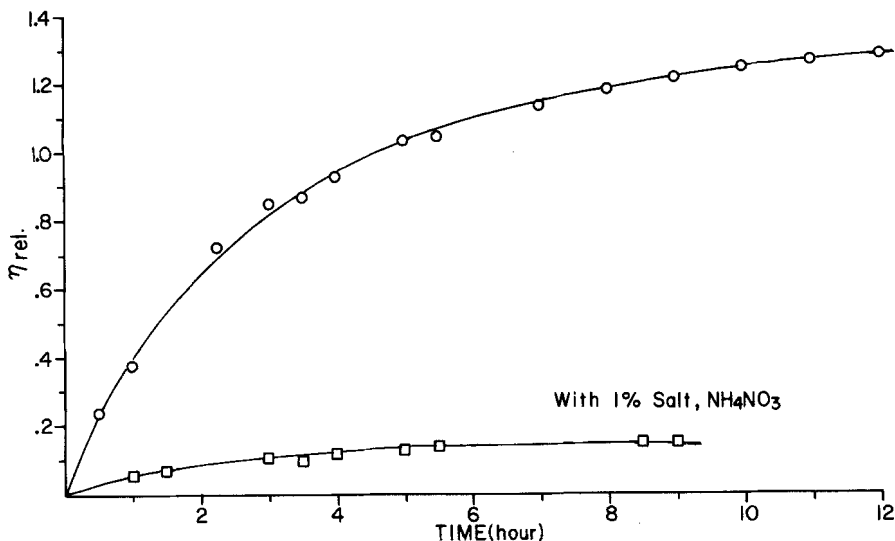


FIG. 3. Relative viscosity of 3 during quaternization with triethylamine in DMSO at 50 C. (○)  $[-\text{CH}_2\text{Cl}]$ , 0.024 meq/mL; [TEA], 0.0505 mmol/mL. (□)  $[\text{CH}_2\text{Cl}]$ , 0.024 meq/mL; [TEA], 0.0505 mmol/mL, 1 wt%  $\text{NH}_4\text{NO}_3$ .

kinetics with an  $E_a$  of 10.4 kcal/mol. Noda and Kagawa also observed the same phenomenon in the quaternization of chloromethylated polystyrene with TEA in DMF ( $E_a = 10.5$  kcal/mol) [11]. The major difference between these two systems is the polymer backbone, polysulfone being composed of a sequence of stiff aryl units. In order to investigate this factor in more detail, a condensation polymer with a flexible connecting segment, chloromethylated acetylated phenoxy resin, **5**, was synthesized.

Phenoxy resin was prepared from bisphenol-A and epichlorohydrin, and the secondary hydroxyl groups produced by the condensation were protected by acetylation. After chloromethylation the functional groups are located on the biphenol-A unit ortho to the ether linkage. Functional groups on polysulfone are located in the same relative position, so the activity of  $-\text{CH}_2\text{Cl}$  on either polymer should be identical. In fact chloromethylated phenoxy resin is more active than **3** (see Fig. 4). No appreciable change in the rate profile was observed, but the break point shifted to a higher extent of conversion. The functional groups are more accessible and the charged groups can be stabilized by formation of polar domains.

Introduction of a flexible glyceryl ether repeat unit definitely reduces

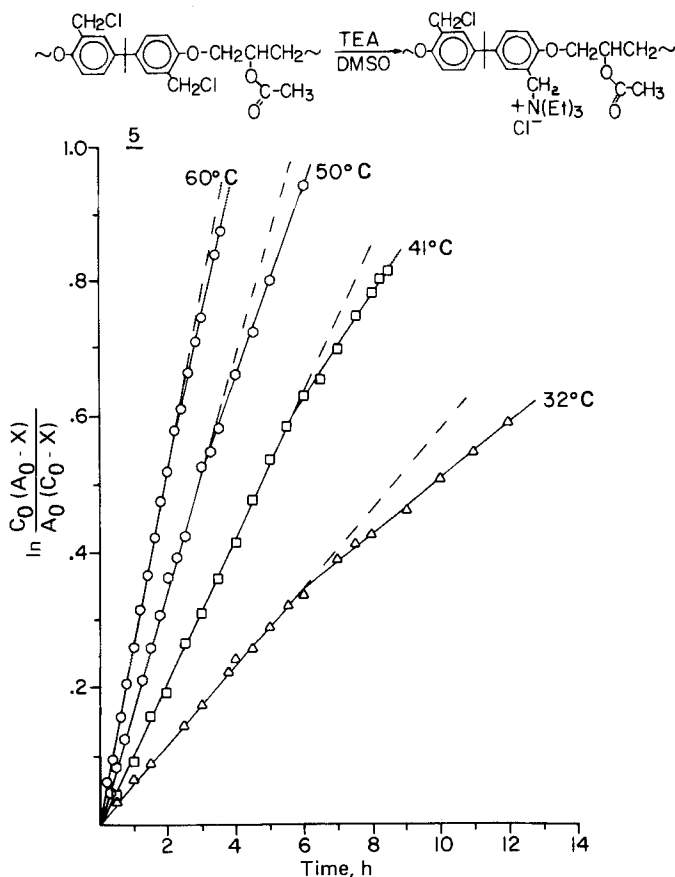


FIG. 4. Quaternization of 5 with triethylamine in DMSO. ( $\circ$ )  $[-\text{CH}_2\text{Cl}]$ , 0.026 meq/mL;  $[\text{TEA}]$ , 0.051 mmol/mL. ( $\diamond$ )  $[-\text{CH}_2\text{Cl}]$ , 0.025 meq/mL;  $[\text{TEA}]$ , 0.052 mmol/mL. ( $\square$ )  $[-\text{CH}_2\text{Cl}]$ , 0.026 meq/mL;  $[\text{TEA}]$ , 0.052 mmol/mL. ( $\triangle$ )  $[-\text{CH}_2\text{Cl}]$ , 0.025 meq/mL;  $[\text{TEA}]$ , 0.051 mmol/mL.

the stiffness of the polymer backbone; for example, the glass transition for bulk phenoxy resin is  $100^\circ\text{C}$  and the  $T_g$  of the chloromethylated acetylated derivative drops to  $60^\circ\text{C}$ . In contrast, chloromethylated polysulfone exhibits a glass transition of  $175^\circ\text{C}$ ; this rigidity must persist in solution and limit free rotation of the polymer chain. The rigid aromatic groups extend the chain and make it difficult for chain folding to create small domains [14].

During quaternization of chloromethylated polymers, the positive charge density gradually increases on the polymer chain. The polyelectrolyte fails to dissociate completely; an equilibrium is established between the macroion and variously bound counterions [15]. The counterions can be classified into three categories: counterions freely moving outside the region occupied by macroions, those bound but mobile within small domains in the macroion, and those bound to individually charged groups on the macroion. The relative concentration of freely moving counterions is very small and can be suppressed completely by adding salts. Thus, the most significant factor controlling introduction of additional charge will be the distribution between bound but mobile and individually bound counterions. In polar solvents, flexible polymers fold into configurations which contain polar domains with high dielectric constants, and most of the ionic functional groups reside within these domains. The number of localized counterions is estimated to be small in strongly dissociative polyelectrolytes.

If the flexibility of the polymer chain is reduced, the tendency to fold into domains must decrease. Each charge must be localized within the polymer backbone, which is a low dielectric region. Solvation of individual counterions will become the primary mode of product stabilization. If the counterions are tightly bound to individual groups, the solvent molecules must be highly ordered to effect solvation. Further, the extent of solvation will have a pronounced impact upon the stability of the transition state, and the reaction rate will be very sensitive to solvent variations. We have noted that DMSO is very difficult to remove quantitatively from quaternized polymers and that the polyquats are extremely hygroscopic. These observations indicate that solvent molecules are very strongly bound to the ionic sites.

Our results to date suggest that the flexibility of the polymer backbone plays the most important role in polymer reactivity, particularly if there is a significant change in the polarity of the polymeric derivative. Rigid polymer chains cannot contribute significantly to solvation. Retardation of substitution rates occurs because the resultant product must be formed in a nonpolar environment and stabilization through solvation is restricted. Thus, accessibility of active sites is not the dominant factor in determining reactivity.

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