J. Am. Chem. Soc. 1983, 105, 1567–1571

in terms of largely inhomogeneous doping, without invoking more elaborate doping–electronic structure relationships.

It is evident that the cofacial assembly strategy offers new means, via stringent structural control, to probe the nature of those factors which stabilize the molecular metallic state. Building upon the methodology and results outlined in the present study, experiments directed at elucidating dopant electronic vs. structural effects, the influence of stack length, the effect of macrocycle and macrocycle substituents, as well as further manipulation of interplanar spatial relationships are logical extensions of the work. In regard to extended molecular arrays, it should also be evident that this strategy offers the possibility of assembling an almost limitless variety of electrically conductive macromolecules. Further efforts at characterizing and processing the most interesting of these materials are in progress.[62]

Acknowledgment. This research was generously supported by the Office of Naval research (to T.J.M.) and by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR79-23573). We thank Professor M. T. Ratajack for helpful discussions concerning the analysis of reflectivity data, Professor J. B. Cohen and Dr. P. Georgopoulos for access to the X-ray diffraction equipment as well as helpful advice, and D. Keszler for helpful advice on the use of LAZY PULVERIX.

Registry No. Ni(Pc)I, 84624-83-9; $[Si(Pc)O]_n$, 39114-20-0; $[Ge(Pc)O]_n$, 55948-70-4; $[Sn(Pc)O]_n$, 57156-42-0.

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[62] (a) Inabe, T.; Lyding, J. W.; Moguel, M. K.; Marks, T. J. *J. Phys.*, in press. (b) Dirk, C. W.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Polymn. Sci., Polym. Chem. Ed.*, in press.

Kinetic Features of an Intraresin Reaction[1]

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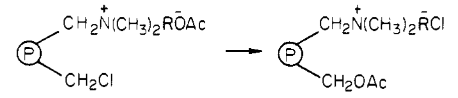
Abstract: The kinetic features of the intraresin displacement by pendant ammonium acetate groups on chloromethylated polystyrene have been investigated as a function of temperature, swelling solvent, and cross-link density. In all cases, intraresin displacement proceeds with a rapid initial rate followed by a very slow second stage; the latter represents that fraction of reactants which become "kinetically isolated". The free energy of activation for the first stage, under the various swelling conditions used, lies in the range 24.4–26.8 kcal mol^{-1}, which is similar to that found for analogous homogeneous reactions. The absolute rates measured for the homogeneous and the initial intraresin displacement in dioxane were similar; with *n*-hexane and toluene as solvents, polymeric rates were considerably slower than those of their homogeneous counterparts. Intraresin displacement was rapid even when a poor swelling solvent (*n*-hexane) was used. As the rate of intrapolymeric reaction decreased (through a decrease in temperature, increase in cross-link density, or change in solvent), the percent of "kinetically isolated" sites increased.

The study of "site–site interactions" in cross-linked polymers has attracted considerable interest over the past 12 years.[2,3] Surprisingly, however, very little attention has focused on the rates of such processes.[4] In this paper we report the first direct kinetic study of an intraresin reaction, i.e., the intrapolymeric displacement by pendant ammonium acetate on chloromethylated polystyrene (eq 1). Our reasons for choosing this specific system for investigation were 3-fold. First, a simple nucleophilic displacement such as this should have a significant activation energy. While "kinetic isolation" within cross-linked polymers has been clearly demonstrated for the dimerization of *o*-benzyne[4] its existence has not been rigorously proven for reactions which possess appreciable energy barriers. Second, reaction 1 proceeds without a change in cross-link density and charge concentration. Since each of these factors can influence "site-isolation" effectiveness, both should be constant in any resin system designed for kinetic study.[5,6]



(1)

Table I. Influence of Onium Salt Structure, Temperature, and Solvent on the Rate of Homogeneous Displacement

$$PhCH_2N(CH_3)_2R^+\,OAc^- + PhCH_2Cl \rightarrow PhCH_2N(CH_3)_2R^+Cl^- + PhCH_2OAc$$

R	solvent	temp, °C	$10^5 k_2$, M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	$\Delta G^\ddagger$ at 333.15 K, kcal mol^{-1}
n-C_4H_9	dioxane	60	499	14.1	−27.3	23.1
		50	277			
		40	121			
n-$C_{16}H_{33}$	dioxane	60	522	16.5	−19.8	23.1
		50	400			
		40	100			
n-$C_{16}H_{33}$	toluene	60	200	18.7	−15.0	23.7
		50	100			
		40	32			
n-$C_{16}H_{33}$	n-hexane	60	350	12.0	−33.9	23.3
		50	170			
		40	100			

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[1] Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG 77-S-02-4446) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

[2] A preliminary account of this work has been published: Regen, S. L.; Bolikal, D. *J. Am. Chem. Soc.* **1981**, *103*, 5248.

[3] For recent reviews of "site–site interactions", see: Kraus, M. A.; Patchornik, A. *Macromol. Rev.* **1980**, *15*, 55. Kraus, M. A.; Patchornik, A. *Isr. J. Chem.* **1978**, *17*, 298. Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *135*. Hodge, P.; Sherrington, D. C. "Polymer-Supported Reactions in Organic Synthesis"; Wiley: New York, 1980. Mathur, N. K., Narang, C. K.; Williams, R. E. "Polymers as Aids in Organic Chemistry"; Academic Press: New York, 1980.

[4] Mazur, S.; Jayalekshmy, P. *J. Am. Chem. Soc.* **1979**, *101*, 677. Rebek, J., Jr.; Trend, J. E. *Ibid.* **1979**, *101*, 737.

[5] Chang, Y. H.; Ford, W. T. *J. Org. Chem.* **1981**, *46*, 5364.

[6] Regen, S. L.; Lee, D. P. *J. Am. Chem. Soc.* **1974**, *96*, 294.

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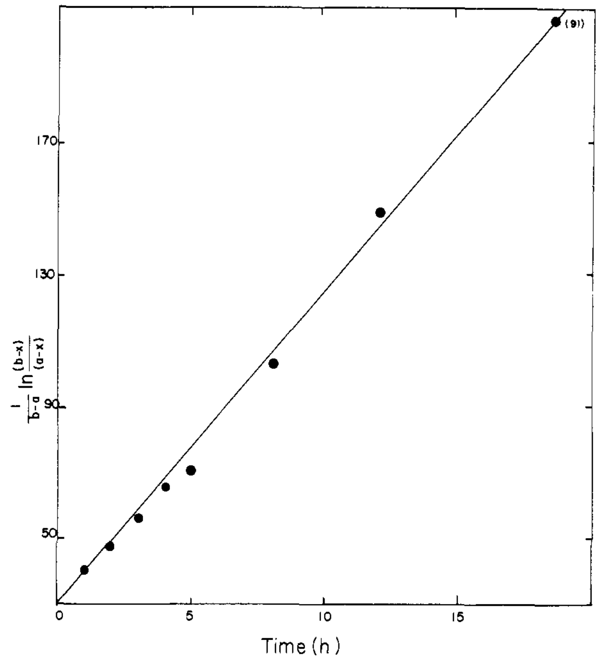
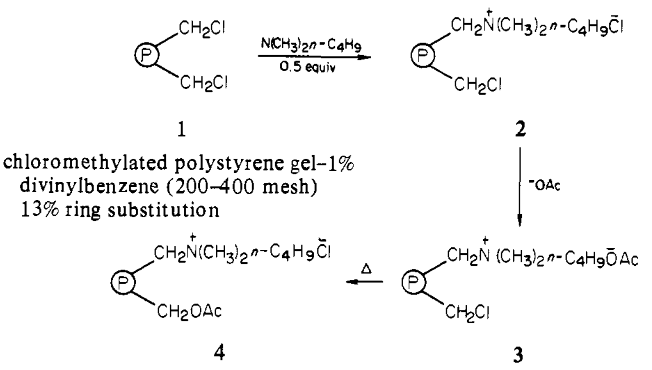


Figure 1. Second-order plot of the reaction of 0.037 M benzylchloride with 0.031 M *n*-butyldimethylbenzylammonium acetate in dioxane at 40 °C.

Scheme I



Third, polymers of this type have a close relationship to onium-based triphase catalysts.[7] Kinetic examination of reaction 1 under triphase conditions could, therefore, provide insight into the dynamic properties of such catalysts.

Results

Homogeneous Nucleophilic Displacement. In order to have a reference from which to judge the influence that the polymer lattice has on reaction 1, the kinetics of analogous reactions occurring in homogeneous solution were first investigated. Reaction of benzyl chloride with *n*-butyldimethylbenzylammonium acetate in dioxane or with cetyldimethylbenzylammonium acetate in dioxane, toluene, and *n*-hexane obeyed clean second-order kinetics (eq 2). A typical kinetic plot is presented in Figure 1. Specific

$$\mathrm{PhCH_2\overset{+}{N}(CH_3)_2R\overset{-}{O}Ac + PhCH_2Cl \rightarrow PhCH_2\overset{+}{N}(CH_3)_2R\overset{-}{Cl} + PhCH_2OAc} \quad (2)$$

$$R = n\text{-}C_4H_9 \text{ or } n\text{-}C_{16}H_{33}$$

second-order rate constants measured between 40 and 60 °C along with the corresponding activation parameters are reported in Table I. Both the observed rates and the free energy of activation (ca. 23 kcal mol^{-1}) showed little dependence on the length of the alkyl chain of the ammonium salt and on the solvent employed.

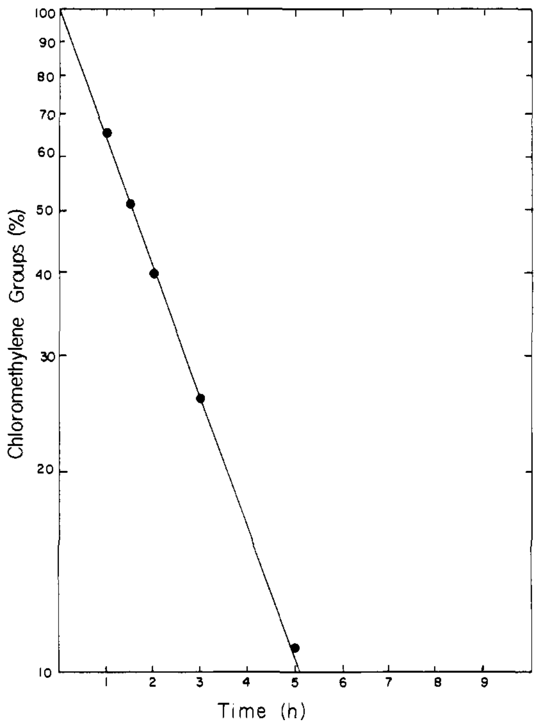


Figure 2. Pseudo-first-order plot of the quaternization of 1 with excess *N*,*N*-dimethyl-*n*-butylamine in toluene at 40 °C (see Experimental Section).

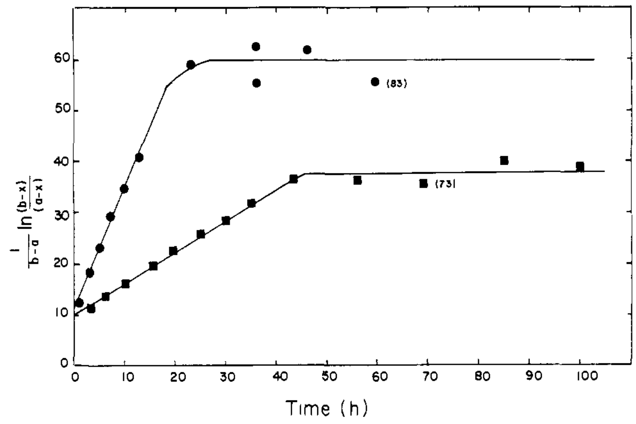


Figure 3. Second-order plot of intraresin displacement of 1 in dioxane at 40 °C (■) and 60 °C (●); b = 0.16 M; a = 0.13 M. Numbers in parentheses indicate the percent conversation based on a.

Resin-Bound Reactants. Scheme I outlines the synthetic approach used for the preparation of resin 3. All chloromethylated polystyrenes used in this work (including 1, which was a commercial sample) were prepared by suspension copolymerization of styrene, vinylbenzyl chloride, and divinylbenzene.[8] Since the reactivity ratios for styrene and vinylbenzyl chloride are very similar, an approximately random distribution of chloromethylene groups must be present throughout the polymer beads.[9] In addition, quaternization of 1 using a 10-fold excess of *N*,*N*-dimethyl-*n*-butylamine in toluene at 40 °C obeyed clean pseudo-first-order kinetics over 90% conversion (Figure 2). This fact further indicates that nearly all of the pendant groups are uniformly reactive. Since a minimum volume of solvent was used in reacting 0.5 equiv of *N*,*N*-dimethyl-*n*-butylamine with 1 (>95% of the toluene solution was *within* the polymer) and since the

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(7) Regen, S. L. *Ang. Chem., Int. Ed. Engl.* **1979**, *18*, 421.

(8) Regen, S. L.; Bolikal, D.; Barcelon, C. *J. Org. Chem.* **1981**, *46*, 2511.

(9) Copolymer reactivity ratio for vinylbenzyl chloride (m$_1$) and styrene (m$_2$) are r_1 = 1.08 and r_2 = 0.72 at 60 °C: Young, L. J. In "Polymer Handbook", 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; pp 11–344.

Table II. Intraresin Conversion of 3 to 4

solvent	swelling ratio[a]	temp, °C	10^5-k_2, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ at 333.15 K, kcal mol^{-1}	kinetic isolation, %
dioxane	2.7	60	67	13.6	−32.6	24.4	10
		40	17				25
toluene	2.9	80	27	21.4	−14.7	26.3	10
		70	13				25
		60	4				57
n-hexane	0.12	60	8.2	13.0	−38.5	25.4	30
		50	4.2				44
		40	2.2				47
toluene/ water	3.0[b]	80	19	25.2	−4.7	26.8	38
		70	5				65
		60	2				75

[a] Swelling (grams of solvent/grams of dry resin) determined at room temperature. [b] Imbibed solvent was 93% toluene.

chloromethylene groups are kinetically equivalent, the resulting quaternary ammonium sites in **2** should be close to being randomly distributed. Resin **2** was then converted into the acetate form **3**, using ion-exchange procedures described in the Experimental Section.

Kinetic Features of the Intraresin Displacement. Intraresin nucleophilic displacement of **3** was conveniently monitored by following the appearance of ionic chloride, using a one-vial, one-kinetic-point technique. Effective concentrations of reactants used in all kinetic plots are defined as the number of millimoles of resinous acetate or chloromethylene groups present in the reaction mixture at a given time divided by the total volume taken up by the solvent-swollen polymer (see Experimental Section).

Second-order plots for the conversion of dioxane-swollen **3** to **4** are shown in Figure 3. In sharp contrast to the analogous homogeneous reactions, the rate profiles were characterized by two distinct stages. At 40 °C a rapid initial rate was observed which was linear up to 75% conversion. Beyond that point, the intraresin reaction showed an abrupt decrease in rate. Swelling measurements made at 0 and 75% conversion indicated that the effective reaction volume remained unchanged. At 60 °C the first stage of the reaction was extended to 87% conversion and was approximately 4 times faster than at 40 °C. Specific rate constants and activation parameters characterizing this first stage were similar to those found for the corresponding homogeneous displacement and are reported in Table II.

In order to establish that the remaining chloromethylene and acetate groups in the second stage of the reaction were accessible and active for displacement, 0.20-g samples of **3** (75% conversion to **4**) were reacted separately with 5 mL of 0.05 M benzyl chloride and 5 mL of 0.05 M *n*-butyldimethylbenzylammonium acetate at 40 °C. In both cases the total yield of chloride ion, based on the polymeric reactant, increased to 90% after 2 h.[10] These results, taken together, clearly show that a significant fraction of the pendant groups in **3** become "kinetically isolated" at 40 °C.

In order to ensure that the initial intraresin displacement was not the result of soluble acetate (generated from trace ionic impurities) reacting with resinous chloromethylene groups, a "three-phase test" was performed.[11] Resin **1** was fully quaternized with *N*,*N*-dimethyl-*n*-butylamine and converted into its acetate form. Mixing this polymer with a portion of **1** in dioxane and subsequent heating at 40 °C for 24 h did not yield any detectable chloride ion.

Second-order plots for the conversion of **3** to **4** using toluene, *n*-hexane, and toluene–water as the swelling media are shown in Figures 4, 5, and 6, respectively. In all cases, two distinct stages were observed, and the linearity of the first stage was extended as the temperature increased. The transition between the first and second stage was, however, less abrupt at 80 °C. At 60 °C the relative rates of the initial intraresin reaction for toluene–water, toluene, *n*-hexane, and dioxane were 1.0, 2.0, 4.1, and 33.5, respectively. Corresponding free energies of activation were in the range of 24.4–26.8 kcal mol^{-1} (Table II).

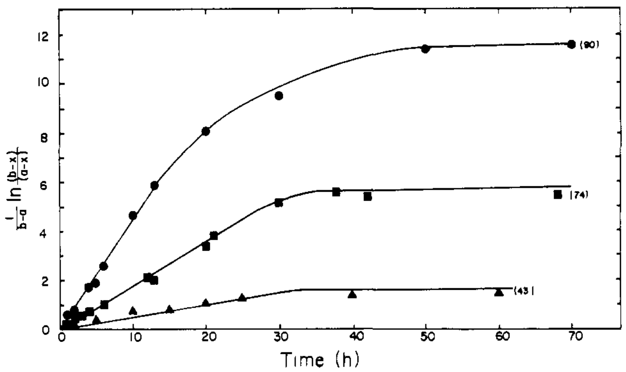

Figure 4. Second-order plot of intraresin displacement of **1** in toluene at 60 °C (▲), 70 °C (■), and 80 °C (●); b = 0.21 M; a = 0.18 M. Numbers in parentheses indicate the percent conversion based on a.

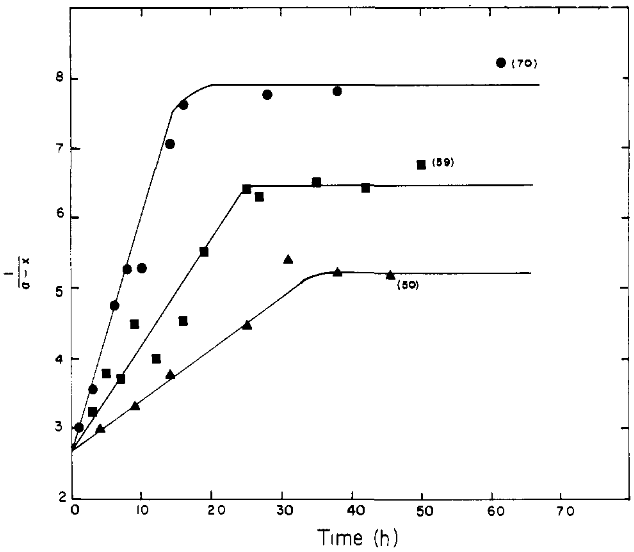

Figure 5. Second-order plot of intraresin displacement of **1** in *n*-hexane at 40 °C (▲), 50 °C (■), and 60 °C (●); a = b = 0.44 M. Numbers in parentheses indicate the percent conversion.

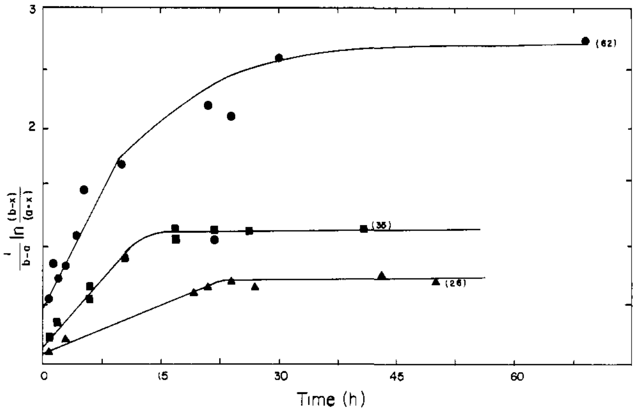

Figure 6. Second-order plot of intraresin displacement of **1** in toluene–water at 60 °C (▲), 70 °C (■); and 80 °C (●); b = 0.18 M; a = 0.13 M. Numbers in parentheses indicate the percent conversion based on a.

Influence of Cross-Link Density on the Intraresin Displacement. In order to measure the effect that cross-linking had on reaction **1**, analogous resins were prepared having 4% and 10% divinyl-

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[10] Under the reaction conditions used, absorption of benzyl chloride by **3** was negligible; *n*-butyldimethylbenzylammonium acetate was absorbed to a small extent (0.25 mmol/g of dry polymer).

[11] For a description of the "three-phase test", see: Rebek, J.; Gavina, F. *J. Am. Chem.* **1975**, *97*, 3453.

Table III. Influence of Cross-Link Density on Intraresin Displacement[a]

DVB[b] (%)	swelling ratio[c]	$10^5 k_2$, M^{-1} s^{-1}	kinetic isolation, %
1[d]	2.7	17	25
1	3.2	12	20
4	1.7	12	20
10	0.7	3	50

[a] Reaction in dioxane at 40 °C with 40-120 mesh beads, having, initially, an 11% ring substitution of chloromethylene groups. [b] Divinylbenzene (mol %). [c] Swelling (grams of dioxane/grams of resin) determined at room temperature. [d] Resin 3.

benzene incorporated into the matrix. In addition, a 1% cross-linked polymer was synthesized and compared to resin **3**. The swelling ratio measured for the latter two polymers differed somewhat, which probably reflects a difference in the *true* cross-link density and/or the small difference in the loading of pendant groups. Intraresin reaction at 40 °C in dioxane showed well-defined two stage kinetic plots in all cases. Rate constants determined for the initial stage of the 1 and 4% cross-linked polymers were similar (Table III); also, approximately 20% of the pendant groups were "kinetically isolated". With 10% cross-linking, however, the initial rate was significantly lower and the number of "isolated" groups increased to 50%.

Discussion

A tacit assumption which underlies this study is that resinous acetate reacts as a pendant group and not as a free ion. Previous studies have shown that similar quaternary ammonium salts exist almost exclusively as ion pairs in dioxane.[12] Based on correlations made between cation-anion interaction energies and S_N2 reactivity, convincing arguments have been made which suggest that such salts do indeed react in nucleophilic displacement processes as ion pairs.[13] The results presented herein substantially strengthen this view by showing that pendant acetate and chloromethylene groups in **3** become "kinetically isolated" with respect to each other, but react readily with soluble analogues. If **3** is considered as a model for closely related ammonium-based triphase catalysts,[7] these results further show that ion pairs are the reactive species even when such polymers are contacted with an organic solvent plus an aqueous phase. Comparison of the kinetic profile observed for **3** under biphase and triphase conditions indicates that the apparent resin flexibility is, however, somewhat reduced by the presence of water.

Initial intraresin displacement of dioxane-swollen **3** proceeds with a rate which is very similar to that of an analogous homogeneous process; with *n*-hexane and toluene as solvents, polymeric rates were considerably slower. The precise origin of this solvent effect is not clear at the present time. It may, however, be related to changes in the dynamic and/or conformational properties of the polymer backbone.[14] It is, nonetheless, significant to note that displacement can occur at a rate which is faster in a very poor swelling solvent such as *n*-hexane than in a good swelling solvent (toluene). This result is in agreement with our earlier findings that a small degree of swelling is sufficient to allow for extensive site-site interactions.[15] Finally, an interesting correlation is revealed from a plot of the observed second-order rate constants reported in Tables II and III vs. the percent of kinetic isolation (Figure 7). When the initial intraresin rate is decreased (by lowering the temperature, increasing the cross-link density, or changing the solvent), there is a corresponding increase in the percent of "kinetically isolated" sites.

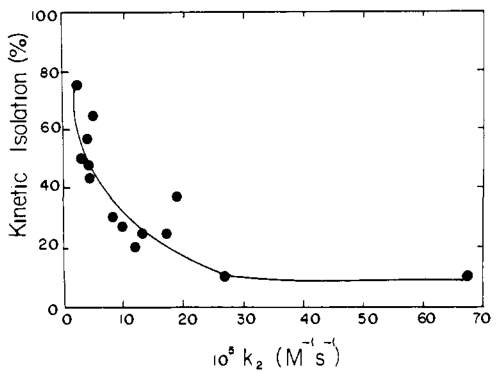

Figure 7. Plot of kinetic isolation (%) at 60 °C vs. $10^5 k_2$.

The results of this study clearly demonstrate that "kinetic isolation" exists even for pendant reactants of low intrinsic reactivity, bound to lightly cross-linked gels. This finding should provide further stimulus for the continued mechanistic and synthetic use of cross-linked polymer supports as isolating media in organic chemistry.

Conclusions

The kinetic features of the intrapolymeric displacement by pendant ammonium acetate groups on chloromethylated polystyrene have been investigated as a function of temperature, swelling solvent, and cross-link density. Principal conclusions which emerge from this study are the following: (1) Intraresin displacement proceeds with a rapid initial rate followed by a very slow second stage; the latter represents that fraction of reactants which become "kinetically isolated". (2) Pendant ammonium acetate reacts as ion pairs under two-phase (polymer/liquid organic) and three-phase (aqueous/polymer/liquid organic) conditions. (3) The free energy of activation for the first stage of the intraresin reaction (under various swelling conditions) lies in a range (24.4–26.8 kcal mol^{-1}) which is similar to that found for analogous homogeneous reactions. (4) Absolute rates measured for the homgoeneous and the initial intraresin displacement in dioxane at 60 °C were similar; with *n*-hexane and toluene as solvents, polymeric rates were considerably slower than their homogeneous counterparts. (5) Intraresin displacement was rapid even when a poor swelling solvent (*n*-hexane) was used. (6) As the rate of intrapolymeric reaction decreased (through a decrease in temperature, increse in cross-link density, or change in solvent), the percent of "kinetically isolated" sites increased.

Experimental Section

General Methods. Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. Dioxane, toluene, and *n*-hexane were distilled from sodium benzophenone ketyl under nitrogen. Deionized water was purified by distillation from $KMnO_4/Ba(OH)_2$. Cetyldimethylbenzylammonium chloride was purchased from ICN, K and K Laboratories, and used directly. Resin **1** was purchased from Bio-Rad Laboratories. Procedures used for the preparation of other chloromethylated resins have been described elsehwere.[8] Chloride ion analyses were determined by a modified Volhard titration.[16] The temperature of the oil bath used for kinetic experiments was controlled (±0.5 °C) with the aid of a THERM-O-WATCH electronic controller, Model L6-1000 (I^2R Co., Cheltenham, PA). Product mixtures from solution reactions were analyzed by GLC on a Hewlett-Packard Model 5830-A flame ionization instrument, equipped with a 2 ft × 0.125 in. UCW-982 on Chromosorb W column.

Conversion of AGl-X2 into Acetate Form. An anion-exchange resin (120 g of Bio-Rad AGl-X2, 100-200 mesh, chloride form, 3.5 mequiv/g of dry polymer) was packed into a glass tube (4.5 cm i.d.) and washed with 1.0 M NaOH until chloride ion could not be detected in the eluent. The polymer was then washed with 1 L of deionized water followed by 1.0 M acetic acid solution, until the pH of the eluent was 2.5. Finally, the resin was rinsed with deionized water until the pH of the eluent was 4.8 and then washed with 100 mL of methanol.

Cetyldimethylbenzylammonium Acetate. Cetyldimethylbenzylammonium chloride (7.12 g) was dissolved in 30 mL of methanol and was passed through a column (2.0 cm i.d.) packed with 150 g of meth-

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[12] Ugelstad, J.; Ellingsen, T.; Berge, A. *Acta Chem. Scand.* **1966**, *20*, 1593.

[13] Starks, C. M.; Liotta, C. L. "Phase Transfer Catalysis"; Academic Press: New York, 1978; pp 31–37.

[14] Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 708.

[15] Regen, S. L.; Lee, D. P. *Macromolecules* **1977**, *10*, 1418.

[16] Stewart, J. M.; Young, J. D. "Solid Phase Peptide Synthesis"; W. H. Freeman: San Francisco, CA, 1969; p 55.

anol-swollen AG1-X2 in the acetate form. The column was washed with 400 mL of methanol and the combined eluent evaporated to dryness. The resulting colorless waxy solid was then dissolved in a minimum volume of methanol and recrystallized by pouring into 150 mL of hexane, followed by cooling (0 °C). Cetyldimethylbenzylammonium acetate (7.2 g, 94%) obtained after drying [65 °C, 24 h (0.05 mm)] contained no detectable chloride ion (Volhard titration). Reaction of 0.108 g (0.257 mmol) of cetyldimethylbenzylammonium acetate with 10 equiv of benzyl chloride in 5 mL of dioxane at 60 °C for 24 h produced 0.244 mmol of benzyl acetate (*n*-tridecane used as a GLC internal standard), indicating that the purity of the ammonium salt was ≥95%.

***n*-Butyldimethylbenzylammonium Acetate.** A mixture of benzyl chloride (3.80 g, 30.0 mmol) plus *N*,*N*-dimethyl-*n*-butylamine (3.03 g, 30.0 mmol) was purged with nitrogen and heated for 5 h at 90 °C in a sealed 50-mL culture tube. The resulting ammonium salt was triturated with toluene (cooled to 5 °C) and dried [24 h, 100 °C (0.05 mm)], affording 6.01 g (88%) of pure product. Anal. Calcd for $C_{13}H_{22}NCl$: Cl, 4.40 mequiv/g. Found: 4.39 mequiv/g. *n*-Butyldimethylbenzylammonium chloride was converted into its corresponding acetate form using procedures similar to that described for the preparation of cetyldimethylbenzylammonium acetate. Analysis by Volhard titration indicated no detectable chloride ion.

Reaction of Soluble Quaternary Ammonium Acetate with Benzyl Chloride. Procedures similar to that used for the reaction of cetyldimethylbenzylammonium acetate with benzyl chloride were used in all of the homogeneous displacement reactions. A 20-mL culture tube was charged with a mixture of *n*-tridecane (0.023 g, 0.123 mmol), cetyldimethylbenzylammonium acetate (0.130 g, 0.295 mmol), and 11 mL of *n*-hexane and sealed with a Teflon-lined screw cap. After the mixture was warmed for 1 h at 40 °C, a clear solution was obtained. Benzyl chloride (0.039 g, 0.295 mmol) was then added, and the progress of the displacement was monitored by analyzing for benzyl acetate and unreacted benzyl chloride (GLC). Reactions were normally followed to 80–90% conversion. Stirred reactions yielded second-order rate constants which were identical with unstirred reactions.

Kinetics of Quaternization of 1. Into each of five 50-mL culture tubes was placed 0.2 g of **1** (dry) plus 2 mL of a 1.65 M solution of *N*,*N*-dimethyl-*n*-butylamine in toluene. The tubes were placed in an oil bath maintained at 40 °C and withdrawn successively at regular time intervals, and the contents were analyzed for chloride ion. Quaternization obeyed clean pseudo-first-order kinetics over 90% conversion.

Partial Quaternization of Chloromethylated Polystyrene. In a typical preparation, a 250-mL two-necked round-bottomed flask was charged with 50 mL of freshly distilled toluene plus 0.78 g (7.7 mmol) of *N*,*N*-dimethyl-*n*-butylamine and the resulting solution purged with nitrogen for 10 min. Chloromethylated polystyrene (10.0 g of **1**, 12.2 mmol of chlorine) was then added and the mixture allowed to equilibrate for 10 min at room temperature. The flask was then placed in an oil bath (65 °C) for 48 h and cooled to room temperature, and the resin was filtered and washed successively with 50 mL of toluene and 100 mL of methanol. After the resin dried [65 °C, 24 h (0.05 mm)], a 0.2-g sample of the resin was treated with a mixture of 30 mL of 50% acetic acid in water (v/v) and 5 mL of concentrated nitric acid and analyzed for chloride ion. The total chlorine content was determined by analyzing a second 0.2-g sample in a similar way, after the remaining chloromethylene groups were first quaternized with pyridine.[16] Found: 0.59 mmol of Cl^-/g; 1.22 mmol of total chlorine/g.

Conversion of Partially Quaternized Chloromethylated Polystyrene into the Acetate Form and Sample Preparation for a Kinetic Run. Acetate was exchanged for *ionic* chloride by stirring 3.0 g of resin with a mixture of 15 mL of toluene, 3 mL of glacial acetic acid, and 15 mL of saturated sodium acetate for 3 h at 22 °C. The resin was then (1) washed sequentially with 150 mL of distilled water, 150 mL of 50% dioxane–water (v/v), and 100 mL of dioxane, (2) divided into 0.3-g samples (dioxane-swollen polymer was weighed directly into 50-mL culture tubes), and (3) suspended in 5 mL of dioxane maintained at the desired temperature. The total time spent for the final washing and weighing of samples and the start of the kinetic run was ca. 20 min.

Kinetic Methods. Intraresin displacement was monitored by using a one-vial, one-kinetic-point technique, withdrawing appropriate samples, and analyzing for ionic chloride. For intraresin reactions performed in *n*-hexane, toluene, or toluene–water, the polymer was washed further (after washing with 100% dioxane) with 10 mL of *n*-hexane, toluene, and toluene, respectively. Intraresin displacement was carried out with 0.3-g samples (solvent swollen) suspended in 5 mL of *n*-hexane, 5 mL of toluene, or 5 mL of toluene plus 3 mL of water, respectively.

Swelling ratios (g of solvent/g of dry polymer) for **3** determined at 25 °C were as follows (solvent, swelling ratio): **3**, dioxane, 2.7; **3**, *n*-hexane, 0.12; **3**, toluene, 2.7; **3**, toluene + water, 3.0. The imbibed water content under three-phase conditions was determined as previously described.[17] The swelling ratio measured for **3** in dioxane after the intraresin displacement was allowed to proceed for 50 h at 40 °C was the same as that determined at the start of the reaction.

The initial effective concentration of pendant ammonium acetate and chloromethylene groups was estimated by using the following equations:

$$a = \frac{(a_0 - C_0)W_r}{\dfrac{W_r}{d_r} + \dfrac{W_s}{d_s}}$$

$$b = \frac{(b_0 - C_0)W_r}{\dfrac{W_r}{d_r} + \dfrac{W_s}{d_s}}$$

where a = initial effective concentration of pendant ammonium acetate groups (M), b = initial effective concentration of pendant chloromethylene groups (M), a_0 = mmol of OAc^-/g of dry resin, b_0 = mmol of CH_2Cl^-/g of dry resin, C_0 = mmol of Cl^-/g of dry resin produced from intraresin displacement at time zero, W_r = weight of dry polymer, W_s = weight of imbided solvent at room temperature, d_r = density of dry resin taken as 1.0 g/cm^3, and d_s = density of solvent.

In all experiments, C_0 accounted for less than 10% of the total polymer-bound chlorine. Depending upon the relative amounts of pendant chloromethylene and ammonium acetate groups initially present, second-order plots were made in one of two ways. When the difference between these groups was ≤0.02 mmol/g of dry resin, the average of these values was used in a plot of $1/(a - x)$ vs. time, where $x = (C - C_0)/[(W_r/d_r) + (W_s/d_s)]$ and C represents the millimoles of ionic chloride per gram of dry polymer at a given time. When the molar difference in pendant groups present was >0.02 mmol/g, a plot of $1/(b - a) \ln [(b - x)/(a - x)]$ vs. time was made. Second-order rate constants were calculated from the early stages of the reaction where good linearity was observed.

Three-Phase Test for Ionic Impurities. Chloromethylated polystyrene (**1**) which had been completely quaternized with *N*,*N*-dimethyl-*n*-butylamine was converted quantitatively into its acetate form by using procedures similar to that described above. The resulting dioxane-swollen polymer (1.0 g) was placed in a culture tube along with 0.3 g of **1** and 10 mL of dioxane. The tube was immersed in an oil bath at 40 °C for 24 h, and the contents were analyzed for ionic chloride; none was detected.

Evidence for Kinetic Isolation. Procedures similar to the following were used in all cases. Resin **2** (0.6 g) was changed into the acetate form (**3**), which was divided equally (while swollen) into three fractions. Each fraction was placed in a 50-mL culture tube and heated with 5 mL of dioxane for 24 h at 40 °C. Analysis of the contents of one of the tubes showed a 72% intraresin conversion. Into a second tube was added 0.031 g (0.276 mmol) of benzyl chloride, and the tube was then heated for 2 h at 40 °C. Chloride ion analysis revealed that 90% of the pendant acetate had undergone reaction. Similarly, introduction of 0.057 g (0.27 mmol) of benzyldimethyl-*n*-butylammonium acetate to the third tube followed by heating for 2 h at 40 °C resulted in a chloride ion analysis indicating that 90% of the total pendant chloromethylene groups reacted. Results of similar "kinetic isolation" experiments carried out for **3** were as follows (swollen polymer used per tube, g; solvent, mL; reaction temperature, °C; reaction time for intraresin displacement, h; cetyldimethylbenzylammonium acetate added, g; benzyl chloride added, g; reaction time with soluble reactant, h; intraresin conversion prior to addition of soluble reactant, %; total conversion based on limiting pendant group after addition of excess soluble reactant, %): (0.3 g; 5 mL of *n*-hexane; 40 °C; 40 h; 0.08 g; 0.0 g; 20 h; 53%; 81%), (0.03 g; 5 mL of *n*-hexane; 40 °C; 40 h; 0.0 g; 0.2 g; 20 h, 53%; 77%), (0.47 g; 3 mL of toluene, 80 °C; 68 h; 0.08 g; 0.0 g; 3 h; 82%; 92%), (0.47 g; 3 mL of toluene; 80 °C; 68 h; 0.0 g; 0.027 g; 3 h; 82%; 90%), (0.47 g; 2.5 mL of toluene + 0.5 mL of water; 80 °C; 48 h; 0.17 g; 0.0 g; 4 h; 61%; 77%), (0.47 g; 2.5 mL of toluene + 0.5 mL of water; 80 °C; 48 h; 0.0 g; 0.072 g; 4 h; 61%; 78%). Control experiments carried out in which 0.044 g of benzyl chloride or 0.54 g of **2** was heated for 4 h at 80 °C in a mixture of 2.5 mL of toluene plus 0.5 mL of water showed no detectable release of chloride ion into the aqueous phase.

Registry No. Styrene–vinylbenzyl chloride–divinylbenzene copolymer, 55844-94-5; *N*,*N*-dimethyl-*n*-butylamine, 927-62-8; benzyl chloride, 100-44-7; *n*-butyldimethylbenzylammonium acetate, 78607-82-6.

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