Kinetic Observations of the Quaternization of Poly-(ar-vinylbenzyl Chloride) with Trimethylamine

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Synopsis

The quaternization of poly(ar-vinylbenzyl chloride) with trimethylamine is shown to be a nucleophilic displacement reaction, the kinetics of which are complicated by several factors, notably differences in the reactivities of o- and p-chloromethyl groups (position isomerism), differences in the reactivities of groups as a function of the reacted or unreacted status of immediately adjacent groups (neighboring group effect), and differences in the reactivities of groups arising from the microtacticity of the polymer segment (configurational effects). Estimates of mean rate constants, activation energies, and preexponential factors are given for high purity poly-p-vinylbenzyl chloride and for the analogous *ortho* polymer.

INTRODUCTION

The preparation of poly[trimethyl(ar-vinylbenzyl)ammonium chloride] by reaction of trimethylamine with poly(ar-vinylbenzyl chloride) (PVBC) has been described previously.[1,2] The PVBC, prepared by emulsion polymerization,[2,3] may be linear or, by incorporation of 0.05–0.10% divinylbenzene, a lightly crosslinked microgel. The aqueous latex emulsion is very readily attacked by trimethylamine at room temperatures, yielding the clear, water-soluble polyquaternary in a matter of minutes at 10–20% concentrations.

This reaction is an extremely interesting one with regard to the polymer chemistry involved: it involves charge reversal on the latex particle surface, as well as the possibilities of neighboring-group effects, architectural factors, and configurational, conformational, and position isomerism. Since the reaction proceeds with unusual facility, and is readily tracked titrimetrically, an examination of its kinetic character may be not only of specific relevance to the preparation of polycationics by displacement reactions upon hydrophobic polymers, but also of some general interest in illuminating the various factors which are also encountered in other less accessible reactions.

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Completeness of Reaction

When PVBC is treated with excess trimethylamine at room temperature, the reaction gives the impression of going to completion, in that the system undergoes a visually dramatic change from an opaque, water-thin milk to a sparklingly clear, viscous syrup or gel. This transformation in appearance, however, occurs at about 60–70% conversion. When the reaction mixture is allowed to stand for 24 hrs., then dried on steam rollers, the elemental analysis of the raw product polymer is often surprisingly good.[1] However, carefully dialyzed polymer samples are found to be consistently low in chlorine (typically 86–91% of theoretical) and lower in nitrogen (typically 80–86% of theoretical). Some typical data are shown in Table I.

TABLE I
Analyses of Dialyzed
Poly[trimethyl(ar-vinylbenzyl)ammonium Chloride][a]

Sample	VBC +	Structure	Analyses				
			N, %	Cl, %	C, %	H, %	HOH, %
A	DDM, 0.3%	Linear	4.96	14.08	62.76	8.82	7.80
B	DDM, 0.1%	Linear	5.32	13.79	63.84	8.67	6.58
C	DDM, 0.05%	Linear	5.05	13.62	64.12	8.66	6.60
D	—	Linear	5.00	13.64	63.75	8.82	7.12
E	DVB, 0.05%	Microgel	4.86	13.64	63.33	8.89	6.67
F	DVB, 0.1%	Microgel	4.76	13.51	64.37	9.05	6.70
G	DVB, 0.2%	Microgel	5.04	13.34	63.55	8.65	7.65
H	DVB, 0.4%	Microgel	5.11	13.54	65.89	9.18	6.47

[a] VBC = ar-vinylbenzyl chloride; DDM = tert-dodecyl mercaptan; DVB = divinylbenzene.

The first five columns in Table I show the raw elemental analyses (uncorrected for water) and the Karl Fischer water determinations. As these samples have been exhaustively dialyzed and thoroughly vacuum-dried, it is reasonable to assume that all nitrogen present is in the form of vinylbenzyl quaternary groups. The molar excess of chlorine over nitrogen is taken as a measure of unreacted vinylbenzyl chloride groups. The balance (based on carbon determination) is assumed to be due to vinylbenzyl alcohol groups owing to hydrolysis in the aqueous alkaline reaction system. (This last assumption is approximative. It has been shown[2] that PVBC readily undergoes a small amount of alkaline hydrolysis. However, a slow partial replacement of Cl⁻ counterions during extended dialysis could account for an equivalent ternary mixture of quaternary chloride, quaternary hydroxide, and unreacted benzyl chloride.)

This analysis accounts for 98+% of the polymers. It indicates that quaternized units make up only some 80–85% of these homopolymers, with some 2–7% of the chloromethyl groups remaining unreacted, and some 10–13% having been (we believe) hydrolyzed. It is inferred that the better analyses on undialyzed samples include the hydrolysis by-product,

trimethylamine hydrochloride.   The variation in molecular architecture among the eight samples in Table I is not reflected in any systematic manner by the elemental analyses; over this range of architectural modifications there is no first-order effect of architecture upon extent of reaction.

Temperature Range

The temperature range of the reaction was explored qualitatively by treating PVBC with trimethylamine at several temperatures, from -15 to $100°C$.   Portions of diluted PVBC latex ($0.50M$ in benzyl chloride groups, in 1:1 water/ethylene glycol) were treated with equal volumes of 12.5% (about $2M$) trimethylamine (also in 1:1 water/glycol).   The opaque latex mixture was converted to a clear viscous fluid in less than 5 min. at $100°C$., in about 10 min. at $30°C$., in about 150 min. at $0°C$., and overnight (between 200 and 1050 min.) at $-15°C$.   All of these clear samples were readily dilutable in water, and represent reaction of at least about 65% of the chloromethyl groups.

EXPERIMENTAL PROCEDURE

Monomers

ar-Vinylbenzyl chloride (mixed isomers), prepared by the method of McMaster and Stowe,[4] was flash-redistilled and stored at $-15°C$. with 0.1% *tert*-butylcatechol, under which conditions the monomer may be kept for at least a year.   Several samples of carefully fractionated vinylbenzyl chloride of high isomer purity were kindly provided by Dr. D. C. Mac-Williams.   The highest purity *ortho* isomer contained less than 5% *para* isomer, no detectable *meta* isomer, and 1.9% ethylbenzaldehyde; the highest purity *para* isomer contained no detectable *ortho* isomer, less than 1% *meta* isomer, and less than 0.8% aldehyde (analyses by infrared). Immediately prior to polymerization monomer samples were washed with cold dilute caustic solution to remove inhibitor, then washed repeatedly with deionized water until neutral.

Polymerization

The emulsion polymerization of vinylbenzyl chloride monomers was carried out according to the procedure previously described.[1-3]   In all cases the polymerization was found to have gone to essentially complete conversion.

Quaternization

In a typical run, PVBC latex, prepared as above, was diluted to about 10% polymer solids and the polymer content of the emulsion redetermined accurately.   Fresh reagent trimethylamine (Matheson, Coleman and Bell white label, 25% in water) was diluted to about $0.8M$, and aliquots of the two reactants placed in a thermostatted waterbath, in 100-ml. stoppered

serum bottles. Three additional serum bottles, containing appropriate amounts of water, were also placed in the constant-temperature bath. The following transfers were then made. To an amine control bottle containing 60.0 ml. water was added 10.00 ml. of the trimethylamine solution. To a latex control bottle, also containing 60.0 ml. water, was added 10.00 ml. of the diluted PVBC latex. To the reaction bottle containing 50.0 ml. water was added 10.00 ml. of the diluted PVBC latex and 10.00 ml. of the trimethylamine solution. All bottles were immediately stoppered, shaken vigorously for 30 sec. to ensure complete mixing, and maintained at the bath temperature.

The quaternization reaction was tracked by periodic removals, by syringe, of 2–5 ml. portions of the reaction mixture, these being immediately transferred into small stoppered serum bottles each containing an accurately measured excess of standard dilute HCl (typically, 10.00 ml. of 0.1N HCl in 50 ml. deionized water). These bottles had also been weighed accurately, so that the exact quantity of reaction mixture transferred into them by the syringe could be determined gravimetrically. Addition of the PVBC–amine reaction mixture to the excess acid immediately arrested the quaternization.

In the course of a quaternization run, one to two dozen samples of the reaction mixture were thus transferred by syringe to receiving bottles. During this time, several samples each were withdrawn from the two control bottles and similarly transferred into receiving bottles.

At the end of a quaternization run all samples were titrated with 0.1000N aqueous NaOH, using a Precision-Dow automatic titrimeter. Very sharp endpoints (at about pH 6) were obtained.

Normality of the base titrant was determined for each run by triplicate blanks. Initial total amine strength was determined by the several titrations of the amine and control samples. (These also provided a running check on basicity loss due to volatilization, absorption, or CO_2 neutralization.) The extent of initial hydrolysis (and of running thermal hydrolysis) of the PVBC was determined by the titrations of the latex-control samples. (Both the control amine basicity and the extent of hydrolysis of the latex control were found to be invariant within experimental error during the quaternization runs.) With this reference information determined concurrently with each kinetic run, the actual quaternization was tracked by following the loss of free basicity of the reaction mixture with time.

RESULTS

Position Isomer Effects

A lightly crosslinked (0.050% divinylbenzene) PVBC latex was prepared from monomer consisting of about 60% *para* and 40% *ortho* isomer. The latex and a standard trimethylamine solution were thermostatted at 30°C. and combined with water of dilution at the same temperature, to yield a reaction mixture containing initially 0.0827 g.-equiv./l. of vinyl-

benzyl chloride units and $0.1054N$ with respect to amine.   The quaterniza-
tion curve is shown in Figure 1.   The most conspicuous feature of this
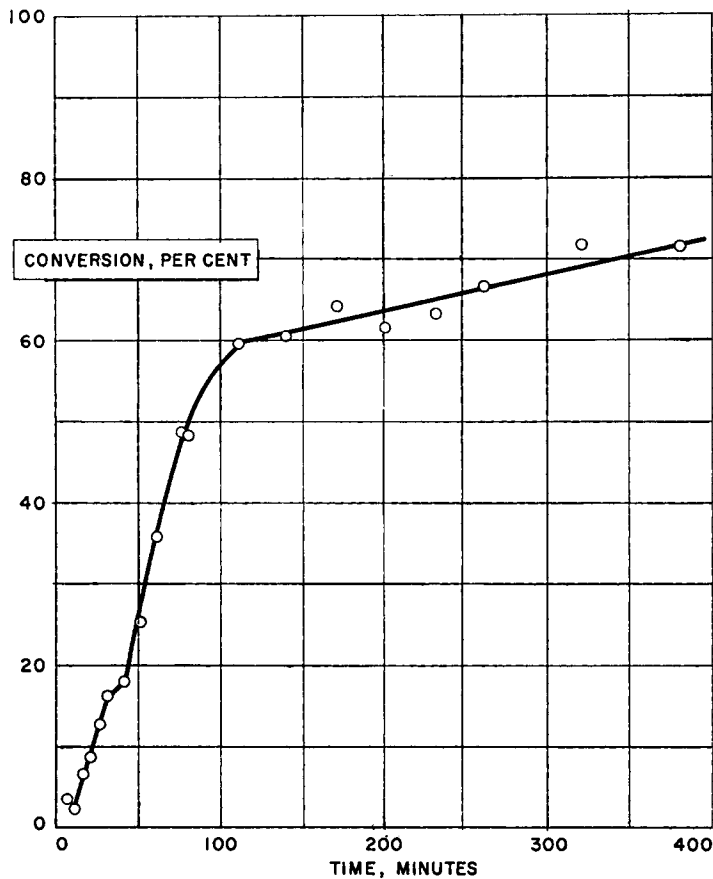quaternization is a marked deceleration at somewhat more than 50% con-
version.

Fig. 1. Quaternization of PVBC (0.0827 g.-equiv./l.) with trimethylamine (0.1054 N)
at 30.0°C.   Polymer contains about 40% o-vinylbenzyl chloride.

If we assume that this deceleration is due to differing reactivities of o-
and p-chloromethyl sites on the polymer chain, and if this is the major
"special factor" in this quaternization, then the kinetics may be expected
to follow a predictable pattern.   For simultaneous first-order reactions,

$$A/A_0 = \alpha e^{-k_1 t} + (1 - \alpha)e^{-k_2 t} \tag{1}$$

where A_0 is the original concentration of reactants, α is the fraction of
isomer 1 reacting at rate constant k_1, and $(1 - \alpha)$ is the fraction of isomer
2 reacting at rate constant k_2.   For the case that k_1 is substantially greater
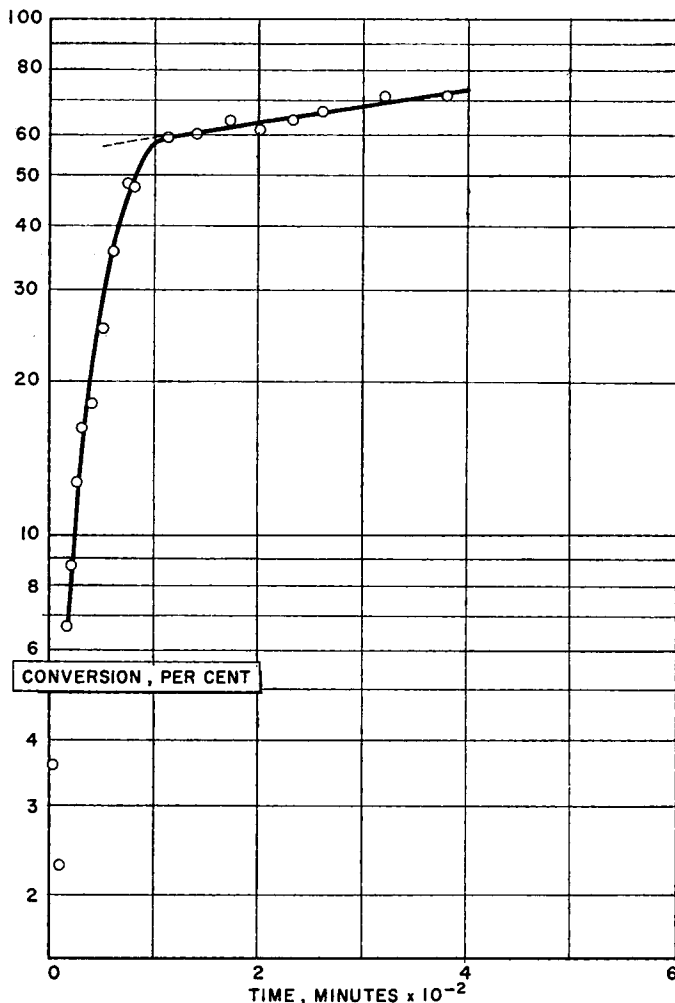than k_2, the "fast" fraction will be nearly completely reacted at some time

Fig. 2. Quaternization of PVBC with trimethylamine.   Data of Fig. 1 replotted to show
a distinct break in the conversion curve.

at which very little of the slow fraction will have reacted.   At this point,

$$A/A_0 \cong (1 - \alpha)e^{-k_2 t} \tag{1a}$$

and a distinct break in the reaction curve will obtain in a plot of log conversion against time.   The semilog plot of this same run is shown in Figure 2.   The rather well-defined break in the curve suggests 55–60% "fast" chloromethyl sites and 40–45% "slow" chloromethyl sites.

This estimate is in close agreement with the analytically determined isomer ratio of the vinylbenzyl chloride monomer.   To verify the differences in reactivities of o- and p-chloromethyl groups in PVBC, two similar PVBC latexes were prepared, from 99% para isomer and from 95% ortho isomer,
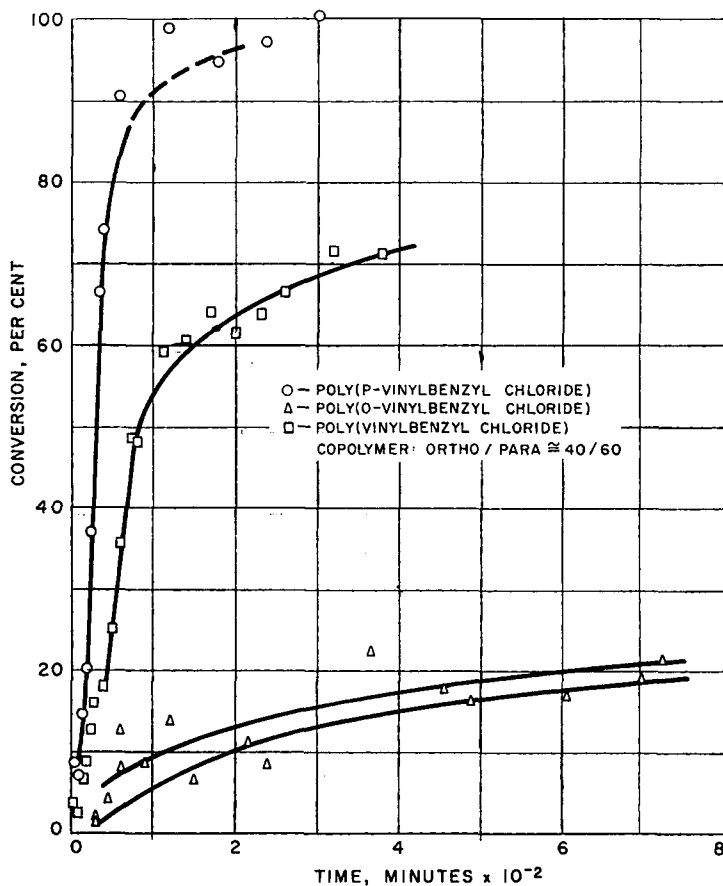
Fig. 3. Effect of position isomer composition upon quaternization of PVBC at 30.0°C. Concentrations for the *ortho-* and *para*-polymer reactions shown in Table III.

and quaternizations run under similar conditions. The three conversion curves are compared in Figure 3. It is evident that the *p*-PVBC reacts

TABLE II

Quaternizations of Polyvinylbenzyl Chloride at 30°C.

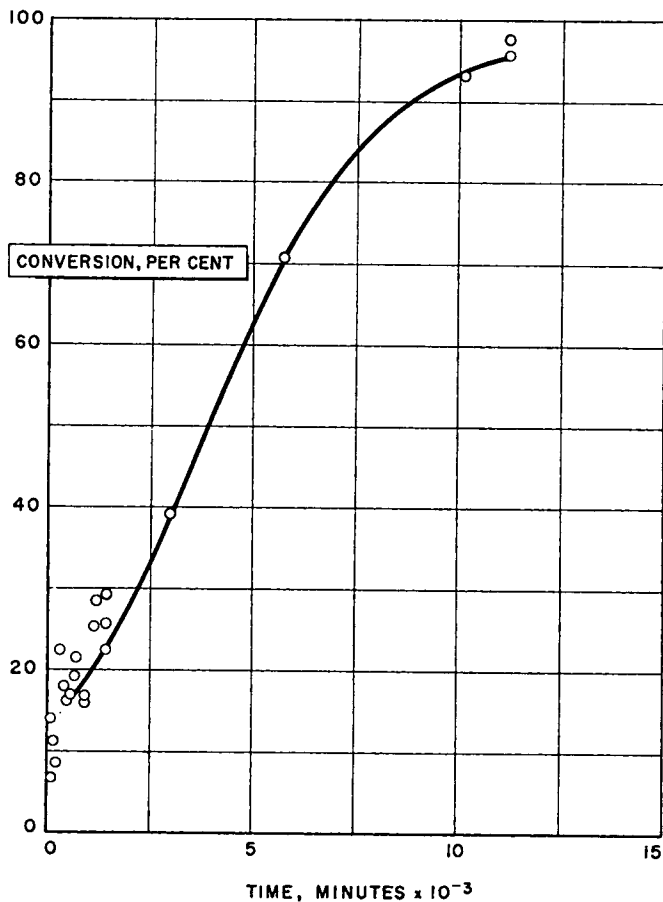| Run	$[Me_3N]_0$, M	$[VBC]_0$, M	*p*-Isomer (approx.), %	$t_{5\%}$, min.
1	0.292	0.200	92	1.3×10^1
2	0.201	0.143	92	1.5×10^1
3	0.302	0.200	67	2.1×10^1
4	0.300	0.200	67	2.5×10^1
5	0.109	0.093	99	2.9×10^1
6	0.105	0.083	60	8.4×10^1
7	0.310	0.200	20–25	5.1×10^2
8	0.107	0.078	5	3.7×10^3

Fig. 4. Quaternization of poly(o-vinylbenzyl chloride) with trimethylamine at 30.0°C. Reagent concentrations shown in Table III.

very readily, while the high-*ortho* analog, after an initial surge, reacts much more sluggishly.

o-PVBC does, however, undergo reaction to high conversions when given sufficient time. This is shown in Figure 4, wherein the time scale is compressed 20-fold as compared with Figure 3. The steric hindrance to reaction at o-chloromethyl sites is a sizeable kinetic factor but is not an absolute barrier.

The range of reaction rates for a group of eight PVBC samples at 30°C. is shown in Figure 5. The composition and concentration data for these samples is given in Table II.

Reaction Order

Since even secondary benzylic bromides undergo nucleophilic displacement with optical inversion,[5] it seems highly probable that the nucleophilic

displacement with trimethylamine upon a primary benzylic chloride will proceed by an S_n2 mechanism. Although determination of kinetic orders for high polymer reactions may be difficult, especially in the later stages,[6]
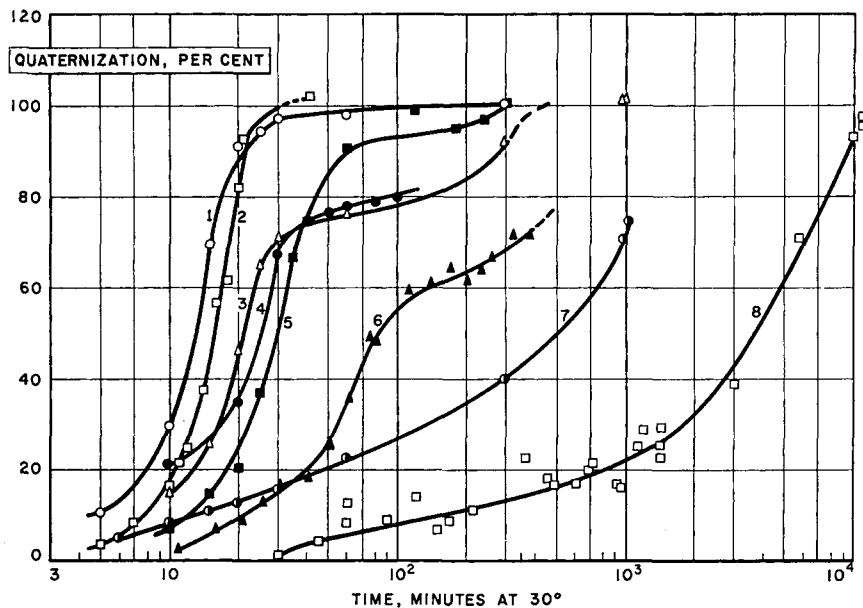

Fig. 5. Quaternization of PVBC (varying isomer compositions) with trimethylamine. Compositions and concentrations for various runs shown in Table II.

the data of Figure 5 may be examined at low conversions for kinetic consistency. For a second-order reaction starting with an initial *p*-vinylbenzyl chloride concentration C_0, the general kinetics should obey the relationship (for $A_0 \neq C_0$):

$$\int k\,dt = \frac{1}{A_0 - C_0} \ln \frac{C_0(A_0 - x)}{A_0(C_0 - x)} \tag{2}$$

As a test for the presumed second-order kinetics, the time required for conversion corresponding to 20% of the *para* isomer may be compared with $\int k\,dt$ in eq. (2) (for which $x = 0.2\ C_0$). The relationship between $k\,dt$ and t for the seven runs for which data are available is shown in Figure 6.

The *para*-rich runs are in excellent agreement, defining a straight line passing through the origin. With increasing *ortho* content, both precision of the data and agreement with the linear relationship tend to fall off. Nevertheless, the overall pattern indicates a bimolecular reaction the rate of which is dependent upon the concentrations of free amine and chloromethyl groups.
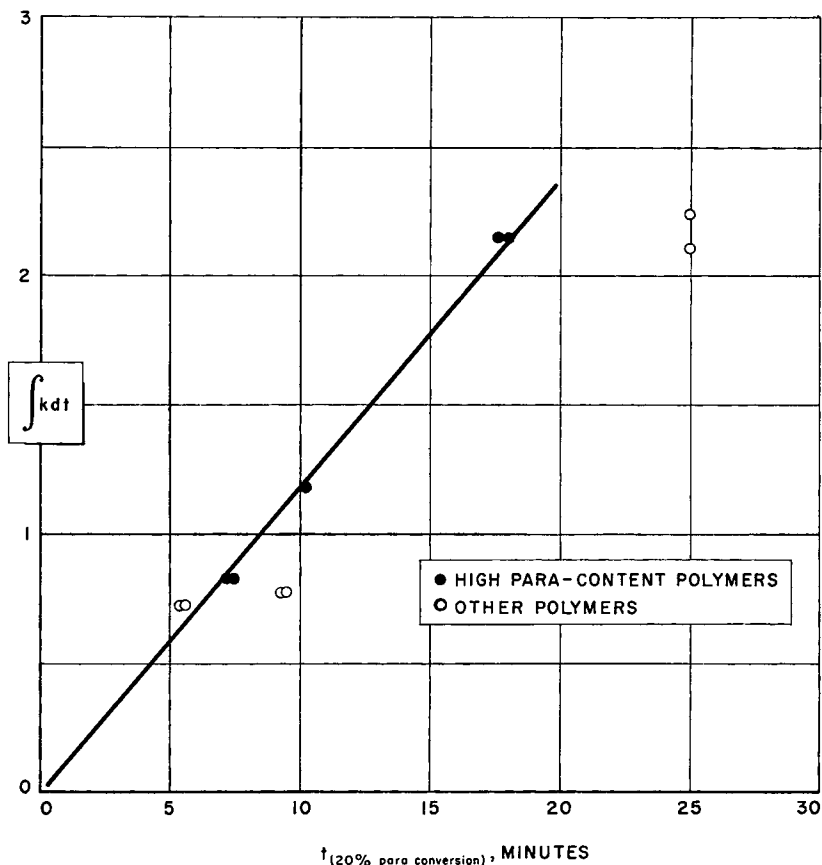
Fig. 6. Test for second-order reaction kinetics. Ordinate defined by eq. (2). Abscissa is time for quaternization of 20% of the *p*-vinylbenzyl chloride groups.

Temperature Dependencies

The effect of varying temperature upon the conversion curves of substantially pure poly(*p*-vinylbenzyl chloride) and poly(*o*-vinylbenzyl chloride) is shown in Figures 7 and 8. The rate constants are not directly accessible from the complex curves which these polymeric systems yield. Again, however, useful information may be obtained from the times required for 20% conversion ($t_{0-20\%}$). Since

$$t_{0-20\%} \cong 1/\bar{r} \qquad (3)$$

where $\bar{r}$ is the average rate of conversion during this interval, and since for the second-order reaction

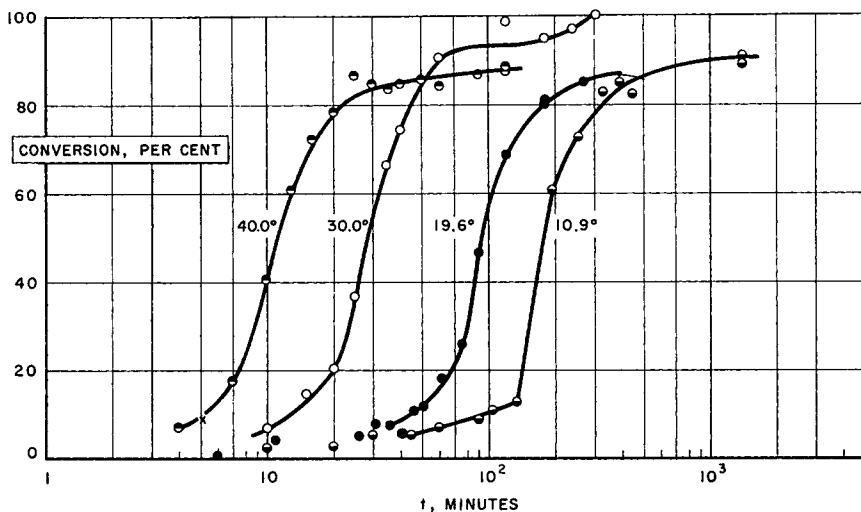$$\bar{r} = \bar{k}(\bar{A})(\bar{C}) \qquad (4)$$

Fig. 7. Quaternization of poly(*p*-vinylbenzyl chloride) at 10.9–40.0°C.   Concentrations shown in Table III.
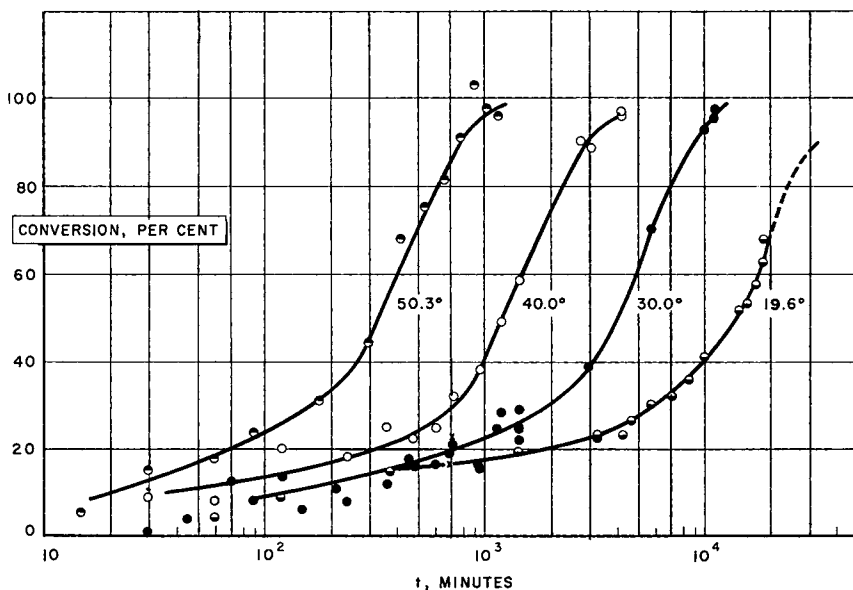

Fig. 8. Quaternization of poly(*o*-vinylbenzyl chloride) at 19.6–50.3°C.   Concentrations shown in Table III.

where $(\bar{A})$ and $(\bar{C})$ are the mean concentrations of reactants in this interval of reaction, it follows that

$$\bar{k}_{0-20\%} \cong 1/[(\bar{A})(\bar{C})(t_{0-20\%})] \tag{5}$$

These reactions, however, are noticeably different from small-molecule bimolecular reactions.   This is intuitively evident by inspection of the con-

TABLE III

Temperature Effects in the Quaternization of Poly(p- and o-vinylbenzyl Chlorides)[a]

Isomer	Temp., °C.	$[Me_3N]_0$, M	$[PVBC]_0$, M	$t_{20\%}$, min.	$t_{50\%}$, min.	$k_{0-20\%}$	$k_{20-50\%}$
p-PVBC	10.9	0.1284	0.0898	143.0	180.0	0.72_5	4.77
	19.6	0.1016	0.0914	68.0	93.0	1.93	9.67
	30.0	0.1085	0.0927	19.6	29.0	6.17	23.2
	40.0	0.1006	0.0926	7.3	11.2	18.0	$62._5$
o-PVBC	19.6	0.1053	0.0754	1750.0	14000.0	0.086_1	0.021_1
	30.0	0.1067	0.0760	700.0	4020.0	0.211	0.076_1
	40.0	0.0999	0.0745	310.0	1220.0	0.521	0.308^b
	50.3	0.1314	0.0758	68.0	335.0	1.74	0.725

a Second-order rate constants estimated as described in text.
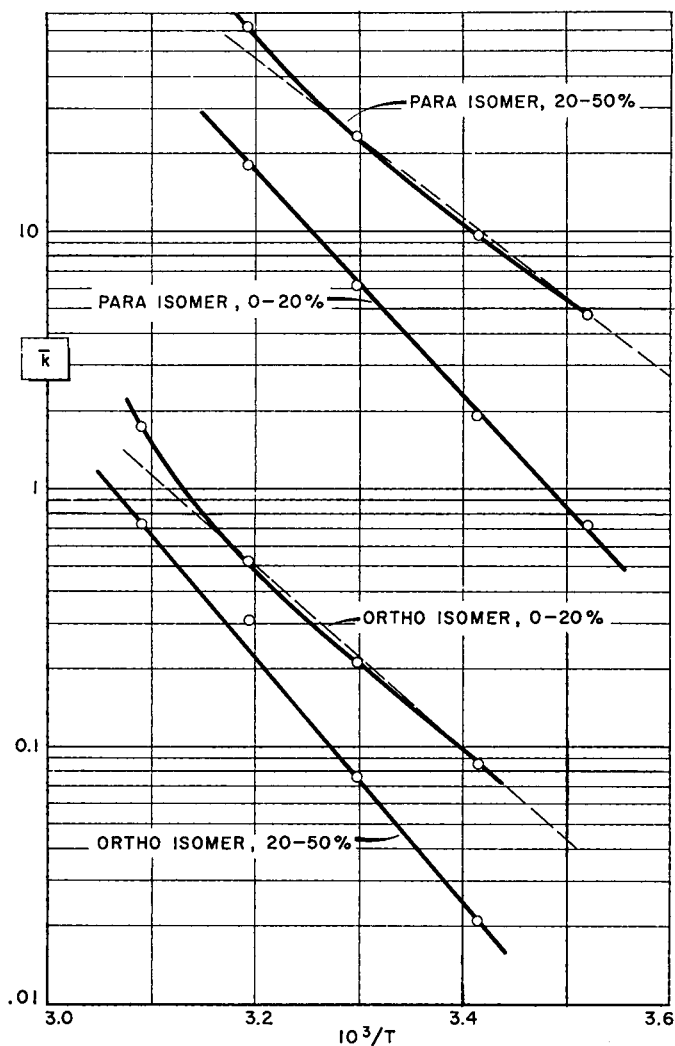b This datum is questionable; see Figure 9.

Fig. 9. Temperature dependencies for the mean quaternization rate constants at low (0–20%) and moderate (20–50%) conversions.

version curves, and may be shown in a rough-quantitative fashion by noting the values for $t_{50\%}$ on Figures 7 and 8, and similarly calculating the mean values for the rate constants between 20% and 50% conversion ($\bar{k}_{20-50\%}$'s). The reactant concentrations and estimated values of $\bar{k}$'s for these runs are summarized in Table III.

All rate constants have the expected moderate temperature dependence. In the case of *p*-PVBC, the medium conversion (20–50%) rate constant is consistently and significantly greater than the initial (0–20%) rate constant, the ratio $\bar{k}_{20-50\%}/\bar{k}_{0-20\%}$ varying smoothly from 6.6 at 10.9°C. to 3.5 at 40°C. On the other hand, the reverse effect is observed with *o*-PVBC;

here the ratio $\bar{k}_{20-50\%}/\bar{k}_{0-20\%}$ is consistently less than unity, increasing from 0.24 at 19.6°C. to 0.42 at 50.3°C.

Owing to these opposed drifts of $\bar{k}$'s with conversion, the comparison between rate constants for p-PVBC and o-PVBC differs sharply in proceeding from the initial to the medium-conversion stages. In the 0–20% conversion range, $\bar{k}_{para}/\bar{k}_{ortho}$ increases from 22 at 19.6°C. to 35 at 40.0°C. In the 20–50% conversion range, $\bar{k}_{para}/\bar{k}_{ortho}$ is much larger, and decreases with increasing temperature, from 458 at 19.6° to 203 at 40.0°.

The temperature dependencies of the rate constants in Table III may be seen from the Arrhenius plot in Figure 9. Estimates of the activation energies and pre-exponential factors are shown in Table IV.

TABLE IV
Estimated Arrhenius Constants for the Quaternization of
Poly(Vinylbenzyl Chlorides) with Trimethylamine

	p-PVBC	o-PVBC
Low conversion range (0–20%)		
log pre-exponential	13.1 ± 0.2	10.7 ± 1.0
Activation energy, kcal.	19.5 ± 0.3	18.3 ± 1.4
Medium conversion range (20–50%)		
log pre-exponential	10.8 ± 0.6	13.1 ± 0.9
Activation energy, kcal.	15.6 ± 0.8	22.2 ± 1.2

With the mixed-isomer polymer (about 60% *para*, 40% *ortho* isomers) a similar temperature dependency is obtained, except that a sharp break in the conversion curves is consistently evident at about 60% conversion (cf. Figs. 1 and 2).

DISCUSSION

Potential Sources of Complexity

A priori, four major sources of kinetic complexity may be anticipated: (1) differences in the reactivities of o-chloromethyl and p-chloromethyl functional groups (position isomerism); (2) differences in the reactivities of groups as a function of the number of quaternized nearest neighbors (0, 1, or 2) (neighboring group effects); (3) differences in the reactivities of groups arising from the pattern of microtacticity of the polymer segment (configurational differences); and (4) for o-vinylbenzyl chloride units, differences which would arise in the event of hindered rotation of the aromatic nucleus, giving rise to "boxed" and "open" o-chloromethyl groups (conformational isomerism).

In addition to these major sources, the kinetics might be skewed by diffusion control of rate. It was particularly anticipated that the transient coagulation of the reacting mixture at low extents of quaternization, arising from charge neutralization of the initially anionic-stabilized PVBC latex, might give rise to notable discontinuities of reaction rate. Neither of

these latter factors appear to be important, however.   The accelerating rate of reaction of p-PVBC is clearly counter to the geometric deceleration required of a diffusion-controlled reaction of polymer spheres, while the generally smooth conversion curves fail to show any important retardation at low conversion associated with the isoelectric zone portion of the reaction.

Analysis of Results

The position isomer effect is clearly shown by the preceding data to be of substantial significance.   Furthermore, the conversion curves of mixed-isomer polymers indicate that the differences in reaction rate between units of differing position isomerism are sufficiently large that o- and p-chloromethyl groups may usefully be treated as two separate species.

The neighboring group effects also appear to be real and important (Tables III and IV).   With increasing conversion of p-PVBC both the pre-exponential and the activation energy decrease, suggesting that the big neopentyl-sized quaternized groups tend to shield neighboring chloromethyl groups, but that this adverse steric effect is offset by their contributions to a more polar (E_a-lowering) environment for their unreacted neighbor sites.   With increasing conversion of o-PVBC both the pre-exponential and the activation energy increase.   It may be suggested that the effect of introducing quaternary functions this close to the backbone gives rise to electrostatic repulsive forces which lead to chain uncoiling, hence to an increase in the accessibility of unreacted o-chloromethyl groups.   This is overridden by the increase in activation energy, implying deactivation of an o-chloromethyl group by an adjacent o-quaternary group.   Such a deactivation is consistent with the observations of Fuoss and his co-workers[6,7] in studies of the quaternization of polyvinylpyridines.   For the model compound 1,3-di-(4-pyridyl)propane, Chow has shown that in the quaternization reaction $k_2 \cong 0.7\ k_1$.[8]   If this interpretation is correct, then the overall effect of a quaternized nearest neighbor upon the activation energy of quaternization of a nearest neighbor may depend rather closely upon the distance of the functional groups from the chain backbone.   Thus, for the above instances,[6-8] and for the present work with o-PVBC, there are three carbon atoms separating the quaternary (or incipient quaternary) nitrogens from the backbones, and in all these cases a quaternized neighbor tends to increase the activation energy; but for p-PVBC, with five carbon atoms separating the nitrogen from the backbone, a quaternized neighbor clearly decreases the activation energy.

The problem of tacticity is the least clearly illuminated by the present work.   A curious observation is that the fast-reacting p-PVBC, in three runs out of four, appears to be virtually arrested after 85–90% conversion (Fig. 7), while the slow o-PVBC goes essentially to completion (Fig. 8).   A possible explanation of this may be advanced, assuming that these "atactic" radical-initiated polymers are perhaps about 90% syndiotactic, consisting of short segments of alternating configurations, separated by ad-

jacent units of like configuration. It has recently been shown that other nominally atactic polymers have configurational distributions which are very far from random, and which tend toward high frequencies of alternating configurations.[9,10]

If this mostly syndiotactic configuration is assumed for p-PVBC, there will occur kinks at the points of tactic inversion which, for extended chain models, lead to points of very high steric hindrance with respect to backside nucleophilic attack. This assumption explains both the absence of other breaks in the conversion curves for p-PVBC and also the cut-off in the vicinity of 90% conversion. Furthermore, this is consistent with the essentially quantitative conversion of o-PVBC, for in addition to the probability of a greater syndiotacticity, the hindrance at points of tactic inversion for this case may be relieved simply by rotation of the C(backbone)—C(aromatic) bond.

These results fail to support the hypothesized conformational isomerism of o-PVBC. Conversion curves with these polymers fail to show the kind of break associated with two species of differing reactivity (cf. Figs. 1 and 2). Conversion discontinuities occur only with mixed-isomers polymers, they conform closely to the isomer composition of the starting monomer used, and they show no tendency to shift with temperature of quaternization. Hence, rotation of the C(backbone)—C(aromatic) bond in o-vinylbenzyl chloride units, while surely not completely "free," is insufficiently hindered to lead to the existence of distinct conformational species.

The elemental analysis pattern appears to be accounted for in terms of the concurrent hydrolysis of chloromethyl groups, and to incomplete reaction of p-rich polymers, this latter possibly arising from kinking hindrance at sites of tactic inversion. The overall quaternization kinetics are clearly sensitive to position isomerism. The dependency of rate upon the reacted or unreacted status of vicinal functional groups may be better understood in the light of recent theoretical attacks upon this problem.[11–13]

References

1. Lloyd, W. G., and J. F. Vitkuske, *J. Appl. Polymer Sci.*, **6**, 557 (1962).

2. Lloyd, W. G., and T. E. Durocher, *J. Appl. Polymer Sci.*, **7**, 2025 (1963).

3. Vitkuske, J. F., and F. C. Rutledge (to Dow Chemical Co.), Brit. Pat. 880,338 (October 18, 1961).

4. McMaster, E. L., and S. C. Stowe (to Dow Chemical Co.), Brit. Pats. 792,859–60 (April 2, 1958).

5. Siegel, S., and A. F. Graefe, *J. Am. Chem. Soc.*, **75**, 4521 (1953).

6. Chow, L.-Y., and R. M. Fuoss, *J. Polymer Sci.*, **27**, 569 (1958).

7. Coleman, B. D., and R. M. Fuoss, *J. Am. Chem. Soc.*, **77**, 5472 (1955).

8. Chow, L.-Y., thesis, Yale University, New Haven, Conn., 1957.

9. Glavis, F. J., *J. Polymer Sci.*, **36**, 547 (1959).

10. Smets, G., and W. De Loecker, *J. Polymer Sci.*, **45**, 461 (1960).

11. Keller, J. B., *J. Chem. Phys.*, **37**, 2584 (1962); *ibid.*, **38**, 325 (1963).

12. Alfrey, T., Jr., and W. G. Lloyd, *J. Chem. Phys.*, **38**, 318 (1963).

13. Arends, C. B., *J. Chem. Phys.*, **38**, 322 (1963).

Résumé

On montre que la quaternisation des chlorures de poly(*ar*-vinylbenzyle) par la tri-méthylamine est une réaction de déplacement nucléophile dont la cinétique est compliquée par différents facteurs, par de notables différences de réactivité des groupes *ortho* et *para*-chlorométhylés (isomérie de position), par des différences de réactivité des groupes qui sont fonctions de l'état réactif ou non-réactif du groupe immédiatement adjacent (effet de voisinage), et par des différences de réactivité des groupes augmentant avec la microtacticité du segment de polymère (effets de configuration). On donne des estimations des constantes de vitesse, des énergies d'activation et des facteurs pré-exponentiels pour des chlorures de poly-*p*-vinylbenzyle de haute pureté et pour des polymères *ortho* analogues.

Zusammenfassung

Die Quaternisierung von Poly(*ar*-vinylbenzylchlorid) mit Trimethylamin ist eine nukleophile Verdrängungsreaktion, deren Kinetik durch mehrere Faktoren kompliziert wird. Dazu gehören Reaktivitätsunterschiede von *ortho*- und *para*-Chlormethylgruppen (Stellungsisomerie), Reaktivitätsunterschiede von Gruppen als Funktion des Reaktionszustandes unmittelbar benachbarter Gruppen (Nachbargruppen-effekt) und Reaktivitätsunterschiede als Folge der Mikrotaktizität von Polymersegmenten (Konfigurationseffekte). Mittlere Geschwindigkeitskonstanten, Aktivierungsenergien und präexponentielle Faktoren für hochgereinigtes Poly-*p*-vinylbenzylchlorid und für das analoge *ortho*-Polymere werden mitgeteilt.