794. *Reactions of Macromolecules. Part V.* *Kinetics of the Quatern- isation of Poly-*(4-NN-*dimethylaminostyrene*) *by Methyl Iodide.*

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The initial second-order constant for the reaction of poly-(4-NN-di- methylaminostyrene) with methyl iodide in dimethylformamide at 0° (10.5×10^{-3} l. mole^{-1} min.$^{-1}$) is almost unaltered by change in molecular weight and by greater separation of amino-groups by inert styrene units. Under the conditions above, the constants for dimethylaniline and *p*-iso- propyl-NN-dimethylaniline are 5·1 and 15.4×10^{-3}. These values imply electron-release from the main chain to the side-groups in the polymers, for which the Hammett σ function is evaluated at σ $= -0.101$. After 20—25% reaction, the development of a charged envelope about the macromolecule leads to a fall in the rate of quaternisation.

A KINETIC study of some reactions of polystyrene side-groups has been undertaken, and the following method of investigation has been developed. Rate and order of reaction are determined at the same solvent composition and temperature for: (i) two specimens of homopolymer of different average molecular weight; (ii) a coplymer in which the reactive units are separated by inert units; (iii) the appropriate phenyl compound, representing the individual side-group; and (iv) the isopropylphenyl compound, re- presenting the side-group together with the chain-carbon atom to which it is combined and the two adjacent atoms. It may then be inferred how far the macromolecular reaction is similar in rate and order to that for the phenyl compound; where differences are found they are ascribed to the macromolecular environment, and the effects of the following factors may be distinguishable: molecular weight, from (i) above; interaction between adjacent reactive groups, from comparison of (ii) with (i); electron-release from the main chain, from comparison of (i) and (ii) with (iii) and (iv).

The investigation of a representative unimolecular reaction, the decomposition of a diazonium cation, was reported earlier,[1] and that of a bimolecular reaction, the formation of a quaternary ammonium iodide by the action of methyl iodide on a dimethylanilino- group is now described.

Evans, Watson, and Williams [2] have found the reaction of a series of *para*-substituted dimethylanilines with methyl iodide in methanol to be accurately of the second order for at least the first 50% of quaternisation, and the order of velocities *p*-OMe > *p*-Me > H > *p*-Cl to be consistent with a reaction which is favoured by accession of electrons to a nucleophilic centre. Reaction, it is concluded, proceeds by the S_N2 mechanism:
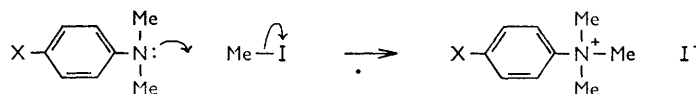
Harman, Stewart, and Ruben,[3] for the reaction of tritium-labelled methyl iodide with dimethylaniline in ethanol and in benzene, found no entry of labelled methyl into unused amine, whence it was inferred that quaternisation is not reversible under the present experimental conditions.

EXPERIMENTAL

Melting points are corrected.

Dimethylformamide, the liquid amines, and styrene were throughout distilled and kept under nitrogen.

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* Part IV, *J.*, 1963, 1175.

[1] Arcus and Halliwell, *J.*, 1961, 3708.
[2] Evans, Watson, and Williams, *J.*, 1939, 1345.
[3] Harman, Stewart, and Ruben, *J. Amer. Chem. Soc.*, 1942, **64**, 2294.

The following purification of dimethylformamide is based on the findings of Thomas and Rochow.[4] Benzene (200 ml.; dried over calcium hydride) was added to dimethylformamide (2 l.) and then removed by distillation at atmospheric pressure through a 30 cm. column, the temperature at the head of which was not allowed to exceed 80°. Magnesium sulphate (50 g.), which had been heated for 8 hr. at 300—400°, was added to the dimethylformamide, and the whole was shaken for 1 day, then filtered. Distillation through a 90 cm. vacuum-jacketed column packed with Fenske helices gave dimethylformamide having b. p. 42°/11 mm., n_D^{25} 1·4275; it was kept in a wash-bottle, the orifices of which were normally stoppered, and dispensed by application of nitrogen pressure. A single stock of dimethylformamide was used; the first three runs with dimethylaniline (Table) were conducted at the beginning and the last two at the end of the series; the values of k are not significantly different, indicating the solvent to have remained unchanged.

Methyl iodide was dried (Na_2SO_4), then distilled and the fraction of b. p. 42·0—42·4° taken; it was kept in a dark bottle containing a coil of copper wire.

Dimethylaniline (150 ml.) was refluxed for 3 hr. with acetic anhydride (65 ml.). After three distillations the dimethylaniline had b. p. 192—193°, n_D^{25} 1·5557.

p-Isopropyl-*NN*-dimethylaniline was prepared by the method of Sachs and Sachs.[5] It was twice distilled and had b. p. 110°/8 mm., n_D^{25} 1·5304 (Found: C, 81·15; H, 10·1; N, 8·85. Calc. for $C_{11}H_{17}N$: C, 80·9; H, 10·5; N, 8·6%). Its methiodide had m. p. 204—205°.

Polymers.—*p*-*NN*-Dimethylaminobenzaldehyde (75 g.) was allowed to react with methyl-magnesium iodide (from magnesium 15 g., and methyl iodide 90 g.) as described by Marvel and his co-workers.[6] However, their method of decomposition was not followed; next day, the ethereal layer was decanted from the solid complex, which was shaken with ether (300 ml.), a saturated solution of ammonium chloride (60 g.), ice, and aqueous ammonia (*d* 0·88; 30 ml.); the aqueous layer was separated and extracted with ether (100 ml.); the ethereal solutions were washed with ammoniacal ferrous hydroxide suspension (to remove peroxides) and dried (Na_2SO_4); evaporation (bath temperature 45°) gave 4-*NN*-dimethylamino-α-methylbenzyl alcohol (60 g.) which, after recrystallisation from light petroleum (b. p. 40—60°), had m. p. 58·5—59°. The decanted ethereal layer, above, yielded a further small quantity of the alcohol. The best yields of 4-*NN*-dimethylaminostyrene (60%) were obtained when the freshly prepared alcohol (m. p. ≮56°; 8-g. portions) was distilled at 5 mm. from a Claisen flask (25 ml.) with air-leak, connected to receivers cooled in ice and solid carbon dioxide; heating was by micro-burner, and considerable reflux from the flask-neck was allowed. The monomer, to which 1% of t-butylcatechol had been added, was dried (K_2CO_3) and filtered. Redistillation, after addition of a further 1% of t-butylcatechol, with heating by oil-bath, yielded 4-*NN*-dimethyl-aminostyrene, b. p. 81°/0·3 mm., n_D^{25} 1·6084.

Styrene was purified as described earlier.[1]

αα'-Azoisobutyronitrile [m. p. 103—104°; (i) 0·0304, (ii) 0·0127 g.] was dissolved in 4-*NN*-di-methylaminostyrene [(i) 3·04, (ii) 3·02 g.], which was then sealed under nitrogen in a thin-walled soft-glass tube and kept for 21 hr. at 70°. The resultant glass was crushed and dissolved in benzene (15 ml.). The solution was added slowly to stirred propan-2-ol (150 ml.). A white, fibrous homopolymer was precipitated. It was filtered off, washed with propan-2-ol, and dried under reduced pressure in the presence of potassium hydroxide, calcium chloride, and paraffin wax, and finally to constant weight at 50°/2 mm. [Found: for homopolymer (i), N, 9·65; for homopolymer (ii), N, 9·5. Calc. for $C_{10}H_{13}N$: N, 9·5%]. By the procedure above, styrene (4·20 g.), 4-*NN*-dimethylaminostyrene (2·97 g.), and αα'-azoisobutyronitrile (0·0416 g.) yielded the 2 : 1 *copolymer* (Found: C, 88·15; H, 8·1; N, 3·85. $C_8H_8 : C_{10}H_{13}N = 2·00 : 1$ requires C, 87·8; H, 8·2; N, 3·95%).

The logarithmic viscosity numbers, $(1/c) \ln (\eta_{soln.}/\eta_{solv.})$, where $c =$ g. of solute in 100 ml. of solution, were determined for solutions of each homopolymer and the copolymer in toluene at 25·0° and $c = 1·2, 0·8, 0·6,$ and 0·4; extrapolation yielded the limiting intrinsic viscosity, $[\eta]$. The flow-times of solutions of the copolymer did not alter with time; those of the homo-polymers fell during 3 days by up to 6% and then remained constant; the final values were used in the calculation of logarithmic viscosity numbers. Homopolymers (i) and (ii) and the copolymer had respectively $[\eta]$ 0·338, 0·450, 0·565.

[4] Thomas and Rochow, *J. Amer. Chem. Soc.*, 1957, **79**, 1843.
[5] Sachs and Sachs, *Ber.*, 1905, **38**, 520.
[6] Marvel, Overberger, Allen, and Saunders, *J. Amer. Chem. Soc.*, 1946, **68**, 737.

Rate-determination Procedure.—Methyl iodide (0·2720 equiv.) and the tertiary amine (0·1360 equiv.) were weighed into separate flasks; to each, dimethylformamide (5 ml.) was added; the polymeric amines dissolved in an hour at room temperature. The flasks, together with a third flask containing solvent, were placed in a bath of ice and water. After 30 min., the solution of the amine was added and washed into that of the methyl iodide, and the whole was brought to 25 ml. with dimethylformamide, and mixed. At intervals from this point, portions (2 ml.) were transferred by syringe into methanol (45 ml.) containing 2N-sulphuric acid (6 ml.). Iodide ion was titrated potentiometrically with 0·01391N-silver nitrate by means of a glass and a silver electrode. At the end-point the polarity of the electrodes became reversed and a change in potential of ~200 mv occurred.

It was found, from runs conducted in the absence of amine, that a slow, pseudo-first-order reaction rate-constant 6×10^{-6} min.$^{-1}$, occurred between methyl iodide and dimethylformamide. The quaternisation runs were corrected for iodide ion so liberated; the corrections were small, 1·3% of the titre for the homopolymer at 8 hr.

RESULTS AND DISCUSSION

By initiation with $\alpha\alpha'$-azoisobutyronitrile, there were prepared two specimens of poly-(4-*NN*-dimethylaminostyrene) of different molecular weights, and a 2 : 1 styrene–4-*NN*-dimethylaminostyrene copolymer. The equation, $[\eta] = KM^\alpha$, relating limiting
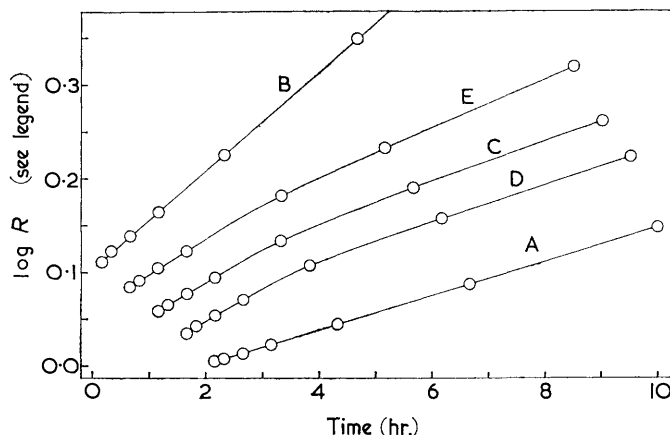

FIG. 1. Reaction of tertiary amines with methyl iodide in dimethylformamide at 0°: A, dimethylaniline; B, *p*-isopropyl-*NN*-dimethylaniline; C, D, poly-(4-*NN*-dimethylaminostyrene) (i) and (ii); E, 2 : 1 styrene–4-*NN*-dimethylaminostyrene copolymer. The origin has been displaced successively by 0·025 unit of the ordinate from right to left, and 0·5 hr. of the abscissa from left to right. Log R denotes $\log_{10} a(b - x)/b(a - x)$.

intrinsic viscosity to viscosity-average molecular weight, has not been evaluated for poly-(4-*NN*-dimethylaminostyrene). In order to obtain numerical values permitting a comparison of molecular weights, the equation for solutions of polystyrene in toluene, for which Green[7] has determined the values $K = 1·16 \times 10^{-4}$ and $\alpha = 0·72$, has been applied to the limiting intrinsic viscosities of the homopolymers and the copolymer of 4-*NN*-dimethylaminostyrene; it leads to the values given below.

Order and Rates of Quaternisation.—Exploratory experiments showed that the homopolymers and the copolymer, both before and after quaternisation, were soluble, together with methyl iodide, in dimethylformamide at 0°. Representative examples of runs of dimethylaniline, *p*-isopropyl-*NN*-dimethylaniline, the two samples of poly-(4-*NN*-dimethylaminostyrene), and the 2 : 1 styrene–4-*NN*-dimethylaminostyrene copolymer are shown

[7] Green, *J. Polymer Sci.*, 1959, **34**, 514.

in Fig. 1. The logarithmic plots for dimethylaniline and *p*-isopropyl-*NN*-dimethylaniline are linear, and the second-order constants (*k*) recorded in the Table hold throughout the run. The plots for the homopolymers and copolymer are substantially linear for the first 20—25% of reaction and then become concave towards the abscissa. The values of *k* given in the Table are derived from straight lines drawn through these first sections. The rate constants are considered to be those for the dimethylamino-groups attached to the macro-molecules, before the incidence of a perturbing factor due to the accumulation of ammonium ions on the chain has become appreciable.

The values of *k* for homopolymer (i) (*M*, 65,000), homopolymer (ii) (*M*, 97,000), and the copolymer (*M*, 130,000) are nearly equal. Change in molecular weight and in the spacing of amino-groups by the insertion of inert units has thus little effect on the initial second-order constant, for which the average value is 10.5×10^{-3} l. mole^{-1} min.$^{-1}$. This

Reaction with methyl iodide in dimethylformamide at 0°.

	k (10^{-3} l. mole^{-1} min.$^{-1}$)					
Amine	Individual runs					Average
Dimethylaniline	5·0	5·0	5·1	5·1	5·1	5·1
p-Isopropyl-*NN*-dimethylaniline	15·4	15·4				15·4
Poly-(4-*NN*-dimethylaminostyrene) (i)	10·4	10·4				10·4
(ii)	10·6	10·4				10·5
2 : 1 Styrene–4-*NN*-dimethylaminostyrene copolymer	10·6	10·5	10·6			10·6

rate, and that for *p*-isopropyl-*NN*-dimethylaniline are, respectively, about twice and three times that for dimethylaniline. The results imply that quaternisation is promoted by inductive electron-release towards the amino-group, and that the release from the main chain of the polymers is some fraction of that from an isopropyl group.

It is useful to consider the polystyrene main chain, the structure outside the square brackets in (I), as a substituent in the phenyl side-group, and to treat it by Hammett's
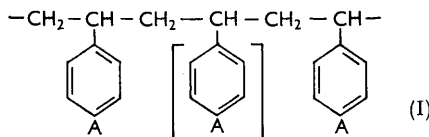
σ_p procedure.[8] At the beginning, all reacting groups (A) are in the situation of the central group in (I). Increasingly thereafter, they may be flanked by phenyl bearing the group which is the product of the reaction.

For a substituent X in a phenyl group, the σ constant is given by:

$$\sigma_x = \log K_{C_6H_4X} - \log K_{C_6H_5}, \qquad (1)$$

where $K_{C_6H_4X}$ and $K_{C_6H_5}$ are, respectively, the dissociation constant of the substituted and unsubstituted benzoic acid, in water at 25°. The dissociation behaviour of poly(styrene-4-carboxylic acid) has not been recorded. However, insertion of the dissociation constants for *p*-isopropylbenzoic and benzoic acid[9] in (1) yields, for the σ constant of the *p*-isopropyl group: $\sigma_i = -0.154$. (This value has been derived by the use of the best value for the dissociation constant of benzoic acid as assessed by Kortüm, Vogel, and Andrussow[9] and differs slightly from Hammett's value, -0.151.[8]) Further, where ρ is the constant for the reaction of dimethylanilines with methyl iodide in dimethylformamide at 0°, σ_p the σ-constant for the polystyrene chain as a *para*-substituent, and k_H, k_i, k_p are, respectively,

[8] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, pp. 184—189.

[9] Kortüm, Vogel, and Andrussow, " Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961, pp. 353, 358.

the average values of the rate-constants of the Table for dimethylaniline, *p*-isopropyl-*NN*-dimethylaniline, and poly-(4-*NN*-dimethylaminostyrene), we have:

$$\log (k_i/k_H) = \rho\sigma_i; \quad \log (k_p/k_H) = \rho\sigma_p;$$

on insertion of the values above for σ_i, k_H, k_i, k_p, there are found $\rho = -3\cdot11$ and $\sigma_p = -0\cdot101$.

The last value is, rigorously, that for the main chain of poly-(4-*NN*-dimethylamino-styrene) considered as a *para*-substituent. However, the initial rates for the copolymer and homopolymers are almost identical, whence replacement of two-thirds of the dimethyl-amino-groups by hydrogen in the polymeric substituent of (I) does not appreciably alter σ_p. It is inferred that the value found is substantially that for the main chain bearing phenyl groups on the carbon atoms β and δ to the point of attachment to the side-group under consideration.

Deceleration during Quaternisation.—During the progress of the kinetic runs of the homopolymers and copolymer, the second-order rate constant alters little during the first part of the reaction, but thereafter falls. In Fig. 2 are shown the initial rates, forming the
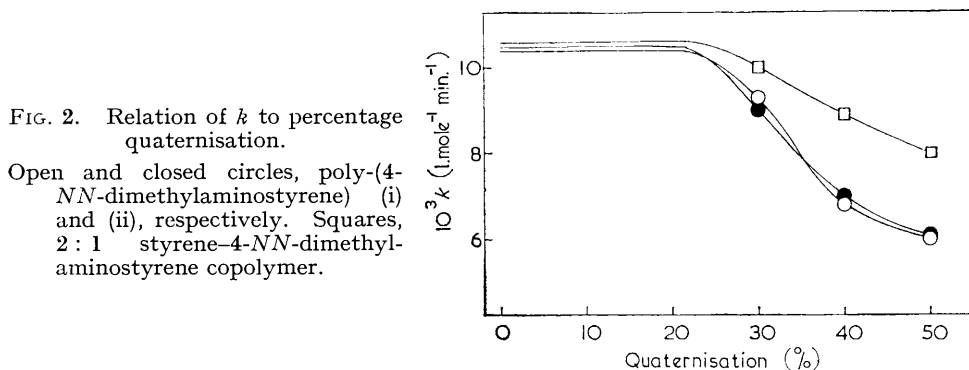
FIG. 2. Relation of k to percentage quaternisation.

Open and closed circles, poly-(4-*NN*-dimethylaminostyrene) (i) and (ii), respectively. Squares, 2 : 1 styrene–4-*NN*-dimethyl-aminostyrene copolymer.

horizontal part of the plots, and the instantaneous second-order constants derived from the slopes of plots of the kinetic runs at the times when 30, 40, and 50% of quaternisation had occurred. The points are the average values from the runs for each polymer. When 50% quaternisation has occurred, the rate-constants for the homopolymers are seen to fall to about 60%, and that for the copolymer to about 75%, of the initial value.

The plots of k against percentage quaternisation are nearly identical for the two homopolymers, whence it is concluded that change in molecular weight, within the range above, does not appreciably affect the course of deceleration. In the copolymer, the charges are separated by distances, measured along the chain, which average three times those between charges on the homopolymer at the same percentage quaternisation. This difference is associated with a less-marked, though still considerable, deceleration during the growth of a charged envelope.

A similar fall in rate has been observed by Coleman and Fuoss [10] for the quaternisation of poly-(4-vinylpryidine) by n-butyl bromide in tetrahydrothiophen 1,1-dioxide. Possible modes of action of the accumulating positive charges on the bimolecular reaction have been discussed by these authors, but no decision was reached on their relative importance.

It is concluded, with respect to the population of dimethylanilino-groups attached to the polyvinyl main chain, that quaternisation is at first essentially similar to that of dimethylaniline and *p*-isopropyl-*NN*-dimethylaniline. Electron-release from the main chain is somewhat less than that from the *p*-isopropyl group and is expressible by the value $\sigma_p = -0\cdot101$. Neither change in molecular weight of the polymer nor spacing by means

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[10] Coleman and Fuoss, *J. Amer. Chem. Soc.*, 1955, **77**, 5472.

of inert styrene units affects the initial rate appreciably. The accumulation of positive charge on the macromolecule as the quaternary ammonium groups are formed causes a fall in reaction rate in both homopolymers and copolymer. The effect is more marked for the homopolymers, which possess the greater charge-density at a given degree of quaternisation.