

1007. Anionic Polymerization of Styrene: Conductivity Measurements.

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Measurements have been made, over a wide range of concentrations, of the conductance of solutions which contain the anionically polymerizing species formed from styrene and sodium naphthalene in tetrahydrofuran solution. The active chain ends have been shown to be primarily ion pairs with the sodium gegenion, with a dissociation to free ions which has a dissociation constant of 1.5×10^{-7} .

THE polymerization of vinyl compounds by acidic and basic catalysts is usually assumed to involve some form of ionic intermediate, the preferred species being the ion pair. But consideration of the probable concentration of polymerizing chain ends, and the wide range of dielectric constants of the solvents used, leads to some doubt if the ion pair as defined by Fuoss and Kraus¹ is always the predominant species. It is generally agreed that dissociation into free ions is negligible in such non-polar solvents as hydrocarbons, but when the dielectric constant is increased to 10 or above in solvents such as chlorinated hydrocarbons, nitrobenzene, or dimethylformamide the possibility that free ions are the major species should be considered. It is, however, difficult to determine the state of the ions in normal ionic reactions owing to the transitory nature of the reacting species. Some systems that have recently been defined lend themselves to measurement, particularly the anionic polymerization of olefins where termination reactions are negligible and the polymer chains carrying negative charges on their ends are stable over extended time intervals.²

The present work presents some measurements of the conductivity of the polymerizing species produced by the action of sodium naphthalene on styrene in tetrahydrofuran solution. The results have been treated by the methods of Kraus *et al.* to show the salt-like nature of the chain ends and to determine the degree of ionic dissociation in this solvent of moderately low dielectric constant. This initiator has the advantage of being clean in its method of preparation and free from salts which could affect the conductivity. It has the disadvantage that it produces a polymer chain



with an ionic centre at each end, but they are sufficiently far apart to be considered independent, and the degree of dissociation is sufficiently low so that any complication due to doubly charged species is negligible.

EXPERIMENTAL

The tetrahydrofuran was purified by refluxing and distillation from phosphorus pentoxide and potassium hydroxide in turn, followed by refluxing with sodium-potassium alloy and fluorenone until the green colour of the disodium salt of fluorenone was well established. This was followed by fractional distillation through a column of reputedly more than 100 theoretical plates. After degassing and storage over calcium hydride on the vacuum-system the product was, before use, distilled on to, and stirred with, sodium-potassium alloy, to form the deep blue colour associated with potassium solutions.

Styrene was fractionally distilled under a reduced pressure of nitrogen and then distilled in a high vacuum on to a fresh sodium film. The monomer was stirred magnetically until the colour began to change, at which point the stirring was stopped and the styrene was distilled as rapidly as possible in the vacuum-system to an evacuated storage bulb, leaving a large proportion of the original material behind as polymer. When stirring was for too long,

¹ Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 1019.

² Swarc, Levy, and Milkovitch, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

explosive polymerization occurred, but it was necessary to prolong the stirring for a sufficient time to polymerize some monomer and thus to remove reactive impurities.

All further manipulations were performed in evacuated systems.

It was desired to measure conductivities at known concentrations as low as $10^{-5}M$ where, owing to the sensitivity of the reactants to traces of impurities, concentration measurements which depended on successive dilutions were found to be unreliable. These low concentrations were determined photometrically by an extrapolation of the concentration-optical density relation established at concentrations ten times higher by use of the technique described below. The optical cells were constructed of 10 mm. square Pyrex tubing; when necessary, 9 mm. quartz blocks were used, to convert the cells into 1 mm. cells. The cells were calibrated with potassium chromate solutions. The apparatus used for the optical-density measurements, shown in Fig. 1, contained fragile bulbs of naphthalene (1) and styrene (2), together with

FIG. 1. Apparatus used in the measurement of spectra.

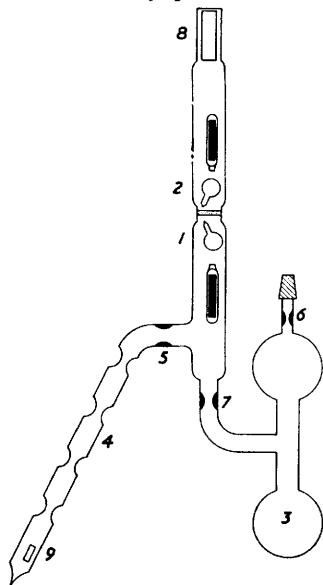
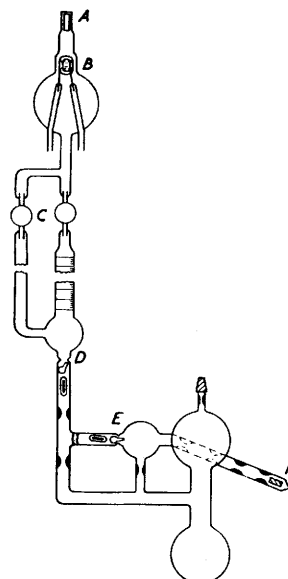


FIG. 2. Apparatus used in the measurement of conductivities.



A, optical cell. B, conductivity cell.
C, brass stopcocks. D, styrene. E, naphthalene. F, sodium.

magnetic breakers. Solvent was distilled on to loose naphthalene in the bulb (3) after sodium (9) had been distilled from the side-arm (4) which was removed at (5). The apparatus was sealed off at (6) and the solution of sodium naphthalene formed was rinsed around the apparatus for an hour or more. The solution was then drained back to the bulb (3) and the apparatus was rinsed by refluxing. The apparatus was inverted, sufficient solvent was distilled into the left-hand side, and the bulbs were sealed and removed at (7). Despite the excess of sodium present, it was always found that the solvent distilled from the sodium naphthalene solution gave, on recontact with the sodium film, a pale green solution of sodium naphthalene. The spectrum of this solution was measured on a Beckman D.U. spectrophotometer, then the naphthalene bulb was broken and the main sodium naphthalene solution spectrum measured by use of the 1 mm. optical cell (8). The difference was taken as that due to the weight of naphthalene in the bulb. When the styrene bulb was broken the polystyryl salt was formed and its spectrum was measured. The volume of solvent was found by weighing, and hence the concentration and extinction coefficients were calculated.

The conductivities were measured on a Leeds Northrup a/c conductance bridge with a frequency of 1000 c./sec. only, as the effect of changing the frequency was found to be very

small. The measurements were made in an oil-bath held at $20^{\circ} \pm 0.01^{\circ}$. The conductivity cell (Fig. 2) with a constant of *ca.* 0.09 consisted of a 500 ml. flask with the electrode assembly, two concentric platinum cylinders, in a well at the bottom with the optical cell joined immediately below this. The silica block converting the cell from 10 mm. to 1 mm. could be manœuvred in and out of the optical cell. The cell was connected to a burette through an all-brass, vacuum-tight, needle-valve. The burette contained a small fragile bulb of styrene and a breaker and was connected through a glass filter to a further flask in which the sodium film was formed, and into which a small fragile bulb of naphthalene could be broken. The whole was joined by two flasks joined neck to neck as before. A similar procedure was adopted of washing the apparatus and rinsing by refluxing. From time to time the conductance of samples of solvent distilled into the cell was measured until it fell to a value of 10^{-10} ohm⁻¹ cm.⁻¹, then the conductivity cell was half-filled with distilled solvent. The cell was isolated by shutting the needle-valve, and the sodium polystyryl salt was prepared as before.

Successive additions of this solution in the burette were then made to the solvent in the cell, and the conductivity and the optical density and hence the salt concentration were measured. For runs at concentrations beyond that where the optical-density method was applicable, the concentrations were determined volumetrically from the amounts of solution added from the burette. The concentration of the solution in the burette was estimated optically from the dilution ratio and the optical density of the more dilute solutions prepared. The most concentrated solutions of all were estimated directly from the weight of naphthalene used and were successively diluted by weighed amounts of solvent distilled into the cell.

The polymer chain had a molecular weight of 5000, the Szwarc relation mol. wt. = $[M]/\frac{1}{2}[C]$ being assumed.

RESULTS AND DISCUSSION

The spectrum of sodium naphthalene agreed well with published spectra.^{3,4} When the material was prepared under these conditions no change in the optical density was observed in 24 hours.

The freshly prepared sodium polystyryl salt showed one absorption peak only in the range measured (310—900 m μ), with a maximum at 343 m μ of $\epsilon = 1.18 \times 10^4$. However, this peak decreased with time and two smaller peaks appeared, one at 560 m μ , and a weaker one at about 420 m μ which later disappeared. The original peak disappeared fairly rapidly at first, decreasing about 30—40% in the first day, but its rate of disappearance became slower and even after six months about 15% remained. Efforts were made to ensure that this reaction was not due to some contaminant or the presence of naphthalene, and it appears characteristic of this salt.

Because of this, and the finite time it took to perform the rather cumbersome experiments in the measurement of the conductivities, the conductivity measured was not that of the pure species desired, but of a mixture. It was found that the conductivity did increase with time: one solution left for 72 hr. showed an 18% increase. Hence every effort was made to decrease the time taken to carry out the experiments and to minimize the concentration of extraneous species; three hours was the average time from the formation of the polystyryl salt to the completion of the measurements. One other source of error could be the destruction of the sodium polystyryl salt by impurities to give other conducting salts. It was found, however, that in preliminary experiments, the complete decoloration of dilute solutions by contaminants gave solutions with conductivities negligible compared with those recorded for proper solutions.

The results are shown in Fig. 3 as a plot of $\log \Lambda$ against $\log c$, which give a straight line of slope -0.51 . This behaviour is expected when the conductance is determined by an ionization to free ions governed by the law of mass action⁵ when the principal species is the ion-pair, and the dissociation constant is small. In this case, it was possible to treat

³ Balk, Hoytink, and Schreurs, *Rec. Trav. chim.*, 1957, **76**, 813.

⁴ Paul, Lipkin, and Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.

⁵ Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 21.

the results by Kraus and Bray's method,⁶ which assumes that the effects of interionic attraction are negligible. They derived the equation

$$1/\Lambda = 1/\Lambda_0 + c\Lambda/K\Lambda_0^2$$

so that in the plot of $1/\Lambda$ against $c\Lambda$ the slope is $1/K\Lambda_0^2$, and the intercept is $1/\Lambda_0$, where K is the ion-pair dissociation constant. The results plotted in this manner gave a straight line of slope 1.60×10^3 , but the intercept was too small to be read accurately because of the low degree of ionization, so Walden's rule was used to evaluate Λ_0 .

Tetrahydrofuran has not been often used as a solvent for conductivity measurements, and it was not possible to determine from the literature if Walden's rule was valid in this solvent. Conductivity measurements were made on both tetrabutylammonium and tetraethylammonium picrate at 20° in tetrahydrofuran solution, over the concentration range 1×10^{-5} to 2×10^{-4} M to test the validity of this rule. The results were treated by Fuoss's method⁷ to determine Λ_0 and K , the dissociation constant. The values of the

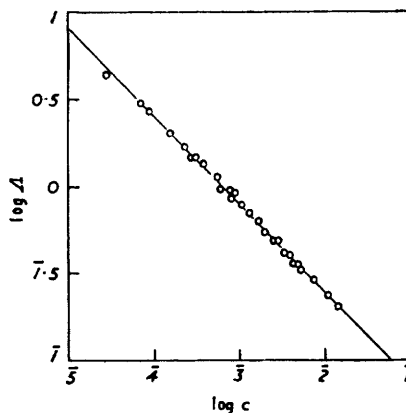


FIG. 3. Conductance data for the sodium polystyryl salt in tetrahydrofuran plotted as $\log_{10} \Lambda$ against \log_{10} concentration.

viscosity⁸ and dielectric constant⁹ were taken as 4.86 millipoises and 7.58 respectively. The results were $\Lambda_0 = 126$ and 107 , $K = 4.05 \times 10^{-6}$ and 2.92×10^{-6} , for the tetraethylammonium and the tetrabutylammonium salt respectively. These give for the product $\eta\Lambda_0$ 0.61 and 0.52 respectively, and as the average values in the literature are 0.56 and 0.45 the agreement is sufficiently close to justify the use of Walden's rule. The average value of $\eta\lambda_+$ for Na^+ was taken as 0.233, which gives $\lambda_{\text{Na}^+} = 48$ in tetrahydrofuran. No simple application of Walden's rule can be applied to the anion, but the product $\eta\lambda$ for an ion of molecular weight 5000 was estimated to be 0.068 by applying Stokes's law to the figures given by Pickering and Kraus¹⁰ for long-chain electrolytes in various solvents, hence λ_- in tetrahydrofuran was estimated to be 14. This value is in agreement with a similar calculation on the figure given for sodium trimesitylboron in tetrahydrofuran¹¹ if the above value of λ_{Na^+} is assumed. The estimated value of Λ_0 for the sodium polystyryl salt is thus 62.

This value of Λ_0 , when inserted in the Kraus and Bray equation, gives $K = 1.63 \times 10^{-7}$. Use of the Fuoss method⁷ which makes allowance for long-range interionic attractions gives $K = 1.50 \times 10^{-7}$, but the plot of F/Λ against $c\Lambda^2/F$ curves slightly upwards as expected, above the concentration 3×10^{-7} D³ which Fuoss gives as the limit for linearity.

⁶ Kraus and Bray, *J. Amer. Chem. Soc.*, 1913, **35**, 1315.

⁷ Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

⁸ Kuss, *Z. angew. Physik*, 1955, **7**, 376.

⁹ Critchfield, Gibson, and Hall, *J. Amer. Chem. Soc.*, 1953, **75**, 6044.

¹⁰ Pickering and Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 3288.

¹¹ Chu and Weismann, *J. Phys. Chem.*, 1956, **60**, 1020.

From the latter figure of K the interionic distance of the ion-pair was calculated as 3.9 Å which is of the right order of magnitude, even though probably of little absolute significance. The value of K is less by a factor of 20 than that for tetra-alkylammonium salts in tetrahydrofuran but, in general, in all solvents, sodium salts have dissociation constants this order of magnitude smaller.

The major anomaly found in treating the sodium polystyryl salt as a normal ion-pair is the slight evidence for any aggregates such as triple ions which might be expected to be formed at the highest concentration in a solvent of this dielectric constant, and so to cause the equivalent conductance to pass through a minimum. This absence of higher aggregates is, however, in accord with the observation¹² of an increase in viscosity of these solutions on addition of ethylene oxide, or to a smaller extent carbon dioxide, which converts the carbanion into alkoxide or carboxylate anion. The viscosity of the polystyryl carbanion solution was, in contrast to this, identical with the viscosity of the parent uncharged polystyrene solution. Szwarc has suggested that the lack of association of carbanions can be correlated with delocalization of the charge over the benzyl group to give a reduced charge density. Alternatively, the appearance of triple ions could be masked by the increase in viscosity of the solution at the higher concentrations to give a resultant depression of the specific conductance which would offset the increase due to the conductance of the triple ions. 0.01N-Solutions of the polymer with molecular weight 5000 increase the viscosity by only 15%, so the effect can only be minor.

The results indicate that in anionic polymerization of styrene with sodium counterions in tetrahydrofuran solution, at normal initiator concentrations of 10^{-3} — 10^{-4} M, the major species present is the ion-pair in equilibrium with about 1% of free ions. It would be interesting to compare this result with kinetic measurements. In this system, if the free ion were the reactive species the rate of propagation would be proportional to the half-power of initiated-chain concentration; if both ion and ion-pair were equally active the order would be first; but if the free ion had a somewhat different activity from the ion-pair, deviations from first-order kinetics would appear at lower initiator concentrations. The only relevant kinetic data refer to α -methylstyrene,¹³ so only a qualitative comparison is possible. The reaction at the highest initiator concentrations was of the first order in initiator, but some deviations did occur at the lowest concentration; however, as the experimental error increases rapidly with dilution it is doubtful if any concrete conclusions should be drawn.

The dissociation constant of an ion-pair has been found to increase rapidly with dielectric constant,¹ so that serious consideration should be given to the state of ionic dissociation of reacting species in other ionic polymerization systems in solvents of rather higher dielectric constant, as such dissociation could profoundly affect the kinetics of the reaction.

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¹² Brody, Richards, and Szwarc, *Chem. and Ind.*, 1958, 1473.

¹³ Worsfold and Bywater, *Canad. J. Chem.*, 1958, **36**, 1141.