138. *Anionic Polymerisation. Part I. The Polymerisation of Styrene in Liquid Ammonia Solution catalysed by Potassium Amide.*

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In an earlier paper (Evans, Higginson, and Wooding, *Rec. Trav. chim.*, 1949, **68**, 1069) a mechanism was suggested for the polymerisation of styrene in liquid ammonia as solvent, catalysed by potassium amide. The study, there reported, of the dependence of molecular weight on reactant concentrations has been extended and measurements of the rate of styrene disappearance have been made. These results confirm the mechanism previously suggested which involves : initiation by addition of the amide ion to a styrene molecule, propagation by reaction of the resulting carbanion with further monomer molecules, and termination by reaction of the growing polymer chain with the solvent ammonia leading to re-formation of the amide ion.

The activation energy and frequency factor of the initiation reaction have been found.

In contrast to the many detailed investigations of the polymerisation of vinyl monomers by radical and cationic initiators, the studies of polymerisation by anionic catalysts have been almost entirely qualitative in character. Such anionic polymerisation is known to occur in the bulk monomer, and in solution in inert hydrocarbons, diethyl ether, and liquid ammonia, the catalysts including alkali metals (Beaman, *J. Amer. Chem. Soc.*, 1948, **70**, 3115; Schlenk and Bergmann, *Annalen*, 1928, **463**, 1; Ziegler *et al.*, *ibid.*, 1934, **511**, 13, 64), sodium amide (Sanderson and Hauser, *J. Amer. Chem. Soc.*, 1949, **71**, 1595), triphenylmethylsodium (Beaman, *loc. cit.*), metal alkyls (Ziegler *et al.*, *Annalen*, 1934, **511**, 13, 45; 1940, **542**, 90), and Grignard reagents (Landler, *Rec. Trav. chim.*, 1949, **68**, 922). In aqueous solution the polymerisation of nitro-olefins (Blomquist, Tapp, and Johnson, *J. Amer. Chem. Soc.*, 1945, **67**, 1519) probably involves an anionic mechanism also, but for most vinyl monomers the strongest base obtainable in water, the hydroxyl ion, is unreactive.

Of the various reaction systems which could be investigated in detail, homogeneous polymerisation in liquid ammonia as solvent with the amide (NH_2^-) ion as catalyst seemed likely to present least interpretative difficulties. In particular, information is available as to the state of dissolved salts in this solvent. From the findings reported in a preliminary communication (Evans, Higginson, and Wooding, *loc. cit.*) it was evident that styrene, methyl methacrylate, and acrylonitrile undergo polymerisation under conditions suitable for kinetic measurements, and the following mechanism for the reaction was proposed :

$$NH_2^- + CH_2{:}CHR \longrightarrow NH_2{\cdot}CH_2{\cdot}\overset{(-)}{C}HR \quad (\textit{Initiation})$$

$$NH_2{\cdot}[CH_2{\cdot}CHR]_m{\cdot}CH_2{\cdot}\overset{(-)}{C}HR + CH_2{:}CHR \longrightarrow NH_2{\cdot}[CH_2{\cdot}CHR]_{m+1}{\cdot}CH_2{\cdot}\overset{(-)}{C}HR \quad (\textit{Propagation})$$

$$NH_2{\cdot}[CH_2{\cdot}CHR]_n{\cdot}CH_2{\cdot}\overset{(-)}{C}HR + NH_3 \longrightarrow NH_2{\cdot}[CH_2{\cdot}CHR]_n{\cdot}CH_2{\cdot}CH_2R + NH_2^- \quad (\textit{Termination})$$

Sanderson and Hauser (*loc. cit.*) have suggested a similar reaction mechanism.

The main purpose of the work here described has been the verification of the above reaction scheme in one specific case. Styrene was selected as a suitable monomer since here side reactions proved to be unimportant.

Experimental

1. *Materials.—Styrene.* The commercial product was washed twice with 10% sodium hydroxide solution, then six times with distilled water. After drying ($CaCl_2$), the monomer was distilled under water-pump vacuum in a stream of dry, oxygen-free nitrogen, at about 30°. The purified styrene, which was prepared in small quantities as required, was tested for polymer

by dilution in excess of pure methanol before use; small amounts of polymer cause a turbidity in the solution.

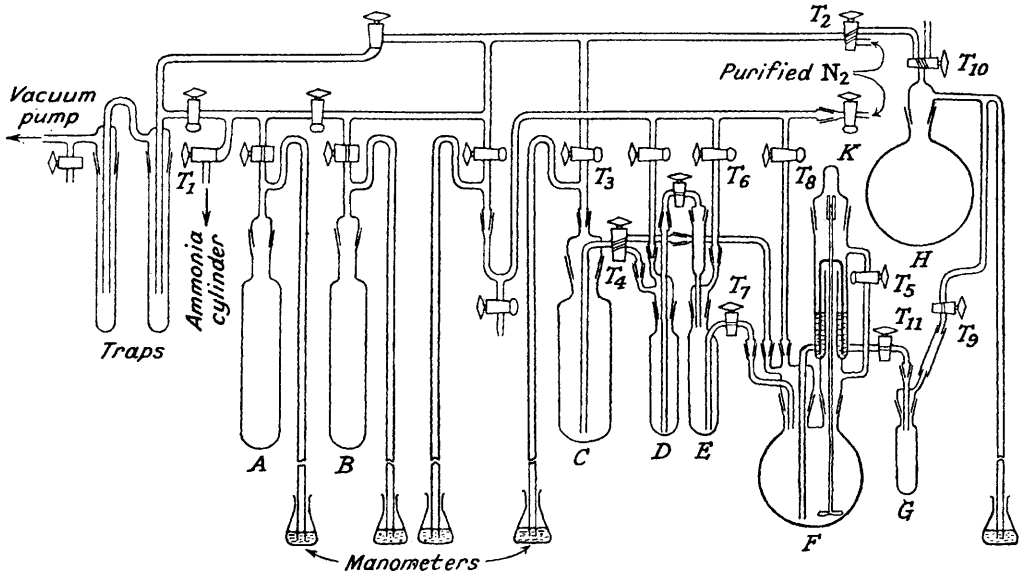
Toluene and light petroleum (b. p. 40—60°) were purified by distillation and stored over metallic potassium.

For freezing-point determinations, spectroscopic *cyclo*hexane (m. p. 2·4°) was purified by fractional crystallisation, and was then fractionally distilled over sodium through a 14″ glass column, the 80·5—80·8° fraction being retained (m. p. 4·8°; lit., 6·5°).

Benzene for viscosity determinations was either " molecular weight benzene, cryoscopically pure " or " AnalaR " grade.

Iodine monochloride reagent was prepared in 0·1M-solution by dissolving the appropriate amount of pure iodine monochloride in glacial acetic acid. Alternatively, chlorine was passed slowly into a cooled 0·1N-solution of iodine in glacial acetic acid, until the titration against sodium thiosulphate solution was almost doubled. A slight excess of iodine remained, but was preferable to an excess of chlorine, for in the latter case irreproducible results were obtained in

FIG. 1.



the determination of styrene. The reagent was kept in absence of light and was stable for a month.

Other reagents used were either obtained pure, or were purified by the usual methods.

Nitrogen from a cylinder was purified by slow passage through a trap surrounded by liquid air, which removed most of the moisture present, and then through three traps in series containing a concentrated solution of potassium in liquid ammonia, cooled to −78°. These traps removed any remaining moisture and also oxygen. A 2-l. bulb and mercury blow-off prevented sudden pressure fluctuations during withdrawal of pure nitrogen.

2. *Liquid Ammonia Apparatus.*—The apparatus for manipulation of liquid ammonia solutions in absence of air follows accepted practice (see, *e.g.*, Kraus and Hawes, *J. Amer. Chem. Soc.*, 1933, **55**, 2776; Laitinen and Nyman, *ibid.*, 1948, **70**, 2241; Zintl, Goubeau, and Dullenkopf, *Z. physikal. Chem.*, 1931, *A*, **154**, 1) and is shown in Fig. 1. Those parts of the apparatus through which ammonia was passed as liquid were detachable for cleaning. Taps and joints were greased with silicone tap grease.

(a) *Purification of ammonia.* Cylinder ammonia, led in as gas through tap T_1, was condensed on to sodium in vessel *A*, which was cooled to −78° (approx.) by acetone–solid carbon dioxide. By warming *A* and cooling *B* ammonia was then distilled into vessel *B*, which also contained metallic sodium. The ammonia was then distilled into the storage vessel *C*. Two such distillations from sodium were found adequate to free the ammonia from water and oxygen, both of which can react with potassium amide or with carbanions in liquid ammonia. From *C*

the ammonia can be either distilled into vessels *D*, *E*, or *F*, or forced directly into *D* or *F* by application of a pressure of pure nitrogen through taps T_2 and T_3 to vessel *C*, the receiving vessel being cooled.

(b) *Preparation of the potassium amide solutions.* An appropriate quantity of pure potassium (0·1—5·0 g.), cut free from contaminated surfaces, was weighed under toluene and transferred to flask *E* under light petroleum (b. p. 40—60°). A small amount of baked platinised asbestos (5% Pt, as supplied by B.D.H. Ltd.) wrapped in platinum gauze was added as catalyst for amide formation.

The light petroleum was pumped off, and ammonia distilled from *C* up to a previously determined mark in *E*. In absence of moisture and oxygen, potassium amide formed slowly during several hours at −33·5°, and at complete conversion a clear, pale yellow solution remained. The presence of moisture or oxygen resulted in a cloudy solution due to the formation of insoluble potassium hydroxide or potassium peroxide and the rate of disappearance of the blue colour of the potassium solution was comparatively rapid. Potassium amide solutions thus contaminated were rejected.

(c) *Preparation of solutions of styrene in liquid ammonia.* Solutions of styrene were prepared in *F* by pipetting in the appropriate quantity of purified styrene, which was then frozen at −78°. After evacuation, liquid ammonia was passed in from *C* through tap T_4 up to a predetermined mark. The temperature was then altered to −33·5°, the ammonia pressure then being equal to that of the atmosphere. Tap T_5 on the mercury-seal stirrer was now closed, cap *K* removed, and the stirrer operated by connecting it with a flexible metal drive. When the solid styrene had dissolved, the temperature was lowered if necessary to the appropriate value (between −33·5° and −64°), and the pressure kept at 1 atm. with nitrogen. A Dewar vessel surrounding the reaction vessel *F* was fitted with a copper circulating coil through which acetone at −78° was continually pumped. Thermostatic control could be effected at any temperature from −70·0° upwards by a heating coil controlled by a " Sunvic " type TS3 bimetallic strip regulator. The temperature variation measured on a standard pentane thermometer was ±0·5°.

(d) *Production of polymer samples for molecular-weight determination.* With the styrene dissolved, the stirrer was disconnected, and after nitrogen had blown out through the seal for several minutes, cap *K* was replaced and T_5 opened. Application of a small excess pressure of nitrogen through T_6 with, if necessary, slight suction applied to *F* enabled a suitable amount of potassium amide solution to be transferred from vessel *E* through T_7 into *F*. Tap T_7 was closed, and the pressure in *F* brought up to that of the atmosphere with nitrogen through T_8. The stirrer was connected as before, and the mixture continually stirred. After an appropriate time, solid ammonium chloride was added through a stoppered side tube (not shown in diagram) to vessel *F*. The mixture was stirred for several minutes to allow neutralisation of the potassium amide, and then the stirrer was disconnected, cap *K* replaced, the Dewar vessel removed, and the ammonia distilled back to vessel *A*.

(e) *Kinetic experiments.* The potassium amide solution was added to the styrene solution as described above. At the same time a stop-watch was started. Vessel *G* contained 1 g. of solid ammonium nitrate and was immersed in acetone–solid carbon dioxide (−78°) and evacuated through T_9 and T_{10}. After a suitable time T_{10} was closed and T_{11} opened. In ten seconds about 20—40 ml. of the reaction mixture passed over into *G*, and the ammonium nitrate immediately stopped the reaction by neutralising the potassium amide. The pressure in *F* remained constant as nitrogen at 1 atm. pressure had access to this vessel through T_8. No liquid remained in the tube connecting *F* and *G* after sampling, for on closure of T_{11} the ammonia near this tap boiled and blew the solution back into *F* and *G* respectively. After sampling, the cooling bath was removed from *G*, and the pressure brought up to that of the atmosphere through T_{10}; *G* was then removed and replaced by a similar vessel, also containing 1 g. of ammonium nitrate, which was evacuated ready for taking the next sample. The amount of the reaction sample was determined to ±2% by measuring the height of the liquid in the calibrated vessel *G*. The contents of *G* were transferred to a cooled, 500-ml., conical flask and *G* was then washed three times with pure chloroform, the washings being added to the bulk liquid in the conical flask. Ammonia was allowed to boil off in a fume cupboard, and the sample analysed for styrene as described below. With this procedure samples could be taken every two minutes if required. The volume of reaction mixture before sampling was 400—500 ml. and up to 15 samples were taken in each kinetic experiment. Values for the initial styrene concentration could be obtained by taking a sample before adding the potassium amide solution: the above procedure was used except that ammonium nitrate in *G* was not necessary.

The values thus found agreed well with those obtained from the volumes of styrene and liquid ammonia used.

3. *Molecular-weight Determinations.*—(a) *Purification of polymer.* After polymerisation, the ammonia was distilled off and the polystyrene and unchanged styrene remaining in vessel *F* were dissolved in a total of 60 ml. of ethyl methyl ketone. The solution was stirred mechanically, and *F* was washed with 60 ml. of water, the washings being added to the ethyl methyl ketone solution; 400 ml. of methanol were then added slowly, and stirring was continued for two hours. The precipitated polymer was collected on a sintered filter, washed with water and methanol, and then redissolved through the filter with 60 ml. of ethyl methyl ketone. This solution was mechanically stirred, and 600 ml. of methanol followed by 100 ml. of water were added slowly. After 2 hours' stirring, 5 g. of potassium chloride were added, and stirring was continued for a further 2 hours. The polymer was then filtered off, washed thoroughly with water and with methanol, and then dried (P_2O_5) in high vacuum for 48 hours.

(b) *Viscosity determinations.* Viscosity determinations were made at 25° in benzene as solvent, an Ostwald viscometer, B.S.S. type, No. 1, being used. Solutions of polymer were prepared by weighing the requisite amount, less than 1 g. per 100 ml. of benzene, into a standard flask. The solutions were kept at 25° before being made up to the mark, and before use, 10 ml. of solution were pipetted into the viscometer, which was held vertically in a clamp fitted with a spirit-level and adjusting screws. The time of flow was taken with a $\frac{1}{5}$-second stop-watch. The average of five determinations with a given solution was taken, and two separate solutions were made up for each concentration of a particular polymer sample. The time of flow of the pure benzene was also determined.

(c) *Nitrogen determinations.* Nitrogen in the polymer was determined by the standard Kjeldahl method. A mixed catalyst of 0·25 g. of metallic selenium with 0·25 g. of copper sulphate was used in the conversion of nitrogen in the polymer into ammonium sulphate by ashing with concentrated sulphuric acid. The amount of polymer used was not less than 0·4 g. The ammonia was distilled into a known excess of 0·01N-sulphuric acid, and the solution back-titrated with 0·01N-sodium hydroxide solution, bromocresol-green being used as indicator.

(d) *Freezing-point determinations.* The freezing-point apparatus consisted of a 3-cm. diameter tube fitted with a stirrer and Beckmann thermometer, and was held by a cork ring in an 8-cm. diameter tube. The latter was immersed in an ice–water mixture which was mechanically stirred. The freezing point was determined from the cooling curves, the rate of cooling at 3·5° being approximately 0·05° per min. The molecular depression constant for 100 g. of the solvent used, *cyclo*hexane (m. p. 4·8°), was determined as 204·7 (±1·0) by using pure naphthalene [compare the value of 201·5 for pure *cyclo*hexane (m. p. 6·5°)]. Polymer solutions were examined at several concentrations, from 0·8 to 3·4 g. of polymer per 100 g. solvent.

4. *Determination of Unchanged Styrene in the Presence of Polymer.*—The usual bromine method for the determination of styrene (Ulrig and Levin, *Ind. Eng. Chem. Anal.*, 1941, **13**, 90) was inapplicable to the polystyrene–styrene mixtures obtained during kinetic experiments, high and irreproducible values being obtained. Experiments showed that 2-phenylethylamine, the simplest compound obtained by the attack of potassium amide on styrene in liquid ammonia, reacted slowly with bromine under the conditions of the estimation. However, the iodine chloride method of determining vinyl groups (see, *e.g.*, Jeu and Alyea, *J. Amer. Chem. Soc.*, 1933, **55**, 575) was found to give exact and reproducible results for styrene even in the presence of similar amounts of 2-phenylethylamine and of a large excess of ammonium acetate. On the other hand, the polymer, freed from styrene and the lower molecular weight polystyrenes (up to about tetramer) by the precipitation procedure described above, showed no sign of unsaturation even when bromine in chloroform–acetic acid was used as solvent. The average molecular weight was sufficiently low to enable one ethylenic link per polymer chain to be detected.

The procedure adopted for determining unchanged styrene in the kinetic experiments was as follows. A conical flask containing the sample, dissolved in chloroform and saturated with ammonia, was cooled to −50°, and glacial acetic acid added slowly with continuous shaking till present in excess. After this had attained room temperature, an approximately 50% excess of 0·1M-iodine monochloride reagent was added, and the stoppered flask kept for 15 minutes with occasional shaking. Low results were obtained if the time of standing was less than 10 minutes; 10—30 minutes' standing gave reproducible results. At the end of the 15 minutes a small excess of 10% aqueous potassium iodide solution was added, and liberated iodine titrated against 0·1N-sodium thiosulphate solution. For each set of samples analysed, blank titrations

were done in duplicate to standardise the iodine chloride solution, the same conditions being used except for the absence of reaction mixture.

It was thus possible to determine styrene in amounts of 0·1 g. and over with an accuracy of ±3%. The most dilute samples determined were approximately 0·01M in styrene, and as for these samples 40 ml. of the reaction mixture were taken, the amount of styrene determined was about 0·04 g.; here the error was ±10%, *i.e.*, ±0·004 g. of styrene, approximately the same as the error found in determining larger quantities of styrene.

5. *Conductivity Measurements.*—A 500-ml. flask fitted with platinum electrodes of approximately 1 sq. cm. area and 0·5 cm. apart was used as a conductivity cell and was attached to the liquid-ammonia apparatus in the same manner as vessel *F*. The electrodes were platinised according to Popoff, Kunz, and Snow's procedure (*J. Physical Chem.*, 1928, **32**, 1056). After being washed with water they were dried by washing with ethanol and then with dry ether.

Potassium amide solutions were prepared in the conductivity vessel by using known amounts of metallic potassium and liquid ammonia. The platinised electrodes served as catalyst for the conversion of the potassium solution into potassium amide. Measurements were made in the low-temperature thermostat described above.

The resistance of the solution was determined by using an A.C. bridge fitted with a variable condenser for balancing stray capacitance. The oscillator provided 5 v at 1000 cycles per second. The detector circuit consisted of an amplifier giving a D.C. output fed to a "magic eye" indicator for rough balancing and to a D.C. galvanometer for more precise adjustment.

Results

1. *Molecular Weights.*—(a) *Molecular weights by viscosity measurements.* The intrinsic viscosity, $[\eta]$, can be found by extrapolation of plots of either $(\eta \text{ spec.})_c/c$ against c or $\ln (\eta \text{ rel.})_c/c$ against c to infinite dilution. Here $(\eta \text{ spec.})_c$, the specific viscosity at concentration c, is $[(\eta \text{ solution})_c - (\eta \text{ solvent})]/(\eta \text{ solvent})$, and $(\eta \text{ rel.})_c$, the relative viscosity at concentration c, is $(\eta \text{ solution})_c/(\eta \text{ solvent})$. As $(\eta \text{ spec.})_c/c$ increases with increase in c while $\ln (\eta \text{ rel.})_c/c$ decreases with c, $[\eta]$ can be found if c is small by taking the arithmetic means of $(\eta \text{ spec.})_c/c$ and $\ln (\eta \text{ rel.})_c/c$ (cf. Baxendale, Bywater, and Evans, *J. Polymer Sci.*, 1946, **1**, 241). This procedure was used here. In a few cases values of $[\eta]$ were found from measurements at more than one concentration between 0·2 and 0·8 g. of polymer per 100 ml. of solution in benzene. The largest difference found between any two values of the intrinsic viscosity for a given polymer sample was less than 10%, and in one or two cases differences of this magnitude were found between intrinsic viscosities obtained from solutions of similar concentrations.

In Table 1 are tabulated the intrinsic viscosity $[\eta]$ and the corresponding weight-average molecular weight W calculated by using the Staudinger equation constant of Kemp and Peters (*Ind. Eng. Chem.*, 1942, **34**, 1097) for low molecular weight polystyrenes. For the concentration units used here (c = g. of polymer per 100 ml. of solution in benzene), $K = 3{\cdot}6 \times 10^{-5}$. In addition, molecular-weight values obtained by using Bamford and Dewar's constants (*Proc.*

Table 1. *Molecular weights from viscosity, nitrogen content, and freezing-point depression measurements.*

Sample from expt.	$[\eta]$	Viscosity mol. wts. ($\overline{W}$) *: K. & P.	B. & D.	Number average mol. wts. ($\overline{N}$): N content	F.-p. depn.	Sample from expt.	$[\eta]$	Viscosity mol. wts. ($\overline{W}$.) *: K. & P.	B. & D.	Number average mol. wts. ($\overline{N}$): N content	F.-p. depn.
MW	0·0418	1160	1110	—	—	MH	0·0806	2240	3040	2180, 2800	2200
MA	0·0515	1430	1520	—	—	MG	0·0825	2290	3150	1980, 2180	2625
MX	0·0540	1500	1640	1410	—	MN	0·0856	2380	3360	2400, 2450	—
MB	0·0558	1550	1720	—	—	MQ	0·0882	2450	3480	—	—
NA	0·0591	1640	1880	—	2050	MD	0·0887	2460	3510	—	—
MR	0·0595	1650	1890	—	—	MF	0·0907	2520	3640	—	—
NB	0·0649	1800	2170	2630, 2700	<3000	ML	0·0962	2670	4000	—	—
MC	0·0703	1950	2450	—	—	MP	0·1016	2820	4330	—	—
ME	0·0735	2040	2630	2270, 2880	—	ND	0·1180	3280	5480	3700	—
MT	0·0739	2050	2650	—	—	MU	0·1184	3290	5500	—	—
MS	0·0752	2090	2730	—	—	MJ	0·1230	3410	5820	3320	—
NC	0·0768	2130	2820	2880, 3190	2760	MK	0·1310	3640	6410	3020, 3400	—
MM	0·0774	2150	2840	—	—	MV	0·1531	4250	8150	—	—

* K. & P. = Kemp and Peters (*loc. cit.*); B. & D. = Bamford and Dewar (*loc. cit.*).

Roy. Soc., 1948, *A*, **192**, 329) are tabulated. These authors use Mark and Houwink's modification of the original Staudinger equation and find $K = 4{\cdot}39 \times 10^{-4}$, c being expressed in the same units as above and β, the molecular-weight exponent, being taken as 0·65; these values appear to be applicable to low molecular weight polystyrenes.

(b) *Molecular weights by nitrogen determination.* The molecular weights found by nitrogen determination in the polymer are also recorded in Table 1. They have been calculated by assuming one nitrogen atom per polymer molecule.

(c) *Molecular weights by freezing-point depression.* The molecular weight of 2-phenylethylamine as calculated from the depression of freezing point of *cyclo*hexane was found to increase with concentration. Linear extrapolation to zero concentration led to a value of 119·8 (Calc. : 121·2). A few polymer molecular weights were determined in this way and are recorded in Table 1. Two freezing-point depression measurements at each of several different concentrations were made and extrapolated to zero concentration. The concentrations varied between 0·7 and 3·4 g. of polymer per 100 g. of *cyclo*hexane. The method was limited to polymer samples of molecular weight below about 3000. Above this figure the polymer was found to be incompletely soluble in *cyclo*hexane.

Although the accuracy of the molecular weights by freezing-point depression and by nitrogen content determination is not high, comparison shows a fair agreement, much better than that obtained by assuming two nitrogen atoms per polymer molecule in calculating the molecular weight from nitrogen content, which would give double the molecular weights tabulated. This correlation between the two sets of figures, both number-average molecular weights, may be taken as evidence for one nitrogen atom per polymer chain. The two sets of viscosity molecular weights, derived from the same values of $[\eta]$, but using different intrinsic viscosity–molecular weight relationships may now be compared with the molecular weights by nitrogen content. In general, the weight-average and the number-average molecular weights of an unfractionated polymer sample are not identical. For these polymers, however, up to a molecular weight of about 2500—3000 both sets of viscosity (weight-average) molecular weights are in reasonable agreement with the nitrogen content (number-average) molecular weights. Above this value, although fair agreement between the molecular weights found by using Kemp and Peters's constants and the molecular weights found by nitrogen content determination is still apparent, yet the corresponding values found by using Bamford and Dewar's constants are very much larger. The values based on the work of Kemp and Peters have therefore been chosen, as it seems probable that the agreement between number-average and weight-average molecular weights found at the lower molecular weights would still be found at the higher molecular weights.

Conductivity Measurements : Variation of the Dissociation Constant of Potassium Amide with Temperature.—Although $K_{\text{diss.}}$ for potassium amide in liquid ammonia has been accurately measured at −33·5° (Hawes, *J. Amer. Chem. Soc.*, 1933, **55**, 4422), no measurements have been made at lower temperatures. The purpose of the conductivity measurements was to determine the approximate magnitude of the variation with temperature.

In the calculation of the dissociation constant of potassium amide from conductivity measurements, extrapolation of the equivalent conductivity to infinite dilution is valueless unless measurements of high accuracy at concentrations lower than 10^{-3}M have been made (see Fuoss and Kraus, *ibid.*, p. 487). On the other hand, 10^{-3}M-potassium amide is the lowest concentration for which reasonably accurate measurements can be made without recourse to laborious high-precision work of the type described by Hnizda and Kraus (*ibid.*, 1949, **71**, 1565). However, we may in general assume that the equivalent conductivity at infinite dilution of a given solute at a particular temperature is inversely proportional to the viscosity of the solvent at the same temperature (Walden, *Z. physikal. Chem.*, 1912, **78**, 257). Thus, provided that Λ_0 is known at a given temperature and the temperature dependence of the solvent viscosity is known, Λ_0 can be calculated for any temperature.

Hawes (*loc. cit.*) has found the value 343 mhos for $(\Lambda_0)_{KNH_2}$ at −33·5°, and Fredenhagen (*Z. anorg. Chem.*, 1930, **186**, 13) and Monosson and Pleskov (*Z. physikal. Chem.*, 1931, *A*, **156**, 192) have determined the viscosity of liquid ammonia at various temperatures from −33·5° to −69°. Hence, for an approximate measure of the temperature variation of $K_{\text{diss.}}$ it is necessary only to take conductivity measurements at a potassium amide concentration of about 10^{-2}M, where reasonable accuracy is possible and no extrapolation to infinite dilution is needed. Since only approximate $K_{\text{diss.}}$ values are required, the Ostwald dilution law may be used provided the concentration of potassium amide is not too high.

The conductivity of solutions of potassium amide in liquid ammonia was determined at

$-33{\cdot}5°$, $-45°$, $-60°$, and $-70°$ at six different concentrations between $1{\cdot}7 \times 10^{-3}$ and $2{\cdot}79 \times 10^{-2}$M. Measurements were made at each of the four temperatures, the same solutions being used. Over this range of concentrations a plot of $(\Lambda_c)_T$ against $(\sqrt{c})_T$ is approximately linear (cf. Fuoss and Kraus, *loc. cit.*), though, as mentioned previously, the extrapolation of such a plot to zero concentration yields an incorrect value for $(\Lambda_0)_T$. From these linear plots the value of $(\Lambda)_T$ at a concentration of 10^{-2}M-potassium amide was taken, and with the appropriate values of $(\Lambda_0)_T$ the use of the Ostwald dilution law enables $(K_{\text{diss.}})_T$ to be calculated (Table 2).

TABLE 2.

Temp.	$-33{\cdot}5°$	$-45°$	$-60°$	$-70°$
$(\eta)_T$, centipoise	0·260	0·304	0·383	0·486
$(\Lambda_0)_T$, mhos	343	287	228	191
$(\Lambda_{c=0{\cdot}01})_T$, mhos	33·0	31·0	26·0	22·5
$10^4\ (K_{\text{diss.}})_T$	1·02	1·31	1·47	1·57

A value of $c = 0{\cdot}01$ was taken as being the lowest possible consistent with reasonable accuracy in c. Higher values of c were not used in the calculation since, the Ostwald dilution law being used, the effect of ionic strength on ionic mobility would lead to greater inaccuracy in $K_{\text{diss.}}$.

We see from Table 2 that $K_{\text{diss.}}$ varies little with temperature from $-33{\cdot}5°$ to $-70°$. This small temperature dependence of $K_{\text{diss.}}$ is probably not significant in view of the approximate nature of these results and we conclude that $(\Delta H)_{\text{diss.}} = 0 \pm 2$ kcal./mole. The value of $1{\cdot}02 \times 10^{-4}$ for $K_{\text{diss.}}$ at $-33{\cdot}5°$ compares with $7{\cdot}0 \times 10^{-5}$ (Franklin, *Z. physikal. Chem.*, 1909, **69**, 290) and $7{\cdot}3 \times 10^{-5}$ (Hawes, *loc. cit.*). The latter value is probably the most accurate recorded and is used throughout this work over the temperature range $-33{\cdot}5°$ to $-70°$.

General.—(a) *Molecular weights.* (i) Dependence of weight-average molecular weight on the concentrations of potassium amide, amide ion, and potassium ion. The figures in Table 3 show

TABLE 3.

Temperature = $-33{\cdot}5°$.

Expt.	Viscosity mol. wt.	$[C_8H_8]$,* mole/l. $\times 10^2$	$[KNH_2]$, mole/l. $\times 10^2$	[KI], mole/l. $\times 10^2$	$[K^+]$, mole/l. $\times 10^3$	$[NH_2^-]$, mole/l. $\times 10^3$	Formation of visible polymer
MW	1160	9·0	1·54	5·50 †	13·06	0·086	Slow
MX	1500	11·3	1·64	1·96 †	7·13	0·168	Slow
MC	1950	9·7	1·34	—	0·99	0·99	Immediate
MB	1550	9·5	4·96	—	1·90	1·90	Immediate
MA	1430	8·45	6·48	—	2·17	2·17	Immediate

* In this and later tables, C_8H_8 is used for styrene.

† The potassium-ion concentration in MW and MX was calculated by using the value of $4{\cdot}067 \times 10^{-3}$ for the dissociation constant of potassium iodide at $-34°$ (Hnizda and Kraus, *loc. cit.*).

that the molecular weight is relatively unaffected by the concentration of the amide ion or of undissociated potassium amide, the deviations being apparently random. Experiments MW, MX, and MC also show that the presence of different amounts of potassium ion has no marked effect on the molecular weight.

(ii) Dependence of weight-average molecular weight on concentration of styrene. In Table 4 are shown the results of experiments in which the concentration of potassium amide was kept roughly constant, while that of styrene was varied. It can be seen (Fig. 2) that the molecular weight shows an approximately linear dependence on the initial styrene concentration up to about 0·3M-styrene. At concentrations greater than this, the linear relationship breaks down and the molecular weights are very much lower than would be expected.

It will be noted that the percentage yield of polymer increases with the initial concentration of styrene. This is to some extent due to the higher proportion of low molecular weight polymer separated with unchanged styrene after reaction in the experiments at lower initial styrene concentrations. The rate of polymerisation is lower in the low styrene concentration experiments, but this was partly offset by increasing the time of polymerisation from 25 minutes for the more concentrated solutions to 60 minutes for the more dilute. A constant percentage conversion of styrene was not attained in these experiments, as this requires a knowledge of the rate of disappearance of styrene and the corresponding kinetic experiments were done subsequently.

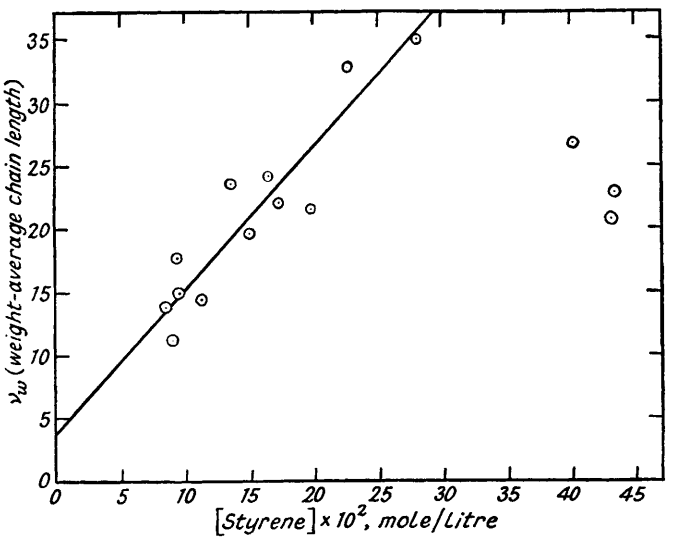
TABLE 4.

Temperature = − 33·5°.

Expt.	$[C_8H_8]$, mole/l. × 10^2	$[NH_2^-]$, mole/l. × 10^3	Approx. yield, % *	W	ν_w †	$\overline{W}$ (B. & D.)
MA	8·45	2·13	26·5	1430	13·75	1520
MW	9·0	0·09	—	1160	11·1	1110
MB	9·5	1·86	38·5	1550	14·9	1720
MC	9·7	0·97	35·0	1950	18·75	2450
MX	11·3	0·17	—	1500	14·4	1640
MD	13·5	0·94	50·0	2460	23·65	3510
ME	15·0	0·86	66·5	2040	19·6	2630
MF	16·55	1·28	43·5	2520	24·2	3640
MG	17·3	0·92	68·0	2290	22·0	3150
MH	19·8	0·97	76·0	2240	21·55	3040
MJ	22·7	0·86	62·0	3410	32·8	5820
MK	28·2	0·65	76·5	3640	35·0	6410
ML	40·2	0·93	83·0	2670	25·67	4000
MM	43·2	0·77	—	2150	20·67	2840
MN	43·5	0·97	82·0	2380	22·9	3360
MP	62·5	0·88	81·0	2820	27·1	4330
MQ	65·1	0·97	86·0	2450	23·55	3480

* Measured on polymer separated by precipitation procedure.
† Weight-average chain length.

FIG. 2.



Under otherwise equivalent conditions there appeared to be a small decrease in the molecular weight of the polymer as the time of reaction was increased, *i.e.*, the molecular weight decreased slightly with increased yield of polymer. This effect was barely greater than the overall experimental error of the polymerisation experiments. Sanderson and Hauser (*loc. cit.*) have observed similar behaviour in the styrene–sodium amide–liquid ammonia system.

(iii) Dependence of the weight-average molecular weight on temperature. In the case of the molecular weights determined at temperatures lower than −33·5°, recorded in Table 5, the corresponding kinetic measurements had been made previously and it was therefore possible by adjusting the time of reaction to ensure 50% reaction in each case, with a corresponding yield of polymer of rather less than this figure. These results show that the molecular weight increases with decrease in temperature, a drop of 25° causing a 2—3-fold increase in W.

(b) *Kinetic results.* (i) Dependence of rate of disappearance of styrene on styrene concentration. In Table 6 are summarised the results of six kinetic experiments at −33·5° in which the concentration of potassium amide was kept constant and the initial styrene concentration was varied. It was found that the rate of disappearance of styrene was of second order with respect to the styrene concentration, as good linear plots of $1/[\text{Styrene}]_t$

against t were obtained (Fig. 3). Other kinetic expressions led to curved plots of the appropriate function of the styrene concentration against time.

TABLE 5.*

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
From gradient of Fig. 2		−33·5°	—	—	—	—	5·28	—	3·7226	—	4·171
MR	½	−33·5	10·2	1·01	1650	15·85	5·58	4·28	3·7463	3·6316	4·171
MS	¾	−36·0	12·5	1·13	2090	20·05	6·16	4·63	3·7898	3·6653	4·215
MT	3	−44·0	8·6	0·91	2050	19·7	8·76	6·59	3·9426	3·8186	4·363
MU	6	−54·0	10·0	0·93	3290	31·6	13·24	9·60	4·1221	3·9823	4·562
MV	9¼	−59·0	10·9	1·00	4250	40·8	16·20	11·52	4·2096	4·0614	4·669

* *Key*: Col. I, Expt.
,, II, Time of reaction (hrs.) for 50% conversion.
,, III, Temperature (°c.).
,, IV, Initial styrene concn., moles/l. × 10^2.
,, V, $[KNH_2]$, moles/l. × 10^2.
Col. VI, $\overline{W}$.
,, VII, Average chain length, ν_w.
,, VIII, $k_p/k_t \times 10^{-3}$ (equation 11).
,, IX, $k_p/k_t \times 10^{-3}$ (,, 10).
,, X, log k_p/k_t (,, 11).
,, XI, log k_p/k_t (,, 10).
,, XII, $10^3/T$.

FIG. 3.

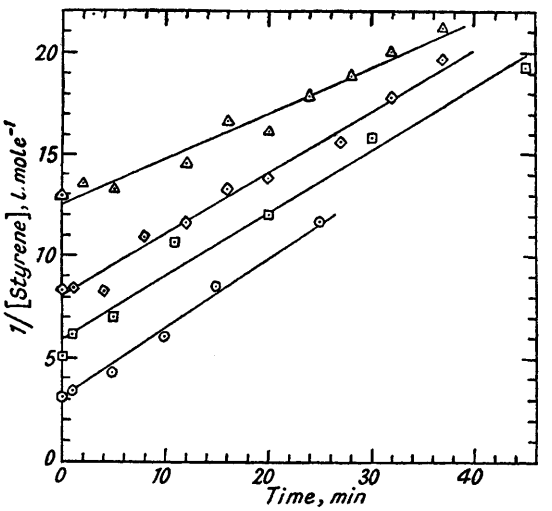


TABLE 6.

Temperature = − 33·5°.

Expt.	Initial $[C_8H_8]$, mole/l. × 10^2	$[KNH_2]$, mole/l. × 10^2	$[NH_2^-]$, mole/l. × 10^3	$d(1/[C_8H_8])/dt$, l. mole^{-1} min.$^{-1}$
KA	5·75	1·15	0·88	0·357
KB	11·90	1·25	0·92	0·300
KC	14·35	1·00	0·82	0·233
KD	19·70	1·02	0·83	0·317
KE	21·80	1·07	0·85	0·248
KF	32·40	1·23	0·91	0·328

TABLE 7.

Temperature = − 33·5°.

Expt.	Initial $[C_8H_8]$, mole/l. × 10^2	$[KNH_2]$, mole/l. × 10^2	$[NH_2^-]$, mole/l. × 10^3	Slope = $d(1/[C_8H_8])/dt$, l. mole^{-1} min.$^{-1}$	k' = Slope / $[KNH_2]^{\frac{1}{2}}$	k'' = Slope / $[NH_2^-]$
KG	9·80	0·36	0·48	0·100	1·67	208
Average of KA to KF	5·75—32·4	1·12 (av.)	0·87 (av.)	0·297	2·81	342
KB	11·90	1·25	0·92	0·301	2·69	326
KH	9·60	9·4	2·58	1·185	3·86	458
KJ	9·23	15·1	3·29	1·420	3·65	431
KK	9·90	22·3	4·00	1·815	3·84	453

(ii) Dependence of rate on potassium amide and amide ion concentrations. To determine the dependence of the rate on potassium amide concentration, experiments were done in which the concentration of potassium amide was varied from $3{\cdot}6 \times 10^{-3}$ to 0·223M. These are recorded in Table 7. Plots of the slopes of these reaction plots against the square root of the potassium amide concentration and against the amide-ion concentration are shown in Figs. 4*a* and 4*b*. Fairly good straight lines are obtained. The overall kinetic expression can thus be written as

$$\mathrm{d[Styrene]}/\mathrm{d}t = -k'[\mathrm{Styrene}]^2[\mathrm{KNH_2}]^{\frac{1}{2}}$$

or

$$\mathrm{d[Styrene]}/\mathrm{d}t = -k''[\mathrm{Styrene}]^2[\mathrm{NH_2^-}]$$

Since under the experimental conditions $[\mathrm{NH_2^-}]^2 \simeq K_{\mathrm{diss.}} \times [\mathrm{KNH_2}]$, it is not possible to differentiate between these two expressions on experimental grounds and they do not necessarily imply the same detailed kinetic mechanism. Reasons for preferring the second expression will be given later.

FIG. 4*a*.

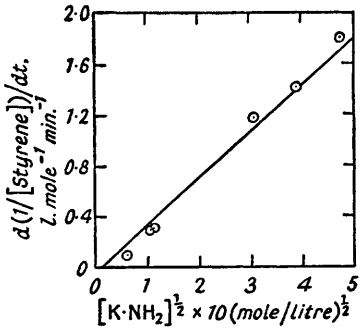
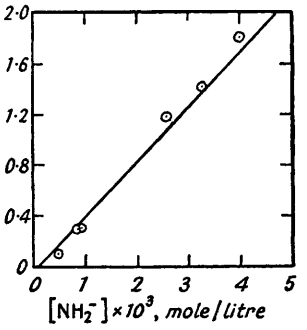


FIG. 4*b*.



(iii) The dependence of the rate of the reaction on the temperature was investigated over the temperature range −33·5° to −64° and the results are summarised in Table 8. The

TABLE 8.

Expt.	Initial $[C_8H_8]_2$, mole/l. × 10^2	$[NH_2^-]$, mole/l. × 10^3	Temp.	$10^3/T$	k''	$\log_{10} k''$
Average of KA to KF	5·75—32·4	0·87 (av.)	−33·5°	4·171	342	2·534
KB	11·9	0·92	−33·5	4·171	326	2·513
KL	10·0	0·74	−35·0	4·198	280	2·447
KM	12·95	0·90	−39·0	4·270	177	2·248
KN	10·55	0·76	−44·0	4·363	97	1·987
KP	9·77	0·74	−49·0	4·460	121	2·083
KQ	11·69	0·79	−54·0	4·562	63	1·799
KR	10·65	0·71	−59·0	4·669	46	1·663
KS	12·0	0·82	−64·0	4·780	16·5	1·218

corresponding Arrhenius line (Fig. 5) shows that the overall activation energy for the polymerisation reaction is 8·8 ± 2·0 kcal./mole.

(iv) The rate of styrene disappearance at high monomer concentrations. The linear dependence of average molecular weight on initial styrene concentration only holds up to a concentration of 0·3M-styrene and two kinetic experiments summarised in Table 9 were done at initial styrene concentrations above this value to see if the kinetic behaviour was also anomalous. In such experiments sampling and stirring were difficult, as the heavy precipitate of polymer caused the reaction mixture to assume a thick, mud-like consistency. The plots of 1/[Styrene] against time show that the reaction was initially of the second order with respect to styrene concentration, but particularly in the case of the experiment at higher styrene concentration, there was a noticeable falling off in the reaction rate after about two-thirds reaction. The

TABLE 9.

Temperature = − 33·5°.

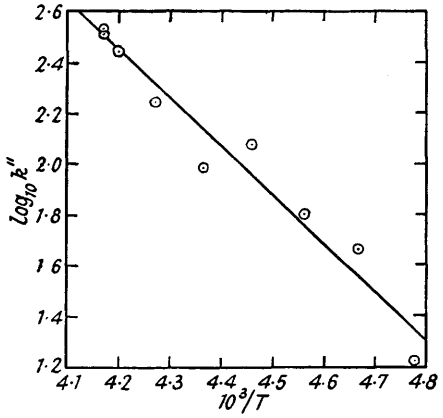
Expt.	Initial $[C_8H_8]$, mole/l. × 10^2	$[NH_2^-]$, mole/l. × 10^3	k''
KT	38·35	0·88	138
KU	58·1	0·81	135
Average of KA to KF	5·75—32·4	0·87 (av.)	342 (av.)

value of k'' calculated from the linear part of the plots was less than half that to be expected for the reaction at $-33{\cdot}5°$.

Discussion

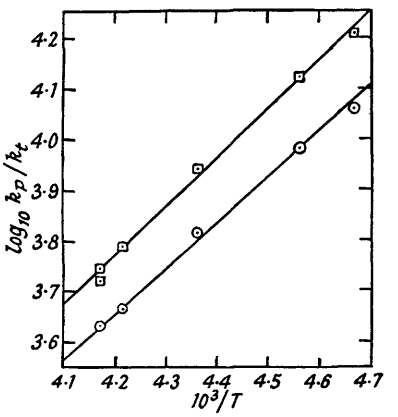
The main features of the polymerisation in dilute solutions of the reagents (up to 0·3M-styrene and 0·25M-potassium amide) may be summarised as follows. (*a*) The polymer contains one nitrogen atom per polymer molecule. (*b*) The polymer chain is saturated. (*c*) The molecular weight of polymer produced is independent of the potassium amide concentration and of the amide-ion concentration. (*d*) The molecular weight at constant conversion is independent of the potassium-ion concentration. (*e*) The molecular weight depends linearly on the initial styrene concentration up to 0·3M-styrene. (*f*) The molecular weight decreases slightly with increasing degree of conversion of monomer into polymer. (*g*) The molecular weight increases with a decrease in temperature. (*h*) The rate expression for consumption of styrene is $d[\text{Styrene}]/dt = k'[\text{Styrene}]^2[KNH_2]^{\frac{1}{2}} = k''[\text{Styrene}]^2[NH_2^-]$. (*i*) For a given potassium amide concentration the time of formation

FIG. 5.



$E = 8{\cdot}8 \pm 2{\cdot}0$ *kcal./mole.*

FIG. 6.



$E_p - E_t = 4{\cdot}4$ *kcal./mole (simple equation).*
$E_p - E_t = 4{\cdot}15$ *kcal./mole (full equation).*

of visible polymer decreases greatly with increase in potassium-ion concentration for a given potassium amide concentration. (*j*) The rate of reaction decreases with a decrease in temperature. (*k*) Consumption of potassium amide during the polymerisation is small, possibly nil (see below).

Plausible mechanisms which can be suggested for the polymerisation all involve the same initiation and propagation reactions, *i.e.* :

$$(I, a)\quad (K^+)NH_2^- + CH_2{:}CHPh \longrightarrow NH_2{\cdot}CH_2{\cdot}\overset{(-)}{C}HPh + (K^+) \quad (\textit{Initiation})$$

$$(P)\quad NH_2{\cdot}CH_2{\cdot}\overset{(-)}{C}HPh + CH_2{:}CHPh \longrightarrow NH_2{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}\overset{(-)}{C}HPh \quad (\textit{Propagation})$$

The possibility of the alternative initiation steps

$$(I, b, \text{i})\quad (K^+)NH_2^- + CH_2{:}CHPh \longrightarrow (K^+)CH_2{:}\bar{C}Ph + NH_3$$

followed by

$$(I, b, \text{ii})\quad (K^+)\overset{(-)}{C}H_2{:}CPh + CH_2{:}CHPh \longrightarrow CH_2{:}CPh{\cdot}CH_2{\cdot}\overset{(-)}{C}HPh(K^+)$$

is unlikely, for some unsaturation would be found in the polymer chain, contrary to the experimental findings.

For the termination (*T*) three alternative reactions can be suggested :

(a) *Termination by the potassium ion.* This would involve a consumption of one molecule of potassium amide for each polymer chain. On this basis, in kinetic experiments

with an initial potassium amide concentration of the order 10^{-2}M, the consumption of potassium amide after $\frac{3}{4}$ of the styrene originally present had reacted would be approximately $0{\cdot}6 \times 10^{-2}$M. The resulting change in amide-ion concentration would cause a marked curvature of the plots of 1/[Styrene] against time, but they were in nearly all cases good straight lines. In addition, experiments in which the reaction mixture was filtered after almost complete polymerisation, showed that there was little change in the potassium amide concentration in the ammonia filtrate. Though the accuracy of such experiments was not high, it was certain that any consumption of potassium amide must be very much less than one potassium amide molecule per polymer chain. Finally, termination by the potassium ion should lead to a dependence of molecular weight on the potassium-ion concentration, which did not appear experimentally.

(b) *Proton transfer from a monomer molecule, giving* $CH_2{:}\overset{(-)}{C}Ph$. The monomer anion, if formed, can react either with ammonia or with a monomer molecule, starting a second polymerisation cycle. In the latter case, as with the corresponding initiation mechanism, some unsaturation would be expected in the polymer, but none was found. As, in general, for acids of comparable strength, proton-transfer reactions in which a C–H bond is broken proceed much less easily than those involving an N–H bond, it is difficult to imagine this termination mechanism predominating over the third termination possibility (c).

(c) *Termination by proton transfer from a solvent ammonia molecule, thus* :

$$(T,c)\quad NH_2{\cdot}(CH_2{\cdot}CHPh)_n{\cdot}CH_2{\cdot}\overset{(-)}{C}HPh + NH_3 \longrightarrow NH_2{\cdot}(CH_2{\cdot}CHPh)_n{\cdot}CH_2{\cdot}CH_2Ph + NH_2^-$$

This termination mechanism does not suffer from the objections applicable to (a) and (b) and is consistent with the experimental evidence.

The effect of added potassium ions in greatly retarding the rate of formation of visible polymer, *i.e.*, in decreasing the rate of polymerisation, seems to indicate that the amide ion alone and not the potassium amide ion-pair is involved in the formation of the transition complex of the initiation step. An increase in the potassium-ion concentration for a given potassium amide concentration would greatly reduce the amide-ion concentration in solution and hence the stationary concentration of the transition complex, but is unlikely to have any great effect if the potassium ion is also present in this complex, even though salt effects are likely to be more pronounced in liquid ammonia than in water. In addition, the dependence of the rate of reaction on the square root of the potassium amide concentration, which at these concentrations is proportional to the amide-ion concentration, is also evidence in favour of the amide ion as the initiating species.

The polymerisation mechanism involving the three steps (I, *a*), (*P*), and (*T*, *c*) thus seems to be the most likely and can best be checked by comparing the experimental kinetic and molecular weight dependences on reactant concentrations with those predicted by a stationary-state treatment of the above mechanism.

The various kinetic steps in the polymerisation reaction can be represented as follows :

$$\text{Initiation}: \quad M + NH_2^- \xrightarrow{k_i} M_1^-$$

$$\text{Propagation}: \quad M_1^- + M \xrightarrow{k_p} M_2^-$$

$$M_j^- + M \xrightarrow{k_p} M^-_{(j+1)}$$

$$\text{Termination}: \quad M_r^- + NH_3 \xrightarrow{k_t} M_rH + NH_2^-$$

If it is assumed that k_p and k_t are independent of the chain length of the growing polymer, and if $M^- = \Sigma M_j^-$, application of the stationary-state condition to the concentration of active centres,

$$d[M^-]/dt = 0 = k_i[M][NH_2^-] - k_t[M^-][NH_3] \quad . \quad . \quad . \quad . \quad (1)$$

leads to

$$\frac{-d[M]}{dt} = k_i[M][NH_2^-]\left(1 + \frac{k_p[M]}{k_t[NH_3]}\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Under the experimental conditions $k_p[M]/k_t[NH_3]$ is generally large compared with unity, and within the accuracy of the kinetic experiments (2) can be simplified to

$$\frac{-d[M]}{dt} = \frac{k_i k_p}{k_t}\frac{[M]^2[NH_2^-]}{[NH_3]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{If } P_r = [M_rH],\ dP_r/dt = k_t[M_r^-][NH_3]$$

and, applying the stationary-state condition $d[M_r^-]/dt = 0$, we have

$$d[M_r^-]/dt = 0 = k_p[M][M_{(r-1)}^-] - k_p[M][M_r^-] - k_t[NH_3][M_r^-] \quad . \quad (4)$$

and

$$\frac{dP_r}{dt} = \left(\frac{k_i k_t[NH_2^-][M][NH_3]}{k_p[M] + k_t[NH_3]}\right)\left(\frac{k_p[M]}{k_p[M] + k_t[NH_3]}\right)^{r-1} \quad . \quad . \quad . \quad . \quad (5)$$

Now

$$-dP_r/d[M] = (dP_r/dt) \div (-d[M]/dt)$$

hence from (2) and (5)

$$\frac{-dP_r}{d[M]} = \left(\frac{k_t^2[NH_3]^2}{(k_t[NH_3] + k_p[M])^2}\right)\left(\frac{k_p[M]}{k_p[M] + k_t[NH_3]}\right)^{r-1}$$

$$-dP_r = \int_{[M_0]}^{[M_f]}\left(\frac{k_t^2[NH_3]^2}{(k_t[NH_3] + k_p[M])^2}\right)\left(\frac{k_p[M]}{k_p[M] + k_t[NH_3]}\right)^{r-1} d[M]$$

where M_f and M_0 are respectively the final and the initial monomer concentration, *i.e.*,

$$P_r = \frac{k_t}{k_p}[NH_3]\frac{1}{r}\left[\left(\frac{k_p[M_0]}{k_p[M_0] + k_t[NH_3]}\right)^r - \left(\frac{k_p[M_f]}{k_p[M_f] + k_t[NH_3]}\right)^r\right] \quad . \quad . \quad (6)$$

Now

$$\frac{\overline{W}}{m} = v_w = \frac{\sum_{r=1}^{\infty} r^2 P_r}{\sum_{r=1}^{\infty} r P_r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\overline{W}$ is the weight-average molecular weight, v_w the corresponding average chain length, and m the molecular weight of the monomer.

In the simple case of 100% polymerisation ($[M_f] = 0$), evaluation of (7) by substitution for P_r and summation gives

$$v_w = 1 + k_p[M_0]/k_t[NH_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Now, in purifying the polymer and freeing it from unchanged styrene, it is probable that the lower molecular weight polystyrenes will not be precipitated, but will remain in solution in the methanol–water solvent. In this connection 2-phenylethylamine, the simplest product of the polymerisation reaction, is known to be soluble in both water and methanol. As the method of purification was standardised, we may assume that only chain lengths of j and above are precipitated. Hence the expression for v_w becomes

$$v_w = \sum_{r=j}^{\infty} r^2 P_r / \sum_{r=j}^{\infty} r P_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

whence, if $[M_f] \neq 0$, substitution for P_r and summation give

$$v_w = \frac{Y^j\left(\frac{j-1}{1-Y} + \frac{1}{(1-Y)^2}\right) - Z^j\left(\frac{j-1}{1-Z} + \frac{1}{(1-Z)^2}\right)}{Y^j/(1-Y) - Z^j/(1-Z)} \quad . \quad . \quad (10)$$

where

$$Y = \frac{k_p[M_0]}{k_p[M_0] + k_t[NH_3]} \text{ and } Z = \frac{k_p[M_f]}{k_p[M_f] + k_t[NH_3]}$$

When $[M_f] = 0$ equation (10) reduces to

$$v_w = j + Y/(1-Y) = j + k_p[M_0]/k_t[NH_3] \quad . \quad . \quad . \quad . \quad (11)$$

Thus for complete polymerisation a simple linear relationship between v_w and $[M_0]$ should hold. Fig. 2 shows an approximately linear relation between v_w and $[M_0]$ up to $[M_0] \simeq$

0·3*M*. This plot contains all the values obtained, irrespective of the degree of conversion of monomer into polymer. From the treatment given above it appears that both the degree of conversion and the degree of fractionation of the polymer will affect the value of v_w and it is necessary to determine how variations in these quantities will affect the form of the dependence of v_w on $[M_0]$.

The ratio $v_w(x\%$ conversion$)/v_w(100\%$ conversion) has been calculated by using different values of j in the range 1—6 for values of $x\%\{= 100([M_0] - [M_f])/[M_0]\%\}$ similar to those attained in the experiments summarised in Table 4. (In the experiments with lower initial concentrations of styrene, the percentage conversion was considerably greater than the percentage yield of polymer, owing presumably to the relatively greater proportion of low molecular weight polymer fractionated in the purification procedure.) It was found that a linear connection between v_w and $[M_0]$ should still apply to a series of experiments in which the degree of conversion was approximately the same though different from 100%, that the slope does not give a good value for k_p/k_t, but that the intercept when $[M_0] = 0$ would yield a value for j very similar to that found from a series of experiments at 100% conversion. It is noteworthy that those points which appear to be " high " in Fig. 2 were obtained from experiments in which the percentage conversion, as judged by the yield of polymer, was unduly low relatively to that obtained in experiments at similar concentrations. This positive deviation for low conversions is to be expected from the above treatment of the chain-length dependence. Equation (11) being used, the positive intercept on the molecular weight axis at $[M_0] = 0$ shows that at very low initial concentrations of monomer, the chain length of the polymer separated is 4 and hence polymer of chain length up to, but excluding, 4 is fractionated, *i.e.*, $j = 4$.

Although Fig. 2 may be taken as establishing the linear dependence of v_w on $[M_0]$ up to $[M_0] = 0{\cdot}3$ mole/litre, as the degree of polymerisation was not accurately known these results cannot be used for a satisfactory evaluation of k_p/k_t. In the experiments summarised in Table 5 the ratio $[M_f]/[M_0]$ was 0·5 in each case, and by using the full expression (equation 10) with $j = 4$ and $[M_f] = \frac{1}{2}[M_0]$, a plot of $k_p[M_0]/k_t[NH_3]$ against v_w was constructed over a suitable range of values of v_w. By interpolation in this plot it was possible to find the value of $k_p[M_0]/k_t[NH_3]$ corresponding to a given observed chain length at 50% conversion. As $[M_0]$ and $[NH_3]$ were known, the corresponding value of k_p/k_t could be found. These values at different temperatures, together with the values found by using equation (11), are summarised in Table 5. Here $[NH_3]$ is taken as 48·0 moles/litre in each case. It can be seen from Table 5 that the effect of incomplete conversion on the molecular weight is not large, as k_p/k_t values found by using equation (11), *i.e.*, assuming that the molecular weight is unaffected by the degree of conversion, are only 40% greater than those found by using the full equation (10) for 50% conversion. The plot of log k_p/k_t against $1/T$ (Fig. 6) shows that $E_p - E_t = -(4 \pm 1)$ kcal./mole, where E_p is the activation energy of the propagation reaction and E_t that of the termination reaction.

The overall kinetic expression found for the rate of disappearance of monomer is of the same form as that deduced (equation 3). Here, as in the case of the dependence of molecular weight on styrene concentrations, the similarity between the experimental and the theoretical relationships provides good confirmation for the proposed mechanism. The other mechanisms previously mentioned lead to different expressions for both the dependence of polymer-chain length and rate of disappearance of monomer on reactant concentrations and hence these mechanisms are considered to be inapplicable. It appears therefore that the overall reaction velocity constant found experimentally, k'', is equal to $k_i k_p/k_t[NH_3]$.

At the amide concentrations used, the rate expression can be written

$$\frac{-\mathrm{d}[M]}{\mathrm{d}t} = \frac{k_i k_p}{k_t} \cdot K^{\frac{1}{2}}_{\text{diss. } KNH_2} \cdot \frac{[M^2][KNH_2]^{\frac{1}{2}}}{[NH_3]}$$

and hence the overall activation energy E is given by

$$E = E_i + E_p - E_t + \tfrac{1}{2}\Delta H_{(\text{diss. } KNH_2)}$$

where E_i is the activation energy of the initiation reaction and is therefore given by

$$E_i = E - (E_p - E_t) - \tfrac{1}{2}\Delta H_{(\text{diss. } KNH_2)}$$

It has been shown above that $\Delta H_{(\text{diss. } KNH_2)} = 0 \pm 2$ kcal./mole and so from the observed overall activation energy (Fig. 5) of 9 ± 2 kcal./mole and the value of $-(4 \pm 1)$ kcal./mole for $(E_p - E_t)$, we have $E_i = 13 \pm 4$ kcal./mole.

These experimental findings can be summarised as follows: (i) The overall velocity constant $k_i k_p/k_t$ at $-33{\cdot}5° = 274$ l. mole^{-1} sec.$^{-1}$ (from $k'' = 342$, Table 7). (ii) The overall energy of activation $(E_i + E_p - E_t) = 9 \pm 2$ kcal./mole. (iii) k_p/k_t at $-33{\cdot}5° = 4{\cdot}28 \times 10^3$ (Table 5). (iv) $(E_p - E_t) = -(4 \pm 1)$ kcal./mole. (v) k_i at $-33{\cdot}5° = 6{\cdot}4 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. (vi) $k_i = 4{\cdot}4 \times 10^{10} \exp(-13\,000/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

Although the proposed mechanism evidently holds up to initial styrene concentrations of the order 0·3M, yet the anomalously low rate of reaction and molecular weights found above this concentration may indicate that other reactions are occurring at these higher concentrations. However, the reaction solution becomes of mud-like consistency after only a few seconds' reaction, owing to the heavy precipitate of polymer formed and so the reaction medium was very different in such properties as viscosity from that obtaining at the lower concentrations of styrene. In the case of radical polymerisation, an increase in the viscosity of the medium generally results in an increase in the average molecular weight, whereas here the reverse is the case. However, in a polymerisation of ionic mechanism other factors such as a change in the dielectric constant of the medium—which, for example, might markedly affect the dissociation of potassium amide in this reaction—are also likely to affect the rates of the various reactions. It is therefore difficult to suggest any satisfactory interpretation of the anomalies observed. They cannot be ascribed to the use of an inappropriate molecular weight–intrinsic viscosity relation in calculating the relevant molecular weights, for a decrease in the intrinsic viscosity is observed on increasing the initial styrene concentration above 0·3M. In addition, the rate of disappearance of monomer also becomes unexpectedly low above this concentration.

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