139. *Anionic Polymerisation. Part II.* The Acid–Base Character of Anionic Polymerisation.*

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A qualitative survey has been made of the reactivity of various anion bases in initiating the polymerisation of vinyl monomers in liquid ammonia and in diethyl ether as solvents. The observed correlation between base strength and reactivity is in accord with the anionic mechanism of these polymerisation reactions.

The relative p*K* of acetylene in liquid ammonia as solvent has been estimated.

In the preceding paper a detailed mechanism has been established for the polymerisation of styrene by potassium amide in liquid ammonia. This mechanism follows that suggested by Sanderson and Hauser (*J. Amer. Chem. Soc.*, 1949, **71**, 1595) who first reported quantitative measurements in a similar system, styrene–sodium amide–liquid ammonia, and was also suggested in a preliminary communication (Evans, Higginson, and Wooding, *Rec. Trav. chim.*, 1949, **68**, 1069). It seems probable that in all such cases of anionic polymerisation of vinyl monomers the initiation reaction involves the addition of a base to a monomer molecule, forming a carbanion :

$$(X^+)B^- + {>}C{=}C{<} \longrightarrow B{-}\overset{|}{\underset{|}{C}}{-}\overset{(-)}{C}{<}(X^+)$$

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* Part I, preceding paper.

The propagation reaction then follows :

$$\mathrm{B{-}\overset{|}{\underset{|}{C}}{-}\overset{(-)}{C}{<}(X^+) + {>}C{=}C{<} \longrightarrow B{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{(-)}{C}{<}(X^+)}, \text{ etc.}$$

and the termination reaction, which competes with the propagation reaction, involves the addition of a Lewis acid, *i.e.*, electron-pair acceptor, to the growing polymer chain :

$$\mathrm{B{-}[{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}]_n{-}\overset{|}{\underset{|}{C}}{-}\overset{(-)}{C}{<}(X^+) + A^+ \longrightarrow B{-}[{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}]_n{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}A\ (+\ X^+)}$$

(compare Beaman, *J. Amer. Chem. Soc.*, 1948, **70**, 3115). In the styrene–potassium amide–liquid ammonia system ($A^+ = H^+$), the termination is due to proton transfer from a solvent ammonia molecule, the conjugate acid to the catalyst base.

In the work now reported an attempt has been made to correlate qualitatively the base strength of the catalyst with its catalytic activity in the polymerisation of various vinyl monomers in liquid ammonia and in diethyl ether as solvents. All the cases dealt with here appear to fall into the class where termination is by proton addition to the growing polymer chain rather than by addition of any other electron-pair acceptor.

Liquid ammonia was used as reaction medium for certain of the experiments which were an extension of those previously reported (Evans, Higginson, and Wooding, *loc. cit.*). (With styrene as monomer and sodium anilide as initiating species there is a discrepancy between the previous and the present findings. The present experiments were done under standard conditions which differed from those previously used. The anilide ion is evidently only just an effective catalyst for the polymerisation of styrene in liquid ammonia.)

In other experiments, diethyl ether was used, since in this solvent semi-quantitative data on the strengths of weak acids have been obtained by Conant and Wheland (*J. Amer. Chem. Soc.*, 1932, **54**, 1212) and by McEwan (*ibid.*, 1936, **58**, 1124). In many ways the use of ether rather than liquid ammonia as solvent leads to a simpler interpretation of the effect of various catalyst bases. Unlike liquid ammonia, this solvent is inert and cannot enter into proton-transfer equilibria with the polymerisation catalysts. As solvent termination cannot occur in ether there are two possible termination reactions :

(1) Termination can be effected by proton transfer to the growing polymer chain from the acid conjugate to the catalyst base. For complete conversion of monomer into polymer and with no fractionation of the polymer, this leads to an expression of the weight-average molecular weight similar to that deduced for the styrene–potassium amide–liquid ammonia system under similar conditions, *viz.* :

$$\nu_w = 1 + k_p[\mathrm{M_0}]/k_t[\mathrm{HB}] \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(For a definition of the symbols used, see preceding paper.) Unlike polymerisation in liquid ammonia, in the ether system the acid, HB, conjugate to the catalyst base is not the solvent and so the concentration of the terminating species can be varied in this solvent.

(2) In addition to the above mechanism, the termination reaction can in principle occur by proton transfer from a monomer molecule to the growing chain :

$$\overset{(-)}{\mathrm{M}_x} + \mathrm{{}^{H}{>}C{=}C{<}} \longrightarrow \mathrm{M_xH}\ \text{(dead polymer)} + \mathrm{{-}\overset{(-)}{C}{=}C{<}} \qquad . \quad . \quad (2)$$

an alternative reaction to the propagation step

$$\overset{(-)}{\mathrm{M}_x} + \mathrm{{}^{H}{>}C{=}C{<}} \longrightarrow \overset{(-)}{\mathrm{M}_{x+1}}$$

The species $\mathrm{{-}\overset{(-)}{C}{=}C{<}}$ can of course react with monomer, and commence a second polymer chain :

$$\mathrm{{>}C{=}C{<} + {-}\overset{(-)}{C}{=}C{<} \longrightarrow {>}\overset{(-)}{C}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{C}{=}C{<}}$$

and thus this second termination reaction is of the chain-transfer type. In this case the chain length is independent of reactant concentrations and depends only on the ratio of k_p to k_t.

With methyl methacrylate as monomer and triphenylmethylsodium as catalyst in ether solution an attempt was made to decide whether termination reaction (2) occurred. Triphenylmethylsodium is the most strongly basic catalyst used in the experiments in ether and the conjugate acid triphenylmethane is thus the weakest in these experiments. These conditions are likely to be the most favourable to termination by proton transfer from a monomer molecule.

In Table 1 is shown the effect of an increase in monomer concentration on the molecular weight, the concentration of triphenylmethylsodium and triphenylmethane being kept as far as possible constant. Table 2 shows, for approximately constant monomer and triphenylmethylsodium concentrations, the effect of an increase in triphenylmethane concentration on the molecular weight. Qualitatively, the increase in molecular weight with increase in monomer concentration and with decrease in triphenylmethane concentration is to be expected if termination reaction (1) occurs, but the quantitative correlation between the concentrations and the molecular weight which equation (1) predicts, *viz.*, $(\nu_w - 1) \propto [M_0]$; $(\nu_w - 1) \propto 1/[CHPh_3]$, does not appear. The dependence observed can, however, be explained on the assumption that, though termination reaction (2) does occur, reaction (1) predominates. More certain evidence that termination reaction (2) occurs only to a small extent is the absence of olefinic unsaturation in the polymer. (In polymer of chain length approximately 60 the presence of one double bond per polymer chain in one of every ten polymer molecules can be detected by bromine absorption.) It thus seems fairly certain that termination reaction (1) predominates, though reaction (2) cannot be excluded completely.

TABLE 1.

Temp. $\simeq 20°$; $[CPh_3Na] \simeq 0{\cdot}04$ mole/l.; $[CHPh_3] \simeq 0{\cdot}04$ mole/l.

[Monomer], mole/l.	[η]	Mol. wt.*
0·43	0·0925	6,150
0·82	0·1073	7,600
1·26	0·1225	9,250
1·76	0·1382	11,000

TABLE 2.

Temp. $\simeq 20°$; $[CPh_3Na] \simeq 0{\cdot}06$ mole/l.; [Monomer] = 0·15 mole/l.

[Monomer], mole/l.	[η]	Mol. wt.*
0·01	0·1665	18,600
0·08	0·1157	8,500
0·14	0·0987	6,700

* Calculated from [η] by using Baxendale, Bywater, and Evans's intrinsic viscosity–molecular weight relation for methyl methacrylate (*J. Polymer Sci.*, 1946, **1**, 237).

EXPERIMENTAL

Reagents.—Xanthen was prepared by Heller and Kostanecki's method (*Ber.*, 1908, **41**, 1324), and phenylacetylene by the procedure of "Organic Syntheses" (Coll. Vol. 1, p. 428). Other acids were available and were purified by the appropriate methods. Monomers were freed from stabiliser if present and purified by the usual methods. Ammonia was purified by two distillations from metallic sodium. Ether was partially purified by refluxing over metallic sodium in an atmosphere of nitrogen, followed by distillation.

Procedure.—Experiments in liquid ammonia were carried out in absence of air in the apparatus described in the preceding paper. The catalyst base solutions were prepared by adding a potassium amide solution to a slight excess of the conjugate acid. Except for butadiene, this solution was then mixed with a solution of the monomer in liquid ammonia. After about 30 minutes at −33·5° the catalyst was neutralised with ammonium chloride. After the ammonia had boiled off, polymer, if formed, was extracted with the appropriate solvent and reprecipitated in the case of methyl methacrylate and styrene. In all experiments with acrylonitrile, polymer was produced and here it was sufficient to remove unchanged monomer together with ammonium chloride and potassium chloride by solution in water. Butadiene appeared to have a low solubility in liquid ammonia, and the purified gas was condensed into the vessel containing the potassium amide catalyst solution until the undissolved liquid butadiene was present in considerable excess. After several hours the potassium amide was neutralised with ammonium chloride. In none of the experiments in liquid ammonia were traces of polymer found after the ammonia and butadiene had boiled off. Because of the low solubility of this monomer in liquid ammonia, and as negative results were obtained with potassium amide, the strongest base which could be used, experiments with other bases were not carried out.

Experiments in diethyl ether were carried out in an all-glass apparatus similar to that used for the liquid-ammonia experiments. Manometers and connecting tubes were fitted with small heating coils to prevent condensation of ether vapour. A solution of triphenylmethylsodium in ether was prepared (Renfrow and Hauser, *Org. Synth.*, Coll. Vol. 2, p. 607) and the concentration was determined by titrating the alkali formed by addition of a known amount of the solution to excess of water against standard acid. With the exceptions noted below, solutions of other catalysts were prepared by adding the triphenylmethylsodium solution to a known amount of the conjugate acid of the catalyst base until a faint colour due to the red triphenylmethyl ion remained. With xanthen and fluorene the colour of the corresponding carbanions is sufficiently similar to that of the triphenylmethyl ion to make the use of this method impossible; and hence, the weight of acid present being known, the equivalent volume of triphenylmethylsodium solution was added. Solutions of sodium ethoxide and sodium methoxide were prepared by allowing a known amount of the corresponding alcohol to react with excess of sodium in ether. The solution was decanted from excess of sodium when reaction ceased. In both the experiments in ether and in ammonia the monomer concentration was approximately molar except for butadiene, and the catalyst concentration was about 0·04 M.

Polymerisation in ethereal solution at 20° occurred rapidly as compared with the slow reaction in liquid ammonia at −33·5° and appeared to be complete in about one minute. After a few minutes polymer was filtered off from the solution. If required pure for molecular-weight determination, as in the experiments with methyl methacrylate and triphenylmethylsodium, the polymer was thoroughly washed with methanol, water, and again with methanol, and finally dried in high vacuum (P_2O_5) for 48 hours. Where no polymer was visible after a few minutes, the time of standing in the presence of catalyst was extended but in no instance was slow formation of visible polymer observed. The ether was then distilled off, and the monomer remaining examined for polymer. In all cases where no visible polymer was observed, no trace of polymer was found—the polymer if formed was always insoluble in ether.

Determination of the Relative Acid Strength of Acetylene in Liquid Ammonia.—The approximate acid strength of acetylene relative to other acids can be found by similar methods to those used by Conant and Wheland (*loc. cit.*) and McEwan (*loc. cit.*). In preliminary experiments, dried acetylene gas was passed into solutions of various carbanions in liquid ammonia; the pertinent observations are summarised in Table 3.

TABLE 3.

Hydrocarbon	$pK_{rel.}$*	Colour of corresponding carbanion	Concn.	Effect of passing C_2H_2
Fluorene	25	Orange	M/50	No change
Fluorene	25	Orange	M/1000	No change
Xanthen	29	Red	M/50	Completely and rapidly decolorised
Triphenylmethane	33	Red	M/50	Completely and rapidly decolorised

* The $pK_{rel.}$ values are those found by Conant and Wheland (*loc. cit.*) and by McEwan (*loc. cit.*) in ethereal solution.

TABLE 4.

Temperature − 33·5°.

Time, min.	Resistance, ohms		Time, min.	Resistance, ohms	
0	247	0·01M-Potassium anilide	0	259	0·01M-Sodium acetylide
10	247		10	259	
13		C_2H_2 passed for 0·5 min.	15		Aniline solution added to make test solution M/20 in NH_2Ph
14	299				
17	299				
20		More C_2H_2 passed	17	261	
21	288		22	262	
23	287		30	262	
27		More C_2H_2 passed			
28	289				
32	288				

As the acetylide ion is colourless, these results are interpreted as showing that acetylene is a stronger acid than xanthen and triphenylmethane, but weaker than fluorene. Hence, assuming that the order of acid strengths in ether is paralleled by that in ammonia (cf. Bell, "Acid–Base Catalysis," 1941, p. 108, Oxford,) we have $25 < pK_{rel.(acetylene)} < 29$. To reduce these limits, comparison with aniline was made. The anilide ion is colourless in liquid ammonia, and so a conductivity method of determining the position of equilibrium in the anilide ion–acetylene system was used. The conductivity apparatus was that previously described.

Sodium acetylide solution in liquid ammonia was prepared by passing acetylene through a 0·01M-solution of sodium in liquid ammonia for 5 minutes after the blue colour of the sodium had disappeared. (It was assumed that this procedure gave a solution containing $\text{NaC}\vdots\text{CH}$ and no $\text{NaC}\vdots\text{CNa}$.) Sodium anilide solution was prepared as described above. The results are summarised in Table 4.

These results suggest that, although acetylene reacts with the anilide ion, yet there is little or no reaction between the acetylene ion and aniline, *i.e.*, the equilibrium $\text{HC}\vdots\text{CH} + \text{Ph·NH}^- \rightleftharpoons \text{HC}\vdots\overset{(-)}{\text{C}} + \text{Ph·NH}_2$ is well over to the right. Thus pK (acetylene) $<$ pK (aniline) $= 27$. Since pK (acetylene) > 25 (Table 3), on the above arbitrary scale of acid strength the p$K_{\text{rel.}}$ of acetylene is $\simeq 26$.

DISCUSSION

The experimental findings are summarised in Table 5. The absence of polymerisation may be due to two factors : either the catalyst is an insufficiently strong base to add to the monomer, or the termination reaction may be so effective that the polymer is of very short chain length and would escape detection under the experimental conditions. In ethereal solution, with the exception of sodium methoxide and ethoxide, the catalyst solutions were prepared by addition of a slight excess of triphenylmethylsodium to the conjugate acid of the catalyst base and the only acid species present is triphenylmethane. Hence, the predominating termination reaction will in all cases involve proton transfer from triphenylmethane to the growing polymer chain, which, as polymer is formed in certain cases, must be a slow reaction compared with the propagation reaction. Therefore it appears that the factor responsible for absence of polymerisation is the absence or comparative slowness of the addition of the catalyst base to the monomer. The ease of such addition would be expected to increase with an increase in the base strength of the catalyst and with an increase in the Lewis acid strength of the monomer. This is analogous to the connection between catalyst acid or base strength and catalytic power found in proton-transfer reactions (Brönsted relation). The results in Table 5(*a*) indicate that the monomers can be put in order of Lewis acid strength : acrylonitrile > methyl methacrylate > styrene $\simeq$ butadiene. This order for anionic polymerisation has also been found by Walling,

TABLE 5.

			Monomers *			
Acid	p*K* (ether)	Colour of anion	Acrylo-nitrile	Methyl methacrylate	Styrene	Butadiene
		(*a*) Ethereal solution : 20°.				
Methanol	17	Colourless	+	—	—	
Ethanol	18	Colourless	+	—	—	
Acetophenone	19	Yellow	+	—	—	—
Triphenylcarbinol	19	Green	+	—	—	
Indene	21	Yellow	+	+	—	—
Phenylacetylene	21	Colourless	+	+	—	—
Diphenylamine	23	Colourless	+	+	—	—
Fluorene	25	Red	+	+	—	—
Aniline	27	Colourless	+	—	—	—
p-Methoxyaniline	27	Colourless	+	—	—	
Xanthen	29	Red	+	+	+	+
Triphenylmethane	33	Red	+	+	+	+
		(*b*) Liquid-ammonia solution : — 33·5°.				
Ethanol	18	Colourless	+	—		
Acetophenone	19	Yellow	+	—		
Triphenylcarbinol	19	Green	+	—		
Indene	21	Yellow	+	—		
Phenylacetylene	21	Colourless	+	—	—	
Diphenylamine	23	Colourless	+	+	—	
Fluorene	25	Orange	+	—	—	
Acetylene	26	Colourless	+	+	—	
Aniline	27	Colourless	+	+	+	
Xanthen	29	Red	+	+	+	
Triphenylmethane	33	Red	+	+	+	
Ammonia	36	Colourless	+	+	+	—

* + Indicates formation of polymer; — indicates absence of polymer.

Briggs, Cummings, and Mayo (*J. Amer. Chem. Soc.*, 1950, **72**, 48) from copolymerisation studies (see also Mayo and Walling, *Chem. Reviews*, 1950, **46**, 280). It would also be expected that for each monomer there would be a definite region of the p*K* of the catalyst below which polymerisation would become very slow. With the exception of the anilide and the *p*-methoxyanilide ions with methyl methacrylate as monomer, this is observed. These experiments were repeated carefully with the same negative result and there appears to be no simple explanation for this surprising anomaly.

In liquid ammonia, a small amount of the acid conjugate to the catalyst base was present, and the stronger acids may act as terminating species in addition to the solvent ammonia. However, the general picture is similar to that found in ether. Polymerisation was not found with butadiene, though this may be connected with the low solubility of this monomer in liquid ammonia. The only anomaly appears to be the carbanion formed from fluorene, which does not polymerise methyl methacrylate, though the apparently weaker base, the anilide ion, was effective.

In connection with these anomalies it should be emphasised that only an approximate correlation can be expected between the strength of a base and its effectiveness as a polymerisation catalyst. This correlation is in principle subject to the limitations of the Brönsted relation itself; for example, this relation often breaks down completely if applied to a series of catalysts in which the atom to which the acid hydrogen is attached changes, or in which a profound alteration in the structure of the catalyst as a whole occurs. This effect is likely to be accentuated here, for unlike the proton-transfer reactions to which the Brönsted relation applies, the bond formed in the polymerisation reaction is a bond between the catalyst and a carbon atom as distinct from a bond between the catalyst and hydrogen. In addition, steric effects are likely to be more marked than those found in proton-transfer reactions.

As only a qualitative measure of the reaction rate has been considered, *i.e.*, a reasonably rapid rate of polymerisation on the one hand and extremely slow or zero reaction on the other, fairly large deviations from a strict correlation between base strength and catalyst activity will generally pass unnoticed. Thus there appear to be relatively few catalysts for which the catalyst activity cannot be inferred from the corresponding p*K* value. Were more quantitative rate measurements available, however, it is probable that an exact parallelism between catalyst reactivity and base strength would not be found.

Colour of Polymers.—Though the poly(methyl methacrylate), polystyrene, and polybutadiene formed were in almost every case colourless, it is of interest that with all catalysts the polyacrylonitrile was orange-yellow and was soluble in liquid ammonia to give a yellow solution. Unlike polyacrylonitriles prepared by other methods, the yellow polymer was sparingly soluble in pyridine and in acetone. It is possible that the polymer, even though solid, was of very low molecular weight. The colour, which was permanent in air and partly retained even on solution in concentrated nitric acid followed by precipitation with water, suggests the presence of conjugated double bonds. This implies that the cyano-group may take part in the polymerisation, and that the polymer may contain groupings such as $CH_2{:}CH{\cdot}\overset{|}{C}{:}N{\cdot}C(CH{:}CH_2){:}N{\cdot}$.

Another observation was that the polymer formed from both acrylonitrile and methyl methacrylate with the acetylide ion as initiating species was highly coloured and the colour was again permanent. The polyacrylonitrile was brick-red in colour as distinct from the usual yellow to orange, while the poly(methyl methacrylate) was yellow, though in all other cases this polymer was white. Possibly the acetylene also present copolymerised to some extent with these monomers and again gave rise to conjugated double bonds in the polymer. No evidence was obtained for the polymerisation of acetylene itself in liquid ammonia.

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