

Electroinitiated polymerization of butyl isocyanate: 2. Polymerization kinetics

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Electrolysis of a solution of a quaternary ammonium perchlorate or tetrafluoroborate produces a transient species capable of polymerizing *n*-butyl isocyanate: some direct reduction of the monomer also occurs. High molecular weight polymer is produced during the early stages of the reaction, and small but measurable quantities of cyclic trimer are formed during the later stages. Kinetic analysis of the polymerization indicates a complex reaction mechanism; above a certain current density the overall rate of reaction appears to be zero order in current. The rate also shows an unusual acceleration and appears to depend on the quantity of monomer already consumed.

INTRODUCTION

We have previously attempted to elucidate a mechanism of initiation for the polymerization of *n*-butyl isocyanate under electrolytic conditions using dimethylformamide (DMF) as solvent, and quaternary ammonium salts as electrolytes¹. This paper describes the kinetics of polymerization.

In the electroinitiated polymerization of phenyl isocyanate it has previously been suggested² that yield increases with decreasing temperature and current density; increasing monomer concentration and polymerization at the electrode resulted in a crystalline product. Using butyl isocyanate, limits of concentration and current density appear to apply.

EXPERIMENTAL

Materials

Butyl isocyanate, quaternary ammonium salts and dimethyl formamide were purified and stored as described in Part 1.

Butyl isocyanurate was prepared using the method of Kitano³ but without the addition of the appropriate alcohol as a further cocatalyst and taking precautions to exclude moisture from the reaction mixture. The product was purified by fractionation through an alumina column using a toluene-methanol mixture as the mobile phase with an increasing methanol content.

Procedure

For preparative experiments the electrolysis cell consisted of a 500 ml resin flask fitted, via a flange joint, to a lid having five glass sockets through which passed a stirrer, a reference electrode or gas exit with tap, an electrical connection to the mercury cathode, a counter electrode (in effect a platinum electrode fitted inside a tube, the end of which consisted of a grade 4 glass sinter) and finally a sampling device. The sampling device allowed liquid samples (1–3 g) only to be taken through a wide tube, the end of which was packed with glass wool, into tared round bottom flasks (100 ml capacity). Samples were either forced from the reactor

under argon pressure or, during the later stages, because of the increased viscosity, drawn from the reactor under reduced pressure. Rapid draining of the residual liquid in the tube back into the reactor could be effected by the application of a slight excess pressure. After careful washing and drying the whole assembly was flamed for several minutes under a stream of dry argon.

To a solvent transfer vessel, dried and rinsed with purified DMF, was added a given weight of dry clean mercury to give a pool of approximately 20 cm² when transferred to the reaction vessel. Dried electrolyte was then added, followed by the appropriate volume of DMF directly from the vacuum purification system to give a 0.1 M solution. After complete dissolution the total contents of the transfer vessel were transferred to the reaction vessel. Monomer was transferred again through a transfer vessel in a dry box and thence to the reaction cell directly under a pressure of argon.

The electrolysis cell was maintained at –60°C during electrolysis and reactions were carried out at constant current.

In the kinetic experiments, chemical methods of analysis were unavoidable because the polymer formed was insoluble in the reaction medium.

Analysis of samples

Unreacted isocyanate. Isocyanates are generally analysed by reaction with an excess of an amine to give the corresponding urea⁴ followed by back-titration of the unreacted amine. The procedure adopted is a development of that recommended by David and Stanley⁴ which was found to give poor reproducibility in the presence of DMF. Instead of using dibutylamine dissolved in toluene, the amine was dissolved in DMF. Bromophenol-blue was found to be an improvement on the bromocresol-green indicator previously described. However, further improvement was obtained using a pH titration technique with an end-point at pH = 5.5, care being taken because of the comparatively slow response of the glass electrode in a partly non-aqueous solution. Precise determinations could be obtained at low isocyanate concentration by weighing the amine added.

Because of the range of sample weights taken during an

electrolysis and thus the considerable variation in the volume of acid added during the titration, significant results were obtained only if distilled water was added to give a constant total volume before the final addition of acid. This gave only a trivial difference (± 0.1 ml), but this is important in samples of low free isocyanate content.

The procedure adopted was as follows.

- (i) Samples (1–3 g) added to tared flask and weighed;
- (ii) dibutylamine in DMF (10–25 ml 0.5–1.0 M) added;
- (iii) flasks reweighed and stored for a minimum of 1 h;
- (iv) isopropanol added (75–100 ml);
- (v) hydrochloric acid (0.1–0.25 M) added to pH 5.5;
- (vi) distilled water added to give total volume of 175 ml;
- (vii) hydrochloric acid added to return pH to 5.5
- (viii) three blanks treated in same manner, the average value of their titres being used to calculate the blank for each individual sample.

Isocyanurate (trimer)

Isocyanurate concentration was determined using a Pye–Unicam series 104 gas chromatograph fitted with twin columns and twin flame ionization detectors. The peak areas were obtained using a Kent Mark II electronic integrator.

The columns used were 10% Phascarb L on a Universal support. Dibutylamine used as the assay agent produced 1,1,3-tributyl urea which was used as internal standard for the trimer since the molar concentration of the urea was known from the titration value obtained above. The urea gave a symmetrical peak. Blank determinations showed that the presence of isopropanol, water, HCl and DMF in the sample did not interfere with the results.

Relative weight sensitivities using Phascarb L (10%) on a universal support at 100°C using nitrogen as carrier gas at a flow rate of 50 cm³ s⁻¹ were:

1,1,3-tributyl urea	1.00
butyl isocyanurate trimer	0.769 ($\sigma = 0.0103$)

RESULTS AND DISCUSSION

Attempts to use constant potential electrolysis failed because of coating of the cathode (either mercury or platinum) by polymer, resulting in a cessation of the electrolysis. Attempts to stir the solution were unsuccessful because the turbulence caused slight changes in the resistance between the reference and working electrode. This caused slight changes in the potential difference which was amplified and transmitted to the cell aggravating the oscillations at the reference electrode which were further amplified making operation of the potentiostat impossible.

Analysis of reaction mixtures after electrolysis at constant current showed the presence of small but significant amounts of cyclic n-butyl isocyanate trimer. A series of polymerizations at decreasing temperatures indicated that only at temperatures below -40°C did polymerization occur when using either a platinum or a solid mercury cathode, eliminating the possibility that a tetraethylammonium–mercury amalgam was responsible for initiation, as reported in the polymerization of acrylonitrile at below -10°C ⁵.

Experiment showed that passage of current through the monomer/electrolyte system only, followed by subsequent immediate addition of monomer gave rise to an extremely rapid polymerization. Delay in the addition of monomer resulted in no polymerization, indicating the transitory

nature of the initiating species. Additionally, the efficiency of initiation depended on the rate of passage of current rather than on total current passed. Subsequent monomer addition also curtailed the formation of cyclic trimer. When phenyl isocyanate was used as the monomer, trimer was the major product using this technique and also occurred as the major product when electrolysis was carried out in the presence of this monomer.

Considerable difficulties were experienced when attempting to study the kinetics when monomer was added subsequent to electrolysis because the margin between no reaction and an exceedingly fast reaction was small, and especially since the progress of the polymerization could only be determined in retrospect because of the nature of the techniques used to measure the residual monomer. For completeness, the only successful experiment is described at the end of the paper. The results confirm that an initiating species was formed from the solvent and that it had a relatively short lifetime.

Electrolysis using tetrahydrofuran as solvent in the presence of monomer resulted in polymer formation with a conversion curve similar to that observed when using DMF. However, the rate of polymerization is much slower. Conversion of solutions of similar molarity were complete in 840 min in THF at 70 mA (the maximum obtainable) whilst in DMF at 50 mA conversion was complete after 50 min. This may be due to the lower dielectric constant of THF but other results suggest that it is due to the lower reactivity of the reduced monomer.

In the study of polymerization kinetics, a preparative cell was used with a mercury cathode and a known, approximately molar, butyl isocyanate at -60°C . Results were obtained for the various current values these are illustrated in *Figure 1*, by considering the value at 50 mA which is typical for other current values and which indicates an accelerating reaction and the formation of isocyanurate trimer in the later stages. Acceleration is feasible in electroinitiation if there is no termination. It is possible to show for a propagating dianion with no termination that, for a constant current, a plot of $\ln M_0/M$ versus t^2 should be linear⁶ and that, when termination occurs a plot of $\ln M_0/M$ versus t should be linear. *Figure 2* shows that, applying both these conditions, there is some residual acceleration over the above that to be expected from the special circumstances of electroinitiation. Traditionally an accelerating polymerization may be explained on several grounds: a decreasing rate of termination or of the rate constant because of an increase in the viscosity of the medium (Trommsdorff effect); or a dual polymerization by two initiating species in which the second is more active,

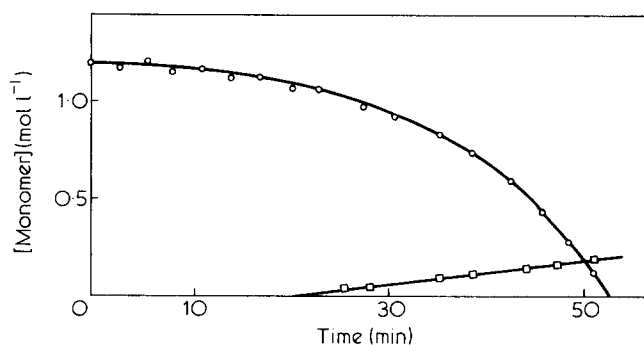


Figure 1 Dependence of butyl isocyanate concentration on time during electrolysis at 50 mA and -60°C . \square , production of trimer ($\times 3$)

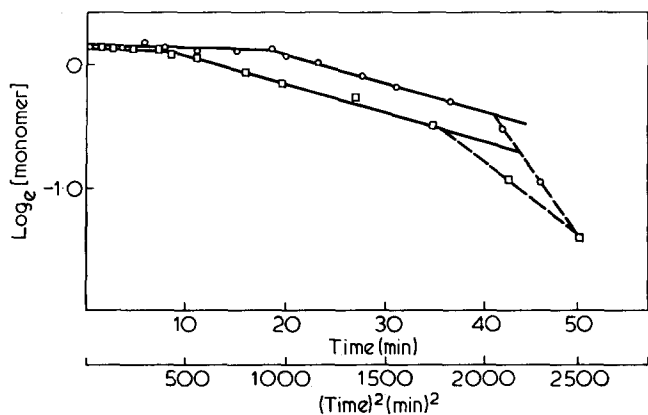
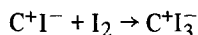
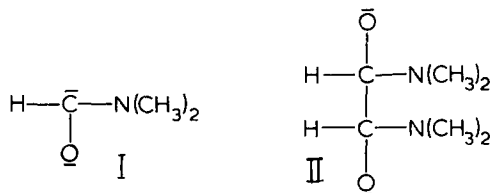


Figure 2 Residual acceleration in the polymerization of butyl isocyanate electrolysis at 50 mA and -60°C . \circ , Log_e [monomer]: t ; \square , \log_e [monomer]: t^2

but is formed more slowly in the reaction mixture an example of this is the polymerization of vinyl ethers with iodine⁷ where the tri-iodide is more reactive due to the greater proportion of free ions than with the initial iodide.

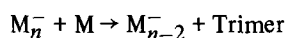


In the present system the DMF dianions (both monomeric and dimeric) mentioned in Part I and the polymer anions themselves are not likely to form a second series of ion pairs with the quaternary ammonium counterion. Conceivably both the DMF dianions I and II are active



and probably initiate the polymerization at different rates. However, the dimer is readily formed from the DMF dianion and after a short time period both species remain at a constant concentration, the net effect being that of a single initiating species.

A possible variation in the termination reaction could be the result of trimer formation which occurs at all the current densities used and which involves the monomer, possibly by the mechanism:

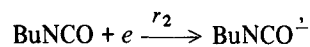
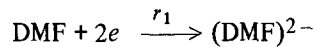


This would result in a linear % conversion with time because the ratio of the propagation rate to that of the rate of termination would remain constant. A similar result would obtain if trimer formation occurred by the spontaneous splitting of a trimer anion without the addition of a monomer unit. The rate of termination could also decrease if initial impurities were removed during the early stages of the electrolysis; this would not agree with the possible kinetic treatment to be presented in this paper. Increase in viscosity is not important as the polymer produced became insoluble at fairly low conversions.

Considering the results outlined in Part 1 together with the preliminary results using pre-electrolysis prior to addition of the monomer and the fact that some polymerization occurs when THF is used as the solvent, it would seem

reasonable to suppose that a variable initiation rate was responsible for the acceleration of reaction.

It may be assumed that only a fraction of the current reduces the solvent (r_1) and that the remaining current reduces the monomer (r_2):



$$(r_1 + r_2 = 1)$$

$$\frac{d(\text{DMF})^{2-}}{dt} = \frac{r_1\theta}{2} = \frac{(1-r_2)\theta}{2} \quad (1)$$

where $\theta = I/nFv$; n is the number of electrons transferred; F is the Faraday; and v is the volume of solvent.

r_2 is dependent on monomer concentration and will decrease as polymerization proceeds. $[(\text{DMF})^{2-}]$ increases with time, increasing the rate of initiation, whether DMF^{2-} or $(\text{DMF})_2^{2-}$ or both are responsible for initiation. Equation (1) may be rewritten as:

$$\frac{d[(\text{DMF})^{2-}]}{dt} = \frac{(1+k_2[\text{M}])\theta}{k_2}$$

The value of k_2 can be evaluated if the initial values of r_1 and r_2 are known. r_2 is probably larger than r_1 , since the isocyanate is reduced more readily than the solvent.

If it is assumed that the rate of initiation is insufficient seriously to affect the equilibria established in the solvent (Part 1) the concentration of $(\text{DMF})^{2-}$ may be expressed as:

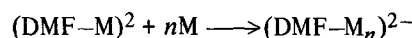
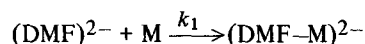
$$[(\text{DMF})^{2-}] = \frac{I(1-k_2[\text{M}])}{2FVk_B} \quad (2)$$

where k_B is the rate constant for conversion of $(\text{DMF})^{2-}$ into $(\text{DMF})_2^{2-}$

During electrolysis the concentration of the initiating species is not depleted and the rate of polymerization may be given by:

$$\frac{-d[\text{M}]}{dt} = \frac{k_p k_i}{2FVk_B} [\text{M}]^2 I(1-k_2[\text{M}]) \quad (3)$$

where there is a two-stage process:



Substituting numerical values for k_B , suitably corrected for monomer concentration and taking $V = 225$ ml and $I = 50$ mA.

$$\frac{-d[\text{M}]}{dt} = 5.456 \times 10^{-5} k_p k_i [\text{M}]^2 (1-k_2[\text{M}]) \quad (4)$$

differentiation with respect to $[\text{M}]$ yields:

$$\frac{d(-d[\text{M}]/dt)}{d[\text{M}]} = 5.456 \times 10^{-5} k_p k_i (2[\text{M}] + 3k_2[\text{M}]^2)$$

a second differentiation, i.e.:

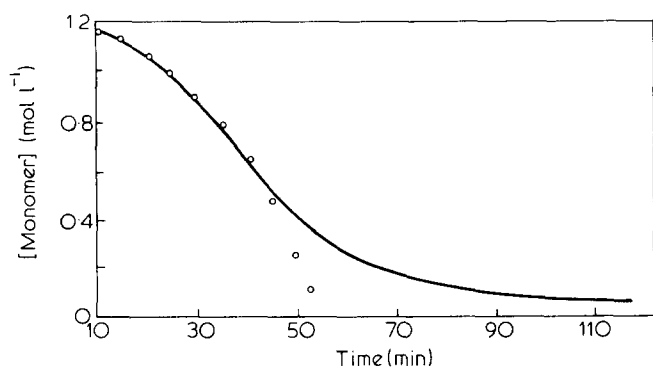


Figure 3 Comparison of theoretical treatment and experimental results for the electroinitiated polymerization of butyl isocyanate at 50 mA and -60°C . \circ , Experimental;

$$---, M = - \int_0^t kM^2(1-0.81)dt$$

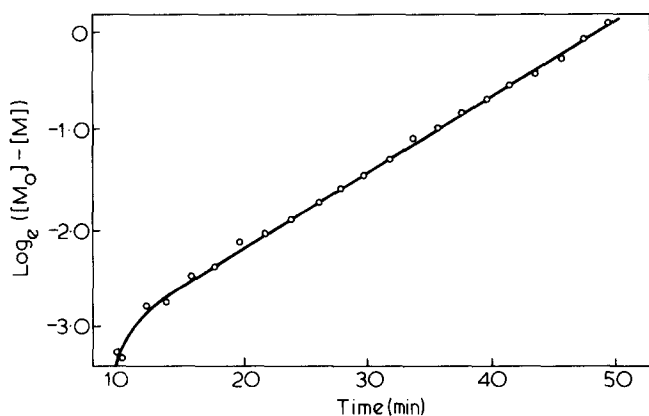


Figure 4 Dependence of polymerization of butyl isocyanate on concentration of monomer which has already polymerized, 50 mA, -60°C . Slope = $7 \times 10^{-2} \text{ min}^{-1}$

$$\frac{d^2(-d[M]/dt)}{d[M]^2}$$

indicates that the relationship exhibits a maximum and that a point of inflection occurs in the $[M]:t$ curve when $[M]_I = 2/3k_2$.

At 50 mA if r_2 is 0.99 and initially $k_2 = 0.8164$ and $[M]_I = 0.788 [M]$, when r_2 is less than 0.99, the point of inflection occurs at higher values of the monomer concentration; when $[M] > 1.75 \text{ mol l}^{-1}$, the slope of the rate of reaction becomes positive and polymerization cannot occur (see later).

If the product $k_p k_i$ is evaluated, equation (4) can be solved and a curve of $[M]:t$ constructed. Using a numerical approach in which $[M]$ is assumed constant for short periods of time, substitution into the integrated form of equation (4) where $[M_0]$ is the monomer concentration at the beginning of each time period and $k_2 = 0.8164$:

$$\frac{1}{[M_0]} - \frac{1}{[M]} = 5.456 \times 10^{-5} k_p k_i t (1 - 0.8164 [M_0]) \quad (5)$$

A value of $k_p k_i = 52.89$ was evaluated from experimental data for periods of 300 s. Equation (5) then becomes:

$$\frac{1}{[M]} - \frac{1}{[M_0]} = 0.8658(1 - 0.8164 [M_0]) \quad (6)$$

The curve is shown in Figure 3 with the superimposed experimental data at 50 mA. The experimental results agree well during the early stages of the theoretical curve, but acceleration still occurs after a decline in rate is predicted theoretically.

The position at which

$$\frac{d(-d[M]/dt)}{dM} = 0 \text{ (i.e., } 0.788 \text{ M)}$$

remains unchanged even when a termination reaction is postulated and when the theoretical rate curve becomes:

$$\frac{-d[M]}{dt} = \frac{k_p k_i}{kt} [M]^2 (1 - k_2 [M]) (1 - \exp k_i t) \quad (7)$$

Further differentiation with respect to $[M]$ gives a curve of the same general character as that already discussed, although the individual points may vary slightly.

Thus a fresh explanation is necessary to interpret the results. If the experimental data are represented in the form:

$$\frac{-d[M]}{dt} = k([M_0] - [M]) \quad (8)$$

a linear relationship of $\ln([M_0] - [M]):t$ is obtained after an initial period (Figure 4). This equation is extraordinary in that the rate of polymerization depends on the concentration of the monomer which has already been polymerized. One explanation would be that the polymer is active as a catalyst for the polymerization, which, because of the primary molecular structure, is difficult to envisage. Additionally the presence of added polymer produced under identical conditions in a separate experiment caused no change in the observed acceleration.

In order to analyse the situation further the overall rate constant k in equation (8) was investigated for its current dependence by taking the slopes of the plots of $\ln([M_0] - [M])$ versus time for various currents; all the experiments indicate a similar acceleration and trimer formation. The overall result is shown in Figure 5. The overall rate of polymerization is independent of the current above a certain value (about 15 mA) and there appears to be a minimum current required (about 8 mA) before polymerization occurs. The

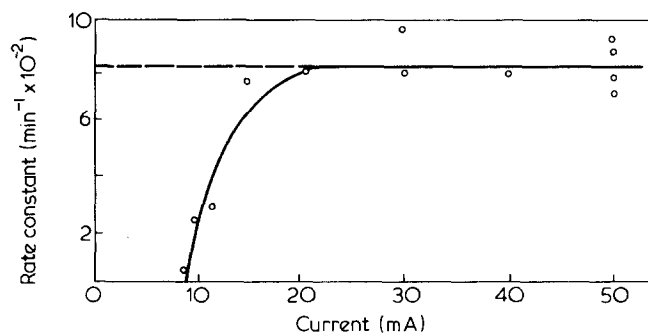


Figure 5 Dependence of rate of polymerization of butyl isocyanate on current (-60°C)

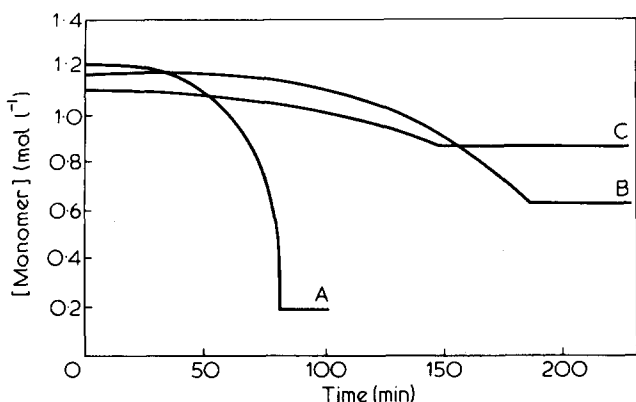


Figure 6 Polymerization of n-butyl isocyanate at low current values A, 15 mA; B, 11.5 mA; C, 9.0 mA

value of the overall rate constant along the horizontal portion of the graph is $8.2 \times 10^{-2} \text{ min}^{-1}$.

The acceleration in the rate of polymerization may be rationalised on the basis of a solid-state polymerization for which the rate constant is much greater than in the homogeneous analogue. It must be remembered that the onset of precipitation occurred quite early in the polymerization. It might be expected that this would lead to the usual decrease in polymerization rate as the monomer concentration decreases. It would appear that there is no simple dependence of monomer concentration included in the composite rate constant k , i.e.:

$$\frac{-d[M]}{dt} = k'[M] ([M_0] - [M])$$

otherwise a plot of $[M] : t$ would give a sigmoidal curve with a point of inflection at $2[M] = [M_0]$. This would imply that under rapidly stirred conditions, the rate of diffusion of monomer to the active centres in the solid particles is much greater than the rate of polymerization. The possible dependence on monomer concentration in a quiescent solution could not be ascertained because of the coating of the electrodes under these conditions.

The greater reactivity of the solid polymer may be due to the increased free-ion nature of the negative polymeric ions enforced by the withdrawal of the tetraethyl ammonium Gegen ions to the other side of the solid/liquid interface. Alternatively the solid may have an inherently higher propagation rate constant. This was shown to be the case when butyl isocyanate was irradiated with X-rays although the whole system was in the solid phase⁸. It may be significant in the context of solvent participation that these workers found that the rate was further enhanced if a frozen solution of isocyanate in DMF was irradiated with X-rays.

If equation (8) is rewritten as:

$$\frac{-d[M]}{dt} = k [\text{active centres}]$$

then

$$\frac{[\text{active centres}]}{([M_0] - [M])} = \text{Constant}$$

which suggests that the number of chains is fixed by the

current value giving a zero-order dependence at $> 20 \text{ mA}$. This could be a manifestation of a steric arrangement within the polymer particle. This is a controversial subject: nylon-1 polymers represent polymers with extremely stiff chains where the Mark-Houwink exponent $\alpha \geq 1$ ⁹. There is also considerable evidence that a rod-helix transformation occurs.

The degree of polymerization at which this phenomenon occurs varies according to the solvent and technique used for its determination. Rather wide limits have been proposed ($\bar{P}_n = 500-1500$)¹⁰. X-ray measurements on the crystalline solid poly(n-butyl isocyanate) suggest a helical arrangement of the molecules with 8 n-butyl isocyanate monomer units occupying three turns of the helix¹¹. There is also a strong indication that the conformation of the polymer is essentially the same in cyclohexane solution¹⁰. One hypothesis is that the molecule can propagate more rapidly in the helical form because of the position of the side groups.

One considerable drawback with the present work was that the polymer proved to be almost totally insoluble in the solvents which have been reported for poly(n-butyl isocyanate) and thus conventional techniques for molecular weight measurement could not be used. X-ray diffraction studies indicated that the polymers were crystalline and their infrared spectra were identical with the spectra reported by Natta for polymers produced using ethyllithium¹² in toluene and also for polymers produced by radiation-initiated polymerization⁸. These polymers are also insoluble, whilst those produced by the reaction of NaCN in DMF are soluble¹².

A further interesting feature of the polymerization is the appearance of a maximum in the degree of conversion at currents up to 15 mA as illustrated in Figure 6, where it can be seen that the acceleration in rate occurs until a limit is reached, after which a sharp cut off occurs.

The polymerization of isocyanates gives rise to an equilibrium concentration of polymer¹³, complicated in this case by depolymerization to trimer rather than monomer. Such a polymerization may normally be expressed as

$$\ln \frac{[M_0] - [M_e]}{[M] - [M_e]} = kt \quad (9)$$

where $[M_e]$ is the equilibrium concentration of monomer. This does not obtain here, presumably because the acceleration effect is still dominant. A linear relationship is found to apply if the results are considered in terms of the relationship

$$([M_0] - [M_e]) = kI + C \quad (10)$$

as can be seen from Figure 7. This may possibly be rationalized on the basis that there is a maximum degree of polymerization. The conversion of monomer to polymer may thus be decreed by the number of chains and this is fixed by the current. The absence of a time dependence probably indicates that the polymerization is much faster than the rate of initiation. The higher currents ($> 15 \text{ mA}$) may lead to a situation where the maximum degree of polymerization has not been reached when the monomer is totally depleted. Figure 7 also indicates a minimum current which must be reached before polymerization can occur. It is not apparent why further chains are not initiated when current is passed continuously. It could be argued that polymerization would occur until all the monomer was used up, whatever the limit to the degree of polymerization.

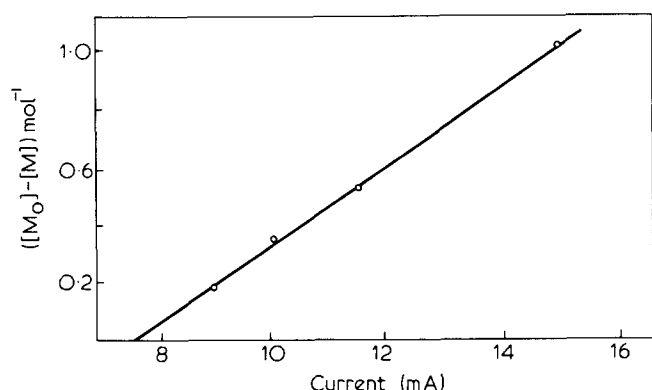
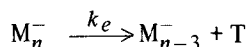
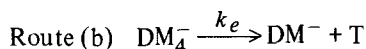
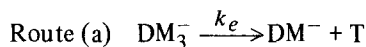


Figure 7 Relationship between electrolysis current and extent of total reaction for the polymerization of butyl isocyanate at -60°C . Slope = $0.137 \text{ mol l}^{-1} \text{ mA}^{-1}$

The effect of higher currents was also investigated, i.e. using 200 and 100 mA. In the former case, a slow reaction ensued, giving a low yield of polymer. It was also observed that dark-coloured particles were produced which floated on mercury, typical of alkyl ammonium amalgams⁵. A similar effect was observed, although to a lesser extent at 100 mA, when polymerization proceeded at a rate only slightly lower than that at 50 mA, giving a slightly reduced yield of polymer. In both cases however, polymer samples exhibited a slightly different colour to those produced at lower currents.

Trimerization to produce butyl isocyanurate occurred during electrolysis under these conditions, in turn giving rise to polymer formation. Such a material could be produced either directly from the monomer or by depolymerization of the growing polymer chains.



where D = DMF residue; M = monomer; and T = trimer.

Routes (a) and (b) are identical if the minimum number of monomer units (3 or 4) required for termination is regarded as a polymer of low molecular weight. In the present system a distinction between the routes can be made if M_n^- (in route b) is assumed to be insoluble polymer whilst route (a) occurs in the preceding homogeneous state. Different kinetic systems then apply.

$$\text{Route (a):} \quad \frac{dT}{dt} = k_e [\text{Anionic centres}]$$

$$T = \frac{k_e I t}{n F v} \quad \text{or} \quad \frac{k_e I t^2}{N F v} \quad (\text{if no termination})$$

$$\text{Route (b):} \quad \frac{dT}{dt} = k_e \int_0^t ([\text{Mo}] - [\text{M}]) dt$$

It would appear, therefore, that a linear increase in trimer with time should be observed if trimer is formed in the homogeneous state. An exponential increase in trimer concentration should be observed if its formation is via the

polymer, that is, assuming that only the centres active for polymerization are active for trimerization. The experimental evidence is not definitive on the mechanism of trimer formation. The theory that trimer is formed from the polymer is supported by the observation that formation occurs only during the accelerating phase of the reaction. In experiments at low currents ($<15 \text{ mA}$) the trimer concentration did not increase markedly when the limiting monomer concentration was reached, although current continued to be passed. However, at higher currents, trimer is formed linearly with time until the monomer concentration approaches zero when the trimer concentration remains constant. When the temperature was allowed to rise, samples indicated that the monomer was removed entirely but that the trimer increased only to the level of the residual monomer, not to the original monomer concentration. The non-formation of trimer when monomer was added subsequent to the electrolysis of solvent only may also indicate that trimer is not formed from the polymer. Certainly an improved fit of the experimental points to the derived equations is obtained if a slight adjustment for trimer is made to the monomer concentration. The formation of trimer would then be extra to the polymerization and therefore probably from the homogeneous stage. Figure 8 illustrates the influence of current on the rate of formation of trimer where it can be seen that the curve exhibits the same general form as Figure 5, which may indicate that the trimerization reaction suffers from the same constraints as polymerization.

The results presented so far refer to solutions containing known concentrations ($\sim 1 \text{ M}$) of monomer. When the concentration was increased to 4 M , no polymerization occurred after 2 h electrolysis at 50 mA. Dilution to 2.5 M gave no polymerization even after a further 2 h electrolysis. It was only after dilution to 1.9 M and after further electrolysis that polymerization occurred together with the now familiar acceleration effect. Again trimer was produced only during this stage. It would therefore appear that there is a maximum in the monomer concentration above which polymerization does not occur, thus lending support to the scheme developed in Part 1. Solvent is reduced to provide the species necessary to initiate polymerization. The overall rate constant of $12.7 \times 10^{-2} \text{ min}^{-1}$ (at 50 mA) is comparatively high (Figure 5) indicating some dependence on monomer concentration on the rate of polymerization. These results suggest that a solution of $< 1 \text{ M}$ monomer should polymerize more readily; this was found to be so when using a current of 30 mA at a monomer concentration of 0.5 M . The rate constant ($7.93 \times 10^{-2} \text{ min}^{-1}$) was slightly below that recorded for a 0.9 M solution but that appears to be a high value (Figure 5).

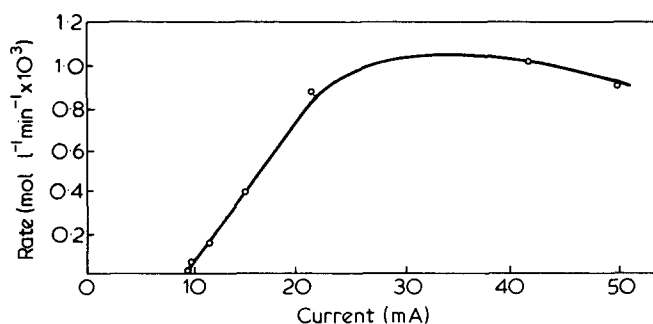


Figure 8 Rate of isocyanurate trimer formation as a function of applied current

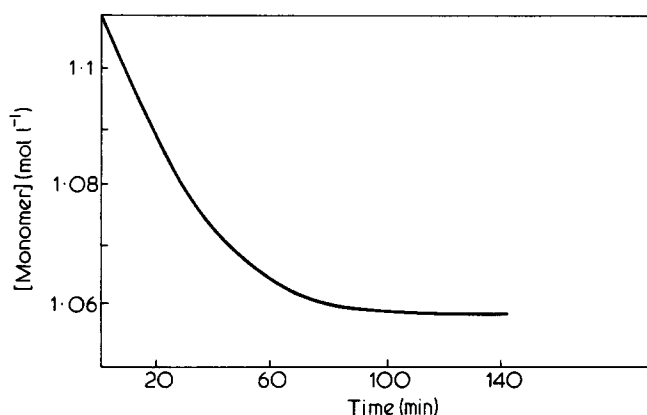


Figure 9 Rate of decay of polymerization of butyl isocyanate at -60°C following electrolysis at 50 mA for a period of 5 min at -60°C

The initial linear portion of the plot of $\log[M]$ versus time (Figure 2) suggests the possibility of a termination reaction being present. Experiments were carried out to test this hypothesis in which the current (50 mA) was switched off after 5 and 10 min, respectively. The decay curves were similar: that obtained in the former case is shown in Figure 9. The reaction continues almost unabated and then is terminated quite rapidly. A possible explanation for this phenomenon is that chains are still being initiated by the DMF anions until these are removed by protonation, when the activity of the chain ends is quenched fairly rapidly by the termination reaction. The curves illustrate the relatively low rate constant for the formation reaction. The half-life is of the order of 10 min or more which is about 5 times longer than the half-life for solvent protonation.

Figure 10 illustrates the conversion of monomer when immediately added to solvent plus electrolyte electrolysed for 1 h at 30 mA. The curve is quantitatively similar to those described earlier when electrolysis took place in the presence of monomer in that an accelerating reaction occurs, followed by a limit to the extent of reaction. However, the linear plot of $\log_e[\text{residual monomer}]$ versus time (Figure 10) has a slope of 0.79 min^{-1} which is about an order of magnitude greater than those in experiments when monomer was present throughout (Figure 5). This may possibly be interpreted in terms of an increased number of active polymerization sites caused by the complete availability of the current for reducing the solvent rather than some (probably most) of it being diverted into producing inactive reduced monomer. The rapid quenching of the reaction, when the gradient of the line $\log_e([M] - [M_0])$ versus time changes from positive to zero, may be explained in terms of the termination reaction mentioned previously. In all probability the number of active centres in this 'subsequent polymerization' is equivalent to a current of several hundred milliamps when monomer is present. However, such a high current was not practicable. The initial high readings in Figure 10 are interpreted as being due to incomplete mixing rather than any particular effect and the dotted line is therefore taken as the true curve.

CONCLUSIONS

This paper possibly represents the first published attempts to understand the kinetics of polymerization of isocyanates

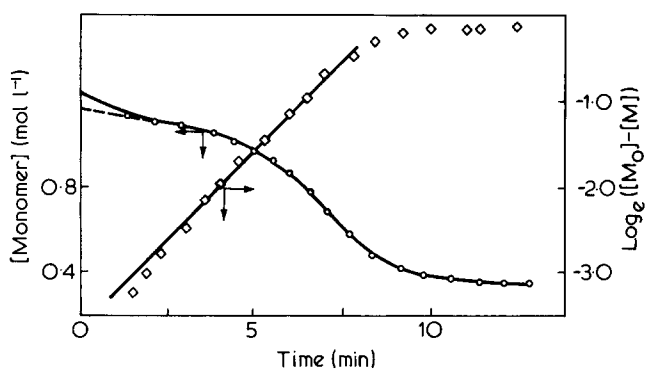


Figure 10 Subsequent polymerization of butyl isocyanate at -60°C . Monomer added following pre-electrolysis at 30 mA for 60 min

to produce linear addition polymers of the nylon-1 type. The polymerization shows several complicating features, including timer formation and a residual acceleration additional to that which may be expected in electroinitiated polymerization. The problems are further exacerbated by the transient nature of the initiating species which it is believed are derived from the electrolysis of the DMF although there is indeed some direct reduction of the monomer.

The reaction proceeds through an anionic mechanism leading rapidly to the production of an insoluble polymer. This will no doubt affect the course of the reaction and the accompanying kinetics, which show some remarkable features, in that it would appear that the rate of polymerization depends on the quantity of monomer already consumed and that the overall rate of polymerization is independent of current above a given value: however, a minimum current is required for polymerization to occur. Other factors which limit polymerization are monomer concentration and temperature.

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