ANIONIC POLYMERIZATION OF PROPIOLONITRILE; CONDUCTOMETRIC INVESTIGATION OF THE COURSE OF REACTION BETWEEN PROPIOLONITRILE AND BUTYLLITHIUM

J.Peška and M.J.Beneš

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

The polymerization of propiolonitrile with butyllithium in tetrahydrofuran at 25°C was followed conductometrically. A mechanism has been suggested according to which the reaction proceeds *via* cyanocetylide by route of a system of consecutive reactions. The rate constant of the growth steps decreases with the length of the conjugated chain. In this way, the general hypothesis about the kinetic stabilization of the growing centre during the polymerization of substituted acetylenes is supported.

The polymerization of substituted acetylenes proceeds only to low degrees of polymerization[1,2]. In theoretical quantum mechanical papers a hypothesis has been forwarded on the resonance stabilization of the growing centre[3,4] which in the limiting cases can be either thermodynamic or kinetic[5]. For the case of kinetic influence, a system of consecutive reactions is assumed fulfilling the condition $k_1 > k_2 > k_3$, while for the thermodynamic influence the system of the polymerization–depolymerization equilibria is supposed to exist, with $K_1 > K_2 > K_3$. In this paper, a contribution to this topic was made by investigating the conductometric response in the system propiolonitrile–tetrahydrofuran–butyllithium.

EXPERIMENTAL

The compounds were the same as in the preceding communication[2]. The conductivity cell with smooth platinum electrodes having an area of 2.2 cm^2 each with the constant 0.204 cm^{-1} and the working volume 10 cm^3 was adapted for working in an inert atmosphere, and provided with a thermostating jacket and magnetic stirrer. The conductivity was followed by means of an LF 39 (WTW Weinheim) conductometer using an EZ 4 recorder (LP Prague). The solution of reaction components were prepared and stored under an inert atmosphere and dosed from magnetically controlled burettes against a flow of argon. On adding the components the dosage opening was closed and the apparatus was maintained under an overpressure of the inert throughout the reaction time.

RESULTS

The electrical conductivity of the system increases during the polymerization. Fig. 1 shows the concentration dependence of the conductivity of propiolonitrile and butyllithium in tetrahydrofuran. The dependence of the conductivity of lithium chloride is also attached; it is analogous to that of butyllithium and could be measured more easily and in greater detail. The difference between the conductivities of propiolonitrile and butyllithium corresponds to the change observed during the polymerization. Fig. 1 shows further that the difference depends on concentration, and indicates the concentration range within which it is advantageous to follow the polymerization conductometrically. The cause of the different conductometric behaviour of components of the polymerizing system is a difference in association which amounts to several orders of magnitude (Fig. 2).

The polymerization itself was carried out so that an excess of propiolonitrile (M) was maintained throughout the reaction. This reduces the number of independent variables. A few typical records are given in Fig. 3. The relationships found do not satisfy a first order equation. As will be shown later, they are easy to interpret if two consecutive reactions
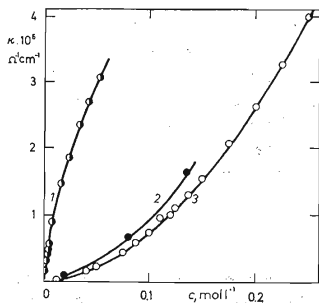
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad\qquad (A)$$

are taken into consideration, with $k_1 > k_2$. The integral solution of the above scheme is given by equations (1)–(3):

$$[A] = [A]_0 \exp\left(-k_1 t\right), \tag{1}$$

$$[B] = [A]_0 \frac{k_1}{k_1 - k_2} \left(\exp\left(-k_2 t\right) - \exp\left(-k_1 t\right)\right), \tag{2}$$

$$[C] = [A]_0 - [A] - [B]. \tag{3}$$

To proceed further, the relationship between the conductometric response and conversion must be examined — the conductometric response, r, is an additive property (Eq. 4a), relationship 4b defines the molar response of compound J, R_J, and the limiting response for time $t \to \infty$, $r_{\lim}$, is related to R_C (Eq. 4c):

$$r = r_A + r_B + r_C, \tag{4a,b,c}$$

$$r_J = R_J [J],$$
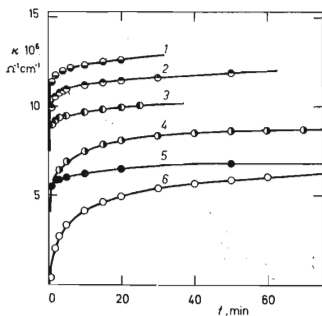
$$r_{\lim} = R_C [A]_0.$$

FIG. 3

Conductivity Response of the Polymerization of Propiolonitrile at 25°C

Concentration of the monomer or butyllithium respectively (mol/l): ○ 0·051, 0·0020, ● 0·118, 0·0019, ◐ 0·060, 0·0039, ◖ 0·118, 0·0038, ◓ 0·067, 0·0074, ◑ 0·115, 0·0074.
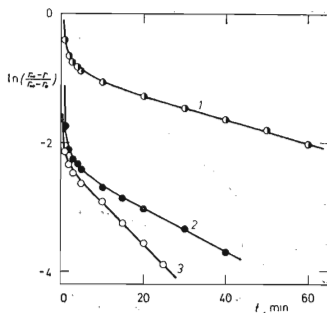
FIG. 4

Treatment of Conductivity Data According to Relationship (5)

Concentration of the monomer or butyllithium respectively (mol/l): ○ 0·117, 0·0038, ● 0·067, 0·0074, ◑ 0·034, 0·0020; temperature 25°C.

The response at the onset of the reaction which is related to R_A in a similar way was found to be negligible with respect to the response in the further course of reaction, *i.e.* $R_A = 0$. For a further mathematical treatment, it was necessary to find an analogous relationship for R_B, which in contrast with the above relationships for R_A and R_C cannot be obtained experimentally. We take the first approximation: R_B is a fraction of R_C, and therefore $R_B = \beta R_C$, By this, the coefficient β is defined which we only assume to remain constant during each individual experiment. The justification of such assumption and its indirect verification are discussed in the latter part of this paper. By rearrangement we obtain

$$\frac{r_{\lim} - r}{r_{\lim} - r_0} = \frac{\beta k_1 - k_2}{k_1 - k_2} \exp\left(-k_1 t\right) + \frac{(1 - \beta) k_1}{k_1 - k_2} \exp\left(-k_2 t\right). \qquad (5)$$

It can be shown that under the condition $k_1 > k_2$ the first term in the right-hand side of relationship (5) can be neglected with respect to the second term in the further course of the reaction. To analyze the situation at the onset of the reaction we shall use a linear approximation $\exp(-x) = 1 - x$ for $x \to 0$ which leads to the relationship

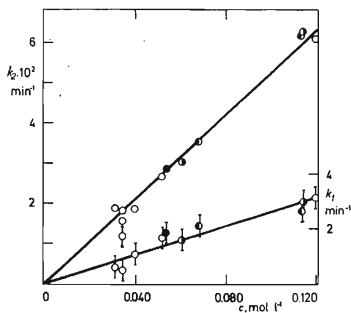$$\left[(r_{\lim} - r)/(r_{\lim} - r_0)\right] = \exp\left(-\beta k_1 t\right). \qquad (6)$$

Fig. 5

First Order Rate Constants Depending on the Original Concentration of Propiolonitrile

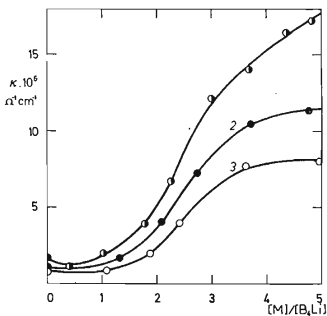Concentration of butyllithium (mol/l) (rounded off): ○ 0·002, ● 0·003, ◑ 0·004, ◐ 0·007; temperature 25°C.

Fig. 6

Limiting Conduction Response after Addition of Propiolonitrile (M) to Butyllithium Depending on the Ratio [M]/[BuLi]

[BuLi]: ○ 0·0039, ● 0·0050, ◑ 0·0101; temperature 25°C.

Consequently, if we rearrange the measured values in the form $(r_{lim} - r)/(r_{lim} - r_0)$ and plot the natural logarithm of this function against time, we obtain curves (Fig. 4) whose linear part corresponds to the second term of Eq. (5). From this linear part, we can read the slope $-k_2$ and (for $t = 0$) the intercept $\ln (1 - \beta) k_1/(k_1 - k_2)$. According to (6), the linear slope at the onset of reaction is then $-\beta k_1$.

For the separation of the individual quantities, a small iterative cycle was used, when $k_1/(k_1 - k_2)$ was first set equal to unity, β was calculated from the intercept and then used to calculate k_1. The latter value was used to calculate a new value for $k_1/(k_1 - k_2)$; the procedure was repeated until after four or five steps constant values had been achieved. The values thus determined are independent of the concentration of butyllithium and proportional to the initial concentration of propiolonitrile (Fig. 5) as corresponds to the simple scheme where $[A]_0$ is proportional to the initial concentration of butyllithium. Fig. 5 was used to read off the mean values for the second order rate constants at $25°C$, $k_1' = 26.1 \pm 10 \, l \, mol^{-1} \, min^{-1}$, $k_2' = 0.54 \pm 0.05 \, l \, mol^{-1} \, min^{-1}$.

$$A + M \rightarrow B, \qquad\qquad\qquad (B)$$

$$B + M \rightarrow C. \qquad\qquad\qquad (C)$$

Analysis of Errors

From the graphic representation (Fig. 4), the individual data can be read off with different accuracy. The slope $-k_2$ is read from the longer linear part so that the reliability of this value, confirmed also by the reproducibility of the individual experiments, is $\pm 7\%$. However, in the case of k_1 the unfavourable situation given by the method of reading off the limiting slope is enhanced by the fact that at the beginning the curves are subjected to a major error given by the problematic determination of the start of reaction in the region of rapidly changing response. It therefore cannot be regarded as surprising that the uncertainty in k_1 in some cases amounts to as much as 50%.

To carry out an evaluation according to Eq. (5), an assumption was made that the coefficient β is constant during each experiment. The molar responses R_J are proportional to the equivalent conductivity Λ_J which is generally dependent on concentration. The character of this dependence is determined mainly by the association constant and was examined for the case of propiolonitrile as given in Fig. 1; it can be described by e.g. Shedlovsky's conductivity equation[6]
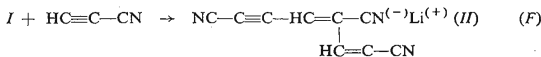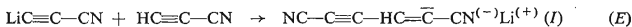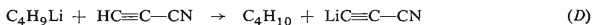
$$1/S\Lambda = 1/\Lambda_0 + (K_{ass}/\Lambda_0^2) \, S\Lambda c f_{\pm}^2 , \qquad\qquad (7)$$

where $S\Lambda = \alpha \Lambda_0$, $(1 - \alpha)$ is the degree of association and S is Shedlovsky's function whose magnitude depends on the ionic strength of the solution. Consequently, for the coefficient β, which is the ratio of the responses or equivalent conductivities of compounds B and C the common value of S is not operative, and β is equal to the ratio of the degrees of dissociation of compounds B and C. If one bears in mind that both compounds produce by dissociation a common counter-ion (Li^+), it can be demonstrated that the ratio of their degrees of dissociation is independent of concentration (equal to the ratio of the dissociation constants) if both degrees of dissociation

α_B and α_C are small. Thus, the assumption about the constant character of the coefficient β is generally satisfied only within a certain limited concentration range. It can be, however, verified indirectly by following the variations of the β values determined in the individual experiments differing by the original concentration. The values thus found (the average from sixteen determinations 0·831, standard deviation 0·077) did not exhibit any dependence on the original concentration of butyllithium in the range from 2 to 7 mmol/l. The calculated coefficient of linear regression (0·0015 l/mmol) corresponds to the predicted increase in β, within the above concentration range, by one order of magnitude lower than the standard deviation of β.

Experiments with an Inverse Addition of Components

If in contrast with the preceding experiments propiolonitrile is added to the solution of butyllithium, the reaction proceeds differently. At the beginning, the reaction mixture remains colourless; colouration sets in only after the third mol of propiolonitrile per one mol of butyllithium has been consumed. The conductometric response was read off only after stabilization to a constant value. The dependences measured and given in Fig. 6 show that the principal change occurs only between the consumption of the third and fourth mol of propiolonitrile per one mol of butyllithium. If one considers, similarly to ref.[5], the following scheme

$$C_4H_9Li + HC{\equiv}C{-}CN \;\rightarrow\; C_4H_{10} + LiC{\equiv}C{-}CN \qquad (D)$$

$$LiC{\equiv}C{-}CN + HC{\equiv}C{-}CN \;\rightarrow\; NC{-}C{\equiv}C{-}HC{=}\bar{C}{-}CN^{(-)}Li^{(+)} \;(I) \qquad (E)$$

$$I + HC{\equiv}C{-}CN \;\rightarrow\; NC{-}C{\equiv}C{-}HC{=}C{-}CN^{(-)}Li^{(+)} \;(II) \qquad (F)$$
$$\underset{\displaystyle HC{=}\underset{\cdot}{C}{-}CN}{|}$$

the fact mentioned above seems somewhat surprising. Lithium acetylides are known[7] to be strongly associated, similarly to butyllithium. However, one would expect for enine I a behaviour essentially identical with that of trimer II, and thus also the change in the molar response to be largest between the consumption of the second and third moles of propiolonitrile. A similar phenomenon, namely, a retarded formation of the product against the kinetic scheme by one molecule per initiator, has already been observed during the polymerization of propyne by lithium methylacetylide in dimethylsulphoxide[5]. We proved that this fact was due to the complex formation between monomer and the anion of the growing centre. The formation of this complex intermediate played a decisive role in determining the rate of polymerization. In the case dealt with here the formation of such a complex will have a still more pronounced character, since it is not interfered with by a strong polar solvent.

REFERENCES

1. Beneš M. J., Janić M., Peška J.: Chem. listy *64*, 1094 (1970).
2. Beneš M. J., Peška J.: This Journal, in press.
3. Manassen J., Rein R.: J. Polymer Sci. *A-1, 8*, 1403 (1970).
4. Kříž J.: J. Polymer Sci. *A-2, 10*, 615 (1972).
5. Kříž J., Beneš M. J., Peška J.: This Journal *32*, 4043 (1967).
6. Shedlovsky T.: J. Franklin Inst. *225*, 739 (1938).
7. Rodionov A. N., Kazennikova G. V., Talalajeva T. B., Šigorin D. N., Kočeškov K. A.: Dokl. Akad. Nauk SSSR *129*, 121 (1959).

Translated by L. Kopecká.