Anionic polymerization of acrylonitrile initiated by electrolytically prepared radical anions of benzophenone and 2,2'-bipyridyl

S. MIERTUŠ, O. KYSEL', and P. MÁJEK

Polymer Institute, Slovak Academy of Sciences,
809 34 Bratislava

Possibilities of the application of radical anions of benzophenone and 2,2'-bipyridyl as initiators of anionic polymerization were studied experimentally. Acrylonitrile polymerization is initiated by both radical anions. In evaluating and investigating anionic polymerization we concentrated on propagation reaction; the propagation rate constant, the effect of the quality as well as the concentration of supporting electrolyte, and the effect of the concentration of initiator on the propagation rate constant were determined.

Экспериментально изучены возможности использования анион-радикалов бензофенона и 2,2'-бипиридила как инициаторов анионной полимеризации. В случае акрилонитрила имеет место инициирование обоими анион-радикалами. При обсуждении и изучении анионной полимеризации мы сосредоточились на реакцию роста цепи, причем мы определили ее константу скорости и влияние типа и концентраций поддерживающего электролита и инициатора на константу скорости.

For anionic polymerization mostly initiators (radical anions or dianions) prepared by chemical reduction with alkali metals have been employed so far [1, 2]. In addition to this procedure there are other ways of preparing radical anions; of these, especially electrolytical reduction [3] has some advantages. The radical anions thus prepared have rarely been used for anionic polymerization [2, 4, 5]. This is connected with the fact that in the electrolysis strongly polar solvents are used in the presence of the supporting electrolyte representing thus a more complex medium able to modify considerably reactivity in polymerization reactions. Since these processes in the electrolytical preparation of radical anions have been relatively little investigated, we concentrated on their study.

Experimental and discussion

Acrylonitrile, styrene, and 4-vinylpyridine were used for polymerization. Benzophenone and 2,2'-bipyridyl radical anions were employed as initiators. They were prepared by electrolytical reduction at large-surface Hg cathode in dimethylformamide (DMF) in the presence of the supporting electrolyte $(n\text{-}C_4H_9)_4NClO_4$ (TBAPC) or $NaClO_4$. The whole system was in an inert nitrogen atmosphere. The reduction potential of the cathode was chosen by 0.1—0.2 V higher than the polarographic half-wave potential and kept constant against SCE by a potentiostat Radelkis OH 404. Details on the preparation of radicals, purification of solvent and nitrogen have been described previously [6].

The generation of radical anion proceeded until the electric current fell below 10% of the initial value. After completion of the preparation of radical anion, the known amount of monomer was added in the electrolytical vessel and kinetics were measured. Monomers deprived of water and air oxygen distilled several times were used for polymerization [6]. Part of solution was transferred to a ground-joint vessel containing the known amount of precipitant (H_2O). After precipitation of polymer, solution with precipitant was filtered and the amount of precipitated polymer was weighed.

Polymerization with benzophenone radical anions was carried out at 298 K. With respect to the low stability of 2,2'-bipyridyl radical anions at $T > 273$ K the polymerization was performed at 243 K. Of the above monomers, only acrylonitrile was successfully polymerized. This result was qualitatively explained by the theoretical study of initiation reactions given in the preceding paper [7].

We focused our attention on the polymerization of acrylonitrile initiated by radical anions, on the determination of the propagation rate constant, and the evaluation of the effect of the quality and concentration of supporting electrolyte and the concentration of initiator.

By kinetic measurements the time dependence of the consumption of monomer was obtained. The apparent rate constant for propagation reaction was calculated from the time dependence of the monomer consumption and the immediate monomer concentration by the equation

$$-d[M]/dt = k_p[M] \qquad (1)$$

Here it is assumed [8] that the concentration of the reactive centres (*i.e.* anionic ends of living polymers — LP) is constant during polymerization. Then the rate constant for propagation of bimolecular reaction k_{ap} is obtained from the relation

$$k_p = k_{ap}[LP] \qquad (2)$$

To simplify matters we assumed the concentration of living anionic chain ends [LP] to be equal to the concentration of initiator.

The real ratios in determining k_{ap} are more complicated since in the initial stage both reactions (*i.e.* initial and propagation) proceed simultaneously as a set of consecutive and competitive reactions

$$I^{\overline{\cdot}} + M \rightarrow I + M^{\overline{\cdot}} \tag{3}$$

$$I^{2-} + M \rightarrow I^{\overline{\cdot}} + M^{\overline{\cdot}} \tag{4}$$

$$M^{\overline{\cdot}} + M \rightarrow {}^{-}M{-}M \cdot \tag{5}$$

We tried to examine also kinetics of initiation reactions. The decay of radical anions was studied after addition of monomer. However, initiation reaction is fast because after 15—20 s the concentration of radical anions falls below the spectrophotometrically observable value. Accordingly, the propagation should then occur and the consumption of monomer should be due to the chain growth. Thus after 1—2 min the propagation reaction can be regarded formally as the first-order reaction and the rate constant determined can be assigned qualitatively to the rate constant of propagation. The order of the reaction was confirmed by the plot of $d[M]/dt$ *vs.* the immediate monomer concentration $[M]$ (Fig. 1) which is linear.
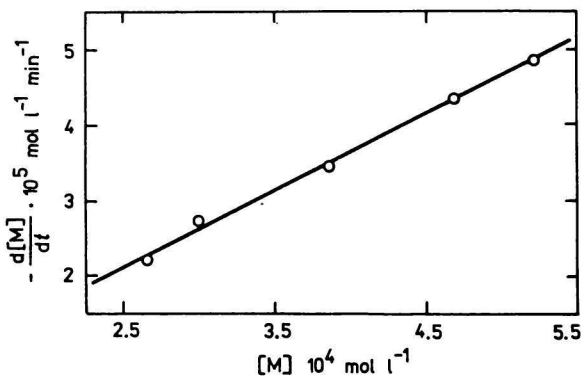

Fig. 1. Plot of the consumption of acrylonitrile *vs.* immediate acrylonitrile concentration.

Tables 1 and 2 contain the results of all measurements of the rate constants for propagation reaction of acrylonitrile determined in this manner.

The values lead to several conclusions. We found that for benzophenone radical anion used as initiator, the propagation rate constant is in the presence of the supporting electrolyte TBAPC (larger cation) higher than in the presence of NaClO$_4$ (cation with smaller radius).

According to experimental works [1, 2] on the systems using radical anion obtained by chemical reduction as initiator and from the theoretical study of this process [9], the reverse order of the reactivity was found. This can be due to the

Table 1

Effect of the concentration of supporting electrolyte on the rate constant for propagation reaction of acrylonitrile

Electrolyte	Concentration of electrolyte $(mol\ l^{-1})\cdot 10^3$	k_{ap} $(l\ mol^{-1}\ s^{-1})\ 10^3$
NaClO₄	2.5	1.81
TBAPC	2.5	4.77
TBAPC	25.0	1.90

$T = 298\ K$; concentration of benzophenone $2.6 \times 10^{-3}\ mol\ l^{-1}$.

Table 2

Effect of the concentration of initiator on the rate constant for propagation reaction of acrylonitrile

Benzophenone $(mol\ l^{-1})\cdot 10^3$	k_{ap} $(l\ mol^{-1}\ s^{-1})\cdot 10^3$
5.0	1.26
2.6	4.77
1.0	11.60

$T = 298\ K$; concentration of TBAPC $2.5 \times 10^{-3}\ mol\ l^{-1}$; initiator: benzophenone.

mentioned more complex medium (presence of excess cations of supporting electrolyte) and thus lead to higher association of the living anion with Na^+ ion, which may decrease reactivity of the anion. Similar anomalies were found in studying the equilibrium of ion pairs of radical anions (prepared electrolytically) with Na^+ or $(C_4H_9)_4N^+$ (from supporting electrolyte) [10].

As the concentration of the supporting electrolyte increases, the rate of propagation reaction decreases (Table 1) as a result of an equilibrium shift ion pair—free ions toward ion pairs; the latter are generally less reactive than the former [1], which is in agreement with theoretical calculations [9].

With the increasing concentration of initiator the rate constants decrease (Table 2). It was found that k_{ap} is a linear function of $[BPh]^{-1/2}$ ([BPh] is the initiator concentration). This indicates that during reaction the equilibrium is established probably between free ions and ion pairs of the living polymer. For this equilibrium, according to [8], the following relation holds

$$k_{ap} = k_{\pm} + \frac{(k_- - k_{\pm})\ K_{dis}^{1/2}}{[LP]^{1/2}} \qquad (6)$$

where $k_{\pm}$ and k_{-} are the propagation rate constants for ion pairs and free ions respectively, and K_{dis} is the equilibrium dissociation constant between free ions and ion pairs.

The dependence found supports assumption that during polymerization the concentration of the living polymer [LP] is almost constant and directly proportional to the concentration of initiator [BPh].

Eqn (6) was obtained for the systems with chemical initiation of polymerization [8] on the assumption that the system contained more ion pairs than free ions. It can be therefore assumed that in the system studied, similar situation arises, *i.e.* in strongly polar medium also ion pairs take part in the propagation reaction.

Results obtained for 2,2'-bipyridyl do not in principle differ from those given for benzophenone. In the case of 2,2'-bipyridyl the mentioned processes are more rapid.

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