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Electroinitiated Polymerization of Acrolein by Direct and Indirect Electron Transfer Via Controlled Potential Electrolysis

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ELECTROINITIATED POLYMERIZATION OF ACROLEIN BY DIRECT AND INDIRECT ELECTRON TRANSFER VIA CONTROLLED POTENTIAL ELECTROLYSIS

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ABSTRACT

Electroinitiated polymerization of acrolein has been achieved by controlled potential electrolysis at the reduction peak potential of the monomer for direct electron transfer. Kinetics and type of mechanism of the polymerization have been investigated. The structure of the polymer has also been examined by IR spectroscopy. In a separate experiment, a small amount of CCl_4 was added to a polymerization system. Since the reduction peak potential of CCl_4 appears at a more anodic region than that of acrolein on mercurized platinum, initiation proceeds via the electrolytic product of CCl_4. The direct and indirect initiation mechanisms are compared. It is found that electroinitiated polymerization of acrolein carried out by direct electron transfer from cathode to monomer (in the absence of CCl_4) proceeds simultaneously via radical and anionic mechanism. On the other hand, when polymerization is carried out by indirect initiation in the presence of CCl_4, propagation proceeds by an anionic mechanism.

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INTRODUCTION

In recent years great attention has been given to the polymerization of acrolein due to new areas of application of the polymer. Most important applications are in the biological and biomedical fields. The polymer can be used as a protein crosslinking agent [1], in the fixation of living cells [2], and as binding agents of antibodies to microspheres of the polymer for immunoresearch and protein immobilizations [3].

The structure of a polymer is a critical factor in the determination of its uses, hence, the type of polymerization is important. Difunctionality of a monomer leads to different polymer structures depending on the type of initiation. The free-radical polymerization of a monomer initiated by free-radical initiators [4], redox pairs [5], UV [6], and gamma rays [7] generally yields insoluble polymers. Polymerization proceeds through the double bond to a great extent and gives pendant aldehyde groups which may be cyclicized. The most commonly encountered structure is
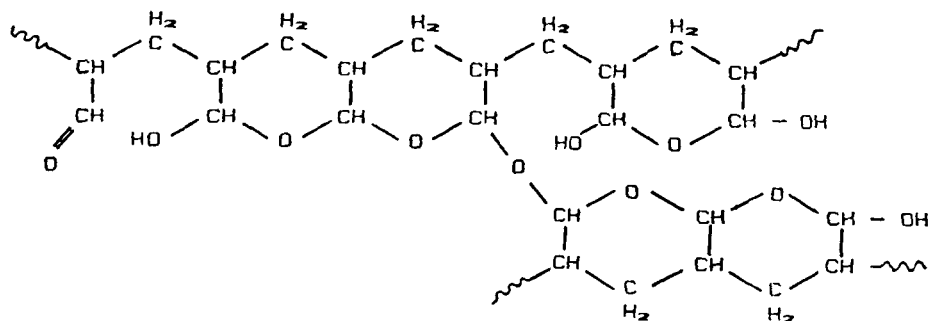
On the other hand, the products of ionic polymerization [4, 8] contain about 70% double bonds and polymerize through the carbonyl group to give etheric linkages in the chain backbone with the structure given below. However, it is almost impossible to have only vinyl-type polymers or polyether-type structures due to the activation of both functional groups.
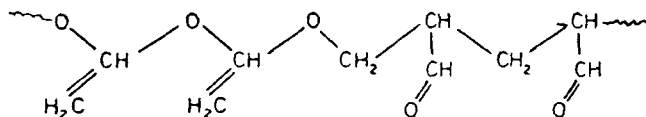
It is suggested that if a suitable method is applied in which only the vinyl group or aldehyde group is activated, a polymer with a desired structure may be synthesized.

Electrochemical initiation by controlled potential electrolysis is a suitable method for this purpose. It is possible to activate only the vinyl group or aldehyde group by applying the suitable potential found by cyclic voltammetry.

The aim of this work is to make use of the high selectivity of electrochemical initiation to synthesize polyacroleins with predetermined structures.

There are few reports on the electrochemical polymerization of acrolein in the literature [9, 11]. However, in most studies the method used was controlled current electrolysis (CCE). In CCE, the type of initiation may be via indirect electron transfer and a species other than the monomer may be activated to initiate or inhibit polymerization. On the other hand, Akbulut et al. [12, 16] showed that it is possible to initiate polymerization by direct electron transfer to the monomer by using the controlled potential electrolysis method. Hence, the same method is used in this work for the proposed aim.

EXPERIMENTAL

Purification of Materials

Purification of acetonitrile and tetrabutylammonium tetrafluoroborate was described earlier [17]. Acrolein was distilled at 40°C before each experiment. *n*-Butyl bromide, hydroquinone, and carbon tetrachloride were used without further purification.

Determination of the Electrochemical Behavior of Acrolein and Carbon Tetrachloride

The electrochemical behaviors of acrolein (AL) and carbon tetrachloride were determined by cyclic voltammetry (CV) with acetonitrile–tetrabutylammonium tetrafluoroborate (TBAFB) as the solvent-supporting electrolyte couple. TBAFB was 0.1 M in each case. The reference electrode was Ag/Ag$^+$ (0.01 M), and two platinum wires were used as the working and counter electrodes during the measurement of the reduction peak potential of AL. The conditions were the same in the presence of CCl$_4$ except for the working electrode which was a mercurized Pt wire. The mercurized Pt electrode was prepared by using the electrode as a cathode in the electrolysis of a solution of 0.1 M mercurous chloride in 70% perchloric acid for a definite time. After plating the Pt with Hg, it was washed with water, dried, and used as the working electrode in CV measurements. The concentration of both substrates (AL and CCl$_4$) was 1 mmol/L.

Direct Initiation and Kinetic Studies

The kinetics of polymerization reactions were followed by cyclic voltammetry during the course of the reactions. For this purpose a specially designed polymerization cell with three compartments was used (Fig. 1).

Cathode and anode compartments were separated by a fritted glass disk. The reference electrode was connected to the cathode compartment with a luggin capillary. Two potentiostats, one for controlling the potential of electrolysis and the other coupled with a function generator for taking the cyclic voltammograms, were used during the studies. Working and counter electrodes in electrolysis (WE_e, CE_e) were both Pt foils having 1 in.² areas. Working and counter electrodes in CV (WE_c, CE_c) measurements were Pt wires. The WE_c was made easily detachable to facilitate flaming of the electrode after each CV run to eliminate coated polymer which affects the CV peaks. There were two Ag wire electrodes in the same compartment, i.e., the reference electrode of the cell.

Polymerization reactions were conducted in acetonitrile–TBAFB at the reduction peak potential of the monomer with known amounts of AL (0.10 M). After taking the
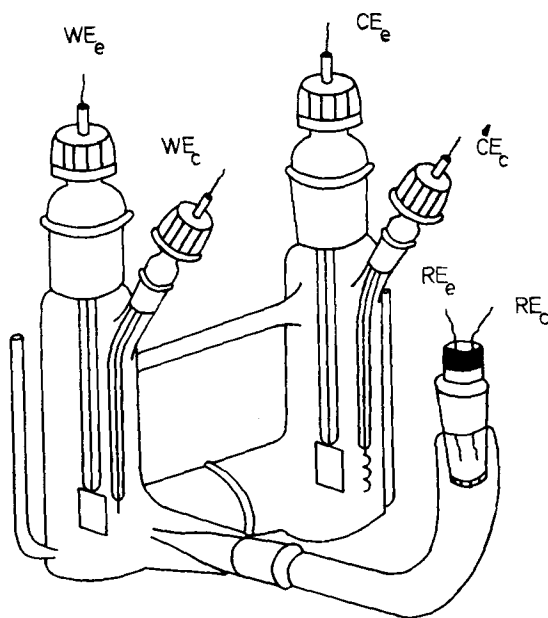
FIG. 1. Polymerization cell for kinetic investigations.

cyclic voltammogram of the monomer for the initial peak height, electrolysis was started and measurements were continued by CV during the course of reaction. WE_c was flamed after each measurement without interrupting the electrolysis. All of the experiments were performed after purging the solutions with N_2. Before each CV measurement, gas was purged into the working compartment for a few seconds. Percent conversions were calculated using the peak heights in the voltammograms of the unreacted monomer.

In the inhibition of the polymerization, electrolyses were carried out up to a definite time, then inhibitors were added and electrolysis was continued. Inhibitors were electroinert at the working potential.

The kinetics of postpolymerization was followed by stopping the current after a definite time and following the decrease in the peak height of the monomer thereafter. For inhibition of postpolymerization, inhibitors were added just after the cessation of the current.

Indirect Initiation and Kinetic Studies

In order to achieve indirect initiation, 2.3×10^{-2} M CCl_4 was used with 0.10 M initial monomer concentration. All the conditions were the same as for the direct initiation case, except that the WE_e was mercurized Pt foil (1 in.²). It was prepared the same as WE_c except that the mercurization times were longer (2 min).

Fourier-Transform Infrared Spectrophotometer (FTIR)

FTIR spectroscopy was used to determine the structure of the polymer. The instrument was Perkin-Elmer Model 1710.

RESULTS AND DISCUSSION

Direct Initiation of Polymerization

In controlled potential electrolysis, the initiating species is the activated monomer itself where the applied potential is the reduction peak potential of monomer as determined by CV. AL has an irreversible reduction peak at −2.4 V vs the Ag/Ag⁺reference electrode (Fig. 2). Therefore, for direct initiation of polymerization, −2.4 V was used as the electrolysis potential.

Polymerizations were heterogeneous in the solvent used (acetonitrile), and the cathode was coated with a whitish polymer layer during electrolysis. In all experiments the polymer obtained was insoluble in ordinary solvents. The IR spectrum of the polymer (Fig. 3) resembles the spectrum of the polymer obtained by redox initiation [8].
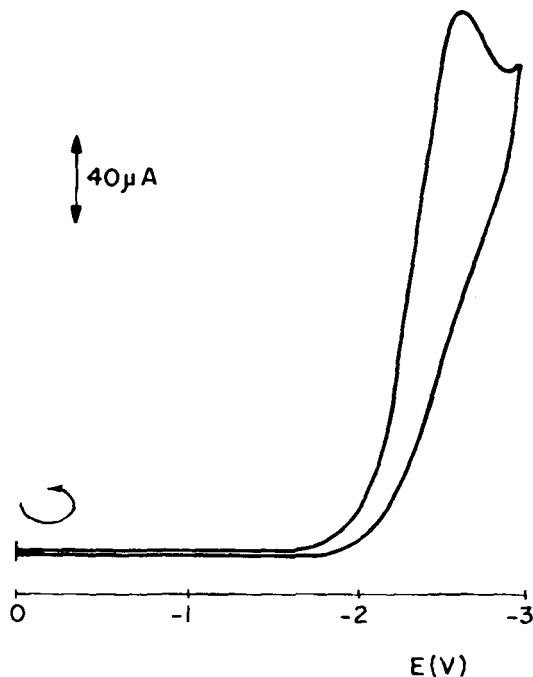
FIG. 2. Cyclic voltammogram of acrolein.

Polymerization mostly propagates through the double bond with pendant aldehyde groups in polymerization systems where the initiating species are free radicals. Therefore, the IR spectrum obtained in this work indicates a free radical mechanism. The validity of this assumption was checked by kinetic and inhibition experiments.

In order to investigate the effect of temperature on the polymerization rate, reactions were carried out at three different temperatures: +25, 0, and −15°C (Fig. 4). There is a direct relationship between the temperature and the rate.

The possibility of a free-radical mechanism was checked by inhibiting the polymerization with hydroquinone. The inhibition experiment was conducted at 25°C. The decrease in monomer concentration was followed up to the 6th minute, hydroquinone was added, and electrolysis was continued. However, instead of complete inhibition, only a decrease in rate was observed (Fig. 5). Such behavior may be an indication of a more complex mechanism. Since the electrochemical reaction is the reduction of acrolein-forming anions or radical anions, the polymerization can be
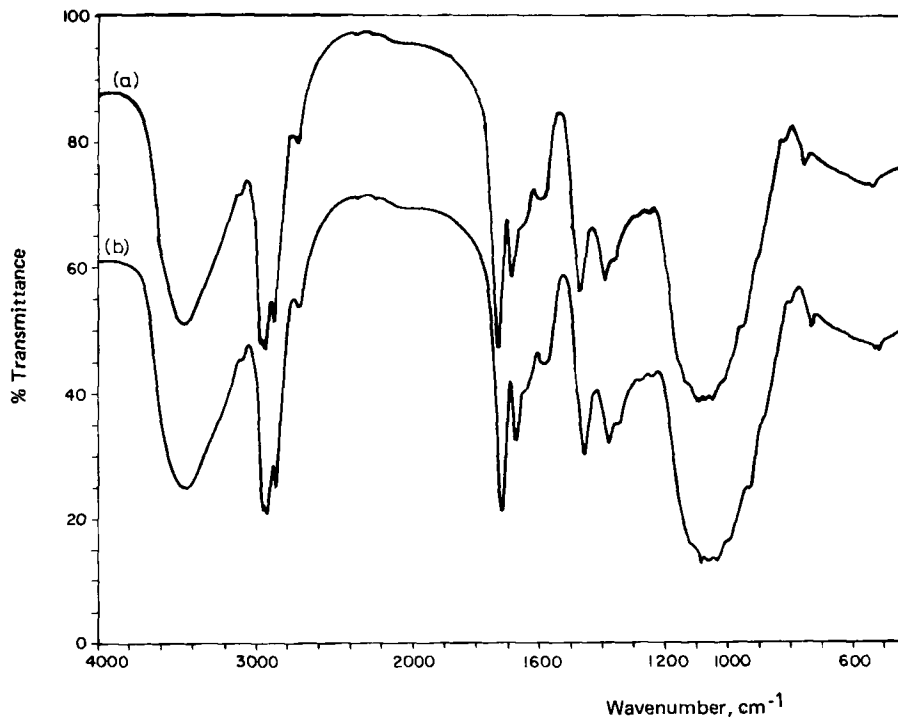
FIG. 3. (a) FTIR spectrum of polyacrolein obtained by direct initiation at 0°C and –2.4 V. (b) FTIR spectrum of polyacrolein obtained by indirect initiation at –1.7 V and –15°C.

assumed to proceed by an anionic mechanism. Therefore, n-butyl bromide was added to the system to trap the anions. From the results it is seen that n-BuBr was effective for inhibiting the anionic sites (Fig. 5).

An interesting observation in the electroinitiated homopolymerization of acrolein was the propagation of polymerization after the cessation of current. The kinetics of postpolymerization was also investigated by performing the electrolysis for 6 minutes and stopping the current. Figure 6 shows the results of the mentioned experiment. The percent conversion reaches from the 40s to the 70s in about 15 minutes, indicating a fast postpolymerization rate.

The occurrence of postpolymerization gave an opportunity to check the inhibition efficiency of hydroquinone in the absence of an electric current.

The two inhibitors mentioned above were also used in these postpolymerization studies. These experiments were performed as in the polymerization case but the
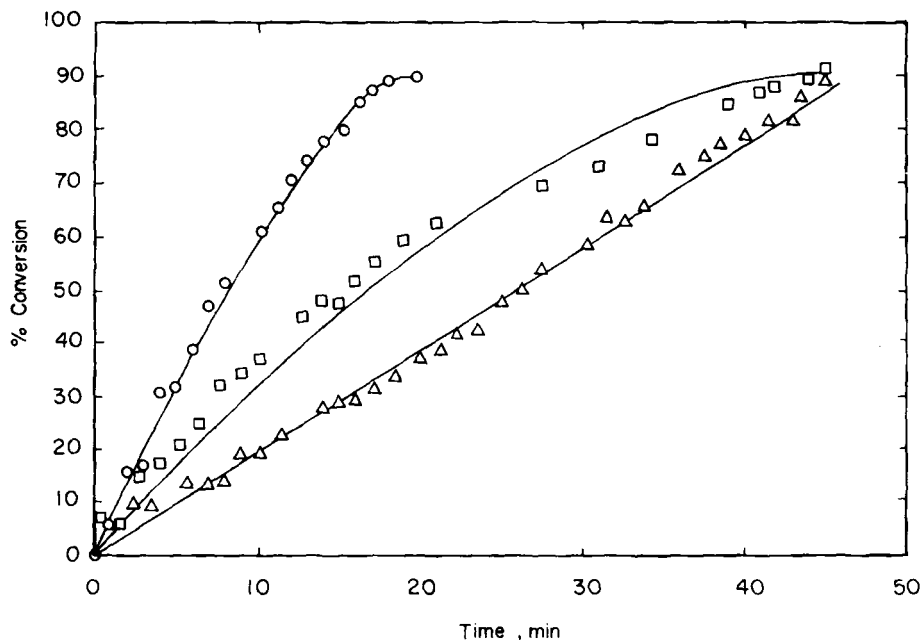
FIG. 4. Percent conversion vs time plots for electroinitiated polymerization of acrolein obtained at (Δ) −15°C, (☐) 0°C, and (O) 25°C.

inhibitors were added just after the cessation of current. In this way the electroreduction of hydroquinone was eliminated and thus the efficiency of the inhibitor on postpolymerization could be emphasized. In such a case the postpolymerization should be stopped completely if the mechanism were purely free radical. Addition of both inhibitors had the same effect on rate as in the usual polymerization case (Fig. 6).

Hydroquinone was more effective in the inhibition. However, complete cessation of postpolymerization cannot be achieved even in this case. Therefore the presence of a complex mechanism involving radical-anions or radicals and anions is proposed for the electroinitiated homopolymerization of acrolein.

The effect of agitation was also investigated for the electroinitiated polymerization of acrolein by continuously bubbling N_2 into the cathode compartment. The rate of polymerization was affected in the positive sense upon agitation (Fig. 7). This behavior is attributed to the continuous refreshment of the electrode surface. The amount of monomer activated under these circumstances must increase. As a result,
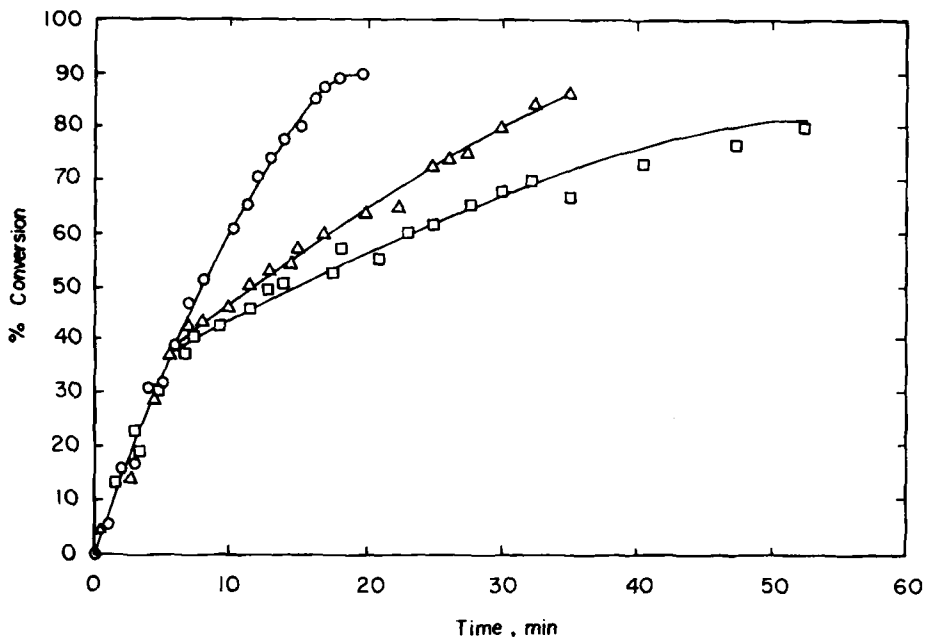
FIG. 5. Percent conversion vs time plots for electroinitiated polymerization of acrolein in the case of (O) polymerization at 25°C, (Δ) inhibition of polymerization with *n*-butyl bromide at 25°C, and (□) inhibition of polymerization with hydroquinone at 25°C.

an increase in the rate of polymerization and the percent conversion was seen. On the other hand, since the propagating active sites do not have enough time to reach a *certain chain length due to agitation, a decrease in the* yield was detected. The yield in the polymerization of acrolein at 25°C in a quiet solution was 75.8% and in an agitated solution was 61.2%. The lack of polymer growth in the electrolysis solution other than on the cathode surface is an expected result.

Further characterization of the polymers could not be accomplished since the polymer is insoluble in any common solvent.

Indirect Initiation of the Polymerization

It is known that CCl_4 is reduced electrochemically in two steps in acetonitrile to give CCl_3^- in the first step and CCl_2^{2-} in the second step [18]:
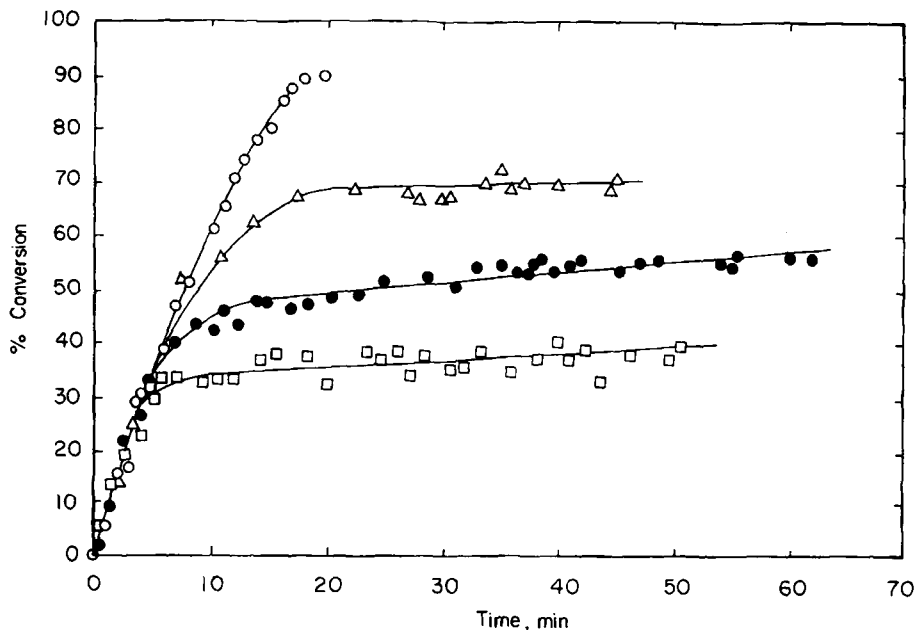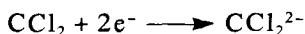
FIG. 6. Percent conversion vs time plots for electroinitiated polymerization of acrolein in the case of (O) polymerization at 25°C, (Δ) postpolymerization at 25°C, (●) inhibition of postpolymerization with n-butyl bromide at 25°C, and (□) inhibition of postpolymerization with hydroquinone at the same temperature.

$$CCl_4 + 2e^- \longrightarrow CCl_3^- + Cl^-$$

$$CCl_3^- \longrightarrow CCl_2 + Cl^-$$

$$CCl_2 + 2e^- \longrightarrow CCl_2^{2-}$$

The cyclic voltammogram of CCl_4 reveals reduction peaks at -1.7 and -2.8 V vs an Ag/Ag^+ reference electrode when mercurized Pt is used as the working electrode (Fig. 8). In the case where Pt was used as WE_c, only the peak at -2.8 V was recorded.

In order to control the mechanism of polymerization, CCl_4 was used for the indirect initiation of the polymerization of AL. Since the first reduction peak potential of CCl_4 is lower than the reduction peak potential of the monomer in the case where WE_c is mercurized Pt, the initiating species will be from CCl_4 only.

Polymerization by indirect initiation was conducted at both 25 and $-15°C$. The applied potential was 1.7 V vs an Ag/Ag^+ reference electrode. The cathode surface
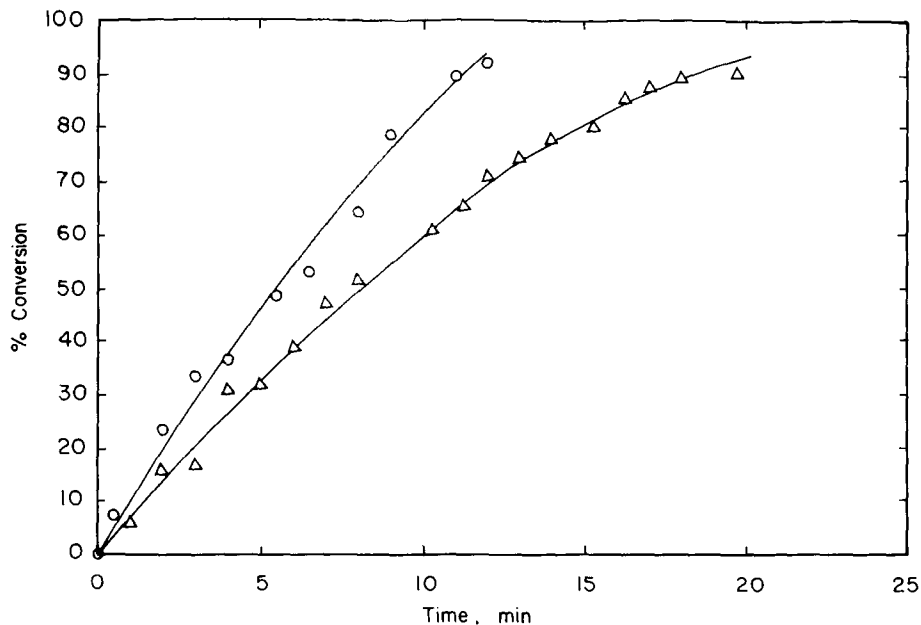
FIG. 7. Percent conversion vs time plots for electroinitiated polymerization of acrolein at 25°C in the case of (O) polymerization in stirred solution and (Δ) polymerization in quiet solution.

was coated with a white polymer layer as in the previous cases. The results of kinetic analysis are presented in Fig. 9. The polymerization rate is slower than the directly initiated one, and there is an inverse relationship between the rate and the temperature.

The rates of polymerization for each experiment are tabulated in Table 1 for comparison.

The IR spectrum of the polymer obtained by indirect initiation is given in Fig. 3. Contrary to expectations, the spectrum resembles the spectrum of the polyacrolein obtained by direct initiation.

In conclusion, it is deduced that the electroinitiated polymerization of acrolein can be achieved by direct electron transfer to the monomer if the reduction peak potential of the monomer is applied as the polymerization potential. A complex mechanism of polymerization is suggested for direct initiation involving radicals and anions. In addition, the cyclic voltammetry technique is proved to be a novel method for following the kinetics of polymerization *in situ*..
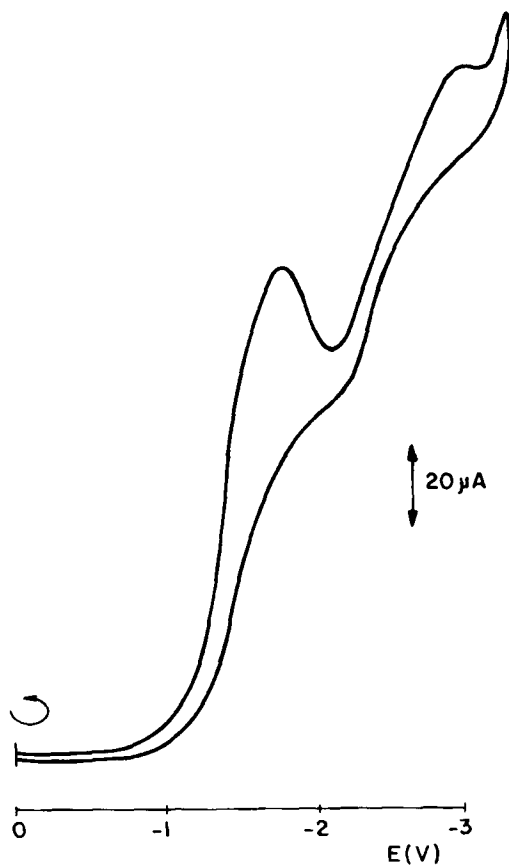
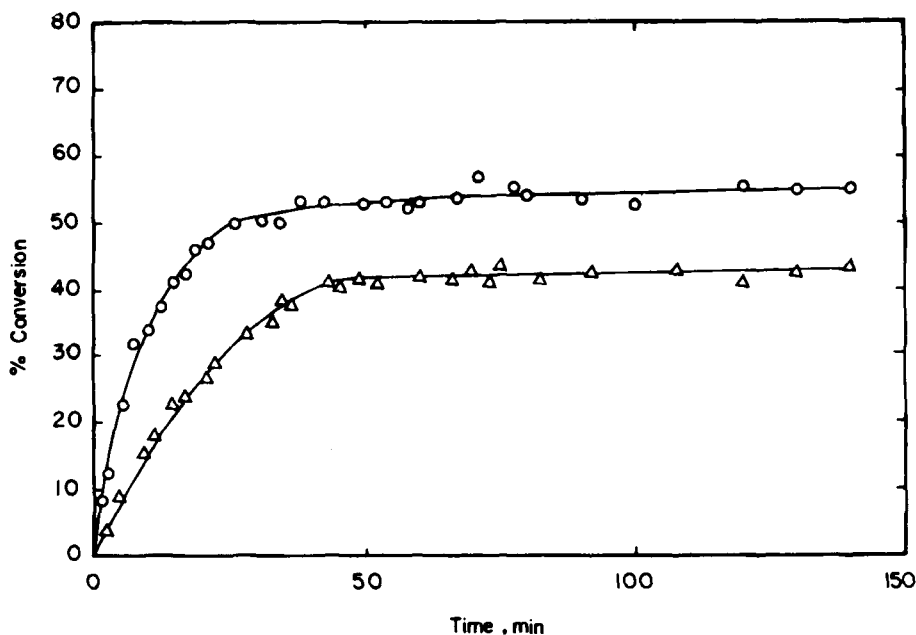FIG. 8. Cyclic voltammogram of carbon tetrachloride.

FIG. 9. Percent conversion vs time plots for electroinitiated polymerization of acrolein by indirect initiation at (O) −15°C and (Δ) 25°C.

TABLE 1. Rates of Electroinitiated Polymerization of Acrolein under Various Experimental Conditions ([M]$_0$ = 0.1 M)

Temperature, °C	Experimental conditions	$R_p \times 10^5$ mol·L^{-1}·s^{-1}
25	Polymerization in quiet solution at −2.4 V	10.00
0	Polymerization in quiet solution at −2.4 V	5.42
−15	Polymerization in quiet solution at −2.4 V	3.07
25	Addition of inhibitor during electrolysis (n-Bu bromide)	3.75[a]
25	Addition of inhibitor during electrolysis (hydroquinone)	2.80[a]
25	Postpolymerization	6.66[b]
25	Addition of inhibitor (n-BuBr) after the cessation of current	4.17[t]
25	Addition of inhibitor (hydroquinone) after the cessation of current	0.51[b]
25	Agitation of solution by bubbling N$_2$	18.33
−15	Indirect initiation via reduction of CCl$_4$ at −1.7 V	7.30
25	Indirect initiation via reduction of CCl$_4$ at −1.7 V	2.62

[a] R_p found after the addition of inhibitor.
[b] R_p found after the cessation of current.

Indirect initiation for the polymerization of acrolein was achieved via the electrolytic product of CCl_4 with a predetermined mechanism (anionic) since the initiating species are anions. However, the structure of the polymer was found to be the same in both the direct and indirect initiation cases.

ACKNOWLEDGMENT

REFERENCES

[1] S. W. Fishman and B. I. Khodorov, *Biochim. Biophys. Acta, 255,* 1 (1971).

[2] D. Hopwood, *Histochem. J., 4,* 267 (1972).

[3] A. Rembaum, R. J. K. Yen, D. H. Kempner, and J. Ugelstad, *J. Immunol. Methods, 52,* 341 (1982).

[4] R. C. Schulz, *Makromol. Chem., 17,* 62 (1955).

[5] R. C. Schulz, H. Cherdron, and W. Kern, *Macromol. Chem., 24,* 141 (1957).

[6] F. E. Blacet, G. H. Fielding, and J. G. Roof, *J. Am. Chem. Soc., 59,* 181 (1937).

[7] A. Henglein, W. Schnabel, and R. C. Schulz, *Makromol. Chem., 31,* 181 (1959).

[8] R. C. Schulz and W. Passmann, *Macromol. Chem., 60,* 139 (1963).

[9] R. C. Schulz and W. Strobel, *Monatsch. Chem., 99,* 1742 (1968).

[10] W. Strobel and R. C. Schulz, *Makromol. Chem., 133,* 303 (1970).

[11] A. Desbene-Monvernay, J. E. Dubois, and P. C. Lacaze, *J. Electroanal. Chem. Interfacial Electrochem., 89*(1), 149 (1978).

[12] U. Akbulut, S. Eren, and L. K. Toppare, *Polymer, 25,* 1028 (1984).

[13] U. Akbulut, L. Toppare, A. Usanmaz, and A. Onal, *Makromol. Chem., Rapid Commun., 4,* 259 (1983).

[14] L. Toppare, S. Eren, L. Türker, and U. Akbulut, *Polymer, 25,* 1655 (1984).

[15] L. Toppare, S. Eren, O. Ozel, and U. Akbulut, *J. Makromol. Sci.—Chem., A21*(10), 1281 (1984).

[16] B. Hacioğlu, L. Toppare, and U. Akbulut, *J. Polym. Sci., Polym. Chem. Ed., 27,* 3875 (1989).

[17] U. Akbulut, R. L. Birke, and J. E. Fernandez, *Makromol. Chem., 179,* 2507 (1978).

[18] S. Wavzanek and R. C. Duty, *J. Electrochem. Soc., 108*(12), 1135 (1961).