## Electroinitiated Polymerization of Acrylonitrile

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# ELECTROINITIATED POLYMERIZATION OF ACRYLONITRILE

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## ABSTRACT

Anionic polymerization of acrylonitrile was achieved by constant-potential electrolysis via direct electron transfer to the monomer. The reduction peak potential in the $(C_4H_9)_4NBF_4$-$CH_3CN$ electrolyte-solvent system was measured by cyclic voltammetry. On the other hand, dimethylformamide-metal salts were not found suitable for the direct electron-transfer process in our system. Polymers produced both anodically and cathodically were found to contain cyclized structures.

## INTRODUCTION

In several studies there exist many reports related to the homo- and copolymerization of acrylonitrile with various initiators [1-3]. Electrochemical polymerization has also been reported. Funt and coworkers studied the elec-

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troinitiated polymerization by constant-current electrolysis (CCE) in dimethyl-formamide (DMF)-NaNO$_3$ solvent-electrolyte couple [4]. They suggested that the polymerization proceeds via direct electron transfer to monomer. However, the DMF-NaNO$_3$ system is not found electroinert up to the reduction peak potential of acrylonitrile in our system, most probably due to the presence of trace amount of water and due to NaNO$_3$. Thus direct electron transfer from the cathode to the monomer is not possible in CCE.

Since the current is kept constant in CCE and the potential is left to vary, the nature of the active species cannot be deduced. However, in constant-potential electrolysis (CPE), the potential is controlled, hence creation of undesired active species is prevented [5, 6]. By cyclic voltammetric measurements (CV), it is shown that the DMF-NaNO$_3$ discharge occurs before any electron transfer to acrylonitrile. On the other hand, in the acetonitrile-tetrabutylammonium fluoroborate solvent-electrolyte couple, the reduction peak potential for acrylonitrile is found to be lower than the solvent-electrolyte discharge potential, which indicates the possibility of direct electron transfer in this system.

In this study, polymerization of acrylonitrile by CPE was achieved. The advantages of CPE over CCE has previously been reported in detail [7, 8]. Cyclic voltammetry measurements of acrylonitrile reveal one reduction peak potential at -2.60 V ($E_{p,c}$) vs Ag$^0$/Ag$^+$ (0.01 $M$) reference electrode. Constant-potential electrolysis was carried out at this measured peak potential.

The total monomer consumption with respect to time in each compartment of electrolysis cell was investigated. The kinetics of polymerization were followed by gas chromatography (gc) of polymer solutions removed from each compartment separately at certain time intervals.

The characterization of polymers were carried out by IR measurements.


## EXPERIMENTAL

### Materials

The preparation and purification of tetrabutylammonium fluoroborate (TBAFB) were discussed in an earlier publication [9].

Acetonitrile (AN) was dried over CaH$_2$ overnight and fractionally distilled over fresh CaH$_2$ under a dry N$_2$ atmosphere.

Dimethylformamide (DMF) was stirred with anhydrous CuSO$_4$ for 48 h and then distilled under vacuum at 30°C and 4 torr.

Acrylonitrile (AcN) was washed several times with dilute H$_2$SO$_4$, then

with dilute $Na_2CO_2$. After washing with distilled water, it was dried over $CaH_2$ for overnight and fractionally distilled under $N_2$.

## Apparatus

Cyclic voltammetry and constant-potential electrolysis cells were discussed in an earlier report [5].

A Hewlett-Packard 5890A gas chromatograph with a column of Porapak Q (1.5 m long, 3.2 mm o.d.) was used.

## Procedure

Freshly distilled AN and dry TBAFB were introduced into the polymerization cell (approximate volume 30 mL) while the polymerization cell was purged with $N_2$. AcN (2.0 mol/L) was added. The cell was placed in a constant-temperature ethanol bath. Just before the application of potential, a 10-$\mu$L sample was removed from each compartment of the cell and transferred into 100 $\mu$L methanol containing 3 $\mu$L internal standard, propionitrile, to determine the initial monomer concentration by gas chromatographic analysis. After the potentiostat was switched on, 10-$\mu$L samples from anode and cathode compartments were separately transferred at definite time intervals into ethanol to follow the kinetics of polymerization by gc. The polymerization was carried out at three temperatures: $-10.0, 0.0, +10.0°C$.
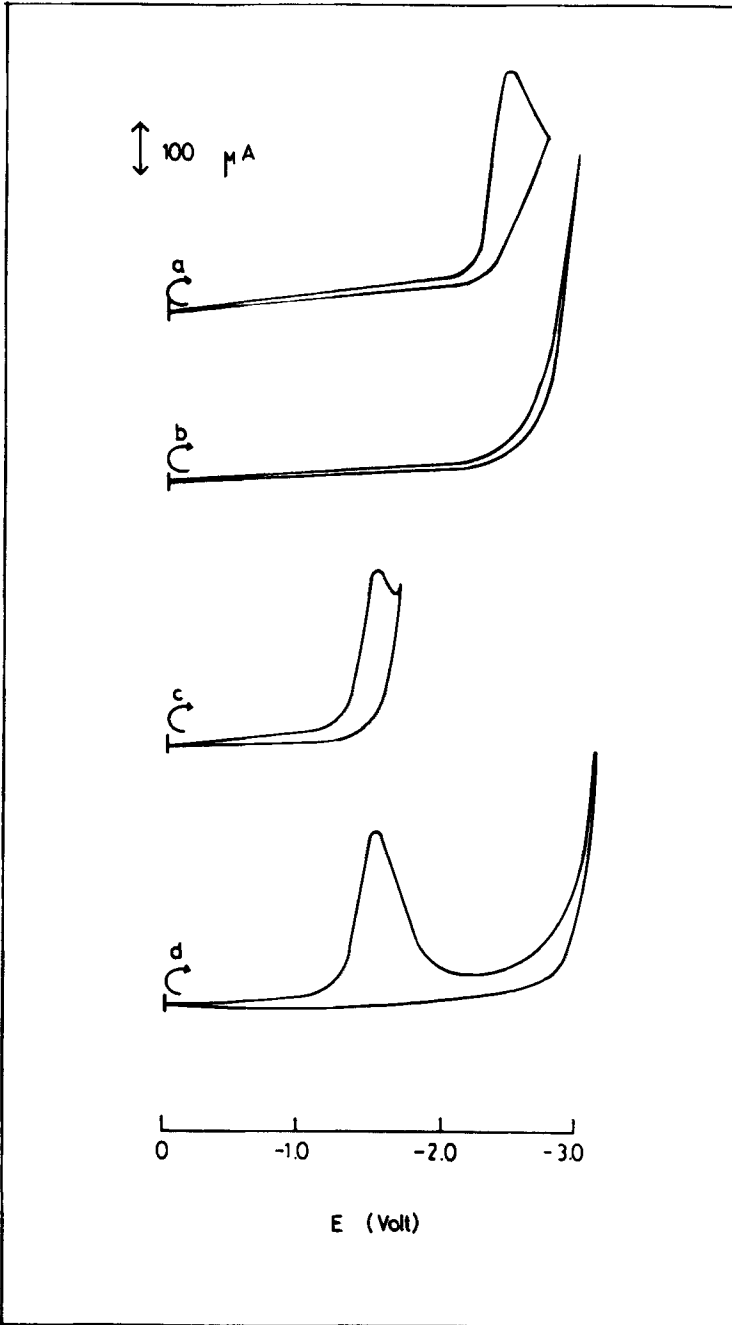
In order to check the mechanism of polymerization in the anolyte, a radical inhibitor was added to the electrolysis cell, and the same electrolysis procedures were applied.

The polymerization was allowed to proceed for 2 h, and the contents of each compartment were separately introduced into methanol. The precipitated polymer was filtered, washed, and dried under vacuum and prepared for IR and viscometric measurements.

## RESULTS AND DISCUSSION

### Cyclic Voltammetry

CPE proceeds selectively through the monomer itself, especially in the initiation step, if a suitable potential is employed. The electrochemical behavior of AcN was obtained in AN-TBAFB (0.1 mol/L) solvent-electrolyte, which is totally electroinert in the potential range of +3.0 V. Only one irreversible re-

duction peak potential was observed at -2.60 V $(E_{p,c})$ vs $Ag^0/Ag^+$ at room temperature. Scanning through the oxidation or reduction side did not affect the place and the number of this peak potential in this range (+3.0 V vs $Ag^0/Ag^+$).

The cyclic voltammogram of AcN in the AN-TBAFB system (Fig. 1) indicates that the polymerization can be initiated selectively through the monomer. In the AN-TBAFB system, solvent-electrolyte discharge occurs at -3.0 V vs $Ag^0/Ag^+$ where $E_{p,c}$ of AcN appears at -2.60 V. By adjusting the polymerization potential to -2.60 V vs $Ag^0/Ag^+$, which is the $E_{p,c}$ of AcN, initiation is primarily through the monomer, i.e., initiation occurs by direct electron transfer.

However, the DMF-NaNO$_3$ system (Fig. 1c) shows an electrolyte discharge potential at about -1.60 V. Thus, in the DMF-NaNO$_3$ system, direct electron transfer to monomer is not found to be possible. Also in the CH$_3$CN-NaNO$_3$ couple, a similar discharge occurs before the $E_{p,c}$ of acrylonitrile (Fig. 1d). Thus, the nature of the initiating species can not be easily determined by CCE.

The reduction peak potentials of monomers can be correlated with the lowest unoccupied molecular orbitals (LUMO) (Fig. 2). After a short time of electrolysis, the energy band of the working electrode, in this case the cathode, becomes comparable to the LUMO of the monomer and, as a consequence of this, an electron transfer occurs from the electrode to the LUMO of the monomer. The electrochemically created active form of the monomer, either radical anion or dianion, propagates polymerization.

Polymerization of AcN in the AN-TBAFB system was carried out at -2.60 V vs $Ag^0/Ag^+$ at three temperatures. The monomer conversion as given by $([M]_t/[M]_0) \times 100$, was obtained from gc data. Unreacted monomer concentrations were calculated by evaluating the gc data, which were further used to determine the monomer consumption in each cell compartment.

In a short time of electrolysis, the concentration of reacted monomer increases very rapidly and tends to a plateau (Figs. 3 and 4).

In the presence of radical inhibitor in both cell compartments, different results were obtained. In the catholyte, no appreciable change in the rate of polymerization was observed. On the other hand, in the anode compartment

FIG. 1. (a) The cyclic voltammogram of acrylonitrile (1.0 mmol/L) measured in AN-TBAFB. (b) Background voltammogram of acetonitrile in the presence of TBAFB. (c) Cyclic voltammogram of DMF in the presence of NaNO$_3$. (d) Cyclic voltammogram of acetonitrile in the presence of NaNO$_3$.
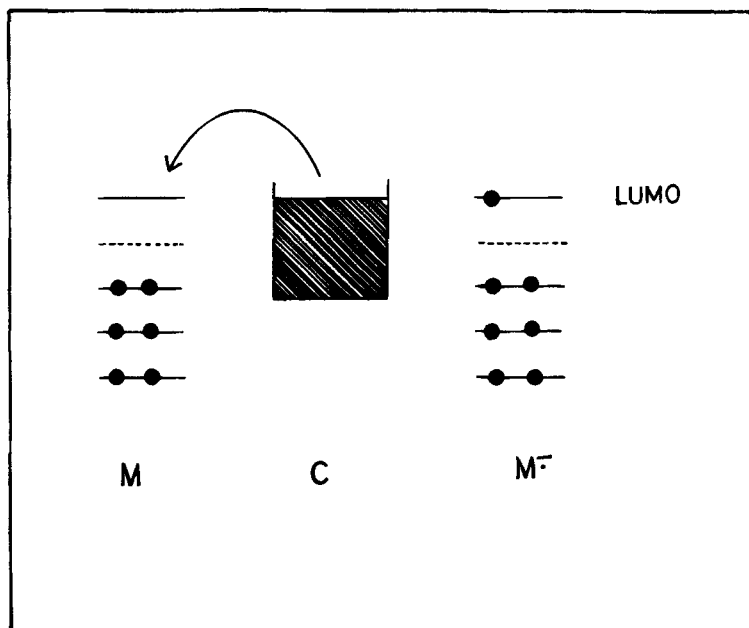
FIG. 2.  Schematic representation of molecular energies of the monomer
(M), the radical anion of the monomer (M⁻), and the energy band of the
cathode (C) for electroinitiated anionic polymerization.

the presence of inhibitor makes an important difference up to 30 min of elec-
trolysis.  Thereafter, due to electrolytical decomposition of inhibitor, the re-
action rate increases (Fig. 5).  Since the cathode potential is kept constant at
-2.60 V, the anode potential can be as high as 10 V, depending on the reac-
tion conditions, the IR drop, the substrate concentration, etc.  No inhibitor
nor any solvent electrolyte or substrate can stand that high a potential.  This
shows that an indirect radical type of initiation occurs in the anolyte.

In our previous studies [7-10], since no polymer was observed other than
in the working electrode compartment, gc sampling was done by removing
equal amounts of solution from each compartment and adding them to the
same methanol tube.  This procedure enables one to follow the conversion
points in the gc measurements rather accurately.  During the electrolysis, de-
pending on the consumption rate of the monomer, there occurs monomer
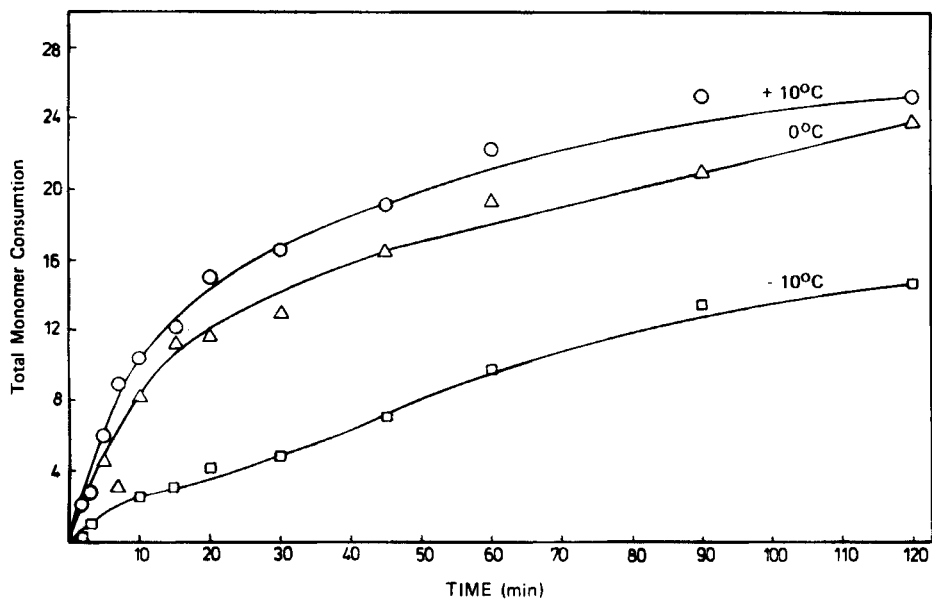passage between the two compartments through the sintered glass disk.  There-

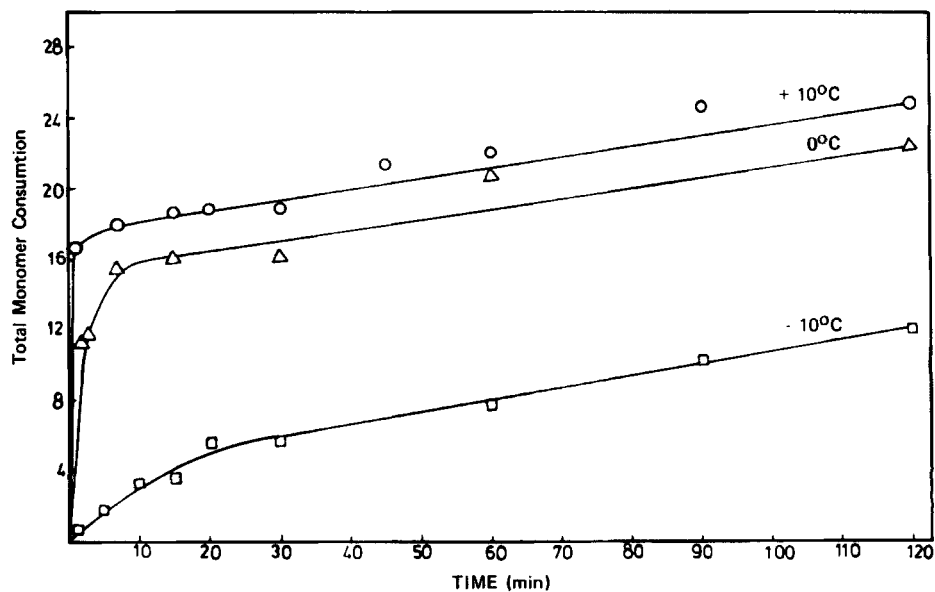FIG. 3. Percent monomer conversion in catholyte versus time: (○) +10.0°C, (△) 0.0°C, (□) –10.0°C.



FIG. 4. Percent monomer conversion in anolyte versus time: (○) +10.0°C, (△) 0.0°C, (□), –10.0°C.
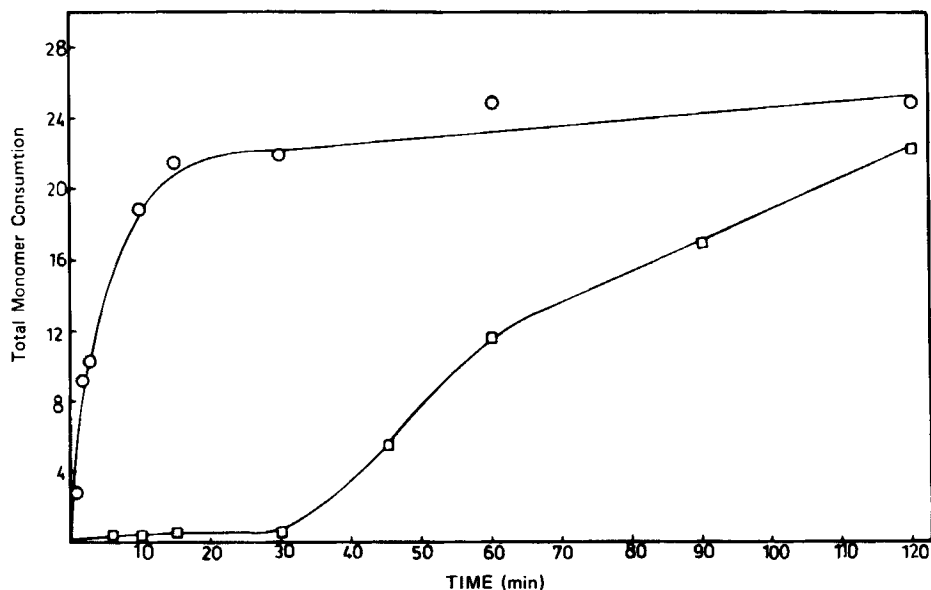
FIG. 5. Percent monomer conversion in the presence of radical inhibitor (hydroquinone) vs time: (O) catholyte, (□) anolyte.

for, sampling from only one side results in erroneous kinetic curves. In this study, in order to obtain reproducible kinetic results, the average of several experiments were taken. In Table 1 it appears as if the total yields are higher than the conversions. This discrepancy arises from the above-mentioned phenomenon, i.e., due to the continuous diffusion of the monomer from and to the working electrode compartment.

The difference between conversion and yield values is most probably due to oligomeric products of very low molecular weight which do not precipitate in methanol.

The physical appearance and IR spectra of the polymers permit some comments on the structure. Insoluble, crosslinked polymers were obtained on the cathode surface. The polymers obtained from anode and cathode compartments can be distinguished. The cathode material was darker, yellow to orange, whereas the anode material was light yellow. The coloration of the polyacrylonitriles was attributed to intermolecular cyclization [4]. Linear polyacrylonitrile has a powdery appearance and is white in color.

**TABLE 1.** Electroinitiated Polymerization of Acrylonitrile Carried out by Constant-Potential Electrolysis at −2.60 V in Acetonitrile on a Pt[o] Electrode

| Polymerization temperature, °C | Conversion in anolyte,[a] % | Conversion in catholyte,[a] % | Yield in anolyte,[b] % | Yield in catholyte,[b] % | Total conversion, % | Total yield, % | $[\eta]$, dL/g[c] |
|---|---|---|---|---|---|---|---|
| +10.0 | 25.0 | 25.3 | 9.3 | 30.4 | 50.3 | 39.7 | 0.041 |
| 0.0 | 22.5 | 23.9 | 11.1 | 25.1 | 46.4 | 36.2 | 0.072 |
| −10.0 | 12.1 | 14.9 | 5.3 | 21.6 | 27.0 | 26.9 | 0.088 |

[a]The % conversions in cell compartments, anode and cathode, were measured by gas chromatography at the end of 2 h of electrolysis, separately.
[b]The % yields in anode and cathode compartments were obtained by precipitation of polymer solution at the end of 2 h of electrolysis, separately.
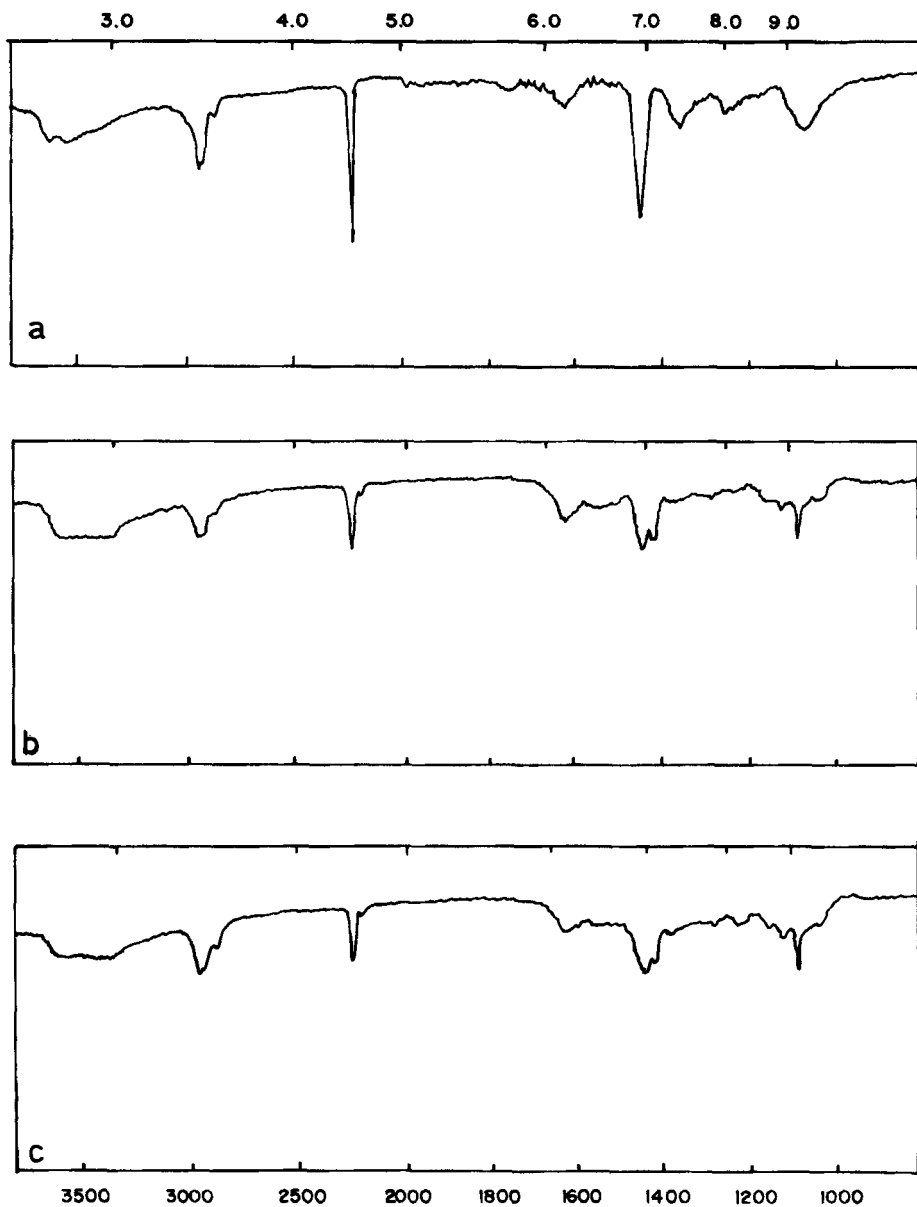[c]At 25°C in DMF.

FIG. 6.  Infrared spectra of (a) linear polyacrylonitrile, (b) electrochemically obtained polyacrylonitrile from anode compartment, (c) same from cathode compartment (at −2.60 V vs $Ag^0/Ag^+$).

Comparison of the IR spectra of the samples with the literature indicates that the colored polyacrylonitrile contains cyclic structures (Fig. 6).

The IR spectra of linear polyacrylonitrile showed mainly two intense peaks. These are the $-C\equiv N$ vibration at 2240 cm$^{-1}$ and the $-CH_2-$ bending vibrations at 1450 cm$^{-1}$. On the other hand colored polyacrylonitriles have the same $-C\equiv N$ absorption at 2240 cm$^{-1}$, but this peak is split into two due to the formation of cyclic sequences in the chains. In addition, the intensity of the 2240 cm$^{-1}$ band decreased. The cyclization of nitrile groups of the polyacrylonitrile has been given as [4]
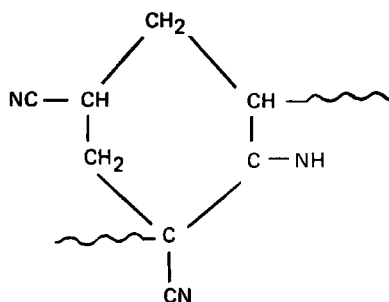


Besides the changes in the $-C\equiv N$ vibration and in the intensity of the $-CH_2-$ bending vibrations, broadening in the frequency range 1400-1700 cm$^{-1}$ due to vibrations of CH and $CH_2$ groups is yet another indication of cyclization.

The IR spectra of anode and cathode materials both have the same basic structure, except for the degree of cyclization (Fig. 6). Both have the 2240 cm$^{-1}$ $-C\equiv N$ band, but the intensity of this peak of the anolyte polymer is higher than that of the cathode material. This verifies the predominance of cyclic sequences in the cathodic polymer. As mentioned earlier, the color of cathodic polymer was darker, indicating that cathode polymer has more cyclic units, in agreement with the IR spectra.

Electrochemically obtained polyacrylonitriles have very low molecular weights (see the intrinsic viscosities in Table 1), and the intrinsic viscosities increase with decreasing polymerization temperature.

## ACKNOWLEDGMENTS

## REFERENCES

[1] T. Hirahara and Y. Minoura, *J. Polym. Sci., Part A-1*, 3, 3391 (1970).
[2] B. L. Funt, I. McGregor, and J. Tanner, *J. Polym. Sci., Part B, 8,* 699 (1970).
[3] D. J. T. Hill, J. H. O'Donnell, and P. W. O'Sullivan, *Macromolecules, 15,* 960 (1982).
[4] B. L. Funt and F. D. Williams, *J. Polym. Sci., A2,* 865 (1964).
[5] U. Akbulut, S. Eren, and L. Toppare, *J. Macromol. Sci.–Chem., A21*(3), 335 (1984).
[6] U. Akbulut, S. Eren, and L. Toppare, *Polymer, 25,* 1028 (1984).
[7] L. Toppare, S. Eren, Ö. Özel, and U. Akbulut, *J. Macromol. Sci.–Chem., A21*(10), 1281 (1984).
[8] U. Akbulut, S. Eren, and L. Toppare, *Polymer, 25,* 1165 (1984).
[9] L. Toppare, S. Eren, and U. Akbulut, *J. Polym. Sci., Polym. Chem., Ed., 22,* 294 (1984).
[10] U. Akbulut, L. Toppare, and B. Yurttas, *J. Polym. Sci., Polym. Lett. Ed., 24,* 185 (1986).