# Electroinitiated Polymerization and Copolymerization of Phenylacetylene

**James J. Jakubowski\* and R. V. Subramanian**

Department of Materials Science and Engineering, Washington State University, Pullman, Washington 99164, USA

SUMMARY

   A linear conjugated polymer $\pm(C_6H_5)C=CH\mathord{\mathrlap{\rule[0.5ex]{1.2em}{0.4pt}}}_n$, with a <u>trans</u> rich, <u>cis-trans</u> copolymer structure results from the electropolymerization of phenylacetylene.

INTRODUCTION

   It was shown in earlier work from this laboratory that electropolymerization of monomers on graphite fiber electrodes has a significant effect on the properties of composites prepared from the electorlytically coated graphite fibers (Subramanian and Jakubowski, 1978). In the course of this research, the elctropolymerization of acetylene-terminated polyimide intermediates was found to occur readily, and phenylacetylene,(PA) was chosen as monomer to establish the occurrence of electroinitiated polymerization through C≡C bonds (Subramanian et.al., 1978). The results of this study are presented here. Following our findings that the polymerization of the carbonitrile group in benzonitrile (BN) is electroinitiated in a facile manner (Subramanian and Garg, 1979), the copolymerization of PA and benzonitrile in an electrolytic cell has also been investigated and is reported in this paper.

EXPERIMENTAL

   PA was polymerized in the cathode compartment of a two-compartment electrolytic cell, separated by fritted glass from the anode compartment. The cathode compartment was charged with 50 ml of a 0.2g per ml PA in a 0.2 N $NaNO_3$-DMF solution. The anode compartment was simlarly charged with 50 ml of 0.2 N $NaNO_3$-DMF solution but without any monomer. Carbon fiber electrodes were then placed in the appropriate compartments. Constant DC voltage was applied for 18 hours, at room temperature. For 36 and 48 volts DC, a cooling bath was found to be necessary because of heating caused by the higher current. The copolymerization experiments were also conducted with the same set-up under a dry nitrogen atmosphere. Upon completion of the electropolymerization, the products were isolated from the cathode and anode solutions sepa-

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\* Present address:  Dow Chemical Co., Midland, Mi 48640

rately, by dilution with distilled water and extraction with
benzene. Viscosity measurements of pPA, were conducted in benzene
solution in an Ostwald type viscometer (Kimax #50), at 35°C.
$M_v$ was calculated using the Mark Houwink equation, $[\eta] = KM^a$
where $K = 1.03 \times 10^{10}$ and $a = 2.42$ (Bigani et.al., 1975).
Molecular weight of the copolymer was measured by vapor phase
osmometry.

## RESULTS AND DISCUSSION

The polymer from PA was formed in the cathode compartment with
the development of a deep red color in $NaNO_3$/DMF solutions, but no
reaction was observed when the monomer was present in the anode
compartment. The migration of the color to the anode compartment
from the cathodic solution was also noted. These observations,
coupled with the high sensitivity to moisture which completely
inhibited the polymerization, suggest an anionic mechanism of poly-
merization.

The polymer was deposited on the cathode and also present in
solution. Though the reaction was conducted for a long time to
collect enough polymer for characterization, polymer formation was
visually observable in only 5 minutes. From the results summarized
in Table 1, it can be seen that the polymer yield, at the cathode,
reaches a maximum at about 24V, after which the yield remains at
a steady level. On the other hand, yield of the polymer from
the anode compartment, where no monomer was initially present,
steadily increased with applied voltage in the range studied.
This indicated that the polymer is an anionic species which is
repelled by the cathode and migrates to the anode compartment
across the fritted glass separator.

TABLE 1

Cathodic Polymerization of Phenylacetylene

| V Applied | Yield (Cathode) % | Yield (Anode) % | $M_v$ (Cathode) | $M_v$ (Anode) |
|---|---|---|---|---|
| 6 | 17.0 | 3.0 | 3,100 | 3,100 |
| 12 | 35.0 | 4.0 | 3,000 | 3,100 |
| 18 | 45.0 | 9.0 | 3,200 | 2,900 |
| 24 | 52.0 | 11.0 | 3,300 | 3,000 |
| 36 | 36.0 | 23.0 | 3,200 | 3,000 |
| 48 | 37.0 | 27.0 | 3,300 | 3,000 |

In order to demonstrate that monomer in the anode compartment
could be polymerized by migrating species from the cathode, a
series of experiments was conducted where the monomer concentra-
tion in the anode compartment was progressively increased while
that in the cathode compartment was maintained constant (Table
2). In this case, the amount of polymer isolated from the anode

compartment steadily increased and even exceeded the total amount
of monomer added to the cathode. However, polymerization
occurred only when there was monomer present in the cathode
compartment and no polymer was isolated when only the anode
compartment contained monomer. Thus, even though the initiating
species are formed in the cathode, polymerization does seem to
occur at the anode compartment also. It is also significant
that the molecular weight remained essentially unchanged with
increasing monomer concentration and was the same in both compart-
ments.

## TABLE 2

Variation of polymer yield with monomer concentration at the anode.

| Monomer[a], g. | | Polymer yeild[b], g. | | Molecular weight | |
|---|---|---|---|---|---|
| Anode | Cathode | Anode | Cathode | Anode | Cathode |
| 1.0 | 0.0 | 0 | 0 | -- | -- |
| 0.0 | 1.0 | 0.2 | 0.3 | -- | -- |
| 1.0 | 1.0 | 0.8 | 0.5 | 3100 | 3100 |
| 2.0 | 1.0 | 1.5 | 0.4 | 3100 | 3100 |
| 5.0 | 1.0 | 2.5 | 0.6 | 3100 | 3100 |
| 10.0 | 1.0 | 3.1 | 0.8 | 3700 | 3300 |

a: in 50 ml electrolytic solution. b: in 19 hours, with 24 VDC
applied voltage.

From viscosity measurements of the red-orange polymer iso-
lated from the reaction mixture, the average molecular weight
was found to be 3000, (Table 1). Fractional precipitation by
methanol and methanol-water separated the polymer into fractions
of molecular weight from 4000 to 2700 which had identical nmr
and ir spectra, but different melt-softening temperatures (155-
167°C, 110-122°C, 55-75°C). X-ray diffraction did not show any
crystallinity.
Carbon hydrogen analyses agreed well with calculated values
for pPA (calculated for $C_8H_6$: C, 94.08; H, 5.92. Found: C,
92.14-93.05; H, 5.75-5.84). The ir spectrum showed absorptions
due to stretching vibrations of poly-conjugated double bonds at
1590 $cm^{-1}$ and those due to C-H out-of-plane deformation of
monosubstituted benzene at 750 $cm^{-1}$ and 690 $cm^{-1}$. Weak absorp-
tions are also seen at 910 $cm^{-1}$ and 840 $cm^{-1}$, the larger of
these being at 910 $cm^{-1}$. This region is believed to be involved
in the unsaturation on pPA, with characteristic absorptions
arising at 910 $cm^{-1}$, 870 $cm^{-1}$, and 840 $cm^{-1}$ (Masuda et.al.,
Kern, 1969 and Sasaki, et.al. 1976). Of these three absorption
bands, the one at 870 $cm^{-1}$, has been taken as characteristic

of cis-structure; it is seen from Figure 1 that this band is not present conspicuously in the ir specturm of the polymer prepared in this study.

Kern (1969) has studied and compared pPA formed from several types of initiation reactions and grouped them into three types of products. Of these, Type III is a yellow solid, readily soluble in acetone and benzene at 20-25°C, having weak ir absorption at 910-840 cm$^{-1}$, and displaying no crystallinity. Kern suggested this polymer to be a cis-trans copolymer and to be richer in trans structure when recovered from solvents like pyridine and dimethylformamide. Polar solvents like pyridine and DMF were found to promote the isomerization of cis to trans unsaturation in pPA.

The yellow methanol insoluble polymer obtained by electropolymerization is similar to this thermal, type III polymer, as it is readily soluble in acetone and benzene, reveals no crystalizability by X-ray diffraction and has absorption bands at 910 cm$^{-1}$ and 840 cm$^{-1}$. Also, since the polymerization and original isolation of polymer products were conducted in DMF, it is likely this product is richer in trans-structure than in cis. This would also explain the absence of absorption at 870 cm$^{-1}$. Other fractions of polymer from the electropolymerization experiments have the same ir's as the yellow methanol insoluble fraction, although they differ in color, MW, and melting point. It is suggested here that these are just lower molecular weight fractions of the same polymer, a trans rich, cis-trans copolymer.
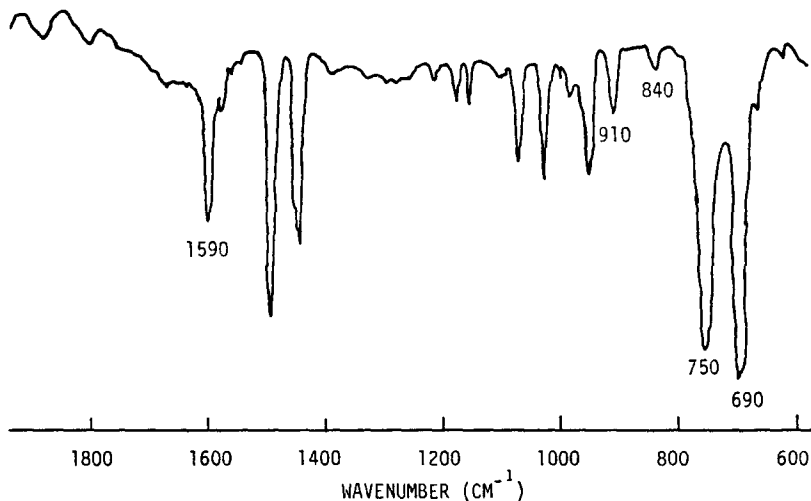


FIGURE 1. IR SPECTRUM OF ELECTROINITIATED POLYMER OF PHENYLACETYLENE.

## $^1$H-NMF Spectra: Polyphenylacetylenes

The proton ($^1$H) NMR spectra were observed using a 60 MHz instrument and checked on a 100 MHz, JEOL spectrometer. Spectra of the polymers were taken in CDCl$_3$ using TMS as an internal standard. The

spectrum consisted of a single broad multiplet centered about 7.0 ppm (Fig. 2). This is consistent with published ^{1}H-NMR spectra of pPA (Sasaki, et.al. 1976). Also, in compounds like 1,4-diphenyl-1, 3-butadiene, the -C=C-H absorption in the NMR occurs at about 6.6 to 6.8 ppm. (Aldrich). An extended chain, and more likely a 1,3-placement of phenyl groups as in the more probable head-to-tail structure could cause a broadening of the phenyl and -C=C-H proton absorptions and perhaps also cause chemical shift of the -C=C-H protons to higher ppm values. This could lead to their being included in the benzene proton absorption resulting in a single broad multiplet about 7.0 ppm.
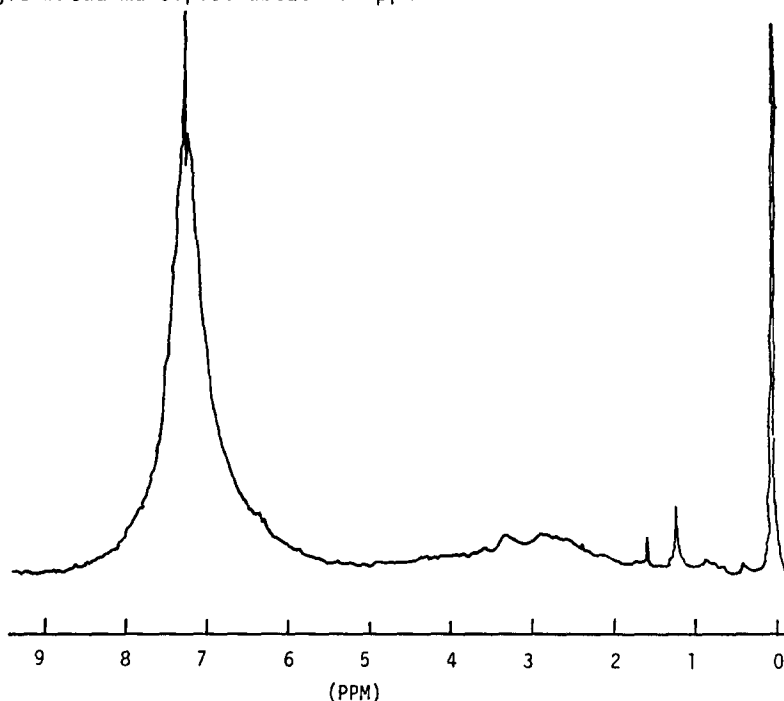


FIGURE 2. ^{1}H NMR SPECTRUM OF ELECTROINITIATED POLYMER OF PHENYLACETYLENE.

The available evidence, indicates the polymer to be a linear polymer with a _trans_ rich polyene structure $(C=CH)_n$, which as suggested earlier, is probably formed by an anionic mechanism initated at the cathode. It should be interesting to investigate the details of the mechanism of electropolymerization of acetylenic monomers which has found independent confirmation in work elsewhere (Farafonov, et.al. 1977). Using perchlorates as electroytes in DMF or DMSO, these authors electropolymerized PA and diphenyl-acetylene. Though the products formed in their experiments were oligomers of low average molecular weight (500-1,000), their ir spectra, as in our work, showed the formation of conjugated bonds through the polymerization of $C \equiv C$ bonds.

Even though the mechanism of polymerization is indicated to be anionic and anionic polymer species migrate from the cathode to the anode, the evidence does not substantiate a "living polymer" system. It was pointed out earlier that the molecular weight is invariant with monomer concentration and with rate of initiation (applied voltage). In fact, all the observations seem to indicate the occurrence of a termination mechanism resulting in self-limiting growth of the polymer chain. It is significant, in the light of these observations in electroinitiated polymerization, that similar behavior has been observed in lithium intiated polymerization of PA (Berlin et.al. 1975). It was found that the polymer yield leveled off after a rapid first stage of polymerization leading to a certain degree of conversion. The propagation rate constant was only 0.3 $(m/1)^{-1}$ $min^{-1}$, surprisingly low for an anionic polymerization. Interestingly, it was also found by spectroscopic techniques, that inactivation of the active center during polymerization was by the generation of a new inactive, anionic species with a characteristic absorption at 660 nm. It is theorized that the observed inactivation of the growing chain is probably due to exchange interaction between the active center and the $\pi$-electron system of the growing pPA chain. The migration of anionic polymer species of essentially constant molecular weight from the cathode to the anode observed in our experiments would suggest the formation of such a stabilized macroanion by electroinitiation and propagation.

TABLE 3

Copolymerization of Phenylacetylene and Benzonitrile[a]

| Monomer Ratio[b] | | | % Yield | | Molecular Weight | |
|---|---|---|---|---|---|---|
| PA | : | BN | Cathode | Anode | Cathode | Anode |
| 5 | : | 1 | 47 | 31 | 760 | --- |
| 3 | : | 1 | 26 | 26 | 570 | --- |
| 1 | : | 1 | 30 | 21 | 500 | 700 |
| 1 | : | 3 | 26 | 15 | 640 | --- |
| 1 | : | 5 | 21 | 13 | 470 | --- |
| 1 | : | 10 | 13 | 7.0 | --- | --- |

[a] 24 VDC, 18 hours.   [b] Total monomer concentration 1.98 m/e.

## Copolymerization of Phenylacetylene with Benzonitrile

The copolymerization of PA and BN was conducted in a two compartment cell, varying the monomer ratios, PA:BN, from 5:1 to 1:10. The polymer yield, as shown in Table 3, decreases steadily in both compartments, as the proportion of BN in the monomer composition is increased. The isolated copolymers have low molecular weights, much lower than those observed in the homopoly-

merization of PA. The CHN analysis for the copolymers (Table 4) is practically invariant over a range of monomer ratios and corresponds closely to that expected for a 1:1 copolymer. It might be tempting, from these results, to infer the presence of a 1:1 copolymer. But, the low molecular weights of the copolymer suggest the need for caution in making such an inference. A molecular weight of only about 600, indicates the incorporation of only six molecules of BN or PA in the copolymer.

TABLE 4

Elemental Analysis of PA/BN Copolymer

| Monomer Ratio | Analysis, % | | | | | |
|---|---|---|---|---|---|---|
| | Observed | | | Calculated[a] | | |
| PA : BN | C | H | N | C | H | N |
| 5 : 1 | 88.63 | 5.96 | 4.07 | 92.00 | 5.71 | 2.28 |
| 3 : 1 | 87.19 | 6.52 | 6.29 | 90.95 | 5.62 | 4.42 |
| 1 : 1 | 85.97 | 6.09 | 6.10 | 87.80 | 5.37 | 68.3 |
| 1 : 3 | 83.98 | 5.36 | 6.98 | 84.67 | 5.11 | 10.22 |
| 1 : 5 | 85.83 | 5.15 | 6.93 | 83.63 | 5.02 | 11.35 |
| 1 : 10 | 85.58 | 5.38 | 6.95 | 82.69 | 4.95 | 12.37 |

a: for copolymer of same composition as monomer feed.

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