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ELECTROINITIATED POLYMERIZATION THROUGH $C\equiv C$ AND $C\equiv N$ BONDS

by

R. V. Subramanian, James J. Jakubowski
and B. K. Garg

To be presented at the
175th National ACS Meeting,
Anaheim, CA, March 1978

Department of Materials Science & Engineering
Washington State University
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The polymerization of monomers through acetylenic and nitrile groups has been studied. In the cathodic polymerization of phenylacetylene in dimethylformamide, an anionic polymerization mechanism is indicated. The polymer of molecular weight ~3000 has been fractionated and the fractions characterized by ir, uv, and nmr spectroscopy. Evidence is presented for a conjugated polyene structure formed from cis and trans structural units combined in a predominantly head-to-tail fashion. Similarly, the polymerization of

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benzonitrile i[illegible]imethylformamide at the cathode leads to a polymer with conjugated -C=N- bonds. Mass spectroscopy did not reveal the presence of any cyclic trimer of benzonitrile. Infrared absorption bands at 1605 cm^{-1} and 1520 cm^{-1} established the formation of -C=N- conjugation in polybenzonitrile.

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ELECTROINITIATED POLYMERIZATION THROUGH $C\equiv C$ AND $C\equiv N$ BONDS

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INTRODUCTION

In the context of a comprehensive study in our laboratories of electroinitiated polymerization on electrodes (1-5) it became of interest to investigate the participation of acetylenic and nitrilic groups in electropolymerization. Phenylacetylene and benzonitrile were chosen for this research and the first results are reported here.

EXPERIMENTAL

Dimethylformamide, Mallinckrodt chemical, analytical grade was refluxed over calcium hydride, Alfa Products, -4+40 mesh, for 24 hours and distilled at 10 torr. Phenylacetylene, Aldrich Chemical, 98% was distilled at 10 torr before use. Sodium nitrate, Mallinckrodt chemical, analytical grade, was dried at 120°C for 48 hours. $NaNO_3$ was then stored in a desiccator until used. Hercules type AU carbon fibers in the form of bundles tied at each end with rayon thread were used as electrodes: wt ≈ .4 to .6 g each.

Phenylacetylene 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 0.2 g per ml phenylacetylene in DMF solution which was 0.2 N $NaNO_3$. The anode compartment was similarly 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. The electrode distance was fixed at 5 cm. Constant DC voltage was applied for 18 hours. All experiments were conducted at room temperature ∿ 25°C. For 36 and 48 volts DC, a water cooling bath was found to be necessary because of heating caused by the higher current.

Upon completion of the electropolymerization, the electrode solutions were removed and the products isolated as follows, from the cathode and anode solutions separately; the electrode solutions were diluted > 8 fold with distilled water and extracted several times with 100 ml portions of benzene. The combined benzene extracts were washed several times with distilled water and dried over magnesium sulfate. After filtering, the benzene was removed by using a roto-vac (steam). The resulting polymer was dried in a vacuum oven at ∿ 60°C for 24 hours.

In the case of benzonitrile, the cathodic polymerizations were conducted in the middle compartment of a three compartment cell partitioned by fritted glass discs with the counter electrodes being placed in the end compartments. Typically, a dry solution of benzonitrile in DMF containing lithium nitrate was electrolyzed for up to 72 hours. The loose polymer deposit formed on the cathode was scraped off, thoroughly washed with water and dried. During washing with water, an ammoniacal odor was quite noticeable.

Viscosity measurements of polyphenylacetylene were conducted in benzene solution in an Oswald type viscometer (Kimax #50), at 35°C at four different concentrations and the results plotted as ln $\eta r/c$ vs. C. Extrapolation to conc = 0 gave the intrinsic viscosity. M_v was calculated using the Mark-Houwink equation $[\eta] = KM_v^a$ where $K = 1.03 \times 10^{10}$ and $a = 2.42$. The intrinsic viscosities of polybenzonitrile were measured at 35°C in conc. H_2SO_4.

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RESULTS AND DISCUSSION

The polymer from phenylacetylene 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 polymerization.

The polymer was deposited on the cathode and was also present in solution. Even though the reaction was conducted for a long time to collect enough polymer for characterization, polymer formation was visually observable in only 5 minutes. The slow reaction after a facile initiation would seem to indicate that the activity of the growing species was attenuated by resonance stabilization.

From viscosity measurements of the red-orange polymer isolated from the reaction mixture, the average molecular weight was found to be 3000. 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 though different melt-softening temperatures (155-167°C, 110-122°C, 55-75°C). X-ray diffraction did not show any crystallinity. The results are summarized in Table 1.

Table 1. Cathodic Polymerization of Phenylacetylene

V applied	Yield (cathode) %	Yield (anode) %	M_v (cathode)	M_v (anode)
6	17.0	3.0	3132	3074
12	35.0	4.0	2969	3074
18	45.0	9.0	3179	2931
24	52.0	11.0	3336	3016
36	36.0	23.0	3247	3030
48	37.0	27.0	3349	3011

Carbon hydrogen analyses agreed well with calculated values for polyphenylacetylene (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 absorptions are also seen at 910 cm^{-1} and 870 cm^{-1}, the larger of these being at 910 cm^{-1}. This region is believed to be involved in the unsaturation in polyphenylacetylenes, with characteristic absorptions arising at 910 cm^{-1}, 870 cm^{-1} and 840 cm^{-1} (6-8). Of these three absortion bands, the one at 870 cm^{-1} has been taken as characteristic of a cis-structure (6); it is seen from Figure 1 that this band is not present conspicuously in the ir spectrum of the polymer prepared in this study.

Kern (7) has studied and compared polyphenylacetylenes formed from several types of initiation reactions and grouped them into three types of products. The methanol insoluble polymer obtained in our study by electropolymerization of phenylacetylene and reprecipitated with methanol from a benzene solution appears to be similar to the thermal polymerization product, Type III described by Kern (7).

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, when recovered from solvents like pyridine and dimethylformamide, to be richer in trans. Polar solvents like pyridine and DMF were found to promote an isomerization of cis unsaturation to trans unsaturation in polyphenylacetylenes (7).

The yellow methanol insoluble portion obtained after electropolymerization is similar to this thermal type III polymers, 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 cis. This would also explain the absence of absorption at 870 cm^{-1} (Fig. 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 other products are just lower molecular weight fractions of the same polymer, a trans rich, cis-trans copolymer.

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

The spectra consisted of a single broad multiplet centered about 7.0 ppm. This is consistent with published ^{1}H-NMR spectra of polyphenylacetylene (8). 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 (9). 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.

The available evidence then indicates the polymer to be a linear polymer with a polyene structure. The polymer, as suggested earlier, is probably formed by an anionic mechanism at the cathode. The presence of polymer at the anode, as seen in Table I, increases with increasing voltage, and probably results from electrophoretic migration of living polymer anions since no monomer was present in the anode compartment. It is significant that the molecular weights of the polymers from both compartments are the same. This might indicate that the living anions had reached equilibrium growth before migrating to the anode. This aspect is being investigated in more detail.

The experiments with benzonitrile provided similar evidence for the formation of a linear, -C=N- conjugated polybenzonitrile by an anionic mechanism. The results are summarized in Table 2. For convenience of isolation of coated polymer, metal plate electrodes were used in these experiments.

Here again, small amounts of water completely inhibited the polymerization reaction, which occurred only at the cathode. An anionic mechanism is thus indicated. The reaction rate was also slow presumably because of the resonance stabilization of the anions of the growing polymer. Such resonance stabilization may also be a limiting factor in the maximum molecular weight achievable by electropolymerization. The intrinsic viscosity of the polymer, measured at 35°C, was found to be 0.07 dl/g in conc. H$_2$SO$_4$ in which the polymer was completely soluble. The polymer was also partially soluble in DMF.

The mass spectroscopic study was conducted at low temperature (50-200°C) in order to volatilize low molecular weight compounds only, as well as to prevent thermal degradation of the polymer. It indicated that the polymer was not predominantly the cyclic trimer 2,4,6-triphenyl-s-triazine; it showed no significant excess of mass 309. The sample also showed significant amounts of mas 103 - presumably benzonitrile, and mass 120 - presumably benzoic acid or benzamide. The infrared spectrum indicated the presence of absorption bands for conjugated $-C=N-$ bonds at 1605 cm^{-1} and 1520^{-1}, (Fig. 3). The facile electropolymerization of benzonitrile under ambient conditions to a linear conjugated polymer is in striking contrast to the general observation that nitriles homopolymerize only under conditions of high temperature and pressure, usually in the presence of a complexing agent such as titanium tetrachloride. The ordering of the $C\equiv N$ dipoles under the influence of the electric field in the electrode region must be a contributing factor in electropolymerization.

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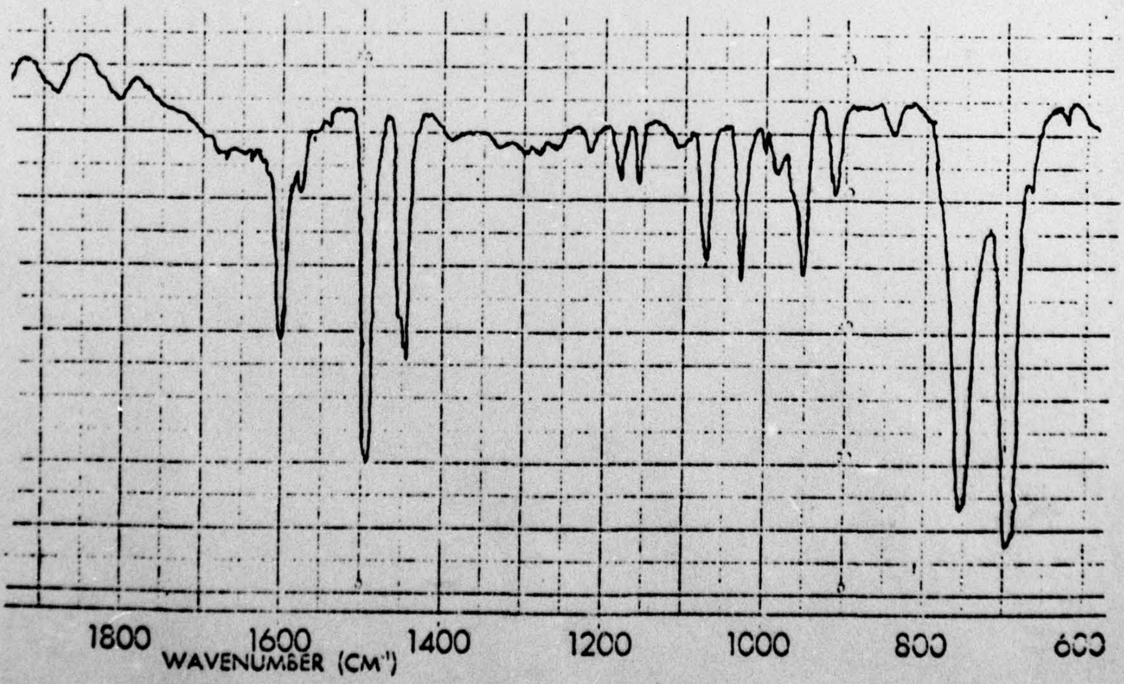

Fig. 1. IR spectrum of electroinitiated polymer of phenylacetylene.

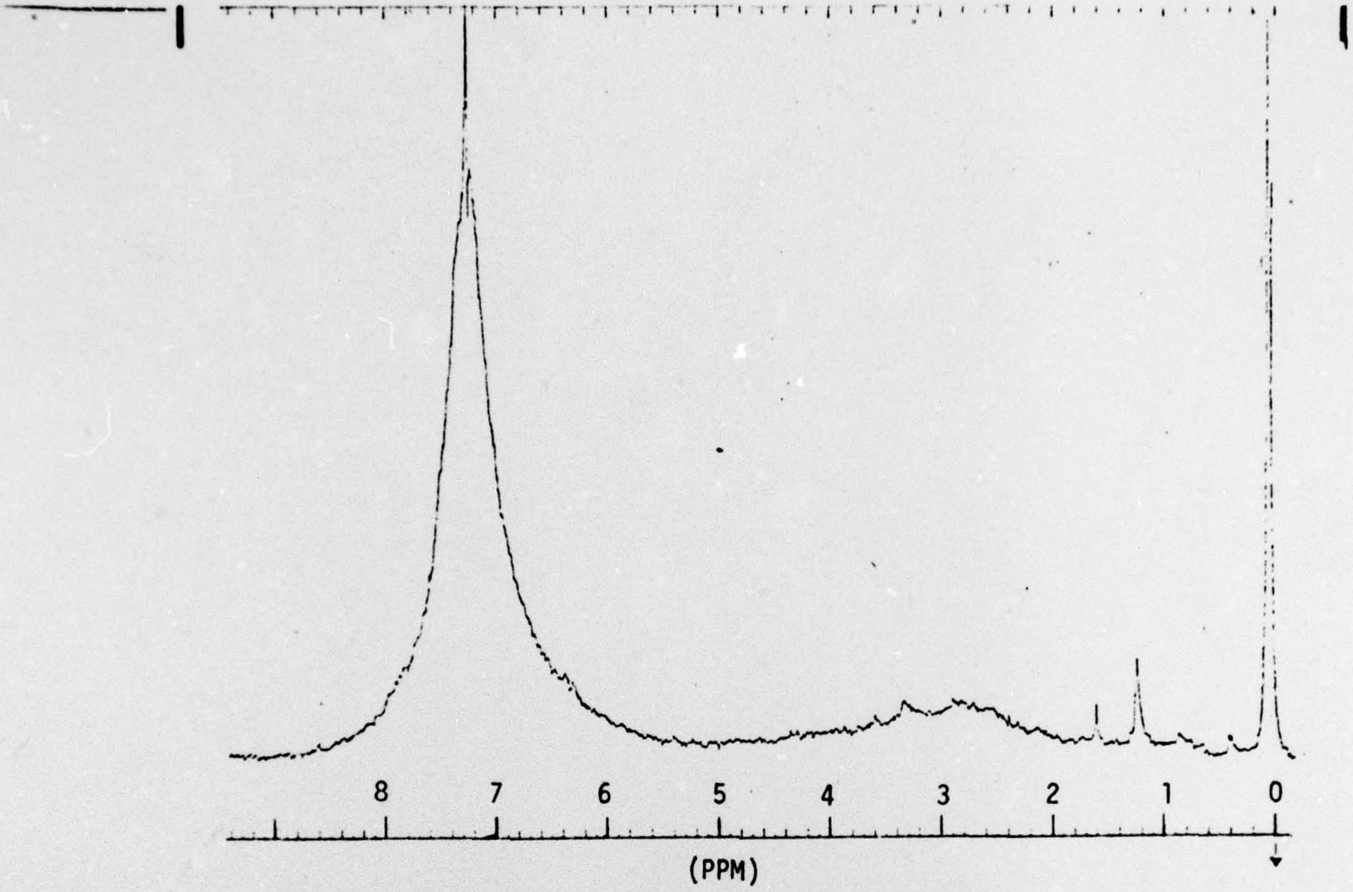

Fig. 2. ^1H NMR spectrum of electroinitiated polymer of phenylacetylene.

Table 2. Electroinitiated Polymerization of Benzonitrile

Composition of Catholyte [b]	Electrode	Cell Voltage Volts	Current (mA) Initial	Current (mA) Final	$[\eta]$ [a] dl/g
1. Benzonitrile (200g) $LiNO_3$ (5g)	steel	12	104	28	0.062
2. Same as above	zinc	12	103	18	0.073
3. Same as above	copper	12	117	20	0.070
4. Benzonitrile (80g) $LiNO_3$ (2g)	aluminum	12	64	17	0.068
5. Benzonitrile (80g) $LiNO_3$ (2g) H_2O (5g)	aluminum	12	108	101	no polymer
6. Benzonitrile Neat	platinum	60	0.1	0.02	no polymer
7. Benzonitrile (200g) $(C_2H_5)_4NBr$	zinc	12	74	56	0.062

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[a] Intrinsic viscosity determined in conc. H_2SO_4 at 35°C.

[b] In DMF solution, except 6.

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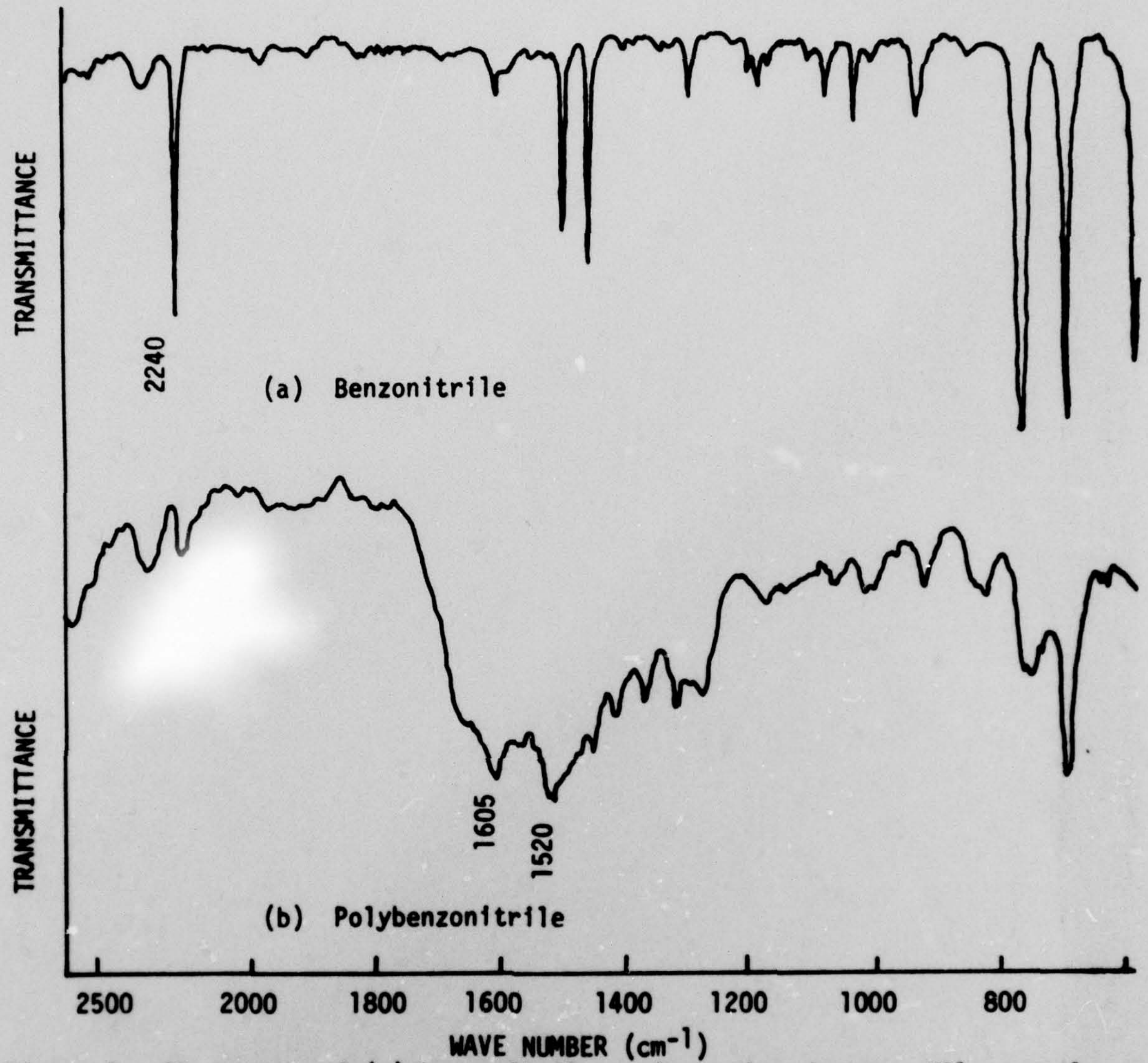

Figure 3. IR spectra of (a) benzonitrile, using a drop between KCl crystals (b) polybenzonitrile, using KBr pellet.

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