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Electroinitiated Polymerization of Benzonitrile

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SUMMARY

The electroinitiated polymerization of benzonitrile yields a linear conjugated polymer, $\left[(C_6H_5)C{=}N\right]_n$. An anionic mechanism of polymerization is indicated.

INTRODUCTION

In the course of a comprehensive study of electropolymerization occurring on electrode surfaces, it became of interest to investigate the participation of nitrile groups in electroinitiated polymerization (GARG et al. (1978), SUBRAMANIAN et al. 1978a,b. The cathodic polymerization of acrylonitrile(AN) in dimethylformamide (DMF) with sodium nitrate as supporting electrolyte yielded an orange colored polymer, the ir spectrum of which revealed the formation of cyclized polyacrylonitrile (pAN) (GARG, et al. 1978). The addition of the pendent, cyano groups to each other apart from the occurrence of main chain polymerization through vinyl bonds was inferred from this observation. Benzonitrile (BN) was therefore chosen as monomer to investigate electropolymerization through C≡N bonds.

EXPERIMENTAL

The cathodic polymerization of BN was 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 BN in DMF containing lithium nitrate was electrolyzed for up to 72 hours. All polymerizations were conducted at room temperature. The loose polymer deposit formed on the cathode was scraped off, thoroughly washed with water and dried. During washing, an ammoniacal odor was quite noticeable.

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RESULTS AND DISCUSSION

The experimental conditions and results of polymerization of BN are summarized in Table 1. It is seen that, without the added electrolyte, the neat monomer caused high cell resistance and negligible current, and that there was no polymer formed. Hence, it is concluded that in the absence of an electrode reaction as indicated by a measurable current, the electric field obtained under the present experimental conditions does not initiate polymerization.

The polymer was partially soluble in several organic solvents including DMF but was completely soluble in concentrated sulfuric acid in which the intrinsic

TABLE 1

Electroinitiated Polymerization of Benzonitrile

Composition of Catholyte[b]	Electrode	Volts	Current (mA) Initial	Current (mA) Final	$[\eta]^a$ dl/g
C_6H_5CN (200g) $LiNO_3$ (5g)	steel	12	104	28	0.062
As above	zinc	12	103	18	0.073
As above	copper	12	117	20	0.070
C_6H_5CN (80g) $LiNO_3$ (2g)	aluminum	12	64	17	0.068
C_6H_5CN (80g) $LiNO_3$ (2g) H_2O (5g)	aluminum	12	108	101	no polymer
C_6H_5CN (Neat)	platinum	60	0.1	0.02	no polymer
C_6H_5CN (200g) $(C_2H_5)_4NBr$	zinc	12	74	56	0.062

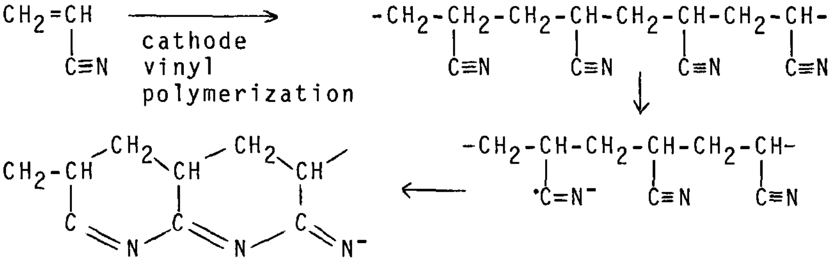
[a] Intrinsic viscosity determined in conc. H_2SO_4 at 35°C

[b] In DMF solution, except 6.

viscosity of the polymer was found to be 0.07 dl/g. From Table 1, it is apparent that the electrode material has neglible influence on polymer molecular weight.

The presence of small amounts of water completely inhibited the electropolymerization reaction. However, the addition of small quantities of a free radical inhibitor had little effect on polymerization. Hence, it was concluded that the polymerization mechanism is anionic. Further, the reaction rate was rather slow, presumably because of the resonance stabilization of the anions at the ends of growing polymer chains. Such resonance stabilization may also be a limiting factor in the maximum molecular weight achievable by electropolymerization.

The cathodic polymerization of acrylonitrile was shown to proceed through a dianion $[CNCH(CH_2)_2CHCN]^{2-}$ formed by a two electron reduction of acrylonitrile monomer (TRIFANOV et al. 1973). The cyclization of pAN and the unique formation of "whiskers" on the cathode during the polymerization of AN in DMF have also been explained by the accumulation of anions trapped in the polymer formed (GARG et al. 1978). During the initial stages of electrolysis, a relatively fast vinyl polymerization leads to the formation of pAN coating on the cathode. Subsequently, some of the nitrile groups accept electrons to become anion radicals, thus initiating anionic polymerization of nitrile groups leading to cyclized pAN. The anions are covalently bonded to the precipitated polymer and thus cannot move away



from the cathode. As the concentration of anions in the coating increases above some critical value, the coulombic repulsion between the cathode and the negatively charged coating will be sufficient to cause the peeling of the coating from the cathode surface. The peeled portions align themselves in the direction of the electric field to give the appearance of whiskers. The formation of cyclized pAN was confirmed by ir absorption at 1570 cm^{-1} for conjugated -C=N- bonds, at 1650 and 1635 cm^{-1} for C=N bonds and at

1220 and 1145 cm^{-1} for C-N bonds. This has also been observed by TRIFONOV and SHOPOV (1972); evidence for the presence of conjugated multiple bonds in the yellow colored polymers was supported by uv absorption at a longer wavelength 304 nm, compared to 271 nm for white pAN prepared by free radical initiation.

Similarly, the ir spectrum of pBN obtained in this study shows the presence of absorption bands for conjugated -C=N-bonds at 1605 cm^{-1} and 1520 cm^{-1} in agreement with published data on pBN (KABANOV et al., 1963) (Fig. 1). A mass spectroscopy study of the polymer was conducted at low temperature (50-200°C) in order to volatilize only low molecular weight compounds while simultaneously preventing the thermal degradation of the polymer. The mass spectrum did not show a significant excess of mass 309. This indicated that the polymer was not predominantly the cyclic trimer 2,4,6-triphenyl-s-triazine (MW=309) which is a typical end product of attempts to polymerize BN at <150°C by chemical means. The sample, however, showed a significant excess of mass 103--presumably the residual BN,

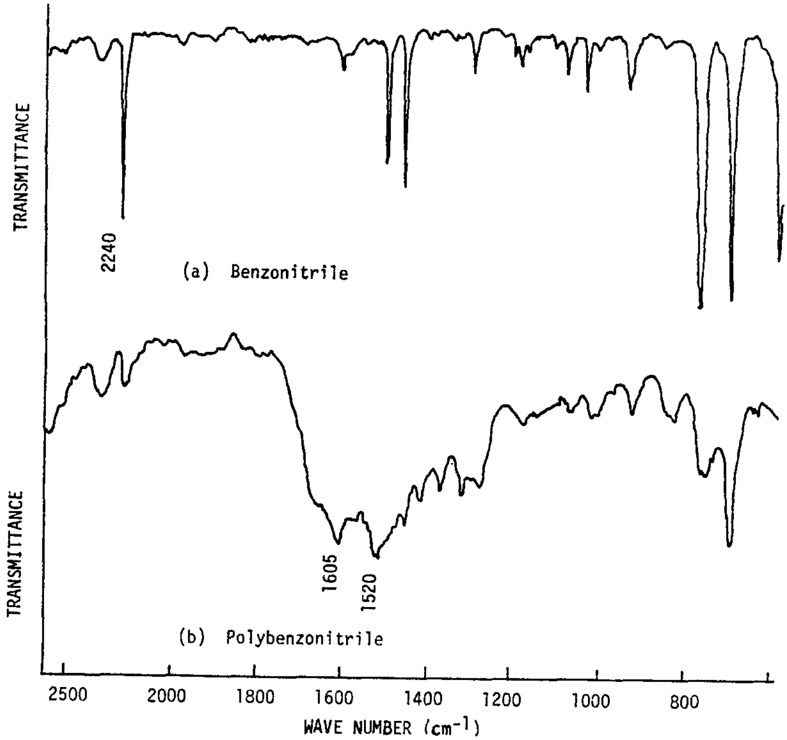


Figure 1. IR spectra of (a) BN, using a drop between KCl crystals (b) pBN, using KB$_r$ pellet.

and also of mass 120--presumably benzoic acid and benzamide generated by hydrolysis of the pBN during aqueous washing.

It is therefore concluded that the polymer obtained by electropolymerization of BN is the polybenzonitrile with a conjugated -C=N- backbone. Kabanov et al., (1963) have suggested that the polymerization of C≡N to the corresponding polyconjugated polymers cannot occur under conditions typical for polymerization of vinyl or acetylenic compounds. Their suggestion was based on the fact that the estimated heat of polymerization at the C≡N bond cannot be substantially more than zero. Since the entropy of polymerization of C≡N to the corresponding $\{C=N\}_n$ polymers is negative, the reaction will lead to an increase in the free energy of the system, making such a polymerization thermodynamically unfavorable. Kabanov et al., (1963) and KARGIN et al., (1961) were able to prepare polyconjugated polymers from aliphatic nitriles and benzonitrile by first preparing stoichiometric complexes of these monomers with titanium tetrachloride, zinc chloride, or boron trifluoride and subsequently heating these complexes, in the presence of polymerization initiators such as phosphoric acid, to 150-250°C in sealed ampoules. The presence of the complexing agent shifts the chemical equilibrium favorably in the direction of polymerization through a preliminary ordering of the monomer molecules. LIEPINS (1968) and LIEPINS et al. (1968) were also able to synthesize polyconjugated polymers from nitriles by using free radical initiators at temperatures of 150-330°C.

The convenient electropolymerization of benzonitrile under ambient conditions to a linear conjugated polymer is thus in striking contrast to the rather severe conditions of temperature and pressure necessary to cause homopolymerization of nitriles by ordinary chemical methods. The preliminary ordering of C≡N dipoles under the influence of an electric field in the electrode region might be a contributing factor in favoring the convenient electropolymerization of nitriles.

The polyconjugated polymers derived from nitriles have been shown to have useful semiconducting properties (WILDI and KATON, 1964, OIKAWA and KAMBARA, 1964, and NORRELL et al., 1974). Similarly, the polymerization of nitrile goups is likely to be used for the curing of nitrile terminated polyimide intermediates (BILOW et al., 1974). It is therefore obvious that a convenient method of converting C≡N compounds to $\{C=N\}_n$ polymers as by electropolymerization, would have many practical applications. The indicated anionic mechanism of polymerization requires further elucidation.

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