ether (1.0 *M*) in acetonitrile (Figure 4). This signal was also unresolvable and of approximately the same width as an authentic sample of the 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion. No significant differences were observed in this signal by varying the flow rate from 1.5 to 3.0 ml/sec.

Kinetic Studies. The kinetic studies of the reaction of tetracyanoquinodimethane and isopropyl vinyl ether were carried out in the apparatus shown in Figure 9, by following the disappearance of the maximum absorbance of tetracyanoquinodimethane at 393.5 nm. After the tetracyanoquinodimethane spectrum was recorded, the reagents were mixed by opening the break seal. The various initial concentrations, temperatures, and kinetics are given in Table VII. The concentration of tetracyanoquinodimethane was found to be linear with absorption.

A Durram-Gibson stopped-flow spectrophotometer was employed in determining the kinetics of the charge-transfer complex disappearance to the cycloaddition product of tetracyanoethylene and alkyl vinyl ethers (Figure 6, Table X), in methylene chloride and acetonitrile. The charge-transfer complex formation was too rapid to follow by this technique. This instrument was also used to follow the kinetics of the free-radical intermediate 2,3-dichloro-5,6-dicyano-*p*-benzoquinone radical anion, in the reaction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and alkyl vinyl ethers (Table IX).

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Polymerization of *N*-Vinylcarbazole with Zinc Bromide. I. Electroinitiated

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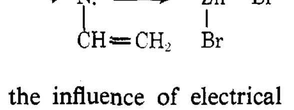
ABSTRACT: The electroinitiated polymerization of *N*-vinylcarbazole is described. The reaction medium consists of monomer dissolved in an acetone–zinc bromide solution. Elemental analysis and infrared and nuclear magnetic resonance spectroscopy identified the reaction product as poly(vinylcarbazole). Molecular weights were obtained from gel permeation chromatography and intrinsic viscosity measurements. Generally, polymer yield increased with increased applied current density. High polymer yields were obtained in short reaction times. Weight-average molecular weights were low and in the range 2000–5000. Molecular weight distributions were very narrow and always in the range 1–1.2.

Breitenbach, *et al.*,[1] studied the electroinitiated polymerization of *N*-vinylcarbazole (VCZ) using techniques not involving donor–acceptor mechanisms. Their studies involved the cationic polymerization of the monomer in nitrobenzene solution using supporting electrolytes such as tetraalkylammonium compounds and silver perchlorate. Good yields of low molecular weight polymers were obtained. However, the perchlorate systems lend themselves to some experimental criticism, since it is known that cationic polymerization can take place with perchlorate catalysts in systems containing trace amounts of water in the absence of electrolytic current.

Recently, several electroinitiated polymerizations have been studied in which donor–acceptor complexes are thought to be part of the reaction mechanism.[2–6] The results can be interpreted on the model proposed by Gaylord,[7] which was arrived at after observing experimental behavior on the copolymerization of pairs of polar monomers in the presence of suitable salts.

The postulate involves the interaction between an electron-donor monomer and an electron-acceptor monomer to form an equimolar charge-transfer complex. This complex formation is enhanced by a metal salt which acts as an electron acceptor. The formation of the complex is then followed by the spontaneous or radical-initiated polymerization to produce an alternating copolymer.

An extension of the Gaylord donor–acceptor theory may be applicable in the case of homopolymerization in the presence of a transition metal salt such as $ZnBr_2$. Such a mechanism was tentatively proposed by Gaylord for acrylonitrile polymerization utilizing $ZnCl_2$.[7] Since VCZ is a very basic monomer it will complex readily with Zn salts, thereby forming a complex in which the VCZ moiety has increased electrophilic character. The complexed VCZ–$ZnBr_2$ molecule (*i.e.*, the acceptor) under the influence of electrical current (electroexcitation) will be vulnerable to nucleophilic attack from a VCZ monomer (*i.e.*, the donor molecule), thereby initiating a cationic-type polymerization.



In electrochemical systems, polymerization of the donor–acceptor complexes is thought to be initiated by activation of these complexes at the electrode, with the rate of formation of the activated complex being dependent on the current. It is likely that elevated temperatures increase the reactivity of the donor–acceptor complexes. However, higher temperatures are also thought to decrease the concentration of the complexes, giving rise to a decrease in reaction rate. Electrochemical initiation offers a tool for investigation these

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opposing effects separately by altering the reaction rate of the complexes at constant temperature.

In this paper, the electroinitiated polymerization of *N*-vinylcarbazole is described using zinc bromide as catalyst.

Experimental Section

Materials. *N*-Vinylcarbazole (BASF Chemicals Ltd.) was recrystallized three times from purified dry *n*-hexane and dried *in vacuo* at 30° for 48 hr (mp 65.5°). The pure crystals were stored *in vacuo* and in darkness until needed. Zinc bromide crystals (Fisher Scientific Co.) were dried for 24 hr *in vacuo* at 140°. Acetone (Fisher Scientific Co., high purity grade) was dried over 4A Molecular Sieves and fractionally distilled prior to use.

Polymerization Procedure and Analysis. The experiments were conducted in a 500-ml darkened reaction flask to avoid the possible occurrence of any extraneous photochemical reactions. The vessel, which was maintained at 25° by means of a jacket through which water flowed, was equipped with stirrer and nitrogen inlet and outlet. The electrolytic cell contained two identical platinium foil electrodes (2.0 × 5.0 cm) separated by 4.0 cm. Polymerizations were performed under conditions of constant current using a dc power supply (Northeast Scientific Corp., Model RI233; 0–230 mA, 0–360 V).

The zinc bromide and *N*-vinylcarbazole monomer were separately dissolved in two equal volumes of acetone contained in darkened vessels. Equal quantities of each solution were mixed just prior to the application of current. The concentration of VCZ was 0.33 *M* in a total volume of 400 ml and the mole ratio of VCZ:$ZnBr_2$ was 5:1. After passage of electrolytic current, the products of the reaction were isolated by precipitation into a large excess of absolute methanol. This procedure served to separate the polymer from monomer, since the monomer is readily soluble in methanol. The crude polymer was further purified by reprecipitation from toluene solution into excess methanol, followed by several methanol washes. After drying the product, yields were determined gravimetrically. In every case, blank reaction solutions (*i.e.*, solutions through which no current has passed), were left standing under ambient conditions to check the possibility of thermal polymerization occurring.

Chemical elemental analyses for C, H, and N were carried out by Galbraith Laboratories, Inc. Zinc contents were estimated by semiquantitative emission spectral analyses.

Results and Discussion

Elemental analyses and infrared and nmr spectral data confirmed that the reaction product was poly(vinylcarbazole).

Typical elemental analyses gave values of C, 86.7; H, 5.8; N, 6.8. (Calcd: C, 87.4; H, 5.8; N, 6.8.) No significant levels of zinc or bromine were found in the products.

The nmr spectrum of poly(vinylcarbazole) has recently been studied by Williams.[8] He reported the following assignments: τ 6.22, 6.937 (methine proton); 8.00, 8.48 (methylene protons); and 2.14, 3.11 (d), 4.77 (aromatic protons). In the spectra of electroinitiated polymer, the aromatic protons have peaks at τ 2.35, 3.20, and 4.80, which are close to those reported by Williams. The aliphatic protons produce a broad overlapping resonance between τ 6.0 and 9.0. From the integral, a ratio of the area under the aromatic proton peaks to that under the aliphatic proton peaks was found to be 2.66. The theoretical value for the polymer is 8/3 or 2.67.

Infrared absorption spectra showed that the vinyl bands (present at 806 and 963 cm^{-1} in the monomer[9]) were absent in the purified product, indicating that reaction had occurred through the *N*-vinyl group. The other absorption bands were almost identical with those quoted by Tazuke[10] for poly(vinylcarbazole).

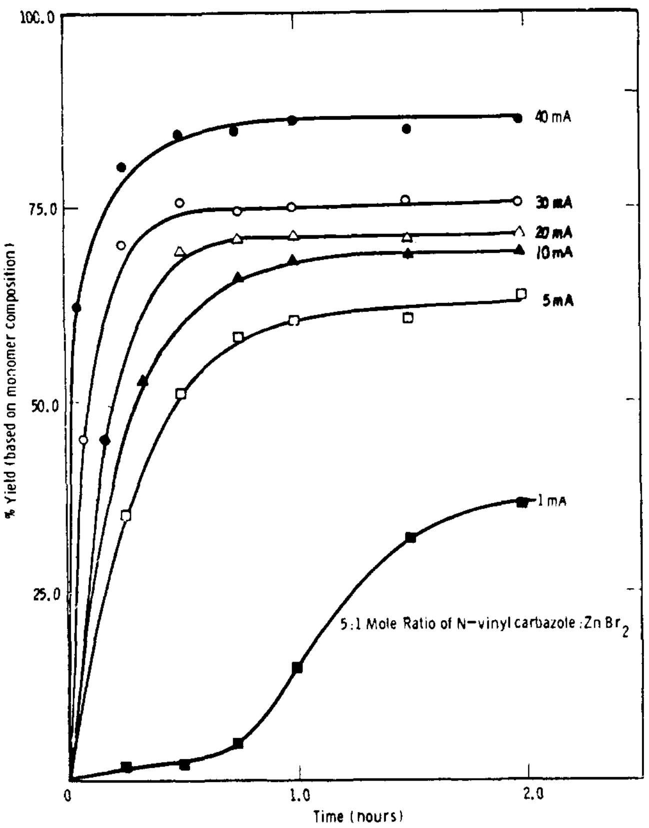

Figure 1. Polymer production as a function of time and electroinitiation current.

Polymer yield, and hence rate of polymerization, increased with increasing applied current density. Figure 1 shows the yield of poly(*N*-vinylcarbazole) as a function of time for six different currents. With higher applied currents, optimum yields were achieved after only a 15-min reaction time, whereas lower current densities did not exhibit this same optimization. In initial experiments, the mole ratio of zinc bromide to *N*-vinylcarbazole monomer was varied. Optimum polymer yields were obtained when the mole ratio of *N*-vinylcarbazole to zinc bromide was $\leqslant$5:1. Generally, the reactant mole ratio of acetone:*N*-vinylcarbazole:zinc bromide was approximately 200:5:1.

Polymer molecular weight estimates were made by employing gel permeation chromatography analyses and intrinsic viscosity determinations. Generally, polymer weight-average molecular weights were very low (2000–5000). However, (weight average)/(number average) distributions were very narrow and always in the range 1–1.2. These gel permeation chromatographic studies also indicated that, under the experimental conditions employed in this work, the yield of the cyclic dimer *trans*-1,2-dicarbazylcyclobutane, which has been reported by Ellinger, *et al.*,[11] was always small (<2%).

The molecular weight of the polymer was also determined by intrinsic viscosity measurements according to the equation[12] $\eta = (3.35 \times 10^{-4})M^{0.58}$ dl g^{-1}, at 25° in benzene. The molecular weights obtained by this latter technique compared very favorably with those obtained by gel permea-

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tion chromatography analysis. It was originally thought that these low molecular weight products could be explained according to a simple donor–acceptor model.[7] That is, a high concentration of initiator gives rise to many polymer chains and hence low overall molecular weight. With this theory in mind, some experiments were carried out with small zinc bromide concentrations together with the application of very low current densities. However, these conditions produced no significant increase in molecular weight. The reason for these low molecular weight values is not very clear at present. Further experimental work is now in progress to elucidate the mechanism of termination in these systems.

Thermal polymerization was not observed in blank experiments conducted under conditions already described for electroinitiated polymerization. In the blank experiments, no current was passed through solutions containing *N*-vinylcarbazole, acetone, and $ZnBr_2$. No polymer was found even after the samples had been left for several days in a darkened reaction vessel at room temperature.

In a separate experiment, the locus of polymerization was found, by separation of the electrode compartments using a porous clay battery cup, to be the anode. The locus of polymerization being at the anode eliminates the possibility of an anionic mechanism.

Calculations based on the number of Faradays transferred and the corresponding number of polymer molecules formed indicated a very high absolute electrical efficiency. After 70% conversion at a 5:1 VCZ:$ZnBr_2$ mole ratio, approximately 70 polymer molecules were formed per electron transferred at the electrode. This is an extremely high efficiency compared with other electrochemical polymerizations and is in sharp contrast to the results obtained by free-radical[13] (< one polymer molecule/electron) or anionic electroinitiation[14] (~ three polymer molecules/electron). It is thought that the high efficiency experienced in this system may be characteristic of donor–acceptor cationic electroinitiated polymerization.

The asymptotic nature of the conversion–time curves is unusual in that all the curves show a high initial rate during the first 55–80% conversion and then decrease sharply. The polymerizations were always incomplete, thus indicating the occurrence of a high degree of termination. The initial reaction rates appear to be directly proportional to the current density, which might be expected if it is assumed that the rate of initiation is dependent on the concentration of electroexcited VCZ–$ZnBr_2$ complexes.

Our results indicate that water has an effect on both the rate of polymerization and molecular weight of the polymer. In initial experiments, the water content of the acetone was found to be 0.15% (w/w) by Karl Fisher titration. However, in relatively anhydrous systems (<0.005% H_2O) low molecular weights were again obtained. These data suggest that the polymerization is proceeding through a cationic mechanism in which chain-breaking reactions or transfer reactions are taking place between the growing polymer cation and VCZ monomer. VCZ monomer is the most basic compound present in this system, and at the concentrations (0.333 *M*) used it seems more likely to be involved in cationic transfer reactions than the water or other basic impurities. The molecular weights obtained in this work are lower than but comparable to those found by Breitenbach.[1]

It seems unlikely that the acetone solvent plays any direct role in determining the molecular weight of the final polymer.

The kinetics and precise mechanism of the reaction will be the subject of further papers involving both electrochemical and photochemical initiation.

Acknowledgment. The authors wish to acknowledge the assistance of Dr. F. Dollish, Mellon Institute, Pittsburgh, Pa., in the nmr analysis.

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Viscoelastic Properties of Poly(phenylene ethers). II. 2-Methyl-6-alkyl-Substituted Polymers

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ABSTRACT: The viscoelastic properties of a series of 2-methyl-6-(secondary alkyl) poly(*p*-phenylene ethers) have been investigated by dynamic mechanical techniques. No tan δ peak was found which could be ascribed to motions of the backbone phenylene unit below T_g, in agreement with previous work on unsymmetrically disubstituted poly(phenylene ethers). For all the materials studied here two tan δ peaks were found between T_g and $-200°$, identified here as the γ and δ peaks to conform to previously used nomenclature. The peak temperatures of the γ relaxation increase drastically with the number of CH_2 groups in the side chain (from *ca.* 100 for the C_5 side chain to -50 for C_{10} at 1 Hz); the activation energies increase linearly from *ca.* 9 to 18 kcal for these materials. This relaxation is assigned to a low-amplitude hindered torsional oscillation of $n - 2$ units of the alkyl side chain, in its all-trans conformation, around an axis which is coincident with the long axis of the all-trans alkyl chain. The peak temperatures of the δ relaxations increase only slightly with increasing side-chain length, the activation energies are uniformly of the order of 6 kcal, and the mechanism seems to be motion of terminal groups (methyl or ethyl).

The poly(phenylene ethers) constitute a series of polymers that can be modified easily by the placement of various substituents in the 2 and 6 positions of the phenylene ring. A large number of investigations on the viscoelastic properties of this important family of materials have already been made. In a previous paper we have reported on a study of the low-temperature relaxations encountered in unsubstituted and methyl- or phenyl-substituted poly(*p*-phenylene ethers)[1] and also reviewed the pertinent literature.

One of the findings of the previous investigation which is

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