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ELECTROINITIATED POLYMERIZATION OF *N*-VINYLCARBAZOLE BY DIRECT ELECTRON TRANSFER

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ABSTRACT

Electroinitiated polymerization of *N*-vinylcarbazole has been accomplished by constant potential electrolysis. It was found that direct electron transfer from the monomer to the anode initiates the polymerization even at a potential as low as +0.95 V versus Ag^0/Ag^+. Dichloromethane was used as the solvent, and the electrolyte was tetrabutylammonium fluoroborate. Conversions as high as 86% were reached even when a microelectrode was used. Effects of electrode area, temperature, and electrode potential on polymerization were studied. Percent conversion was followed by cyclic voltammetry.

INTRODUCTION

Poly(*N*-vinylcarbazole) is known to have high thermal stability and photoconductivity along with good dielectric properties. Polymerization of *N*-vinylcarbazole (NVC) has been studied extensively. Polymerizations by free radical [1-5] and cationic [6-11] initiators have been reported. Attempts at polymerization by anionic initiators have been unsuccessful [12]. There are also no reports on the electroinitiated polymerization of NVC by constant potential electrolysis (CPE).

It is known that electroinitiation can take place by direct electron transfer by CPE [13-18]. When constant current is applied, the working electrode potential will vary during polymerization. In such systems the monomer, solvent, and electrolyte can all be involved in the electron transfer step at some stage of polymerization.

Most electroinitiated polymerization studies on NVC have been carried out by constant current electrolysis (CCE). Breitenbach and Srna [19] reported that when nitrobenzene was used as solvent and tetrabutylammonium perchlorate as electrolyte, high polymer yields were obtained by CCE. Phillips et al. [20, 21] used acetone-zinc halide systems to polymerize NVC by CCE. They obtained polymers with low molecular weights (1000-6000).

Kikuchi [22, 23] applied constant current and rectangular current to a NVC-acetone-$LiClO_4$ mixture and obtained higher polymer yields with decreasing temperature. They proposed a cationic mechanism for the electroinitiated polymerization of NVC in acetone and acetonitrile.

Mano and Calafate [24] reported the electroinitiated polymerization of NVC in dichloromethane by CCE. They employed tetraalkylammonium salts as the electrolyte and claimed that molecular weights as high as 10^5 can be obtained at and below 0°C. The electroinitiated copolymerization [25] of NVC and α-methylstyrene by CCE has also been reported.

The only example of CPE for the polymerization of NVC was reported by Dubois et al. [26]. The purpose of that work was to coat the electrode but not to study the rate or other parameters of polymerization. There are no reports in the literature in which the rate of electroinitiated polymerization of NVC was studied under CPE conditions.

The effects of electrode area and anode potential have not been studied for the electroinitiated polymerization of NVC either in CCE or CPE systems. The aim of the present work was to follow the rate of polymerization by cyclic voltammetry even at the earliest stages of polymerization without interrupting the polymerization. We also aimed to check the possibility of employing a microelectrode with an area of 0.03 cm^2 under CPE conditions since the polymerization reaction is very rapid with conventional electrodes (few cm^2) due to the large surface area. Finally, the effects of polymerization potential and temperature were also studied.

EXPERIMENTAL

Materials

Acetonitrile (Merck, synthetic grade) was dried over CaH_2 for 24 h, filtered, fresh CaH_2 added, refluxed for 10 h, and distilled under N_2 atmosphere.

Dichloromethane (Merck, extra pure) was dried over CaH_2 for 24 h, refluxed, and distilled under N_2 atmosphere.

N-Vinylcarbazole (Aldrich) was recrystallized from methanol in the dark, filtered, dried under vacuum at 20°C for 24 h, and stored in the dark.

Tetrabutylammonium fluoroborate (Sigma), methanol (Merck, synthetic grade), and diethylether (Merck, synthetic grade) were used without further purification.

Procedure

Cyclic Voltammetry

Cyclic voltammograms of NVC were obtained prior to and during polymerization by using the cyclic voltammetry cell. The working electrode was a 2-mm long Pt wire, and the counterelectrode was a 10-mm long Pt wire coiled around the working electrode. An isolated Luggin capillary reference electrode of Ag^0/Ag^+ (0.01 *M*) was used. The supporting electrolyte was 0.10 *M* tetrabutylammonium fluoroborate in dry acetonitrile. A Bank Elektronik LB 75 L potentiostat, a Bank Elektronik Wenking Model VSG 72 function generator, and a Yokogawa Technicorder Type 3073 XY recorder were employed.

Polymerization Procedure

Polymerizations by CPE were accomplished with an H-type cell which was described previously [27]. Platinum foil and wire were used as counter and working electrodes, respectively. The reference electrode was Ag^0/Ag^+ (0.01 *M*). Equal amounts of tetrabutylammonium fluoroborate (0.10 *M*) and NVC (0.035 *M*) were placed into both compartments of the electrolysis cell. The solvent was dichloromethane (60 mL total) unless otherwise stated. The solution was purged with dry nitrogen prior to electrolysis for 20 min. Electrolysis was carried out without bubbling the gas, but the solution was blanketed with dry N_2. The potential of the working electrode (anode) was adjusted to the desired potential (0.95, 1.50, or 3.00 V) and kept constant by the potentiostat. At the end of electrolysis the contents of each compartment were poured into a methanol–ether mixture (1:1) separately to precipitate only the polymer. Precipitated polymers were washed with acetone to remove any traces of dimer [28]. The polymer was filtered and dried under vacuum at 30°C for 24 h.

Before starting the electrolyses, 10–100 μL samples were transferred from the original monomer solution to a CV cell containing 3 mL acetonitrile and 0.1 *M* tetrabutylammonium fluoroborate. From the peak currents of the cyclic voltammograms of the monomer, a calibration curve was obtained in each case by plotting peak currents versus monomer concentration (Fig. 1). The plots of the heights of the peaks at +1.25 and +1.75 V versus monomer concentration gave linear calibration curves with the same slopes.

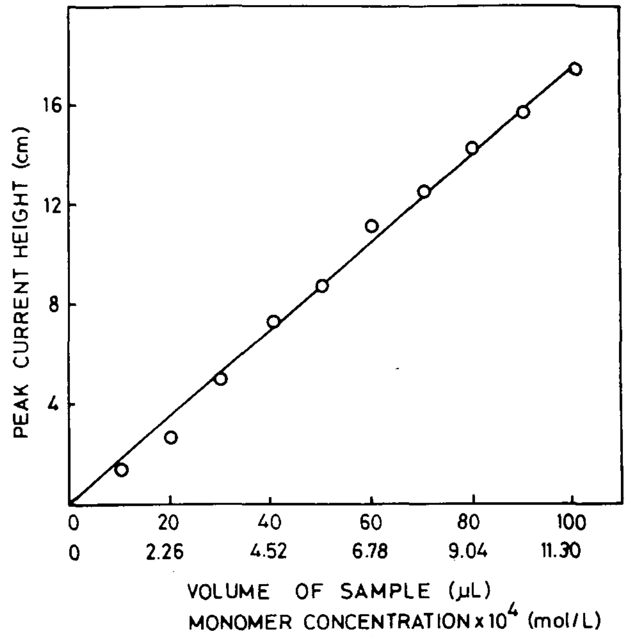

FIG. 1. Calibration curves derived from the peak currents of the cyclic voltammograms of NVC using the peak at +1.25 V.

During electrolysis, 100 μL aliquots from the anode compartment were taken at various time intervals and cyclic voltammograms were obtained as described previously. The concentration of unreacted monomer was found from the calibration curve by using the peak currents of the cyclic voltammograms.

The molecular weights of polymers were obtained at 25°C in benzene with an Ubbelohde viscometer. For calculations, values of $K = 3.05 \times 10^4$ dL/g and $\alpha = 0.58$ were used [29]. A Perkin-Elmer 1710 Model FTIR was used to obtain an IR spectrum of the polymer in KBr.

RESULTS AND DISCUSSION

The cyclic voltammogram of NVC was obtained in acetonitrile at room temperature. Two oxidation peaks were observed at +1.25 and +1.75 V versus Ag^0/Ag^+ (Fig. 2c). There were no cathodic peaks. As seen in Fig. 2, dichloromethane and acetonitrile exhibit no oxidation peaks in the potential range where NVC is oxidized. The data clearly indicate that when electrolysis is carried out at potentials in the range of 0 to +3.00 V,

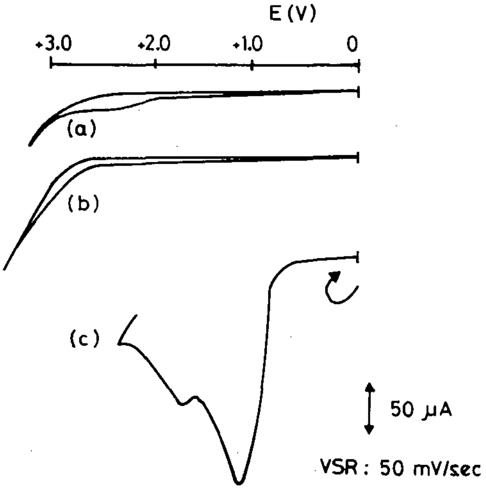

FIG. 2. Cyclic voltammograms of (a) dichloromethane, (b) acetonitrile, and (c) *N*-vinylcarbazole in acetonitrile. VSR is the voltage scan rate. The supporting electrolyte was tetrabutylammonium fluoroborate in each case.

only the monomer can be oxidized. If polymerization occurs by constant potential electrolysis, the oxidized form of monomer, NVC$^{\cdot+}$, should be the only species capable of initiating polymerization. Therefore, it can be said that the electroinitiated polymerization of NVC via CPE proceeds by direct electron transfer in that potential range.

$$\mathrm{NVC} \xrightarrow{-e^-} \mathrm{NVC}^{\cdot+}$$

The area of the anode (working electrode) was found to greatly affect the rate of polymerization. Figure 3 shows that when the anode area is 3.60 cm², over 85% conversion is reached in 10 min of electrolysis in dichloromethane at +1.5 V. In order to decrease the extremely fast rate of polymerization, the anode area was reduced by a factor of 120× to 0.03 cm². The use of an anode with a surface area of 0.03 cm² (microelectrode) caused the percent conversion to drop to 20% after 10 min of electrolysis. For the rest of our work, that microelectrode was used as the anode. The area of the working electrode is directly proportional to the current

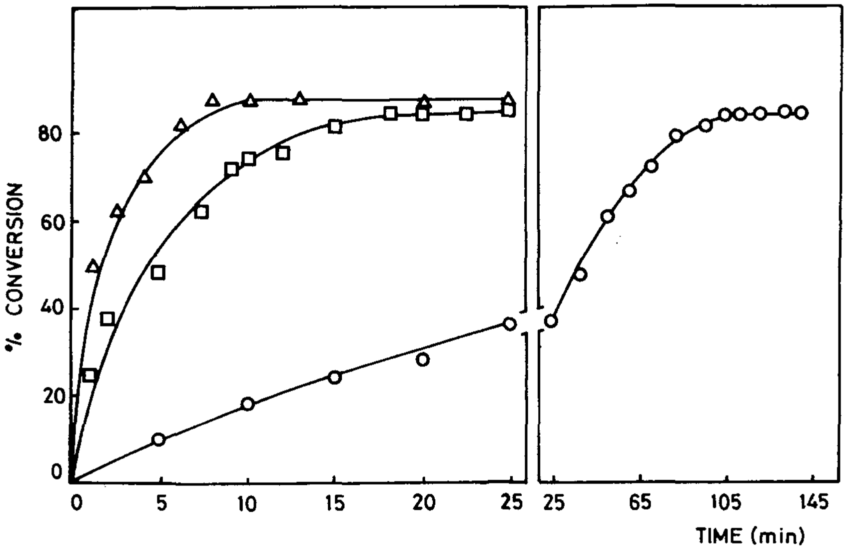

FIG. 3. The effect of working electrode (anode) area on rate of polymerization of NVC. Anode areas were (○) 0.03 cm², (□) 0.30 cm², and (△) 3.60 cm².

passing through the solution. The amount of current, on the other hand, determines the number of radical cations of NVC. The concentration of NVC^{+} should influence the rate of polymerization since it initiates the reaction. Figure 3 therefore represents the effect of initiator concentration on the rate of polymerization via the anode area.

When the potential was applied, the working electrode surface was instantly coated with a green film. Formation of the green film on the anode was attributed to the presence of a cyclic dimer of NVC [26]. Davies et al. [20] reported that the cyclic dimer in the NVC system is *trans*-1,2-dicarbazylcyclobutane. When a Pt foil with a large area (3.60 cm^2) was used as the anode, the color of the reaction mixture turned green after 10 min of electrolysis. This resulted in the precipitated polymers being a light green color. When the microelectrode was used as the anode, the anolyte was colorless throughout the electrolysis. The polymers precipitated were white powders. The use of a microelectrode as the anode therefore minimized the formation of the cyclic dimer in bulk.

Figure 4 shows plots of percent conversion versus time for polymeriza-

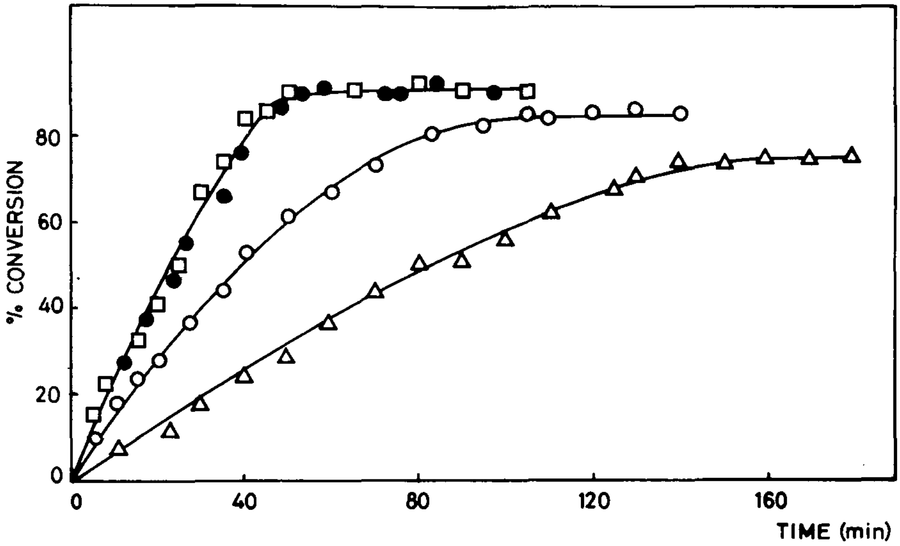

FIG. 4. Electroinitiated polymerization of NVC in dichloromethane at polymerization potentials of (△) +0.95 V, (○) +1.50 V, (□) +3.00 V, and (●) postpolymerization at +3.00 V vs Ag^0/Ag^+.

tions conducted at potentials of +0.95, +1.50, and +3.00 V versus Ag^0/Ag^+. As seen in the figure, the polymerization rate increases as the potential increases.

As a result of increasing the polymerization potential, the amount of current and thus the concentration of radical cations ($NVC^{\cdot +}$) should increase. In addition, at higher oxidation potentials (Epol > +1.75 V), active species which were formed by a second electron transfer to anode can also initiate the polymerization. No polymers were obtained at potentials below +0.95 V versus Ag^0/Ag^+, apparently because sufficient amounts of radical cations cannot be produced. Above +3.00 V, polymers can still be obtained. However, it is likely that oxidation of solvent and/or electrolyte can also take place above +3.00 V. It can be concluded that electroinitiated cationic polymerization of NVC by direct electron transfer can be accomplished within the potential range of +0.95 to +3.00 V versus Ag^0/Ag^+.

The possibility of postpolymerization was checked by carrying out the

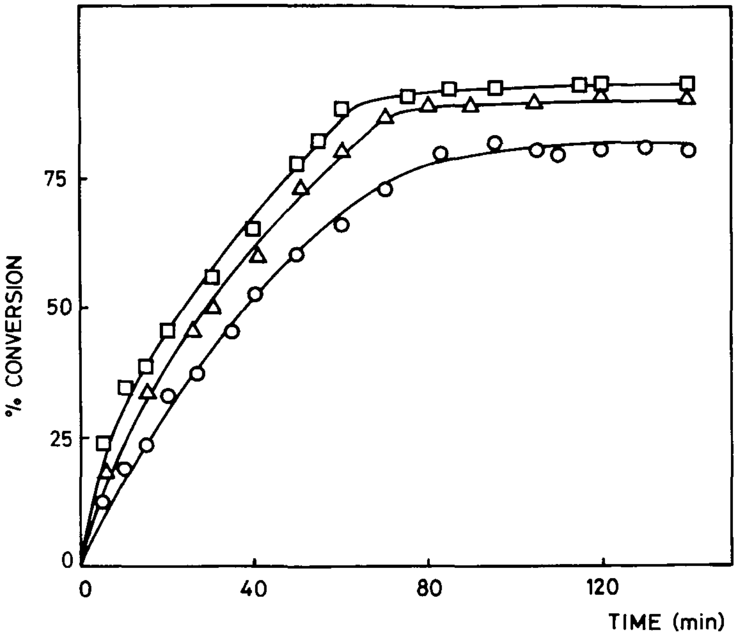

FIG. 5. Electroinitiated polymerization of NVC at three different temperatures: (○) 20°C, (△) 0°C, (□) −30°C.

polymerization at +3.00 V up to 25% conversion. The electrolysis was stopped at 20 min, and it was found that polymerization continued in the absence of current at the same rate as if the current were not stopped, as shown in Fig. 4. The active centers therefore must be very stable.

The effect of temperature on polymerization was also studied. As seen in Fig. 5, the rate of polymerization increases as the temperature decreases. This observation supports the cationic mechanism suggested previously by Kikuchi [22, 23].

The molecular weights of the polymers were not affected significantly by temperature nor by electrolysis potential. As seen in Table 1, the molecular weights are in the order of 1.0–1.2 × 10^4 when the initial monomer concentration was 0.035 *M*. The initial monomer concentration, $[M]_0$, was found to affect the molecular weight. When $[M]_0$ was increased to 0.10 *M*, the molecular weight of the polymer was calculated to be 2.00 × 10^4 (Table 1).

TABLE 1. Percent Yields and Molecular Weights of Polymers Isolated at the End of the Electroinitiated Polymerization of NVC on a Microelectrode

Polymerization potential, V	Temperature, °C	$[M]_0$,[a] mol/L	Percent yield[b]	M[c]
+3.00	20	0.035	83	12,000
+1.50	20	0.035	79	11,500
+0.95	20	0.035	62	–
+1.50	0	0.035	75	11,000
+1.50	−30	0.035	86	10,000
+1.50	20	0.100	80	20,000
+3.00[d]	20	0.035	81	–

[a] Initial monomer concentration.

[b] Calculated from the amount of polymer precipitated in a methanol–ether mixture (1:1) at the end of electrolysis.

[c] Calculated from viscosity measurements made in benzene at 25°C.

[d] Postpolymerization after cessation of the current at 20 min.

Percent conversions were calculated by CV measurements during electrolysis. Percent yields, however, were calculated from the amounts of polymers precipitated at the end of electrolysis, as given in Table 1. There were no significant changes in the amounts of polymers isolated, which indicates that the formation of cyclic dimers is negligible.

The infrared absorption spectrum of the electrochemically produced poly(*N*-vinylcarbazole) is given in Fig. 6.

When the FTIR spectrum given in Fig. 6 was compared with the spectrum given in the literature [30], they were found to be the same. The FTIR spectrum of poly(*N*-vinylcarbazole) produced by electroinitiation under various conditions indicates that it has the same structure as the polymers obtained chemically.

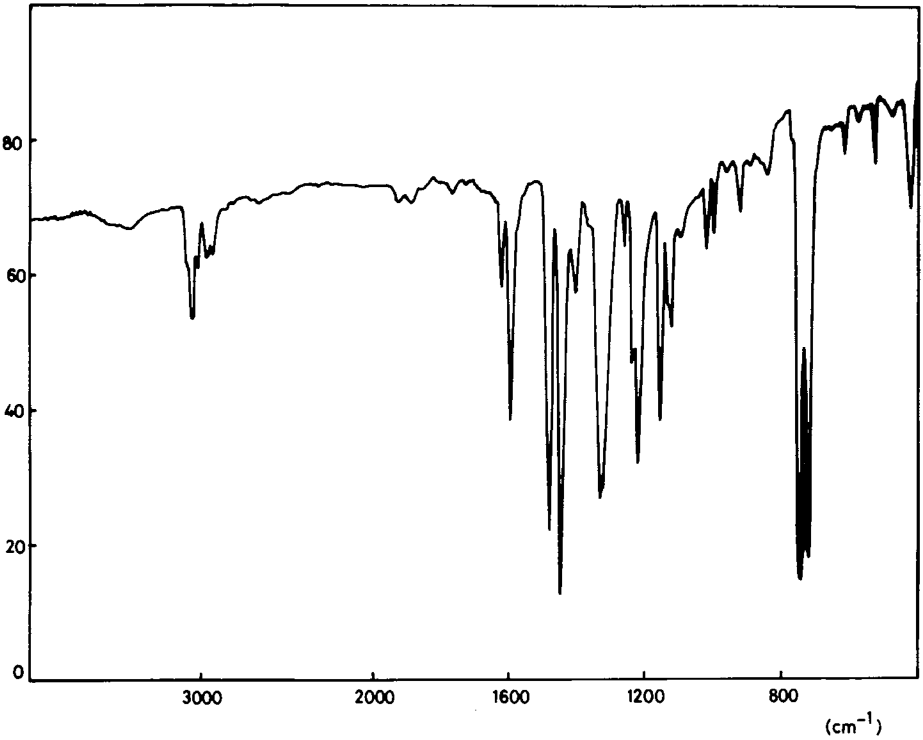

FIG. 6. FTIR absorption spectrum of poly(NVC) obtained by electroinitiation in KBr.

In conclusion, we have shown that NVC can be polymerized by electroinitiation on a microelectrode. The rate of polymerization can be controlled by electrode area, by potential, as well as by temperature. The active species produced by constant potential electrolysis are stable enough to cause postpolymerization. The molecular weights of the polymers are not significantly affected by temperature, electrode area, or potential.

The only notable effect on molecular weight was due to monomer concentration. We have also shown that the rate of electroinitiated polymerization of NVC can be followed by cyclic voltammetry, even in the early stages of polymerization, without interrupting the polymerization.

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