

Electrochemical Polymerization of *N*-Vinylcarbazole

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SYNOPSIS

The electrolysis of *N*-vinylcarbazole in the solution of quaternary ammonium salts in dichloroethane leads to polymer formation in the anolyte. The effect of monomer concentrations, current levels, and nature of supporting electrolytes on the polymerization has been investigated. The polymerization is free radical with bromide salt and cationic with perchlorate or hexachloroantimonate salt. The poly(*N*-vinylcarbazole) gets oxidized at the anode and can be cycled between the oxidized and neutral states. The oxidized polymers at the electrode may exhibit electrical conductivity.

INTRODUCTION

A great deal of attention has been given to the polymerization of *N*-vinylcarbazole (NVCZ) because its polymers display unusual electrical and photoelectrical properties.^{1,2} There are several reports on the electrochemical polymerization of NVCZ.³⁻⁹ Here we describe the electrically initiated polymerization of NVCZ and the anodic oxidation of the resulting polymers.

EXPERIMENTAL

Materials

NVCZ was analytical grade and used without further purification after proper drying. Tetrabutyl ammonium bromide was dried prior to use. Hexachloroantimonate salts were prepared and purified as described in the literature.^{10,11} Dichloroethane (DCE) was purified by fractional distillation after proper drying.

Polymerization Method

Polymerization was carried out in a simple H-shaped cell which could hold approximately 25 mL of a solution and accommodate two Pt electrodes of the area $0.7 \times 2.5 \text{ cm}^2$. The cell compartments were divided by a fine fritted glass disc 1 cm in diameter.

The rate of polymerization was followed gravimetrically. In order to determine the amount of polymers formed at a desired time, the electrolysis was terminated at that time, and the whole anolyte was poured into cold methanol to recover the polymers.

RESULTS AND DISCUSSION

When a solution of NVCZ in DCE containing $(\text{C}_4\text{H}_9)_4\text{NBr}$ was subjected to a constant current electrolysis, polymerization occurred only in the anode compartment. A green mass coated the anode and the initial colorless anolyte turned finally to pale brown. There was no polymerization if the reaction mixture was not electrolysed. The yields of polymers at different impressed constant currents for 4 h of electrolysis time and a fixed initial concentration of NVCZ are presented in Figure 1, which shows that the polymer yields are dependent on impressed currents. Figure 2 shows that the polymer yields linearly increase with increasing initial NVCZ concentration. The free-radical scavenger, 2,2-diphenyl-1-picrylhydrazyl, inhibited the polymerization, suggesting a likelihood of a free-radical mechanism. The anodic process might have involved the oxidation of bromide anion, Br^- , to generate bromide radical, Br^\cdot , which initiates a free-radical polymerization of NVCZ in the anolyte. In order to explore this view, a solution of $(\text{C}_4\text{H}_9)_4\text{NBr}$ was electrolyzed at 6 mA for 4 h in DCE without NVCZ. The resulting anolyte contained free bromine, as was confirmed by chemical analysis.¹² When 0.4 g of NVCZ was added to

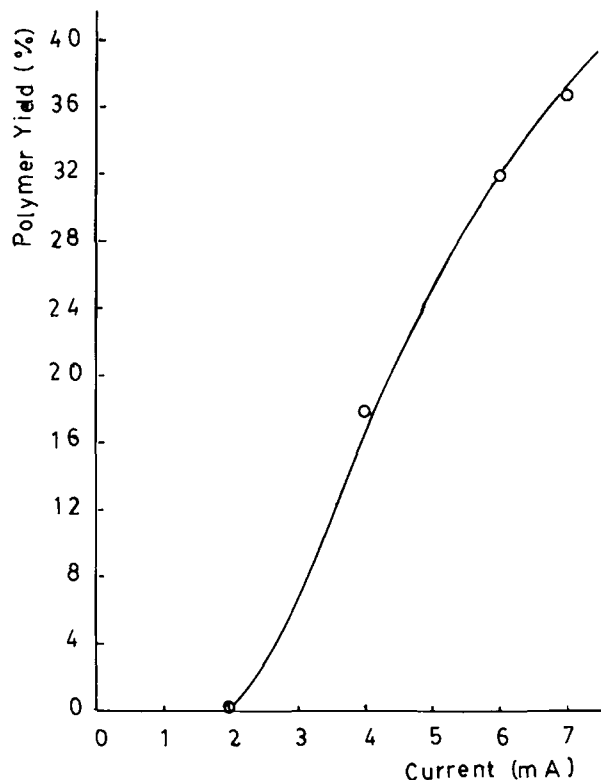


Figure 1 Effect of impressed current on the anodic polymerization of NVCZ (0.207 mol L^{-1}) in DCE solutions of $(\text{C}_4\text{H}_9)_4\text{NBr}$ ($6.2 \times 10^{-2} \text{ mol L}^{-1}$) at 40°C ; electrolysis time 4 h.

such an anolyte, the monomer polymerized to give a 30% conversion to polymers. Furthermore, the anolyte retained its ability to cause the polymerization for 24 h after the termination of electrolysis.

NVCZ was also subjected to electrolysis separately with $(\text{C}_2\text{H}_5)_4\text{NSbCl}_6$, $(\text{C}_4\text{H}_9)_4\text{NBrSbCl}_5$, and $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ in DCE. Table I shows the yields and colors developed in the anolyte with these supporting electrolytes during electrolysis. Unlike $(\text{C}_4\text{H}_9)_4\text{NBr}$, the free-radical inhibitor 2,2-diphenyl-1-picrylhydrazyl could not inhibit the polymer formation for these supporting electrolytes. Under a constant current electrolysis, two possibilities of initiation are open, direct electron exchange either between anode and the monomer or between the radical generated by the anion discharged at the anode¹³⁻¹⁵ and the monomer resulting in the formation of monomeric radical cation. The radical cations may dimerize to a dication and grow according to the schemes of cationic addition polymerization. Alternatively, it was presumed that the radical end of the radical cation remained dormant in the cationic polymerization of NVCZ.¹⁶

If perchlorate and hexachloroantimonate salts are not completely anhydrous, the polymerization of NVCZ takes place without the passage of electric current through the reaction mixture. No color formation occurs in such chemical polymerization of the monomer.

The average molecular weight of resulting poly(NVCZ) was not found to be high as indicated by the limiting viscosities, the average value being 0.101 dL g^{-1} in DCE at 30°C . The high degree of termination, plausibly due to NVCZ which is a basic compound,¹⁷ might be responsible for low molecular weights.

When the solution of poly(NVCZ) was subjected to electrolysis with $(\text{C}_4\text{H}_5)_4\text{NSbCl}_6$ or $(\text{C}_4\text{H}_9)_4\text{NBrSbCl}_5$ in DCE, the same green color which formed during the polymerization of NVCZ had developed in the anolyte. The reversal of electrode polarities decolorized the solution. Thus the polymer gets oxidized at the anode and can be cycled between the oxidized and neutral states. The oxidized polymers are green while the neutral one white. The green color formation in the anolyte is due to the oxidized polymers. The electrochemical oxidation of poly(NVCZ) and of several other carbazole polymers have been reported recently.^{8,9} The suggested mechanism of anodic oxidation of poly(NVCZ) (I) is the formation of carbazyl radical cation (II), which on subsequent dimerization at the 3,6- posi-

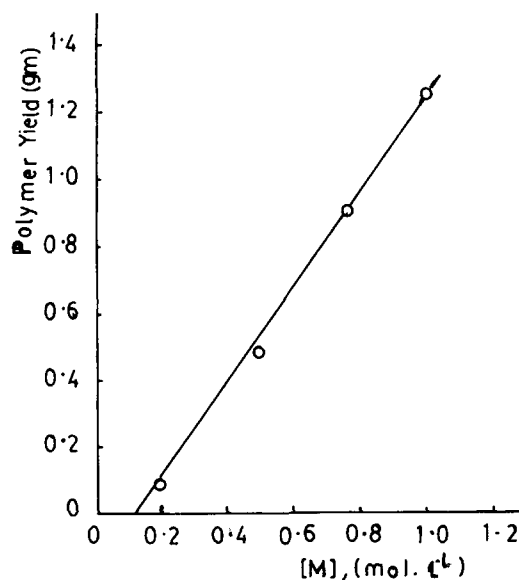
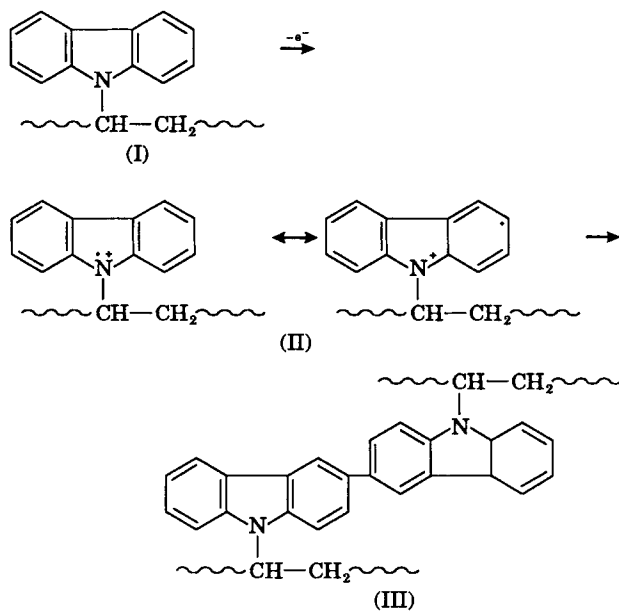


Figure 2 Dependence of polymer yields on the concentration of NVCZ in the solution of $(\text{C}_4\text{H}_9)_4\text{NBr}$ in DCE ($6.2 \times 10^{-2} \text{ mol L}^{-1}$) at 4 mA and 40°C ; electrolysis time 4 h.

Table I Anodic Polymerization of *N*-Vinylcarbazole (NVCZ) (0.203 mol L⁻¹) in the Dichloroethane (DCE) Solution of Different Supporting Salts at 5 mA for 1 h

Salt	Concn of Salt (mol L ⁻¹)	Polymer Yield (%)	Color of Anolyte
(C ₂ H ₅) ₄ NSbCl ₆	0.012	86	Green
(C ₄ H ₉) ₄ NClO ₄	0.023	79	Pink
(C ₄ H ₉) ₄ NBrSbCl ₅	0.012	47	Green

tion gives 3,3'-dicarbazyl (III), a crosslinked material with electrical conducting behavior. The conductivity of up to 10⁻⁵ Ω⁻¹ cm⁻¹ has been attributed to electron hopping between the dimer sites¹⁸:



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