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Oxidative Polymerization of *N*-substituted Carbazoles

A. Sezai Saraç,* Esma Sezer and Belkis Ustamehmetoğlu
Istanbul Technical University, Faculty of Science, Department of Chemistry, 80626 Maslak, Istanbul, Turkey

ABSTRACT

Poly(N-vinylcarbazole), poly(N-carbazole) and poly(N-ethylcarbazole) powders were chemically synthesized by the reaction of ceric ammonium nitrate (CAN) with N-vinylcarbazole carbazole and N-ethylcarbazole in acetonitrile. Products were characterized by elemental analysis, Fourier transform infrared spectroscopy, scanning electron microscopy and viscosity, X-ray fluorescence and four-probe conductivity measurement. It is found that when a suitable concentration of CAN is used in the polymerization process, the conductivity of chemically synthesized polymers can be improved further by controlling the CAN addition. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The preparation of poly(*N*-vinylcarbazole) (PVCz) by electrochemical polymerization has been known for many years [1–4]. The first stage of electropolymerization involves the oxidation of monomer to the cation radical. Then, depending on the electrochemical conditions, several pathways of polymerization are possible and, in consequence, the obtained films reveal different structures and properties [5].

* Correspondence to: A. Sezai Saraç, Istanbul Technical University, Faculty of Science and Letters, Chemistry Department, 80626 Maslak, Istanbul, Turkey.

The electrolysis of *N*-vinylcarbazole (NVCz) solution usually results in a coating on the anode surface with a green conducting polymer. Besides this, in the bulk of the solution the formation of the nonconducting colorless PVCz, in which the polymer chain is formed exclusively by bonds between vinyl groups, is also possible [6, 7]. Results presented in the study published by Papez *et al.* [6] show that PVCz polymerized electrochemically in solution is photoconductive. However, no photoconductivity of the PVCz films electropolymerized on the electrode surface was observed.

In spite of great interest in the electrochemical preparation of PVCz, the oxidative polymerization of NVCz in nonaqueous systems, using metal salts, has not been studied systematically. Although the process has been reported [8–11], there is still considerable confusion as to the exact mechanism involved.

Although PVCz prepared electrochemically and prepared by suspension polymerization using $FeCl_3$ in toluene/water solvent have the conductivity values 10^{-4}–10^{-6} S/cm [2, 3, 12], the electrical conductivity of PVCz obtained by conventional methods shows it behaves essentially as an insulator (10^{-10}–10^{-16} S/cm) [13, 14].

Only a few papers have described the electrodeposition of films from carbazole and their properties [15–17]. On the other hand, the anodic oxidation of *N*-ethyl carbazole (ECz) in acetonitrile does not produce films [15] except on Au and glassy carbon electrodes in aqueous $HClO_4$ with conductivities of between 10^{-8} and 10^{-4} S/cm [18].

As noted above the oxidative polymerization of carbazoles by using metal salts have not been investigated systematically so far. The aim of the present work was to investigate systematically the oxidative polymerization of NVCz, carbazole (Cz) and ECz comparatively by using cerium (IV), which was used very effectively for the polymerization of

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