

Short communication

Oxidative polymerization of *N*-vinylcarbazole in polymer matrix

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Abstract: A new class of soluble conductive poly(*N*-vinylcarbazole) (PVCz) compounds has been developed by oxidative matrix polymerization of *N*-vinylcarbazole (NVCz) by Ce(IV) in the presence of poly(ethylene glycol) (PEG). PEG was found to be a more suitable matrix with which to obtain a stable homogenous ternary complex solution when compared with poly(acrylic acid) (PAA) and poly(vinylpyrrolidone) (PVP). The role of PEG, NVCz and Ce(IV) concentration, order of component addition, the structure of the polymer matrix, molecular weight of polymer and the effect of solvent have been investigated. Obtaining soluble PEG–Ce(III)–PVCz ternary complexes was shown by cyclic voltammetric measurements, and the initial rate of formation NVCz cation radicals as calculated using UV–visible spectrophotometry. Advantageously with these soluble complexes, conductivities could be measured both in solution and in the solid state.

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INTRODUCTION

Due to its interesting electrical and optoelectronic properties, chemical and electrochemical polymerizations of *N*-vinylcarbazole (NVCz), have been extensively studied. There are several reports on its electrochemical polymerization.^{1–3} The electrolysis of NVCz solution usually results in a coating on the anode surface of a green conducting polymer. Besides this, in the bulk of the solution, the formation of the non-conducting colourless poly(*N*-vinylcarbazole) (PVCz), in which the polymer chain is formed exclusively by bonds between vinyl groups is also possible.^{4–6} Our previous studies on chemical oxidative polymerization of NVCz using Ce(IV) salts also indicates the same mechanism.⁷ Depending on the molar ratio of ammonium cerium(IV) nitrate (CAN) and NVCz ($n_{\text{CAN}}/n_{\text{NVCz}}$), it is possible to obtain either a white photoconductive form polymerized via vinyl groups or a brown conductive form polymerized through Cz rings. PVCz polymerized electrochemically in solution is photoconductive and soluble in common solvents.⁵ However, the conductive dark green form is not soluble like other five membered heterocyclic conductive polymers such as polypyrrole (PPy).⁷ Because of this insolubility, the structures of polymers and polymerization mechanisms have not been well defined and cannot be characterized by conventional methods. Spectroelectrochemical studies

of the effect of anions on the behaviour of PVCz could be performed only on thin films on the electrode surface.⁸

The difficulty in solubilizing the conducting polymer originates from its delocalized π -electron structure which is the very same molecular characteristic that gives rise to its novel optical and electronic properties necessary for device applications. The delocalized π -electron structure leads to large interchain π - π attractions which favour aggregation instead of polymer solvation. The delocalized electron structure leads to large electronic polarizability and a stiff polymer backbone. Knowing the origin of insolubility, a simple approach to increase solubility would be to decrease the electronic polarizability and make the polymer backbone flexible. To achieve all of these aims simultaneously by structural modifications would mean that the polymer would lose all its useful optical and electronic properties; it would be processable but no longer useful.

In recent years, water soluble polymerization systems such as methyl, cellulose, poly(vinyl alcohol), polyvinylpyrrolidone (PVP), polyacrylamide and poly(ethylene glycol), (PEG) have been examined with $\text{Fe}^{3+}/\text{Fe}^{2+}$ oxidation systems to overcome the solubility problem of polypyrrole (PPy).¹⁰ Oxidative polymerization in the presence of a polyanion has been carried out with polyaniline.¹¹ Recently the synthesis

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