

Direct Electrodeposition of Thin-Layer (Phenylene-Carbazolyene) Copolymers

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SYNOPSIS

Thin (phenylene-carbazolyene) copolymer films of controlled composition can be directly deposited onto solid cathodes such as indium tin oxide (ITO) glass or glassy carbon through a dehalogenative polycondensation of 4,4'-dibromobiphenyl and 3,6-dibromo-*N*-alkylcarbazole mixtures in the presence of an electrogenerated zero-valent nickel catalyst. The electrochemical and optical properties of the resulting thin films have been studied. The electrochemical behavior reveals two distinct electronic states that depend on the copolymer composition and structure. The first electronic state is characterized by either only one redox process, attributed to the presence of phenylene-disubstituted carbazolic units in the case of copolymers with the highest proportion of phenylene, or two successive redox processes, attributed to the occurrence of a radical cation and dication of carbazolic diades, in the case of copolymers with the lowest proportion of phenylene. The second electronic state shows in all cases a single redox system occurring at a higher potential than the first state and due to phenylene moieties in the copolymer. All the electrodeposited copolymer films were found to be reducible in the same manner as pure poly(*p*-phenylene). © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the field of conducting polymers, obtention of electroactive copolymers has been recently the subject of great interest, because of the adjustable physical and electronic properties that can be obtained through the control of both their composition and structure.¹⁻⁶ For example, pyrrole-thiophene copolymers¹⁻⁴ that display electronic transport properties¹ and electrochemical behavior² intermediate between those of each homopolymer were described and phenylene-thiophene copolymers with a continuous molar ratio of monomers have been studied.⁵ We recently reported⁶ some results on the synthesis of phenylene-*N*-alkylcarbazolyene random copolymers obtained from a dehalogenative polycondensation of mixtures of 4,4'-dibromobiphenyl and 3,6-dibromo-*N*-alkylcarbazole in the

presence of electrogenerated zero-valent nickel. These copolymers are partly soluble in polar solvents. For a given composition, their solubility increases with the length of the aliphatic substituent on the nitrogen atom. Owing to this solubility, thin film can be cast onto various substrates from a solution. Electrochemical properties of these films are strongly dependent on the copolymer composition and structure.^{6b,c} These materials have conductivities upon doping lying between those of each homopolymer.

The formation of thin conducting films is of great technological interest and electrocoating is found to be a very attractive technique.⁷ Indeed, this could be used as a batch or continuous process that could be completed in a single step. Furthermore, the coating thickness can be controlled by monitoring either the electrodeposition time or current.

The aim of this article was to demonstrate that a thin layer of phenylene-carbazolyene copolymers with controlled proportions of phenylenic and carbazolic units can be directly deposited onto a conducting support through a dehalogenative coupling

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reaction. Characterizations of these films have been carried out by optical spectroscopy and their electrochemical behavior has been investigated.

As a reminder, neutral poly(1,4-phenylene) (PPP) film can be deposited onto a conducting support such as glassy carbon (GC) or indium tin oxide (ITO) glass through the electrochemical coupling of 4,4'-dibromobiphenyl in the presence of zero-valent nickel catalyst.⁸⁻¹⁰ The mechanism of nucleation and growth of insulating transparent yellowish PPP films onto ITO glass has been recently investigated, using chronoamperometry and scanning electron microscopy.¹⁰ On the other hand, and under the same experimental conditions, i.e., using dipolar aprotic solvent such as *N,N*-dimethylacetamide (DMA), the electrodeposition of a thin layer of poly(*N*-alkylcarbazole) (PCZ) from cathodic reduction of dihaloderivatives¹¹ is not possible, owing to its solubility in such a solvent. The electrodeposition of these types of materials is only achievable while using a nonsolvent of PCZ such as acetonitrile.

EXPERIMENTAL

Reagents

Synthesis and purification of 3,6-dibromo-*N*-alkylcarbazole (DBCZ) (alkyl = ethyl or *n*-butyl) has been described previously.^{6c} 4,4'-Dibromobiphenyl (DBB, Aldrich) was used without further purification. The NiBr₂/2,2'-bipyridine complex (NiBr₂ bipy) was prepared as described.^{6c}

The supporting salts (LiClO₄, LiBF₄, NBu₄BF₄) were dried under vacuum at 120°C for 24 h. *N,N*-Dimethylacetamide (DMA) and acetonitrile were distilled under reduced pressure over calcium hydride just prior to use. Tetrahydrofuran, chloroform, ethanol, hexane, and diethyl ether (Merck) were used as received.

Electrochemical Experiments

Electrochemical studies were performed with a Solea-Tacussel apparatus (PJT 35-2 potentiostat, GSTP4 generator, IG5N coulometer) connected to an X-Y SEFRAM (TGM 101) recorder.

Film Preparation by Electrodeposition

In a one-compartment cell under argon were introduced 30 mL of freshly distilled DMA, 10 mmol of LiBF₄, 0.1 mmol of NiBr₂ bipy complex with an excess of bipy, and mixtures of DBCZ and DBB with

variable ratios (between 0.25 and 2). A three-electrode system was used, with the working cathode being either glassy carbon (GC) or ITO plate, the reference electrode a saturated calomel electrode (SCE), and the counterelectrode usually a platinum wire. The electrolysis was carried out at the reduction potential of the catalytic precursor^{6a} and stopped after the integrated charge was about 0.2–0.3 C cm⁻². The homogeneous and transparent films were rinsed with acetone and then dried at 60°C prior to characterization and study.

Electrochemical Study of Copolymer Film

Electrochemical behaviors of the copolymer films were investigated in acetonitrile with LiClO₄ or NBu₄BF₄ as the supporting salt. The working electrodes were films electrodeposited on conducting supports (GC or ITO glass), whereas reference and auxiliary electrodes were the same as above.

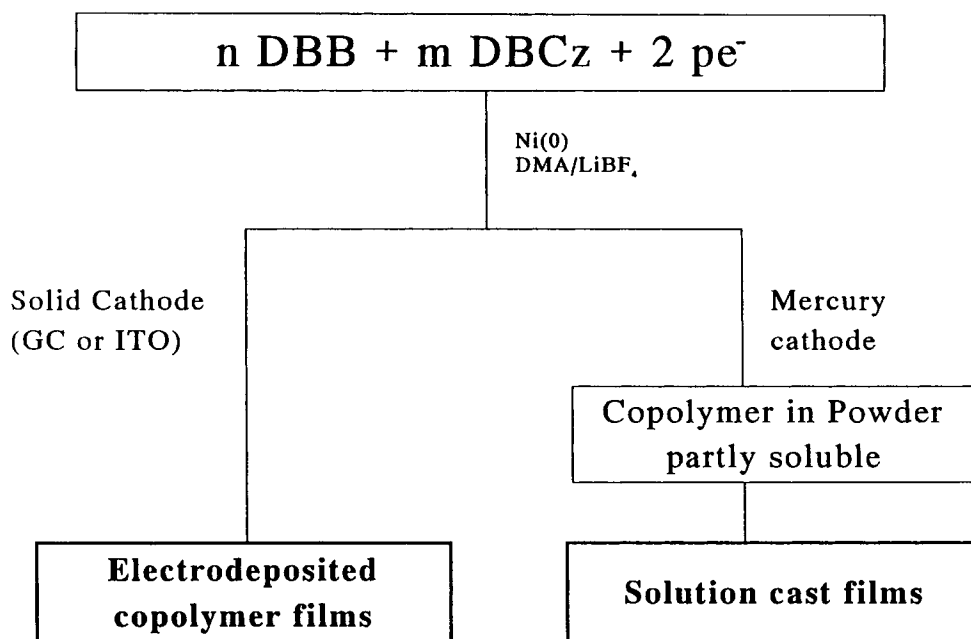
IR and UV-visible Spectroscopy

Spectra of the electrodeposited samples were recorded using, respectively, a Perkin-Elmer 580 and a Varian DMS 100 spectrometer.

RESULTS AND DISCUSSION

Copolymer Film Formation and Characterization

Depending on the nature of the cathode used, two different paths may be followed that lead to film deposition according to Scheme 1. Using a mercury pool as the cathode,⁶ it has been found that an increase in the proportion of carbazolyene units in the copolymers improves their solubility in polar solvents. These copolymers were characterized with various techniques. Infrared spectra of the copolymers⁶ show a $\delta(\text{C—H})$ out-of-plane deformation in intermediate positions between that of poly(*p*-phenylene) (PPP), around 808–810 cm⁻¹, and that of poly(*N*-alkylcarbazolyene) (PCZ), close to 795 cm⁻¹. A continuous shift of this single band is observed from 810 to 795 cm⁻¹ as the percentage of the carbazolyene unit (determined by the nitrogen content from elemental analysis) increases in the copolymer. Meanwhile, a diminution of the intensity of the band at 1000 cm⁻¹ (in-plane deformations of the *para*-substituted phenylene unit) and an increase of the one at 874 cm⁻¹ (out-of-plane deformations of 1,2,4-trisubstituted benzene of the carbazole unit) take place.



Scheme 1

The soluble fractions of the various copolymers were characterized by optical spectroscopy.^{6c} A first absorption peak, between 312 and 320 nm, has been found and is attributed to carbazolyene units, whereas a more or less pronounced shoulder, attributed to phenylene units, is observed between 340 and 350 nm. The relative intensities of these two signals depend on the copolymer composition.

The ¹³C-NMR spectrum of the phenylene-*N*-butylcarbazolyene copolymer reveals the chemical shifts of PPP¹² at 128 and 139 ppm and those of poly (*N*-butyl-3,6-carbazolyene);^{6c} furthermore, supplementary signals were found at 131–132.8 and 140.6 ppm, disclosing the presence of heterocoupling between phenylene and carbazolyene units.⁶

Direct electrodeposition of copolymer films has been carried out through the electrolysis of mixtures of monomers (DBCZ/DBB) with different ratios (between 0.25 and 2) in the presence of the Ni-Br₂bipy complex. A thin layer with a homogeneous appearance is visually detected on ITO glass. These films, slightly whitish for the highest ratios, change to yellow for the lowest ones.

The optical spectra of electrodeposited film are characterized mainly by the presence of two broad weakly defined absorptions at about 310 and 350 nm. However, with increase in the concentration of DBB in the initial mixture, low DBCZ/DBB ratios, the optical spectra of these thin films show the presence of three absorptions peaks, respectively, at 317 nm (carbazolyene units) and at 337 and 360 nm

relative to phenylene sequences of different length (Fig. 1).

Moreover, the infrared spectrum of a scratched powder of electrodeposited film onto a carbon plate (5 cm² in area) shows the characteristic adsorption bands of the phenylene unit (808 and 1000 cm⁻¹) together with that of the carbazolyene one (795 and 875 cm⁻¹). As the electrodeposition of poly (*N*-alkyl-3,6-carbazolyene) film is not achievable in a solvent such as DMA, the detection of the carbazolic signature, both by NMR and IR, indicates that a thin copolymer layer has been formed in these conditions.

To confirm these conclusions, we studied the electrochemical behavior of various electrodeposited films using acetonitrile as the solvent and LiClO₄ or NBu₄BF₄ as the supporting salt.

Electrochemical Characterization of Electrodeposited Film of Copolymers

Electrochemical study of cast copolymer films⁶ revealed three main types of redox behavior: The first type is characterized by the presence of three anodic signals at +0.85, +1.15, and +1.4/+1.5 V/SCE. The two first anodic processes have been attributed to the occurrence of a radical cation and a dication of the carbazolyene diades, whereas the third anodic peak is due to the oxidation of phenylene units. This behavior is observed mainly in copolymers rich in phenylene units.

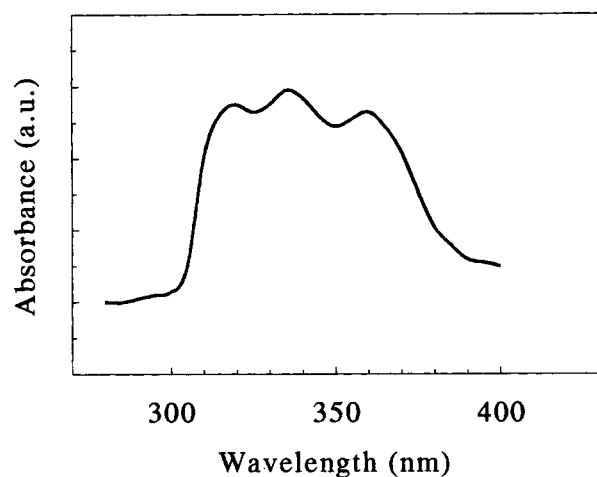


Figure 1 UV spectrum of an electrodeposited phenylene-*N*-butylcarbazolyene copolymer onto ITO glass from a monomer ratio DBUC/DBB = 0.5.

In the second type, two redox processes occur at +1.2 V and between +1.4 and +1.5 V/SCE. In this case, the first signal corresponds to the oxidation of an isolated and disubstituted carbazolyene unit and

the second oxidation process has been attributed to the oxidation of phenylene moieties. The third type of redox behavior consisted only of two anodic signals at +0.85 and +1.20 V/SCE and is related to copolymers that are rich in carbazolyene units.

In the case of electrodeposited copolymer films, the two first types of electrochemical behavior previously described were observed. These two redox behaviors are very similar to those found in cast copolymer films, whereas the third type, which consists of an electrochemical behavior close to that of poly(*N*-alkyl-3,6-carbazolyene), was not observed for copolymers obtained by direct electrodeposition.

Figure 2 shows cyclic voltammetry studies, carried out using acetonitrile/LiClO₄, of electrodeposited films onto glassy carbon from two different monomer ratios using 3,6-dibromo-*N*-ethylcarbazole (DBEC) as the carbazolic monomer. When the potential range is limited between 0 and +1.3 V/SCE (curves a and c), two electrochemical systems are observed and are due to carbazolyene units. Indeed, anodic and cathodic peak potentials (see Table I) are near those determined for PCZ film deposited by electrolysis in acetonitrile.¹¹

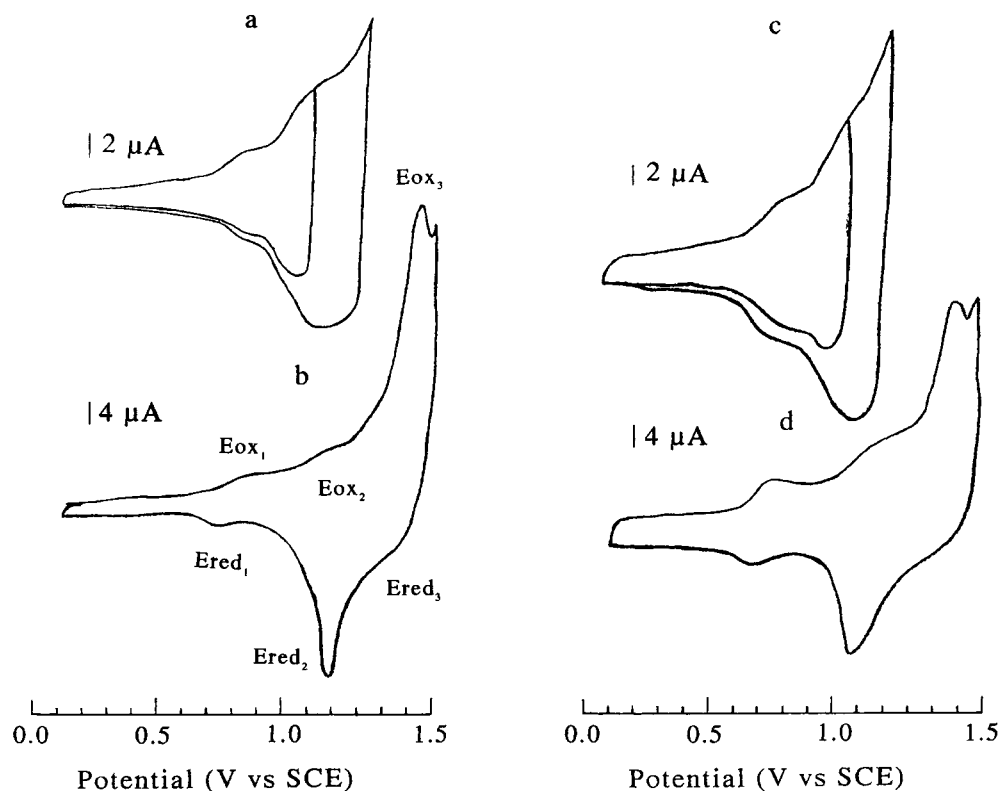


Figure 2 Cyclic voltammograms of electrodeposited phenylene-*N*-ethylcarbazolyene copolymers onto glassy carbon from two different monomer ratios: (a,b) DBEC/DBB = 0.5; (c,d) DBEC/DBB = 2 (in acetonitrile/0.3 mol l⁻¹ LiClO₄) (scan rate: 0.1 V S⁻¹).

Table I Peak Potential (V/SCE) of Electrodeposited Phenylene-*N*-ethylcarbazolyene Copolymers and Corresponding Homopolymer Film on a Glassy Carbon Electrode in Acetonitrile/LiClO₄ as the Medium (Scan Rate 0.1 V S⁻¹)

DBEC/DBB ^a	First System		Second System		Third System		Ref.
	Eox ₁	Ered ₁	Eox ₂	Ered ₂	Eox ₃	Ered ₃	
DBEC only ^b	0.88	0.73	1.2	1.1	—	—	11
2	0.85	0.75	1.2	1.1	1.47	1.40 ^d	
1	0.82	0.70	1.25	1.16	1.50	1.35 ^d	
0.5	0.85	0.74	1.18	1.09	1.50	1.35 ^d	
0.25	0.85	^c	1.2	^c	1.45	1.30	
DBB only	—	—	—	—	1.58	1.20	8, 9

^a Molar monomer ratio to obtain copolymer film by electrodeposition in DMA.

^b Electrodeposited film of poly(*N*-ethylcarbazolyene) is achievable only in acetonitrile.

^c Indeterminable value.

^d Ill-defined peak.

The nature of the substituent has only a limited impact on the redox behavior of the electrodeposited copolymer films; the different peak potentials remains unaltered if the ethyl group is replaced by butyl. Moreover, the molar monomer's ratio has only a little effect on the peak potential (Table II). However, and in the case of butyl *N*-substituted carbazole, the two redox systems are only observed for the highest monomer ratio, i.e., when the starting mixture was rich enough in the carbazolic monomer.

A second difference between cast and electrodeposited thin films consists of the smaller difference between anodic and the corresponding cathodic peak potential of each system of the electrodeposited films compared to the cast ones as described previously.^{6b,c} These observations, already made in the case of PCZ film,¹² indicate that a better electrochemical reversibility is achieved in the case of electrodeposited films than in the case of the cast copolymers.

When the potential range is extended to +1.7 V

(Fig. 2, curves b and d, and Tables I and II), a third oxidation peak is observed at a potential (Eox₃) between +1.42 and +1.6 V. As shown in Figure 2, peak current increases when the DBCZ/DBB ratio decreases. When increasing the proportion of DBB in the starting mixtures, DBCZ/DBB ratio ≤ 0.25, the two first electrochemical processes become very weak compared to the third one; in that case, the voltammograms are close to that of PPP.^{6c,9,13} Consequently, this third signal can be attributed to the oxidation of phenylene units of various lengths. On reversing the scan, three reduction processes generally appear along with the corresponding oxidation steps.

However, and upon cycling, an abnormal decrease of the cathodic peak current of the third redox system (Ered₃) and, simultaneously, an increase of the cathodic current of the second system (Ered₂) have been observed compared with the corresponding oxidation peak current (respectively, Eox₃ and Eox₂).

Table II Peak Potential (V/SCE) of Electrodeposited Phenylene-*N*-butylcarbazolyene Copolymers on a Glassy Carbon Electrode in Acetonitrile/LiClO₄ as the Medium (Scan Rate: 0.1 V S⁻¹)

DBuC/DBB ^a	First System		Second System		Third System		Ref.
	Eox ₁	Ered ₁	Eox ₂	Ered ₂	Eox ₃	Ered ₃	
DBuC only ^b	0.92	0.74	1.25	1.07	—	—	11
2	0.85	0.75	1.18	1.05	1.42	1.35	
1	—	—	1.20	1.06	1.60	1.40	
0.5	—	—	1.15	1.05	1.55	1.35	

^a Molar monomer ratio to obtain copolymer film by electrodeposition in DMA.

^b Electrodeposition of poly(*N*-butylcarbazolyene) films is achievable only in acetonitrile.

In the present state, we have no satisfactory explanations concerning this surprising behavior; nevertheless, it may be possible that an electronic transfer takes place inside the material between the most oxidized form of the copolymer, probably bipolarons of phenylene units, and carbazolyene units partly or not oxidized yet. According to this hypothesis, such a reaction could lead mainly to the formation of the bipolaronic form of carbazolic diades and could explain together the weakening and the increment of cathodic current, corresponding, respectively, to peaks occurring at E_{red_3} and E_{red_2} . As this electrochemical behavior is quite similar to that of the first type of copolymer cast film, we can assume that this kind of electrodeposited copolymer is rich in phenylene units. Furthermore, it is all the more rich in phenylene units as the peak current of the third anodic process is high compared with the intensity of the two first oxidation peaks.

In the case of electrodeposited copolymer obtained from a mixture of DBUC/DBB ratio ≤ 1

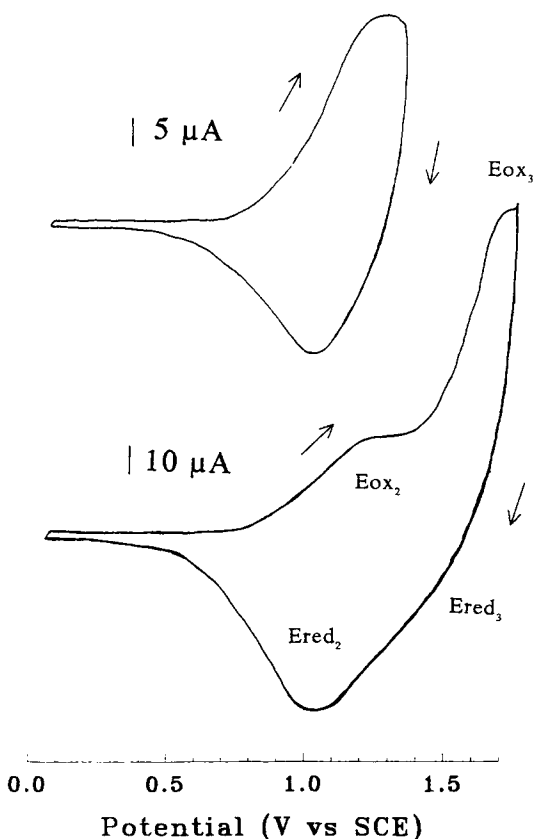


Figure 3 Cyclic voltammograms of electrodeposited phenylene-*N*-butylcarbazolyene copolymer onto glassy carbon from DBUC/DBB = 0.5 in acetonitrile/0.3 mol l⁻¹ LiClO₄ (scan rate: 0.1 V S⁻¹).

(Table II), the electrochemical study shows that the obtained deposit is appreciably different (see Fig. 3). Indeed, the voltammogram discloses only one redox process whose anodic peak occurs at +1.15 V when the studied range potential is limited between 0 and +1.3 V.

This redox process can be attributed to the oxidation of the isolated and disubstituted carbazolic unit in the radical cation as has been observed for some cast copolymer films⁶; this behavior is in good agreement with the moderately stable cation formation of several 3,6-disubstituted *N*-ethylcarbazoles by anodic oxidation as reported previously.¹⁴ When the range of study was extended to +1.7 V, a second redox process is observed at about +1.55 V. This signal can be due to the oxidation of phenylene moieties as described above.

The electrochromic behavior of all these copolymers electrodeposited on ITO glass is quite similar. Films become green around +0.9 V/SCE and turn red to red-brown when the applied potential reaches +1.4 or +1.5 V. The last color change is much more pronounced with increase of the DBB proportion in the starting mixture, indicating a high proportion of phenylene units in the material.

Formation of electrodeposited copolymer with a controlled composition is corroborated by the electrochemical characterization in the acetonitrile/NBu₄BF₄ medium (Fig. 4). This cathodic reduction, not observable in the case of poly(*N*-alkyl-3,6-carbazolyenes), takes place from -1.8 V without limitation of current in the same manner as for the electrochemical reduction of PPP.^{8b,c} On reversing the scan at -2.3 V/SCE, an oxidation peak of the reduced form occurs near -2.1 V. Although, surprisingly, no color change is detected during the scanning, these different results are additional indications that copolymerization took place and that the copolymer compositions can be adjusted by simply controlling the monomer's ratio.

CONCLUSION

We have shown that the thin-film (phenylene-carbazolyene) copolymer with a controlled proportion of each monomeric type can be obtained by a direct electroreductive process from mixtures of 1,4-dibromobiphenyl and 3,6-dibromo-*N*-alkylcarbazole. These films were characterized by optical measurement and by electrochemical behavior and compared with cast copolymer films.

Electrochemical properties in CH₃CN/LiClO₄ as the medium reveals two main behaviors already ob-

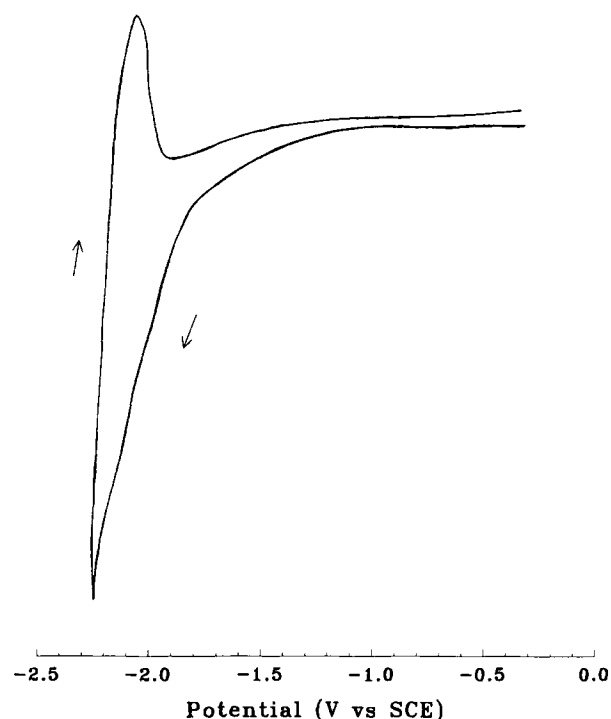


Figure 4 Electrochemical reduction of phenylene-*N*-ethylcarbazolyene copolymer obtained by electrodeposition on a glassy carbon from DBEC/DBB = 1 in acetonitrile/0.1 mol l⁻¹ NBu₄ BF₄ (scan rate: 0.1 V S⁻¹).

served in the case of cast films. These electrochemical behaviors are characterized by two distinct electronic states depending on the copolymer composition and structure. The first oxidation level is characterized by one or two redox processes attributed to the carbazolic chain structure. The second oxidation level is due to the phenylene units. Furthermore, all the electrodeposited films are reducible in CH₃CN/NBu₄BF₄, confirming that copolymers rich in phenylenic units have been obtained.

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