A Single-Layer Approach to Electrochromic Materials

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ABSTRACT: This study is focused on the development of electrochromic (EC) materials that could be incorporated into electrically-driven switchable devices such as electrochromogenic glasses. The ultimate goal of this research is to depart from the complexity of the EC device construction which is in use today. Such construction consists of three layers each of them incorporating a specific functionality: the electrochromophore, the electrolyte and the ion storage, assembled between two transparent or reflective electrodes. In most of these conventional devices the electrolyte layer is a liquid or a gel. Since solid-state EC devices are of high commercial interest, we are exploring various avenues to reduce the number of layers to one layer that is all-solid and electrochromically/electrolytically and ionically functional. The design strategy is based on the use of polymers such as poly(epichlorohydrin-*co*-ethylene

oxide), poly(vinyl butyral) and poly(ethylene-*co*-methacrylic acid) ionomer, to which EC properties were introduced by grafting reactions with specifically synthesized carbazole derivatives. A combination of analytical techniques was used to characterize the monomers and the carbazole-grafted polymers. A proof of concept was demonstrated for a single-layer, all-solid-state EC device consisting of a film of poly(ECH-*co*-EO) containing pendent carbazole groups, assembled between two transparent electrodes, Sn-doped In_2O_3 oxide-coated glasses. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 361–368, 2011

KEYWORDS: electrochromic device; functionalization of polymers; phase transfer catalysis; polyelectrolytes; redox polymers

INTRODUCTION Our research is directed toward the construction of simpler and all solid-state electrochromic (EC) devices. This is a very challenging task as most of the existing technologies are based on liquid or gel electrolytes. From a commercial standpoint, EC solid-state devices are more desirable, because they eliminate the problems associated with solvent evaporation and leakage. EC systems based on solid polymeric electrolytes have been known for some time.¹ The most successful application of the polymer electrolyte principle² relies on polymer solvents such as poly (ethylene oxide) and lithium salts. However, there are some disadvantages associated with these polymer electrolytes. The most notable are related to their glass transition (T_g) temperature, which is not low enough to allow ionic conductivity at room temperature. Alternative methods of improving the conductivity are, therefore, desirable. Finding combinations of EC materials with polymer electrolytes exhibiting higher conductivity at room temperature could have a significant impact on the applications of EC materials.³⁻⁶

This article describes how polymer EC compositions obtained by the modification of different types of polymers show potential to be utilized in solid-state EC devices. The EC compositions consist of polymer matrices selected from (a) low $T_{\rm g}$ elastomers, (b) hydrophilic polymers that can tolerate a high level of plasticizers, and (c) ionomers. Exam-

ples include poly(epichlorohydrin-co-ethylene oxide) [poly (ECH-co-EO)], poly(vinyl butyral) (PVB), and Na neutralized poly(ethylene-co-methacrylic acid)7 [poly(E-co-MA)] or Surlyn[®], respectively. All three types of polymers are chemically modified to incorporate the EC moieties via alkyl or alkyl oxide linkers. In the case of poly(ECH-co-EO), the chlorine side groups are used as grafting sites for derivatives of carbazole. The carbazole-modified poly(ECH-co-EO) retains elastomer functionality capable of dissolving inorganic salts and permitting their transport in a dissociated state. In the case of PVB and poly(E-co-MA), the -OH and -COONa groups, respectively, serve as grafting sites for carbazole derivatives. In both cases, the alkyl spacers act as internal plasticizers, which compensate for the conformational stiffness of the polymer backbone. In addition, their T_g can be further controlled by the addition of plasticizers. The attached pendant electroactive species exhibit new optical absorption bands (e.g., show a new color) in conjunction with an electron transfer or redox reaction in which they either gain or lose electrons. The new absorption can arise from photoexcitation of an electron from a lower energy level (or ground state) to a higher one, either in the same molecule, which is an intramolecular excitation, or within a neighboring moiety, which involves an optical charge transfer. The grafting design offers the possibility of achieving

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control of EC properties by placing appropriate redox-active chromophores in selective positions along the polymer backbone. This approach is quite versatile, allowing the attachment of various EC groups to different polymer backbones. Alternatively, different electroactive moieties can be used to substitute different positions of the aromatic and heteroaromatic electrochromophores to vary the conduction properties and/or achieve a controlled response with voltage fluctuations. The ends of the electrochromophore molecules can be individually functionalized with groups such as -SH, pyridyl, -CN, and -SCN to promote the absorption and self-assembly (SA) on metal surfaces, including Au, Cu, Pd, Pt, Ni, and Al. Other functional groups such as -COOH and $-P(O)(OH)_2$ can also be introduced with the specific aim of providing binding or SA to Sn-doped In₂O₃ oxide (ITO) surfaces. Another possibility is to attach two or more types of chromogenic groups, with similar or different substituents (e.g., one electron-donor and the other electron-acceptor to the metal). Self-doped chromophores can be also obtained by incorporating ionic groups (e.g., Na⁺, K⁺, or Li⁺ as cationic groups, and SO_3^- or ClO_4^- as anions) on the electrochromophore. This report will be limited to the synthesis of electrochromophores and their reactions with poly(ECHO-co-EO), PVB, and poly(E-co-MA).

EXPERIMENTAL

Materials

All reagents were obtained from Sigma–Aldrich unless otherwise indicated. Poly(E-*co*-MA) sodium salt ionomer was obtained as Surlyn[®] from E. I. du Pont de Nemours (DuPont), Wilmington, DE. PVB was also obtained from DuPont. Sndoped-ITO was obtained from Southwall Technologies, Palo Alto, CA.

Methods

Infrared Spectroscopy

Infrared spectroscopy (IR) analyses were carried out with a Nicolet instrument, model Magna-IR 760 E.S.P.

¹H NMR

The ¹H NMR characterization of the monomers was obtained at 400 or 500 MHz using chloroform- d_1 as solvent and tetramethylsilane as internal standard.

Cyclic Voltammetry

Cyclic voltammetry (CV) experiments of the chromogenic compounds and devices were obtained with a voltammetric analyzer, CV-50W from Bioanalytical Systems.

Synthesis of Monomers

All reactions were carried out under an inert atmosphere. All reagents were used without further purification unless otherwise indicated. Thin-layer chromatography (TLC) analysis was performed using EM Science silica gel 60 (F254) plates (0.25 mm). Chromatographic purifications were performed by flash chromatography on EM Science silica gel (230–400 mesh).

Preparation of 2-(*N***-Carbazolyl)propionitrile.** 2-(*N*-Carbazolyl)propionitrile was synthesized via cyanoethylation of

carbazole with acrylonitrile in the presence of benzyltrimethylammonium hydroxide (Triton[®] B) as catalyst using a procedure adapted from the literature.8 Carbazole (1.7 g, 0.0055 mol) and acrylonitrile (20 g, 0.369 mol) were introduced into a 100-mL round-bottomed glass flask equipped with magnetic stirrer. The flask was placed in an ice-bath and allowed to cool for 15 min. Then, Triton[®] B (40% in MeOH) was added dropwise (four drops) via a 50- μ L syringe for a total of 40 μ L. The paste changed color from white to yellow. The reaction mixture was allowed to warm-up slowly, but there was no sign of an exothermic reaction. After 2 h, heat was supplied via a heating mantle. Once the temperature reached 65 °C, the paste became an orange solution. The flask was heated for 1 h at 70 °C. The product precipitated in the flask after it had cooled. The precipitate was then filtered and recrystallized from acetonitrile.

Preparation of the Potassium Salt of 2-(*N***-Carbazolyl)-propionitrile.** The potassium salt of 2-(*N*-carbazolyl)propionitrile was obtained by reacting 2-(*N*-carbazolyl)propionitrile with potassium hydroxide in ethanol at reflux. KOH (1.7 g) was dissolved in water (10 g), and then added to a mixture of EtOH (15.8 g) and *N*-propionitrile carbazole (0.293 g, 0.00132 mol) in a 100-mL round-bottomed glass flask equipped with magnetic stirrer. After the addition of the KOH, a condenser was attached, and the reaction mixture was heated to reflux for 3 h. The flask was then attached to a rotary evaporator, and the EtOH and water were removed until a precipitate formed. The precipitate was filtered and recrystallized from EtOH. The recrystallized material was dried overnight at room temperature under nitrogen.

Preparation of Bromohexyl Carbazole. Tetrabutylammonium bromide (TBAB) (2.622 g, 0.008 mol) and NaOH (50%, 3 mL) were placed in a 50-mL round-bottomed flask. 1,6-Dibromohexane (4.392 g, 0.018 mol), benzene (3 mL), and carbazole (1 g, 0.00598 mol) were mixed, forming a suspension. This suspension was then poured into the reaction flask while stirring. The flask was then stoppered and allowed to stir at room temperature. The reaction was allowed to continue at room temperature for 1.5 h and then overnight (16 h). The reaction product was extracted three times with 25-mL methylene chloride followed by a final washing with water (pH = 7). A ¹H NMR spectrum taken of the resulting compound indicated that further purification was needed to remove the unreacted dibromohexane. To purify the product, a silica column was loaded with the crude product. Then, the column was flushed with 500 mL of hexane to remove the unreacted dibromohexane compound. Subsequently, the eluent was changed to a 50/50 hexane/methylene chloride mixture to collect the final product. An oily product was isolated and diluted with EtOH. The precipitate that formed on cooling was filtered off and dried under vacuum. The ¹H NMR spectrum of this compound is consistent with the expected product. Bromobutyl carbazole was obtained in a similar manner by the reaction of carbazole with dibromobutane.

Synthesis of 2-(2-Carbazol-9-yl-ethoxy)ethanol. The title compound was produced in two steps. In the first step, 2[2-

(chloroethoxy)ethoxyl]tetrahydropyran was prepared by the reaction of 2-(2-chloropethoxy)ethanol and 3,4-dihydro-2Hpyran in the presence of concentrated hydrochloric acid. In a dry box, 2-(2-chloroethoxy)ethanol (50.0 g, 0.401 mol) and 135-mL chloroform were added to a 500-mL three-necked flask equipped with a stirring bar, addition funnel and septum. 3,4-Dihydo-2H-pyran (39.7 g, 0.472 mol) in 35-mL chloroform was added dropwise over 30 min using an addition funnel. At the end of the addition, the flask was warm. The addition funnel was removed from the flask and replaced with a stopper, and the flask was transferred to the hood and placed under an atmosphere of nitrogen. Twelve drops of concentrated HCl were added dropwise via a syringe. The septum was then replaced with a water condenser. The reaction was heated at 40° for 1 h, and then allowed to cool to room temperature. The flask was opened to the air, K₂CO₃ (9 g) was added to the reaction mixture, and the mixture was stirred for 2 min before filtering. The solvent was removed via rotary evaporation, and the product was dried under vacuum for 8 h at room temperature to give 84 g (0.406 mol) of 2[2-(2-chloroethoxy)ethoxyl]tetrahydropyran. In the second step, 2-(2-carbazol-9-yl-ethoxy)-ethanol was prepared in the following manner. Carbazole (20 g, 0.12 mol), 2[2-(chloroethoxy)ethoxyl]tetrahydropyran (38 g, 0.12 mol), benzyltriethylammonium chloride (TEBA) (4.2 g, 0.025 mol), NaI (1.0 g, 0.0055 mol), 100 mL of 50% NaOH solution, and 100-mL benzene were added to a flask equipped with a stir bar, condenser, and a nitrogen inlet. The mixture was refluxed under nitrogen for 6 h. The reaction mixture was diluted with 100 mL of benzene and the organic phase was separated, washed with water, dried over MgSO₄ and filtered through acidic Al₂O₃. The solvent was removed via rotary evaporation. The product was dissolved in 400-mL MeOH. Concentrated HBr (2 mL) was added to the flask, and the reaction was stirred overnight at room temperature. The reaction was neutralized with 10% aqueous NaOH. The MeOH was removed by rotary evaporation to give a dark orange oil. The final product was further purified by recrystallization twice from methanol.

Preparation of the Carboxylic Acid of 2-(2-Carbazol-9-ylethoxy)ethanol. The 2-(2-carbazol-9-yl-ethoxy)ethanol was transformed into its carboxylic acid in two steps. In the first step, 2-(2-carbazol-9-yl-ethoxy)ethanol (0.584 g, 0.00227 mol) and 12.5-mL THF were introduced into a 100-mL round-bottomed glass flask equipped with stirring in a dry box. Separately, sodium hydride (0.0546 g, 0.00227 mol) was mixed with 12.5-mL THF. The slurry obtained was added very slowly to the flask. After complete addition, the reaction mixture was allowed to stir under nitrogen at room temperature overnight (16 h). Then, to this mixture, methyl chloroacetate (0.326 g in 25 mL THF) was added dropwise under nitrogen at room temperature. This mixture was allowed to stir at room temperature for 4 h. Then, the flask was taken out from the dry box and 30 mL of distilled water were added, followed by the addition of 75 mL of brine solution. The resulting solution was transferred into a separatory funnel. The THF was then separated. Two additional extractions were performed using 100-mL THF. The THF extracts were subjected to column chromatography to give a purified carboxylic acid derivative.

Reaction of Poly(E-co-MA) with Bromoalkyl Carbazole

Bromoalkyl carbazole prepared as shown before was reacted with poly(E-*co*-MA) sodium salt ionomer according to the following procedure. Poly(E-*co*-MA) (0.5 g), DMAc (1.4 g), and 1,2-dichlorobenzene (8.1 g) were added to a 25-mL round-bottomed glass flask that was attached to a condenser. This mixture was heated at 110° for 1 h until poly(E-*co*-MA) was completely dissolved. TBAB (0.0281 g) and bromobutane carbazole (0.0263 g) were added with stirring. The reaction was heated for 4 h and allowed to stir at room temperature under N₂ overnight. Approximately 0.5 mL of the reaction mixture was added to 20 mL of a 1:9 methylene chloride:hexane solution. The precipitated polymer was filtered, washed with CH_2Cl_2 and hexane, and dried at room temperature under vacuum.

The Reaction of PVB with Carbazole Propionic Acid

The reaction of PVB with carbazole propionic acid (prepared in multiple steps as previously indicated) was performed in the following manner. PVB (0.185 g) was placed in a 100-mL round-bottomed flask with a stirring bar. THF (10 mL) was added, and the PVB went into solution after 15 min. 9-Propionic acid carbazole (0.239 g, prepared as previously described), 4-(dimethylamino)-pyridine (0.0092 g), and 1,3dicyclohexylcarbodimide (0.206 g) were added, in that order. The solution was homogeneous and colorless. An additional 15 mL of THF were added after 20 min. The reaction was stirred at room temperature under N₂ purge for 2 days. The reaction mixture was then poured in 150-mL distilled water. The resulting precipitated compound was washed twice with 100-mL distilled water, separated by filtration, and dried under vacuum at 85° overnight.

Reaction of PVB with Carboxylic Acid of 2-(2-Carbazol-9-yl-ethoxy)ethanol

PVB (1 g) was placed in a 100-mL round-bottomed flask with a stir bar. DMSO (10 mL) was added, and PVB was solubilized with stirring. 1,3-Dicyclohexylcarbodiimide (0.206 g) was dissolved in 1.5-mL DMSO. 4-(Dimethylamino)-pyridine (0.0092 g) was also dissolved in 1.5 mL of DMSO. Once these solutions were completely homogeneous, they were added to the solution of PVB in DMSO under stirring and nitrogen. Then, the carboxylic acid of 2-(2-carbazol-9-yl-ethoxy)-ethanol (0.62 g, 0.00198 mol) prepared as shown in the previous section, was added to this reaction mixture. The reaction was stirred and kept under a N2 blanket for 2 days. Then, the reaction mixture was poured into 150 mL of distilled water. The water was decanted off, and the polymer was washed two more times with 100 mL of water. The water was decanted off, and the polymer was dried in the vacuum oven at 85 °C overnight.

Reaction of Poly(EPI-co-EO) with Potassium Salt of 2-(N-Carbazolyl)propionitrile

A solution of poly(ECH-*co*-EO) was made from 0.46 g (0.005 mol) of polymer in 30 mL of anhydrous THF. Complete



SCHEME 1 Synthesis of 2-(*N*-carbazolyl)propionitrile and —COOK derivative (a) and bromoalkyl carbazole (b).

dissolution was achieved by stirring it overnight at room temperature. This solution was heated with the potassium carboxylic salt (0.293 g, 0.001 mol) of 2-(*N*-carbazolyl)propionitrile prepared as previously shown (in a ratio CH₂Cl/KOOC = 1:1) in the presence of a stoichiometric amount (0.322 g, 0.001 mol) of tetrabutylammonium bromide. The reaction mixture was heated at 60 °C for 96 h. The resulting polymer was precipitated in water, filtered, and dried in a vacuum oven. A 22-mg sample was dissolved in ~0.7 mL of deuterated THF. The sample was heated to 60 °C until dissolved, and was analyzed by ¹H NMR.

Preparation of an EC Device

The poly(E-*co*-EO) modified with carbazole pendent groups and the salt, lithium perchlorate (LiClO₄), were mixed in anhydrous THF. Separately, two ITO-coated glasses were rinsed with isopropanol and dried under nitrogen. Then, using the THF solution made from the components previously mentioned, an EC film was coated on one piece of clean ITO. The resulting EC film on ITO was sandwiched using another piece of clean ITO. Wire leads were connected to each side of the two ITO slides. An appropriate voltage (depending on the electrochromophore) was applied, and the change in color was observed. Then, the potential applied was reversed and the return to the initial color was detected.

RESULTS AND DISCUSSION

Different types of new electrochromophores have been reported for the synthesis of functionalized polymers.⁸ Organic–inorganic hybrids consisting of polyether phases, which act as a solid solvent for lithium ions are also known.^{9–12} Examples of electrochromophores that can be used for the assembly of solid-state, single-layer devices have not been described in the literature. To be functional, such a layer needs to combine EC, electrolytic, and ionic properties. The main goal of this study was to explore a combination of technical approaches, including grafting and phase-transfer catalysis, for the design and synthesis of novel electrochromophores. Their use in the assembly of a solid-state, single-layer EC device was demonstrated in the case of poly(ECH-co-EO) grafted with carbazole.

Synthesis of Carbazole Derivatives

2-(*N*-Carbazolyl)propionitrile was synthesized via the cyanoethylation of carbazole with acrylonitrile. It is known that the ease with which acrylonitrile reacts with amines is



SCHEME 2 Synthesis of 2-(2-carbazol-9-yl-ethoxy)-ethanol.

dependent on the type of amine.¹³ Aromatic amines such as carbazole do not react without a catalyst. We adopted a procedure from the literature¹⁴ using benzyltrimethylammonium hydroxide (Triton[®] B) as a catalyst, in the presence of which the reaction proceeds vigorously. The potassium salt was obtained with KOH at reflux in ethanol. These reactions are outlined in Scheme 1(a). The *N*-alkylation reaction of carbazole with dibromides is shown in Scheme 1(b). In this case, the bromoalkyl carbazoles were prepared under mild conditions using phase-transfer catalysis. The reactions were carried out in benzene in the presence of TBAB and aqueous 50% sodium hydroxide (NaOH).

2-(2-Carbazol-9-yl-ethoxy)-ethanol was produced according to a literature procedure¹⁵ via protection, deprotection chemistries in two steps, as shown in Scheme 2. Accordingly, 2[2-(chloroethoxy)ethoxyl]tetrahydropyran was synthesized first by the reaction of 2-(2-chloroethoxy)ethanol with 3,4dihydro-2*H*-pyran. In the second step, this compound was reacted with carbazole in benzene and aqueous NaOH using



FIGURE 1 CV of ferrocene in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile using Ag wire as a reference electrode.



FIGURE 2 CV of 2-(2-carbazol-9-yl-ethoxy)-ethanol.

TEBA phase-transfer catalyst to obtain 2-(2-carbazol-9-yl-ethoxy)-ethanol.

CV experiments of 2-(2-carbazol-9-yl-ethoxy)-ethanol were carried out using ferrocene as a reference (Fig. 1). The voltammogram of 2-(2-carbazol-9-yl-ethoxy)-ethanol displays oxidation and reduction peaks (Fig. 2) appearing near two positive voltages, 98 and 140 mV, respectively. The peaks are not symmetrical, probably resulting from the kinetic limitations in the redox reaction.

As it is not possible to react 2-(2-carbazol-9-yl-ethoxy)-ethanol directly with PVB, it was transformed into its carboxylic derivative in two steps. In the first step, it was reacted with sodium hydride and, in the second step, the carboxylic acid derivative was obtained from the ethoxy compound and methyl chloroacetate as is indicated in Scheme 3.

Polymer Modification Reactions with Carbazole Derivatives

The reaction of PVB with the carboxylic acid of 2-(2-carbazol-9-yl-ethoxy)-ethanol was performed according to Scheme 4.

The degree of modification of PVB with the carboxylic acid of 2-(2-carbazol-9-yl-ethoxy)-ethanol was estimated using IR spectroscopy. The OH level was calculated using the following formula that takes into account the IR region from 2150 to 1600 nm.





SCHEME 3 Synthesis of the carboxylic acid of 2-(2-carbazol-9-yl-ethoxy)-ethanol.



where: A = 2070 nm/1705 nm (OH/methylene), B = 1925 nm/1705 nm (water/methylene).

The results indicating the OH% of the PVB starting material and of two samples of PVB after their modification with a low and a high level of carboxylic acid of 2-(2-carbazol-9-ylethoxy)-ethanol can be seen in Table 1.

Reaction of Surlyn[®] with Bromo Alkyl Carbazole

Bromo-alkyl carbazole, prepared as shown in the Experimental section, was reacted with poly(E-*co*-MA) sodium salt ionomer according to Scheme 5.

Redox Properties of Carbazole Modified Surlyn[®]

A film of carbazole-modified Surlyn[®], prepared as is indicated in the Experimental section, was made on Pt foil in a dry box by dissolving the dried polymer in a mixture of 81% 1,2-dichlorobenzene and 14% DMAc at 110 °C. After solvent evaporation, the film was tested for redox properties in an electrochemical cell. The working electrode was the Pt with the film on top. The counter electrode was also Pt. The reference electrode was silver wire. The test solution was acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The CV of Surlyn[®] is shown in Figure 3 and, as expected, indicates no redox activity. The CV of the bromopropyl carbazole is shown in Figure 4. In contrast, Surlyn[®] modified with butyl carbazole (Fig. 5) indicates the presence of two redox peaks (175 and 4 mV), in good agreement with the redox activity exhibited by the bromobutyl carbazole compound (Fig. 4).

TABLE 1 Estimated OH% of the PVB Starting Material and of Two Samples of PVB after Modification with a Low and a High Level of Carboxylic Acid of 2-(2-Carbazol-9-yl-ethoxy)-ethanol

No.	Samples	OH (%)
1	PVB	18.82
2	PVB grafted with a low level of the carboxylic acid of 2-(2-carbazol-9-yl-ethoxy)- ethanol	16.50
3	PVB grafted with a high level of the carboxylic acid of 2-(2-carbazol-9-yl-ethoxy)- ethanol	No measurable OH peak (2070 nm)



SCHEME 5 Reaction of bromoalkyl carbazole with poly(E-*co*-MA) sodium salt ionomer.

Poly(ECH-co-EO) with Pendant Carbazole Groups

Poly(ECH-*co*-EO) contains \sim 66% epichlorohydrin. The intent was to displace the chlorine from the epichlorohydrin by reaction with the potassium salt of 2-(*N*-carbazolyl) propionitrile.

There are major drawbacks regarding the nucleophilic displacement of chlorine from poly(ECH-*co*-EO). They include dehydrochlorination side reactions and degradation resulting from the formation of the vinylether units.¹⁴ For these considerations, to achieve the chemical modification of poly (ECH-*co*-EO), we chose to use phase-transfer catalysis. The synthetic scheme for this preparation is shown in Scheme 6.

The ¹H NMR spectrum of the carbazole-modified resulting polymer was consistent with the proposed structure and shows 57% conversion. This spectrum and the assignments are shown in Figure 6.

¹H NMR 500 MHz, d8-THF: 8.053 (br, 2H), 7.516 (br, 2H), 7.404 (br, 2H), 7.157 (br, 2H), 4.672 (br, 2H), 4.1 (d, 3.5H), 3.687 (br), 2.858 (br, 2H).

The UV-vis spectra of the potassium salt of the carbazole derivative and of poly(ECH-*co*-EO) modified with this derivative can be seen in Figure 7. It can be observed that the modified polymer exhibits the signature of the carbazole derivative.

Characterization of EC Properties

An important aspect of the use of an EC material is how to incorporate it into an EC device. The conventional devices





FIGURE 4 CV of bromopropylcarbazole.



FIGURE 5 CV of Surlyn[®] modified with bromopropylcarbazole.

are electrochemical cells where the EC electrode (transparent ITO modified with electrochromophore) is separated from the counter electrode by an electrolyte. The assembly of solid-state devices offers several advantages in applications requiring large surface area and flexibility and also eliminates problems related to the lifetime of the device such as solvent evaporation and leakage. Although the solid state is commercially highly desirable, it is in a very early stage of development with very few known examples. The example we present is based on the fabrication of solid devices using two optically complementary conductive polymer



SCHEME 6 Reaction of poly(ECH-*co*-EO) with potassium salt of 2-(*N*-carbazolyl)propionitrile.







FIGURE 7 UV-vis spectra of the potassium salt of the carbazole derivative (1) and of poly(ECH-*co*-EO) modified with this derivative (2).

blends deposited on ITO-PET and a polymeric electrolyte.³ In our case, the ultimate goal is to simplify the EC device construction, to reduce the number of layers, and to eliminate



SCHEME 7 Simple schematic of a single-layer EC device.

the use of liquid or gel electrolytes. For proof of concept, we prepared a single-layer solid-state device, the schematic of which is shown in Scheme 7.

First, a mixture was prepared from the 2-(*N*-carbazolyl)propionitrile-modified poly(EPI-*co*-EO) and LiClO₄ in THF. Then, an EC film was coated from this mixture and sandwiched between two ITO-coated glasses, as described in the Experimental section. An appropriate voltage (1 V) was applied for 20 s, and the change in color was observed. Then, the applied potential was reversed, and the return to the initial color was detected.

The EC mechanism associated with the presence of the carbazole moiety is supposed to involve an oxidation reaction to form a delocalized radical cation in one of the positions shown in Scheme 8.



SCHEME 8 EC mechanism associated with the presence of carbazole.



FIGURE 8 Initial color of carbazole-electrolyte-elastomer film (0.3175 mm) sandwiched between two ITO-coated glasses.

The EC response of the EC device made of carbazole-modified poly(EPI-*co*-EO) can be depicted by examining Figures 8 and 9. In Figure 8, the EC layer appears transparent and uncolored, and the text placed under the device can be clearly distinguished. By applying a low voltage (1 V), the color changes to green and the transparency is reduced.

CONCLUSIONS

Several EC derivatives consisting of carbazole equipped with alkyl or alkyl oxide linkers have been synthesized. 2-(N-Carbazolyl)propionitrile was synthesized via a cyanoethylation reaction of carbazole with acrylonitrile in the presence of benzyltrimethylammonium hydroxide as catalyst. Bromoalkyl carbazoles were obtained from carbazole and dibromoalkanes under phase-transfer-catalyzed conditions. 2-(2-Carbazole-9-yl-ethoxy)-ethanol was synthesized via protection, deprotection chemistry using TEBA phase-transfer catalyst. This compound was, then, transformed into its carboxylic acid with methyl chloroacetate in THF. Functionalization of poly(ECH-co-EO) copolymer with pendant carbazole groups was performed using the potassium salt of 2-(N-carbazolyl) propionitrile under phase-transfer catalysis conditions to avoid the dehydrochlorination side reactions and degradation resulting from formation of the vinyl ether units. Surlyn[®] was modified with bromobutyl carbazole in the presence of TBAB, using a solvent mixture consisting of DMAc and 1,2dichlorobenzene. PVB was EC functionalized with 9-propionic acid carbazole in the presence of DCC and DMAP in THF as a solvent. Various degrees of functionalization were obtained, as determined by IR spectroscopy. The EC properties of these devices were investigated using bulk electrolysis with coulometry. The redox properties of EC derivatives, and Surlyn[®] were also identified by cyclic voltammetry experiments. A proof of concept was demonstrated by constructing a simple all-solid EC device consisting of a single layer of carbazole-modified p(ECH-co-EO) elastomer placed between ITO electrodes that changed color when it was subjected to a change in voltage.



FIGURE 9 Change in color of carbazole-electrolyte-elastomer film after applying 1 V for 20 s.

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