

Electrochemical synthesis and characterization of poly(9-benzylfluorene)

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Abstract In this study, we report the electrochemical polymerization of 9-benzylfluorene (9-BF) in acetonitrile solution. The characterization of the resulting poly(9-BF) film obtained on the working electrode has been performed by using attenuated total reflectance infrared spectroscopy. Besides electrochemical properties, the optical and photoluminescent properties of film were also investigated in detail by means of UV–Vis spectroscopy and fluorescence spectroscopy. Fluorescent spectral studies indicate that polymer film in solid state emits blue-green light at around 470/520 nm under irradiation of UV light. In addition, scanning tunneling microscopy was used to investigate the morphology of poly(9-BF) film. The morphological results also reveal that the surface of single crystalline gold electrode is completely covered with the polymer film.

Keywords 9-Benzylfluorene · Electrochemical polymerization · Cyclic voltammetry · Spectroscopic techniques

Introduction

Since, the first discovery of polymer-based light-emitting diodes (PLEDs) in the 1990s, many studies have been focused on the development of efficient, stable, and pure blue-light-emitting conjugated polymers and the fabrication of devices based on these materials [1]. In this regard, interesting results have been obtained with wide-band-gap semiconducting polymers such as poly(*p*-phenylene) (PPP) [2, 3] and poly(*p*-phenylenevinylene) (PPV) [4, 5]. Recently, on the other hand, polyfluorenes (PFs) in organic polymers have emerged as promising candidates for the desired color emission due to their high fluorescence quantum yields and

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good thermal stability [6–9]. However, further studies have shown that PFs have some drawbacks upon PLED applications, such as poor hole-injection balance and undesirable greenish emission [10–13]. In addition, it has been represented that these problems mainly stem from the keto effect and interchain interactions leads to formation of excimers or aggregates in the solid state [6, 7, 14, 15]. There are numerous ways proposed to overcome these problems [14, 16–18]. Among them, modification of chemical structure by substitution of the fluorene unit at the remote C9 position using bulky substituents or long alkyl chains is probably the most preferred one [7, 19–22]. Furthermore, this strategy provides the opportunity for the synthesis of many PF derivatives with different degrees of stability, conductivity, and solubility [23, 24].

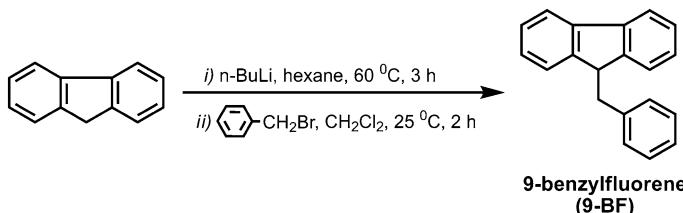
Most fluorene-based polymers are mainly synthesized by a simple chemical polymerization of the monomers using Suzuki, Yamamoto, and Stille coupling reactions [12, 13, 25]. On the other hand, in comparison with chemical approaches, electrochemical polymerization has been proved to be one of the most useful approaches for the synthesis of electronically and optically active polymers [26–29]. This method can form a thin film on the working electrode in one step. In addition, the thickness of the polymer film deposited on the electrode can be easily controlled by the integrated charge passing through the electrochemical cell.

In this study, we have investigated the electrochemical synthesis and characterization of a new polymer, poly(9-benzylfluorene) (9-BF) in acetonitrile solutions. Our main motivation for the synthesis and characterization of this novel homo polymer containing bulky aryl group at the C9 position of the fluorene units is based on the fact that such a benzyl structure directly attached to the C9 carbon may offer the ability to reduce the degree of interchain interactions between polymer chains and, thus, suppress the formation of excimers in the solid state [30, 31]. Furthermore, a methylene unit in between the benzene and the fluorene rings can effectively block the conjugation length among the aromatic side group and polymer backbone. This proper choice of the functionality within the polymer will also allow that the electronic properties of the PF main chain remain relatively unperturbed [32].

Experimental section

Synthesis of 9-BF

9-BF was synthesized following a previously reported procedure (Scheme 1) [33]. The residue was purified by column chromatography on silica-gel eluting with $\text{CH}_2\text{Cl}_2/n$ -hexanes (10%) to afford 9-BF (0.59 mg, 57%) as a light yellow crystal (mp: 130–133 °C, Lit. [34] 131–133 °C). ^1H NMR (400 MHz, CDCl_3) δ 3.14 (d, 2H), 4.26 (t, 1H), 7.18–7.77 (m, 13H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.5, 49.1, 120.2, 125.2, 126.8, 127.1, 127.5, 128.7, 129.9, 140.2, 141.2, 147.2; FTIR (KBr pellet, cm^{-1}) 3088, 3058, 3034, 3004, 2930, 2844, 1603, 1590, 1496, 1477, 1446, 1399, 1353, 1329, 1313, 1287, 1178, 1101, 1078, 1031, 1013, 975, 940, 920.



Scheme 1 Synthesis of 9-BF monomer

Reagents and chemicals

Fluorene, bromomethylbenzene, *n*-butyl lithium, and other chemicals were used as received from Aldrich and Fluka. Acetonitrile (ACN, Fluka for HPLC analysis) was purified by distillation from P_2O_5 and then it was kept under molecular sieves (3 Å, Merck) to eliminate its water content as much as possible. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP) was purchased from Fluka and used without additional purification.

Electrochemical measurements

Cyclic voltammetric experiments were performed in a single-compartment cell (BAS model C3-cell stand) with the use of Bioanalytical Systems BAS 100B electrochemical workstation (Bioanalytical System Inc., Lafayette, IL, USA). For the cyclic voltammetry investigations, the working electrode was a platinum disk (diameter: about 1 mm). A platinum sheet (total area: about 7 cm^2) was used in preparative electrolyses. The working electrodes were successively polished with 1.0, 0.3, and 0.05 μm alumina slurries (Buehler) on microcloth pads (Buehler). After each polishing, the electrodes were rinsed with distilled water and acetonitrile. In all cases, the counter electrode was platinum wire. An $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat})}$ (BAS Model MF-2063) electrode was used as the reference electrode and potentials appearing in this article were referred to this electrode. During the electrochemical measurements, the solutions were degassed with nitrogen and kept in a nitrogen atmosphere.

Spectroscopic measurements

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Varian spectrometer at room temperature. Transmission infrared spectrum of monomer was measured as a KBr pellet using a Perkin-Elmer Spectrum-1 spectrometer. The reflectance IR measurements of the polymer film on platinum were also recorded on the horizontal attenuated total reflection cell of a Perkin-Elmer Spectrum-1 system. The samples were placed directly on the ZnSe window (45° angle of incidence), and the spectra were recorded with a resolution of 4 cm^{-1} and averaged 1,200 scans from. Absorption and steady-state fluorescence measurements were obtained by using Shimadzu UV–Vis–NIR 3101 PC spectrophotometer and Shimadzu RF-5301

PC spectrofluorometer, respectively. For the optical measurements of the polymer film in solid state, an indium-tin-oxide coated quartz sheet (ITO) (ca. 80% transmittance, ca. $300\ \Omega/\text{square}$ resistance, from Balzers, Liechtenstein) was used. Scanning tunneling microscopy (STM) measurements were acquired in ambient conditions, with a Molecular Imaging Model PicoScan instrument. STM tips were mechanically cut Pt–Ir wire. The single crystal gold (Au(111)) electrodes used for STM measurements were prepared as described earlier by Hamelin [35]. First of all, Au wire (Alfa Aesar, 0.762 mm diameter, 99.999% purity) was cleaned by sequential rinsing with distilled water, absolute ethanol, piranha solution (3:1, H_2SO_4 , 30% H_2O_2), distilled water, and absolute ethanol. *Caution: Piranha is a vigorous oxidant and should be used with extreme caution!* After being dried in nitrogen gas stream, the clean Au wire was melted in a H_2/O_2 flame to form a 1.5–2.5 mm diameter droplet at the end of the wire, and then to obtain elliptical (111) facets the droplet was annealed in the flame. Finally, the surface of Au electrode was tested electrochemically in 1 M H_2SO_4 solution.

Results and discussion

Electrochemical polymerization of 9-BF

The electrochemical oxidation process of 9-BF was investigated by cyclic voltammetry in dry ACN solution containing 0.1 M TBAP on a Pt disk electrode (Fig. 1). During the first anodic scan (Fig. 1a), a single irreversible oxidation wave was determined at around 1.85 V vs. Ag/AgCl , corresponding to the oxidation of 9-BF. In the reverse potential scan, a well-defined reduction peak was observed at potential of 1.28 V. After the second positive scan, an additional broad oxidation wave was appeared at 1.49 V. As the cyclic voltammetric scan continued (Fig. 1b), the height of the first anodic peak decreased regularly with time whereas the peak currents of the other anodic and cathodic peaks were remarkably enhanced in the first 10 potential scans, and then these waves gradually diminished in height. Furthermore, when cycling in the range of 0.0–1.85 V over 10 cycles, the growth of a new redox couple between 1.4 and 1.7 V was observed with a concomitant increase in current intensities. These new waves clearly reveal the formation of electroactive polymer film on the electrode surface. This polymeric material possessing a redox potential less than the starting monomer is reoxidized during the successive scans and the increase in the redox wave currents implies that the amount of the polymer on the electrode is increasing.

The oxidative polymerization of 9-BF occurs probably by carbon–carbon coupling through the C2 and C7 fluorene carbon atoms as previously described in the case of classical fluorenes [7, 36]. The first oxidation step is the formation of monomer radical cations. The electrogenerated monomeric radical cations are highly reactive and completely consumed in the following chemical reactions. Thus, new electroactive species (dimer and short-chain oligomers) which oxidize more readily than the 9-BF monomer are produced. The radical cations formed by their oxidation quickly couple with other coexisting radical cations leading to long-chain

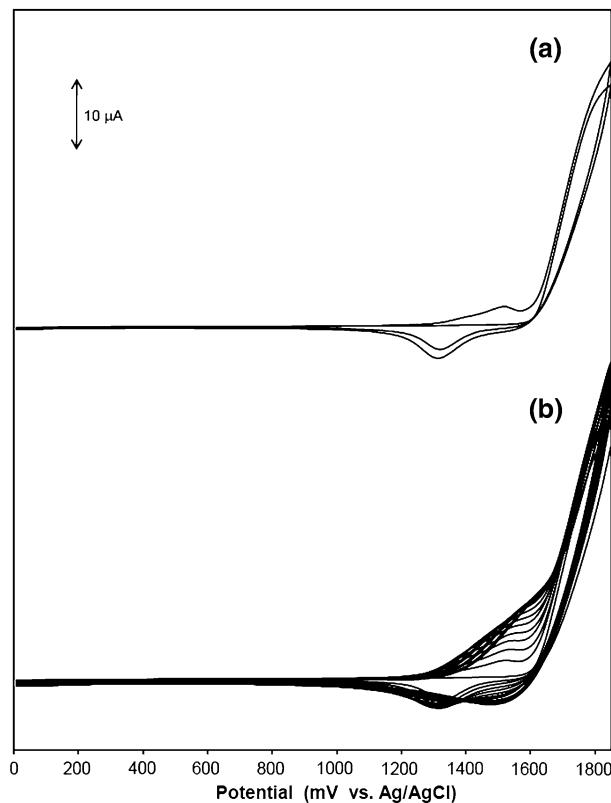


Fig. 1 Cyclic voltammograms in dry ACN containing 0.1 M TBAP. Electropolymerization of 9-BF (10 mM) performed by (a) 4 and (b) 20 repetitive scans between 0.0 and +1.85 V on a platinum electrodes. Scan rate: 100 mV s⁻¹

oligomers and polymer with increasing conjugation length which may precipitate on the electrode.

The electrochemical behavior of fluorene was also investigated under similar conditions as references. For oxidation of the fluorene (1.56 V) relative to the 9-BF (1.58 V), a slightly lower onset potential was obtained. It is well known that the oxidation potentials decrease with increasing conjugation length [37]. However, the steric effects introduced by the multi conjugated rings lead to nonplanar conformations and high torsional angles which increase the oxidation potentials [38, 39]. Therefore, the higher onset potential for 9-BF can be attributed to benzyl substituent at the C9 position which increases the steric interaction on the structure.

Electrochemical behavior of poly(9-BF) film

Cyclic voltammetry was used to assess the redox behavior of the polymer. After electrodeposition, the polymer film coated electrode, as prepared in Fig. 1b, was rinsed with ACN to remove any unreacted monomer and oligomeric species and

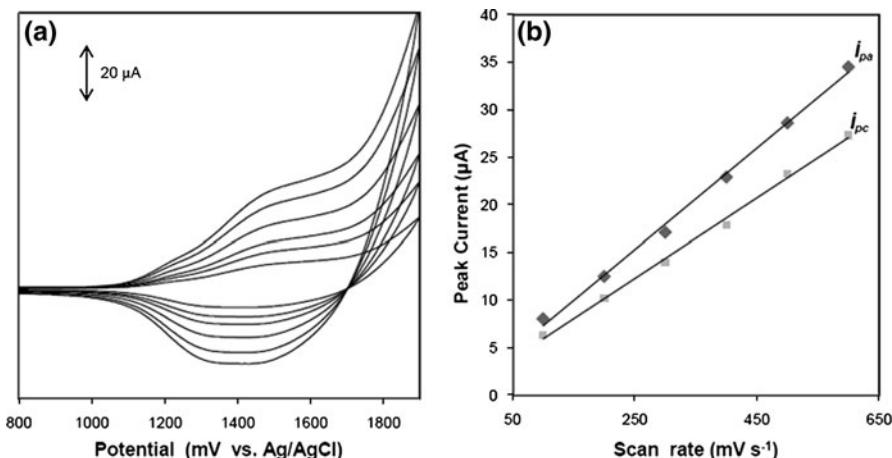


Fig. 2 **a** Cyclic voltammograms of poly(9-BF) in thin film coated on Pt electrode in monomer-free ACN containing 0.1 M TBAP at varying scan rates. **b** Dependence of peak currents on the scan rate

transferred to a monomer-free electrolyte solution. As shown in Fig. 2a, voltammetric analysis of the film showed a reversible electrochemical response between 1.5 and 1.8 V. This couple is associated with the doping and dedoping of the polymer deposited on the electrode. Scan rate dependence experiments showed that anodic and cathodic peak currents increase linearly with increasing scan rate, indicating a well-adhered polymer film and a non-diffusional redox process (Fig. 2b). The potential difference between the anodic and cathodic peaks for poly(9-BF) is also typically very small and close to the theoretical value of 0 for surface confined redox species. Furthermore, this film could be cycled repeatedly between the oxidized and neutral states without significant decomposition of the material. The polymer formed is therefore electrochemically stable and is not destroyed by the charge–discharge processes.

Characterization of poly(9-BF) film

Infrared spectroscopy can provide valuable information on the polymer structure by comparison of the infrared group frequencies of the monomer and polymer. In this regard, the chemical structure of the poly(9-BF) film on Pt electrode was investigated by ATR-FTIR reflectance spectroscopy (Fig. 3b). For comparison, the transmission FTIR spectrum of the monomer in KBr was also included, as depicted in Fig. 3a. The broad and intense bands in the high-frequency part of the spectrum for monomer ($3100\text{--}3000\text{ cm}^{-1}$) (Fig. 3a) are related to the $=\text{C}-\text{H}$ stretching vibrations of the aromatic rings. In the polymer spectrum, these bands are relatively broad because poly(9-BF) has the broad distribution of the polymer chain length (Fig. 3b) [40]. On the other hand, the bands at 2930 and 2845 cm^{-1} can be assigned to the symmetric- CH_2 and asymmetric- CH_2 vibrations. After polymerization, these peaks still exist, however, the positions of these bands shift to higher frequencies (from 2845 to 2870 cm^{-1} and from 2930 to 2938 cm^{-1} , respectively).

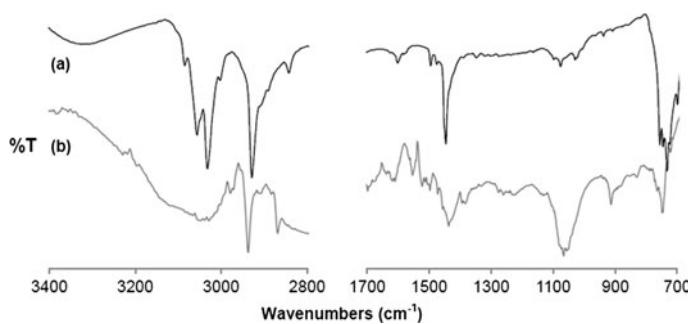


Fig. 3 **a** Transmission infrared spectrum of 9-BF in KBr pellet and **b** ATR infrared spectrum of poly(9-BF) film electrodeposited on Pt

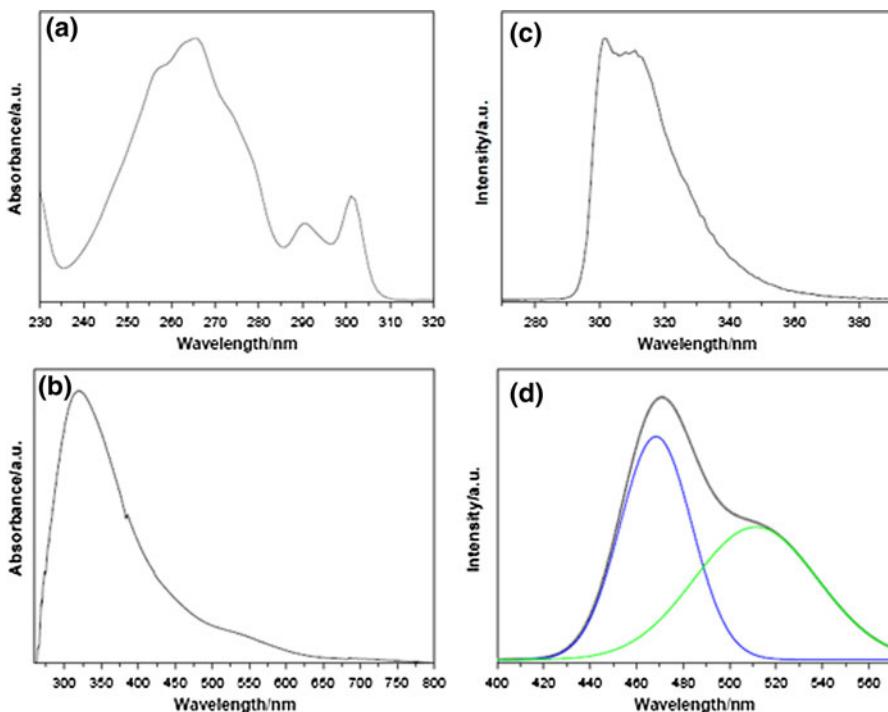


Fig. 4 UV-Vis absorption and emission spectra of the 9-BF in ACN (**a**, **c**) and poly(9-BF) film on ITO (**b**, **d**)

Such an increase in the frequencies of the CH_2 stretching vibrations also implies to decreasing conformational order of the polymer chain [41].

In low frequency region, the peaks in the vicinity of 1400 and 1650 cm^{-1} can be ascribed to the $\text{C}=\text{C}$ stretching modes of aromatic rings. In addition, it should be noted that the band at 1438 cm^{-1} corresponds to the skeleton vibration of the

aromatic ring of fluorene. On the other hand, the characteristic bands of the monomer at 728 and 757 cm^{-1} are assigned to the C–H out-of-plane vibration in the 1,2-disubstituted benzene ring. In this region, the polymer spectrum shows three peaks at 733, 766, and 836 cm^{-1} , attributed to the presence of a tri-substituted benzene aromatic ring. This spectral change points that polymerization mainly occurred at the C2 and C7 positions [25]. Finally, the strong absorption band around 1100 cm^{-1} in the polymer spectrum originates from the ClO_4^- doping species vibration [42].

The optical properties of 9-BF and poly(9-BF) were investigated by UV–Vis and fluorescence spectroscopy. The normalized absorption and emission spectra of the monomer in ACN solution and of polymer film on an ITO electrode are shown in Fig. 4. The absorption spectrum of 9-BF presents a main absorption band centered at 265 nm in combination with two significant shoulders at 291 and 302 nm, which is attributed to the $\pi-\pi^*$ transition (Fig. 4a). On the other hand, as illustrated in Fig. 4b, the UV–Vis spectrum of neutral poly(9-BF) thin film exhibits a much broader absorption from 270 to about 770 nm with a maximum at 327 nm. The absorption maximum of the polymer is red-shifted by about 50–55 nm by comparison with the monomer spectrum. The shift of the band to a longer wavelength indicates an increase in conjugation length of the polymeric material [43]. On the other hand, the absorption curves for both monomer and polymer are almost identical to those of the fluorene and PF in shape, although the absorption peaks are only blue-shifted by 3–5 nm [44].

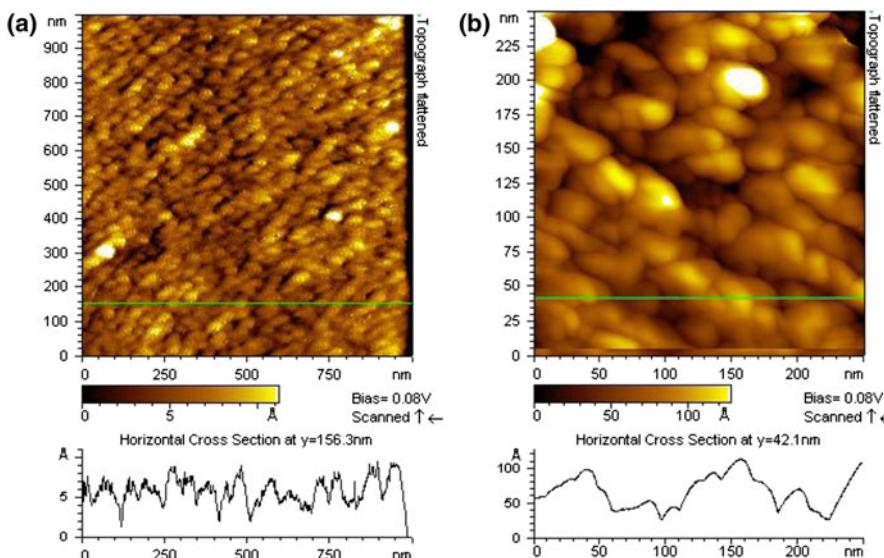


Fig. 5 STM images of poly(9-BF) thin films deposited onto Au(111) single crystalline substrates during **a** 1 and **b** 20 cyclic voltammetric scans between 0.0 and $+1.85\text{ V}$ in ACN solution containing 0.1 M TBAP and 5 mM 9-BF

The emission spectrum of the dilute solution of monomer exhibits a strong peak at 310 nm when excited at 260 nm (Fig. 4c). As seen from Fig. 4d, the photoluminescence of poly(9-BF) film in solid state also shows two major peaks at around 470 and 520 nm when excited at the absorption maximum wavelength. The broad peak around 520 nm is probably due to interchain excimer emission [6, 14]. Thus, this result implies that the polymer film emitted blue-greenish light.

The surface morphology of the polymer film on the Au(111) electrode was examined by STM. Figure 5a shows STM image of film obtained during a single cyclic scan between 0.0 and 1.85 V in an ACN/0.1 M TBAP solution containing 5 mM 9-BF. The image reveals that the gold surface is completely covered with polymer thin film with a thickness of about 5 nm, and the polymer film resembles partially ordered arrangements of the granules with a grain size of 50–60 nm. On the other hand, when the potential is cycled 20 times in a selective range of the electrode potentials, a thicker layer of polymer with different grain sizes (thickness increases from 5 up to 50 nm) is obtained (Fig. 5b). This observation indicates that a longer deposition time results in the forming of three-dimensional structures.

Conclusions

In summary, a new PF derivative, poly(9-BF) was electrochemically synthesized and characterized with respect to its properties. The resulting polymer film showed good redox activity and good stability. The UV–Vis spectral data of polymer film displayed the expected bathochromic shift attributed to the longer conjugated chains than that of the monomer. On the other hand, the emission spectra suggested that the polymer film in the solid state was blue-green emitter because of interchain excimer formation. These results indicated that this kind of polymer film was a good candidate for applications in polymer light-emitting diodes and conducting materials.

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