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Electrochemical polymerization of 9-phenylcarbazole in mixed electrolytes of boron trifluoride diethyl etherate and sulfuric acid

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Abstract Poly(9-phenylcarbazole) (P9PC) films were synthesized electrochemically by direct anodic oxidation of 9-phenylcarbazole in boron trifluoride diethyletherate (BFEE) containing additional 2% sulfuric acid (by volume). The oxidation potential onset of 9-phenylcarbazole in this medium was measured to be 0.9 V vs. SCE, which was much lower than that in acetonitrile containing 0.1 mol L^{-1} Bu_4NBF_4 (1.1 V vs. SCE). P9PC films obtained from this medium showed good electrochemical behavior and good thermal stability with an electrical conductivity of 0.09 S cm^{-1}. The structure and morphology of the polymer were investigated by UV–visible spectroscopy, infrared spectroscopy, and scanning electron microscopy (SEM), respectively. The results of quantum chemistry calculations of 9-phenylcarbazole monomer indicated that the polymerization mainly occurred at C_3 and C_6 positions. Fluorescent spectral studies indicated that P9PC was a blue-light emitter.

Introduction

Inherently conducting polymers (CPs), such as poly(*para*-phenylene) [1], poly(*para*-phenylenevinylene) [2], polythiophene [3, 4], polypyrroles [5], polyindole [6], polyfluorene [7], and polycarbazole [8] are of interest because of their several potential applications. Among them, carbazole and it derivatives are well known to exhibit good electro- and photo-active properties [9]. Polycarbazole, with the advantages of good environmental stability, photoconductivity and electrochromic properties, has attracted great attention due to its potential industrial applications in electroluminescent applications [10, 11], light-emitting diodes (LEDs) [12, 13], electrochromic displays [14], organic transistors [15], and rechargeable batteries [16], as hole-transporting and photoluminescence efficiencies units [17, 18].

It is well know that the properties of conducting polymers strongly depend on their structural characteristics. Therefore, structural consideration is an important factor in the synthesis of new materials. In the case of carbazole-based conjugated polymers, all previous studies were devoted to 3,6-linked, *N*-substituted and 2,7-linked carbazole units [19]. Our previous studies have investigated that electrosyntheses of poly(*N*-octylcarbazole), poly(*N*-(6-bromohexyl)carbazole), poly(1,6-bis-(carbazole)hexane) and poly(1,12-bis(carbazolyl) dodecane) films [20, 21]. They all exhibited high quality, nice structural stability and good light-emitting properties. Recently, the high molecular weight poly(*N*-alkyl-3,6-carbazole)s were successfully synthesized [17]. They possess good solubility, film-forming ability, thermal stability, and moderately high photoluminescence efficiency [17]. Poly(9-alkyl-9*H*carbazole-2,7-diyl) can be considered as promising candidates for application in blue light emitting diodes in view of their

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high fluorescence quantum efficiencies [22]. The HOMO level can be engineered by substitution at the 3, 6, and 9 position of the carbazoles [23]. Moreover, polycarbazoles have possibility of substitution at N position. This facile process provides the opportunity to improve both the solubility and functionality of the resulting polymer. On the other hand, flexible side chains can cause steric hindrance and thereby provide a means to control the effective conjugation length and thus tuning the color of the emitting light in devices [24]. From these points described above, *N*-functionalized carbazole with phenyl substituent is very typical and it is very necessary to investigate the chemical and electrochemical properties of poly(9-phenylcarbazole) (P9PC) films.

Electrochemical polymerization is a very effective approach for the electrosyntheses of conducting polymer films with several advantages such as cheap and one-step conducting polymer film formation, mainly in common organic solvent such as acetonitrile or in water. In recent years, boron trifluoride diethyl etherate (BFEE) was found to be a good electrolyte for electrochemical polymerization of aromatic compounds such as benzene [25], thiophene [26], carbazole [27] and its derivatives, etc. [20, 21]. The addition of a certain amount of sulfuric acid into BFEE as a mixed electrolyte can further improve the properties of corresponding polymer [28].

In this paper, P9PC films were easily prepared by direct anodic oxidation of 9-phenylcarbazole monomer in mixed electrolyte of BFEE containing 2% sulfuric acid. The electrochemical properties, polymerization mechanism, thermal stability, fluorescent properties, and morphology of as-prepared P9PC films were studied in detail.

Experimenral

Materials

Boron trifluoride diethyl etherate (BFEE, Beijing Changyang Chemical Plant) was distilled and stored at −20 °C before use. BFEE is a colorless fuming liquid, often very stable, which can be distilled without decomposition. It is a strong Lewis acid. BFEE is also a very hazard reagents such as extremely destructive to tissues of the mucous membranes and upper respiratory tract, extremely destructive to skin. Swallowing BFEE can cause severe burns of the mouth, throat, and stomach, leading to death. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage. Persons with pre-existing skin disorders, or impaired kidney or pulmonary function may be more susceptible to the effects of this agent. In addition, all our experiments concerning BFEE were performed in draught cupboard. 9-Phenylcarbazole (Aldrich Chem. Co.), commercial high performance liquid chromatography grade acetonitrile (Tianjin Kermel Chemical Reagents Research Institute), sulfuric acid (98% Beijing Chemical Factory), were used as received. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4; Acros Organics; 95%) was dried in vacuum at 60 °C for 24 h before use. Dimethyl sulfoxide (DMSO; analytical-grade) was a product of Tianjin Bodi Chemicals Co., Ltd.

Electrosyntheses of P9PC films

Electrochemical syntheses and examinations were performed in a one-compartment cell by the use of a model 263 potentiostat-galvanostat (EG & G Princeton Applied Research) under a computer control. For electrochemical examinations, the working and counter electrodes were Pt wire with a diameter of 0.5 mm and stainless steel wire with a diameter of 1 mm, respectively. They were placed 5 mm apart during the experiment. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with surface areas of 10 and 12 cm^2 each were employed as the working and counter electrodes, respectively. The electrodes mentioned above were carefully polished with abrasive paper (1,500 mesh) and cleaned with water and acetone successively before each examination. The electrochemical dedoping of P9PC films coated on ITO electrode was performed at a constant potential of −0.27 V vs. SCE in a monomer free BFEE containing 2% EE solution until the current density was close to zero. All potentials were referred to SCE.

The typical electrolytic solution was BFEE containing 2% sulfuric acid and 0.02 mol L^{-1} 9-phenylcarbazole. The amount of the polymer deposited on electrode was controlled by the integrated current density passed through the cell. The P9PC films were prepared from BFEE containing 2% sulfuric acid (by volume) and 0.02 mol L^{-1} 9-phenylcarbazole at a constant applied potential of 1.08 V vs. SCE. To remove the electrolyte, oligomers, and monomer, the electropolymerized films were rinsed with CH_3CN and pure water. As-formed polymer powder was scraped from stainless steel sheets. For spectral analysis, the scraped polymer was dedoped with 25% ammonia for 3 days and then washed repeatedly with water. Finally, it was dried in vacuum at 60 °C for 2 days.

Characterization

The electrical conductivity of as-formed P9PC films was measured by a conventional four-probe technique. Ultraviolet-visible (UV–vis) spectra were taken with a

Perkin–Elmer Lamda 900 ultraviolet-visible-near-infrared spectrophotometer. Infrared spectra were recorded with a Nicolet 510P Fourier transform infa-red (FTIR) spectrometer with KBr pellets. The fluorescence spectra were determined with an F-4500 fluorescence spectrophotometer (Hitachi). The thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA (Perkin–Elmer) thermal analyzer. Scanning electron microscopy (SEM) measurements were taken with a JEOL JSM-6700F scanning electron microscope. The fluorescence quantum yields ($\phi_{overall}$) of P9PC in solution was measured using anthrancene in CH_3CN (standard, $\phi_{ref} = 0.27$) [29] as a reference and were calculated according to the well-known method given as

$$\phi_{overall} = \frac{n^2 A_{ref} I}{n_{ref}^2 A I_{ref}} \times \phi_{ref} \qquad (1)$$

Here, n, A and I denote the refractive index of solvent, the absorbance at the excitation wavelength, and the intensity of the emission spectrum, respectively. Absorbance of the samples and the standard should be similar [30, 31].

Results and discussion

Electrochemical syntheses of P9PC films

Figure 1 shows the anodic polarization curves of 9-phenylcarbazole in the solvents of BFEE mixed with 0 (A), 2% (B), 4% (C), and 6% (D) sulfuric acid (by volume). The oxidation onset of 9-phenylcarbazole was initiated at 0.83 V vs. SCE in pure BFEE (Fig. 1a). The addition of 2, 4 and 6% sulfuric acid to BFEE increased the oxidation potential of the monomer significantly to about 0.9, 0.93, and 0.95 V, respectively (Fig. 1b–d). They all were much lower than that 9-phenylcarbazole in CH_3CN containing 0.1 mol L^{-1} Bu_4NBF_4 (1.1 V vs. SCE), as shown in the insert of Fig. 1. From this point of view, pure BFEE is the best choice because generally the lowering of the monomer oxidation potential onset can prevent side reaction and lead to high quality polymer films. However, no apparent redox waves of the polymer were found in pure BFEE solution (Fig. 2a), indicating that only a trace amount of the polymer was formed [32]. On the contrary, the introduction of a small amount of the sulfuric acid to BFEE led to the formation of high quality film on Pt electrode surface. According to Fig. 1, the oxidation potentials of the monomer increased with sulfuric acid concentration in the mixed electrolytes. Higher oxidation potential usually led to side reactions during the polymerization process and thus resulted in poor polymer film quality. On the basis of these considerations, BFEE containing 2% sulfuric acid was chosen as the best-mixed electrolyte for the electrosyntheses of P9PC.

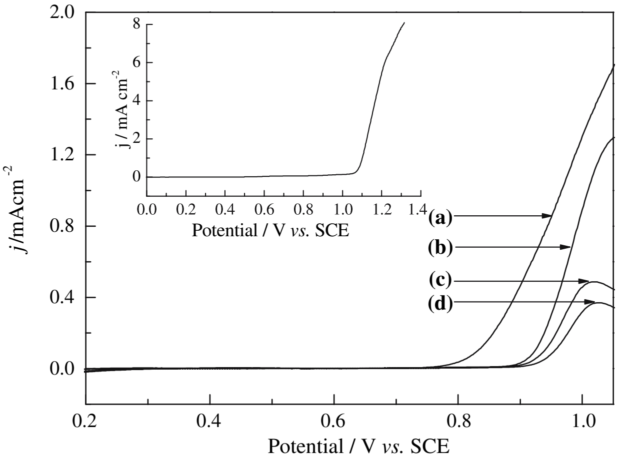


Fig. 1 Anodic polarization curves of 9-phenylcarbazole in mixed electrolytes of BFEE containing 0 (**a**), 2% (**b**), 4% (**c**), and 6% (**d**) sulfuric acid (by volume) and in CH_3CN containing 0.1 mol L^{-1} Bu_4NBF_4 (insert). The potential scanning rate was 20 mV s^{-1}. j = current densities

The successive cyclic voltammograms (CVs) of 0.02 mol L^{-1} 9-phenylcarbazole in the mixed electrolytes on a Pt electrode were shown in Fig. 2. As can be seen from Fig. 2a, the CVs of 9-phenylcarbazole in pure BFEE were not very successful, although a polymer film still can be formed on working electrode. No apparent redox waves of the polymer were found, indicating that only a trace amount of the polymer was formed. This is mainly due to the fact that polymer film was formed on the electrode surface and its electrical conductivity was much lower than that of stainless steel electrode. On the other hand, the successive CVs of 0.02 mol L^{-1} 9-phenylcarbazole in the mixed electrolytes with BFEE containing 2% sulfuric acid on a Pt electrode were very successful (Fig. 2b). As it can be seen from this figure, the cyclic voltammograms of 9-phenylcarbazole in BFEE containing 2% sulfuric acid showed characteristic features of other CPs such as polypyrole and polythiophene during potentiodynamic syntheses. As the CV scans continued, a polymer film was formed on the Pt electrode surface. P9PC can be reduced and oxidized between 0.66 V and 0.8 V. The increases of the redox wave currents implied that the amount of the polymer on the electrode was increased. The potential shift of the wave maximum provide information about the increases in the electrical resistance in the polymer film and over-potential needed to overcome the resistance [33]. When increasing the sulfuric acid content in the mixed electrolytes, a similar phenomenon could be observed (Fig. 2c, d). It can also be seen in Fig. 2b–d that the increases in the redox wave current densities per cycle was the highest in BFEE containing 2% sulfuric acid (Fig. 2b).

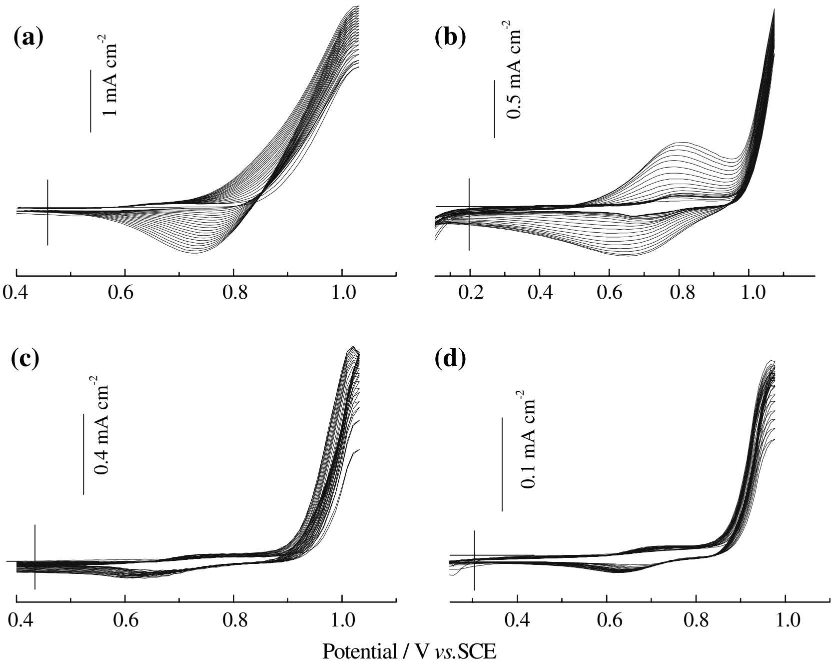


Fig. 2 Cyclic voltammograms of 0.02 mol L^{-1} 9-phenylcarbazole in pure BFEE (**a**), a mixed electrolyte of BFEE containing sulfuric acid 2% (**b**), 4% (**c**), 6% (**d**). The potential scanning rates was 100 mV s^{-1}

As the sulfuric acid concentration was increased further in the mixed electrolytes, the density of current per cycle decreased. This may be ascribed to the fact that oxidation potential of the monomer increased, together with the strong over-oxidation effect of sulfuric acid as the sulfuric acid concentration further increased (Fig. 1b–d). According to the electrochemical kinetics, at a given applied potential (E), the polymerization rate is exponential to the potential difference ($E-E^0$) of E and the oxidation potential of the monomer (E^0). The addition of sulfuric acid increased E^0 of the monomer. Thus, the polymerization rates decreased at the given applied potentials when increasing sulfuric acid content. This resulted in the phenomena shown in Fig. 2c, d. Therefore, the following work was concentrated on the electrosyntheses and characterizations of P9PC films prepared in BFEE containing 2% sulfuric acid.

Electrochemistry of P9PC films

The electrochemical behavior of the P9PC films deposited electrochemically from BFEE containing 2% sulfuric acid was studied in monomer-free BFEE containing 2% sulfuric acid (Fig. 3a) and in concentrated sulfuric acid (Fig. 3b), respectively. Similar to the results in the literature [34], the steady-state cyclic voltammograms represented broad anodic and cathodic peaks. The peak current densities were proportional to the scan rates (inserts of Fig. 3a, b), indicating good redox activity of the polymer. Furthermore, these polymer films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials, indicating high structural stability of the polymer. The polymer film obtained from BFEE containing 2% sulfuric acid can be oxidized and reduced from 1.0 V (E_a) to 0.8 V (E_c) in monomer-free BFEE containing 2% sulfuric acid at potential scan rate of 50 mV s^{-1}. With the scan rates increasing, the potentials needed to oxidize and reduce the polymer film shifted positively and negatively to about 1.08 V (E_a) and 0.75 V (E_c), respectively. This can be mainly ascribed to the slow transfer rate of large doping anions and solvent molecules in BFEE containing 2% sulfuric acid, such as $(\mathrm{EtO})_3\mathrm{BF}_3^-$, especially at higher scan rates [35]. However, the redox potentials of the polymer were very stable, according to the increases of potential scan rates, which is from 0.74 V (E_a) and 0.66 V (E_c) in concentrated sulfuric acid (Fig. 3b). This indicated high stability of P9PC films even in concentrated sulfuric acid. Moreover, the small anions in concentrated sulfuric acid (SO_4^{2-} or HSO_4^-) [35] can facilitate the doping and dedoping process. This led to the good redox activity of P9PC films in concentrated sulfuric acid. On the other hand, the difference of (E_a-E_c) related to the kinetics of the doping-dedoping reactions is equal to 0.08 V in concentrated sulfuric acid for the P9PC prepared from BFEE containing 2% sulfuric acid (Fig. 3a). This implied that the redox properties of P9PC films from BFEE containing 2% sulfuric acid were fairly good in concentrated sulfuric acid. On the basis of this discussion, it can be reasonably concluded that the doping-dedoping reaction of P9PC was very fast, also indicating high quality P9PC film formation.

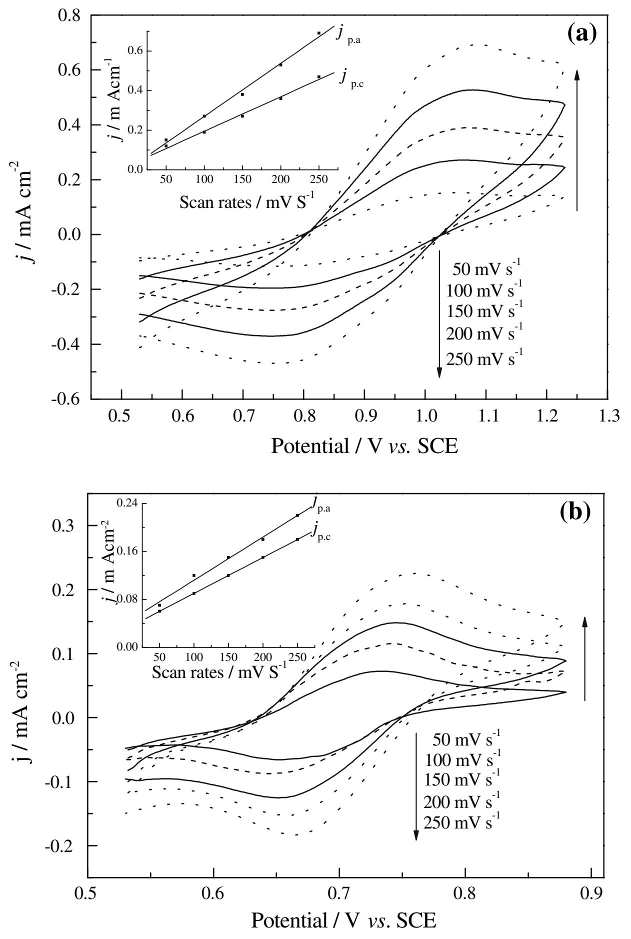


Fig. 3 Cyclic voltammograms of a P9PC film in monomer-free BFEE containing 2% sulfuric acid (**a**) and in concentrated sulfuric acid (**b**), at potential scanning rates of 50, 100, 150, 200, 250 mV s^{-1}. The P9PC film was synthesized electrochemically in BFEE containing 2% sulfuric acid at constant applied of 1.08 V vs. SCE. j, j_{p}, $j_{\mathrm{p.a}}$, $j_{\mathrm{p.c}}$ are defined as the current densities, the peak current densities, the anodic peak current densities, and the cathodic peak current densities, respectively

Structural characterizations of P9PC films

During potentiostatic deposition of P9PC in BFEE containing 2% sulfuric acid, a polymer film was formed on the Pt electrode surface (blue to black as the deposit thickened). The electrolyte solution was changed gradually from slight blue to blue, then to deep blue, and finally to dark blue during the electropolymerization. This implied that part soluble blue oligomer formed during the electropolymerization diffused into the bulk solution.

As-prepared P9PC films from BFEE containing 2% sulfuric acid were in doped state and metallic dark in color. When dedoped by 25% ammonia, their color changed into brown. Doped and dedoped P9PC were soluble in the strong polar solvent DMSO. Therefore, the UV–vis spectra of the 9-phenylcarbzale, doped and dedoped P9PC films dissolved in DMSO were examined, as shown in Fig. 4. The monomer showed several characteristic absorptions at 340, 327, 291, and 286 nm (Fig. 4a). On the contrary, the spectrum of the P9PC films shows a much broader absorption at 306 nm. The overall absorption tails off to about 370 nm. Generally, higher wavelength means higher conjugation length. Therefore, the result of the red shift of UV–vis spectra of P9PC means higher conjugation backbone in comparison with the monomer [36]. The peaks located at 340 and 327 nm were absent for the polymer (Fig. 4a). This proved that higher conjugation length was formed in polymer. However, the doped films showed another strong absorption on the ITO electrode, with peaks at ca. 760 nm, 405 nm, 312 nm (Fig. 4d). These wide absorptions can be assigned to the absorption of conductive species on the main backbone of the P9PC in the doped stated. In comparison with dedoped P9PC films in solution and on ITO (Fig. 4c, e), the spectrum of the doped P9PC films were similar (Fig. 4b, d), respectively. This may be due to the automatic dedoping process of P9PC in DMSO solution, because the counterions in P9PC films obtained from BFEE containing 2% sulfuric acid can be mainly ascribed to BF$_4^-$, [BF$_3$OH]$^-$[37], SO$_4^{2-}$ or HSO$_4^-$. These counterions can move out of the polymer in DMSO solution, resulting in automatic dedoping. On ITO electrode, the polymer film in doped state was very stable, resulting in the similarity of the absorptions of both doped and dedoped polymers on ITO electrode.

Vibrational spectroscopy can provide structural information on neutral and doped conducting polymers. The comparison on the evolution of the vibrational modes appearing in conducting polymers and in some simpler related molecules acting as references usually facilitates the interpretation of the experimental absorption spectra.

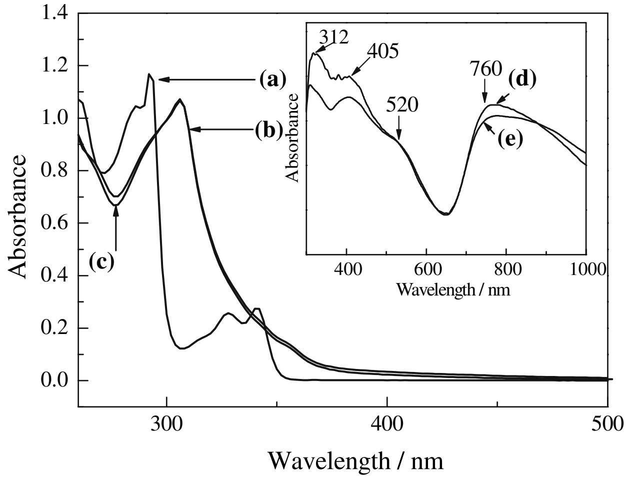
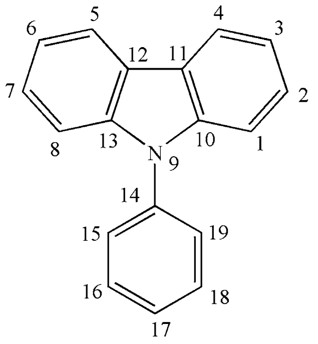


Fig. 4 UV–vis spectra of 9-phenylcarbazole (**a**), doped P9PC films (**b**) and dedoped P9PC films (**c**). Solvent: DMSO. Insert: doped P9PC (**d**) and dedoped P9PC (**e**) films on ITO electrode

Therefore, the FTIR spectra of 9-phenylcarbazole monomer (Fig. 5a), doped P9PC (Fig. 5b) and dedoped P9PC (Fig. 5c) were examined. Absorption vibration bands at 725 and 750 cm^{-1} indicated that existence of a 1,2-di-subsituted benzene ring (Fig. 5a). After polymerization, these bands became very weak (Fig. 5b, c). At the same time, these polymers exhibited a new peak at about 810 cm^{-1}, indicating the emergence of 1,2,4-tri-substituted benzene ring. This can provided the information that the polymer of 9-phenylcarbazole occurred mainly at (C_3, C_6), (C_2, C_7) or (C_2, C_6) positions (Scheme 1). The bands at 1,233 cm^{-1}(Fig. 5a, b, c) were related to the C–C deformation of carbazole [38]. These bands at 1,450, 1,629, and 1,632 cm^{-1} (Fig. 5a, b, c) can be ascribed to the C=C vibration on benzene ring. The bands in the region from 1,600 to 1,100 cm^{-1} were assigned to the stretching and shrinking modes of C=C and C–C, which were selectively broadened for the polymer.

To get deep insight into P9PC structures and the polymerization mechanism, the atomic electron density population and reactivity of 9-phenylcabazole monomer (Scheme 1) were calculated at the B3LYP/6-31G(d,p) level using Gaussian 03 software [39]. The results of main atomic electron density populations showed negative electric charges on $C_{(1)}$, $C_{(3)}$, $C_{(4)}$, $C_{(5)}$, $C_{(6)}$, and $C_{(8)}$ (Table 1), which implied that these atoms will donate electrons when 9-phenylcabazole monomer is electrochemically polymerized because the polymerization is performed through radical cation intermediates. According to the molecular orbital theory, the reaction between the active molecules mainly happens on the frontier molecular orbitals and near orbitals. For 9-phenylcabazole, the proportions of atoms $C_{(1)}$, $C_{(3)}$, $C_{(6)}$, and $C_{(8)}$ in HOMO were higher than other atoms as listed in Table 2. At the same time, $C_{(1)}$, $C_{(3)}$, $C_{(6)}$, and $C_{(8)}$ also had rich negative charges (Table 1). When coupling at $C_{(1)}$ and $C_{(8)}$ position, there would be significant steric effect. Therefore, these theoretical results implied that the polymerization between the monomers would happen preferentially on $C_{(3)}$ and $C_{(6)}$, in well accordance with the results of IR and literatures [19].



Scheme 1 Chemical structures of 9-phenylcarbazole

Table 1 Main atomic electron density populations for 9-phenylcarbazole

Atom	Electric charge	Atom	Electric charge
$C_{(1)}$	−0.111149	$C_{(2)}$	−0.098753
$C_{(3)}$	−0.100856	$C_{(4)}$	−0.133559
$C_{(5)}$	−0.133559	$C_{(6)}$	−0.100856
$C_{(7)}$	−0.098753	$C_{(8)}$	−0.111149
$N_{(9)}$	−0.728497	$C_{(10)}$	0.292927
$C_{(11)}$	0.041265	$C_{(12)}$	0.041265
$C_{(13)}$	0.292927	$C_{(14)}$	0.233045
$C_{(15)}$	−0.089582	$C_{(16)}$	−0.098243
$C_{(17)}$	−0.077862	$C_{(18)}$	−0.098243
$C_{(19)}$	−0.089582		

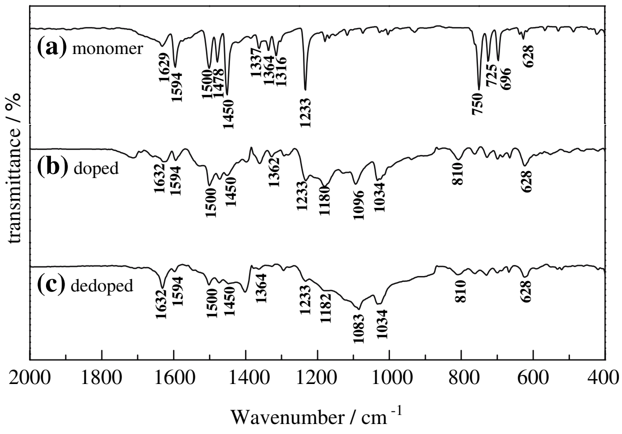


Fig. 5 FTIR spectra of 9-phenylcarbazole monomer (**a**), doped P9PC films (**b**) and dedoped P9PC films (**c**)

The fluorescence spectra of monomer 9-phenylcarbazole, doped P9PC and dedoped P9PC prepared in BFEE containing 2% sulfuric acid were examined in DMSO. As shown in Fig. 6, an obvious emission peak at 390 and 408 nm was found in the fluorescence spectra of doped (Fig. 6b) and dedoped (Fig. 6c) P9PC, respectively. For the monomer, they were located at 350 and 365 nm (Fig. 6a). This implies that there was a large bathochromic shift in the emission wavelength between the monomer and the polymer. The red shift of the emission peak further proved the formation of conjugated backbone of P9PC, in well agreement with the UV–vis spectral results (Fig. 4). These results demonstrate that P9PC may be a good candidate in blue-light-emitting materials, since it is very difficult to achieve blue-light-emitting materials [40–42]. The fluorescence quantum yield of as-formed P9PC in DMSO was measured to be 0.25 according to Eq. 1.

Table 2 Main composition and proportion of the frontier orbitals in 9-phenylcarbazole (%)

Atom	HOMO-1	HOMO	LUMO	LUMO+1
$C_{(1)}$	1.4444	8.9426	10.1078	0.8732
$C_{(2)}$	16.4308	0.0711	14.3361	0.4052
$C_{(3)}$	2.9344	9.7703	0.1334	1.2765
$C_{(4)}$	6.7136	3.7514	14.5165	0.3433
$C_{(5)}$	6.7136	3.7514	14.5165	0.3433
$C_{(6)}$	2.9344	9.7703	0.1334	1.2765
$C_{(7)}$	16.4308	0.0711	14.3361	0.4052
$C_{(8)}$	1.4444	8.9426	10.1078	0.8732
$N_{(9)}$	0.0701	30.5242	1.2310	0.1089
$C_{(10)}$	10.7904	1.6909	1.1430	3.7872
$C_{(11)}$	11.4204	4.5442	8.0026	0.7161
$C_{(12)}$	11.4204	4.5442	8.0026	0.7161
$C_{(13)}$	10.7904	1.6909	1.1430	3.7872
$C_{(14)}$	0.1958	1.3001	0.2150	28.7256
$C_{(15)}$	0.0531	3.3686	0.5664	8.0609
$C_{(16)}$	0.0613	0.4467	0.0695	6.1986
$C_{(17)}$	0.0065	2.7012	0.0063	27.4203
$C_{(18)}$	0.0613	0.4467	0.0695	6.1986
$C_{(19)}$	0.0531	3.3686	0.5664	8.0609

The HOMO, HOMO-1, LUMO, and LUMO+1 are defined as highest occupied molecular orbital, next highest occupied molecular orbital, lowest unoccupied molecular orbital, and next lowest unoccupied molecular orbital

Thermal analysis

The thermal stability of CPs is very important for their potential applications. TGA is a significant dynamic way of detecting the degradation behaviors. The weight loss of a polymer sample was measured continuously, whereas the temperature was changed at a constant rate. To investigate the thermal stability of P9PC films prepared in BFEE containing 2% sulfuric acid, the thermal analysis of doped P9PC was tested, as show in Fig. 7. The thermal analysis was performed under a nitrogen stream in the temperature range of 292–1,054 K at a heating rate of 10 K/min. As shown in Fig. 7, there was a slight weight loss from 292 K to 452 K, up to 6.0%. This degradation can be ascribed to water evaporation or other moisture trapped in the polymer [43]. The decomposition up to 20.1% occurred between 452 K and 716 K. This weight loss was attributed to the degradation of the skeletal P9PC chain structure. In addition, there was still evident decomposition, about 8.0%, between 716 K and 876 K, possibly because of the overflow of some oligomers that decomposed from P9PC with increasing temperature. The last one was about 65.9% from 876 K to 1,054 K, possibly owing to the ashing of carbon. From the differential thermalgravimetry (DTG) curves (Fig. 7b), it can be seen that when the temperature was 585 K, the weight loss rate of P9PC was fastest. These results indicate good thermal stability for the P9PC films obtained from BFEE containing 2% sulfuric acid.

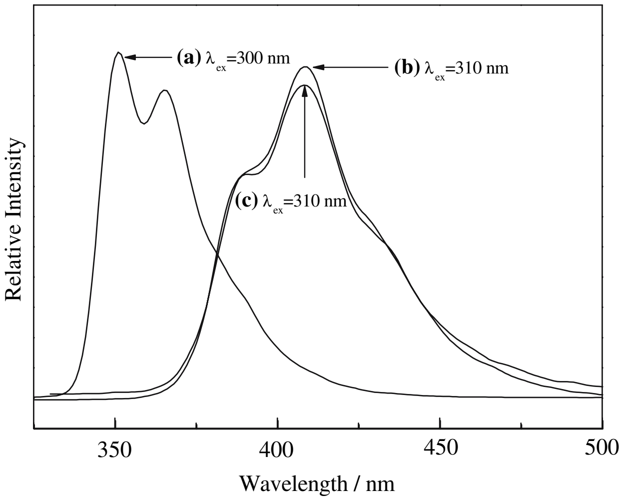


Fig. 6 Emission spectra of 9-phenylcarbazol monomer (**a**), doped P9PC (**b**) and dedoped P9PC (**c**). Solvent: DMSO

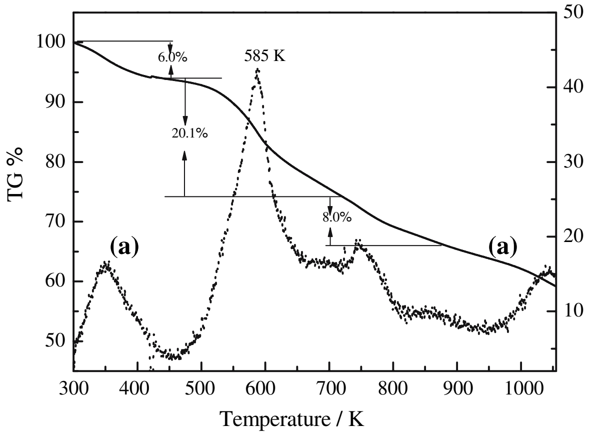


Fig. 7 TGA curves of doped P9PC films obtained potentiostatically at 1.08 V vs. SCE from BFEE containing 2% sulfuric acid

Morphology and conductivity

The SEM images of a P9PC film prepared in BFEE containing 2% sulfuric acid are shown in Fig. 8. Microscopically, the polymer film resembles ordered arrangements of the granules. The growth of nuclei was in the form of clusters. This morphology facilitated the movement of doping anions into and out of the polymer film during doping and dedoping process, in well accordance with the good redox activity of P9PC films (Fig. 3a, b).

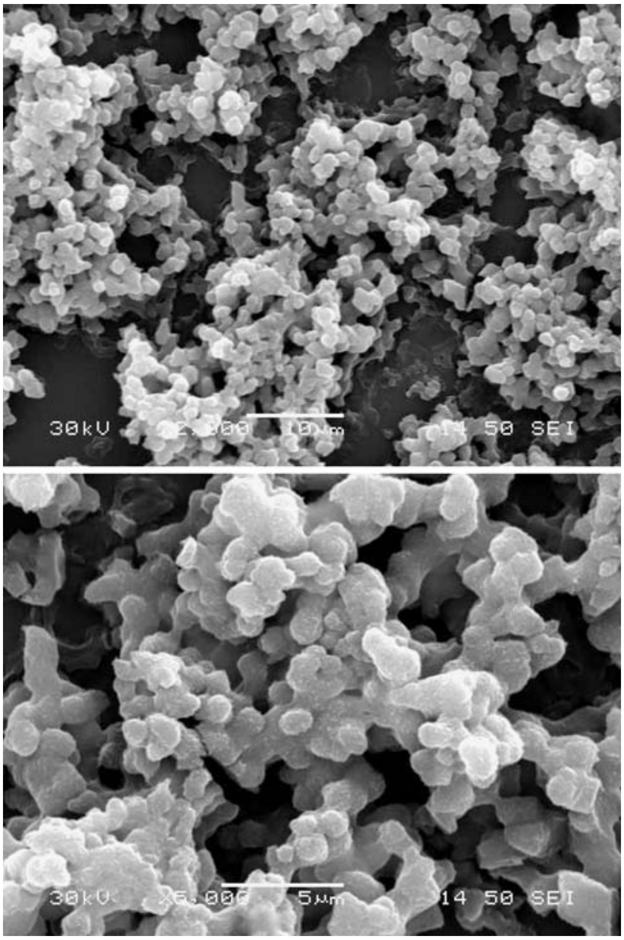


Fig. 8 SEM micrographs of P9PC film deposited on the ITO glass electrode surface from BFEE containing 2% sulfuric acid at applied constant potential of 1.08 V vs. SCE

The conductivity of pressed P9PC pellets from BFEE containing 2% sulfuric acid was measured to be 0.09 S cm^{-1}.

Conclusions

P9PC films with an electrical conductivity of 0.09 S cm^{-1} were electrochemically synthesized by direct anodic oxidation of 9-phenylcarbazole in BFEE containing 2% sulfuric acid. The oxidation potential of 9-phenylcarbazole in this medium was determined to be 0.9 V vs. SCE, which was much lower than that determined in acetonitrile containing 0.1 mol L^{-1} Bu_4NBF_4 (1.1 V vs. SCE). As-formed P9PC films showed good redox activity and high stability both in BFEE containing 2% sulfuric acid and concentrated sulfuric acid. Electrochemical, structural and morphology studies implied that P9PC films could be obtained from BFEE containing 2% sulfuric acid. According to infrared and quantum chemistry calculations, the polymerization of 9-phenylcarbazole mainly occurred at C_3, C_6 positions. TGA results indicated good thermal stability of the P9PC films obtained from BFEE containing 2% sulfuric acid. The fluorescence quantum yield as-formed P9PC in DMSO was measured to be 0.25.

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References

1. Goldenberg LM, Lacaze PC (1993) Synth Met 58:271
2. Burroughes JH, Bradley DDC, Brown AR, Marks RN, MacKay K, Friend RH, Burns PL, Holmes AB (1990) Nature 347:539
3. Leclerc M, Faid K (1997) Adv Meter 9:1087
4. Groenendaal LB, Zotti G, Aubert PH, Waybright SM, Reynold JR (2003) Adv Mater 11:855
5. Subianto S, Geoffrey WD, Serge K (2003) J Polym Sci A: Polym Chem 41:867
6. Xu JK, Nie GM, Zhang SS, Han XJ, Hou J, Pu SZ (2005) J Polym Sci A: Polym Chem 43:1444
7. Xu JK, Zhang YJ, Hou J, Wei ZH, Pu SZ, Zhao JQ, Du YK (2006) Euro Polym J 42:1154
8. Grazulevicius JV, Strohriegl P, Pielichowski J, Pielichowski K (2003) Prog Polym Sci 28:1297
9. Yang L, Feng JK, Ren AM, Sun JZ (2006) Polymer 47:1397
10. Morin JF, Boudreault PL, Leclerc M (2002) Macromol Rapid Commun 23:1032
11. Jegadesan S, Sindhu S, Advincula RC, Valiyaveettil S (2006) Langmuir 22:780
12. Jin YE, Kim JY, Park SH, Kim J, Lee S, Lee K, Suh H (2005) Polymer 46:12158
13. Tokito S, Suzuki M, Sato F, Kamachi M, Shirane K (2003) Org Electron 4:105
14. Donnat-Bouillud A, Mazerolle L, Gagon P, Goldenberg L, Petty MC, Leclerc M (1997) Chem Mater 9:2815
15. Horowitz G (1998) Adv Mater 10:365
16. Saraswathi R, Gerard M, Malhotra BD (1999) J Appl Polym Sci 74:145
17. Zhang ZB, Fujiki M, Tang HZ, Motonaga M, Torimitsu K (2002) Macromolecules 35:1988
18. Liou GS, Hsiao SH, Huang NK, Yang YL (2006) Macromolecules 39:5337
19. Morin JF, Leclerc M, Adès D, Siove A (2005) Macromol Rapid Commun 26:761
20. Wei ZH, Xu JK, Nie GM, Du YK, Pu SZ (2006) J Electroanal Chem 589:112
21. Xu JK, Wei ZH, Du YK, Pu SZ (2007) Mater Lett 61:2486
22. Iraqi A, Simmance TG, Yi H, Stevenson M, Lidzey DG (2006) Chem Mater 18:5789
23. Brunner K, Dijken AV, Börner H, Bastiaansen JJAM, Kiggen NMM, Langeveld BMW (2004) J Am Chem Soc 126:6035
24. Morin JF, Leclerc M (2002) Macromolecules 35:8413
25. Li C, Shi G, Liang Y, Ye W, Sha Z (1997) Polymer 38:5023
26. Shi G, Jin S, Xue G, Li C (1995) Science 267:994
27. Nie GM, Xu JK, Zhang SS, Han XJ (2006) J Appl Electrochem 36:937
28. Xu J, Shi G, Chen F, Wang F, Zhang J, Hong X (2003) J Appl Polym Sci 87:502

29. Zimmermanna C, Mohr M, Zipse H, Eichberger R, Schnabe W (1999) J Photochem Photobiol A: Chem 125:47
30. Tsai FC, Chang CC, Liu CL, Chen WC, Jenekhe SA (2005) Macromolecules 38:1958
31. Xu J, Liu H, Pu S, Li F, Luo M (2006) Macromolecules 39:5611
32. Xu J, Hou J, Pu S, Nie G, Zhang S (2006) J Appl Polym Sci 101:539
33. Otero TF, de Larreta-Azelain E (1988) Polymer 29:1522
34. Pandey PC, Prakash R (1998) J Electrochem Soc 145:4103
35. Xu JK, Zhou WQ, Chen B, Pu SZ, Wang JW, Wan YQ (2006) J Polym Sci A: Polym Chem 44:1125
36. Sak-Bosnar M, Budimir MV, Kovac S, Kukulj D, Duic L (1992) J Polym Sci A: Polym Chem 30:1609
37. Xu JK, Nie GM, Zhang SS, Han XJ, Hou J, Pu SZ (2005) J Polym Sci A: Polym Chem 43:1444
38. Nie G, Xu J, Zhang S, Cai T, Han X (2006) J Appl Polym Sci 102:1877
39. Frisch MJ, Trucks GW, Schlegel HB et al (2003) GAUSSIAN 03, Revision D.01. Gaussian, Inc., Pittsburgh, PA
40. Scherf U, List EJW (2002) Adv Mater 14:477
41. Leclerc M (2001) J Polym Sci A: Polym Chem 39:2867
42. Neher D (2001) Macromol Rapid Commun 22:1365
43. Thieblemont JC, Brun A, Marty J, Planche MF, Calo P (1995) Polymer 36:1605