

Electrochemical Behavior of Chemically Prepared Ring-Substituted Polyanilines

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Polyaniline (PAN) has been known as a promising conducting polymer for technological applications. In research work electrochemically synthesized PAN has been frequently used since electropolymerization is convenient to prepare the polymer film with controllable thickness or doping on electrodes. However, the processibility of electrosynthesized PAN is too poor to produce large area devices because of its insolubility and infusibility. Recently, therefore, chemical polymerization has attracted a considerable attention^[1-3], especially suitably derivatized ring-substituted (e. g. alkyl or alkoxy) polyanilines have been synthesized, and their appreciable solubility in common organic solvents enable the preparation of film on industrial scale by casting. Moreover, emulsion polymerization reduces the amount of water in Pan, being useful for nonaqueous battery system. Although the physical and mechanistic properties of chemically prepared PAN, such as tensile properties, viscoelasticity and electrical conductivity, have been investigated, there are few studies on their electrochemical properties. In this paper, the electrochemical behavior of three chemically synthesized ring-substituted polyanilines, poly-*o*-toluidine (POT), poly-2,5-dimethoxyaniline (PDM An), and poly-*m*-chloroaniline (PClAn) are compared, and the effects of substituents are discussed.

1 Experimental

The polymers were obtained by chemical oxidation with potassium persulfate as oxidant in the solution containing sodium dodecylsulphate, all reagents were A. R grades and used as received. The procedure for preparation of POT, PDMA and PClAn will be given elsewhere in detail.

The molecular weight of polymer was measured by Waters-208 GPC, and IR and NMR(¹H) experiments were carried out by a Nicolet FT-IR spectrometer and a Varian Unityplus-500 NMR spectrometer. The characteristic spectroscopic data for the polymer products are as follows. POT: 3 359 (N-H), 2 916, 1 305 (-CH₃), 1 598, 1 494 (Ar-H), 1 565 cm⁻¹ (Ar=N⁺); δ = 2.1 ~ 2.3, δ = 6.4 ~ 7.2. PDMA: 3 335 (N-H), 2 924 (-CH₃), 2 859, 1 218 (Ar-O-CH₃),

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1 523, 1 032 (Ar), 1 592 cm^{-1} (Ar=N⁻); $\nu = 6.2 \sim 8.6$, $\nu = 3.7 \sim 4.2$. PCIAAn: 3 294 (N-H), 3 065, 1 572, 1 508 (Ar), 779 cm^{-1} (Ar-Cl); $\nu = 6.2 \sim 7.7$.

All the electrochemical experiments were carried out using CHI660 electrochemical instrument (CH company, USA) in a conventional three-electrode cell. The auxiliary electrode was a platinum foil and the reference electrode was a saturated calomel electrode (SCE). Polyaniline membrane electrodes were prepared by casting the DMF solution of respective polymer on platinum base electrodes, and the thickness of membrane was controlled by the amount of casting solution.

2 Results and Discussion

Generally speaking, polyaniline has three oxidation states^[4], i.e. fully reduced, intermediately (or partially) oxidized and fully oxidized, their existence depends on the nature of polymer, the potentials applied as well as the composition of solution. Fig. 1 shows the cyclic voltammograms of Pt electrodes coated with POT, PDMAAn and PCIAAn in 1 mol/L H_2SO_4 solution respectively, indicating that the substituents attached to phenyl ring have great influence on the electrochemistry of polymers. In the case of POT (curve a), the oxidation and reduction proceed by two steps, the first oxidation process at ~ 0.32 V where the emeraldine salt appears and correspondingly the conductivity increases, the second oxidation process near 0.55 V where pernigraniline form appears and then conductivity decreases gradually. These results are in agreement with that observed by Fujita et al^[5] for electrosynthesized POT electrodes in 1 mol/L HCl. Andrade et al^[6] reported the voltammograms of electrosynthesized POT electrodes in 1.5 mol/L H_2SO_4 + 1.5 mol/L HClO_4 , an anodic peak found near 0.3 V, but the upper limit of scanning potential was controlled lower than 0.5 V. This anodic peak should correspond to the first oxidation process. For PDMAAn (curve b), only one anodic peak displays at 0.06 V, implying that the intermediately oxidized state is unstable. Lastly, no redox peak appears on the voltammogram for PCIAAn (curve c).

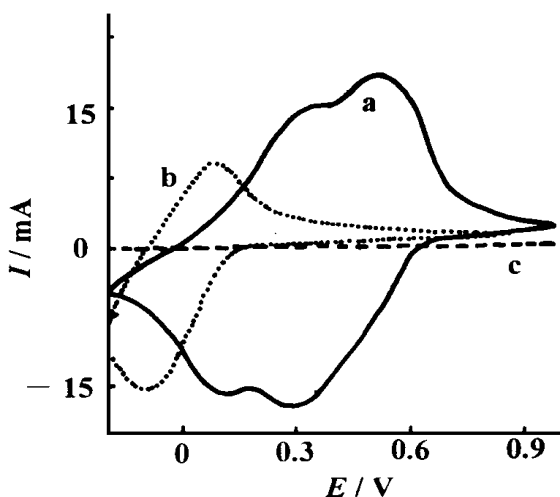


Fig. 1 Voltammograms of Pt electrodes coated with POT (a), PDMAAn (b), PCIAAn (c) in 1 mol/L H_2SO_4 solution. Scan rate 50 mV/s.

Electrochemical impedance spectroscopy (EIS) has been an important technique for study of conducting polymers. Fig. 2 are the ac impedance diagrams (Nyquist plot) for the three polymers at different potentials, the changes of impedance with potentials are relative to the voltammograms in Fig. 1. For example, the Nyquist plot of POT at -0.2 V displays a section of hemi-cy-

cle, from which the sum of solution resistance and polymer film resistance is estimated as 1×10^3 ohm, predicting the polymer is in less electroactive state, on the contrary, the Nyquist plot of POT at 0.2 V exhibits the electron transfer occurring at the polymer electrode. Similar analysis can be done for the other two polymer electrodes. The physical interpretation of ac impedance diagrams depends greatly on the choice of effective circuit. Vorotynev et al^[7] proposed a model for the electrodes coated with electroactive polymer films which takes into account both diffusion-migration of ionic and electronic charge carriers inside the film and charge-transfer across metal/polymer and polymer / electrolyte interfaces. By following their model and fitting the experimental data with Marquardt-Levenberg algorithm, the parameters such as electron diffusion coefficient in the film, D_e , can be obtained. In preliminary work we found the values of D_e decrease in the order of POT, PDMA_n and PCIA_n.

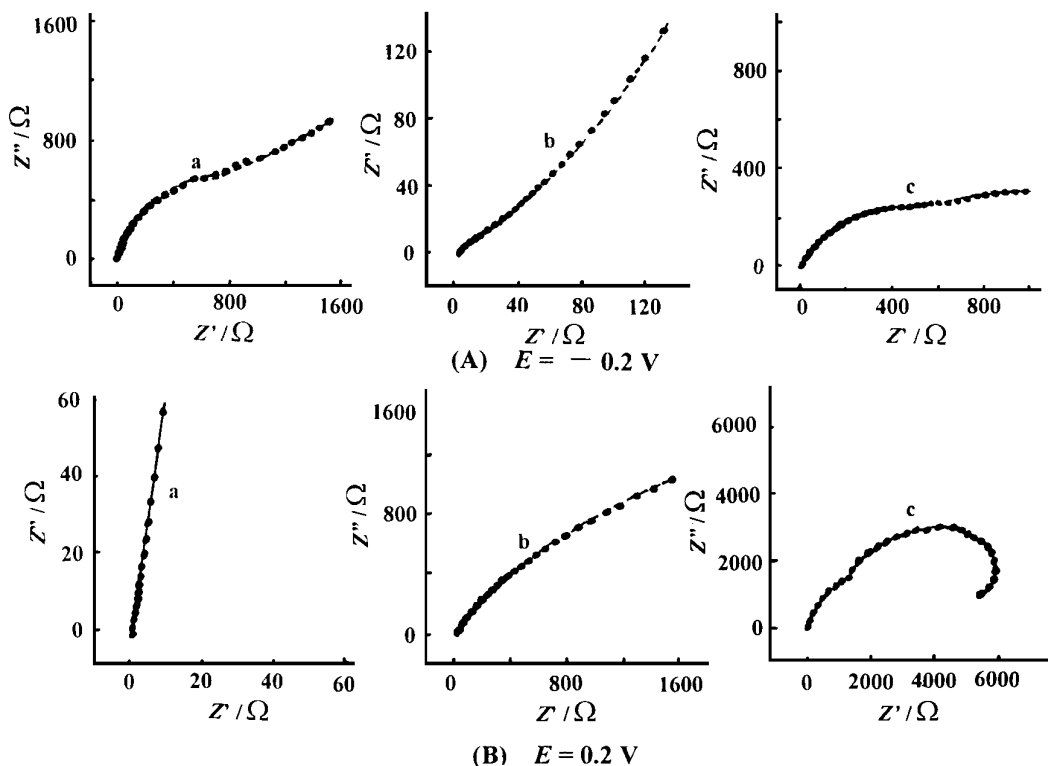


Fig. 2 Nyquist representation of the ac impedance for Pt electrodes coated with POT (a), PDMA_n (b) and PCIA_n (c) in 1 mol/L H₂SO₄ solution

ac frequency: $0.05 \sim 1 \times 10^5$ Hz, electrode potential: (A) - 0.2 V, (B) 0.2 V

The effects of substituents on electrochemical properties of polyanilines can be explained by either electronic effect or steric effect. Both alkyl and alkoxy are electron-donating substituents, whereas Cl is electron-withdrawing. Several authors considered the polyanilines with electron-withdrawing substituents as insulators^[8,9]. The protonation is essential to induce a conduction in

polyanilines, and strong electron-withdrawing groups in polyanilines render this protonation difficult. The structure of PDMA_n is hardly possible to be planar due to steric hindrance by two methoxy groups, one of which is at ortho position with respect to -NH₂-group (see Fig. 3), this may be the reason why its intermediately oxidized state is unstable. It should be also pointed that substituents can influence the polymerization reaction, and lead to the significant difference in molecular weight of each polymer.

According to measurement of molecular weight, the number of unit in a PCIAN chain was found about 13, smaller than that in POT and PDMA_n. Short chain length implies the easy interception of electron transfer in PCIAN matrix. In principle the redox potentials of substituted polymers can be correlated by Hammett law, for this purpose, however, more substituted polyanilines must be investigated.

The electroactivities of polymers manifest themselves in the reaction of redox species on their coated electrodes. Fig. 4 depicts the cyclic voltammograms in 0.5 mol/L K₃[Fe(CN)₆], obviously the reduction of ferricyanide ion is dependent on the nature of polymer. The electron-transfer reactions between conducting polymers and redox ions in electrolytes may take place at the polymer / electrolyte solution interface, or in the polymer film, or at the substrate electrode. The curve c in Fig. 4 indicates that PCIAN is not only insulating but also impenetrable for ferricyanide ion so that the reduction current is negligible. On the other hand, the reduction currents at POT and PDMA_n electrodes are larger since these polymers are electroactive in the potential region for ferricyanide reduction. From the voltammogram of a bare platinum electrode in 0.5 mol/L K₃[Fe(CN)₆], an anodic peak for ferrocyanide oxidation was found at 0.45 V. Therefore, the difference of curve a with curve b can be attributed to that PDMA_n is in insulating state at more positive potentials.

In conclusion, substituents play an important role in tuning electric or electrochemical properties of polyanilines. For different technological applications we need to develop the polymers

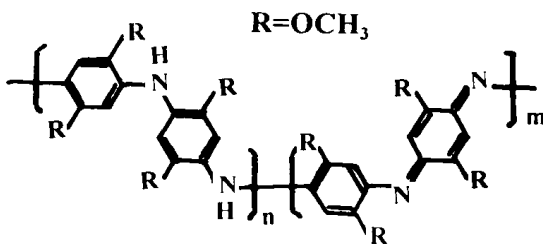


Fig. 3 Structure of PDMA_n
(R = CH₃O)

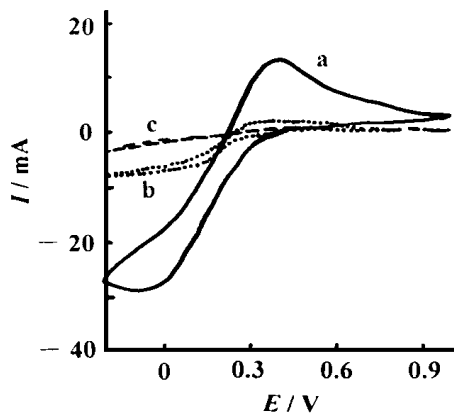


Fig. 4 Voltammograms of Pt electrodes coated with POT (curve a), PDMA_n (b), PCIAN (c) in 0.5 mol/L K₃[Fe(CN)₆], scan rate 50 mV/s

with either high or low conductivity, therefore it is worthy to deeply study the effects of substituents on properties of polymers, the further investigations are in progress.

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化学合成环取代聚苯胺的电化学行为

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摘要 聚邻甲苯胺(POT)、聚2,5-二甲氧苯胺(PDMA_n)和聚间氯代苯胺(PClAn)由化学法合成而得,用它们的二甲基甲酰胺溶液在铂上成膜以制得聚合物修饰电极.循环伏安实验表明:在1 mol/L H₂SO₄中,POT的氧化还原分两步进行,呈现两对氧化还原峰,PDMA_n只在较负的电位区呈现两对氧化还原峰,而PClAn不呈氧化还原活性.不同电位下的交流阻抗特征与循环伏安图相对应.三种聚合物膜电极在0.5 mol/L K₃[Fe(CN)₆]溶液中的伏安图也证明铁氰离子的还原速度依POT > PDMA_n > PClAn的顺序而下降.环取代基的影响用电子效应和几何效应进行解释.可溶性聚苯胺便于制作大面积器件,环取代基对调节聚苯胺的电化学性能具有重要作用,值得进一步研究.

关键词 导电聚合物,聚苯胺,可溶性聚合物,电化学过程