

Synthesis, Characterization and SEESR Spectroscopic Investigations of Indole/Aniline copolymers

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ABSTRACT: Indole/aniline copolymers were synthesized electrochemically and the polymerization mechanism was investigated via *in-situ* simultaneous electrochemical electron spin resonance (SEESR) spectroscopy. The Radical cationic intermediates of substituted indole and aniline were detected during the electrochemical oxidation. The resulting ESR-spectra with hyperfine splitting were simulated and radicalic structures were identified. It was suggested that the polymerization occurs over positions C-3

and C-6 of indole molecule and over the nitrogen and *para*-position of aniline. Furthermore, aniline, indole and aniline/indole copolymers were investigated depending on applied potential via electrochemical impedance spectroscopy (EIS). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3044–3049, 2008

Key words: polyaniline; polyindole; aniline/indole copolymer; SEESR-spectroscopy; polymerization mechanism

INTRODUCTION

Conducting polymers are used widely in many technological areas such as diodes, transistors, rechargeable batteries, capacitors, electrocatalysts, and sensors.^{1–3} Among these type of materials, polyaniline (PAn), polypyrrole (PPy), polythiophene (PTy) and polyindole (PIn) etc. were studied intensively because of their easy processibility and relative stability.⁴ For the polymerization and conductivity of the polymer film, the presence of the π -electrons in the monomer is essential. In contrast to such a wide range of applicability of the conducting polymeric materials, the number of the appropriate monomers is extremely limited which causes a deficit for the preparation of new conducting materials.

Because of the limited number of the monomers, it is a legitimate way to produce copolymers with monomers, whose homopolymers are well known. In previous studies, we introduced different copolymers such as pyrrole/aniline, indole/pyrrole in different media.^{5,6}

Indole has aniline type of configuration in its chemical structure. Especially, these characteristic of indole led us to study its electrochemistry and its copolymerization mechanism with aniline.

In the present article, indole/aniline copolymers were synthesized and the copolymerization mechanism was studied by SEESR spectroscopy. Furthermore, in that course, we employed EIS to study the behaviors and the characteristics of the synthesized materials, for the first time.

EXPERIMENTAL

Aniline (Merck) was freshly distilled before use and indole (Merck) was employed without any purification. 0.1M solution of aniline and indole in acetonitrile/0.1M LiClO₄ were mixed in different mol/mol ratios (1 : 1; 1 : 2; 1 : 3; 1 : 4) and the polymer films were synthesized potentiodynamically between –0.2 and + 1300 mV. Electrochemical measurements were carried out with an electrochemical work station (CHI-660A) in a three electrode H-cell. The working and the counter electrodes were Pt-plates (1 cm²) and the reference electrode was a Ag/AgCl/Cl[–] throughout the measurements. The *in situ* conductivity and the SEESR measurements (Bruker 200 D ESR-spectrometer) were carried out as described before.⁶

The electrochemical impedance spectroscopic measurements were done at various potential values and with various copolymer constitutions. The EIS measurements were carried out at 25°C at different potentials in a frequency range from 10 kHz to 0.1 Hz in acetonitrile/0.1M LiClO₄. Some of the equivalent circuits proposed earlier^{7–10} were used to fit the experimental data (software ZView 2.1b, delivered by Scribner Associates Inc., USA).

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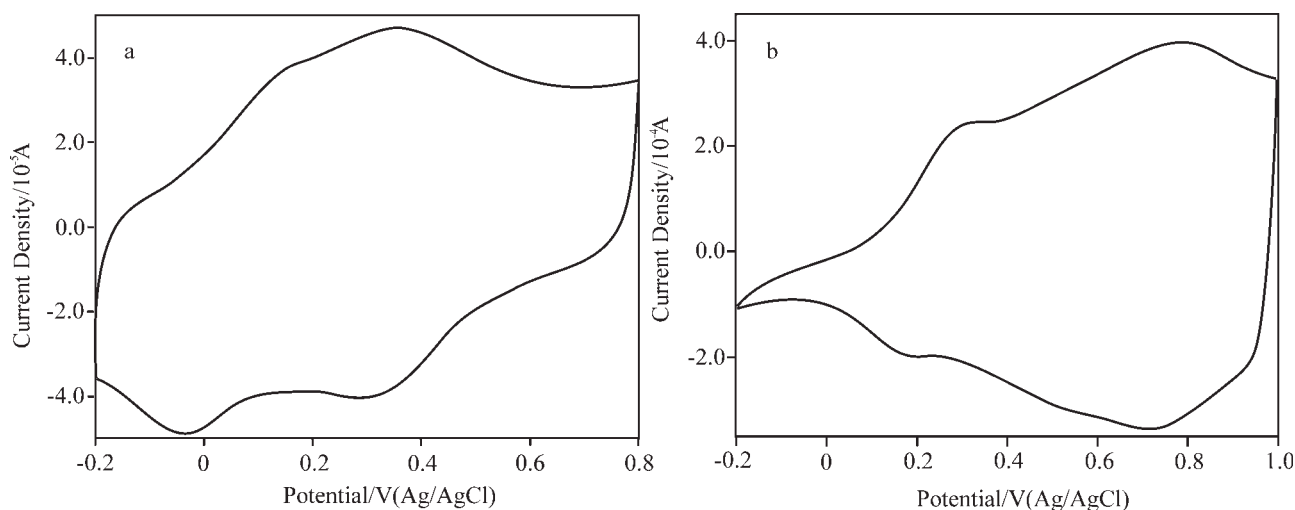


Figure 1 The cyclic voltammograms of polyaniline and polyindole on Pt electrodes with a scan rate of 50 mV/s in AN/LiClO₄ supporting electrolyte; (a)-polyaniline; (b)-polyindole.

RESULTS AND DISCUSSION

In acetonitrile/LiClO₄ electrolyte system, the cyclic voltammogram of aniline shows an oxidation wave at ca 360 mV versus Ag/AgCl on a Pt electrode [Fig. 1(a)]. Polyindole has redox waves at \sim 300 and 750 mV [Fig. 1(b)].

As can be seen in the cyclic voltammograms in Figure 1(a,b), the main oxidation waves in the cyclic voltammograms of both polymers have \sim 380 mV potential difference from each other. This difference in the peak potential changes gradually when a copolymer was synthesized. The cyclic voltammogram of a copolymer (1 : 1) is presented as an example in Figure 2.

In the cyclic voltammogram of aniline/indole copolymer (Fig. 2), a redox wave was observed at 360 mV. A new, black electroactive material was obtained from the oxidation of the mixed solution. The peak potentials of the synthesized materials are presented in Table I.

The peak potentials of the synthesized copolymers shift to more positive values with increasing indole concentration in the electrolyte solution (Table I). This indicates that with increasing indole concentration, the copolymer gets more and more polyindole character.

The polymerization mechanisms of indole and of aniline were described previously.^{11,12} Radical cationic intermediates of the monomers were assumed during the electrooxidation in these studies. However, no ESR-spectrum of these radical cationic intermediates could have been recorded so far. Now, we have investigated the mechanism of the aniline/indole copolymer formation by simultaneous electrochemical electron spin resonance spectroscopy. A record of an ESR-spectrum of unsubstituted aniline

and/or of indole was not possible, due to the fast polymerization of these monomers on the electrode surface. The coating of the electrode surface with a polymer film causes a low concentration of paramagnetic intermediates formed during the oxidation. In that case, the polymer films show only their own typical singlet in the ESR-spectrum.

To find out the structure of the radical cationic species formed during the anodic oxidation, we used *N,N*-dimethylaniline. In that case, the hydrogen atoms of the amino group in aniline were substituted versus methyl groups. This should prevent the fast polymerization and the fast delocalization of the free radical. In fact, when *N,N*-dimethylaniline was used, we were able to record *in situ* a SEESR-signal for the first time which is presented in Figure 3.

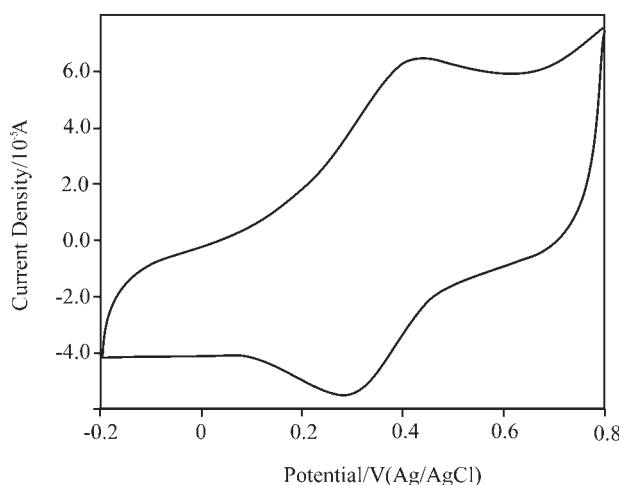


Figure 2 The cyclic voltammogram of the aniline/indole copolymer (1 : 1) on Pt-plate electrode in AN/LiCl₄ electrolyte system. $V = 50$ mV/s.

TABLE I
The Anodic Peak Potentials of Polyaniline, Polyindole, and Synthesized Copolymers in AN/LiClO₄ Supporting Electrolyte

Polymer	PAn : PIn								
	PAn	PIn	1 : 1	1 : 2	1 : 3	1 : 4	2 : 1	3 : 1	4 : 1
Peak potential mV (Ag/AgCl)	380	750	360	400	400	400	600	640	750

The deviations in the shape of the ESR-signal might have been resulted from the high magnetic field applied as well as the reflection of the microwave from the electrode surface in the cylindrical resonator. The number of the lines in ESR spectra was calculated according to the eq. (1)

$$N = \prod_k (2n_k + I_k + 1) \quad (1)$$

where N is the total number of the lines, k is the number of the equivalent nucleus, I is the atom spin and n is the total number of nucleus in a molecule. By using the eq. (1), 378 lines were calculated in the ESR-spectrum of *N,N*-dimethylaniline theoretically, where the nitrogen atom, methyl groups and the hydrogen atoms in the six-membered ring are involved in the coupling process. Because of the overlapping of some signals, all 378 lines could not be seen in the spectrum. For the simulation of the

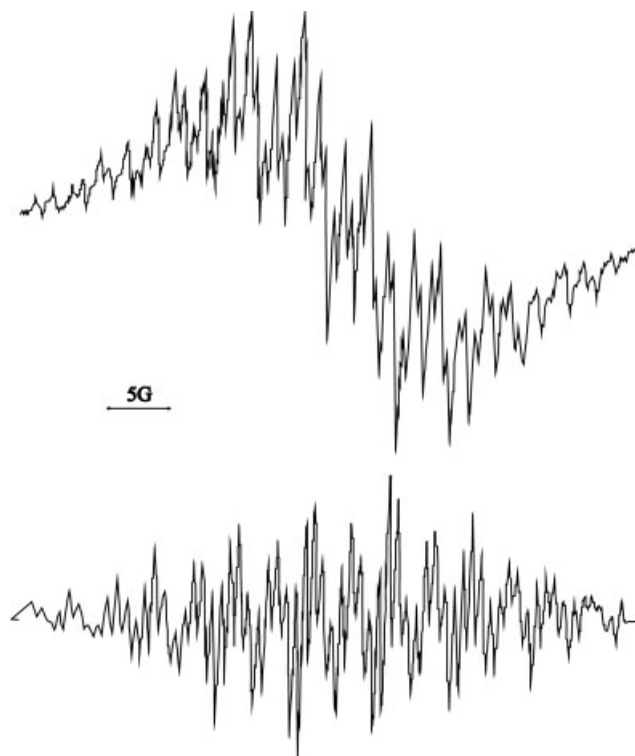


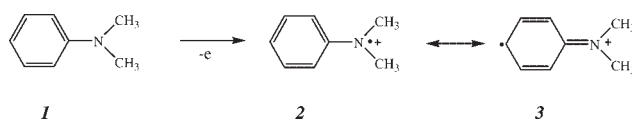
Figure 3 (a) The SEESR-spectrum of *N,N*-dimethylaniline recorded on a Pt electrode in AN/LiClO₄ solution; (b) simulated spectrum.

ESR-spectrum, the following coupling constants are used

$$a_N = 7.75; \quad a_{\text{CH}_3} = 8.54 \text{ G}; \quad a_o = 3.71 \text{ G};$$

$$a_m = 0.95 \text{ G}; \quad a_p = 6.90 \text{ G}$$

The formation and the structure of the radical cationic intermediates can be formulated as follows:



At the first step in the mechanism, an electron abstracted from the *N,N*-dimethylaniline, **1**, and a radical cationic intermediate **2** is formed. Especially, the quinonoid structure **3** is plausible because the positive charge localized on the nitrogen atom which can compensate it easily and the free electron is localized in the *para* position of the ring system. The large coupling constant of 6.9 G supports this suggestion as well.

Indole derivatives, such as *N*-methylindole and 2-methylindole polymerize under anodic conditions and give a polymer film on the electrode surface. When the 2 position (2-methylindole) was substituted with methylgroup, the polymerization became slower and the record of an *in situ* SEESR spectrum was succeeded (Fig. 4). Further substituted indoles,

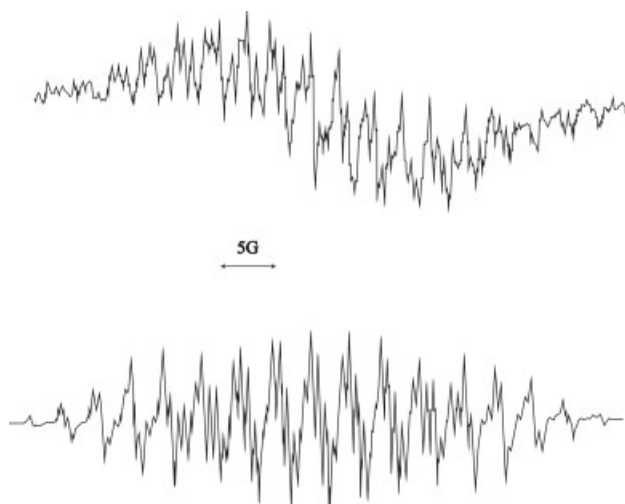


Figure 4 (a) The ESR-spectrum of 2-methylindole; (b) simulated spectrum.

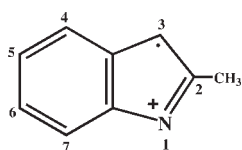
e.g., 3-methylindole 2,3-dimethylindole and 3,6-dimethylindole do not polymerize on the Pt-electrode in acetonitrile/LiClO₄ electrolyte.

Through the experiments with 2-methylindole, we could obtain an ESR-spectrum with hyperfine splitting. However, the recorded spectrum has a slight deviation in its shape and the resolution is not the best, because of the aforementioned reasons. Additionally, 2-methylindole polymerizes continuously during the record of the spectrum and this causes disturbances for recording-process, too. The following coupling-constants were used for the simulation of ESR spectrum of 2-methylindole radical cation

$$a_N = 5.20 \text{ G}; a_H = 4.0 \text{ G}; a_H = 1.80 \text{ G}; a_H = 1.80 \text{ G}$$

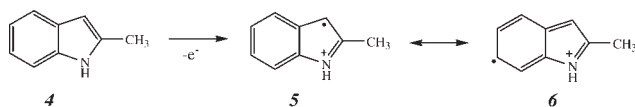
$$a_{CH_3} = 1.50 \text{ G}; a_H = 1.75 \text{ G}; a_H = 1.60 \text{ G}; a_H = 1.55 \text{ G}$$

With simulation data, the structure of the radical cationic species could be suggested



Suggested structure of 2-methylindole radical cation

After an electron abstraction from 2-dimethylindole, **4**, the radical cationic species **5** is formed. In that structure, the free electron is on the 3-position and the positive charge is localized on the nitrogen atom which can compensate the positive charge easily and the six-membered ring keeps its aromatic character as well. The resonance structure **6** is also a plausible one, because the conjugated double-bonds leads to a quinonoid structure in this species.



Our best resulted ESR-spectrum was obtained as 1,2-dimethylindole was used, which polymerizes as well. However, the polymerization rate of this substance appears to be lower than of 2-methylindole as described in.⁵

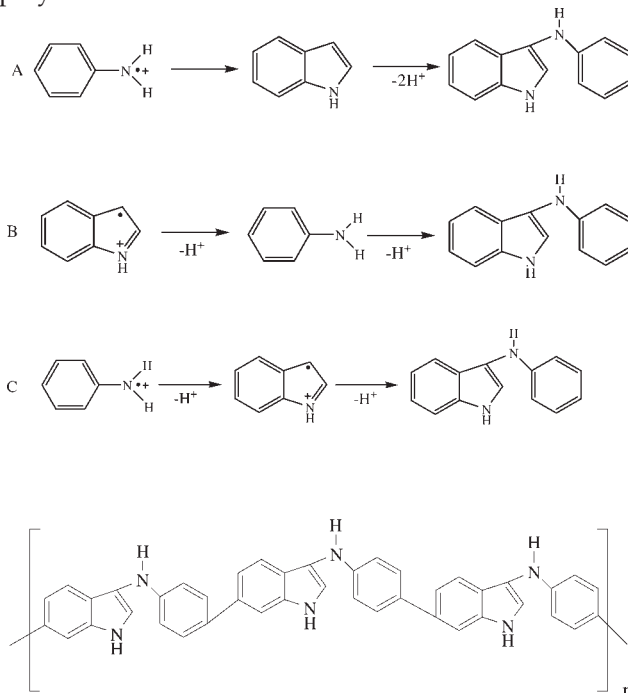
The ring positions of the indole molecule differ in their reactivity. Sundberg has reported that the 3-position of the ring is much more reactive than others. The second reactive position is C-2 and C-7 does not take part in any reaction.¹³ McCord et al. investigated indole molecule intensively with laser chemically induced dynamic nuclear polarization (LCIDNP) and reported the same corresponding results to that of Sundbergs.¹⁴ Cheek and Nelson found for the reactivity of the indole ring after investigations with in 6-

position deuteriated 2,3-diphenylindole via ²D-NMR spectroscopy that the dimerization reaction occurs over the 6 and the 3-position of the ring.¹⁵ Billaud et al. reported that the 3-position as well as the C-2 the most reactive positions of the five membered ring.¹⁶ Also our SEESR spectroscopic results lead to the conclusion that the coupling positions of the ring could mainly be 3 and 6. With the consideration all these results, the reactivity of each position in the ring system could be written as follows:

$$3 > 2 > 6-4 > 1 > 5 > 7$$

In fact, we could observe no polymerization, as 3-methylindole, 2,3-dimethylindole and 3,6-dimethylindole were employed during the oxidation. Additionally, different studies based on MO-calculations related to the reactivity of the ring positions of the molecule with respect to its changes have revealed the same result as well.^{17,18}

The polymerization of aniline occurs in idealized form over the nitrogen atom and the *para*-position of the ring. Depending on all those aspects, there are three possibilities to obtain the structure of the polymer:



The suggested structure of the copolymer film.

First, an aniline radical cation can be added on the indole molecule (path A). Second, an indole radical cation can be added on an aniline molecule (path B) and finally, an indole radical cation can recombine with an aniline radical cation (path C). In all cases, whichever mechanism is considered, it leads to the same product and further electron transfer steps lead to the polymerization of these species.

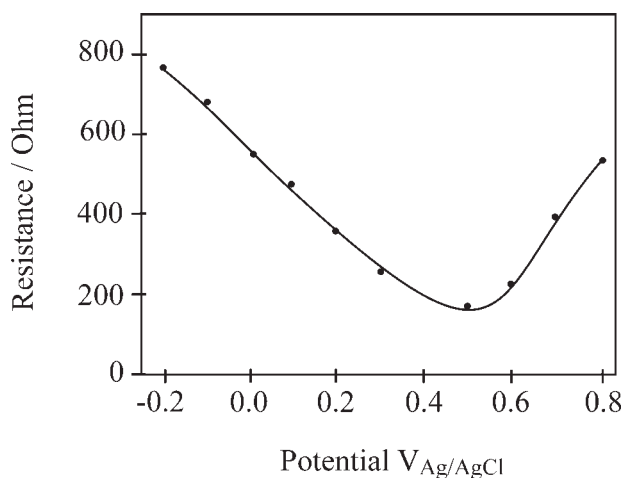


Figure 5 The resistance-potential curve of the PAN/PIIn (1 : 1) copolymer film on Pt in AN/LiClO₄ electrolyte.

The *in situ* conductivity measurements of the copolymer film depending on the potential were carried out by using of a Wheatstone Bridge as described before.⁵ In that previous study, bulk polymers have shown in their conductivity a dependence on the applied potential. Also here, the synthesized

copolymer behaves like their homopolymers, polyaniline and polyindole, and shows a potential dependence in the conductivity.

The resistance-potential curve of the PAN/PIIn (1 : 1) copolymer gives a minimum at ~ 0.4 V (Fig. 5). This potential corresponds to the maximum in the cyclic voltamogram and indicates that at this potential, the copolymer has its maximum conductivity. In the overoxidation region the resistance increases, as expected. Limits in resistance could be obtained due to the fact that polyaniline and polyindole are not durable at more positive potentials because of the overoxidation. It is well-known that fully oxidized or fully reduced films are insulators, while partially oxidized films are excellent conductors. Detailed information about the resistance-potential curve can be found in the papers of Glarum et al.,¹⁹ Bredas et al.²⁰ and Genies et al.^{21–22}

In connection with *in situ* resistance measurements, the electrochemical impedance spectroscopy (EIS) delivers a simple method to attain information about the conductivity of polymer films coated on the electrode surface. In that case, the charge transfer resistance inbetween polymer/electrode layers can be taken as the parameter versus changing potential.

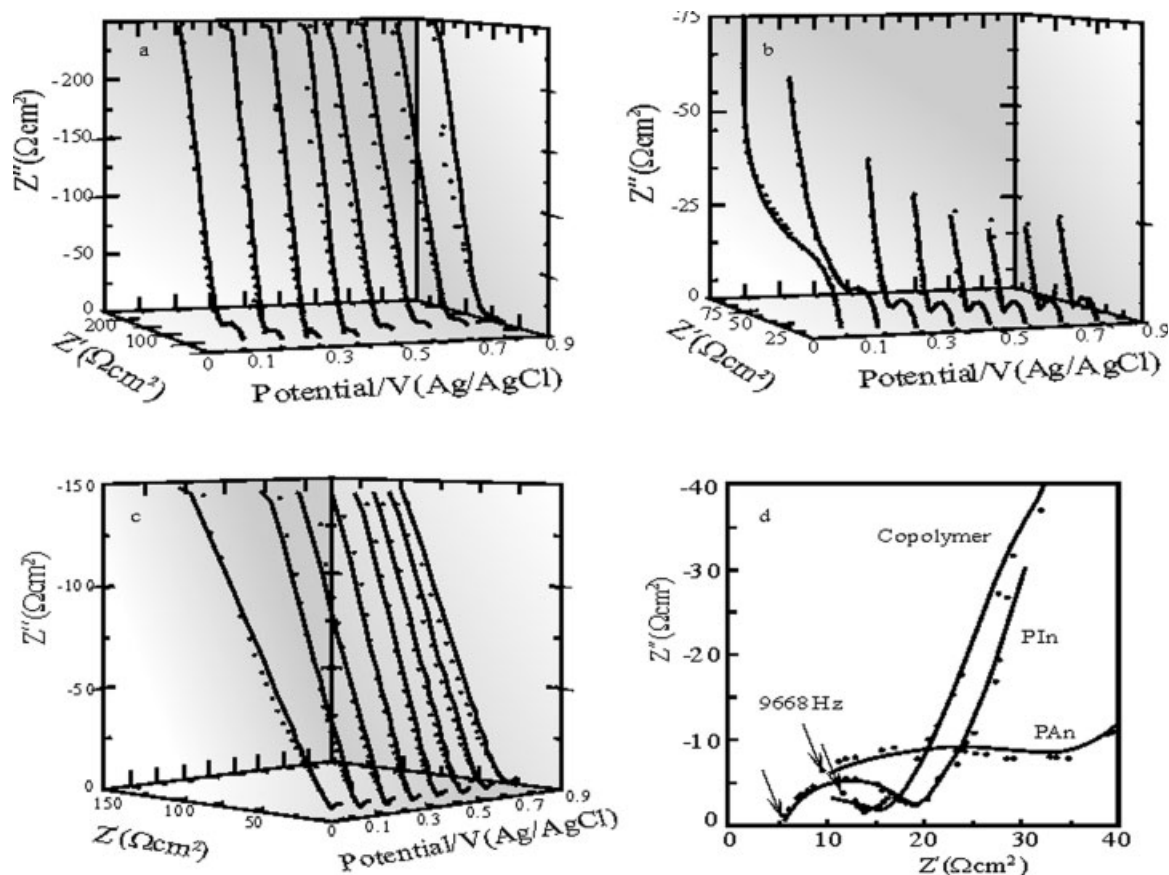


Figure 6 The ac-impedance response of polymer films depend on the applied potential in acetonitrile + LiClO₄. (a) polyindole; (b) polyaniline; (c) aniline/indole copolymer (1 : 1); (d)-three Nyquist diagrams together at 0.4 V

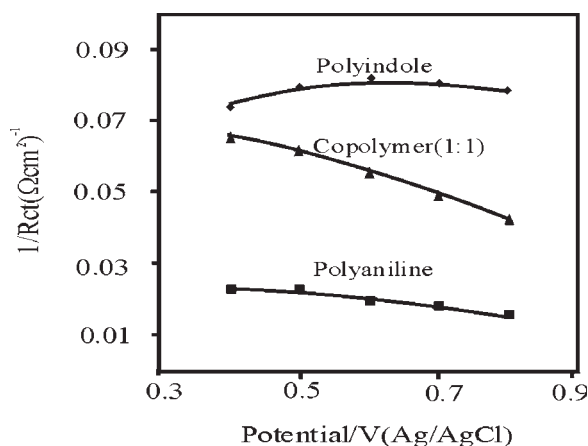


Figure 7 The changes in the charge transfer resistance, R_{ct} , are represented as a function of the applied potential of polyaniline, polyindole and aniline/indole (1 : 1) copolymer. The curves are registered in acetonitrile/0.1M LiClO₄ solution.

In Figure 6(a–c), the resistance values change gradually depending on the applied potential in semicircles. Polyaniline [Fig. 6(b)] has the greatest resistance values in aprotic medium. This is an expected result, because polyaniline needs protons for its conductivity and it conducts better in protic solutions, i.e., in aqueous H₂SO₄. The conductivity of Polyindole is higher in acetonitrile/LiClO₄ electrolyte system [Fig. 6(a)]. The synthesized copolymer (1 : 1) is placed between both homopolymers regarding charge transfer resistance values [Fig. 6(c)]. In Figure 6(d), all three Nyquist diagrams are represented together at the same potential value, to represent the differences in behavior of the polymers clearly.

Also in Figure 7, it can be seen that polyindole is the best conductive material at potentials more positive than ~ 0.6 V in aprotic medium and polyaniline shows here its best conductivity between ~ 0.4 and 0.5 V. The copolymer 1 : 1 shows its maximum conductivity at ~ 0.4 V, although its curve is between the curves of homopolymers (Fig. 7). All these potentials correspond to peak potentials in cyclic voltammograms, as well.

CONCLUSIONS

Aniline and indole were mixed in different ratios and polymerized potentiodynamically on Pt electrodes in acetonitrile/LiClO₄ electrolyte. According to cyclic voltammograms and *in situ* conductivity meas-

urements, new conducting materials are synthesized. The polymerization mechanism of the reaction was studied by simultaneous electrochemical electron spin resonance spectroscopy. No ESR spectra of the unsubstituted monomers could be recorded due to the fast polymerization of both monomers, aniline and indole. However, as the substitute derivatives of aniline (*N,N*-dimethylaniline) and indole (2-methylindole) were used, we could receive ESR-spectra with hyperfine splitting. In the suggested polymerization mechanism, aniline prefers the polymerization over the nitrogen atom and the *para*-position of the ring, and indole molecule reacts over positions C-3 and C-6. The *in situ* conductivity measurements of the copolymers were carried out with a Wheatstonebridge and by using electrochemical impedance spectroscopy as well. The results of these measurements reveal that the copolymers synthesized are also conducting materials having comparable characteristics like their homopolymers.

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