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PARA-PHENYLENE DERIVATIVES OBTAINED BY PLASMA POLYMERIZATION TECHNIQUE

C. NASTASE[a], A. DUMITRU[a], V. BARNA[b], F. NASTASE[a*]
[a]*Polymer Science Group, University of Bucharest, PO Box MG-40, 077125 Magurele, Bucharest, Romania*
[b]*Faculty of Physics, University of Bucharest, PO Box MG-11, 077125 Magurele, Bucharest, Romania*

Obtaining of conjugate oligomers/polymers as thin films with a low degree of cross-linkage and semiconducting properties deposited by plasma polymerization represents an interesting challenge. A plasma-polymerization experimental set-up is developed to use liquid monomers and solid-liquid mixtures as starting materials. In this work, mixtures of p-xylene monomer with isolated polycyclic aromatic precursors (biphenyl and quarterphenyl) are plasma polymerized to obtain polymer films with specific properties related to organic electronic applications. The characteristics of obtained films are analyzed by FT-IR spectroscopy, atomic force microscopy (AFM). In order to explain the conduction mechanism the current-voltage characteristics in asymmetric electrode configuration are investigated.

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1. Introduction

A wide research on the field of plasma polymerization processes has been already achieved [1-3]. The main reason for applying the plasma polymerization technique is that thin, stable, and pinhole-free films are obtained with good adherence to many substrates. Nevertheless, in general are obtained polymer films with poor predictability of the chemical structure, high degree of cross-linkage and very high electrical resistivity [4,5]. Based on many similarities and results with chemical synthesized poly(p-phenylene) (PPP) and poly(p-phenylenevinylene) (PPV) we use p-xylene, biphenyl and quaterphenyl as precursors in an DC-glow discharge reactor for the synthesis of PPP-like films by plasma polymerization.

Since Kovacic's synthesis of PPP, there has been a considerable interest for this class of conjugated polymers due to theirs exceptional properties: thermal stability in neutral state, resistance to environmental oxidation and irradiation and a very wide conductivity range (10^{-18}-10^{2} Scm^{-1}) [6]. Wnek et al reported the syntesis of PPV through direct chemical polymerization reactions [7]. Both materials were chemically synthesized in powder form. The reported results regarding the electropolymerization of benzene as precursor for PPP synthesis and sulfonium or chloride salts for PPV synthesis proved that this is not an appropriate method for film processing [8,9].

The derivative poly [2-methoxy-5-(2'-ethyl-hexyloxy) phenylene vinylene] (MEH-PPV), a solution-processable to PPV still did not reach the performance to be successfully applied in the field of polymer light emitting diodes (PLED). MEH-PPV is an important member of the PPV family because of the excellent processability and favorable electronic and spectroscopic properties. The major drawback of these materials is the multi step synthesis for difunctionalization and stringent process requirements of the condensation polymerization [10].

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[*] Corresponding author: florin.nastase@psg.unibuc.ro

The investigations were extended to make these processable, particularly in thin continuous and homogeneous films [11-15].

The main interest for PPP and PPV is due to theirs common characteristics: n- and p-doping state, non degenerate ground state, similar redox potential, electroluminescence and non linear optical activity (for PPV) [16, 17]. PPP already gained a stable application as electrode in pressed pellet for non-aqueous batteries [18].

Many applications claim submicron films. Thin films at nanometric level are required for electronic applications (materials for electroluminescent devices); the power storage capacity of rechargeable batteries needs PPP thin films; microelectrodes and membranes in redox reactions [19]. Particularly, during the polymer functionalization in order to obtain solution processable properties, the electronic properties become loosely.

Therefore, the chemical and electrochemical synthesis methods give rise to insoluble powders in all common solvents making these compounds not viable for various applications. Moreover, the partial solubility of various PPP derivatives obtained by chemical and electrochemical synthesis includes additional intermediate reactions with the attachment of side polar groups.

The electrochemical synthesis leads to unidentified layers on the electrode surface and insoluble PPP precipitate in solution [20,21]. PPP films with good properties have been obtained by electrochemical polymerization of biphenyl in different organic media [22-24]. Also using Kovacic and other derivative methods, the biphenyl and higher aromatics were obtained. PPV thin films prepared by chemical vapor deposition polymerization were also reported. Although, the brominated PPV film showed the reduction of the polymer rigidity by saturating the vinylene groups of PPV and the insolubility preservation indicated the cross-linking reaction occurring during polymerization [11]. The various PPV derivatives with phenyl substituents have been as well synthesized by the Gilch polymerization method [12].

Based on the above considerations, we introduce an alternative method to chemical synthesis represented by the plasma polymerization technique. In spite of its simplicity this method does not allow a good control over reactions in the plasma bulk because of electron-atoms-ions collisions. The main advantage is the synthesis of thin films ready for use having a controlled thickness, while not sharing the properties of the films developed by chemical synthesis methods. That is a consequence of the high discharge power value that increases the fragmentation degree of the precursors and of the interactions becoming more energetic. With increasing degree of fragmentation a smaller proportion of monomer molecules retain their original chemical structure.

These polymeric films developed by plasma polymerization, could be further successfully used in our research group for designing soft matter responsive systems with liquid crystal composites, for which we have expertise and have already done numerous molecular simulations [25-29].

This paper reports the plasma polymerization of p-xylene with biphenyl (pX-B) and p-xylene with quarterphenyl (pX-Q) mixtures compared with p-xylene plasma polymerized thin films (pX) and proves the similarity of the obtained films' structure and morphology with respect to the PPP. The thin films obtained via plasma polymerization were fully characterized by AFM, FT-IR spectroscopy and I-V electrical measurements.

2. Experimental details

Our designed DC-glow discharge reactor avoids many disadvantages of the plasma polymerization process. In our configuration the monomer is directly sprayed in plasma stream by a special model atomizer coupled on the discharge tube.

In this work the thin films obtained from p-xylene, biphenyl with p-xylene and quaterphenyl with p-xylene as precursors were deposited with special arrangement. When the monomer is introduced in reactor, the residence time of molecules in the plasma stream can be controlled by adjustment of pressure in deposition chamber. If this parameter is suitable chosen, then a high radical concentration can be induced close to the substrate. In this way a lot of destructive phenomena are avoided: pinhole, monomer destruction, excess of ion radicals, etc. In addition, a very fine control of monomer dosage is possible.

The substrate (silicon 100) was positioned at the cathode exit in downstream plasma. The plasma was initiated in Ar (flow 0.138 sccm/s) and for each series of experiments the physical parameters were setup in conformity with Table 1.

Table 1. DC deposition conditions

Precursor	**Plasma power [W]**		**Plasma potential [V]**		**pressure [Pa]**		**Time of deposition [s]**	**Plasma polymer**
	initial	**final**	**initial**	**final**	**initial**	**final**		
Para-xylene	3.7	3.8	370	630	6.7	26.7	420	pX
Para-xylene /biphenyl	4.5	2.9	450	680	6.7	26.7	420	pX-B
Para-xylene /quaterphenyl	4	3.25	400	650	6.7	26.7	420	pX-Q

The solution concentration for p-xylene-biphenyl was set at 0.16 g/0.5ml and for quarter-phenyl at 0.0703g/0.5ml respectively. The dosage of the precursors was set at 0.0375ml/min for 7 min.

FT-IR spectra were acquired on a Thermo-Nicolet Nexus instrument with a resolution of 8 cm^{-1}. AFM measurements were performed by means of a Quesant Instrument Corporation apparatus (model Nomad). I-V characteristics were measured with a homemade assembly device.

3. Results and discussions

3.1. AFM characterizations

The uniformity in the deposition process and surface morphology for the thin films were analyzed by AFM investigations. The AFM images were evaluated on multiple scans on a 5x5 micron area taken in different locations of the films. Firstly, we notice a good uniformity of pX and pX-Q films and a relatively poor uniformity in the case of the pX-B films. Figure 1 shows films with specific morphology and distinctive features. For pX the smoothness, counted of RMS deviation, is about 1.82 nm. That is a very good homogeneous surface topography and gives a first information about the composition and structure, which is constant in the film bulk.

For pX-B the surface topography is considerably changed. The film shows a uniform granular layer that is similar to the other class of conjugated polymers. The surfaces are cover by small droplets. These can be considered nucleation centers for the polymer films initiated in the plasma volume and on substrate. For pX-Q the surface topography shows large plate-like islands close to a lamella stacking. No pinholes are observed in the samples.

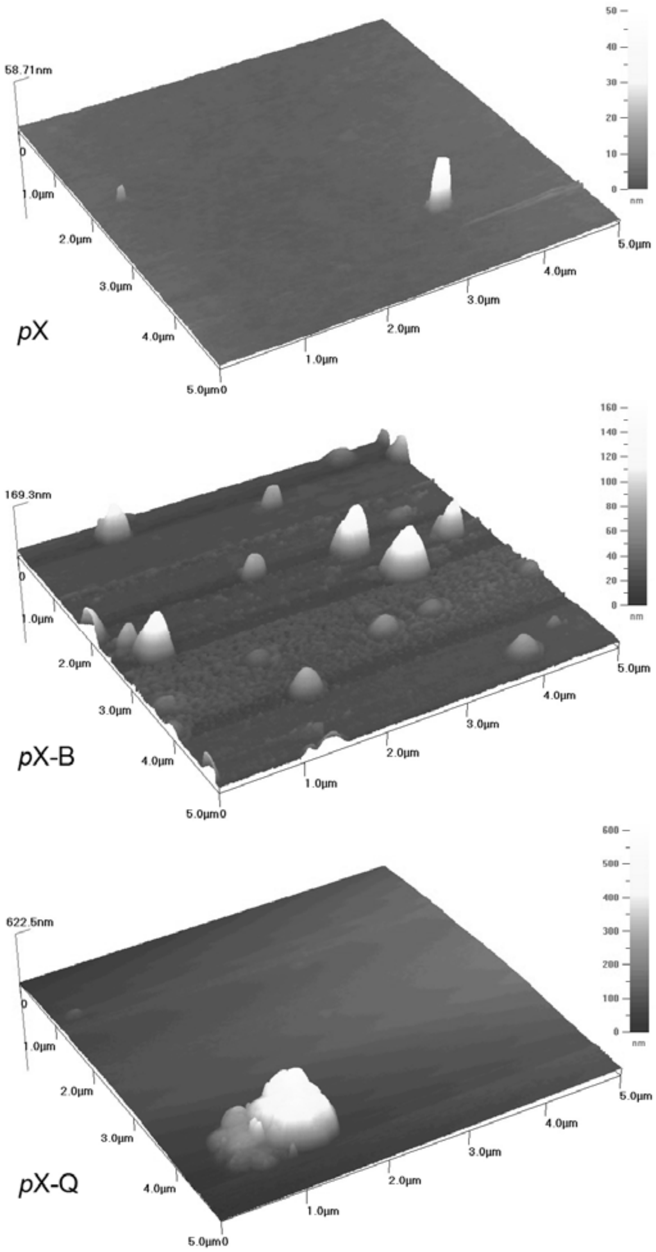

Fig. 1. AFM images for pX, pX-B and pX-Q films

3.2. FTIR investigations

The processing of the FTIR spectra included the subtraction of the silicon base lines. The characteristic peaks of the polymer films are shown in Table 2, where collected features of PPP and PPV are inserted. The assignment of the FTIR absorption bands was carried out according to references of Table 2.

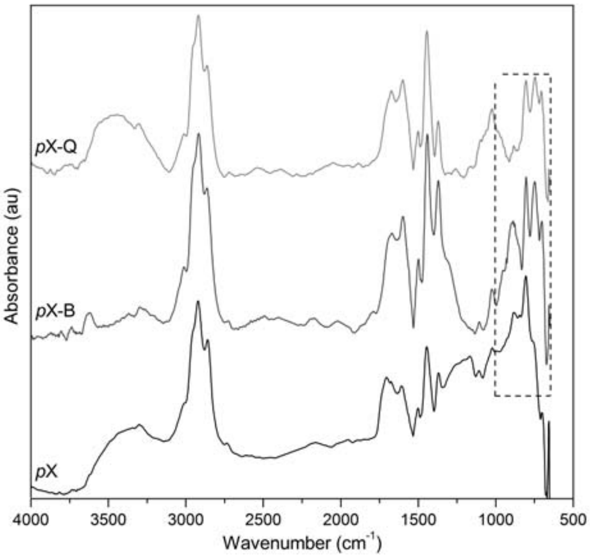

Fig. 2. FTIR spectra for pX, pX-B and pX-Q films

The strongest peaks in their order are in the area where the contribution of C-H derives from: C-H aromatic stretch and CH_2- alkyl stretch. The medium intensity peaks are centered at 1600 and 1670 cm^{-1} and well defined for the pX-B and pX-Q films. The aromatic stretching observed at 1600 cm^{-1} corresponding to a quinoid structure is well shaped. The band at 1670 cm^{-1} is typical for C=C stretch in aromatics. The bands positioned on 1440 - 1500 cm^{-1} represent C-C stretching in phenyls and they are well shaped. C-H, in plane bend, is much more defined in pX-Q case, less for pX-B and weak for pX. In the last two cases is important out-of-plane C-H-trisubstituted (846-900 cm^{-1}). Most of the peaks correspond to the in-plane C-H bands mixed with the complex in-plane ring vibrations. These spectra show clearly a polymerization process where phenyl groups are chained with alkyls by a randomizing interconnection. The intensity rapport between lines close to 800 and 700 cm^{-1} (Figure 3) estimate the number of phenyl rings in each sample as described in references [39]. The results show that the sample originated of p-xylene has only 1 phenyl ring, the second with biphenyl has between 1.8-2.5 phenyl rings and that with quarterphenyl reach a maximum of 4.8 phenyl rings.

Table 2. Peak assignments of FTIR absorption bands

Wave number [cm^{-1}]	**Characteristic bond**	**Sample**		
		pX	**pX-B**	**pX-Q**
692, 760, 768 [30-32]	C-H out of plane vibration mono	700, 759	703, 698, 728	705
750 [33]	1,2 di-substituted benzene ring		750	746
800-817 [30]	out-of-plane C-H vibrations of 1,4-di-substituted benzene ring	804	806	806
846-900 [34], [35]	out-of-plane C-H vibrations of 1,2,4-trisubstituted benzene ring	846, 885	881, 889, 903	885
1013, 1108, 1176 [32]	C-H in plane bend	1022, 1106,	1025,1108	1025

Wave number [cm^{-1}]	**Characteristic bond**	**Sample**		
		1166	1170 miss	
1347	CH2-symm. Alkyl deformation		1344	
1339, 1426, 1502, 1519 [32], [36]	C-C ring stretch & semicircular phenyl stretch	1444, 1500	1502,1442, 1481	1446, 1502
1385, 1390, 1402, 1480 [37]	aromatic C-C stretching vibrations	1367	1373	1371
1630-1650 [30]	C=C ring stretch	1673	1672	1675
1600 [37]	quinoid structure	1608	1600	1600
1706	-C=C aliphatic	1706		
2850-2860	CH2 stretch alkyl	2859	2865	2863
2920 [32]	Aliphatic C-H stretch	2919	2919	2921
2950, 3045, 3077 [32]	Aromatic C-H stretch	2954	2958	2948
3029, 3060 [38]	Aromatic C-H stretch	3010	3014	3010

The PPP-like films grown by plasma polymerization have rather short cross-linked structures. Comparing our results with PPP obtined by electrochemical synthesized of biphenyl and terphenyl where the length chains contain about about 7.4 phenyl rings (biphenyl) and 8.4 phenyl rings (terphenyl), our results indicate that plasma polymerization can be a good challenger for the chemical synthesis method [40].

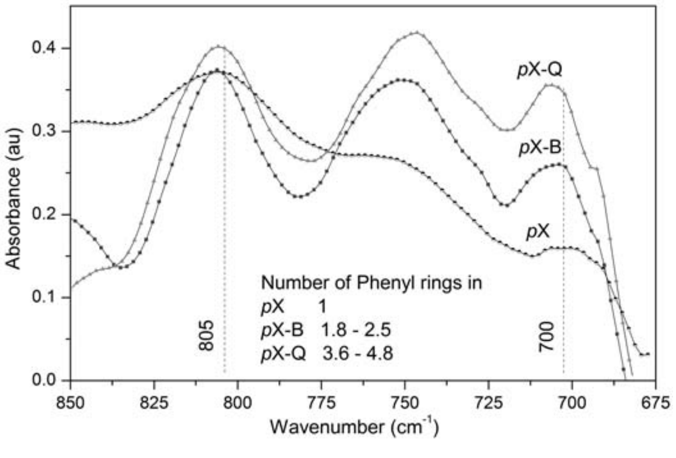

Fig. 3. FTIR spectra for counting the number of phenyls in the polymeric chain pX, pX-B and pX-Q

3.3.Electrical characterization

Our samples obtained by plasma polymerization were investigated close to schottky type diode, as shown in Figure 4. In the case of thin films the behavior is inverse proportional with the conjugation length.

The characteristics are asymmetric and have a rectifying behavior. The interface polymer layer and electrodes play an important role in the charge injection and transfer. Being deposited on

Si-100 intrinsic the characteristics show as for p-doped polymeric films. For biphenyl and quaterphenyl precursors, the polymer exhibits a large band gap.

The structures of the deposited plasma polymer films were significantly influenced by the applied DC voltages during the discharge. Also, the process of plasma thin film deposition depends on the precursor systems. It was concluded that the conduction mechanism controlled by SCLC is dominant in plasma polymerized thin films.

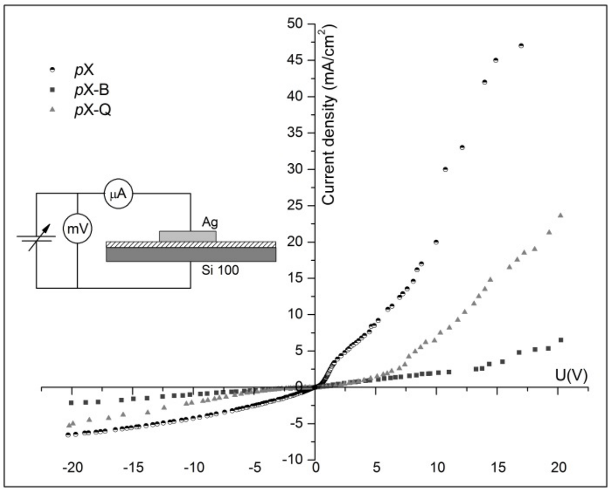

Fig. 4. Current density versus applied voltage for pX, pX-B and pX-Q, at room temperature conditions

4. Conclusions

Thin polymer films obtained from p-xylene (pX) and biphenyl with p-xylene (pX-B), quaterphenyl with p-xylene (pX-Q) as precursors were deposited by means of a special plasma system. Our experimental design of plasma reactor gives the possibility of obtaining thin polymer films with a higher conjugation length than films developed in other plasma configurations.

PPP-like films have a cross-linked structure with a number of up to 4-5 phenyl rings in the chain construction, lower than the ones obtained by electrochemical/chemical methods (which include 10-12 phenyl rings).

The obtained polymer films are highly homogeneous, pinhole free, have an elevated smoothness of the surface topography. The I-V characteristics depend on the conjugation length and have a rectifying behavior. PPP-like films present the structure similarities with literature PPP and PPV films.

We conclude that PPP-like films grown via plasma polymerization in a particular plasma reactor configuration have a relatively low degree of cross-linkage and very good electrical properties. Thus, these new materials could be interesting candidates for a variety of organic electronic applications.

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