

SYNTHESIS AND CHARACTERISTICS OF POLY(PARA-PHENYLENEVINYLENE)

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ABSTRACT

Poly(para-phenylenevinylene) [PPV] films and nanotubes were prepared via chemical vapor deposition polymerization (CVDP) by vapor phase pyrolysis of α, α' -dichloro p-xylene on the quartz plate, silicon wafers and Al_2O_3 membrane substrate with the pore size $\phi = 100$ nm. We prepared graphitic carbon films and carbon nanotubes by carbonizing the poly(para-phenylene vinylene) [PPV] films and nano patterns under thermal treatment range from 500°C to 900°C . When the PPV films on quartz plate were treated at 900°C highly oriented graphitic carbon films were obtained. The characterization of the PPV nanotube and nanotube carbon has been investigated by means of IR, SEM, AFM and Raman scattering study.

Keywords: Nanotube carbon, polymer nanotube

1. INTRODUCTION

Nowadays Poly(para-phenylenevinylene) PPV is still extensively studied due to its promising electrical, optical and electroluminescent properties [1, 2]. The insoluble and infusible below the temperature range of decomposition cause to limit the synthesis, analysis and application of PPV. The polyreactions of PPV in solution result in oligomeric materials. The precursor route for making conjugated materials such as PPV allows to overcome this problem [3]. The chemical vapor deposition polymerization (CVDP) is a method, in which the surface of templates or substrates are utilized to accumulate polymer molecules. Jang *et al.* [4] prepared polypyrrol nanotubes by CVDP method on the inner surface of nano porous anodic aluminum oxide (AAO) membrane template that was presoaked in a FeCl_3 aqueous solution. The deposited FeCl_3 catalyzes the polymerization of the pyrrol monomers in the gas phase. The electrochemical polymerization is applicable also to the preparation of nanotubes of some of the polyconjugated polymer [5]. Nanotubes of soluble polymers simply can prepare by soaking the nano membranes or nano tubes in a polymer solution followed by the evaporation of the solvent. Polyaniline nanotubes and nanorods prepared by self-assembly method in the presence of an inorganic acid as dopant acid as HCl and H_2SO_4 [6]. Kyungkon Kim *et al.* prepared highly electrical graphitic carbon films and nano patterns by carbonizing poly(p-phenylenevinylene) films and nano patterns prepared on the silicon surface, nano porous alumina membrane by the chemical vapor deposition polymerization (CVDP) method of α, α' -dichloro p-xylene [7, 8].

In the course of our studies, we used α,α' -dichloro p-xylene for the preparation of PPV precursor and nano patterns on the substrate aluminum oxide (Al_2O_3) membrane. We carbonized poly(p-phenylenevinylene) nano patterns inside the pores of Al_2O_3 membrane and on the surface of quartz plate. The characterizations of PPV nanotubes and carbon nanotubes were realized by IR, SEM, AFM, and Raman spectroscopy.

2. EXPERIMENTS

2.1 Materials and measurements

For synthesis of PPV via CVDP, we used commercially available nano porous alumina membranes (nominal pore diameter: 100 nm, Whatman, England). The α,α' -dichloro p-xylene (Aldrich Co, Milwaukee, U.S.A) was purified by recrystallization from benzene that was used as better monomers to produce PPVs with fewer chemical structural defects. The scanning electron microscopy (SEM, S-4300, Hitachi, Japan) and Atomic Force Microscope (AFM) were used to determine the morphology of nano patterns. The chemical structure of PPVs was observed through the infrared absorption spectra (Impact 400). Raman spectra were recorded by Jobin-Yvon LabRam HR (high resolution), in which the set up of the 800 nm focal length monochromator with LN_2 cooled CCD multichannel detector. Raman scattering experiments were performed at ambient conditions using a back scattering geometry for the laser excitation line: argon 514.5 nm. The spectral resolution of the system was better than 2 cm^{-1} .

2.2 Synthesis

The synthesis of PPV via CVD was obtained by vapor phase pyrolysis of α,α' -dichloro p-xylene. Figure 1 shows the pyrolysis apparatus used for CVD process.

The CVD polymerization of the α,α' -dichloro p-xylene monomer was conducted in a quartz tube consisting of vaporization, pyrolysis and deposition zone. The commercially available alumina porous filters (nominal diameter 100 nm Anodic Whatman, England) were utilized in the present investigation.

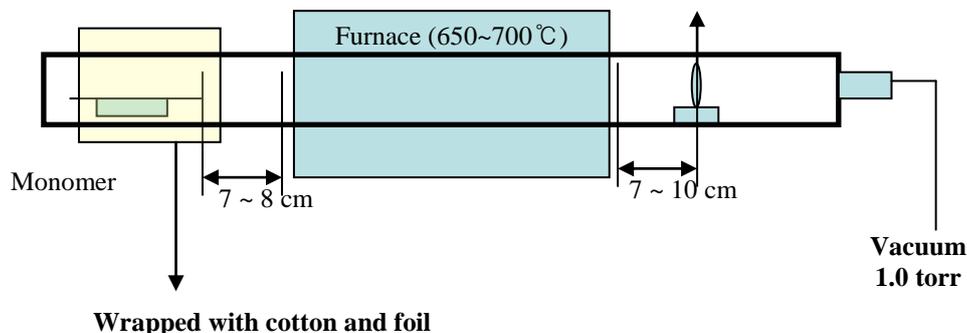


Fig. 1: The pyrolysis apparatus for CVD process

A sample (40 - 60 mg) of purified from benzen α,α' -dichloro p-xylene placed on tungsten boat was evaporized at 90 - 95°C in steady stream 8 ml/min of argon at the pressure of 1.0 torr.

The evaporized monomer passes through the pyrolysis zone preheated to 650°C. The precursor polymer was collected on the inner surface or inside the Al_2O_3 filter placed in the deposition zone. The precursor polymer nanotubes or nanofilms were thermally treated at 300°C for 12 - 15 hours converting them into PPV. The PPV nanotubes and nanofilms were carbonized by heating

at different temperatures from 500 - 900°C for 1 hour under argon in the pyrolysis quartz tube to obtain the carbon tubes and carbon films.

3. RESULTS AND DISCUSSION

3.1 Structure characterization

Figure 2 shows the IR spectrum of the PPV. As indicated in the spectrum, sp^3 saturated C-H stretching absorption are observed at 2858 and 2945 cm^{-1} . In addition, the absorption at 3024 cm^{-1} is belong to unsaturated sp^2 =C-H stretching mode. The final PPV samples prepared by CVDP of α,α -dichloro p-xylene (bis 1,4-chloromethyl benzen) contain a low - level of the saturated 1,4-phenyleneethanediyl (PE) units in addition to the unsaturated 1,4-phenylenevinylene (PV) units.

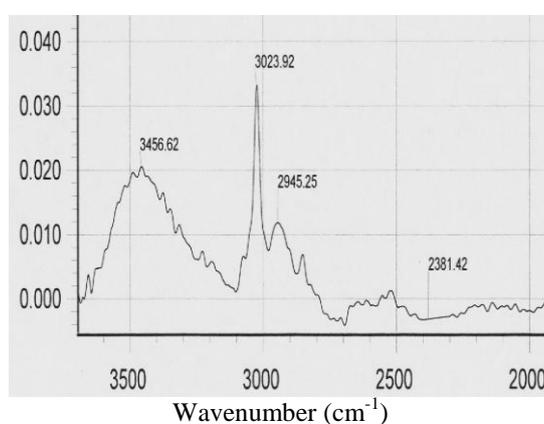


Fig. 2: IR spectrum of the PPV

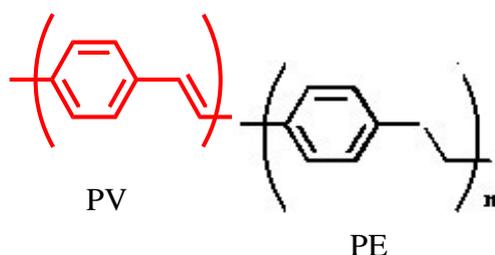


Fig. 3: The formula of 1,4 phenylenevinylene (PV) and 1,4-phenyleneethanediyl (PE) units

Figure 3 shows the formula of 1,4 phenylenevinylene (PV) and 1,4-phenyleneethanediyl (PE) units. This suggests that quinodimethane is formed together with quinodichloro upon pyrolyzing the monomer.

3.2 Surface morphology

The PPV nanotubes formed inside Al_2O_3 membrane by CVDP. Usually, the top surface of the membrane was covered by PPV formed during the CVDP process which was removed by CF_4 -plasma etching and 10% hydrofluorid solution. Figure 4 shows the scanning electron microscopy (SEM) images of PPV nanotubes. The PPV nano objects could be easily carbonized to the graphitic products by thermal treatment as above. The Atomic Force Microscopy (AFM)

images of carbonized PPV nanotubes (CPNT) and carbon nanofilms were presented in Fig. 5. It is clear that the carbon particles on films and inside membrane were of the nanosize. The surface of the carbon films seems to be smooth and the cluster sizes were according to the results in Table 1.

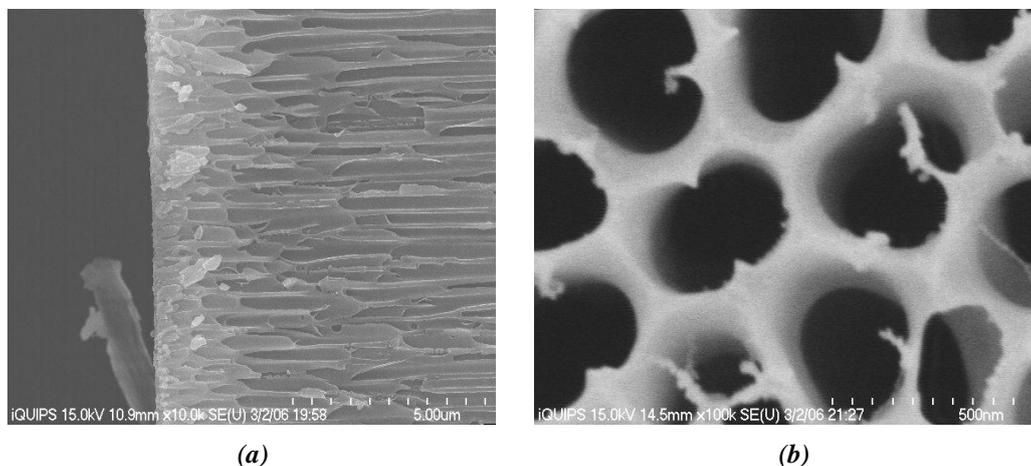


Fig. 4: (a) SEM images of nanotube PPV in an alumina filter membrane with nominal pore diameter of 100 nm from cross section. (b) Nanotube PPV inside Al₂O₃ membrane from top view

Table 1: Calculation results of graphitic cluster diameters

N ⁰	Samples	Treatment temperature (°C)	I _D /I _G	La (nm)
1	NF ₁ (ChAC 500)	500	0.5	9.0
2	NF ₂ (ChAC 700)	700	1.68	2.62
3	NF ₃ (ChAC 900)	900	1.87	2.35
4	NTC ₁ (ChAC 17)	700	2.35	1.87
5	NTC ₂ (ChAC 18)	900	2.31	1.90

3.3 Raman spectra

Raman spectroscopy is a standard nondestructive tool for the characterization of crystalline, nano crystalline and amorphous carbons [8]. In the theoretical works [7, 9] the modes of Raman spectra in disordered and amorphous were given. However it is regretted that the experiments suggestions for nano object carbon obtained from PPV are not full. In order to describe in detail the Raman process of disordered carbons. We focus on D and G Peaks, neglecting other features that sometimes present those at 1100 - 1400 and 1500 - 1600 cm⁻¹. Figure 6 shows the Raman spectra of the graphitized PPV films under 500°C (a), 700°C (2), 900°C (1).

The Raman spectra of graphitized films (the curves in Fig. 6) display two peaks which correspond to the disordered carbon (D peaks) around 1350 cm⁻¹ and a graphitic carbon (G peak) around 1580 - 1600 cm⁻¹, usually assigned to zone center phonons of A_{1g} symmetry and K-point phonons of E_{2g} symmetry, respectively. The G mode of graphite around 1600 cm⁻¹ has E_{2g} symmetry. This mode does not require the presence of six fold rings occurred at sp² sites, while it does in aromatic and olefinic molecules [9].

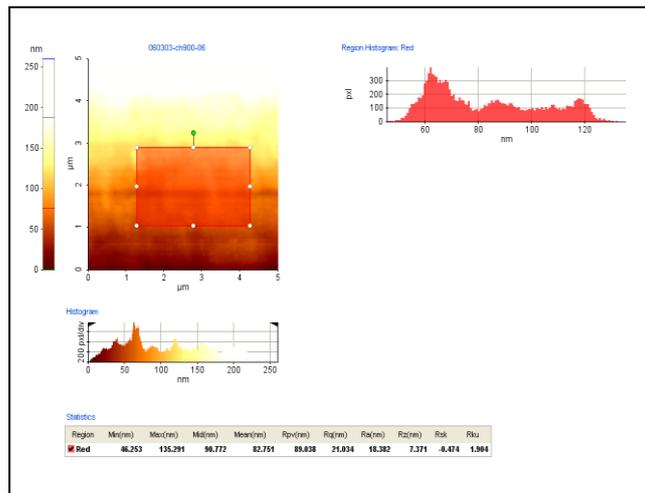


Fig. 5: AFM image of the nanocarbon film on quartz plate carbonized PPV film at 500°C in 1 hour under Ar pressure

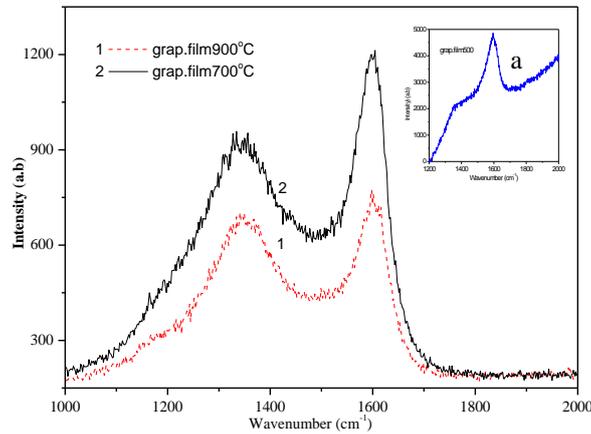


Fig. 6: Raman spectra of the graphitized PPV films under 900°C (1), 700°C (2), 500°C (a)

The peak around 1350 cm^{-1} is very often called D peak which is a breathing mode of A_{1g} symmetry involving phonons near the K-zone boundary. This mode is forbidden in perfect graphite and becomes active only in disordered graphites. The D mode is very dispersive and varies with photon excitation energy, even when the G peak is not dispersive. The intensity of this mode is strictly connected to the presence of six fold aromatic rings.

The peak around 1600 cm^{-1} is the G mode of E_{2g} symmetry [9] and it involves the in-plane bond stretching motion of sp^2 C-atom [7]. Some authors used an alternative to a Gaussian fit line for the G peak and a Lorentzian for the D peak [9] or a double Gaussian fit line for the both peaks [7]. So, a Gaussian fit line has an asymmetric line shape and curve tails increasingly to lower frequencies for the lower coupling coefficient. The Gaussian + Lorentzian line is an excellent means to fit Raman spectra of all carbons from graphite to tetrahedral amorphous carbon (ta.C).

In general, the D peak position will decrease with increasing disorder with Gaussian + Lorentzian fit but will increase for the double - Gaussian fit [9]. When we utilized the Gaussian + Lorentzian fit, we obtained the I_D / I_G ratio values of 0.5; 1.68; 1.86; and 2.30, respectively for

the graphitic carbon films on quartz and nanotube inside Al₂O₃ membranes treated under 500; 700, and 900°C.

According to the Tuinstra and Koenig (TK) equation [10], the ratio of intensity to that of the G peak varied inversely with La (graphitic cluster diameter or in-plane correlation length):

$$I(D)/I(G) = C(\lambda)/L_a \quad (1)$$

where $C(\lambda)$ is the scaling coefficient and depends on the wavelength of the source laser. The wavelength of the laser in our case was 514.5 nm and $C(\lambda)$ is 44 Å⁰. Table 1 tabulates the calculation results of La for the graphitic carbon films and nanotubes treated at different temperatures.

Ferrari A.C. and Robertson J. [9] present a three stage model relating the visible Raman parameters to the sp² nano structure and the content of disordered carbons. The experimental visible Raman Spectra (on Fig. 7) of graphitic carbon films and carbon nanotubes were suitable to a phenomenological three stage model. The main effects in the evolution of the Raman spectrum of graphite to nano crystalline graphite are following:

- a. The G peak moves from 1581 cm⁻¹ a position close to 1600 cm⁻¹
- b. The D peak appears and I_D/I_G increases following the equation (1)
- c. There is no dispersion of the G mode

Table 2 tabulates the positions of the D-peak and the G-peak of the graphitic carbon films and carbon nanotubes.

Table 2: The positions of D-peak and G-peak of the nano objects

N ^o	Samples	Treat. (°C)	D peak (nm)	FWHM	G peak (nm)	FWHM
1	NF ₁ (ChAC 500)	500	1348	86.96	1600	60.87
2	NF ₂ (ChAC 700)	700	1336	172.18	1600	77.39
3	NF ₃ (ChAC 900)	900	1348	139.13	1604	78.26
4	NTC ₁ (ChAC 17)	700	1348	161.73	1604	80.86
5	NTC ₂ (ChAC 18)	900	1340	139.13	1602	78.26

The physical properties of carbon materials strongly depend on the ratio of sp² (graphite like) to sp³ (diamond like) bonds. The G peak displays around 1600 cm⁻¹ in all the cases of our experiment graphitic carbon films and carbon nanotubes prepared by the CVDP method. The I_D/I_G value is about 2,0 tells us that the obtained carbon films are the nanocrystalline graphite [7]. It is known that the G peak moves from 1581 cm⁻¹ to 1600 cm⁻¹ when the disordered graphite becomes the nanocrystalline graphite.

4. CONCLUSION

We have successfully prepared the conjugated polymer (PPV), PPV nanofilms on quartz and inside the pore of Al₂O₃ membrane by the chemical vapor deposition polymerization of α,α'-dichloro p-xylene and the graphitic carbon tubes, carbon films by carbonizing PPV. The increasing of the temperature in a graphitized process from 500 to 900°C leads to decrease the cluster diameter of nanocrystalline graphite films.

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