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Preparation of PPV Nanotubes and Nanorods and Carbonized Products Derived Therefrom

Kyungkon Kim and Jung-Il Jin*

Division of Chemistry and Molecular Engineering, and Center for Electro- and Photo-Responsive Molecules, Korea University, Seoul 136-701, Korea

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ABSTRACT

We report the synthesis of poly(*p*-phenylene vinylene) (PPV), a polyconjugated polymer, in nanotube and nanorod shapes, and carbonized products derived therefrom. PPV tubes and rods could be prepared on the inner surface of or inside the nanopores (10–200 nm diameter) in alumina or polycarbonate membrane filters by the chemical vapor deposition (CVD) polymerization method of α,α′-dichloro-*p*-xylene followed by thermal dehydrochlorination. The PPV nanotubes and nanorods thus obtained could be converted to the corresponding carbonized tubes and nanorods when they were subjected to thermal treatment under an argon atmosphere. Thus prepared nanoobjects were characterized by electron microscopic analyses, IR, UV–vis, and Raman spectroscopy, and photoluminescence fluorometry. This investigation demonstrates that, if one employs membrane filters containing cylindrical pores of uniform diameter, monodisperse nanotubes and nanorods of PPV and carbonized products thereof with controlled diameter and wall thickness can be prepared.

Preparation of polyconjugated organic polymers in nanotube and nanowire shapes can provide us with conducting materials that can find a wide range of applications in nanoelectronic devices such as nanosized transistor rectifiers,[1] sensors,[2] etc.[3−5] Moreover, since PPV is known to exhibit electroluminescence (EL)[6] and nonlinear optical properties,[7] optical nanodevices fabricated with the PPV nanotubes or nanorods may be able to find advantageous uses in light-emitting diodes (LED) and photonics applications such as wave-guiding and all-optical switching. Despite all these potentials, fabrication of PPV in an intended shape of a desired dimension is extremely difficult due to the insolubility of PPV in any solvent and to its intractability. Therefore, one has to rely on synthetic methods that go through soluble precursors that can be converted chemically or thermally to the final composition. In fact, many synthetic methods known for the preparation of PPV involve the soluble precursor routes.[8] The Wessling−Zimmerman method[9] and the Gilch polymerization[10] are two well-known, most widely used representative methods. Water-soluble sulfonium salt precursor is involved in the first method, whereas in the second method organic soluble precursor is formed where saturated chloroethylene or bromoethylene units link the phenylene rings along the main chain.

The precursor polymers can be readily converted to PPV by heating them under an inert atmosphere. Therefore, if one wants to prepare a thin film of PPV or fibers, one first has to form films or fibers of the soluble precursor polymers followed by thermal elimination. During this process, a large amount of solvent and side products have to be removed, which is expected to generate many defects such as bubbles in the final objects and to leave impurities from the solvent. Therefore, fabrication of PPV nanotubes and nanorods of high quality via organic or water-soluble precursor polymers is very difficult, if not prohibitive. We have been studying electrical and luminescent properties of a wide variety of PPV derivatives mainly prepared by these synthetic methods.[11−13]

Nonetheless, there are many interesting and important reports on fabrication of nanotubes and nanorods of conducting polymers using soluble precursor polymers or soluble polyconjugated polymers. For example, Martin et al. pioneered the preparation of nanotubes of conducting polymers by filling the nanopores of alumina or organic polymer filters with polymers or polymer solutions followed by removal of solvents.[14−16] They could prepare polyaniline and other conducting polymer wires by polymerizing aniline and other monomers inside the channels of nanoporous membranes. Recently, Jang et al.[17] prepared polypyrrole/poly(methyl methacrylate) coaxial nanowires through sequential polymerization of methyl methacrylate and pyrrole monomers inside the channels of mesoporous silica.

In this investigation, we prepared PPV nanotubes and nanorods by polymerizing α,α′-dichloro-*p*-xylene by the CVD polymerization method in the pores of alumina or polycarbonate filters having nominal pore diameters of

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* Corresponding author e-mail address: jijin@mail.korea.ac.kr.

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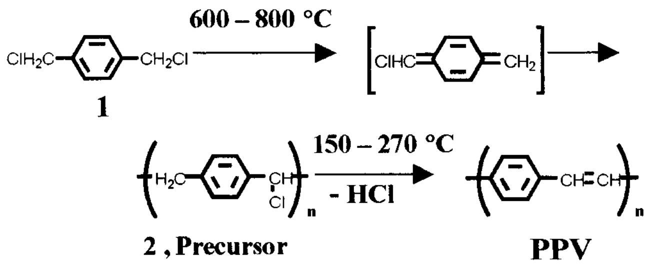
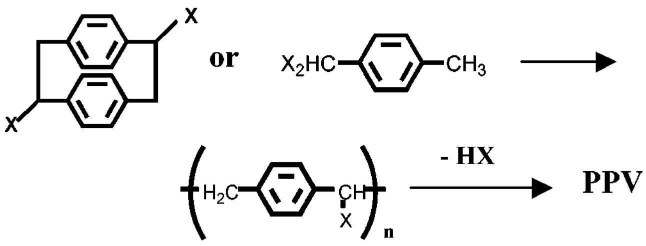
10−200 nm. This synthetic method requires two steps to prepare PPV: In the first step the precursor polymer **2** is



formed, which has to be further converted to PPV at 150−270 °C under vacuum. This method is known to produce some structural irregularities in the final PPV due to some undesirable side reactions.[18] Such side reactions appear to be avoidable if one uses a halogenated paracyclophene or α,α-dihalogenated *p*-xylene in the similar CVD polymerizations:



Schäfer et al.[18] studied in detail the preparation of PPV films via CVD polymerization of α,α′- and α,α-dihalogenated *p*-xylenes. They found that α,α-dihalogenated *p*-xylenes are better monomers that produce PPVs having many fewer chemical structural defects such as the saturated ethanediyl units. Vaeth and Jensen[19] observed that greater aliphatic ethanediyl units are incorporated into the PPV when prepared by CVD of α,α′-dibromo-*p*-xylene as the starting monomer, as compared to the corresponding dichloro compound. Schäfer et al.,[18] Staring et al.,[20] and Vaeth and Jensen[21] separately reported electroluminescence (EL) properties of the light emitting diode (LED) devices fabricated with PPV films prepared by the CVD method.

Despite some of the claimed disadvantages, we utilized α,α′-dichloro-*p*-xylene in the present work, because the main objective was to demonstrate the feasibility of the preparation of PPV in nanotube and nanorod shapes by the CVD method in the channels of nanoporous filters. The CVD polymerization of the α,α′-dichloro-*p*-xylene monomer was conducted in a quartz tube consisting of vaporization, pyrolysis, and deposition zones equipped with a pressure control system, a tungsten boat, a heating stripe, an electrical furnace, argon gas inlet, vacuum line, and a holder for the nanoporous filters. The experimental setup was practically the same as described by Schäfer et al.[18] The commercially available nanoporous (nominal pore diameter of 200 nm; ANODISC 6809−7003, Whatman, England) alumina and polycarbonate filters (nominal diameter of 100 and 10 nm; Poretics K01SH01300 and KN1CP01300, Osmonics Inc., U.S.A.) were utilized in the present investigation. α,α′-Dichloro-*p*-xylene (Aldrich Co, Milwaukee, U.S.A.) purchased was purified by recrystallization rom benzene. A sample (60 mg) of purified α,α′-dichloro-*p*-xylene (**1**) placed on a tungsten boat was vaporized at 93−95 °C in a steady stream (8 mL/min) of argon at the pressure of 1.0 Torr. The vaporized monomer was allowed to pass through the pyrolysis zone preheated to 625

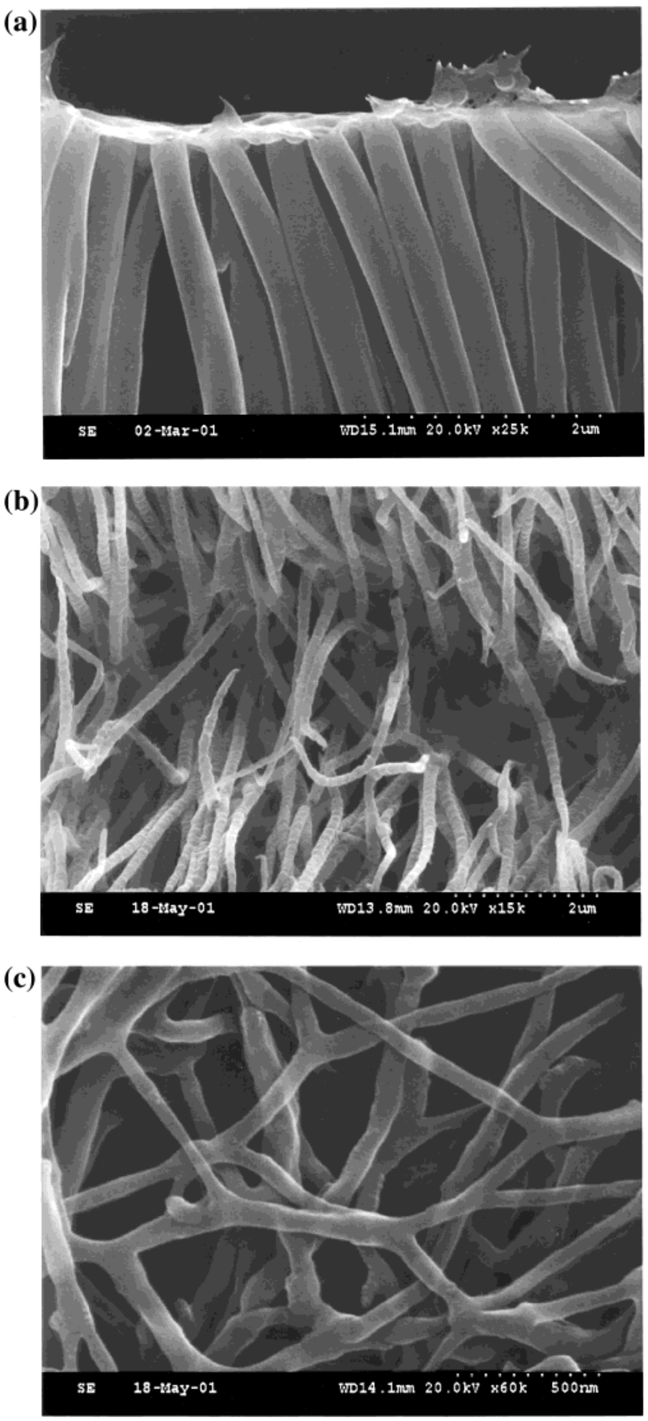


Figure 1. SEM images of PPVs after being isolated from the filters: (a) nanotubes (AL-200) prepared in an alumina filter membrane with nominal pore diameter of 200 nm; (b) nanotubes (PC-100) prepared in a polycarbonate filter membrane with nominal pore diameter of 100 nm; and (c) nanorods (PC-10) prepared in a polycarbonate filter membrane with nominal diameter of 10 nm. (The micrographs were obtained for the platinum replicas.)

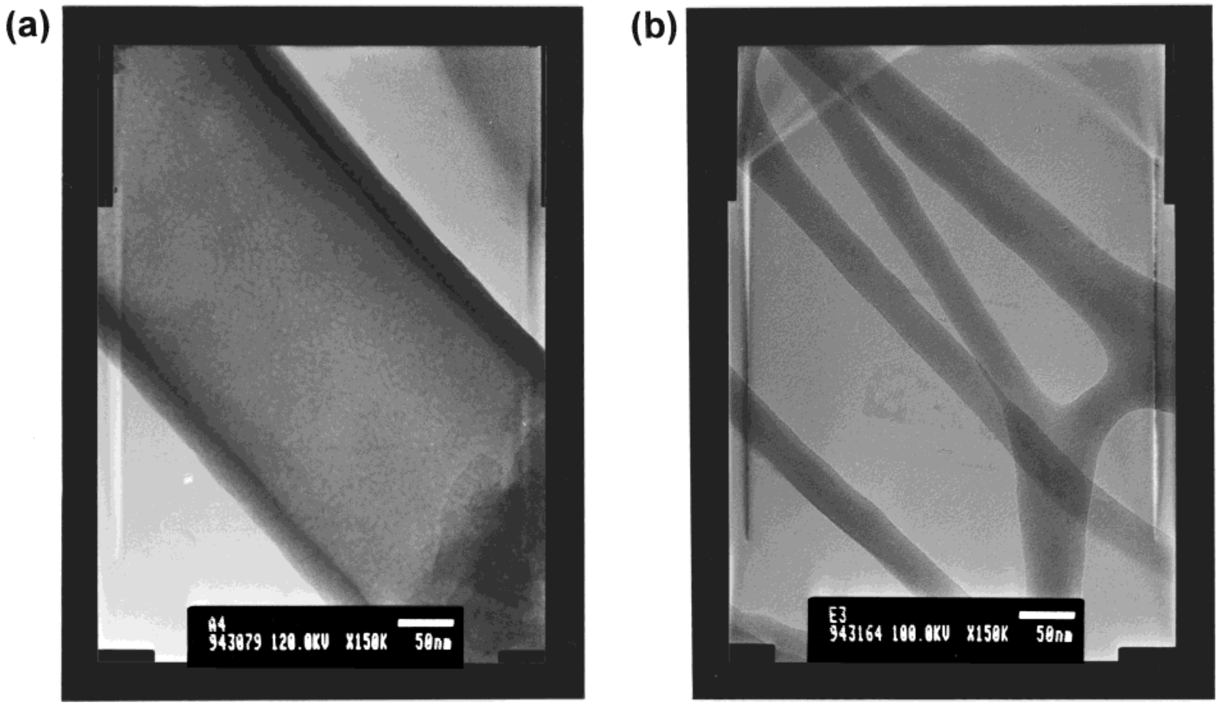


Figure 2. TEM images of (a) a PPV nanotube (AL-200) and (b) PPV nanorods (PC-10). (The micrographs were taken after the samples were stained with osmium tetroxide.)

°C. The precursor polymer was collected on the inner surface of or inside the channels of nanoporous filters placed in the deposition zone. The precursor polymer (**2**) nanotubes or nanorods formed inside the nanopores were thermally treated at 270 °C for 14 h, converting them into PPV. The PPV nanotubes (AL-200, PC-100) and nanorods (PC-10) were carbonized by heating them at 850 °C for 1 h under argon in a pyrolysis quartz tube. AL and PC stand for alumina and polycarbonate membrane filters, respectively. The numbers following AL and PC signify the nominal pore diameters.

Figure 1 shows the scanning electron microscopy (SEM; S-4300, Hidachi, Japan) photographs of PPV nanotubes (AL-200 and PC-100) (Figure 1a and b) and nanorods (PC-10) (Figure 1c) obtained after removing the alumina or polycarbonate filters by dissolution either in 3M NaOH solution or in 1,1,2,2-tetrachloroethane at room temperature. Figure 1c clearly shows the presence of multibranches, indicating that the pores inside the filter substrate are very much interconnected. It is noted that no pinholes are found in the nanotubes and nanorods of the present PPVs within the limit of detection of SEM. The wall thickness of the nanotubes AL-200 is estimated to be 28 ± 3 nm as shown by the transmission electron micrograph (TEM; JEM-2000EXII, JEOL, Japan) in Figure 2a. The TEM micrograph shown in Figure 2b confirms completely filled morphology of the PPV nanorods (PC-10) of a diameter of about 31 ± 3 nm. The outer diameter of the PPV tubes (AL-200) shown in Figure 2a is 285 ± 25 nm. And the outer diameter of PC-100 prepared using the polycarbonate filter with pore sizes of 100 ± 20 nm was 134 ± 20 nm. Although the TEM micrograph of PC-100 nanotubes is not given (refer to Supporting Information), the wall thickness was found to

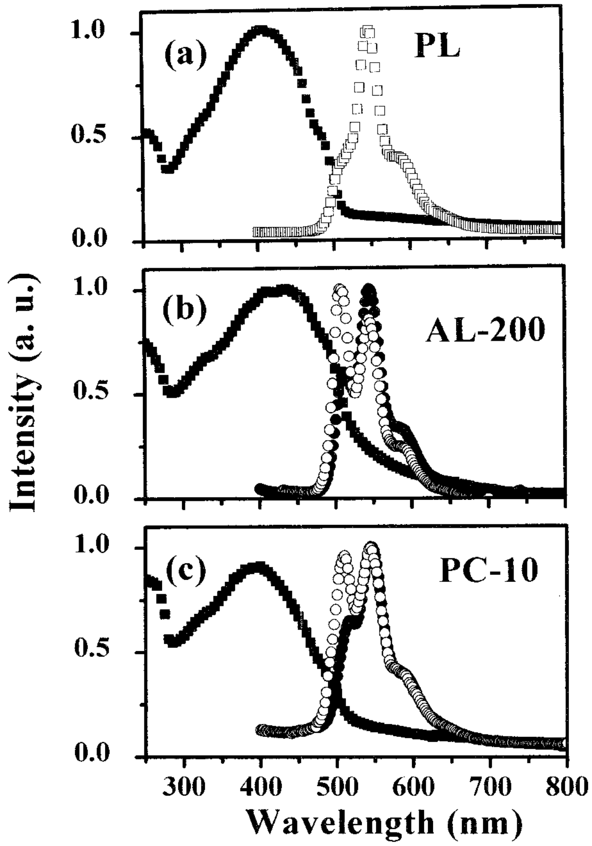


Figure 3. Comparison of UV−vis absorption and photoluminescence (PL) spectra. ■: UV−vis absorption spectra ((a): bulk PPV film; (b): PPV nanotubes (AL-200) in the methanol suspension; (c): PPV nanorods (PC-10) in methanol suspension); □: PL spectrum of bulk film; ●: PL spectra of nanotubes and nanorods in filter membranes; ○: PL spectra of nanotubes and nanorods suspended in methanol. (All the PL spectra were obtained at the excitation wavelength of 350 nm.)

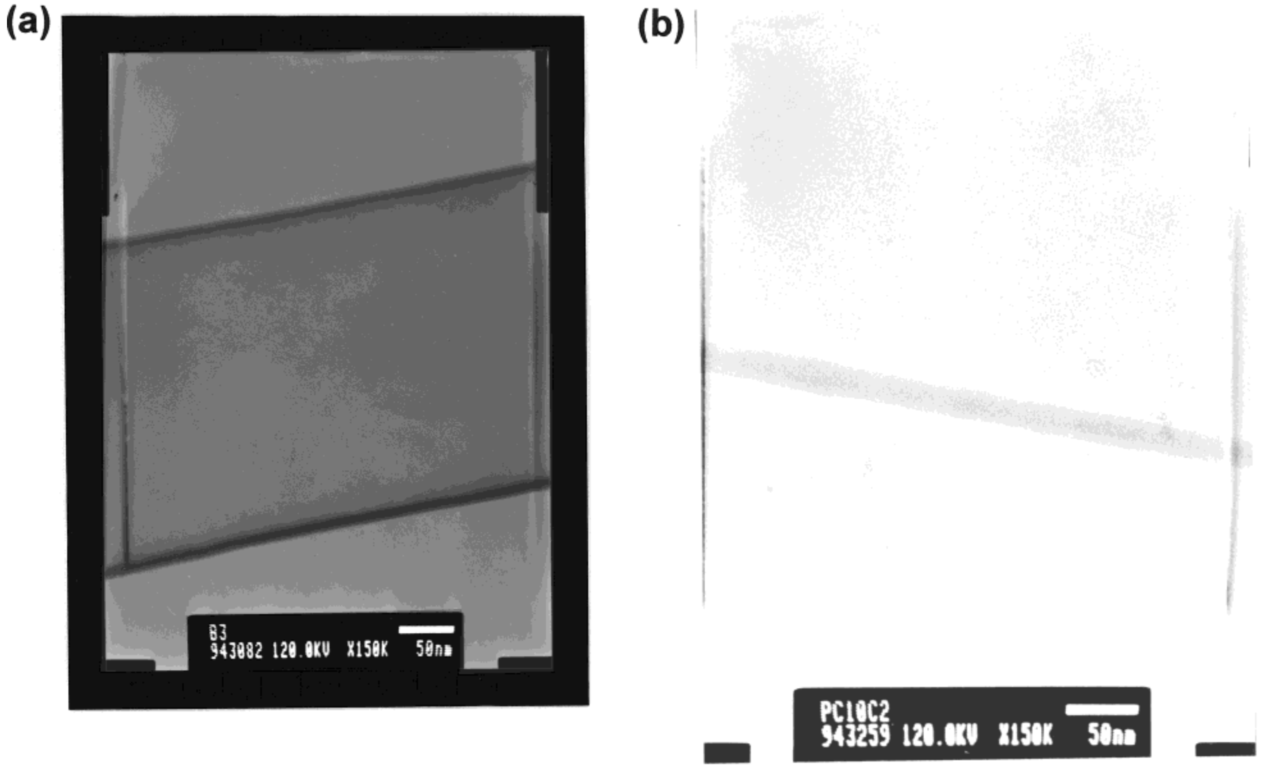


Figure 4. TEM images of (a) a carbon nanotube and (b) a nanorod obtained at 850 °C from PPV nanotubes (AL-200) and nanorods (PC-10), respectively.

be 38 ± 3 nm. Needless to say, the wall thickness depends on the polymerization time, flow rate of the inert gas, and the pressure in the reactor tube. In general, we found that diameters of PPV nanotubes and nanorods prepared in the present investigation are significantly larger than those of the pores in the filter templates. It is very possible that during the removal process of the templates the solvents expand PPV nanotubes and nanorods and the expanded shapes do not return upon drying to the original compact morphology.

As far as their chemical structures are concerned, the FT-IR spectra of the present PPVs are same as described earlier by Schäfer et al.,[18] which show absorption peaks observed for PPVs prepared by Wessling and Zimmerman's sulfonium salt precursor route. They, however, show aliphatic C−H stretching absorption bands in the region of 2900 cm^{-1} indicating the presence of sp^3 carbons that were derived from structural defects as was earlier discussed about in detail by Schäfer[18] and co-workers and Vaeth and Jensen.[19] Schäfer et al.[18] reported that they obtained up to 10 mol % of aliphatic structure, i.e., the 1,4-phenyleneethanediyl unit, in the final product when α,α′-dichloro-*p*-xylene was utilized as the starting material. Vaeth and Jensen[19] proposed that incorporation of dimerization byproducts of monomer pyrolysis into the PPV chain may be the source of aliphatic segments.

Figure 3 shows the UV−vis spectra of the bulk PPV film (30 nm thick) prepared by the Wessling − Zimmerman's route, PPV nanotubes (AL-200) suspended in methanol, and PPV nanorods (PC-10) suspended in methanol at the concentration of 2 mg/ml and 0.6 mg/ml, respectively. They are basically the same and maximum absorption was observed at 410 nm for all the samples, which correspond to $\pi-\pi^*$ transition of the PPV backbone. Their photoluminescence behavior, however, depends on their preparation method and also whether the PPV nanotubes and nanorods were remaining inside the pores of substrate filters or isolated from them. The range of wavelengths (475−625 nm) of luminescence emission is practically the same for the three samples and their PL spectra have emission at three positions (510, 545, and 585 nm). The fine details of the PL spectra, however, are quite different: the major peculiarity lies in the fact that the relative emission intensity at the shortest wavelength (510 nm) grows in the order of the bulk film < nanosamples in the filter < nanotubes or nanorods suspended in methanol. This emission peak has been claimed to be from $S_1 \rightarrow S_0$ 0−0 transition, i.e., highest electronic energy transition involving π-electrons[22]. The additionally enhanced $S_1 \rightarrow S_0$ 0−0 emission for the methanol suspensions of nano-PPVs is a very intriguing phenomenon that requires further studies. It, however, may be due to reduced reabsorption by neighboring chains of the emitted light originated from the 0−0 transition of a given chain because of complete isolation of the nanoparticles suspended in the solvent that consist of much fewer polymer chains compared to bulk films. In contrast, when the nanotubes and nanorods remain in the filter pores, the PPV molecules in the interface would interact with the substrate surface causing a reduced emission for the 0−0 transition compared to suspensions. Smith et al.[23] observed earlier the same phenomenon for PPV nanocomposites prepared in photochemically polymerized matrix of a lyotropic liquid-crystalline monomers. They also studied

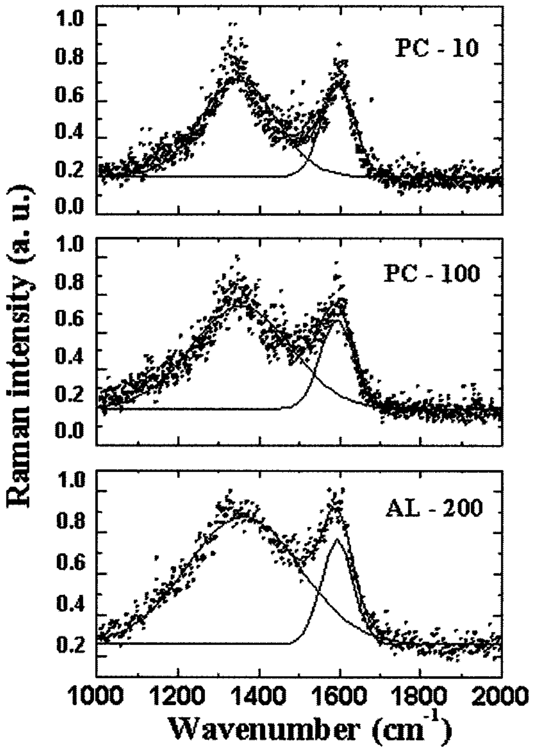


Figure 5. Raman spectra of carbon nanotubes and nanorods obtained from PPV. An Ar laser of 514.5 nm was employed as a light source.

photoluminescence detected magnetic resonance (PLDMR) of the composites confirming that increased PL quantum yield was resulted from the isolation of the PPV chains.[24]

According to the wide-angle X-ray diffractogram (refer to Supporting Information), the PPVs prepared by the present method are amorphous. Gagnon et al.[25] implied that unoriented PPV is amorphous whereas oriented sample is semicrystalline. Staring et al.,[18] Schäfer et al.,[20] and Bradley[26] separately reported that PPV can become crystalline if properly annealed or precursor polymer was converted to PPV at higher temperatures. Probably, PPV chains in the present nanotubes and nanorods are randomly oriented resulting in an amorphous morphology. We also could not observe any X-ray scattering in the small-angle region.

We subjected the PPV nanotubes and nanorods to thermal treatment at 850 °C for 1 h to convert them into corresponding carbon nanotubes and nanorods. It was earlier reported by Ueno et al.[27] that PPV could be carbonized thermally in an inert atmosphere at elevated temperatures. Figure 4 shows TEM micrographs of a carbon nanotube (Figure 4a) and a nanorod (Figure 4b) thus obtained. The wall thickness of the carbon nanotube shown in Figure 4a is 15 ± 2 nm, which is thinner than that (28 nm) of the original PPV nanotubes (AL-200). Such a reduction in wall thickness after carbonization appears to be general, which can be ascribed to the formation of more compact structures accompanied by removal of hydrogens and aromatization. The same phenomenon was observed also for nanorods. When we carbonized PPV nanorods (PC-10) of diameter of 31 ± 3 nm, the resulting carbon nanorods exhibited the rod diameter of 25 ± 2 nm. Finally, Figure 5 compares Raman (NR1100, JASCO, Japan) spectra of the carbonized products obtained at 850 °C. They show the coexistence of amorphous and crystalline regions. We observe the crystalline aromatic C=C (E_{2g} mode; G-mode) Raman shift at 1592 cm^{-1} and the aromatic C=C (A_{1g} mode; D-mode) Raman shift in the disordered structure at 1355 cm^{-1},[28] whose ratios are about 70−80:20−30 in area. Carbonization of PPVs at higher temperatures is expected to produce further graphatized products. Earlier, we found that poly(*p*-phenyleneethynylene) undergoes carbonization faster than PPV.[29] The acetylenic structure in the former evidently facilitates the formation of aromatic graphitic structures than the vinylene groups in the latter.

There are numerous papers describing preparation methods and properties of different types of carbon nanotubes including single and multiwall structures.[30] And applicability of the carbon nanotubes has been discussed about much in the literature,[31] and is not repeated in this article. It, however, is emphasized that the present investigation provides an alternative and easy way to prepare carbon nanotubes and nanorods that can be utilized as conducting materials in nanodevices and high surface supports useful in catalysis.

In summary, we successfully prepared PPVs in the shapes of nanotubes and nanorods by the CVD polymerization of α,α′-dichloro-*p*-xylene inside the nanopores of alumina and polycarbonate filters. They also could be converted into carbonized products by thermally treating them in an inert atmosphere. This approach is expected to open up new fabrication methods for the preparation of insoluble organic polymers in intended nano shapes and dimensions. Study on the electrical and optical properties of the present PPVs and carbonized nano objects is expected to lead to new information useful in nano technologies.

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Supporting Information Available: Figure S-1 (TEM micrographs of PC-100 and carbonized PC-100) and Figure S-2 (wide-angle X-ray diffractograms of Al-200, PC-100, and PC-10). This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting

This article was released ASAP on 8/29/2001. Figure 5 has been revised and the correct version was posted on 10/31/2001.

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