

## Preparation of a Graphite-like Structured Polymer from 1-Phenylpenta-1,3-diyne-5-ol

Heung Jae Lee and Sang Chul Shim\*

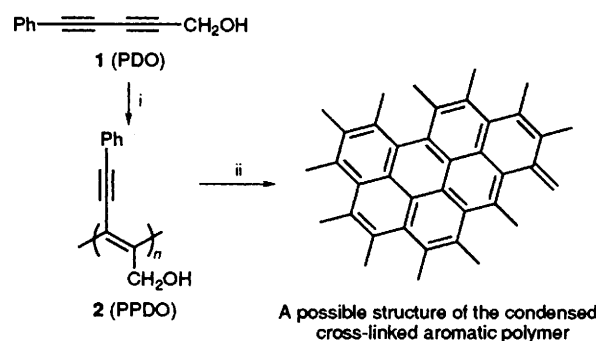
Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusong-Ku, Taejon, 305-701, Korea

Poly(1-phenylpenta-1,3-diyne-5-ol) (PPDO), prepared by  $\text{NbCl}_5/(\text{Bu}^n)_4\text{Sn}$  catalysed metathesis of PDO, is converted into a graphite-like structure with a high conductivity in the absence of dopants by heat treatment at  $800^\circ\text{C}$  under vacuum.

Conductive or semi-conductive organic polymers such as poly(acetylene) derivatives have received much recent attention.<sup>1-4</sup> However, doped conductive polymers are not known to be very stable in air. Some synthetic graphites are known to be stable in air and have a high conductivity without dopants.<sup>5-9</sup> Calculations predicted that graphite-subunits possess a low band gap and offer distinct electronic advantages over linear  $\pi$ -systems,<sup>10,11</sup> stimulating an interest in the synthesis of polymers having a graphite-like structure.

In order to prepare such a graphite-like structured polymer, poly(1-phenylpenta-1,3-diyne-5-ol) (PPDO) **2** was prepared as a possible precursor by the metathesis polymerization of 1-phenylpenta-1,3-diyne-5-ol (PDO)† **1** (Scheme 1). Thus-prepared PPDO was heat treated at  $800^\circ\text{C}$  for 30 min under

vacuum to obtain the final product; a graphite-like structured polymer formed probably through cyclization and condensation reactions. A typical polymerization procedure of PDO is as follows. A toluene (0.2 ml) suspension of  $\text{NbCl}_5$  (40 mg, 0.2



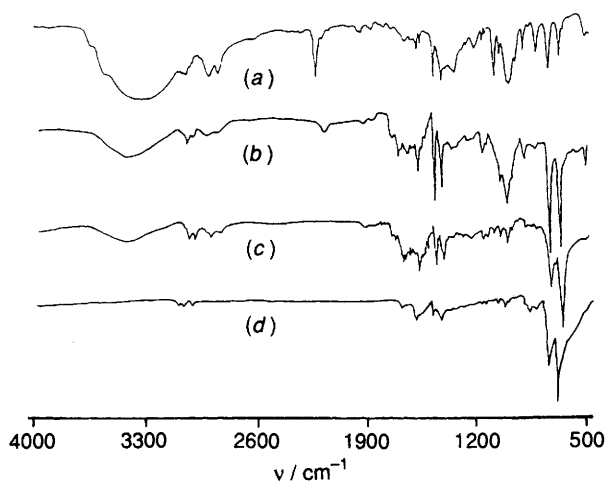
† PDO **1** was prepared by the Chodkiewicz and Cadiot Coupling<sup>12</sup> of phenylacetylene and 1-bromopropynyl alcohol:<sup>13</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.14 (2H, s), 4.39 (1H, s), 7.2–7.5 (5H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  51.51, 70.23, 73.16, 78.43, 80.56, 121.36, 128.36, 129.28, 132.53 MS  $m/z$  156 ( $\text{M}^+$ ).

**Scheme 1** Reagents and conditions: i,  $\text{NbCl}_5$  or  $\text{TaCl}_5$ , cocatalyst:  $\text{Et}_3\text{SiH}$ ,  $\text{Bu}^n_4\text{Sn}$ ,  $\text{Ph}_4\text{Sn}$ , toluene,  $80^\circ\text{C}$ , 2 days; ii,  $>800^\circ\text{C}$ , under vacuum

**Table 1** The effects of the substituents on the polymerization of R-≡≡-R'

R	R'	Polymerization yield (%) <sup>a</sup>	M <sub>w</sub>	Colour	λ <sub>max</sub> /nm
Ph	-CH <sub>2</sub> OH	82	3200 <sup>b</sup>	Dark-brown	446.5 <sup>d</sup>
MeOC <sub>6</sub> H <sub>4</sub>	-CH <sub>2</sub> OH	76	5300 <sup>b</sup>	Dark-brown	451 <sup>d</sup>
Ph	-C(Me <sub>2</sub> )OH	43	2065 <sup>b</sup>	Brown	449 <sup>d</sup>
-CH <sub>2</sub> OH	-CH <sub>2</sub> OH	88	? <sup>c</sup>	Dark-yellow	365 <sup>e</sup>

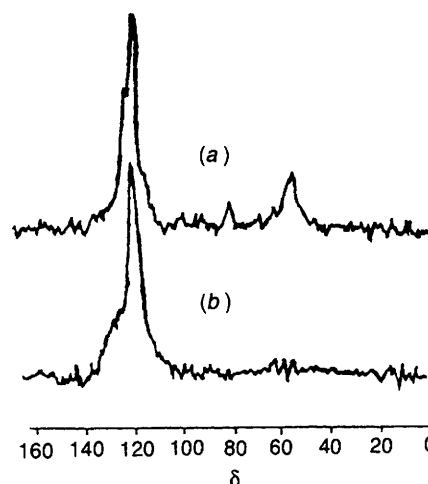
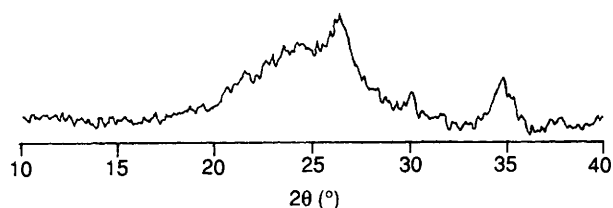
<sup>a</sup> NbCl<sub>5</sub> and Bu<sub>4</sub>Sn catalysts used. <sup>b</sup> Determined by GPC method in THF. <sup>c</sup> Not determined by GPC method in DMF. <sup>d</sup> In THF. <sup>e</sup> In DMF.

**Fig. 1** IR spectra of (a) PDO; (b) PPDO; (c) heat-treated PPDO under 200 °C; (d) under 330 °C

mmol) and Bu<sub>4</sub>Sn (0.12 ml, 2 mmol) under nitrogen atmosphere was stirred at 80 °C for 30 min and a toluene (50 ml) solution of PDO (800 mg, 5 mmol) was added with the continuous stirring at 80 °C for 2 days. Tetrahydrofuran (THF) was added to the mixture, and a small amount of insoluble inorganic materials were removed by filtration. After the evaporation of solvents, PPDO (656 mg, 82%) was precipitated by adding hexane. The results of polymerization of PDO and several disubstituted buta-1,3-diyne are shown in Table 1.

The PPDO and heat-treated PPDO were analysed by the IR, Raman, CPMAS <sup>13</sup>C NMR and X-ray diffraction spectroscopic methods. Important informations on the structure of PPDO and heat-treated PPDO at 200 and 330 °C were obtained from the IR spectra as shown in Fig. 1. The following vibrations were of particular importance when comparing the spectra of monomer [Fig. 1(a)] and polymer [Fig. 1(b)]. (i) The stretching vibration of the triple bond in monomer and PPDO was observed near 2200 cm<sup>-1</sup>. (ii) The stretching vibration of the double bond in PPDO near 1600 cm<sup>-1</sup>. Interestingly, when the heat-treatment temperature was raised, the stretching vibrations of the triple bond (2200 cm<sup>-1</sup>) and the C-O bond (1050 cm<sup>-1</sup>) disappeared. The two strong bands between 650–760 cm<sup>-1</sup> in the spectra [Fig. 1(c) and 1(d)] were assigned to the C-H out-of-plane vibrations of monosubstituted phenyl ring which were also observed in the spectrum of the monomer [Fig. 1(a)], suggesting that the partial structure of PPDO contains monosubstituted phenyl moiety that remains intact after the thermal treatment at 330 °C.<sup>14</sup>

Raman spectroscopy provided important information on a graphite-like structure.<sup>15,16</sup> The laser Raman spectrum of the heat-treated PPDO at 800 °C shows two peaks around 1350

**Fig. 2** Solid-state <sup>13</sup>C NMR CPMAS spectra of (a) PPDO; (b) heat-treated PPDO (at 800 °C)**Fig. 3** Powder X-ray diffraction pattern for PPD pyrolysed at 800 °C

cm<sup>-1</sup> (disorder-induced line) and 1580 cm<sup>-1</sup> (Raman allowed graphite-like E<sub>2g</sub> mode). The results of the IR and Raman spectral analysis indicated that all the oxygen atoms and some of the hydrogen atoms were released during the heat treatment to give graphite-like structures having defects.

Fig. 2 shows the CPMAS <sup>13</sup>C NMR spectra of PPDO and heat-treated PPDO. The peaks at δ 110–140 [Fig. 2(a)] correspond to the sp<sup>2</sup> carbons of the polymer backbone and the phenyl group of the side chains, while those at δ 80–90 are the sp carbons of the side chains in PPDO, and those at δ 50–60 are due to the hydroxy methyl carbons of the side chains. In the spectrum of heat-treated PPDO at 800 °C [Fig. 2(b)] the peaks at δ 80–90 and δ 50–60 have disappeared. The broad peaks of olefinic carbons in the <sup>13</sup>C NMR spectra suggested an irregularity in the structure of imperfect graphite-like products.

Fig. 3 shows the powder X-ray diffraction pattern (with Cu-Kα radiation) of the heat-treated PPDO at 800 °C. The interlayer distance ( $d_c = 3.37 \text{ \AA}$ ) is derived from the peaks around  $2\theta = 21\text{--}28^\circ$ , which may be considered as the (002) band, in reference to the (002) peak of a graphite.<sup>17</sup> The results indicated that the heat-treated PPDO at 800 °C has quasi-crystalline forms ranging from near amorphous to the crystalline graphite-like state.

PPDO is an insulator, but its thermal annealed product gave some conductivity. The conductivity change of pelletized PPDO and heat-treated PPDO is shown in Table 2. When PPDO is thermally annealed at 200 and 300 °C for 30 min under N<sub>2</sub> atmosphere, it became a semiconductor ( $5.3 \times 10^{-8}$ – $1.5 \times 10^{-6} \text{ S cm}^{-1}$ ) without appreciable changes in the dimension or appearance, except that the original brown powder become black lustre. The reason for this remains unclear, but it may be due to π-conjugation enlargement of the main chain. This increase in the electrical conductivity from  $10^{-6}$  to  $10^{-1} \text{ S cm}^{-1}$  by the heat-treatment at 800 °C is supportive of the formation of a graphite-like structure. But the resulting electrical conductivities are not of metallic

**Table 2** Conductivity of PPDO and heat-treated PPDO

$T/^{\circ}\text{C}$	Iodine doping	Form	$S_{\text{max}}/\text{cm}$
Room temp.	Doped	Pellet	$1.9 \times 10^{-4}$
	Undoped	Pellet	$5.3 \times 10^{-8}$
200 <sup>a,b</sup>	Doped	Pellet	$9.0 \times 10^{-5}$
	Undoped	Pellet	$1.5 \times 10^{-6}$
330 <sup>a,b</sup>	Doped	Pellet	$7.3 \times 10^{-4}$
	Undoped	Pellet	$3.2 \times 10^{-1}$
800 <sup>a,c</sup>	Doped	Pellet	
	Undoped	Pellet	

<sup>a</sup> Heat treatment for 30 min. <sup>b</sup> Under  $\text{N}_2$ . <sup>c</sup> Under vacuum.

nature. This is because the heat-treated PPDO at  $800^{\circ}\text{C}$  has a condensed cross-linked aromatic rings with defects.

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