Synthesis and Properties of Poly(1-phenyl-3-butyn-1-ol)

Yun-Hi Kim and Soon-Ki Kwon*

Department of Polymer Science & Engineering and Advanced Material Research Institute,
Gyeongsang National University, Chinju 660-701, Korea
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Substituted polyacetylenes are of interest to many research groups due to their better stability and solubility than polyacetylene in spite of somewhat low electrical conductivity.[1]

Polymerization of polyacetylene derivatives containing functional group such as ester, acid, pyridine, halide, sulfide, and alcohol etc. has been extensively studied because of their capacity to show hydrophilic properties, chemical reactivity, and complex formation ability.[2] The polymers of acetylene derivatives with ionic functional groups has also been reported.[3] Among these polymers, polyacetylene derivatives containing a hydroxy functional group are of interest because of unique structures and difficulty in the synthesis of soluble polymer with high molecular weight.[4]

It has been reported that some acetylene derivatives containing hydroxy functional group were polymerized but the resulting polymers were insoluble or has considerably low molecular weight.[5,10] In the previous paper,[6] we reported the cyclopolymerization of dipropargyl carbinol derivatives by transition metal catalysts. However, there is no report on the polymerization of acetylene derivative containing β-hydroxy functional group except the polymerization of 3-butyn-1-ol which gave insoluble polymer.[5b]

In the present paper, we examined the selective synthesis and polymerization of a acetylene derivative containing a β-hydroxy group, 1-phenyl-3-butyn-1-ol(PBO). Further, the structure and properties of the resulting polymer were elucidated.

Experimental

PBO is prepared by Grignard reaction. 4.3 g (0.18 mol) of magnesium turnings and 22 g (0.18 mol) of propargyl bromide were reacted with 16 g (0.15 mol) of benzaldehyde. [Yield : 68%, B.p. : 75 °C/1 mmHg]; ^{1}H NMR δ 7.2 (m, 5H, ring protons), 4.7 (m, 1H, benzylic proton), 2.8 (b, 1H, O-H), 2.5 (m, 2H, -CH$_2$-), 2.1 (t, 1H, ≡CH), ; IR (NaCl, cm^{-1}) 3500 (O-H), 3300 (≡C-H), 2150 (C≡C).

Instruments and Measurements. ^{1}H- and ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer and a Bruker AM 300 spectrometer. Infrared spectra were taken on a Perkin-Elmer 283B and a Bomem Michelson series FT-IR spectrometer using KBr pellet or NaCl disk. UV-visible spectrum were obtained with a Beckman DU-6 spectrometer. The number average molecular weights (Mn) were measured by means of GPC-150C of waters in THF solution using a calibration curves for polystyrene standards. Thermogravimetric analysis (TGA) was performed with a DuPont 951 TGA under nitrogen atmosphere at a heating rate of 5 °C/min. Wide-angle x-ray diffractograms were obtained on a Rigaku-Rotaflex. Elemental analysis was made on a 240C Elemental Analyzer. Electrical conductivity were measured by the 2-pont probe dc method employing a Hewlett-Packard 6216A power supply and a Keithley picoameter.

Polymerization. All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere. The polymers were synthesized by the same method as described in a previous paper.[6a]

Results and Discussions

The PBO was prepared by a Grignard reaction of propargyl magnesium bromide and benzaldehyde contrary to difficult literature method[8] in which PBO was synthesized from lithium acetylide and styrene oxide in liquid ammonia. As the reaction temperature lowered and the reaction time shortened, the yield of internal acetylene derivative, 1-phenyl-2-butyn-1-ol, was decreased. The monomer, PBO was selectively synthesized, when the reaction temperature and time are below − 30 °C and within 3 min, respectively. (Scheme 1)

The polymerization of PBO was carried out by various transition metal catalysts (Table 1). It has been known that MoCl$_5$-based catalysts are very effective for the polymerization of some acetylene derivatives, especially those containing oxygen atoms, such as propiolic acid, dipropargyl ether, and dipropargylcarbinols.[5,6,9] The polymerization of PBO was also effectively carried out by MoCl$_5$-based catalyst systems.

The polymerization of PBO by WCl$_6$-based catalyst system was also carried out. The WCl$_6$-EtAlCl$_2$ catalyst system gave only 10% low yield of poly(PBO). On the other hand, the polymerization of PBO was not proceeded by WCl$_6$ itself and WCl$_6$-(n-Bu)$_4$Sn. The low catalytic activity of WCl$_6$-based catalysts for the polymerization of PBO is thought to be due to poisoning of WCl$_6$ by the hydroxy group. Similar results were observed for the polymerization of such hydroxy group-containing acetylenes as dipropargylcarbinol, 1-octyne-3-ol and 1-ethynyl-1-cyclohexanol.[5,6] TiCl$_4$ catalyst system known as good catalyst system for the acetylene was not effective, while the polymerization by PdCl$_2$ was carried out at low yield. Furthermore, TaCl$_5$ and NbCl$_5$
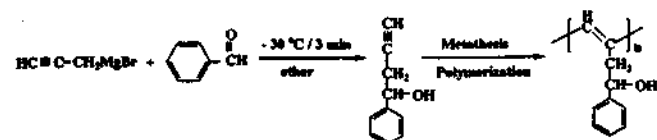
Scheme 1.

which are good catalysts for the disubstituted acetylene and monosubstituted acetylene with bulky substituents, showed no catalytic activity for the polymerization of PBO.

The number average molecular weight of the poly(PBO) obtained by $MoCl_5$-based catalysts is about 4×10^3-7×10^3 and is somewhat high as compared with that of other monosubstituted polyacetylenes containing a hydroxy functional group[5] but is as low as ever in comparison with that of other non-polar polyacetylene derivatives. This is probably due to the reduction of catalytic activity through the coordination of hydroxy functional group to the active center of catalyst during polymerization.

The polymer structure was identified by ^{1}H, ^{13}C NMR and IR spectroscopy. In the ^{1}H NMR spectrum of poly (PBO), protons of conjugated double bond appeared at δ 6.0-7.5 ppm in company with aromatic protons. The infrared spectrum of poly(PBO) showed neither acetylenic hydrogen bond nor the carbon-carbon triple bond stretching absorption band presented in the IR spectrum of PBO. Instead, new carbon-carbon stretching absorption band of conjugated double bond appeared at about 1650 cm^{-1}, which indicates that a highly conjugated polymer was formed (Figure 1). In

Table 1. Polymerization of PBO by Various Transition Metal Catalysts[a]

Exp. No	Catalyst (mole ratio)	Polymer Yield (%)	$\overline{Mn}$[b]
1	$MoCl_5$	80	4900
2	$MoCl_5$ (n-Bu)$_4$Sn (1:2)	85	6800
3	$MoCl_5$ Et$_2$AlCl (1:2)	47	5200
4	$MoCl_5$ EtAlCl$_2$ (1:2)	61	3700
5	PdCl$_2$	32	3800
6	TiCl$_4$ EtAlCl$_2$ (1:2)	0	-
7	WCl$_6$	0	-
8	WCl$_6$ (n-Bu)$_4$Sn (1:2)	0	-
9	WCl$_6$ EtAlCl$_2$ (1:2)	10	-
10	TaCl$_5$	0	-
11	NbCl$_5$	0	-

[a]Polymerization was carried out at 80 °C for 24 h. in chlorobenzene. Initial monomer concentration ($[M_o]$) was 1.0 M and the mole ratio of monomer to catalyst is 50. [b]Number Average Molecular Weight ($\overline{Mn}$) of Poly(PBO) by GPC in THF.
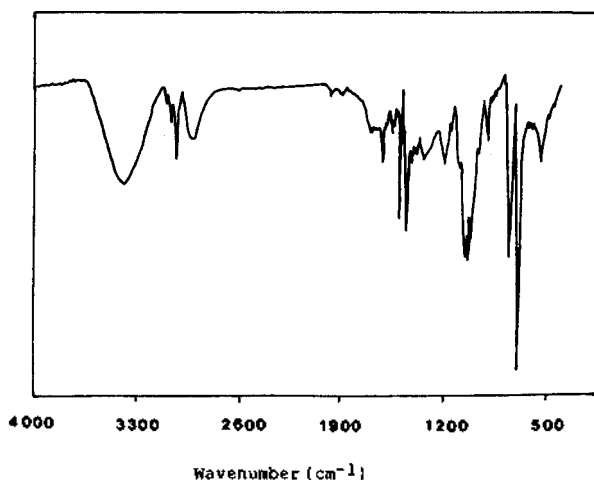
the ^{13}C NMR spectrum (Figure 2), olefinic carbons appeared at 125 and 135 ppm while the acetylenic carbon peak disappeared at 72 and 79 ppm. The UV-visible spectrum of the polymer was obtained in chloroform solution (Figure 3). A broad π→π* absorption peak (λ_{max}=315 nm) of conjugated double bonds in the polymer main chain, which are absent in the monomer, extended to the visible region (400-550 nm). These spectral data suggest that poly (PBO) has conjugated double bond as shown in Scheme 1.

The obtained yellow poly(PBO) was soluble in various organic solvents such as toluene, benzene, CHCl$_3$, THF, and acetone, but insoluble in non-polar solvents such as petroleum ether, hexane, cyclohexane, and CCl$_4$. These solubility
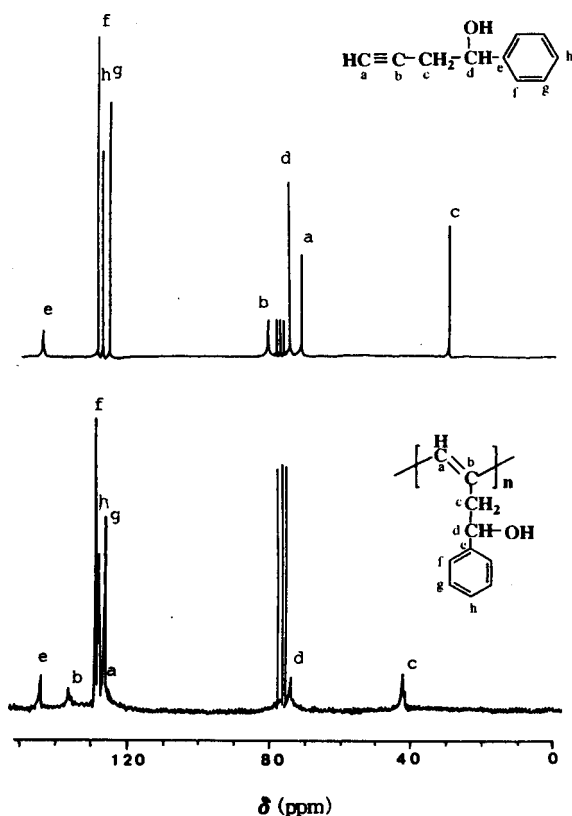

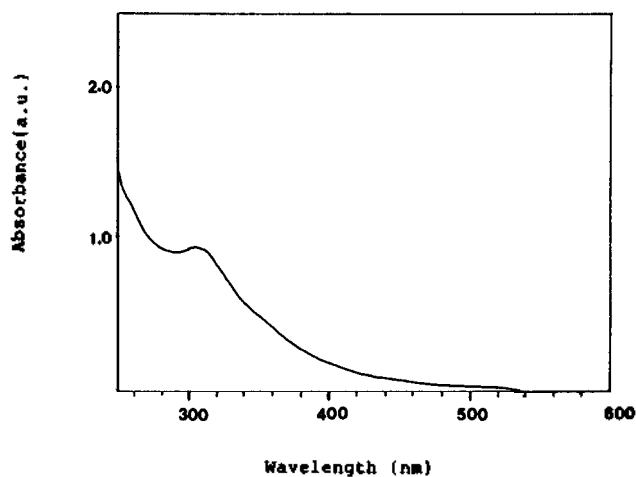**Figure 2.** ^{13}C NMR spectra of PBO and poly(PBO).

Figure 1. A IR spectrum of poly(PBO).

Figure 3. A UV-visible absorption spectrum of poly(PBO).

Notes

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behaviors were probably due to the hydroxy and phenyl functional group of the product polymer.

The morphology of poly(PBO) was also investigated by x-ray diffraction analysis. In general, when the X-ray diffraction pattern of amorphous polymer is broad, the ratio of the half-height width to diffraction angle ($\triangle 2\theta/2\theta$) is greater than 0.35 and when crystalline diffraction peak are sharp, values of $\triangle 2\theta/2\theta$ are smaller than 0.05.[1a] On this basis, it is concluded that poly(PBO) is amorphous [2θ, ($\triangle 2\theta/2\theta$)= 8.5°, (1.04); 16.1°, (0.68)]. The electrical conductivity of iodine-doped poly(PBO) was 7.5×10^{-4} Scm^{-1}. The electrical conductivity and morphology of poly(PBO) is similar with that of other monosubstituted polyacetylenes.[1b]

The TGA thermogram of poly(PBO) showed the weight loss begins about 150 °C. The first weight loss of 13% at the range of 150-220 °C is probably due to the dehydration of poly(PBO). The first weight loss is consistent with weight percent of H_2O in the repeating unit. The residual weight of poly(PBO) at 600 °C is about 40%. This is probably due to the carbonization of dehydrated poly(PBO) with extended conjugation.

The studies on the dehydration of poly(PBO) and the electrical conductivity of dehydrated poly(PBO) are now in progress.

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CORRECTION

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1) In the figure caption of Figure 3, from bottom to top should be changed to **from top to bottom**.   2) In the figure caption of Figure 5, (A) PEO-powder, (B) PEO-sheet, and (C) PEO-pellet should be changed to (A) **PEO-pwd**, (B) **PEO-sht**, and (C) **PEO-plt**.   3) In the second line of Results and Discussion section, HEPE should be **HDPE**.