



Polymerization of 4-ethynylbiphenyl by transition metal catalysts



JooHwan Tak^{a,1}, Sung-Ho Jin^{a,*}, Yeong-Soon Gal^{b,*}

^a Department of Chemistry Education, Pusan National University, Busan 46279, Republic of Korea

^b Department of Fire Safety, Kyungil University, Gyeongsan 38428, Gyeongsangbuk-do, Republic of Korea

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ABSTRACT

The polymerization of 4-ethynylbiphenyl (4-EBP) was performed by various transition metal catalysts. The polymerization of 4-EPB proceeded well to give a high yield of polymer. The W-based catalysts were found to be more effective for this polymerization than the Mo-based catalysts. The EtAlCl_2 showed high cocatalytic activity for the polymerization of 4-EPB by WCl_6 or MoCl_5 . The $[\text{Rh}(\text{nbd})\text{Cl}]_2/\text{Et}_3\text{N}$ catalyst showed high catalytic activities, whereas the poly(4-EBP)s obtained by Rh catalyst were mostly insoluble in organic solvents. The analytical results for the polymer structure revealed that the resulting polymer have a conjugated polymer backbone system with the biphenyl substituents. The poly(4-EPB)s prepared by W- and Mo-based catalysts were completely soluble in such organic solvents such as benzene, carbon tetrachloride, chloroform, 1,4-dioxane, methylene chloride, THF, and toluene. The maximum peak of photoluminescence spectrum of polymer was located at 474 nm corresponding to the photon energy of 2.62 eV, which is sky blue region. The cyclic voltammograms of poly(4-EBP) exhibited not only irreversible oxidation and reduction peaks but also the electrochemically stable window in the range of -1.3 to 1.3 V. HOMO and LUMO levels and band gap of poly(4-EBP) were 5.43, 2.72 eV and 2.71 eV, respectively.

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Introduction

Over the past five decades, there has been a permanent interest in the design and synthesis of π -conjugated oligomers and polymers [1–10]. The conjugated polymers are expected to show such general properties as semiconductivity, optical nonlinearity, high gas permeability, helix formation, magnetic properties, electro-optical properties, etc. [2,3,6,11,12]. These properties of conducting polymers have been applied in wide ranges of applications including light-emitting diodes, solar cells, nonvolatile memory devices, photosensing devices, organic field-effect transistors, batteries, and biological and chemical sensors [5,6,13–20]. Various conducting polymer-based nanocomposites or nanoparticles have also been fabricated and characterized, which the conducting polymers were based on polyanilines and/or polypyrroles [21–27].

Polyacetylene itself is the simplest representative of conjugated polymer class having the alternating single and double bonds. The

free-standing thin polyacetylene films with metallic luster were firstly prepared by Ito et al. [28,29]. Polyacetylene itself is a typical semiconductor, however the electrical conductivity of polyacetylene film was dramatically increased by over 14 orders of magnitude by the chemical doping using electron donors or acceptors [7,30]. However, this material is notoriously intractable and unstable to air oxidation, and these natures of polyacetylene prevented their potential use in technological applications. Various conjugated polymers have been designed and prepared from acetylene derivatives including monosubstituted and disubstituted acetylenes, and cyclopolymerizable α,ω -diynes [1–10,31–34]. The introduction of substituents onto the conjugated polymer backbone has helped to overcome the problems of insolubility, instability, and degradation and has yielded relatively more stable and readily more processable conjugated polymers [2–6]. Substituted polyacetylenes have been known to be stable enough in air for a long period of time and generally soluble in organic solvents.

The polymerization of phenylacetylene, a mostly simple aromatic acetylene, have been carried out by various initiators and catalysts [1]. Masuda et al. firstly synthesized polyphenylacetylene with high molecular weights by using the WCl_6 and MoCl_5 catalyst, which had been used for the metathesis reaction of olefins and the metathesis polymerization of cycloolefins [35]. After then,

* Corresponding authors.

E-mail addresses: shjin@pusan.ac.kr (S.-H. Jin), ygal@kiu.ac.kr (Y.-S. Gal).

¹ Present address: Busan II Science High School, Busan 242, Republic of Korea.

there have been a number of study for the polymerization of functional arylacetylenes including phenylacetylene using W- and Mo-based catalyst systems [1,36,37]. We have also studied the polymerization behaviors of phenylacetylene using the catalyst systems such as $\text{MoCl}_5/2\text{-propyn-1-ols}$, $\text{Mo}(\text{OEt})_5\text{-EtAlCl}_2$, and $\text{Cp}_2\text{MoCl}_2/\text{EtAlCl}_2$ catalysts [38–41]. A few study on the synthesis and characterization of substituted polyacetylene with biphenyl substituents has been performed [42,43]. $[\text{RhCl}(\text{NBD})]_2$ (NBD: norbornadiene) and $[\text{Rh}(\text{NBD})\text{acac}]$ catalysts were used for the synthesis of optically active poly(phenylacetylene) and fluorescent polyacetylene-type conjugated polymers with biphenyl moieties, respectively [42,43].

In this paper, we report the synthesis of poly(4-EBP) via the transition metal catalyzed polymerization of 4-EBP, and the characterization for the polymer structure, and the physical properties of the resulting poly(4-EPB).

Experimental

Materials

4-EBP (97%), tungsten (VI) chloride (WCl_6 , 99.91%), molybdenum(V) chloride (MoCl_5 , 99.91%) and $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = 2,5-norbornadiene) were purchased from Sigma–Aldrich and used without further purification. Triethylamine (Et_3N) and ethylaluminum dichloride (EtAlCl_2) (Sigma–Aldrich, 25 wt%, 1.8 M solution in toluene) were used as received. Tetraphenyltin (Ph_4Sn , Sigma–Aldrich, 97%) was purified by recrystallizing by using carbon tetrachloride. Chlorobenzene (Sigma–Aldrich, 99.8%) was dried with calcium hydride and distilled. Toluene was distilled over sodium/benzophenone.

Polymerization

General procedures

The procedures for catalyst system preparation and polymerization with MoCl_5 and WCl_6 were performed under dry nitrogen atmosphere because the catalyst systems are sensitive to oxygen or moisture. The catalyst solutions of MoCl_5 and WCl_6 were prepared in chlorobenzene as 0.2 M solution. The polymerization procedures are as follows.

Polymerization of 4-EBP by MoCl_5

In a magnetic-stirred 30 mL flask capped by rubber septum, 0.5 g (2.81 mmol) of 4-ethynylbiphenyl, chlorobenzene (1.4 mL, $[\text{M}]_0 = 0.5 \text{ M}$), and 0.47 mL of 0.2 M MoCl_5 solution (0.0935 mmol, $\text{M}/\text{C} = 30$) were added in the order given. After that, the polymerization was performed at 60 °C for 24 h. Then the polymerization was terminated by adding a small amount of methanol. The polymer solution was diluted with 10 mL of chloroform, precipitated into a large excess of methanol. The precipitated polymer was filtered using Pyrex Buchner funnel (60 mL, 10–15 M) from the solution and dried under vacuo at 40 °C for 24 h. The polymer was obtained in 51% yield.

Polymerization of 4-EBP by $\text{WCl}_6\text{-EtAlCl}_2$

In a magnetic-stirred 30 mL flask tube capped by rubber septum, the catalyst solution of 0.47 mL (0.0935 mmol, $\text{M}/\text{C} = 30$) of 0.2 M WCl_6 solution and 0.104 mL (0.187 mmol, the mole ratio of catalyst:cocatalyst = 1:2) of 1.8 M EtAlCl_2 solution was shaken at 30 °C for 15 min. After that, the catalyst solution was injected into the reaction flask. Then the monomer solution of 0.5 g (2.81 mmol) of 4-ethynylbiphenyl and chlorobenzene (1.4 mL, $[\text{M}]_0 = 0.5 \text{ M}$) was added to the reaction flask containing the catalyst solution slowly. The polymerization was performed at 60 °C for 24 h. Then the polymerization was terminated by adding a small amount of

methanol. The polymer solution was diluted with 10 mL of chloroform, precipitated into a large excess of methanol. The precipitated polymer was filtered using Pyrex Buchner funnel (60 mL, 10–15 M) from the solution and dried under vacuo at 40 °C for 24 h. The polymer was obtained in 81% yield.

Polymerization of 4-EBP by $[\text{Rh}(\text{nbd})\text{Cl}]_2\text{-Et}_3\text{N}$ catalyst systems

In a magnetic-stirred 30 mL flask tube capped by rubber septum, a toluene solution (2.0 mL) of 4-ethynylbiphenyl (0.356 g, 2 mmol) was added to a toluene solution (2.0 mL) of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (0.0092 g, 0.02 mmol, $\text{M}/\text{C} = 100$) and 0.0202 g of Et_3N (0.2 mmol, catalyst:cocatalyst = 1:10). Then the polymerization was performed at 30 °C for 1 h. After a given time of polymerization, the polymer solution was diluted with 10 mL of chloroform, precipitated into a large excess of methanol. The precipitated polymer was filtered using Pyrex Buchner funnel (60 mL, 10–15 M) from the solution and dried under vacuo at 40 °C for 24 h. The polymer was obtained in 79% yield.

Measurements

The Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in CDCl_3 using tetramethylsilane as an internal standard was used to measure ^1H and ^{13}C NMR spectra for polymers and the chemical shifts are reported in ppm units. Infrared spectra of monomer and polymer were obtained on a Varian 800 spectrometer in KBr pellet. The elemental analyses were performed with FISON EA1110 elemental analyser. The X-ray diffractograms of polymer were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The number- and average-molecular weight (M_n and M_w , respectively) and polydispersity (M_w/M_n) of polymers were determined by GPC analysis relative to polystyrene calibration (Agilent 1100 series GPC, PL gel 5 μm MIXED-C, refractive index detector) in THF solution. The thermal analyses were carried out on a Mettler Toledo TGA/SDTA851 and DSC 822 analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. The optical UV–vis absorption spectrum was measured using a HP 8453 UV-visible Spectrophotometer in solution. A PerkinElmer luminescence spectrometer LS55 (Xenon flash tube) was used to obtain PL spectroscopy. It was measured by a lock-in amplifier system using a chopping 150 Hz frequency. Electrochemical property of polymers was measured with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research) cyclic voltammetry (CV) at a scan rate of 100 mV/s. All electrochemical measurements were carried out in air condition at room temperature. 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBAT) in anhydrous acetonitrile was used as electrolyte and polymer solution was prepared in *N,N*-dimethylformamide. A platinum wire and Ag/AgNO_3 were used as the counter electrode and reference electrode, respectively.

Results and discussion

Polymerization

Various types of W- and Mo-based catalysts had been used as an effective catalysts for the olefin metathesis polymerization and the metathesis polymerization of mono- and di-substituted acetylenes, and nonconjugated diynes [3,4,44,45]. Herein, the polymerization of 4-EBP, a substituted acetylene with biphenyl substituents, was performed by various transition metal catalysts (Scheme 1). We selected the chlorobenzene as the polymerization solvent because it was good solvent for not only the catalyst but also the monomer and polymer.

Table 1 shows the polymerization results of 4-EBP by W- and Mo-based transition metal catalysts. Generally, the

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