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Synthesis and characterization of poly(9-ethynyl-9-hydroxyfluorene)

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ABSTRACT

Transition metal-catalyzed polymerizations of 9-ethynyl-9-hydroxyfluorene (EHF) were investigated. EHF was easily polymerized by various transition metal catalysts to give in relatively high yields of polymer. The $MoCl_5$-based catalysts exhibited high catalytic activities, whereas the WCl_6-based catalysts showed low catalytic activities for the present polymerization. The highest polymer yield (85%) was obtained when the $(NBD)PdCl_2$ catalyst was used. The polymer structure was identified by such various instrumental methods as NMR, IR, and UV–visible spectroscopies to have a conjugated backbone with the fluorene and hydroxy groups. Poly(EHF) was stable to air oxidation and was soluble in such organic solvents as benzene, chlorobenzene, chloroform, DMF, and DMSO. The cyclovoltammograms of polymer exhibited the irreversible electrochemical behaviors. The oxidation of poly(EHF) was started to occur at 0.42 V (vs $Ag/AgNO_3$), where the vinylene unit of conjugated polymer backbone might be oxidized in the scan. And poly(EHF) also shows the irreversible reduction starting at −1.15 V.

Introduction

Semiconducting organic polymers are of particular interest in material science because of their extraordinary optical and electronical properties [1,2]. The polymers having a conjugated backbone shows such unique properties as electrical and photoconductivity, migration and transfer of energy, chemical reactivity and complex formation ability, high gas permeability, and high nonlinear optical susceptibility [3–9]. The unique properties based on the π-conjugated systems enabled these materials to be used in a wide range of applications such as electric semiconductors, photonics, nonlinear optical applications, gas or liquid separation membranes, chemical sensors, liquid crystals, photovoltaic cells, and organic light-emitting diodes (OLEDs) [10–17].

Over the past decades, significant progress has been made in the synthesis, characterization, and applications of polyacetylene and its derivatives [3,4,18–20]. Polymerization of acetylene by using various transition metal catalysts yielded the simplest conjugated polymer in organic systems. The applications of polyacetylene had been restricted because of the insolubility in organic solvents and the unstability to air oxidation. Unlike polyacetylene, substituted polyacetylenes are generally soluble in organic solvents and stable enough in air for a long period of time. The progress of various transition metal-based catalysts enabled the synthesis of a wide variety of functional conjugated polymers from acetylene monomers including monosubstituted and disubstituted acetylenes [3–5,21–24].

The organic polymers obtained from fluorene and its derivatives as monomers have been a potential candidate materials as blue light-emitting organic materials for light-emitting devices for display and other purposes [25,26] because these materials have advantages to impart solubility while maintaining a high degree of delocalization [27].

The palladium-catalyzed Sonogashira coupling of terminal alkynes to aromatic bromides or iodides in amine solvents is one of the most frequently used C–C bond forming processes in organic synthesis. Soluble fluorene-based copolymers for the applications as light-emitting diode and bulk heterojunction photovoltaic cell were prepared from the palladium catalyzed Suzuki polymerization of the corresponding monomers [28,29]. The conjugated cyclopolymer, poly(9,9-dipropargylfluorene), was synthesized via the ring-forming polymerization of 9,9-dipropargylfluorene by using various transition metal catalysts [30].

The polymer having two ethynyl and aromatic functional groups in the main chain had been prepared via the oxidative coupling of 9,9-dipropargylfluorene itself and its electro-optical

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and thermal properties were studied. And also, poly(9,9-dipropargylfluorenylene-phenylene) and poly(9,9-dipropargylfluorenylene-biphenylene) were prepared by palladium-catalyzed cross-coupling condensation reaction [31,32].

Attempted polymerization of EHF, an alkyne carrying a bulky substituents, had been performed by using classical transition metal catalysts. They found that some part of the pendant groups are converted into 9-fluorenone in solution [33]. In this article, we report the polymerization behaviors of EHF by using various transition metal catalysts, and the characterization on the electro-optical and electrochemical properties of the resulting poly(EHF).

Experimental

Materials

EHF (TCI Chemicals) was used without any further purification. $PdCl_2$ (Aldrich Chemicals, 99.9+%), (Bicyclo[2.2.1]hepta-2,5-diene)dichloropalladium(II) [(NBD)$PdCl_2$, Aldrich Chemicals), $PtCl_2$ (Strem), and $RuCl_3$ (Aldrich Chemicals) were used as received. $MoCl_5$ (Aldrich Chemicals, 99.9+%), WCl_6 (Aldrich Chemicals., 99.9+%), and $EtAlCl_2$ (Aldrich Chemicals., 25 wt.% in toluene) were also used without further purification. Ph_4Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. All the solvents were analytical grade.

Polymerization

All procedures for catalyst system preparation and polymerization were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. The catalyst solutions of WCl_6, $MoCl_5$, and $EtAlCl_2$ were prepared in 0.1 M or 0.2 M solutions in chlorobenzene before use. The polymer yield was determined by gravimetry. Typical synthetic procedures of poly(EHF) are as follows.

Polymerization of EHF by $PdCl_2$

A catalyst solution is prepared by mixing 28.7 mg (0.162 mmol, $M/C = 30$) of $PdCl_2$ and 5.0 mL of DMF ($[M]_0 = 0.81$ M). To this solution is added EHF (1.0 g, 4.85 mmol), followed by purging with the purified nitrogen. Then the polymerization was carried out at 80 °C for 24 h. The polymerization is terminated after the polymerization time and the polymer formed is isolated by the precipitation of the polymer solution diluted with additional 5 mL DMF into a large excess of benzene/petroleum ether. The precipitated polymer was filtered and dried in vacuum oven at 40 °C for 24 h. The light brown powder was obtained in 45% yield.

Polymerizaion of EHF by $MoCl_5$-$EtAlCl_2$

A mixture of $MoCl_5$ (1.62 mL of 0.1 M $MoCl_5$ solution, 0.162 mmol, $M/C = 30$) and $EtAlCl_2$ (1.62 mL of 0.2 M $EtAlCl_2$ solution, 0.324 mmol, $MoCl_5/EtAlCl_2$ mole ratio = 1/2) is aged at 30 °C for 15 min. This catalyst mixture was injected into the mononer (EHF, 1.0 g, 4.85 mmol) solution in chlorobenzene (1.61 mL, $[M]_0 = 1.0$ M). After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The diluted polymer solution was poured into an excess of benzene/petroleum ether, filtered from the solution, and then dried under vacuum at 40 °C for 12 h. The polymer yield was 62%.

Characterization

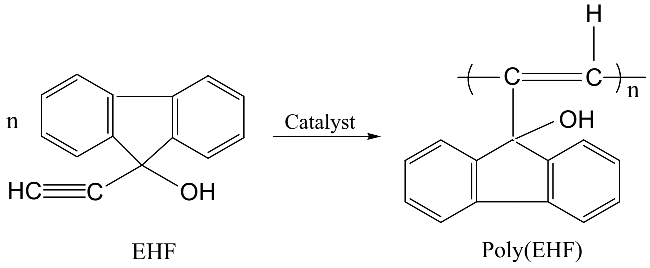
NMR spectra of poly(EHF) were performed in $CDCl_3$ as solvent on a 600 MHz Agilent FT-NMR spectrometer and the chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were recorded in KBr pellet on Bruker EQUINOX 55 spectrometer in the range of 400–4000 cm^{-1}. The molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with respect to polystyrene calibration (Waters high-pressure GPC assembly: M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500 and 100 Å, and refractive-index dectors) in THF solutions. Ultraviolet (UV)–visible spectra of monomer and polymer in DMF solvent were recorded on HP 8453 UV–visible spectrophotometer in the range of 200–800 nm. The non-isothermal thermogravimetric analyses of polymer were carried out using Perkin Elmer Diamond 3-II thermogravimetric analyzer under nitrogen atmosphere with a heating rate of 10 °C/min in the temperature range of 40–700 °C. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research). To examine electrochemical properties, the polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate (TBAT) solution containing acetonitrile. ITO, Ag/$AgNO_3$, and platinum wire were used as a working, reference and counter electrode, respectively.

Results and discussion

The polymerization of acetylene derivatives having hydroxy functional groups are of interests because of their unique structures and facile modification of hydroxy groups with other interesting functional groups. Soluble polyacetylene derivatives with hydroxy functional groups had been prepared by introducing substituents at the α-carbon of propargyl alcohol [34,35].

The polymerization of EHF, an acetylene derivative containing 9-hydroxyfluorenyl groups, was carried out by the Pd, Pt, W, and Mo-based catalysts (Scheme 1), which had been found to be very effective for the polymerization of some monosubstituted acetylenes [3–5,34–36].

Table 1 shows the results for the polymerization of EHF by various transition metal catalysts. The present polymerizations proceeded well in mild homogeneous monomer to give relatively high yields of polymer. $PdCl_2$ and $PtCl_2$ catalysts polymerized EHF to give moderate yields of poly(EHF) (45%, 43%, respectively). We also used the (NBD)$PdCl_2$ catalyst, which shows excellent solubility in the polymerization solvents whereas the $PdCl_2$ and $PtCl_2$ catalysts were not completely soluble in reaction medium. The (NBD)$PdCl_2$ catalyst polymerized the monomer in homogeneous manner to give the highest polymer yields (85%). This result may be explained by the high catalytic activity and/or the good solubility of (NBD)$PdCl_2$. It has been known that the $MoCl_5$-based catalyst systems exhibited the higher catalytic activity for the polymerization of acetylene derivatives with polar functional groups [3,4]. In the present polymerization, $MoCl_5$ alone gives a moderate yield of polymer (42%), whereas WCl_6 alone failed to polymerize EHF. A typical organoaluminium cocatalyst, $EtAlCl_2$,



Scheme 1. Synthesis of poly(EHF) by transition metal catalysts.