

Synthesis and Spectroscopic Properties of Conjugated Cyclopolymer

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1. INTRODUCTION

Fluorene group is very useful for electro- and optical property and highly efficient chromophore. Fluorene containing poly(phenylene vinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices for display and other purposes [1-3]. The diacetylene polymer via oxidative coupling of fluorene compound and poly(fluorenyleneethylene)s by alkyne metathesis of (9,9-dialkyl)fluorene-2,7-yleneethynylene were prepared and characterized [4,5]. In 9,9'-spirofluorene in the polymer chains, the fluorene rings are orthogonally arranged and connected via a common tetracoordinated carbon [6]. This structural features would be expected to reduce the probability of interchain interactions and prevent the close packing of the polymer chains, resulting in good solubility of polymers.

In our previous paper, we have studied the polymerization behaviors for the cyclopolymerization of dipropargylfluorenes by W- and Mo-based catalysts [7-9]. In some cases, the resulting polymers were insoluble at any organic solvents because of the crosslinking reaction during the polymerization. Now we report the synthesis of soluble poly(9,9-dipropargylfluorene) by the cyclopolymerization of 9,9-dipropargylfluorene by Pd, Pt, and Ru-based catalysts, and the electro-optical and electrochemical properties of the resulting polymer.

2. EXPERIMENTAL

All procedures for polymerization were carried out under dry nitrogen atmosphere. A typical procedure for the polymerization of 9,9-dipropargylfluorene by (NBD)PdCl₂ was as follows. In a magnetic-stirred 30 mL reactor, 9,9-dipropargylfluorene (2.0 g, 3.25 mmol), (NBD)PdCl₂ [7.41 mg, 0.275 mmol, monomer to

catalyst mole ratio (M/C) = 30], and DMF (8.0 mL, [M]₀ = 0.825) were added in that given order and sealed with a rubber septum after flushing with purified argon gas. The polymerization was carried out at 90 °C for 24 hrs. The polymerization proceeded homogeneously. Then the polymer solution diluted with DMF was precipitated into a large excess amount of methanol. The precipitated polymer was filtered and dried under vacuum oven at 40 °C for 24 hrs.

The optical absorption spectra were measured by a HP 8453 UV-Visible Spectrophotometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence Spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. NMR spectra of polymer were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in CDCl₃ and the chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. Molecular weights were determined by a gel permeation chromatographer (Waters 150C) equipped with μ -Styragel columns using THF as an eluent. Monodisperse polystyrene standard samples were used for molecular weight calibration.

3. RESULTS AND DISCUSSION

In general, the present cyclopolymerization of 9,9-dipropargylfluorene by the Pd, Pt- and Ru-chlorides proceeded well to give relatively high yield of polymer. The catalytic activity of PdCl₂ and RuCl₃ was found to be slightly higher than that of PtCl₂. We used the homogeneous (NBD)PdCl₂ catalyst, which shows excellent solubility in the polymerization solvents and have not been used for the cyclopolymerization of nonconjugated diynes.

This catalyst polymerized the monomer in mild homogeneous manner to give the highest polymer yield (91%) and the number-average molecular weight of this polymer was 10,100. The number-average molecular weights (Mns) and the polydispersities (Mw/Mn) were in the range of 4,300-10,100 and 2.50-3.23, respectively. The relatively low molecular weights and high polydispersities may be originated by the mild polymerization manner. On the other hand, the WCl_6 alone gives only a low yield of oligomeric products. The polymer obtained by $MoCl_5$ was mostly insoluble in organic solvents although the yield was quantitative. The reason for the formation of insoluble poly(9,9-dipropargylfluorene) may be originated by the relatively rapid polymerization, which causes the inter-chain cross-linking reaction of activated allyl protons of the resulting polymer during the process. We used the poly(9,9-dipropargylfluorene) sample prepared by (NBD) $PdCl_2$ for the identification of polymer structure and the elucidation on the electro-optical and electrochemical properties of polymer.

The 1H -NMR spectrum of poly(9,9-dipropargylfluorene) prepared showed the aromatic fluorene proton peaks at the aromatic region of 6.4-8.0 ppm. The vinyl protons of conjugated polymer backbone were also observed around 6.0 ppm. Fig. 1 shows the ^{13}C -NMR spectrum of poly(9,9-dipropargylfluorene) in $CDCl_3$. It did not show any acetylenic carbon peaks (72.76, 80.99 ppm) of monomer. Instead, the ^{13}C -NMR spectrum of polymer showed the aromatic carbons of fluorene groups and the olefinic carbon peaks of the conjugated polymer backbone at the region of 118-156 ppm. More informations on the microstructures of poly(1,6-heptadiyne)-based conjugated cyclopolymers can be obtained from the studies on the resonance for the quaternary carbon atoms [9].

The electro-optical and electrochemical properties of poly(9,9-dipropargylfluorene) were studied by UV-visible and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). The UV-visible spectrum of poly(9,9-dipropargylfluorene) solution (0.025 wt. %, DMF) was measured. In our previous paper, we had reported the PL spectrum of an ionic poly(2-ethynylpyridinium bromide) with propargyl side chain, it showed 708 nm PL maximum value at excitation wavelength of 525 nm. Poly(9,9-dipropargylfluorene) showed characteristic UV-visible absorption band at 307 and 324nm and violet-blue PL spectrum at 411 nm, corresponding to a photon energy of 3.01 eV. This polymer includes the chromophores of fluorene and conjugated polyene moieties. Fluorene group exhibited UV maximum

absorption of 307 and 314 nm and PL maximum emission of 411 nm. Conjugated polyene in main chain of this polymer showed relatively weak visible light absorption at around 500 to 600 nm and very weak PL emission at around 700 nm region originated from mono-substituted polyacetylene structure. In this compound, two chromophores are separated and they emit their own emission light although the intensity of polyacetylene is very weak. The energy band gap of polymer was estimated to be 2.81 eV from the analysis of the absorption edge between 500 and 600 nm region with a plot of (hv) vs. $(ahv)^2$, where a , h , and v are absorbance, Plank's constant, and the frequency of light, respectively.

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