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Journal of Industrial and Engineering Chemistry 14 (2008) 468–472

JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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Electro-optical and electrochemical properties of an conjugated cyclopolymer: Poly(9,9-dipropargylfluorene)

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Received 5 October 2007; accepted 2 February 2008

Abstract

The conjugated cyclopolymer, poly(9,9-dipropargylfluorene), was prepared by the ring-forming polymerization of 9,9-dipropargylfluorene by (bicyclo[2.2.1]hepta-2,5-diene)dichloropalladium(II) in high yield. The chemical structure of poly(9,9-dipropargylfluorene) was characterized by such instrumental methods as NMR (^{1}H, ^{13}C), IR, UV–vis spectroscopies, and elemental analysis to have the conjugated polymer backbone bearing fluorene moieties. Poly(9,9-dipropargylfluorene) showed characteristic UV–vis absorption band at 307 and 324 nm and violet-blue PL spectrum at 411 nm, corresponding to a photon energy of 3.01 eV. The cyclic voltamograms of the polymer exhibited reversible electrochemical behaviors between the doped and undoped peaks. It was found that the kinetics of the redox process of polymer is controlled by the diffusion process mixed with the electron transfer process from the experiment of the oxidation current density of polymer *vs.* the scan rate.

Keywords: Polyacetylene; Conjugated polymer; Cyclopolymerization; Photoluminescence; Cyclic voltammogram

1. Introduction

The polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1–7]. Because of these properties, polyacetylene and its homologues have been promising as organic semiconductors, as membranes for gas separation and for liquid-mixture separation, as chiro-optical materials, as side-chain liquid crystals, as materials for chemical sensors, and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties [8–15].

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 [16–19]. The diacetylene polymer via oxidative coupling of fluorene compound and poly(fluorenyleneethylene)s by alkyne metathesis of (9,9-dialkyl)fluoren-2,7-yleneethylenes were prepared and characterized [20,21]. In 9,9′-spirofluorene in the polymer chains, the fluorene rings are orthogonally arranged and connected via a common tetracoordinated carbon [22]. These 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.

We have studied the polymerization behaviors for the cyclopolymerization of dipropargylfluorenes by W- and Mo-based catalysts [23,24]. 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.

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doi:10.1016/j.jiec.2008.02.001

Table 1
Cyclopolymerization of 9,9′-dipropargylfluorene by transition metal catalysts[a]

Exp. No	Catalyst	M/C[b]	$[M]_0$[c]	Solvent	P.Y. (%)[d]	M_n[f]	M_w/M_n[f]
1	$PdCl_2$	30	0.5	DMF	86	7,500	2.51
2	$PtCl_2$	30	0.5	DMF	75	4,300	2.80
3	$RuCl_3$	30	0.5	DMF	83	8,100	3.23
4	$(NBD)PdCl_2$	30	0.5	DMF	91	10,100	2.72
5	$(NBD)PdCl_2$	50	0.5	DMF	81	8,200	2.50
6	WCl_6	50	0.25	Chlorobenzene	6	–	–
7	$MoCl_5$	50	0.25	Chlorobenzene	100[e]	–	–

[a] Polymerization was carried out at 60 °C (in chlorobenzene) and 90 °C (in DMF) for 24 h.
[b] The mole ratio of monomer to catalyst.
[c] Initial monomer concentration (M).
[d] Methanol-insoluble polymer yield.
[e] Insoluble polymer.
[f] Molecular weights obtained by GPC.

2. Experimental

(Bicyclo[2.2.1]hepta-2,5-diene)dichloropalladium(II) [$(NBD)PdCl_2$] (Aldrich Chemicals.) and fluorene (Aldrich chemicals, 98%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution in toluene) was dried with K_2CO_3 and distilled under reduced pressure. The synthesis of 9,9-dipropargylfluorene was performed according to the literature procedure [23]. All procedures for polymerization were carried out under dry nitrogen atmosphere. A typical procedure for the polymerization of 9,9-dipropargylfluorene by $(NBD)PdCl_2$ was as follows. In a magnetic-stirred 30 mL reactor, 9,9-dipropargylfluorene (2.0 g, 3.25 mmol), $(NBD)PdCl_2$ (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 h. 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 h. The polymer yield was 91%.

NMR spectra of polymer were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in $CDCl_3$ 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.

The optical absorption spectra were measured by a HP 8453 UV–vis Spectrophotometer. The photoluminescence spectra were obtained by PerkinElmer luminescence Spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. 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 solution containing acetonitrile. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

3. Results and discussion

We used the Pd, Pt, Ru-based catalysts including WCl_6 and $MoCl_5$ itself for the synthesis of conjugated cyclopolymer by the ring-forming polymerization of dipropargyl monomer carrying fluorene moieties. Table 1 shows the results for the polymerization of 9,9-dipropargylfluorene by these catalyst systems. In general, the present polymerization by the Pd, Pt- and Ru-chlorides proceeded well to give relatively high yield of polymer. The catalytic activity of $PdCl_2$ and $RuCl_3$ was found to be slightly higher than that of $PtCl_2$. We used the homogeneous $(NBD)PdCl_2$ 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 (M_ns) and the polydispersities (M_w/M_n) were in the range of 4300–10,100 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 crosslinking reaction of activated allyl protons of the resulting polymer during the process. We used the poly(9,9-dipropargylfluorene) sample prepared by $(NBD)PdCl_2$ (Exp. No. 4) for the identification of polymer structure and the elucidation on the electro-optical and electrochemical properties of polymer.

The polymer structure of poly(9,9-dipropargylfluorene) was characterized by such instrumental methods as NMR (^1H, ^{13}C), IR, UV–vis spectroscopies. The FT-IR spectrum of polymer did not show the acetylenic C≡C bond stretching (2119 cm^{-1}) and