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Microwave-assisted $FeCl_3$-mediated rapid synthesis of poly(9,9-dihexylfluorene) with high molecular weight

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ABSTRACT

Poly(9,9-dihexylfluorene) with high molecular weight (M_w ~ 81,000) is obtained in 25 min using a microwave-assisted $FeCl_3$-mediated oxidative polymerization. The effects of microwave power, time, solvent, monomer and catalyst's concentration on the polymerization have been systematically investigated. The structures and thermal properties of obtained polymers are fully characterized using FTIR, NMR, TGA, DSC, UV–visible absorption and fluorescence spectra. The results show that well-defined polymers have been obtained. XPS, ICP and elemental analysis are used to check the residue of iron catalyst, and almost no residue of $FeCl_3$ is detected in polymers.

1. Introduction

In the past decades, π-conjugated polymers have been the subject of increasing interests due to their potential applications in electronic devices such as organic light emitting diodes (OLEDs), organic solar cells (OSCs) and organic field effect transistors (OFETs) [1–6]. To date, Yamamoto [7–9] and Suzuki [10–12] polycondensations are the most frequently used methods to synthesize π-conjugated polymers. These reactions generally need to be catalyzed by transition metal complex, such as Ni complex and Pd complex. However, using these catalysts suffers from several drawbacks, in particular, the complication in preparation and operation process of Ni catalysts, and prohibitive price of noble metal Pd. There is an urgent need to develop convenient and sustainable synthetic method with low cost for the large-scale preparation of π-conjugated polymers. Iron (Fe) represents one of the most abundant, inexpensive, low toxic and environmental friendly metal [13,14]. As we know, $FeCl_3$ as one of the earliest catalysts has been used for producing conjugated polymers through oxidative polymerization [15–17]. However, only oxidative coupling of thiophene and pyrrole [18–21] (electron-rich π_5 [6] system) have been reported to obtain polymers with high molecular weights under mild conditions. While, for the monomers with decreased electron-cloud density, such as carbazole (π_{13}^{14}), the catalytic ability of $FeCl_3$ is reduced significantly, and the degree of polymerization is low [22]. This method has been even rarely reported for the non-electron-rich system – *c.a.* fluorene (π_{13}^{13}). [16]

Recently, we have successfully applied microwave (MW) as efficient heating source to prepare conjugated polymers with high molecular weights and narrow polydispersity in very short time *via* Yamamoto and Suzuki polycondensations [23,24]. The alternating electric field of MW can induce local reorganization of charges, and this is the physical origin of polarization phenomenon. As similar with polar molecule, a nonpolar molecule may have a distribution of charge which can be regarded as two equal and opposite dipoles centered at different positions. Such a distribution results in a total charge of zero and a total moment of zero, but it will has a quadrupole moment (such as CS_2) [25]. It is proposed that when the intermolecular distances in liquids are not different much with molecular dimensions, quite strong interactions may arise between MW and molecule, which may lead to change the local electron-cloud density, so as to accelerate the polymerization of non-electron-rich system.

In the current paper, taking 9,9-dihexylfluorene as an example, we report an efficient $FeCl_3$-mediated oxidative polymerization of PDHF under MW irradiation (Scheme 1). It is found that the polymerization can be accomplished in a relatively short duration of 25 min and PDHF with weight-average molecular weight (M_w) up to 81,000 can be obtained under optimized condition.

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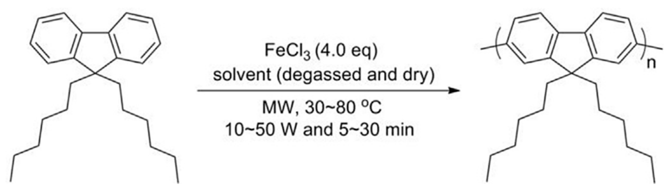

Scheme 1. The pathway and reaction conditions of the oxidative polymerization of PDHF assisted by MW.

2. Experimental

2.1. Materials

$CHCl_3$ (chloroform), toluene, ethanol, hexane, DMF (dimethylformamide), DMSO (dimethyl sulfoxide), THF (tetrahydrofuran) and CH_2Cl_2 (dichloromethane) were distilled and dried before use. All other starting materials were purchased from Acros and Aldrich, and used as received.

2.2. Characterization

MW reactions were performed using CEM Discover single-mode MW reactor. All reactions were carried out under nitrogen atmosphere. The polymerizations were carried out in 10 mL standard Pyrex vessels sealed with a Teflon septum cap. The temperature profiles of the polymerization were monitored using a calibrated infrared temperature control mounted beneath the reaction vessel. The reaction parameters (temperature, power, time, cooling, stirring, etc.) were set manually. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a high performance liquid chromatography (HPLC) Waters 510 pump using a series of low-polydispersity polystyrene standards in THF (HPLC grade, Aldrich) at 308 K. IR spectra were obtained on a Bruker IFS-66V FTIR spectrophotometer with a Mid IR (MIR) globar source ^{1}H NMR spectra were recorded on a Bruker AVANCZ 500 spectrometer at 298 K using $CDCl_3$ as solvent and tetramethylsilane as standard. UV–visible absorption spectra were recorded on a UV-3100 spectrophotometer. Photoluminescence (PL) spectra were carried out with an RF-5301PC fluorometer. X-ray photoelectron spectroscopy (XPS) was recorded on a America ESCALAB250 instrument. Trace metal concentration (Fe) was determined using Perkin Elmer Optima 3300DV Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Elemental analysis was performed by Flash EA 1112, CHNS–O elemental analysis instrument. Thermogravimetric analysis (TGA) was performed on a TA TGA Q500 instrument. Differential scanning calorimetry (DSC) experiments were recorded on a NETZSCH DSC-204 instrument at 10 °C min^{-1} while flushing with nitrogen.

2.3. Synthesis of 9,9-dihexylfluorene

A typical procedure [26] is as follows: a DMSO solution (20 mL) of fluorene (1.66 g, 10 mmol) and tetrabutyl ammonium bromide (166.2 mg, 0.5 mmol) was degassed with nitrogen and heated to 80 °C. A H_2O solution (6 mL) of NaOH (50%, w/w) and 1-bromohexane (3.6 mL, 26 mmol) were added dropwise to the mixture. The solution was stirred at 80 °C for 12 h. The reaction mixture was cooled and poured into water. The water was then extracted three times with dichloromethane. The organic layer was subsequently washed with saturated brine and dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silicagel with cyclohexane as eluent to give product as colorless transparent liquid. Yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.70–7.68 (d, 2H, Ar–H), 7.33–7.29 (m, 6H, Ar–H), 1.92–1.90 (m, 4H, CH_2), 1.12–1.01 (m, 12H, CH_2), 0.77–0.74 (m, 6H, CH_3), 0.61 (m, 4H, CH_2); MS (m/z) 334.3; Anal. Calcd for $C_{25}H_{34}$: C, 89.76; H, 10.24. Found: C, 89.94; H, 10.36.

2.4. MW-assisted synthesis of PDHFs

The monomer 9,9-dihexylfluorene (66.8 mg, 0.2 mmol) was added to a 10 mL vial in a glovebox. $FeCl_3$ (130 mg, 0.8 mmol) and $CHCl_3$ solution (4 mL) were then added into the vial. The vial was sealed under nitrogen and then irradiated by MW. The mixture was precipitated into MeOH/HCl (50 mL, 10:1) to give PDHF as a yellow solid.

3. Results and discussion

Conventional polycondensation of 9,9-dihexylfluorene was carried out at room temperature by stirring the monomer and $FeCl_3$ in $CHCl_3$ for 24 h under the protection of N_2 atmosphere. It gave a PDHF product with M_w of only 4000. When the reaction mixture was irradiated by microwave for 15 min, a large number of polymer-like product was obtained. The GPC measurement indicated that there existed some low-molecular-weight product. So the obtained PDHF was purified by Soxhlet extraction overnight using n-hexane to remove low-molecular-weight oligomeric components. And then the M_w of ~27,100 of the polymer was measured, although the yield was low (15.8%) (Table 1, entry 1).

And then, a series of screening of reaction conditions involving reaction temperature, MW power, reaction time, solvent and monomer's concentration were subsequently investigated (Scheme 1). When the reaction temperature was varied from 30 to 80 °C (Table 1, entries 1–6), it was revealed that the polymers with high molecular weights could be obtained when the temperature was around 40–60 °C. As reaction at temperature of 50 °C, the product was achieved with a relatively high M_w of 45,200 and a PDI of 1.45 after precipitation, but the yield of high molecular weight product was still low (24.1%). At temperature of 70–80 °C, PDHFs with higher yields of about 80% and moderate molecular weight with higher PDI could be obtained.

Table 1
Effect of MW conditions on the polymerization.[a]

Entry	Temp. (°C)	Power (W)	Time (min)	M_w[b]	PDI[c]	S[d]	Yield[e] (%)
1	30	20	15	27,100	2.17	√	15.8
2	40	20	15	40,400	1.58	√	22.0
3	50	20	15	45,200	1.45	√	24.1
4	60	20	15	45,000	1.61	√	21.8
5	70	20	15	26,200	2.39	√	80.3
6	80	20	15	22,300	2.83	√	78.5
7	50	10	15	44,000	1.52	√	11.4
8	50	30	15	37,000	1.61	√	16.8
9	50	40	15	20,300	2.26	√	6.9
10	50	50	15	17,200	2.46	√	6.7
11	50	20	5	5100	2.13	√	10.7
12	50	20	10	27,700	2.04	√	13.6
13	50	20	20	48,700	1.50	√	27.0
14	50	20	25	50,300	1.48	√	29.5
15	50	20	30	48,100	1.51	√	28.5

[a] Reaction conditions: 9,9-dihexylfluorene (0.1 mmol), $FeCl_3$ (0.4 mmol) in 2.0 mL $CHCl_3$ under MW irradiation.
[b] Estimated by GPC in THF on the basis of a polystyrene calibration. M_w = weight-average molecular weight.
[c] M_w/M_n = polydispersity index (PDI).
[d] Solubility tested in common organic solvents; √ = completely soluble.
[e] Yield after Soxhlet extraction.