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Ultrasound-assisted Suzuki coupling reaction for rapid synthesis of polydihexylfluorene

Xu Gao, Ping Lu*, Yuguang Ma

State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, People's Republic of China

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ABSTRACT

Ultrasound-assisted synthesis of conjugated polymer is reported taking PF as an example. It is found that ultrasound can dramatically accelerate the Suzuki coupling reaction. The effects of ultrasonic amplitude, time, monomer and catalyst's concentration on the polymerization have been investigated. PF with high M_w of 39,100 g/mol is obtained in 20 min under optimized condition.

1. Introduction

Conjugated polymers have already attracted great interests of worldwide researchers because they have written down amazing accomplishments in many fields, such as organic lighting emitting diodes (OLEDs) [1,2], organic photovoltaics (OPVs) [3,4], organic field effect transistors (OFETs) [5,6], and etc. Many conjugated polymers are synthesized by the metal-catalyzed coupling reactions. Suzuki coupling reaction represents one of the most powerful, versatile and popular method for the synthesis of conjugated polymers in the past decades [7–10]. It has the advantages of high yields, less amount of catalyst, non-sensitive of water, and tolerating a large number of functional groups. Although varied conjugated polymers has been successfully synthesized by Suzuki coupling reaction [11,12], the long reaction period (48 h) required for a high molecular weight product is still an obstacle for their mass produce. Microwave irradiation as the heating source has been widely used in organic synthesis to effectively reduce the reaction time. [13–15] Our recent reports have shown microwave-assisted polymerization can afford polydihexylfluorene (PF) with high molecular weights (M_w = 37,200 g/mol) in 14 min [16]. However, some insoluble gels are inevitably formed during the reaction and affect the yield of conjugated polymers [17]. New platform-like synthetic tool towards high-quality conjugated polymers in a short time is significantly needed to be developed.

The study of sonochemistry is concerned with understanding the effect of sonic waves especially ultrasound on chemical systems [18]. Previous studies have shown that the ultrasound does not interact directly with molecules to induce the chemical change. Instead, it creates acoustic cavitation which causes local extremes of temperature and pressure in the liquid providing a physical and chemical micro-condition where the reaction happens [19,20]. It also breaks up solid and removes passivating layers of materials to give a larger surface area for the reaction to occur [21]. Thus sonochemistry is especially suitable for heterogeneous liquid–liquid and liquid–solid system to greatly enhance the chemical reactivity. While some organic compounds, particularly polymeric materials, would be destroyed or degraded sonochemically [22,23], that is why less investigation is reported for polymerization reactions under ultrasonic irradiation. In fact, lots of metal-catalyzed polymerization reactions occur heterogeneously and some of them require increasing reaction activity ulteriorly, therefore, it is of great signification to take investigation for the sonochemical effect on polymerization reactions. Typically, palladium-catalyzed Suzuki coupling reaction for the synthesis of conjugated polymers involves heterogeneous solvent (e.g. water and toluene) and heterogeneous catalysts ($Pd(PPh_3)_4$ and Na_2CO_3) [24,25]. Based on above consideration, here we report the investigation of ultrasound-assisted Suzuki coupling reaction for the synthesis of conjugated polymers, taking PF as an example. We found that ultrasound could dramatically accelerate the Suzuki coupling reaction and obtain high-quality conjugated polymers in very short period. The obtained PFs were fully soluble in common organic solvents. The structures were characterized spectroscopically, demonstrating

* Corresponding author. Tel.: +86 431 85167057; fax: +86 431 85193421.
E-mail address: lup@jlu.edu.cn (P. Lu).

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well-defined PFs had been prepared through this new method. And the mechanism for the polymerization under ultrasonic irradiation was discussed preliminarily.

2. Experimental

2.1. Instrumentation

Ultrasound-assisted reactions were performed using VCX 750 Watt ultrasonic processor. All reactions were carried out under nitrogen atmosphere. The ultrasound-assisted polymerizations were carried out in 10 mL standard vessels. The reaction parameters (amplitude, time, etc.) were set manually. Elemental analysis was performed by Flash EA 1112, CHNS–O elemental analysis instrument. 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. FTIR spectra were obtained on a Bruker IFS-66V 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 a solvent and tetramethylsilane as a standard. UV–visible absorption spectra were recorded on a UV-3100 spectrophotometer. Photoluminescence (PL) spectra were carried out with a RF-5301PC fluorometer.

2.2. Materials

Toluene and THF were distilled before use. All starting materials were purchased from Acros and Aldrich, and used as received.

2.3. Ultrasound-assisted synthesis of PFs

To the mixture of degassed toluene and Na_2CO_3 (2 M) in vessel, 2,7-dibromo-9,9-dihexyl-9H-fluorene (1, 0.1 mmol), 2,2′-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2, 0.1 mmol), and tetrakis(triphenylphosphine) palladium were added. And then, the ultrasonic time and amplitude were set. The vessel was sealed under nitrogen and then irradiated by ultrasonic waves. When the reaction ended, the reaction mixture was extracted with chloroform. The organic phase was washed with distilled water and dried over anhydrous magnesium sulfate. The mixture was filtered and the solvent was removed by rotary evaporation. The residue was dissolved in chloroform and precipitated into 50 mL (10:1) MeOH/HCl to give poly(9,9-dihexylfluorene) as a light yellow solid.

3. Results and discussion

The monomers and the PF (under oil heating condition) were synthesized according to our reported procedure [26] and detailed synthesis processes for them are available in Supporting Information. A commonly used Suzuki reactive condition was adopted for the investigation of ultrasound effect on the polymerization, which applied 2,7-dibromo-9,9-dihexyl-9H-fluorene (1, Scheme 1) and 2,2′-(9,9-dihexyl-9H-fluorene-2,7-diyl) bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2) as the monomers, $Pd(PPh_3)_4$ and Na_2CO_3 as the catalyst, and mixture of water and toluene as the solvent. The ultrasonic irradiation supplied by 20 kHz ultrasonic generator VCX 750 was firstly used here to replace the stirrer and oil bath in conventional Suzuki coupling reaction. The input power of ultrasound could be adjusted by amplitude. With the amplitude of 30% was applied for 10 min, we found a large number of polymer-like product (yield over 70%) appeared. The GPC measurement for purified product indicated the M_n of ~6200 g mol^{-1}, and index of polydispersion (M_w/M_n) of 2.33. The NMR and FTIR analysis showed that the structure of product was the same as PF obtained from routine Suzuki polymerization. This demonstrated that Suzuki coupling reaction could occur and the most importantly be greatly accelerated by ultrasound.

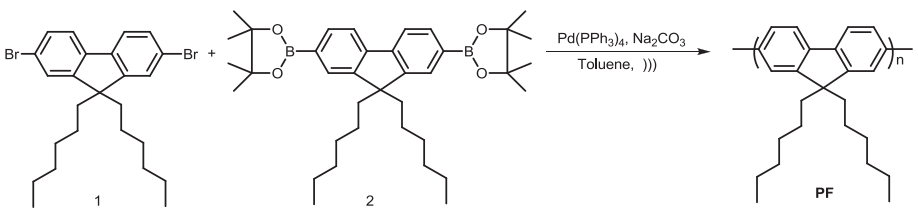
In order to explore whether ultrasound-assisted polymerization had an optimal condition, we then studied the influence of ultrasonic amplitude on the reaction. Holding an amplitude of 30%, the M_n of products was increased steadily with increasing the reaction time. The M_n of ~8700 g mol^{-1} was obtained when the reaction time was increased to 30 min (Table 1, entry 3). When the reaction was performed at higher amplitude of 50%, the reaction proceeded slowly in the first 10 min. Products with higher yield and M_n could be achieved at longer reaction time, e.g. reaction time of 20 min, M_n of ~11,000 g mol^{-1} (Table 1, entry 5). However, at strong amplitude, the yield and M_n of products were decreased as extended reaction time of 30 min. This reflected that the slight degradation of polymer chains might occur at strong ultrasound input. The investigation demonstrates that it is possible to obtain conjugated polymers with high molecular weight by ultrasound-assisted Suzuki coupling reaction under optimized condition.

Besides the ultrasound parameter, the effect of solvents and concentration of monomers and catalyst on polymerization reaction were carried out in order to understand the ultrasound-assisted Suzuki coupling reaction comprehensively. Product with M_n of ~11,000 g mol^{-1} was obtained in toluene, which was twofold higher than that obtained in THF under the same conditions (Table 2). This further demonstrates that sonochemical reaction

Table 1
Effect of amplitude and reaction time on polymerizations.

No.[a]	Amp (%)	t (min)	M_n[b]	M_w	M_w/M_n	S[c]	Yield (%)
1	30	10	6200	14,400	2.33	√	72
2	30	20	7200	13,900	1.92	√	70
3	30	30	8000	9900	1.24	√	78
4	50	10	1300	1700	1.33	√	50
5	50	20	11,000	20,500	1.86	√	75
6	50	30	8300	18,700	2.26	√	40

[a] Polymerization carried out in toluene at room temperature under nitrogen; [cat.] (mol%) = 4, [M_0] = 0.04 M.
[b] Estimated by GPC in THF on the basis of a polystyrene calibration. M_w = weight-average molecular weight; M_n = number-average molecular weight; M_w/M_n = polydispersity index (PDI).
[c] Solubility tested in common organic solvents; √ = completely soluble.



Scheme 1. Palladium-catalyzed Suzuki coupling reaction of polydihexylfluorene under ultrasonic irradiation.