Chain-Growth Horner-Wadsworth-Emmons Condensation Polymerization Initiated with an Aliphatic Aldehyde

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The effective initiation for the chain-growth Horner-Wadsworth-Emmons (HWE) condensation polymerization was succeeded by utilizing an aliphatic aldehyde. Due to the higher electrophilicity of the aliphatic aldehyde compared with the aromatic one, the reactivity of the initiation might be accelerated, producing uniform intermediates to result in the formation of well-defined poly(3-(2-ethylhexyl)thienylene vinylene) (P3EHTV). Consequently, P3EHTV possessed the predictable molecular weight and lower molar-mass dispersity ($D_M = 1.16$) value than that of P3EHTV obtained by employing aromatic aldehyde compounds as the initiators. In this polymerization system, neither transition metals nor halogens are utilized to realize low environmental-load synthesis of well-defined π-conjugated polymers.

Keywords: Horner-Wadsworth-Emmons Reaction, Condensation Polymerization, Chain-Growth Polymerization, Low Environmental-load, π-Conjugated Polymers

1. Introduction

In the past couple of decades, π-conjugated polymers have received much attentions due to their unique properties such as light weight, flexibility and applicability for printing processes. Together with the increase in demands for high performance materials, a wide variety of their synthetic methods have been developed [1-10]. Recently, lots of π-conjugated polymers have been synthesized by transition-metal-catalyzed cross-coupling polycondensation methods [11,12]. Especially, a Catalyst-Transfer Polycondensation (CTP) system has been widely applied in this research area, because this system could precisely control the primary structures of polymers such as number-average molecular weight ($M_n$), $D_M$, regioregularity and be accessible to block copolymers [13-27]. However, it always requires both of halogenated monomers and transition-metal catalysts.

Kuwabara et al. reported that the residual halogenated terminal of a semiconducting polymer and the residue of transition metal catalysts negatively affected the optoelectrical device performance [28,29]. Moreover, from the viewpoint of environmentally friendly synthesis, such potentially hazardous reagents should not be employed.

Recently, some researchers have developed alternative controllable procedures without either of transition metals or halogen moieties [30-32]. In addition, Zhang et al. reported the transition-metal free and halogen-free polymerization based on the aldol condensation reaction for the first time [33]. In this polymerization system, only water is eliminated as a condensate.

However, since these polymerization systems follow a step-growth manner, the primary structures of the polymer could not be precisely controlled in terms of $M_n$ values while maintaining low $D_M$ values. Our research group recently succeeded in realizing a chain-growth condensation polymerization system under transition-metal-free and halogen-free conditions utilizing the Horner-Wadsworth-Emmons (HWE) condensation reaction [34]. In this system, we could tune the reactivity of the generated anionic monomer, suppressing its homopolymerization probably by the delocalization of the anion via an intramolecular resonance effect.

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as shown in Scheme 1. After reacting the anionic monomer with the aromatic aldehyde, the polymerization initiated and propagated in a chain-growth manner by cancelling such a delocalization. Since the developed methodology is only adopted for aromatic aldehydes as initiators, we intend to pursue the alternative initiator to extend and generalize the methodology.

In this work, hexanal, an aliphatic aldehyde, is employed for the chain-growth HWE condensation polymerization for the first time. The aliphatic aldehyde has higher electrophilicity than the aromatic one, so that the initiation readily underwent to obtain well-defined P3EHTV with an $M_n$ of 5,000 and low $D_M =1.16$ value.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF, stabilizer free, 99.5%, Kanto Chemical Co., Inc.) was dried over sodium benzophenone under nitrogen and distilled before use. 3-(2-Ethylhexyl)-5-formyl-thiophene-2-ylmethyl)phosphonic acid diethyl ester (1) was synthesized according to the previous report [34]. All other reagents were purchased from Sigma-Aldrich Japan K. K., Tokyo Chemical Industry Co., Ltd., Kanto Chemical Co., Inc. or Wako Pure Chemical Industries and used without further purification.

2.2. Synthesis of P3EHTV using 2a as an initiator

All glass apparatuses were dried over under vacuumed pressure prior to use. Dehydrated THF (18 mL), 15-crown-5-ether (0.10 mL, 0.51 mmol) and a 1.9 M THF solution of sodium hexamethyldisilazide (NaHMDS, 0.27 mL, 0.51 mmol) were placed in a 20 mL two-necked flask purged with N2 and cooled down to −78 °C. A 1 solution (2 mL), which was prepared in another 5 mL two-necked flask with 1 (184 mg, 0.491 mmol) and dehydrated THF (2 mL) cooled down to −78 °C, was immediately added to the mixed solution. After stirring for 5 min, hexanal (2a, 2.16 mL, 0.022 mmol), which was dissolved in THF (0.5 mL), was added to start the polymerization. The polymerization was carried out at −40 °C for 2 h, followed by quenching with 5 N HCl aq. (2 mL). The quenched solution was extracted with chloroform, washed with water, and analyzed by size exclusion chromatography (SEC) directly before precipitation. The crude solution was poured into a large amount of methanol/water (200 mL/ 100 mL) to precipitate the polymer. After filtering and drying under vacuum, P3EHTV was obtained as a dark blue solid (101 mg, 94%). $M_n$ (SEC) = 8,000, $M_n$ (1H NMR) = 5,000, $D_M$ (SEC) = 1.16.

2.3. Measurements

The proton nuclear magnetic resonance (1H NMR) spectra were recorded with a JOEL JNM-ECX400 spectrometer at 25 °C. Deuterated chloroform was chosen as a solvent and standard ($\delta$H: 7.26 ppm). The $M_n$ and weight-average molecular weight ($M_w$) values were measured by SEC on a JASCO GULLIVER 1500 equipped with a pump, an absorbance detector (UV, $\lambda$ = 254 nm), and three polystyrene gel columns, based on a calibration curve using polystyrene standards. THF (40 °C) was selected for a carrier solvent at the flow rate of 1.0 mL / min.
side chains around 0.7-1.8 ppm, methylene protons next to the thiophene unit (d) at 2.54 ppm, thienylene protons (b) at 6.74 ppm, and vinylene protons (c) at 6.85-6.99 ppm are clearly observed (Fig. 2).

The formyl proton at the terminal unit of the polymer could also be observed at 9.80 ppm. Comparing their signal intensities, the $M_n$ value was determined to be 5,000, which is in good agreement with that calculated ($M_n = 5,000$). The higher $M_n$ value determined by SEC ($M_n = 8,000$) may be caused by overestimation using a calibration using polystyrene standards for rigid-rod $\pi$-conjugated polymers.

The results of the polymerization are summarized in Table 1. The polymerization system employing 2a afforded P3EHTV with the objective $M_n$ value of 5,000 with the lowest $D_M$ value ($D_M = 1.16$) among all runs.

The controllability of polymerization is sometimes related to a rapid and uniform initiation reaction. In practice, it was found that 2a acted as the best initiator so far, suppressing undesired polymer-polymer linking reactions. In addition, owing to high electrophilicity of such an aliphatic initiator, more rapid and uniform initiation step (Scheme 3, Path A) may possibly be promoted rather than using 2b-2d (Scheme 3, Path B using 2b).

After the initiation reaction, the propagation reaction underwent preferably in the chain-growth manner.

![Fig. 2. $^1$H NMR spectrum of P3EHTV initiated with hexanal (2a).](image)

**Table 1. Results of the HWE condensation polymerization of 1 initiated with 2a-2d.**

| Run | Initiator | [1]$_0$/[2]$_0$ | Calcd. | SEC$^a$ | $^1$H NMR | $D_M^a$ | Yield (%)$^b$ |
|-----|-----------|----------------|--------|---------|-----------|--------|-------------|
| 1   | 2a        | 23             | 5,000  | 8,000   | 5,000     | 1.16   | 80          |
| 2   | 2b        | 23             | 5,000  | 7,600   | –         | 1.20   | 94          |
| 3   | 2c        | 23             | 5,000  | 6,400   | –         | 1.20   | 98          |
| 4   | 2d        | 23             | 5,000  | 7,900   | –         | 1.23   | 88          |

$^a$ $M_n$ and $D_M$ were determined by SEC (THF) using polystyrene standards. $^b$ Yields were determined by gravimetry after reprecipitation in MeOH/H$_2$O. $^c$ Data were extracted from the previous report [34].
manner, minimizing the occurrence of step-growth polymerization reactions to afford the well-defined P3EHTV.

4. Conclusion

In conclusion, we have successfully improved the controllability of the chain-growth HWE condensation polymerization by utilizing the simple aliphatic aldehyde as an initiator. Indeed, the well-defined P3EHTV with the predicted $M_n$ value of 5,000 with the lowest $D_n$ value ($D_n = 1.16$) could be obtained. The higher electrophilicity of the aliphatic aldehyde compared with the aromatic one may possibly accelerate the initiation step to minimize the occurrence of step-growth polymerization reactions. Since the proposed system is free of transition-metals as well as halogens, optoelectronic performances of the $\pi$-conjugated polymers should be improved and the related works are now under investigation.

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