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Synthesis and Characterization of a Crystalline Triblock Copolymer Containing a Conjugated Rod Segment

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A crystalline conjugated block copolymer(PLA-b-PF-b-PLA) of poly(9,9′-didodecylfluorene) (PF) and poly(L-lactide) (PLA) was synthesized by a ring opening polymerization method. The oligofluorene with hydroxyl ends was prepared by the Yamamoto-type coupling of 2,7-dibromo-9,9-didodecyl-fluorene using a $Ni(COD)_2$ catalyst as reductive transition metal-base coupling agent. The molecular structure of PLA-b-PF-b-PLA was characterized by ^{1}H-NMR, GPC, DSC and PL techniques. The photoluminescence of PLA-b-PF-b-PLA was highly influenced by the crystalline PLA blocks.

Keywords: crystalline conjugated block copolymer; poly(9,9′-didodecylfluorene); poly(L-lactide)

INTRODUCTION

There have been many efforts to enhance the solubility and performance of conjugated polymers by either introducing either various substituents/end groups in the polymer backbone or copolymerizing with conjugated or non-conjugated comonomers [1–3]. Recently, a series of conjugated block copolymers of poly(*p*-phenylene)s, poly(*p*-phenylene vinylene)s and polyfluorenes has been synthesized for photonic and electronic applications [1,4–7]. The combination of conjugated rod blocks with flexible coil blocks in a single polymer chain, exhibiting a great variety of phase-separated morphologies both in solid state

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and selective solvents, extends the areas of optoelectronic applications to other fields [7,8].

In this report, we synthesized a symmetric, crystalline triblock copolymer of poly(L-lactide)-*b*-poly(9,9-didodecyl fluorene-2,7-diyl)-*b*-poly(L-lactide) (denoted PLA-*b*-PF-*b*-PLA) by using an ring opening polymerization technique. The oligofluorene midblock segment was synthesized by a Yamamoto-type coupling reaction, followed by ring-opening polymerization of L-lactide. Because of the crystallization of poly(L-lactide) end blocks, the photoluminescence behavior of the spin-coated films of poly(9,9-didodecyl fluorene-2,7-diyl) was highly affected.

EXPERIMENTAL SECTION

Materials and Characterization

2,7-Dibromo-9,9-di-n-dodecylfluorene (97%), toluene (anhydrous, 99.8%), N,N-dimethylformamide anhydrous (99.8%), hydrazine, bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), bypyridine (99+%), 1,5-cyclooctadiene (COD, 99+%), 4-bromobenzyl alcohol (99%), Tin(II) 2-ethylhexanoate (95%) (all from Aldrich) were all used as received. L-lactide (from PURAC) was also used as received.

^1H spectra were recorded on a Bruker AC 250 spectrometer at 250 and 63 MHz, respectively, and were referenced to TMS. The thermal transition temperatures were measured by using a Thermal Analysis DSC 2920 under nitrogen atmosphere at a heating rate of 10°C/min. Molecular weights and molecular weight distributions were determined using a GPC equipped with a Waters Associates 410 RI detector, 510 HPLC pump, and *i*-Styragel columns with pore sizes of 102, 500, 103, and 104 Å. The eluant was THF, and the molecular weights were calibrated with polystyrene standards.

Synthesis of Hydroxyl End-Functionalized Polyfluorene (2)

$Ni(COD)_2$, COD, bipyridine and anhydrous DMF were mixed with stirring at 70°C for 30 min under dry N_2 gas. In this dark blue solution, 2,7-dibromo-9,9′-didodecylfluorene**1** and 4-bromobenzyl alcohol in anhydrous toluene were added *via* a syringe. Then, the reaction continued with stirring at slightly-elevated temperature, 85°C in the absence of light for additional 2 days. After the reaction, the mixture was then cooled to room temperature and diluted with THF and aqueous hydrazine solution. The mixture solution was stirred overnight. The organic layer of the mixture solution where the product was assumed to be dissolved was separated, filtered, concentrated and

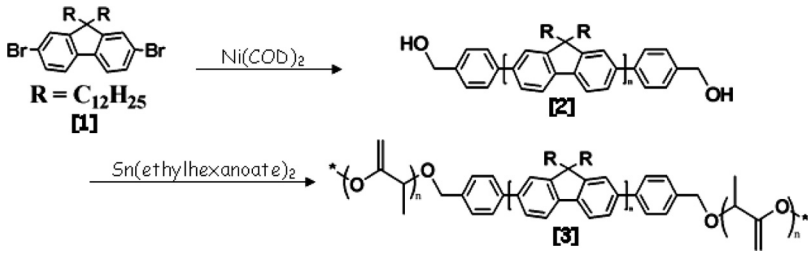
poured into methanol. The precipitated powder product was purified by extraction with methanol, and reprecipitated into methanol.

Synthesis of PLA-b-PF-b-PLA (3)

Compound **2**, L-lactide, anhydrous toluene were added in a round-bottom flask and then the mixture was heated at 120°C. Tin octoate (stannous 2-ethyl-hexanoate) was added, and then the solution was stirred 7 hours. The resulting solution was precipitated into methyl ether. The obtained, tint yellow polymer powder was filtered and dried in vacuum oven at 40°C.

RESULTS AND DISCUSSION

The syntheses of the compounds **2** and **3** were schematically described in Scheme 1. The oligofluorene with hydroxyl ends **2** was prepared by the Yamamoto-type coupling of 2,7-dibromo-9,9-didodecyl-fluorene **1** using a $Ni(COD)_2$ catalyst as a reductive transition metal-base coupling agent. It has been known that the alkyl substituents at C9 position of a fluorene unit do not influence its optical and optoelectronic properties in dilute solutions. We therefore used a fluorene having didodecyl substituents at C9 position which is commercially available. The long alkyl substituents may enhance the solubility of polyfluorene during the reaction. Both **1** and **2** were highly soluble in organic solvents. Toluene was used as a reaction medium which dissolved $Ni(COD)_2$ catalyst in DMF. The monofunctional comonomer of bromobenzyl alcohol was used as an end-capper to functionalize the ends of **1** into hydroxyl ends. The reaction was carried out in dark to avoid the formation of fluorenone defects and their absence was confirmed by ^{1}H-NMR data as shown in Figure 1(a). In this figure, we found the peak at 4.79 ppm for Ar–CH_2–OH, confirming the end-capping of the–Ar–CH_2–OH units on the 2,7-positions of 9,9-didodecylfluorene. The weakness of the peak arose from the increased molecular weight



SCHEME 1 Synthetic route.

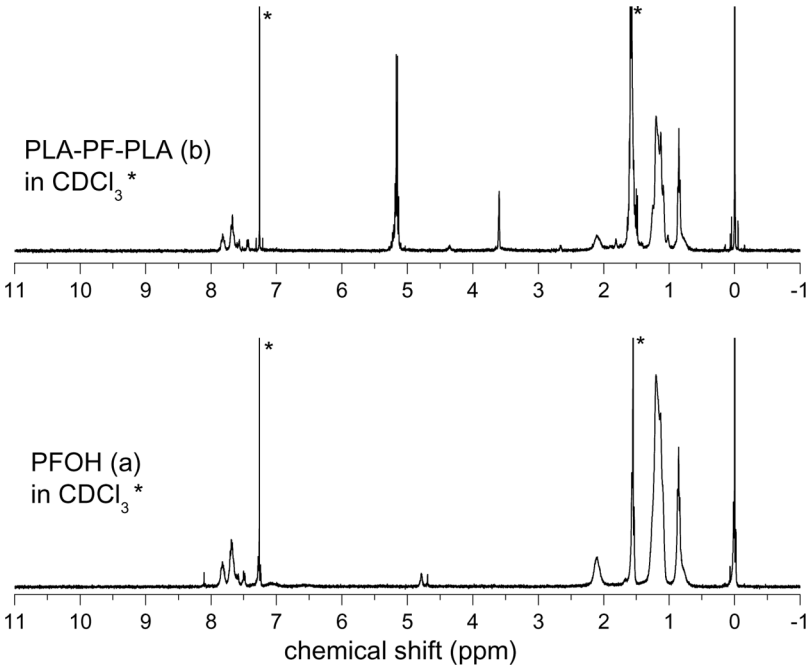


FIGURE 1 ^{1}H NMR of (a) PFOH and (b) PLA-*b*-PF-*b*-PLA.

of the coupled fluorenic units, which reduced the relative concentration of $-Ar-CH_2-OH$ unit at the same concentration.

The synthesis of a symmetric block copolymer of PLA-*b*-PF-*b*-PLA **3** was carried out by ROP at 120°C for 7 hrs in toluene. The chemical structure of **3** was confirmed by ^{1}H NMR as shown in Figure 1(b). In this figure, a peak at $\delta = 5.15$ ppm and 3.60 ppm, with the absence of the peak at $\delta = 4.78$ ppm, was indicative of the complete transformation of $-Ar-CH_2-OH$ units into $-Ar-CH_2-O-CH(CH_3)$-C=O−. To synthesize a triblock copolymer of PL-*b*-PF-*b*-PL, tin octoate was used as a catalyst. Polymerization was carried out at 120°C for 7 hrs in order to achieve the complete monomer conversion without increasing the polydispersity (PDI) of final polymer. The M_ns of **2** and **3** were determined by GPC and measured as 4000 g/mol and 8000 g/mol and their polydispersity indices (PDIs) were 1.5 and 1.3, respectively. The PDI of **3** was high because of the intermolecular coupling reaction of **1**, which also led to a high PDI of **2**. The lower PDI of **3**, as compared with one measured from **2**, was caused by the increase of molecular weight of the final polymer.

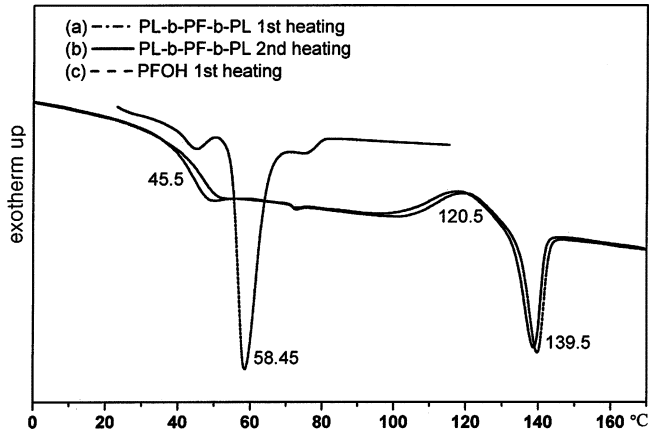


FIGURE 2 DSC data, (a) measured from the first heating and (b) the second heating of PLA-*b*-PF-*b*-PLA, and (c) measured from the first heating of PFOH.

Figure 2(a) and (b) show the DSC data of the compounds **3** which was measured during the first and the second heating scans of the as-prepared sample in the temperature range between 0°C and 170°C. Figure 2(c) also shows the data measured from the oligofluorene mid-block. The characteristic feature shown in Figures 2(a) and (b) was almost similar. Since the melting of the oligofluorene was shown in the temperature range between 40°C and 80°C in Figure 2(c), we assumed that the crystallization of the oligofluorene moieties was prohibited by the block copolymerization. Therefore, it was proposed that the transition near 45°C and the endothermic peak occurred near 140°C were the glass transition and melting of the PLA end blocks.

The photoluminescence property of PLA-*b*-PF-*b*-PLA depends on the crystallization of the PLA blocks. Figure 3 shows the fluorescence spectra of the film of PLA-*b*-PF-*b*-PLA. The block copolymer was initially melted at 150°C, and then (a) quenched in the air or (b) annealed at 120°C for 24 hrs. In Figure 3(a), the fluorescence maximum of PLA-*b*-PF-*b*-PLA was found at 451 nm which was longer than one measured from the solution. It may be due to the increase of the effective conjugated length of PLA-*b*-PF-*b*-PLA by a dense packing of the molecules in film. During annealing the similar film specimen (Fig. 3(b)), the fluorescence maximum peak was not changed as compare with one measured in Figure 3(a), but the intensities of the vibronic bands were increased (475 and 515 nm). It may be caused by the increase of the keto-formation at C9 position by the high temperature heat treatment.

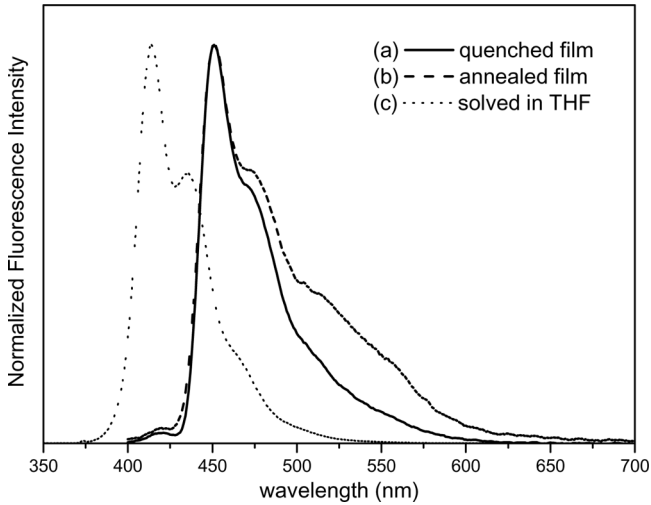


FIGURE 3 PL spectra of PLA-*b*-PF-*b*-PLA: (a) quenched film, (b) annealed film, and (c) THF solution.

CONCLUSIONS

We were successfully synthesized the conjugated triblock copolymer of PLA-*b*-PF-*b*-PLA. The PF midblock was synthesized by the Yamamoto coupling reaction and the ring opening polymerization and PLA endblocks were attached by ring-opening polymerization. PLA was highly crystalline and photoluminescence behavior of PF block was influenced by the crystallization of PLA endblocks.

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