Photo-induced Excimer Formation of Pyrene-labeled

Polymers for Optical Recording

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Supplementary Information

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Figure S9   Single-exponential fitting curves for time profiles of normalized fluorescence for excimer emission of pyrene-labeled PLA thin-film sample recorded at different annealing temperatures; T=25, 40, 60 and
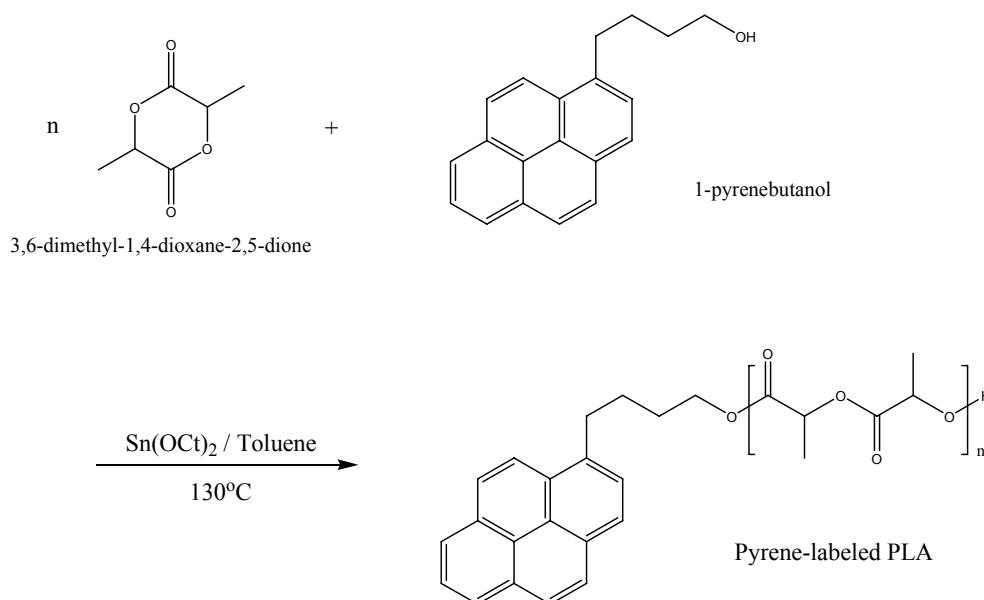
80°C; output power of 8mW, λ_{exc}=340nm, λ_{em}=480nm and emission slit=10nm.

Figure S10   Single-exponential fitting curves for time profiles of fluorescence for excimer emission of PLP thin-film samples recorded at output power of 6mW; (a) pyrene-labeled PLA, (b) pyrene-labeled PLLA, (c) pyrene-labeled PDLA; λ_{exc}=340nm, λ_{em}=480nm and emission slit=10nm.

Figure S11   Time profiles of fluorescence for excimer emission of PLP thin-film samples recorded at output power of 1.7mW; λ_{exc}=340nm, λ_{em}=480nm and emission slit=10nm.

Characterization of the pyrene-labeled polymers

Scheme S1. Synthesis of Pyrene-labeled PLA

n [3,6-dimethyl-1,4-dioxane-2,5-dione] + [1-pyrenebutanol]

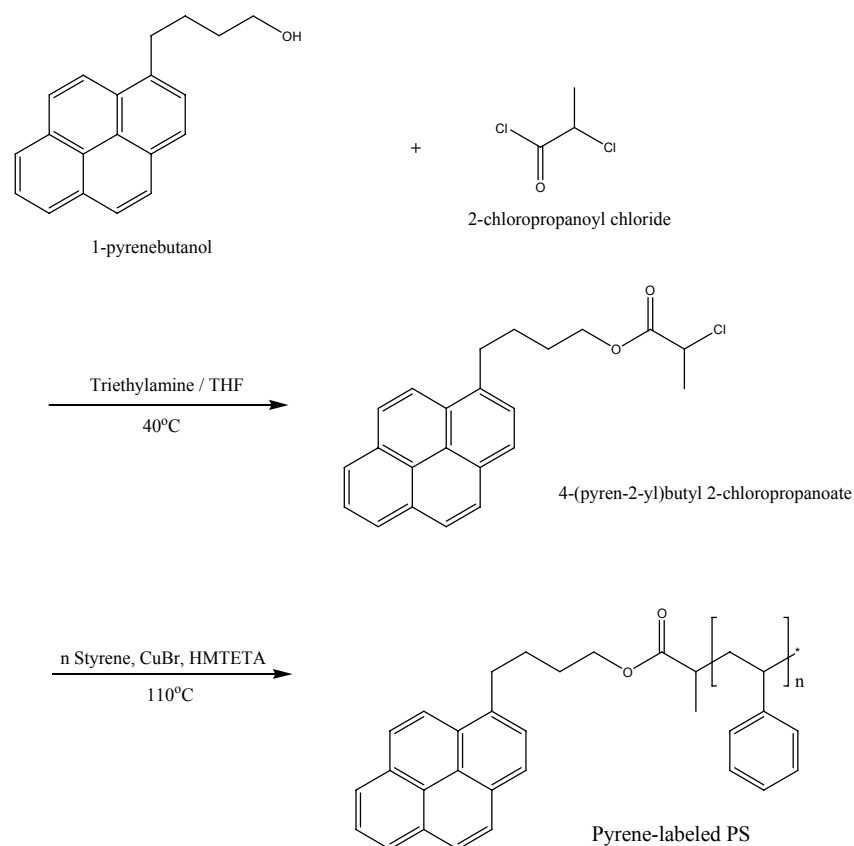$\xrightarrow[130^{\circ}C]{Sn(OCt)_2 / Toluene}$ Pyrene-labeled PLA

The detailed procedures for the synthesis of the pyrene-labeled PLA were described in following procedures; a mixture of D,L-lactide (i.e., 3,6-dimethyl-1,4-dioxane-2,5-dione), 1-pyrenebutanol, stannous(II) 2-ethyl hexanoate (Sn(Oct)$_2$) and Toluene was mixed in a round-bottom flask under nitrogen at room temperature. The system was then sealed and heated at 120°C in oil bath for 6h to yield pyrene-labeled PLA. The mixture was then quenched by the addition of methanol and the resulting polymer was precipitated to give white solids. The product was then collected by vacuum filtration to give white solids. The final solid was washed by MeOH and dried under vacuum at 50-60°C overnight to yield pyrene-labeled PLA. **Fig. S1** shows the NMR analysis of pyrene-labeled PLA;

^{1}H NMR (500 MHz, Chloroform-d$_3$, δ): 7.85–8.25 (m, 9H, pyrene), 5.16 (q, 1H, CH(CH$_3$)), 1.58 (d, 3H, CH(CH$_3$)).

The procedures of synthesizing the pyrene-labeled PLLA and PDLA were almost the same with the synthesizing the pyrene-labeled PLA via ROP except for replacing D,L-lactide with L-lactide and D-lactide, respectively. **Fig. S2** shows the NMR analysis of pyrene-labeled PLLA; ^{1}H NMR (500 MHz, Chloroform-d$_3$, δ): 7.85–8.25 (m, 9H, pyrene), 5.13 (q, 1H, CH(CH$_3$)), 1.56 (d, 3H, CH(CH$_3$)). **Fig. S3** shows the NMR analysis of pyrene-labeled PDLA; ^{1}H NMR (500 MHz, Chloroform-d$_3$, δ): 7.85–8.25 (m, 9H, pyrene), 5.13 (q, 1H, CH(CH$_3$)), 1.54 (d, 3H, CH(CH$_3$)).

Scheme S2. Synthesis of Pyrene-labeled PS

1-pyrenebutanol

+

2-chloropropanoyl chloride

Triethylamine / THF
40°C

4-(pyren-2-yl)butyl 2-chloropropanoate

n Styrene, CuBr, HMTETA
110°C

Pyrene-labeled PS

The detailed procedures for the synthesis of the pyrene-labeled PS were

described in following procedures; a mixture of 1-pyrenebutanol, 2-chloropropionyl

chloride, triethylamine and THF was mixed in a round-bottom flask under nitrogen at

room temperature. The system was heated at 40°C for 6h to yield intermediate

product, 4-(pyren-2-yl) butyl 2-chloropropanoate served as initiator for ATRP.

Subsequently, the pyrene-labeled PS was prepared by ATRP of styrene with

4-(pyren-2-yl) butyl 2-chloropropanoate and CuBr/HMTETA (1, 1, 4, 7, 10, 10,

hexamethyl triethylene tetraamine) as the catalyst/ligand. The system was then sealed

and heated at 110°C in oil bath for 8h to yield pyrene-labeled PS. The mixture was

then quenched by the addition of methanol and the resulting polymer was precipitated

to give white solids. The product was then collected by vacuum filtration to give

white solids. The final solid was washed by MeOH and dried under vacuum at 70-80

°C overnight to yield pyrene-labeled PS. **Fig. S4** shows the NMR analysis of

pyrene-labeled PS; ^1H NMR (500 MHz, Chloroform-d_3, δ): 7.85–8.25 (m, 9H,

pyrene), 6.46-7.09 (br, 5H, ArH), 1.82 (br, 1H, CH), 1.40 (br, 2H, CH2).

All manipulations were carried out under a dry nitrogen atmosphere. Solvents,

1-pyrenebutanol, D, L-lactide, L-lactide, D-lactide, styrene and Chloroform-d_3 were

purified before uses. ^1H nuclear magnetic resonance (NMR) spectra were recorded on

a Varian Unityinova 500 NMR spectrometer with chemical shifts given in ppm from

the central line of CHCl$_3$. The GPC measurements were performed on Waters 1515

isocratic HPLC pump equipped with a Waters 2414 RI detector using THF (HPLC

grade) as an eluent. Molecular weight and molecular weight distributions were

calculated using polystyrene as standard. The number average molecular weight and

polydispersity (PDI) of pyrene-labeled polymers were obtained by GPC analysis. The

DSC measurements were performed on Perkin Elmer DSC-7 differential scanning

calorimeter equipped with a mechanical intracooler. **Fig. S5** shows the DSC analysis

of pyrene-labeled polymers. Table S1 summarizes the characterization of the PLPs.

Table S1. Characterization of pyrene-labeled polymers

Sample Code	Mn (g/mol)	PDI	Tg(℃)	Tm(℃)
Pyrene-labeled PS	17,629	1.45	101.6	amorphous
Pyrene-labeled PDLA	17,290	1.45	56.5	153.3
Pyrene-labeled PLLA	16,638	1.48	45.0	148.7
Pyrene-labeled PLA	16,734	1.46	38.5	amorphous

a. M_n and Polydispersity index (PDI) of the pyrene-labeled polymers were determined by GPC which was calibrated with polystyrene standards. b. Tg and Tm of the pyrene-labeled polymers were determined by DSC with a scan rate 10 ℃/min. The DSC was calibrated with an indium standard previously.
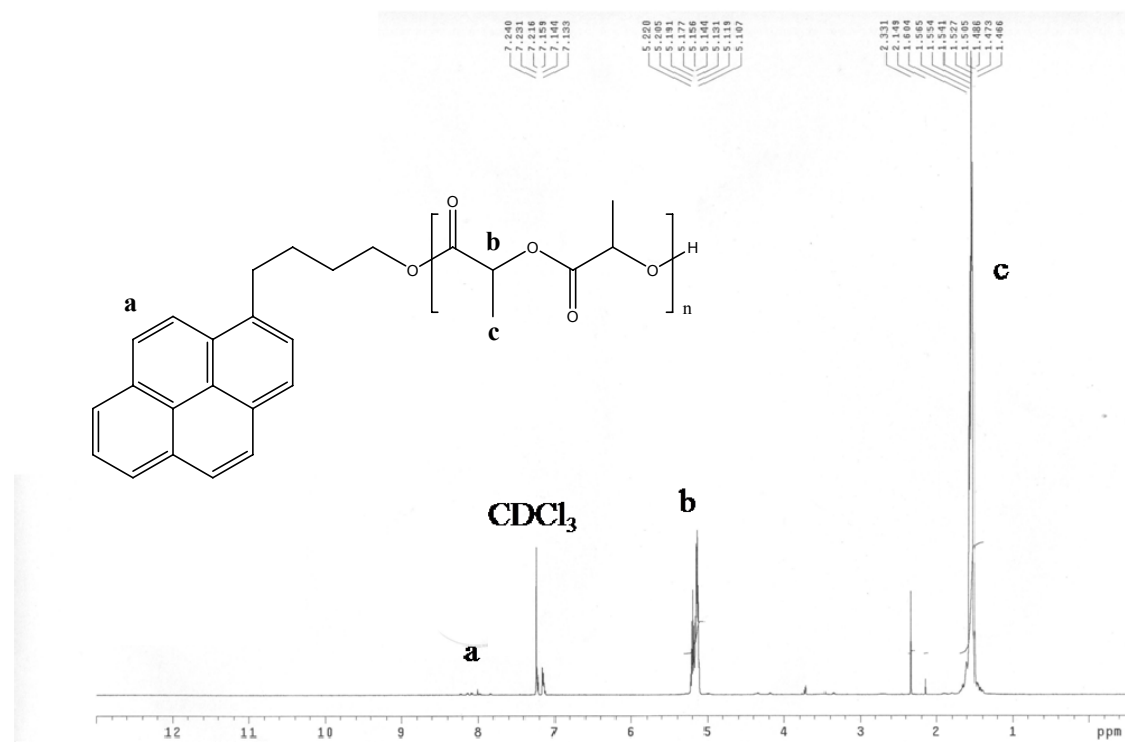
Figure S1. ^{1}H NMR spectrum of pyrene-labeled PLA
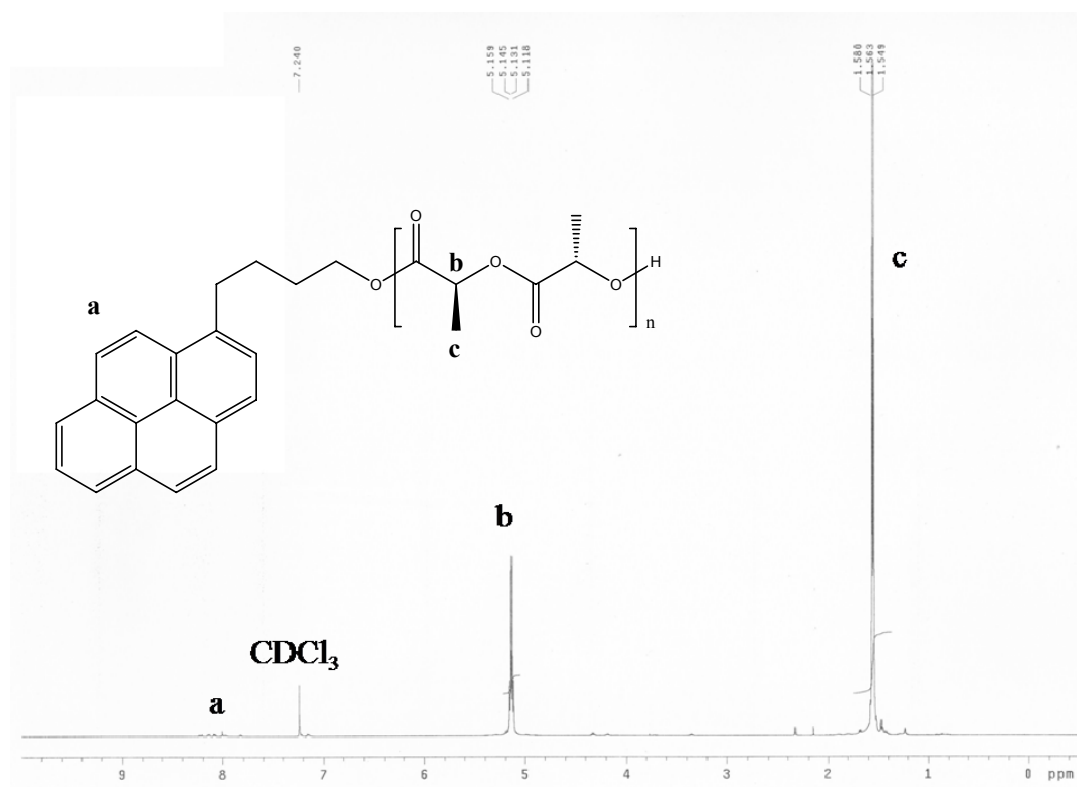
Figure S2. ^{1}H NMR spectrum of pyrene-labeled PLLA
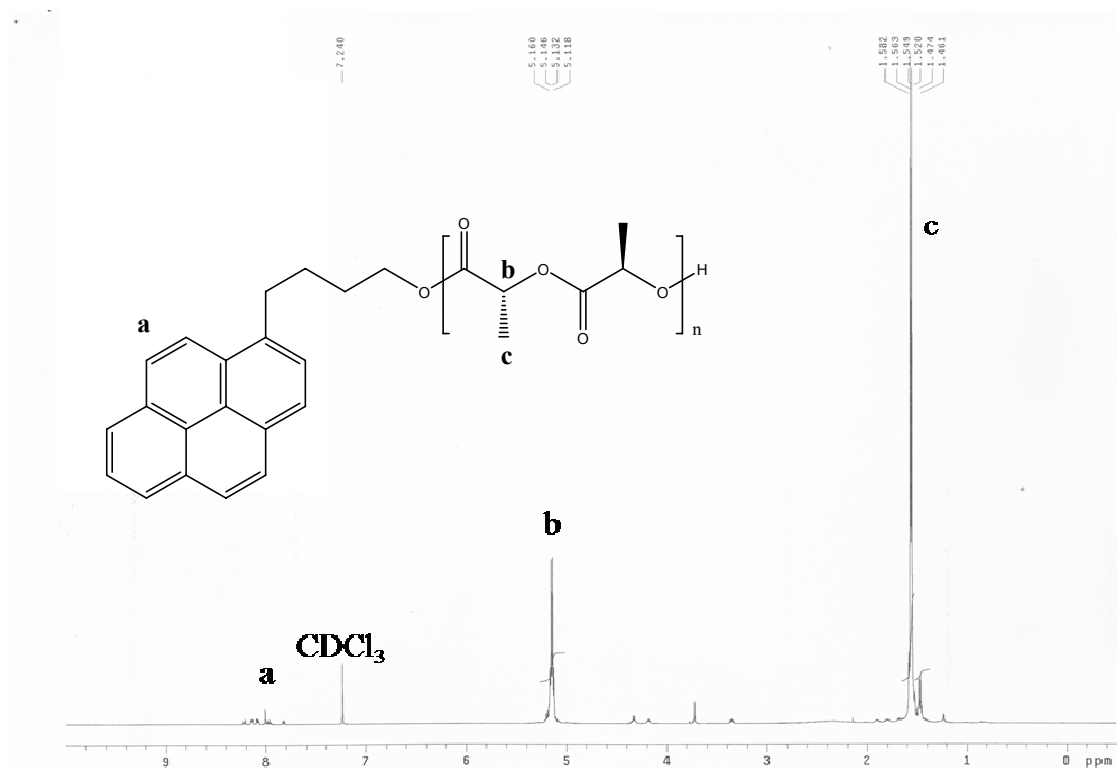
Figure S3. ^{1}H NMR spectrum of pyrene-labeled PDLA
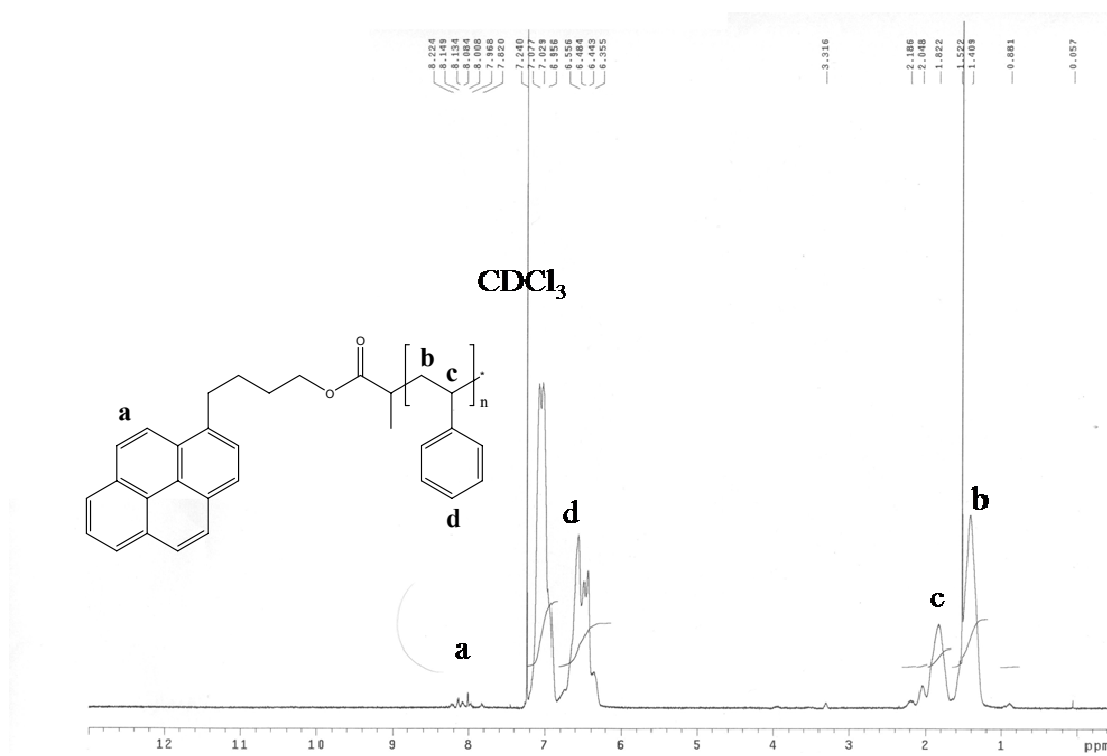
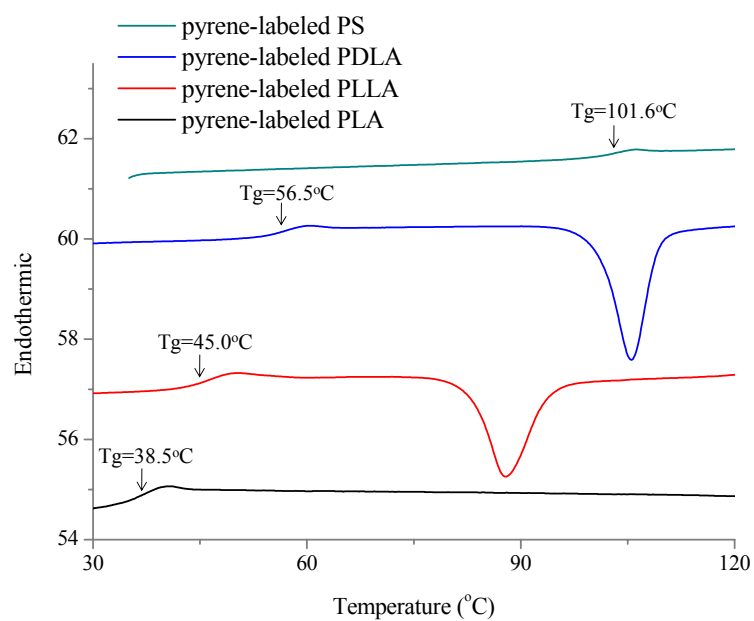**Figure S4.** ^{1}H NMR spectrum of pyrene-labeled PS

Figure S5. DSC thermograms of pyrene-labeled polymers. All samples were annealed

at 160 °C for 3 min., then rapidly cooled to 20°C, and held at 20 °C for 30min before

measuring.

The absorption curve of the polymer (pyrene-labeled PLA) is shown in Fig. S6;

the absorbance bands of pyrene are in the ranges of 250-270nm and 300-350nm and

the absorbance band of PLA polymer is in the range of 200-230nm. Therefore, the

incident UV radiation with the wavelength centered at 340nm was used as optical
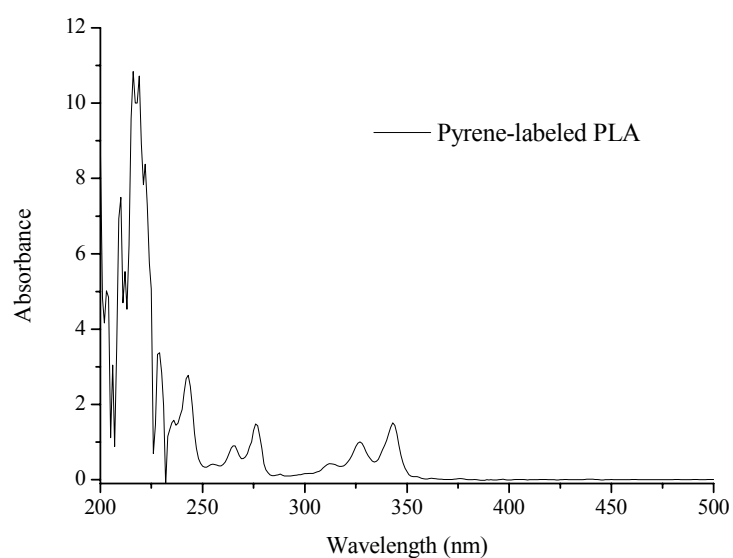
recording light source for the formation of excimers.

Figure S6. Absorption spectrum of pyrene-labeled PLA thin-film sample.

The details on the of experimental procedure

As shown in Fig. S7 of ESI, a sandwich-like thin-film sample of amorphous PLPs was prepared by hot impression at 160°C for 30min between two glass slides, and then rapidly cooled to room temperature (i.e., T=25°C); the film thickness was about 10μm., after it had been stored at room temperature in atmosphere for 1 hour, a Xenon-lamp light was focused onto the thin-film sample with different output powers through a monochromator for optical recording experiments; the wavelength centered at 340nm, a region of the sample with a dimension of approximately 2mm x 3mm was recorded. After recording, a Xenon-lamp light was then de-focused onto the recorded thin-film sample. Accordingly, the fluorescence contrast could be read in light blue and purple fluorescence upon reading illumination; the wavelength centered at 340nm.

Fluorescence spectra and time profiles of fluorescence for the excimer emission of pyrene-labeled polymer thin-film samples were acquired with a fluorescence spectrophotometer (Hitachi F-2500). To examine the effect of temperature on the association of pyrene molecules in PLP, a Hitachi F-2500 fluorescence spectrophotometer equipped with a hot stage was utilized to observe fluorescence spectra and time profiles of fluorescence for the excimer emission of PLP thin-film samples at different annealing temperatures; T=25, 40, 60, 80, 100, and 120°C. The

thin-film samples were attached on the hot stage which was held isothermally at the

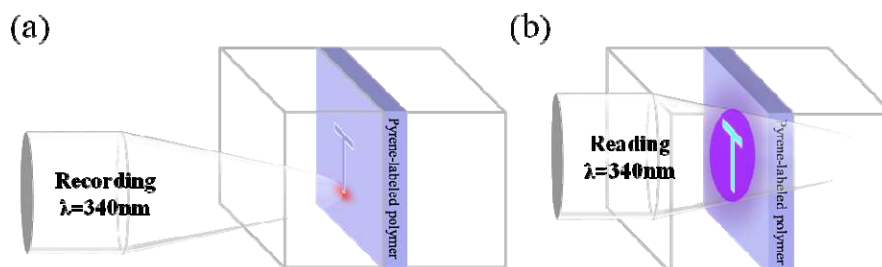prescribed temperatures during recording.

Figure S7. Schematic illustration of (a) optical recording and (b) reading experiment
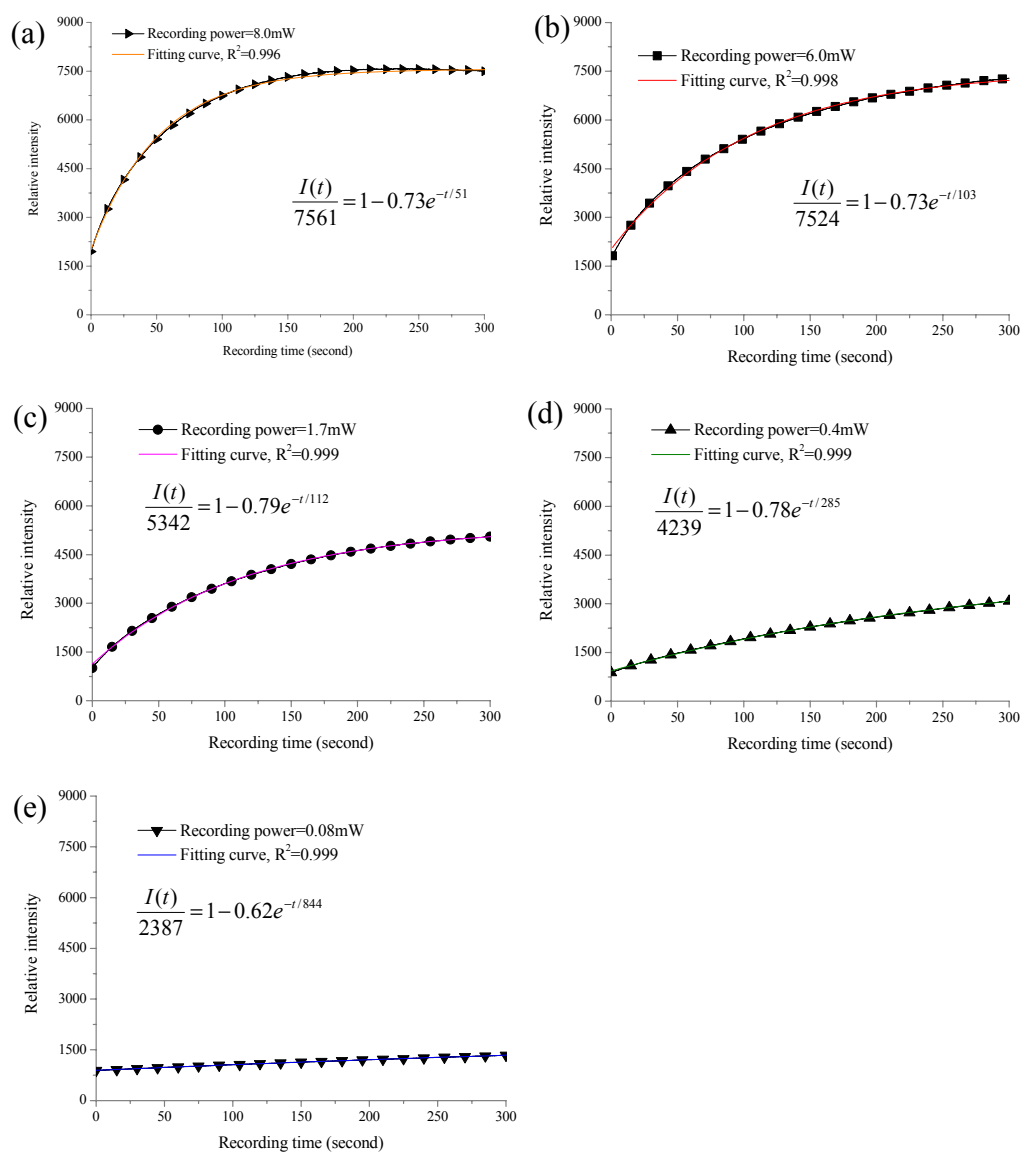
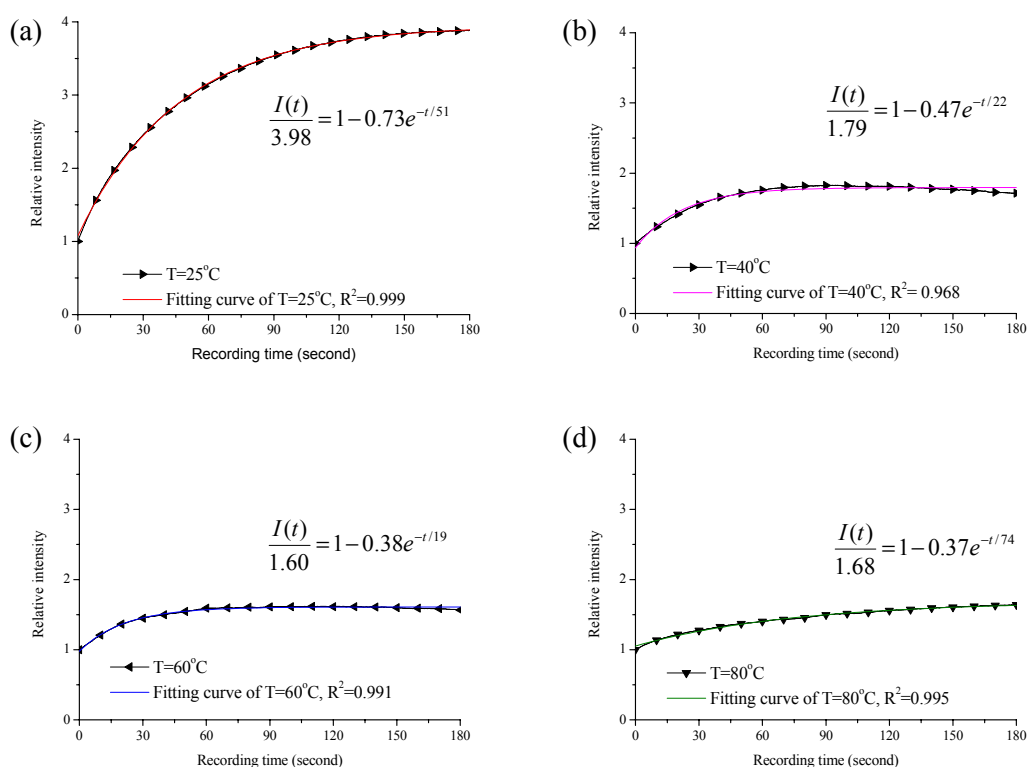**Figure S8.** Single-exponential fitting curves for time profiles of fluorescence for excimer emission of pyrene-labeled PLA thin-film sample recorded at different output powers; the output powers are (a) 8mW, (b) 6mW, (c) 1.7mW, (d) 0.4mW, (e) 0.08mW; λ_{exc}=340nm, λ_{em}=480nm and emission slit=10nm.

Figure S9. Single-exponential fitting curves for time profiles of normalized fluorescence for excimer emission of pyrene-labeled PLA thin-film sample recorded at different annealing temperatures; T=25, 40, 60 and 80°C; output power of 8mW, λ_{exc}=340nm, λ_{em}=480nm and emission slit=10nm.
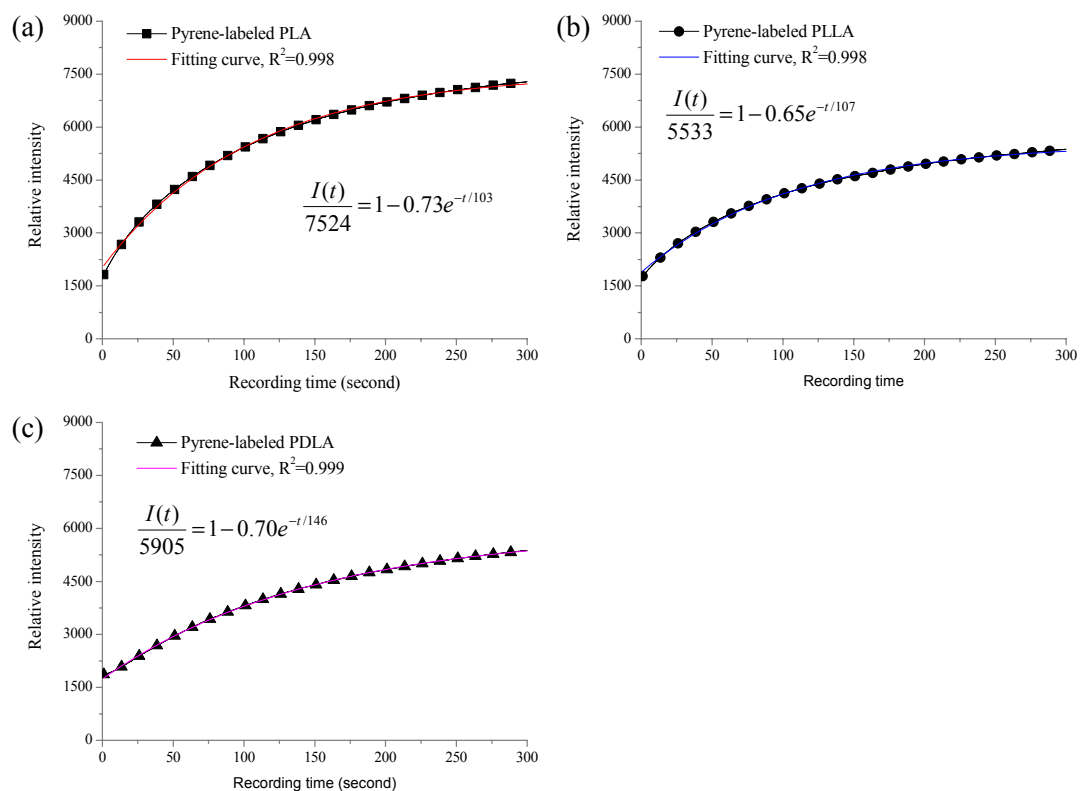
Figure S10. Single-exponential fitting curves for time profiles of fluorescence for excimer emission of PLP thin-film samples recorded at output power of 6mW; (a) pyrene-labeled PLA, (b) pyrene-labeled PLLA, (c) pyrene-labeled PDLA; λ_{exc}=340nm, λ_{em}=480nm and emission slit=10nm.
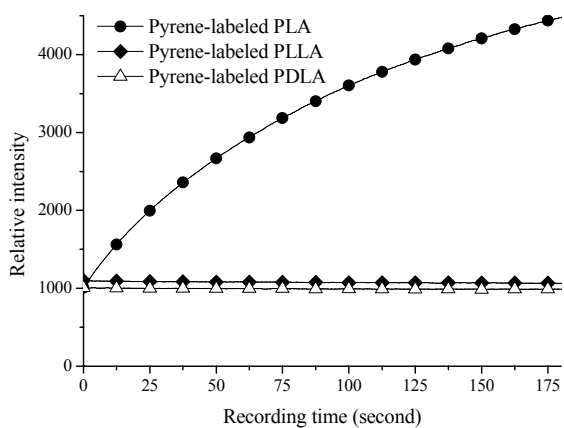
Figure S11. Time profiles of fluorescence for excimer emission of PLP thin-film

samples recorded at output power of 1.7mW; λ_{exc}=340nm, λ_{em}=480nm and emission

slit=10nm.