Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Block Copolymer Synthesis in One Shot: Concurrent Metal-Free ATRP and ROP Processes Under Sunlight

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Experimental

Materials

Methyl methacrylate (MMA, 99%; Aldrich) was washed with NaOH and distilled over CaH_2 prior to use. ε-caprolactone (ε-CL, 97%; Aldrich), was also vacuum distilled over CaH_2 and collected in molecular sieves before use. (3S)-cis-3,6-Dimethyl-1,4-dioxane-2,5-dione (L-Lactide, LLA, 98%; Aldrich) was crystallized from ethanol and dried prior to use. Tetrahydrofuran (THF; Aldrich HPLC grade) was dried on sodium wire under reflux in the presence of traces of benzophenone until a blue color persisted and was used directly after distillation. Perylene (98%, Sigma Aldrich) was crystallized from methanol prior to use. Phosphazene base P_2-*t*-Bu (~2.0 M THF solution, Sigma-Aldrich) was used as received.

Characterization

^{1}H NMR of the intermediates and final polymers were recorded at room temperature at 500 MHz on an Agilent VNMRS 500 spectrometer. Molecular weights and polydispersities of the polymers were measured using gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer using THF as the eluent at a flow rate of 0.3 mL min−1 at 30 °C and polystyrene standards. For the molecular weight analysis of poly((N-isopropyl acrylamide)-*b*-(ε-caprolactone)) was performed on Agilent 1100 instrument equipped with differential refractometer using DMF as eluent at a flow rate of 1 mL min^{-1} at 30 °C with poly(methyl methacrylate).

Synthesis of 3-hydroxypropyl 2-bromo-2-methylpropanoate (HBM)

1,3-Propanediol (1.8 mL, 3eq.) and triethylamine (1.22 mL, 1 eq.) was taken into a 100 mL round bottom flask containing dry dichloromethane (50 mL) and cooled in an ice bath under continuous mixing. 2-bromo-2-methylpropanyl bromide (1 mL, 1 eq.) was dissolved in dry dichloromethane (10 mL), taken into a dropping funnel and slowly added to the reaction flask. The reaction was left mixing for overnight and filtrated to remove the inorganic residues. Afterwards, the mixture was extracted with dilute HCl solution (2 × 50 mL), saturated potassium carbonate (K_2CO_3) solution (2 × 50 mL) and then with brine (2 × 50 mL). The organic layer was dried over $MgSO_4$ and dichloromethane was removed under reduced pressure. The product was then purified by column chromatography (2/8, ethyl acetate/hexane) (Yield: 71%).

General procedure for block copolymer synthesis: Concurrent Metal-Free ATRP and ROP Processes Under Sunlight:

In a typical experiment, the following chemicals were taken in a dry Schlenk tube containing dry THF under nitrogen atmosphere: [MMA] or [St]/[Perylene]/[HBM]: 300/3/1, [ε-CL]/[P_2-t-Bu]/[HBM]: 200/5/2, V_{MMA}=V_{THF}= 1 mL. The tube was exposed to sun light irradiation for 2 hours and the mixture was precipitated in methanol. The precipitate was filtered off and dried under vacuum.

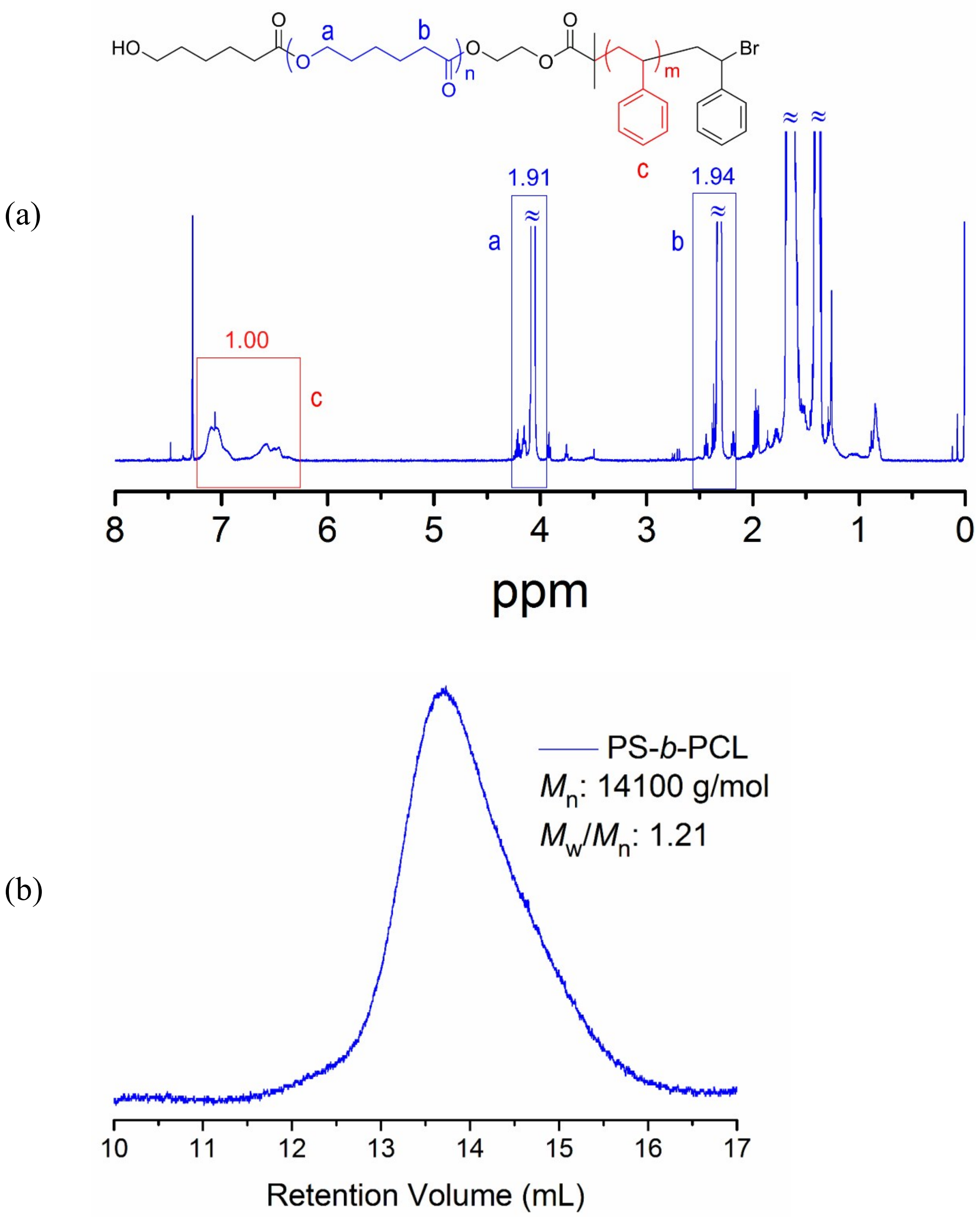
Synthesis of PNiPAM-*b*-PCL:

Identical experimental conditions and purification procedures were applied except using NiPAM (1 g) and using appropriate volume of THF to adjust the same concentration of perylene as described above.

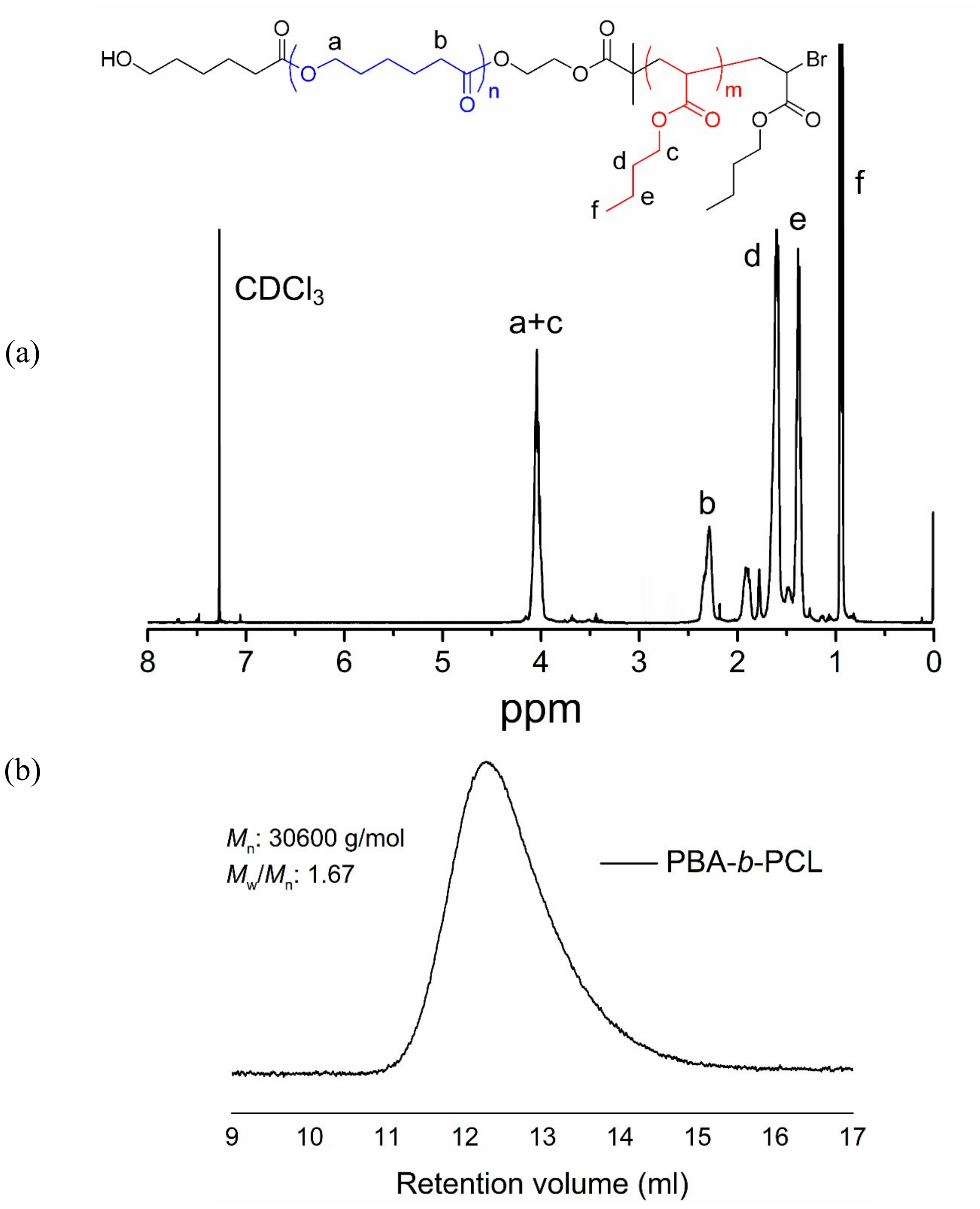
Synthesis of PMMA-*b*-PCL-*b*-PLLA

The following chemicals were taken in a dry Schlenk tube containing dry THF under nitrogen atmosphere: [MMA]/[Perylene]/[HBM]: 300/3/1, [ε-CL]/[P_2-t-Bu]/[HBM]: 20/5/2,

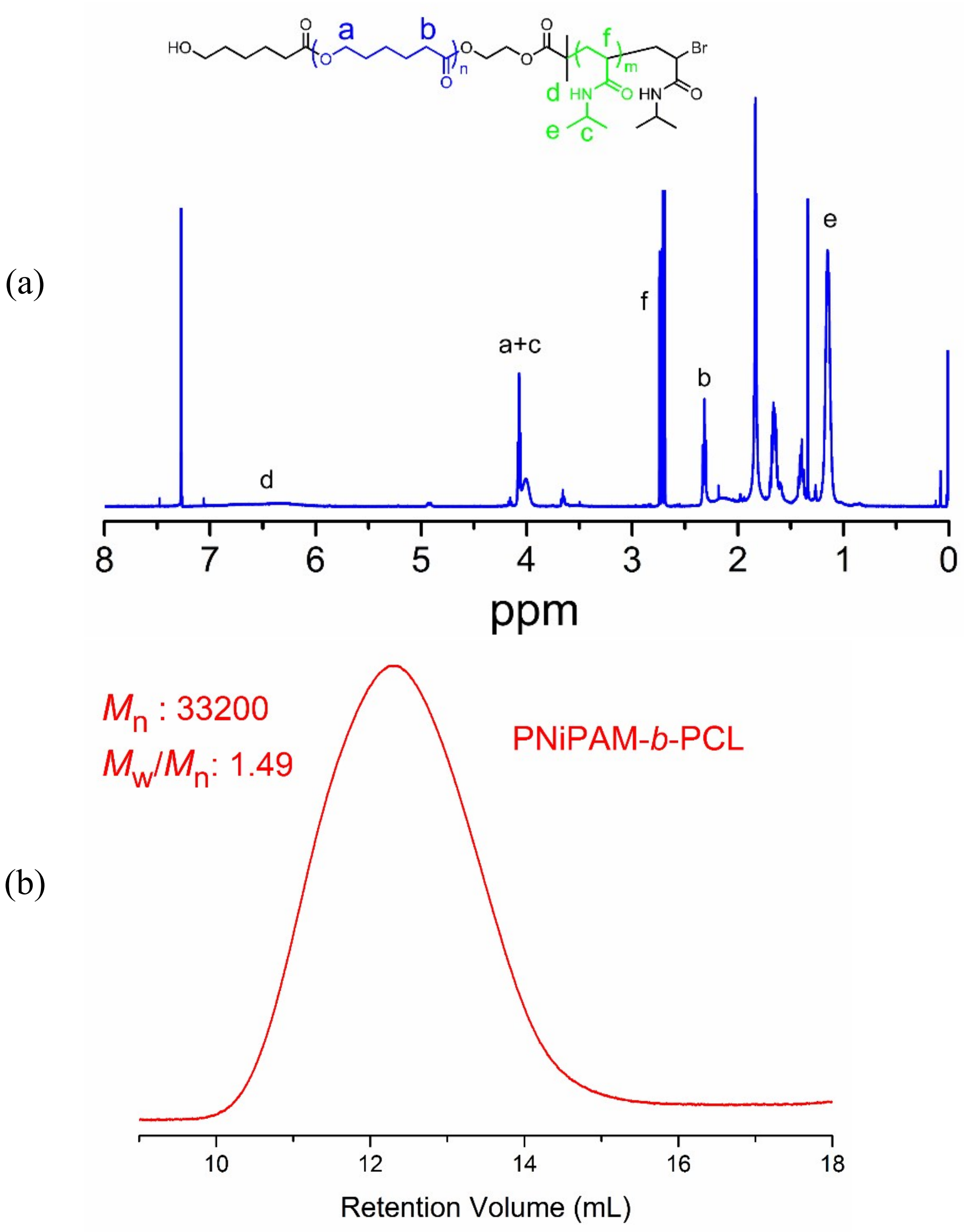
$V_{MMA}=V_{THF}$= 0.6 mL. After 2 hours of sunlight irradiation, LLA ([LLA]/[ε-CL]: 9/1), which was dissolved in dry THF (5.20 mL) was injected to the system via a syringe and the resulting mixture was further mixed under sunlight for 2 hours. Finally, the mixture was poured into excess methanol. The resulting material was filtered off ad dried under vacuum.



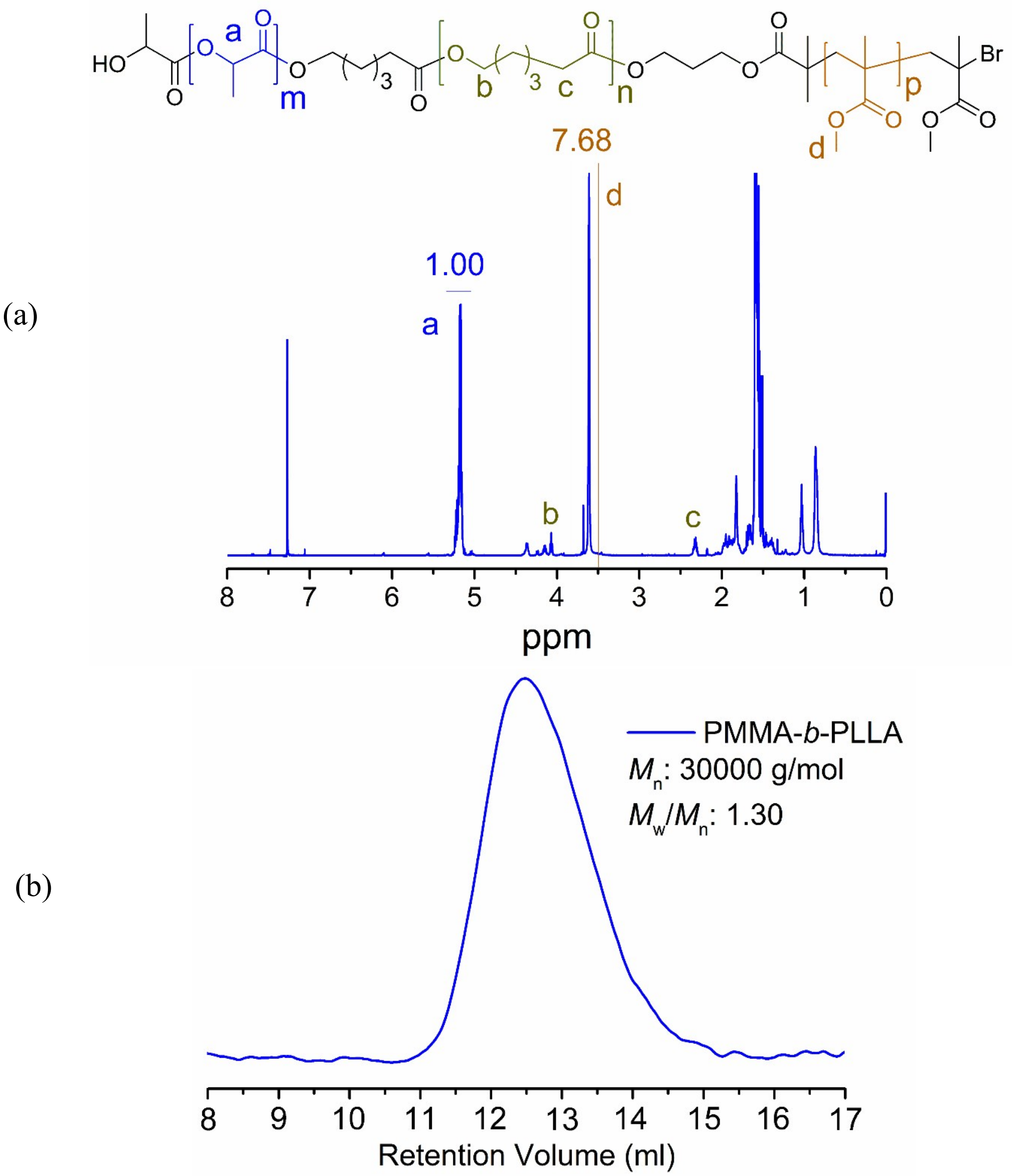
SF1. ^{1}H-NMR spectrum (a) and GPC chromatogram (b) of PS-*b*-PCL



SF2. ^{1}H-NMR spectrum (a) and GPC chromatogram (b) of PBA-*b*-PCL



SF3. ^{1}H-NMR spectrum (a) and GPC chromatogram (b) of PNiPAM-*b*-PCL



SF4. ^{1}H-NMR spectrum (a) and GPC chromatogram (b) of PMMA-*b*-PLLA