Supplementary Material (ESI) for Chemical Communications

Synthesis of amino acid-based polymers *via* atom transfer radical polymerization in aqueous media at ambient temperature

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Supplementary Materials

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Synthesis of Acryloyl β-alanine (ABA)

To a three-neck flask, equipped with a thermometer and a mechanical stirrer, containing 0.5 mol of β-alanine and 1 mol of NaOH aqueous solution, acryloyl chloride equivalent to the amino group on the β-alanine was added dropwise with vigorous stirring at a temperature below 5 °C. After addition was completed, an additional hour was allowed to complete the reaction. The solution was acidified to pH = 2 with a solution of concentrated HCl (37%), and extracted four times with ethyl acetate. The extract was separated, dried with anhydrous $MgSO_4$, filtered and concentrated using a rotary evaporator to obtain white crystals. The crystals were recrystallized from ethyl acetate to obtain pure ABA.

^{1}H NMR (D_2O, 400 MHz): δ = 6.09 (m, 2H), 5.62 (m, 1H), 3.40 (t, 2H), 2.51 (t, 2H).

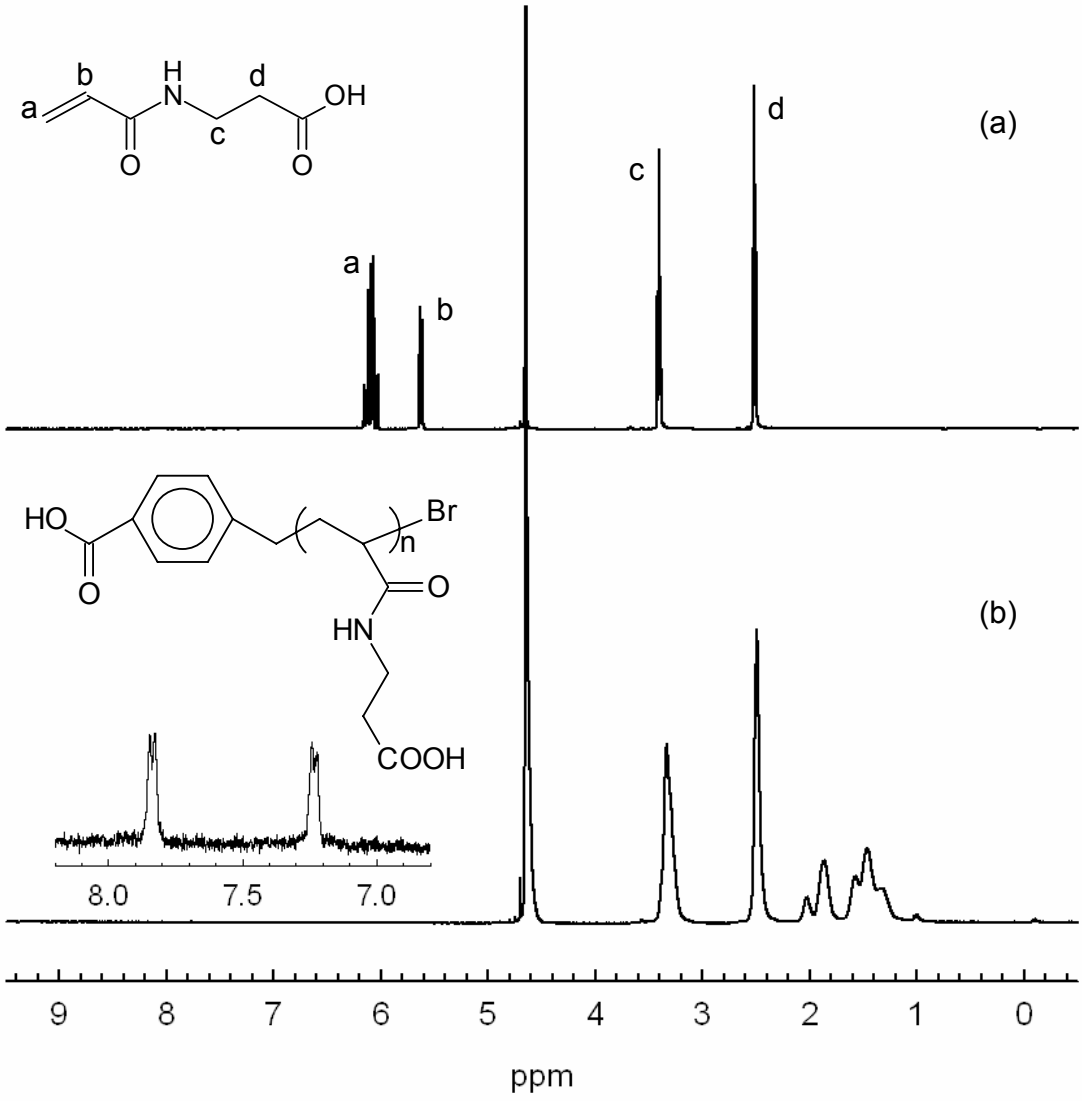

Fig. 1. ^{1}H NMR spectra of (a) ABA monomer and (b) its homopolymer synthesized by ATRP using initiator **3** at ambient temperature (D_2O).

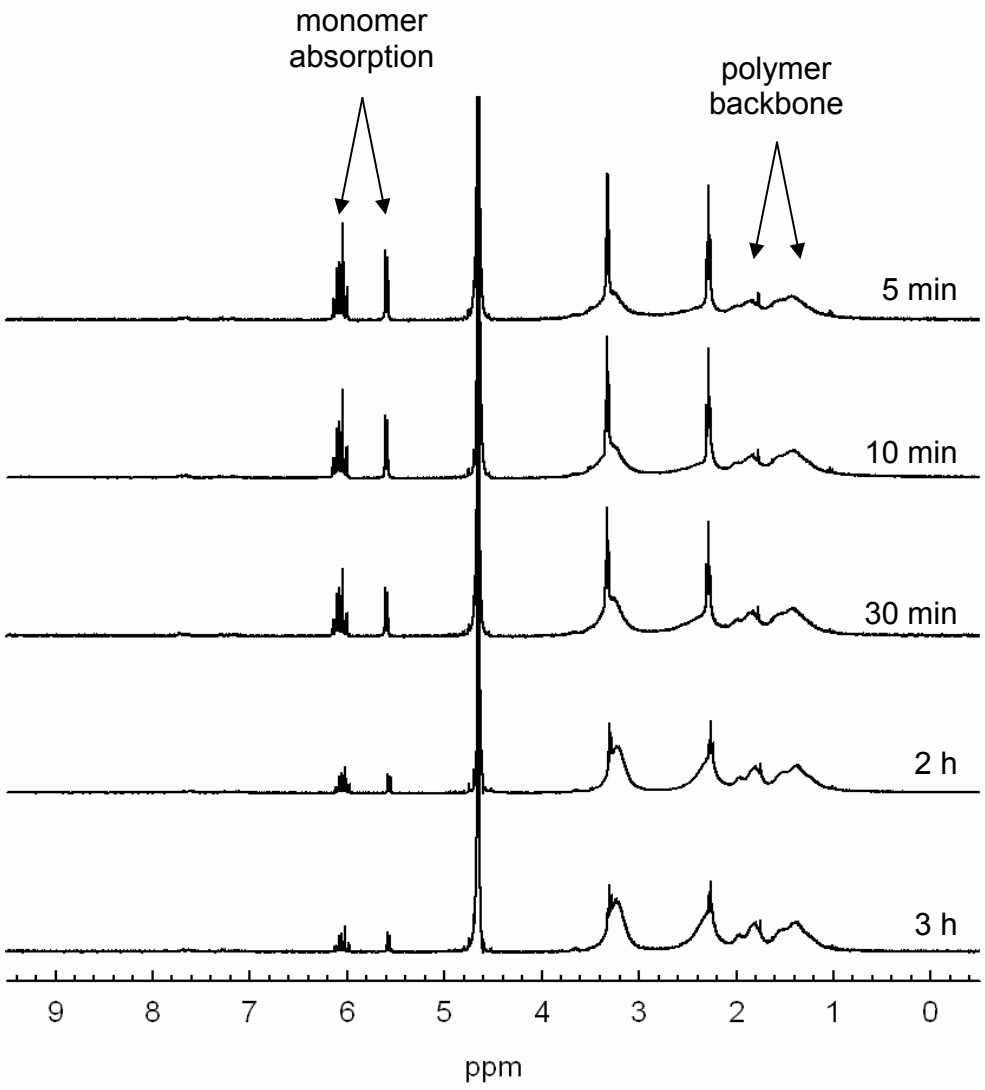

Fig. 2. Evolution of ^{1}H NMR spectra with reaction time for the ATRP of ABA in aqueous media using initiator **3** at ambient temperature (in D_2O).

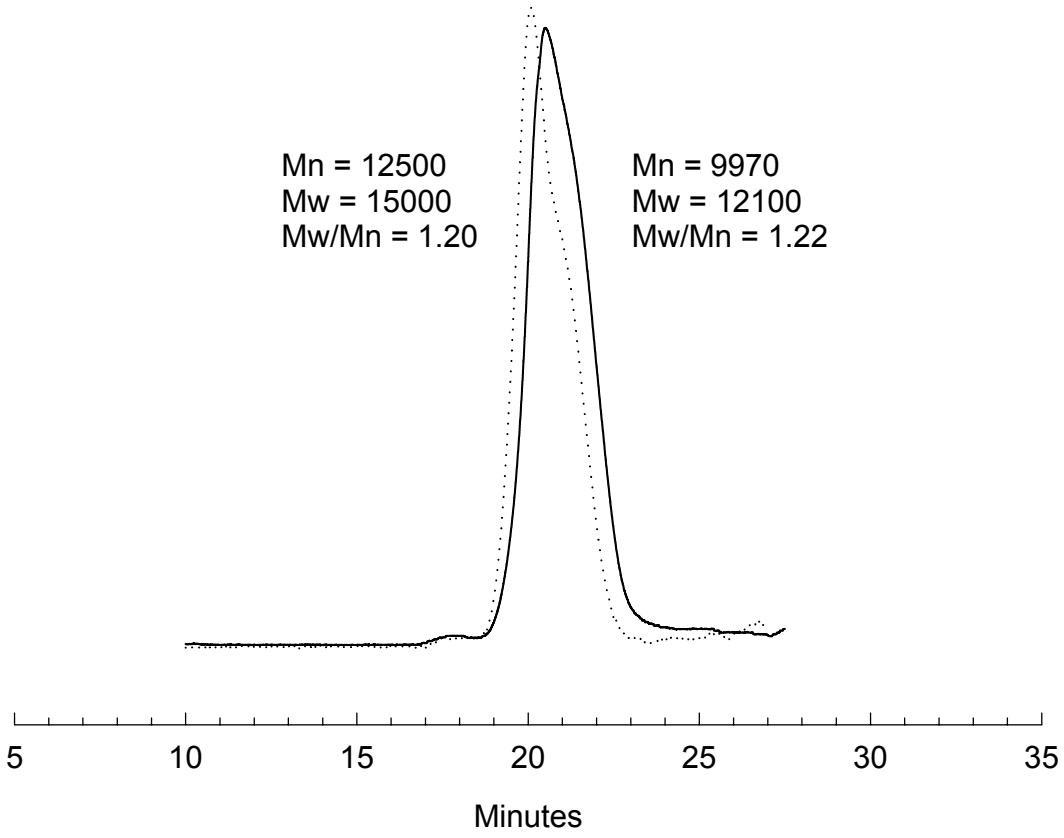

Fig. 3 GPC traces for ABA homopolymers synthesized by ATRP using initiator **2** at 20 °C in 60:40 water–MeOH mixture.

d*n*/d*c* Determination

The refractive index increments (d*n*/d*c*) were determined by the injection of five different concentrations into the interferometric refractometer (Wyatt OPTILAB DSP) in water for PABA at 20 °C, and in THF for methylated PABA at 40 °C. Concentrations (mg/mL) for the solutions were estimated by the following equation: $c_i = i/\{30 \times (\mathrm{d}n/\mathrm{d}c)\}$, where i = 1,2,3,4, or 5. During these measurements, the injector, equipped with a syringe pump, was connected to the refractometer directly. The flow rates employed were 0.2 mL/min, which was found to be sufficient for obtaining consistent data.

Multi-angle Light Scattering Characterization

Light scattering measurements were made at 20 °C using a Wyatt DAWN EOS multi-angle photometer at the wavelength of 690 nm.

Toluene and a narrow distributed polystyrene sample with the molecular weight being 8,000 were used to calibrate the right angle detector and to normalize the other scattering detectors, respectively. Water was used as the eluent; the flow rate was set to 1 mL/min. Molecular weights were determined by injecting five samples at different concentrations, which were determined by the equation, $c_i = i/\{n^2 \times (\mathrm{d}n/\mathrm{d}c)^2 \times Mw\}$, where i = 1,2,3,4, or 5, n is the refractive index of the solvent and the concentrations have the units of g/mL. The specific refractive index increment for PABA in water at 20 °C was taken to be 0.1572 $cm^3\ g^{-1}$ to determine weight average molecular weight.