Supplementary information

Multicomponent Polymerization System Combining Hantzsch Reaction and Reversible Addition−Fragmentation Chain Transfer to Efficiently Synthesize Well-Defined Poly(1,4-dihydropyridine)s

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Materials

2-(Acetoacetoxy)ethyl methacrylate (AEMA, Aladdin, 95%), benzaldehyde (Aladdin, 99%), dimedone (Aladdin, 99%), ammonium acetate, glycine（SCRC, 99%）, 2-thenaldehyde (Alfa, 98%), 4-fluorobenzaldehyde (Alfa, 98%), p-hydroxybenzaldehyde (Aladdin, 98%), 1-naphthaldehyde (Aladdin, 97%), hexanaldehyde (Aladdin, 97%) were used as purchased. Azodiisobutyronitrile (AIBN, Aladdin, 99%) was recrystalized twice from acetone prior to use. 4-cyano-4-(ethylthiocarbonothioylthio)pentanoic acid[1] was used as the chain transfer agent (CTA). Solvents as acetonitrile, and methanol were purchased from Sinopharm Chemical Reagent and used directly without further purification.

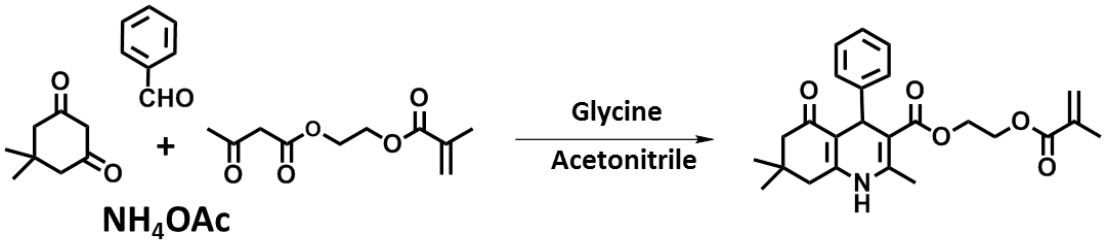
Measurements

Gel permeation chromatography (GPC) analyses of polymers were performed using N,N-dimethyl formamide (DMF) as the eluent. The GPC system was a Shimadzu LC-20AD pump 45 system consisting of an auto injector, a MZ-Gel SDplus 10.0 μm

guard column(50 × 8.0 mm, 10^2 Å) followed by a MZ-Gel SDplus 5.0 µm bead-size column (50 – 10^6 Å, linear) and a Shimadzu RID-10A refractive index detector. The system was calibrated with narrow molecular weight distribution polystyrene 50 standards ranging from 200 to 10^6g mol^{-1}. ^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL JNM-ECA400 (400 MHz) spectrometer for all samples. The ESI-MS data were collected using a Micro TOF-QII Bruker. The FT-IR spectra were made in a transmission mode on a Perkin-Elmer Spectrum 100 spectrometer (Waltham, MA, USA). The fluorescence measurements were obtained on a Perkin-Elmer LS-55 spectrometer equipped with quartz cuvettes of 1 cmpath length.

Methods

Synthesis of 1,4-dihydropyridines monomer



AEMA (428 mg, 2 mmol), dimedone (280 mg, 2 mmol), benzaldehyde (212 mg, 2 mmol), ammonium acetate (231 mg, 3 mmol) and glycine (22.5 g, 0.3 mmol) were dissolved in 2 mL of acetonitrile. The mixture was then kept at 70 °C for 4 hours, then the product was purified through column gel chromatography using ethyl acetate/petroleum ether (1:8) as eluent.

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.25 (m, 5H, C_6H_5), 6.27 (S, 1H, NH), 6.06, 5.55 (m, 2H, CH_2=C), 5.02 (s, 1H, CH), 4.25 (m, 4H, CH_2CH_2), 2.34 (s, 3H, NHCC$\underline{H}_3$), 2.18 (m, 4H, C=OCH_2C, CC$\underline{H}_2$CCH_3), 1.05, 0.91 (m, 6H, C(CH_3)$_2$).

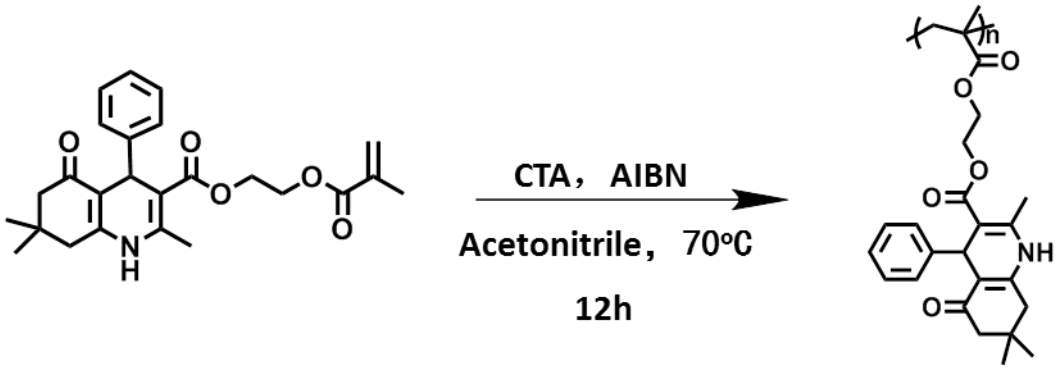
^{13}C NMR (100 MHz, DMSO, δ/ppm): 194.7 167.1 (167.9), 149.9 (148.1), 146.2, 136.1, 128.2 (127.9), 126.6 (126.2), 110.6, 103.4, 63.2, 61.6, 50.7, 36.3, 32.6, 29.6,

27.0, 18.9, 18.5.

IR (ν/cm^{-1}): 3280, 1721, 1792, 1607, 1482, 1380, 1274, 1209, 1160, 1106, 1079, 1046, 996, 945, 762, 715, 699, 657.

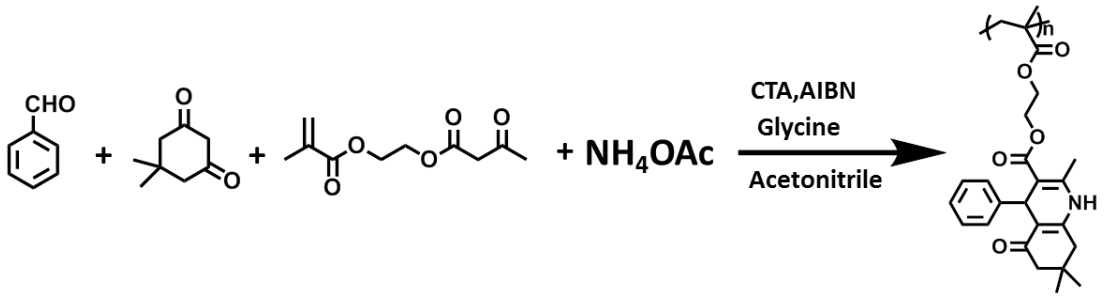
ESI-MS: observed (expected): 424.2120(424.2118) [M+H^{+}].

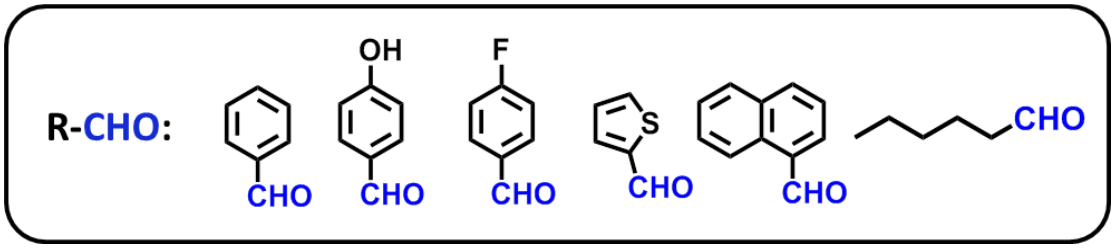
Preparation of poly(1,4-dihydropyridines) (poly(1,4-DHPs)) via RAFT process of 1,4-dihydropyridines monomer



1,4-Dihydropyridines monomer (846 mg, 2.0 mmol), CTA (5.26 mg, 0.02 mmol) and AIBN (0.66 mg, 0.004 mmol) were charged into a schlenk tube with 4.0 mL of acetonitrile. The schlenk tube was sealed with a rubber septum and purged by nitrogen flow for 20 min, the tube was then kept in a 70 °C oil bath. After 12 h, the polymerization was exposed to the air, and the mixture were dialysed against methanol (MWCO: 7000) for 2 days to get the target polymer.

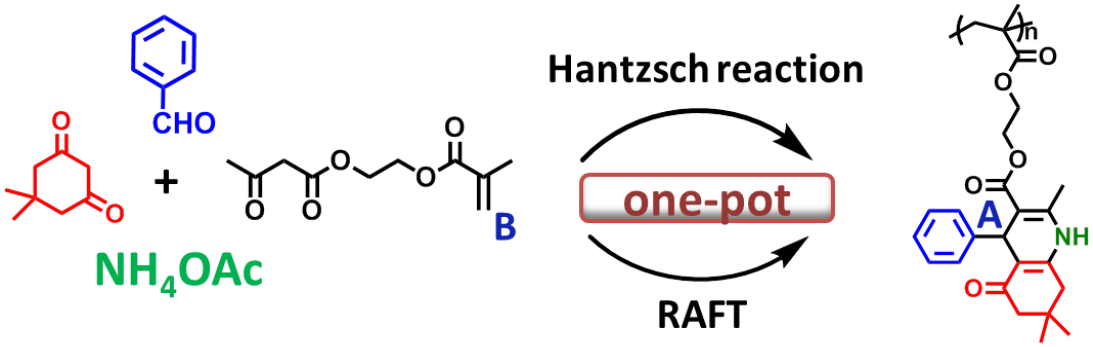
Preparation of poly(1,4-DHPs) via one-pot Hantzsch-RAFT process.





AEMA (428 mg, 2.0 mmol), dimedone (280 mg, 2.0 mmol), benzaldehyde (212 mg, 2.0 mmol), ammonium acetate (231 mg, 3.0 mmol), glycine (22.5 mg, 0.3 mmol) were firstly dissolved in 2.0 mL of acetonitrile. Afterwards, CTA (5.26 mg, 0.02 mmol), AIBN (0.66 mg, 0.004 mmol) were added into the schlenk tube. The schlenk tube was sealed with a rubber septum and purged by nitrogen flow for 20 min, the tube was then kept in a 70 °C oil bath. Samples were withdrawn periodically under N_2 to perform ^{1}H-NMR and GPC analyses. After 12 hours, the polymerization was exposed to the air, and the mixture were dialysed against methanol (MWCO: 7000) for 2 days. The final polymer was obtained after solvent evaporation. All the other aldehyde substituted poly(1,4-dihydropyridines) (poly(1,4-DHPs)) via one-pot Hantzsch-RAFT process were performed in a similar process except that benzaldehyde was replaced by different aldehydes.

Supporting Data



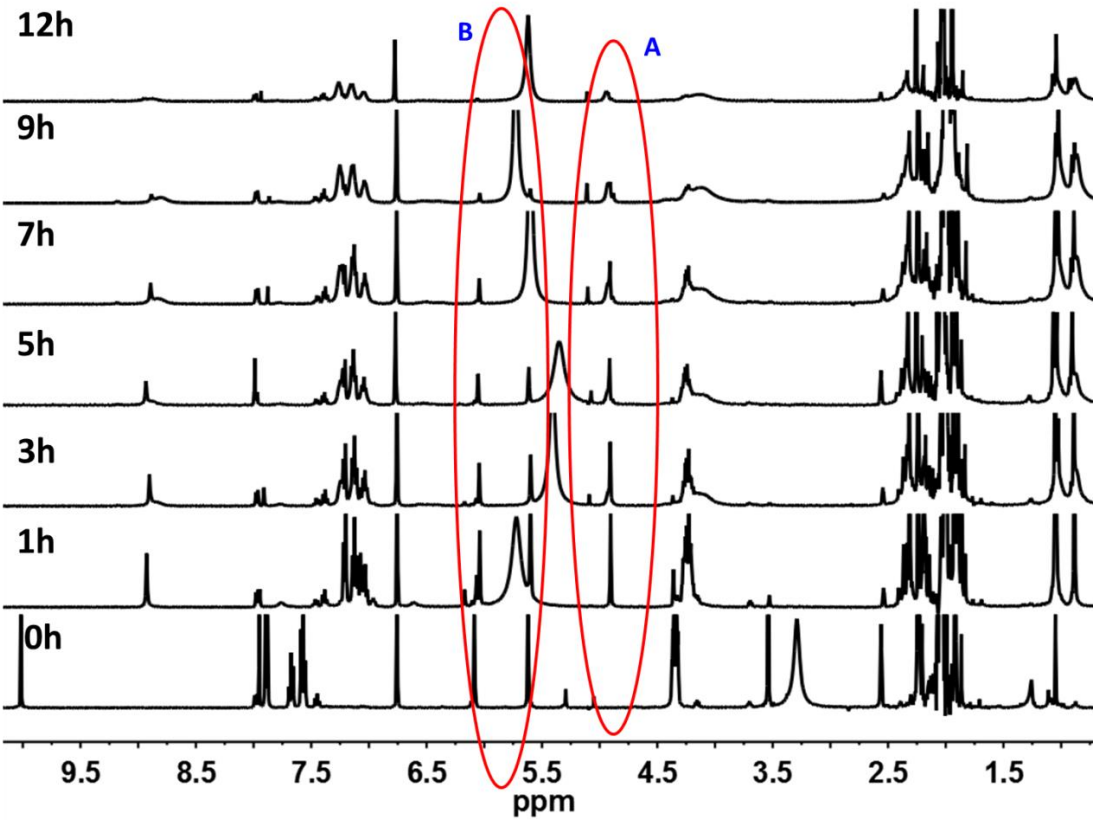


Figure S1. ^{1}H-NMR spectra of Samples were withdrawn periodically under N_2 during the preparation of poly(1,4-dihydropyridines) (poly(1,4-DHPs)) via one-pot Hantzsch-RAFT process.

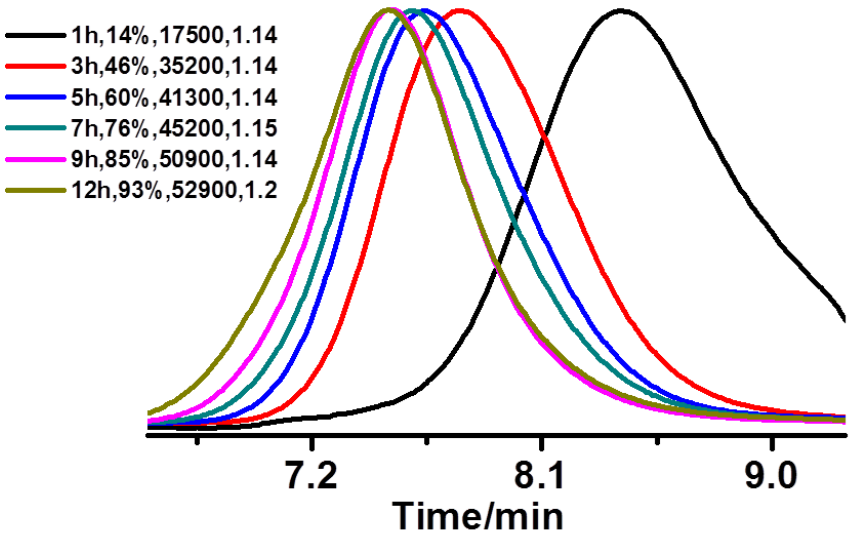


Figure S2. GPC curves of samples during polymerization with detailed data information of Mn and PDI.

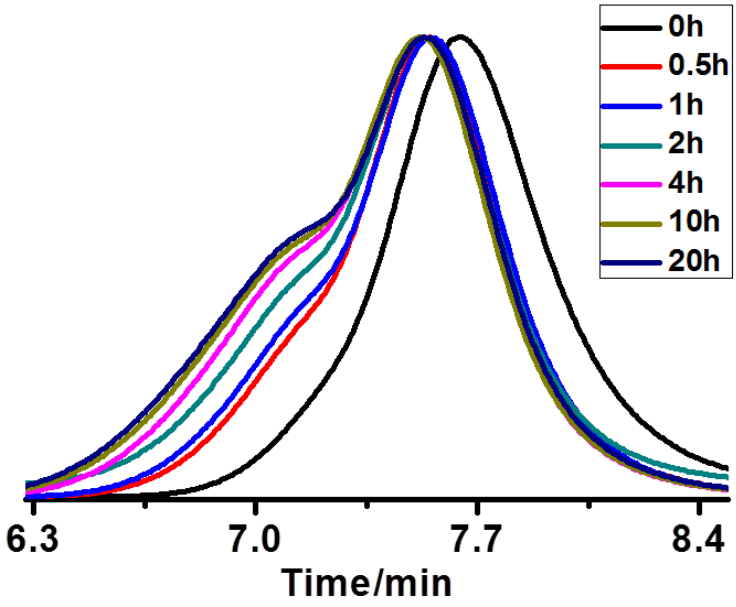


Figure S3. GPC of poly(1,4-DHP)s during the post-modification.

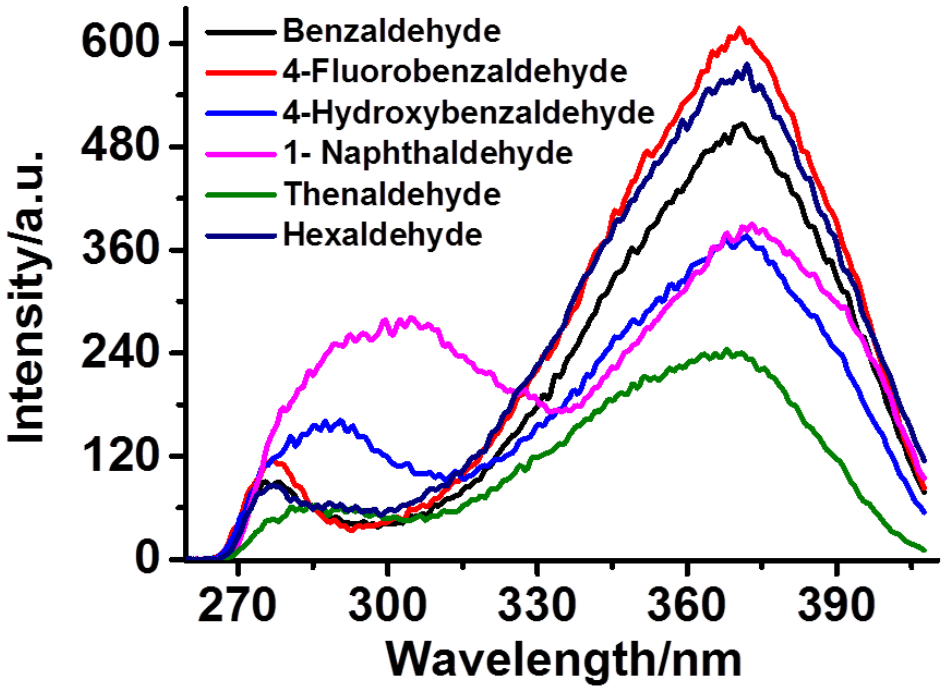


Figure S4. Excitation spectrum of poly(1,4-dihydropyridines) with different aldehyde substituted via one-pot Hantzsch-RAFT process (the emission wavelength is 438 nm).

Reference

(1) Tao, L.; Liu, J.; Davis, T. P. *Biomacromolecules* **2009**, *10*, 2847.