Electronic Supplementary Material
For

A facile one pot strategy for synthesis of well-defined polyacrylates from acrylic acid via RAFT polymerization

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Experimental Section

1. Materials and measurements

Acrylic acid (AA) and 1, 1, 3, 3-tetramethylguanidine (TMG) were distilled under reduced pressure before using. All other chemicals were analytical-grade reagents and used directly without further purification.

Gel permeation chromatography (GPC) measurements were carried out at 35℃in THF with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards.

^{1}H NMR spectra were obtained using a Bruker Avance 400 spectrophotometer for all samples.

2. Methods

Synthesis of benzyl dithiobenzoate. The preparation of this compound is described elsewhere.[1] A mixture of benzoic acid (3.66 g, 30 mmol), benzyl alcohol (3.24 g, 30 mmol), and phosphorus pentasulfide (6.67 g, 30 mmol) in benzene (60 mL) was refluxed for 12 h. It was cooled to room temperature and the product purified by column chromatography packed with neutral alumina eluting with petroleum ether. After removal of solvent, vacuum distillation of the residue gave benzyl dithiobenzoate as red oil. ^{1}H NMR, δ: 4.60 (s, 2H, C$\mathbf{H}_2$-Ph), 7.30-7.60 (m, 8H, Ar**H**), 8.02 (m, 2H, Ar**H**).

Determination of the yield of TMG promoted esterification reaction of acrylic acid with ethyl iodide in DMF at 70℃. Acrylic acid (171 μL, 2.5 mmol) and TMG (314 μL, 2.5 mmol) were mixed in 0.5 mL DMF, and the reaction mixture was put in an oil bath thermostated at 70℃. The reaction time was set 0 when ethyl iodide (201 μL, 2.5 mmol) was added immediately. Samples were withdrawn periodically for ^{1}H NMR in $CDCl_3$ for yield determination. The ^{1}H NMR spectrums of reaction mixtures at different reaction time were shown in **Fig. S1**.

One pot synthesis of polyacrylate from acrylic acid. A typical procedure is as follows. In a two-necked round-bottom flask equipped with a condenser, acrylic acid (3.43 mL, 50 mmol) and 1, 1, 3, 3-tetramethylguanidine (6.27 mL, 50 mmol) were mixed in DMF (10 mL) in nitrogen atmosphere, then AIBN (4.1 mg, 0.025 mmol), benzyl dithiobenzoate (61.1 mg, 0.25 mmol) and ethyl iodide (4.04 mL, 50 mmol) were added. The reaction mixture was immersed in an oil bath thermostated at 70℃. Samples were withdrawn periodically for ^{1}H NMR and GPC analyses for conversion and molecular weight determination, respectively. The purified polymer was obtained via precipitation into water, then dissolving into THF, and precipitating into petroleum ether for three times, and finally dried under vacuum.

Synthesis of hyperbranched polymer. A typical procedure is as follows. Acrylic acid (343 µL, 5 mmol), and 1, 1, 3, 3-tetramethylguanidine (627 µL, 5 mmol) were mixed in DMF (4 mL), then AIBN (1.6 mg, 0.01 mmol), benzyl dithiobenzoate (24.4 mg, 0.1 mmol) and 1,4-bis(bromomethyl)benzene (660 mg, 2.5 mmol) were added. After being degassed by three freeze-vacuum-thaw cycles, the reaction mixture was immersed in an oil bath thermostated at 70℃ for a prescribed time. After polymerization, the reaction mixture was precipitated in methanol two times and washed with water. The precipitate was collected and dried by vacuum freezing. The degree of branch is calculated based on the following equation:

$$DB = \frac{I_a - 4I_b}{I_a} \qquad \textbf{(1)}$$

where I_a is the integration of peak a at 5.17 ppm corresponding to the methylene protons of $-$COOC**H**$_2$ArC**H**$_2$OOC$-$, and I_b is the integration of peak b at 6.16 ppm corresponding to the methine protons originating from CH_2=**CH**COOCH_2—.

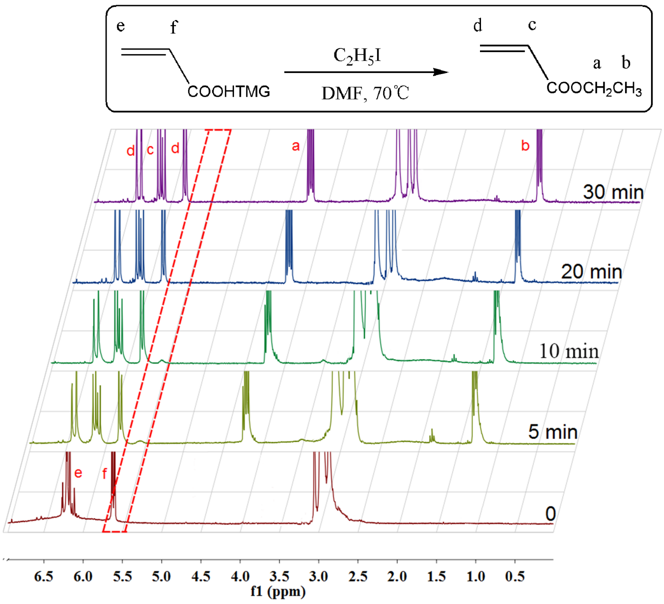

Fig. S1 ^{1}H NMR spectrums of the TMG promoted esterification reaction of acrylic acid with ethyl iodide at 70℃ at different reaction time. The signals between 2.5 and 3.5 ppm are assigned to methyl protons of DMF and TMG salt.

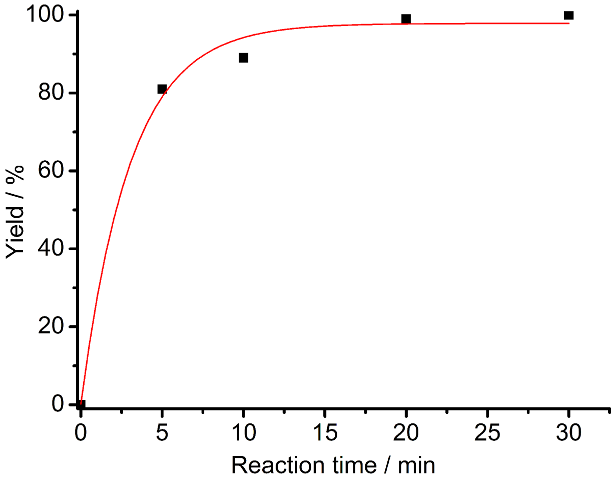

Fig. S2 Plot of product yield versus reaction time for the reaction of acrylic acid with ethyl iodide in DMF using TMG as promoter at 70℃.

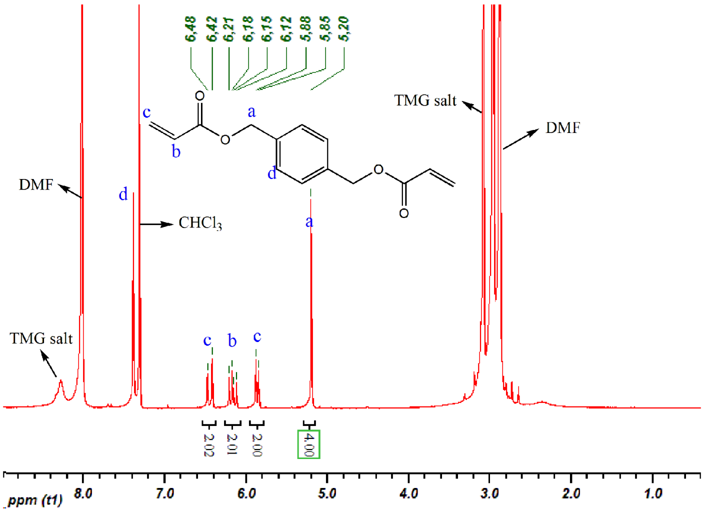

Fig. S3 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of the TMG promoted esterification reaction of acrylic acid with 1,4-bis (bromomethyl) benzene at 70℃ in DMF. The sample was withdrawn after reaction for **5 min** and dissolved in $CDCl_3$ for ^{1}H NMR analyse. The yield is 100% calculated according the spectrum.

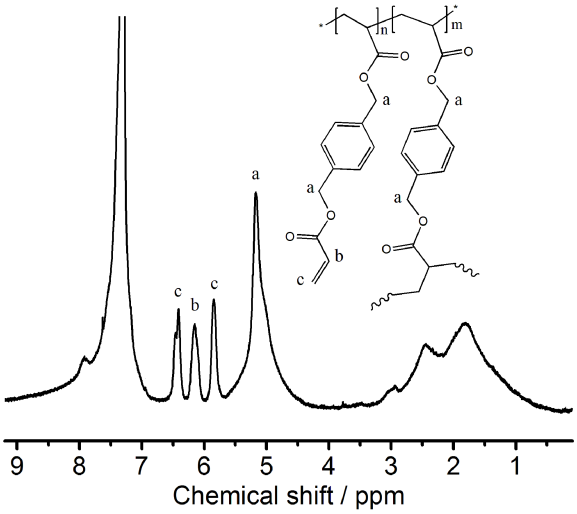

Fig. S4 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of hyperbranched polyacrylate synthesized by one pot stategy.

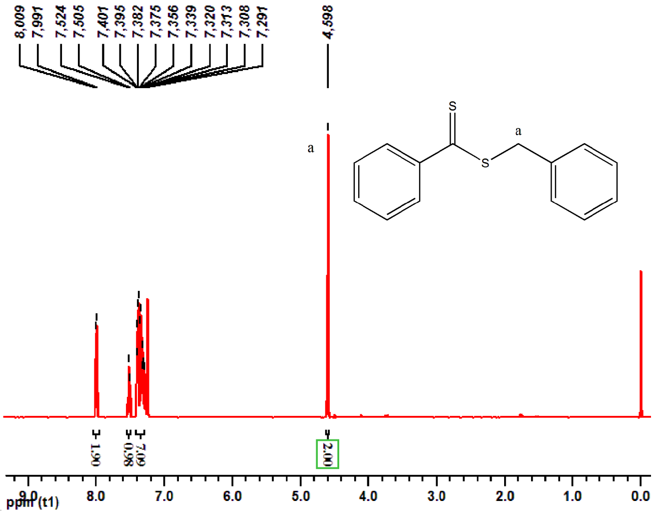

Fig. S5 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of benzyl dithiobenzoate.

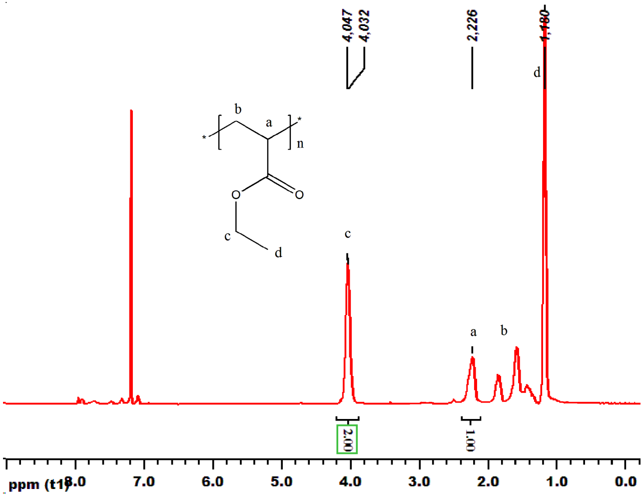

Fig. S6 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (ethyl acrylate) obtained via one pot strategy.

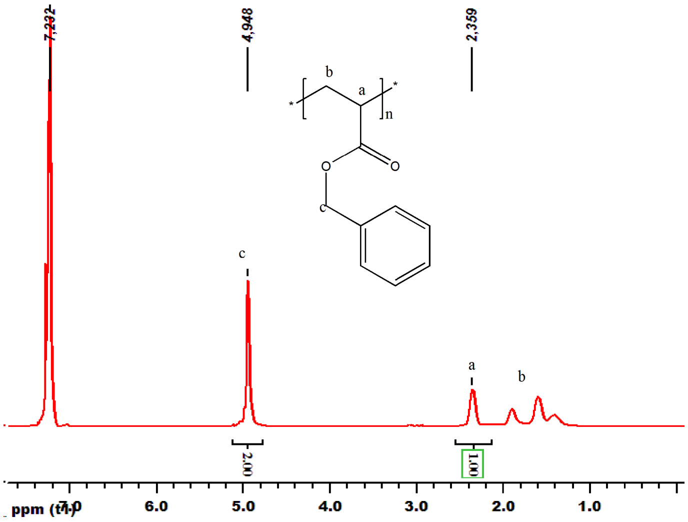

Fig. S7 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (benzyl acrylate) obtained via one pot strategy.

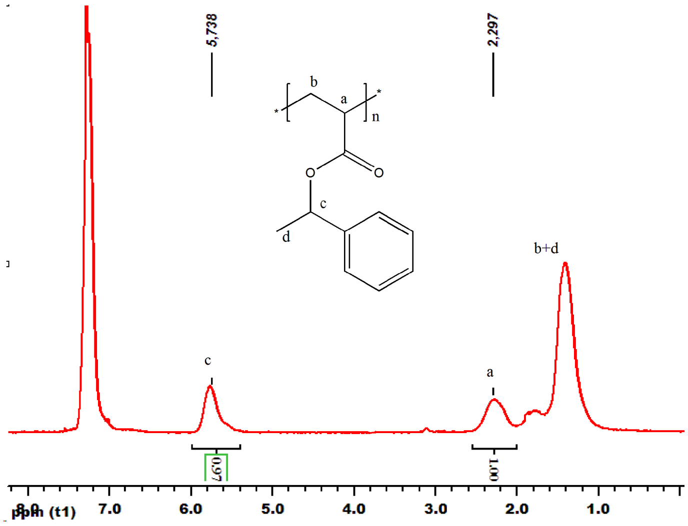

Fig. S8 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (1-phenylethyl acrylate) obtained via one pot strategy.

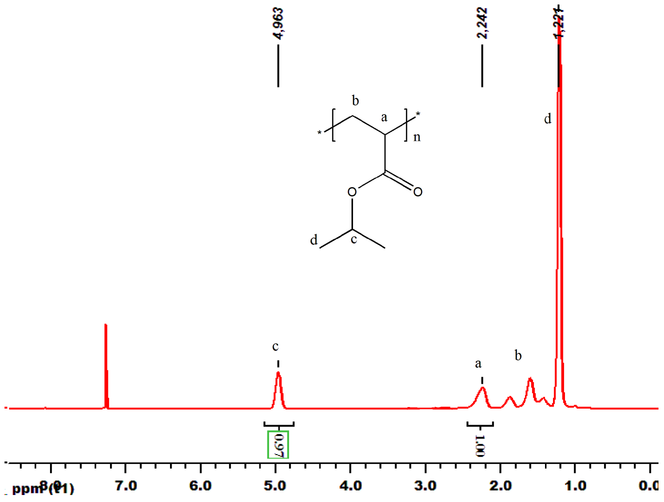

Fig. S9 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (isopropyl acrylate) obtained via one pot strategy.

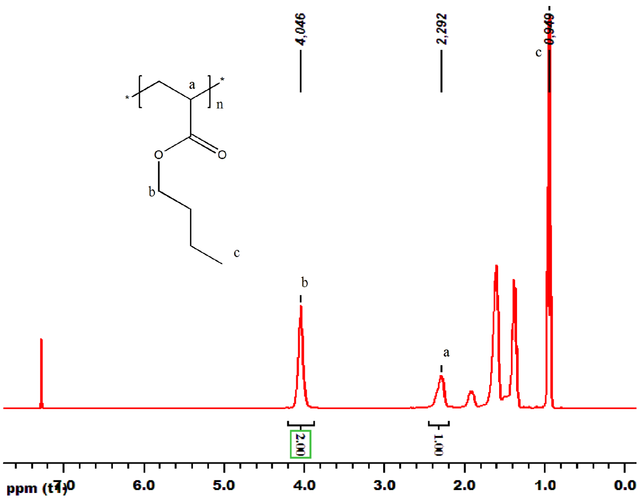

Fig. S10 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (n-butyl acrylate) obtained via one pot strategy.

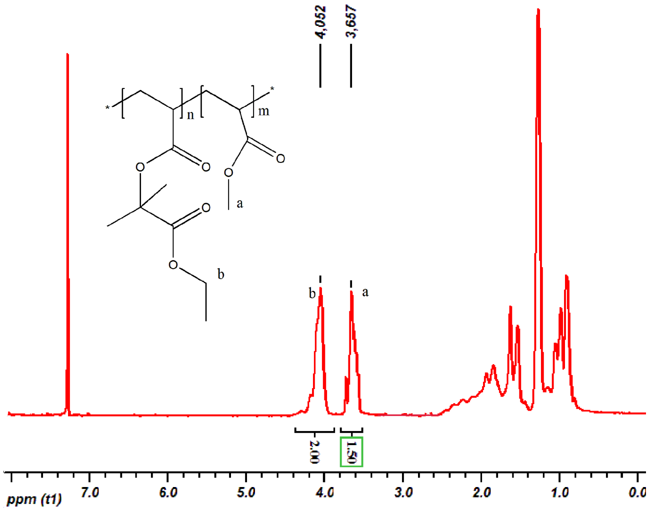

Fig. S11 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly (1-ethoxy-2-methyl-1-oxopropan-2-yl acrylate-block-methyl acrylate) after methylation of poly (1-ethoxy-2-methyl-1-oxopropan-2-yl acrylate) with methyl iodide obtained via one pot strategy.

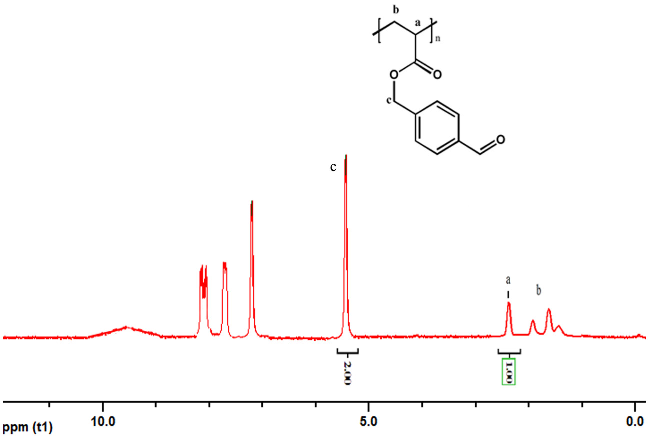

Fig. S12 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of poly(4-formylbenzyl acrylate) obtained via one pot strategy.

Stability of CTA in the presence of TMG

In order to investigate the influence of TMG on the RAFT agent, a model reaction was performed, which was similar to the polymerization system except for the absence of AIBN. The reaction mixture was characterized by ^{1}H NMR spectroscopy after reaction for 8h or 24h at 70℃, and the signal at 4.57 ppm belongs to the methylene of RAFT agent (PhC(S)SC**H**$_2$Ph) still existed, and no signals of aminolysis products of RAFT agent, such as PhC**H**$_2$SH, and PhC**H**$_2$SSC**H**$_2$Ph, were found. These results indicate that TMG did not affect the RAFT agent and the RAFT polymerization.

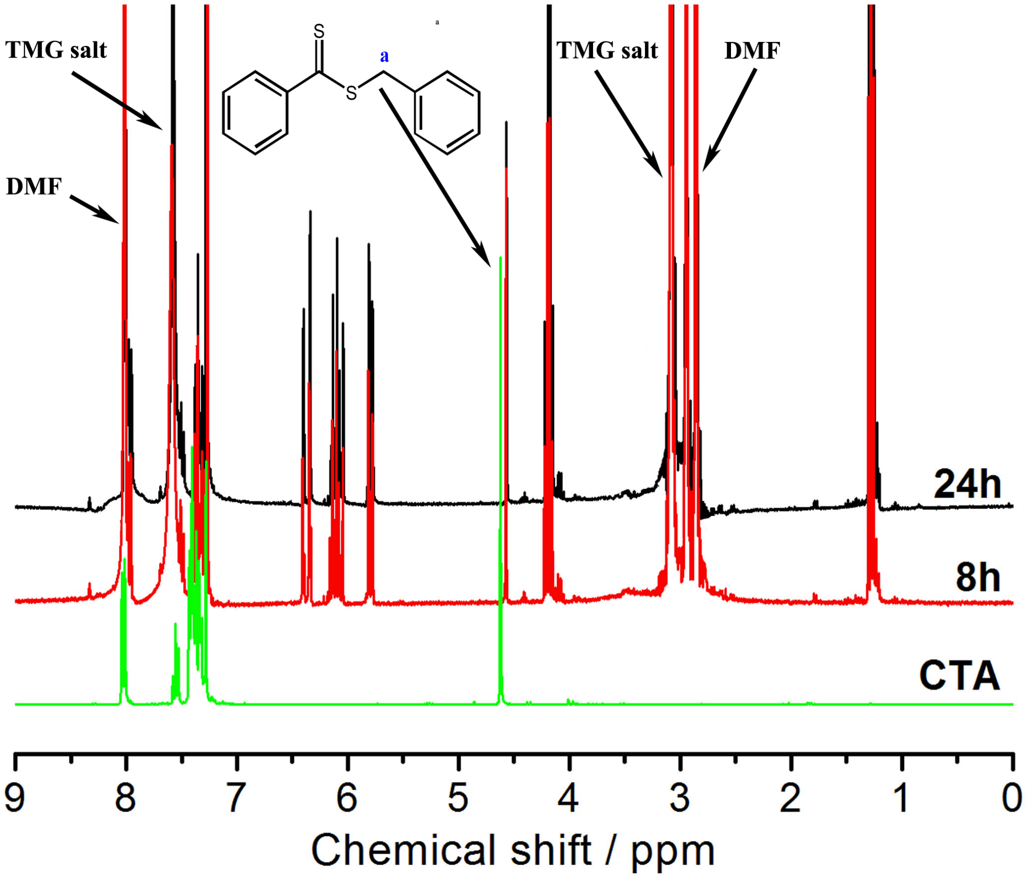

Fig. S13 The ^{1}H NMR spectrum of polymerization mixture (acrylic acid, TMG, ethyl iodide, and CTA in DMF) after reaction for 8h or 24h at 70℃.

Reference

1. A. Sudalai, S. Kanagasabapathy, and B. C. Benicewicz, *Org. Lett.*, 2000, **2**, 3213.