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Electronic Supplementary Information

One-pot sequential multicomponent reaction and multicomponent polymerization method for the synthesis of differently topological polymers

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1. The MS of the intermediate produced in one-pot sequential multicomponent reaction and multicomponent polymerization method.

Propargyl methacrylate (248 mg, 2 mmol), *N*-acethomocysteine thiolactone (318 mg, 2 mmol), *N,N*-dimethyldipropylenetriamine (319 mg, 2 mmol) and triethylamine (1g, 10 mmol) were dissolved in DMF (3 mL), subsequently, the mixture was degassed with argon for 2 min. The reaction was performed under stirring at room temperature. After 3 hours' reaction, we injected the reaction mixture into LC-MS instrument for MS analysis. Only the peaks for the target molecule were observed. The signal at 443.2 is for the in situ formed intermediate (C21H38N4O4S, 442.2+1, [M+H$^+$], 100%), and the signal observed at 444.2 (25%) is originated from the isotopic molecule of C21H38N4O4S.

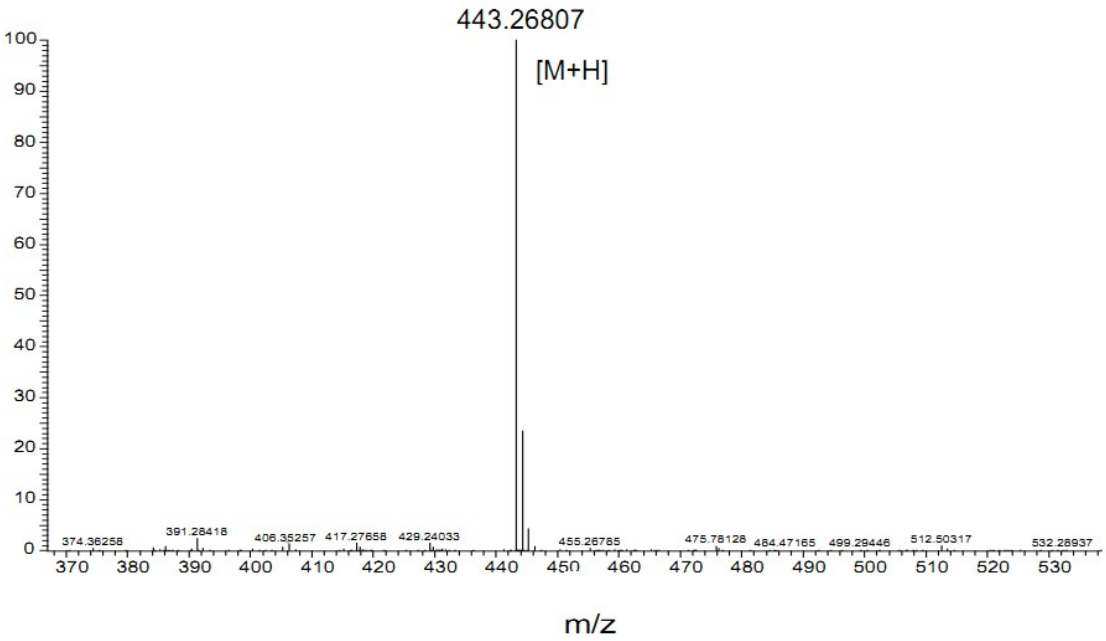


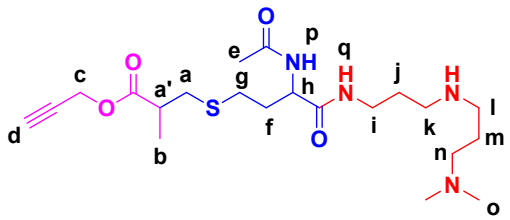
Figure S1. The MS spectrum of the intermediate in reaction mixture produced in one-pot sequential multicomponent reaction and multicomponent polymerization method.

2. The controlled experiment by a stepwise process to synthesis sequenced-

controlled linear polymer.

(1) The multicomponent of propargyl methacrylate, *N*-acethomocysteine thiolactone and *N,N*-dimethyldipropylenetriamine.

Propargyl methacrylate (248 mg, 2 mmol), *N*-acethomocysteine thiolactone (318 mg, 2 mmol) and *N,N*-dimethyldipropylenetriamine (319 mg, 2 mmol) were dissolved in DMF (3 mL), subsequently, the mixture was degassed with argon for 2 min. The reaction was performed under stirring overnight at room temperature. Then the mixture was purified by a silica column (methanol/ethyl acetate: 1/9) to furnish the intermediate molecular as slight yellow viscous oil, yield was 86 %. (Because of the strong polarity of second amine and third amine groups, the intermediate molecular was flowed very slowly in silica column).



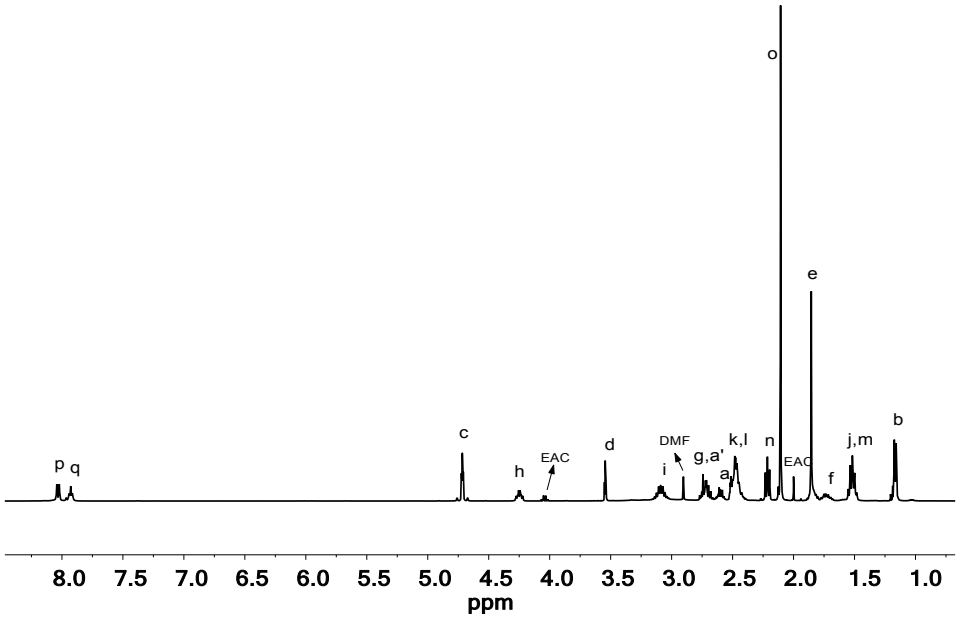
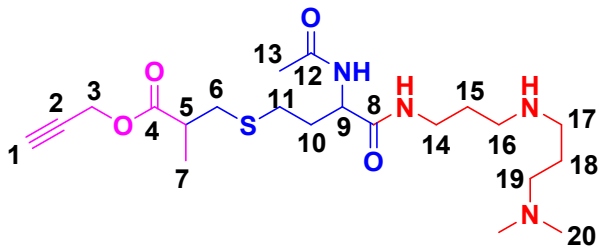


Figure S2. ^{1}H NMR spectrum of the intermediate obtained after purified by a silica column in DMSO-d6.



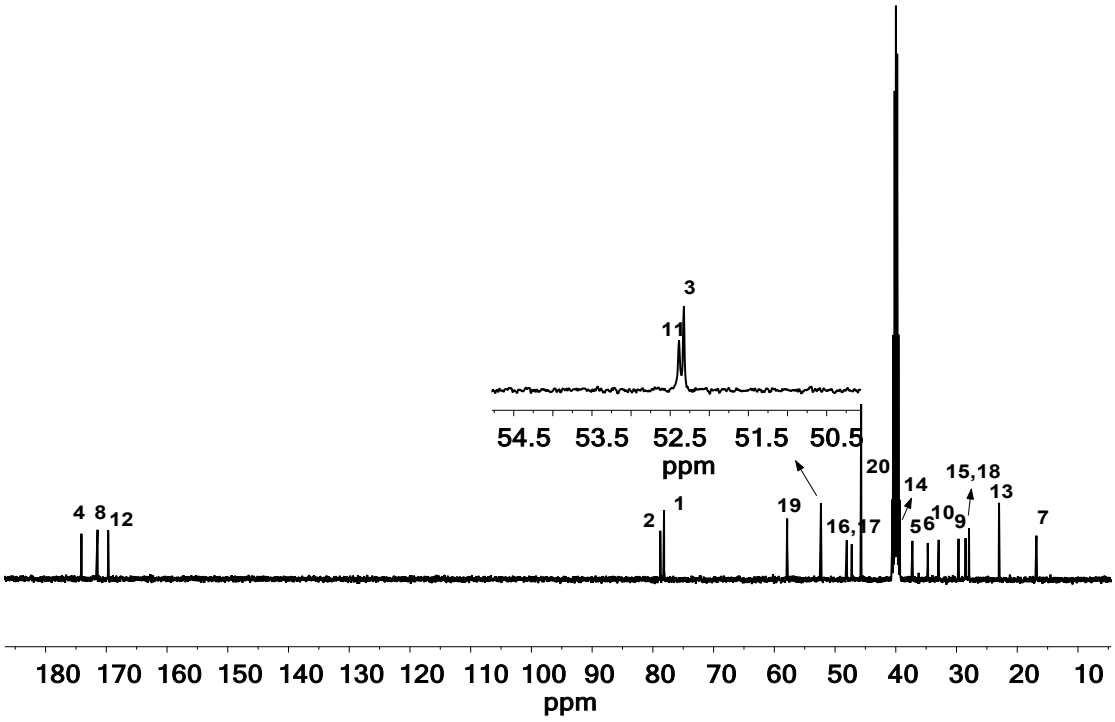


Figure S3. ^{13}C NMR spectrum of the intermediate obtained after purified by a silica column in DMSO-d6.

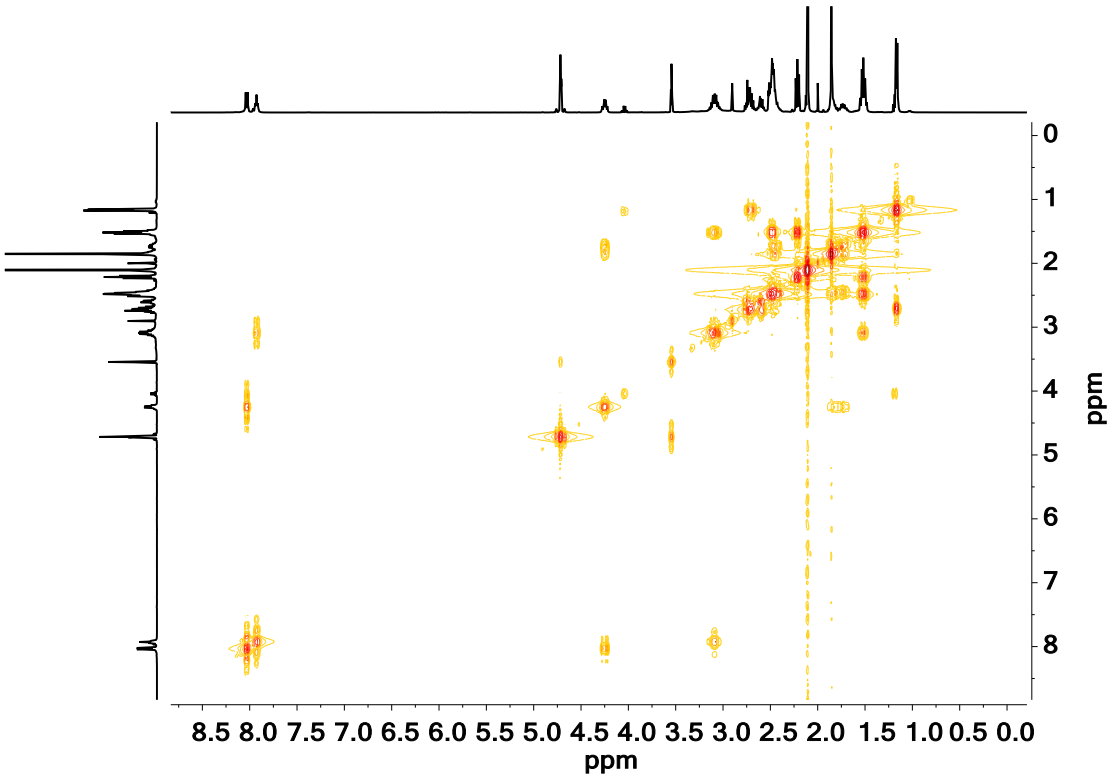


Figure S4. H,H COSY 90° spectrum of the intermediate obtained after purified by a silica column in DMSO-d6.

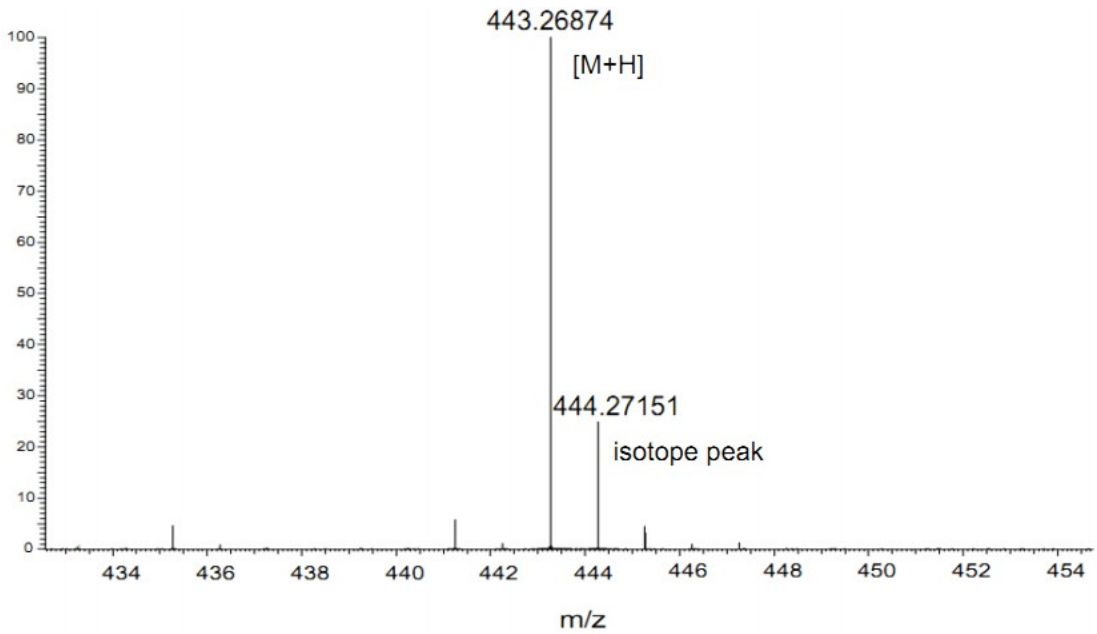


Figure S5. MS spectrum of the intermediate obtained after purified by a silica column.

(2) The multicomponent reaction of alkyene, secondary amine and azide.

The intermediate molecular (442 mg, 1 mmol) was dissolved in DMF (3 mL), then CuCl (15 mol%) and TEA (500 mg, 5 mmol) was added under argon atmosphere. After additional 15 min's stirring, *p*-toluenesulfonyl azide (394 mg, 2 mmol) in 1 mL DMF was slowly added into the reaction mixture in 20 min using an injector. The polymerization was carried out at 70 ºC for 10 h. Subsequently, the reaction solution was precipitated into diethyl ether and isopropanol. Then the linear polymer (390 mg) was separated by filtration and dried in vacuum to obtain the product linear polymer as brown solid. Yield was 64 %.

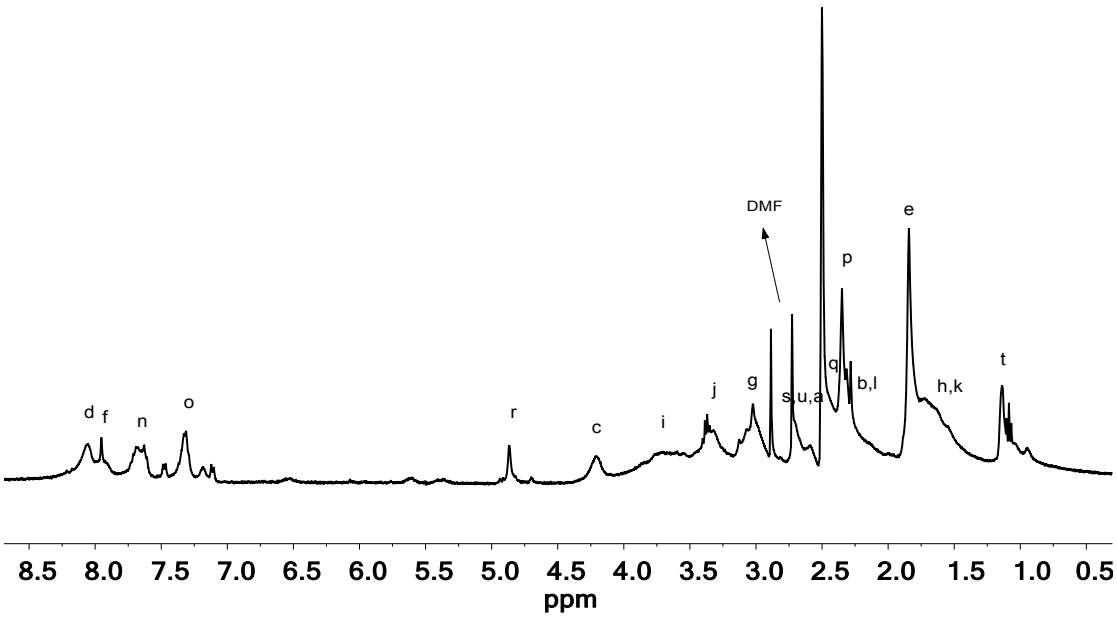


Figure S6. ^{1}H NMR spectrum for the linear polymer prepared via multicomponent

polymerization between the intermediate molecular containing one alkyne unit and one second amine unit with *p*-toluenesulfonyl azide in DMSO-d6.

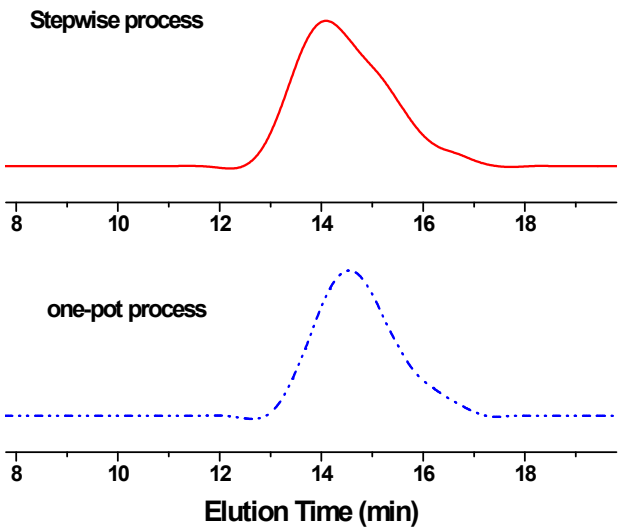


Figure S7. SEC curves of the sequence-controlled linear polymers prepared by the stepwise process (red) and one-pot process (blue).