Electronic Supplementary Information

One-pot synthesis of polyamides with various functional side groups via Passerini reaction

Yao-Zong Wang, Xin-Xing Deng, Lei Li, Zi-Long Li, Fu-Sheng Du and Zi-Chen Li*

Beijing National Laboratory for Molecular Sciences (BNLMS),
Key Laboratory of Polymer Chemistry & Physics of Ministry of Education,
Department of Polymer Science & Engineering,
College of Chemistry and Molecular Engineering,
Peking University, Beijing 100871, China

Experimental

Materials. Undecanoic acid (98%), 10-undecyanoic acid (96%), 10-undecenoic acid (99%), 2-bromoisobutyric acid (98%), 3-hydroxy-2,2-dimethylpropionic acid (98%), 1,6-diisocyanohexane (98%), *N, N, N',N",N"*-pentamethyldiethyltriamine (PMDETA, 99%), *trans*-cyclohexane-1,2-diol (98%) and benzyl bromide (99%), were purchased from Alfa Aesar and used as received. All other chemicals were purchased from Beijing Chem. Reagent Co. and used as received unless otherwise noted. *N, N*-dimethylformamide (DMF) was refluxed with KOH and distilled under reduced pressure. Dichloromethane (CH_2Cl_2) and triethylamine were refluxed with CaH_2 and distilled. Cuprous bromide (CuBr) was washed with acetic acid, methanol and ethyl ether and dried in vacuum. 2, 2'-Azobisisobutyronitrile (AIBN) was recrystallized twice in methanol.

Measurements. Molecular weights and polydispersity index (PDI=M_w/M_n) of polymers were measured with a gel permeation chromatography (GPC) equipped with a 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, HT4). The columns were thermostated at 35 °C and

THF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was made against standard monodisperse linear polystyrene (PSt), the obtained datum was processed on professional software. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Varian Gemini 300 spectrometer with tetramethylsilane (TMS) as the internal reference for chemical shifts (δ, ppm).

Thermal gravimetric analysis (TGA) was carried out using a Q600-SDT thermogravimetric analyzer (TA Co., Ltd.) with nitrogen purging rate set at 50 mL/min. Measurements were conducted from room temperature to 500 ^{o}C at a heating rate of 10 ^{o}C/min. Calorimetric measurement was performed using a Q100 differential scanning calorimeter (TA Co., Ltd.) with nitrogen purging rate set at 50 mL/min. The program was set to finish two cycles in a temperature range of -80 to 160 ^{o}C at a heating/cooling rate of 10 ^{o}C/min. Data of endothermic curve were acquired from the second scan data for each polymer sample. TA Universal Analysis software was applied for data acquisition and processing in the two measurements.

Synthesis of adipaldehyde [1]

A hot aqueous solution of $NaIO_4$ (1.08 M, 65 mmol, 60 mL) was added to the vigorously stirred suspension of silica gel (50 g). Afterwards a solution of *trans*-cyclohexane-1, 2-diol (5.81 g, 50 mmol) in CH_2Cl_2 (250 mL) was added drop-wise to the suspension and the reaction was stirred for 24 h at room temperature. The mixture was filtered and the silica gel was washed with CH_2Cl_2 for three times. Adipaldehyde (4.38 g, 75% yield) was obtained as a colorless oil after the evaporation of CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.65 (4H, t, J=6.9 Hz), 2.45 (4H, dt, J=1.4, 6.9 Hz), 9.76 (2H, t, J=1.4 Hz).

Synthesis of benzyl azide [2]

To a suspension of NaN_3 (2.54 g, 0.039 mol) in DMF (50 mL) was added benzyl bromide (5.13 g, 0.03 mol). The solution was stirred for 24 h at room temperature. The mixture was treated with ice water and extracted with CH_2Cl_2 for three times. The corresponding organic phase was washed thoroughly with water and dried with anhydrous $MgSO_4$. The concentrated benzyl azide with trace of DMF was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 4.35 (2H, s), 7.26-7.45 (5H, m).

General procedure for the polymerization based on Passerini reaction

Take the synthesis of **P5** as an example. In a polymerization tube containing a stir bar, undecanoic acid (0.4099 g, 2.2 mmol) was added along with $CHCl_3$ (1 mL). Then adipaldehyde (0.1141 g, 1 mmol) and 1, 6-diisocyanohexane (0.1362 g, 1 mmol) were added sequentially, and the tube was sealed under nitrogen. The reaction was conducted at 40°C for 48 h. Afterwards the solution was immediately diluted with $CHCl_3$, and precipitated into cold ethyl ether for three times. The obtained polymer was dried in vacuum and kept in a desiccator (90% yield).

Kinetics of the polymerization

Undecanoic acid (1.6396 g, 8.8 mmol), adipaldehyde (0.4564 g, 4 mmol) and 1, 6-diisocyanohexane (0.5448 g, 4 mmol) were mixed in $CDCl_3$ (4 mL) in a Schlenk flask and kept at 40°C. Samples were taken periodically with a syringe to follow the kinetics of the polymerization. The conversions of the isocyano groups were determined via ^{1}H NMR measurement with the carboxylic acid as the internal reference by comparing the integration of methylene protons adjacent to isocyano group ($-CH_2-NC$, δ 3.39 ppm) with those adjacent to carboxyl group ($-CH_2-COO-$,δ 3.24 ppm).

Postmodification by copper(I) catalyzed 1,3-dipolar cycloaddition

In a polymerization tube, the polymer, benzyl azide (2 eq, with respect to the pendant alkynyl group), CuBr (1 eq), and PMDETA (1 eq) were dissolved in a minimal amount of DMF. After three freeze-pump-thaw cycles, the tube was sealed and subjected to 30°C for 24 h. The solution was diluted with $CHCl_3$ and filtered over alkali alumina. The obtained solution was then concentrated and precipitated into cold ethyl ether for three times to recover the corresponding polymer.

Postmodification by thiol-ene coupling [3]

In a polymerization tube, the polymer, n-dodecanethiol (10 eq, with respect to the pendant alkenyl group), and AIBN (0.55 eq) were dissolved in a minimal amount of DMF. After three freeze-pump-thaw cycles, the tube was sealed and subjected to 80°C for 24 h. The solution was diluted with $CHCl_3$ and precipitated into cold petroleum ether for three times to recover the corresponding polymer.

References

1. S. Lopez, F. Fernandez-Trillo, P. Midon, L. Castedo and C. Saa, *Journal of Organic Chemistry*, 2005, **70**, 6346-6352.
2. F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *European Journal of Organic Chemistry*, 2010, 1875-1884.
3. L. M. Campos, K. L. Killops, R. Sakai, J. M. J. Paulusse, D. Damiron, E. Drockenmuller, B. W. Messmore and C. J. Hawker, *Macromolecules*, 2008, **41**, 7063-7070.

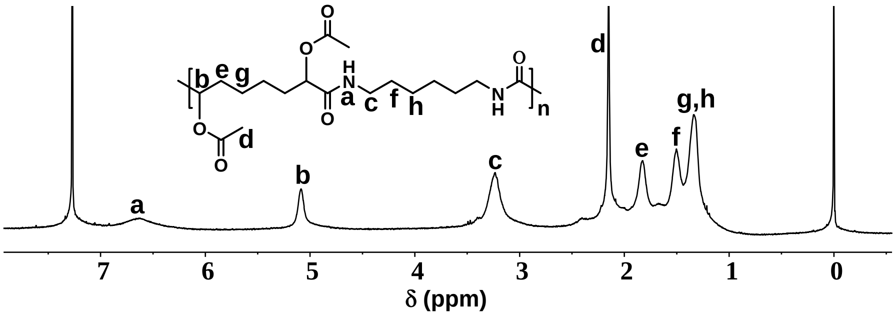

Fig. S1 ^{1}H NMR spectrum of the polyamide obtained by the reaction of 1,6-diisocyanohexane (1 M), adipaldehyde (1 M) and acetic acid (2.2 M) in CH_2Cl_2 at 30°C for 48 h. M_n=56.0 kDa, PDI=1.50, which was measured by GPC using DMF as the eluent, due to the poor solubility in THF.

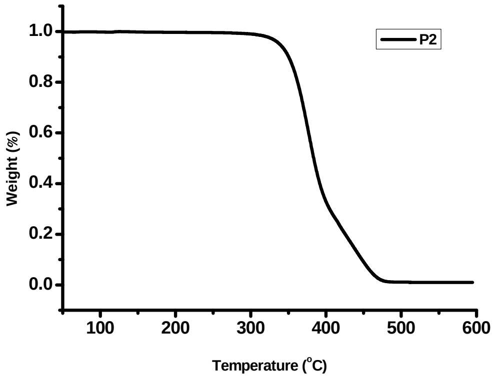

Fig. S2 TGA curve of **P2**.

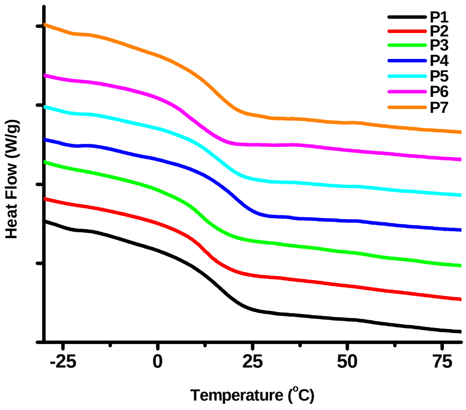

Fig. S3 DSC curves of **P1-P7**.

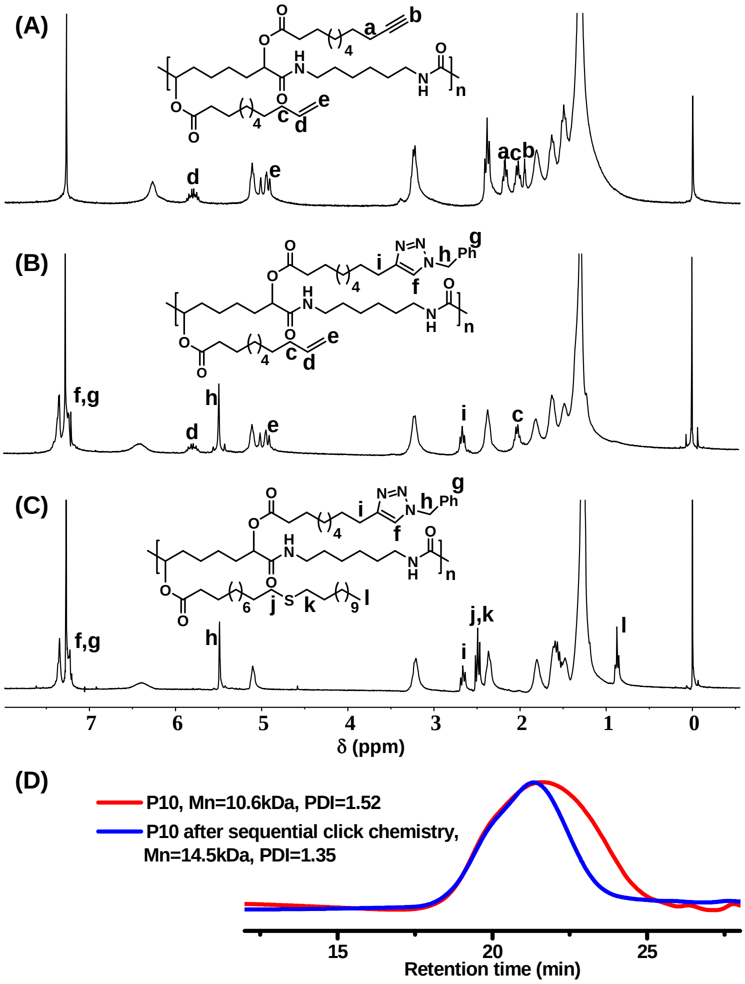

Fig. S4 ^{1}H NMR spectra of **P10** (A), the product after CuAAC cycloaddition with benzyl azide (B) and the product after subsequent thiol-ene click chemistry with n-dodicanethiol (C); corresponding GPC traces (D).

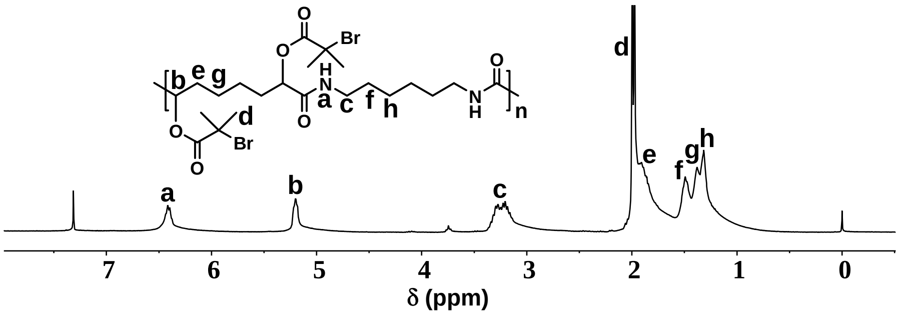

Fig. S5 ^{1}H NMR spectrum of **P11** obtained by the reaction of adipaldehyde (1 M), 1,6-diisocyanohexane (1 M) and 2-bromoisobutyric acid (2.2 M) in $CHCl_3$ at 40°C for 48 h. M_n=10.4 kDa, PDI=2.25.

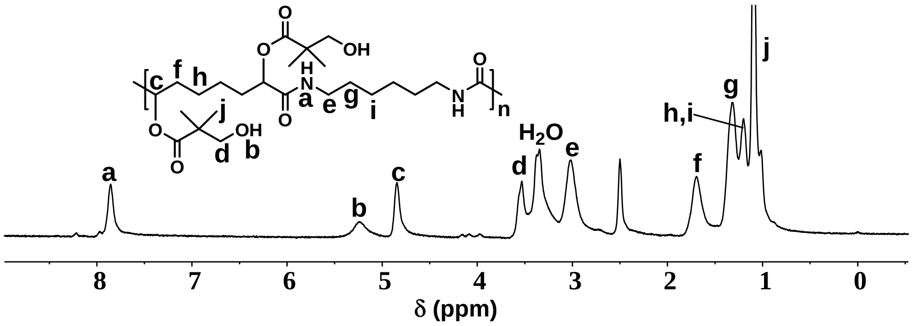

Fig. S6 ^{1}H NMR spectrum of **P12** obtained by the reaction of adipaldehyde (1 M), 1,6-diisocyanohexane (1 M) and 3-hydroxy-2,2-dimethylpropionic acid (2.2 M) in THF at 40°C for 48 h. M_n=73.7 kDa, PDI=2.21 (measured by GPC using DMF as the eluent). The reason we used DMF for GPC measurement was that the polyamide could not be redissolved in THF after precipitation, which was attributed to the formation of strong hydrogen bond between hydroxyl and amide groups.