

Supporting Information for

Highly Dispersible Silver Nanowires via Diblock Copolymer Approach for Potential Application in Transparent Conductive Composite

Zhiwei Yu,^{1,2,3,4} Shudong Lin,^{1,2,4} Guojun Liu,^{1,2,4,6} Jiwen Hu,^{*1,2,3,4} Pei Zhang,^{1,2,3,4}
Yuanyuan Tu,^{1,2,4} Hailiang Zou,^{1,2,4} and Yanlong Wei,^{1,2,3,4} and Zhenzhong Gao^{*,5}

¹*Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou, P. R.
China, 510650;*

²*Key Laboratory of Cellulose and Lignocellulosics Chemistry, Chinese Academy of
Sciences, Chinese Academy of Sciences, P. R. China, 510650;*

³*The University of the Chinese Academy of Science, Beijing, P. R. China, 100039;*

⁴*Guangdong Provincial Key Laboratory of Organic Polymer Materials for
Electronics, 510650, P. R. China;*

⁵*College of Materials and Energy, South China Agriculture University, Guangzhou,
510642, PR China;*

⁶*Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario,
Canada K7L 3N6*

S1. Materials and reagents

N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA 98%), 4,4'-di(5-nonyl)-2,2'-bipyridyl (dNbpy), diethyl ether (99%), *tert*-butyl methacrylate (*t*BA, 99%), trifluoroacetic acid (TFA, 99%), dichloromethane (DCM, 99.8%) diphenyl ether (DPE) and CuBr (98%) were all obtained from Aladdin Reagent of China. Methyl methacrylate and *tert*-butyl acrylate were purified by passage through an alumina column before they were dried over molecular sieves. DPE was dried over molecular sieves and degassed with argon for 15 min before use. CuBr was purified according to our previously reported procedures.¹ Methoxyethyl 2-bromoisobutyrate (MEBrIB) was synthesized and purified according to a previously reported

procedure.²

Synthesis of the diblock copolymer (PMMA-*b*-PtBA)

Synthesis of the macroinitiator (PMMA-Br, PM1 as an example). PMMA-Br was prepared via ATRP by using MEBriB as the initiator and CuBr/dNbpy as the catalyst. CuBr (0.035 g, 0.25 mmol), MMA (10.0 g, 100 mmol), DPE (8.0 mL) and MEBriB (0.055 g, 0.50 mmol) were added into a dry Schlenk flask. This mixture was deoxygenated with argon by performing four freeze-pump-thaw cycles. The mixture of dNbpy (0.21 g, 0.52 mmol) and DPE (2.0 mL) was then added via a degassed syringe under an argon atmosphere. The Schlenk flask was transferred into a preheated oil bath at 90 °C and stirred for 2.0 h. The reaction was stopped by freezing the flask with liquid nitrogen before introducing air inside the flask, causing the color of the reaction mixture to change from deep green to blue. The mixture was then diluted with 10 mL of CH₂Cl₂ and passed through an activated neutral alumina column to remove the catalyst. After the solvents were removed under reduced pressure via rotary evaporation at 60 °C, the residue (2.0 mL) was added into 20 mL of cold alcohol to precipitate the polymer. Finally, the obtained product (PMMA-Br) was dried under vacuum at 60 °C for 24 h, thus yielding 5.78 g of the product as a white powder in a 57.8 % yield.

Synthesis of the diblock copolymer (PMMA-*b*-PtBA, PM1-*t*BA1 as an example). A series of PMMA-*b*-PtBA diblock copolymers were prepared through the ATRP of *t*BA using PMMA-Br as the macroinitiator. In a typical synthesis, PMMA-Br (0.50 g, 62.5 μmol), toluene (2.0 mL), *t*BA (1.3 g, 0.010 mol) and CuBr (28 mg, 0.20 mmol) were added into a dry Schlenk flask. This mixture was deoxygenated with argon by performing four freeze-pump-thaw cycles. Subsequently, PMDETA (0.068 g, 0.40 mmol) was added via a degassed syringe under an argon atmosphere. The solution was stirred in order to dissolve the solid and then placed into an oil bath that was preheated at 90 °C. After 4 h, the reaction was stopped by freezing the mixture with liquid nitrogen and exposing the mixture to air. The reaction mixture was diluted with 10 mL of CH₂Cl₂ before it was passed

through a neutral alumina column to remove the copper complex. The filtrate was concentrated to 2 mL via rotary evaporation and added into 50 mL of water/methanol (1:1, v:v) to precipitate the copolymers. The crude product was redissolved into 2 mL of CH₂Cl₂ and precipitated from 50 mL of water/methanol (1:1, v:v). This process was repeated. The final precipitate was dried under vacuum overnight to generate 0.89 g of the copolymer as a white powder in a 49.5 % yield.

Synthesis of silver nanowires (AgNWs)

0.60 mL of FeCl₃ (5.0 mM) was added into a flask with 42 mL of EG and then 0.42 g of PVP and 0.30 g of AgNO₃ was added. The mixture was stirred for 30 min, and then was maintained at 160 °C for 1.5 h, before it was allowed to naturally cool to room temperature. The cooled-down solution was then centrifuged three times at 3000 rpm for 30 min to remove the solvent (EG), PVP and other impurities in the supernatant. The supernatant containing silver particles could be easily removed using a pipette. The precipitate was washed with water/ethanol (1:1) and then centrifuged (removing PVP as soon as possible). The process was repeated six times and the precipitate consisting of AgNWs was redispersed in methanol.

S2. Characterization

The X-ray diffraction patterns (XRD). XRD of AgNWs composite particles were obtained using a Siemens D/max-1200 diffractometer using Cu K α radiation from 2 θ = 30-90° with a scan step of 0.2°.

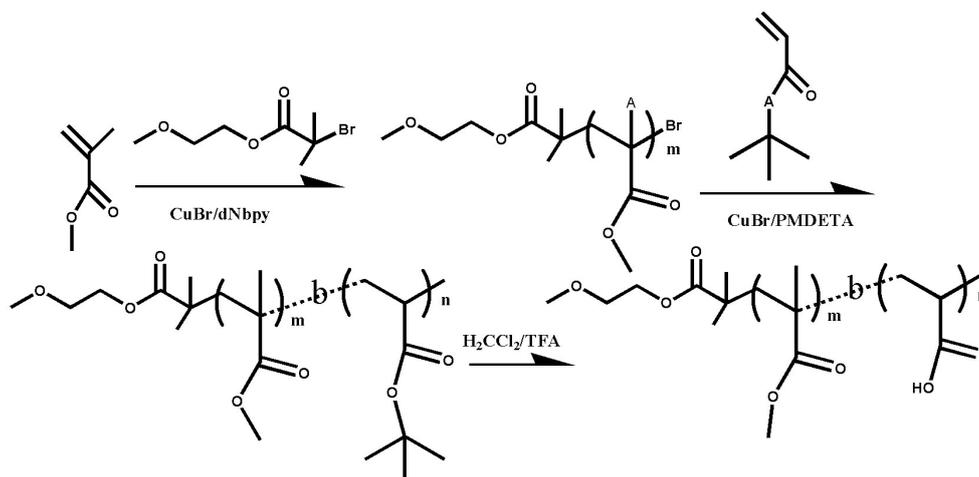
UV-visible spectroscopy. UV-visible absorption spectra were recorded between 300 and 600 nm for AgNWs and 500 and 800 nm for TCG using a Shimadzu UV-1750 PC instrument.

Nuclear magnetic resonance (NMR) spectroscopy. ¹H NMR spectra were recorded using a Bruker DMX-400 spectrometer. The samples were dissolved in deuterated chloroform (CDCl₃) or dimethyl sulfoxide (DMSO-*d*₆) at 25 °C. The concentration of each sample NMR recording was ~10 mg/mL.

Size exclusion chromatography (SEC). The number average molecular

weights (M_n) and polydispersity index (M_w/M_n) values of the polymers were determined at 30 °C using a Waters 1515 size exclusion chromatography (SEC) system equipped with a Waters 2414 refractive index (RI) detector. The SEC system was equipped with a guard column in addition to styragel HR3 and HR4 (DMF) columns, which were calibrated using mono-disperse PS standards. A DMF solution containing tetrabutylammonium bromide (0.050 mg/mL) was used as the eluent at a flow rate of 0.60 mL min⁻¹. The samples were dissolved in DMF and passed through a 0.45 μm PTFE filter before analysis.

S3. Additional results



Scheme S1. Synthetic routes for preparation of PMMA-*b*-PAA diblock copolymers.

Table S1 Synthetic conditions and molecular characteristics of the PMMA-*b*-PtBA diblock copolymers.

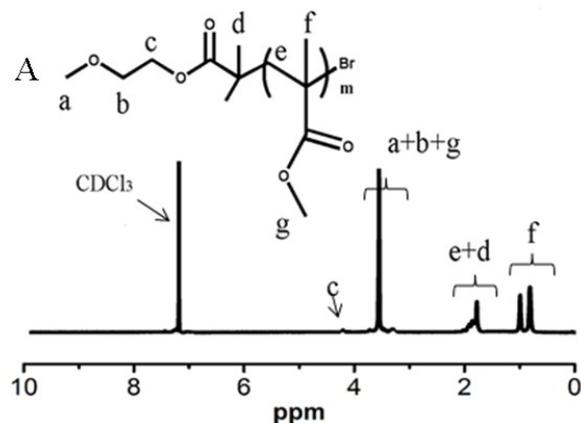
Entry	Molar feed ratio	Time (min)	M_n^a	M_n^b	m/n^a	PDI ^b	Conv. ^c (%)	f_{PtBA} %
PM1	200:1:0.5:1	120	12010	12850	120	1.05	57.8	---
PM1- <i>b</i> -PtBA1	250:1:2.5:5	300	22265	23930	120/80	1.13	49.5	40.0
PM1- <i>b</i> -PtBA2	250:1:2.5:5	480	27420	28870	120/120	1.15	52.6	50.0
PM2	400:1:0.5:1	240	23530	24670	235	1.17	58.8	---
PM2- <i>b</i> -PtBA3	200:1:2.5:5	300	30570	32370	235/55	1.19	61.7	19.0
PM2- <i>b</i> -PtBA4	250:1:2.5:5	900	40170	41230	235/130	1.25	71.5	36.1

Molar feed ratio is denoted as $[\text{M}]_0/[\text{I}]/[\text{Cu}]_0/[\text{L}]_0$.

^a The DPs of m and n were evaluated via ¹H NMR.

^b M_n and PDI were evaluated by SEC using DMF as the eluent and PS standards. $f_{\text{PtBA}}\%$ was calculated according to the weight composition of the PtBA block in the copolymer.

^c The conversion were evaluated by the finally weight.



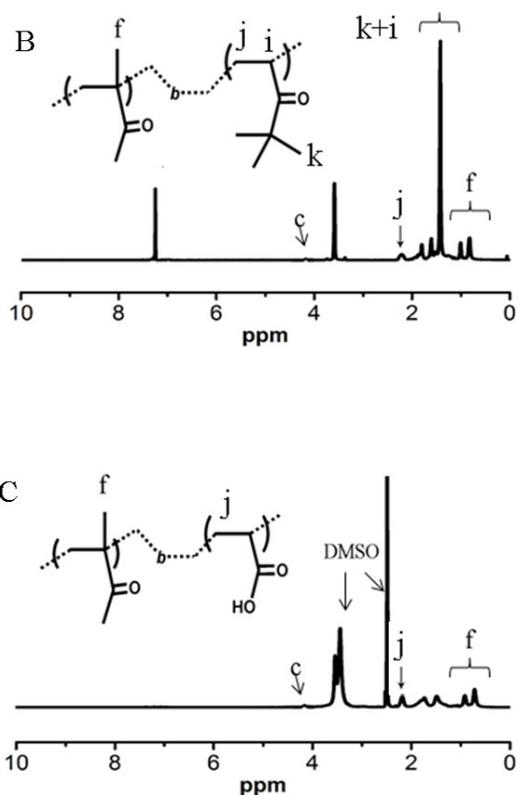


Figure S1. ¹H NMR spectra of PMMA (A), PMMA-*b*-PtBA (B) and the hydrolysis copolymers PMMA-*b*-PAA (C).

The degree of polymerization (DP) for PMMA was evaluated by comparing the intensity of peak at 4.3 ppm (c) from the methylene groups and at 1.0-0.7 ppm (f) methyl groups of the copolymer. The DP for PtBA (or PAA) was evaluated from by comparing the intensity of peak at 2.1 ppm (j) from the methylene groups and at 1.0-0.7 ppm (f) from methyl groups of the diblock copolymer. The average molecular weights (M_n) from ¹H NMR were evaluated based on the above DPs.

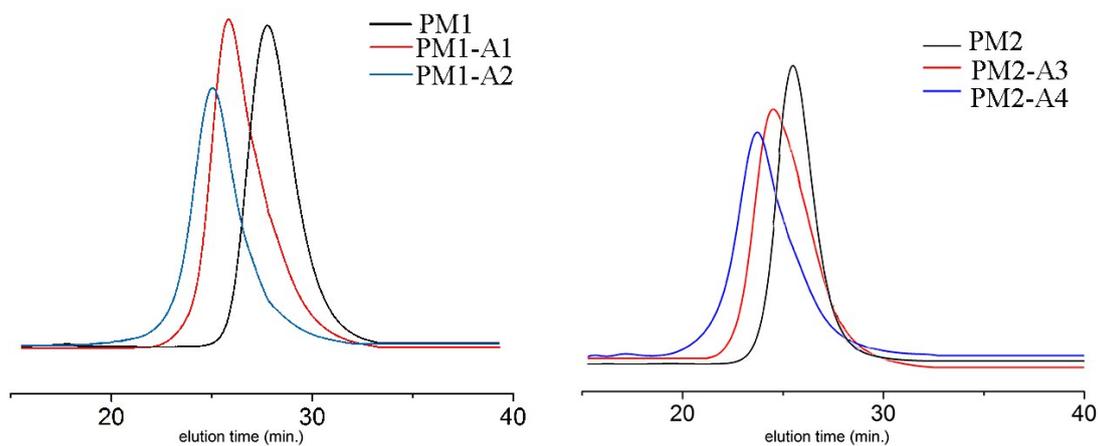


Figure S2. The SEC traces of PMMA (PM1 and PM2) and PMMA-*b*-PAA (PM1-A1, PM2-A3 and PM2-A4).

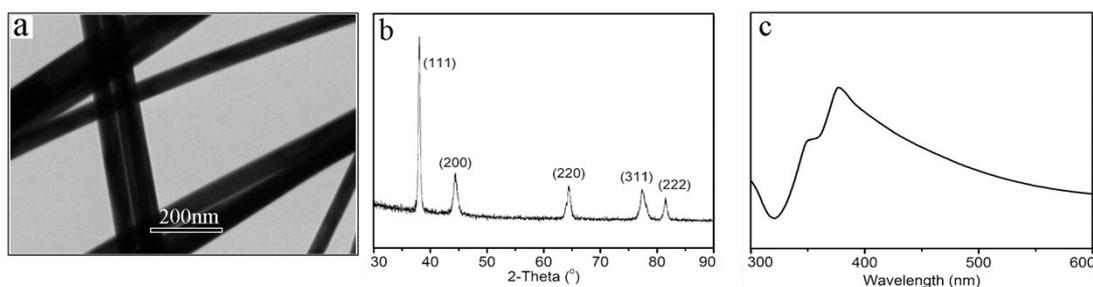


Figure S3. A TEM image (a), a XRD spectrum (b) and a UV-visible spectrum (c) of the silver nanowires prepared by the one-step method described in this article.

From Figure S3, the obtained silver nanowires had an average diameter of approximately 55 ± 5 nm and lengths ranging from 5 to 15 μm . With regard to the XRD spectrum, all of the diffraction peaks could be indexed to the (111), (200), (220), (311), and (222) planes of pure face-centered-cubic silver crystals, which was very consistent with the standard value according to JCPDS Card no. 04-0783. For the UV-visible curve, two sharp peaks at 350 and 380 nm were observed confirming the formation of high-purity AgNWs.

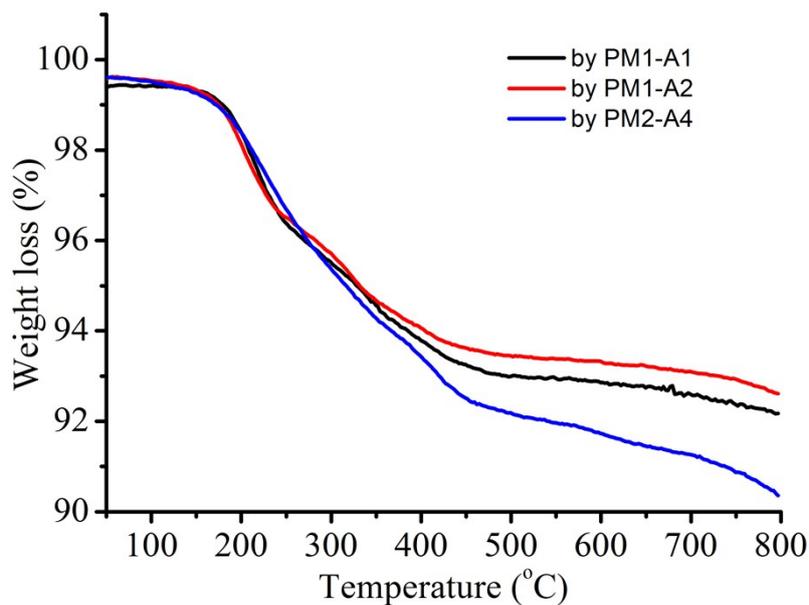


Figure S4. TG curves of AgNWs that had been modified with PM1-*b*-A1, PM2-*b*-A3 and PM2-*b*-A4, respectively.

The calculations for the thickness of PM1-A1, PM1-A2, PM2-A3, and PM2-A4 on the surfaces of the AgNWs from TGA measurements were the followings.

$$v = \frac{m1}{\rho1}$$

$$v = \pi(R^2 - r^2)l$$

$$d = R - r$$

V the volume of copolymers adsorbed onto the surface of silver nanowires.

$\rho1$ a rough density of $\sim 1.2 \text{ g/cm}^3$ for the copolymers.

$m1$ the mass of copolymers adsorbed onto the surface of silver nanowires.

R the radius of AgNWs with copolymers adsorbed.

r the radius of AgNWs without copolymers adsorbed.

l the total length per unit mass of AgNWs.

d the thickness of copolymers on the surfaces of the AgNWs.

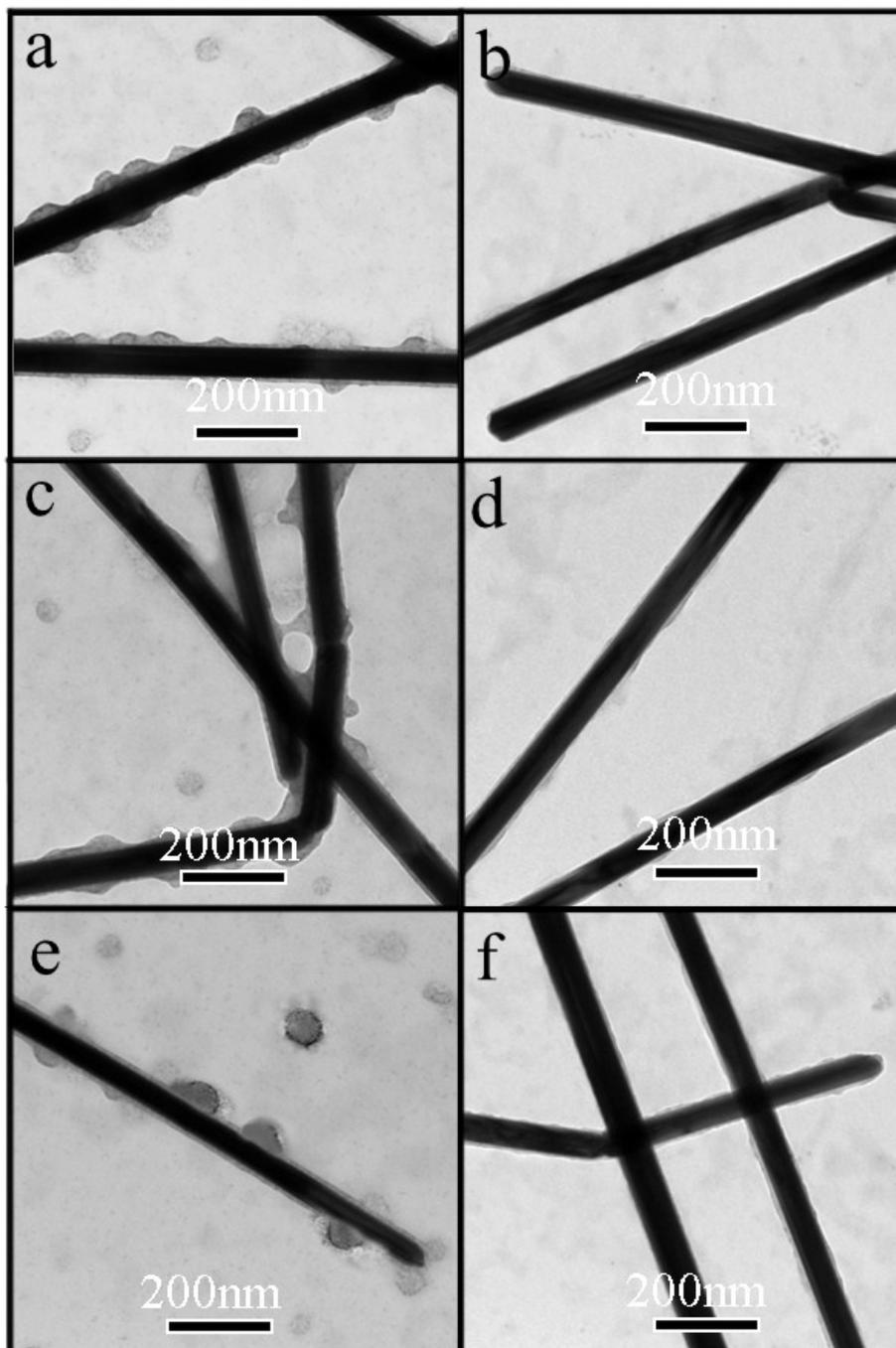


Figure S5. Typical TEM images of AgNWs during the modification process (a, c and e) and after modification with PM1-A1, PM2-A3 and PM2-A4, respectively, and subsequent purification and dispersal in chloroform (b, d and f).

S4. References

1. F. Liu, J. Hu, G. Liu, C. Hou, S. Lin, H. Zou, G. Zhang, J. Sun, H. Luo and Y. Tu, *Macromolecules*, 2013, **46**, 2646-2657.

2. H. Zou, S. Lin, Y. Tu, G. Liu, J. Hu, F. Li, L. Miao, G. Zhang, H. Luo and F. Liu, *Journal of Materials Chemistry A*, 2013, **1**, 11246-11260.