

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

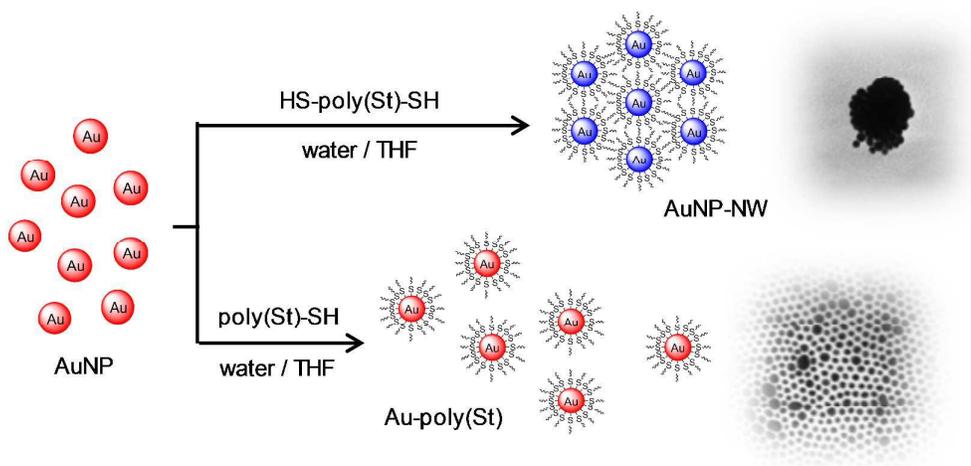
Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Table of contents

Synthesis and optical properties of gold nanoparticle networks cross-linked with chain-length-controlled polymers

Emi Sugata and Seiya Kobatake\*

We synthesized gold nanoparticle networks by a cross-linking of gold nanoparticles with chain-length-controlled polymers having SH groups at both termini.



## ARTICLE

# Synthesis and optical properties of gold nanoparticle networks cross-linked with chain-length-controlled polymers

Cite this: DOI: 10.1039/x0xx00000x

Emi Sugata<sup>a</sup> and Seiya Kobatake<sup>a,\*</sup>

Received 00th January 2015,

Accepted 00th January 2015

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

In order to control the absorption band ascribed to localized surface plasmon resonance (LSPR) of gold nanoparticles (AuNPs) in solution, we newly synthesized a gold nanoparticle network (AuNP-NW) cross-linked with chain-length-controlled polymers. The chain-length-controlled polystyrene (poly(St)) having dithiobenzoate groups at both termini was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization with a novel RAFT agent which enables the precise control of the chain length of polymers. Both terminal groups of poly(St) were reduced from the dithiobenzoate groups to thiol groups. AuNP-NW was prepared by the self-organized cross-linking of individual AuNPs with poly(St) having the thiol groups at both termini. Transmission electron microscopic images and absorption spectra of AuNP-NW indicate the presence of the network structures. The absorption band due to LSPR of AuNP-NW could be changed by the precise control of the distance between AuNPs.

## Introduction

Gold nanoparticles (AuNPs) show different properties compared to bulk state. Localized surface plasmon resonance (LSPR) is one of their representative characters. AuNPs have the absorption band in the visible region ascribed to LSPR and the maximum wavelength in the LSPR band depends on the particle size, the particle shape, the distance between particles, and the environment around the particles.<sup>1-5</sup> From this specific property, there are various researches on AuNPs for application to sensing materials and materials used in medical field.<sup>6-8</sup>

The distance between AuNPs supported on the solid substrate affects to the LSPR band. As decreasing the distance between the particles, the absorption band due to LSPR is shifted to the long wavelength side.<sup>9</sup> The change of LSPR induced by the interaction between AuNPs can be observed even when the distance between the particles is changed in the order of nanometers. Moreover, the two-photon photopolymerization using LSPR at the gap between AuNPs on the solid substrate has also been reported.<sup>10,11</sup> The control of the distance between AuNPs is strongly required not only on solid substrates but also in solutions to expand a possibility in application of this phenomenon.

To control the distance between AuNPs in solutions, the approaches to cross-link the nanoparticles using ion bonding,<sup>12</sup> hydrogen bonding,<sup>13</sup> alkane dithiol,<sup>14</sup> entanglement of polymer chains<sup>15</sup> and photoresponsive molecules<sup>16,17</sup> have been so far reported. However, in all case, the precise control of the

distance between the nanoparticles has never been accomplished. In this work, we newly synthesized a gold nanoparticle network (AuNP-NW) by the cross-linking of AuNPs using polystyrene (poly(St)) with well-controlled chain length having thiol groups at both termini. The precise control of the distance between the nanoparticles has been performed and their optical properties have been evaluated. The polymers used for the cross-linking have been synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization, which can easily control the chain length.

## Experimental

### General

Solvent used were spectroscopic grade and purified by distillation before use. <sup>1</sup>H NMR (300 MHz) spectra were recorded on a Bruker AV-300N spectrometer with tetramethylsilane as the internal standard. Mass spectra were obtained on a JEOL JMS-700/700S mass spectrometer. The number- and weight-average molecular weight ( $M_n$  and  $M_w$ , respectively) and polydispersity ( $M_w/M_n$ ) were determined by gel-permeation chromatography (GPC) calibrated by standard poly(St)s. GPC was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns at 40 °C using tetrahydrofuran (THF) as the eluant. Absorption spectra were measured with a JASCO V-560 absorption spectrometer. Transmission electron microscopy (TEM; Hitachi H-7000) was measured at an accelerating voltage of 75 kV. TEM samples

were prepared by dropping a solution on a carbon-coated copper grid and dried in air.

### Materials

Chemicals used for synthesis were commercially available and used without further purification. 1,1'-Azobis(cyclohexane-1-carbonitrile) (ACN) was recrystallized from methanol. Styrene (St) was purified by distillation under reduced pressure before use. 1,4-Bis(thiobenzoylthiomethyl)benzene (BTTMB) was synthesized according to the method described in literature.<sup>18</sup>

### Synthesis of 1,4-bis(1-thiobenzoylthioethyl)benzene (BTTEB)

Bromobenzene (1.00 mL, 9.49 mmol) in dry THF (10 mL) was slowly added into a flask containing magnesium turnings (0.230 g, 9.66 mmol) and dry THF (8 mL) at 0 °C under argon atmosphere, and the mixture was stirred for 1 h at room temperature. Carbon disulfide (0.575 mL, 9.52 mmol) was slowly added to the THF solution of the Grignard reagent at 0 °C and stirred for 30 min at room temperature. To the reaction mixture was slowly added a solution of 1,4-bis(1-bromoethyl)benzene<sup>19</sup> (1.25 g, 4.27 mmol) in dry THF (10 mL) at 0 °C, refluxed for 17 h. The reaction mixture was quenched with water and extracted with diethyl ether. The organic layer was washed with water and saturated brine, dried over MgSO<sub>4</sub>, filtrated, and concentrated in vacuo. The crude product was purified by silica gel column chromatography using *n*-hexane as the eluant. The product was further purified by recycle high performance liquid chromatography (HPLC; JAI LC-908) using JAI Gel IH and 2H columns with chloroform as the eluant, and HPLC (Hitachi L-7150 pump system) using Kanto Chemical Mightysil Si 60 column with *n*-hexane/ethyl acetate (98:2) as the eluant to give 0.540 g of BTTEB in 28.8% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.80 (d, *J* = 7.1 Hz, 6H), 5.25 (q, *J* = 7.1 Hz, 2H), 7.3–7.4 (m, 4H), 7.42 (s, 4H), 7.4–7.6 (m, 2H), 7.9–8.0 (m, 4H). HR-MS (ESI<sup>+</sup>): *m/z* = 438.0610 (M<sup>+</sup>). Calcd. for C<sub>24</sub>H<sub>22</sub>S<sub>4</sub>: 438.0604.

### Synthesis of poly(St) with thiol groups at both termini

RAFT polymerization was performed into a glass tube. Appropriate amounts of styrene (St), ACN, and RAFT agent (BTTMB or BTTEB) were put in a glass tube. The tube was degassed by several freeze-pump-thaw cycles and sealed off under vacuum. After polymerization for a prescribed time at 70 °C, the polymerization mixture was poured into methanol to precipitate the resulting polymer. The polymer was purified by reprecipitation and then dried in vacuo. The resulting poly(St) having dithiobenzoate groups at both termini was stirred with sodium borohydride (NaBH<sub>4</sub>) in THF/water.<sup>20</sup> The reaction mixture was poured into methanol to precipitate the resulting poly(St) having thiol groups at both termini (HS-poly(St)-SH). The resulting polymer was dried in vacuo.

### Synthesis of AuNP-NW

AuNPs were synthesized by citrate reduction as follows. Appropriate amounts of trisodium citrate in ultra-pure water (105 mL) was quickly added to the boiling solution of hydrogen

tetrachloroaurate(III) tetrahydrate (88 mg, 0.21mmol) in ultra-pure water (210 mL), refluxed for 30 min, and then cooled to room temperature. HS-poly(St)-SH (0.6 μmol) dissolved in THF (20 mL) was dropwise added to the AuNP solution (50 mL) and stirred for 20 min at room temperature. AuNP-NW was transferred into the organic phase when appropriate amounts of ethyl acetate were added to the reaction mixture. The organic phase was collected and dried in vacuo. The resulting solid was dissolved to diethyl ether/THF, centrifuged at 6000 rpm for 15 min, and removed supernatant solution. The color of supernatant solution was become from red to colorless as this cycle was repeated. After repeating this cycle four times, the resulting precipitate was dried in vacuo.

## Results and Discussion

### Synthesis of polymer with well-controlled chain length having thiol groups at both termini

Poly(St) with well-controlled chain length having thiol groups at both termini was synthesized by RAFT polymerization. RAFT agents used in this work are shown in Chart 1. First, we performed the polymerization using BTTMB as listed in Table 1. The conversion increased with the polymerization time. *M<sub>n</sub>* of the resultant polymers also increased with the polymerization time. This indicates that the polymerization proceeded as controlled/living radical polymerization. However, *M<sub>w</sub>*/*M<sub>n</sub>* of the polymers is slightly larger than that of usual RAFT polymerization (*M<sub>w</sub>*/*M<sub>n</sub>* = 1.05~1.10)<sup>21</sup>. Figure 1a shows <sup>1</sup>H NMR spectrum of the polymer obtained with 10.9% conversion. The broad peaks at 6.0-7.5 ppm are assigned to the aromatic protons of the St unit in the polymer. The broad peaks at 1.0-2.5 ppm are assigned to the methylene and methine protons of the polymer main chain. The small peaks at 4.6-5.0 ppm, expressed as *b* in Figure 1a, are assignable to the methine protons bound to the dithiobenzoate end group.<sup>20</sup> The small peaks at 7.75-7.90 ppm, expressed as *a* in Figure 1a, are assignable to the *ortho*-aromatic protons in the dithiobenzoate group. The peak intensity of *a* and *b* was determined to be 2 : 1. However, the peaks at 4.4-4.6 and 7.95-8.05 ppm, expressed as *b'* and *a'* in Figure 1a, respectively, are considered to be ascribed to an irregular structure. Their intensity ratio was determined to be 1 : 1. Because these peaks are similar to the chemical shifts of methylene and *ortho*-aromatic protons in BTTMB, we considered that the polymer chain was propagated to the one side, expressed as poly(St)-II in Chart 2. Therefore, poly(St) synthesized using BTTMB as the RAFT agent is the mixture of poly(St)-I and poly(St)-II structures shown in Chart 2. The peak intensity of *a'* and *b'* decreased with the polymerization time. This indicates that the structure of poly(St)-II changed to that of poly(St)-I by propagating the polymer chain at both sides. Table 1 also shows the contents of poly(St)-I and poly(St)-II structures. When the polymerization was carried out over 48 h, the peaks of *a'* and *b'* disappeared and all structures became poly(St)-I. The presence of poly(St)-II at the early state of the polymerization is ascribed to the large

bond-dissociation energy of C-S bonds. The carbon radical produced by the addition of the poly(St) radical to BTTMB can dissociate whether methylene-sulfur bond or methine-sulfur bond. The bond-dissociation energy of the C-S bond generated by the addition of the poly(St) radical to the RAFT agent is smaller than that of the original methylene-sulfur bond in the RAFT agent. Therefore, the dissociation of the original C-S bond is prevented.

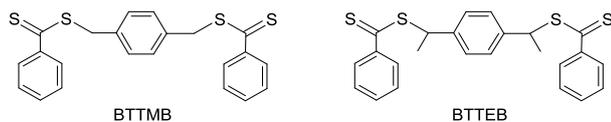


Chart 1. Structure of chain transfer agents.

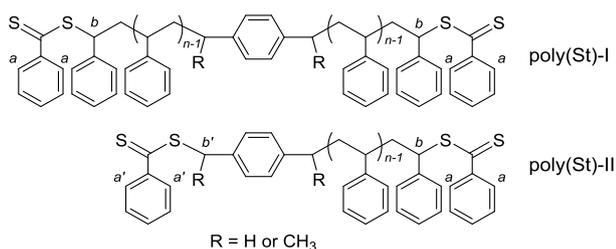


Chart 2. Structure of poly(St) synthesized by RAFT polymerization using BTTMB or BTTEB as the RAFT agent.

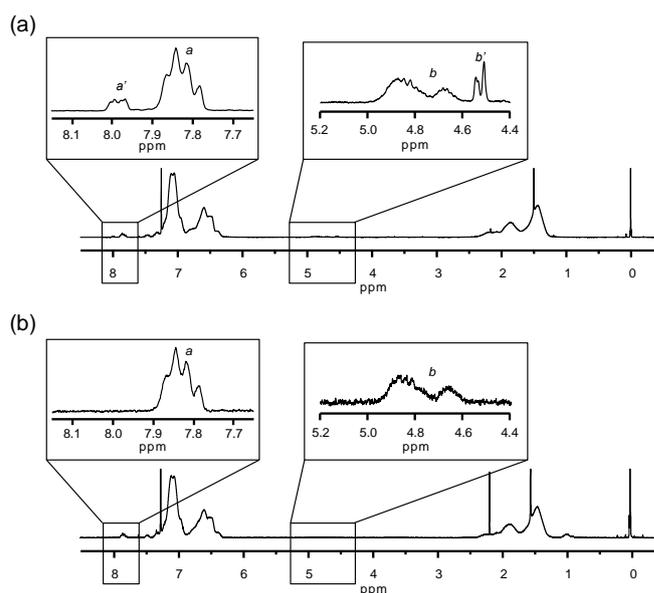


Figure 1.  $^1\text{H}$  NMR spectra of poly(St) synthesized with BTTMB (a) and BTTEB (b) for 18 h at 70 °C, respectively.

To obtain poly(St) having the structure of poly(St)-I at the early stage of the polymerization, the bond-dissociation energy of the original C-S bond in the RAFT agent is required to be the same or smaller than that of the bond generated by the addition of the poly(St) radical to a RAFT agent. Therefore, we synthesized a new RAFT agent, 1,4-bis(1-thiobenzoylthioethyl)benzene (BTTEB).

The polymerization results using BTTEB as the RAFT agent are also summarized in Table 1. The conversion increased with the polymerization time.  $M_n$  of the resultant polymers also

Table 1. Characterization of poly(St) synthesized by RAFT polymerization.<sup>a)</sup>

RAFT agent	Time / h	Conversion / %	poly(St)-I / %	poly(St)-II / %	$M_n$ (GPC)	$M_w/M_n$ (GPC)
BTTMB (R = H)	18	10.9	76.6	23.4	5700	1.21
	24	15.3	84.6	15.4	7400	1.25
	30	19.1	89.7	10.3	9500	1.25
	36	23.3	93.3	6.7	10900	1.25
	42	26.4	93.8	6.2	13000	1.24
	48	30.5	100	0	14500	1.28
	54	32.8	100	0	16200	1.30
	60	35.8	100	0	17400	1.29
BTTEB (R = CH <sub>3</sub> )	12	7.0	100	0	3100	1.11
	18	12.5	100	0	6200	1.08
	24	16.9	100	0	8500	1.10
	30	21.1	100	0	10100	1.11
	36	24.9	100	0	12700	1.12
	42	28.4	100	0	13400	1.16
	48	29.3	100	0	14000	1.17
	54	34.9	100	0	16400	1.17
	60	37.5	100	0	19000	1.20
	42	28.4	100	0	13400	1.16

a) [St] = 8.7 M, [RAFT agent] = 20 mM, [ACN] = 7 mM, 70 °C

increased with the polymerization time. These results are

similar to those using BTTMB as the RAFT agent. As expected,  $M_w/M_n$  of the polymers is smaller than that using BTMB ( $M_w/M_n \sim 1.1$ ). Figure 1b also shows  $^1\text{H}$  NMR spectrum of the polymer obtained with 12.5% conversion. The peaks of  $a'$  and  $b'$  disappeared as compared with the spectrum in Figure 1a. These results indicate that the polymer chain length can be well controlled by using BTTEB.

Next, dithiobenzoate groups of poly(St) at both termini were reduced to thiol groups using  $\text{NaBH}_4$  in THF/water. The results were summarized in Table 2. The polydispersity of polymers before and after the reduction was similar. This indicates that the polymer chain length is precisely constant even after the reduction from the dithiobenzoate groups to thiol groups.

**Table 2.** Characterization of poly(St) synthesized by reduction reaction in the end groups.

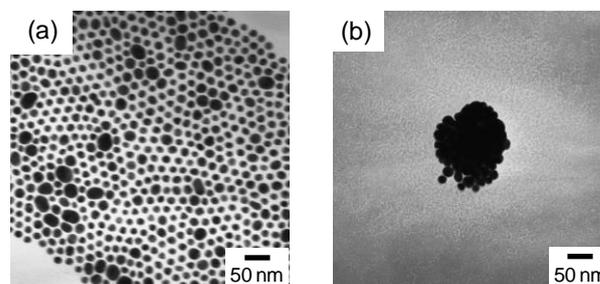
Before reduction		After reduction	
$M_n$ (GPC)	$M_w/M_n$ (GPC)	$M_n$ (GPC)	$M_w/M_n$ (GPC)
3100	1.11	3100	1.10
6200	1.08	5700	1.11
8500	1.10	8200	1.12
10100	1.11	9500	1.13
12700	1.12	12300	1.15
13400	1.16	13100	1.15
14000	1.17	13400	1.18
16400	1.17	15600	1.19
19000	1.20	18300	1.21

### Synthesis of gold nanoparticle networks

The gold nanoparticle networks (AuNP-NW) were synthesized by stirring the poly(St) having thiol groups at both

termini and individual AuNPs prepared by citrate reduction in water/THF, as shown in Scheme 1. As the control, single AuNP covered with poly(St) (Au-poly(St)) was synthesized by the same method using poly(St) having thiol group at only one side. Both samples of AuNP-NW and Au-poly(St) were dried under vacuum and dissolved in toluene. After 4 h, the supernatant solution of both samples was used for absorption spectra and TEM measurements.

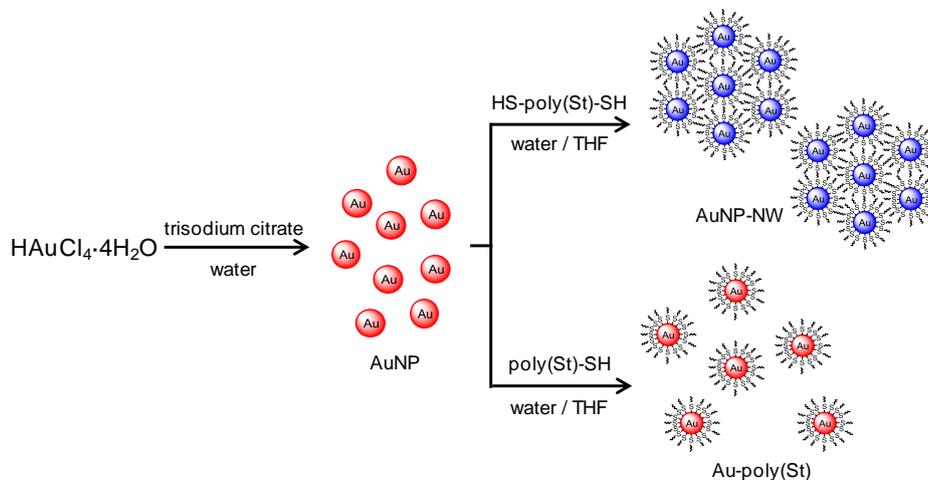
Figure 2 shows the TEM images of Au-poly(St) and AuNP-NW. Only a gold part can be seen as black image and the polymer segments cannot be seen in the TEM image.<sup>22</sup> Au-poly(St) has the average particle size ( $d$ ) of 17.9 nm and size distribution ( $\sigma/d$ ) of 33%. Au-poly(St)s are well-dispersed without agglomeration on the TEM grid, and there is no overlap of the nanoparticles. On the other hand, in the case of the AuNP-NW, the three-dimensionally overlapped structure of the nanoparticles was observed as shown in Figure 2b. This result indicates that the network was successfully obtained using poly(St) having thiol groups at both termini. Moreover, AuNP-NWs having the different Au particle size and the different chain length of poly(St) were also prepared.



**Figure 2.** TEM images of Au-poly(St) (a) and AuNP-NW (b). The diameter of gold nanoparticle is about 17.9 nm.  $M_n$  of poly(St) is 6300 (a) and 3100 (b).

### Optical properties of AuNP-NW

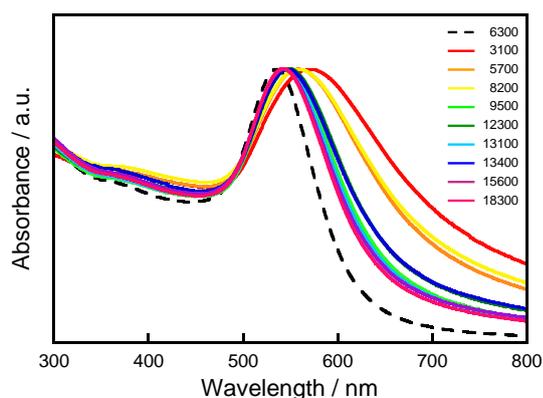
Figure 3 shows the absorption spectra of Au-poly(St) and AuNP-NW prepared using poly(St) with different chain length



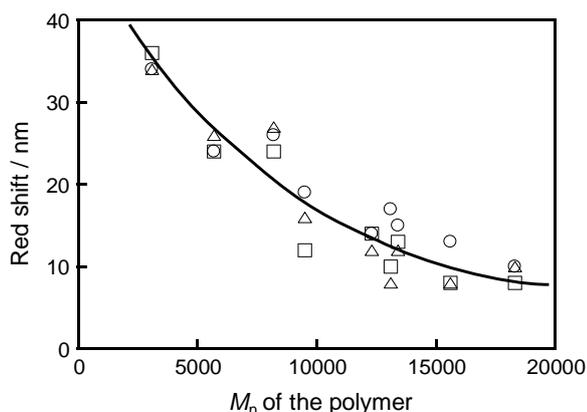
**Scheme 1.** Synthetic routes of AuNP-NW and Au-poly(St) covered with poly(St).

in toluene. The maximum wavelength in the LSPR band depends on the particle size, the particle shape, the interparticle distance, and the environment around the particles.<sup>1-5</sup> The absorption maxima of AuNP-NW were red-shifted in comparison to Au-poly(St), and the degree of the red shift depended on the chain length of the polymer. This indicates that the dependence is due to the difference in the interparticle distance.

Figure 4 shows the relationship between  $M_n$  and the degree of the red shift. As decreasing the chain length, the degree of the red shift became large. In spite of using AuNPs having different particle size ( $d = 18\sim 30$  nm), the similar results were obtained. These results indicate that the red-shift does not depend on the size of AuNP in the range of 18–30 nm in diameter and the LSPR band can be changed depending on the interparticle distance between AuNPs in the network in solution.



**Figure 3.** Absorption spectra of Au-poly(St) (dashed line) and AuNP-NW (solid line) in toluene. The diameter of gold nanoparticle is about 17.9 nm.  $M_n$  of poly(St) used for AuNP-NW is shown in the figure.



**Figure 4.** The relationship between  $M_n$  and red shift of the LSPR band of AuNP-NW in toluene. The diameters of gold nanoparticle are about 29.7 nm ( $\circ$ ), 18.9 nm ( $\Delta$ ), and 17.9 nm ( $\square$ ).

## Conclusion

In conclusion, we synthesized a new RAFT agent (BTTEB) which enables the polymerization of St at both termini of the agent at the early stage of the polymerization. The chain-length-

controlled poly(St) was prepared by using BTTEB. The polydispersity of the polymers synthesized using BTTEB becomes smaller than that of polymers synthesized using BTTMB. Moreover, we newly synthesized the gold nanoparticle networks by the cross-linking of individual gold nanoparticles using above mentioned polymers. The structure of the gold nanoparticle networks was confirmed by the TEM measurement. Moreover, the absorption band due to LSPR of the gold nanoparticle networks was different from that of individual nanoparticles in solution. The absorption maximum of the LSPR band was red-shifted as decreasing the chain length of polymers. Thus, we could control the LSPR band in solution.

## Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (C) (No. 24550161) from the Japan Society for the Promotion of Science (JSPS) and a Grant-in-Aid for Scientific Research on Innovative Areas "Photosynergetics" (No. 26107013) from The Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

## Notes and references

<sup>a</sup> Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan. E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp; Tel & Fax: +81-6-6605-2797

<sup>†</sup> Electronic Supplementary Information (ESI) available: <sup>1</sup>H NMR spectrum of BTTEB and GPC curves of polymers. See DOI: 10.1039/C5RA000000/

- P. N. Njoki, I.-I. S. Lim, D. Mott, H.-Y. Park, B. Khan, S. Mishra, R. Sujakumar, J. Luo and C.-J. Zhong, *J. Phys. Chem. C*, 2007, **111**, 14664.
- C. A. Mirkin, R. L. Letsinger, R. C. Mucic and J. J. Storhoff, *Nature*, 1996, **382**, 607.
- H. Ahn, A. Chandekar, B. Kang, C. Sung and J. E. Whitten, *Chem. Mater.*, 2004, **16**, 3274.
- T. Uwada, R. Toyota, H. Masuhara and T. Asahi, *J. Phys. Chem. C*, 2007, **111**, 1549.
- M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293.
- N. L. Rosi and C. A. Mirkin, *Chem. Rev.*, 2005, **105**, 1547.
- M. E. Stewart, C. R. Anderton, L. B. Thompson, J. Maria, S. K. Gray, J. A. Rogers and R. G. Nuzzo, *Chem. Rev.*, 2008, **108**, 494.
- A. M. Gobin, M. H. Lee, N. J. Halas, W. D. James, R. A. Drezek and J. L. West, *Nano Lett.*, 2007, **7**, 1929.
- W. Huang, W. Qian, P. K. Jain and M. A. El-Sayed, *Nano Lett.*, 2007, **7**, 3227.
- K. Ueno, S. Juodkazis, V. Mizeikis, K. Sasaki and H. Misawa, *Adv. Mater.*, 2008, **20**, 26.
- K. Ueno, S. Juodkazis, T. Shibuya, Y. Yokota, V. Mizeikis, K. Sasaki and H. Misawa, *J. Am. Chem. Soc.*, 2008, **130**, 6928.
- M. Sethi and M. R. Knecht, *Langmuir*, 2010, **26**, 9860.
- M. Chandra, A. Dowgiallo and K. L. Knappenberger, *J. Am. Chem. Soc.*, 2010, **132**, 15782.
- I. Hussain, Z. Wang, A. I. Cooper and M. Brust, *Langmuir*, 2006, **22**, 2938.

## ARTICLE

- 15 M. Q. Zhu, L. Q. Wang, G. J. Exarhos and A. D. Q. Li, *J. Am. Chem. Soc.*, 2004, **126**, 2656.
- 16 Y. Wei, S. Han, J. Kim, S. Soh and B. A. Grzybowski, *J. Am. Chem. Soc.*, 2010, **132**, 11018.
- 17 Y. Shiraishi, E. Shirakawa, K. Tanaka, H. Sakamoto, S. Ichikawa and T. Hirai, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7554.
- 18 D. L. Patton, M. Mullings, T. Fulghum and R. C. Advincula, *Macromolecules*, 2005, **38**, 8597.
- 19 C. Zhang, J. Ling and Q. Wang, *Macromolecules*, 2011, **44**, 8739
- 20 H. Nishi and S. Kobatake, *Chem. Lett.*, 2008, **37**, 630.
- 21 G. Moad, E. Rizzardo and S. H. Thang, *Chem. Asian J.* 2013, **8**, 1634.
- 22 H. Nishi and S. Kobatake, *Dyes Pigm.*, 2012, **92**, 847.