Preparation of polymeric vesicles and their application for catalyst carriers

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Abstract. The catalytic property of the silver nanoparticles (AgNPs) decorated polymeric vesicles were studied. Cross-linked polymeric vesicles were used as the templates for AgNPs deposition. The effect of the degree of polymerization (DP) of the hydrophilic block mPEG was evaluated and good shaped vesicles could be obtained with DP of mPEG at 43. Monomer molar ratio of DIPEMA/GlyMA had big effect on particle morphology, and pure polymeric vesicles could be produced when monomer molar ratio was equal to or higher than 7:3. The catalytic study indicated good catalytic property of the AgNPs decorated vesicles.

Keywords: polymeric vesicles; reversible addition-fragmentation chain transfer (RAFT); silver nanoparticles; catalytic property.

1. Introduction

Nanoparticles could be widely used in drug delivery, nanoreactors, imaging, et al.,[1,2] and among the nanopartciles, polymeric vesicles have attracted more and more attention for the existing of hollow cavity. The polymeric vesicles could be applied as carriers for metal deposition to prepare organic/inorganic composites, and polymeric vesicles with high stability by cross-linking of the vesicle membrane are more attractive for the good stability in different kinds of environments.[3,4]

Polymeric vesicles decorated with silver nanoparticles (AgNPs) have been reported to study the catalytic property. The photoinitiated[5] and enzyme catalysis-induced[6] reversible addition-fragmentation chain transfer (RAFT) polymerization method were reported to prepare glycidyl methacrylate (GlyMA) based vesicles, and AgNPs were deposited on the vesicles via the reduction of AgNO3 using sodium borohydride (NaBH4) or polyvinylpyrrolidone (PVP), after cross-linking of the vesicle membrane, and good catalytic property was found by the reduction of methyl blue using NaBH4. And Tan et al.[7] reported the good catalytic property of the prepared AgNPs/poly(acrylic acid)-block-polystyrene composite vesicles.

Herein, poly(ethylene oxide)-b-p[2-(diisopropylamino)ethyl methacrylate-co-glycidyl methacrylate](mPEG-b-P(DIPEMA-co-GlyMA)) vesicles were prepared, and the membrane of the produced vesicles could be cross-linked by using ethylene diamine (EDA), as reported previously.[8] And then the cross-linked vesicles were used as the templates for AgNPs deposition. The effect of the DP of the hydrophilic block mPEG and the molar ratio of the monomers were evaluated, and the catalytic performance of the AgNPs decorated vesicles were studied.

2. Experiment

2.1 Materials

The α-methoxy-ω-hydroxypoly(ethylene oxide) (mPEG) (DP of 23, 43 and 113), 4-(dimethylamino)pyridine (DMAP), 4-(4-Cyanopentanoic acid) dithiobenzoate (CPADB), dicyclohexylcarbodiimide (DCC) and Polyvinylpyrrolidone (PVP) were purchased from Aladdin. 2-(diisopropylamino)-ethyl methacrylate (DIPEMA) and glycidyl methacrylate (GlyMA) were purchased from Aladdin and purified by passing through the Al_2O_3 column to remove the inhibitor. Potassium persulfate (KPS) was purchased from United Initiators (Shanghai) Co., Ltd., and sodium bisulfite (SBS) was purchased from Damao Chemical Reagent Factory. Silver nitrate ($AgNO_3$) was purchased from Tianjin Tiangan Chemical Technology Development Co., Ltd. and used as received.

2.2 Preparation of of AgNPs decorated vesicles

The preparation of the macro-chain transfer agent (macro-CTA) poly(ethylene oxide)-4-(4-Cyanopentanoic acid) dithiobenzoate (mPEG-CPADB) and the cross-linked polymeric vesicles was done according to the previously reported RAFT dispersion polymerization method,[8] and the cross-linked vesicles were used as templates to deposite AgNPs. Followed was an example: firstly the cross-linked vesicles were dispersed in ethanol/water solution (solid content 0.003 g/mL, 6 mL), and AgNO3 (0.006 g) was added and stirred at 24 ˚C for 30 min in the dark, and then 0.006 g PVP was added to the solution. The reaction was proceeded for 24 h at 50˚C, and then the samples were purified via centrifugation-redispersion cycles for evaluation.

2.3 Characterization

Transmission electron microscopy (TEM, JEM-2100 Plus electron microscope) was used to evaluate the morphology of the produced particles, and the samples were stained with phosphotungstic acid before observations. Gel permeation chromatograph (GPC, Waters 2695) was used for the the molecular weight analysis, and 1H NMR spectra (Bruker DMX500 spectrometer) and Fourier transform infrared spectroscopy (FTIR, PerkinElmer Frontier) were done to check the chemistry structure of the polymers. The average diameter of the particles were tested on a commercial dynamic light scattering spectrometer (DLS, PPS Z3000). UV-vis (TU-1901) was applied to track the reduction reaction catalized by the AgNPs decorated vesicles.

3. Results and discussion

3.1 Preparation of the polymeric vesicle templates

For the preparation of the polymeric vesicles, mPEG-CPADB was used as the macro-CTAs. The DP of the hydrophilic block mPEG is one of the main factors that affects the particle morphology[9], mPEG with DP of 23, 43 and 113 were used for the study. GPC (Figure 1 (a)) and 1H NMR (Figure 1 (b)) were done to analyze the three synthesized macro-CTAs. Mn of mPEG23-CPADB was 1215 with Mw/Mn=1.20, while mPEG43-CPADB showed Mn=2693 with Mw/Mn=1.17, and mPEG113-CPADB showed Mn=6270 with Mw/Mn=1.16, and all of them showed relatively narrow Mw/Mn. 1H NMR spectroscopy results indicated the esterification was successful based on the integral values of signals of ester methylene protons at δ=4.3(f). The average end-functionality of mPEG23-CPADB, mPEG43-CPADB and mPEG113-CPADB was 86.2%, 98.3% and 96.0% respectively by calculating the integral ratio of methoxy protons of PEG at δ= 3.4 (h) and aromatic protons at δ=7.3-8.0 (a, b, c), as shown in Figure 1 (b).

And the three macro-CTAs produced above were used as the macro-CTA for the vesicle preparation, and Figure 2 showed the TEM images of the produced nanoparticles. Pure vesicles could only be obtained by using $mPEG_{43}$-CPADB as the macro-CTA, while $mPEG_{113}$-CPADB can only produce solid spherical particles and $mPEG_{23}$-CPADB produced mixtures of solid spherical particles and vesicles, and delamination was observed for the solution that produced by using $mPEG_{23}$-CPADB after deposition for a while. The macro-CTA in the RAFT dispersion polymerization acted as both stabilizer and chain transfer agent. The stability of the nanoparticles mainly depended on the hydrophilic segment of the macro-CTA, and it was more liable to form higher order morphologies by using macro-CTA with low DP, where the barrier was not enough and favored particle fusion for vesicle fabrication.[10]

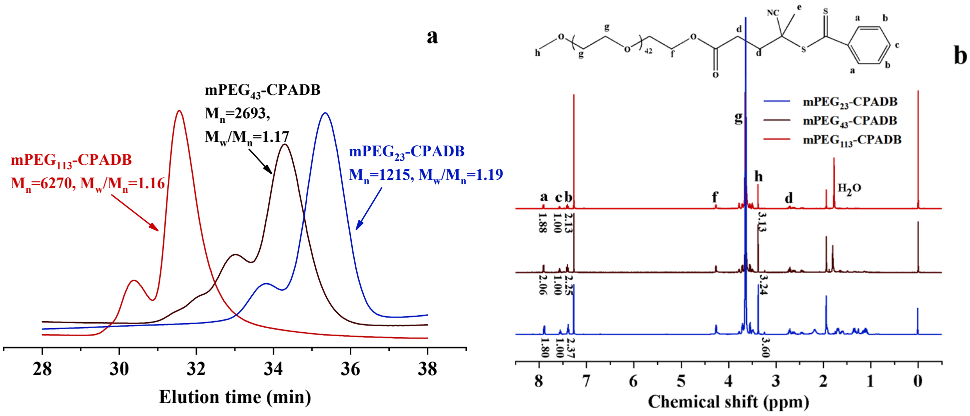

Figure 1. (a) GPC curves of mPEG-CPADB with different DP. (b) ^{1}H NMR spectrum of mPEG-CPADB with different DP in $CDCl_3$.

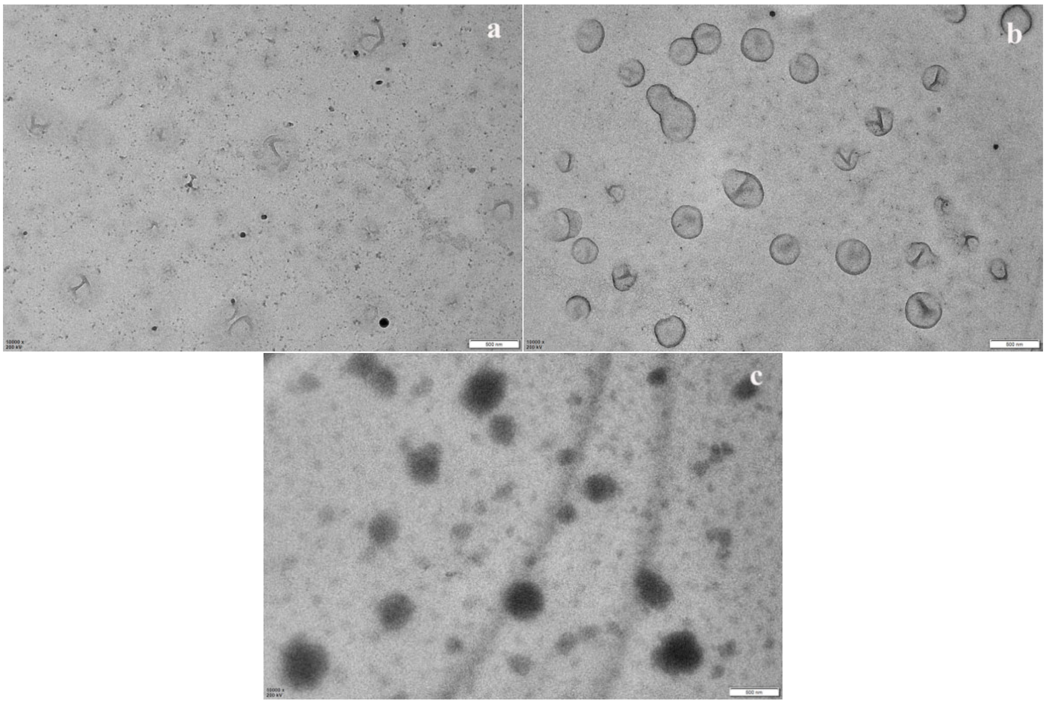

Figure 2. TEM images of the produced product with varying DP of the macro-CTAs and the hydrophobic block: (a) mPEG$_{23}$-CPADB, (b) mPEG$_{43}$-CPADB, (c) mPEG$_{113}$-CPADB.

DIPEMA and GlyMA were used as the copolymerization monomers, and the higher GlyMA content may generate more epoxy groups on the vesicles, which might be helpful for the AgNPs deposition. So the effect of the GlyMA ratio was studied by using mPEG$_{43}$-CPADB as the macro-CTA, and each sample was characterized by its morphology, FTIR, molecular weight (Mn) and molecular weight distribution (Mn/Mw). Figure 3 shows the TEM images of the produced nanoparticles, and Figure 4 shows the FTIR and GPC traces of Mn and Mw/Mn versus the monomer molar ratio. It could be seen that pure polymeric vesicles could be produced when monomer molar ratio of DIPEMA/GlyMA was equal to or higher than 7:3, and vesicle and solid particle mixtures with monomer molar ratio at 6:4, while no vesicles could be observed when the monomer molar ratio decreased to 5:5. Figure 4 (a) showed the molecular weight (Mn) and molecular weight distribution (Mn/Mw) of the produced copolymers, and it is found that Mn decreased with the increasing of the GlyMA loading ratio, and when the Mn was lower than 14700, corresponding to monomer molar ratio of DIPEMA/GlyMA at 6:4, pure vesicles could not be produced, while the Mn/Mw maintained at a relative lower value, less than 1.25. From Figure 4 (b), it can be seen that with the increasing of the GlyMA loading ratio, the absorption peaks at 842 cm−1 and 907 cm−1 (characteristic absorption peaks of epoxide ring[11]) increased for the produced copolymer. Thus, vesicles produced with

DIPEMA/GlyMA molar ratio of 8:2 was cross-linked for the vesicle membrane by reaction with EDA and used as templates for the AgNPs deposition.

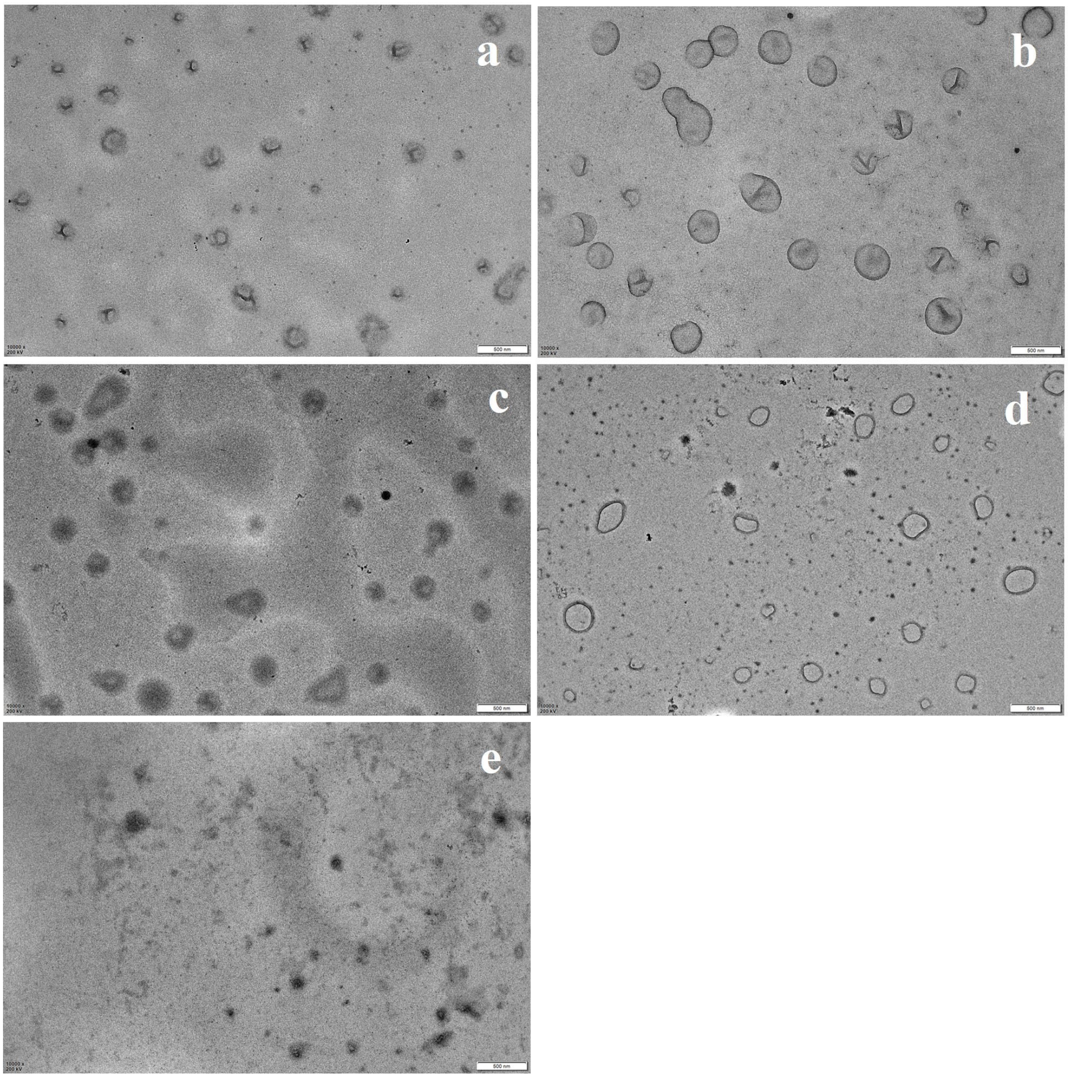

Figure 3. TEM images of mPEG-b-P(DIPEMA-co-GlyMA) nanoparticles prepared under different monomer molar ratio of DIPEMA/GlyMA, (a) 9:1, (b) 8:2, (c) 7:3, (d) 6:4, (e) 5:5.

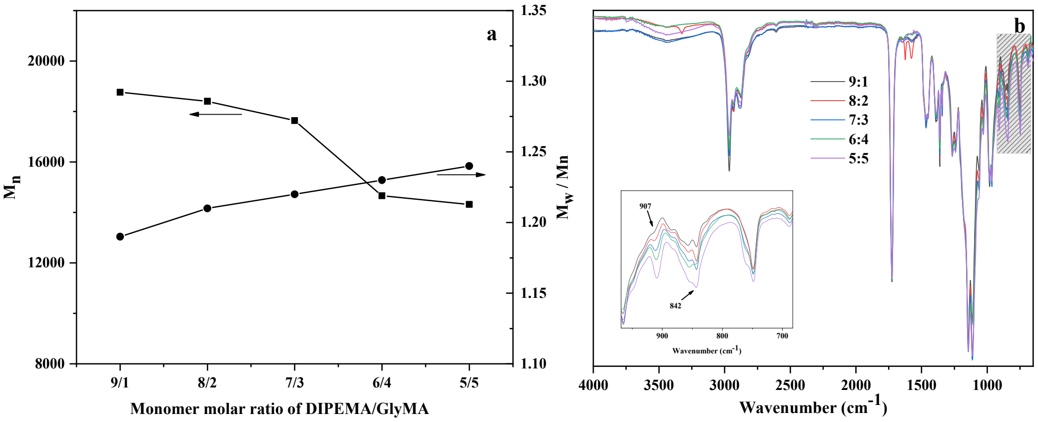

Figure 4. (a) the number average molecular weight and molecular weight distribution, (b) FTIR spectrum of mPEG-b-P(DIPEMA-co-GlyMA) versus monomer molar ratio of DIPEMA/GlyMA.

3.2 Preparation of AgNPs decorated vesicles and their catalytic performance

AgNPs decorated vesicles were prepared via in situ reduction of AgNO3 using the cross-linked polymeric vesicles as the template, and the color of the produced AgNPs decorated vesicles solution was brown. Figure 5 (a) showed the morphology of the AgNPs decorated vesicles, and small black dots could be observed on the vesicles. The reduction of 4-nitrophenol (4-NP) by NaBH4 was studied to check the catalytic performance of the AgNPs decorated vesicles. At first, excess amount of NaBH4 was added to the 4-NP solution, and no change could be observed after 2 hours. Then for the other bottle, after NaBH4 were added to the 4-NP solution, AgNPs decorated vesicles solution were added, and the color of the solution changed from brown to colorless gradually within 60 min, and the reaction was monitored via UV-vis, as shown in Figure 5 (b). As the increasing of the reaction time, the absorption peak at 400 nm decreased gradually, while a new peak at about 300 nm increased continuously, which indicated the reduction of 4-NP to 4-aminophenol, and also confirmed the catalytic capability of the AgNPs decorated vesicles.

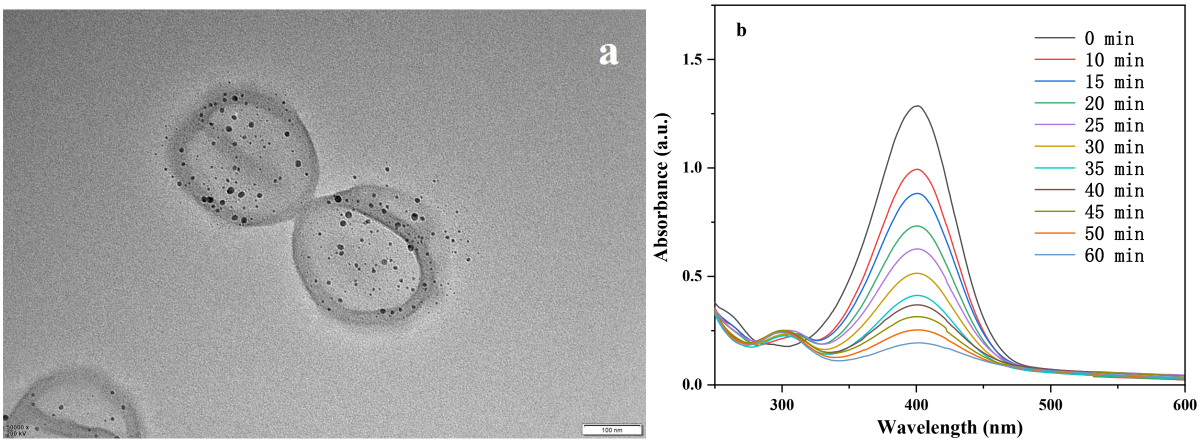

Figure 5. (a) TEM image of AgNPs decorated vesicles; (b) UV-vis spectra of 4-NP reduced by NaBH$_4$ catalyzed with AgNPs decorated vesicles at different reaction time

4. Conclusion

The cross-linked vesicles were used as the templates for the preparation of AgNPs decorated vesicles. The polymeric vesicles were fabricated via the redox-initiated RAFT dispersion polymerization, and post cross-linking was applied to cross-link the vesicle membrane. Pure vesicles could be obtained with DP of the hydrophilic block mPEG at 43. High GlyMA monomer ratio would cause lower Mn of the produced polymers and affect the particle morphology a lot. Good catalytic property of the AgNPs decorated vesicles was found via the UV-vis evaluation of 4-NP reduced by NaBH$_4$.

Acknowledgements

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