

Video Article

Using Polystyrene-*block*-poly(acrylic acid)-coated Metal Nanoparticles as Monomers for Their Homo- and Co-polymerization

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Abstract

We present a template-free method for “polymerizing” nanoparticles into long chains without side branches. A variety of nanoparticles are encapsulated in polystyrene-*block*-poly(acrylic acid) (PSPAA) shells and then used as monomers for their self-assembly. Spherical PSPAA micelles upon acid treatment are known to assemble into cylindrical micelles. Exploiting this tendency, the core-shell nanoparticles are induced to aggregate, coalesce, and then transform into long chains. When more than one type of nanoparticles are used, random and block “copolymers” of nanoparticles can be obtained. Detailed procedures are reported for the PSPAA encapsulation of nanoparticles, homo- and co-polymerization of the core-shell nanoparticles, separation and purification of the resulting nanoparticle chains. Transformations of single-line chains into double- and triple-line chains are also presented. The synergy between the polymer shell and the embedded nanoparticles leads to an unusual chain-growth polymerization mode, giving long nanoparticle chains that are distinct from the products of the traditional step-growth aggregation process.

Video Link

The video component of this article can be found at <https://www.jove.com/video/52954/>

Introduction

Despite great advances in the synthesis of nanoparticles over the past two decades, their orderly assembly remains a great challenge. Our synthetic capabilities in putting the basic building blocks together are of critical importance for the exploration and exploitation of their synergistic effects and collective properties. Thus, developing new reaction pathways and exploring the underlying mechanisms are the stepping stones towards the rational synthesis of complex nanodevices.

Among the rich structural variety of possible nanoparticle assemblies, one-dimensional (1D) chains have shown useful applications in nanoelectronics, optoelectronics, and biosensors.¹⁻⁴ Typically, self-assembly of nanoparticles into chain-like structures requires magnetic or electric dipole interactions, anisotropic electrostatic repulsion, or external templates.⁵⁻¹¹ For dipole-induced assembly, one needs nanoparticles with permanent dipoles, such as magnetic nanoparticles and semiconductor nanoparticles under special environments.¹²⁻¹⁵ For nanoparticles with no permanent dipole, it has been shown that the relatively weaker electrostatic repulsion at the ends of the nanoparticle chains can promote the selective attachment of nanoparticle thereon and thus, 1D chain growth.^{16,17} Because the nanoparticles can aggregate with each other and with the oligomers, the aggregation often follows the intrinsic step-growth mode, leading to short chain length and the lack of control over branching. Lastly, nanoparticles can be adsorbed onto 1D templates to form chains, but usually it is very difficult to achieve secure anchoring and avoid gaps among the nanoparticles.

With these existing methods, hetero-assembly or “co-polymerization” of nanoparticles is particularly difficult. A few pioneer works have demonstrated the “co-polymerization” of short nanoparticle chains exploiting magnetic dipole¹⁸ or electrostatic repulsion.¹⁹

Recently, we reported the homo- and co-polymerization of PSPAA-coated nanoparticles into chains.^{20,21} This new synthetic pathway involves facile colloidal synthesis and generic use of different types of nanoparticles. It affords ultralong chains without branching and allows ready control of their length and width (single-, double-, and triple-line chains). Most importantly, random- and co-polymers of nanoparticles can be synthesized with improved structural control. In this work, we provide video protocols for the related syntheses, intending to give a detailed demonstration and presentation.

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS). Some chemicals used in these syntheses are corrosive, toxic and possibly carcinogenic. Nanomaterials may have unrecognized hazards as compared to their bulk counterparts. Please use appropriate safety practices

when performing reaction, including the use of fume hood and personal protective equipment (safety glasses, gloves, lab coat, full length pants, closed-toe shoes, etc.).

1. Synthesis of Metal Nanoparticles

Note: All glassware used in the syntheses are washed with *aqua regia* (CAUTION: highly acidic and corrosive, handle with caution and dispose following the regulations), thoroughly rinsed, and then dried in 60 °C oven. Metal impurity or residue may lead to premature nucleation and failure of the nanoparticle synthesis.

1. Synthesis of 16 and 32 nm Au nanoparticles (AuNPs)
 1. Dissolve 10 mg of hydrogen tetrachloroaurate(III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) into 100 ml of deionized (DI) water in a round-bottom flask equipped with a condenser and a stir bar.
 2. With stirring on, heat the solution to reflux (boiling, 100 °C). The yellow color of the HAuCl_4 remains unchanged.
 3. Prepare a 1% sodium citrate solution by dissolving 30 mg of sodium citrate into 3 ml of DI water.
 4. To synthesize 16 nm AuNPs, inject 3 ml of 1% sodium citrate solution (1.1.3) into the boiling HAuCl_4 solution (1.1.2). The solution turns grey within 1 min, and then gradually turns red.
 1. To synthesize 32 nm Au NPs, use 1.5 ml of the sodium citrate solution instead. The smaller amount of reductant leads to less extensive homogeneous nucleation, so that each nucleus can grow larger.
 5. Keep the solution at boiling for another 30 min, and then cool down to RT for use in the subsequent reactions.
 6. Confirm the size and morphology of the resulting AuNPs by transmission electron microscopy (TEM).
 1. To prepare the TEM sample, first concentrate the AuNPs by transferring 1.5 ml of the as-synthesized solution into a microcentrifuge tube, and centrifuge it at 16,000 x g for 15 min. After removing the transparent supernatant, drop a 10 μl aliquot of the residue solution onto a TEM copper grid. Wick off the excess liquid sample using a filter paper and dry the copper grid in air.
 2. To conduct the TEM characterization, load the copper grid sample into the TEM holder, secure the sample, and load the holder into the specimen chamber following the standard operation procedures (specific to the type/brand of instrument).²²
2. Synthesis of Au nanorods (AuNRs)
 1. Prepare the seed solution. Under vigorous stirring, add 0.6 ml of 10 mM ice-cooled sodium borohydride (NaBH_4) to 10 ml of 0.25 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ prepared in 0.1 M hexadecyltrimethylammonium bromide (CTAB) solution. Continue stirring for 10 min.
 2. Add 95 ml of 0.1 M CTAB, 1 ml of 10 mM silver nitrate (AgNO_3), 5 ml of 10 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in sequence into a 200 ml conical flask.
 3. Add 0.55 ml of 0.1 M L-ascorbic acid to the solution, and shake gently to homogenize the solution.
 4. Immediately add 0.12 ml of the seed solution (Step 1.2.1). Mix the solution by gentle shaking and leave it undisturbed O/N (14–16 hr).
3. Synthesis of *t*-Te nanowires (TeNWs)
 1. Prepare 10 ml of N_2H_4 solution by mixing 1 ml of neat $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ with 9 ml of DI water.
 2. Add 16 mg of TeO_2 powder slowly to the N_2H_4 solution (Step 1.3.1) in a beaker at RT under constant stirring. In about 10 min, the powder completely dissolves. The solution would change from colorless to amber, to purple, and eventually to blue, indicating the formation of *t*-Te nanowires.
 3. Dilute the solution 10 times with sodium dodecylsulfate (10 mM) to terminate the reaction. The blue color of the solution becomes less intense after the dilution.

2. Synthesis of PSPAA Encapsulated Metal Nanoparticles (the Monomers)

Note: In the following, precise amounts are used to achieve a precise ratio of the final DMF/water solvent mixture. Because the residue volume after centrifugation and extraction of the supernatant is always different, roughly measure the residue volume by pipette and then compensate for this volume when adding DMF/water to make the final solutions. Small variations of the solvent ratio are usually not a problem.

1. Encapsulate AuNPs ($d_{\text{Au}} = 16 \text{ nm}, 32 \text{ nm}$) with PSPAA (AuNP@PSPAA)
 1. Purification of the AuNP solution. Add 3 ml of the as-synthesized AuNP solution (Step 1.1) to two microcentrifuge tubes (1.5 ml each), centrifuge at 16,000 x g for 15 min and remove the supernatant. Dilute the concentrated solution (~20 μl) with 160 μl of DI water.
 2. Prepare the PSPAA stock solution by dissolving 8 mg of PSPAA ($\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ or $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$) in 1 ml of DMF.
 3. Prepare a PSPAA solution by mixing 740 μl of DMF with 80 μl of $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ stock solution. For encapsulating the AuNPs in $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$ shells, use 80 μl of $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$ stock solution.
 4. In a glass vial, add the AuNPs (~180 μl solution, step 2.1.1) to 820 μl of the PSPAA solution (Step 2.1.3). The final mixture has a volume of 1 ml with $V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 4.5:1$.
 5. Add 40 μl solution of 1,2-dipalmitoyl-*sn*-glycero-3-phosphothioethanol (P-SH) in ethanol (2 mg/ml).
 6. Incubate the mixture at 110 °C for 2 hr to allow polymer self-assembly.
 7. Slowly cool the solution to RT in the oil bath. The sample can be stored at this state for weeks.
 8. Confirm the formation of AuNP@PSPAA with TEM.
 1. To prepare the TEM sample, concentrate the AuNP@PSPAA by transferring 200 μl of the as-synthesized solution into a microcentrifuge tube, add 1.3 ml of DI water and centrifuge it at 16,000 x g for 15 min.
 2. Mix a 5 μl aliquot of concentrated sample solution with 5 μl of 1% ammonium molybdate stain solution (Note: stain is used for samples containing PSPAA to improve the contrast of the polymers), and drop the mixture onto a TEM copper grid. Wick off the excess liquid sample using a filter paper and dry the copper grid in air.

2. Encapsulate AuNRs with PSPAA (AuNR@PS₁₅₄-*b*-PAA₄₉)
 1. Purify the as-synthesized AuNR solution (Step 1.2) twice to remove the excess CTAB. Add 3 ml of the AuNR solution into two microcentrifuge tubes, and then centrifuge them at 8,100 x g for 15 min. After removing the supernatant, add 1.5 ml of DI water and centrifuge again to remove the supernatant.
 2. Combine the concentrated AuNR solutions, and add 160 µl of DI water.
 3. In a glass vial, add the AuNR solution (~180 µl) to 820 µl of the PS₁₅₄-*b*-PAA₄₉ solution (Step 2.1.3). The final mixture has a volume of 1 ml with $V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 4.5:1$.
 4. Add 40 µl solution of 2-naphthalenethiol (NpSH) in ethanol (2 mg/ml) into the mixture.
 5. Incubate the mixture at 110 °C for 2 hr to allow polymer self-assembly.
 6. Slowly cool the solution to RT.
3. Encapsulate TeNWs with PSPAA (TeNW@PS₁₅₄-*b*-PAA₄₉)
 1. Purify the as-synthesized TeNWs (Step 1.3) to remove the excess SDS. Add 3 ml of the TeNW solution into two microcentrifuge tubes, and centrifuge them at 2,900 x g for 10 min. After removing the supernatant, add 1.5 ml of ethanol and centrifuge the tubes again. Repeat this purification process once more (total 3 rounds of centrifugation).
 2. Combine the concentrated TeNWs solutions, and add 160 µl of DI water.
 3. Add the TeNWs solution (~180 µl) to 820 µl of PS₁₅₄-*b*-PAA₄₉ solution (Step 2.1.3). The final mixture has a volume of 1 ml with $V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 4.5:1$.
 4. Incubate the mixture at 110 °C for 2 hr.
 5. Slowly cool the solution to RT.
4. Encapsulate carbon nanotubes (CNTs) with PSPAA (CNT@PS₁₅₄-*b*-PAA₄₉)
 1. Mix 730 µl DMF with 80 µl of the PS₁₅₄-*b*-PAA₄₉ stock solution (Step 2.1.2).
 2. Disperse about 0.05 mg of single-wall CNTs into the PS₁₅₄-*b*-PAA₄₉ solution.
Note: It is hard to measure the small weight of the CNTs; usually 0.2 mg of CNTs is weighed and about ¼ of the sample (by estimated volume) is added.
 3. Sonicate the mixture in an ice-water bath until it becomes a transparent dark solution. Use the clear solution and discard the insoluble residue CNTs.
 4. Add 180 µl of DI H₂O drop-wise to the solution. The final mixture has a volume of 990 µl with $V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 4.5:1$.
 5. Sonicate the solution at about 50 °C for 2 hr.
 6. Slowly cool the solution to RT.
5. Prepare spherical micelles of PS₁₅₄-*b*-PAA₄₉.
 1. Add 80 µl of the PS₁₅₄-*b*-PAA₄₉ stock solution (Step 2.1.1) to 740 µl of DMF, then add 180 µl water, making a solution of $V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 4.5:1$.
 2. Incubate the polymer solution at 110 °C for 2 hr.
 3. Slowly cool the solution to RT.

3. Homo-polymerization of the PSPAA Encapsulated Metal Nanoparticles

1. Synthesis of single-line chains from the AuNP@PSPAA
 1. Purify the AuNP@PSPAA.
 1. Dilute 800 µl of the as-synthesized AuNP@PSPAA (section 2.1) with 11.2 ml of water, divide the solution into individual microcentrifuge tubes (1.5 ml each), and centrifuge them at 16,000 x g for 30 min. Carry out two separate reactions, using the 16 nm AuNPs encapsulated in PS₁₅₄-*b*-PAA₄₉ and the 32 nm AuNPs encapsulated in PS₁₄₄-*b*-PAA₂₂ as the monomers.
 2. Remove and discard the supernatant, add 1.5 ml of 0.1 mM NaOH (pH = 10) to each tube and centrifuge them again at 16,000 x g for 30 min to remove the supernatant.
Note: The pH of the NaOH used for centrifugation in the purification process should not be too high. Higher pH would lead to aggregation during the centrifugation, and the residue base would comprise the effects of acid in the chain-growth step, leading to globular aggregates.
 2. Disperse the concentrated AuNP@PSPAA (combine all the tubes) in 1 ml of DMF/H₂O ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 6:1$) in a glass vial, and add 5 µl of 1 M HCl.
Note: It is important to control the residue NaOH and loss of the AuNP@PSPAA in the previous steps, so that the HCl amount required in the assembly process is consistent among the different batches. Vortex the reaction mixture before incubation to ensure complete mixing of the components.
 3. Incubate the mixture at 60 °C for 2 hr to allow the aggregation, coalescence, and morphological transformation of the core-shell nanoparticles.
 4. Cool the mixture to RT.
 5. For homo-polymerization of the AuNR@PS₁₅₄-*b*-PAA₄₉ and TeNW@PS₁₅₄-*b*-PAA₄₉, follow the same procedures, including the purification processes.
Note: In the experiments, plastic microcentrifuge tubes are typically used for purification and centrifugation, and glass vials are used for the reactions at elevated temperature. The PSPAA-coated nanoparticles are usually stable in solutions, except that when dispersed in high-DMF content solution in microcentrifuge tubes, they will stick to the plastic surface. To avoid this situation, high-DMF content solutions of the nanoparticles are only prepared in glass vials.
2. Synthesis of double-line chains from the AuNP@PSPAA
 1. Purify the AuNP@PSPAA (by following Step 3.1.1). Only the 16 nm AuNPs encapsulated in PS₁₅₄-*b*-PAA₄₉ shells have been tested.
 2. Disperse the concentrated AuNP@PSPAA in 1 ml of DMF/H₂O ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 7:3$) in a glass vial, and add 5 µl of 1 M HCl.

3. Incubate the mixture at 60 °C for 2 hr.
4. Cool the mixture to RT.
3. Purification of the nanoparticle chains

Note: The as-synthesized solutions contain the product nanoparticle chains, small chains/clusters, large agglomerates, AuNP@PSPAA monomers, empty PSPAA micelles, DMF and excess acid.

 1. Remove the empty PSPAA micelles, DMF and acid.
 1. Dilute 800 μ l of the as-synthesized solution with 11.2 ml of 0.1 mM NaOH, divide the solution into individual microcentrifuge tubes (1.5 ml each), and centrifuge them at 16,000 x g for 30 min.
 2. Add 1.5 ml of 0.1 mM NaOH to dilute the concentrated solutions, and centrifuge the tubes again at 16,000 x g for 30 min. Repeat this step once more.
 2. Enrich the AuNPs chains

Note: The purified solution contains the product nanoparticle chains, small chains/clusters, and AuNP@PSPAA monomers. They were separated by differential centrifugation.

 1. Centrifuge the tube at 300 x g for 25 min to isolate and remove the large agglomerates.
 2. Collect the supernatant, centrifuge it at 2,000 x g for 30 min. Remove the supernatant containing mostly monomers and small chains/clusters.
 3. Collect the bottom solution, dilute it in 1.5 ml of 0.1 mM NaOH, and centrifuge at 2,000 x g for 20 min to remove excess monomers. Repeat the process once more.

Note: The pH of the NaOH used in the centrifugation in the all purification process should not be too high. Higher pH would lead to aggregation during the centrifugation, causing the formation of globular aggregates.
4. Transformation of single-line nanoparticle chains to double-/triple-line chains
 1. Purify the single-line chains (Step 3.3.1, without the enriching step).
 2. Concentrate 800 μ l of the purified solution to ~20 μ l by centrifugation.
 3. To transform to double-line chains, disperse the solution in 1 ml of DMF/H₂O mixture solvent ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 7:3$) and add 2.5 μ l of 1 M HCl, $[\text{HCl}]_{\text{final}} = 2.5$ mM. To transform to triple-line chains, use 1 ml of DMF/H₂O ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 3:2$) and 2.5 mM $[\text{HCl}]_{\text{final}}$.
 4. Incubate the solution at 70 °C for 1 hr to allow the transformation of the nanostructures.
 5. Slowly cool the solution to RT.

4. Co-polymerization of the PSPAA Encapsulated Metal Nanoparticles

1. Random co-polymerization of the 16 nm AuNP@PS₁₅₄-b-PAA₄₉ and the 32 nm AuNP@PS₁₄₄-b-PAA₂₂. The process is very similar to Step 3.1 except that two monomers are used.
 1. Purify the two types of the as-synthesized AuNP@PSPAA separately (Step 3.1.1).
 2. Disperse the concentrated 16 nm AuNP@PS₁₅₄-b-PAA₄₉ and 32 nm AuNP@PS₁₄₄-b-PAA₂₂ in 1:1 ratio into 1 ml of DMF/H₂O mixture ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 6:1$).
 3. Add 5 μ l of 1 M HCl, $[\text{HCl}]_{\text{final}} = 5$ mM.
 4. Incubate the solution at 60 °C for 2 hr to allow co-assembly of the nanoparticles.
 5. Cool the solution to RT.
2. Random co-polymerization of the 16 nm AuNP@PS₁₅₄-b-PAA₄₉ and AuNR@PS₁₅₄-b-PAA₄₉
 1. Purify the AuNP@PS₁₅₄-b-PAA₄₉ and AuNR@PS₁₅₄-b-PAA₄₉ separately (Step 3.1.1).
 2. Disperse the AuNP@PS₁₅₄-b-PAA₄₉ and AuNR@PS₁₅₄-b-PAA₄₉ in 1:1 ratio into 1 ml of DMF/H₂O mixture ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 6:1$).
 3. Add 5 μ l of 1 M HCl, $[\text{HCl}]_{\text{final}} = 5$ mM.
 4. Incubate the solution at 60 °C for 2 hr to allow co-assembly of the nanoparticles.
 5. Cool the solution to RT.
3. Random co-polymerization of the 16 nm AuNP@PS₁₅₄-b-PAA₄₉ and PS₁₅₄-b-PAA₄₉ micelles
 1. Purification of the 16 nm AuNP@PS₁₅₄-b-PAA₄₉ (Step 3.1.1).
 2. Add the concentrated AuNP@PS₁₅₄-b-PAA₄₉ and 60 μ l of the spherical PS₁₅₄-b-PAA₄₉ micelles (Step 2.5) into 940 ml of DMF/H₂O. In the final solution, $V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 6:1$.
 3. Add 5 μ l of 1 M HCl, $[\text{HCl}]_{\text{final}} = 5$ mM.
 4. Incubate the solution at 60 °C for 1.5 hr.
 5. Cool the solution to RT.
4. Random co-polymerization of AuNP@PS₁₅₄-b-PAA₄₉ and PS₁₅₄-b-PAA₄₉ vesicles
 1. Follow the same procedures as Step 4.3.1-4.3.3.
 2. Incubate the solution at 60 °C for 6 hr to allow shape transformation of the PSPAA cylinders to vesicles.
 3. Cool the solution to RT.
5. Block-copolymerization of TeNWs with AuNPs
 1. Purify the 16 nm AuNP@PS₁₅₄-b-PAA₄₉ and TeNW@PS₁₅₄-b-PAA₄₉ (Step 3.1.1)
 2. Disperse the concentrated TeNW@PS₁₅₄-b-PAA₄₉ in 1 ml of DMF/H₂O mixture ($V_{\text{DMF}}/V_{\text{H}_2\text{O}} = 6:1$)
 3. Add 2 μ l of 1 M HCl.
 4. Incubate the mixture at 60 °C for 20 min.
 5. Add the concentrated 16 nm AuNP@PS₁₅₄-b-PAA₄₉ and 3 μ l of 1 M HCl.

6. Incubate the mixture at 60 °C for 2 hr.
7. Cool the solution to RT.
8. For block-copolymerization of CNTs with AuNPs, follow the same procedures as Step 4.5.1-4.5.7 by using CNT@PS₁₅₄-*b*-PAA₄₉ (Step 2.4).

Representative Results

The nanoparticle monomers and chains are characterized by TEM. **Figure 1** shows the representative TEM images of the PSPAA encapsulated monomers, confirming the morphologies and sizes (**Figure 1**). As some monomers typically remain in the sample after the “polymerization”, the sample is usually purified and concentrated before being used for TEM characterization. A stain was introduced during the preparation of the TEM samples by mixing the sample solution with 1% ammonium molybdate, in order to render the polymer shell with clear contrast in the TEM images. The representative TEM images of the “homo-polymers” and “co-polymers” are presented in **Figure 2** and **Figure 3**.

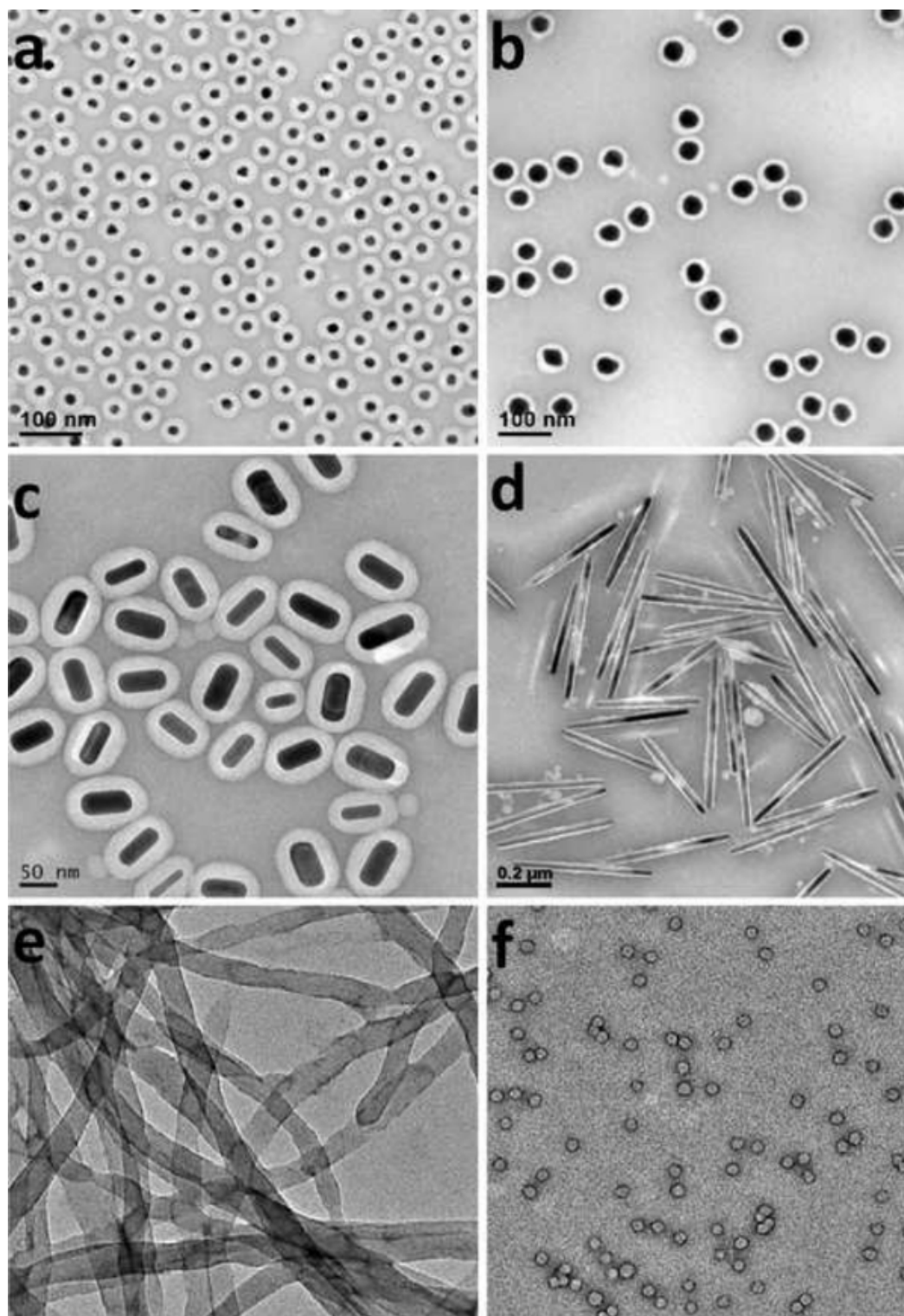


Figure 1. TEM images of the monomers. (A) 16 nm AuNP@PS₁₅₄-*b*-PAA₄₉, **(B)** 32 nm AuNP@PS₁₄₄-*b*-PAA₂₂, **(C)** AuNR@PS₁₅₄-*b*-PAA₄₉, **(D)** TeNW@PS₁₅₄-*b*-PAA₄₉, **(E)** CNT@PS₁₅₄-*b*-PAA₄₉ and **(F)** PS₁₅₄-*b*-PAA₄₉ micelles. [Please click here to view a larger version of this figure.](#)

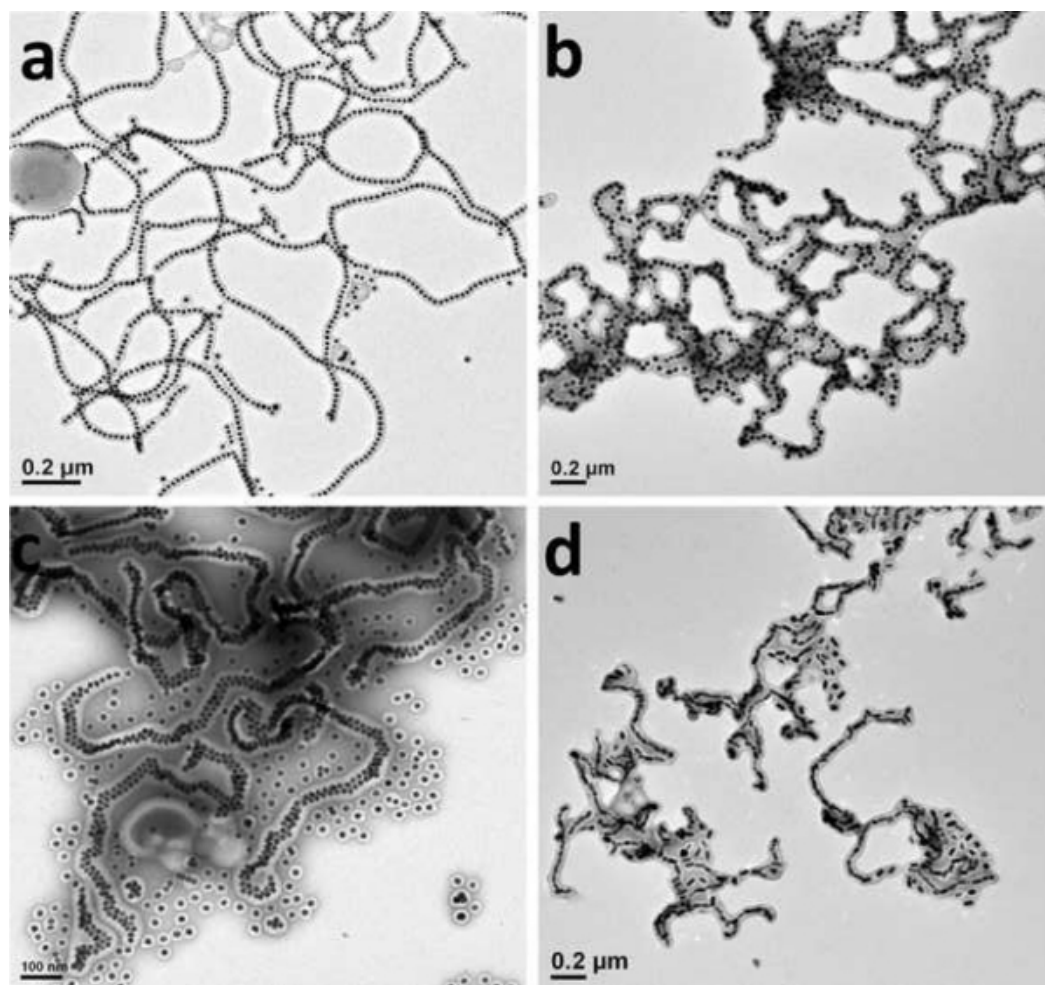


Figure 2. TEM images of the “homo-polymers” of nanoparticles. (A) Single-line chains of 16 nm AuNP encapsulated in PS₁₅₄-b-PAA₄₉, (B) single-line chains of 32 nm AuNPs encapsulated in PS₁₄₄-b-PAA₂₂, (C) double-line chains of 16 nm AuNPs encapsulated in PS₁₅₄-b-PAA₄₉ and (D) single-line chains of AuNR@PS₁₅₄-b-PAA₄₉. [Please click here to view a larger version of this figure.](#)

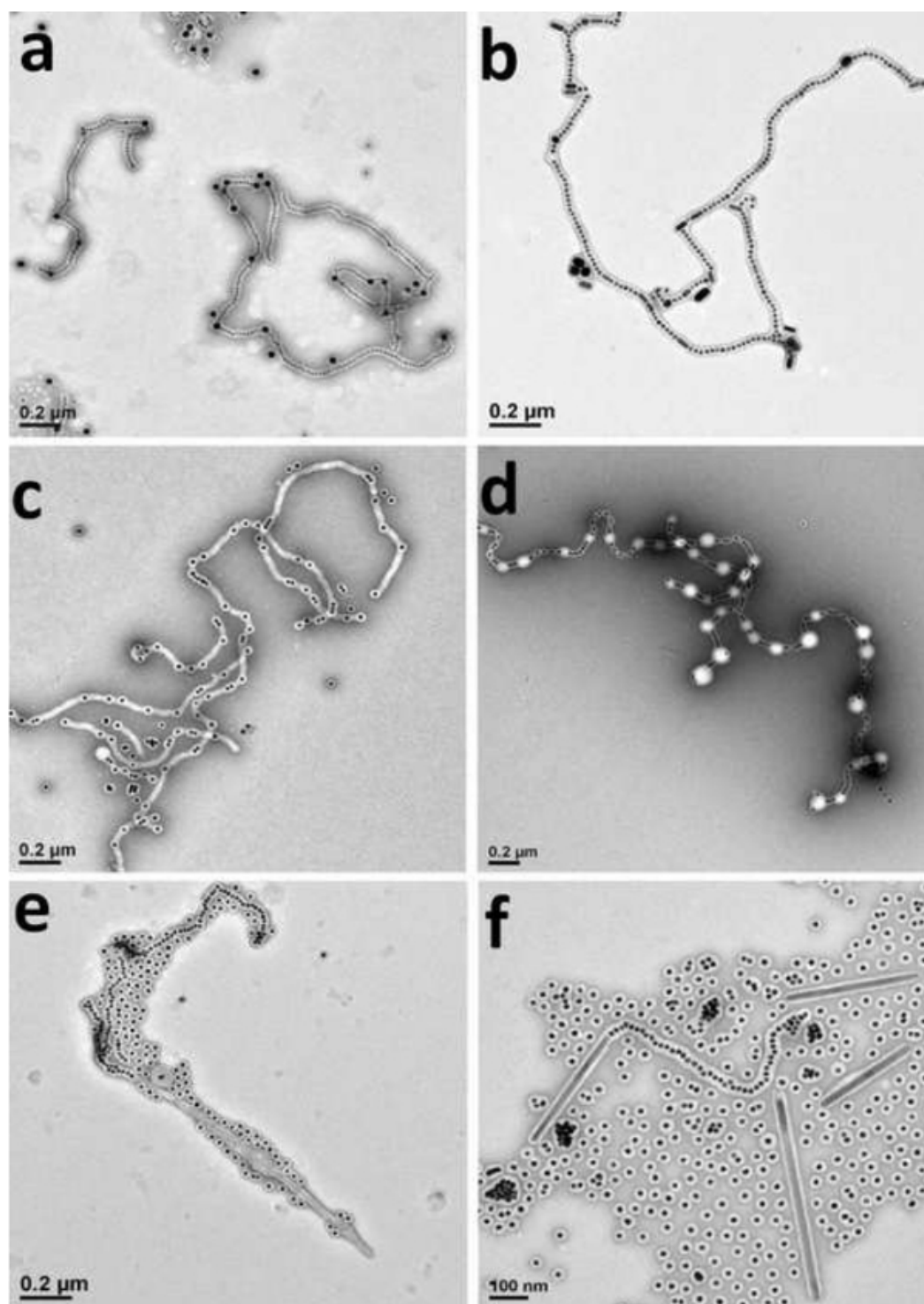


Figure 3. TEM images of “co-polymers” of nanoparticles. (A) random chains of 16 nm AuNP encapsulated in $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ and 32 nm AuNP encapsulated in $\text{PS}_{144}\text{-}b\text{-PAA}_{22}$, (B) random chains of 16 nm AuNP encapsulated in $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ and AuNR@ $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$, (C) random chains of 16 nm AuNP encapsulated in $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ and $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ micelles, (D) random chains of 16 nm AuNP encapsulated in $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ and $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ vesicles, (E) block chains of CNT@ $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ and 16 nm AuNP encapsulated in $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$. (F) block chains of TeNW@ $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$ and 16 nm AuNP encapsulated in $\text{PS}_{154}\text{-}b\text{-PAA}_{49}$. [Please click here to view a larger version of this figure.](#)

Discussion

The mechanistic details of the syntheses are reported and discussed in the previous publications.^{20,21} Here we focus on the rationales of the synthetic conditions. For the polymerization of nanoparticles, it is preferred that nanoparticles of uniform size are used. We follow literature procedures to obtain the uniform Au nanoparticles,²³ Au nanorods,²⁴ and Te nanowires.²⁵ In general, better size uniformity can be obtained when

the nucleation and growth stages are separated.²⁶ After the initial burst of homogeneous nucleation, all nuclei grow at the same rate for a same period, giving nanoparticles of similar sizes. Thus, the size of the nanoparticles depends on the total amount of growth material and total number of nuclei formed at the initial nucleation stage.

The encapsulation of the nanoparticles by PSPAA has been previously reported and discussed.²⁷⁻²⁹ The driving force of the PSPAA self-assembly is the phase segregation between PS and PAA domains.^{30,31} In a polar solvent, PSPAA forms micelles, with the PS blocks in the center and PAA blocks dissolved in the solvent facing outwards. In the presence of nanoparticles that are functionalized with hydrophobic ligands, the PS blocks can adsorb on the nanoparticle surface via van der Waals and hydrophobic interactions, forming a micellar shell with surface PAA blocks (**Figure 1A-E**). In the synthesis here, excess PSPAA is used to achieve single encapsulation of the nanoparticles.²⁷ The excess polymer remains as empty PSPAA micelles (without nanoparticles) after the encapsulation and can be easily separated by centrifugation. The -SH ended hydrophobic ligands (P-SH and Np-SH) are used to render the surface of AuNPs and AuNRs hydrophobic. We add the ligands after PSPAA to minimize the aggregation among the hydrophobic nanoparticles. For TeNWs, no surface ligand is necessary as their surface is intrinsically hydrophobic. The solvent ratio ($V_{\text{DMF}}:V_{\text{H}_2\text{O}}$) is of importance, in terms of improving the mobility of PS domains by swelling³² and controlling the morphology of PSPAA micelles.^{33,34} Elevated temperature (60–110 °C) is used to promote the association/dissociation dynamics of the polymer micelles so that near equilibrium conditions can be attained.

The polymerization of nanoparticle chains is driven by the tendency of the PSPAA micelles to transform from spheres to cylinders. As acid is added to protonate the surface PAA blocks and reduce their mutual repulsion, the transformation towards cylindrical micelles is thermodynamically favorable in terms of reducing the surface-to-volume ratio (S/V) of the micelles. The $V_{\text{DMF}}:V_{\text{H}_2\text{O}}$ solvent ratio affects the polymer-solvent interfacial energy. The PS domain with a lower degree of swelling is more dissimilar to the solvent and thus the polymer-solvent interfacial energy is higher. In the synthesis, elevated temperature (60 °C) is used to promote the coalescence of PSPAA domains after the nanoparticles aggregate. High DMF content solvent ($V_{\text{DMF}}:V_{\text{H}_2\text{O}} = 6:1$) is used for synthesizing single-line nanoparticle chains (**Figure 2A, 2B, 2D**), whereas solvent with higher water content ($V_{\text{DMF}}:V_{\text{H}_2\text{O}} = 7:3$) is used for synthesizing double-line chains (**Figure 2C**).

The extent of monomer aggregation depends on their mutual charge repulsion and reaction time. For 32 nm AuNPs, their large size leads to stronger charge repulsion (assuming a same surface charge density). Addition of more acid can lead to more extensive aggregation but it compromises the selectivity of chain formation.²⁰ Thus, polymers with shorter PAA blocks (PS₁₄₄-b-PAA₂₂) are employed to reduce the charge repulsion without compromising the selectivity (**Figure 2B**).

To achieve “co-polymerization” of nanoparticles, two types of PSPAA-coated monomers are used in the self-assembly. When they are mixed before the addition of acid, random “copolymer” chains would be obtained (**Figure 3A-B**). The ratio of two types of nanoparticles in the resulting chains depends on, but is not directly proportional to, the initial concentration ratio of the monomers. Empty PSPAA micelles can also be used as monomers, giving cylindrical polymer segments within the nanoparticle chains (**Figure 3C**). Such segments can be transformed to vesicles upon prolonged heating (6 hr) at 60 °C (**Figure 3D**). Block-chains of nanoparticles are more difficult to prepare, as the chains after synthesis and purification cannot be readily re-activated for the addition of 2nd type of monomers. Without purification, monomers remained in the sample after forming the 1st block would interfere with the growth of the 2nd block. We use CNTs and TeNWs with a high aspect ratio to construct the 1st block, so that nanoparticles can “polymerize” within the same reaction mixture for the growth of the 2nd block (**Figure 3E-F**).

In conclusion, we demonstrate a general method to prepare the PSPAA encapsulated nanoparticles chains. Metal nanoparticles with different size and aspect ratios are shown to aggregate into “homo-polymers”, which can be controlled from single-line to triple-line chains. Random or block “copolymers” of nanoparticles are also prepared by combining two types of the PSPAA encapsulated nanoparticles. Developing these new reaction pathways and exploring the underlying mechanisms are the stepping stones towards the rational synthesis of complex nanodevices.

Disclosures

The authors have nothing to disclose.

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