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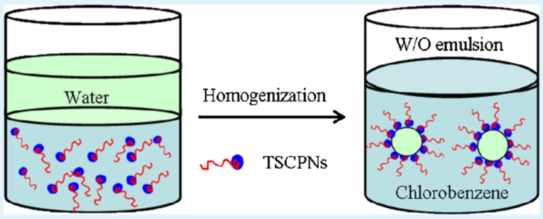
# Water in Oil Emulsion Stabilized by Tadpole-like Single Chain Polymer Nanoparticles and Its Application in Biphase Reaction

Fugui Xu,[†] Zhihui Fang,[†] Duanguang Yang,[†] Yong Gao,*[,†] Huaming Li,[†,‡] and Daoyong Chen[§]

[†]College of Chemistry and [‡]Key Lab of Environment Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105, Hunan Province, P. R. China

[§]The State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai, 200433, China

Ⓢ *Supporting Information*



**ABSTRACT:** In this study, tadpole-like single chain polymer nanoparticles (TSCPNs) were efficiently synthesized by intramolecularly cross-linking P4VP block of commercial block polymer of PMMA$_{2250}$-*b*-P4VP$_{286}$ in *N*,*N*-dimethylformamide using propargyl bromide as cross-linking agent. The intramolecular cross-linking reaction led to the production of TSCPNs with a linear tail and a cross-linked head. The as-prepared TSCPNs were then applied as emulsifier to stabilize water in chlorobenzene emulsion, and an extremely stabilized water in oil (W/O) emulsion was generated at a low TSCPNs concentration. The TSCPNs concentration was as low as 0.0075 wt % versus total weight of water and chlorobenzene for emulsion formation. The emulsifying performance of TSCPNs was better than that of low molecular surfactant, such as Span-80. The generated W/O emulsion provided an ideal medium for the reduction of oil-soluble *p*-nitroanisole by water-soluble sulfide to *p*-anisidine, an effective contact problem between the two reactants with different solubility was well solved through interfacial reaction.

**KEYWORDS:** *Pickering emulsion, single chain polymer nanoparticles, intramolecular cross-linking, interfacial reaction*

## ■ INTRODUCTION

Colloid particles stabilized emulsion, termed as Pickering emulsion, was named by Pickering in 1907.[1] The advantages distinguishing Pickering emulsion from traditional emulsion stabilized by low molecular weight surfactant are its ultrahigh stability, low toxicity, and well adjustable droplet size.[2−5] In recent years, Pickering emulsion has received considerable attention in diverse fields, such as pharmaceuticals, cosmetics, food science, oil recovery, and wastewater treatment.[6−8] It is well-known that the stability of Pickering emulsion is mainly controlled by the wettability and concentration of particles. Stabilized Pickering emulsion requires the colloid particles to be partially wetted by oil and water,[2] and the solid particles are thus strongly irreversibly absorbed on the liquid−liquid interface, resulting in large reduction in interface tensile. At the same time, the entire surface of the droplets are required to be covered by absorbed colloid particles, and the formed densely packed particle layer at the oil−water interface could effectively prevent droplet coalescence by a steric barrier mechanism.[9,10] During the past decades, much effort has been focused on developing particulate emulsifiers for Pickering emulsions. A broad range of inorganic rigid particles, including SiO$_2$ particles,[11] clay,[12] carbon naomaterials,[13−16] and polymer soft particles, such as star-structured polymer,[17−20] polymer nanoaggergates,[21−23] natural macromolecules,[24−27] and so forth, have been successfully applied to stabilize emulsions. Although much progress has been made, exploiting new colloid particles with excellent emulsification performance for Pickering emulsions is still interesting and challenging work.

Owing to their anisotropy in chemistry and/or polarity, Janus particles are the most excellent candidate for solid surfactants.[28] By comparison with uniform particles, Janus particles demonstrated more strengthened adsorption at the interface because of their high surface activity. Binks and Fletcher[29] have calculated that the surface activity of Janus particles at an oil−water interface is three times higher than that of uniform particles. However, to date, reports on emulsions stabilized by Janus particles are still limited,[30−35] and this is mainly ascribed to the difficulty in synthesis of Janus particles on a large scale. Therefore, developing an efficient synthesis method for Janus particles is important and interesting work.

Tadpole-like single chain polymeric nanoparticles (TSCPNs) with a cross-linked head and linear tail were regarded as the smallest polymer Janus nanoparticles, which have attracted intensive focus owing to their easily tunable dimensions and properties by the molecular weight and the quantity of intramolecular bonds as well as the composition of their linear polymer precursors.[36] A newly developed strategy for facile preparation TSCPNs is intramolecularly cross-linking one block of a block copolymer.[37−40] For example, Chen et al.[39] have reported a facile method for the preparation of

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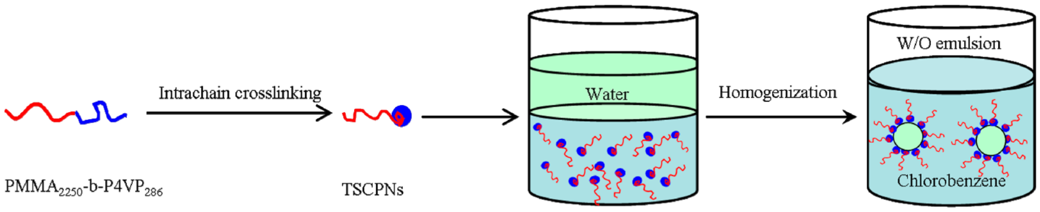
Scheme 1. Water in Chlorobenzene Emulsion Stabilized by TSCPNs



unimolecular polymeric Janus nanoparticles in relatively large quantity. The experiment was carried out by cross-linking the middle P2VP block of PS-*b*-P2VP-*b*-PEO using 1,4-dibromobutane in DMF at a higher polymer concentration (20 mg $mL^{-1}$) under required conditions. The intermolecular cross-linking reaction could be excluded by reason of the shielding effect of PS and PEO end blocks. Wen et al.[40] also reported PS tethered PDMAEMA single-chain nanoparticles with a tunable size by intramolecularly cross-linking PDMAEMA block of PDMAEMA-*b*-PS diblock copolymer using 1,4-diiodobutane as cross-linking agent. Inspired by these, TSCPNs were synthesized by intramolecularly cross-linking P4VP block of diblock polymer of poly(methyl methacrylate)-*block*-poly(4-vinylpyridine) ($PMMA_{2250}$-*b*-$P4VP_{286}$) using propargyl bromide (PB) as the cross-linker in this study. The obtained TSCPNs were then used as emulsifier to stabilize water in chlorobenzene emulsion, and the overall procedure is shown in Scheme 1. In addition, the generated water in chlorobenzene emulsion was employed as an heterogeneous reaction platform for the reduction of *p*-nitroanisole by sulfide to *p*-anisidine.

## EXPERIMENTAL SECTION

**Materials.** The block copolymers poly(methyl methacrylate)-*block*-poly(4-vinylpyridine) ($PMMA_{2250}$-*b*-$P4VP_{286}$, the subscripts represent degree of polymerization of the respective blocks, $M_w/M_n$ =1.13) were purchased from Polymer Source Inc. Propargyl bromide (PB) (Shanghai Bangcheng Chemical Reagent, AR) and *N*,*N*-dimethylformamide (DMF, Shanghai Qiangsheng Chemical Reagent, AR) were purified by reduced pressure distillation over $CaH_2$ before use. *p*-Nitroanisole was purchased from Sinopharm Chemical Reagent Co., Ltd., China.

**Synthesis of TSCPNs by Intrachain Cross-Linking Reaction.** In a typical experiment, diblock copolymer of $PMMA_{2250}$-*b*-$P4VP_{286}$ was first dissolved in DMF at a concentration of 1 mg $mL^{-1}$. Then, PB was added into the block copolymer solution, and the molar ratio of PB to the pyridine groups of the block copolymer was 2:1. After three freeze−pump−thaw cycles, the flask was sealed and then stirred at 60 °C for 24 h. The polymer was first precipitated in a large amount of cold mixture of diethyl ether and petroleum ether (v/v 1:1), and the titled polymer product was separated by centrifugation, and then dried under reduced pressure at 25 °C.

**Preparation of Water in Oil (W/O) Pickering Emulsion Stabilized by TSCPNs.** A certain quality of TSCPNs were first dissolved in 2 mL of chlorobenzene, and then 2 mL of deionized water was added. The concentration of TSCPNs in chlorobenzene was varied from 0.105 to 2.1 mg $mL^{-1}$. The chlorobenzene−water biphase wwas homogenized by ultrasonic processor with 3 mm probe (Sonics, VCX130, American) with a Branson 130 W instrument at 60% amplitude. During sonication, the vial was immersed in an ice bath to avoid overheating. The diluted emulsion was placed on a glass slide and viewed with the optical microscope. The type of emulsion was determined by a drop test as well as conductivity measurement. The emulsions were kept at room temperature after homogenization.

**Reduction Reaction of *p*-Nitroanisole on the Interface of Oil−Water.** In a typical experiment, 3 mg of *p*-nitroanisole was added into the vial containing 4 mL of Pickering emulsion stabilized by 0.05% of TSCPNs concent versus the total weight of oil and water. The $Na_2S$ concentration in water phase was 0.1 mol $L^{-1}$. After 1 min of stirring, the vial was transferred to 80 °C oil bath. After a certain reaction time period, the reaction was stopped. The mixture was first added into the large amount of cold mixture of diethyl ether and petroleum ether (v/v 1:1). The water phase containing polymer was washed three times with 20 mL of cold mixture of diethyl ether and petroleum ether (v/v 1:1). The organic phase was collected, and then the solvent was removed under reduced pressure. The remaining was diluted with chlorobenzene. The conversion of *p*-nitroanisole was analyzed by high performance liquid chromatography (HPLC).

**Characterization.** Fourier transform infrared (FTIR) spectra were recorded on a NEXUS-470 spectrometer from Thermofisher. $^1H$ NMR spectra were recorded on a Bruker DMX400 spectrometer in deuterated solvents. The number-average molecular weight $M_n$ and polydispersity were determined by gel permeation chromatography (GPC). GPC analysis was carried out on a PL-GPC120 setup equipped with polymer standards service columns (guard; $10^2$, $10^3$, and $10^5$ Å), and a Waters 410 refractive index detector calibrated against linear PS standards in DMF. Transmission electron microscopy (TEM) observations were conducted on a JEOL-2010 electron microscope at an acceleration voltage of 200 kV. Emulsion droplets were imaged with an optical microscope (DM-BA450, Motic China Group Co., LTD) fitted with a digital camera after dilution in the continuous-phase liquid. Droplet diameter was measured by image analysis using the motic images advanced software. Interfacial tension measurements were measured by the Wilhelmy plate method, and the experiments were performed with a Kruss tensiometer K20 equipped with a Wilhelmy slide. The hydrodynamic diameters of the polymer samples were measured on a Brookhaven instrument equipped with a 100 mW solid-state laser emitting at 532 nm. The results were analyzed in CONTIN mode. Zeta potentials of TSCPNs in chlorobenzene and emulsion droplets were measured using a MALVERN Zetasizer Nano ZS instrument. HPLC measurments were performed using an Agilent 1200 system. The water/acetonitrile mobile phase composition was 30/70 (v/v), and the method was run with a mobile phase flow rate of 1 mL $min^{-1}$. All measurements were made with 10 $\mu$L injection volume and UV detection at 300 nm.

## RESULTS AND DISCUSSION

**Synthesis of TSCPNs.** Intramolecularly cross-linking one block of diblock polymer provides an ideal method for synthesis of TSCPNs. where the cross-linking reaction from different chains in solution could be effectively prevented by steric hindrance shielding from noncrosslinked block.[39,40] In this study, we intended to synthesize TSCPNs by intramolecularly cross-linking P4VP block of commercial diblock copolymer of $PMMA_{2250}$-*b*-$P4VP_{286}$ in DMF using PB as cross-linker, as depicted in Scheme 1. The cross-linking reaction was conducted at polymer concentration of 1 mg $mL^{-1}$. The cross-linking reaction mechanism using PB as cross-linker has been described in some previous reports.[41,42] In brief, PB was first reacted with 4VP units of block polymer, and the grafted propargyl groups were activated and then intramolecularly self-polymerized with each other, resulting in the cross-linking of the P4VP block. The reaction was first testified by comparing the FTIR spectra of $PMMA_{2250}$-*b*-$P4VP_{286}$ before and after reaction with PB. Typical absorbing peak at 1640 $cm^{-1}$,

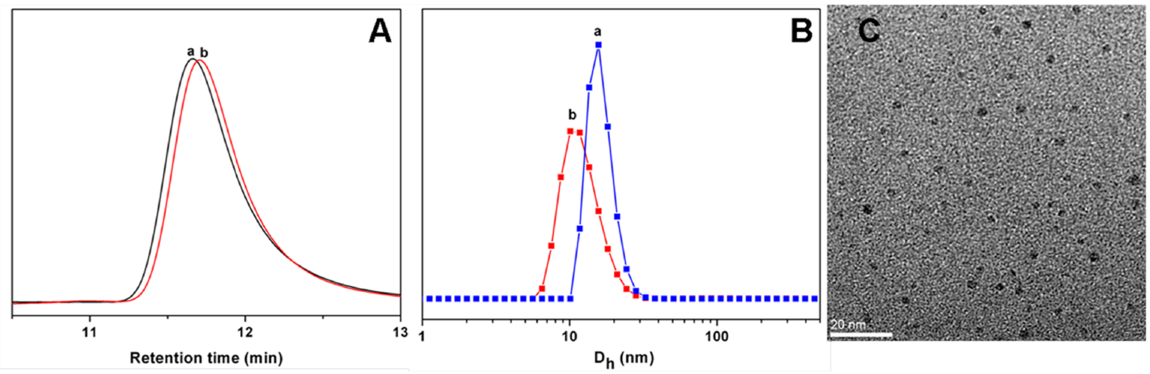


**Figure 1.** (A) GPC traces of the linear $PMMA_{2250}$-*b*-$P4VP_{286}$ copolymer (a) and the TSCPNs (b). (B) DLS curves of the linear $PMMA_{2250}$-*b*-$P4VP_{286}$ copolymer (a) and the TSCPNs (b). (C) Typical TEM image of TSCPNs.

corresponding to the pyridinium signals, appeared, while no obvious absorbing peak at 1640 $cm^{-1}$ was observed in the FTIR of virgin $PMMA_{2250}$-*b*-$P4VP_{286}$ (Figure S1, Supporting Information). Successful intramolecular cross-linking reaction was further verified by GPC and dynamic light scattering (DLS) measurements. Figure 1A shows the GPC traces of the collapsed nanoparticles and the starting linear copolymers. As indicated in curve b, the GPC trace shifted toward the low molecular weight region with a higher retention time after reaction with PB, revealing a reduction in hydrodynamic volume. No peak was monitored at the high molecular weight region in GPC trace, suggesting the exclusively intramolecular self-polymerization reaction of grafted propargyl groups. This conclusion was consistent with the DLS measurement. Figure 1B shows the DLS curves of the $PMMA_{2250}$-*b*-$P4VP_{286}$ diblock polymer before and after reaction with PB. As shown in Figure 1B, the average hydrobynamic diameter ($\langle D_h \rangle$) of linear $PMMA_{2250}$-*b*-$P4VP_{286}$ precursor was about 16 nm with PDI of 0.173 (curve a). After reaction with PB, the average value of $\langle D_h \rangle$ decreased to about 12 nm with PDI of 0.252 (curve b). Both GPC and DLS results indicated the cross-linking of P4VP block by PB was an exclusively intramolecular reaction. Our present result was different from that previously reported by Huang et al.;[42] polymer stars with core−shell structure rather than single chain collapsed nanoparticles were obtained by cross-linking the P4VP block of $PS_{891}$-*b*-$P4VP_{311}$ diblock copolymer using PB as the cross-linker at polymer concentration of 5 mg $mL^{-1}$. The main reason was that the current polymer reaction concentration was far lower than that required for micellization induced by chemical cross-linking.[42−44] Our control experiment indicated that improving the polymer reaction concentration, such as 5 mg $mL^{-1}$, was favorable to the intermolecular cross-linking reaction, which was verified by DLS measurement (Figure S2, Supporting Information). On the other hand, the block length ratio of non-cross-linked PMMA to cross-linked P4VP block also largely increased, and the steric hindrance effect was thus largely enhanced. Therefore, reduction in polymer concentration and the increased length of non-cross-linked PMMA block remarkably decreased the probability of interchain reaction.

The morphologies of TSCPNs were further characterized by TEM. As shown in Figure 1C, spherical nanoparticles with average diameter of about 4 nm were observed, and the enhanced contrast was due to the counterions of pyridinium of $Br^-$. The size of TSCPNs was smaller than that predicted by the polymer structure, and the reason was that the low contrast region formed by PMMA block could not be observed.

The $^1H$ NMR spectra of $PMMA_{2250}$-*b*-$P4VP_{286}$ before and after reaction with PB were also recorded (Figure S3, Supporting Information). In order to investigate whether the non-cross-linked PMMA block was embedded in the cross-linked P4VP block during self-polymerization of the grafted propargyl groups, quantitative $^1H$ NMR analysis was performed using dimethyl sulfoxide (DMSO) as internal standard. As shown in Figure S3 (Supporting Information), all protons signals were observed in the $^1H$ NMR spectrum of virgin $PMMA_{2250}$-*b*-$P4VP_{286}$. The resonance peaks at 6.3 and 8.3 ppm were assigned to the protons of pyridine rings of 4VP repeat units; the resonance peaks at 0.83 and 3.58 ppm were assigned to the protons of $-CH_3$ and $-OCH_3$ of PMMA block. Based on $^1H$ NMR analysis, the integral area ratio of peak at 3.58 ppm to that at 8.3 ppm was 12.2, which was almost equal to the theoretical value of 11.8 according to the structure parameter of block polymer, indicating molecular dispersing of $PMMA_{2250}$-*b*-$P4VP_{286}$ in deuterated $CHCl_3$ (curve A). After reaction with PB, the protons signals of P4VP block disappeared completely due to the low mobility. The resonance peaks at 0.83 and 3.58 ppm, corresponding to the protons of $-CH_3$ and $-OCH_3$ of MMA repeat units, could still be observed (curve B). However, the integral peak area ratio at 3.58 ppm of curve B to that of curve A was about 0.90 using integral peak area at 2.5 ppm, corresponding to protons of $-CH_3$ of DMSO internal standard, as reference, revealing about 10% of PMMA block was wrapped in the cross-linked P4VP block during cross-linking reaction. Most of PMMA block was still solvated. In summary, TSCPNs consisting of a linear PMMA tail and a cross-linked P4VP head were successfully synthesized through intramolecular cross-linking reaction based on GPC, DLS, and $^1H$ NMR analysis.

**W/O Emulsion Stabilized by TSCPNs.** Among the diverse applications of the polymer Janus nanoparticles, one of the most fascinating applications is acting as solid particles emulsifier to stabilize emulsion. For the present synthesized TSCPNs, it consisted of a cross-linked quaternized head and a linear tail. The quaternized head and linear PMMA tail conferred the TSCPNs hydrophilicity and hydrophobicity, respectively. Zeta potential measurement indicated that the surface of the TSCPNs was negatively charged (about −4 mV) in chlorobenzene. Consequently, such amphiphilic TSCPNs was a perfect particle emulsifier. By the ultrasonic homogenization, they could be absorbed on the oil−water interface in a similar fashion as solid particles in Pickering emulsions to stabilize the emulsion droplets. The hydrophilic cross-linked head and the hydrophobic linear tail faced the water and oil phase, respectively. Previous studies revealed that suitable particles concentration, approximately 1−5 wt % was necessary required for the stabilized Pickering emulsion, and emulsion destabilization usually occurred at low concentration of particles due to the insufficient protecting the droplets against coalescence.[45,46] However, recent study demonstrated that PEO-based star polymer stabilizer exhibited excellent emulsifying performance, and stable emulsions could be generated at an extremely low surfactant concentration, <0.01 wt % versus total weight of water and oil.[17] In order to investigate the emulsifying performance of TSCPNs, a series of water in chlorobenzene emulsions with fixed oil/water volume ratio (1:1) and varied TSCPNs content ranging from 0.1% to 0.005% was prepared. TSCPNs were first dissolved in chlorobenzene, and the emulsion was prepared by addition of water into the chlorobenzene containing TSCPNs, followed by 1 min of ultrasonic homogenization emulsification. Figure 3 shows photographs of water/chlorobenzene biphase containing different content of TSCPNs after ultrasonic treatment. As shown in Figure 2A−D, stabilized gelled emulsion layer could be generated by ultrasonic treating when the content of TSCPNs ranged from 0.1% to 0.0075%. The generated emulsion layer fraction slightly increased with the increase of TSCPNs content. However, a thin emulsion layer accompanied by about 30 vol % water phase was observed when the TSCPNs content was as low as 0.005% (Figure 2E). This suggested that 0.0075% versus the total weight of water and oil for emulsion formation was the required lowest TSCPNs concentration for complete emulsification of the water phase. The difference of emulsifying performance of the TSCPNs from that of the regular low molecular surfactant, such as Span 80, was also studied. The surfactant Span 80 is well-known to form W/O emulsions due to a low hydrophile−lipophile balance (HLB) value of 4.3,[47] while only a thin layer emulsion was formed when 0.05% versus the total weight of oil and water of Span 80 was used (Figure 2F).

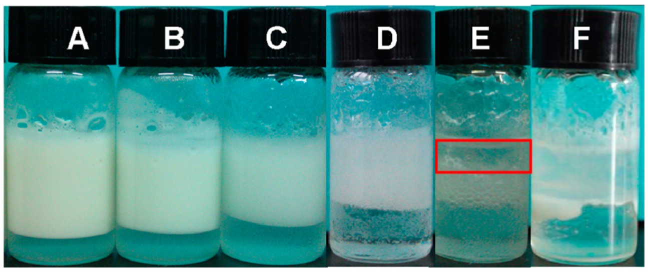


**Figure 2.** Photographs of water in chlorobenzene emulsions stabilized by varied concentration of TSCPNs ((A) 0.1%; (B) 0.05%; (C) 0.01%; (D) 0.0075%; (E) 0.005%) and (F) 0.05% of Span-80 at pH 7. The content represents the weight percent of TSCPNs versus the total weight of water and oil for emulsion formation. The photographs were taken after 24 h of standing at room temperature.

The optical microscope images of emulsion droplets stabilized by didfferent TSCPNs content are shown in Figure 3. Evidently, the size of emulsion droplets gradually increased with the decreasing of TSCPNs content. For example, the average size of droplets was about 10 and 18 $\mu$m, corresponding to 0.1% and 0.05% of TSCPNs content, respectively (Figure 3A and B). When the TSCPNs content decreased to 0.005%, the droplets size increased to 1.5 mm (Figure 3E). The larger droplets size was a result of fewer nanoparticles available on the oil/water interface. The long-term stability of the emulsion was examined by monitoring the variation of the droplets size with the prolonging of placement time. Figure 3F and G shows the optical microscope images of emulsion droplets stabilized by TSCPNs with 0.05% of TSCPNs after 24 h and 45 days placement durations, respectively. Although the droplet size increased and reached 39 $\mu$m after 45 days displacement, an obvious water layer separated from the emulsion was not observed even within a time period of more than 4 months.

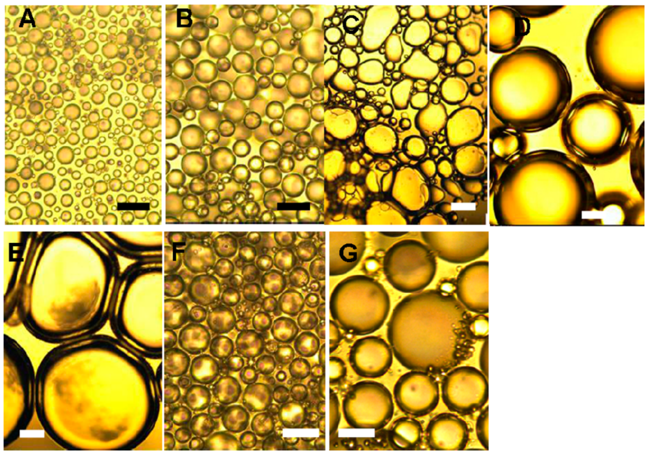


**Figure 3.** Optical microscope images of water in chlorobenzene emulsions stabilized by TSCPNs with varied concentrations versus the total weight of liquid phase at pH 7 ((A) 0.1%; (B) 0.05%; (C) 0.01%; (D) 0.0075%; (E) 0.005%) after homogenization and optical microscope images of water in chlorobenzene emulsions stabilized by 0.05% of TSCPNs at pH 7 after different placement durations ((F) 24 h; (G) 45 days). Scale bar: 30 $\mu$m for (A), (B), (F), and (G); 300 $\mu$m for (C), (D), and (E).

The ultrastability of emulsion originated from the reduction in oil−water interfacial tension. Interfacial tension experiment indicated that 0.125 wt % TSCPNs content in cholorbenzene could effectively lower the chlorobenzene−water interfacial tension from the clean interface value of 37.4 mN m$^{-1}$[48,49] to 15 mN m$^{-1}$. Furthermore, the stabilized O/W emulsion could be easily broken by addition of the poor solvent of TSCPNs. When the emulsion droplets were added to the poor solvent of TSCNPs, the TSCPNs were precipitated and detached from the interface, leading to the coalescence of the droplets.

**Reduction Reaction of *p*-Nitroanisole on the Interface of Oil−Water.** Many water-soluble compounds were necessary required to be participated in some organic reactions. However, the most troublesome problem is the insolubility of organic reactants in water. For Pickering emulsion system, reactants with different solubility could be dissolved separated in different phase, and the reaction could be smoothly carried out on the interface. Therefore, Pickering emulsion could be used as an ideal platform for reactions that are highly favorable in a heterogeneous phase. Many studies on biphase interfacial reaction based on Pickering emulsion have been reported in recent years.[16,22,50,51] Because the catalysis takes place at the interface of the emulsion droplets, a large interfacial area is desirable for a fast conversion. In some cases, the reactants and products could automatically entered the different phase due to the difference in solubility. Therefore, tedious separation was not necessary. In order to demonstrate the potential advantage of the current emulsion system in interfacial reaction, reduction

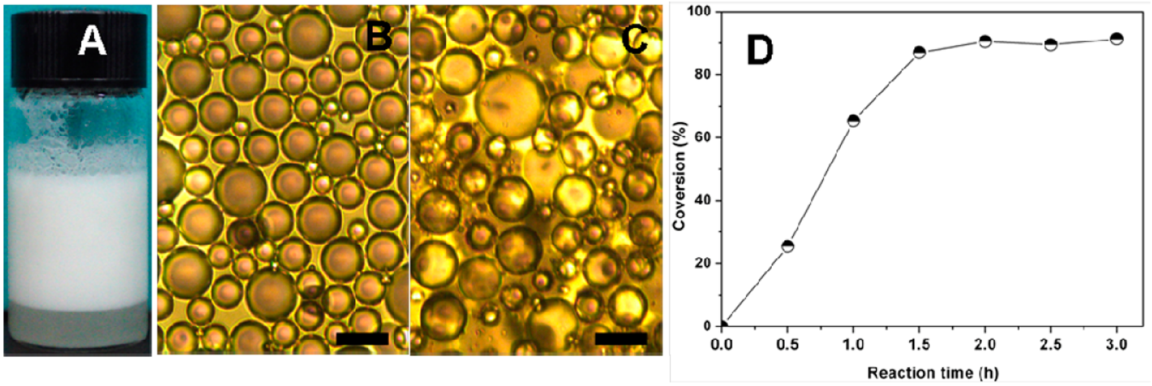


**Figure 4.** Photograph of sodium sulfide (0.1 mol $L^{-1}$) aqueous solution in chlorobenzene emulsions stabilized by 0.05% TSCPNs after homogenization (A). Optical microscope images of sodium sulfide (0.1 mol $L^{-1}$) aqueous solution in chlorobenzene emulsions stabilized by 0.05% of TSCPNs after homogenization (B) and after 24 h of placement durations at 80 °C oil bath (C). Scale bar: 30 $\mu$m. (D) Plot of the conversion of *p*-nitroanisole verse reaction time.

reaction of *p*-nitroanisole by sulfide to *p*-anisidine[16,52,53] was chosen as a model reaction to be studied.

The disperse phase of water was first replaced by 0.1 mol $L^{-1}$ $Na_2S$ aqueous solution, and the stability of the generated emulsion under reaction conditions was studied. Figure 4 shows a photograph of sodium sulfide (0.1 mol $L^{-1}$) aqueous solution in chlorobenzene emulsion stabilized by 0.05% TSCPNs after homogenization (A) and optical microscope images of the formed emulsions after homogenization (B) and 24 h of placement durations at 80 °C (C). No macrophase separation except for a slight increase in droplets size was indicative of a stabilized Pickering emulsion at experimental conditions. Subsequently, a series of reduction reactions of *p*-nitroanisole by $Na_2S$ was carried out at 80 °C in water in chlorobenzene emulsion system. The volume ratio of water to chlorobenzene was fixed to be 1, and the mole ratio of $[Na_2S]$ to [*p*-nitroanisole] was 10. The reaction was stopped after varied time period. After separation of oil from water, the conversion of *p*-nitroanisole was analyzed by HPLC. Figure 4D shows the conversion of *p*-nitroanisole versus reaction time plot. After 3 h of reaction, the conversion of *p*-nitroanisole reached 91.3% based on HPLC analysis. For comparison, reduction reactions of *p*-nitroanisole were also carried out both in emulsion without sodium sulfide and in chlorobenzene/water macroscopical biphase system in the absence of TSCPNs. However, no conversion was found in the absence of sodium sulfide, indicating that there was no reaction between the *p*-nitroanisole and TSCPNs. The conversion of *p*-nitroanisole was only 14.7% in chlorobenzene/water macroscopical biphase system even though the reaction time was prolonged to 5 h. This revealed that the reduction reaction rate was substantially prompted owing to the a large interfacial area.

## CONCLUSIONS

TSCPNs has been efficiently synthesized by intramolecularly cross-linking P4VP block of $PMMA_{2250}$-*b*-$P4VP_{286}$ in DMF using PB as the cross-linker. Owing to the low polymer reactive concentration and an effective steric hindrance shielding from long non-cross-linked PMMA block, the intermolecular cross-linking reaction was prohibited. The synthesized amphiphilic TSCPNs showed a high emulsifying performance, and a stabilized W/O Pickering emulsion could be generated at a extremely low TSCPNs content of 0.0075% versus the total weight of oil and water. The generated W/O emulsion demonstrated a high long-term stability, and no water layer separated from emulsion was observed within a period of more than 4 months. The prepared stabilized emulsion provided an ideal medium for heterogeneous reaction. A large interfacial area facilitated the fast conversion. In addition, some active species, such as catalysis, could be incorporated into the cross-linked head of TSCPNs, and the application of the interface of the emulsion will be widened.

## ASSOCIATED CONTENT

### Supporting Information

FTIR spectra of $PMMA_{2250}$-*b*-$P4VP_{286}$ and TSCPNs, DLS curves of $PMMA_{2250}$-*b*-$P4VP_{286}$ polymer before and after reaction with PB at the polymer concentration of 5 mg·$mL^{-1}$, and $^1H$ NMR spectra of virgin $PMMA_{2250}$-*b*-$P4VP_{286}$ and TSCPNs in *d*-$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: gydx.1027@163.com. Fax: +86 731 58293264. Tel: +86 731 58293264.

### Notes

The authors declare no competing financial interest.

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