Facile Mechanochemical Preparation of Polyamide-derivatives via
Solid-state Benzoxazine-isocyanide Chemistry

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Electronic Supplementary Information

Abstract With the exploration of novel sustainable protocol for functional polyamides’ (PAs) construction as the starting point, herein, the small molecular model compound (M1-ssBIC) was prepared firstly by manual grinding of monofunctional benzoxazine (1a) and isocyanide (1b) via solid-state benzoxazine-isocyanide chemistry (ssBIC) to evaluate the feasibility of ssBIC. Linear PAs (P1-series polymers) were subsequently synthesized from bifunctional benzoxazine (2a) and isocyanide (2b), and the influence of the loading of catalyst (octylphosphonic acid (OPA)) on the polymerization was investigated. Afterwards, two kinds of cross-linked PAs were successfully constructed via ssBIC by using trifunctional benzoxazine (3a) and cross-linked polybenzoxazine (4a) as reaction substrates, respectively, thus verifying the adaptability of ssBIC. Structural characterization indicates that amide, phenolic hydroxyl and tertiary amine substructures, with metal-complexing capability, have been successfully integrated into the obtained PAs. A type of representative PA/silver composite (P3-AgNPs) was prepared subsequently via in situ reduction treatment, and its application as recyclable reduction catalyst for organic pollutant p-nitrophenol (4-NP) was preliminarily investigated here to provide the example for possible downstream application of ssBIC. We think that this current work could provide a new pathway for the construction of functional PAs through facile and sustainable ssBIC protocol.

Keywords Mechanochemistry; Solid-state synthesis; Benzoxazine; Isocyanide; Polyamide

INTRODUCTION

Compared with the liquid-state reaction, the solid-state reaction (SSR) (usually categorised as typical mechanochemical reaction (MCR)) shows the advantages of being independent of the solubility of reaction substrates/intermediates, no need to use solvents, easy scaling up and high reaction speed, etc. Therefore, SSR has attracted intensive attention in recent years to act as a sustainable synthetic approach.[11–14] Up to now, SSR has been successfully utilized in reactions of Scholl,[8] Sonogashira,[6] Michael,[7] Click,[8] and Ritter,[9] etc. Despite the high efficiency of SSR in the preparation of small molecular compounds, there are much fewer reports regarding the preparation of polymers by SSR. In general, mechanical force has been considered as the destruction power for polymer structure.[15–17] The utilization of mechanochemical activation to achieve the growth of polymer chain in solid-state has limited success.[18–20] The exploration of novel solid-state polymerization protocol will provide effective supplement for the development of polymer chemistry.

As one of the typical engineering plastics, the synthesis and application of polyamides (PAs) have been extensively studied. PAs can be used as structural materials with excellent mechanical performance, and have certain application prospect in the fields of functional materials.[20–22] However, traditional syntheses of PAs are mainly carried out by solution/interfacial polymerization in liquid state, and there are only scarce reports on the preparation of PAs by SSR.[23–25] It can be seen from these reports that to realize the preparation of PAs via SSR, it is inevitably to adopt highly reactive, multifunctional aromatic acyl chloride as monomers to propagate with primary amines. It is well known that the preparation, purification and storage of acyl chloride are difficult to be implemented, and sometimes strong alkali solutions have to be introduced as acid-binding agent in SSR preparation of PAs.[23–25] These aspects have brought significant limitations to structural design and subsequent performance modulation of PAs via SSR. Thus, the exploitation of new SSR for the preparation of PAs, which can be carried out under mild condition and with good substrate designing flexibility, is desirable. In 2016, Juaristi et al. reported the preparation of a series of small-molecular amides through mechanical force-activated Ugi and Passerini multicomponent reactions.[26] This
work provided a new idea for the preparation of amides by MCR, but their work did not involve the construction of polymeric amides. Recently, our group exploited novel benzoxazine-isocyanide chemistry (BIC) to act as a powerful tool to construct PAs, and this reaction system displayed some attractive advantages, such as high flexibility in substrates designing, mild reaction condition, practical simplicity, and insensitivity to water/oxygen. However, the above-mentioned BIC reactions were implemented in solution state, and the environmentally unfriendly solvent, chloroform, was used as the solvent. The characteristics of BIC made it possible to be an ideal candidate to realize SSR preparation of PAs. To the best of knowledge, the relevant research has not been reported yet.

Based on the above research background, as a continuation of our recent work regarding BIC (ssBIC), we tested firstly by the synthesis of model compound (M1-ssBIC). Subsequently, linear PA (P1) was successfully prepared via ssBIC to verify its adaptability in polymer construction, and the feed loading of catalyst (OPA) in ssBIC process was optimized. On this basis, the corresponding cross-linked polymer (P2) was prepared by ssBIC [3+2] polymerization between trifunctional benzoxazine (3a) and bifunctional isocyanide (3b) monomers. In addition, an insoluble cross-linked polybenzoxazine (4a) was used as the precursor to obtain corresponding PA (P3) via ssBIC post-polymerization, proving the excellent universality of ssBIC. Structural characterization implies that some functional segments (phenolic hydroxyl, tertiary amine and amide), which possess good metal complexing capability, have been simultaneously introduced into PA’s structure after ssBIC process. Based on this, P3 was selected as the representative polymer to act as the platform for the in situ preparation of polymer/Ag nanoparticles composite (P3-AgNPs). Further study revealed that P3-AgNPs can act as active agent to catalyze the chemical reduction of organic pollutant p-nitrophenol (4-NP).

**EXPERIMENTAL**

### Materials and Instruments

Organic solvents, such as 1,4-dioxane, THF and toluene were used as the solvent. The characteristics of BIC made it possible to be an ideal candidate to realize SSR preparation of PAs. To the best of knowledge, the relevant research has not been reported yet.

Based on the above research background, as a continuation of our recent work regarding BIC (ssBIC) was tested firstly by the synthesis of model compound (M1-ssBIC). Subsequently, linear PA (P1) was successfully prepared via ssBIC to verify its adaptability in polymer construction, and the feed loading of catalyst (OPA) in ssBIC process was optimized. On this basis, the corresponding cross-linked polymer (P2) was prepared by ssBIC [3+2] polymerization between trifunctional benzoxazine (3a) and bifunctional isocyanide (3b) monomers. In addition, an insoluble cross-linked polybenzoxazine (4a) was used as the precursor to obtain corresponding PA (P3) via ssBIC post-polymerization, proving the excellent universality of ssBIC. Structural characterization implies that some functional segments (phenolic hydroxyl, tertiary amine and amide), which possess good metal complexing capability, have been simultaneously introduced into PA’s structure after ssBIC process. Based on this, P3 was selected as the representative polymer to act as the platform for the in situ preparation of polymer/Ag nanoparticles composite (P3-AgNPs). Further study revealed that P3-AgNPs can act as active agent to catalyze the chemical reduction of organic pollutant p-nitrophenol (4-NP).

### Preparation of Benzoxazines

#### Preparation of trifunctional benzoxazine (3a)

4,4′,4′-Trihydroxytriphenylmethane (1.168 g, 4 mmol), aniline (1.116 g, 12 mmol), paraformaldehyde (750 mg, 25 mmol) and toluene (10 mL) were added to a two-necked bottle under N2. The mixture was heated to reflux for 12 h. After cooling to room temperature, the mixture was washed 3 times by distilled water, and the organic layer was separated and dried over anhydrous MgSO4. After evaporation of partially solvent, the concentrate was added dropwise to petroleum ether (200 mL). The precipitate was collected and dried under vacuum at 50 °C for 24 h to obtain white powder (2.341 g, yield ~91%). FTIR (KBr, cm⁻¹): 3035, 2897, 1600, 1497, 1239, 1022, 940. 1H-NMR (400 MHz, CDCl3, δ, ppm): 7.25 (m, 6H), 7.06 (d, J=8 Hz, 6H), 6.91 (m, 3H), 6.79 (d, J=12 Hz, 3H), 6.70 (d, J=8 Hz, 3H), 6.66 (s, 3H), 5.32 (s, 6H), 5.22 (s, 1H), 4.53 (s, 6H). 13C-NMR (101 MHz, CDCl3, δ, ppm): 152.81, 148.46, 136.69, 129.26, 128.85, 127.20, 121.19, 120.58, 118.10, 116.86, 79.27, 54.68, 50.55. TOF-MS Calcd. for C24H28N2O3: 643.2901, Found [M+H]+: 644.2935, [M+H+Na]+: 667.2720, [M+H+2K]+: 722.4346.

#### Preparation of cross-linked poly(benzoxazine) (4a)

4,4′,4′-Trihydroxytriphenylmethane (1.168 g, 4 mmol), 4,4′-diamino diphenyl (1.104 g, 6 mmol), paraformaldehyde (750 mg, 25 mmol) and 1,4-dioxane (15 mL) were added to a two-necked bottle under N2. The mixture was heated to reflux for 12 h. After cooling to room temperature, the precipitate was collected by filtration and purified by Soxhlet extracting (THF as solvent) for 12 h to remove unreacted monomers and oligomers. The product was dried under vacuum at 50 °C for 24 h to obtain yellowish powder (1.675 g, yield ~56%). FTIR (KBr, cm⁻¹): 3026, 2917, 1603, 1494, 1218, 1091, 935.

### Preparation of Model Compound (M1-ssBIC)

1a (106 mg, 0.5 mmol), 1b (90 mg, 0.5 mmol) and OPA (19 mg, 0.1 mmol) were mixed in an agate mortar (with diameter of 5 cm), and ground manually for 15 min. The crude product was purified by column chromatography (silica gel, tetrahydrofuran: petroleum ether=1:8, V/V) and dried under vacuum at 50 °C for 24 h to give white powder (155 mg, yield ~76%). Structural characterization data of M1-ssBIC are consistent with the
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RESULTS AND DISCUSSION

Feasibility Assessment of ssBIC

The main aim of this study is to evaluate the feasibility of ssBIC under ambient conditions (room temperature and without additional water/oxygen isolation). Based on this, the simplest and the most convenient mechanochemical protocol, manual grinding, was selected to implement ssBIC due to its operational convenience and can be implemented with relatively small amount of reaction substrate (as compared to ball milling). In order to verify the feasibility of ssBIC, model molecule (M1-ssBIC) was prepared firstly via ssBIC by using monofunctional benzoxazine (1a) and isocyanide (1b) as reaction substrates with OPA (20 mol%) as catalyst (Scheme 1). Thin-layer chromatography (TLC) monitoring indicated that ssBIC occurred rapidly at room temperature. After 15 min of manual grinding, the yield (purified) of M1-ssBIC (76%) was comparable to that of liquid-state BIC by using chloroform as solvent (reaction time is 6 h).[28] and further extension of grinding time endowed very slight influence to the yield. NMR (Fig. S1 in the electronic supplementary information, ESI) and TOF-MS (Fig. S2 in ESI)

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analyses of M1-ssBIC confirmed that it is consistent with the product obtained by solution method.

To further verify the feasibility of ssBIC in the construction of polymers, bifunctional benzoazine (2a) and isocyanide (2b) were used as monomers (with functionality ratio of 1:1), and OPA (addition of 20 mol%) as catalyst for ssBIC polymerization. After 15 min of manual grinding, the product was dissolved in THF and reprecipitated with ethyl ether. Unfortunately, the dispersion looked like a turbid emulsion, and the corresponding polymer was not obtained after filtration, suggesting that only oligomers were formed at this stage. We speculate that the relatively short reaction time did not provide sufficient contacting opportunities for active oligomer chain ends. The target polymer (P1-20) was successfully obtained after extending the reaction time to 1 h, while the yield was unsatisfactory (~16%). As reflected by Fig. 1, \(^1\)H-NMR spectrum of P1-20 is consistent with reported result of polymer obtained by solution method.\(^{[28]}\) By carefully analyzing Fig. 1 one can find that specific methylene signals, which correspond to N—CH\(_2\)—O (circle) and N—CH\(_2\)—Ar (square) in benzoxazine ring, appear at δ~5.30 and ~4.57 ppm, respectively, suggesting the presence of unreacted benzoxazine end groups in P1-20. We presume that this might be due to the insufficient encountering between catalyst (OPA) and benzoxazine, which stems from the difficulty in diffusion and migration of OPA in solid state. According to previous literatures, compared with traditional solution method, the solid-state protocol sometimes required much more catalyst to promote the extent of reaction.\(^{[14,17]}\) Based on this, the influence brought by the feed ratios of OPA (from 20 mol% to 100 mol%) was investigated. Experimental results (Table S1 in ESI) show that with the increase of OPA, the yields of P1 gradually raise. When the feed of OPA is increased to 100 mol%, the yield of P1-100 reaches ~60% (Table S1 in ESI), which is slightly higher than that of the liquid phase polymerization system (50%).\(^{[28]}\) \(^1\)H-NMR spectrum of P1-100 (Fig. 1) reveals that the benzoxazine methylene signals almost vanish, suggesting that the participation of monomers in ssBIC has been effectively improved by increasing the dosage of OPA.

The effect of OPA addition on the molecular weight of P1 was also explored. The molecular weights of corresponding polymers were analysed by GPC, and the results are summarized in Table S1 (in ESI). GPC results reveal that all polymers possess satisfactory molecular weight (with Mn>8000). Molecular weight dispersity index (PDI) values of P1-20 and P1-40 are 4.73 and 3.66, respectively, which are much greater than PDIs of other three polymers. This indicates that there are molecular chains with considerable discrete chain lengths in P1-20 and P1-40, which might be brought by the insufficient OPA dosage. When the OPA dosages surpass 60%, PDI values tend to be stable. Mn (1.27×10\(^4\)) of P1-100 was comparable to the corresponding value of the product prepared in liquid phase.\(^{[28]}\) Based on this, 100 mol% addition of OPA was selected as a catalyst dosage for subsequent ssBIC experiments.

**Preparation of Cross-linked PAs from ssBIC**

ssBIC [3+2] to construct cross-linked PA (P2) After verifying the feasibility of ssBIC in the construction of linear PAs, we subsequently explored ssBIC’s application in the preparation of cross-linked PAs. In order to construct cross-linked PAs via ssBIC, we need firstly to prepare multifunctional (with functionality>2) benzoxazine or isocyanide monomers. Here 4,4’,4”-trihydroxytriphenylmethane (1), aniline (2) and paraformaldehyde were used as reaction substrates to prepare a novel bifunctional benzoxazine (3a) (Scheme 2), and the bifunctional isocyanide (3b) was chosen as comonomer. The structure of 3a was analysed by \(^1\)H- and \(^{13}\)C-NMR (Figs. 2A and 2B). As shown in Fig. 2(A), methylene proton signals of benzoxazine ring (N—CH\(_2\)—O (a) and N—CH\(_2\)—Ar (b)) appear at δ~5.32 and ~4.53 ppm, respectively, and the proton signal (c) of methine in triphenylmethane appears at 5.22 ppm. There are six groups of aromatic proton signals in the low field (7.25~6.66 ppm), and their respective assignments are shown in Fig. 2(A). Further analysis reveals that the integral of each proton signal is consistent with its structure. As shown in Fig. 2(B), methylene carbon atom signals of benzoxazine (N—CH\(_2\)—O (a) and N—CH\(_2\)—Ar (b)) appear at δ~79.27 and ~50.55 ppm, and the signal (c) of methine appears at 54.68 ppm. Aromatic carbon signals resonate at δ~152.81~116.86 ppm, and their respective assignments are marked. In the TOF-MS spectrum (Fig. S3 in ESI) of 3a, three distinctive mass signals appear at m/z 644.2935 ([M+H]+), 667.2720 ([M+H+Na]+) and 722.4346 ([M+H+2K]+), respectively, in good agreement with the calculated mass value (C\(_{44}\)H\(_{32}\)N\(_2\)O\(_8\), 643.2901). These analyses verify that 3a has been successfully prepared.

Cross-linked PA (P2) was synthesized via ssBIC [3+2] reaction (Scheme 2). Solubility test revealed that P2 was insoluble in common solvents (toluene, CHCl\(_3\), DMSO, THF, etc.), which is reasonable due to its cross-linked molecular skeleton. Chemical structure of P2 was analyzed by FTIR spectrum subsequently (Fig. 3a). As shown in Fig. 3(a), distinct from 3a and 3b, FTIR spectrum of P2 displays distinctive bands at ~1673 and ~3279 cm\(^{-1}\), which belong to the stretching vibration of amide (\(\overset{\equiv}{C}—\text{NH}\)) and phenolic hydroxyl (\(—\text{OH}\)) groups, respectively. In addition, as compared to that of 3a, the characteristic absorption of benzoxazine ring (~940 cm\(^{-1}\)) in P2 significantly weakens. Besides, there is no appearance of

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*Fig. 1* \(^1\)H-NMR spectra of P1-20 and P1-100.
−NC band at ~2120 cm$^{-1}$ in the FTIR spectrum of P2, indicating that benzoxazine/isocyanide groups sufficiently participated in ssBIC. Parallel experiment of the preparation of P2 in solution state (P2-solution) was also carried out, and one can note that the FTIR spectra (Fig. S4 in ESI) of P2-ssBIC and P2-solution highly resemble each other, suggesting the feasibility of ssBIC in the construction of cross-linked PA. By carefully analysing the FTIR spectrum of P2-solution, one can find...
the weak band of residual $-$ NC at $\sim$2120 cm$^{-1}$ (Fig. S4 in ESI). In contrast to this, the $-$ NC signal is hard to be detected in the FTIR spectrum of P2-ssBIC, suggesting that ssBIC displays superiority to liquid-reaction in the preparation of cross-linked polymer, owing to the ignorance of solubility issue during solid-state process.

Solid-state $^{13}$C-NMR (CP/MAS) spectrum of P2 suggests the presence of C=O, C–O&C–N, aromatic carbons and methylene/methine carbons (Fig. S5 in ESI). XPS analysis was also carried out to investigate the chemical composition and state of elements contained in P2. As shown in Fig. 3(b), the full scan spectrum of P2 shows the presence of C, N and O elements. High-resolution C 1s XPS spectrum (Fig. 3c) displays three obvious peaks at 284.4 eV (C$-$C/C$-$H), 285.6 eV (C$-$OH/C$-$N) and 287.7 eV (C$=$O).$^{[34,35]}$ High-resolution N 1s spectrum (Fig. 3d) splits into two peaks at 400.3 and 399.7 eV, which can be assigned to amide (O$=$C$-$N) and tertiary amine (C$-$N) groups, respectively. O 1s spectrum in Fig. 3(e) displays two obvious peaks at 532.8 eV (O$=$C$-$N) and 531.4 eV (C$=$OH). The composition of each element is summarized in Table S2 (in ESI).

The microstructure characteristic of P2 was analysed by SEM and TEM. SEM (Fig. 4a) shows that P2 has a loose block structure, with rough surface and many wrinkles. As shown in

![Fig. 3](https://doi.org/10.1007/s10118-021-2510-6)
Fig. 4(b), TEM image of P2 exhibits agglomerated structure with bright and dark contrast, suggesting there might be preliminary pore structure inside. Figs. 4(c) and 4(d) display the isothermal adsorption-desorption and pore size distribution curves of P2. The BET specific surface area (SSA) of P2 was 11.5 m²·g⁻¹, and the pore was dominated by mesopores (DFT method) (Fig. 4d). The small SSA of P2 might be due to the presence of flexible methine and amide substructures, which caused partial pore structure collapse during polymerization.

Constructing cross-linked polyamide (P3) by ssBIC post-polymerization

In order to further verify the adaptability of ssBIC, an insoluble, cross-linked polybenzoxazine precursor (4a) was selected as the reaction substrate to investigate the feasibility of ssBIC in post-polymerization modification. 4,4',4''-Trihydroxytriphenylmethane (1), 4,4'-diaminobiphenyl (3) and paraformaldehyde were used as starting materials to prepare a cross-linked polybenzoxazine (4a). Subsequently, 4a and 3b were reacted to construct the cross-linked PA (P3) by ssBIC (Scheme 2). FTIR analyses reflect the presence of amide (~1667 cm⁻¹) and phenolic hydroxyl (~3222 cm⁻¹) groups relative to that of 4a and 3b, respectively. Solid-state ¹³C-NMR (CP/MAS) spectrum of P3 (Fig. S5 in ESI) resembles that of P2, which is resolvable due to the similar structural skeletons of both polymers. As the discussion for P2, XPS analysis (Figs. 5b–5e) of P3 indicates that P3 also contains amide, phenolic hydroxyl and tertiary amine groups.

SEM image reflects that the surface of P3 (Fig. 6a) is rough and with many gullies and wrinkles. TEM image (Fig. 6b) of P3 exhibits a contrast between light and dark regions, indicating that P3 has preliminary pore structure. Figs. 6(c) and 6(d) are the isothermal adsorption-desorption and pore size distribution curves of P3. The BET results (Fig. 6c) show that the SSA of P3 is 23.7 m²·g⁻¹, and the pore size distribution (Fig. 6d) is also dominated by mesopores. As can be seen from Table S2 (in ESI), P3 displays higher SSA and overall pore volume than those of P2, which might be due to the stabilization effect brought by the cross-linked skeleton structure of ssBIC precursor (4a).

The above analyses reveal that ssBIC can work smoothly even when using insoluble cross-linked polybenzoxazine as substrate. The summarization of mechanochemical preparation of polyamide-derivatives by us and other groups has been carried out here (Table S3 in ESI). As revealed by Table S3 (in ESI), compared to available reports about mechanochemical preparation of PAs, the ssBIC polymerization protocol utilized in this work displayed advantages in wide range of monomers, high structural designing flexibility and no requirement for basic additives, etc.

Preparation and Characterization of P3-AgNPs

According to previous literatures, thanks to the containing of lone pair electrons on O/N atoms, molecular fragments such as amide, phenolic hydroxyl and tertiary amine groups...
display strong complexation with metal ions. These functional substructures have been successfully integrated into the target PAs by ssBIC (Scheme 2), suggesting that these PAs might complex with metal ions and can be used as substrates to load metal nanomaterials by further in situ reduction treatment. Since P3 has rough surface (Fig. 6a) and relatively large SSA than P2, it was selected here to act as matrix for the loading of metal nanomaterials. Compared with other metal nanoparticles such as Au, Pt and Pd, Ag nanoparticles are relatively inexpensive and possess special chemical activity. Therefore, the preparation of P3/Ag nanocomposite (P3-AgNPs) was attempted. Firstly, Ag⁺ and P3 were stirred in a mixed solvent (methanol:H₂O=1:5, V/V) overnight to uniformly load Ag⁺ on P3 (P3-Ag⁺). The reaction mixture was centrifuged to remove free Ag⁺, and the corresponding P3-AgNPs were obtained by subsequent in situ reduction of P3-Ag⁺ by NaBH₄. As shown in FTIR spectra of P3 and P3-AgNPs (Fig. 7a), relative to that of pristine P3 (−1662 cm⁻¹), the absorption of amide group in P3-AgNPs (−1685 cm⁻¹) displays ~23 cm⁻¹ shift to the higher wavenumber region,[25,27] hinting that the amide groups in P3 play an important role in the loading of AgNPs. Further XPS analysis provides more direct evidence for the successful loading of AgNPs. Full scan XPS spectrum of P3-AgNPs displays an obvious signal at 368.11 eV (Fig. 7b), which belongs to the

Fig. 5 FTIR spectra of P3, 4a, 3b (a), the full scan (b), C 1s (c), N 1s (d) and O 1s (e) XPS spectra of P3.
Fig. 6  SEM image (a), TEM image (b), isothermal adsorption-desorption curve (c) and pore size distribution curve (d) of P3.

Fig. 7  FTIR spectra of P3 and P3-AgNPs (a), full scan (b) and Ag 3d scan (c) XPS spectra and XRD pattern (d) of P3-AgNP.
signal of Ag 3d.[39−41] High-resolution XPS spectrum of Ag 3d (Fig. 7c) clearly shows peaks at 368.4 and 374.4 eV, which can be assigned to Ag 3d_{5/2} and Ag 3d_{3/2}. The spin energy difference between these two peaks is ~6.0 eV, indicating that Ag exists in the zero-valent state here.[39−41] Moreover, XRD pattern of P3-AgNPs (Fig. 7d) exhibits distinctive diffraction signals at 38.1°, 44.2°, 64.4°, and 77.3°, corresponding to (111), (200), (220), and (311) lattices of AgNPs (JCPDS 89-3722), and the average crystalline size calculated by the Scherrer equation is ~12.8 nm.

As shown in the SEM image of P3-AgNPs (Fig. 8a), P3-AgNPs were formed by the accumulation of microplates, and with rough surface. DLS characterization tells that the average diameter of P3-AgNPs is ~1062 nm (Fig. 56 in ESI). In TEM image (Fig. 8b) one can clearly observe that AgNPs have been loaded in polymer matrix. No detached free AgNPs were observed in TEM image (Fig. 8b), suggesting the strong affinity between P3 and AgNPs, which might be due to the presence of metal-complexing amide, hydroxyl and ternary amine segments in P3’s structure. Locally enlarged TEM image (Fig. 8c) shows that AgNPs with diameters of 8 ± 3 nm (evaluated by one hundred randomly selected points) uniformly distribute in polymer platform. As shown in HR-TEM image of P3-AgNPs (Fig. 8d), the lattice spacing of AgNP equals 0.233 and 0.209 nm, corresponding to (111) and (200) plane of silver, respectively.[39] The corresponding selected area electron diffraction (SAED) pattern is shown in Fig. 8(e), which reflects the polycrystalline nature of AgNPs.[39] ICP-MS analysis tells that the composition ratio of silver in P3-AgNPs is ~5.78%.

**Catalytic Reduction of 4-NP by P3-AgNPs**

AgNPs have excellent catalytic reduction activity and have been applied to realize the chemical degradation of dyeing wastewater and nitro compounds.[37,39,40] It can be seen from above analyses that AgNPs have been uniformly loaded in P3 platform, and the presence of inert polymer substrate might be helpful to improve AgNPs’ catalytic stability and thus can afford recyclable catalyst. Here we selected the toxic p-nitrophenol (4-NP) as the degradation target, and used NaBH₄ as the reducing agent to investigate the catalytic reduction activity of P3-AgNPs. With the introduction of aqueous NaBH₄ solution, 4-NP solution shows yellow colour due to the formation of p-nitrophenolate ion, and its concentration can be monitored by the absorption at ~400 nm.[30,42] As shown in Fig. 9(a), after the addition of P3-AgNPs, with the extension of reaction time, the absorption at ~400 nm gradually decreases. At the same time, the absorption of reduction product, 4-aminophenol (4-AP), appears at ~300 nm,[30] and its intensity increases continuously. The apparent color of reaction system gradually changes from yellow to colourless (inset of Fig. 9a). After 8 min of reaction, the absorption at ~400 nm almost disappears, indicating that 4-NP has been completely reduced. Parallel experiment tells that NaBH₄ alone cannot reduce 4-NP and the apparent color retains after stirring at room temperature overnight, indicating that P3-AgNPs have good catalytic reduction activity for 4-NP.

The catalytic kinetic of 4-NP by P3-AgNPs was evaluated by a pseudo first-order kinetic equation as:

$$\ln \left( \frac{c_t}{c_0} \right) = kt$$

where $k$ is the rate constant (min$^{-1}$), $t$ is the reaction time (min), $c_0$ and $c_t$ are the initial and $t$ time concentrations of 4-NP, respectively.

As shown in the ln($c_t/c_0$)-t relationship curve (Fig. 9b), the rate constant is evaluated to be 0.816 min$^{-1}$, indicating that P3-AgNPs have high catalytic activity. The catalytic stability of P3-AgNPs was evaluated by catalyst recovery experiments. As shown in Fig. 9(c), the catalytic efficiency maintains ~92% of the initial value after 5 cycles of catalyzing/recovery process, indicating that the presence of polymer substrate effectively improved the chemical stability of AgNPs.
Multifunctional benzoxazines were used subsequently as reaction substrates to construct cross-linked PAs (P2 and P3) by ssBIC, further testifying the universality of ssBIC to construct PAs. To exploit the possible application of the synthesized PAs, P3 was selected as the substrate to prepare polymer/AgNPs composites (P3-AgNPs) by in situ reduction treatment. We found that P3-AgNPs can act as efficient and recyclable catalyst for the reduction of 4-NP. The ssBIC reported here displayed advantages of simple operation, mild condition, high efficiency, high substrate designing flexibility and with no solubility limitation, which can act as prospective pathway for sustainable preparation of functional PAs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-021-2510-6.

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