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## Poly(N-cyanoethylethyleneimine): A new nanoscale template for biomimetic silicification

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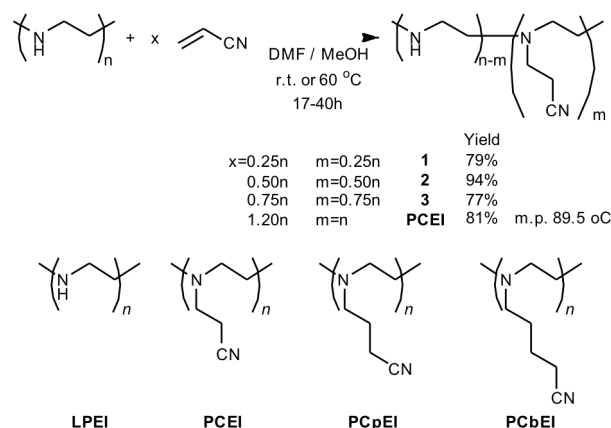
**Poly(N-cyanoethylethyleneimine) (PCEI) obtained by Michael addition of linear poly(ethyleneimine) (LPEI) with acrylonitrile provided novel nanocrystalline entities which could play as catalytic templates affording nanosheet-based structured silica under mild conditions.**

Beautiful shapes and precise patterns seen in diatoms biosilica have received considerable attention from materials scientists. In silica biomineralization, proteins and natural polyamines are generally acting as matrices to promote the condensation of silicic acid.<sup>1</sup> Mimicry of silica biomineralization has been actively investigated in the presence of certain additives and templates.<sup>2,3</sup> Especially, synthetic polyamines such as poly(L-lysine) and its block copolymers,<sup>4,5</sup> amine-terminated dendrimers,<sup>6</sup> branched poly(ethyleneamine),<sup>7</sup> poly(allylamine)-hydrochloride,<sup>4,8</sup> and poly(propyleneimine) and its derivatives<sup>3c,9</sup> are frequently used as templates and catalysts for biomimetic silica deposition. The method based on synthetic polyamines is advantageous over the conventional methods as a preparative method of nanosilicas, because the polyamines not only play as templates but also work as catalysts to direct successfully the nanostructured silicas. In our previous papers, we reported unique catalytic templates with tunable crystalline morphologies consisted of linear poly(ethyleneimine)s (LPEI) which are capable of producing tube, ribbon, fiber, and sheet-based nanostructured silicas.<sup>10,11</sup> The easy formation of such divergently controlled silica structures is due to the crystalline feature of LPEI possessing secondary amine in its backbone. Therefore, finding out polyamines with crystalline feature is still a challenge for developing templating-chemistry of mineralization. Herein, we report the synthesis of poly(N-cyanoethylethyleneimine) (PCEI) via Michael addition reaction of LPEI with acrylonitrile and its unique feature of forming crystallites which play effectively as catalytic templates for biomimetic silica deposition under neutral aqueous conditions without any additives.

Synthesis of PCEI was performed by treatment of LPEI with acrylonitrile by a similar procedure that used for the reaction of LPEI with methyl acrylate.<sup>12</sup> LPEI was synthesized by hydrolysis of commercially available poly(2-ethyloxazoline) (Mw = 50000).<sup>10</sup> As shown in Scheme 1, treatment of LPEI with an excess of acrylonitrile (AN) at 60°C for 40 h in DMF/MeOH afforded PCEI in 81% yield. In contrast, when the feeding ratio of AN to the EI unit was lower than 1, the corresponding polymers were random copolymers poly(CEI<sub>m</sub>-co-EI<sub>n</sub>) such as m : n = 25 : 75 (**1**), 50 : 50 (**2**), and 25 : 75 (**3**), respectively. We also synthesized two PCEI analogues of poly(3-cyanopropylethyleneimine) (PCpEI) and poly(3-cyanopropylethyleneimine) (PCbEI) with side chains of

cyanopropyl and cyanobutyl via reaction of iodobutylonitrile or iodovaleronitrile with –NH– site of LPEI in the presence of Et<sub>3</sub>N in DMF/MeOH at 55°C for 67 h. The isolated yields of the products PCpEI and PCbEI were about 20%, but the secondary NH group of LPEI were completely substituted by the cyanoalkyl group. All the polymers were identified by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FT-IR (Fig. S1-S5). <sup>1</sup>H-NMR spectrum of PCEI showed two broad triplets due to methylene protons of the cyanoethyl group at 2.50 and 2.78 ppm, and one singlet due to the methylene group at 2.58 ppm in the main chain of PCEI (Fig. S1e). In the <sup>13</sup>C NMR spectrum of PCEI, a singlet assigned to the methylene carbon in LPEI chain is accompanied by three singlets due to the three carbons in the group of –CH<sub>2</sub>CH<sub>2</sub>CN (Fig. S3). These data are accordance with PCEI synthesized by a ring opening polymerization of N-cyanoethyl aziridine.<sup>13</sup> FT-IR spectra showed one strong absorption band around 2243~2245 cm<sup>-1</sup>, which is assigned to the –C≡N stretching vibration of cyanoethyl group (Fig. S4). In comparison, <sup>1</sup>H and <sup>13</sup>C-NMR spectra for **1**, **2** and **3** are not straightforward (Fig. S1-3).

We confirmed the solubility of PCEI in different media (see Table S1). In contrast to LPEI, PCEI is insoluble in water even heated about to 90°C. Methanol is also non-solvent but DMF and acetonitrile are good solvents to completely dissolve PCEI. When mixed solvent containing DMF and water or methanol was used, PCEI becomes soluble at 60°C. As cooling the solution to room temperature, PCEI precipitates. We found that the non-solubility of PCEI in water or methanol is due to its strong crystalline property.



Scheme 1. Schematic representation of the synthesized polymers: the derivatives of LPEI substituted by cyanoethyl group with 0.25 equiv. (**1**), 0.50 equiv. (**2**), and 0.75 equiv. (**3**) of acrylonitrile; as well as LPEI, PCEI, PCpEI and PCbEI.

Different to LPEI which crystallizes in water with association of water molecules, the crystallites PCEI forms in the mixed medium of DMF containing a small non-solvents such as water and methanol. We prepared the PCEI crystallites by heating (60°C) and cooling (room temperature) cycle of mixtures containing certain amount of 5wt% PCEI solution in DMF and a small amount of water. The precipitates after washing by water were subjected to XRD measurement. Figure 1 showed XRD patterns of solidified samples of PCEI, **1**, **2**, **3** as well as LPEI. We can see that PCEI shows four sharp peaks at  $2\theta=14.8$ , 19.1, 20.3 and 21.9°, with several broad peaks. These diffractions were completely different from those of LPEI, indicating that crystalline structure was different than that of LPEI. No peak appeared for random copolymers **1** and **2** (Fig. 1a, b), but the diffraction of **3** showed a weak peak at 21.9° (Fig. 1c). It seems that the higher component of N-cyanoethyl ethyleneimine unit in the copolymer backbone is benefit to give crystallites. We also compared PCpEI and PCbEI in XRD and found that PCpEI trended to crystallization but PCbEI did not (Fig S6e, f). Furthermore, we subjected the crystalline PCEI to TG and DSC measurements and found that there is no or little weight loss until 120°C and melting

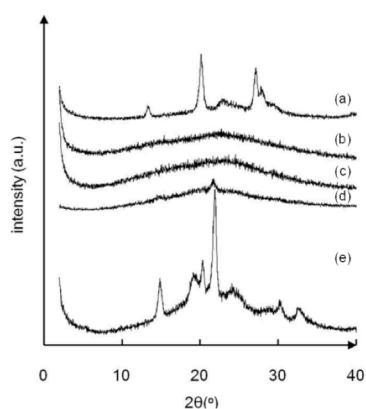


Fig. 1. XRD patterns of (a) LPEI dehydrate and the derivatives of LPEI (b) **1**, (c) **2**, (d) **3**, and (e) PCEI.

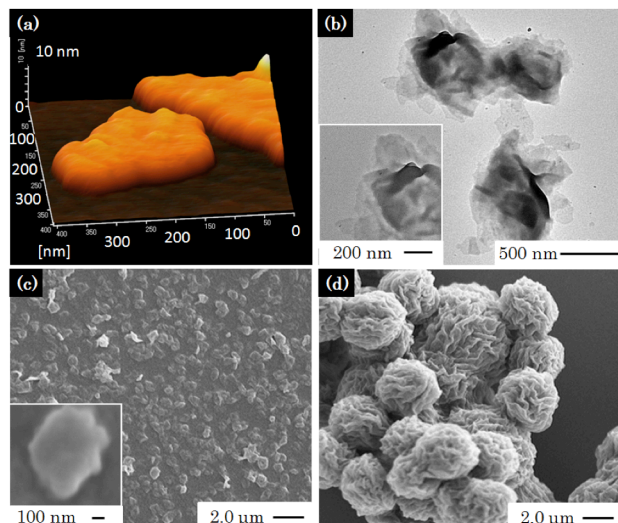


Fig. 2. AFM (a) and TEM (b) images of PCEI-NS. SEM images of PCEI-NS (c) and PCEI-G (d).

point (89–92°C) almost unchanged between the first and the second heating runs (Fig. S7). This is indicative of the absence of water molecules in PCEI crystalline structure and is distinguishable with the crystallites of LPEI which always associated with water molecules as crystallization in atmosphere.<sup>12</sup> No water association in the formation of PCEI crystallites would be favour to enhance the stability of the crystalline morphologies and thus be adaptive for using them as versatile templates in mineralizations.

In order to understand the morphology of the PCEI crystallites, we visualized the PCEI crystallites obtained from DMF/H<sub>2</sub>O medium by AFM, SEM and TEM. Interestingly, the crystallites developed from the medium of DMF/H<sub>2</sub>O = 3.2 appeared as isolated nanosheets with major width of about 300 nm and the thickness of about 6 nm (Fig. 2a). TEM and SEM images also supported the nanosheets structure with several hundred nanometers width (PCEI-NS; Fig. 2b, c). When DMF content lowered somewhat to DMF/H<sub>2</sub>O = 2.5, there appeared micrometer scale globular aggregates with crumpled surface image (Figure 2d). It seems that the lower content of DMF could not make the nanosheets crystallites keep as isolated state and causes the aggregation of the nanosheets into globular morphology. Such globular morphology was also available by neutralization of aqueous solution of protonated PCEI-HCl in the absence of DMF (Fig. S8). †

We examined whether the two entities with different crystalline morphologies, PCEI-nanosheets (PCEI-NS) and PCEI-globe (PCEI-G), behaved as catalytic templates for silica deposition. The powders of PCEI-NS or PCEI-G dispersed in distilled water (which showed pH 6.1) were mixed with tetramethoxysilane (TMOS) and the mixture was stirred at room temperature for 3 hrs. This procedure yielded white solids of SiO<sub>2</sub>@PCEI-NS and SiO<sub>2</sub>@PCEI-G, respectively. We characterized the solids fractions by FT-IR, TG-DTA, SEM and TEM. In FT-IR spectrum, a strong vibration peak due to Si-O-Si bond of silica appeared at 1079 cm<sup>-1</sup> indicating the silica formation on the PCEI templates to form silica/PCEI hybrids. From TG-DTA measurement, we confirmed 45wt% and 31wt% weight loss in a temperature range 100–800°C for SiO<sub>2</sub>@PCEI-NS and SiO<sub>2</sub>@PCEI-G, respectively, indicating that the 55wt% and 69wt% residues belong to silica. From the SEM observation, it is evident that the silica SiO<sub>2</sub>@PCEI-NS mediated from PCEI-NS showed very thin, curved, and elliptical morphology similar to the shape of the PCEI-NS prior to the silica deposition (Fig. 3a, b, c). The silica nanosheets were separated well each other. The width of the silica nanosheets was around 0.4–1 μm, whereas the thickness was about 15 nm (Fig. 3c). On the other hand, SEM images of the silica SiO<sub>2</sub>@PCEI-G mediated from PCEI-G showed globular appearance with ca. 2 μm diameters, but the every globe is piled up by a lot of nanosheets (Fig. 3d) similar to the appearance of PCEI-G. Interestingly, the curved nanosheet and globular morphologies remained without changes even after calcination of the silica/PCEI hybrids at 800°C (see Fig S9). This result strongly support that the nanosheet silica is thermo-resistance when the PCEI was removed. Remarkably, the crystalline PCEI entities based on nanosheets structures play effectively as catalytic templates to promote silicification of TMOS. In this process, the crystalline morphologies can be completely transferred to the resulting silica without deformation. We also examined silica deposition on the polymers **1**, **2**, and **3** under similar conditions as above. No detectable silica deposition occurred from **1** and **2**. In sharp contrast, globular silica with piling many nanosheets, which is similar to those formed from PCEI-G, was selectively templated from **3** regardless of DMF/water ratios (Fig. S10). Also, PCpEI promoted the hydrolytic polycondensation of TMOS to give silica with a mixture of spheres (100–500 nm) and nanosheets (Fig. S11a). Silica from PCbEI was a mixture of bulk materials (Fig. S11b). These results clearly suggest

the importance of the cyanoethyl group in PCEI for silicification, which enables to construct nanosheet-based silica structures.

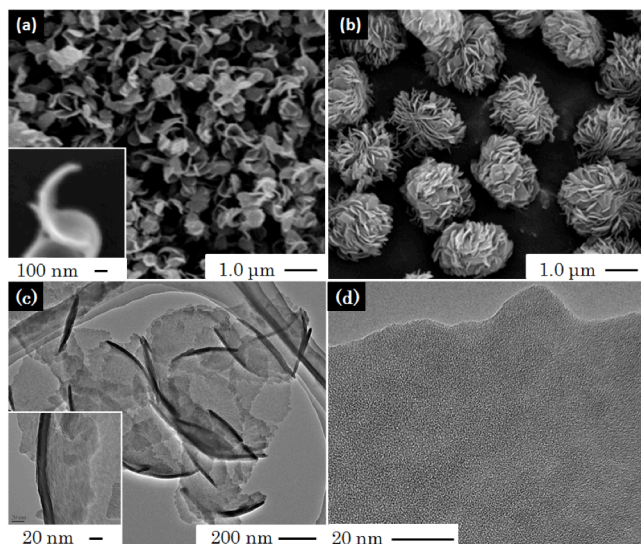


Fig. 3. SEM images of (a)  $\text{SiO}_2$ @PCEI-NS and (b)  $\text{SiO}_2$ @PCEI-G. TEM and HR-TEM images of (c)  $\text{SiO}_2$ @PCEI-NS and HR-TEM (d). The inset in (c) showed edge of curved silica.

We speculate that the nanosheet formation of PCEI is related to the lamella crystallites. In the sense of the formation of very thin nanosheet, we can say that the PCEI crystallites would be single layered lamella structure. Probably, the dipole-dipole interaction of the cyanoethyl groups hanged on the LPEI backbone is non-negligible in the growth of 2-dimensional crystallites. When the cyanoethyl was replaced by the cyanopropyl and cyanobutyl, the corresponding polymers such as PCPEI and PCBPEI did not show crystallinity. Further investigation on the poly(cyanoalkylethyleneimines) is required for understanding their crystalline features. Nevertheless, it is worth to point out that the 2-dimensional lamellae-based crystalline behavior of the PCEI and its catalytic templating function are very unique and desirable in the mineralization for design of nanostructured materials.

In summary, we synthesized PCEI and P(EI-co-CEI) copolymers via conjugate addition of LPEI with acrylonitrile under the mild conditions. The other two polymers with cyanopropyl and cyanobutyl groups as analogues of PCEI were also prepared by different synthetic routes. All of the polymers prepared were employed in silica deposition, and two of them having crystalline feature, PCEI and **3**, were confirmed as effective candidates for templating nanosheet-based silica materials. Further work for templating other metal oxides is currently undergoing.

## Notes and references

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† As shown in Fig. S8, crystallization behavior of LPEI and PCEI was compared by acid-base titration. Both LPEI and PCEI are soluble in water

under acidic conditions ( $\text{pH} < 5$ ). Titration of an acidic solution of LPEI by NaOH (aq) led to the crystallization of LPEI as pH arrived at 9~10, whereas PCEI crystallization occurred under slightly acidic conditions ( $\text{pH} = 5\text{--}6$ ). It means that crystallites of PCEI are more stable than that of LPEI in a wide range of pH values and thus usable as templates even under slightly acidic conditions. Electronic Supplementary Information (ESI) available: Experimental sections, spectra of NMR and FT-IR, XRD patterns, DSC and titration curves, SEM and TEM images (Fig. S1-11, Table S1). See DOI: 10.1039/c000000x/

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Table content entry

Nanocrystalline entities of poly(N-cyanoethylethyleneimine) (PCEI) could play as catalytic templates affording nanosheet-based structured silica under mild conditions.

