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# Supramolecular Template-Directed Synthesis of Perfect Phenelenediimino-Bridged Ladderlike Polyphenylsiloxanes

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**Abstract:** A template synthesis of the soluble, high molecular weight ($M_w$), and perfect *p*-phenylenediimino (*p*-PDA)-bridged ladderlike polyphenylsiloxane (PLPS) is reported. First, *N,N'*-bis(phenyldichlorosilyl)-*p*-PDA monomers were self-assembled into a perfect ladder superstructure (LS) by concerted interaction of aromatic π–π stacking and hydrogen bonding. Then the LS underwent a novel stoichiometric hydrolysis/dehydrochlorination–condensation reaction instead of the usual hydrolysis/dehydration–condensation reaction, leading to the PLPS. The perfect ladder structures of both the PLPS and, in particular, the unstable supramolecular LS were confirmed as follows. 1) There are two Bragg peaks in solid and/or solution X-ray diffraction (XRD) spectra representing the ladder width (*w*) and ladder thickness (*t*); these peaks were consistent with those calculated by molecular simulation. 2) Both the PLPS and LS have extremely sharp absorption peaks with small half-peak widths ($\Delta_{1/2} < 0.3$ ppm) in $^{29}$Si NMR spectra, suggesting the presence of the perfect ladder structure for PLPS and LS. 3) Moreover, no noticeable absorption peaks for the Si–OH and $NH_2$ groups were observed in FT-IR and $^{29}$Si NMR spectra, indicating that the Si–N bond of the ≡Si-NH-$C_6H_4$-NH-Si≡ ladder rung of PLPS and LS is not cleaved. 4) Both PLPS and LS show similar emission peaks (in fluorescence spectroscopy) attributed to the excimer formed by face-to face π–π stacking of phenyl groups along the ladder chain rather than a branched direction. 5) Differential scanning calorimetry (DSC) measurements indicate a high glass temperature ($T_g = 176.4$ °C) for PLPS. As circumstantial evidence, this result further indicates very high stiffness of PLPSs ladder backbone as compared with flexible single-chain polyphenylmethylsiloxane with a low $T_g = -69.4$ °C.

**Keywords:** hydrolysis · ladder superstructure · self-assembly · silicon · supramolecular chemistry

## Introduction

It is known that ladderlike polymers, that is, a special type of double-stranded polymer, possess much higher resistance to thermal, chemical, mechanical, and biological degradation, relative to the common single chain polymers. The reason for this is that the probability of breaking of two bonds on the same ladder rung is far less than breaking of a single bond. Furthermore, ladderlike polysiloxanes, including organo-bridged polysiloxanes, and ladderlike polysilsesquioxanes are attractive for radiation- and heat-resistant applications, since the bond energy of the Si–O linkage is much higher than that of the C–C and C–O ones.[1] They possess considerable interest as "self-healing" high-temperature nanostructured materials, space-survivable coatings,[2,3] low-*k* dielectric materials,[4] and, in particular, promising candidates of microstructure-controllable tubular and sieve-plate polymers.[5] However, preparation of the real ladderlike polysiloxane from a multifunctional monomer has many straightforward difficulties, that is, insolubility, cross-linking, and statistical considerations. As early as 1960, Andrianov et al. attempted to synthesize a *p*-phenylene-bridged polysiloxanes,[6] but they only obtained some oil-like oligomers and cross-linked gels. Recently, our group prepared a series of ordered organo-bridged ladderlike polysiloxanes through intermediate ladder superstructures (LSs) constructed by concerted interaction of aromatic π–π stacking and/or hy-

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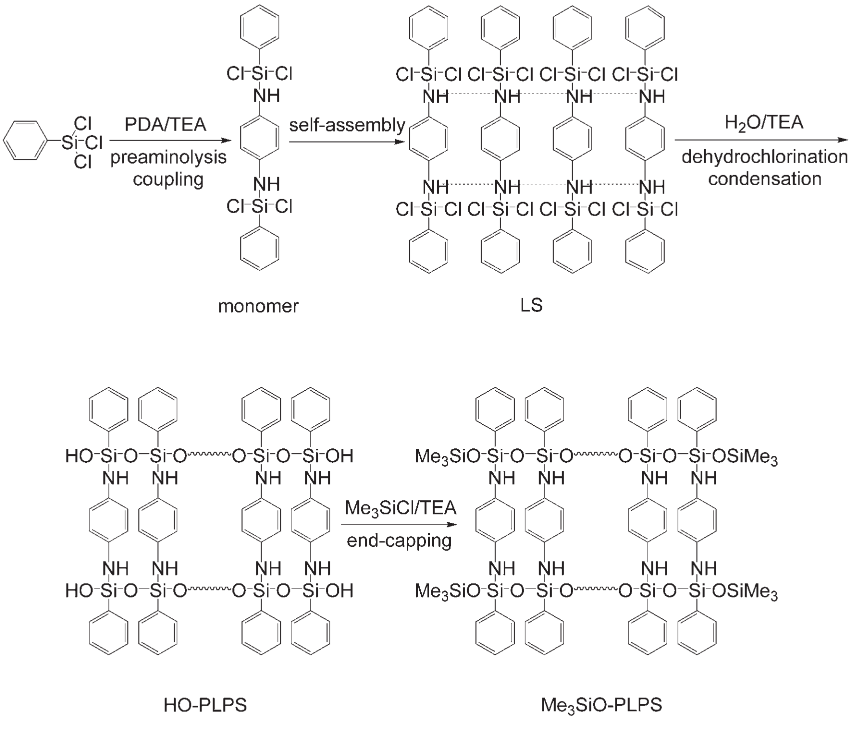
drogen bonding.[7–12] Generally, the $\Delta_{1/2}$ values of $=\mathrm{SiO}_{2/2}$ moieties of these polymers range from 0.6 to 2 ppm, suggesting that these organo-bridged ladderlike polysiloxanes are not perfect ladderlike polymers. The reason is that monomers containing strongly polar groups (such as hydroxyl or amide ones) are only dissolved in specific polar solvents (such as DMF or DMSO) rather than the less polar solvents. As a result, hydrogen-bonding interactions in the monomer are greatly weakened and the ladder regularity of organo-bridged ladderlike polysiloxanes is also decreased. On the other hand, with respect to the polysilsesquioxane ladder, Brown et al.[13] first reported the synthesis of a soluble polyphenylsilsesquioxane ladder by means of an "equilibration polymerization" method in 1960. However, his result was refuted 11 years later by Frye et al.,[14] who pointed out that the polyphenylsilsesquioxane ladder is not a complete ladderlike polymer, but "partially opened polycyclic cages". In 2004, Yamamoto et al.[15] reported an oligomeric polyphenylsilsesquioxane ladder with low ladder regularity. As Brook mentioned, the ladderlike polyphenylsilsesquioxane is not universally accepted[16] and the ladder structure may result under certain conditions (i.e., bioprocess). The crux of the failure was that the reactive intermediates (phenylsilanetriols) or its derived oligomers easily formed some randomly interlaced aggregates rather than the ordered LSs. Evidently, the key to preparation of the perfect ladderlike polymer is that either both sides of the ladder must be formed simultaneously or no reaction occurs. We have tried to prepare perfect ladderlike polyphenylsilsesquioxanes by conventional hydrolysis/dehydration–condensation reactions of the monomer, *N*,*N*′-bis(phenyldichlorosilyl)-*p*-PDA (PDA = phenylenediimino), but we have not got satisfied results yet from this methodology. Our preliminary research showed that the $\Delta_{1/2}$ was about 4 ppm due to the unavoidable hydrolytic rupture of the Si–N bonds of monomer during condensation.[17,18]



Scheme 1. Synthetic route for the formation of PLPS.

In summary, for over 45 years, the question of whether the high $M_w$ and perfect ladderlike polysiloxanes can be synthesized has remained unanswered. This problem has become a tantalizing target for polymer chemists. Here, we report a new approach—a stoichiometric hydrolysis/dehydrochlorination–condensation reaction—to the perfect ladderlike polysiloxane (PLPS) instead of the conventional hydrolysis/dehydration–condensation reaction used before. By using this new method not only can the perfect PLPS be obtained, but also the perfect ladderlike polyphenylsilsesquioxane could be derived from PLPS because PLSP has sacrificial ladder rungs of Si–N bonds that can be readily converted into an ordered ladderlike polyphenylsilsesquioxane by means of a mild acid-catalyzed hydrolysis in polar solvent and condensation.[19] In addition, it is worth noting that the LSs, which are extremely susceptible to ambient environment (pH, humidity, solvent polarity and temperature, etc.), have been substantiated by X-ray diffraction (XRD), NMR and fluorescence spectroscopy, and a series of control experiments (adding hydrogen-bonding blocking reagent, urea, to destroy template effect of the LS) for the first time.

## Results and Discussion

**Dehydrochlorination–condensation reaction**: The polymerization mechanism for PLPS is shown in Scheme 1. To prepare the perfect PLPS it is extremely important to bring the template effect of the LS into full play throughout the synthetic process.

Generally, there are two main problems associated with the traditional hydrolytic/dehydration–condensation process. One is that the excess water can readily hydrolyze the Si–N bonds of ladder rungs during the hydrolysis of the Si–Cl groups and invalidate the template effect of LS. Another is that four Si–Cl bonds of each coupled *N*,*N*′-bis(phenyldichlorosilyl)-*p*-PDA monomer are completely converted to the strongly polar intermediate Ph-$(OH)_2$Si-NH-$C_6H_4$-NH-Si$(OH)_2$-Ph, resulting in the LS being dissolved in only very strongly polar solvents, such as acetone and so forth, which would further weaken hydrogen-bonding effect of the LS. In contrast, the stoichiometric hydrolytic/dehydrochlorination–condensation reaction only converts, on an average, two Si–Cl bonds of each monomer into two Si–OH bonds and, moreover, the dehydrochlorination–condensation reaction generates HCl, which can be immediately absorbed by triethylamine (TEA) rather than destroy the Si–N bonds. Thus, less polar mixture solvents (toluene/*p*-dioxane) can be utilized and consequently LS can continuously play an efficient template role. As shown in the $^{29}$Si NMR spectrum of the PLPS and LS (see discussion below), no noticeable silanol groups, derived from the ladder rungs of PLPS (Ph-$(O_{2/2})$Si-NH-$C_6H_4$-NH-Si$(O_{2/2})$-Ph) by hydrolysis, are observed, suggesting no rupture of Si–N bonds occurs.

Scheme 1 indicates the important role of PDA during the reaction process producing the coupled monomer which, in turn, spontaneously forms LSs through the concerted interaction of hydrogen bonding and aromatic π–π stacking. Because these weak interactions can be maintained only in mild conditions, some necessary reaction conditions should be emphasized.

*Medium polarity*: Generally, hydrogen-bonding interactions decrease with increasing polarity of the reaction medium. Therefore, less polar or nonpolar solvents are preferred. However, the selected solvent must possess a suitable solution power for the LS and PLPS. If polar THF or acetone were chosen, the LS would be destroyed due to the rupture of the Si–N bonds during the hydrolytic process.[19] Here, a less polar mixture of solvents, toluene/*p*-dioxane (DOX), was chosen based on the balance between the polarity and solution power of the solvent.

*Reaction temperature*: hydrogen-bonding interaction becomes very week or disappears at higher temperature, while low temperature trends to the formation of stable **LS** alignment. Nevertheless, too low temperature may lead to very slow condensation. Accordingly, it is necessary to control the reacting temperature to guarantee the suitable reaction speed and the as strong hydrogen-bonding template effect as possible throughout the synthetic process. Hence, the temperature was fixed at 50 °C.

*Monomer concentration*: A higher monomer concentration is beneficial to the fast formation of LSs. On the other hand, it may lead to a cross-linking reaction between neighboring ladder structures. Thus, the monomer concentration was controlled at a range of 1–2 %.

*Dropping speed of water*: A very slow dropping speed of water should be maintained strictly to guarantee that all the Si–OH formed from the hydrolytic reaction condenses rapidly with the neighboring excess Si–Cl groups. In fact, some gel (cross-linked polymer) may form if the stoichiometric water is added too fast. In addition the HCl released in the condensation reaction must be absorbed by TEA so as to get the high molecular weight PLPS.

### Confirmation of ladder structure of PLPS and LS

*Molecular weight determination of PLPS*: Generally, the gel permeation chromatograph (GPC) using polystyrene as the standard samples is only suitable instrument to characterize the flexible single-chain polymers. For this reason, molecular weight ($M_w$) of the PLPS was determined by vapor pressure osmometry (VPO; THF as solvent). The result shows that PLPS has $M_w \sim 30200$.

*FT-IR analysis of PLPS*: The following absorption peaks (KBr) were observed: 3375 (N–H), 1593, 3070, 3047, 2972 (Ph), 1514 (Si–N), 1430, 1131 (Si–C), 1078, and 1024 $cm^{-1}$ (Si-O-Si). Importantly, no absorption peaks indicative of Si–OH and PDA $NH_2$ groups derived from the Ph-$(O_{2/2})$Si-NH-$C_6H_4$-NH-Si$(O_{2/2})$-Ph ladder rung, by means of a hydrolysis reaction, were observed, indicating that the rupture of Si–N bond is avoided.

*XRD analysis—polymer PLPS*: The XRD spectrum of PLPS (Figure 1) demonstrates two distinct peaks. Referring to the literature,[6,13] these peaks give the ladder width ($w$ = 1.56 nm) and thickness ($t$ = 0.49 nm). Evidently, the first peak is not only sharp and narrow, but also has very high intensity, indicating the existence of the significant ladder structure on the macromolecule framework. In addition, there is a decent coincidence between the XRD data and the calculated dimensions $w$ = 1.63 nm and $t$ = 0.57 nm by simulation software (Alchemy 2000 V1.0).

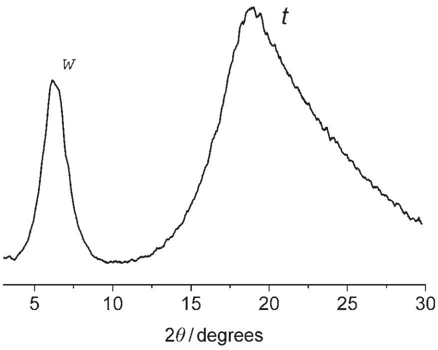


Figure 1. X-ray diffraction patterns of the solid polymer PLPS; *w* and *t* stand for the width and the thickness of PLPS, respectively.

*X-ray analysis—ladder superstructure*: As shown in Figure 2 the solution XRD pattern of the LS also demonstrates two diffraction peaks, though their location is shifted with respect to those of PLPS. This similarity clearly indicates that the LS also possesses ladder structure in the solution through the hydrogen-bonding and π–π interactions. For fur-

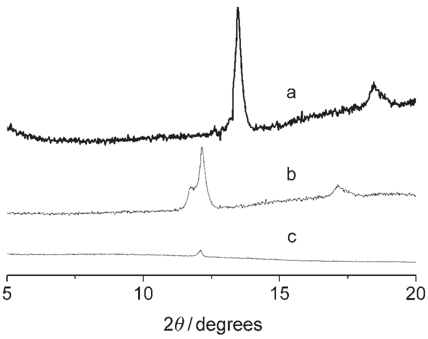


Figure 2. X-ray diffraction patterns of a) the polymer PLPS, b) the LS, and c) the LS + urea in toluene (4 g per 100 mL).

ther substantiation of the ladder structure of the superstructure, a control experiment was carried out. If urea used as a hydrogen-bonding blocking agent in the system, the Bragg diffraction peaks (characteristic of ladder structure) completely disappeared. This result states clearly that the LS is seriously destroyed. If this system was continuously condensed, the final polymer PLPS derived becomes very irregular. As shown in Figure 3, the $\Delta_{1/2}$ is as large as $>4$ ppm.

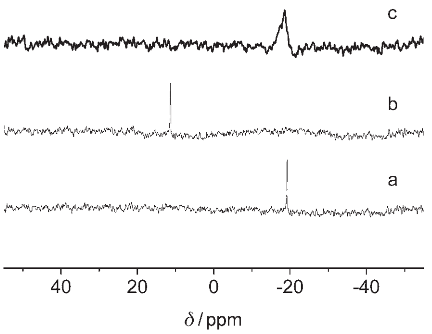


Figure 3. $^{29}$Si NMR spectra of a) the polymer PLPS, b) the LS, and c) the polymer PLPS derived from the LS + urea.

*$^{29}$Si NMR measurements—polymer PLPS*: It is known that the higher the regularity of organo-bridged ladder polysiloxane, the narrower the resonance peak of the $=SiO_{2/2}$ moiety on the ladder backbone, and the smaller the half-peak width $\Delta_{1/2}$. As shown in Figure 4, an extremely small half-peak width of $\Delta_{1/2} < 0.3$ ppm for the $=SiO_{2/2}$ unit at $\delta = -18.5$ ppm is observed for PLPS and clearly indicates that the polymer only consists of regular structure units without any noticeable branched moieties. Similarly, no noticeable absorption peaks of Si–OH groups are observed in the $^{29}$Si NMR spectrum, suggesting that the Si–N bond of the Ph-$(O_{2/2})$Si-NH-$C_6H_4$-NH-Si$(O_{2/2})$-Ph ladder rung of the PLPS is not cleaved. Combining the information obtained from the $^{29}$Si NMR spectrum with the XRD patterns, it can be deduced that PLPS possesses the expected perfect ladder structure.

*$^{29}$Si-NMR measurements—ladder superstructure LS*: Similarly, as shown in Figure 3, an extremely small $\Delta_{1/2} < 0.3$ ppm of the $=SiO_{2/2}$ unit at $\delta = 10.5$ ppm clearly indicates that the **LS** only consists of regular ladder structure of Ph-$(Cl)_2$Si-NH-$C_6H_4$-NH-Si$(Cl)_2$-Ph, rather than of randomly interlaced or branched structures. Similarly, no any noticeable absorption peaks of Si–OH groups were observed in the $^{29}$Si NMR spectrum, suggesting that the Si–N bond of the Ph-$(Cl)_2$Si-NH-$C_6H_4$-NH-Si$(Cl)_2$-Ph ladder rung of the LS is not cleaved. If a hydrogen-bonding blocking reagent such as urea is added to the LS system, as shown in Figure 3, the $\Delta_{1/2}$ of final polymer PLPS becomes as large as $>4$ ppm, further demonstrating that the LS is seriously destroyed and the resultant PLPS became more irregular.

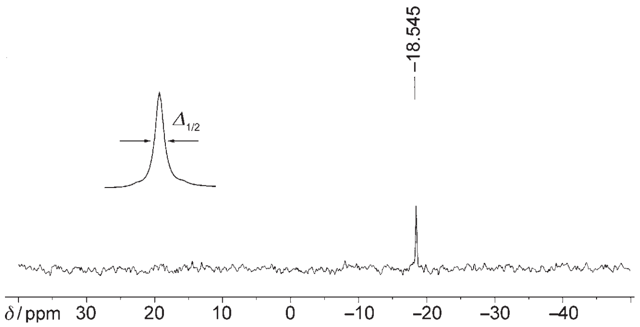


Figure 4. $^{29}$Si NMR spectra of the polymer PLPS with the $\Delta_{1/2} < 0.3$ ppm.

*Fluorescence spectroscopic analysis—polymer PLPS*: Figure 5 shows fluorescence emission spectra of PLPS and the LS. The fluorescence spectrum of PLPS gives an emission peak at 329 nm when it was excited by UV light with a wavelength of 299 nm. It is reasonable to attribute the emission at 329 nm to the excimer formed by aromatic chromophores along the ladder chain direction in PLPS.[20,21]

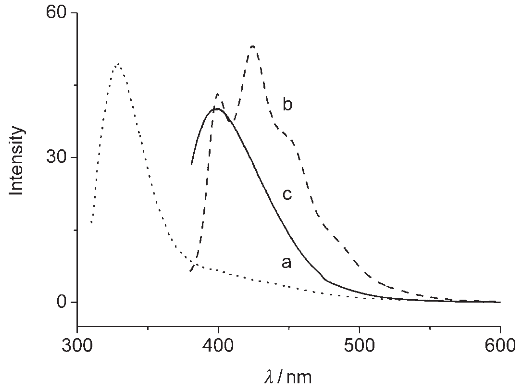


Figure 5. Fluorescence emission spectra of a) the polymer PLPS excited at 299 nm, b) the LS excited at 366 nm, and c) the LS + urea excited at 366 nm, in toluene (0.3 g L$^{-1}$).

*Fluorescence spectroscopic analysis—ladder superstructure*: The fluorescence spectrum of the LS shows two new broad emission peaks at 424 and 400 nm when excited by UV light with a wavelength of 366 nm. If urea was added in the monomer solution, a single emission peak was observed at 400 nm when it was excited at 366 nm. This phenomenon is attributed to the π–π stacking of phenyl and the -NHR chromophores. By contrast, the fluorescence profile of the superstructure LS sample in high-wavelength region suggests that there are the intramolecular interactions in solutions of the monomer, namely, hydrogen-bonding and π–π interactions.[22–24]

*DSC measurement of PLPS*: Compared with the lower $T_g$ for the single-chain polysiloxane (e.g., $T_g = -69.4$ °C for polyphenylmethylsiloxane[25]), the much higher Tg for the PLPS ($T_g = 176.4$ °C) indicates higher stiffness, which arises from fact that the internal rotation of the -Si-O-Si- main chain are greatly restricted. If PLPS possesses some branched structure its $T_g$ should be greatly decreased. Therefore, the higher Tg indirectly confirms the double-chain structures of PLPS.

## Conclusion

The first soluble, high molecular weight, perfect ladder polymer, PLPS, has been successfully synthesized through ladder superstructure (LS) constructed by the concerted interaction of hydrogen-bonding and aromatic π–π stacking by means of a stoichiometric hydrolysis/dehydrochlorination–condensation reaction. The perfect ladder structures of PLPS and LS were confirmed by VPO, FT-IR, $^{29}$Si NMR, and fluorescence spectroscopy, XRD, DSC and control experiments based-on addition of hydrogen-bonding blocking reagent.

## Experimental Section

**Materials and techniques**: The Fourier transform infrared spectra (FT-IR) were recorded using a Perkin–Elmer 80 spectrometer. $^1$H, $^{13}$C, and $^{29}$Si NMR spectra were obtained on Bruker FT-AM 400 spectrometers with 400.1, 100.6 and 79.5 MHz respectively; for the $^{29}$Si spectra toluene was used as the solvent and TMS as the external reference. The X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2400 diffractometer. The fluorescence spectra of samples PLPS were measured on a F-4500 FL spectrophotometer in toluene with a concentration of 0.3 g L$^{-1}$. The DSC investigation was carried out on a Mettler Toledo Star 822 differential scanning calorimeter with heating rate 10 °C min$^{-1}$. Vapor pressure osmometry (VPO) analysis was measured in dry THF at room temperature on a Knauer VPO instrument. All reagents were obtained from commercial sources and used without additional purification. Toluene, 1,4-dioxane (DOX), and tetrahydrofuran (THF) were distilled from sodium and benzophenone under argon. Triethylamine (TEA) was dried from sodium and degassed before use.

**Preparation of monomer *N*,*N*′-bis(phenyldichlorosilyl)-*p*-PDA**: The monomer was prepared and characterized according to our previously reported work.[26] Because the monomer is very air-sensitive, we converted it by means of a methanolysis reaction to stable crystalline *N*,*N*′-bis(phenyldimethoxysilyl)-*p*-PDA. M.p. 99–100 °C; $^1$H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 7.75$–$7.65$ (m, 10H; $C_6H_5$), 6.61 (s, 4H; $HNC_6H_4NH$), 3.60 (s, 12H; $CH_3O$), 3.50 ppm (br, 2H; $NH$); $^{13}$C NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 135.8$, 129.8, 128.1 ($C_6H_5$), 136.7, 115.9 ($HNC_6H_4NH$), 42.8 ppm ($CH_3O$); FAB-MS: *m*/*z* 440 $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{28}N_2O_4Si_2$: C 60.00, H 6.36, N 3.62; found: C 59.98, H 6.34, N 3.65).

**Preparation of polymer PLPS**: The synthetic route to PLPS is shown in Scheme 1. After standard cycles of evacuation and back-fill with dry and pure argon, a dry Schlenk flask, equipped with a magnetic bar, was charged with $PhSiCl_3$ (3.2 mL, 20 mmol) and toluene (200 mL) by syringe at room temperature. The solution of TEA (16.8 mL, 0.12 mol) and PDA (1.08 g, 10 mmol) in DOX (50 mL) was then slowly added into the flask by syringe under vigorous stirring at 10 °C. After that, the reaction mixture was kept stirring at room temperature for 48 h. After finishing the coupling reaction, water (0.18 g) dissolved in a DOX/toluene mixture (100 mL; 40:60) was added very slowly dropwise into the flask at 50 °C. The following dehydrochlorination–condensation reaction proceeded for 12 h. Finally, a solution of $Me_3SiCl$ (10 mL; 0.01 M, dissolved in toluene) was charged, and the end-capping reaction proceeded for 6 h. The mixture was filtered, reduced under pressure distillation, and vacuum dried at 30 °C to yield a light yellow powder of PLPS in 80.1 % yield.

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