Aza-Wittig Polymerization: Kinetic Study and Efficient End Functionalization of Poly(azomethine)s

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ABSTRACT: We have revealed the kinetic advantage of the aza-Wittig polymerization over the conventional diamines/dialdehydes polycondensation system for the effective preparation of end-functionalized π-conjugated poly(azomethine)s. The synthesized polymers **P1** and **P2** possess hexyl groups and POSS units at the chain ends, respectively. Both polymers were highly soluble in common organic solvents including $CHCl_3$, CH_2Cl_2, THF, benzene, and toluene at room temperature. The thermal stability of POSS-modified poly(azomethine) **P2** (temperature of 10% weight loss; $T_{10} = 381$ °C) was high as compared to that of poly(azomethine) without POSS units **P1** ($T_{10} = 372$ °C) because of the siliceous bulky POSS segments at the chain ends. Further, UV−vis absorption study in dilute $CHCl_3$ solution (1.0×10^{-5} M) demonstrated that both polymers had the same absorption maxima at 454 nm, resulting from the extension of the π-electron delocalization length of both polymers via the π-conjugated poly(azomethine) backbone. In the film state, UV−vis absorption spectra, fluorescence quantum yields (Φ_F), XRD patterns, and TEM images supported that bulky three-dimensional POSS groups at the chain ends effectively suppress intermolecular aggregations of the individual poly(azomethine).

Introduction

Semiconducting polymers have gained immense interest over the past few years, in part stimulated by their applicability to devices such as organic photovoltaic cells (OPVs), polymer-based light-emitting diodes (LEDs), and field-effect transistors (FETs).[1] Among these polymers, π-conjugated poly(azomethine)s[2] have been widely studied due to their prominent properties including excellent thermal stability,[3] the ability to chelate with metals,[3] electrical conductivity,[4] second- and third-order nonlinear optical properties,[5] and fiber-forming property.[6] To further alter the properties and explore the full potential of these functional materials, chemical modifications of π-conjugated poly(azomethine)s have been actively performed.[7] Most of these efforts are focused on main-chain and/or side-chain functionalization of π-conjugated poly(azomethine)s. Although end group functionalization would also broaden the range of applications of these polymers, the synthesis of end-functionalized π-conjugated poly(azomethine)s has been rarely reported. The importance of π-conjugated polymer-end-capping as they pertain to physical and electronic properties can be illustrated with poly(*p*-phenylenevinylene)s (PPVs) and polyfluorenes (PFs). One of the most prominent results was demonstrated by tethering polyhedral oligomeric silsesquioxanes (POSS) units covalently to the chain ends of poly(2-methoxy-5-[2-ethylhexyloxy]-1,4-phenylenevinylene) (MEH-PPV) and poly(9,9′-dioctylfluorene), which resulted in the enhanced electroluminescence and thermal stability of the devices prepared from these modified hybrid-type π-conjugated polymers.[8]

Basically, the methodology for the synthesis of π-conjugated poly(azomethine)s is the condensation reaction of A_2B_2 monomers: a dialdehyde and a diamine. So far, many kinds of A_2B_2 poly(azomethine)s have been prepared by this manner. However, because the reaction between primary amines and aldehyde compounds is a chemical equilibrium reaction (a reversible reaction), it is likely to be difficult to introduce functional groups quantitatively to the chain ends of π-conjugated poly(azomethine)s. Another potential choice of imine group-forming reaction is the aza-Wittig reaction,[9] which is the reaction of phosphazenes, obtainable by Staudinger reaction from organic azides and phosphorus(III) reagents, with carbonyl compounds. This process has become one of the most efficient methods for the creation of imine group due to its high reactivity, selectivity, and irreversibility. Recently, we have developed novel and highly efficient polymerization methods utilizing aza-Wittig reaction for the construction of various poly(azomethine) derivatives, that is, aza-Wittig polymerization.[10] Therein, it has been shown that the reactivity of the aza-Wittig polymerization could be dramatically improved only by optimizing the steric and electronic features of phosphines employed. These results prompted our interest in not only the detailed kinetic study of the aza-Wittig polymerization but also the efficient end functionalization of π-conjugated poly(azomethine)s. In this Article, we first describe the kinetic advantage of the aza-Wittig polymerization over the conventional polycondensation reaction involving diamine monomers, and then we demonstrate the construction of end-functionalized π-conjugated poly(azomethine)s with POSS units.

Results and Discussion

Scheme 1 illustrates both (a) aza-Wittig polymerization and (b) conventional polycondensation reaction for the kinetic experiments. Note that the conditions employed here were adapted from studies previously reported by us[10a] and Andersson,[7d] respectively. All kinetic experiments performed during the present study were conducted as follows: (i) The equimolar amounts of monomers were dissolved in anhydrous toluene-d_8 solutions (40 mM) in an argon atmosphere; (ii) the excess amounts of additives (phosphorus(III) reagents for aza-Wittig polymerization and lithium chloride for conventional polycondensation reaction) were added to the solution; (iii) after heating at 80 °C for a certain period, samples were transferred to an NMR tube (0.5 mL) and were then kept in liquid nitrogen to terminate further polycondensation reaction; and (iv) monomer consumption rate was estimated by the integrals of the ^{1}H NMR spectral features corresponding to the azomethine ($-CH{=}N-$) protons of polymers at around 9 ppm and to the aldehyde protons of monomers and/or polymer end groups at around 10.5 ppm.

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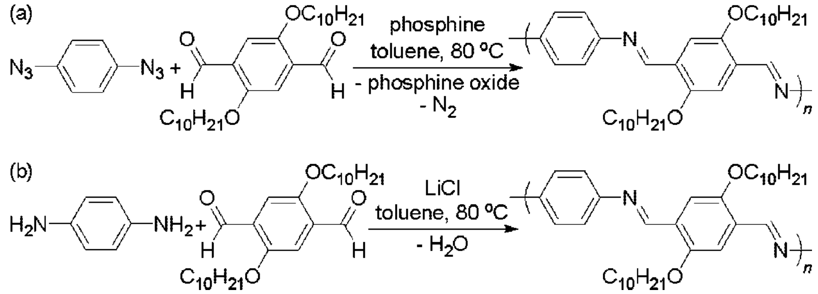
Scheme 1. (a) Aza-Wittig Polymerization and (b) Conventional Polycondensation Reaction



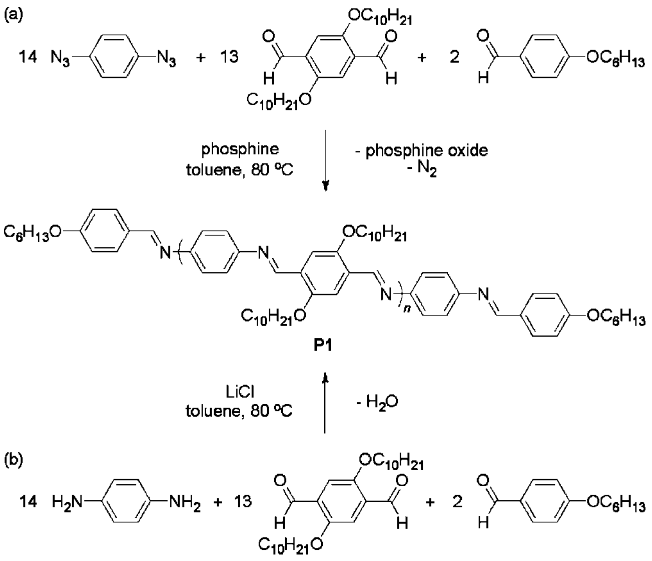
As shown in Figure 1, when the consumption rate of monomers was plotted with reaction time, the initial gradient of the curve was found to be in good agreement with a second-order equation. If the concentration of CHO at t minutes is represented by C and the initial concentration is represented by C_0:

$$v = -\mathrm{d}C/\mathrm{d}t = kC^2$$

$$1/C = kt + 1/C_0$$

The estimation of the kinetic parameters (k) was done by plotting $1/C - 1/C_0$ versus time and determining the slopes in the linear region. The results are summarized as follows: (i) The monomer conversion of aza-Wittig polymerization with methyldiphenylphosphine ($PMePh_2$) immediately reached 90% within 2 h, whereas that of the conventional polycondensation reaction only reached 50% in 2 h; (ii) $PMePh_2$ was much more effective than triphenylphosphine (PPh_3), presumably due to the steric hindrance caused by three phenyl rings of PPh_3 in addition to the high stability of the corresponding phosphazene; and (iii) the k value ($k = 4.56$ M^{-1} min^{-1}) for aza-Wittig polymerization using $PMePh_2$ was 13.4 times larger than that for conventional polycondensation reaction ($k = 0.34$ M^{-1} min^{-1}). This large difference of kinetics would also affect the efficiency of the polymer-end-capping reaction. Scheme 2 demonstrates the synthetic routes for end-functionalized poly(azomethine) involving both monomers and terminal aldehyde compound. The molecular weight of the target polymer here was controlled by the molar ratio of the monomers and end-capping unit (14:13:2). We first checked the consumption rate of the terminal aldehyde compound by ^{1}H NMR spectra. Therein, we found that the aza-Wittig polymerization consumed almost all of the end-capping unit within 2 h, while the conventional polycondensation reaction remained about 40% (Figure 2). These results must come from the difference of the reaction manner; that is, the aza-Wittig polymerization proceeds almost irreversibly, whereas the conventional polycondensation reaction experiences chemical equilibrium. Thus, only in the case of the aza-Wittig polymerization did the analytic data agree well with the expected molecular structure of the resultant poly(azomethine) **P1** (conventional polycondensation reaction yielded ill-characterized poly(azomethine) **P1′**).

Scheme 2. Synthesis of End-Functionalized Poly(azomethine) P1 via (a) Aza-Wittig Polymerization and (b) Conventional Polycondensation Reaction



To demonstrate the utility of the aza-Wittig polymerization, we performed the introduction of polyhedral oligomeric silsesquioxanes (POSS) units covalently into the chain ends of

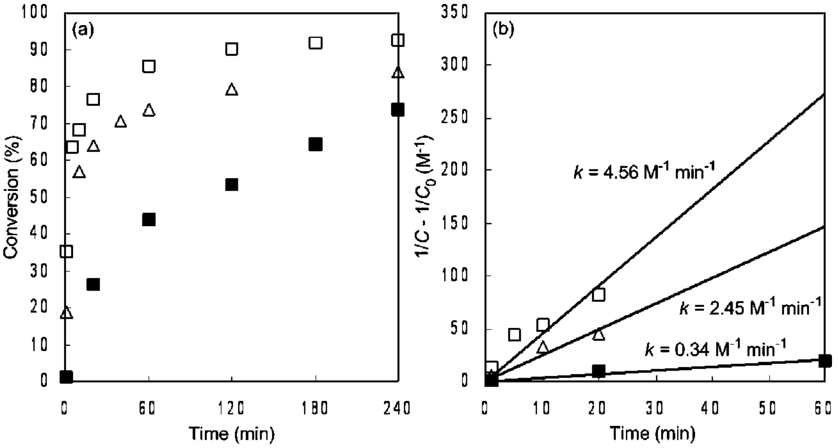


Figure 1. (a) Time−conversion relationships of aza-Wittig polymerization with $PMePh_2$ (□), PPh_3 (△), and conventional polycondensation reaction (■); (b) kinetic plots of aza-Wittig polymerization with $PMePh_2$ (□), PPh_3 (△), and conventional polycondensation reaction (■).

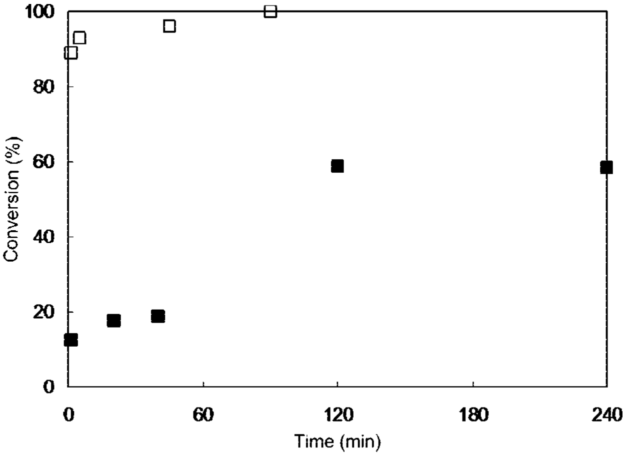


Figure 2. The consumption rate of end-capping group utilizing the aza-Wittig polymerization with $PMePh_2$ (□) and the conventional polycondensation reaction (■).

poly(azomethine). Scheme 3a illustrates the synthetic route for **POSS-Aldehyde** as an end-capping group. Treatment of 4-hydroxybenzaldehyde with **POSS-I** in the presence of K_2CO_3 resulted in the etherification to give **POSS-Aldehyde** in 80% yield. Subsequently, POSS-containing poly(azomethine) **P2** was synthesized via aza-Wittig polymerization with $PMePh_2$, as outlined in Scheme 3b. The polymerization was carried out in dilute toluene solution (20 mM) because of the low solubility of **POSS-Aldehyde**. Note that the condition performed here is rather unfavorable; that is, a polycondensation reaction under a low monomer concentration tends to cause cyclization reaction, which results in the generation of undesirable macrocycles without any end-capping units. Nevertheless, the obtained POSS-containing poly(azomethine) **P2** via aza-Wittig polymerization possessed the adequate polymer structure (conventional polycondensation reaction yielded ill-characterized poly(azomethine) **P2′**).

Table 1 summarizes the polymerization results and properties of the obtained end-functionalized poly(azomethine)s. Both polymers **P1** and **P2** possessed similar molecular weights and polydispersity (PDI). In addition, **P1** and **P2** were highly soluble in a variety of common solvents including $CHCl_3$, CH_2Cl_2, THF, benzene, and toluene. In both cases, no phase transition was observed by differential scanning calorimetry (DSC) from 0 to 200 °C. On the other hand, the effect of POSS moieties on polymer property could be observed by thermogravimetric analysis (TGA). The thermal stability of POSS-modified poly(azomethine) **P2** (temperature of 10% weight loss; $T_{10} = 381$ °C) was high as compared to that of poly(azomethine) without POSS units **P1** ($T_{10} = 372$ °C) due to the siliceous bulky three-dimensional POSS segments at the chain ends.

To evaluate the electronic structure of the obtained π-conjugated poly(azomethine)s, Figure 3 displays the UV−vis absorption spectra both in $CHCl_3$ (1.0×10^{-5} M) and in the film state. In dilute $CHCl_3$ solution (Figure 3a), both polymers possessed the same absorption maxima at 454 nm, suggesting the extension of the π-electron delocalization length of both polymers via the π-conjugated poly(azomethine) backbone. In the solid state, poly(azomethine) without POSS units **P1** and POSS-modified poly(azomethine) **P2** exhibited apparently different behavior (Figure 3b). Although both absorptions were red-shifted in the solid state relative to the solution probably due to the strong intermolecular interaction between the polymer main chains, **P2** ($\lambda_{max} = 471$ nm, $\lambda_{edge} = 604$ nm) had less contribution at the bathochromic side than did **P1** ($\lambda_{max} = 477$ nm, $\lambda_{shoulder} = 505$ nm, $\lambda_{edge} = 640$ nm). This result indicates that bulky POSS groups at the chain ends effectively suppress the intermolecular aggregation of π-conjugated poly(azomethine) backbone. We then checked whether the existence of POSS units at the chain ends could alter the photoluminescence properties of the obtained poly(azomethine)s both in $CHCl_3$ (1.0×10^{-5} M) solution and in the film state (Figure 4). Although both polymers possessed completely the same emission maxima both in solution ($\lambda_{max} = 508$ nm) and in the film state ($\lambda_{max} = 570$ nm), the absolute quantum yield (Φ_F) of POSS-modified poly(azomethine) **P2** in the film state ($\Phi_F = 0.8\%$) showed 2-fold larger value relative to **P1** ($\Phi_F = 0.4\%$). This result suggests that the isolation effect of the nanosized POSS units inhibited the interchain aggregation/quenching, and hence POSS-modified polymer **P2** exhibited an enhanced Φ_F value in the film state.

To further examine the effect of POSS units on polymer property in the solid state, X-ray diffraction (XRD) measurements were conducted (Figure 5). XRD samples were prepared by depositing one drop of a polymer solution on a glass substrate and dried to remove the solvent at room temperature. Both polymers **P1** and **P2** had distinct diffraction peaks at 2θ of 4.6°, corresponding to an interlayer spacing of 19.2 Å. These results suggest that the obtained polymers form a layered order structure in which the rigid-rod main chains are separated by the alkyl side chains. **P1** exhibited additional diffraction peaks centered at 9.2°, 13.4°, 18.0°, and 25.7°, whereas **P2** had only one additional diffraction peak centered at 18.0°. This result supports the high crystalline nature of **P1** in the solid state and indicates that bulky POSS units located at the chain ends of poly(azomethine)s effectively suppress the intermolecular aggregation.

To gain information for the effect of POSS moieties on polymer morphology, transmission electron microscopy (TEM) measurements were carried out after drying the $CHCl_3$/CF_3CH_2OH (20/80, v/v) solutions on a carbon-coated copper grid. Note that CF_3CH_2OH was used as a poor solvent to induce effective polymer aggregations. As shown in Figure 6a, the TEM image of **P1** revealed the presence of nanometer-sized particles and further aggregations of each particle, whereas that of **P2** showed well-dispersed nanometer-sized particle structures (Figure 6b). These data support that bulky three-dimensional POSS units at the chain ends not only suppress intermolecular self-assembly of the individual poly(azomethine) backbone but also disturb further aggregations of each particle.

Conclusions

We have demonstrated the kinetic advantage of the aza-Wittig polymerization over the conventional polycondensation reaction using diamine and dialdehyde monomers for the effective synthesis of end-functionalized π-conjugated poly(azomethine)s. Polymers **P1** and **P2** possess hexyl groups and POSS units at the chain ends, respectively. Both polymers showed excellent solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, THF, benzene, and toluene at room temperature. The thermal stability of POSS-modified poly(azomethine) **P2** was high as compared to that of poly(azomethine) without POSS units **P1** due to the siliceous bulky POSS segments at the chain ends. Further, UV−vis absorption study in dilute $CHCl_3$ solution revealed that both polymers possessed the same absorption maxima, suggesting the extension of the π-electron delocalization length of both polymers via the π-conjugated poly(azomethine) backbone. In the film state, UV−vis absorption spectra, fluorescence quantum yields (Φ_F), XRD data, and TEM images supported that bulky three-dimensional POSS groups at the chain ends not only suppress intermolecular aggregations of the individual poly(azomethine) but also disturb further aggregations of each particle.

Scheme 3. Synthetic Route for (a) POSS-Aldehyde and (b) POSS-Containing Poly(azomethine) P2

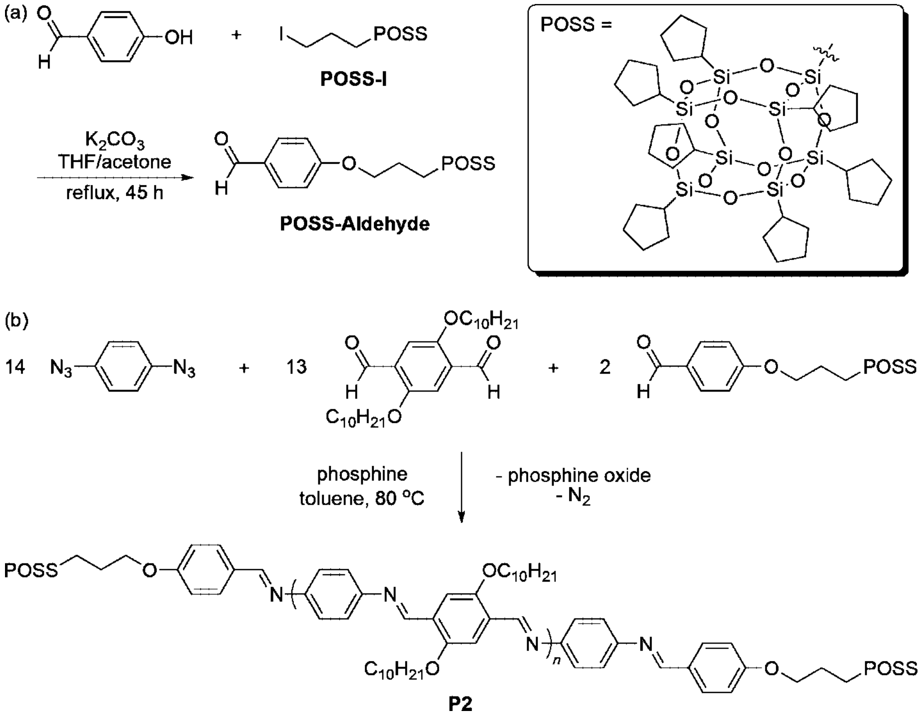


Table 1. Properties of End-Functionalized Poly(azomethine)s

polymer	yield (%)	M_n[a]	PDI[a]	T_d[b] (%)	λ_{max} (nm)[c]	λ_{max} (nm)[d]	shift (nm)
P1	96	19 600	1.60	372	454	477, 505	23, 51
P2	91	19 800	1.64	381	454	471	17

[a] Determined by GPC ($CHCl_3$), polystyrene standards. [b] Temperature resulting in a 10 wt % loss based on the initial weight. [c] Measured in $CHCl_3$ (1.0×10^{-5} M) at room temperature. [d] Measured in the film state.

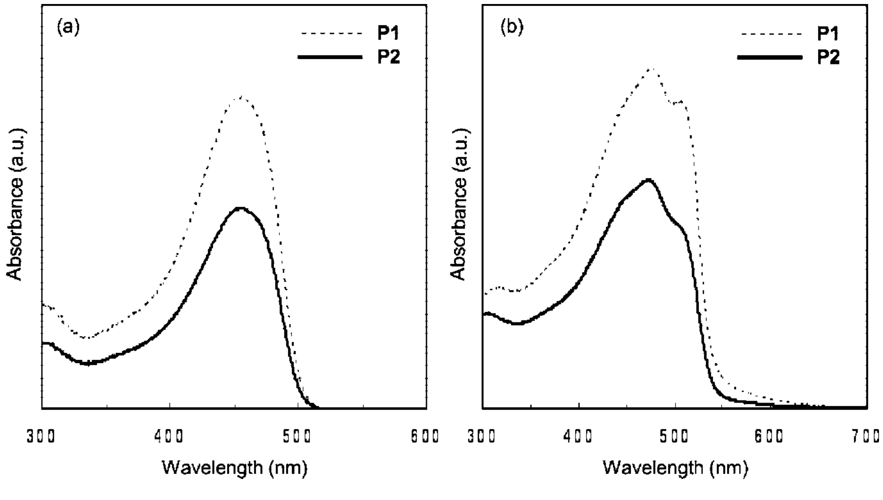


Figure 3. UV−vis absorption spectra of polymers **P1** (- - -) and **P2** (−) (a) in $CHCl_3$ (1.0×10^{-5} M) and (b) in the film state.

Experimental Section

Materials. Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. All synthetic procedures were performed under argon atmosphere. Tetrahydrofuran (THF) and triethylamine (TEA) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). *p*-Phenylenediamine was obtained from Wako Chemical, Co. Ltd. (97%). 2,5-Bis(3,7-dimethyloctyloxy) terephthalaldehyde was obtained from Aldrich Chemical, Co. Ltd. (98%). 4-(Hexyloxy)benzaldehyde was obtained from TCI, Co. Ltd. 1,4-Diazidobenzene was prepared according to the reported procedure.[11]

Measurements. ^1H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (80 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer utilizing 0.05% tetramethylsilane (TMS) as an internal standard in $CDCl_3$ at room temperature. Number-average molecular weight and molecular weight distribution values of all polymers were estimated on a TOSOH size exclusion chromatography (SEC) system equipped with a polystyrene gel column (TOSOH gel: G3000HXL) using refractive-index (RI-8020) and ultraviolet (UV-8020) detectors at 40 °C. The system was operated at a flow rate of 1.0 mL/min with $CHCl_3$ as an eluent after calibration with the standard polystyrene samples. FT-IR spectra were obtained on a Perkin-Elmer 1600 infrared spectrometer. Thermogravimetric analy-

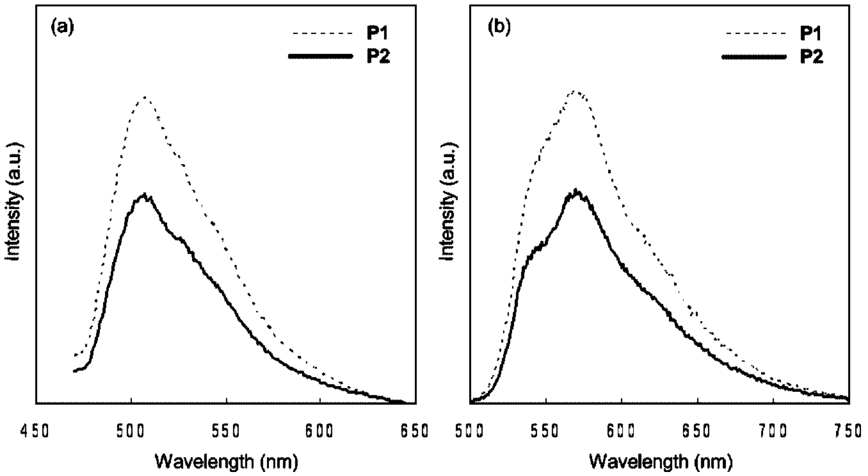


Figure 4. Fluorescence spectra of polymers **P1** (- - -) and **P2** (—) (a) in $CHCl_3$ (1.0×10^{-5} M) and (b) in the film state.

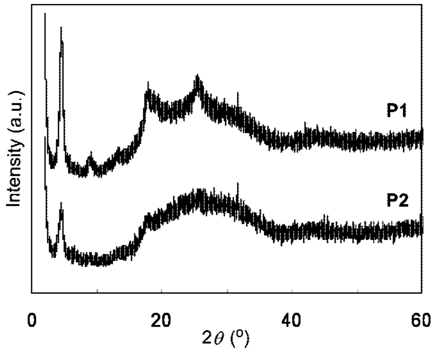


Figure 5. XRD patterns of polymers **P1** and **P2**.

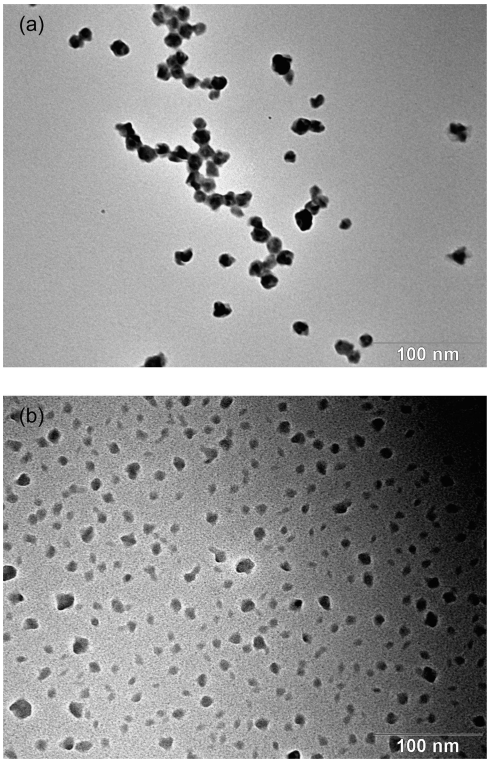


Figure 6. TEM micrographs of (a) **P1** and (b) **P2** from $CHCl_3$/CF_3CH_2OH (20/80, v/v) solutions. The concentration of both samples is 1.0×10^{-4} M.

sis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of 10 °C/min in air. UV—vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Transmission electron microscopy (TEM) images were observed with a JEOL JEM-100SX operating at an accelerating voltage of 100 kV. TEM samples were prepared by depositing one drop of a desired solution on a 200 mesh copper grid covered with a carbon film and dried to remove the solvent at room temperature. X-ray diffraction (XRD) patterns were taken by using Cu Kα radiation with a Shimadzu XRD-600. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Synthesis of POSS-Aldehyde. In a round-bottom flask were charged 2.42 g of **POSS-I** (2.26 mmol) and 0.20 g of 4-hydroxybenzaldehyde (1.64 mmol). To this were added 0.45 g of anhydrous K_2CO_3 (3.28 mmol), 80 mL of anhydrous THF/acetone cosolvent (3/1, v/v), and a stir bar. The reaction was then left to stir for 45 h in a thermostatic oil bath at 80 °C, after which the solvent was removed via vacuum distillation. Dichloromethane was then added to the residue, and the resulting suspension was filtered to remove excess K_2CO_3 and insoluble byproducts. Afterward, the solvent was removed with a rotary evaporator, and the crude product was purified by column chromatography with an eluent of hexane/$CHCl_3$ (1/1, v/v) to give **POSS-Aldehyde** (80% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 9.88 (s, 1H), 7.82 (d, 2H), 6.98 (d, 2H), 4.03 (m, 2H), 1.93 (m, 2H), 1.81−1.40 (br, 56H), 0.96 (m, 7H), 0.76 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ (ppm) 190.8 (*C*HO), 164.2 (C_{Ar}—O), 132.0 (C_{Ar}—H), 129.7 (C_{Ar}—C), 114.7 (C_{Ar}—H), 70.0 (CH_2O), 28−22 (aliphatic carbons), 8.2 (CH_2Si). ^{29}Si NMR ($CDCl_3$): δ (ppm) −66.4, −66.7. Anal. Calcd: C, 50.81; H, 7.01. Found: C, 51.12; H, 6.62.

Aza-Wittig Polymerization. A general polymerization procedure is as follows. In a round-bottom flask were placed monomers, the corresponding end-capping group (4-(hexyloxy)benzaldehyde for **P1** and **POSS-Aldehyde** for **P2**, respectively), dry toluene (20 mM), and an excess amount of phosphine at room temperature. The reaction mixture was thoroughly deoxygenated, filled with high-purity argon, and placed in a thermostatic oil bath at 80 °C for 72 h. After being cooled, the reaction mixture was concentrated. Exhaustive extraction of the resulting solid with methanol (Soxhlet extraction) afforded the target polymer. **P1**, ^{1}H NMR ($CDCl_3$): δ (ppm) 9.01 (br, 2H), 7.80 (br, 2H), 7.33 (br, 4H), 4.19 (br, 4H), 1.91 (br, 4H), 1.80−0.76 (br, 34H). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.2 (C_{Ar}—O), 153.4 (*N*=*C*H), 150.4 (C_{Ar}—N), 128.3 (C_{Ar}—CH), 122.1 (C_{Ar}—H), 110.4 (C_{Ar}—H), 67.5 (CH_2O), 40−19 (aliphatic carbons). Anal. Calcd: C, 77.76; H, 9.62; N, 5.43. Found: C, 76.95; H, 9.76; N, 5.18. **P2**, ^{1}H NMR ($CDCl_3$): δ (ppm) 9.01 (br, 2H), 7.80 (br, 2H), 7.33 (br, 4H), 4.20 (br, 4 H), 1.91 (br, 4H), 1.86−0.71 (br, 34H). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.3 (C_{Ar}—O), 153.4 (*N*=*C*H), 150.4 (C_{Ar}—N), 127.8 (C_{Ar}—CH), 122.1 (C_{Ar}—H), 110.4 (C_{Ar}—H), 67.5 (CH_2O), 40−19 (aliphatic carbons), 8.2 (CH_2Si). ^{29}Si NMR ($CDCl_3$): δ (ppm) −66.4, −66.8. Anal. Calcd: C, 72.25; H, 9.04; N, 4.39. Found: C, 71.33; H, 8.83; N, 4.44.

Conventional Polycondensation Reaction. A general polymerization procedure is as follows. In a round-bottom flask were placed monomers, the corresponding end-capping group (4-(hexyloxy)benzaldehyde for **P1′** and **POSS-Aldehyde** for **P2′**, respectively), dry toluene (20 mM), and an excess amount of LiCl at room temperature. The reaction mixture was thoroughly deoxygenated, filled with high-purity argon, and placed in a thermostatic oil bath at 80 °C for 72 h. After being cooled, the reaction mixture was concentrated. Exhaustive extraction of the resulting solid with methanol (Soxhlet extraction) afforded the target polymer. **P1′**, ^{1}H NMR ($CDCl_3$): δ (ppm) 9.02 (br, 2H), 7.81 (br, 2H), 7.34 (br, 4H), 4.20 (br, 4H), 1.91 (br, 4H), 1.83−0.73 (br, 34H). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.2 (C_{Ar}−O), 153.4 (N=CH), 150.4 (C_{Ar}−N), 128.3 (C_{Ar}−CH), 122.1 (C_{Ar}−H), 110.4 (C_{Ar}−H), 67.5 (CH_2O), 40−19 (aliphatic carbons). Anal. Calcd: C, 77.76; H, 9.62; N, 5.43. Found: C, 79.83; H, 9.41; N, 5.32. **P2′**, ^{1}H NMR ($CDCl_3$): δ (ppm) 9.01 (br, 2H), 7.80 (br, 2H), 7.33 (br, 4H), 4.20 (br, 4H), 1.91 (br, 4H), 1.86−0.70 (br, 34H). ^{13}C NMR ($CDCl_3$): δ (ppm) 155.3 (C_{Ar}−O), 153.4 (N=CH), 150.4 (C_{Ar}−N), 127.8 (C_{Ar}−CH), 122.1 (C_{Ar}−H), 110.4 (C_{Ar}−H), 67.5 (CH_2O), 40−19 (aliphatic carbons), 8.2 (CH_2Si). Anal. Calcd: C, 72.25; H, 9.04; N, 4.39. Found: C, 75.34; H, 8.99; N, 4.91.

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