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NOTE

Aza-Wittig Polymerization: An Improved Molecular Design for Preparing AB-Type Poly(azomethine)s Utilizing Air-Stable Triphenylphosphine

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Introduction

Aromatic poly(azomethine)s,[1] often termed poly(Schiff base)s, have been currently recognized as a special class of high-performance polymers due to their salient properties such as excellent thermal stability,[2] the ability to chelate with metals,[2] electrical conductivity,[3] and nonlinear optical properties.[4] In particular, AB-type poly(azomethine)s have gained much interest because they should have large dipole moment along the polymer backbone in addition to their inherent notable properties of aromatic poly(azomethine)s. Though several types of A_2B_2-type poly(azomethine)s have been prepared by the condensation reaction of a dialdehyde and a diamine,[5] very few AB-type poly(azomethine)s have been achieved mainly due to the ease of self-condensation between the aldehyde and amine functionalities.[6]

The aza-Wittig reaction,[7] which is the reaction of phosphazenes—obtainable by the Staudinger reaction from organic azides and phosphorus(III) reagents—with carbonyl compounds, has become one of the most efficient methods for the construction of azomethine compounds due to its high reactivity, chemo-selectivity and irreversible nature. Recently, we have developed a novel and efficient polymerization method utilizing the aza-Wittig reaction for the creation of various poly(azomethine)s, i.e., aza-Wittig polymerization.[8] Therein, it has been shown that A_2B_2-type aza-Wittig polymerization possess kinetic advantage over the conventional diamines/dialdehydes polycondensation system,[8d] and its reactivity can be dramatically improved only by optimizing the steric and electronic features of phosphines employed.[8a] Subsequently, we have also demonstrated that the aza-Wittig polymerization of AB-type monomers having both aldehyde and azide functionality within single molecules gave the first example of AB-type poly(azomethine)s,[8b] and their chiral derivative exhibited a unique optical activity and nanometer-sized fiber-forming property.[8c]

However, only medium-low molecular weight AB-type poly(azomethine)s were obtained even in the usage of electron-rich phosphorus(III) reagents such as tributylphosphine, dimethylphenylphosphine and methyldiphenylphosphine because the nucleophilic phosphazene and the electrophilic aldehyde are connected by a conjugated phenyl moiety to form a push-and-pull system in addition to the negative effect of electron-donating alkoxy side chains on the electrophilic aldehyde group. Furthermore, triphenylphosphine, which is one of the most useful reagents in the aza-Wittig reaction because of its air-stable nature and low cost, displayed no activity on AB-type aza-Wittig polymerization. In order to improve the AB-type aza-Wittig polymerization system, we report herein a novel molecular design for the synthesis of AB-type poly(azomethine)s using air-stable triphenylphosphine.

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Results and Discussion

Figure 1 displays a novel molecular design (**M1a, b**) for the effective AB-type aza-Wittig polymerization. Note that the positive effect of electron-donating alkoxy side chains on the nucleophilic phosphazene group can be expected.

Scheme 1 illustrates the synthetic route to **M1a** and **M1b**, novel AB-type monomers containing both the aldehyde and azide functionality. The synthetic strategy was adapted from a procedure previously reported by us.[8b] Methyl 4-amino-3-hydroxybenzoate **1** was converted into methyl 4-azido-3-hydroxybenzoate **2** by azidation. Then, methyl 4-azido-3-alkoxybenzoates **3a** and **3b** were obtained by alkylation. Long and branched alkyl side chain on the phenyl ring is introduced to improve the polymer solubility because aromatic poly(azomethine)s generally have poor solubility in common organic solvents. Treatment of methyl 4-azido-3-alkoxybenzoates **3a** and **3b** with DIBAL-H resulted in the selective reduction of the esters to yield 4-azido-3-alkoxybenzyl alcohols, followed by oxidation of the free alcohols using a Dess-Martin reagent gave the desired 4-azido-3-alkoxybenzaldehydes **M1a** and **M1b** in high yields after purification by flash chromatography. The structures of the obtained monomers were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analyses.

AB-type poly(azomethine)s (**P1a, b**) were first synthesized by adding excess amounts of tributylphosphine ($P(Bu^n)_3$) to anhydrous toluene solutions (200 mM) of monomers (**M1a, b**), respectively, at 80 °C (Scheme 2). In the initial stage of the polymerization, the color of the reaction mixture immediately changed from light yellow to deep orange in addition to the generation of N_2 bubble, indicating the successful progress of the Staudinger reaction. Note that, in the case of **P1a**, a large amount of precipitation was observed at the initial stage of the polymerization (within 6 h) since **P1a** had limited solubility in common organic solvents. After the polymerization, the reaction mixture was concentrated, and the obtained polymers were purified by Soxhlet extraction with methanol to remove low molecular weight fragments and phosphine byproduct.

The polymer structure was first examined by FT-IR spectroscopy. The FT-IR spectra showed a strong absorption band at 1575 cm^{-1}, assigned to the azomethine (−CH=N−) stretching. The ^{1}H NMR spectrum of **P1b** displayed a signal at 8.50 ppm, which is also attributed to the azomethine proton. Size exclusion chromatography (SEC) of **P1b** in $CHCl_3$, using polystyrene standards for calibration, gave a number-average molecular weight (M_n) of 12 000 g mol^{-1} and a polydisersity index

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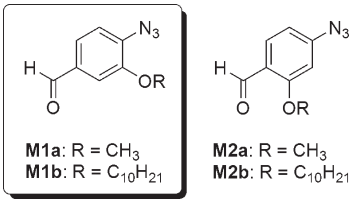
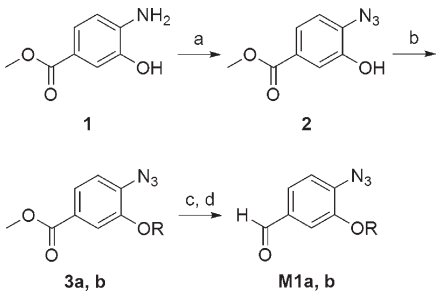


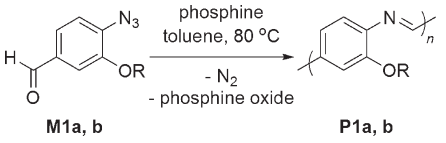
Figure 1. New monomer design for the effective AB-type aza-Wittig polymerization.

Scheme 1. Synthetic Route to Monomers



[a] Reagents and conditions: (a) HNO_2, NaN_3; (b) RX, K_2CO_3, acetone, reflux; (c) DIBAL-H, CH_2Cl_2, −78 °C; (d) DMP, CH_2Cl_2, rt.

Scheme 2. Synthesis of AB-Type Poly(azomethine)s



(M_w/M_n) of 2.25, respectively. Importantly, it was found that the molecular weight of the obtained **P1b** here was much higher than that of the previously synthesized **P2b** (M_n = 6000 g mol^{-1}), probably resulting from the positive effect of electron-donating alkoxy side chains on this new monomer system. Further, UV−vis absorption study in dilute $CHCl_3$ solution (1.0×10^{-5} M) demonstrated that **P1b** had an absorption maximum at 415 nm, which is comparable to the previously synthesized **P2b** (λ_{max} = 425 nm), resulting from the extension of the π-electron delocalization length via the AB-type π-conjugated poly(azomethine) backbone. Note that the new molecular design described here gave higher molecular weight AB-type poly(azomethine)s without changing their optical properties significantly.

In order to evaluate the reactivity of monomers, we checked the consumption rate of the new monomer **M1b** and the previous monomer **M2b**, respectively. The kinetic study was performed as follows: (i) the equimolar amounts of monomers (**M1b** and **M2b**) were dissolved in anhydrous toluene solutions (200 mM) in an argon atmosphere; (ii) an excess amount of $P(Bu^n)_3$ was added to the solution; (iii) after heating at 80 °C for a certain period, samples were transferred to an NMR tube and were then kept in liquid nitrogen to terminate further polymerization; (iv) monomer consumption rate was estimated by the integrals of the ^{1}H NMR signals (Figure 2a) corresponding to the azomethine (−CH=N−) protons of polymers (8.50 ppm for **P1b** and 8.94 ppm for **P2b**, respectively) and to the aldehyde protons (9.68 ppm for **P1b** and 10.2 ppm for **P2b**, respectively); (v) the consumption rate of monomers was plotted with reaction time (Figure 2(b)). As we expected, the consumption rate of the previous monomer **M2b** was very slow, whereas the new monomer **M1b** showed much higher activity on the AB-type aza-Wittig polymerization system.

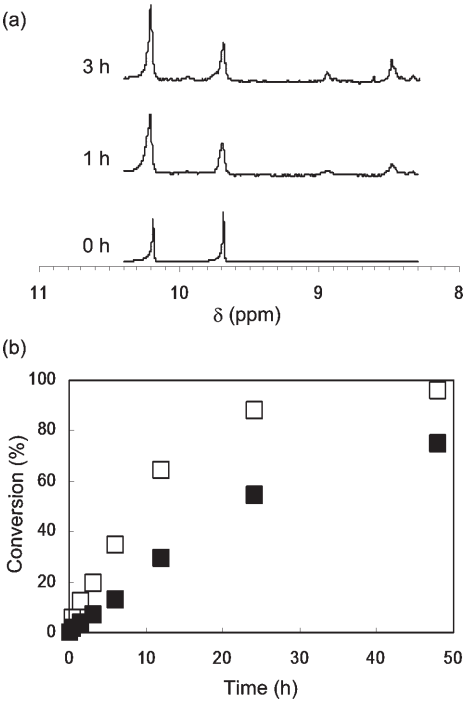


Figure 2. (a) Typical ^{1}H NMR spectra at the initial stage of the AB-type aza-Wittig polymerization and (b) consumption rate of **M1b** (open squares) and **M2b** (filled squares).

To further demonstrate the advantage of the new monomer **M1b**, we then examined triphenylphosphine (PPh_3). It should be noted that PPh_3 is a relatively electron-poor phosphorus(III) species, thus making it possible to be treated under air. In our previous work, however, it was found that PPh_3 displayed no activity on the AB-type aza-Wittig polymerization with the previous monomer **M2b**, which resulted in the corresponding phosphazene in a quantitative yield.[8b] On the other hand, the new monomer **M1b** underwent AB-type aza-Wittig polymerization even with the use of PPh_3, which resulted in the corresponding poly(azomethine) **P1b** with moderate molecular weight (M_n = 2100 g mol^{-1}, M_w/M_n = 2.10). This result can be rationalized in terms of the difference of the electron density between the resultant phosphazene moieties, and it is suggested again that the positive effect of electron-donating alkoxy side chains on the nucleophilic phosphazene group in **M1b** could effectively promote the AB-type aza-Wittig polymerization.

Conclusions

We have developed a novel monomer design for the effective synthesis of AB-type poly(azomethine)s. The obtained AB-type poly(azomethine) **P1b** showed moderate solubility in common organic solvents such as $CHCl_3$, THF, and toluene. UV−vis absorption study in dilute $CHCl_3$ solution revealed that **P1b** possessed an absorption maximum at 415 nm, suggesting the extension of the π-electron delocalization length of **P1b** via the AB-type π-conjugated poly(azomethine) backbone. Most importantly, in comparison with the previously reported AB-type monomer system, not only tributylphosphine ($P(Bu^n)_3$) but also air-stable triphenylphosphine (PPh_3) were effective, which resulted in the corresponding AB-type poly(azomethine) with moderate molecular weight.

Experimental Section

Materials. All synthetic procedures were performed under argon atmosphere. Unless stated otherwise, all reagents were obtained from commercial sources and used without further

purification. Tributylphosphine ($P(Bu^n)_3$) and triphenylphosphine (PPh_3) were purchased from Wako Chemical, Co. Ltd.

Measurements. ^1H (400 MHz) and ^{13}C (100 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 (M_n) and molecular weight distribution value (M_w/M_n) 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. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Methyl 4-Azido-3-hydroxybenzoate (2). A round-bottomed flask was charged with 5.00 g (30.0 mmol) of methyl 4-amino-3-hydroxybenzoate (**1**) dissolving 100 mL of aqueous solution. After cooling down to 0 °C, 25 mL of conc. H_2SO_4, 2.76 g (40.0 mmol) of $NaNO_2$, and 3.25 g (50.0 mmol) of NaN_3 were then added dropwise. The reaction mixture was left to stir for 12 h at room temperature. The mixture was extracted with EtOAc, washed with H_2O, and the organic layer was dried over $MgSO_4$. Afterward, the solvent was removed with a rotary evaporator, and the crude product was purified by flash chromatography on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3. Yield: 87%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (d, 1 H), 7.54 (s, 1 H), 6.99 (d, 1 H), 6.60−5.75 (br, 1 H), 3.83 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.6 (CH_3OOC), 147.4 (C_{Ar}−N), 131.1 (C_{Ar}−C), 127.4 (C_{Ar}−O), 122.6 (C_{Ar}−H), 118.4 (C_{Ar}−H), 117.2 (C_{Ar}−H), 52.3 (CH_3OOC). MS (EI) m/z: 193.0488 ($C_8H_7N_3O_3$ requires 193.0487).

General Procedure for Methyl 4-Azido-3-alkoxybenzoates (3a, b). A round-bottomed flask was charged with methyl 4-azido-3-hydroxybenzoate (**2**) and a large excess of the corresponding alkyl halides. To this were added a large excess of anhydrous K_2CO_3, anhydrous acetone, and a stir bar. The reaction mixture was then left to stir for 12 h at 80 °C, after which the solvent was removed via vacuum distillation. CH_2Cl_2 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 flash chromatography on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3.

Methyl 4-Azido-3-methoxybenzoate (3a). The above general procedure was performed with 1.93 g (10.0 mmol) of methyl 4-azido-3-hydroxybenzoate (**2**), 25.0 g (176.0 mmol) of methyl iodide, 8.30 g (60.0 mmol) of K_2CO_3, and 50 mL of acetone. The crude product was purified by column chromatography to give **3a** (82% yield, 1.70 g). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (d, 1 H), 7.55 (s, 1 H), 7.00 (d, 1 H), 3.91 (s, 3 H), 3.89 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.2 (CH_3OOC), 151.6 (C_{Ar}−O), 133.1 (C_{Ar}−C), 127.2 (C_{Ar}−N), 123.0 (C_{Ar}−H), 119.8 (C_{Ar}−H), 112.7 (C_{Ar}−H), 56.0 (CH_3O), 52.1 (CH_3OOC). MS (EI) m/z: 207.0642 ($C_9H_9N_3O_3$ requires 207.0644). Anal. Calcd: C 52.17, H 4.38, N 20.28, O 23.17. Found: C 51.72, H 4.40, N 20.26, O 23.67.

Methyl 4-Azido-3-(3′,7′-dimethyloctyloxy)benzoate (3b). The above general procedure was performed with 1.93 g (10.0 mmol) of methyl 4-azido-3-hydroxybenzoate (**2**), 6.00 g (27.0 mmol) of 1-bromo-3,7-dimethyloctane, 8.30 g (60.0 mmol) of K_2CO_3, and 50 mL of acetone. The crude product was purified by column chromatography to give **3b** (72% yield, 2.40 g). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, 1 H), 7.55 (s, 1 H), 6.94 (d, 1 H), 4.10 (t, 2 H), 3.90 (s, 3 H), 1.90 (m, 1 H), 1.80−0.80 (br, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.3 (CH_3OOC), 151.6 (C_{Ar}−O), 133.0 (C_{Ar}−C), 127.1 (C_{Ar}−N), 122.7 (C_{Ar}−H), 120.2 (C_{Ar}−H), 113.3 (C_{Ar}−H), 67.6 (CH_2O), 52.1 (CH_3OOC), 40−19 (aliphatic carbons). MS (EI) m/z: 333.2049 ($C_{18}H_{27}O_3N_3$ requires 333.2052). Anal. Calcd: C 64.84, H 8.16, N 12.60, O 14.40. Found: C 64.69, H 8.05, N 12.50, O 14.61.

General Procedure for 4-Azido-3-alkoxybenzaldehydes (M1a, b). A round-bottomed flask was charged with methyl 4-azido-3-alkoxybenzoates dissolving CH_2Cl_2 solution. After the reaction was allowed to cool down to −78 °C, a large excess of DIBAL-H (1.0 M hexane solution) was added dropwise. The reaction mixture was then left to stir for 1 h at −78 °C, after which the reaction was quenched by adding a large excess of MeOH. After warming up to room temperature, the solution was poured into aqueous potassium sodium tartrate, and the resulting mixture was stirred for 1 h. The mixture was diluted with CH_2Cl_2 and washed with H_2O, and the organic layer was dried over $MgSO_4$. Afterward, the solvent was removed with a rotary evaporator, and the crude product was purified by flash chromatography on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3. Then, a solution of 4-azido-3-alkoxybenzyl alcohols in CH_2Cl_2 was added to a stirred solution of Dess-Martin periodinane (DMP) in CH_2Cl_2 over 5 min. The solution came to a spontaneous boil for about 5 min. After 1 h, the solution was poured into saturated aqueous $NaHCO_3$ containing $Na_2S_2O_3$, and the resulting mixture was stirred for 1 h. The mixture was diluted with CH_2Cl_2 and washed with H_2O, and the organic layer was dried over $MgSO_4$. Afterward, the solvent was removed, and the crude product was chromatographed on silica with an eluent of hexane/EtOAc adjusted to give an R_f for the product of 0.2−0.3.

4-Azido-3-methoxybenzaldehyde (M1a). The reaction was carried out by following the procedure described above. Yield: 60%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.90 (s, 1 H), 7.44 (d, 1 H), 7.41 (s, 1 H), 7.12 (d, 1 H), 3.96 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.6 (*C*HO), 152.5 (C_{Ar}−O), 135.0 (C_{Ar}−C), 133.9 (C_{Ar}−N), 125.3 (C_{Ar}−H), 120.3 (C_{Ar}−H), 110.1 (C_{Ar}−H), 56.1 (CH_3O). MS (EI) m/z: 177.0536 ($C_8H_7O_2N_3$ requires 177.0538). Anal. Calcd: C 54.24, H 3.98, N 23.72, O 18.06. Found: C 54.27, H 3.91, N 23.58, O 18.30.

4-Azido-3-(3′,7′-dimethyloctyloxy)benzaldehyde (M1b). The reaction was carried out by following the procedure described above. Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.88 (s, 1 H), 7.42 (d, 1 H), 7.40 (s, 1 H), 7.06 (d, 1 H), 4.13 (t, 2 H), 1.90 (m, 1 H), 1.80−0.80 (br, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.6 (*C*HO), 152.4 (C_{Ar}−O), 134.8 (C_{Ar}−C), 133.8 (C_{Ar}−N), 125.0 (C_{Ar}−H), 120.1 (C_{Ar}−H), 110.7 (C_{Ar}−H), 67.7 (CH_2O), 40−19 (aliphatic carbons). MS (EI) m/z: 303.1945 ($C_{17}H_{25}O_2N_3$ requires 303.1947). Anal. Calcd: C 67.30, H 8.31, N 13.85, O 10.55. Found: C 67.10, H 8.21, N 13.78, O 10.85.

Polymerization Procedure. A general polymerization procedure is as follows. In a round-bottom flask were placed a monomer, dry toluene (200 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 cooling down, the reaction mixture was concentrated. Exhaustive extraction of the resulting solid with methanol (Soxhlet extraction) afforded the target polymer. **P1a**: IR (ν, cm^{-1}): 1575 (−CH=N−). **P1b**: ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.50 (br, 1 H), 7.65 (br, 1 H), 7.10 (br, 2 H), 4.15 (br, 2 H), 1.95−0.80 (br, 19 H). IR (ν, cm^{-1}): 1575 (−CH=N−).

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