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# The Aza-Wittig Polymerization: An Efficient Method for the Construction of Carbon−Nitrogen Double Bonds-Containing Polymers

**Junpei Miyake and Yoshiki Chujo***

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

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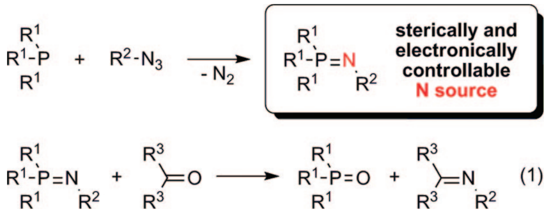
ABSTRACT: A novel and efficient polymerization method based on the aza-Wittig reaction was developed for the construction of carbon−nitrogen double bonds-containing polymers. In contrast to the conventional diamines/dialdehydes polycondensation system, the reactivity of the aza-Wittig polymerization was easily tunable only by changing the steric and electronic features of phosphines employed. The obtained $\pi$-conjugated poly(azomethine)s here consisted of only one trans conformation, which is consistent with the previous reported paper employing the theoretical study of the aza-Wittig reaction. Moreover, it was found that the aza-Wittig polymerization can also be applied not only to the aromatic and aliphatic diazido-containing compounds but also to the heteroatom-containing diazido monomers.

## Introduction

Carbon−nitrogen double bonds-containing compounds have been given much attention because they are used as the key components in coordination complex[1] and dynamic combinatorial chemistry.[2] Among them, $\pi$-conjugated poly(azomethine)s[3] have been widely recognized as a special class of high-performance polymers due to their salient properties including electrical conductivity,[4] second- and third-order nonlinear optical properties,[5] and fiber-forming properties.[6] In general, the special role of poly(azomethine)s among $\pi$-conjugated polymers can be explained by the presence of the nitrogen atom in the imine group and its free electron pair, which may take part in the formation of complexes with many electrophilic substances.[7] So far, several types of poly(azomethine)s have been prepared by the typical polycondensation reactions of aromatic/aliphatic dialdehydes and diamines.[8] Since the nucleophilicity of primary amines to aldehyde compounds is uncontrollable, it was impossible to control the reactivity of the conventional polycondensation reactions utilizing amine and aldehyde compounds.

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, has become one of the most efficient methods for the creation of the imine group under mild reaction conditions (eq 1). In recent works employing the aza-Wittig reaction, it became evident from the excellent yields in many of these syntheses that the aza-Wittig reaction might lend itself to the construction of C═N group-containing polymers. In addition, the reactivity of phosphazenes depends on the polarity of the phosphorus−nitrogen bond as well as the basicity of these systems so that the reactivity of the aza-Wittig polymerization is also thought to be controllable by changing the substituents on the phosphorus and nitrogen atoms. Herein, we wish to report a novel polymerization method for the construction of C═N group-containing polymers utilizing the aza-Wittig reaction.



(1)

## Results and Discussion

To begin our study, we discovered that 1,4-diazidobenzene and terephthalaldehyde derivative readily underwent polycondensation reaction in the presence of tri-*n*-butylphosphine, resulting in a soluble $\pi$-conjugated poly(azomethine) with high molecular weight (**1a**; $M_n$ = 31 000, PDI = 2.03). Long and branched alkyl side chains on the phenyl ring are introduced to enhance the solubility of the polymers (Scheme 1). The motivation to prepare this type of polymer first was its potential use in photonic devices as thin films spin-casted from solutions. Especially, $\pi$-conjugated poly(azomethine)s, made by the vapor deposition technique of the monomers in a vacuum chamber, have been used as electron transporting layers in polymer light-emitting diodes.[4a,b]

1,4-Diazidobenzene was synthesized using a modified literature procedure starting from commercially available 1,4-diaminobenzene.[10] The aza-Wittig polymerization took place by utilizing an equimolar amount of 1,4-diazidobenzene and substituted terephthalaldehyde with an excess amount of phosphine in anhydrous toluene at 80 °C for 72 h. In the initial stage of the polymerization (within 30 min), 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. After the reaction, the reaction mixture was concentrated, and the obtained polymer was purified by Soxhlet extraction using methanol to remove low molecular weight fragments and phosphine byproduct.

The polymer structure was investigated by FT-IR, $^1$H NMR, $^{13}$C NMR spectroscopy, and elemental analyses. The FT-IR spectrum showed a strong absorption band at 1604 cm$^{-1}$, assigned to the azomethine (−CH═N−) stretching. The $^1$H NMR spectrum displayed a signal at $\delta$ 9.02, which is attributed to the azomethine proton. The presence of a single signal, in good agreement with the earlier result,[8d] for the azomethine proton suggested the occurrence of only one isomer, which is presumably the thermodynamically more stable trans isomer. Previous reports employing the theoretical study of the aza-Wittig reaction supported the preferential or exclusive formation of ($E$)-imines so that the obtained poly(azomethine) here would also have trans conformation.[11] Gel permeation chromatography (GPC) of this polymer in chloroform, using polystyrene

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* Corresponding author: e-mail chujo@chujo.synchem.kyoto-u.ac.jp, Fax +81-75-383-2605, Ph +81-75-383-2604.

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**Scheme 1. Aza-Wittig Polymerization**

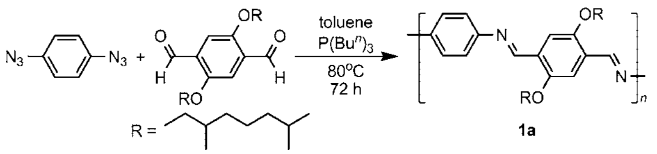

**Table 1. Steric Effect of Phosphines on the Aza-Wittig Polymerization**

| entry | phosphine | yield (%) | $M_n$[a] | $M_w$[a] | PDI[a] |
|---|---|---|---|---|---|
| 1 | $P(Bu^n)_3$ | 91.7 | 31000 | 63000 | 2.03 |
| 2 | $PCy_3$ | 24.5[b] | 1900 | 3600 | 1.89 |
| 3 | $P(Bu^t)_3$ | 18.9[b] | 1000 | 1200 | 1.20 |

[a] Determined by GPC ($CHCl_3$), polystyrene standards. [b] Low molecular weight fractions were removed by HPLC.

**Table 2. Electronic Effect of Phosphines on the Aza-Wittig Polymerization**

| entry | phosphine | yield (%) | $M_n$[a] | $M_w$[a] | PDI[a] |
|---|---|---|---|---|---|
| 4 | $PMe_2Ph$ | 94.7 | 33000 | 69000 | 2.09 |
| 5 | $PMePh_2$ | 93.2 | 55000 | 133000 | 2.42 |
| 6 | $PPh_3$ | 58.4[b] | 2200 | 4500 | 2.05 |
| 7 | $P(p\text{-}OMeC_6H_5)_3$ | 60.5[b] | 2000 | 4200 | 2.10 |
| 8 | $P(p\text{-}FC_6H_5)_3$ | 51.5[b] | 2400 | 4900 | 2.04 |
| 9 | $P(p\text{-}CF_3C_6H_5)_3$ | 53.1[b] | 2300 | 4800 | 2.09 |

[a] Determined by GPC ($CHCl_3$), polystyrene standards. [b] Low molecular weight fractions were removed by HPLC.

**Scheme 2. Aza-Wittig Polymerization Utilizing Aliphatic Diazido Monomers**

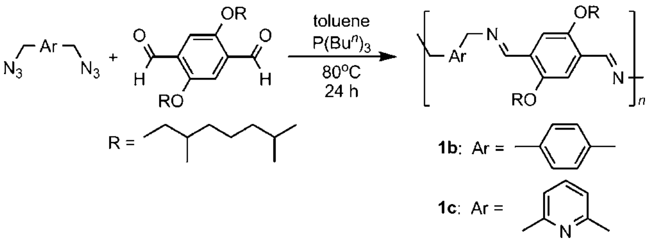

**Table 3. Polymerization Results Utilizing Aliphatic Diazido Monomers**

| entry | polymer | phosphine | yield (%) | $M_n$[a] | PDI[a] |
|---|---|---|---|---|---|
| 10 | **1b** | $PMePh_2$ | 90.7 | 35000 | 3.06 |
| 11 | **1b** | $PPh_3$ | 90.4 | 10000 | 2.60 |
| 12 | **1c** | $PMePh_2$ | 81.5 | 7800 | 2.31 |

[a] Determined by GPC ($CHCl_3$), polystyrene standards.

standards for calibration, gave a number-average molecular weight of 31 000 and a polydispersity of 2.03. This result is consistent with the results of $^1H$ NMR and elemental analyses that no aldehyde and phosphazene end groups could be detected.

We have examined other kinds of trialkylphosphines and found that steric features of phosphines significantly affected on the aza-Wittig polymerization (Table 1). In the case of trialkylphosphines (entries 1−3), only tri-*n*-butylphosphine (entry 1) was effective for the polymerization reaction in spite of the similarity of the electronic state. This result can be rationalized in terms of the reported phosphine cone angles,[12] and it is suggested that steric hindrance caused by bulky organic substituents on phosphorus atom (entries 2 and 3) strongly suppressed the aza-Wittig polymerization.

As shown in Table 2, we have also evaluated the electronic effect of phosphines on the aza-Wittig polymerization. It is well-known that the electronic state on phosphorus atom can be varied by modification of the substituents. For example, the electronic density on phosphorus atom of aryl groups-substituted phosphine is lower than that of trialkylphosphine; thus, the reactivity of the Staudinger reaction utilizing aryl groups-substituted phosphine is also predicted to be low. However, in contrast to our expectation, $PMe_2Ph$ (entry 4) and $PMePh_2$ (entry 5) were much more effective than tri-*n*-butylphosphine (entry 1), which resulted in higher molecular weight poly(azomethine)s. Although more detailed studies on this behavior are currently underway, a plausible explanation for the observations is that the phosphazene derived from tri-*n*-butylphosphine, a relatively unstable species, would react with adventitious moisture or other protic impurities.

Interestingly, triphenylphosphine ($PPh_3$), which is one of the most employed reagents in the aza-Wittig reaction, displayed much lower activity on the aza-Wittig polymerization (entry 6). It was already reported that *p*-phenylenebis(phosphine imide)s are so stable that they can be isolated in the presence of atmospheric oxygen and moisture for weeks with no apparent degradation.[13] Therefore, it is suggested that not only the steric hindrance caused by three phenyl rings but also the high stability of the corresponding phosphazene are both unfavorable for the aza-Wittig polymerization. We then checked whether the difference of the electron density on phosphorus atom derived from the modification of $PPh_3$ with electron-donating or electron-withdrawing substituents could alter the reactivity of the aza-Wittig polymerization. However, in contrast to our expectation, we could not see any distinct difference in the degree of polymerization (entries 7−9).

In order to further demonstrate the versatility of this new polymerization method, we have also examined other diazido-containing monomers (Scheme 2). As a result, the polymerizations of these aliphatic diazido monomers with substituted terephthalaldehyde in the presence of phosphines were also successfully carried out, and the results are summarized in Table 3. Interestingly, in comparison with the results of the aza-Wittig polymerization using aromatic diazido monomers (Tables 1 and 2), not only $PMePh_2$ (entry 10) but also $PPh_3$ (entry 11) were effective, which resulted in the corresponding C═N group-containing polymers with high molecular weights. Moreover, it was found that the aza-Wittig polymerization can also be applied to heteroatom-containing diazido monomers (entry 12).

## Conclusions

We have developed a novel and efficient polymerization method for the construction of carbon−nitrogen double bonds-containing polymers utilizing the aza-Wittig reaction. In contrast to the conventional diamines/dialdehydes polycondensation system, the reactivity of the aza-Wittig polymerization was easily tunable only by changing the steric and electronic features of phosphines employed. The obtained $\pi$-conjugated poly(azomethine)s here had only one isomer, which is the thermodynamically more stable trans isomer. Moreover, it was found that the aza-Wittig polymerization can also be applied not only to the aromatic and aliphatic diazido-containing compounds but also to the heteroatom-containing diazido monomers. Application of the aza-Wittig polymerization to the design of novel backbone-containing polymers will be reported in forthcoming papers.

## Experimental Section

**Materials.** Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was purified by passage through solvent purification columns.[14] $\alpha,\alpha'$-Diazido-*p*-xylene and 2,6-bis(azidomethyl)pyridine were synthesized and characterized according to the literature.[15]

**Measurements.** $^1$H and $^{13}$C NMR measurements were recorded on a JEOL EX-400 at 400 and 100 MHz in $CDCl_3$ (0.05% TMS as an internal standard) at room temperature (rt). UV−vis measurements were carried out on JASCO V-530 spectrometer at rt. PL spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer at rt. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8020 and RI-8020 (TOSOH TSKgel $\alpha$-3000 column) using $CHCl_3$ as an eluent at 40 °C, after calibration with the standard polystyrene samples. Recyclable preparative high-performance liquid chromatography (HPLC) was performed on a JAI LC-918 using $CHCl_3$ as an eluent. FT-IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Powder X-ray diffraction (XRD) patterns were taken by using Cu K$\alpha$ radiation with a Shimadzu XRD-600.

**Monomer Synthesis.** 1,4-Diazidobenzene was synthesized using a modified literature procedure starting from commercially available 1,4-diaminobenzene.[10] In a 100 mL round-bottom flask, 1,4-diaminobenzene (1.62 g, 15 mmol) was dissolved in dry $CH_3CN$ (50 mL) and cooled to 0 °C in an ice bath. To this stirred mixture was added *t*-BuONO (4.64 g, 5.35 mL, 45 mmol) followed by $TMSN_3$ (4.14 g, 4.78 mL, 36 mmol) dropwise. The resulting solution was stirred at room temperature for 20 h. The reaction mixture was concentrated under vacuum, and the crude product was purified by silica gel chromatography (hexane) to give 1,4-diazidobenzene as a brown solid (1.51 g, 63%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.01 (s, 4 H).

**Polymerization Procedures.** A general polymerization procedure is as follows. In a round-bottom flask was placed equimolar amounts of monomers, 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 cooling down, the reaction mixture was concentrated. Exhaustive extraction of the resulting solid with methanol (Soxhlet extraction) afforded the target polymer. **1a:** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 9.02 (br, 2 H), 7.81 (br, 2 H), 7.35 (br, 4 H), 4.22 (br, 4 H), 1.91 (br, 4 H), 0.75−1.84 (br, 34 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 155.2 ($C_{Ar}$−O), 153.4 (N═$C$H), 150.5 ($C_{Ar}$−N), 128.3 ($C_{Ar}$−CH), 122.1 ($C_{Ar}$−H), 110.4 ($C_{Ar}$−H), 67.5 ($CH_2O$), 40−20 (aliphatic carbons). IR ($\nu$, cm$^{-1}$): 1604 (−CH═N−). Anal. Calcd: C 78.72, H 9.71, N 5.40. Found: C 78.68, H 9.58, N 5.38. **1b:** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.82 (br, 2 H), 7.57 (br, 2 H), 7.33 (br, 4 H), 4.82 (br, 4 H), 4.05 (br, 4 H), 1.81 (br, 4 H), 0.75−1.84 (br, 34 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 157.9 ($C_{Ar}$−O), 152.7 (N═$C$H), 138.1 ($C_{Ar}$−$CH_2$), 128.2 ($C_{Ar}$−H), 127.5 ($C_{Ar}$−CH), 110.4 ($C_{Ar}$−H), 67.4 ($CH_2O$), 65.5 ($C_{Ar}$−$CH_2$), 40−20 (aliphatic carbons). **1c:** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.78 (br, 2 H), 7.79 (br, 2 H), 7.40 (br, 3 H), 4.82 (br, 4 H), 4.00 (br, 4 H), 1.79 (br, 4 H), 0.70−1.75 (br, 34 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 158.0 ($C_{Ar}$−O), 152.8 (N═$C$H), 134.8 ($C_{Ar}$−$CH_2$), 132.5 ($C_{Ar}$−H), 128.2 ($C_{Ar}$−CH), 126.0 ($C_{Ar}$−H), 110.4 ($C_{Ar}$−H), 67.4 ($CH_2O$), 65.4 ($C_{Ar}$−$CH_2$), 40−20 (aliphatic carbons).

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