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Synthesis of Polyphosphazenes by a Fast Perfluoroaryl Azide-Mediated Staudinger Reaction

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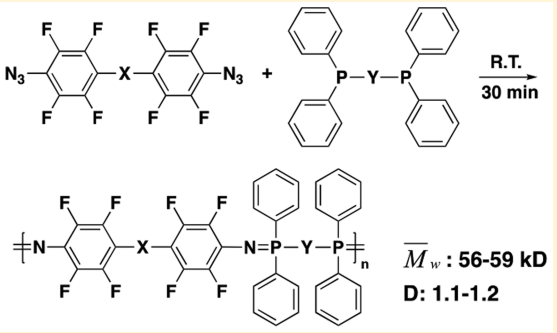
Supporting Information

ABSTRACT: We report the synthesis of polyphosphazenes by a fast Staudinger reaction between a bis-PFAA (perfluoroaryl azide) and a bis-phospine. Polymerization was completed within 30 min after mixing the two monomers (20 mM) in CH_3CN under ambient conditions to give polyphosphazene with molecular weight of up to over 59 000 and a narrow dispersity ($Đ$) of 1.1−1.2. This is a significant improvement over the polyphosphazenes obtained from the classic Staudinger reaction which had lower molecular weight ($\bar{M}_n$ = 10 000−25 000) and higher $Đ$ (1.7). This reaction applies to bis-PFAAs and bis-phosphines with either an aromatic or an aliphatic linker. Polarity of the solvent influenced the degree of polymerization, and more polar solvents such as acetonitrile gave higher molecular weight polymer in comparison to less polar solvents such as dichloromethane. The synthesized polyphosphazenes showed high thermal stability, with the aromatic polyphosphazenes giving decomposition temperature and char yield of up to of 441 °C and 53%, respectively.



INTRODUCTION

Polyphosphazenes, inorganic−organic hybrid polymers consisting of the P═N repeating unit, possess several unique properties such as unusual elasticity,[1] high thermal stability,[2] flame resistance,[3] and high stability toward harsh chemicals such as acids and bases.[4] It has been used in many applications including drug and vaccine delivery,[5−8] microarray and biosensors,[9−11] superhydrophobic surface,[12−14] and tissue engineering.[15−17]

One of the early methods for the synthesis of polyphosphazenes was developed by Allcock and co-workers.[18,19] It consists of two steps, starting from the ring-opening of hexachlorocyclotriphosphazene to give polydichlorophosphazene having 10 000−15 000 repeating units, which is then treated with a nucleophile such as amine or an alcohol to introduce the desired substituent (R) to the polymer (Scheme 1A).[20,21] This method remains the most popular and is still in use today.[3,19,22] However, this method suffers from several drawbacks such as low hydrolytic stability of hexachlorocyclotriphosphazene and polydichlorophosphazene.[23] High temperature (250 °C) and vacuum are required for the ring-opening polymerization which may cross-link or degrade the polymer.[24] In addition, the nucleophilic substitution step may not give complete replacement of all Cl atoms in the polymer, especially when the substituent is large. Substituent exchange reaction can also occur depending on the nucleophilicity and the steric hindrance.[25] Furthermore, the P−Cl bond is prone to hydrolysis.[24] Other methods have also been developed, such as living cationic polymerization,[26] where the polymerization can be carried out at room temperature, yielding polymers with defined molecular weight and narrow size distribution.[27] However, living cationic polymerization typically requires strict polymerization conditions such as high vacuum and high purity of the reagents.[27]

The Staudinger reaction, the reaction between an azide and a phosphine, generates an iminophosphorane, i.e., phosphazene product in almost quantitative yield under relatively mild conditions.[28] It has been used to synthesize polyphosphazenes. For example, Herring reported a polymerization reaction between 1,4-diazido-benzene with 1,4-bis(diphenylphosphino)-benzene at room temperature for 4 h. However, the polymer precipitated out of the solution, and the molecular weight was impossible to analyze.[29] The first high molecular weight polyphosphazene ($\bar{M}_n$ = 10 000−25 000) synthesized through Staudinger reaction was reported by Matyjaszweski and co-workers.[30] By mixing trimethylsilyl azide with bis-(trifluoroethyl)(phenyl)phosphonite at 70 °C, the polyphosphazene product was obtained in 60−80% yield.

Perfluoroaryl azides (PFAAs), originally developed as highly efficient photoaffinity labels owing to the increased lifetime of the singlet perfluoroaryl nitrene generated by photoactivation of the azide, have been applied for the functionalization of materials and surfaces[31,32] and for the conjugation of a wide range of structures including drug molecules,[33] polymers,[34,35] carbohydrates,[36−41] and nanoparticles.[42−45] Additionally, the azide in PFAA is a highly electrophilic dipole activated by the

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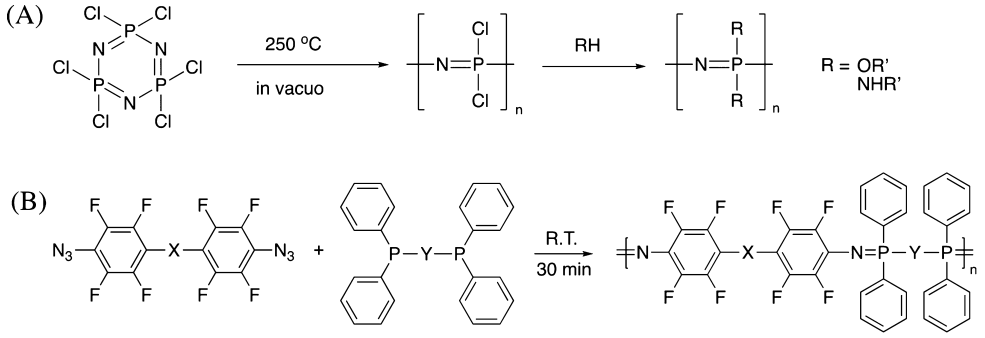
Scheme 1. Synthesis of Polyphosphazene: (A) Ring-Opening of Hexachlorocyclotriphosphazene Followed by Nucleophilic Substitution with an Alcohol or an Amine; (B) PFAA-Mediated Staudinger Polymerization



multiple fluorine atoms. For instance, the LUMO of pentaphenyl azide is 3.06 eV compared to 3.68 eV in the case of phenyl azide.[46,47] This electrophilic activation results in orders of magnitude increase in the reaction rates and enables new reactions of PFAAs that are unique and impossible with phenyl azide, for example, azide−thioacid amidation,[48] azide−aldehyde amidation,[49,50] azide−alkyne cycloaddition,[46,51−53] and Staudinger reaction.[54] In the PFAA-Staudinger reaction, the reaction occurs under ambient conditions, and the rate constant of the reaction between PFAA and triarylphosphine reached 15 M^{-1} s^{-1}.[54] In addition, the iminophosphorane product is stable toward hydrolysis and aza−ylide reactions. In this work, we demonstrate the use of this reaction for the synthesis of polyphosphazenes (Scheme 1B). The polymerization occurs at room temperature in air to give polyphosphazenes with $\bar{M}_w$ of up to above 59 000 and narrow $Đ$ (1.1−1.2). The scope of the polymerization was investigated with regard to the structure of the monomers, and the impact of the solvent was also studied. The resulting polyphosphazenes showed high thermal stability, with the decomposition temperature and char yield of up to 441 °C and 53%, respectively.

EXPERIMENTAL SECTION

Materials. Sodium azide (≥99.5%), cesium carbonate (99%), copper(I) iodide (≥99.5%), ethylene glycol (≥99.5%), *N*′-ethyl-*N*-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDAC) (≥99%), 3-(diphenylphosphino)propionic acid (97%), 1,3-bis-(diphenylphosphino)propane (97%), diphenylphosphine (98%), decafluorobiphenyl (99%), DMAP (4-(dimethylamino)pyridine) (≥99%), 1,4-diiodobenzene (99%), methyl pentafluorobenzoate (99%), sodium chloride (≥99.5%), sodium sulfate (≥99%) and poly(bis(phenoxy)phosphazene (PBPP) were purchased from Sigma-Aldrich. *N*,*N*-Dimethylformamide (DMF), ethyl acetate, hexanes, toluene, diethyl ether, acetone, methanol, methylene chloride, and acetonitrile were purchased from Fisher Scientific. NMR spectra were recorded on a Bruker Avance Spectrospin DRX 500 spectrometer (500 MHz) or a Bruker Avance Spectrospin DPX 200 spectrometer (200 MHz) referenced to either nondeuterated residual solvent peak or tetramethylsilane peak (TMS, δ 0 ppm). Trifluoroacetic acid (CF_3COOH, δ −76.55 ppm) was used as the external reference for ^{19}F NMR, and 85% phosphoric acid (H_3PO_4, δ 0 ppm) was used as the external reference for ^{31}P NMR. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific, West Palm Beach, FL).

Synthesis of 4,4′-Diazido-2,2′,3,3′,5,5′,6,6′-octafluoro-1,1′-biphenyl (1a). Compound **1a** was synthesized following a previously developed protocol.[55,56] To the solution of decafluorobiphenyl (5.0 g, 15 mmol) in 5 mL of DMF, a solution of sodium azide (1.95 g, 30.0 mmol) in 5 mL of DMF was added. The solution was stirred at room temperature overnight. The reaction mixture was diluted with 20 mL of water, and diethyl ether (20 mL) was added to the mixture. The organic layer was washed with water (3 × 100 mL) and brine (100 mL) and dried over sodium sulfate. The collected organic phase was concentrated under vacuum, and the crude product was purified by column chromatography with hexanes as the eluent to obtain **1a** as a white solid powder (5.2 g, 91%). ^{19}F NMR (188 MHz, $CDCl_3$): δ −134.69 to −134.88 (m, 4F), −147.58 to −147.71 (m, 4F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.85 (dd, $^1J_{CF}$ = 253 Hz, $^2J_{CF}$ = 14 Hz), 140.73 (dd, $^1J_{CF}$ = 253 Hz, $^2J_{CF}$ = 16 Hz), 122.48 (t, $^2J_{CF}$ = 13 Hz), 102.31 (t, $^2J_{CF}$ = 15 Hz).

Synthesis of Ethane-1,2-diyl Bis(4-azido-2,3,5,6-tetrafluorobenzoate) (1b). Compound **1b** was synthesized according to the reported protocol.[57] In brief, a solution of 4-azido-2,3,5,6-tetrafluorobenzoic acid[58] (1.00 g, 4.30 mmol) in dry dichloromethane (20 mL) was stirred with ethylene glycol (132 mg, 2.10 mmol) and DMAP (53 mg, 0.43 mmol) under Ar at room temperature for 30 min. Afterward, EDAC (908 mg, 4.70 mmol) was added to the solution, and the solution was further stirred at room temperature overnight. Then 20 mL of water was added, and the mixture was stirred for 30 min. The mixture was extracted with 20 mL of CH_2Cl_2 for 3 times, and the combined organic layers were washed with water (3 × 100 mL) and brine (100 mL) and dried over sodium sulfate. The compound was purified by column chromatography using hexanes:ethyl acetate (3:2, v:v) as the eluent to give **1b** as a white powder (729 mg, 70%). ^1H NMR (500 MHz, $CDCl_3$): δ 4.71 (s, 4H). ^{19}F NMR (188 MHz, $CDCl_3$): δ −136.10 (dd, $^1J_{FF}$ = 21 Hz, $^2J_{FF}$ = 10 Hz, 4F), −148.65 (dd, $^1J_{FF}$ = 19 Hz, $^2J_{FF}$ = 8 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.05 (s), 145.57 (ddt, $^1J_{CF}$ = 260 Hz, $^2J_{CF}$ = 13 Hz, $^3J_{CF}$ = 4 Hz), 140.56 (dd, $^1J_{CF}$ = 252 Hz, $^2J_{CF}$ = 16 Hz), 123.96 (tt, $^2J_{CF}$ = 12 Hz, $^3J_{CF}$ = 3 Hz), 107.04 (t, $^2J_{CF}$ = 15 Hz), 63.38 (s).

Synthesis of Ethane-1,2-diyl Bis(3-(diphenylphosphanyl)-propanoate) (2b). Monomer **2b** was synthesized in a similar manner as monomer **1b** from 3-(diphenylphosphino)propionic acid (595 mg, 2.30 mmol), ethylene glycol (71 mg, 1.15 mmol), EDAC (220 mg, 1.15 mmol), and DMAP (14 mg, 0.12 mmol) in dry CH_2Cl_2 (20 mL). The crude product was purified by column chromatography using hexanes:ethyl acetate (20:3, v:v) to give a thick yellow liquid (499 mg, 80%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.45−7.38 (m, 8H), 7.36−7.28 (m, 12H), 4.20 (s, 4H), 2.48−2.30 (m, 8H). ^{31}P NMR (81 MHz, $CDCl_3$): δ −14.12 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.84 (d, $^3J_{CP}$ = 15 Hz), 137.73 (d, $^1J_{CP}$ = 13 Hz), 132.72 (d, $^2J_{CP}$ = 19 Hz), 128.84 (s), 128.57 (d, $^3J_{CP}$ = 7 Hz), 62.30 (s), 30.60 (d, $^1J_{CP}$ = 20 Hz), 22.99 (d, $^2J_{CP}$ = 13 Hz).

Synthesis of 1,4-Bis(diphenylphosphanyl)benzene (2c). Monomer **2c** was synthesized following the reported procedures.[59] In brief, cesium carbonate (978 mg, 3.00 mmol) and copper iodide (46 mg, 0.24 mmol) were mixed in a flame-dried round-bottom flask. Afterward, a solution containing 1,4-diiodobenzene (792 mg, 2.40 mmol) and diphenylphosphine (372 mg, 2.00 mmol) in toluene (5 mL) was added. After heating at 110 °C for 24 h, the mixture was filtered through a packed Celite and rinsed with dichloromethane (3 × 20 mL). The solution was then washed with water (3 × 100 mL) and

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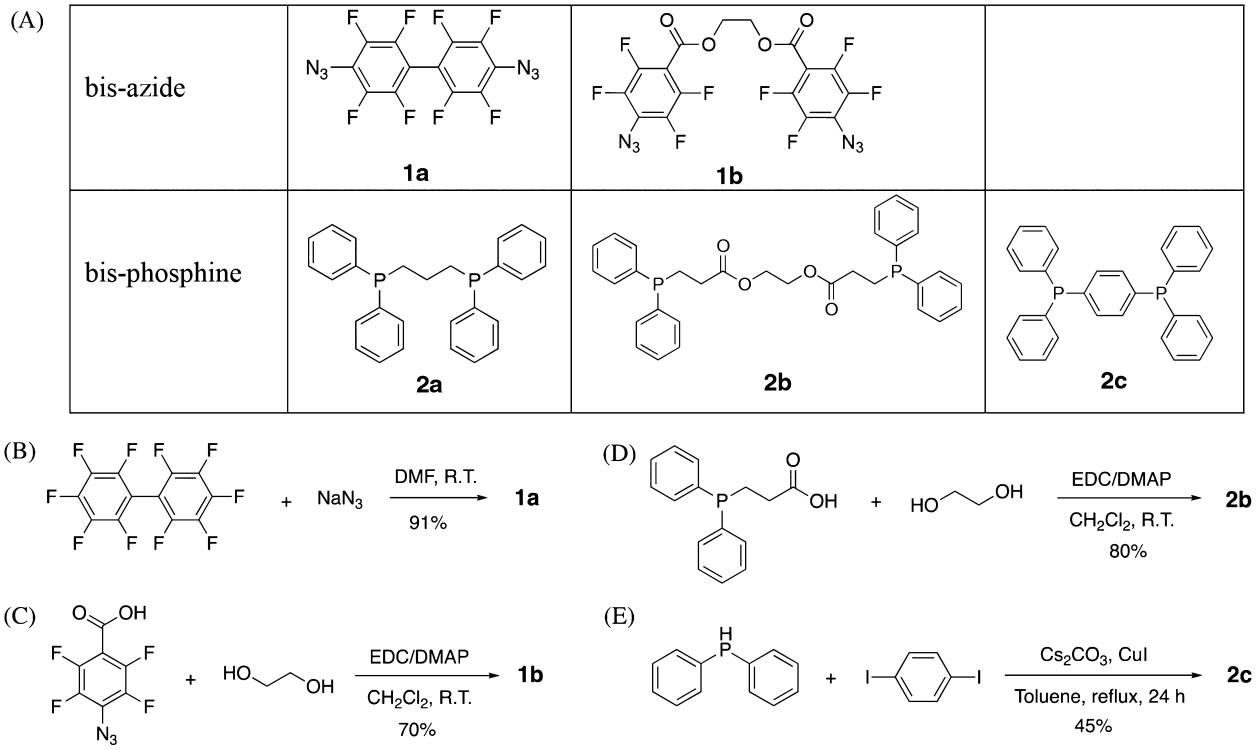
Scheme 2. (A) Bis-Azide (1a, 1b) and Bis-Phosphine (2a, 2b, 2c) Used in This Study; Syntheses of 1a (B), 1b (C), 2b (D), and 2c (E)



dried over sodium sulfate. After the solvent was removed on a Rotovap, the crude was purified by column chromatography using hexanes:dichloromethane (2:1, v:v) as the eluent to give **2c** as a white powder (385 mg, 73%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.47−7.35 (m). ^{31}P NMR (81 MHz, $CDCl_3$): δ −3.97 ppm.

General Polymerization Procedure. Polymers **3aa**, **3ab**, **3ba**, and **3bb** were synthesized as follows. A solution of PFAA monomer **1a** or **1b** (0.26 mmol) in CH_3CN (6.5 mL) was added to a solution of phosphine monomer **2a** or **2b** (0.26 mmol) in CH_3CN (6.5 mL). The solution was stirred at room temperature for 30 min. Typically, precipitates were observed after stirring for 15 min. The precipitate was collected by centrifugation, and the supernatant was removed. The polymer was then redissolved in 1 mL of DMF and was precipitated by the addition of diethyl ether (13 mL). The precipitation/centrifugation process was repeated three times, and the obtained light yellow solid was then dried under vacuum.

Polymer **3ac** was synthesized as follows. A solution of PFAA monomer **1a** (0.26 mmol) in CH_3CN/CH_2Cl_2 (1/1) (6.5 mL) was added to a solution of phosphine monomer **2c** (0.26 mmol) in CH_3CN/CH_2Cl_2 (1/1) (6.5 mL). The solution was stirred at room temperature for 30 min. It was then purified following the purification method above.

Polymer 3aa. Yield: 71.6 mg, 34%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67−7.64 (m, 8H), 7.46−7.45 (m, 4H), 7.41−7.38 (m, 8H), 2.74−2.67 (m, 4H), 1.85−1.75 (m, 2H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 7.56 (t, $^3J_{PF}$ = 5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −147.76 (m, 4F), −159.02 (m, 4F).

Polymer 3ba. Yield: 88.4 mg, 37%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67−7.64 (m, 8H), 7.46−7.45 (m, 4H), 7.41−7.38 (m, 8H), 2.74−2.67 (m, 4H), 1.85−1.75 (m, 2H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 9.75 (t, $^3J_{PF}$ = 5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −146.37 (m, 4F), −158.81 (m, 4F).

Polymer 3ab. Yield: 136 mg, 56%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78−7.74 (m, 8H), 7.52−7.49 (m, 4H), 7.46−7.43 (m, 8H), 4.12 (s, 4H), 2.86−2.81 (m, 4H), 2.58−2.53 (m, 4H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 6.76 (t, $^3J_{PF}$ = 5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −147.92 (m, 4F), −158.86 (m, 4F).

Polymer 3bb. Yield 28.9 mg, 37%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74−7.70 (m, 8H), 7.55−7.51 (m, 4H), 7.48−7.44 (m, 8H), 4.55 (s, 4H), 4.12 (s, 4H), 2.85−2.80 (m, 4H), 2.55−2.50 (m, 4H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 9.12 (t, $^3J_{PF}$ = 5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −146.54 (m, 4F), −158.64 (m, 4F).

Polymer 3ac. Yield; 60.0 mg, 30%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.78−7.62 (m, 10H), 7.49−7.36 (m, 14H). ^{31}P NMR (81 MHz, $CDCl_3$): δ 9.67 (t, $^3J_{PF}$ = 5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$): δ −140.48 (m, 4F), −149.80 (m, 4F).

Thermal Stability. Thermal stability studies were conducted by thermal gravimetric analysis (TGA 5500, TA Instruments, New Castle, DE). Typically, about 2.5 mg of the polymer sample was added to the TGA pan. The polymer was then heated under Ar at a heating rate of 10 °C/min until the temperature reached 800 °C.

RESULTS AND DISCUSSION

Polymer Synthesis. Bis-PFPAs and bis-phosphines with aromatic or aliphatic linkers were used in this study (Scheme 2). The electron-deficient nature of the perfluorinated aryl azide allows the straightforward synthesis of bis-PFPA **1a** by nucleophilic aromatic substitution of decafluorobiphenyl with NaN_3 at room temperature in high yield (91%) (Scheme 2).[60] Monomer **1b** was synthesized by esterification of EDAC-activated 4-azido-2,3,5,6-tetrafluorobenzoic acid with 1,2-ethylene diol in 70% yield. Phosphine **2b** was synthesized by esterification of EDAC-activated 3-(diphenylphosphino)-propanoic acid with 1,2-ethylene diol in 80% yield. Phosphine **2d** was synthesized by a CuI-catalyzed cross-coupling of diphenylphosphine and 1,4-diiodobenzene under toluene reflux in 45% yield.[59]

Monomers **1a** and **2a** were used as the model system to determine the optimized conditions for the polymerization (Figure 1A). The polymerization was carried out by mixing equal mole amount of **1a** and **2a** in acetonitrile at room temperature at the monomer concentration of 20, 30, or 40

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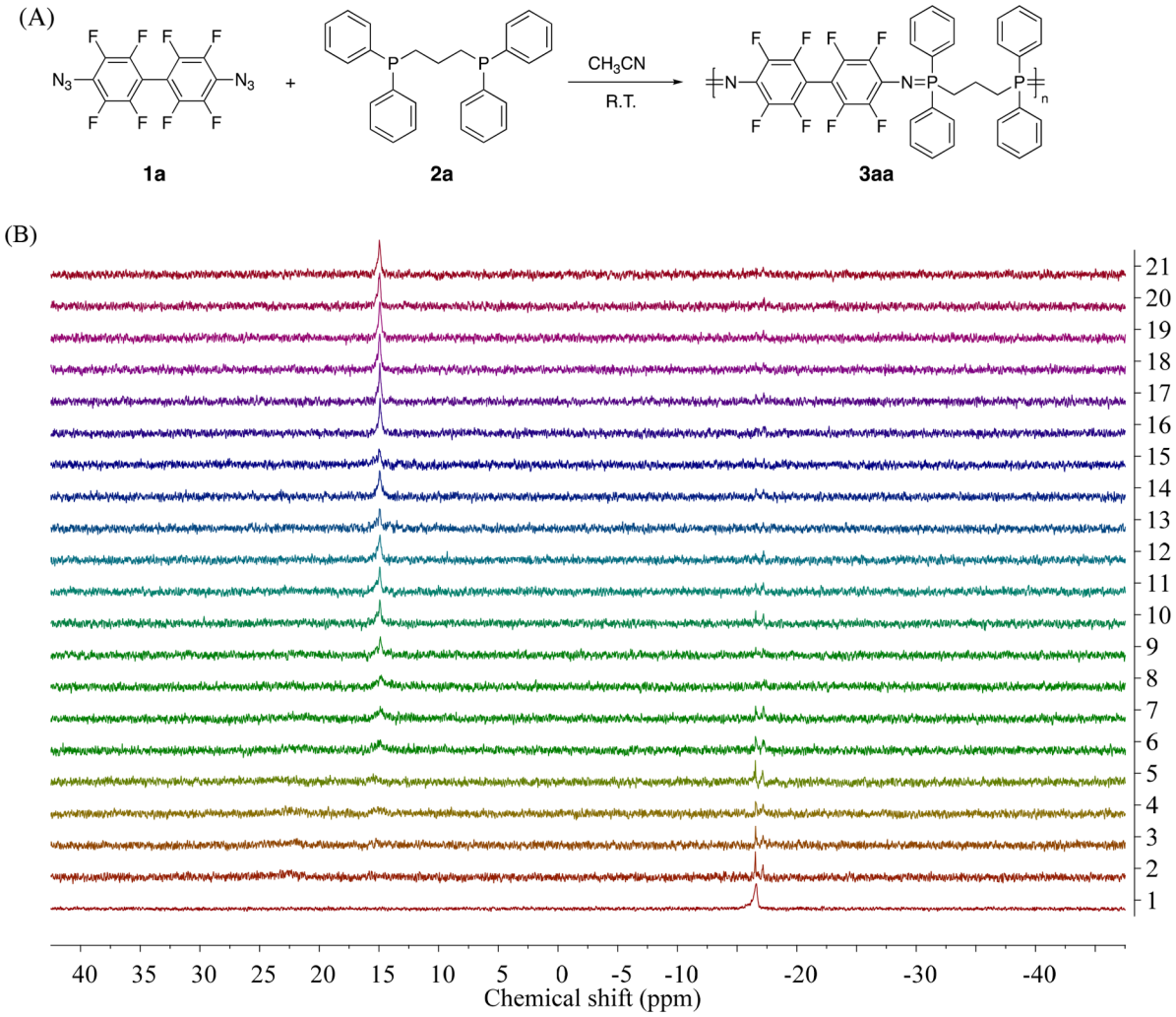

Figure 1. (A) Synthesis of polymer **3aa**. (B) ^{31}P NMR spectra of the polymerization mixture of **1a** and **2a** in acetonitrile (20 mM) over the course of 40 min. A spectrum was taken every 2 min. Spectrum 1 was that of **2a** before **1a** was added.

mM. Upon mixing the two monomers, precipitate started to form immediately. After stirring for 30 min, the precipitate was collected and was purified by three cycles of dissolving in DMF and precipitating with diethyl ether.

The progress of polymerization was monitored using ^{31}P NMR at the monomer concentration of 20 mM over the course of 40 min (Figure 1B). The ^{31}P NMR spectrum of **2a** (spectrum 1) contains a single peak at −16.54 ppm which corresponds to the P in **2a**. Upon addition of **1a**, the peak at −16.54 ppm decreased, and a new peak at −17.11 ppm appeared. This could be assigned the chain terminus of the polymer which gradually decreased in relative intensity as the polymer chain grew. The peak at −16.54 ppm continued to decrease and was consumed by the end of the reaction. A new peak at 14.89 ppm started to appear at 6 min into the polymerization (spectrum 4). This peak is typical of phosphazene formed from the PFPA-Staudinger reaction,[54] which can be assigned to the P in the polyphosphazene product **3aa**. As the high molecular weight polymer precipitated out from the reaction, the phosphazene product detectable by NMR in the supernatant solution should be low molecular weight fractions. The intensity of the peak at 14.89 ppm continued to grow with the progress of the polymerization and plateaued at the end of 30 min (spectrum 16). Before the formation of polyphosphazene, a broad peak at around 22.49 ppm appeared immediately after mixing the two monomers (spectra 2−4). This peak can be assigned to the phosphazide intermediate[54,61] formed from the reaction between the azide and the phosphine, as the Staudinger reaction proceeds through a phosphazide intermediate before converting into phosphazene.[62]

The polymerization was also monitored by IR (Figure 2). After polymerization, the characteristic azide peak at 2120/2148 cm^{-1} in the IR spectrum of **1a** (Figure 2A) disappeared, indicating the full conversion of the monomer **1a** (Figures 2C−E). The N=P band at 1175 cm^{-1}, which was absent in both monomers, appeared in all polymers (Figures 2C−E).[63] The aliphatic −CH and aromatic =CH stretching at around 2900−3100 cm^{-1} in monomer **2a** (Figure 2B) together with the aromatic C=C ring stretch around 1470 and 1640 cm^{-1} in both monomers **1a** (Figure 2A) and **2a** (Figure 2B) also appeared in the polymer (Figures 2C−E).

The product **3aa** is furthermore characterized by ^{31}P and ^{19}F NMR (in $CDCl_3$, Figure 3). The ^{31}P NMR spectrum of the polymer contained only one peak at 7.56 ppm, which belonged to the P in the phosphazene structure (Figure 3A). The ^{31}P NMR spectra of the starting material **2a** and the phosphazide intermediate formed between **1a** and **2a** appeared at −22.3

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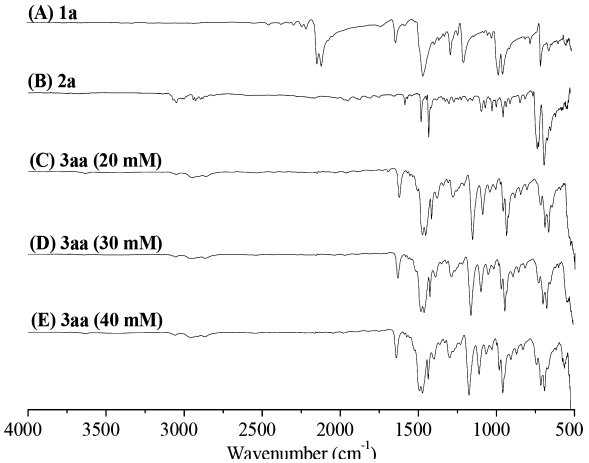

Figure 2. IR spectra of monomer **1a** (A), **2a** (B), and polymer **3aa** synthesized from **1a** and **2a** at 1:1 mole ratio at monomer concentration of 20 (C), 30 (D), or 40 mM (E) in acetonitrile for 30 min.

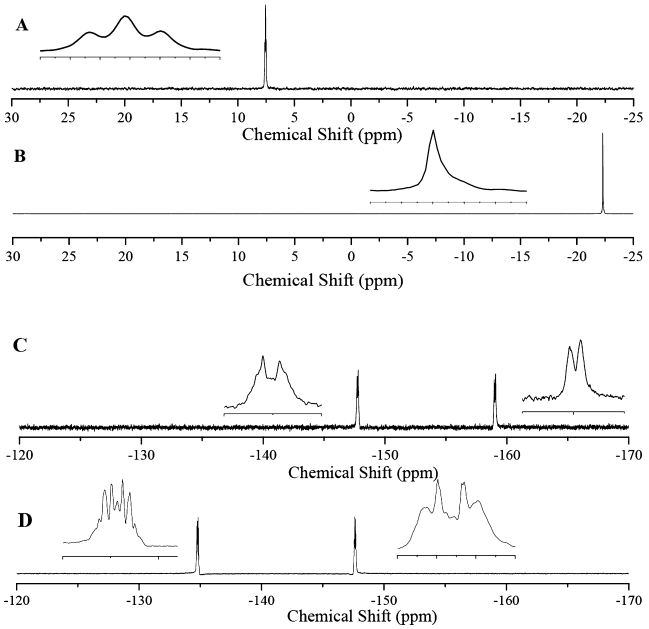

Figure 3. ^{31}P NMR (A) and ^{19}F NMR (C) spectra of polymer **3aa** synthesized from monomer **1a** and monomer **2a** (20 mM) at room temperature for 30 min. (B) ^{31}P NMR spectrum of **2a**. (D) ^{19}F NMR spectrum of **1a**. The insets are the enlarged peaks. All spectra were taken in $CDCl_3$.

ppm (Figure 3B) and ~25 ppm,[54] respectively. In addition, the P peak in the polymer **3aa** showed the triplet splitting pattern (Figure 3A, inset), resulting from the coupling to the nearest two F atoms, which is typical of the P from the phosphazene structure that was not observed in the starting material **2a** (Figure 3B, inset).[54] The formation of the polymer was furthermore confirmed by the two distinct peaks at −147.76 and −159.02 ppm in the ^{19}F NMR spectrum of polymer **3aa** (Figure 3C), which shifted upfield from those of the monomer **1a** at −134.79 and −147.71 ppm, respectively (Figure 3D).

The molecular weight and molecular weight distribution of polymer **3aa** prepared at different monomer concentration in CH_3CN were analyzed by GPC (Table 1, entries 1−3). The polyphosphazenes synthesized by PFAA-Staudinger reaction

Table 1. Effect of the Monomer Concentration and Solvent on the Molecular Weight and Dispersity of Polymer 3aa

entry	monomer concn (mM)	solvent	solvent polarity index[64,65]	$\bar{M}_w$[a]	$\bar{M}_n$[a]	$Đ$[a]
1	20	CH_3CN	6.2	59 516	54 051	1.1
2	30	CH_3CN	6.2	54 141	44 303	1.2
3	40	CH_3CN	6.2	57 041	47 730	1.2
4	20	EtOAc	4.3	41 254	29 706	1.4
5	20	CH_2Cl_2	3.1	21 706	15 384	1.4

[a]Measured by GPC (THF, room temperature, polystyrene standard).

had higher molecular weight ($\bar{M}_n$ = 44 000−50 000) and narrower dispersity ($Đ$: 1.1−1.2) than those prepared by the classic Staudinger reaction. The narrowest molecular weight distribution of the polymer ($Đ$: 1.1, entry 1) was obtained from the lowest monomer concentration used (20 mM), whereas $Đ$ increased to 1.2 at higher monomer concentrations of 30 and 40 mM (entries 2 and 3). The molecular weight of the polymer was also slightly higher at the lowest monomer concentration (entry 1 vs entries 2 and 3). The low dispersity can be attributed to the fast reaction and the low solubility of the polymer in the polymerization solvent CH_3CN. The high molecular weight polymer precipitated immediately upon mixing the two monomers. The low molecular weight polymer remained in the solution (Figure 1) and was removed during the work-up. The collected polymer product contained only the high molecular weight fractions with more uniform molecular weight distribution. Increasing monomer concentration would further accelerate premature termination of the growing polymer chains, contributing to increased dispersity.

The influence of solvent on the polymerization was next tested while keeping the monomer concentration at 20 mM (Table 1, entries 1, 4, and 5). The molecular weight of the polymer increased with the polarity of the solvent. The molecular weight was also more homogeneous for polymer obtained in more polar solvent, giving $Đ$ of 1.1 in CH_3CN (entry 1) and 1.4 in ethyl acetate and dichloromethane (entries 4 and 5). The Staudinger reaction goes through a polar transition state that is more stabilized in the polar solvent and hence faster reaction.[62] In the PFAA-Staudinger reaction, the reaction rate increased with the polarity of the solvent.[54] We expect that the rate of PFAA-Staudinger polymerization increases with the polarity of the solvent in the order of CH_2Cl_2, EtOAc, and CH_3CN. The solubility of the polymer differs considerably in different solvents. Acetonitrile is a poor solvent for the polymer. When the polymerization was carried out in acetonitrile, precipitate was formed immediately, resulting from a combination of fast rate and poor solubility of the polymer. CH_2Cl_2 is a less polar but better solvent for the polymer. The slower polymerization as well as the higher solubility of the polymer contributed to the lower molecular weight and increased dispersity.

To test the scope of the polymerization, monomers having aliphatic, aromatic and ester linkers were used to investigate the effect of the monomer structure on polymerization (Schemes 1 and 3). The polymerization was carried out by stirring 20 mM of monomer **1** and monomer **2** in CH_3CN at room temperature for 30 min. Typically, precipitates were observed after stirring for 15 min. The polymer was collected by centrifugation, and was purified by repetitive dissolution/

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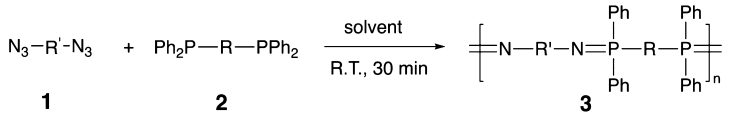
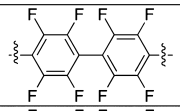
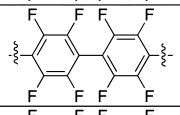
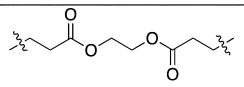
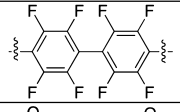
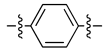
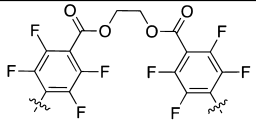
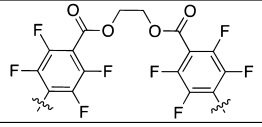
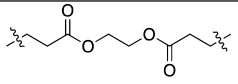
Scheme 3. Scope of PFAA-Staudinger Polymerization



	R'	R
3aa		
3ab		
3ac		
3ba		
3bb		

precipitation from DMF/ether to give the polymer as light yellow solids.

Diphosphine **2c** was chosen to test whether the aromatic structure would affect the reactivity of the phosphine as extended conjugation may reduce the reactivity of the phosphine.[66] Dichloromethane was initially used as the solvent for the synthesis of polymer **3ac** due to the lower solubility of monomer **2c** in CH_3CN; however, the polymerization was incomplete after 1 h as shown by the presence of the phosphine monomer after purification. The slow reaction could be due to the lower polarity of the solvent in addition to the conjugated structure. The reaction was then carried out in 1:1 CH_3CN:CH_2Cl_2. Under this condition, the reaction was completed in 1 h as shown by the absence of the phosphine peak in the polymer product (Figure S22).

^{31}P NMR analysis of the polymers **3aa**, **3ba**, **3ab**, and **3bb** showed the phosphazene peak in the range of 6.8−9.8 ppm (Figures S10, S13, S16, and S19), indicating that the polyphosphazene products were successfully synthesized. Polymers **3aa**, **3ba**, **3ab**, and **3bb** have $\bar{M}_w$ in the range of 52 724−59 516 and low $Đ$ of 1.1−1.2 (Table 2, entries 1−4). The molecular weight of polymers **3ac** was not analyzed due to its poor solubility in THF.

Thermal Stability. The high nitrogen and phosphorus contents in polyphosphazenes make them intrinsically fire resistant.[67] These polymers have high thermal stability, which can be characterized by high thermal decomposition temperatures and high char yields. Thermal decomposition temperature is the temperature that corresponds to a significant decrease of the polymer weight.[68] The char yield is defined as the percentage of the polymer weight that remains unchanged at the end of a heating process.[67] For example, **PBPP** (Figure 4), a commercially available polyphosphazene, has a thermal degradation temperature of 395 °C and a char yield of 37%.[67]

Table 2. Molecular Weight, Dispersity, Decomposition Temperature, and Char Yield of Synthesized Polyphosphazenes

					decomposition temperature (°C)[d]			
entry	polymer	$\bar{M}_w$[a]	$\bar{M}_n$[a]	$Đ$[a]	T_{onset}	T_{max}	T_{end}	char yield (%)[e]
1	**3aa**[b]	59 516	54 051	1.1	353	410	455	28
2	**3ba**[b]	52 724	43 282	1.2	266	328	473	22
3	**3ab**[b]	57 018	49 303	1.2	251	340	441	21
4	**3bb**[b]	56 158	45 369	1.2	267	310	446	7
7	**3ac**[c]	N.D.	N.D.	N.D.	351	441	520	53
8	**PBPP**				255	395	510	21

[a]Measured by GPC (THF, room temperature, polystyrene standard), N.D. = not determined because the polymer was insoluble in THF. [b]Synthesized in CH_3CN. [c]Synthesized in CH_2Cl_2:CH_3CN (1:1, v:v). [d]Measured from differential thermogravimetric analysis (DTG, Figure S24). Data are presented as the temperature at the onset (T_{onset}), maximal (T_{max}), and end (T_{end}) of decomposition. [e]Measured by TGA under argon from Figure 4.

The thermal stability of the synthesized polyphosphazenes was studied using TGA and DTG, from which the decomposition temperature and char yield were obtained. The polymer sample was gradually heated under argon and the weight of the sample was monitored by TGA. The weight of the sample was normalized against the initial sample weight, and the percent weight was then plotted against the heating temperature (Figure 4). The thermal decomposition temperatures were obtained from the differential thermogravimetric curve shown in Figure S24,[69] from which the decomposition temperatures at the onset, the maximal rate, and the end of decomposition were obtained (Table 2). Several factors influence the thermal stability of the polymer, including the

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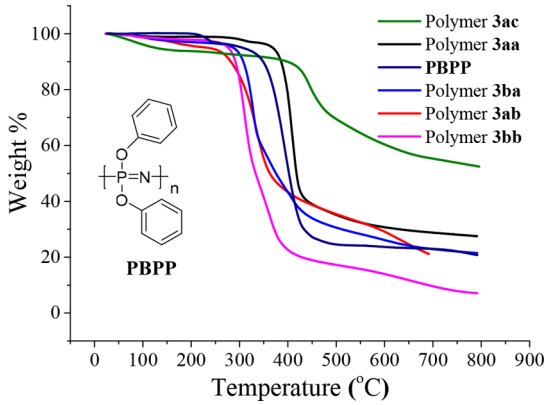

Figure 4. TGA thermograms of polymers tested. Samples were heated at 10 °C/min under Ar.

structure of the monomer and the strength of the chemical bond.[70,71] Studies on the thermal degradation of polyphosphazenes conclude that the chain scission typically occurs randomly followed by both depolymerization and some degree of cross-linking.[72−75] The decomposition temperatures of polymers **3aa**, **3ab**, and **3ac** synthesized from **1a** having a diphenyl linker are in general higher than polymers **3ba** and **3bb** synthesized from **1b** that has an ester linker (entry 1 vs 2, entry 3 vs 4, entry 5 vs 6). The ester bond typically decomposes around 263−284 °C as compared to the Ph−Ph bond which decomposes around ∼400 °C.[76,77] The highest thermal decomposition temperature was obtained from polymer **3ac** (441 °C, entry 7), which was synthesized from the aromatic monomers **1a** and **2c**. Both polymers **3ac** and **3aa** have higher thermal decomposition temperature than **PBPP**.

Similar to the decomposition temperature, the char yields of polymers **3aa**, **3ab**, and **3ac** synthesized from **1a** were higher than those of polymers **3ba** and **3bb** synthesized from **1b** (Table 2, entry 1 vs 2, entry 3 vs 4, entry 5 vs 6). This is also consistent with other studies that associate highest char yields with aromatic structures.[67,78] With the exception of **3bb** and **3ab**, all other polyphosphazenes synthesized had the same or a substantially higher char yield than **PBPP** (21%). Polymer **3ac** has the highest char yield (53%, entry 7), which is higher than EYPEL-A rubber (20%), a material that had been used by US Navy as a helicopter seating material.[67]

CONCLUSIONS

In this work, the fast PFAA-Staudinger reaction has been demonstrated in the synthesis of polyphosphazenes. The polymerization was carried out under ambient conditions to give polyphosphazenes with molecular weight close to 60 000 and $Đ$ as narrow as 1.1. This is a significant improvement over the polyphosphazenes obtained from classic Staudinger reaction which had lower molecular weight ($\bar{M}_n$ = 10 000−25 000) and higher $Đ$ (1.7). The molecular weight was influenced by the solvent polarity, with the polar solvent such as CH_3CN giving higher molecular weight than the less-polar solvent like CH_2Cl_2. In addition, most polymers synthesized gave higher thermal decomposition temperatures and char yields and showed higher thermal stability than the commercial poly(bis(phenoxy)phosphazene). Polymer **3ac** has the decomposition temperature and the char yield reaching 441 °C and 53%, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b00618.

Experimental protocols; ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra of monomers and polymers (PDF)

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Notes

The authors declare no competing financial interest.

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