

Synthesis and characterization of polyphenylaminophosphazene and fluorinated polyarylamino phosphazene

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ABSTRACT: Two polyarylamino phosphazenes, poly[bis(phenylamino)phosphazene] (PBAP) and poly[bis(*p*-trifluoroethoxyphenylamino)phosphazene] (PBTAP), were successfully synthesized by ring-opening polymerizations and nucleophilic substitution reactions. Their chemical structures, thermal properties, and surface properties were investigated by NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and water contact angles (WCA). The results indicate that the glass-transition temperature (T_g), thermal stability, and WCAs of PBAP and PBTAP presented obvious differences; this suggested that PBTAP possessed the lower T_g and higher contact angle than PBAP. This was attributed to the influence of trifluoroethoxy at the para position of aniline. TGA measurements indicated that PBAP possessed a higher thermal stability than PBTAP; this was attributed to the strong electron-withdrawing influence of the trifluoroethoxy. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42542.

KEYWORDS: fluorinated; polyphosphazenes; polyarylamino phosphazene; thermal property; water contact angle

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INTRODUCTION

Polyphosphazenes have attracted abundant attention in recent decades for wide applications because of its unique structures.^{1,2} They are macromolecules with a backbone of alternating phosphorus and nitrogen atoms and have two adjustable side groups on the backbone.^{3–5} Generally, polyphosphazenes are prepared by two-step reactions. First, polydichlorophosphazene (PDCP) is synthesized by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene (HCCP). Second, chlorine atoms on the PDCP are substituted by nucleophilic substitution reactions with inorganic, organic, or organometallic side groups, such as sodium alkoxides or aryloxides, primary or secondary amines, or organometallic reagents (Figure 1).⁶ The activity of the P–X bond allows X to be substituted by a nearly unlimited variety of nucleophiles. Previous studies have indicated that the side groups on polyphosphazenes have a significant influence on the properties, such as the high refractive index, color, ultraviolet filtration, flexibility, hydrophobicity, hydrophilicity, or even water solubility, ion conduction, and biomedical compatibility.^{7–11} Liu *et al.*^{12,13} described the differences in polymer properties brought about by substituent exchange reactions. When the homosubstituted poly[bis(2,2,2-trichloroethoxy)phosphazene] was converted to cosubstituted derivatives with trifluoroethoxy unities, the solubility in common organic solvents, film-forming properties, and fire-resistant applications were

improved obviously. Polyphosphazenes have been widely used in many aspects, such as in elastomers, membranes, biomedical materials, liquid-crystal polymers, lubricant stabilizers and additives, fire-resistant materials, polymer electrolytes, dyes, and resins.^{14–18}

Polyaryloxyphosphazenes and polyalkoxyphosphazenes have been studied extensively because of their excellent thermal stability and mechanical properties.^{19–23} Fluoroalkoxyphosphazenes and fluoroaryloxyphosphazenes are perhaps the most important polyphosphazene derivatives for their synthetic versatility, structural variability, and outstanding properties.^{24,25} Fluorinated polyphosphazenes mainly include two categories, homopolymers and copolymers.^{26,27} Homopolymers are further divided into two groups, in which fluorine atoms attach to phosphorus directly or fluorine-containing moieties are linked to phosphorus through aliphatic or aromatic groups. Copolymers are further divided into three classes: First, two or more fluorinated chains are attached to the backbone. Second, two or more fluorinated macromolecules are linked to the backbone to form linear or block copolymers. Third, the fluorinated phosphazene materials as the main substrates are grafted onto organic macromolecules. Furthermore, poly[bis(trifluoroethoxy)phosphazene] is considered as the most prominent member of fluorine-containing polyphosphazenes; it is extremely stable against solvents, such as water, alcohols, acetic acid, and pyridine. This

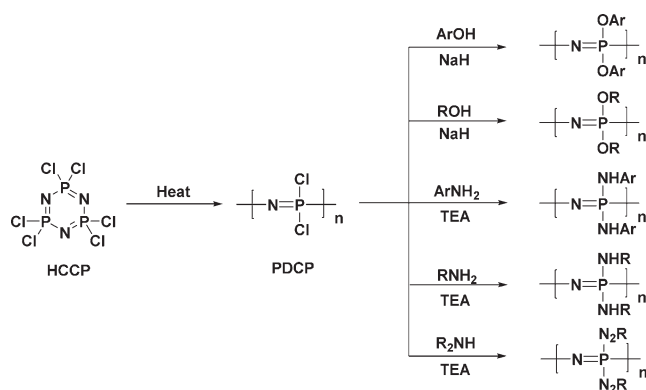


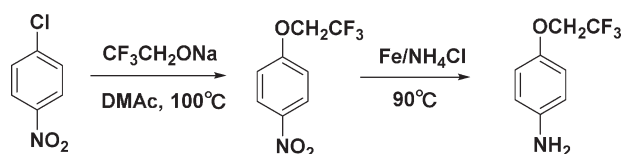
Figure 1. Primary synthesis pathway for the polyphosphazenes.

polymer also presents excellent thermal stability, with a low glass-transition temperature ($T_g = -66^\circ\text{C}$) and high limiting oxygen index (48.0).^{28–30}

Polyaminophosphazenes, which possess biodegradability under physiological conditions, are mainly studied in the field of biodegradable polymers and permeable membranes.^{31–33} Polyphosphazenes with simple amino acid ester as side groups are hydrolytically sensitive to release phosphate, ammonia, amino acid, and alcohol, which should be nontoxic.³⁴ Morozowich *et al.*³⁵ reported the synthesis and characterization of polyphosphazenes containing serine and threonine substituents, which were connected to the polyphosphazene backbone by N and O termini, respectively. A hydrolysis study revealed that the polymers were sensitive to hydrolysis and yielded bioacceptable products, and N-linked side chain polymers were hydrolyzed faster than O-linked polymers. Hu *et al.*³⁶ prepared a novel self-healing elastomer via the reversible photochemical [2+2] cycloaddition through the introduction of ethyl 4-aminocinnamate to polyphosphazenes. Within about 0.5 h under UV irradiation, the damaged polyphosphazenes could be almost completely rehealed. The double bonds of ethyl 4-aminocinnamate could be cross-linked easily, and the retro [2+2] cycloaddition occurring under 254 nm made the polymer able to be reprocessed. Study of polyarylamino phosphazenes is rarely reported because of their higher T_g 's and lower thermal decomposition temperatures.^{37,38}

Different classes of polyphosphazenes are formed by the replacement of chlorine atoms of PDCP with diverse substituent groups; these have different physical and chemical properties. Researchers have paid much attention to the influence of different side groups connecting directly to the phosphorus atoms on the backbone. Few studies have focused on the effect of groups linked to linear polyphosphazenes indirectly, for instance, with an aromatic as spacer.

In this study, poly[bis(phenylamino)phosphazene] (PBAP) and poly[bis(*p*-trifluoroethoxyphenylamino)phosphazene] (PBTAP) were synthesized and characterized by $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and water contact angle (WCA) measurements were occupied to explore the influence of trifluoroethoxy on PBTAP in comparison to PBAP. We aimed to determine the effect when side groups were connected indirectly to polyorganophosphazenes.



Scheme 1. Synthesis of 4-(2,2,2-trifluoroethoxy)aniline.

EXPERIMENTAL

General

All of the polymerization and substituted reactions were carried out under a dry nitrogen atmosphere with a standard Schlenk line technique. HCCP was recrystallized from petroleum ether and sublimed (60°C and 0.05 mmHg). 2,2,2-Trifluoroethanol was distilled over calcium hydride, and sodium hydride (NaH) and aluminum chloride were used as received. All solvents were purchased from commercial sources and purified with standard methods. 4-(2,2,2-Trifluoroethoxy)aniline was synthesized according to the literature (as shown in Scheme 1).³⁹ The polymers PBAP and PBTAP were synthesized with the following procedure, as shown in Scheme 2. $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$ spectra were recorded on a Bruker Avance 400-MHz spectrometer operated at 400 and 162 MHz, respectively. The spectra were recorded with TMS as an internal standard or with 85% phosphoric acid as an external reference.

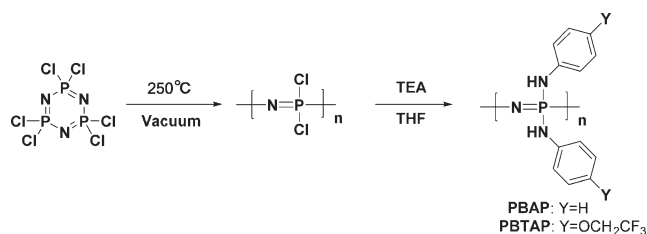
Synthesis of (2,2,2-Trifluoroethoxy)nitrobenzene

To a mixture of NaH (1.90 g, 79.3 mmol, 2.5 equiv) and *N,N*-dimethylacetamide (DMAc) in a 150-mL, round-bottomed flask, 2,2,2-trifluoroethanol (6.35 g, 63.5 mmol, 2 equiv) was added dropwise in an ice bath and stirred at room temperature for 3 h. 4-Chloronitrobenzene (5.0 g, 31.7 mmol, 1 equiv) was added to the previous reaction mixture and stirred at 100°C for 5 h. After it was cooled to room temperature, the mixture was adjusted to a pH value of 6 with diluted hydrochloric acid and filtered. The filter cake was dissolved in ethyl acetate. The organic layer was washed with brine and subsequently dried over Na_2SO_4 . Removing the solvent by rotary evaporation, we provided the crude product by recrystallization with EtOH/ H_2O to afford (2,2,2-trifluoroethoxy)nitrobenzene as a dark yellow acicular crystal with a yield of 94.2%.

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 8.28–8.21 (m, 2H), 7.07–7.00 (m, 2H), 4.47 (q, $J = 7.9$ Hz, 2H).

Synthesis of 4-(2,2,2-Trifluoroethoxy)aniline

Fe powder (3.80 g, 67.8 mmol, 3 equiv) and NH_4Cl (3.63 g, 67.8 mmol, 3 equiv) were added sequentially to a solution of (2,2,2-trifluoroethoxy)nitrobenzene (5.0 g, 22.6 mmol, 1 equiv) in EtOH/ H_2O (3:1) and then refluxed at 90°C overnight. The



Scheme 2. Synthesis route of polyarylamino phosphazenes.

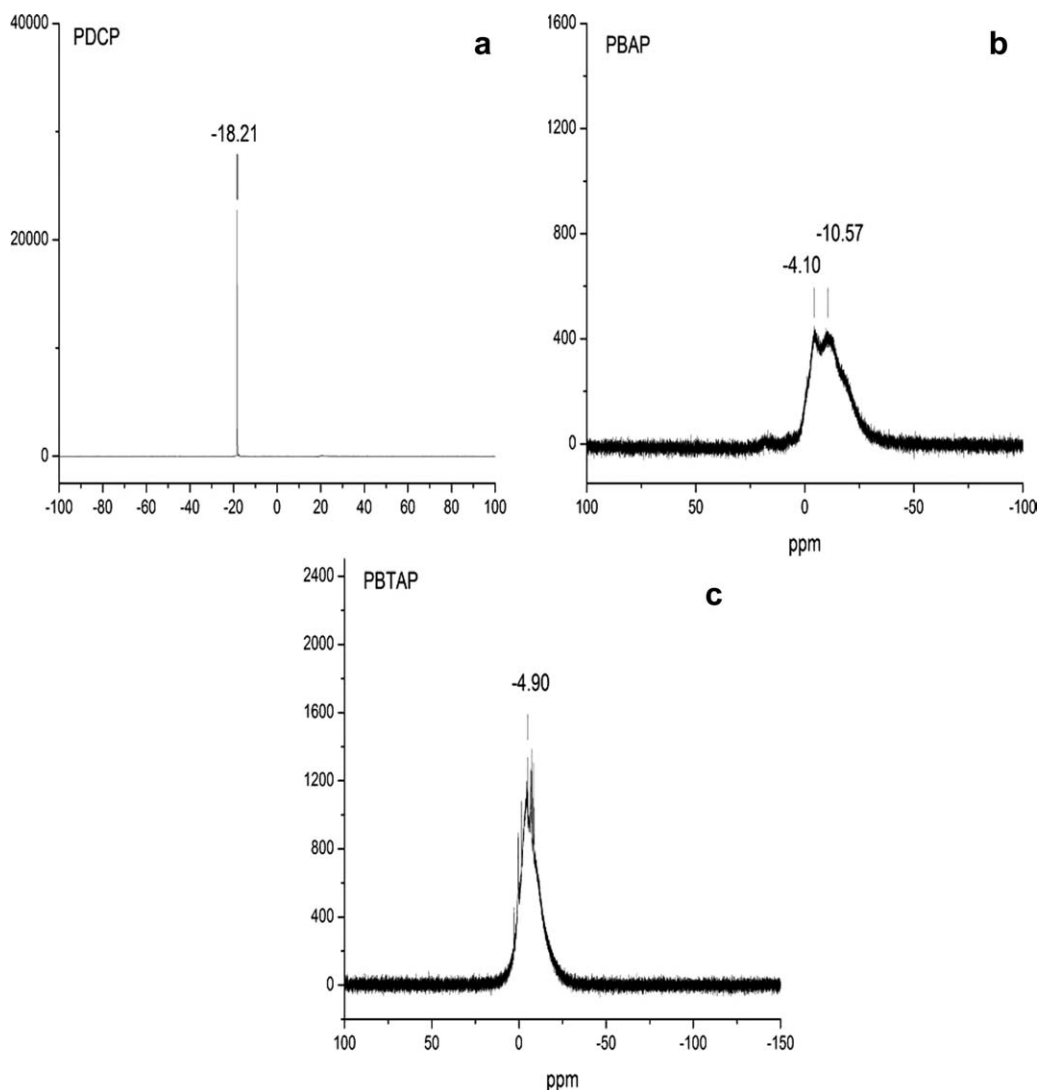


Figure 2. ^{31}P -NMR spectra of PDCP, PBAP, and PBTAP.

reaction mixture was concentrated under reduced pressure, extracted with chloroform, washed with saturated salt water, and dried on Na_2SO_4 . After the solvent was removed, the crude product was purified by recrystallization with dichloromethane/petroleum ether to yield a brown solid with a yield of 95.1%.

^1H -NMR (400 MHz, CDCl_3 , δ): 8.32–8.26 (m, 2H), 7.07–6.99 (m, 2H), 4.46–4.39 (m, 2H).

Synthesis of PDCP

Sublimated HCCP (2.00 g) and anhydrous AlCl_3 (1.25 mg) were placed in a glass tube and then evacuated for 30 min at pressure of 0.1 mmHg and sealed. The sealed glass tube was put into a muffle furnace and reacted for 10 h at 250°C to produce PDCP via ring-opening polymerization. After cooling to room temperature, a transparent immobile substance was acquired. The mixture was washed by petroleum ether several times to wash out trimer and oligomers. The polymer was dissolved in anhydrous tetrahydrofuran (THF) for subsequent use.

^{31}P -NMR [162 MHz, hexadeuterated dimethyl sulfoxide ($\text{DMSO}-d_6$), δ]: -18.21 (s, 1P).

Synthesis of PBAP

A solution of triethylamine (TEA; 4.71 g, 46.60 mmol, 4.5 equiv) and aniline (2.89 g, 31.06 mmol, 3 equiv) in THF was added dropwise to a stirred solution of PDCP (1.2 g, 10.35 mmol, 1 equiv) in THF under an N_2 atmosphere in a Schlenk line. Precipitate began forming almost immediately after the addition was begun. After addition was complete, the mixture was heated to reflux and stirred for 4 days. After the reaction mixture was cooled to room temperature, it was filtered to remove TEA hydrochloride. The filtrate was concentrated under reduced pressure, precipitated from THF into water three times and from THF into hexanes three times, and dried under high vacuum to afford a white solid, which was soluble in THF.

^1H -NMR (400 MHz, $\text{DMSO}-d_6$, δ): 7.54–6.13 (m, 10H).
 ^{31}P -NMR (162 MHz, $\text{DMSO}-d_6$, δ): -4.10 to -10.57 (1P).

Synthesis of PBTAP

Under an N_2 atmosphere, a mixture of TEA (4.71 g, 46.60 mmol, 4.5 equiv) and *p*-trifluoroethoxyaniline (5.94 g, 31.06 mmol, 3 equiv) was slowly added to the solution of PDCP

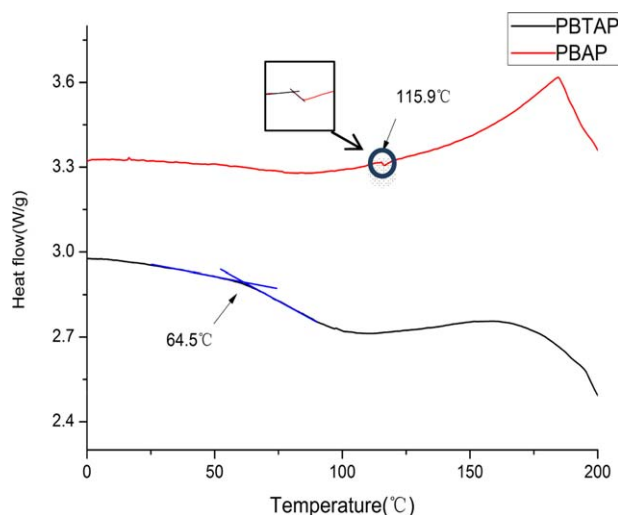


Figure 3. DSC curves of PBAP and PBTAP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(1.2 g, 10.35 mmol, 1 equiv) in THF in a Schlenk line. The precipitate appeared immediately after the addition was begun. The reaction mixture was stirred and refluxed for 4 days and then filtered to remove TEA hydrochloride. The filtrate was concentrated under reduced pressure and precipitated from THF into water three times and from THF into hexanes three times. It was then dried under high vacuum to afford a brown solid.

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ): 7.67–6.21 (m, 8H), 4.55 (b, 4H). $^{31}\text{P-NMR}$ (162 MHz, $\text{DMSO-}d_6$, δ): –4.90 (s, 1P).

T_g

DSC (Mettler Toledo DSC1) was used to study the T_g values of these polyarylamino phosphazenes. The weight of the specimens was approximately 5–10 mg. Specimens were placed in sealed aluminum pans. The specimens were heated from –30 to 200°C at the ramp rate of 10°C/min under nitrogen atmosphere.

Thermal Stability

TGA measurements were carried out on a TA thermogravimetric analyzer Q50. Specimens of about 20 mg were heated from room temperature to 850°C at a rate of 10°C/min under a nitrogen atmosphere. Polymer systems were weighed in the same thermobalance with an accuracy of 0.001 g.

WCA

WCA measurements were obtained with a Dataphysics OCA 15EC contact angle goniometer. Water was dispensed from a needle attached to a Gilmont microliter syringe filled with ultrapure water. The needle was adjusted to allow minimal falling distance for the droplet after detachment from the needle tip via the force of gravity. Water droplets were placed on the surface of the spun-cast film of the polymer, and images of the drop silhouette were recorded with a video camera and stored for analysis on a computer.

RESULTS AND DISCUSSION

$^{31}\text{P-NMR}$

Figure 2 shows the $^{31}\text{P-NMR}$ spectra of PDCP, PBAP, and PBTAP. PDCP showed a sharp peak at –18.21 ppm. The $^{31}\text{P-}$

NMR spectrum of PBAP exhibited broad peak at –4.10 and –10.57 ppm, and the phosphorus spectrum signal of PBTAP was detected at –4.90 ppm; this corresponded to the phosphorus resonance of the –N–P–N– branch. No signal peak was detected at –18.21 ppm in the spectra of PBAP and PBTAP; this indicated that the chlorine atoms of polyphosphazene were fully substituted by aniline groups.

T_g

The T_g values of PBAP and PBTAP were measured by DSC (Figure 3) and were found to be 115.9 and 64.5°C, respectively. They were rather high compared with those of polyalkoxyphosphazenes and polyaryloxyphosphazenes; this suggested a lower torsional mobility of the amino compared with the oxy analogs. We found that connection with trifluoroethoxy at the para position of aniline decreased T_g of PBTAP because, as a flexible group, trifluoroethoxy improved the torsional freedom of the backbone.

Thermal Stability

TGA was used to probe the thermal decomposition behavior of the polymers, as shown in Figure 4. The initial decomposition temperatures of PBAP and PBTAP were 153 and 160°C, respectively. They were lower than those of the polyalkoxyphosphazenes and polyaryloxyphosphazenes; this suggested that these two polymers showed poor thermal stability. Both the samples experienced a three-step thermal degradation, as shown clearly from the TGA curves. The first thermal degradation step occurred from 24 to 150°C; this was attributed to the evaporation of the residual solvent. The second stage was due to the cleavage of side groups in the temperature range from 150 to 400°C. The last weight loss stage started at 400°C and may have been imputable to the degradation of the polyphosphazene backbone. The weight losses of PBAP and PBTAP in the temperature range between 200 and 800°C and the temperatures in the weight loss range between 5 and 50% are enumerated separately in Table I and Table II. These data reveal that PBAP had a higher char yield at elevated temperature than that of PBTAP; this indicated that PBAP possessed a higher thermal stability than PBTAP. This was ascribed to the strong electron-

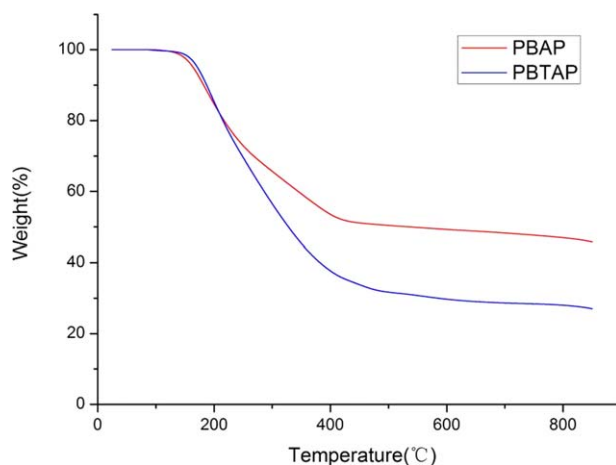


Figure 4. TGA curves for PBAP and PBTAP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Weight Loss by TGA for PBAP and PBTAP

Polymer	200°C	400°C	600°C	800°C
PBAP	15.5	46.5	50.8	53
PBTAP	14.9	62.3	70.3	72.0

withdrawing influence by the trifluoroethoxy at the para position of aniline; this decreased the bond energy of P—N. Therefore, PBAP and PBTAP presented poor thermal stability.

WCA

The surface properties of PBAP and PBTAP were analyzed by static WCA measurements, as shown in Figure 5. It was clear that their surface displayed evident differences. The WCA values of PBAP and PBTAP were 82.8 and 101° and were considered to be hydrophilic and hydrophobic, respectively. Hydrophilicity of PBAP may mainly contribute to hydrogen bonds between secondary amines and water. With the addition of trifluoroethoxy, PBTAP turned out to be hydrophobic. We conjectured that the steric hindrance of trifluoroethoxy decreased the effect of hydrogen bonds; even trifluoroethoxy is usually identified as a flexible group. Moreover, trifluoroethoxy itself as a side group in polyphosphazenes also shows the hydrophobic properties.^{28,29}

Unlike most polyalkoxyphosphazenes and polyaryloxyphosphazenes, as elastomers, PBAP and PBTAP are solid powders, so the solution-cast films of these two samples are quite brittle.

CONCLUSIONS

Polyarylamino phosphazene was designed and synthesized. In a comparison, aniline polyphosphazene was also synthesized successfully. These two polymers were characterized by ¹H-NMR, ³¹P-NMR, DSC, TGA, and WCA. With the effect of the trifluoroethoxy, the T_g value of PBTAP (64.5°C) was lower than that of PBAP (115.9°C), the WCA of PBTAP (101°) was larger than that of PBAP (82.8°). Although the initial decomposition temperature of PBTAP (160°C) was a little higher than that of PBAP (153°C), the char yield was lower than PBTAP above 600°C. We concluded that trifluoroethoxy possessed the ability to improve the flexibility of backbones and the hydrophobic properties of polyarylamino phosphazenes but had no obvious influence on the thermal stability. This indicated that the properties of polyphosphazenes could also be changed by connection with side groups indirectly, even with an aromatic spacer.

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Table II. Thermal Decomposition Temperatures of PBAP and PBTAP

Polymer	T_5 (°C)	T_{10} (°C)	T_{20} (°C)	T_{30} (°C)	T_{40} (°C)	T_{50} (°C)
PBAP	164	182	217	268	344	535
PBTAP	171	187	215	248	286	328

T_x temperature at which X% of weight loss takes place.

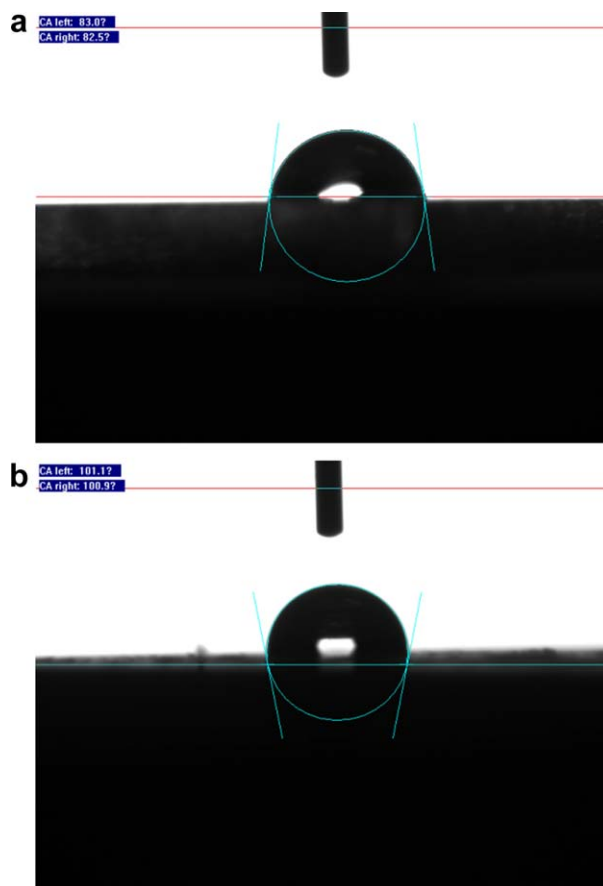


Figure 5. WCA measurement images of PBAP (left) and PBTAP (right) on the spun-cast film. WCA: water contact angle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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