

# Thermal Properties, Adhesive Strength, and Optical Transparency of Cyclolinear Poly(aryloxycyclotriphosphazenes)

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**ABSTRACT:** Four cyclolinear poly(aryloxycyclotriphosphazenes) derived from poly[4,4'-(isopropoylidene)diphenoxytetrachlorocyclotriphosphazene] and poly[4,4'-(hexafluoroisopropylidene)diphenoxytetrachlorocyclotriphosphazene] were synthesized from the reaction of hexachlorocyclotriphosphazene (HCP) with 4,4'-(isopropoylidene)diphenol (bisphenol A) or 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol AF) in molar ratio 1 : 1 via a one-step condensation polymerization. Subsequent reaction of the resulted chlorine-bound polymers with adequate amount of the sodium salts of 4-methoxycarbonylphenoxide or 4-propoxycarbonylphenoxide yielded the corresponding chlorine-free polymers, [poly(tetra-4-methoxycarbonylphenoxy)-4,4'-(isopropoylidene)diphenoxycyclotriphosphazene] (MBACP), [poly(tetra-4-propoxycarbonylphenoxy)-4,4'-(isopropoylidene)diphenoxycyclotriphosphazene] (PBACP), [poly(tetra-4-methoxycarbonylphenoxy)-4,4'-(hexafluoroisopropylidene)diphenoxycyclotriphosphazene] (MBAFCP), [poly(tetra-4-propoxycarbonylphenoxy)-4,4'-(hexafluoroisopropylidene)diphenoxycyclotriphosphazene] (PBAFCP), respectively. The chemical structures were characterized by Fourier transformer infrared, <sup>1</sup>H, and <sup>13</sup>C-NMR. Thermal properties of polymers were investigated using DSC and TGA analysis. The obtained polymers were thermoplastic, having moderate *T<sub>g</sub>* values in the range of 26–78°C and good

thermal stability up to 350°C in N<sub>2</sub> and O<sub>2</sub> gases. The thermal decomposition of the isopropylidene-containing polymers is a one-step process, while that of hexafluoroisopropylidene-containing polymers is a two-step process. However, presence of the latter group in the polymers backbone showed negligible effects on the thermo-oxidative stability. The adhesive strength was measured by lap-shear strength test on glass–glass bonded joint and found to be in the range of 1.78–2.62 MPa, this property may be attributed to the physical interactions between glass–glass interfaces and the polar-pendant units present at the polymers backbone. The products showed high optical transparency when they applied between two glass surfaces, the adhesive layers were colorless, with the UV cut-off wavelength of 300–302 nm, and the maximum transparency of about 90% was observed within the wavelengths range of 400–700 nm. Because of their properties, the cyclolinear poly(aryloxycyclotriphosphazenes) synthesized in this study are recommended as potential candidates for high thermally stable, transparent adhesives required in industrial applications. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1058–1065, 2011

**Key words:** cyclophosphazenes; thermal properties; adhesives; transparency; glass bonded joints

## INTRODUCTION

Hexachlorocyclotriphosphazene (HCP; phosphonitric chloride trimer) is inorganic molecule that contains three N=PCl<sub>2</sub> units. All chlorines on the phosphorus atoms can be readily replaced with a wide variety of functional organic groups via nucleophilic substitution reaction, affording different organocyclotriphosphazenes and poly(organocyclotriphosphazenes) depending on the number of functional groups of the substituents.<sup>1–5</sup> Phosphazene is a ver-

satile compound, which has a wide range of industrial applications such as preparation of phosphazene-based epoxy resin,<sup>6–8</sup> inherent fire- and heat-resistant polymers,<sup>9,10</sup> copolymers with organic backbones and cyclotriphosphazene as pendant units,<sup>11,12</sup> additives for improving thermal degradation and flame retardancy,<sup>13–15</sup> precursor for curing agents,<sup>16</sup> lubricants,<sup>17</sup> photocurable,<sup>18</sup> antioxidants,<sup>19</sup> coatings,<sup>20</sup> and adhesives.<sup>21</sup> The phosphazene backbone is completely transparent from the mid-UV to the near infrared region, this due to the unfavorable geometry of the –P=N– bond present in the phosphazene polymer chain; therefore, no delocalization of the charges or  $\pi$  electron is allowed in these materials, their resonance forms being limited within the three P–N–P atomic system.<sup>22</sup>

During the last two decades, attentions have been focused on preparation of thermally stable poly-cyclotriphosphazenes with reactive side groups.

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Curing of these polymers at high temperatures afforded insoluble, nontransparent, crosslinked cyclomatrix polymers with good adhesive strength applicable for metal–metal bonded joints.<sup>23</sup> Devadoss<sup>24</sup> reported some aspects of the structural property relationships of a phosphazene-modified epoxy-base cyclomatrix system formed from the direct condensation reaction of HCP with a variety of aromatic diamines, 4,4'-diaminodiphenylmethane, benzidine, 4,4'-diaminodiphenylether, and 4,4'-diaminodiphenylsulfone. The adhesive, heat resistance, and thermophysical profiles of these thermosetting systems and those of epoxy-rich compositions were good as the degree of substitution of chlorine increased. Presence of a thermally stable, flexibilizing group (viz., —O—) in the aromatic diamines conferred higher level of adhesion. On the other hand, Devadoss and Nair<sup>25</sup> have reported the synthesis of novel cyclomatrix polymers obtained from the reaction of HCP with the monosalt of bisphenol A, thiodiphenol, and hydroquinone followed by the replacement of the residual chlorine atoms by methyl aziridine to give condensates. Curing at high temperature afforded a thermally stable (up to 350°C) hard, insoluble cyclomatrix polymer, which showed moderately good adhesion at room temperature. Kumar<sup>26</sup> prepared new adhesive materials formed from the direct reaction of HCP with phloroglucinol, hydroquinone, resorcinol, bisphenol, and benzilic acid in different molar ratios. Stainless steel, duralumin test panels were used for the measurement of adhesive strength (shear and peel) and film toughness. The polar density, molecule geometry, London forces, and temperatures play important role to determine the adhesive bonding strength.

Adhesives for bonding glass and related substrates are selected based on polarity, available functional groups, and compatibility. The polymeric materials used to bond glass are generally transparent and does not change the optical characteristics of the glass, heat-setting resins, water, and UV resistant (to meet the requirement of outdoor applications). The most useful polymeric adhesive materials are polyvinyl butyral, phenolic butyral, phenolic nitrile, styrene-modified polyesters and styrene monomer-based adhesives, thermosetting epoxies, and acrylics are also used.<sup>27</sup> Because glass is a nonporous adherend; therefore, any adhesive-containing water or solvent will not be suitable for bonding applications. The UV curable and heat-setting resin adhesives are widely used for glass adhesive bonding.<sup>28</sup>

In the present work, new poly(aryloxycyclotriphosphazenes) adhesive materials were synthesized. Investigations of their thermal, mechanical, and optical properties revealed that the characteristics of the products meet the general requirements needed for practical applications for glass–glass bonded joints,

such as, moderate melting (softening) temperatures (to avoid inner tension through thermal stress), thermoplastic (to offer a possibility to disconnect the bonded joint by heat supply required in view of recycling process), fillers and solvents free, resistance to thermo-oxidative degradations, and high optical transparency with invisible glue line between the bonded glass plates.

## EXPERIMENTAL

### Materials

Hexachlorocyclotriphosphazene (NPCl<sub>2</sub>)<sub>3</sub> (HCP, Aldrich) was purified by recrystallization from *n*-hexane. Bisphenol A (BA, Fluka), methyl 4-hydroxybenzoate, and propyl 4-hydroxybenzoate (MHB and PHB, Fluka) were purified by recrystallization from hot toluene and bisphenol AF (BAF, Fluka) recrystallized from hot ethanol. 1,4-Dioxane (AJAX Chemicals) was freshly distilled before use from sodium benzophenone ketyl. Anhydrous sodium sulfate, methanol, and methylene chloride (Merck) were used as received. Sodium metal (AJAX Chemicals) rods were sliced into thin pieces before use.

### Measurements

#### FTIR spectra

Fourier transformer infrared (FTIR) spectra in the range of 4000–400 cm<sup>-1</sup> were recorded on a SHIMADZU 8400s FTIR spectrophotometer. The spectra were obtained from a thin film of the products casted on a potassium bromide window from methylene chloride solutions.

#### <sup>1</sup>H- and <sup>13</sup>C-NMR spectra

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded using an Oxford Varian 300 NMR spectrometer operated at 300 MHz for proton and 75 MHz for carbon. Samples were dissolved in CDCl<sub>3</sub>, and the solvent was used as an internal lock. Chemical shifts were recorded in parts per million relative to tetramethylsilane (0.00 ppm) as an internal reference.

#### Differential scanning calorimetry

The differential scanning calorimetry (DSC) analysis was performed on a NETZSCH DSC 204 F1 Phoenix Germany, at a heating rate of 10°C/min under atmosphere of N<sub>2</sub> gas. All samples were annealed over the temperature range of –20 – 200°C for both heating and quenching. The samples were hold for 3 min at 200°C before cooled. The second scan was performed after 3 min of waiting time at –20°C. The glass transition temperatures (*T*<sub>g</sub>) were determined

from the inflection point of the DSC thermograms of the second scan.

#### Thermogravimetric analysis

The thermal gravimetric analysis (TGA) were obtained on a STA 409 PC, Luxx Germany at a heating rate of 20°C/min in the range of ambient temperature to 800°C under atmosphere of N<sub>2</sub> and O<sub>2</sub> gases.

#### Tensile shear strength

Measurements of the tensile shear strength (adhesive strength) of a single-lap bonded joint were carried out according to the standard DIN EN 1465 using INSTRON 1195 tensiometer with pulling rate of 2 mm/min and maximum applied force of 100 kg at room temperature using glass test plates with the dimensions of 100 × 25 mm. The adherends were degreased by washing with acetone and then dried at 70°C in an oven; no further treatment such as chemical etching or sandblasting was made at the surface of the adherends. Small amount of the product (about 0.1 g) was placed on each glass plate and heated on a hot plate until the material started melt and flow. The plates were overlapped with each other and initially pressed, the material was equally spread within the adhesion zone (25 × 12.5 mm), air bubbles were removed, the thickness of the adhesive layer was minimized until the glueline became invisible, and then the plates were tightly pressed (35 kg) against each other while gradually cooled down to room temperature. The thickness of the adhesive layer was found to be ≈0.016 mm (±0.003 mm) for all specimens. To avoid cracking or slipping of the specimens during the test, 10-mm thick glass were used, and two uniform holes with diameter of 4 mm were made at the non-bonded ends. The specimen was hooked from the holes via steel wires and properly aligned by the jaws of the tensile testing machine before starting the test.

#### UV-vis spectra

The UV-vis spectra of the specimens were recorded on a T80 UV/vis spectrophotometer at room temperature. A cut-off wavelength is defined here where the transmittance decreased below 1% in the spectrum. The specimens were prepared by melting of about 0.05 g of the product between two microscopic slides on a hot plate, the slides were gently pressed to remove the air bubbles and to minimize the thickness of the adhesive layer until disappearance of the glueline, and then the specimens were allowed to cool down to room temperature. The thickness of

the adhesive layer was measured at different spots of the bonded area by a digital micrometer, and it was found to be ≈0.026 mm (±0.002 mm) for all specimens.

#### Synthesis of cyclolinear poly(aryloxycyclotriphosphazenes)

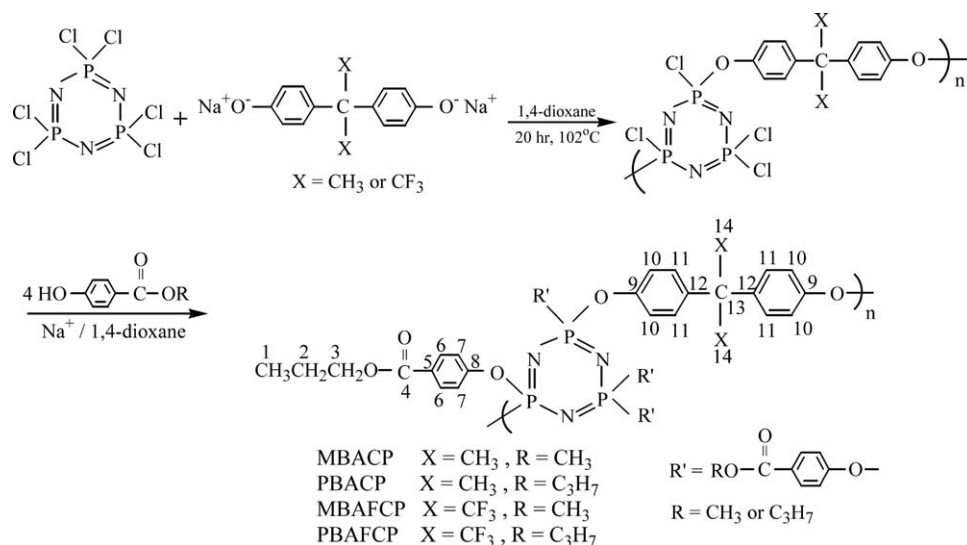
Because the method of synthesis was the same for all the reactions, only that of [poly(tetra-4-methoxycarbonylphenoxy)-4,4'-(isopropoylidene)diphenoxycyclotriphosphazene] (MBACP) is described in detail.

Sodium metal (0.66 g, 0.02 mol) was made into finely dispersed particles by melting it in boiling 1,4-dioxane and stirring vigorously while cooling inside a 250-mL two-necked round-bottomed flask equipped with a condenser, a guard tube, and a magnetic stirring bar. A solution of BA (3.27 g, 0.01 mol) in 20 mL of freshly distilled 1,4-dioxane was added, and the contents of the flask were stirred and refluxed. After 5 h, a dense white slurry of the disodium salt was formed and precipitated. Then, a solution of HCP (5.00 g, 0.01 mol) in 20 mL of 1,4-dioxane was added drop wise via a dropping funnel over a period of 5 min. The content of the flask was stirred for 4 h at room temperature and refluxed for 20 h. Sodium chloride salt that was precipitated was filtered off, and the filtrate was dried under reduced pressure. The product was redissolved in a suitable amount 1,4-dioxane and carefully added via an addition funnel over a period of 30 min to sodium 4-methoxycarbonylphenoxide formed from the reaction of MHB (9.18 g, 0.06 mol) with sodium metal (1.38 g, 0.06 mol) and refluxed in 50 mL of 1,4-dioxane for 5 h. The resulting mixture was stirred for 30 min and then refluxed for 20 h. Sodium chloride, which was precipitated, was removed by suction filtration, and the filtrate was concentrated using a rotary evaporator. Upon the addition of chilled distilled water (250 mL), a whitish material was precipitated, which was collected and redissolved in 50 mL of methylene chloride. The solution was further washed with distilled water in separatory funnel before drying over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the resulting solid material was thoroughly washed with 200 mL of hot methanol. Finally, a pale yellow product was obtained and then dried at 120°C for 3 h in a vacuum oven.

## RESULTS AND DISCUSSION

#### Characterization of cyclolinear poly(aryloxycyclotriphosphazenes)

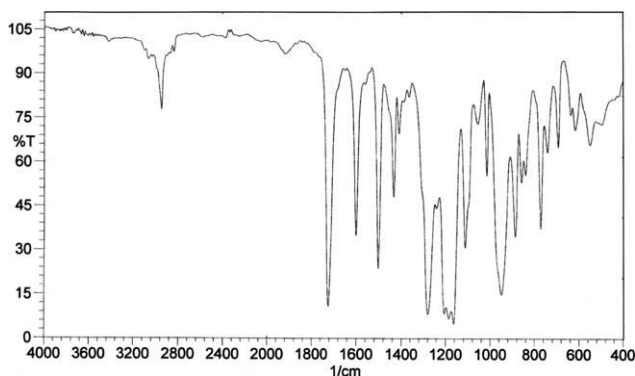
Poly(aryloxycyclotriphosphazenes) bearing different phenoxy groups (di- and mono-) were synthesized from reacting of HCP with bisphenol A or bisphenol AF followed with 4-alkoxycarbonylphenoxide in a



**Scheme 1** Synthesis of cyclolinear poly(aryloxycyclotriphosphazenes).

molar ratio of 1 : 1 : 4. The schematic outline of the synthetic reactions of the products is presented in Scheme 1. The first step involved reaction between HCP and BA or BAF disodium salt, which has previously been shown to be quantitative, with the substitution taking place in nongeminal mode.<sup>29</sup> In the second step, the substitution of the residual chlorines that still bonded to the polymer backbone was achieved using excess amount of the sodium salt of MHB or PHB under refluxing condition for 20 h.

The FTIR spectrum of MBACP depicted in Figure 1 shows the characteristic bands of the phosphazene ring, mainly at 1278, 1205  $\text{cm}^{-1}$  assigned to the asymmetric, and symmetric stretching of P=N group, respectively, and at 1161  $\text{cm}^{-1}$  assigned to the stretching PO—C bond (of PO—Ar groups). The C=O and CO—O—C absorption frequency of methoxycarbonylphenoxide appeared at 1724 and 1184  $\text{cm}^{-1}$ , respectively. The characteristic absorption peaks due to P—Cl bonds of the ArOP—Cl and P—Cl<sub>2</sub> groups are not discernible from the IR spectrum, suggesting that the substitution reaction



**Figure 1** FTIR spectrum of MBACP.

(replacement of chlorine by 4-methoxycarbonylphenoxide) had proceeded to completion affording the chlorine-free polymer, MBACP. Assignments of the related peaks in the FTIR, <sup>1</sup>H-NMR spectra, and other data of the products are given in Table I, and <sup>13</sup>C-NMR spectral data are tabulated in Table II. These data clearly confirm that the products prepared herein are consistent with the proposed molecular structures shown in Scheme 1.

### Thermal properties

A stack plot of DSC thermograms of the products is depicted in Figure 2. Clear single endothermic transitions appeared at the thermograms are corresponded to the  $T_g$  transitions. MBACP and [poly(tetra-4-methoxycarbonylphenoxy)-4,4'-(hexafluoroisopropylidene)-diphenoxycyclotriphosphazene] (MBAFCP) have  $T_g$  of 73 and 78°C, whereas [poly(tetra-4-propoxycarbonylphenoxy)-4,4'-(isopropylidene)diphenoxycyclotriphosphazene] (PBACP) and [poly(tetra-4-propoxycarbonylphenoxy)-4,4'-(hexafluoroisopropylidene)-diphenoxycyclotriphosphazene] (PBAFCP) possess lower  $T_g$  that appeared at 26 and 34°C, respectively. The decrease of the  $T_g$  values is attributed to the presence of 4-propoxycarbonylphenoxy-pendant groups, which increase the free volume, chain mobility, and consequently  $T_g$  dropped. However, presence of hexafluoroisopropylidene group in the backbone of MBAFCP and PBAFCP somewhat increased the  $T_g$  values compared to that of the MBACP and PBACP. This increase can be assigned to the polar interactions between C—(CF<sub>3</sub>)<sub>2</sub> groups and aryloxy moieties present in the polymer backbones.

The TGA curves in atmosphere of nitrogen and oxygen gas show good thermal stability, indicated



**TABLE I**  
**FTIR, <sup>1</sup>H-NMR Spectral Data, and Yields of the Products**

Product	Frequency (cm <sup>-1</sup> )	<sup>1</sup> H-NMR in CDCl <sub>3</sub> δ ppm	Yield (%)	Color
MBACP	C=O (1724)	8.2–7.6 (m, 8H, arom. H)	86	Pale yellow powder
	P=N asym. 1278	7.4–6.6 (m, 16H, arom. H)		
	P=N sym. 1205	3.9 (m, 12H, –OCH <sub>3</sub> )		
	P=N Skeletal vib. 887	1.5 (m, 6H, C–CH <sub>3</sub> )		
	CO–O–C 1184			
	PO–C 1161			
PBACP	P–OC 949		85	Faint yellow to colorless transparent
	C=O (1720)	8.1–7.7 (m, 8H, arom. H)		
	P=N asym. 1273	7.2–6.7 (m, 16H, arom. H)		
	P=N sym. 1205	4.2 (m, 8H, –OCH <sub>2</sub> )		
	P=N Skeletal vib. 887	1.7 (m, 8H, –CH <sub>2</sub> –)		
	CO–O–C 1184	1.5 (b, 6H, –C–CH <sub>3</sub> )		
MBAFCP	PO–C 1161	1.0 (m, 12H, –CH <sub>3</sub> )	90	Whitish powder
	P–OC 949			
	C=O (1726)	8.2–7.6 (m, 8H, arom. H)		
	P=N asym. (1280)	7.4–6.7 (m, 16H, arom. H)		
	P=N sym. (1211)	3.8 (m, 12H, O–CH <sub>3</sub> )		
	P=N Skeletal vib. (887)			
PBAFCP	CO–O–C and C–(CF <sub>3</sub> ) <sub>2</sub> (1176) <sup>a</sup>		92	Faint yellow to colorless transparent
	PO–C (1163)			
	P–OC (950)			
	C=O (1720)	8.2–7.7 (m, 8H, arom. H)		
	P=N asym. (1273)	7.4–6.7 (m, 16H, arom. H)		
	P=N sym. (1211)	4.2 (m, 8H, –OCH <sub>2</sub> )		
	P=N Skeletal vib. (887)	1.7 (m, 8H, –CH <sub>2</sub> –)		
	CO–O–C and C–(CF <sub>3</sub> ) <sub>2</sub> (1176) <sup>a</sup>	1.0 (m, 12H, –CH <sub>3</sub> )		
	PO–C (1161)			
	P–OC (950)			

<sup>a</sup> Overlapped appearance.

by the absence of any significant weight loss up to 350°C as illustrated in Figures 3 and 4. Although there were no major differences in their thermal stability, the presence of chemically stable C–(CF<sub>3</sub>)<sub>2</sub>

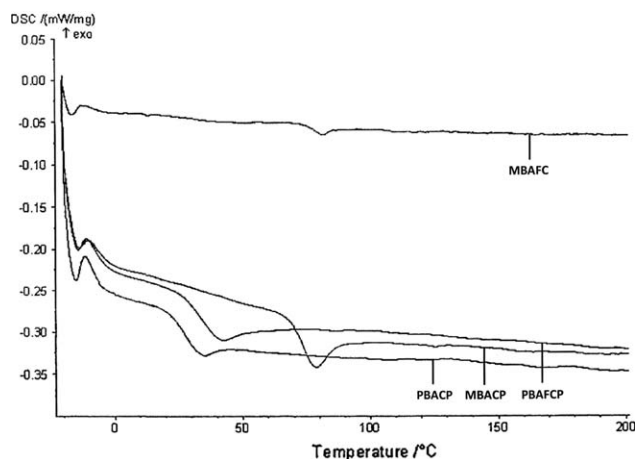
groups at the polymer backbones was slightly improved the thermal stability to MBAFCP and PBAFCP. In both atmospheres, the thermograms of products containing isopropylidene groups showed one major decomposition step, whereas those containing hexafluoroisopropylidene groups showed two discernable decomposition steps. The TG curves

**TABLE II**  
<sup>13</sup>C-NMR Spectral Data of the Products

Labeled <sup>a</sup>	MBACP δ ppm	PBACP δ ppm	MBAFCP δ ppm	PBAFCP δ ppm
1	52.4	10.7	52.4	10.7
2	–	22.3	–	22.2
3	–	66.9	–	66.9
4	166.2	165.7	166.1	165.7
5	120.4	120.4 <sup>b</sup>	120.7 <sup>b</sup>	120.7 <sup>b</sup>
6	131.5	131.4	131.7	131.4
7	121.0	120.8 <sup>b</sup>	120.8 <sup>b</sup>	120.7 <sup>b</sup>
8	154.0	154.0	153.8	153.8
9	148.3	148.5	150.9	150.9
10	128.0	128.0	130.2	130.2
11	127.4	127.8	127.6 <sup>b</sup>	127.9 <sup>b</sup>
12	147.5	147.8	127.9 <sup>b</sup>	127.9 <sup>b</sup>
13	42.4	42.4	64.4	64.1
14	30.9	31.0	126.0	126.0

<sup>a</sup> Carbon atoms numbered according to the overall structure of products given in Scheme 1.

<sup>b</sup> Overlapped appearance.



**Figure 2** DSC thermograms of the products.

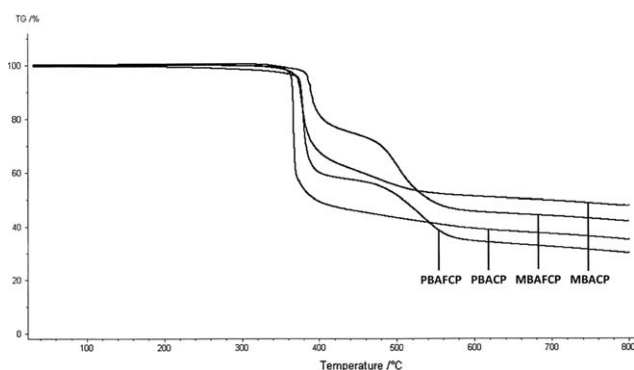


Figure 3 TG curves of the products in N<sub>2</sub> gas.

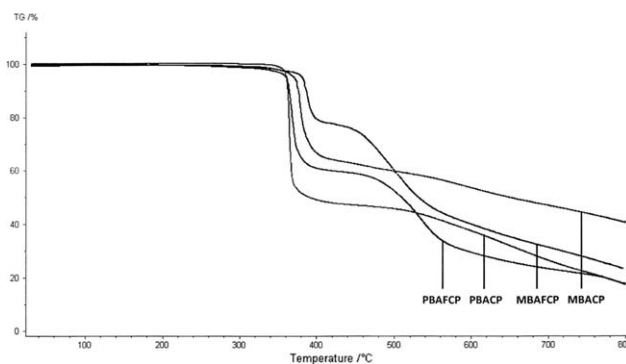


Figure 4 TG curves of the products in O<sub>2</sub> gas.

TABLE III  
A Summary of the Thermal Properties of the Products in N<sub>2</sub> and O<sub>2</sub> Gas

Product	$T_g$ (°C)	First decomposition step		Second decomposition step		Char yield 800°C	
		N <sub>2</sub> Temp. (°C) (wt %) <sup>a</sup>	O <sub>2</sub> Temp. (°C) (wt %) <sup>a</sup>	N <sub>2</sub> Temp. (°C) (wt %) <sup>a</sup>	O <sub>2</sub> Temp. (°C) (wt %) <sup>a</sup>	N <sub>2</sub> (wt %)	O <sub>2</sub> (wt %)
MBACP	73	380 (32)	380 (32)	—	—	47	40
PBACP	26	370 (50)	365 (52)	—	—	35	17
MBAFCP	78	395 (25)	390 (21)	510 (30)	520 (44)	42	22
PBAFCP	34	380 (41)	370 (39)	530 (23)	525 (29)	33	17

<sup>a</sup> Weight loss % at indicated temperature.

of MBACP and PBACP under nitrogen gas given in Figure 3 show main thermodegradation step occurred at 380 and 370°C, respectively. This step is attributed to the cleavage of P—OAr bonds of both aromatic moieties present at the polymer backbone. The TG curve of MBACP also shows minor decomposition step at 480°C with weight loss of about 13%, this step is due to the scission and partial volatilization of —P=N— groups. On the other hand, the curves of MBAFCP and PBAFCP show two decomposition steps, and the former is assigned to the cleavage of P—OAr bonds while the latter may be due to the loss of bulky C—(CF<sub>3</sub>)<sub>2</sub> linking group. Under oxygen gas, the TG curves given in Figure 4 show that the thermo-oxidative decomposition of all products processed slightly faster than that in nitrogen without any major differences. It is worthwhile to note here that the presence of hexafluoroisopropylidene unit has minor effect on the thermo-oxidative

stability of the products. Furthermore, the TG curves shows presence of appreciable amount of char residue in the range of 47%–17% at 800°C. This observation is in keeping with the corresponding increase in phosphorus–nitrogen content of products.<sup>30–32</sup> A summary of the thermal analysis data is presented in Table III.

### Adhesive strength

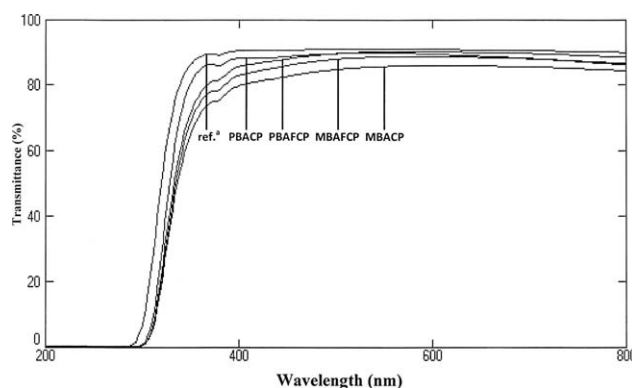
Adhesive strength is defined as the maximum force ( $F_{max}$ ) at the break of the bonded joint in relation to adherend surface area ( $A$ ). The adherend surface area results from the test plate width of 25 mm and the overlap length of 12.5 mm. An average of five readings was taken for calculating the ( $F_{max}$ ) values

TABLE IV  
Adhesive Strength of the Products Measured Over Glass Specimens

Specimen <sup>a</sup>	Setting temp. (°C)	Adhesive strength (MPa) <sup>b</sup>
MBACP	160	2.25
PBACP	125	2.62
MBAFCP	170	1.78
PBAFCP	130	2.48

<sup>a</sup> Products applied between two glass pieces.

<sup>b</sup> Evaluated in term of lap-shear strength.



<sup>a</sup> Blank microscopic slide.

Figure 5 UV-vis spectra of the products.

**TABLE V**  
**Optical Properties of the Products at Various Wavelengths**

Product	Transparency (%) <sup>a</sup>						
	$\lambda_{\text{cut-off}}$ nm	$\lambda_{80\%}$ nm	$\lambda_{400}$ nm	$\lambda_{500}$ nm	$\lambda_{600}$ nm	$\lambda_{700}$ nm	$\lambda_{800}$ nm
Ref. <sup>b</sup>	291	338	91	91	91	91	90
PBAFCP	302	364	86	90	90	90	89
PBACP	300	349	88	90	90	88	87
MBACP	302	400	80	85	86	85	85
MBAFCP	302	384	83	88	89	88	87

<sup>a</sup> The wavelength range of UV–vis measurements was 200–800 nm.

<sup>b</sup> Blank microscopic slide is used as a reference.

with standard deviation of  $\approx \pm 6.60$ . The adhesive strength values were calculated from the below equation, and data are tabulated in Table IV. Also of noteworthy to mention here that some of the glass test specimens were cracked or broken before disconnect (or break) of bonded joint during the test, their readings were excluded.

$$\text{Adhesive strength} = F_{\text{max}}/A \text{ (MPa)}$$

The adhesive strength of bonded joints is attributed to the physical interactions between the active hydroxy sites on glass with the polar alkoxy-carbonylphenoxy-pendant units. The slightly higher strength of PBACP and PBAFCP than that of MBACP and MBAFCP may be due to the effective hyperconjugation of propoxycarbonylphenoxy groups present at the polymer backbone.

### Optical properties

A stack plot of UV–vis spectra of the specimens is depicted in Figure 5. In the same figure, the transmittancy of the blank microscopic slide is also presented as a reference (ref.) for comparison. All products exhibit good optical transparency at various wavelengths as illustrated in Table V. The UV cut-off wavelength ( $\lambda_{\text{cut-off}}$ ) of the ref. was 289 nm, whereas those of the products were about 300 nm, and their wavelengths of 80% transparency ( $\lambda_{80\%}$ ) were in the range of 347–400 nm. The maximum transparency of about 90% was observed within the wavelength range of 400–700 nm. The high optical transparency of the products is attributed to the absence of the intermolecular conjugation probably because of the slightly puckered structure of phosphazene ring,<sup>33,34</sup> together with the presence of isopropylidene units in the polymer backbones, which prohibit the extensive conjugation of the aromatic moieties. The slightly higher transparency of PBACP and PBAFCP compared to others is attributing to the larger size of propoxy-pendant groups. Incorporation of bulky pendant groups into the polymer backbone serves to increase the free volume of the

polymers, thereby improving various properties including of optical transparency.<sup>35,36</sup>

### CONCLUSIONS

Four thermally stable, good adhesive strength, and transparent poly(aryloxycyclotriphosphazenes) containing different bisphenols (biphenol A or bisphenol AF) linkage groups and 4-alkoxycarbonylphenoxy-pendant units have been successfully synthesized via a two-step substitution reaction. The thermal analysis of the products exhibited moderate glass transition temperatures and good thermal stability under atmosphere of N<sub>2</sub> and O<sub>2</sub> gases. Products containing isopropylidene linkage group showed one main decomposition step while those containing hexafluoroisopropylidene showed two decomposition steps and also limited effects on the thermo-oxidative stability. For glass–glass bonded joint, the products exhibited good adhesive strength at room temperature, superior optical properties, and entire transparency within the wavelengths range of 400–700 nm.

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