Preparation and Properties of Transparent Copolymers Based on Cyclotriphosphazene and Styrene as Potential Flame-Retardant Optical Resins

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ABSTRACT: Transparent copolymers composed of hexa(allyl 4-hydroxybenzoate) cyclotriphosphazene (compound **1**) and styrene as potential halogen-free, flame-retardant optical resins were prepared by radical copolymerization. The thermal performances of the cured resins were studied with thermogravimetric analysis; the decomposition mechanism of the copolymers was investigated with integrated thermogravimetry–Fourier transform infrared analysis. Compared with conventional polystyrene, the synthesized copolymers exhibited a higher refractive index and a higher thermal stability both under nitrogen and air atmospheres at elevated temperature, and the visible-light transmittance of the copolymers decreased slightly. With increasing ratio of compound **1** to styrene in the copolymers, the onset decomposition temperature and the char yield both increased gradually. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3137–3144, 2011

Key words: copolymers; degradation; flame retardance; thermogravimetric analysis (TGA)

INTRODUCTION

As one of the most popular plastics, polystyrene (PS) is used widely in fields such as automobiles, furniture, electronic casings, and interior decor. It can also be used as optical materials for its high refractive index (n_d), good transparency, and low percentage water absorption (W_a). However, its flammability and easy thermal and oxidative decomposition prevent it from being used in certain commercial applications. Generally, flame-retardant additives are blended with polymers to improve their fire retardance and heat resistance by reducing the rate of burning, flame spread, and smoke generation. Halogen-containing additives, such as hexabromo-*cyclo*-dodecane and tetrabromo bisphenol A bis(2,3-dibromopropylether), are found to be efficient flame retardants and have always been blended with PS to improve its flame-resistant properties.[1–3]

However, these additives have some negative aspects, in particular, the release of toxic and corrosive gases. The growing number of restrictions and recommendations from the European Community has promoted the development of halogen-free flame-retardant additives and polymers. As one excellent alternative, phosphorus-containing additives, both inorganic and organic compounds, have been paid more and more attention in recent years.[4–11]

In past decades, researchers in science and industry fields have shown strong interest in phosphazene compounds, including linear polyphosphazenes and cyclomatrix-type polyphosphazenes, for their superior performance.[12–18] Materials containing phosphazenes not only possess a wide range of thermal and chemical stabilities but also provide improved flame-retardant and heat-resistant properties to reinforced polymers. More important, phosphazene-based materials are halogen free and friendly to the environment.[19–21]

In our previous study, a series of halogen-free, flame-resistant optical resins were prepared via the copolymerization of hexa(allyl 4-hydroxybenzoate) cyclotriphosphazene (compound **1**) with methyl methacrylate.[22] As a part of this continuous research, in this study, we focused on the preparation of potential flame-resistant optical copolymers based on compound **1** and styrene. Our analysis
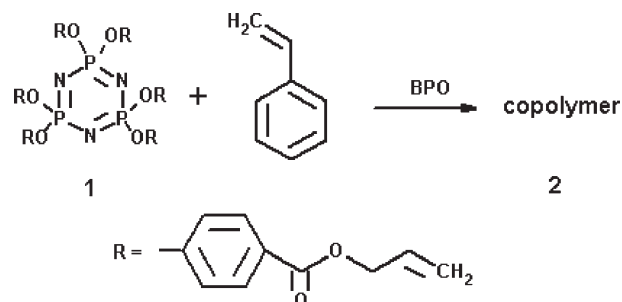
Scheme 1 Synthesis route of the copolymers based on cyclotriphosphazene and styrene.

emphasized the behavior and mechanism of thermal decomposition of the products by thermogravimetric analysis (TGA) and integrated thermogravimetry (TG)–Fourier transform infrared (FTIR) analyses. Values of n_d, water resistance, and density of the products were also determined. The experiment data showed clear evidence for a higher n_d and higher thermal stability of the copolymers in the presence of cyclotriphosphazene units.

EXPERIMENTAL

Materials

All of the chemicals and solvents were reagent grade. Compound **1** was synthesized in our laboratory according to a procedure described in the literature.[22] Styrene (St) was purified by washing with a 5% aqueous sodium hydroxide solution and then with water, dried overnight with anhydrous sodium sulfate (Na_2SO_4), and distilled over cuprous chloride (Cu_2Cl_2) before polymerization.

Instrumentation

The n_d values of the cured resins were measured with a WZS-IAbbé refractometer (Shanghai Changfang Optical Instrument Co.,Ltd., China) at 20°C. The visible-light transmittance of the cured resins was measured by a S721 visible spectrophotometer at a wavelength of 550 nm. Thermal stability studies were carried out on a synchronous thermal analysis instrument (STA 409 PC/4/H LUXX, Germany) under nitrogen and air, respectively, as the purge gases at a 10°C·/min scanning rate from 40 to 900°C. The morphology of the cyclomatrix resin and the solid residue after pyrolysis were observed on a FEI Sirion 200 field emission scanning electron microscope (FEI Company, Holland). Integrated TG–FTIR analyses were used to study the decomposition mechanism. The integrated TG–FTIR analyses were performed on a combination of a simultaneous differential scanning calorimetry–TGA instrument (SDT Q600, USA) and a

Nicolet IR-380 infrared spectrometer (Thermo Nicolet Corporation, Madison Wisconsin, USA). A sample of 18.162 mg was heated at a heating rate of 10°C·/min from ambient temperature to 900°C under a steady flow of nitrogen (200 mL/min), and the volatile gas produced from thermal decomposition was recorded by FTIR online. The density of the cured resins was determined according to GB1033-86 (test method for the density and relative density of plastics, test method B). The W_a values in water and at 75% relative humidity were determined by GB/T 1034-1998 (plastics determination of W_a). W_a at 75% relative humidity was determined by the simulation of constant humidity in closed container with an ammonium sulfate saturated aqueous solution at 23°C.

Polymer synthesis

The synthesis procedure for the optical resins composed of cyclotriphosphazene is illustrated in Scheme 1. The detailed procedure of the phosphazene cyclomatrix homopolymer was reported previously.[22] Similarly, 10 g of an admixture of compound **1** and styrene according to a certain proportion and 0.2 g of benzoyl peroxide (BPO) were placed in a three-necked flask equipped with a stirrer, thermometer, and nitrogen inlet; the temperature of the reaction mixture was increased to 80°C and stirred for 0.5 h. Then, the preformed polymer was cast slowly into a glass mold and placed in a vacuum oven; the temperature was kept at 75°C for 20 h, 85°C for 2 h, 95°C for 2 h, and 100°C for 2 h, and the oven was turned off. After the temperature of the oven was cooled to room temperature, the molds were removed, and colorless and sheetlike resin samples with a thickness of 3 mm were obtained.
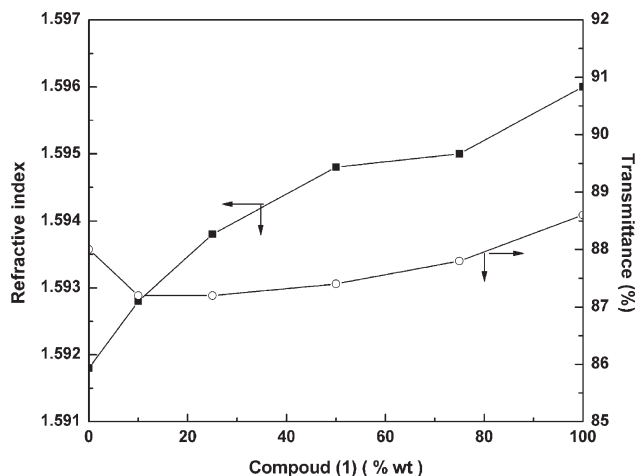

Figure 1 Effect of the content of compound **1** in the formulations on the n_d values and the transmittance of the cured resins.
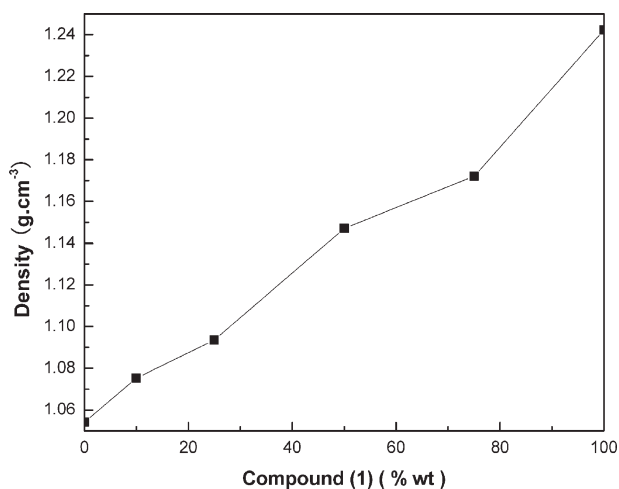
Figure 2 Relationship between the density of the cured resins and the content of compound **1** in the formulations.

RESULTS AND DISCUSSION

n_d's and densities

The n_d values, visible-light transmittances, and densities of the cured resins are shown in Figures 1 and 2. The n_d values of the pure PS was 1.592, and its density was 1.054. With increasing content of compound **1** in the experimental formulas, the n_d and density values of the cured resins increased gradually. The n_d value of the pure cyclomatrix homopolymer was 1.596, and its density was 1.242. The n_d values and the densities of the copolymers were located between those of the two homopolymers. The visible-light transmittances of the pure PS and pure cyclomatrix homopolymer at 550 nm were 88 and 88.6%, respectively, and those of all of the copolymers were above 87%. The results show the cyclotriphosphazene units were advantageous for
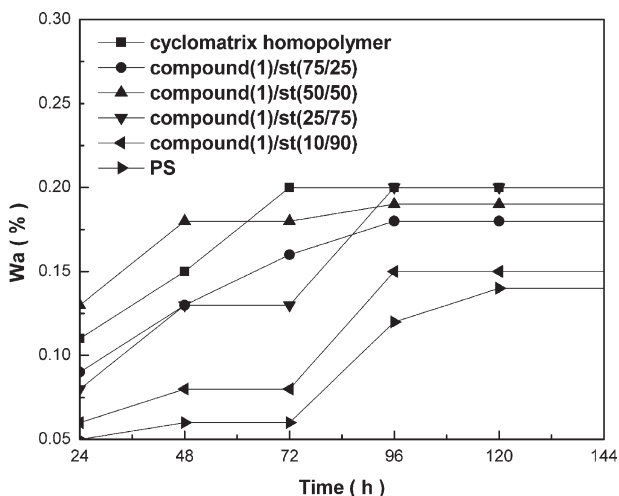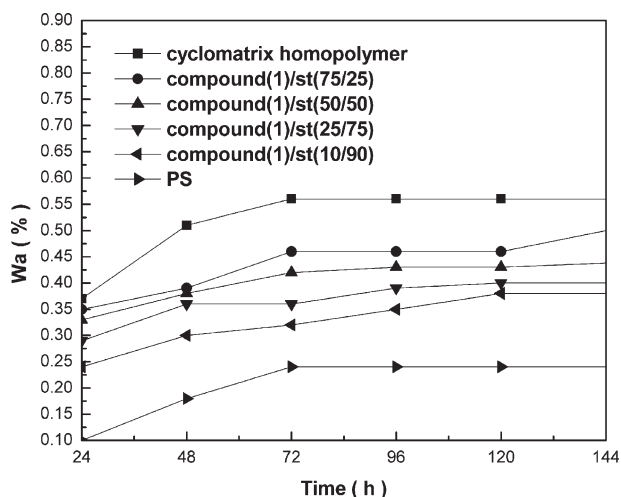

Figure 4 Effect of the time on W_a of the cured resins in water.

increasing n_d of the copolymers, and they had less impact on the visible-light transmittance. The result was due to the fact that the $-P{=}N-$ construction of

Figure 3 Effect of the time on W_a of the cured resins at 75% relative humidity.
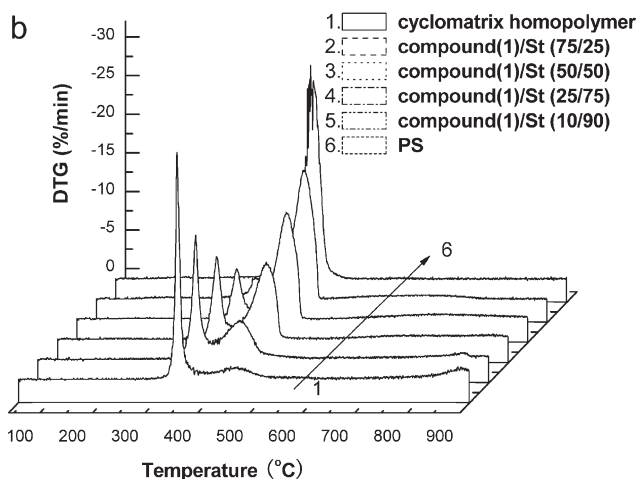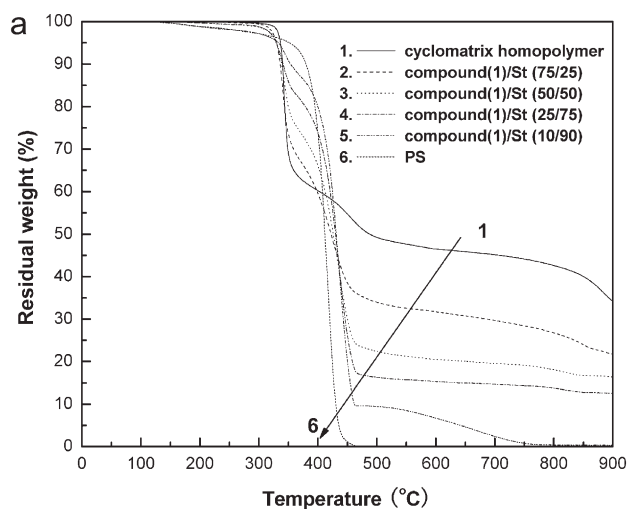
Figure 5 Dynamic (a) TGA and (b) DTG curves for the cured resins under a nitrogen atmosphere.

TABLE I
Thermal Decompositions of All of the Formulations Under a Nitrogen Atmosphere

Compound 1/styrene (weight ratio)	$T_{2\%}$ (°C)	Stage I			Stage II		Residue (wt %)	
		Mass loss (wt %)	T_{max} (°C)		Mass loss (wt %)	T_{max} (°C)	900°C	850°C
PS	260	100	411.3					
10 : 90	261	12.8	343.7		77.8	438.4	0.3	0.3
25 : 75	314	17.4	341.7		66.3	436.1	12.6	12.8
50 : 50	314	26.0	342.5		51.3	435.6	16.4	16.7
75 : 25	321	33.4	340.7		33.7	423.6	21.8	24.0
Cyclomatrix homopolymer	331	41.0	341.6		9.8	451.1	34.3	40.0

T_{max} = temperature at the maximum mass loss rate.

cyclotriphosphazene had the potential to generate high n_d values because of its relatively high electron density, and it is optically transparent in the region between 220 and 800 nm because the skeletal bonding structure in phosphazenes is quite different from the situation found in electron-rich organic compounds.[12,23–25]

Water resistance

The relationships between the W_a values of the cured resins and the time at 75% relative humidity and in water are shown separately in Figures 3 and 4, respectively. At 75% relative humidity condition and in water, the W_a values of the cured resins increased with the time, and W_a reached a constant value after 120 and 96 h, respectively. The pure cyclomatrix homopolymer had the highest W_a, and the pure PS possessed the lowest W_a. The W_a values of the copolymers were located between those of the two homopolymers. This was due to the fact that PS contained only hydrophobic atoms (C, H), whereas

the cyclomatrix homopolymer and the copolymers contained both hydrophobic atoms and hydrophilic atoms (N, P, O). The total weigh percentage of hydrophilic atoms in the formulas increased with the addition of cyclotriphosphazene monomer, and this resulted in an increase in W_a of the copolymers.
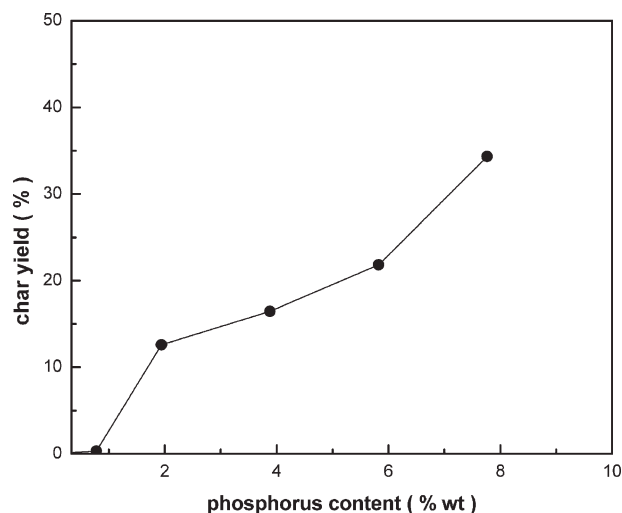

Figure 6 Effect of the calculated phosphorus content of the formulas on the char yields of the copolymers under a nitrogen atmosphere at 900°C.
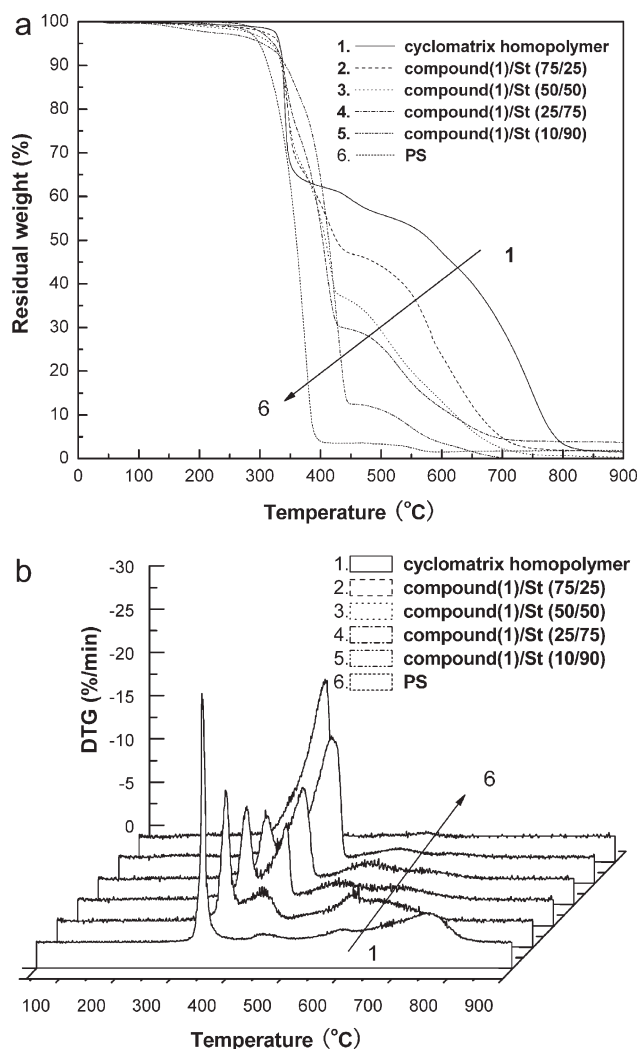
Figure 7 Dynamic (a) TGA and (b) DTG curves for the cured resins under an air atmosphere.

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TABLE II
Thermal Decompositions of All of the Formulations Under an Air Atmosphere

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Compound **1**/styrene (weight ratio)	$T_{2\%}$ (°C)	Stage I			Stage II		Stage III	
		Mass loss (wt %)	T_{max} (°C)	Mass loss (wt %)	T_{max} (°C)	Mass loss (wt %)	T_{max} (°C)
PS	199	100	385.5				
10 : 90	193	17.1	353.2	70.0	424.4	13.0	546.8
25 : 75	296	25.4	341.7	44.7	409.3	30.0	545.5
50 : 50	268	31.8	345.2	30.7	416.5	35.5	511.7
75 : 25	297	33.2	344.1	19.8	409.8	46.9	575.1
Cyclomatrix homopolymer	321	35.9	338.5	7.8	450.2	56.3	750.9

T_{max} = temperature at the maximum mass loss rate.

Thermal behavior

Mass loss of the polymers

Figure 5(a,b) shows the TG and differential thermogravimetry (DTG) curves of the PS, cyclomatrix homopolymer, and copolymers under a nitrogen atmosphere. The thermogravimetric results are summarized in Table I. When the decomposition behaviors of the two homopolymers and the copolymers were compared, PS started to decompose at a much lower temperature (at 260°C) than the cyclomatrix homopolymer (at 331°C), whereas the pyrolysis behaviors of the copolymers were between those of the two homopolymers. With increasing ratio of cyclotriphosphazene to styrene in the copolymers, the beginning pyrolysis temperature increases, herein indicated as the temperature of 2% mass loss ($T_{2\%}$).

One-step decomposition behavior was observed for PS in the temperature range between 120 and 460°C, with a maximum decomposition rate at 411.3°C [Fig. 5(b)], and it lost all of its mass at 460°C [Fig. 5(a)]. In addition, the cyclomatrix homopolymer

and all of the copolymers of styrene with cyclotriphosphazene were characterized by two-stage decomposition behaviors in the temperature range between 120 and 500°C. The first stage of the cyclomatrix homopolymer decomposition began at about 330°C and reached a plateau at about 400°C, with a maximum decomposition rate at 341.6°C. The second stage ranged from 400 to 500°C, with a maximum decomposition rate at 451.1°C [Fig. 5(b)]. The mass loss in stage I (41.0%) was much lager than that in stage II (9.8%). With increasing ratio of cyclotriphosphazene to styrene in the copolymers, the mass loss of stage I increases, whereas that of stage II decreased. At the same time, the temperature of maximum decomposition rate in stage II decreased, and that in stage I changed a little.

Figure 6 shows the relationship between the char yields under nitrogen at 900°C and the content of phosphorus in the copolymers. With increasing content of phosphorus in the copolymers, the char yields of the copolymers under nitrogen at 900°C increased. The limiting oxygen indices (LOIs) of the
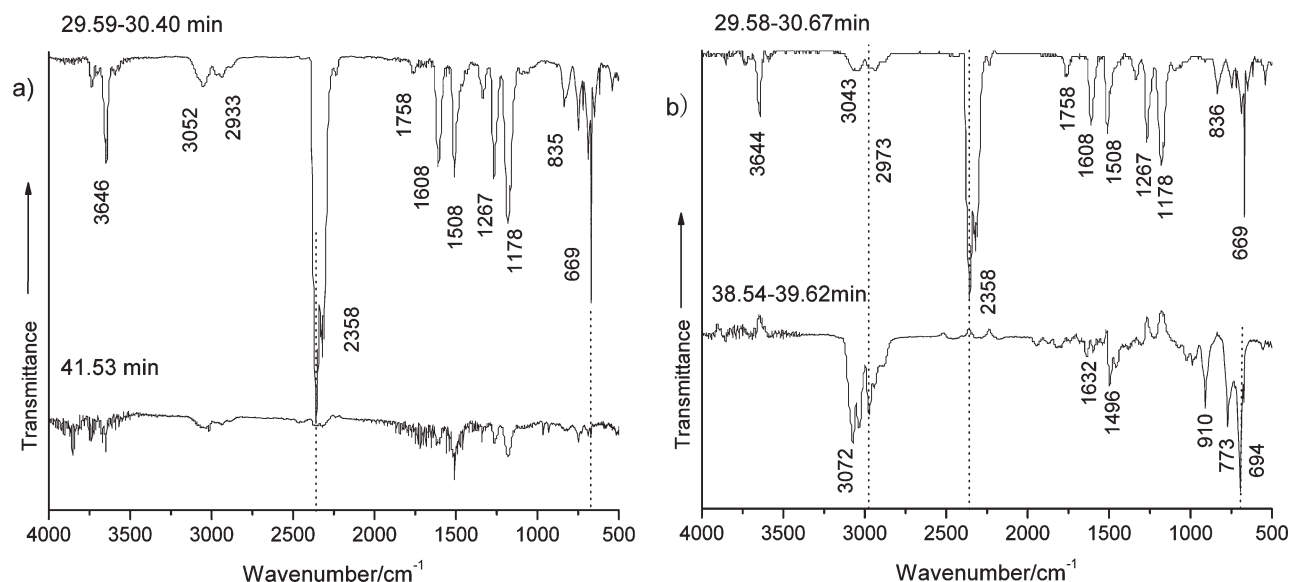

Figure 8 FTIR spectra of the volatile gas produced from thermal decomposition in nitrogen atmosphere: (a) cyclomatrix homopolymer and (b) copolymer (compound **1**/styrene = 50 : 50 weight ratio formulation).

copolymers calculated from the char yield at 850°C based on the semiempirical eq. (1) proposed by Ven Krevelen[22,26] were larger than 22% when the content of cyclotriphosphazene was up to 25%, where CR indicates the char yield at 850°C. Standard flammability tests were still required to authenticate the calculated value. We will report the results in a subsequent article, comparing them with those of poly(methyl methacrylate), polycarbonate, and CR-39 based polymers:

$$LOI = 17.5 + 0.4CR \qquad (1)$$

Figure 7(a,b) shows the TG and DTG curves of the PS, cyclomatrix homopolymer, and copolymers

under an air atmosphere. The thermogravimetric results are summarized in Table II. The overall decomposition behaviors of all of the samples under air were similar to those under a nitrogen atmosphere at temperatures lower than 500°C. However, $T_{2\%}$ and the temperatures at the maximum mass loss rate under an air atmosphere were lower than those under a nitrogen atmosphere. The finishing temperature of stage II decreased about 40°C as well (from 470°C under a nitrogen atmosphere to 430°C under an air atmosphere). At temperatures higher than about 500°C, the ordinary thermooxidative decomposition happened to the residues from the former stages under the air atmosphere, and all of the samples exhibited few residues at temperatures higher than 800°C. Similar results were obtained by Lejeune et al.[7] and Allcock et al.[27]

Volatile decomposition products and solid residues

Figure 8 shows the FTIR spectra of the volatile gas produced from the two-stage thermal decompositions of the cyclomatrix homopolymer and the
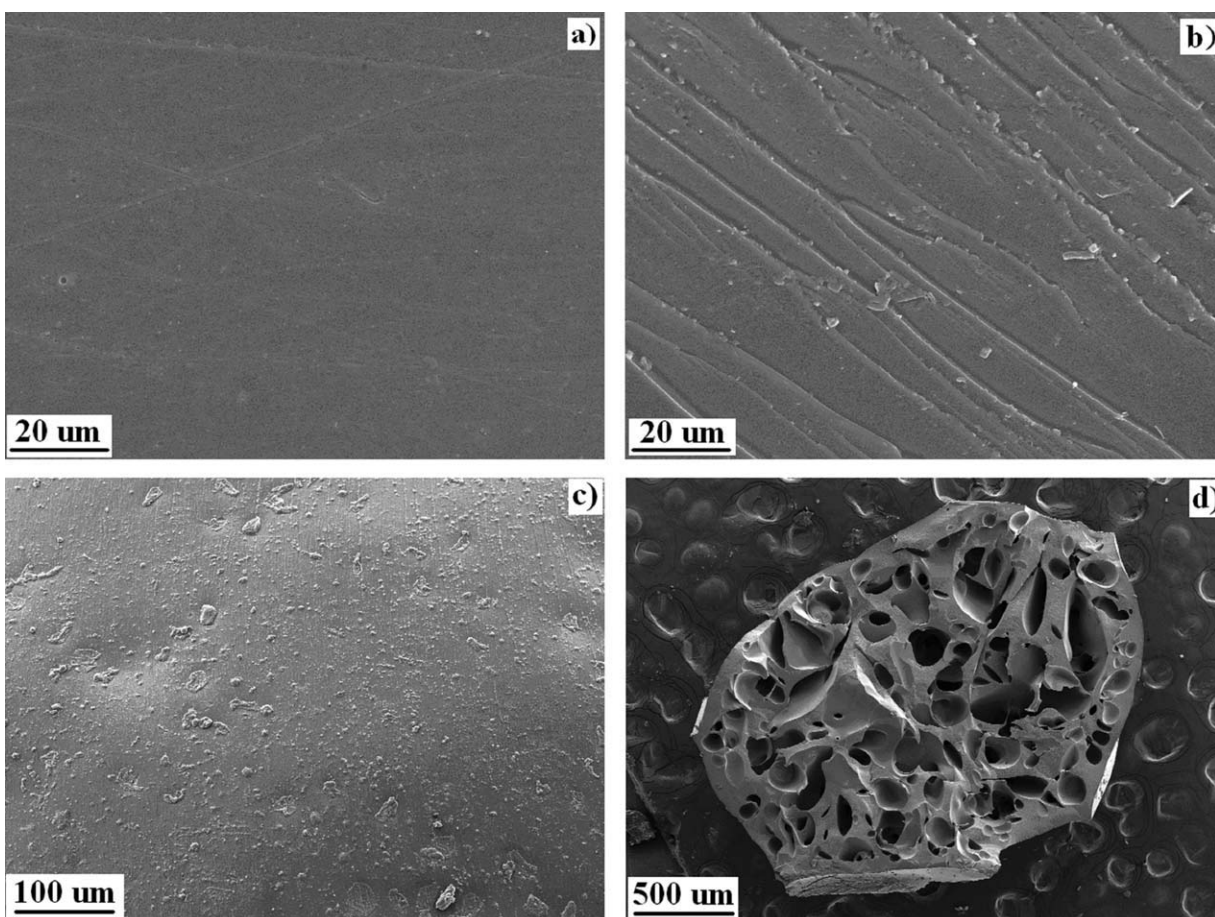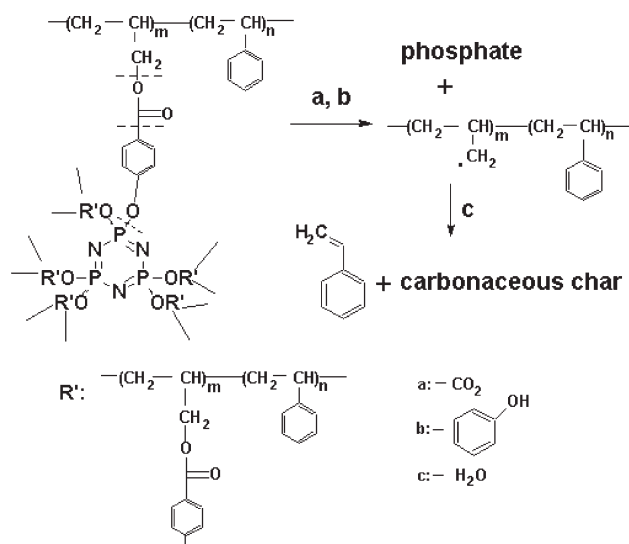

Figure 9 Morphology of the cured resin and the solid residues of the copolymer (compound **1**/styrene = 50 : 50 weight ratio formulation) after pyrolysis: (a) surface of the resin, (b) inside morphology of the resin, (c) surface of the solid residue after pyrolysis, and (d) inside morphology of the solid residue after pyrolysis.

Scheme 2 Possible mechanism involved in the two stages of decomposition of the copolymers under a nitrogen atmosphere.

copolymer [compound **1**/styrene (50 : 50) formulation] under a nitrogen atmosphere. The main signals from the gas phase spectra were assigned and are summarized in Table III. The main evolved gases from the cyclomatrix homopolymer decomposition in stage I included carbon dioxide, phenol, and benzoic acid. As shown in Figure 8(a), in the first stage of decomposition (29.59–30.40 min), a significant amount of CO_2 (2358 and 669 cm^{-1}) and phenol (3616, 1608, 1508, and 1267 cm^{-1}) were released. At the same time, a little benzoic acid (3580, 1758, 1178 cm^{-1}) was released. In the second stage of decomposition, phenol and a little water were released. The main evolved gases from the copolymer decomposition in stage I (29.58–30.67 min) were similar to those of the cyclomatrix homopolymer. Styrene was the main product during the second-stage (38.54–39.62 min) of copolymer decomposition [Fig. 8(b)].

The morphologies of the copolymer [compound **1**/styrene (50 : 50) formulation] and its solid residues after pyrolysis are shown in Figure 9. Both the surface and the inside of the resin before pyrolysis were smooth, compact, and imporous. After pyrolysis, the bulk had a continuous surface with many solidified molten drops on it but was porous inside; this was similar to that of the cyclomatrix homopolymer.[22]

Thermal degradation mechanism

The proposed decomposition model of the copolymers under a nitrogen atmosphere is illustrated in Scheme 2, which is based on the results of thermal analysis, DTG, FTIR spectral analysis of the volatile gases, and analysis of the condensed residues. In stage I, the decomposition came from the breaking of the C—O and P—O bonds of the cyclotriphosphazene structural units, produced phosphates such as ammonium phosphate, and released a large amount of CO_2 and phenol. In stage II, the carbon chains broke, and the main volatile products were styrene and a little water. The residues were carbonaceous char and some phosphorus compounds such as polyphosphoric acid and pyrophosphoric acid.[28–31]

CONCLUSIONS

Transparent copolymers containing cyclotriphosphazene and styrene were prepared by radical copolymerization. Compared with conventional PS, the copolymers exhibited a higher n_d and a higher thermal stability both under nitrogen and air atmospheres at elevated temperature; this resulted from the crosslinking in the copolymer. The visible-light transmittance of the copolymers decreased slightly. With increasing content of cyclotriphosphazene in the copolymers, the onset decomposition temperature and the char yield increased.

The cyclomatrix homopolymer and all of the copolymers of styrene with cyclotriphosphazene were characterized by two-stage decomposition behaviors in the temperature range between 120 and 500°C under a nitrogen atmosphere. The breaking of the C—O and P—O bonds of the cyclotriphosphazene structural units released CO_2 and phenol in stage I, and the depolymerization of styrene units was responsible for the mass loss in stage II. The decomposition behaviors of all of the samples under air were similar to those under a nitrogen atmosphere at temperatures lower than 500°C. At temperatures higher than about 500°C, ordinary thermooxidative decomposition happened to the residues of the former stages under the air atmosphere, and all of the samples exhibited few residues at temperatures higher than 800°C.

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