Polym. Bull. (2009) 62:421–431
DOI 10.1007/s00289-008-0035-6

ORIGINAL PAPER

Synthesis and properties of the optical resin composed of cyclotriphosphazenes

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Received: 14 September 2008 / Revised: 11 December 2008 / Accepted: 20 December 2008 /

Abstract Cyclomatrix polyphosphazenes attract more and more interest because they possess thermal stability and halogen-free flame retardant property. The hexa(Allyl 4-hydroxybenzoate)cyclotriphosphazene is synthesized using hexachlorocyclotriphosphazene (HCTP), 4-hydroxybenzoic acid and allyl alcohol, its structure is confirmed by FTIR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and mass spectrometer. Through radical homopolymerization of itself and copolymerization with methyl methacrylate (MMA), a series of optical resins containing cyclotriphosphazene units are obtained. The refractive indices, the visible light transmittance, the density, the water absorption, the thermal and flame-retardant characteristic of the cured resins are studied. Among the tested cured resins, the cyclomatrix homopolymer has the highest refractive index ($n_{\mathrm{d}} = 1.596$), the highest thermal stability (starting decomposed at 337 °C) and the best halogen-free flame-retardant characteristic (limited oxygen index is 34.33% via the 40.03% char yield data at 850 °C by the semi-empirical formula).

Keywords Cyclomatrix polyphosphazene · Optical resins · Halogen-free flame retardant · Heat-resistant

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Introduction

Most of the high refractive index materials available for optical applications are inorganic-based glasses which are heavy and brittle. Organic polymers offer the advantages of lightness of weight, toughness, and ease of fabrication. Many high refractive index polymers have been reported. These systems usually consist of highly conjugated, aromatic-type, π-electron systems that bear heavy elements such as bromine [1], iodine or sulfur [2–4]. Some systems are inorganic/organic nanocomposites or consist of heavy-metal ion such as Pb [5], Ti [6, 7], etc. However, above mentioned materials either are inflammable and thermolabile or obtain the flame-retardant characteristic via halogens which burn to give smoke and toxic gas. This is a disadvantage for being used in certain areas such as aviation and space, etc.

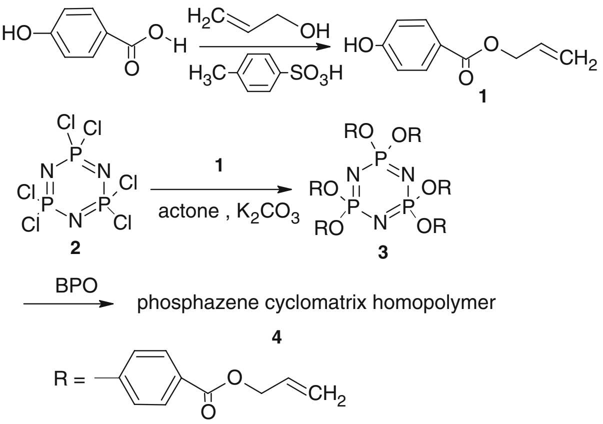
Linear polyphosphazenes are a broad class of polymers which have the wide range refractive indices from 1.59 to 1.75 according to the nature of the side groups [8, 9]. Addition to the high refractive index values, the polymers containing phosphazenes are also fire-retardant and heat-resistant. However, their main disadvantage, in further widening the application of linear polyphosphazenes, is low yield, high cost and difficult to process. In order to overcome the shortcomings, other types of phosphazenes, for instance, cyclomatrix-type polyphosphazenes, have attracted much attention recently. In past decades, a series of phosphazene cyclomatrix polymers have been reported [10, 11], which have been used as coating materials [12], fire- and heat-resistant binders with high anaerobic char yields useful for reinforced composites [13], flame-retardant polymeric additives [14], and thermoset resins [15, 16] for their high thermal stability. But little attention has been paid to the application of phosphazene cyclomatrix in optical materials.

In this article, we report the synthesis and properties of a series of halogen-free flame retardant optical resins composed of cyclotriphosphazenes prepared via the homoplymerization of allylic group [C=C] and the copolymerization with MMA, the preparation route and the ideal structure of the homopolymer are presented in Scheme 1. Subsequently, the optical characteristics and the thermal and flame-retardant properties were evaluated comparing to the corresponding copolymers and poly(methyl methacrylate) (PMMA). The process offers the advantages of ease of synthesis and fabrication.

Experimental

Materials

All of the chemicals and solvents were reagent grade. 4-hydroxybenzoic acid and p-toluene sulfonic acid were used as received without further purification. Allyl alcohol was distilled before use. Acetone was dried with potassium carbonate and distilled prior to use. Hexachlorocyclotriphosphazene (HCTP, Compound **2**) was synthesized in the lab as described in the literature [17, 18], recrystallized from heptane and sublimed (60 °C, 0.05 mmHg) before use (m.p. = 110.0–112.0 °C).



Scheme 1 Synthetic route of cyclomatrix homopolymer of phosphazene (see "Experimental" section for further details)

Potassium carbonate was activated at 140 °C for 2 h. Methyl methacrylate (MMA) was washed 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) prior to polymerization.

Instruments

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Equinox 55 Fourier Transfer Infrared Spectrophotometer (Germany), using a KBr plate and measured in atmosphere. ^{1}H NMR (400 MHz), ^{13}C NMR (400 MHz) and ^{31}P NMR (400 MHz) spectra were obtained with a Bruker AV 400 spectrometer (Switzerland). An 85% H_3PO_4 aqueous solution assigned to 0 ppm was used as an external reference for the ^{31}P NMR spectrum, deuterated DMSO (DMSO-d_6) as the solvent. As convention, the ^{1}H NMR and the ^{13}C NMR spectra were referenced to tetramethylsilane, deuterated chloroform ($CDCl_3$) as the solvent. The molecular weight was measured on an Autoflex III MALDI-TOF mass spectrometer (Bruker Daltonics Inc.). The refractive indices (n_d) of the cured resins were measured by a WZS-IAbbé-Refractometer at 20 °C. The visible light transmittance of the cured resins was measured by a S721 visible spectrophotometer at a wavelength of 550 nm. Calorimetric studies and thermal stability studies were carried out on a synchronous thermal analysis instrument (STA 409 PC/4/H LUXX, Germany) with nitrogen as the purge gas at a 10 °C min^{-1} 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 (Holland).

Synthesis of Allyl 4-hydroxybenzoate (**1**)

Compound **1** was synthesized according to the literature [19]. A solution of 4-hydroxybenzoic acid (27.6 g, 0.2 mol) and p-toluene sulfonic acid (2.0 g, 0.012 mol) in a large excess of allyl alcohol(116 g, 2 mol), cyclohexane (50 ml) was placed in a 250 ml round-bottomed flask, the mixture was heated at refluxing to ensure the complete removal of water for 18 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature, and the excess of allyl alcohol was distilled under reduced pressure. The remaining solid was washed with a 5% $NaHCO_3$ solution, then with water, and recrystallized from ethanol–water (2:3), dried in a vacuum oven at 50 °C to give 33.3 g (0.187 mol, 93% yield) of white thin crystals(m.p. 98–99 °C). IR (KBr, cm^{-1}): 1,446, 1,518, 700–900 (aromatic); 1,603(allyl double bond); 1,672, 1,126, 1,168, 1,232, 1,284 (ester group stretching); 3,233 (hydroxyl). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.79–4.81(m, $J = 1.2$, 2.8 Hz, 2H; O–CH_2), 5.26–5.29 (m, $J = 9.2$, 1.2 Hz, 1H; C=CH_2), 5.37–5.42 (m, $J = 15.6$, 1.6 Hz, 1H; C=CH_2), 5.98–6.07 (m, $J = 5.6$, 5.2 Hz, 1H; CH_2=C–H), 6.23 (s, 1H, OH), 6.87–6.89 (d, $J = 8.8$ Hz, 2H; Ph), 7.97–7.99 (d, $J = 8.8$ Hz, 2H; Ph). ^{13}C NMR ($CDCl_3$, 400 MHz): 65.64 (s, 1, OCH_2); 115.4 (s, 2, aromatic); 118.3 (s, 1, =CH_2); 122.0 (s, 1, aromatic); 132.0 (s, 2, aromatic); 132.1 (s, 1, -CH=); 160.5 (s,1, aromatic,C-OH); 166.8(s,1,C=O).

Synthesis of hexa-(Allyl 4-hydroxybenzoate)cyclotriphosphazene (**3**)

Compound **3** was synthesized according to the literature [20]. Compound **2** (10.4 g, 0.03 mol), compound **1** (38.5 g, 0.216 mol), and activated potassium carbonate (29.8 g, 0.216 mol) were placed in a three-necked flask provided with a stirrer, a reflux condenser, and a nitrogen inlet. After reaction at 60 °C for 48 h under nitrogen atmosphere, the mixture was cooled to room temperature and the potassium carbonate was separated by filtration, and the solvent was removed under distillation. The residue obtained was then dissolved in methanol in order to remove the excessive allyl 4-hydroxybenzoate, filtrated, and dried in a vacuum oven at 40 °C, a white solid was obtained. Yield: 27 g, 75%, m.p. = 52–53 °C. IR (KBr, cm^{-1}): 1,503, 1,603 (aromatic, allyl double bond); 1,724, 1,272, 1,116 (ester group stretching); 1,161, 1,182, and 1,206 (cyclotriphosphazene ring P=N); 951 (P–O–Ph). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.80 (m, $J = 1.2$, 3.2 Hz, 2H; O–CH_2), 5.28–5.31 (m, $J = 9.2$, 1.2 Hz, 1H; C=CH_2), 5.38–5.43 (m, $J = 13.2$, 1.6 Hz, 1H; C=CH_2), 5.99–6.09 (m, $J = 5.6$, 4.8 Hz, 1H; CH_2=C–H), 7.00–7.02 (d, $J = 8.8$ Hz, 2H; Ph), 7.89–7.91 (d, $J = 8.8$ Hz, 2H; Ph). ^{13}C NMR (400 MHz, $CDCl_3$, δ):65.75(s, 1, OCH_2), 118.4 (s, 2, aromatic), 120.5 (m, 1, =CH_2), 127.4 (s, 1, aromatic), 131.4 (s, 2, aromatic), 132.2 (s, 1, –CH=), 153.7 (m, 1, aromatic, C–O), 165.1 (s, 1, C=O). ^{31}P NMR (400 MHz, DMSO-d_6, δ): 9.05 (s, 3, P=N). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{60}H_{54}N_3O_{18}P_3$, 1220.9908; found, 1220.5.

Synthesis of the phosphazene cyclomatrix homopolymer (**4**)

Ten gram compound **3**, 0.2 g benzoyl peroxide were placed in a three-necked flask equipped with a stirrer, thermometer, nitrogen inlet, the temperature of the reaction mixture was increased to 75 °C and stirred for 0.5 h. Then, the preformed polymer was cast slowly in a glass-mould and placed in the vacuum oven, the temperature was kept at 70 °C for 20 h, 80 °C for 2 h, 90 °C for 2 h, 100 °C for 2 h and then the oven was turned off. After the temperature of the oven was cooled to room temperature, the mold was removed from the cured resin and a colorless and sheet-like polymer with 3 mm thickness was obtained.

Synthesis of phosphazene cyclomatrix (**3**)/MMA copolymers

Similarly, 10 g admixture of compound **3** and MMA according to certain proportion, 0.2 g benzoyl peroxide were placed in a three-necked flask equipped with a stirrer, thermometer, nitrogen inlet, the temperature of the reaction mixture was increased to 75 °C and stirred for 0.5 h. Then, the preformed polymer was cast slowly in a glass-mould and placed in the vacuum oven, the temperature was kept at 70 °C for 20 h, 80 °C for 2 h, 90 °C for 2 h, 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 from the cured resins and the colorless and sheet-like resins with 3 mm thickness were obtained.

Results and discussion

Design and synthesis of the optical resins

In order to obtain the halogen-free flame retardant optical resins, two problems are required to be resolved. The first one is the complete substitution of the chlorine atoms in hexachlorocyclotriphosphazene(HCCP) by Allyl 4-hydroxybenzoate to ensure the halogen-free flame retardant property. The second one is that the colorless and transparent products containing benzene rings are needed to ensure the optical properties. The synthetic procedure for the optical resin composed of cyclotriphosphazenes is summarized in Scheme 1. Firstly, the compound **1** (Allyl 4-hydroxybenzoate) was synthesized via esterification of 4-hydroxybenzoic acid and allyl alcohol. Secondly, compound **3** (hexa-(Allyl 4-hydroxybenzoate)cyclotriphosphazene) was obtained via nucleophilic substitution of compound **1** and compound **2** (HCCP), six allyl groups were grafted onto the cyclotriphosphazene core. Finally, the optical resins were attained through radical homopolymerization or copolymerization with MMA.

Characterization of chemical structure

The chemical structures of compound **1** and compound **3** were characterized by FTIR spectroscopy, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as mass spectrometer, and the results are presented in the "Experimental" section.

FTIR spectrum of compound **3** compared with that of compound **1** are given in Fig. 1. Both in the curve (a) and curve (b), the characteristic absorption peaks of the aromatic group and the ester group stretching, the characteristic absorption peaks of the allyl double bond at 1,603 cm^{-1} were observed. The characteristic peak of the hydroxyl group appeared at 3,233 cm^{-1} in curve (a), whereas it was disappeared in

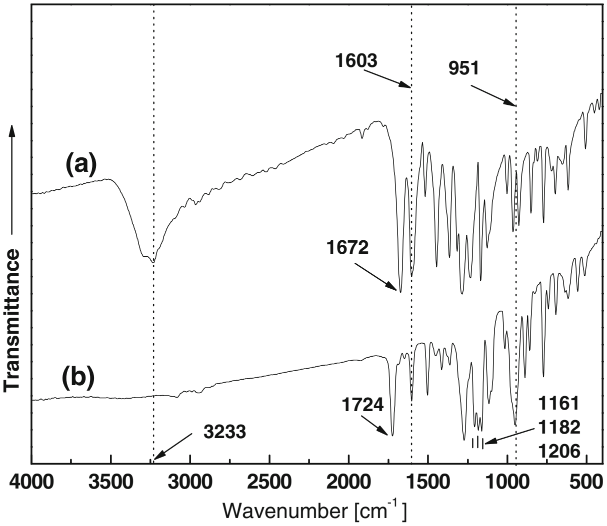


Fig. 1 FTIR spectra of compound **1** (**a**) and compound **3** (**b**)

curve (b). At the same time, in curve (b), the characteristic absorption peak of the (P–O–Ph) appeared at 951 cm^{-1}, the characteristic bands of cyclotriphosphazene ring (P=N) were observed at 1,161, 1,182, and 1,206 cm^{-1}.

A sharp singlet resonance peak at 9.05 ppm was observed in the ^{31}P NMR spectrum of compound **3** instead of the singlet resonance peak corresponding to compound **2** at 20.1 ppm, indicating the almost complete substitution of the chlorine atoms in compound **2**. HRMS (ESI, m/z): $[M + \mathrm{Na}]^+$ calcd for $C_{60}H_{54}N_3O_{18}P_3$, 1220.9908; found, 1220.5.

The characteristic bands in the FTIR spectra, the characteristic resonance peaks in the ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, and the mass spectrometric analysis are consistent well with the structure of compound **3** in Scheme 1.

Optical characteristics

The refractive indices (n_d) and the visible light transmittance of the cured resins are shown in Fig. 2. The n_d of pure PMMA is 1.493, and its visible light transmittance at 550 nm is 93.5%. With increasing ratio of compound **3** to MMA in the copolymer, the n_d of the cured resin increases gradually, the visible light transmittance lightly decreases slightly. The n_d of pure cyclomatrix homopolymer **4** is 1.596, and its visible light transmittance at 550 nm is 88.6%. The relationship between the densities of cured resins and the ratio of compound **3** to MMA is shown in Fig. 3. The densities of the pure PMMA and the pure cyclomatrix homopolymer **4** are 1.165 and 1.242, respectively, the densities of the copolymers are located between the two homopolymers.

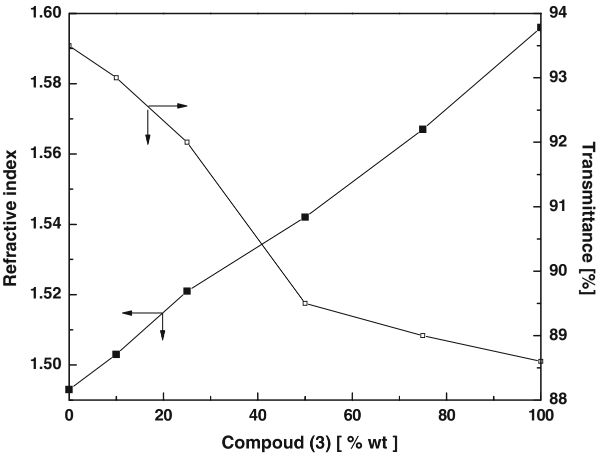


Fig. 2 The effect of the ratio of compound 3 to MMA on the refractive indices and the transmittance of cured resins

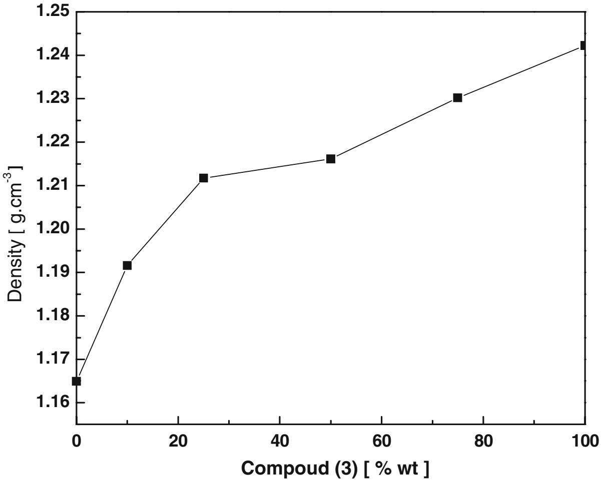


Fig. 3 The relationship between the density of cured resins and the ratio of compound **3** to MMA

Water resistance

The relationships between the water absorption (Wa) of the cured resins and the time at 75% relative humidity and in water are separately shown in Figs. 4 and 5. Either at 75% relative humidity or in water, the Wa of the cured resins increase with the time within 120 h, the Wa is nearly saturated at 120 h. The pure cyclomatrix homopolymer **4** has the lowest Wa and the pure PMMA possess the highest Wa, the Wa of the copolymers are located between the two homopolymers.

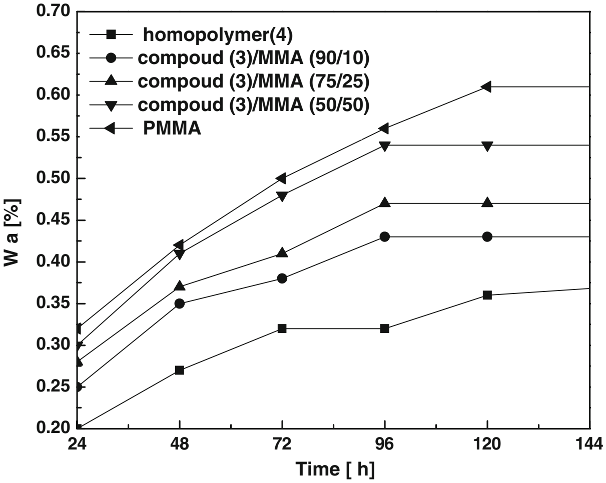


Fig. 4 The effect of the time on the water absorption of cured resins at 75% relative humidity

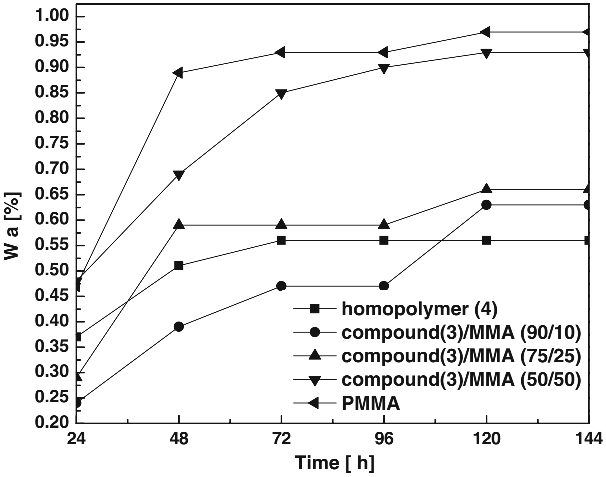


Fig. 5 The effect of the time on the water absorption of cured resins in water

Thermal properties

The thermal stabilities of cyclomatrix homopolymer **4**, the pure PMMA and the copolymers were analyzed by TGA. As shown in Fig. 6, pure PMMA begins to decompose at 210 °C, with increasing ratio of compound 3 to MMA in the copolymer, the pyrolysis temperature increases, cyclomatrix homopolymer **4** do not decompose until at 337 °C. The char yields of cyclomatrix homopolymer **4** in nitrogen at 850 °C and at 900 °C are high up to 40.03 and 34.33%, respectively. The limiting oxygen index (LOI) can be calculated as about 33.5% via the char yield

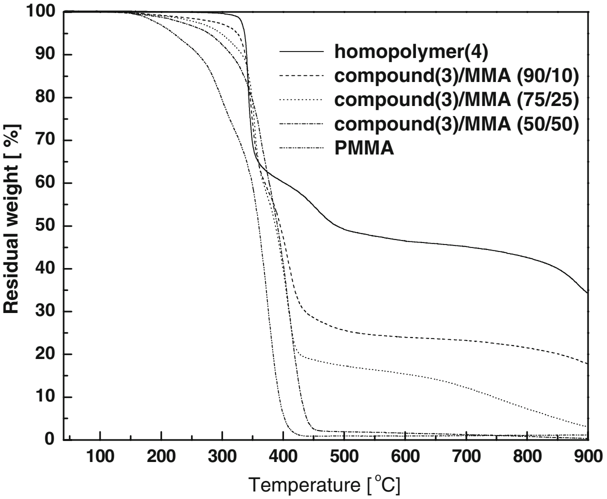


Fig. 6 Dynamic TGA curves for cured resins in nitrogen atmosphere

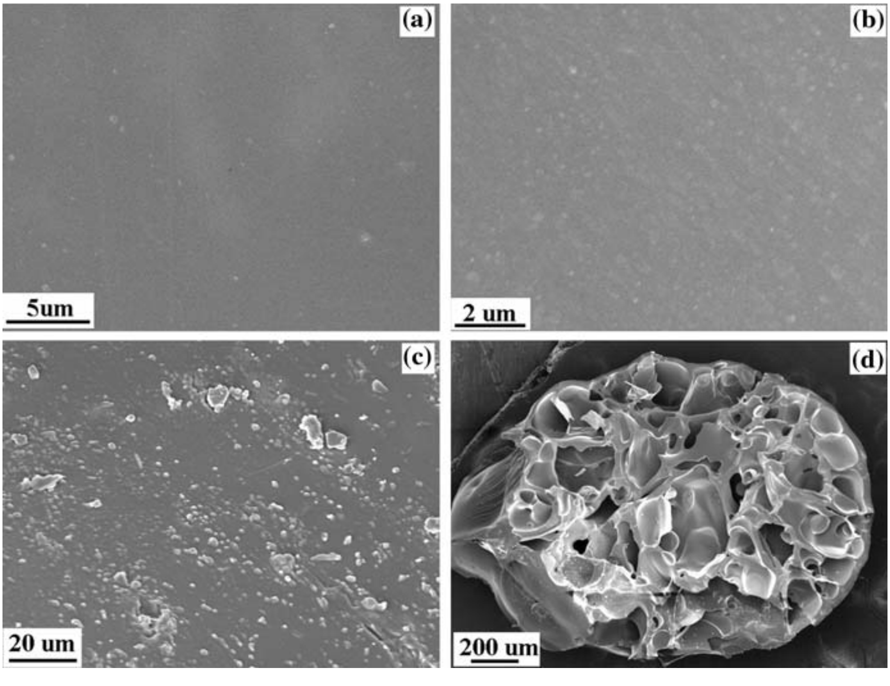


Fig. 7 Morphology of the cured resin and the solid residues of polymer 4 after pyrolysis: **a** surface of the resin, **b** inside morphology of the resin, **c** surface of the solid residue after pyrolysis, **d** inside morphology of the solid residue after pyrolysis

data at 850 °C by the following semi-empirical formula proposed by Ven Krevelen [21],

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

where CR means the char yield at 850 °C. The results show that cyclomatrix homopolymer **4** has the highest thermal stability and the best flame-retardant characteristic in all the experimental cured resins.

The morphologies of the cyclomatrix homopolymer **4** and its solid residues after pyrolysis are shown in Fig. 7. Both the surface and the inside of the resin before pyrolysis are smooth, compact and imporous. After pyrolysis, the bulk has a continuous surface with many solidified molten drops on it but is porous inside, which is accordant with the flame-retardant mechanism proposed in literature [10].

Conclusions

Halogen-free flame retardant optical resins with high refractive index composed of cyclotriphosphazenes have been obtained through the following procedure. Firstly, the hexa-(Allyl 4-hydroxybenzoate)cyclotriphosphazene (compound **3**) has been synthesized by esterification and nucleophilic substitution, which has six allyl double bonds. Secondly, its cyclomatrix homopolymer **4** and copolymers composed of cyclotriphosphazenes have been obtained through radical homopolymerization or copolymerization with MMA. When the ratio of compound **3** to MMA in the copolymer is increased, the n_d, the density, the thermal stability and the flame-retardant characteristic of the cured resin increase, but the Wa decrease gradually. The n_d of the cyclomatrix homopolymer **4** reaches to 1.596. At the same time the cyclomatrix homopolymer **4** has a high light transmittance at 550 nm (89%). The cyclomatrix homopolymer **4** has a compact morphology but it is porous inside after pyrolysis. Among the experimental cured resins, the cyclomatrix homopolymer **4** has the highest thermal stability (starting decomposed at 337 °C) and the best flame-retardant characteristic (40.0% char yield at 850 °C), its LOI is up to 34.3% via the char yield data at 850 °C by the semi-empirical formula.

All the results indicate the cyclomatrix homopolymer **4** has a potential superiority both as a high refractive index optical resin itself with good thermal stability and flame-retardant property and as a modifier to improve the corresponding performances of PMMA through copolymerization.

Acknowledgment This work was supported by the National Natural Science Foundation of China (No. 20374022, 50703013).

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