

Soluble Polyarylates Containing Phosphorus in Main Chains with Thermal Stability

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ABSTRACT: A series of polyarylates containing phosphorus (pho-PARs) were synthesized from bisphenol A with different molar ratios of bis-(4-carboxyphenyl) phenyl phosphine oxide (BCPPO) to terephthalic acid (TPA). When the contents of BCPPO are in the range of 0.4–1.0, the pho-PARs are readily soluble in a wide range of organic solvents and have the glass transition temperatures of 243.0–260.4°C. The initial degradation temperatures of these pho-PARs are all above 450°C and their char yields at 800°C under nitrogen atmosphere are in the range of 28.7–33.0%, suggesting they have excellent thermal stability. The results of TG-FTIR and FT-IR show the introduction of BCPPO change the decomposition model of the pho-PARs. The limiting oxygen indexes are at a range of 30.7–34.5%, which suggests that the pho-PARs are a kind of excellent inherent flame retardant materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3521–3529, 2013

KEYWORDS: flame retardance; mechanical properties; thermal properties

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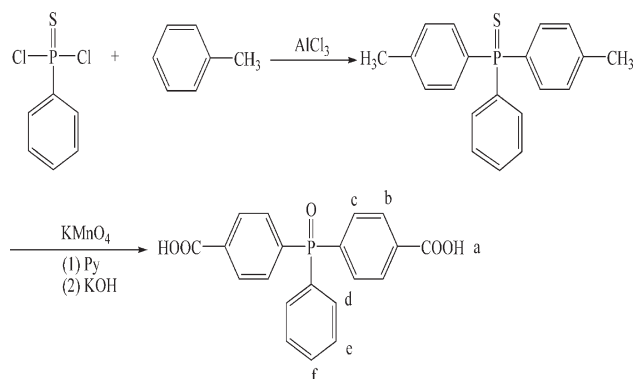
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INTRODUCTION

Bisphenol A based polyarylate (U-polymer) derived from bisphenol A (BPA) and aromatic diacids is a type of high-performance engineering materials due to its excellent heat resistance, chemical resistance, good mechanical properties, and good flame retardance. These properties are attributed due to the high packing density, stiffness of the polymer chain, and the presence of a large number of phenyl rings in the polymer backbone.^{1,2} However, it is generally difficult to soluble in the common organic solvents, which greatly limits the application in the fields of coatings and films. Thus, much work has been done to obtain good solubility for processing. There were several achievements on modification methods in the past few years. The main modification methods were reported as follows: (1) introduction of flexible main chain segment in main chain;^{3,4} (2) introduction of bulky pendent groups in repeating unit;^{5,6} (3) introduction of asymmetric units in the main chains;^{7,8} (4) introduction of distorted and non-coplanar structures;^{9,10} (5) copolymerization of several aromatic monomers to obtain a more random backbone.^{11,12} For example, Wang et al. synthesized a series of novel perfluorononyloxy group containing polyarylates from 5-(perfluorononyloxy)-isophthaloyl chloride with various aromatic diols. All polymers would be soluble in many organic solvents and had good thermal properties and

extraordinary mechanical properties.¹³ Zadrozna et al. synthesized some polyarylates from 2,4-dihydroxy-benzaldehyde and formyl-bisphenol A. These polymers showed high thermal stability and their films had good mechanical properties.¹⁴ Hsiao et al. reported a new series of fluorine-containing polyarylates were highly soluble in a variety of solvents, but they did not show significant thermal stability.¹⁵ The above methods have been applied with several disadvantages: (1) most of the monomers were complex in structure, which made them hard to be synthesized and applied in polymerization; (2) though the solubility can be improved by introducing these monomers, it may diminish the heat resistance and thermal stability. In order to improve the thermal stability of the polyarylates, some researchers brought phosphorus to the main chain of polyarylates. For example, Balabanovich et al. showed a new fire retardant 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide containing aliphatic–aromatic polyester. The polymer had good thermal stability and flame retardance with anti-flammable structure. Though these polyarylates had good thermal stability and flame retardance properties, they could not dissolve in some common organic solvents; moreover, the preparation of monomers was very difficult, which greatly limited their applications.^{16,17}

In our previous work, Liu et al.¹⁸ synthesized some polyarylates containing aryl ether units by melt transesterification reaction.



Scheme 1. The synthetic route of BCPPO.

The processability of these polyarylates is improved through reducing the melting peak temperature. For further improvement of the polyarylates' application, the focus of our present work is improvement of processability and thermal stability at the same. In order to improve the processability of polyarylates (PARs) without extreme loss of the other properties, such as thermal stabilities and mechanical properties, etc., we introduced flame retarding structure with triaryl phosphine oxide moiety (TPO) to the main chains. A series of novel polyarylates containing phosphorus (pho-PARs) were synthesized by high temperature solution polycondensation from bisphenol A and different molar ratios of bis-(4-carboxyphenyl) phenyl phosphine oxide (BCPPO) to terephthalic acid (TPA). First, introducing the bulky pendent phenyl increase the solubility of PARs to improve the processability. Moreover, introduction of BCPPO may contribute to promoting their flame retardance, heat resistance, and thermal stabilities. Therefore, these novel pho-PARs can be used in the harsher conditions. The properties of these pho-PARs were systematically characterized by a series of experimental methods, such as gel permeation chromatography (GPC), differential scanning calorimetry (DSC), dynamic mechanical analyses (DMA), thermogravimetric analyses (TGA), wide angle X-ray diffraction (WAXD), thermogravimetry–Fourier transform infrared spectroscopy analysis (TG-FTIR), tensile test, limiting oxygen index (LOI), etc.

EXPERIMENTAL

Materials

Potassium permanganate (KMnO_4), sublimed sulfur, toluene, phenol, tetrachloromethane (CCl_4), ethanol (EtOH), chloroform (CHCl_3), methanol (MeOH), cyclohexane, and anhydrous aluminum chloride (AlCl_3), 1,1,2,2-tetrachloroethane (TCE), dichlorophenylphosphine sulfide (DCPPS, from Dubang Chemical Plant, Zibo, China) and benzenesulfonyl chloride (BsCl, from Xilong Chemical Plant, Guangdong, China) were analytically pure and used as received. *N,N*-dimethylformamide (DMF) and pyridine (Py) were used after reflux with CaH and the vacuum distillation. BPA was used after vacuum drying at 80°C . All reagents are purchased from Chengdu Kelong Chemical Reagent Factory except DCPPS and BsCl.

Monomer Synthesis

According to the method of Wang et al., bis-(4-methylphenyl) phenyl phosphine sulfide (BMPPS) was synthesized through the

Friedel–Crafts reaction of DCPPS, which was prepared by the reaction of sulfide, DCPPS, and toluene with AlCl_3 as catalyst.¹⁹ Then BMPPS was oxidized to BCPPO using KMnO_4 as oxidizing agent. The synthetic route is shown in Scheme 1.

Polymerization

The pho-PARs were synthesized by high temperature solution polycondensation from BPA with different molar ratios of BCPPO to TPA (Figure 1). The synthesis of PAR-2 was used as an example to illustrate the general synthetic route. In a four-neck, 250 mL round-bottom flask equipped with a mechanical stirrer, a condenser and a nitrogen inlet, DMF (0.22 g, 3 mmol), a mixture of Py (10 mL) and BsCl (2.29 g, 13 mmol) were added, and the mixture was stirred for 30 min at 25°C under nitrogen atmosphere. Then a solution of BCPPO (0.3660 g, 1 mmol) and TPA (0.6640 g, 4 mmol) in Py (10 mL) was added to the above flask. The mixture was vigorously stirred for 10 min at 25°C , and then was heated to 120°C and held for 10 min to obtain a clear solution. Then BPA (1.1400 g, 5 mmol) in 10 mL of Py was added dropwise to the reaction flask over a period of 20 min and the whole solution was stirred at 120°C for another 3 h. Extending reaction time has no effect on improving the molecular weight. After the reaction, the viscous polymer solution was poured into methanol for precipitation. The prepared polymer was washed with hot water repeatedly, and then dried at 100°C . And it was repeatedly washed using ethanol in Soxhlet Extractor before testing, and the residual monomers can be completely removed. The inherent viscosity of the PAR-2 was 0.47 dL g^{-1} , which was measured at a concentration of 0.25 g dL^{-1} in a mixed solvent of TCE and phenol (6:4, v/v) at 30°C .

Preparation of the pho-PARs Films

The films were prepared by casting chloroform solutions containing 10 wt % pho-PARs onto glass plates and dried for 3 h at room temperature. Then the films were peeled off and further vacuum dried for 12 h at 70°C to ensure the complete removal of the solvent. The obtained films were about 0.1 mm in thickness and were used for DMA, tensile test, and limiting oxygen index tests.

Characterization

^1H NMR spectra were measured with a Bruker 400 MHz Ultra Shield NMR spectrometer. The chemical shifts were calibrated using tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Nicolet 560 spectrometer. The inherent viscosities of polyarylates were determined by an Ubbelohde capillary viscometer at a concentration of 0.25 g dL^{-1} in TCE/phenol (6 : 4, v/v) at $30.0 \pm 0.1^\circ\text{C}$. GPC measurement was carried out on a Water 1515 chromatography. All GPC analyses were performed using dilute solution of polymers in THF at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$ and calibrated with narrow polystyrene standards. Qualitative solubility was tested with 10 mg sample in 1 mL solvent at room temperature or on heating if needed. The solubility parameters (δ_p) were calculated according to the turbidity method described by Wu et al.¹⁹ We used TCE [$\delta = 10.4 \text{ (cal cm}^{-3})^{1/2}$] as solvent (polymer concentration of 0.6 g dL^{-1}) and methanol [$\delta = 14.6 \text{ (cal cm}^{-3})^{1/2}$] and cyclohexane [$\delta = 8.2 \text{ (cal cm}^{-3})^{1/2}$] as precipitants in this method.

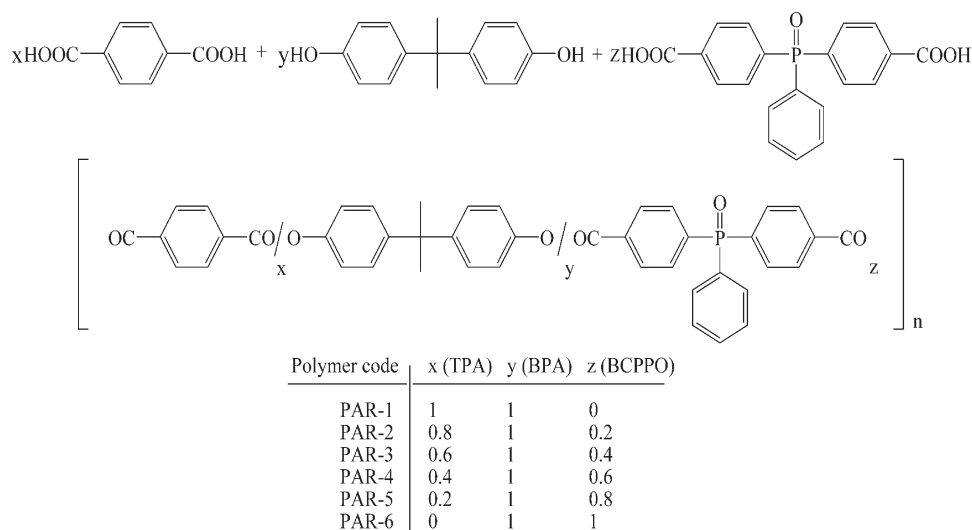


Figure 1. The synthetic route of PARs.

DSC measurement was carried out using a NETZSCH DSC 204F1 at a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen ($20\text{ cm}^3\text{ min}^{-1}$), and the scanning scope was $30\text{--}370^{\circ}\text{C}$. The temperature and heat enthalpy were calibrated with indium standard before the equipment running. WAXD patterns were measured with X'Pert Pro X-ray diffractometer. The scanning rate was $12^{\circ}\text{ min}^{-1}$ over a range of scattering angle $2\theta = 5\text{--}45^{\circ}$. The dried polymer powder was used for WAXD measurement. TGA were performed with a TA SDT Q600 thermal analyzer using a heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen ($100\text{ cm}^3\text{ min}^{-1}$). DMA was performed with a TA Q800 DMA. The storage modulus G' and $\tan \delta$ were studied when the pho-PAR films were subject to the temperature scan mode of a heating rate $10^{\circ}\text{C min}^{-1}$ from 30 to 300°C at a frequency of 1 Hz. A sample (50 mm in length, 10 mm in width, and 0.1 mm in thickness) was used. TG-FTIR was performed via a Perkin Elmer Pyris-1 TG analyzer and Nicolet IR-560 infrared spectrometer equipped with a TG-FTIR interface. The sample was heated at $10^{\circ}\text{C min}^{-1}$ from ambient temperature to 800°C under a steady flow of nitrogen (10 mL min^{-1}) and the volatile gas produced from thermal decomposition was recorded online by FT-IR. According to GB/T2406-93 standard, LOI measurements were performed on a LOI-1045 G05 ATLAS with film specimens (140 mm in width, 52 mm in length, and about 0.10 mm in thickness), and an average of at least four replicas was used. All the readily soluble pho-PARs could be convenient to process into flexible film and an Instron 5567 tester was used to test the stress-strain behavior of pho-PAR films samples. A gauge length of 25 mm and a crosshead speed of 5 mm min^{-1} were used for this test. Measurement were performed at room temperature with film specimens (10 mm in width, 70 mm in length, and about 0.10 mm in thickness), and an average of at least five replicas was used.

RESULTS AND DISCUSSION

Monomer Synthesis

The structure of the BCPPPO was confirmed by $^1\text{H NMR}$ spectrum shown in Figure 2. It is found that the area ratio, chemical shift, and signal splitting of each peak are completely consistent

with the structure of BCPPPO. There is no small miscellaneous peak in the $^1\text{H NMR}$ spectrum, suggesting the obtained product has very high purity. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ , ppm): 13.374 (s, 2H, H_a), 8.099 (s, 4H, H_b), 7.776 (s, 4H, H_c), 7.660 (s, 3H, H_e , H_f), 7.587 (s, 3H, H_d). In the reaction of monomer, the quality of the product is mainly determined by the reaction temperature, the degree of oxidation, feeding order, etc. To reduce the side reaction, the temperature needs to be controlled at $65\text{--}70^{\circ}\text{C}$ which is the reflux temperature of toluene. The excessive oxidation agent should be added to ensure the complete oxidation reaction. If DCPSPS was added dropwise to the toluene solution, the yield would be improved efficiently. According to the previous researches about the synthesis of BCPPPO in references and study in our article, the exorbitant reaction temperature would reduce the yield of the monomer. In order to ensure the polycondensation, the quality of the

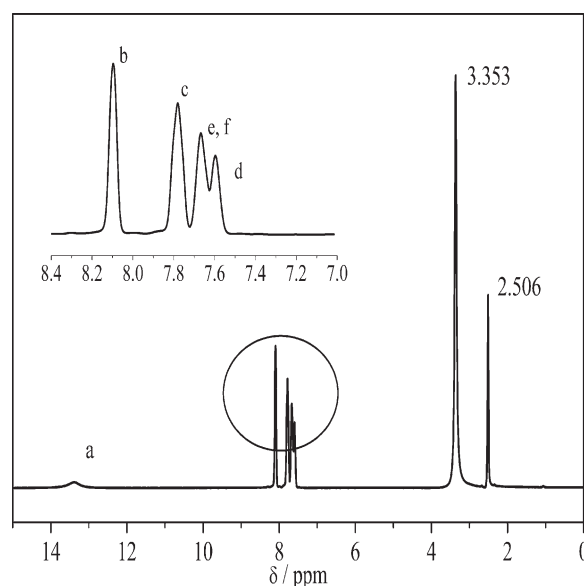


Figure 2. $^1\text{H NMR}$ spectrum of BCPPPO.

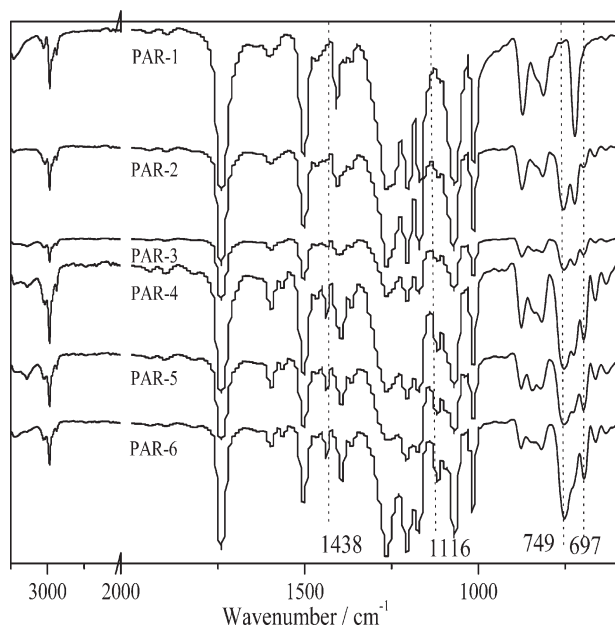


Figure 3. The FT-IR spectra of PARs.

monomer is very important. The sufficient degree of oxidation would ensure that BMPPS be oxidized into diacid completely. Also, when DCPPS was added dropwise to the toluene solution, the amount of toluene was excessive relative to DCPPS at this time, which was conducive to react with DCPPS completely. After optimizing above factors, the yield of the monomer would be up to 84%.

Preparation of PARs

The PARs were prepared by the high temperatures solution polycondensation with BsCl/Py/DMF as the condensation agents.²⁰ The optimized reaction conditions for this high temperature solution polycondensation are obtained as follows: the monomer concentration is 0.167 mol L^{-1} , the reaction temperature is 120°C , and the reaction time is 3 h. The typical FT-IR spectra of the PARs exhibit characteristic ester absorption band (Figure 3).

Table I. Inherent Viscosities and Molecular Weights of PARs

Polymer code	$\eta_{\text{inh}}^{\text{a}}$ ($\text{dL} \cdot \text{g}^{-1}$)	Molecular weights ^b		
		M_n ($\text{g} \cdot \text{mol}^{-1}$)	M_w ($\text{g} \cdot \text{mol}^{-1}$)	PDI ^c
PAR-1 ^d	0.36	–	–	–
PAR-2 ^d	0.47	–	–	–
PAR-3	0.53	11,004	18,639	1.504
PAR-4	0.62	10,590	17,485	1.431
PAR-5	0.84	6,740	9,961	1.276
PAR-6	0.91	3,600	4,700	1.178

^a Measured at a polymer concentration of 0.25 g dL^{-1} in chloroform at 30°C .

^b Calibrated with polystyrene standards, using THF as the eluent at a constant flow rate of 1 mL min^{-1} .

^c Polydispersity index (M_w/M_n).

^d No GPC data of PAR-1 and PAR-2 because they cannot dissolve in THF.

IR (KBr): 1740 cm^{-1} (ester $\text{C}=\text{O}$), around 1262 and 1170 cm^{-1} (ester $\text{C}-\text{O}-\text{C}$), 1599 , 1560 , 1460 cm^{-1} (aromatic $\text{C}=\text{C}$).^{21,22} In addition the pho-PARs has other typical absorption band. IR (KBr): 1116 cm^{-1} ($\text{Ar}_3-\text{P}=\text{O}$), 1438 cm^{-1} ($\text{P}-\text{Ar}$), 697 cm^{-1} and 749 cm^{-1} (mono-substituted phenyl $\text{C}-\text{H}$).

The inherent viscosities and relative molecular weights of PARs are listed in Table I. PARs have the values of η_{inh} in the range of 0.36 – 0.91 dL g^{-1} , and their M_n and M_w determined by GPC are 3600 – $11,004 \text{ g mol}^{-1}$ and 4700 – $18,639 \text{ g mol}^{-1}$, respectively. PAR-1 has the lowest inherent viscosity. It could be explained that the molecular chain has high symmetry and rigidity, and the movement of oligomer molecular chain is very difficult, which would limit the growth of molecular chain. It is observed that the inherent viscosities of the pho-PARs increase with increasing the content of BCPPO. A reasonable explanation is that the symmetry of the backbone decrease due to the bulky pendent phenyl of monomer, which leads to the reduction of interaction and the increase of chain space among the molecular chains. This would be beneficial to the dissolution of polymer in the solvents and the movement of oligomers, which can be confirmed by the test of the qualitative solubility. Therefore, introduction BCPPO would be beneficial to the growth of the chain. Nevertheless, the maximum value of molecular weight is at the molar ratio of 0.4 (PAR-3) among PAR-3–PAR-6. This may be caused that the bulky pendent benzene rings in the main chains raise the steric hindrance, which would limits the growth of the chain.

Properties of Polymers

The Qualitative Solubility. The qualitative solubility of PARs was studied in various solvents, and the results are summarized in Table II. PAR-1 reveals a relatively poor solubility, because of its closely packed and stiff structures. With the increase of the content of BCPPO, the solubility of the pho-PARs improves obviously. The pho-PARs are soluble in a wide range of organic solvents such as toluene, CHCl_3 , dichloromethane (CH_2Cl_2), THF, Py, NMP, and DMF at room temperature or higher temperature. However, all polymers are insoluble in methanol. Their high solubility is attributed to the loss of packed structures. The introduction of bulky pendent phenyl in the repeating unit plays an important role in increasing free volume of

Table II. Solubility Parameters of PARs

Polymer code ^a	$\delta_{\text{mh}}^{\text{b}}$ ($\text{cal} \cdot \text{cm}^{-3}$) ^{1/2}	$\delta_{\text{ml}}^{\text{c}}$ ($\text{cal} \cdot \text{cm}^{-3}$) ^{1/2}	$\delta_{\text{p}}^{\text{d}}$ ($\text{cal} \cdot \text{cm}^{-3}$) ^{1/2}
PAR-1 ^e	–	–	–
PAR-2	11.86	9.04	10.45
PAR-3	12.13	9.07	10.60
PAR-4	12.24	9.13	10.69
PAR-5	12.37	9.12	10.75
PAR-6	12.43	9.16	10.80

^a Tested by turbidimeter.

^b δ_{mh} : Upper limit of the solubility parameter.

^c δ_{ml} : Lower limit of solubility parameter.

^d δ_{p} : Solubility parameter of polymer.

^e No the data of PAR-1 because it cannot dissolve in TCE.

Table III. Qualitative Solubility of PARs

Polymer code ^a	Solvents ^b /solubility parameter										
	CCl ₄ 8.6	C ₇ H ₈ 8.9	CHCl ₃ 9.3	CH ₂ Cl ₂ 9.7	THF 9.1	Acetone 9.9	Py 10.7	NMP 11.3	DMF 12.1	DMSO 14.5	CH ₃ OH 14.5
PAR-1	--	--	--	--	--	--	--	--	--	--	--
PAR-2	--	++	--	++	--	--	++	++	++	+-	--
PAR-3	--	++	++	++	++	--	++	++	++	+-	--
PAR-4	--	++	++	++	++	--	++	++	++	+-	--
PAR-5	--	++	++	++	++	--	++	++	++	+-	--
PAR-6	--	++	++	++	++	--	++	++	++	+-	--

^aQualitative solubility was determined by using 10 mg sample in 1 mL of solvent. ++, soluble in a short time at room temperature; +t, soluble in a long time at room temperature; +h, soluble on heating; +-, partial soluble or swelling on heating; --, insoluble on heating.

^bSolvent: THF, tetrahydrofuran; Py, pyridine; NMP, N-methyl-2-pyrrolidone; DMF, N,N-dimethyl formamide; DMSO, dimethyl sulfoxide; MeOH, methanol.

the polymer chains and decreasing the packing density so as to allow much solvent to diffuse in. The excellent solubility made these polymers able to process into products by cast, spin- or dip-coating.

In order to further substantiate the effect of the introduction of BCPPO on the solubility of the pho-PARs, the solubility parameters of the pho-PARs were tested by turbidity and the results are shown in Table III. The pho-PARs have solubility parameters in the range of 10.45–10.80 (cal cm⁻³)^{1/2} and the lower limit δ_{ml} is 9.04 (cal cm⁻³)^{1/2}, the upper limit δ_{mh} is 12.43 (cal cm⁻³)^{1/2}. Therefore, they can dissolve in the solvents, with the soluble solubility parameters from 9.04 to 12.43 (cal cm⁻³)^{1/2}, which corresponds to the result of solubility test (Table III).

Aggregation Structure. The DSC curves of the polymers are shown in Figure 4. The semicrystalline PAR-1 shows an obvious melting endothermic peak at 368°C, while PAR-2 reveals an endothermic peak at 290°C. However, the other pho-PARs have

no melting endothermic peaks up to 370°C in the DSC heating curves and belong to the amorphous polymers, indicating the introduction of BCPPO to the molecular chain can decrease the crystallization ability and result in dropping the melting temperature of PAR-2.

The crystallization behaviors of the polymers were also evaluated by wide-angle X-ray diffraction (WAXD). The WAXD patterns of the PARs at room temperature are shown in Figure 5. It is found that PAR-1 and PAR-2 show strong diffractions at 16.0° and 19.2° while PAR-3–PAR-6 have very broad diffraction in their WAXD patterns. This indicates that PAR-1 and PAR-2 have typical crystal structure and PAR-3–PAR-6 are amorphous, which is consistent with the DSC analysis.

Thermal Properties. The thermal properties of PARs were evaluated by means of DMA and TGA. The results are listed in Table IV.

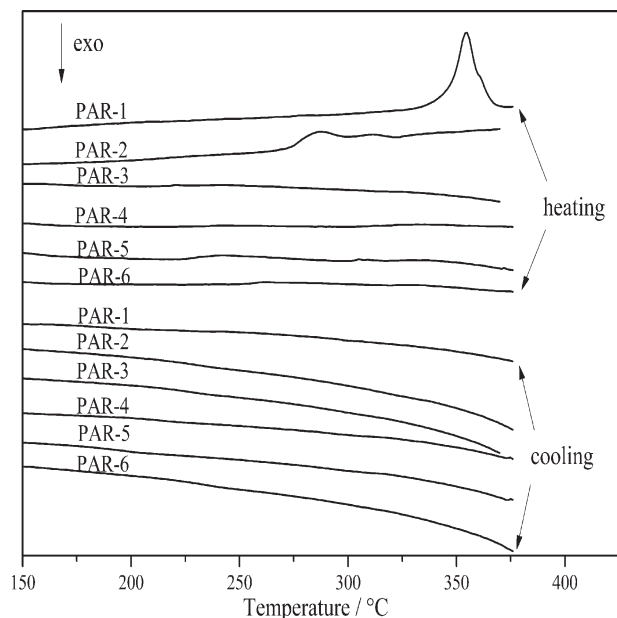


Figure 4. The DSC curves for PARs.

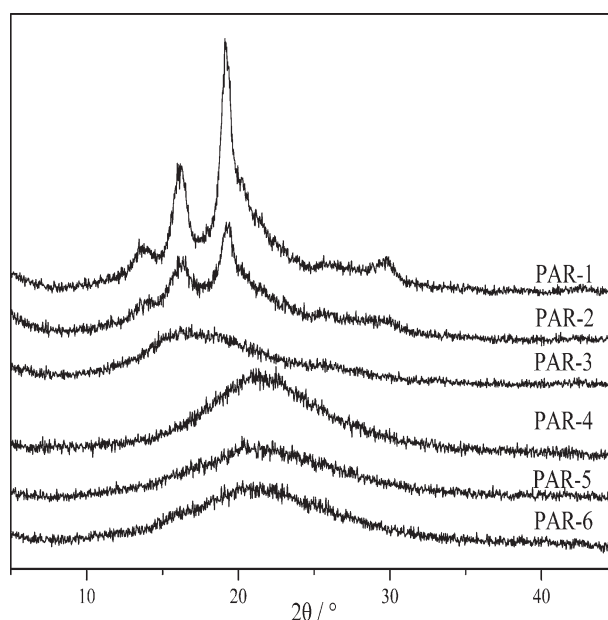


Figure 5. The WAXD patterns of PARs.

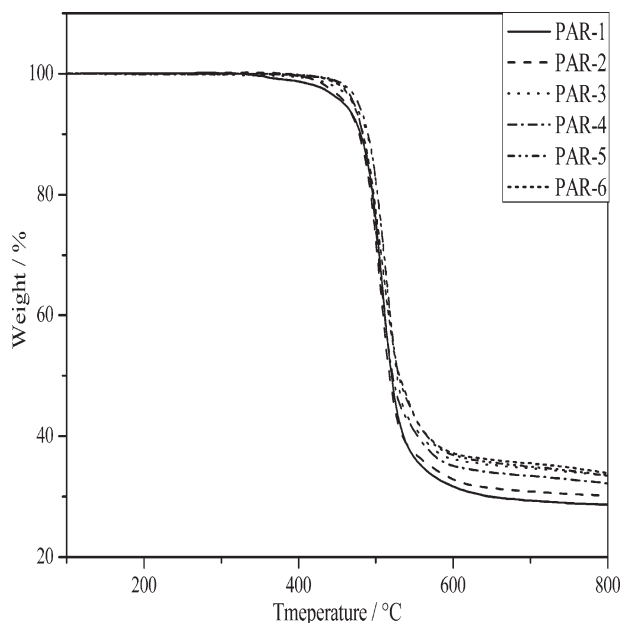
Table IV. Thermal Properties Data of PARs

Polymer code	T_g^a (°C)	$\tan \delta$	T_{id}^b (°C)	T_{md}^c (°C)	Char Yield ^d (%)
PAR-1 ^e	-	-	458	492.3	28.7
PAR-2 ^e	-	-	460	495.0	30.1
PAR-3	243.0	1.29	469	503.0	33.0
PAR-4	251.9	1.71	471	490.0	32.0
PAR-5	258.3	2.61	473	498.9	32.8
PAR-6	260.4	2.87	470	494.6	33.0

^aTested by DMA.^b5% weight loss temperature.^cMaximal rate of weight loss temperature.^dResidual weight percentage at 800°C.^eNo T_g data of PAR-1 and PAR-2 because they cannot dissolve in CHCl_3 to make the films.

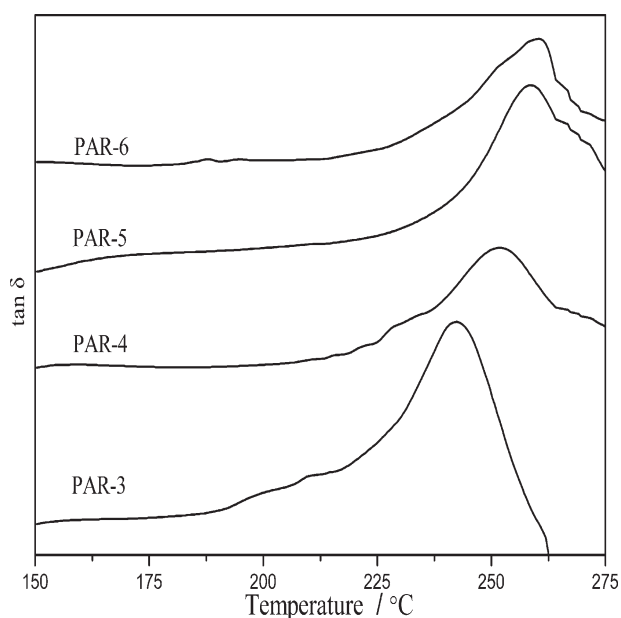
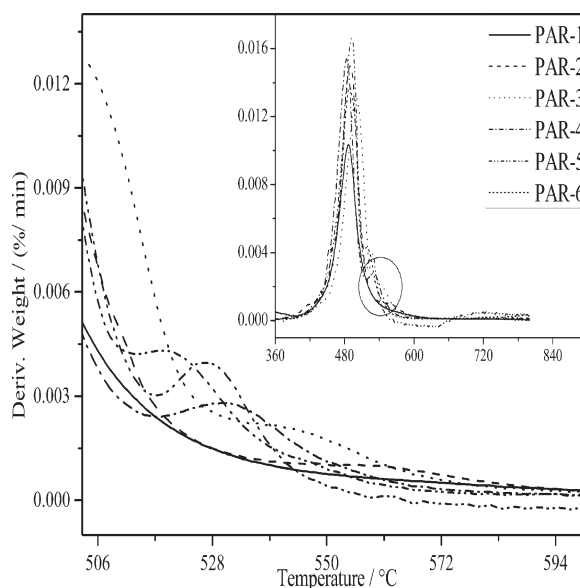
The peak of $\tan \delta$ was identified as the glass transition temperature (T_g) of polymer, because a great decrease in storage modulus (G') occurred at this point. The T_g values of PAR-3–PAR-6 are 243.0, 251.9, 258.3, and 260.4°C (Figure 6), respectively, indicating that the heat resistance of the pho-PARs can be promoted with the increase of BCPPO. A reasonable explanation is that the introduction of bulky pendent phenyl in the repeating unit is conducive to reducing the movement ability of the molecular chain.

Thermal stabilities of these polyarylates were evaluated by TGA under nitrogen atmosphere shown in Figure 7. The different shapes of DTG curves in nitrogen environment result from that the thermal decomposition mechanisms of PARs are changed by the introduction of BCPPO (Figure 8). PAR-1 has a initial thermal degradation temperature (T_{id}) of 458°C, while the T_{id} of the pho-PARs increase from 460 to 473°C and the char yield at

**Figure 7.** The TGA curves of PARs.

800°C ranges from 28.7% to 33.0% with the increase of BCPPO in the repeating unit, suggesting the introduction of the BCPPO can improve the thermal stability.

For a better understanding, the thermal decomposition behavior of the proposed polymers was monitored by FT-IR. Figure 9 shows the FTIR spectra of the volatile gases of PAR-1 and PAR-5 at their respective maximal rate of weight loss temperature (T_{md}) in nitrogen atmosphere. The volatile gases analysis for PAR-1 exhibited characteristics bands of the carbon dioxide around 2349 cm^{-1} ($\text{O}=\text{C}=\text{O}$), ester absorption band around 1756 cm^{-1} (ester $\text{C}=\text{O}$), 1261 and 1172 cm^{-1} (ester $\text{C}-\text{O}-\text{C}$).

**Figure 6.** DMA curves of PARs.**Figure 8.** The DTG curves of PARs.

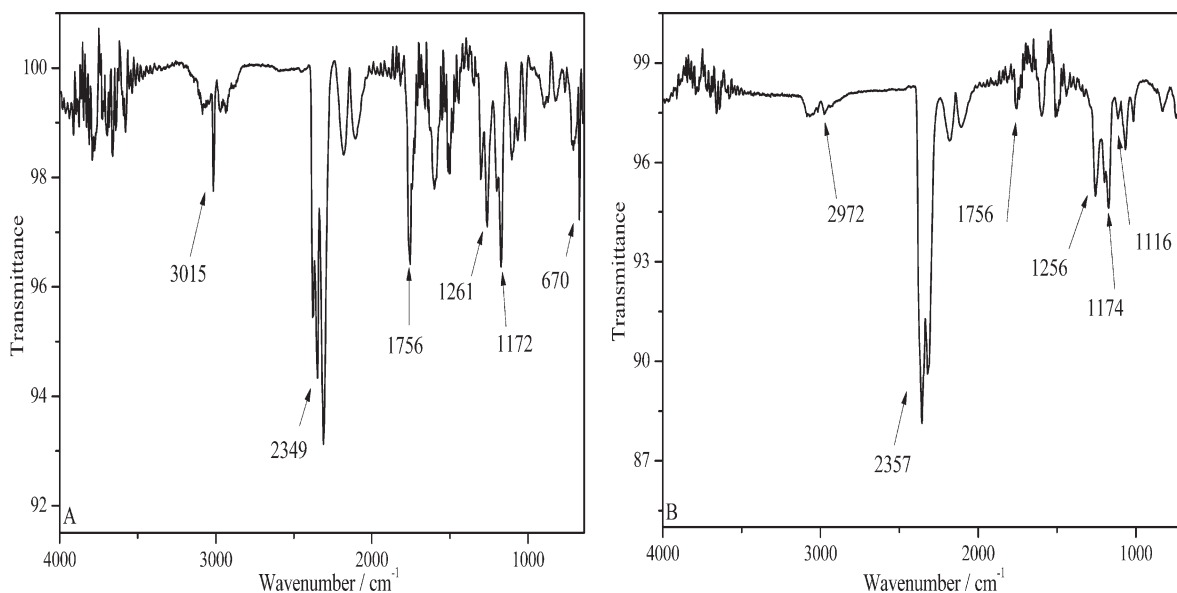


Figure 9. The volatile gases spectra measured by TG-FTIR for (A) PAR-1 and (B) PAR-5.

The volatile gases analysis of PAR-5 exhibited characteristics bands of the carbon dioxide around 2357 cm^{-1} ($\text{O}=\text{C}=\text{O}$), ester absorption band around 1756 cm^{-1} (ester $\text{C}=\text{O}$), 1256 and 1174 cm^{-1} (ester $\text{C}-\text{O}-\text{C}$), and the absorption around 1116 cm^{-1} ($\text{P}=\text{O}$), suggesting the phosphorus exist in gas phase. It is believed that phosphorus-containing compounds can quench flammable particles like $\text{H}\cdot$ or $\text{OH}\cdot$ and reduce the energy of the flame in the gas phase.²³ After heating the samples up to 460, 490, and 520°C , respectively, the FT-IR spectra of the residues of PAR-1 and PAR-5 are displayed in Figure 9. In Figure 10(A), with the temperature increasing, there is no appearance of new peak, and only the signals of the characteristic absorption become weaker. The decrease in intensity of the ester absorption bands (ester $\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$), the aromatic absorption bands ($\text{C}=\text{C}$), associated with the decomposition of

the macromolecule can be observed. So the thermal decomposition of PAR-1 is just the chain scission. Figure 10(B) shows the FT-IR spectra of the residues of PAR-5. During heating process, it is found that a new absorption band of 1630 cm^{-1} is observed in FT-IR spectrum (a) at 460°C (T_{id}), which is attributable to the carbonyl absorption ($\text{C}=\text{O}$) of the associated diaryketones.²⁴

This suggests the existence of BCPPO changes the decomposition model of the pho-PARs. When the treatment temperature rises to 490°C (T_{md}), the intensity of ester absorption band is decreased sharply. A new FT-IR peak appears at 920 cm^{-1} , which is attributed to the absorption of $\text{P}-\text{O}-\text{P}$. The FT-IR spectra confirm that both $\text{P}-\text{O}-\text{P}$ and $\text{P}=\text{O}$ structural groups are present in charred layers, which suggests the existence of

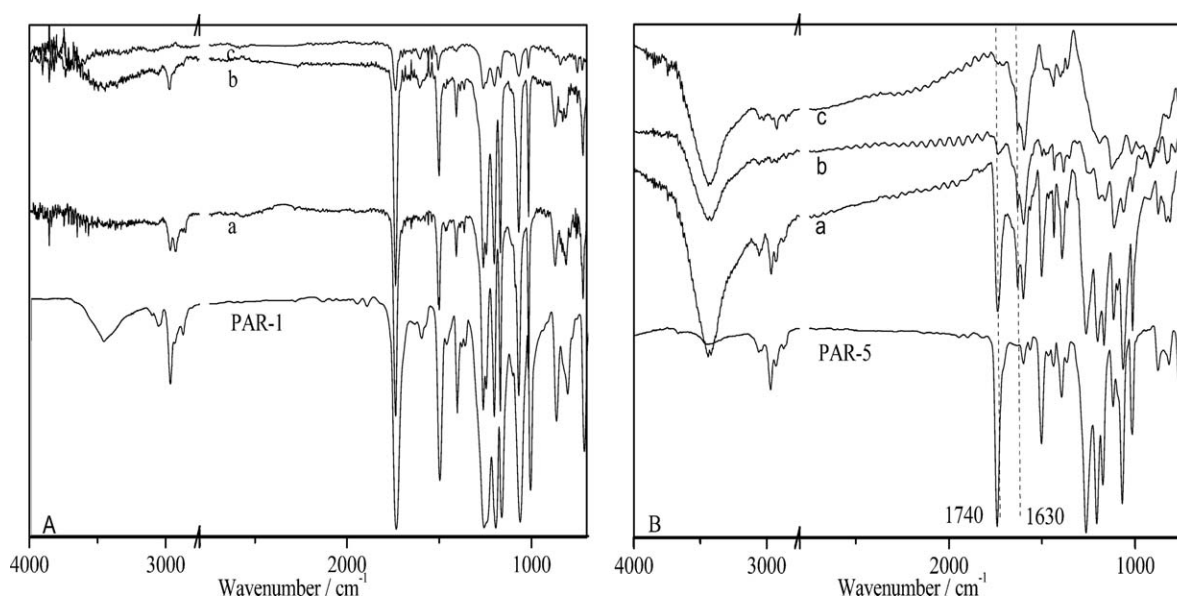


Figure 10. The FT-IR spectra of residues of (A) PAR-1 and (B) PAR-5 heated to various temperatures (a: 460°C , b: 490°C , c: 520°C).

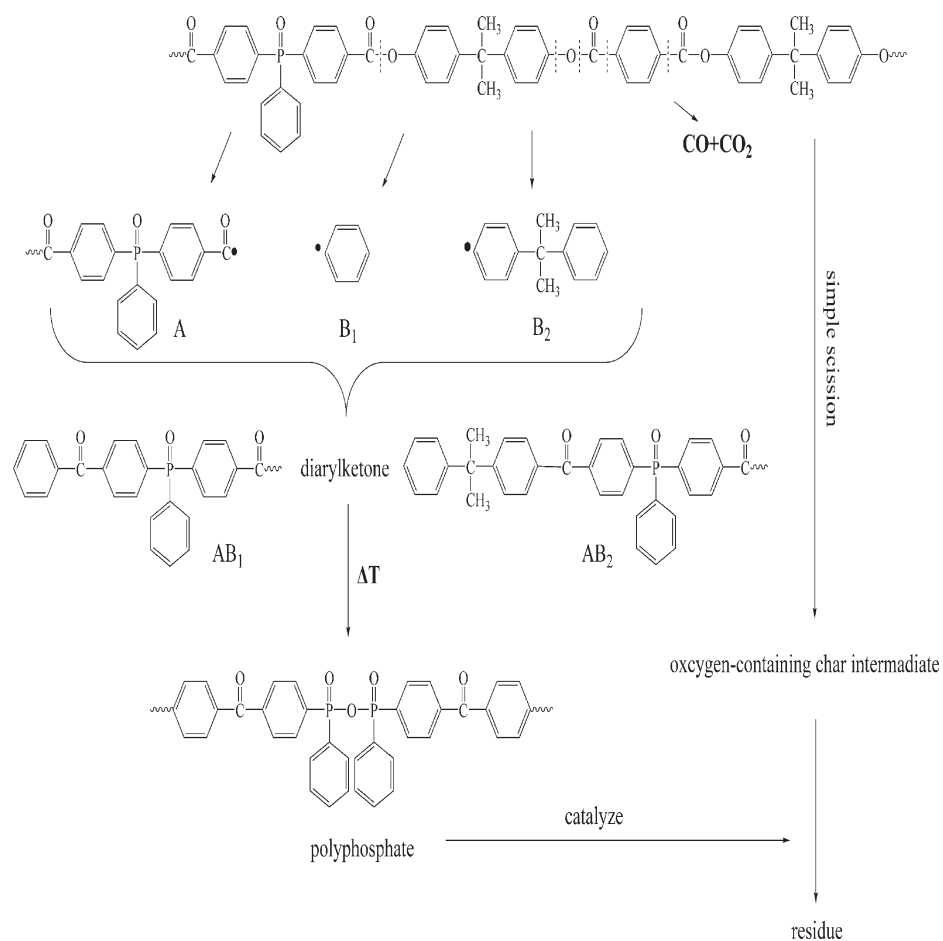


Figure 11. Possible decomposition mechanisms of the pho-PARs.

polyphosphate. With the increasing of temperature, the aliphatic hydrocarbons (C—H) can be observed, which indicates the BPA structure is still in the solid residue. The ester absorption band around 1740, 1260, and 1170 cm^{-1} (ester, C=O, and C—O—C) and the absorption around 1116 cm^{-1} (P=O) disappear at 520°C, which corresponds to the 60% weight loss. However, the absorptions around 1128 cm^{-1} (P—C—O) and 920 cm^{-1} (P—O—P) could be observed. The signal of P—O—P and P—C—O suggest phosphorus still be in residue.

Possible Decomposition Mechanism. Based on the characteristics of the decomposition processes (decomposition temperature, volatile gases, and residue structure), the possible decomposition mechanism of the pho-PARs is illustrated in Figure 11. Generally, the high temperature decomposition products of polymer containing phosphorus are triarylphosphine and TPO.²⁵ At the decomposition temperature, the radicals containing TPO structure would react with the radicals from the decomposition of molecular chain to form diarylketone compounds, which have the better thermal stability. With the increase of temperature, the diarylketone compounds containing phosphorus produces polyphosphate. The phosphonate units would more efficiently promote char formation in the oxygen-containing polymers. The FT-IR spectrum of the residue confirms the existence of polyphosphate and the oxygen-containing

char intermediate, which jointly form the high char containing phosphorus.^{24–26} Therefore, increasing the content of the BCPPO has good effect on improving the thermal stability.

Flame Retardance. In the degradation of polymers, phosphorus promotes the formation of the char, which serves as a protective layer and prevents the transfer of combustible gases to the surface of the materials, thus increasing the flame retardance of the pho-PARs. So the LOI value of pho-PAR increases from 30.7% to 34.5% with the increase of content of BCPPO (Figure 12), which demonstrates that the pho-PARs have very good flame retardance and all belong to flame retardant materials.

The Tensile Mechanical Properties of PAR Films. The tensile properties of these films are also summarized in Table V. These PAR films have tensile strengths of 30.57–57.54 MPa, elongations to break of 2.59–12.61%. With the increase of content of BCPPO in repeating units, the tensile strengths and elongations reduced gradually. A reasonable explanation is that introducing BCPPO in the molecular chain, the space of the polymer increases and the interaction of chains reduces, which would cause the tensile strengths and elongation decrease. Another possible reason is that the tensile strengths reduce with the decrease of the pho-PARs' molecular weight. The elongation

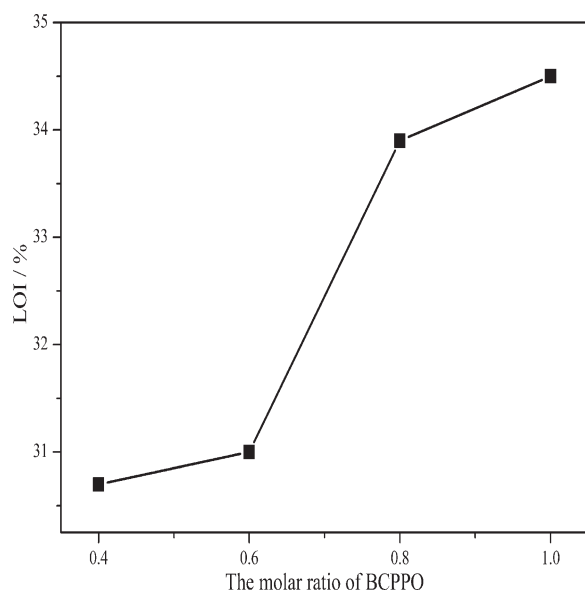


Figure 12. The LOI values of the pho-PARs.

reduces because the bulky pendent phenyl limits the movement of the molecular chain.

CONCLUSIONS

A series of novel polyarylates were synthesized from BPA with BCPPO and TPA. The results show that the polyarylates with the content of BCPPO above 20% have good solubility, and are readily soluble in a wide range of organic solvents inasmuch as the introduction of bulky pendent phenyl, which is able to increase the free volume in the polymer chains and decrease the packing density so as to allow much solvent to come in. Furthermore, these readily soluble PARs can prepare tough and transparent films. Moreover, the bulky phenyls and phosphorus improve the thermal stability, the glass transition temperatures of the phosphorus containing polyarylates range from 243.0 to 260.4°C, which suggest the pho-PARs have good heat resistance. It is believed that phosphorus not only act in the gas phase but also in the solid phase. Therefore, the formed phosphorus-rich residues serve as a protective layer to flame. LOI values are 30.7–34.5%, indicating that pho-PARs have very good flame retardance and all

Table V. Tensile Properties of the pho-PARs Films

Polymer code	Tensile strengths (MPa)	Elongation to break (%)
PAR-1 ^a	–	–
PAR-2 ^a	–	–
PAR-3	57.54	12.61
PAR-4	45.99	11.3
PAR-5	36.91	3.22
PAR-6	30.57	2.59

^aNo the data of PAR-1 and PAR-2 because they cannot dissolve in CHCl₃ to make the films.

belong to flame retardant material. Above all, it follows that the introduction of BCPPO in the repeating unit can significantly improve both the solubility and thermal stability of pho-PARs, which can be applied under tougher environments.

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