Thermal-resistantand Soluble Copoly(Phenyl-s-triazine)s Containing both Diphenylfluorene and Phthalazinone Units in Backbones

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Abstract   A series of novel copoly(phenyl-s-triazine)s were prepared by solution polycondensation of 2,4-bis(4-fluorophenyl)-6-phenyl-1,3,5-s-triazine (BFPT) with 9,9-bis(4-hydroxyphenyl)fluorine (BHF) and 4-(4-hydroxylphenyl)(2*H*)-phthalazin-1-one (HHPZ) to investigate the effects of bulky diphenylfluorene units on solubility as well as thermal and mechanical properties.Moreover, the introduction of diphenylfluorenemoieties in the main chains leads to the outstanding modification in the solubility of the copolymers in common organic solvents, such as chloroform, chlorobenzene (CB) and*N*-methylpyrrolidone (NMP). Simultaneously, the copolymers exhibitremarkable dimensional stability as evidenced by DMA, and maintain excellent thermal properties with glass transition temperatures (T_gs) ranging from 307℃ to 340℃, 5% mass-loss temperatures lying between 525℃ and 551℃, and char yieldsat 800℃ higher than 55% in N_2. Their solubility increaseswith the increase of diphenylfluorene content in the polymer backbone,whereas the thermal properties decrease slightly. The films obtained via solution casting technologypossesscommendable mechanical properties, even at elevated temperatures.
Keywords: Poly(phenyl-s-triazine)s,Diphenylfluorene,Phthalazinone, Solubility, Thermal stability

Introduction

Poly(arylene ether)s (PAEs) is one of the most important classes of high-performance polymers that have attracted much attention in recent years. These materials can be used as structural materials in automotive, aerospace, microelectronic industries[1-6] and polymer electrolyte membrane fuel cells[7-11]for possessing a combination of interesting properties, such as excellent mechanical strength perunitweight, highly thermal stability and good insulating properties.

In the research of PAEs, thePAEsbearing rigid phenyl-s-triazine rings (PAEPs)in the main chain are particularly valuable, for example, as thin membranes forfuel cells[12, 13]and matrix resins for advanced composites[14, 15], especially at elevated temperature applications, due to the merits brought bythe high resonance energy of the phenyl-s-triazine units. Simultaneously, the high electron affinity and structural symmetry of the phenyl-s-triazine units in favor of electron injection and transport encouraged the researchers to explore their application in electroluminescent devices [16-18]. However, the plane-structural characteristic of phenyl-s-triazine units, in general, has limited solubility in common organic solvents, even with the incorporation of flexible ether linkages[18]. Additionally, gels always take place in the later stage of their polymerization. Thus, the high molecular weights of poly(aryl ether phenyl-s-triazine)s were hardly attained.

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As known, most high performance polymers composed of rigid rod-like main chain are extremely difficult to be dissolved in normal organic solvents or hardly to be melt processed due to their highly rigid molecular structure.Incorporating heterocyclic structure into the main chain has been proved to be an effective approach to promote the comprehensive properties of PAEs[19-24], especially mechanical properties and thermal stability with improving the solubility for some kinds of polymers with the large bulky heterocyclic structure in polymer backbone.

Diphenylfluorene is a bulky moiety. Bae and coworkers[25] estimated its approximate molecular size via semiempirical molecular orbital calculation. The plane of the hydroxyphenyl units runs vertically rather than horizontally to the fluorene plane in 3D (Fig. 1). As a result, the polymers containing diphenylfluorene units were generally soluble in most of solvents[26-28], while maintaining the thermal stabilities[29].To the best of our knowledge, there is little research on introducing diphenylfluorenemoieties into the backbone of poly(aryl ether phenyl-s-triazine)s.

In this paper, we describe the synthesis of novel polymeric phenyl-s-triazines containing diphenylfluorene and phthalazinone moieties. The effects of the introduction of diphenylfluorenemoieties on the solubility, thermal and mechanical properties as well as crystallinityof the copolymers were investigated in details. Additionally, several factors that would affect the molecular weight of the polymers were also discussed.

Polymer synthesis

PAEPs could be readily derived from a step-growth solution polycondensation of the BFPT, HHPZ and BHF, as Fig. 1 shows. The fluorine in BFPT monomer towards the S_{NAr} reaction was activated by the electron withdrawing group s-trizaine unit. NMP was chosen as the reaction solvent because it isa favorablereaction mediate for the synthesis of phenyl-s-triazine containing polymers with adequate solubility and reaction temperature. A one-step feed methodwas adopted, that is HHPZ, BHF and BFPT were added into reaction flask together. The synthetic details along with polymeric results for PAEPs are summarized in Table1.Several sets of tests including FT-IR, NMR and elemental analysiswere carried out to investigate the chemical structure of the copolymers obtained.The results are consistent with the exact nature of polymer structure.
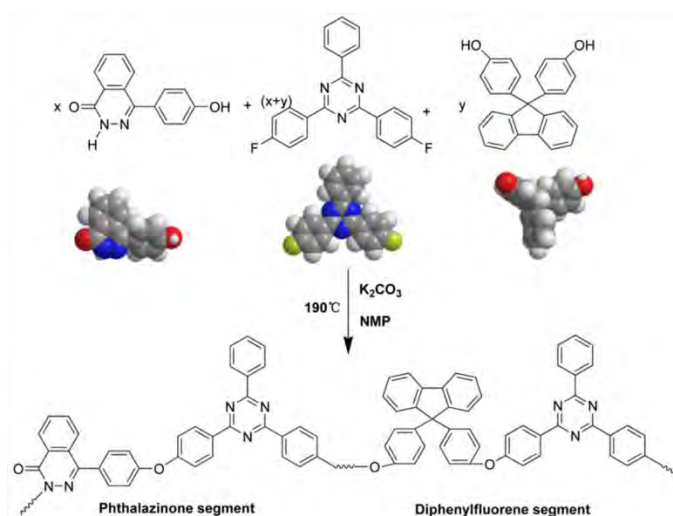

Fig. 1 Synthesis of PAEPs via a step-growth solution polycondensation and 3D structural patterns of the monomers used.

Table 1 Synthetic condition, inherent viscosity and molar masses of PAEPs.

Polymer	Composition HHPZ/BHF	Reaction time(h)	η_{inh}(dL/g)^a	$M_n{}^b$	PD^b	Yield(%)

PAEP1000	100/0	5.0	1.35[c]	-[d]	-[d]	90
PAEP7525	75/25	7.0	0.60	22,800	2.7	93
PAEP5050	50/50	7.0	0.67	38,400	2.7	94
PAEP2575	25/75	7.0	0.91	38,600	3.4	95
PAEP0100	0/100	6.0	1.17	43,000	2.2	95

[a] Inherent viscosity of PAEPs was determined at a concentration of 0.5 g/dL in NMP at 25℃.

[b] Number-average molar mass (M_n) and polydispersity (PD) of PAEPs was measured by GPC in NMP calibrated with polystyrene standards.

[c] Inherent viscosity of PAEP1000 was determined at a concentration of 0.5 g/dL in concentrated sulfuric at 25℃.

[d] Number-average molar mass and polydispersity of PAEP1000 could not be detected by GPC.

The polymers exhibit reasonable solubility in several aprotic solvents at ambient temperature, such as NMP, chlorobenzene, $C_2H_2Cl_4$ andchloroform, when the fraction of diphenylfluorene segments in polymer backbone is higher than 50 percent. In poly(aryl 1,3,5-trazine)s system, diphenylfluorene segments possessing bulky volume in space were incorporated into polymer backbone for increasing the free volume of polymer chains to a higher degree. The increasing steric congestion between macromolecular chains makes solvent molecules diffuse into more easily, eventually resulting in a visible modification of the solubility. The desirable solubility behavior of PAEPs will undoubtedly facilitate the syntheticprocess of polymers under milder conditions and broaden the application of the polymers in coating and film fields.

Polymer thermal property

The glass transition temperatures (T_gs) of the polymerswere detected by differential scanning calorimetry (DSC, Fig. 2) and dynamic mechanical analysis (DMA, Fig. 3). As Fig. 2 depicts, a clear glass transition is found at 307, 312, 324, 328 and 340℃for PAEP0100-PAEP1000, respectively. T_g values of the copolymers decrease with the diphenylfluorene contents increase in polymer backbone.This phenomenon could be attributed to the introduction of diphenylfluorene units, enlarging the intermolecular free volume,in turn to causing the polymer chains much easier to move, and finally leading to a decrease in T_g value. Moreover, the T_gs of all the polymers surpass 307℃, higher than (60-70℃) those of reported phenyl-1,3,5,-triazine polymers (T_g=240-255℃), implying the outstanding thermal properties of the copolymers.
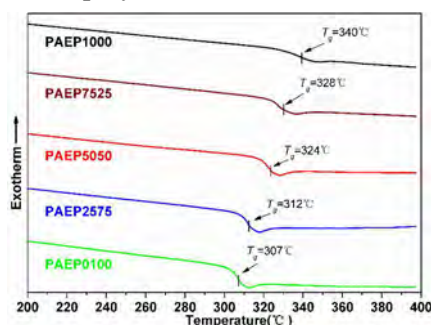

Fig.2 DSC traces of PAEPs.

The glass transition temperatures of polymers were also detected on thin film samples by dynamic mechanical analysis (DMA), which described the transition via detecting relaxation of molecular motion (Fig. 3).In Fig. 3, the maximum tan δvalues of the films represent the appearance of the glass transition at 328℃, 337℃,348℃,360℃ for PAEP 0100-PAEP7525, respectively, indicating that the copolymers possesscommendable dimensional stability at elevated temperature as well.
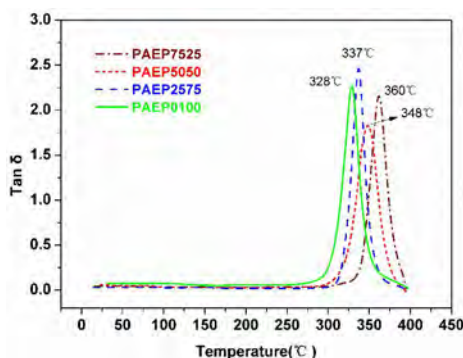
Fig. 3 Tan δ traces of PAEP films.

The thermal stabilities of the polymers were evaluated using thermogravimetric analysis (TGA)as shown in Fig. 4. The polymers are stable before 500℃under nitrogen atmosphere. They retain 95% weight at 499-580℃ and 90% weight at 538-590℃ in N_2, respectively. PAEP0100 containing no fraction of phthalazinone reveals a superior performance of thermal stability with the weight retention at 95% higher than 580℃. The char yields of all polymers obtained aregreater than 55%, suggesting that phenyl-s-triazine units endow PAEPs with a more stable polymer backbone. The5% mass loss temperatures decrease and the C_y values at 800℃increase with the increase of the fraction of phthalazinoneunits in the main chain. The nitrogen atoms of phthalazinone and phenyl-s-triazine units lead to high C_y values.
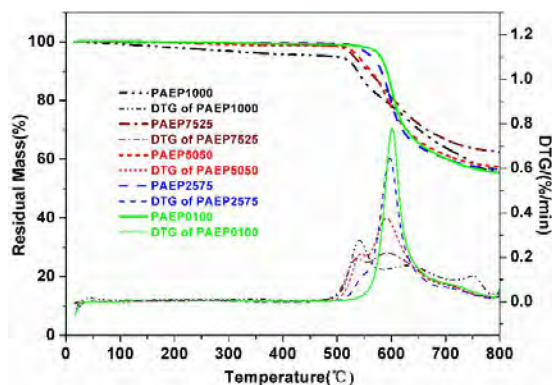

Fig.4TGA and DTG thermograms of the PAEPs.

Polymer mechanical property

The mechanical properties of PAEP7525 to PAEP0100 films were tested by tensile measurement at the stretching speed of 2 mm/min, as shown in Table 2. The samples have tensile stress at maximum load of 73-112 MPa, tensile moduli of 1.8-2.4 GPa, and elongation at break of 6% to 8%at room temperature, respectively. Furthermore, film samples were treated in ovenunder air atmosphereat 150℃ and 250℃ for 4h, respectively, followed by investigating their residual mechanical properties. As evidenced in Table 4, all the film specimens treated at 150℃ for 4 h exhibit better tensile strength. However, when treated at 250℃, their tensile strengths exhibit a slightly decrease. The results indicate that the PAEPs materials have good mechanical properties, especially at elevated temperatures, indicating their excellent thermal stabilities.

Table 2 Mechanical properties of PAEPs[a].

Polymer	Tensile Strength/MPa			Elongation at break (%)			Tensile Modulus/GPa		
	A	B	C	A	B	C	A	B	C
PAEP7525	84	89	53	6	8	4	2.0	2.2	1.9
PAEP5050	73	84	64	6	6	6	1.8	2.0	1.6
PAEP2575	106	118	110	8	9	8	2.1	2.8	2.1
PAEP0100	112	130	112	8	8	6	2.4	2.4	2.3

[a]Key: A: original samples before thermal degradation; B: samples thermally degraded at approximately 150°C for 4 h; C: samples thermally degraded at approximately 250°C for 4 h.

Conclusions

A series of novel organosoluble and thermally stable poly(phthalazinoneether 1,3,5-triazine)s were prepared by the polymerization reaction of BFPTwith BHF and HHPZ. The obtained random copolymers were characterized by FT-IR and NMR for convincing their accurate structure. Diphenylfluorene units in polymer main chain have brought aboutan improvement on solubility while maintaining desirable thermal properties. The copolymers with more than 50% content of diphenylfluoreneaugmentscould be dissolved in chloroform and NMP at room temperature. Thus,they could be readily processed from solution to derive flexible transparent films. Their films havecommendable mechanical properties at both room and elevated temperatures. All the polymers possess excellent thermal properties with high T_gs, decomposition temperatures and C_y values in comparison with previously reported analogues. Combining all the above merits suggests a good application of the resulting PAEPs for processable and heat-resistant structural materials.

Acknowledgements

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