

Synthesis of Novel Poly(arylene ether)s Bearing Phthalazinone and Aryl-s-triazine in the Main Chain

Jianyan Wang^{a,b} (王锦艳), Cheng Liu^a, Guipeng Yu^a, Xigao Jian^{a,b*} (蹇锡高)

^aDepartment of Polymer Science & Materials, Dalian University of Technology (大连理工大学)

^bLiaoning Province Engineering Center of High Performance Resins, Dalian 116012, China

ABSTRACT: Phenyl-s-triazine-based polymers are well-known for their outstanding comprehensive properties including excellent thermal stability, high strength and modulus, good flame retardance and chemical resistance, unique electronic and optical properties. However, they always exhibit high melt temperatures and poor solubility. Therefore, it is rather difficult to process this type of thermally stable polymers, which hamper their widespread application as insulating coatings, adhesives and membranes. This paper reported the novel poly(aryl ether phenyl-s-triazine)s containing phthalazinone and Aryl-s-triazine in the main chain by a solution nucleophilic polycondensation polymerization. The obtained polymers are amorphous and readily resolve in NMP and DMAc at room temperature. The incorporation of sulfone or phthalazinone moieties into the polymer backbone is more effective in improving the overall solubility than that of meta-ether linkages. They exhibit high thermal stabilities and oxidative stabilities (T_g s > 241 °C; N₂: $T_{d5\%}$ > 536 °C; Air: $T_{d5\%}$ > 529 °C).

Key words: phthalazinone; Aryl-s-triazine; N–C coupling reaction

1. Introduction

Phenyl-s-triazine-based polymers (PSTs) are well-known for their outstanding comprehensive properties including excellent thermal stability, high strength and modulus, good flame retardance and chemical resistance, unique electronic and optical properties [1–3]. However, they are frequently prepared at extremely high temperatures under super high pressures. In addition, such polymers always exhibit high melt temperatures and poor solubility. Therefore, it is rather difficult to process this type of thermally stable polymers, which hamper their widespread application as insulating coatings, adhesives and membranes. In addition, the synthetic reaction conditions for these PSTs are rigorous since the polymers may crystallize and precipitate from the organic solvent media before the formation of a high-molecular-weight polymer [4]. These problems have initiated a search for soluble PSTs by using structural modification of chain recently, with a view to simplifying synthesis, improving processability and hence broadening their applications, especially adhesives, coatings and membranes. The incorporation of non-linear moieties [5], flexible groups [6], kink [7] or non-coplanar units [8] into the thermally stable polymer backbones has been employed to achieve good solubility in typical organic solvents while maintaining the other unique properties. In this way, our laboratory has disclosed the preparation of poly(ether phenyl-s-triazine)s containing meta-ether linkage, sulfone or phthalazinone segments in the main chain [9]. The obtained amorphous polymers possess improved solubility in polar solvents and show acceptable thermal properties.

2. Experimental

2.1. Materials

* Corresponding author. Tel.: +86-411-83653426; fax: +86-411-83639223.
E-mail address: jian4616@dl.cn (X. Jian).

2-Phenyl-4,6-bi(4-fluorophenyl)-1,3,5-triazine (BFPT) was synthesized according to the procedure reported previously^[4]. The product was obtained as white long thin needles; m.p.: 260.2–260.8 °C; the product was confirmed by MALDI-TOF/MS. GC/MS (M^+ Calcd. as C₂₁H₁₃N₂F₂ 345.1078): m/z 345.1067 (M^+). Hydroquinone (HQ) was purified by sublimation and dried under vacuum before use. Resorcinol (RS) was distilled under reduced pressure and dried under vacuum. 4-(4-Hydroxyphenyl) (2*H*)-phthalazin-1-one (DHPZ) was prepared as white powder by the method reported in Ref.^[9]. The product was obtained as white powder; m.p.: 310.0–310.8 °C; yield: 90 wt%; the product was confirmed by MALDI-TOF/MS. GC/MS (M^+ Calcd. as C₁₄H₁₀O₂N₂ 238.0742): m/z 238.0750 (M^+). 4,4'-Dichlorodiphenyl sulfone (DCS) was purified by recrystallization from isopropanol and dried in a vacuum oven for 24 h. Anhydrous potassium carbonate was ground and dried in vacuum at 100 °C for 24 h before use. Sulfolane was dried and vacuum-distilled over sodium hydroxide pellets. N-methyl-2-pyrrolidone (NMP) was vacuum-distilled over calcium hydride and stored over molecular sieves (type 4Å) before use. Toluene was distilled over calcium hydride under reduced pressure. Unless otherwise specified, all other solvents and reagents were used as received.

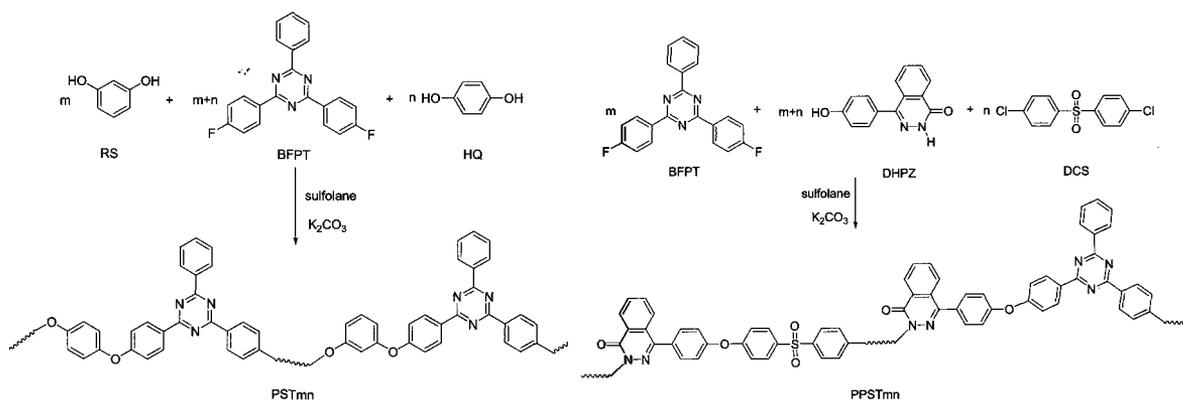
2.2. Instruments

Inherent viscosities (η_{inh}) of the copolymers were measured by Ubbelohde capillary viscometer at a concentration of 0.5 g/dL in *N*-methylpyrrolidone (NMP) or concentrated sulfuric acid at 25 °C according to their solubility. Infrared measurements were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer. ¹H NMR (400 MHz) spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using CDCl₃ or H₂SO₄-*d*₂ as a solvent and the data were listed in parts per million downfield from tetramethylsilane (TMS). Gel permeation chromatography (GPC) analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4×500Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were performed on a Micromass GC-TOF CA 156 MALDI-TOF/MS. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) of the copolymer were performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C/min from 100 to 800 °C. Decomposition temperature (T_d) was taken as the temperature of 5% and 10% weight loss. Temperature for the maximum weight loss rate (T_{max}) in nitrogen was also measured at a heating rate of 20 °C/min. Char yield (C_y) was calculated as the percentage of solid residue after heating from 100 to 800 °C in flowing nitrogen. The glass transition temperature (T_g) was determined with a Mettler DSC822 differential scanning calorimeter in flowing nitrogen at a heating rate of 10 °C/min from 50 to 400 °C. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu Kα radiation (40 V, 100 mA).

2.3. Polymer synthesis

The PSTs copolymers were synthesized via a nucleophilic aromatic substitution (SNAr), as depicted in Scheme 1 and Scheme 2, respectively. The numbers of the sample name indicate the molar fractions of HQ and RS or of BFPT and DCS. For example, the resultant copolymer in the copolymerization starting from 70 mol percents of HQ and 30 mol percents of RS could be labeled as

PST7030. The copolymer starting from 60 mol percents of DCS and 40 mol percents of BFPT could be labeled as PPST64. All copolymers were prepared in similar procedures. Therefore, only the synthesis of PST5050 was given as a typical example. A 100 mL three-necked round-bottomed flask, equipped with a mechanical stirrer, a nitrogen gas inlet tube and an outlet tube, and a Dean–Stark trap was charged with HQ (5.0 mmol), RS (5.0 mmol), K_2CO_3 (excess, 12.0 mmol) and BFPT (10.0 mmol), and rinsed with 2 mL sulfolane and 25 mL toluene. The mixture was stirred and heated at 150 °C for 4 h to dehydrate by azeotroping off with toluene under the protection of nitrogen before the reaction mixture was heated stepwise to 190 °C. During the polymerization, another 2.5 mL sulfolane in batches (0.5 mL each time) was added to dilute the solution when the reaction mixture apparently became extremely viscous. The reaction system was kept at this temperature for 5 h, until the solution viscosity exhibited no obvious increase. Subsequently, the resultant viscous solution was slowly poured into a mixture of distilled water:methanol (500 mL, v:v=1:3) with vigorous stirring to precipitate the copolymer. The crude product was washed six times with hot water to remove inorganic salts. The dried copolymer was further purified by dissolving in NMP and being filtered through a thin layer of celite. The filtrate was then slowly poured into methanol with stirring, and the resulting suspension was filtered. Finally, the purified fibrous product was dried at 120 °C under vacuum for 24 h. The yield of PST55 was 96 wt%. FT-IR (KBr, cm^{-1}): 3066 (w, =C-H), 1589, 1518, 1496 (s, C=N or C=C), 1477, 1445, 1411, 1369 (s, C-N), 1222 (s, C-O), 1142, 859 (w, C-H), 826 (w, γ_{C-H}), 777 (w, γ_{C-H}), 722 (w, γ_{C-H}), 690 (w, δ_{phenyl}). 1H NMR (400 MHz, $H_2SO_4-d_2$, ppm): δ : 8.45–8.92 (m, 12H), 8.22–8.44 (m, 4H), 7.98–8.15 (m, 3H), 7.72–7.89 (m, 3H), 6.99–7.61 (m, 12H). ^{13}C NMR (100 MHz, $H_2SO_4-d_2$, ppm) δ : 172.45, 170.92, 167.98, 164.25, 157.29, 147.12, 141.63, 136.92, 135.98, 130.32, 130.26, 127.31, 124.96, 123.79, 122.65. Elem. Anal. Calcd. for PST5050 ($C_{54}H_{34}N_6O_4$) $_n$ (830.8) $_n$: C, 78.06; H, 4.12; N, 10.11%. Found: C, 78.95; H, 4.09; N, 10.21%.



Scheme 1 Synthetic route of PSTs copolymers. Scheme 2 Synthetic route of PPSTs copolymers

Selected data of PPST64: IR (KBr, cm^{-1}): 3064 (=C-H), 1669 (C=O), 1587, 1502 (C=C or C=N), 1445, 1364 (C-N), 1304 (SO₂, symmetric), 1237 (C-O), 1152 (SO₂, asymmetric), 846, 685 (C-S-C). 1H NMR (400 MHz, $CDCl_3$, ppm) δ : 8.71–8.82 (m, 12H), 8.55 (s, 5H), 8.01–8.03 (d, 12H), 7.92–7.99 (m, 15H), 7.71–7.74 (d, 4H), 7.64–7.66 (d, 10H), 7.46–7.48 (d, 4H), 7.20–7.22 (d, 8H), 7.19–7.20 (d, 10H), 7.11–7.16 (d, 12H), 7.10–7.13 (d, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ : 171.45, 170.75, 161.3, 160.54, 158.78, 157.48, 156.23, 147.93, 147.52, 146.98, 145.80, 145.63, 145.32, 140.19, 139.63, 136.05, 135.69, 134.96, 133.71, 133.43, 132.16, 131.42, 131.14, 129.34, 128.61, 128.17, 126.82, 126.98, 125.43, 120.15, 119.50, 118.59, 118.41. Elem. Anal. Calcd. for PPST64 ($C_{148}H_{90}O_{16}N_{16}S_3$) $_n$ (2442.59) $_n$: C, 73.50; H, 3.60; N, 8.91%. Found: C, 71.27; H, 3.81; N, 8.89%.

3. Results and Discussion

3.1 Polymer Synthesis and Characterization

A new series of PST copolymers with different compositions were prepared via aromatic nucleophilic displacement polycondensation of BFPT with various ratios of HQ and RS (Scheme 1) or of DHPZ and DCS (Scheme 2). In these copolymerization reactions, sulfolane was experimentally more suitable for reaction medium than other polar aprotic solvents, because it allows higher reaction temperatures which is required to maintain solubility of high-viscosity copolymers, and it also effectively solvates the monomers and the polar intermediates formed. The excess base here was used to convert the bisphenols into the more reactive phenolates. Since K_2CO_3 is a weak base, no hydrolytic side reaction with BFPT was observed. The dehydration of bisphenols was promoted by using a minimal amount of toluene to allow azeotropic distillation of the water formed as a byproduct in the reactions. All copolymerization reactions proceeded homogeneously and smoothly in common organic solvents, thus the synthetic conditions for these copolymers are much milder than those for the known poly(arylene ether)s.

Note that the homopolymers prepared by the reactions of BFPT with HQ or RS, respectively, exhibited either low-viscosity or intractable resins under the reaction conditions described above because of their precipitation out directly from the solvent medium in the early stage before the formation of a high-molecular-weight polymer. Expectedly, the intrinsic viscosity (η_{inh}) of PST0100 was up to 0.60 dL/g when the polycondensation time prolonged to 8 h (Table 1) in spite of the lower reactivity of RS compared to that of HQ. The solubility of the PST obtained in the system of BFPT and HQ, RS improved with the increase of RS content in monomer compositions, indicating that the resorcinol-based PST segments are helpful to improve the overall solubility of copolymers in the reaction medium and hence facilitate the generation of truly high molecular-weight polymers.

Table 1 Composition and physical properties of PST copolymers.

Polymers	Composition	Time (h)	η_{inh}^a (dL/g)	Yield (%)	Color
PST0100	HQ/RS: 0/100	8	0.60	94	White
PST1090	HQ/RS: 10/90	6	0.66	95	White
PST3070	HQ/RS: 30/70	6	0.71	95	White
PST5050	HQ/RS: 50/50	5	0.63	94	White
PST7030	HQ/RS: 70/30	5	0.61	93	White
PST9010	HQ/RS: 90/10	4	0.58	94	White
PST1000	HQ/RS: 100/0	4	0.45	94	White
PPEP	DCS/BFPT: 0/100	4	0.57 ^b	98	White
PPST28	DCS/BFPT: 20/80	4.5	0.80	93	White
PPST46	DCS/BFPT: 40/60	5.5	0.62	93	White
PPST55	DCS/BFPT: 50/50	5.5	0.76	93	White
PPST64	DCS/BFPT: 60/40	6	1.18	92	White
PPST82	DCS/BFPT: 80/20	6	0.91	93	White
PPES	DCS/BFPT: 100/0	6	1.21	94	White
PPES	DCS/BFPT: 100/0	14	2.25	95	White

a: Determined at a concentration of 0.5 g/dL in NMP at 25°C.

b: Determined at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25°C

For comparison, poly(phthalazinone ether sulfone) (simplified as PPES) and poly(phthalazinone ether phenyls-triazine) (simplified as PPEP) homopolymers were also prepared in the similar procedures. Although the incorporation of phthalazinone groups into the backbone tends to be effective in improving the overall solubility of the PAEPs to some extent, high-viscosity polymers (exceeding 0.60 dL/g) could hardly be obtained under the described conditions. The intrinsic viscosity (η_{inh}) of the PPES synthesized is 1.21 dL/g, and it significantly increases and reaches a maximum (2.25 dL/g) when the polycondensation time was prolonged to 14 h. In these copolymerizations, sulfolane or dipolar aprotic solvents such as NMP, *N,N*-dimethyl acetamide (DMAc), were experimentally suitable solvents, because they effectively dissolve the monomers, the polar intermediates and the high-molecular-weight polymers formed. Although NMP or DMAc tends to be good solvents and is easier to handle, sulfolane was used in these copolymerization reactions since allowing higher reaction temperatures (e.g., 190 °C, etc) which is required to maintain solubility of the copolymers.

The key structural features of the copolymers synthesized were characterized using instrumental techniques including FTIR, NMR and elemental analysis. As shown in Fig. 1, disappearance of absorptions in the range of 3200–3500 cm^{-1} indicates the complete conversion of O–H or N–H groups. The presence of phenyl-*s*-triazine is identified by the strong absorption bands at around 1589, 1518 cm^{-1} (C=N stretch) and 1369 cm^{-1} (C–N stretch). The absorption bands for Ph–O–Ph linkages appear at around 1222 cm^{-1} , which correlates sufficiently well with the expected structure of the copolymers. In the system of PPST, characteristic stretching bands of sulfone groups appearing at 1304 cm^{-1} (SO₂, symmetric), 1152 cm^{-1} (SO₂, asymmetric) and 685 cm^{-1} (C–S–C), whose intensity increases with the increase of sulfone content, indicate that different content of sulfone group has been introduced into the polymer chain.

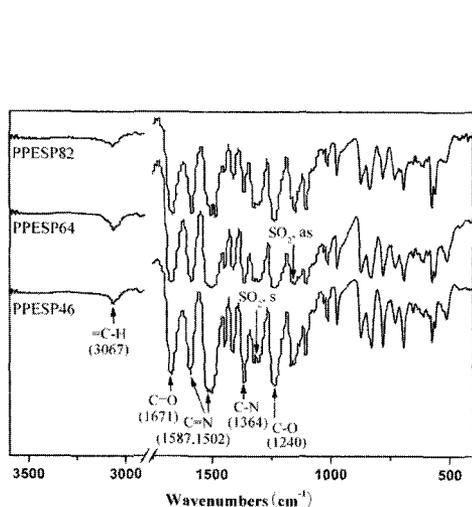


Fig. 1. FTIR spectra of PPST82, PPST64 and PPST46.

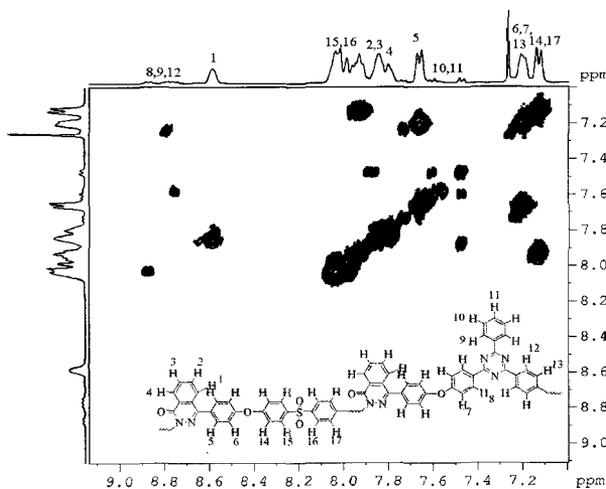


Fig. 2. H–H gcosy NMR spectrum of PPST55 in CDCl₃

As a representative example, H–H gcosy NMR spectrum of PPST55 and the chemical shift assignment of relative hydrogen protons are illustrated in Fig. 2. A comparison of ¹H NMR spectra of several representative copolymers, PPST46, PPST64 and PPST82, are shown in Fig. 3. The characteristic peaks shifting downfield at 8.55 ppm, which can always be used as the reference signal to assign the other atoms, is diagnostic for the presence of ortho-hydrogen (H-1) of lactam in phthalazinone. The presence of phenyl-*s*-triazine in the main chain of copolymers is identified by signals at 8.71–8.82, 7.71–7.74, 7.46–7.48 and 7.20–7.22 ppm. The hydrogen protons (H-8, H-9, H-12)

ortho to s-triazine nuclei appear at high frequencies (8.71–8.82) due to the deshielding ring current effect of the strong electron-withdrawing s-triazine nuclei. The four signals at 8.01–8.03 ppm are ascribed to the aromatic hydrogen protons (H-15, H-16) ortho to sulfone group. In addition, the integration intensity of characteristic peaks of H-15 and H-16 increases while that of H-8, H-9 and H-12 reduces with an increase in the content of sulfone. As shown in Figs. 2 and 3, ^1H NMR spectrum of PPST82 is well distinguished in the region of 7.8–8.2 ppm, whereas the protons in PPST64, PPST55 and PPST46 cannot be separated clearly in the same region, suggesting that the sequences in the latter copolymers are somewhat “short block” or “random”. ^{13}C NMR spectra of the obtained copolymers in CDCl_3 were also found to be in well accordance with their chemical structure. For example, in a representative ^{13}C NMR spectrum of PPST64, the signals for the carbon protons of the lactam carbonyl groups in phthalazinone appear at 158.59 ppm. The presence of phenyl-s-triazine groups is also identified by signals at 171.45 and 170.75 ppm which are assigned to the carbon protons of the s-triazine nuclei. The carbon signals of the s-triazine nuclei appear at high frequencies due to its deshielding ring current effect. ^1H NMR spectrum of PST55 and the chemical shift assignment of relative hydrogen protons are illustrated in Fig. 4. The presence of phenyl-s-triazine in the main chain of the copolymer is identified by signals at 8.45–8.92, 8.22–8.44, 7.98–8.15 and 6.99–7.11 ppm. The signals of hydrogen protons (H-2, H-3) in benzene rings ortho to s-triazine nuclei appear at the highest frequencies, due to the deshielding effect of the strong electro-withdrawing s-triazine nuclei. ^{13}C NMR spectra of the obtained copolymers in CDCl_3 are also found to be in well accordance with their chemical structure.

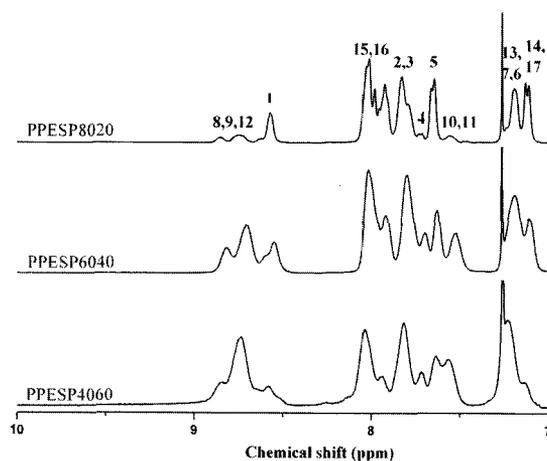


Fig. 3. ^1H NMR spectra of PPST82, PPST64 and PPST46 in CDCl_3 .

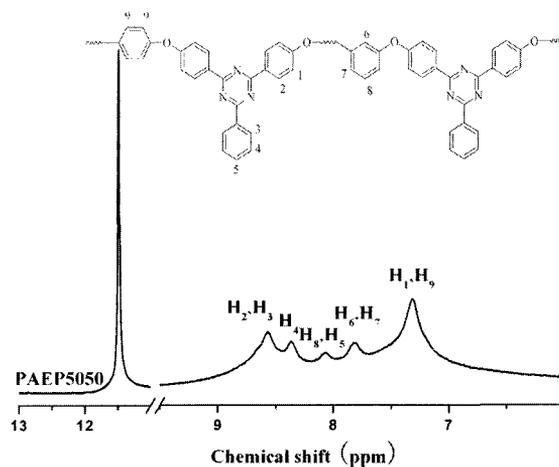


Fig. 4. ^1H NMR spectrum of PST5050 in CDCl_3

3.2. Polymer Properties

The solubility behavior of the resulting copolymers was studied in various organic solvents by dissolving 0.04 g of the polymers in 1 mL solvent (4%, w/v) at different temperatures. As summarized in Table 2, all copolymers are soluble in selected aprotic polar solvents such as N,N-dimethylacetamide (DMAc) and NMP at room temperature. In addition, they can readily resolve in less efficient solvents like N,N-dimethylformamide (DMF) at elevated temperatures except PST7030 and PST9010. All copolymers can be easily cast into films through spin coating or other solution casting techniques. The improved solubility may be resulted from the introduction of multiply meta-ether linkages, or the crank,

twisted non-coplanar phthalazinone and the kinked sulfone moieties into the main chain which cumpers the close packing of the intermolecular chains and enlarges the average intermolecular into the main chain that cumpers the close packing of the intermolecular chains and enlarges the average intermolecular distance of polymers, thus enabling solvent molecules to diffuse easily into the polymer chains. All copolymers can hardly resolve in other common organic solvents including THF, acetone, toluene and sulfolane, even at elevated temperatures (Table 2). This may be attributed to the strong charge transfer interactions between phenyl-s-triazine rings and aromatic rings that hamper solvent molecules to diffuse into the copolymer chains.

Table 2 Solubility of PST and PPST copolymers.

Polymers	Solubility ^a							
	NMP	DMA	DMF	CHCl ₃	CH ₂ Cl ₂	AC	THF	TO
PST0100	++	++	+	—	—	—	—	—
PST1090	++	++	+	—	—	—	—	—
PST3070	++	++	+	—	—	—	—	—
PST5050	++	++	+	—	—	—	—	—
PST7030	++	++	—	—	—	—	—	—
PST9010	+	+	—	—	—	—	—	—
PST1000	—	+	—	—	—	—	—	—
PPEP	++	++	—	—	—	—	—	—
PPST28	++	+—	—	—	—	—	—	—
PPST46	++	++	+	++	—	—	—	—
PPST55	++	++	++	++	+	—	—	—
PPST64	++	++	++	++	+	—	—	—
PPST82	++	++	++	++	++	—	—	—
PPES	++	++	++	++	++	—	—	—

NMP: *N*-methylpyrrolidone; DMAc: *N,N*-dimethyl acetamide; CHCl₃: chloroform; CH₂Cl₂: dichloromethane; AC: acetone; To: toluene; THF: tetrahydrofuran..

a Solubility: ++, soluble in room temperature; +, soluble on heating; —, insoluble.

Thermal properties of the resulting copolymers were determined by applying DSC, TGA and DTG measurements in nitrogen and air atmosphere. The detailed thermal results are summarized in Table 3. The glass transition temperatures of PSTs are recorded in the range of 241 – 305 °C (taking as the midpoint of the change in slope of the baseline in DSC curve), indicating their good heat resistance, and no clear evidence of crystallinity was observed by the DSC measurements in any case. It is apparent that all DSC heating scans reveal only single distinct T_g for each copolymer. The T_g s of PST series are lower than that of PPSTs. The values increase gradually with the decreasing content of meta-ether linkages, or with the increasing sulfone content. The introduction of the multiply meta-ether linkages into the backbone leads to a decrease in polymer chain rigidity, and the introduction of the polar sulfone groups into the backbone leads to an increase in intermolecular chain interactions that hampers the movement of the polymer chains as shown by T_g .

Table 3 Thermal properties of PSTs and PPSTs.

Polymers	T_g ¹⁾ (°C)	T_g ²⁾ (°C)	$T_{5\%}$ ³⁾ (°C)	$T_{10\%}$ ³⁾ (°C)	$T_{5\%}$ ⁴⁾ (°C)	$T_{10\%}$ ⁴⁾ (°C)	T_{max} ⁵⁾ (°C)	C_y ⁶⁾ (%)
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PST0100	241	–	575	594	529	567	602	50
PST1090	241	242	575	595	541	574	603	50
PST3070	242	243	579	596	548	578	604	51
PST5050	244	244	581	599	559	588	604	51
PST7030	247	246	585	603	571	590	607	51
PST9010	248	247	590	605	582	601	609	52
PST1000	249	–	591	608	585	602	609	52
PPEP	269	-	536	563	529	567	536, 617	67
PPESP2080	271	275	519	534	524	544	529, 620	63
PPESP4060	279	282	508	517	517	532	526, 619	60
PPESP5050	283	285	515	526	512	526	526, 617	56
PPESP6040	289	289	513	524	511	522	527	55
PPESP8020	300	297	503	515	509	525	529	53
PPES	305	-	505	512	-	-	527	53

a Glass transition temperature (T_g) tested by DSC.

b T_g calculated from Fox Equation (Formula I).

c Temperature for 5% and 10% mass-loss in nitrogen determined by TGA.

d Temperature for 5% and 10% mass-loss in air determined by TGA.

e Temperature for the maximum in nitrogen determined by DTG.

f Char yield in nitrogen determined by TGA.

g Data according to Ref. [10].

TGA and DTG thermograms of the PST copolymers under nitrogen atmosphere demonstrated excellent thermal and thermo-oxidative stability with no significant weight loss up to temperatures of approximately 520 °C in nitrogen, as shown in Table 3. The 5% weight loss temperatures of the copolymers under nitrogen and air atmosphere determined by TGA are respectively higher than 575 °C and 541 °C. These two values decrease gradually with the increase in RS content in the copolymerization. The temperatures for 5% and 10% mass-loss of the copolymers are higher than 503 °C and 515 °C under nitrogen, respectively. In addition, these two values decrease gradually with the increase in sulfone content except those of PPST46. In case of PPST46, these values are slightly lower than those of the PPST55 and PPST64. This is possibly due to the higher concentration of chain ends of PPST46 relative to the others, as implied by the low inherent viscosity and M_n . Among the investigated copolymers, highest T5% and T10% values are exhibited by PPST28, due to the highest content of the phenyl-s-triazine units that endows the copolymer with the highest resonance energy along the chain. The thermal stability of these copolymers is only a little lower than that of PPEP analogue and much higher than that of the PPES homopolymers, as evidenced by thermogravimetric data listed in Table 3. Therefore, good thermal stability of the copolymers is maintained relative to PPEP with the introduction of the sulfone moieties into the backbone. The copolymers show char yields (Cy) of 53 – 63%, when heated to 800 °C under a nitrogen atmosphere, confirming their excellent thermal stability. The Cy value increases gradually with increase of the content of the phenyl-s-triazine unit in the copolymer chains, most probably due to the phenyl-s-triazine that has higher char concentration than sulfone at the elevated temperatures.

Based on the results as listed in Table 3, it can be concluded that all these synthesized copolymers exhibit high T_g , T5%, T10% and Cy values, thus being extremely thermally stable. The overall thermal

stability increases with the decreasing content of sulfone in the main chain. The high thermal stability of PPESP copolymers will make them as potential high-temperature polymeric materials in a wide range of applications (e.g., high-temperature fuel cells, advanced composites, etc). Further efforts in these aspects are currently underway by our group.

3.3 Polymer Crystallinity

Crystallinity of the copolymers synthesized was investigated by means of wide-angle X-ray diffraction (WAXD) on powder or film samples at room temperature. Fig. 5 illustrates the WAXD patterns of the typical copolymers. The calculated crystallinity degree of the copolymers is almost negligible, and therefore, they are amorphous. Interestingly, four weak diffraction peaks are displayed in the WAXD pattern of PPST28, giving a pattern typical of micro-crystalline nature. In addition, the intensity of these diffraction peaks reduces gradually as the content of sulfone ranges from 20 to 80 mol%, indicating that the presence of sulfone groups hampers the crystallization process. In the system of PST, four weak diffraction peaks ($2\theta=18, 20, 22, 29^\circ$) are displayed in the WAXD pattern of PST9010 film which were annealed at 270°C for 4 h, giving a pattern typical of micro-crystalline nature. In addition, the intensity of these peaks becomes smaller with the increase of meta-ether linkage content in the copolymer backbone. The amorphous nature of most copolymers is also reflected in their good solubility in common organic polar solvents, whereas the PPST28 with highest crystallinity exhibits worse solubility than others. Therefore, it was observed that the presence of kinked sulfone units in each of these copolymers might increase intermolecular freedom and polymer-polar solvent interaction significantly, resulting in the improved solubility in organic polar solvents.

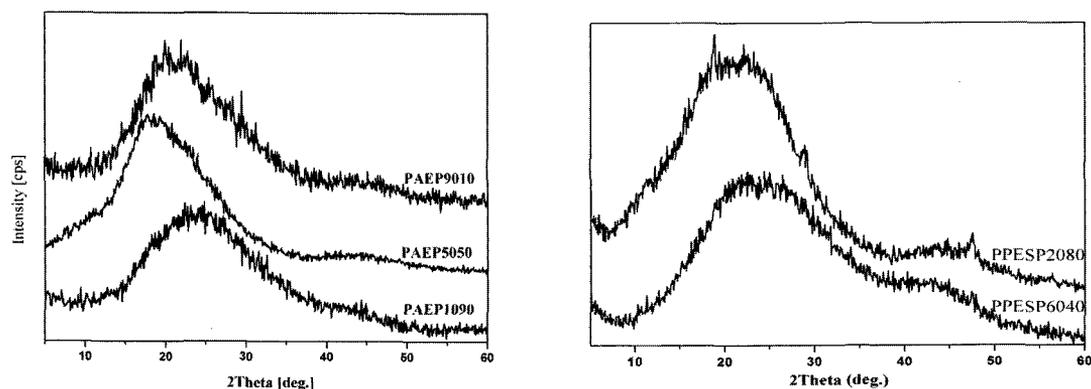


Fig. 5. WAXD diffractograms of PST and PPST.

4. Conclusion

New copoly(arylene ether phenyl-s-triazine)s have been prepared and their solubility, crystallinity, thermal and mechanical properties investigated. They have been synthesized by direct solution nucleophilic displacement polycondensation in essentially quantitative yields under mild reaction conditions. The obtained copolymers show good solubility in common polar solvents and can be promising for practical applications in the field of high-temperature membranes, coating or adhesives. All copolymers are amorphous except PST9010 gives a pattern typical of micro-crystalline nature as evidenced by WAXD. (Next see p220)