

# Synthesis and property investigation of poly(arylene ether)s with pendant cyclohexyl units

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**Abstract** A series of poly(arylene ether)s with pendant cyclohexyl units had been prepared by solution polycondensation of 4,4'-cyclohexane-1,1'-diyldiphenol (CHDP) and 4,4'-difluorobenzophenone (DFBP) (or 4,4'-difluorodiphenylsulfone (DFDPS)). The inherent viscosities of obtained poly(arylene ether)s were in the range of 0.49–0.97 dLg<sup>-1</sup>. They were found to have high glass transition temperatures ( $T_g$ ) of 158–208 °C, and good thermal stability with 5% weight-loss temperature ( $T_{5\%}$ ) of 442–484 °C. The tensile test and dynamic mechanical analysis results indicate the good mechanical properties of poly(arylene ether)s. Their Young's Modulus were found to be 2.2–2.3 GPa, tensile strengths were 81.0–97.7 MPa, storage modulus were over 1.5 GPa even near glass transition temperature. The complex viscosities of the resultant polymers melt maintained a narrow range of 308–313 Pas at 260 °C or 2700–4600 Pas at 340 °C during the testing time. That indicates the resultant resins have good melt flowability and stability. In addition, these poly(arylene ether)s were found to have good solubility in various solvents such as CHCl<sub>3</sub>, THF, NMP, DMAc, DMI, etc., and have good optical transmittance (>80%) at 450 nm. It suggests that the obtained poly(arylene ether)s not only can be processed by melt method, but also can be applied with solution method easily, and can be applied to tough and transparent films.

**Keywords** Poly(arylene ether)s · Cyclohexyl · Synthesis · Processability

## Introduction

Poly(arylene ether)s (PAEs) are a kind of important high-performance thermoplastics that have rigid aromatic rings and flexible ether linkage in their backbones. The typical PAEs, such as poly(arylene ether ketone)s (PAEKs) and poly(arylene ether sulfone)s (PAESs) exhibit outstanding thermal stability, good mechanical properties and excellent chemical resistance [1–4]. Due to above excellent combination of properties, the applications of PAEs in the aerospace, automobile, energy, medical care, electrical and optical industries had attracted significant attention in the last several decades [5–10]. However, most of these PAEs have some drawbacks, such as high melt processing temperature, high melt viscosity and poor solubility, and these drawbacks make themselves difficult to process and limit their application in various technological fields. For example, a good balance between the film-forming ability and corrosion resistance of polymer is required for membrane application, good melt stability and flowability of polymer are necessary for injection molding process. Therefore, In order to enlarge their application field, chemical modifications of these polymers are becoming essential and critical.

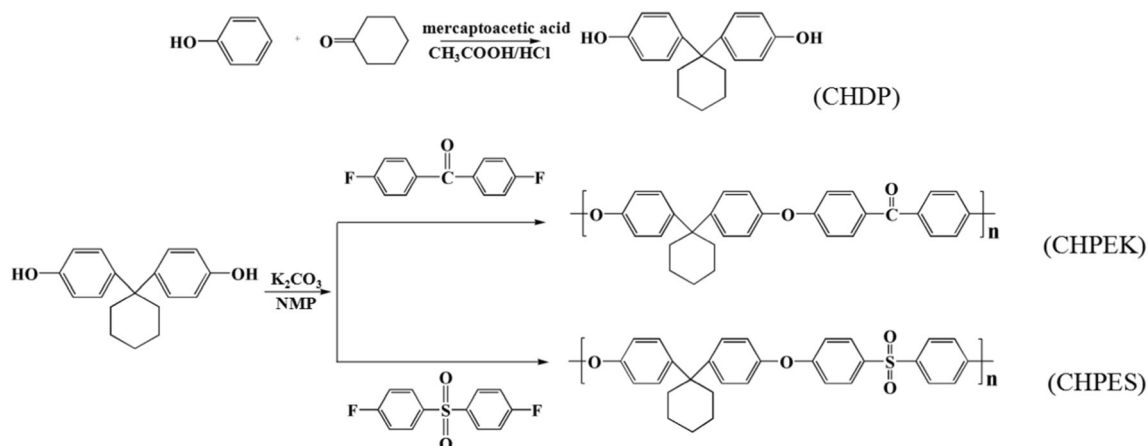
To solve this problem, the studies on improving their melt processability by the introduction of flexible moiety, such as alkyl [11, 12], thioether [13] and amide [14] into the polymer backbone, and raising the ratio of ether linkage to polar groups [3] have been reported. In addition, the effort to improve their solution processability by

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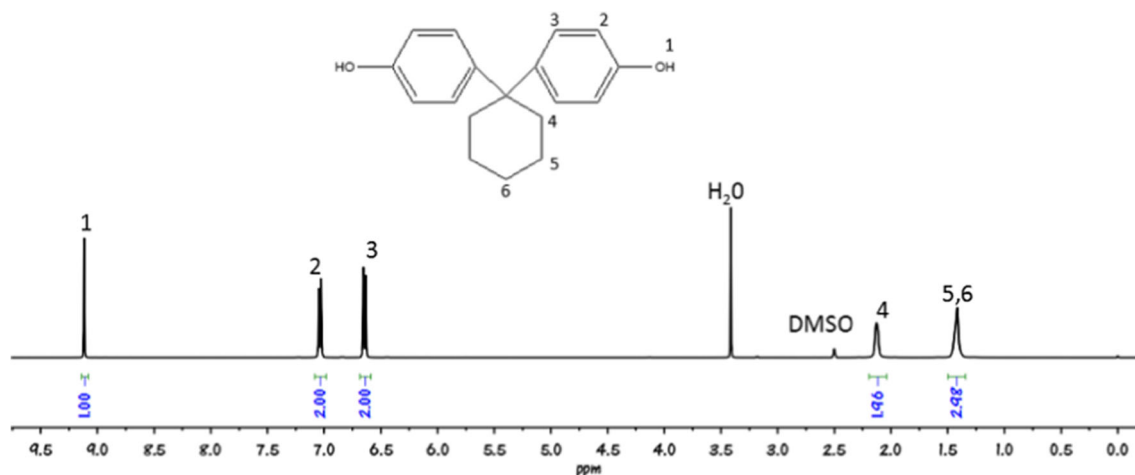
**Scheme 1** Synthesis routes of CHDP, CHPEK and CHPES

incorporation of cardo groups, such as phthalazine [15], spirodilactam [16], phenolphthalein [17], xanthene [18], fluorene [19], decahydronaphthalene [20] and isophorone [21] into the polymer chain, and the introduction of pendant trifluoromethyl [5], polychloro [22], cyano [23, 24], aryl [25–27] and alkyl [27–29] groups onto the polymer chain have been afforded.

It is well known that the introduction of flexible moiety into the polymer backbone can effectively soften the polymer backbone and lower the melt point of polymers, but their crystallization properties still result in the poor solubility. The incorporation of bulk groups into the polymer chain is an effective way to weaken the molecular regularity and improve their solubility, but it also leads to a great increase in the glass transition temperature, and requires a harsh melt processing environment. Besides, the earlier studies on chemical structure modification of PAEs were mostly focused on the relationship between thermal properties and their aggregated structures, while just a few studies about their rheological properties.

Therefore, the aim of this work is to synthesize the poly(arylene ether)s with excellent thermal and mechanical properties, as well as good melt and solution processability, which is estimated by the testing of their rheological behavior and solubility. To achieve this aim, the cyclohexyl units with good thermal stability and moderate rigidity were introduced into the polymer backbone. The pendant cyclohexyl groups are expected to weaken the molecular packing and the interaction of chain so as to lower the crystallinity and melt viscosity of the polymers, and improve their processabilities.

In this paper, 4,4'-cyclohexane-1,1'-diylidiphenol (CHDP) was synthesized. The pendant cyclohexyl groups containing PAEs were prepared by the solution polycondensation of 4,4'-cyclohexane-1,1'-diylidiphenol (CHDP) and 4,4'-difluorobenzophenone (DFBP) (or 4,4'-difluorodiphenylsulfone (DFDPS)). The effects of pendant cyclohexyl units on their thermal, mechanical, rheological, optical properties and solubility were discussed in detail.



**Fig. 1**  $^1\text{H-NMR}$  spectrum of CHDP in DMSO- $\text{D}_6$

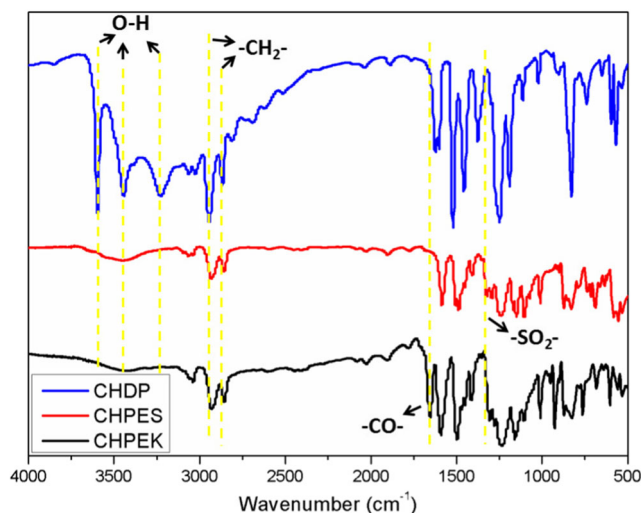


Fig. 2 FT-IR spectra of CHDP, CHPEK and CHPES

### Experimental

#### Materials

4,4'-difluorodiphenylsulfone (DFDPS) (AR, Aladdin Reagent Company), 4,4'- difluorobenzophenone (DFBP) (poly grade, Sino-High(China) Co., Ltd.), potassium carbonate (AR, Chengdu Kelong Chemical Industry Company),

methylbenzene (AR, Chengdu Kelong Chemical Industry Company), N-methyl-2-pyrrolidone (NMP) (99.5%, Jiangsu NanJing JinLong Chemical Industry Company), hydrochloric acid (HCl) (AR, Chengdu Kelong Chemical Industry Company), acetic acid (AR, Chengdu Kelong Chemical Industry Company), phenol (AR, Chengdu Kelong Chemical Industry Company), cyclohexanone (AR, Aladdin Reagent Company), mercaptoacetic acid (AR, Aladdin Reagent Company) were used without further purification. The other solvents and reagents were commercially obtained.

#### Measurements

**Intrinsic viscosity analysis** The intrinsic viscosity ( $\eta_{int}$ ) of the resultant polymers were measured by one-point method at  $30 \pm 0.1$  °C with 0.500 g of polymer dissolved in 100 ml of NMP, and using a Cannon-Ubbelohde viscometer. The results were calculated with following equation:

$$\eta_{int} = \frac{\sqrt{2(\eta_{sp} - \ln \eta r)}}{C} \tag{1}$$

Where  $\eta r = \eta/\eta_0$  and  $\eta_{sp} = \eta/\eta_0 - 1$ .

**Chemical structure analysis** The <sup>1</sup>H-NMR spectra were recorded on a BRUKER-600 NMR spectrometer with

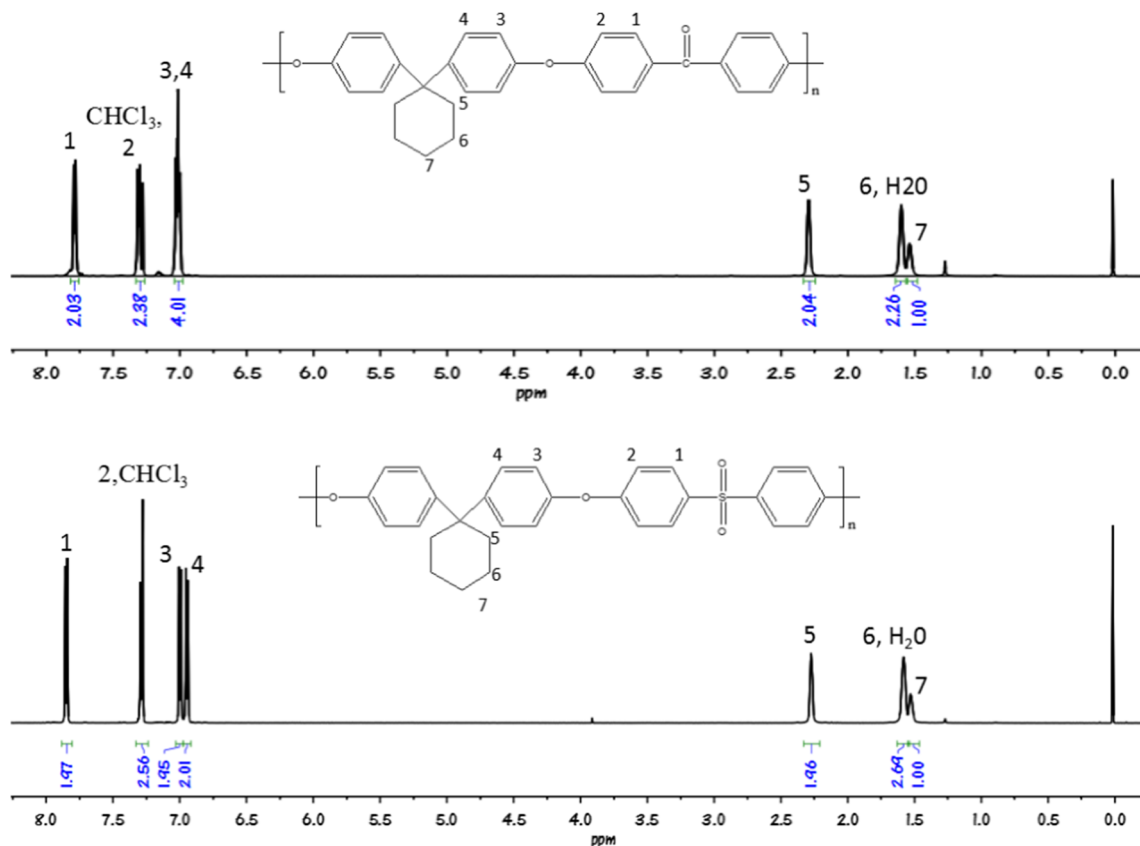


Fig. 3 <sup>1</sup>H-NMR spectra of CHPEK and CHPES in CDCl<sub>3</sub>

**Table 1** Intrinsic viscosity ( $\eta_{\text{int}}$ ), yield and elemental analysis of CHPEK and CHPES

Sample	$\eta_{\text{int}}^a$ (dLg <sup>-1</sup> )	Yield (%)	Elemental analysis <sup>b</sup> (wt%)		
			C	H	S
CHPEK	0.49	95.78	85.32 (84.35)	5.09 (4.76)	<1.0
CHPES	0.97	97.38	75.15 (75.47)	4.86 (4.40)	6.92 (6.71)

<sup>a</sup>  $\eta_{\text{int}}$ s of polymers were measured at  $30 \pm 0.1$  °C with the concentration of 0.500 g/100 ml NMP

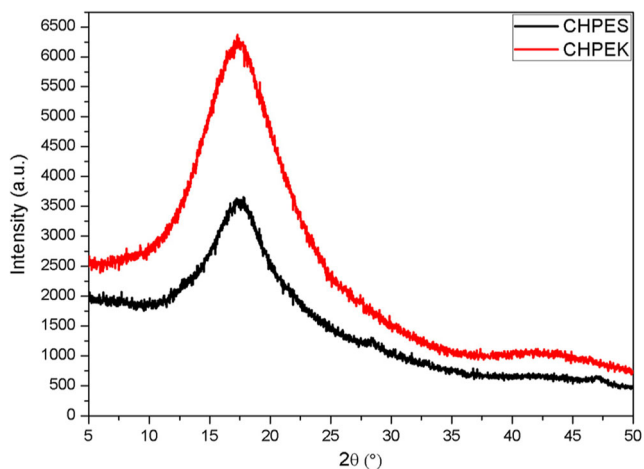
<sup>b</sup> The values in bracket are calculated data

deuterated dimethyl sulfoxide (DMSO-D6) or deuterated chloroform (CDCl<sub>3</sub>) as solvents. The FT-IR spectra were obtained by a NeXuS670 FT-IR instrument. The results of elemental analysis were obtained by an elemental analyzer (EURO EA-3000). The X-ray diffraction (XRD) was performed with Philips X'pert Pro MPD.

**Thermal analysis** Thermal analysis of the resultant polymers were obtained by Thermogravimetric analysis (TGA, Q500) and Differential scanning calorimetry (DSC, NETZSCH DSC 200 PC) at a heating rate of 10 °C/min under nitrogen atmosphere.

**Mechanical test** The stress-strain behavior of the polymer casting films were studied by the Instron Corporation 402. The speed of testing was 10 mm/min. Dynamic mechanical analysis (DMA) was performed on TA-Q800 apparatus operating in the tensile mode at air atmosphere with a heating rate of 5 °C/min and a frequency of 1 Hz.

**Rheological test** The rheological properties of the resultant polymers were measured by using a parallel plate rheometer with 2.5 cm diameter stainless steel parallel plates. Temperature sweep (shear frequency: 1 Hz, shear strain: 2%, temperature scanning rate: 5 °C min<sup>-1</sup>) and time sweep (shear frequency: 1 Hz, shear strain: 2%) were performed under air atmosphere.

**Fig. 4** XRD patterns of CHPEK and CHPES

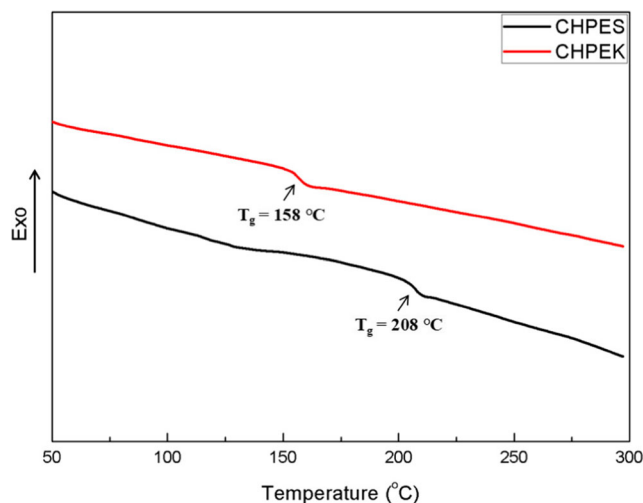
**Experiment of solubility** The solubility of the resultant polymers in various solvents was tested at room temperature for 12 h and at the boiling of the solvents for 10 min.

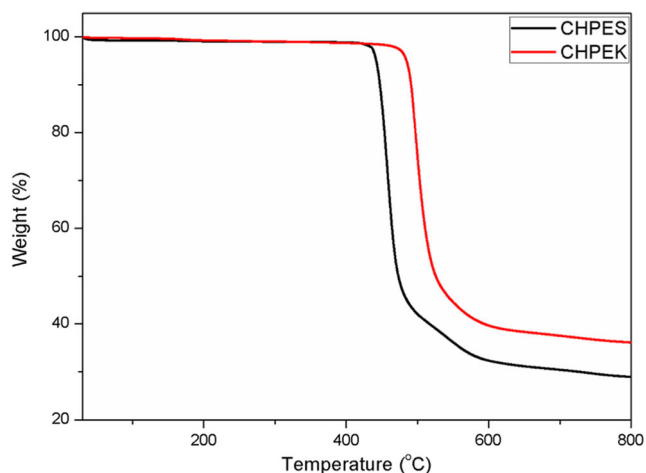
**Optical properties** The optical transmittance of the prepared polymer films was determined by UV-Visible spectroscopy (U-2310II). The samples were prepared by the solution-casting method to form a thin film, whose thickness is about 10–15 μm.

### Monomer synthesis

*4,4'-cyclohexane-1,1'-diylidiphenol (CHDP)* (shown in scheme 1)

Phenol (37.64, 0.4 mol), mercaptoacetic acid (0.5 g), a mixture of hydrochloric acid and acetic acid (90 ml, 2:1 by volume) were added into a 250 ml three-necked flask. The mixture was stirred at 50 °C for 0.5 h. Then cyclohexanone (9.82 g, 0.1 mol) was added dropwise within 0.5 h, and the reaction was kept for 12 h. Afterwards, the mixture was filtered and washed 3 times with hot deionized water to remove excess phenol. Then, the crude product was recrystallized from methanol aqueous solution. Finally, the product was dried under vacuum at 50 °C for about 24 h. That afforded CHDP as white crystals (yield: 94.54%).

**Fig. 5** DSC curves of CHPEK and CHPES at a heating rate of 10 °C/min in N<sub>2</sub>



**Fig. 6** TGA curves of CHPEK and CHPES at a heating rate of 10 °C/min in N<sub>2</sub>

### Polymer synthesis

*Poly[(4,4'-cyclohexane-1,1'-diyl)diphenol]-  
-alt-(4,4'-difluorobenzophenone)] (CHPEK)*

A typical polymerization was carried out as shown in Scheme 1. CHDP (26.8 g, 0.1 mol), DFBP (21.8 g, 0.1 mol), toluene (15 ml), potassium carbonate (27.6 g, 0.2 mol) and NMP (120 ml) were added into a 250 ml three-necked flask fitted with a mechanical stirrer, thermometer and nitrogen inlet. The mixture was heated to 160 °C for 1 h to remove the byproduct water. Next, the reaction temperature was raised up to 200 °C and kept for another 6 h. After the reaction was over, the reaction solution was poured into deionized water to obtain fibrous precipitate, and then the precipitate was crushed into powder and washed with hot deionized water several times. After dried at 100 °C for 12 h, 42.62 g (yield: 95.78%) of CHPEK was obtained, the inherent viscosity ( $\eta_{\text{int}}$ ) was 0.49 dLg<sup>-1</sup>.

*Poly[(4,4'-cyclohexane-1,1'-diyl)diphenol]-  
-alt-(4,4'-difluorodiphenylsulfone)] (CHPES)*

CHPES was prepared following a similar procedure as that of CHPEK. The yield and inherent viscosity ( $\eta_{\text{int}}$ ) of CHPES were 97.38% and 0.97 dLg<sup>-1</sup>, respectively.

**Table 2** Thermal and mechanical properties of CHPEK and CHPES

Sample	T <sub>g</sub>	T <sub>5%</sub>	Tensile strengths (MPa)	Elongation at break (%)	Young's modulus (GPa)	Storage modulus (GPa)	
CHPEK	158 <sup>a</sup>	180 <sup>b</sup>	484	81.0 ± 5.6	7.3 ± 0.14	2.2 ± 0.16	1.5 <sup>c</sup>
CHPES	208 <sup>a</sup>	234 <sup>b</sup>	442	97.7 ± 4.8	10.0 ± 0.60	2.3 ± 0.20	—
							1.6 <sup>d</sup>

<sup>a</sup> Measured by DSC at a heating rate of 10 °C/min under nitrogen atmosphere

<sup>b</sup> Measured by DMA at a heating rate of 5 °C/min under nitrogen atmosphere

<sup>c</sup> Measured by DMA at 110 °C under air atmosphere

<sup>d</sup> Measured by DMA at 200 °C under air atmosphere

## Results and discussion

### Monomers

#### *Synthesis and chemical structure of CHDP*

The monomer CHDP was synthesized by condensation of phenol with cyclohexanone in a mixture acid solvent (as shown in Scheme 1). Its structure was confirmed by <sup>1</sup>H-NMR and FT-IR spectra. The <sup>1</sup>H-NMR spectrum of the monomer is shown in Fig. 1. The signal at 9.1 ppm was attributed to the units of -OH. While the signals at 7.0 and 6.6 ppm were assigned to the protons on benzene ring. The signals rang from 1.4 to 2.1 ppm were assigned to the cyclohexyl units. The ratio of corresponding integral curves was about 1:2:2:2:3, that was in good agreement with the calculated value. From the FT-IR spectrum of CHDP (Fig. 2), we could observe the characteristic absorption bands of -OH at 3200–3600 cm<sup>-1</sup> and the absorption bands of C-O stretching vibration at 1250 cm<sup>-1</sup>. The bands at 2935 and 2852 cm<sup>-1</sup> in the spectrum indicated the existence of cyclohexyl units. The bands at 1612, 1513 and 1442 cm<sup>-1</sup> were for the C = C stretching vibrations of benzene ring. Besides, the absorption bands of C-H stretching vibration and out-plane bending vibration of benzene ring could be observed at 3044 and 820 cm<sup>-1</sup>, respectively. Combining the results of <sup>1</sup>H-NMR and FT-IR, we confirmed that CHDP was successfully synthesized as shown in Scheme 1.

### Polymers

#### *Synthesis and chemical structure of CHPEK and CHPES*

The synthetic route of polymers were shown in Scheme 1. The polymerizations were carried out with potassium carbonate as the base. The FT-IR, <sup>1</sup>H-NMR spectra and elemental analysis were used to confirm the chemical structure of the resultant polymers. The FT-IR spectra (Fig. 2) of CHPEK and CHPES both showed the characteristic absorption bands of C-O stretching vibrations at 1238 cm<sup>-1</sup>. The bands at 2932 and 2857 cm<sup>-1</sup> in the spectra indicated existence of cyclohexyl



units. The absorption bands at 1592 and 1496  $\text{cm}^{-1}$  were for C = C stretching vibrations of benzene ring. Besides, the C-H stretching vibrations and out-plane bending vibrations of benzene ring appeared at 3060  $\text{cm}^{-1}$  and 827  $\text{cm}^{-1}$ , respectively. Comparing with the spectrum of CHDP, the characteristic absorption bands of O-H at 3200–3600  $\text{cm}^{-1}$  had almost disappeared. Besides, the new absorption band at 1654  $\text{cm}^{-1}$  of ketone group or the absorption band at 1324  $\text{cm}^{-1}$  of sulfone group could be observed, respectively. The  $^1\text{H-NMR}$  spectrum of CHPEK is shown in Fig. 3. The signals at 7.8, 7.3 and 7.0 ppm were assigned to the aromatic protons. While the signals at 2.3, 1.6 and 1.5 ppm were attributed to the cyclohexyl units. The ratio of corresponding integral curves was about 2:2:4:2:2:1. The  $^1\text{H-NMR}$  spectrum of CHPES in Fig. 3 appeared familiar signals with a same intensity at 7.8, 7.3, 7.0, 6.9, 2.3, 1.6 and 1.5 ppm, indicated there are benzene ring and cyclohexyl units in this resultant polymer. The chemical composition of CHPEK and CHPES was measured by elemental analysis. As shown in Table 1, the test results are very close to the calculated values. When combining the results of FT-IR,  $^1\text{H-NMR}$  and elemental analysis, we can confirm that the polymerization proceeds as what we have described in Scheme 1.

#### X-ray diffraction analysis of polymers

The structure of aggregating state of CHPEK and CHPES were estimated by X-ray diffraction analysis. As shown in Fig. 4, no crystalline peaks could be observed, only a Gaussian distribution appeared. It signifies that the polymers were amorphous. The amorphous structure of the polymers was mostly due to the existence of pendant cyclohexyl groups and strong polarity of sulfone or ketone groups that weakened the molecular regularity and inhibited the close packing of the molecular chains.

#### Thermal properties

The thermal properties of CHPEK and CHPES were investigated by DSC (Fig. 5), and TGA (Fig. 6) (summarized in Table 2). As shown in Fig. 5, the glass transition temperatures of CHPEK and CHPES were 158 and 208  $^{\circ}\text{C}$ , respectively. It was much higher than that of bisphenol A polyketone (144  $^{\circ}\text{C}$ ) [30] and bisphenol A polysulphone (187  $\pm$  3  $^{\circ}\text{C}$ ) [31], respectively. From the DSC curve, it could find that the resultant polymers had no endothermic melting peak. It also suggests the amorphous nature of polymers. This result was consistent with the results from XRD. Figure 6 showed the thermal degradation curves of CHPEK and CHPES. The 5% weight loss temperatures of CHPEK and CHPES in nitrogen were 484 and 442  $^{\circ}\text{C}$ , respectively, which was greatly higher than their glass transition temperature. Above results indicate

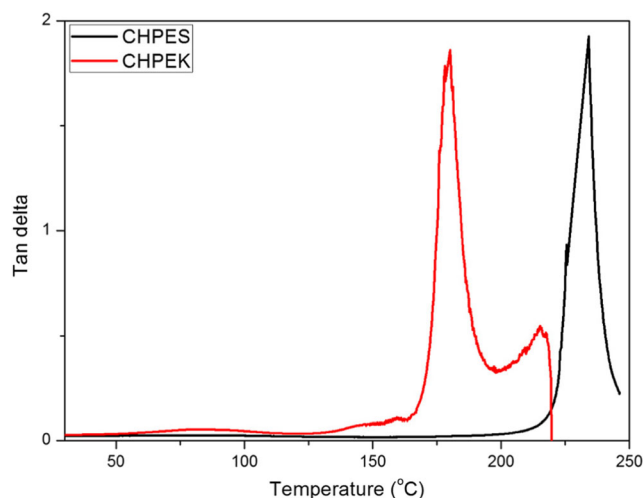


Fig. 7 The tan delta curves of CHPEK and CHPES

that these polymers have good thermal stability and can be processed with melt method.

#### Mechanical properties

The tensile strength of the casting films of polymers was tested by a universal testing machine (as shown in Table 2). The average tensile strength of CHPEK and CHPES was 81.0 and 97.7 MPa, respectively. And the Young's modulus of CHPEK and CHPES were 2.2 and 2.3 GPa, respectively. Besides, the elongation at break of CHPEK and CHPES were both more than 5%. It suggests that the casting films of CHPEK and CHPES both have good mechanical properties. Furthermore, the thermal mechanical properties of polymers were characterized by dynamic thermomechanical analysis (DMA). From the tan delta curves of CHPEK and CHPES in Fig. 7, one obvious transition peak could be observed. Through the transition peak temperatures, we could obtain that the  $T_g$ s of CHPEK and CHPES were 180 and 234  $^{\circ}\text{C}$ , respectively. The  $T_g$ s are

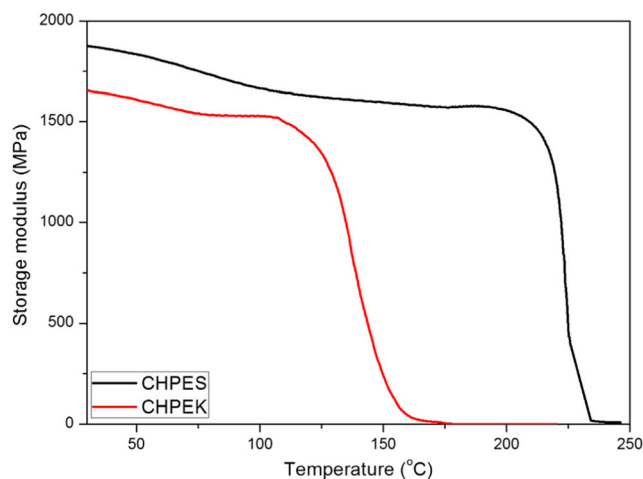
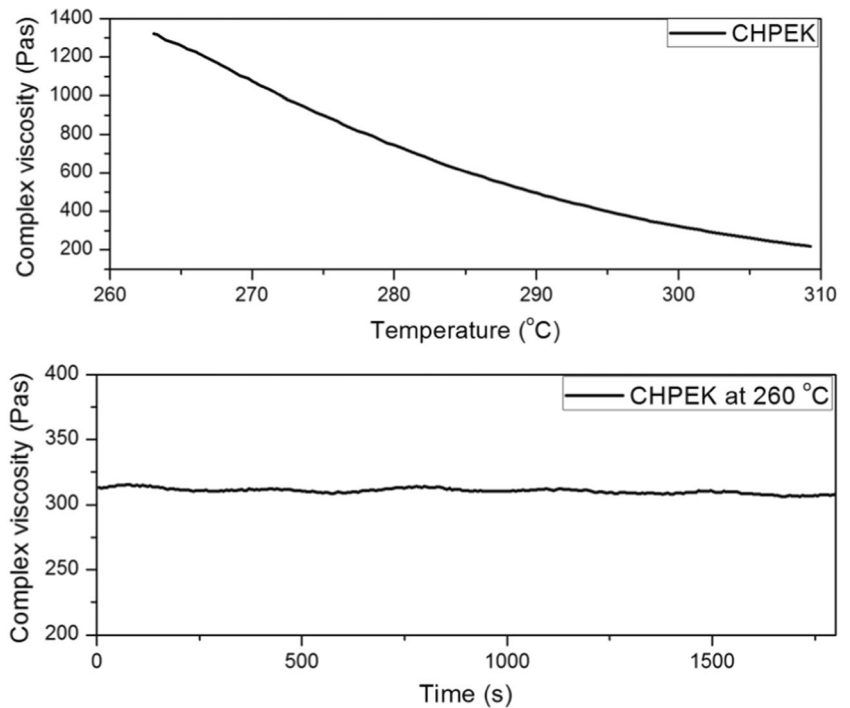


Fig. 8 The storage modulus curves of CHPEK and CHPES

**Fig. 9** The curves of complex viscosities versus temperature and time for CHPEK

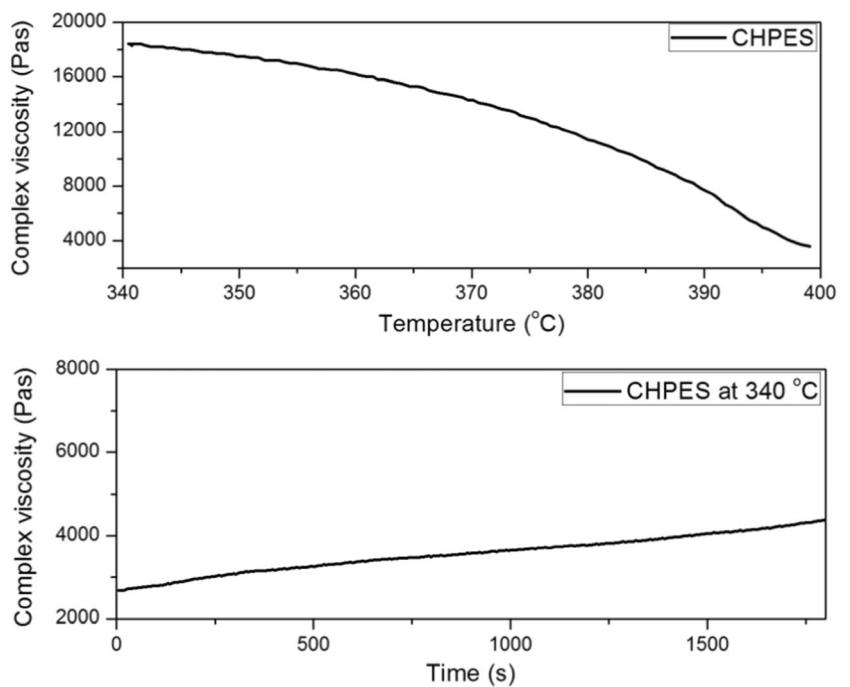


slightly higher than those tested by DSC. The slight differences are mainly due to the different responses of the polymers with these two measurements. Moreover, as the storage modulus curves shown in Fig. 8, CHPEK and CHPES showed high storage modulus of 1.7 and 1.9 GPa, respectively. Most importantly, the storage modulus of CHPEK and CHPES still remained over 1.5 GPa even near the glass transition temperature. It indicates that CHPEK and CHPES both have good thermal mechanical performance.

*Rheological properties*

The rheological properties of CHPEK and CHPES were studied with a parallel plate rheometer. In order to study the melt stability and melt processing temperature of the resultant polymers, a time and temperature sweep were investigated, respectively. As shown in Fig. 9, the complex viscosity of CHPEK were in the range of 219–1322 Pas from 260 °C to 310 °C, meanwhile the complex viscosity of CHPEK almost remained

**Fig. 10** The curves of complex viscosity versus temperature and time for CHPES



**Table 3** Solubility behavior of CHPEK and CHPES

Solvent	CHPEK		CHPES	
	Room temperature	High temperature <sup>a</sup>	Room temperature	High temperature <sup>a</sup>
HCl (6 molL <sup>-1</sup> )	–	–	–	–
NaOH (1 molL <sup>-1</sup> )	–	–	–	–
Concentrated sulfuric acid	+	+	+	+
Formic acid	–	–	–	–
CF <sub>3</sub> COOH	–	–	–	–
Acetone	–	–	–	–
Ethanol	–	–	–	–
Diethyl ether	–	–	–	–
Chloroform	+	+	+	+
Toluene	+	+	–	–
1,4- Dioxane	+	+	+–	+–
THF	+	+	+	+
NMP	+	+	+	+
DMAc	+	+	+	+
DMF	+–	+	+–	+
DMSO	–	+–	–	+
DMI	+	+	+	+

+ soluble, +– partly soluble or swelling, – insoluble

<sup>a</sup> the boiling of the solvents

at 310 Pas during the whole testing time (0–1800 s at 260 °C). It suggests that CHPEK has good melt flowability and stability. Figure 10 showed a decrease in the complex viscosity of CHPES with temperature increase could be observed, and the complex viscosity of CHPES kept at the range of 2700–4600 Pas during the whole testing time (0–1800 s at 340 °C), it also indicates the good melt flowability and stability of CHPES. Comparing with poly(arylene ether ketone) resins, such as PEEK and PEKK, the melt processing window of CHPEK had a significant improve. Besides, for the classical poly(arylene ether sulfone) resins, 340 °C is a relatively low melt processing temperature. These results were mainly caused by the incorporation of pendant cyclohexyl groups weaken the molecular packing and interaction of chain.

#### Solubility experiment

The results of the solubility experiments of CHPEK and CHPES were summarized in Table 3. According to Table 3, it was found that CHPEK and CHPES could be dissolved in various solvents, such as CHCl<sub>3</sub>, THF, NMP, DMAc, DMI and etc. It suggests that the resultant polymers have outstanding solubility, and can be processed by solution method. In particular, the solution processability of CHPEK was greatly improved when compared with traditional poly(arylene ether ketone) resins,

such as PEEK, PEKK and PEEKK. It was attributed to the incorporation of pendant cyclohexyl groups caused its amorphous structure. On the other hand, CHPEK and CHPES were insoluble in acetone, ethanol, diethyl ether, alkali and acid solution (except concentrated sulfuric acid). It suggests that these polymers still keep moderate corrosion resistance.

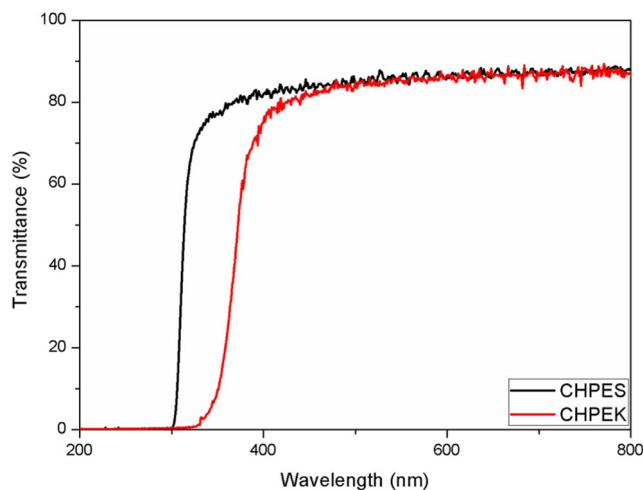
#### The optical properties of films

The optical properties of CHPEK and CHPES films were determined by UV-Visible spectroscopy. The cutoff wavelength ( $\lambda_{\text{cutoff}}$ ) and optical transmittance at 400 nm ( $T_{400}$ ) and 450 nm ( $T_{450}$ ) of the prepared polymers films were summarized in Table 4. As shown in Fig. 11, the cutoff wavelength ( $\lambda_{\text{cutoff}}$ ) of CHPEK and CHPES films were 337 and 302 nm, respectively. The transparencies of CHPEK and CHPES films measured at 400 and 450 nm were 71.31–81.95% and 81.31–83.46%, respectively. It indicates that the resultant poly(arylene ether)s can be

**Table 4** Optical properties of CHPEK and CHPES

Sample	d (μm)	$\lambda_{\text{cutoff}}$ (nm)	$T_{400}$ (%)	$T_{450}$ (%)
CHPEK	9	337	71.31	81.31
CHPES	9	302	81.95	83.46





**Fig. 11** UV-vis spectra of CHPEK and CHPES

applied as the candidate materials for the optical films, that need good transparent and thermal properties.

## Conclusion

A series of poly(arylene ether)s with pendant cyclohexyl units were designed and synthesized in order to develop high performance PAEs with great melt and solution processability. The poly(arylene ether)s were prepared by solution polycondensation of 4,4'-cyclohexane-1,1'-diyldiphenol (CHDP) and 4,4'-difluorobenzophenone (DFBP) (or 4,4'-difluorodiphenylsulfone (DFDPS)). The resultant poly(arylene ether)s showed good mechanical and thermal properties. Their Young's Modulus were found to be 2.2–2.3 GPa, tensile strengths were 81.0–97.7 MPa, storage modulus were over 1.5 GPa even near glass transition temperature. Moreover, these poly(arylene ether)s exhibited high glass transition temperatures ( $T_g$ ) of 158–208 °C, and good thermal stability with 5% weight-loss temperature ( $T_{5\%}$ ) of 442–484 °C. Most importantly, all poly(arylene ether)s showed good melt stabilities, low melt processing temperatures and outstanding solubilities, mostly due to the introduction of pendant cyclohexyl groups weakens the molecular packing and interaction of chain. It suggests that the resultant poly(arylene ether)s have excellent processability, and they can be processed by either melt or solution methods. In addition, their solution-casting films exhibited high optical transmittance (>80%) at 450 nm. Hence, the prepared poly(arylene ether)s with pendant cyclohexyl units could be applied as heat resistant, tough and transparent films.

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## References

1. Labadie JW, Hedrick JL, Ueda M (1996) Poly(aryl ether) synthesis. ACS Symp Ser 624:210–225
2. Rose JB (1997) Preparation and properties of poly(arylene ether sulphones). Polymer 15:456–465
3. Attwood TE, Dawson PC, Freeman JL, Hoy LRJ, Rose JB, Staniland PA (1981) Synthesis and properties of polyaryletherketones. Polymer 22:1096–1103
4. Shukla D, Negi YS, Uppadhyaya JS, Kumar V (2012) Synthesis and modification of poly(ether ether ketone) and their properties: a review. Polym Rev 52:189–228
5. Dhara MG, Banerjee S (2010) Fluorinated high-performance polymers: poly(arylene ether)s and aromatic polyimides containing trifluoromethyl groups. Prog Polym Sci 35:1022–1077
6. Miyatake K, Chikashige Y, Higuchi E, Watanabe M (2007) Tuned polymer electrolyte membranes based on aromatic polyethers for fuel cell applications. J Am Chem Soc 129:3879–3887
7. Bursal JDS, Peeva LG, Kumbharkar S, Livingston A (2015) Organic solvent resistant poly(ether-ether-ketone) nanofiltration membranes. J Membr Sci 479:105–116
8. Song Y, Wang JY, Li GH, Sun QM, Jian XG, Teng J, Zhang HB (2008) Synthesis, characterization and optical properties of fluorinated poly(aryl ether)s containing phthalazinone moieties. Polymer 49:4995–5001
9. Zhao Z, AH W, Luan SJ, Zhang CY (2015) Preparation and characterization of a positively charged nanofiltration membrane based on poly(arylene ether sulfone) with tertiary amine groups. J Polym Res 22:168
10. Pei XL, Zhai WT, Zheng WG (2015) Preparation of poly(aryl ether ketone ketone)-silica composite aerogel for thermal insulation application. J Sol-Gel Sci Technol 76:98–109
11. Xia JQ, Zhang J, Liao GX, Jian XG (2007) Copolymerization and blending of poly(phthalazinone ether ketone)s to improve their melt processability. J Appl Polym Sci 103:2575–2580
12. Zhang G, Zhou YX, Kong Y, Li ZM, Long SY, Yang J (2014) Semiaromatic polyamides containing ether and different numbers of methylene (2–10) units: synthesis and properties. RSC Adv 4: 63006–63015
13. Wang YZ, Lin CH, Chan BW, Hsieh KH (2004) Synthesis and properties of thio-containing poly(ether ether ketone)s. Polym Int 53:320–325
14. Wang Y, Wang PP, Xu Q, Yan T, Cai MZ (2014) Synthesis and properties of novel copolymers of poly(ether ketone biphenyl ketone ether ketone ketone) and poly(ether ketone sulfone amide). J Polym Res 21:533
15. Liu YJ, Jian XG, Liu SJ, Zhang J (1999) Synthesis and characterization of poly(ether ketone ketone) contain the phthalazinone moiety. Acta Polym Sin 1:37–41
16. Zhou H, Bucio E, Venumbaka SR, Fitch JW, Cassidy P (2006) New spirodilactam polymers. Polymer 47:6927–6930
17. Gao N, Zhang SB, JP X (2012) Phenolphthalein-based Cardo poly(arylene ether sulfone): preparation and application to separation membranes. J Appl Polym Sci 128:1–12
18. Sheng SR, Ge WW, Huang ZZ, Liu XL, Song CS (2009) Synthesis and characterization of novel soluble cardo poly(arylene ether ketone)s containing xanthene structures. J Appl Polym Sci 114:570–576
19. Kawasaki S, Yamada M, Kobori K, Jin FZ, Kondo Y, Hayashi H, Suzuki Y, Takata T (2007) Synthesis and chemical, physical, and optical properties of 9,9-Diarylfuorene-based poly(ether-ether-ketone). Macromolecules 40:5284–5289
20. Honkhambe PN, Pasale SK, Bhairamadgi NS, Kumbhar KP, Salunkhe MM, Wadgaonkar PP (2010) Poly(ether ether ketone)s and poly(ether ether ketone ketone)s containing Cardo

- Decahydronaphthalene groups: synthesis and characterization. *J Appl Polym Sci* 122:1607–1613
21. Zhang G, Zhou YX, Li Y, Wang XJ, Long SR, Yang J (2015) Investigation of the synthesis and properties of isophorone and ether units based semi-aromatic polyamides. *RSC Adv* 5:49958–49967
  22. Huang ZZ, LM Y, Sheng SR, Ge WW, Liu LX, Song CS (2008) Synthesis and characterization of novel soluble poly(ether ketone sulfone)s with pendant polychloro groups. *J Appl Polym Sci* 108:1049–1054
  23. Cai MZ, Zhu MH, YK Y (2009) Synthesis and characterization of poly(ether ketone ether ketone ketone)/poly(ether ether ketone ketone) copolymers containing naphthalene and pendant cyano groups. *J Appl Polym Sci* 112:3225–3231
  24. Zhu XJ, Yan T, Xu Q, Cai MZ (2016) Synthesis and characterization of novel poly(aryl ether ketone)s containing biphenylene moieties and pendant cyano groups. *J Polym Res* 23:24
  25. Zhao XY, Wang CY, Zhang K, Zhou Z, Zhu MF (2010) Soluble poly(aryl ether)s containing naphthalene pendant group: synthesis, characterization and electrospinning. *Colloid Polym Sci* 288:907–914
  26. Wu T, Liu PQ, Shi MW, Lu J, Ye GD, JJ X (2011) Novel copoly(ether ether ketone)s with pendant phenyl groups: synthesis and characterization[J]. *Polym Int* 60:1318–1323
  27. Risse W, Sogah DY (1990) Synthesis of soluble high molecular weight poly(aryl ether ketones) containing bulky substituents. *Macromolecules* 23:4029–4033
  28. Lin C, Lei Y, Feng J, Wang CY, Li JL, Xu Z (2007) Novel heterocyclic poly(arylene ether ketone)s: synthesis and polymerization of 4-(4'-hydroxyaryl)(2H)phthalazin-1-ones with methyl groups. *J Polym Sci Polym Chem* 45:1525–1535
  29. Yildiz E, Inan TY, Yildirim H, Kuyulu A, Gungor A (2007) Thermal and mechanical properties of poly(arylene ether ketone)s having pendant tertiary butyl groups. *J Polym Res* 14:61–66
  30. Sayyed MM, Maldar NN (2010) Novel poly(arylene-ether-ether-ketone)s containing preformed imide unit and pendant long chain alkyl group. *Mater Sci Eng B* 168:164–170
  31. Riley DJ, Gungor A, Srinivasan SA, Sankarapandian M, Tchatchoua C, Muggli MW, Ward TC, Mcgrath JE (1997) Synthesis and characterization of flame resistant poly(arylene ether)s. *Polym Egn Sci* 37:1501–1511