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RESEARCH ARTICLE

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# Synthesis and characterization of polyarylene sulfide sulfone/ketone amide

**Abstract** High-molecular-weight polyarylene sulfide sulfone amide (PASSA) and polyarylene sulfide ketone amide (PASKA) were synthesized from diamine monomers containing sulfone or ketone group by a low temperature solution polycondensation reaction in anhydrous *N*-methylpyrrolidone (NMP). The structures of the monomers and corresponding polymers were identified by IR-spectra and UV spectra. The maximum intrinsic viscosities of the polymers were 0.72 dL/g in NMP (PASSA) and 0.62 dL/g in $H_2SO_4$ (PASKA) at $30 \pm 0.1$°C, respectively. The polymers possess excellent thermal properties with the glass transition temperature ($T_g$) for PASSA and PASKA are 274.9°C and 195.2°C, respectively. The initial degradation temperatures ($T_i$) for PASSA and PASKA are 461.55°C and 467.08°C, respectively, which suggests that PASSA and PASKA are excellent heat-resistant materials. The dissolvability experiments show that PASSA and PASKA are also corrosion resistance materials.

**Keywords** polyarylene sulfide sulfone, polyarylene sulfide amine, polyarylene sulfide sulfone amide, polyarylene sulfide ketone amide, 4,4′-bis(4-aminothio phenyl)diphenyl sulfone, 4,4′-bis(4,-aminothiophenyl) diphenyl ketone

## 1 Introduction

Poly(arylene sulfide) (PAS), including commercially available poly(phenylene sulfide) (PPS), poly(phenylene sulfide sulfone) (PPSS), poly(phenylene sulfide ketone) (PPSK), poly(phenylene sulfide ketone ketone) (PPSKK), etc. is one of the most important classes of high performance polymers which are known for their excellent mechanical and thermal properties [1–3]. Semicrystalline poly(polyarylene sulfide amine) (PASA) is also a kind of PAS with amine in the backbone of polymer chains, which inherits many excellent properties of polyarylene sulfide (PAS) such as excellent mechanical and thermal properties. However, PASA bears several inborn shortcomings such as low glass transition temperature and poor corrosion resistance in many polar organic solvents. By far, only low molecular weight PASA was obtained which further limited its application [4]. In order to improve the properties of PASA, sulfone or ketone were introduced into the main chain of PASA in this work. Two new kinds of special engineering resin with outstanding performances, namely PASSA and PASKA, were synthesized. The high glass transition temperatures, high temperature stability, good chemical resistance and self- extinguishing property of these two polymers imply their enormous technical and economic importance in the future.

## 2 Experiments

### 2.1 Materials

Commercially available 4,4′-dichloro diphenyl sulfone (DCDPS) (polygrade, Shanghai Yinsheng chemical plant), 4,4'-difluodibenzophenone (polygrade, Jinshan chemical reagents company) and 4-Aminothiophenol terephthalyl chloride (TPC) were used as received. *N*, *N*-dimethylformamide (DMF) and dimethyl acetamide (DMAC) were dried with anhydrous $MgSO_4$ for 24 h, followed by distillation under reduced pressure. *N*-methylpyrrolidone (NMP) had large amounts of water removed by azeotropic distilled with benzene, followed by distillation under reduced pressure [5]. The fraction boiled at middle temperature was collected and stored over molecular sieves before use.

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## 2.2 Methods

### 2.2.1 Synthesis of monomers [6–9]

The 4, 4′-bis(4-aminothiophenyl) diphenyl sulfone (BAPS) and 4, 4′-bis(4-aminothiophenyl) diphenyl ketone (BAPK) was synthesized by the same procedure. For example, a mixture of DCDPS, DMAC or DMF, 4-aminothiophenol and NaOH, $K_2CO_3$ were charged into a three-necked flask fitted with a mechanical stirrer, a thermometer and a nitrogen inlet. The mixture was heated to 150°C and kept for 5 h under nitrogen atmosphere. After the reactant was cooled to room temperature, it was poured into water (150 mL) to precipitate the product and then filtered to remove the inorganic salts. The crude material was collected, crushed and charged into a flask with 400 ml of boiling ethanol for reflux for 0.5 h to obtain the purified product.

### 2.2.2 Synthesis of polymers [10–14]

#### 2.2.2.1 Synthesis of PASSA

The polymerization happened in a 100 mL 3-necks flask equipped with a mechanical stirrer, thermometer and a $CaSO_4$ drying tube. First, 4.66 g (0.01 mol) BAPS was added into the flask, followed by the addition of 40 mL of dry NMP. Stirring was started and the flask was placed in a crushed ice-salt water bath and cooled to $-10$ to 5°C for 15 min. When this step was completed, 2.05 g (0.0101 mol) TPC was added slowly under constant stirring over a period of 0.5 h. Then, the cooling bath was removed and the polymerization temperature [of the polymerization reaction] was allowed to rise gradually to $-20$°C and maintained for 5 h with stirring. Afterwards, a clear, deeply yellow and highly viscous solution was obtained. After this period, stirring was continued for another 2 h at 70°C. Finally, the polymer solution was slowly poured into 200 mL of sodium hydroxide solution with rapid stirring to obtain a slightly yellow precipitate of polymer in fibrous form. The polymer was separated by filtration, and dried, crushed and washed for several times with hot water to remove possible residual NMP and inorganic salts. After the purified polymer was filtered, the solid powder was vacuum-dried at 100°C for at least 12 h up to constant weight.

#### 2.2.2.2 Synthesis of PASKA

The synthesis routing of PASKA was similar to that of PASSA described above. The polymerization reaction maintained for about 3 h at room temperature until the solution became a ceraceous solid. The solid was poured into water with rapid stirring. Yellow precipitate was gained. The purification procedure of the polymer is the same as that of PASSA.

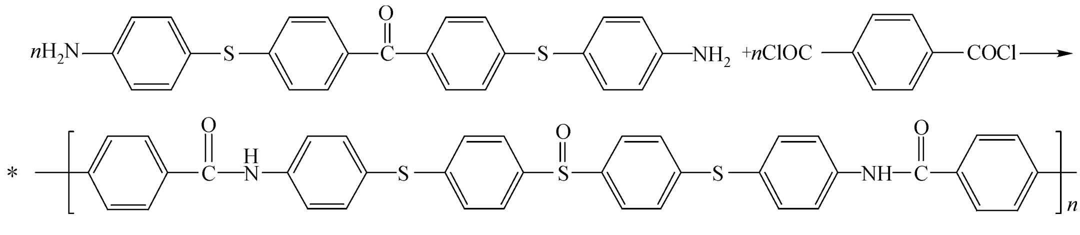
### 2.2.3 Polymers and monomers identification

Infrared spectra of the prepared polymers and monomers were measured on an infrared spectrophotometer (Nicolet-500 SX FT-IR). The samples were coated on KBr disks. All spectra were recorded within the wave number range of $4000-600\ cm^{-1}$ at 25°C. Nuclear magnetic resonance ($^1$H-NMR) analysis was carried out on a Varian INNOVA-400 NMR spectrometer for the monomers dissolved in dimethylsulfoxide.

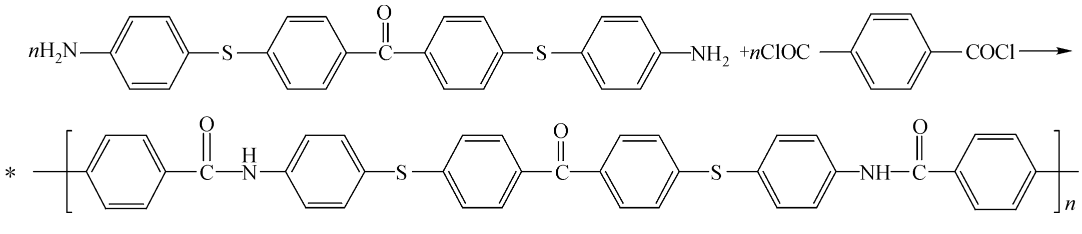
### 2.2.4 Polymers characterization

#### 2.2.4.1 Intrinsic viscosity

The intrinsic viscosity of the product was measured at 30 ± 0.1°C in NMP or $H_2SO_4$ solvent with 0.5 g of polymers



**Scheme 1** Synthesis of PASSA



**Scheme 2** Synthesis of PASKA

dissolved in 100 ml NMP or $H_2SO_4$ using a Cannon-Ubbelodhe viscometer and the result was obtained by the formula as below:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln\eta_r)}}{C}, \tag{1}$$

where $c$ is the concentration of solution, $\eta_{sp} = t/t_0 - 1$ and $\eta_r = t/t_0$.

#### 2.2.4.2 Solubility

The solubility of polymers in various amide solvents namely, DMF, DMAC, NMP, HMPA and common solvents was determined at 25°C and at solvent boiling temperatures, respectively.

#### 2.2.4.3 Characterization of aggregation structure

X-ray diffraction studies were conducted using X-ray diffractometer (XRD) (Philips X'pert Pro MPD).

#### 2.2.4.4 Thermal properties test

Differential scanning calorimetry (DSC) was performed with Dupont 2900 thermal analysis equipment, fitted with a cooler system using liquid nitrogen. It was calibrated with an indium standard and operated at a gas rate of 10 mL/min under nitrogen atmosphere. The heating rate of DSC measurement is 10 K/min. Thermogravimetric analysis (TGA) measurements were conducted using Dupont TA2100 thermal analysis equipment with a heating rate of 10 K/min at nitrogen atmosphere.

## 3 Results and discussion

### 3.1 Synthesis of monomers

The diamine monomers were prepared by nucleophilic aromatic substitution reaction utilizing 4-aminothiophenol as the nucleophile and DCDPS or 4,4'-difldibenzophenone as the activated aromatic halide. Various influences such as solvent, activator, materials ratio, reaction temperature and time were examined. The optimized reaction conditions can be summarized as follows: solvent is DMAc or DMF; reaction time is 5 h; charge ratio is $n$ (PATP):$n$(DCDPS/DFDPK):$n$(NaOH) = (1 − 2.2):(0.5 − 1):(1 − 2.2). Under this condition, the yield of the monomers can reaches 70%–85% and the purity is ~99%.

### 3.2 Synthesis of polymers

PASSA and PASKA had been synthesized by polycondensation reaction of diamine monomers with TPC in anhydrous NMP at low temperature. The basic reaction employed here is the Schotten–Baumann condensation of an aromatic acid chloride and a diamine, which is generally known to be fast and quantitative. Although, it could be expected that there is a competition between the growing polymer molecules and the solvent (NMP), the solvent is more basic than the polymeric product and the monomer to yield the products with high molecular weight. Through optimizing selection, the best reaction conditions were obtained. The viscosity of PASSA (in NMP) and PASKA (in concentrated sulfuric acid) under optimum conditions was determined to be 0.72 g/dL and 0.62 g/dL, respectively.

### 3.3 Polymers and monomers Identification [15–17]

The structure of the prepared monomers and polymers were proposed on the basis of their IR, UV and $^1$H-NMR spectra. Five groups of peaks are shown in the NMR spectrum of the monomers in Fig. 1. Each group splits into two peaks. The ratio of corresponding integral curves is 1 : 1 : 1 : 1 : 1, implying the symmetric disubstitution of the benzene ring. Combining the result of the FT-IR, these five groups of peaks are ascribed to the construction units of Ha, Hb, Hc, Hd and He. The chemical shifts ($\delta$) of monomers are listed in Table 1.

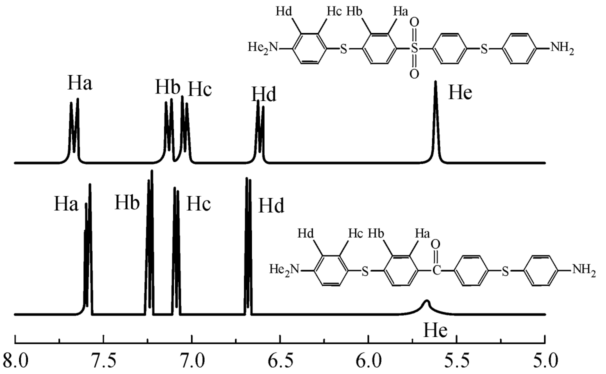


**Fig. 1** $^1$H-NMR spectra of BAPS and BAPK

**Table 1** Chemical shifts ($\delta$) of the monomers

| Chemical shifts $\delta$ | Ha | Hb | Hc | Hd | He |
|---|---|---|---|---|---|
| BAPS | 7.661 | 7.134 | 7.038 | 6.615 | 5.620 |
| BAPK | 7.577 | 7.225 | 7.074 | 6.667 | 5.656 |

Figures 2 and 3 show the FT-IR spectrum of PASSA, PASKA and the corresponding monomers. Comparing with the IR spectra of the polymers and monomers, it can be found that the absorption peaks has an obvious red shift. Detail analysis of these absorption peaks can prove the molecular structure of the polymers.

Figures 4 and 5 are the UV absorption spectra of the polymers and their corresponding monomers. It is obvious that there is a red-shift in the corresponding characteristic absorption peaks, which can be ascribed to the formation of long conjugate π bonds. According to the FT-IR and UV analysis results, it can be safely concluded that the structures of the polymers are in good agreement with the expected ones.

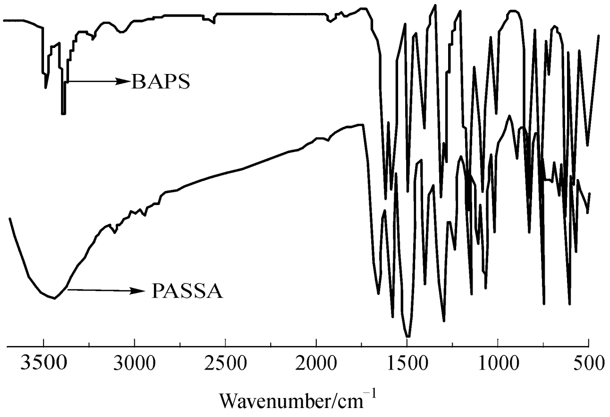


**Fig. 2** FT-IR spectrum of PASSA and corresponding monomer

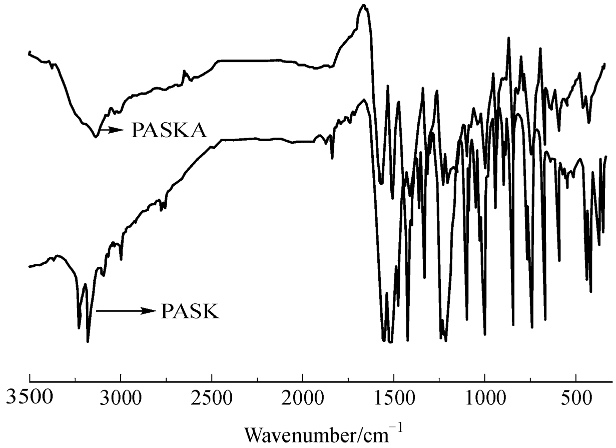


**Fig. 3** FT-IR spectrum of PASKA and corresponding monomer

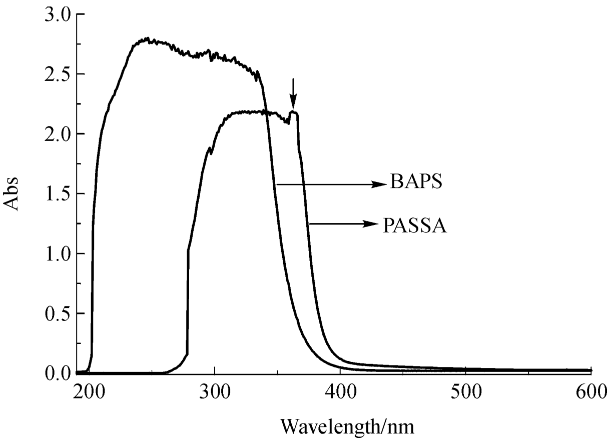


**Fig. 4** UV spectra for PASSA and BAPS

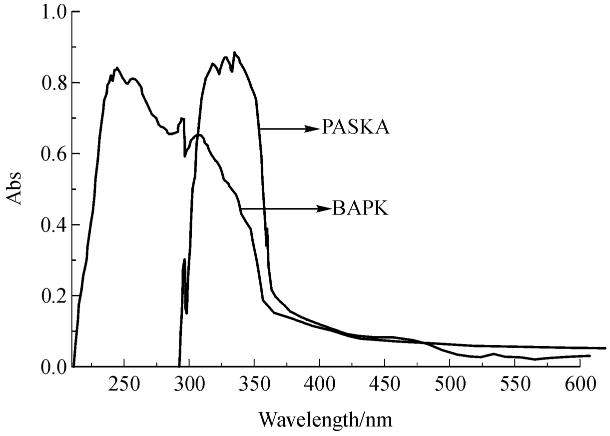


**Fig. 5** UV spectra for PASKA and BAPK

## 3.4 Polymer characterization

### 3.4.1 Solubility

It is well-known that poly(phenylene sulfide) (PPS) is insoluble in any solvent at normal temperature. Comparatively, PASSA and PASKA have better solubility than PPS, as shown in Table 2. PASSA can be soluble in NMP and concentrated sulfuric acid. Some organic polar solvents or mixed solvents can also partly dissolve PASSA and PASKA [2]. From the research of the dissolvability of PASSA and PASKA, it can be obviously confirmed that both PASSA and PASKA are kinds of resins with excellent chemical corrosion-resistant properties.

### 3.4.2 The thermal properties of PASSA and PASKA

Thermal properties of the polymers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are shown in Fig. 6 to Fig. 9 respectively. The glass transition temperature ($T_g$), the initial degradation temperatures ($T_i$), the maximum degradation rate temperature ($T_{max}$) and final degradation temperature ($T_f$) are listed in Table 3. Compared with PPS, PASSA and PASKA have better thermal properties. The $T_g$ of PASSA and PASKA are 274.9°C and 195.2°C, respectively, which are higher than that of PPS (around 85°C) [1]. The rest of the thermal properties of PASSA and PASKA are also much better than PPS, PPSS or PPSK [18–20].

### 3.4.3 The aggregation of PASSA and PASKA

X-ray diffraction patterns of the polymers were shown in Fig. 10. According to the X-ray diffraction result, it can be confirmed that the as-prepared PASSA and PASKA sample shows amorphous structure, which differ from the semicrystalline structure of PASA. The introduction of

**Table 2** Solubility behavior of PASSA and PASKA

| Agent | PASSA | | PASKA | |
|---|---|---|---|---|
| | 25°C | Refluxing temperature | 25°C | Refluxing temperature |
| Hydrochloric acid | insoluble | insoluble | insoluble | insoluble |
| Concentrated sulfuric acid | soluble | soluble | soluble | soluble |
| Acetic acid | insoluble | insoluble | insoluble | insoluble |
| Trifluoroacetic Acid | slightly soluble | slightly soluble | insoluble | insoluble |
| Acetone | insoluble | insoluble | insoluble | insoluble |
| Hexahydropyridine | insoluble | insoluble | insoluble | insoluble |
| Toluene | insoluble | insoluble | insoluble | insoluble |
| Chloroform | insoluble | insoluble | insoluble | insoluble |
| Dimethyl sulfoxide | insoluble | insoluble | insoluble | insoluble |
| Dimethyl formamide | slightly soluble | slightly soluble | insoluble | insoluble |
| Dioxane | insoluble | insoluble | insoluble | insoluble |
| Phenol + dichloroethane | slightly soluble | slightly soluble | insoluble | slightly soluble |
| NMP | soluble | soluble | insoluble | slightly soluble |

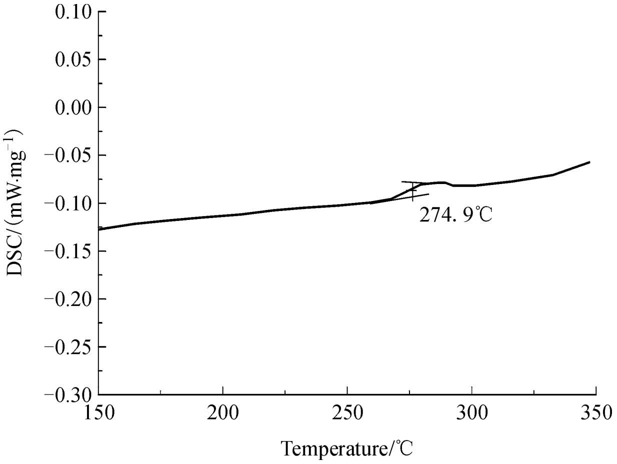


**Fig. 6** DSC analyses of PASSA

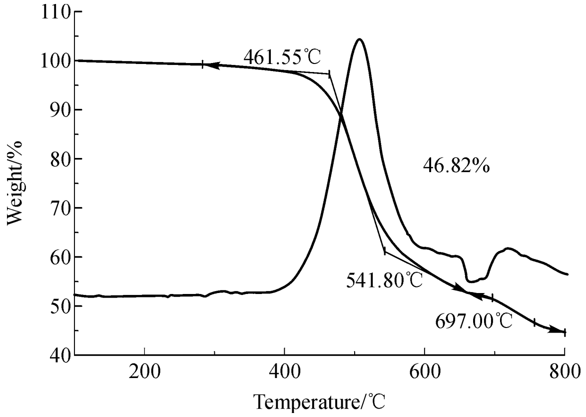


**Fig. 8** TGA weight loss behavior of PASSA

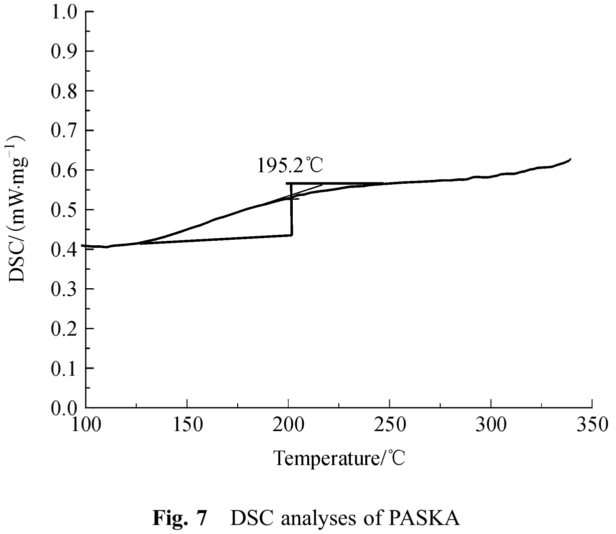


**Fig. 7** DSC analyses of PASKA

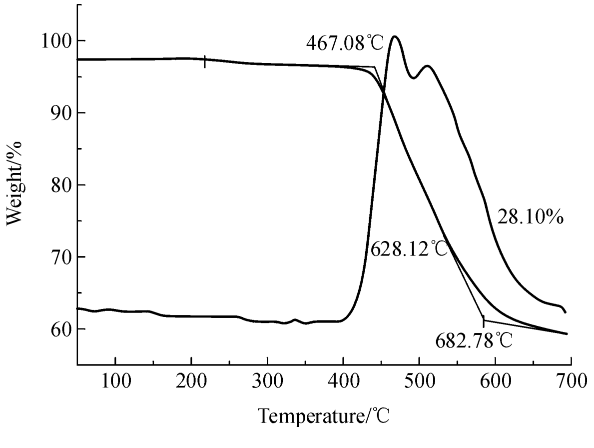


**Fig. 9** TGA weight loss behavior of PASKA

**Table 3** Thermal properties of PASSA and PASKA

| Polymers | $T_g$ | $T_i$ | $T_{max}$ | $T_f$ |
|---|---|---|---|---|
| PASSA | 279.9 | 461.55 | 541.80 | 697.00 |
| PASKA | 195.2 | 467.08 | 529.12 | 592.78 |

Note: $T_i$ is the initial degradation temperature, $T_{max}$ is the maximum degradation rate temperature and $T_f$ is the final weight lost temperature.

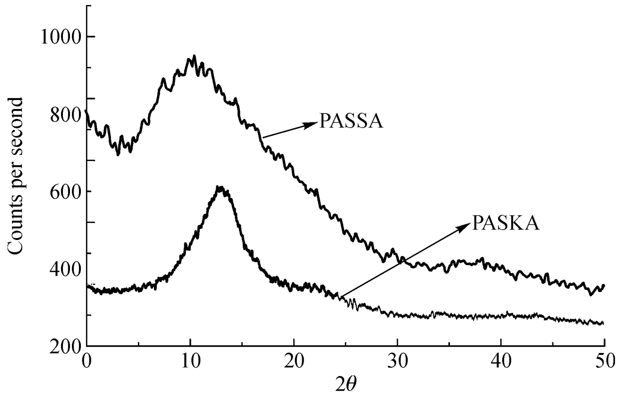


**Fig. 10** XRD spectra of PASSA and PASKA

polar sulfone or ketone groups may be responsible for the change in the aggregation.

## 4 Conclusion

In this paper, high molecular weight PASSA and PASKA were prepared by an amidation reaction at low temperature, which is different from other studies which were conducted at high temperatures. Through optimizing the polymerization conditions, such as solvent, molar ratio, reaction time and temperature, the best reaction conditions were obtained. The viscosity of under optimum conditions was 0.75 g/dL for PASSA and 0.62 g/dL for PASKA. The X-ray diffraction revealed that the as-prepared PASSA and PASKA samples are amorphous. Benefiting from their high glass transition temperatures and good corrosion resistance, these polymers maybe used as high performance engineering plastics. The disadvantage of these polymers is their poor fluidity which may cause difficulty in processing and probably limit their application.

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