#### Polymer 52 (2011) 1013-1018

Contents lists available at ScienceDirect

# Polymer

journal homepage: www.elsevier.com/locate/polymer

# Thermal cross-link behavior of an amorphous poly (para-arylene sulfide sulfone amide)

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#### ARTICLE INFO

Article history: Received 13 September 2010 Received in revised form 10 December 2010 Accepted 1 January 2011 Available online 9 January 2011

Keywords: Poly (para-arylene sulfide sulfone amide) Thermal curing Cross-link behavior

# ABSTRACT

Cross-link behavior of an amorphous poly (para-arylene sulfide sulfone amide) synthesized via low temperature solution polycondensation was observed for the first time, when the polymer was subject to a series of thermal curing at 260 °C in air condition. The formation of cross-link network was demonstrated by the DSC and TGA results that  $T_g$  of the polymer enhanced from 259.17 °C to 268.89 °C, and the 1% weight loss temperature increased remarkably from 243.75 °C to 345.87 °C. EPR analysis further suggested that two kinds of free radicals, CO• and C•, induced by thermal curing were responsible for this cross-link behavior. According to FT-IR spectrum, the origin of these free radicals was confirmed as amide C==O group in the polymer backbone. The cross-linking type was attributed to conventional radical cross-link reaction and the cross-link mechanism was discussed in detail subsequently.

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## 1. Introduction

Poly (phenylene sulfide) (PPS) is a semi-crystalline thermoplastic engineering polymer, which has attracted much attention from researchers due to its excellent mechanical properties, good solvent resistance, high temperature resistance and so on [1-10]. As a structurally modified material of PPS, an amorphous poly (arylene sulfide sulfone amide) (PASSA) was synthesized via low temperature solution polycondensation in our laboratory [11]. It possesses the desirable dimensional stability and chemical resistance of PPS as well as the high strength of polyamide (PA); in addition, it has higher glass-transition temperature than PPS which makes up for the disadvantage of PPS. PASSA is soluble in some polar solvents due to its improved solubility compared to PPS, such as N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF), but it still has much higher chemical resistance than PA. The superior characteristics of PASSA make it valuable and potentially applicable in polymer electrolyte membranes, composite bipolar plates, conductive materials, surface mounted devices, vehicle sensors and so on [12-15].

Thermal behavior is one of the most significant characteristics of polymers due to its crucial influence in application. So it is of great importance to understand the changes in chemical structures and

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physical properties, which may occur during thermal histories. In recent years, a large number of experimental data have established the thermal properties of PPS [16–19]. Gies et al. [20] reported that PPS thermal curing in the presence of oxygen leaded to oxygen uptake in the form of sulfoxides in the PPS backbone. Perng [21] researched the mechanism and kinetic model for thermal decomposition behavior of PPS by stepwise pyrolysis/gas chromatography/ mass spectrometry and thermogravimetry analysis/mass spectrometry techniques. However, there were few literatures that discussed the thermal properties of amorphous structurally modified materials of PPS. Wang [22] studied the thermal degradation of poly (phenylene sulfide sulfone) (PPSS) by thermogravimetric analysis, and suggested the reaction mechanism was a Dn deceleration type. It is not yet clear about the thermal behavior before degradation of these amorphous polymers. For the purpose of theoretical research and application, it is necessary to study the thermal properties of this PASSA resin.

In our previous work, the effect of annealing treatment on meta-PASSA in nitrogen atmosphere was studied [23]. The result showed that decarboxylation of the terminal carboxylic acid group occurred during the annealing treatment, and annealed *m*-PASSA exhibited different thermal properties compared to the untreated one. However, no cross-link behavior of the polymer was discovered in this work.

In the recent study, we present experimental results on thermal curing of para-PASSA in air condition. Our aim is to learn the thermal property of this polymer and the changes of chain





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structure in different thermal histories. Thermal cross-link behavior of the polymer is demonstrated for the first time via the enhancement of glass-transition temperature and 1% weight loss temperature. Amide C=O group in the polymer backbone produces two kinds of free radicals which are responsible for this cross-link behavior, and the reaction mechanism is discussed.

# 2. Experimental

# 2.1. Materials

4,4'-Dichloro diphenyl sulfone (DCDPS) was supplied by Jinsheng Chemical Reagents Company (Huaian, China). 4-Aminothiophenol was acquired from Shouerfu Chemical Reagent Corporation (Jinyun, China). 1,4-Benzenedicarbonyl chloride was purchased from Lianda Chemical Reagent Corporation (Nanchang, China). Sodium hydroxide (NaOH) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were gained from Changlian Chemical Reagent Corporation (Chengdu, China). *N*,*N*-dimethylformamide (DMF) and anhydrous alcohol were obtained from Kelong Chemical Reagent Corporation (Chengdu, China). *N*-methyl-2-pyrrolidone (NMP) was provided by Jinlong Chemical Industry Company (Nanjing, China). All the above chemicals were commercial products and used as received.

#### 2.2. Synthesis of p-PASSA

The monomer, 4,4'-bis(4-aminophenylthio) diphenyl sulfone, was synthesized using DCDPS via an aromatic nucleophilic substitution reaction. The typical reaction condition was at 150  $^{\circ}$ C in nitrogen atmosphere.

The synthesis of para-PASSA was performed following the polycondensation method in a glass batch reactor. The proper amounts of 4,4'-bis(4-aminophenylthio) diphenyl sulfone and appropriate 1,4-benzenedicarbonyl chloride with a molar ratio of 1.01/1.00 were charged into the reaction tube of the polycondensation apparatus. The reaction mixture was dissolved in NMP at freezing temperature remaining for hours [11]. The product was washed repeatedly with hot water and then dried at 120 °C for 48 h. The synthesis route is shown in Fig. 1.

#### 2.3. Preparation of the p-PASSA membranes

The *p*-PASSA membranes were prepared by dissolving the polymer powders in NMP, and then casting the solution on microscopy slides directly. The films were subsequently dried in an oven at 80 °C for 24 h to remove the residual solvent.

#### 2.4. Thermal curing

The prepared polymer (powder or membrane) was subject to a series of thermal histories by being heated at 260 °C for 2 h, 6 h and 10 h, respectively, in air, oxygen and nitrogen environment, followed



The synthesis route of monomer 4,4'-bis(4-aminophenylthio) diphenyl sulfone



The synthesis route of p-PASSA

Fig. 1. Schematic illustrations of synthesis route of *p*-PASSA.



by the cooling in air until the temperature drops to the indoor one. The samples for ESR measurement should be quenched into ice water after the treatment to freeze the unreacted free radicals.

#### 2.5. Thermal property measurements

Differential scanning calorimetry (DSC) was performed using the NETZSCH DSC 200 PC thermal analysis equipment with polymer powders, fitted with a cooler system using liquid nitrogen. It was operated at a gas rate of 10 ml/min in nitrogen atmosphere. The heating rate of DSC measurement was 10 °C/min.

Thermogravimetric analysis (TGA) measurements were conducted using the TGA Q500 V6.4 Build 193 thermal analysis equipment with a heating rate of 10 °C/min in nitrogen atmosphere.

# 2.6. Characterization of the polymer structure and molecular weight

Fourier-transform infrared (FT-IR) spectroscopic measurements were characterized by examining thin, homogeneous membranes in the NEXUS670 FT-IR instrument.

Nuclear magnetic resonance (<sup>1</sup>H NMR) instrument was used to provide the chain structure with a BRUKER-400 NMR Spectrometer. The samples were dissolved in deuterated dimethyl sulfoxide.

X-ray diffraction (XRD) analyses were carried out with a Philips electronic instrument (X'pert Pro MPD) using Cu–Ka radiation at 40 kV and 150 mA with scanning from 0° to 50°.

Molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 515 Isocratic HPLC pump, a Waters 2414 refractive index detector, GPC measurements were carried out at 60 °C using DMF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards.

#### 2.7. Characterization of free radicals

Electron Paramagnetic Resonance (EPR) measurements were conducted at 15 °C on an X-band JEOL JES-FA200 EPR spectrometer, and operated at a 9.4 GHz modulation field with microwave power of 1 mW. When the microwave power saturation method was used, the microwave power was changed from 0.04 mW to 49 mW. The radical concentration was characterized by the ESR spectrum intensity compared to a standard sample of weak pitch. The sample powders or membranes (18.5  $\pm$  0.2 mg) were examined in a quartz cell.

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Chemical shifts	<i>(δ)</i>	of the	monomer.

 Chemical shifts δ (ppm)
 Ha
 Hb
 Hc
 Hd
 He

 BAPS
 7.661
 7.134
 7.038
 6.615
 5.620



Fig. 3. FT-IR spectrum of p-PASSA before curing (black line), and after curing in air at 260 °C for 10 h (dash line).



**Fig. 4.** Wide-angle X-ray diffraction of *p*-PASSA before curing (black line), and after curing in air at 260 °C for 10 h (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

# 3. Results and discussion

#### 3.1. Structure and molecular weight characterization

The chemical structures of monomer and polymer were characterized with <sup>1</sup>H NMR and FT-IR spectrometer. <sup>1</sup>H NMR spectra for 4,4'-bis(4-aminophenylthio) diphenyl sulfone (BAPS) is shown in Fig. 2 and details are tabulated in Table 1. Five groups of peaks appear in the NMR spectrum, and the ratio of corresponding integral curves is 1:1:1:1:1, which implies the symmetric disubstitution of the benzene ring. This structure can also be verified by the representative FT-IR spectrum of the polymer (Fig. 3).

The presence of sulfuryl S=0 stretch in the backbone of the polymer is indicated by absorption at  $1313 \text{ cm}^{-1}$  and  $1155 \text{ cm}^{-1}$  [24], and the broad band in the  $3245-3341 \text{ cm}^{-1}$  region corresponds to the N–H stretch [25,26]. The absorption peaks around 763 cm<sup>-1</sup> and 827 cm<sup>-1</sup> are attributed to the C–H out of plane stretch of 1,4-disubstituted benzene, which indicate a linear or 1,4-conjugated phenyl structure. This fact is in agreement with Wang's work on synthesis of poly (phenylenesulfidephenylenamine) by self-polycondensation of methyl-(4-anilinophenyl) sulfide [27].

The aggregative structure of *p*-PASSA was determined by the XRD analysis. The presence of strong polar O=S=O bonds in a repeated unit of the polymer backbone imparts a highly amorphous character to the polymer as is evident from the presence of a broad amorphous diffraction peak (Fig. 4) [28]. The position of a quite wide peak in the range of 15–25° is taken as a measure of the most probable intersegmental spacing [29], and the narrow peak of *p*-PASSA after curing compared to the untreated one results from the reduction of distances among molecules.

Molecular weight of the polymer was determined by GPC analysis with  $M_n$  value of 59,565, and  $M_w$  value of 215,930.

## 3.2. TGA measurements

TG and DTG curves of the polymer, measured in nitrogen, are presented in Fig. 5 and details are listed in Table 2. The onset degradation temperature is as high as 456.37 °C, which is a good indication of the polymer thermal stability.

The comparison in Table 2 indicates that thermal stability of the polymer is improved after curing. The 1% weight loss temperature rises remarkably from 243.75 °C to 345.87 °C, and weight loss at 800 °C decreases by about 2%. The mass loss is due to the elimination of volatile species from the polymer. The low 1% weight loss temperature of *p*-PASSA before treatment implies that some volatiles and low molecular weight oligomers are contained in the samples [30]. The enhanced temperature of 1% weight loss and reduced weight loss at 800 °C after curing suggest that thermal cross-link behavior of the polymer could exist and the oligomers are efficiently incorporated into the cross-linked structure during the treatment process. To identify the existence of cross-link behavior, DSC measurements were employed as described below.

#### 3.3. DSC measurements

Fig. 6 represents the DSC curves of *p*-PASSA samples which were subject to different thermal histories. The endothermic peaks



Fig. 5. TG and DTG curves of *p*-PASSA before curing (a), and after curing in air at 260 °C for 10 h (b) heated at 10 °C/min in nitrogen.

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#### Table 2

Thermal properties of *p*-PASSA: results of TGA measurements.

Samples	1% weight loss temperature (°C)	Onset degradation temperature (°C)	Maximal degradation temperature (°C)	Weight loss at 800 °C (%)
p-PASSA before curing	243.75	456.37	490.69	59.12
p-PASSA after curing	345.87	457.84	490.84	57.54



Fig. 6. DSC thermograms of p-PASSA before curing (a), and after curing in air at 260 °C for 10 h (b) measured with a 10 °C/min heat-cool-heat cycle in nitrogen.

revealed in the scans are attributed to the glass transition of the polymer [23]. In Fig. 6a, the  $T_g$  value increases by nearly 4 °C in the second heating curve. This is indicative of curing and indicating the presence of cross-link structure [31]. After thermal curing at 260 °C for 10 h in air, the  $T_g$  value increases from 259.17 °C to 268.64 °C (Fig. 6b), and the  $T_g$  values in the first and second heating curves are almost the same. This fact implies that the cross-link structure has already formed. Furthermore, the second sample was put in a vial with ~3 mL of NMP. After 1 week, the sample was not dissolved in the solvent. This also illustrates that thermal curing has occurred to a sufficient extent to form the cross-link material.

#### 3.4. EPR measurements

EPR analysis is used to identify the generation of free radicals [32], and confirm the cross-link reaction type. The effect of thermal curing on *p*-PASSA powders in a time span of 0-10 h was studied by using the EPR spectrum. As it can be seen from Fig. 7, a typical single line shape (g = 2.0023) is exhibited in the spectrum. R<sub>1</sub> is used hereinafter to represent this kind of free radicals. A comparison of



Fig. 7. EPR spectrum of p-PASSA samples for different thermal curing times at 260 °C in air.

the line feature clearly shows an enhancement of the peaks with the increase of curing time, which indicates a rise of  $R_1$  free radical concentration.

The variation of radical concentration with time is shown in Fig. 8. The curve of concentration versus treatment time can be divided into three stages. The first 3-h is a stage of activating free radicals. In this stage, free radicals have little chance to impact each other, which is caused by their few existences, so the concentration rises with time linearly from  $0.007 \times 10^{13}$  spins mg<sup>-1</sup> to  $4.36 \times 10^{13}$  spins mg<sup>-1</sup>. The radicals increase slightly in the next stage from 3 to 6 h, only from  $4.36 \times 10^{13}$  spins mg<sup>-1</sup> to  $6.62 \times 10^{13}$  spins mg<sup>-1</sup>. It is considered that the free radicals are initiated and consumed via the cross-linking reaction in this stage [33]. The rate of radical generation is only a little above the rate of consumption, which results in the mildly rise of concentration. When the treatment time is above 6 h, the concentration enhances linearly again. It is inferred that a network structure has already formed in this stage, and the free radicals produced are not consumed anymore. This fact corresponds to the DSC result at the same curing temperature.

From the line shape in Fig. 7 one can see that the left side of the peak is a little wider than the right one, which is highlighted by an



Fig. 8. Concentration of R1 free radicals vs. time of thermal curing.



**Fig. 9.** EPR spectrum of *p*-PASSA samples cured in air at 260 °C for 10 h with different power.



Fig. 10. Schematic illustrations of EPR signals at different microwave power: (a) 2 mW; (b) 36 mW.

arrow. It is possible that another weak peak  $(R_2)$  covered by  $R_1$  exists, so the microwave power saturation method is employed to confirm and differentiate them [34].

With the increase of microwave power in Fig. 9a,  $R_2$  signal appeared gradually, which could be observed in the amplifying signal of 8 mW (Fig. 9b). Due to the few number of  $R_2$  free radicals, the  $R_2$  signal is so weak that covered the  $R_1$  signal. Meanwhile, the EPR signal enhanced to maximum at 2 mW, and then weakened gradually. The variations of signal intensities are attributed to the saturated characteristic of  $R_1$  radicals [33], which is easily saturated by microwave power at a level around 2 mW. The phenomenon that left side of the peak widened with the increase of power could be explained by the existence of  $R_2$  free radicals. As shown in Fig. 10, the EPR signal is the superposition of  $R_1$  (blue line) and  $R_2$  (red line). When microwave power grows above 2 mW,  $R_1$  signal is saturated and weakens gradually. However,  $R_2$  signal does not saturate with power easily, which increases slightly in the power range (Fig. 10b).

In conclusion, the different saturated characteristics of  $R_1$  and  $R_2$  are the reason for broadened left side of the peak in EPR signals.

The phenomenon that EPR signal enhanced with the increase of thermal curing time suggested that  $R_1$  may be oxygen free radicals because of the treatment environment in air. In order to analyze the origin of these free radicals, a group of contrast experiments were carried out in  $N_2$ , air and  $O_2$  atmosphere, respectively, with a thermal curing at 260 °C for 10 h.

A comparison of the three signals in EPR spectrum (Fig. 11a) clearly shows that the radical concentration produced in  $N_2$  is much lower than that in air, and close to the untreated one, meanwhile  $O_2$  environment induces the highest radical concentration. Fig. 11b is the amplifying signal of the sample cured in  $N_2$ , from which one can see that the  $R_1$  signal decreased sharply due to the curing environment, and  $R_2$  signal is clearer in this picture (highlighted by an arrow). So it is considered that the production of  $R_1$  and  $R_2$  is closely related to  $O_2$ , and  $R_1$  could be RO• free radicals.



Fig. 11. EPR spectrum of *p*-PASSA samples cured in different atmosphere at 260 °C for 10 h.



Fig. 12. Schematic illustrations of the cross-link reaction process.

According to the FT-IR spectrum of the polymer (Fig. 3), an obvious decrease in the amide C=O peak at 1644  $\text{cm}^{-1}$  after curing is observed, which coincides with our inference. Therefore it can be concluded that the origin of  $R_1$  and  $R_2$  is the amide C=O group. Combined with EPR analysis it is reasonable that R<sub>1</sub> are CO• free radicals, and R<sub>2</sub> are C• free radicals. The cross-linking reaction mechanism is suggested as below.

#### 3.5. Possible reaction mechanism of cross-link

Based on the research hereinbefore, the thermal cross-link behavior of *p*-PASSA could be explained by the following mechanism.

The double bonds of amide C=O are opened when they are subject to thermal curing in air, and two kinds of free radicals, C• and CO•, are produced consequently. With the effect of O<sub>2</sub>, most C• are transformed into CO• free radicals, which causes the higher concentration of R<sub>1</sub> than R<sub>2</sub>. The cross-linking network was formed afterward which was induced by these two kinds of free radicals. The cross-linking reaction type belongs to conventional radical cross-link reaction, and the reaction process is shown in Fig. 12.

## 4. Conclusions

An amorphous *p*-PASSA was synthesized via low temperature solution polycondensation. The polymer with high glass-transition temperature (259 °C) and thermal stability suggests a potential use in heat-resistant materials.

We have demonstrated, for the first time, the thermal cross-link behavior of the polymer at 260 °C in air condition. The results showed that the formation of cross-link network enhanced the  $T_{\sigma}$ from 259.17 °C to 268.89 °C, and the 1% weight loss temperature of the polymer increased remarkably from 243.75 °C to 345.87 °C. Two kinds of free radicals, CO• and C•, existed in the polymer, and concentration of the former was much higher than that of the latter. These two kinds of free radicals were responsible for the intermolecular cross-linking behavior. The cross-linking type was attributed to conventional radical cross-link reaction, and the reaction mechanism was also suggested.

This cross-linkable polymer represents a new class of super engineering plastic with great thermal stability. Further investigations regarding the processing and mechanical properties of this material are in active progress and the results will be presented in our future articles.

#### Acknowledgements

This work is financially supported by the National High Technology Research and Development Programme of China (863 program) with the project No. 2007AA03Z561. We would like to express our sincere thanks to Dr. Guodong Li of Jilin University for his kind assistance in Electron Paramagnetic Resonance (EPR) measurement.

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