

SYNTHESIS AND MORPHOLOGICAL STRUCTURE OF POLY(PHENYLENE SULFIDE AMIDE)

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ABSTRACT

Poly (phenylene sulfide amide) (PPSA) has been synthesized by using sulfur as S source which reacts with dichlorobenzamide (DCBA) and alkali in polar organic solvent at the atmospheric pressure. The polymer structures were determined by elemental analysis, FT-IR and $^1\text{H-NMR}$. It is shown that the yielded polymer has linear structure and its structure unit is $-\text{p-C}_6\text{H}_4\text{-CONH}-\text{p-C}_6\text{H}_4\text{-S}-$. The polymer morphology was studied by X-ray diffraction and polarized microscopy. The results show that PPSA is a crystalline polymer and its spherulites are the aggregation of nontwisting lamella or micro-thread structure. Under shearing force, these crystals are dispersed to form micro-fibrillar structure. The decomposition kinetics of PPSA was also studied at different heating rates. The decomposition energy of PPSA is higher than that of PPS.

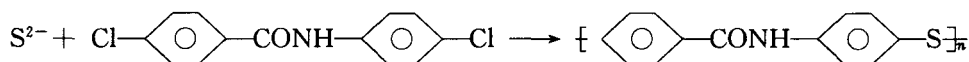
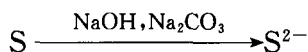
INTRODUCTION

Poly (phenylene sulfide amide) is a new polymer of poly (phenylene sulfide) (PPS) family. It has good comprehensive properties and processibility. The syntheses of PPSA by using Na_2S as S source were reported^[1-3]. To omit the time-consuming dehydration process of sodium sulfide, a new preparing route for the synthesis of PPSA by using sulfur as S source in polar solvent which reacts with dichloro-benzamide (DCBA) and alkalis, and the characterization of the polymer are reported in this paper. The aggregative morphology of PPSA was studied by X-ray diffraction and

under polarized microscope in the present work. The decomposition kinetics of PPSA was also studied at different heating rates, The decomposition energy is higher than that of PPS.

EXPERIMENTAL

1. Preparation of PPSA



Into a tri-necked flask fitted with a stirrer and a reflux condenser, solvent N-methyl-pyrrolidone (NMP) was added. Under heating and stirring, S, NaOH, Na₂CO₃, DCBA and catalysts were charged successively. The flask was heated below 200°C for 6 hours. At the end of reaction, the contents were cooled to 120°C and then poured into cold water. The yielded polymer was precipitated. It was recovered by filtration through a glass funnel and washed several times with deionized water and acetone, and then dried in an oven. After milled, the polymer was purified by extraction with deionized water and acetone for 24 hours and dried in vacuum oven.

2. The analysis and determination of polymer

Viscosity measurement: NMP with LiCl on weight ratio 95 : 5 as a solvent. The reduced viscosities were measured at 30 ± 0.05°C with polymer concentration of 0.1g/100ml.

Elemental analysis: C, H, N, O were determined by Carlo Erba Elemental analyzer; S was analyzed by combustion in triangular flask followed by ion chromatograph.

FT-IR Spectra were recorded on a Nicolet 170SX FT-IR Spectrometer.

Nuclear Magnetic Resonance Spectra were obtained on a JNX-FX90Q FT-NMR spectrometer by using (CD₃)₂SO as a solvent and TMS as reference compound.

X-ray diffraction spectra were obtained on Rigaku Model 3014 X-ray diffractometer.

Cross polarized microscope (CPM) determination: The polymer samples were heated on a heating plate in a PHMK model CPM up to 320°C

for 5 hours then cooled to 15°C. The photos were taken on a XPT-7 model CPM.

Thermogravimetric analysis (TGA) with heating rate 5, 10, 15, 20°C/min and differential scanning calorimetric (DSC) data were measured on a Du Pont 1090 TGA and a Perkin-Elmer 7 DSC in N₂, respectively.

RESULTS AND DISCUSSION

1. Synthesis and chain structure

In the above-mentioned reaction conditions, the polymers obtained have the reduced viscosities of $\eta_{\text{red}} > 0.18$ dl/g, a little higher than that of the polymer synthesized with Na₂S as S source^[2]. The results of elemental analysis are: C: 67.86 ~ 68.01%, H: 3.64 ~ 3.89%, N: 6.09 ~ 6.17%, O: 7.14 ~ 7.36%, S: 13.64 ~ 13.86%. The calculated data are: C: 68.72%, H: 3.96%, N: 6.17%, O: 7.00%, S: 14.10%. Obviously, the determination data coincide with the calculated data.

Figs. 1 and 2 are the IR spectra of DCBA and PPSA respectively. The spectrum in Fig. 2 is the same as that of PPSA made from Na₂S and DCBA. Comparing the Figs. 1 and 2, we found:

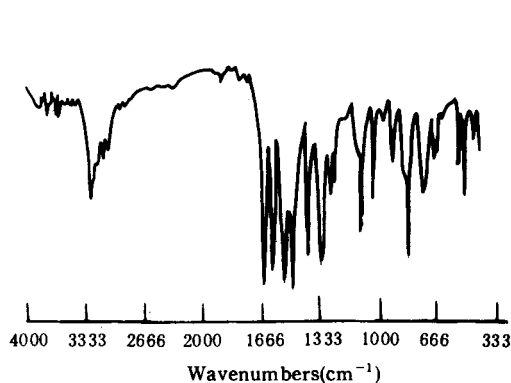


Fig. 1 FT-IR spectrum of DCBA

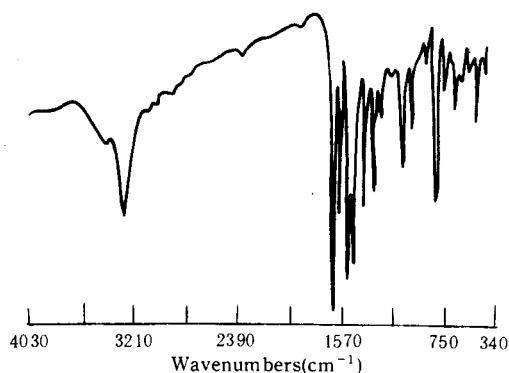


Fig. 2 FT-IR spectrum of PPSA

(1) There are absorption peaks at 3100 ~ 3250 cm⁻¹ (V_{N-H}) and 1630 ~ 1690 cm⁻¹ (V_{C=O}) in both DCBA and PPSA spectra;

(2) There are absorption peaks at 820 ~ 830 cm⁻¹ for para-disubstituted benzene in both spectra;

(3) The absorption peak at 736 cm^{-1} for C—Cl in DCBA spectrum disappeared in the PPSA spectrum. But the weak absorption peak at $1010\sim 1100\text{ cm}^{-1}$ for C—S in PPSA was not observed, because the absorptions of other groups in PPSA also appeared at this region which covered the absorption of C—S bond.

Fig. 3 is the ^1H -NMR spectrum of PPSA. There are a group peaks at $\delta\ 7.3\sim 8.4\text{ ppm}$ and a peak at 10.4 ppm . The intensity ratio between the group and the peak is $8:1$ and it can be assigned to eight H atoms in the two benzene nuclei and one H atom in —NH group.

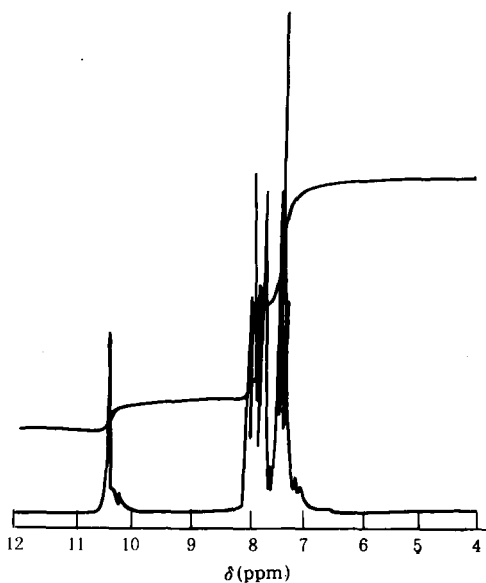


Fig. 3 ^1H -NMR spectrum of PPSA

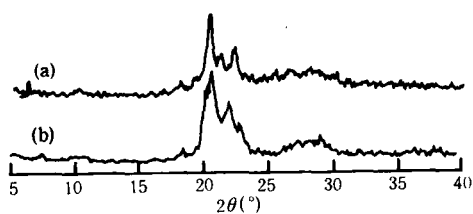


Fig. 4 X-ray diffraction spectra of PPSA
(a) PPSA-20 (Na_2S as S source)
(b) PPSA-40 (S as S source)

2. Aggregation morphology

Fig. 4 shows that PPSA samples from different S sources appear the same X-ray diffraction spectra. The intensive diffraction peak indicates that PPSA is a crystalline polymer.

Figs. 5 and 6 are the cross polarized photographs of PPS and PPSA respectively. From the photographs, we can observe that PPS does not obviously appear to be crystalline aggregation, while PPSA shows obvious crystalline aggregation in the same conditions. The spherulites of PPSA are

constituted by non-twisting lamellae (a) or fine-thread structure (b).

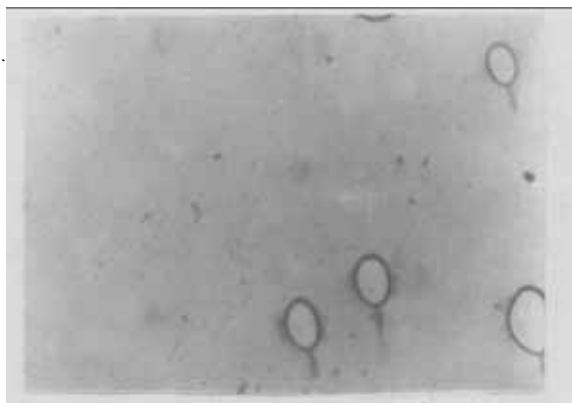


Fig. 5 Cross polarized photograph of PPS ($\times 50$)

Fig. 6 (a) shows that the direction of chain lamellae are parallel to the radius direction of spherulites, the widths of lamellae being $10 \sim 20 \mu\text{m}$. Under shearing force, the fine-thread aggregation becomes micro-fibrillar structure as shown in Fig. 7. The diameter of micro-fibrils is about $5 \mu\text{m}$.

According to the photographs, the crystallization rate of PPSA is faster than that of PPS. From the fact that the micro-fibrillar structure is present in PPSA, we postulate that PPSA has possessed higher mechanical strength by self-reinforcement.

The formation of nontwisting lamellar structure or micro-fibrillar structure may be explained by the higher rigidity of PPSA molecular chain and formation of H-bonds with the strong polarity of amide groups.

3. Thermal analysis and decomposition kinetics of PPSA

Fig. 8 is the TGA curve of PPSA. The initial and maximum decomposition temperatures were found to be 300°C and 447°C , respectively.

From DSC curve in Fig. 9, the melting point (T_m), glass transition temperature (T_g) and melting enthalpy (ΔH_m) of PPSA were obtained. The results are: $T_m = 294 \sim 304^\circ\text{C}$, $T_g = 104 \sim 107^\circ\text{C}$ and $\Delta H_m = 107 \text{ J/g}$, respectively.

According to the thermal decomposition rate equation:

$$\frac{dc}{dt} = kf(c) \quad (1)$$

We can obtain the following equation^[4]:

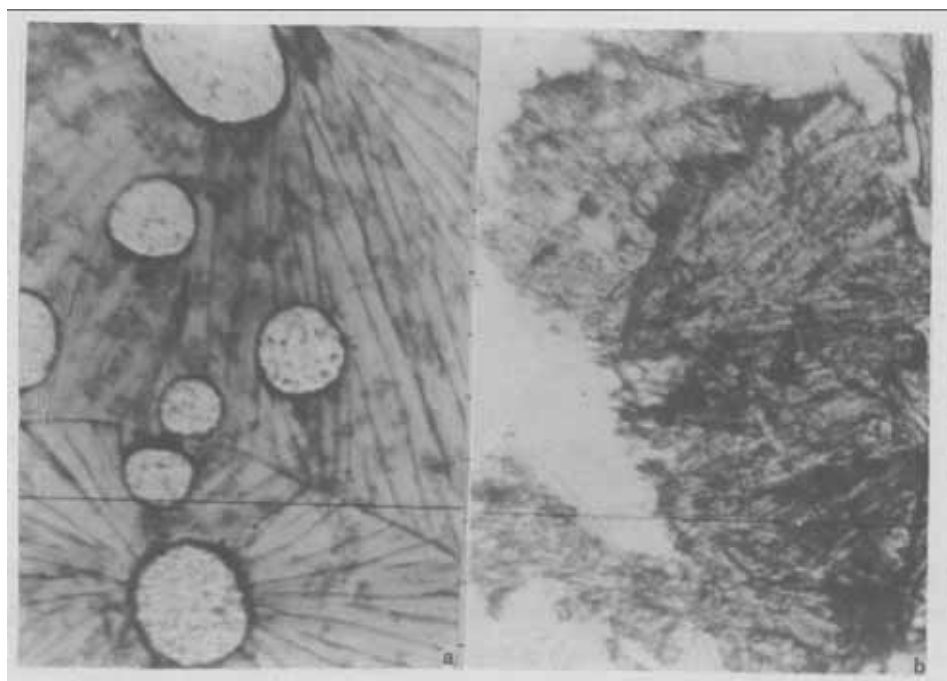


Fig. 6 Cross polarized photograph of PPSA ($\times 100$)

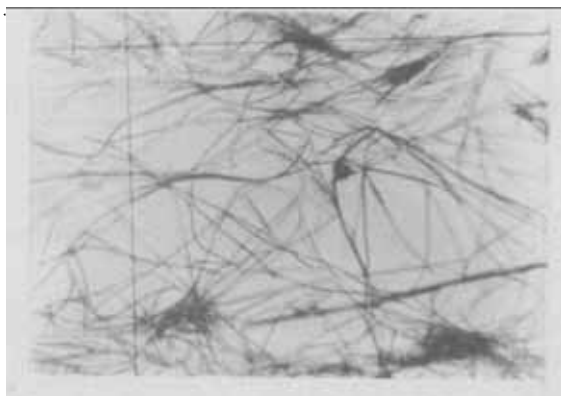


Fig. 7 The micro-fibrillar structure of PPSA ($\times 100$)

$$\lg \beta = \lg \frac{AE}{Rf(c)} - 2.315 - \frac{0.457E}{RT} \quad (2)$$

In the Eq. (2), β is the heating rate ($^{\circ}\text{C}/\text{min}$); A is the pre-exponential factor of decomposition (S^{-1}); E is activation energy of decomposition

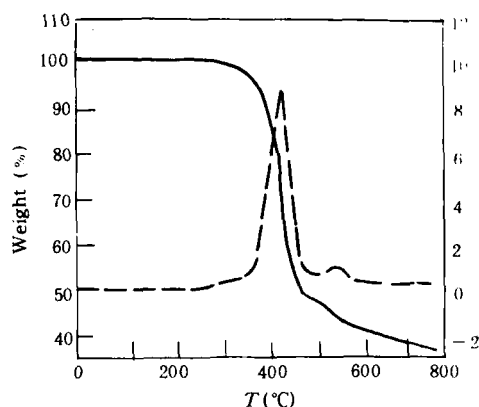


Fig. 8 The TGA curve of PPSA

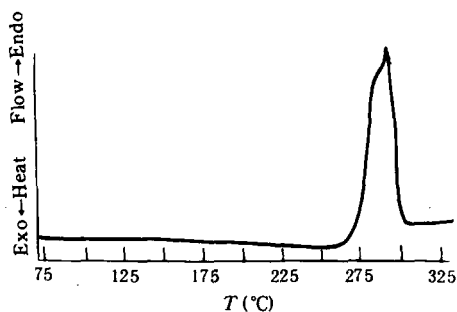


Fig. 9 The DSC curve of PPSA

(J/mol); R is gas constant (8.314 J/mol. K). The $f(c)$ is a function of degree of conversion (weight loss) which relies on the type of reaction or reaction mechanism, for a given reaction system it is a constant. For one sample, the plots of $\lg \beta$ versus $1/T$ should be straight lines according to Eq. (2). From the slope of the straight line E can be obtained.

Through mathematical transformation, some other kinetic parameters can also be obtained, such as half life:

$$t_{\frac{1}{2}} = \frac{\ln(1/2)}{K(T)} \quad (3)$$

From Eq. 3, the 60 second half-life temperature can be calculated.

$$T_{t_{\frac{1}{2}}=60} = \frac{E}{R \cdot \ln[\ln(1/2)/t_{\frac{1}{2}} \cdot A]} \quad (4)$$

These calculations can be performed by programmed computer connected with thermal analysis instruments.

By different heating rates, the parameters of decomposition kinetics of PPSA are calculated and the results are listed in Table 1.

It can be seen that when the conversion approaches to 25%, the data of decomposition energy become almost constant.

The thermal decomposition kinetics of PPS has been reported in our previous paper^[4]. For PPS, the decomposition energy is about 85.7~95.7 kJ/mol, less than that of PPSA. So the thermal stability of PPSA is higher than that of PPS.

Table 1 The parameters of decomposition kinetics of PPSA

Conversion(%)	E (kJ/mol)	A (S ⁻¹)	T _{t_{1/2}-60} (°C)
1.0	120		
2.5	128		
5.0	140		
10.0	127		
20.0	123		
25.0	132	2.90×10 ⁶	360.2
30.0	134		
35.0	134		
40.0	135		
45.0	135		

CONCLUSIONS

The structures of PPSA made either from sulfur or from Na₂S are just the same. Both are crystalline polymer. Their spheric crystals are constituted with non-twisting chain lamellae or fine-thread aggregation.

The activation energy of decomposition of PPSA is higher than that of PPS, so PPSA possesses higher thermal stability than PPS.

Keywords:

Polyarylene sulfide; Poly (phenylene sulfide amide); Synthesis; Morphological structure

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