Polymer Bulletin 54, 251–261 (2005)
DOI 10.1007/s00289-005-0392-3

Polymer Bulletin

Synthesis and characterization of poly(p-phenylene sulfide sulfone/ketone) copolymer

Shuang-xi Xu[1], Jie Yang[2] (✉), Sheng-ru Long[2], Yong-rong Chen[2], Guang-xian Li[3]

[1]The Faculty of Chemistry, Sichuan University, Chengdu 610064, P.R.China
[2]Institute of Materials and Technology, Sichuan University, Chengdu 610064, P.R.China
[3]The College of Polymer Materials Science and Engineering, Chendu 610065, P.R.China
E-mail: ppsf@scu.edu.cn

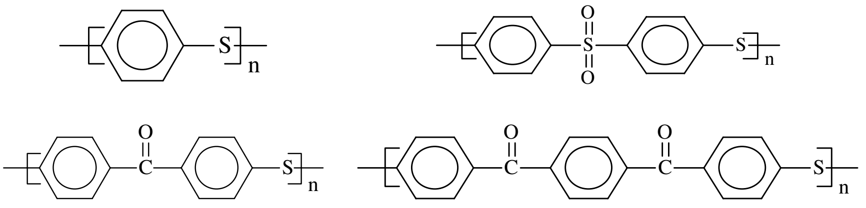
Received: 11 January 2005 / Revised version: 5 May 2005 / Accepted: 25 May 2005

Summary

High molecular weight poly(phenylene sulfide sulfone/phenylene sulfide ketone) copolymer was synthesized by the step polycondensation of sodium sulfide ($Na_2S{\cdot}xH_2O$) with 4,4'-dichlorobenosulfone (DCDPS), 4,4'-difldibenzophenone (DFBP) between 180~202ºC at normal pressure. The copolymer was characterized by FT-IR spectrum, UV spectrum, ^{1}H-NMR spectrum, X-ray diffraction and small angle light scattering (SALS), DSC and TGA. The more ketone in the copolymer chain, the better thermal properties of the PPSS/Ks resins have. The copolymer was found to be amorphous but has little local ordering structures with the content of ketone in the range of 0~45% which is different from other high pressure polymerization.

Introduction

A special kind of thermoplastic material poly(arylene sulfide)s (PAS) such as poly(phenylene sulfide) (PPS), poly(phenylene sulfide sulfone) (PPSS), poly(phenylene sulfide ketone) (PPSK), poly(phenylene sulfide ketone ketone) (PPSKK) etc. (shown below) have excellent fire ,chemical resistance, outstanding mechanical and thermal characters under rigorous operation conditions[1]. As a consequence, much more researches have been directed toward the development of new or improved thermoplastic materials. It reported that poly(phenylene sulfide sulfone) is amorphous and has high glass transition temperature (Tg) about 217ºC while poly(phenylene sulfide ketone) (PPSK) is crystalline with more palmary chemical resistance and better thermal properties. However, PPSK is hard to be processed due to its high crystalline degree and high melting points. It is well known that both poly(phenylene sulfide sulfone) (PPSS) [2-8] and poly(phenylene sulfide ketone) (PPSK) [9-13] can be prepared by aromatic nucleophilic substitution from their respective dihalogenation monomers. And all these researches were focused on high temperature and high pressure which had a high risk on the apparatus operation and security. In this paper, the normal pressure synthesis was used to obtain poly(phenylene sulfide sulfone/ketone) copolymer which dramatically reduced the experimental cost. And this new kind of modified PPSS material combined the good qualities of the two kinds of resins.



Scheme 1.

For the purpose of obtaining a new kind of modified PPSS material that possesses the good qualities of excellent thermal, chemical mechanical and physical characters, random poly(phenylene sulfide sulfone/ketone) copolymer was successfully synthesized by aromatic nucleophilic substitution step polymerization reaction at normal pressure. The copolymers with the content of ketone in the range of 0~45% were amorphous but little local ordering structures. It was different from the result of Dwayne R[14], in his paper the copolymers had clarified that with sulfon/ketone mole ratios (S:K)>25:75 are amorphous, the copolymers with (S:K)≤25:75 are crystalline. The complex effects of process conditions at atmospheric pressure were examined; the chain and aggregation structure of PPSS/Ks were characterized. Differential scanning calorimetry (DSC) and thermogravimetic analysis (TGA) were employed to understand the thermal properties of PPSS/Ks.

Experimental

Materials

Commercially available 4,4'-dichlorobenosulfone (poly grade, Shanghai Yinshen chemical reagents Company), sodium sulfide ($Na_2S \cdot xH_2O$ $Na_2S\% \approx 60\%$) (Nanfeng Group), sodium hydroxide (NaOH) (AR, Tianjing 3rd chemical agent plant), N-methyl pyrrolidone (NMP) (BASF Chemical Corporation, Germany), 4,4'-difl-dibenzophenone (poly grade, Jinshan chemical reagents Company) All of them were used without further purification. Catalyzer A and catalyzer B were made in our lab [15]. Other reagents and solvents were obtained commercially.

Polymerization

High molecular weight PPSS/Ks were synthesized by the aromatic nucleophilic substitution step polymerization reaction of 4,4'-dichlorodiphenyl sulfone (DCDPS), 4,4'-difluorobenzophenone (DFBP) with sodium sulfide and base at elevated reaction temperature and normal pressure. The polymerization happened in a 500 ml 3-necks flask equipped with a nitrogen inlet, reflux condenser, mechanical stirrer and thermometer. The polymerization reaction was divided into two steps [16]. The first step was the synthesis of PPSS oligomer and then the second step was the formation of poly(phenylene sulfide sulfone/ketone) copolymer.

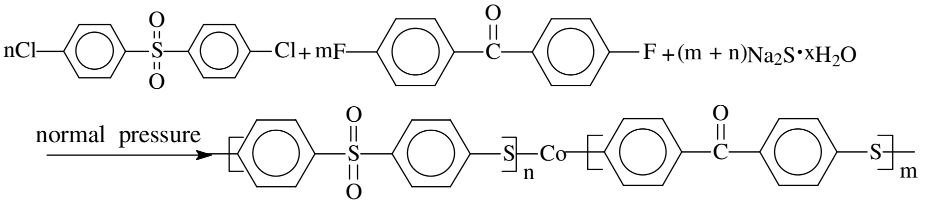
Formation of PPSS oligomer

A typical preparation of PPSS oligomer is described below. Firstly, the reactor was filled with nitrogen gas. Then the reactor was added 200 ml NMP and 5 ml deionized water, 39.00 g (0.30 mol) sodium sulfide, 5.00 g (0.0174 mol) DCDPS, 12 g

(0.30 mol) of sodium hydroxide, 6.0 g Cat. A, 9.0 g Cat.B, and then the reactor was heated to 180°C in 30 minutes; during this course ,15 ml water was taken off and at the same time, the PPSS oligomer was achieved.

Formation of PPSS/K copolymer

When the above reaction vessel was cooled to 100°C, 73.40 g (0.2556 mol) DCDPS and 6.546 g (0.03 mol) DFBF were added into the reactor. After 45 minutes, the reactor was heated to 200°C and kept for 4 h. After the reactor was cooled to room temperature, the product was poured into the cold deionized water to precipitate the copolymer under the stirring condition. The crude product, fibrous copolymer, was then smashed, and washed for several times with hot water to remove possible residual inorganic salts. After the purified polymer was filtered, the result solid powder was further vacuum-dried at 100°C for more than 12 h.



Scheme 2.

Characterizations

Intrinsic viscosity

Intrinsic viscosity was measured at 30±1°C in NMP solvent with 0.500 g of copolymer dissolved in 100 ml NMP, using a Cannon-Ubbelodhe viscometer and the result was obtained by some formulas as below:

$$[\eta]=\frac{\sqrt{2\left(\eta_{sp}-\ln\eta_{r}\right)}}{C}, \qquad (1)$$

where $\eta_{sp}=t/t_0-1$ and $\eta_r=t/t_0$.

Characterization of chain structure

The samples of PPSS/K casting film were prepared. FT-IR spectroscopic measurements were determined by using a Nicolet-170 SX FT-IR instrument at a resolution of 1 cm^{-1}.

The UV spectra were scanned with a Shimadzu UV-2100 spectrophotometer. Before examination, PPSS/Ks samples were first dissolved in the NMP solvent. Then the solution contained samples were diluted in absolute ethyl alcohol. UV spectra of both polymer and monomer were performed.

Nuclear magnetic resonance (^{1}H-NMR) instrument for the determination of the samples structure were provided with a Warian INOVA-400 NMR Spectrometer. The samples were dissolved in deuterated sulfuric acid.

Characterization of aggregation structure

The samples obtained were characterized by X-ray diffraction (XRD) (DX-1000). Films of PPSS/K were prepared by casting NMP solution on microscopy slide glass. Samples were subsequently dried at 110ºC in vacuum or annealed at 220ºC for 4 h. Samples (PPSS/K=65:35) for SALS were prepared using the same method as described in X-ray diffraction but annealed at 220ºC for 4 h. The thickness of as-cast films was about 50 µm. A He-Ne laser beam with a wavelength of 632.8 nm was used. Linearly polarized laser light was scattered by the sample and then filtered with an analyzer polarized parallel (VV) to the polarization direction of the incident light.

Thermal properties test

Thermal analysis of the samples was measured by differential scanning calorimetry (DSC) measurement (Seiko EXSTAR 6000 DSC6200). Thermogravimetric analysis (TGA) was performed on a Dupont Thermo gravimetric TA2100 instrument. The samples were heated at a rate of 10ºC/min in the nitrogen atmosphere.

Results and discussion

Effect of the modes of adding monomer on molecular weight

Based on the previous research work [2, 17], two modes of adding monomers were investigated in order to obtain product with higher molecular weight. In the first mode, we added all of the reaction monomers to the reactor, and then heated to 200ºC. The result (η_{inh}=0.3302 dl/g) showed that much higher molecular weight copolymers could not be obtained at this condition. The main reason was that tempestuous polymerization was induced during the reaction course after adding all of the monomers, and vast of heat was given out, so some sulfide was taken out of the reaction vessel by vapor, and the balance of the molar ratios between the monomers was broke. In the second mode, the reaction monomers were added into the reactor after the formation of PPSS oligomer to produce moderate conditions for polymerization, which made $Na_2S{\cdot}xH_2O$ disperse well in NMP and kept the balance of the molar ratios between the monomers. The higher molecular weight copolymers were achieved in the latter method compared to the first method. The normal pressure synthesis equation of poly(phenylene sulfide sulfone/ketone) copolymers (PPSS/Ks), was showed in scheme 2.

Effect of water on molecular weight

In order to disperse well $Na_2S{\cdot}xH_2O$ in solvent, effect of the content of H_2O on molecular weight was studied. The experiment showed that 7.00 ml added water is helpful to reach sufficient disperse of inorganic $Na_2S{\cdot}xH_2O$ in organic NMP, More sulfide will be taken off when much more added water turns into vapor. Higher molecular weight resin can not be obtained if $Na_2S{\cdot}xH_2O$ can not be well dissolved in sufficient water. Our further research would be focus on the accurate molar ratios and intrinsic reaction mechanism.

Effect of reaction temperature and time on molecular weight

In order to get higher molecular weight resin under normal pressure, the reaction temperature and time were investigated while the other synthesis conditions were maintained constant. The intrinsic viscosities of products were listed in Figure1.

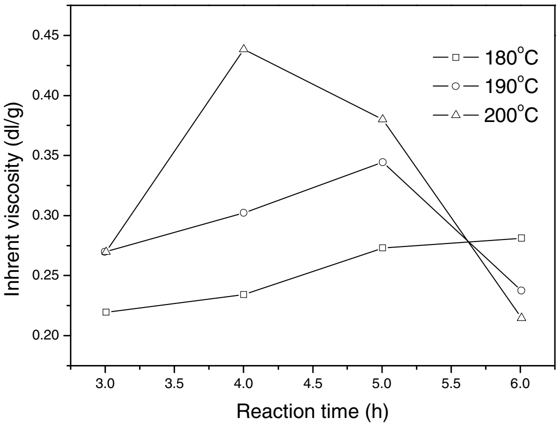


Figure 1. Effect of reaction temperature and time on molecular weight

It showed that the reaction temperature had a significant effect on the molecular weight from Figure 1. The maximum of intrinsic viscosity (0.4392 dl/g) was obtained at 200ºC, which is much higher than that at 180ºC. We ascribe this phenomenon to kinetic effects.

The effect of reaction time on molecular weight was also examined by varying time from 3 h to 6 h, while the other conditions were kept constant. The reaction temperature was kept 180ºC or 200ºC, respectively. The results indicated that it took longer reaction time to obtain the high intrinsic viscosity at the lower temperature (180ºC), however, the polymerization completed in 4 h at the higher temperature (200ºC), and the longer reaction time such as 5 h or 6 h, however, will resulted in lower intrinsic viscosity due to the balanced reaction between polymerization and depolymerization turned to the side of depolymerization.

Effect of different monomer ratios of materials

A 90:10 PPSS/Ks copolymer was prepared at four different monomer ratios of DCDPS and DFBP to $Na_2S{\cdot}H_2O$. The amount of $Na_2S{\cdot}xH_2O$ was constant while the DCDPS was varied in the reaction mixture. The aryl halides reactive behavior was lower than that of $Na_2S{\cdot}xH_2O$ in the normal pressure reactive environment. In the reaction, a little excess of DCDPS relative to the moles of $Na_2S{\cdot}xH_2O$ was expected in a typical condensation polymerization. As shown in Table 1, higher molecular weight PPSS/K was obtained using DCDPS-to-$Na_2S{\cdot}xH_2O$ molar ratio of 0.91:1.00 and DFBP-to- $Na_2S{\cdot}xH_2O$ molar ratio of 0.10:1.00.

Table 1. The effect of monomer molar ratios on molecular weight and yields of PPSS/K*

No.	DCDPS/ Na_2S	DFBP/ Na_2S	η_{inh} (dl/g)	Yield (%)
1	0.89:1.00	0.10:1.00	0.3347	96.8
2	0.90:1.00	0.10:1.00	0.3576	97.6
3	0.91:1.00	0.10:1.00	0.4393	98.7
4	0.92:1.00	0.10:1.00	0.3321	94.6

*Reaction time: 4 h; reaction temperature: 200ºC

The chain structure of PPSS/K

Figure 2 showed the FT-IR spectrum of PPSS/Ks. It indicated that the more ketone in the copolymer chain, the stronger absorption of the carbonyl group near the 1656 cm^{-1} in the FT-IR spectrum. At the same time, when the mount of the sulfone decreased, its absorption at 1320 cm^{-1} and 1158 cm^{-1}, had not obviously weakened because of the interference of other groups. While the other groups' absorption peaks were corresponding, and there was no absorption at 860 cm^{-1} to be ascribed to tri-substituted benzene, combined with the ^{1}H-NMR spectrum analysis, it indicated that the copolymer was a linear or 1,4-conjugated structure. Detail analysis of these absorption peaks was listed in Table 2. Figure 3 was the UV absorption spectrum of DFBP, PPSS and PPSS/Ks. In the Figure 3, there is a red-shift could be identified in corresponding characteristic absorption peaks, which can be ascribed to the formation of long conjugate π bonds and the effect of polar carbonyl group.

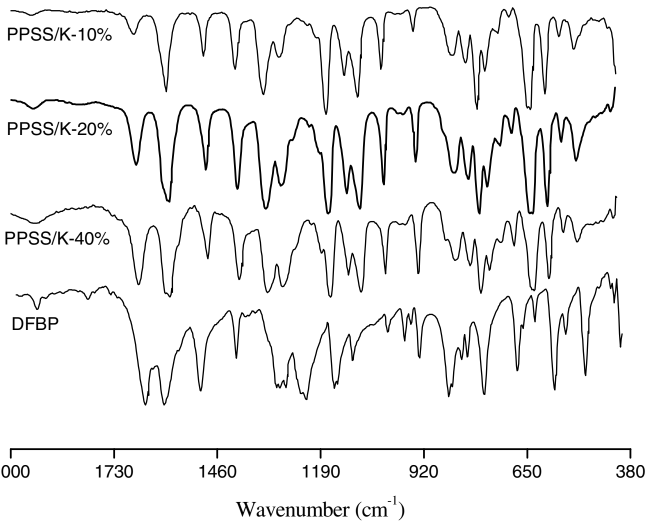


Figure 2. FT-IR spectrum of PPSS/Ks under different monomer ratios

Table 2. Infrared absorption peaks and assignments of different PPSS/Ks

Assignment		Wave number, cm^{-1}			
		PPSS/K-10%	PPSS/K-20%	PPSS/K-40%	DFBP
C–H stretch (phenyl)		3087.0	3088.351	3080.66	3112.0
ring C–C stretch		1574.41	1575.933	1581.585	1599.386
		1476.179	1475.218	1475.632	1503.312
		1393.050	1391.867	1395.851	1408.195
C–H out-of-plane bend		826.836	827.699	828.925	819.79
phenyl-sulfide bond		1076.062	1076.167	1076.976	-
sulfonyl	asym.	1322.375	1322.027	1320.695	-
	sym.	1158.816	1158.683	1158.050	-
ketone	sym.	1658.472	1656.863	1656.882	1649.273

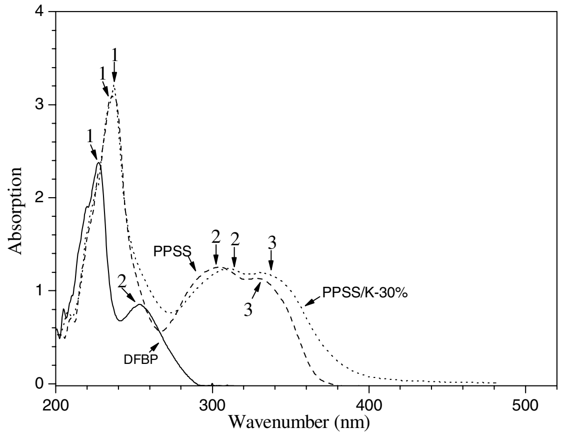


Figure 3. UV absorption spectrum of DFBP, PPSS and PPSS/K

Table 3. UV data of DFBP, PPSS and PPSS/K-30%

NO.	λ1 (nm)	λ2 (nm)	λ3 (nm)
DFBP	227.50	253.50	-
PPSS	230.00	295.00	310.00
PPSS/K-30%	232.00	299.50	318.50

Two groups of peeks were appeared in the NMR spectrum of PPSS/K-5% in Figure 4. Each group should be split into two peeks, but the high viscosity of the solution restrained molecule oscillation, and so the weak split signal were shielded or not be detected The ratio of corresponding integral curves was 1:1 and belonged to the type of AA'BB', which imply the symmetric disubstitution of benzene ring. Combining the results of FT-IR, these two groups of peaks were ascribed to the construction units of HA, HB, HC and HD[a]. The chemical shifts (δ) of PPSS/K-5% were listed in Table 4.

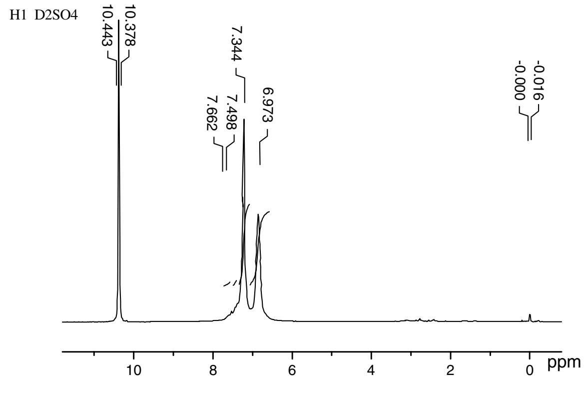
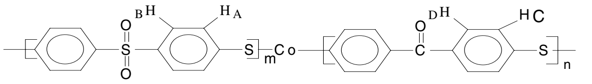


Figure 4a. ^{1}H-NMR spectrum of PPSS/K-5%

---

a 

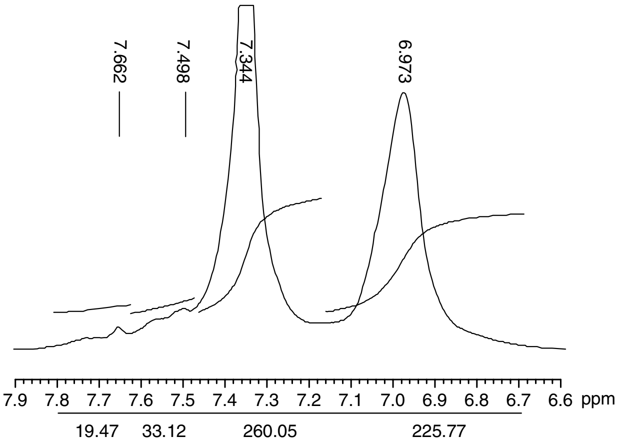


Figure 4b. Magnified ^{1}H-NMR spectrum of PPSS/K-5%

Table 4. Chemical shifts (δ) of PPSS/K-5%

Chemical shifts	HA	HB	HC	HD
δ (ppm)	6.973	7.344	7.498	7.652

The aggregative structure of PPSS/Ks

X-ray diffraction of PPSS/Ks untreated and annealed at different temperature was listed in Figure 5. As manifested in the Figure 5, as shown in Figure 5 the copolymer took on little local ordering structures.

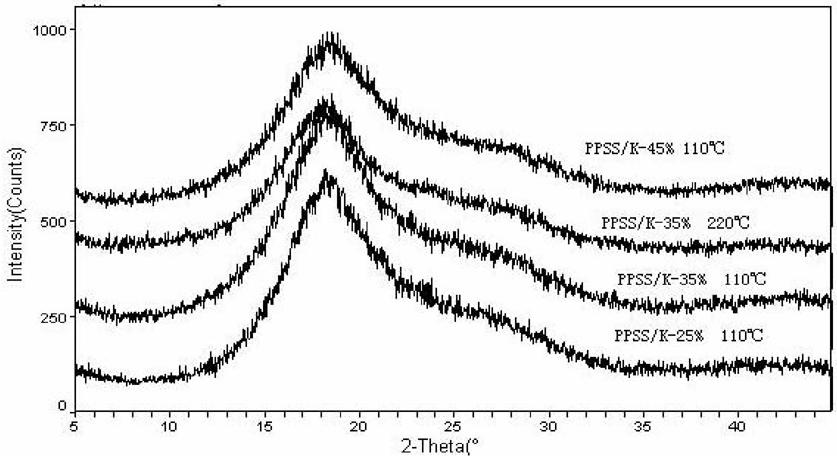
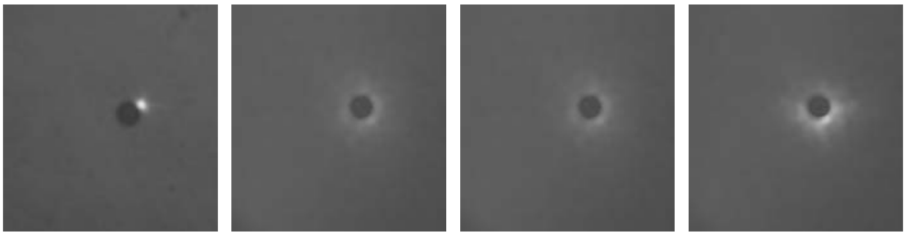


Figure 5. XRD spectra of PPSS/Ks treated at different temperatures for 4h

It can be found that a small shoulder located between 22~34° appears in each spectrum. The appearance of this shoulder may be ascribed to the fact that a small quantity of ordering chain structure was formed. At the same time, these local ordering structures were surrounded by lots of random chains which prohibited the further development of fine sticks.

As manifested in the Figure 5, the copolymer with the ratios of ketone in PPSS/Ks varying in the range of 25~45% was mainly amorphous but little local ordering structures, The PPSS/Ks resins were not blending polymer or block copolymer but random copolymer, for the PPSS was amorphous, the PPSK was crystalline. If the product was block copolymer or blending polymer, the distinctly crystalline can be seen form the XRD. This is different from other researcher reported [14] and need further research.

Light scattering originates from the density or polar inhomogeneity of material. Account for that the local ordering structure of PPSS/Ks may be not as distinct as crystalline or blend sample, the experiment was conducted under Vv mode. The scattering patterns were smoothed with Photoshop. The resulting pictures were given in Figure 6. As showed in Figure 6, no light scattering occurred for PPSS untreated sample, which implied a homogenous structure in the sample. However, light scattering appeared in the photos of PPSS-220ºC PPSS/K-untreated and PPSS/K-220ºC, which implied the formation of some local ordering structure [18].



PPSS-untreated PPSS-220ºC PPSS/K-untreated PPSS/K-220 ºC

Figure 6. SALS patterns of PPSS and PPSS/K-35% treated at different temperatures for 4 h

The thermal properties of PPSS/Ks

Thermal properties of PPSS/Ks of various molecular weights were examined by differential scanning calorimetry (DSC) and thermogravimetic (TG) analysis. The selected results were displayed in Figure 7 and Figure 8. The values of corresponding thermal properties were listed in Table 5.

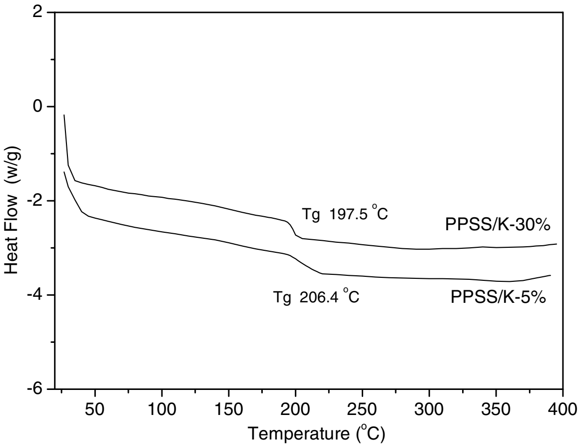


Figure 7. DSC analyses of PPSS/K-5% and PPSS/K-30%

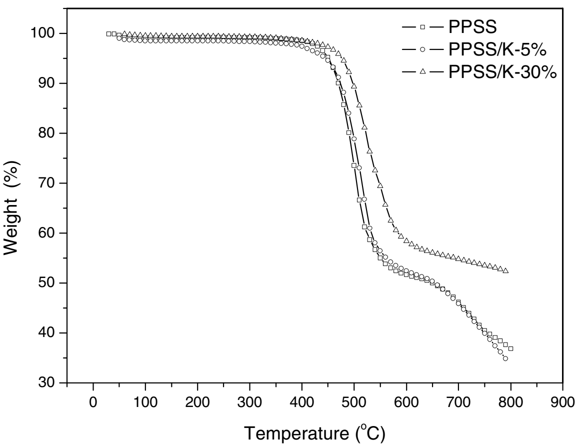


Figure 8. TGA weight loss behavior of PPSS/Ks at a heat rate of 10°C/min in N_2

Table 5. Thermal of property of PPSS/Ks with different ratio

PPSS-No.	Tg (°C)	T_m (°C)	T_i (°C)	T_{max} (°C)	T_f (°C)	Remainder (%)
PPSS	216.20	-	465.25	505.77	527.89	57.65
PPSS/Ks-5%	206.40	-	472.71	519.62	537.93	61. 97
PPSS/Ks-30%	197.50	-	486.92	523.70	567.69	63.44
PPSK	155.7	342.0	507.3	545.00	630.0	70.20

The Figure 7 showed that only one Tg was achieved at each different monomer ratio, and combine the FT-IR spectrum, we concluded that it was the copolymer but not the blends of PPSS with PPSK. When the ratio of ketone in PPSS/Ks varied in the range of 5~30%, the glass transition temperature(Tg) shifted from higher temperature(206.4°C) to lower temperature(197.5°C), while the initial degradation temperature(T_i) the maximum temperature (T_{max}) and the final degradation temperature(T_f) shifted to higher temperatures (seen Figure 8) . The results suggested that high temperature performance, thermal stability and easily processed of material can be achieved by increasing the ratios of ketone in the PPSS/Ks copolymers.

Conclusions

In this paper, high molecular weight PPSS/Ks were prepared successfully by aromatic nucleophilic substitution step polymerization reaction at normal pressure.

The modes of adding monomers and water have great effect on the molecular weight of PPSS/Ks.

The PPSS/Ks resins synthesizes by this means were random copolymer and the samples with the mount of ketone in the range of 0~45% were amorphous but little local ordering structures, which is different from other studied and need further research.

The more ketone in the copolymer chain, the better thermal properties of the PPSS/Ks resins have.

Acknowledgements. This work was supported by research grants from the 863 program of China (Grant No.: 2001AA334020-1).

References

1. Yang Jie, Chen Yongrong, Yu Zili, et al. Synthesis and characterization of micro-branch-high molecular-weight poly(phenylene sulfide). Polymer Materials Science & Engineering 1996;12(2):52-56
2. Wang Huadong, Yang Jie, Long Shengru, et al. Study on the high performance polymers polyphenylene sulfide sulfone. Polymer Materials Science & Engineering 2003; 19(3):54-57
3. Y.Liu, A. Bhatnagar, et al. Influence of polymerization conditions on the molecular structure stability and physical behavior of poly(phenylene sulfide sulfone) homopolymers. Polym 2000;41:5137-5146
4. Bobsein R L,Jr E C.US Pat 4,808,698
5. Campbell R W. US Pat 4,102,875
6. Campbell R W. US Pat 4,016,145
7. Campbell R W. US Pat 4125525
8. Campbell R W. US Pat 4301274
9. Durvasula V. R., Stuber F. A., D. Bhattacharjee, Synthesis of polyphenylene ether and thioether ketones. J.Polym. Sci. Part.A, 1989; 27(2):661-669.
10. Yoshikatsu S., et al. EP Pat 0,293,113
11. Duane C. M., et al. EP Pat 0,285,874
12. Frederick,G.J.,et al., EP Pat 0,274,754.
13. Edward,O.J., et al., EP Pat 0,270,955
14. Dwayne R. Senn. Synthesis characterization of ran-copoly(p-phenylene sulfide sulfone/ketone)s. J. Polym. Sci. Part.A 1994; 32:1175-1183.
15. Wang Huadong,Yang Jie, Chen Yongrong, et al.ZL:02113803.6(CN)
16. Yang Jie, Xu Shuangxi et al. CN Pat. Appl.: 10040365.3, 2004, Agu.
17. WANG Hua-dong,YANG Jie, CHEN Yong-rong, et al. Synthesis and characterization of poly(phenylene sulfide sulfone). China Plastics Industry 2003; 31(5):9-12.
18. JieYang, Huadong Wang Shuangxi Xu et al. Study on polymerization condition and structure of poly(phenylene sulfide sulfone). J.Polym.Research 2004(accepted)