

Studies on the Thermal Properties of Poly(phenylene sulfide amide)

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Received 20 June 1996; accepted 15 March 1997

ABSTRACT: Thermal properties of poly(phenylene sulfide amide) (PPSA) prepared using sodium sulfide, sulfur, and thiourea as sulfur sources which reacted with dichlorobenzamide (DCBA) and alkali in polar organic solvent at the atmospheric pressure, were studied. The glass transition temperature (T_g), melting point temperature (T_m), and melting enthalpy (ΔH_m) of the related polymers were obtained by use of differential scanning calorimetry analysis. The results are: $T_g = 103.4\text{--}104.5^\circ\text{C}$, $T_m = 291.5\text{--}304.7^\circ\text{C}$, and $\Delta H_m = 104.4\text{--}115.4\text{ J/g}$. Thermal properties such as thermal decomposition temperature and decomposition kinetics were investigated by thermogravimetric analysis under nitrogen. The initial and maximum rate temperatures of degradation were found to be $401.5\text{--}411.7^\circ\text{C}$ and $437\text{--}477^\circ\text{C}$, respectively. The parameters of thermal decomposition kinetics of PPSAs were worked out to be: activation energy of degradation was 135 to 148 kJ/mol and the 60-s half-life temperature was 360 to 371°C . © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1227–1230, 1997

Key words: poly(phenylene sulfide amide); thermal transition behavior; thermal decomposition kinetics

INTRODUCTION

Poly(phenylene sulfide) (PPS) has found a wide application as an engineering thermoplastic which combines high thermal, chemical, and environmental stabilities with toughness and excellent electrical properties. Since the high-insolubility property leads to difficulty in testing, regular introduction of an amide group into the main chain of aromatic polythioethers is expected to improve the solubility and processability of the corresponding polymer. Poly(phenylene sulfide amide) (PPSA) with a repeating structural unit of $-(\text{—}p\text{—C}_6\text{H}_4\text{—CONH—C}_6\text{H}_4\text{—S—}p\text{—})\text{—}$ is a new polymer of PPS class. It has good compre-

hensive properties and processability. Until now, there has been very limited literature concentrating on its synthesis. Ishikawa and Kondo¹ reported a manufacturing route for it that is the polycondensation of dichlorobenzamide (DCBA) and Na_2S at 240°C for 8 h in N_2 atmosphere under high pressure. We have explored a route for preparing PPSA without pressurizing. The synthesis using Na_2S , sulfur (S), and thiourea, respectively, as S sources which reacted with DCBA, alkali, and catalyst in polar organic solvent at atmospheric pressure were reported in our earlier articles.^{2–4} The structures have been characterized and compared with each of the other yielding polymers using different S sources. To have a deeper understanding of this new polymer, systematical studies on its thermal properties, such as thermal transition behavior and thermal degradation kinetics, are reported in the present article.

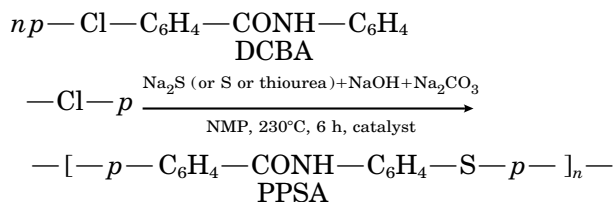
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Journal of Applied Polymer Science, Vol. 66, 1227–1230 (1997)
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EXPERIMENTAL

Materials

PPSAs for this study were prepared by polycondensation of DCBA and sodium sulfide, S, and thiourea in NMP (N-methylpyrrolidone) in the presence of alkali and catalyst at atmospheric pressure. The reaction can be expressed as:



In the present paper, they are denoted as PPSA-20, sodium sulfide as S source, reduced viscosity of 0.173 dL/g²; PPSA-40, sulfur as S source, reduced viscosity of 0.176 dL/g³; and PPSA-60, thiourea as S source, reduced viscosity of 0.150 dL/g⁴.

All the samples were purified by extraction with deionized water and acetone for 48 h and then dried in a vacuum oven before being used. The viscosity of 0.1 g/dL polymer solution in NMP 5 wt % LiCl was measured using a Ubbelohde viscosimeter at 30 ± 0.05°C.

Instruments and Methods

The glass transition temperature (T_g), melting point temperature (T_m), and melting enthalpy (ΔH_m) were determined by a Perkin-Elmer 7 Se-

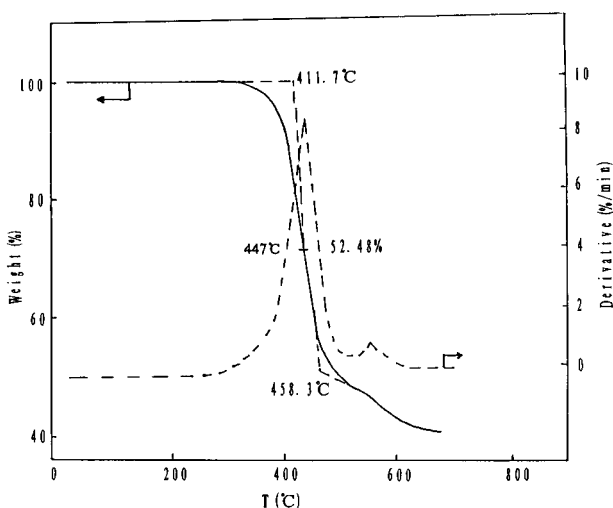


Figure 1 TGA analysis of PPSA-20.

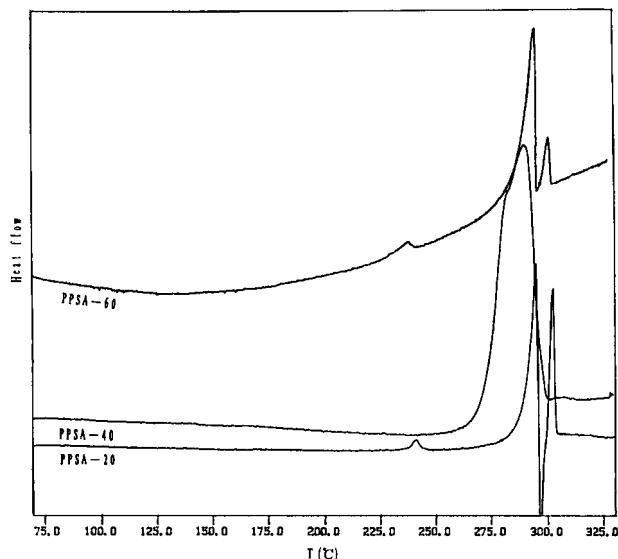


Figure 2 DSC curves of PPSAs.

ries thermal analysis instrument using the differential scanning calorimetry (DSC) program with a heating rate of 10°C/min under nitrogen. Thermogravimetric analysis (TGA) was conducted on a Dupont 1090 thermal analysis system. The TGA curve (Fig. 1) was recorded with a heating rate of 10°C/min, and the thermal decomposition kinetics parameters were obtained with heating rates of 5, 10, 15, and 20°C/min in nitrogen atmosphere.

RESULTS AND DISCUSSION

DSC Analysis

From Figure 2, which displays the DSC traces of samples synthesized from the related three kinds of sulfur sources, the basic thermal parameters were obtained and are summarized in Table I.

Table I Results of DSC Analysis of PPSAs

Samples	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PPSA-20	104.5	304.7	104.4
PPSA-40	104.3	297.8	115.4
PPSA-60	103.4	291.5	107.0

^a T_m was chosen as the highest peak of all the peaks in a curve.

^b ΔH_m was calculated as the total value under the peaks in a curve.

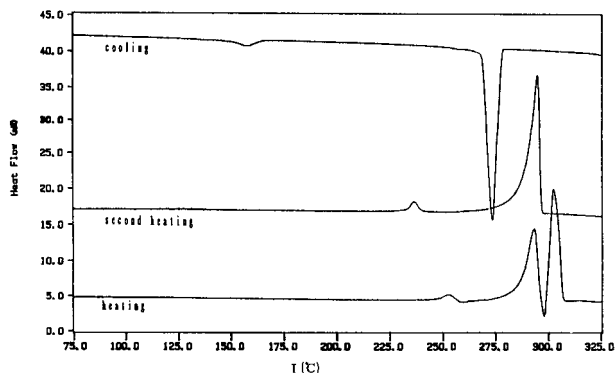


Figure 3 DSC analysis of PPSA-20.

From Figure 3, which records the heating, cooling, and second heating traces of DSC of PPSA-20, it was suggested that multiphase crystalline may be existing in the aggregate of this polymer. Multiphase transition may occur during the heating treatment (as here, heating and cooling). Therefore, the second heating curve in Figure 2 shows only two peaks instead of three on the heating curve. The peaks near 250°C of the DSC curves may result from the existence of a separate crystalline phase. This is consistent with the result of the X-ray diffraction analysis.³

TGA Analysis

The TGA curves of PPSAs under nitrogen appear in Figure 1. It shows the initial and maximum rate temperatures of degradation, which were found to be 411.7 and 447.1°C, respectively, and at the point of maximum rate of 447.1°C, the polymer weight remains 52.48%. From the derivative curve in Figure 1, we see that the decomposition of PPSA shows a two-stage weight loss which is similar to that of PPS.⁵

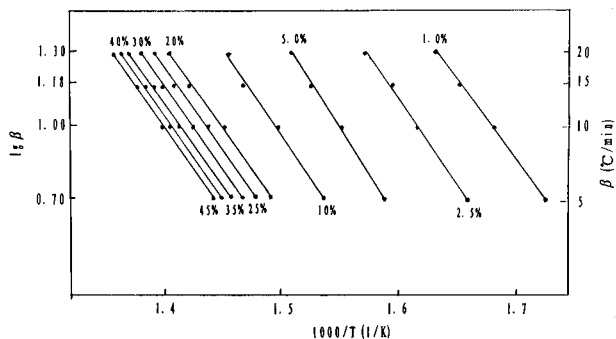


Figure 4 Plots of log β versus 1/T of PPSA-20 at different decomposition conversions.

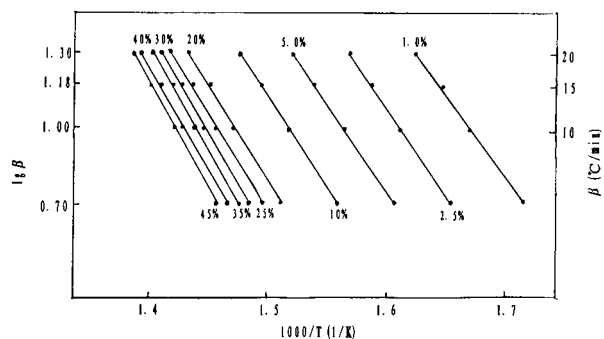


Figure 5 Plots of log β versus 1/T of PPSA-40 at different decomposition conversions.

Thermal decomposition kinetics can be expressed by the following equation^{6,7}:

$$\log \beta = \log[AE/Rf(c)] - 2.315 - (0.457E/RT) \tag{1}$$

where β is the heating rate (°C/min), A is the preexponential factor of decomposition (1/S), E is the activation energy of decomposition (J/mol), R is the gas constant (8.314 J/mol), T is temperature, and f(c) is a function of degree of conversion and relies on the type or mechanism of reaction. For a given reaction system at a given conversion, f(c) can be considered a constant. Therefore, for a given sample at a given conversion of degradation, the plots of log β against 1/T should be a straight line according to eq. (1), and E and A can be obtained from the slope and the tangent distance of the line, respectively. From Figures 4–6, which display the plots of log β versus 1/T of PPSAs at different conversions of the decomposition, it is apparent that straight lines are obtained which consist with the theoretical expectation from the

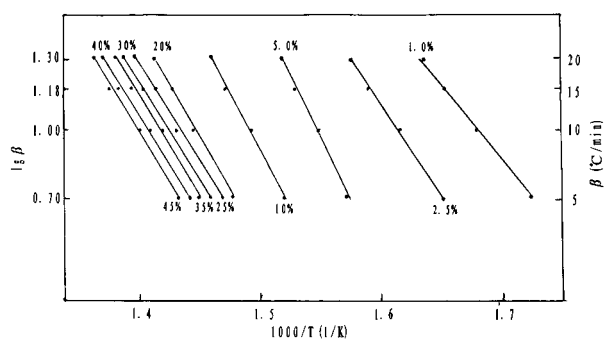


Figure 6 Plots of log β versus 1/T of PPSA-60 at different decomposition conversions.

Table II Results of Thermal Decomposition Kinetics of PPSAs

Conversion	<i>E</i> (kJ/mol)			<i>A</i> (1/S)			<i>T</i> (°C)		
	PPSA-20	PPSA-40	PPSA-60	PPSA-20	PPSA-40	PPSA-60	PPSA-20	PPSA-40	PPSA-60
1.0	115	120	109						
2.5	125	128	132						
5.0	124	140	180						
10.0	130	127	165						
20.0	139	123	149						
25.0	144	132	148	5.3×10^9	8.8×10^{10}	1.3×10^{10}	371.9	360.5	368.4
30.0	146	134	147						
35.0	148	134	147						
40.0	143	135	148						
45.0	144	135	148						

above equation. The percentile data nearing the straight lines are the relevant conversions.

The 60-s half-life temperature can be calculated as

$$T_{t(1/2)=60s} = E/[R \times \ln(A \times t_{1/2}/\ln 2)] \quad (2)$$

From the results of decomposition kinetics summarized in Table II, which were calculated by a programmed computer connected with the thermal analysis instrument, it was found that the *E* of a sample tended to be a constant when conversion was over 25%.

CONCLUSIONS

From the above study, we obtained the following conclusions:

1. PPSAs prepared from the three kinds of sulfur sources had similar thermal properties.
2. The T_g , T_m , and activation energy of thermal decomposition of PPSA were higher

than those of PPS, which were reported to be about 90, 185, and 90 kJ/mol, respectively. It was suggested that PPSA can be used at higher temperature than PPS.

3. The process of thermal decomposition of PPSA is similar to that of PPS, and also appears to be a two-stage process.
4. A separate crystalline phase may exist in the aggregate of PPSA.

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