

Polymerization Characteristics and Thermal Degradation Study of Poly(phenylene sulfide ketone)

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ABSTRACT: Poly(phenylene sulfide ketone) (PPSK) was synthesized by the reaction of sodium sulfide with 4,4'-dichlorobenzophenone in *N*-methyl-2-pyrrolidinone through the Phillips process. The effect of water hydration of sodium sulfide in solution, polymerization temperature, polymerization time, and stoichiometric ratio of monomers on the polymerization behavior of PPSK were investigated with respect to inherent viscosity and yield. Thermal degradation parameters of PPSK synthesized were investigated by dynamic thermogravimetry. To determine thermal degradation energy, Kissinger, Ozawa, and Friedman methods were used and activation energies were 202.3, 233.6, and 232.2 kJ/mol, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1329–1337, 2000

Key words: poly(phenylene sulfide ketone); polymerization; thermal properties; degradation

INTRODUCTION

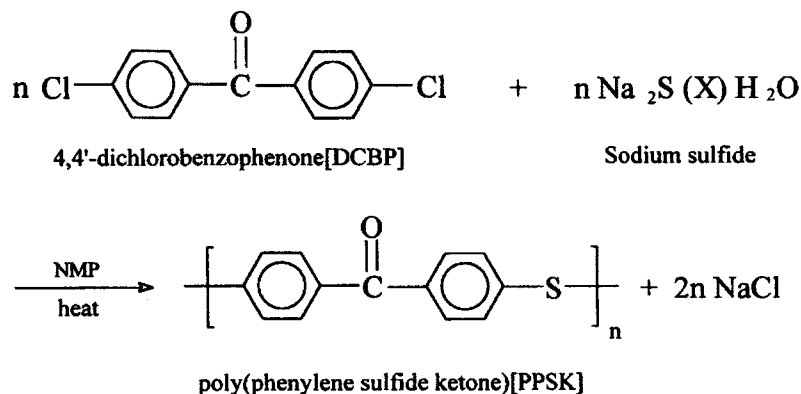
Poly(phenylene sulfide) referred to as PPS is classified as an engineering semicrystalline thermoplastic. PPS shows excellent mechanical, electrical, thermal, and chemical resistance properties in addition to the polymer being inherently self-extinguishing. This polymer has found uses in applications such as coatings, injection molding, film, fiber, and advanced composites.^{1–2} New applications are being discovered and demands are increasing.

In 1973, Phillips Petroleum Co. (Bartlesville, OK) began the world's first commercial production of Ryton PPS based on the reaction of *p*-dichlorobenzene with sodium sulfide in a polar organic solvent such as *N*-methyl-2-pyrrolidinone (NMP) at elevated temperature. Phillips was granted a U.S. patent for this method.^{3–4} How-

ever, it is difficult to achieve high-molecular weight for PPS because of the premature precipitation of the product and the low reactivity of dichlorobenzene with sodium sulfide during the polymerization. This material has low-molecular weight, low-melt viscosity, and too much creep. Thus, processibility, impact strength, and other mechanical properties are affected. Many researchers have tried to solve these problems by syntheses of new PPS derivatives.^{5–6} We have already reported on the synthesis of poly(phenylene sulfide sulfone) and poly(phenylene sulfide ether).⁶ In particular, poly(phenylene sulfide ketone) (PPSK), which is one of PPS derivatives, includes carbonyl groups in the polymer backbone. For the reason of being a polar group in the polymer backbone, PPSK has high-intermolecular interaction and crystalline regularity. Glass transition temperature (T_g) and melting temperature (T_m) of PPSK are higher than those of PPS. When this material is applied at high temperature, it is expected to show excellent thermal stability.

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Scheme 1

In 1981, Mukherjee and Pramanik examined the conductivity of PPSK which was synthesized in dimethyl formamide (DMF) to make a semiconducting polymer.⁷ Durvasula and his coworkers reported the polymerization characteristic of PPSK in *N*-cyclohexyl-2-pyrrolidinone (CHP) and diphenylsulfone (DPS) as solvents,⁸ and in 1989, Senn tried to synthesize copoly(*p*-phenylene sulfide sulfone/ketones) in NMP from 4,4'-dichlorobenzophenone (DCBP), bis-(4-chlorophenyl) sulfone, and sodium hydrosulfide (NaSH) and investigated thermal analyses and solution properties of these copolymers.⁹ However, the results of the study on the Phillips process, which was widely used to synthesize PPS and its derivatives, were mostly covered under patents.¹⁰⁻¹² Accordingly, we wish to report the results of studies on various reaction conditions in the polymerization of PPSK by using the Phillips process.

These materials associated with these high-temperature polymers have the need for test procedures to assess and predict performance under service conditions. In polymer science, the measurement of weight loss as a function of temperature or time, thermogravimetric analysis (TGA), represents a technique which has been widely used to predict thermal stability because of its simplicity and the information afforded from a simple thermogram. There are many proposed methods to calculate kinetic parameters and these reported values have been described and discussed in several publications.¹³⁻¹⁶ Kissinger, in 1957, proposed the relatively simple method which is initially used to determine the apparent activation energy E for each of the stages.¹⁷ Ozawa¹⁸ and Flynn and Wall¹⁹ proposed independently an isoconversional method with an approximate solution²⁰ of the integrated rate equation.

The difference-differential method of Freeman and Carroll²¹ was proposed for the kinetic analysis of thermogravimetric data and a generally applicable differential method was developed by Friedman.²² Thermal stability of poly(ether ether ketone) structurally similar to PPSK was reported by Day et al. in 1989.²³

It is thus the aim of the present work to deal with the polymerization characteristics using the Phillips process and the thermal degradation study of PPSK.

EXPERIMENTAL

Materials

DCBP and lithium acetate dihydrate ($\text{LiAc} \cdot 2\text{H}_2\text{O}$) used in this study were obtained from Aldrich Chemical Co. (Milwaukee, WI). Sodium sulfide ($\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$) was obtained from Showa Chemical Co. and used as received. Acetone and sulfuric acid were obtained from Duksan Chemical Co. (Youngin-City, Korea) and used without further purification. NMP was distilled several times in the usual manner before use.

Polymerization

The synthesis scheme for PPSK is as shown in Scheme 1.

A polymerization procedure is as follows. A mixture of sodium sulfide, DCBP, and NMP (150 mL) was placed in a 350-mL bomb-type reactor made of corrosion-resistant alloy under a dry argon atmosphere. Then it was stirred and heated at various reaction conditions. After being allowed to cool, the product mixture was poured

into acetone. The precipitates were filtered. To remove the salt and water-soluble by-products and unreacted monomer, the polymer was washed several times in hot distilled water and acetone with stirring. Then, residual PPSK was dried in a vacuum oven at 100°C for 72 h.

To investigate the effect of water content in the polymerization system, dehydration of sodium sulfide was carried out. A 300-mL three-necked flask provided with a condenser, Dean-stock apparatus, and dry-gas line was charged with NMP (150 mL) and a measured amount of sodium sulfide under a dry argon atmosphere. It was heated to 150°C until the mixture was fairly dehydrated. Then the mixture was transferred to the reactor with the addition of measured amounts of DCBP and distilled water. Then the previously described procedure was followed.

Analyses

The synthesized polymer is practically insoluble in commercially available polar and nonpolar solvents but is soluble only in concentrated sulfuric acid. Inherent viscosities of each polymer were measured by using a Ubbelohde viscometer in concentrated sulfuric acid solvent: 0.1 g PPSK/10 mL 95 wt % sulfuric acid at 30°C.

IR spectrum was obtained on Midac FTIR. The sample was thoroughly washed to get rid of residual monomers, then dried.

Thermal properties of PPSK were investigated with a DuPont Thermal Analyzer DSC-2000 and Thermogravimetric Analyzer TGA-2100. Glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and melting temperature (T_m) were recorded during a second heating run. In TGA scanning, a sample was heated from room temperature to 200°C at 30°C/min in less than 15 min to purge with nitrogen, and then it was heated to 700°C at 0.5, 1, 5, 10, 50, and 100°C/min.

RESULTS AND DISCUSSION

Characterization

IR spectrum for PPSK synthesized is shown in Figure 1.

PPSK has sulfur groups and carbonyl groups and the absorption bands are assigned at 1655 and 800–840 cm^{-1} , respectively.²⁴

Reaction Temperature

We considered first the effect of reaction temperature on polymerization of PPSK. The changes of inherent viscosity and yield of PPSK with respect to reaction temperature are shown in Figure 2.

As Figure 2 shows, the yield is not affected by increasing reaction temperature, and inherent viscosity is the highest value at 230°C reaction temperature. In 1991, Lyon and coworkers reported that PPSK's optimum polymerization temperature was about 250°C,^{8–25} but in this study we observed different results. In the case of PPS polymerization by the Phillips process, which was successfully carried out within the range of about 240–250°C,²⁶ PPSK possesses a carbonyl group between two phenyl rings in the polymer backbone and this electron-withdrawing group should increase the reactivity of chlorine of DCBP. Therefore, the reaction temperature of PPSK is lower than that of PPS. We guess that the decrease of inherent viscosity was due to side reactions at temperatures above 230°C. Considering the above results in respect to yield and inherent viscosity, we think that 230°C is an appropriate reaction temperature for PPSK.

Reaction Time

The reaction temperature was fixed at 230°C. Then with reaction time increasing, the changes of yield and inherent viscosity were investigated. These results are shown in Figure 3.

The inherent viscosity of PPSK, as shown in Figure 3, rise with longer reaction time, but the yield was not affected by the reaction temperature within the experimental range. In the case of the short reaction time, like half-hour reaction times, polymerization yield was still high. We think the reaction time should be about 4 h to achieve appropriate molecular weight.

Monomer Feed Ratio

The results in Figure 4 were examined with varying monomer feed ratios of sodium sulfide and DCBP under these fixed reaction conditions: reaction time (4 h) and reaction temperature (230°C) with $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$. It is different from the traditional expected condensation polymerization behavior and is assumed because of the different reactivity of two monomers. Within the experimental range, the ratios of sodium sulfide/DCBP above 1.0 cause the material to have higher inherent viscosity. These

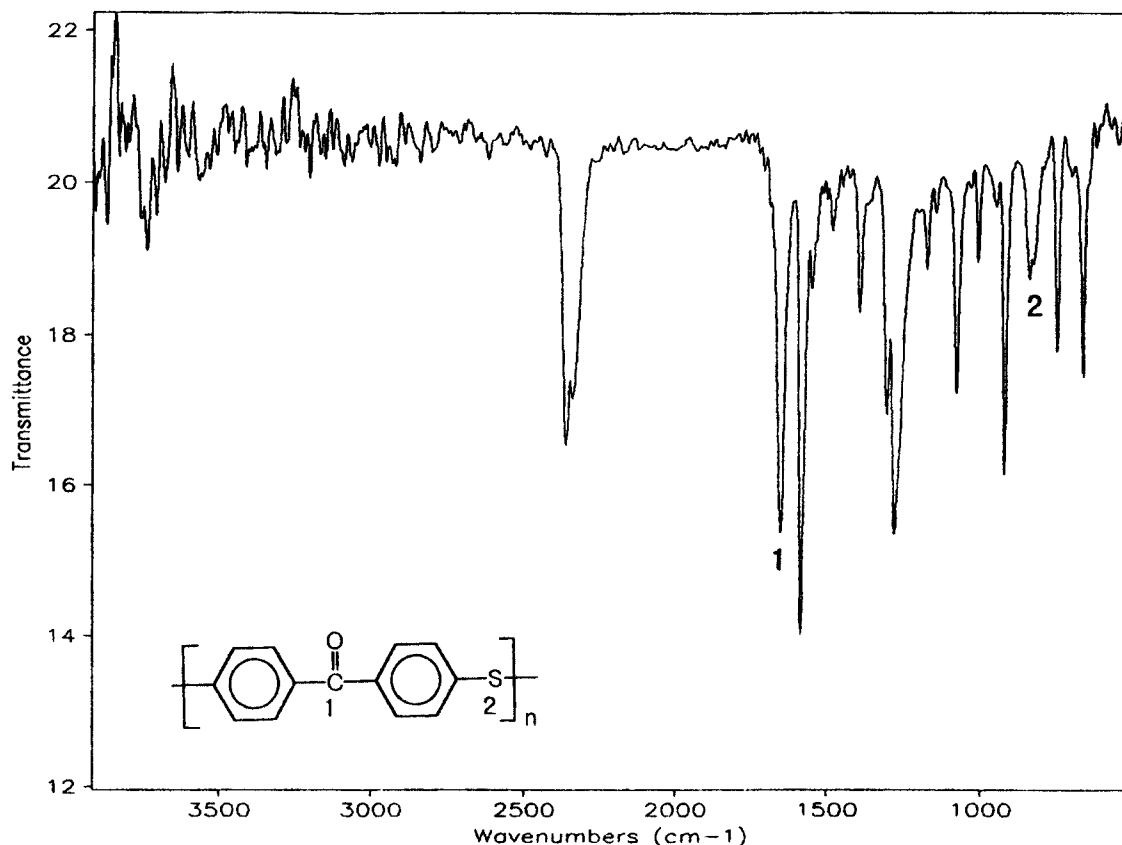


Figure 1 IR spectrum for poly(phenylene sulfide ketone).

results differ from the patent.¹⁰ In contrast, it agrees exactly with Durvasula's research.⁸ Because sodium sulfide is very hygroscopic, it includes some

amount of impurity. To obtain high molecular weight PPSK, it was found necessary to add more sodium sulfide than DCBP.

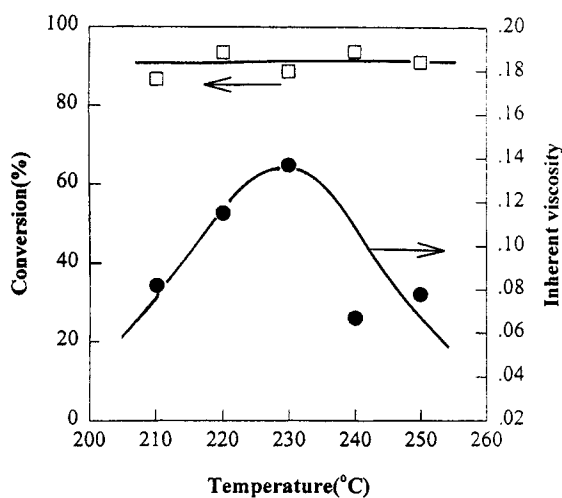


Figure 2 Effect of reaction temperature on the conversion and inherent viscosity of PPSK: $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ was used, reaction time 4 h, mole ratio $\text{Na}_2\text{S}/\text{DCBP} = 1/1$.

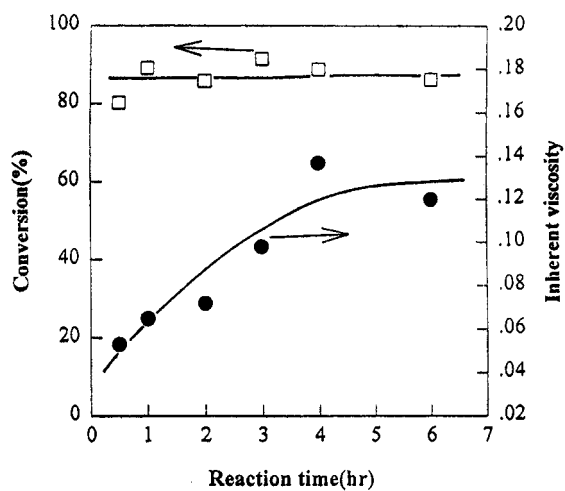


Figure 3 Effect of reaction time on the conversion and inherent viscosity of PPSK: $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ was used, reaction temperature 230°C , mole ratio $\text{Na}_2\text{S}/\text{DCBP} = 1/1$.

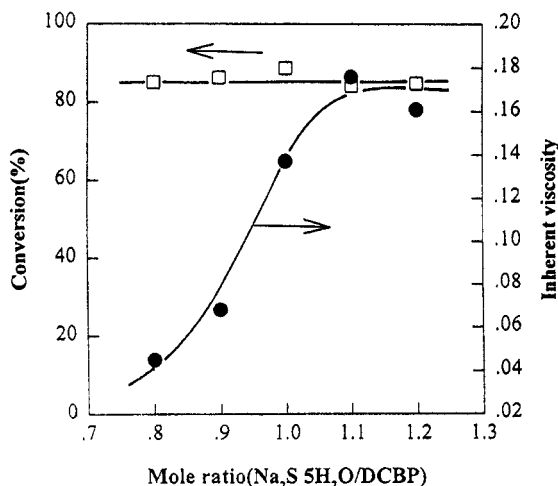


Figure 4 Effect of mole feed ratio on the conversion and inherent viscosity of PPSK: Na₂S 5H₂O was used, reaction temperature 230°C, reaction time 4 h.

Crystal Waters of Sodium Sulfide

When the reaction temperature is fixed at 230°C and other reaction conditions are the same as before, the changes of inherent viscosity and yield of PPSK are shown along with the increase in water hydration of sodium sulfide, as in Figure 5.

In this figure, we can observe that polymerization yields are not largely changed and inherent viscosity values are increased along with decreasing water hydration. In syntheses of PPS derivatives, it was reported that when hydrated sodium

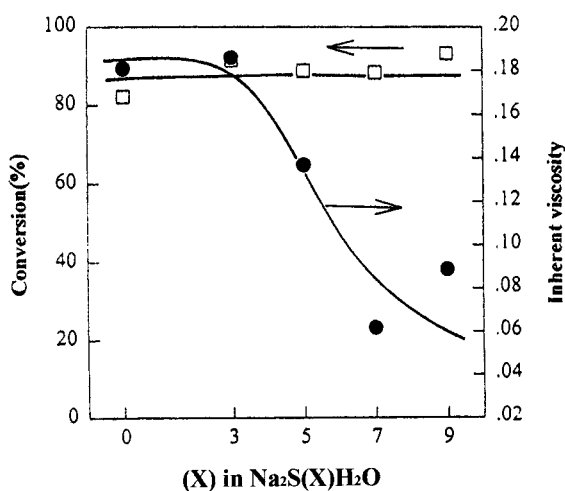


Figure 5 Effect of crystal waters of sodium sulfide on the conversion and inherent viscosity of PPSK: reaction temperature 230°C, mole ratio Na₂S/DCBP = 1/1, reaction time 4 h.

Table I Effect of Additives on the Conversion and Inherent Viscosity of PPSK

Additives	Conversion (%)	Inherent Viscosity ^a
None	89	0.12
Lithium acetate	91	0.10
Sodium benzoate	87	0.11

^a Conc.: 0.1 g PPSK/10 mL 95 wt % sulfuric acid at 30°C. Reaction condition: reaction temperature, 230°C; reaction time, 4 h; crystal water, Na₂S 5H₂O; mole ratio, sodium sulfide/DCBP = 1/1.

sulfide dissolved in NMP at elevated temperatures, a chemical reaction occurred, yielding a separable complex product.²⁷ This product was involved in syntheses of PPS derivatives; however, the role of water in the polymerization system is not clear.

On the other hand, Lenz et al. and Brady suggested that the chemistry of PPS growth from sodium sulfide and *p*-chlorobenzene in NMP is dominated by the ionic S_NAr (aromatic nucleophilic substitution reaction) mechanism,^{28,29} whereas, the possibility of the S_{RN}1 (unimolecular radical nucleophilic substitution) mechanism²⁷ in commercial high-temperature reaction remains an open question. Recently, Percec et al. reported the polyetherification of bis(aryl chlorides) activated by carbonyl groups with hydroquinones.³⁰ This report explained that the aromatic nucleophilic substitution and the reductive dehalogenation reactions are based on a competition between polar and single electron transfer (SET) pathways. In this case, reductive elimination of chlorine from the chlorobenzophenone-propagating chain results in the unreactive benzophenone chain end. This side reaction can be explained by a S_{RN}1 mechanism. We reason that crystal water was involved with the side reaction.

Additives

PPS produced through the use of alkali metal carboxylates was superior to the PPS produced in the absence of alkali metal carboxylates, as indicated by the values for inherent viscosity.³¹ So we introduced lithium acetate and sodium benzoate that were equimolar to sodium sulfide in the polymerization system of PPSK. Reaction conditions were at 230°C for 4 h; pertinent results are listed in Table I. The inherent viscosity and conversion

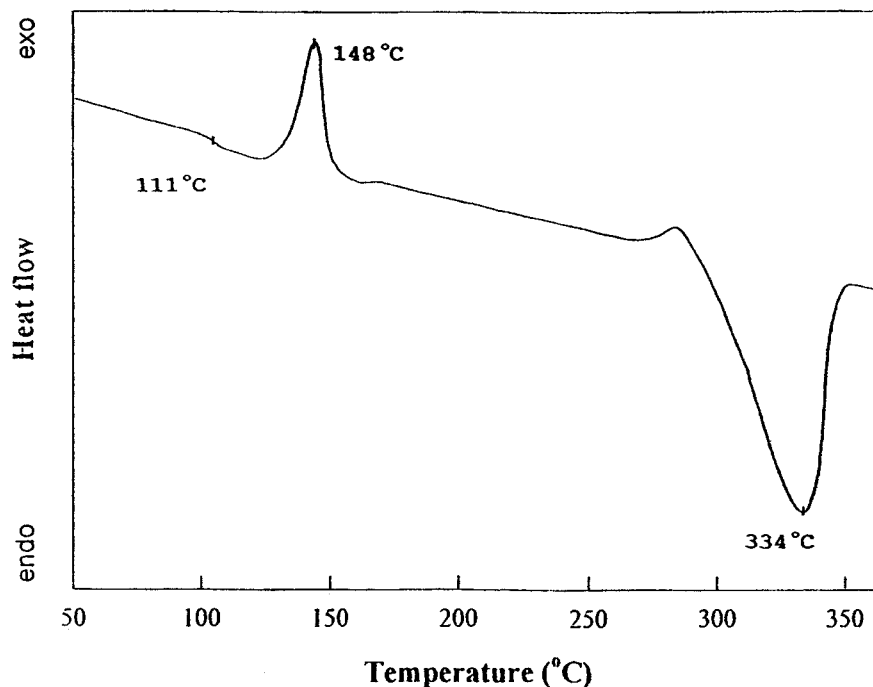


Figure 6 DSC thermogram for PPSK at heating rate of 20°C/min, 2nd run.

of PPSK was not affected with alkali metal carboxylates used in this experiment.

Thermal Behaviors

DSC thermogram for PPSK is shown in Figure 6. As seen in this figure, PPSK has $T_g = 111^\circ\text{C}$, $T_{cc} = 148^\circ\text{C}$, and $T_m = 334^\circ\text{C}$. In 1994, according to Senn's report,⁹ PPSK has $T_g = 144^\circ\text{C}$ and $T_m = 345^\circ\text{C}$, but the exact condition of thermal analysis was not presented.

In Table 2, data of maximum degradation temperatures and residues at 700°C in accordance with various heating rates are listed. In the case of the slowest heating rate (0.5°C/min), its maxi-

mum degradation temperature is over 450°C, and so good thermal stability is expected in various applications of PPSK. We studied its thermal stability in view of thermal degradation kinetics.

Kinetic Methods

The foundation for the study of kinetic data from the mass-loss curve is based on the basic rate equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where α is the fractional conversion, k is the Arrhenius rate constant, A is the preexponential factor, E is the activation energy, R is the universal gas constant, $f(\alpha)$ is the function of conversion, T is the temperature, n is the apparent order of reaction, and β is the heating rate. The equation expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the reactant concentration loss and rate constant. In the case of polymer degradation, it is assumed that the rate of conversion is proportional to concentration of material that has to react,

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

Table II TGA Thermogram for PPSK with Heating Rate 0.5, 1, 5, 10, 50, and 100°C/min

Heating Rate (°C/min)	Maximum Degradation Temperature (°C)	% of Residues at 700°C
0.5	488	30
1	502	59
5	536	60
10	561	65
50	597	65
100	618	66

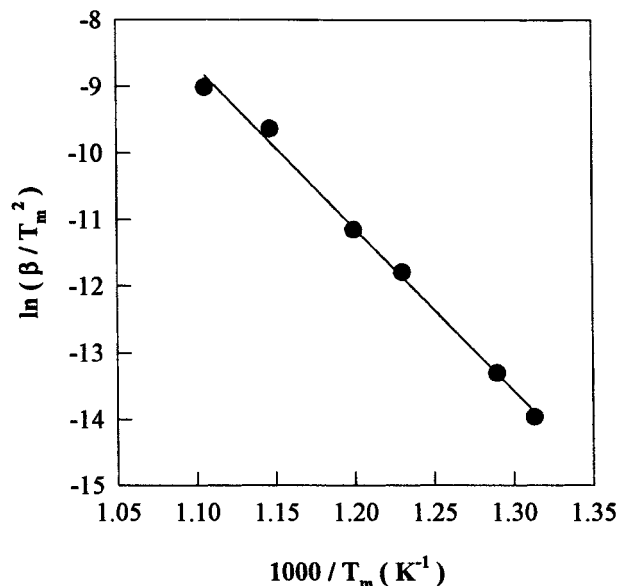


Figure 7 Kissinger plot of PPSK degraded in nitrogen.

The combination of these equations and the empirical Arrhenius expression gives the following relationship:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (3)$$

and introducing the heating rate, β :

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

This is the fundamental expression of analytical methods used to calculate kinetic parameters on the basis of thermogravimetry data. These methods can be distinguished and are based on the degree of conversion, α , and heating rate, β .

The relatively simple Kissinger method was initially used to determine the apparent activation energy E in the case of $n = 1$ with a relationship between maximum degradation temperature (T_{\max}) and rate of maximum degradation. This method involves the following expression derived by Kissinger¹⁷:

$$\frac{d \ln\left(\frac{\beta}{T_{\max}^2}\right)}{d\left(\frac{1}{T_{\max}}\right)} \cong -\frac{E}{R} \quad (5)$$

A plot of $\ln(\beta/T_{\max}^2)$ as a function of $(1/T_{\max})$ then gives E from the slope of the line. The plot obtained for PPSK degraded in nitrogen is shown in Figure 7. E value of 202.8 kJ/mol was calculated from the slope, confirming the apparent simple kinetics in nitrogen. Although the Kissinger method is relatively simple, it relies on the accuracy of maximum degradation temperature, but the data in the vicinity of the maximum rate usually has the least sensitivity due to a rapid change of their weight.

The most general of differential methods was developed by Friedman,²² who utilized eq. (2) in logarithmic form, for instance,

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln \beta \frac{d\alpha}{dT} = \ln A + n \ln(1-\alpha) - \frac{E}{RT} \quad (6)$$

Thus, by plotting $\ln(d\alpha/dt)$ against $1/T$ at constant α , it is possible to obtain values for activation energies and preexponential factors.

In Figure 8, a Friedman plot is presented from 0.05 to 0.2 of conversion. We can obtain a mean value of each activation energy of fractional conversion 232.2 kJ/mol and preexponential factor $1.7673 \times 10^{12} \text{ min}^{-1}$ but cannot observe a lineal relationship above 0.25 of conversion. We then use the isoconversional method proposed independently by Ozawa¹⁸ and Flynn and Wall¹⁹ in

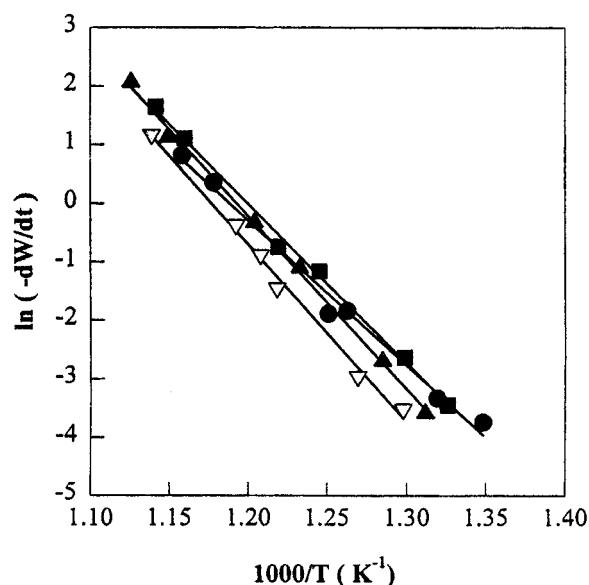


Figure 8 Friedman plots of $\ln(\text{rate of weight loss})$ versus $1/T$ for PPSK fractional conversion (α): ●, 0.05; ■, 0.1; ▲, 0.15; ▽, 0.2.

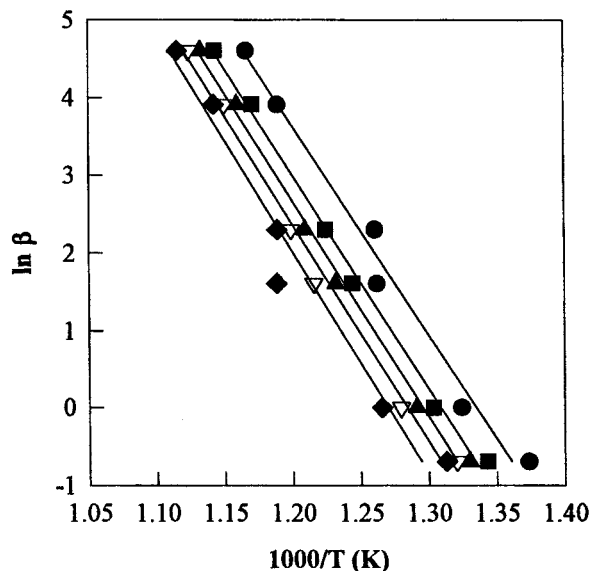


Figure 9 Ozawa plots of $\ln(\text{heating rate})$ versus $1/T$ for PPSK fractional conversion (α): ●, 0.05; ■, 0.1; ▲, 0.15; ▽, 0.2; ◆, 0.25.

this work. This integral method is based on the following expression, which is an approximate solution of the integrated rate equation:

$$\ln F(\alpha) \cong \ln \frac{AE}{R} - \ln \beta - 5.305 - 1.052 \frac{E}{RT} \quad (7)$$

By using this equation, the activation energies E can then be obtained from a plot of $\ln \beta$ against $1/T$ for a fixed degree of conversion since the slope of such a line is given by $-0.1052E/R$. In addition, the derived E values can be used to calculate $\ln A$ from the intercept value.

Figure 9 shows some of the Ozawa plots for the thermal degradation of PPSK in nitrogen for the range of heating rates employed in this study. The nearly straight lines over the fractional conversion range 0.05–0.35 indicate that a single reaction mechanism works in the initial stage. We can also obtain a mean value of each activation energy of fractional conversion 233.6 kJ/mol and preexponential factor $8.9643 \times 10^{13} \text{ min}^{-1}$ but cannot observe a lineal relationship above 0.35 of conversion. Judging from the above two methods of Ozawa and Friedman [the higher conversions of thermal degradation (above 0.35)], a more complex mechanism is involved.

CONCLUSION

In this work, PPSK was synthesized by reacting sodium sulfide with DCPB in NMP. The effect of

water contents, reaction time, reaction temperature, and stoichiometric ratio of monomers on the polymerization behavior of PPSK were investigated. Optimum polymerization condition of PPSK with Phillips process was determined in view of inherent viscosity and conversion. Optimum polymerization condition of PPSK with the Phillips process was found at 230°C (polymerization temperature), 4 h (polymerization time), and low content of water in solvent. Its inherent viscosity increases with increased molar ratio of sodium sulfide to dichlorobenzophenone. There is no effect for additives such as sodium benzoate and lithium acetate.

Thermal properties of PPSK were investigated with DSC and TGA in nitrogen atmosphere. T_g of PPSK appeared at 111°C and T_m was 334°C (2nd run). To determine activation energy of thermal degradation, Kissinger, Ozawa, and Friedman method were used and activation energy was 202.8, 233.6, and 232.2 kJ/mol, respectively.

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