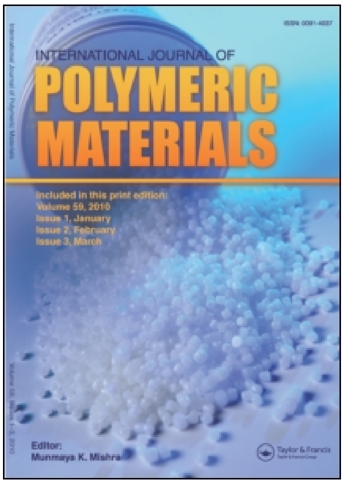

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Cure Kinetics and Thermal Property of Bisphenol-S Epoxy Resin and Phthalic Anhydride

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The cure kinetics of bisphenol-S epoxy resin (BPSER) and curing agent phthalic anhydride, with N,N-dimethyl phenzylamine as an accelerator, were studied by means of differential scanning calorimetry (DSC). Analysis of DSC data indicated that an autocatalytic behavior showed in the first stages of the cure. The autocatalytic behavior was well described by the model proposed by Kamal including two rate constants, k_1 and k_2, and two reaction orders, m and n. The overall reaction order, $m+n$, is in the range $2 \sim 3$. The activation energies for k_1 and k_2 were 111.69 and 80.47 KJ/mol, respectively. Diffusion control was incorporated to describe the cure in the latter stages. The glass transition temperatures (T_gs) of the BPSER/anhydride samples isothermally cured partially were determined by means of torsional braid analysis (TBA) and the results showed that the reaction rate increased with increasing T_g in terms of the rate constant, but decreased with increasing conversion. The T_g of completely cured BPSER/anhydride system is about 40 K higher than that of BPAER. The thermal degradation kinetics of this system was investigated by thermogravimetric analysis (TGA). It illustrated that the thermal degradation of the BPSER/phthalic anhydride has n-order reaction kinetics.

Keywords: Bisphenol-S epoxy resin; Phthalic anhydride; Cure reaction kinetics; Glass transition temperature; Thermal degradation kinetics

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INTRODUCTION

The improved epoxy resin based on bisphenol-S (BPS) are considered worthy of further study in terms of its good thermal stability, chemical resistance, mechanical properties, and modification than that of the bisphenol-A epoxy resin (BPAER) [1,2] because of the introduction of sulfonyl groups into the backbone of the resins. The cure process and the thermal properties of this thermosetting material affect its macroscopic properties, which govern its end-use performance. The bisphenol-S epoxy resin (BPSER) synthesized by bisphenol-S and epichlorohydrin was described for the first time by Beavers in 1953 [3]. The formation kinetics of this epoxy resin have been studied [4, 5], but the description of cure reaction kinetics and the description of thermal property and degradation kinetics of BPSER with anhydrides have been lacking until now.

In order to provide a basis for the theory about curing process for the application of BPSER, it is necessary to conduct the research in the curing kinetics of BPSER/anhydride system. A kinetic model arising from an autocatalyted reaction mechanisms [6–8] was applied to isothermal DSC data. In general, a good fit to experimental data was obtained in the early stages of the cure, but deviations were observed in the later stages, particularly near vitrification when the reaction was primarily diffusion controlled.

In this work to be described herein, the DSC technique was used to study the curing kinetics of BPSER and phthalic anhydride. The curing reactions in the kinetic control stage followed an autocatalytic kinetics and a four-parameter semiempirical equation proposed by Kamal [9]. To our best knowledge, this is the first time that such a model and diffusion controlled process is applied to the BPSER and phthalic anhydride system.

The glass transition temperature (T_g) can be used effectively to illustrate the curing reaction process [10]. In this paper, torsional braid analysis (TBA) was used to determine the T_g of the BPSER/anhydride system due to T_g is a particularly convenient index for relating cure to properties. The glass transition temperatures were measured for BPSER/anhydride samples cured isothermally at different temperatures for various periods. Structure changes during curing process were investigated by Fourier transition infrared analysis (FTIR).

The mechanism of thermal degradation was studied by means of thermogravimetric analysis (TGA).

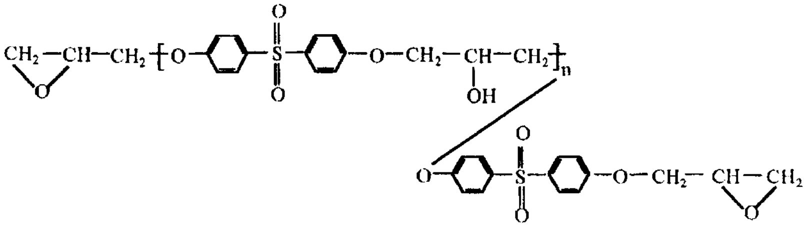
EXPERIMENTAL

Materials

Bisphenol-S was recrystallized from the toluene, and a crystal with a melting point of 240°C was obtained. Bisphenol-A epoxy resin E44 was commercially available. Epichlorohydrin, NaOH, KOH, acetone, ethylalcohol, hydrochloric acid and phthalic anhydride were all analytically pure grade and were supplied by Beijing Chemical Reagent Co.

Synthesis of BPSER

Epoxy resin based on bisphenol-S used in this work was synthesized according to Rainer *et al.* [11]. The molecular structure of this resin has the following approximate form.



where $n = 0 \sim 1$. The epoxy value was determined according to Jay [12] to be 0.31 mol/100 g.

IR Measurements

The BPSER/phthalic anhydride samples were prepared with a stoichiometric ratio of one epoxy group with one hydrogen, and they were mixed uniformly. During the isothermal curing, an FTS-40 IR spectrophotometer was used for the investigation of the structure changes of the curing system. The sample was dissolved in acetone, then coated it into a thin film on a potassium bromide plate and completely evaporated in vacuum, the potassium bromide plate was first scanned by the IR instrument. Thereafter, the plate was placed in a heated oven with a fixed temperature of 413 K. During the curing reaction at this temperature, the plate was repeatedly withdrawn at a regular time interval for analysis.

DSC Method

Curing studies were carried out by a Shimadzu DT-41 differential scanning calorimeter operating in a nitrogen atmosphere. The DSC was calibrated with high-purity indium, α-Al_2O_3 was used as the reference material. Isothermal and dynamic-heating experiments were carried out according to Opalicki *et al.* [6] under a nitrogen flow of 40 ml/min.

Resin and hardener with an accelerator were used as received and mixed under 5°C at a 1:1 equivalent ratio. Approximately 10 mg samples of the mixture were weighed accurately into an aluminum DSC sample pan and covered with an aluminum lid. The entire operation was carried out in a dry chamber.

Samples were placed in thermostatic baths at curing temperatures T_c between 110 and 130°C in 5°C increments. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of reaction, was used to calculate the isothermal heat of cure, ΔH_i, at a given temperature. After each isothermal run, the sample was cooled rapidly in the DSC cell to 10°C and then reheated at 10°C/min to 300°C in order to determine the residual heat of reaction, ΔH_r. The total heat evolved during the curing reaction is $\Delta H_0 = \Delta H_i + \Delta H_r$.

Torsional Braid Analysis (TBA)

Specimens, prepared by dipping heat-cleaned glass fiber braid in the solution of BPSER/phthalic anhydride system and an accelerator mixed at an equivalent ratio of 1:1, were completely evaporated in vacuum. The air oven was first heated up to a desired curing temperature T_c, and kept for a certain period of time until the system reached the equilibrium state. Specimens were quickly set into the thermostatic baths at T_c between 433 and 453 K for 10, 20, 30, 40, 50, 60, 120 minutes, respectively. Then took them out and cooled them to the room temperature and determined their T_gs with the heating rate of 2 K/min. The T_g of completely cured specimen prepared by BPAER and phthalic anhydride (with a ratio of 1 : 1.1) was determined with the heating rate of 2 K/min, too.

TGA Measurements

BPSER and hardener mixed at a ratio of 1:1.1. After curing at 413 K for 6 hrs, thermal analysis was carried out on a Shimadzu DT-40 thermogravimetric analysis (TGA). About 3 mg of the sample, which had been completely cured, was put into a platinum cell and placed on the detector plate, then the furnace was heated to 500°C.

RESULTS AND DISCUSSION

Isothermal Curing

The FTIR spectrums of BPSER/anhydride system detected are shown in Figure 1. The most significant feature is the appearance of the epoxide group absorption at 914 cm^{-1} (marked by an arrow). It is observed that this absorption finally becomes a tiny peak when the curing time increases to 10 hrs. Obviously, the system still cured incompletely when the curing time was so long at 413 K. So in the practice the curing agent should be a little overdosed. The absorbance of each sample was shown in Table I. We can see that the absorbance decreased with the increasing of the curing time. In addition, the IR absorption in carbonyl region is almost no change.

The mechanisms of the curing reaction of thermosetting resins have the two general kinetic models; that is, *n*th-order and autocatalytic mechanism [13]. The *n*th-order kinetics can be expressed as:

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \qquad (1)$$

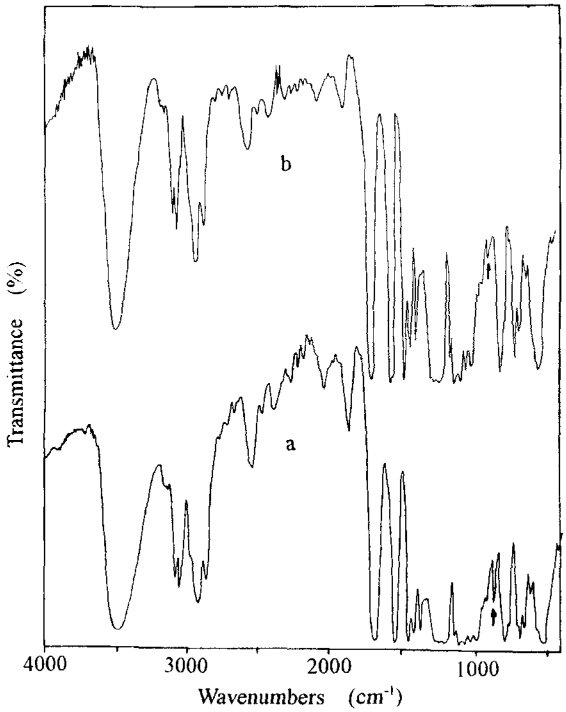


FIGURE 1 The FTIR spectrum of BPSER/anhydride system after curing at 413 K for (a) 30, (b) 600 min.

TABLE I The absorbance of BPSER/anhydride curing for different time

Cure time (min)	0	30	90	600
A	0.392	0.220	0.200	0.086

The autocatalytic kinetics can be expressed by Kamal [9] as:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \tag{2}$$

where α is the extent of reaction, and α is given by $\alpha = \Delta H_t/\Delta H_0$. ΔH_t is the partial area under a DSC trace up to time t; k_1 and k_2 are the specific rate constants at these models, which are the functions of temperature; and m and n are the reaction orders. According to nth-order kinetic model, the maximum reaction rate will be observed at $t = 0$, and according to the autocatalytic model, the reaction rate is zero initially and attains a maximum value at some intermediate conversion.

During the curing reaction of the thermosetting resins, the heat evolution recorded by DSC is proportional to the extent of consumption of the epoxide group in the epoxy resin or the reactive group in the curing agent [14, 15]; namely, the heat is proportional to the extent of the reaction. According to this assumption, curing kinetics was studied; and the kinetics data were determined [16, 17]. If the cure reaction is the only thermal event, then the reaction rates $d\alpha/dt$ is proportion to the heat flow [13], dH/dt, that is:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \tag{3}$$

The rate of cure can be determined by the curing exotherm.

Figure 2 shows plots of the curing reaction conversion α *versus* time t at different isothermal temperatures, and isothermal DSC curves are shown in Figure 3 plotted as $d\alpha/dt$ *versus* time. The reaction rate at any temperature is seen to increase with time at the initial stage of cure and passes through a maximum. The reaction rate peak becomes higher and shifts to lesser times with an increase in isothermal temperature. The plots show a maximum reaction rate at time $t > 0$, thereby negating simple nth-order kinetics. The autocatalytic kinetic

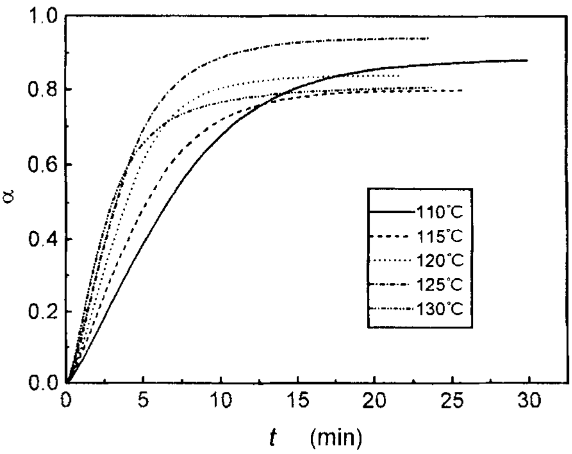


FIGURE 2 Conversion, α, *versus* time curves at different temperatures.

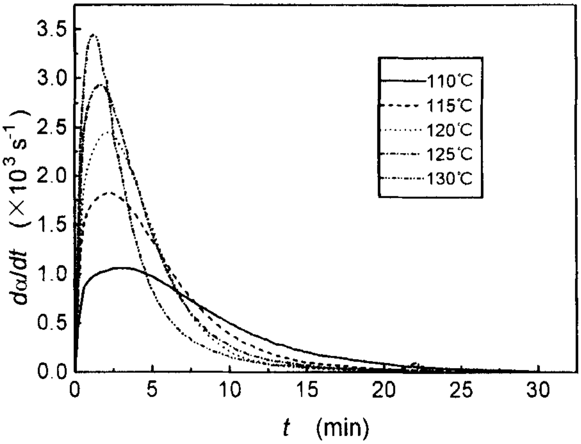


FIGURE 3 Reaction rate, $d\alpha/dt$, *versus* time curves at different temperatures.

TABLE II Kinetic parameters for isothermal curing of BPSER/anhydride

$T(°C)$	110	115	120	125	130
$k_1(\times 10^{-4})$	3.29	4.86	9.59	11.7	19.31
$k_2(\times 10^{-3})$	3.38	4.94	7.75	8.40	12.78
m	0.29	0.75	0.93	0.62	0.67
n	1.84	1.91	1.96	1.43	2.30
$m+n$	2.13	2.66	2.89	2.05	2.97

model (2) is appropriate to describe this isothermal curing behavior. In the Eq. (2), $m+n$ is the over-all reaction order. The kinetics parameters can be obtained by fitting the data with nonlinear least-squares procedures and shown in Table II.

It is observed that the k_1 values were small compared with that obtained for k_2 which affect the reaction more. Furthermore, k_1 and k_2 values are observed to increase with increasing temperature, respectively. The overall reaction order, $m+n$, is in the range $2 \sim 3$.

The reaction rate constants k_1 and k_2 depend on the temperature and follow the Arrhenius relationship:

$$k = A\exp(-E/RT) \tag{4}$$

Rate constants k_1 and k_2 are shown as an Arrhenius plot in Figure 4, which yields the values of 111.69 KJ/mol and 80.47 KJ/mol for the associated activation energies E_1 and E_2. It is observed that the

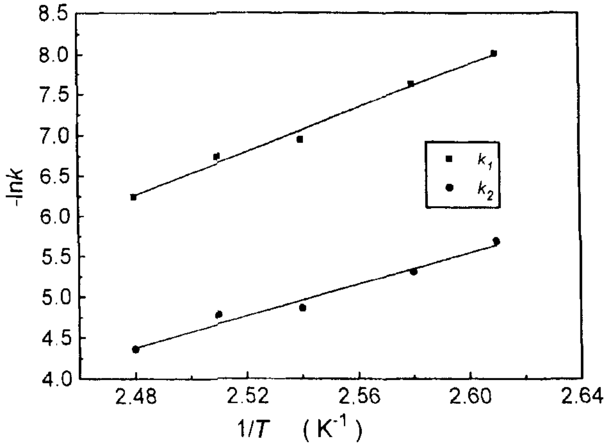


FIGURE 4 Rate constants of curing reaction, k_1 and k_2, *versus* temperature.

linear correlation coefficients for k_1 values is 0.9946 and for k_2 is 0.9872.

Comparison between typical experimental DSC data under two temperatures 110 and 115°C and predictions of the autocatalytic model, with values of model parameters determined above, are shown in Figure 5. The kinetic behavior described by the kinetics model coincides with the experimental data in the early stage. Whereas in the later stage, the chemical kinetics cannot be satisfactorily represent the experimental data, and the system becomes controlled mainly by diffusion. Since the effect of the diffusion was not taken into account in the kinetic model, deviations are observed when the conversions beyond 0.5 at 110°C and 0.6 at 115°C. This is due to the onset of gelation and the system becomes controlled by diffusion at the latter stage of cure. Differences between model predictions and experimental data are observed to be greater when curing temperature decreases under the same conversion. This may be associated with the T_g of fully cured material. If the curing temperature is in the vicinity of the glass transition region of the highly cured material, the free volume is reduced, and the segmental mobility within the polymer decreases, thus reducing the rate of diffusion of molecular to reactive sites, which reduces the reaction rate. So it is evidently observed that the reaction rate is seriously affected by the diffusion when curing at 110°C.

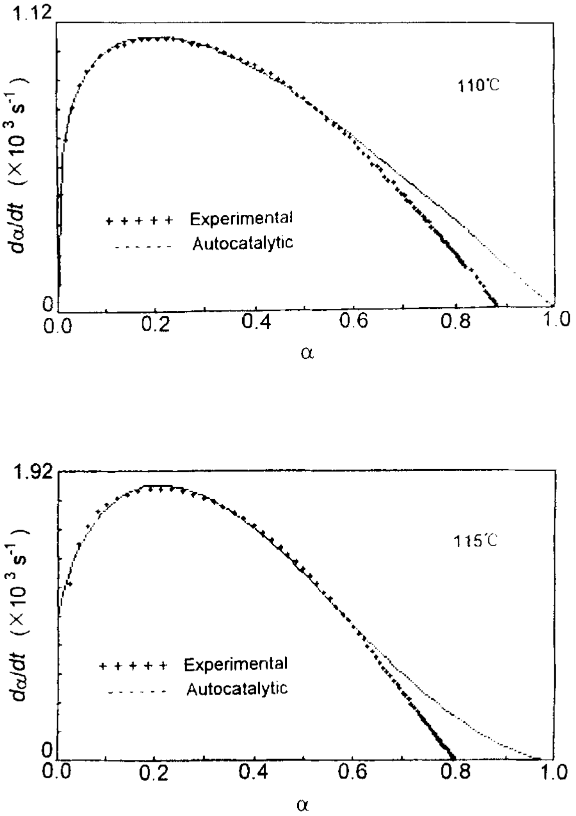


FIGURE 5 Comparisons of experimental data with model prediction: reaction rate, $d\alpha/dt$, *versus* conversion, α, at 110°C and 115°C.

To consider diffusion effect, we introduced a diffusion factor $f(\alpha)$ [6] defined as the ratio k_e/k_c, k_c, being the rate constant for chemical kinetics and k_e the overall effective rate constant. This diffusion factor is given by

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{5}$$

where α_c is the critical conversion and C is the diffusion coefficient. When α is much smaller than the critical value, $\alpha \ll \alpha_c$, the $k_e = k_c$, then $f(\alpha)$ approximates unity, the reaction is kinetically controlled, and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$

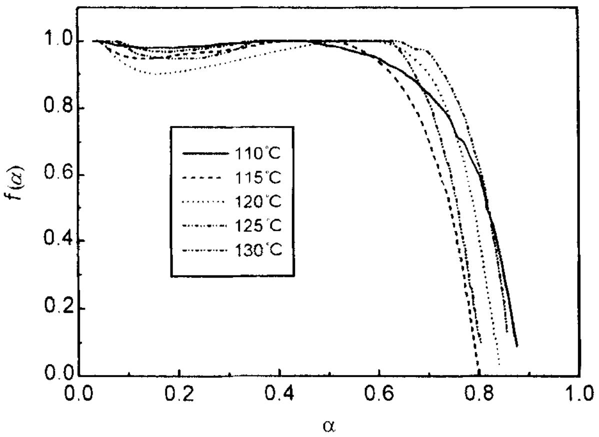


FIGURE 6 Plot of diffusion factor, $f(\alpha)$, *versus* conversion at different curing temperatures.

begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$ and beyond this point, approaches zero as the reaction effectively stops. It shows that with conversion increasing the effect of diffusion developed gradually. The effective reaction rate k_e at any conversion is equal to the chemical reaction rate k_c multiplied by $f(\alpha)$.

Figure 6 shows the plots of $f(\alpha)$ *versus* conversion α at different curing temperatures. As the cure progresses, the resin crosslinks, the glass transition temperature T_g of the system rise. When it approaches T_c, the resin passes from a rubbery state to a glassy state. At this stage, the mobility of the reacting groups is hindered and the rate of conversion is controlled by diffusion rather than by chemical factors. The k_e and $f(\alpha)$ are decreased with the conversion increasing, and approaches zero when T_g is raised.

T_g Value and the Curing Process

T_g has been used directly as a parameter for conversion in analysis of reaction kinetic models [18, 19], and there is a one-to-one relationship between the T_g and the degree of cure. It is a sensitive parameter because of the ease of measurement of T_g by TBA, and is particularly useful at high conversion and after vitrification because of the non-linearity of T_g *versus* conversion reaction [20, 21]. The T_g values are measured for the BPSER/anhydride specimen cured isothermally at different temperatures for various periods. T_g obtained from TBA measurements is plotted *versus* cure time in Figure 7. As seen from Figure 7, different glass transition behaviors occurred for the samples with different degrees of cure.

At low T_cs, as observed, T_g increases during the early stages of cure. Then levels off and remains a low temperature value compared with higher T_cs. Even if we prolong the curing time under low T_cs, the resin system is difficult to reach high conversion. At T_c of 453 K, T_g quickly reaches the maximum, and a high degree crosslinked structure is formed after a short period. Because the process of vitrification usually drastically lowers the reaction rate, complete cure usually involves temperatures in the vicinity of the maximum of glass transition temperature. This is indicative of autocatalytic kinetics in the first stages and diffusion-controlled reaction as the T_g rises [19]. Similar results have been obtained based on our study of the conversion or reaction rate *versus* time at different isothermal cure temperatures.

At the beginning of the curing reaction process, the degree of cure is low, and the sample gives low T_g value. At this stage, the process is characterized by a gradual increase in molecular weight, and this

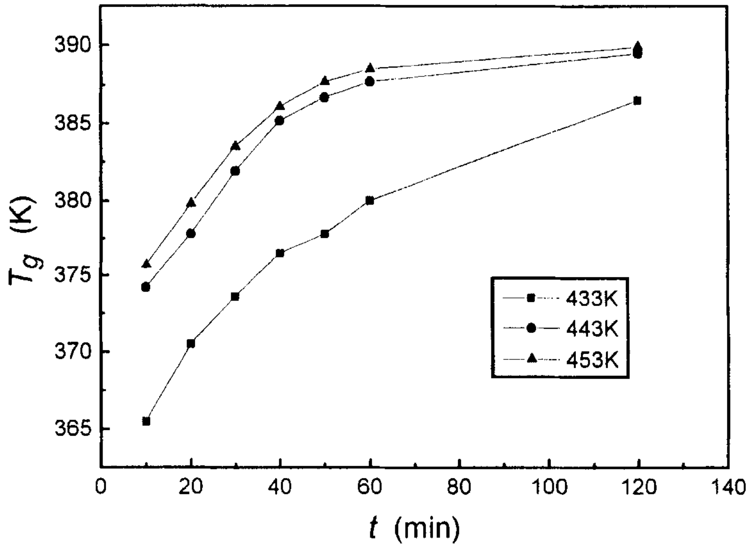


FIGURE 7 T_g values of the BPSER/anhydride cured isothermally at different temperatures for various periods.

transition behavior is the reflection of the movement of linear molecular chain in the system. Since only linear molecular chains exist in this stage, there are many chances for the molecular to collide and it results in a high reaction rate. With the weight-average molecular weight increasing, the T_g value increases. With the molecular weight increases, the mobility of the chains is decreased, and the chances for the molecular to collide with each other are reduced. The crosslinking density further increases with the reaction time rising, and the T_g of the network is enhanced with a decrease in the distance between crosslink points. Correspondingly, the increasing crosslinking density makes the intramolecular reaction not to proceed any longer. At this time, the sample has been highly cured and the T_g value is get higher.

T_g of BPAER/phthalic anhydride system is determined to be 355 K, and it's almost 40 K lower than that of BPSER's. It illustrates that BPSER has better thermal resistance. This is due to the different molecular structure of the BPSER and BPAER. Bisphenol-S has an electron-withdrawing group, $-SO_2-$, which effects the intermolecular forces in the polymers and effects epoxide group more than $-C(CH_3)_2-$ group of the bisphenol-A. Higher T_g values were found at polymers with higher polar group $-SO_2-$ in comparison with the $-C(CH_3)_2-$ group. We can say that the $-SO_2-$ group in the resin raises the T_g of the cured material. Thus, investigation of molecular structure-macroscopic property relations is the principal theme of polymer material science.

Thermal Degradation

The weight loss fractions of resin were calculated, and the weight loss rates were shown as a function of temperatures in Figure 8 and Table III. The following kinetic equation was assumed to hold for the thermal degradation reaction [13]. When the reaction order $n = 1$, it follows as:

$$\ln\left(-\frac{\ln C}{T^2}\right) = \ln\left[\frac{AR}{\varphi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (6)$$

where $C = (W/W_0)$, W is the remained weight, W_0 is the total weight loss, E is the activation energy, A is the frequency factor, φ is the

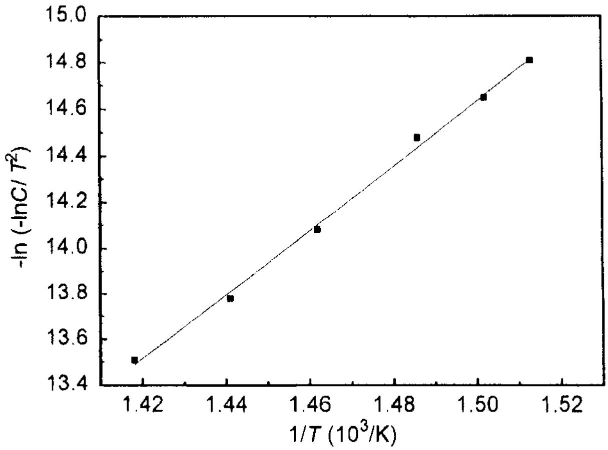


FIGURE 8 Weight loss function, $-\ln(-(\ln C/T^2))$, *versus* reaction temperature T of the thermal degradation.

TABLE III Thermal weight loss (%) of BPSER/anhydride at different temperatures

$T(K)$	603	623	643	653	673	683	693	703
$C(\%)$	4.29	6.18	9.55	12.69	20.82	30.02	39.43	49.13

heating rate, and R is the ideal gas constant. According to this equation, a plot of $\ln(-(\ln C/T^2))$ against $(1/T)$ will be shown in Figure 8. It is observed that the activation energy of thermal degradation for the system is 116.11 KJ/mol, and the linear correlation coefficient is 0.9985.

CONCLUSIONS

1. The cure reaction for the system of BPSER/phthalic anhydride system is shown as an autocatalytic behavior in the kinetic control stage, and can be well described with the model proposed by Kamal, which includes two rate constants, k_1 and k_2, and two reaction orders, m and n. The overall order, $m+n$ is in the range $2 \sim 3$. With the proceeding of the cure reaction, the cross-linking structure appears, and the reaction is mainly controlled by diffusion in the latter stages.

2. T_gs were investigated for BPSER/anhydride samples cured partially; and by monitoring the difference in these T_gs, the curing reaction process and the thermal property of BPSER/anhydride are illustrated. The results show that the T_gs increase with the increasing of the cure conversion.
3. The thermal stability of the material studied by TGA illustrates that the BPSER/anhydride has n-order reaction kinetics. The activation energy of this system E_d is 116.11 KJ/mol and $n = 1$.

References

[1] Kreps, R. W. F., Klootwijk, A. and Goppel, J. M. (1989). *U.S. Pat. 3,364,178.*
[2] Stutz, H., Tesch, H., Neumann, P. and Schaefer, G. (1987). *De 3,523,318.*
[3] Beavers, E. M. (1953). *U.S. Pat. 2,765,322.*
[4] Masters, J. E. (1956). *U.S. Pat. 2,767,157.*
[5] Gao, J. G. (1993). *J. Appl. Polym. Sci.*, **48**, 237.
[6] Opalicki, M., Kenny, J. M. and Nicolais, L. (1996). *J. Appl. Polym. Sci.*, **61**, 1025.
[7] Khanna, U. and Chanda, M. (1993). *J. Appl. Polym. Sci.*, **49**, 319.
[8] Duswlt, A. A. (1974). *Thermochim. Acta*, **8**, 57.
[9] Kamal, M. R. (1974). *Polym. Eng. Sci.*, **14**, 23.
[10] Kenny, J. M. and Opalicki, M. (1993). *Makromol. Chem., Macromol. Symp.*, **68**, 41.
[11] Rainer, E., Udo, G., Heinrich, H. W. and Eruin, B. (1985). *Ger. Pat. DD228,279.*
[12] Jay, R. R. (1964). *Anal. Chem.*, **36**, 665.
[13] Liu, Z. H., *Thermoanalysis Introduction*, Beijing, Chemical Industry Publishing Co., 1991.
[14] Woo, E. M. and Seferis, J. C. (1990). *J. Appl. Polym. Sci.*, **40**, 1237.
[15] Ghaemy, M. and Riahy, M. H. (1996). *Eur. Polym. J.*, **32**, 1207.
[16] Keenan, M. R. (1987). *J. Appl. Polym. Sci.*, **33**, 1725.
[17] Barton, J. M. (1985). *Adv. Polym. Sci.*, **72**, 111.
[18] Simon, S. L. and Gillham, J. K. (1993). *J. Appl. Polym. Sci.*, **47**, 461.
[19] Wisanrakkit, G. and Gillham, J. K. (1990). *J. Appl. Polym. Sci.*, **41**, 2885.
[20] Wisanrakkit, G., Gillham, J. K. and Enns, J. B. (1990). *J. Appl. Polym. Sci.*, **41**, 1895.
[21] Venditti, R. A. and Gillham, J. K. (1997). *J. Appl. Polym. Sci.*, **64**, 3.