

The Preparation, Characterization, and Cure Reactions of New Bisbenzocyclobutene-Terminated Aromatic Imides

Yingqiang Zhang,¹ Jianying Gao,² Xuening Shen,¹ Farong Huang¹

¹The School of Materials Science and Engineering, Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai 200237, People's Republic of China

²Department of Chemistry, East China University of Science and Technology, Shanghai 200237, People's Republic of China

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ABSTRACT: Several new bisbenzocyclobutene-terminated aromatic imides, 2,2'-bis(*N*-4-benzocyclobutenyl)phthalimide, 2,2'-bis[4-(*N*-4-benzocyclobutenylphthalimide)]-ether, 2,2'-bis[4-(*N*-4-benzocyclobutenylphthalimide)]-ketone, and 2,2'-bis[4-(*N*-4-benzocyclobutenylphthalimid-4-oxy)phenyl]-propane, have been synthesized in high yields and characterized by FTIR, MS, EA, and ¹H NMR spectroscopy. The polymers cured from benzocyclobutene-terminated imides have high glass transition temperature and good thermal stabilities. The cure reaction of an imide was studied by FTIR-ATR (attenuated total reflection) and DSC techniques. Appar-

ent kinetic parameters of the cure reaction are obtained. The apparent cure reaction order, activation energy, and pre-exponential factor determined by isothermal DSC method are 1, 143.4 kJ/mol, and $3.88 \times 10^{13} \text{ min}^{-1}$, and by nonisothermal DSC methods 1, 139.4 kJ/mol, and $2.27 \times 10^{13} \text{ min}^{-1}$, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1705–1719, 2006

Key words: bisbenzocyclobutene-terminated aromatic imides; cure reaction; reaction kinetics

INTRODUCTION

Benzocyclobutene-terminated resins can thermally be cured at 180–250°C without giving off volatiles. The cured polymers have good heat-resistant properties and low moisture sensitivity, which makes them a promising material for high performance composite systems^{1–5} and functional films and coatings of insulation.^{6–10}

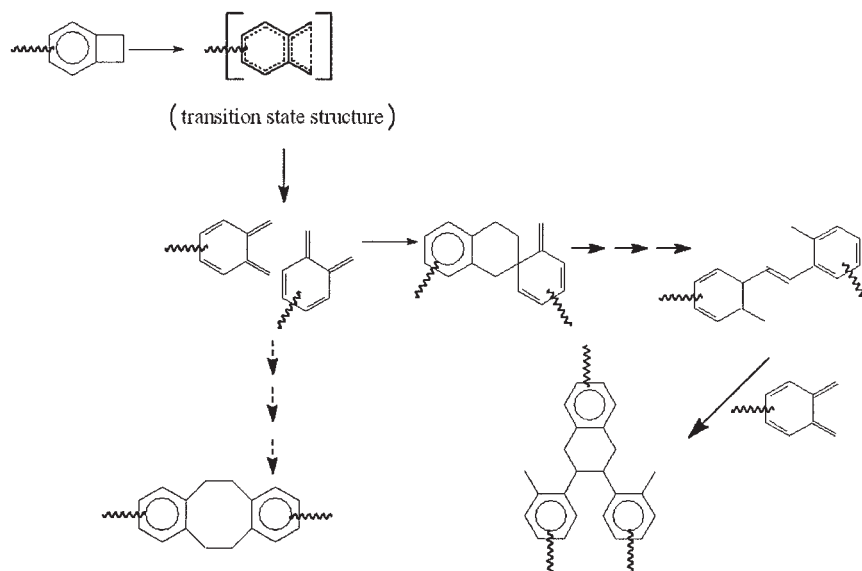
As well known, the performances of materials based on thermosetting resins mainly depend on chemical structures of resins and network structures formed in the course of resin processing. However, the processing of thermosetting resins is complicated because of involvement of complicated chemical reactions. Therefore, the understanding of curing is the fundamental in the analysis, design, and control of any processing operation.

Studies concerning the thermal cure of various bisbenzocyclobutene resins^{11–13} and other benzocyclobutene resins^{14–17} in an attempt to understand the chemistry of the processing of benzocyclobutene materials have been reported in recent years and good

kinetics results of cure reaction have been obtained by both HPLC and thermal analysis methods. People have also paid great attention to the cure mechanism and crosslinking structures formed from bisbenzocyclobutene resins. It was believed in previous work^{18,19} that cure reaction of bisbenzocyclobutenes follows the biradical mechanism to form a three-dimensional poly-*o*-xylylene network. However, research results in recent reports^{20,21} showed that the cure of bisbenzocyclobutene does not follow the suggested biradical mechanism, but a pericyclic reaction mechanism (Scheme 1). According to the pericyclic reaction mechanism, the cure reaction and formed crosslinked structures of bisbenzocyclobutene resins can be well described. Bisbenzocyclobutenes undergo a slow and thermally allowed ring-opening reaction to *o*-quinodimethane (reaction intermediate), which then quickly reacts with each other by Diels–Alder cycloadditions and other reactions to form mainly two characteristics structures in two different pathways. One structure formed by the cycloadditions and rearrangements reaction in one way shown by void arrowhead in Scheme 1 is dibenzocyclooctadiene structure (structure I) and another structure formed by other cure reactions in other way shown by solid arrowhead in Scheme 1 is tetrahydronaphthalene structure (structure II). The rate-controlled step of the whole crosslinking reactions of bisbenzocyclobutenes is the opening of strained four-membered ring of benzocyclobutene.

Correspondence to: F. Huang (fhuanglab@ecust.edu.cn).

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Scheme 1. Mechanism of cure reaction of bisbenzocyclobutenes.

Undoubtedly, it is very important to investigate the cure reaction behavior, kinetics, and process parameters of a bisbenzocyclobutene-terminated imide, which will help to better understand the control technology and chemical reaction characteristics of bisbenzocyclobutene during the processing of bisbenzocyclobutene-terminated imides. The objective of the present work is to synthesize and characterize some bisbenzocyclobutene-terminated aromatic imides with new structures and investigate cure behaviors and reaction kinetics of these imides to further understand the cure reaction of bisbenzocyclobutene resins.

EXPERIMENTAL

Reagents and solvents

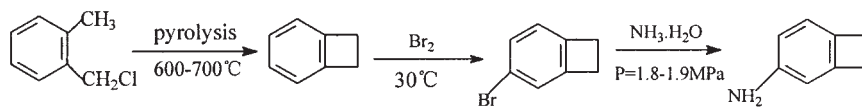
Pyromellitic dianhydride (PMDA) was purchased from Shanghai No.1 Reagent Factory and recrystallized from acetic anhydride before use. Benzophenone-3,3',4,4'-tetracarboxylic acid dianhydride (BTDA) was purchased from Shanghai Synthetic Resin Institute and recrystallized from acetic anhydride before use. Oxydiphthalic dianhydride (ODPA) and 2,2'-bis[4,4'-di(3,4-dicarboxyphenoxy)phenyl]propane dianhydride were purchased from Shanghai Synthetic Resin Institute and used as received. Acetic anhydride (Analytical Re-

agent Grade) was purchased from Xin Da Chemical Factory and used as received.

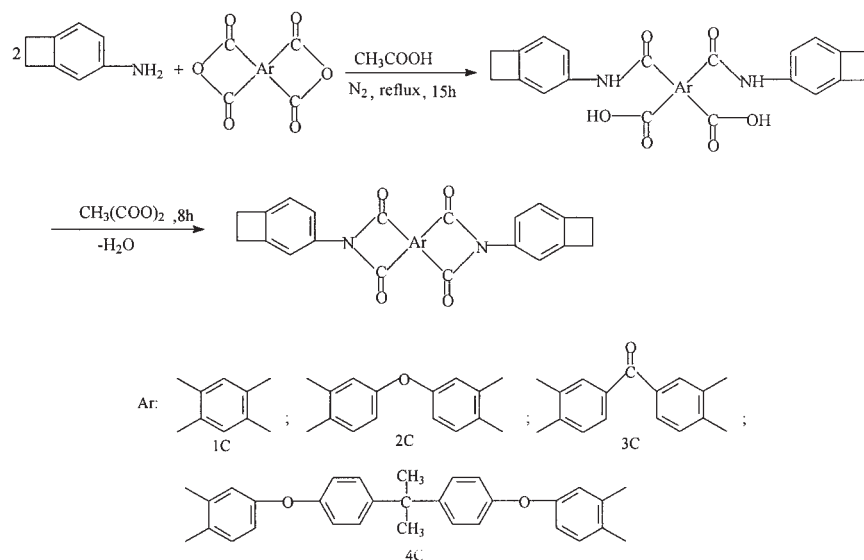
Preparation of imides

The preparation of 4-amino-benzocyclobutene was performed according to the procedures described in the literature²² (Scheme 2). Bisbenzocyclobutene-terminated aromatic imides, 2,2'-bis(*N*-4-benzocyclobutenyl)phthalimide (designated as 1c), 2,2'-bis[4-(*N*-4-benzocyclobutenyl)phthalimide]-ether (2c), 2,2'-bis[4-(*N*-4-benzocyclobutenyl)phthalimide]-ketone (3c), and 2,2'-bis[4-(*N*-4-benzocyclobutenyl)phthalimid-4-oxo]phenyl]propane (4c) were prepared according to procedures described in the literatures^{23,24} (Scheme 3). The colors and yields of 1c, 2c, 3c, and 4c were light yellow, 93%; white, 90%; light yellow, 94%; and light yellow, 95%, respectively. The melting point of 4c was 179°C, and those of others were not observed.

Anal. Calcd for 1c (C₂₆H₁₆O₄N₂): C, 73.66; H, 3.81; N, 6.67. Found: C, 74.01; H, 3.80; N, 6.43. Anal. Calcd for 2c (C₂₆H₂₀O₅N₂): C, 75.00; H, 3.91; N, 5.47. Found: C, 74.87; H, 3.92; N, 5.26. Anal. Calcd for 3c (C₃₃H₂₀O₅N₂): C, 75.57; H, 3.82; N, 5.34. Found: C, 75.26; H, 3.83; N, 5.14. Anal. Calcd for 4c



Scheme 2. The preparation of 4-amino-benzocyclobutene.



Scheme 3. Synthesis route of benzocyclobutene-terminated imides.

($C_{47}H_{34}O_6N_2$): C, 78.16; H, 4.71; N, 3.88. Found: C, 77.88; H, 4.80; N, 3.61.

Polymerization

4c was cured in a stove under air at 230°C/1 h, 240°C/1 h, 250°C/1 h, and 275°C/1 h and postcured at 300°C/3 h. The obtained polymer is referred to as 4p. The other imides, 1c, 2c and 3c, were polymerized in air at 250°C/2 h, 270°C/2 h, 290°C/1 h, and 300°C/1 h and then postcured at 315°C/3 h. The cured polymers, corresponding to imides 1c, 2c, and 3c, are referred to as 1p, 2p, and 3p, respectively, throughout the text. The colors of 1p, 2p, and 3p were found to be yellow, brown yellow, and brown yellow, respectively. The film of 4p was found to be light yellow and transparent.

Measurements

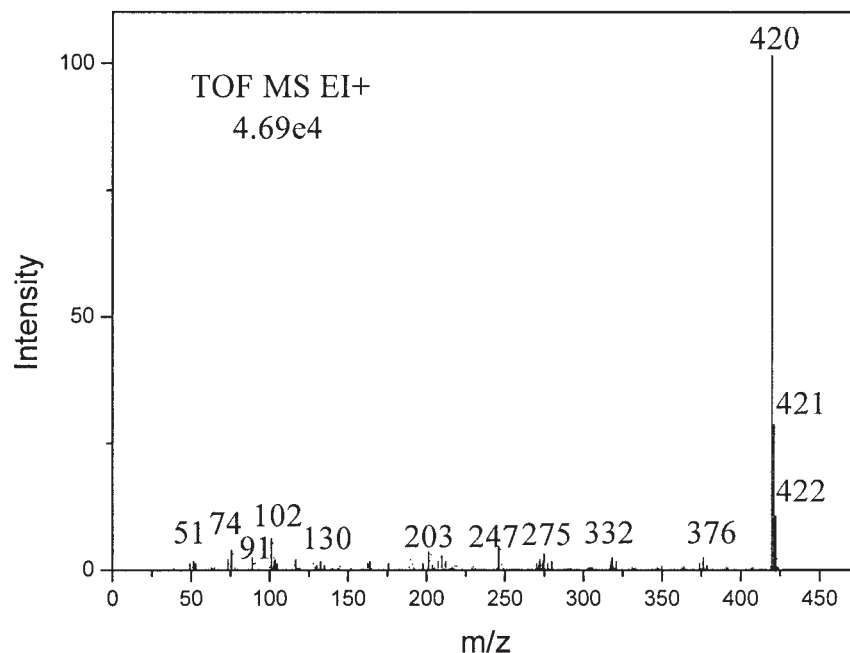
SPI-MS (electrospray ionization mass spectrometry) analysis was carried out on Micromass LCT KC317 and EI-MS (electron ionization mass spectrometry) analysis was conducted on Micromass GCT. Elemental analyses were conducted with Elementar vario EL III analyzer. Proton nuclear magnetic resonance (1H NMR) spectra were obtained in deuteriochloroform and tetramethylsilane was used as an internal standard. The instrument used was BRUKER AVANCE 500 (500 MHz). The thermal stability of cured polymers was characterized by TGA using METTLER TGA/SDTA 851 under N_2 at a heating rate of 20°C/min from 30 to 800°C. Dynamic mechanical analysis (DMA) was utilized primarily for the identification of glass transition temperature (T_g). DMA was carried

out on UBM Rheogel-E4000 operating in the tension mode from 100 to 350°C at a frequency of 11 Hz with a programmed heating rate of 3°C/min. The imide resins were characterized by Fourier transform infrared (FTIR) spectroscopy with Nicolet 550. Solid samples were pressed into pellets with KBr or a thin film of samples was cast from CH_2Cl_2 solution on a KBr plate for FTIR analyses. FTIR-ATR technique was used to follow the cure reaction of a sample with Nicolet AVATAR360, by casting film from a 30 wt % 4c solution in CH_2Cl_2 on the foil of aluminum. The samples were cured at a given temperature and measured at given time intervals. Differential Scanning Calorimetric (DSC) measurements were performed with Universal V2.3 TA instruments 2910 modulated system for nonisothermal cure reaction of the imides and NETZSCH DSC 204 system for isothermal cure experiments. For the isothermal experiments, the samples were placed in the cell and the cell was heated to 100°C and then kept for 1 min to get rid of the humidity of sample and thereafter the cell was quickly heated to a test temperature. Then the scanning of DSC was conducted. For nonisothermal experiments, the heating rate of 5, 10, 15, and 20°C/min were chosen and used.

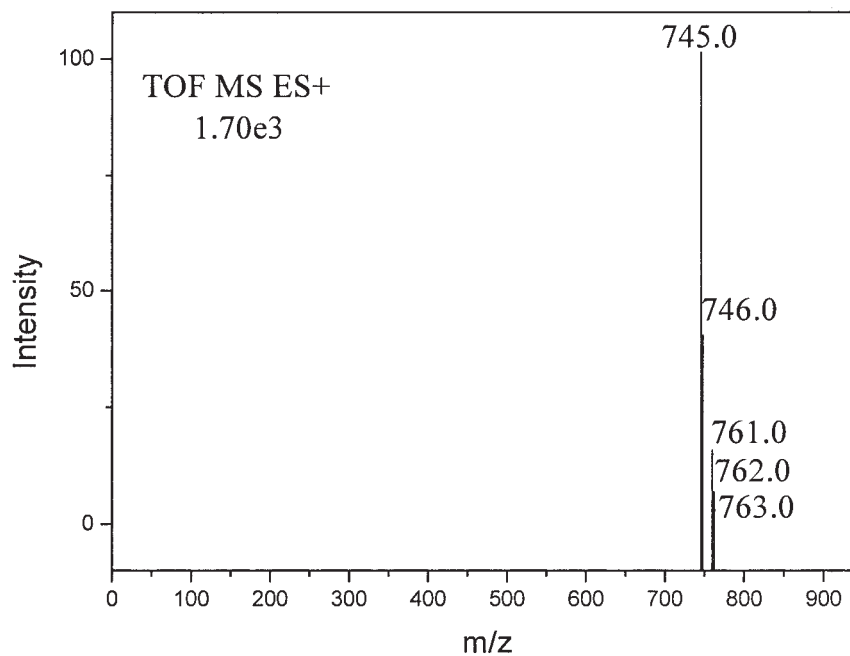
RESULTS AND DISCUSSION

Characterization of imides

The chemical structures of 1c, 2c, 3c, and 4c are determined by MS, FTIR, and 1H NMR spectrometry. Mass spectra of the prepared imides are shown in Figure 1. EI-MS is used to determine the structure of 1c, 2c, and 3c. 1c m/z : 420(M^+); 2c m/z : 512(M^+); and 3c m/z :



(a)



(b)

Figure 1 Typical EI-MS spectra of 1c (a) and SPI-MS spectra of 4c (b).

524(M^+). SPI-MS is used to determine the structure of 4c. 4c m/z : 745.0($M^+ + Na^+$), 746.0(isotope peak of $M^+ + Na^+$), 761.0($M^+ + K^+$), 762.0, and 763.0(isotope peak of $M^+ + K^+$).

FTIR spectra of purified bisbenzocyclobutene-terminated aromatic imides, 1c, 2c, 3c, and 4c, are shown in Figure 2. The characteristic band at 2930 cm^{-1} is as-

signed to C—H asymmetric stretching vibration of methylene of four-membered ring of benzocyclobutene. Another characteristic band is aromatic in-plane ring stretching mode at 1470 cm^{-1} for all the imides, which associates with the strain of four-membered ring of benzocyclobutene. In addition, the characteristic band at 1776 cm^{-1} is assigned to asymmetric

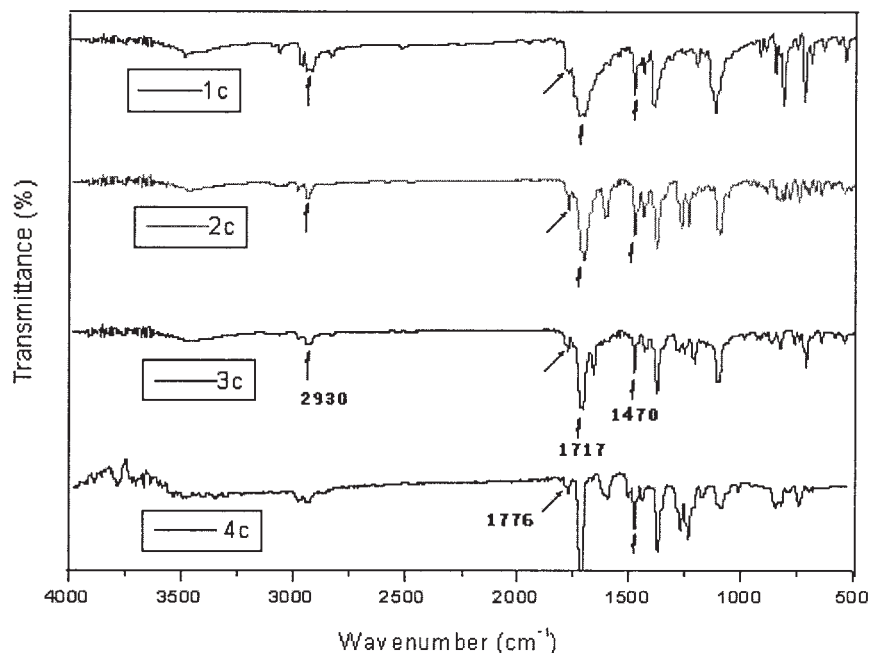


Figure 2 FTIR spectra of 1c–4c.

stretch of imide group and at 1717 cm^{-1} assigned to symmetric stretch of imide group. Characteristic C—N stretching vibration of imide groups can be found at 1380 cm^{-1} , which is also present in the spectra of all the imides studied.

^1H NMR spectra of 1c, 2c, 3c, and 4c are shown in Figure 3. The singlet at 3.25 ppm is a characteristic peak for the alicyclic protons. The aromatic protons appear as a multiplet at 6.9–8.4 ppm, which are observed for all the imides. For 4c, the peak at 1.68 ppm is attributed to the protons of methyl groups $-\text{C}(\text{CH}_3)_2-$.

Solubility of imides

The solubility of 1c, 2c, 3c, and 4c in various organic solvents is listed in Table I. As shown in Table I, 4c dissolves not only in strong polar solvents such as DMAC, DMF, and NMP but also in halohydrocarbon such as CH_2Cl_2 and chloroform. Other imides made from PMDA, BTDA, and ODPA only dissolved in NMP. This indicates that the imides with a stiff structure in the backbone have less solubility in solvents. The good solubility of 4c mainly results from the introduction of bisphenol A group which probably makes the molecular structure pack more loose.

Cure behaviors of imides

The cure behaviors of the imides are traced by DSC. Figure 4 shows the typical DSC curves of 1c and 4c. DSC curves of 2c and 3c are similar to 1c. There is not

any endothermic peak of DSC curve, which indicates these imides have no melting points. A sharp exothermic peak is observed for 1c, 2c, 3c, and 4c and is caused by ring-opening polymerization. All analyses results are tabulated in Table II. The onset temperatures of exothermic cure reaction of samples 1c, 2c, and 3c are higher than that of 4c. Although 4c has the lower concentration of benzocyclobutene groups compared with other benzocyclobutene-terminated imides, it has the highest ΔH_{polym} (Heat of cure reaction). This is probably owing to the restricted molecular mobility of 1c, 2c, and 3c, and not all of benzocyclobutene groups react with each other in a short period of time during cure process. In addition, 4c shows the lower cure temperature, whereas 1c, 2c, and 3c exhibit higher cure reaction temperatures, which indicates that the crosslinking reaction of 4c easily take place. Therefore, the chemical structure of benzocyclobutene-terminated imide could influence to some extent the cure behavior.

Glass transition temperature of cured polymers

Dynamic DSC is normally used for the determination of glass transition temperature T_g of polymers. However, T_g s of the 1p, 2p, 3p, and 4p could not be detected by DSC, presumably because these imide polymers are highly crosslinked and any change in specific heat capacity (C_p) is too small to be detected. DMA is usually an alternative technique used to measure T_g of polymers networks. DMA curve of 4p is given in Figure 5. The peak of $\tan \delta$ curve results from the glass

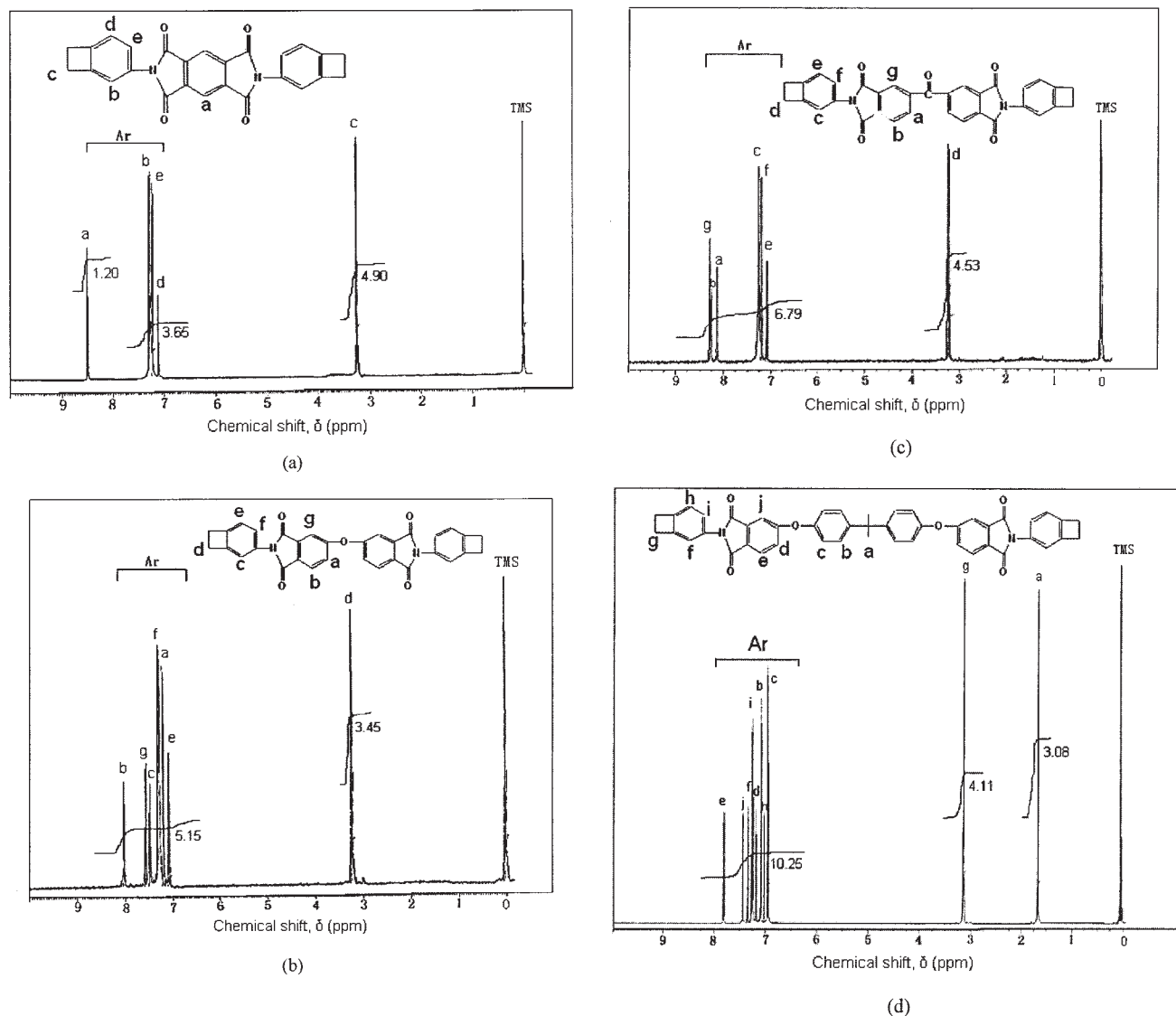


Figure 3 ^1H NMR spectra of 1c (a), 2c (b), 3c (c), and 4c (d).

transition and the temperature at the peak is considered as T_g . As shown in Figure 5, 4p displays a T_g of 300°C. Samples of 1p, 2p, and 3p for DMA measurement could not be made because of insoluble and unmelted properties of 1c, 2c, and 3c.

Thermal stabilities of cured polymers

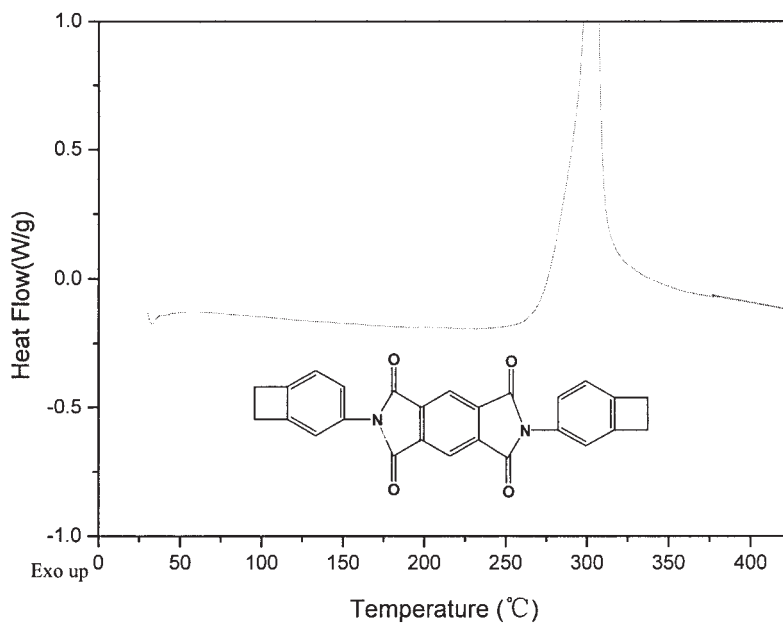
The typical TGA and DTGA curves of 4p are shown in Figure 6 and the initial thermal decomposition tem-

peratures (IDT)* of 1p–4p are listed in Table III. As shown in Figure 6 and Table III, IDT of 1p, 2p, 3p, and 4p are all higher than 483°C, which indicates that these imide polymers have high thermal stabilities and is similar to that reported.^{23–25} Additionally, only one peak is observed on the DTGA curve, which indicates that the thermolysis behavior of 4p is simple. The similar thermolysis behaviors are also observed for 1p, 2p, and 3p.

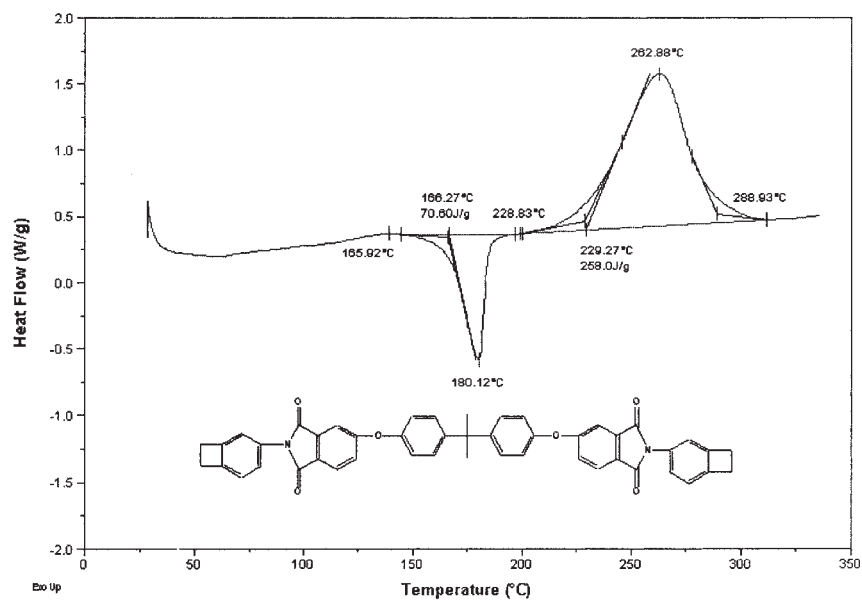
TABLE I
Solubility of 1c, 2c, 3c, and 4c in Various Organic Solvents (25°C)

Monomers	CH_2Cl_2	CH_2Cl_3	Acetone	DMF	DMAC	NMP	<i>N</i> -hexane	Ethanol
1c	*	*	–	–	–	+	–	–
2c	–	–	–	–	–	+	–	–
3c	*	*	–	–	–	+	–	–
4c	+	+	+	+	+	+	–	–

+, soluble; *, partially soluble; and –, insoluble.



(a)



(b)

Figure 4 DSC curves of 1c (a) and 4c (b).

TABLE II
DSC Analyses Results of 1c, 2c, 3c, and 4c

Imide	Exothermic peak temperature (°C)			ΔH_{polym} (J/g)
	Initial (T_i)	Max (T_p)	Final (T_f)	
1c	295.1	301.7	307.4	231.7
2c	293.4	299.8	306.3	202.7
3c	296.3	298.8	303.5	193.3
4c	229.3	262.9	288.9	258.0

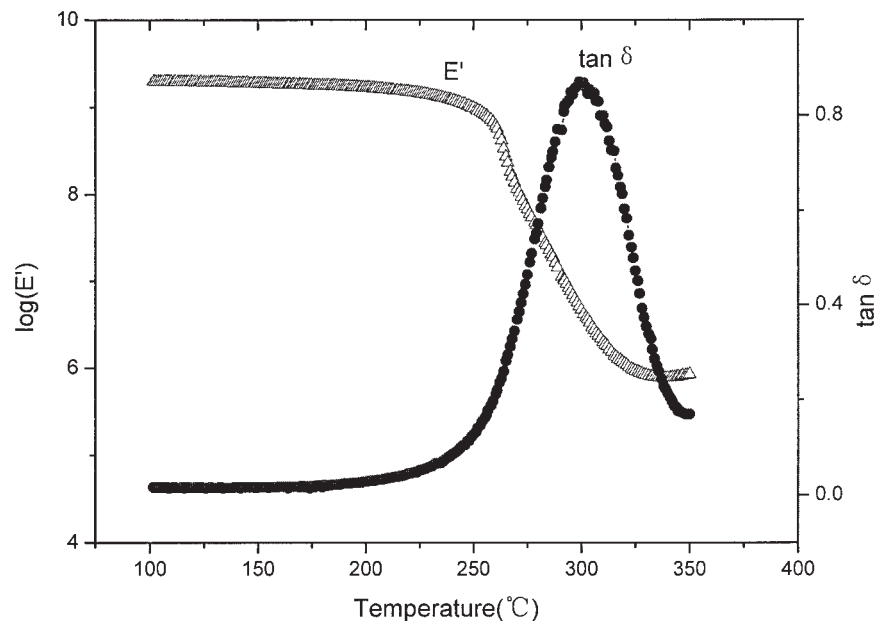


Figure 5 DMA of 4p.

Investigation of cure behavior by isothermal FTIR

FTIR-ATR technique is used to trace changes of active reactive group of 4c during cure process. FTIR spectra of 4c at 200, 215, 230, 245, 260, and 275 °C are measured and typical spectra are shown in Figure 7. The analytical results are tabulated in Table IV. The characteristic peak of aromatic in-plane ring stretching vibration at 1475 cm^{-1} gets smaller and smaller with the increas-

ing cure reaction time and simultaneously, another peak at 1505 cm^{-1} strengthens and gets stronger and stronger during the cure process, which is also associated with the incessant release of strained four-membered ring of benzocyclobutene.^{25,26} Based on the Beer-Lambert's law, the absorbance of groups is related to the content of the groups in the sample. The absorbance of the characteristic peak of aromatic in-plane ring stretching vibration (1475 cm^{-1}) of reactant as a function of time at specified

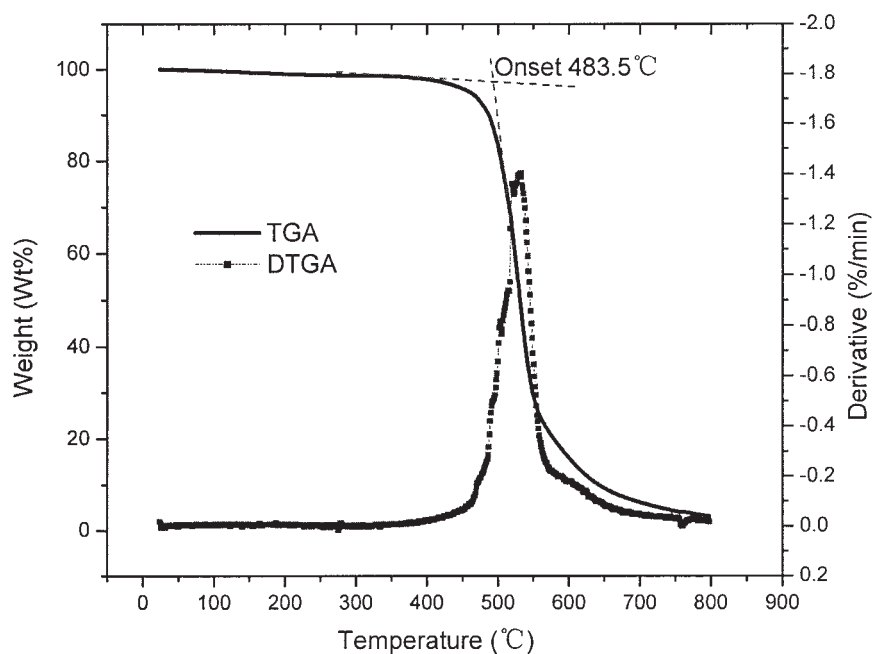


Figure 6 TGA and DTGA curves of 4p (N_2 , heating rate: $20^\circ\text{C}/\text{min}$).

TABLE III
Initial Thermal Decomposition Temperatures (T_d)^a of Cured Polyimides

Polymer	IDT ^b (°C)
1p	501.5
2p	520.1
3p	513.6
4p	483.5

^a N₂, heating rate: 20°C/min.

^b Initial decomposition temperature derived by extrapolation.

temperature are measured and the area of peak at 1475 cm⁻¹, A_{1475} , is calculated by integrating the area under FTIR curve of the characteristic absorbance peak, and normalized to the total area of the peaks of the imide carbonyl group bands at 1778 cm⁻¹ (asymmetric stretch) and 1716 cm⁻¹ (symmetric stretch).

All of data in Table IV indicate that high temperature accelerates the ring-opening reaction of benzocyc-

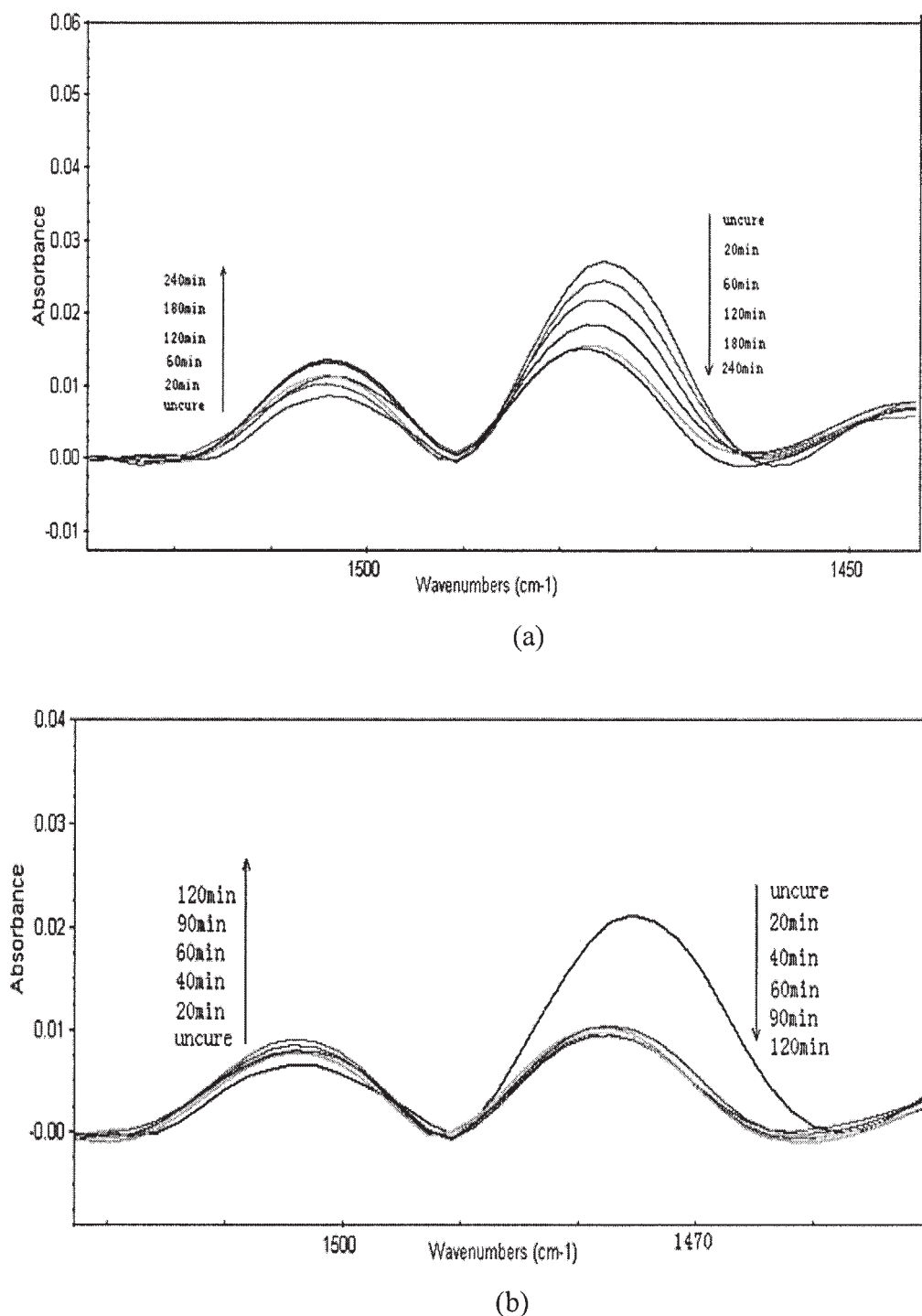


Figure 7 FTIR spectra of 4c cured isothermally at 200°C (a) and 260°C (b).

TABLE IV
Absorption Band Area Ratio $A_{1475}/A_{c=0}$ ^a of 4c at Various Temperatures for Different Cure Time

Temperature(°C)	Reaction time (min)						
	20	40	60	90	120	180	240
200	0.225	—	0.196	0.166	0.130	0.113	0.111
215	0.181	—	0.132	—	0.115	0.105	0.103
230	0.123	0.103	0.097	0.094	0.086	—	—
245	0.111	0.103	0.108	0.108	0.107	—	—
260	0.105	0.101	0.098	0.097	0.093	—	—
275	0.096	0.093	0.093	0.093	0.093	—	—

^a $A_{c=0}$ is the total area of two peaks for asymmetric and symmetric stretching of the carbonyl group of imide.

clobutene and thereby the cure reaction would be finished in short time at high temperature. At 200°C, the cure reaction had not been completed even for 240 min, as indicated in Figure 7(a). However, at 275°C, the ratio of $A_{1475}/A_{c=0}$ hold the same value 0.093 after 20 min, which indicates that the cure reaction can be finished in 20 min. In addition, it is also observed that the intensity of the peak at 1475 cm^{-1} gradually decreases with the reaction time increasing at 200°C, whereas the intensity at 260°C decreases fast at the beginning (in 20 min) and then change less. This means the cure reaction quickly takes place at temperatures higher than 250°C.

Kinetics for cure reactions

Isothermal DSC

A DSC is used to measure the heat of cure reaction during an isothermal cure process. A single exother-

mic peak is observed in a DSC curve and it is assumed that the cure reaction originates from a single chemical process as the first approximation. In addition, it has to be assumed that all the heat generated only comes from the cure reaction, which is irreversible ring-opening reaction. It is assumed that no reaction takes place before the experiments started and there is no volatilization in sample pans. Thus, it is feasible to relate the area under the exothermic curves to the heat of reaction.

The DSC curves of heat flow of cure reaction vs. time at different temperatures are given in Figure 8. The rate of heat release ($d\Delta H_1/dt$) measured by DSC is directly converted into overall reaction rate ($d\alpha/dt$) as a function of time using the following formula:

$$d\bar{\alpha}/dt = (dH/dt)_{ISO}/\bar{\Delta}H_T$$

where ΔH_T is the total heat of reaction, averaged from nonisothermal experiments at different heating rates.

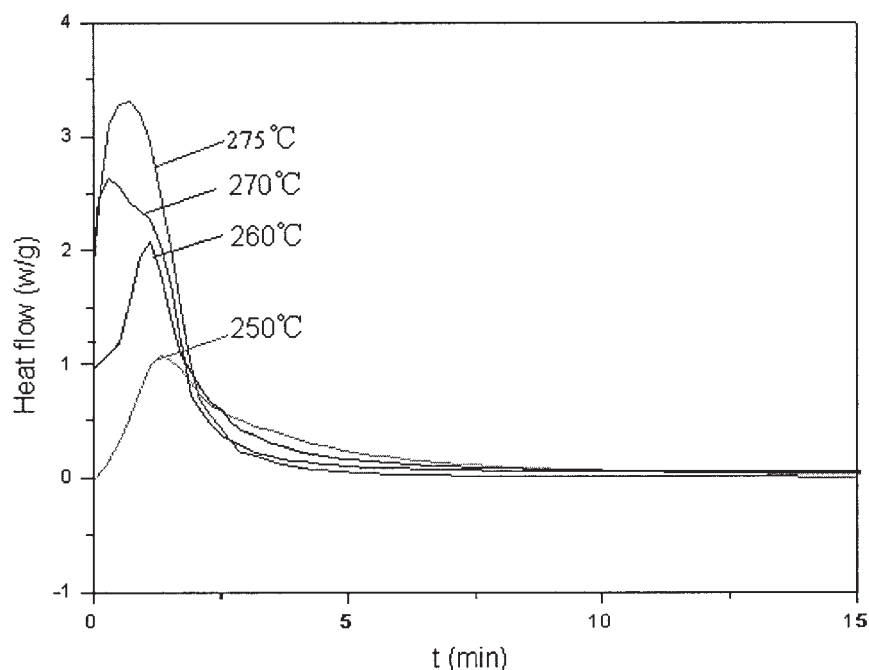


Figure 8 The heat flow of cure reaction vs. time for 4c at different temperatures by DSC.

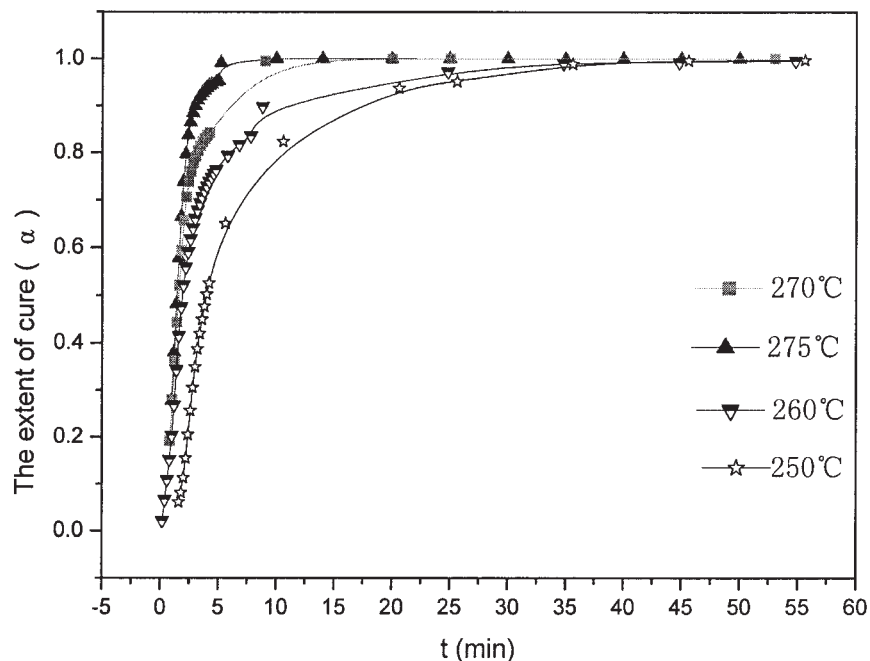


Figure 9 The extent of reaction *vs.* time of 4c at different temperatures.

The extent of reaction α is calculated from the partial areas in the DSC trace divided by ΔH_T .

In Figure 9, the extent of reaction is plotted as a function of isothermal cure temperatures. The relationship of $(1-\alpha)$ *vs.* time (Fig. 10) agrees with the first order kinetics model very well, and the value of reaction rate constant at different temperature is obtained by fitting $\ln(1-\alpha)$ with t with a high regression coef-

ficient, and listed in Table V. As shown in Table V, the higher the reaction temperature, the larger the reaction rate constant, and the faster the cure reaction takes place. The polymerization at 275°C is 4.5 times faster than that at 250°C.

Assuming that the Arrhenius relationship $k = Ae^{-E_a/RT}$ between temperature and reaction rate constant holds, an apparent activation energy $E_a = 143.4$

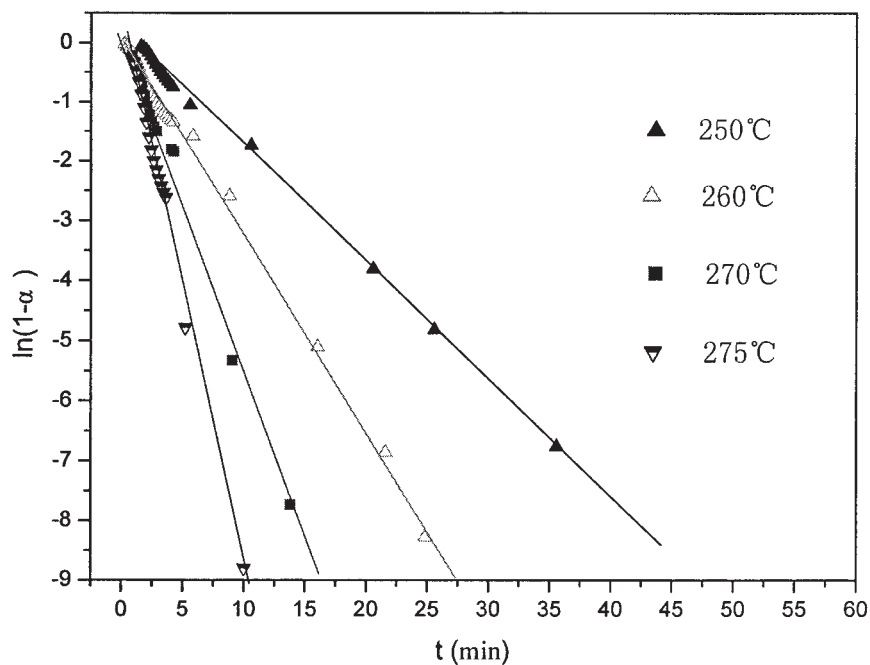


Figure 10 Kinetic plots of $(1-\alpha)$ *vs.* time of 4c at various temperatures.

TABLE V
Kinetic Analyses Results of the Thermal Curing
of 4c by DSC

Temperature (°C)	Reaction rate constant k (min ⁻¹)	Linear regression coefficient
250	0.194	0.999
260	0.320	0.989
270	0.581	0.996
275	0.901	0.978

kJ/mol is obtained from the slope and preexponential factor $A = 3.88 \times 10^{13}$ from the intercept of the plot of $\ln k$ vs. $1/T$ (Fig. 11). Therefore the polymerization reaction rate equation is expressed as follows:

$$d\alpha/dt = 3.88 \times 10^{13}(1 - \alpha)\exp(-143400/RT)$$

(Isothermal)

Nonisothermal DSC

We studied the cure reactions using nonisothermal DSC to better understand the cure process and check the kinetic parameters. Heat flow and temperature data are obtained through exothermic peaks of DSC curves at various heating rates. By using nonisothermal data at different heating rates, we have an alternative way of calculating the apparent activation energy of cure reaction. Nonisothermal DSC curves is shown in Figure 12.

According to the Kissinger equation²⁷ $d[\ln(\beta/T_p^2)]/d(1/T_p) = -E_a/R$, and Ozawa equation²⁸ $d[\ln(\beta)]/$

$d(1/T_p) = -1.052E_a/R$, where β is the heating rate (°C/min), R the universal gas constant (8.314 J/(mol K)), E_a the apparent activation energy (J/mol), and T_p the exotherm peak temperature (K). Thereby, the apparent activation energy is obtained by the plot of $\ln(\beta/T_p^2)$ vs. $1/T$ and $\ln(\beta)$ vs. $1/T$. The activation energy of cure reaction of the benzocyclobutene-terminated imide is calculated by Kissinger equation from the slope of the plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ and the slope of a plot of $\ln(\beta)$ and $1/T_p$ by Ozawa equation (Fig. 13) and the values of E_a are 139.0 and 139.9 kJ/mol, respectively. This result is consistent with kinetic parameters of benzocyclobutene resins reported previously,¹⁰ in which apparent activation energies of various benzocyclobutene-terminated resins are a range of 117.0–175.6 kJ/mol, which depends on molecular structures of resins. In addition, the apparent activation energy for the bisbenzocyclobutene-terminated imide we measured is a bit lower than the values of compound D (175 ± 13) and E (171 ± 3) in Table VI. The lower reaction activation energy of benzocyclobutene-terminated imide could be attributed to electron-withdrawing characteristics of imide groups bonded to the benzocyclobutene group. Kirchhoff et al.¹⁰ have shown that both electron-withdrawing group on arene or electron-donating group on the cyclobutene four-membered ring can lower the energy of the transition state (Scheme 4). Their explanation was that electron-withdrawing group on arene or electron-donating group on the cyclobutene (four-membered ring) can stabilize HOMO and LUMO of the transition state and make transition state structure more accessible.

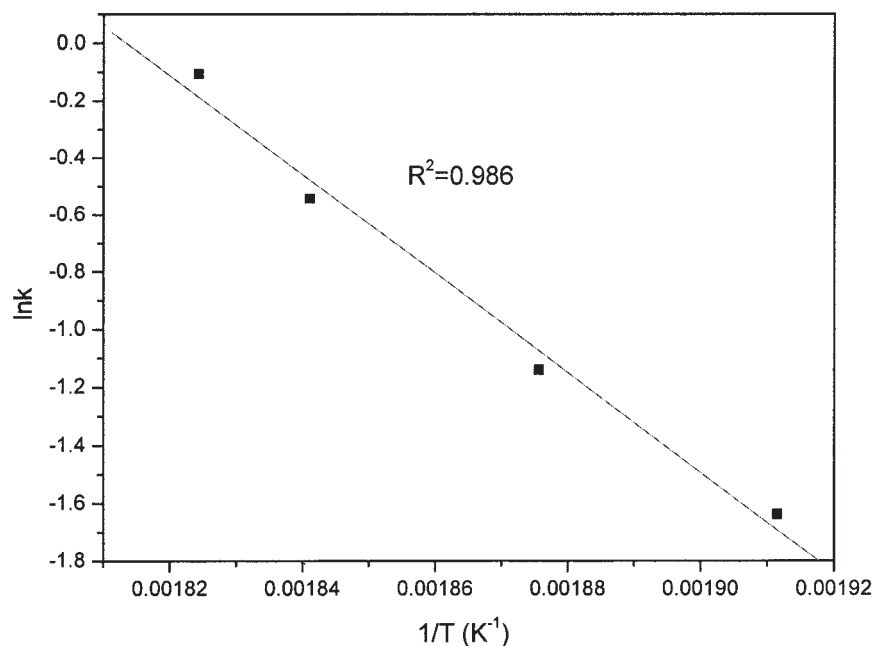


Figure 11 Kinetic plot of $\ln k$ vs. $1/T$ of 4c.

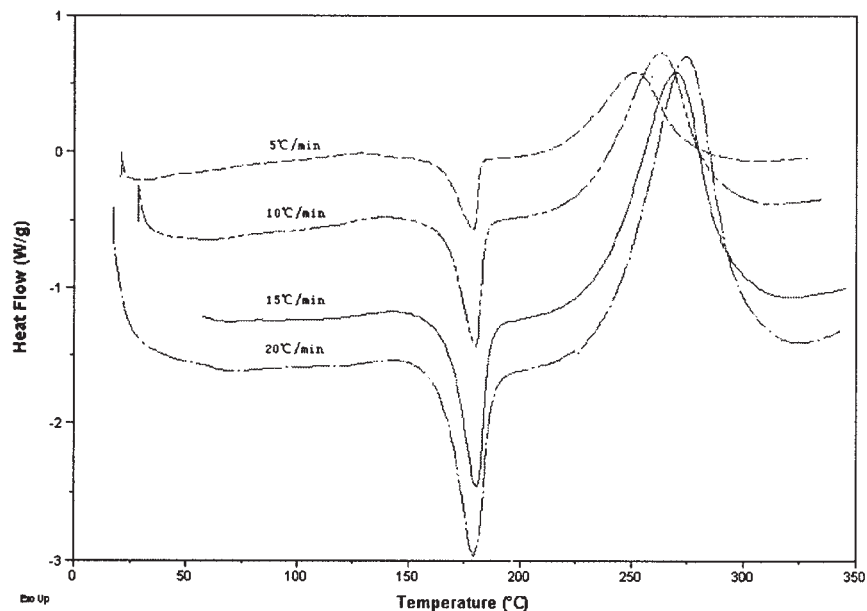


Figure 12 DSC cure exotherms of 4c at different heating rates.

The cure reaction order can be obtained, according to Crane equation,²⁹ $d(\ln\beta)/d(1/T_p) = -E_a/nR - 2T_p$. A straight line is obtained by fitting line of $\ln\beta$ vs. $1/T_p$, when $(E_a/nR) \gg 2T_p$, and then the reaction order n is 0.997, calculated from the slope of the line. The result is consistent with the previous report.¹⁰ The polymerization rate of the benzocyclobutene system is controlled by the

first-order ring-open reaction of benzocyclobutene to the *o*-quinodimethane intermediate.

Preexponential factor at different heating rates is calculated according to following Kissinger equation:²⁷ $A = \beta E_a \exp(E_a/RT_p) / [RT_p^2 n (1 - \alpha_p)^{n-1}]$, where α_p is the extent of reaction at the exothermal peak. The calculated results are listed in Table VII. Thus, according to Arrhenius equation, the cure

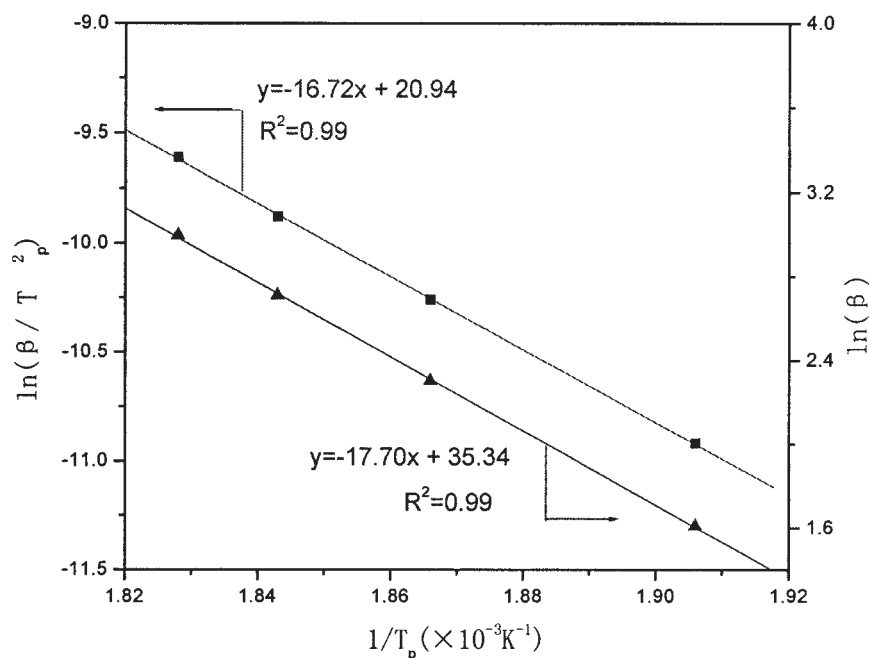
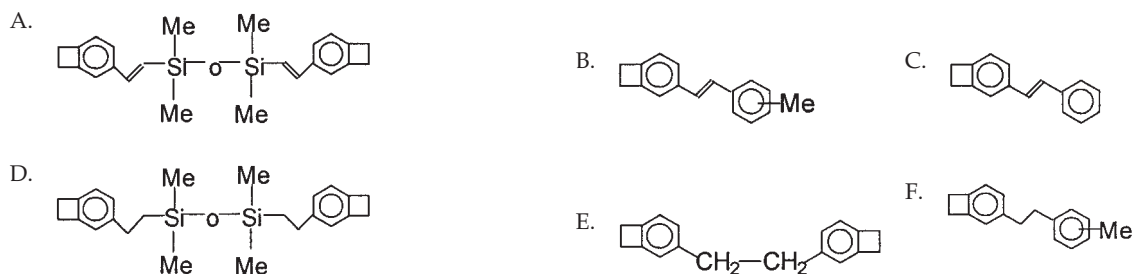


Figure 13 The plots of d vs. $1/T_p$ (Kissinger's method) and $\ln(\beta)$ vs. $1/T_p$ (Ozawa's method).

TABLE VI
Apparent Activation Energy and Order of Cure Reactions of Benzocyclobutene Compounds

Monomers	E_a (KJ/mol)	Reaction order (n)	Reference
A	161 ± 1	1.03 ± 0.01	10
B	150 ± 10	0.86 ± 0.13	11
C	119 ± 20	0.43 ± 0.27	10
D	175 ± 13	1.24 ± 0.3	10
E	171 ± 3	1.07 ± 0.03	10
F	171 ± 3	1.02 ± 0.18	11
4c	139 ± 4	1	

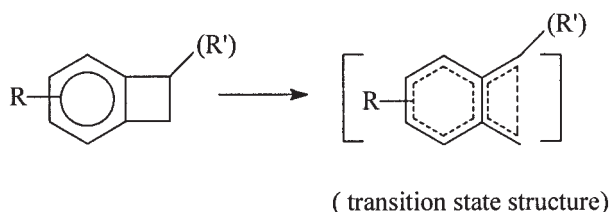


reaction rate of bisbenzocyclobutene is expressed as follows:

$$d\alpha/dt = 2.27 \times 10^{13}(1 - \alpha)\exp(-139400/RT)$$

(nonisothermal)

It is interesting to compare the kinetics results obtained from isothermal and nonisothermal experiments. The apparent kinetic parameters obtained by isothermal experiment are close to those by nonisothermal experiment. This illustrates that the obtained kinetic parameters are with credibility.



Scheme 4. Ring-open reaction of benzocyclobutene.

TABLE VII
Preexponential Factor at Different Heating Rates

Heating rate β ($^{\circ}\text{C}/\text{min}$)	Exothermic peak temperature T_p (K)	Preexponential factor A (min^{-1})
5	524.7	2.32×10^{13}
10	536.0	2.17×10^{13}
15	542.6	2.26×10^{13}
20	547.0	2.32×10^{13}

Average value of Preexponential factor at different heating rates (sample 4c): 2.27×10^{13} .

CONCLUSIONS

Four new bisbenzocyclobutene-terminated imides with high purity are synthesized in high yields, which are thermally polymerized to yield highly crosslinked polymers. The glass transition temperature of 4p is 300°C . The thermal decomposition temperature of the cured polyimides arrives at higher than 483°C , depending on the chemical structures of the imides. The ring-open cure reaction was confirmed by FTIR and DSC. The study on kinetics of cure reaction shows that the analysis results for isothermal and nonisothermal DSC are similar. The kinetic equations are expressed as follows:

$$d\alpha/dt = 3.88 \times 10^{13}(1 - \alpha)\exp(-143400/RT)$$

(isothermal)

$$d\alpha/dt = 2.27 \times 10^{13}(1 - \alpha)\exp(-139400/RT)$$

(nonisothermal)

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