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Thermal stability and degradation products analysis of benzocyclobutene-terminated imide polymers

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Abstract

Benzocyclobutene-terminated imides were prepared and fully characterized with ^{1}H NMR, MS, and FT-IR. The thermal degradation of polymers was investigated by using thermogravimetric analyzer (TGA) and high-resolution pyrolysis-gas chromatography–mass spectrometry (HR-Py-GC–MS). TGA showed that thermal degradation of the polymer was a single-stage process in N_2, whereas a three-stage degradation in air atmosphere. The major involved products were found to be CO_2, naphthalene and naphthalene derivatives. Degradation mechanism of the polymer was suggested and the relationship between structures of the polymer and degradation products was also discussed.
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Keywords: Benzocyclobutene-terminated imide; Thermal stability; Thermal degradation; Degradation mechanism

1. Introduction

Thermosetted polymers are commonly referred to as network polymers or cross-linked polymers. The mobility of the molecular chain is limited due to cross-linking. Thus, thermosetted polymers possess excellent dimensional stability and thermal stability.

Recently, a kind of novel thermosetting resins based on benzocyclobutene (BCB) attracted people more attentions [1–5] owing to their superior properties. They have low melting points or are soluble in some common solvents, and they could be easily cured and processable and form crosslinked polymers with good properties at elevated temperatures. It was due to the advantages that benzocyclobutene resins would find a variety of applications in aerospace, electronics, etc. [6–10]. One of the important properties in these applications is their thermal stability at elevated temperature.

High heat-resistance of cured benzocyclobutene resins usually associates with the network structure formed during polymerization. People paid great attention to the curing mechanism and crosslinking structures formed of the benzocyclobutene resin. It was believed in previous work [11–13] that polymerization reaction of benzocyclobutenes follows the biradical mechanism to form a three-dimensional poly-*o*-xylylene network. However, research results in recent reports [14–16] showed that polymerization of benzocyclobutene does not follow the suggested biradical mechanism, but a pericyclic reaction mechanism (Scheme 1). It is an interesting subject that the relationships between the structure of cured BCB resin and their degradation stability which will be benefit to design and develop a new benzocyclobutene resin with excellent heat-resistance for demanding applications.
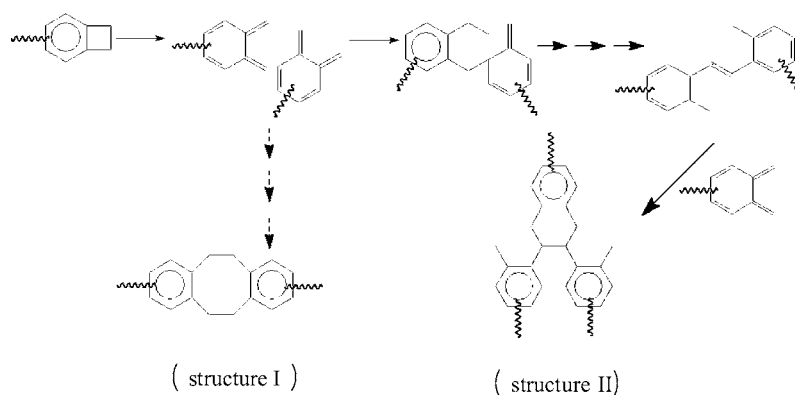
Our work is focusing on thermal and thermo-oxidative stability of cured polymers of benzocyclobutene-terminated imide and the thermal degradation mechanism.

2. Experimental

2.1. Reagents and solvents

Pyromellitic dianhydride (PMDA) was purchased from Shanghai No. 1 Reagent Factory and recrystallized from

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Scheme 1. Mechanism of polymerization of bisbenzocyclobutenes.

acetic anhydride before used. 2,2′-Bis[4,4′-di(3,4-di car-boxyphenoxy)phenyl]propane dianhydride (BPADA) was purchased from Shanghai Synthetic Resin Institute and used as received. Acetic anhydride (analytical reagent grade) was purchased from Xing Da Chemical Factory and used as received.

2.2. Analyses and characterization

Electrospray ionization-mass spectrometry (SPI-MS) analysis was carried out on the Micromass LCT KC317 and electron ionization-mass spectrometry (EI-MS) analysis was conducted on Micromass GCT. Elemental analyses were conducted with Elementar vario EL III analyzer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained in deuterochloroform solvent and tetramethylsilane (TMS) was used as an internal standard. The instrument used was BRUKER AVANCE 500 (500 MHz). The imide resins were characterized by Fourier transform infrared (FT-IR) spectroscopy with Nicolet 550. Solid samples were pressed into pellets with KBr or a thin film of the

sample was cast from CH_2Cl_2 solution of the product on a KBr plate for IR analyses. The thermal stability of cured polymers was investigated by dynamic TGA. The analyses is conducted by using METTLER Toledo TGA 851 in N_2 and air at heating rate of 10 °C/min from 30 to 800 °C. HR-Py-GC–MS was used to study the degradation mechanism. Polymers cured from benzocyclobutene-terminated imides were decomposed in the pyrolytic instrument at different temperatures. The separation and identification of fragments produced in the degradation was carried out through QP-2010 GC–MS (Shimadzu). The inert helium was used as a carrier gas, with a total flow of 84.3 ml/min and a split ratio of 100:1.

2.3. Preparation of imides

Fig. 1 shows the chemical structures of the imides. The preparation of imide, 2,2′-bis[4-(N-4-benzocyclobut-enylphthalimid-4-oxy)phenyl]-propane, 1c, was completed by condensation between a dianhydride (BPADA) and two 4-amino-benzocyclobutene (4-NH$_2$-BCB). A solution of
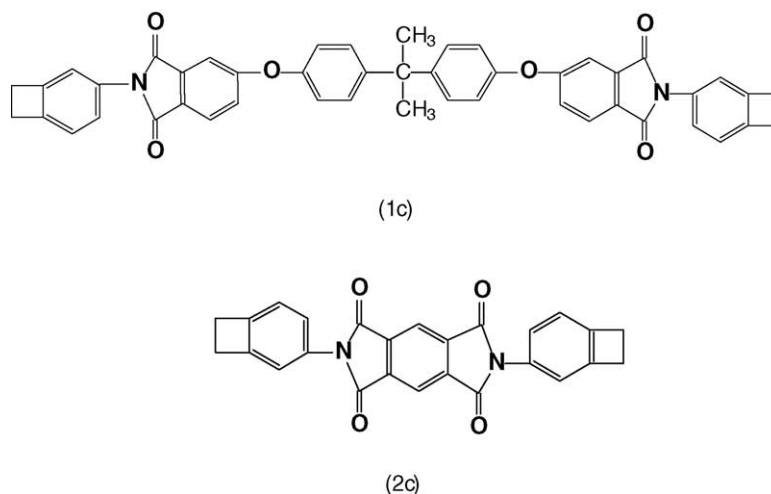

(1c)

(2c)

Fig. 1. The chemical structures of imide 1c and 2c.

BPADA (9.44 g, 18.1 mmol in 25 ml of DMAC) was slowly added to a solution of 4-NH$_2$-BCB (4.3 g, 36.1 mmol) freshly prepared under the protection of N$_2$. After the reaction mixture was stirred for 5 h at room temperature, 30 ml of acetic anhydride was added. The mixture was heated and kept at 90 °C for 5 h and then precipitated in 1000 ml of distilled water. The precipitate was filtered, and washed with a saturated solution of Na$_2$CO$_3$ and finally with water. The product was obtained as light yellow microcrystals. Yield: 95%; mp: 179 °C. Imide 1c can be dissolved not only in strong polar solvents such as DMAC, DMF, NMP, but also in halohydrocarbon such as CH$_2$Cl$_2$ and chloroform.

1c: SPI-MS, m/z: 745.0 ($M_{1c}^+ + \text{Na}^+$), 746.0 (isotope peak of $M_{1c}^+ + \text{Na}^+$), 761.0 ($M_{1c}^+ + \text{K}^+$), 762.0 and 763.0 (isotope peak of $M_{1c}^+ + \text{K}^+$). Infrared spectroscopy (cm^{-1}): 2930 (benzocyclobutenyl CH$_2$ stretching vibration), 1470 (aromatic in-plane ring stretching vibration), 1776 (asymmetric stretching vibration of imide group), 1717 (symmetric stretching vibration of imide groups) and 1380 (C–N stretching vibration of imide groups). ^{1}H NMR (CDCl$_3$, TMS, ppm): 3.25 (singlet, alicyclic protons), 6.8–7.9 (multiplet, aromatic protons) and 1.68 (singlet, methyl protons of C(CH$_3$)$_2$). EA: Anal. Calcd. (C$_{47}$H$_{34}$O$_6$N$_2$) (%): C, 78.16; H, 4.71; N, 3.88. Found (%): C, 77.88; H, 4.80; N, 3.61. The analysis results consist with the structure of imide 1c.

Another benzocyclobutene-terminated imide, 2,2′-bis(N-4-benzocyclo-butenyl)phthalimide, designated as 2c, was prepared by the same process as 1c. Yield: 93%. The melting point of 2c was not observed and 2c only dissolved in NMP.

2c: EI-MS, m/z: 420 (M_{2c}^+). Infrared spectroscopy (cm^{-1}): 2930 (benzocyclobutenyl CH$_2$ stretching vibration), 1471 (aromatic in-plane ring stretching vibration), 1777 (asymmetric stretching vibration of imide group), 1720 (symmetric stretching vibration of imide groups) and 1383 (C–N stretching vibration of imide groups). ^{1}H NMR (CDCl$_3$, TMS, ppm): 3.23 (singlet, alicyclic protons), 7.1–8.8 (multiplet, aromatic protons). EA: Anal. Calcd. (C$_{26}$H$_{16}$O$_4$N$_2$) (%): C, 73.66; H, 3.81; N, 6.67. Found (%): C, 74.01; H, 3.80; N, 6.43. The analysis results consist with the structure of imide 2c.

2.4. Polymerization

The imide 1c was polymerized in air at 230 °C/1 h, 240 °C/1 h, 250 °C/1 h, 275 °C/1 h and then postcured at 300 °C/3 h. Another imide 2c was 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 related to imides 1c and 2c are referred to as 1p and 2p, respectively, throughout the text.

Infrared spectroscopic analyses of 1p and 2p indicate that the peak of aromatic in-plane ring stretching vibration at 1470 cm^{-1} move to high wavenumber peak at 1505 cm^{-1}, which is due to the releasing of the ring strain of four-membered ring of benzocyclobutene during polymerization.

3. Results and discussion

3.1. Thermal degradation of 1p and 2p in N$_2$ and air

The TG and DTG curves of 1p and 2p are shown in Fig. 2 and analysis data are tabulated in Table 1. As shown in Table 1, $D_{0.1}$'s (temperature for 10% decomposition of polymer) of 1p and 2p in N$_2$ are 491 and 500 °C, respectively. A weight loss of 43 and 28% at 550 °C are observed for 1p and 2p, respectively. Char yields at 800 °C are 44 and 46% for 1p and 2p, respectively. It also can be seen that $D_{0.1}$'s of 1p and 2p in air are 483 and 494 °C, respectively, which is a little bit lower than those in N$_2$. This may indicate that 1p and 2p are more thermostable in N$_2$ than in air. As shown in Fig. 2, it is obvious that the decomposition of 1p and 2p show a single-stage degradation process in N$_2$, whereas a three-stage degradation process is found in air. This indicates that the three-stage degradation associates with the existence of oxygen in the air. The degradation curve of 1p in air shows that its degradation begins at about 461 °C. There is a 12% weight loss at 495 °C and a weight loss of 32% below 550 °C after which rapid degradation occurs. The biggest weight loss of 67% is observed between 550 and 700 °C. TG curve of 2p in air is similar to that of 1p. In addition, char yields for 1p and 2p at 800 °C in air are near to zero, which illustrate that 1p and 2p decompose completely. Thereby, thermal stability of 1p and 2p is better than thermo-oxidative stability of them.

3.2. Thermal degradation products analysis

HR-Py-GC–MS is a very useful technique used to determine the thermal degradation mechanisms and the structures of a polymer [17,18]. 1p and 2p were pyrolyzed at 750 °C to investigate their degradation behaviors. The GCs (gas chromatographies) of 1p and 2p are shown in Fig. 3 and the components of the pyrolyzates are tabulated in Table 2. It is observed that the major degraded fragments are CO$_2$ and 3,4-dimethyl-benzenamine. Some pyrolyzates, including benzocyclobutene, aniline, naphthalene, 2-ethenyl-naphthalene, 2-naphthalenamine, 1-amino-2-methyl-naphthalene are observed. Other pyrolyzates, such as 3-methyl-aniline, 2,4,5-trimethyl-aniline, and 3-phenyl-1H-indene are determined in the degradation fragments of 2p.

It is known to us that bisbenzocyclobutenes react with each other by Diels–Alder cycloadditions and other reactions to form mainly two characteristics structures in two different

Table 1
TGA results for 1p and 2p (heating rate: 10 °C/min)

Polymer	N$_2$		Air	
	$D_{0.1}{}^a$ (°C)	Y^b (%)	$D_{0.1}{}^a$ (°C)	Y^b (%)
1p	491	44	483	0
2p	500	46	494	0

^{a} Temperature for 10% decomposition of polymer.
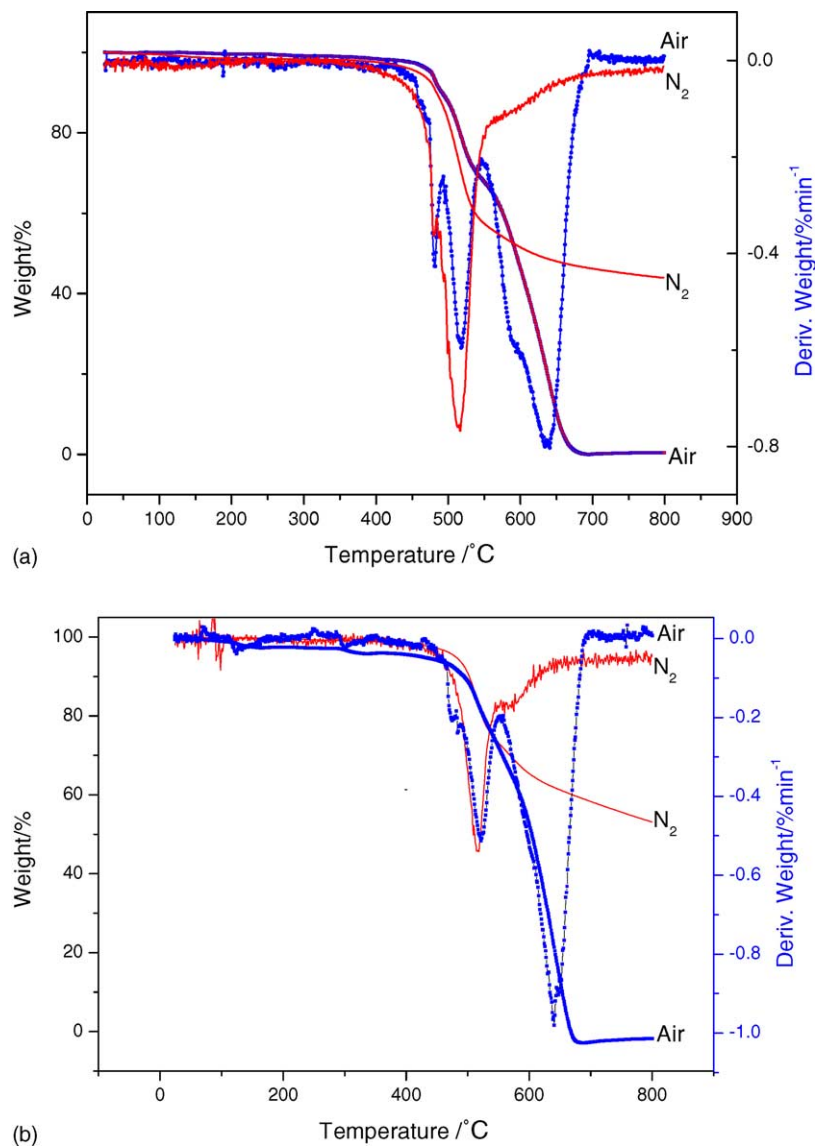^{b} Char yield at 800 °C.

Fig. 2. TG and DTG curves of 1p (a) and 2p (b) in N_2 and air (heating rate: $10\,^{\circ}C/min$).

Table 2
Pyrolyzates of the cured polymers of benzocyclobutene-terminated imide identified by Py-GC–MS

No.[a]	Structure	Name	MW	The contents of fragments		
				1p-550[b]	1p-750[c]	2p-750[d]
1	CO_2	Carbon dioxide	44	40.69	38.22	31.56
2		Benzene	78	–	18.65	–
3		Toluene	92	–	6.93	–
4		Ethylbenzene	106	–	1.89	–
5		*p*-Xylene	106	–	1.82	–

Table 2 (*Continued*)

No.[a]	Structure	Name	MW	The contents of fragments		
				1p-550[b]	1p-750[c]	2p-750[d]
6		Benzocyclobutene	104	5.61	2.48	–
7		Aniline	93	7.97	0.99	–
8		*p*-Aminotoluene	107	3.72	0.42	–
9		Naphthalene	128	–	2.15	–
10		3,4-Dimethyl-benzenamine	121	16.40	1.81	39.94
11		2-Ethenyl-naphthalene	154	–	23.42	–
12		Phenanthrene	178	–	0.84	–
13		2-Phenyl-naphthalene	178	–	0.38	–
14		2-Naphthalenamine	143	13.34	–	–
15		1-Amino-2-methyl-naphthalene	157	12.27	–	–
16		3-Methyl-aniline	107	–	–	8.72
17		2,4,5-Trimethyl-aniline	135	–	–	7.98
18		3-Phenyl-1H-indene	192	–	–	11.80

(–) Not observed.
[a] Corresponds to the number in Fig. 3(a–c).
[b] 1p was pyrolyzed at 550 °C.
[c] 1p was pyrolyzed at 750 °C.
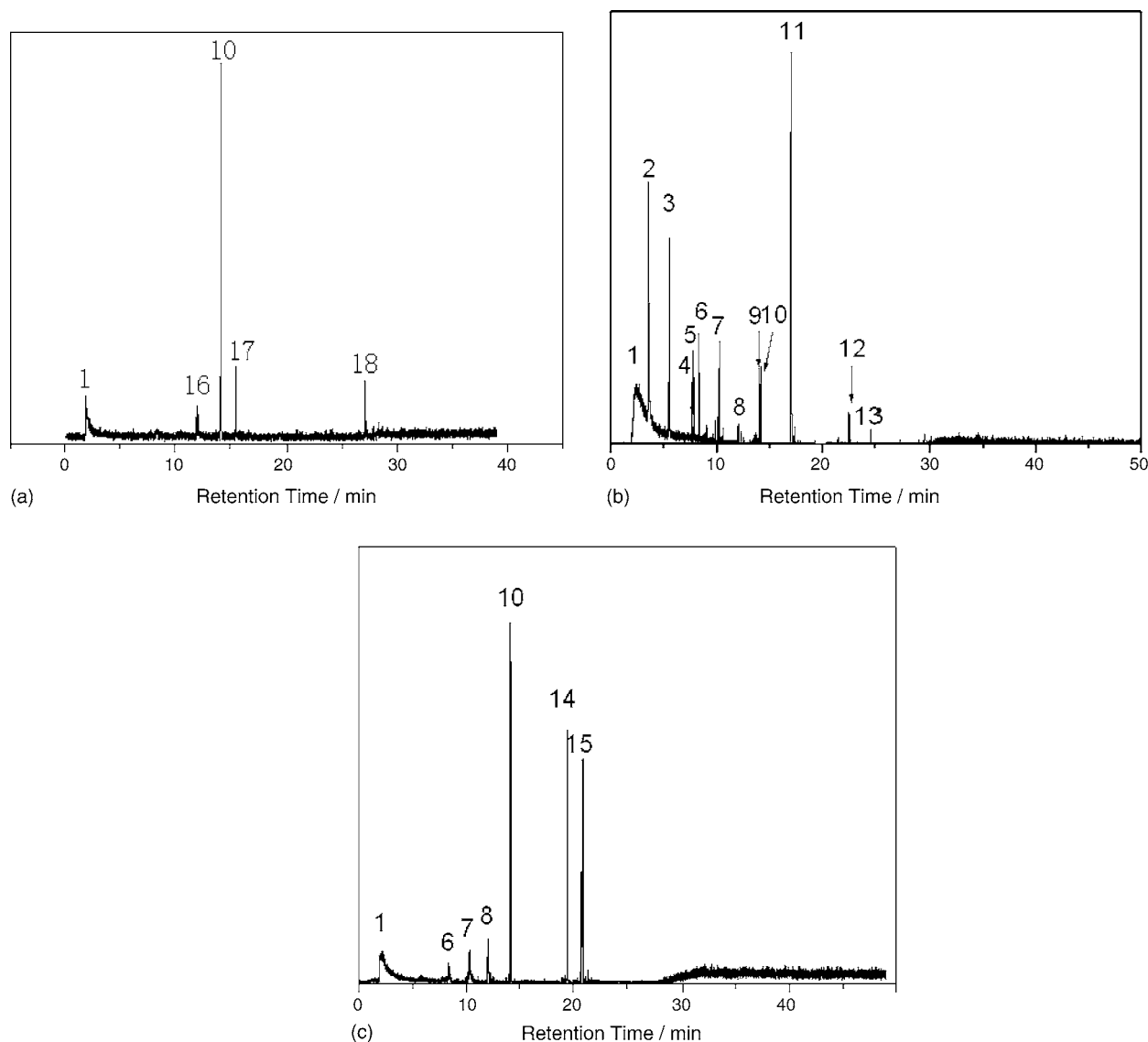[d] 2p was pyrolyzed at 750 °C.

Fig. 3. GC analyses of degradation products of the cured polymers of benzocyclobutene-terminated imides: (a) 2p, pyrolyzed at 750 °C; (b) 1p, pyrolyzed at 750 °C; (c) 1p, pyrolyzed at 550 °C.

ways. One structure formed by cycloadditions and rearrangements reaction shown by void arrowhead in Scheme 1 is dibenzocyclooctadiene structure (structure I), and another structure formed by other curing reactions shown by solid arrowhead in Scheme 1 shows the tetrahydronaphthalene structure (structure II). On the basis of the analyses of degradation products and structures of cured polymer, we suggest the thermal degradation mechanisms shown in detail in Fig. 4. The thermal degradation is initiated by thermal cleavage of C–N, C–C, and C–O bonds in the chain of the polymer, and these cleavages give rise to chain free radicals, which would involve in further complicated reaction process at elevated temperature, including chain transfer, rearrangement, isomerization, cyclizations, etc.

According to the mechanism of degradation, the degradation results could be explained. Naphthalene and other

naphthalene derivatives such as 2-ethenyl-naphthalene, 2-naphthalenamine, phenanthrene, 1-amino-2-methyl-naphthalene, and 2-phenyl-naphthalene could be produced by cleavage of structure II in cured polymers. As shown in Table 2, the degraded components of 1p contain more components than those of 2p. The main products for the degradation of 1p are CO_2, benzene, benzocyclobutene, naphthalene, 2-ethenyl-naphthalene, 2-naphthalenamine, 1-amino-2-methyl-naphthalene, whereas, the major fragments for the degradation of 2p are CO_2, 3-methyl-aniline, 2,4,5-trimethyl-aniline. The decomposition of 1p easily produces the fragments of naphthalene derivatives, whereas, 2p produce the fragments of aniline derivatives. The difference probably results from the structures of 1p and 2p. These results indicate that there is the structure I in the cured polymer 1p, whereas, there is not or little the structure II
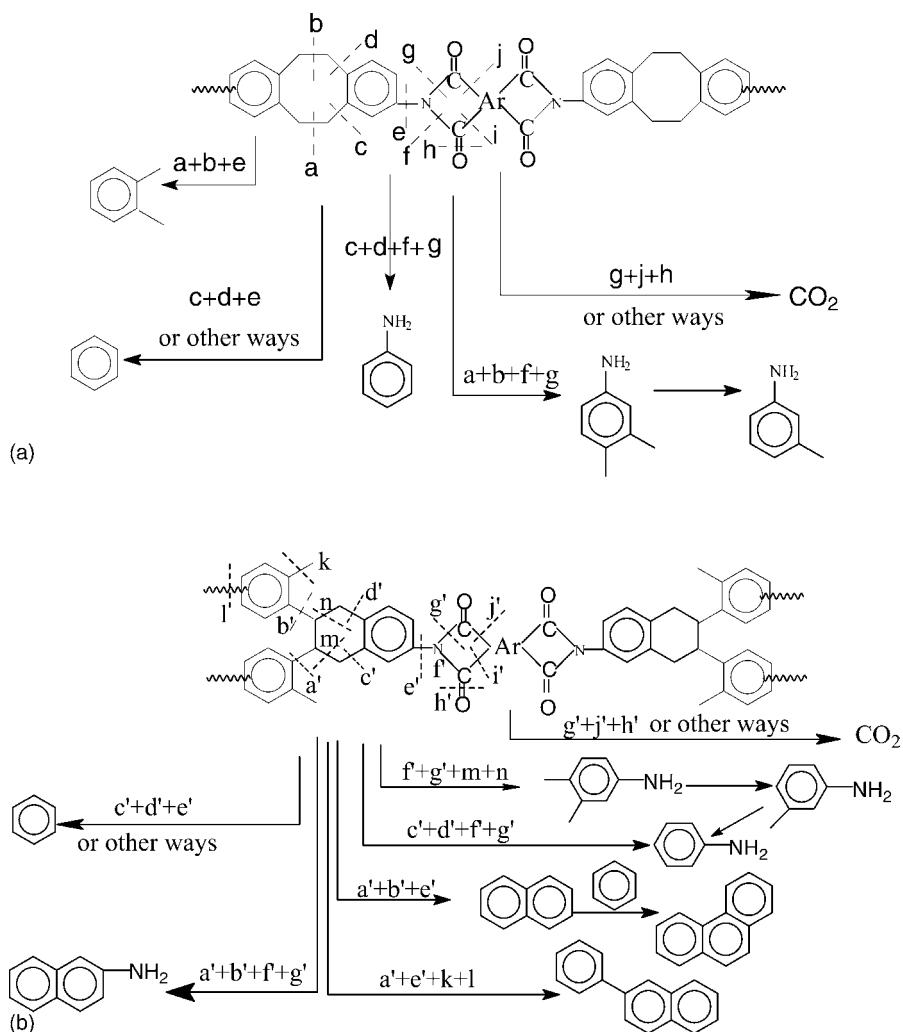
Fig. 4. The thermal degradation mechanisms and products of the cured polymers of benzocyclobutene-terminated imides: (a) based on structure I; (b) based on structure II.

in the cured polymer 2p. This is related to the structure of imide. There is the ether group in imide 1c, which is flexible group. As shown in Scheme 1, the formation of structure II needs a lot of reactions including additions rearrangement and isomerization. The flexibility of chain will cause rearrangement reaction easily. Thereby, 1p has more structure II than 2p. The structure II in the cured polymer 1p gives the warrant fact for supporting the curing mechanism suggested by Marks et al. [14–16]. This also indicates there is not or little structure II in the cured polymer with rigid imide chain. A lot of CO_2 are produced during the degradation of 1p and 2p. As well known, the degradation of polyimide is easily to produce CO [19]. However, GC analysis do not determine the presence of CO. The production of CO_2 probably results from the combination of CO with oxygen [20].

The effect of pyrolysis temperature on the thermal degradation reaction of 1p has been investigated. 1p was pyrolyzed at 550 and 750 °C separately and the degradation fragments are analyzed. The main compositions of the pyrolyzates are tabulated in Table 2. It is observed that different pyrolysis temperature leads to different distribution of pyrolyzates. Some naphthalene derivatives with amino groups, such as 1-amino-2-methyl-naphthalene and 2-naphthalenamine are found at 550 °C, while some naphthalene derivatives with unsaturated and condensed ring structures, such as 2-ethenyl-naphthalene, phenanthrene, and 2-phenyl-naphthalene are found at 750 °C. In addition, more fragments in pyrolyzates including benzene, toluene, ethylbenzene, and p-xylene are observed. It indicates that more complicated reactions and further degradation take place at higher pyrolysis temperature.

4. Conclusion

As discussed above, we can come to the following conclusion. The cured polymers of benzocyclobutene-terminated imides have excellent thermal and thermo-oxidative stability. The thermal decomposition temperatures of the polymers arrive at above 490 and 480 °C in N_2 and air, respectively. Based

on the analyses of degradation products, two major thermal degradation mechanisms have been proposed for cured benzocyclobutene-terminated imides. We believe that the difference of degradation fragments of the polymers results from the different structures. The different degradation products of the polymers are obtained at different temperatures.

Acknowledgements

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