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Thermal stability of a novel polytriazole resin

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Abstract

A novel poly(1,2,3-triazole) (PTA) resin was prepared from a diazide and a multialkyne. The thermal stability and degradation kinetics of the cured PTA resin were investigated with the aid of the thermogravimetric analysis (TGA) technique. The degradation temperature of the cured PTA resin reaches 360 °C (T_{d5}). Apparent kinetic parameters of the degradation of the cured resin is obtained by using Ozawa's method. The average apparent degradation activation energies of the PTA resin are about 190 kJ/mol under nitrogen and 160 kJ/mol under air. The cured PTA resin was pyrolyzed at 400 and 570 °C separately and the pyrolysis fragments were determined by using the Py/GC/MS combined technique. The results show that the degradation of the cured PTA resin initiates at CH_2—N bonds. Nitrogen and related compounds which result from the cleavage of C—N and N—N bonds of 1,2,3-triazole ring were found in the pyrolysis products at 570 °C but no at 400 °C. Finally, a degradation mechanism of the cured polytriazole resin was proposed.

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Keywords: Polytriazole; Thermal degradation kinetics; Pyrolysis; Degradation mechanism; High performance resin matrix

1. Introduction

In the past 30 years, advanced composites have become main structural materials of aviation and aerospace. Among these composites materials, people have paid great attention to low temperature molding (LTM) materials, which not only possess low manufacture cost but also exhibit high performance. In 1970s, the ACG Corporation (U.K.) and the Air Tech Corporation (U.S.A.) started the exploitation of the LTM materials and developed a series of LTM products [1].

1,3-Dipolar cycloaddition reaction of an azide and an alkyne easily takes place and forms a triazole substance. The reaction is exothermal and usually occurs at low temperatures, e.g. 70 °C, which could be utilized for the synthesis of both aromatic and non-aromatic five-membered ring heterocycles [2–5] and the preparation of LTM materials. In 1960s, Johson et al. synthesized several linear polytriazoles from monomers containing both azide and acetylene groups [6,7]. The obtained polytriazoles were thermally stable but hardly processable polymers due to the rigid molecular chains. No more details and further work on polytriazoles have been reported since then. Recently, we have been developing and synthesized a series of polytriazole (PTA) resins with good processability made from diazides and multialkynes [8,9]. The PTA resins are a novel kind of crosslinkable polymers, which are expected to be used as a matrix of advanced composites with LTM features [10].

With our continuing efforts on developing PTA materials, it is necessary to study the relationship between the structures and degradation stability of PTA resins, which would be benefit to design and prepare new PTA resins with high performances in the future. In this paper, the thermal stability, degradation kinetics, and degradation mechanisms of the cured PTA resin were investigated.

2. Experimental

2.1. Raw materials

Propargyl bromide was purchased from KeLiDa Chemical Factory and distilled before use. 4,4′-Diaminodiphenylmethane (Chemical Purity), sodium azide (Chemical Purity), 4,4′-

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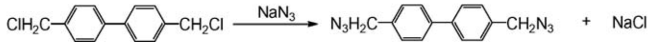
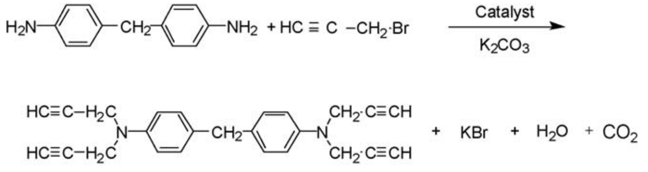


Scheme 1. The synthesis of DAMBP.

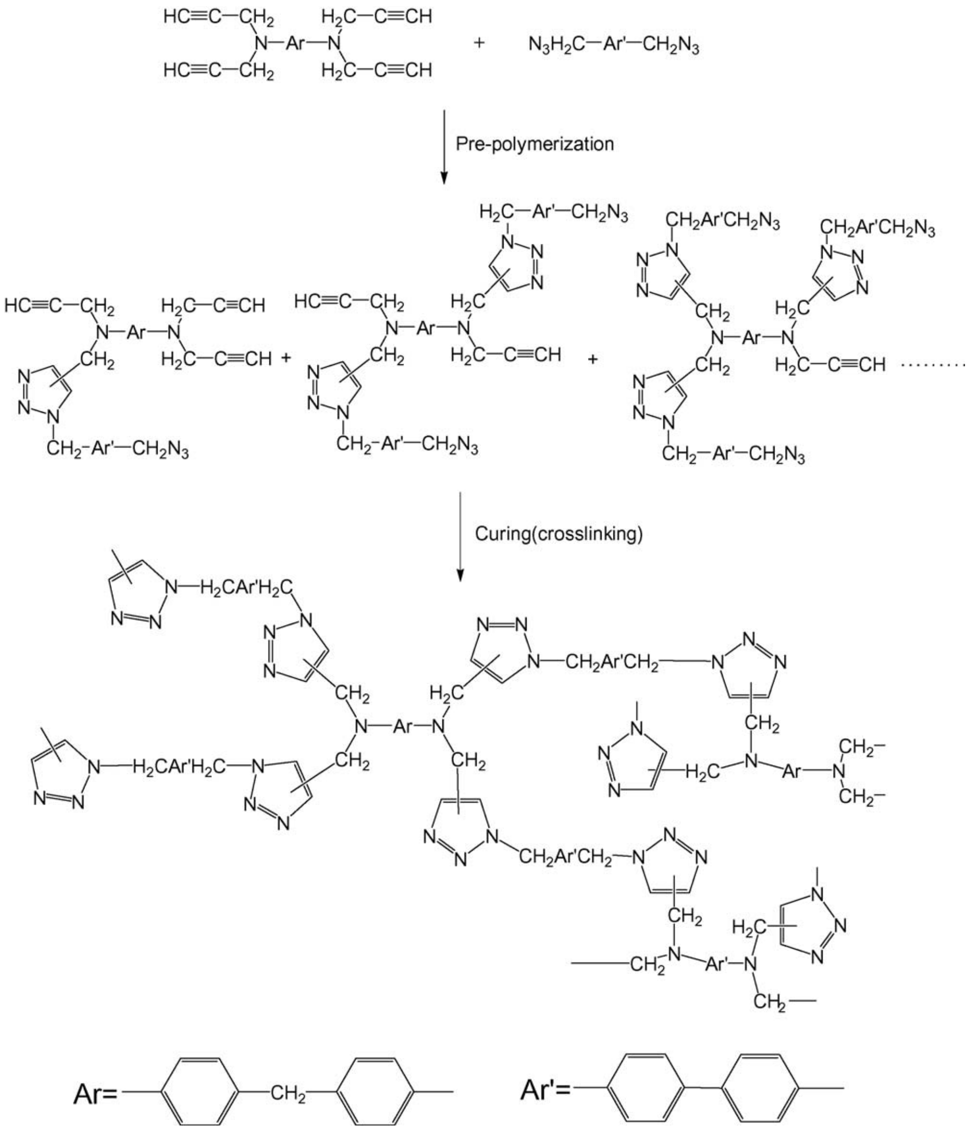


Scheme 2. The synthesis of TPDDM.

dichloromethylbiphenyl, dimethylformamide, benzene, dichloroethane, potassium carbonate, magnesium sulfate, and tetrabutyl-ammonium bromide (all analytical reagent grade), were purchased from Sinopharm Chemical Reagent Co. Ltd. and used as received.

2.2. Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained in deuteron chloroform solvent on BRUKER AVANCE 500 (500 MHz) instrument, and tetramethylsilane (TMS) was used as an internal standard. FT-IR spectra were recorded on a Nicolet 550 instrument. Solid samples were pressed into pellets with KBr for the FT-IR analyses. Electron ionization-mass spectrometry (EI-MS) analysis was conducted on Micromass GCT. The pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) were conducted on a Frontier Lab Single-shot Pyrolyzer PY-2020i (PY Single-shot Pyrolyzer, quartz tube, temperature: 400 and 570 °C) and a Shimadzu GCMS-QP2010 chromatograph/mass spectrometer (Chromatographic column, 30 m × 0.25 mm × 0.25 μm; carrier gas, helium gas; pressure, 34.0 kPa; total flow, 84.3 ml/min; column flow, 0.80 ml/min. The temperature of column was held at 40 °C for 1 min, and then increased with a heating rate of 10 °C/min, at last maintained



Scheme 3. Schematic polymerization of DAMBP and TPDDM.

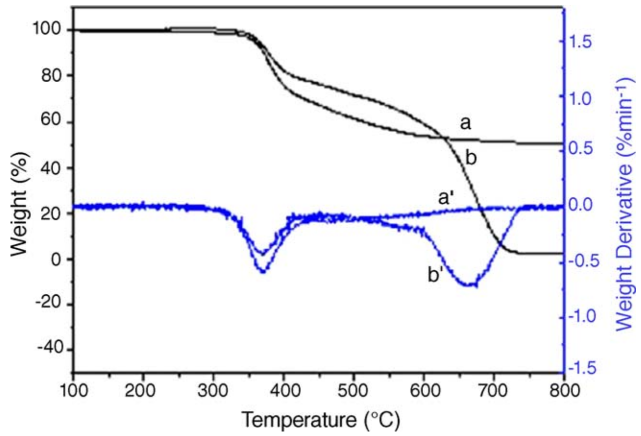


Fig. 1. TGA and DTG thermograms of the cured PTA resin. a and a′: under N_2; b and b′: under air (heating rates: 10 °C/min).

at 260 °C for 10 min. Mass spectroscopy: ion source, EI; ion source temperature, 200 °C; electric energy, 70 eV; scan range for *m*/*z*, 25–600). The pyrolysis time of the cured resin in the pyrolyzer was 10 s.

2.3. Preparation of a polytriazole (PTA)

2.3.1. Preparation of 4,4′-diazidomethylbiphenyl (DAMBP) and N,N,N′,N′-tetrapropargyl-p,p′-diaminodiphenyl methane(TPDDM) [11]

6.30 g 4,4′-dichloromethylbiphenyl, 6.50 g sodium azide, 20 ml dimethylformamide, and 20 ml benzene (be careful because benzene is a carcinogen) were added into a three-necked round bottom flask (100 ml) with a mechanical stirrer and a reflux condenser. The reaction mixture was slowly heated to 75 °C and kept at this temperature for 6 h. Then the reaction mixture was poured into a beaker with 200 ml deionized water. The organic benzene layer was separated and the aqueous layer was extracted with 20 ml benzene. The process was repeated three times. The organic benzene layers were combined and dried by anhydrous magnesium sulfate and the benzene was then distilled out. A solid product of DAMBP 5.94 g was obtained. Yield: 90.0%; mp: 71–72 °C. ^{1}H NMR ($CDCl_3$, TMS): 4.40 (s, 4H, CH_2), 7.41 (d, 4H, *J* = 8.00, Ar–H), 7.61 (d, 4H, *J* = 8.00, Ar–H); MS (EI) *m*/*z*: 264 $(M)^+$, 236 $(M\text{–}N_2)^+$, 222 $(M\text{–}N_3)^+$, 208 $(M\text{–}N_3\text{–}CH_2)^+$, 180 $(M\text{–}N_3\text{–}N_2\text{–}CH_2)^+$, 166 $(M\text{–}2N_3\text{–}CH_2)^+$. The reaction for the synthesis of DAMBP is shown in Scheme 1.

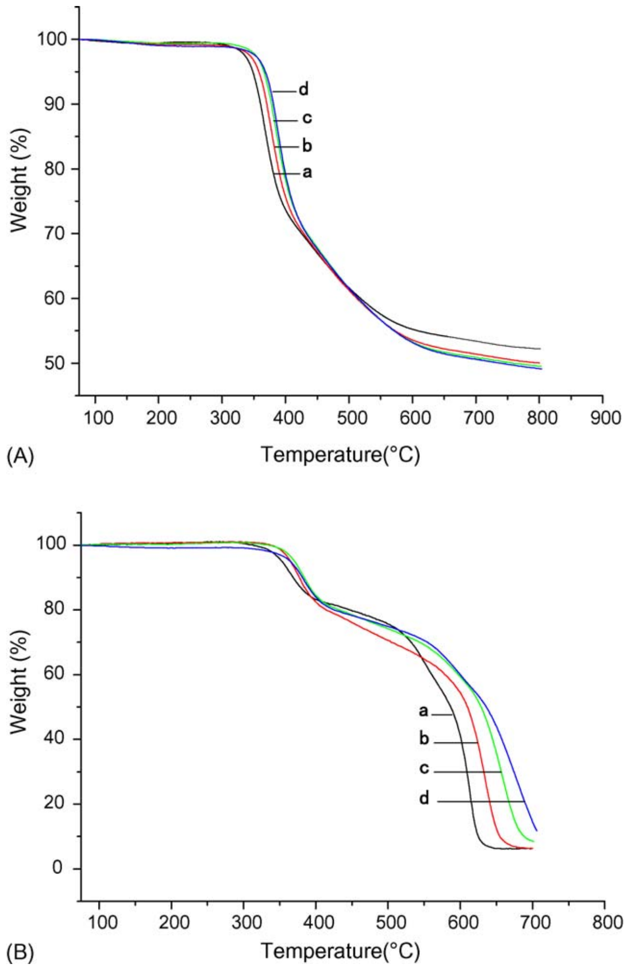


Fig. 2. Thermogravimetric curves of the cured PTA resin under N_2 (A) and air (B) at a variety of heating rates: a, 5; b, 10; c, 15; d, 20 °C/min.

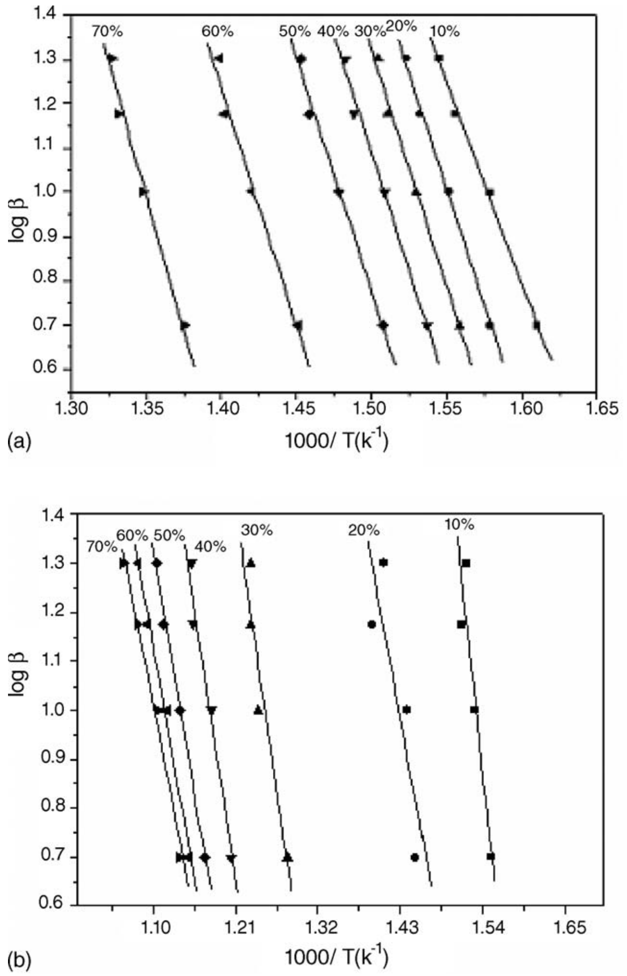


Fig. 3. The Plot of log *β* vs. 1/*T* of the cured PTA resin at different degradation conversion under N_2 (a) and air (b).

4.90 g 4,4′-diaminodiphenylmethane, 10.35 g anhydrous potassium carbonate, 15.00 g deionized water, 15.00 g dichloroethane, and 0.40 g tetrabutyl-ammonium bromide were charged into a three-necked round bottom flask (250 ml) with a mechanical stirrer, a nitrogen bypass, and a reflux condenser and a dropping funnel and stirred vigorously under the atmosphere of N_2 at 70 °C. And then 20.80 g propargyl bromide was then dropwise added in 3 h. After the completion of the addition, the mixture was remained at 70 °C for 6 h. Thereafter, the reaction products were cooled to room temperature and poured into a separation funnel and the dichloroethane layer was separated from the aqueous layer. The organic layer was washed with deionized water several times, the unreacted reagents and solvent were removed by using an evaporator, and a crude product was obtained. The product was then purified by the extraction with 50 ml petroleum ether, which was repeated in three times. The extracted product was then recrystallized with methanol three times. A yellow solid crystal of 7.44 g TPDDM was obtained. Yield: 85.0%; mp: 50–51 °C; ^{1}H NMR ($CDCl_3$, TMS): 2.20 (s, 4H, $\equiv$CH), 3.80 (s, 2H, Ar–CH_2–Ar), 4.10 (s, 8H, CH_2–C$\equiv$C), 6.80 (d, 4H, $J = 8.63$, N–Ar–H), 7.10 (d, 4H, $J = 8.52$, CH_2–Ar–H). The synthetic reaction for TPDDM is shown in Scheme 2.

2.3.2. Preparation of a poly(1,2,3-triazole) resin

DAMBP and TPDDM monomers were well-proportioned (the molar ratio [DAMPB]/[TPDDM] = 2:1), added into a three-necked round bottom flask with a mechanical stirrer and a reflux condenser, and stirred. The flask was heated to 80 °C with an oil bath and kept at this temperature. After the mixture of the monomers became homogenous, a polytriazole resin was obtained. The resin was then poured into an aluminum pan and cured in an oven under air at 80 °C for 10 h, 120 °C 2 h, 150 °C 2 h, 170 °C 2 h, and 200 °C 2 h. The polymerization reaction is schematically shown in Scheme 3. The polymerization were traced by an Infrared spectroscopy technique [10]. The peak at 3292 cm^{-1} is the characteristic absorption of the alkyne and the peak at 2098 cm^{-1} the characteristic absorption of N=N=N and C$\equiv$C stretching vibrations (overlapped). The two absorption peaks disappear at the end of the cure, while the peak at

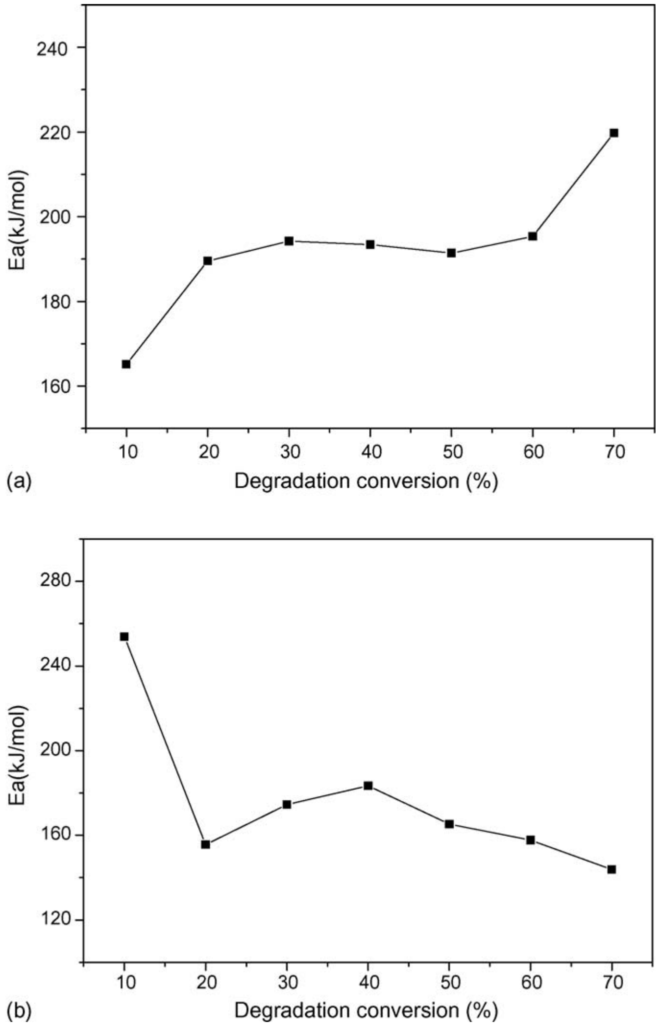


Fig. 4. The degradation conversion dependence of apparent activation energy for the degradation of the cured PTA resin under N_2 (a) and air (b).

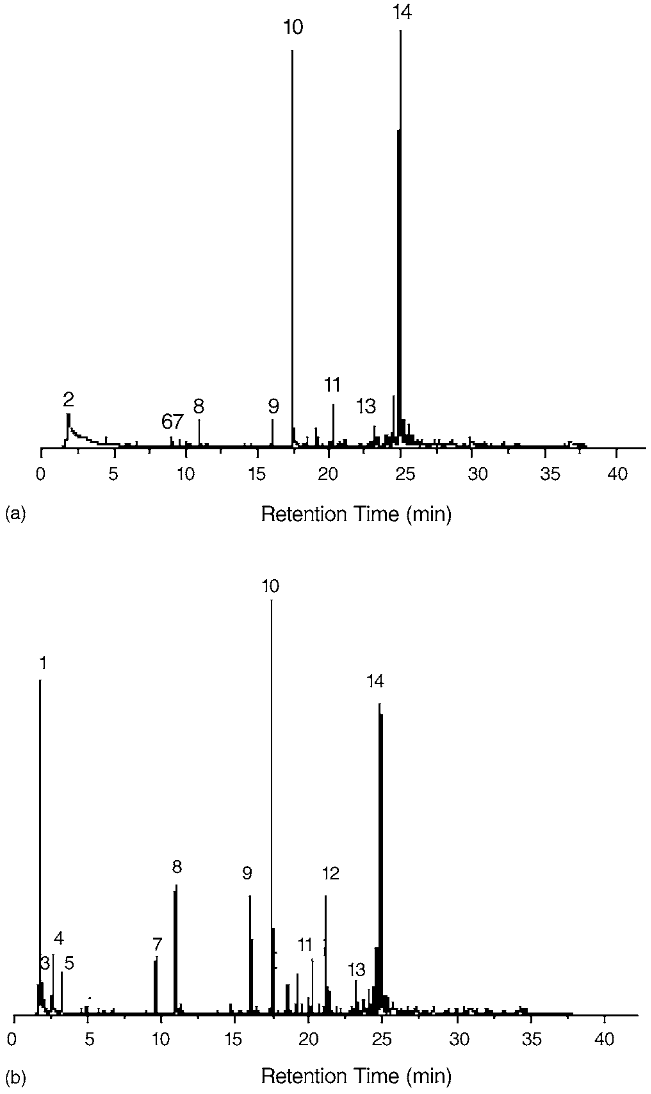


Fig. 5. The gas chromatogram of the pyrolysis fragments of the cured PTA resin pyrolyzed at 400 °C (a) and 570 °C (b).

3126 cm^{-1} occurs for the characteristic absorption of C–H on the triazole ring, which indicates that poly(1,2,3-triazole) had been formed [8–10]. The structures of the triazoles in polymer chains was also confirmed by the NMR technique [11]. Elemental analysis results [%, found (calculated)] for the resin: C 71.75 (72.44); H 5.31 (5.24); N 21.41 (22.32); and the cured resin: C 70.84 (72.44); H 5.36 (5.24); N 21.08 (22.32). The cured resin was used for the investigation of thermal stability.

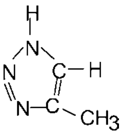
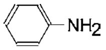
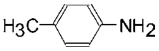
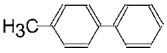
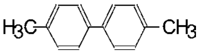
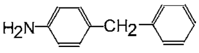
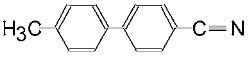
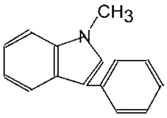
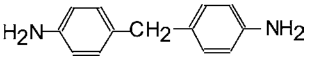
3. Results and discussion

3.1. Thermal and thermo-oxidative stability of the cured polytriazole resin

The thermal stability of the cured poly(1,2,3-triazole) (PTA) resin has been investigated by the thermogravimetry analysis (TGA). Fig. 1 shows the TGA and DTG thermograms of the investigated resin under both nitrogen and air atmosphere. It can be seen that the decomposition process is performed in one stage under nitrogen atmosphere and in two stages under air atmosphere. The degradation temperature T_{d5} (the temperature of degradation at 5% weight loss) is 360 °C and the temperature at maximum degradation rate is around 380 °C under both nitrogen and air atmospheres in the first stage. As shown in the figure, the second stage of the decomposition under air initiates at 580 °C and the maximum rate at this stage of the decomposition occurs at 621 °C.

The weight loss of the cured resin in the range of 400–620 °C under air was relatively lower than that under nitrogen. Oxygen might take part in the degradation reactions of PTA resin, i.e., the thermal-oxidative degradation and the uptake of oxygen increases the weight. It is possible that some char is formed at lower temperatures (<600 °C) in which oxygen must participate and degrades at a higher temperature [12]. Thus, the oxidative products are quickly decomposed with the temperature increasing further and finally the residue weight at 800 °C is near zero.

Table 1
Pyrolyzates of the cured PTA resin identified by Py/GC/MS at different pyrolysis temperatures

Peak no.	Structures	MS fragments (m/z)[a]	Relative abundance (%)[b]	
			400 °C	570 °C
1	$N\equiv N$	28 $(M)^+$ (s)	–	48.18
2	$H_2C{=}C{=}CH_2$	40 $(M)^+$ (s), 39 $(M{-}H)^+$ (s), 38 $(M{-}2H)^+$ (m), 37 $(M{-}3H)^+$ (w), 28 $(M{-}C)^+$ (w)	7.31	UD[c]
3	$H{-}C\equiv N$	27 $(M)^+$ (s), 26 $(M{-}H)^+$ (w)	–	5.42
4	$NC{-}CH{=}CH_2$	53 $(M)^+$ (s), 52 $(M{-}H)^+$ (m), 51 $(M{-}2H)^+$ (w), 26 $(M{-}CH{=}CH_2)^+$ (s)	–	8.98
5	$NC{-}CH_2{-}CH_3$	55 $(M)^+$ (m), 54 $(M{-}H)^+$ (s), 28 $(M{-}HCN)^+$ (s), 27 $(M{-}CH_2{=}CH_2)^+$ (w), 26 $(M{-}CH_2CH_3)^+$ (w)	–	6.03
6		83 $(M)^+$ (s), 56 $(M{-}HCN)^+$ (m), 54 $(M{-}N_2{-}H)^+$ (m), 42 $(M{-}CH_3{-}CN)^+$ (m), 28 $(N_2)^+$ (m), 27 (HCN) (m)	1.53	–
7		93 $(M)^+$ (s), 66 $(M{-}H{-}CN)^+$ (m), 65 $(M{-}2H{-}CN)^+$ (w)	1.23	11.43
8		107 $(M)^+$ (s), 106 $(M{-}H)^+$ (s),	4.04	15.25
9		168 $(M)^+$ (s), 167 $(M{-}H)^+$ (m), 153 $(M{-}CH_3)^+$ (w), 152 $(M{-}CH_3{-}H)^+$ (w)	2.59	14.42
10		182 $(M)^+$ (s), 181 $(M{-}H)^+$ (w), 167 $(M{-}CH_3)^+$ (m)	44.47	88.42
11		183 $(M)^+$ (s), 182 $(M{-}H)^+$ (m), 165 $(M{-}NH_4)^+$ (w), 106 $(M{-}C_6H_5)^+$ (m)	4.25	7.36
12		193 $(M)^+$ (s), 178 $(M{-}CH_3)^+$ (m),	–	18.31
13		207 $(M)^+$ (s), 192 $(M{-}CH_3)^+$ (w), 165 $(M{-}CH_3{-}HCN)^+$ (m)	1.95	4.54
14		198 $(M)^+$ (s), 197 $(M{-}H)^+$ (m), 182 $(M{-}NH_2)^+$ (w), 180 $(M{-}NH_2{-}2H)^+$ (w), 106 $(M{-}C_6H_4NH_2)^+$ (m)	100	100

[a] s, strong; m, medium; w, weak.

[b] -: Not observed.

[c] Undetermined.

3.2. Degradation kinetics of the cured polytriazole resin

Thermograms of the cured PTA resin at heating rates of 5, 10, 15, and 20 °C/min under nitrogen and air atmospheres are shown in Fig. 2. The kinetics of thermal degradation of a polymer is usually treated by several methods [13–15]. One of the methods is Ozawa's. The apparent activation energy (E_a)for the degradation can be obtained by the following Ozawa's equation:

$$\log\beta = \log\frac{AE_a}{Rf(c)} - 2.315 - 0.457\frac{E_a}{RT} \qquad (1)$$

where β is the heating rate (°C/min), A the pre-exponential factor of degradation (s^{-1}), E_a the apparent activation energy (kJ/mol), T the temperature (K), c the conversion of degradation, and $f(c)$ is the function of conversion. Therefore, for a given sample at a given conversion of degradation, the plots of $\log\beta$ versus $1/T$ should be a straight line and E_a can be obtained by the slope of the line.

The plots of $\log\beta$ versus $1/T$ at different conversion of degradation were shown in Fig. 3(a and b). Moreover, the dependence of the activation energy on the conversion of degradation was shown in Fig. 4(a and b). It can be observed that average apparent activation energies approach to about 190 kJ/mol except for those at low or high conversion of degradation under nitrogen atmosphere. Under air atmosphere, an average value of the activation energy is near 160 kJ/mol except for that at less than 20% conversion of degradation. The activation energy of degradation under nitrogen is higher than that under air. This implies that the thermo-oxidative degradation of the cured PTA resin is a bit easier than thermal degradation.

3.3. Degradation mechanism of the cured polytriazole resin

In order to trace thermal degradation of the PTA resin, the Py/GC/MS combined technique, which is usually used to determine the thermal degradation mechanisms and the structures of a polymer [16,17], was utilized. Fig. 5 shows the gas chromatograms of the pyrolytic products of the cured PTA resin at 400 and 570 °C. The pyrolysis fragments are identified by MS analyses. The main compounds identified from the thermal pyrolysis of the cured PTA resin are tabulated in Table 1.

As shown in Fig. 5 and Table 1, the main pyrolysis products for the cured PTA resin pyrolysized at 400 and 570 °C are 4,4′-dimethylbiphenyl (peak 10) and 4,4′-diaminodiphenylmethane (peak 14). The other pyrolysis products are aniline, aniline derivatives and benzene derivatives such as 4-methylbenzenamine, 4-(phenylmethyl)benzenamine, 4-methylbiphenyl, etc. These products are related to the breakage of the C–N bonds of the TPDDM and DAMBP chain units in the crosslinked PTA network. This implies the weakest points

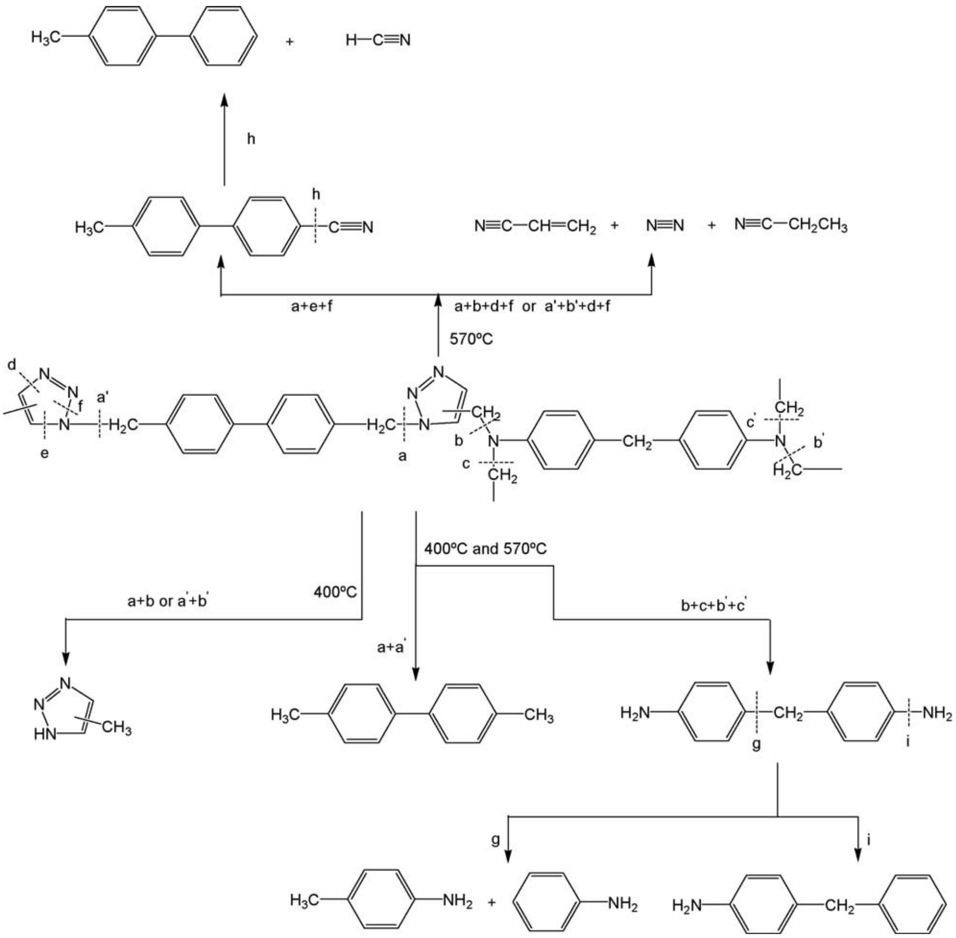


Fig. 6. A suggested thermal degradation mechanism of the cured PTA resin.

of cleavages in the crosslinked PTA network is CH_2–N bonds and the degradation of the cured PTA resin initiates at these bonds. The covalence energies for the bonds C–C and C–N are 334 and 276 kJ/mol, respectively. This further demonstrates that the breakage of C–N bond is easier than that of C–C bond and corresponds with our research results.

As seen from Table 1, the fragments such as nitrogen, hydrogen cyanide, acrylonitrile, propionitrile, etc. occurs when the cured resin was pyrolyzed at 570 °C. Especially, the nitrogen (peak 1) escaped from the decomposition of the cured resin increased largely. These compounds are related to the breakage of 1,2,3-triazole ring [18,19]. This demonstrates that the cleavage of the C–N and N–N bonds of the 1,2,3-triazole ring at 570 °C takes place. By comparison, there is no such fragments when the cured PTA resin was pyrolyzed at 400 °C. However, 4-methyl-1,2,3-triazole (related to peak 6 in Fig. 5) was detected in the degraded products of the resin pyrolyzed at 400 °C but the amount of the product is small. This demonstrates the triazole ring is stable at 400 °C but opened at 570 °C. As mentioned above, the degradation temperature T_{d5} of the cured TPA is 360 °C, which is lower than 400 °C. It probably happens that the breakage of the CH_2–N bonds in the crosslinked polytriazole network occurs at 360°C, whereas the triazole ring is stable at this temperature. Some reported work also demonstrated that the triazole ring formed from azide and allyl resins is stable at 400 °C [19]. It is possible that all of fragments with the triazole ring do not run out during the decomposition at 400 °C because of the crosslinking network of the polytriazole. Some of fragments with the triazole rings would remain in the residues. Thereby, the yield of methyl-1,2,3-triazole detected is low. Besides, 1,2-propadiene was identified when the resin was pyrolyzed at 400 and 570 °C. 1,2-Propadiene could probably be produced by the cleavage of C–N bond of TPDDM unit with propargyl groups unreacted in the cured PTA resin.

Based on the above results and discussion, we suggest that the degradation of the cured PTA resin was firstly the breakage of the CH_2–N bonds in the crosslinked network and then the formed fragments further decompose. A thermal degradation mechanisms of the cured PTA resin is proposed as shown in Fig. 6.

4. Conclusion

In summary, the thermal dedegradation temperature T_{d5} of the cured PTA resin arrives at 360 °C under air and under nitrogen atmosphere. The cured PTA resin is a kind of thermally and thermo-oxidatively stable polymers. The apparent activation energies of the degradation of the cured PTA resin are obtained by using Ozawa's method and are 190 and 160 kJ/mol (*ca*) for thermal degradation and thermo-oxidative degradation, respectively. The thermal decomposition of the cured PTA resin has been traced. The investigations show that the degradation of the cured PTA resin easily occurs at the CH_2–N bonds of the TPDDM and DAMBP units in the crosslinked polymer network. 1,2,3-Triazole ring is splited off nitrogen and relative products at higher than 400 °C in a pyrolyzer. At last, a degradation mechanism of the cured PTA resin is suggested.

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References

[1] C. Ridgard, Aircraft Eng. 59 (1987) 4–6.
[2] H.L. Cohen, J. Polym. Sci.: Polym. Chem. Ed. 19 (1981) 1337–1347.
[3] T. Sasaki, K. Minamoto, J. Org. Chem. 44 (1979) 1424–1429.
[4] H. Robert, S. Gupta, J. Org. Chem. 36 (1971) 2553–2556.
[5] S.T. Abu-Orabi, M.A. Atfah, I. Jibril, J. Heterocycl. Chem. 26 (1989) 1461–1468.
[6] K.E. Johson, J.A. Lovinger, C.O. Parker, J. Polym. Sci. Part B: Polym. Lett. 4 (1966) 977–979.
[7] M.G. Baldwin, K.E. Johson, J.A. Lovinger, J. Polym. Sci. Part B: Polym. Lett. 5 (1967) 803–805.
[8] Y.H. Hu, Y.H. Luo, L.Q. Wan, F.R. Huang, et al., Acta. Polym. Sinica 4 (2005) 560–565.
[9] S.L. Liu, Y.H. Hu, F.R. Huang, et al., Chin. J. Org. Chem. 24 (2004) 1228–1232.
[10] Y.H. Luo, Y.H. Hu, L.Q. Wan, F.R. Huang, et al., Chem. J. Chin. Univ. 27 (2006) 170–173.
[11] (a) L. Wan, J. Tian, F. Huang, et al., J. Macromol. Sci., Part A: Pure Appl. Chem., A44(2006), in press.;
(b) L. Wan, J. Tian, F. Huang, et al., J. Appl. Polym. Sci., (2006), in press.
[12] R.T. Conley, Thermal Stability of Polymers, vol. 1, Marcel Dekker, New York, 1970.
[13] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881–1886.
[14] F. Huang, X. Wang, S. Li, Polym. Degrad. Stab. 18 (1987) 247–259.
[15] J. Cardoso, L. Rubio, J. Appl. Polym. Sci. 73 (1999) 1409–1414.
[16] M. Day, J.D. Cooney, J. Anal. Appl. Pyrolysis 52 (1999) 199–224.
[17] Y.Q. Zhang, X.N. Shen, F.R. Huang, Thermochim. Acta 430 (2005) 15–22.
[18] B. Hans, D. Ralph, A. Sitki, J. Am. Chem. Soc. 105 (1983) 7681–7685.
[19] B. Gaur, B. Lochab, V. Choudhary, I.K. Varma, J. Therm. Anal. Calorim. 71 (2003) 467–479.