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Study on the flash pyrolysis of polyacrylamide: accelerator of Al–H_2O-based propellants

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Abstract The flash pyrolysis of polyacrylamide (PAM) in Ar atmosphere was carried out in a tube-type pyrolyzer at 700 °C for 5 min. The volatile products were detected and identified by gas chromatography combined with mass spectrometry (GC/MS). Twenty four kinds of pyrolysis products were identified. In particular, some products, such as acetaldazine and 4-hydroxy-4-methyl-2-pentanone, were the first reported existing in the PAM pyrolysis products, which should play an important role in improving the igniting and combustion performance of Al–H_2O-based propellants. Moreover, the flash pyrolysis residues were analyzed by FTIR. The experimental results show that the pyrolysis products of PAM can be roughly divided into five types. The products of five types promote the igniting and combustion performance of Al–H_2O-based propellants, and the mechanisms of formation of every type are discussed.

Introduction

The aluminum (Al)–water (H_2O) reaction is important to combustion and explosive systems. Aluminum and water as propellants applied in both space [1, 2] and underwater propulsion [3, 4] have been proposed. Especially, the combustion of Al with seawater is of interest in underwater propulsion, since the reaction is extremely exothermic and the water (oxidizer) need not be carried onboard [3]. The research has been initiated in the 1940s and continued in the early 1960s. For propulsion system, if the reaction takes place between metal fuels and water, the specific impulse will be remarkably increased. The reaction of metal and H_2O has the notable volume energy density because it does not bear the weight of water under the water propulsion system. However, because of higher melting and boiling point of Al and its oxide coating, Al–H_2O reaction activity is low. Moreover, the start-up of Al–H_2O reaction is particularly difficult. These facts indicate that it is enormously difficult to make the Al–H_2O propulsion system put into practice unless nano-sized Al particles are used. However, concerning the energy density, the amounts of producing gas, the stability of storing, price, and so on, the reaction of Al with H_2O is the best in metal–fuel system. Furthermore, the reaction of Al–H_2O with high energy density can attain better propulsion performance.

Polyacrylamide (PAM), which has the chemical structure as shown in Structure 1, is also called flocculating agent. PAM is not toxic, but unpolymerized acrylamide can be present in the polymerized acrylamide [5]. For PAM, one of the largest uses is to flocculate or coagulate solids in a liquid. Moreover, it is highly water absorbent, forming a soft gel used in such applications as PAM gel electrophoresis and in manufacturing soft contact lenses.

In recent years, PAM has been introduced into combustion field, including the component of hydrogen fuel cell, and the important additive of Al–H_2O propellant. Especially, the addition of PAM to the Al–H_2O propellant increases propellant combustion stability and makes propellant ignite easily [6]. In some engine, the addition of PAM to Al–H_2O propellant directly determines whether the propellant can be successfully ignited [7–11]. Therefore, it can be found that PAM plays an important role in the combustion process of Al–H_2O propellant. However,

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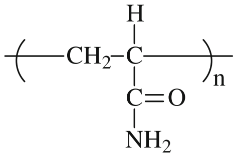
Structure 1



$$-\!\!\left(\mathrm{CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle NH_2}{C{=}O}}{C}}}\right)\!\!-_n$$

considerable uncertainty remains in the understanding of how PAM affects the Al–H_2O propellant combustion. Few fundamental studies have been conducted on pure PAM polymer. Han et al. [12] have studied PAM aqueous solution flash pyrolysis and indicated that oxygen-free radicals can accelerate the pyrolysis of PAM. However, some problems are not yet clearly understood, such as pure PAM flash pyrolysis, flash pyrolysis mechanism, and the effect of pure PAM on the ignition and combustion of Al–H_2O-based fuels. Therefore, it is of great importance to investigate thermal behaviors of pure PAM polymer.

In this study, in order to simulate actual environment of Al–H_2O-based propellants' combustion, the flash pyrolysis of PAM was carried out at 700 °C in argon. The pyrolysis products were detected and identified by pyrolysis-gas chromatography combined with mass spectrometry (Py-GC/MS), and the residues were analyzed by Fourier transform infrared (FTIR) spectra. The flash pyrolysis mechanism of PAM was also preliminarily discussed.

Experimental

Raw material

The sample used in the experiment is PAM, its purity is 90%, and molecular weight is 3,000,000.0 g/mol. Solvent is acetone (CH_3COCH_3), its purity is 99.5%, which was used for collecting pyrolysis products. PAM and acetone were both purchased from Shanghai Chemical Reagent Inc. of Medicine Group of China.

Flash pyrolysis

Flash pyrolysis of PAM was performed in a furnace-type pyrolyzer, using off-line detections. It mainly consists of a tube-type furnace, a temperature controller, a quartz tube, a quartz boat, and a U-tube collector. Most of the devices and their operations have been detailed in [13], but a U-tube collector was used in our experiments instead of the Cambridge pad assembly reported in [13]. An experimental arrangement is shown in Fig. 1. The U-tube collector was placed in a water/ice/salt bath, and about 5 ml acetone was injected into the collector before experiment each time. 0.1 g sample was pyrolyzed for 5 min in Ar atmosphere for each experiment. After pyrolysis, about 25 ml acetone was injected into the U-tube collector to dilute the products. The solution in the collector after experiment was then transferred into a Kuderna–Danish concentrator and was concentrated to about 1 ml for analysis of products.

Analysis of flash pyrolysis products

The collected products were analyzed by GC/MS using Rtx-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness), with the following temperature programming: the initial oven temperature was 40 °C, holding for 2 min, and then was heated to 250 °C with the heating rate of 4 °C min^{-1}, holding for 5 min. Helium was used as the carrier gas with a constant flow rate of 3.0 ml min^{-1}. Programming temperature vaporizer (PTV) injector temperature was 250 °C, and the split value was 30:1. The

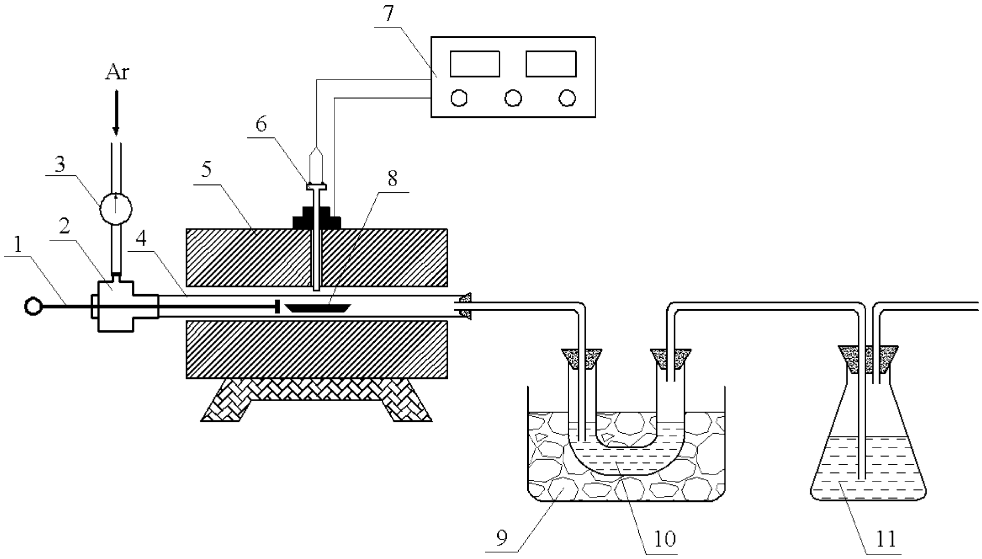


Fig. 1 A schematic of the pyrolysis system: *1* step push pot, *2* packing gland, *3* flow meter, *4* quartz tube, *5* tubular heater, *6* thermocouple, *7* temperature controller, *8* quartz boat, *9* water/ice/salt bath, *10* U-tube collector, and *11* NaOH solution

temperature of the GC/MS transfer line was 250 °C. The mass spectrometer worked in the electron impact (EI) mode with the ionization energy of 70 eV, and the MS detector scanned from 40 to 600 m/z. Mass spectral identification was assisted by comparing the mass spectra with those in NIST MS library.

FTIR spectra were obtained with a Nicolet IS10 FTIR spectrometer in the range of 4000–400 cm^{-1}. The samples for FTIR analysis were prepared by thin film method.

Results and discussion

Flash characterization of PAM

Pyrolysis experiments were carried out at 700 °C for 5 min. The total ion chromatograms (TICs) of the products from PAM flash pyrolysis and partial enlarged detail are shown in Fig. 2. Most products were separated and detected before 15 min. Twenty-four principal products which were released from flash pyrolysis of the PAM are listed in Table 1, and their structures are exhibited in Schemes 3, 4, 5, 6, 7, 8 at 700 °C.

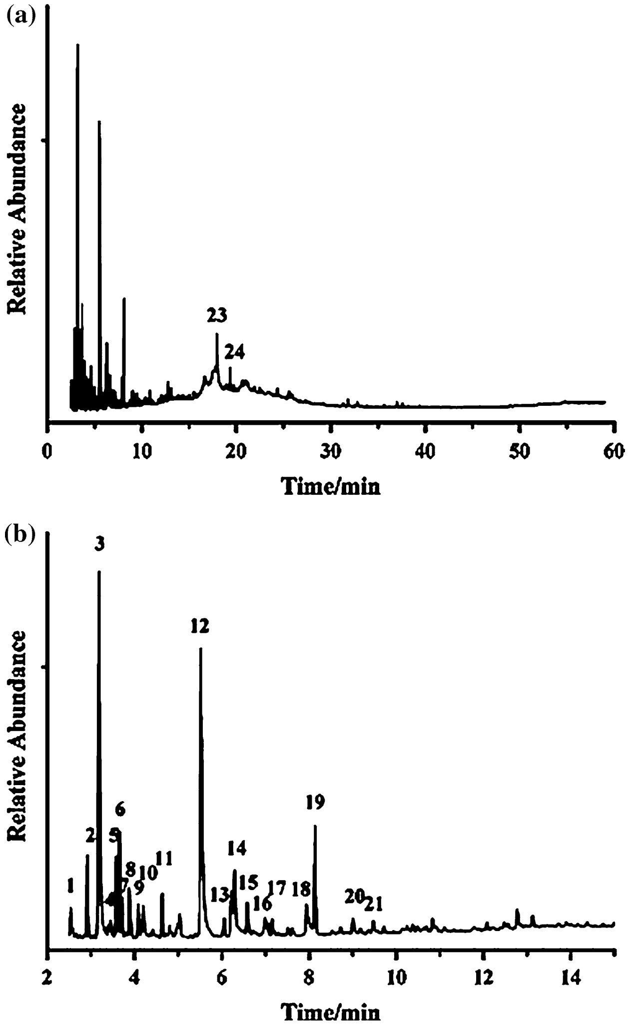


Fig. 2 The total ion chromatograms of PAM flash pyrolysis at 700 °C (**a**) and partial enlarged detail (**b**)

It can be recognized that all the compounds identified are flammable, and some of them are observed for the first time in PAM pyrolysis. It should be mentioned that numerous aromatic hydrocarbons, nitrogenous compounds, and ketone, including toluene, xylene, styrene, 1-methylethyl-benzene, acetone cyanohydrin, acetaldazine and, 4-hydroxy-4-methyl-2-pentanone are detected, which are believed to be mutagenic or carcinogenic [14, 15].

It can be found from Fig. 2 that the main peaks in the pyrogram of PAM are acetaldazine, 4-hydroxy-4-methyl-2-pentanone, and 1-methylethyl-benzene—especially for acetaldazine and 4-hydroxy-4-methyl-2-pentanone, which account for approximately 50% of total identified peak areas. The mass spectra of two compounds are shown in Fig. 3.

It is well known that the combustion of Al and H_2O must initially proceed through a surface reaction like boron and carbon because the flame temperature of Al–H_2O reaction is lower than the vaporization temperature of Al [16]. However, unlike boron and carbon, the final oxide product, such as Al_2O_3, if formed or present on the particle surface, will not leave the surface since their vaporization temperatures are considerably higher than both the Al vaporization and adiabatic flame temperature, and isolate Al particles from reacting with H_2O. This process directly causes an obstacle to sustain combustion of fuels. However, the addition of PAM to the Al–H_2O reaction can offer significant advantages over that without the addition of PAM. We predict the two mechanisms would favor PAM-promoting effects on combustion performance of Al–H_2O-based fuels. One is that the pyrolysis products such as 4-hydroxy-4-methyl-2-pentanone and most of aromatic hydrocarbons presented in Table 1 would react with Al forming some metal–organic chelate compounds, which may provide an effect to diminish the formation of aluminum oxides—especially for 4-hydroxy-4-methyl-2-pentanone, which is the main product of PAM flash pyrolysis, even at room temperature, is incompatible with Al [17]. These metal–organic chelate compounds are easier to be ignited and burned. Therefore, these would enhance the igniting and combustion performance of Al–H_2O-based fuels. The mechanisms are explained in Scheme 1.

Other products are nitrogenous compounds, such as acetaldazine, 2-methyl-2-butenenitrile, acetone cyanohydrin, 2-pentenenitrile, 3-methyl-2-methylene-butanenitrile, 3, 4, 4, 5-tetramethyl-pyrazole, 1-hydroxymethyl-5, 5-dimethyl-2, 4-imidazolidinedione, and 3, 3-dimethylpyrrolidine-2, 5-dione. At very high temperature, these substances are expected to decompose to give NH_3. In particular,

Table 1 PAM flash pyrolysis products detected and identified by GC/MS

Products	Molecular weight	Formula	Compounds	Rt/min	Area%
(1)	86	$C_5H_{10}O$	3-Pentanone	2.536	1.09
(2)	81	C_5H_7N	2-Methyl-2-butenenitrile	2.916	3.04
(3)	84	$C_4H_8N_2$	Acetaldazine	3.182	21.69
(4)	96	C_7H_{12}	1-Ethylcyclopentene	3.446	0.69
(5)	85	C_4H_7NO	Acetone cyanohydrin	3.574	3.61
(6)	92	C_7H_8	Toluene	3.654	4.65
(7)	96	C_7H_{12}	1-Methyl-cyclohexene	3.716	1.63
(8)	81	C_5H_7N	Butanenitrile	3.877	3.35
(9)	81	C_5H_7N	2-Pentenenitrile	4.085	1.58
(10)	102	$C_5H_{10}O_2$	1,2-Cyclopentanediol	4.195	2.19
(11)	95	C_6H_9N	3-Methyl-2-methylene- butanenitrile	4.632	1.98
(12)	116	$C_6H_{12}O_2$	4-Hydroxy-4-methyl-2-pentanone	5.518	21.39
(13)	106	C_8H_{10}	Ethylbenzene	6.058	0.70
(14)	106	C_8H_{10}	*O*-Xylene	6.293	3.53
(15)	111	$C_7H_{13}N$	*N*-cyclohexylidene-methanamine	6.581	1.81
(16)	104	C_8H_8	Styrene	6.991	0.86
(17)	98	$C_6H_{10}O$	Cyclohexanone	7.155	0.95
(18)	124	$C_7H_{12}N_2$	3,4,4,5-Tetramethyl-pyrazole	7.940	2.93
(19)	120	C_9H_{12}	1-Methylethyl-benzene	8.136	6.47
(20)	112	$C_7H_{12}O$	2-Methyl-cyclohexanone	9.007	0.85
(21)	120	C_9H_{12}	1-Ethyl-3-methyl-benzene	9.475	0.51
(22)	124	$C_8H_{12}O_2$	4,4-Dimethyl-2–cyclohexen-1-one	12.773	1.13
(23)	128	$C_5H_8N_2O_2$	5,5-Dimethyl-2,4-imidazolidinedione	17.929	3.73
(24)	127	$C_6H_9NO_2$	3,3-Dimethylpyrrolidine-2,5-dione	19.349	1.72

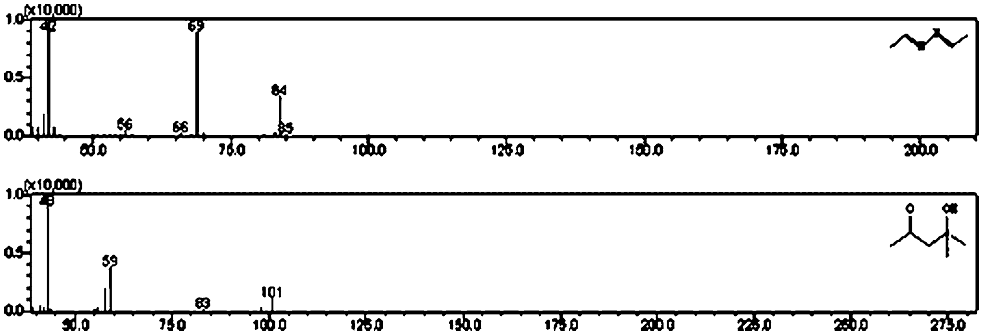


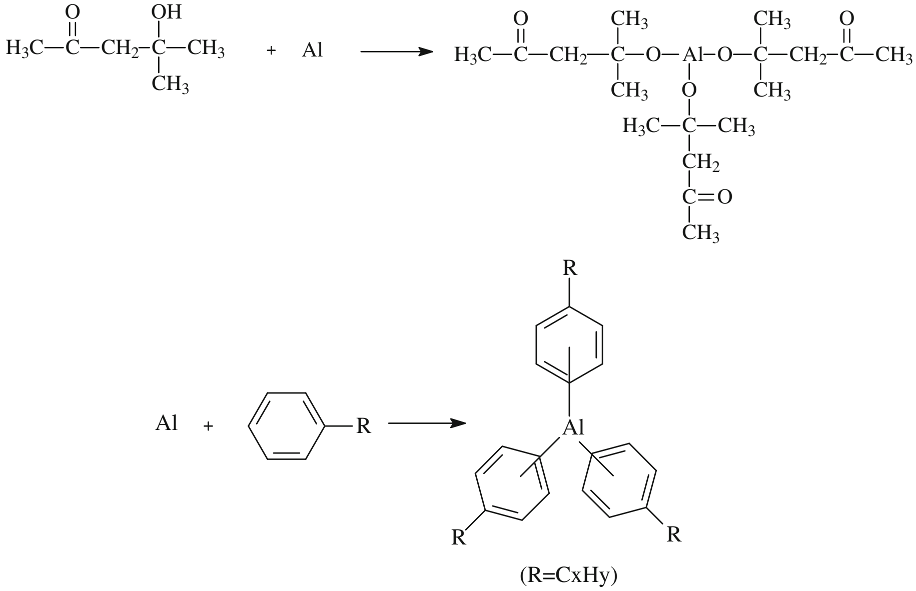
Fig. 3 The mass spectra of acetaldazine and 4-hydroxy-4-methyl-2-pentanone

acetaldazine, which is the main product of PAM flash pyrolysis, emits toxic vapors of NO_x when it is heated to decomposition in oxidizing agents. These substances such as NH_3 and NO_X can enhance the performance of fuels in normal combustion process.

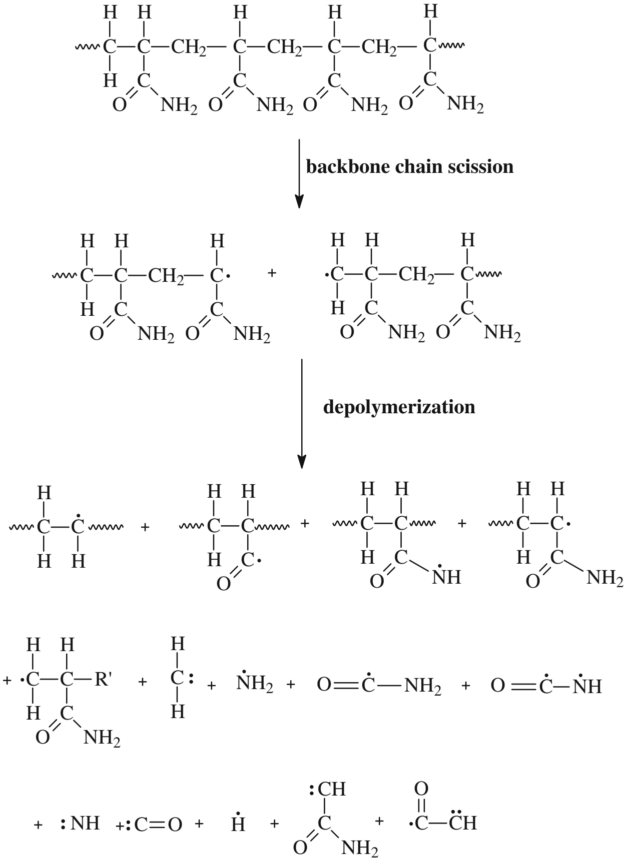
FTIR spectra of PAM and solid residues

FTIR spectra were adopted to assist mass spectra analysis in our experiment. Figure 4 shows the FTIR spectra, representing functional group compositional analysis of pure PAM and the solid residues obtained from the flash pyrolysis of PAM. For pure PAM, the bands at about 3440 and 1620 cm^{-1} are assigned to N–H stretching vibrations and the NH_2 bending, respectively. 2925 and 1455 cm^{-1} are, respectively due to the stretching vibrations and bending vibrations of C–H. The peak at 1130 cm^{-1} is assigned to the asymmetric stretching vibrations of C–C [18]. The peaks at 637 and 616 cm^{-1} correspond to C–O wagging vibrations and C–C rocking vibrations, respectively.

The FTIR spectra for flash pyrolysis residues of PAM at 700 °C are displayed in Fig. 4 for comparison. The intensity of the peak at 1455 cm^{-1} exhibits an obvious increase.

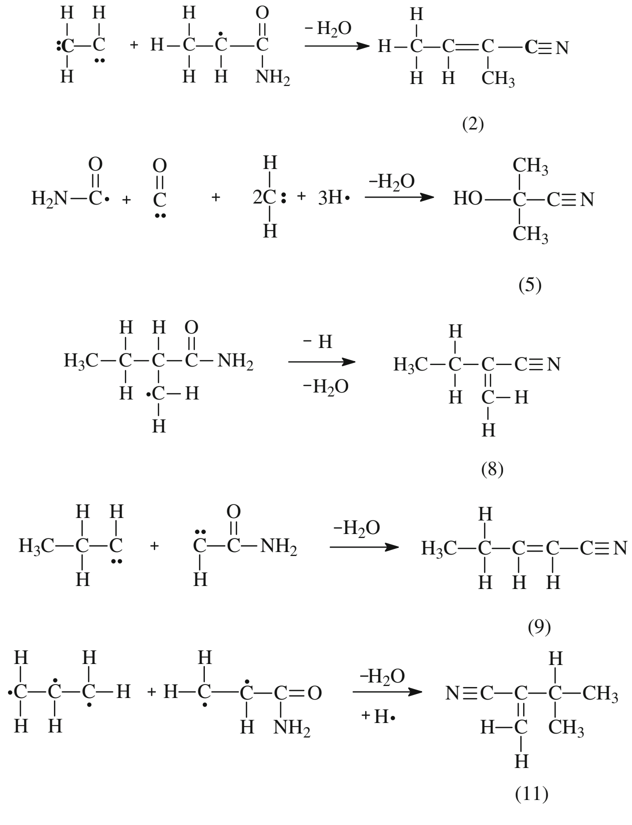


Scheme 1 The reacting mechanisms of 4-hydroxy-4-methyl-2-pentanone and aromatic hydrocarbons with Al



Scheme 2 The pathways of backbone chain scission of PAM polymer

A new sharp peak (876 cm^{-1}) can be observed at 700 °C, which can be assigned to the stretching vibration of C–C bond; this indicates that the flash pyrolysis has formed some new compound containing this structure.



Scheme 3 The formation pathways of low aliphatic nitriles

Flash pyrolysis mechanism of PAM

The pyrolytic decomposition of PAM has been studied in the recent past [19]. This study has shown that PAM decomposition takes place first, (a) chain scission, (b) loss of water and ammonia, forming nitrile functional groups

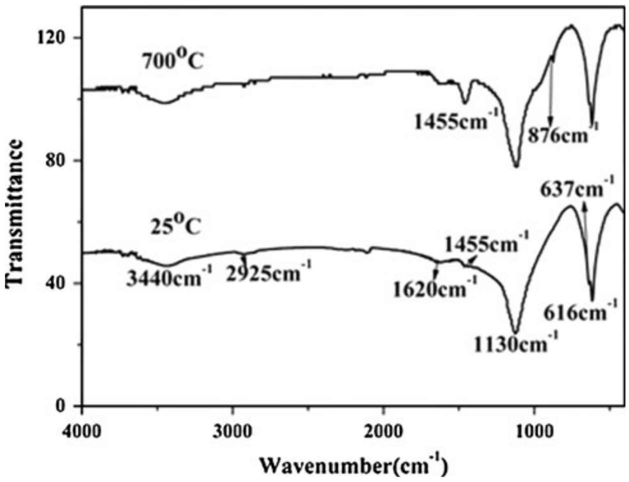
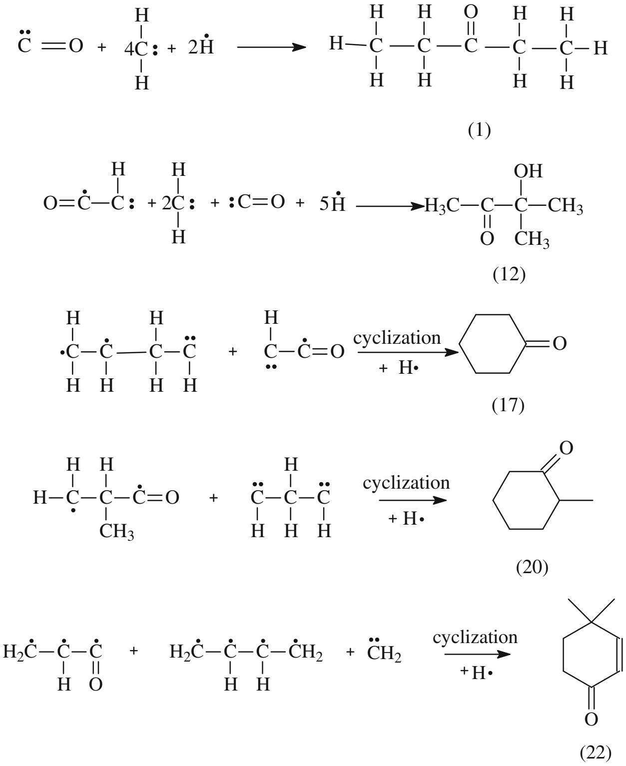
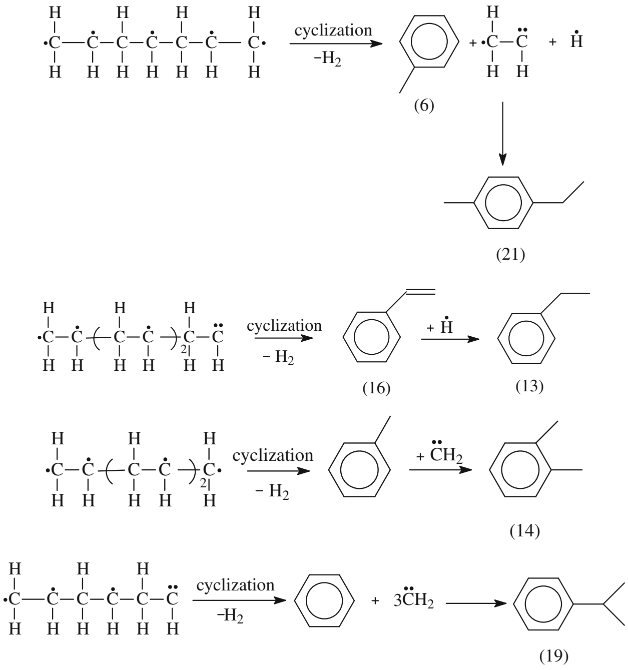


Fig. 4 FTIR spectra of pure PAM at 25 °C and flash pyrolysis residues of PAM at 700 °C

and the cyclic ring structure of glutarimide, followed by polymer chain scission to form saturated and unsaturated low aliphatic acrylonitrile and glutarimide. In addition, the polymer backbone chain scission is a part of the mechanism by which monomers, dimers, trimers, and tetramers are formed. It can be found from the above discussion that the major pyrolysis products of PAM are compounds containing nitrile functional groups and diimide functional groups. A few researches have been reported on the formation mechanisms of acetaldazine, 4-hydroxy-4-methyl-2-pentanone, and some aromatic compounds in the decomposition of PAM. In this study, water, ammonia, monomers, dimers, and trimers have not been detected because of the collection methods. On the contrary, many compounds (such as acetaldazine, 4-hydroxy-4-methyl-2-pentanone, aromatic compounds, etc.) have been found. Tutaş et al. [20] has detected that the decomposition of PAM at 500 °C can form acetonitrile, acrylonitrile, propionitrile, methacrylonitrile, and isobutyronitrile. However, there are few compounds containing nitrile functional groups observed at the end of the PAM pyrolysis. It has been suggested that the compounds (such as acetaldazine, 4-hydroxy-4-methyl-2-pentanone, aromatic compounds, etc.) arise from the high-temperature pyrolysis of the products which are formed from the backbone chain scission at lower heating temperatures. Therefore, it is possible that these products which are formed at lower heating temperatures can further be transformed to some steadier compounds at a relatively high temperature. In other words, the compounds collected and detected in our experimental processes are likely to assume root in the backbone chain scission products. Scheme 2 displays the formed pathways of backbone chain scission products, via C–C bond scission of polymer chains. These products of the backbone chain scission then can further decompose and form some free radicals and intermediates, which generate the final products by various pathways.

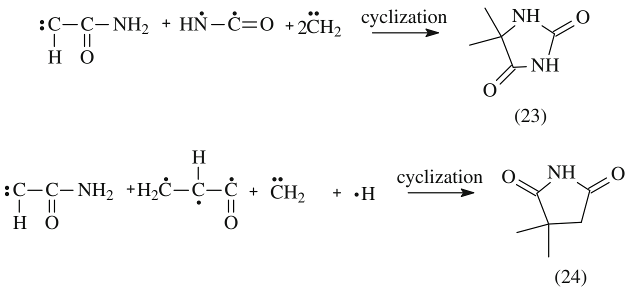


Scheme 4 The formation pathways of aliphatic ketones

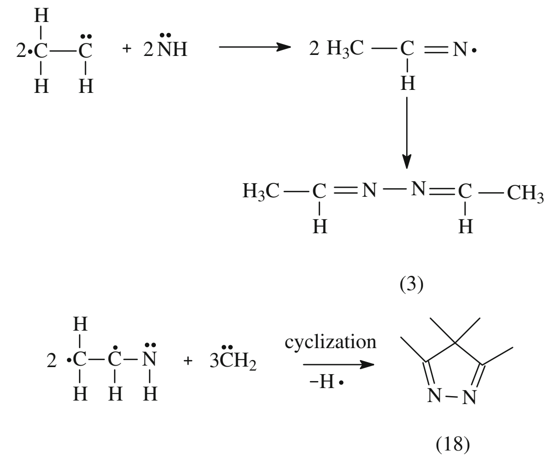


Scheme 5 The formation pathways of aromatic hydrocarbons

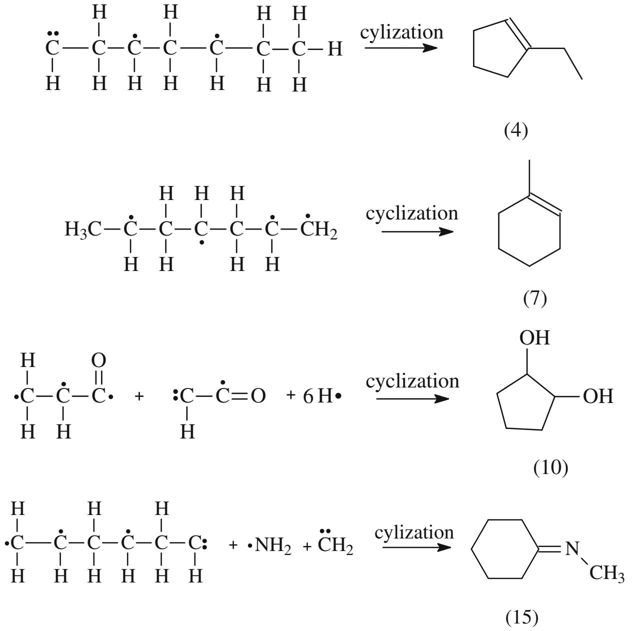
The formation of free radicals on the backbone of the polymer may cause the polymer to undergo scission to



Scheme 6 The formation pathways of aliphatic diimides



Scheme 7 The formation pathways of compounds containing =N–N= functional groups



Scheme 8 The formation pathways of alkane derivatives, glycol and nitrogenous compounds

form a propagating free radical on the backbone. The random scission, which occurs at relatively higher temperatures, involves the formation of free radicals producing fragments of varying lengths thus giving rise to primary and secondary macro radicals. Both macro radicals can further react to give a variety of products, though the primary macro radical undergoes an almost quantitative depolymerization.

The mechanism is discussed in the following reactions. According to the identification products shown in Table 1, the pyrolysis products of PAM can be roughly divided into low aliphatic nitriles, aliphatic ketones, aromatic hydrocarbons, aliphatic diimides, and compounds containing =N–N= functional groups. The low aliphatic nitriles generally result from the reaction of alkyl-free radicals and free radicals containing amido functional groups and amido functional groups with loss of water. In other words, the low aliphatic nitriles are formed from free radicals and dehydration reaction, as shown in Scheme 3.

As shown in Scheme 4, aliphatic ketones are formed from free radical and addition reactions. Some free radicals via cyclization process form six-membered ring of ketones. Scheme 5 illustrates the possible formation pathways of aromatic hydrocarbons. Besides forming some benzene ring structures by cyclization process, some aromatic derivatives via intermolecular H-abstraction reactions and disproportionation intermolecular reactions can also be formed. Some aliphatic diimides, such as 2,4-imidazolidinedione and 3,3-dimethylpyrrolidine-2,5-dione, can be produced by cyclization reactions, as shown in Scheme 6. Compounds containing =N–N= functional groups via free radical reactions or cyclization process are formed, as shown in Scheme 7. In addition, some alkane derivatives, glycol, and nitrogenous compounds are formed by the cyclization process, as shown in Scheme 8.

Conclusions

In this study, the flash pyrolysis of PAM at 700 °C was investigated. The flash pyrolysis products and their formation mechanisms were identified and discussed. The analysis of GC/MS results shows that the flash pyrolysis products are roughly divided into five types, which promote the igniting and combustion performance of Al–H_2O-based fuels. Among these chemicals, higher amounts of acetaldazine and 4-hydroxy-4-methyl-2-pentanone are produced, which play important roles in enhancing the igniting and combustion performance of Al–H_2O-based fuels. At high temperature, the flash pyrolysis of PAM first takes place by backbone chain scission, which then further decomposes and forms some free radicals and intermediates. It could be predicted that two mechanisms would favor PAM-promoting effects on combustion performance of Al–H_2O-based fuels. The flash pyrolysis products of PAM, such as 4-hydroxy-4-methyl-2-pentanone and aromatic compounds, can protect aluminum from aluminum oxide's coating by forming metal chelates. Moreover, the combustion of nitrogenous compounds, such as acetaldazine which is energy material, enhances the igniting and combustion performance of fuels.

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