Hydrolysis of Aromatic Heterocyclic Polymers in High Temperature Water. I. Hydrolysis of Polyphenyl-1,2,4-triazine

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ABSTRACT: The hydrolytic behaviors of polyphenyl-1,2,4-triazine (As–PPT) at high temperatures were investigated both experimentally and theoretically. The hydrolytic experiments of As–PPT film and a reasonably designed model compound for the polymer were carried out in distilled water at 250°C/3.97 MPa under N_2 atmosphere, respectively. The hydrolytic reactions were monitored by FTIR and UV-Vis spectra, and their hydrolysates were identified by FTIR, HPLC, and MS. The results confirmed that the two reactions gave the same major hydrolysate, terephthalic acid. In addition, the electronic structure of its model compound, given by *ab initio* calculation at the 4-31G level, indicated that the triazine ring is the hydrolytically active part at which the N atoms are to be protonated. On the basis of these results, a hydrolytic mechanism is proposed, which suggests that the cleavage of one C—N bond takes place, primarily on the triazine rings, followed by a gradual rupture of the polymer chain and the formation of the intermediate terephthalonitrile, the further hydrolysis of which produces terephthalic acid. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 907–915, 2001

Key words: aromatic heterocyclic polymer; poly-1,2,4-triazine; high-temperature hydrolysis; heat- and water-resistant polymer; *ab initio* calculation

INTRODUCTION

Polymeric materials with considerable stability at high temperatures, both in air and in water, are of great importance in many fields of modern science and technology because high-temperature water is commonly used and polymeric materials can be employed as coatings, adhesives, insulat-

ing materials, and structural materials in these situations. For example, high-temperature water serves as a heat-transport carrier in nuclear power stations and as a clean energy source in the heat-energy utilization of underground geothermal water. High-temperature water is also used in oil exploration and in some chemical industries. In these situations, water of 250°C or higher is encountered, thus the polymeric materials used in these rigorous circumstances should have good heat and water resistance. As an example, underwater electric motors are frequently used in the above-mentioned conditions, which demands
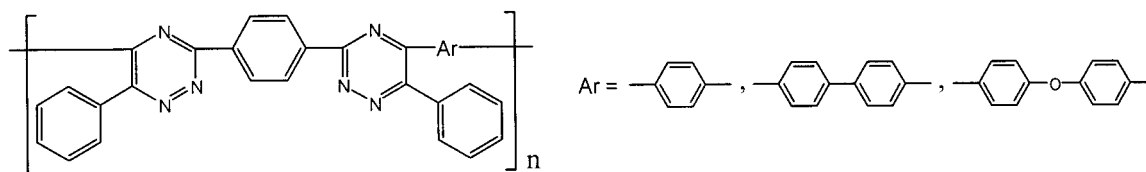
Scheme 1

that the insulating coating on the enamel wires maintains good stability in high temperature water.

A number of excellent heat-resistant polymers, such as aromatic polyimides, polyquinoxalines, polybenzimidazoles, polypyrrones, and so forth, have been well developed since the 1950s.[1] Since then, some investigators focused attention on the hydrolytic stabilities of some polymers in water at 25–100°C,[2–8] whereas the polymers' water resistance in temperatures higher than 100°C has not normally been considered as a notable polymer property, and thus has not yet been studied systematically, even though it may be of great importance in many cases, as mentioned earlier and in the literature.[9] Apparently, the uses of excellent heat-resistant polymers would be limited if their stability in high-temperature water is poor. Hence, it is necessary and important to investigate the stability of some available or reported heat-resistant polymers.

As it is known, aromatic heterocyclic polymers exhibit good heat resistance as well as outstanding mechanical strength and electric insulation, and thus have good potential to be used as structural and functional materials in, for example, the aerospace, electronic, manufacturing, and chemical industries.[9] For instance, because of their excellent heat resistance and cost performance, polyimides (PI) have been popularly used in industry for some time and some of them have a ready market. Some investigations on the be-

haviors of PIs (primarily the Kapton-H films from Du Pont were used as test samples), in aqueous solutions of various pH values as well as in distilled water at temperatures below 100°C, were previously reported.[2–8] As it turns out, PI polymers showed adequate stabilities in water below 100°C for general purposes (e.g., the mechanical durability of Kapton-H films in boiling water could last for as long as 1 year[2]). However, their hydrolysis behaviors at higher temperatures have received very little attention.

To verify whether some chosen heat-resistant polymeric materials are eligible for use in higher-temperature water, Lu and coinvestigators[10] made a comparison of the behaviors of Kapton-H and polyphenylquinoxaline (PPQ) films in distilled water at 250°C/3.97 MPa (the vapor pressure of pure water at this temperature is 3.97 MPa) for 60 h and found that the Kapton-H film was completely destroyed, whereas the PPQ film lost only a little of its weight. This implies that the thermal decomposition and the high-temperature hydrolysis of a polymer may be dominated by different mechanisms. Our present investigation is an extension of the earlier work.

Another type of good heat-resistant polymers, polyphenyl-1,2,4-triazines (As–PPTs), was first reported in 1969.[11] Since then, a number of As–PPTs, characterized by their good thermooxidative stability, solubility, water resistance, and processability, have been developed.[12,13] In this study, experimental investigations were carried

model compound I   model compound II
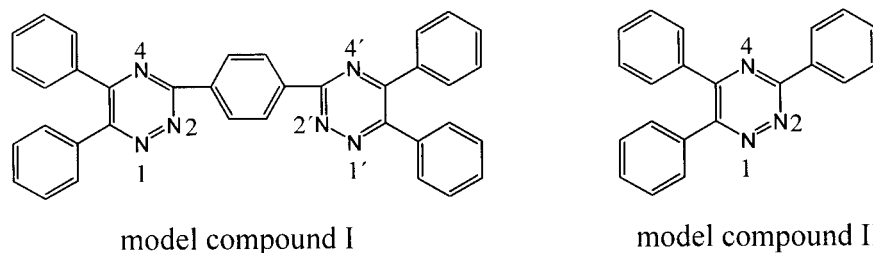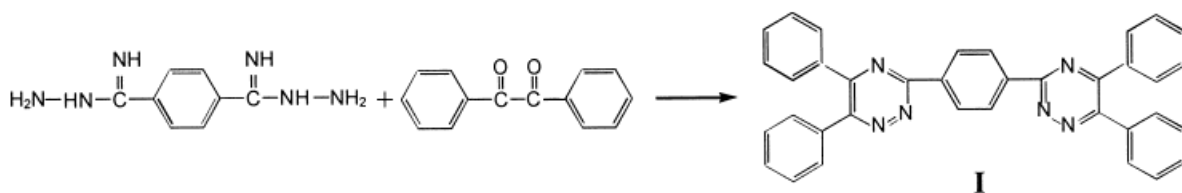
Scheme 2

Scheme 3

out on the hydrolysis of As–PPT film and its model compound in distilled water at 250°C/3.97 MPa. In combination with the experimental observation, quantum chemical calculations of the theoretically designed model compounds were also performed to understand the relationship between the hydrolysis resistance and the macromolecular structure of the polymer.

MODEL COMPOUNDS

The typical chain structures of As–PPTs are shown in Scheme 1. In the present study we confine ourselves to the polymer with Ar = $-C_6H_4-$, the same as previously reported.[13,14]

As shown in Scheme 1, each of the repeated units in the polymer chain of As–PPTs contains two 1,2,4-triazine rings spaced off by a phenylene group, and every two units are joined through a substitutive aromatic group. Thus, two molecules were designed to serve as the model compounds of the chosen As–PPT polymer, with the structure as shown in Scheme 2, where each of the 1,2,4-triazine rings is connected with three benzene rings, that is, in a surrounding that is chemically similar to that in the polymer.

Model compound **I**, composed of a single unit of polymer and a terminal phenyl, was employed to carry out a parallel hydrolysis test as a comparison with the As–PPT polymer. This makes it easier to identify the hydrolysates and to determine the reaction mechanism. Model compound **II**, a

compound with the smallest unit, was used to perform *ab initio* calculations to give a better approximation to the local electronic structure on the heterocyclic part of the polymer because it remains impossible to do an immediate *ab initio* calculation with a polymer molecule, despite the development of computer technology and advances in methods of calculation.

EXPERIMENTAL

Materials

The As–PPT film and model compound **I** were prepared following a well-known scheme as previously proposed.[14,15] Model compound **I** was prepared from a cyclocondensation reaction of stoichiometric quantities of terephthalamidrazone with benzil in refluxing ethanol, according to **Scheme 3**. The crude product of As–PPT was recrystallized in dimethylformamide (DMF) solution. Finally, the needlelike grains of yellow color were obtained.

As–PPT film was prepared by a conventional two-step method: polymerization was carried out in a solution of cresol at ambient temperature, followed by film casting and curing at high temperature, as shown in Scheme 4.

The first stage of the procedure includes the preparation of a solution of polymer precursor, resulting from the reaction of stoichiometric amounts of terephthalamidrazone and 1,4-bis-
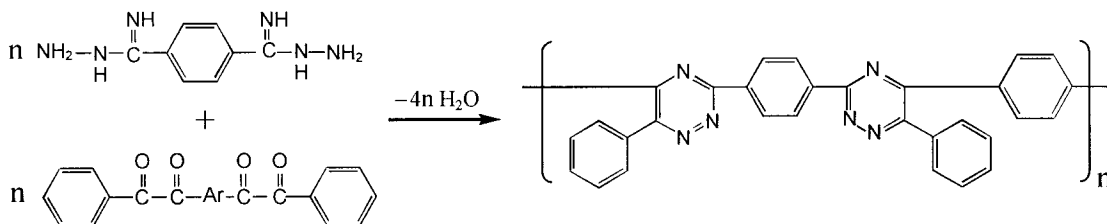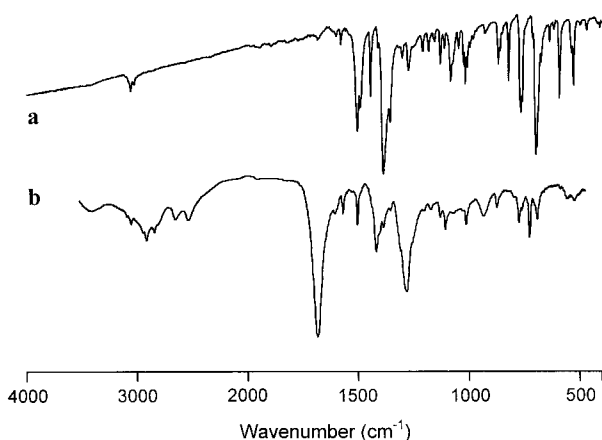

Scheme 4

Figure 1 FTIR spectrum of the extracted hydrolysates (b) compared with the untreated model compound **I** (a), determined in pellets of KBr.

(phenylglyoxalyl)benzene in cresol under drastic stirring at room temperature for 2 h at a solids content of 10%. The given filtrated precursor solution exhibited an inherent viscosity (η_{inh}) of 0.66 dL/g (0.5 wt % in cresol at 30°C). In the second stage, an appropriate volume of the precursor solution was slowly poured onto a clean glass plate, followed by heating at 80–90°C, to evaporate most of the solvent, and then curing at 300°C under argon atmosphere for 1.5 h. Finally, a light yellow film of about 15 μm thickness was obtained.

Hydrolysis in Water at High Temperature

The experiments of high-temperature hydrolysis of model compound **I** and As–PPT film in distilled water were carried out in a 100-mL autoclave with temperature autocontrol. At first, about 100 mg of sample and 30 mL of distilled water were added into the reactor. After the oxygen in the

autoclave was cleared out by vacuuming and alternately filling with nitrogen, the reactants were heated up to 250°C, at the rate of about 5°C/min, and then maintained for a predetermined time.

The hydrolysis of model compound **I** lasted continuously for 20 h. The obtained solid residue and the hydrolysates in aqueous solution were identified by FTIR and MS. On the other hand, the hydrolysis reaction of As–PPT film was carried out for 100 h in all, with periodic sampling every 20 h to monitor the gradual change in the hydrolysis process. The samples, recovered every time from the aqueous solution and solid residue, were characterized by UV-Vis and IR spectra, respectively. Additionally, MS determinations of hydrolysates were performed with the final aqueous solutions of the two reaction systems to identify their major hydrolysates.

Spectroscopy and Chromatography Identification

A Nicolet-560 FTIR spectrophotometer (Nicolet Instruments, Madison, WI) and a Hewlett–Packard 8452A UV-Vis spectrophotometer (Hewlett–Packard, Palo Alto, CA) with diode array were employed for the spectra determinations. Mass spectra analysis was carried out on an MS-50 mass spectrometer with an inlet of solid sample. IR determinations were done immediately with the original As–PPT film as well as with the film that underwent hydrolysis in a shorter time but was not yet broken off. In the case of the film that had been chipped, the solid residues sampled at different reaction times were washed with water and dried in vacuum, and then pelletized together with KBr for recording their IR spectra. A similar procedure was applied to the original sample of model compound **I**. UV determinations were made directly toward all the samplings of aqueous solutions, whereas the samplings from the
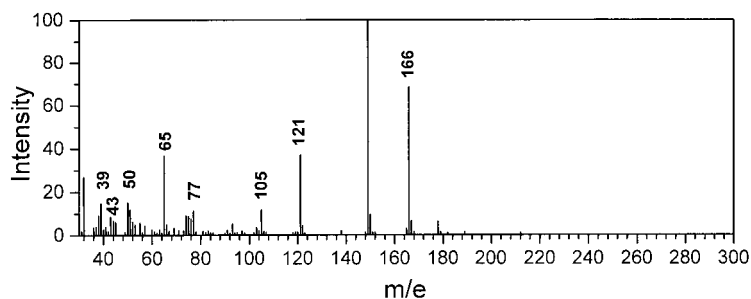

Figure 2 MS spectrum of the hydrolysates of model compound **I** with an inlet of solid sample.
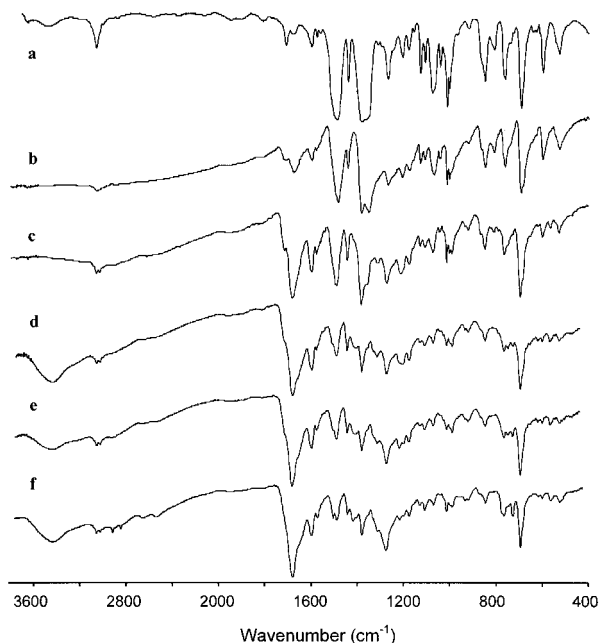
Figure 3 FTIR spectra of the hydrolyzed residue of As–PPT film varies with time: (a) untreated film; residue after (b) 20 h, (c) 40 h, (d) 60 h, (e) 80 h, and (f) 100 h. (a) and (b) were determined with the film, whereas (c)–(f) were determined with the KBr-supported pellets.

film and residue were recorded in the solutions of concentrated sulfuric acid. The hydrolysates in the final hydrolyzed solutions of both model compound **I** and As–PPT film were extracted with ethyl acetate at about pH 1.0 (acidified by using dilute hydrochloric acid). After clearing the solvent off by distilling and vacuum drying, white solids of extractive were obtained for MS and IR determinations.

Quantum Chemical Calculations

A full geometry optimization for the molecule of model compound **II** was carried out by using a semiempirical method of quantum chemistry, PM3, followed by an *ab initio* calculation at the RHF/4-31G level, to theoretically predict the electronic structure and bonding property of the molecule. All the calculations were performed by using the Mulliken 2.0 program provided by the IBM Company (Armonk, NY).

RESULTS AND DISCUSSION

Behaviors of Model Compound I

Model compound **I** presented high stability in distilled water below 100°C because no weight loss
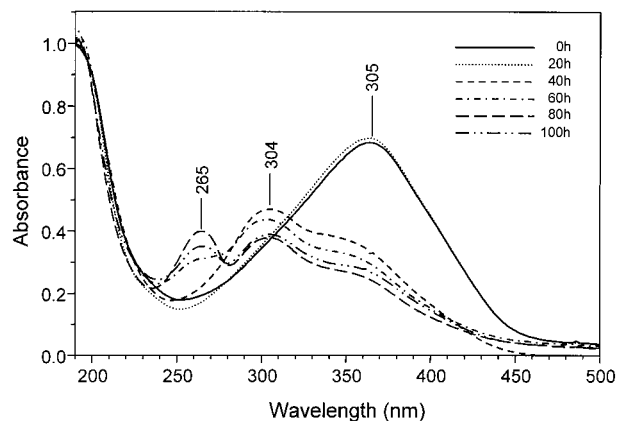

Figure 4 UV-Vis spectrum of the solid residue of As–PPT film varies with time; all the determinations were done with a residue solution in concentrated sulfuric acid.

or IR spectrogram changes could be observed with a sample after treatment in boiling water for 200 h. However, it was found that the hydrolysis was accelerated with increasing temperature (e.g., a sample lost its weight by about 10%), and the pH value of the aqueous phase decreased from 7 to 5 after hydrolysis in water at 250°C/3.97 MPa for 20 h. Meanwhile, no perceptible change was found with the IR spectrum of the solid residue.

The IR spectra of the solid residue and the extractive of hydrolysates are shown by curves (a) and (b), respectively, in Figure 1. It can be seen that the characteristic bands of the 1,2,4-triazine ring[16] at 1490, 1445, 1385–1390, and 1016 cm^{-1} disappear in curve (a) entirely, whereas two new absorptions
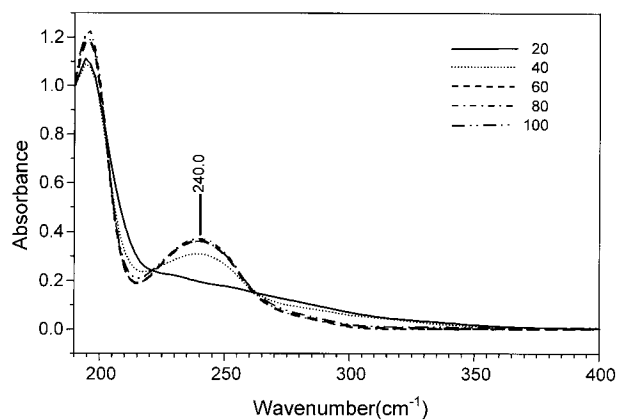

Figure 5 UV-Vis spectrum of the hydrolysis solution of As–PPT film varies with time; all the determinations were done directly with the aqueous solution.
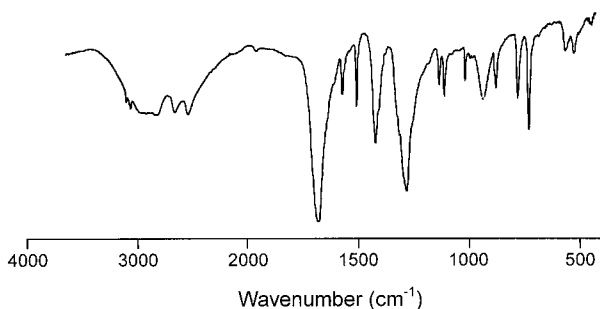
Figure 6 FTIR spectrum of the hydrolysates extracted from the final hydrolyzed solution of As–PPT film, determined with a KBr-supported pellet.

corresponding to aromatic acids show up in curve (b): a broad band ranging from 2500 to 3000 cm^{-1} and another sharp band at 1688 cm^{-1}. The agreement of curve (b) with the standard spectrum of terephthalic acid indicates that the latter is the basis of the aqueous phase. This is further confirmed by the mass spectrum of the extractives shown in Figure 2, where the molecular ion peak arises at $m/e = 166$. Hence, the major hydrolysate is terephthalic acid [$C_6H_4(COOH)_2$, $M_w = 166$].

Behaviors of As–PPT Film

During the hydrolysis of As–PPT film in distilled water at 250°C/3.97 MPa, its color gradually varied from light yellow to black, while the film became increasingly brittle. Finally, it shattered into small pieces completely after 40 h, which indicates that the water resistance of As–PPT is remarkably poorer at 250°C than it is at 200°C.[14]

The stack IR spectra diagram of the solid residue is given in Figure 3 to illustrate the hydrolysis progress. The diagram shows that all the absorption bands characteristic of the 1,2,4-tri-

azine ring,[16] at 1491, 1445, 1385–1390, and 1016 cm^{-1}, grew increasingly weaker, whereas the absorption bands characteristic of aromatic acid, at 2500–3000 and 1684 cm^{-1}, gradually grew stronger. This indicates the gradual breaking down of the heterocyclic ring in the polymer.

Figure 4 presents the stack of UV-Vis spectra for the solid residues, where the UV absorption band at 364 nm, characteristic of the 1,2,4-triazine ring,[17] decreases with a slight blue shift. This indicates the decrease of the content of the triazine rings during the reaction. A decrease in absorbance by 50% after 40 h implies that about half of the 1,2,4-triazine rings in the polymer have broken down. Meanwhile, the characteristic absorption of the benzene ring at 304 and 264 nm emerges and increases.

The pH value of the aqueous solution decreased from 7 to 5 with time, similarly to the case of model compound **I**. In its UV-Vis stack diagram given by Figure 5, the absorbance at 240 nm increases incrementally, which indicates the formation of some aromatic compounds.

The IR spectrum of the extracted hydrolysates from the finally aqueous solution, shown in Figure 6, is quite analogous to that of model compound **I** [see curve (b) in Fig. 1]. Two intensive absorption bands, at 2500–3000 and at 1688 cm^{-1}, confirm the existence of aromatic acids.

Furthermore, the mass spectrum of the hydrolysates, shown in Figure 7, looks very much like a copy of Figure 2. In the range of $m/e \geq 50$, all the peaks are almost reproduced with a relative abundance approximately equal. This means that As–PPT and its model compound give the same major hydrolysate, terephthalic acid, and thus there should be a similar mechanism to dominate the hydrolysis reactions.
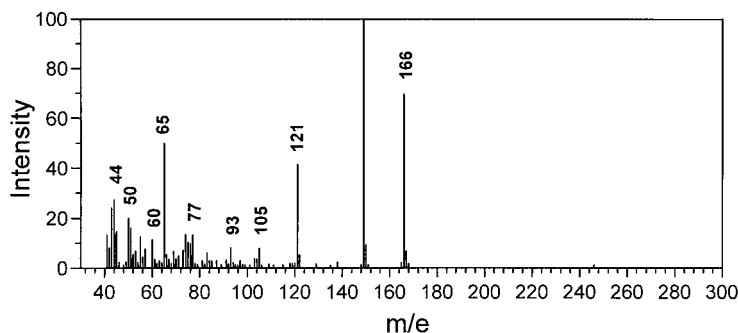

Figure 7 MS spectrum of the extractives from the hydrolyzed solution of As–PPT film, determined with the solid sample from which the solvent was removed.
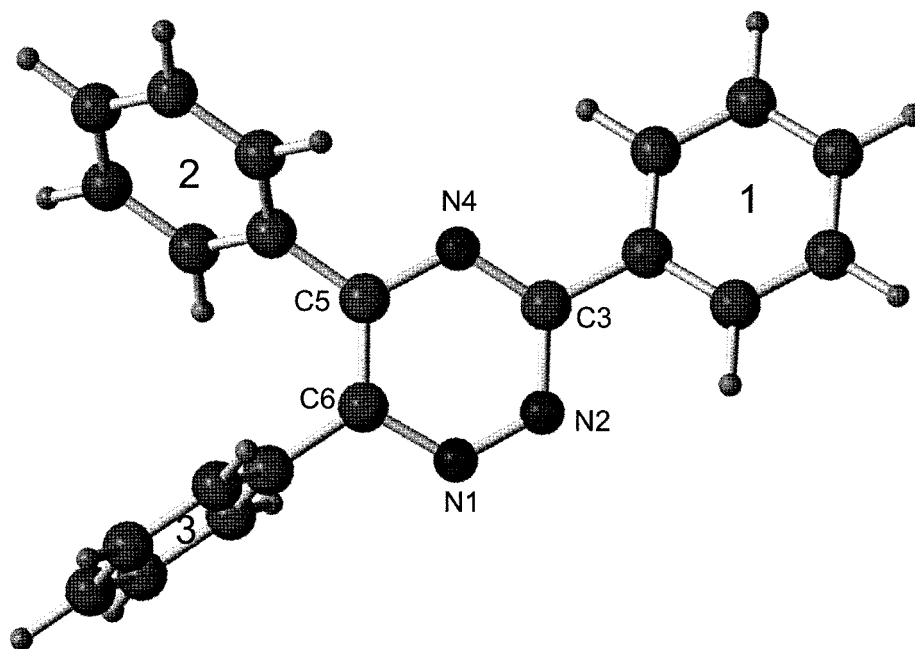
Figure 8 Equilibrium geometry of the molecule of model compound **II**, theoretically predicted by semiempirical method of quantum chemistry, PM3.

Theoretical Computations

Prior to calculation, we computed the electronic structures of the oligomers of As–PPT at the RHF/STO-3G level with repeated units from 1 to 4. The computational results showed that the chain length of oligomers exerts only a slight effect on the electronic distribution on the atoms and bonds of the heterocyclic ring. This suggested that model compound **II** can serve as the simplest entity to reasonably simulate the local electronic structure on the heterocyclic ring of As–PPT.

Full geometry optimization calculation by using the PM3 method showed that the geometry of model compound **II** is nonplanar, as shown in Figure 8, where the benzene rings 1, 2, and 3 twist against the heterocyclic plane at an angle of 23.0, 79.6, and 52.8°, respectively, as a consequence of the spatial obstruction.

Based on the theoretically predicted equilibrium geometry, an *ab initio* calculation was performed and followed by Mulliken electronic population analysis to give the net charge distribution on each atom and the interatomic overlap of electrons between each pair of bonding atoms. The results are illustrated in Figures 9 and 10, where the interatomic overlap populations that correspond to all C—H bonds, ranging from 0.758

to 0.767, are omitted because the data are of less significance to the discussion of the reaction mechanism.

The chemical bond strength and reactivity of a molecule strongly depend on its electronic structure.[18–20] It is well known that Mulliken population analysis provides brief and intuitional infor-
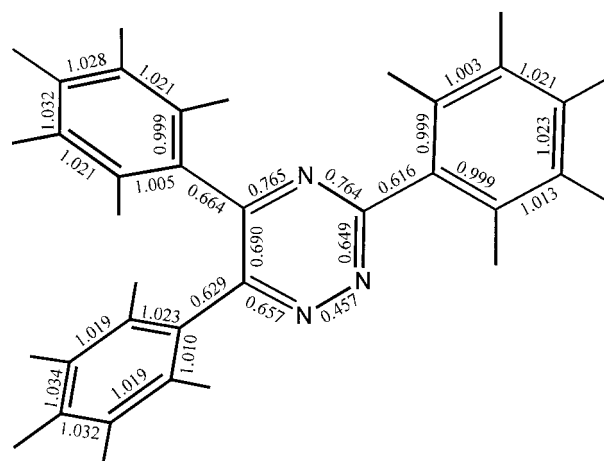

Figure 9 Mulliken interatomic overlap populations between two adjacent atoms of model compound **II**, given by *ab initio* calculation at the RHF/4-31G level; the overlap populations on all C—H bonds are omitted.
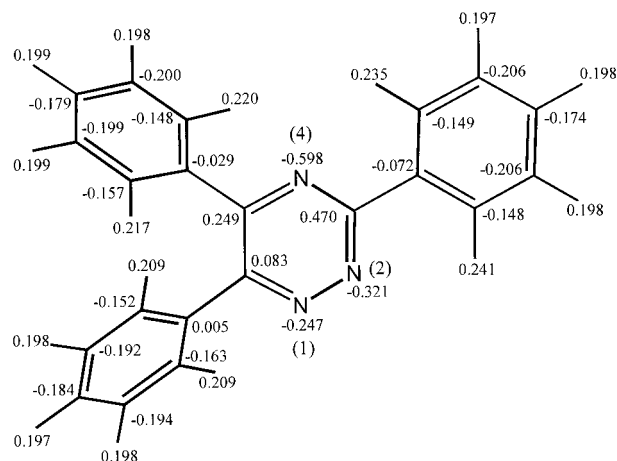
Figure 10 Net atomic charge distribution of model compound **II**, given by *ab initio* calculation at the RHF/4-31G level.

mation about the molecular electronic structure. The magnitude of interatomic overlap population is evidence of the relative strength of the corresponding chemical bond. From Figure 9 it can be seen that the 1,2,4-triazine ring is less stable than the benzene rings because the interatomic overlap in the former is remarkably less than that in the latter. Thus, the high-temperature hydrolysis degradation of As–PPT should first take place on the heterocyclic rings.

The hydrolysis reactions of aromatic heterocyclic polymers are generally catalyzed by acid[3,10] and it is the initiating step that the atom with the most negative charge and the least spatial obstruction is attacked by a hydrated proton. As shown in Figure 10, significantly more negative charges are concentrated on the three nitrogen atoms. In addition, there is almost no steric hindrance for a hydrated proton to approach the nitrogen atoms. Thus, each of the atoms N1, N2, or N4 has the tendency to be protonated. Under this consideration, three protonated intermediates, related to N1, N2, and N4, respectively, of model compound **II** were proposed. The equilibrium geometries and the interatomic overlap populations

of electrons of these intermediates were obtained using the same method as that for the original model compound. A comparison of the interatomic overlap populations on the heterocyclic ring between model compound **II** and its protonated intermediates is presented in Table I. From the table it can be seen that the interatomic overlap of electrons on the C—N bond connected to the protonated nitrogen decrease considerably and become the weakest. As a result, this bond would break down first in the high-temperature hydrolysis process. This is a case unlike that of the thermal degradation of As–PPT, where primarily the weakest N—N ruptures.[21,22]

HYDROLYSIS MECHANISM

On the basis of the experimental results and the preceding theoretical considerations, a reaction mechanism, as shown in Scheme 5, is suggested to explain the formation of the major hydrolysate.

It is considered that the hydrolysis of As–PPT in high-temperature water is initiated by the attack of a hydrated proton toward a nitrogen atom on the heterocyclic rings of the polymer. The protonation lowers the stability of the heterocyclic rings, in particular, by sharply weakening one or more carbon–nitrogen bonds on the rings. Then, the gradual scission of the C—N bonds leads to the formation of terephthalonitrile, which is easy to hydrolyze and produces terephthalic acid.

The increase of temperature speeds up the hydrolysis in three aspects:

1. It heightens the dissociation degree of the water and then the concentration of the hydrated protons. (The pH value may reach 5.53 in distilled water of 250°C/3.97 MPa.)
2. It intensifies the molecular vibration of the polymer and thus significantly lowers the strength of the C—N bonds.
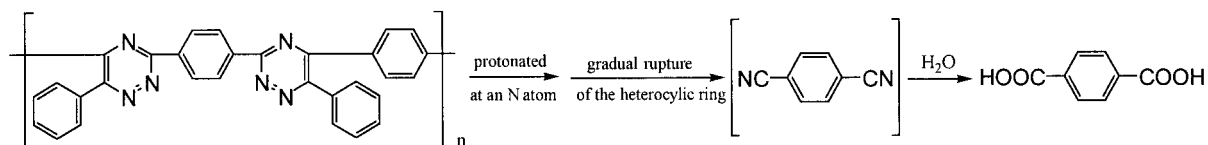
Scheme 5

Table I Interatomic Overlap Populations of Electrons on the Heterocyclic Ring Model Compound II and Its Protonated Intermediates Given by *ab Initio* Calculation at RHF/4-31G Level

	N1–N2	N2–C3	C3–N4	N4–C5	C5–C6	N1–C6
Before protonation	0.457	0.649	0.764	0.765	0.690	0.657
Protonated at N1	0.226	0.773	0.669	0.765	0.622	0.220
Protonated at N2	0.262	0.109	0.873	0.766	0.571	0.888
Protonated at N4	0.434	0.706	0.182	0.262	0.782	0.604

3. It increases the rate constants of all the reaction steps.

Taken together, these outcomes can reasonably explain why the hydrolysis resistance of As–PPT degrades at a high temperature (about 250°C). Further investigations are under way.

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