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# Thermal degradation kinetics of poly(aryl ether sulfone 1,3,5-triazine)s containing phthalazinone moieties

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ABSTRACT

Thermal degradation of phthalazinone-based poly(aryl ether sulfone 1,3,5-triazine) copolymers (PPESTs) has been investigated under nitrogen flow in dynamic heating conditions. Model-free kinetic approaches were applied to data for decomposition processes of PPESTs with different molecular structure. The activation energy was calculated as a function of the degradation extent by using Kissinger–Akahira–Sunose and Vyazovkin method. The effect of polymer composition and structure on the characteristic temperatures and kinetic parameters of thermal degradation was also investigated. The replacement of sulfone by 1,3,5-triazine in polymer main chain significantly increases initial decomposition temperature and $E_a$, and its stabilizing effect may be explained by the existence of two-stage decomposition process that suppresses unzipping of the copolymers. This assumption is supported by the experimental fact that the complete replacement of sulfone by 1,3,5-triazine increases the initial decomposition temperature by 31 °C and $E_a$ by at least 57 kJ/mol according to Vyazovkin method.

## 1. Introduction

Most frequently, heterocyclic-containing poly(aryl ether)s such as poly(aryl ether phenylquinoxaline)s [1], poly(aryl ether benzimidazole)s [2], poly(aryl ether imide)s [3], poly(aryl ether 1,3,5-triazine)s (PAETs) [4], etc, have assumed intensive attention due to their outstanding comprehensive properties. Among of them, PAETs are normally thought of as one of the most thermally stable polymer materials potentially utilized in automotive, aerospace, microelectronic and military [5,6]. The incorporation of 1,3,5-triazine units into the polymer backbone remarkably enhances the chain rigidity and aromaticity, and the polarizable *p*-electrons always lead to strong intermolecular interactions. Therefore, such materials are always featured by certain fascinating advantages over those without heterocyclic units, including good chemical resistance, high glass transition temperatures ($T_g$s), excellent thermal resistance, high tensile strength and module at elevated temperatures.

To date, there are many reports in the literature of thermally stable high-molecular-weight PAETs synthesized by the nucleophilic displacement polycondensation between commercially available aromatic diols and 1,3,5-triazine activated dihalides [4–12]. In general, the obtained PAETs are a class of amorphous polymers with $T_g$s exceeding 240 °C as well as acceptable mechanical properties and good chemic resistance. However, it is rather difficult to process this type of thermally stable polymers, since the strong charge transfer interactions among the aromatic rings and heterocyclic rings always make the synthesized PAETs insoluble in most organic solvents [4]. Therefore, a number of research efforts have devoted to the structural modification of main chain of PAETs for the purpose of improving their organic solubility, thus simplifying synthesis and broadening their applications as adhesives, coatings or membranes [5–12]. Among of them, several papers have reported the synthesis of organosoluble sulfone-containing or cyano-containing PAET copolymers [8–10]. A notable feature of these copolymers is that they exhibit good solubility in *N*-methyl pyrrolidone, *N*,*N*-dimethylacetamide and trifluoroacetic acid. Among them, sulfonated PAET copolymers containing sulfone segments in the main chain show higher proton conductivity than Nafion 117 whose chemical formula is $[CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2CF_2SO_3H]_n$ [8]. Such copolymers may be promising candidates of proton exchange membranes for high temperature applications. Very recently we have also disclosed the development of several new series of organosoluble thermoplastic PAET copolymers [10,11]. In particular, we have made great progress in study on the structural modification of main chain of PAETs by incorporating kink phthalazinone and sulfone moieties [10]. Unlike the conventional PAETs, this novel series of phthalazinone-based poly(aryl ether sulfone

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1,3,5-triazine)s (PPESTs) demonstrate excellent solubility in common polar organic solvents, and can be easily cast into transparent flexible films through either simple solution casting or melt compressing techniques. Additionally, PPESTs also exhibit good mechanical properties and thermal stability together with considerably high $T_g$s and decomposition temperatures. These promising properties make the PPEST copolymers good candidates for high performance polymeric materials.

Although a number of published reports have described the excellent thermal and oxidative stability of 1,3,5-triazine polymers [13–16], no systematic study has been carried out to evaluate their thermal degradation, thus up to now the degradation kinetic remains fully unclear. In addition, since most 1,3,5-triazine polymers must be processed at high temperatures, often exceeding 300 °C, they may be sensitive to degradation and modification not only in the manufacturing, compounding and processing stage, but also in service or during repair. Thermal analysis methods have proved useful not only in defining suitable processing conditions for the polymers as well as useful service guidelines for their application, but also in drawing information on properties–chain structure relationships [17,18]. Therefore, the determination of kinetic parameters associating with thermal degradations of the 1,3,5-triazine polymers appears to be a research topic of great interest.

Representatives of the 1,3,5-triazine polymers chosen for study was the phthalazinone-based poly(aryl ether sulfone 1,3,5-triazine)s (PPESTs) which is reported to be of many attracting properties [10]. In this paper, thermal stability and degradation kinetics of the PPEST copolymers with different molecular structure have been studied by the combination of thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG). The purpose is to evaluate the influence of polymer composition and structure on the characteristic temperatures and kinetic parameters of thermal degradation, and hence to find some useful correlations between the physico-chemical properties and the structure, which could be used in designing new high performance polymers.

## 2. Experimential

### 2.1. Materials

Phthalazinone-based poly(aryl ether sulfone 1,3,5-triazine)s (PPESTs) were prepared by the solution polycondensation of 4-(4-hydroxylphenyl)(2*H*)-phthalazin-1-one (HPPZ) with 2,4-bis(4-fluorophenyl)-6-phenyl-1,3,5-triazine (BFPT) and 4,4′-dichlorodiphenyl sulfone (DCS) following the procedures previously reported [10]. The numbers of the sample name indicate the molar fractions of DCS and BFPT. For example, the resultant copolymer in the copolymerization starting from 40 mol% of DCS and 60 mol% of BFPT could be designated as PPEST4060. All polymer samples were used in the form of powders and dried at 120 °C under vacuum for 24 h before test.

### 2.2. Viscosity and number-average molecular weight measurements

Inherent viscosity ($\eta_{inh}$) of sample was measured by Ubbelohde capillary viscometer at a concentration of 0.5 g/dL in *N*-methylpyrrolidone (NMP) or concentrated sulfuric acid at 25 °C according to their solubility. Number-average molecular weight ($M_n$) of the sample was measured in chloroform by Gel permeation chromatography (GPC). GPC analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4 × 500 Å) arranged in series with chloroform as a solvent and a UV detector at 254 nm. The obtained values were calibrated versus polystyrene standard.

### 2.3. DSC measurements

Glass transition temperature ($T_g$) of the sample was determined with a Mettler DSC822 differential scanning calorimetry (DSC). Both heat flow and temperature calibrations were performed following the procedures suggested by the supplier and reported in the operating instructions of equipment. The first DSC scan was operated in flowing nitrogen at a heating rate of 10 °C/min from 50 to 400 °C. The second DSC run was also performed under nitrogen after quenching at the end of the first scan (10 °C/min). $T_g$ value of the sample was taken at the inflection point at the second scan.

### 2.4. TG and DTG measurements

Thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) of the polymers were conducted on a Mettler TG/SDTA851 thermogravimetric analysis instrument. The measurements were performed in the scanning mode of TG and DTG from 100 °C up to 800 °C under nitrogen flow (50 mL/min) or in a static air atmosphere. Each sample mass was around 8 mg, and heated in alumina platinum crucibles at five selected heating rates ($\beta$: 5; 10; 15; 20 and 30 °C/min), respectively.

## 3. Results and discussion

### 3.1. Physico-chemical properties of PPESTs

Shown in Fig. 1 is the chemical structure of PPESTs which possess both phthalazinone and 1,3,5-triazine moieties in the main chain. The PPEST copolymers with different compositions were synthesized in 92–98% yields via the simple solution polycondensation of HPPZ with various ratios of DCS and BFPT. Inherent viscosity ($\eta_{inh}$) and number-average molecular weight ($M_n$) of the polymer samples were preliminarily determined, and the obtained values are specified in Table 1. The $\eta_{inh}$ values of the copolymers and PPEST1000 are all higher than 0.60 dL/g, and their $M_n$ values measured in chloroform by GPC, range from 16,700 to 25,400, indicative of the successful preparation of high-molecular-weight polymers. In cases of PPEST0100 and PPEST2080, the $\eta_{inh}$ values are 0.57 and 0.80 dL/g, respectively, while the $M_n$ values were not detected because of their insolubility in the chloroform or tetrahydrofuran eluents.

### 3.2. Thermal properties of PPESTs

The glass transition temperature ($T_g$) was determined for each polymer by DSC scans (Table 1), and the $T_g$ values are all exceeding 269 °C (taking as the midpoint of the change in slope of the baseline in DSC curve) and far higher than those of the known PAETs [7,8], suggesting their better heat resistance. The high $T_g$ values of the investigated polymers could be attributable to their rigid molecular structure, due to the incorporation of heterocyclic phthalazinone moieties into polymer main chain. For all these copolymers and homopolymers, it is not possible to detect any melting temperature because of their amorphous structure previously disclosed [6,10]. As can be clearly seen from the DSC scans, only single distinct $T_g$ is detected for each copolymer and the $T_g$ value increases gradually with the increasing sulfone content, which approximately fits the rule of random copolymers. The increase of $T_g$ can be easily explained considering the following two factors: an enhancement in intermolecular chain interaction that hampers the movement of the polymer chains due to the introduction of the polar sulfone groups into the backbone; a decrease in free volume of the polymers

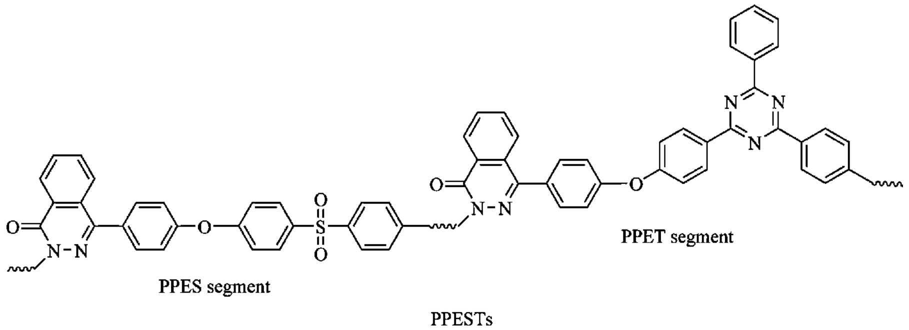

**Fig. 1.** Chemical structure of PPESTs.

**Table 1**
Physico-chemical and thermal properties of PPESTs.

| Polymers | $\eta_{\text{inh}}$[a](dL/g) | $M_n$[b](g/mol) | PD[b] | $T_g$[c](°C) | $T_g$[d](°C) | $T_{N2,5\%}$[e](°C) | $T_{\text{air},5\%}$[f](°C) | $T_{\max}$[g](°C) | $C_y$[h](%) |
|---|---|---|---|---|---|---|---|---|---|
| PPEST0100 | 0.57 | – | – | 269 | – | 536 | 529 | 536,617 | 67 |
| PPEST2080 | 0.80 | – | – | 271 | 275 | 519 | 524 | 529,620 | 63 |
| PPEST4060 | 0.62 | 16,700 | 3.2 | 279 | 282 | 508 | 517 | 526,619 | 60 |
| PPEST5050 | 0.76 | 18,900 | 3.5 | 283 | 285 | 515 | 512 | 526,617 | 56 |
| PPEST6040 | 1.18 | 22,500 | 2.5 | 289 | 289 | 513 | 511 | 527 | 55 |
| PPEST8020 | 0.91 | 19,800 | 3.4 | 300 | 297 | 503 | 509 | 529 | 53 |
| PPEST1000 | 1.21 | 25,400 | 3.1 | 305 | – | 505 | – | 527 | 53 |

[a] Determined at a concentration of 0.5 g/dL in NMP at 25 °C.
[b] Determined number-average molecular weight ($M_n$) and polydispersity (PD) by GPC calibrated with polystyrene standards.
[c] Tested by DSC at a heating rate of 10 °C/min in nitrogen.
[d] Calculated from Fox equation (1)
[e] Temperature for 5% weight loss in nitrogen, heating rate of 20 °C/min.
[f] Temperature for 5% weight loss in air, heating rate of 20 °C/min.
[g] Temperature for the maximum in nitrogen, heating rate of 20 °C/min.
[h] Calculated as the percentage of solid residue after heating from 100 to 800 °C in nitrogen.

that is attributable to the decreasing content of bulky 1,3,5-triazine units. In addition, the $T_g$s of random copolymers could be well predicted based on the feed ratio of the dihalides during the polymerization using the following Fox equation [20]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{1}$$

where $T_g$ is the glass transition temperature of the investigated copolymer, $W_1$, $W_2$ are respectively the weight fractions of BFPT and DCS relative to the total dihalides, $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of PPET ($T_{g1} = 269\,^\circ\text{C}$) [6] and PPES ($T_{g2} = 305\,^\circ\text{C}$) [19], respectively. A good agreement of the detected $T_g$ values of PPESTs with values predicted by Fox equation according to the feed ratios is also observed (Table 1). Therefore, the $T_g$s of the copolymers can be tailored by simply varying the molar 1,3,5-triazine content in the main chain.

Thermal analysis methods have paramount importance for evaluating the thermal stability of polymers, and also for drawing useful information on the relationships of thermal properties and polymer chain structure. Here TG and DTG measurements at a heating rate of 20 °C/min were applied to study thermal behavior of the copolymers in nitrogen or air atmosphere. Thermal parameters including decomposition temperatures for 5% mass-loss ($T_{N2,5\%}$, $T_{\text{air},5\%}$), temperature for the maximum weight loss rate in nitrogen ($T_{\max}$) together with the percentage of solid residue at 800 °C ($C_y$) values obtained from TG and DTG are listed in Table 1. Comparisons of TG and DTG thermograms of all copolymers in nitrogen are illustrated in Figs. 2 and 3, respectively. As described in Fig. 2 and Table 1, all investigated samples exhibit high thermal stability without significant weight loss up to temperatures of approximately 450 °C in nitrogen. The $T_{N2,5\%}$ and $T_{\text{air},5\%}$ values of the copolymers are respectively higher than 503 °C and 509 °C. Additionally, these two parameters decrease gradually with the increasing sulfone content except those of PPEST4060. In case of PPEST4060, these values are a little lower than those of PPEST5050 and PPEST6040, possibly due to the relative low $M_n$ of PPEST4060. Among the investigated copolymers, the highest $T_{N2,5\%}$ and $T_{\text{air},5\%}$ values are exhibited by PPEST2080, due to the highest 1,3,5-triazine content that endows the corresponding copolymer with the high resonance energy along the chain. The thermal stability of the copolymers is only a little inferior to PPET and the known PAETs, but it is still much higher than that of PPES and its analogues, as evidenced by thermogravimetric data (Table 1). Therefore, good thermal and oxidative stability of the 1,3,5-triazine polymers is maintained with the introduction of the sulfone moieties into the backbone.

The thermal behavior studies indicate that the copolymers are stable in air up to 450 °C and exhibit considerably high $T_{5\%}$ values (exceeding 509 °C) and $T_{10\%}$ values (exceeding 521 °C), sug-

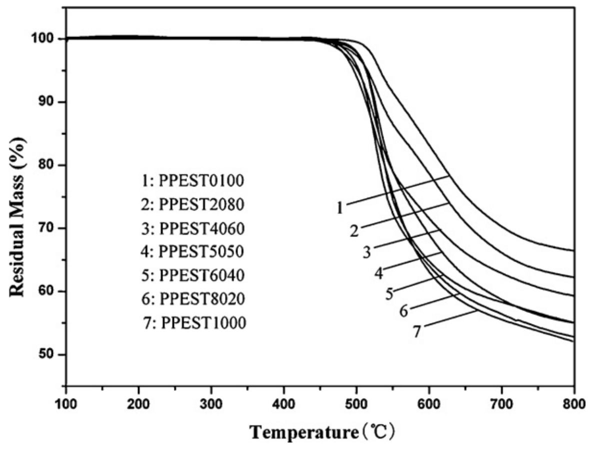

**Fig. 2.** TG thermograms of PPESTs in nitrogen at heating rate of 20 °C/min$^{-1}$.

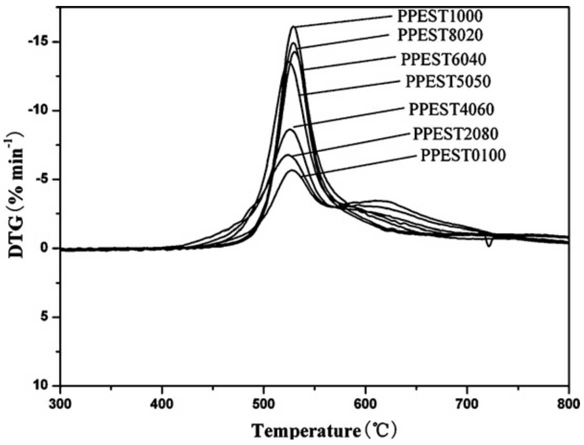

**Fig. 3.** DTG thermograms of PPESTs in nitrogen at heating rate of 20 °C/min$^{-1}$.

gesting their excellent oxidative stability. Similarly, the thermal oxidative stability of polymers is also significantly influenced by 1,3,5-triazine content in the copolymer main chain. The highest $T_{\mathrm{air,5\%}}$ value was exhibited by PPEST2080, while PPEST8020 exhibits the lowest, which indicates that the introduction of 1,3,5-triazine groups attributes their polymers better oxidative stability than sulfone groups.

The copolymers show moderately high char yields ($C_{\mathrm{y}}$) of 53–63%, when heated to 800 °C at a rate of 20 °C/min under a nitrogen atmosphere, confirming their excellent thermal stability. The $C_{\mathrm{y}}$ value increases gradually with the increase of the 1,3,5-triazine content in the copolymer chains, most probably due to such structural unit that has higher char concentration than sulfone at the elevated temperatures. The TG curves from thermal experiments in nitrogen atmosphere show that, at all heating rates used, all copolymers degrade with the formation of a residue stable up to 800 °C (Table 1). As can be noted in Fig. 3, the DTG curves of PPEST2080, PPEST4060 and PPEST5050 exhibit an initial broad and irregular decomposition stage at lower temperatures (530 °C), immediately followed by a continuous and slow degradation process up to 800 °C. We attributed the first stage to random chain scission, which is not a single process, as shown by the broad and irregular DTG peak profiles. However, the sulfone-rich copolymers including PPEST6040 and PPEST8020 demonstrate a clearly different decomposition behavior. Shown in Fig. 3 is a single slightly broad decomposition stage of each sulfone-rich copolymer, similar to that of PPES. Accordingly, the broad DTG peak of sulfone-rich copolymers indicates that the two-stage processes are almost simultaneous in these conditions. As for the investigated samples except the sulfone-rich copolymers, the degradation stage at higher temperatures might be ascribed to the following two aspects: branching and crosslinking processes which superimpose on the initial ones, as supported by the formation of residue stable up to 800 °C; the decomposition of 1,3,5-triazine-containing segments possessing high resonance energy along the chain, as supported by the two-stage degradation processes similar to that of PPET homopolymer. The existence of two-stage degradation process is probably helpful to suppress unzipping of the polymer, as evidenced by the experimental fact that the complete substitution of sulfone by 1,3,5-triazine in the main chain increases the initial decomposition temperatures by more than 30 °C. Obviously, as illustrated in Fig. 2 the 1,3,5-triazine-rich copolymers degrade more slowly than the sulfone-rich copolymers, which also provides useful evidence for identifying the suppression of unzipping in the degradation. Since unzipping is suppressed, degradation occurs through random scission of PPES segments that produces only a small amount of low molecular weight species capable of vaporizing. As a result, the TGA experiments conducted of 1,3,5-triazine-rich copolymers show a noticeable delay in the mass loss compared to those of sulfone-rich copolymers performed in same conditions.

### *3.3. Kinetic study of PPESTs*

To investigate kinetic parameters, thermal degradation processes of PPEST copolymers were investigated in a flowing nitrogen atmosphere under dynamic heating conditions by using TG and DTG measurements. For comparison, the degradation processes of PPET and PPES homopolymers were also performed under the same conditions, and the results were used as references to compare with those of the PPEST copolymers investigated. The TG curves of copolymers at all scanning rates are recorded, and the percentage of undegraded polymer $(1-\alpha)\%$ could be plotted as a function of temperature, where conversion $\alpha=(W_0-W)/(W_0-W_\infty)$, $W_0$ refers to the initial weight of the sample (mg), $W$ refers to sample weight (mg) at any temperature $T$, and $W_\infty$ refers to final sample weight (mg). For all copolymers investigated, initial decomposition temperatures and temperatures of the DTG peaks associated with the first degradation stage are mainly dependent on the heating rates ($\beta$). Obviously, by increasing the heating rates TG and DTG curves move towards higher temperatures, and the weight loss percentage for the first DTG peak of the comprehensive weight loss increases significantly. At a selected heating rate, the degradation of the sulfone-rich copolymers, which is qualitatively similar to that of PPES analogues, show lower DTG peak temperatures and far higher associated mass losses than those of 1,3,5-triazine-rich polymers. For instance, the DTG peak temperature of PPEST8020 at a heating rate of 20 °C/min is recorded to be 529 °C which is a little lower than that of PPEST2080 at the same heating rate. The associated weight loss of PPEST8020 is 18% which is far higher than that of PPEST2080 (6%). The quite sharp DTG peak observed at high heating rates indicates that, in these conditions the two-stage processes are almost simultaneous and that the rate of branching and crosslinking are comparable with the scission rate, as also supported by the high $C_{\mathrm{y}}$ values. By contrast, at a low heating rate the scission process is much quicker than branching and crosslinking processes, and the complete or around complete degradation of polymers is observed. This kind of behavior shown in inert atmosphere is in good agreement with some literatures on polymers having structure similar to that of our copolymers [17,18].

The data obtained from the non-isothermal tests such as decomposition temperature and extent of conversion were collected for kinetic analysis of the decomposition processes. Integral isoconversional methods, such as Kissinger–Akahira–Sunose (KAS) [21,22], are suited to analysis of TGA curves since they do not require the experimental data to be differentiated beforehand. In this paper, KAS method was chosen since it was shown to be correct for a wide interval of activation energies.

For decomposition, the rate combined with the Arrhenius approach of the temperature function of reaction rate constant can be expressed using the following equation:

$$g(\alpha)=\int\frac{1}{f(a)}da=\frac{k_0}{\beta}\int\exp\left(\frac{-E}{RT}\right)dT \qquad (2)$$

where $\alpha$ is the extent of polymer conversion (%), $T$ is the temperature (K), $R$ is the gas constant, $\beta$ is the heating rate (K/min$^{-1}$), $E_{\mathrm{a}}$ is the activation energy (J mol$^{-1}$), $f(\alpha)$ is a function that represents the reaction model. By using the Coats–Redfern approximation and considering that $2E/RT$ is much lower than 1 [23], and substituting the temperature integral, rearranging and logarithming, gives the

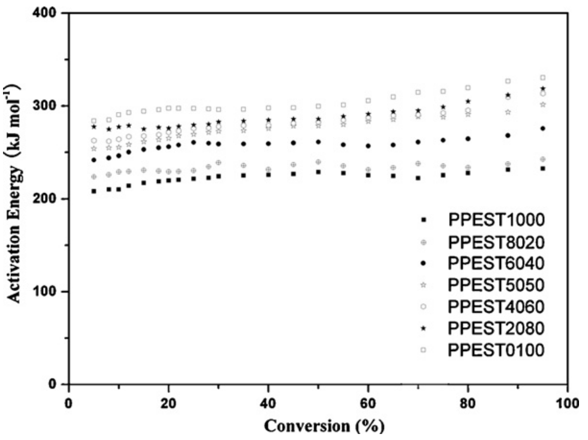

**Fig. 4.** Dependence of activation energy on conversion for PPESTs according to KAS method.

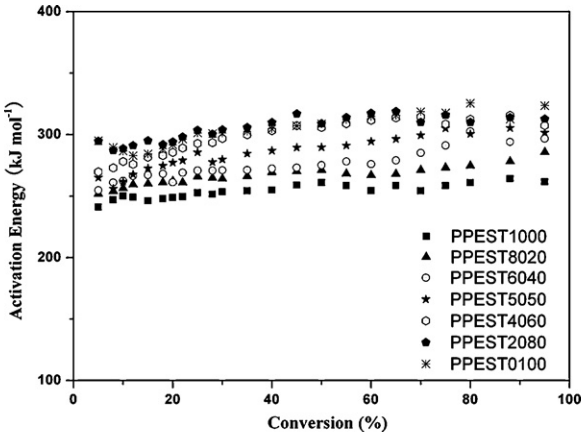

**Fig. 5.** Dependence of activation energy on conversion for PPESTs according to Vyazovkin method.

Kissinger–Akahira–Sunose method as presented bellow:

$$\ln\frac{\beta}{T_a^2}=\ln\left[\frac{Rk_0}{E_a g(a)}\right]-\frac{E_a}{R}\frac{1}{T_a} \qquad (3)$$

where $k_0$ is the pre-exponential factor ($s^{-1}$).

The dependence of $\ln(\beta/T_\alpha^2)$ on $1/T_\alpha$, calculated for the same $\alpha$ values at the different heating rates $\beta$ can be used to calculate the activation energy. In this case, the range $\alpha = 0.05–0.95$ was chosen to evaluate the $E_a$ values of PPESTs. The dependency of activation energy on conversion is illustrated in Fig. 4, and the determined $E_a$ values for the thermal degradation of PPESP6040 as well as correlation coefficients at different conversions are listed in Table 2.

Since the macroscopic kinetics are complex as they always include information about simultaneously occurring multiply steps by their nature, one should investigate the complexity of decomposition process by determining the dependence of activation energy ($E_a$) on $\alpha$ prior to any kinetic analysis [24]. Meanwhile, due to this complexity, decomposition process of most polymers cannot be described simply by Eq. (2) in the whole temperature region. As suggested in many references [24–29], this $E_a - \alpha$ dependence is considered to be the highly reliable criterion of the process complexity and isoconversational methods are considered as the most reliable ones for the calculation of $E_a$ and $E_a - \alpha$ dependence of thermally activated decompositions. Results of the ICTAC Kinetic Project also showed that isoconversational methods are among the few methods that are up to the disentanglement of macroscopic kinetics. The popular representatives of isoconversationl methods include the methods of Kissinger–Akahira–Sunose [21,22], Friedman [30] and Ozawa [31], while the full potential of the isoconversion methods has been appreciated as Vyazovkin [24–29]. It is well-known that Vyazovkin method brought analysis of the $E_a$ - $\alpha$ dependence to the forefront and it is very useful for exploring the mechanisms of processes and for predicting kinetics. Also, this isoconversion method allows complex (i.e., multi-step) processes to be detected via a variation of $E_a$ with $\alpha$ [24,25]. Conversely, independence of $E_a$ on $\alpha$ is a sign of a single-step process. Therefore, Vyazovkin model-free method was selected to determine the $E_a$ values and understand the variation of activation energy $E_a$ with $\alpha$ in this paper, by employing integration method that makes use of the following function:

$$\Phi(E_\alpha)=\sum_{i=1}^{n}\sum_{j\neq 1}^{n}\frac{I(E_{a,\alpha},T_{a,i})\beta_j}{(E_{a,\alpha},T_{a,i})\beta_i} \qquad (4)$$

where $\Phi$ is a function representing the activation energy, activation energy is determined at any particular value of $\alpha$ by finding $E_a$, which minimizes the function, $I(E_{a,\alpha}, T_{\alpha,i})$ and $I(E_{a,\alpha}, T_{\alpha,j})$ are the integral formula of $\exp(-E_a/RT)$ that result from heating rate $\beta_i$ and $\beta_j$, respectively.

Dependency of activation energy on conversion for nonisothermal decomposition of all copolymers is presented through Fig. 5. The detected $E_a$ values of a typical PPEST6040 are listed as examples in Table 2. It is concluded that the activation energy is practically independent on $\alpha$ in a conversion range from $0.05 \le \alpha \le 0.95$ for PPEST1000, PPEST8020 and PPEST6040. This means that from the kinetic point of view the investigated process of sulfone-rich polymers is simple (one-step process) and can be described by unique kinetic triplet. This is in a good agreement with the investigation reported in Section 3.2 and some literatures who have established that poly(aryl ether sulfone)s and their analogues decompose in a single-stage by random scission of the chain links [18,19]. However, for 1,3,5-triazine-rich copolymers it is found that initially $E_\alpha$ is a slowly increasing function of $\alpha$ and then becomes a very strong function of $\alpha$ towards the end of the decomposition phenomenon. For example, the maximum increase of activation energy of 41 kJ/mol was obtained for PPEST2080 from the conversion 12% to 95%. This may be explained by the fact that the thermal decomposition becomes tougher relative to the initial process. As proposed by Vyazovkin [24–29], it can be assumed that the thermal degradation of 1,3,5-triazine-rich copolymers is most probably

**Table 2**
Kinetic parameters for PPEST6040 obtained by KAS method and relative errors with Vyazovkin method chosen as standards.

| $\alpha$ | 5 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|
| $E_a$[a] | 241.6 | 246.4 | 257.3 | 259.2 | 259.8 | 261.2 | 265.6 | 264.5 | 266.7 | 276.0 |
| $r$[b] | 0.990 | 0.985 | 0.996 | 0.991 | 0.983 | 0.991 | 0.985 | 0.993 | 0.978 | 0.989 |
| $E_a$[c] | 254.7 | 262.3 | 261.1 | 271.0 | 272.4 | 275.2 | 275.9 | 285.2 | 302.6 | 296.7 |
| RE[d](%) | 5.14 | 6.06 | 1.47 | 4.35 | 5.66 | 6.11 | 3.73 | 7.25 | 11.86 | 6.98 |

[a] $E_a$ (kJ/mol): activation energy for PPEST6040 determined by using KAS method.

[b] $r$: correlation coefficients of linearships of versus $1/T_\alpha$.

[c] $E_a$ (KJ/mol): activation energy for PPEST6040 determined by using Vyazovkin method.

[d] RE: relative errors (%) of $E_a$ obtained by KAS method with Vyazovkin method chosen as standards.

a multiple-step process from the shapes of our curves that describe dependence of $E_\alpha$ on $\alpha$ (Fig. 4).

It can be clearly observed that the 1,3,5-triazine-rich copolymers have remarkably high $E_a$ values associating with its first thermal degradation stage relative to the sulfone-rich copolymers in a conversion range from $0.05 \leq \alpha \leq 0.95$. The largest activation energy of thermal degradation of the investigated copolymers in whole range of conversion, was obtained for PPEST2080. It is recorded to be 318 kJ/mol according to KAS method and to be 327 kJ/mol according to Vyazovkin method at a conversion of 0.95, respectively. For PPEST8020, the activation energy starts increasing slightly in the beginning of degradation process and then stabilizing at about 220 kJ/mol in the rest conversion range. Table 2 shows the relative errors of $E_\alpha$ for PPEST6040 obtained by KAS method with Vyazovkin method chosen as standards computing model. The relative error for PPEST6040 associated with KAS method ranges from 1.47% to 11.86%, and the average is about 5.86% at the selected conversations.

As shown in Figs. 4 and 5 the substitution of sulfone groups with 1,3,5-triazine units in polymer chain significantly increases the activation energy, thus making the degradation process far more difficult from the kinetic viewpoint. This phenomenon can be rationalized, in our opinion, on considering that the degradation of 1,3,5-triazine-rich polymers exhibits an obviously different mechanism with the sulfone-rich copolymers as discussed above. The stabilizing effect of the 1,3,5-triazine unit may be easily explained by the existence of two-stage decomposition process that suppresses unzipping of the polymer. Generally, degradation starts at the weak linkages (i.e., sulfone group), whose concentration is very high at low extents of degradation. Therefore, the overall degradation rate is controlled by unzipping of the polymer chain. With the increasing content of 1,3,5-triazine, the concentration of the weak linkages decreases. As a result, the rate-limiting step shifts from unzipping to initiation, branching and crosslinking, which have significantly higher activation energy values. This assumption is supported by the experimental fact that the complete replacement of sulfone by 1,3,5-triazine in the main chain increases the initial decomposition temperatures by more than 30 °C and the $E_\alpha$ values at least by 57 kJ/mol according to Vyazovkin method, respectively. The determined $E_\alpha$ values of PPEST copolymers are not much lower than those of the PAET analogous, which indicates that good thermal stability is maintained with the incorporation of the sulfone groups and phthalazinone moieties into the polymer backbone. Furthermore, it is notable that the $E_a$ values of the PPESTs are far higher than that of the commercial available poly(aryl ether sulfone)s (PAESs) such as A-300® PES (AMOCO Polymers Alpharetta, $E_a$ = 178.0 kJ/mol under argon) [32], suggesting their superior thermal stability relative to the conventional PAESs. These results demonstrate an important role of the 1,3,5-triazine units in enhancing the thermal stability of the PAES polymers.

## 4. Conclusion

The high-molecular-weight poly(aryl ether sulfone 1,3,5-triazine) copolymers (PPESTs) containing phthalazinone moieties in the main chain show outstanding comprehensive properties. The $T_g$ values are determined to be in the range of 269–305 °C, and no obvious weight loss is observed below 450 °C. Thermal degradations of PPESTs investigated under nitrogen flow in dynamic heating conditions by using Vyazovkin model-free kinetic method indicate that the apparent activation energy values for first degradation stages increase with the increasing content of 1,3,5-triazine. The substitution of the sulfone group with a 1,3,5-triazine unit in polymer main chain increases the initial decomposition temperature and $E_a$ significantly, and its stabilizing effect may be explained by the existence of two-stage decomposition process. The model-free kinetics applied in this investigation has proven to be a useful evaluation in the study of the thermal degradation process of copolymers with different molecular structure. The thermogravimetric study provides an important link between the polymer composition, structure and characteristic thermal degradation parameters in copolymers.

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