

THERMAL ANALYSIS OF A NEW THIOPHENE DERIVATIVE AND ITS COPOLYMER

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Thermal characteristics of a new thiophene derivative, 2-(thiophen-3-yl)-ethyl octanoate (OTE), its homopolymer (POTE), and copolymer with thiophene P(OTE-co-Th) were investigated via pyrolysis mass spectrometry. Thermal degradation of the copolymer started by lose of side chains and thiophene involving products evolved almost in the same temperature range where PTh degradation was detected, at slightly higher temperatures than PTh backbone decomposed during the pyrolysis of POTE. The extent of doping and network structure decreased in the order POTE<P(OTE-co-Th)<PTh.

Keywords: *conducting polymers, copolymers, polythiophene, polythiophene derivatives, pyrolysis mass spectrometry*

Introduction

During the last two decades, conducting polymers have been an interdisciplinary for chemists, physicists and biologists. Due to the conjugation in the backbone of the conducting polymers, there exists a band gap which manifests semiconductor properties [1–3]. Furthermore, since conducting polymers can easily be coated on large surfaces of numerous substrate types, they have potential applications in areas such as light-emitting diodes [4], chemical sensors [5], electrochromic devices [6–8], microactuators [9] and batteries [10]. The molecular structure of conducting polymers can be adjusted in order to tailor several applicable attributes such as color of the electrochromic devices depending on the modified optical band gap [11].

Among the polymeric emissive materials, functionalized polythiophenes are proven to be better candidates due to their synthetic versatility and solubility [12, 13]. The selection of emissive materials for LEDs, even though primarily depend on fluorescence and electroluminescence (EL) characters, also depend on thermal stability, as, the EL conversion efficiency is around 5% and the remaining electrical energy may dissipate in the form of heat. The thermal energy instantaneously raises the temperature of the emissive layer, thus, the polymer should have good thermal stability too [14–16]. In a recent thermal study, it has been determined that though the melting and the isotropic temperatures of thiophenes containing mesogenic side chains at the 3rd position decrease linearly with the increase of aliphatic segment, for such polymers no characteristic relation has been determined between the alkoxy chain length and degradation [17].

We have recently prepared some functionalized thiophene monomers such as *bis*-(2-thiophen-3-yl-ethyl) decanedionate (DATE) and 2-(thiophen-3-yl-ethyl) octanoate (OTE), their homopolymers, and copolymers with thiophene to improve physical characteristics of PTh [7, 8]. Our former direct pyrolysis mass spectrometry studies revealed that copolymerization of thiophene with other monomers also improved electroactivity and increased the thermal stability [7, 8]. In direct pyrolysis mass spectroscopy (DPMS) technique as pyrolysis is conducted within the high vacuum system of the mass spectrometer, secondary reactions and condensation of pyrolysate can largely be avoided. Consequently, the pyrolysis mass spectra generated can be used to investigate thermal degradation mechanisms [18–23]. We applied direct pyrolysis mass spectrometry to investigate the structural and thermal characteristics of homopolymers of DATE and *bis*-(2-thiophen-3-yl-ethyl) terephthalate (TATE) and their copolymers with thiophene [18, 19]. The growth of polymer occurred through both 2 and 5 positions when the ester linkages contain hydrocarbon chains. However, when the ester linkages contain more rigid groups such as a phenyl, polymerization proceeded via coupling of thiophene moieties mainly at 5 position yielding a polymer with lower conductivity [18]. Pyrolysis of the samples prepared by electrochemical oxidation of DATE, or TATE in the presence of Th indicated an increase in thermal stability of ester linkages compared to pure homopolymers, PDATE and PTATE [19].

In the present study, direct pyrolysis mass spectroscopy (DPMS) and thermogravimetry analyses (TG) were applied to investigate the structural and thermal characteristics of a new thiophene derivative, 2-(thiophen-3-yl-ethyl) octanoate and its homopolymer and copolymer with thiophene.

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Experimental

Materials

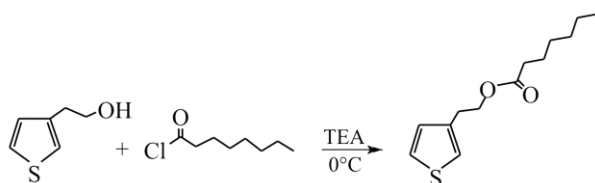
Reagents

2-Thiophen-3-yl-ethanol (Aldrich), octanoyl chloride (Aldrich), triethylamine (TEA) (Merck), tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich), acetonitrile (ACN) (Merck) and boron-trifluoride ethylether (BFEE) (Aldrich) were used without further purification. Thiophene (Th) (Aldrich) was distilled before used.

Methods

Synthesis of thiophene derivative monomer

The synthesis and characterization by NMR and FTIR of OTE was described in detail previously [7, 13]. The schematic representation of synthesis is shown in Scheme 1.



Scheme 1 Synthesis route for OTE monomer

Electrochemical synthesis of polymers

The homopolymer POTE and the copolymer P(OTE-co-Th) were potentiostatically prepared in a one-compartment cell with two platinum foils (1.5 cm^2) as the working and counter, while an Ag

wire was utilized as the pseudo-reference electrode. The homopolymer synthesis was carried out under nitrogen atmosphere in ACN/BFEE (8:2, v/v) containing 0.01 M OTE and 0.1 M TBAFB. Copolymerization with thiophene was achieved in ACN/BFEE (8:2, v/v) containing 0.01 M OTE, 0.1 M TBAFB and 15 μL of thiophene (Scheme 2). For both cases, a constant potential of 1.5 V was applied via a Wenking POS 73 potentiostat for 1 h. The freestanding films were washed with ACN several times and dried under high vacuum.

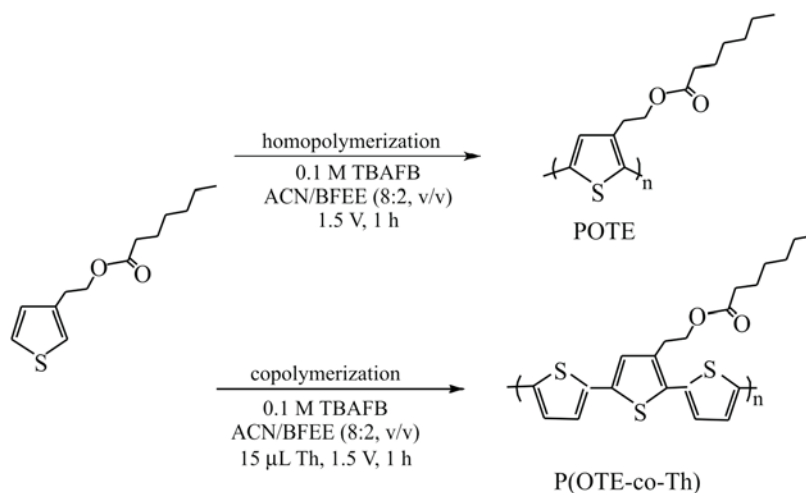
Details of electrochemical polymerization of BF_4^- doped polythiophene (PTh) were given in [21].

Conductivity of POTE, P(OTE-co-Th) and PTh were $3.2 \cdot 10^{-4}$, $9.1 \cdot 10^{-2}$ and 1.5 S cm^{-1} , respectively, via 4-probe technique. This method utilizes 4-osmium tips where a current is passed through the outer terminals and voltage drop between the inner tips is measured.

Instrumentation

Direct pyrolysis mass spectrometry (DPMS) system consisting a 5973 HP quadrupole mass spectrometer with a mass range of 10–800 Da was coupled to a JHP SIS direct insertion probe ($T_{\text{max}} = 445^\circ\text{C}$). In each experiment, the temperature was increased up to 445°C at a heating rate of $10^\circ\text{C min}^{-1}$, and kept constant for an additional 10 min at 445°C . 0.010 mg samples were pyrolyzed in the flared glass sample vials. Pyrolysis mass spectra were recorded using 70 and 19 eV EI ionization to differentiate the extent of dissociative ionization in the ion source.

TG experiments were performed by DuPont 2000 Thermal Gravimetry Analyzer (TG) at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere.



Scheme 2 Schematic representation of electrochemical syntheses of POTE and P(OTE-co-Th)

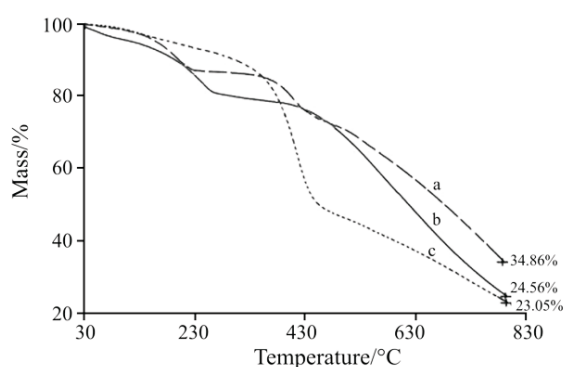


Fig. 1 TG curves of potentiostatically synthesized a – P(OTE-co-Th), b – P(Th) and c – POTE

Results and discussion

For both PTh and the copolymer P(OTE-co-Th), TG curves revealed two mass losses; at 230 and 440°C for PTh, and at 203 and 414°C for the copolymer. The low temperature mass losses were attributed to the removal of dopant anion from the matrices and the high temperature ones were associated with the decomposition of the polymer itself (Figs 1a and b). The homopolymer, POTE showed only a single step decomposition at 415°C, leaving 23.05% residue. It may be thought that since the degree of doping was too low as reflected by the very low conductivity measured for this polymer, removal of the dopant from the matrices would not lead to a significant mass loss.

The total ion current curve (variation of total ion yield as a function of temperature), (TIC), curves for

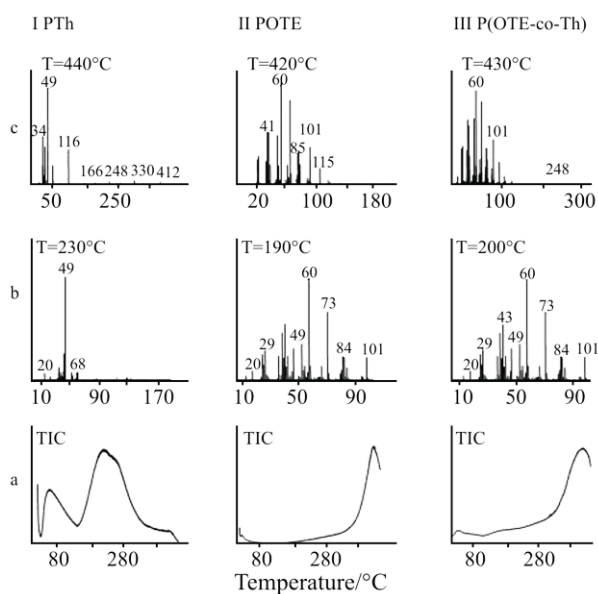


Fig. 2 Total ion current (TIC) curves for I – PTh, II – POTE and III – P(OTE-co-Th) and pyrolysis mass spectra at selected temperatures

PTh, POTE and P(OTE-co-Th) and the pyrolysis mass spectra recorded at the maximum of the peaks present in the TIC curves given in Fig. 2 show significant differences. In order to minimize further dissociation of degradation products in the mass spectrometer, the pyrolysis experiments were also performed by decreasing ionization energy to 19 eV. Yet, no significant change in fragmentation patterns was observed which indicates that secondary dissociation due to the ionization inside the ion source was not critical. Thus, discussions were made on the more reproducible 70 eV data.

Polythiophene

Recent pyrolysis studies on BF₄ doped PTh revealed that the first step of thermal degradation is due to the loss of the dopant, and the second step is due to the degradation of the polymer backbone producing segments of various conjugation lengths in accordance with the literature results [21, 22]. The cleavage of the thiophene ring at elevated temperatures was confirmed by evolution of H₂S and C₂H₂ and associated with a network structure [22]. In Fig. 3. single ion evolution profiles of some characteristic dopant products such as HF ($m/z=20$ Da), BF₂ ($m/z=49$ Da) and PTh based products such as thiophene monomer, dimer and trimer ($m/z=84$, 166 and 248 Da, respectively) and H₂S ($m/z=34$ Da) are shown. Evolution profiles of dopant

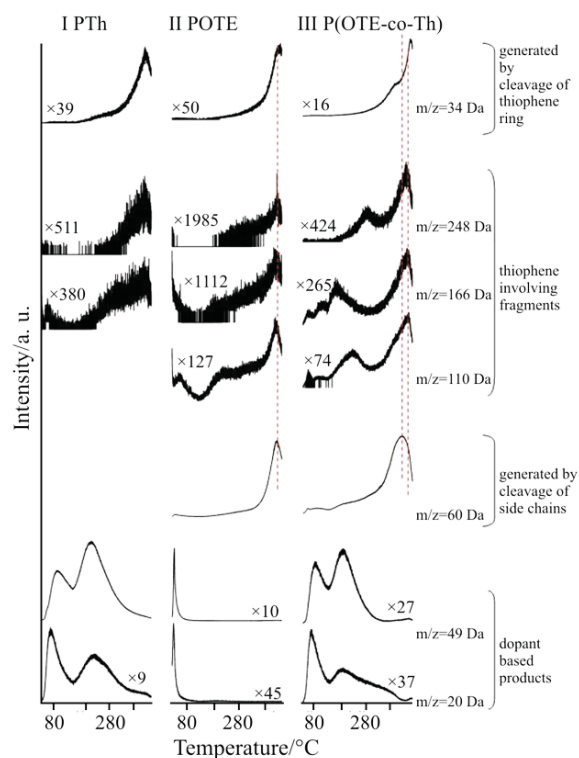


Fig. 3 The single ion evolution profiles of most intense and/or characteristic peaks recorded during pyrolysis of I – PTh, II – POTE and III – P(OTE-co-Th)

based products showed two maxima at 90 and 230°C. The low temperature evolutions were assigned to the adsorbed dopant on the polymer matrix and previous studies showed that although the relative intensity of the first maximum increased linearly, the relative intensity of the second maximum reached to a threshold value upon increasing dopant to monomer ratio during synthesis. After this threshold value, the conductivity was also independent of dopant concentration [21].

Homopolymer of octanoic acid 2-thiophene-3-yl-ethyl ester (POTE)

The detailed analyses of the mass spectra of the monomer indicated that the fragmentation follows the classical ester degradation mechanism, together with long hydrocarbon chain and thiophene fragmentation routes. The base peak at $m/z=110$ Da was assigned to 3-vinyl thiophene (C_4H_3S)CH=CH₂, due to the cleavage at α -position to the CO group. Other intense peaks were detected at $m/z=143$, 127, 60 and 57 Da due to OCO(CH₂)₆CH₃, OC(CH₂)₆CH₃, C(OH)₂=CH₂ and C₄H₉, respectively. The peak at $m/z=84$ Da was also quite intense and was attributed to CH₂=CH(CH₂)₃CH₃ fragment, yet, contribution of thiophene ion ($m/z=84$ Da) to the intensity should also be considered.

The TIC curve and the pyrolysis mass spectra recorded at the peak maximum at 420 and around 200°C are shown in Fig. 2.II. Pyrolysis data pointed out that the evolution of low molecular mass compounds such as unreacted monomer and BF₃, occurred below 80°C indicating extensive adsorption. The diagnostic dopant peaks were only present in this region. Peaks that can be attributed to degradation of the polymer were observed above 250°C. The mass spectra recorded around 420°C indicated that the fragmentation of the side chains of the polymer follows the classical ester fragmentation pattern as in the case of the monomer. Yet, the relative intensities of the product peaks changed significantly. The peak at $m/z=110$ Da, the base peak in the mass spectrum of OTE, was also present in the pyrolysis mass spectra of the polymer, though weakly. For the polymer, the base peak was at $m/z=60$ Da and assigned to both C₄H₁₂ and HOC(OH)=CH₂ fragments. The peak at $m/z=84$ Da was now more pronounced and weak dimer and trimer peaks were observable. A great degree of similarity between the mass spectrum of the monomer and pyrolysis mass spectra of the corresponding homopolymer can only be observed if the thermal degradation proceeds through a depolymerization mechanism. Thermal degradation of polymers involving labile side chains usually starts with the cleavages of weak bonds substituted on the main chain. Thus, significant differences noted between the

pyrolysis mass spectra of POTE and its monomer was in accordance with our expectations.

In order to get a better insight, the single ion pyrograms (variation of ion yield as a function of temperature, evolution profiles) of characteristic products were studied. Products due to the supporting electrolyte such as BF₃, BF₂, BF and HF appeared at the first stage of pyrolysis and showed identical trends. The evolution profiles of products due to degradation of POTE were quite similar and showed a maximum at 435°C. Presence of dimer and trimer peaks, though weak confirmed polymerization through the thiophene moieties. The relative yield of H₂S was quite low and its evolution profile was slightly shifted to higher temperatures ($T_{max}=445^\circ\text{C}$). The single ion pyrograms of HF ($m/z=20$ Da), BF₂ ($m/z=49$ Da), HOC(OH)=CH₂ ($m/z=60$ Da), (C₄H₃S)CH=CH₂ ($m/z=110$ Da), thiophene dimer and trimer ($m/z=166$ and 248 Da) and H₂S ($m/z=34$ Da) recorded during the pyrolysis of BF₄ doped of POTE are shown in Fig. 3.II. Previous studies revealed that H₂S evolution, indicating cleavage of the thiophene ring is more likely when there existing a network structure [21, 22]. Hence, it may be concluded that extent of network structure is quite low for POTE.

Copolymer of OTE with thiophene P(OTE-co-Th)

The TIC curve of the copolymer is shown in Fig. 2.III. The decomposition of P(OTE-co-Th) occurred in a broad temperature range as can be noted from the figure. Besides the low temperature peak, a broad and intense peak with a tail at moderate temperatures was observed at elevated temperatures in the TIC curve.

Analyses of the pyrolysis mass spectra recorded at the low temperature ranges pointed out that the first peak in the TIC curve of P(OTE-co-Th) corresponds to the evolution of low molecular mass compounds such as H₂O, BF₃, C₂H₅ and C₃H₇. In the temperature range 200–300°C peaks due to dopant were recorded together with the peaks diagnostic to degradation of polymer. Peaks due to the cleavage of side groups were again the most intense and the base peak was again at 60 Da through out the pyrolysis as in the case of the homopolymer, POTE. In the last stage of the pyrolysis, the peaks due to the products attributed directly to products characteristic to side chains and PTh backbone increased significantly similar to POTE. Yet, for the copolymer, the relative intensities of dopant based peaks increased significantly. Furthermore, the peaks due to fragments involving thiophene units and H₂S were more pronounced compared to the homopolymer.

The single ion pyrograms of the same characteristic degradation products of P(OTE-co-Th) which were

discussed for PTh and POTE are given in Fig. 3.III. For the copolymer, one of the most significant differences was the trends observed in the evolution profiles of dopant based products. Unlike POTE, two maxima, at 80 and 200°C appeared in the single ion pyrograms of dopant based products as in the case of PTh. Yet, the second maximum was shifted about 30°C to lower temperatures compared to what was detected for PTh (Figs 3.I and III). This may indicate that the interaction between the dopant and the polymer in the copolymer was stronger compared to POTE whereas weaker compared to PTh. The evolution profiles of products involving Th units such as vinyl thiophene, thiophene dimer and trimer followed almost the same trends at elevated temperatures and these products reached to maximum yield at 440°C when generated from the copolymer. This value was very close to the temperature at which H₂S yield was maximized. Yet, evolutions of thiophene involving products were also noted below 300°C indicating presence of low molecular mass oligomers. The differences observed in the evolution profiles of fragments involving thiophene units and those generated by cleavage of the side chains were quite interesting. Evolution profiles of fragments such as HOC(OH)=CH₂ (*m/z*=60 Da) and (CH)_x where *x*=2 to 7 showed a maximum at 420°C, at about 20°C lower temperature than the temperature at which the yield of thiophene involving fragments reached to maximum value. Thus, it may be concluded that electrochemical polymerization of thiophene and octanoic acid 2-thiophene-3-yl-ethyl ester has been achieved yielding a copolymer having a network structure. Upon copolymerization thermal stability of thiophene backbone increased mainly due to the increase in extent of network structure. However, decompositions of side chains follow an identical path with POTE.

Another point that should be noted was the change in the ratios of H₂S:thiophene dimer: thiophene trimer. It was 1:22:40 for POTE, 1:10:13 for PTh, and 1:15:25 for P(OTE-co-Th) pointing out that extent of network structure increased in the order POTE<P(OTE-co-Th)<PTh.

Conclusions

In this study, thermal degradation of BF₄ doped PTh, POTE, P(OTE-co-Th) were investigated via pyrolysis mass spectrometry. It has been determined that the extent of doping decreased significantly for POTE chains compared to PTh which in turn also caused a decrease in conductivity. Thiophene involving products evolved almost in the same temperature range during the pyrolysis of both PTh and the copolymer, at slightly higher temperatures than those evolved

during the pyrolysis of POTE. Yet, for the copolymer, degradation started by loss of fragments due to the cleavage of side chains which in turn decreased the stability of polymer matrix. Furthermore, for the copolymer, dopant evolution also occurred at lower temperatures indicating a weaker interaction between the dopant and the polymer.

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