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A Kinetic Evaluation for Phenothiazine Base Copolymers

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ABSTRACT

In here, the nonisothermal decomposition kinetics of co-polymers based phenothiazine was present-ed. For this, firstly, 3, 7-di-2-thienyl-10H-phenothiazine (TF) was prepared via an optimized Suzu-ki–Miyaura cross-coupling reaction. After monomer (TF) characterization, the copolymerization re-actions with EDOT and thiophene were performed by the electrochemical technique. The molecular masses of the co-polymers were found by gel permeation chromatography (GPC) analysis. Thermal characterizations of the resulting polymers were conducted by thermogravimetric analyses. The thermal decomposition kinetics of the resulting polymers was also performed. For this, the kinetic methods (Tang, FWO, KAS, Kissinger, and Friedman) based on the multiple heating rates were used. Several kinetic parameters related to the decomposition kinetics of the solid-state were revealed.

Keywords:
Thermal decomposition; Kinetic; Phenothiazine; Copolymer.

INTRODUCTION

The first conductive polymers were discovered in 1975. Then, they have attracted considerable attention due to their interesting electrical conductivity [1]. Nowadays, the studies related to conductive polymers have gained a new acceleration due to the rapid developments in science and technology. In most of these studies, it is aimed to give to the polymeric materials some properties of semiconductors. Some properties which do not naturally exist in semiconductors are trying to be imparted to conductive polymers synthetically [2]. Since conductive polymer compounds, which are the product of polymerization, have a wide area in polymer technology, comprehensive studies have been carried out to date [3,4]. Among these conductive polymers, phenothiazine based polymers has been extensively studied for their applications in various electronic and electrochemical legal devices [5,6]. They are good electron-donor and hole transport materials, since the phenotiazine rings have electron-rich sulfur and nitrogen heteroatoms. However, many of their features are still known to be limited. On the other hand, to date, various methods have been used for the synthesis of conductive polymers. Chemical, enzymatic, oxidative, and electrochemical polymerization methods are used effectively for the conversion of monomers carrying groups such as thiophene, pyrrole, and carbazole to conductive polymers. Electrochemical polymerization is one of the most important polymerization methods of recent years. The first electrochemical synthesis is the production of PANi polymer by Letheby [7]. Later this method was used by Szaways [8]. Since then, conductive polymers such as polypyrrole (PPy), polythiophene (PTh), polypurane (PF), polyphenylene (PP), and polycarbazole (PCz) with π-electron conjugate structure have been synthesized for use in many applications [9]. Electrochemical polymerization is highly advantageous over other polymerization methods because of its superior properties such as the reaction being carried out at room temperature, controlling the film thickness by varying the applied voltage or current, the homogeneity of the films, and not requiring purification [10]. Here, it is aimed to synthesize phenothiazine copolymers by constant potential electrolysis. For this, the monomer was prepared as described in the literature [11]. The structure of the synthesized monomers was illuminated by FT-IR, UV-Vis, ^{1}H- and ^{13}C-NMR techniques. Characterizations of copolymers were carried out by TG-DTA, CV, and GPC. In the final stage of the research, the solid-state degradation kinetics of phenothiazine based conductive polymers were calculated using TG-DTG data under non-isothermal conditions. Accordingly, to our knowledge, this study is the first report to examine the kinetics related to the solid state degradations of phenothiazine based conductive polymers.

EXPERİMENTAL METHODS

Materials

Phenothiazine, 3-thiophene boronic acid, Aliquot 336, N-bromosuccinimide (NBS), silicon diox-ide (SiO_2), tetrakis (triphenylphosphine) palladium (0) [$Pd(PPh_3)_4$], 3,4-ethylenedioxydiophene (EDOT), Potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), thiophene, 18-crown-6, DMSO, DMF, THF, ethyl acetate, ethyl alcohol, methyl alcohol, chloroform, ether, acetone, acetonitrile, 2-methoxy ethanol, hexane, heptane, 1,4-dioxane, $CHCl_3$, and CCl_4 were obtained from Merck (Germany) and used in the experiments without pre-purification.

Measurement Techniques

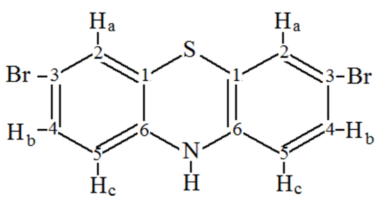
HEIDOLPH branded magnetic stirrers were used for the synthesis processes. To dry glassware and chemicals J.P. Selecta brand vacuum oven was used. Column chromatography was performed using silica gel. UV-vis spectra of copolymers were obtained from indium–tin oxide (ITO, solid phase) surface using an Analytic Jena Speedcord S-600 diode-array spectrophotometer. Fourier Transform Infrared (FT-IR) Spectrometer (Perkin Elmer FT-IR Spectrum one) and Nuclear Magnet-ic Resonance (NMR) Spectrophotometer (JEOL ECX II 400 MHz) were used for structural charac-terization of synthesized substances. ^{1}H and ^{13}C-NMR analysis used DMSO-d_6 as a solvent. UV-vis analyzes were performed using a double beam path spectrophotometer and quartz cuvet. DMSO was used as a solvent in UV measurements. The number average molecular weight (M_n), Mass aver-age molar mass (M_w), and polydispersity index (PDI) of the copolymers were found by Viscotek GPC/SEC systems. To determine the electrochemical properties of resulting polymers, cyclic volt-ammograms were taken using CH Instruments 660 C Electrochemical Analyzer (CH Instruments, Texas, USA). The copolymers were coated on platinum or ITO. A platinum wire was used as a counter electrode. The non-aqueous Ag/Ag+ was determined as a reference electrode. After the coating of resulting copolymers was on ITO/glass surface via electro-oxidative polymerization, the films were rinsed with ACN. The thermal properties of synthesized polymers were determined by using Thermogravimetry-Differential Thermal Analysis (TG-DTA Perkin Elmer Diamond Thermal Analysis System) [12,13]. The measurements were carried out in an N_2 atmosphere between 20-1000°C, at the heating rate of 5, 10, 15, and 20°C/min.

Synthesis of 3,7-dibromo-10H-phenothiazine

A solution of 10 mmol (1.99 g) phenothiazine in 20 mL THF was placed in a 100 mL two-necked flask in an ice bath. To the resulting yellow solution, a solution of 22 mmol (3.91 g) of NBS dis-solved in 45 mL of THF was added dropwise for 1 hour. The dark green solution formed after the drop was cooled to room temperature and stirred for a further 24 hours. After the solvent removal, the residue was purified over silica gel. A light green product was obtained (2.50 g, yield: 70%) [14]. The reaction scheme for the synthesis of 3, 7-dibromo-10H-phenothiazine is given in Fig. 1

Synthesis of 3,7-di-2-thienyl-10H-phenothiazine (TF Monomer)

In a 100 mL flask, 4 mmol (1.42 g) of 3, 7-dibromo-10H-phenothiazine was dissolved in a boil-ing ethoxyethanol-water (40: 4, 44 mL) mixture. 20 mmol (2.76 g) of K_2CO_3 was added to the re-sulting green solution and stirred at 130 0C for half an hour. Then 11.2 mmol (1.43 g, 2.8 eq.)



FTIR (ATR, cm^{-1}): 3337 ν (NH stretch, thiomorpholine ring), 1592, 1566, 1441 ν (C = C stretch, phenyl), 1311 ν (C=N bending, thiomorpholine ring), 737 ν (C-S bending, thiomorpholine ring), 649 ν (C-Br bending)

^{1}H-NMR (DMSO-d_6, ppm, δ): 8.85 (s, 1H, -NH), 6.59 (d, 1H, Ar-HC), 7.14 (dd, 1H, Ar-H_a), 7.11 (s, 1H) (Ar-H_b)

^{13}C-NMR (DMSO-d_6, ppm, δ): 141.43 (6-C), 130.12 (3-C), 128.62 (1-C), 118.72 (5-C), 116.55 (2-C), 113.19 (4-C)

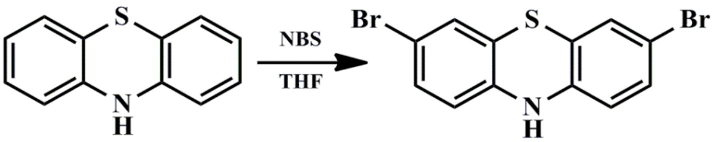
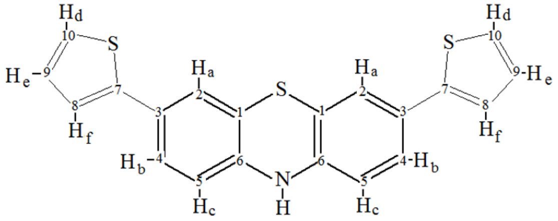


Figure 1. Synthesis of 3, 7-Dibrom-10H-phenothiazine



FTIR (ATR, cm^{-1}): 3334 ν (NH stretch, thiomorpholine ring), 1592, 1566, 1465 ν (C = C stretch, phenyl), 1298 ν (CH-N bending, thiomorpholine ring), 798 ν (CH-S bending, thiomorpholine ring);
^{1}H-NMR (DMSO-d$_6$, ppm, δ): 8.96 (s, 1H, -NH), 7.49 (d, 1H, Ar-Hd), 7. 42 (d, 1H, Ar-Hf), 7.33 (s) , 1H, Ar-Ha), 7.28 (d, 1H, Ar-Hb), 7.13 (t, 1H, Ar-He), 6.75 (d, 1H, Ar-HC);
^{13}C-NMR (DMSO-d 6, ppm, δ): 143.12 (6-C), 141.10 (7-C), 128.86 (1-C), 128.30 (10-C), 125.50 (8-C), 124.88, 123.36 (3-C), 122.89 (9-C), 117.17 (4-C), 115.25 (5-C)

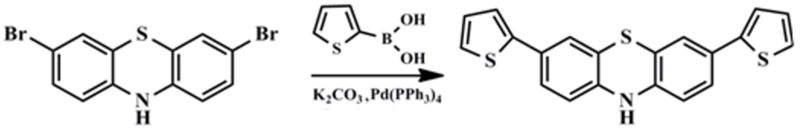


Figure 2. Synthetic scheme of 3, 7-di-2-thienyl-10H-phenothiazine

of 2-thiophene boronic acid and 0.06 mmol (70 mg) [Pd (PPh)$_3$]$_4$ as catalyst was added and the mixture was refluxed at 130 °C for 2 hours. After two hours, the mixture was cooled down to room temper-ature and precipitated with the distilled water. The precipitation was carried out by stirring the mix-ture continuously with a magnetic stirrer. The precipitate was filtered and washed with an ethanol-acetone (1:1 v/v) solvent mixture. The resulting light yellow product was dried in a vacuum oven at 40°C for 6 hours (1.16 g, yield: 81%) [15]. The reaction scheme for the synthesis of 3, 7-di-2-thienyl-10H-phenothiazine is given in Fig. 2.

Electrochemical Characterization

Data from voltammograms were used to determine the electrochemical properties of the resulting copolymers on the ITO surface [16]. Electrochemical measurements were performed in a quartz cell using non-aqueous Ag/Ag+ as the reference electrode, platinum wire as the counter electrode, and ITO as the working electrode. 0.1 M TBAPF$_6$ was used as a support electrode.

Electrochemical Copolymerization of TF Monomer with Thiophene and EDOT

To determine the electrochemical properties of synthesized TF monomer by using cyclic voltam-mograms, CH Instruments 660 C Electrochemical Analyzer was used. The resulting copolymers were obtained by cyclic voltammograms repeated at a scanning rate of 50 mV/s in 0.1 M TBAPF$_6$/ACN. For this, 20 mg TF monomer and 0.9 ml thiophene (d: 1.05 g/cm^3) were dissolved in 9 ml 0.1 M TBAPF$_6$/ACN and 1 ml BF$_3$.OET$_2$ support electrolyte solution. Copolymerization was then performed on the ITO surface at a scanning speed of 50 mV/s, with a potential range of (+1.8)-(-0.4) V. In the case of copolymerization of TF monomer with EDOT, 20 mg of TF monomer and 0.7 ml of 3,4-ethylene dioxythiophene (d:1.33 g/cm^3, EDOT) were dissolved in 9 ml of 0.1 M TBAPF$_6$/ACN and 1 ml of BF$_3$.OET$_2$ support electrolyte solution. Copolymerization was performed by the electrochemical method to the ITO surface at a scanning speed of 50 mV/s, in the potential range (-1.6)-(+1.6) V. Synthetic pathway for electrochemical copolymerizations of the TF monomer with thiophene or EDOT is given in Fig. 3. The films of the resulting copolymer were coated onto the ITO surface by electro oxidative polymerization and then washed with ACN.

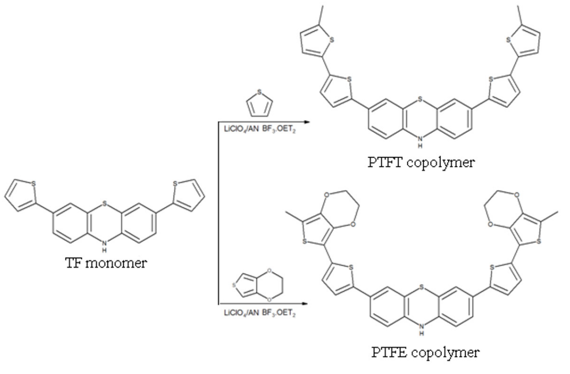


Figure 3. Electrochemical copolymerization of TF monomer by EDOT and thiophene

RESULTS AND DISCUSSION

Structural Characterization

3,7-di-2-thienyl-10H-phenothiazine used in electropolymerization was synthesized from 3,7-dibromo-10H-phenothiazine according to standard literature procedures [11]. The chemical structure of each compound was confirmed by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra. Significant changes were also observed in the FT-IR spectra of each compound relative to the starting material pheno-thiazine. The C-Br bending peak of 3,7-dibromo-10H-phenothiazine was observed at 649 cm^{-1} in the FTIR spectrum. Also, the N-H tensile peak of the thiomorpholine ring was determined at 3337 cm^{-1}, and the C-N peaks at 1311 cm^{-1}. In the 1H-NMR spectrum, the hydrogen atom in the thiomorpholine ring showed a single signal at 8.85 ppm. Thus, both the FT-IR and ^{1}H-NMR spectra of this compound showed that the Bromine did not bind at the N-position. Also, the aromatic proton signal at 6.59 ppm (1H, binary) and 7.11 ppm (1H, single) was observed. On the other hand, it was deter-mined that the Hb proton at 7.14 ppm split into the doublet of the doublet due to the remote group interaction with the Ha proton. In the ^{13}C-NMR spectrum, characteristic resonance peaks of six dif-ferent carbon atoms between 113-141 ppm were determined. All these results confirm that the -NH group on phenothiazine is protected and that the halogenation reaction takes place via the aromatic ring. However, in the FTIR spectrum of 3,7-di-2-thienyl-10H-phenothiazine, the C-Br peak at 649 cm^{-1} was lost and the C-S peak in the thiomorpholine ring was observed at 798 cm^{-1}. The N-H and C-N peaks in the thiomorpholine ring were also observed, respectively, at 3334 cm^{-1} and 1298 cm^{-1}. In the ^{1}H-NMR spectrum, the N-H bond in the thiomorpholine ring was exhibited as a single peak at 8.96 ppm. Also, this compound gave peaks at 7.49 ppm (1H, doublet), 7.42 ppm (1H, doublet), 7.33 ppm (1H, singlet), 7.28 ppm (1H, doublet), 7.13 ppm (1H, triplet)) and 6.75 ppm (1H, doublet). However, in the ^{13}C-NMR spectrum, this compound showed resonance signals of ten different car-bon atoms between 115-143 ppm.

Optical and Electrochemical Properties

UV-vis spectra of PTFT and PTFE copolymers were taken from the ITO surface and given in Fig. 4. The UV-vis spectrum of the TF monomer exhibited a maximum absorption (λmax) at 364 nm. This maximum peak is attributed to π- π* transitions in the aromatic ring. The UV-vis spectrum of PTFT copolymer showed a peak at 397 nm shifting to 33 nm red when compared to the TF mon-omer. This is related to the higher conjugation of PTFT than the TF monomer. On the other hand, PTFE showed two peak absorption peaks at 460 nm and 643 nm due to high conjugation compared to both TF and PTFT copolymer. The lowest spectral energy edge bands of the absorption spectra of FT and PTFT copolymer were measured as 481 and 494 nm, respectively. Accordingly, the optical band gaps were 2.57 eV for TF monomer and 2.5 eV for PTFT. In the case of PTFE, the lowest spectral energy edge bands λmax_1 and λmax_2 were determined to be 567 and 783 nm, respectively. Accordingly, the optical band gap for PTFE was calculated as 2.18 eV for λmax_1 and 1.58 eV for λmax_2.

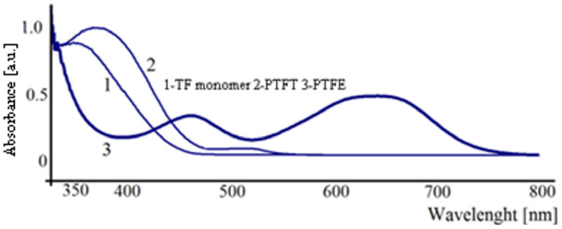


Figure 4. UV-vis spectra of TF, PTFT, and PTFE on ITO surface

On the other hand, PTFT and PTFE copolymers were formed by electrochemical cyclic Voltam-metry at a scanning rate of 50 mV/s. The first cyclic voltammograms for TF, PTFT, and PTFE co-polymers are given in Fig. 5.

Fig. 5 show the first cyclic voltammograms of PTFE and PTFT at a scanning speed of 50 mV/s. According to Fig. 5, the first oligomeric products were taken in the range of -1.4-1.6 V for PTFT and -0.4-1.6 V for PTFE. The oxidation peak of PTFE was observed at 0.51 V. İts reduction peak was at -0.39 V. Also, the oxidation peak and reduction of PTFT was exhibited at 0.82 V and 0.44 V, respectively. Accordingly, each voltammogram showed a single oxidation and reduction peak with a reversible character. Functioned thiophene compounds such as thiophene or 3,4-ethylene dioxythiophene (EDOT) can be very easily oxidized. The radicals formed as a result of this oxidation can be joined together to form a polymerization reaction easily on the ITO electrode. İn here PTFE and PTFT copolymers were obtained by cyclic Voltammetry. Voltagram collection was continued until no electroactive species could be recovered from the monomer. The copolymeriza-tion reaction of TF monomer with EDOT was carried out between -1.4-1.6 V. In the voltammogram of PTFE, the oxidation peak at 0.51 V shifted

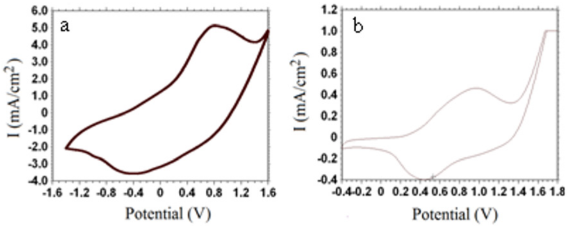


Figure 5. First cyclic voltammograms of PTFE (a) and PTFT (b) at a scanning speed of 50 mV/s

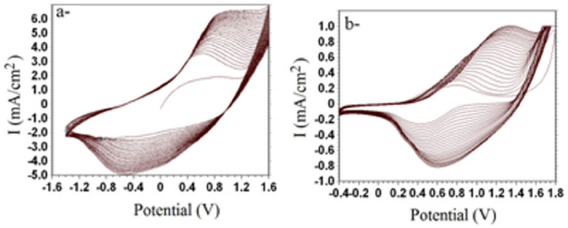


Figure 6. Sequential cyclic voltammograms of PTFE (a) and PTFT (b) in the repeated potential screening of FT.

to 0.88 V and the reduction peak at -0.39 V shifted to 0.62 V. On the other hand, the copolymerization reaction of TF monomer with thiophene was carried out between -0.4-1.8 V. Here, the oxidation potential shifted from 0.82 V to 1.27 V and the reduction potential shifted from 0.44 V to 0.62 V. The sequential voltammograms obtained by con-sequently the shift of the reaction to the high potentials by binding of the active species showed that the copolymerization reactions took place [17]. Cyclic voltammograms for electroactive PTFE and PTFT copolymers deposited on ITO are given in Fig. 6

Furthermore, the dependence of the scanning speed versus the current density of copolymers de-posited on ITO in the 0.1 M TBAPF₆/ACN support solution is shown in Fig.s 7 and 8. Fig.s 7 and 8 showed a linear relationship between current density and scanning speed. This event was at-tributed to the non-diffusion process.

It was determined that there is a linear relationship between scanning velocities and current in-tensives in Fig.s 7 and 8, which shows the scanning velocity dependence in copolymerization re-actions. GPC was used to calculate the average molar masses of the soluble portions of the PTFE and PTFT. The results are given in Table 1. According to GPC analysis, polymers have low PDI values. Low PDI indicates a controlled polymerization reaction [18].

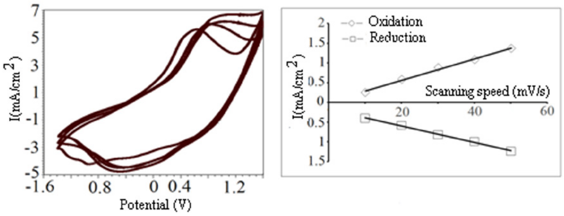


Figure 7. The current density of PTFE at scanning speeds of 10, 20, 40, 60, 80 mV/s

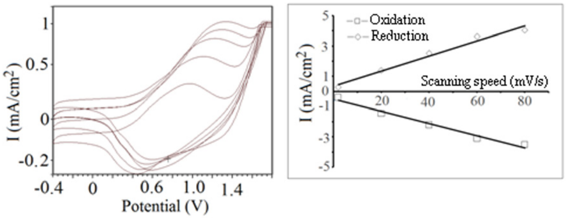


Figure 8. Current density of PTFT at scanning rates of 1, 20, 40, 60, 80 mV/s

Table 1. GPC analysis of PTFE and PTFT

Copolymers	M_n(gmol^{-1})	M_w(gmol^{-1})	PDI
PTFT	22782	32578	1.43
PTFE	13850	19113	1.38

Kinetic Evaluation

Non-isothermal methods are often used for the evaluation of mechanisms and kinetics of solid-state reactions. Most of these thermo analytic methods are based on the Arrhenius equation.

$$k = A\exp(-E/RT) \qquad (1)$$

and rate expression occurs

$$da/dt = kf(a) \qquad (2)$$

Here, f (α) is the kinetic function. α is the conversion fraction. If f (α) = (1-α) n and dT / dt = β occur equally at constant temperature, Eq. 2 can be written as follows.

$$g(a) = \int_0^a \left[\frac{1}{(1-n)^n}\right] da = \frac{\mathrm{A}}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right)dT \qquad (3)$$

Here; n is the degree of reaction. Eq. 4 can be written for the special case n = 1. On the other hand, Eq. 5 can be written for n ≠ 1 values.

$$\int_0^a \left[\frac{1}{(1-n)}\right] da = -\ln(1-a) \qquad (4)$$

$$\int_0^a \left[\frac{1}{(1-n)^n}\right] da = -\frac{1-(1-a)^{1-n}}{1-n} \qquad (5)$$

Many techniques are using different approximations to solve Eq. 3. The following isoconver-sional methods were used to calculate kinetic parameters related to the solid-state degradation of copolymers.

Tang Method

When an appropriate approach is used for the solution of Eq. 2 and the logarithm of both sides is taken, the equation given below can be obtained [19].

$$\ln\left(\frac{g(a)}{T^{1.894661}}\right) = \begin{bmatrix} \ln\dfrac{AR}{Rg(a)} \\ +3.635041 \\ -1.894661\ln E \end{bmatrix} - \left(\frac{1.001450E}{RT}\right) \qquad (6)$$

Here, the activation energy (E_a) can be found from the slopes of the Arrhenius plots at different heating rates.

Kissenger-Akahira-Sunose Method

This method is an integral isoconversional method and E_a is calculated in similar ways as in other methods. According to the Kissenger-Akahira-Sunose method, an equation is obtained as follows [20,21].

$$\ln\left(\frac{g(a)}{T^2}\right) = \ln\left[\frac{AR}{Eg(a)}\right] - \frac{E}{RT} \tag{7}$$

Kissinger Method

E_a can be calculated without using any reaction mechanism, by using the following equation [20].

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \left\{\frac{AR}{E} + \ln\left[n(1-a_{\max})^{n-1}\right]\right\} - \frac{E}{RT_{\max}} \tag{8}$$

where β, T_{max}, A, α_{max} and n are the heating rate, temperature, pre-exponential factor, the maxi-mum conversion fraction, and reaction order. E_a can be calculated from the graph of ln ($\beta/T2_{max}$) ver-sus 1000 /T_{max}.

Flynn-Wall-Ozawa Method

This is an integral method. In this technique, A, f (α), and E_a are independent of both conversion fraction and the temperature. This technique uses the following logarithmic equation [22,23].

$$\log\beta = \log\left[\frac{AE}{R}\right] - \log\beta + \log p\left(\frac{E}{RT}\right)\frac{E}{RT} \tag{9}$$

Using Doyle approximation and assuming E/RT> 20 for the integral function, the above equation can be simplified as follows

$$\log\beta = \log\left[\frac{AE}{R}\right] - \log g(g(a)) - 2.315 - 0.4567\frac{E}{RT} \tag{10}$$

Friedman Method

The Friedman method uses Eq. 11 based on the Arrhenius equation for thermal decomposition kinetics [24].

$$\ln\left(\frac{da}{dt}\right) = \ln(A) + \ln(1-n) - \frac{E}{RT} \tag{11}$$

In the above equations, α, g(α), β, T_m, A, and R are the degree of reaction, integral function, heating rate, temperature, pre-exponential factor, and gas constant, respectively. A line is obtained by plot-ting 1/T versus ln (dα /dt) and E/R is determined from the slope of this line.

Thermal Decomposition Kinetic

The decomposition kinetics of the copolymers were performed by the TG technique. Kinetic pa-rameters were calculated using multiple heating rate methods. The TG curves obtained in the dy-namic nitrogen atmosphere of the copolymers were given in Fig. 9. TG experiments were carried out in nitrogen of 50 mL min^{-1} gas at heating rates of 5, 10, 15, and 20 °C min^{-1}. Analyses were performed by using 8-10 mg samples. All TG curves showed that copolymers degrade in one step.

The first decomposition temperature (T_{on}) in addition to the temperatures at which 20% and 50% mass losses occurred were found from the TG thermograms. Furthermore, DTG curves were used to determine temperatures (T_{max}) corresponding to the maximum decomposition rate. DTA curves were used to determine the exothermic and endothermic nature of decomposition. According to the TG curve of PTFE copolymer at a heating rate of 5 ° C/min, the initial decomposition temperature was 104 ° C. 20% and 50% mass loss was observed at 245 °C and 328 °C, respectively. The amount of residue at 1000˚C was calculated to be about

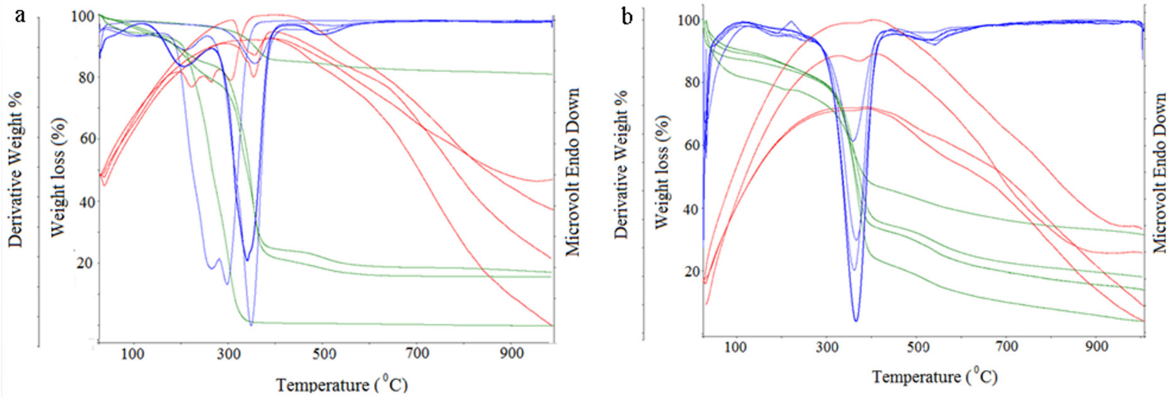


Figure 9. TG / DTG and DTA thermograms of PTFE (a) and PTFT (b) at different heating rates

11%. This compound was degraded in one step and T_{max} was found as 303 °C. During the decomposition of the PTFE copolymer, the presence of an endothermic peak at 318 °C was observed in the DTA curve. According to the TG curve obtained at a heating rate of 5 oC/min of PTFT copolymers the initial decomposition temperature was deter-mined as 231 oC. The temperatures at which 20% and 50% mass loss were observed were 283 ° C and 347 °C, respectively. The amount of residue at 1000˚C was calculated to be approximately 8%. This compound was determined to be degraded in one step. From the DTG curve, T_{max} was calculated as 381 °C. During the decomposition of PTFT copolymers, the presence of an endothermic peak at 399 ° C was observed in the DTA curve.

Kinetic Studies

There are many techniques for the solution of Eq. 3. In this study, several techniques were used to investigate the kinetic parameters of copolymers. These techniques are FWO, KAS, Tang, and Kissinger methods. For these methods, the TG curves at multiple heating rates are used. For the calculation the kinetic parameters of copolymers, firstly Kissinger method and isoconversional meth-ods were used. According to the Kissinger method, E_a related to the thermal decomposition kinetics of PTFE and PTFT was found to as 75.23 kJ mol^{-1} and 83.47 kJ mol^{-1}, respectively. According to equation [6], E_a can be found from the graph of 1000 / T versus ln ($\beta/T^{1.894661}$). The average value of E_a for PTFE and PTFT was found to as 75.8 kJmol^{-1} and 93.8 kJmol^{-1}, respectively. The values obtained for copolymers were given in Table 2. KAS is an another method used in this study. In the conversion fractions given α = 0.05-0.95, E_a determined from the slope of the graph of ln (β/T^2) ver-sus 1000/T was calculated as 74.7 and 92.8 kJmol^{-1} for PTFE and PTFT, respectively. The result is very close to the value obtained by the Tang method. Another method used in this study is FWO. At a constant conversion, the slope of the line obtained from log β versus 1000/T graph is equal to 0.456 E/RT. E_a can be found from here. In Fig. 15, the plots of ln β versus 1000/T at a different conver-sion value are plotted, and the values found here are 75.7 and 93.1 kJmol^{-1} for PTFE and PTFT, re-spectively. As a result, the E_a obtained by all three methods for copolymers were very close to each other. Finally, Ea for PTFE and PTFT using the Friedman method was determined as 78.8 and 97.9 kJmol^{-1}, respectively.

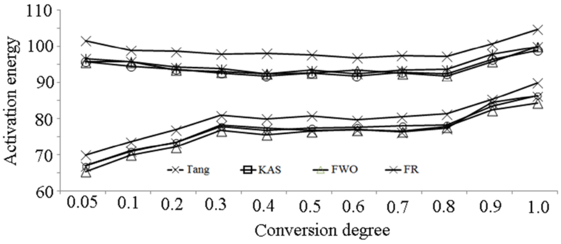


Figure 10. E_a values as a function of the conversion degree

Fig. 10 shows the Arrhenius type curves in the range of α = 0.05-0.95. As given in Fig. 10, the minimum E_a values required for copolymers to start degradation is 64.3 and 94.6 kJmol^{-1} for PTFE and PTFT, respectively. E_a required for the degradation step of PTFE and PTFT copolymer are very close to each other within the limits of 0.2 <α <0.9. When the

Table 2. E_a values obtained by Tang, KAS, FWO, and Friedman methods

Decomposition Steps								
	PTFE				*PTFT*			
α	*Tang*	*KAS*	*FWO*	*FR*	*Tang*	*KAS*	*FWO*	*FR*
0.05	*65.8*	*64.3*	*65.9*	*68.9*	*91.6*	*94.6*	*94.6*	*100.5*
0.1	*69.8*	*68.9*	*70.1*	*72.5*	*94.7*	*93.4*	*94.6*	*97.8*
0.2	*72.3*	*71.1*	*72.4*	*75.8*	*93.2*	*92.6*	*92.4*	*97.5*
0.3	*76.8*	*75.6*	*77.1*	*79.8*	*92.7*	*91.6*	*91.9*	*96.7*
0.4	*75.7*	*74.5*	*76.4*	*78.9*	*91.4*	*90.7*	*91.4*	*96.9*
0.5	*76.4*	*75.4*	*75.6*	*79.7*	*92.3*	*91.5*	*91.6*	*96.5*
0.6	*76.5*	*75.8*	*75.9*	*78.6*	*91.4*	*90.8*	*92.3*	*95.7*
0.7	*76.9*	*75.4*	*75.2*	*79.4*	*92.3*	*91.7*	*91.5*	*96.4*
0.8	*77.1*	*76.7*	*76.3*	*80.2*	*92.5*	*91.4*	*90.8*	*96.2*
0.9	*82.3*	*81.3*	*83.5*	*84.3*	*96.8*	*95.3*	*94.7*	*99.6*
0.95	*85.2*	*83.2*	*85.2*	*88.9*	*98.9*	*97.8*	*98.8*	*103.6*
Average	*75.8*	*74.7*	*75.7*	*78.8*	*93.8*	*92.8*	*93.1*	*97.9*

α; conversion fraction

mass loss reaches 90%, co-polymers have required energy of 90 kJmol^{-1}

CONCLUSION

Here, a phenothiazine monomer whose preparation was previously presented in the literature was again synthesized and its PTFE and PTFT were prepared by the electropolymerization method. Characterization of the phenothiazine-based monomer was performed by UV-Vis, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra. Also, the average molecular mass of PTFE and PTFT by the GPC was found as approximately 13850 g mol^{-1} and 22782 g mol^{-1}, respectively. In the following study, the solid-state decomposition kinetics of PTFE and PTFT were evaluated by using thermal curves. The kinetic parameters of the decomposition were determined using Kissinger, Tang, KAS, FWO, and Fried-man methods based on multiple heating rates. Accordingly, the mean values of Ea obtained by the Tang method for PTFE and PTFT were 75.8 and 93.8 kJmol^{-1}, respectively. The obtained co-polymers can be used in various applications such as organic field-effect transistors [25], chemilumi-nescence [26] and light-emitting diodes [27] due to their the electro-optical properties

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