

*Dedicated to the memory of  
Professor Cristofor I. Simionescu (1920–2007)*

## THERMAL DEGRADATION BEHAVIOUR AND KINETIC ANALYSIS OF POLYSTYRENE WITH PENDENT VILOGEN GROUPS

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Polystyrene containing viologene groups in the side chain is a polystyrene having N-(p-H, p-NO<sub>2</sub>, p-Cl)-phenacyl-4,4'-bipyridinium chloride/bromide and N- carboxymethyl/ethyl-4,4'- bipyridinium chloride/bromide (4a-4e) as pendant groups. The influence of the chemical structure of these viologene groups on the thermal degradation of the polymers was studied. As the reaction of thermal degradation is a complex process, the kinetical parameters and characteristics of the thermal degradation were established. The kinetical study of the thermal degradation of chemically modified polystyrene was done using three different heating rates (° C/min.): 5; 10 and 20. Energy of activation of degradation processes for the polystyrene containing viologene groups was determined by isoconversional method proposed by Vyazovkin with a standard deviation +/-7 kJ/mol.

### INTRODUCTION

Polystyrene with quaternary groups in the side chain is of great interest due to the important area of applications: modifiers of the textile surfaces, antistatic agents, agents for the activation of the flotation processes, coagulation and sedimentation agents, corrosion inhibitors, growing regulators, antiseptically agents.<sup>1-4</sup> The presence of viologene group in the side chain of the polymer provides it with special properties and make it useful as electron transfer catalyst for redox processes, to obtain hydrogen from water<sup>5-7</sup>, as electrochromic and photochromic materials.<sup>8-12</sup>

The present paper deals with a study of the thermal behavior of polystyrene containing viologene groups in the side chain; the kinetical parameters of the thermal degradation reactions were determined.

### RESULTS AND DISCUSSION

Fig. 1 plots the FTIR spectra of CMPS and 4c sample. The decrease of the absorption band at

1260 cm<sup>-1</sup> shows the consumption of – CH<sub>2</sub>Cl groups involved into the quaternization reaction. Figs. 2-5 show TGA thermograms of 3b and 3c low molecular compounds and of the corresponding quaternized CMPS 4b and 4c. These thermograms show that the thermal degradation of PS containing viologene groups in the side chain is a quite complex process.

The thermal degradation of samples 4a-4e proceeds in four steps, depending on the chemical structure of pendant viologene group (Table 1).

The last step corresponds probably to a thermal-oxidative process of the carbon residue formed around 400 °C which is a characteristic process for polymers containing aromatic rings. The temperature differences, recorded for the samples analysed at 400 °C, depend on the chemical structure of the viologene groups.

It was established in a previous paper<sup>13</sup> that the thermal stability of the low molecular weight compounds 3a-3e decrease in the order: 3c > 3a > 3e > 3d > 3b. The same order was found for PS with viologene groups in the side chain: 4c > 4a > 4e > 4d > 4b. The thermogravimetric characteristics

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showed a significant modification of the thermal stability for PS containing viologene groups depending on the heating rate. Also, their thermal stability is strongly diminished when compared with that of PS and CMPS. We believe that the

modified polymers possessed an amorphous morphology, which facilitates the thermal attack to the unstable bonds. The next steps proceed at temperatures comparable with those of low molecular weight compounds.

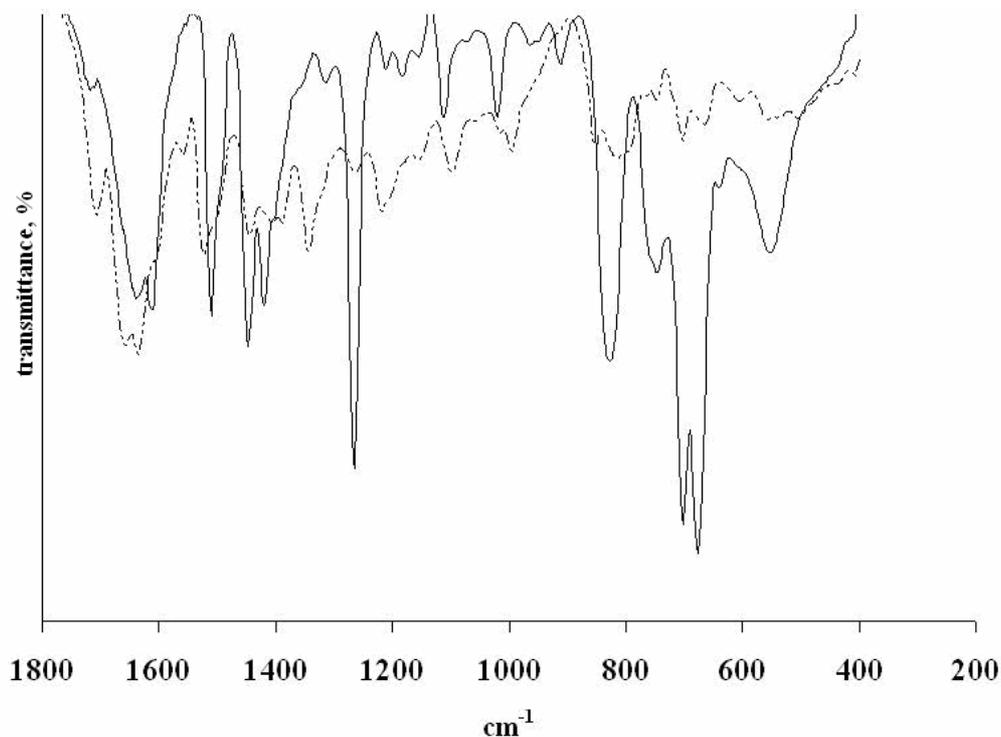


Fig. 1 – FT-IR spectra of Chloromethylated Polystyrene (—) and **4c** (----).

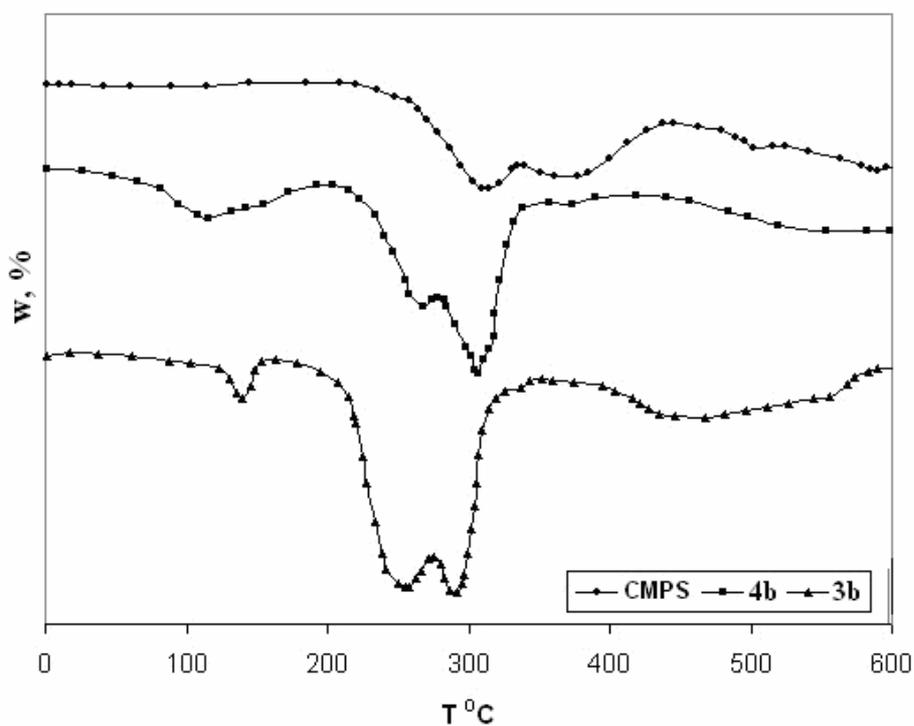


Fig. 2 – DTG curves for Chloromethylated Polystyrene, **4b**, **3b**.

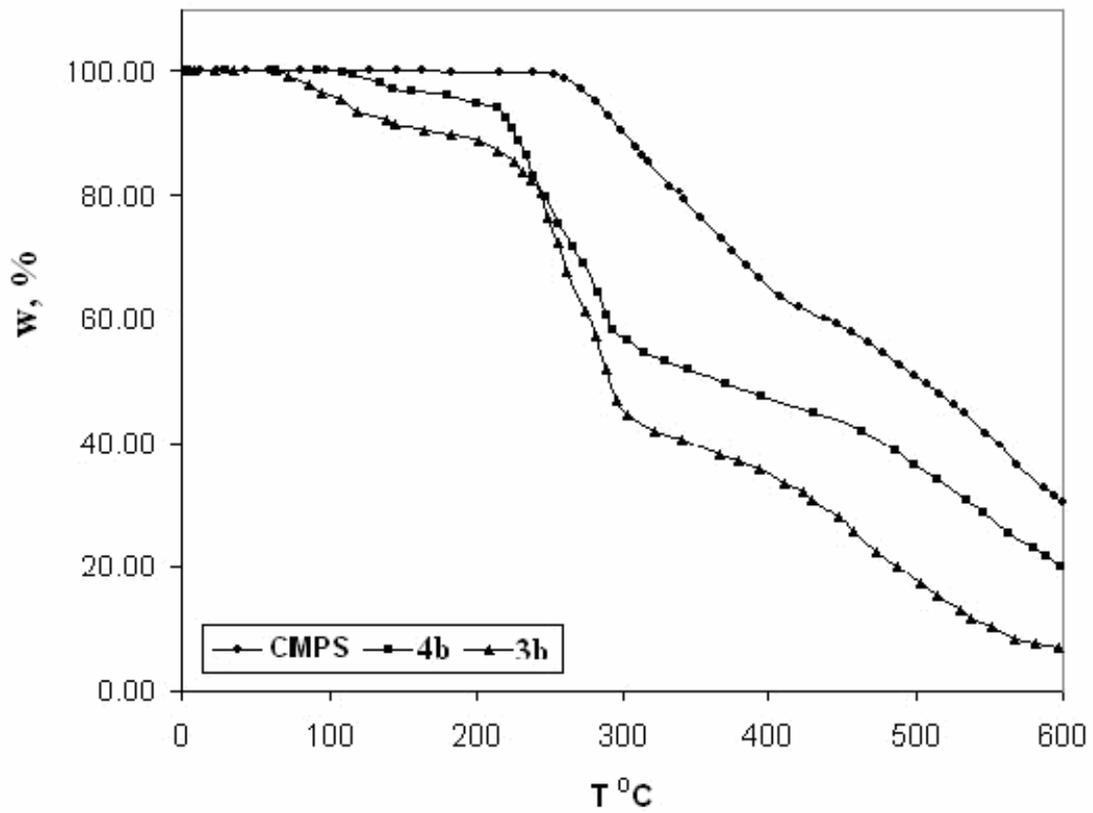


Fig. 3 – TG curves for Chloromethylated Polystyren, 4b, 3b.

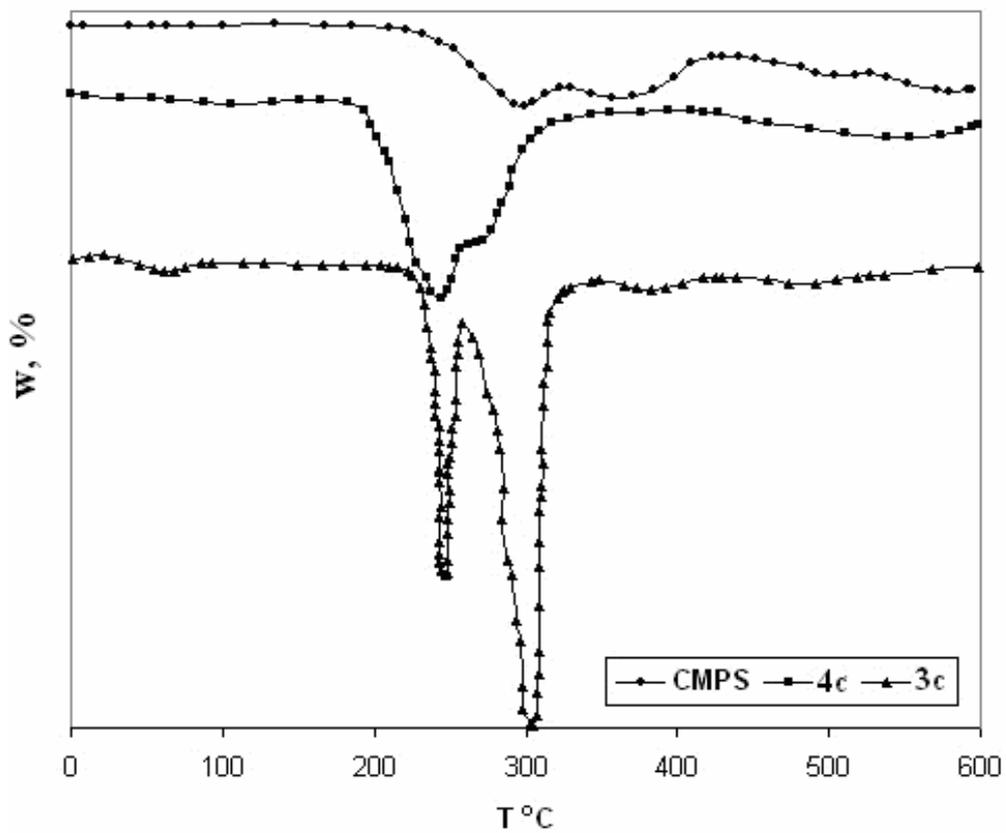


Fig. 4 – DTG curves for Chloromethylated Polystyren, 4c, 3c.

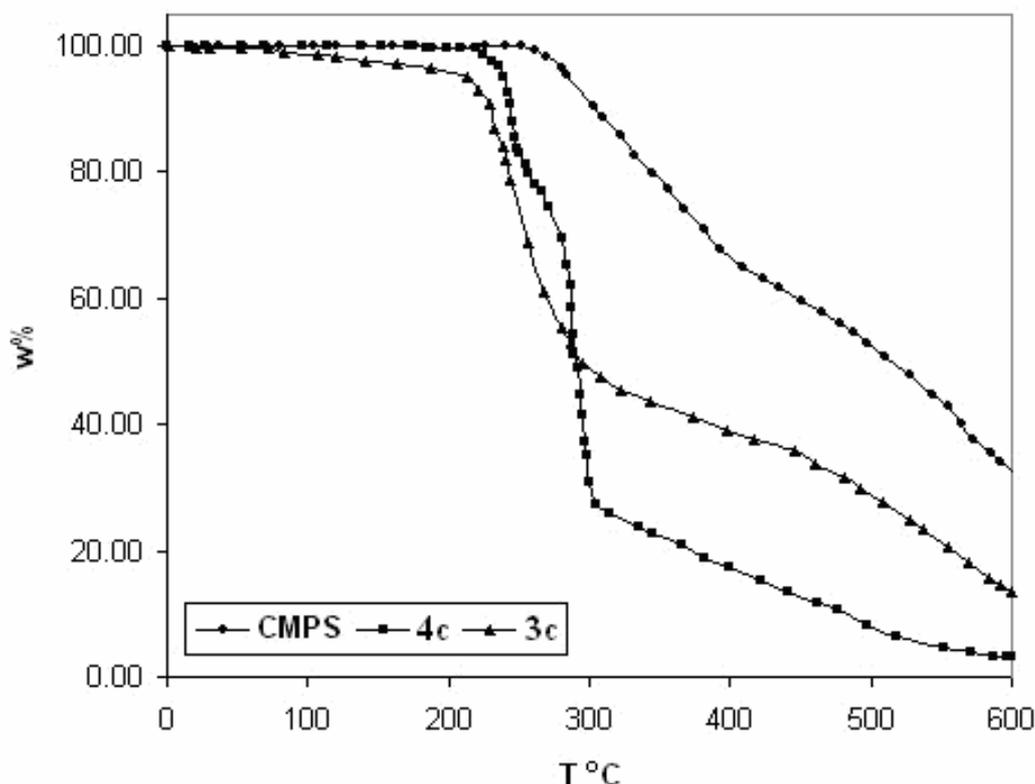


Fig. 5 – TG curves for Chloromethylated Polystyren, 4c, 3c.

Kinetic information can be extracted from dynamic experiments by means of various methods. A rigorous study was done by applying the method proposed by Vyazovkin<sup>14-16</sup>, which involved data obtained at least three heating rates (°C/min.): 5; 10; 20. The advanced isoconversional method proposed by Vyazovkin is free of these approximations because it is based on numerical integration, and it takes into account a possible variation in the activation energy. According to this method, for a set of  $n$  experiments carried out at different arbitrary heating programs  $T_i(t)$ , the activation energy is determined at any particular value of  $\alpha$  by finding the value of  $E_\alpha$  that minimizes the function:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (1)$$

In equation (1), the integral

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (2)$$

is evaluated numerically for a set of experimental heating programs. The minimization procedure is repeated for each value of  $\alpha$  to determine the  $E_\alpha$  – dependence.

The application of Vyazovkin's method confirmed the existence of correlation between the activation energy and the degree of conversion. Figs. 6-10 shows such results for PS containing viologen groups into side chain.

These results could be arranged into, narrow temperature intervals and it was observed that often the activation energy increases with the increase of the conversion degree. In agreement with figures 6-10, the dependence of activation energy on the conversion degree exhibits a variation comprised between 45 kJ/mol and 250 kJ/mol. This fact confirms the complexity of the degradation mechanism of PS with viologen groups into side chain. A different behavior was observed in case of sample 4d, which had the last two steps in other temperature intervals.

Table 1

Thermogravimetric data for polystyrene with pendent viologen groups (10 °C/min) 4a-4e

Sample	Step I				Step II				Step III				Step IV				Residue
	T <sub>i</sub> <sup>1)</sup> (°C)	T <sub>max</sub> <sup>2)</sup> (°C)	T <sub>f</sub> <sup>3)</sup> (°C)	W <sup>4)</sup> (%)	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	W (%)	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	W (%)	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	W (%)	
PS	–	–	–	–	–	–	–	–	240	375	600	82.5	–	–	–	–	17.5
CMPS	–	–	–	–	–	–	–	–	220	315	440	36.5	440	550	600	27.5	36
4a	53	60	120	10	120	140	210	9	210	310	330	27	330	470	550	50	4
4b	35	90	146	7.5	146	162	200	36.5	200	253	330	14.5	330	566	620	21.5	20
4c	55	105	130	14	130	164	204	6	204	288	390	53	390	487	540	24	3
4d	40	210	230	4	230	290	300	14	300	400	435	23	435	550	600	56	3
4e	50	80	140	20	140	170	230	10	230	310	380	31	380	545	600	36	3

1) T<sub>i</sub> = initial temperature of the decomposition process

2) T<sub>max</sub> = temperature corresponding to the maximal degradation rate

3) T<sub>f</sub> = final temperature of the decomposition process

4) W(%) = weight loss of the polymer after the end of the decomposition process

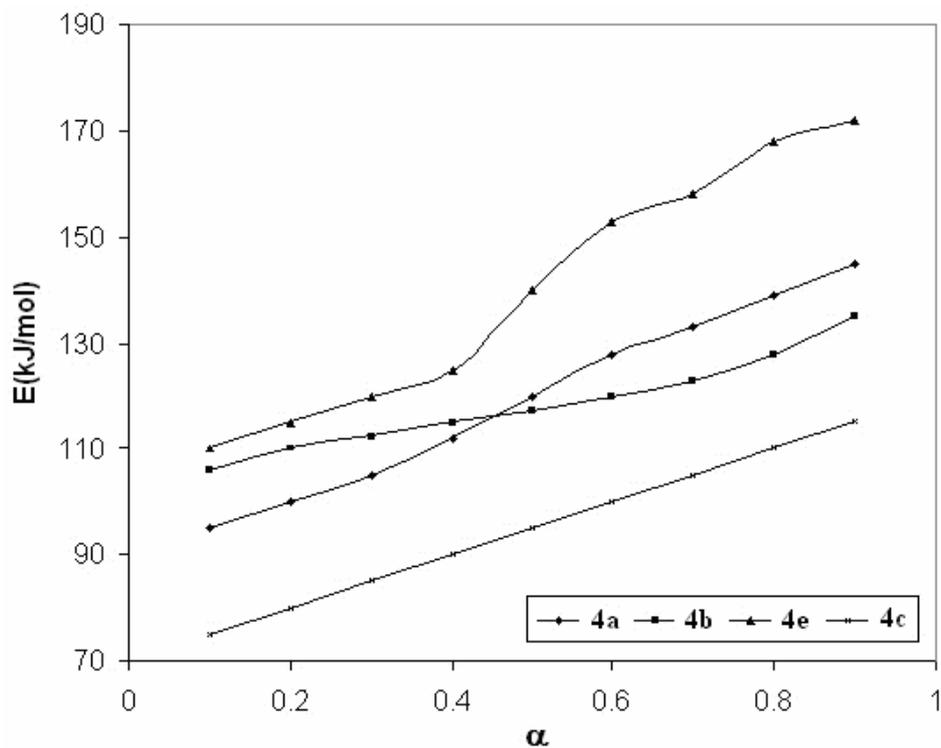


Fig. 6 – The dependence of activation energy *versus* conversion degree of the second process of polymer decomposition (some 120-200 °C).

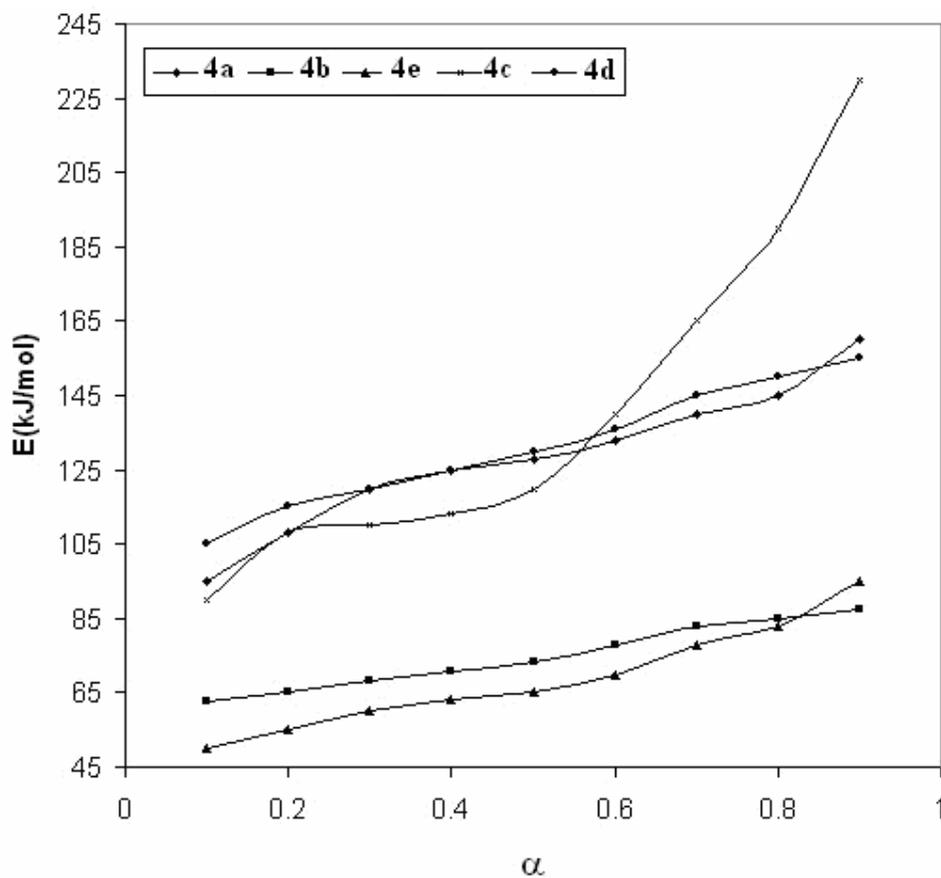


Fig. 7 – The dependence of activation energy *versus* conversion degree of the third process of polymer decomposition (some 200-300 °C).

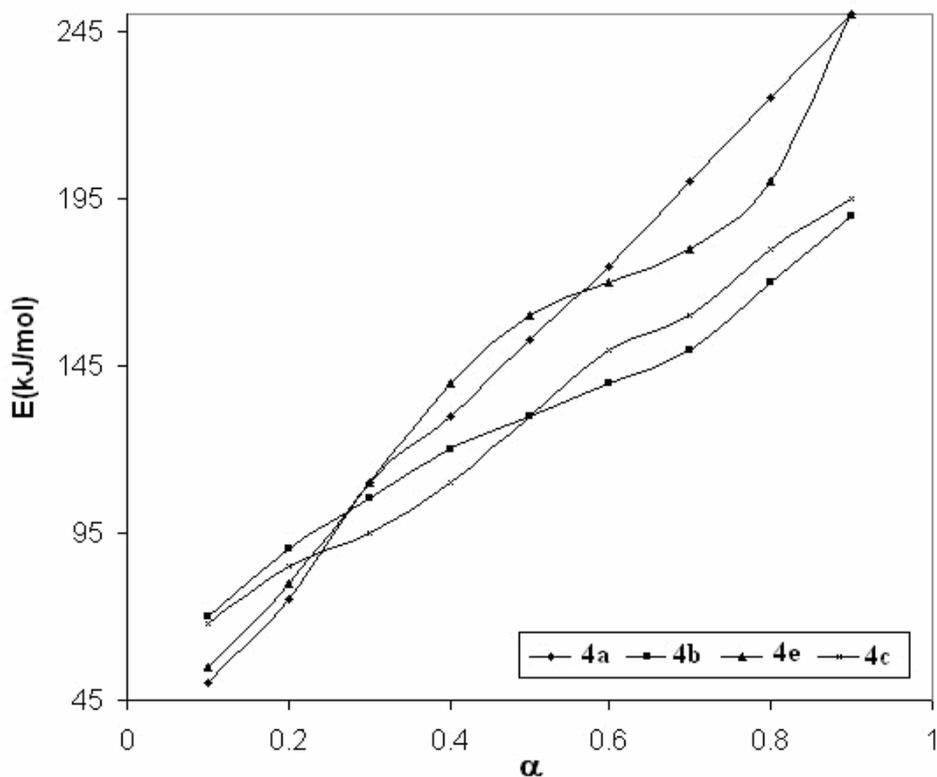


Fig. 8 – The dependence of activation energy *versus* conversion degree of the final process of polymer decomposition (some 350-600 °C).

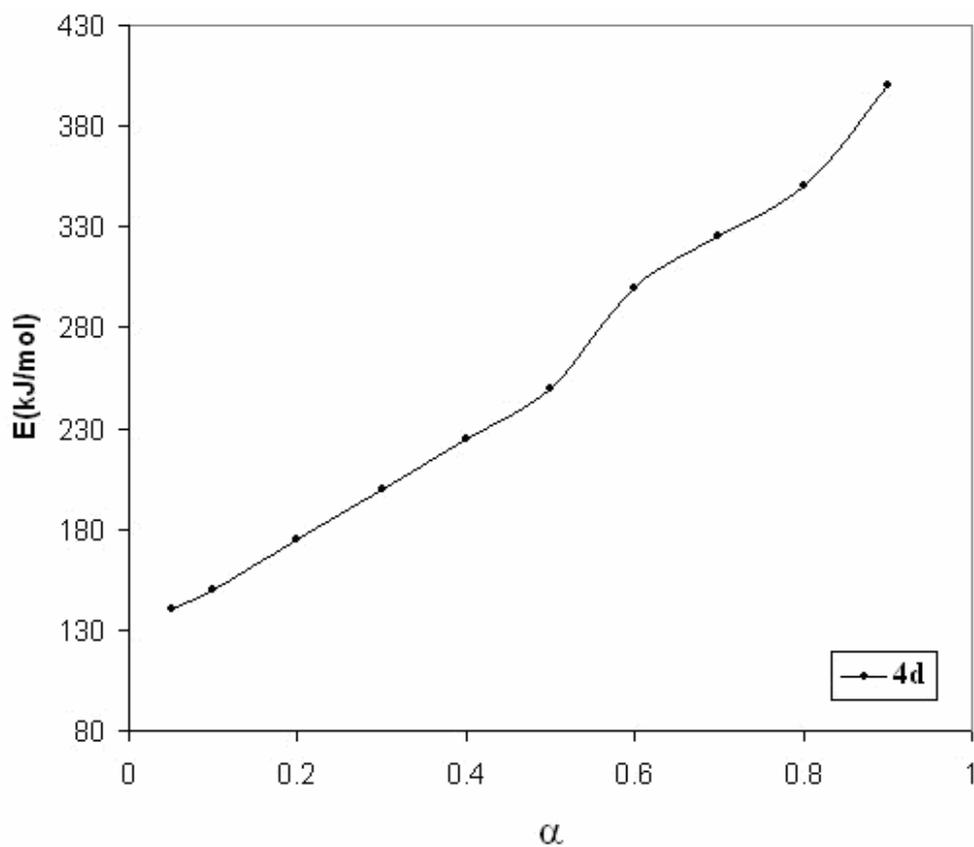


Fig. 9 – The dependence of activation energy *versus* conversion degree of the third process of polymer decomposition for sample **4d** (300-435 °C).

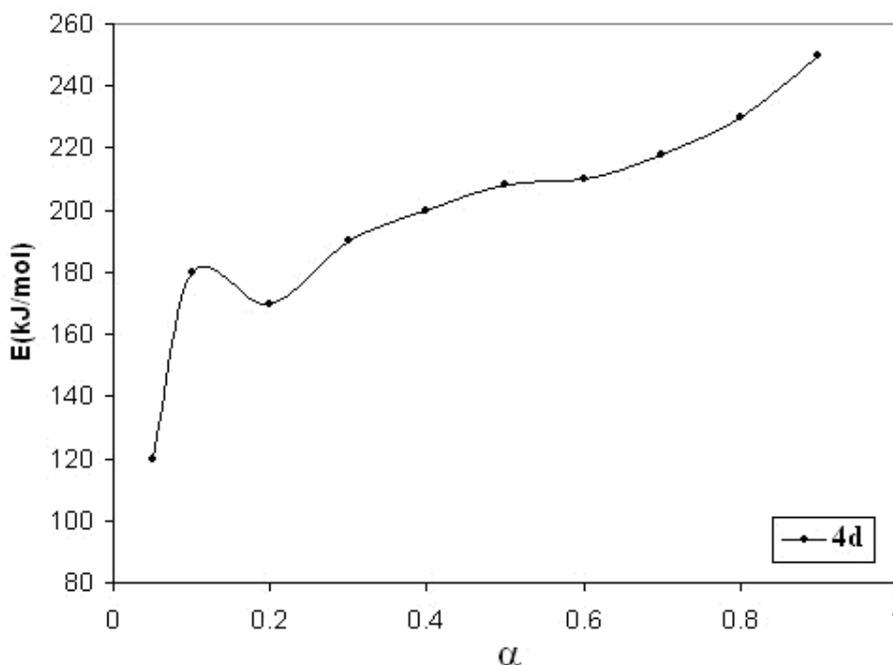


Fig. 10 – The dependence of activation energy *versus* conversion degree of the final process of polymer decomposition for sample **4d** (435-600 °C).

## EXPERIMENTAL

### Reagents and materials

Polystyrene (PS) was prepared by radical polymerization in suspension of styrene. Its numerical average molecular weight ( $\bar{M}_n = 41.000 \text{ g}\cdot\text{mol}^{-1}$ ) was determined by viscosimetry, in benzene at 25°C.<sup>17</sup> Chloromethylated polystyrene (CMPS) was synthesized by the reaction of polystyrene with a mixture of paraformaldehyde and trimethylchlorosilane.<sup>18</sup> The chlorine content (21.57 %) of the resulting chloromethylated polystyrene was determined by Schöninger's method.<sup>19</sup> The corresponding molar degree of substitution with chloromethyl groups, DS, was calculated using the equation:

$$DS = \frac{104 \times m_{Cl}}{35.45 \times 100 - 48.45 \times m_{Cl}}$$

where: 104 = molecular weight of polystyrene;  
 35.45 = atomic weight of chlorine;  
 48.45 = molecular weight of -CH<sub>2</sub>Cl functional group;  
 m<sub>Cl</sub> = weight of chlorine (gram) determined experimentally.

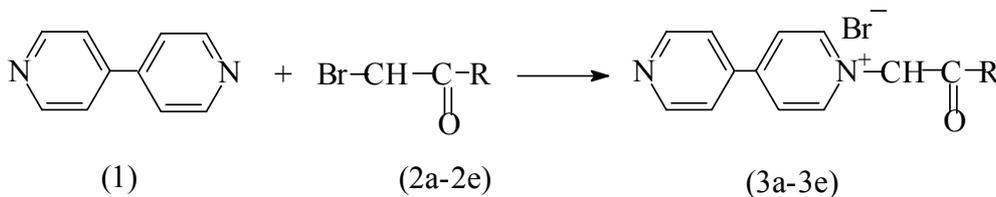
The presence of -CH<sub>2</sub>Cl groups was evidenced by the absorption band at 1260 cm<sup>-1</sup> in FTIR spectra, and an additional peak at 4.45 ppm in <sup>1</sup>H-NMR spectra.

### Synthesis of N-phenacyl (p-H, p-NO<sub>2</sub>, p-Cl) and N-acetoxyalkyl-4,4'-bipyridinium bromides (3a-3e)

The N-phenacyl(*p*-H, *p*-NO<sub>2</sub>, *p*-Cl)-4,4'-bipyridinium bromides (3a-3c) and N-acetoxyalkyl-4,4'-bipyridinium bromides (3d, 3e) were synthesized by reaction of the 4,4'-bipyridyl (1) with the *p*-substituted bromoacetophenone (2a-2e) as described in Scheme 1.

The 4,4'-bipyridyl (4,4'-bpy, Merck) was purified by recrystallization from diethylether, mp.110 °C; 2-bromoacetophenone (*p*-H, *p*-NO<sub>2</sub>, *p*-Cl) (Merck) were purified by recrystallization from benzene and petroleum ether. Methyl/ethylbromoacetate (Merck) were distilled under vacuum. Analytical grade acetone was distilled over K<sub>2</sub>CO<sub>3</sub>.

The N-monoquaternized derivatives of 4,4'-bipyridyl (3a-3e) were purified by multiple recrystallization from diethylether until the complete removal of the unreacted 4,4'-bipyridyl traces.



Scheme 1

R:	3a	C <sub>6</sub> H <sub>5</sub>	(4,4'-bipyridinium N-phenacyl bromide)
	3b	C <sub>6</sub> H <sub>4</sub> (p-NO <sub>2</sub> )	(4,4'-bipyridinium N(p-nitro)-phenacyl bromide)
	3c	C <sub>6</sub> H <sub>4</sub> (p-Cl)	(4,4'-bipyridinium N-(p-chloro)-phenacyl bromide)
	3d	OCH <sub>3</sub>	(4,4'-bipyridinium N-carbomethoxymethyl bromide)
	3e	OC <sub>2</sub> H <sub>5</sub>	(4,4'-bipyridinium N-carbomethoxyethyl bromide)

### Synthesis of N-phenacyl-4,4'-bipyridinium bromide (3a)

A solution of  $\omega$ -bromoacetophenone (2a) (1.99g; 10 mmol) in anhydrous acetone (10 ml) was added to a stirred solution of (1) (1.575g; 10.1 mmol) in anhydrous acetone (10 ml) at room temperature. The mixture was stirred for 3 h then kept at room temperature for 12 h without stirring. The resulted precipitate was filtered and wash three times with anhydrous diethylether (10 ml) to recover the unreacted reagents. Finally, the product was kept over  $P_2O_5$  under vacuum at room temperature for 48 h.

Analysis:

N-phenacyl-4,4'-bipyridinium bromide (3a): White-blue crystals, yield 88 %, mp. 203 °C.  $C_{18}H_{15}N_2OBr$ : calculated (%): C 60.84; H 4.22; N 7.88; Br 22.54; found (%): C 61.11; H 4.30; N 7.82; Br 22.34. IR (KBr,  $cm^{-1}$ ): 3050 ( $\nu_{C-H}$  aromatic); 1693 ( $\nu_{C=O}$ ); 1637, 1598, 1540, 1493 ( $\nu_{C=C}$ ,  $\nu_{C=N}$  aromatic).  $^1H$ -NMR (DMSO- $d_6$ , TMS)  $\delta$ : 9.216 (d, 2H, ortho  $>N^+<$ ); 8.90-8.65 (m, 4H, Ph-Ph); 8.175-7.65 (m, 5H, -Ph, 2H, ortho  $>N$ ); 6.55 (s, 2H,  $-CH_2-$ ).

N-(p-nitro)-phenacyl-4,4'-bipyridinium bromide (3b): Blue crystals, yield 93%, mp. 148 °C.  $C_{18}H_{14}N_3O_3Br$ : calculated (%): C 54.00; H 3.50; N 10.50; Br 20.00; found (%): C 54.25; H 3.73; N 10.77; Br 19.86. IR (KBr,  $cm^{-1}$ ): 3040 ( $\nu_{C-H}$  aromatic); 1703 ( $\nu_{C=O}$ ); 1635, 1596, 1481 ( $\nu_{C=C}$ ,  $\nu_{C=N}$  aromatic); 1528 ( $\nu_{NO_2}$  asym.), 1346 ( $\nu_{NO_2}$  sym.).  $^1H$ -NMR (DMSO- $d_6$ , TMS)  $\delta$ : 9.212 (d, 2H, ortho  $>N^+<$ ); 8.90-8.675 (m, 4H, Ph-Ph); 8.375 (m, 4H, -Ph); 8.05 (m, 2H, ortho  $>N$ ); 6.725 (s, 2H,  $-CH_2-$ ).

N-(p-chloro)-phenacyl-4,4'-bipyridinium bromide (3c): Pink-lilac crystals, yield 91%, mp. 270 °C.  $C_{18}H_{14}N_2OBrCl$ : calculated (%): C 55.45; H 3.59; N 7.19; found (%): C 55.73; H 3.81; N 7.33. IR (KBr,  $cm^{-1}$ ): 3050 ( $\nu_{C-H}$  aromatic); 1666 ( $\nu_{C=O}$ ); 1637, 1597, 1540, 1514, 1478 ( $\nu_{C=C}$ ,  $\nu_{C=N}$  aromatic);

1090 ( $\nu_{C-Cl}$  aromatic).  $^1H$ -NMR (DMSO- $d_6$ , TMS)  $\delta$ : 9.425 (d, 2H, ortho  $>N^+<$ ); 8.950-8.675 (m, 4H, Ph-Ph); 8.125-8.025 (m, 2H, 2H ortho  $>N$ ); 7.225 (d, 2H); 6.525 (s, 2H,  $CH_2$ ), 4.0 (s, 3H,  $-OCH_3$ ).

N-[1-(2-methoxy-2-oxo)ethyl]-4,4'-bipyridinium bromide (3d):

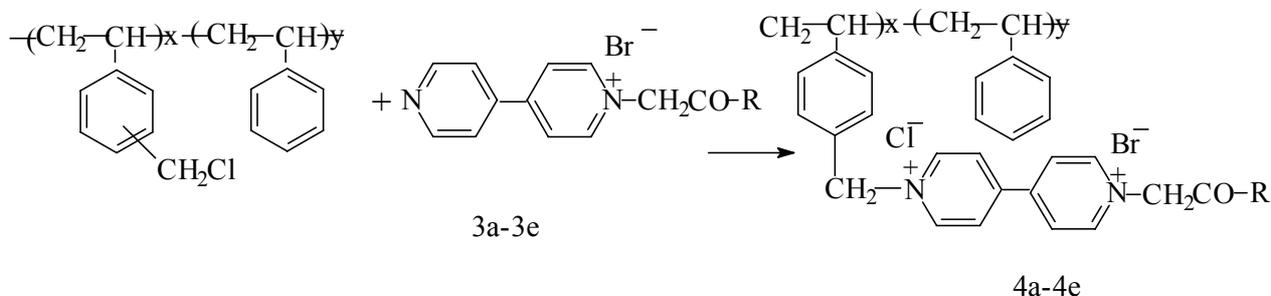
Beige crystals, yield 78%, mp. 176 °C.  $C_{13}H_{13}N_2O_2Br$ : calculated (%): C 50.42; H 4.20; N 9.06; Br 25.89; found (%): C 50.52; H 4.34; N 9.12; Br 26.02. IR (KBr,  $cm^{-1}$ ): 3040 ( $\nu_{C-H}$  aromatic); 1730 ( $\nu_{C=O}$ ); 1636, 1584, 1541, 1482, ( $\nu_{C=C}$ ,  $\nu_{C=N}$  aromatic); 1238, 1178 ( $\nu_{C-O-C}$  ester).  $^1H$ -NMR (DMSO- $d_6$ , TMS)  $\delta$ : 9.17 (d, 2H, ortho  $>N^+<$ ); 8.67 (m, 4H, Ph-Ph); 7.90 (m, 2H, ortho  $>N$ ); 5.87 (s, 2H,  $-CH_2-$ ); 3.85 (s, 3H,  $-CH_3$ ).

N-[1-(2-ethoxy-2-oxo)ethyl]-4,4'-bipyridinium bromide (3e):

Beige crystals, yield 72%, mp. 198 °C.  $C_{14}H_{15}N_2O_2Br$ : calculated (%): C 52.01; H 4.64; N 8.67; Br 24.76; found (%): C 51.78; H 4.71; N 8.72; Br 24.85. IR (KBr,  $cm^{-1}$ ): 3050 ( $\nu_{C-H}$  aromatic); 1722 ( $\nu_{C=O}$ ); 1635, 1597, 1580, 1478, ( $\nu_{C=C}$ ,  $\nu_{C=N}$  aromatic); 1240, 1182 ( $\nu_{C-O-C}$  ester).  $^1H$ -NMR (DMSO- $d_6$ , TMS)  $\delta$ : 9.17 (d, 2H, ortho  $>N^+<$ ); 8.65 (m, 4H, Ph-Ph); 7.92 (m, 2H, ortho  $>N$ ); 5.82 (s, 2H,  $-CH_2-$ ); 4.30 (m, 2H,  $-CH_2-$ , ethyl); 1.30 (s, 3H,  $-CH_3$ , ethyl).

### Synthesis of polystyrene with N-(p-H, p-NO<sub>2</sub>, p-Cl)phenacyl 4,4'-bipyridinium bromides and N-acetoxyalkyl-4,4'-bipyridinium bromides pendent groups

The polystyrene containing viologen groups was synthesized by quaternization reaction of  $-CH_2Cl$  reactive group in chloromethylated polystyrene with monoquaternary bromides of 4,4'-bipyridinium (3a-3e). The reaction proceeded in DMF at 40°C for 6 h, using a molar ratio of 1/1.2 CMPS/3a-3e (see Scheme 2):



Scheme 2

The reaction mixture was poured into acetone, filtered and washed three times with absolute methanol, to remove traces of low molecular reagent. Finally, the product was dried at 40°C for 48 h.

### Measurements

The FTIR spectra were recorded on a DIGILAB, Scimitar Series, USA Spectrophotometer. The  $^1H$ -NMR spectra were registered on a Jeol 80MHz spectrometer using  $CDCl_3$  and DMSO- $d_6$  as solvent and TMS as internal reference, respectively. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded on a Paulik-Paulik-Erdey-type Derivatograph, MOM made in Budapest in the following conditions: sample weight  $m_w = 50$  mg,  $Al_2O_3$  as reference material, quartz melting pot, heating rate

5 °C/min, 10°C/min and 20 °C/min in static air atmosphere, temperature range 20-600°C.

### CONCLUSIONS

The thermal stability of polystyrene with viologen groups into side chain depends on the nature of the viologen group. The evaluation of the kinetically parameters suggested that the mechanism of thermal degradation is complex, probably due to the presence of functional groups into side chain. The use of Vyazovkin's method

evidenced existence of correlation between the activation energy and the degree of conversion.

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