Thermogravimetric and Kinetics of Thermal Degradation of Powdered Laboratory Examination Gloves: 2. Analysis of Isotherm and Thermal Scan Traces from 307-455ºC

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Authors' contributions

This work was carried out in collaboration between all authors. Author NH designed and set-up the experiment, selected the materials, performed the experiment, operated TGA, and, analyzed the results, and wrote the first draft and finalized the manuscript. Author MM participated in performing the experiments, collected the data and reviewed the manuscript. Author SS participated in performing the experiments, collecting the data, and data analysis. Author CTL participated in experiments, and revision of manuscript, author MG participated in analysis of the data and literature searches. All authors read and approved the final manuscript.

ABSTRACT

The kinetics of pyrolysis of powdered laboratory safety examination gloves (PLEG) by the thermogravimetric analysis (TGA) was studied and the corresponding parameters were evaluated. The goal was to look for approaches to save the condensed energy within the PLEG wastes in

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order to reduce the environmental pollution caused by an ever increasing amount of laboratory safety examination gloves (LEG) in the landfills. The study was conducted in the Department of Biological and Physical Sciences at South Carolina State University (SCSU), Orangeburg, SC, USA, during the spring and summer of 2014. Twelve TGA experiments were performed on twelve samples of PLEG under three distinct conditions. From the thermal scans and isotherms, the highest rate of weight loss, the temperature at the maximum weight loss, the apparent order of reaction (wlo), the apparent rate constant (k) and the apparent activation energy of weight loss (Ea) were estimated. The experimental results confirmed keeping the PLEG in temperatures near to 340°C for a period of 30 min resulted in production of new materials with more thermal stability than the original PLEG.

ABBREVIATIONS

PLEG: powdered laboratory examination glove, LSG: laboratory safety glove, w: the non-vaporized mass percent of the materials in the TGA reaction pan, r: the rate of reaction, wlr: weight loss rate of reaction; wlo: weight loss order of reaction; PVC: poly(vinyl chloride); PMMA: poly(methyl methacrylate); PS: poly(styrene); PE: poly(ethylene); PET: poly(ethyleneterephthalate); RT: retention time, TIC: total ion chromatogram; GC-MS: gas chromatography-mass spectrometry, WHO: world health organization, Ea: activation energy, TGA: thermogravimetric analysis, kR =8.314 x 10³ j/mol.K; MR = 8.314 x 10⁶ j/mol.K

1. INTRODUCTION

This work is the continuation of the previous study [1] on the thermogravimetric analysis (TGA) of powdered laboratory examination glove (PLEG). The objective is converting chlorine-containing plastic waste materials, such as neoprene, into "clean fuels" and useful chemicals. In the previous paper, the thermal scans were analyzed; here, the thermal scans and isotherms were considered. Based on our previous experiments [2] and the results reported by other researchers, one possible process for recovering valuable chemicals and petrochemical products from plastic waste is the stepwise thermal degradation of recovered waste plastics [3]. This study reports the effects of temperature on the kinetics of thermolysis of PLEG, the one that is made of chloroprene rubber.

2. MATERIALS, INSTRUMENTATION AND METHODS

Materials, methods and instrumentation were described previously [1]. The experiments were carried out to investigate the PLEG decomposition under various temperatures and their impact on the kinetics of the pyrolysis process. Briefly, a Perkin-Elmer (USA) thermogravimetric analyzer (TGA-7) was used to study the thermal stability of the PLEG from 50°C to 850°C. The experimental tests, both under dynamic and isothermal conditions, were performed in the same thermogravimetric analyzer, TGA-7. The atmosphere was fluxed by argon with a flow rate of 10 mL min⁻¹. The heating rate in all dynamic experiments was kept at the maximum capacity of the TGA instrument, 200°C min⁻¹, starting from 50°C and rising to the first isotherm. The isothermal tests were performed in two steps. In first step, the sample was rapidly heated up (~ 200°C min) to the first temperature level (e.g. 310°C) and then the temperature was kept constant for 30 min. In succession, the temperature was rapidly increased to the second isothermal step (410°C, the highest decomposition rate of PLEG) and maintained for 30 min; successively, the temperature was rapidly increased to 850°C and maintained there for two min; this led to the complete degradation of the organic substances. The fast temperature ramps to the isothermal conditions did not show significant overheating.

The initial sample weights varied between 4 and 8 mg; however, in calculations, the weight was normalized to the weight percentage of the samples. The experimental data, such as time (min), sample temperature (°C), weight percentage of sample, and derivative of weight loss over time (dw/dt), were downloaded from

Pyris program to Microsoft Office for calculation, graphing, and word processing.

3. RESULTS AND DISCUSSION

Fig. 1a shows the thermograms of 12 samples of PLEG. The sample S340 that was kept for 30 min at 340°C obtained higher thermal stabilities than any other sample. This was due to the chemical changes in the structure of the material during 30 min at 340°C; such a change in thermal properties of PLEG was not observed for the other samples which were heated in other temperatures. The rate of weight loss of S340 at 410°C was slower than any other sample (Fig. 1). The remains of S340 at 475°C was about 40% of its original weight, while for the other samples at the same temperature the remaining reached below 30%. Residues of the PLEG at the other isotherms (S325 and S355) also produced some thermal stabilities but not comparable to the S340 (Fig. 1b).

Kinetics of Pyrolysis of PLEG

Fig. 1 shows the thermograms of thermolysis of powdered PLEG where the mass of PLEG (w) decreased by time and temperature. The thermolysis process can be described by a typical reaction (1) where w is the mass percent of reactants in the TGA reaction pan:

$$w \rightarrow Products \qquad (1)$$

The reaction rate, r, for a typical chemical reaction, such as reaction (1), with reaction order, n, rate constant, k, at the time, t, can be described by Eq (2):

$$r = -\frac{dw}{dt} = akw^n \qquad (2)$$

The logarithmic form of Eq 2 produces a linear function of Ln r versus Ln w:

$$Ln\ r = Ln\ ak + n\ Ln\ w \qquad (3)$$

Fig. 2 shows the double logarithmic plot of variation of the rate of weight loss, Ln r, versus Ln w for the eleven samples of PLEG. According to Eq (3), the slope of these graphs at any w represents the order of reaction, n, and the intercept of it represents the rate constant, ak. As the temperature of the isotherm increased, the rate of weight loss reaction (wlr) also increased. This was within expectations based on the

Arrhenius equation, Eq (4). Four samples that had their first isotherm under 380°C (S340, S355, S370, and S375-) had a very particular form in the double logarithmic plot (Fig. 2) due to small weight loss.

Analysis of the first thermal scans. The entire range of thermal scan did not follow Eq (3) as was expected for a pure compound. Fig 3 represents the variations of Ln r versus Ln w for the portion of thermogram belonging to the first temperature scan, prior to the first isotherm process for 11 samples of PLEG. This portion of the diagram was not very visible in Fig. 2, so it was expanded for proper analysis (Fig. 3).The variation of Ln r versus Ln w of the thermal scans below 370°C had the common feature of an "N" form. At the initial state of thermal scan, as the temperature increased above 100°C, the weight loss reaction rate (wlr) decreased to a minimum. The weight loss order (wlo) was a large positive number although the amount of weight loss was below 1% of the reactants. As the temperature increased, the amount of reactants (ln w) decreased; suddenly, there was a change in course of wlr, creating a second trace. In this step the wlo value (the slope of the line fitted by list-square into experimental data) was a large negative number. The wlo at the max and min points was zero. Afterward, the wlr decreased by increasing Ln w; in this stage, the wlo values were large positive numbers for S310, S325, S340 and S355. The wlo decreased as the temperature of isotherm increased. This behavior was more pronounced in the first four samples where their thermal scans were below 355°C. The first two sections were compressed in the samples that were heated to temperatures above 370°C due to rapid weight loss (Fig. 3). Therefore, the variation of Lnr versus Lnw, instead of being one straight line as was expected; it has segments of straight lines. The slops of each segment vary depending on the initial and final temperature. Therefore, there were many n values instead of one single n. Each n value was related to a particular reaction. Thus, there are many concurrent reactions instead of one single reaction.

The end of the third trace, at temperatures above 370°C, looked like a concave upward curve, and it was the bearer of the highest wlr. Near to the end of thermal scan, the tail converged to form a plateau where the slope of the tangent line to it was zero. As weight loss increased, the values of slope increased; it initiated with a large negative number and ended with a positive number. The

different shapes of the curve indicate that different type of decomposition and polymer modification chemical reactions were taking place at each given temperature. Identification of these type of reactions, products related to them at a given temperature is essential for a product driving pyrolysis process.
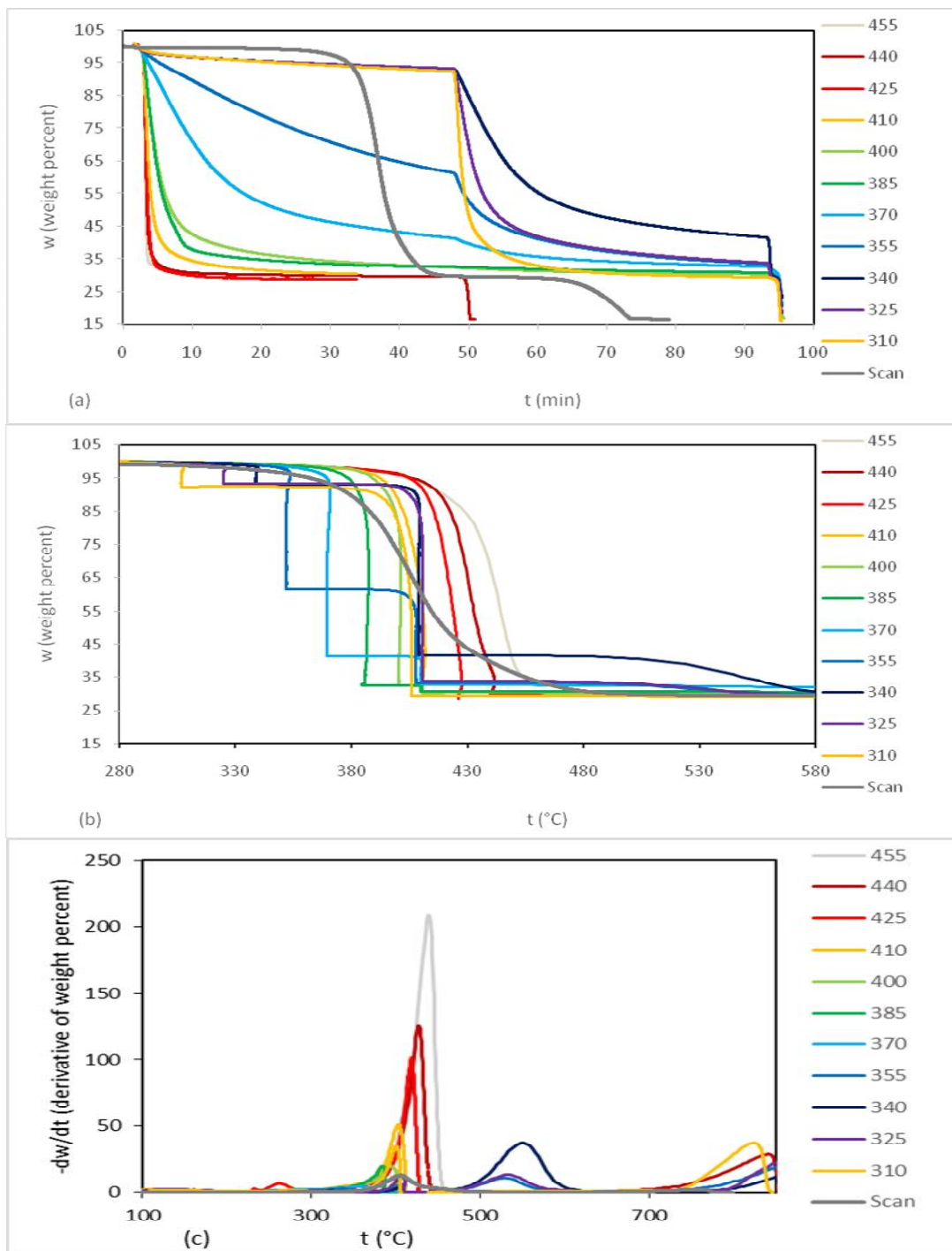
Fig. 1. Thermogravimetric analysis of 12 samples of PLEG: (a) weight-loss versus time; (b) weight loss versus temperature, and (c) rate of weight loss with time (-dw/dt) versus temperature.
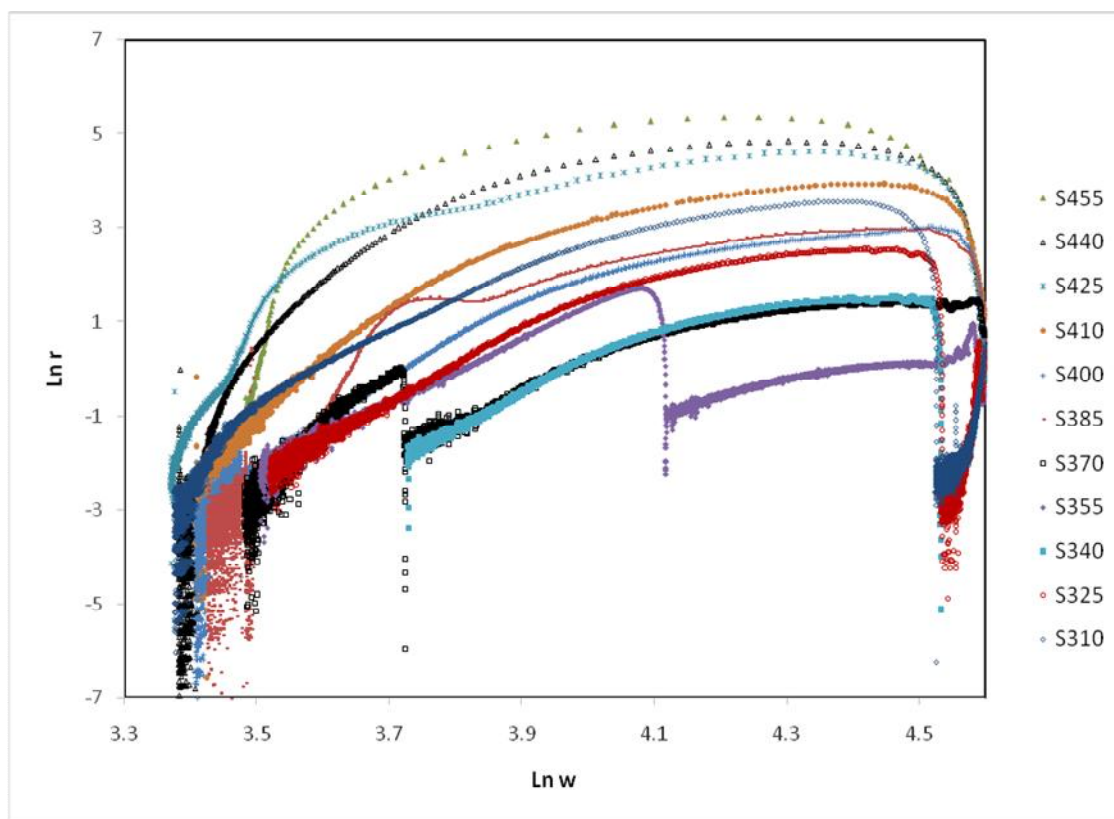
Fig. 2. Double logarithmic variation of wlr versus w (Ln r versus Ln w), according to Eq (3) for 11 samples of PLEG.

The wlr that reached to its maximum at temperatures 100°C < t < 200°C may be related to evaporation of the trapped moisture in the PLEG complex network or compounds resulted from decomposition of PLEG ingredients and other volatiles used to manufacture the PLEG besides the essential oils added for a pleasant aroma. As the temperature increased (200°C< t < 273°C), more volatile components of PLEG were released which caused the wlr increased and reached its max, where negative values of wlo were observed. A large scale pyrolysis of PLEG indicated that the composition of very first condensate drops were water, hydrochloric acid, CO_2, NO, C2 to C5 hydrocarbons, and phthalic acid esters and its derivatives [2].

The detailed study of each of these samples follows:

S310. The sample was heated with a rate of 200°C/min from room temperature to 307°C, maintained for 30 min in 307°C, and then heated (200°C/min) to 407°C and held there for another 30 min. Fig 4 shows the plots of variation of rate of weight loss of the isotherms and thermal scans according to Eq (3) for S310.

S310: Thermal Scan 100-307°C. The thermal scan from 100-307°C produced three traces with wlo (slope) positive, negative, and positive (Fig 3 S310). The decrease of wlr (114-212°C) resulted in high value of wlo ~ 252. At the minimal of wlr, the wlo was zero (212°C). The next trace (213-271°C), the wlr was increased regularly, the wlo was a high negative value (-495). Again, around 272-273°C (the max of wlr), the wlo was zero. The decrease of wlr began around 273°C and continued to the end of scan at 307°C. The wlo value of the third trace (274-308°C) was very high (109). The length of thermal scan (100-308°C) was about 2.5 min, the amount of weight loss (1.5%) was small. Table 1 summarizes the important points of pyrolysis such as the initial and final time, the time of process, the initial and final temperature, the change in temperature, the initial and final weight of sample, the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S310.
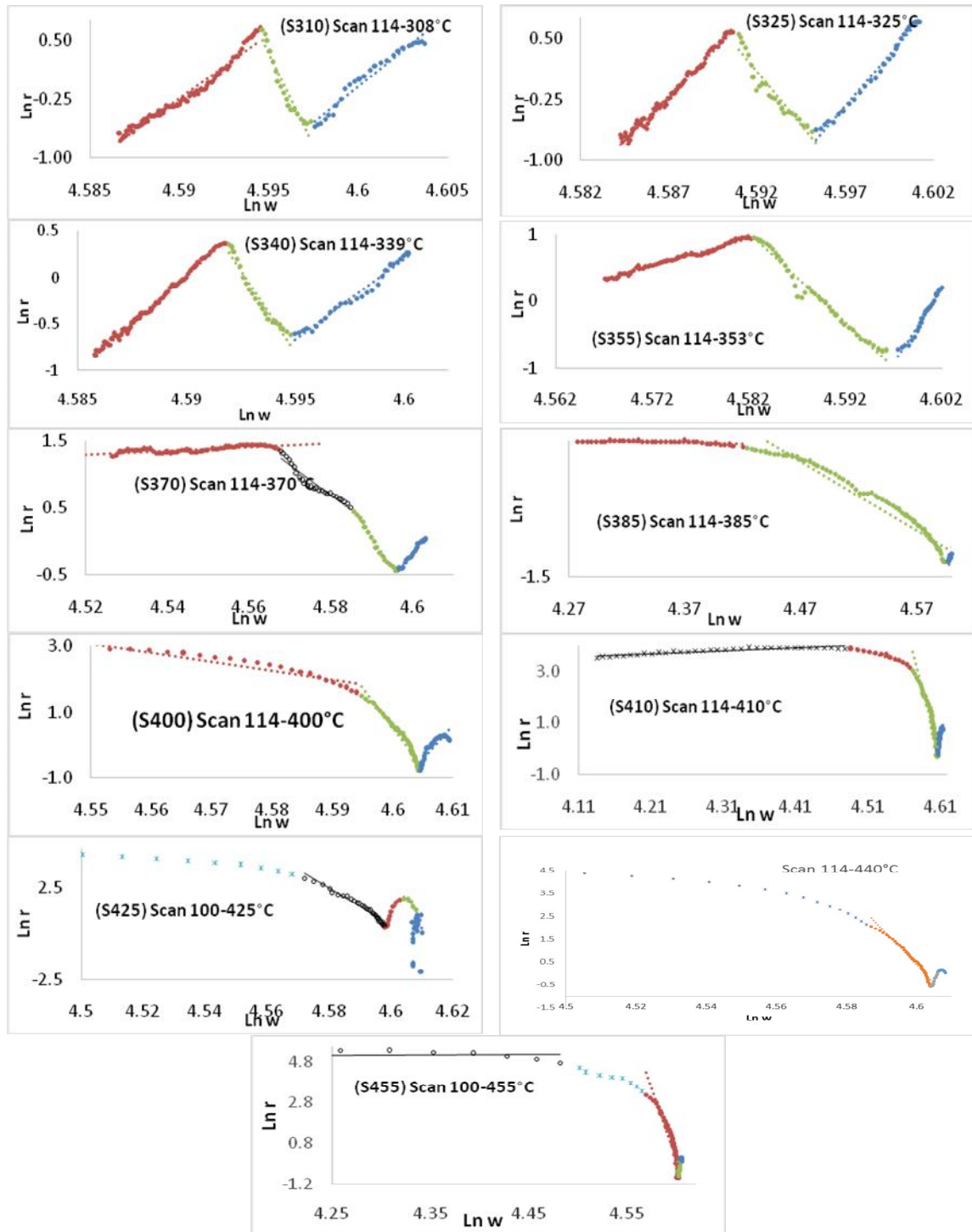
Fig. 3. Variation of Ln r (-dw/dt) versus Ln w (weight percent) of 11 samples of PLEG from 100°C to the isotherm temperatures. The temperature range and the sample name is indicated on each plot.
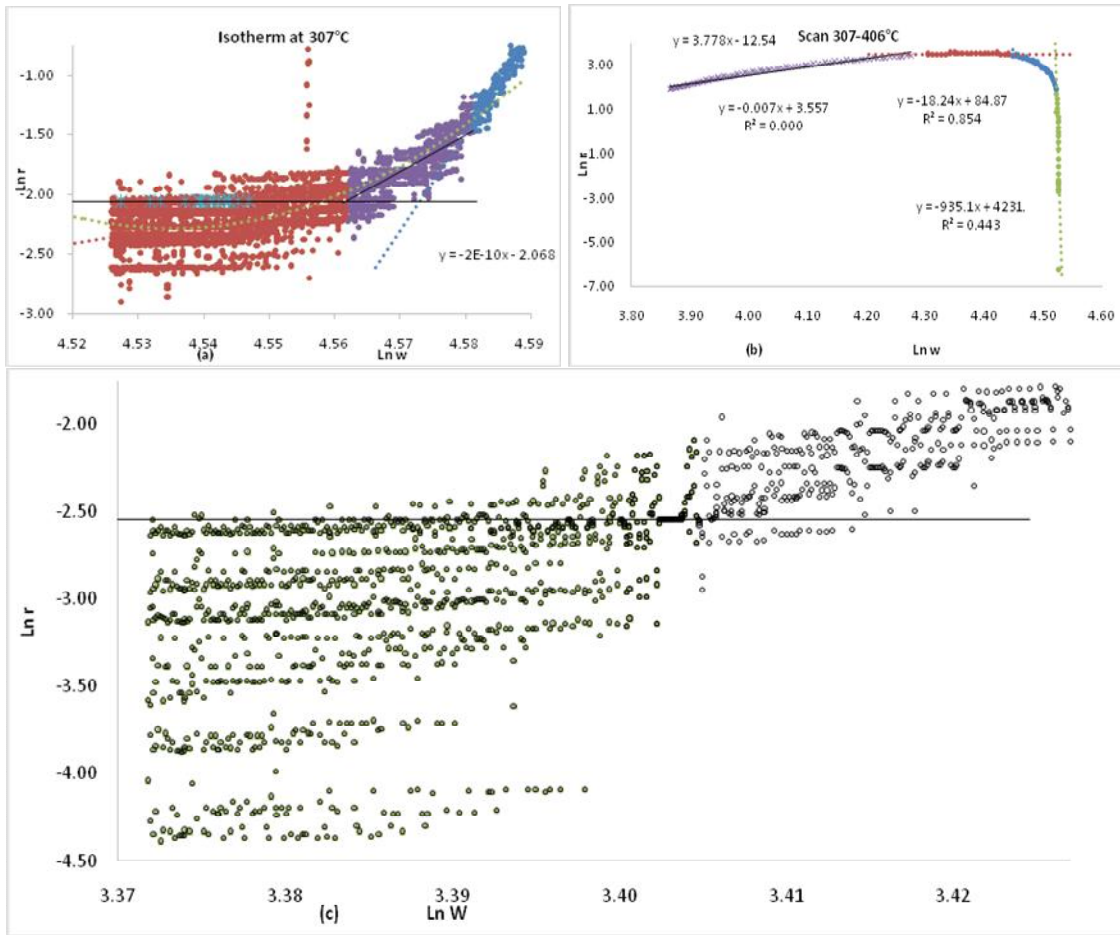
Fig. 4. Variation of Ln r versus Ln w for S310. (a) Isotherm at 307; (b) thermal scan from 307°C to 406°C; (c) expansion of the tail of isotherm at 407°C.

Table 1. The initial and final time, the time of process, the initial and final temperature, the change in temperature, the initial and final weight of sample, the weight loss amount, the wlo, and Ln ak resulted from TGA analysis of S310.

Time (min)			Temperature (°C)			Weight Percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
1.70	2.12	0.42	114	212	98	100.42	99.96	0.46	252	-1161
2.13	2.42	0.28	215	271	56	99.95	99.68	0.27	-495	2280
2.43	3.85	1.42	274	308	34	99.64	98.42	1.22	109	-501
3.87	5.53	1.67	308	308	0	98.41	97.81	0.61	88.2	-405
5.55	17.18	11.63	308	307	-1	97.80	95.76	2.04	33.4	-155
17.20	45.33	28.13	307	307	-0.04	95.76	92.56	3.20	9.33	-44.60
45.35	47.23	1.88	307	307	0.02	92.56	92.37	0.19	0.25	-3.44
47.25	47.92	0.67	307	378	71	92.37	91.98	0.39	-935	4231
47.93	49.22	1.28	380	405	25	91.87	58.10	33.76	-0.14	-5
50.32	64.90	14.58	406	406	0	46.55	31.32	15.23	8.27	-30
73.23	92.82	19.58	406	406	0	30.19	29.22	0.97	35.1	-122

S310: Isotherm at 307°C. The first isotherm of S310 was at 307° C for 30 min, where about 6% of total weight loss was observed. The wlo was started with the value of 88 and it decreased slowly to 33 when a kind of plateau was

observed at the end with a slope near to zero (Fig. 4a, Table 1).

The plot presented two major irregularities: First, the experimental data points were not following a simple line as was the theoretical expectations, and second, the values of wlo do not appear to be within the values of a reaction order, since in a solid and liquid state a reaction order over 3 is rarely ever expected. Another concern centered on the variety of chemicals presented in the scene of reaction (TGA pan), a mixture of a wide range of chemicals, both original components of the PLEG and products of degradation of PLEG during thermolysis. A close analysis of the experimental points indicates that their orientation is not a merely random distribution (Fig. 4c). Many of the experimental points are oriented together forming parallel straight lines with the value of slope near to zero (similar wlo), but their intercepts (ak values) are different from each other. Therefore, the best hypothesis is that the value of ak of wl for the chemicals under TGA conditions is different while their wlo are near to zero. Filtering the data, regrouping and adjusting a list-square regression line to the experimental points that had similar visual trend, yields the wlo and ak for each separated hypothetical reaction. The kinetics characteristics of 28 hypothetical parallel reactions, such as the values of wlo, initial weight of sample (wi), final weight of sample (wf), and the amount of weight loss(δw) of pyrolysis of S310 at 307°C were summarized in Table 2.

The existence of these hypothetical chemical reactions also could be confirmed by referring to a previous work, where total ion chromatogram (TIC) obtained by gas chromatography mass spectrometry (GC-MS), of any samples of PLEG pyrolysis, showed over 150 chemicals [3,4,5]. Postulating many chemical reactions at high temperatures for pure polymeric materials has been reported by other researchers [eg 6]. For example, Kruse et al. [6] presented a detailed mechanism of PS pyrolysis based on population balance equations and the method of the moments in which up to 93 species and 4500 reactions were used to describe product distribution and average molecular weight. Similarly, detailed kinetics models of polyethylene (PE), polypropylene (PP) and PS pyrolysis were presented and discussed by other researchers [eg 5,7]. In fact, the considerable attention given to plastic waste has seen several research projects focusing on the thermal degradation of plastic blends and their mutual interactions [8,9,10]. These results do not completely agree since each research group depending on their particular interests focused on different effects. Postulating many simultaneous reactions at higher temperatures, such as in the case of reactions shown in Tables 2, is also in line with the work of other researchers [10]. For example, the researchers who studied the decomposing of polymer mixtures [11] discovered that the pyrolysis of' a particular polymer in a polymeric mixtures behaves quite similarly to the pyrolysis of a pure polymer. Thus, the additive rule was applicable to the pyrolysis of a mixture of polymers. Therefore, the pyrolysis of PLEG, which made of a mixture of many chemical ingredients, will be similar to pyrolysis of each individual ingredient of the sample.

S310: Thermal Scan 307 to 406°C. At the beginning of the thermal scan from 307-410°C, the wlr increased exponentially, which led to the decrease of the wlo to a high negative value (~ -935, 11th column Table 1). The wlr reached a maximum at 399°C, about 7°C before ending the heating scan. As the temperature increased, the wlr became slower; a plateau was observed with wlo near to zero around 398°C < t <403°C, 75< w <85. The plateau with wlo of zero covered 10% of the total weight loss of sample. As thermal scan continued, the wlr decreased slowly, hence, the wlo increased gradually. At the end of the thermal scan, the wlo ~ +3 was observed. The reaction order, one and two, in the liquid and solid state are well understandable, while higher orders are not so easy to interpret, particularly, when it is about simultaneous decomposition and vaporization of many compounds. This kind of behavior was observed for all 11 PLEG samples (Fig. 2). It was interpreted as simultaneous combination of many reactions at the same time rather than one simple decomposition reaction (for details see S310: Isotherm at 307°C).

S310: Isotherm at 406°C. The highest weight loss of the S310 (63%) happened when it was held at temperature 406°C for 30 min (10th column Table 1). The maximum value of wlr of this sample at 406°C was smaller than the maximum values of wlr of the other samples that were held at 410°C (Fig 2). This behavior was related to the differences in the thermal history of samples. Moreover, heating the sample for 30 min at 307°C caused internal structural changes that triggered the reduction of the wlr of sample at 406°C. These kinds of thermal retardation caused by recombination of materials at higher

temperature were also observed for other samples, particularly S340.

The pyrolysis rate for a fare section of thermogram 84.9 <w% < 31.3 of S310 pyrolysis could be described by equation,

$wlr = -5.123 (Ln\ w)^2 + 45.306(Ln\ w) - 96.634$, with $R^2 = 0.9964$.
$wlo = -10.246 (Ln\ w) + 45.306$.

The above equations cover part of thermal scan above 398°C and about half of isotherm, (15 min). The wlo in this trace began with a value near to zero (-0.2) and increased ending with wlo ~10.

Therefore, S310 isotherm process inherited the wlo ~3 from previous thermal scan as the base value; then wlo by starting the isotherm began to increase in response to the decreases of wlr which was within expectations. The wlo at the end of isotherm reached ~+34 (11th column, Table 1).

A close inspection of an expanded section of the end of the isotherm (similar to Fig. 4c) showed a parallel array of many sets of experimental data that lined together forming a straight lines with a slope near to zero or very low values such as 1 or 2, but with different values of intercepts. Similar to the previous section, the experimental points that were aligned in straight lines were taken as references for a concurrent reaction. By this method, over 43 different reactions were recognized.

Table 2. The values of slope (wlo), the intercept (Ln ak), initial weight of sample (wi), final weight of sample (wf), and the amount of weight loss (δw) for the hypothetical weight loss reactions of PLEG during the isotherm 307°C.

Reaction	Wlo	Ln ak	wi	wf	δw
1	0.62	-7.43	29.25	29.50	0.26
2	0.67	-7.53	29.24	29.63	0.39
3	0.41	-6.34	29.28	29.22	0.06
4	0.24	-5.15	29.24	29.26	0.02
5	-0.24	-3.44	29.22	29.34	0.12
6	-0.62	-0.90	29.80	29.37	0.43
7	-0.15	2.13	29.43	29.44	0.01
8	0.19	-4.35	29.24	29.22	0.02
9	0.61	-6.18	29.30	29.30	0.00
10	0.51	-8.69	29.36	29.57	0.21
11	0.25	-4.14	29.61	29.72	0.11
12	0.97	-8.59	29.47	29.50	0.03
13	0.05	-3.39	29.31	29.74	0.44
14	-0.32	-2.08	29.83	29.28	0.55
15	1.00	-6.47	29.59	29.25	0.34
16	0.73	-5.56	29.41	29.49	0.07
17	0.01	-9.70	29.43	29.92	0.50
18	-0.71	-0.55	29.99	29.23	0.76
19	0.17	-3.47	29.52	29.51	0.01
20	0.84	-5.68	29.62	29.91	0.28
21	1.19	-7.59	29.30	29.85	0.54
22	0.63	-6.44	29.88	30.02	0.15
23	-0.65	-0.43	29.69	29.51	0.18
24	-0.23	-1.81	29.37	29.38	0.01
25	0.30	-3.58	29.71	29.98	0.27
26	0.23	-3.29	29.84	30.02	0.18
27	0.49	-8.89	29.98	30.08	0.09
28	0.25	-3.16	30.18	30.05	0.13

Evaluation of Ea by k and T. Arrhenius (Eq 4) related the rate constant, k, to the activation energy of reaction E_a, the absolute temperature of the reaction T, the ideal gas constant, R = 8.314 J mol^{-1} K^{-1} and another constant such as z to describe the efficiency of the molecular collisions in a chemical reaction.

$$k = ze^{-\frac{E_a}{RT}} \qquad (4)$$

The logarithmic form of Eq (4), linearly relates Ln k to the inverse of temperature, 1/T (K):

$$Ln\ k = Ln\ z - Ea/RT \qquad (5)$$

Fig. 5 represents the application of Eq (5) to the data tabulated in the Table 1 (assuming a = 1); the initial and final temperatures (5th and 6th column) of each trace and the Lnk value belonging to that particular trace (12th column). The slope of the line fitted to these data represents Ea/R value for the weight loss process according to Eq (5). The highest values of k belonged to initial interval of each thermal scan, for example, the intervals of 215-271°C and 307-378°C of S310. The k value of thermal scan of the trace at 114-212°C was the lowest k values in the Table 1, although it was in line with the other two highest k values (Fig. 5). The slopes of lines fitted to these three extreme values of k (both negative and positive, Fig. 5) represent the values of -Ea/R (9.9 to 9.5 MR) for

the weight loss. These values are about five to eight times higher than the slopes of the lines representing the other k and T data (1.12 to 1.3MR). Ignoring the results of the thermal scan from 112-307°C (because of low value of weight loss), the Ea/R = 21 -24 kR (~232 kj/mol) was obtained. The obtained Ea (~232 kj/mol) at temperatures below 410°C can be related to the decomposition of PLEG by break of Cl-C bonds (331 kJ/mol at 25°C) and C-C single bond (346 kJ/mol) by radical mechanism. Ea ~ 232 kj/mol is smaller than the energy required for radical initiation reaction of neoprene at room temperature, but not at higher where enough thermal energy was available. The higher values of Ea was related to decomposition of PLEG by chain scissoring of CC bonds (346 single bond and 602 C=C both in kJ/mol).

Table 3 summarizes the values of Ea obtained for eleven samples of PLEG from the graphs similar to the Fig. 5. One set of Ea values was calculated using initial temperature, and another set of Ea values was calculated considering the final temperature. Also, since the extreme values of k were arranged into a line by themselves, they resulted in another set of Ea values which represented the extreme values. Each trace of the data had two temperatures, initial and final, for each sample two trends were observed (Fig. 5) and the Ea was evaluated and tabulated in the Table 3.
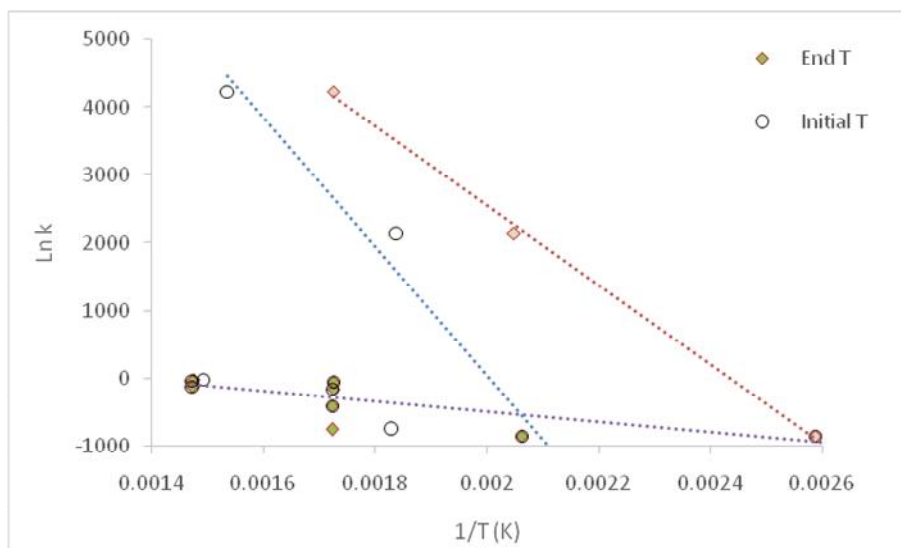
Fig. 5. Variation of the values of the Ln k of weight loss of S310 versus invers of initial and final temperatures (1/T in 1/K, data Table 1)

Table 3. Ea obtained from the slope of variation of Ln k versus 1/T (K) (Fig 5).

	Lower values of k		Higher values of k	
Sample	Initial T	Final T	Initial T	Final T
S310	1.04	0.80	6.27	10.04
S325	1.78	1.47	17.57	38.55
S340	2.56	2.57	42.17	69.49
S355	1.27	0.39	3.13	4.09
S370	-0.02	0.02	20.67	29.81
S385	1.07	2.67	1.36	2.80
S400	0.82	1.72	3.30	4.67
S410	0.57	1.09	2.16	1.96
S425	2.13	4.88	-	--
S440	0.33	0.31	1.09	0.86
S455	0.33	0.02	0.52	0.84

The values of Ea obtained from the slope of extreme k values were about 5-9 times higher than the values obtained using lower k values. Considering the lower k values belong to the regions that most significant weight loss of materials was observed. Thus, such Ea could be related to the weight loss of sample by vaporization alone, not including any chemical reaction. Contrary to the extreme k values which belonged to the region that the materials in the TGA pan were undergoing internal changes such as decomposition, rearrangements, and other possible chemical reaction including a significant vaporization. An important factor that must be recognized is the inaccuracy of the k values. One of the factors that make the value of k inaccurate is the assumption a =1.

As the temperature of the isotherm experiment increased, the values of Ea of extreme k and the middle one approached each other as it was expected (Table 3).

S325. This sample was (200°C/min) from room temperature to 325°C, retained for 30 min at 325°C, then heated (200°C/min) to 411°C and held there for another 30 min. The variation of Ln r versus ln w of this sample was similar to the previous one (Figs. 2 and 3). Table 4 summarizes the initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k of S325. After S325 was held for 30 min at 411°C, detained 33.8% of its mass, contrary to the S310 which after being held for 30 min at 407°C, retained 29.2% of its mass. Therefore, heating the PLEG in certain temperatures above 325°C produced new materials (4.4%) that are more thermally resistant than the original compounds; such as this case S325 produced about 4% materials that were more thermal resistant than original sample (Table 4).

The highest wlr of S325 was at ~533°C, while for the previous sample (S310) the highest wlr was observed at ~402°C. The tails of the isotherms at 325°C and 411°C were similar to the tails of S310; therefore, to include a separated analysis here was omitted.

Table 4. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S325.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
1.62	2.10	0.48	109	225	116	100	99.69	0.55	247.9	-1140
2.10	2.50	0.40	225	300	76	99.69	99.30	0.39	-272.7	612
2.53	3.77	1.23	300	325	25	99.33	98.17	1.16	217.7	-746
3.80	5.47	1.67	325	325	0	98.16	97.59	0.57	83.7	-385
5.48	17.12	11.63	325	325	-1	97.58	95.81	1.77	50.7	-234
17.13	42.37	25.23	325	325	0	95.80	93.63	2.17	15.7	
42.38	47.18	4.80	325	325	0	93.63	93.28	0.35	-0.1	-74
47.20	47.87	0.67	325	382	57	93.28	93.20	0.08	-4136	18757
49.38	48.20	-1.18	410	403	-7	93.18	91.41	1.76	-67.3	16109
48.20	48.63	0.43	403	409	5	91.07	85.96	5.11	-3.0	16
48.88	51.53	2.65	411	411	0	82.87	57.84	25.0	2.2	-7
48.90	51.55	2.65	411	411	0	82.66	57.74	24.9	2.2	-7
51.53	92.53	41.00	411	411	0	57.84	33.80	24.0	7.9	-30

S340. This sample was heated (200°C/min) from room temperature to 340°C, kept for 30 min at 340°C, then heated (200°C/min) to 409°C and held there for another 30 min. The variation of Ln r versus Ln w for this sample was also similar to the previous samples (Fig. 2). Table 5 summaries the initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S340. At the end of 409°C isotherm 41.7% of materials remained contrary to the previous samples, S310 and S325. For example, the remaining of S310 after being hold for 30 min at 410°C was 29.2% and of S325 was 33.8%. This suggested that about 12.5% of the materials were not evaporated at 410°C; which was not within the expectations. The highest wlr of this sample was at 550°C instead of the expected temperature, 410°C. Therefore, some significant internal reactions took place during the isothermal process at 340°C which were not observed in the other isotherms. Therefore, during the isotherm 340 a number of internal reactions occurred in the TGA pan, with no considerable weight loss, resulting in the formation of new materials with unique properties including higher thermal resistance than PLEG itself.

The tails of the isotherms, similar to the previous case, composed of a very scattered range of data. The list-square line fitted to the trace 98.55< w < 93.11 showed a slope = 10.4 for reaction order. However, we may assume that this tail of isotherm, similar to the previous cases, was made of many parallel reactions with slopes near to zero. The list-square line fitted to all of these data will not give a correct reaction order since the weight loss corresponded to numerous simultaneous chemical and physical reactions.

S355. This sample was heated (200°C/min) from room temperature to 355°C, kept for 30 min at 355°C, then heated (200°C/min) to 410°C and held there for another 30 min. The plot of variation of Ln r versus Ln w for this sample was different from the three previous samples (Fig. 4: S340, S325, S310). S355 held 61.2% of its mass at the end of the first isotherm at 352°C contrary to the S310, S325, and S340 where they held 92.4%, 93.3%, and 93.1% of their total mass, respectively, after being for 30 min in their corresponding isotherm. The S355 had lost about 38.4% of its weight at 355°C for 30 min (Table 6). PLEG samples held about 30% of their mass at temperature below 550°C (Fig. 1) which could be the mass of inorganic fillers and other higher thermal resistant materials that were added to neoprene for processing, or they were the products of internal reactions at higher temperatures. Pure neoprene also contains about 40% chlorine by mass. Therefore, chlorine makes about 28 to 29% mass of PLEG. If the entire weight loss at this stage is related to the loss of water, and HCl from PLEG, the remains could be chlorine free materials. Further research will be conducted to confirm or refuse this assumption.

Table 5. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S340.

Time (min)			Temperature (°C)			Weight Percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	LnaK
1.80	2.23	0.43	157	244	88	99.96	99.59	0.38	259	-1192
2.25	2.57	0.32	248	310	62	97.11	99.31	-2.20	-392	1802
2.58	3.80	1.22	312	339	27	99.29	98.32	0.97	129	-591
3.83	5.50	1.67	339	340	0	98.30	97.74	0.56	82.2	-378
5.52	17.15	11.63	340	339	-1	97.74	95.88	1.86	41.6	-192
17.17	47.20	30.03	339	339	0	95.88	93.11	2.77	10.4	-50
46.57	47.93	1.37	361	390	29	93.12	93.04	0.08	-3580	16228
47.95	46.68	-1.27	392	404	13	93.02	91.97	1.06	-1600	380
48.37	48.90	0.53	405	408	4	91.90	89.66	2.24	-1.21	6.89
48.92	50.58	1.67	408	409	1	89.59	82.37	7.23	0.25	0.34
50.60	55.60	5.00	409	409	0	82.29	64.11	18.19	1.91	-6.88
55.58	92.82	37.23	409	409	0	64.11	41.66	22.45	7.11	-28

S370. was heated (200°C/min) from room temperature to 370°C, kept for 30 min at 370°C, then heated (200°C/min) to 410°C and held there for another 30 min. At the end of being 30 min in 370°C, the weight of the sample was 41.5% of its original mass (Table 7) and the wlr was about 0.25 (weight percent per min). After being this sample for 30 min at 410°C, w = 32.58% with the initial wlr = 0.81%/min. Therefore, heating the sample at higher temperature (410°C) resulted about 9% additional weight loss. Perhaps one of the most economical ways to decompose the PLEG is to keep it at 370°C for longer. The variation of Ln r versus Ln w for this sample was different than S370 (Fig. 4), since, at the end of isotherm more than 68% weight of sample were lost (Table 7). Therefore, keeping the sample at 370°C did not produce appreciable amount of

materials that can be stable at 410°C as in the case of S340 (see below).

S385. This sample was heated (200°C/min) from room temperature to 385°C, kept for 30 min at 385°C, then heated (200°C/min) to 410°C and held there for another 30 min. At the end of 30 min at 385°C, the weight of sample was 33.0% of its original mass (Table 8). Most of sample was decomposed, and evaporated at 385°C during the 30 min period. After 30 min at 385°C, while the weight loss was active, the sample was scanned to 410°C. After being 30 min at 410°C, w = 31% of its original mass. During 30 min at 410°C, only about 2% of weight loss was observed. Therefore, a temperature near to 385°C is a suitable and economical way to decompose the PLEG at lower temperatures.

Table 6. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S355.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
1.65	2.10	0.45	119	217	97	100.2	99.82	0.42	217.2	-999
2.12	2.77	0.65	220	335	115	99.82	99.02	0.80	-135.3	631
2.78	3.75	0.97	336	353	17	99.02	97.13	1.90	41.3	-187
3.78	7.73	3.95	353	353	0	97.08	92.11	4.97	5.9	-26
7.75	17.10	9.35	353	352	-1	92.09	81.91	10.18	0.6	-3
17.12	47.15	30.03	352	352	0	81.90	61.63	20.27	3.5	-15
47.52	47.92	0.40	352	389	37	61.49	61.32	0.17	-793.6	-382
47.92	48.35	0.43	389	404	15	61.32	59.70	1.63	-42.2	175
48.35	48.55	0.20	404	405	2	59.70	58.61	1.09	0.5	0
48.57	92.77	44.20	406	408	2	58.52	33.33	25.19	7.1	-27

Table 7. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S370.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
1.70	2.00	0.30	137	200	63	100.3	100.0	0.25	189.6	-874
2.02	2.30	0.28	203	261	58	100.0	99.74	0.27	-363	1673
2.32	3.73	1.42	264	370	105	99.71	94.74	4.97	2.8	-12
3.77	7.72	3.95	370	370	0	94.63	79.10	15.52	-0.2	2
7.73	17.08	9.35	370	369	-1	79.10	55.52	23.58	2.9	-11
17.10	47.13	30.03	369	369	0	55.50	41.55	13.94	6.6	-26
47.67	47.90	0.23	370	393	23	41.45	41.43	0.02	-4675	17410
47.90	48.23	0.33	395	406	11	41.42	41.12	0.29	-55.3	206
48.25	49.13	0.88	406	410	4	41.11	40.31	0.80	9.1	-34
49.15	54.13	4.98	410	410	0	40.30	37.38	2.92	8.9	-33
54.15	92.73	38.58	410	410	0	37.37	32.58	4.79	16.2	-60

The variation of Ln r versus Ln w for this sample was different than the previous samples (Fig. 2); since at the end of isotherm at 385°C, the thermal scan began with a smooth and gentle increase on the rate of reaction as it is visible (Fig. 4). These values are summarized in Table 8 for S385. The appearance of the variation of "Ln r" versus "1/T" of this sample was also similar to the previous samples (310, 325,..); therefore the graphic presentation of the data was omitted and the resulted Ea were tabulated in the Table 3, 7th row.

The wlo was around -2 at the end of scan to 385°C. The isotherm beginning wlo was ~ -2 (similar to the sample 370). However, the wlo increased as weight of the sample decreased, reached to zero and continued to increase. A large trace of data, 94.2 < w <32.7, about 61% of total mass of the sample, had a wlo ~ 2 (Table 8). Afterward, the wlo began to decrease; a trace of data with wlo ~ 0.6 was characterized at the 46 < w < 41% of weight of the sample. Later on, the wlo continued to increase, wlo ~ 17, and 30, then decreased to 18. Considering the high wlo values for the reactions at the end of isotherm is not understandable. A deep looking at the patterns of data showed that many reactions with order zero and one were occurred simultaneously. In the cases similar to this, adjusting a list-square line to all data that belong to a number of concurrent reactions is not an appropriate procedure to find the wlo.

S400. This sample was heated (200°C/min) from room temperature to 400°C, kept for 30 min at 400°C, then heated (200°C/min) to 410°C and held there for another 30 min. At the end of being 30 min at 400°C, the weight of the sample was 32.3% of its original mass (Table 9). Compared with the previous samples after 30 min at 385°C the w ~33.0% and the other at 370°C for 30 min w ~41.6%. Comparing these results indicates that there is not too much advantage in increasing the decomposition temperature of pyrolysis if time is not a factor. As the temperature increased the rate of the weight-loss increased as was observed in the graphs of Fig 2. The variation of Ln r versus Ln w for this sample was different than the one for the previous samples (Fig. 2), since, at end of isotherm at 400°C the weight loss was almost complete (w ~32.3%).

S410. This sample was heated (200°C/min) from room temperature to 410°C, and held there for 30 min. After 30 min at 410°C, the weight of

sample was 30.2% of its original mass (Table 10); which is near to the maximum amount of weight loss that could be reached at temperatures below 550°C. Also, this temperature is the one at which the highest decomposition rate of PLEG was reached in a dynamic scanning from room temperature to 850°C [1]. As the temperature increased the wlr increased as was observed in the graphs of Fig 4. Based on the variation of Ln r versus Ln w for this sample, the order of reaction during the thermal scan was similar to the previous ones. The highest rate of weight loss occurred when w ~ 83.0%. The isotherm was divided into several traces in order to analyze it properly. The trace at 88% < w < 61% where the weight loss order obtained was 1.0. Afterward, the order began to increase, the trace 61% < w < 44% had the average order of~ 4. From this point the order increased and the last trace w < 44% had the average wlo of 25 and higher. These values are summarized in Table 10 for S410. Similar to all isotherm that were studied before, under these conditions, many reactions occurred simultaneously with order near to zero. Adjusting a list-square line to the data that belong to a wide range of reactions is not appropriate for estimation of order of the reactions. It is more appropriate to identify each reaction and consider it separately as we did in the previous cases (S310). For sake of brevity, here omitted the table contains the kinetic parameters of the reactions and the corresponding figure.

S425. It was heated (200°C/min) from room temperature to 425°C, then it was held there for 30 min. During this period of time, it lost all its volatiles (w ~ 28.6% Table 11). This is the maximum amount of weight loss that could be reached at temperatures below 550°C. The temperature 425°C is about 15°C above the temperature at which the highest decomposition rated of PLEG was reached in a dynamic scanning from room temperature to 850°C (Fig. 2). The highest value of wlr was obtained when 78.0% mass of PLEG remained, where the wlo was zero. Based on the variation of Ln r versus Ln w for this sample, the wlo during the thermal scan was similar to the previous samples (Table 11). Two traces of the isotherm at 425°C were selected to analyze. The first, when the mass of the sample was 91-80% of its original mass where wlo was ~ -3. The next trace was 78% <w <36% where the wlo was +3. Also the traces in-between these two traces were analyzed and tabulated in Table 11.

329

Table 8. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S385.

Time (min)			Temperature (°C)			Weight percent				
Start	End	Dt	start	end	DT	start	end	-DW	slope = n	intercept
1.57	1.98	0.42	108	202	94	100.22	99.88	0.34	355.5	-1637
2.00	3.12	1.12	206	379	174	99.88	94.54	5.33	-71.2	328
3.13	3.55	0.42	380	385	6	94.27	86.37	7.90	-1.8	11
3.13	7.23	4.10	387	387	-1	94.27	32.72	61.55	2.3	-7
7.25	8.32	1.07	387	386	0	45.72	41.06	4.67	0.6	-1
8.33	34.32	25.98	386	386	-1	40.99	32.96	8.03	16.9	-62
34.33	48.72	14.38	386	409	23	32.96	32.44	0.52	29.6	-107
48.72	92.65	43.93	409	410	1	32.44	30.71	1.74	18.4	-67

Table 9. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S400.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
1.58	2.08	0.50	106	217	111	100.4	99.95	0.48	194.8	-897
2.10	2.73	0.63	221	350	129	99.94	98.97	0.97	-245	1127
2.75	3.15	0.40	353	391	38	98.90	93.98	4.92	-46.0	122
2.77	3.17	0.40	357	392	35	98.81	93.67	5.15	-23.3	205
3.02	3.18	0.17	386	392	6	96.36	93.35	3.01	-6.9	34
3.20	3.37	0.17	392	396	3	93.03	89.72	3.31	0.1	3
3.38	4.17	0.78	396	401	5	89.40	75.77	13.63	1.3	-3
4.18	5.67	1.48	401	401	0	75.51	57.65	17.86	2.3	-7
5.70	47.78	42.08	401	400	-1	57.51	32.32	25.20	9.3	-35
47.92	48.47	0.55	405	410	4.66	32.32	32.24	0.08	66.06	-232
48.48	54.30	5.82	410	410	0.42	32.05	31.64	0.41	17.24	-62.0
54.32	92.80	38.48	410	411	0.13	31.64	30.19	1.45	51.13	-179

Table 10. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S410.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
1.58	2.02	0.43	106	201	94.6	100.9	100.2	0.66	147.8	-681
2.02	2.93	0.92	204	387	182.9	100.2	96.68	3.52	-106	487.6
2.40	3.15	0.75	282	400	117.6	99.79	88.87	10.92	-8.29	41.16
3.17	3.25	0.08	400	403	2.42	88.06	83.89	4.17	-0.97	8.21
3.27	3.32	0.05	403	404	1.12	83.04	80.48	2.56	0.07	3.63
3.17	3.47	0.30	405	407	2.25	79.63	73.14	6.50	1.19	-1.28
3.18	3.48	0.30	405	407	2.16	85.58	59.83	25.75	2.01	-4.78
3.78	4.83	1.05	410	412	1.89	60.86	43.90	16.96	4.02	-13.0
4.85	19.83	14.98	412	410	-1.40	43.78	31.48	12.30	12.37	-44.4
19.85	33.75	13.90	410	410	0.12	31.48	30.23	1.24	24.54	-86.5

Table 11. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of PLEG sample 425.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Dt	Initial	Final	DT	Initial	Final	-DW	wlo	Ln ak
2.22	2.28	0.07	249	262	14	100.3	99.88	0.40	-412	756
2.30	2.47	0.17	266	300	34	99.76	99.29	0.46	313	-1441
2.48	2.90	0.42	303	387	83	99.27	97.53	1.74	-113	521
2.92	3.07	0.15	390	410	20	97.30	92.23	5.07	-25.5	119
3.08	3.20	0.12	411	417	6	91.22	81.35	9.87	-2.9	17
3.22	3.27	0.05	418	419	2	79.77	74.57	5.20	-0.1	5
3.28	3.32	0.03	420	420	1	72.89	69.68	3.21	1.2	0
3.33	3.47	0.13	421	423	2	68.15	57.74	10.41	1.9	-4
3.48	3.65	0.17	423	425	2	56.68	48.56	8.12	3.4	-10
3.67	4.23	0.57	425	427	2	47.96	35.80	12.16	4.0	-12
4.22	5.53	1.32	427	427	0	35.98	31.77	4.21	22.9	-79
5.57	13.75	8.18	427	426	-1	31.74	29.15	2.59	24.0	-83
13.75	33.75	20.00	426	426	0	29.15	28.57	0.58	48.2	-163

S440. This sample was heated (200°C/min) from room temperature to 440°C, then held there for 30 min. The highest weight loss occurred during the thermal scan to 440°C, and before reaching the isotherm at 440°C (w ~32%). During 6.8 min of thermal scan to 440°C, the sample lost most of its weight w~ 31.5% (Table 12) where during the 30 min time period in the isotherm at 440°C, a small amount of wl (31.6% < w <29.5% , Table 12) was reached. This was within expectation since this temperature is about 30° above the temperature at which the highest decomposition rate of PLEG was obtained in a dynamic scanning from room temperature to 850°C (Fig. 1). As the temperature increased, the rate of the weight-loss increased as it was expected (Fig. 4). The highest wlr ~ 126 min^{-1} was reached at w ~ 73.9% and t = 427.4°C, where the wlo was zero.

Based on the variation of Ln r versus Ln w for this sample, the order of reaction during the thermal scan was similar to the previous one, large negative values, reaching to zero, followed by large positive values reaching to zero, followed with large negative values that increased fast passing zero at the max wlr and continued to high positive values. Seven traces of thermal scan and three traces of the isotherm 440°C were selected to analyze (Table 12). At the 80% < w < 61% the wlr was the highest and the wlo was near to zero (n = 0.4). As wlr values decreased, the order of reaction increased. At the next trace, 44% < w < 60%, order of n =3.6 was calculated. All relevant data related to this experiment are tabulated in Table 12. When the wlo is large, the TGA data can be divided into

various set of concurrent reactions with order near to zero as in the previous cases.

S455. This sample was heated fast (200°C/min) from room temperature to 459°C, then it was hold there for one min. After one min in 459°C w ~ 32.5% (Table 13) was reached which is equivalent in weight loss of keeping the sample for 30 min in 400°C. The pyrolysis temperature was about 45°C above the temperature at which the highest decomposition rate of PLEG was reached in a dynamic scanning from room temperature to 850°C (Fig. 1, Scan). The highest rate of weight loss was reached (209 min^{-1}) when 70.7% mass of PLEG was remained at t = 439°C, where the wlo became zero. Based on the variation of Ln r versus Ln w for this sample, the wlo of thermal scan was similar to the previous one (Fig. 3), a large negative value, flowed with a high positive value, immediately followed with negative values. The negative slope gradually increased to zero (Table 13). At 88% < w <47% the wlo was near to zero (n = 0.2) where the highest wlr was reached. As wlr values decreased the order of reaction increased. At the next trace, 43% > w >35%, the wlo ~ 8 was calculated. This section of thermogram records the data that belong to numerous simultaneous reactions as was shown in the previous cases. We omit to report the full analysis, otherwise the paper would become lengthy. All relevant data related to this experiment are tabulated in the Table 13.

Analysis of the weight losses of the first thermal scans. The full circles in Fig. 6 show the variation of the temperature versus weight loss of the 11

samples of PLEG at the end of the first fast thermal scan (200°C/min) to a given temperature. The continuous line is the variation of weight loss by temperature increase (10 °C /min, under argon environment). The position of the circles (the weight of sample after a fast scan to a given temperature) are near to the positions of weight loss of a PLEG sample when it was scanned from 50°C to 850°C with a rate of 10°C/min. This again confirmed the reproducibility of the TGA data. The comparison of the two sets of the weight losses by temperatures indicated that at lower temperatures (t < 385 °C) the maximum weight loss was similar in both cases. However, at higher temperatures (t >400), the weight loss at

higher heating rates (200°C/min) was slightly smaller than the weight loss at lower heating rate. This is within expectations since at the higher heating rate, the sample did not have enough time to absorb necessary energy to undergo the chemical decompositions reactions to produce similar amount of volatile materials.

Reaction Rate Constant and Temperature. Fig. 7 shows the application of the logarithmic form of Arrhenius relationship, Eq (5), to the values of Ln k versus 1/T (K) using all values of k and T from the above Tables. The data are scattered; however, a list-square adjusted line to these data helped to calculate an average value for the Ea of weight loss (Fig. 7) to be Ea = 1.57 MR.

Table 12. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S440.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$	wlo	Ln ak
1.58	1.72	0.13	109	143	34	100.3	100.2	0.15	-64.8	299
1.73	2.03	0.30	147	208	61	100.1	99.90	0.24	335.6	-1546
2.05	2.85	0.80	211	374	163	99.90	98.08	1.82	-156	717
2.87	3.17	0.30	378	424	46	97.93	82.23	15.70	-13.3	64
3.18	3.33	0.15	425	431	6	80.23	61.82	18.42	0.4	3
1.68	3.60	1.92	431	436	5	60.04	44.01	16.03	3.6	-10
3.62	6.83	3.22	437	441	4	43.48	31.57	11.92	13.5	-47
7.73	14.00	6.27	441	440	-1	31.55	30.27	1.28	62.0	-214
14.08	24.33	10.25	440	439	-2	30.27	29.90	0.37	55.2	-191
24.33	47.33	23.00	440	440	0	29.90	29.45	0.45	118.8	-407
47.35	50.25	2.90	440	853	413	29.45	16.75	12.70	658.5	-2231
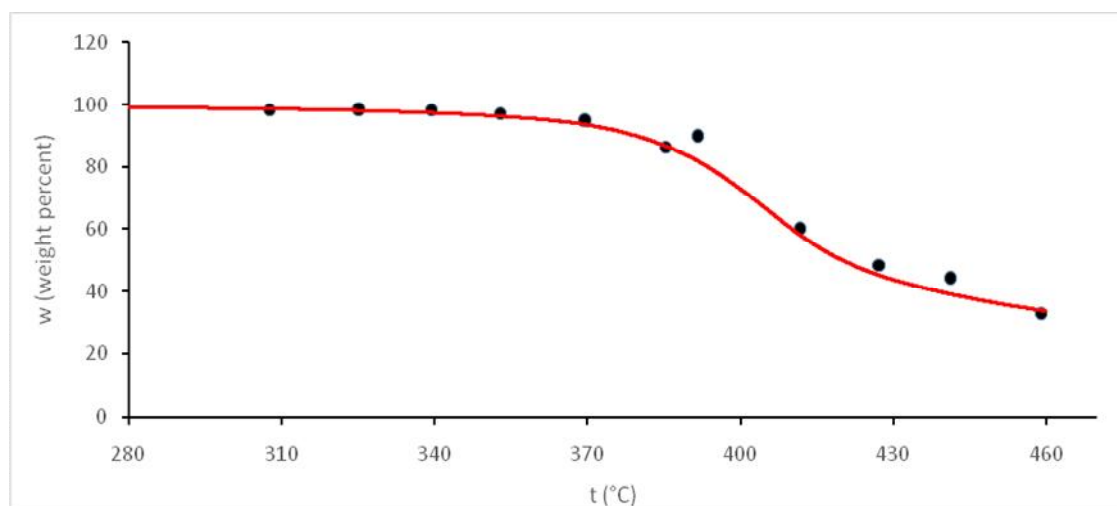
Fig. 6. Comparisons of the variation of the weight loss of PLEG samples versus temperatures. The dark dots show the weight loss at the end of each thermal scan; the continue line shows the weight loss of a thermal scan with the rate of 10°C/min form 50 °C to 850°C.

Table 13. The initial and final time, the time of process, the initial and final temperature, and the change in temperature, the initial and final weight of sample and the weight loss amount, the wlo, and Ln k resulted from TGA analysis of S455.

Time (min)			Temperature (°C)			Weight percent				
Initial	Final	Δt	Initial	Final	ΔT	Initial	Final	$-\Delta W$	wlo	Ln ak
1.55	1.68	0.13	106	142	36	100.1	99.96	0.14	-60.8	280
1.70	1.97	0.27	145	200	54	99.94	99.76	0.18	397.4	-1830
1.98	2.92	0.93	203	394	190	99.75	96.52	3.23	-140	646
2.93	3.05	0.12	397	420	23	96.10	90.19	5.91	-15.1	72
3.07	3.30	0.23	423	447	23	88.43	47.03	41.40	0.2	4
3.32	3.62	0.30	448	453	5	43.83	35.25	8.58	7.8	-25
3.58	4.47	0.88	454	459	5	35.04	32.93	2.10	52.6	-184
4.48	5.23	0.75	459	459	0	32.92	32.54	0.38	42.8	-150
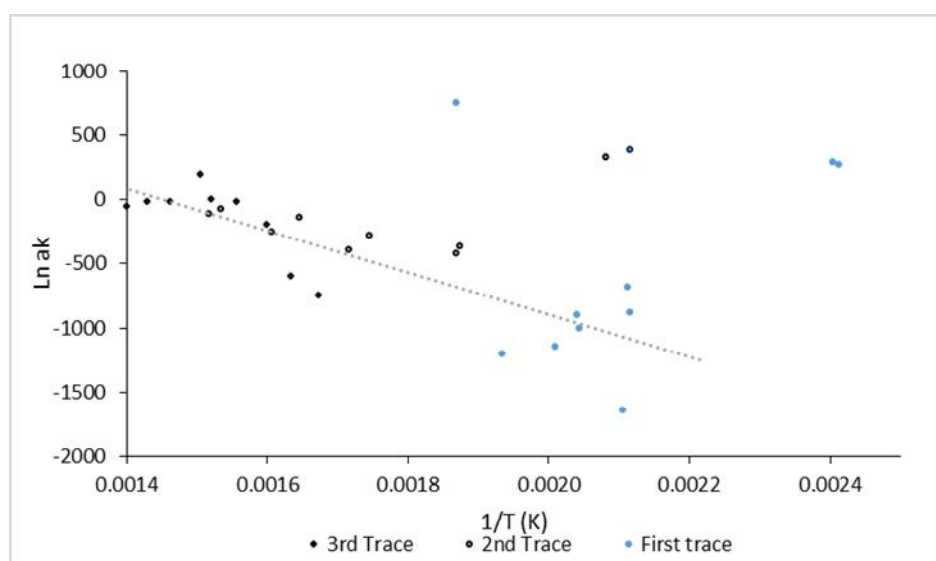
Fig. 7. Variation of all "Ln k" versus "1/T" (K^{-1})

4. CONCLUSION AND REMARKS

The variation of Ln r versus Ln w of the first thermal scans showed three distinguished tendencies (Fig. 2), which were analyzed, accordingly. The weight losses of the first and second traces were negligible; the third trace bore the highest weight-loss of the process of the thermal scan. This by no means indicates that there were no physical and chemical changes in the structure of the materials under study at higher temperatures. In fact, prior to any visible weight loss in TGA many chemical and physical changes had already occurred in the structure of materials at high temperatures. These changes are the precursors to posterior wlr detected in TGA.

The variation of Ln r versus Ln w of the thermal scans had a concave downward curve form; they were converged to a plateau before reaching the final temperature; thus, the intermediate trace was always a curve. Adjusting a straight-line to it produced inaccurate and arbitrary results which are reflected in the scatterings of the data (Fig. 7).

It is universally accepted that the detailed description of the overall degradation of materials at high temperatures, particularly PLEG which is composed of a complex mixture of minerals, polymers, organic plasticizers, and inorganic fillers, is quite a complex process involving a large number of chemical reactions and intermediate species at high temperatures. The TGA alone is not able to provide a complete set of information about the nature of the volatiles at a given temperature. Therefore, without chemical identification of the thermolysis products, it is hard to propose a mechanism for degradation. However, from the information obtained from gas chromatography mass spectrometry analysis of

the thermolysis products of LEGs [2] and the results published by other researchers who had developed kinetic models with an in-depth discussion for the pure polymers [e.g.4-12], we may assume a type of radical degradation mechanism.

In the case of PLEG, the presence of chlorine and double bonds favor the initiation radical reactions and this fact reduces the activation energy of decomposition compared with PE chains, similar to PS decomposition [4]; due to the preferential formation of the long lived resonantly stabilized radicals.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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