

Thermal Degradation of Statistical Copolymers of 2-Vinyl Pyridine with Functional Methacrylates

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Abstract: *Conventional free radical polymerization was employed for the synthesis of statistical copolymers of 2-vinyl pyridine (2VP) with either 2-butoxyethyl methacrylate (BuOEMA), di(ethylene glycol) methyl ether methacrylate (DEGMA) or oligo(ethylene glycol) methyl ether methacrylate bearing a side chain with an average number of 5 ethylene glycol units (OEGMA300). Copolymers having different compositions in the two monomers were obtained. The thermal decomposition of these statistical copolymers was studied by Thermogravimetric Analysis (TGA) and Differential Thermogravimetry (DTG). The Ozawa-Flynn-Wall (OFW) and Kissinger methodologies were adopted for the calculation of the activation energies of the thermal decomposition. The results of these studies were compared with those measured for the corresponding P2VP, PBuOEMA, PDEGMA and POEGMA300 homopolymers so as to correlate the structures of the copolymers with their properties.*

Keywords: *statistical copolymers, 2-vinyl pyridine, functional methacrylates, thermogravimetric analysis, differential thermogravimetry, thermal decomposition*

Abbreviations:

TGA- Thermogravimetric Analysis, DTG- Differential Thermogravimetry, 2VP- 2-vinyl pyridine, BuOEMA - 2-butoxyethyl methacrylate, DEGMA -di(ethylene glycol)methyl ether methacrylate, OEGMA300-oligo(ethylene glycol) methyl ether methacrylate, OFW - Ozawa-Flynn-Wall method, SEC-Size Exclusion Chromatography, NMR- Nuclear Magnetic Resonance

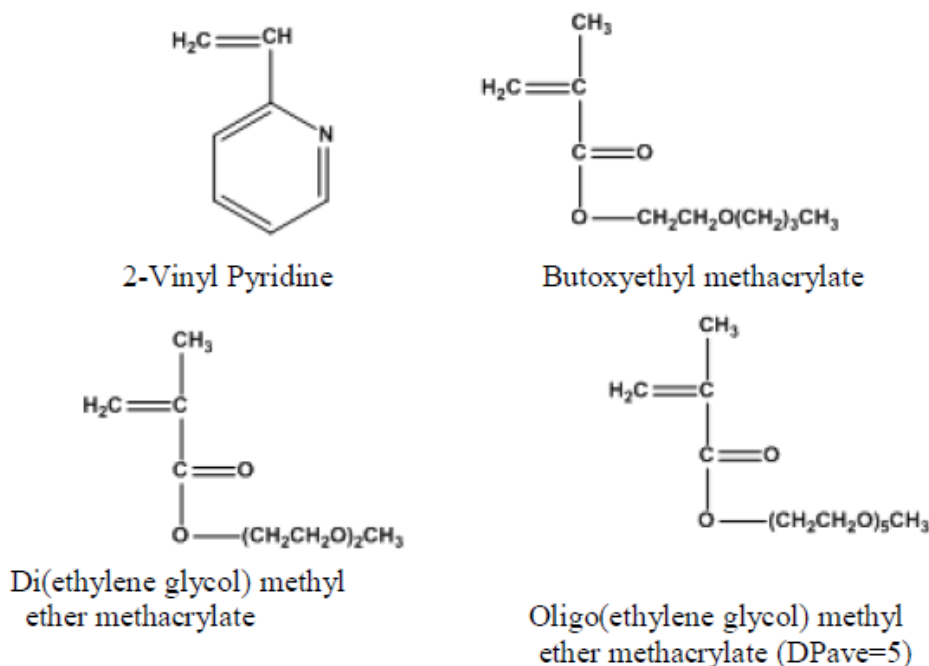
1. INTRODUCTION

Copolymerization is a very important tool in polymer science because it provides scientists the possibility to manipulate the physical and chemical properties of a polymer chain, e.g. solubility [1], crystallinity [2] and glass transition temperature (Tg) [3] in order to create new materials of scientific interest as well as diverse applications, such as drug transfer systems [4], photoresists for lithography [5] and smart materials [6]. Its utility is stressed by the large number of commercial applications and investigations that have been conducted to correlate the structure with the properties of the materials [3], [7].

Copolymerization has been studied extensively, both experimentally and theoretically [8]. The main body of work is focused on the elucidation of the copolymer composition, the determination of the monomer reactivity ratios, the monomer sequence distribution and the kinetics of the copolymerization [9].

Free radical copolymerization is the most important copolymerization technique, since it is experimentally less demanding compared to other copolymerization methodologies and it can be applied to a wide range of monomers. The free radical copolymerization of 2-vinyl pyridine (2VP) with either 2-butoxyethyl methacrylate (BuOEMA), di(ethylene glycol) methyl ether methacrylate (DEGMA), or oligo(ethylene glycol) methyl ether methacrylate with number average molecular weight 300 g/mol (OEGMA₃₀₀) was the focus of previous studies. The monomer structures are given in Scheme 1. It was found that the reactivity ratios of 2VP, r_{2VP} were higher in all statistical copolymers ($r_{2VP}=3.04$ and $r_{BuOEMA}=0.48$ for the P2VP-co-PBuOEMA copolymers [10], $r_{2VP}=1.57$ and $r_{DEGMA}=0.92$ for the P2VP-co-PDEGMA copolymers [10], whereas $r_{2VP}=1.08$ and $r_{OEGMA300}=0.23$ for the P2VP-co-POEGMA300 copolymers [11]) indicating a kinetic preference for the incorporation of the 2VP units in the copolymer structure. These findings prompted the present study of the kinetics of

the thermal decomposition of these statistical copolymers by Thermogravimetric Analysis (TGA) and Differential Thermogravimetry (DTG). These results were correlated with those obtained from the corresponding homopolymers P2VP, PBuOEMA, PDEGMA and POEGMA₃₀₀ to study the effect of the copolymer structure and composition on the thermal properties of the copolymers.



Scheme 1. Structure of the Monomers

2. EXPERIMENTAL SECTION

2.1. Materials

The synthesis of the statistical copolymers has been described in detail elsewhere [10], [11]. Briefly, all manipulations were performed using high vacuum techniques. The monomers were vacuum distilled from calcium hydride just prior to use in order to remove inhibitors and humidity. The copolymerization reactions were performed in glass reactors in bulk. 2,2' Azobisisobutyronitrile (AIBN) in the concentration of 0.1% wt was the initiator. The mixture of the two monomers and the initiator was degassed using three freeze–thaw cycles, and the reactors were flame-sealed. The copolymerizations were conducted at 50–60°C for 2–3 hours. The polymers were precipitated in n-heptane, redissolved in chloroform and reprecipitated once more. The same procedure was repeated as many times as necessary in order to remove all remaining quantities of the unreacted monomers. Finally, the polymers were dried overnight in a vacuum oven.

2.2. Thermogravimetric Analysis

The thermal stability of the homopolymers and the copolymers was studied by thermogravimetric analysis (TGA) and Differential Thermogravimetry (DTG) with a Q50 TGA model from TA instruments. The samples were placed in platinum crucibles and an empty platinum crucible was used as reference. The samples were heated from ambient temperatures up to 600°C in a 60 mL/min flow of N₂ at heating rates of 3, 5, 7, 10, 15 and 20°C/min.

3. RESULTS AND DISCUSSION

3.1. Free Radical Homopolymerization and Copolymerization Reactions

The free radical copolymerizations of VP, BuOEMA, DEGMA and OEGMA₃₀₀ were conducted in bulk using AIBN as the initiator. The conversions in all cases were lower than 10% in order to satisfy the differential copolymerization equation. The molecular characteristics of both the homopolymers and the copolymers are shown in Table 1. The molecular weights were measured by Size Exclusion Chromatography, SEC using a calibration curve constructed by polystyrene standards. The compositions of the copolymers in the various monomers were measured by NMR or UV analysis at 252 nm, where only the 2VP monomer units absorb. The copolymers are symbolized by the various

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feed molar ratios of the monomers prior the copolymerization, e.g. 2VP-BuOEMA 20-80 is used for the copolymer P2VP-co-PBuOEMA, synthesized from a molar feed composition 20% 2VP and 80% BuOEMA.

Table1. Macromolecular characteristics of the homopolymers and the statistical copolymers

Sample	^a M _n x 10 ⁻³	^a I=M _w /M _n	^b 2VP moles %
P2VP	214.0	1.46	100
PBuOEMA	81.5	1.23	0
PDEGMA	280.0	1.41	0
POEGMA ₃₀₀	288.5	1.28	0
2VP-BuOEMA 20/80	83.5	1.36	45.6
2VP-BuOEMA 40/60	77.2	1.39	61.2
2VP-BuOEMA 50/50	65.8	1.73	72.7
2VP-BuOEMA 60/40	65.3	1.34	82.0
2VP-BuOEMA 80/20	78.4	1.37	92.1
2VP-OEGMA ₃₀₀ 20/80	465.0	1.42	35.8
2VP-OEGMA ₃₀₀ 50/50	363.1	3.50	66.2
2VP-OEGMA ₃₀₀ 60/40	472.6	1.40	70.3
2VP-OEGMA ₃₀₀ 80/20	430.1	1.80	82.6
2VP-DEGMA 20/80	1078	1.34	33.9
2VP-DEGMA 40/60	1358	1.43	61.0
2VP-DEGMA 50/50	1182	1.41	72.3
2VP-DEGMA 60/40	1091	1.39	78.1
2VP-DEGMA 80/20	695.0	1.36	91.0

a. by SEC in CHCl₃ at 40°C, b. by ¹H-NMR in CDCl₃ at 25°C or by UV analysis at 252 nm.

3.2. Thermal Decomposition of the Homopolymers and the Statistical Copolymers

The homopolymers and the statistical copolymers were thermally degraded at different heating rates under inert atmosphere. The temperatures where the thermal decomposition is initiated and completed along with the temperatures at the maximum rate of thermal decomposition are provided in Tables 2 (homopolymers) and 3 (statistical copolymers) and characteristic thermograms from DTG are given in Figures 1-7. Additional plots are given in the supporting information section.

Table2. TGA results for the homopolymers at the heating rate 10°C/min

Sample	Start (°C)	Finish (°C)	Peak 1 (°C)	Peak 2 (°C)
P2VP	363.91	457.16	414.40	--
PBuOEMA	210.18	408.49	305.70	317.98
PDEGMA	180.62	396.66	262.85	327.07
POEGMA 300	237.93	390.75	331.62	338.44

Table3. TGA results for the copolymer samples at the heating rate 10°C/min

Sample	Start (°C)	Finish (°C)	Peak (°C)
P2VP-PBuOEMA 20-80	272.04	425.32	365.75
P2VP-PBuOEMA 40-60	270.22	424.86	373.92
P2VP-PBuOEMA 50-50	300.24	440.33	377.56
P2VP-PBuOEMA 60-40	291.60	437.14	378.01
P2VP-PBuOEMA 80-20	304.79	433.96	388.93
P2VP-POEGMA ₃₀₀ 20-80	282.50	425.32	366.64
P2VP-POEGMA ₃₀₀ 50-50	279.77	441.24	369.37
P2VP-POEGMA ₃₀₀ 60-40	299.33	442.13	378.47
P2VP-POEGMA ₃₀₀ 80-20	270.22	448.06	393.48
P2VP-PDEGMA 20-80	258.50	392.09	322.99
P2VP-PDEGMA 40-60	271.74	404.18	356.39
P2VP-PDEGMA 50-50	278.08	403.61	355.81
P2VP-PDEGMA 60-40	267.13	413.40	360.42
P2VP-PDEGMA 80-20	290.74	415.70	368.48

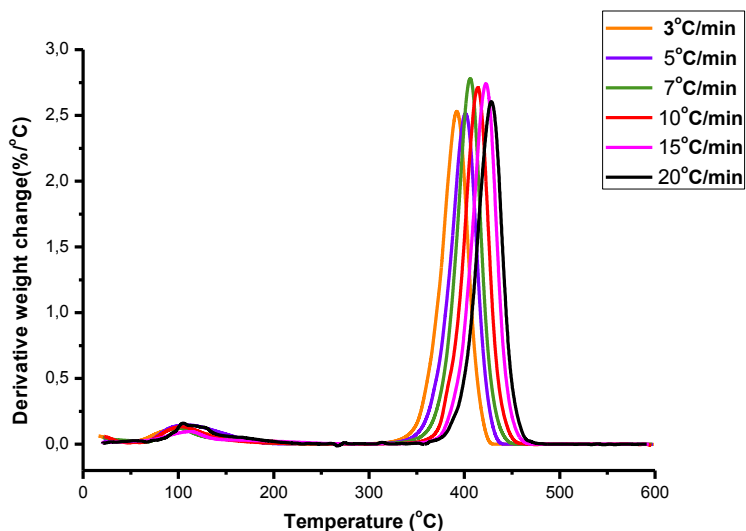


Figure1. Derivative Weight Loss with Temperature for P2VP under Different Heating Rates

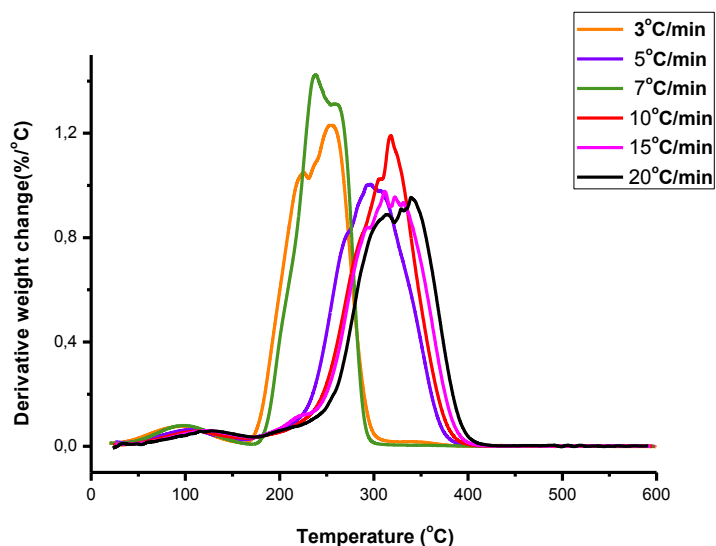


Figure2. Derivative Weight Loss with Temperature for PBUOEMA under Different Heating Rates

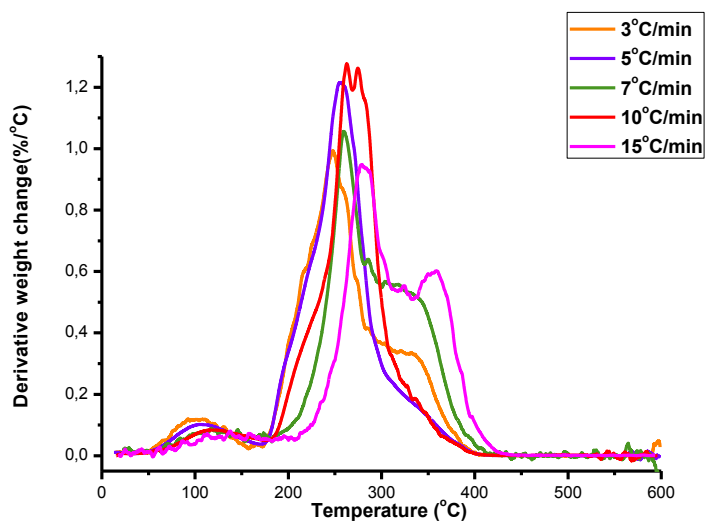


Figure3. Derivative Weight Loss with Temperature for PDEGMA under Different Heating Rates

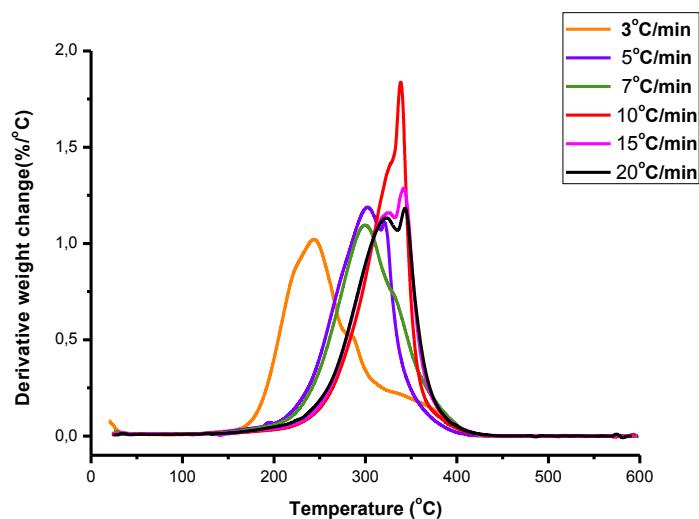


Figure4. Derivative Weight Loss with Temperature for POEGMA300 under Different Heating Rates

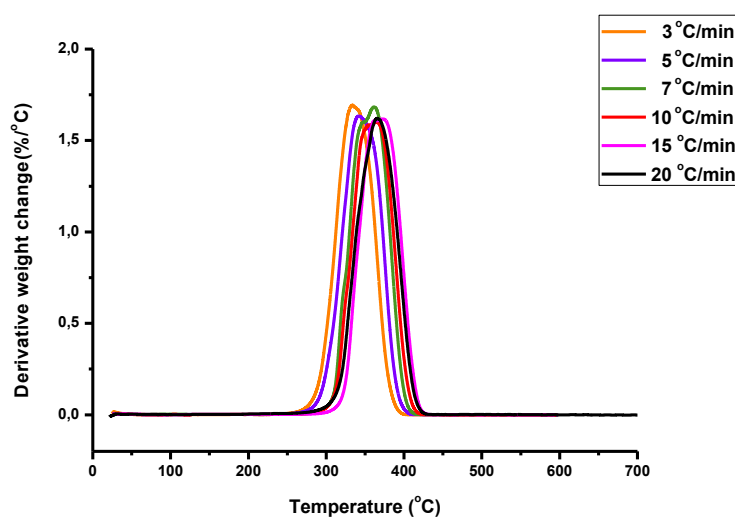


Figure5. Derivative Weight Loss with Temperature for P2VP-PBuOEMA 20-80 under Different Heating Rates

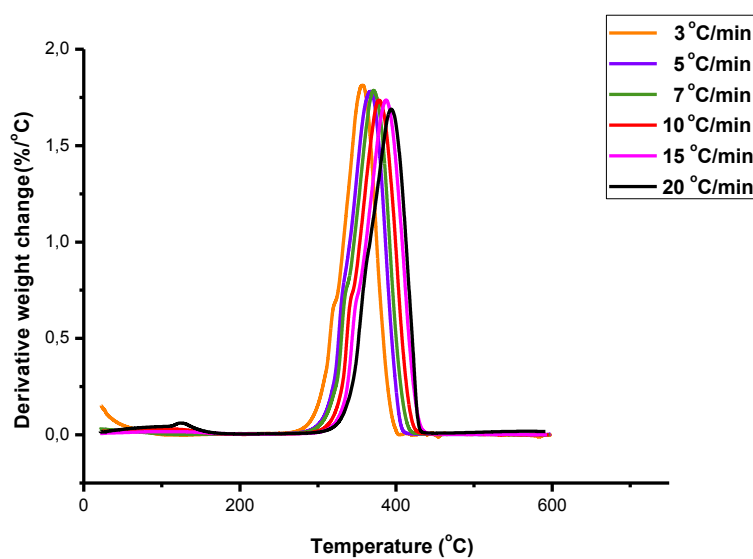


Figure6. Derivative Weight Loss with Temperature for P2VP-POEGMA300 60-40 under Different Heating Rates

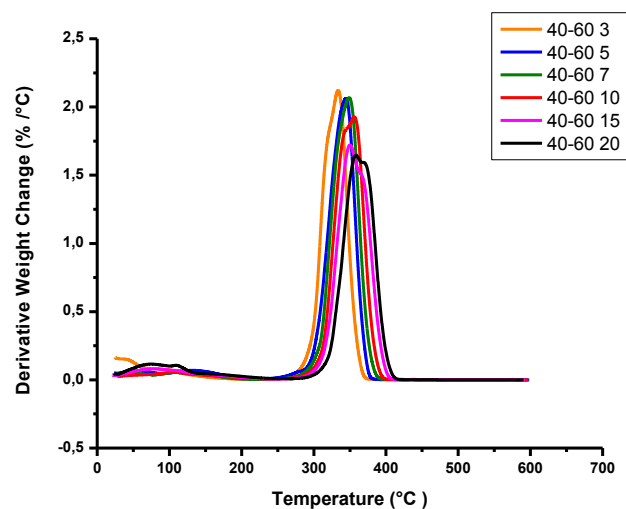


Figure 7. Derivative Weight Loss with Temperature for P2VP-PDEGMA 40-60 under Different Heating Rates

DTG revealed that single decomposition peaks appear for P2VP at different heating rates. For PBuOEMA, however, DTG indicated the presence of a single decomposition peak at lower heating rates, while at higher heating rates a more complex pattern consisting of two peaks appeared. A similar decomposition behavior was also observed for PDEGMA and POEGMA₃₀₀ homopolymers, obviously due to the similar chemical structure of these polymers, since all three are polymethacrylates bearing ethylene glycol side groups. These results indicate that for the specific polymethacrylates the decomposition pattern is complex and involves the simultaneous decomposition of the polymer backbone and the side chains.

The thermal decomposition of P2VP is initiated and completed at higher temperatures compared to the three polymethacrylates. In addition, the decomposition peaks in DTG graphs occur at higher temperatures for P2VP as well. These data unambiguously indicate that P2VP is thermally more stable than the corresponding polymethacrylates, obviously due to the presence of the aromatic pyridine ring. The range of decomposition temperatures is narrower for P2VP than that of PBuOEMA, PDEGMA and POEGMA₃₀₀ supporting the conclusion that a simpler thermal decomposition mechanism exists for P2VP. Comparing the temperatures of decomposition at the maximum rate of decomposition, T_p , the following order is noted: $T_{pP2VP} > T_{pPOEGMA300} > T_{pPDEGMA} > T_{pPBuOEMA}$ and seems to be the order of thermal stability of the homopolymers. Among the polymethacrylates it is evident that upon increasing the size of the side groups (number of ethylene oxide units) the thermal stability increases. The higher thermal stability of PDEGMA compared to PBuOEMA leads to the conclusion that the introduction of a higher number of oxygen atoms at the side chain leads to increased thermal stability. These conclusions can be further supported considering the thermal stability of poly(ethylene oxide).

In the case of the statistical copolymers P2VP-co-PBuOEMA DTG revealed that only a single decomposition peak is observed, similar to the behavior of the P2VP homopolymer. Thus, the thermal decomposition behavior of P2VP prevails in the copolymer. This observation can be attributed to the much higher reactivity ratio of 2VP over that of BuOEMA, which leads to copolymers with much higher contents in 2VP units. Upon increasing the 2VP content, the temperatures where thermal decomposition is initiated and completed, as well as that of the decomposition peak in DTG all increase. These temperatures are within those found for the respective homopolymers but are closer to those of the P2VP homopolymer, further demonstrating the effect of 2VP monomer units on the overall behavior of the copolymer.

Similar behavior was observed for the P2VP-co-PDEGMA and P2VP-co-POEGMA₃₀₀ copolymers. The thermal degradation behavior of the copolymers is dominated by the 2VP content. In addition to the previous comments it should be noted that the range of the temperatures of decomposition is much narrower for the copolymers compared to the respective polymethacrylates. Comparing the temperatures of decomposition at the maximum rate of decomposition, T_p , it can be concluded that they follow the order: $T_{pP2VP-co-PBuOEMA} > T_{pP2VP-co-POEGMA300} > T_{pP2VP-co-PDEGMA}$. This should also be the order of thermal stability of the copolymers. It is rather surprising that the copolymers with the

BuOEMA are thermally more stable since the corresponding homopolymer presents the lowest thermal stability of all the homopolymers. This discrepancy can be explained by the fact that the P2VP-co-PBuOEMA copolymers have higher 2VP contents compared to the other copolymers.

3.3. Kinetics of the Thermal Decomposition of the Homopolymers and the Statistical Copolymers

The kinetics of the thermal decomposition of the statistical copolymers was studied by TGA measurements. The activation energy, E_a , of mass loss upon heating was calculated using both the isoconversional Ozawa-Flynn-Wall (OFW) [12] and Kissinger [13] methods. The OFW approach is a "model free" method which assumes that the conversion function $F(\alpha)$, where α is the conversion, does not change upon altering of the heating rate, β , for all values of α . The OFW method involves the measurement of the temperatures corresponding to fixed values of α from experiments at different heating rates β . Therefore, plotting $\ln\beta$ vs $1/T$ in the form:

$$\ln\beta = \ln \frac{AE}{R} - \ln F(\alpha) - \frac{E}{RT}$$

This should result in straight lines with slopes directly proportional to the activation energy where T is the absolute temperature. A is the pre-exponential factor (min^{-1}) and R is the gas constant ($8,314 \text{ J/K.mol}$). If the determined activation energy is the same for the various values of α , then a single-step degradation reaction can be concluded. The OFW method is the most useful method for the kinetic interpretation of thermogravimetric data, obtained from complex processes like the thermal degradation of polymers. This method can be applied without knowing the reaction order.

The activation energy E_a was also calculated from plots of the logarithm of the heating rate vs. the inverse of temperature at the maximum reaction rate in constant heating experiments, according to the Kissinger method. The equation for the Kissinger method is the following:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln \frac{AR}{E} + \ln[n(1 - \alpha_p)^{n-1}] - \frac{E}{RT_p}$$

where T_p and α_p are the absolute temperature and the conversion at the maximum weight loss and n is the reaction order. The E_a values can be calculated from the slope of the plots of $\ln(\beta/T_p^2)$ vs. $1/T_p$.

The activation energy values, E_a , of the homopolymers resulting from the OFW method are displayed in Table 4, whereas characteristic plots are given in Figures 8-11. It is obvious that the E_a values depend on the degree of thermal decomposition, especially for sample POEGMA300. This is a manifestation of the rather complex mechanism of thermal degradation of these polymers. The E_a values of samples vary with the following order: $E_{aP2VP} > E_{aOEGMA300} > E_{aPDEGMA} > E_{aPBuOEMA}$, in agreement with the thermal stability of the homopolymers, as previously discussed. Similar conclusions were drawn by the Kissinger method. Characteristic plots are given in Figures 12-15, and the E_a values are displayed in Table 5.

Table4. Activation Energies for the Homopolymers from the OFW Method

Weight Loss (%)	P2VP	PBuOEMA	PDEGMA	POEGMA300
10	--	53.10	64.75	73.50
20	167.49	54.92	61.82	78.34
30	181.44	54.75	74.48	81.73
40	189.20	50.56	80.90	86.69
50	193.99	46.71	75.95	93.41
60	197.77	45.12	64.96	102.63
70	201.19	44.87	65.42	142.75
80	204.46	44.92	62.40	140.46
90	208.12	46.76	81.83	--

Table5. Activation Energies for the Polymers from the Kissinger Method

Sample	E_{a1} (J)	E_{a2} (J)
PBuOEMA	86.88	115.18
P2VP-PBuOEMA 20/80	118.2	
P2VP-PBuOEMA 40/60	161.3	
P2VP-PBuOEMA 50/50	198.0	

P2VP-PBuOEMA 60/40	177.7	
P2VP-PBuOEMA 80/20	181.3	
P2VP	188.3	
P2VP-POEGMA300 20/80	203.0	
P2VP-POEGMA300 50/50	122.7	
P2VP-POEGMA300 60/40	168.1	
P2VP-POEGMA300 80/20	115.3	
POEGMA300	38.99	154.01
P2VP-PDEGMA 20-80	111.72	
P2VP-PDEGMA 40-60	215.16	
P2VP-PDEGMA 50-50	151.23	
P2VP-PDEGMA 60-40	159.17	
P2VP-PDEGMA 80-20	158.63	
PDEGMA	24.67	61.62

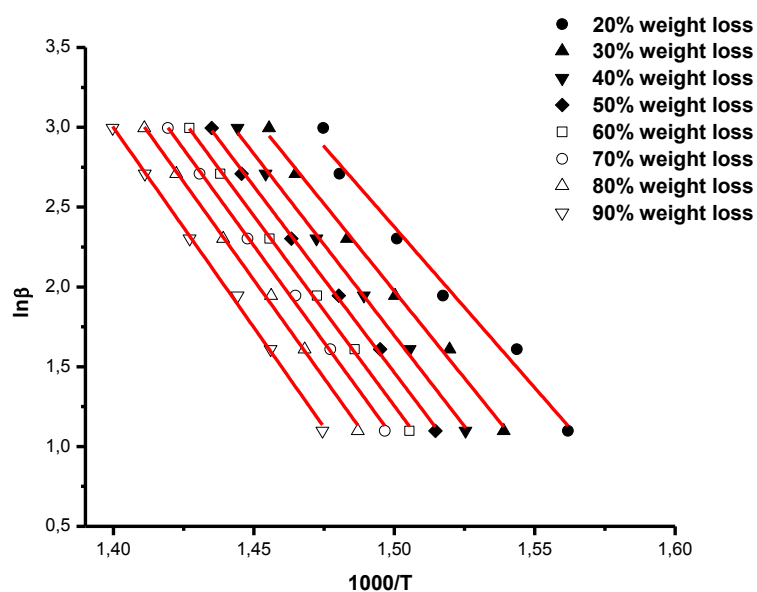


Figure8. OFW plots for P2VP

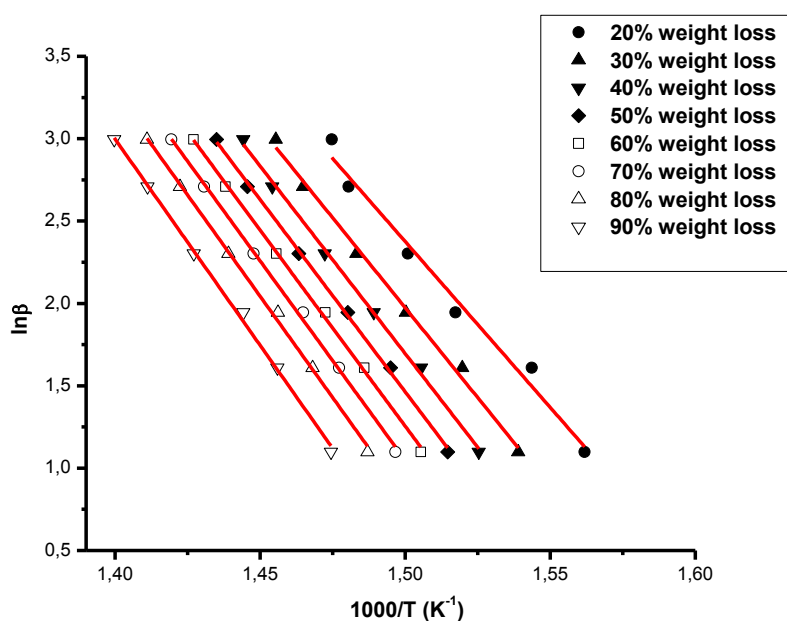


Figure9. OFW plots for PBuOEMA

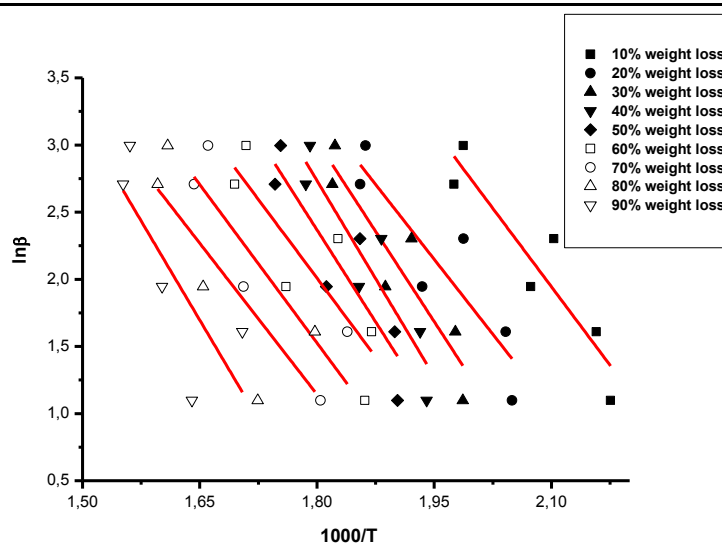


Figure10. OFW plots for PDEGMA

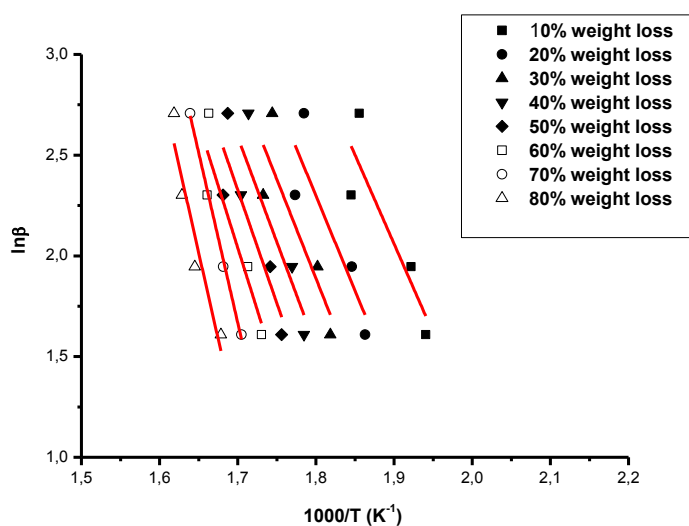


Figure11. OFW plots for POEGMA 300

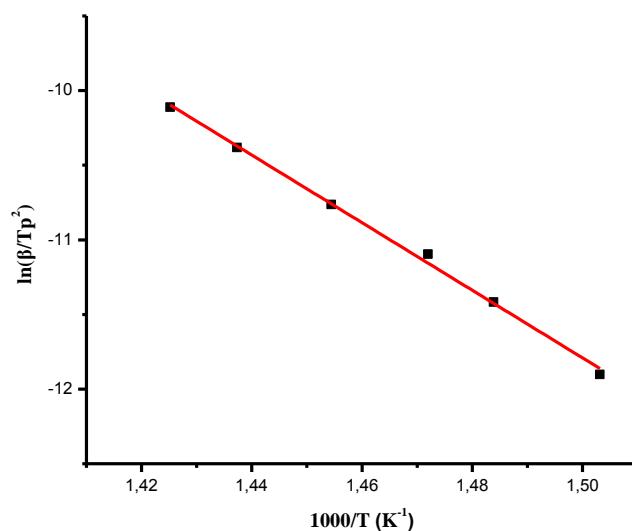


Figure12. Kissinger plot for P2VP

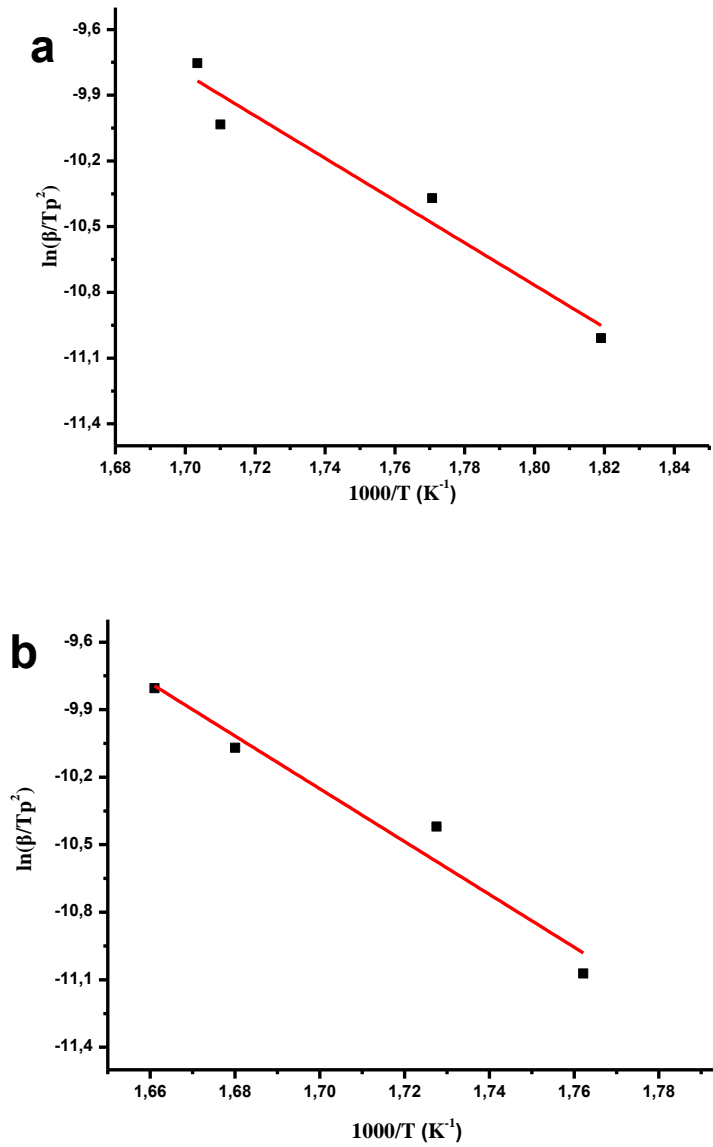
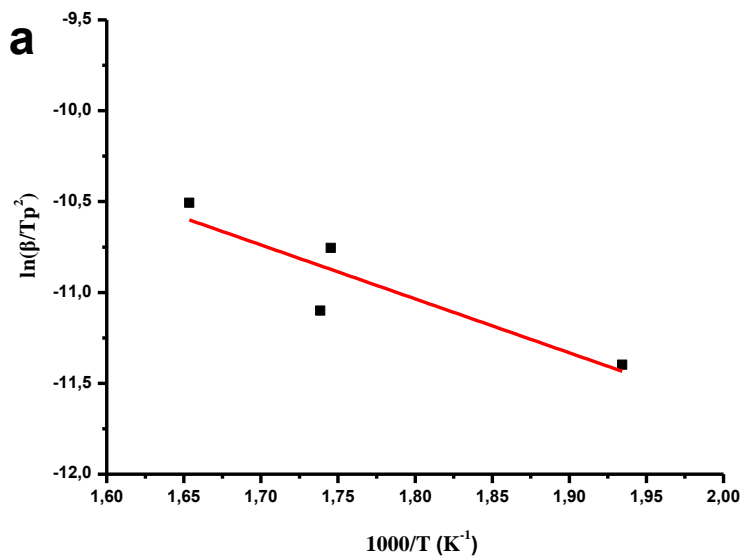


Figure13. (a) Kissinger plot for PBuOEMA first peak (b) Kissinger plot for PBuOEMA second peak



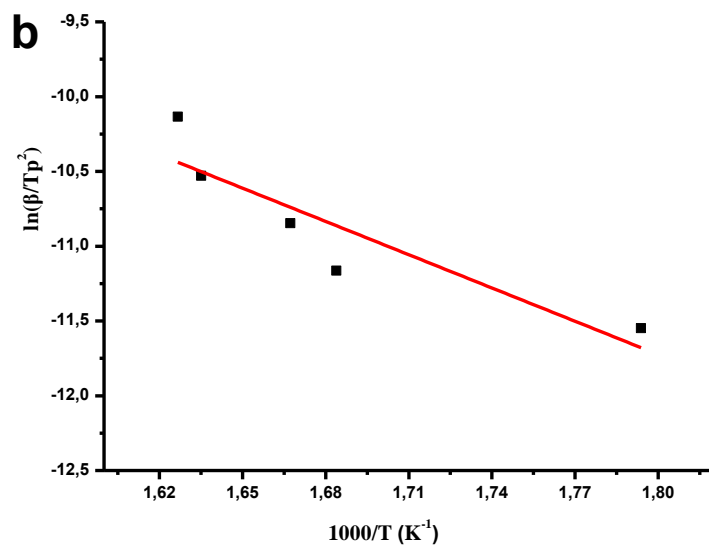


Figure14. (a) Kissinger plot for PDEGMA first peak (b) Kissinger plot for PDEGMA second peak

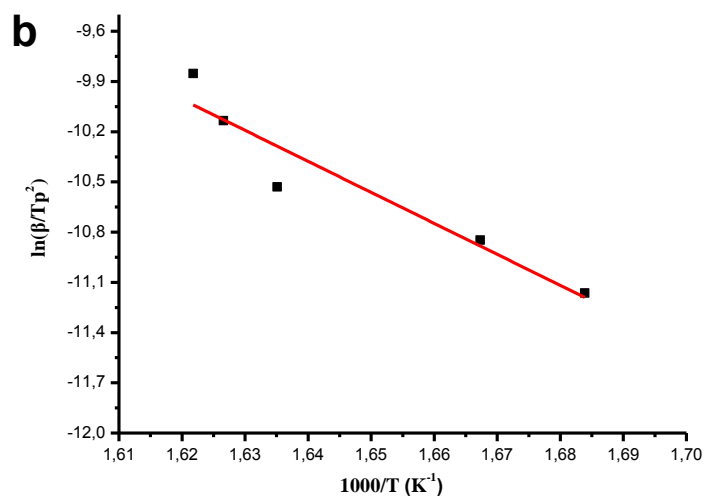
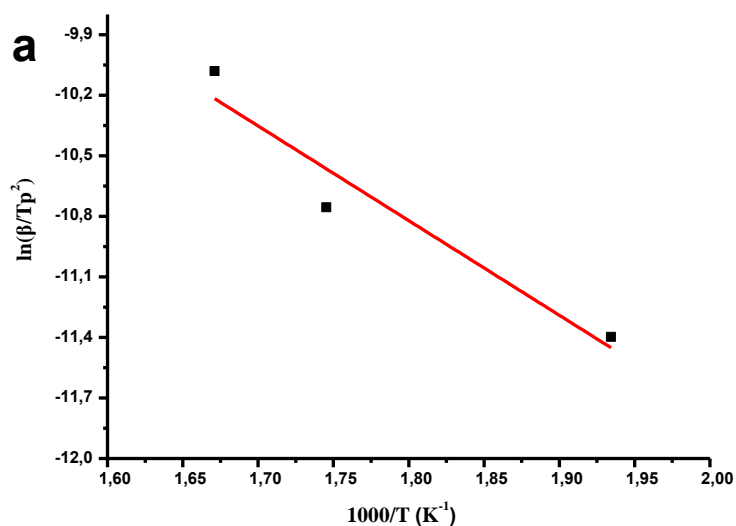


Figure15. (a) Kissinger plot for POEGMA300 first peak (b) Kissinger plot for POEGMA300 second peak

The activation energies E_a of the various copolymers at different weight losses are shown in Tables 6-8 and characteristic OFW plots are provided in Figures 16-18. These values generally increase upon increasing the degree of decomposition. However, this change is not so pronounced as in the case of the polymethacrylate homopolymers, since the presence of the 2VP monomer units dominates and affects the thermal decomposition behavior of the copolymers. The obtained values are located between those measured for the respective homopolymers, but are always closer to the E_a values of P2VP, due to the higher 2VP content in all copolymers. Comparison of the E_a values of the various copolymers leads to the general conclusion that they follow the order: $E_{a_{P2VP-co-PBuOEMA}} > E_{a_{P2VP-co-OEGMA300}} > E_{a_{P2VP-co-DEGMA}}$. The same order was found for the temperatures of decomposition at the maximum rate of decomposition of the copolymers, confirming their thermal stability. The E_a values were also calculated by the Kissinger method and results are given in Table 5 and characteristic plots in Figures 19-21. It is obvious that the Kissinger equation leads to lower activation energies. However, the same trend regarding the variation of the E_a values with the structures was observed with the OFW approach.

Table6. Activation Energies for the P2VP-PBuOEMA Copolymers from the OFW Method

Weight Loss (%)	P2VP-PBuOEMA 20-80	P2VP-PBuOEMA 40-60	P2VP-PBuOEMA 50-50	P2VP-PBuOEMA 60-40	P2VP-PBuOEMA 80-20
10	142.86	182.58	182.08	189.54	173.67
20	152.79	186.81	192.11	184.50	180.70
30	157.64	187.86	196.73	191.84	183.92
40	160.96	186.20	200.12	192.23	185.80
50	161.82	185.56	201.95	193.86	187.88
60	163.79	185.21	201.68	194.90	189.48
70	167.54	185.45	202.32	197.46	191.89
80	172.61	186.52	202.30	200.17	190.60
90	178.24	188.70	206.16	204.07	197.76

Table7. Activation energies for the P2VP-PDEGMA copolymers from the OFW method

Weight loss (%)	P2VP-PDEGMA 20-80	P2VP-PDEGMA 40-60	P2VP-PDEGMA 50-50	P2VP-PDEGMA 60-40	P2VP-PDEGMA 80-20
10	12.06	2.03	2.67	10.64	61.38
20	112.39	200.68	171.12	170.25	153.30
30	191.97	199.13	169.72	171.98	165.35
40	172.84	196.28	168.84	173.17	171.45
50	160.67	195.26	167.49	172.40	170.04
60	149.45	191.64	166.36	171.47	168.77
70	142.30	184.48	166.75	170.61	167.98
80	141.50	179.17	167.50	169.95	166.62
90	153.41	176.39	170.31	169.46	166.63

Table8. Activation Energies for the P2VP-POEGMA300 Copolymers from the OFW Method

Weight Loss (%)	P2VP-POEGMA ₃₀₀ 20-80	P2VP-POEGMA ₃₀₀ 50-50	P2VP-POEGMA ₃₀₀ 60-40	P2VP-POEGMA ₃₀₀ 80-20
10	19.85	138.06	176.04	50.33
20	--	145.12	181.25	--
30	--	158.11	183.45	143.76
40	136.61	166.10	184.10	159.60
50	165.50	171.70	185.75	173.54
60	196.51	176.21	166.35	172.07
70	199.41	196.53	183.12	179.42
80	196.08	202.45	187.83	176.20
90	195.51	182.85	196.54	183.36

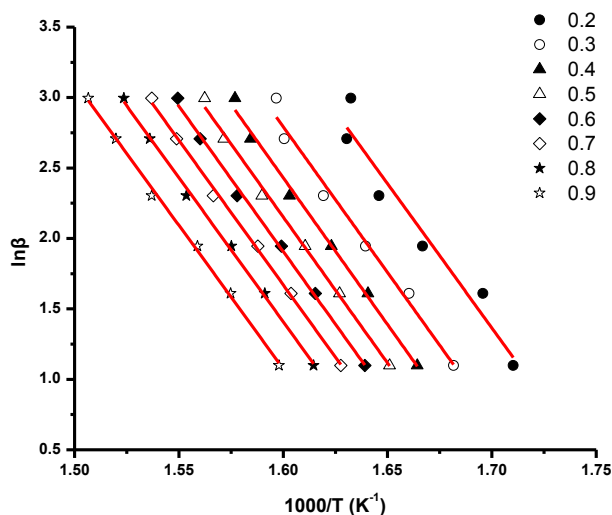


Figure16. OFW plots for P2VP-PDEGMA 60-40

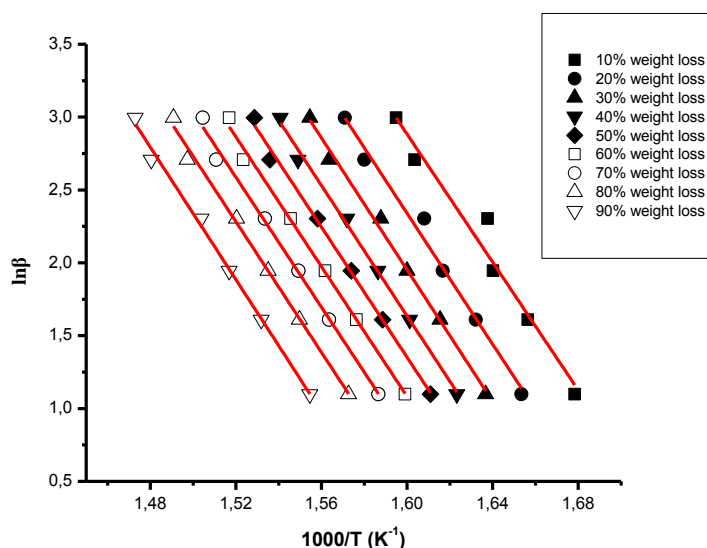


Figure17. OFW plots for P2VP-PBuOEMA 40-60

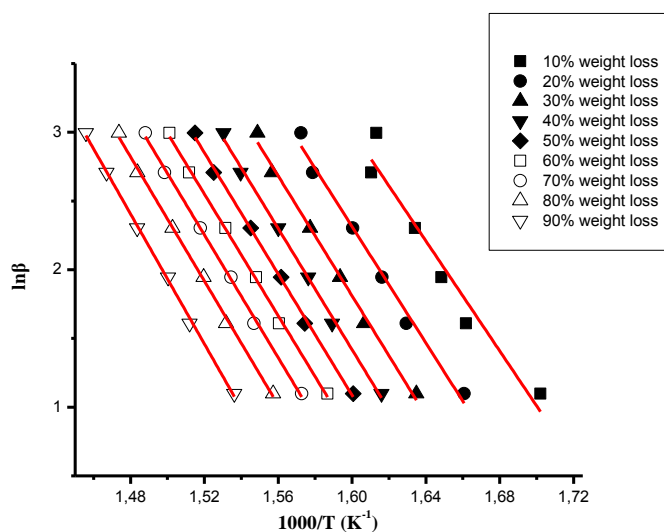


Figure18. OFW plots for P2VP-POEGMA300 60-40

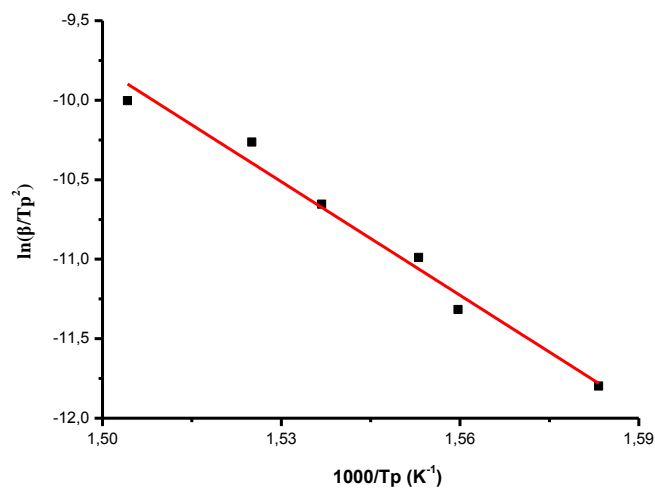


Figure19. Kissinger plot for P2VP-PBuOEMA 50-50

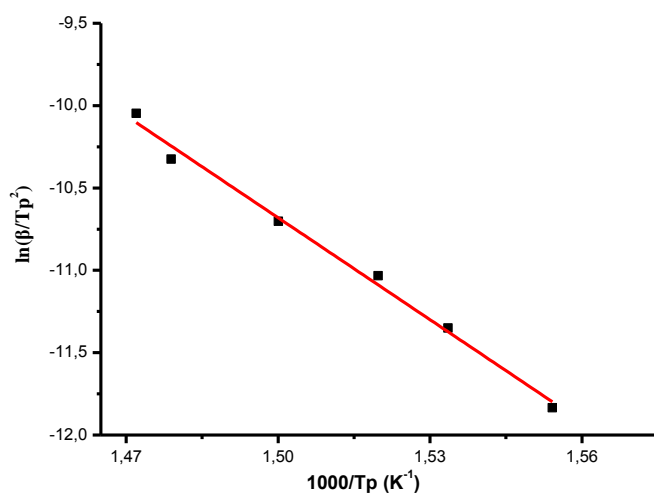


Figure20. Kissinger plot for P2VP-POEGMA300 80-20

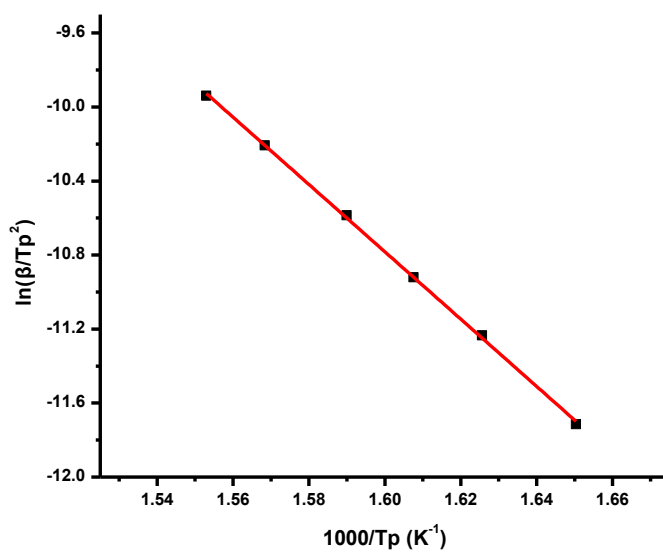
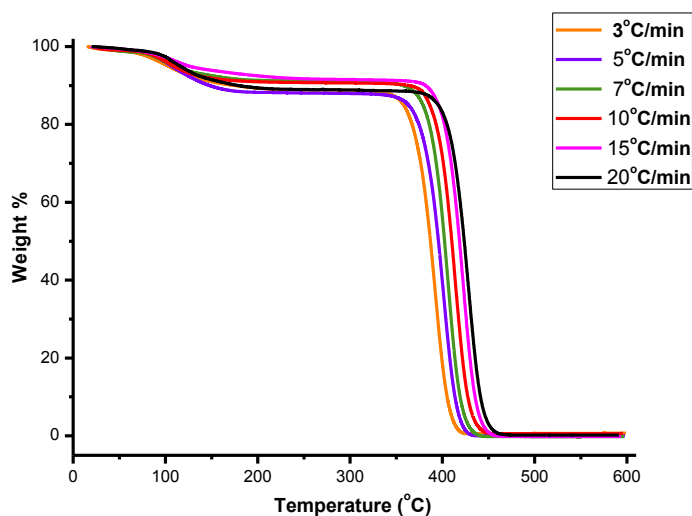
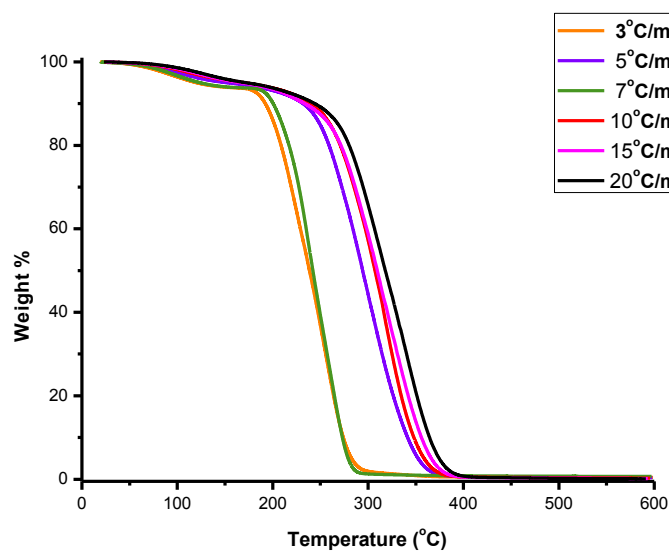


Figure21. Kissinger plot for P2VP-PDEGMA 50-50

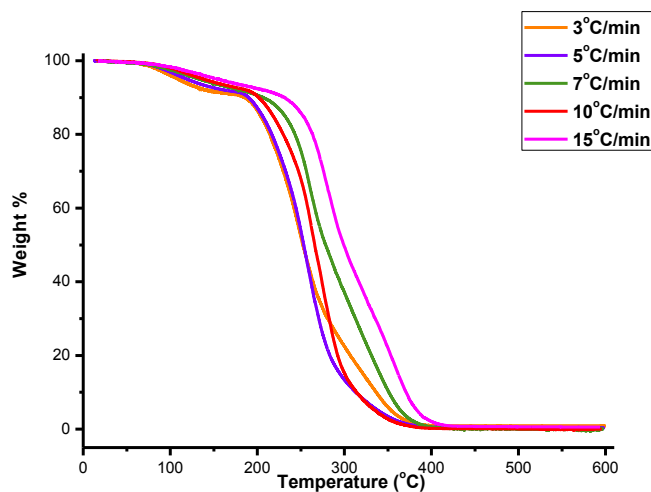
SUPPORTING INFORMATION



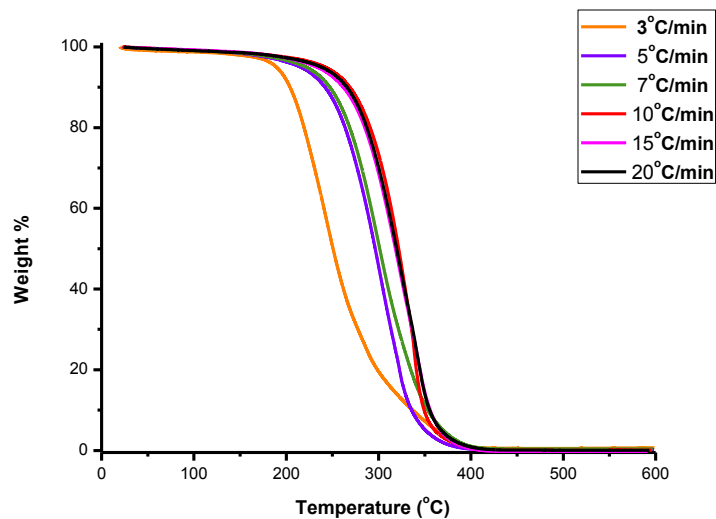
TGA curves for P2VP



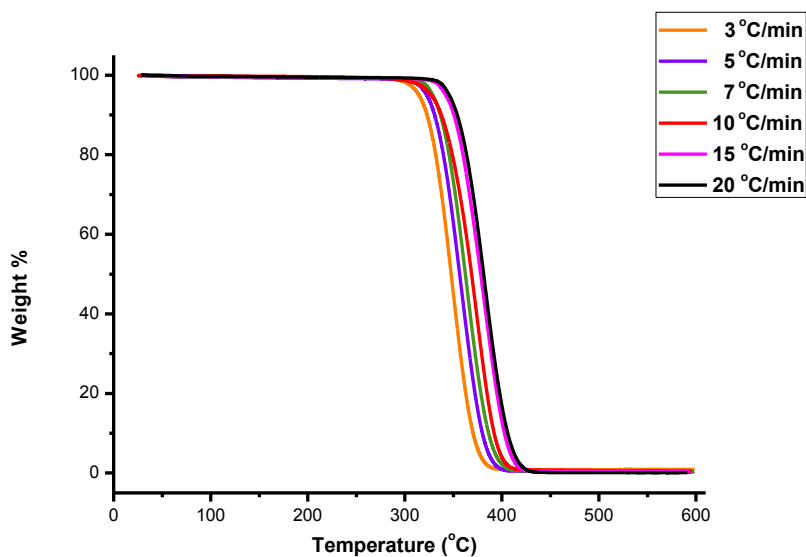
TGA curves for PBuOEMA



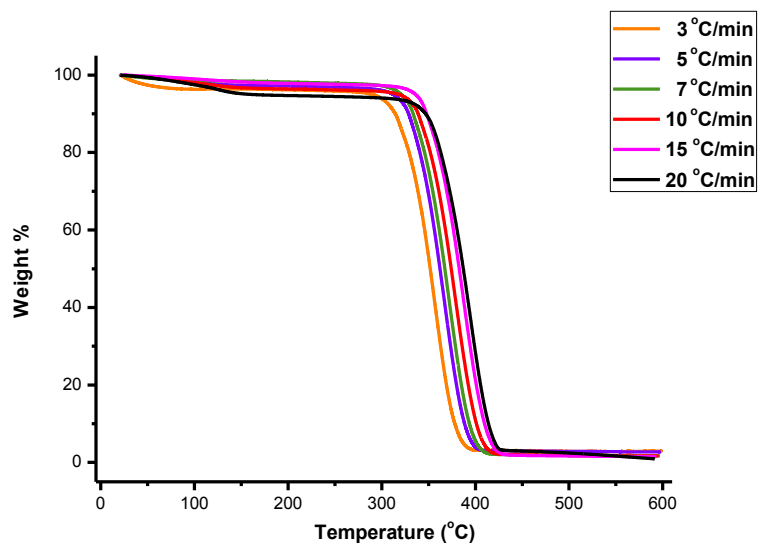
TGA curves for PDEGMA



TGA curves for POEGMA 300



TGA curves for P2VP-PBuOEMA 40-60



TGA curves for P2VP-POEGMA300 60-40

It is clear that it is possible to manipulate the thermal decomposition behavior of the statistical copolymers by affecting small changes in the comonomer chemical structure.

4. CONCLUSION

The kinetics of the thermal decomposition of statistical copolymers of 2-vinyl pyridine (2VP) with 2-butoxyethyl methacrylate (BuOEMA), di(ethylene glycol) methyl ether methacrylate (DEGMA) and oligo(ethylene glycol) methyl ether methacrylate with number average molecular weights 300 g/mol (OEGMA₃₀₀) were studied by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). The results of the corresponding homopolymers revealed that the thermal stability decreases in the order P2VP>POEGMA300>PDEGMA>PBuOEMA. Single decomposition peaks were obtained by DTG for P2VP, whereas a more complex decomposition pattern was obtained for the polymethacrylates, indicating a more complex mechanism of decomposition. The statistical copolymers showed only single decomposition peaks at temperatures located between those of P2VP and the respective polymethacrylate. However, the decomposition temperature at the maximum rate of decomposition is closer to that of P2VP, since the copolymers are richer in 2VP units. The activation energies of the thermal decomposition were calculated by the Ozawa-Flynn-Wall (OFW) and Kissinger methods. Comparison of the E_a values of the various copolymers leads to the general conclusion that they follow the order: $E_{aP2VP-co-PBuOEMA} > E_{aP2VP-co-OEGMA300} > E_{aP2VP-co-DEGMA}$. The same order was found for the decomposition temperatures at the maximum rate of decomposition of the copolymers, confirming their thermal stability.

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