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Araştırma Makalesi / Research Article

Investigation of Thermal Degradation Kinetics of Poly(Ɛ-caprolactone) Grafted onto PEMA-co-PHEMA

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Thermal Degradation Kinetic; ε-caprolactone; TGA.

Abstract

Poly(ethyl methacrylate)-co-poly(2-hydroxyethyl methacrylate), PEMA-co-PHEMA, which containing 5% 2-hydroxyethyl methacrylate (HEMA) was synthesized by the free radical polymerization. ε-caprolactone was grafted -OH side group of PEMA-co-PHEMA via ring opening polymerization method. A newly synthesized PEMA-co-PHEMA-g-PCL which grafted onto PEMA-co-PHEMA were characterized by experimental measurements such as FTIR, ^{1}H NMR and TGA techniques. The reaction mechanism of degradation process and the kinetic parameters of the polycaprolactone grafted onto PEMA-co-PHEMA in nitrogen environment were investigated by thermogravimetric analysis (TGA) at different heating rates. The evident activation energies of thermal degradation for polycaprolactone, as defined by the Kissinger's, Flynn–Wall–Ozawa and Tang methods, which does not necessary knowledge of the reaction mechanism (RM), were 108.58, 113.88 and 108.35 kJ/mol, respectively. These values were compared using different integral and differential methods. An analysis of the experimental results proposed that the reaction mechanism was an R3 deceleration type in the conversion range (2-40%) studied.

PEMA-ko-PHEMA Üzerine Aşılanan Poly(ε-kaprolakton)' un Termal Bozunma Kinetiğinin İncelenmesi

Anahtar Kelimeler:
Termal Bozunma Kinetiği; ε-kaprolakton; TGA.

Özet

Serbest radikal polimerizasyonuyla sentezlenen %5 oranında 2-hidroksietilmetakrilat (HEMA) içeren poli(etilmetakrilat)-ko-poli(2-hidroksi etilmetakrilat), PEMA-ko-PHEMA, kopolimerinin –OH ucuna, Ɛ-kaprolakton halka açılması polimerizasyonu metoduyla aşılandı. Sentezlenen polimerler FTIR ve ^{1}H-NMR teknikleriyle karakterize edildi. PEMA-ko-PHEMA-a-PCL aşı kopolimerinin termal degradasyon kinetiği farklı ısıtma hızlarında termogravimetrik analizle araştırıldı. Aktivasyon enerjisi Kissinger, Flynn–Wall–Ozawa ve Tang metotlarıyla, reaksiyon mekanizması bilinmeden, sırasıyla 108.58, 113.88 ve 108.35 kJ/mol olarak hesaplandı. Farklı integral ve diferansiyel metotlar kullanılarak bu değerler karşılaştırıldı. Deneysel sonuçların analiziyle, çalışılan dönüşüm aralığında (%2-40) reaksiyon mekanizması R_3 olarak belirlendi.

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1. Introduction

Nowadays, functional polymers are synthesized to investigation of macromoleculer properties and explored use for various purpose of this polymer. The studies about this polymers showed that structure and position of substituent linked monomers change the many properties of polymer. For this purpose the most commonly used polymer is methacrylate polymers. Acrylate and methacrylate based polymers have wide application area [1].

Poly (2-hydroxyethylmethacrylate), PHEMA, polymer is remarkable hydrogel with viscoelastic mechanical properties, high water content and the similarity to the basic structural macromolecules in the body. [2-4]. PHEMA have high chemical stability, good biocompatibility, excellent mechanical properties and hydrophilic character [5-7]. PHEMA is widely used as the main chain for the synthesis of stimuli sensitive hydrogel [8-10].

Linear polycaprolactone (PCL) polyester is synthesized by ring-opening polymerization of caprolactone. It is a semi-crystalline polymer with about 50% of crystals. It has a relatively low glass transition temperature and melting temperatures. PCL chain is flexible and exhibits low modulus, high elongation [11]. PCL is one of the most widely used synthetic polymers and approved by the FDA for medical applications. In addition, the PCL applications may be limited by slower resorption kinetics and degradation of other aliphatic polyester because of its hydrophobic character and high crystallinity [12]. Long linear chains for PCL leads to high crystallinity and a slow degradation [13]. Because of its solvable in a broad range of organic solvents PCL have high processability. Therefore it is miscible with a wide range of polymers. PCL is widely used in medical applications due to the particularly harsh and soft tissue compatibility feature[14].

In this study, the thermal degradation kinetics of poly(Ɛ-caprolactone), PEMA-co-PHEMA-g-PCL, grafted onto polyethylmetacrylate-co-poly(2-hydroxymethacrylate), PEMA-ko-PHEMA, was investigated.

2. Experimental

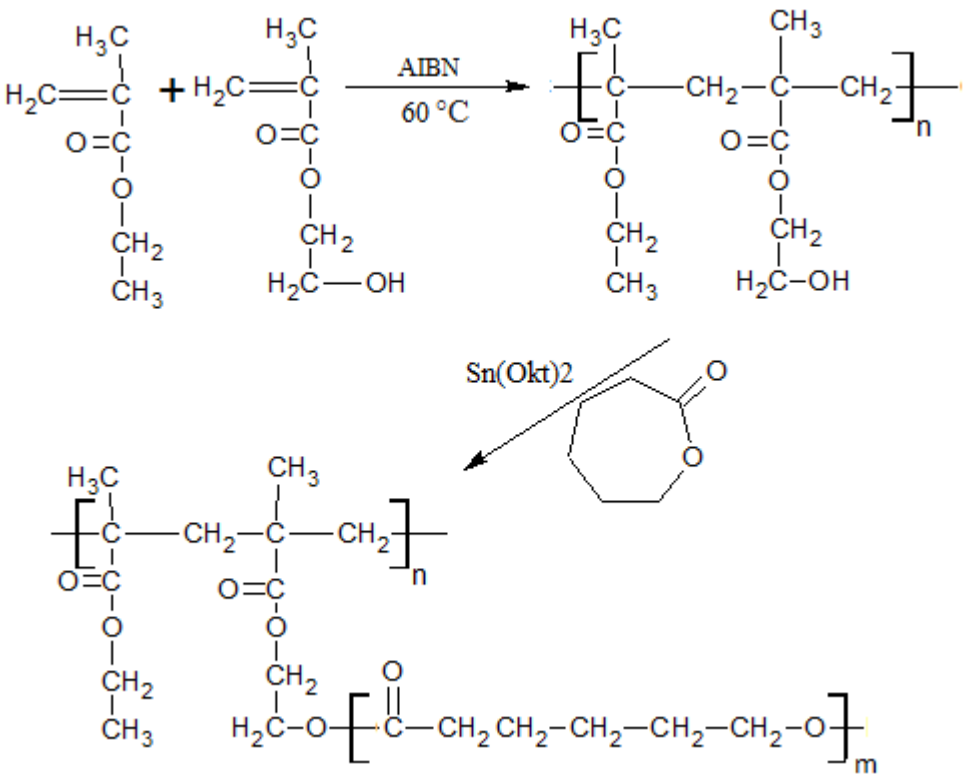
2.1. Materials

Ethylmethacrylate and 2-hydroxymethacrylate monomers was distilled before using. Ɛ-caprolactone, Tin(II)octoate catalyst and solvents was used as received.

2.2. Synthesis of Poly(Ɛ-caprolactone) Graft Copolymer

Primarily, PEMA-co-PHEMA polymers containing 2-hydroxyethyl methacrylate in 5 % rates was synthesized via free radical polymerization technique. for this purpose, for accounted amounts EMA: HEMA (95: 5) monomers was placed in a polymerization tube. 1% AIBN initiator was added into the monomer mixture and it was placed in an oil bath set at 60 ^{0}C. After 24 hours, the copolymer was removed from oil bath and dissolved in chloroform, precipitated from n-hexane. Then it dried in vacuum oven at 35 ^{0}C. -OH end group of copolymer was used as initiator for the ring opening polymerization of Ɛ-caprolactone. For this purpose, the copolymer were solved in N, N-dimethylformamide (DMF). In the calculated amount Ɛ-caprolactone monomer was added in a

solution. The polymerization was continued in the presence of tin-II-octoate catalyst in oil bath set at 100 ^{0}C for 6 hours. Thus PEMA -co-PHEMA-g-PCL copolymer was obtained with the grafting of ε-caprolactone onto -OH end groups of PHEMA. Copolymer was precipitated into methylalcohol and dried in vakuum oven at room temperature. The polymers were characterizated with FTIR ve ^{1}H-NMR tecniques. Synthesis reaction of polymers were showed at scheme 1.



Scheme 1. Synthesis Reaction of Polymers

2.3. Instrumental Techniques

Polymers were characterized with FTIR ve ^{1}H-NMR techniques. The infrared spectra was recorded on the Perkin–Elmer Spectrum One Fourier transform infrared spectrometer. 1H NMR spectra was recorded on the 400 MHz Bruker AVIII 400 machines, using tetramethylsilane as an interior standard and d- chloroform as the solvent. Thermogravimetric analysis (TGA) polymers were recorded using a Shimadzu TGA-50 (by heating rate of 10 ^{0}C min-1) under a nitrogen flow, respectively. TGA measurements were carried out on approximately 4-7 mg samples at a heating rate of 10 ^{0}C min^{-1} under conditions of nitrogen flow (10 cm^3 min^{-1}). Activation energy measurements of thermal stability and decomposition were performed from 25^{0}C to 500^{0}C at heating rates of 5, 10, 20, 30 and 40^{0}C/min. All the experiments were performed under N_2 atmosphere. The optimum gas flux rate was used 25 mL/min for the TGA-50 analyzer. For thermogravimetric analysis, the polyurethane were considered as 4–8-mg weights.

2.4. Thermal Degradation Kinetics

Dynamic thermogravimetric methods application holds an important place as a means to solve the mechanisms of physical and chemical operations occurring during the polymer degradation. The solid state isothermal decomposition reaction ratio can be explained as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (1)$$

wherein α is the conversion degree, T is the absolute temperature (K), A is the pre-exponential factor (min $^{-1}$), E is the activation energy (kJ / mol), R is the gas constant (8.314 J mol^{-1} K^{-1}) and f (α) is a function depending on the reaction mechanism. Equation (1) is reorganization and integral taking with both sides of the equation is obtained the following equation.

$$g(\alpha) = \int_0^{\alpha p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{Tp} e^{-E/RT} \mathrm{dT} \quad (2)$$

where g (α) is an integral function of the conversion. The polymer degradation process follows either deceleration or sigmoid function. Tp is dependent on the peak temperature and αp is the conversion grade at peak temperature. Table I indicates for dissimilar solid state mechanisms the differential expression of g(α) [15-17].

2.4.1. Kissinger method

Activation energy using Kissinger method determined without knowing of the reaction mechanism by the following equation:

$$\ln\left(\frac{\beta}{Tmax2}\right) = \{ln\frac{AR}{E} + ln[\mathrm{n}(1\text{-}\alpha_{\mathrm{max}})^{\mathrm{n-1}}]\} - \frac{E}{RTmax} \quad (3)$$

Wherein β is the heating rate. Tmax is related to the temperature of the inflection point of the TGA graph. αmax is the maximum conversion degree in the temperature point. n is the reaction scheme. The activation energy, E, was computed from slope of the plot ln [β / T ^{2} max] versus 1 / Tmax. [18].

2.4.2. Flynn–Wall–Ozawa method

This method is derived from integration method which determines the activation energy of the without knowing reaction mechanism. used to determine the activation energy for a given conversion value. The integrating of Doyle approach[19] and equal(2) was obtained the following logarithmic formula:

$$\log(\beta)=\log[\frac{AE}{g(\alpha)R}] - 2.315 - \frac{0.457E}{RT} \quad (4)$$

the activation energy was computed from the slope of the plot Ln (β) versus 1000 / T ; slope will be −0.4567E/R [20-21].

2.4.3. Tang method

By taking the logarithms of both sides and the formula used for solving Equation (2), the following formula can be acquired:

$$\ln(\frac{\beta}{\mathrm{T}1.894661}) = \ln(\frac{AE}{Rg(\alpha)}) + 3.635041 - 1.894661\ln E - \frac{1.001450E}{RT} \quad (5)$$

Plots of ln(β/T$^{1.894661}$) versus 1/T can be drawn. Slope will be _1.001450E/R [22].

2.4.4. Coats–Redfern method

The Coats–Redfern method uses an asymptotic approximation for the solution of eq. (2):

$$\ln g(\alpha)/T^2 = \ln(\frac{AE}{\beta E}) - \frac{E}{RT} \quad (6)$$

The activation energy for each degradation operate listed inTable I can be defined from plot of g (α) versus 1000 / T[23].

2.4.5. Van Krevelen metodu and Horowitz–Metzger metodu

$$\log g(\alpha) = \log B + \left(\frac{E}{RTr} + 1\right) + \log T \quad (7)$$

wherein;

B is $=\frac{A}{\beta}\left(\frac{E}{RTr} + 1\right)^{-1}\left(\frac{0.368}{Tr}\right)^{E/RTr}$. the activation energy can be determined from plot of log g(α) versus log [24, 25].

TABLE I. Algebraic Expressions for g(a) for the Most Frequently Used Mechanisms of the Solid-State Processes

Symbol	g(α)	Solid-state processes
Sigmoidal curves		
A2	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami eq. (1))
A3	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami eq. (2))
A4	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami eq. (3))
Deceleration curves		
R1	α	Phase boundary controlled reaction (One-dimensional movement)
R2	$[1-(1-\alpha)^{1/2}]$	Phase boundary controlled reaction (contraction area)
R3	$[1-(1-\alpha)^{1/3}]$	Phase boundary controlled reaction (contraction volume)
D1	α^2	One-dimensional diffusion
D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
D3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D4	$(1-2/3\alpha)(1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling-Brounshtein equation)
F1	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
F2	$1/(1-\alpha)$	Random nucleation with two nuclei on the individual particle
F3	$1/(1-\alpha)^2$	Random nucleation with three nuclei on the individual particle

3. Result and Discussion

3.1 Polymer Characterization

FT-IR spectrum of PEMA-co-PHEMA display characteristic peak of C=O stretching vibrations at 1720 cm^{-1}. PEMA-co-PHEMA-g-PCL spectrum display characteristic peaks of C=O stretching vibrations at 1726 cm−1, CH_2 bending modes at 1361, 1397 and 1473 cm−1 and CH_2 asymmetric stretching at 2942 and symmetric stretching at 2862 cm−1. The C—O—C stretching vibrations yield peaks at 1042, 1107 and 1233 cm−1. The FTIR spectrum of polymers was showed Figure 1.

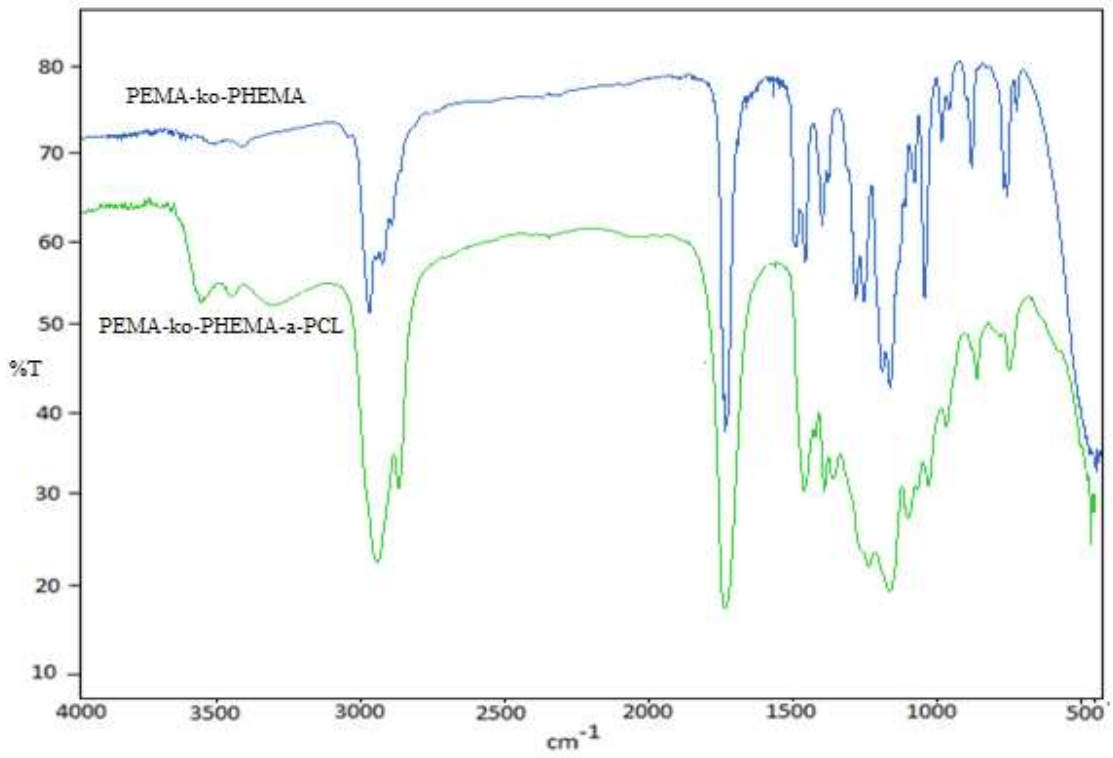


Figure1. FTIR Spectrum of Polymers

The ^{1}H NMR spectrum of PEMA-co-PHEMA showed the characteristic signal at 2.1 ppm (CH-C=O), 1.2–2.2 ppm (–CH2– and –CH– protons in the polymeric chain), and 4.5 ppm [O–CH_2-]. The ^{1}H NMR spectrum of PCL showed characteristic signals at 3.75 ppm(-OH), 2.3 pmm (CH_2-C=O) and 4.2 ppm (CH_2-OH). The ^{1}H-NMR spectrum of polymer was showed Figure 2.

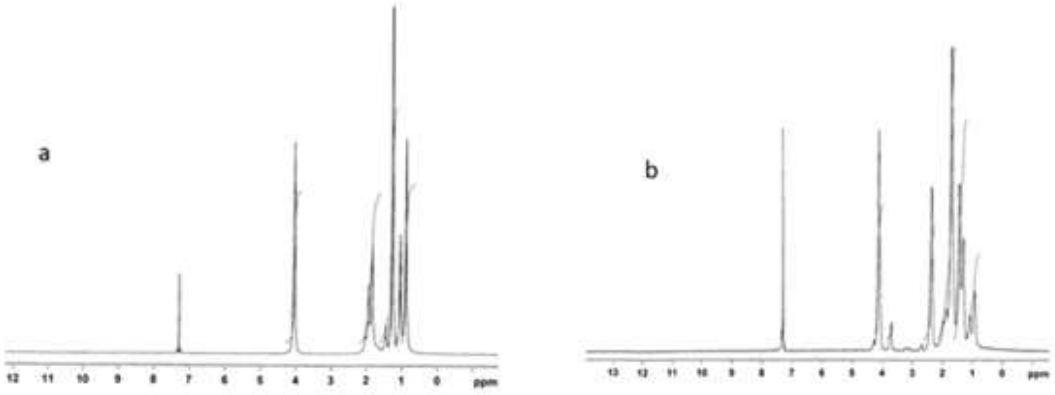


Figure 2. ^{l}H-NMR Spectrum of polymers a. PEMA-co-HEMA, b. PEMA-co-PHEMA-g-PCL

3.2. Thermal Properties of Polymers

Thermogravimetric analysis (TGA) for PEMA-co-PHEMA and PEMA-co-PHEMA-g- with a heating rate of 10 °C/min ranging from room temperature 30–500 °C. The initial and the 50% decomposition temperature were 229 °C and 283 °C for PEMA-co-PHEMA, 243 °C and 361 °C for PEMA-co-PHEMA-g-PCL, respectively. PEMA-co-PHEMA-g-PCL exhibited two degradation stages located ca. 243 and 372 °C. The weight losses for

the first and second stages were 55 and 90% w/w, respectively. TGA curves were showed Figure 3. Datas were given Table II.

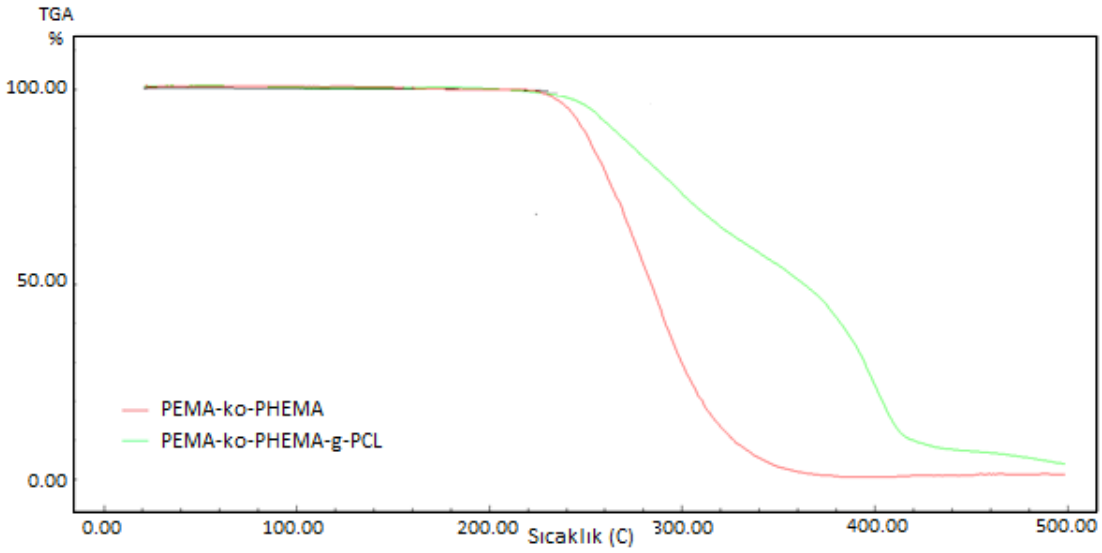


Figure 3. TGA Curves of polymers

TABLE II. Thermal Properties of Polymers

Polymer	$T_{initial}$(^{0}C)	$T_{\%50.}$(^{0}C)	$\%_{residue}$
PEMA-co-PHEMA	229	283	4.12
PEMA-co-PHEMA-g-PCL	243	361	7.07

3.3. Thermal Characterization

The thermal degradation curves of PEMA-co-PHEMA-g-PCL performed different heating rate 5, 20, 30 ve 40 0C/min indicated in Figure 4. The initial degradation temperature (T_i), degradation temperature at 50% weight decrement, % weight decrement at 300^{0}C and % residue at 500^{0}C were determined with this curves and datas were given Tablo III. The analysis of this curve showed that the % residue at 500 ^{0}C was 1.9 % with a 40 ^{0}C / min heating rate. The 10^{0}C /min gaps among measurements have selected to refrain the overlapping of inflection point temperatures[26]

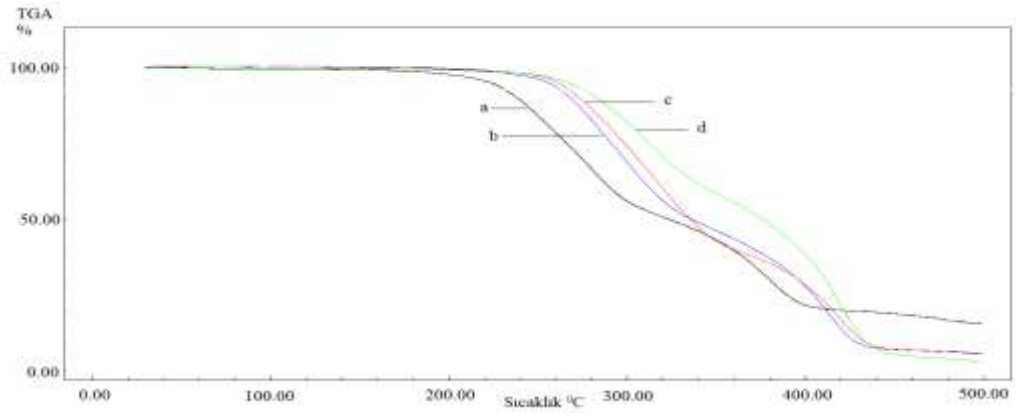


Figure 4. Experimantal TGA Curves at Different Heating Rates (a) 50C/min, (b) 200C/min, (c) 300C/min, (d) 400C/min.

TABLE III. Thermogravimetric Analysis Data at Different Heating Rates

Heating Rate (^{0}C/min)	T_i[a] (^{0}C)	$T_{50\%}$ (^{0}C)[b]	(%) weight loss at 300^{0}C	500^{0}C (%) residue
5	243.7	323.1	44.7	13.1
20	271.7	335.8	31.1	5.1
30	277.5	334.8	25.4	5.2
40	286.4	376.9	17.1	2.1

a Initial decomposition temperature (0C).

bTemperature at 50% decomposition

According to the method of Kissinger activation energy was calculated from plot of ln (β / 2 Tmax) versus 1000 / Tmax. the activation energy of PCL for this method calculated 108.58 kj/mol (Figure 5). Activation energy was calculated with Flynn-Wall-Ozawa method from plot of log β versus 1000 / T at different conversions (Figure 6). The activation energy values which calculated for different conversions with Flynn method were given Table IV. The average activation energy with this method was calculated113.88 kJ / mol. The activation energies with Tang method were determined using equation 5. For this, the graph of ln ($\beta/T^{1.894661}$) versus 1/T were drawn for different conversions (Figure 7). The average activation energy with this method was calculated 113.88 kJ/mol. This value is very close to the calculated values with the other two methods. When compared to other methods, these metots which enables to calculate the activation energy without knowing the reaction mechanism is advantageous. To check thermodegradation mechanism models, these methods have been used by some authors [20,25].

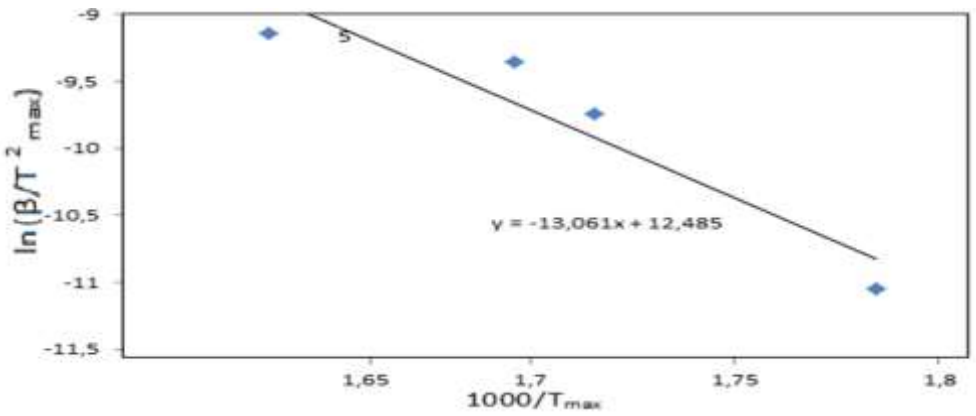


Figure 5. Kissinger method applied to the experimental data at different heating rates.

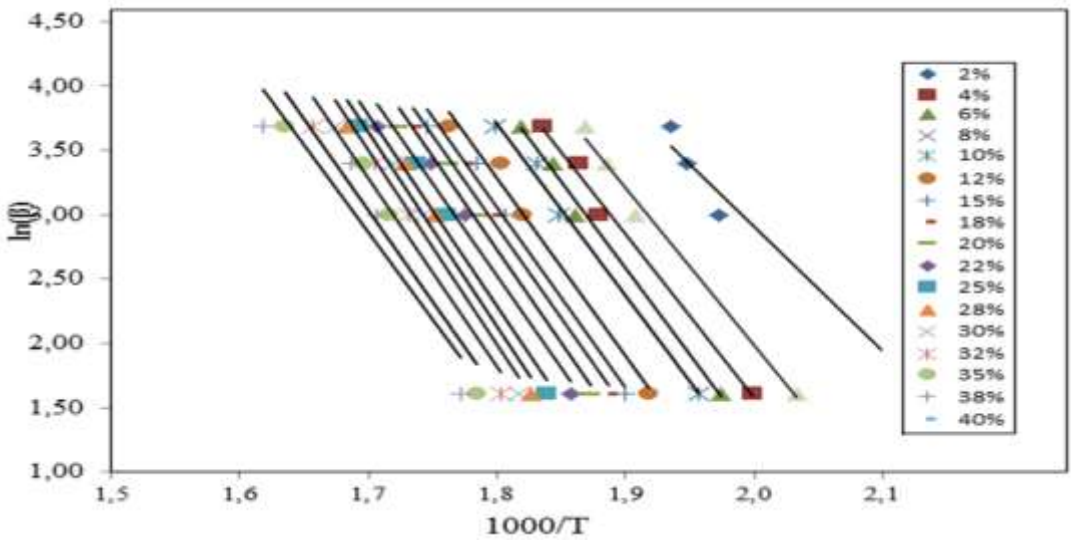


Figure 6. Flynn–Wall–Ozawa method applied to the experimental data (2–40%).

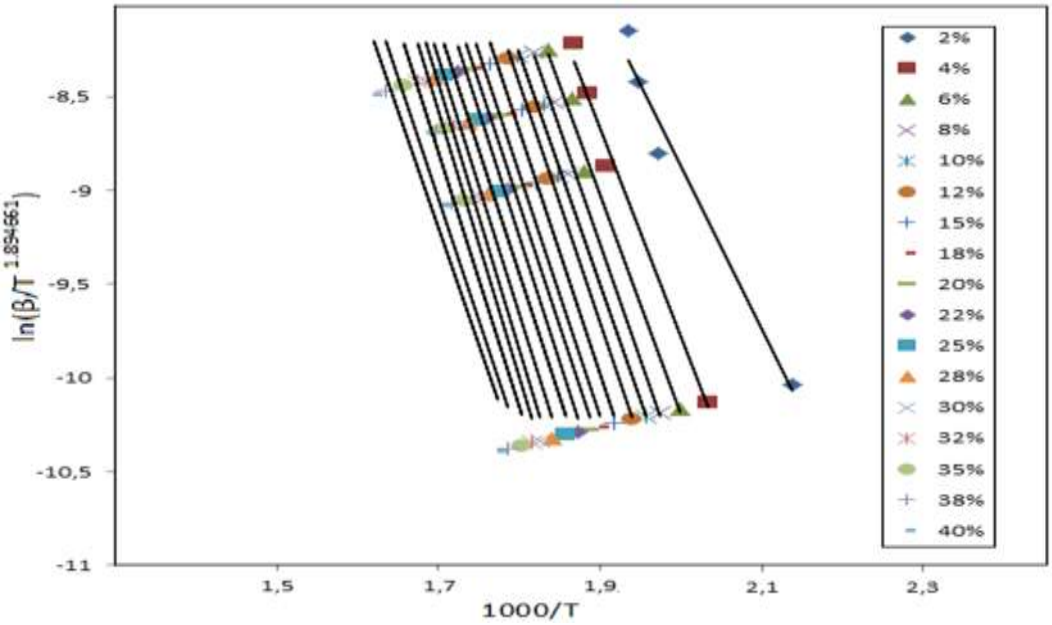


Figure 7. Tang method applied to the experimental data (2–40%).

Table IV. Activation Energy (Ea) Values Obtained by Flynn–Wall–Ozawa and Tang Methods

	Flynn–Wall–Ozawa method		Tang method	
α (%)	Ea (kJ/mol)	R	Ea (kJ/mol)	R
2	80,31324	0,9778	72,5193	0,9732
4	101,3227	0,9889	93,13971	0,9871
6	106,0783	0,9903	97,7473	0,9887
8	110,9088	0,9938	102,4711	0,9929
10	110,5928	0,9932	102,0809	0,992
12	110,5928	0,9932	106,3481	0,993
15	116,0551	0,9858	107,3527	0,9833
18	116,396	0,9838	107,61	0,981

20	117,9923	0,9809	109,1542	0,9775
22	119,4306	0,982	110,5323	0,9788
25	119,4306	0,9711	110,441	0,9661
28	122,8809	0,9646	113,8116	0,9587
30	125,4915	0,958	116,352	0,9513
32	125,6994	0,9551	116,518	0,9478
35	121,8417	0,9407	112,5746	0,9308
38	118,3165	0,9038	108,9466	0,8881
40	112,7545	0,8735	103,3096	0,8524
Mean	113,88		108,35	

The activation energy for all g(α) function which registered in Table I was suggested by Coats and Redfern. These worths were get at fixed heating rates from the fitting of $\ln[g(\alpha)/T^2]$–1000/T plots. Similar conversion worths were used in this study. Table V and VI displayed activation energies and correlation in the range of 2-40% conversion at 5, 20, 30 and 40 ^{0}C / min heating rate, respectively. From the analysis of these values, at all heating rates the activation energy in a very good fit with obtained Kissinger method correspond to the Rn type mechanism. Kissinger, Tang and Flynn-Wall-Ozawa methods were chosen, because they are not dependent to mechanism. From these tables, the activation energy value which calculated at 20 ^{0}C / min optimum heating rate and depending on R3 mechanism (106.85 kJ / mol) is very close Tang (108.35 kJ / mol) and Kissinger (108.58 kJ / mol) method. This result strongly expressed that the graft copolymer is followed deceleration (R3) type solid state thermodegradation mechanism.

TABLE V: Activation Energy (Ea) Values Obtained by Coats–Redfern Method for Multiple Solid-State Processes at Heating Rates of 5 and 20 0C/min.

	5^{0}C/min		20^{0}C/min	
Mechanism	Ea (kJ/mol)	R	Ea (kJ/mol)	R
A1	40,68705	0,9814	54,98048	0,9769
A2	27,12443	0,9814	36,65393	0,9769
A3	20,34353	0,9814	27,49024	0,9769
R1	74,76614	0,9759	100,907	0,969
R2	77,99613	0,9789	105,3301	0,9732
R3	79,10522	0,9798	106,8515	0,9745
D1	149,5356	0,9759	201,8057	0,969
D2	153,7425	0,9779	207,5756	0,9718
D3	158,2071	0,9798	213,7031	0,9745
D4	17,58078	0,8938	24,10312	0,9158
F1	81,37328	0,9814	102,961	0,9769
F2	13,8054	0,8884	18,9343	0,9111
F3	27,60996	0,8884	37,86944	0,9111

TABLE VI: Activation Energy (Ea) Values Obtained by Coats–Redfern Method for Multiple Solid-State Processes at Heating Rates of 30 and 40 ^{0}C/min.

	30^{0}C/min		40^{0}C/min	
Mekanizma	Ea (kJ/mol)	R	Ea (kJ/mol)	R
A1	54,29042	0,9788	45,8409	0,9733
A2	36,19417	0,9788	30,5606	0,9733
A3	27,14604	0,9788	22,92004	0,9733
R1	99,59341	0,9699	84,03791	0,9634
R2	103,9832	0,9746	87,7709	0,9686
R3	105,4963	0,9761	89,05957	0,9703
D1	199,1785	0,9699	168,0841	0,9634
D2	204,9152	0,973	172,9478	0,9669
D3	210,9927	0,9761	178,1108	0,9703
D4	23,92852	0,9274	20,32939	0,9337
F1	101,5808	0,9788	91,67848	0,9733
F2	18,79629	0,9225	15,97535	0,9295
F3	37,59258	0,9225	31,94987	0,9295

The activation energy calculation using Van Krevelen [29] and Horowitz-Metzger methods [30] results can also support this mechanism. Using Equation (7), activation energy values which obtained plot of log g(α) versus log T are given in Table VII. Activation energy and correlation for Rn mechanism at different heating rates were shown in this table. As can be seen from these tables, activation energy values which obtained by R3 type mechanism at 20 and 30 ^{0}C / min heating rates are best agreement with calculated by other methods.

TABLE VII. Activation Energy (Ea) Values Obtained by Van Krevelen Method for Phase-Boundary-Controlled Reaction Processes at Different Heating Rates

		Mechanism		
Heating Rate ^{0}C/min		R1	R2	R3
5	Ea (kJ/mol)	89,3615	93,2636	94,6089
	R	0,9708	0,9748	0,976
20	Ea (kJ/mol)	103,8307	107,8720	112,6040
	R	0,9632	0,9681	0,9697
30	Ea (kJ/mol)	100,9184	105,85	109,55
	R	0,9636	0,969	0,9709
40	Ea (kJ/mol)	91,4182	95,5265	96,9337
	R	0,954	0,9601	0,962

4. Conclusions

The newly synthesized polycaprolactone graft copolymer was characterized by FTIR, ^{1}H-NMR and TGA techniques. Thermal degradation kinetics of copolymer was researched by TGA at different β values. Activation energy values of thermal degradation of the copolymer computed with Kissinger's, Flynn–Wall– Ozawa and Tang method in a nitrogen atmosphere were 108.58, 113.88 and 108.35 kJ/mol. respectively. Additionally, we

debated the workability of the main plots based on the first derivative of a for detecting the mechanism of a solid-state process. Analysis of the experimental conclusions proposed that the reaction mechanism was an R3 deceleration type that is phase boundary controlled reaction (contraction volume) in the %2-40 conversion.

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