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Research Article

Synthesis, Characterization and Thermal Degradation Kinetics of Poly(methylmethacrylate-*co*-methacrylic acid)

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Abstract
In this study, poly (methyl methacrylate-*co*-methacrylic acid) (poly(MM-*co*-MA)) was synthesized at 70 ^{O}C in the presence of benzoyl peroxide, methacrylic acid and methyl methacrylate monomers by free radical addition polymerization method. The obtained structure of poly (methyl methacrylate-*co*-methacrylic acid) was characterized by GPC(Gel permeation chromatography), FT-IR(Fourier transform infrared spectroscopy) and ^{1}H-NMR(Nuclear magnetic resonance) analyses. (M_n=39800 g/mol PDI: 2.04) Radical polymerization yield was obtained at 42%. The thermal decomposition kinetics of poly (methyl methacrylate-*co*-methacrylic acid) was also investigated by the thermogravimetric process. The thermal degradation of the poly(MM-*co*-MA) was observed in two steps. Kinetic parameters were computed by the Flynn-Wall-Ozawa process and the Kissinger process. The first step and second step activation energy was determined to be 108,34 kJ / mol, 253,41 kJ / mol according to the Flynn-Wall-Ozawa process. According to the Kissinger-Akahira-Sunose process, the activation energy of the first step was 114,40 kJ/mol and activation energy of the second step was 231,13 kJ/mol.

Keywords: Thermal degradation, polymer synthesis, radical polymerization, poly(methyl methacrylate-*co* methacrylic acid)

Poli (metilmetakrilat-ko-metakrilik asit) Sentezi, Karakterizasyonu ve Termal Bozunma Kinetiği

Öz

Bu çalışmada, poli (metil metakrilat-ko-metakrilik asit) (poli (MM-ko-MA))) 70 ° C'de benzoil peroksit , metakrilik asit ve metil metakrilat monomerleri varlığında serbest radikal polimerizasyon yöntemiyle sentezlenmiştir. Poli (metil metakrilat-ko-metakrilik asit) yapısı, GPC, FT-IR ve 1H-NMR metotları analizleri ile karakterize edildi. Mn = 39800 g / mol PDI: 2.04 Radikal polimerizasyon verimi% 42 olarak elde edildi. Poli (metil metakrilat-ko-metakrilik asit) 'in termal bozunma kinetiği ayrıca araştırılmıştır. Poli (MM-ko-MA) 'nın ısıl bozulması iki aşamada gözlenmiştir. Kinetik parametreler Flynn-Wall-Ozawa işlemi ve Kissinger metodu ile hesaplandı. Birinci adım ve ikinci adımın aktivasyon enerjisinin Flynn-Wall-Ozawa metoduna göre 108,34 kJ / mol, 253,41 kJ / mol olduğu belirlenmiştir. Kissinger-Akahira-Sunose metoduna göre, ilk adımın aktivasyon enerjisi 114,40 kJ / mol ve ikinci adımın aktivasyon enerjisi 231,13 kJ / mol bulunmuştur.

Anahtar Kelimeler: Termal bozunma, polimer sentezi, radikal polimerizasyon, Poli (metilmetakrilat-ko-metakrilik asit)

1. Introduction

Functional polymers have widely used in many areas due to their potential applications, such as drug delivery, targeted, drug carrier, biosensors, and microreactors. PMMA (poly(methyl methacrylate)) is a sophisticate thermoplastic with a spacious field of implementations like automobile shadow, electronics pieces, as food containers, optical equipment, and home decoration products (Duarte, 2007). However, poly(methacrylic acid) is a pH-responsive polymer within implementations of distinct areas as like the drug delivery system in the improvement of engineering tools for medicine and bioseparation in biotechnology (Govender,

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1999). MA copolymers are used membrane bilayers by pH-triggered conformational change (Liang, 2019; Yessine, 2003). For the purpose of taking advantage of the features of both polymers, So it is important to synthesize poly(MM-*co*-MA) copolymers and also to know the properties of these polymers. In this work, the goal was to synthesize poly(MM-*co*-MA) using a radical polymerization method and also to investigate the thermal properties of poly(MM-*co*-MA).

Kinetic process (Lee, 2006; Wang, 2010; Yuzay, 2010)

Thermal degradation kinetic analysis may be used for the definition of many polymers. In common, the thermal degradation reaction of a solid polymer may be indicated in:

$$A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$$

where B_{solid} and C_{gas} are the solid char and the gas yield, A is the starting material [3].

The kinetics of thermal degradation of polymers is usually stated by the typical kinetic equation :

$$r = d\alpha/dt = k\,(T) \times f(\alpha) \qquad (1)$$

A lot of methods for the compute of kinetic parameters A, E, n based upon differential or integral methods are used.

Differential Process

Kissenger process (Badia, 2006; Hamciuc, 2007)

Activation energy may be computed using Equation (2) by the Kissenger process without knowing the solid-state degradation reaction mechanism.

$$\ln (\beta/T^2_{\max}) = \ln AR/E_a + \ln (n(1-\alpha_{\max})^{n-1}) - (E/RT_{\max}) \quad (2)$$

A is the pre-exponential factor, β is the heating rate, $\alpha_{\max}$ is maximum degradation fraction n is reaction order, $T_{\max}$ is temperature related to maximum reaction rate. Plotting

$\ln (\beta/T^2_{\max})$ against $(1000/T_{\max})$ gives activation energy from the slope.

Integral Process

Flynn-Wall-Ozawa Process [Cekingen,2012; Fraga, 2001; Dogan,2008)

This process is one of the integration processes that may be explained the activation energy without information on the reaction mechanism. The activation energy (E_a) does not depend on degradation fraction, nevertheless, they depend on the temperature, pre-exponential factor (A) and This process use Equation (3).

$$\log g(\alpha) = \log (AE_a/R) - \log \beta + \log p(E/RT) \quad (3)$$

$$\log \beta = \log (AE_a/R) - \log g(\alpha) - 2.315 - 0.4567(E/RT) \quad (4)$$

the plot of $\log \beta$ against 1000/T should be linear with the slope E_a/R, from which E_a may be acquired.

2. Materials and Methods

2.1 Materials

Methyl methacrylate (99%, Aldrich), Methacrylic acid (99%, Aldrich). Benzoyl peroxide (99% Sigma Aldrich). Triethylamine (TEA, 98% Aldrich) Dichloromethane (DCM, 99.9% Aldrich) Diethyl ether (98%, Aldrich)

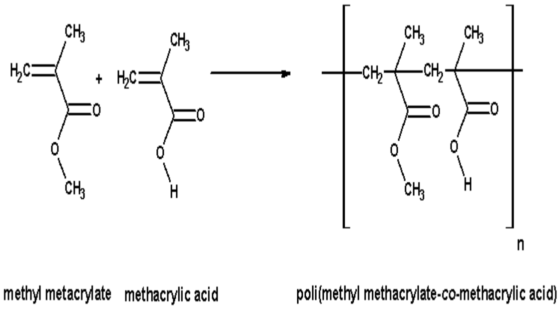
Tetrahydrofuran (THF, 98% Sigma Aldrich) Methanol (98% Sigma-Aldrich) and N, N-Dimethyl formamide (99% Aldrich).

Instrumentation

^{1}H NMR measurements were saved using a Varian AS-400 (400 MHz) appliance. FT-IR spectra were saved on a Perkin-Elmer FTIR Spectrum One-B spectrometer. Molecular weights were designated by gel permeation chromatography (GPC) appliance equipped with a Waters styragel column (HR series 2, 3, 5E) with THF. TG was performed on Perkin–Elmer Diamond TA/TGA from 25 to 600°C at different heating rates (5-10-15-20 °C/min), under a fixed flow of 100 mL/min of N_2 atmosphere.

2.1.1.1.Synthesis of Poly (methylmethacrylate-*co*-methacrylic acid)

Three necks balloon with were taken and then methyl methacrylate, (2.5 ml, 0.0234 mol) and methacrylic acid (0.5 ml, 0.00592 mol) and benzoyl peroxide (3%; 0.2131 g) were added. The balloon in the oil bath was vacuumed and purged with nitrogen. The balloon's mouth was closed on the magnetic rod inside the chili balloon. The magnetic stirrer and heater were turned on to adjust the reaction temperature to 70 °C. After 90 minutes, the reaction was stopped. The mixture was precipitated in 100 ml of ether. Filter under vacuum to obtain the polymer as a solid. The oven was dried for 1 day (scheme1). FTIR and ^{1}H NMR spectra are given in Figure 1 and Figure 2, respectively. (M_n=39800 g/mol PDI: 2.04)



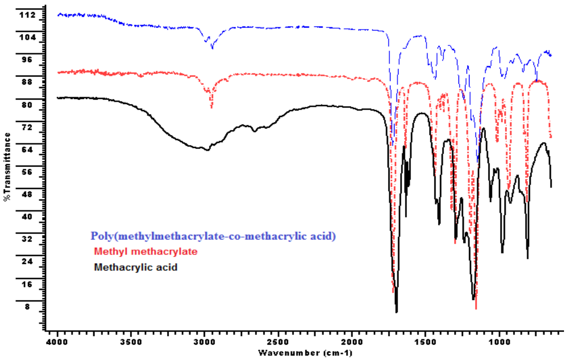


Figure 1: FT-IR Spectra of Monomers and Poly(methylmethacrylate-*co*-methacrylic acid)

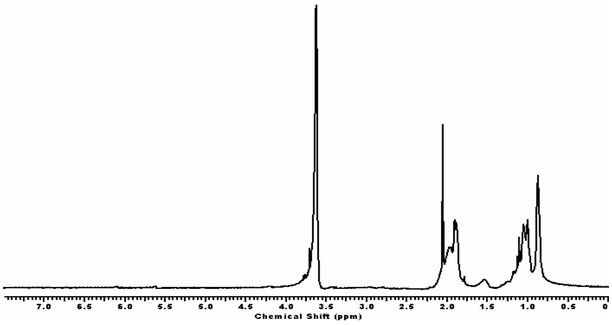


Figure 2: ^{1}H- NMR Spectrum of Poly(methylmethacrylate-*co*-methacrylic acid)

3. Results and Discussion

As mentioned above, our strategy toward the direct preparation of copolymer base upon radical polymerization technic and to investigate thermal degradation of poly(MM-*co*-MA). The whole method is showed in Scheme 1. To this strategy, poly(MM-*co*-MA) copolymers containing two different monomers were prepared over free radical addition polymerization. The components of copolymers as explained by using ^{1}H NMR spectroscopy approved in agreement with the expected values and copolymer structure. In the ^{1}H NMR spectrum of poly(MM-*co*-MA), while the signal around at 3.7 ppm was attributed to $-CH_3$ linked to the oxygen atom. Also, the FTIR spectral analysis promotes this result (Figure 2). According to the FTIR spectrum in Figure 2, both methacrylic acid and methyl methacrylate were found to be lost in the methacrylate-co-methacrylic acid copolymer peak of C = C sp^2 hybridization on the straight chain at about 1600 cm^{-1}. In addition, 2900 cm^{-1} wide and strong peak in the structure of the existing -COOH belongs to the 1700 cm^{-1} and the peak in the structure of 1750 cm^{-1} C=O was observed. The peak of 3000 cm^{-1} shows the C-H stresses present in the structure.

The corresponding derivative curves (DTG) and TG curves for poly(MM-*co*-MA) are indicated in Figure 3 and figure 4. The degradation of poly(MM-*co*-MA) demonstrates two-step. The first step reaction arises to start around 100 °C and stop around 200 °C with a maximum rate around at 150 °C for heating rate 20 °Cmin^{-1}. The second reaction step arises between 360 °C and 460 °C with the maximum rate of weight loss around 425 °C for heating rate 20 °Cmin^{-1}. The thermogravimetric characteristics, maximum degradation temperature (T_{max}), and residual mass (1-α) can be obtained from figure 3 at the distinct heating rates (5- 10-15-20 °C/min). When the heating rate raised, degradation inception temperatures of the DTG curves and maximum degradation temperatures were raised. This temperature shift could be ought to heat transfer influence. No ash observed after thermal degradation of the poly(MM-*co*-MA) sample with increasing heating rates.

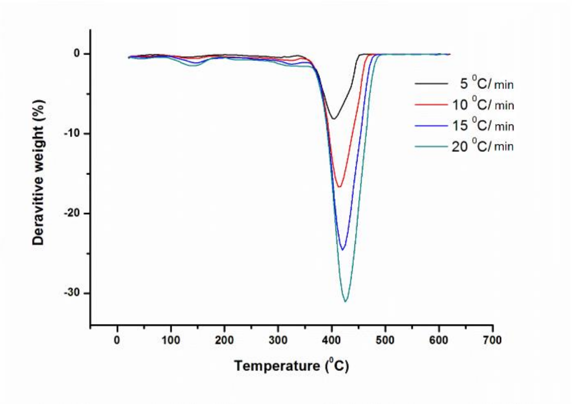


Figure 3: DTG curves of poly(MM-*co*-MA)

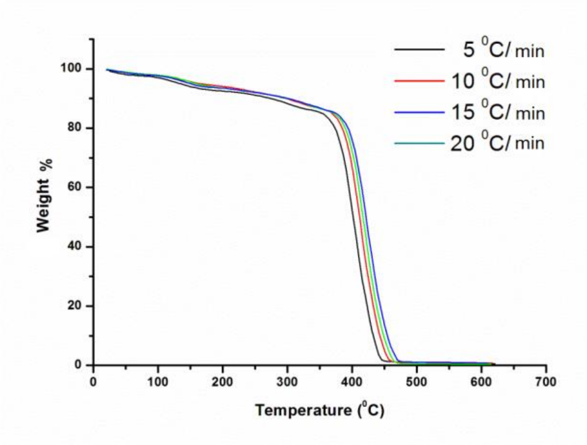


Figure 4: TG curves of poly(MM-*co*-MA)

Table 1: Kissinger method into (β/T^2_{max}) and 1000 / T_{max} values at different heating rates (First step)

β	T_{max} (°C)	T_{max} (K)	T^2_{max}	$\ln(\beta/T^2_{max})$	$1000/T_{max}$
5	404	677	458329	-11,426	1,477
10	414	687	471969	-10,762	1,456
15	422	695	483025	-10,380	1,439
20	426	699	488601	-10,104	1,431

Table 2: Kissinger method ln (β/T^2_{max}) and 1000 /T_{max} values at different heating rates(second step)

β	T_{max} (°C)	T_{max} (K)	T^2_{max}	$\ln(\beta/T^2_{max})$	$1000/T_{max}$
5	135	408	166464	-10,413	2,451
10	142	415	172225	-9,754	2,410
15	148	421	177241	-9,377	2,375
20	142	415	172225	-9,061	2,410

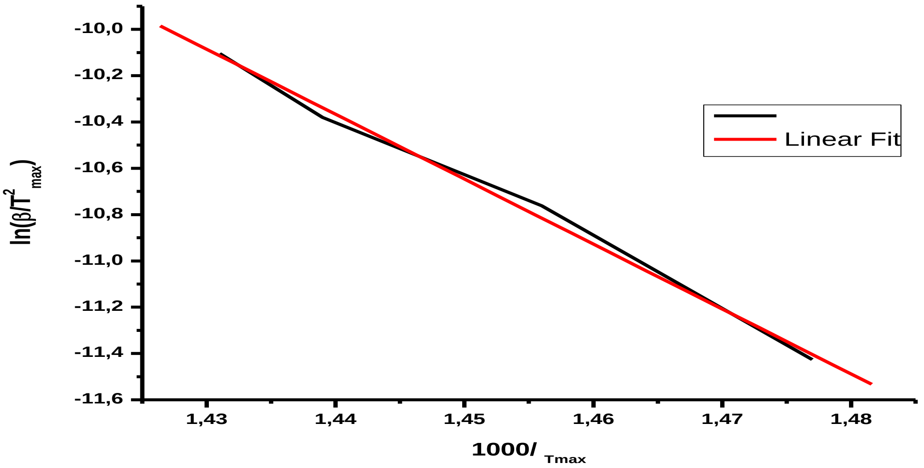


Figure 5: ln (β/T^2_{max}) with 1000 /T_{max} first step activation energy graph

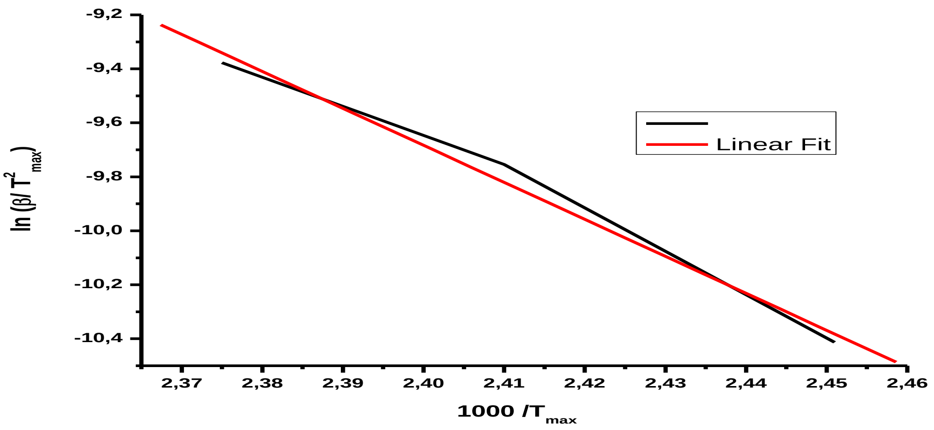


Figure 6: ln (β / T^2_{max}) with 1000/T_{max} second step activation energy graph

Table 3: Log (β) values for poly (Methyl methacrylate-*co*-methacrylic acid)

	log(β)	0,95	0,9	0,85	0,8	0,75	0,7	0,65
5	0,70	2,46	1,83	1,60	1,55	1,53	1,51	1,51
10	1,00	2,29	1,75	1,56	1,52	1,50	1,49	1,48
15	1,18	2,32	1,75	1,55	1,51	1,49	1,48	1,47
20	1,30	2,36	1,74	1,54	1,50	1,48	1,47	1,46

	log(β)	0,55	0,5	0,45	0,4	0,35	0,3	0,25
5	0,70	1,49	1,49	1,48	1,47	1,46	1,46	1,45
10	1,00	1,47	1,46	1,45	1,45	1,44	1,43	1,43
15	1,18	1,46	1,45	1,44	1,44	1,43	1,42	1,41
20	1,30	1,45	1,44	1,43	1,43	1,42	1,41	1,40

	log(β)	0,15	0,1	0,05
5	0,70	1,43	1,42	1,41
10	1,00	1,41	1,40	1,39
15	1,18	1,40	1,39	1,37
20	1,30	1,39	1,37	1,36

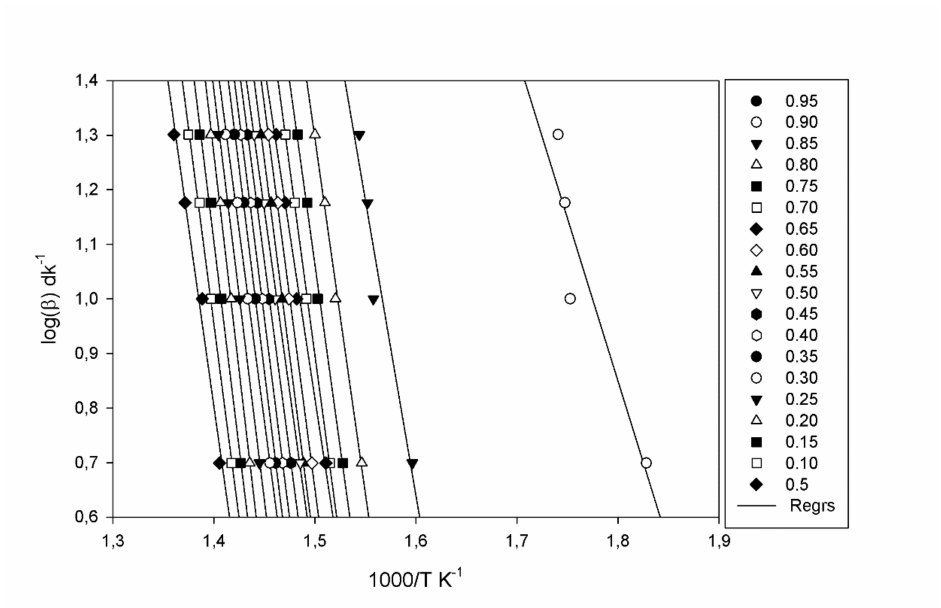


Figure 7: Poly(Methyl methacrylate-*co*-methacrylic acid) change of log (q) to 1000/T for different heating rates

Table 4: The obtained (1-α) and activation energy values of TG thermograms for poly (Methyl methacrylate-*co*-methacrylic acid)

1-α	α	m	E (kJ)/mol	R^2
First Step				
0,95	0,05	-5,951	108,34	0,96
0,9	0,1	-5,951	108,34	0,96
Average			108,34	
Second step				
0,85	0,15	-10,849	197,50	0,96
0,8	0,2	-13,019	237,00	1
0,75	0,25	-13,438	244,63	0,87
0,7	0,3	-13,729	249,93	0,96
0,65	0,35	-12,172	221,59	0,96
0,6	0,4	-14,070	256,14	1
0,55	0,45	-14,394	262,04	1
0,5	0,5	-13,241	241,05	1
0,45	0,55	-14,137	257,36	1
0,4	0,6	-14,684	267,32	1

0,35	0,65	-14,902	271,28	1
0,3	0,7	-14,010	255,05	1
0,25	0,75	-14,902	271,28	0,99
0,2	0,8	-15,880	289,09	0,96
0,15	0,85	-15,062	274,20	0,96
0,1	0,9	-14,240	259,23	0,98
Average			253.41	

The first (T_{max}) was in the range of 100-200 ^{o}C and might be because of the destruction of decarboxylation of the methacrylic acid group. For example, aliphatic polyesters are degrading over β- and α- hydrogen bond scission of macromolecular chains, forming low molecular weight volatile products like allyl compounds alcohols, ketones, aldehydes, acids and H_2O, CO_2, (Nanaki, 2011). The second maximum of decomposition (T^2_{max}) was in the range of 360-460 ^{o}C and might be because of the ester unit thermal degradation is dominated by random scission of β- and α-hydrogen bonds and the degradation of polymer chain itself. For the purpose of acquiring more knowledge about the thermal stability of the poly(MM-*co*-MA), kinetic parameters were calculated using integral and differential methods. The Kissenger and Flynn-Wall-Ozawa process was applied to examine the TG datum of poly(MM-*co*-MA) because they were sovereign of any thermal degradation mechanism. The activation energies and correlations acquired from the classical process of the Kissenger for poly(MM-*co*-MA) are 114,40 kJ\mol (r^2=0.9959) for the first step and 231,13 kJ \ mol (r^2=0.9895) for the second step. (Figure 5 and Figure 6). Tmax values are tabulated in Table 1 and Table 2. Plotting log β and 1000/T as a function of conversation as per the Flynn-Wall-Ozawa process is indicated in Figure 6. Finally, the KAS process is based upon Equation (10) and must be a few thermograms (at least four) at distinct heating rates. The worth of activation energies was examined from plots of ln(β/T^2) against 1000/T at similar α values (Table 3 and Table 4). Table 1-2 and Table 3-4 sum up the activation energies of the first and second steps acquired by the Kissenger, Flynn-Wall-Ozawa process respectively. The activation energies acquired from Flynn-Wall-Ozawa, the process was higher than Kissenger the worth from in the second step. It can to the second peaks on DTG curves were not sharp enough to examine the peak point and this broadness could bring some difference.

4. Conclusion

A Functional copolymer was synthesized via a free radical addition polymerization method. Poly(MM-*co*-MA) was characterized by FTIR, ^{1}H-NMR, TG, and GPC. MA copolymers are widely used membrane bilayers by pH-triggered conformational change. The thermal degradation of poly(MM-*co*-MA) in nitrogen is a two-step reaction. The thermal degradation kinetics of poly(MM-*co*-MA) was appraised by using two processes. The average activation energies for the first step acquired using Kissenger, Flynn-Wall-Ozawa, process were calculated 114,40 and 108, 34 kJ/mol, respectively. For the second step, the average activation energies worth from Kissenger, Flynn-Wall-Ozawa, were taken as 231,20, 253,41 kJ/mol, respectively.

Ethics

There are no ethical issues after the publication of this manuscript.

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