

Synthesis, Characterization and Thermal Behavior of Novel Acrylate Polymers Based on N-(benzothiazole-2-yl) Maleimide

F. Abdel Hai, H. Abdel Wahab, A. Galal* and H. S. Nassar
Department of Applied Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt.

IN the present study novel acrylate polymers were prepared from different feed compositions of ethyl acrylate (EA), methyl methacrylate (MMA), styrene (St) and N-(benzothiazole-2-yl) maleimide (BTM) monomer via emulsion polymerization technique using sodium lauryl sulfate as a surfactant and ammonium persulfate as an initiator. The chemical structure of BTM monomer was confirmed by elemental analysis in addition to FT-IR, ¹H-NMR and mass spectroscopy. The prepared acrylate polymers of different compositions were also investigated by FT-IR, GPC, TGA and DSC. The solubility of both BTM monomer and the formed polymers of different compositions in various solvents was also investigated. The obtained results showed that the thermal decomposition of the prepared polymers which has taken place occurred in a single step in the temperature range from 345 to 436°C. The mechanism of the thermal degradation of the prepared polymers was confirmed via kinetic analysis of their thermal degradation using Broido, Coats-Redfern and Horowitz-Metzger methods.

Keywords: Acrylate polymer, N-(benzothiazole-2-yl) maleimide, Thermal gravimetric analysis and Kinetic analysis.

In the recent years some comprehensive work has been published on the synthesis of new types of plastic materials by modification of commodity polymers in order to improve their properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization. Polymers of N-substituted maleimides and their derivatives can be classified as polyimides, important high performance engineering plastics, being a class of rigid polymers because of the imide rings in the backbone. This provides the polymers with superior mechanical and thermal stability. The peculiar homo- and copolymerization characteristics of the maleimide group make it an attractive monomer for designing special vinyl polymers. Although maleimide undergoes homopolymerization with great difficulty, it copolymerizes

*Corresponding author. Tel.: (02) 01115492817; E-mail: ahmed_20201422@yahoo.com

quite readily with a variety of vinyl monomers. Apart from enhancing the thermal stability and glass transition temperature of the resultant copolymers, the maleimide group can effectively serve as a vehicle for many functional groups for their predefined distribution in a vinyl polymer backbone through free radical copolymerization. One of the main advantages offered by functional maleimides, is the fact that new monomers with desired substituents to the imino nitrogen can be readily prepared. Free radical polymerization and copolymerization of N-substituted maleimides, with various vinyl monomers, have been reported in a number of papers⁽¹⁻³⁾.

The utilization of thermo gravimetric analysis (TGA), to study the thermal stability and degradation behavior of the polymeric systems, has attracted much attention. Many reports were carried out in this field⁽⁴⁻⁷⁾. Hanzhou Liu *et al.* introduced acrylonitrile onto poly ethylene nonwoven fabric via a pre-irradiation induced emulsion graft polymerization method. The thermal stability of the grafted polymer is measured by thermo gravimetric analysis (TGA)⁽⁸⁾. Sinem Kadriye Cekingen *et al.* synthesized a novel 2-[[2-(3-thienyl) acetyl]oxy]ethyl 2-methylacrylate (HEMAT) monomer. Polymer and random copolymer of HEMAT and methyl methacrylate (MMA) were prepared. Thermal behavior of HEMAT polymer and copolymer with MMA was also investigated by thermo gravimetric analysis (TGA). The apparent activation energies for thermal degradation were obtained by Kissinger and Tang methods⁽⁹⁾. The present work focused on synthesis, characterization and thermal stability behavior of the novel acrylate polymers based on a new monomer containing benzothiazol ring. Degradation kinetic parameters such as energy of activation (E_a) for the prepared polymers were calculated using three mathematical models namely; Broido's (BR)⁽¹⁰⁾, Coats-Redfern (C-R)⁽¹¹⁾ and Horowitz-Metzger (H-M)⁽¹²⁾ for comparison purposes.

Experimental

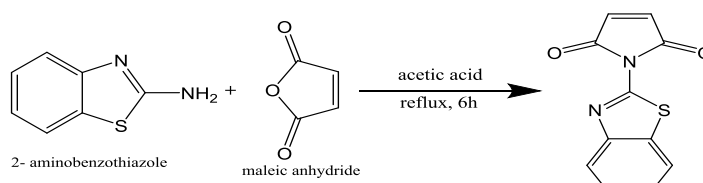
Materials

The maleic anhydride, 2-aminobenzothiazole, anhydrous sodium acetate, acetic acid and poly vinyl alcohol (PVA) used were produced by Sigma-Aldrich Company Ltd based in UK. The ethyl acrylate (EA), methyl methacrylate (MMA) and styrene (St) used were produced by EIF chem. (ATCO) company in France. Sodium lauryl sulfate (SLS), ammonium persulfate and other chemicals were all supplied by the El-Naser Pharmaceutical Chemical Company in Egypt. Deionised water was used throughout the work.

Synthesis of *N*-(benzothiazole-2-yl) maleimide (BTM) monomer

A mixture of maleic anhydride (0.1 mole, 9.8 g), 2-amino-benzothiazole (0.1 mole, 15 g) and anhydrous sodium acetate (0.5 g) in acetic acid (200 ml) was refluxed for 6 hr. Then the resulting solution was poured into a crushed ice water mixture, where a yellowish white colored monomer was separated out. The solid obtained was filtered and washed several times with cold water and then dried. Further the monomer was recrystallized from an ethanol/benzene mixture. The *Egypt. J. Chem.* **56**, No.4 (2013)

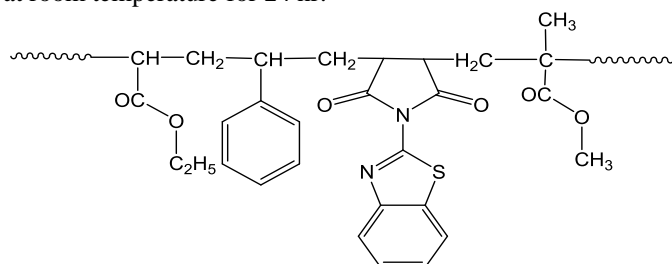
reaction yield was then determined, as well as the physicochemical characteristics such as colour and melting point.



Scheme 1. Synthesis of N-(benzothiazole-2-yl) maleimide (BTM) monomer.

Synthesis of the acrylate polymers based on N-(benzothiazole-2-yl) maleimide (BTM)

Ethyl acrylate (24g), methyl methacrylate (1g), styrene (variable), N-(benzothiazole-2-yl) maleimide (BTM) (variable) and sodium lauryl sulfate - emulsifier (SLS, 0.8 g) were dispersed in 30 g of 1% PVA solution (0.3 g PVA in 29.7g deionized water) to get a pre-emulsion by fast agitation. Then, 10% of the pre-emulsion, 15g of 1% PVA solution, 0.5 g ammonium hydroxide (25%) and 20% of the ammonium persulfate initiator weight (0.096 g) were added to a 500ml five-necked round-bottom flask fitted with a reflux condenser, a thermometer, a magnetic stirring bar and two separate feed streams, and the agitation was maintained at 200 rpm. Initially, the reaction flask was purged with nitrogen for 15 min and immersed in a water bath. When the temperature was raised to 80°C the remaining pre-emulsion, and the solution of the remaining initiator (0.384 g in 5.22 g deionized water), were added to the flask over a 3 hour period. When the addition was complete, the reaction was kept at 80°C for a further 2 hr, to ensure complete monomer conversion, and then cooled. Part of the emulsion was diluted with water and the polymers were precipitated into excess acetone and extracted from ethanol for 12 hr to remove all traces of water, surfactant and unreacted monomer residue. They were then dried under reduced pressure at room temperature for 24 hr.



Scheme 2. Chemical structure of acrylate polymer containing thiazole moiety.

Characterization techniques

The elemental analysis for the synthesized N-(benzothiazole-2-yl) maleimide (BTM) monomer was undertaken at the National Research Center, Micro Analytical Centre, Giza, Egypt. The FT-IR spectra of the synthesized N-

(benzothiazole-2-yl) maleimide (BTM) monomer and new acrylate polymers were recorded on a Nicolet 400D FT-IR spectrometer, using KBr pellets. The Mass spectra and the $^1\text{H-NMR}$ spectra of the synthesized N-(benzothiazole-2-yl) maleimide (BTM) monomer were recorded on a Shimadzu QP-2010 (Tokyo, Japan) using the electron ionization mode and a Varian Mercury VX-300 NMR (Tokyo, Japan) spectrometer (δ , ppm) in DMSO- d_6 at (300) MHz, respectively. Thermal properties were examined using a simultaneous DSC-TGA (USA) Q600-SDT System from TA Instruments. The temperature range covered was 25–600 °C and the scanning rate 10°C min $^{-1}$, under nitrogen atmosphere. The molecular weight of the copolymers was obtained using WATERS 410-gel permeation chromatography equipped, fitted with a differential refractive index detector. Tetrahydrofuran was used as the eluent and polystyrene standards were employed for the calibration.

Solid content and monomer conversion (%)

Total solid content (TSC) and monomer conversion (MC) were determined by a gravimetric analysis method using Equations 1 and 2, respectively.

$$\text{TSC (\%)} = \frac{\text{weight of dry latex}}{\text{weight of latex}} \times 100 \quad (1)$$

$$\text{MC (\%)} = \frac{\text{weight of dry latex}}{\text{total weight of monomers}} \times 100 \quad (2)$$

Solubility studies

Solubility of the synthesized N-(benzothiazole-2-yl) maleimide (BTM) monomer and the synthesized acrylate polymers were tested in various polar and non-polar solvents. About 5–10 mg of the sample was added to about 2 ml of the respective solvent in a test tube and kept overnight with the tube tightly closed. The solubility of the polymers was noted after 24 hr⁽¹³⁾.

Results and Discussion

Synthesis and characterization of N-(benzothiazole-2-yl) maleimide (BTM) monomer

In the present study, N-(benzothiazole-2-yl) maleimide (BTM) monomer was prepared by refluxing maleic anhydride with 2-aminobenzothiazole in an acetic acid/ anhydrous sodium acetate mixture as described in the experimental section. The chemical structure of the obtained BTM monomer is represented in Scheme 1. Elemental analysis, reaction yield and physical properties, such as melting point and product color, were measured and listed in Table 1. The good agreement between the experimental and theoretical values of the C, H and N levels reveals that the methods of synthesis and purification of the product were performed successfully.

TABLE 1. Physico- chemical properties of N-(benzothiazole-2-yl) maleimide (BTM) monomer.

Elemental analysis						m.p °C	Mol. Formula	Yield %	Color
% C		% H		% N					
found	Calc.	found	Calc.	found	Calc.				
57.67	57.38	2.67	2.63	12.33	12.17	160	C ₁₁ H ₆ N ₂ O ₂ S	88	Yellowish white

Spectral analysis of N-(benzothiazole-2-yl) maleimide (BTM) monomer

Structural features of the synthesized N-(benzothiazole-2-yl) maleimide (BTM) monomer were confirmed using FT-IR, ¹H-NMR and mass spectroscopy, as shown from Fig. 1, 2 and 3, respectively. This combination of techniques was utilized for structure confirmation. The key characteristic peaks of the FT-IR spectrum of the BTM monomer are as follows: (KBr, cm⁻¹) functional groups observed [3052 (aromatic C-H), 2930 (aliphatic C-H), 1712 (C=O), 1602 (C=N), 1545, 1505 (aromatic ring), 1448 (C-N), 1272 (C-S) and 755 (maleimide moiety)] are all typical for N-(benzothiazole-2-yl) maleimide (BTM) monomer. The ¹H-NMR spectrum was measured in DMSO-d₆ solvent and showed peaks (ppm) at δ = 7.82 (d, 2H, CH=CH), 7.97-8.02 (d, 2H, Ar C-H adjacent to thiazole ring), 7- 7.75(m, 4H, ArH). The calculated mass spectra (m/z) for a BTM monomer of chemical formula C₁₁H₆N₂O₂S using the electron ionization mode was found to be 230, which reveals that the methods of synthesis and purification of the products were performed successfully.

Solubility studies of N-(benzothiazole-2-yl) maleimide (BTM) monomer

The N-(benzothiazole-2-yl) maleimide (BTM) monomer was found to be soluble in ethyl acetate, acetone, dioxane, tetrahydrofuran (THF), Dimethylsulfoxide (DMSO), Dimethylformamide (DMF), methylene chloride, chloroform, diethylether (sparingly) and also in alcohols such as methanol, ethanol and isopropanol. However, it was not soluble in distilled water, petroleum ether and hydrocarbon (e.g., n-hexane, benzene, toluene and xylene).

Synthesis and characterization of new acrylate copolymers based on N-(benzothiazole-2-yl) maleimide (BTM)

In the present study new acrylate polymers of different feed compositions were prepared by means of emulsion polymerization in water, using sodium lauryl sulfate as a surfactant and ammonium persulfate as a water-soluble radical initiator, as described in the experimental section. The generalized chemical structure of the produced polymer is represented in Scheme 2 and the recipe and weight changes for the various polymer compositions are illustrated in Table 2. The amount of BTM used in the polymerization was 0, 1, 2, 3, 4 wt%, corresponding to E₀, E₁, E₂, E₃ and E₄, respectively.

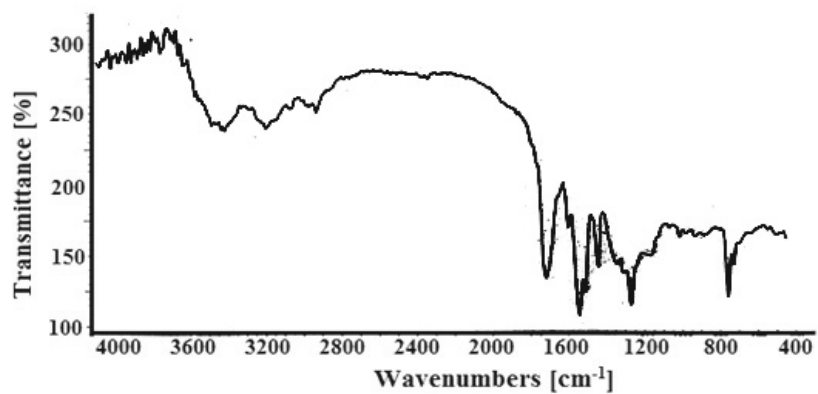


Fig. 1. IR spectra of N-(benzothiazole-2-yl) maleimide (BTM) monomer.

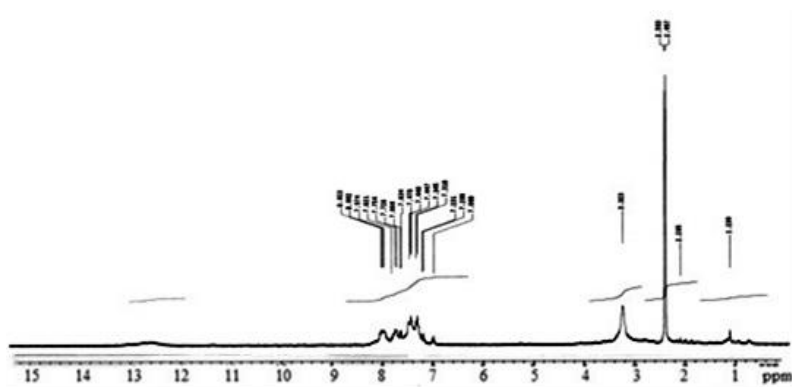


Fig. 2. ¹H-NMR spectra of N-(benzothiazole-2-yl) maleimide (BTM) monomer.

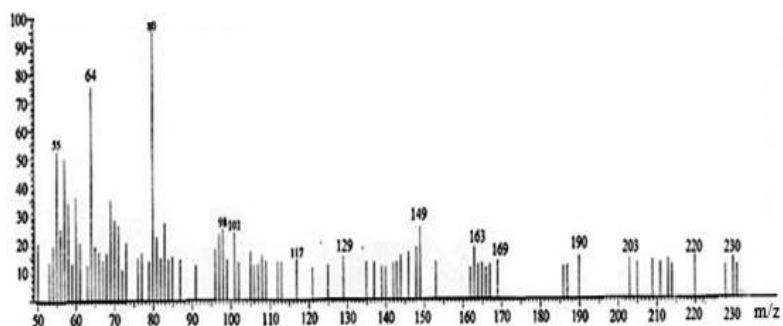


Fig. 3. Mass spectra of N-(benzothiazole-2-yl) maleimide (BTM) monomer.

TABLE 2. Polymerization recipe for various formulations at 80 °C.

Ingredient	E ₀	E ₁	E ₂	E ₃	E ₄
Reaction vessel charge					
Deionized water(g)	14.85	14.85	14.85	14.85	14.85
Protective colloid (PVA) (g)	0.15	0.15	0.15	0.15	0.15
Ammonium persulfate (g)	0.096	0.096	0.096	0.096	0.096
Ammonium hydroxide(25%)(g)	0.5	0.5	0.5	0.5	0.5
Pre-emulsion					
Ethyl acrylate (EA) (g)	24	24	24	24	24
Methyl methacrylate (MMA) (g)	1	1	1	1	1
Styrene (St) (g)	23	22.52	22.04	21.56	21.08
N-(benzothiazole-2-yl) maleimide (BTM) (g)	0	0.48	0.96	1.44	1.92
Sodium lauryl sulfate (SLS) –emulsifier (g)	0.8	0.8	0.8	0.8	0.8
Deionized water (g)	29.7	29.7	29.7	29.7	29.7
Protective colloid (PVA) (g)	0.3	0.3	0.3	0.3	0.3
Initiator solution					
Deionized water (g)	5.22	5.22	5.22	5.22	5.22
Ammonium persulfate(g)	0.384	0.384	0.384	0.384	0.384

Solubility studies and spectral analysis of new acrylate copolymers based on N-(benzothiazole-2-yl) maleimide (BTM)

The polymers basically have low solubility, or no solubility, in organic solvents. The prepared acrylate polymers, which have been synthesized with or without BTM, are no exception. They become soluble by heating in DMF, THF and toluene, but are insoluble in acetone, Dioxane, DMSO, chloroform, n-hexane, methanol and ethanol. The characterization of these polymers is very difficult due to their limited solubility. The key peaks of the IR spectra of the prepared polymers are shown in Fig.4. It is shown from the figure that specific bands at 1708 cm^{-1} and 1715 cm^{-1} can be attributed to C=O stretching vibration of the ester groups. The bands at 2925 cm^{-1} and 2977 cm^{-1} are assigned to aliphatic C-H stretching vibration of methyl and methylene groups. The C-H stretching vibration of the aromatic ring is assigned to a band around 3025 cm^{-1} . The bands at 1450 cm^{-1} and 1495 cm^{-1} are assigned to an aromatic ring. The absorption around 1377 cm^{-1} may be traced to the in plane bending vibrations of methyl or methylene groups. The band at 1150 cm^{-1} may be attributed to the C-O stretching vibration of the ester group. Characteristic bands around 1600 cm^{-1} and 1449 cm^{-1} are attributed to C=N and C-N stretching vibrations, respectively. These absorption bands indicate that the BTM monomer is involved in the polymerization process. The absorption around 1380 cm^{-1} may be traced to the in plane bending vibrations of methyl or methylene groups. The C-O stretching vibration of ester groups is indicated by a band at 1160 cm^{-1} . The main evidence for the copolymer formation is certainly the disappearance of the characteristic band of vinyl groups at 1680 cm^{-1} .

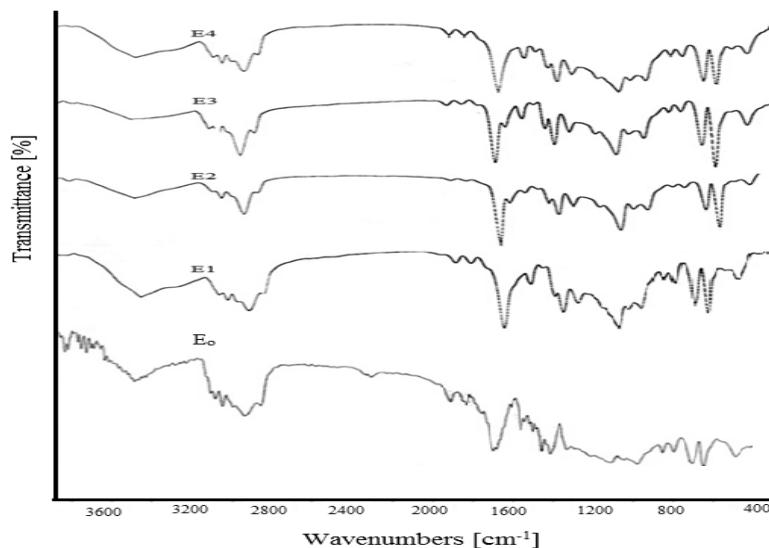


Fig. 4. IR spectra of new acrylate copolymers formulations.

Average molecular weights of new acrylate copolymers based on N-(benzothiazole-2-yl) maleimide (BTM)

The average molecular weight of the prepared polymers (E₀-E₄) was determined by gel permeation chromatography (GPC). The results obtained are shown in Table 3. It is clearly seen from the data shown in the table that the average molecular weight (M_w) decreases as the BTM content increases. It was shown also from the polydispersity index (M_w/M_n), listed in Table, 3 that the polymers are polydisperse. It is well known from the literature that the theoretical values of the polydispersity indexes for polymers, produced by radical combination and disproportionation, are 1.5 and 2.0, respectively⁽¹⁴⁾. The results shown in Table 3 reveal that the chain termination takes place predominantly by disproportionation, rather than coupling, during the polymerization of BTM monomer with St, MMA and EA. The effect of the BTM concentration on monomer conversion is shown in Fig. 5. It can be observed that the monomer conversion decreases with increasing amounts of BTM. This is likely due to the stability of the π bond of malimide moiety.

TABLE 3. Average molecular weights of new acrylate polymers determined by GPC.

Polymer	M_n	M_w	M_z	Polydispersity (M_w/M_n)	Conversion (%)	Solid content (%)
E ₀	98505	156648	229517	1.590	78.33	37.6
E ₁	67032	231347	413283	3.451	65.35	31.37
E ₂	49037	159184	381834	3.246	53.56	25.71
E ₃	48757	207598	511137	4.258	32	15.36
E ₄	35724	152335	352015	4.264	44.9	21.56

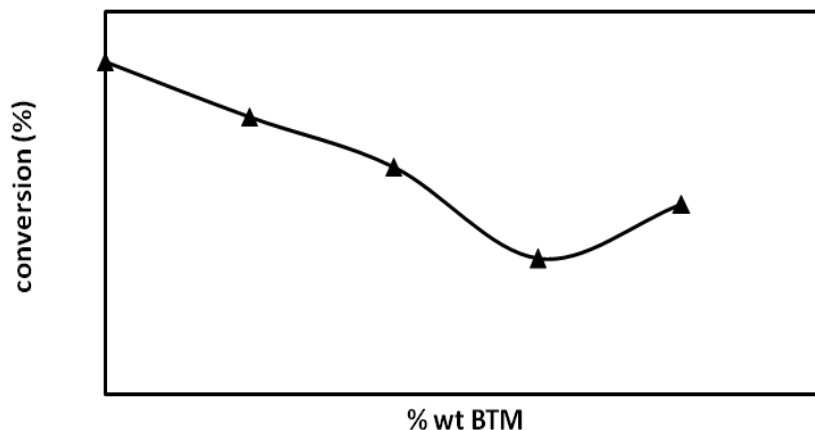


Fig. 5. Effect of BTM monomer concentration on conversion.

Thermal gravimetric analysis (TGA) & Differential scanning calorimetry (DSC)

The results obtained from the TGA work are shown in Table 4 and Fig. 6-10. It is observed from the data in Table 4 and the figures that as the temperature increases, various components of the sample are decomposed and the weight percentage of each resulting mass decreased. The results obtained from the DSC test are shown in Table 5 and Fig. 11. It is shown from the data in Table 5 and Fig. 11 that the control formulation E_0 [without BTM monomer] undergoes single step decomposition in the temperature range 345-435 °C, with one DTG peak at 409 °C. This observation is supported by an exothermic peak at 411.69 °C. Also, all the polymer formulations (E_1 - E_4) containing BTM monomer, undergo single step decomposition over the temperature range from 345 to 436°C. It was observed also that the synthesized polymers were stable up to $350 \pm 5^\circ\text{C}$ and the thermal stability does not depend on the BTM content in the polymers, *i.e.* it may increase or decrease randomly with decrease in BTM content. The data obtained from the DSC curves were in good agreement with that obtained from the TGA thermograms.

TABLE 4. TGA data of the synthesized polymers.

Polymer	% Wt loss at various temperature (°C)					Decomposition Temp. (°C)	T_{15} (°C)	T_{50} (°C)	T_{90} (°C)	T_{Max} (°C)
	200	300	400	500	600					
E_0	2.58	5.68	37.15	93.81	94.34	345 - 435	383	405	423	409
E_1	4.03	6.86	41.78	97.43	98.02	356 - 426.41	382	403	419	405
E_2	4.74	7.96	44.12	-	-	356 - 426.41	379	402	416	406
E_3	2.98	5.45	40.09	96.53	97.09	352- 434.84	382	404	426	406
E_4	3.20	7.65	46.37	-	-	345- 435.90	374	401	422	405

TABLE 5. DSC data of the synthesized copolymers.

Polymer	DSC decomposition temperature (°C)		
	Initial temp. (°C)	Peak temp. (°C)	Final temp. (°C)
E ₀	362.96	411.69	437
E ₁	364.99	408.9	434
E ₂	365.29	409.81	436
E ₃	367.88	409.11	444
E ₄	368.44	406.51	444

Kinetic analysis of thermal degradation

Thermal degradation kinetic parameters were determined for the acrylate polymer samples from the TGA curves using Broido's (BR), Coats-Redfern (C-R) and Horowitz-Metzger (H-M) methods which provide overall kinetic data.

The mathematical expression for Broido's (BR) method is as follows;

$$\log[-\log(1-\alpha)] = -\frac{E_a}{2.303 RT} + \log \left[\frac{ART_s^2}{\beta E_a} \right]$$

where α is the fraction decomposed at time t and is given by $\alpha = \frac{w_i - w_t}{w_i - w_f}$ (w_i is

the mass at the beginning of the decomposition step, w_t is the mass at time t , w_f is the mass at the end of the decomposition step), where $(1-\alpha)$ is the fraction of the number of initial molecules not yet decomposed, T is the temperature in Kelvin and R is the gas constant. β is the heating rate and A is the frequency factor. In this method a straight line should be observed between $\log\{-\log(1-\alpha)\}$ and $1/T$ with a slope of $-(E_a/2.303R)$.

Coats-Redfern (C-R) relation used to evaluate the degradation kinetic is;

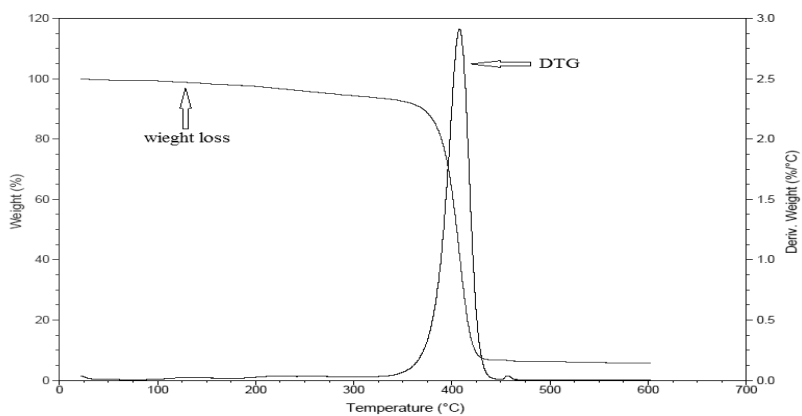
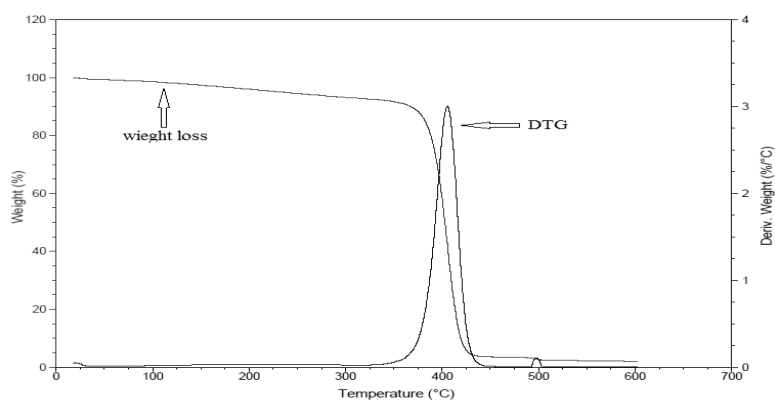
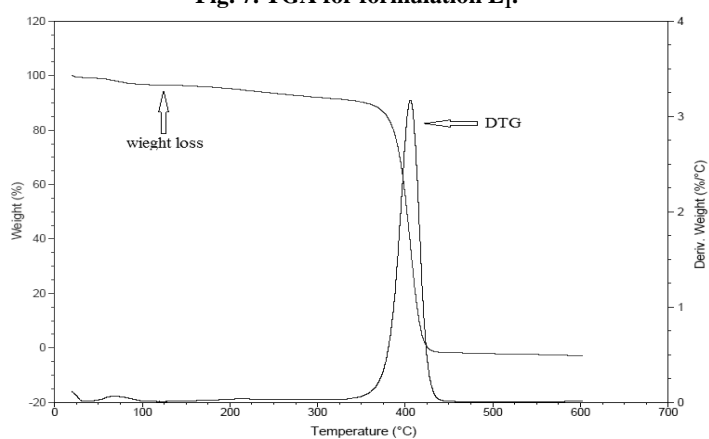
$$\log \left[\frac{-\log(1-\alpha)}{T^2} \right] = \log \left[\frac{AR}{\beta E_a} \right] - \frac{E_a}{2.303 RT}$$

A Plot of $\log\{-\log(1-\alpha)/T^2\}$ versus $1/T$ gives straight lines where E_a and A (Arrhenius pre-exponential factor) were calculated from the slope and the intercept, respectively.

Horowitz-Metzger (H-M) relation used to evaluate the degradation kinetic is;

$$\log[-\log(1-\alpha)] = \frac{\theta E_a}{2.303 RT_s^2} \dots \dots \dots$$

where $\theta = T - T_s$, T is the temperature corresponding to weight loss; w_t , T_s is the temperature at maximum degradation rate. Plot of $\log\{-\log(1-\alpha)\}$ versus θ should give a straight line whose slope is $E_a/2.303RT_s^2$.

**Fig. 6. TGA for formulation E₀.****Fig. 7. TGA for formulation E₁.****Fig. 8. TGA for formulation E₂.**

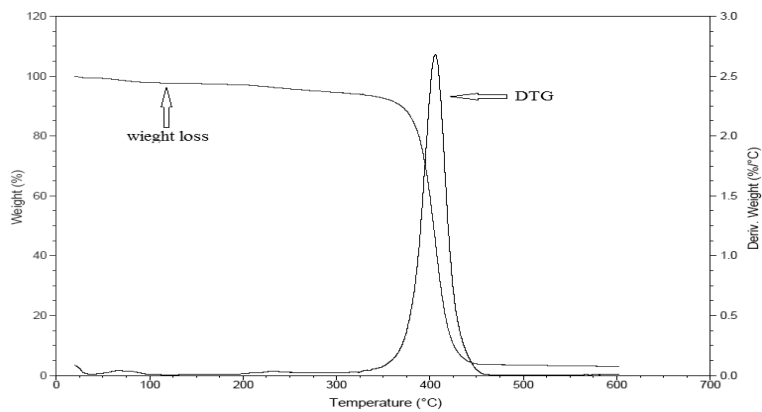


Fig. 9. TGA for formulation of E₃.

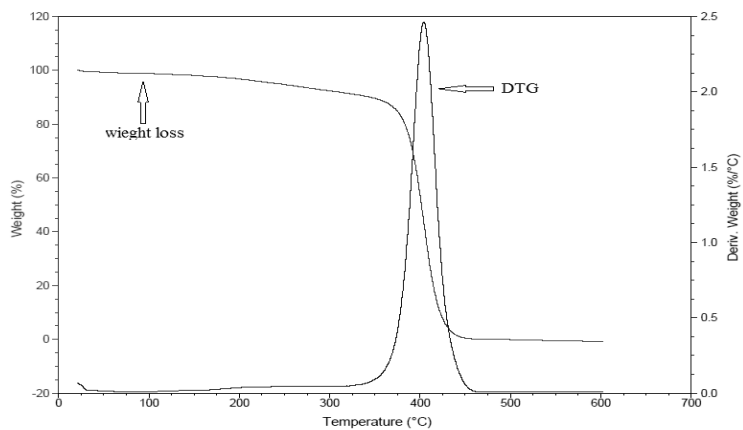


Fig.10. TGA for formulation E₄.

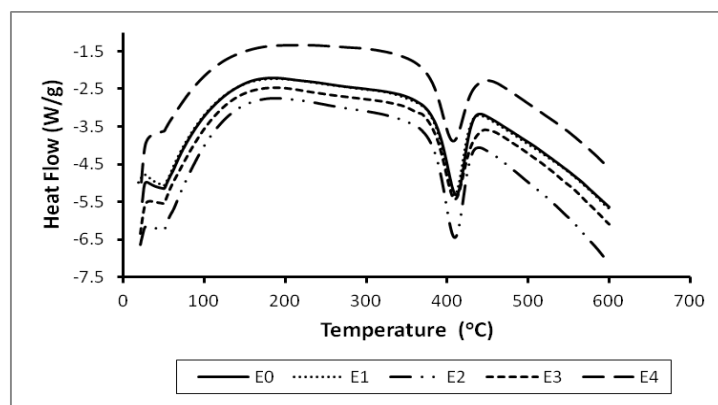


Fig.11. DSC curves for copolymers (E₀-E₄).

Representative plots of $\text{Log}\{-\log(1-\alpha)\}$ versus $1/T$ (BR), $\text{Log}\{-\log(1-\alpha)/T^2\}$ versus $1/T$ (C-R) and $\text{Log}\{-\log(1-\alpha)\}$ versus θ (H-M) for polymers are shown in Fig. 12, 13 and 14, respectively. The regression analysis gives the slopes, constants and R^2 for the degradation process. The linear plot, with a concurrency value (R^2) closer to one, was chosen for both methods. The activation energy (E_a), Arrhenius pre-exponential factor (A) and correlation coefficient (R^2) for the thermal degradation process and for each method, are tabulated in Table 6. The correlation coefficient (R^2) of the linearization plots of the thermal decomposition steps, using the three calculation methods, were found to lie in the range (0.9803-0.9992) showing a good fit with the linear function. The activation energy (E_a) values lie in the range 295.1 – 373.1 kJ/mol for Broido's method, 284.1-362.2 kJ/mol for Coats–Redfern method and 310 – 394.8 kJ/mol for Horowitz–Metzger method. Variation of (E_a) values calculated by the three mathematical methods, with %wt of BTM monomer in the acrylate polymer, is shown in Fig.15. It was observed that the difference in the values of the activation energies, due to the three calculation methods used for the same sample, are relatively small. The data indicates a tendency for higher activation energies when calculating with the HM method.

TABLE 6. Kinetic parameters of new acrylate polymers by Broido's (BR), Coats–Redfern (CR) and Horowitz-Metzger (HM) methods.

Polymer	BR			C-R			H-M		
	E_a (KJ/mol) 4±	R^2	A (min ⁻¹)	E_a (KJ/mol) 4±	R^2	A (min ⁻¹)	E_a (KJ/mol) 4±	R^2	A (min ⁻¹)
E ₀	354.3	0.9896	1.3×10^{27}	343.3	0.9983	1.4×10^{33}	377.6	0.9992	7.7×10^{28}
E ₁	368.5	0.9852	1.7×10^{28}	357.5	0.9916	4.9×10^{55}	385.7	0.9903	5×10^{29}
E ₂	373.1	0.9833	4.2×10^{28}	362.2	0.9918	3.9×10^{56}	394.8	0.9803	2.3×10^{30}
E ₃	295.1	0.9834	2.6×10^{22}	284.1	0.9902	2.6×10^{42}	310	0.989	5.4×10^{23}
E ₄	308.6	0.9919	3.2×10^{23}	297.6	0.9864	8.1×10^{44}	320.8	0.9933	4.6×10^{24}

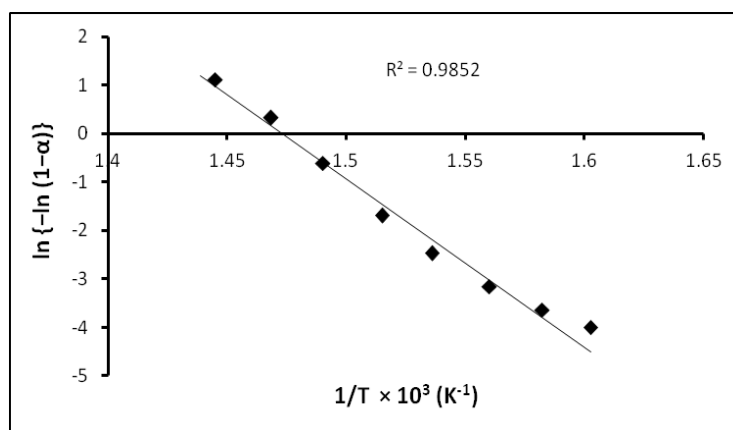


Fig. 12. Kinetic analysis of thermal degradation using Broido's plot method.

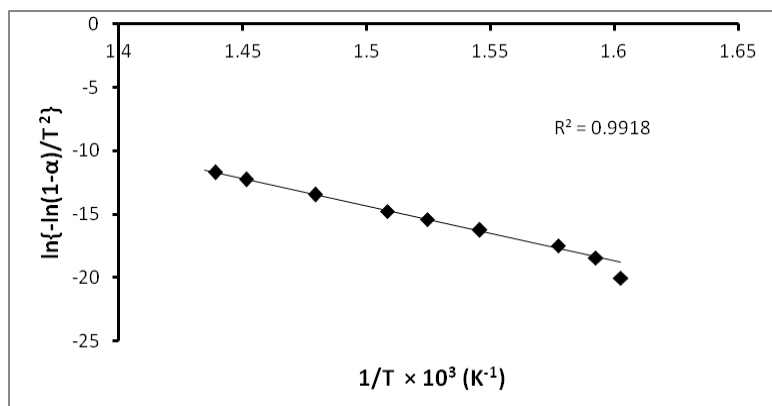


Fig. 13. Kinetic analysis of thermal degradation using Coats-Redfern plot method.

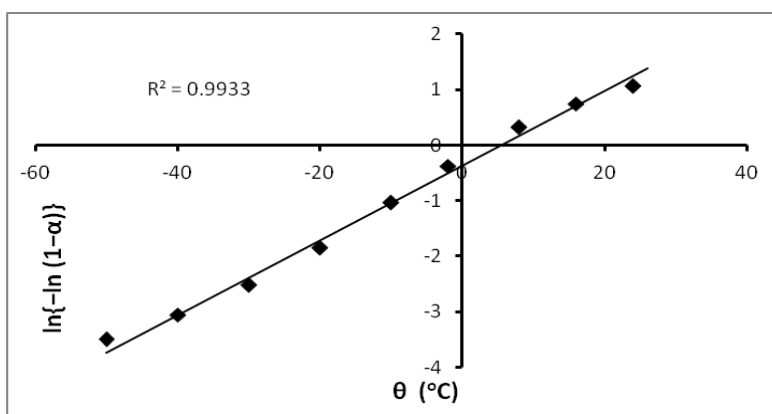


Fig. 14. Kinetic analysis of thermal degradation using Horowitz-Metzger plot method.

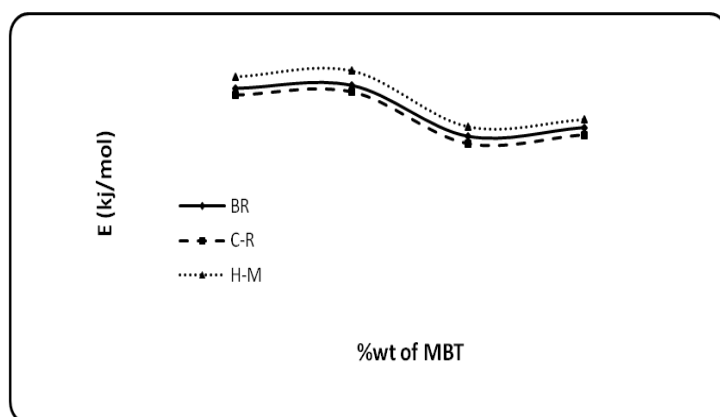


Fig. 15. Variation of activation energy (E) with %wt of MBT monomer.

Conclusion

Synthesis and characterization of the new monomer, N-(benzothiazole-2-yl) maleimide (MBT) is reported. Novel acrylate polymers were prepared from different feed compositions of ethylacrylate (EA), methyl-methacrylate (MMA), styrene (St) and BTM by emulsion polymerization in water, using sodium lauryl sulfate as a surfactant and ammonium persulfate as a water-soluble radical initiator. The synthesized monomer and polymers were characterized by spectroscopic methods. Thermal stability of the obtained polymers was reported. Thermo gravimetric curves showed that all polymers undergo single step decomposition. The mechanism of polymer degradation was confirmed by studying kinetic analysis, using Broido, Coats-Redfern and Horowitz-Metzger plot methods.

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تحضير وتوصيف ودراسة السلوك الحرارى لبوليمرات أكريلات جديدة محتوية على بنزوئايزول-2-يل-ماليميد N

فرج عبد الحى، حماده عبد الوهاب، أحمد جلال و هشام نصار
قسم الكيمياء- كلية العلوم- جامعة الأزهر- القاهرة- مصر .

تضمنت هذه الدراسة تحضير مونومر جديد، N- بنزوئايزول-2-يل-ماليميد، بتفاعل انهدريد حمض الماليك مع 2- أمينو بنزوئايزول في خليط من حمض الأستيك وخلات الصوديوم اللامائية كوسط للتفاعل وعمل ارتداد لمدة 6 ساعات. ولقد تم إثبات التركيب البنائى للمونومر الناتج باستخدام طيف الأشعة تحت الحمراء (IR) والرنين النووى المغناطيسى ($^1\text{H-NMR}$) ومطياف الكتله (Mass spectra) بالإضافة الى التحاليل الدقيقة للعناصر (elemental analysis; C,H,N). تم تحضير بعض بوليمرات الأكريلك الجديدة من مونومرات الماليميد بنزوئايزول، الاستيرين، أكريلات الإيثيل، وأكريلات ميثا الميثيل بتقنيه البلمره بالإستحلاب فى وسط مائى عند درجة حرارة (80 ± 1 °C) مستخدما فوق كبريتات الأمونيوم كبادئ بلمره بالشق الحر يذوب فى الماء وكبريتات ليوريل الصوديوم كعامل استحلاب. تم توصيف البوليمرات المحضرة باستخدام طيف الأشعة تحت الحمراء. كما اختبرت ذوبانية المونومر المحضر وكذلك البوليمرات المحضرة فى المذيبات القطبية والغير قطبية. تم تقدير الأوزان الجزئية للبوليمرات المحضرة عن طريق (gel permeation chromatography). كما تم دراسة الثبات الحرارى للبوليمرات المحضرة عن طريق التحليل الحرارى الوزنى (TGA) و الفحص التفاضلى الكالوريمترى (DSC) وقد تبين من الدراسة ان البوليمرات الناتجة ثابتة حراريا حتى 345 °م. كما تم احتساب طاقة التنشيط لعملية التفكك الحرارى للبوليمرات المحضرة من منحنيات التحليل الحرارى الوزنى باستخدام طريقة برويدو (Broido; BR) وطريقة كوتس-ريدفرن (Coats-Redfern; C-R) و طريقة هوروتز- منزجر (Horowitz-Metzger; H-M) وتمت مقارنة النتائج.