



International Journal of Biology and Medicine

Research Article

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Study of Copolymerization Acrylamide with Methyl Methacrylate

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Received Date: Jan 09, 2020 / Accepted Date: Jan 23, 2020 / Published Date: Jan 24, 2020

Abstract

Copolymer of acrylamide (AM) with methyl methacrylate (MMA) was synthesized by free radical technique using dimethylsulfoxide (DMSO) as solvent and benzoyl peroxide (BPO) as initiator. The overall conversion was kept low ($\leq 15\%$ wt/wt) for all studies copolymer's samples. The synthesized copolymers were characterized using fourier transform infrared spectroscopy (FT-IR), and their thermal properties were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The copolymers compositions were determined by elemental analysis. The monomer reactivity ratios have been calculated by linearization methods proposed by Kelen-Tudos and Fineman-Ross. The derived reactivity ratios (r_1, r_2) for (AM-co-MMA) are: (0.03, 0.593). The microstructure of copolymers and sequence distribution of monomers in the copolymers were calculated by statistical method based on the average reactivity ratios and found that these values are in agreement with the derived reactivity ratios. Copolymers of AM with MMA formed alternating copolymers.

Keywords: Acrylamide; Methyl methacrylate; Reactivity ratios; Sequence distribution

Cite this article as: Ameen Hadi Mohammed, Susan Rasheed Jubair. 2020. Study of Copolymerization Acrylamide with Methyl Methacrylate. Int J Biol Med. 2: 01-09.

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Introduction

The properties of polymers can be most effectively modified with the help of the technique of copolymerisation [1-4]. This technique is designed to manipulate the intra- and inter-molecular forces that are exerted amongst similar and dissimilar polymer segments, engendering broad variation in properties like temperature of glass transition, melting point, solubility, permeability, dyeability, adhesion, elasticity and chemical reactivity. The basic explorations of structure property correlations and the variety of commercial and biological applications all attest to the fact that copolymerisation is highly useful [5]. A copolymer composition equation

relies greatly on reactivity ratios, which not only indicate the relative reactivity of pairs of monomers, but also outline the elements making up the copolymers. To understand how its utility has developed, it is first necessary to understand the copolymer composition itself. As emphasised above, the reactivity ratios are essential for copolymer composition and the manner in which it is distributed. The empirical data regarding copolymer composition and monomer feed mixtures must be mathematically processed before the monomer reactivity ratios can be determined. The reactivity of various comonomers can be calculated via a range of techniques. Furthermore, different analytical methods have been proposed to find out how much of a comonomer has been included in the copolymer

[6]. New scientifically and commercially relevant materials can be obtained when two distinct monomers with various physical and or chemical attributes are incorporated in the same polymer molecule at different ratios. The monomer reactivity ratios of copolymerisation enable the determination of the relative reactivity of a monomer toward a specific polymer radical. A copolymers composition is a critical factor in the assessment of its uses. Controlling the polymer property parameters, for example, molecular weight averages, sequence distribution, and copolymer composition, which is a specific significance in the copolymerization forms [7]. To figure the rate of polymerization or polymer profitability and copolymer synthesis, monomer reactivity proportions must be known [8]. The technique which is utilized frequently recently for evaluating monomer reactivity ratios is to perform low conversion copolymerization at different starting monomer feed compositions. In this way, the copolymer composition is resolved for every reaction. Conventional techniques for evaluating monomer reactivity ratios depend on, first, changing the momentary copolymer composition equation into a frame that is straight in the parameters r_1 and r_2 and after that assessing the monomer reactivity ratios by graphical plotting or by the direct minimum squares technique. Linearization of the copolymer composition condition will contort the blunder dispersions related with the information [9-11]. The aim of this work is to copolymerize AM, a hydrophilic monomer with MMA, a hydrophobic monomer, and to study the best synthetic conditions and characterization of the copolymer. This study also determines the reactivity ratios of AM and MMA. From these parameters, a specific comonomer distribution is estimated.

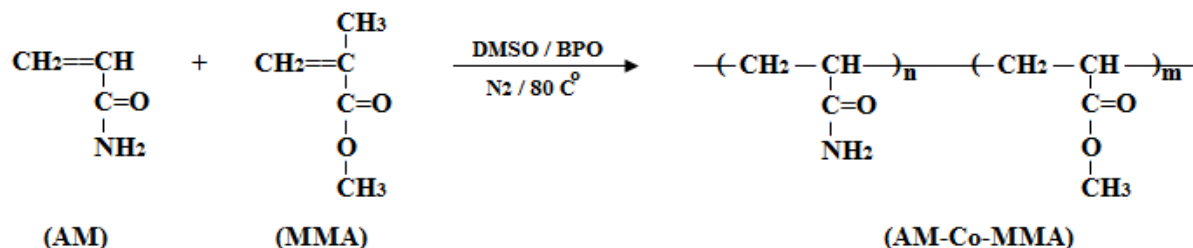
Experimental

Materials

The monomers, initiator, and solvents were obtained from Aldrich-oma chemical Co. The monomer AM was purified by recrystallization from methanol and dried in a vacuum. MMA was freed from the inhibitor by shaking with 10% W/V aqueous NaOH. After washing with water, it was vacuum distilled immediately prior to the copolymerization experiment. Initiator (benzoyl peroxide) was purified by twice recrystallizations from chloroform and refrigerated prior to use. Solvents were used as received.

Copolymerization

Copolymerization of (AM) with (MMA) was carried out using (10 ml) dimethylsulfoxide (DMSO) as solvent and (1×10^{-3} mol dm^{-3}) (BPO) as initiator. In quick fit test glass tubes, the prescribed amount of monomers, initiator and solvent were charged, and then put in water bath at (80 °C). As shown in table 1, the feed ratio was varied in a series of copolymerization of (AM) with (MMA) (AM-co-MMA) whilst the total molar composition of the monomer mixture was maintained at (1 mol dm^{-3}). Before starting the reaction, Nitrogen gas was bubbled through the mixture for 10 minutes in order to remove all Oxygen. Low conversion (<15%) of copolymers was obtained by controlling the time of copolymerization. Petroleum ether (b.p. 40-60°C) was used to precipitate the obtained copolymers. All the copolymers were filtered off, dissolved again in dimethylsulfoxide and precipitated in petroleum ether prior to constant weight in vacuum at 40°C. In order to determine the copolymer compositions, samples of the copolymer (0.2 mg) were checked by elemental analysis. Scheme 1 shows the reaction of copolymerization (AM) with (MMA).



Scheme 1: The process formation of AM-co-MMA from AM and MMA as monomers.

Characterization

Perkin Elmer-1650 spectrometer was used to record FTIR spectra of the copolymers on KBr Pellets in the range 200-4000 cm^{-1} . Intrinsic viscosity $[\eta]$ was determined according to the Solomon Gotessman relationship [12] by using an Ostwald Viscometer with negligible kinetic energy correction. By following the variation of estimated nitrogen content arising from (AM) comonomers units, copolymer compositions were determined by elemental analysis. DSC-Mettler calorimetric system was employed to determine the glass transition temperature (T_g) whilst Perkin Elmer in a nitrogen atmosphere at a heating rate of 10 $^\circ\text{C} / \text{min}$ from 0 to 800 $^\circ\text{C}$

was used to study the thermal degradability of the copolymers.

Results and Discussion

The absorption bands which appear in the FTIR spectra of the copolymer Figure 1 (c) belong to the stretching vibration in different functional groups of corresponding homopolymers Figure 1 (a,b). The absorption bands of AM/MMA copolymer as follows: 3400 cm^{-1} (amide N-H), 1670 cm^{-1} (amide C=O), 1750 cm^{-1} (ester C=O), 1450 cm^{-1} (methyl C-H), 1200 cm^{-1} (amide C-N), 1030 cm^{-1} (ester C-O), 2850 cm^{-1} (alkane C-H).

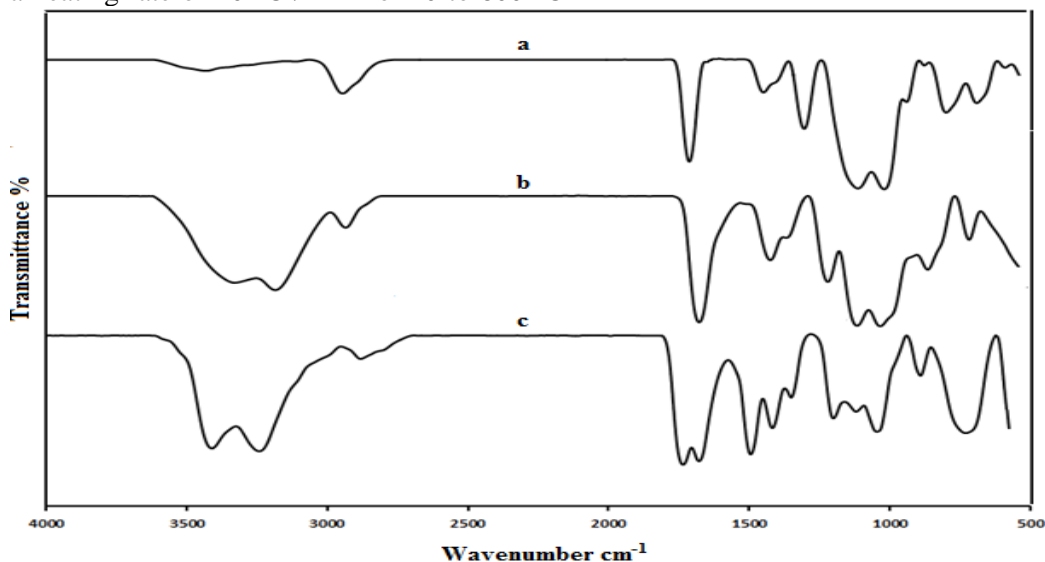


Figure 1: FT-IR of: a- Poly MMA, b- Poly AM, c- AM-co-MMA.

Copolymer Composition

It is very useful to study the monomer reactivity in the copolymer system because the composition of the copolymer depends mainly

on the monomer feed composition. In AM/MMA copolymers, composition of the monomer in the copolymer was assessed by assurance N % in the copolymers and this proportion indirectly gave the mole fraction of AM in the copolymer. The monomer

composition and the results of elemental analysis in addition to intrinsic viscosity values $[\eta]$ for samples of five different compositions are listed in table 1. The values of $[\eta]$ should be used in estimating qualitatively degree of polymerization. Figure 2 shows the plots of mole fraction of AM in the copolymer (F_1) vs. that of mole fraction of MMA in the feed (f_1).

presence of carbonyl and amide groups for each AM and MMA monomers units gave rise to a significant attraction of free electron in the double bond and generate a positive charge in the growing polymer chain and stabilization of the corresponding macroradical. Since both monomers are electron rich, it forms the bond easily with electron deficient species, thus they easily involved in polymerization.

In AM/MMA system, AM forms alternate copolymer with MMA (Figure 2). Here, the

Table 1: Feed and copolymer compositions, conversion, nitrogen analysis and intrinsic viscosity values $[\eta]$ of AM/MMA copolymer.

Sample Code	f_1 (feed)	Conversion%	N%	F_1 (copolymer)	$[\eta]$ (dL/g)
AM/MAA-1	0.10	12.3	1.91	0.128	0.52
AM/MAA-2	0.25	11.5	3.81	0.254	0.71
AM/MAA-3	0.50	13.7	4.51	0.296	0.78
AM/MAA-4	0.75	10.9	6.93	0.437	1.06
AM/MAA-5	0.90	12.8	12.3	0.691	1.74

(a) f_1 is the mole fraction of monomer-1 (AM) in the initial feed; $f_2 = 1 - f_1$
 (b) F_1 is the mole fraction of monomer-1 (AM) in the copolymer; $F_2 = 1 - F_1$

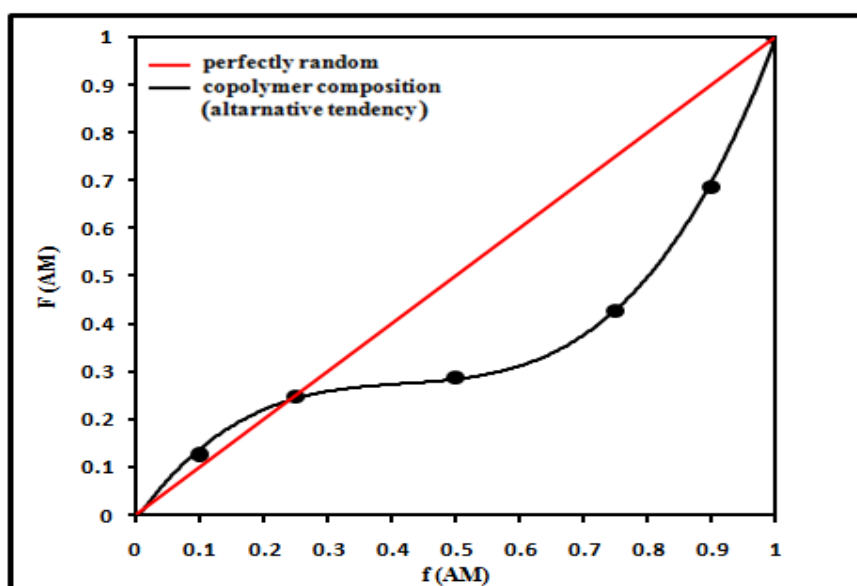


Figure 2: Variation of copolymer composition F_1 (AM) with feed composition f_1 (AM) for AM/MMA copolymer.

Reactivity Ratio

The sort of copolymer framed can be best comprehended from the information of reactivity ratios of the copolymers. The most widely recognized scientific model of

copolymerization depends on finding the connection between the composition of the monomer feed and the composition of copolymers in which the monomer reactivity ratios are the parameters to be resolved [13]. In our work two procedures have been used for the best fitting of (r_1 & r_2) pair from a set of $[M_1]$,

[M₂], d [M₁] and d [M₂] pair, using linearization methods representing by Kelen-Tudos and Fineman-Ross. The references [14,15] of these methods should be consulted for more details

about the mathematical processes. The values are showed in figure 3 and figure 4, and represented in table 2.

Table 2: Kelen-Tudos and Fineman-Ross parameters of AM/MMA copolymer.

Sample Code	f ₁ (feed)	G	X	η	ζ
AM/MAA-1	0.10	-7.702	11.53	-0.638	0.952
AM/MAA-2	0.25	-1.996	3.012	-0.551	0.840
AM/MAA-3	0.50	-0.588	0.412	-0.600	0.420
AM/MAA-4	0.75	-0.081	0.084	-0.124	0.128
AM/MAA-5	0.90	0.142	0.028	0.238	0.047

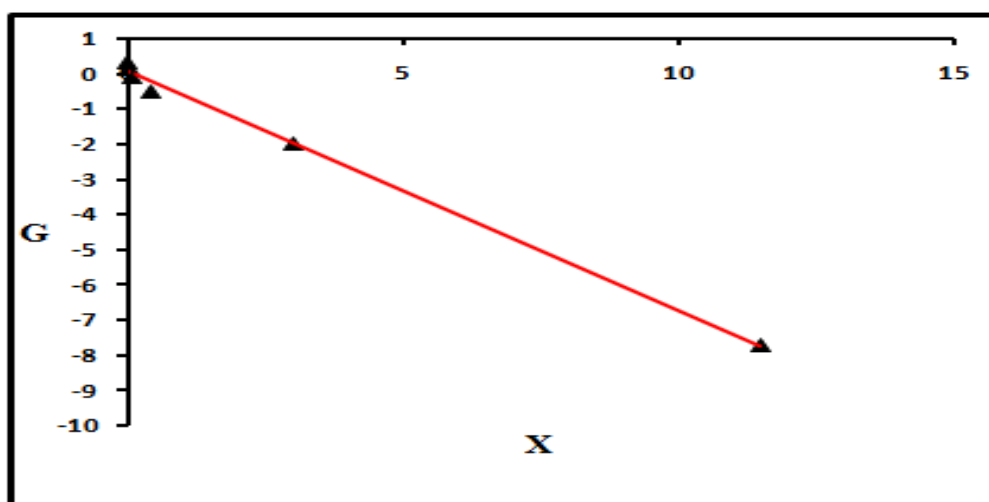


Figure 3: Fineman-Ross plot of AM/MMA copolymer.

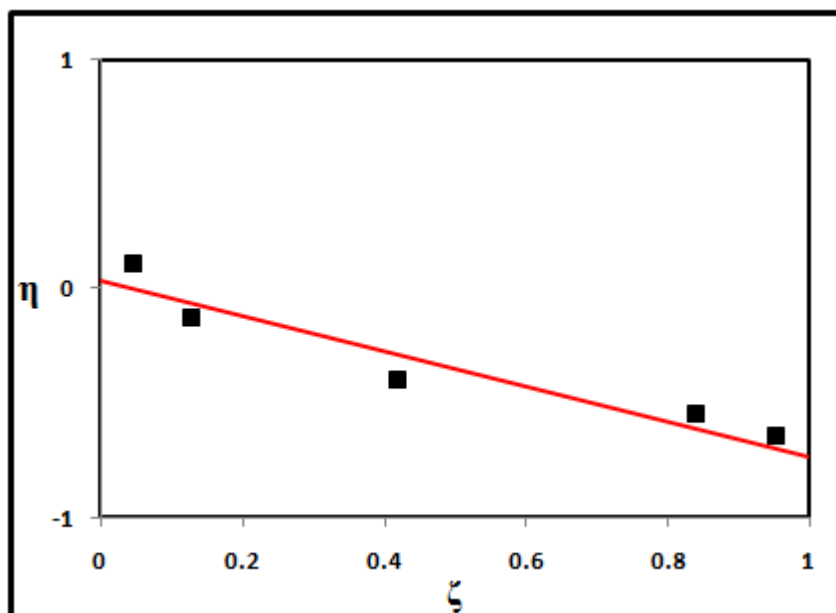


Figure 4: Kelen-Tudos plot of AM/MMA copolymer.

Table 3: Monomer reactivity ratios values for AM/MMA copolymer.		
Procedure $r_1 r_2$		
Kelen-Tudos	0.032	0.575
Fineman-Ross	0.029	0.612
Average values	0.030	0.593

Table 3 shows the values of reactivity ratios by different methods, the values (r_1, r_2) from the different methods are very close. It is easy to observe that (AM/MMA) copolymer has the $r_1 r_2$ values less than unity demonstrating the alternation behavior of the monomers. The alternative behavior for the two monomers (AM and MMA) could be explained in terms of increasing the stabilization of their radicals by the carbonyl groups resonance. On the other hand, the value of r_2 is slightly greater than r_1 which lead to a greater incorporation of MMA units compared to AM units. In this case, the double bond of MMA appears to have slightly more positive charge due to the presence of carbonyl ester bond. The charge density generated on carbonyl carbon atom would favor a significant electron attraction in MA radicals, which creates a slightly more positive charge on the double bond. A similar behavior was observed in our earlier case [16] wherein acrylamide was copolymerized with 3-(Trimethoxysilyl) Propyl Methacrylate, which contained similar carbonyl ester bond attached to the double bond.

When the reactivity ratios of the two monomers are less than unity, the synthesized copolymer shows an alternating behavior. Each monomer prefers to react with other monomer more than itself [17]. The possibility of an azeotropic composition increases in case of r_1, r_2 are both > 1 and < 1 . For (AM/MMA) copolymer system, this condition is fulfilled since r_1 and $r_2 < 1$. Figure 2 (copolymer composition curve) proves this fact, in which a value of 0.25 for f_1 (az.) could be clearly observed. The azeotropic feed composition f_1 (az.) can be expressed by the following equation:

$$f_1(\text{az}) = (1-r_2) / (2-r_1-r_2) \quad (1)$$

The results of reactivity ratios were then utilized for microstructural figuring. The

microstructure of the copolymers is required to be critical in deciding the arrangement properties which the copolymer shows [18]. Igarashi's [19,20] procedures are used to calculate the fraction of M_1-M_1, M_2-M_2 and M_1-M_2 units in the copolymers, the data are listed in table 4.

$$S_{1-1} = m_1 - \frac{2m_1 m_2}{1 + [(2m_1 - 1)^2 + 4r_1 r_2 m_1 m_2]^{1/2}} \quad (2)$$

$$S_{2-2} = m_2 - \frac{2m_1 m_2}{1 + [(2m_1 - 1)^2 + 4r_1 r_2 m_1 m_2]^{1/2}} \quad (3)$$

$$S_{1-2} = \frac{4m_1 m_2}{1 + [(2m_1 - 1)^2 + 4r_1 r_2 m_1 m_2]^{1/2}} \quad (4)$$

where: m_1 (AM) and m_2 (MMA)- the mole fractions in the copolymer, S_{1-1}, S_{2-2} , and S_{1-2} - the mole fractions of 1-1, 2-2, and 1-2 sequences, respectively, r_1 and r_2 - the reactivity ratios.

The following equations were then used to calculate the probabilities of finding the sequence and the average length sequences of AM and MMA units [21,22]; the data are listed in Table 4.

$$P11 = r_1[A] / (r_1[A] + [B]) \quad (5)$$

$$P22 = r_2[B] / (r_2[B] + [A]) \quad (6)$$

$$P12 = [B] / (r_1[A] + [B]) \quad (7)$$

$$P21 = [A] / (r_2[B] + [A]) \quad (8)$$

$$\mu_1 = 1/P12 \quad (9)$$

$$\mu_2 = 1/P21 \quad (10)$$

Where: A (AM) and B (MMA) are the mole fractions in the feed. In these equations, P11, P22, P12 and P21- the probability of a AM or MMA unit to be followed by AM or MMA unit.

For (AM/MMA) copolymer system, $[M_1]-[M_1], [M_1]-[M_2], P11$ and $P21$ increase as (AM) increases in the feed, whilst $[M_2]-[M_2], P22$ and $P12$ increase as (MMA) increases. At the same time, the mean sequence length of AM, μ_1 , varied from 1.003 to 1.270. For these copolymer compositions, values of μ_2 were between 6.369 and 1.066, respectively. From these results, (AM) have a tendency to react with other monomer (MMA) more than it selves in the growing chain, whilst (MMA) have a tendency to react with it selves more than other monomer (AM) to form alternation copolymer and block (MMA) units distributes

in the growing chain. These results are in agreement with the values of r_{AM} (0.03) and r_{MMA} (0.593).

Table 4: Statistical data of AM/MMA copolymer.

Sample code	Blockness (mol%)	Alternation (mol%)	Sequence probability (mol%)	Sequence length
M_1-M_1	M_2-M_2	M_1-M_2	P_{11} P_{22} P_{12} P_{21}	μ_1 μ_2
AM/MMA-1	0.10	74.39	25.51 0.003 0.842 0.996 0.157	1.003 6.369
AM/MMA-2	0.30	49.51	50.19 0.009 0.639 0.990 0.360	1.010 2.777
AM/MMA-3	0.40	41.25	58.35 0.029 0.371 0.970 0.628	1.031 1.592
AM/MMA-4	2.18	14.71	83.11 0.082 0.164 0.917 0.835	1.094 1.197
AM/MMA-5	38.3	0.510	61.17 0.212 0.061 0.787 0.938	1.270 1.066

Thermal properties

For (AM and MMA) homopolymers, T_g value observed around 155 °C and 90 °C respectively whereas AM/MMA-1 copolymer showed the T_g around 110 °C. It is found that by increasing the amount of AM content in the copolymers result in increased T_g , this may be due to the presence of rigid amide group in the backbone in AM side chain. TGA results are presented in Figure 5. The AM/MMA copolymer is more stable than the homopolymer of MMA with 10 % weight loss at about 350 °C of AM/MMA-1 which is higher than 100 °C of Poly (MMA). This result could be attributed to the presence of methyl group in the backbone in MMA side chain which significantly lowers the T_g value and the thermal stability of AM/MMA copolymer. Values of T_g and data of TGA are given in table 5.

Table 5: Thermal data of AM/MMA copolymers.

Samples	T_g (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	Residual at 800 °C (wt %)
PAM	155	370	490	35
AM-co-MMA-1	90	100	475	28
PMMA	110	350	420	8

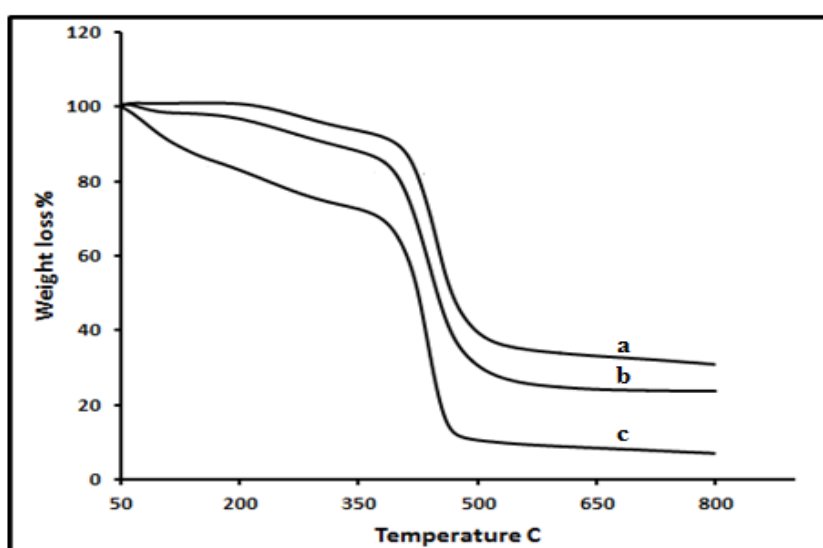


Figure 5: TGA thermogram of: (a) Poly AM, (b) AM-co-MMA-1, (c) Poly MMA.

Conclusions

The copolymer AM/MMA was successfully synthesized. The structure of synthesized copolymer was confirmed by FT-IR technique. Elemental analysis test was employed to determine the copolymer compositions. Then, the results of N% were used to calculate the reactivity ratios by different methods: Kelen-Tudos and Fineman-Ross methods and a good agreement was observed between the two procedures. The copolymer tends to be alternative ($r_1=0.03$, $r_2=0.593$). The results of sequence distribution of monomers and microstructure show a good agreement with the obtained reactivity ratios. DSC and TGA analysis were used to study the thermal properties of the (AM and MMA) homopolymers and copolymer.

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