

SYNTHESIS AND CHARACTERIZATION OF NON-IONIC GRAFT COPOLYMERS

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ABSTRACT

Graft copolymers are prepared by graft polymerization using poly (ethylene glycol) methyl ether (mPEG) macromonomers and methyl methacrylate (MMA) ratios of 10:90, 20:80 and 30:70 in presence of benzoyl peroxide as an initiator. A macro free radical initiator technique affected by heating in toluene is applied. The graft copolymers P(mPEG-g-MMA) thus formed are characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermo gravimetric analyzes (TGA), nuclear magnetic resonance (¹H NMR, ¹³C NMR) and Fourier transform infrared FT-IR spectroscopies. The optimization parameters of mPEG graft copolymerization are determined by studying the effect of the initiator and monomer concentrations, the reaction time and the temperature of the polymerization. The results of the characterization techniques show the formation of the copolymer P(mPEG-g-MMA) under optimum conditions referring to a monomer concentration of 0.42 mole L⁻¹, a 10:90 ratio, a reaction temperature of 60°C - 85°C and reaction time of 3 h.

Keywords: poly (ethylene glycol) methyl ether, methyl methacrylate, synthesis, graft polymerization, catalyst, optimum conditions.

INTRODUCTION

Graft copolymerization is a process in which monomers are bonded to the polymer chain through strong covalent bonds. The polymer acts as a backbone, while the monomers - as branches. This process can be used to produce copolymers of desirable properties based on a proper selection of monomers [1]. In other words, graft copolymers are also multi-component polymers in which some side chain blocks are grafted on a single main polymer chain. The graft copolymerization is an important aspect of polymer science, which continues to attract considerable attention. The graft copolymers obtained by this process find a variety of potential applications because of the different properties of the components forming the hybrid branched macromolecule [2]. The

graft copolymers also exhibit good phase separation which in turn provides their use as impact-resistant plastics, thermoplastic elastomers, compatibilizers and polymeric emulsifiers. Because of their branched structure, they generally melt easily, which is advantageous for their processing. They have a great potential in terms of new properties because of their structural variables referring to the composition, the backbone length, the branch length, the branch spacing, etc. [3, 4]. They are also widely used as compatibilizers of polymer blends, dispersion stabilizers, surfactants and surface modifiers.

Various polymerization methods have been used to synthesize graft copolymers. They refer to procedures based on free radicals, an anionic and cationic coordination, group transfers and coupling, which change the polymerization mechanism and the step growth, intro-

duce initiators, etc. [5 - 8]. Furthermore, the methods of block copolymers preparation include ionic, free radical and metal-catalyzed polymerization procedures [9]. The ionic polymerization is the most frequently used among them. But it is somewhat limited because of the rigor conditions and the narrow range of the monomers. Moreover, the scientists have focused on a free radical block copolymerization because it requires mild conditions, while the range of the monomers is wide [10]. As far as the reaction mechanism of the free radical graft polymerization is concerned (shown in Fig. 1), the free radical generation results from the homolytic dissociation of compounds such as benzoyl peroxide using heat or light as shown in step I and II [11]. It leads to the reaction initiation. The free radical combines with the trunk polymer during step III providing a site for the monomer to attach to the main polymer backbone. This step is responsible for the synthesis of the desired copolymer as shown by step IV.

The hydrophilic nature of poly (ethylene glycol) derivatives and their wide availability in terms of molecular weights have received great attention. Due to their unique properties such as solubility, flexibility, etc., they find potential applications in different fields including life science, surface chemistry, electrochemistry, etc. They also play a vital role in biomedical and other industrial fields due to their useful properties such as biocompatibility and a high solubility in water [12]. Based on the above-mentioned details, many researchers have focused on the grafting copolymerization with

poly (ethylene glycol) derivatives [13 - 16]. Furthermore, many of them [17 - 23] have reported the chemical modification of poly (ethylene glycol) derivatives via graft copolymerization. The present communication describes the synthesis of graft copolymers P(mPEG-g-MMA) by a simple method, i.e. by free radical polymerization. The synthesized material thus formed is characterized by different useful techniques such as FT-IR, ^1H NMR, ^{13}C NMR, DSC, TGA and SEM. The various parameters that affect the grafting process such as the monomer concentration, the initiator concentration, the temperature and the time are also studied aiming to determine the optimal conditions as this is essential for any process of a practical application.

EXPERIMENTAL

Materials

Poly(ethylene glycol) methyl ether or methoxy poly(ethylene glycol) mPEG, $M_n=5000$, methyl methacrylate MMA (contains 30 ppm, hydroquinone monomethyl ether (MEHQ) as inhibitor, > 99 %), benzoyl peroxide, toluene (American Chemical Society (ACS) reagent, reagent ISO, > 99.7 %) and hexane (HPLC) were purchased from Sigma Aldrich.

A preparation of the grafted P(mPEG-g-MMA) copolymer

The grafted copolymers containing different ratios were prepared in a 500 ml three-necked flask using a condenser. Constant stirring was applied. During the

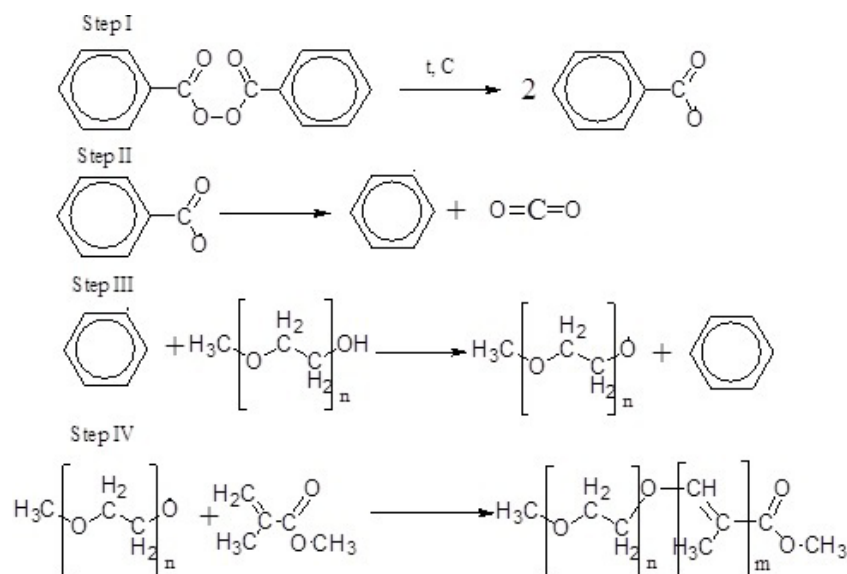


Fig. 1. A mechanism of free radical graft copolymerization.

first step, mPEG was dissolved in toluene and a catalyst was added (0.1 wt. % in respect to the monomer). Benzoyl peroxide was the catalyst used. It was initially recrystallized, then dried in an oven at a temperature lower than 40 °C and in a desiccator over silica gel to remove the water content. During the second step, the monomer (MMA) was fed to the system drop-wise and the temperature of system was increased to 70°C for 1 h. The polymerization was conducted using mPEG to methyl methacrylate ratios of 10:90, 20:80 and 30:70. A thermometer was fixed to record the temperature. The rate of the stirrer was adjusted to about 100 rpm. The temperature was increased to 85°C for 1 h during the final stage. After that, the reaction product was precipitated with the addition of hexane. The precipitated copolymer was filtered and then dried overnight at a room temperature.

Characterization

Fourier Transform Infrared (FTIR) spectroscopy

The samples were characterized by recording the IR spectra of mPEG and the copolymer formed after grafting, i.e. P(mPEG-g-MMA) using a Fourier-transform infrared spectroscopy at a room temperature within the wave number range of 4000 cm^{-1} – 600 cm^{-1} . These spectra were recorded by a Bruker model Alpha infrared

spectrophotometer using potassium bromide (KBr) pellets (500 mg). The latter contained 2 mg - 6 mg of the powdered sample.

Nuclear Magnetic Resonance (NMR) spectroscopy

The nuclear magnetic resonance (NMR) spectra (^1H and ^{13}C) of mPEG and the grafted P(mPEG-g-MMA) copolymers were recorded on a BRUKER AVANCE spectrometer at 500 MHz. An acetone- D_6 solvent was used at a room temperature ($T = 298 \text{ K}$). The acetone residual peak ($\delta = 2.5 \text{ ppm}$) was treated as an internal reference.

Thermogravimetric Analyses (TGA) and Differential Scanning Calorimetry (DSC)

The thermogravimetric analyses (TGA) of mPEG and its grafted copolymer were carried out with a thermo-gravimetric analyzer Perkin Elmer STA 6000, while DSC was applied using a differential scanning calorimeter Perkin Elmer Pyris 1 DSC. The samples were subjected to a constant heating rate of 20°C min^{-1} . The thermal studies were performed over a temperature range from 30°C to 920°C in case of TGA. The changes of the samples during the DSC analyses were recorded up to a temperature of 200°C, i.e. at heating from 30°C to 200°C.

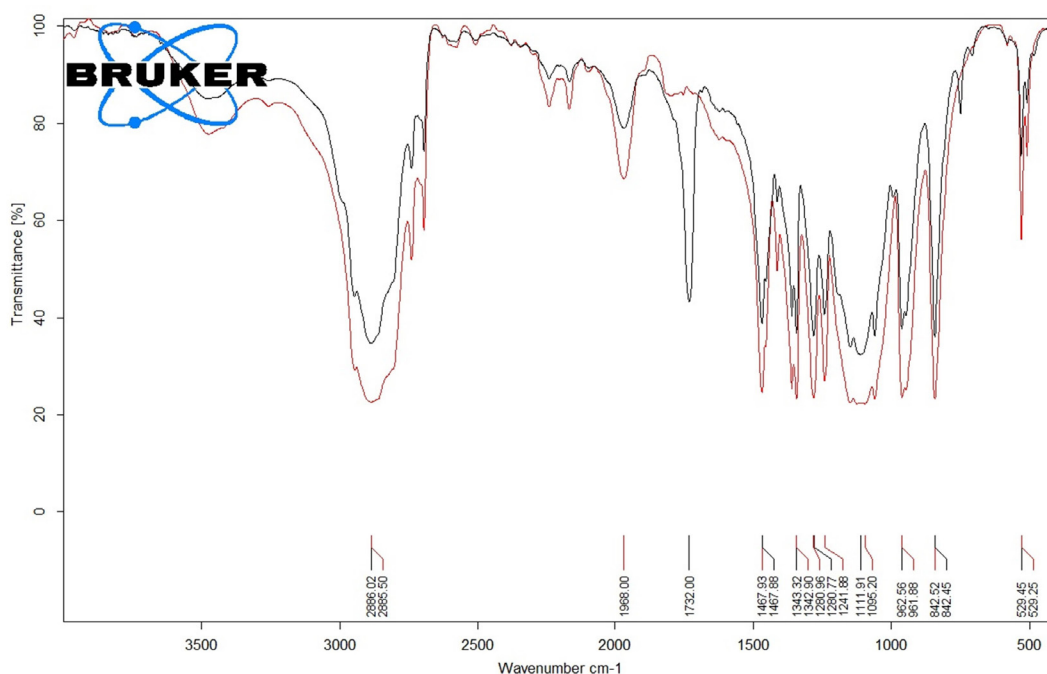


Fig. 2. IR spectra of mPEG and P(mPEG-g-MMA) copolymer (the red spectrum refers to mPEG, the black spectrum refers to P(mPEG-g-MMA)).

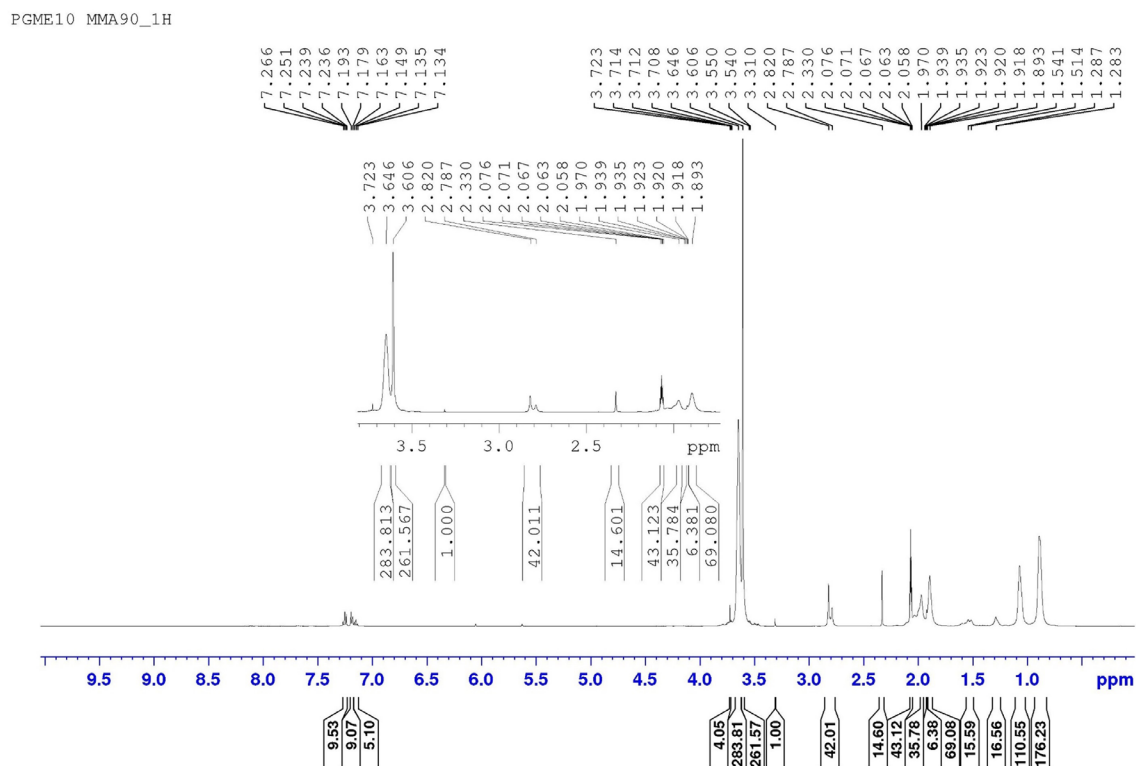


Fig. 3. ^1H NMR spectrum of the P(mPEG-g-MMA) copolymer obtained.

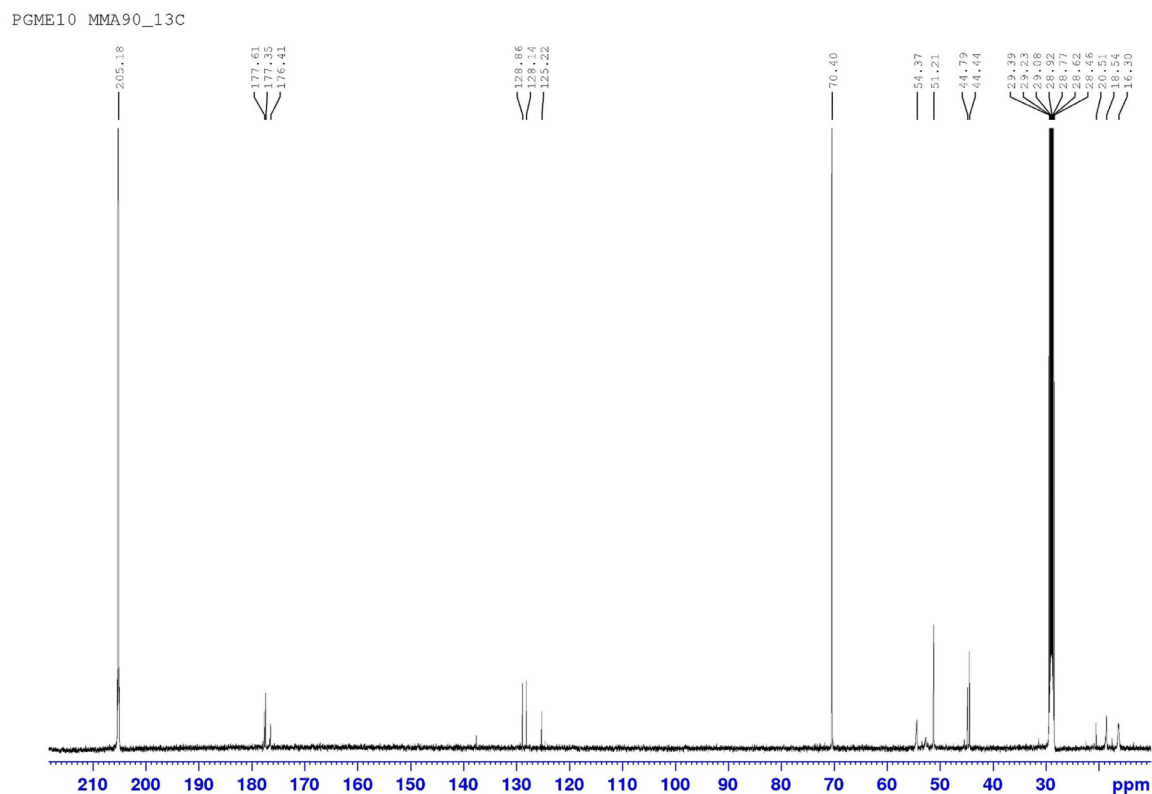
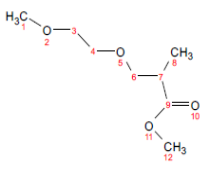


Fig. 4. ^{13}C NMR spectrum of the P(mPEG-g-MMA) copolymer obtained.

Table 1. Values of carbon chemical shifts of P(mPEG-g-MMA) copolymer.

Node	Shift	Structure
C ₁	59.3	
C ₃	71.6	
C ₄	70.1	
C ₆	72.6	
C ₇	40.9	
C ₈	13.2	
C ₉	176.1	
C ₁₂	52.2	

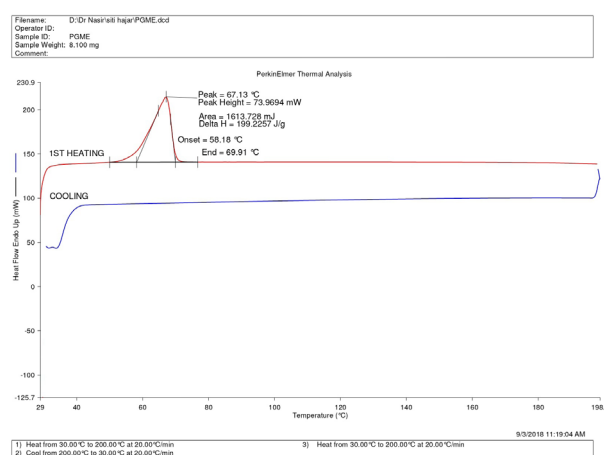
Scanning Electron Microscopy (SEM)

The mPEG and graft copolymers P(mPEG-g-MMA) of different ratios were characterized by using the microscopic methods to provide an information on the morphology. The SEM analysis was carried out by a scanning electron spectroscopy (XHR-FESEM) model FEI Verios 460L. The samples were coated with a thin layer of gold and examined by an electron probe micro analyzer at 10 KV.

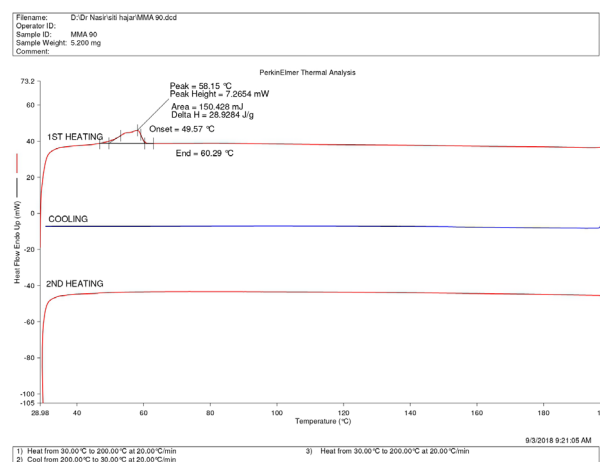
RESULTS AND DISCUSSION

FTIR studies

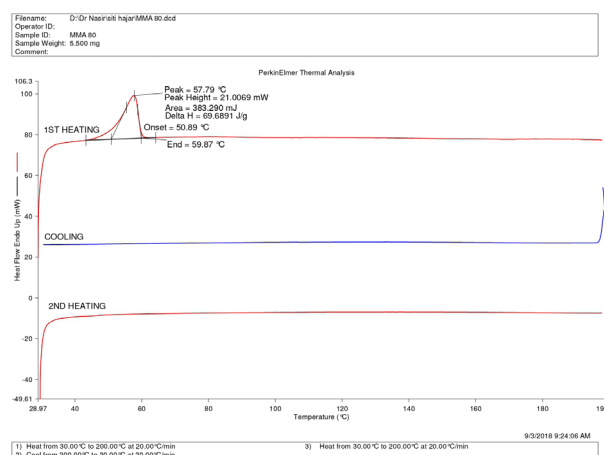
The FTIR spectra of mPEG and a P(mPEG-g-MMA) copolymer are shown in Fig. 2. -C-O-C- and -OH stretching peaks are observed at 1113 cm⁻¹ and 3353 cm⁻¹ in the spectrum of mPEG. The absorption peaks at 1732



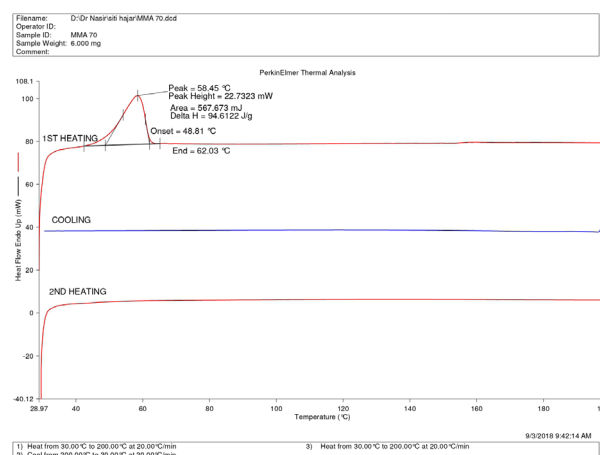
a)



c)



b)



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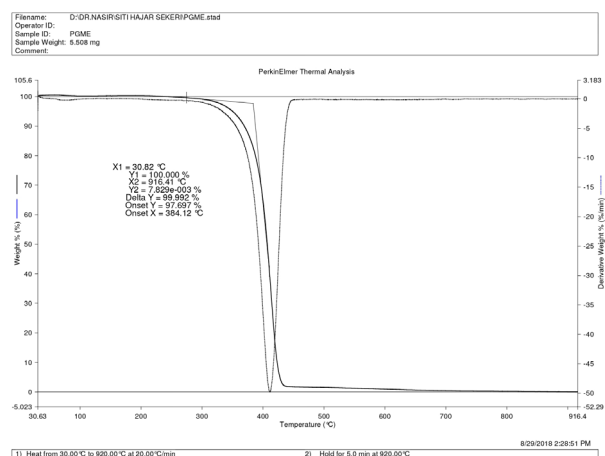
Fig. 5. DSC thermograms of mPEG and P(mPEG-g-MMA) copolymers of varying ratios: a) mPEG; b) 10:90; c) 20:80; d) 30:70.

Table 2. mPEG and P(mPEG-g-MMA) weight losses.

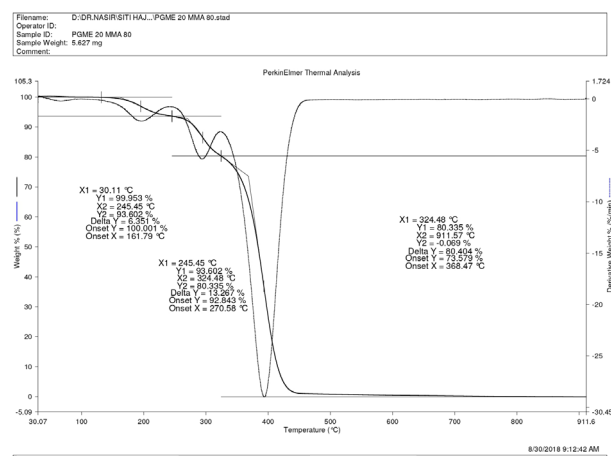
Name	Stage	Temperature range, °C	Weight loss, %
mPEG	1	30.82-384.12	99.992
P(mPEG-g-MMA)	1	30.72-156.29	12.028
	2	246.59-274.38	19.227
	3	330.55-363.60	68.377

cm^{-1} and 2886 cm^{-1} are detected after are formation of the grafted copolymer due to a carbonyl group and C-H bond, respectively. Moreover, C–O stretching is also present at 1241 cm^{-1} and 1280 cm^{-1} . The increment of the

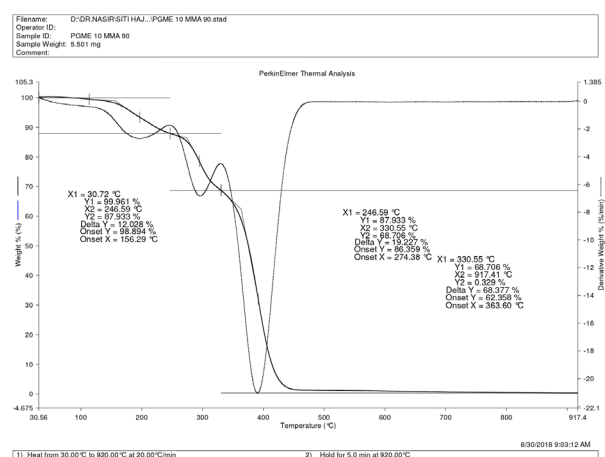
peak intensity in case of -C-O-C-, the decrease of that of -OH and the presence of a carbonyl group peak in the spectra of the grafted copolymer confirm the synthesis of P(mPEG-g-MMA) copolymer [18].



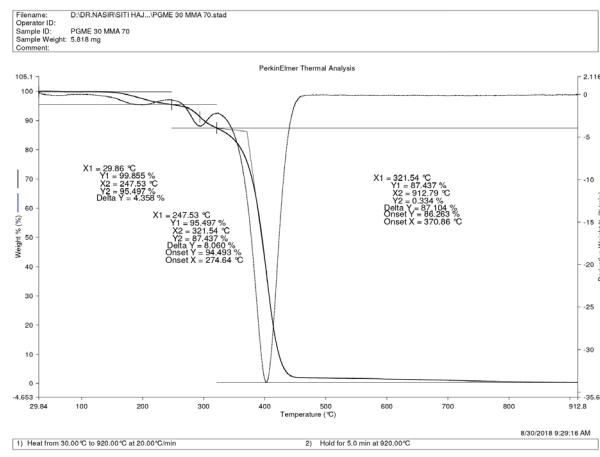
a)



c)



b)



d)

Fig. 6. TGA thermograms of mPEG and P(mPEG-g-MMA) copolymers of varying ratios: a) mPEG; b) 10:90; c) 20:80; d) 30:70.

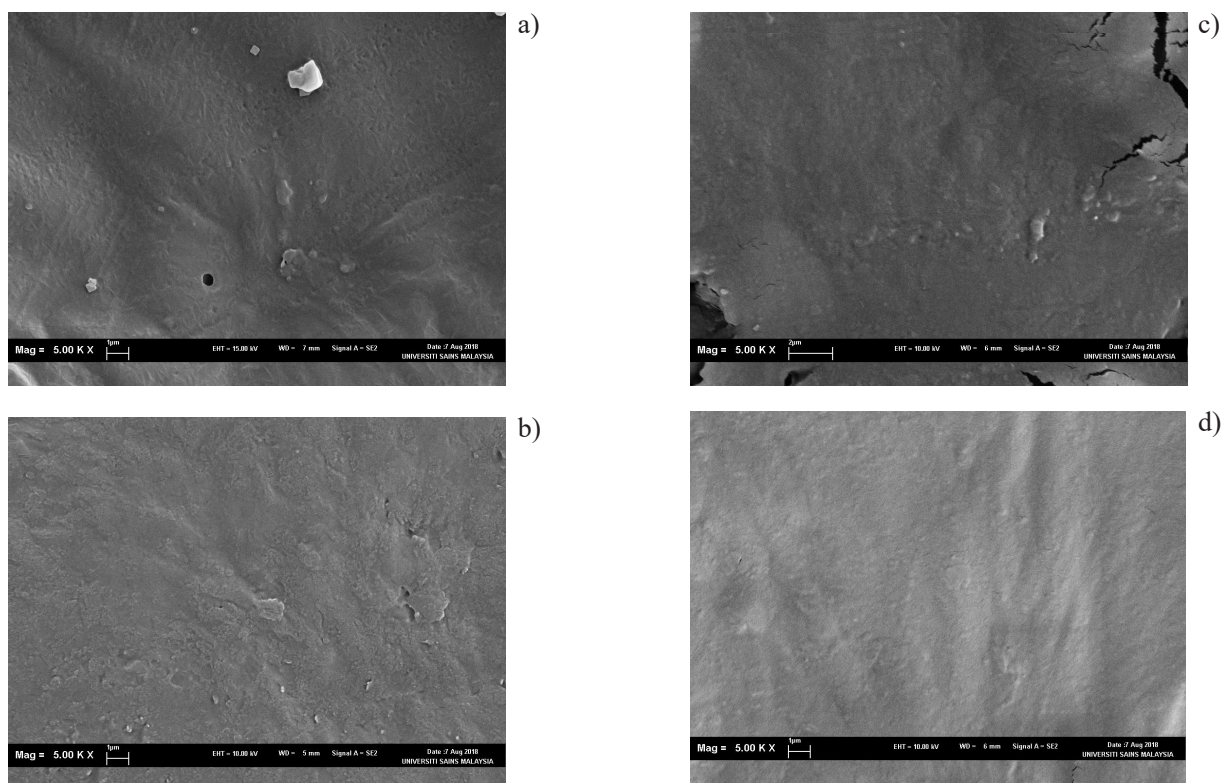


Fig. 7. SEM (Mag = 5000) data referring to pure mPEG and P(mPEG-g-MMA) copolymers of varying ratios: a) mPEG; b) 10:90; c) 20:80; d) 30:70.

¹H and ¹³C NMR studies

¹H and ¹³C NMR studies are carried out aiming to obtain more evidence in respect to the synthesized material. The results are shown in Fig. 3 and Fig. 4, respectively.

Various peaks are found referring to P(mPEG-g-MMA). They are shown in Fig. 3 having different values of the chemical shift. They are assigned to the synthesized copolymer structure as shown in the inset. The values of the chemical shift δ of 3.40 ppm and 3.70 ppm for H-C(1), of 3.54 ppm, 3.55 ppm and 3.83 ppm for H-C(2), of 1.12 ppm for H-C(3), and of 2.63 ppm for H-C(4) correspond to the protons bonded to C-1, C-2, C-3, C-4, respec-

tively. P(mPEG-g-MMA) is dissolved in acetone-D₆ and analyzed aiming to obtain its ¹³C-NMR spectrum. The corresponding spectroscopic data is shown in Fig. 4 suggesting the molecular formula of C₈H₁₆O₄. The ¹³C NMR spectroscopic data displays 8 carbon signals, including 3 methyl, 1 secondary, 1 tertiary carbon and 3 carbon signals for acetone. Table 1 presents the values of the chemical shifts of each carbon of P(mPEG-g-MMA) copolymer.

DSC analysis data

The DSC data of the initial mPEG and the P(mPEG-g-MMA) copolymer obtained using different ratios is shown

Table 3. A monomer concentration effect on the grafting copolymerization.

No	Concentration of monomer (mole)	Graft yield, %	Grafting efficiency, %	Homopolymer, %
1	0.42	93.6	92.3	5
2	0.37	89.3	85.5	6.5
3	0.32	64.0	71.9	4.7

* mPEG amounts to 5 g; MMA amounts to 45 ml; a temperature of 85 °C; reaction time of 3 h.

in Fig. 5. The glass transition temperature of the copolymers is determined by the chemical composition, while the structure of their chain is not attributed to a strictly defined value as the transition to a glass-shaped state usually occurs in a fairly wide temperature range. Fig. 5 shows that T_g moves toward the low temperatures of mPEG-g-MMA - the value of T_g of pure mPEG is 58.18°C, while that of mPEG-g-MMA is 49.57°C. The glass transition temperature increases with the molecular mass increase in the area of small values of the molecular mass, when the polymer passes from a glassy to a viscous state. The glass

transition temperature becomes virtually independent of the molecular mass as soon as it reaches the value of the molecular mass of the macromolecule statistical segment.

TGA data

The TGA data of the initial mPEG and the copolymers obtained are shown in Fig. 6. In case of mPEG, the temperature range is between 30.82 °C and 384.12 °C. It shows about 99.992 % loss of the weight that can be seen in Fig. 6 (a) and Table 2.

This may be attributed to the degradation of pure

Table 4. An initiator concentration effect on the grafting copolymerization.

Sample	Initiator concentration, mole	Graft yield, %	Grafting efficiency, %
1	0.1	70.7	82.5
2	0.2	72.2	83.5
3	0.3	75.1	84.7
4	0.4	79.3	86.2
5	0.5	83.8	87.1

* mPEG amounts to 5 g; MMA amounts to 45 ml; a temperature of 60°C; duration of 3 h.

Table 5. A temperature effect on the grafting copolymerization

Sample name	Mode	Graft yield, %	Grafting efficiency, %
P(mPEG-g-MMA)	1	87.3	91.1
P(mPEG-g-MMA)	2	77.7	81.2

* mPEG amounts to 5 g; MMA amounts to 45 ml; a temperature of 60-85 °C; duration of 3 r.

Table 6. A reaction time effect on the grafting copolymerization.

Sample name	Time (min)	Graft yield, %	Grafting efficiency, %
P(mPEG-g-MMA)	60	70.1	84.5
P(mPEG-g-MMA)	90	71.3	85.5
P(mPEG-g-MMA)	120	73.1	86.7
P(mPEG-g-MMA)	150	78.3	87.2
P(mPEG-g-MMA)	180	79.9	89.1

* mPEG amounts to 5 g; MMA amounts to 45 ml; a temperature of 85°C.

mPEG. The TGA of the P(mPEG-g-MMA) copolymers shown in Fig. 6 (b, c, d) reflect three stages of a weight loss between 30°C and 364°C (Table 2).

The temperature range during the first stage is between 30.72°C and 156.29°C, while the loss amounts to 12.028 % attributed to bound water or impurities. The second stage of the weight loss starts at 246.59°C and continues to 274.38°C. It amounts to about 19.227 % due to the ungrafted mPEG degradation. The third stage of the weight loss starts at 330.55°C and continues to 363.60 °C. It reaches a value of 68.377 %. The weight loss during the third stage is determined by the decomposition process of P(mPEG-g-MMA). This is an indication that the grafted copolymer has an excellent thermal stability providing different applications.

SEM data

The scanning electron micrographs of pure mPEG and P(mPEG-g-MMA) copolymers are shown in Fig. 7. The SEM image of mPEG shows a smooth surface because of the stronger interaction between the mPEG molecules. On the other hand, the SEM images of the P(mPEG-g-MMA) copolymers prove the uniform distribution of MMA. The graft copolymerization of MMA modifies the surface morphology of mPEG. Homogenous grafted P(mPEG-g-MMA) copolymers are obtained.

A monomer concentration effect on the grafting copolymerization

The effect of the monomer concentration on the degree of grafting is investigated by using MMA decomposed within 3 h in toluene at 60°C, 70°C and 85°C. Three ratios of mPEG and monomer concentrations are used, i.e. 10:90; 20:80 and 30:70. The results indicate an increase of the graft yield (G, %), the grafting efficiency (GE, %) and the amount of the homopolymer (H, %) with an increase of the concentrations of methyl methacrylate in the solution as shown in Table 3. The values of G(%), GE (%) and H (%) are calculated in accordance with the following equations:

$$G(\%) = [(W_1 - W_0)/W_0] \times 100 \quad (1)$$

$$H(\%) = [(W_2 - W_1)/W_3] \times 100 \quad (2)$$

$$GE(\%) = (W_1/W_2) \times 100 \quad (3)$$

where W_0 and W_1 are the weights of the initial matrix and the grafted matrix, i.e. the weight of the product after extraction, W_2 is the crude product weight prior to the extraction, while W_3 is the weight of the monomer [8].

The maximum grafting yield is found equal to 93.6 % in case the monomer concentration is 0.42 mole L⁻¹, the temperature is 85°C and the reaction time is 3 h. This trend may be due to increased homopolymer formation during the proton transfer to the MMA monomer. Such transfer can occur with an increase of the graft copolymer chain. Furthermore, the opportunity of further addition to the growing chain increases in case of the monomer concentration increase at a higher methyl methacrylate concentration, i.e. the grafting process is facilitated. On the other hand, the decrease of the homopolymer amount provides an easier interaction of the initiator molecule with mPEG prior to the monomer addition. The portion wise addition of MMA is another factor favoring the grafting yield. The results clearly reveal an increase of the graft yield and the grafting efficiency, while the homopolymer is decreased with the increase of the monomer concentration.

An initiator concentration effect on the grafting copolymerization

The more common method of a radical generation during conventional free radical polymerization refers to homolytic dissociation of compounds such as benzoyl peroxide with the application of heat or light. Two radicals are obtained per decomposition. This explains the choice of benzoyl peroxide as a catalyst of the monomer double bond destruction. Furthermore, the choice made is determined by the good solubility of benzoyl peroxide in toluene. The amount of the catalyst is calculated using the following formula: 0.1 wt. % in respect to the monomer used. The amount of the catalyst varies between 0.1 moles and 0.5 moles. An increase of the catalyst concentration up to a concentration of 0.1 moles (0.1 wt. %) results in an increase of the grafting. The further increase of the catalyst concentration leads to an increase of the graft yield and the graft efficiency as shown in Table 4.

A temperature effect on the grafting copolymerization

The synthesis is carried out in two modes, i.e. mode 1: 60-70-85°C; mode 2: 70-80-85-90°C. The results referring to this parameter effect are shown in Table 5. The first mode results show that the degree of polymerization is much higher than that of the second case. This observation verifies the fact that the mechanism of

grafting is affected by the presence of benzoyl peroxide and the temperature change.

A time effect on the grafting copolymerization

The effect of the reaction time (60 min, 120 min and 180 min) on the grafting at 85°C is investigated. Table 6 shows that the reaction time increase provides a slight increase of the yield and the efficiency. The duration of 180 min is taken as the optimal time on the ground of the values presented.

CONCLUSIONS

The graft copolymers P(mPEG-g-MMA) are successfully synthesized by the free radical polymerization method using benzoyl peroxide as an initiator. The characterization is performed using various techniques such as FT-IR, SEM, nuclear magnetic resonance (^1H NMR, ^{13}C NMR), DSC, and TGA. The effect of the various parameters such as the concentration of the initiator and the monomer, the reaction time and the temperature of the graft copolymerization of mPEG and MMA is investigated. The experimental results obtained reveal that the optimum conditions for grafting P(mPEG-g-MMA) copolymer refer to a ratio of 10:90, a monomer concentration of 0.42 mole L^{-1} , a reaction temperature of 60 - 85°C and reaction time of 3 h. At a lower initiator concentration (0.1 %), the monomer conversion is found good. The NMR study confirms that all groups are present in the copolymer. The results also show that the grafted copolymer has an excellent thermal stability, which provides numerous applications. Moreover, the rate of decomposition is highly improved through grafting and polymerization of the grafted samples. Therefore, these copolymers can be widely used even as surfactants in chemical technology.

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REFERENCES

1. V. Lele, S. Kumari, H. Niju, Syntheses, Characterization and Applications of Graft Copolymers of Sago

- Starch – A Review, Starch - Stärke, 70, 2018, 7-8.
2. D. Jenkins, S. Hudson, Review of Vinyl Graft Copolymerization Featuring Recent Advances toward Controlled Radical-Based Reactions and Illustrated with Chitin/Chitosan Trunk Polymers, Chem. Rev., 101, 2001, 3245-3273.
3. J. Ueda, M. Kamigaito, M. Sawamoto, Calixarene-Core Multifunctional Initiators for the Ruthenium-Mediated Living Radical Polymerization of Methacrylates, Macromolecules, 31, 20, 1998, 6762-6768.
4. H. Shinoda, P. Miller, K. Matyjaszewski, Improving the Structural Control of Graft Copolymers by Combining ATRP with the Macromonomer Method, Macromolecules, 34, 10, 2001, 3186-3194.
5. A. Noshay, J. E. McGrath, Block Copolymers: Overview and Critical Survey, Academic Press, New York, 1977.
6. Ceresa R.J (ed.), Block and Graft Copolymerization, Wiley, London papers, 12, 11, 1976.
7. M. Ueda, Sequence control in one-step condensation polymerization, Prog. Polym. Sci., 24, 5, 1999, 699-730.
8. A. Bhattacharya, B.N. Misra, Grafting: a versatile means to modify polymers: Techniques, factors and applications, Prog. Polym. Sci., 29, 8, 2004, 767-814.
9. I.W. Hamley, In The Physics of Block Copolymers, Oxford University Press, New York, 1998.
10. Y. Liu, L. Bai, R. Zhang, Y. Li, Y. Liu, K. Deng, Block Copolymerization of Poly(ethylene glycol) and Methyl Acrylate Using Potassium Diperoxodisulfate(III), Journal of Applied Polymer Science, 96, 2005, 2139-2145.
11. G. Odian, Principles of Polymerization, Wiley-Interscience, New York, 1991, p. 212-226.
12. C. Allen, D. Maysinger, A. Eisenberg, Nano-engineering block copolymer aggregates for drug delivery, Colloids and Surfaces B: Biointerfaces, 16, 3, 1999, 3-27.
13. B. Bogdanov, A. Vidts, E. Schacht, H. Bergmans, Isothermal Crystallization of Poly(ϵ -caprolactone-ethylene glycol) Block Copolymers, Macromolecules 32, 3, 1999, 726-731.
14. H.R. Kricheldorf, S. Rost, Syntheses of L-Lactide-PEG Multiblock Copolymers by Means of Spirocyclic Ge-PEG Initiators, Macromol. Chem. Phys., 205, 8, 2004, 1031-1038.

15. Raechelle A. D'Sa, Brian J. Meenan, Poly(ethylene glycol) methyl ether methacrylate (PEGMA) onto polystyrene (PS) and poly(methyl methacrylate) (PMMA) surfaces (Chemical Grafting of Poly(ethylene glycol) Methyl Ether Methacrylate onto Polymer Surfaces by Atmospheric Pressure Plasma Processing, *Langmuir*, 26, 3, 2010, 1894-1903.
16. B. Tsai, O. Garcia-Valdez, P. Champagnem M. Cunningham, Poly(Poly(Ethylene Glycol) Methyl Ether Methacrylate) Grafted Chitosan for Dye Removal from Water, *Water Processes*, 5, 12, 2017, doi: 10.3390/pr5010012.
17. R. Krishnan, K.S.V. Srinivasan, Synthesis and Characterization of Amphiphilic Block Copolymers of Methyl Methacrylate with Poly(ethylene oxide) Macroinitiators Formed by Atom Transfer Radical Polymerization, *Journal of Applied Polymer Science*, 97, 3, 2004, 989-1000.
18. Ren-Shen Lee, Yi-Ting Huang, Synthesis and Characterization of Amphiphilic Block-Graft MPEG-b-(PaN3CL-g-alkyne) Degradable Copolymers by Ring-Opening Polymerization and Click Chemistry, *Journal of Polymer Science Part A: Polymer Chemistry*, 46, 13, 2008, 4320 - 4331.
19. Y. Liu, L. Bai, R. Zhang, Y. Li, Y. Liu, K. Deng, Block Copolymerization of Poly(ethylene glycol) and Methyl Acrylate Using Potassium Diperoxodisulfate(III), *Journal of Applied Polymer Science*, 96, 6, 2005, 2139-2145.
20. K. Inomata, E. Nakanishi, Y. Sakane, M. Koike, T. Nose, Side-chain crystallization behavior of graft copolymers consisting of amorphous main chain and crystalline side chains: Poly(methylmethacrylate)-graft-poly(ethylene glycol) and poly(methyl acrylate)-graft-poly(ethylene glycol), *Journal of Polymer Science Part B: Polymer Physics*, 43, 1, 2005, 79-86.
21. E. S. Khalil, B. Saad, El-Sayed Negim, M. I. Saleh, Novel water-soluble chitosan derivative prepared by graft polymerization of dicyandiamide: synthesis, characterization, and its antibacterial property, *Journal of Polymer Research*, 22, 6, 2015, 1-12.
22. R.R. Mohamed, M.W. Sabaa, Graft Copolymerization of Acrylonitrile and its Amidoxime Derivative onto Chitosan // *Journal Appl. Polym. Sci.*, 116, 2010, 413-421.
23. M.W. Saba, N.A. Mohamed, R.R. Mohamed, N.M. Khalil, S.M. Abd El Latif, Synthesis, characterization and antimicrobial activity of poly (N-vinyl imidazole) grafted carboxymethyl chitosan, *Carbohydrate Polymers*, 79, 4, 2010, 998-1005.