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# Synthesis and characterization of vinyl acetate graft copolymers

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**Abstract.** Graft copolymer P(mPEG-g-VAc) have been prepared by the graft polymerization with a different ratios of mPEG with Mn=2000 macromonomers and Vinyl acetate VAc in the presence of benzoyl peroxide as an initiator using a macro radical initiator technique under influence of heating in toluene has been observed. The graft copolymer P(mPEG-g-VAc) thus formed was characterized with scanning electron microscope SEM, nuclear magnetic resonance <sup>1</sup>H NMR, <sup>13</sup>C NMR, differential scanning calorimeter DSC, thermo gravimetric analyzer TGA and Fourier transform infrared FT-IR techniques. The results of characterization techniques shows formation of copolymer P(mPEG-g-VAc) while the optimum condition among the studied parameters were as follows; monomer concentration 0.4 mole L<sup>-1</sup>, ratio (10:90), reaction temperature is 60-85 °C and reaction time is 3 h.

**Key words:** polyethylene glycol methyl ether, vinyl acetate, free radical polymerization, catalyst, characterization.

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## Introduction

Graft copolymerization is the process in which monomers are bonded to starch backbone through strong covalent bonds. Graft copolymers also exhibit good phase separation and are used for a variety of applications, such as thermoplastic elastomers, compatibilizers, concrete additives, polymeric emulsifiers and surfactants. Due to their branched structure, they melt easily and have potential to achieve a new field of application because of their structures, which is advantageous for processing. [1-5, 13-16].

In addition to other complex polymer systems comprised of star, block, and dendritic architectures, graft copolymer synthesis is an important aspect of polymer science, which continues to receive considerable attention. Graft copolymers can be described as having the general structure 1, where the main polymer backbone A, commonly referred

to as the trunk polymer, has branches of polymer chain B emanating from different points along its length. The common nomenclature used to describe structure 1, where polymer A is grafted with polymer B, is A-graft-B, which can be further abbreviated as A-g-B. Graft copolymers have a variety of potential applications resulting from the wide range of properties available when different polymer chains are connected to form a hybrid branched macromolecule [2].

Many authors [6–8] have distinguished chemical modification of mPEG via graft copolymerization. Much of their work has focused on the synthesis and copolymerization of mPEG macro monomers using anionic, cationic, free radical, and condensation polymerizations, depending on the type of monomer used to prepare the macro monomer.

In this paper the graft copolymer P(mPEG-g-VAc) thus formed was characterized with FT-IR,

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DSC, TGA, SEM techniques and shown in Figures 1-7.

## 2 Experimental

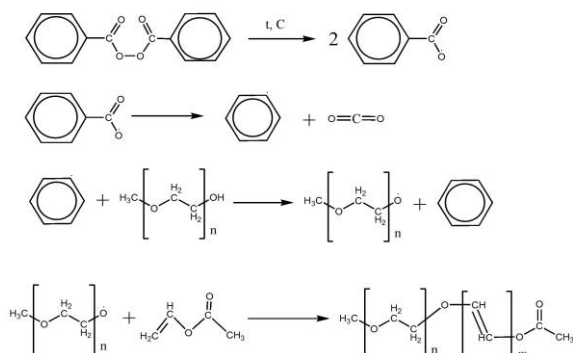
### 2.1 Materials

Polyethylene glycol methyl ether or methoxy poly(ethylene glycol) mPEG,  $M_n=2000$ , Toluene (ACS reagent, reagent grade, ISO, >99.7 %) and Hexane (HPLC) were purchased from Sigma Aldrich. Vinyl acetate (99 % stabilized, nitrogen flushed) was purchased from Acros Organics. Dibenzoyl peroxide, 97% (dry wt.), wet with 25% water was purchased from Alfa Aesar.

### 2.2 Preparation of grafted copolymer P(mPEG-g-VAc)

Firstly, 5 g of mPEG was dissolved in 100 mL of toluene and charged into a 250 mL three-necked reaction flask equipped with a reflux condenser, dropping funnel and thermometer. The reaction flask was involved in a water bath (with automatic temperature control) with settled temperature  $60\text{ }^\circ\text{C}$ . Benzoyl peroxide (0.1 % weight mass of mPEG) was added to the mixture and heated to  $60\text{ }^\circ\text{C}$  under reflux condition. The recrystallization of benzoyl peroxide carried out, dried in an oven at less than  $40\text{ }^\circ\text{C}$  and then in desiccator over silica gel to remove water content. In second step, the monomer vinyl acetate (VAc) was fed to the system drop-wise for 40 minutes at  $60\text{ }^\circ\text{C}$ .

### 2.3 Mechanism of grafting polymerization



**Figure 1** Mechanism of the polymerization

The mechanism of free radical graft polymerization is shown (Fig. 1), and in the step I and II going homolytic dissociation of compounds

such as benzoyl peroxide using heat, that causes the initiation of reaction. In Step III, free radical combines with the trunk polymer and provide a site to attach the Vinyl acetate (VAc) monomer which is provide attaching on the main polymer backbone. Step III is the major step in the synthesis for obtaining the desired copolymer in step IV.

## 3 Characterization

### 3.1 Fourier-transform infrared spectroscopy

The samples were characterized by recording the IR spectra of mPEG and P(mPEG-g-VAc) using a Fourier-Transform Infrared Spectroscopy (FTIR) within the wave number range of  $4000\text{--}600\text{ cm}^{-1}$  and 32 scans at room temperature. These spectra were measured with a Bruker model Alpha infrared spectrophotometer equipped with diamond crystal.

### 3.2 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectra ( $^1\text{H}$  and  $^{13}\text{C}$ ) of grafted copolymer P(mPEG-g-VAc) were recorded on a Bruker Avance spectrometer at 300 MHz. The spectra were recorded in acetone- $d_6$  solvent at room temperature ( $T = 298\text{ K}$ ) using acetone residual peak ( $\delta = 2.5\text{ ppm}$ ) as internal reference. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) and coupling constants (J) are given in hertz (Hz).

### 3.3 Thermogravimetric analysis and Differential Scanning Calorimetry analysis

The thermogravimetric analysis (TGA) of mPEG and its grafted copolymer was carried out with thermo-gravimetric analyzer Mettler Toledo Stare System while Differential Scanning Calorimetry (DSC) by differential scanning calorimeter mettler toledo stare system. The samples were subjected to a constant heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Thermal studies were performed over a temperature range of  $30\text{ }^\circ\text{C}$  to  $800\text{ }^\circ\text{C}$  in case of TGA. In DSC studies, the changes in the samples were recorded up to a temperature of  $100\text{ }^\circ\text{C}$  i.e. heating from  $-50\text{ }^\circ\text{C}$  to  $100\text{ }^\circ\text{C}$ .

### 3.4 Scanning electron microscopy

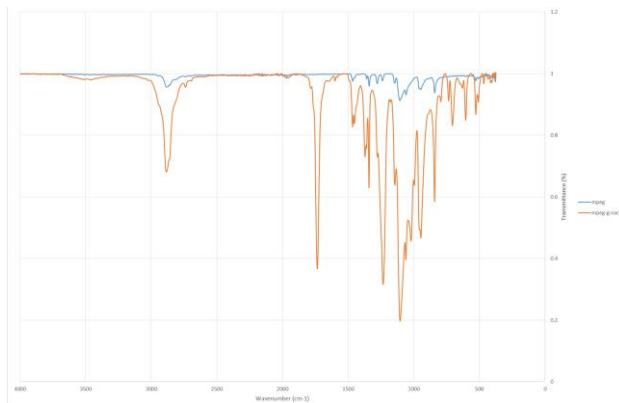
The mPEG and grafted copolymer P(mPEG-g-VAc) were characterized by using the microscopic methods to provide information about morphology

of obtained samples. The Scanning Electron Microscopy (SEM) analysis was made by scanning electron spectroscopy (XHR-FESEM) model FEI Verios 460L. Samples were coated with thin layer of gold and examined by electron probe micro analyzer at 5 KV.

## 4 Results and discussion

### 4.1 Fourier-transform infrared spectroscopy studies

The FTIR spectra of mPEG and copolymer P(mPEG-g-VAc) are shown in Fig 2. In the spectrum of mPEG, the -C-O-C- and -CH<sub>2</sub>- stretching peaks were observed at 1113 and 2880 cm<sup>-1</sup>. The FT-IR spectra showing typical peaks for C=C at 1634cm<sup>-1</sup>, C=O at 1735cm<sup>-1</sup> and C-O-C at 1099 cm<sup>-1</sup>, O-CH<sub>3</sub> at 1466 cm<sup>-1</sup> are in agreement with the structural characteristics of mPEG-g-VAc. After the formation of grafted copolymer the peaks at 1735 cm<sup>-1</sup> and 2886 are due to carbonyl group and C-H bond respectively. Furthermore, C-O stretching at 1241 and 1280 cm<sup>-1</sup> is also present. Vinyl group =C-O-C- stretching at 1234 and 1341 cm<sup>-1</sup> is also present. The increment in the peak intensity in case of -C-O-C-, the reduction for -OH and presence of carbonyl group peaks in the spectra of grafted copolymer confirm the synthesis of copolymer P(mPEG-g-VAc).

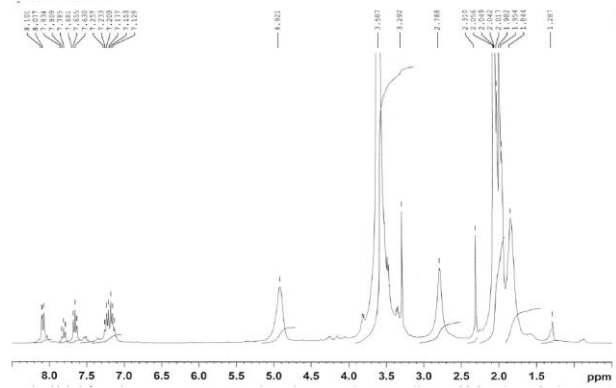


**Figure 2** IR spectra of mPEG and copolymer P(mPEG-g-VAc)

### 4.2 <sup>1</sup>H and <sup>13</sup>C NMR studies

To obtain more evidence for the synthesized material, the <sup>1</sup>H and <sup>13</sup>C NMR studies also carried out and the results are shown in Fig 3 and Fig 4 respectively.

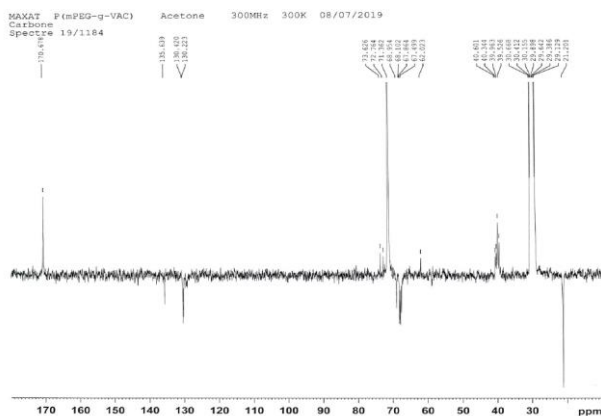
Various peaks can be seen for mPEG-g-VAc in Fig 3 with different values of chemical shift.



**Figure 3** <sup>1</sup>H NMR spectrum of the obtained copolymer P(mPEG-g-VAc)

These values of chemical are assigning on the synthesized copolymer structure as shown in inset. The value of chemical shift for H-C(1) was  $\delta = 3.40$  and 3.70 ppm, for H-C(2)  $\delta = 3.54$ , 3.55 and 3.83, for H-C(3)  $\delta = 1.12$ , for H-C(4) was  $\delta = 2.63$  correspond to the protons bonded to C-1, C-2, C-3, C-4 respectively. The <sup>1</sup>H NMR spectra also showed the typical signals attributed to vinyl acetate (4.5 and 5.2 ppm), methyl groups (-CH<sub>3</sub>) (1.9 ppm), methylene group (-CH<sub>2</sub>) (3.6 and 4.1 ppm).

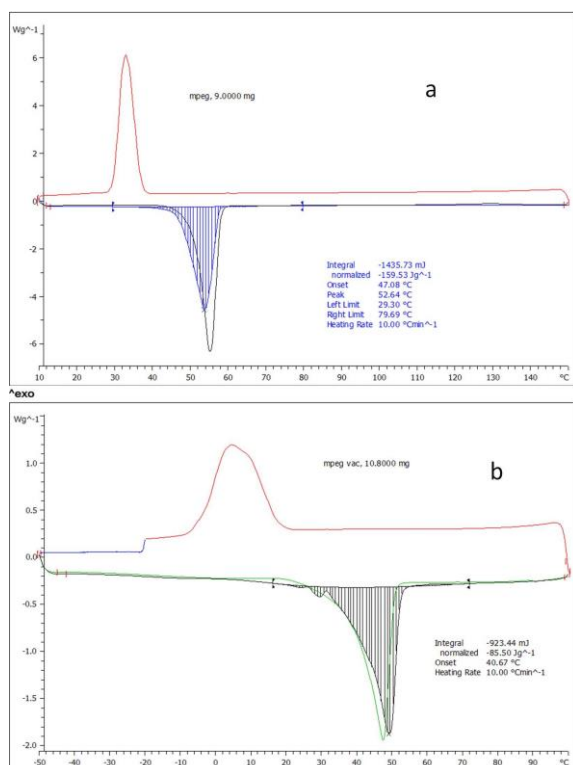
For obtaining the <sup>13</sup>C-NMR spectrum of P(mPEG-g-VAc), it was dissolved in acetone and analyzed. The <sup>13</sup>C NMR spectroscopic data of copolymers P(mPEG-g-VAc) as shown in Fig 4, suggested a molecular formula of C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>. The <sup>13</sup>C NMR spectroscopic data displayed 8 carbon signals, including 3 methyls, 1 secondary, 1 tertiary carbon and 3 carbon signals for acetone. A broad O-H stretching absorption in the region of 1500–1700 cm<sup>-1</sup> is ascribable to a carbonyl group, which was evidenced by the carbon resonance. Table 1 also show the value of chemical shift in copolymer P(mPEG-g-VAc) for each carbon.



**Figure 4** <sup>13</sup>C NMR spectrum of the obtained copolymer P(mPEG-g-VAc)

### 4.3 Differential Scanning Calorimetry analysis

The Differential Scanning Calorimetry (DSC) data's of the initial mPEG and obtained copolymer P(mPEG-g-VAc) are shown in Fig 5. The glass transition temperature of copolymer is determined by the chemical composition and structure of their chain and is not a rigidly defined value, as the transition to a glass-shaped state usually occurs in a fairly wide temperature range. Fig 5 shows that the  $T_g$  moves toward the low temperatures in mPEG-g-VAc, the value of  $T_g$  in pure mPEG is 58.18 °C and in copolymer mPEG-g-VAc it is not defined. In the area of small values of polymer molecular mass, when it passes from glassy to viscous, the glass transition temperature increases with the growth of molecular mass. As soon as the molecular mass reaches the value of the molecular mass of the statistical segment of the macromolecule, the glass transition temperature is virtually independent of the molecular mass [9, 10].



**Figure 5** DSC thermograms of mPEG (a) and copolymer P(mPEG-g-VAc) (b)

Melting temperatures ( $T_m$ ) and enthalpies ( $\Delta H_m$ ) determined by DSC on the second heating scan at heating rates of 10 °C•min<sup>-1</sup>.

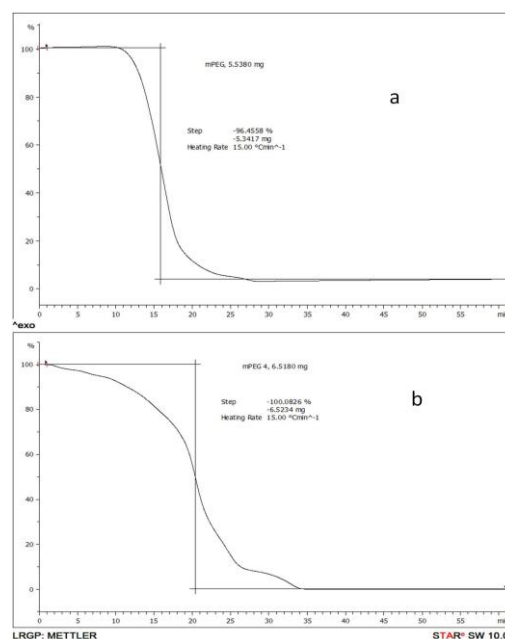
Glass-transition temperature ( $T_g$ ) taken as the inflection point of the second heating DSC curves recorded at 10 °C•min<sup>-1</sup>.

**Table 1** Thermal properties of mPEG and grafted polymer.

Polymer	DSC analysis			TGA analysis	
	$T_m$ , °C	$\Delta H$ , kJ/mol	$T_g$ , °C	$T_i$ , °C	$T_{max}$ , °C
mPEG	47.08	5.7	-		270/405
P(mPEG-g-VAc)	40.67	2.6	-		390/525

### 4.4 Thermogravimetric analysis

Thermogravimetric Analysis (TGA) of methoxy poly(ethylene glycol) mPEG and copolymer P(mPEG-g-VAc) are shown in the Fig 6. In case of mPEG, the temperature range was between 30 °C and 200 °C and it shows about 99.992 % loss in weight that can be seen in Fig 6 and Table 1. This may be corresponding to the degradation of pure mPEG.



**Figure 6** TGA thermograms of mPEG (a) and copolymer P(mPEG-g-VAc) (b)

The TGA of the copolymer P(mPEG-g-VAc) shown in Fig. 6 reflect two stages of weight loss between 30 and 200 °C (Table 2). In the first stage, the temperature range was between 30 and 120 °C with the loss of about 18 % due to the impurities. The second stage of weight loss starts at 120 °C and continues to 200 °C, corresponding weight loss of about 82 % due the weight losses of heating promote decomposition process of P(mPEG-g-VAc). This proves that grafted copolymer has excellent thermal stability and it can be widely used for different applications. Block copolymers also

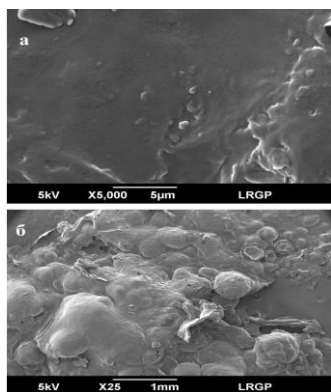


show semicrystalline character with  $T_m$  between 44 °C and 56 °C and superior melting enthalpies for those with longer mPEG. Unlike PDHU, block copolymer do not show detectable  $T_g$ s. Concerning grafted polymers they are amorphous with low  $T_g$ s indicating that grafting mPEG groups prevent crystallization of aliphatic polymer chains. Thermal stability evaluated by TGA shows scarce differences between the homopolymer and its corresponding block copolymers. Different behavior was observed for grafted polymers with a significant decrease in temperature at which 5% weight loss takes place although temperature for maximum degradation rates are similar. This could be related to the higher percentage of labile ester groups and their lower molecular weight [11].

Block or graft copolymers can be self-assembled to form micelles in their selective solvents. Compared with linear block copolymers, graft copolymer can add considerable functionalities on the branched chains with great advantage of convenient chemical modifications in advance of the self-assembly process [12].

#### 4.5 Scanning electron microscopy

The scanning electron micrographs of pure mPEG and copolymer P(mPEG-g-VAc) are shown in Fig 7.



**Figure 7** Results of pure mPEG (a) and copolymer P(mPEG-g-VAc) (b) on scanning electron microscope (Mag = 5000)

The SEM image of mPEG shows a smooth surface, because there is a stronger interaction between mPEG molecules. On the other hand, the SEM images of copolymer P(mPEG-g-VAc) prove the uniform distribution of VAc. The graft copolymerization of VAc modified the surface morphology of mPEG and homogenous grafted copolymers P(mPEG-g-VAc) was obtained.

#### Conclusions

The graft copolymer P(mPEG-g-VAc) was successfully synthesized using benzoyl peroxide as an initiator by free radical polymerization method. The characterization was performed using various techniques such as FT-IR, SEM, nuclear magnetic resonance ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR), DSC, and TGA. The obtained results from this experiments revealed that the optimum conditions for grafting copolymer P(mPEG-g-VAc) were found as follows: ratio is 10:90, monomer concentration 0.42 mol/L, reaction temperature is 60-85 °C and reaction time is 3 h. NMR study confirmed that all the groups present in the copolymers. The results of the thermal stability show that grafted copolymer has excellent thermal stability and it can be widely used for different applications. Moreover, the rate of decomposition is highly improved through grafting and through polymerization of the grafted samples. Therefore, this copolymer can be used for various applications including surfactant in chemical technology.

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## Винилацетатты полимерлердин синтезі мен сипаттамасы

Мырзаханов М.М., Эль Сайд Негим, Мохамад Насыр

**Түйіндеме.** Полиэтилен гликольді метил эфирі  $M_n = 2000$  макромономері мен винил ацетат мономері VAc бос радикалды полимерлеу арқылы алынған сополимер P (mPEG-g-VAc), катализатор ретінде бензойл пероксиді және қыздыру әсерінен алынды. Осылайша пайда болған сополимер P (mPEG-g-VAc) сканерлеуші электронды микроскоппен (SEM),  $^1H$ ,  $^{13}C$  ЯМР спектрометрімен, дифференциалды сканерлеу калориметрімен ДСК, ТГА термогравиметрімен және инфра қызыл-Фурье спектрометрімен сипатталды. P (mPEG-g-VAc) сополимернің сипаттамасының нәтижесінде синтезді жүргізудің оптимальді параметрлері анықталды: мономер концентрациясы  $0,4$  моль  $л^{-1}$ , бастапқы заттардың қатынасы (10:90), температура реакциясы  $60-85$  °C, және синтез уақыты 3 сағат.

**Түйінді сөздер:** полиэтиленгликоль метил эфирі, винил ацетаты, бос радикалды полимеризация, катализатор, сипаттама.

## Синтез и характеристика винилацетатных прививочных полимеров

Мырзаханов М.М., Эль Сайд Негим, Мохамад Насыр

**Аннотация.** Сополимер P(mPEG-g-VAc) был получен путем прививочной полимеризации с различными соотношениями полиэтиленгликоль метилового эфира mPEG с  $M_n=2000$  макромономеров с винилацетатным мономером VAc в присутствии перекиси бензоила в качестве инициатора с использованием метода макрорадикального инициатора под воздействием нагрева в толуоле. Образовавшийся таким образом сополимер P(mPEG-g-VAc) был охарактеризован сканирующим электронным микроскопом СЭМ,  $^1H$ ,  $^{13}C$  ЯМР-спектрометром, дифференциальным сканирующим калориметром ДСК, термогравиметром ТГА и спектрометром ИК-Фурье. Результаты методов характеризации показывают образование сополимера P (mPEG-g-VAc), в то время как оптимальные условия среди изученных параметров были следующими; концентрация мономера  $0,4$  моль  $л^{-1}$ , соотношение (10:90), температура реакции составляет  $60-85$  °C, и время реакции составляет 3 часа.

**Ключевые слова:** полиэтиленгликоль метиловый эфир, винил ацетат, свободнорадикальная полимеризация, катализатор, характеристика.

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