

# Graft of *Polyethylenglycol* With Some Monomers As Fillers For Dentistry

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## **Abstract :**

The aim of this research is to modifying and graft of Polyethylenglycol by using different monomers which are useful in dentistry because some of the prepared graft co polymers can be shaped and molded and then transformed to a solid, such as graft copolymerization of Polyethylenglycol with Indene(A1), with dipenten(A2).with acrylonitrile(A3) ,with acrylamide(A4) , with acrylic acid(A5),by using .dibenzoylperoxide as initiator,

New properties of the substrate of useful derivative as dental material . Due to their structural diversity and stability, onto backbone of polymers are formed , the prepared polymers were characterized by FTIR and H-NMR spectroscopes and thermal analysis TGA & DSC were considered.Sweling percentage s were determined, (A3) & (A5) were found asuitable for fillers .

**Keyword:** *Polyethylenglycol*, Acryl amide , Acrylic acid , Di pentin, , Indine.

## Introduction:

Copolymers are obtained by copolymerization of two or more monomers are sometimes termed bipolymers, those obtained from three monomers gave terpolymers, four monomers gave quaterpolymers. [1]. Examples: Poly(ethylene-co-propylene) (EP) [2]., Poly(styrene-co-butadiene) (SBR) Poly(vinylidene chloride-co-vinyl chloride) (Saran), Acrylonitrile / Butadiene / Styrene (ABS) [3]. These structurally simple polymers constitute by far the largest share among plastics and flexibility to required applications depending on the nature of their repeating units as well as their molecular weight[4]. But the freedom of design is greatly expanded not only by incorporating structurally different repeating units into a given polymer thread but also by

control their ratio and position in the backbone sequence. These give copolymer classes including random copolymers, alternating copolymers with strictly alternating repeating units. Alternating copolymers[5-6]., block copolymers consisting of two or more segments of pure homosequences Block copolymers: [7], graft copolymers in which polymeric side chains of one repeating unit are grafted to a strand of another repeating unit, among others), Different copolymer architectures: random copolymer, alternating copolymer, block copolymer, and grafted copolymer [8]. Amphiphilic and double hydrophilic copolymers enable the formation of micelles An example of Block copolymers for drug delivery .Graft copolymerization Graft copolymerization is a technique for modifying the chemical and physical

properties of natural and synthetic polymers without drastically affecting its basic properties [9]. "Grafting" is a method wherein monomers are covalently bonded (modified) onto the polymer chain [10-11]. Graft copolymers can be obtained with three general approaches [12-15]. 1.

Grafting-onto: A preformed polymer with a reactive end-group is used a precursor, and then attached to the backbone. This method involve reaction of functional groups with another functional [16-17] groups which distributed randomly on the main chain of the other polymer (backbone) [18], 2. Grafting-from: The monomer is grafted from the backbone is significantly more versatile than "grafting-on, 3. Grafting-through in other words grafting via surface-attached monomers [19] are carried out at the presence of polymers (backbone) onto which

functionalized monomers have been attached. The hydroxyl groups of cellulose fiber were converted into thiocarbonyl-thio chain transfer agent [20], and were further used to mediate the RAFT polymerization of styrene graft copolymers became widely studied due to their increased number of applications due to their unique structures relative to other copolymers. Some common applications of graft copolymers include: • Membranes for the separation of gases or liquids [12], • Hydrogels [13], Drug deliverers [14], • Thermoplastic elastomers [15], • Compatibilizers for polymer blends [16-20], • Polymeric emulsifiers, • Impact resistant plastics cellulose microfibers treated with an epoxide and grafted with poly(acrylic acid)" [21]. Synthesis by Atom Transfer Radical

Polymerization". Biomacro molecules [22] . Graft polymerization of vinyl monomers onto cotton fibres were **pretreated with amines gave a new properties [23].**

### Instruments

FT-IR spectra was recorded using solid KBr discs by testing Shimadzu FT-IR 8000 series Fourier Transform, Infrared Spectrophotometer, Al-Mustansiriyah University, College of Science. Thermal analyses were performed using DSC, TGA and DTG. <sup>1</sup>H-

NMR spectra were recorded on a Fourier transform Varian spectrophotometer, company Bruker, model, Ultra shield 500MHZ, origin: Switzerland .Softening points were determined using Thermal Microscope (Kofler-method), and Reichert thermovar. SP.10/0.25 ,160.

.The degree of swelling for each disk sample after 24hrs was calculated, using the following equation:

$$\Delta m = \frac{m_t - m_o}{m_o} \times 100$$

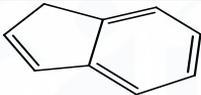
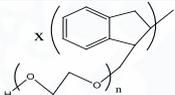
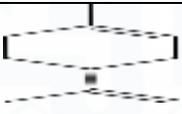
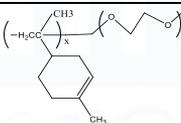
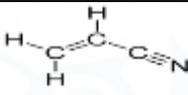
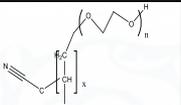
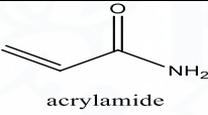
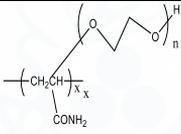
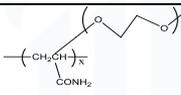
Where  $m_0$  is the weight of a dry drug polymer at  $t = 0$   $m_t$  is the swallowed polymer after 24hrs. Copolymerization of Polyethylen glycol with some monomers :Indene(A1), dipenten(A2), acrylonitrile(A3), acrylamide(A4), acrylic acid(A5) [24].

In a screw capped polymerization bottle (10)gm ) P.E.G dissolved in (5ml) acetone and { (1gm) Indene, or (1gm) dipenten, or (1gm) acrylonitrile (1gm) acrylamide or (1gm) acrylic acid} dissolved in ( 3 ml ) of water , and (0.05gm ) dibenzoylperoxide were

introduced in the polymerization bottle .it was flashed with nitrogen for few minutes inside a glove and resolutely stopped. The mixture was heated at 70°C, using water bath for 2 hr. The

solvent was evaporated under vacuum; the product was obtained, washed three times with ether. Dried in a vacuum oven at 50°C, produced polymers were studied.

**Table(1) Physical properties of prepared graft co polymers**

N	Monomer	Product	Produ	$\mu_{inDL}$	Color	S.P
1			89	0.81	Yellow	150-155
2			78	0.87	Dark brow	160-165
3			67	0.89	White	165-170
4	 acrylamide		88	0.77	White	140-160
5	 acrylic acid		87	0.97	White	190-200

## Results and Discussion

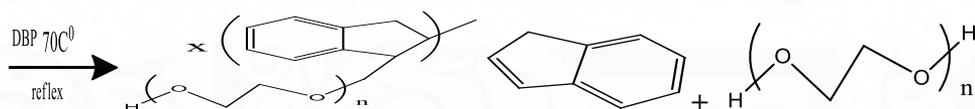
Polyethylene glycol is a linear neutral polyether. Its chemical structure representation is HO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>-

CH<sub>2</sub>CH<sub>2</sub>OH. Polyethylene glycol is non-toxic, odorless, neutral, lubricating, non-volatile and non-irritating and is

used in a variety of pharmaceuticals and in medications as a solvent. Five new graft co polymers were prepared

by the reaction of PEG with different monomers by using dibenzoylperoxide as a radical initiator. as shown below:

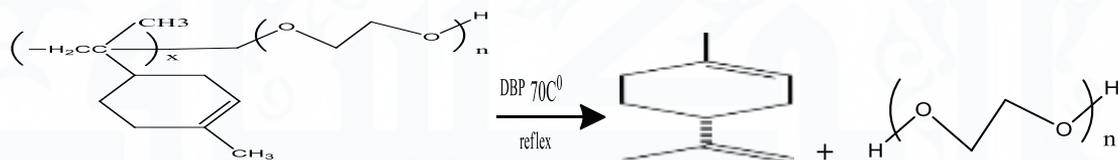
**Polymer 1:**



**PEG**

**Indene**

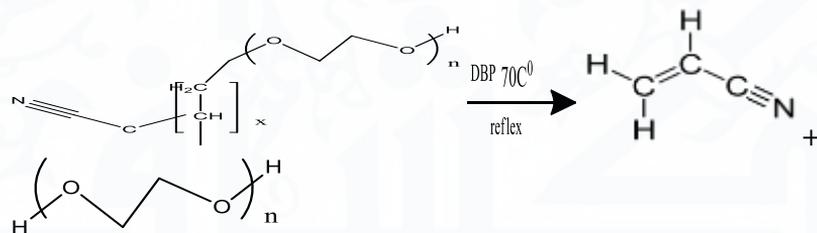
**Polymer 2:**



**PEG**

**dipenten**

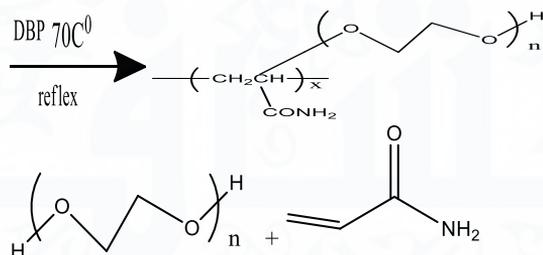
**Polymer 3**



**PEG**

**acrylonitrile**

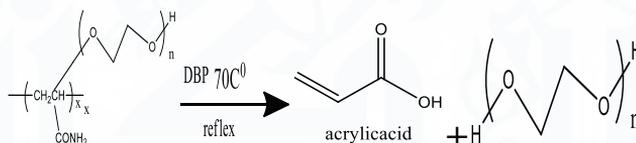
**Polymer 4**



PEG

acrylamide

\*Polymer be quickly (during the approximately 3 minutes) and it gave a white paste in simple heat stiffened, Polymer 5



Fig(1) FTIR spectrum of polymer A1 showed absorption peaks at  $2870.17\text{cm}^{-1}$  (C-H) aliphatic in polyethylen glycol,  $1107.18\text{cm}^{-1}$  (C-O) OF Polyethylen glycol,  $1458.23\text{cm}^{-1}$  (C=C) aromatic ring of indene,  $2881\text{cm}^{-1}$  (=C-H) aromatic ring of indene.

Fig(2) FTIR spectrum of polymer A2 showed absorption peaks at  $2914\text{cm}^{-1}$  (ring-CH<sub>3</sub>),  $1452\text{cm}^{-1}$  (C=C) ring of dipenten,  $1345\text{cm}^{-1}$  (C-CH<sub>3</sub>) of dipenten,  $2872\text{cm}^{-1}$  (CH)

aliphatic in Polyethylen glycol,  $1095.60\text{cm}^{-1}$  (C-O) of Polyethylen glycol

Fig(3) FTIR spectrum of polymer A3 showed absorption peaks at  $1107.18\text{cm}^{-1}$  (C-O) polyethylen glycol,  $2879.82\text{cm}^{-1}$  (C-H) aliphatic in Polyethylen glycol,  $2250\text{cm}^{-1}$  (C≡N) nitrile

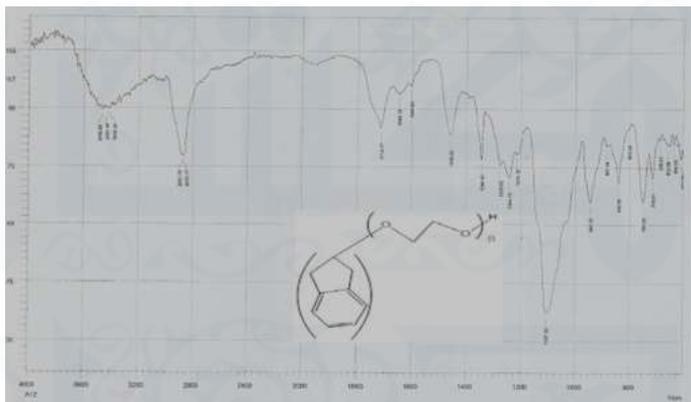
Fig(4) FTIR spectrum of polymer A4 showed absorption peaks at  $1105.25\text{cm}^{-1}$  (C-O) Polyethylen glycol,

2875.96cm<sup>-1</sup> (C-H)  
aliphatic  
inpolyethylenglygol,  
1653.05cm<sup>-1</sup>(C=O)amide,  
3367.82 cm<sup>-1</sup>(N-H) stretch  
amide,1251cm<sup>-1</sup>(C-N)  
amide,1612,54cm<sup>-1</sup>(N-  
H)bending amide,684  
cm<sup>-1</sup>(C-H) amide

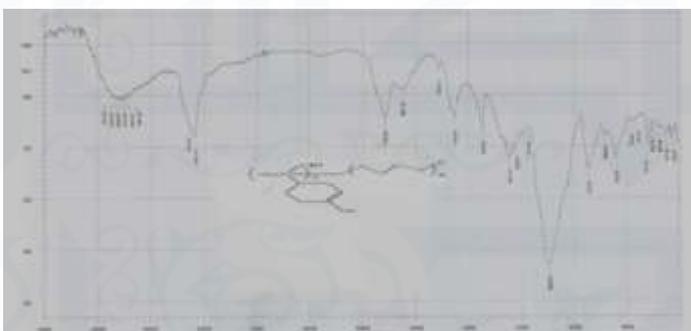
Fig(5) FTIRspectrum of  
polymer A5 showed  
absorption peaks at 1145.  
cm<sup>-1</sup> (C-  
O)polyethylenglygol,  
2881.75cm<sup>-1</sup> (C-H)  
aliphatic in  
Polyethylenglygol,1185  
cm<sup>-1</sup> (C-O)of Acrylic acid  
1730.21cm<sup>-1</sup> (C=O)of  
Acrylic acid, 3462-3000  
cm<sup>-1</sup> (OH)carboxylic acide.

<sup>1</sup>H-NMR spectrum of A3  
showed the signals atδ: 2.9  
ppm (CH-CO, 1H, T.), δ:

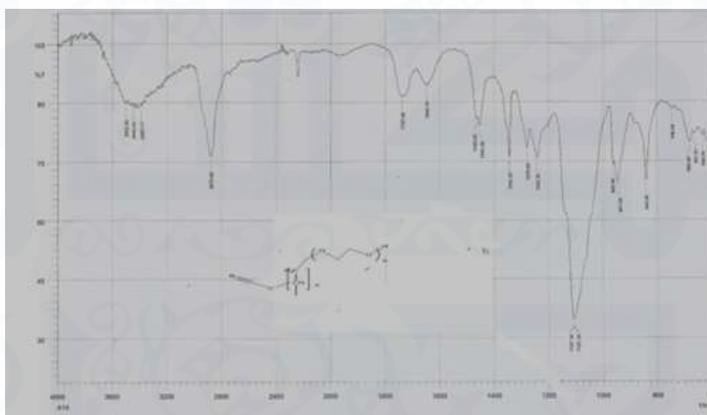
1.17 ppm (CH<sub>2</sub>-CH, 2H, d.)  
polymer, δ: 3.05 ppm  
(CH-CO, 1H, T.), δ: 2.7 ppm  
(CH<sub>2</sub>-CH, 2H, d.), δ: 3.5  
ppm due to (CH<sub>2</sub>-CO, 1H,  
S.), δ: 7.9 ppm (NH-CO, 1H,  
S.),  
Fig (4) <sup>1</sup>H-NMR spectrum of  
polymer A5showed the  
signals 2.7 ppm of 2CH<sub>2</sub>-CO  
(2H) d., 2.9 ppmof  
CH-COOH (1H) and 2.8  
ppm of CH-COOH (1H)S.  
polymer,1.3 ppm of CH<sub>3</sub>  
terminal (3H)d.,δ: 3.6 ppm of  
CH<sub>3</sub>-N (3H) S., and δ: 2.9  
ppm of CH<sub>3</sub>-C (3H) S., δ:  
4.8O-CH-CO (1H) Q.,δ: 7.1  
ppm  
(2H)d.oforthoaromaticring,δ:  
7.6 ppm of(3H) T., of meta  
and para, andδ: 8.1ppm  
ofNH-CO (1H) S.



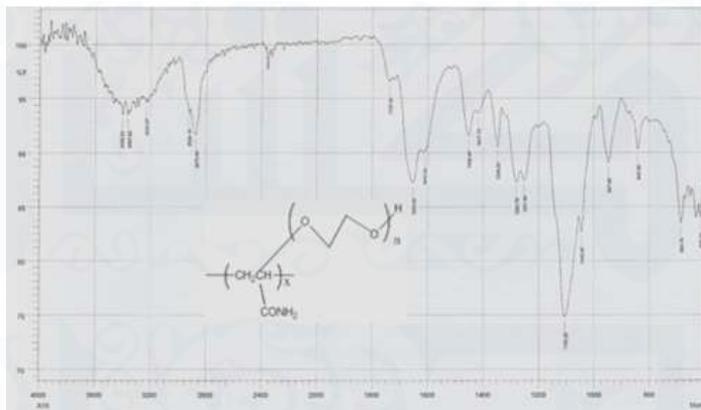
**Fig(1) FTIR spectrum of polymer A1**



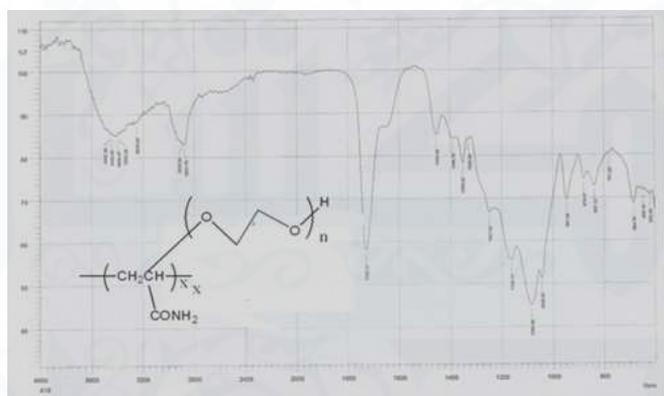
**Fig(2) FTIR spectrum of polymer A2**



**Fig(3) FTIR spectrum of polymer A3**



Fig(4) FTIR spectrum of polymer A4



Fig(5) FTIR spectrum of polymer A5

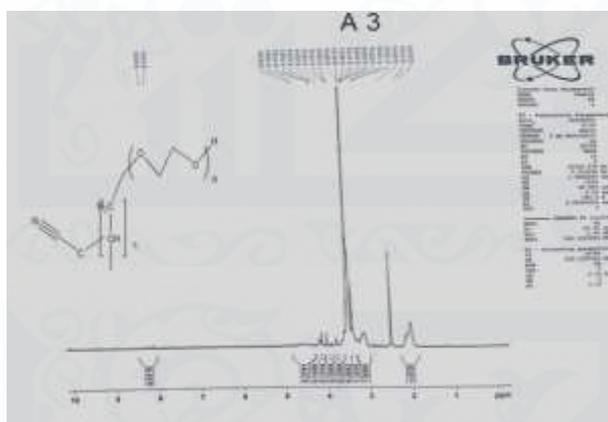


Fig. (6) the <sup>1</sup>H-NMR spectrum of polymer A3

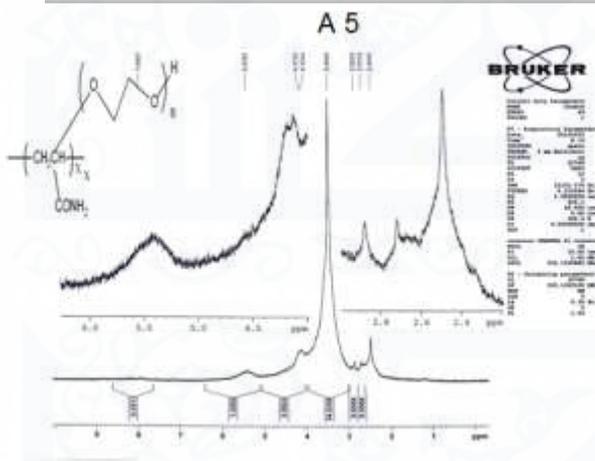


Fig. (7) the  $^1\text{H}$ -NMR spectrum of polymer A5

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