



Research Article

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Esterification of 3,5-dinitrobenzoic acid with 2- hydroxyethyl methacrylate polymers

Nastaran Irani^{1,2*}, Mohammad Hossein Nasirtabrizi², Samaneh Sattar Zadeh³
and Maryam Nedaei²

¹Department of Chemistry, Talesh Center PNU, Payam Noor University, Guilan, Iran

²Department of Chemistry, Ardabil Branch, Islamic Azad University, Ardabil, Iran

³Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

ABSTRACT

In this research, 2- hydroxyethyl methacrylate random copolymers with co-monomer methyl methacrylate (MMA), molar ration (1:1) is synthesized in the demethylformaid by free radical polymerization in presence of AIBN at temperature of 65-70 C °. Then 2-hydroxyethyl methacrylate random copolymers are modified by bonding on 3, 5- dinitrobenzoic acid polymer and modified in presence of DCC and DMAP. DCC plays a fundamental role in organic chemistry and it is used as activator and hydrophilic agent in decomposing of the organic compounds. One of the main methods in esterification is binding of carbodiimid which in acid and alcohol reaction needs to presence of DCC and DMAP as catalyst. The results show that by forming 3, 5- dinitrobenzoic acid bond on the polymer since chains a set of new polymers with new properties are formed which can be used in polymer industry widely. The primary and reactive structures of polymer have been confirmed in each step by techniques H-NMR, DMTA and FT-IR.

Keywords: 2-Hydroxy Ethyl methacrylate, 3, 5- di nitro benzoic acid, chemical modification and dynamic mechanical thermal analysis (DMTA).

INTRODUCTION

Hydroxyl Ethyl methacrylate (HEMA) (Figure 1) is one of the most important functionalized monomers that is a colorless liquid with a melting point of -12 °C and a boiling point of 205 °C at the laboratory temperature and it is a kind of hydrophilic monomers. Many studies and researches have been done on physical and chemical properties of monomers and polymers and applications of these polymers. It is fat-soluble monomers and used extensively in medicine and pharmacy. Copolymers formed from the monomers are soft and elastic. Pure monomer of 2- Hydroxyl Ethyl methacrylate with a purity of 99% is produced by Merck Company and it is available to researchers.

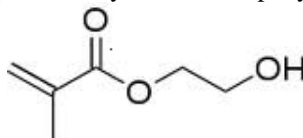


Figure 1. The chemical structure of 2-Hydroxy Ethyl methacrylate (HEMA)

This monomer has two active and substantial center that are as follows:

1. Presence of Alcohol bond in this monomer makes possible the esterification reaction without changing in vinyl double bond and new monomers have ability to perform the polymerization after reaction.
2. Ability to prepare of copolymers is possible because of having a vinyl double bond and this synthesis polymers can also do the esterification reaction with acids with a good yield.

The advantages of acrylic factors (vinyl) and alcohol in monomer can be used as follows:

1. An acrylic body with a functional alcoholic group as a side chain in resultant polymers and having many applications in industry.
2. Easy control of chemical and physical properties such as viscosity and glass transition temperature in polymer produced.
3. Binding of HEMA monomer to propylene and use of alcohol factor ability in the preparation of polymer covers.

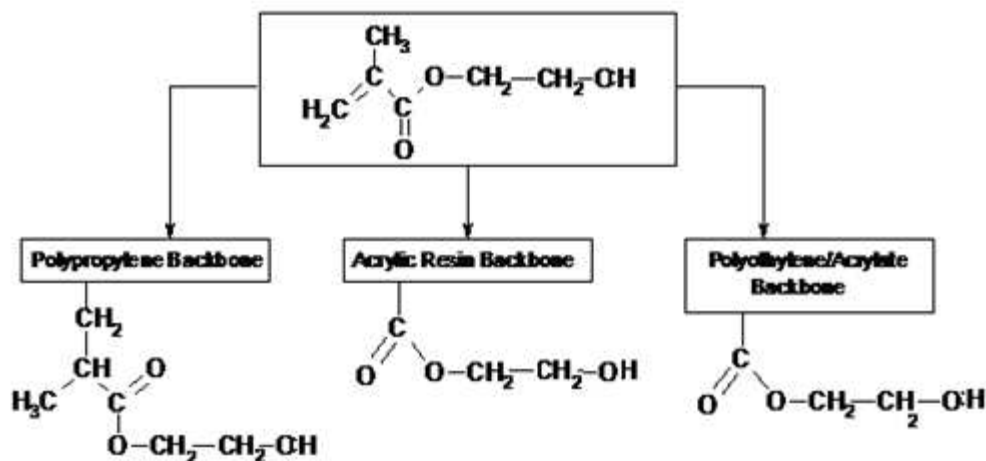


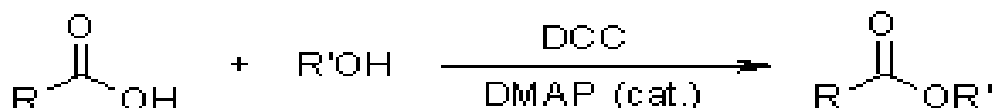
Figure 2. Reaction of HEMA with methacrylate's group

2-Hydroxy Ethyl methacrylate monomer due to the alcohol group (CH₂OH) can be performed the esterification reaction with different acids without changing in vinyl double bond. 2-Hydroxy Ethyl methacrylate reaction (HEMA) with different acids such as 5-Aminosalicylic acid, diclofenac, ibuprofen, salicylic acid is performed for the esterification of alcoholic group. These acids have medicinal properties. The esterification reaction in HEMA monomer is applicable under some specific conditions, if Conditions are not suitable, other reactions can occur. The esterification of a carboxylic acid can be done with alcohol derivations in the presence of basin factor. One of these basins is Dicyclohexylcarbodiimide (DCC), which is converted to Di Cyclohexyl Urea (DCU) in the process of reaction. To speed up this mechanism is requires suitable catalyst such as dimethyl amino pyridine (DMAP), a solvent for used to perform of reaction is dimethylformamide (DMF). Temperature distance that reactions are performed, is between 0 to 20 ° C [1]. Therefore, with control of conditions, we can provide a status to react of alcoholic groups from HEMA with different acids and formed new bonds of carbon with oxygen. In this research, random copolymers of 2-hydroxyethyl methacrylate with comonomer methyl methacrylate (MMA), molar ratio (1: 1), is synthesized solvent dimethylformamide by method of the polymerization of free radicals in the presence of Azobisisobutyronitrile (AIBN) initiator at 65-70 ° C. Then, 2-hydroxyethyl methacrylate copolymer can be modified by binding 3 and 5 di nitro benzoic acid in polymer and in the presence of DCC and DMAP.

2. Theoretical Principles and research background

2.1. Carbon – oxygen bond formation

Acid reacted with DCC to create a bond between carbon and oxygen to form the esterification bond between alcohol and acid and then the resultant compound reacts with alcohol. As a result of this reaction, precipitate of Di Cyclohexyl Urea (DCU) was created and it is removed from environment by smooth out of soluble [2]. Mechanism of this process is shown in Figure 3.



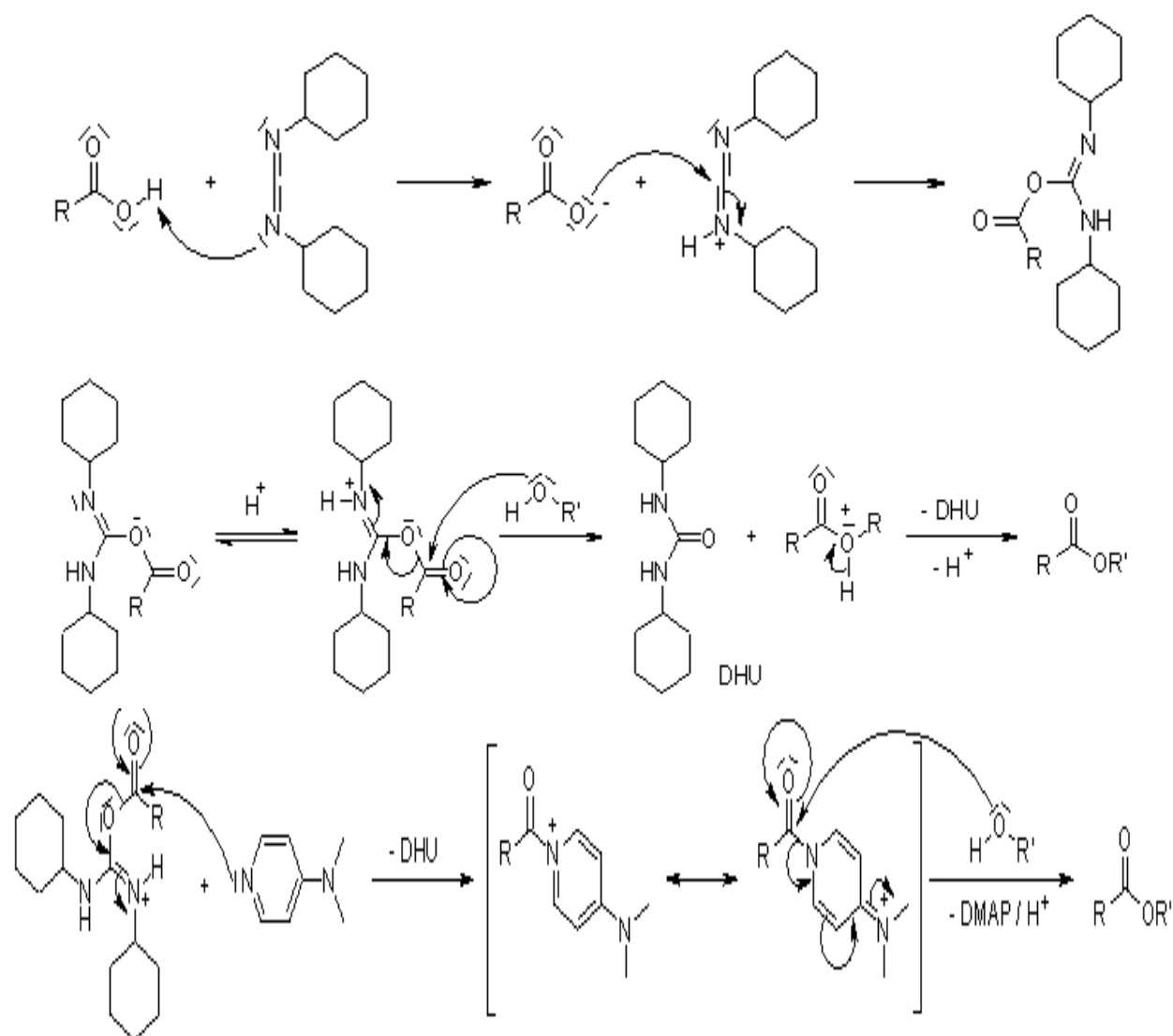


Figure 3. Reaction Mechanisms of acid derivative with alcohol in the presence of DCC

Babazadeh and his colleagues have examined binding of acidic factor in different drugs that we noted to some examples about it. He had done in a research, binding ibuprofen with 2-hydroxyethyl methacrylate (HEMA) monomer and he has been studied modified monomer as a medicinal properties. Then, he polymerized by modified 2-hydroxyethyl methacrylate again with 2-hydroxyethyl methacrylate monomer or butyl acrylate and achieved new compounds with medicinal properties [3].

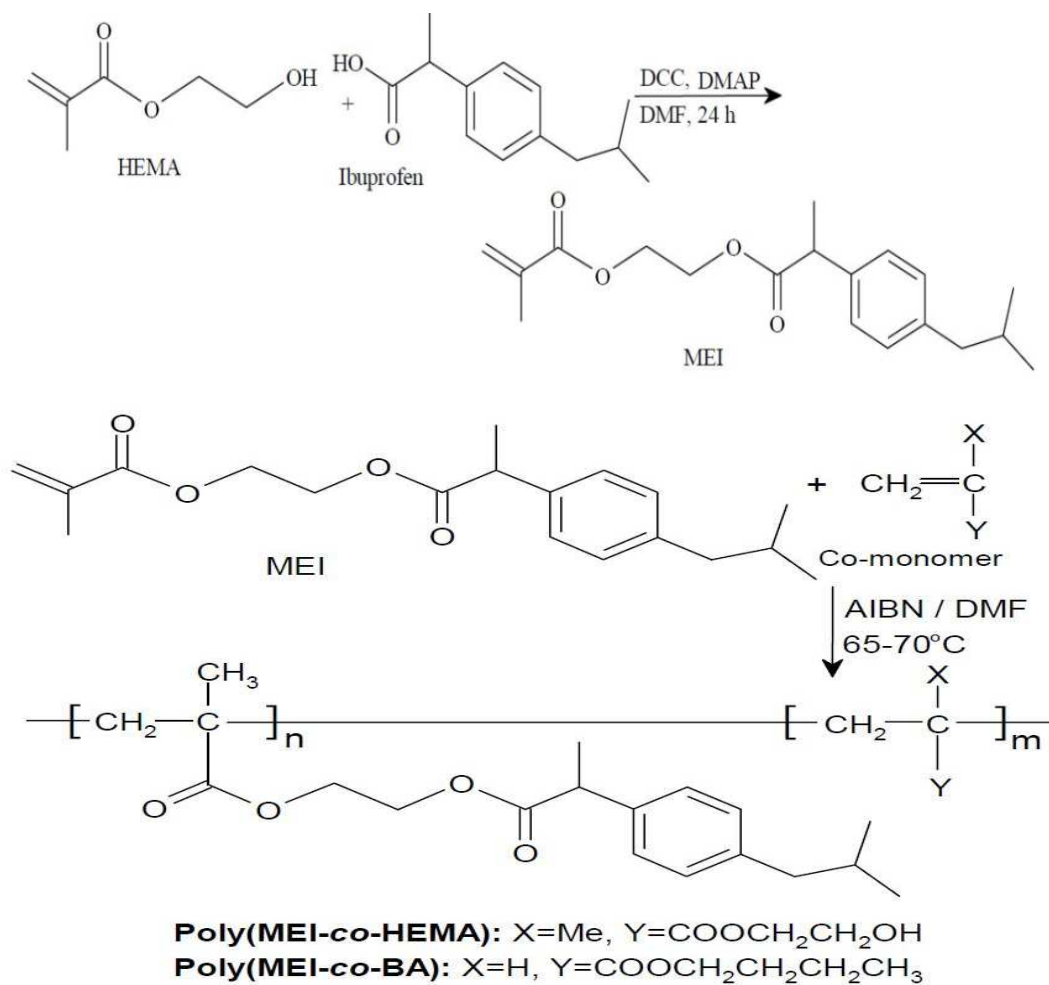


Figure 4. Ibuprofen binding to HEMA

Another example is binding of 5-Aminosalicylic acid monomer to HEMA. He polymerized this monomer of modified with Acrylate commoners and they provided compounds with a new properties [4].

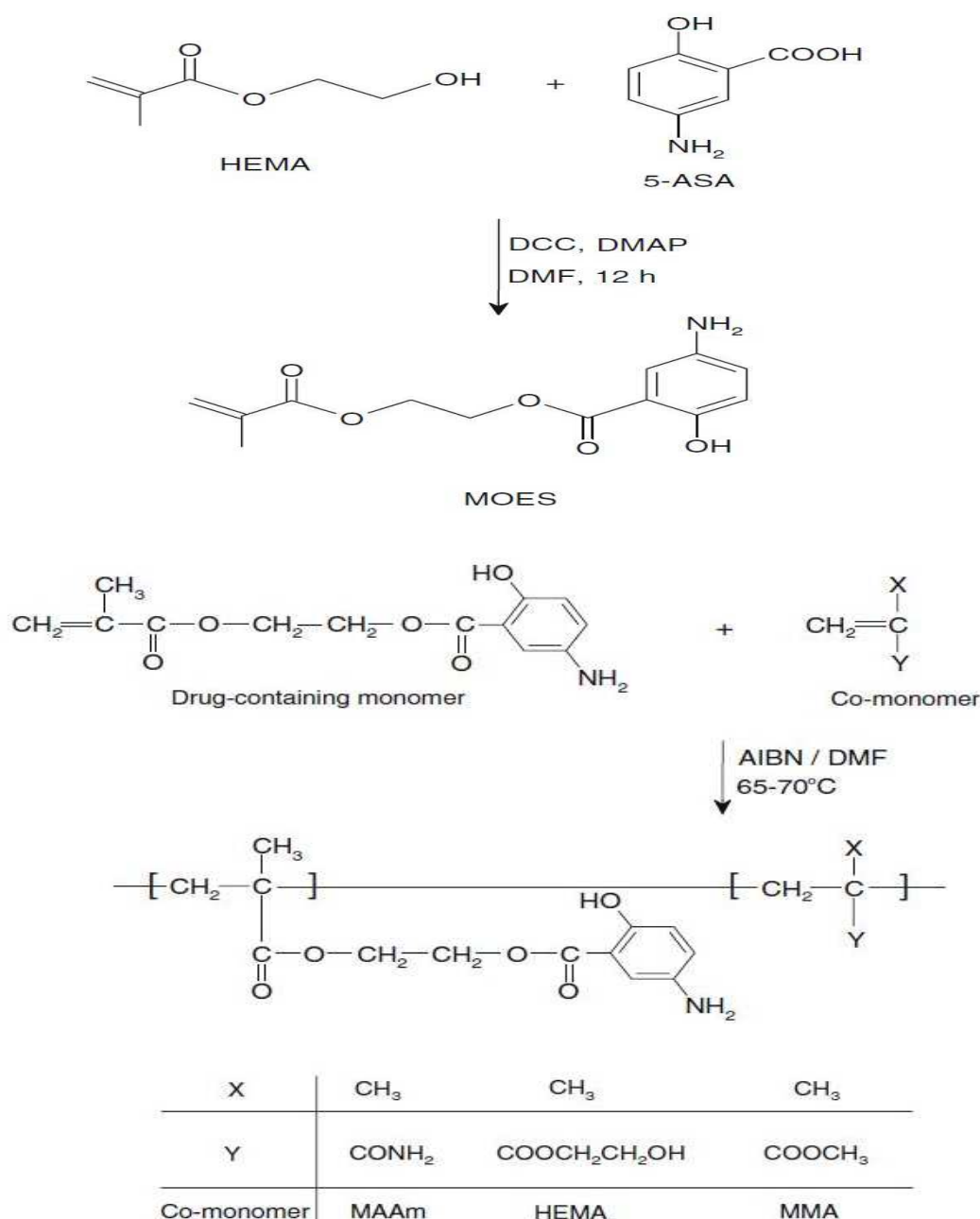


Figure 5. Binding 5-Aminosalicylic acid to HEMA

2.2 Glass transition temperature, (T_g) [5]:

Transition or transfer of glass is a phenomenon that can be seen in amorphous linear polymers such as poly (styrene) or poly (methyl methacrylate). This phenomenon is happened in a specific temperature when mass of materials being breakable and frangible, and their hardness decreases and increases in rubber status. In glassy transition temperature, many of the physical properties is changed, such as thermal expansion coefficient, heat capacity, coefficient of dispersion, impact mechanical resistance, and electrical properties. All of these features are depends on degrees of molecular motion relative freedom in polymer and each of them can be used to determine the glass transition point. Unfortunately, in some cases, the resultant values by different methods are very different. An example of this difference is T_g measured for poly (methyl methacrylate) by using dilatometry method (i.e. showing changes in volume) 110° C and it is obtained by return elasticity method, 160° C. Glass transition phenomena can be studied considering nature of this changes in a specific temperature. When a material is heated up to this temperature, molecular rotation around the simple bonds will done easily. Many factors are effective in this kind of rotation which also effects on amount of glassy transition temperature. Individual mobility of each polymer molecule is important and factors influencing in increasing or decreasing in this mobility will caused differences in the amount of T_g. In addition, interactions between polymer molecules will caused limitations and changes on the

mobility of molecules and T_g , respectively [6]. In summary, the following factors are effective in glassy transition temperature:

1. Presence of groups binding to main polymer (since their existence increases required energy for molecule movement around the simple bonds in main chain). This situation will be seen in branches and side chains.
2. Presence of rigid structures in the main branch of molecules such as phenylene groups.
3. Crosslinks
4. Hydrogen bonds between the polymer chains.
5. Relative molar mass that is effective on T_g . (because whatever molar mass is higher, molecular mobility is more difficult and , it will be provide more limitations in comparison with the polymers of low molar mass).
6. Presence of emollients.

Effect of these factors will be seen In T_g value of some polymers. Some of the values are presented in Table 1, along with a brief explanation of effective cases on the relative amounts of the transition temperature.

Table 1. Glass transition temperature of some polymers

Polymer	T_g (°C)	effective cases
Poly(ethylene)	-20	Flexible main chain
Poly(propylene)	+5	preventing CH_3 groups from free rotation
PVC	+80	Strong polar intermolecular attractions
PTFE	+115	Very difficult main chain

2.3- Dynamic mechanical thermal analysis (DMTA) [7]

Measuring of mechanical properties of materials is basis of dynamic mechanical thermal analysis, when they are under alternating tension. For this purpose, two commonly methods are used:

One of them is free or optional oscillation and other one is mandatory oscillation. Optional oscillation techniques is including use of force to a sample and allowing to its oscillation after the force transmission. Mandatory oscillation is including use of continual force to a sample. Last method is the most common method for use.

DMTA allows to user to view of elastic and inelastic material and Information on changes in cutting and elasticity rate will be achieved with changes in modulus decrease. DMTA is also used to determine of glass transition temperature. Glass transition temperature is measured by DSC technique. But DMTA technique is the most sensitive method to measure of glass transition temperature. An example of a graph is shown in Figure 6.

In DMTA technique, material can determined in terms of modulus of elasticity, viscosity, damping behavior and glass transition temperature and changes in these parameters with strain, strain rate, temperature and frequency of the oscillator. Elastic and viscous tensions is related to properties of materials through the ratio of stress to strain (modulus). Ratio of stress to elastic strain is called the elastic modulus (storage or E' modulus) and ratio of stress to viscous strain, is called the viscous modulus (waste or modulus E''). Glass transition temperature measurement is determined by DMTA with regard to the elastic modulus and peak dependent on the $\tan \delta$ graph. (The ratio of viscous modulus to the elastic modulus is called $\tan \delta$) $\tan \delta = E'' / E'$ which is measure of ability of damping material.

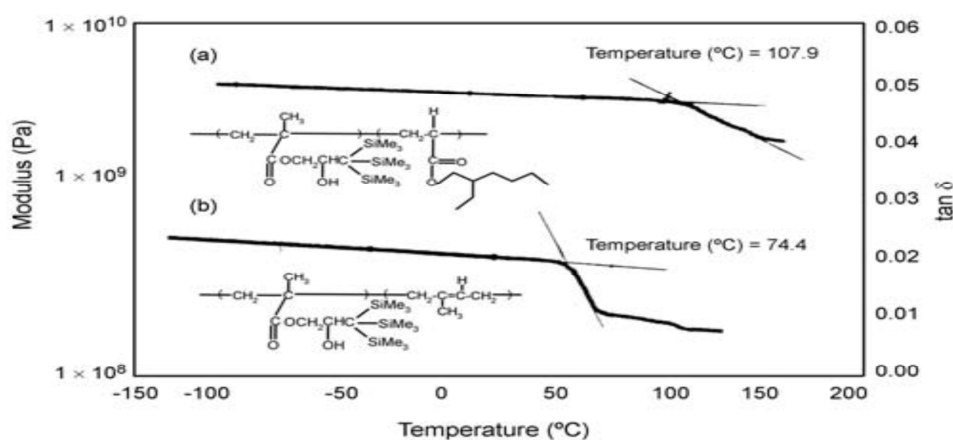


Figure 6. An example of a DMTA graph

2.4. Chemical modification of 2-hydroxyethyl methacrylate polymers:

2-hydroxyethyl methacrylate polymer can be prepared in two methods of the radical polymerization and the esterification through a double bond. These polymers modification happens by the esterification in alcoholic part. These polymers have variety of applications in industry, medicine and pharmacy. The importance of these polymers is because of the functional alcoholic group which provides possibility of further modification of polymer structure [9].

We have mentioned some examples of this research. The modification of this polymer has been studied with salicylic acid in external article. First, Homopolymer is prepared from HEMA monomer and this homopolymer reacts with chloroacetyl chloride and they have been modification the resultant combination with salicylic acid. This amendments follows by spectroscopy of FT-IR and ¹H-NMR and ¹³C-NMR [10].

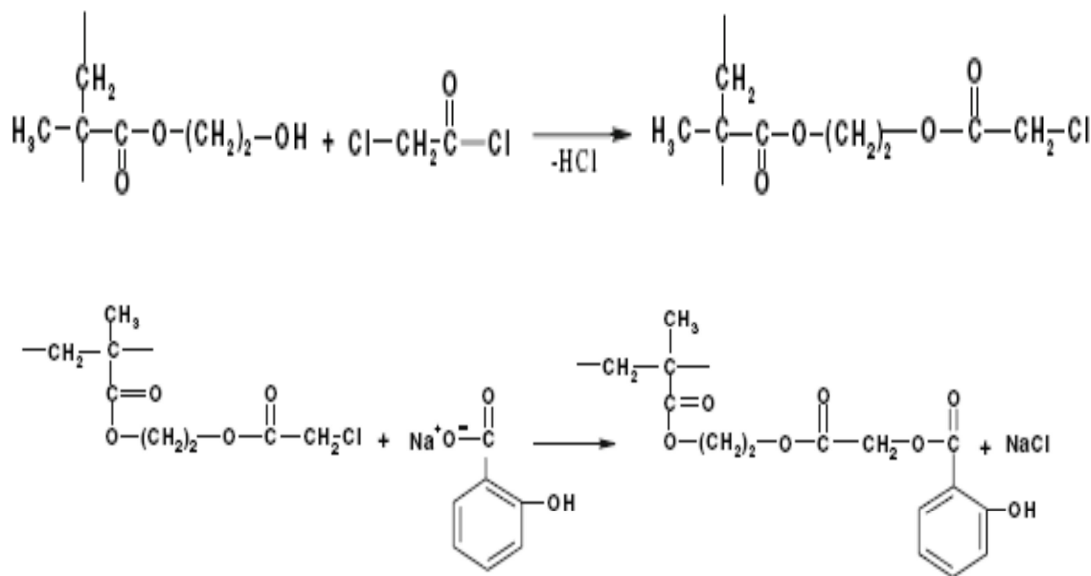


Figure 7. HEMA polymers synthesized with salicylic acid

Another research group, first, modified HEMA monomer with alkoxyethyl compounds and then polymerized HEMA monomer with the resultant combination and reacted with a monomer containing Cuban which makes polymer as a grid [10].

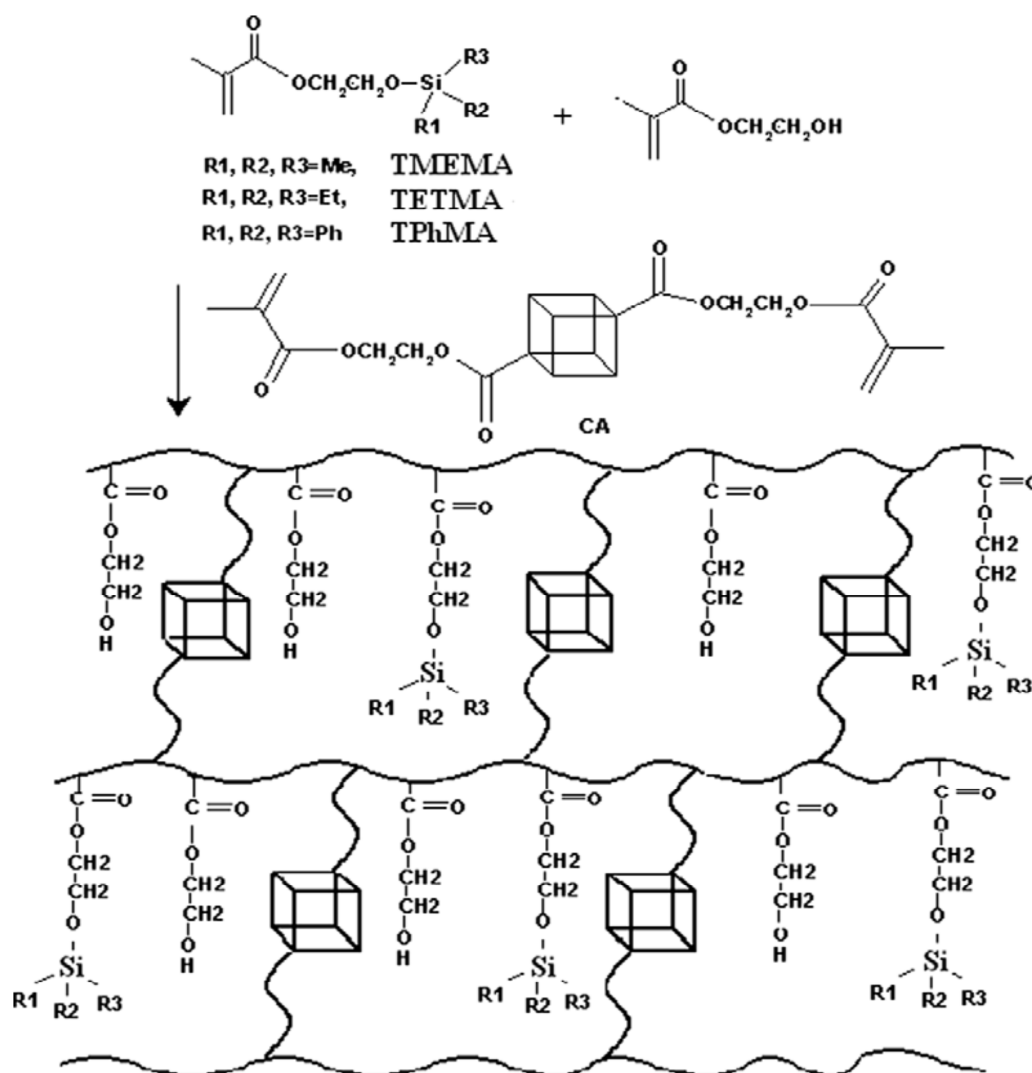
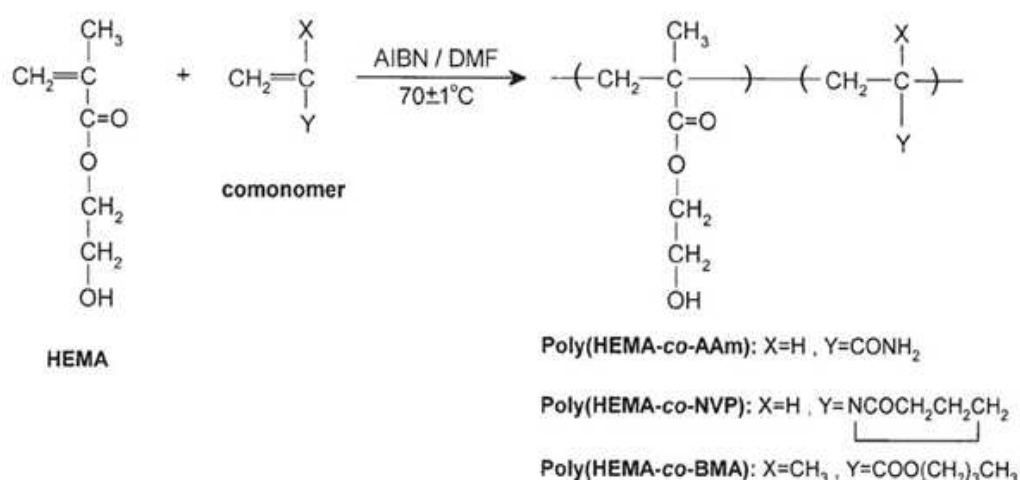


Figure 8. Preparation of cross-linked polymers containing alkoxyethyl group

Another example can be mentioned that is the polymerization of HEMA monomer with acrylate comonomer and modifying it with Diclofenac drug [12].



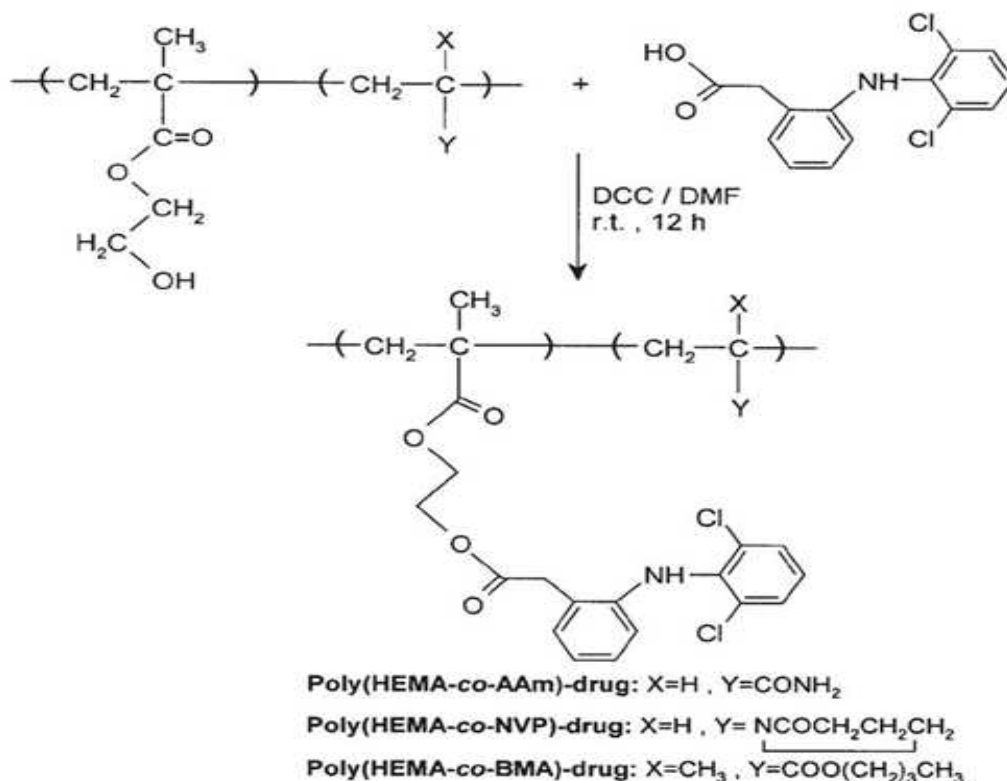


Figure 9. Modification of HEMA copolymer with Diclofenac

2.5. Carboxylic acids

Carboxylic acids is a class of organic compounds that one or more carboxyl functional groups can be found in them. Methanoic Acid is the simplest and most familiar of ethanoic acid. Light carboxylic acids (up to 4 carbon atoms) are as well dissolved in water. But solubility of them in water is low with increasing the carbon chain length, so that most of them are actually insoluble in water. Carboxylic acids are weak acids and the number of their molecules gives its acidic protons to water molecules because of dissolving in water and it quickly reaches to equilibrium state. Examples of 3, 5- carboxylic acids is 3,5-Dinitrobenzoic acid that we noted to some features of them.

2.5.1. General description of 3, 5-Dinitrobenzoic acid

3,5-Dinitrobenzoic acid is a colorless crystalline compound (seen white). This combination is also one of the simplest aromatic carboxylic acid. This combination is a weak acid, which its salts are used as food preservatives. Also benzoic acid is used in making most of other organic compounds.

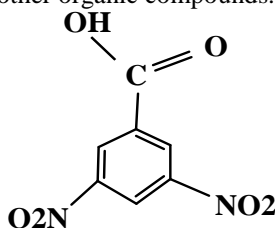


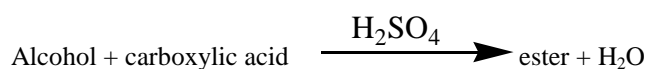
Figure 10. Structure of 3,5-Dinitrobenzoic acid

Table 2. Physical and chemical properties of 3, 5-Dinitrobenzoic acid

Molecular formula	C ₇ H ₄ N ₂ O ₆
Molar mass	197.12g/mol
Form	Solid
Melting point	122/3°C

2.6. The Esterification reaction

The Esterification reaction is the first and oldest synthesis reaction method of esters and organic acids with the alcohol in the presence of mineral acid (usually "sulfuric acid") as a catalyst. With this method, we can directly synthesize many esters, this method is called Fisher reaction.



Dicyclohexylcarbodiimide is used for synthesizing of ester in new methods.

2.7. Dicyclohexylcarbodiimide (DCC)

2.7.1. General description of Dicyclohexylcarbodiimide

Dicyclohexylcarbodiimide is like a yellow solid at room temperature which is insoluble in water but it easily dissolved in soluble organic solvents such as dimethylformamide, tetrahydrofuran, dichloromethane.

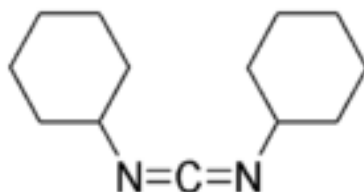


Figure 11. The chemical structure of Dicyclohexylcarbodiimide (DCC)

Table 3. Physical and chemical properties of Dicyclohexylcarbodiimide (DCC)

Molecular formula	C ₁₃ H ₂₂ N ₂
Molar mass	206.33g/mol
Melting point	34-35 °C

DCC as a sluice and an activator factor is for of aromatic carboxylic acid for preparation of ester. Research findings suggest that DCC makes active in slowly and quietly conditions the esterification of the first and second alcohols. While the third type of efficiency is very low in alcohol [13]. DCC is a combination with a strong allergen property. Recently they have been suggested that the combination of N, N- Diisopropylcarbodiimide (DCI) that is not an allergen, can be used. Therefore, it is better to use of DCC under the hood.

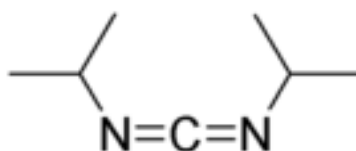


Figure 12. Chemical structure of Diisopropylcarbodiimide (DCI)

2.7.2. Synthesis of Dicyclohexylcarbodiimide

We can noted to some DCC preparation methods in the following ways.

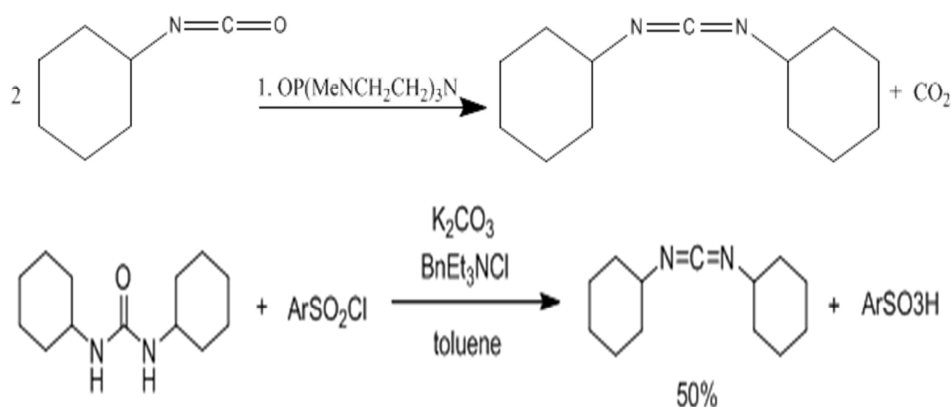


Figure 13. Synthesis of Dicyclohexylcarbodiimide

2.8. Di methyl amino pyridine (DMAP)

2.8.1 General description of Di methyl amino pyridine

Dimethyl amino pyridine as a white to yellowish crystalline powder that is insoluble in water.

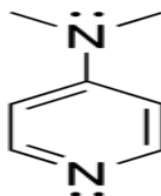


Figure 14. Chemical structure of Di methyl amino pyridine (DMAP)

Table 4. Physical and chemical properties of Di methyl amino pyridine

Molecular formula	C ₇ H ₁₀ N ₂
Molar mass	122.17 g/mol
Form	Powder
Melting point	110-113 °C

DMAP is a nucleophile catalyst that is very suitable for the esterification reactions. This combination is used in the synthesis of drugs and polymers. DMAP is produced from pyridine in two stages.

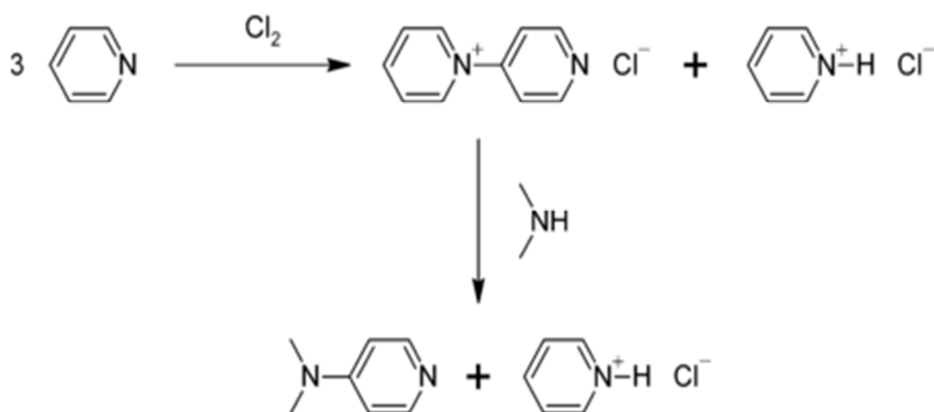


Figure 15. Synthesis of Di methyl amino pyridine

3. Research methodology

Our purpose in this study, modifying physical properties of copolymers of 2-hydroxyethyl methacrylate-comonomer methyl methacrylate, and changes of the glass transition temperature of primary polymer. Preparation of HEMA copolymers have been reported in scientific papers, but modified of polymers does not happen with 3 and 5 di nitro benzoic acid. Modification of these polymers is done by the esterification of alcohol group with carboxylate group and binding on the polymer as lateral group in presence of DCC.

Solvents and chemical materials were purchased from Merck Company. 2-hydroxyethyl methacrylate (HEMA) with a purity of over 99% of the Mark Company and other monomers were purchased from Merck Company.

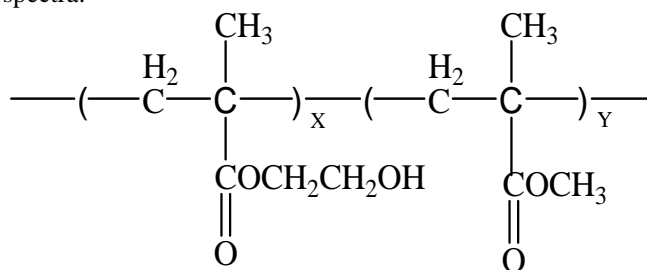
Identification of products is done by infrared spectroscopy methods (IR) and ¹H-NMR. FT-IR spectra by Bruker-IR Scientific and SHIMADZU devices and ¹H-NMR spectra by Bruker 400 MHz device have been done in pure deuterium solvents (CDCl₃ or DMSO-d₆). Chemical shift (δ) is presented in units of parts per million (ppm). DMTA thermograms is recorded by Triton, Tritec2000 model, in nitrogen atmosphere condition and at 10 ° C per minute.

3.1. Preparation of methacrylate Copolymer and their reaction with 3, 5 -di nitro benzoic acid

3.1.1. Preparation of copolymer (2-hydroxyethyl methacrylate-co-methyl methacrylate) with molar ratio of 1:1

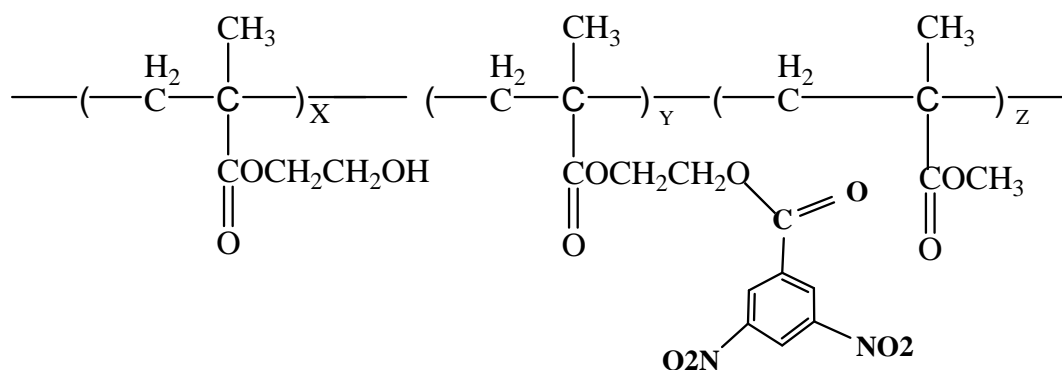
In a 100 ml balloon, 1/0 grams of AIBN initiator (6.0 mmol), 2.6 grams of 2-hydroxyethyl methacrylate monomer (HEMA) 2.6 g (20 mmol), and 2.002 grams of methyl methacrylate comonomer (MMA) (20 mmol) in 20 ml of DMF solvent dimethylformamide was solved, the solvent is DE oxygenation under nitrogen gas and protective tube of calcium chloride (CaCl₂) is protected from moisture, Then the solution was stirred in the oil bath for 48 hours in 70 ° C and the resultant viscous solution was poured as drop by drop in a container containing 150 ml cold ethyl ether while stirred continuously by magnetic stirrer and gradually copolymer sediment of 2- hydroxyethyl methacrylate was formed.

Polymer deposits is isolated by overflowing of Diethyl ether, and the resultant sediment is washed once again with diethyl ether, and it was dried under vacuum condition at room temperature and the final product was a viscous solid and weight of the resultant copolymer is 3 grams and the reaction share is 65%. The formation of copolymer is proved by ¹HNMR, FT-IR spectra.



3.1.2. Preparation of copolymer (2-hydroxyethyl methacrylate - methyl methacrylate) containing of 3, 5 -di nitro benzoic acid

In a balloon with two opening, 0.936 g of 3, 5- di nitro benzoic acid (6.7 mmol), 1.56 g of di cyclohexane ethylhexyl carbo di imide (6.7 mmol), 0.095g of Di methyl-amino pyridine (0.7 mmol) was solved in 10 0 ml of dimethylformamide DMF, balloon is cooled up to -5 ° C, and then 1 g of the resultant copolymer was dissolved in 10 ml of DMF, droplets was added by Brom ampoule to contents of the balloon at this temperature for an hour. Brom ampoule is under nitrogen gas and protective tube (Guard Tube) of calcium chloride. The reaction mixture was stirred with extremely force for an hour at temperature of -5 ° C and it slowly warmed to room temperature. Then,contents of the balloon was stirred at room temperature for 24 hours. They smooth it because of Separation of white yellowish sediment N, N -Di Cyclohexyl Urea (DCU) from modified polymer. Finally, under filter solution was added as drop by drop in 150 ml of distilled water. Gradually precipitate of polymer was formed at the bottom of container. In order to washing unreacted acids, the resultant sediment was washed again twice with 50 ml diethyl ether and it was died for 48 hours at room temperature and one hour under vacuum condition. The weight of final product was 1.25 gram and the reaction share was 65%. The formation of copolymer is proved by ¹HNMR, FT-IR spectra.



4. Research findings

4.1. The preparation conditions of 2-hydroxyethyl methacrylate copolymer with methyl methacrylate

2-Hydroxyethyl methacrylate monomer (HEMA) and methyl methacrylate monomer (MMA) are polymerized in presence of AIBN initiator and Dimethyl form amide solvent. The resultant copolymer is collected by slow and intense commix in anti-solvent of cold diethyl ether and then washing several times by diethyl ether is dried under vacuum condition and at the laboratory temperatures (figure 16).

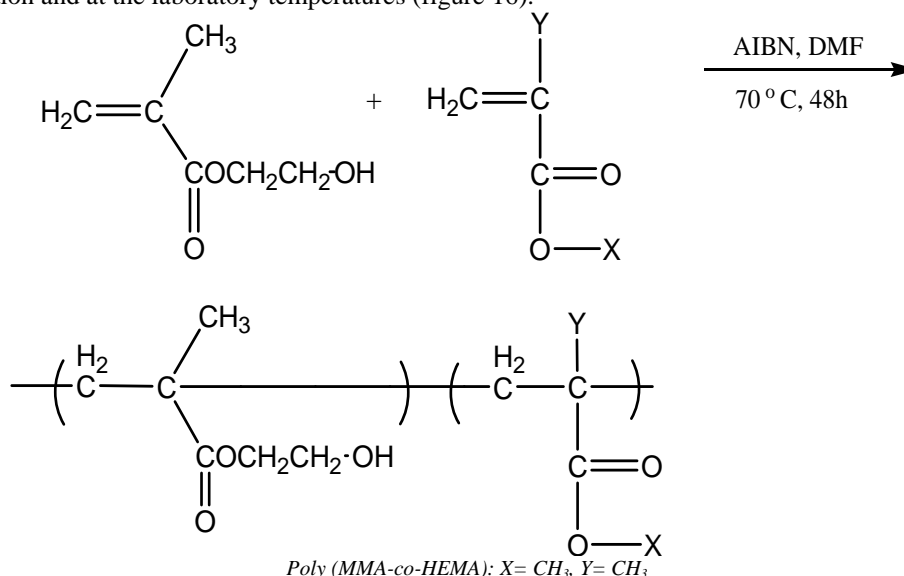


Figure 16. Preparing method of methacrylate copolymer based on 2-hydroxyethyl methacrylate

4.1.1. Study of HNMR and IR spectrums synthesized copolymer before binding of 3, 5- di nitro benzoic acid

4.1.2. Study of IR copolymer (poly (HEMA-co-MMA))

For study of copolymers prepared by IR spectrum in copolymer IR spectrum (poly (HEMA-co-) synthesized is observed wide strip of (OH) in 340 cm⁻¹ areas. Symmetric and asymmetric stretching vibrations of (CH) bonds of aliphatic are observed in 2953 cm⁻¹ and 2996 cm⁻¹. Stretching vibration of carbonyl groups are in 1663-1732 cm⁻¹ that appeared peak in lower absorption frequency of (C = O) is unreacted monomer that is because of hydrogen bonds effects with OH group which reduces the absorption of carbonyl group. Stretching vibrations (C-H) of their esterified is appeared in 1024 cm⁻¹ up to 1277 cm⁻¹ areas.

4.1.3. Study of HNMR spectrum of copolymer poly (HEMA-co-MMA) in CDCl₃ solvent

In spectrum of this copolymer (HNMR), hydrogen's (-CH₃) in 0.34-1.3 ppm and peak of hydrogen's of Methylene group (-CH₂-) are appeared in 1.6-2.3 ppm areas that (CH₃) of two monomers have overlap to each other. Proton of (OH) is appeared in 2.8- 3.1 areas. Peak in 3.7 ppm area shows (O-CH₃) hydrogen. Peaks of 3.8-4 ppm and 4- 4.3 areas shows (-CH₂-) bonds related to (HEMA) monomer. Peak of 7.2 ppm shows CDCl₃ solvent protein.

4.2. Binding of 3, 5- di nitro benzoic acid to methacrylate copolymer

For binding of acid to copolymer and the esterification reaction, 1 gram copolymer, 0.936 gram 3, 5- di nitro benzoic acid are reacting in presence of Di cyclohexyl carbodi imide and Dimethyl amino pyridine. (Being seen precipitate of white to yellowish Di cyclohexane urea (DCU) is indicative of the reaction). In this method, produced copolymer is added as drop by drop to the acidic solution and catalyst. The reaction is done at a temperature -5 ° C (Figure 17).

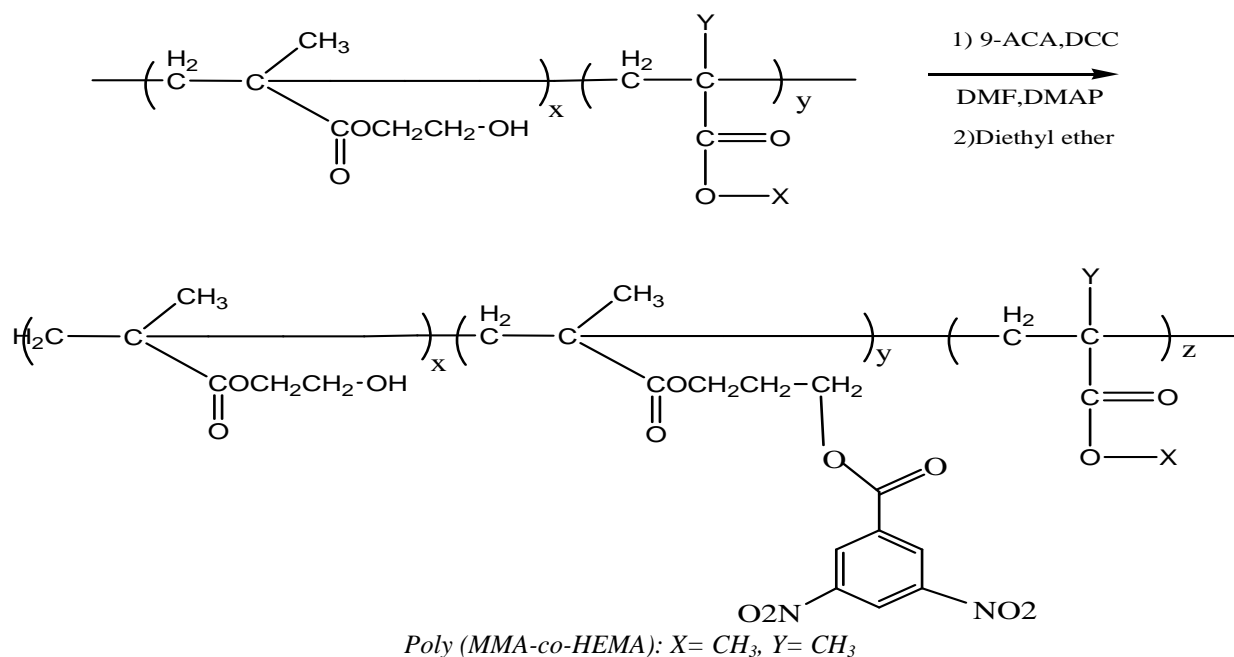


Figure 17. Binding of 3, 5- di nitro benzoic acid to methacrylate copolymer

After the reaction, the acidic polymer product is deposited in distilled water. For washing unreacted acids, we are washing again sediment twice by diethyl ether. In this process, extra acid is washed and separated from polymer.

4.3. Study of binding IR and 1 HNMR spectrum of 3, 5- di nitro benzoic acid to synthesized methacrylate copolymer

4.3.1. Study of 1 IR spectrum copolymer poly (HEMA-co-MMA) containing of 3, 5- di nitro benzoic acid

Presence of peak in 3502 cm^{-1} area is related to unreacted alcoholic group (OH) that its value decreased from baseline of appeared peak in 3111 cm^{-1} area from aromatic ring (C-H) that showed of reaction. Symmetric and asymmetric the stretching vibration of aliphatic bonds (CH) in 2936 cm^{-1} and 2858 cm^{-1} is shown. Appeared peak in 1734 cm^{-1} frequency is related to ester carbonyl group (C = O). Appeared peak in 1628 cm^{-1} area is related to Benzene ring (C = C) and appeared peak in 1546 cm^{-1} and 1344 cm^{-1} is related to (NO₂) group on Benzene ring that it shows of reaction.

4.3.2. Study of 1 HNMR spectrum of copolymer poly (HEMA-co-MMA) containing of 3, 5- di nitro benzoic acid groups in CDCl₃ solvents

In 1 HNMR spectrum copolymer poly (HEMA-co-MMA) containing of 3, 5- di nitro benzoic acid has not been completely disappeared of (OH) hydrogen peak in 2.8 ppm area. Because some groups of (OH) is not reacted with 3, 5 -di nitro benzoic acid, peak of benzene ring hydrogen has been appeared in 7.8-9.2 ppm area. Become visible of this peaks is a reason to proof of binding of 3, 5- di nitro benzoic acid to copolymer. Peaks of primary (CH) is not changed from its original location and it has appeared in 3.5 – 3.9 and 4-4.3 areas.

4.4. Solubility test of synthetic copolymers

Solubility of synthesized polymers before and after binding of 3, 5 -Di nitro benzoic acid and after the esterification is summarized in tables 5 and 6. Results show that these polymers are soluble in Polar aprotic solvents.

Table 5. Solubility of synthesized copolymers in different solvents

Solvent	Poly(HEMA-co-MMA)
Chloroform	-+
Di ethyl ether	-
Water	-
Acetone	+
Ethenol	-
DMF	++
DMSO	++

++ (Soluble), - (insoluble), -+ (less soluble)

Table 6. Solubility of synthesized copolymers with 3, 5 -Di nitro benzoic acid in different solvents

Solvent	Poly(HEMA-co-MMA)Iso nicotinic acid
Chloroform	++
DMF	+
Water	-
Methanol	-

++ (Soluble), - (insoluble), - + (less soluble)

4.5. Solubility tests of 3, 5- Di nitro benzoic acid

Solubility of 3, 5- Di nitro benzoic acid in different solvents is summarized in table 7.

Table 7. Solubility of 3, 5- Di nitro benzoic acid in different solvents

Solvent	Chloroform	DMF	Methanol	Diethyl ether	Water
3,5 Di Nitro Benzoeic acid	++	++	-+	++	-

++ (Soluble), - (insoluble), - + (less soluble)

4.6. Study of DMTA curves in copolymer synthesized

Study of the thermal behavior of copolymer containing of 3 and 5 di nitro benzoic acid were performed by using DMTA and heating rate of 10 ° C per minute. DMTA curve of copolymer synthesized can be seen only a temperature of Tg that indicate of absence of homopolymer mixed in copolymerization system. Tg temperature of a random copolymer in which HEMA is copolymerized with methacrylate monomers, is higher than other monomers. Because presence of α - methyl groups on the copolymers main chain of type 1 was leading to reduce of flexibility of the polymer chains. As a result temperature of Tg is increased. Benzene ring in polymers is caused an increase in the rigidity of polymer and also it cause an increase in Tg temperature.

The rate of increases of Tg temperature of polymers has increased because of modification of 3, 5 -di nitro benzoic acid with getting larger of substitution of alkyl ester group in methacrylate's monomer. Because with increases of space prevention, possibility of the esterification of alcoholic group is low by acid. Increasing of Tg temperature can be seen after binding of benzene ring to this copolymer in the methacrylate's copolymer, because binding of benzene ring (because of esterification reaction) is caused an decrease in chains mobility and it caused an increase in Tg temperature of modified polymer. We will have access to new polymers with completely modified Tg points and it has a great important based on new applications of these polymers.

Table 8. Glass transition temperature of polymers

Name of combination	T _g (°C) of polymer before binding of 3,5-di nitro benzoic acid	T _g (°C) of polymer after binding of 3,5-di nitro benzoic acid
Poly(HEMA-co- MMA)	50	110

CONCLUSION

The result of this research is modification of the physical properties of 2- hydroxyethyl methacrylate polymers and methylmethacrylate copolymer, also in next step modification with 3,5- dinitrobenzoic acid and change of temperature of primary polymers glass transition. The modification of these polymers was done by the esterification of alcohol group with carboxylate group and binding on the polymer as lateral group in presence of DCC that finally led to production of a polymer with high application in polymer, water and sewage industry in order to attract some heavy metals of water.

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