SYNTHESIS OF A NOVEL BENZOPHENONE DERIVED UV ABSORBER ACRYLATE MONOMER

by

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Dayım ve babanneme…

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ABSTRACT

SYNTHESIS OF A NOVEL BENZOPHENONE DERIVED UV ABSORBER ACRYLATE MONOMER

Since the destructive effects of sunlight have been discovered, UV protection of materials have gained more importance. The weathering resistance of organic materials can be increased by coating their surface with UV absorber polymers. Benzophenones and triazines are the most common commercially availible UV absorbers which are sold under different trademarks. In this thesis, we have synthesized a novel benzophenone derived acrylate monomer which undergoes Photo-Fries Rearrangement when exposed to sunlight. The new compound has the ability to absorb the UV portion of the electromagnetic spectrum *via* proton transfer. When the radiation stops, the compound returns to its original form and release the energy as heat so that the material is protected from the UV light. The monomer was polymerized to give homopolymers and methyl methacrylate copolymers at different ratios, then the UV absorption behavior of the polymers before and after the UV radiation were investigated.

ÖZET

YENİ BİR BENZOFENON TÜREVİ UV ABSORBLAYICI AKRİLAT MONOMERİ SENTEZİ

Güneş ışığının yıkıcı etkisinin keşfinden beri, maddelerin UV 'den korunması daha çok önem kazanmıştır. Organik maddelerin hava koşullarına dayanıklılığı, yüzeylerini UV absorblayıcı polimerlerle kaplama ile arttırılır. Benzofenonlar ve triazinler farklı ticari isimler altında en çok bulunan UV absorblayıcılardır. Bu tezde güneş ışığı altında Foto-Fries Kayması yapan, yeni bir benzofenon türevi UV absorblayıcı akrilat monomeri sentezlenmiştir. Oluşan yeni bileşik proton transferi ile elektromagnetik spektrumun UV bölgesini absorblayıcı özelliği vardır. Radyasyon durduğu zaman molekül ısı enerjisi vererek eski haline geri döner böylece madde ultraviyole ışıktan korunmuş olur. Monomer, homopolimer ve farklı oranlarda metil metakrilat kopolimerleri verecek şekilde polimerleştirildi, sonrasında polimerlerin UV radyasyonundan önce ve sonra UV absorpsiyon davranışları incelendi.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS....iv
ABSTRACT....v
ÖZET....vi
LIST OF FIGURES....ix
LIST OF TABLES....xi
LIST OF ACRONYMS/ABBREVIATIONS....xii
1. INTRODUCTION....13
1.1. Nature of Sunlight and the Reason for UV Protection....13
1.2. UV Protectors....15
1.2.1. Inorganic UV Protectors....16
1.2.2. Organic UV Protectors....17
1.2.3. Photo-Fries Rearrangement....20
2. OBJECTIVES....22
3. EXPERIMENTAL....23
3.1. Materials and Methods....23
3.2. Apparatus....23
3.3. Monomer Synthesis....23
3.3.1. Synthesis of 3-(2-hydroxyethoxy)phenyl benzoate....24
3.3.2. Synthesis of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate....25
3.4. Polymer Synthesis....26
3.4.1. Radical Homopolymerization of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate....26
3.4.2. Radical Copolymerizations of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate....27
3.4.2.1. Synthesis of 10% Copolymer with methyl methacrylate....27
3.4.2.2. Synthesis of 20% Copolymer with methyl methacrylate....28
3.4.2.3. Synthesis of 30% Copolymer with methyl methacrylate....28
3.5. Investigation of UV Absorptions....28
3.5.1. UV Spectra of the Monomer....28
3.5.2. UV Spectra of the Homopolymer....29
3.5.3. UV Spectra of the 10% Copolymer....29

3.5.4. UV Spectra of the 20% Copolymer 29
3.5.5. UV Spectra of the 30% Copolymer 30
3.5.6. Photoreaction Procedures 30
4. RESULTS AND DISCUSSION 31
4.1. Synthesis and Characterization of 3-(2-hydroxyethoxy)phenyl benzoate 31
4.2. Synthesis and Characterization of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate 38
4.3. Synthesis and Characterization of the Homopolymer and Copolymers with 1:9, 2:8 and 3:7 Ratios 42
4.4. Analyzing UV Absorption Behaviors of the Polymers 47
4.4.1. UV-Spectra of the Polymers After UV Radiation 51
5. CONCLUSION 55
REFERENCES 56

LIST OF FIGURES

Figure 1.1. Electromagnetic Spectrum....13
Figure 1.2. UV Protection of ozone layer.....14
Figure 1.3. Cycloaddition of Thymine bases in the presence of UV.....15
Figure 1.4. An example of UV transparent polymer 15
Figure 1.5. 2,2,6,6-Tetramethylpiperidine……..16
Figure 1.6. UV absorption by intramolecular hydrogen bonding of oxybenzone.....17
Figure 1.7. Most common UV absorber molecules.....18
Figure 1.8. Examples of benzophenone derived UV absorbers in literature 19
Figure 1.9. UV-Vis Spectrum of 2, 4-hydroxy benzophenone.....20
Figure 1.10. Mechanism for Fries rearrangement in the presence of Lewis acid.....21
Figure 3.1. Synthesis of 3-(2-hydroxyethoxy)phenyl benzoate.....24
Figure 3.2. Synthesis of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate 25
Figure 3.3. Synthesis of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate homopolymer....26
Figure 3.4. Synthesis of the copolymer 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.....27
Figure 4.1. Reaction mechanism of benzoyl chloride with resorcinol hydroxymonoethyl Ether……32
Figure 4.2. ^{1}H-NMR of 3-(2-hydroxyethoxy)phenyl benzoate.....33
Figure 4.3. ^{13}C-NMR of 3-(2-hydroxyethoxy)phenyl benzoate.....34
Figure 4.4. ^{1}H-NMR of 3-(2-benzoyloxy)ethoxy)phenyl benzoate.....36
Figure 4.5. ^{13}C-NMR 3-(2-benzoyloxy)ethoxy)phenyl benzoate.....37
Figure 4.6. Reaction mechanism of acryloyl chloride with 3-(2-hydroxyethoxy)phenyl benzoate 38
Figure 4.7. ^{1}H-NMR of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.....39
Figure 4.8. ^{13}C-NMR of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.....40
Figure 4.9. IR Spectra of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.....41
Figure 4.10. Homopolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate 43
Figure 4.11. ^{1}H-NMR of the 10% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.....44
Figure 4.12. ^{1}H-NMR of the 20% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate

with methyl methacrylate.....45
Figure 4.13. ^{1}H-NMR of the 30% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.....46
Figure 4.14. UV-Spectra of the homopolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).....47
Figure 4.15. UV-Spectra of 30% copolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).....48
Figure 4.16. UV-Spectra of 20% copolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).....48
Figure 4.17. UV-Spectra of 10% copolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).....49
Figure 4.18. Absorbance-Concentration Graph of the homopolymer 49
Figure 4.19. Absorbance-Concentration Graph of the 10% copolymer 50
Figure 4.20. Absorbance-Concentration Graph of the 20% copolymer 50
Figure 4.21. Absorbance-Concentration Graph of the 30% copolymer 51
Figure 4.22. UV-Spectra of homopolymer after UV radiation.....52
Figure 4.23. UV-Spectra of 30% copolymer after UV radiation.....52
Figure 4.24. UV-Spectra of 20% copolymer after UV radiation.....53
Figure 4.25. UV-Spectra of 10% copolymer after UV radiation.....53

LIST OF TABLES

Table 4.1. Molecular weights and polydispersity index of polymers.....42
Table 4.2. Analyzing the absorption results of polymers.....51

LIST OF ACRONYMS/ABBREVIATIONS

AIBN	Azobisisobutyronitrile
$AlCl_3$	Aluminium chloride
$CDCl_3$	Deuterated chloroform
DCM	Dichloro methane
DNA	Deoxyribonucleic acid
GPC	Gel Permeation Chromatography
HALS	Hindered amine light stabilizers
IR	Infra Red
NMR	Nuclear Magnetic Resonance
TLC	Thin Layer Chromatography
UV	Ultra Violet

1. INTRODUCTION

1.1. Nature of Sunlight and the Reason for UV Protection

Sun irradiates electromagnetic waves. Depending on their wavelengths, these waves are divided into regions, also known as " the electromagnetic spectrum".

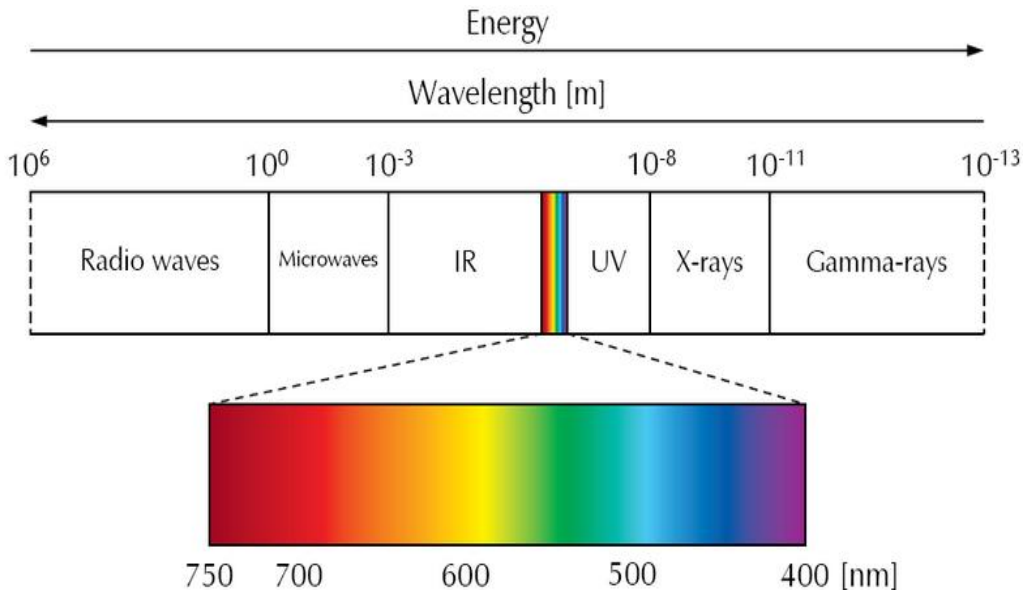


Figure 1.1. Electromagnetic Spectrum.

The visible portion of the electromagnetic spectrum is in between 400-750 nm. UV Light (400-100nm) is divided into UV-A (400-315nm), UV-B (315-280nm) and UV-C (280-100nm) regions. UV-C for example, is the most energetic radiation but is almost completely absorbed by the ozone layer. UV-B is the main reason for the skin cancer and UV-A penetrates the skin the deepest .

UV accounts for 8% of the total solar radiation and 6% of the radiation reaches the ground after the absorbtion by the ozone layer [1]. From the rays reaching the earth's surface UV is the most energetic one. Among them 95 percent is UV-A and the rest is UV-B [2]. Moreover 10% of

UV-B and almost the whole UV-A radiated from the sun reaches the earths surface. UV-C practically can not penetrate through the atmosphere so it can not reach the ground [3].

The ozone molecule is believed to absorb the UV light to form elemental oxygen and oxygen gas. Then these two combine again to produce ozone, as a result harmfull UV is converted into heat energy.

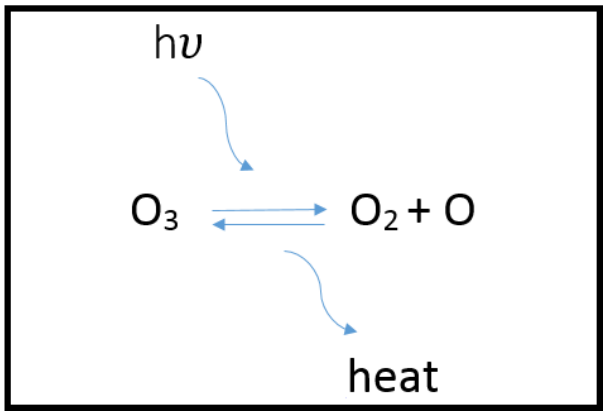


Figure 1.2. UV Protection of ozone layer.

The driving force for this reaction is entrophy. Heat is more disordered form of energy than light so the reaction proceeds in the direction of heat production [4].

Ozone depletion is the decrease in the volume of the ozone gas in the stratosphere and as a result ozone layer no longer prevents the UV-light reaching the surface of the earth. In 1960s Mario Molina, Frank Rowland and Paul Crutzen have found out that the use of CFCs (Chloroflorocarbons) leads to decrease in the amount of ozone concentration in stratosphere and they shared the nobel prize in 1995 for their work [5]. When the ozone layer depletes, more UV-B (280-315nm) rays pentrates through it and reaches the earths surface. As a result, all the living and non-living things are being more exposed to UV light and its detrimental effects.

UV rays has negative effects on both living and non-living things. For example when exposed to sunlight, dyes fade as a result of broken organic chains. Also UV light is known to be one of the most common reason for skin cancer and several mechanisms have been proposed

showing how the UV light damages the DNA. One such mechanism is 2+2 cycloaddition of Thymine bases [6].

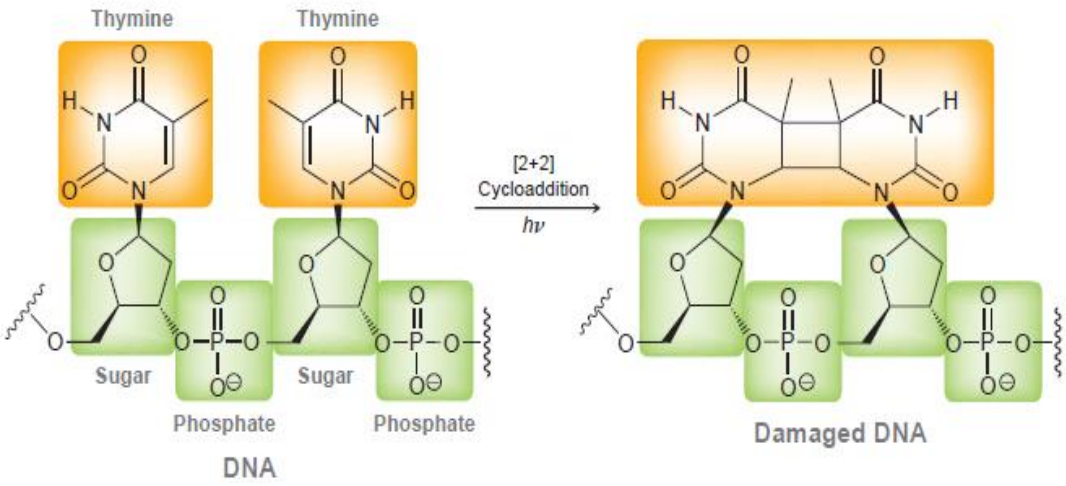


Figure 1.3. Cycloaddition of Thymine bases in the presence of UV [6].

For the reasons listed above, UV protection has a vital importance in many fields of application and many compounds have been investigated for this purpose.

1.2. UV Protectors

UV-C is almost absorbed by the ozone layer, therefore UV protection means stability under UV-A and UV-B radiation of sunlight. This can be acheived in two ways: material can be UV transparent or an UV protecter additive is used to eliminate the destructive effect of light. UV transparent materials have no absorption in the UV region so electromagnetic waves penetrate through the material by giving no damage. One such material is more durable to sunlight, therefore it can be used in outdoor applications.

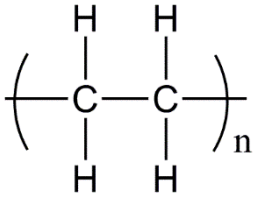


Figure 1.4. An example of UV transparent polymer.

UV protector is any organic or inorganic compound which protects materials from photodegredation. An ideal UV protector should prevent the destructive effect of the whole UV range of the electromagnetic spectrum and show no absorbance in the visible range (400 nm-700 nm) so that it would be colourless. Also, a UV protector should be stable at high temperatures and should not decompose under sunshine. Finally, these chemicals should be compatible with the coatings or polymers they are added to so that they would not change the chemical property of the material [7]. To achieve these goals many organic and inorganic compouds have been developed and often they are used together [8]. The aim of combining these two compounds is to acheive protection in a broader range of wavelenghts. UV protecting materials have been used in many fields since the negative impacts of sunlight exposure have been understood. Sunscreen creams, coatings, textiles are few examples. In most applications, UV protectors are used together with radical scavengers such as hindered amine light stabilizers (HALS) [9]. HALS inhibite the oxidation of polymer chain by trapping the radicals being formed. These are generally the derivatives of 2,2,6,6-Tetramethylpiperidine and they have been used to stabilize polymers since the seventies.

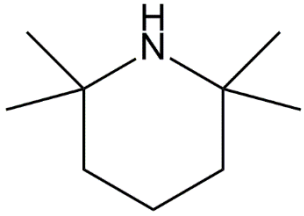


Figure 1.5. 2,2,6,6-Tetramethylpiperidine.

1.2.1. Inorganic UV Protectors

Inorganic UV protectors such as titanium dioxide, zinc oxide, aluminium oxide and silicon dioxide reflect and scatter the UV light, so their protection mechanism is believed to be physical. Because of being non-toxic and more stable under UV exposure, inorganic UV protectors are much preferred [10]. In addition to conventional bulk inorganic compounds, the nanoparticles of these species are used in many fields. These nanoparticles have special properties and some advantages over bulk particles. In textile industry for example; fabrics loose their UV protection property due

to laundering or wearing. However; by using nanoparticles, these treated fabrics become more durable since nanoparticles have large surface area and high surface energy that provide better affinity to fabrics [11].

1.2.2. Organic UV Protectors

Organic UV protectors are conjugated π systems that have strong absorption below 400nm. They are also called UV absorbers because their protection mechanism depends on the absorption of the electromagnetic radiation. When irradiated, these compounds usually make a temporary intramolecular hydrogen bonding and when the irradiation stops they release the absorbed energy as heat.

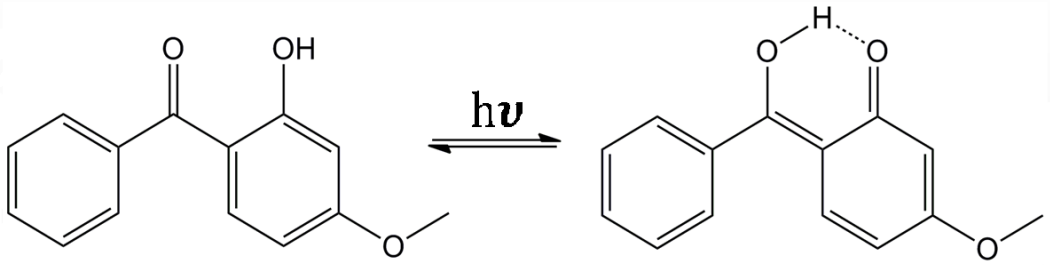


Figure 1.6. UV absorption by intramolecular hydrogen bonding of oxybenzone.

For an effective UV protection, this process should be more rapid than the UV absorption of the protected material to prevent the photodecomposition. Synthesis of new UV absorbers have been reported in the literature during the past years and most of them are derivatives of benzophenones, benzotriazoles and triazines.

There are several examples for each type of absorbers in the literature. For our purposes, benzophenone derivatives are the area of special interest. For instance, Bailey *et al* have synthesized 2,4-Dihydroxy-4'-vinylbenzophenol type UV absorber copolymers [12]. Bojinov and Grabchev has synthesized a combination of 2,2,6,6-tetramethylpiperidine–2-hydroxybenzophenone 1,3,5-triazine derived polymerizable monomers [13]. Zakrzewski and Szymanowki has prepared a 2-hydroxybenzophenone UV absorber containing 4,4,5,5-tetramethylimidazolidine fragment [14].

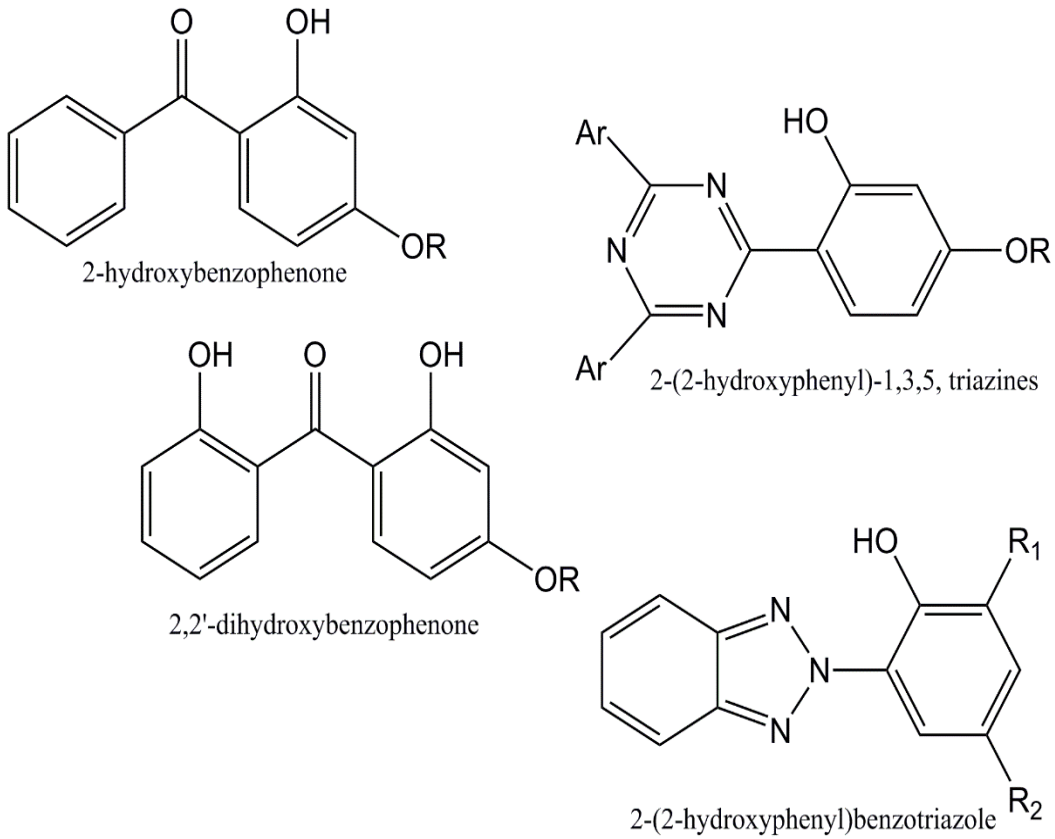


Figure 1.7. Most common UV absorber molecules.

Sunlight exposure can cause surface cracking, increased brittleness, loss of mechanical strength and discoloration of the polymeric materials [15]. Without the use of UV absorbers, polymers would have a shorter lifetime. Mixing 0.5-1% of such substance with a coating material maintains shelter effect and prevents photodecomposition.

Although UV absorbers can be added directly to the material as small additives, polymerizing these compounds with the material have some benefits. For instance, they prevent the small cracks caused by the mobility of these materials on the solid surfaces. When it is used in a solid plastic material, they are chemically bonded to the material so their mobility is restricted. Even if they are used for long periods of time, UV absorber molecules do not migrate to surface,

therefore small cracks do not occur and the homogenous composition is preserved. However; these compounds have also some disadvantages.

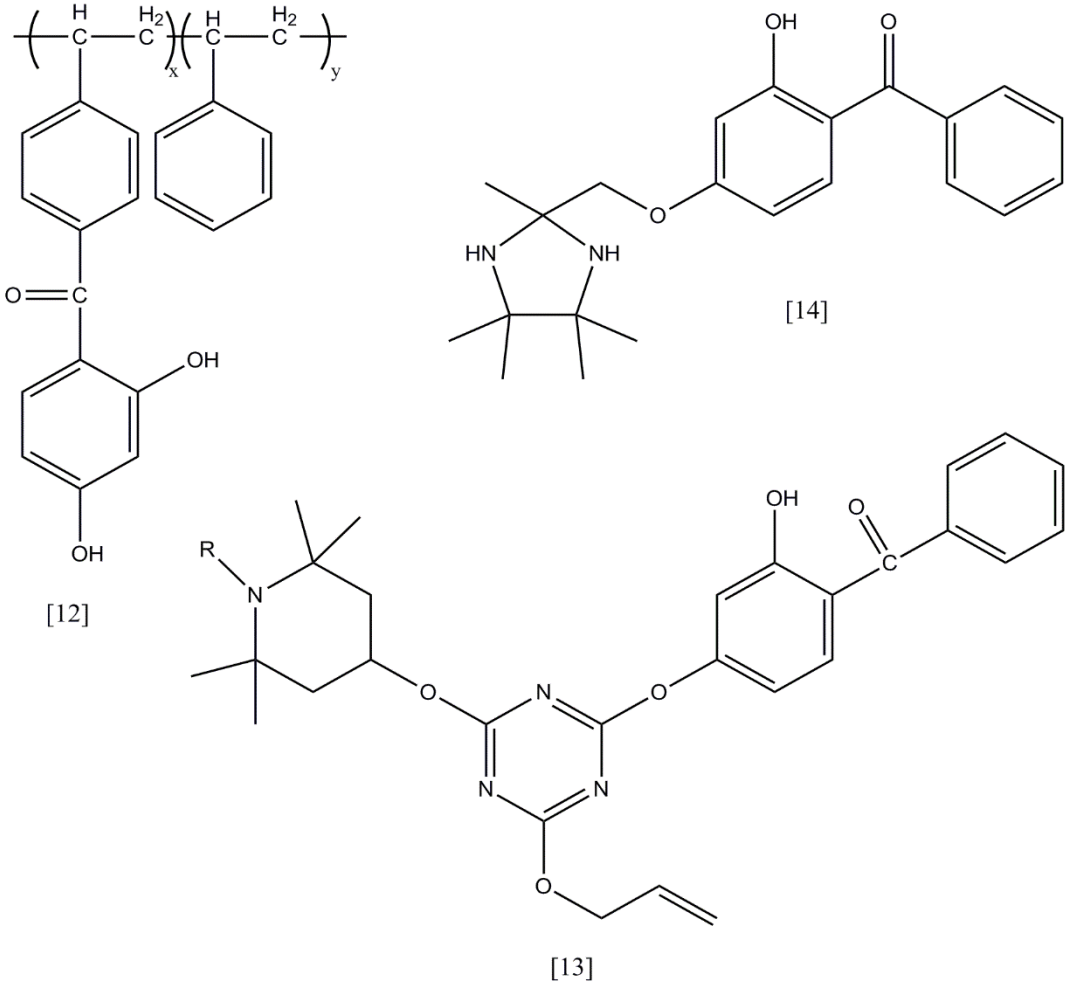


Figure 1.8. Examples of benzophenone derived UV absorbers in literature.

Benzophenones for instance, usually have a small absorption tail at around 400 nm which makes them slightly yellow [16]. This makes harder to obtain some unique color tones when they are employed. If a benzophenone type of UV absorber is used to protect a dye for instance, the color of the dye slightly changes due to this yellowing effect. On the other hand, these type of UV absorber polymers usually have miscibility problem in some organic solvents due to their water soluble functional groups which causes an additional application limitations.

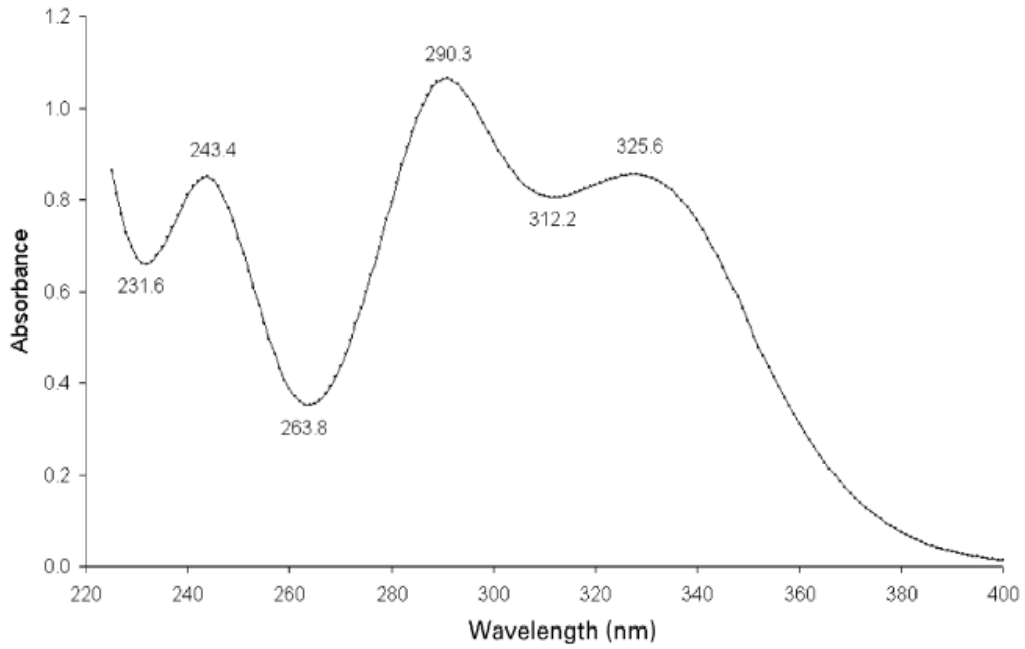


Figure 1.9. UV-Vis Spectrum of 2, 4-hydroxy benzophenone.

1.2.3. Photo-Fries Rearrangement

Fries Rearrangement is the migration of the aryl ester to ortho or para position of the aromatic ring to form phenol in the presence of a Lewis base such as $AlCl_3$. Although different pathways have been proposed for the mechanism, the rearrangement is believed to start with coordination of the ester to the Lewis acid. The same reaction also proceeds in the presence of UV radiation rather than a Lewis acid. This reaction is called "Photo-Fries Reaction" and it enables to overcome the limitations caused by the use of conventional benzophenone type UV absorbers. Before the rearrangement, the compound has no yellow color and is suitable for mixing with organic compounds. Polymerizing a monomer that can undergo Photo-Fries rearrangement with a plastic does not change the original color of the material and makes it also UV absorber. The aim of using a monomer that is capable of making Photo-Fries rearrangement is therefore keeping the material properties invariable while having protection from UV.

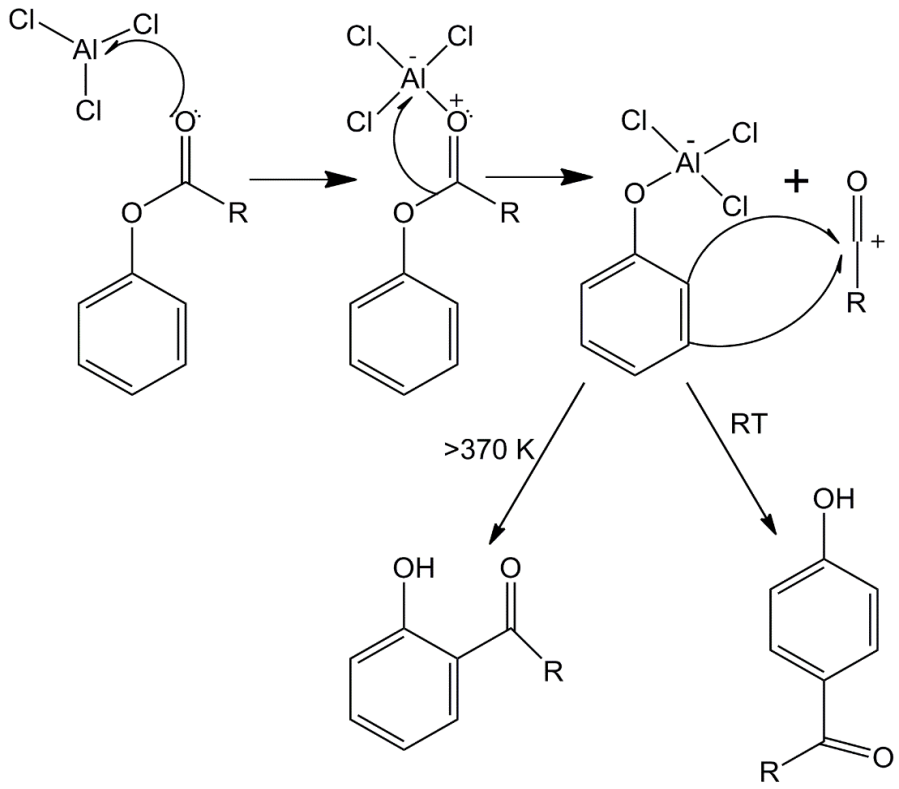


Figure 1.10. Mechanism for Fries rearrangement in the presence of Lewis acid.

When exposed to sunlight, the material creates only a thin yellow UV absorber layer on the surface. This slightly yellow color does not have a pronounced effect on the original color, which enables to obtain a broader range of colors that has UV absorption property. Moreover, conventional UV absorbers lose their property by time or are washed out in long term use. UV absorber polymers that can undergo Fries rearrangement is a key to overcome these limitations which is also the subject of this thesis.

2. OBJECTIVES

UV absorber polymers have been used in many applications to prevent materials from detrimental effects of sunlight such as photodecomposition. Since the first discovery of UV photodegredation, many attempts have been made to synthesize different types of molecules. These molecules are stable under sunlight and most of them make temporary hydrogen bondings when they are exposed to UV radiation. However, most of the commercially available UV absorber molecules absorb in the visible region of the electromagnetic spectrum and therefore they have a slightly undesired yellow colour. Secondly, these coumpounds usually have miscilibility problem with many organic paints and coating due to their hydroxyl groups. This limitation makes these compounds mobile and therefore causes unwanted cracks on the material that ther are added to.

In this thesis, the aim is to synthesize a novel acrylate monomer that is colorless at its original form and it is miscible with many organic solvents and polymeric systems. When this monomer is exposed to UV, it undergoes Photo-Fries rearrangement to give a new molecule that is UV absorber and have a slightly yellow colour just above the surface. By this approach, we create a thin, slightly yellowish UV absorber layer on the surface where it is applied and therefore it does not change the colour of the whole matrix..

The monomer will be polymerized to give homopolymers and its UV absorbtion behavior will be investigated to find out if it is possible for using in outdoor applications. Then its copolymers with methyl methacrylate will be synthesized at different ratios (10%, 20%, 30%) to observe the UV absorbing capacity with the changing UV absorber moities. Finally, stock solutions of these polymers will be prepared and they will be irradiated to give the rearranged product. Same UV absorption tests will be carried out to examine how much radiation is needed for the rearrangement and to compare the UV absorption behaviors of rearranged products with the original molecule.

3. EXPERIMENTAL

3.1. Materials and Methods

Resorcinol monohydroxyethyl ether (MP Biomedicals), benzoyl chloride 99% (Acros Organics), triethylamine 99% (Merck), acryloyl chloride 97% (Aldrich), methyl methacrylate 99% (Acros Organics), sodium hydroxide 97% (Merck), sodium bicarbonate 99% (Merck), anhydrous sodium sulfate 99% (Merck), azobisisobutyronitrile (AIBN) 99% (Aldrich). All glassware and stirring bars were dried overnight in oven at 140 ^{0}C before use. All solvents: methylene chloride, hexane, toluene were used as received from Merck. Column chromatography was performed by using silicagel-60 (0.063-0.200 mm, Merck). Thin layer chromatography (TLC) was performed using silica gel plates (TLC silica gel 60 F_{254}, Merck).

3.2. Apparatus

^{1}H-NMR and ^{13}C-NMR analysis were carried out by using Varian Gemini 400MHz spectrometer. All UV-Vis spectra analysis were done by SHMADZU UV-1700 PharmaSpec UV-Visible Spectrophotometer. GPC analysis were done by Viscotek VE2001 GPC Solvent/Sample Model with a PL Gel 5 µm MIXED-C Column that was calibrated against polystyrene standarts. IR Spectra of compounds was determined by using NICOLET 380 FT-IR, Thermo SCIENTIFIC. All photoreactions were carried out in a custom made UV reactor that uses 256 nm Philips UV lamps.

3.3. Monomer Synthesis

Monomer synthesis was carried out in two steps. First, resorcinol monohydroxyethyl ether and benzoyl chloride were reacted to give 3-(2-hydroxyethoxy)phenyl benzoate. Then 3-(2-hydroxyethoxy)phenyl benzoate and acryloyl chloride were reacted to give 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.

3.3.1. Synthesis of 3-(2-hydroxyethoxy)phenyl benzoate

Resorcinol monohydroxyethyl ether (7.7 g, 0.05 mol), triethylamine (1 mL, 0.007 mol), methylene chloride (60 mL), distilled water (70 mL) and a magnetic stirring bar were added to a 250 mL three-necked round bottom flask. Benzoyl chloride (5.8 mL, 0.05 mol) in methylene chloride (14.2 mL) and sodium hydroxide (2 g, 0.05 mol) in water (20 mL) were added dropwise into the mixture while stirring vigorously at room temperature. Starting from benzoyl chloride, additions continued stepwise and each one of which is 5 mL. Addition was completed in 15 minutes, then stirring continued for 15 minutes. The mixture was washed two times with saturated sodium bicarbonate solution and two times with distilled water. Organic phase was separated, dried with sodium sulfate and methylene chloride was evaporated. Remaining product was dissolved in minimum methylene chloride (2 mL) and purified by silica column chromatography (methylene chloride) to give 93% yield (11.99 g) (Figure 3.1). **^{1}H NMR** ($CDCl_3$), δ: 8.14 (m, 2H, Ar*H*), 8.58 (m, 1H, Ar*H*), 7.44 (m, 2H, Ar*H*), 7.25 (m, 1H, Ar*H*), 6.57 (m, 3H, Ar*H*), 4.01 (t, 2H, C*H*$_2$-CH_2), 3.88 (t, 2H, CH_2-C*H*$_2$) ppm. **^{13}C-NMR** ($CDCl_3$), δ: 61.2 (1C, CH_2-*C*H_2), 69.6 (1C, *C*H_2-CH_2), 108.6 (1C, Ar*C*), 112.4 (1C, Ar*C*), 114.4 (1C, Ar*C*), 128.7 (2C, Ar*C*), 129.4 (1C, Ar*C*), 130.1 (1C, Ar*C*), 130.2 (2C, Ar*C*), 133.8 (1C, Ar*C*), 152.0 (1C, Ar*C*), 159.6 (1C, Ar*C*), 165.2 (1C, *C*=O) ppm.

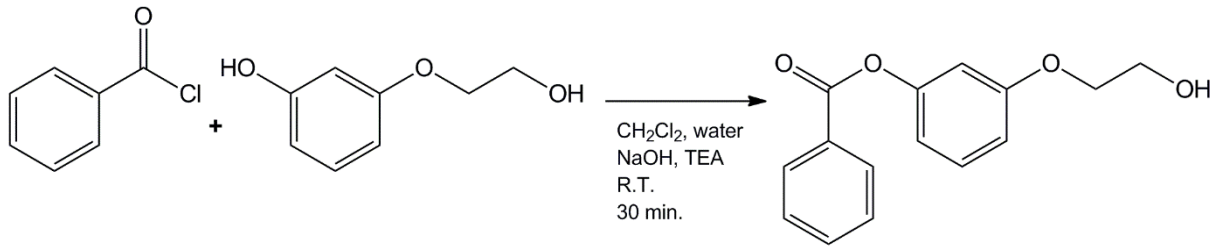


Figure 3.1. Synthesis of 3-(2-hydroxyethoxy)phenyl benzoate.

The reaction has one more product resulting from the reaction of both alcohols with benzoyl chloride. That product was also purified by silica column chromatography (methylene chloride) and put in the oven overnight. **^{1}H NMR** ($CDCl_3$), δ: 4.34 (t,2H, C*H*$_2$-CH_2), 4.69 (t, 2H, CH_2-C*H*$_2$), 6.88 (m, 3H, Ar*H*), 7.36 (m, 1H, Ar*H*), 7.45 (m, 2H, Ar*H*), 7.52 (m, 2H, Ar*H*), 7.57

(m, 1H, Ar*H*), 7.65 (m, 1H, Ar*H*), 8.08 (m, 2H, Ar*H*), 8.22 (m, 2H, Ar*H*) ppm. **^{13}C-NMR** ($CDCl_3$), δ: 63.0 (1C, CH_2-*C*H_2), 66.1 (1C, *C*H_2-CH_2), 108.4 (1C, Ar*C*), 112.2 (1C, Ar*C*), 114.3 (1C, Ar*C*), 128.4 (1C, Ar*C*), 129.3 (1C, Ar*C*), 129.6 (2C, Ar*C*), 129.7 (1C, Ar*C*), 129.8 (1C, Ar*C*), 130.1 (2C, Ar*C*), 133.0 (1C, Ar*C*), 133.5 (1C, Ar*C*), 151.8 (1C, Ar*C*), 159.4 (1C, Ar*C*), 164.8 (1C, *C*=O), 166.4 (1C, *C*=O) ppm.

3.3.2. Synthesis of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate

3-(2-hydroxyethoxy)phenyl benzoate (7.18 g, 0.028 mol), triethylamine (4.2 mL, 0.03 mol), methylene chloride (20 mL) and a magnetic stirring bar were added to a 250 mL erlenmayer flask. Acryloyl chloride (2.4 mL, 0.03 mol) in methylene chloride (10 mL) was added dropwise into the mixture while stirring vigorously under ice bath. Addition was completed in 20 minutes and then mixture was heated to 80 ^{0}C for 30 minutes. The mixture was brought to room temperature and washed two times with saturated sodium bicarbonate solution, then two times with distilled water. Residue was dried with anhydrous sodium sulfate and methylene chloride was evaporated. Remaining product was dissolved in min. methylene chloride (3 mL) and purified by silica column chromatography (methylene chloride) to give 60% yield (5.24 g) (Figure 3.2). **^{1}H NMR** ($CDCl_3$), δ: 4.20 (t, 2H, C*H*$_2$-CH_2), 4.49 (t, 2H, CH_2-C*H*$_2$), 5.84 (quar, 1H, CH=CH*H*), 6.15 (quar, 1H, C*H*=CH_2), 6.44 (quar, 1H, CH=C*H*H), 6.83 (m, 3H, Ar*H*), 7.32 (t, 1H, Ar*H*), 7.49 (m, 2H, Ar*H*), 7.62 (m, 1H, Ar*H*), 8.12 (m, 2H, Ar*H*) ppm. **^{13}C-NMR** ($CDCl_3$), δ: 60.8 (1C, CH_2-*C*H_2), 64.1 (1C, *C*H_2-CH_2), 106.5 (1C, Ar*C*), 110.2 (1C, Ar*C*), 112.4 (1C, Ar*C*), 126.0 (1C, *C*H=CH_2), 126.6 (2C, Ar*C*), 127.4 (1C, Ar*C*), 127.9 (1C, Ar*C*), 128.1 (2C, Ar*C*), 129.3 (1C, CH=*C*H_2), 131.6 (1C, Ar*C*), 149.9 (1C, Ar*C*), 157.4 (1C, Ar*C*), 163.0 (1C, C=O), 163.9 (1C, C=O).

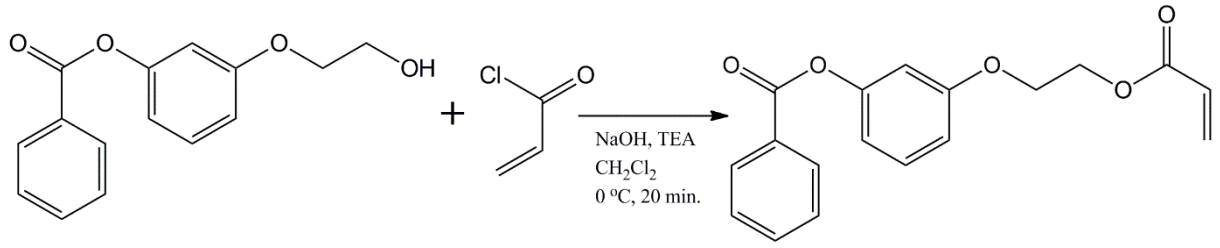


Figure 3.2. Synthesis of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.

3.4. Polymer Synthesis

In each polymerization, total monomer to initiator ratio is adjusted to 100:1 by moles. The volume of toluene is about 2-4 times than the monomer volume. In such conditions polymerizations were carried out 4 hours at 70 ^{0}C.

3.4.1. Radical Homopolymerization of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate

3-(2-(acryloyloxy)ethoxy)phenyl benzoate (0.7 g, 2.147x10^{-3} mol), toluene (1.3 mL), AIBN (3.6x 10^{-3} g, 2.147x10^{-3} mol) and a magnetic stirrer were put into a 25 mL one-neck round bottom flask equipped with a reflux condenser. Nitrogen gas passed through the mixture for 10 minutes and the mixture was set to 70 ^{0}C for 4 hours. The polymer was precipated into hexane. White precipitate was collected and dissolved in methylene chloride, then precipitated in hexane two times more. The residue was collected and dried in a vacuum oven overnight. **^{1}H NMR** ($CDCl_3$), δ: 3.92 (m, 2H, C*H*$_2$-CH_2), 4.21 (m, 2H, CH_2-C*H*$_2$), 6.68 (m, 3H, Ar*H*), 7.15 (m, 1H, Ar*H*), 7.37 (m, 2H, Ar*H*), 7.50 (m, 1H, Ar*H*), 8.05 (m, 2H, Ar*H*) ppm.

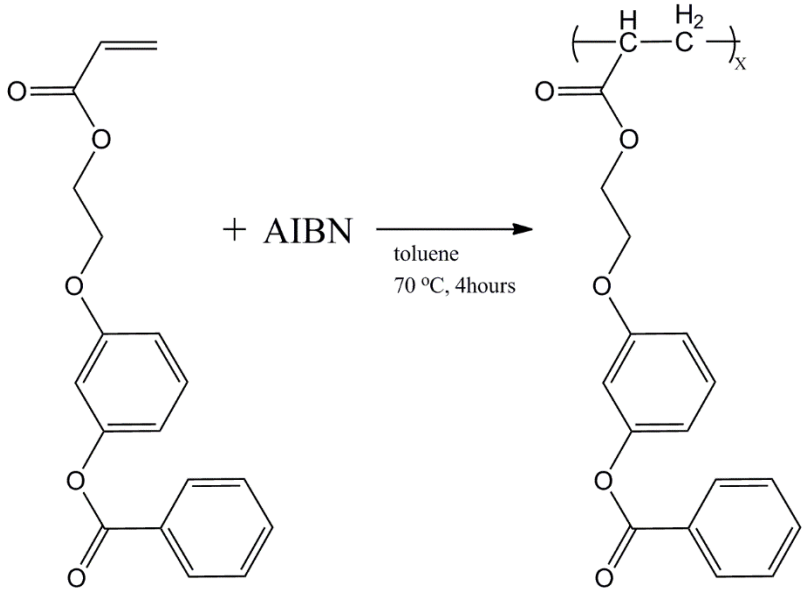


Figure 3.3. Synthesis of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate homopolymer.

3.4.2. Radical Copolymerizations of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate

The same procedure was followed for each copolymerization to run the reaction below.

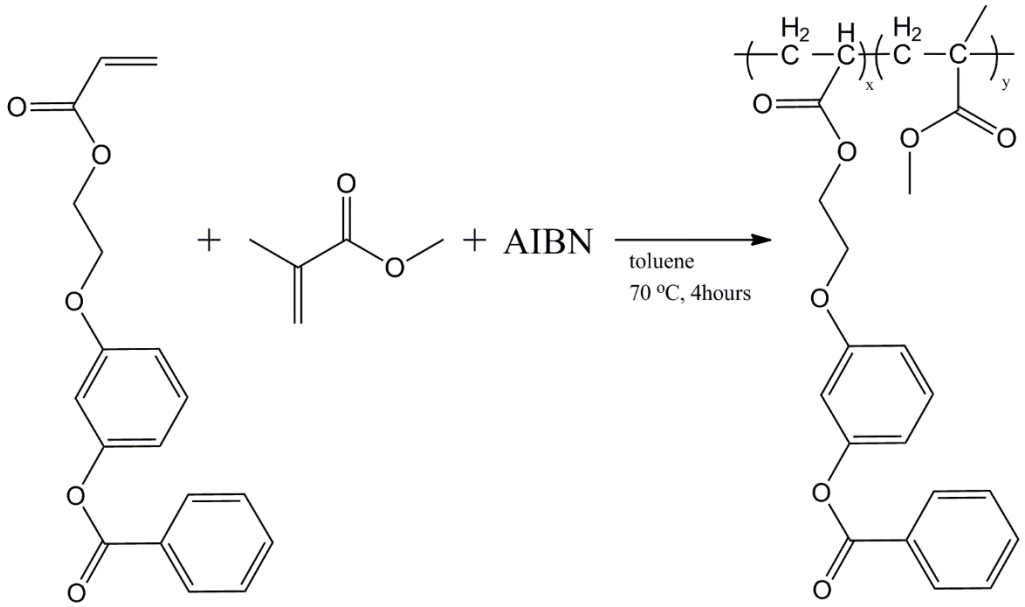


Figure 3.4. Synthesis of the copolymer 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.

3.4.2.1. Synthesis of 10% Copolymer with methyl methacrylate. 3-(2 (acryloyloxy)ethoxy) phenyl benzoate (0.30 g, 9.61×10^{-4} mol), methyl methacrylate (0.87 g, 8.65×10^{-3} mol), toluene (2.3 mL), AIBN (15.8×10^{-3} g, 9.6×10^{-5} mol) and a magnetic stirrer were put into a 25 mL one-neck round bottom flask equipped with a reflux condenser. Nitrogen gas passed through the mixture for 10 minutes and the mixture was set to 70 ^{0}C for 4 hours. The polymer was precipated into hexane. White precipitate was collected and dissolved in methylene chloride, then precipitated in hexane two times more. The residue was collected and dried in a vacuum oven overnight. **^{1}H NMR** ($CDCl_3$), δ: 8.20 (m, 2H, Ar*H*), 7.64 (m, 1H, Ar*H*), 7.52 (m, 2H, Ar*H*), 7.34 (m, 1H, Ar*H*), 6.82 (m, 3H, Ar*H*), 4.36 (m, 2H, C*H*$_2$-CH_2), 4.15 (m, 2H, CH_2-C*H*$_2$)

3.4.2.2. Synthesis of 20% Copolymer with methyl methacrylate. 3-(2-(acryloyloxy)ethoxy)phenyl benzoate (0.30 g, $9.61x10^{-4}$ mol), methyl methacrylate (0.38 g, $3.846x10^{-3}$ mol), toluene (3 mL), AIBN ($7.89x10^{-3}$ g, 4.8×10^{-5} mol) and a magnetic stirrer were put into a 25 mL one-neck round bottom flask equipped with a reflux condenser. Nitrogen gas passed through the mixture for 10 minutes and the mixture was set to 70 ^{0}C for 4 hours. The polymer was precipated into hexane. White precipitate was collected and dissolved in methylene chloride, then precipitated in hexane two times more. The residue was collected and dried in a vacuum oven overnight. **^{1}H NMR** ($CDCl_3$), δ: 8.20 (m, 2H, Ar*H*), 7.64 (m, 1H, Ar*H*), 7.52 (m, 2H, Ar*H*), 7.34 (m, 1H, Ar*H*), 6.82 (m, 3H, Ar*H*), 4.36 (m, 2H, C*H*$_2$-CH_2), 4.15 (m, 2H, CH_2-C*H*$_2$)

3.4.2.3. Synthesis of 30% Copolymer with methyl methacrylate. 3-(2-(acryloyloxy)ethoxy) phenyl benzoate (0.30 g, $9.61x10^{-4}$ mol), methyl methacrylate (0.22 g, $2.24x10^{-3}$ mol), toluene (2 mL), AIBN ($5.25x10^{-3}$g, $3.2x10^{-5}$ mol) and a magnetic stirrer were put into a 25 mL one-neck round bottom flask equipped with a reflux condenser. Nitrogen gas passed through the mixture for 10 minutes and the mixture was set to 70 ^{0}C for 4 hours. The polymer was precipated into hexane. White precipitate was collected and dissolved in methylene chloride, then precipitated in hexane two times more. The residue was collected and dried in a vacuum oven overnight. **^{1}H NMR** ($CDCl_3$), δ: 8.20 (m, 2H, Ar*H*), 7.64 (m, 1H, Ar*H*), 7.52 (m, 2H, Ar*H*), 7.34 (m, 1H, Ar*H*), 6.82 (m, 3H, Ar*H*), 4.36 (m, 2H, C*H*$_2$-CH_2), 4.15 (m, 2H, CH_2-C*H*$_2$)

3.5. Investigation of UV Absorptions

3.5.1. UV Spectra of the Monomer

3-(2-(acryloyloxy)ethoxy)phenyl benzoate (0.00210 g) was dissolved in methylene chloride (10 mL) to obtain 0.210 g/L solution. This stock solution was then diluted by 50% each time and five other solutions were prepared (0.105, 0.052, 0.026, 0.013, 0.006 g/L). UV spectra of these solutions were measured by UV-Visible Spectrophotometer and molar absorption coefficients were determined from the concentration versus absorption graph. The stock soution

was then irradiated with UV in the photoreactor and the UV spectra was measured at 5, 10, 15, 20 minutes.

3.5.2. UV Spectra of the Homopolymer

3-(2-(acryloyloxy)ethoxy)phenyl benzoate (0.0021 g) was dissolved in methylene chloride (10 mL) to obtain 0.210 g/L solution. This stock solution was then diluted by 50% each time and five other solutions were prepared (0.105, 0.052, 0.026, 0.013, 0.006 g/L). UV spectra of these solutions were measured by UV-Visible Spectrophotometer and molar absorbtion coefficients were determined from the concentration versus absorption graph. The stock soution was then irradiated with UV in the photoreactor and the UV spectra was measured at 5, 10, 15, 20 minutes.

3.5.3. UV Spectra of the 10% Copolymer

10% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate and methyl methacrylate (0.0021 g) was dissolved in methylene chloride (10 mL) to obtain 0.210 g/L solution. This stock solution was then diluted by 50% each time and five other solutions were prepared (0.105, 0.052, 0.026, 0.013, 0.006 g/L). UV spectra of these solutions were measured by UV-Visible Spectrophotometer and molar absorbtion coefficients were determined from the concentration versus absorption graph. The stock soution was then irradiated with UV in the photoreactor and the UV spectra was measured at 5, 10, 15, 20 minutes.

3.5.4. UV Spectra of the 20% Copolymer

20% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate and methyl methacrylate (0.0021 g) was dissolved in methylene chloride (10 mL) to obtain 0.210 g/L solution. This stock solution was then diluted by 50% each time and five other solutions were prepared (0.105, 0.052, 0.026, 0.013, 0.006 g/L). UV spectra of these solutions were measured by UV-Visible Spectrophotometer and molar absorption coefficients were determined from the concentration versus absorption graph. The stock soution was then irradiated with UV in the photoreactor and the UV spectra was measured at 5, 10, 15, 20 minutes.

3.5.5. UV Spectra of the 30% Copolymer

30% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate and methyl methacrylate (0.0021 g) was dissolved in methylene chloride (10 mL) to obtain 0.210 g/L solution. This stock solution was then diluted by 50% each time and five other solutions were prepared (0.105, 0.052, 0.026, 0.013, 0.006 g/L). UV spectra of these solutions were measured by UV-Visible Spectrophotometer and molar absorbtion coefficients were determined from the concentration versus absorption graph. The stock soution was then irradiated with UV in the photoreactor and the UV spectra was measured at 5, 10, 15, 20 minutes.

3.5.6. Photoreaction Procedures

All the photoreactions above were carried out in a custom made photoreactor which uses 256 nm lambs. The samples which are put in a kuartz tube were irradiated with UV light and UV-spectra of solutions were measured in each 5 minutes.

4. RESULTS AND DISCUSSION

The purpose of this study is to synthesize a novel benzophenone derived UV absorber acrylate monomer and to investigate the UV absorption behavior of the corresponding polymers. The monomer was synthesized in two steps. First, resorcinol mono hydroxyethyl ether was reacted with benzoyl chloride to obtain 3-(2-hydroxyethoxy)phenyl benzoate. Then acryloyl chloride and 3-(2-hydroxyethoxy)phenyl benzoate were reacted to give 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.

In this section, we examine the synthetic pathways and proposed mechanisms. Also the factors that affect the reaction yields will be discussed.

4.1. Synthesis and Characterization of 3-(2-hydroxyethoxy)phenyl benzoate

This reaction is a condensation reaction of benzoyl chloride with phenolic alcohol and carried out in a biphasic system where organic phase is methylene chloride. The reaction condition is typical for Schotten Baumann reaction which has a relatively complex mechanism than a conventional condensation reaction. The reason for running this reaction in Schotten Baumann condition is that the reaction is fast and in the end we directly get rid of the water soluble impurities. Triethylamine was used as a phase transfer agent rather than to scavenge the liberated HCl, therefore it is used in catalytic amounts. Benzoyl chloride, which has a higher solubility in methylene chloride than water, makes a complex with triethylamine and makes it water soluble. The reaction is believed to occur in the aqueous phase where resorcinol mono hydroxyethyl ether is more soluble. When the reaction finishes, the product of the reaction is once again transferred to the organic phase where it has a higher solubility.

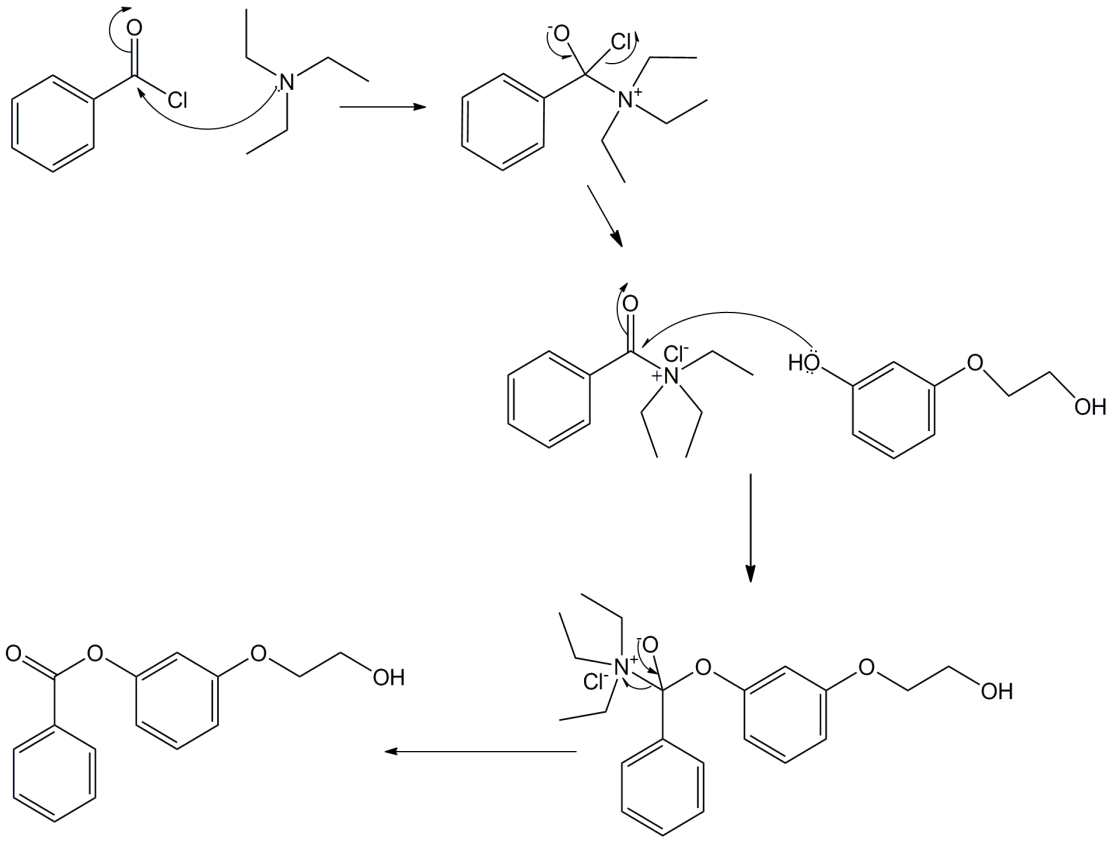


Figure 4.1. Reaction mechanism of benzoyl chloride with resorcinol hydroxymonoethyl ether.

The reaction is very sensitive to pH; therefore, the liberated hydrochloric acid was neutralized by sodium hydroxide. The aim of adding benzoyl chloride and sodium hydroxide stepwise is to adjust the pH just below 9. When pH is higher, benzoyl chloride reacts with both alcohols.

The purification of the compound was done by silica column chromatography and then the final yield is 93%. Vigorous stirring has also a critical role on the yield because it enables the contents of the phases to interact more with each other in a biphasic system.. Figure 4.2 shows the ^{1}H-NMR, and Figure 4.3 shows the ^{13}C-NMR of the monomer.

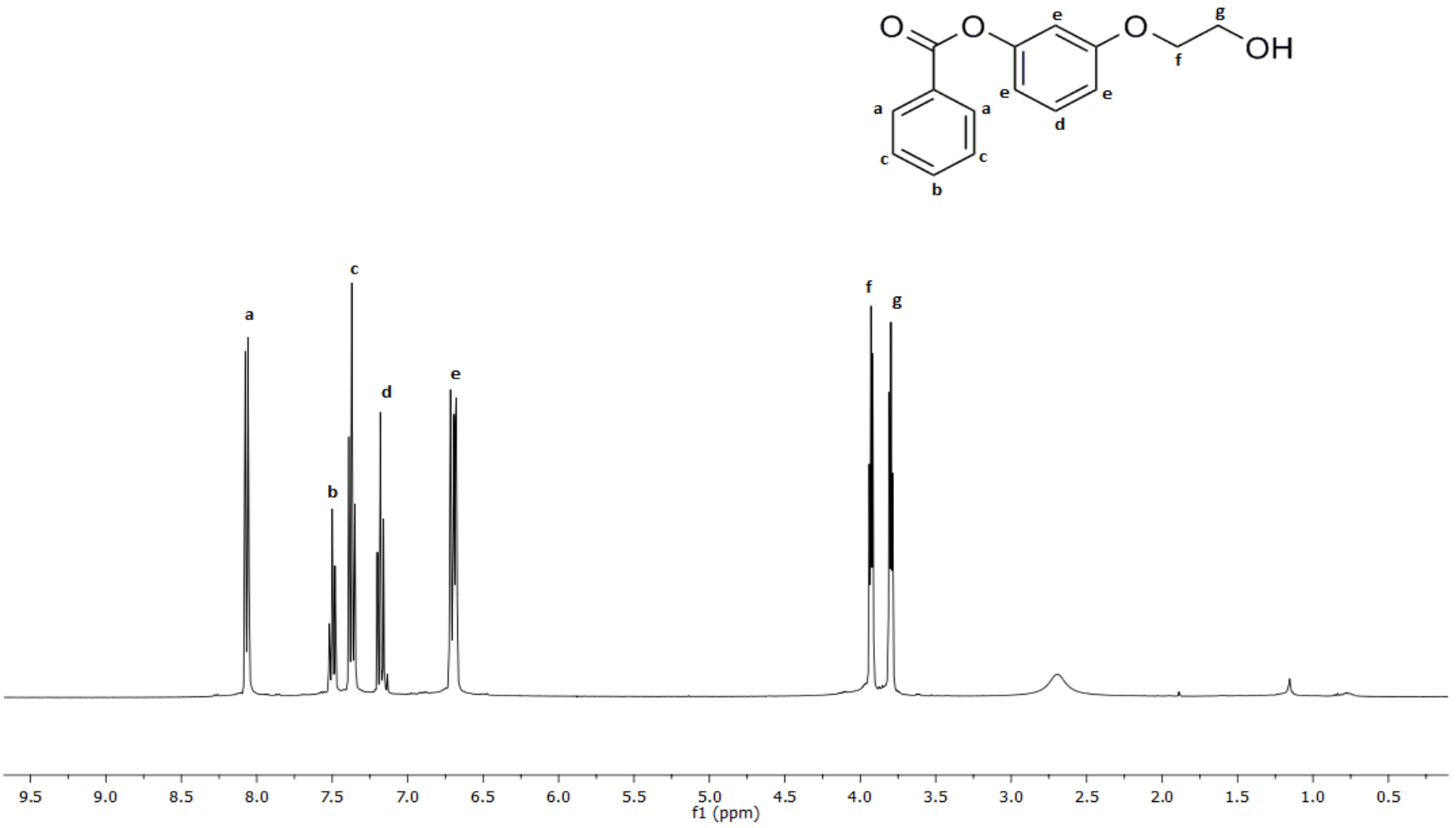


Figure 4.2. ^{1}H-NMR of 3-(2-hydroxyethoxy)phenyl benzoate.



Figure 4.3. ^{13}C-NMR of 3-(2-hydroxyethoxy)phenyl benzoate.

The reaction has one more product, resulting from the reaction of primary alcohol with benzoyl chloride. When the pH is higher than 10, the reaction favors more the formation of this byproduct as mentioned earlier. This byproduct "3-(2-benzoyloxy)ethoxy)phenyl benzoate" which moves faster on TLC due to its non-polar groups, is also purified by silica column chromatography with methylene chloride. Figure 4.4 shows the ^{1}H-NMR and Figure 4.5 shows the ^{13}C-NMR of the product.

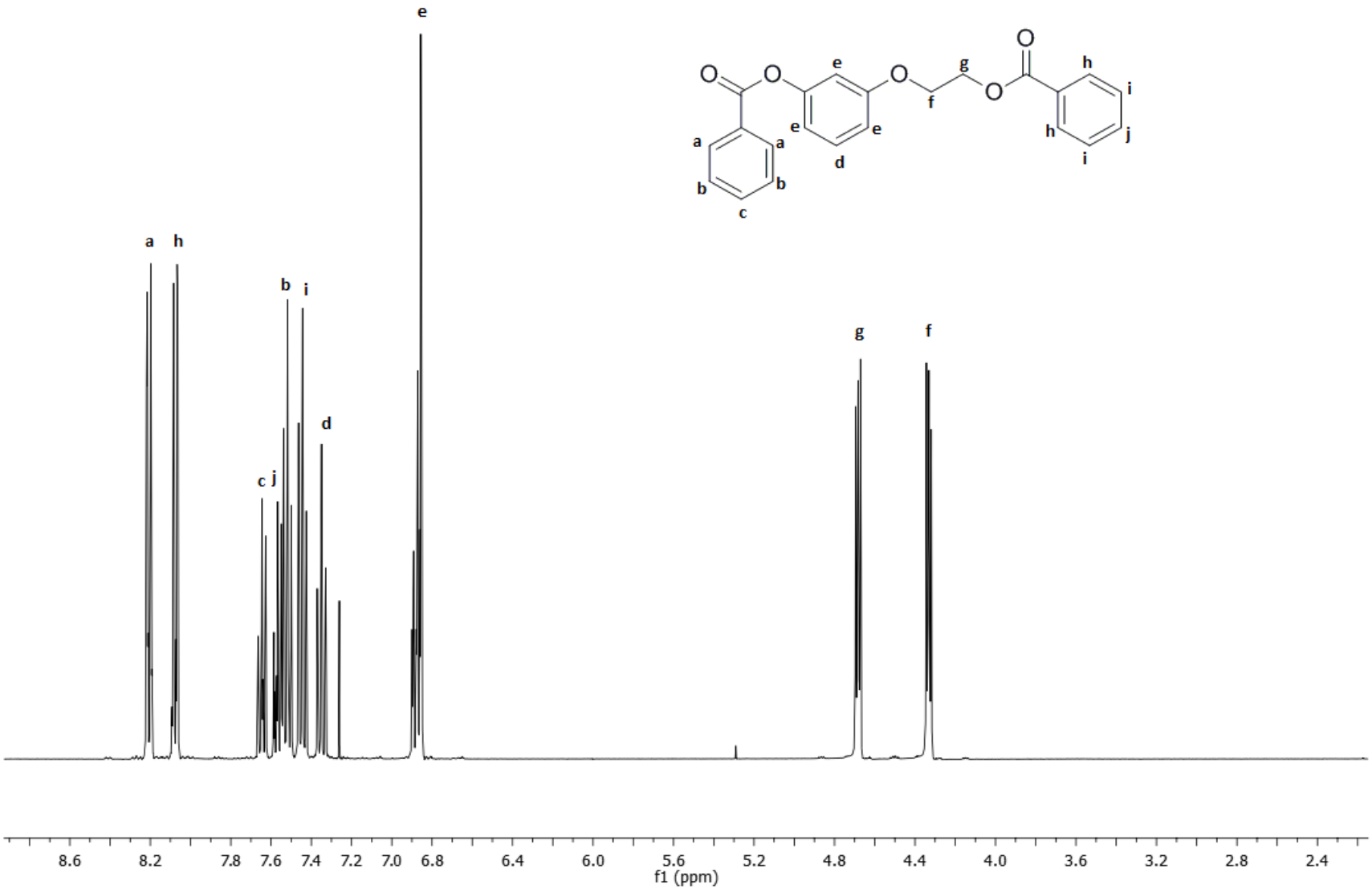


Figure 4.4. ^{1}H-NMR of 3-(2-benzoyloxy)ethoxy)phenyl benzoate.

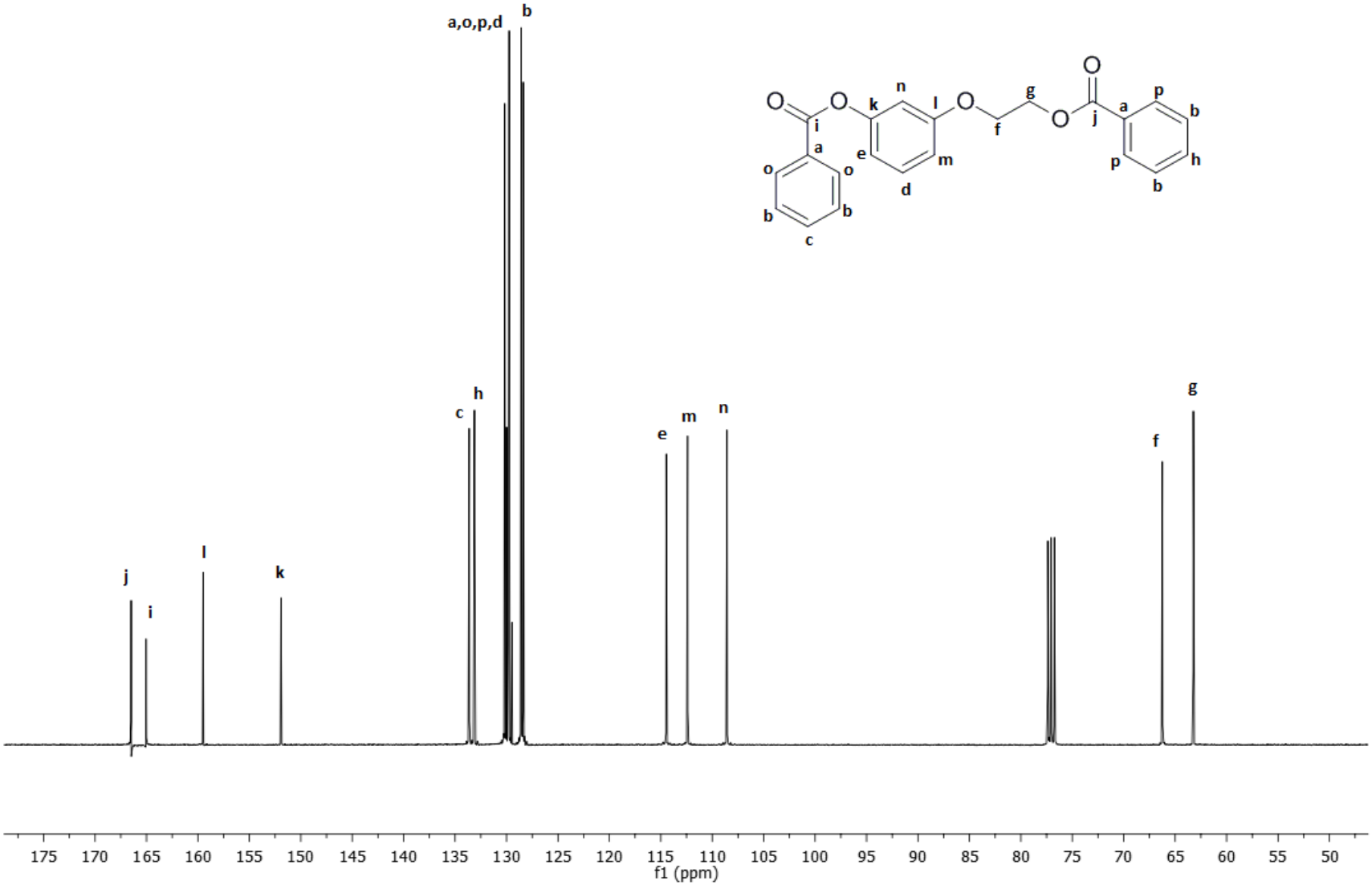


Figure 4.5. ^{13}C-NMR 3-(2-benzoyloxy)ethoxy)phenyl benzoate.

4.2. Synthesis and Characterization of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate

This step is acrylation of an alcohol group. The reaction is highly exothermic therefore it is carried out under ice bath and acrylate is diluted with methylene chloride before adding into the mixture. Triethylamine is used to trap the liberated HCl this time, therefore it is used in equivalent amount. Acrylate is used slightly more than one equivalent to increase the probability of compounds finding each other when acrylate concentration decrease as the reaction proceeds. The reaction starts with the attack of the alcohol to the carbonyl carbon then chloride leaves as a leaving group which then forms hydrochloric acid.

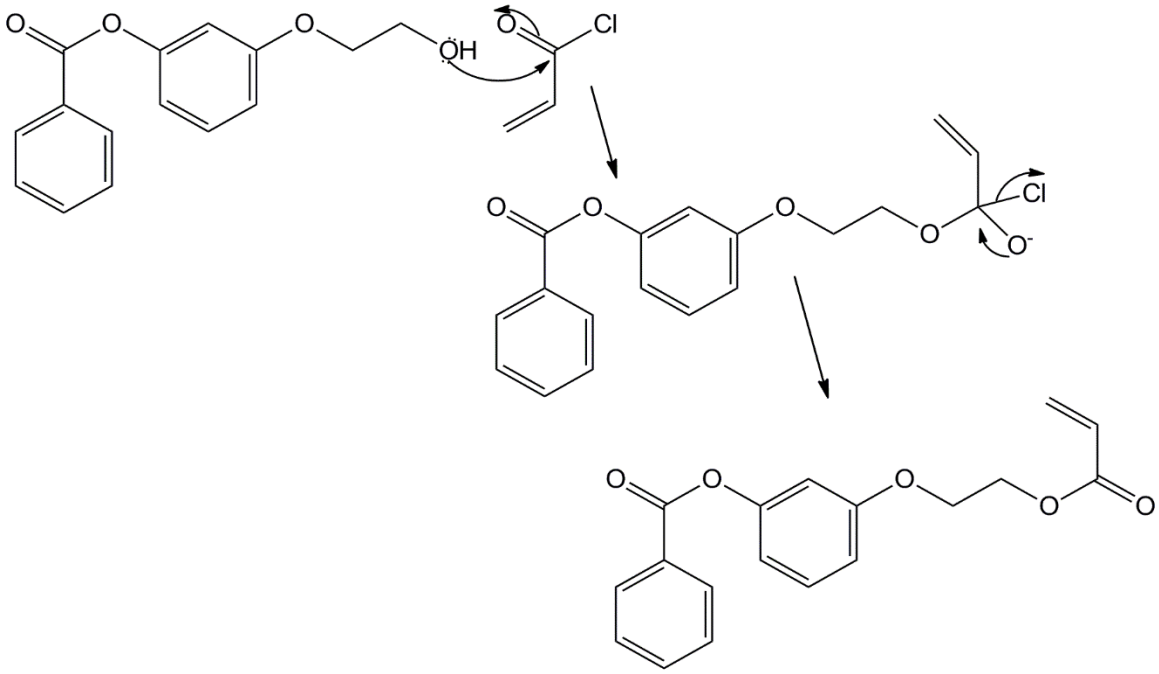


Figure 4.6. Reaction mechanism of acryloyl chloride with 3-(2-hydroxyethoxy)phenyl benzoate.

The product was purified by using silica-gel column chromatography and the yield is calculated 60%. Figure 4.7 shows the ^{1}H-NMR, Figure 4.8 shows the ^{13}C-NMR and Figure 4.9 shows the IR Spectra of the product.

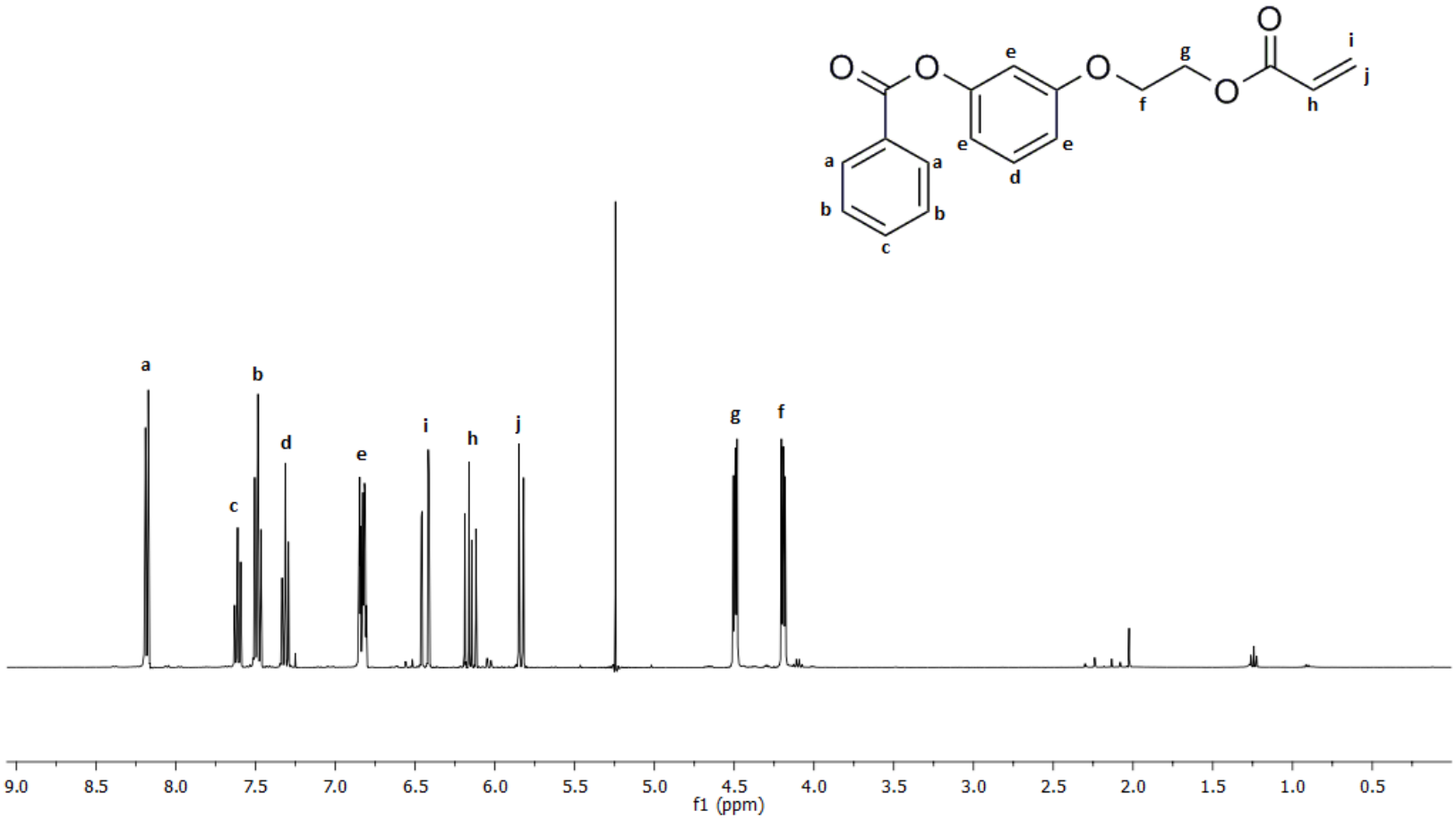


Figure 4.7. ^{1}H-NMR of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.

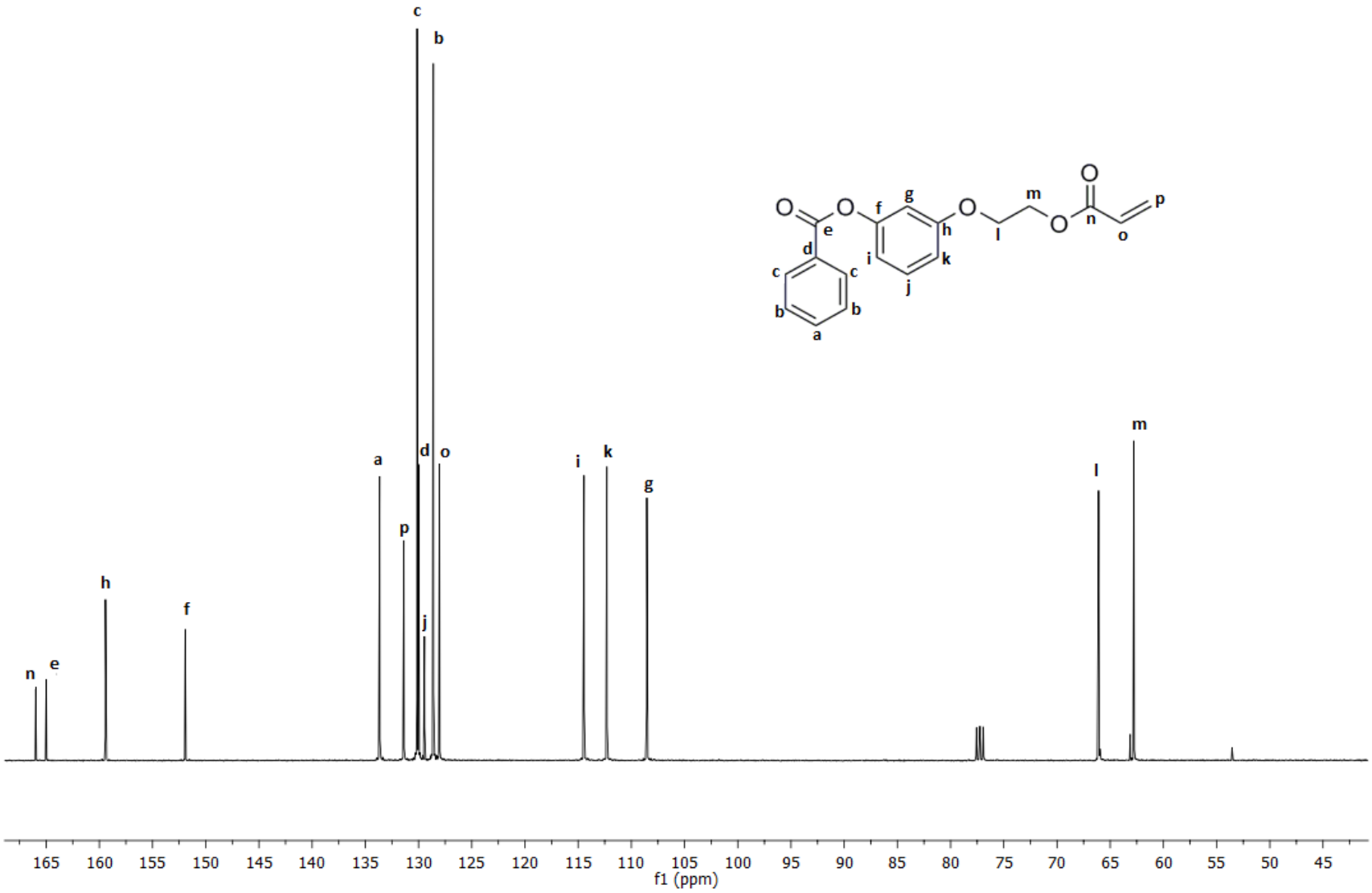


Figure 4.8. ^{13}C-NMR of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.

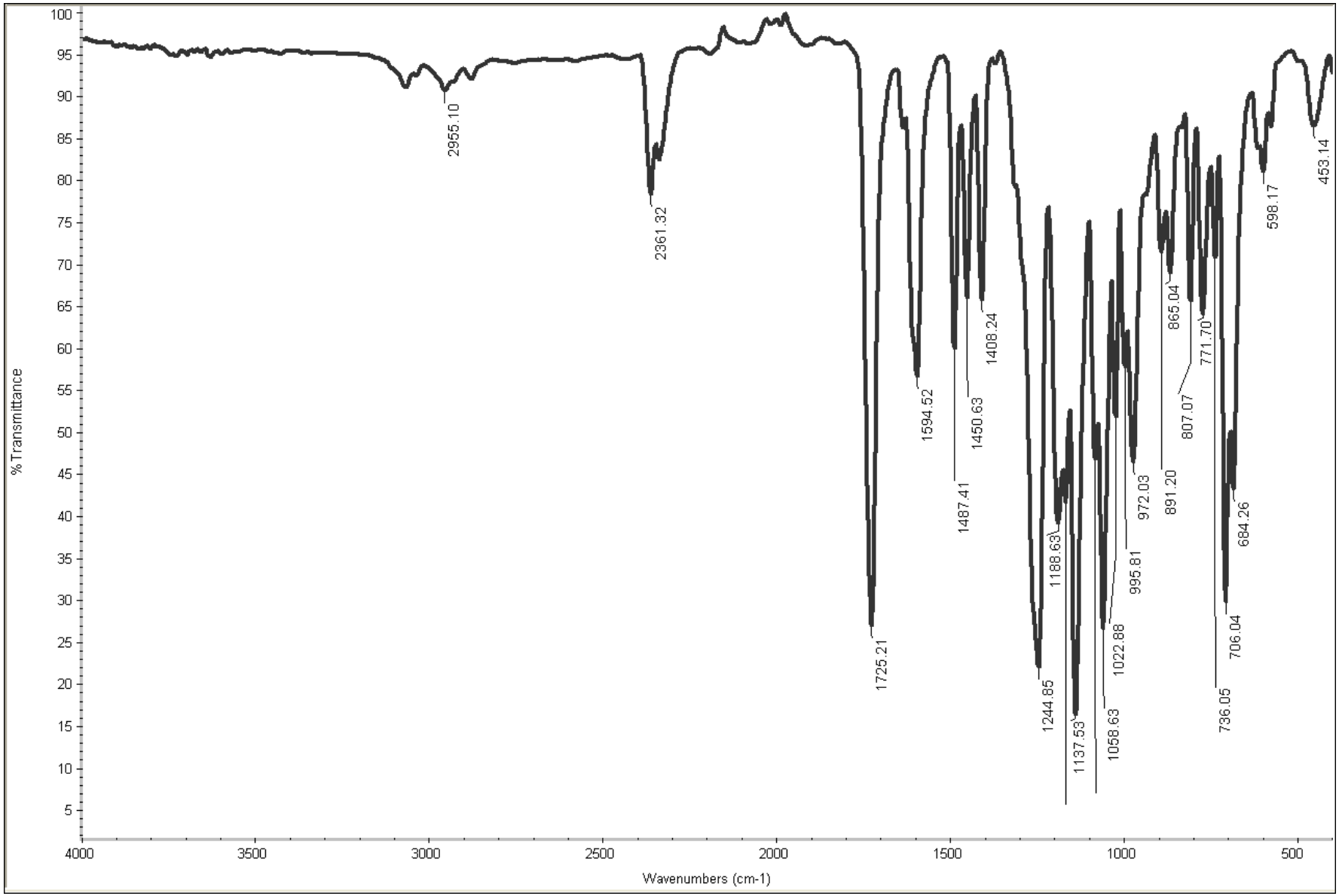


Figure 4.9. IR Spectra of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate.

The same reaction also was carried out with methyl methacrylate rather than acrylate. Reaction had a similar amount of yield but during the removal of the solvent, it polymerized. Addition of hydroquinone in small amounts could prevent the unwanted polymerization; however we focussed our attention to acrylates not to deal with additional impurities.

4.3. Synthesis and Characterization of the Homopolymer and Copolymers with 1:9, 2:8 and 3:7 Ratios

Homo and copolymers of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate monomer were obtained *via* radical polymerization by using AIBN initiator. Before the reactions started, nitrogen was purged into the mixtures to prevent the unwanted reactions of air oxygen. Once started, all the reactions were carried out 4 hours at 70 ^{0}C which is a common procedure for these type of solution polymerizations. Copolymers were synthesized in 10%, 20%, 30% ratios to compare the UV absorption behaviors with increasing UV absorber moieties in the polymer chains.

All the polymers have been precipitated in hexane three times to get higher purities for UV absorption analysis. Polymers have been characterized by ^{1}H-NMR and GPC analysis.

Table 4.1. Molecular weight and polydispersity index of polymers.

Copolymer Ratio	**Molecular Weight (g/mol)**	**Polydispersity index (PDI)**	**NMR Ratio of the polymers**
10%	15.768	1.98	12%
20%	14.249	1.86	18%
30%	27.677	2.14	26%
Homopolymer	58.810	5.07	100%

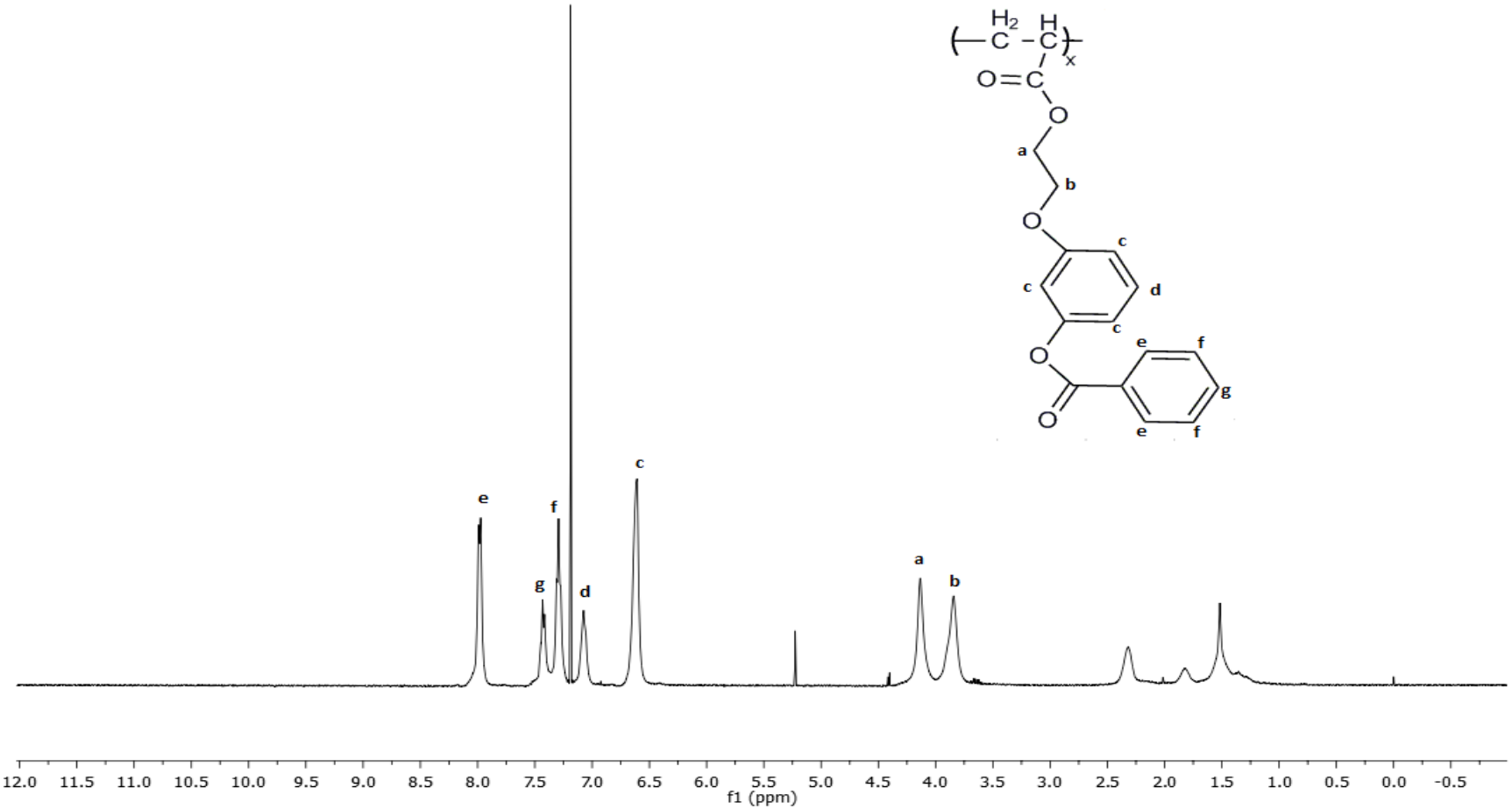


Figure 4.10. ^{1}H-NMR of the 3-(2-(acryloyloxy)ethoxy)phenyl benzoate homopolymer.

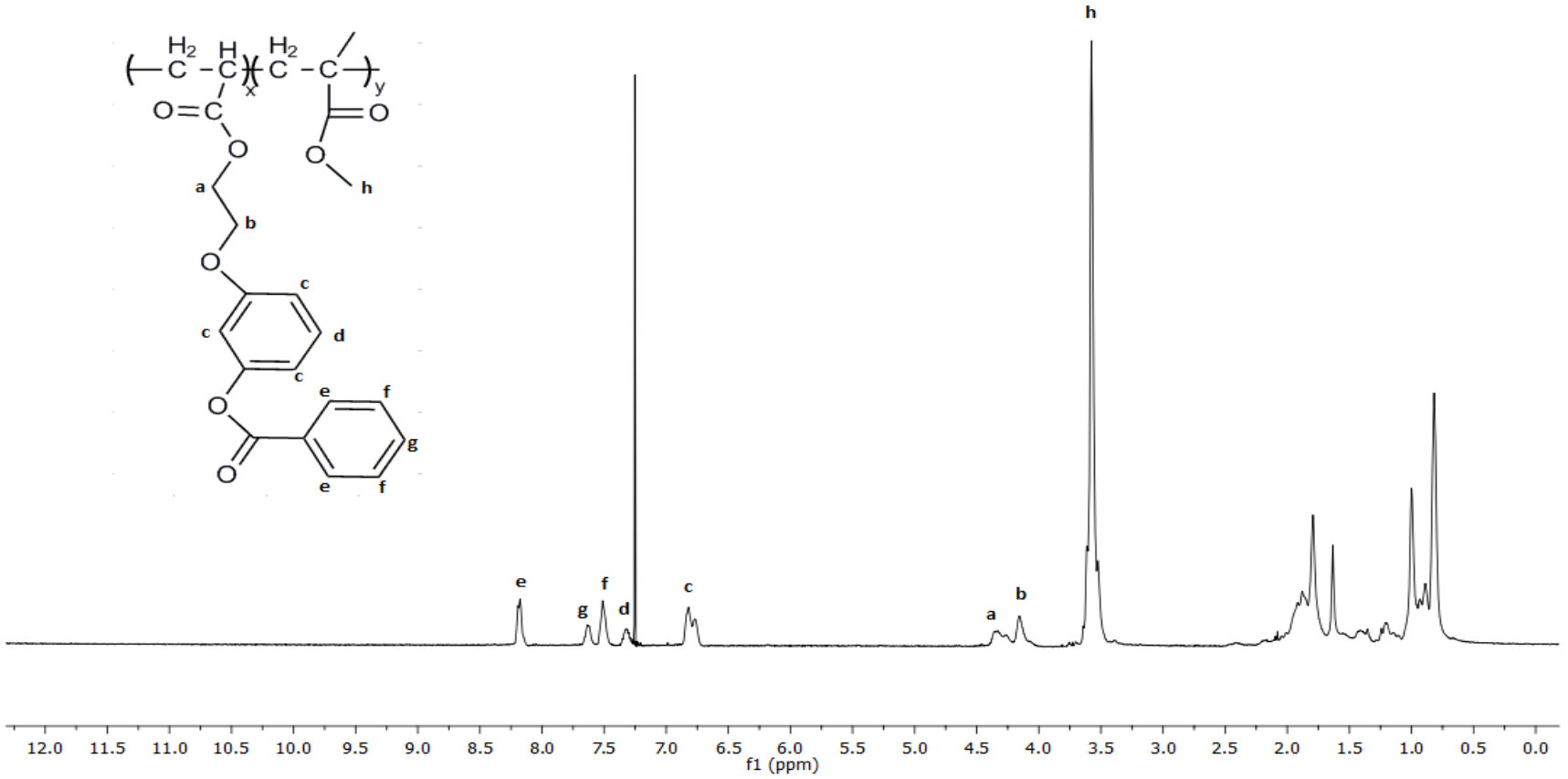


Figure 4.11. ^{1}H-NMR of the 10% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.

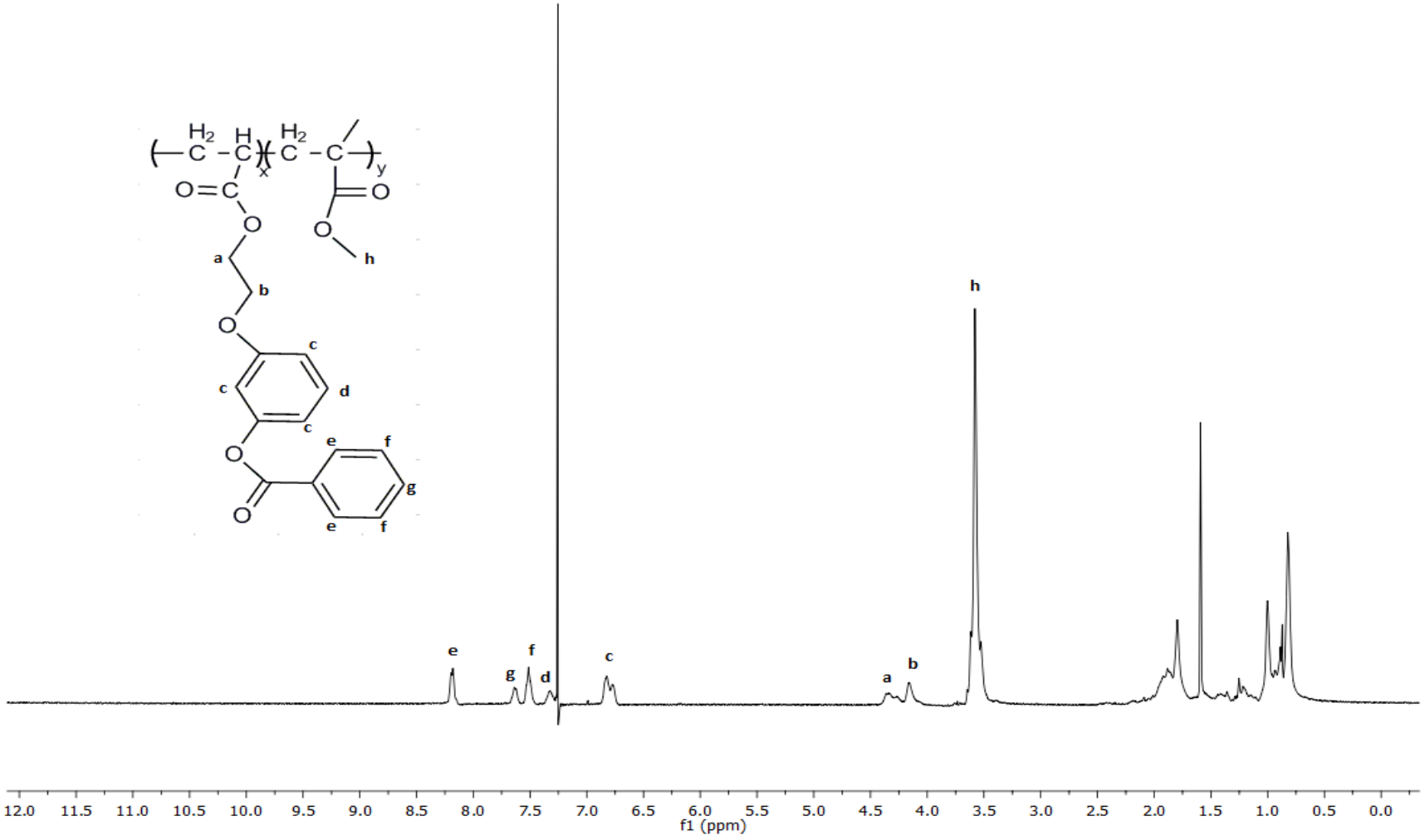


Figure 4.12. ^{1}H-NMR of the 20% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.

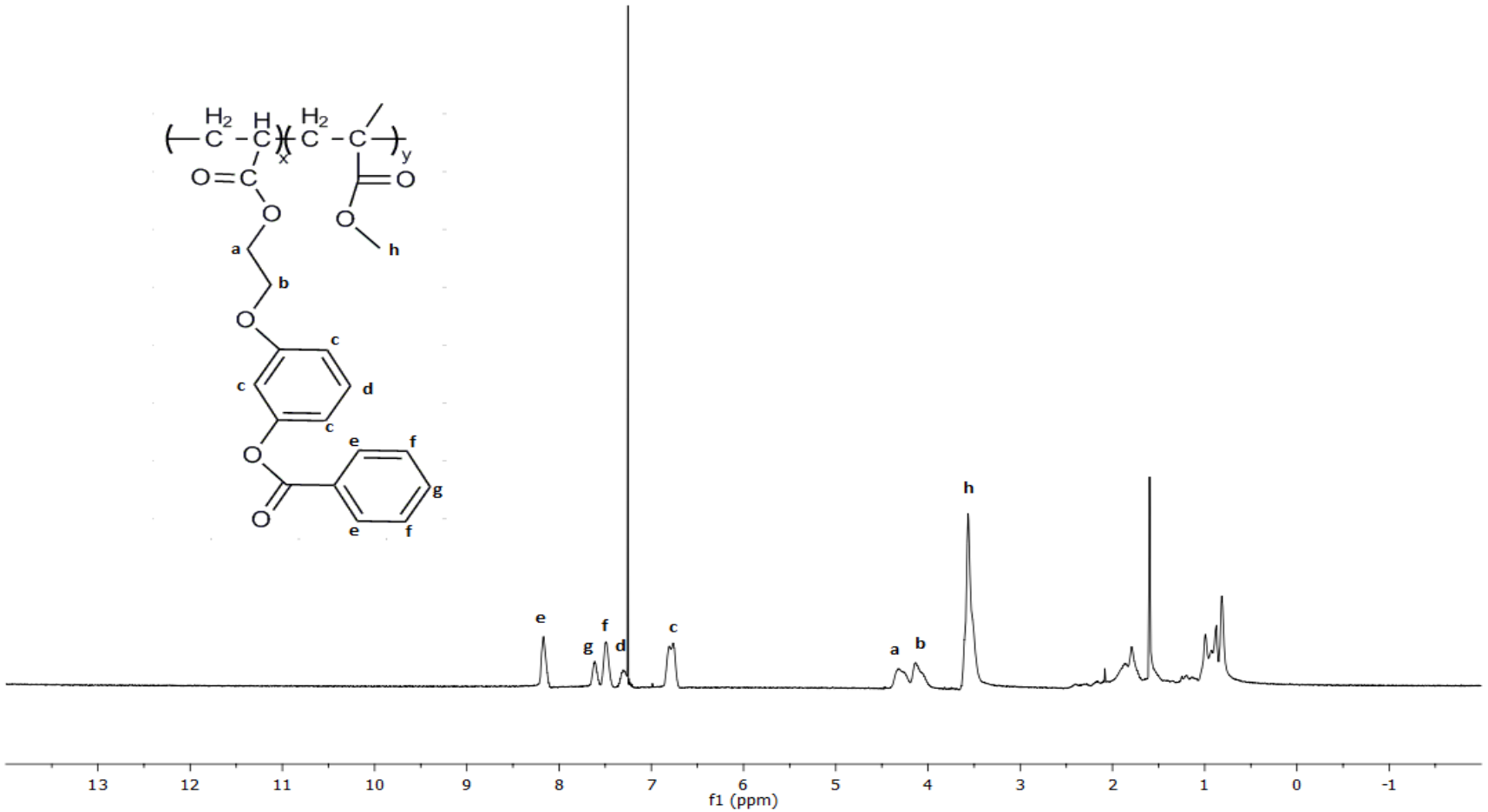


Figure 4.13. ^{1}H-NMR of the 30% copolymer of 3-(2-(acryloyloxy)ethoxy)phenyl benzoate with methyl methacrylate.

4.4. Analyzing UV Absorption Behaviors of the Polymers

Six solutions with different concentrations have been prepared for each polymer and their UV absorption behaviors were investigated to optimize the amount of UV absorber needed. UV absorbance of each polymer increased with the increasing UV absorber concentrations. Moreover, 30% copolymer showed the highest UV absorbance as expected among the other copolymers.

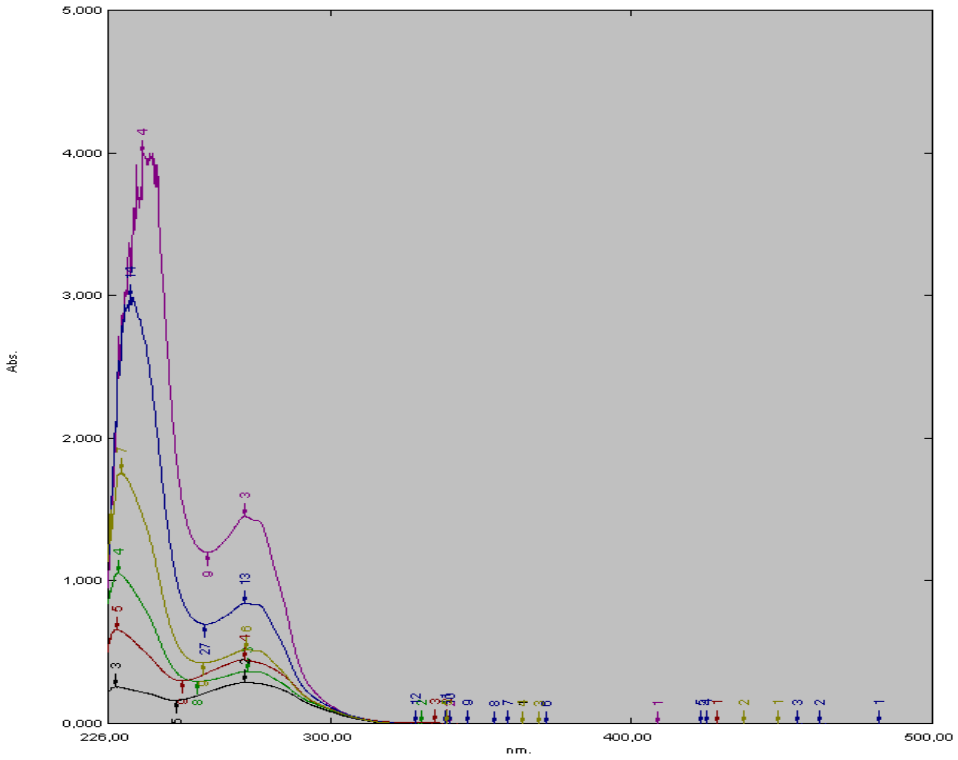


Figure 4.14. UV-Spectra of the homopolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).

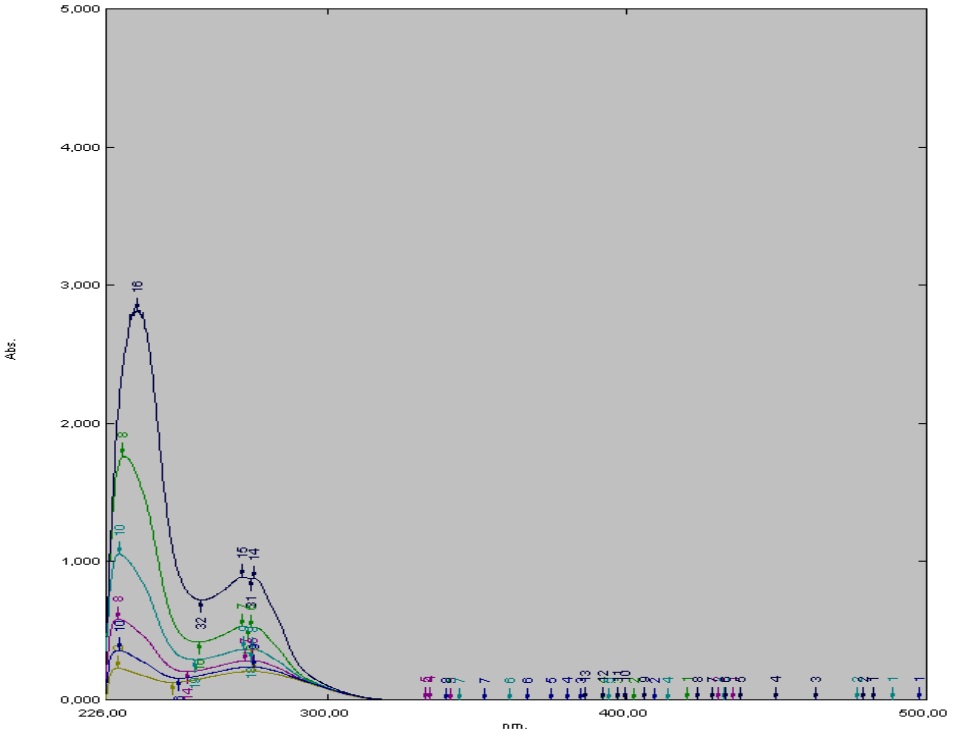


Figure 4.15. UV-Spectra of 30% copolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).

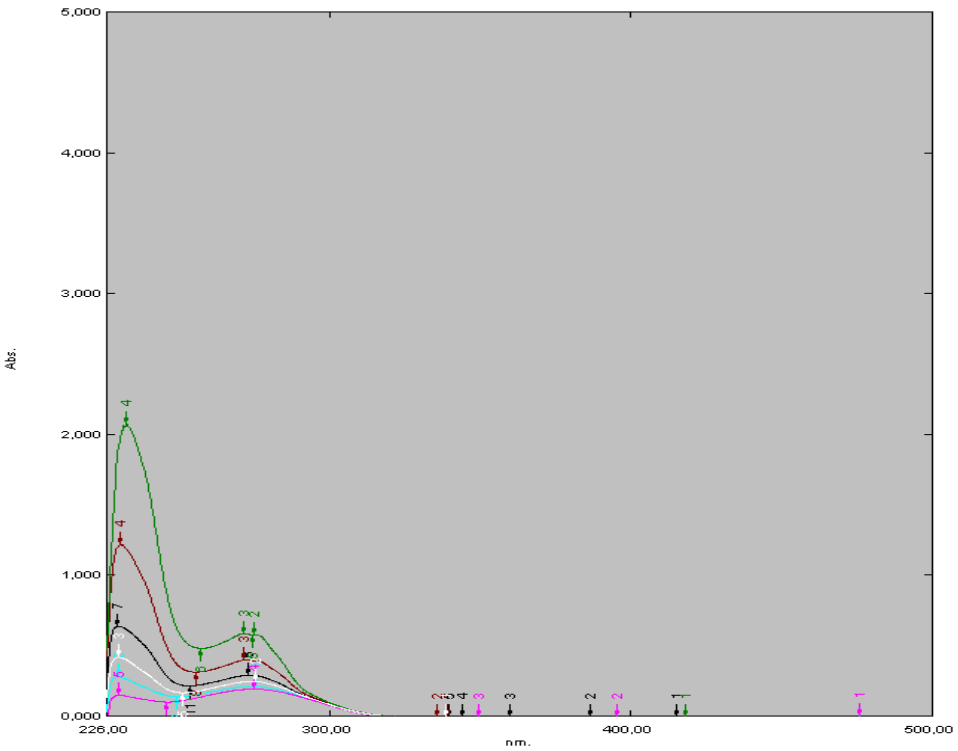


Figure 4.16. UV-Spectra of 20% copolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).

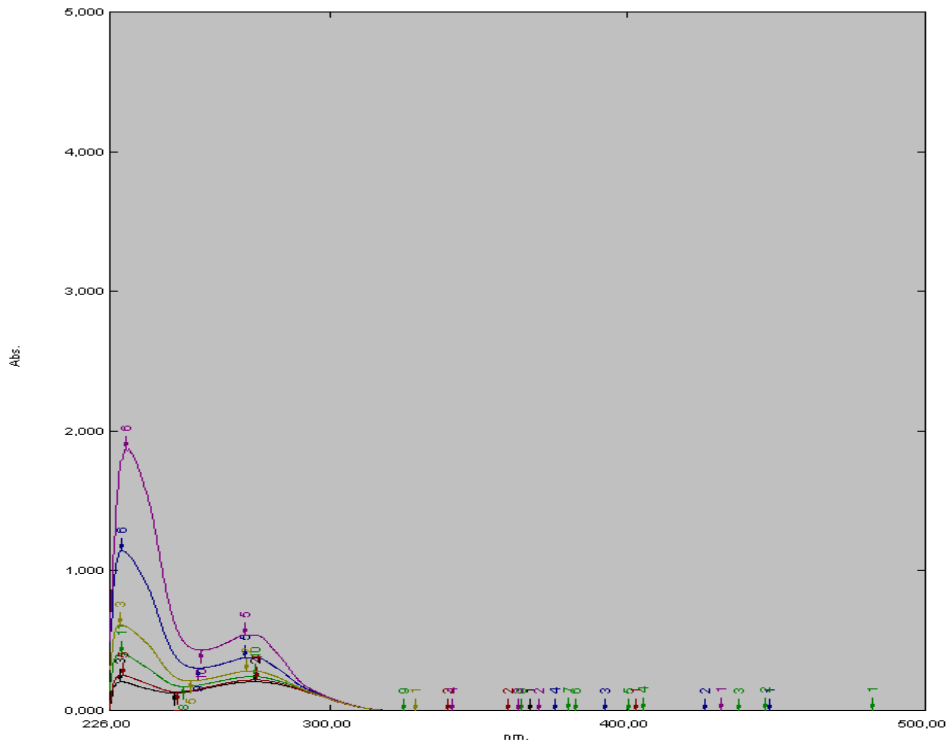


Figure 4.17. UV-Spectra of 10%-copolymer (0.210, 0.105, 0.052, 0.026, 0.013, 0.006 g/L).

The maximum absorption values were used to plot concentration-absorbance graph to find out the mass extinction coefficients (ε) of each polymer.

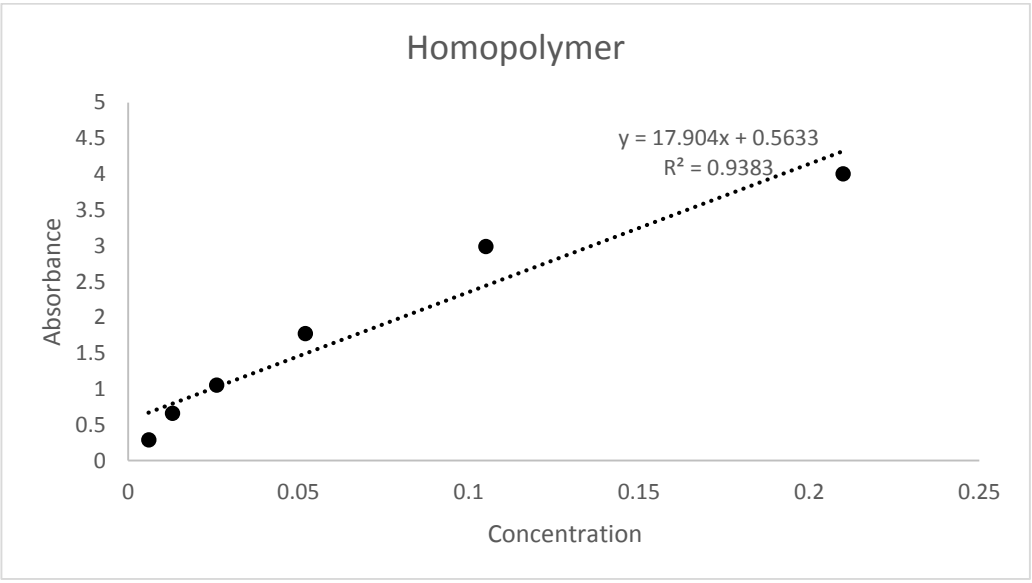


Figure 4.18. Absorbance-Concentration Graph of the homopolymer.

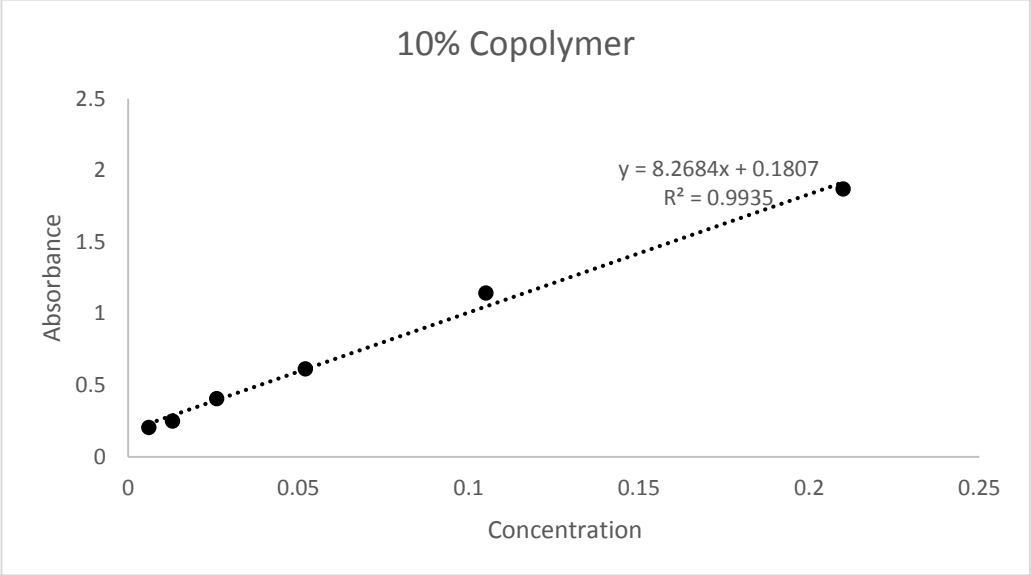


Figure 4.19. Absorbance-Concentration Graph of the 10% copolymer.

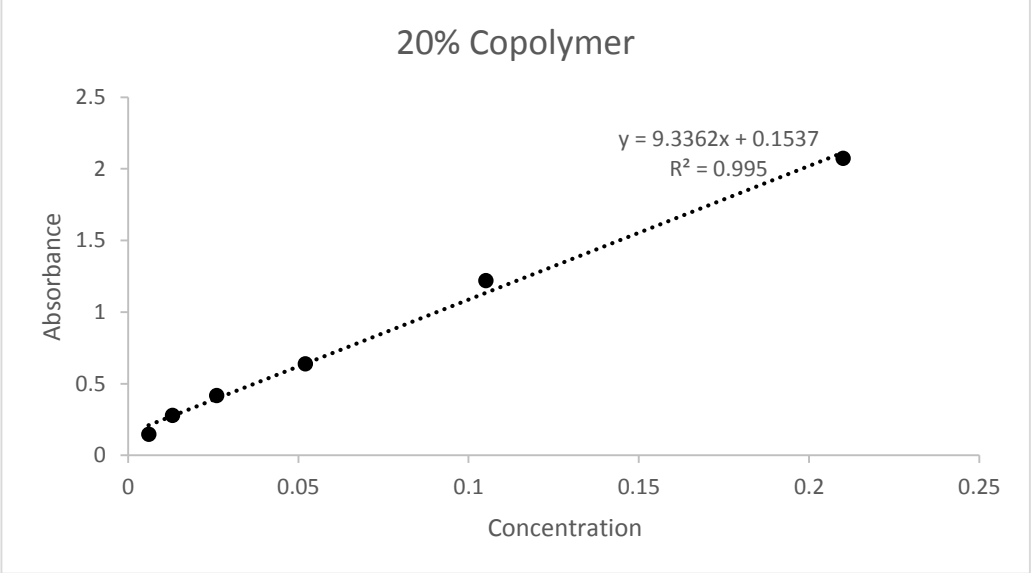


Figure 4.20. Absorbance-Concentration Graph of the 20% copolymer.

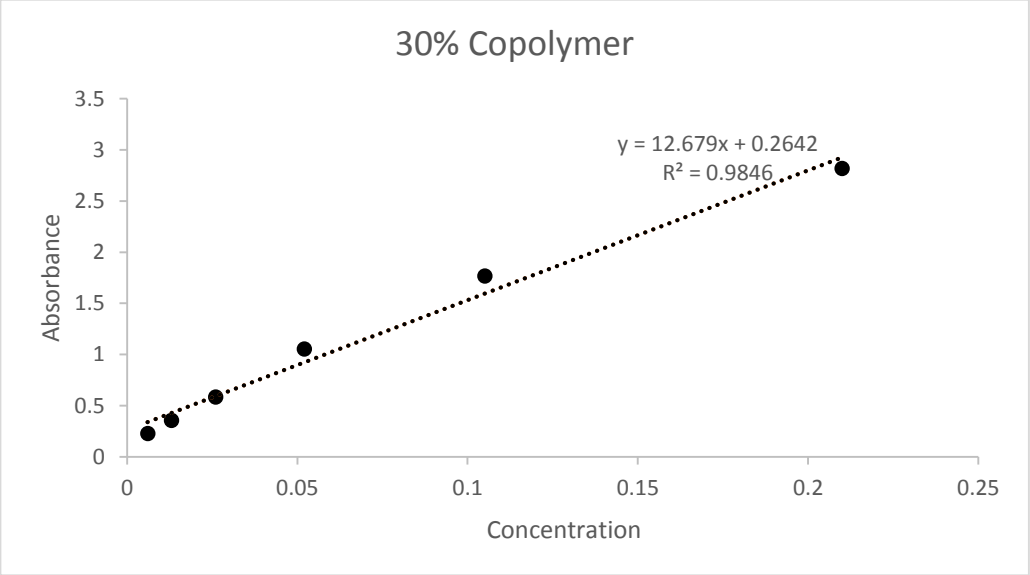


Figure 4.21. Absorbance-Concentration Graph of the 30% copolymer.

Table 4.2. Analyzing the absorption results of polymers.

Compound	**Mass extinction coefficient (ε_m/g^{-1}L cm^{-1})**	**Maximum Absorption Value**	**Wavelength of maximum absorption (nm)**
10% Copolymer	8.268	1.87	231.2
20% Copolymer	9.336	2.07	232.6
30% Copolymer	12.679	2.82	236.2
Homopolymer	17.904	4	237.6

4.4.1. UV-Spectra of the Polymers After UV Radiation

The polymers which have the same concentration (0.052 g/mL) were irradiated with UV light to induce Photo-Fries Rearrangement to compare the change in UV absorbance before and after the rearrangement. Figures shows the UV spectra of the polymer after 5, 10, 15, 20 minutes radiation respectively.

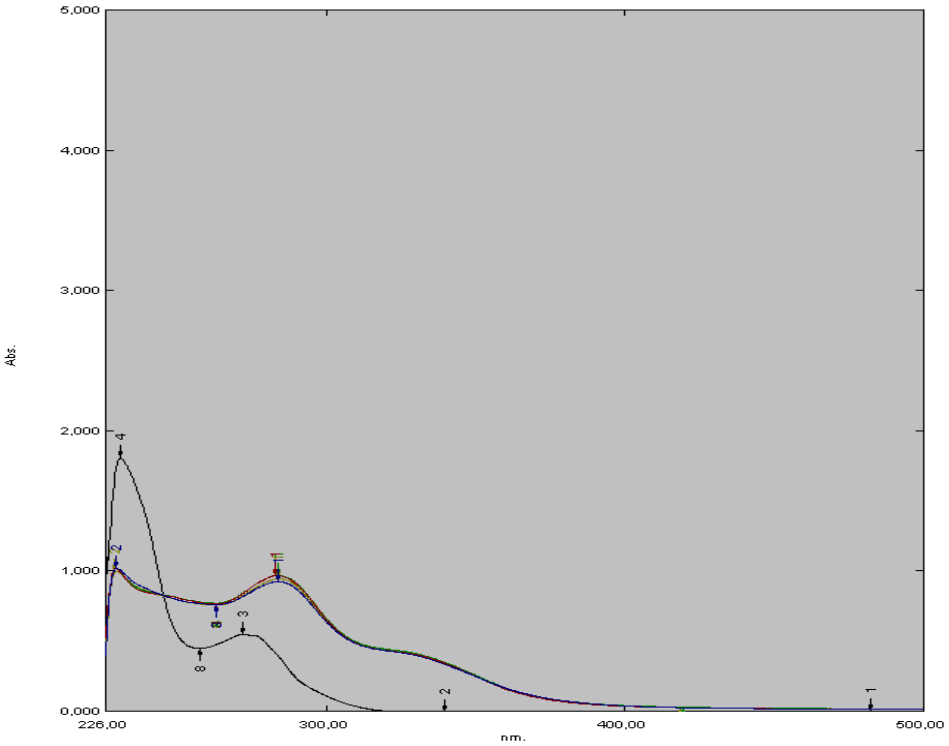


Figure 4.22. UV-Spectra of homopolymer after UV radiation.

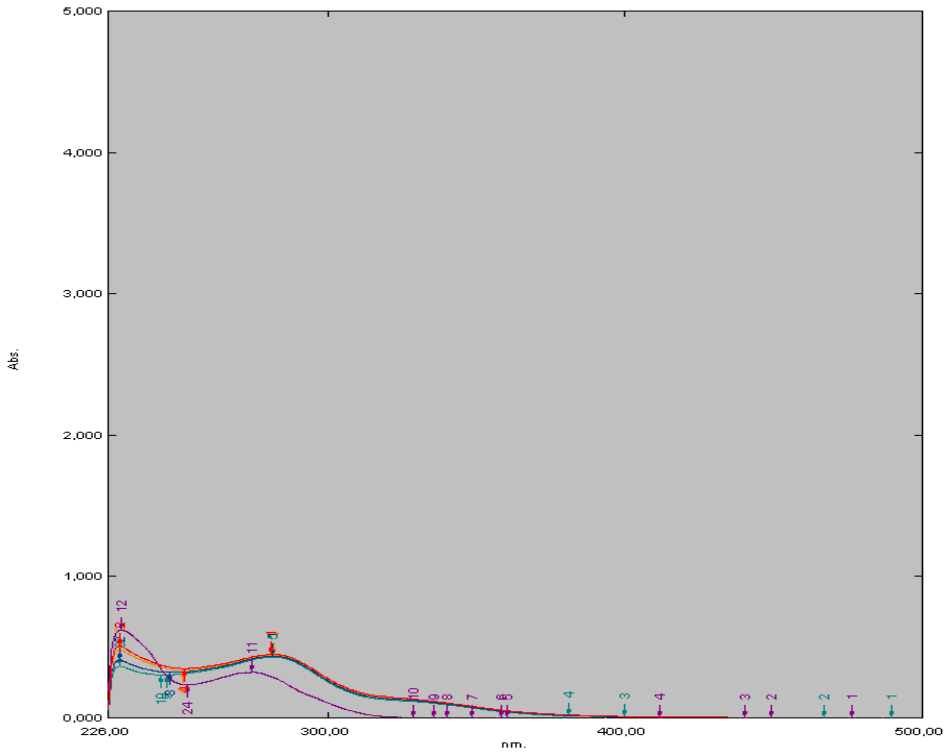


Figure 4.23. UV-Spectra of 30% copolymer after UV radiation.

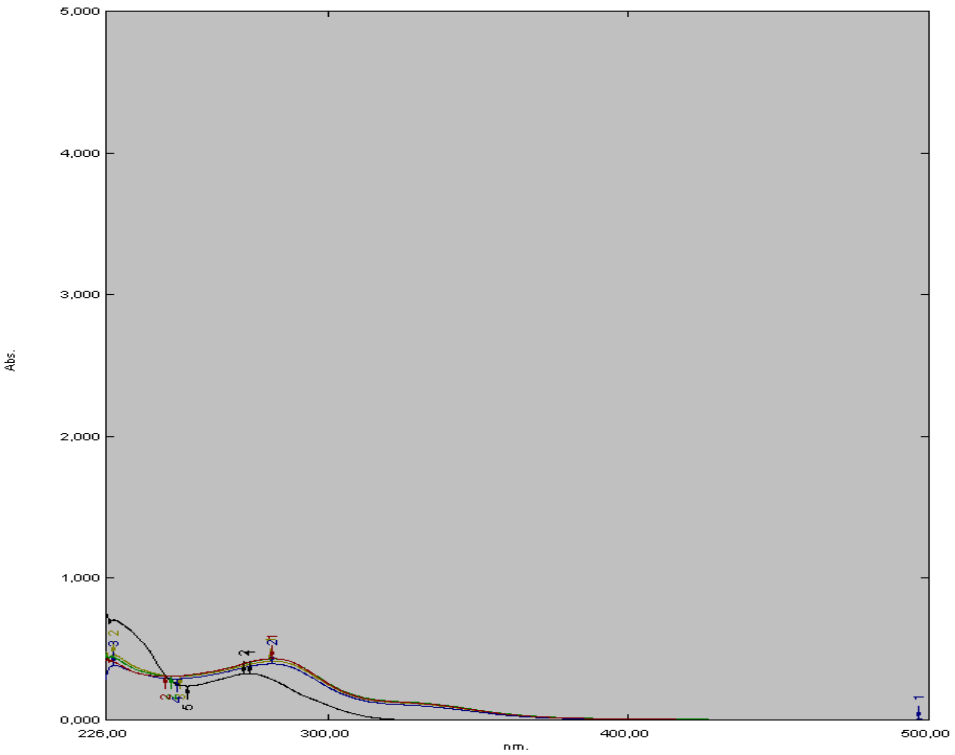


Figure 4.24. UV-Spectra of 20% copolymer after UV radiation.

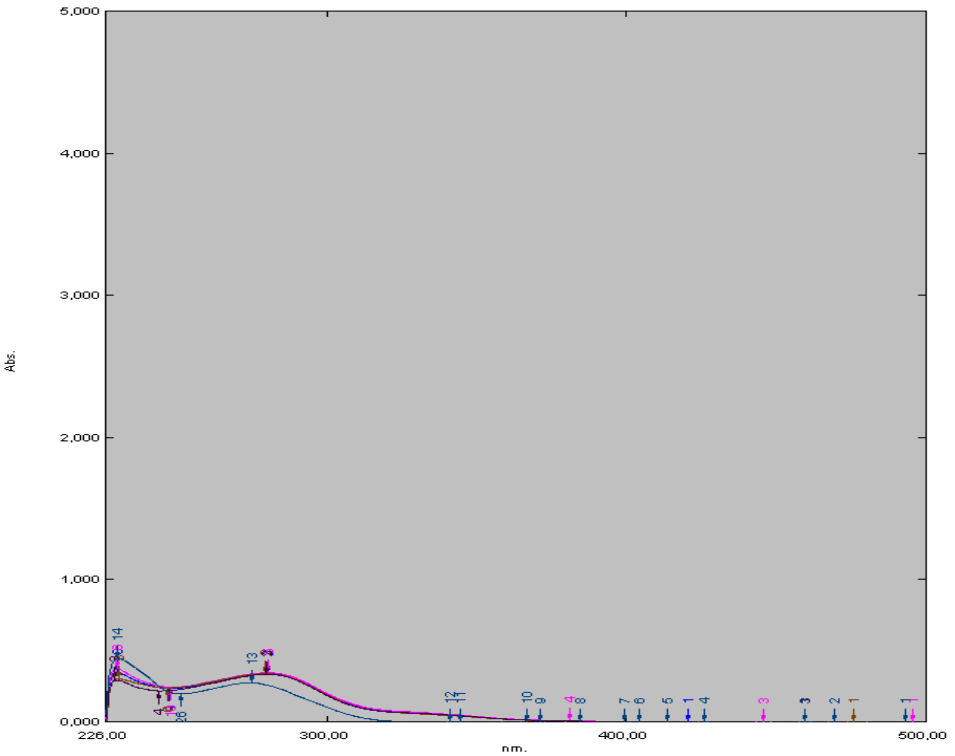


Figure 4.25. UV-Spectra of 10% copolymer after UV radiation.

As can be seen from the figure, the absorbance highly increases after the first 5 minutes radiation. As the radiation gets longer, no significant change in absorbance is observed, therefore we can conclude that almost all the molecules undergo Photo Fries rearrangement in the first 5 minutes. The rearranged product has a higher UV absorbance than the original compound near 300 nm, however near 230 nm absorption slightly decreases. Having this data, one can simply adjust the UV absorbance of the material just by changing the copolymer ratio or concentration.

A more concentrated solution of the monomer is prepared to observe the color change resulting from the Photo-Fries rearrangement. The prepared solution was colorless at first. After 5 minutes UV radiation, the solution had a yellow color which is typical for benzophenone type of monomers.

5. CONCLUSION

In this thesis, we have synthesized a novel UV absorber acrylate monomer and its copolymers with methyl methacrylate. The monomer was characterized by ^{1}H-NMR, ^{13}C-NMR and IR Spectrophotometer. The polymers were characterized by ^{1}H-NMR and GPC instrument. Their UV absorption behaviors before and after the UV radiation were investigated by UV- Spectrophotometer. UV absorption of the copolymers were increased as the UV absorber moiety increased on the polymer chain. Moreover, as the concentration of the polymer solution was increased, the absorption also increased as expected.

Although there are several benzophenone type UV absorbers, they have some limitations as mentioned earlier. To overcome these problems, we have synthesized a monomer that undergoes Photo-Fries Rearrangement under UV light. The monomer is colorless and miscible in organic solvents. When exposed to UV light it undergoes rearrangement and becomes slightly yellow. Therefore yellowing, which is a common problem for these type of UV absorbers, is prevented. Moreover, due to the presence of hydroxyl groups these compounds are usually immiscible in organic solvents which limits their use in applications. Because of having no hydroxyl group before the rearrangement, our synthesized monomer have no miscibility problem in organic solvents.

To sum up, we have synthesized a new compound that would be used as a UV protecting material in outdoor applications. The UV absorber moiety on the polymer chain can be adjusted to optimize the conditions in any applications which can be the subject of a further study.

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