SYNTHESIS AND PROPERTIES OF WEATHERABLE POLYMERS FROM HYDROXYBENZOPHENONES

by

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To My Sisters;

Helin and Sevgi

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ABSTRACT

SYNTHESIS AND PROPERTIES OF WEATHERABLE POLYMERS DERIVED FROM HYDROXYBENZOPHENONES

In this thesis, we have synthesized polymers with UV absorbing moieties in their structure which give them resistance to the sunshine and thus, make them suitable for outdoors applications. These moieties were chosen such that they are rearranged to hydroxy benzophenone type of UV absorbers under ultraviolet radiation via Photo-Fries Rearrangement. In other words, these polymers had an improved weatherability. The project involved first the synthesis of the monomer, then the homo-polymerization of the monomer followed by the co-polymerization of it with methyl methacrylate and finally investigation of absorption behaviors of the polymers under ultraviolet radiation before and after Photo-Fries Rearrangement. Thus, synthesis and properties of polymers with potentially increased weatherability will be discussed.

ÖZET

HİDROKSİBENZOFENON İÇERİKLİ AÇIK HAVAYA DAYANIKLI POLİMERLERİN SENTEZİ VE ÖZELLİKLERİ

Bu tezde, güneşe ve açık hava şartlarına dayanıklı maddeler içeren polimerler sentezlendi. Polimerdeki bu maddeler morötesi ışımaya maruz kaldıklarında Foto-Fries Dönüşümüyle hidroksibenzofenonlara dönüşme özelliğine sahipler. Bu sayede, morötesi ışıması altında iken ilk olarak hidroksibenzofenon tipi morötesi ışıma absorplayan maddelere dönüşerek ikinci kez morötesi ışımadan gelen enerjiyi soğurma özelliği edinmiş oldular. Bu da polimerlerin daha uzun süre güneşe ve açık havaya dayanıklı hale gelmesini sağladı. Projedeki sentez aşamalarını öncelikle monomer sentezi daha sonra sentezlenen monomerlerin homo- ve metil metakrilat ile co-polimerlerinin sentezi ve en son olarak da bu polimerlerin morötesi ışıma altındayken absorplama özelliklerinin belirlenmesi ve bunların morötesi ışıma yapan bir reaktörde polimerlerin Foto-Fries Dönüşümüne maruz kaldıktan sonraki absorplama özellikleri ile kıyaslanması oluşturmaktadır.

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LIST OF ABBREVIATIONS

AIBN	Azobisisobutyronitrile
ESIPT	Excited State Intramolecular Proton Transfer
GPC	Gel Permeation Chromatography
IR	Infrared
NMR	Nuclear Magnetic Resonance
PDI	Poly Dispersity Index
PS	Poly Styrene
SEC	Size Exclusion Chromatography
TEA	Three Ethyl Amine
TLC	Thin Layer Chromatography
UV	Ultraviolet

1. INTRODUCTION

Weatherable Polymers

Polymeric materials that are used for outdoor applications must have resistance against long term outdoor exposure. Therefore, their resistance has to be improved by structural modifications or additives. These types of polymers are called weatherable polymers. Their physical properties are stabilized by incorporation of the several chemical additives into their structures. As a result, degradation of polymers by the effects of air (oxygen), light, temperature and other stimulants can be prevented. [1]

Weatherable polymers should contain many properties. They have to be:

- Stable under sunshine
- Resistant to scratch
- Resistant to chemicals
- High impact resistant
- Stable over a broad range of temperature

There are many applications of weatherable polymers in industry. Most commonly, they are used in automotive, textile, agriculture, cosmetics industries where they are used to protect the goods from the negative effects of the outdoor conditions.

Negative effects of sunshine are the most important problems for materials that are used in outdoor. Since the sun also emits ultraviolet light this cause degradation of the materials under this high energy radiation. Therefore, protection from the solar radiation is crucial for these materials. They can be protected from the ultraviolet radiation in two ways. First, materials may be designed such that they are UV transparent as a result they become resistant to UV radiation since they do not absorb light at the UV region. Second, materials may contain UV responsive chemicals in their structure which protect them from the negative effect of the light.

1.1.1. UV Transparent Polymers

UV transparent polymers are not influenced by the UV radiation coming from the sunshine. Such polymers do not contain any chromophores that absorb ultraviolet radiation. Therefore, UV light exposed by the sun is transmitted through the material without any degradation on the polymer matrix (Figure 1.1).

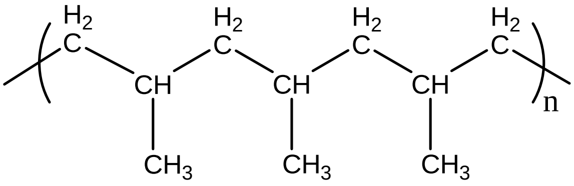


Figure 1.1. An example of transparent polymer

1.1.2. UV Responsive Polymers

Protection of materials from degradation by exposure of sunlight can be managed by adding UV responsive polymer (example in Figure 1.2.) into the material. Such UV responsive polymers have incorporated UV absorber moieties in their structure. Therefore, the UV absorbers in such polymers make materials that are coated with these polymers stable under UV radiation.

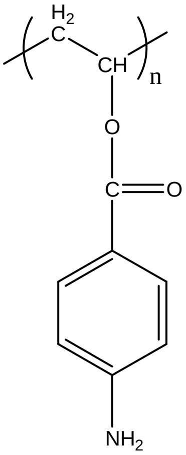
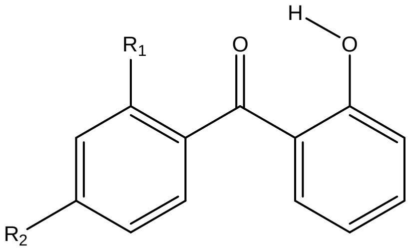


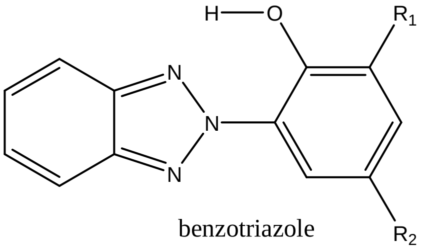
Figure 1.2. An example of UV responsive polymer used in cosmetics [2]

1.2. UV Absorbers

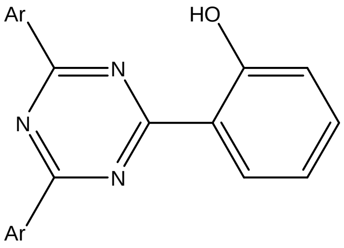
UV absorbers are additives that are protecting materials from the harmful effects of the UV radiation coming from the sunshine. In general, these materials show the following properties; absorption between 290 and 400 nm coupled with transparency in the visible range, stability during long term exposure to light and chemical inertness to their environment [3]. There are many commercially available compounds that have UV absorber properties. The most common ones are benzophenones, benzotriazoles, triazines, oxanilides, and cyanoacrylates (Figure 1.3.)



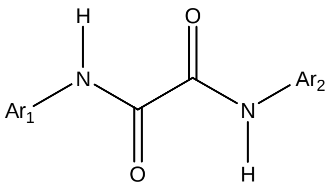
benzophenone



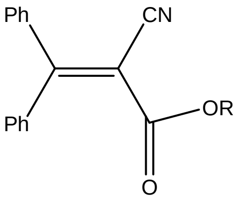
benzotriazole



triazine



oxanilide



cyanoacrylate

Figure 1.3. Examples of some common UV absorbers

1.2.1. Principle of UV Absorbers

For most of the UV absorbers, UV-protection of materials is achieved by a similar mechanism; they all make intramolecular hydrogen bonding (Figure 1.4.).

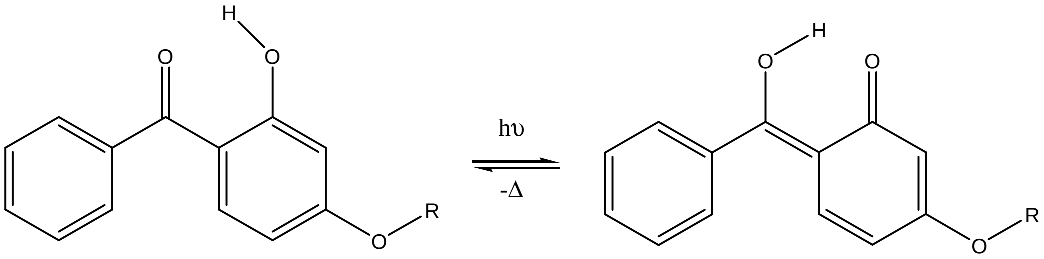


Figure 1.4. An example of reversible intramolecular proton transfer

The UV absorber molecules are excited to their first excited singlet state (S_1) by the UV radiation. Then, they undergo excited state intramolecular proton transfer (ESIPT) to create proton transferred species in their first excited singlet state (S'_1). The excited proton-transferred species (S'_1) then loses their energy by a nonradiative decay process in the form of thermal energy which is transferred to the matrix to form the ground state proton transferred species (S'_0). Thus in the overall process, the solar energy is dissipated in a nonradiative way and materials are protected from the UV radiation (Figure 1.5.). [4]

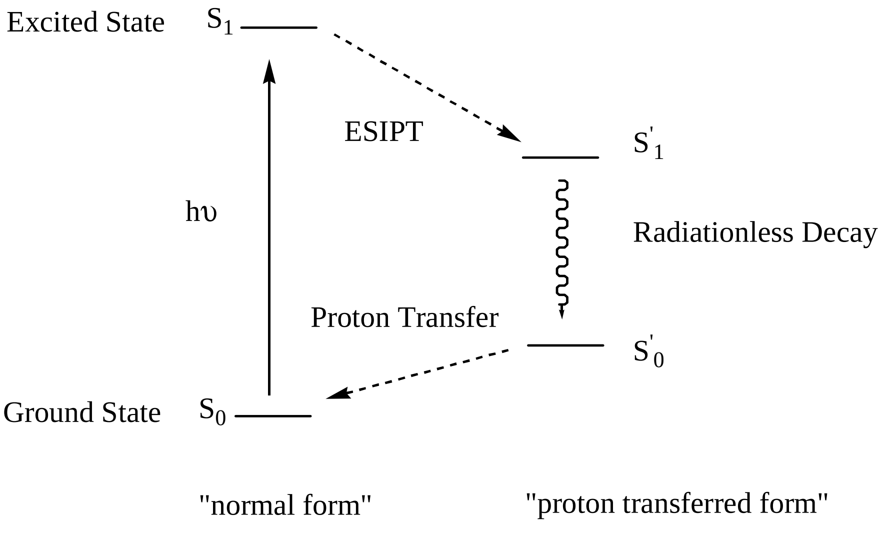
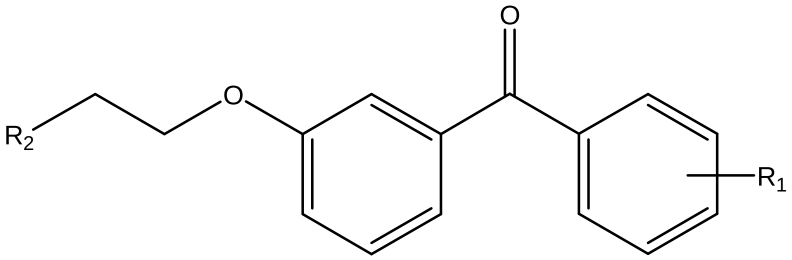


Figure 1.5. Energy dissipation of UV absorbers by intramolecular proton transfer

1.2.2. UV Absorbers in Application

UV absorbers can be introduced in two ways: they can be added directly into the material as small organic additives (Figure 1.6.) or they can be used in polymeric forms. Direct addition of UV absorbers into the polymeric matrices of materials is a very rapid and easy way to protect these materials from the harmful effects of the solar radiation. However, some problems may be encountered by this method. Firstly, small UV absorber molecules have a tendency to migrate to the surface of the polymeric matrices, and as a result, homogeneous distribution can not be obtained. This may reduce the life times of the UV absorbers. Secondly, stabilizer molecules may change the physical properties of the polymeric matrices. Therefore, materials may lose some important physical properties while protected from the UV radiation.



R_1: Alkyl or aryl

R_2: Hydrocarbyl acyloxy

Figure 1.6. An example of small molecule UV additives [5]

1.3. Polymeric UV Absorbers

UV absorbers are incorporated into the polymers rather than added directly into. Although these polymers may have some disadvantages, that is the most effective method to use UV absorbers. There are two ways to incorporate the UV absorbers into polymers: they can be added to the backbone as a repeat unit or they can be incorporated as pendant groups.

1.3.1. UV Absorbers at the Backbone of the Polymers

There are many examples of the polymers having polymeric backbone with UV absorbing moieties. Such polymers are obtained by condensation polymerization methods.

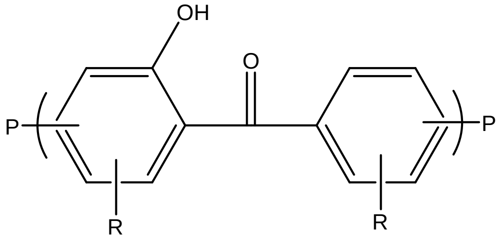


Figure 1.7. An example of polymer with UV absorber containing backbone [6]

The example in Figure 1.7. displays hydroxy benzophenone moieties belonging to a polyarylate polycarbonate blend. These types of blends or copolymers have the ability to absorb UV radiation.

1.3.2. UV Absorbers on the Pendant Group of the Polymers

UV absorber moieties can be added as pendant groups. The UV absorber molecules can be condensed with an olefinic acrylic chloride (methacrloyl-, acryloyl- chloride) and then the olefinic part of the resulting monomer will be polymerized via radical polymerization techniques. There are many examples of UV stable polymers containing the UV-stabilizers on their pendant groups (Figure 1.8.).

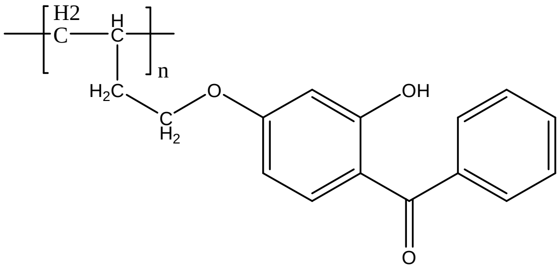


Figure 1.8. An example of a monomer which contains UV stabilizer on the pendant group [2]

Polymeric UV absorbers have many advantages when compared with the small UV absorber molecules. However, they may also have some problems. For examples polymers having hydroxy benzophenone type of UV absorbers in their repeating units have some miscibility and solubility problems due to the phenolic groups. In the literature, to cope with these problems aromatic esters which can undergo *in situe* Photo-Fries Rearrangement and give the hydroxybenzophenone moieties were used. Our project as will be discussed in the following sections mainly involves a similar process where this time the pendant groups will undergo the Photo-Fries Rearrangement.

1.4. Photo-Fries Rearrangement

Fries Rearrangement is known as the rearrangement of aromatic esters and amides into the corresponding phenol and aniline in the presence of $AlCl_3$. Although the mechanism has not been clarified yet the most accepted mechanism is the radical mechanism (Figure 1.9.).

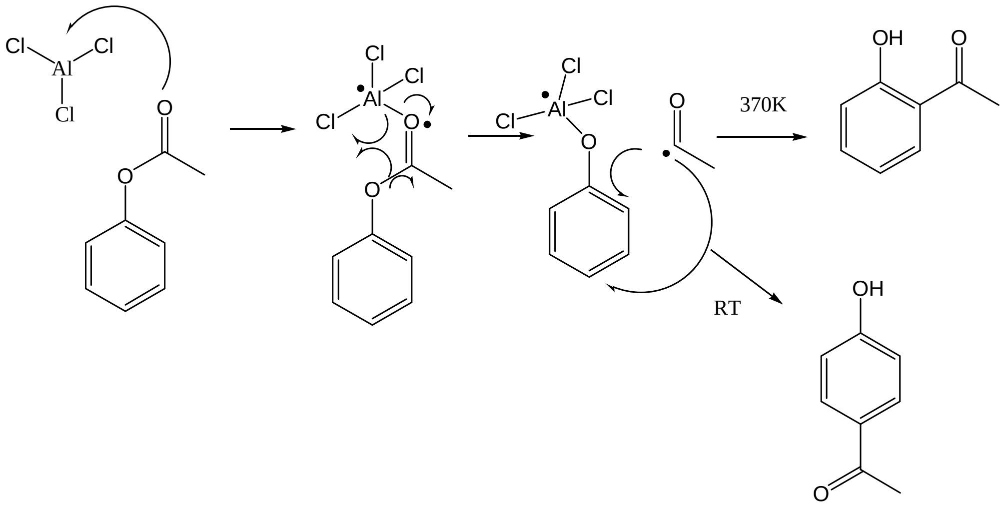


Figure 1.9. Mechanism for the Fries Rearrangement [7]

The same rearrangement can be carried out via a photochemical process called Photo-Fries Rearrangement. This type of rearrangement occurs under UV radiation via, again, a radical mechanism. Photons cleave ester (amide) bond homolytically and radical on the oxygen is delocalized in the aromatic ring (Figure 1.10.). Then, termination step occurs by coupling with the carbonyl carbon radical.

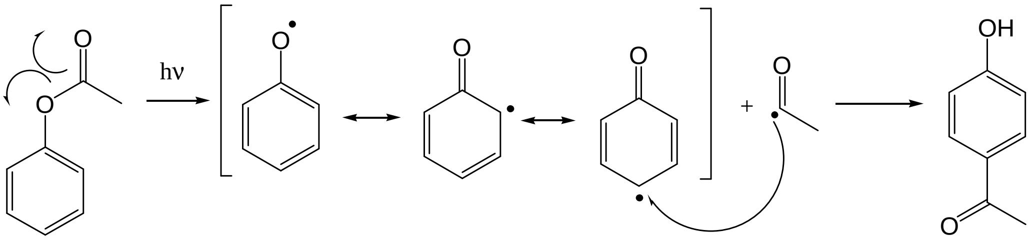


Figure 1.10. Mechanism of Photo-Fries Rearrangement [8]

This type of rearrangement gives ortho- and para- products as a result of different pathways described in the literature by Bellus [8]. However, the ortho- one is the major product.

1.4.1. Polymers Capable of Forming UV Stabilizers via Photo-Fries Rearrangement

Hydroxy benzophenone types of UV stabilizers have some problems as mentioned earlier. The first problem is the process called photo yellowing. Most of the hydroxy benzophenones absorb radiation around UV region with a tail through 400 nm that results in a yellow appearance of the materials. [9] The Figure 1.11. displays the UV spectrum of 2, 4-hydroxy benzophenone (2, 4$(OH)_2$-benzophenone) in ethanol at 25 °C. We can see the characteristic absorption behaviors of hydoxy benzophenones from this spectrum. It has a tail through 400 nm that is typical for hydroxy benzophenones. The second problem with hydroxy benzophenone is the solubility. Because of the hydroxy unit on the stabilizer molecules, solubility in organic solvents becomes a problem. After polymerization step, also miscibility problems occur with other polymers.

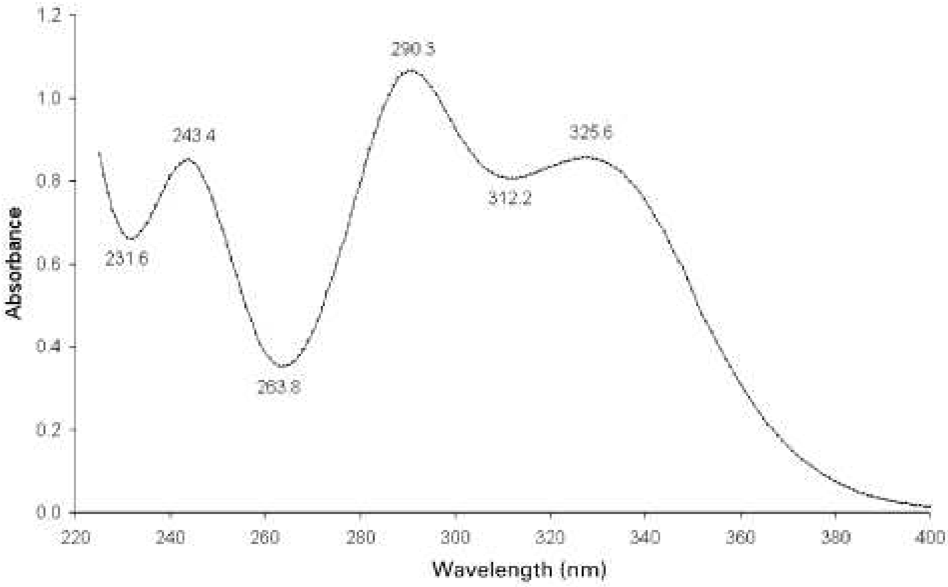


Figure 1.11. UV-Vis Spectrum of 2, 4$(OH)_2$-benzophenone in Ethanol at 25 °C [9]

Photo-Fries Rearrangement in principle should enable the synthesis of hydroxybenzophenone type of polymers where aromatic esters can be used as precursors for the uv absorbing hydroxybenzophenone moities. These type of polymers should have the ability to protect materials from the solar radiation by undergoing Photo-Fries Rearrangement to form the UV absorbing moieties.

In addition, UV absorbers obtained by Photo-Fries Rearrangement formed at the surface of the polymers may protect the remaining polymer matrix underneath. When they are washed out with time, the remaining part will be ready to undergo the rearrangement to form a new hydroxy benzophenone. By this way, polymers will have an elongated life time.

Such polymers with hidden (precursor) stabilizers which can be converted to hydroxy benzophenone via Photo-Fries Rearrangement under solar radiation have been reported in condensation polymers. Block copolyestercarbonate in the Figure 1. 12. is an example of such polymers.

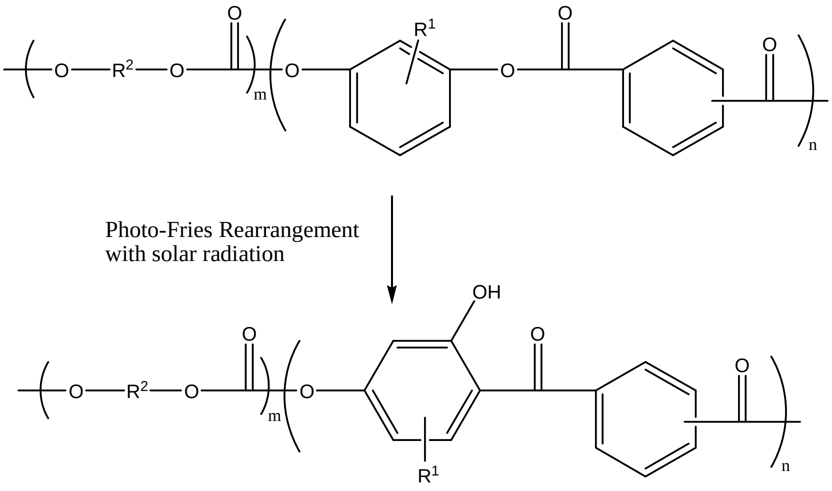


Figure 1. 12. Example of Weatherable Polymers Having UV Stabilizer via Photo Fries Rearrangement on the Backbone [10]

2-vinyl-resorcinol monobenzoate is another example of a monomer of the polymers that is forming UV stabilizer via Photo-Fries Rearrangement under solar radiation (Figure 1. 13.). This is an example of polymer that has a hidden stabilizer unit at the pendant group of the polymer.

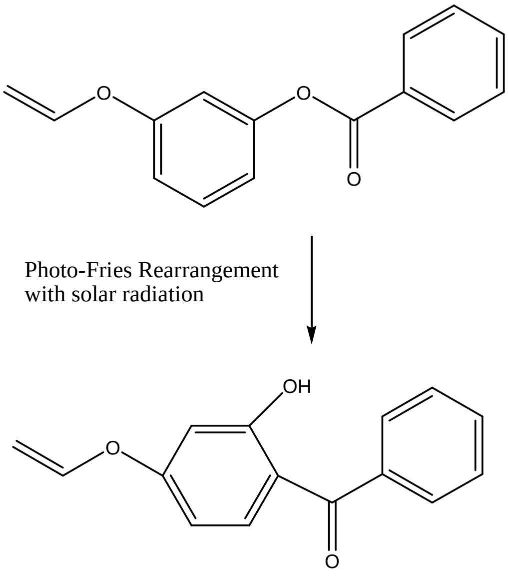


Figure 1. 13. Example of the Monomer of a Weatherable Polymer that have UV Stabilizer via Photo Fries Rearrangement at the Pendant Group [11]

2. OBJECTIVES

UV stabilizing moieties have been used in polymeric forms to form weatherable polymers that are stable for years. There are many examples of weatherable polymers having hydroxy benzophenone type of stabilizer in their repeating units. However, these types of stabilizers have problems: firstly, they absorb radiation through 400 nm which creates a yellow appearance for the polymer as mentioned earlier. The second problem is the solubility and miscibility problems of the UV absorbing polymers due to the hydroxyl units on the benzophenone structure.

In the literature, there were several attempts to solve these problems by using Photo-Fries Rearrangement. Synthesis of polymers having repeating units that are capable to form hydroxy benzophenone under solar radiation via Photo-Fries Rearrangement helped to solve problems. However these polymers were made by only condensation polymerization techniques.

In this study, the goal was to synthesize a photo-responsive olefinic monomer, 3-(methacryloyloxy) phenyl benzoate, and its corresponding homo- and copolymers with methyl methacrylate. The resulting polymers and copolymers should undergo the Photo-Fries Rearrangement under solar radiation which will result in a uv resistant weatherable polymer. Thus, the investigation of the absorption behavior of these polymers under UV radiation was also targeted.

A second target of this study was the synthesis of a second set of polymer from the monomer, 3-(2-(methacryloyloxy) ethoxy) phenyl benzoate which again should give a uv-responsive weatherable polymer.

EXPERIMENTAL

3.1. Monomer Synthesis

3.1.1. Materials

Resorcinol (Acros Organic, 98%), benzoyl chloride (Acros Organic, 99%), triethylamine (Aldrich, 99.5%), sodium bisulfate (Fluka, 95%), metacryloylchloride (Aldrich, 97%), ethylene carbonate (Aldrich, 99%), triphenylphosphine (Fluka, 98.5%), aluminum oxide (Fluka, basic) were used as received without purification. Methyl methacrylate (Aldrich, 99%) was used as it is received. Azobisisobutyronitrile (AIBN) (Aldrich, 99%) was purified by recrystallyzation in methanol. All glassware, needles, and stirring bars were dried overnight in an oven at 150 ^{o}C and purged with nitrogen before use.

The solvents: methylene chloride, toluene, methanol, hexane, ethyl acetate and toluene were all obtained from Merck and used as received.

3.1.2. Apparatus

^{1}H-NMR and ^{13}C-NMR were recorded using a Varian Gemini 400MHz spectrometer. GPC analyses were done using a Viscotek VE2001 GPC Solvent/Sample Model with a PL Gel 5 μm MIXED-C Column that was calibrated against polystyrene standards. All UV-Vis spectra were measured with the UV-2401PC (Shimadzu) UV spectrophotometer. Photoreactions were performed in a custom made UV reactor.

3.1.3. Synthesis of Resorcinol Monobenzoate

Resorcinol (55 g, 0.5 mol), triethylamine (101.19 g, 1 mol) , methylene chloride (280 mL) were added into 1000 mL three-necked round bottom flask fitted with a condenser and magnetic stirring bar. Benzoyl chloride (14 g, 0.1 mol) in methylene chloride (25 mL) was added into the mixture dropwise. Addition was complete in 20 min. The mixture was washed with 2N HCl, then three times with 250 mL water. The organic layer was separated, dried over sodium bisulfate and solvent was evaporated under reduced pressure to give 17.28 g of mixture of resorcinol mono- and diesters. Resorcinol monoester was purified via basic aluminum oxide column chromatography (hexane: ethyl acetate / 4: 1) in 54 % yield.

^{1}H NMR ($CDCl_3$): δ= 6.71 (d, 2H, aromatic *H*), 6.78 (d, 1H, aromatic *H*), 7.26 (t, 1H, aromatic *H*), 7.51 (t, 2H, aromatic *H*), 7.64 (t, 1H, aromatic *H*), 8.20 (d, 2H, aromatic *H*) ppm.

^{13}C NMR ($CDCl_3$): δ= 165.68 [*C*=O], 152.01 (aromatic C, *C*O), 156.96 (aromatic C, *C*O), 133.95 (aromatic C), 130.46 (aromatic C), 130.38 (aromatic C), 129.65 (aromatic C), 128.83 (aromatic C), 114.00 (aromatic C), 113.96 (aromatic C), 113.55 (aromatic C), 113.52 (aromatic C), 109.63 (aromatic C) ppm.

3.1.4. Synthesis of 3-(Methacryloyloxy) Phenyl Benzoate

Resorcinol monobenzoate (10 g, 0.0467 mol), triethylamine (4.73 g, 0.0467 mol), methylene chloride (25 mL) were added in into 100 mL three-necked round bottom flask fitted in ice on magnetic stirring bar. Methacryloyl chloride (5.37 g, 0.0514 moles) in methylene chloride (5 mL) was added into the mixture drop wise. After addition was complete, the mixture was brought to room temperature. The mixture was washed with sodium bicarbonate (saturated, 50 mL), then three times with 50 mL water. The organic layer was separated, dried over sodium bisulfate and solvent was evaporated under reduced pressure to give 10 g of monomer in 76 % yield.

^{1}H NMR ($CDCl_3$): δ= 2.06 (s, 3H, *H*, $COCH_3$), 5.77 (s, 1H, *H*, HC=C), 6.36 (s, 1H, *H*, HC=C), 7.11 (m, 3H, aromatic *H*), 7.44 (t, 1H, aromatic *H*), 7.51 (m, 2H, aromatic *H*), 7.64 (m, 1H, aromatic *H*), 8.20 (m, 2H, aromatic *H*) ppm.

^{13}C NMR ($CDCl_3$): δ= 165.72 [*C*=O], 165.06 [*C*=O], 151.67 (aromatic C, *C*O), 135.87 (olefinic C), 134.07 (aromatic C), 130.04 (aromatic C), 128.87 (aromatic C), 127.89 (olefinic C), 18.64 (aliphatic C) ppm.

3.1.5. Synthesis of 3-Acetoxyphenyl Benzoate

Resorcinol monobenzoate (0.235 g, 1.1 mmol.), triethylamine (0.111 g, 1.1 mmol), methylene chloride (7 mL) were added into a 25 mL three-necked round bottom flask fitted with a condenser and magnetic stirring bar. Acetyl chloride (0.079 g, 1 mmol) in methylene chloride (3 mL) was added into the mixture drop wise. Addition was complete in 5 min. Reaction was monitored with thin layer chromatography (TLC) and completed at 2 hours. The mixture was washed first with NaOH (5 %) to remove excess resorcinol monobenzoate and second with 2N HCl to remove triethylamine, then three times with 250 mL water. The organic layer was separated, dried over sodium bisulfate and solvent was evaporated under reduced pressure to give 0.132 g of 3-acetoxyphenyl benzoate with 51 % yield.

^{1}H NMR ($CDCl_3$): δ= 2.22 (s, 3H, CH_3 *H*), 6.98 (m, 3H, aromatic *H*), 7.44 (m, 3H, aromatic *H*), 7.57 (m, 1H, aromatic *H*), 8.12 (m, 2H, aromatic *H*) ppm.

^{13}C NMR ($CDCl_3$): δ= 20.07 (OC*C*H_3), 114.63 (aromatic), 118.04 (aromatic), 118.14 (aromatic), 127.60 (aromatic), 128.27 (aromatic), 128.75 (aromatic), 129.18 (aromatic), 132.71 (aromatic), 150.17 (aromatic), 150.37 (aromatic), 163.73 [*C*=O], 168.03 [*C*=O] ppm.

3.1.6. Synthesis of Symmetrical Resorcinol Diether by the Reaction of Resorcinol Monobenzoate and Ethylene Carbonate

Resorcinol monobenzoate (3.85 g, 0.014 moles), ethylene carbonate (2.46 g, 0.028mol) and triphenylphosphine (0.011 g, 4.2×10^{-5} mol) were added into 25 mL one-necked round bottom flask fitted and magnetic stirring bar in constant pressure. Reaction was carried out under nitrogen at 170 ^{o}C for 5 h. The resulting mixture was dissolved in methylene chloride and washed three times with 25 mL water. The product was purified by silica column chromatography (methylene chloride) in 17% yield. [14]

^{1}H NMR ($CDCl_3$): δ= 4.20 (t, 4H, *H*, O-CH_2), 4.57 (t, 4H, *H*, O-CH_2), 6.48 (m, 3H, aromatic *H*), 7.12 (m, 1H, aromatic *H*), 7.34 (t, 4H, aromatic *H*), 7.45 (m, 2H, aromatic *H*) 7.96 (d, 4H, aromatic *H*) ppm.

^{13}C NMR ($CDCl_3$): δ= 63.52 (O*C*H_2), 66.33 (O*C*H_2), 102.36 (*C*, aromatic), 107.69 (*C*, aromatic), 128.59 (*C*, aromatic), 129.97 (*C*, aromatic), 130.16 (*C*, aromatic), 130.30 (*C*, aromatic), 133.31 (*C*, aromatic), 160.10 (O*C*H, aromatic), 166.72 [*C*=O] ppm

3.2. Polymer Synthesis

3.2.1. The Solution Polymerization of Olefinic Monomers with AIBN

All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization was conducted in a one-necked round bottom flask. The solid initiator Azobisisobutyronitrile (AIBN) and the monomer(s) were added into a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 minutes. Toluene (1:1 in volume with monomers) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the initiator and monomer were dissolved. Polymerization was carried out under nitrogen at 70 ^{o}C for 4 h. The final polymer was dissolved in methylene chloride, precipitated into hexane and dried in a vacuum oven overnight. [15]

Monomer conversion was determined by gravimetric methods. The determination of the molar masses and the molecular weight distributions has been carried out by size exclusion chromatography (SEC) with a refractometric detector with poly (styrene) (PS) standards. Characterization of the polymer samples has been performed by proton and carbon NMR spectroscopy.

3.2.2. The Procedure for the Purification of the Resulting Polymers

Resulting polymers were precipitated into methylene chloride / hexane and dried in a vacuum oven overnight. The pure polymers were dissolved in chloroform and analyzed by GPC and NMR.

3.2.3. Solution polymerization of 3-(methacryloyloxy) phenyl benzoate

All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization was conducted in a one-necked round bottom flask. The solid initiator Azobisisobutyronitrile (AIBN) ($1.74x10^{-3}$ g, $1.06x10^{-5}$ mmol) and 3-(methacryloyloxy) phenyl benzoate (0.6 g, 0.0021 mol) were added into a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 minutes. Toluene (1 mL) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the initiator and monomer were dissolved. Polymerization was carried out under nitrogen at 70 ^{o}C for 4 h. The final polymer was dissolved in methylene chloride, precipitated into hexane and dried in a vacuum oven overnight.

^{1}H NMR ($CDCl_3$): δ= 0.87 (m, *H*, at the backbone), 1.43 (m, *H*, at the backbone), 1.49 (m, *H*, at the backbone), 1.70 (s, *H*, at the backbone), 1.73 (s, *H*, at the backbone), 2.21 (m, *H*, at the backbone), 6.96 (m, aromatic *H*, on the pendant group), 7.39 (m, aromatic *H*, on the pendant group), 7.52 (m, aromatic *H*, on the pendant group), 8.06 (m, aromatic *H*, on the pendant group), ppm.

3.2.4. Solution copolymerization of 3-(methacryloyloxy) phenyl benzoate with methyl methacrylate

Experiment 1. (Preparation of 10 % copolymer), All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization was conducted in a one-necked round bottom flask. The solid initiator Azobisisobutyronitrile (AIBN) ($8.3x10^{-3}$ g, $5.09x10^{-2}$ mmol) and 3-(methacryloyloxy) phenyl benzoate (0.3 g, 1.1 mmol) were added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 minutes. Toluene (1 mL) and methylmethacrylate (0.957

g, 9.56 mmol) were added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the initiator and monomer were dissolved. Polymerization was carried out under nitrogen at 70 ^{o}C for 4 h. The final polymer was dissolved in methylene chloride, precipitated into hexane and dried in a vacuum oven overnight.

^{1}H NMR ($CDCl_3$): δ= 0.86 (m, *H*, at the backbone), 0.96 (m, *H*, at the backbone), 1.38 (m, *H*, at the backbone), 1.43 (m, *H*, at the backbone), 1.70 (s, *H*, at the backbone), 1.73 (s, *H*, at the backbone), 1.81 (m, *H*, at the backbone), 1.92 (m, *H*, at the backbone), 2.11 (m, *H*, at the backbone), 7.07 (m, aromatic *H*, on the pendant group), 7.42 (m, aromatic *H*, on the pendant group), 7.52 (m, aromatic *H*, on the pendant group), 7.63 (m, aromatic *H*, on the pendant group), 8.18 (m, aromatic *H*, on the pendant group) ppm.

Experiment 2. (Preparation of 20 % copolymer), All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization was conducted in a one-necked round bottom flask. The solid initiator Azobisisobutyronitrile (AIBN) ($5.8x10^{-3}$ g, $3.55x10^{-2}$ mmol) and 3- (methacryloyloxy) phenyl benzoate (0.4 g, 1.42 mmol) were added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 minutes. Toluene (2 mL) and methylmethacrylate (0.567 g, 5.67 mmol) were added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the initiator and monomer were dissolved. Polymerization was carried out under nitrogen at 70 ^{o}C for 4 h. The final polymer was dissolved in methylene chloride, precipitated into hexane and dried in a vacuum oven overnight.

Experiment 3. (Preparation of 30 % copolymer), All liquid chemicals were purged with nitrogen for at least 20 minutes prior to use. The polymerization was conducted in a one-necked round bottom flask. The solid initiator Azobisisobutyronitrile (AIBN) ($5.8x10^{-3}$ g, $3.55x10^{-2}$ mmol) and 3 (methacryloyloxy) phenyl benzoate (0.6 g, 2.12 mmol) were added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 minutes. Toluene (2 mL) and methylmethacrylate (0.496 g, 4.96 mmol) were added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the initiator and monomer were dissolved. Polymerization was carried out under nitrogen at 70 ^{o}C for 4 h. The final polymer was dissolved in methylene chloride, precipitated into hexane and dried in a vacuum oven overnight.

3.3. Investigation of Absorption Behaviors at UV region

3.3.1. UV Spectra of 3-Acetoxyphenyl Benzoate, Resorcinol Diether and Polymers

For the measurements parent stock solutions using methylene chloride were prepared and other solutions were obtained from the dilution of the parent ones. Molar absorptivity constants were calculated from the absorption versus concentration graphs drawn with Microsoft Excel. Photoreactions were performed in a UV reactor (Ultraviolet Co, RPR-2537 A^o Temp lamps were used)

3.3.2 UV Spectra of 3-Acetoxtphenyl Benzoate

2.1 mg 3-acetoxyphenyl benzoate was dissolved in 25 mL methylene chloride (3.28 x 10^{-4} M 3-acetoxyphenyl benzoate). This stock solution was then diluted to 0.82 x 10^{-4} M, 0.41 x 10^{-4} M, 0.21 x 10^{-4} M for other measurements. UV spectra of these four solutions were taken with the spectrophotometer and molar absorptivity coefficients were calculated from the absorption versus concentration graph.

3.3.3 UV Spectra of Resorcinol Diether

25.8 mg resorcinol diether was dissolved in 100 mL methylene chloride (1 x 10^{-3} M resorcinol diether). This stock solution were diluted to 5 x 10^{-4} M, 1 x 10^{-4} M, 5 x 10^{-5} M. UV spectra of these three diluted solutions were taken with the spectrophotometer and molar absorptivity coefficients were calculated from the absorption versus concentration graph. [12]

3.3.4. UV Spectra of Polymers

10.4 mg of polymers was dissolved in 50 mL methylene chloride (0.208 g/L of polymer). Five solutions (0.104, 0.052, 0.026, 0.013 and 0.0065 g/L) were prepared by dilution of stock one. UV spectra of these six solutions were taken with the spectrophotometer and molar absorptivity coefficients were calculated from the absorption versus concentration graph.

3.3.5. Procedure for the Photoreactions

The prepared stock solutions of materials were put into the irradiation box where they were exposed to UV radiation for 25 min. The changes in absorption behaviors of materials were monitored with the UV spectrophotometer at 3rd, 6th, 9th, 15th, 25th minutes of the reaction.

4. RESULTS AND DISCUSSION

The aim of this project is to obtain UV absorbing polymers with improved weatherability and elongated life time.

In this section, we report the synthesis and purification of UV absorber monomers, polymers. Then, the absorption behaviors of the synthesized polymers will be discussed. In addition, we will report the formation of an unexpected resorcinol diether product from the reaction of resorcinol monobenzoate and ethylene carbonate.

4.1. Synthesis and Purification of the monomer (3-(Methacryloyloxy) Phenyl Benzoate

3-(Methacryloyloxy) Phenyl Benzoate was synthesized in two steps. In the first step, resorcinol and benzoyl chloride were reacted in the presence of triethylamine in methylene chloride at room temperature to form resorcinol monobenzoate (Figure 4.1). At the second step, resorcinol monobenzoate was reacted with methacryloyl chloride in the presence of triethylamine in methylene chloride at room temperature to form the monomer 3-(Methacryloyloxy) Phenyl Benzoate (Figure 4.7).

4.1.1. Synthesis of Resorcinol Monobenzoate

This reaction gave two products; resorcinol mono- and dibenzoate. To obtain resorcinol monobenzoate as the major product we used resorcinol in excess amount. In this reaction, TEA was used for three reasons. The first reason is to neutralize HCl that formed during the reaction. The second reason is to make resorcinol soluble in methylene chloride. TEA can also act as an accelerator since it may form a acyl ammonium intermediate with benzoyl chloride which is a better leaving group than chloride and thus the reaction is accelerated. Figure 4.2. displays the reaction mechanism in the presence of TEA.

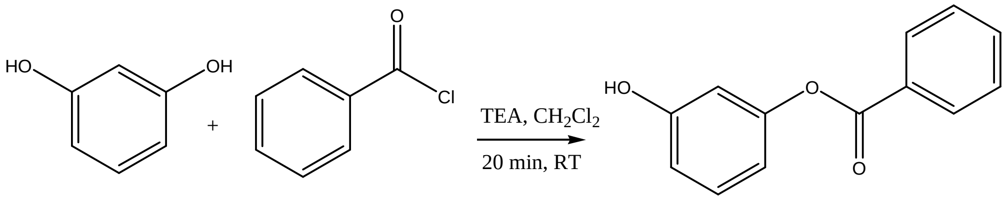


Figure 4.1. Synthesis of Resorcinol Monobenzoate

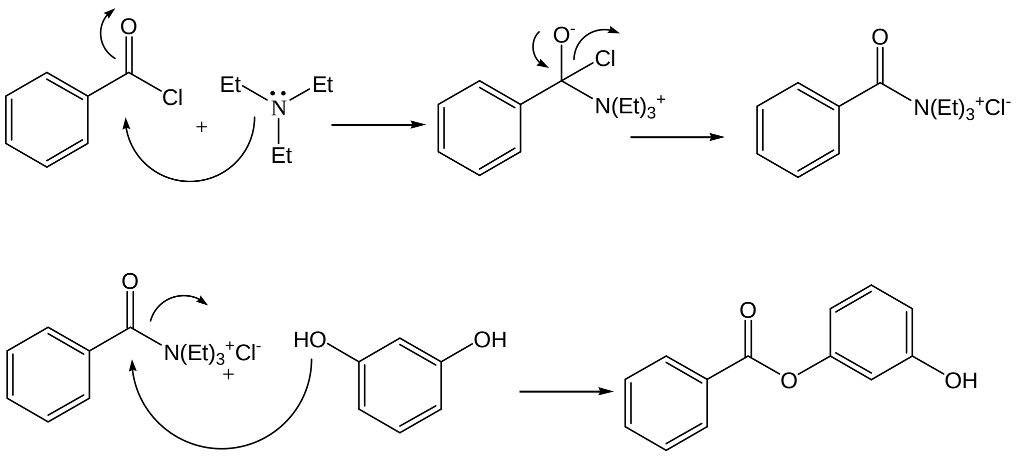


Figure 4.2. Mechanism of the Reaction of Resorcinol with Benzoyl Chloride

4.1.2. Characterization of Resorcinol Monobenzoate

In the synthesis of resorcinol monobenzoate, purification was carried out with basic aluminum oxide column chromatography. We confirmed the purity of resorcinol mono- and dibenzoate by ^{1}H- and ^{13}C- NMR as indicated at the experimental section.

Figure 4.3 shows the ^{1}H-NMR of the product of the reaction of resorcinol and benzoyl chloride before purification. This spectrum indicates the formation of resorcinol mono- and dibenzoate in the reaction. We calculated the percentages of these two products by looking at the integration values in the proton NMR. Calculations show that, resorcinol monobenzoate was formed in 75 %.

For the purification, we tried to separate resorcinol mono- and dibenzoate by deprotonation of monoester with NaOH (5 %) during extraction. However, monoester was hydrolyzed rapidly by the addition of NaOH. Therefore, we purified resorcinol monobenzoate by column chromatography. The purification was carried out with basic aluminum oxide packed column with solvent system hexane: ethyl acetate (4: 1). Resorcinol monobenzoate was obtained with an overall yield of 54 %.

The ^{1}H and ^{13}C NMR of the purified resorcinol monobenzoate and ^{1}H NMR of resorcinol dibenzoate are shown in Figure 4.4., 4.5. and 4.6 respectively. The corresponding peaks for each carbons and protons are indicated in the experimental section.

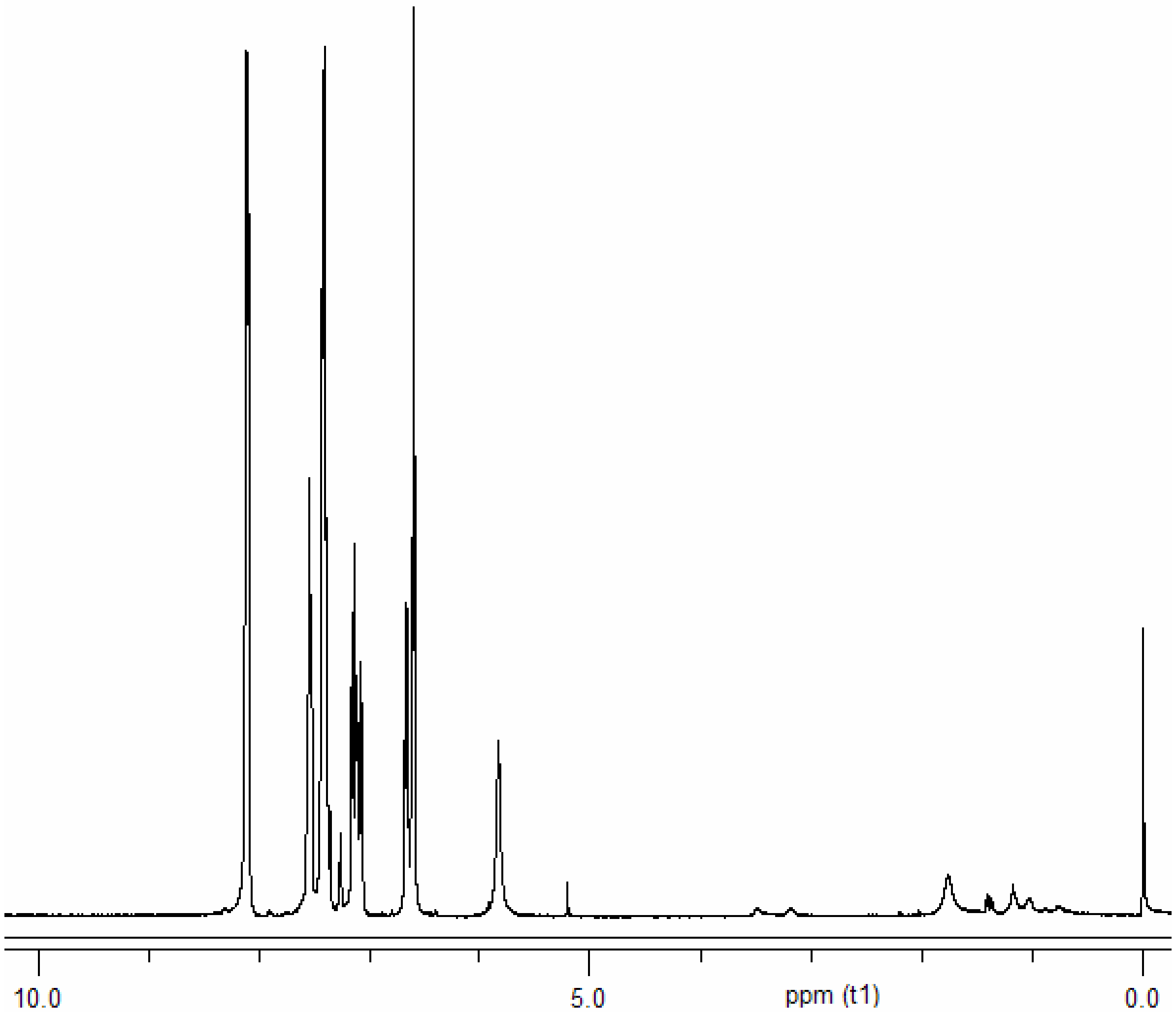


Figure 4.3. ^{1}H NMR of the Product of the Reaction between Resorcinol and Benzoyl Chloride before any Purification.

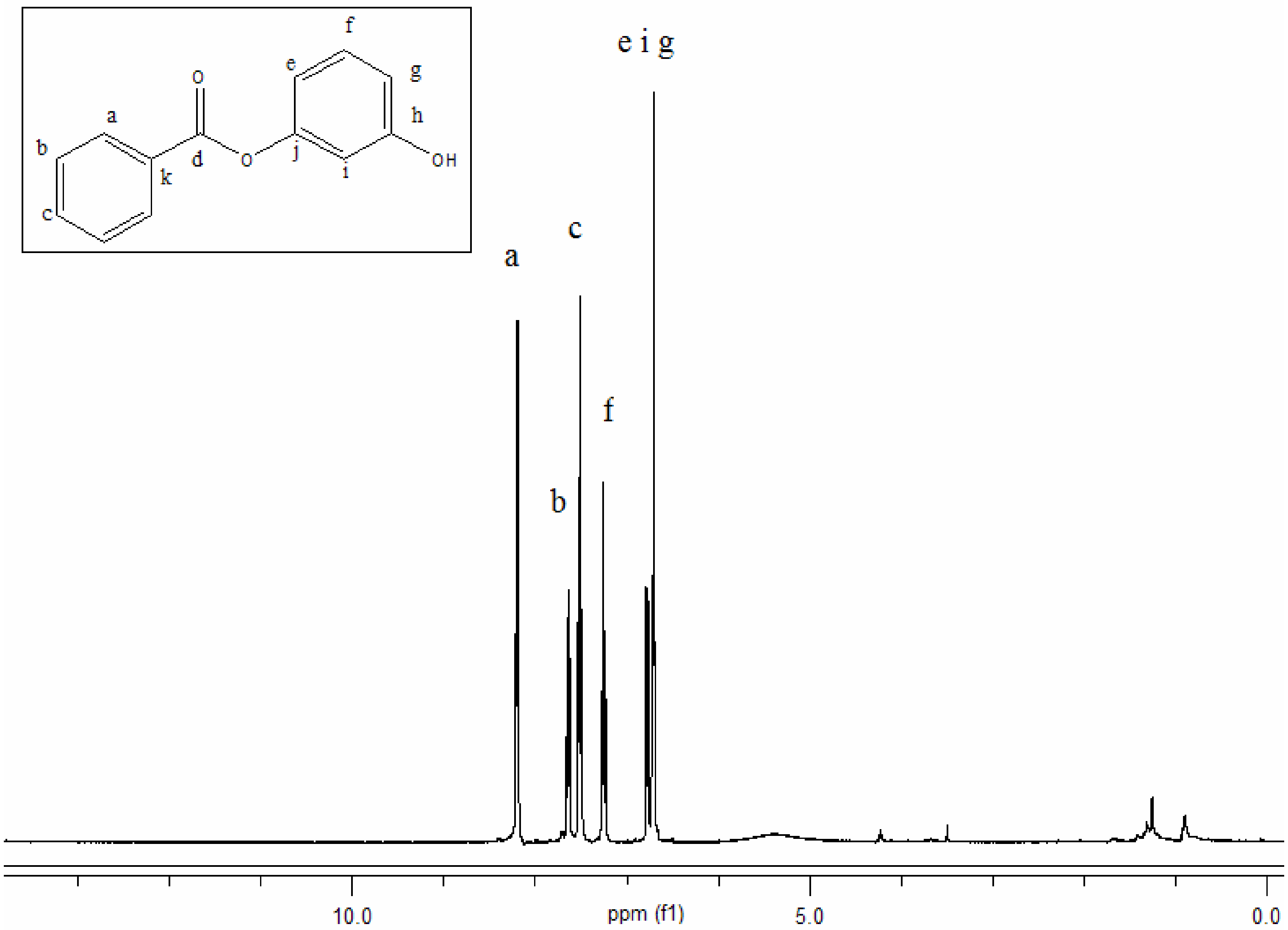


Figure 4.4. ^{1}H NMR of Resorcinol Monobenzoate

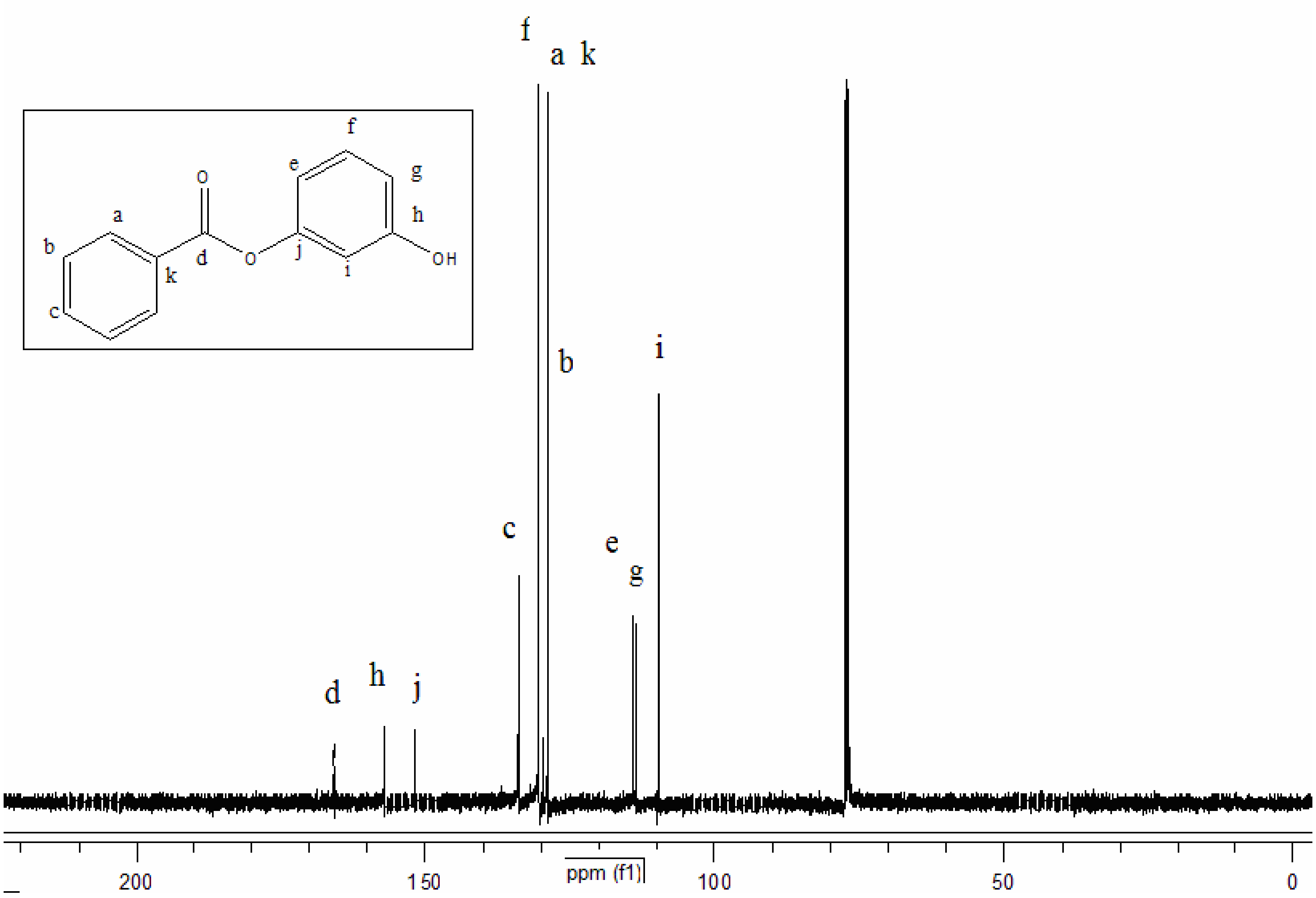


Figure 4.5. ^{13}C NMR of Resorcinol Monobenzoate

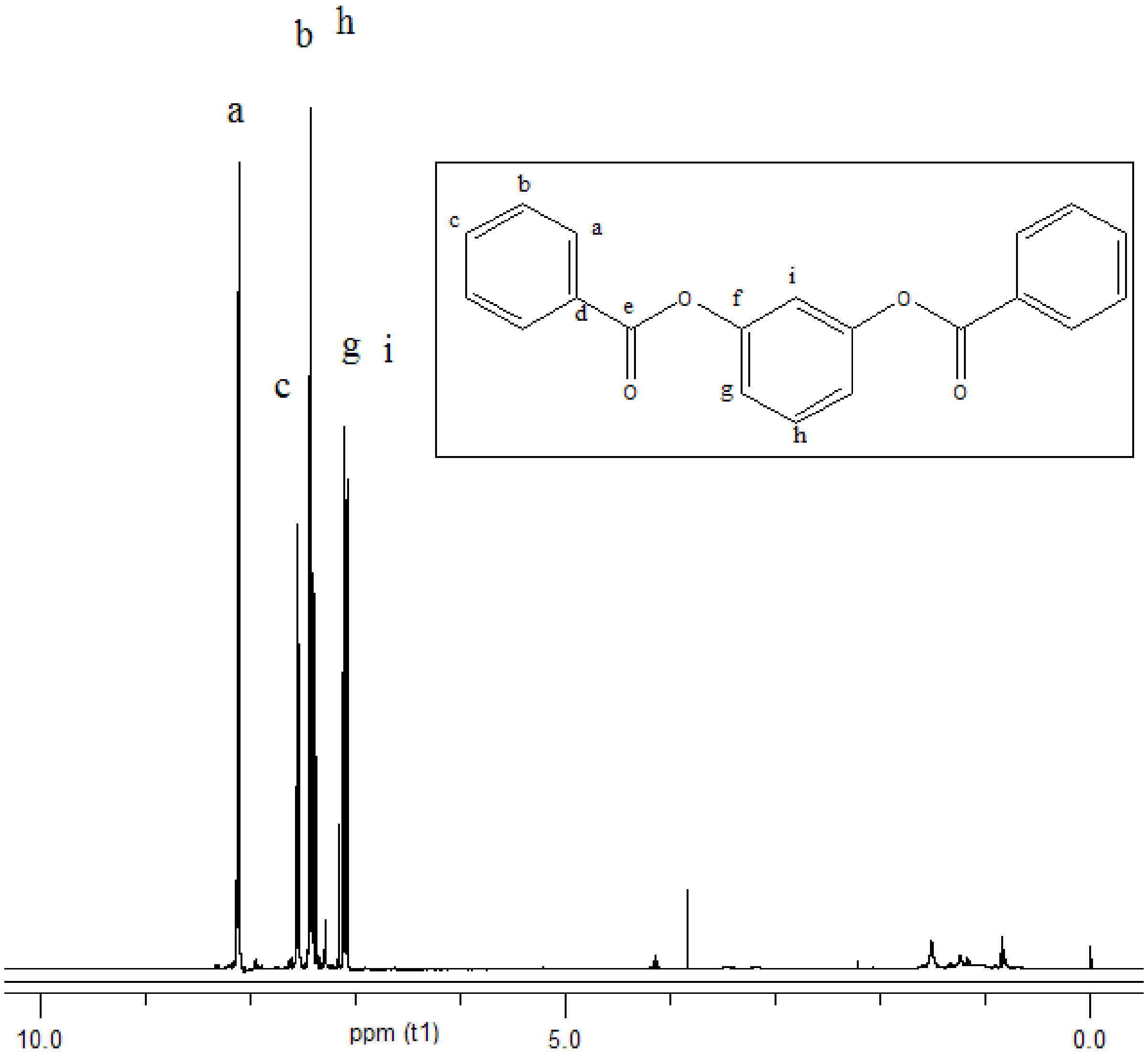


Figure.4.6. ^{1}H NMR of Resorcinol Dibenzoate

4.1.3. Synthesis of (3-(Methacryloyloxy) Phenyl Benzoate from Resorcinol Monobenzoate

In this synthesis, resorcinol monobenzoate and methacryloyl chloride were used as reactants, methylene chloride was used as solvent and TEA was used as catalyst and base scavenger (Figure 4.7.). Methacryloyl chloride was added in excess amount to simplify the purification step where the excess acid chloride can be extracted out easily in the form of an acid salt by simple basic extraction. This reaction was carried out at room temperature and it was monitored with TLC (silica plates with methylene chloride).

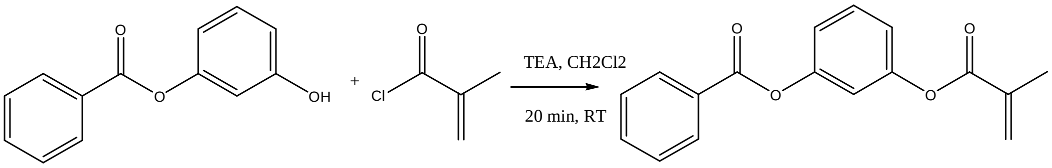


Figure 4.7. Reaction of Resorcinol Monobenzoate with Methacryloyl Chloride

4.1.4. Characterization of (3-(Methacryloyloxy) Phenyl Benzoate

Purification of the monomer, (3-(Methacryloyloxy) Phenyl Benzoate, was done by extraction with saturated $NaHCO_3$. Purity of the monomer was verified by ^1H and ^{13}C NMR as listed in the experimental section.

Figure 4.8. and 4.9. displays the ^1H and ^{13}C NMR of (3-(Methacryloyloxy) Phenyl Benzoate respectively.

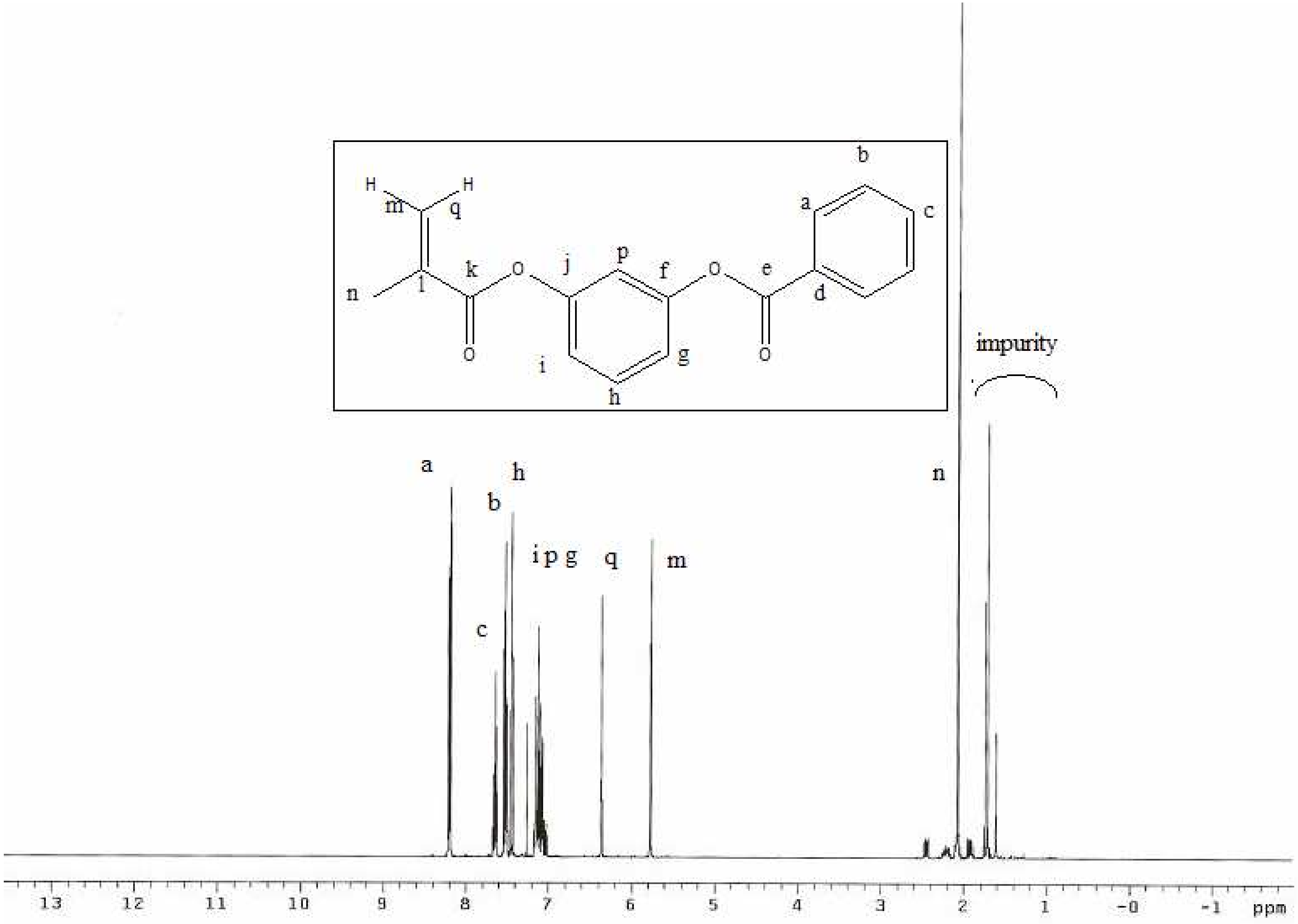


Figure 4.8. ^{1}H NMR of (3-(Methacryloyloxy) Phenyl Benzoate

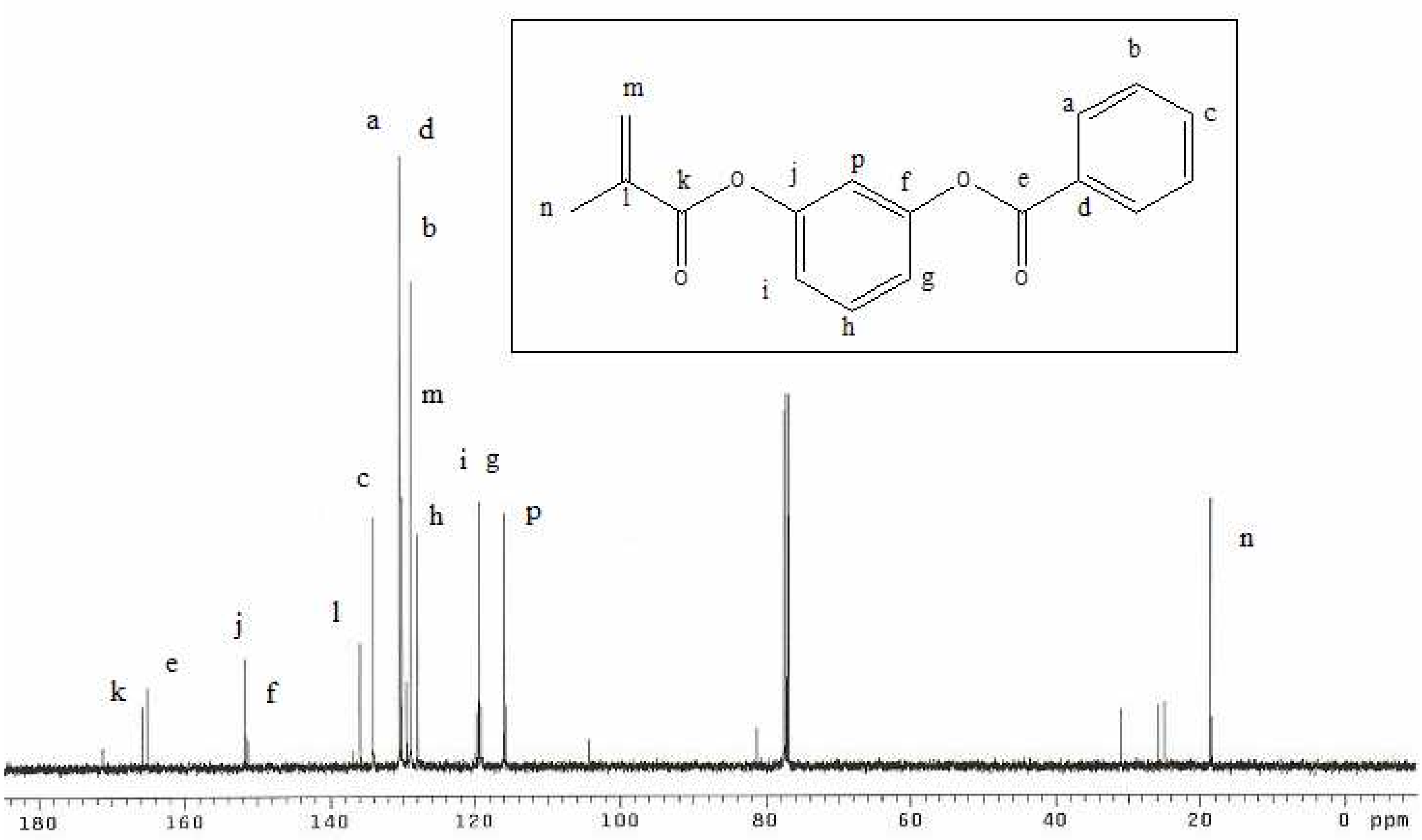


Figure 4.9. ^{13}C NMR of (3-(Methacryloyloxy) Phenyl Benzoate

4.2. Homo- and Copolymerization of the monomer (3-(Methacryloyloxy) Phenyl Benzoate

The monomer was polymerized via conventional radical polymerization in solution. Polymers were synthesized at 70 ^{o}C in toluene. Homopolymer of (3-(Methacryloyloxy) Phenyl Benzoate, and copolymers with 10, 20, 30 % of this monomer with methyl methacrylate were synthesized. This allowed us to compare absorption behaviors of polymers that contain different amounts of the UV stabilizer moieties (resorcinol esters). [13]

Purification was done by precipitation in hexane. Polymers were characterized by ^{1}H NMR (figure 4.10., 4.11., 4.12., and 4.13.) and GPC (table 4.1.).

Table 4.1. Molecular Weights and Polydispersity Index Data of Polymers

Entry	Polymers				
	Monomer 1^{i}	Monomer 2^{ii}	M_n (g/mol)	NMR ratio of Monomer 1	PDI
1	10 %	90 %	32,126	16 %	2.052
2	20 %	80 %	39,364	23 %	2.126
3	30 %	70 %	36,555	28 %	2.639
4	100 %	0 %	68,952	100 %	4.509

i: (3-(Methacryloyloxy) Phenyl Benzoate

ii: Methyl Methacrylate

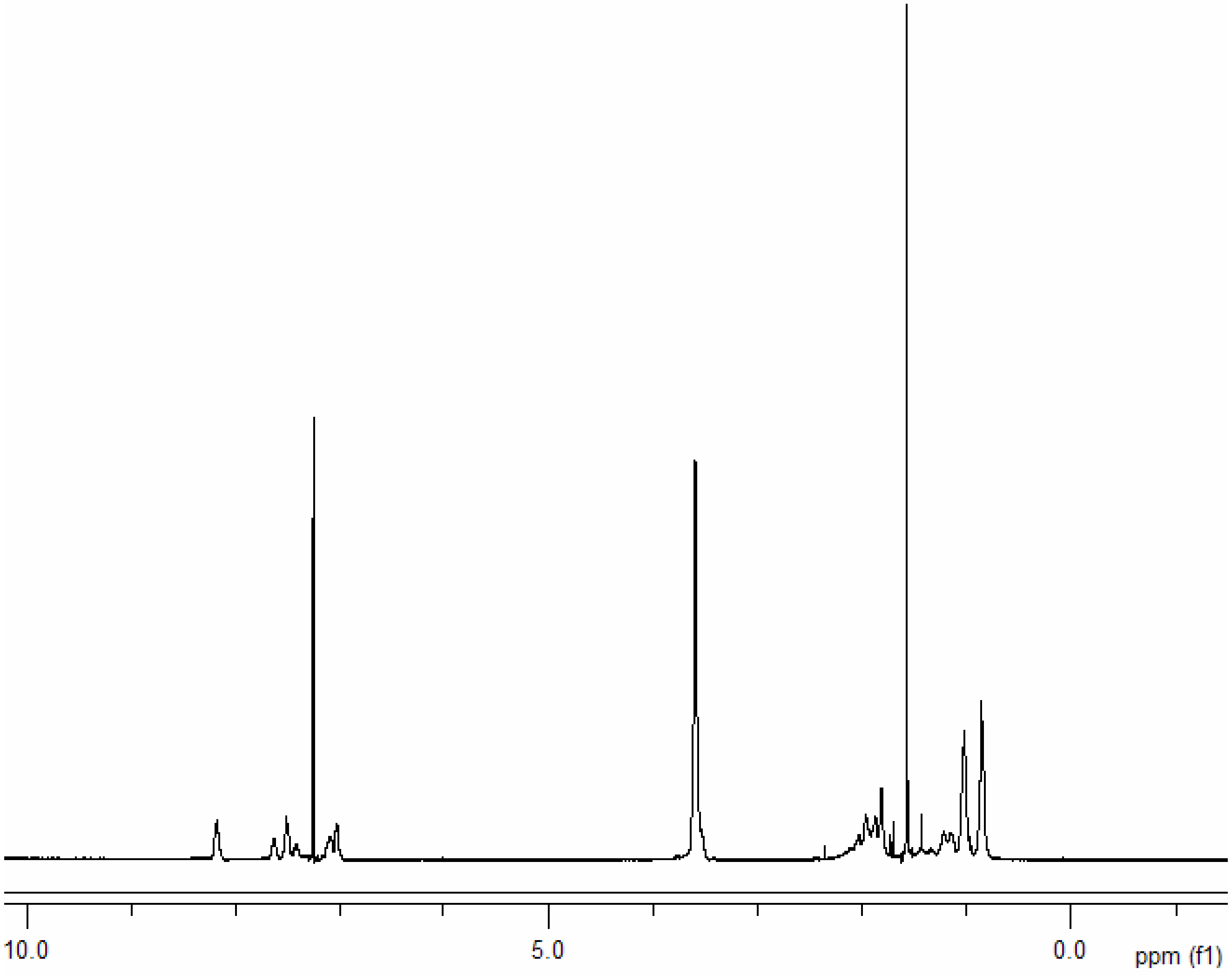


Figure 4.10. ^{1}H NMR of Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (10 %) with Methyl Methacrylate

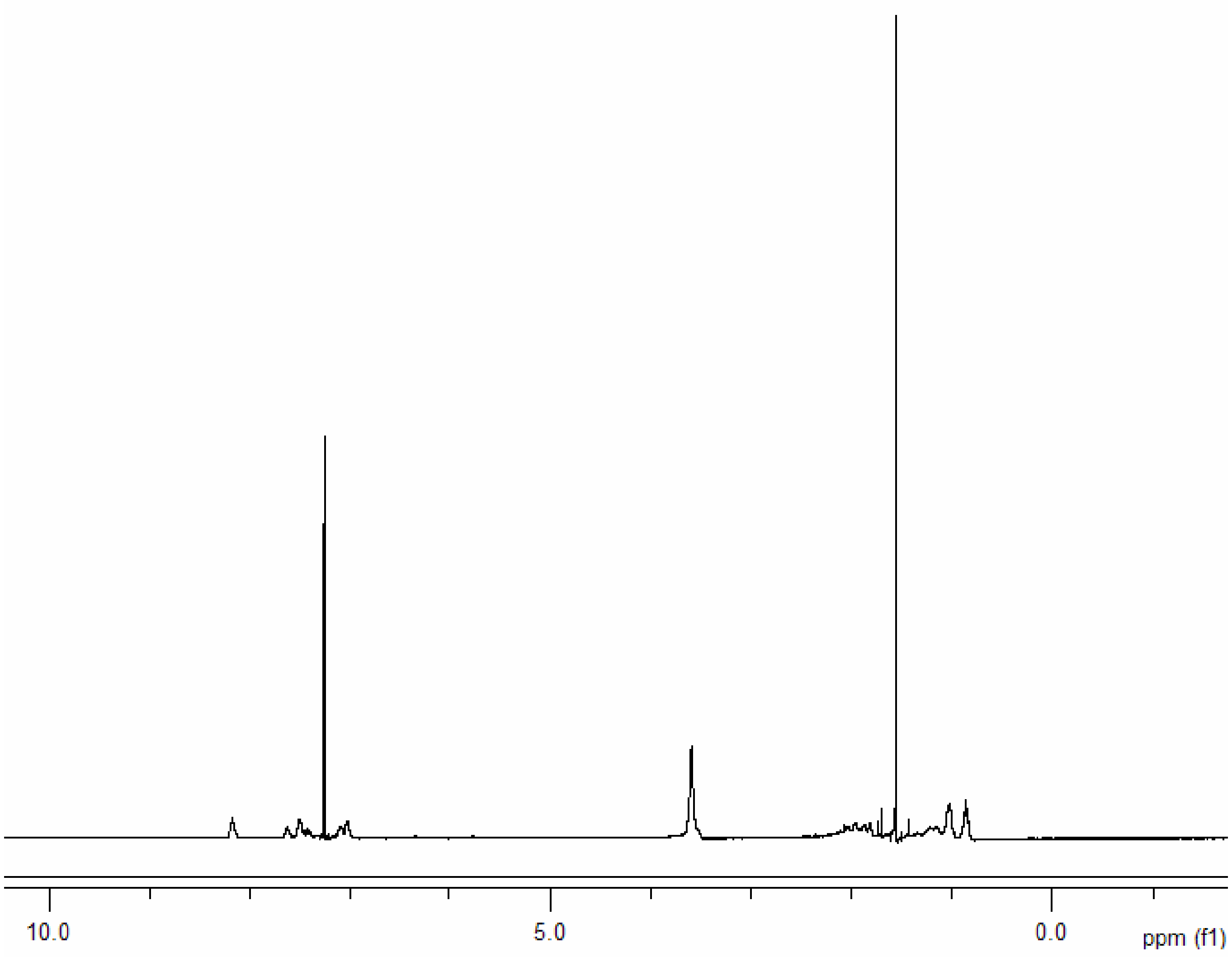


Figure 4.11. ^{1}H NMR of Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (20 %) with Methyl Methacrylate

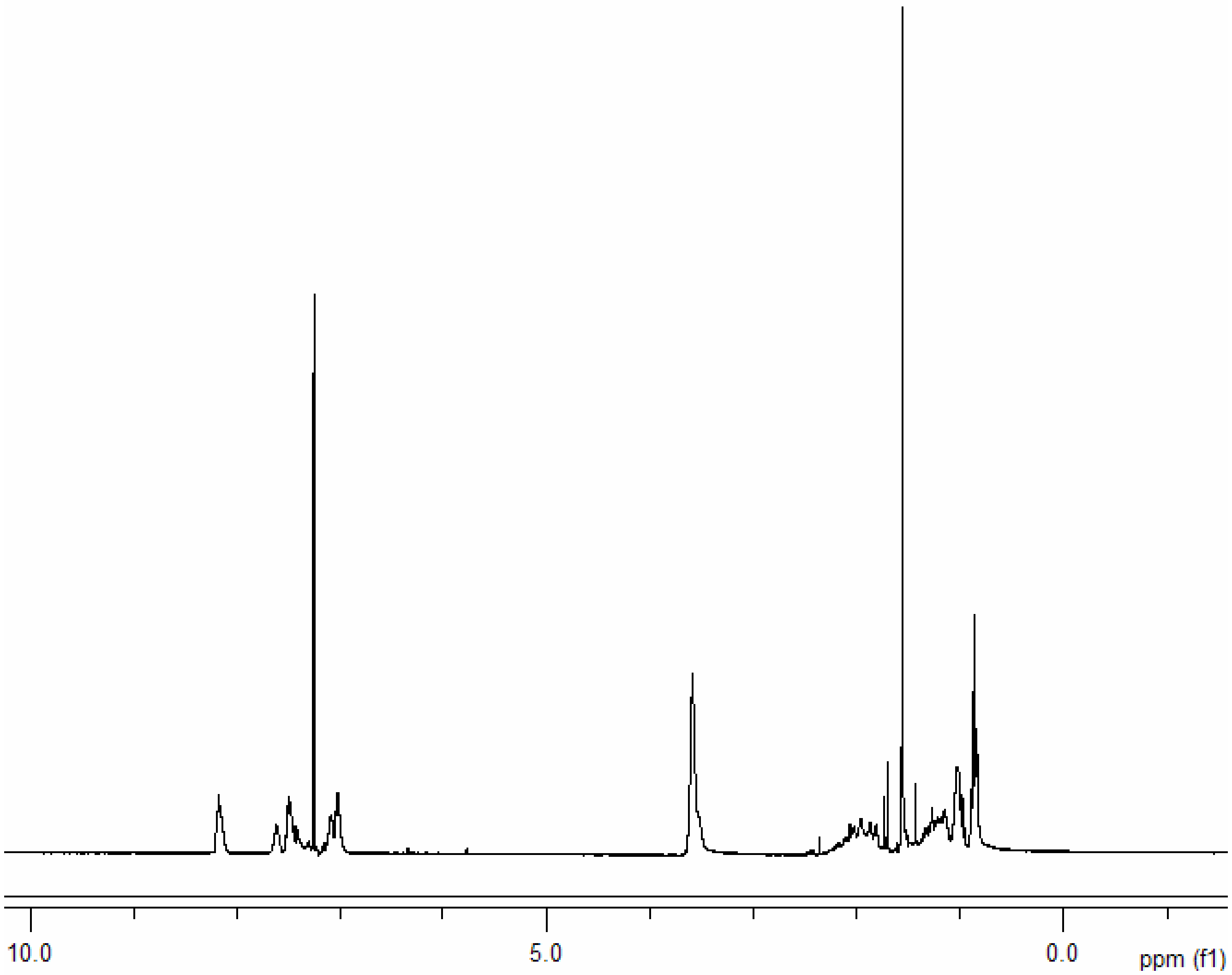


Figure 4.12. ^{1}H NMR of Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (30 %) with Methyl Methacrylate

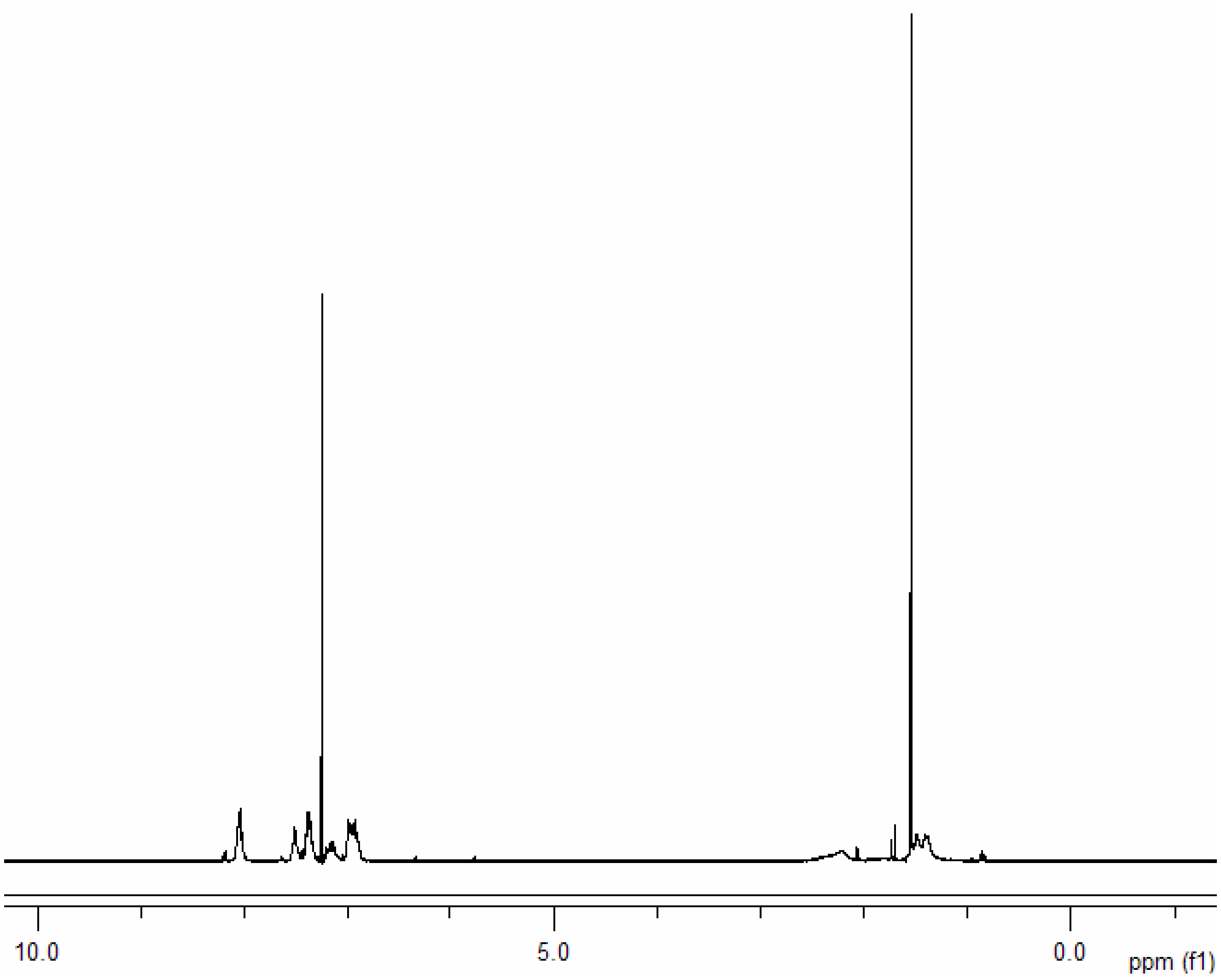


Figure 4.13. ^{1}H NMR of Homopolymer of (3-(Methacryloyloxy) Phenyl Benzoate

4.2.1. UV Absorption Behavior of Polymers Before and After Performing Photo-Fries Rearrangement

Absorption behaviors of the polymers in the UV region were investigated to find out the relationship of these behaviors with the percentages of the uv absorbing moieties in the polymers. For each polymer, a stock solution and from this stock solution five solutions wich differ in concentrations were prepared in methylene chloride. Their UV spectra (Figure 4.14., 4.15., 4.16. and 4.17.) were taken at the wavelengths between 200 and 600 nm. The maximum wavelength shifted to the longer wavelengths as the UV absorber contents of the polymers were increased. Calibration curves (absorption vs. concentration curves) at the maximum wavelength of each polymer were drawn (Figure 4.18., 4.19., 4.20. and 4.21.) to find out ε (mass extinction coefficient) values. Table 4.2. displays the ε values of each polymer.

As the concentration of the polymer was increased the maximum absorbance point was increased also. When concentration is increased aromatic rings of polymers get closer to each other. Consequently, electron mobilities on the polymers increase also. This results a bathochromic shift in the UV spectra. The similar effect was seen when we compared polymers with different percentages of the uv-absorbing moities at same concentrations. As the UV absorber content of the polymer increased, the maximum wavelength increased also. This can be explained by the increase of electron mobilities also.

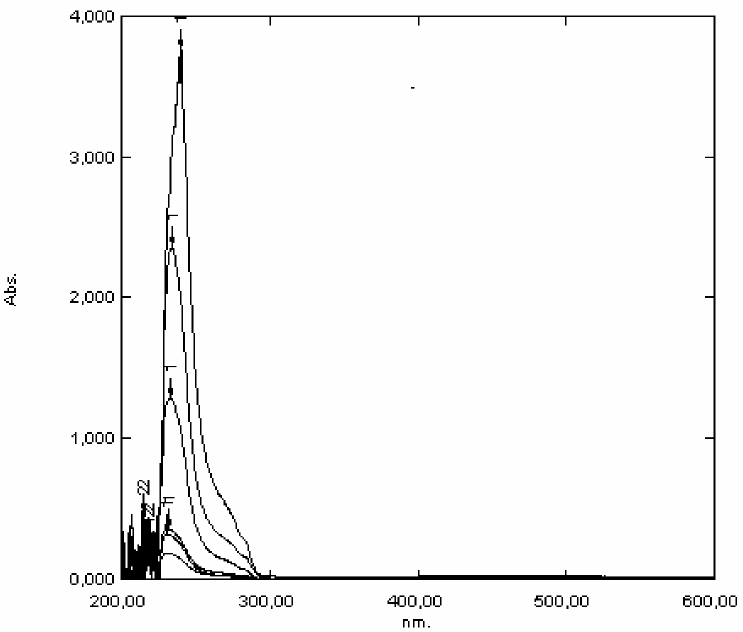


Figure 4.14. UV Spectrum of the Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (10 %) and Methyl Methacrylate for the concentrations 0.0065, 0.013, 0.026, 0.104 and 0.208 g/L

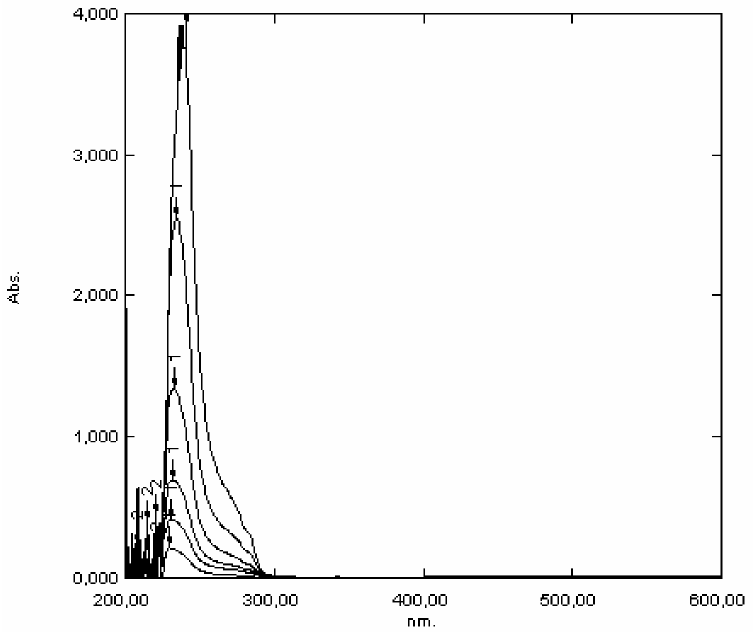


Figure 4.15. UV Spectrum of the Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (20 %) and Methyl Methacrylate for the concentrations 0.0065, 0.013, 0.026, 0.052, 0.104 and 0.208 g/L

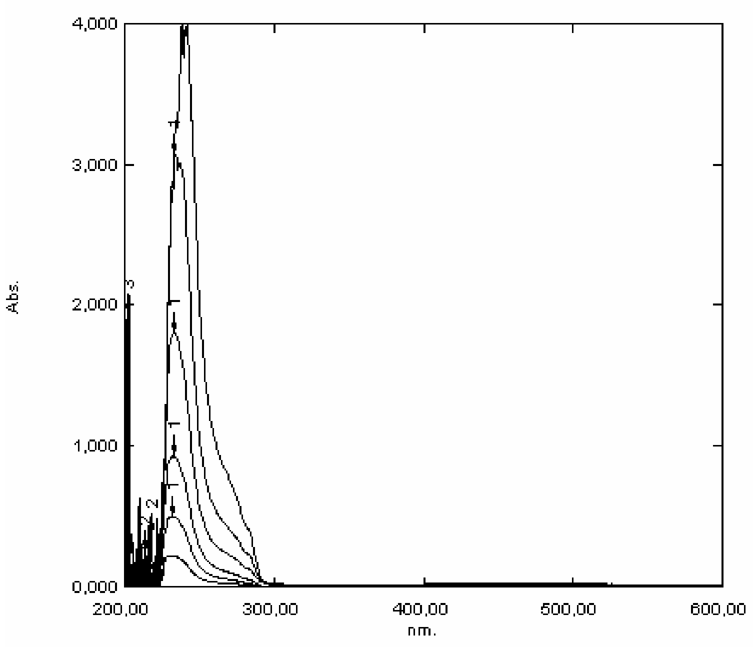


Figure 4.16. UV Spectrum of the Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (30 %) and Methyl Methacrylate for the concentrations 0.0065, 0.013, 0.026, 0.052, 0.104 and 0.208 g/L

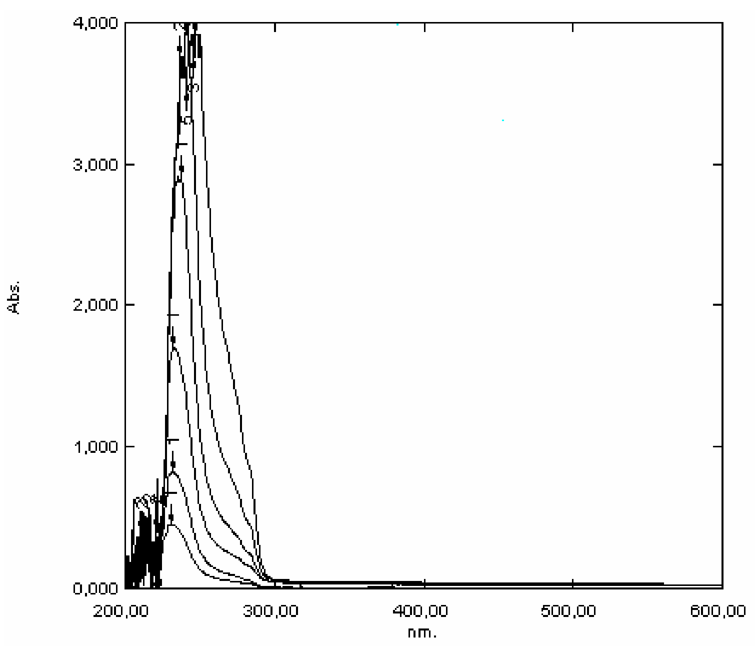


Figure 4.17. UV Spectrum of the Homopolymer of (3-(Methacryloyloxy) Phenyl Benzoate for the concentrations 0.0065, 0.013, 0.026, 0.052, 0.104 and 0.208 g/L

For the homopolymer, the last two solutions (0.104 and 0.208 g/L) gave the same absorbance results. This shows that, the amount of absorption of the polymer does not change after a certain amount of UV content of the polymer. In other words, our polymers get saturated with a certain amount of UV absorber moieties. This result tells us the use of copolymers can protect materials from the solar radiation in same amount with the homopolymer by adjusting the concentration of the copolymers.

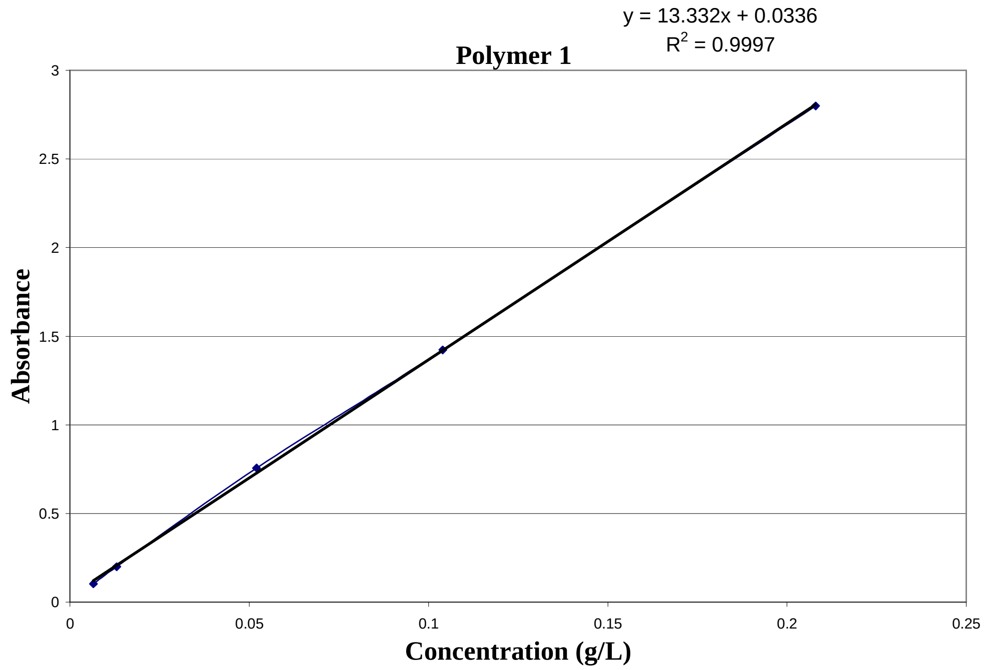


Figure 4.18. Absorbance *vs.* Concentration Graph of Polymer 1 (Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (10 %) with Methyl Methacrylate)

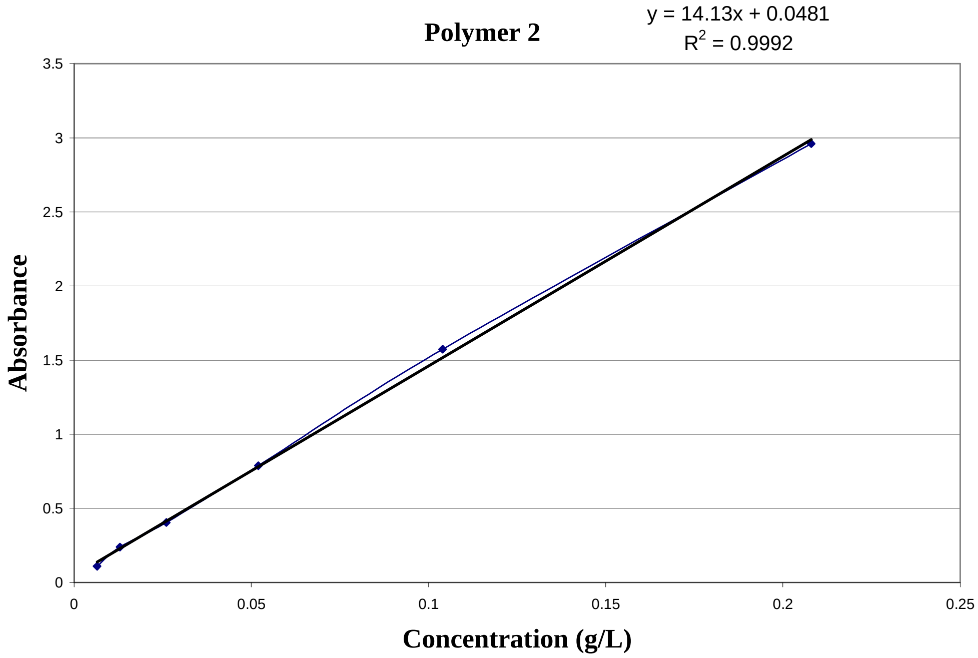


Figure 4.19. Absorbance *vs*. Concentration Graph of Polymer 2 (Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (20 %) with Methyl Methacrylate)

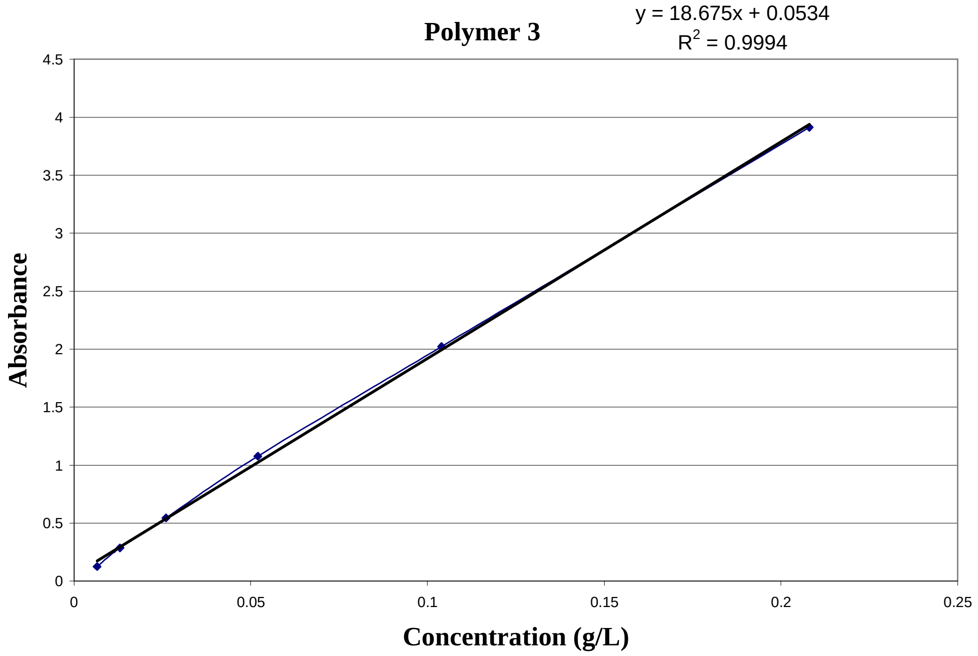


Figure 4.20. Absorbance *vs*. Concentration Graph of Polymer 3 (Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (30 %) with Methyl Methacrylate)

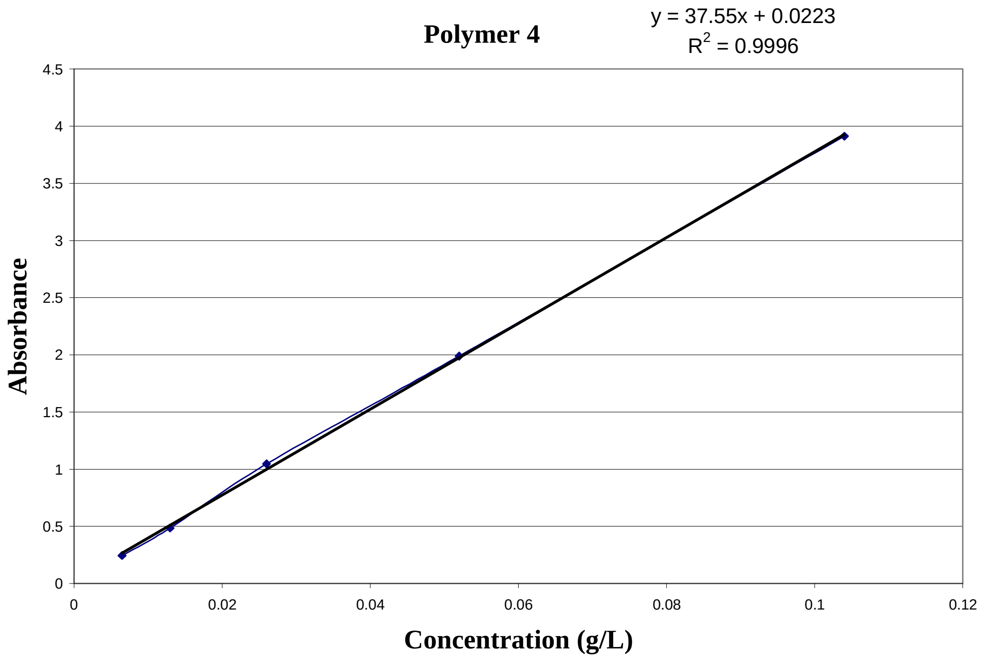


Figure 4.21. Absorbance *vs.* Concentration Graph of Polymer 4 (Homopolymer of (3-(Methacryloyloxy) Phenyl Benzoate)

Table 4.2. The results from the UV spectra of the polymers

Entry	Polymers				
	Monomer 1^i	Monomer 2^{ii}	NMR Ratio of Monomer 1	Mass Extinction Coefficient (ε_m / g^{-1} L cm^{-1})	Maximum Wavelengths (λ_{max} /nm)
1	10 %	90 %	16 %	13.33	238
2	20 %	80 %	23 %	14.13	240
3	30 %	70 %	28 %	18.68	243
4	100 %	0 %	100 %	37.55	244

From the table 4.2., it is seen that, mass extinction coefficient increases as the UV absorbance content of the polymers increases. This means that, polymers that have higher UV absorber moieties have stronger absorbing abilities in the UV region as expected.

As we discussed earlier our polymers contain moieties that are susceptible to Photo-Fries Rearrangement. It is after this rearrangement that our polymers behave like a real UV stabilizer. Thus, we investigated the absorption behavior of our polymers after the rearrangement. To induce rearrangement, the polymers were dissolved in methylene chloride, were irradiated with light with a wavelength of 254 nm for 25 minutes. As expected there has been a considerable change in the absorption behavior of the polymers after the rearrangement. We observed a shift in the UV spectra to longer wavelengths as seen in the Figure 4.22. and these spectra resembled the uv-vis spectra of hydroxyl benzophenones reported in the literature [16]. This observation support that Photo-Fries Rearrangement occurred to form hydroxy benzophenone units at the pendant groups of the polymer.

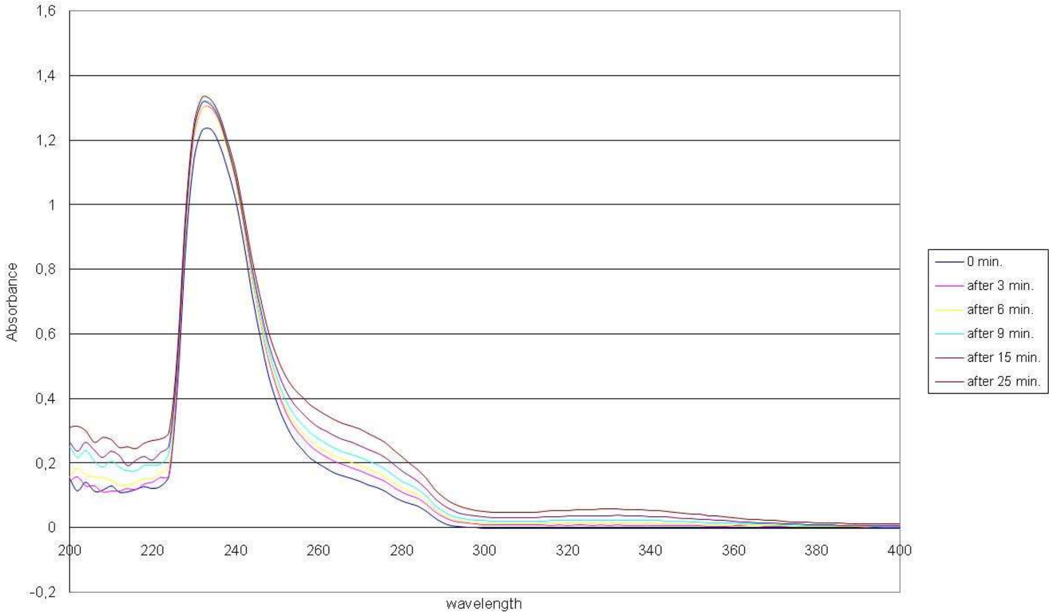


Figure 4.22. UV Spectra of the Copolymer of (3-(Methacryloyloxy) Phenyl Benzoate (10 %) and Methyl Methacrylate and Its Rearranged Products during the Photo-Fries Rearrangement Process.

In addition to these, we synthesized a test compound to see the effect of the polymers backbone to the uv absorbing unit. Thus, we synthesized a small molecule additive, 3-Acetoxyphenyl Benzoate, from the reaction of resorcinol monobenzoate with acetyl chloride. Purity of compound was confirmed by the ^{1}H and ^{13}C NMR that were displayed in Figure 4.23. and 4.24. respectively.

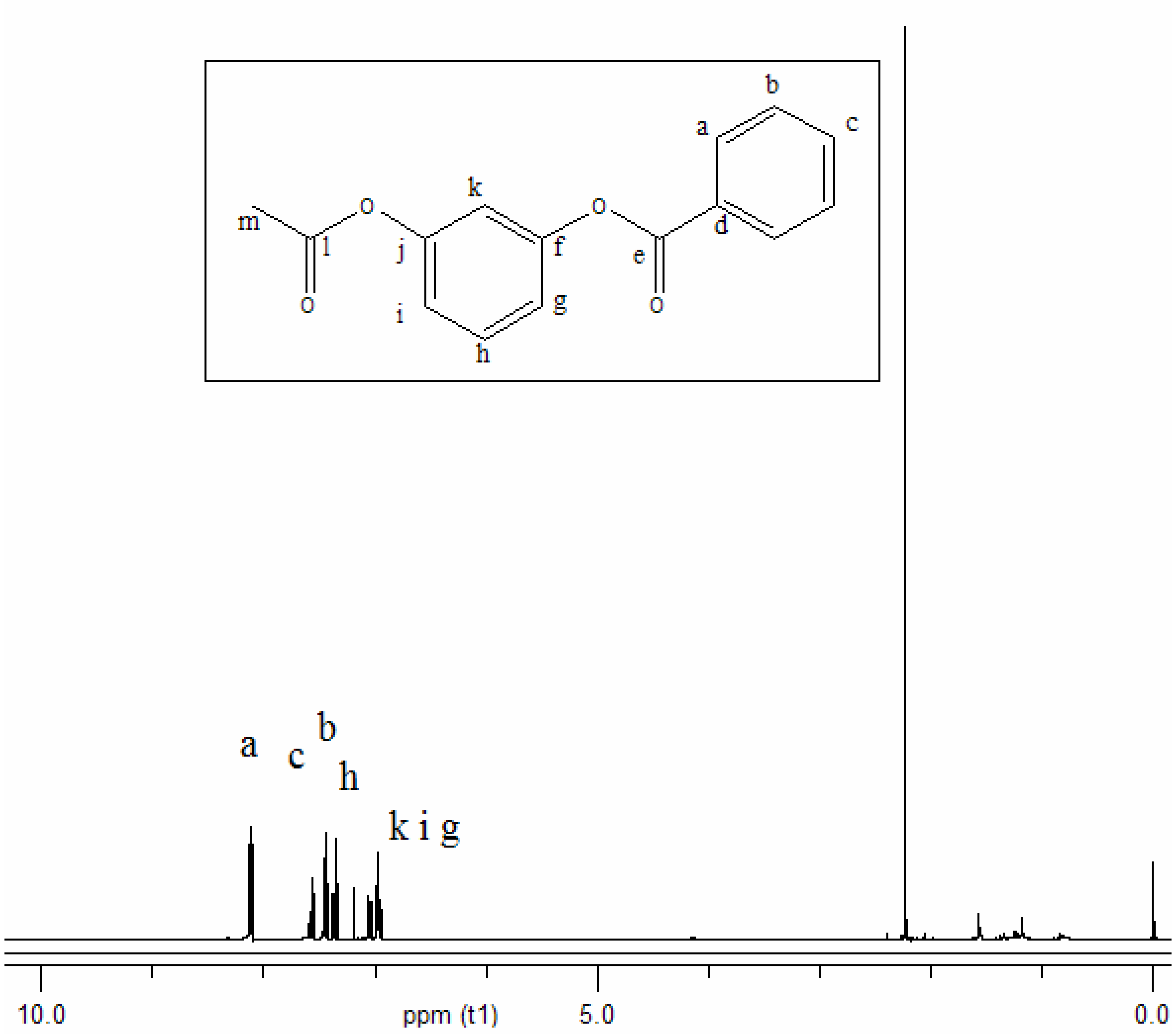


Figure 4.23. ^{1}H NMR of 3-Acetoxyphenyl Benzoate

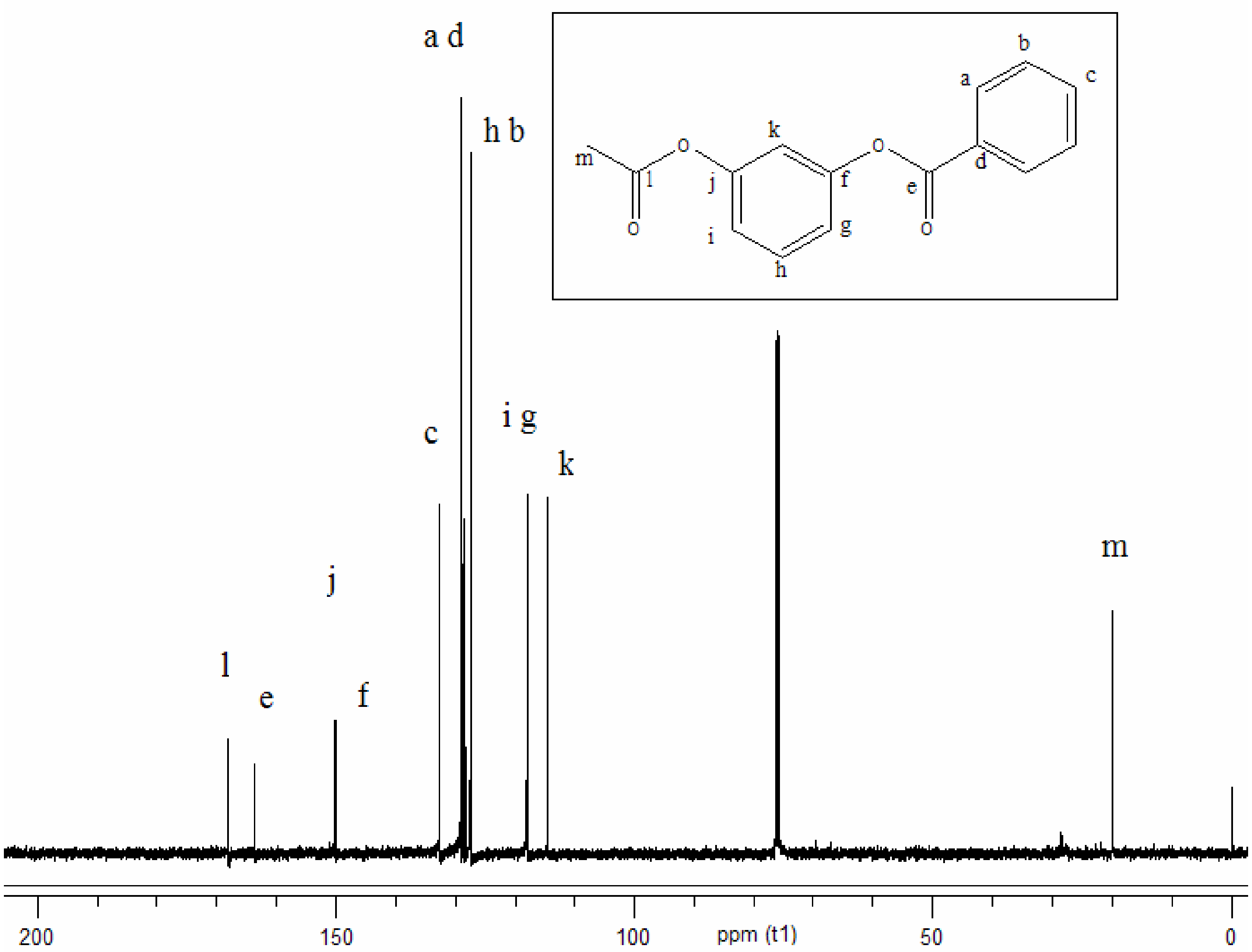


Figure 4.24. ^{13}C NMR of 3-Acetoxyphenyl Benzoate

UV spectra of 3-Acetoxyphenyl Benzoate were taken at different concentrations. Absorbance *vs* concentration graph (Figure 4.25.) was drawn and ε_m value equals to slope of the curve (45.22 g^{-1} L cm^{-1}). The mass extinction coefficient of this compound is close to that of the homopolymer. Therefore, our UV absorber polymer has approximately similar absorption strength with this small absorber compound.

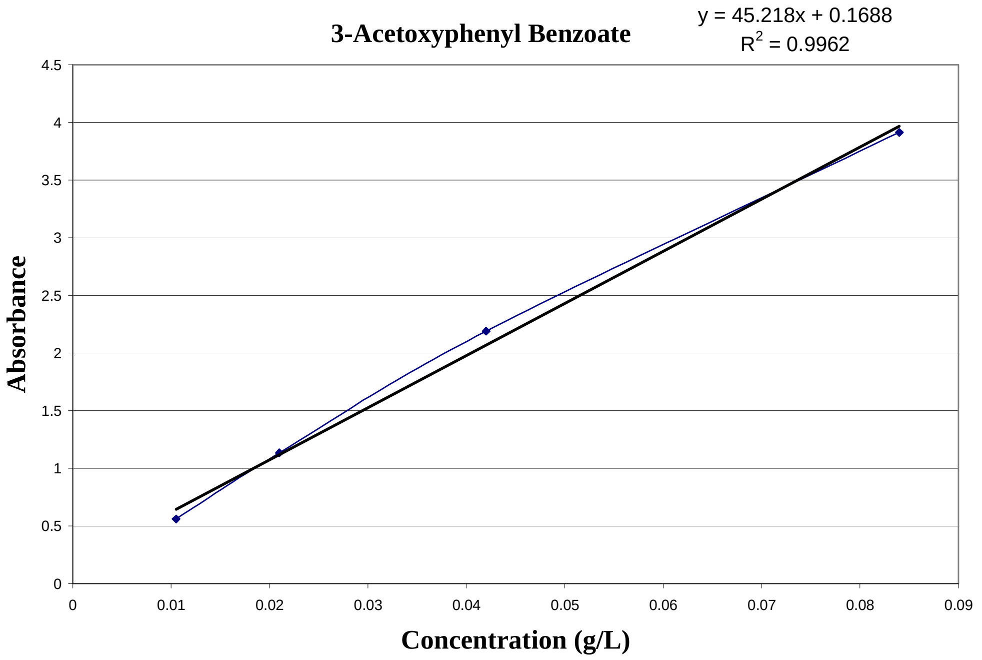


Figure 4.25. Absorption vs. Concentration Graph of 3-Acetoxyphenyl Benzoate

4.3. Formation of Unexpected Resorcinol Diether from the Reaction of Resorcinol Monobenzoate with Ethylene Carbonate

Resorcinol monobenzoate was reacted with ethylene carbonate, to prepare a second set of polymers. The expected reaction was the attack of free phenolic hydroxyl-group to the ethylene carbonate, in other words a ring opening reaction. Then, to obtain the final product the resulting product would be reacted with methacryloyl chloride to form the second methacrylic monomer. Figure 4.26. displays the expected reaction of the mono ester with ethylene carbonate.

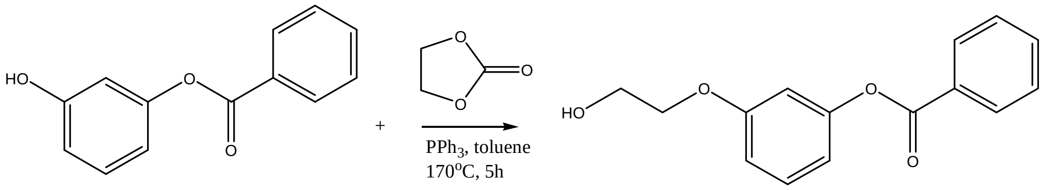


Figure 4. 26. Expected Reaction of Resorcinol Monobenzoate with Ethylene Carbonate

However, the reaction between ethylene carbonate and resorcinol monobenzoate (Figure 4. 27.) gave an unexpected product that seems to be the result of an initial hydrolysis of resorcinol monobenzoate before the opening of ethylene carbonate.

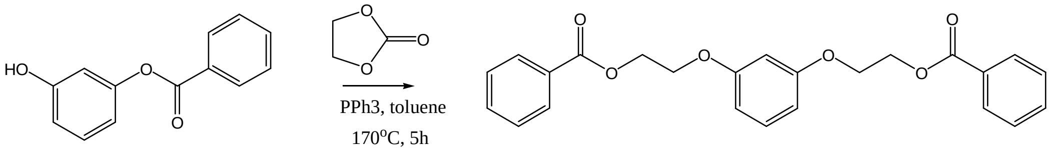


Figure 4. 27. Unexpected Product Formation from the Reaction of Resorcinol Monobenzoate with Ethylene Carbonate

The purification was carried out with silica packed column. The purity was verified with ^{1}H and ^{13}C NMR which are displayed in the Figure 4. 28. and 4. 29. respectively.

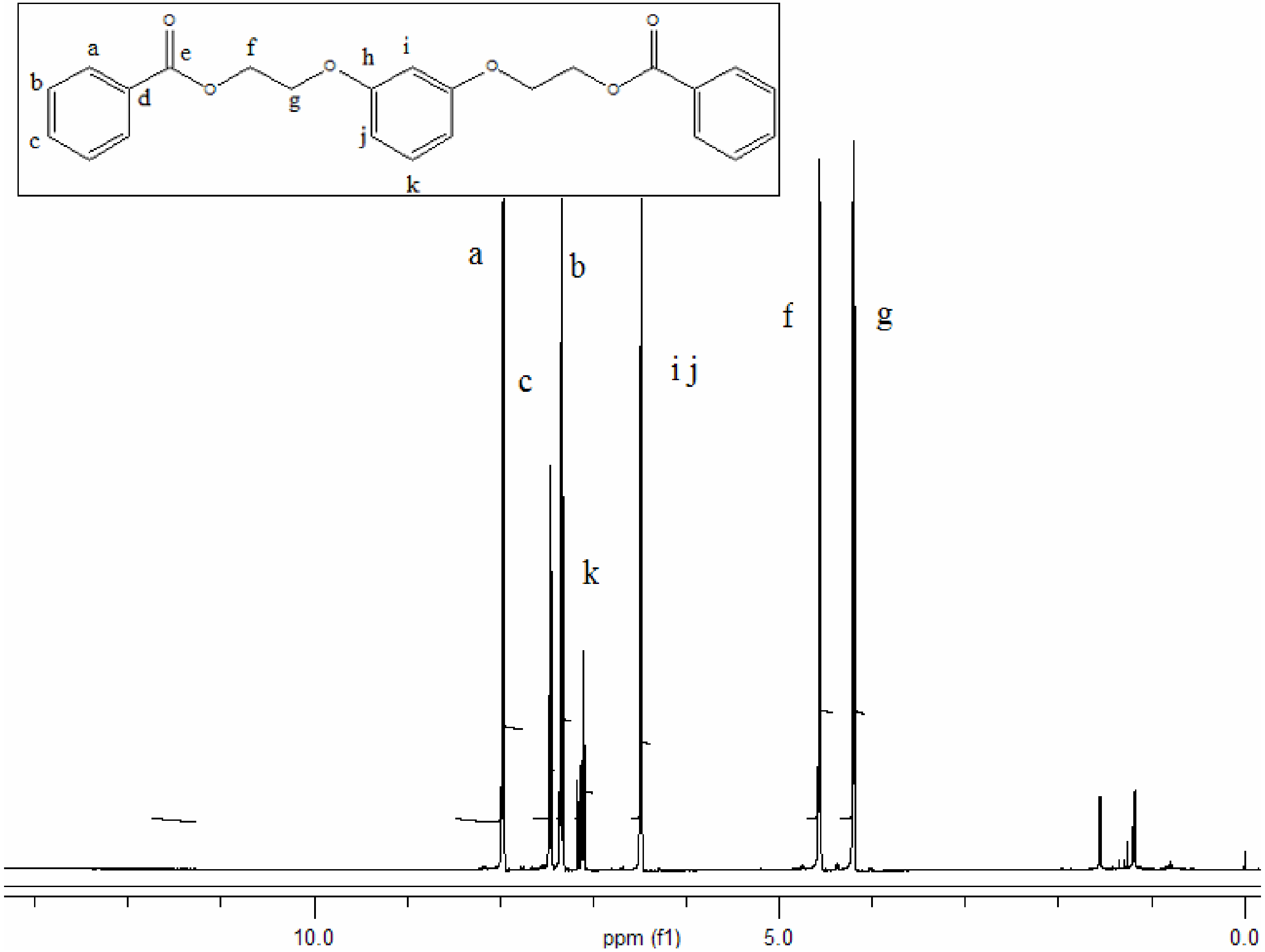


Figure 4.28. ^{1}H NMR of Resorcinol Diether

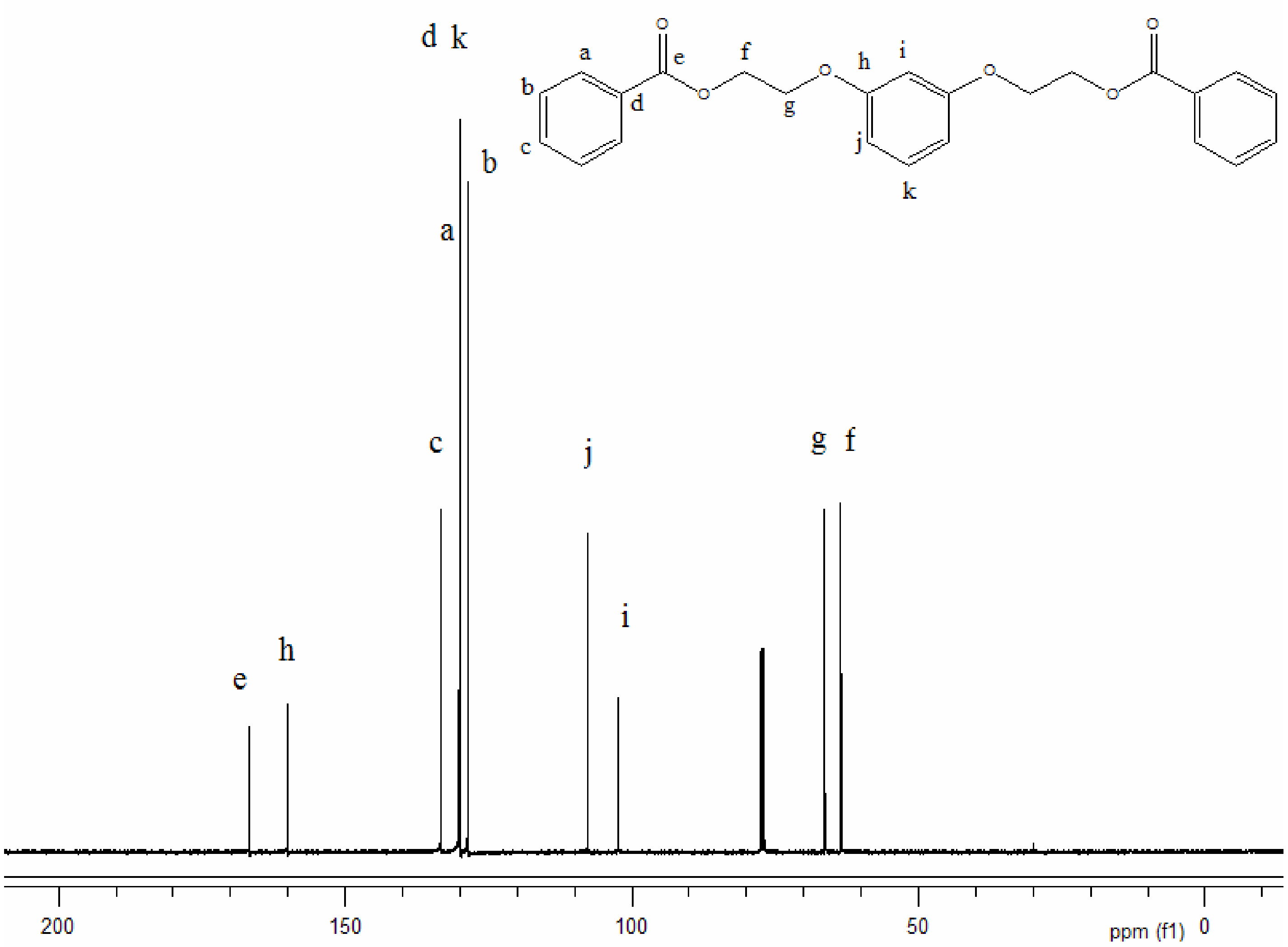


Figure 4.29. ^{13}C NMR of Resorcinol Diether

The obtained compound does not have any hydroxyl group in its structure. This was verified by the IR spectrum of the compound which is displayed in the Figure 4.30.. This proves that, this compound is not the expected product from the reaction. The integration values in the NMR are another proof of that.

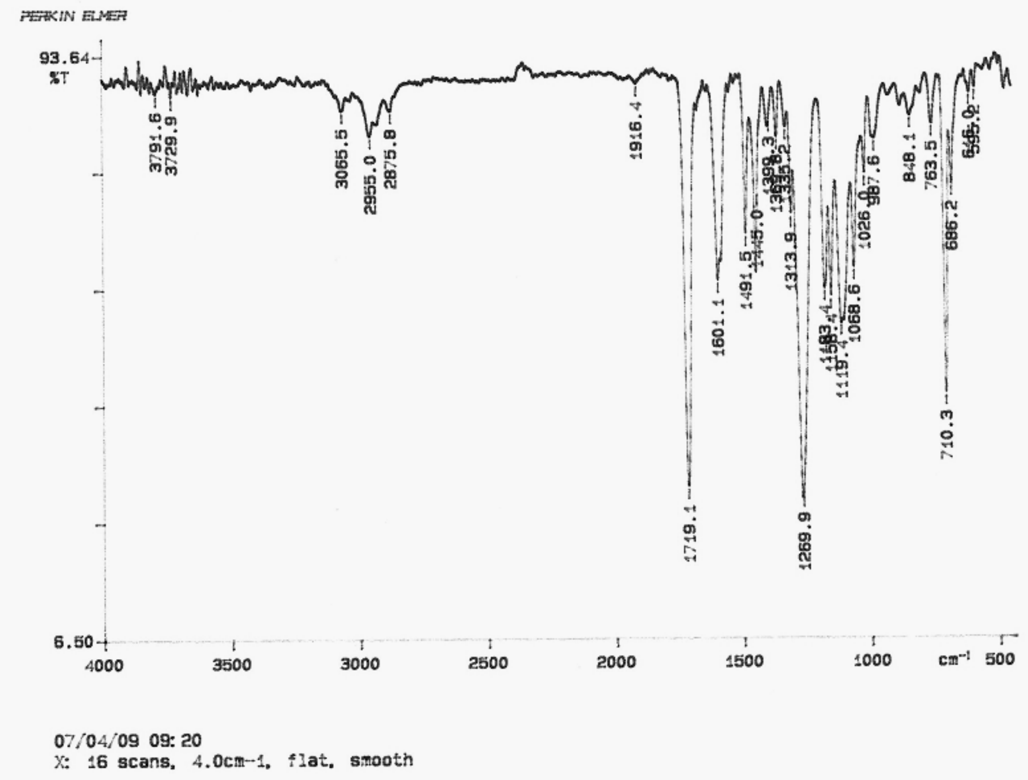


Figure 4. 30. IR Spectrum of Resorcinol Diether

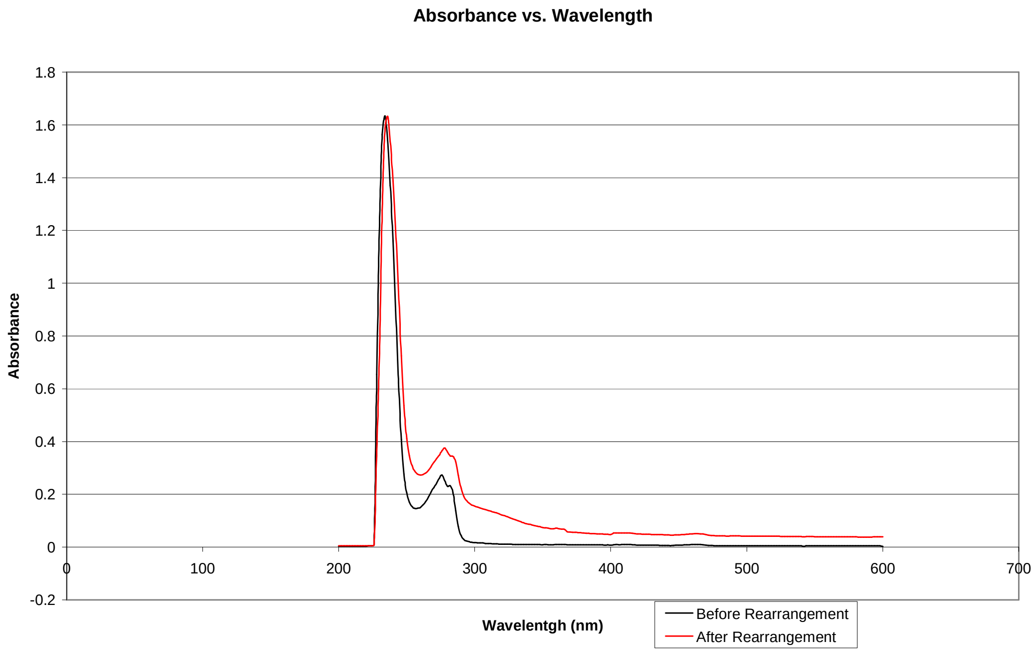


Figure 4. 31. UV Spectra of Resorcinol Diether before and after uv-irradiation

Absorption behavior of the compound was investigated by the UV-Vis spectrophotometer. Two absorption maxima were observed in the UV spectrum of the compound due to the two aromatic units in the compound with different electronic environment. In addition to this, resorcinol diether compound do not perform any rearrangement when it is exposed to UV radiation. In Figure 4. 31., we do not observe any change in the maxima of the spectrum. There is a tail through 400 nm which may be due to secondary decompositions by UV radiation.

5. CONCLUSION

In summary, we have synthesized potentially weatherable polymers that have UV absorbing moieties at their pendant groups. The important property of these moieties is that they are converted to hydroxy benzophenones, a common class of UV absorbers, under solar radiation so that the polymer they are incorporated in can gain an improved resistance to outdoor conditions, in other words, the weatherability of these polymers is improved.

The synthesized polymers were characterized with GPC and NMR instruments. Their absorption behaviors were investigated with UV spectrophotometer. As the UV absorber content increases, the electron mobility on the aromatic ring increases and as a result the maximum wavelength of the polymers increases also. It is expected that, there is an increase in the absorption strength of the polymer as the UV absorber content increases and the mass extinction coefficients of the polymers gave this expected result.

UV spectra of polymers show that, copolymers of 3-(methacryloyloxy) phenyl benzoate with methyl methacrylate absorb UV radiation at the same region with the homopolymer of (3-(methacryloyloxy) phenyl benzoate. Therefore, using copolymers of our UV responsive monomer can be enough to protect materials from solar radiation. Weathering tests for our polymers have to be investigated with a weathering test instrument.

Finally, another result of this study was the formation of an unexpected product from the reaction of ethylene carbonate with resorcinol monobenzoate. The reaction mechanism of this reaction can be studied to enlight the formation of this unexpected product.

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