REPUBLIC OF TURKEY
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GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

TRIAZINE-BASED NEW PLASTIFYING AGENTS

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Ammar AL-OBAID

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ABSTRACT

TRIAZINE-BASED NEW PLASTIFYING AGENTS

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New series of triazine derivatives were successfully designed and synthesized. The synthesis protocol can be carried out with one pot reaction or two-step starting from cyanuric chloride as starting material. Cyanuric chloride has wide application in chemical industries, agriculture, polymer, dye and leather and commercially cheap. In this study (2-chloro-4, 6-bis ((2-ethylhexyl)oxy)-1, 3, 5-triazine) as intermediate compound was synthesized starting from 2, 4, 6-trichloro-1, 3, 5-triazine and used further in substitution reactions with aromatic and aliphatic alcohols. The synthesized compounds were characterized and confirmed by H-NMR, C-NMR and mass spectra. Some of thcompounds synthesized were successfully tested as plastifying agent for PVC.

Keyword: Triazines-based plasticizer, plasticizer agent, Triazines characterization and properties

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ÖZET

TRİAİZN ESASLI YENİ PLASTİFİYANLAR

Ammar AL-OBAIDI

Kimya Bölümü
Yüksek Lisans Tezi

Tez Danışmanı: Prof. Dr. Lokman TORUN

Yeni triazin türev serileri, dizayn edilerek sentezlenmiştir. Sentez; çıkış bileşiği olarak siyanürik klorürden başlanarak, tek-kap reaksiyonu ya da iki basamaklı reaksiyonla gerçekleştirilir. Siyanürik klorür; kimya endüstrileri, tarım, polimer, boya ve deri endüstrilerinde geniş bir uygulama alanına sahip olup ve ticari olarak, ucuz bir bileşiktir. Bu çalışmada, ara bileşik olarak; 2-kloro-4,6-bis ((2-etilhekzil)oksi)-1,3,5-triazin ve çıkış bileşiği olarak da 2,4,6-trikloro-1,3,5-triazinden sentezlenmiş, aromatik ve alifatik alkollerle substitüsyon reaksiyonlarında kullanılmıştır. Sentezlenen bileşikler; H-NMR, C-NMR ve kütle spektrumları ile karakterize edilmiştir. Sentezlenen bileşiklerden bazıları PVC için plastikleştirici olarak başarıyla kullanılmıştır.

Anahtar kelimeler: Triazin temelli plastikleştirici, substitüsyon reaksiyonu, triazin nitelik ve özellikleri

YILDIZ TEKNİK ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

CHAPTER 1

INTRODUCTION

1.1 Literature Review

The development in science and technology has taken the growing interest in the synthesis and investigation of new plasticizer compounds**.** The triazine molecular is interested molecular in the industrial chemistry "able to interact via coordination bonds, hydrogen bonding, electrostatic and charge-transfer attractions, and aromatic–stacking "with wide applications in host-guest chemistry, catalysis, anion recognition, sensors, electronics and magnetism[1].

The importance of the plasticizer is to increase the mechanical properties of the polymers by "decreasing tensile strength, increasing flexibility and lowering the second order transition temperature". Plasticizers, which have low molecular weights, inert, high boiling points and low vapor pressures, are used the modify some properties of polymers that otherwise difficult to process"[2].

"The International Union of Pure and Applied Chemistry (IUPAC) developed a definition for a plasticizer as a “substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability" or dispensability” [3].

The use of plasticizers for modifying the polymers properties, often they are low molecular weight with inert organic compounds, that are used as polymer additives

The main reason behind using plasticizers because of the low extractability with water, oils, and detergents, smart interaction with the polymer, low volatility, chemical stability, plasticizing performance, nontoxicity, and not costly [4, 5].

According to literature about 80% of plasticizers e produced worldwide started from "poly (vinyl chloride) (PVC) formulations and the plasticizers which used for PVC are diesters of phthalic acid" is about 90% [6, 7]. However, the researchers was studied the toxicity of phthalates early in 1940s.

The phthalate plasticizers used in several application such as children's toys, since 1990s the researchers showed that phthalate plasticizers such as "di(ethylhexyl) phthalate (DEHP) were suspected of being carcinogenic agents and endocrine disruptors" [8,9]. As a result many countries have taken strict actions against the use of phthalate plasticizers because of the above mentioned health reasons[10].

1.2 Objective of the Thesis

1,3,5-triazine is becoming a remarkable unit in industrial chemistry as it has been used in chemical industries such as agriculture, dye, polymer, leather and drug. It is a cheap compound, commercially available and also its substitution reaction can be controlled easily. However "s-triazine and its derivatives have their own importance in heterocyclic compounds due to their very good activities"[11].

The aim of project is to produce new series of plasticizer based on triazine moieties and investigate their properties and characterization, starting with cyanuric chloride as starting material to obtain new compounds.

1.3 Hypothesis

Cyanuric chloride treated with two equvelent of 2-ethylheexanol to yield di-substituted 1,3,5-triazine as intermediate compounds and used for further subsitutions with aromatic and aliphatic alcole asnew plasticizer agent . They can potentially be used in severalindustrial and biotechnological applications.

CHAPTER 2

GENERAL INFORMATION

2.1 Triazines

Triazines arearomatic compoundswith six-memberedheterocycles comprised of three nitrogen atoms replacing carbon and hydrogen in the benzene ring to form the molecular formaula ($C_3H_3N_3$).The name of three isomers signify the position of the nitrogen atoms on the aromatic heterocyclic ring. The triazines isomers (see Figure 2.1), "1,2,3-triazine (**1**), 1,2,4-triazine (**2**), and 1,3,5-triazine (**3**)"."The 1,3,5-triazines are the most extensively studied of the isomeric forms" (1,2) Given and oldest one.s-triazinesreferred to "1,3,5-triazine is a symmetrical molecule". The triazine which will be used in this work is"1,3,5-derivatives". [12,13].

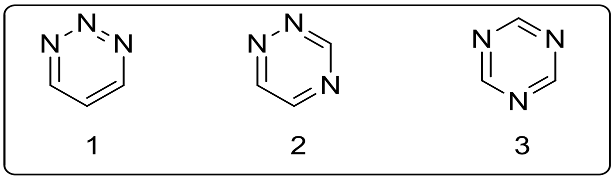


Figure 2.1 Triazine Isomer

2.1.1 1, 2, 3-Triazine

1,2,3-triazine is also called ν-triazine which is the least studied compound among other triazine isomers since the nitrogen atoms in the ring are adjacent and therefore the ring is fragile [12, 14].

Clinically 1,2,3-triazine derivatives are more acceptable because of potent efficacy and minimal side effect. "1,2,3-triazine represents a widely used lead structure with multitude of interesting applications in the numerous pharmacological fields, Thus various pharmacological activities have been reported and explored out till date"(see figure 2.2).

But the "1,2,3-triazines are the least studied triazine family and result in only a few scientific reports per year" [13 -15].

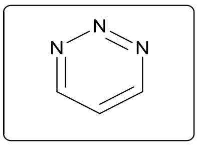


Figure 2.2 1,2,3-Triazine

2.1.2 1,2,4-Triazine

α-triazine or *s*-triazine which means asymmetric triazine. After 1960, the literature on 1,2,4-triazine was increased because its derivatives have biochemical and herbicide properties [12,14].

Usually, "the 1,2,4-triazines attract much greater attention than their 1,2,3-relatives because of the abundance of nitrogen atoms in the cycle and electron deficiency, they are widely explored in reactions of nucleophilic substitution, inverse-electron-demand DA cycloaddition and other ring transformations, as coordinating ligands for metal ion binding and bioactive agents. So the points of interest involve 1,2,4-triazine synthesis, their transformation" and fictionalization.

"1,2,4-triazine"unit is extensively considered as "scaffold of many biological active compounds, natural or synthetic, with a great variety of pharmacological effects, especially active as antitumor agents, anti-AIDS agents"[19]."CRF receptor antagonists,[18] antimicrobial and anti-inflammatory agents"[15]. "The NCNN sequence of 1,2,4-triazine ring was considered fundamental for various pharmacological activities"(see figure 2.3).

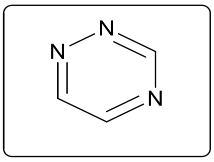


Figure 2.3 1,2,4-Triazine

2.1.3 1,3,5-Triazine

"1,3,5-triazine" was for the first time synthesized by "Nef in 1895 by treating hydrogen cyanide with ethanol in an ether solution saturated with hydrogen chloride. The resulting salt was then treated with base and distilled to give 1,3,5-triazine in low yields, 10%. Nef incorrectly identified the product as a dimeric species"(see figure 2.4). However "in 1954, Grundmann and Kreutzberger proved the compound to be a trimer of hydrogen cyanide" "s-triazine".[12,14].

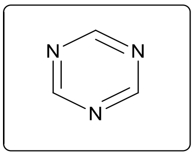


Figure 2.4 1,3,5-Triazine

1,3,5-triazine also isnamed β-triazine and *s*-triazine which refers to a symmetric triazine. It known for almost 200 years. It is the most common and the oldest molecule among the other isomers and it is usually used in many application area such as herbicides, biological active molecules, drug delivery agents, optical brightener, reactive dye, UV-light stabilizer, cross linker, water treatment, flame retardant, textile auxiliary and oil additive [12,13].

2.2 Stability of Triazine

"triazine is thermally stable compound, unless "heated to above 600 °C where it decomposes to form hydrogen cyanide". The "triazine"unit is "less resistant to the substitution of electrophonic". However, "it may readily undergo ring cleavage with nucleophiles and is very sensitive to hydrolysis by water and other hydroxyl-compounds to a lesser degree"[12,14]. A "variety of heterocyclic can be prepared from 1,3,5-triazine by treatment with bifunctional amines or related compounds, and it may be used as an alternative for HCN in reactions"[14]."The most commonly used triazine derivatives (see figure 2.5), cyanuric acid, melamine, and cyanuric chloride".

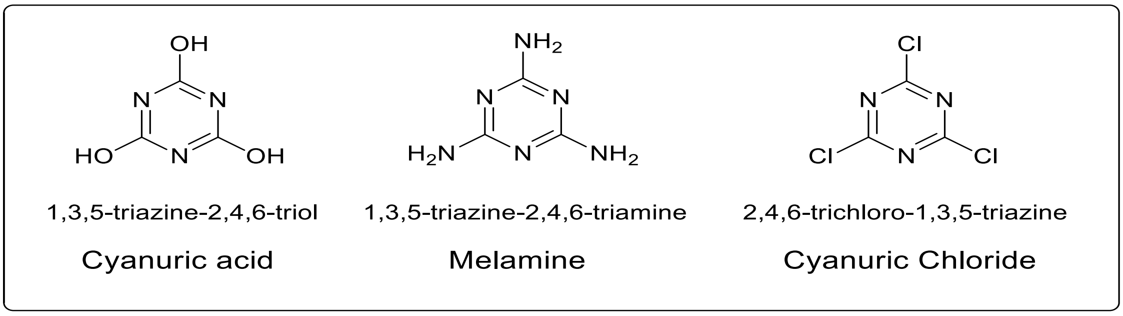


Figure 2.5 Common Triazine Derivatives

The first synthesized compound from triazines were cyanuric acid [15]. "In 1776, Scheele produced cyanuric acid through the pyrolysis of uric acid. The common name of cyanuric acid was developed because, at that time, the compound was considered to be composed of cyanide groups, and it had been produced from uric acid. In 1820, Serullas repeated the work of Scheele to obtain cyanuric acid from cyanogens in water"[20]. It was discovered in "1830 that the two products were indeed the same, and the structure was elucidated by Liebig and Wohler" [22].

2.3 Cyanuric Chloride

"2,4,6-trichloro-1,3,5-triazine or cyanuric chloride" known since 1827,[21]as well as "it was considered to be the trichloride of cyanogens". Liebig"[22],"recognized its composition after obtained the compound bypassing "chlorine over dry potassium thiocyanate". "Serullas converted cyanogen chloride to cyanuric chloride with sunlight"[21] However, "the product was believed for many years to be an isomer rather than the trimer of cyanogens chloride". Aslate as 1867,[23**].** Firstly "the trimer to monomer relationship of cyanuric chloride and cyanogen chloride was not clearly understood".

"Infrared and ultraviolet spectra" [24] now "support the triazine structure" and demonstrate that the chlorines are situated on the carbon atoms.

"Cyanuric chloride is readily hydrolyzed by water vapor to cyanuric acid and hydrochloric acid. cyanuric acid producing by treating cyanuric chloride with hot alcohols [25] and the corresponding alkyl halide with no esterification". Cyanuric chloride reacting with alkaline earth alkoxides to give "mono-, di**-,** and tri-alkyl esters of cyanuric acid"[26,27] or with "Alcohols in the presence of basic acceptors".[27]**.**"To carry out a stepwise substitution, the preferred base is either sodium carbonate or sodium hydroxide". [28].

"Cyanuric chloride, also named tricyanogen chloride, cyanuric trichloride and cyanuryl chloride, is a white, easy hydrolytic degradation monoclinic crystal of pungent odor"."Its soluble in acetonitrile, ether, ketones, and chlorinated hydrocarbons, but nearly insoluble in water"[29]."As a useful organic intermediate, cyanuric chloride is most used to produce triazine derivation which has been widely used in the dye industry"[30]"agriculture chemistry"[31]"plastic and rubber industry"[32].

"Cyanuric chloride" has a "symmetric structure bearing three chlorines "atoms "which can be "substituted by nucleophilic substance step-by-step, such as hydroxybenzene, sulfide, amine in the presence of a hydrochloride scavenger". "The stepwise manner can be controlled at a well-defined temperature. However, the substitution pattern also depends on the structure of the nucleophile, its basic strength and steric factors, the substituent already present in the *s*-triazine ring and the nature of solvent used". For example, "Menicagli achieved nearly quantitative yields of both symmetric and nonsymmetrical" "mono-, di- and trisubstituted alkoxy and amino 1,3,5-triazines by nucleophilic substitution of cyanuric chloride in one pot reaction in the presence of a catalytic amount of 18-crown-6"[33].

"1,3,5-triazine derivatives that have wide practical applications are 2,4,6- mono, di- or tri-substituted, symmetrical and nonsymmetrical compounds". "The most important precursor to these compounds is cyanuric chloride (CC)" whose structure below, due the high "reactivity of its chlorine bearing atoms toward nucleophiles" which give clean reactions. "It is also important to emphasize that cyanuric chloride is a commercially available and a inexpensive material, which makes its applications even more attractive" [30, 34].

"1,3,5-triazine unit has been widely used as a strong electron-accepting center to construct optoelectronic materials due to its high electron affinity and symmetric structure. Many organic and polymeric triazine-based compounds have been synthesized and employed as electron injection and transport materials"[35].

Cyanuric chloride is a colorless "crystalline solid", "it melts at 145 C and boils" at 198°C. It is soluble in many organic solvents such as acetonitrile, acetone, ethanol, heptane and acetic acid. "It is insoluble in cold water and undergoes hydrolysis in water above 10 °C". Cyanuric chloride is commonly prepared by one of three methods.

2.3.1 Cyanuric Chloride Synthesis

2.3.1.1 Trimerization of Cyanogen Chloride.

1- The reaction is conducted in a chloroform dioxane mixture in "the presence of catalytic hydrogen chloride" at 0 °C. The product can be readily isolated due to solubility of cyanuric chloride in chloroform. "On the other hand, dioxane dissolves the hydrogen chloride but not cyanuric chloride". [36].

2.3.1.2 From Hydrocyanic Acid

The "procedure consists of adding chlorine and hydrogen chloride to a solution of hydrogen cyanide in cold chloroform which contains a trace of alcohol" to produce chloral which serves as an intermediate. Chloral reacts with HCN to form the addition compound which "then decomposes in the presence of chlorine to give cyanuric chloride"(see figure 2.6). [37, 38].

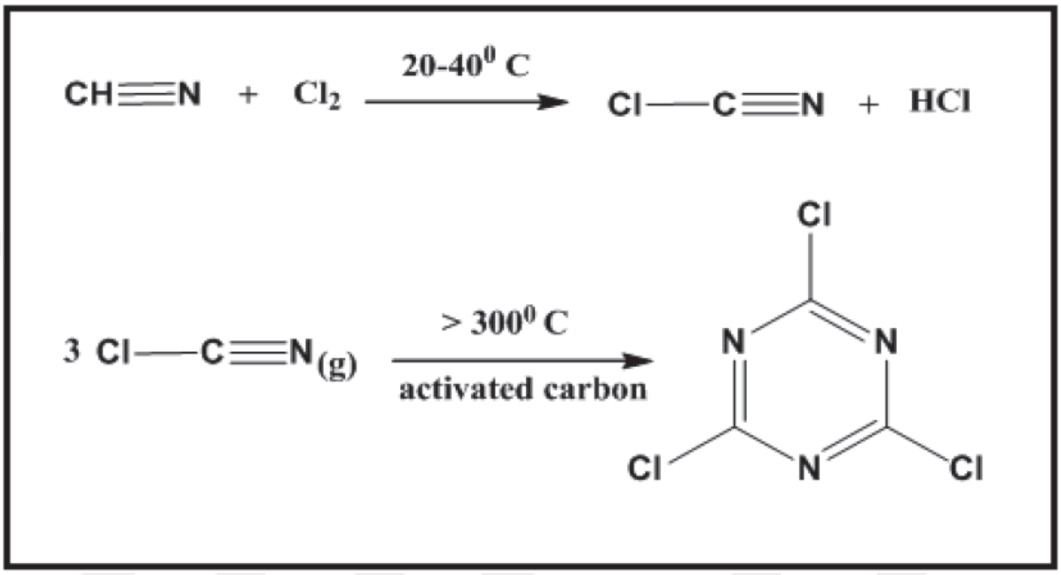


Figure 2.6 Synthesis of Cyanuric Chloride

2.3.1.3 From Cyanuric Acid

Cyanuric chloride can be obtained by reaction of cyanuric acid with phosphorous pentachloride (see figure 2.7)[38].

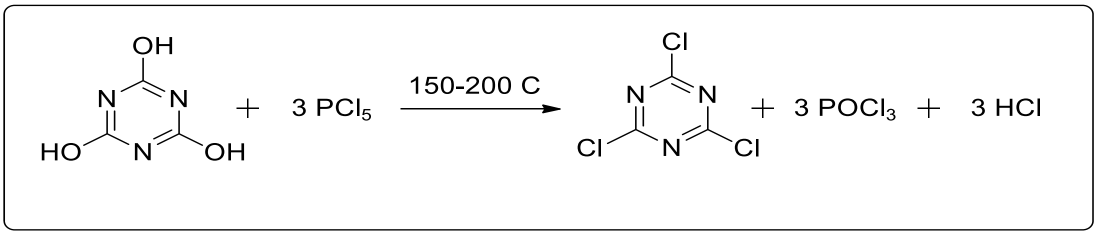


Figure 2.7 Synthesis of Cyanuric Chloride via Cyanuric Acid

2.3.2 Physical and Chemical Properties of Cyanuric Chloride

IUPAC name of cyanuric chloride is 2,4,6-trichloro-1,3,5-triazine. The physical properties are shown in Table 2.1 [39].

Table 2.1 Summary of Physical and Chemical Properties

Property	Value	Reference
Physical state	Solid	
Melting point	145-146 ^{0}C	1,22
Boiling point	190-198 ^{0}C (at 760 mm Hg)	3, 21, 83
Relative density	1.32 (20 ^{0}C)	
Vapour pressure	1.2 Pa 2.5 Pa (20 ^{0}C) 267 Pa (70 ^{0}C)	 17 45
Water solubility	440 mg/L (20 ^{0}C)	7, 17
Partition coefficient noctanol/water (log value)	0.51 >1.7 1.73	6 50 Epiwin
Henry’s law constant	0.04 Pa.m^3/mol	17
Flash point	>190 ^{0}C	106
Ignition temp.	> 650 ^{0}C	106

2.3.3 Chemical Properties

"Under anhydrous conditions, cyanuric chloride can act as a chlorinating agent. Alcohols and tertiary amines are converted to alkyl chlorides"[39,40]."Carboxylic acids form acid chlorides in anhydrous acetone in the presence of triethylamine"(see figure 2.8).

"The acid chloride can be isolated or treated in situ to give the ester, amide, etc.[41]. In both cases cyanuric acid is formed as byproduct".

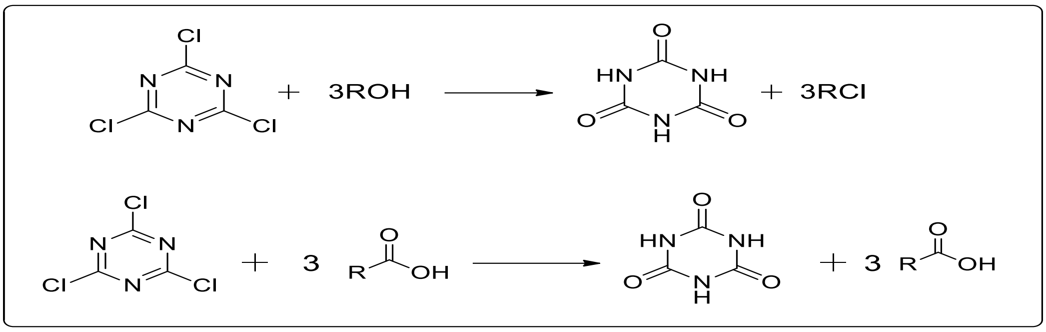


Figure 2.8 Synthesis of 1,3,5-Triazinane-2,4,6-Trione via Cyanuric Chloride

"Cyanuric chloride can be used as a condensation(water-withdrawing) reagent in chemical synthesis. Amides and thioamides can be converted to nitriles"(see figure 2.9).

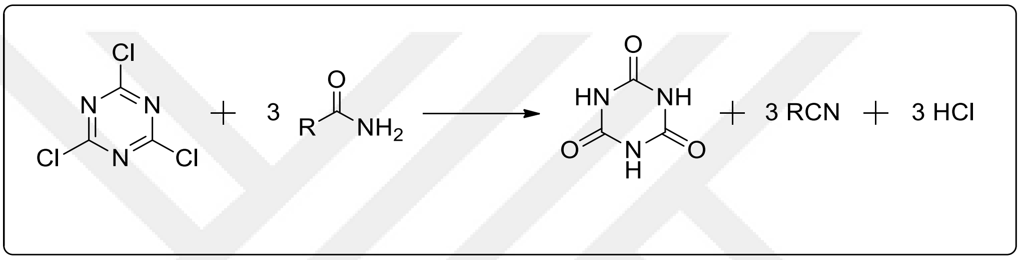


Figure 2.9 Synthesis of Nitriles via Cyanuric Chloride

"Aldoximes react in an analogous way. Aselection of important reactions in which cyanuric chloride acts as chlorination/condensation reagent".

"Under anhydrous conditions tertiary aliphatic amines are converted to substituted melamine derivatives. At the same time one alkyl group is removed and converted to the corresponding alkyl chloride"(see figure 2.10).[40].

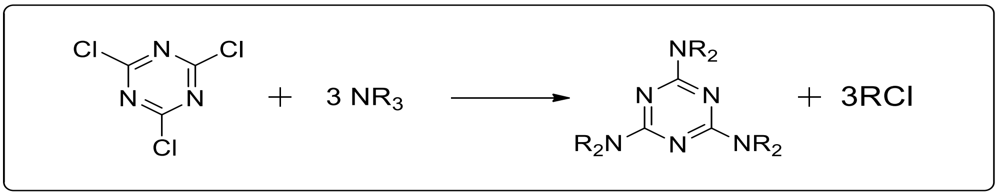


Figure 2.10 Tertiary Amines Converted to Substituted Melamine Derivatives

"Cyanuric chloride usually reacts like an acid chloride with formation of hydrogen chloride"(see figure 2.11).

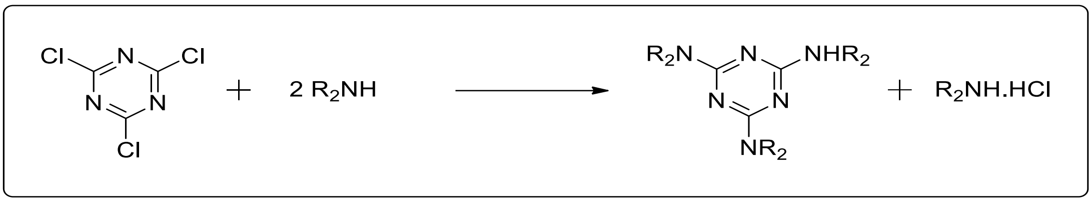


Figure 2.11 Formation of Hydrogen Chloride via Cyanuric Chloride

"According to Fierz – David [42] a suspension of cyanuric chloride in ice water (0 °C) is fairly stable for nearly 12 h. Above 10 °C hydrolysis occurs rapidly; for example, at 30 °C" more than40% of the cyanuric chloride is hydrolyzed within 1 hr".

"The final hydrolysis product is cyanuric acid, the dependence of the hydrolysis of cyanuric chloride (c ¼50 g/L) inwater as a function of hydrolysis time at different temperatures"(see figure 2.12)."In an alkaline aqueous medium, e.g., in the presence of NaOH or NaHCO3, at 40 °C, 2,4-dichloro-6-hydroxy-1,3,5-triazine is formed".

"With an excess of base 2,4-dihydroxy-6-chloro-1,3,5-triazine is formed. Trisodium cyanurate is formed only above 125°C".Anumber of "processes take advantage of the temporary stability of cyanuric chloride in water by reacting a suspension of finely divided cyanuric chloride in ice water with a strong nucleophilic agent such as an alcohol, a thiol, or a primary or secondary amine" [43].

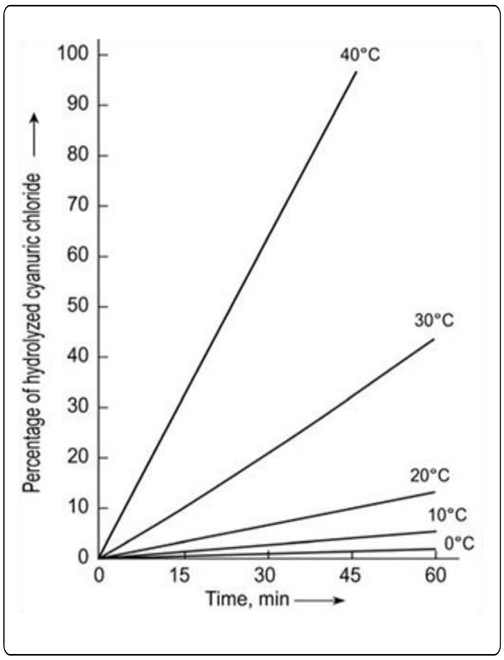


Figure 2.12 Hydrolysis of Cyanuric Chloride as A Function of Temperature

"These reactions often proceed stepwise to trisubstitution at a well-defined temperature. An empirical rule for amine substituent's states that the first chlorine substituent is replaced at(0 –5)°C, the second at (30–50)°C, and the third at (70–100) °C" [42]" Sodium hydroxide, sodium hydrogen carbonate, disodium hydrogen phosphate, and tertiary amines can be used as HCl scavengers"(see figure 2.13).

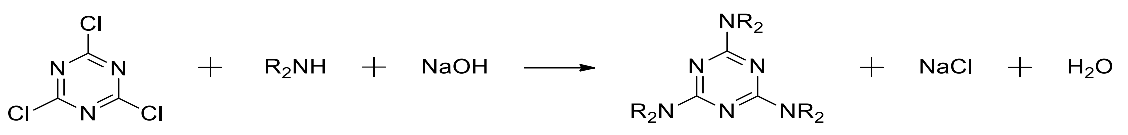
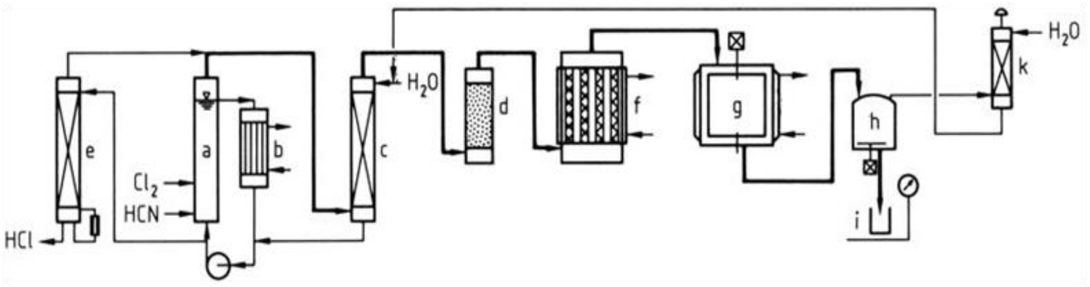


Figure 2.13 Tri-Substitution of Cyanuric Chloride with Tertiary Amines

The "triazine product is usually isolated by filtration or centrifugation. Solvents such as acetone, methyl ethyl ketone, or toluene are of tenused for these reactions. Cyanuric chloride, melt or powder, is dissolved or suspended in the solvent with the nucleophile and treated with aqueous NaOH. The product is filtered or is isolated from the organic layer by evaporation".

"Both methods are used to introduce different substituent's successively at different temperatures. Replacement of the third chlorine atom is sometimes carried out by employing high-boiling solvents or simply the molten reactant. Care must be taken to neutralize the liberated hydrochloric acid and to dissipate the heat of reaction".

"Otherwise, the exothermal hydrolysis of cyanuric chloride (DH ¼ _ 2164 kJ/kg) can become uncontrollable, especially in the manufacture of cyanurates from alcohols"(see figure 2.14). [44].



a) ClCN reactor; b) Heat exchanger; c) Scrubber; d) Dryer; e) Effluent stripper; f) Trimerizer; g) Condenser; h) Storage; i) Drum; k) Tail gas scrubber

Figure 2.14 Production of Cyanuric Chloride from Chlorine and Hydrocyanic Acid

"**Hydrolysis** is accelerated by water-miscible solvents. Storage of solutions of cyanuric chloride in aqueous acetone without heat removal can result in arun-away reaction, which can even start at room temperature". DMF reacted with "cyanuric chloride to form Gold's salt [20353-93-9]"(see figure 2.15). [45].

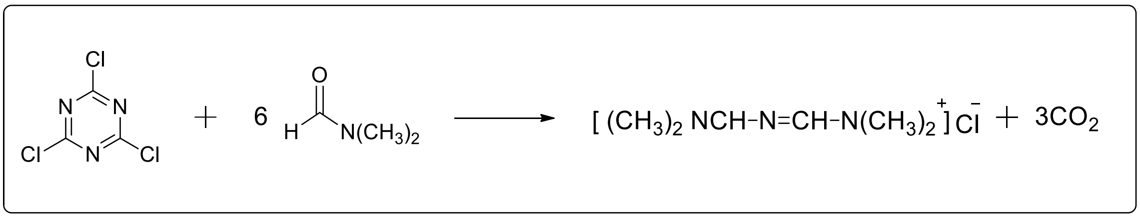


Figure 2.15 Cyanuric Chloride Reaction with DMF

2.3.4 Substituted of Cyanuric Chloride

The substituted of triazine described to be synthesized starting from "cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) and different nucleophiles as the chlorine atoms of cyanuric chloride can be replaced successively by substituted or non– substituted with different amino groups". The nucleophiles substitution can be easily proceed to displace the chlorine atoms depending on temperature the reaction [46].

"In general, the first chlorine can be displaced while the temperature is maintained at (0-5)°C, the second between (27- 50) °C and the third substitution happens at reflux temperature. Other important factors that have to be considered for the preparation of the different derivatives are the nature of the reactive group and the order of entry of the group".

"When different amino groups are introduced, the less reactive one is introduced before the more reactive one. The reactions, in most cases, are carried out in aqueous suspensions, since the products precipitate from solution, simplifying their isolation"[47]."The cyanuric chloride is previously dissolved in acetone and then poured into ice-water to get a very fine suspension and to increase the reactivity and the yield". "The reaction of cyanuric chloride with different amines gives 2-sustituted-4,6-dichloro-1,3,5-triazines"[48-49]."The 2,4-disubstituted-6-chloro-1,3,5-triazines are obtained by reaction of a further amine with the 2-substituted-4,6-dichloro-1,3,5-triazine in the presence of base. The displacement of the last chlorine is carried out at reflux temperature affording the product in good yields"(see figure 2.16)."The product had a low solubility in most organic solvents, except DMSO. However, purification was achieved by recrystallization from methanol-water solution. The elegance of this method lies in its simplicity in use and handling to achieve the desired target".

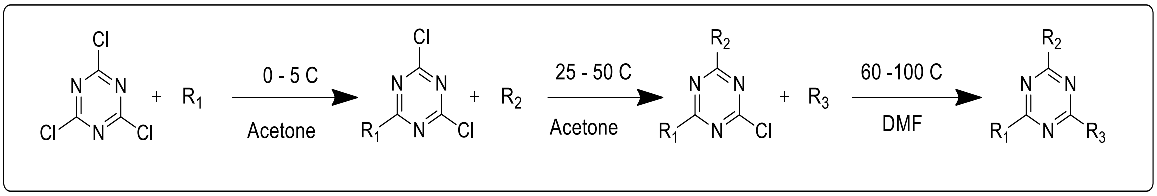


Figure 2.16 Nucleophilic Substitution of Cyanuric Chloride

2.3.5 Hazards To The Environment

2.3.5.1 Aquatic Effects

"The aquatic toxicity of cyanuric chloride is not directly determinable due to its poor solubility and its hydrolytic properties. Only difficult to define hydrolytic mixtures, which are affected by Ph value, the temperature, the amount added and the time period between production and the test run, can be studied. In order to transverse this boundary which applies for all studies of cyanuric chloride in aqueous systems, results of tests with hydrolytic products capable of isolation, such as 2-chloro-4,6-dihydroxy-1,3,5-triazine and cyanuric acid, were included here". Additionally "QSAR calculations on acute toxicity towards fish, daphnia and algae were performed" (see Table 2.2).[50,51,52]

Table 2.2 QSAR Calculations On Acute Toxicity

	Fish (LC50 mg/L)	**Daphnia (EC50 mg/L)**	**Algae (EC50 mg/L)**
Method	ECOSAR	ECOSAR	Log EC50 = -1.00 logKow -1.23 (ref. Van Leeuwen)
Cyanuric chloride	245	258	202
2-chloro-4,6-dihydroxy-1,3,5-s-triazine	994	993	909
Cyanuric acid	1940	1890	1866

2.3.5.2 Environmental Exposure and Fate

"The atmospheric oxidation potential" (AOP)" predicted from the Epiwin program indicates that cyanuric chloride is not photolytically reactive (degradation half-life of > 15 year). A summary ofthe Epiwin calculations is attached as Appendix A"."Cyanuric chloride reacts readily with nucleophilic substances like ammonia, diethylamine, aniline, methanol and water" (53).

"Cyanuric chloride hydrolyses quickly to cyanuric acid in water via formation of 2,4-dichloro-6-hydroxy-s-triazine and 2-chloro-4,6-dihydroxy-s-triazine" (see figure 2.17) [54,55,56].

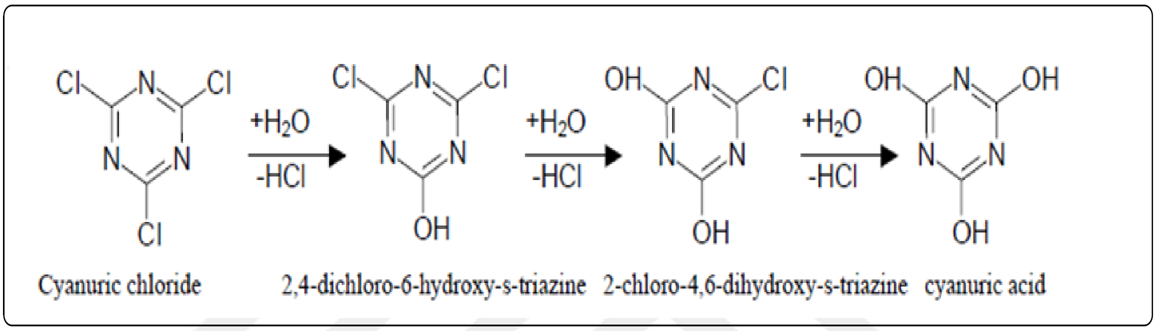


Figure 2.17 Hydrolysis of Cyanuric Chloride

The "reactivity of cyanuric chloride is comparable to that of an acid chloride. The hydrolysis ofcyanuric chloride takes place by a step-wise substitution of all three chlorine atoms by hydroxylgroups. In the 3-step reaction, the first intermediate formed is 2,4-dichloro-6-hydroxy-1,3,5-triazinewhich further reacts to 2-chloro-4,6-dihydroxy-1,3,5-triazine. The final product of the subsequent reaction is cyanuric acid, which is stabilized by tautomerism (tautomer: isocyanuric acid)".

"Compared with its hydrolytic products, cyanuric chloride is relatively poorly soluble in water. Therefore, precise and dependable statements on the hydrolytic degradation are difficult to make".

"The nucleophilic reaction in all partial steps can be described by a first-order reaction rate equation. Reaction rate constants of the single partial reactions differed by one to two orders of magnitude, i.e. at the time of the concentration maximum of the respective hydrolytic product, its predecessor was already extensively degraded. The half-lives of cyanuric chloride and its hydrolysis products depend on pH value, the temperature and partially also on the type of buffer system used. The lowest reaction rate was calculated for a pH value of about 5.5. The reaction rate constant rises sharply towards higher as well as lower pH values, whereby the reaction of cyanuric chloride to cyanuric acid is faster in acidic solution than in alkaline solution. The relative decrease of the rate of hydrolysis with increasing basicity compared to increasing acidity is caused by the fact that although k1 (cyanuric chloride to 2,4-dichloro-6-hydroxy-1,3,5-triazine) increases, k2 (2,4- dichloro-6-hydroxy-1,3,5 triazine to 2-chloro-4,6dihydroxy-1,3,5-triazine) and k_3 (2-chloro-4,6-dihydroxy-1,3,5-triazine to cyanuric acid) are nonetheless lower than the corresponding values in the acidic range".

"The reason for the slower reaction rate in neutral or alkaline media than in an acidic medium lies in the dissociation of the hydroxyl groups and formation of mono- or di-sodium salts of the hydroxyl chlorotriazines. The reactivity of the remaining chlorine atom(s) on the triazine ring is reduced upon formation of these salts, which leads to a stabilization of the hydrolytic intermediate products in form of its anions under neutral or alkaline conditions. In fact, under alkaline conditions, the hydrolysis can almost come to a standstill at the step of 2-chloro-4,6-dihydroxy-1,3,5-triazine" .

2.3.5.3 Human Health

Cyanuric chloride showed a "high toxicity of oral LD50 of ~320 mg/kg bw and a dermal LD50 of >2000 mg/kg bw. The high acute inhalation toxicity of cyanuric chloride (LC50 170 mg/m3) is likely to be secondary to its highly irritating/caustic properties". The cyanuric chloride is "highly effected to the skin, the eyes and the respiratory tract (RD50 5.9 mg/m3)". "When cyanuric chloride exposure to humans causes irritation and caustic effects to eyes and respiratory tract, skin. Cyanuric chloride is sensitizing. Asthma and contact dermatitis are also reported in humans".

Ideally "cyanuric chloride repeated dose studies effected to body weight loss and stomach erosion and ulceration". Severe dermal irritation was seen "in a 21-day dermal study decreased body weight was reported at 150 and 500 mg/kg bw" at all dose levels tested. "Since it cannot be excluded that the effects on body weight" were secondary to stress by the treatment, no systemic NOAEL was derived". "The LOAEL for local effects is 50 mg/kg bw. From a 90-day inhalation study a NOAEC of 0.25 mg/m3 (the highest concentration tested) for systemic toxicity was derived". "The NOAEC for local effects in the respiratory tract of rats displaying"inter current respiratory infection was found to be 0.05 mg/m3. The effects included inflammation in the nose and lungs".

Because of "low solubility (440 mg/L) and easily hydrolysis properties, the actual concentration of cyanuric chloride in water is very low as the cyanuric chloride has a low vapour pressure and log Kow of 1.7". The hydrolysis products of cyanuric chloride by biodegradation process "are much more relevant than cyanuric chloride itself. these hydrolysis products has Studied and showed very limited biodegradability of these compounds under standard test".

2.3.6 Reactivity of Cyanuric Chloride

Cyanuric chloride is a weak base because of its low basicity as well as ring nitrogen atom . The substituted of "chlorine atom in cyanuric chloride by basic group is greatly facilitated by the ring nitrogen" atoms. Although reaction occurs at "ring nitrogen atoms most of the reactions of cyanuric chloride involve the chlorine atom which react selectively one or more at a time with nucleophilic reagents". The high reactivity of cyanuric chloride derivative seem to be due to "maximum resonance stabilization of a charge which can be achieved in transition state". Even "the deactivated mono and di-substituted products of trichloro-s-triazine show high reactivity". Trisubstitution sometimes proceed to completion readily at 20 °C [57].

2.3.6.1 Substitution Reactions by Nucleophiles and Reactivity

Cyanuric chloride is suitable for the nucleophilic substitution reactions. The reaction percentage of cyanuric chloride is dependent on temperature, solubility and the nature of the nucleophilic reactant. "The ease of displacement of chlorine atoms in cyanuric chloride by various nucleophiles makes this reagent useful for the preparation of mono-, di- and tri-substituted 1,3,5-triazines in the presence of a hydro chloride scavenger" such as "sodium carbonate, sodium bicarbonate, sodium hydroxide, disodium hydrogen phosphate or tertiary amines"(see figure 2.18) [58, 59].

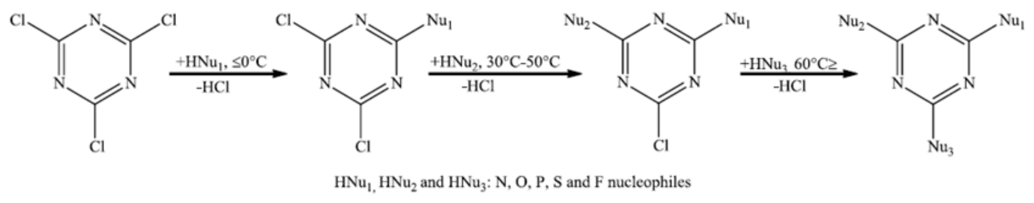


Figure 2.18 Substitution Reactions of Cyanuric Chloride At Different Temperature

2.3.6.2 Reactions of Cyanuric Chloride with Nitroxyalcohols

This reaction was the first nitrate ester reported in the s-triazineseries, has taken place to "determine whether nitroxy groups-affected esterification or the subsequent stability of the products. Pentaerythrtl trinitrate (PETriN) and pentaerythritol dinitrate were the nitroxyalcohols used in this reactions.

The product was successfully obtained by the reaction of pentaerythritol trinitrate and cyanuric chloride in aqueous acetone solution with potassium hydroxide as the acid acceptor"(see figure 2.19)[22].

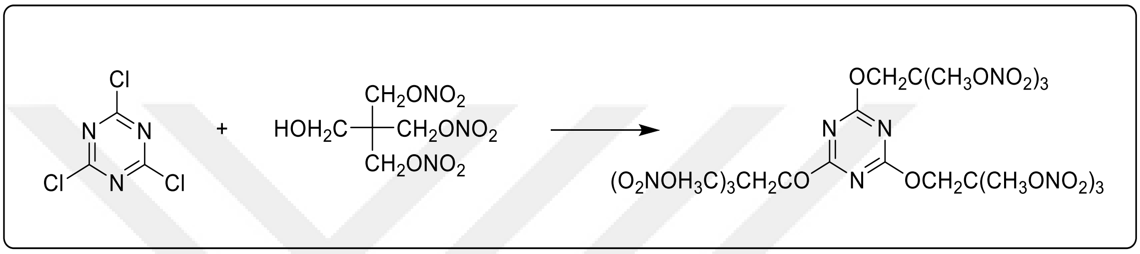


Figure 2.19 Cyanuric chloride with nitroxyalcohols

2.3.6.3 Reactions of Cyanuric Chloride with Polyhalogen Alcohols:

The starting materials for the reaction are "trifluoroethanol and tribromoethanol were reacted with cyanuric chloride". The purpose of using alcohols to "determine whether electron withdrawing halogen substituent's affected the stability" of the final product or the reactivity of the alcohol with cyanuric chloride (see figure 2.20).

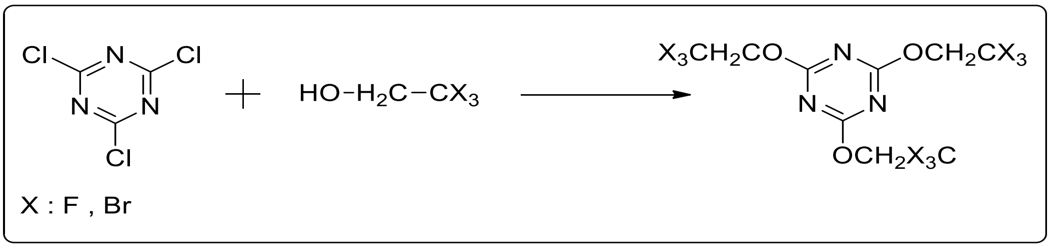


Figure 2.20 Cyanuric Chloride with Polyhalogen Alcohols

Both "reactions proceeded smoothly to give the corresponding product in good yields indicating that the electronegative groups did not affect or hinder ester formation. The products appeared to be thermally stable up to and above 1900 °C"[23].

2.3.6.4 Trans-Esterification Reaction of Alkoxy-s-Triazines

The reaction of cyanuric chloride with alcohols easily as mentioned above. These derivatives of cyanuric chloride are called alkoxy-s-triazines [55].

The trans-esterification reaction of alkoxy-s-triazines occurs between volatile and less volatile alcohols by heating(see figure 2.21).

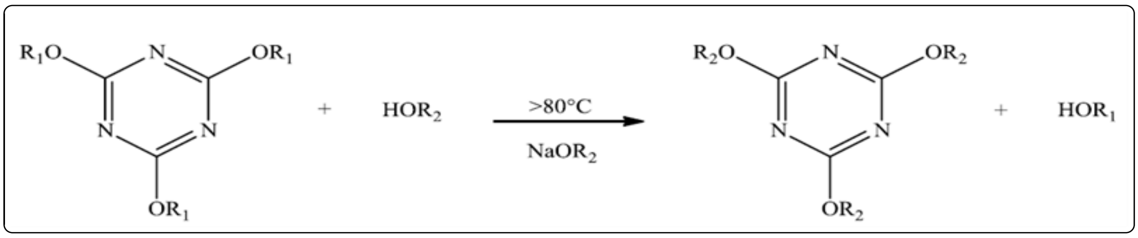


Figure 2.21 The Trans-Etherification Reaction of Alkoxy-S-Triazines with Alcohols.

A low boiling alcohol is displaced by less volatile alcohol. Usually, only a catalytic amount of an alkoxide is required and the temperature should be above 80^oC to yield tri-substituted triazines [55].

2.3.6.5 Synthesis of THEIC-ESBO Based on Triazine

The synthesis of "PVC plasticizers which derived from renewable resources" has reported in recent publications. Ye et al. (2013)[56]started with acetic acid, glycerol, and "benzoic acid as materials and developed a new series of triglyceride plasticizers"(see figure 2.22)."Badra found that the di-(2-ethyl hexyl) phthalate could be replaced by epoxidized sunflower oil as bio-based plasticizer for flexible PVC"[57]. "Desmond et al. (2014) investigated the palm oil-based compound as a polymeric plasticizer for PVC"[58].

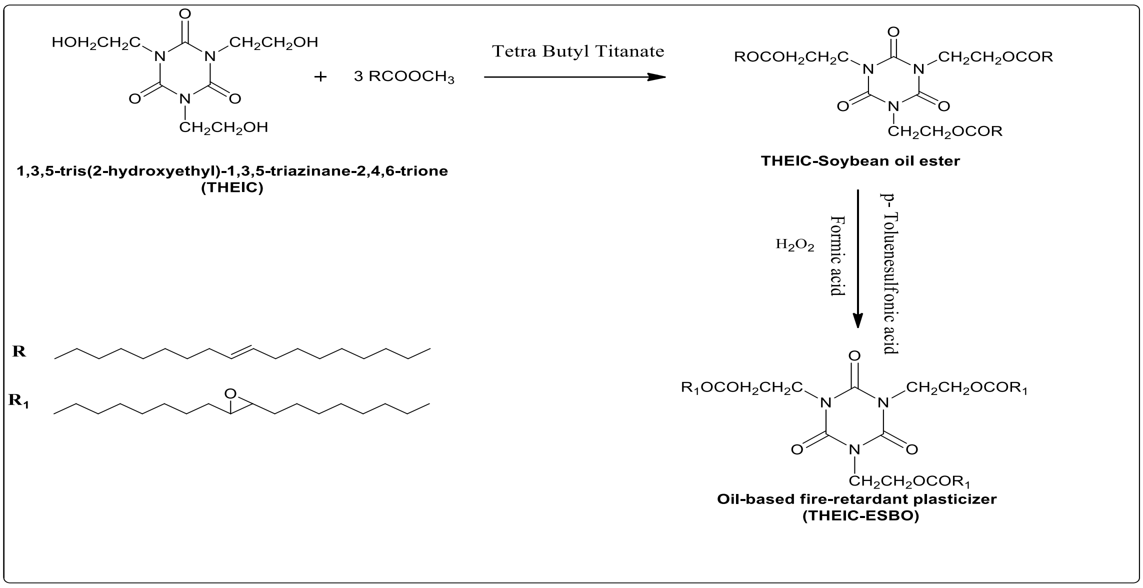


Figure 2.22 Synthesis Route of THEIC-ESBO

2.3.6.6 Reagent for The Activation of Carboxylic Acids for Reduction to Alcohols

"Cyanuric Chloride is also used for the activation of carboxylic acids" for reduction to alcohols (see figure 2.23)

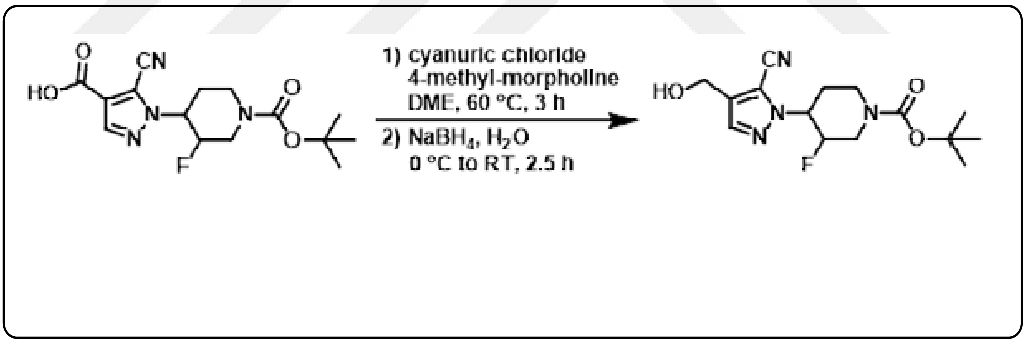


Figure 2.23 Cyanuric Chloride Reagent for Activation Carboxylic Acids

2.4 Application of Triazine Derivatives

Triazine-based chemistry has a wide range of applications as agrochemicals, inhibitors, antitumors and flame retardants, but also shows a high affinity for different enzymes, thereby increasing the interest in triazine containing processes.

2.4.1 In Agriculture

The in triazine derivatives stems has gain much interested due to their potential application as agrochemicals. Triazine based "herbicides have gained worldwide recognition. The major problem experienced due to herbicides is the contamination of soil, surface water, and possibly ground water with their residuals. Systematic studies on residual s-triazines and related compounds are necessary"[60-61]. "Studies are therefore needed to evaluate the toxicities of several substituted triazines and their metal complexes in order to understand the role of substituent and metal complexation in modifying the activities of s-triazine herbicides".

"Many chlorine-containing herbicides, for example 2-chloro-*s*-triazines, are of great concern both environmentally and toxicologically"[62]. "Two approaches are currently validated in the detoxification of remnant herbicides. One of them is derivatization of the herbicides into the less harmful compounds after crop development while the other is the metal ion associated degradation or deactivation of the herbicides". Reports have determined that "metal ions can show remarkable effect in catalyzing the decomposition of herbicides"[63, 64].

This is because the introduction of metal ion causes a change in the chemical structure of herbicides which in turn cause the dramatic shift in the herbicides performance. Consequently, this affects remarkably the fate of herbicides by either catalyzing their decomposition or inactivating them. "Yared Merdassa described the basic chemistry of derivatization and metal complexation of selected herbicide systems that can be used as a means for modifying their activities".

Cyanuric chloride has the most numerous applications among the triazine derivatives. Cyanuric chloride usually used as agrochemicals, dyestuffs, optical brighteners, tanning agents, reactive dyes, UV-absorbing agents, softening agents, pharmaceuticals and cross linking agents (see figure 2.24.

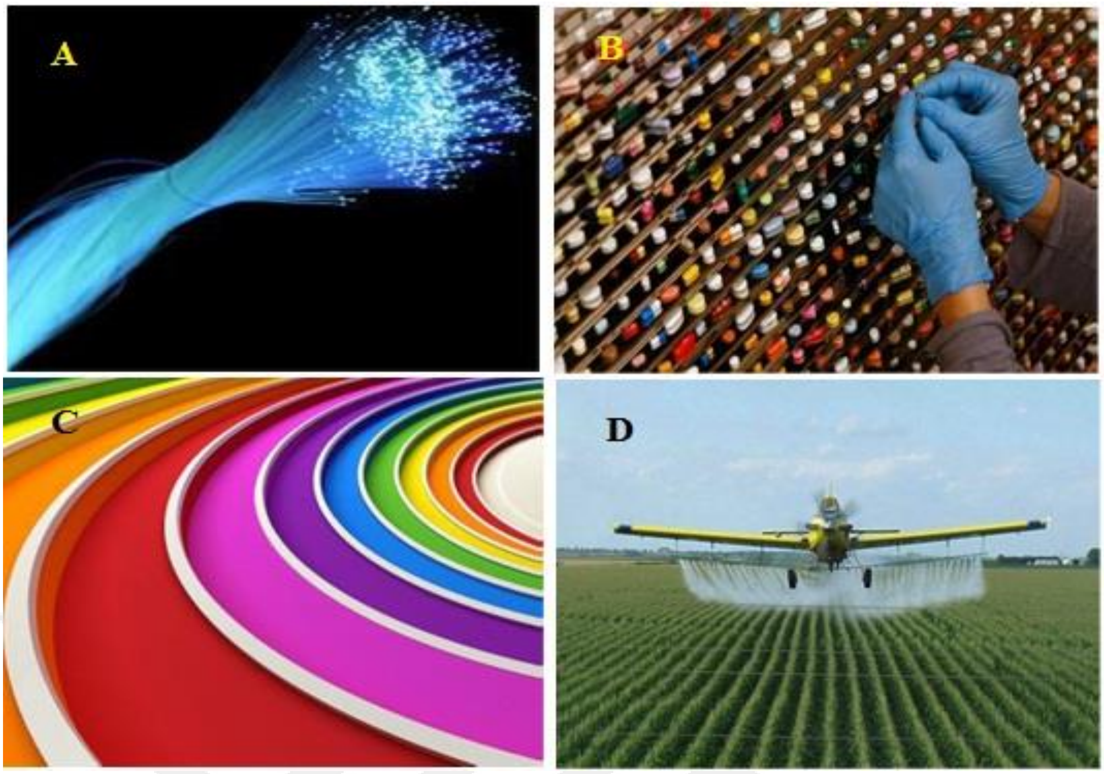


Figure 2.24 Some Examples Use Triazine Related Materiesas in Various Industries Such As (A) In Fiber Optics (C) In Pharmaceuticals, (C) In Paints And (D) Agriculture.

The "most important cyanuric chloride derivatives are the aminotriazines. Alkylaminotriazines are used as pesticides and herbicides" in agricultural industry. The"triazines are still among the biggest selling herbicides, most of derivatives are 2-chloro- or 2- methylthio-4,6-dialkylamino-1,3,5-triazines is one of the oldest" **(**Simazine) and atrazine is the most important triazine-based herbicide[65,66] (see figure 2.25).

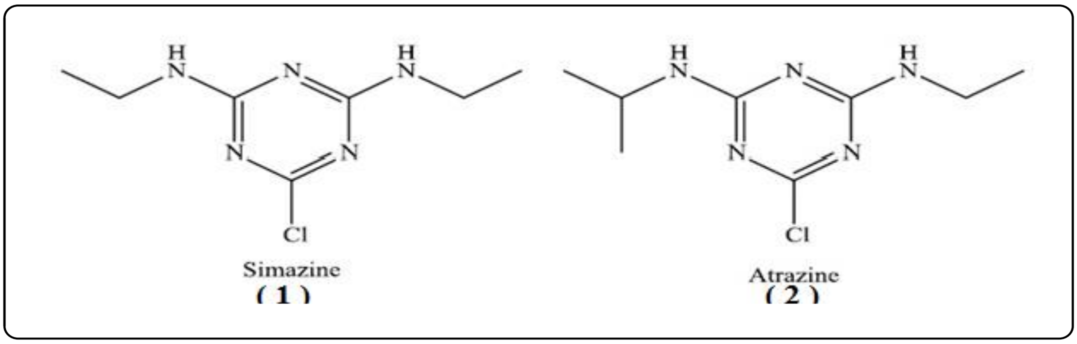


Figure 2.25 Simazine and Atrazine

2.4.1.1 In Polymer Chemistry

"Derivatives of 1,3,5-triazine often show light-emitting and molecularly assembling properties"[67,68]. "1,3,5-triazine-based polymers", "especially those with a πconjugated connecting group between the 1,3,5-triazine units, is desired to reveal the usefulness of the 1,3,5-triazine-based polymers as electronic materials". Alkyl and amino-1,3,5-triazine-based polymers are photo luminescent in nature. "Because the polymer is transparent in most parts of the visible light region, 1,3,5-triazine-basedpolymers may be useful materials for photo devices such as photocopiers, photovoltaic cells and electroluminescence devices" [69] (see figure 2.26).

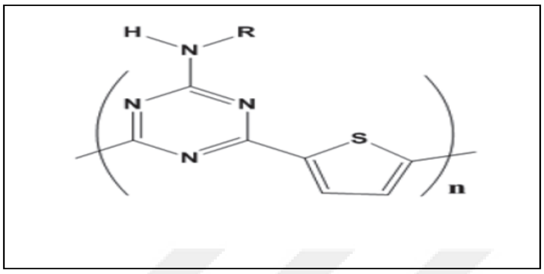


Figure 2.26 Poly 1,3,5-Triazines

2.4.1.2 In Catalysis

"Design and development of nitrogenous materials and their utilization in catalysis is of great interest". Depending upon " the type of N-moieties these materials have been enormously utilized in catalyzed organic transformations such as Knoevenagel condensation [70], aldol condensation[71], C-H bond activation"[72], isomerization[73], oxidation [74] and epoxidation [75]. "Chehard oli et al. reported that melamine have potential to catalyze the chemo- and homo selective oxidation of thiols and sulfides[76] by hydrogen peroxide". With respect to these viewpoints "Mohd Bismillah Ansari etal. synthesized triazine based microporous polymeric (TMP) network (see figure 2.27)was found to be an efficient metal-free catalyst for the epoxidation of styrene".

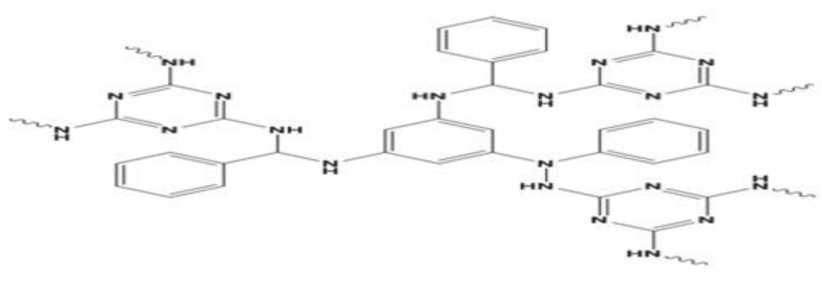


Figure 2.27 Triazine Based Microporous Polymeric (TMP) Network

"A.S.Ramasubramanian et al. [77] reported the synthesis of transition metal complexes of 5-bromosalicylidene-4-amino-3-mercapto-1,2,4-triazine-5-one (see figure 2.28),with metal precursors" such as "copper(II), nickel(II),cobalt(II) and palladium(II)" ions. "The newly synthesized complexes are good catalysts for the oxidation of alcohols to the corresponding carbonyl compounds. The catalytic efficiency was high when N-methylmorpholine-N-oxide (NMO) was employed as the co-oxidant".

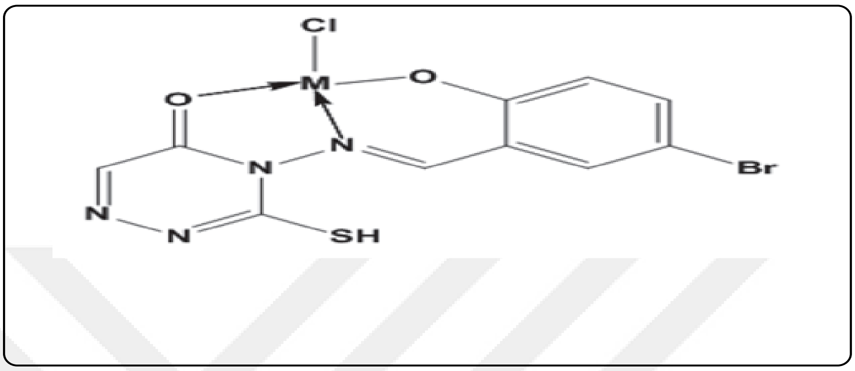


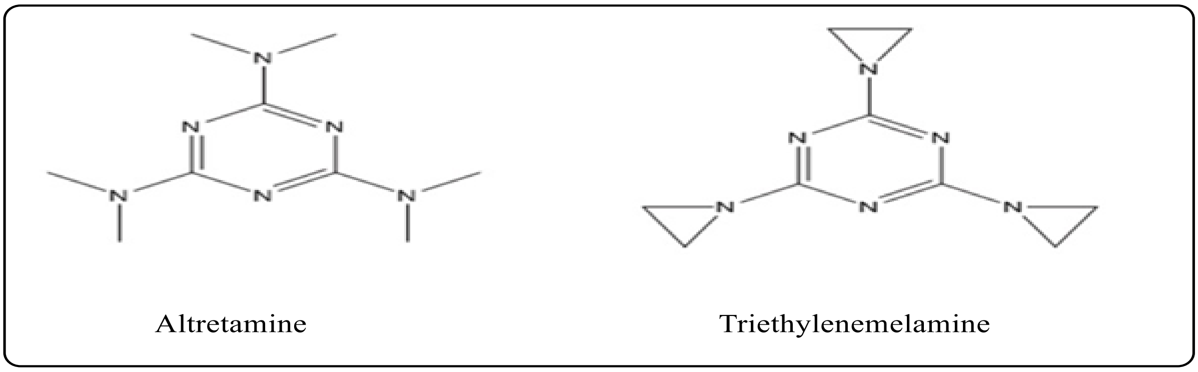
Figure 2.28 5-Bromosalicylidene-4-Amino-3-Mercapto-1,2,4-Triazine-5-One Complexes

2.4.2 In Medicinal Chemistry

"Tri-substituted 1,3,5-triazines are one of the oldest classes of organic compounds that continue to be used as important core structure in many chemotherapeutic agents dueto their interesting pharmacological properties, including anticancer" [78], antiangiogenes[79], anti-HIV [80], antimalarial [81], antibacterial [82] and antimicrobial activity [83]. "The triazine compounds presumably act by inhibiting the action of an inducible membrane protein that normally functions to increase the efflux of thecytotoxic agent". The triazine compounds "(1,3,5-triazine derivatives) also exhibit antiulcer, anti-depressant and antiviral activity" [84].

2.4.2.1 Anticancer Activity

Altretamine"is an Antineoplastic agent. It was approved by the FDA in 1990.It is used to treat refractory ovarian cancer. It is not considered a first-line treatment, but it can be useful as salvage therapy. It also has the advantage of being less toxic than other drugs used for treating refractory ovarian cancer"[85,86]. Triethylenemelamine is a drug used in chemotherapy(see figure 2.29).



Altretamine

Triethylenemelamine

Figure 2.29 Altretamine and Triethylenemelamine

2.4.2.2 Antimicrobial Activity

"The development of natural and synthetic antimicrobial peptides" have contributed to numerous studies"as a prospective source of antibiotic agents". According to this concept we could say "the major factors determining antibacterial activity in these peptides are cationic charge, bulk, and lipophilicity, designed and screened several combinatorial libraries based on 1,3,5-triazine as a template". "A set of compounds were identified to show potent antimicrobial activity together with low hemolytic activity" [87] (see figure 2.30).

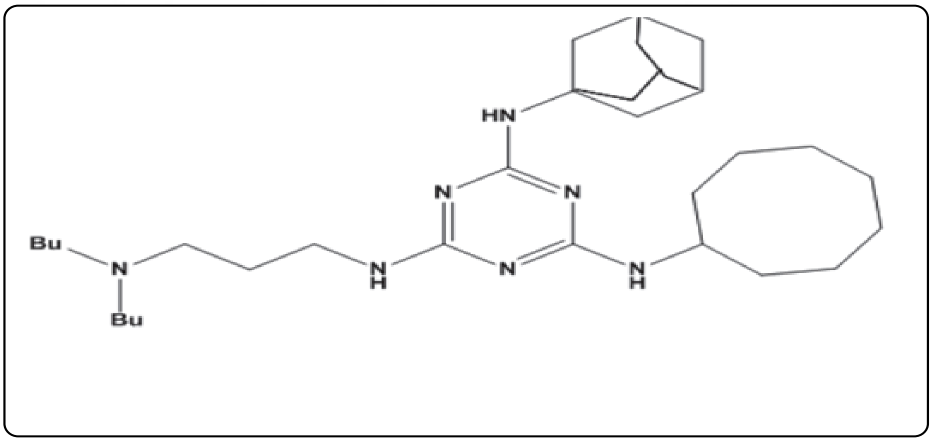


Figure 2.30 Antimicrobial Peptide

2.4.2.3 Antimalarial Activity

"A series of new class of hybrid 4-aminoquinoline triazines "were synthesized and used as antimalarial agents regarding the "emergence and rapid spread of chloroquine resistant strains of plasmodium falciparumhas dramatically reduced the chemotherapeutic options"[94] (see figure 2.31).

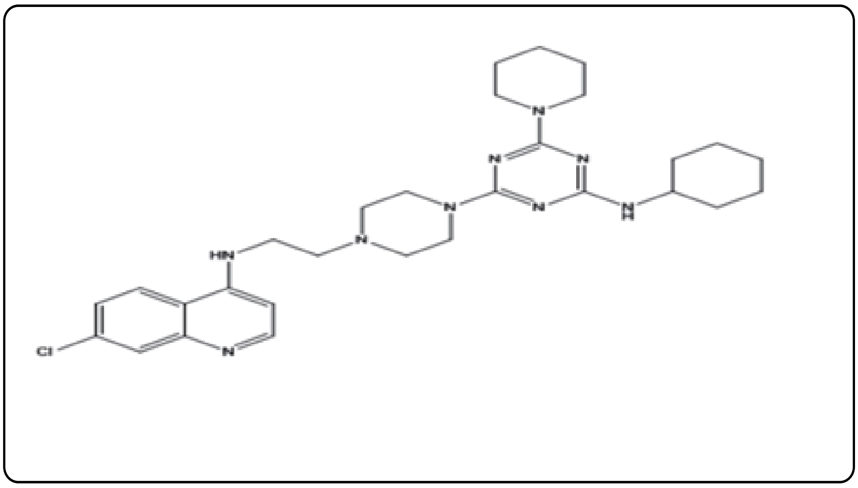


Figure 2.31 4-Aminoquinoline Triazine

2.4.2.4 Antitumor Activity

"A novel series of triaminotriazine derivatives and evaluated for their inhibition activities to colorectal cancer (CRC) cell lines (HCT-116 and HT-29)". "Most of the synthesized compounds demonstrated moderate anti-proliferatory effects on both HCT-116 and HT-29 cell lines [89] (see figure 2.32).

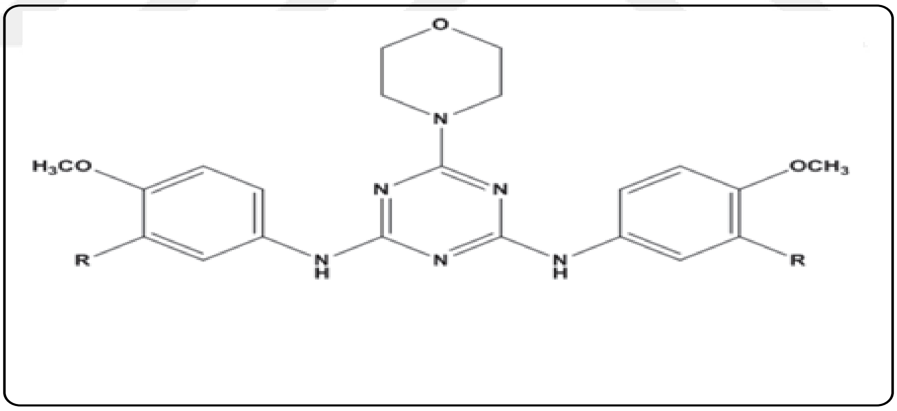


Figure 2.32 Triamino Triazine Derivative

2.5 Plasticizer

"Plasticizer is a substance incorporated into a plastic or elastomer to increase its flexibility, workability" or dispensability as defined by ASTM" [90].

Plasticizers are organic compounds used for modifying of polymer properties. plasticizers do not react chemically with macromolecular compounds, but are incorporated into the polymer matrix, making it elastic, decreasing the processing temperature and the melt viscosity, and enhancing the dielectric properties of articles and their resistance to heat, frost, water, and organic media. The main requirements to plasticizers are low extractability with water, oils, and detergents, good compatibility with the polymer, low volatility, chemical stability, plasticizing performance, nontoxicity, and low cost [91, 92].

Organic compounds of different classes can be used as plasticizers: esters of dicarboxylic and phosphoric acids, hydrocarbons and their derivatives, vegetable oils, products of their modification, etc.

Esters plasticizers are the most widely used (90% of the market), of which *o*-phthalic acid esters make up more than 80%. The other esters (adipates, trimellitates, terephthalates, sebacates, azelates, acrylates, methacrylates, maleates, phosphates, polyesters) are used in considerably smaller amounts(see figure 2.33).

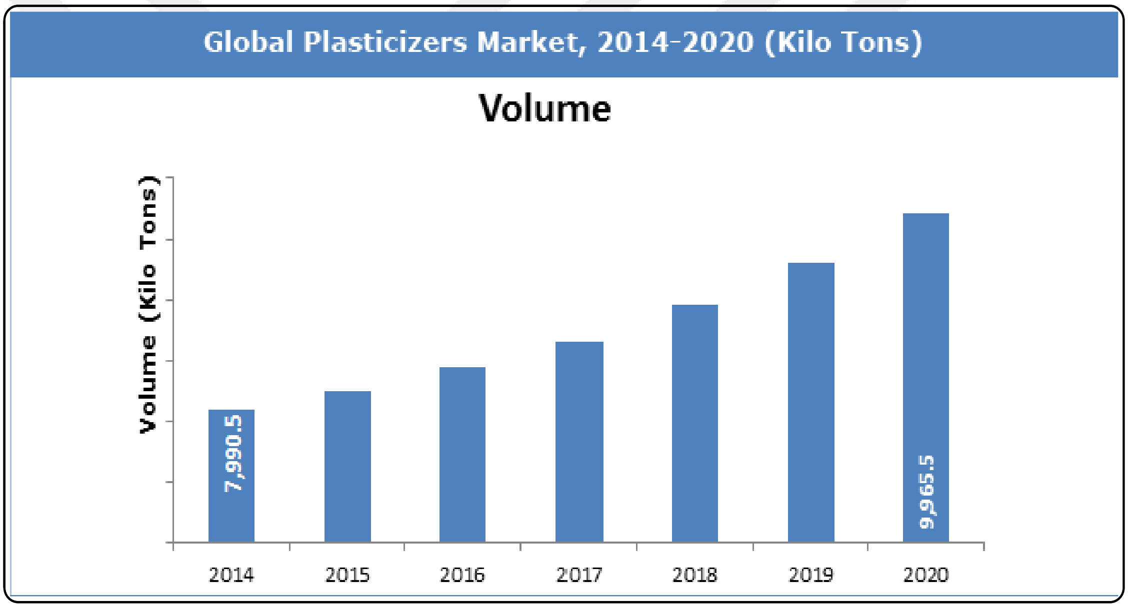


Figure 2.33 Global Plasticizers Market

The growing requirements to environmental safety and exhaustion of crude oil resources stimulated in the recent period active development of studies in the field of synthesis and use of biodegradable plasticizers derived from renewable vegetable raw materials. These include citrates, esters of epoxidized fatty acids, and esters of glycerol, polyglycerol, etc., which can be used for plasticization of both polyvinyl chloride (PVC) and biopolymers such as polylactic acid, polyhydroxyalkanoates, thermoplastic starch, protein plastics, cellulose acetates [93,94].

Plasticizers which consumed in production of PVC items are more than 90% . Since PVC plasticizers are subdivided into three groups with respect to characteristics of their action [95]:

A- General-purpose plasticizers imparting to PVC the required flexibility at optimum balance of the required properties and low cost; these mainly include dialkyl phthalates.

B- Functional plasticizers imparting additional properties to PVC, such as strongly solvating, low-temperature, and weakly volatile plasticizers.

C- Specialty plasticizers imparting special properties to elastic PVC, such as weakly diffusing, stabilizing, and fire-retarding agents.

2.5.1 Literature Summary

Historically, since 1800s plasticizers started used as a polymer additives [95]. "The worldwide demand in 2009 was about 5.7 million tons of plasticizer constituting 51.8% share of global polymer additives market" The worldwide produced around 1200 different plasticizers and about 100 of them are classified as commercially important [96]. The plasticizers which "are used in plasticized or flexible poly(vinyl chloride) (PVC) products" about 90% approximately.

Plasticizers are required for a "polymer systems as poly(vinyl butyral), poly(vinyl acetate), acrylic polymers, poly(vinyldiene chloride), nylon, polyamides, cellulose molding compounds", polyolefin's and certain fluoroplastics [97,98]. "The largest group and most significant of PVC plasticizers is esters of phthalic acid with the share of 97% of all plasticizers used". Plasticizers of "phthalate esters are mostly based on carboxylic acid esters containing linear or branched aliphatic alcohols of chain lengths C_6-C_{11}".

"Since the 1920s the phthalate esters have been used as plasticizers in plastic materials. Widely used phthalates such as, di-isononyl phthalate (DINP), dioctyl phthalate (DOP), di(2-ethylhexyl)phthalate (DEHP), di-isodecyl phthalate (DIDP), di-butyl phthalate (DBP) and butyl benzyl phthalate (BBP). The (DOP),is the most widely used since 1930s as phthalate plasticizer has been"[99]."Phthalate esters are usually added in concentrations up to 50% of the final weight of the products"[100,101]. According to "Ceresana Research report, plasticizer market in 2010 was dominated by phthalate esters, with 54% share of DOP, as the most widely used.

Ceresana Research forecasts that over the next year's DOP will be increasingly replaced by alternative plasticizers due to worldwide growing concerns about the potential toxicity of phthalate esters to humans and the environment" [102]. The application of "phthalate plasticizers is being questioned because as low molecular weight compounds they migrate out of the polymer matrix. Since they are commonly used in a variety of products: flexible plastics, toys, flooring and car dashboards, food contact materials, packaging systems, synthetic leather, medical devices like blood transfusion bags and haemodialysis tubing, cosmetics, as a result, they have been found in terrestrial and aquatic" "ecosystems, in domestic foods and wastes, and also in animals and humans". "Main human exposure pathways to phthalates include inhalation of air contaminated due to off-gassing from plasticized products, also food and drinking water containing plasticizers that exude from packaging materials designed for victuals or are extracted by the foodstuff"[99,110,103].

"Unfortunately, the exposure to a number of phthalates among the general population is wide, with the highest doses for infants and children, due to additional intake caused by the mouthing behavior of toys. Important exposure pathways of phthalates are food and intensive medical care" [99,104]. "There are numerous reports showing that phthalates exert adverse effects on animals’ liver, heart, kidney, lungs" [105]. "A number of studies have been also conducted to evaluate the potential toxicity of phthalate plasticizers on human health. The results showed several implications: hormonal disorders, inducing hepatic peroxisome proliferation, reproductive toxicity, carcinogenicity, allergic symptoms in children" [106, 107].

2.5.2 Plasticizing Theories

There are three theories of plasticization, the first one were "developed in 1930– 1950". "Three of them are still used nowadays", "the gel and lubricity theory has developed in a parallel way", and the third one which is the "free volume theory which originated some years later than the other two"(see figure 2.34).

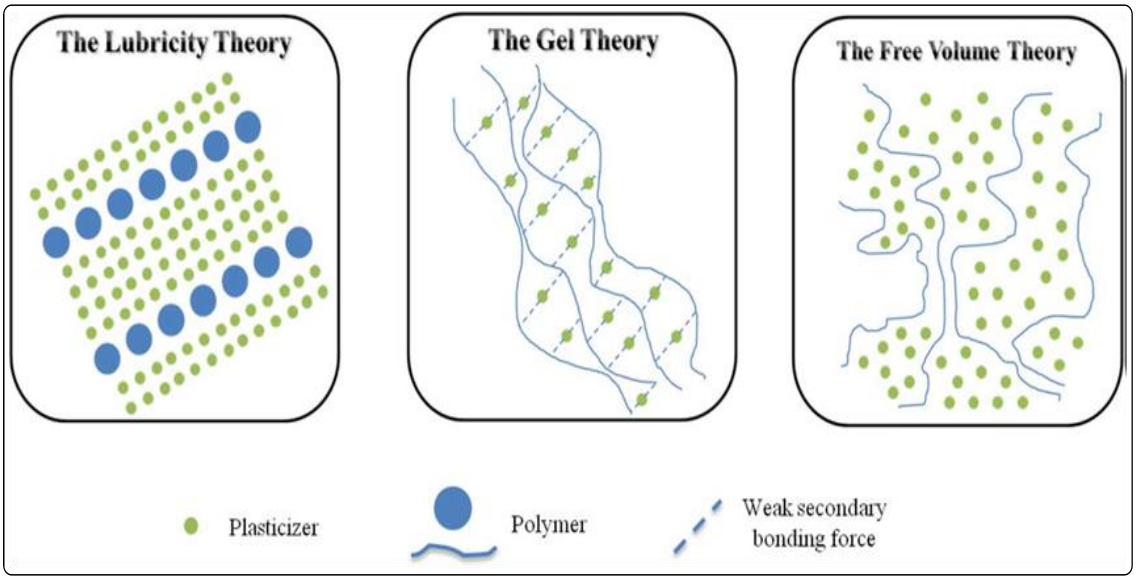


Figure 2.34 Mapping of Plasticization Theories

Generally "it is recognized that the low molecular weight of a plasticizer allows reducing secondary forces" ("hydrogen bonding", "Vander Waals forces") between chains of the polymer by occupying "intermolecular spaces". Thus, "plasticizers change the three-dimensional molecular organization of polymers, decreasing the energy required for molecular motion".

"The lubricity theory provides that the plasticizer diffuses into the polymer, inserting into the polymer chains and reducing the intermolecular frictions". "The macromolecules slip over each other when a plastic part is flexed". Then, "the plasticizer lubricates the movement of the molecules reducing their internal resistance to slide and to prevent the re-formation of the rigid matrix". According to concept theory, "a plasticized plastic can be represented as parallel alternating layers of polymer and plasticizer" [108,109].

"The gel theory is based on the assumption that the plasticized polymer is considered to be a three-dimensional network with plasticizer molecules bonded to resin chains by weak secondary forces". The plasticizer acts by "breaking the polymer–polymer bonds and interactions, masking these centers of attachment from each other and preventing their reformation". "By comparing to the lubricity theory assumes that the rigidity of polymers comes from internal frictions and that plasticizers act by lubricating the layers of polymer whereas the gel theory supposes that it comes from points of attachments of polymer to polymer and that plasticizers reduce the number of these sites".

"The free volume is the internal space available within a polymer, when the resin plasticizer mixture is cooled down after melting. Free volume comes from three principal sources: motion of chain ends, motion of side chains and motion of the main chain"[108,109]. "The free volume theory allowed Chandola and Marathe to predict the behavior of 25 PVC plasticizers"[110]."This theory is giving more explanation on plasticization since it is based on relationships between properties "such as ("specific volume", "viscosity") and "variables (molecular weight, terminal groups content) of polymers that were not yet explained at the time the other two theories appeared".

"A rigid polymer possesses very little free volume". When" a plasticizer is added, it increases the free volume making the polymer soft and rubbery, increasing motion of polymer molecules".

2.6 Plasticizer Classification

The classification of plasticizer depending on "modifying the polymer or monomer so that the flexibility of the polymer is increased. Alternatively""a rigid polymer can be externally plasticized by the addition of a suitable plasticizing agent". "The external plasticizing route is more common because of lower overall costs, and the use of external plasticizers allows the processor a certain degree of freedom in developing formulations for a range of products"[111].

There are two techniques for plasticization (see figure 2.35), external and internal. "External plasticization is a method that provides plasticity through physical mixing".

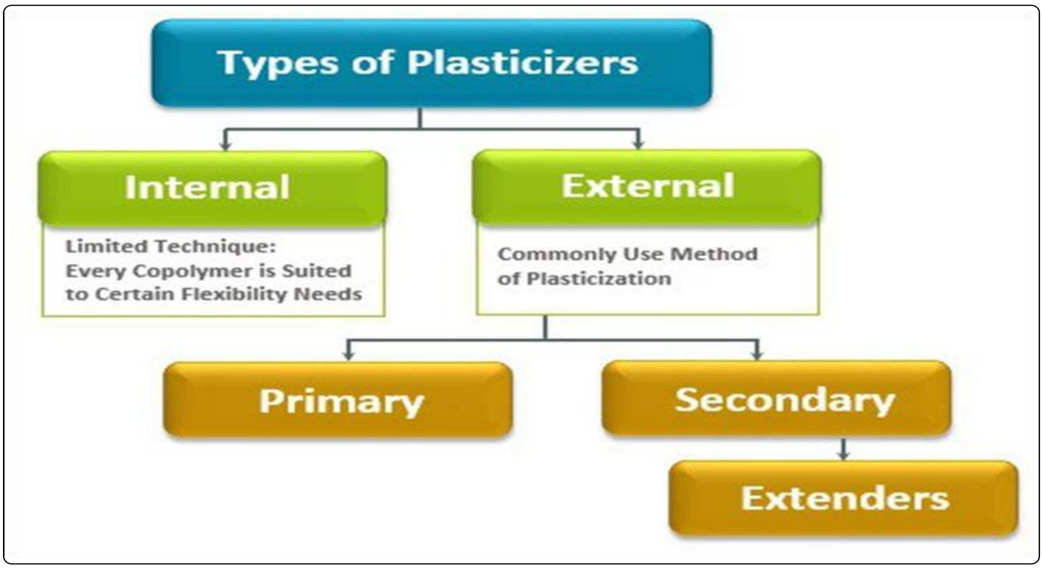


Figure 2.35 Plasticizer Classification

2.6.1 Internal Plasticizers.

"There has been much dedicated work on the possibility of internally plasticized PVC (FPVC)"(see figure 2.36). However, "in achieving this by copolymerization significant problems exist.[112] the affinity of the growing polymer chain for vinyl chloride rather than a co-monomer implies that the incorporation of a co-monomer into the chain requires significant pressure" [113] "since the use of recovered monomer in PVC production is standard practice, contamination of vinyl chloride with co-monomer creates additional problems"[114].

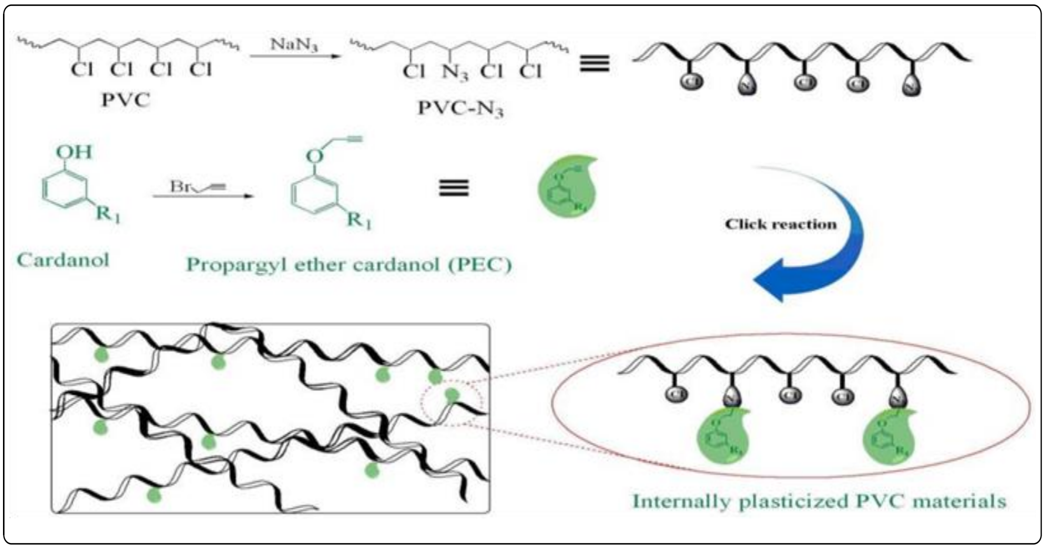


Figure 2.36 Internal Plasticizers of PVC Materials

"The complexity of the reaction can lead to longer reaction times and increased costs. The interaction of "external plasticizers are not chemically bound to the polymer and can evaporate, migrate or exude from polymer products by liquid extraction" [115]. "Plasticization of polymers by incorporation of co-monomers or reaction with the polymer, providing flexible chain units is called an internal plasticization". "Internal plasticizers are groups (flexible segments) constituting a part of a basic polymer chain" which may be "incorporated regularly or irregularly between inflexible monomers ("hard segments") or grafted as side chains thus reducing intermolecular forces" [116,117]. "According to the compatibility with the polymer"(see figure 2.37).

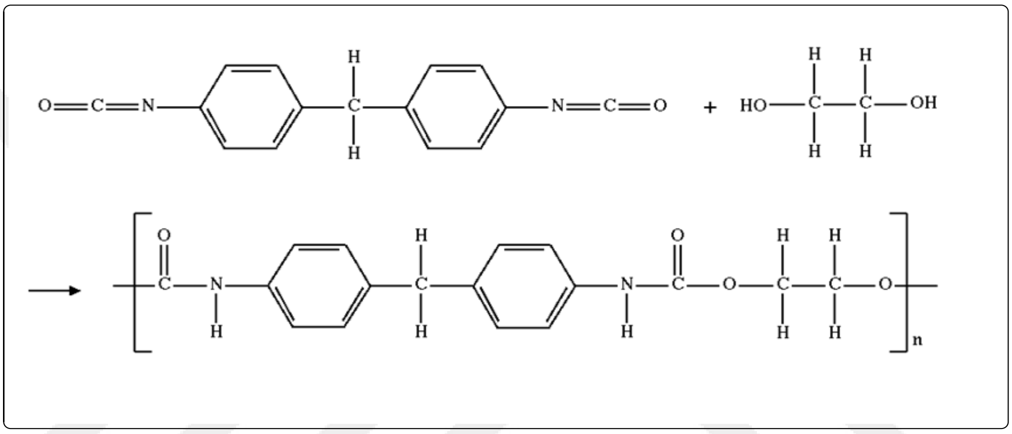


Figure 2.37 Internal Plasticizers of Polyurethanes

2.6.2 External Plasticizers

"External plasticizers can be classified into two principal groups: primary and secondary"(see figure 2.38).

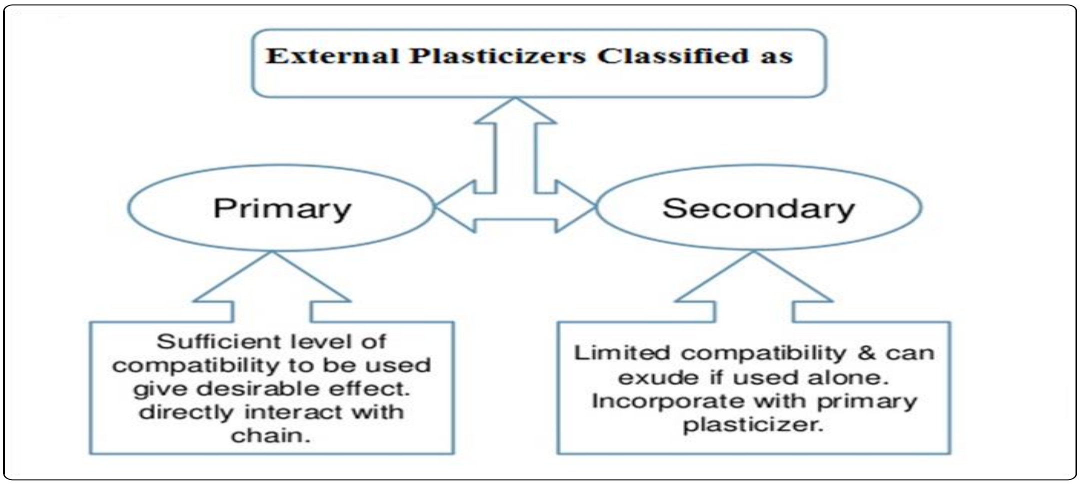


Figure 2.38 Classified of External Plasticizers

2.6.2.1 Primary Plasticizers

Also called as a chemical "plasticizers, Primary plasticizers are compatible with PVC and those containing polar groups are characterized by high salvation capabilities". "They are also defined as real solvents". "These include sulphates and esters of alkylsulphite acids, alcohols and phenols. Diesters of ortho-phtalic acid produced from phthalic anhydride and alcohols containing from 4 to 13 carbon atoms in a molecule are the most common.

They cause the polymer to gelate quickly, which facilitates the processing of PVC in typical temperatures". "Similar properties are demonstrated by terephthalic diesters and alcohols containing 4-8 carbon atoms in the molecule, which thanks to the so-called safe, non-ortho-phthalic application profile, are becoming more and more popular among PVC manufacturers".

"A primary plasticizer, when added to a polymer, causes elongation and softness to be increased. Primary plasticizers have a sufficient level of compatibility with polymer to be able to be used as sole plasticizer in all reasonable proportions, giving a desirable modifying effect"[118].

2.6.2.2 Secondary Plasticizers

"Also known as extenders, secondary plasticizers continue to play a significant role in flexible PVC formulations"(see figure 2.39). "They do not impart flexibility to the PVC resin alone, but when combined with a primary plasticizer act in such a way as to add flexibility and other properties to the final product" [119]. "The majority of secondary plasticizers in use are chlorinated paraffin's, which are hydrocarbons chlorinated to a level of 30–70%. For a given hydrocarbon chain, viscosity increases with chlorine content, as does the fire retardancy imparted to the formulation", Chlorinated paraffin's of the same chlorine content may have different volatilities and viscosities if they are based on different hydrocarbon chains.

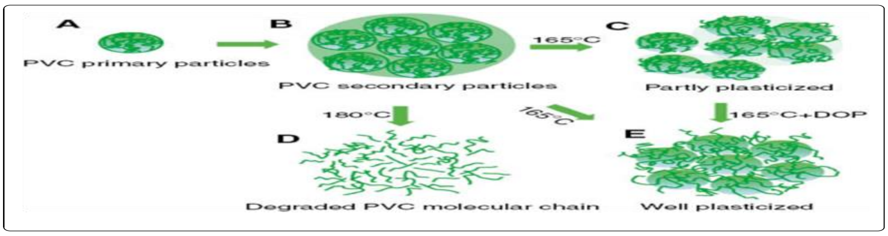


Figure 2.39 Secondary Plasticizers of PVC

"A secondary plasticizer, when added to the polymer alone, does not bring about these changes and may have limited compatibility with the polymer. Secondary plasticizers have limited compatibility and will exude from the polymer if used alone. They are used along with the primary plasticizer, as a part of plasticizer system, to meet a secondary performance requirements (cost, low-temperature properties, permanence)". However "when added to the polymer in combination with a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer".

"Extenders can be used as lower cost, partial replacement for a primary plasticizer. It is possible that a plasticizer used in one formulation as a primary plasticizer could be used in a second formulation as a second one"[117,118]. "Plasticizers, especially used in""biopolymer-based films, can also be classified as water soluble and water insoluble. Hydrophilic plasticizers dissolve in polymeric aqueous dispersions and may cause an increase of water diffusion in the polymer when added in high concentration. On the contrary, hydrophobic plasticizers can lead to a decrease in water uptake, due to the closing of micro-voids in the polymer" [116].

2.7 Mechanism of Plasticizer Action

"There are several theories that describe the effects of plasticizers and a combination of them allows to explain the concept of polymer plasticization"."Some theories involve detailed analysis of polarity, solubility, and interaction parameters and the thermodynamics of polymer behavior, whereas others treat plasticization as a simple lubrication of chains of polymer from each other". An understanding of the plasticization process can be gained by combining ideas from each theory, and an overall theory of plasticization must include all these aspects[128, 114,121].

"The steps involved in the incorporation of a plasticizer into a PVC product can be divided into five distinct stages":

(1) "Plasticizer is mixed with PVC resin—adsorption step".
(2) "Plasticizer penetrates and swells the resin particles—adhesion step".
(3) "Polar groups in the PVC resin are freed from each other—absorption step".
(4) "The structure of the resin is re-established, with full retention of plasticizer—intermolecular plasticizing step".

"Steps 1 and 2 can be described as physical plasticization, and the precise details of how this is carried out depends on the applications technology involved i.e. suspension or dispersion PVC".

"The rate at which step 2 occurs depends on the plasticizer viscosity, degree of branching, resin pore size and free volume, and particle size".

"Steps 3 and 4, however, can be described as chemical plasticization since the rate at which these processes occur depends on the chemical properties of molecular polarity, molecular volume, and molecular weight". "An overall mechanism of plasticizer action must give adequate explanations for this as well as the physical plasticization steps".

A. Lubricity Theory, "developed by Kilpatrick, Clark and Houwink, among others, states that" plasticizer acts as a lubricant, reducing intermolecular friction between polymer molecules responsible for rigidity of the polymer"."On heating, the plasticizer molecules slip between polymer chains and weaken the polymer-polymer interactions (Vander Waals' forces), shielding polymer chains from each other(see figure 2.40). This prevents the reformation of a rigid network, resulting in more flexible, softener and distensible polymer matrix.

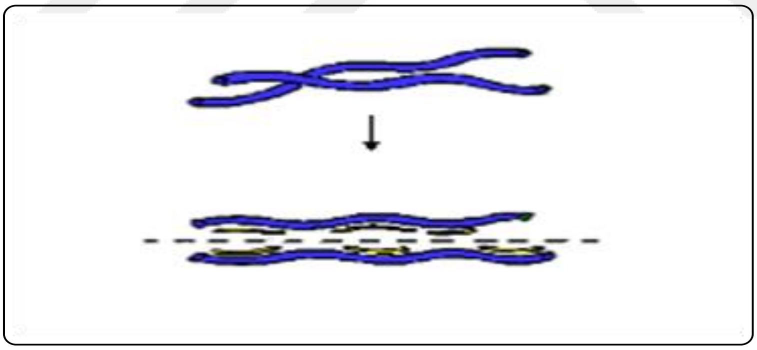


Figure 2.40 Plasticizer Polymer Response Based on Lubricity Theory

B. Gel Theory, developed by Aiken and others, holds that polymers are formed by an "internal three-dimensional network of weak secondary bonding forces (VanderWaals' forces, hydrogen bonding) sustained by loose attachments between the polymer molecules along their chains". These bounding forces, are easily overcome by external strain applied to the material, allowing the plasticized polymer to be bend, stretch, or compress"(see figure 2.41).

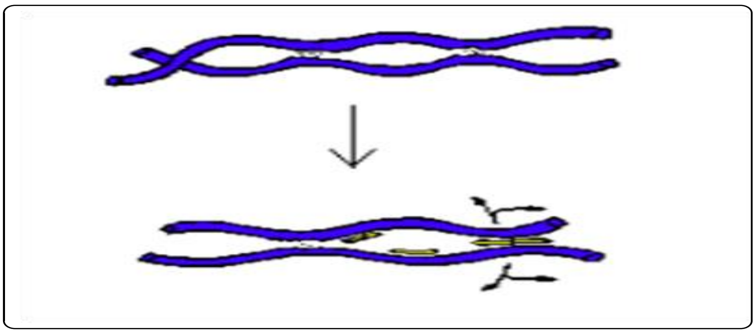


Figure 2.41 Gel Theory of Plasticizers

"Plasticizer molecules that are not attached to polymer tend to aggregate allowing the polymer molecules to move more freely, thus enhancing the gel flexibility".

C. Free Volume Theory, "holds that the presence of a plasticizer lowers the glass transition temperature (Tg) of the polymer". "Free volume is a measure of internal space available within a polymer matrix". "There are three main sources of free volume in polymer" motion of polymer end groups, motion of polymer side groups, and internal polymer motions". "When the free volume increases, more space or free volume is provided for molecular or polymer chain movement"(see figure 2.42). "A polymer in the glassy state has an internal structure with molecules packed closely and small free volume".

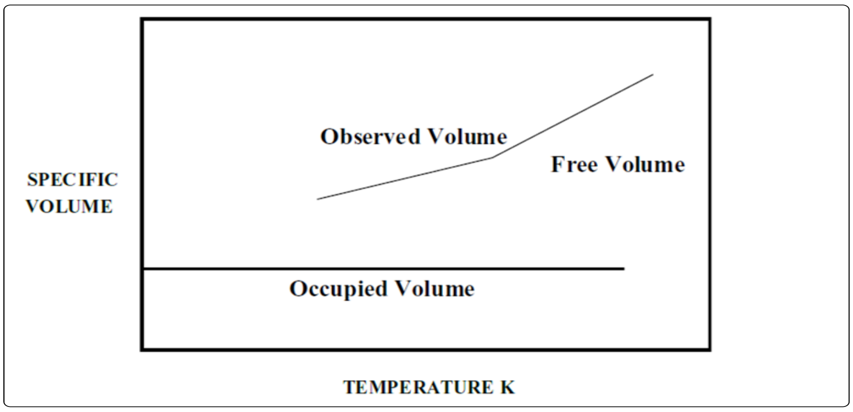


Figure 2.42 Free Volume Theory of Plasticization

D. Mechanistic Theory, "plasticization considers" that plasticizer molecules are not bound permanently to the polymer, but rather there is a dynamic exchange process whereby, a constant associations and disassociations of polymer-polymer, polymer plasticizer and plasticizer-plasticizer molecules form. "Some plasticizers form stronger associations with polymer than others" (see figure 2.43).

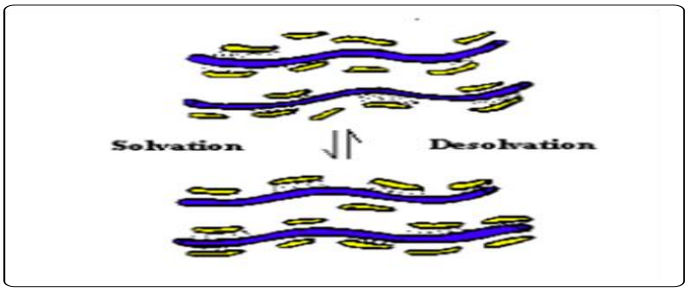


Figure 2.43 Mechanistic Theory of Plasticization

"At low plasticizer levels, the plasticizer polymer interactions are the dominant interactions""what explains "antiplasticization". At high plasticizer loadings plasticizer-plasticizer associations predominate".

2.8 Physicochemical Properties of Plasticizers

"The most important physical parameters for evaluating potential human and environmental exposures are water solubility, octanol/water partition coefficient and leaching data. Furthermore the vapour pressure of the plasticizers at the use temperature may in some cases be important. Whereas the solubility and vapour pressure data are available to some extent, very little information is available on leaching. Summarizes important physical chemical characteristic, some of which have been estimated (in Italics in the table) limiting their validity"(see table 2.3).

Table 2.3 Overview of Some Physical Properties of The Assessed Plasticizers

Substance	**Vapor pressure at 20 ^{0}C (Pa)**	**Water Solubility (mg/L)**	**log K$_{ow}$**	**Water extractability (%)^{a}**	**Kerosene extractability (%)^{b}**
COMGHA	<2.8 x 10^{-4} at 100^{0}C (4)	7 x 10^{3} (4)	6.0 – 7.7 (4)		
ATBC	6 x 10^{-4} (3)	6 x 10^{2} (3)	4.3 (3)		
BTHC	8 x 10^{-8} (3)	6 x 10^{-2} (3)	8.2 (3)		
DEHA	4 x 10^{-4} (3)	0.5 (3)	8.1 (3)	0.10	>70
DEHP	3.4 x 10^{-5} (1)	3.0 (1)	7.5 (1)	0.01	44.3
DINCH	<2.8 x 10^{-4} at 100^{0}C (4)	20 (4)	10.0 (4)		
DINP	6 x 10^{-5} (2)	0.6 (2)	8.8 (2)	0.07	77

It is possible to predict the relative exposure to be expected from the use of different plasticizers. The rate of leaching is dependent on the lipophilicity of the compound and of the material stored, duration of storage, storage temperature, contact area and, in some cases, agitation. In general, the plasticizers show a higher extent of leaching in lipohilic solutions. The clearest conclusion that can be drawn is that there is a severe lack of data on solubility, water/oil partition coefficients and especially leaching of the plasticizers under conditions relevant to the usage in plasticized products"[122].

"Plasticizers are polymer modifiers, as are all the other ingredients included for the formation of an elastomeric compound. Plasticizers may be thought of according to their function in a compound or by their type". Some of those classifications might be "internal, external, chemical, physical, esters, oils, primary, secondary, etc". "Internal plasticizers include flexible monomers (soft segments) incorporated regularly or irregularly between inflexible monomers (hard segments) of a polymer chain". "Flexible polymers may be added to rigid polymers, for example" "nitrile rubber to polyvinyl chloride (PVC), or grafted as side chains that reduce crystallinity and Tg through the reduction of intermolecular forces".

"External plasticizers are materials that interact physically with the elastomer but that do not chemically react with the polymer". "Solvent and non-solvent are two distinct types of external plasticizers".

"Common esters and polymeric polyesters are both external and physical plasticizers. Physical plasticizers may have some weak attraction to the polymer, such as through hydrogen bonding or Vander Waals forces, but, as with external plasticizers, they do not chemically react with the elastomer"."An exception to this can occur under the right conditions provided one of the reactants used to make the plasticizer, after the esterification reaction, retained a reactive group. A potential problem arises here, however, as materials reacted with the polymer molecules will make the polymer molecule larger and thus less flexible. Chemical plasticizers attack, thereby reducing the molecular weight of the elastomer chain"[123]."We have stated that plasticizers can have two distinctly different uses as their different functions and in general the effects as process aids and property modifiers explained"(see table 2.4).

Generally, "a process aid should reduce the temperature of processing without affecting the softening temperature of the final product"(see figure 2.44)."The softening temperature will be the upper limit of usefulness of that final product". "A plasticizer as a final property modifier will ideally lower the Tg temperature or softening temperature without lowering the flow temperature".

Table 2.4 The Different Functions as Processing Aids and Property Modifiers

As Processing Aids	
Lower the processing temperature	Increase tackiness
Increase lubricity	Improve flow out
Reduce mixer sticking	Improve wetting
Reduce mold sticking	Reduce nerve
As Elastomer Property Modifiers	
Soften the polymer	Increase the temperature
Lower the modulus	range of usefulness
Lower the tensile strength	Increase cohesion
increase flexibility	Improve surface appearance
Lower glass transition	Decrease static charge Increase tear strength
Increase elongation	Modify frictional character

"This represents a broadening of the temperature range of usefulness desired from the plasticizer". "The softening temperature will now be the lower limit of usefulness of the finished product". "As an example, apply that reasoning to rubber tires used in arctic regions. Plasticizer added to the recipe lowers the compound Tg, providing the compound with improved low temperature for the cold climate. This allows the tire to have a colder softening temperature but does not alter the flow temperature of the compound".

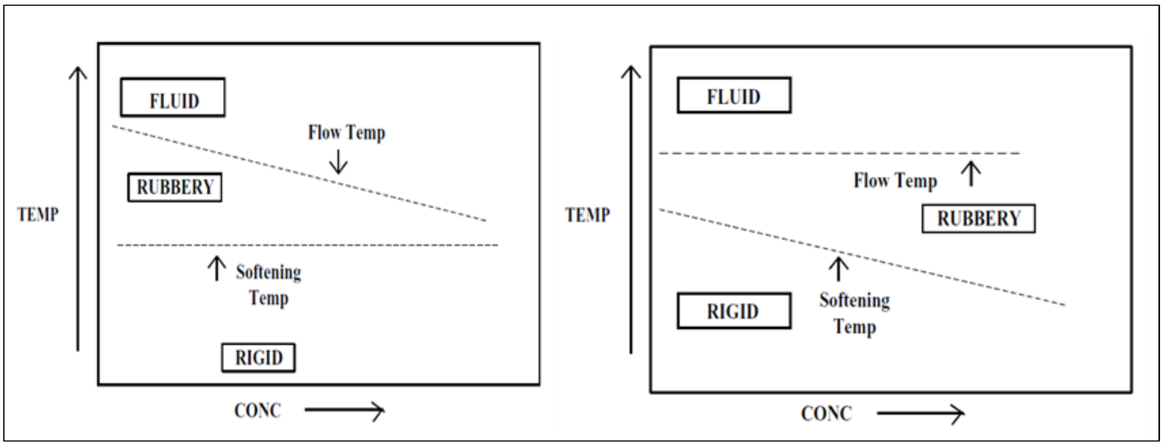


Figure 2.44 Response to Plasticizer as Process Aid and Response to Plasticizer for End Use

2.9 Plasticizer Markets

"Plasticizers are used to produce flexible PVC products for many different end uses or market segments".(see figure 2.45)"depicts a worldwide analysis of plasticizer consumption by PVC market segments". "The largest market segment is film, sheeting, and coated substrates. In this segment", "the majority of plasticizer consumed is for products produced in calendaring operations". "The primary factors in plasticizer selection are low cost and ease of processing, with DOP meeting this requirement in most parts of the world"."In North America and Europe, DINP is the preferred plasticizer choice based on the above criteria and factoring in regulatory issues regarding the use of DOP". "If greater permanence is required, plasticizers such as DIDP, L9P, 911P, and DUP may be used. For coated substrates prepared through a coating process, plastisol viscosity, gelatin or fusion behavior, and emissions are all-important concerns. DINP is found to give a more consistent, stable viscosity than DOP while reducing emissions".

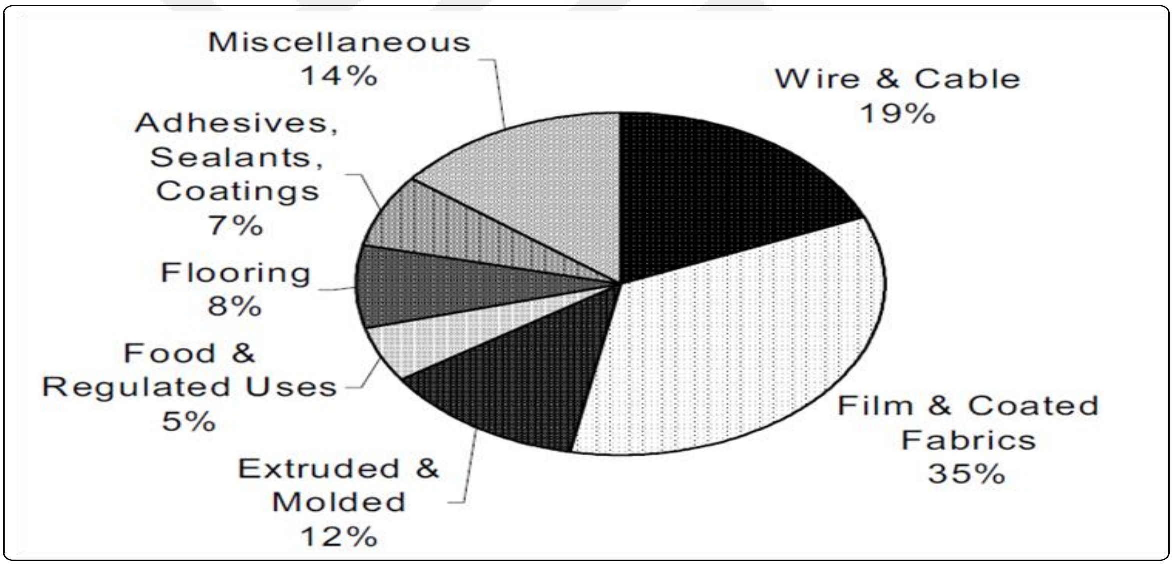


Figure 2.45 End Use Markets for Plasticized PVC

The products which need a slight reduction in "gelation or fusion temperature, DIHP (diisoheptyl phthalate) or BBP can be used to replace a small portion of the primary plasticizer. Vinyl flooring is another major market for plasticized PVC". "There are basically three types of products, vinyl tile, resilient vinyl sheet flooring, and vinyl backed carpeting or carpet squares".

"Floor tiles are comprised of about 80% calcium carbonate held together by the fused flexible PVC binder. The most commonly used plasticizers in floor tiles are DOP and DINP"[124].

2.10 Classification of Plasticizers

There are over 100 types of plasticizers available commercially which can be categorized into general purpose plasticizers, specialty plasticizers,organic plasticizers and others. Some commonly used plasticizers are discussed as follow.

2.10.1 Phthalates

The most abundantly produced worldwide plasticizers are phthalate esters, commonly refer to esters of orthophthalic acid . They can be produced by reacting "two moles of monohydride "alcohol with one mole of phthalic anhydride". The alcohol used are normally range from C_4 to C_{13} as phthalates produced from alcohols below C_4 are too volatile while from "alcohols above C_{13} have limited compatibility" [125]. The general structural formula of phthalates is shown below where the functional groups R, can either be linear aryl groups or alkyl groups with aromatic ring[126] (see figure 2.46).

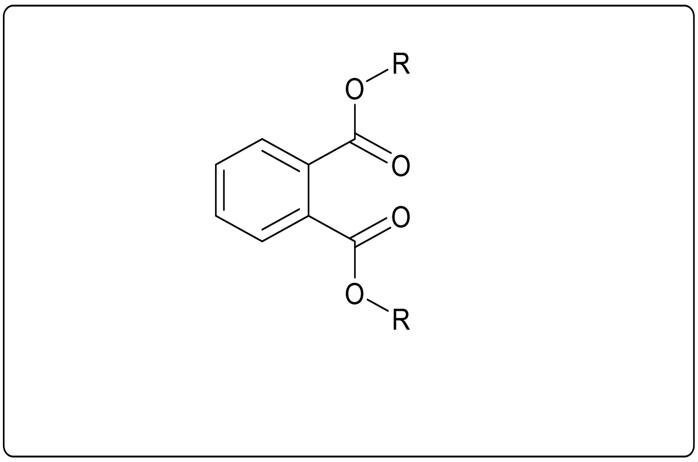
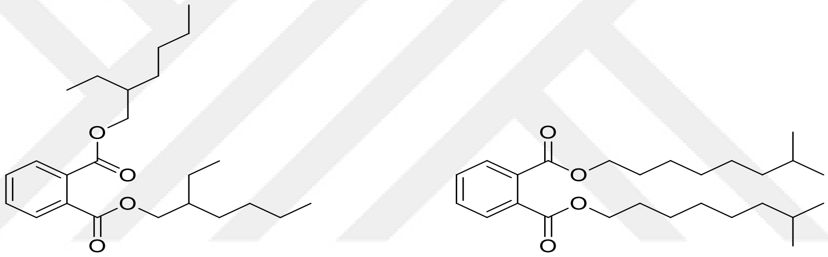


Figure 2.46 General Structural Formula of Phthalates

In general, phthalates possess "most desirable properties of plasticizers including good compatibility, high gelling capacity, relatively low volatility at ambient temperature, water resistant and low cost" [127]. As the length of functional group increases, the plasticizing effect, gelling capacity and volatility decreases. This means that "higher concentration of plasticizer is required to achieve" same flexibility but the extractability will be reduced.

"Some of the examples of phthalates plasticizers are di(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP)" is shown below (see figure 2.47).Among all these, DEHP which was introduced in "1930 is the most widely used plasticizers in the world. DEHP having shorter chain offers higher compatibility and plasticizing effect".

"However, leaching problems occurs especially in medical device have hindered its application". The trend is gradually changed to higher "molecular weight phthalates such as DINP" that has comparable price. "Although DINP offers lower plasticizing efficiency, the problem of plasticizer leaching can be greatly reduced" (Krauskopf & Godwin, 2005) [128].



DEHP
bis(2-ethylhexyl) phthalate
(12)

DINP
bis(7-methyloctyl) phthalate
(13)

Figure 2.47 DEHP and DIDP

2.10.2 Adipates

Adipates are esters of adipic acid which are produced by esterification reaction with monohydride alcohol range from C_8 to C_{10}. Generally, "lower molecular weight alcohols are reacted with higher molecular weight acids or vice versa" to produce adipates range between C_{18} and C_{26}. "This is to maintain the apolar/polar ratio to provide sufficient PVC compatibility along with low temperature properties" [133]. Adipates with molecular weight of 300 – 350 tend to be too volatile while those with molecular weight more than 400 have limited compatibility with PVC [137]. The structural formula of adipates is shown below,where R is alkyl group [130] (see figure 2.48).

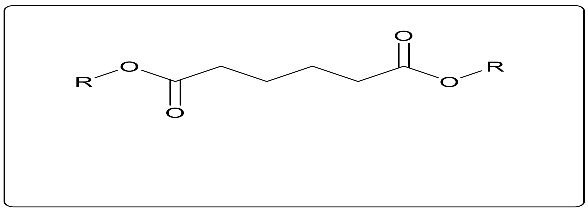


Figure 2.48 General Structural Formula of Adipates

The glass transition temperature reduced by adipates is lower compared to the corresponding phthalates, "but they flexibilize the amorphous sites of PVC more efficiently". Thus, they impart "higher flexibility with lower molecular weight and specific gravity" [131]. Besides that "adipates perform better in low temperature flexibility and are relatively safe compared to phthalates".

However, they have higher volatility which causes high migration rate and are more costly than phthalates. As the molecular weight of adipates increases, the volatility decreases but at the same time the solubility and compatibility with PVC will also decrease. Fortunately, the influence of compatibility is very small and a substantial increase in volatility is capable to compensate the changes in compatibility. Thus, adipate plasticizers are more permanent when their molecular weight increases.

Examples of adipate plasticizer are "di-2-ethylhexyl adipate (DEHA)", dibutyl adipate (DBA), diisononyl adipate (DINA) and diisodecyl adipate (DIDA). DEHA as the most commonly used adipate plasticizer in PVC is a product of "esterification of 2-ethylhexanol with adipic acid" is shown below[125].Other than that, for application requiring lower plasticizer volatility, DINA with higher molecular weight is a good alternative is shown below.Due to the high cost of adipates, they are commonly blended with other plasticizers such as phthalates to "compromise low temperature properties and the cost" [128] (see figure 2.49).

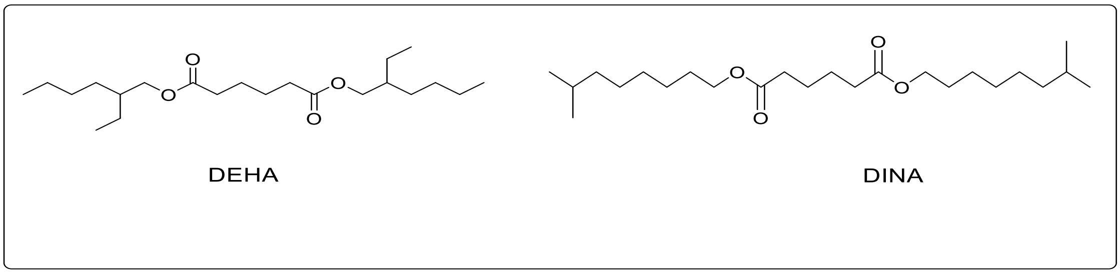


Figure 2.49 DEHA and DINA

2.10.3 Epoxides

Epoxides "plasticizers are epoxidized natural products having oxirane oxygen groups in their molecules" that are produced by the olefinic double bond epoxidation in their raw material. They normally come from soybean oil or linseed oil with double bond fatty acids such as oleic, linoleic and linolenic (see figure 2.50),that can be epoxidised with hydrogen peroxide or peracetic acid [132].

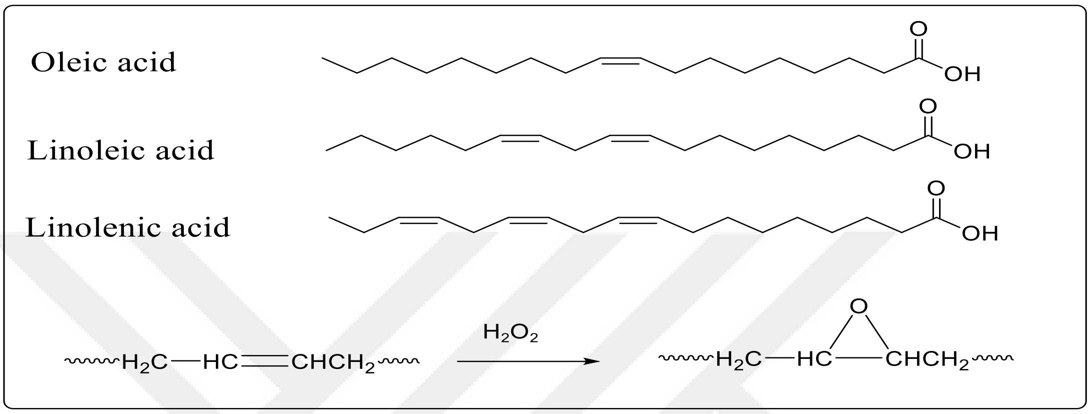


Figure 2.50 Epoxidation Reaction of Unsaturated Fatty Acid of Soybean Oil

Two examples of "most widely used epoxides plasticizers are epoxidised soybean oil (ESO) and epoxidised linseed oil (ELO)". They are used as secondary plasticizer and "secondary stabilizer in PVC due to their ability to form bonds with the hydrogen chloride" when "PVC" is decomposed. Epoxides plasticizers""are the only class of plasticizers that undergo side chain bonding onto PVC chain at the site of labile chlorides in the presence of stabilizers" [125]. They have very high molecular weight (approximately 1000), hence they have low volatility and can hardly migrate out. ESO was previously tested as primary plasticizer with high concentration (approximately 50 phr), but the result is not satisfactory as photo oxidation or hydrolysis of the oxirane oxygen occurs after long time UV-exposure, resulting in sticky surfaces [141].

Thus, ESO structure is shown below is normally work as secondary plasticizers and blended with other plasticizers such as phthalates during application [126] (see figure 2.51).

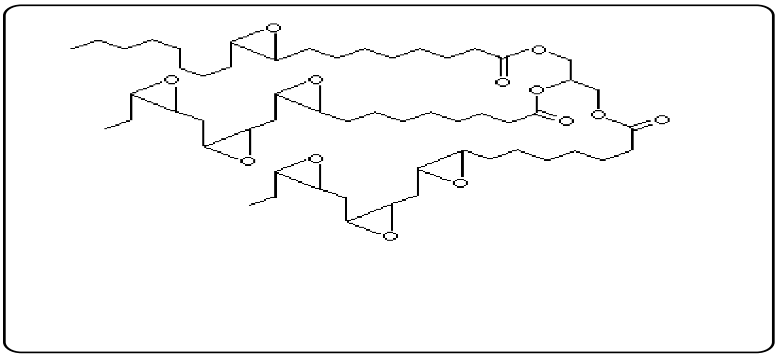


Figure 2.51 Structural Formula of Epoxidised Soybean Oil

2.10.4 Terephthalates

"Terephthalates refer to para-phthalates that are one of the isomeric structures of phthalates". They are esters which are produced by reacting terephthalic acid with monohydride alcohol similar to phthalates. The most common terephthalates is di(2-etylhexyl) terephthalates (DEHTP) or sometime refers as dioctyl terephthalate (DOTP) is shown below(see figure 2.52).

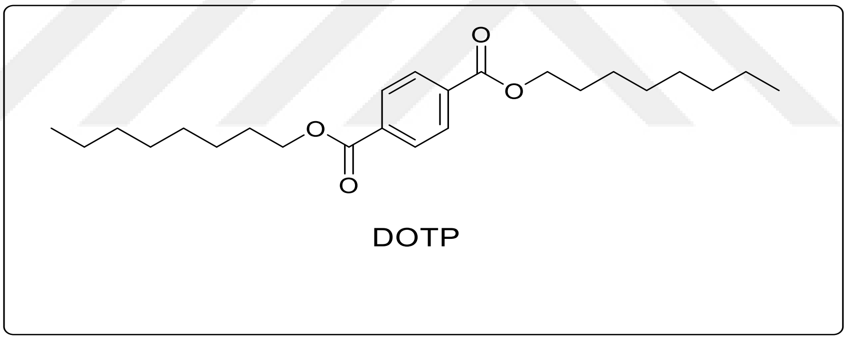


Figure 2.52 Structural Formula of Dioctyl Terephthalate

The manufacturing cost and plasticizing efficiency is "similar to DEHP but with better low temperature properties and significant lower volatility due to high molecular weight and long hydrocarbon chain". Thus, DOTP can be considered as a good alternative to replace volatile and toxic DEHP.

2.10.5 Trimellitates

Trimellitates are the products of esterification between three equivalent of monohydride alcohols and one equivalent of trimellitic anhydride (TMA) as seen the structure below (see figure 2.53),which has similar structure with phthalic anhydride except for the third carbonyl group on the aromatic ring. This additional" carbonyl group has contributed to larger molecular weight compared to phthalates and the "third ester group contributes sufficient polarity to maintain PVC compatibility" [125,130].

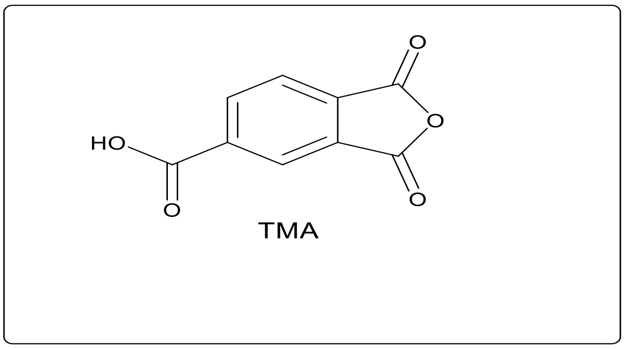
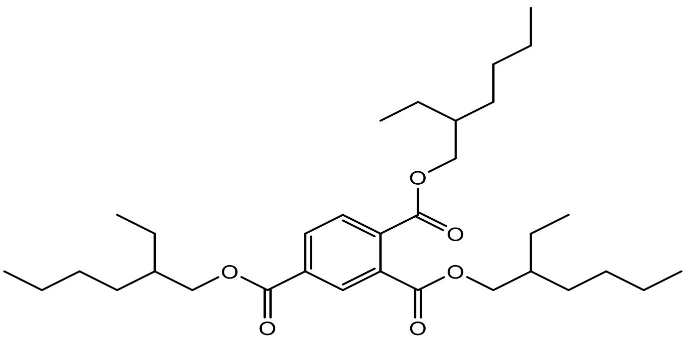


Figure 5.53 Structural Formula of Trimellitic Anhydride

Due to "high molecular weight and highly branched isomeric structures", trimellitates plasticizer possessed very low diffusivity and high temperature stability. The oxygen and carbon dioxide permeability is also enhanced as plasticizer concentration increases. These features have encouraged their application in medical device especially for blood and intravenous solution container and tubing where leaching and permeability are the major concern. However, the oil extraction resistance is similar to phthalates. The plasticizing efficiency is also relatively low and the cost is higher as compared to phthalate. Thus, higher concentration is needed to attain the required flexibility consequently induce higher manufacturing cost. Besides that, at high plasticizer level, PVC will become very soft and sticky especially after sterilization by autoclaving. In view of the high manufacturing cost and relatively low efficiency, trimellitates plasticizer is not suitable for application in disposable medical devices such as urine bag and tubing.

Common trimellitate plasticizers are trimethyl trimellitate (TMTM), tri-2- ethylhexyl trimellitate is shown below (see figure 2.54).

(TEHTM, also called trioctyl trimelliate (TOTM)) and octyl dibenzyl trimellitate. TOTM is the most widely used trimellitate plasticizer due to its extremely low diffusivity and low toxicity. If the price can be reduced by mass production, it is a good consideration for medical application [130].

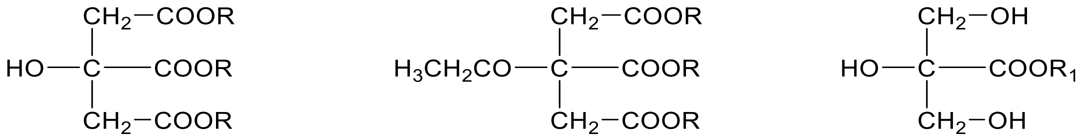


TEHTM

Figure 2.54 Structural Formula of Tri-2-Etylhexyl Trimellitate

2.10.6 Citrates

Citrates are bio-derived tetraesters that are produced by reacting one mole of citric acid with three moles of alcohols is shown below (see figure 2.55).Citrate plasticiser being commercialized for more than 35 years, is one of the major contenders to replace toxic phthalate plasticizer typically DEHP due to its high miscibility, high efficiency and low toxicity. "Toxicity tests conducted by the Pfizer Drug Safety Evaluation Department have proved that citrates are safe through acute dermal toxicity and ocular irritation tests in rabbits, and acute oral toxicity tests in mice and rabbits"[135]. It is approved for use in sensitive application such as "pharmaceutical tablet coatings, medical devices including blood bag, toys, food wraps and cosmetic products". Apart from that, a test "conducted by Morflex Inc. showed that Citroflex B-6" (n-butyryltri-n-hexyl citrate) combined with ESO give similar properties to PVC as DEHP does [135]. However, it is easily extracted by lipid medium and the cost is much higher than DEHP [130].



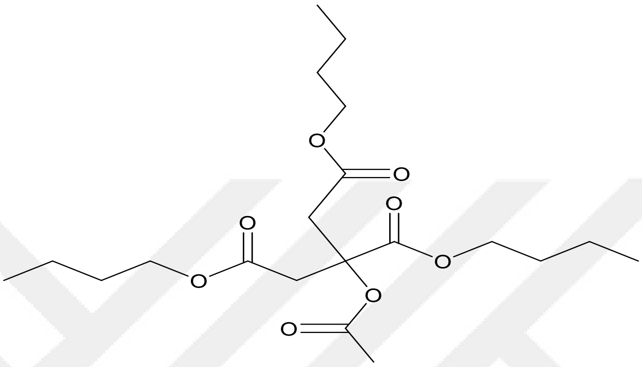
$$HO-\overset{\displaystyle CH_2-COOR}{\underset{\displaystyle CH_2-COOR}{C}}-COOR \qquad H_3CH_2CO-\overset{\displaystyle CH_2-COOR}{\underset{\displaystyle CH_2-COOR}{C}}-COOR \qquad HO-\overset{\displaystyle CH_2-OH}{\underset{\displaystyle CH_2-OH}{C}}-COOR_1$$

R: ethyl, butyl, hexyl

R_1: Stearyl

Figure 2.55 Chemical Structures of Citrates Used in Commercial Plasticizers

Examples of citrate plasticizer used in PVC are trimethyl citrate (TMC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC) is shown below (see figure 2.56), "acetyl trihexyl citrate (ATHC)", and "butyryl trihexyl citrate(BTHC)". In 2004, the European Unhexion Scientific Toxic Committee stated that "ATBC did not possess safety concern when young children placed PVC toys in their mouths" and had approved its use in soft PVC toys [134]. Besides that, ATBC offers high "heat stability and does not discolor when processed in compounded resins.



ATBC

Figure 2.56 Structural Formula of Acetyl Tributyl Citrate

2.10.7 Di-Isononyl-Cyclohexane-1,2-Dicarboxylate (DINCH)

"Di-isononyl-cyclohexane-1,2-dicarboxylate (DINCH)" is an"ester produced by hydrogenation of the aromatic ring in DINP in the presence of noble catalyst" as shown below. It was introduced in 2002 by the company BASF and marketed under the Hexamoll name "for sensitive applications such as medical devices, toys and food packaging" where exposure to toxicological material is of great concern. "According to BASF, Hexamoll "DINCH is a colorless, clear andpractically anhydrous liquid with hardly noticeable odour and is compatible with almost all of the monomeric plasticizers "commonly used in PVC" (see figure 2.57).

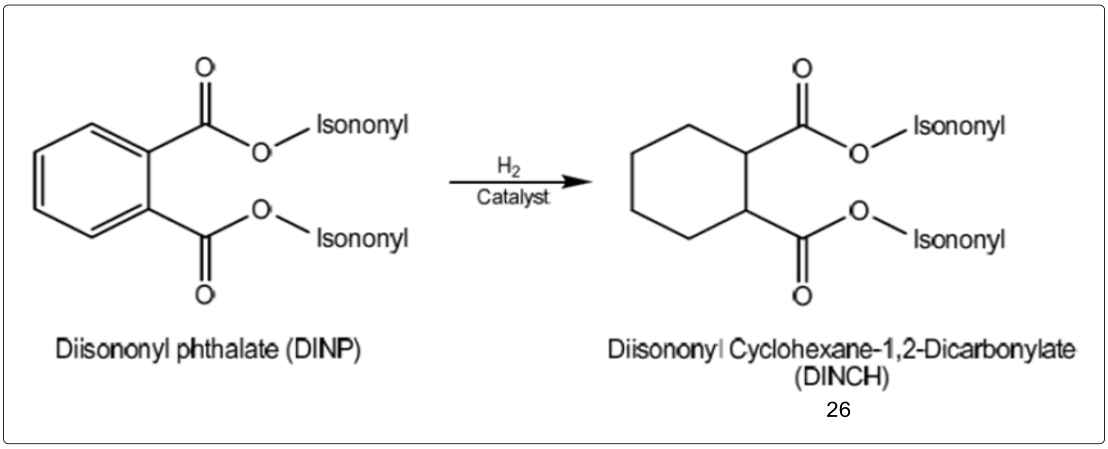


Figure 2.57 Production of DINCH by Hydrogenation of DINP.

The performance characteristic of DINCH "in PVC is expected to be similar" to the hydrogenated product of DINP but with lower compatibility due to increasing a polarity. According to this , more plasticizer is needed to achieve the same flexibility. However, high loading of DINCH will cause the PVC to become very soft and sticky typically after autoclaving [135]. To overcome this problem, PVC resins with higher K value should be used.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Targeted Compounds

The targeted plasticizers prepared in this study are given in (Figure 3.1)

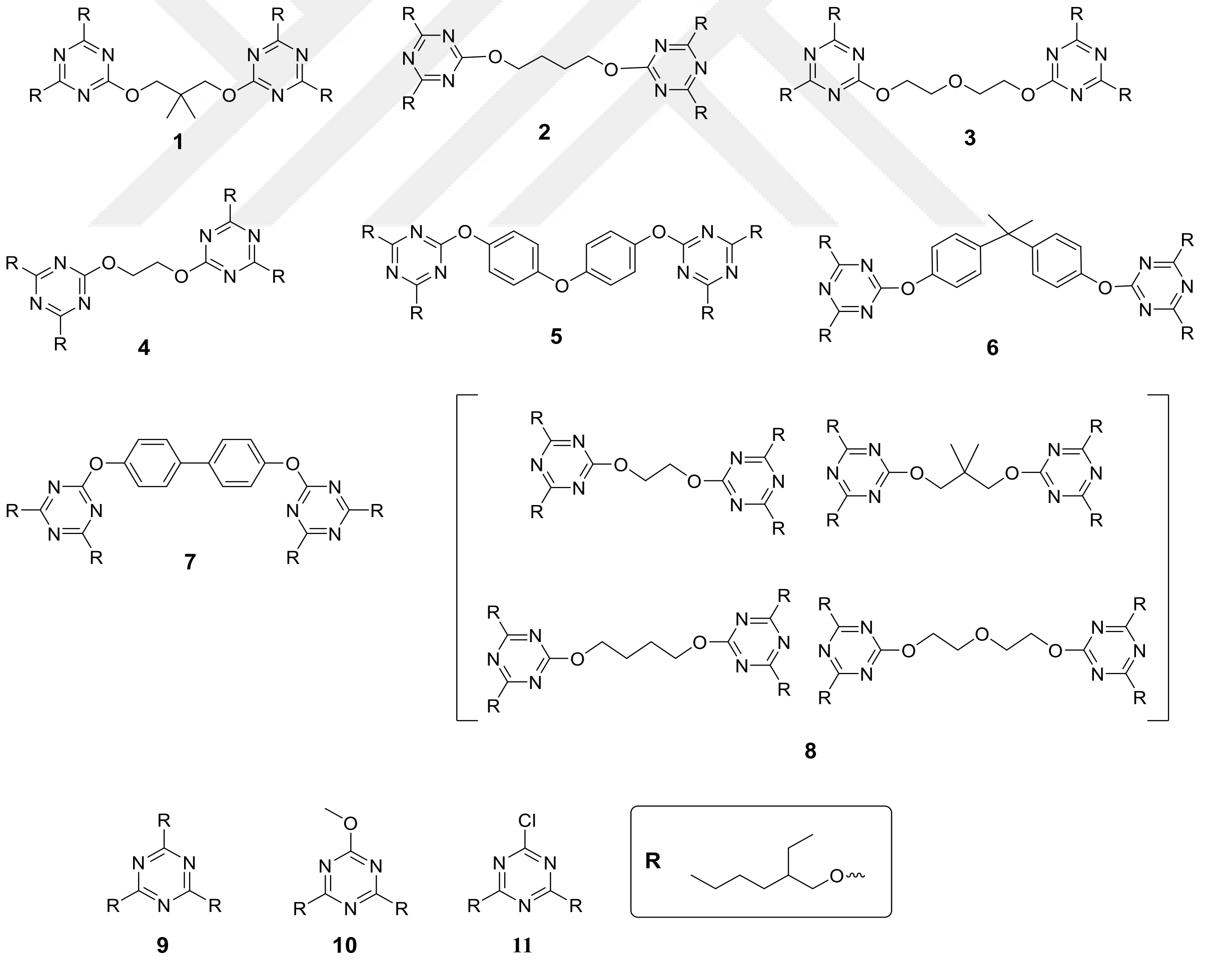


Figure 3.1 Target Triazine Macromolecular Structures Prepared in This Study As Well As The Mixtures of Compounds with Four Different Aliphatic Spacers.

3.2 Resuls and Discussion

Synthesis of 6,6'- ((2,2dimethylpropane - 1,3 - Diyl) Bis (Oxy)) Bis (2,4-Bis ((2-Ethylhexyl) Oxy)-1,3,5-Triazine) (1).

Synthesis of compound 1 is seen in (Figure 4.2) below. The intermediate compound **11** was reacted with dimethylpropane-1,3-diolin the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 86.5% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 1). The QTOF spectrum indicated the presence of $(M+Na)^+$ and $(M+H)^+$ peaks at 775.59and 797.58, respectably. H-NMR showed the –O-CH_2- peaks at 4.2 ppm and 3.6 ppm as singlet while -CH_3- peak at 3.4 ppm as a triplet. In the C-NMR, the triazine peaks are seen at 172 ppm and 171 ppm while the –O-CH_2- three peaks are seen in the (71, 70, 69) ppm.

Synthesis of 1,4-Bis((4,6-Bis((2-Ethylhexyl)Oxy)-1,3,5-Triazin-2-Yl)Oxy)Butane(2).

Synthesis of compound 2 is seen in (Figure 4.3) below. The intermediate compound **11** was reacted with 1,4-butandiol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 84.3% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 2). The QTOF spectrum indicated the presence of $M^+$and $(M+Na)^+$ peaks at 760.58 and 783.55, respectably. H-NMR showed the –O-CH_2- peaks at 4.1 ppm as multiplet while the second –O-CH_2- peaks appear at 3.5 ppm as a multiplet . In the C-NMR, the triazine peaks are seen at 171 ppm and 170 ppm while the –O-CH_2- three peaks are seen in the (71, 70, 69) ppm.

Synthesis of 6,6'-((Oxybis (Ethane-2,1-Diyl)) Bis(Oxy))Bis(2,4-Bis ((2-Ethylhexyl) Oxy) -1,3,5-Triazine) (3).

Synthesis of compound 3 is seen in (Figure 4.4) below. The intermediate compound **11** was reacted with 2,2'-oxybis(ethan-1-ol) in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 72.2%

yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 3). The QTOF spectrum indicated the presence of M^+ and $(M+Na)^+$ peaks at 776.56 and 799.57, respectably. H-NMR showed the –O-CH_2- peaks at 4.15 ppm and 3.5 ppm as. In the C-NMR, the triazine peaks are seen at 172 ppm and 170 ppm while the –O-CH_2- three peaks are seen in the (71, 70, 69) ppm.

Synthesis of 1,2-Bis((4,6-Bis((2-Ethylhexyl)Oxy)-1,3,5-Triazin-2-Yl)Oxy)Ethane(4).

Synthesis of compound 4 is seen in (Figure 4.5) below. The intermediate compound **11** was reacted with ethane-1,2-diol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 91% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 4). The QTOF spectrum indicated the presence of (M+2H)+2 peaks at 367.778. H-NMR showed the –O-CH_2- peaks at 4.1 ppm and 3.5 ppm as multiplets. In the C-NMR, the triazine peaks are seen at 172 ppm and 170 ppm while the –O-CH_2- three peaks are seen in the (71, 70, 69) ppm.

Synthesis of 4,4'-Bis((4, 6- Bis((2- Ethylhexyl) Oxy)- 1, 3, 5-Triazin-2-Yl)Oxy)- 1,1'-Biphenyl(5).

Synthesis of compound 5 is seen in (Figure 4.6) below. The intermediate compound **11** was reacted with [1,1'-biphenyl]-4,4'-diol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 80.4% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 5). The QTOF spectrum indicated the presence of M+2[-H_2O] and (M+2) peaks at 427.28 and 436.78, respectively. H-NMR Showed the aromatic hydrogen peaks at 7.6 ppm and 7.5 ppm as doublet while the –O-CH_2- peaks at 4.2 ppm as triplet .

In the C-NMR, the triazine peaks are seen at 168 ppm and 165 ppm and the aromatic carbon are showed five peaks between (134–128), while the –O-CH_2- two peaks are seen in the 68 and 67 ppm.

Synthesis of 6,6'-((Propane-2,2-Diylbis (4,1-Phenylene)) Bis(Oxy))Bis(2,4-Bis((2-Ethylhexyl) Oxy)-1,3,5-Triazine)(6).

Synthesis of compound 6 is seen in (Figure 4.7) below. The intermediate compound **11** was reacted with 4,4'-(propane-2,2-diyl)diphenol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 74.8% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 6). The QTOF spectrum indicated the presence of $(M+H)+[-H_2O]$ and $(M+NH_4)^+$ peaks at 881.62 and 916.66, respectively. H-NMR showed the aromatic hydrogen peaks at 7.2 ppm and 7.1 ppm as doublet while the $–O-CH_2-$ peaks at 4.2 ppm as triplet . In the C-NMR, the triazine peak are seen at 173 ppm and the aromatic carbon are showed five peaks between (138-125), while the $–O-CH_2-$ peaks are seen at70 ppm.

Synthesis of 6,6'-((Oxybis (4,1-Phenylene)) Bis(Oxy)) Bis(2,4-Bis ((2-Ethylhexyl) Oxy)-1,3,5-Triazine)(7).

Synthesis of compound 7 is seen in (Figure 4.8) below. The intermediate compound **11** was reacted with 4,4'-oxydiphenol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 68% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 7). The QTOF spectrum indicated the presence of $M+[-H_2O]$ and $(M+NH_4)^+$ peaks at 838.57 and 874.64, respectively. H-NMR showed the aromatic hydrogen peaks at 7.62 ppm and 7.45 ppm as doublet while the $–O-CH_2-$ peaks at 4.2 ppm and 3.5 ppm as triplet. In the C-NMR, the triazine peak are seen at 172 ppm and 170 ppm and the aromatic carbon are showed five peaks between (138-125), while the $–O-CH_2-$ showed three peaks are seen at (71,70,69) ppm.

Synthesis of Complex(8).

Synthesis of compound 8 is seen in (Figure 4.9) below. The intermediate compound **11** was reacted with 2,2-dimethylpropane-1,3-diol, butane-1,4-diol, 2,2'-oxybis(ethan-1-ol), ethane-1,2-diol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude mixture of compounds obtain colorless oily material in 89%% yield. The structure was confirmed by mass spectroscopic method as seen in (Figure A 8). The

QTOF spectrum indicated the presence of the four different compounds in the mixture as following (M+)and $(M+Na)^+$ peaks at 760.57 and 784.58 respectively, (M+H) and (M+) peaks at 775.6 and 774.6 respectively, M+[-H_2O] and (M+Na)+[-H_2O] peaks at758.56 and 781.55 respectively, (M+)and $(M+Na)^+$peaks at 732.53 and 755.53respectively.

Synthesis of 2,4,6-Tris((2-Ethylhexyl)Oxy)-1,3,5-Triazine(9).

Cyanuric chloride was used as starting material reacted with 2-ethylhexan-1-ol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 72.5% yield.

Despite the fact that the obtained tri-substituted triazines has a high viscosity and sensitivity to high temperatures, it showed plastifying properties when used with PVC. The film obtained is seen in Figure 3.2. The figure also shows the film obtained with standard plastifying agent used in the PVC industry.

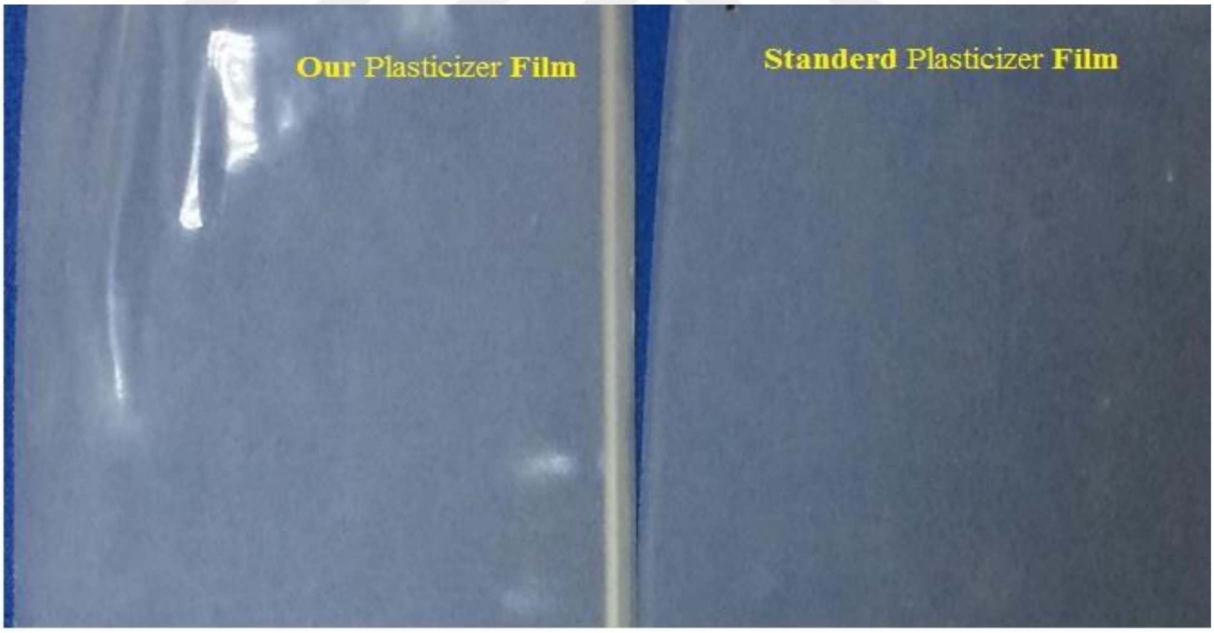


Figure 3.2 Our Synthesize Plasticizer Film and Standard Plasticizer Film

So we decided to synthesis less viscosity compound by replacing one equivalent of 2-ethylhexan-1-ol into methanol which is successfully done.

Synthesis of 2,4-Bis((2-Ethylhexyl)Oxy)-6-Methoxy-1,3,5-Triazine(10).

The intermediate compound 11 was reacted with methanol in the presence of K_2CO_3 in THF at reflux temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 81% yield. The structure was confirmed by mass spectroscopic method as seen in (Figure A 10). The QTOF spectrum indicated the presence of [M+H] and $(M+Na)^+$ peaks at 368.29 and 390.26, respectively.

The compound 10 as synthesized has same desired properties such as stable at high temperature and low viscosity, which may have an application as plastifying agent for PVC.

Synthesis of 2-Chloro-4,6-Bis((2-Ethylhexyl)Oxy)-1,3,5-Triazine(11).

Cyanuric chloride was used as starting material reacted with 2-ethylhexan-1-ol in the presence of Et_3N in THF at room temperature. After work up, the crude compound was passed through a short bed of silica gel column using hexane/ethyl acetate (9:1) to obtain colorless oily material in 71.5% yield. The structure was confirmed by spectroscopic methods as seen in (Figure A 10). The H-NMR showed the $–O-CH_2-$ peaks at 4.3 ppm and 4.2 ppm as triplets. In the C-NMR, the triazine peaks are seen at 173 ppm and 167 ppm while the $–O-CH_2-$ two peaks are seen in the 70 ppm and 78 ppm.

The approach of synthesis new series of different plasticizer molecular has showed desirable properties such as high boiling point and low volatility which reduce its loss during processing and further more highly versatile with properties that may be adjusted to a broad range of applications from highly flexible to semi rigid.

CHAPTER 4

PRACTICAL WORK

4.1 Materials

4.1.1 Chemicals and Reagents

Cyanuric chloride, dodecan-1-ol, 2ethylhexan-1-ol, 2,2-dimethylpropane-1,3-diol, butane-1,4-diol, 2,2'-oxybis(ethan-1-ol), ethane-1,2-diol, [1,1'-biphenyl]-4,4'-diol, 4,4'-(propane-2,2-diyl)diphenol, ,4'-oxydiphenol, potassium carbonate, potassium hydroxide, were used without further purification.Thesolvent wereused dry (THF, DMF, DMAC) were obtained from distilling over phosphorous pentoxide (merck).

4.1.2 Mesurments

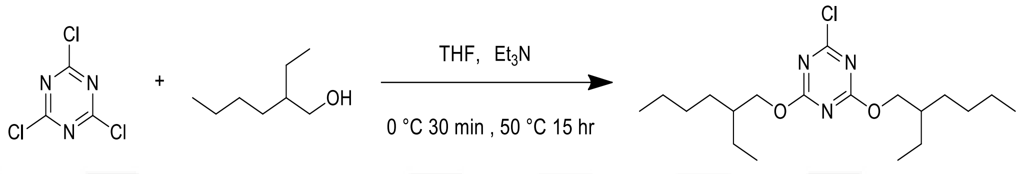
Purity of the compounds was to be checked by TLC on silica gel 60 F254 (Merck). Synthesized compounds are to be characterized by 1H-NMR and 13C-NMR spectra using CDCl3 / DMSO-d6 as a solvent with TMS as an internal standard. IR spectra were to be recorded in KBr on a Shimadzu FTIR 8400S spectrophotometer. Mass spectra were to be recorded on a GCMS-QP 1000 mass spectrometer.

4.2 Experimental Section

4.2.1 Synthesis of Target Compound 11

In a round bottom flask, 2,4,6-trichloro-1,3,5-triazine (12),(10 g, 54.2 mmol), 2-ethylhexan-1-ol(13) (14.12 g,108,4 mmol) in 50 ml of THF were added in order given. The mixture was stirred at room temperature 30 min. After that added trimethylamine (10.9 g,107.7 mmol). The mixture was stirred at 50 °C over night. The completion of the reaction was checked by TLC plate. The solvent was removed under vacuum on a rotator evaporator.

The reaction mixture was washed with methanol/ water (2:1).The combined organic layer was separated. The extracted organic layer was dried over Na2SO4. The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (14.3g, %71.5).



12 **13** **11**

Figure 4.1 Synthesis of Target Compound 11

The structure of compound 11 was confirmed by H1-NMR and C13-NMR spectra as seen in (Figure A 1). The relevant chemical shift of the protons were observed at (4.3 (t, 2×(OCH2), (4.2 (t, 2×(OCH2), 1.75 (m 2×(CH), 1.4 (m2×(CH2), 1.1 (t 2×(CH3),0.9 (t 2×(CH3)), and C13-NMR of the compound showed signals of carbon at (173, 172, 70, 69, 65, 42, 40, 31, 30, 23, 22, 14, 13, 11).

4.2.2 Synthesis of Target Compound 1

In a round bottom flask, 2-chloro- 4, 6-bis ((2-ethylhexyl) oxy) - 1, 3, 5-triazine (11) (2.0g,5.37mmol),2,2-dimethylpropane-1,3-diol (14) (0.28g, 2.68mmol) and K2CO3 (0.74g, 5.35mmol) in 10 mL of THF were added in order given. The mixture was stirred at 60°C over night .The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4, the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.8 g, 86.5%).

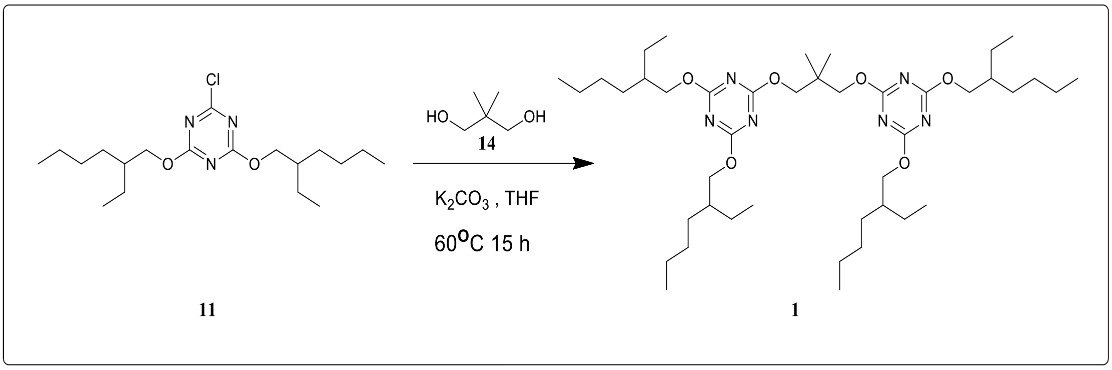


Figure 4.2 Synthesis of Target Compound 1

The structure was confirmed by spectroscopic methods as seen in (Figure A 2).The structure of the compound 1 was confirmed by the presence of (M+Na)+ and (M+H)+ peaks at 775.59 and 797.58 respectively. Structure of compound 1 was also confirmed by 1H-NMR and C13-NMR spectra. The relevant chemical shift of the major protons were observed at (4.2 (t 4×(OCH2), 3.6 (s 2× CH2, 3.4 (t 4× (OCH2), 1.75 (m 4×(CH), 1.5 (t 4×(CH2), 1.3 (t 4×(CH2), 1.1 (t 4×(CH3), 0.9 (t 4×(CH3)) and C-NMR of the compound showed signals of carbon at (172, 171, 71, 70, 69, 42, 38, 30, 28, 24, 23, 15, 14, 10).

4.2.3 Synthesis of Target Compound 2

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine (11) (2.0 g,5.37 mmol), butane-1,4-diol (15) (0.24g, 2.66 mmol) and K2CO3 (0.74 g, 5.35 mmol) in 10 mLof THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4, the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.73g, 84.3%).

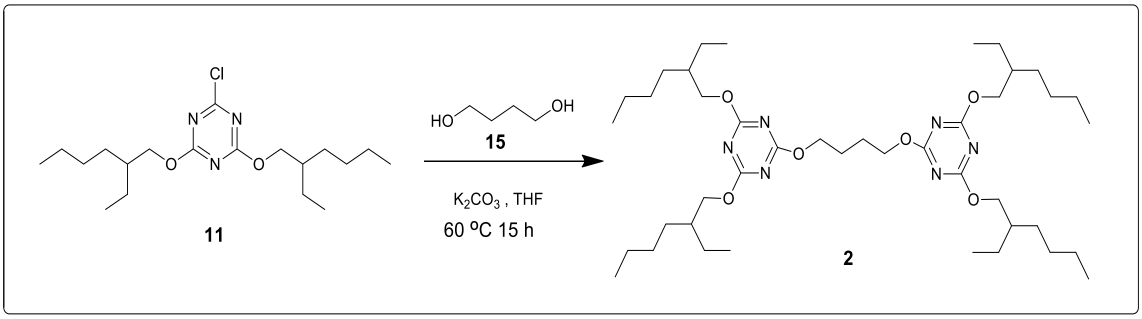
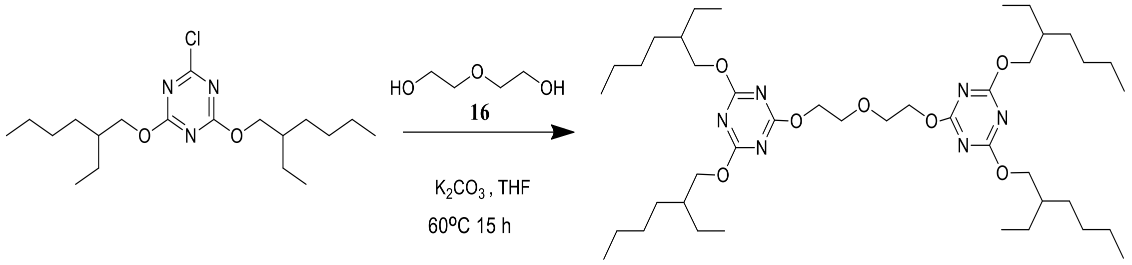


Figure 4.3 Synthesis of Target Compound 2

The structure was confirmed by spectroscopic methods as seen in (Figure A 3).The structure of the compound 2 was confirmed by the presence of M+ and (M+Na)+ peaks at 760.58 and 783.55 respectively. The structure of compound 2 was also confirmed by 1H-NMR and C13-NMR spectra. The relevant chemical shift of the major protons were observed at (4.1 (m 2×(OCH2), 3.5 (m 2×(OCH2), 2.2 (t 2×(CH2), 1.7 (m 4×(CH), 1.45 (t 4×(CH2), 1.2 (m 4×(CH2), 1.1 (m 4×(CH3), 0.8 (t 4×(CH3)), and C NMR of the compound showed signals of carbon at (171, 170, 71, 70, 69 , 42, 40, 31, 30, 23, 22, 14, 13, 11).

4.2.4 Synthesis of Target Compound 3

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11) (2.0g, 5.37mmol), 2,2'-oxybis(ethan-1-ol) (16) (0.28 g, 2.63mmol) and K2CO3 (0.74 g, 5.35 mmol) in 10 mLof THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4, the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.51 g,72.2%).



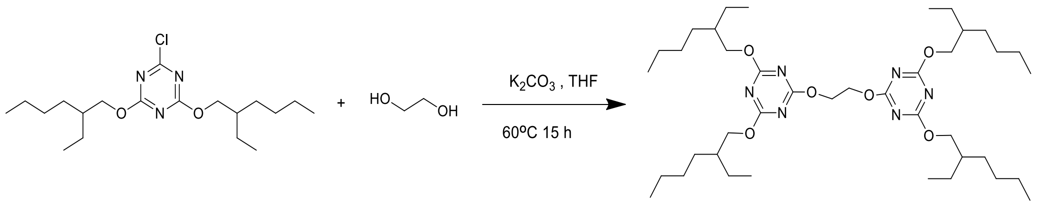
11 3

Figure 4.4 Synthesis of target compound 3

The structure was confirmed by spectroscopic methods as seen in (Figure A 4).The structure of the compound 3 was confirmed by the presence of M+ and (M+Na)+ peaks at 776.56 and 799.57 respectively. The structure of compound 3 was also confirmed by 1H NMR and C NMR spectra as seen in (). The relevant chemical shift of the protons were observed at (4.15 (m 2×(OCH2), 3.6 (m 2×(OCH2), 1.7 (m 4×(CH), 1.3 (m 4×(CH2), 1.1 (t 4×(CH3), 0.8 (t 4×(CH3)), and C NMR of the compound showed signals of carbon at (172, 170, 71, 70, 69, 42, 40, 31, 30, 23, 22, 14, 13, 11).

4.2.5 Synthesis of Target Compound 4

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11)(2.0 g, 5.37mmol), ethane-1,2-diol (17) (0.16 g, 2.57 mmol) and K2CO3 (0.74 g, 5.37 mmol) in 10 mLof THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4 the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.8 g, 91%).



11 17 4

Figure 4.5 Synthesis of Target Compound 4

The structure was confirmed by spectroscopic methods as seen in (Figure A 5).The structure of the compound 4 was confirmed by the presence of (M+2H)+2 peaks at 367.778. The structure of compound 4 was also confirmed by 1H-NMR and C13-NMR spectra. The relevant chemical shift of the protons were observed at (4.1 (m 2×(OCH2), 3.5 (m 2×(OCH2), 1.7 (m 4×(CH), 1.3 (m 4×(CH2), 1.1 (t 4×(CH3), 0.8 (t 4×(CH3)), and C NMR of the compound showed signals of carbon at (172, 170, 71, 70, 69, 42, 40, 31, 30, 23, 22, 14, 13, 11).

4.2.6 Synthesis of Target Compound 5

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11)(2.0 g, 5.37 mmol), [1,1'-biphenyl]-4,4'-diol (18) (0.5 g, 2.68 mmol) and K2CO3 (0.74 g, 5.35 mmol) in 10 mL of THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL). The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4 the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.85g, 80.4%).

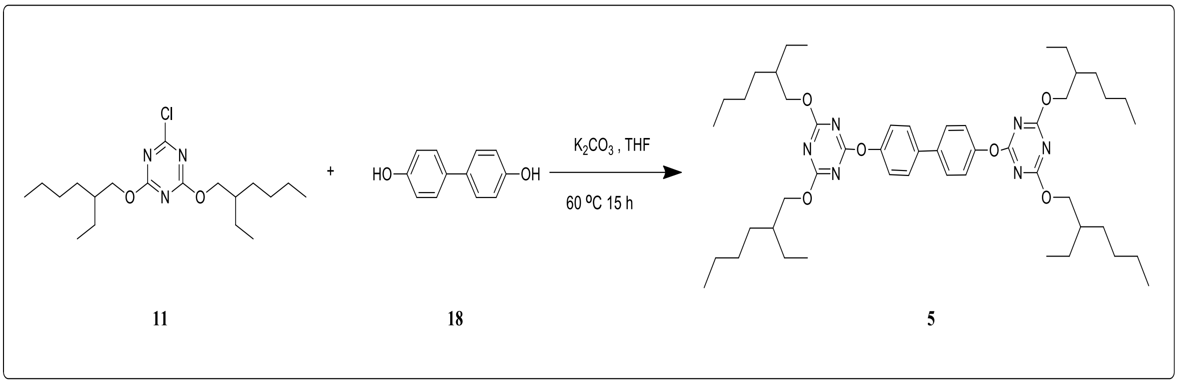


Figure 4.6 Synthesis of Target Compound 5

The structure was confirmed by spectroscopic methods as seen in (Figure A 6).The structure of the compound 5 was confirmed by the presence of M+2[-H2O] and (M+2) peaks at 427.28 and 436.78 respectively. The structure of compound 5 was also confirmed by H1-NMR and C13-NMR spectra. The relevant chemical shift of the protons were observed at (7.6 (d 2H), (7.5 (d 2H), (4.2 (t 4×(OCH2), 1.7 (m 4×(CH), 1.25 (m 4×(CH2), 0.8 (t 4×(CH3), 0.7 (t 4×(CH3)), and C NMR of the compound showed signals of carbon at (168, 165, 134, 132,131, 130, 129, 68, 67, 39, 30, 28, 23, 22, 13, 10).

4.2.7 Synthesis of Target Compound 6

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11)(2.0 g, 5.37 mmol), 4,4'-(propane-2,2-diyl)diphenol (19) (0.61 g, 2.67 mmol) and K2CO3 (0.74 g, 5.35 mmol) in 10 mL of THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4 the solvent was evaporated under vacuum.The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.81g, 74.8%).

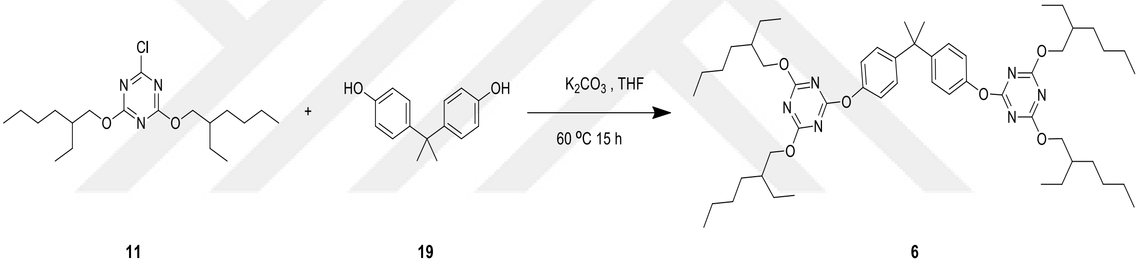
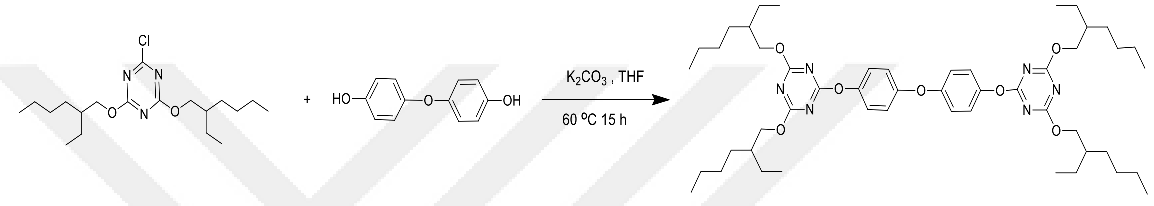


Figure 4.7 Synthesis of Target Compound 6

The structure was confirmed by spectroscopic methods as seen in (Figure A 7).The structure of the compound 6 was confirmed by the presence of (M+H)+[-H2O] and (M+NH4)+ peaks at 881.62 and 916.66 respectively. The structure of compound 6 was also confirmed by 1H-NMR and C13-NMR spectra. The relevant chemical shift of the protons were observed at (7.2 (d, 2H), (7.1 (d 2H), (4.2 (t, 4×(OCH2), 2.25 (t 4×(CH2), 1.7 (t 4×(CH), 1.4 (m 4×(CH2), 1.2 (t 4×(CH2), 0.8 (m 4×(CH3)), and C NMR of the compound showed signals of carbon at (173, 138, 129,128,126, 125,70, 42, 40, 32, 31, 25, 23, 22, 14, 11).

4.2.8 Synthesis of Target Compound 7

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11)(2.0 g, 5.37 mmol), 4,4'-oxydiphenol (20) (0.54 g, 2.67 mmol) and K2CO3 (0.74 g, 5.35 mmol) in 10 mL of THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL). The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4 the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (1.6 g, 68%).



11 20 7

Figure 4.8 Synthesis of Target Compound 7

The structure was confirmed by spectroscopic methods as seen in (Figure A 8). The structure of the compound 7was confirmed by the presence of M+[-H2O] and (M+NH4)+ peaks at 838.57 and 874.64 respectively. The structure of compound 7 was also confirmed by 1H-NMR and C13-NMR spectra. The relevant chemical shift of the protons were observed at (7.62 (d, 2H), (7.45 (d 2H), (4.2 (t, 4×(OCH2), 3.5 (t 2×(OCH2), 1.6 (t 4×(CH), 1.4 (m 4×(CH2), 1.1 (t 4×(CH3), 0.8 (m 4×(CH3)), and C NMR of the compound showed signals of carbon at (172, 170, 138, 131, 129, 128, 125, 71,70, 69, 42, 40, 30, 29, 23, 22, 14, 13, 10).

4.2.9 Synthesis of the Complex (8)

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11)(4.0 g,10.75mmol), 2,2-dimethylpropane-1,3-diol (14),(0.14g, 1.34mmol), butane-1,4-diol (15)(0.12 g, 1.33mmol), 2,2'-oxybis(ethan-1-ol) (16),(0.14 g, 1.31mmol), ethane-1,2-diol (17), (0.08 g, 1.28mmol) and K2CO3 (1.48 g, 10.7 mmol) in 40 ml of THF were added in order given. The mixture was stirred at 64°C over night. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4 the solvent was evaporated under vacuum. The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (3.65g , 88%) .

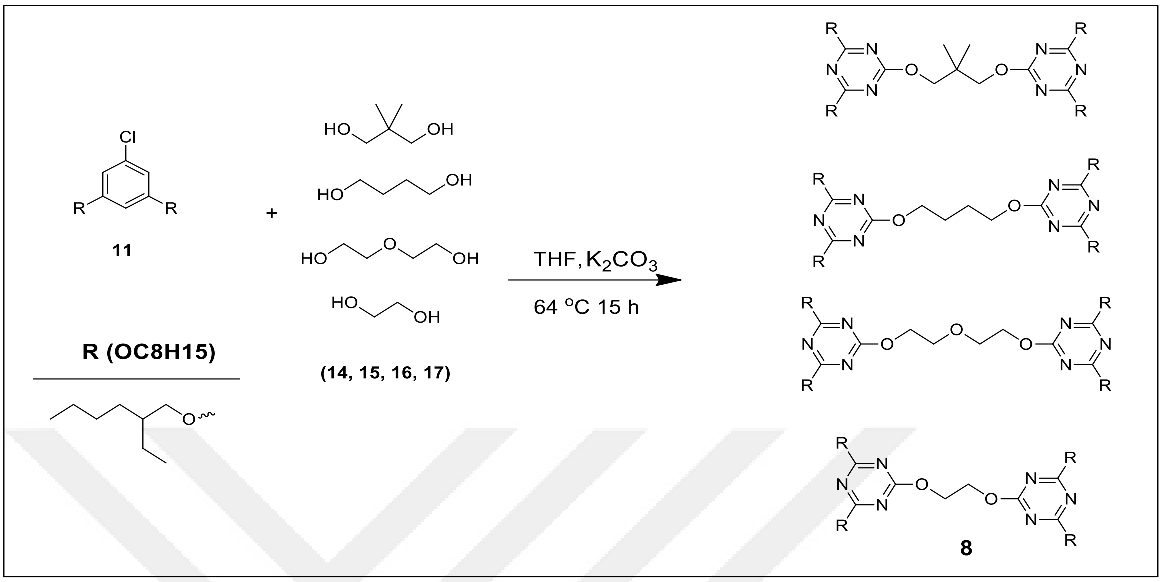


Figure 4.9 Synthesis of Target Compound 8

The structure was confirmed by mass spectroscopic method as seen in (Figure A 9).The structure of the compound 8 was confirmed by the presence of the four different compounds in the mixture as following (M+)and (M+Na)+ peaks at 760.57 and 784.58 respectively, (M+H) and (M+) peaks at 775.6 and 774.6 respectively, M+[-H2O] and (M+Na)+[-H2O] peaks at758.56 and 781.55 respectively, (M+)and (M+Na)+ peaks at 732.53 and 755.53 respectively.

4.2.10 Synthesis of Target Compound 9

In a round bottom flask, 2,4,6-trichloro-1,3,5-triazine (12) (25g, 135.5mmol), 2-ethylhexan-1-ol(13) (52.96g, 406 mmol) andK2CO3 (61.8g, 447 mmol) in 150 ml of THF were added in order given. The mixture was stirred at 60°C over night. The completion of the reaction was checked by TLC plate. The reaction mixture was extracted with hexane (100 mL).The combined organic layer was washed with water (3 x 50 mL). The extracted organic layer was dried over Na2SO4.The solvent was removed under vacuum on a rotator evaporator. The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (45.8 g, 72.5%).

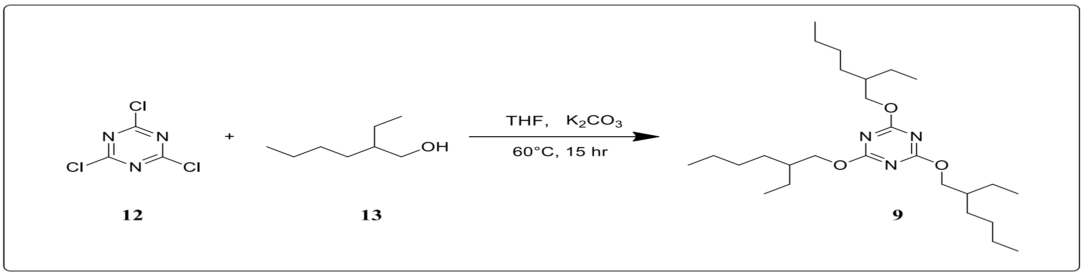


Figure 4.10 Synthesis of Target Compound 9

4.2.11 Synthesis of Target Compound 10

In a round bottom flask, 2-chloro-4,6-bis((2-ethylhexyl)oxy)-1,3,5-triazine(11)(40g, 216.9 mmol), methanol(21) (6.9g, 215.6mmol) and K2CO3 (56.5g, 433.8mmol) in 200 mL of THF were added in order given. The mixture was stirred at 40°C for six hours. The completion of the reaction was checked by TLC plate. After naturalization with 1N HCl, the reaction mixture was extracted with hexane (200 mL). The combined organic layer was washed with water (3 x 100 mL). The extracted organic layer was dried over Na2SO4 the solvent was evaporated under vacuum .The residue was purified by column chromatography with hexane/ethyl acetate (9:1) as an eluent to yield (32g, 81%).

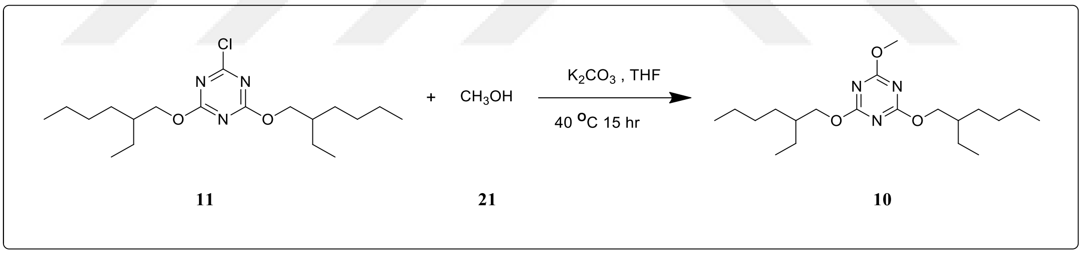


Figure 4.11 Synthesis of Target Compound 10

The structure was confirmed by mass spectroscopic method as seen in (Figure A 10). The structure of the compound 10 was confirmed by the presence of [M+H] and (M+Na)+ peaks at 368.29 and 390.26 respectively.

CHAPTER 5

CONCLUSIONS

In this study, novel of triazines-based plasticizer were succefully synthesized and their spectroscopy characterizations were confirmed by spectroscopic methods as new plasticizer agent for PVC.

The first step of this study, di-substituted triazines were successfully synthesized as intermediate compound and purified were conformed with NMR spectra.

The second step, di-substituted triazines were reacted further in substitution reactions with aromatic and aliphatic alcohols to produced new family of plasticizer agent.

Despite the fact that the obtained tri-substituted triazines as seen in (Figure 4.10) have a high viscosity and sensitivity to high temperatures, it showed plastifying properties when used with PVC. The film obtained is seen in (Figure 3.2). The figure also shows the film obtained with standard plastifying agent used in the PVC industry. So we reduced the high viscosity of the compound by replacing one equivalent of 2-ethylhexan-1-ol into methanol which is successfully done as seen in (Figure 4.11).

As a result the approach of synthesis new series of different plasticizer molecular has showed desirable properties such as high boiling point and low volatility which reduce its loss during processing and further more highly versatile with properties that may be adjusted to a broad range of applications from highly flexible to semi rigid.

REFERENCES

[1] Ge, L. N., Xian, S. W., Huang, Y., Min, Y., Lv, J. M., Tian, M., D. S., (2018). “Synthesis and mesomorphism of novel multi-arm liquid crystals with cholic acid as chiral centre linking Schiff base moieties as mesogens”, Liquid Crystals, 45(7):1055-1067.

[2] Rahman, M., and Brazel, C. S., (2004). “The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges”, Progress in polymer science, 29(12):1223-1248.

[3] Vieira, M. G. A., Da Silva, M. A., Dos Santos, L. O., Beppu, M. M., (2011). “Natural-based plasticizers and biopolymer films: A review”, European Polymer Journal, 47(3): 254-263.

[4] Dainyte, A., Gudeika, D., Buika, G., and Grazulevicius, J. V., (2014). “Synthesis and Properties of the Derivatives of 2, 4, 6-Tris (Phenoxy)-1, 3, 5-Triazine”, Molecular Crystals and Liquid Crystals, 590(1):73-79.

[5] Barshtein, R.S., Kirilovich, V.I., and Nosovskii, Yu.E., (1982). Plastifi Katory Dlya Polimerov (Plasticizers For Polymers), Khimiya, Moscow.

[6] Lindström, A., and Hakkarainen, M., (2007). “Migration resistant polymeric plasticizer for poly (vinyl chloride)”, Journal of applied polymer science, 104(4):2458-2467.

[7] Daniels, P. H., (2009). “A brief overview of theories of Pvc plasticization and methods used to evaluate PVC-plasticizer interaction”, Journal of vinyl and additive technology, 15(4):219-223.

[8] Cartwright, C. D., Thompson, I. P., and Burns, R. G., (2000). “Degradation and impact of phthalate plasticizers on soil microbial communities”, Environmental Toxicology and Chemistry, 19(5):1253-1261.

[9] Reddy, N. N., Mohan, Y. M., Varaprasad, K., Ravindra, S., Vimala, K., and Raju, K. M., (2010). “Surface treatment of plasticized poly (vinyl chloride) to prevent plasticizer migration”, Journal of applied polymer science, 115(3):1589-1597.

[10] Kim, W., Choi, I., Jung, Y., Lee, J., Min, S., and Yoon, C., (2013). “Phthalate levels in nursery schools and related factors”, Environmental science and technology, 47(21):12459-12468.

[11] Banerjee, R., Brown, D. R., and Weerapana, E., (2013). “Recent developments in the synthesis of bioactive 2, 4, 6-trisubstituted 1, 3, 5-triazines”, Synlett, 24(13):1599-1605.

[12] Hatfield, S. E., (2010). Applications of triazine chemistry education, remediation, and drug delivery (Doctoral dissertation, Texas A and M University).

[13] Neunhoeffer, H., and Wiley, P. F. (Eds.)., (2009). Chemistry of 1 2 3-Triazines and 1 2 4-Triazines, Tetrazines, and Pentazin (Vol. 108), John Wiley and Sons.

[14] Brunet, P., Simard, M., and Wuest, J. D., (1997). “Molecular tectonics. Porous hydrogen-bonded networks with unprecedented structural integrity”, Journal of the American Chemical Society, 119(11):2737-2738.

[15] Arshad, M., Kahn., Taki A. K., Meraj, A., (2014). “1, 2, 4-Triazine Derivatives Synthesis and Biological Aplications”, International Journal of Pharma Sciences and Research (Ijpsr), 4:149-162.

[16] Kumar, R., Deep Singh, A., Singh, J., Singh, H., Roy, R. K., and Chaudhary, A., (2014). “1, 2, 3-Triazine scaffold as a potent biologically active moiety: a mini review”, Mini reviews in medicinal chemistry, 14(1):72-83.

[17] Shimokawa, J., (2018). “Synthetic Studies on Heteropolycyclic Natural Products: Development of Divergent Strategy”, Chemical and Pharmaceutical Bulletin, 66(2):105-115.

[18] El-Gendy, Z., Morsy, J. M., Allimony, H. A., Ali, W. R., and Abdel-Rahman, R. M., (2001). “Synthesis of heterobicyclic nitrogen systems bearing the 1, 2, 4-triazine moiety as anti-HIV and anticancer drugs, part III”, Die Pharmazie, 56(5):376-383.

[19] Schmitz, W. D., Brenner, A. B., Bronson, J. J., Ditta, J. L., Griffin, C. R., Li, Y. W., and Macor, J. E., (2010). “5-Arylamino-1, 2, 4-triazin-6 (1H)-one CRF 1 receptor antagonists”, Bioorganic and medicinal chemistry letters, 20(12):3579-3583.

[20] Baldaniya, B. B., (2010). “Synthesis and Characterizations of N2 (Aryl)-N4, N6-bis (6, 7-dichloro-1, 3-benzothiazol-2-yl)-1, 3, 5-triazine-2, 4, 6-triamines as Biological Potent Agents”, Journal of Chemistry, 7(1):210-214.

[21] Chang, M., and Matuszko, A., (1962). Synthesis and Properties of Some Cyanuric Chloride Derivatives (No. Navweps-7109), Bureau of Naval Weapons, U. S. Naval Propellant Plant, Washington Dc.

[22] Fischer, G., Geith, J., Klapötke, T. M., and Krumm, B., (2002). “Synthesis, properties and dimerization study of isocyanic acid”, Zeitschrift für Naturforschung B, 57(1):19-24.

[23] Dömling, A., and Ugi, I., (2000). “Multikomponentenreaktionen mit isocyaniden”, Angewandte Chemie, 112(18):3300-3344.

[24] Klotz, I. M., and Askounis, T., (1947). “Absorption spectra and tautomerism of cyanuric acid, melamine and some related compounds”, Journal of the American Chemical Society, 69(4):801-803.

[25] Qian, Z. H., and Abruzzese, D., (2009). “Fatigue failure of welded connections at orthotropic bridges”, Frattura ed integrità strutturale, 3(9):105-112.

[26] Kallitsas,P., (2016). Fatigue Loads İdentification On Orthotropic steel Decks, MSc. Thesis, Delft University of Technology, Civil Engineering and Geosciences, Delft.

[27] Ya, S., Yamada, K., and Ishikawa, T., (2010). “Fatigue evaluation of rib-to-deck welded joints of orthotropic steel bridge deck”, Journal of Bridge Engineering, 16(4):492-499.

[28] Fierz-David, H. E., and Matter, M., (1937). “Azo and anthraquinonoid dyes containing the cyanuric ring”, Journal of the Society of Dyers and Colourists, 53(11):424-436.

[29] Huthmacher, K., and Most, D., Cyanuric acid and cyanuric chloride, Ullmann's Encyclopedia of Industrial Chemistry, https://onlinelibrary.wiley.com/, 15 June 2000.

[30] Hosseini-Monfared, H., Mojtabazadeh, F., Bikas, R., Eigner, V., Dusek, M., and Gutiérrez, A., (2014). “Cyanuric chloride reagent as a chloride ion donor: synthesis, crystal structure, and magnetic properties of [Cu2 (2-Apm) 2 (μ-Cl) 2 (μ-Och3) 2] n coordination polymer”, Journal of Coordination Chemistry, 67(21):3510-3518.

[31] Bester, K., and Hühnerfuss, H., (1993). “Triazines in the Baltic and North Sea”, Marine pollution bulletin, 26(8):423-427.

[32] Blotny, G., (2006). “Recent applications of 2, 4, 6-trichloro-1, 3, 5-triazine and its derivatives in organic synthesis”, Tetrahedron, 62(41):9507-9522.

[33] Samaritani, S., Peluso, P., Malanga, C., and Menicagli, R., (2002). “Selective Amination of Cyanuric Chloride in the Presence of 18-Crown-6”, European Journal of Organic Chemistry, 2002(9):1551-1555.

[34] Vollbrecht, H. R., and Wagner, F., (1982). U.S. Patent No. 4,329,325., Cyanuric Chloride Mixtures and Process for Producing Same, U.S. Patent and Trademark Office, Washington, Dc.

[35] Kumar, R., Sirohi, T. S., Singh, H., Yadav, R., Roy, R. K., Chaudhary, A., and Pandeya, S. N., (2014). “1, 2, 4-triazine analogs as novel class of therapeutic agents”, Mini Rev Med Chem, 14(2):168-207.

[36] Liu, Y. Q., Zhao, G. Y., Yan, Y. Z., and Zhang, X. C., (2016). “Effect on Stresses of Structural Details of Orthotropic Steel Deck with Thin Surfacing”, DEStech Transactions on Materials Science and Engineering, AMST 2016, 30-31 October 2016, Shenzhen.

[37] Oxley, J. C., Smith, J. L., and Moran, J. S., (2009). “Decomposition of azo-and hydrazo-linked bis triazines”, Journal of Energetic Materials, 27(2):63-93.

[38] Salman, A. W., Rehman, G. U., Abdullah, N., Budagumpi, S., Endud, S., Abdallah, H. H., and Wong, W. Y., (2014). “Sterically modulated palladium (II)-N-heterocyclic carbene complexes for the catalytic oxidation of olefins: Synthesis, crystal structure, characterization and DFT studies”, Polyhedron, 81, 499-510..

[39] Brown, S. B., H. P. Brack, A. Jella and D. Karlik, (2007). Triazine Compounds, Polymers Comprising Triazine Structural Units and Method, United States Patent, Patent No:7, 235, 611

[40] Solankee, A., Kapadia, K., Ćirić, A., Soković, M., Doytchinova, I., and Geronikaki, A. (2010). “Synthesis of some new S-triazine based chalcones and their derivatives as potent antimicrobial agents”, European journal of medicinal chemistry, 45(2):510-518.

[41] Bandgar, B. P., Joshi, N. S., and Kamble, V. T., (2006). "2, 4, 6-Trichloro-1, 3, 5-triazine catalyzed synthesis of thiiranes from oxiranes under solvent-free and mild conditions", Tetrahedron letters, 47(27), 4775-4777.

[42] Fierz-David, H. E., and Matter, M., (1937). "Azo and anthraquinonoid dyes containing the cyanuric ring", Journal of the Society of Dyers and Colourists, 53(11):424-436.

[43] Zheng, M., Xu, C., Ma, J., Sun, Y., Du, F., Liu, H., and Jiang, H., (2007). "Synthesis and antitumor evaluation of a novel series of triaminotriazine derivatives", Bioorganic and medicinal chemistry, 15(4):1815-1827.

[44] Lees, F., (2012). Lees' Loss prevention in the process industries: Hazard identification, assessment and control, Butterworth-Heinemann.

[45] Hinkens, R., Promel, R., and Martin, R. H. (1961). "Synthèse de dihydro-6, 7-imidazo [1, 2− a] triazines-1, 3, 5 disubstituées", Helvetica Chimica Acta, 44(1):299-309.

[46] GOI, M., (1960). "Reactivities of cyanuric chloride derivatives. I", Journal of Synthetic Organic Chemistry, Japan, 18(5):327-331.

[47] Goi, M., (1960). "Reactivities of Cyanuric Chloride Derivatives II", Journal of Synthetic Organic Chemistry, Japan, 18(5):337-342.

[48] Sarmah, K. N., Sarmah, N. K., Kurmi, K. B., and Patel, T. V., (2012). "Synthesis of novel derivatives containing s-triazine moiety as potential antibacterial agents", Archives of Applied Science Research, 4(2):805-808.

[49] Qian, L., Qiu, Y., Liu, J., Xin, F., and Chen, Y., (2014). "The flame retardant group-synergistic-effect of a phosphaphenanthrene and triazine double-group compound in epoxy resin", Journal of Applied Polymer Science, 131(3).

[50] Inspection Center and Testing Institute, (1992). Biodegradation and Bioaccumulation Data of Existing Chemicals Based on the CSCL Japan, Japan Chemical Industry Ecology-Toxicology and Information Center, 2-109, Tokyo.

[51] Grisley, Jr. D., Gluesenkamp, E., and Heininger, S., (1958). Reactions of nucleophilic reagents with cyanuric fluoride and cyanuric chloride, The Journal of Organic Chemistry, 23(11):1802-1804.

[52] Rys, P., Schmitz, A., and Zollinger, H., (1971). "Der Mechanismus der Hydrolyse von Chlortriazinen in protischen Lösungsmitteln. II", Mitteilung Über nukleophile uromatische Substitutionen. Helvetica Chimica Acta, 54(1):163-176.

[53] Chambers, R. D., and Sargent, C. R., (1981). "Polyfluoroheteroaromatic compounds", Advances in Heterocyclic Chemistry, 28, 1-71.

[54] Afonso, C. A., Lourenco, N. M., and Rosatella, A. D. A., (2006). "Synthesis of 2, 4, 6-Tri-substituted-1, 3, 5-Triazines", Molecules, 11(1):81-102.

[55] Moran, J. S., (2008). The synthesis, reduction, and decomposition of novel high-nitrogen bis s-triazinyl hydrazines and diazenes, MSc. Thesis, University of Rhode Island, Analytical Chemistry, Kingston.

[56] Ye, J., Liu, S., Xiang, J., Lei, J., and Zhou, C., (2013). " Preparation and application of triglyceride plasticizers for poly (vinyl chloride) ", Journal of Applied Polymer Science, 129(4):1915-1921.

[57] Bouchareb, B., and Benaniba, M. T., (2008). “Effects of epoxidized sunflower oil on the mechanical and dynamical analysis of the plasticized poly (vinyl chloride) ”, Journal of applied polymer science, 107(6):3442-3450.

[58] Bouchareb, B., and Benaniba, M. T., (2008). “Effects of epoxidized sunflower oil on the mechanical and dynamical analysis of the plasticized poly (vinyl chloride)”, Journal of applied polymer science, 107(6):3442-3450.

[59] Singh, K., Kumar, Y., Puri, P., Sharma, C., and Aneja, K. R. (2012). “Synthesis, spectroscopic, thermal and antimicrobial studies of Co (II), Ni (II), Cu (II) and Zn (II) complexes with Schiff base derived from 4-amino-3-mercapto-6-methyl-5-oxo-1, 2, 4-triazine”, Medicinal Chemistry Research, 21(8):1708-1716.

[60] Dean, J. R., Wade, G., Barnabas, I. J., (1996). “Determination of triazine herbicides in environmental samples”, Journal of chromatography A, 733(1-2):295-335.

[61] Pacáková, V., Štulík, K., and Jiskra, J., (1996). “High-performance separations in the determination of triazine herbicides and their residues”, Journal of chromatography A, 754(1-2):17-31.

[62] Fernandez Cid, M. V., Buijs, W., and Witkamp, G. J., (2007). “Application of molecular modeling in the optimization of reactive cotton dyeing in supercritical carbon dioxide”, Industrial and engineering chemistry research, 46(12):3941-3944.

[63] Kebede, B., Retta, N., Raju, V. J. T., and Chebude, Y., (2006). “Synthesis and Characterization of 2, 4, 6-tris (hydrazino)-s-triazine and its Metal Complexes”, Transition metal chemistry, 31(1):19-26.

[64] Dinku, W., Megersa, N., Raju, V. J. T., Solomon, T., Jönsson, J. A., and Retta, N., (2003). “Studies on transition metal complexes of herbicidal compounds. II: Transition metal complexes of derivatized 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine)”, Bulletin of the Chemical Society of Ethiopia, 17(1).

[65] Parry, Z. A., and Pandey, R., (2017). Dendrimers in Medical Science, Apple Academic Press, Ontario.

[66] Doelle, H. W., Fiechter, A., van Griensven, M., Kasper, C., Pörtner, R., Schlegel, G., and Zorn, H., (2009). Biotechnology, 6. Special Applications, Ullmann's Encyclopedia of Industrial Chemistry.

[67] Ramírez Díaz, J. R., (2013). Síntesis sostenible de nuevos derivados de Triazina, Estudio de sus propiedades ópticas, PhD Thesis, University of Seville, Department of Inorganic, Organic and Biochemical Chemistry, Seville.

[68] Dambal, H. K., and Yelamaggad, C. V., (2012). “Technologically promising, room temperature luminescent columnar liquid crystals derived from s-triazine core: molecular design, synthesis and characterization”, Tetrahedron letters, 53(2):186-190.

[69] Yamamoto, T., Watanabe, S., Fukumoto, H., Sato, M., and Tanaka, T., (2006). “New Heteroaromatic Polymers Consisting of Alkyl-and Amino-1, 3, 5-triazine Units Their Basic Optical Properties and n-Type Time-of-Flight Drift Mobility”, Macromolecular rapid communications, 27(5):317-321.

[70] Fioravanti, S., Pellacani, L., Tardella, P. A., and Vergari, M. C., (2008). “Facile and highly stereoselective one-pot synthesis of either (e)-or (z)-nitro alkenes”, Organic Letters, 10(7):1449-1451.

[71] Wahler, D., and Reymond, J. L., (2002). “Methylamine adenine dinucleotide (Mad): a co-factor to turn alcohol dehydrogenases into aldolases”, Canadian journal of chemistry, 80(6):665-670.

[72] Rios, I. G., Novarino, E., van der Veer, S., Hessen, B., and Bouwkamp, M. W., (2009). “Amine Catalyzed Solvent C− H Bond Activation as Deactivation Route for Cationic Decamethylzirconocene Olefin Polymerization Catalysts”, Journal of the American Chemical Society, 131(46):16658-16659.

[73] Ansari, S., (2012). “The return of the public”, Journal of Communication, 62(2):E5-E7.

[74] Imada, Y., Iida, H., Ono, S., and Murahashi, S. I., (2003). “Flavin catalyzed oxidations of sulfides and amines with molecular oxygen”, Journal of the American Chemical Society, 125(10):2868-2869.

[75] Aggarwal, V. K., Lopin, C., and Sandrinelli, F. (2003). “New insights in the mechanism of amine catalyzed epoxidation: dual role of protonated ammonium salts as both phase transfer catalysts and activators of oxone”, Journal of the American Chemical Society, 125(25):7596-7601.

[76] Ghorbani-Choghamarani, A., Zolfigol, M. A., and Azadbakht, T., (2010). “1, 2-Dipyridiniumditribromide-ethane (DPTBE) as a New Oxidizing Agent for the Chemoselective Oxidation of Sulfides to the Sulfoxides”, Phosphorus, Sulfur, and Silicon, 185(3):573-577.

[77] Ramasubramanian, A. S., Bhat, R. B., Dileep, R., and Rani, S., (2011). “Transition metal complexes of 5-bromosalicylidene-4-amino-3-mercapto-1, 2, 4-triazine-5-one: Synthesis, characterization, catalytic and antibacterial studies”, Journal of the Serbian Chemical Society, 76(1):75-83.

[78] Brzozowski, Z., Sączewski, F., and Gdaniec, M., (2000). “Synthesis, structural characterization and antitumor activity of novel 2, 4-diamino-1, 3, 5-triazine derivatives”, European journal of medicinal chemistry, 35(12):1053-1064.

[79] Ono, M., Kawahara, N., Goto, D., Wakabayashi, Y., Ushiro, S., Yoshida, S., and Sato, Y., (1996). “Inhibition of tumor growth and neovascularization by an anti-gastric ulcer agent, irsogladine”, Cancer research, 56(7):1512-1516.

[80] Daeyaert, F. F. D., De Corte, B., De Jonge, M. R., Heeres, J., Ho, C. Y., Janssen, P. A. J., and Ludovici, D. W., (2000). U.S. Patent No. 6,150,360., Trisubstituted 1,3,5-Triazine Derivatives, U.S. Patent and Trademark Office, Washington, Dc.

[81] Agarwal, A., Srivastava, K., Puri, S. K., and Chauhan, P. M., (2005). “Syntheses of 2, 4, 6-trisubstituted triazines as antimalarial agents”, Bioorganic and medicinal chemistry letters, 15(3):531-533.

[82] Stone, G. W., Ellis, S. G., Cox, D. A., Hermiller, J., O'shaughnessy, C., Mann, J. T., and Popma, J. J., (2004). “A polymer-based, paclitaxel-eluting stent in patients with coronary artery disease”, New England Journal of Medicine, 350(3):221-231.

[83] Leon, M. B., Smith, C. R., Mack, M., Miller, D. C., Moses, J. W., Svensson, L. G., and Brown, D. L., (2010). “Transcatheter aortic-valve implantation for aortic

stenosis in patients who cannot undergo surgery", New England Journal of Medicine, 363(17):1597-1607.

[84] Srinivas, K., Srinivas, U., Bhanuprakash, K., Harakishore, K., Murthy, U. S. N., and Rao, V. J., (2006). "Synthesis and antibacterial activity of various substituted s-triazines", European journal of medicinal chemistry, 41(11):1240-1246.

[85] Klionsky, D. J., Abdalla, F. C., Abeliovich, H., Abraham, R. T., Acevedo-Arozena, A., Adeli, K., and Ahn, H. J., (2012). "Guidelines for the use and interpretation of assays for monitoring autophagy", Autophagy, 8(4):445-544.

[86] Keldsen, N., Havsteen, H., Vergote, I., Bertelsen, K., and Jakobsen, A., (2003). "Altretamine (hexamethylmelamine) in the treatment of platinum-resistant ovarian cancer: a phase II study", Gynecologic oncology, 88(2):118-122.

[87] Basedia, D. K., Shrivastava, B., Dubey, B. K., andSharma, P., (2014). "Synthesis, characterization and antimicrobial activity of novel substituted aryl-1, 3, 4-oxadiazolo-[3, 2-a]-1, 3, 5-triazine derivatives", International Journal of Drug Delivery, 5(4):379-388.

[88] Kumar, R., Gupta, L., Pal, P., Khan, S., Singh, N., Katiyar, S. B., and Lochab, S. (2010). "Synthesis and cytotoxicity evaluation of (tetrahydro-β-carboline)-1, 3, 5-triazine hybrids as anticancer agents", European journal of medicinal chemistry, 45(6):2265-2276.

[89] Zheng, M., Xu, C., Ma, J., Sun, Y., Du, F., Liu, H., and Jiang, H., (2007). "Synthesis and antitumor evaluation of a novel series of triaminotriazine derivatives", Bioorganic and medicinal chemistry, 15(4):1815-1827.

[90] Giam, C. S., and Wong, M. K., (1987). "Plasticizers in food", Journal of Food Protection, 50(9):769-782.

[91] Thinius, K., (1960). Chemie, Physik und Technologie der Weichmacher: ein Handbuch für die Lack-und Plastindustrie, Verlag Technik, Berlin.

[92] Barshtein, R. S., Kirilovich, V. I., and Nosovskii, Y. E., (1982). "Plasticizers for polymers", Moscow: Khimiya, Moscow.

[93] Mekonnen, T., Mussone, P., Khalil, H., and Bressler, D., (2013). "Progress in bio-based plastics and plasticizing modifications", Journal of Materials Chemistry A, 1(43):13379-13398.

[94] Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., and Beppu, M. M., (2011). Natural-based plasticizers and biopolymer films: A review. European Polymer Journal, 47(3):254-263.

[95] Handbook, P. V. C., (2005). Wilkes, Ce, Summers, Jw, and Daniels, Ca, Eds, Munich: Hanser.

[96] Shatkin, J. A., Wegner, T. H., Bilek, E. T., and Cowie, J., (2014). "Market projections of cellulose nanomaterial-enabled products-Part 1: Applications", Tappi Journal, Volume 13, Number 5, 2014, pp 9-16, 13(5):9-16.

[97] Wojciechowska, P., (2012). Recent advances in plasticizers: 8. The Effect of Concentration and Type of Plasticizer on the Mechanical Properties of Cellulose acetate Butyrate Organic-inorganic Hybrids, InTech, The Poznan University of Economics, Poznan.

[98] Craver, C., and Carraher, C. (Eds.)., (2000). Applied polymer science: 21st century. 1st Edition Elsevier Science, New York.

[99] Rahman, M., and Brazel, C. S., (2004). “The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges”, Progress in polymer science, 29(12):1223-1248.

[100] Lindström, A., and Hakkarainen, M., (2006). “Environmentally friendly plasticizers for poly (vinyl chloride)-Improved mechanical properties and compatibility by using branched poly (butylene adipate) as a polymeric plasticizer”, Journal of applied polymer science, 100(3):2180-2188.

[101] Eyerer, P., Weller, M., and Hübner, C. (Eds.)., (2010). Polymers-Opportunities and Risks II: sustainability, product design and processing (Vol. 12), Springer Verlag GmbH, Heidelberg.

[102] Wojciechowska, P., (2012). Recent advances in plasticizers: 8. The Effect of Concentration and Type of Plasticizer on the Mechanical Properties of Cellulose acetate Butyrate Organic-inorganic Hybrids, InTech, The Poznan University of Economics, Poznan.

[103] Cao, X. L., (2010). “Phthalate esters in foods: sources, occurrence, and analytical methods”, Comprehensive reviews in food science and food safety, 9(1):21-43.

[104] Wittassek, M., Koch, H. M., Angerer, J., and Brüning, T., (2011). “Assessing exposure to phthalates–the human biomonitoring approach”, Molecular nutrition and food research, 55(1):7-31.

[105] Yin, B., and Hakkarainen, M., (2011). “Oligomeric isosorbide esters as alternative renewable resource plasticizers for PVC”, Journal of Applied Polymer Science, 119(4):2400-2407.

[106] Babu, B., and Wu, J. T., (2010). “Biodegradation of Phthalte Esters By Cyanobacteria1”, Journal of phycology, 46(6):1106-1113.

[107] Imai, Y., Kondo, A., Iizuka, H., Maruyama, T., and Kurohane, K., (2006). “ Effects of phthalate esters on the sensitization phase of contact hypersensitivity induced by fluorescein isothiocyanate”, Clinical and Experimental Allergy, 36(11):1462-1468.

[108] Wypych, G., (2018). Handbook of material weathering, 6th Edition, ChemTec Publishing.

[109] Daniels, P. H., (2009). “A brief overview of theories of PVC plasticization and methods used to evaluate Pvc-plasticizer interaction”, Journal of vinyl and additive technology, 15(4):219-223.

[110] Chandola, M., and Marathe, S., (2008). “Aqspr for the plasticization efficiency of polyvinylchloride plasticizers”, Journal of Molecular Graphics and Modelling, 26(5):824-828.

[111] Wadey, B. L., (2002). Plasticizers, Encyclopedia of Polymer Science and Technology, Wiley, New Jersey.

[112] Barton, A. F., (2017). CRC handbook of solubility parameters and other cohesion parameters, 2nd Edition, Routledge, Abingdon.

[113] Daniels, P. H., (2009). "A brief overview of theories of Pvc plasticization and methods used to evaluate PVC-plasticizer interaction", Journal of vinyl and additive technology, 15(4):219-223.

[114] Cramer, C. J., (2013). Essentials of computational chemistry: theories and models, 2nd Edition, Wiley, New Jersey.

[115] Rahman, M., and Brazel, C. S., (2004). "The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges", Progress in polymer science, 29(12):1223-1248.

[116] Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., and Beppu, M. M., (2011). "Natural-based plasticizers and biopolymer films: A review", European Polymer Journal, 47(3):254-263.

[117] Pionteck, J., Pionteck, J., and Wypych, G., (2007). Handbook of Antistatics, 2nd Edition, ChemTec Publishing, Ontario.

[118] Wiley-VCH., (2016). Ullmann's Polymers and Plastics, 4 Volume Set: Products and Processes Vol. 1, Wiley, New Jersey.

[119] Wadey, B. L., (2002). Plasticizers, Encyclopedia of Polymer Science and Technology.

[120] Daniels, P. H., (2009). "A brief overview of theories of Pvc plasticization and methods used to evaluate PVC-plasticizer interaction", Journal of vinyl and additive technology, 15(4):219-223.

[121] Wojciechowska, P., (2012). Recent advances in plasticizers: 8. The Effect of Concentration and Type of Plasticizer on the Mechanical Properties of Cellulose acetate Butyrate Organic-inorganic Hybrids, InTech, The Poznan University of Economics, Poznan.

[122] Barber, E. D., and Topping, D. C., (1995). "Subchronic 90-day oral toxicology of di (2-ethylhexyl) terephthalate in the rat", Food and chemical toxicology, 33(11):971-978.

[123] Darby, J. R., Touchette, N.W. and Sears, J.K., (1968). "Benefits and Problems of External Modifiers for Thermoplastic Polymers, 1. Plasticizers and Related Materials", SPE Vipag Newsletter, 4(4):39-50.

[124] Rahmah, M., Nurazzi, N. M., Nordyana, A. F., and Anas, S. S., (2017). "Effect of epoxidised soybean oil loading as plasticiser on physical, mechanical and thermal properties of polyvinylchloride". IOP Conference Series: Materials Science and Engineering, 223:1-12048, IOP Publishing, Bristol.

[125] Elias H. G., (2003). An Introduction To Plastics, 2nd Edition, WILEY-VCH Gmb, Weinheim.

[126] Mok, W. R., (2012). Effects Of Plasticiser Mixtures On Physical And Mechanical Properties Of Medical Grade Polyvinyl Chloride (Pvc), PhD Thesis, Universiti Tunku Abdul Rahman, Engineering and Science, Kampar.

[127] Rahman, M., and Brazel, C. S., (2004). "The plasticizer market: An assessment of traditional plasticzers and research trends to meet new challenges", Progress in Polymer Science, 29, 1223-1248.

[128] Gil, N., Saska, M., and Negulescu, I. (2006). “Evaluation of the effects of biobased plasticizers on the thermal and mechanical properties of poly (vinyl chloride)”, Journal of applied polymer science, 102(2):1366-1373.

[129] Krauskopf, L. G., (1988). Plasticizers: Types, properties, and performance, Marcel Dekker, Encyclopedia of Pvc., 2, 143-261.

[130] Wypych, G., (2004). Plasticizer types, Handbook of Plasticizers, 5-71, 1st Edition, ChemTec Publishing, Ontario.

[131] Wilkes, C. E., Summers, J. W., Daniels, C. A., Berard, M. T., (2005). PVC Handbook, Cincinnati.

[132] Renuka, M., Nishadh, P., Jigar, S., and Tejal, M. (2012). “Mucoadhesive wound healing film of doxycycline hydrochloride”, International Journal of Drug Development and Research, 4(3):128-140.

[133] Nagorka, R., Conrad, A., Scheller, C., Süßenbach, B., and Moriske, H. J., (2011). “Diisononyl 1, 2-cyclohexanedicarboxylic acid (Dinch) and Di (2-ethylhexyl) terephthalate (Deht) in indoor dust samples: concentration and analytical problems”, International journal of hygiene and environmental health, 214(1):26-35.

[134] Mok, W. R., (2012). Effects Of Plasticiser Mixtures On Physical And Mechanical Properties Of Medical Grade Polyvinyl Chloride (Pvc), PhD Thesis, Universiti Tunku Abdul Rahman, Engineering and Science, Kampar.

[135] Edenbaum, J., (1992). Plastics Additives And Modifiers Handbook, Van Nostrand Reinhold Company, New York.

APPENDIX-A

SPECTROSCOPY DATA

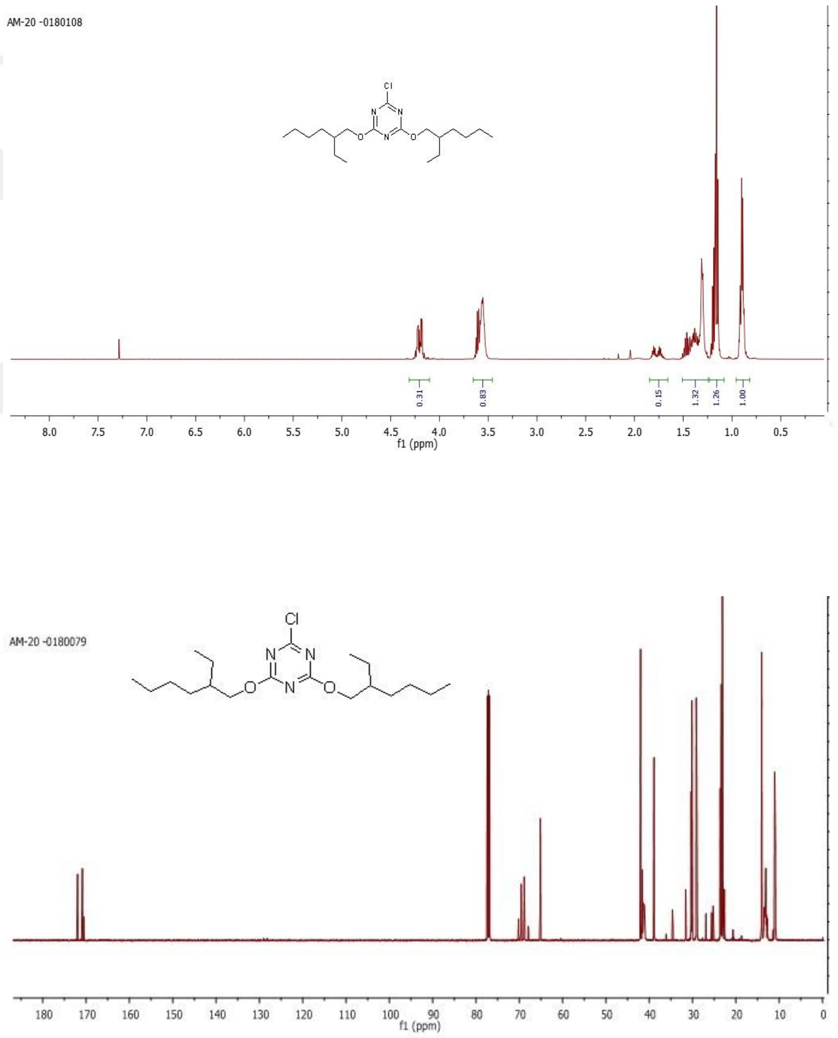
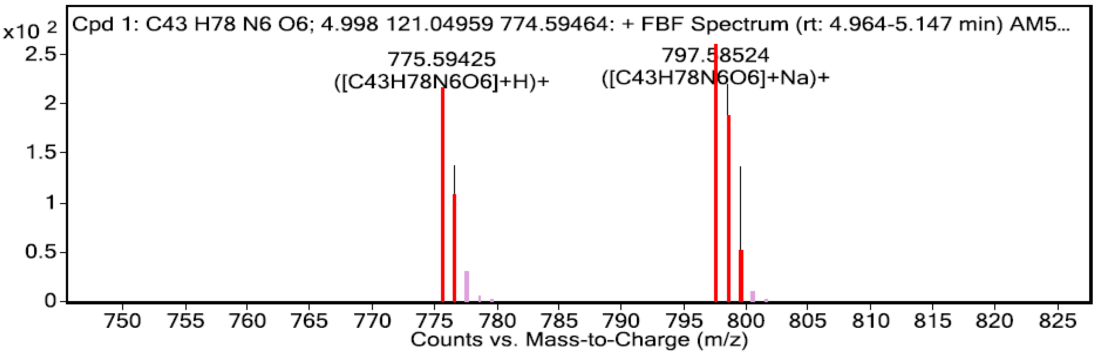
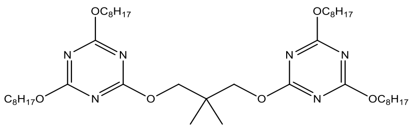


Figure A.1 Spectroscopy Date of Compound 11

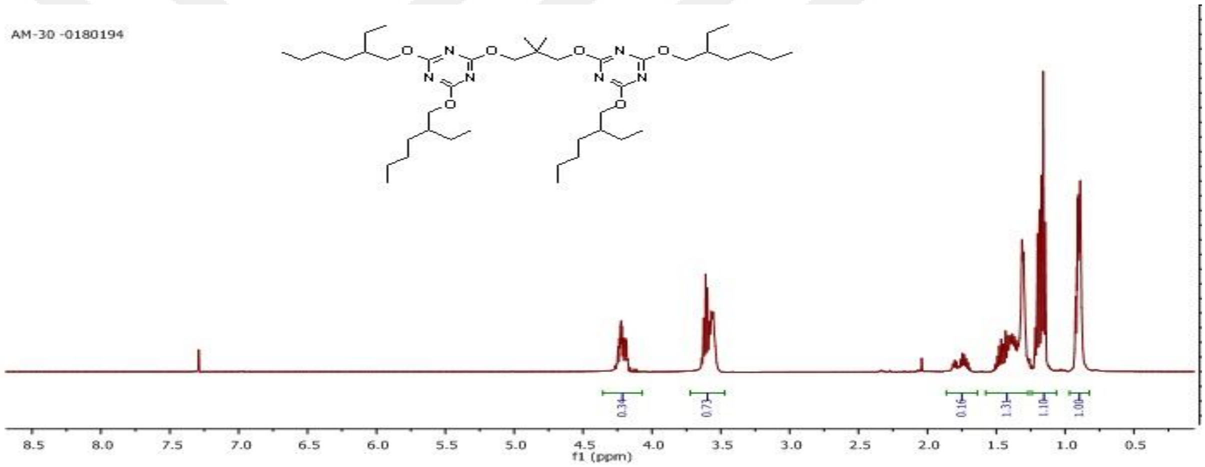


MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
775.59425	1	186.74	C43H78N6O6	(M+H)+
776.62045	1	137.84	C43H78N6O6	(M+H)+
797.58524	1	260.82	C43H78N6O6	(M+Na)+
798.57463	1	219.39	C43H78N6O6	(M+Na)+
799.60217	1	136.13	C43H78N6O6	(M+Na)+



Chemical Formula: $C_{43}H_{78}N_6O_6$
Molecular Weight: 775.12



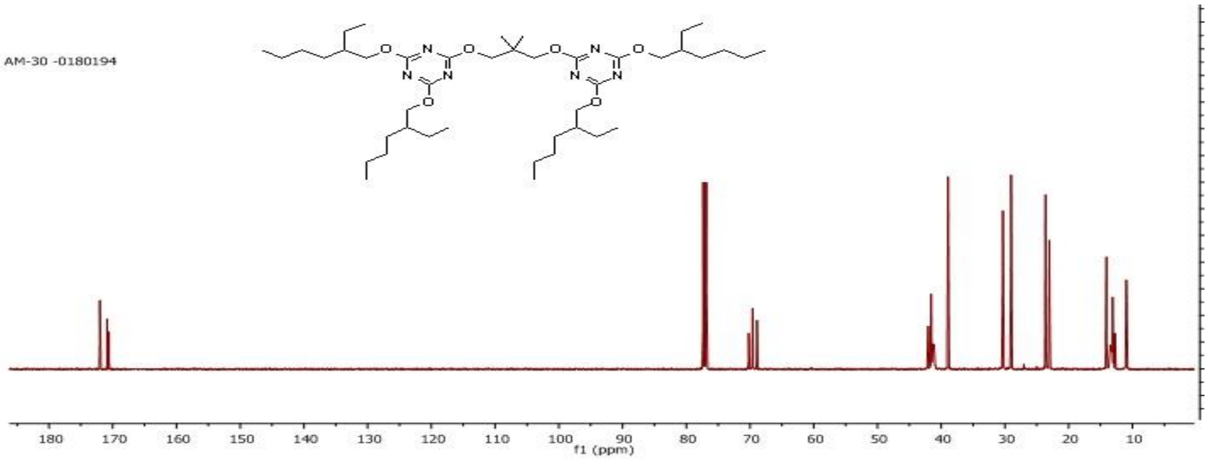
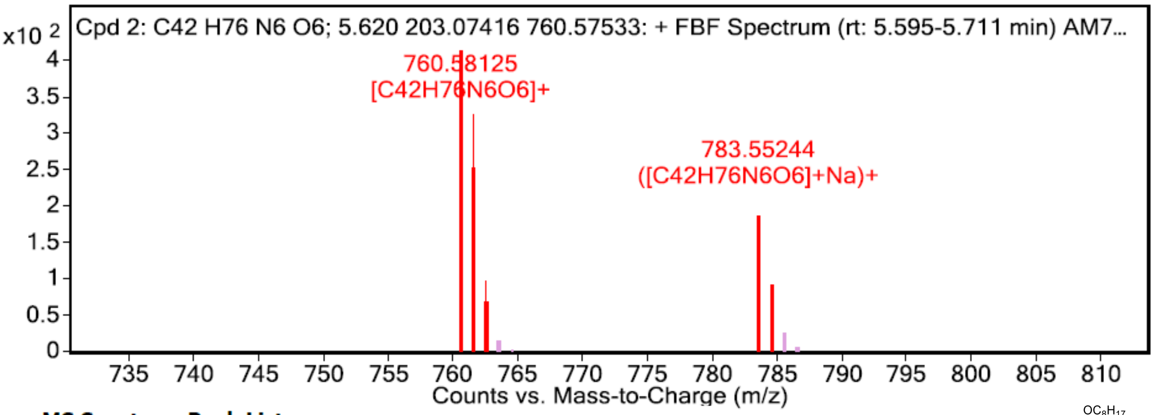
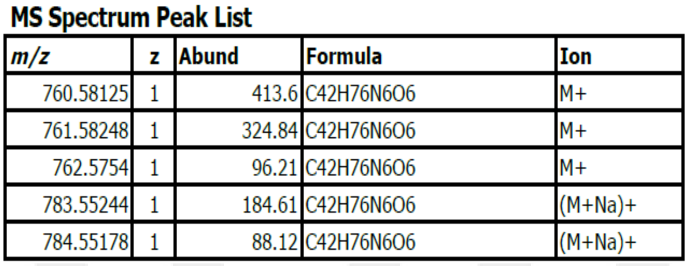


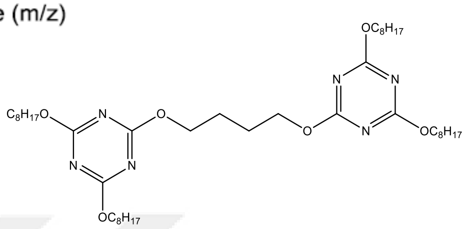
Figure A.2 Spectroscopy Date of Compound 1



MS Spectrum Peak List



m/z	z	Abund	Formula	Ion
760.58125	1	413.6	C42H76N6O6	M+
761.58248	1	324.84	C42H76N6O6	M+
762.5754	1	96.21	C42H76N6O6	M+
783.55244	1	184.61	C42H76N6O6	(M+Na)+
784.55178	1	88.12	C42H76N6O6	(M+Na)+



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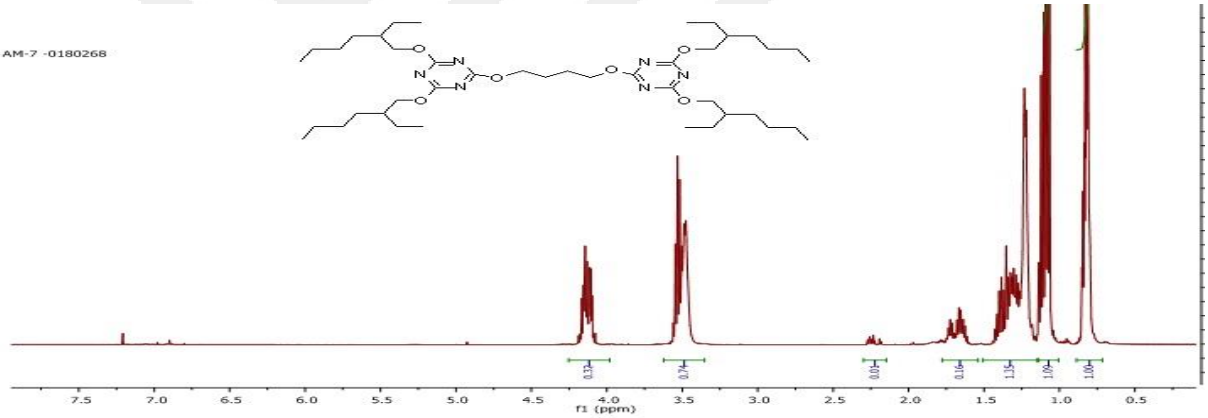


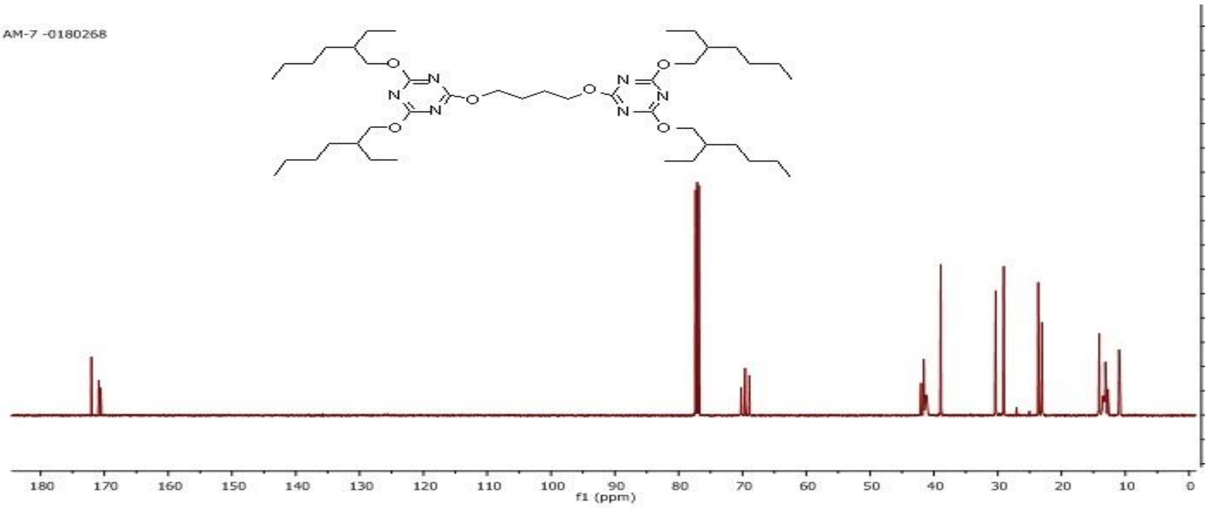
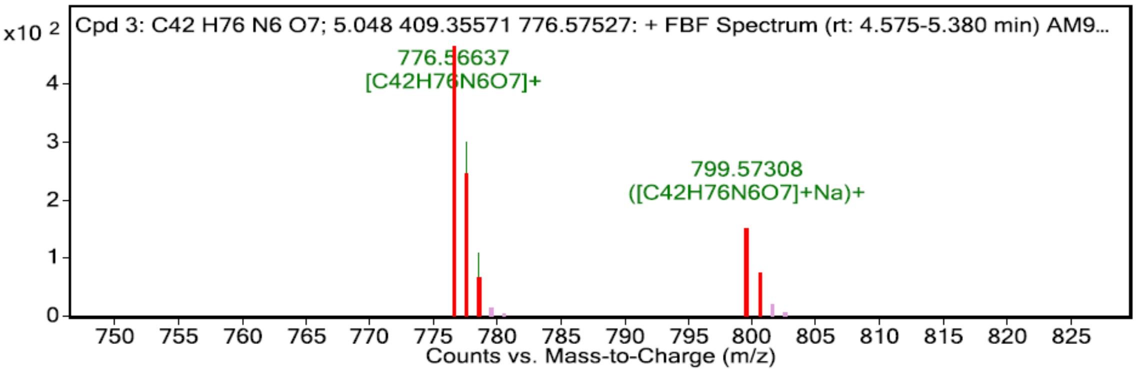
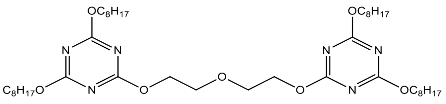


Figure A.3 Spectroscopy Date of Compound 2



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
776.56637	1	407.48	C42H76N6O7	M+
777.5924	1	298.61	C42H76N6O7	M+
778.55121	1	107.91	C42H76N6O7	M+
799.57308	1	148.45	C42H76N6O7	(M+Na)+
800.58572	1	53.63	C42H76N6O7	(M+Na)+



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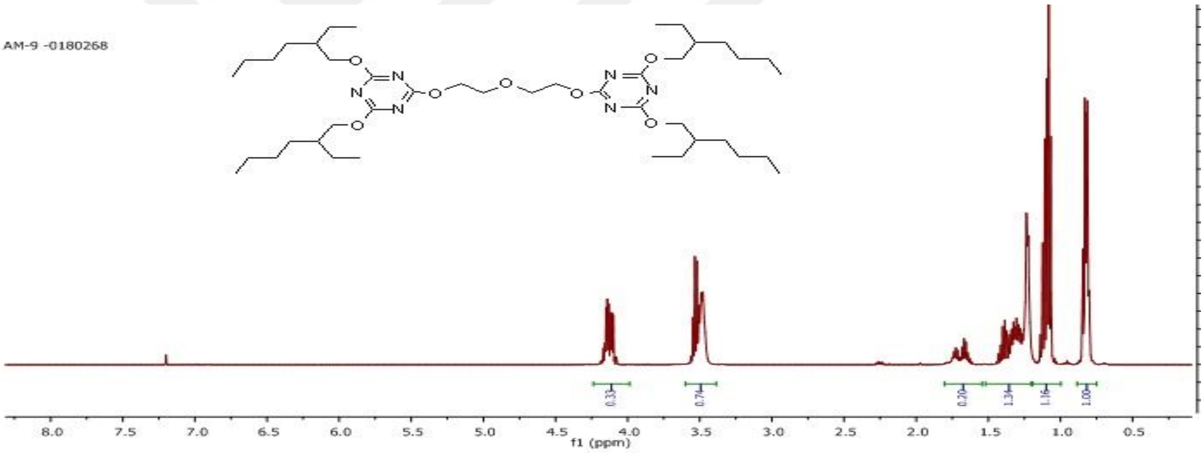
Molecular Weight: 777.09



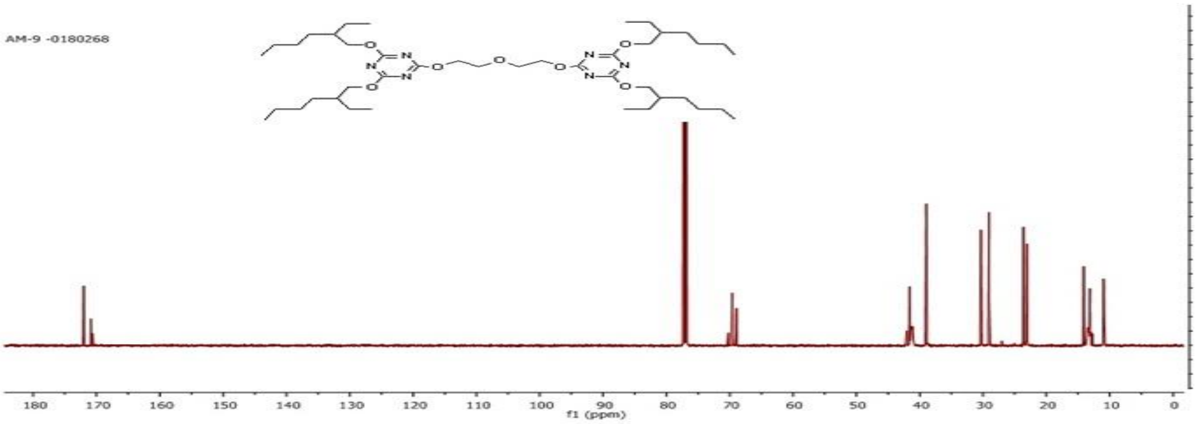
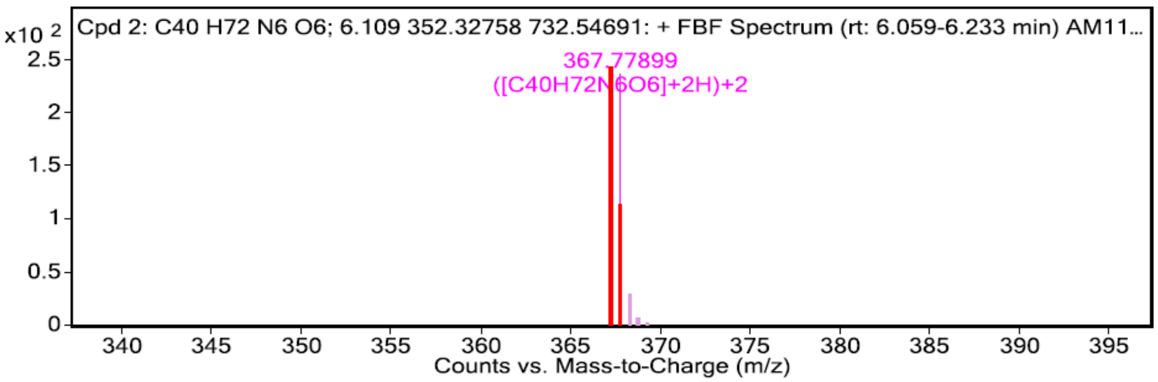
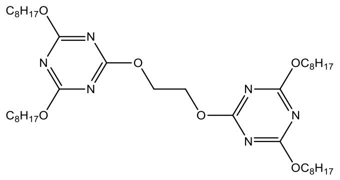


Figure A.4 Spectroscopy Date of Compound 3

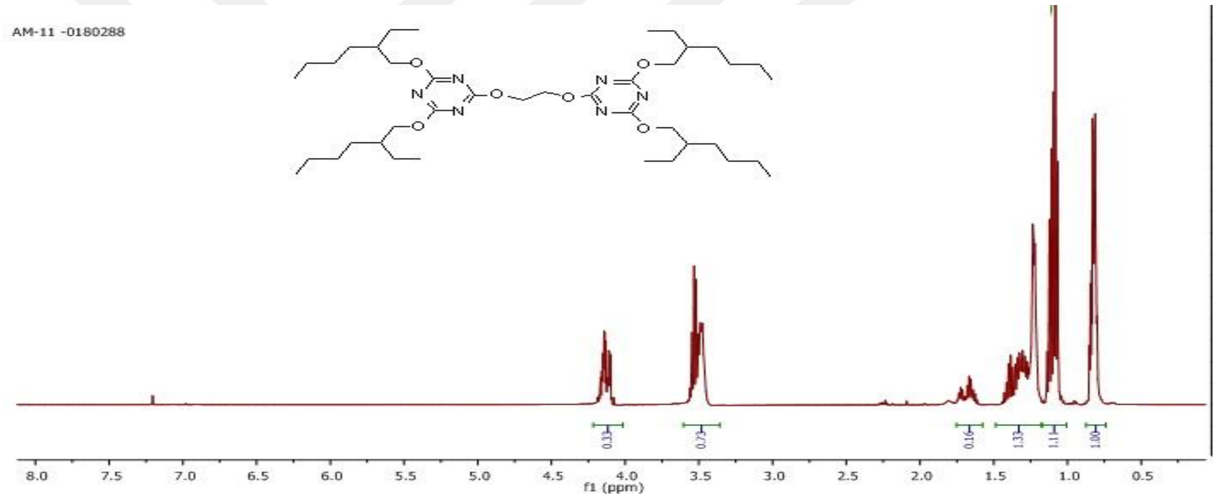


MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
367.28721	2	120.2	C40H72N6O6	(M+2H)+2
367.77899	2	236.21	C40H72N6O6	(M+2H)+2



Chemical Formula: $C_{40}H_{72}N_6O_6$
Molecular Weight: 733.04



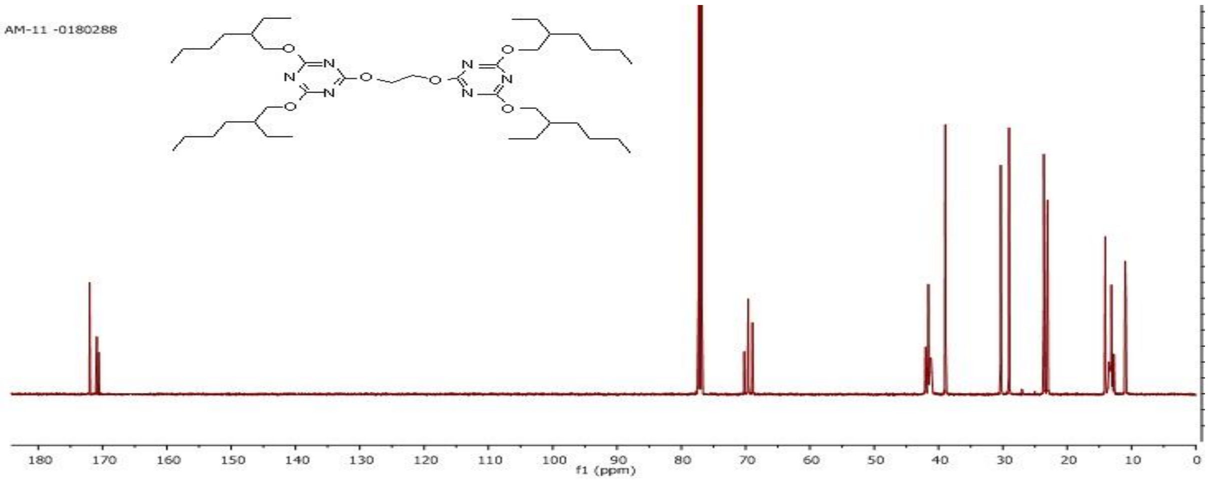
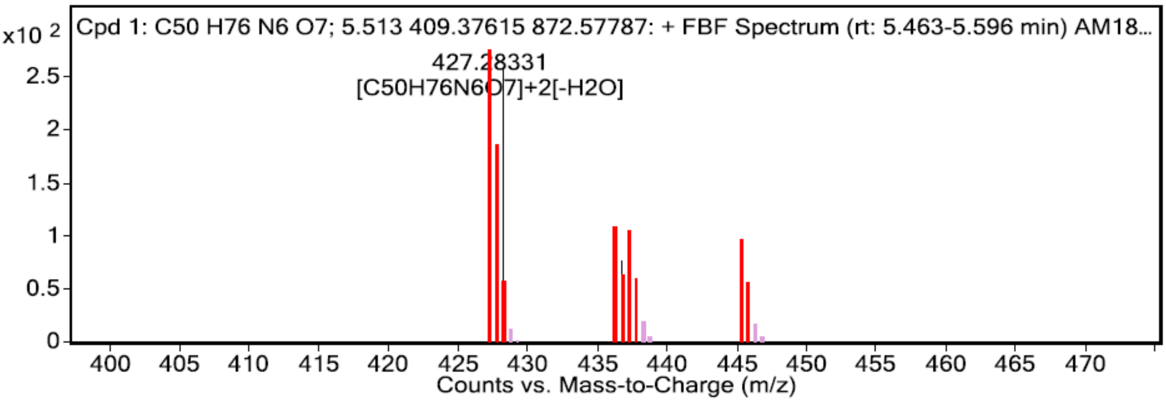
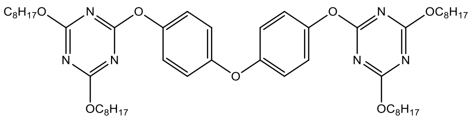


Figure A.5 Spectroscopy Date of Compound 4

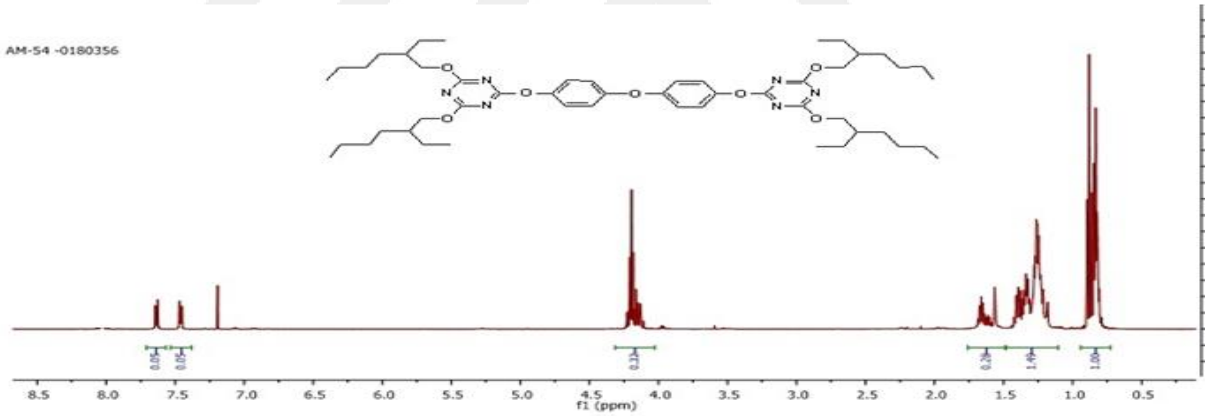


MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
427.28331	2	276.14	C50H76N6O7	M+2[-H2O]
427.79752	2	35.82	C50H76N6O7	M+2[-H2O]
428.27623	2	257.61	C50H76N6O7	M+2[-H2O]
436.28612	2	95.07	C50H76N6O7	M+2
436.78801	2	75.8	C50H76N6O7	M+2
437.29439	2	103.64	C50H76N6O7	(M+2H)+2
437.80855	2	50.27	C50H76N6O7	(M+2H)+2
445.3285	2	94.82	C50H76N6O7	(M+2(NH4))+2[-H2O]
445.84135	2	45.38	C50H76N6O7	(M+2(NH4))+2[-H2O]



Chemical Formula: $C_{50}H_{76}N_6O_7$
Molecular Weight: 873.17



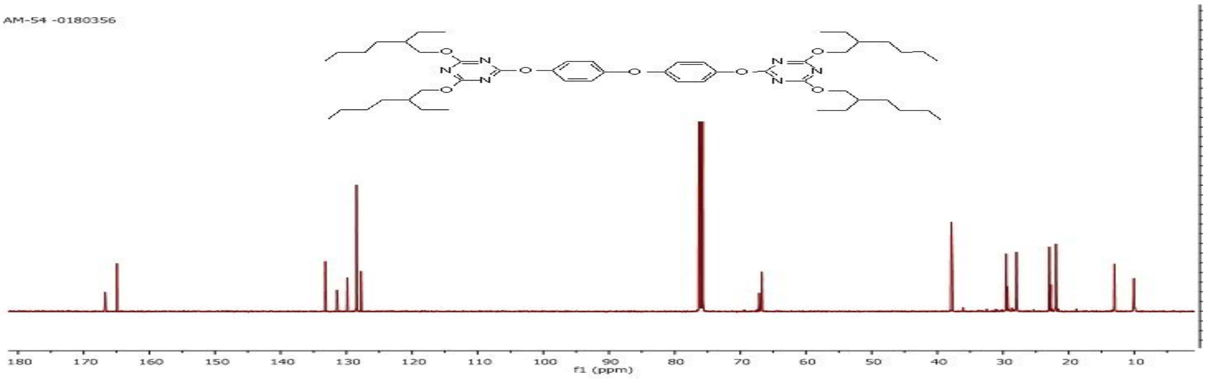
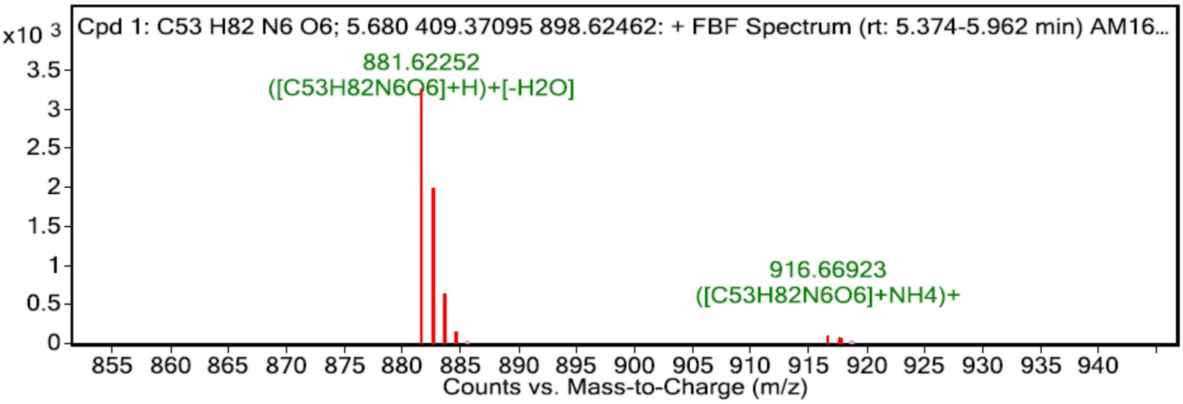
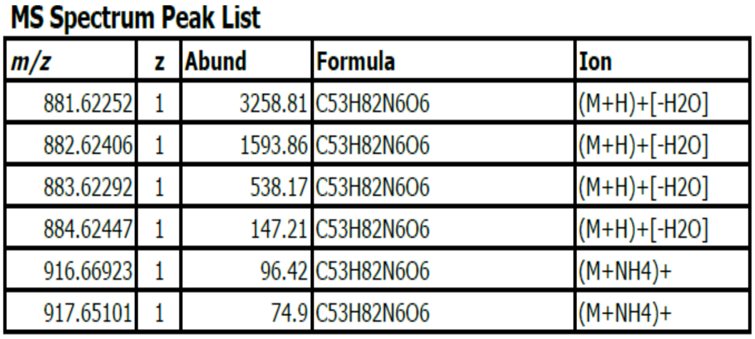


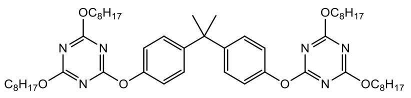
Figure A.6 Spectroscopy Date of Compound 5



MS Spectrum Peak List



m/z	z	Abund	Formula	Ion
881.62252	1	3258.81	C53H82N6O6	(M+H)+[-H2O]
882.62406	1	1593.86	C53H82N6O6	(M+H)+[-H2O]
883.62292	1	538.17	C53H82N6O6	(M+H)+[-H2O]
884.62447	1	147.21	C53H82N6O6	(M+H)+[-H2O]
916.66923	1	96.42	C53H82N6O6	(M+NH4)+
917.65101	1	74.9	C53H82N6O6	(M+NH4)+



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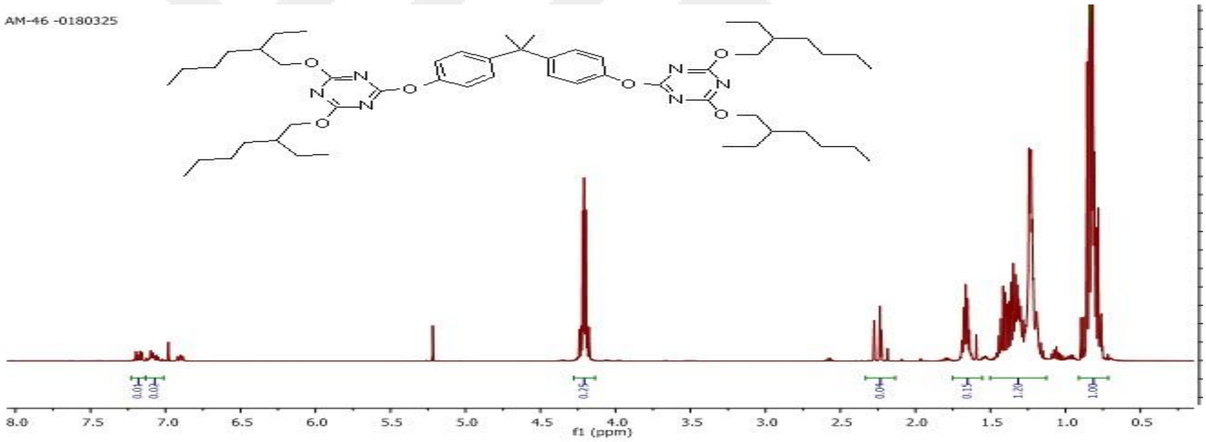

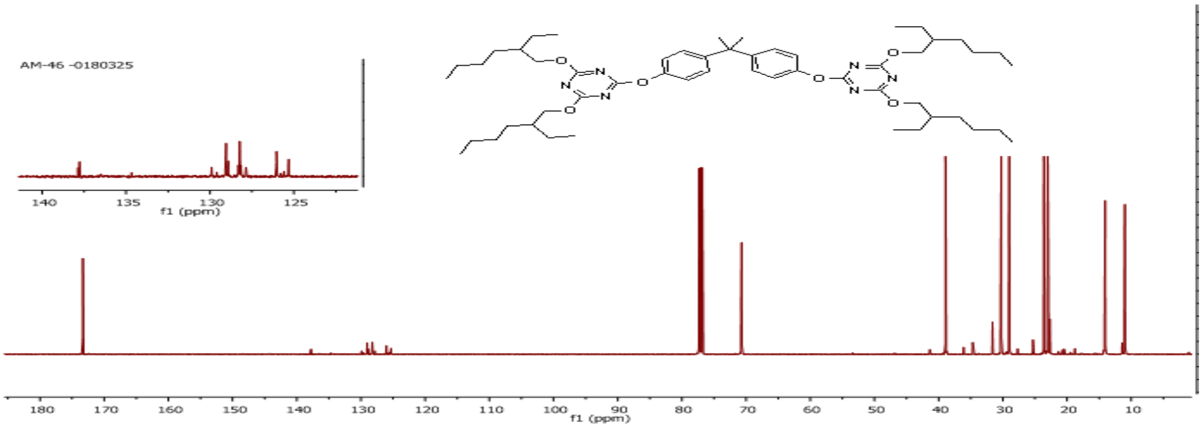

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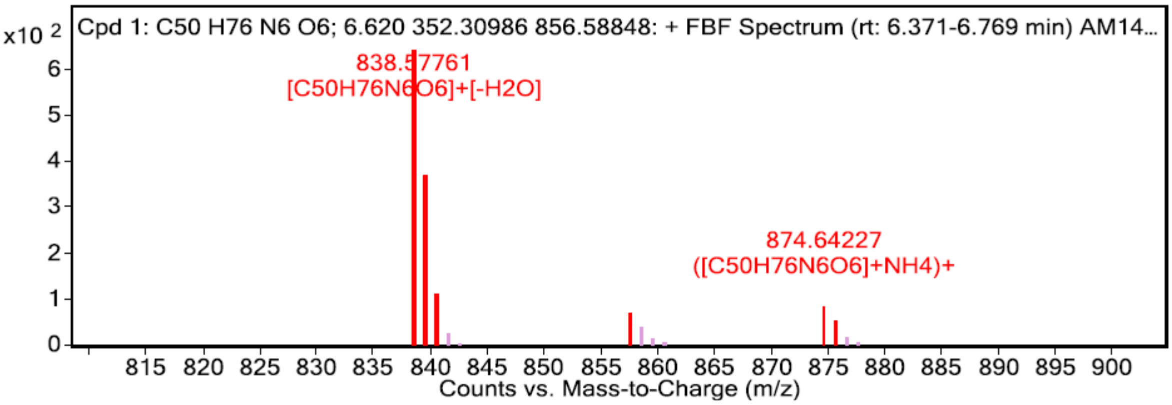

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
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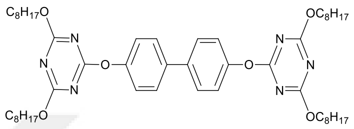
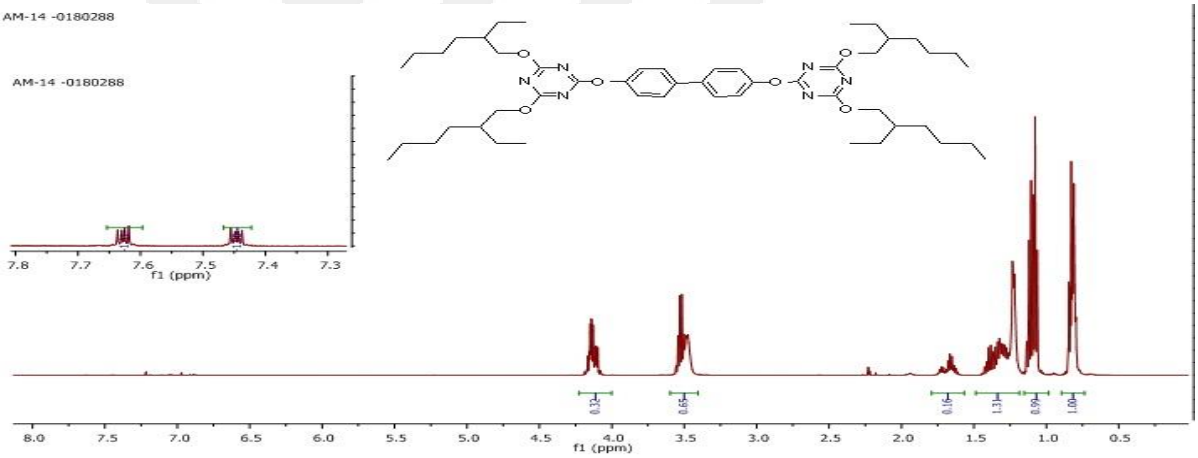
839.57778	1	263.62	C50H76N6O6	M+[-H2O]
840.57335	1	63.2	C50H76N6O6	M+[-H2O]
857.57472	1	68.85	C50H76N6O6	(M+H)+
874.64227	1	83.86	C50H76N6O6	(M+NH4)+
875.6563	1	31.94	C50H76N6O6	(M+NH4)+



Chemical Formula: C50H76N6O6
Molecular Weight: 857.18



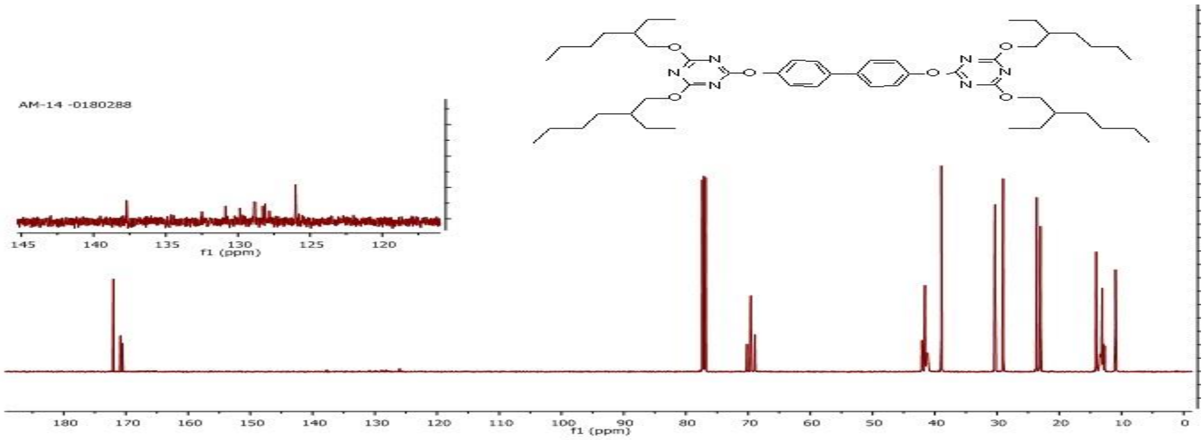
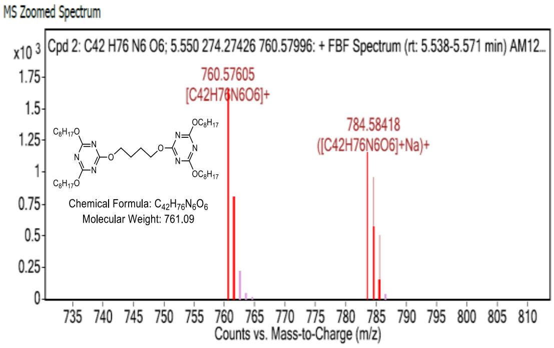
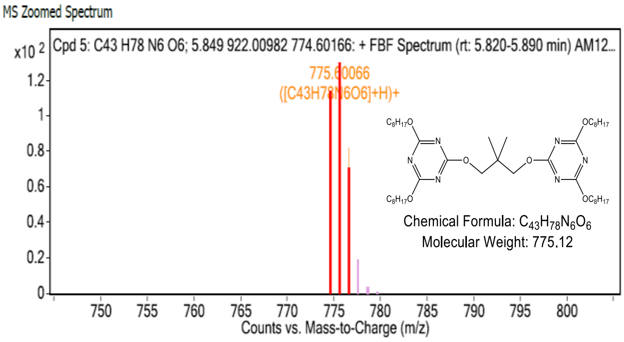
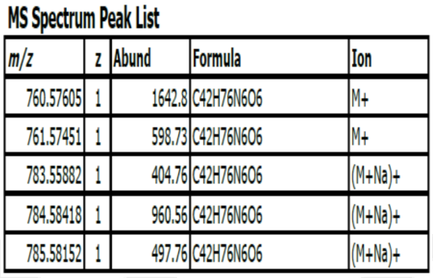


Figure A.8 Spectroscopy Date of Compound 7

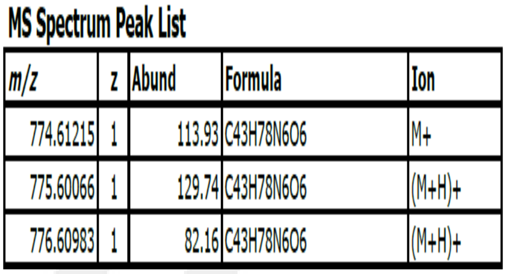






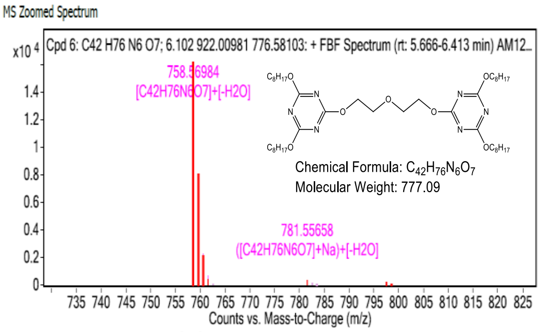
MS Spectrum Peak List

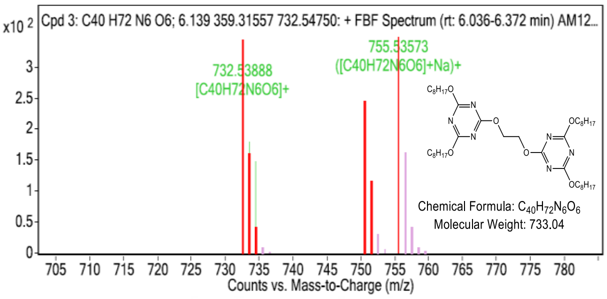
m/z	z	Abund	Formula	Ion
760.57605	1	1642.8	C42H76N6O6	M+
761.57451	1	598.73	C42H76N6O6	M+
783.55882	1	404.76	C42H76N6O6	(M+Na)+
784.58418	1	960.56	C42H76N6O6	(M+Na)+
785.58152	1	497.76	C42H76N6O6	(M+Na)+

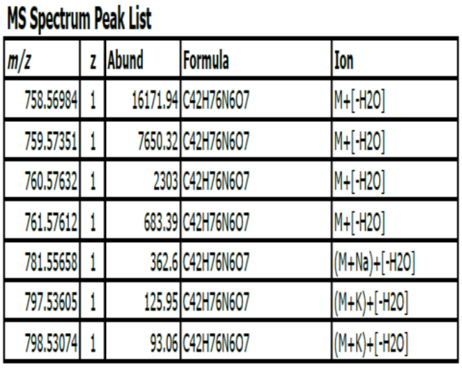


MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
774.61215	1	113.93	C43H78N6O6	M+
775.60066	1	129.74	C43H78N6O6	(M+H)+
776.60983	1	82.16	C43H78N6O6	(M+H)+

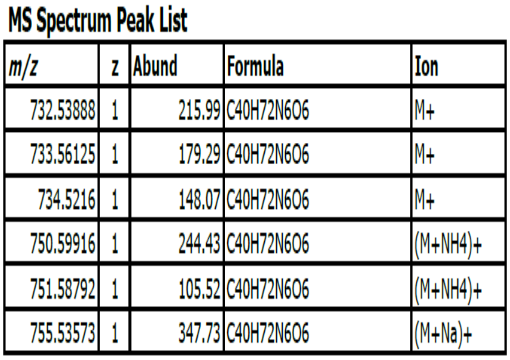






MS Spectrum Peak List

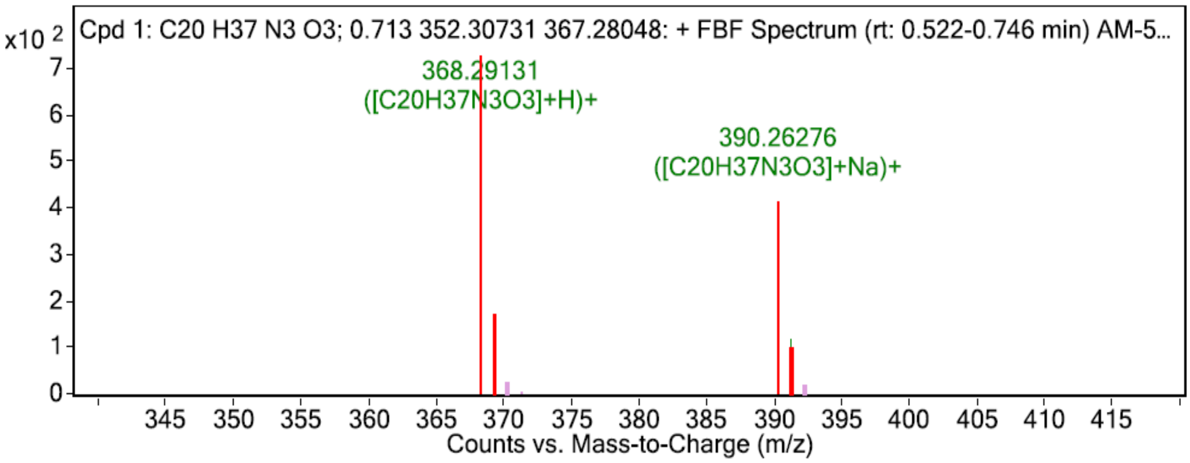
m/z	z	Abund	Formula	Ion
758.56984	1	16171.94	C42H76N6O7	M+[-H2O]
759.57351	1	7650.32	C42H76N6O7	M+[-H2O]
760.57632	1	2303	C42H76N6O7	M+[-H2O]
761.57612	1	683.39	C42H76N6O7	M+[-H2O]
781.55658	1	362.6	C42H76N6O7	(M+Na)+[-H2O]
797.53605	1	125.95	C42H76N6O7	(M+K)+[-H2O]
798.53074	1	93.06	C42H76N6O7	(M+K)+[-H2O]



MS Spectrum Peak List

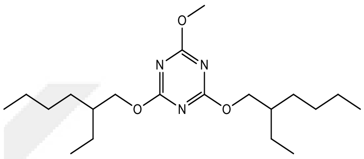
m/z	z	Abund	Formula	Ion
732.53888	1	215.99	C40H72N6O6	M+
733.56125	1	179.29	C40H72N6O6	M+
734.5216	1	148.07	C40H72N6O6	M+
750.59916	1	244.43	C40H72N6O6	(M+NH4)+
751.58792	1	105.52	C40H72N6O6	(M+NH4)+
755.53573	1	347.73	C40H72N6O6	(M+Na)+

Figure A.9 QTOF Spectra of Mixture of Compounds 8



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
368.29131	1	725.57	C20H37N3O3	(M+H)+
369.2904	1	123.83	C20H37N3O3	(M+H)+
390.26276	1	387.31	C20H37N3O3	(M+Na)+
391.27422	1	118.08	C20H37N3O3	(M+Na)+



Chemical Formula: $C_{20}H_{37}N_3O_3$
Molecular Weight: 367.53

Figure A.10 QTOF Spectra of Compound 10

CURRICULUM VITAE

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EDUCATION

Degree	Department	University	Date of Graduation
Undergraduate	Chemistry	Baghdad University	2003
High School	Scientific part	AL-Mutasim	1996

WORK EXPERIENCE

Year	Corporation/Institute	Enrollment
1999	Ministry of Science and Technology	19.04.1999

PUBLISHMENTS

Conference Papers

1. AL-Obaidi A(2018). "Synthesis and Properties of Banana-Shaped and Six-Armed Macromolecular Structures", International Conference on Paint and Coatings Industry, 19-21 March 2018.