

**SYNTHESIS OF PHOTOACTIVE URETHANE ACRYLATES**

**M.Sc. Thesis by  
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## ABBREVIATIONS

<b>PU</b>	: Polyurethane
<b>IPDI</b>	: Isophorone diisocyanate
<b>PEG</b>	: Polyethyleneglycol
<b>BDO</b>	: 1,4- butanediol
<b>HDI</b>	: Hexamethylene diisocyanate
<b>MDI</b>	: Methylene diphenyl diisocyanate
<b>TDI</b>	: Toluene diisocyanate
<b>RIM</b>	: Reaction Injection molding
<b>VOC</b>	: Volatile organic compounds
<b>HEMA</b>	: 2-Hydroxy ethyl methacrylate
<b>UV</b>	: Ultra Violet
<b>NMR</b>	: Nuclear Magnetic Resonance
<b>TGA</b>	: Thermal Gravimetical Analysis
<b>FT-IR</b>	: Fourier Transform Infrared
<b>DPGDA</b>	: Dipropyleneglycoldiacrylate
<b>DBTL</b>	: Dibutyl Tinlaurate
<b>HDDA</b>	: 1,6-hexanedioldiacrylate
<b>UAC</b>	: Chalcone modified urethane acrylate



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## SYNTHESIS OF PHOTOACTIVE URETHANE ACRYLATES

### SUMMARY

UV-curing technology is well accepted for the fast curing of polymeric materials, and it has been widely used in coatings, adhesives, inks, printing plates, and microelectronics because of its fast cure response, economical energy consumption and low contribution to environmental pollution. UV curable coatings have gained more and more attention and are expected to substitute the conventional solvent-based coatings, because of their superior properties and processing advantages such as excellent chemical resistance, solvent-free technology, ultrafast polymerization, and good weathering characteristics. Among the oligomers used for UV-curable coatings, polyurethane acrylate (PUA) oligomers have gained more and more attention and speedy development due to a wide range of excellent application properties, such as high impact and tensile strength, abrasion resistance and toughness combined with excellent resistance to chemicals and solvents. On the other hand, photosensitive polymers with photocrosslinkable groups have gained a considerable interest in recent years owing to a wide variety of applications in the field of macro- and microlithography, printing, liquid crystalline display, nonlinear optical materials, holographic head-up-display, integrated circuit technology, photocurable coatings, photoconductors, energy exchange materials, etc. UV radiation curing has been revealed as a powerful tool to crosslink rapidly the heat sensitive polymers and modifies, selectively in the illuminated areas, their physico-chemical characteristics. Among the various photocrosslinkable groups,  $\alpha,\beta$ -unsaturated carbonyl unit has attracted particular attention due to its excellent photoreactivity at UV absorption wavelength. Crosslinking with ultraviolet light is an excellent method for obtaining articles with thick cross-sections, with or without reinforcement, without significant heat buildup in the interior, which could damage the plastic. Polymers with chalcone or cinnamoyl group either in the backbone or side chain undergo crosslinking through  $[2\pi + 2\pi]$  cycloaddition of the carbon-carbon double bond upon irradiation with UV light and such polymers are regarded as negative-type photoresists. These polymers with the properties of high photosensitivity, the ability to form films, good solubility before irradiation, resistance towards solvents, plasmas and etching agents after crosslinking and good thermal stability are very important for commercial photoresist applications.

In this work, UV curable chalcone modified urethane acrylates (UA-C) containing isophorone diisocyanate and polyethyleneglycol segments were synthesized and employed in UV curable formulations. Crosslinking behaviour and film properties were investigated.



## FOTOAKTİF ÜRETAN AKRİLAT SENTEZİ

### ÖZET

UV ışınları ile kütleme teknolojisi, hızlı kütleme duyarlılığı, ekonomik enerji tüketimi ve çevre kirliliğine duyarlılığı sayesinde polimerik maddelerin kürlenmesinde kabul görmüş olup, kaplamalarda, mürekkeplerde, baskı plakalarında ve mikroelektronik endüstrisinde yaygın olarak kullanılmaktadır. UV ışınları ile kürlenebilen kaplamalar ise, üstün özellikleri ve mükemmel kimyasal dayanım, çözücüsüz teknoloji, çok hızlı polimerleşme ve iyi yaşlanma özellikleri gibi uygulama avantajlarından dolayı dikkati çekmiş ve gelecekte geleneksel çözücü bazlı kaplamaların yerini almaları öngörülmektedir. UV ışınları ile kürlenebilen kaplamalar için kullanılan oligomerler arasında, yüksek darbe ve gerilme kuvveti, aşınma dayanımı, kimyasallara ve çözücülere dayanımla birlikte tokluk gibi geniş yelpazedeki mükemmel uygulama özelliklerinden dolayı polüretan akrilat oligomerler daha çok ilgi çekmiş ve hızlı gelişme sağlamıştır. Diğer taraftan, ışık etkisi ile çapraz bağ yapabilen gruplar taşıyan ışığa duyarlı polimerler, makro ve mikro ölçekte taşbaskı, matbaacılık, sıvı kristal görüntüleme, doğrusal olmayan optik malzemeler, hologramlı görüntüleme sistemleri, birleşik devre teknolojisi, ışık etkisi ile kürlenebilen kaplamalar, ışık iletkenleri, enerji değiştirme malzemeleri gibi geniş çeşitliliğe sahip alanlardan dolayı son yıllarda dikkate değer ilgi toplamıştır. UV ışını ile kütleme, ısıya duyarlı polimerleri hızla çaprazbağ yapmak, onların fizikokimyasal özelliklerini değiştirmek için güçlü bir araç olarak ortaya çıkmıştır. Çeşitli ışık ile polimerleşebilen gruplar arasında  $\alpha,\beta$ -doymamış karbonil fonksiyonallitesi, UV absorpsiyon dalgaboyunda mükemmel fotoreaktivite gösterdiğinden dolayı dikkat çekmiştir. UV ışığı ile çapraz bağlanma, plastiğe zarar verebilecek belirgin bir iç ısınma olmaksızın, takviyeli veya takviyesiz biçimde kalın kesit alanına sahip malzemeleri elde etmek için mükemmel bir yoldur. Omurgasında veya yan zincirinde kalgon veya sinnamoil grubu olan polimerler, UV ışığı ile uyarıldıklarında karbon-karbon çift bağının siklo katılma reaksiyonu ile çapraz bağ yaparlar ve bu polimerlere negatif tipte fotorezistler denir. Bu tür polimerlerin yüksek fotoduyarlılık, film oluşturma yeteneği, uyarılmadan önce iyi çözünme, çapraz bağlandıktan sonra çözücülere, plazmalara ve aşındırıcı ajanlara karşı direnç gösterme ve yüksek ısıl kararlılık gösterme gibi özellikleri ticari fotorezist uygulamaları için büyük önem arzetmektedir.

Bu çalışmada, kalgon modifiyeli, isoforondiizosiyanat ve polietilenglikol segmentleri içeren ve UV ışını ile kürlenebilen üretan akrilatlar sentezlenip UV ışını ile kürlenebilen formülasyona uygulanıp çapraz bağlanma ve film özellikleri araştırılmıştır.







## 1. INTRODUCTION

Because of their excellent property profile, polyisocyanate resins and polyurethanes (PU) have special significance as binders for the formulation of coatings. Since their technical value was first recognized by the coatings industry in the 1950s, their development has been dramatic. Originally, the term polyurethane was used to describe only those coating systems which exploited the high reactivity of isocyanates in their chemical curing process. However, it has now become accepted to apply the term to a large number of different coating resins. Their common characteristic is that monomeric diisocyanates or homologues are incorporated as building blocks in their formation by polyaddition. The resulting products have a high molecular weight and may contain reactive isocyanate groups which are capable of further reaction. A particular characteristic of polyurethanes is that both the raw material manufacturer and, to a large extent, the paint formulator can customize the coating systems through the selection of the components. The building block principle makes it possible to produce coatings with an unparalleled range of properties. This is reflected in the extraordinarily wide range of applications for these coating systems, covering virtually every segment of industrial and non-industrial coating[1-5].

This thesis will concern the preparation of novel urethane acrylates prepared by the reaction of isophorone diisocyanate with polyethyleneglycol and 4,4'-dihydroxychalcone at different modification ratios. Resulting polymers, containing photoactive chalcone units in the main chain, are crosslinked by photo polymerization at the second stage and effect of chalcone moieties on crosslinking and coating performance was examined by analysis of various properties such as hardness, gloss, and stress-strain test. The thermal behaviour of coatings is also evaluated.



## **2. THEORETICAL PART**

### **2.1 Overview of Polyurethanes**

#### **2.1.1 Introduction**

The pioneering work on polyurethane polymers was conducted by Otto Bayer and his coworkers in 1937 at the laboratories of I.G. Farben in Leverkusen, Germany [6]. They recognized that using the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols seemed to point to special opportunities, especially when compared to already existing plastics that were made by polymerizing olefins, or by polycondensation. The new monomer combination also circumvented existing patents obtained by Wallace Carothers on polyesters [7]. Initially, work focused on the production of fibres and flexible foams. With development constrained by World War II (when PUs were applied on a limited scale as aircraft coating), it was not until 1952 that polyisocyanates became commercially available. Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams (initially called imitation swiss cheese by the inventors) was thanks to water accidentally introduced in the reaction mix. These materials were also used to produce rigid foams, gum rubber, and elastomers. Linear fibres were produced from hexamethylene diisocyanate (HDI) and 1,4-butanediol (BDO) [7]. The first commercially available polyether polyol, poly(tetramethylene ether) glycol, was introduced by DuPont in 1956 by polymerizing tetrahydrofuran. Less expensive polyalkylene glycols were introduced by BASF and Dow Chemical the following year, 1957. These polyether polyols offered technical and commercial advantages such as low cost, ease of handling, and better hydrolytic stability; and quickly supplanted polyester polyols in the manufacture of polyurethane goods. Other PU pioneers were Union Carbide and the Mobay corporation, a U.S. Monsanto/Bayer joint venture [7]. In 1960 more than 45,000 tons of flexible polyurethane foams were

produced. As the decade progressed, the availability of chlorofluoroalkane blowing agents, inexpensive polyether polyols, and methylene diphenyl diisocyanate (MDI) heralded the development and use of polyurethane rigid foams as high performance insulation materials. Rigid foams based on polymeric MDI (PMDI) offered better thermal stability and combustion characteristics than those based on TDI. In 1967, urethane modified polyisocyanurate rigid foams were introduced, offering even better thermal stability and flammability resistance to low-density insulation products. Also during the 1960s, automotive interior safety components such as instrument and door panels were produced by back-filling thermoplastic skins with semi-rigid foam. In 1969, Bayer AG exhibited an all plastic car in Düsseldorf, Germany. Parts of this car were manufactured using a new process called RIM, Reaction Injection Molding. RIM technology uses high-pressure impingement of liquid components followed by the rapid flow of the reaction mixture into a mold cavity. Large parts, such as automotive fascia and body panels, can be molded in this manner. Polyurethane RIM evolved into a number of different products and processes. Using diamine chain extenders and trimerization technology gave poly(urethane urea), poly(urethane isocyanurate), and polyurea RIM. The addition of fillers, such as milled glass, mica, and processed mineral fibres gave rise to RRIM, reinforced RIM, which provided improvements in flexural modulus (stiffness) and thermal stability. This technology allowed production of the first plastic-body automobile in the United States, the Pontiac Fiero, in 1983. Further improvements in flexural modulus were obtained by incorporating preplaced glass mats into the RIM mold cavity, also known as SRIM, or structural RIM. Starting in the early 1980s, water-blown microcellular flexible foam was used to mold gaskets for panel and radial seal air filters in the automotive industry. Since then, increasing energy prices and the desire to eliminate PVC plastisol from automotive applications have greatly increased market share. Costlier raw materials are offset by a significant decrease in part weight and in some cases, the elimination of metal end caps and filter housings. Highly filled polyurethane elastomers, and more recently unfilled polyurethane foams are now used in high-temperature oil filter applications. Polyurethane foam (including foam rubber) is often made by adding small amounts of volatile materials, so-called blowing agents, to the reaction mixture. These simple volatile chemicals yield important performance characteristics, primarily thermal insulation. In the early 1990s, because of their impact on ozone depletion, the Montreal Protocol led to the greatly reduced use of

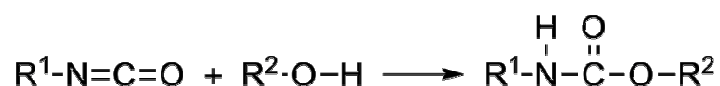
many chlorine-containing blowing agents, such as trichlorofluoromethane (CFC-11). Other haloalkanes, such as the hydrochlorofluorocarbon 1,1-dichloro-1-fluoroethane (HCFC-141b), were used as interim replacements until their phase out under the IPPC directive on greenhouse gases in 1994 and by the Volatile Organic Compounds (VOC) directive of the EU in 1997 (See: Haloalkanes). By the late 1990s, the use of blowing agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) became more widespread in North America and the EU, although chlorinated blowing agents remained in use in many developing countries[8]. Building on existing polyurethane spray coating technology and polyetheramine chemistry, extensive development of two-component polyurea spray elastomers took place in the 1990s. Their fast reactivity and relative insensitivity to moisture make them useful coatings for large surface area projects, such as secondary containment, manhole and tunnel coatings, and tank liners. Excellent adhesion to concrete and steel is obtained with the proper primer and surface treatment. During the same period, new two-component polyurethane and hybrid polyurethane-polyurea elastomer technology was used to enter the marketplace of spray-in-place load bed liners. This technique for coating pickup truck beds and other cargo bays creates a durable, abrasion resistant composite with the metal substrate, and eliminates corrosion and brittleness associated with drop-in thermoplastic bed liners. The potential for polyols derived from vegetable oils to replace petrochemical-based polyols began garnering attention beginning around 2004, partly due to the rising costs of petrochemical feedstocks and partially due to an enhanced public desire for environmentally friendly green products [9]. One of the most vocal supporters of these polyurethanes made using natural oil polyols is the Ford Motor Company [10].

### **2.1.2 Isocyanates**

Isocyanate is the functional group of atoms  $\text{-N=C=O}$  (1 nitrogen, 1 carbon, 1 oxygen), not to be confused with the cyanate functional group which is arranged as  $\text{-O-C}\equiv\text{N}$  or with isocyanide,  $\text{R-N}\equiv\text{C}$ . Any organic compound which contains an isocyanate group may also be referred to in brief as an isocyanate. An isocyanate may have more than one isocyanate group. An isocyanate that has two isocyanate groups is known as a diisocyanate. Diisocyanates are manufactured for reaction with polyols in the production of polyurethanes.

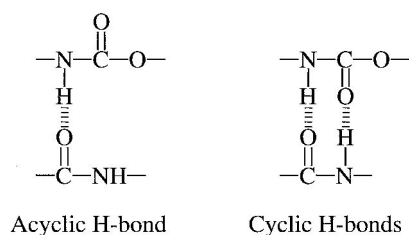
### 2.1.2.1 Synthesis of polyurethanes

Polyurethanes are in the class of compounds called reaction polymers, which include epoxies, unsaturated polyesters, and phenolics [11-15]. A urethane linkage is produced by reacting an isocyanate group,  $-N=C=O$  with a hydroxyl (alcohol) group,  $-OH$ . Polyurethanes are produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol) in the presence of a catalyst and other additives. In this case, a polyisocyanate is a molecule with two or more isocyanate functional groups,  $R-(N=C=O)_n$   $n \geq 2$  and a polyol is a molecule with two or more hydroxyl functional groups,  $R'-(OH)_n$   $n \geq 2$ . The reaction product is a polymer containing the urethane linkage,  $-RNHCOOR'$ . Isocyanates will react with any molecule that contains an active hydrogen. Importantly, isocyanates react with water to form a urea linkage and carbon dioxide gas; they also react with polyetheramines to form polyureas. Commercially, polyurethanes are produced by reacting a liquid isocyanate with a liquid blend of polyols, catalyst, and other additives. These two components are referred to as a polyurethane system, or simply a system. The isocyanate is commonly referred to in North America as the 'A-side' or just the 'iso'. The blend of polyols and other additives is commonly referred to as the 'B-side' or as the 'poly'. This mixture might also be called a 'resin' or 'resin blend'. In Europe the meanings for 'A-side' and 'B-side' are reversed. Resin blend additives may include chain extenders, cross linkers, surfactants, flame retardants, blowing agents, pigments, and fillers.



**Figure 2.1:** Method for synthesis of epoxy rings

Urethane groups form intermolecular hydrogen bonds between polymer molecules; they may be acyclic and/or cyclic (Figure 2.2).



**Figure 2.2:** Intermolecular hydrogen bonds

Under mechanical stresses, energy (about 20 to 25 kJ mol<sup>-1</sup> of acyclic hydrogen-bonds) may be absorbed by separation of hydrogen-bonds, which can re-form (probably in different positions) when the stress is removed. Energy absorption by this reversible bond-breaking/bond re-forming process reduces the likelihood of irreversible breaking of covalent bonds leading to degradation. In addition, the urethanes can be designed with "soft" and "hard" segments: that is, segments having low  $T_g$  and high  $T_g$ , respectively. When stress is applied, the soft segments can extend between the hard segment anchors. This factor, combined with the hydrogen-bonding, permits the preparation of coatings with 2H hardness and 300% extension. These properties permit the design of polyurethanes that are abrasion resistant while still resisting swelling with solvents. Polyurethanes tend to absorb water by hydrogen-bonding with water, which plasticizes the coatings. The isocyanate group is highly reactive, so polyisocyanates can be used to make coatings that cure at ambient temperature or at moderately elevated temperatures. Coatings based on aliphatic diisocyanates exhibit exceptional exterior durability when stabilized with hindered amine light stabilizers. The resistance of urethane coatings to environmental etching is superior to that of many melamine-formaldehyde (MF) cross-linked coatings [16].

#### 2.1.2.2 Base isocyanates for polyurethane resins

There are large number of synthesized isocyanates which are suitable in principle for the manufacture of polyurethane resins. However, given the requirements of large-scale availability and cost-efficiency, very few of these products are actually used. These can be divided into aromatic and aliphatic isocyanates [17].

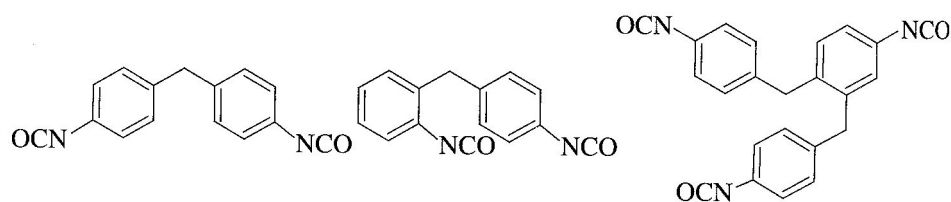
Chemical name (synonym)	Abbreviation	Empirical formula	Molecular weight
Diisocyanatomethylbenzene* (toluene diisocyanate)	TDI	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	174
Diisocyanatodiphenylmethane* (diphenylmethane diisocyanate)	MDI	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	250
1,6-Diisocyanatohexane (hexamethylene diisocyanate)	HDI	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	168
3,5,5-Trimethyl-1-isocyanato-3-isocyanato- methylcyclohexane*(isophorone diisocyanate)	IPDI	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	222
4,4'-Diisocyanato-dicyclohexylmethane*	H <sub>12</sub> MDI	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	262
1,3-Bis(isocyanatomethyl)benzene (m-xylylene diisocyanate)	XDI	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	188
1,6-Diisocyanato-2,2,4(2,4,4)-trimethylhexane*	TMDI	C <sub>11</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	210

\* isomer blend

**Figure 2.3:** Base diisocyanates for polyurethane resins

### Aromatic isocyanates

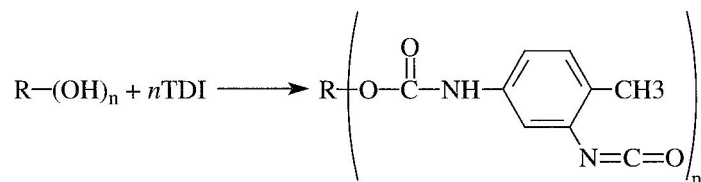
The aromatic isocyanates most widely used are based on MDI. MDI is available in several grades: bis(4-isocyanatophenyl)methane, a mixture of 55% of the 2,4' isomer and 45% of the 4,4' isomer; and several oligomeric (frequently called polymeric) MDI with longer chains of methylene phenyl groups. MDI is also used as a prepolymer with polyether polyols. The volatility (particularly of the oligomeric grades) is low enough to reduce toxic hazard, especially as compared to toluene diisocyanate (TDI).



**Figure 2.4:** 4,4'-and 2,4'-MDI isomers and an example of an oligomer

Due to toxic hazards, TDI is not used in final coating formulations. For coatings in which unreacted isocyanate groups are needed, TDI is converted into derivatives of higher molecular weight and higher functionality. Higher molecular weight reduces the toxic hazard, and the higher functionality yields solvent resistant films more rapidly. 2,4-TDI has the advantage of a differential in

reactivity between the ortho- and the para-isocyanate groups with alcohols, which makes possible synthesis of isocyanurates and prepolymers with narrower molecular weight distribution than with diisocyanates, in which the isocyanate groups are equally reactive. At 40° C, the /para-isocyanate group of TDI is about seven times more reactive than the ortho group. Furthermore, no matter which isocyanate group reacts first, the second group is less reactive than the first. Overall, after reaction of the para-isocyanate, the remaining ortho group is 20 times less reactive than a para-isocyanate on a second TDI. The difference in reactivity decreases as the temperature increases; at temperatures above 100°C, the ortho- and para-isocyanate groups have similar reactivities. Thus, for maximum selectivity a prepolymer should be prepared at a low temperature; of course, this means that the reaction is slow. Catalysts can be used, but the catalyst stays in the product and therefore sets a lower limit on the amount of catalyst in the final formulation. Studies of the reaction of TDI with alcohols catalyzed with tertiary amines and with organotin compounds showed that the amines tended to equalize the reactivity of the two NCO groups [18]. In a study of the ratio of para-to-ortho urethane formation in the reaction of TDI with n-butanol in benzene with several catalysts, the lowest ratio (2.8) was obtained with SnCl<sub>4</sub>, the highest ratio (9.9) with tin octanoate, DBTDL, and triisopentylphosphine. For the uncatalyzed reaction at 20°C the ratio was 11.5 [19]. Almost any polyhydroxy compound can be reacted with TDI to make prepolymers. Low molecular weight hydroxy-terminated polyesters or mixtures of diols and triols are commonly used. For safety, the levels of unreacted TDI in the prepolymer must be very low. Low levels of TDI can be assured by using an NCO/OH ratio below 2: 1 and pushing the reaction to completion, but chain extension (caused by reaction of both NCO groups of some TDI molecules) increases the molecular weight of the product. An alternative process, used when low molecular weight prepolymers are needed, is to react the polyhydroxy compound, often trimethylolpropane (TMP), with a large excess of 2,4-TDI, then remove the excess TDI using a vacuum wiped-film evaporator. Very low levels of free TDI and minimal chain extension are attainable, yielding low molecular weight products suitable for high-solids coatings.

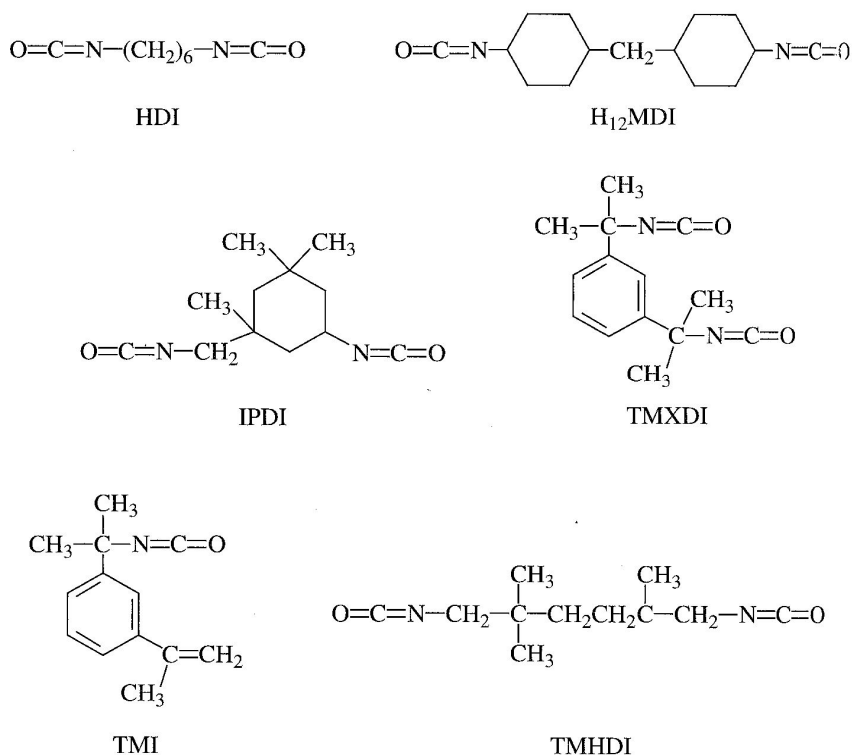


**Figure 2.5:** Idealized TDI prepolymer formation

The isocyanurate derived from TDI made by trimerizing TDI has a lower toxic hazard than that of monomeric TDI. The trimerization reaction occurs exclusively with the para-isocyanate group.

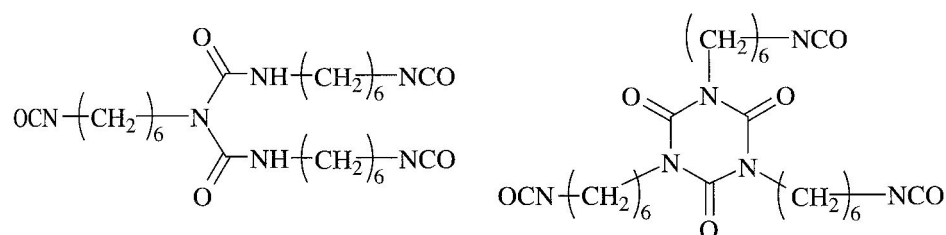
### Aliphatic isocyanates

The principal aliphatic isocyanates used are 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), bis(4-isocyanatocyclohexyl)methane (H12MDI), 1,3-xyllylenediisocyanate (XDI), tetramethyl-m-xylidene diisocyanate (TMXDI), m-isopropenyl- $\alpha,\alpha$ -dimethylbenzylisocyanate (TMI), and 2,2,5-trimethylhexane diisocyanate (TMHDI). Diisocyanates are usually converted to derivatives before use in coatings to increase functionality and reduce toxic hazard.



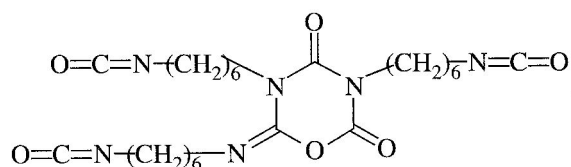
**Figure 2.6:** Some Important Aliphatic Isocyanates

HDI is especially hazardous and is handled on a large scale only in chemical plants. The first less hazardous derivative was a biuret, which can be made by reacting HDI with a small amount of water and removing the excess HDI. The structure of HDI biuret shown below is idealized. The presence of oligomeric biurets makes the average functionality higher than 3. These polyfunctional isocyanates give coatings with good color retention and weather resistance.



**Figure 2.7:** HDI biuret and HDI isocyanurate oligomers

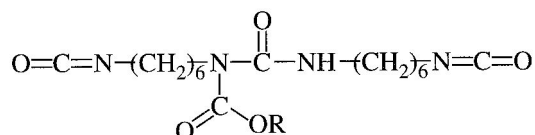
HDI isocyanurates are used on a larger scale. The isocyanurate gives coatings with greater heat resistance and even better long-term exterior durability than does HDI biuret. With ammonium fluoride as a catalyst, an isomeric trimer, an iminooxadiazenedione (called an unsymmetrical trimer) of HDI, is made as an approximately 50:50 mixture with HDI isocyanurate. It has the advantage that viscosity at the same oligomer content is lower than that of the corresponding HDI isocyanurate: 1 Pa.s versus 3 Pa.s [20]. A very low viscosity unsymmetrical trimer with a viscosity of 0.7 Pa.s has been made available, it is useful in very high-solids coatings and because of the low viscosity is easily incorporated in 2K waterborne urethane coatings [21].



**Figure 2.8:** iminooxadiazenedione, an unsymmetrical trimer of HDI

Allophanate derivatives of HDI and IPDI are another type of polyfunctional isocyanate. They are made by reacting an alcohol or diol with excess isocyanate, then removing unreacted diisocyanate with a wiped film evaporator giving an isocyanate-terminated allophanate [22]. The properties can be varied by using

different alcohols to make the starting urethane, to make the compounds with different R substituents shown in the structure. For example, the cetyl alcohol urethane from HDI yields an allophanate diisocyanate that is soluble in aliphatic hydrocarbons. Derivatives with higher functionality are made by reacting a glycol with excess diisocyanate.



**Figure 2.9:** Isocyanate-terminated allophanate

The uretdione dimer of HDI also has lower volatility with low viscosity and can be used for cross-linking in ambient cure coatings. Very low viscosity grades (<100 mPa.s) are reported to permit formulation of very low VOC coatings [23]. Commercial IPDI is a mixture of Z (cis) and E (trans) isomers in a 75:25 ratio. The isomers are difficult to separate. Isophorone diisocyanate has two different types of NCO groups. Studies performed under different conditions show that with DBTDL catalysis, the secondary NCO group of both Z and E isomers are more reactive than the primary NCO group [24-26]. The selectivity decreases with increasing temperature, and selectivity is greater with sec-butyl alcohol than with n-butyl alcohol [26]. DABCO promotes selective reaction of the primary isocyanate group of IPDI in contrast to other amines and DBTDL, where selectivity favors reaction with the secondary isocyanate groups. Selectivity decreases with increasing temperature [25-26]. High selectivity is particularly important in making IPDI prepolymers when low molecular weight and narrow distribution of molecular weight are desired. It was concluded that the optimal conditions for prepolymer synthesis based on IPDI are temperatures between 40 and 60°C using DBTDL catalyst. Isocyanurate derivatives of IPDI analogous to the HDI isocyanurates mentioned above are widely used cross-linkers. The rigidity of IPDI affords films with higher T<sub>g</sub>. By blending IPDI and HDI isocyanurates, formulators can dial the T<sub>g</sub> desired for a particular application. Bis(4-isocyanatocyclohexyl)methane (H12MDI) is less volatile than HDI and IPDI and is sometimes used as a free diisocyanate in coatings to be applied by roll coating but not by spray coating. It is a mixture of stereoisomers; since both isocyanato groups are secondary, reactivity

is lower than HDI or IPDI. XDI, TMXDI, and TMI have aromatic rings, but give color retention and exterior durability equivalent to those of aliphatic isocyanates. The exterior durability of their urethanes probably results from the absence of isocyanate groups directly substituted on the aromatic ring, as well as from the absence of abstractable hydrogens on the carbons adjacent to nitrogen in the cases of TMXDI and TMI. Since the isocyanate group is on a tertiary carbon, the reactivity is lower than that of less sterically hindered aliphatic isocyanates. This difference can be offset by using higher catalyst levels and sterically accessible tin catalysts such as DMTDA instead of DBTDL. TMXDI is offered as a low molecular weight, essentially diisocyanate-free prepolymer with trimethylolpropane. TMI is used as a comonomer with acrylic esters to make 2000 to 4000 MW copolymers with 40 to 50 mole % TMI; thus, each molecule has several isocyanate groups [27].

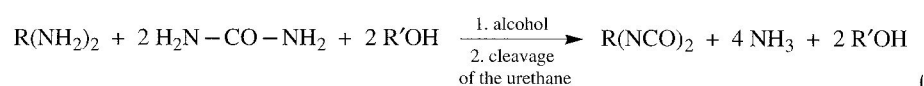
### 2.1.2.3 Basic reactions of isocyanates

Organic isocyanates are derived in their formula from isocyanic acid (H-N=C=O). They are manufactured by reacting amines with phosgene.



**Figure 2.10:** Synthesis of organic isocyanates

As polyfunctional isocyanates are required for the synthesis of polyurethane resins, poly-amines are used as the base products, preferably diamines. Alternative phosgene-free manufacturing processes have been proven. One example of such an alternative process is the reaction of diamines with urea and alcohols. The diisocyanate is formed via a urethane or diurethane intermediate stage which is then thermally decomposed as shown in Figure 2.11.



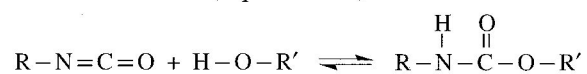
**Figure 2.11:** Reaction of diamines with urea and alcohols

Isocyanates usually react extremely readily by addition with virtually all compounds containing "active" hydrogen. The reactions shown below are of particular interest in

the manufacture of polyurethane precursors and for the chemical curing of reactive coatings.

#### Formation of urethanes

Isocyanates react with alcohols and phenols to form urethanes which are equivalent in formula to carbamic acid esters.

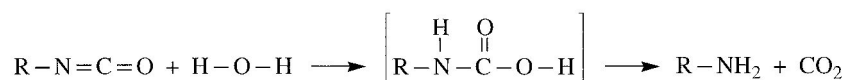


**Figure 2.12:** Formation of urethanes

The reaction is reversible at elevated temperatures. This property is of particular significance in the curing reaction of blocked polyisocyanates. Primary isocyanate groups are more reactive than secondary or tertiary groups. As a rule, the reaction rate with alcohols as the co-reactants follows the same order. Isophorone diisocyanate is the exception.

#### Formation of amines

Isocyanates react with water via carbamic acids as the intermediate stage to form amines and carbon dioxide. The reaction rate of the water approximates that of secondary alcohols.

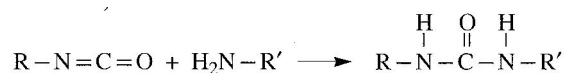


**Figure 2.13:** Formation of amines

The amines formed react with the excess isocyanate to form ureas.

#### Formation of substituted ureas

Isocyanates react spontaneously with primary and secondary amines to form substituted ureas.

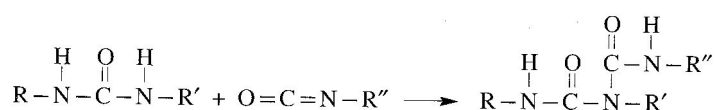


**Figure 2.14:** Formation substituted ureas

The amines formed react with the excess isocyanate to form ureas.

Formation of biurets

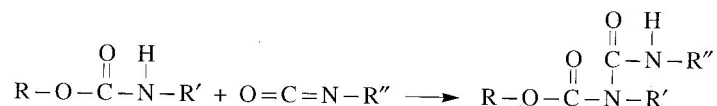
As a rule, isocyanates react with ureas at elevated temperatures to form biurets.



**Figure 2.15:** Formation of biurets

Formation of allophanates

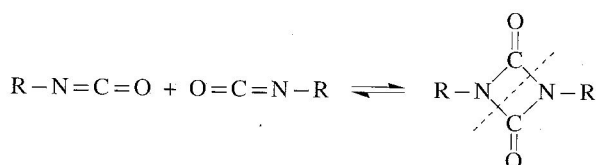
When suitably catalysed or at elevated temperatures, urethanes can be reacted with additional isocyanate groups to form allophanates.



**Figure 2.16:** Formation of allophanates

Formation of uretdiones

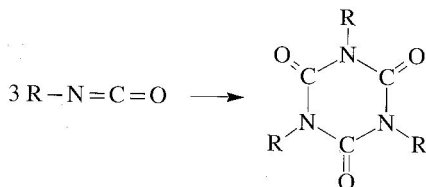
Isocyanates can be dimerized under special conditions to form an uretdione ring. This is an equilibrium reaction whose stable state is quickly destroyed at high temperatures, forming a monomer.



**Figure 2.17:** Formation of uretdiones

## Formation of isocyanurates

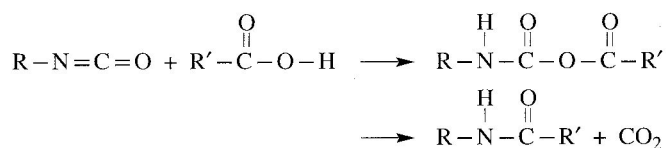
Trimerization of isocyanates forms an isocyanurate ring which, unlike the uretdione ring, is also stable at high temperatures



**Figure 2.18:** Formation of isocyanurates

## Formation of substituted acid amides

At high temperatures, isocyanates react with carboxylic acids with the intermediate formation of mixed anhydrides. These dissociate to form amide and carbon dioxide.



**Figure 2.19:** Formation of substituted acid amides

## Formation of carbodiimides

Isocyanates can react with each other, splitting off carbon dioxide [28].



**Figure 2.20:** Formation of carbodiimides

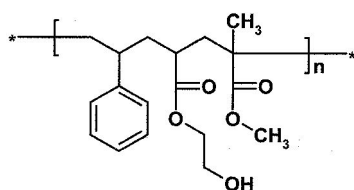
### 2.1.3 Coreactants

The properties of polyurethanes are not only affected by the polyisocyanate, but also in large measure by the hydroxyfunctional coreactant, the polyol. Selecting suitable polyols and polyisocyanates makes it possible to control key characteristics of the coating and the resulting paint film. Solids content, drying, gloss, elasticity and hardness, resistance to chemicals and hydrolysis, and cost-effectiveness are just some

examples in this respect. Research in the past has therefore concentrated greatly on the development of new and improved resins. The most important coreactants for polyisocyanates are hydroxyl-bearing polymers such as polyacrylate, polyester and polyether polyols. Of lesser importance are polycarbonate, polycaprolactone and polyurethane polyols. Products containing amino groups have much higher reactivity with isocyanates, and thus are used only in special applications or when blocked [29].

### 2.1.3.1 Polyacrylate polyols

The term polyacrylate polyols covers copolymers of acrylic and/or methacrylic acid esters - ethyl acrylate, butyl acrylate and methyl methacrylate - which also bear hydroxyl groups. In practice, other comonomers are frequently used together with these, e.g. styrene, vinyl ester or maleates. The hydroxyl groups needed for reaction with isocyanate groups are usually introduced directly via functionalized esters of acrylic and methacrylic acid, e.g. hydroxyethyl acrylate, hydroxyethyl methacrylate or hydroxypropyl methacrylate.

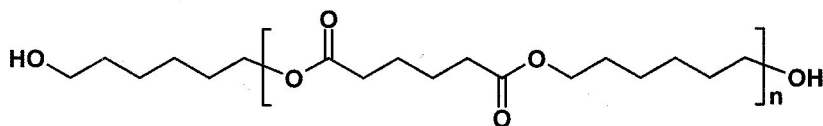


**Figure 2.21:** Structure of polyacrylate a polyol

Another way of generating hydroxyl groups is by polymer-analog reactions on finished polyacrylates [30].

### 2.1.3.2 Polyester polyols

Polyester polyols are produced by the polycondensation of di- and polycarboxylic acids with an excess of polyfunctional alcohols (polyols) (Figure 2.22). The most important polycarboxylic acids and their anhydrides which are available on an industrial scale for the manufacture of polyester polyols include the aromatic acids phthalic acid and isophthalic acid, the aliphatic acids adipic acid and maleic acid, and the cycloaliphatic acids such as tetrahydrophthalic acid and hexahydro-phthalic acid.

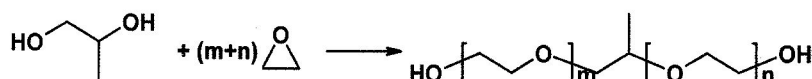


**Figure 2.22:** Structure of a linear polyester polyol based on the 1,6-hexanediol/adipic acid

The polyols used are aliphatic alcohols such as ethane diol, 1,2-propanediol, 1,6-hexanediol, neopentyl glycol, glycerol and trimethylolpropane, and cycloaliphatic alcohols such as 1,4-cyclohexanedimethanol. In addition, monofunctional alcohols or carboxylic acids such as 2-ethyl hexanol or 2-ethyl hexanoic acid can be used as chain terminators.

### 2.1.3.3 Polyether polyols

Polyether polyols are formed by the addition of ethylene oxide and/or propylene oxide to polyfunctional starter molecules.



**Figure 2.23:** Manufacture of a polyether polyol based on 1,2-propanediol

Polyvalent alcohols such as ethylene glycol, 1,2-propanediol, glycerol and trimethylolpropane, or amines such as ethylenediamine (which yields tetrafunctional polyether alcohols) are used as the starter molecules. The addition of the alkene oxide is usually performed in an alkaline medium with sodium hydroxide as the base. Key properties of the polyether such as the melting point, viscosity, hydrophilicity and compatibility can be controlled via the ratio of the ethylene oxide to propylene oxide. Due to their low viscosity, polyether polyols are used mainly in solvent-free coating systems. However, because of the poor weather stability of polyethers - a consequence of oxidative polyether chain degradation - their use is restricted to interior applications or to the formulation of primers. On the other hand, these systems are characterized by particularly good resistance to hydrolysis and mechanical stability. For these reasons, they are often used in the construction sector for coatings on mineral substrates such as concrete.

#### **2.1.3.4 Polycarbonate polyols**

Polycarbonate polyols are esterification products formed by the reaction of carbonic acid with polyols. In practice, the carbonate structure is introduced using phosgene or carbonic acid diesters [31]. Because of their poor solubility, aromatic polycarbonates based on bisphenol A are not used in coating applications. In contrast, linear aliphatic polycarbonates are used both as binders in high-quality polyurethane coatings and in the production of polyurethane binders, especially polyurethane dispersions [32-33]. Aliphatic polycarbonate polyols are characterized by their low viscosity, and the resulting coatings by good weather stability and very good resistance to hydrolysis.

#### **2.1.3.5 Polycaprolactone polyols**

Polycaprolactone polyols are produced by the ring-opening polymerization of  $\epsilon$ -caprolactone. Suitable starter molecules are polyfunctional alcohols such as ethylene glycol, 1,2-propanediol, glycerol and trimethylolpropane [34-36]. The ring-opening polymerization takes place at temperatures of approximately 120 to 200 °C and can be accelerated by the addition of catalysts such as organometallic compounds. The process yields low viscosity products with defined functionality. These are used either as sole binders or as reactive thinners in solvent-free or high solid two-component polyurethane coatings. Polycaprolactone polyols are also used as polyol building blocks in the manufacture of high molecular weight polyurethanes. A further use of the ring-opening polymerization of  $\epsilon$ -caprolactone is in the modification of higher molecular weight polyols, e.g. polyacrylate polyols [37]. The technical advantages of polycaprolactone polyols include their flexibility and weather stability, in addition to their low viscosity. The main applications for these materials are in two-component polyurethane coatings for plastics (automotive sector) and in solvent-free coatings for construction applications.

#### **2.1.3.6 Polyurethane polyols**

Polyurethane polyols are produced using the diisocyanate polyaddition process in which diisocyanates are reacted with an excess of diols and/or polyols [38-40]. On account of their high viscosity, these products are as yet of little importance in the field of solventborne coating systems. By contrast, hydroxyfunctional aqueous polyurethane dispersions are used successfully in one-component and two-

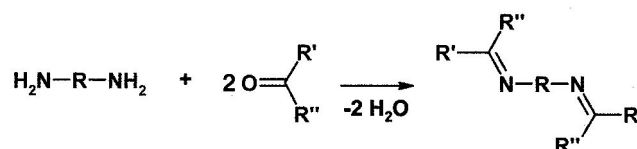
component systems for wood and plastic coatings, e .g. for producing soft-feel effects, and for glass coatings.

### 2.1.3.7 Polyamines

Unblocked amino groups have very high reactivity with isocyanate groups. Polyurea coatings can therefore only be applied using two-component application equipment developed for this purpose. Poly ether amines are normally used in combination with aromatic isocyanate prepolymers. Aliphatic prepolymers have only played a subordinate role up to now. The main applications are coatings for concrete or systems for heavy-duty corrosion protection [41-42]. The reactivity can be lowered by significantly reducing the reactivity of one of the coreactants, e.g. by blocking. One example of this is the reaction of TDI prepolymers with aromatic amines. Such combinations are frequently used to flexibilize epoxy/amine systems [43-44].

Blocking reactions

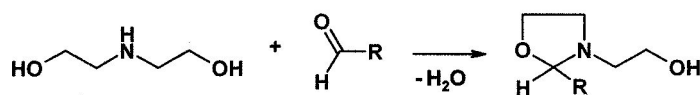
Low molecular weight blocked diamines have become particularly significant as reactive thinners for high solid polyurethane coatings, e.g. for automotive refinishing. The most important blocking reactions for amines are those with aldehydes to form aldimines and with ketones to form ketimines [45-49].



R = (cyclo)alkylene, R' = (cyclo)alkyl, R'' = (cyclo)alkyl, H

**Figure 2.24:** Aldimine and ketimine formation as blocking reactions for amines

On contact with water, e.g. atmospheric humidity, the blocking reaction is reversed to produce the starting amines, which are then available to react with isocyanate groups [49-50]. Even in the absence of water, crosslinking can be achieved - especially under the influence of heat. In this case, cyclic ureas are formed by disproportionation [51]. Reacting amino alcohols with aldehydes or ketones (Figure 2.25) splits off water and yields 1,3-oxazolanes (oxazolidines), another class of blocked amines [52-54].



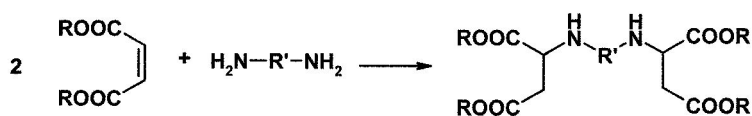
R = (cyclo)alkyl

**Figure 2.25:** Formation of 1,3-oxazolanes

These can react with diisocyanates via available hydroxyl groups to form bifunctional blocked amines (bisoxazolidines).

### Polyaspartics

Polyaspartic esters are special polyamines with secondary amino groups. These can be produced either by the addition of primary aliphatic diamines to maleic or fumaric acid di(cyclo)alkyl esters or by the addition of primary aliphatic amines to unsaturated oligoesters or polyesters [55-57].



R = (cyclo)alkyl, R' = (cyclo)alkylene

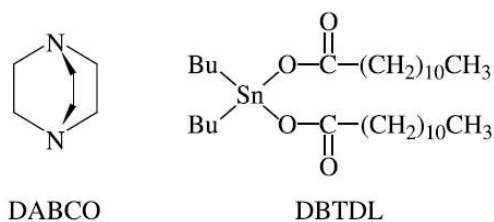
**Figure 2.26:** Polyaspartic esters

Polyaspartic esters based on diethyl maleate and cycloaliphatic diamines are solvent-free, low viscosity substances with secondary amino groups, whose reactivity is reduced by electronic and steric effects to such an extent that they can be used to formulate highly reactive two-component polyurethane coatings with an adequate pot life. This specifically adjustable reactivity enables the formulations of fast-drying coatings for highly productive, modern coating concepts. These systems are of particular interest for use in automotive refinish, large vehicle and industrial coatings, corrosion protection and construction. The polyaspartics are used as the main binder or as reactive thinners [58-60].

### 2.1.4 Catalysts

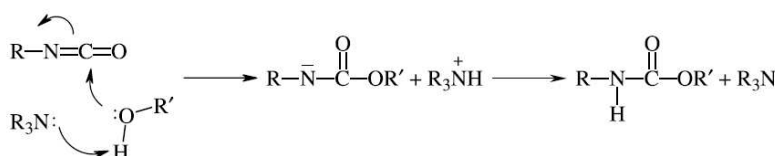
Reactions of isocyanates with alcohols are catalyzed by a variety of compounds, including bases (tertiary amines, alkoxides, carboxylates), metal salts and chelates, organometallic compounds, acids, and urethanes. Most primary aliphatic amines

react so rapidly with isocyanates at room temperature that their reaction rates and effect of catalysts have not been determined. The reactions of amines with isocyanates are catalyzed by carboxylic acids and water. The most widely used catalysts in coatings are tertiary amines, commonly diazabi-cyclo[2.2.2]octane (“DABCO”), and organotin(IV) compounds: most commonly, dibutyltin dilaurate (DBTDL).



**Figure 2.27:** “DABCO” and DBTDL

The mechanisms by which these and other catalysts operate are controversial. A reasonable explanation for catalysis by amines is that they facilitate proton transfer from the alcohol to the isocyanate (and similarly to alcohols and urethanes). Proton removal from the alcohol may occur during reaction with the isocyanate, thereby avoiding formation of the positive charge on oxygen and lowering the energy of the reactive intermediate, which may proceed to product by a proton transfer from the protonated amine, as shown in Figure 2.28 [61].



**Figure 2.28:** Catalysis reaction by amines

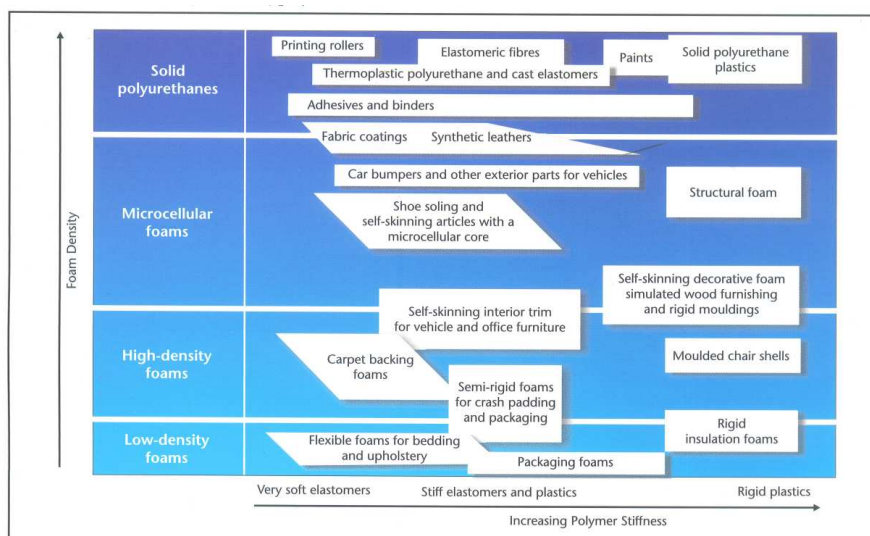
Proton removal by amines at an earlier stage than by alcohols and urethanes is reasonable, owing to the greater basicity of amines [62]. Catalysis of urethane formation by 1-8-diazabicyclo[5.4.0]undec-7-ene (DBU) is reported to result from the formation of the ammonium ion and a hydrogen-bond type complex with the polyol [63]. Comparisons are complicated because catalysts also catalyze allophanate formation and trimerization of aromatic isocyanates to form isocyanurates. For example, reaction of phenyl isocyanate with n-butyl alcohol (at 50°C in acetonitrile)

in the presence of pentamethyldipropylenetriamine (PMPTA) yielded 30% urethane, while 70% of the isocyanate was converted into triphenylisocyanurate [64]. On the other hand, when DABCO was used as a catalyst, the urethane was the principal product, with a small amount of an allophanate also formed. Possibly, urethane formation is favored by sterically accessible amines (e.g., DABCO) and isocyanurate formation is less sensitive to this factor. The zinc complex of 2,4-pentanedione [Zn(AcAc)<sub>2</sub>], tin octanoate, and quaternary ammonium compounds such as tetramethylammonium octanoate specifically catalyze allophanate formation [65]. Acids also catalyze the reaction, perhaps by protonating the isocyanate group. Carboxylic acids act as catalysts [66]. Acetic acid has been reported to be a more effective catalyst than a carboxylic acid functional polyether polyester [67]. The effect of temperature on the reaction rate of m-chlorophenyl isocyanate with n-butanol in heptane catalyzed with acetic acid has been studied and mechanisms proposed for the nonlinear increase in reactivity with temperature [68].

## 2.1.5 Properties, types and applications of polyurethanes

### 2.1.5.1 Properties of polyurethanes

Polyurethanes can be manufactured in an extremely wide range of grades, in densities from 6 to 1,220 kg/m<sup>3</sup> and polymer stiffness from flexible elastomers to rigid, hard plastics. Although an over simplification, the following chart, figure 2.29, illustrates the broad range of polyurethanes, with reference to density and stiffness.



**Figure 2.29:** Property matrix of polyurethanes

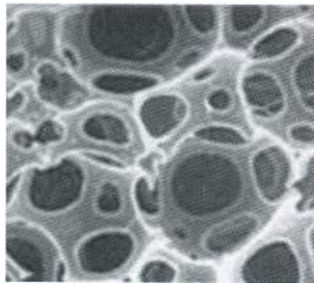
### **2.1.5.2 Types of polyurethanes**

A consideration of particular properties of certain grades of polyurethanes and the way these are used serves to demonstrate their versatility.

#### **Foamed Polyurethanes**

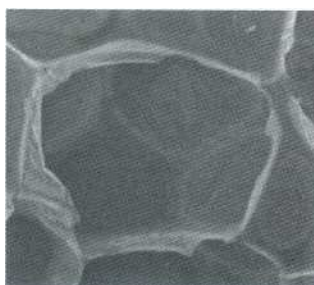
By itself the polymerisation reaction produces solid polyurethane and it is by forming gas bubbles in the polymerising mixture, often referred to as 'blowing', that a foam is made. Foam manufacture can be carried out continuously, to produce continuous laminates or slabstock, or discontinuously, to produce moulded items or free-rise blocks. Flexible foams can be produced easily in a variety of shapes by cutting or moulding. They are used in most upholstered furniture and mattresses. Flexible foam moulding processes are used to make comfortable, durable seating cushions for many types of seats and chairs. The economy and cleanliness of flexible polyurethane foams are important in all upholstery and bedding applications. Strong, low-density rigid foams can be made that, when blown using the appropriate environmentally acceptable blowing agents, produce closed cell structures with low thermal conductivities. Their superb thermal insulation properties have led to their widespread use in buildings, refrigerated transport, refrigerators and freezers. A fast, simple moulding process can be used to produce rigid and flexible foam articles, having an integral skin, that are both decorative and wear resistant. Fine surface detail can be reproduced in the integral skin of the foam allowing for the simple manufacture of simulated wood articles, 'leather-grain' padded steering wheels and textured surface coatings. Three foam types are, in quantity terms, particularly significant: low-density flexible foams, low-density rigid foams and high-density flexible foams, commonly referred to as microcellular elastomers and integral skin foams. Low-density flexible foams have densities in the range 10 to 80 kg/m<sup>3</sup>, made from a lightly cross-linked polymer with an open cell macro structure. There are no barriers between adjacent cells, which results in a continuous path in the foam, allowing air to flow through it. These materials are used primarily as flexible and resilient padding material to provide a high level of comfort for the user. They are produced as slabstock, which is then cut to size, or as individually moulded cushions or pads. There are semi-rigid variants of this material, where the chemistry of the building blocks has been changed, and these are mainly used in energy management

systems such as protective pads in cars. An example of the cellular structure is shown in Figure 2.30.



**Figure 2.30:** Scanning electron micrograph showing the open cells of flexible foam

Low-density rigid foams are highly cross-linked polymers with an essentially closed cell structure and a density range of 28 to 50 kg/m<sup>3</sup>. The individual cells in the foam are isolated from each other by thin polymer walls, which effectively stop the flow of gas through the foam. These materials offer good structural strength in relation to their weight, combined with excellent thermal insulation properties. The cells usually contain a mixture of gases and depending on their nature and relative proportions the foams will have different thermal conductivities. In order to maintain long-term performance it is necessary for the low thermal conductivity gases to remain in the cells, consequently more than 90 per cent of the cells need to be closed. An example of the cellular structure is shown in Figure 2.31. Recently, fully open celled rigid foams specifically developed for vacuum panel applications have been developed.



**Figure 2.31:** Scanning electron micrograph showing the closed cells of rigid foam

High-density flexible foams are defined as those having densities above 100 kg/m<sup>3</sup>. This range includes moulded self-skinning foams and microcellular elastomers. Self-skinning or integral skin foam systems are used to make moulded parts having a cellular core and a relatively dense, decorative skin. There are two types: those with an open cell core and an overall density in the range up to about 450 kg/m<sup>3</sup> and those

with a largely closed cell or microcellular core and an overall density above 500 kg/m<sup>3</sup>. The microcellular elastomers have a much more uniform density in the range of 400 to 800 kg/m<sup>3</sup> and mostly closed cells, which are much smaller than those in the low-density applications. The biggest applications for integral skin and microcellular elastomers are in moulded parts for upholstery, vehicle trim and shoe soling. Another similar material is the microporous elastomer in which the porous structure is often created in ways other than by the expansion of gases. Often produced in thin films these materials have an open cell like structure, which allows movement of gases, but have the appearance and physical integrity of a solid film.

### Solid polyurethanes

Although foamed materials account for a substantial proportion of the global polyurethanes market there is a wide range of solid polyurethanes used in many, diverse applications. Cast polyurethane elastomers are simply made by mixing and pouring a degassed reactive liquid mixture into a mould. These materials have good resistance to attack by oil, petrol and many common non-polar solvents combined with excellent abrasion resistance. They are used amongst other things in the production of printing rollers and tyres, both low speed solid relatively small units and to fill very large, pneumatic off-road tyres. Polyurethane elastomeric fibres are produced by spinning from a solvent, usually dimethylformamide (DMF), or by extrusion from an elastomer melt. The solvent process is the dominant one and has two forms, one in which the completed elastomer is dissolved and then a fibre spun as the solvent is removed and the other in which the isocyanate and polyol are mixed into a DMF solution and the fibre spun as the reaction occurs. The major applications are in clothing where these fibres have effectively replaced natural rubber. Thermoplastic polyurethanes are supplied as granules or pellets for processing by well-established thermoplastic processing techniques such as injection moulding and extrusion. By these means elastomeric mouldings having an excellent combination of high strength with high abrasion and environmental resistance, can be mass-produced to precise dimensions. Applications include hose and cable sheathing, footwear components and high-wear engineering applications. Recent advances have shown the possibility to foam the polymer during injection moulding, extending even further the range of applications. Polyurethanes are also used in flexible coatings for textiles and adhesives for film and fabric laminates. Paints and coatings give the

highest wear resistance to surfaces such as floors and the outer skins of aircraft and for the automotive industry. Binders are used increasingly in the composite wood products market for oriented strand board and laminated beams for high performance applications.

### **2.1.5.3 Applications of polyurethanes**

#### Automotive

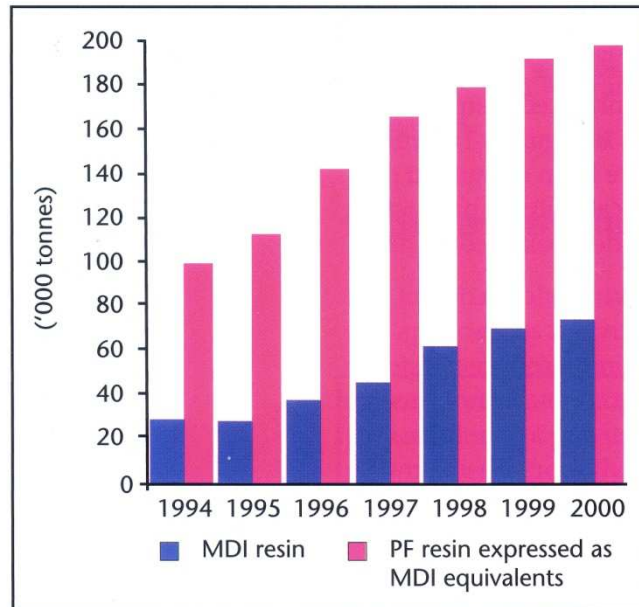
The transport industry uses the widest variety of polyurethane products spanning almost the entire product range and physical properties achievable. Polyurethane products are used to make car seats, head rests, liners, internal body parts, dashboards, fascias, bumpers, energy absorption parts, sound insulation, clear top coats, powder coatings, lacquers and refinishes. Flexible foams are used in car seats, cut and shaped from slabstock or moulded, with the major driver being weight reduction, through using lower density materials and/or thinner seats. The second driver is an enhanced comfort level, which often conflicts with the drive for reduced weight. Other uses for flexible foams are: improved sound insulation, carpet underlay and headrests both sometimes made from bonded scrap foam. Semi-rigid foams are used to make liners, some internal body parts and energy absorbing structures whilst elastomers are used to produce gaskets to seal doors and windows. Integral skin foams, based on microcellular polyurethane elastomers, are used for steering wheels, armrests and dashboards. RIM or reinforced RIM (RRIM) products are used to produce fascias, body panels and other components for cars and trucks, but some of these products are threatened by the substitution pressure of thermoplastic polyolefins. However, glass fibre-reinforced polyurethane panels are in direct competition with the polyolefins and the low tooling cost of the polyurethane RRIM technology provides a cost advantage in the trend towards more customised car trims. Overall, the transport applications for polyurethane are expected to grow above GDP level, despite the sluggish progress of the automotive industry, due to the continuing growth of plastic materials used in cars, required to achieve the continuing weight reductions demanded by environmental legislation. Polyurethane products will be in direct competition with other engineering plastics, but are expected to maintain or slightly increase their proportion of the total amount of plastics used in a vehicle.

## Coatings

The polyurethane coatings industry consists of a broad range of products that are used across all application areas and the market growth has significantly exceeded the rise in GDP for all regions. Two-component systems, water-borne and powder coatings have shown the highest growth rates and increased awareness and acceptance of these products, in combination with environmental pressure, will be the key drivers for future growth, which is expected to be 8 to 10 per cent per year. Coatings for wood products have a major share of the market segment and are primarily two-component systems applied to furniture with future growth expected to be at GDP level with a tendency for increased use of water-borne systems. Architectural coatings, used mainly for interior clear wood finishes, represents another significant market segment and growth in this area has been driven by the enhanced use of water-borne systems supported by increasing legislative pressure on solvent-based systems. Polyurethane anti-corrosion coatings are increasingly used instead of traditional coatings because their superior properties and longer lifetimes greatly lengthen the intervals between refurbishment. Growth of the anti-corrosion market segment is expected to follow GDP, but polyurethane coatings may see a faster growth due to their ability to meet the increasingly more stringent environmental demands. High-performance light-resistant coatings are dominated by products based on aliphatic diisocyanates, which are mainly used in the more demanding application areas such as automotive refinishing. This is mainly due to the penetration of water-based coating technology replacing the traditional solvent-based coatings, increased use of powder coating technology and higher penetration of clear topcoats in the automotive industry.

## Construction

The growth of the polyurethane construction market segment has mainly been driven in the past 10 years by the penetration of polyurethanes into the wood binding area. The use of composite wood products is widespread in the North American construction industry and MDI-based resins are replacing the phenolic resins, traditionally used to produce bonded wood composites. About 27 per cent of the North American oriented strand board (OSB) market now uses MDI as the bonding material, Figure 2-15.



**Figure 2.32:** Market penetration of MDI resins in the North American OSB industry

The use of MDI-based resins has only recently entered the European market, but new mills are now starting to make panels that are immediately manufactured using polyurethane technology for the core of the material. It is clear that the continuing growth in the wood composite market will mainly be captured by polyurethane-based materials as they more efficiently use fast growth timber, natural resources and support the spreading trend for wood driven construction, as currently used in the USA. Polyurethanes will continue to replace phenolic resins through a blend of lower resin usage and shorter production cycles. The use of polyurethane insulation panels is expected to grow due to the need for higher energy efficiencies and the drive towards reduced emission of green house gases. Polyurethane panels offer the best insulation value per unit thickness and are the material of choice when space is restricted. The market is expected to grow, as more stringent legislation will come into effect in the European Union and the United States, regarding building energy efficiency. Renovation of existing buildings will be another main driver for growth with a focus on a major rise in demand for spray and cavity filling technologies. New buildings will be required to be built with less construction time, as the average wealth of the population increases and the cost of labour becomes more expensive. This favours the use of prefabricated panels for rapid construction on site, leading to the increased demand for panels, either rigid or flexible faced, that use the structural

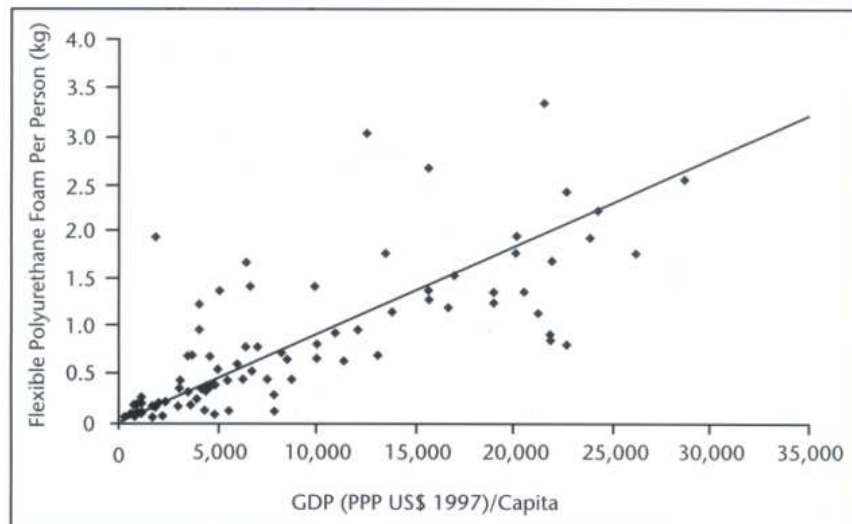
strength of rigid polyurethane foams in combination with its excellent thermal insulation.

## Footwear

The footwear segment is declining in Western Europe, due to the relocation of the industry to the Asian region with China now dominating the global production of footwear and there is a rapid growth in demand for both microcellular polyurethane elastomers, for soling, coatings for the production of artificial leather and polyurethane adhesives. The major production of the polyurethane raw material is still mainly in Western Europe, the USA and Japan which all export to China, but increasingly production units are starting up in China. Other key footwear producing areas besides China are Latin America, Eastern Europe, the Middle East and specific countries such as Italy, which is still seen as the design trend setter, Thailand and Vietnam. Growth in the footwear industry is driven strongly by population growth and societal pressures - most people need basic footwear for protection and increasing numbers buy shoes to make a statement about their position in society. The dynamics of the footwear market are driven by import-export with shoes specified in developed countries made in low-cost labour countries, often using components and raw materials from the developed countries, before being transported back to the developed markets.

## Furniture

Replacement sales will be the main driver for growth in developed countries due to the demand for enhanced cushioning and comfort that is achieved with higher density materials. This comfort premium will become more important as the average wealth per capita increases and has already been seen in the USA and Western Europe. As the wealth of other regions increases the need for comfort seating will grow proportionally. This trend for enhanced foam performance and flexible foam consumption is illustrated in Figure 2.33, which shows a linear correlation between the amounts of flexible foam consumed per capita versus the average purchasing power per capita. Local shifts in production location towards the lowest cost producing country provide a balanced scatter around the trend.



**Figure 2.33:** Flexible foam consumption versus wealth

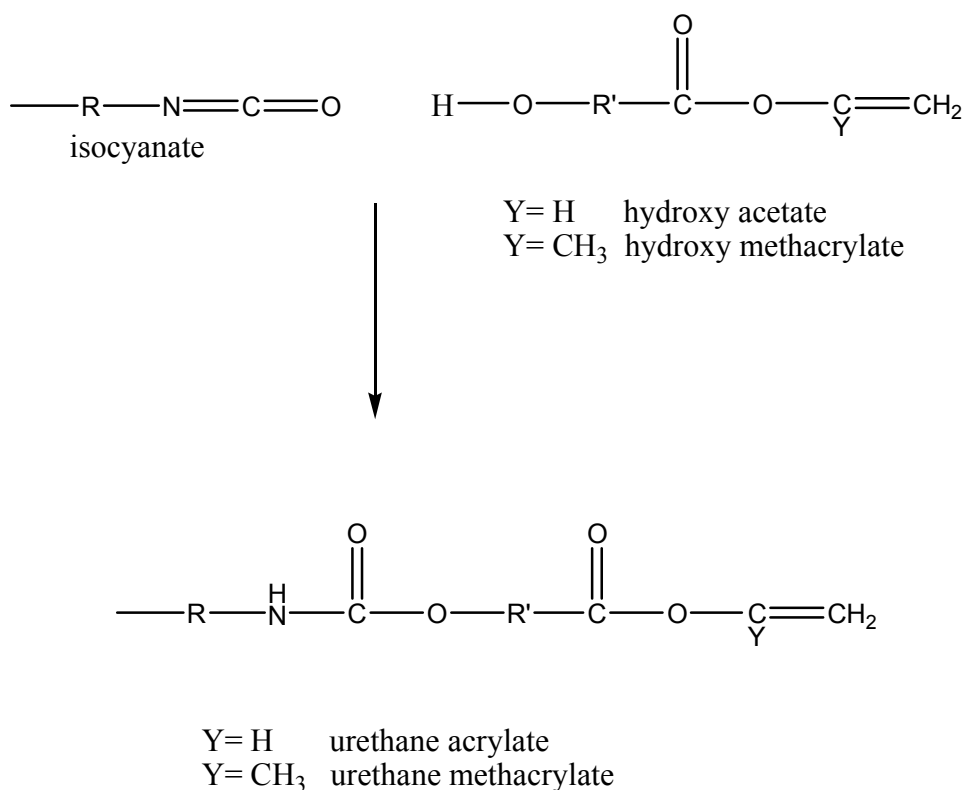
Large growth can be expected from regions with fast growing disposable incomes such as in Asia where many populations are increasing their standard of living very rapidly.

#### Thermal insulation

An increasing world population will require more efficient use of food, with the emphasis on better food preservation to avoid waste. This can only be done through more efficient insulation during transport and storage. Developed regions will see growth through replacement of existing or old units by more energy-efficient units driven by increasing environmental pressure and legislation. Larger units, having thicker walls, will increase the demand for polyurethane insulation, which provides both insulation and structural support. The fast-growing population in the developing regions will need more refrigerated transport and storage. As the population keeps growing, food will need to be transported in larger quantities over longer distances. Government investments in infrastructure will enhance the sales of units in developing regions. Increasing personal wealth will further drive the demand for polyurethane insulated appliances [69].

## 2.2 Urethane Acrylates

The reaction of isocyanate group with the hydroxyl group of an acrylic or methacrylic monomer (Figure 2.34) will give the corresponding urethane acrylate or methacrylate.



**Figure 2.34:** Isocyanate-Hydroxyl Acrylate Reaction

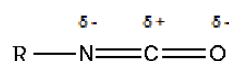
If diisocyanates are utilised, then acrylate di-functionality may be obtained. In contrast with epoxy acrylates, where only a few similar starting materials are available, urethane acrylates can be prepared from a large, diverse range of raw materials. This results in many possible variations in preparation and a very large range of properties of finished products. The diisocyanates which may be acrylated include toluene diisocyanate (TDI), tetramethylxylene diisocyanate (TMXDI), hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI, and its chain isomer, trimethylhexamethylene diisocyanate (TMDI), dicyclohexylmethane diisocyanate (H<sub>12</sub>MDI), xylene diisocyanate (XDI) and diphenylmethane diisocyanate (MDI). HMDI and TDI are extremely hazardous, being relatively volatile. To minimize this problem, oligomers of HMDI are used. TDI is reacted with a triol to give a relatively safe product. H<sub>12</sub>MDI consists of three stereoisomers because of the reduction of the

aromatic MDI. Hydroxy functional monomers include hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and hydroxyethyl methacrylate (HEMA). If other hydroxy containing compounds are also present, like polyethers, polyesters or polyols that contain more than one hydroxyl group per molecule, then chain extension is possible. This results in a wide range of prepolymers that vary in functionality and molecular weight with corresponding variations in final film properties [70]. Urethane acrylates probably offer a far wide range of final film properties than any other class of radiation curable oligomers.

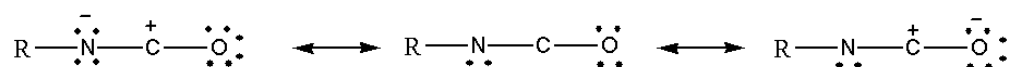
### 2.2.1 Mechanism

The isocyanate group is extremely reactive undergoing the following reactions. Nucleophilic addition (both catalysed and uncatalysed), cycloaddition, insertion and homopolymerisation. With compounds containing active hydrogen (labile hydrogen) like water, amines, hydroxyls and acids, the reaction is a nucleophilic attack on the electrophilic carbon atom of the isocyanate group. Isocyanate groups are very reactive because there are a large number of nucleophiles containing OH, SH, NH, and PH groups that will readily react. In addition, some hydrogen-halide groups and hydrogen-carbon bonds in materials, like nitromethane, malonates, and hydrogen cyanide have been added to aliphatic and aromatic isocyanates [71]. The isocyanate group contains delocalised electrons and with the electronegativity of the O and N atoms an electron deficient C atom is formed, as shown in Figure 2.35. An alternative approach is to consider different resonance forms of the isocyanate structure. These are also shown in Figure 2.35.

#### (A) Delocalised Electrons



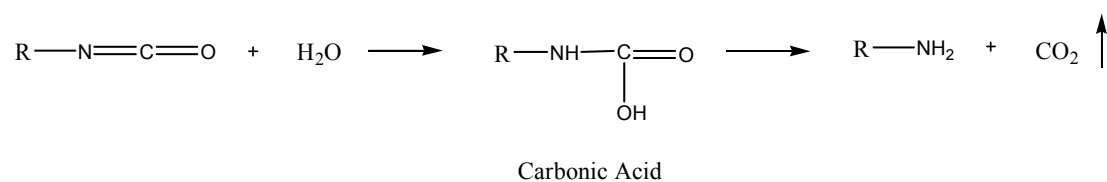
#### (B) Resonance Structures



**Figure 2.35:** Structure of the Isocyanate Group

Such structures make the isocyanate group susceptible to reaction by electron donors attacking the carbonyl carbon and electron acceptors attacking oxygen or nitrogen. These structures are also susceptible to catalysis by Lewis acid and bases. Because the isocyanate group is extremely reactive, there is a range of reactions in which it can participate. For the purposes of acrylation, these can be classified as unwanted side reactions. Some of the unwanted side reactions that may occur during the formation of a urethane acrylate are given in Figure 2.36.

**(A) Reaction with Water**



The amine is available for further reaction

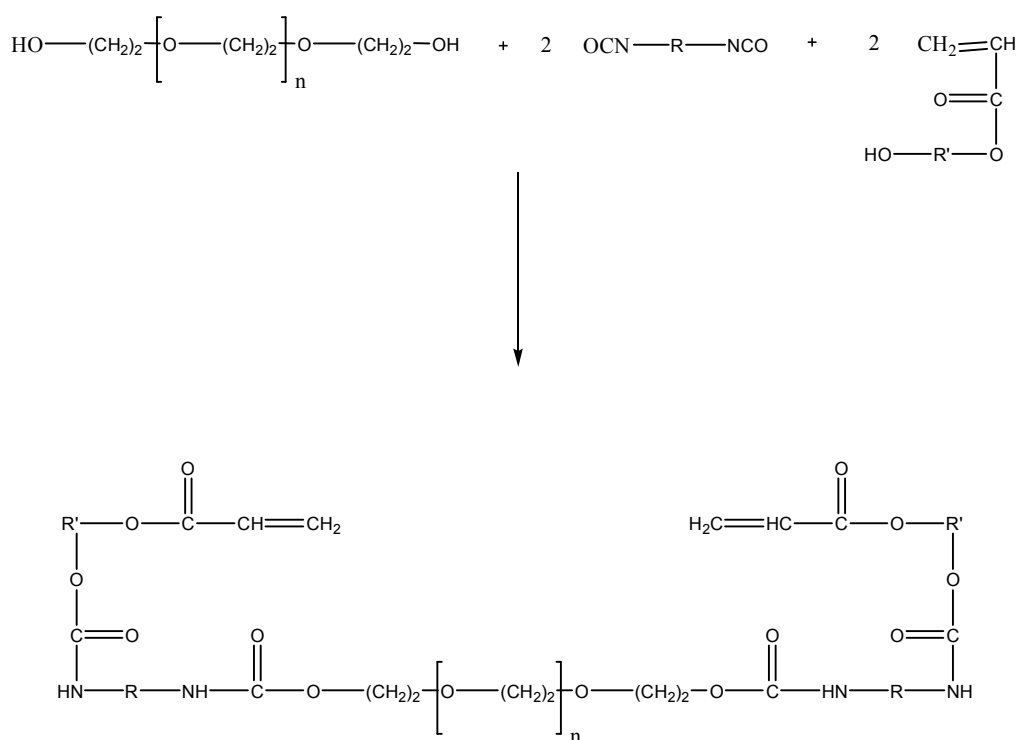
**Figure 2.36:** Some Unwanted Side Reactions that may occur during Urethane Acrylate Preparation



## 2.2.2 Types of urethane acrylates

### 2.2.2.1 Polyether urethane acrylates

Polyether urethane acrylates or methacrylates can be considered to consist of three components. Polyether polyol, multifunctional isocyanate and hydroxy acrylate or methacrylate. An isocyanate functional adduct is produced by capping a polyether with a diisocyanate, which is then reacted with an unsaturated hydroxy compound, such as 2-hydroxyethyl acrylate. Substituting 2-hydroxyethyl methacrylate (for 2-hydroxyethyl acrylate), results in the corresponding polyether urethane methacrylate.



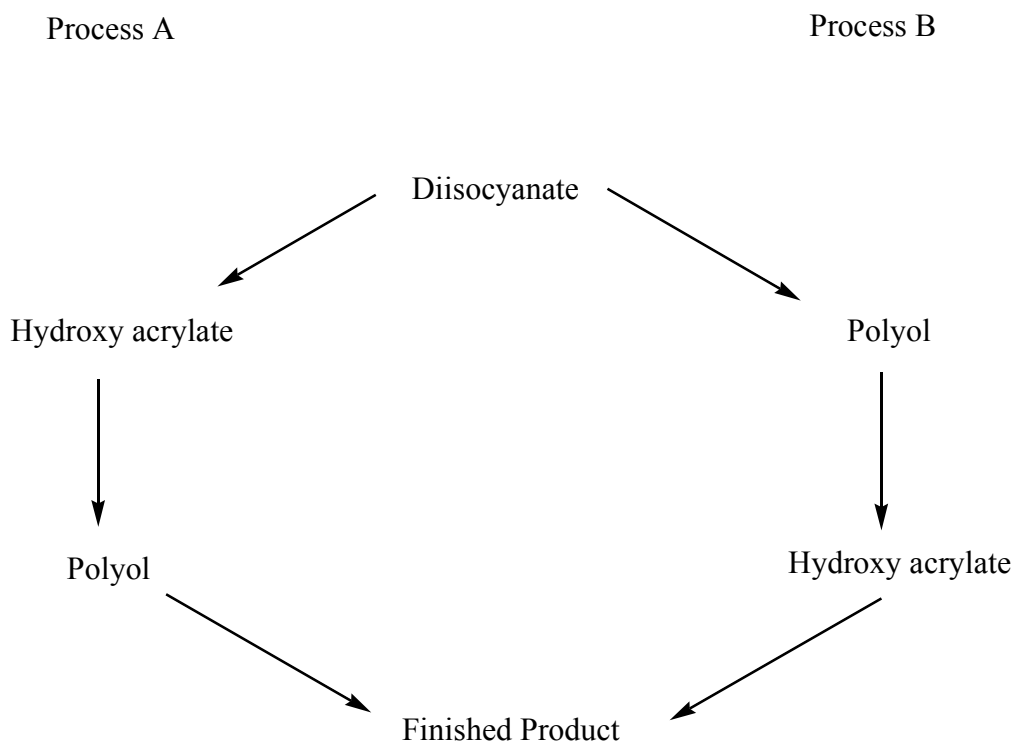
**Figure 2.38:** Formation of a Polyether Urethane Acrylate

Processes similar to those for the polyester urethane acrylates can be used. An example for a product used in the preparation of magnetic media, comprises the reaction of partial urethanes of diisocyanates with hydroxylated polyethers [72]. In this case, 2-hydroxyethyl acrylate is reacted with isophorone diisocyanate in the presence of a dibutyltin dilaurate catalyst, followed by reaction with a bisphenol 'A' epoxy resin. For optical fibre coatings, a copolymer of 2,4-TDI and 4000-polyisopropylene polyoxytetraethylene glycol, and hydroxyethyl acrylate is mixed

with phenyloxyethyl acrylate, N-methyl-pyrrolidone, and alpha-methacryloylpropyl trimethoxysilane. This is UV cured using benzildimethylketal as photoinitiator [73].

### **2.2.2.2 Multicomponent urethane acrylates**

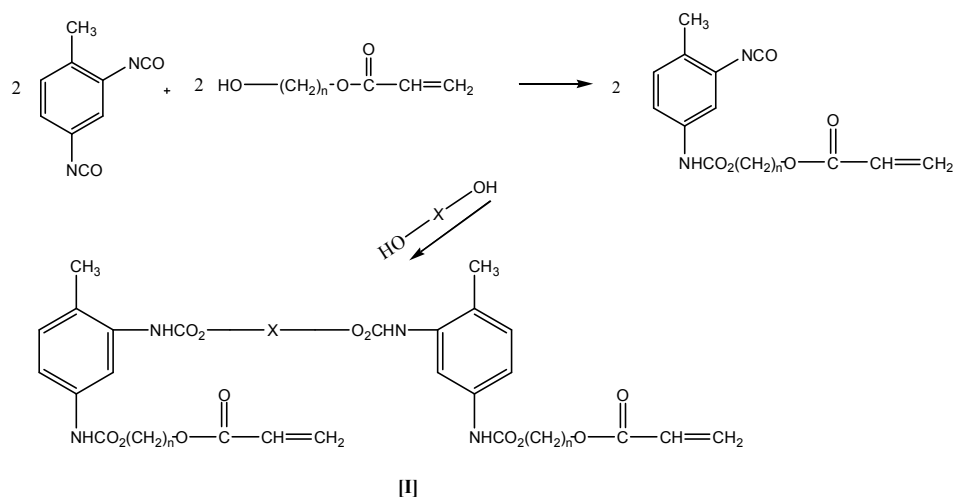
If instead of totally reacting a diisocyanate with a hydroxy acrylate, a portion of the acrylate is replaced by one or more hydroxy functional materials, then an immense range of structures is possible. This possibility is enhanced if the alternative hydroxy materials have multi-hydroxy functionality. Therefore, the range of properties is too large for typical urethane acrylate properties to be given. Owing to the complexity of these materials, even identical stoichiometric mixtures may yield products with significantly different properties under different reaction conditions. Viscosity is one example of a property that can vary dramatically. Flexible urethane acrylates can be made by the reaction of a diisocyanate with a long chain glycol. The half adduct of a diisocyanate acrylate may also be used. Aliphatic diol polyethers, such as polyethylene glycol, polypropylene glycol and caprolactone polyols, are widely used for this purpose, as are polyesters with an excess of hydroxy groups. As the flexibility increases, the hardness, speed of cure, and solvent resistance of the films decrease. A hard urethane acrylate could be formed from a highly branched multifunctional polyol like pentaerythritol, and a diisocyanate and hydroxy acrylate, or a diisocyanate and hydroxy acrylate half adduct. It may be necessary to select reactants to ensure that steric hindrance does not cause incomplete reaction. There are two possible methods of preparing the same urethane acrylate when a modifying hydroxyl component is used. In the first method, the diisocyanate and the hydroxy acrylate (or methacrylate) are reacted and the half (or partial) adduct is then reacted with the modifying hydroxy compound. In the second method, the modifying hydroxy compound is reacted with the diisocyanate and the resulting product is then reacted with the hydroxy acrylate. The two processes can be summarised as in Figure 2.39.



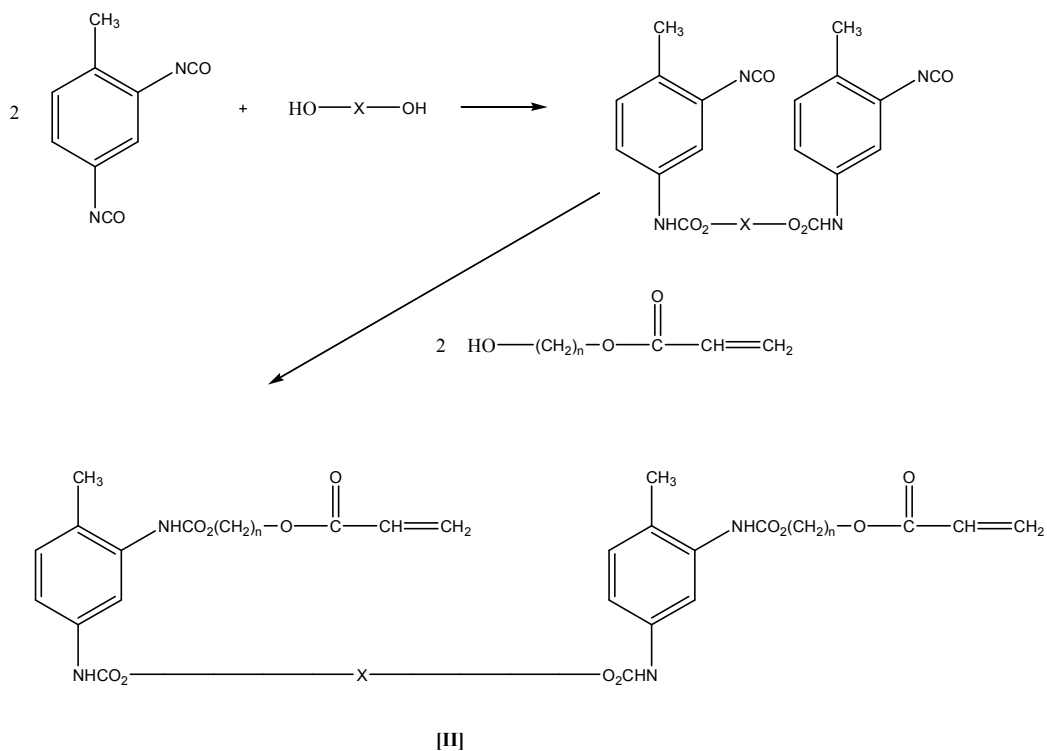
**Figure 2.39:** Two alternative processes for preparing a modified urethane acrylate

The incorporation of non-acrylate (or non-methacrylate) hydroxyl containing components into urethane acrylate structures can vary. The order of addition to the reaction mixture, the type of hydroxyl functionality, the difference in reactivity between the isocyanate groups, and possible differences in reactivity of the hydroxyl groups, may all have different impacts. For symmetrical diisocyanates, the order of addition is unimportant. For asymmetric diisocyanates (like 2,4 TDI and IPDI) and equivalent amounts of hydroxy acrylate and polyol hydroxyl groups, the order of addition is important. Consider 2,4 TDI for the purposes of illustration. The same argument applies for IPDI. If the hydroxy acrylate is added before a polyol, represented as HO-X-OH (Figure 2.40), then structure [I] is the predominant product, whereas structure [II] predominates if the hydroxy acrylate is added after the polyol.

(A) Hydroxy acrylate before polyol



(B) Polyol before hydroxy acrylate

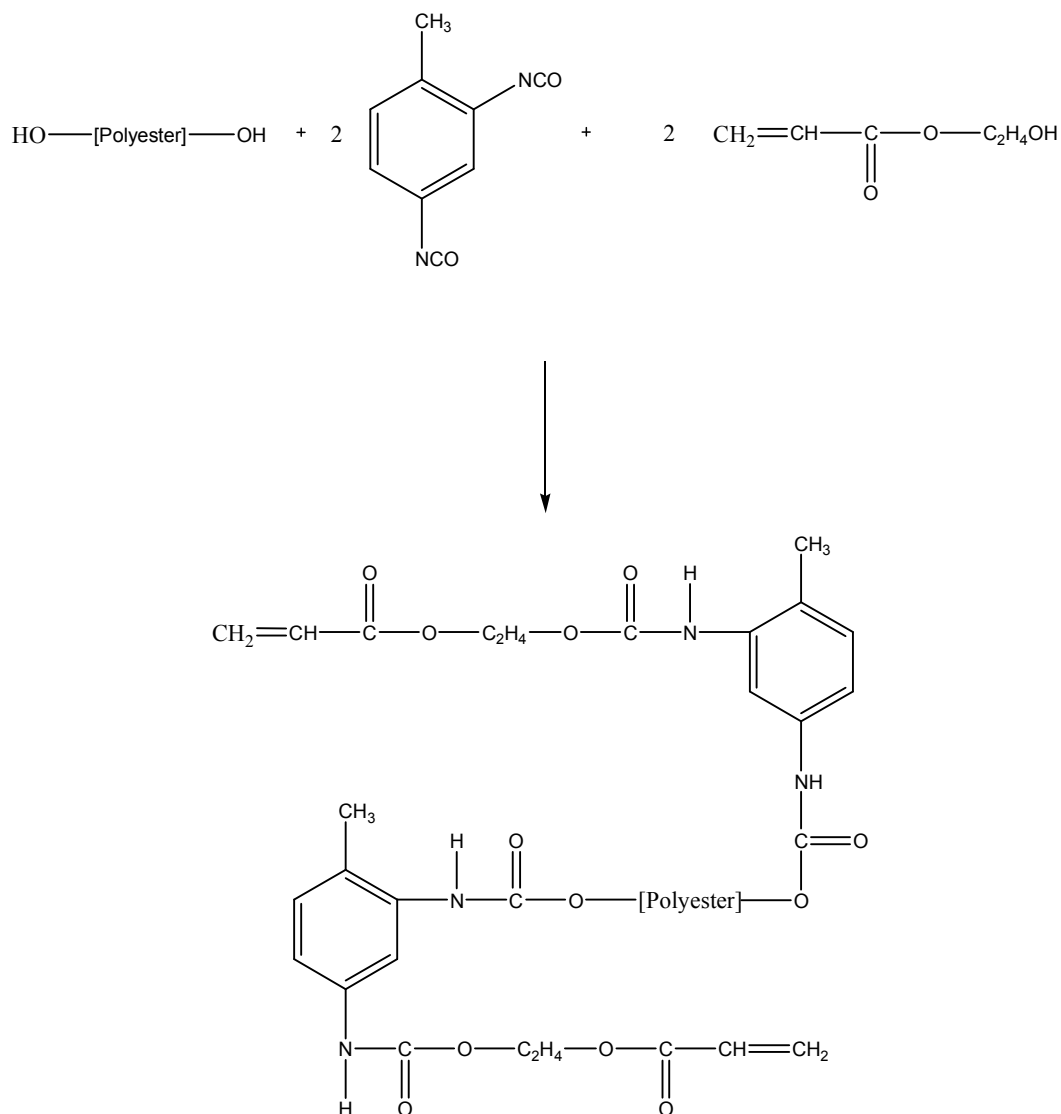


**Figure 2.40:** Resulting Structures from the Reaction of 2,4 TDI, Polyol, and Hydroxy Acrylate, and their Order of Addition

The reactions are not restricted to diisocyanates. An example is a triisocyanate of the structure given in Figure 35, where “R” is C1-4 alkyl. This isocyanate is reacted with methylhydroxyalkyl methacrylates [74].



Reaction of this polyester (represented as HO-[Polyester]-OH) with TDI and hydroxyethyl acrylate (HEA) to produce a polyester modified urethane acrylate of approximate molecular weight of 1500 is shown in Figure 2.43.



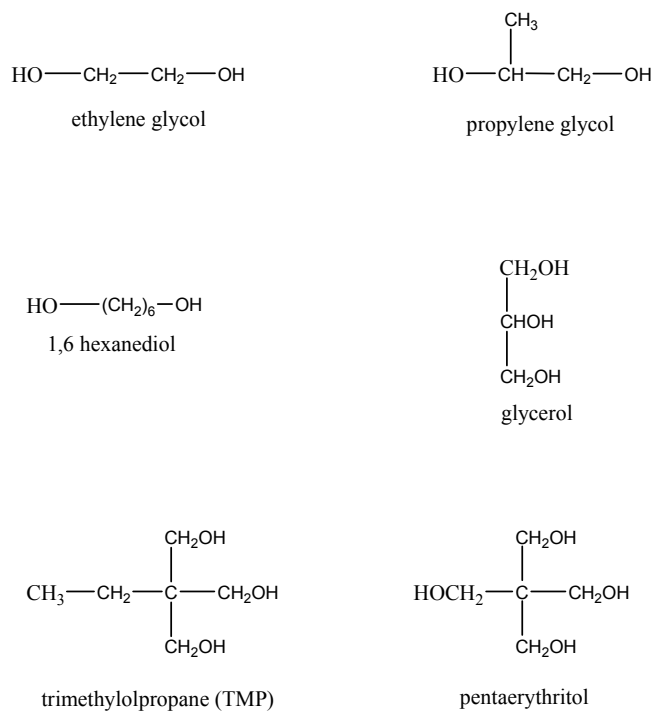
**Figure 2.43:** Preparation of polyester urethane acrylate

There are two possible methods. In the first, the polyester polyol, TDI, inhibitor, catalyst, and diluent (if necessary) are all charged to the reactor, and the air sparge started. The temperature is held at 30-40°C. The HEA is charged to the reactor when the isocyanate level reaches its theoretical value for complete reaction with the polyester polyol. The reaction is held at 50-60°C until there is less than 1 % of -NCO remaining at which time the temperature is raised to 80-90°C. The reaction is continued until the -NCO level is undetectable and, if necessary, -NCO scavengers are added. The prepolymer is cooled, diluted, if necessary, and discharged. In the

second method, the TDI, HEA, and inhibitor are charged to the reactor, heated to 30-50°C, and held until the isocyanate level reaches its theoretical value. The polyester, catalyst and diluent are then charged to the reactor and the temperature is held for 1-3 hours at 50-60°C. The process is then continued, as in the first case above. The first method is preferred by some manufacturers because there is less chance of an acrylate gel. The second method is preferred by other manufacturers because the former method results in free HEA. Obviously, TDI can be replaced by other diisocyanates and a variety of commercial products based on other diisocyanates exists.

#### 2.2.2.4 Polyol urethane acrylates

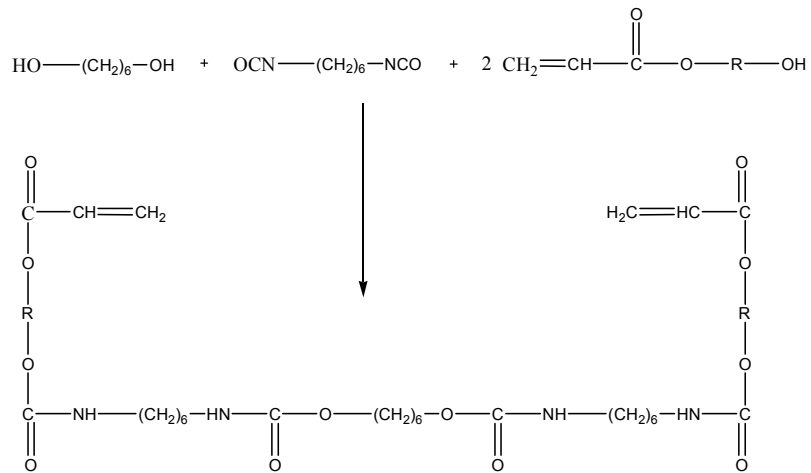
Hydroxyl groups are also present in molecules other than polyesters or polyethers. If there is more than one hydroxyl group per molecule, then the molecule can be described as a polyol. Most polyols that are not polyethers or polyesters, which might be used to form urethane acrylates, are relatively simple molecules (di-, tri-, or tetra-polyols) that are often used in polyester formulation. Examples of some of these polyols include ethylene glycol, propylene glycol, 1,6 hexanediol, glycerol, trimethylolpropane (TMP), and pentaerythritol. Structures of these molecules are shown in Figure 2.44.



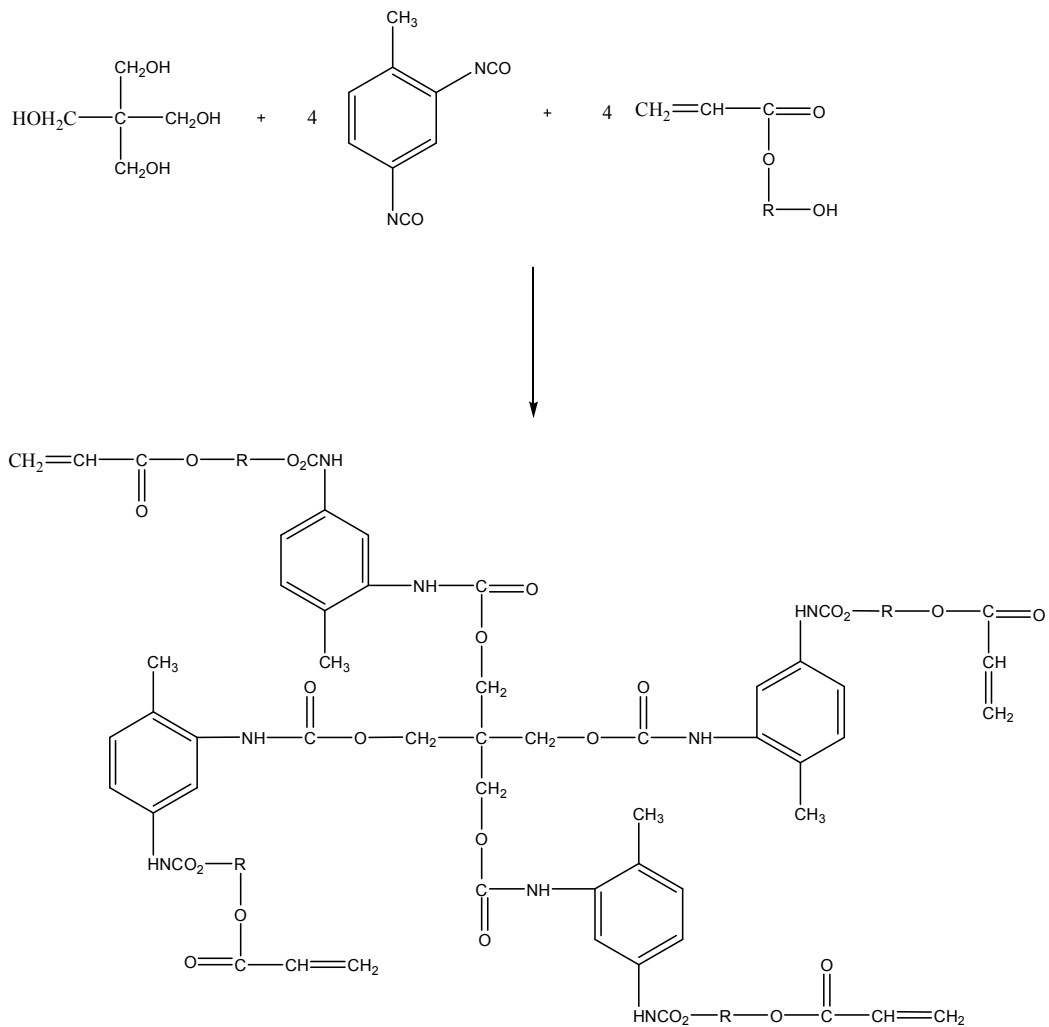
**Figure 2.44:** Structures of some non-polyether, non-polyester polyols

If a flexible chain polyol like 1,6 hexanediol is used to modify a urethane acrylate rather than the shorter chain ethylene glycol (on an OH/OH basis), then the resulting product is more flexible. This is partly due to the flexible nature of the longer polyol chain, but it is also due to the resulting lower crosslink density of the cured film. The groups between the hydroxyl groups can be considered to have a form of diluting effect. Urethane acrylates containing ethylene glycol tend to give a harder film than propylene glycol. If a highly structured polyol is used, then a rigid urethane acrylate can be formed. Frequently, the terms 'soft' and 'hard' are used interchangeably with 'flexible' and 'rigid'. Hard urethane acrylate prepolymers can be obtained through the reaction of diisocyanates with tri-, or higher functionality polyols, such as pentaerythritol and hydroxy monomers. Rigid branched structures are produced which are capable of high levels of crosslinking which give rise to hard, durable, and sometimes even brittle films. Such systems have a high viscosity and consequently a diluent must be added. Aromatic isocyanates tend to give harder films than aliphatic ones. Thus, if the end use permits, a hard urethane acrylate might be based on TDI, whilst a soft urethane acrylate may utilise HMDI (or an oligomer of HMDI). Formulations and processes for soft and hard urethane acrylates are similar to those for other modified urethane acrylates. Examples are shown in Figure 2.45.

**(A) Soft Urethane Acrylate "G"**



**(B) Hard Urethane Acrylate "H"**



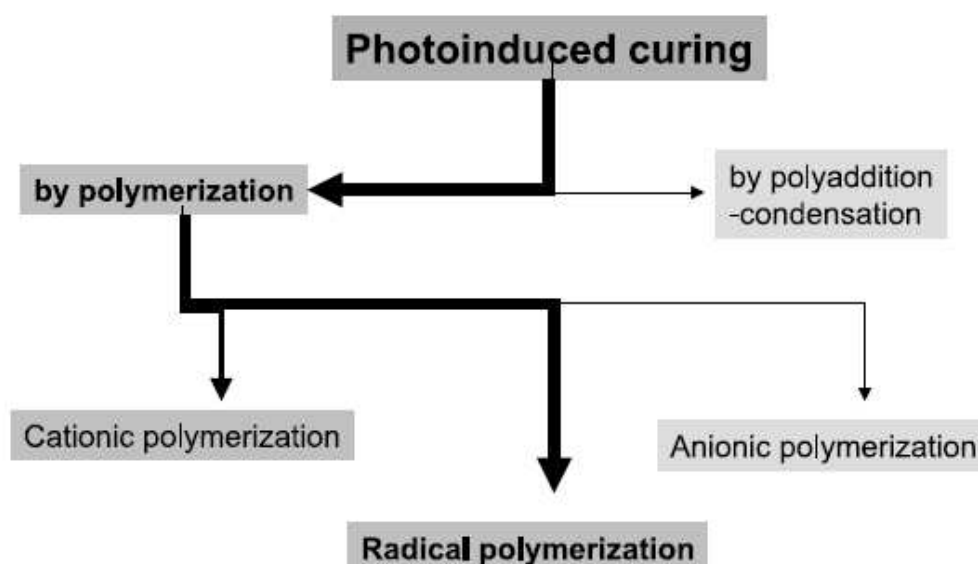
**Figure 2.45:** Preparation of a hard and a soft urethane acrylate

The use of hydroxypropyl acrylate (HPA), rather than hydroxyethyl acrylate (on a OH/OH) basis will further increase the flexibility of the cured film. This is due to three factors, namely. HPA is more flexible than HEA, HPA reduces the crosslink density of the resulting film and HPA, being slower curing, gives the film more time to relax during the crosslink process, thereby relieving some internal stresses.

## 2.3 UV curing

### 2.3.1 Photoinduced curing chemistry

Photoinduced curing can be realized as in the preparation of conventional linear polymers by a step like process, as used in polyaddition and polycondensation reactions or by a chain process occurring in polymerization reactions (Figure 2.46).



**Figure 2.46:** Possibilities of photoinduced curing

The photoinduced polyaddition technology has been for a long time the workhorse of photoresist technology, for example, the crosslinking of resins was achieved by photoinduced dimerization of cinnamates. This photodimerization is an example of a direct photoreaction where every step of polymer built-up is initiated by an absorbed photon, thus every single reaction step is dependent on the quantum yield of the photoreaction (generally very much smaller than 1) [75]. On the contrary, in polymerization reactions induced by light only the initiating step is dependent on the

photoreaction ( $\Phi < 1$ ). The photopolymerization reaction then is a chain reaction, where one produced initiator radical can add up to several thousand monomer units, thus the overall quantum yield of the total reaction is much bigger than 1. Whereas the photoinduced radical polymerization is now the mainstream technology, the photoinduced ionic curing reactions are not so well explored and developed, mainly due to the lack of easily available photoinitiators [76-78]. The basic principles of curing and network formation are similar in radical and cationic induced curing. The cationic curing has its main advantages in the oxygen insensitive curing and in the good adhesion mainly to metals achieved with the cationic curable epoxy systems. The UV curing technology is based on the photoinitiated rapid transformation of a reactive liquid formulation into a solid coating film. The initiating species may be a cation, an anion or a radical. The vast majority of UV curable coatings are based on radical producing photoinitiators. The main components of such formulations based on radical polymerizations are reactive resins containing a plurality of polymerizable double bonds, which govern mainly the desired properties of the final coating; copolymerizable, monomeric diluents, which are responsible for the reduction or adjustment of the viscosity of the formulation, a function taken by the solvent in conventional formulations; photoinitiators or a photoinitiating system containing photoinitiator and photosensibilizer or coinitiators; and, if necessary, other coating additives, like surface active additives, slip additives, fillers, pigments, light stabilizers, etc. The chemistry involved in the radical initiated UV induced crosslinking can be divided into the three steps, initiation, propagation and termination. Although the UV energy applied in photocuring may cleave C–C and C–H bonds, the commonly used monomers do not produce sufficient amounts of initiating species, which is due to low absorbance and poor cleavage efficiency. Thus, a special photoinitiator is usually applied, which is excited and ultimately yields via intersystem crossing, accompanied by various deactivation reactions, the formation of a radical species, which can initiate radical polymerization. The following polymerization reaction follows almost exactly the rules of conventional radical polymerization. Thus, only the initiation step is different to thermal initiated radical polymerization. The light absorption and the following processes are outlined in a Jablonski diagram (Figure 2.47). The process starts with the absorption of a photon by the photoinitiator molecule, which results in excitation of an electron into higher singlet states.

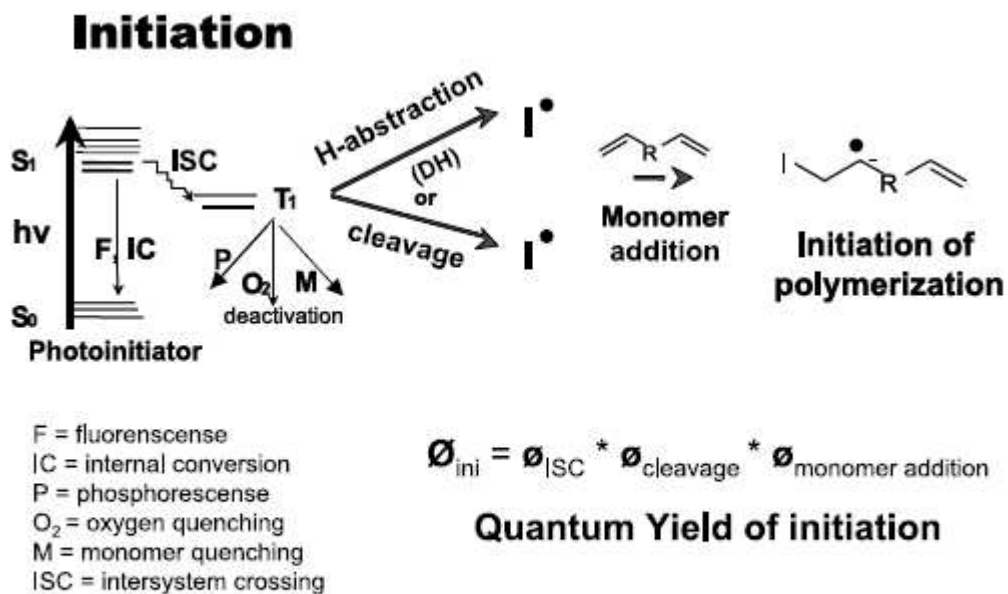
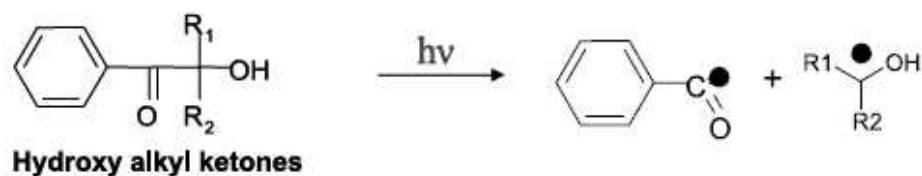


Figure 2.48: Jablonsky-type diagram for photoinduced radical photoinitiation

### $\alpha$ - cleavage type photoinitiators (type I)



### H-abstraction type photoinitiators (type II)

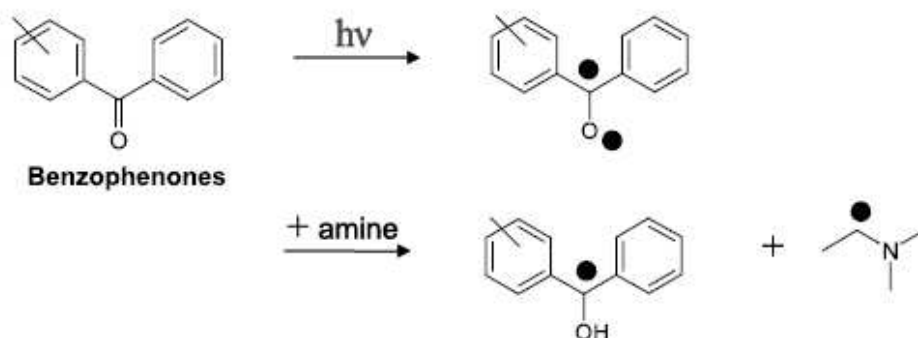


Figure 2.49: Photoinitiator types

From these excited states, various processes can follow. First, deactivation can proceed by radiationless internal conversion and evolution of heat back to the ground state or by emission of fluorescence. Second, by intersystem crossing (ISC) an electron spin inversion leads to the excited triplet state. The photochemical processes which lead to the desired active species (e.g., free radicals) often take place from the excited triplet state, where the molecule possesses two unpaired electrons, rather than from the singlet state. The formation of the reactive species, namely free radicals, competes with further deactivation processes, like monomer quenching, oxygen quenching and phosphorescence. The direct oxygen quenching of the photoinitiator excited states is not very likely in the case of the extremely shortlived triplet states of  $\alpha$ -cleavable type photoinitiators, but much more pronounced in the hydrogen abstraction type owing to the relatively long-lived triplet states [79]. From the triplet state two main reactions can lead to initiating species, the intramolecular scission of an  $\alpha$ -bond, or the intermolecular abstraction of a hydrogen atom. The intramolecular scission is the most effective process in the formation of radicals, since the hydrogen abstraction is a bimolecular type reaction, which is diffusion controlled and may be accompanied by several deactivation reactions. The quantum yield of initiation, representing the number of growing chains per photon absorbed reflects the importance of the processes leading to initiation over all the indicated processes of deactivation. The efficiency of the photoinitiation is a function of different quantum yields, since several side reactions can occur in every step. Thus, the overall yield of initiation is a complex function of different quantum yields, represented exemplarily in Figure 2.49. Two examples of photoinitiators, an alpha type scission initiator and a hydrogen abstraction type photoinitiator are shown in Figure 2.49. Propagation (Figure 2.50) is the key step to very efficient curing, since it is a chain reaction where for instance one produced radical can add more than 1000 monomer units within a fraction of a second. The steps after the initiation are very similar to the normal radical polymerization of monofunctional monomers, which are widely used to synthesize thermoplastic polymers, like polyethylenes, polypropylene or polystyrenes. The main difference in coating systems is the use of multifunctional monomers or oligomers, which leads to the formation of networks. In the propagation reaction transfer reactions also often play a significant role, where the growing radical chain does not add to another monomer unit, but abstracts hydrogen radical from a neighbouring R-H group. The remaining radical can then start another

growing chain, thus leading to the termination of the growing polymer chain, but not to the termination of the chain reaction. The reaction of the radicals with oxygen does not play a significant role in the polymerizations of linear polymers, since they are normally conducted under inert conditions. However, the curing of coatings is normally performed under atmospheric conditions, thus, the oxygen interference plays a major role. The termination reactions are also manifold (Figure 2.51). Besides the termination with an initiator radical, several other termination reactions play a role, especially the recombination of growing radical species or elimination reaction of the chain end.

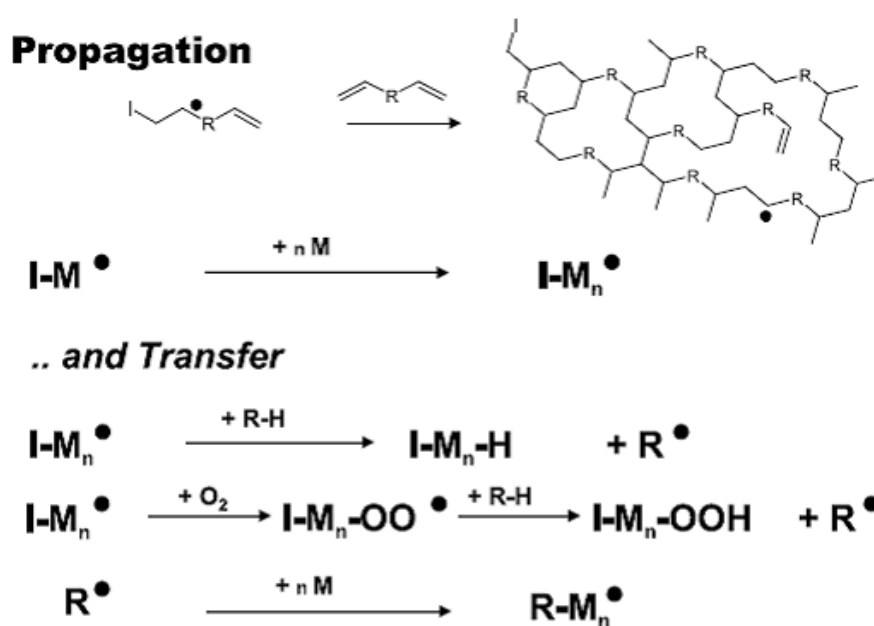


Figure 2.50: Propagation and transfer

**Termination**

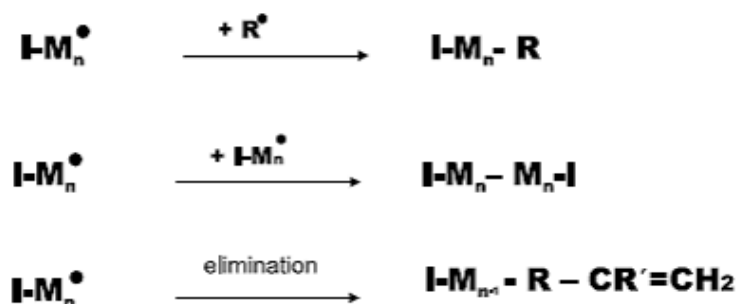


Figure 2.51: Termination reaction

### **2.3.2 Advantages and drawbacks of uv coatings**

Economical advantages are energy saving (commonly rapid cure at room temperature), high production speed, small space requirements and immediate post cure processing possible.

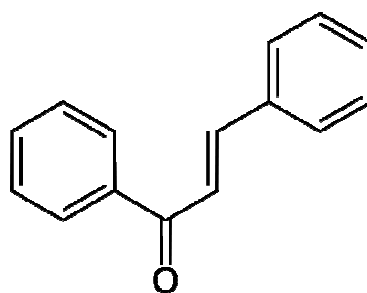
Ecological advantages are in general solvent free formulations (VOC reduction), possibility of easy recycling (waste reduction) and energy saving.

Performance advantages are low substrate heating, high product durability, application versatility, high scratch resistance and chemical resistance, exceptional abrasion, stain and solvent resistance and superior toughness.

Drawbacks are material costs are higher than, e.g., alkyds, polyesters or epoxies, 3D curing equipment development is in its infancy, UV curing in the presence of UV stabilizers decelerated, oxygen inhibition at the surface (in many radical curing systems), sensitivity to moisture (cationic curing system), difficult through-cure of pigmented coatings (at thicknesses  $>5 \mu\text{m}$ ), topics to eliminate weaknesses, improving adhesion to metal, plastics, minimizing skin irritation caused by some reactive diluents, reducing odor (of the formulations), reducing extractables of cured coatings, improving photoinitiators (cost, migration, volatility) and direct food contact packaging approval.

### **2.3.3 Chalcones**

Chalcone (and related compounds "chalconoids") is an aromatic ketone that forms the central core for a variety of important biological compounds, which are known collectively as chalcones. They show antibacterial, antifungal, antitumor and anti-inflammatory properties. Some chalcones demonstrated the ability to block voltage-dependent potassium channels [80].

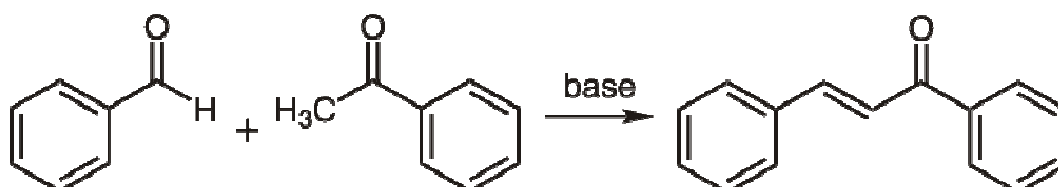


**Figure 2.52:** Chalcone group

They are also intermediates in the biosynthesis of flavonoids, which are substances widespread in plants and with an array of biological activities. Chalcones are also intermediates in the Auwers synthesis of flavones. Methyl hydroxychalcone, found in cinnamon, was thought to be an insulin mimetic, improving insulin response of diabetics [81]. It has since been determined that a flavonoid is responsible for the insulin-like biological activity [82].

### 2.3.3.1 Chemical synthesis of chalcones

Chalcones can be prepared by an aldol condensation between a benzaldehyde and an acetophenone in the presence of sodium hydroxide as a catalyst.



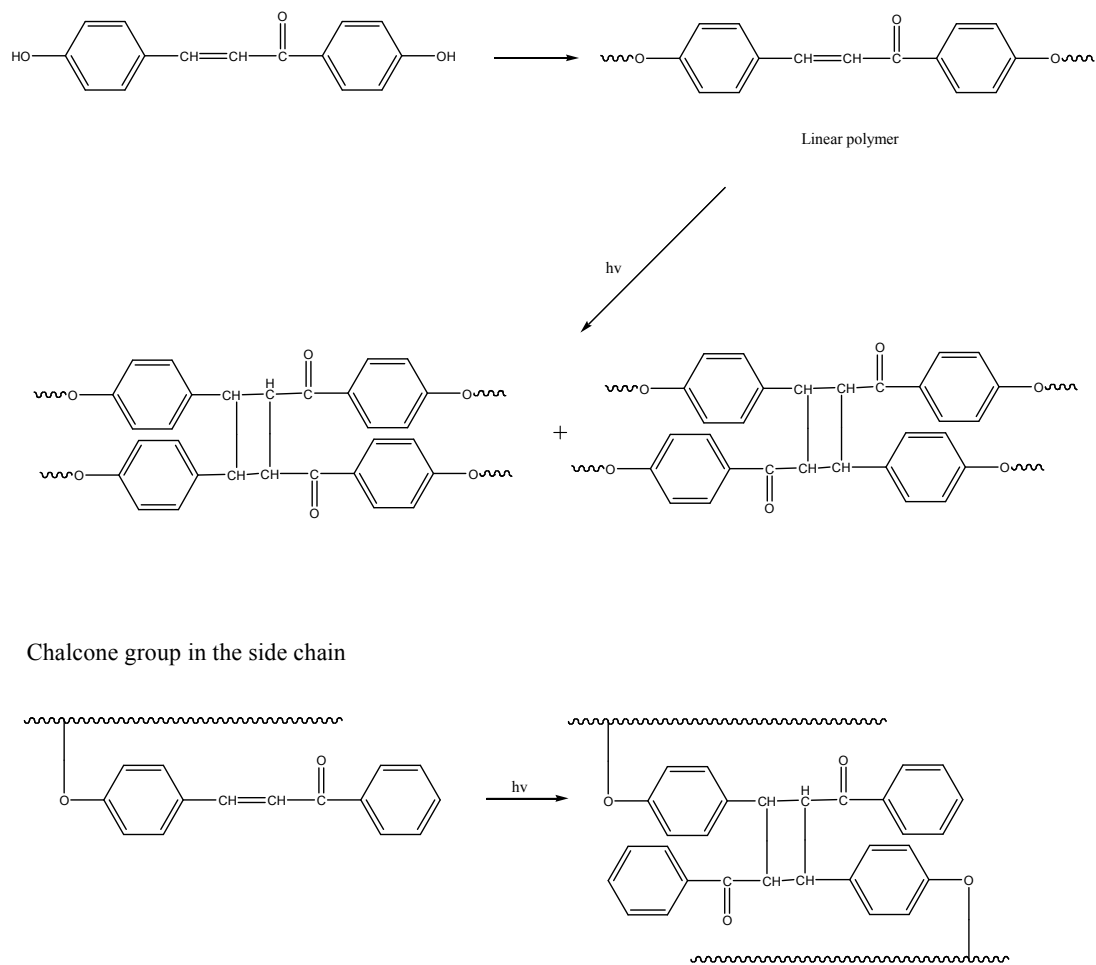
**Figure 2.53:** Formation of chalcones

This reaction has been found to work without any solvent at all - a solid-state reaction [83]. In a study investigating green chemistry synthesis, chalcones were also synthesized from the same starting materials in high temperature water (200 to 350 °C) [84].

### 2.3.3.2 Photocycloaddition reaction of chalcones

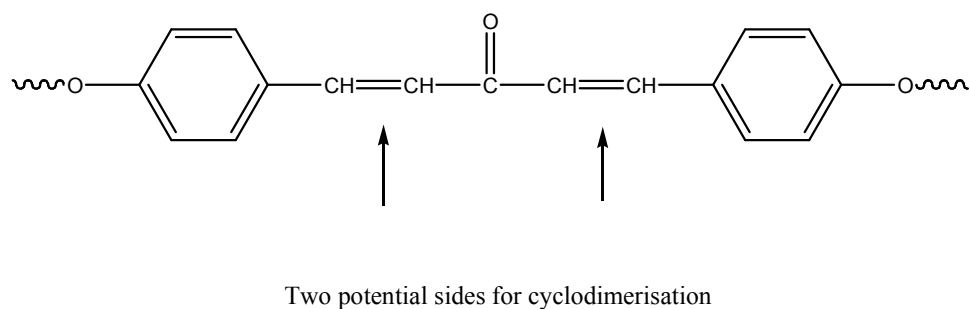
Photosensitive polymers with photocrosslinkable groups have gained a considerable interest in recent years owing to a wide variety of applications in the field of macro- and microlithography, printing, liquid crystalline display, nonlinear optical (NLO) materials, holographic head-up-display, integrated circuit technology, photocurable

coatings, photoconductors, energy exchange materials, DNA microchips, tissue engineering, biosensors, in column materials in chromatography etc. UV radiation curing has been revealed as a powerful tool to crosslink rapidly the heat sensitive polymers and modifies, selectively in the illuminated areas, their physico-chemical characteristics. Photo-tuneable technology have found major openings in various industrial applications where its distinct advantages such as fast cure, selective cure and ambient temperature have allowed this environmental friendly technology to outclass more conventional processing techniques [85]. The photosensitivity of the materials is based mainly on the  $\pi$ -electron density of the photoactive chromophore (e.g.  $-\text{CH}=\text{CH}-$ ) [86]. Among the various photocrosslinkable groups,  $\alpha,\beta$ -unsaturated carbonyl unit has attracted particular attention due to its excellent photoreactivity at UV absorption wavelength [85]. It affords high sensitivity to UV radiation ( $\lambda = 300\text{-}350\text{ nm}$ ). Moreover, the absorption spectrum of the chalcone group closely matches the emission spectrum from a high pressure mercury lamp so that it is possible to achieve improved photocrosslinking efficiency [86]. Crosslinking with ultraviolet light is an excellent method for obtaining articles with thick cross-sections, with or without reinforcement, without significant heat buildup in the interior, which could damage the plastic. Polymers with chalcone or cinnamoyl group either in the backbone or side chain undergo crosslinking through  $[2\pi + 2\pi]$  cycloaddition of the carbon-carbon double bond upon irradiation with UV light and such polymers are regarded as negative-type photoresists (Figure 2.54).



**Figure 2.54:** Examples of the chalcone group in the backbone and in the side chain

To increase the probability of cycloaddition reaction, chalcones of the type shown in 2.55 were introduced.



**Figure 2.55:** Chalcone having enhanced reactivity

A statistical model was set up to investigate how the nature of the chalcone would influence the reactivity of the system and the one shown in Figure 2.55 was found to have the highest predicts reactivity [87]. These polymers with the properties of high photosensitivity, the ability to form films, good solubility before irradiation,

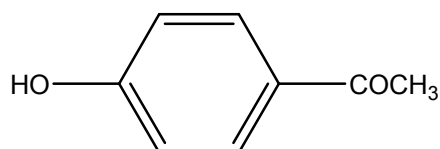
resistance towards solvents, plasmas and etching agents after crosslinking and good thermal stability are very important for commercial photoresist applications [85].

### 3.EXPERIMENTAL PART

#### 3.1 Materials

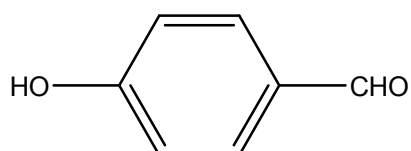
In the synthesis of chalcone modified urethane acrylates (UA-C) , 4-hydroxyacetophenone (Merck), 4-hydroxybenzaldehyde (Merck), 3,4-dihydro-2H-pyran (Merck), toluene-4-sulfonic acid monohydrate (Merck), isophorone diisocyanate (BAYER), polyethyleneglycol 1000 (Merck), 2-hydroxyethyl methacrylate (Laporte Performance Chemicals), hydroquinone, dibutyltinlaurate (Henkel), dipropyleneglycoldiacrylate (CYTEC Chemicals), 1,6-hexanedioldiacrylate (Sartomer Chemicals) and irgacure 819 (Ciba Chemicals) were used.

**4-hydroxyacetophenone** is an aromatic ketone with a hydroxyl group. It is used as a reactant in the synthesis of 4,4'-dihydroxychalcone.  $M_w$  is 136.15 g/mol.



**Figure 3.1:** 4-hydroxyacetophenone

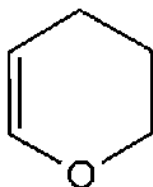
**4-hydroxybenzaldehyde** is an aromatic aldehyde with a hydroxyl group. It is used as a reactant in the synthesis of 4,4'-dihydroxychalcone.  $M_w$  is 122.12 g/mol.



**Figure 3.2:** 4-hydroxybenzaldehyde

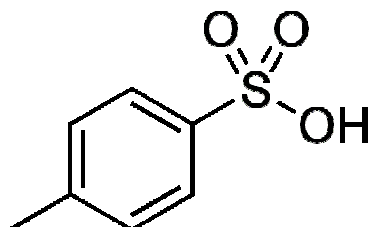
**3,4-dihydro-2H-pyran** is an organic molecule that protects OH groups as their tetrahydropyranyl, (THP) ethers, stable to bases, Grignard or organolithium reagents,

metal hydrides, etc, but readily removed by mild acid generally p-TsOH. It is used to protect OH groups of 4-hydroxyacetophenone and 4-hydroxybenzaldehyde in the synthesis of 4,4'-dihydroxychalcone.



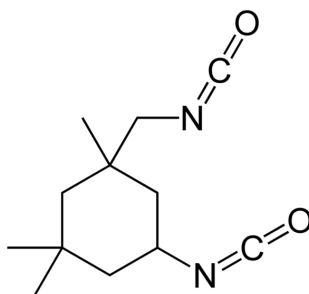
**Figure 3.3:** 3,4-dihydro-2H-pyran

**Toluene-4-sulfonic acid monohydrate (p-toluene sulfonic acid)** is an organic compound that is soluble in water, alcohols, and other polar organic solvents. Most often, TsOH refers to the monohydrate, TsOH.H<sub>2</sub>O. TsOH is a strong organic acid, about a million times stronger than benzoic acid. It is one of the few strong acids that are solid and, hence, conveniently weighed. Also, unlike some of the strong mineral acids (especially nitric acid, sulfuric acid, and perchloric acid), TsOH is non-oxidizing. It is used in the deprotection reaction of 4,4'-dihydroxychalcone.



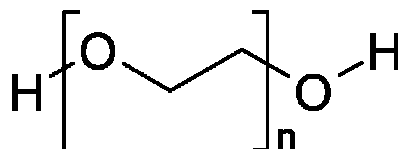
**Figure 3.4:** 3,4-dihydro-2H-pyran

**Isophorone Diisocyanate** is an aliphatic diisocyanate with a  $M_w$  of 222 g/mol. Density of IPDI is 1.061 g/ml. It is the least reactive among the isocyanates. It is used as a reactant in the synthesis of urethane acrylate.



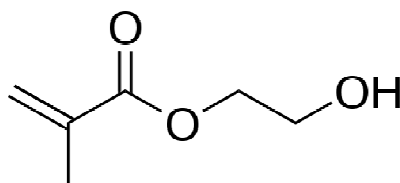
**Figure 3.5:** Isophorone diisocyanate

**Polyethyleneglycol 1000** is polyether polyol that was used in polyurethane synthesis. Its hydroxyl value is 107-108 and average molecular mass is 950 g/mol.



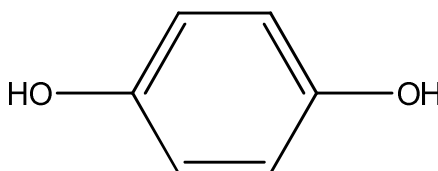
**Figure 3.6:** PEG 1000

**2-hydroxyethyl methacrylate** is used a monoacrylate used to give polyurethane system curability with UV light. Its molecular weight is 130.14 g/mol.



**Figure 3.7:** HEMA

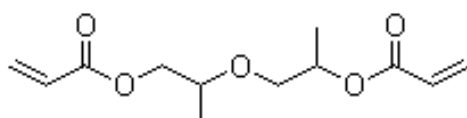
**Hydroquinone (benzene-1,4-diol)** was used as inhibitor. It is white solid and its density is 1,3g/cm<sup>3</sup>.



**Figure 3.8:** Hydroquinone

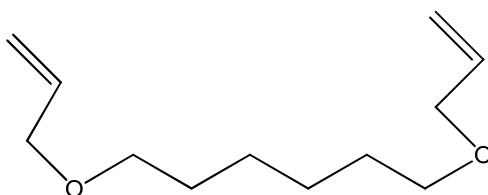
**Dibutyl tin laurate (DBTL)** is an organometallic tin compound that is used as a catalyst in the synthesis of polyurethaneacrylate. It allows allow the reaction to take place at a rapid rate and at lower temperatures

**Dipropylene glycol diacrylate (DPGDA)** is a difunctional monomer used to increase the gelation stability of UV film formulations at elevated temperatures. It has low viscosity, high  $T_g$ , and fast cure speed. It was used as a crosslinking agent in photopolymerization system.



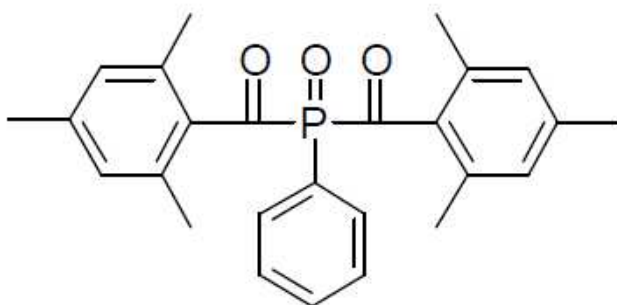
**Figure 3.9** Dipropylene glycol diacrylate

**HDDA (1,6-hexanedioldiacrylate)** is a low viscosity, fast curing monomer with low volatility, a hydrophobic backbone, and good solvency for use in free radical polymerization. It was used for lower viscosity and crosslinking in polymerization.



**Figure 3.10:** HDDA

**Irgacure 819** is a versatile photoinitiator for radical polymerisation of unsaturated resins upon UV light exposure.



**Figure 3.11:** Irgacure 819

## **3.2 Equipments**

### **3.2.1 Infrared analysis (IR)**

Infrared analyses were performed with Thermo Scientific Nicolet IS10 FT-IR spectrometer.

### **3.2.2 Nuclear magnetic resonance (NMR)**

<sup>1</sup>H-NMR analyses were performed with a Bruker 250 MHz Spectrometer.

### **3.2.3 UV spectroscopy analysis**

UV spectroscopy analyses were performed with Shimadzu PharmaSpec UV-1700 UV-Visible Spectrophotometer.

### **3.2.4 Thermogravimetric analysis (TGA)**

Thermogravimetric analyses were performed with a TA TGA Q50 instrument at a heating rate of 20 °C/min.

### **3.2.5 Contact angle meter**

The contact angles of cured UA-C films were measured by KSV CAM 100 instrument.

### **3.2.6 Gloss meter**

The gloss (20°, 60° and 85°) of cured urethane acrylate films were measured by BYK-Gardner (Micro-TRI) gloss meter.

### **3.2.7 Pendulum hardness tester**

A König Pendulum Hardness (BYK-Gardner) tester was used to measure the film hardness of the urethane acrylate films.

### **3.2.8 Tensile loading machine**

Zwick Z010 Universal Tensile Tester was used to determine properties such as modulus, elongation at break and strength.

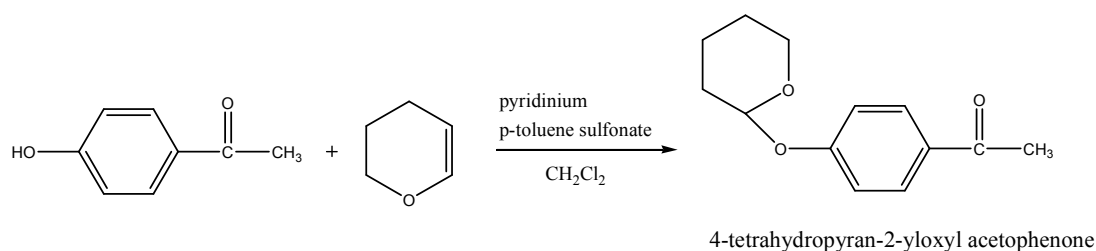
### 3.3 Synthesis

#### 3.3.1 Synthesis of 4,4'-dihydroxychalcone

4,4'-dihydroxychalcone was synthesized by Claisen-Schmidt condensation between 4-hydroxyacetophenone and 4-hydroxybenzaldehyde. For this purpose hydroxyl groups of 4-hydroxyacetophenone and 4-hydroxybenzaldehyde were protected with 3,4-dihydro-2H-pyran before the condensation reaction.

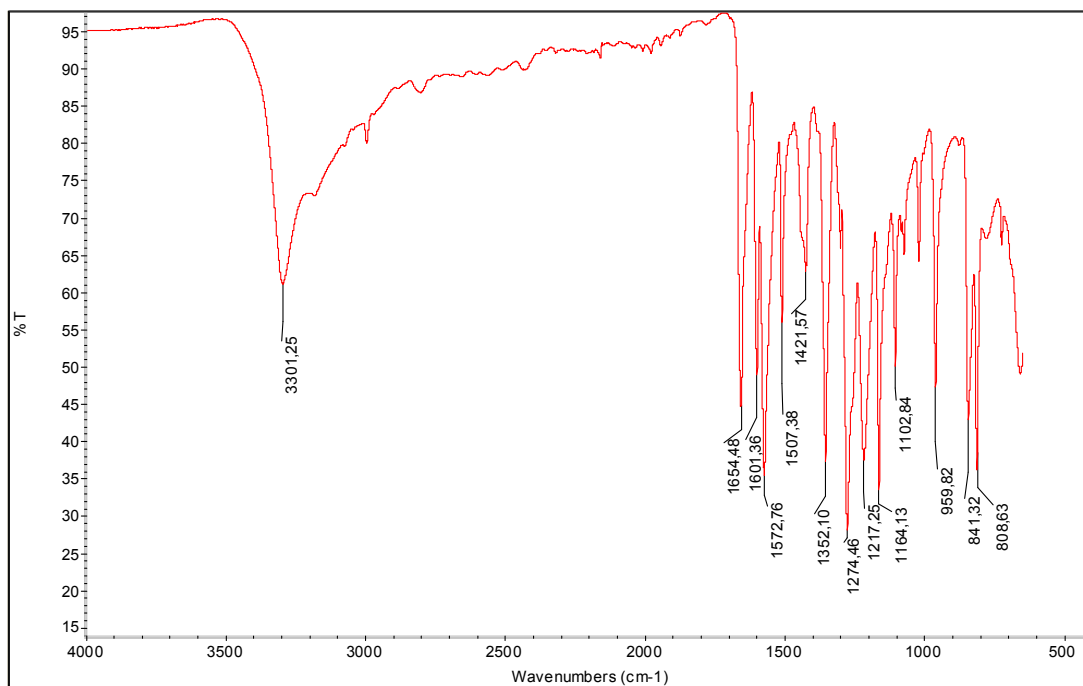
##### 3.3.1.1 Synthesis of 4-tetrahydropyran-2-yloxy acetophenone

The reaction was carried out in a three-necked 500 ml round bottom flask equipped with a magnetic stirrer. 73.4 mmol (10 g) 4-hydroxyacetophenone and 2.94 mmol (0.74 g) pyridinium p-toluenesulfonate (PPTS) were dissolved in 200 ml of  $\text{CH}_2\text{Cl}_2$  and stirred for 30 minutes. After that 146.9 mmol (13.4 ml) 3,4-dihydro-2H-pyran was added dropwise into the mixture. Then the reaction mixture was stirred for 4 hours at room temperature. Finally, the mixture was washed with distilled water for 2 times and once with a saturated NaCl aqueous solution. The solvent was evaporated and the product was dried in vacuum evaporator. Yield of the reaction is 80 % and the melting point is  $63^\circ\text{C}$  [88-89]. The yielding molecule is 4-tetrahydropyran-2-yloxy acetophenone. Completion of reaction was checked by both FT-IR and  $^1\text{H-NMR}$  spectroscopy techniques.

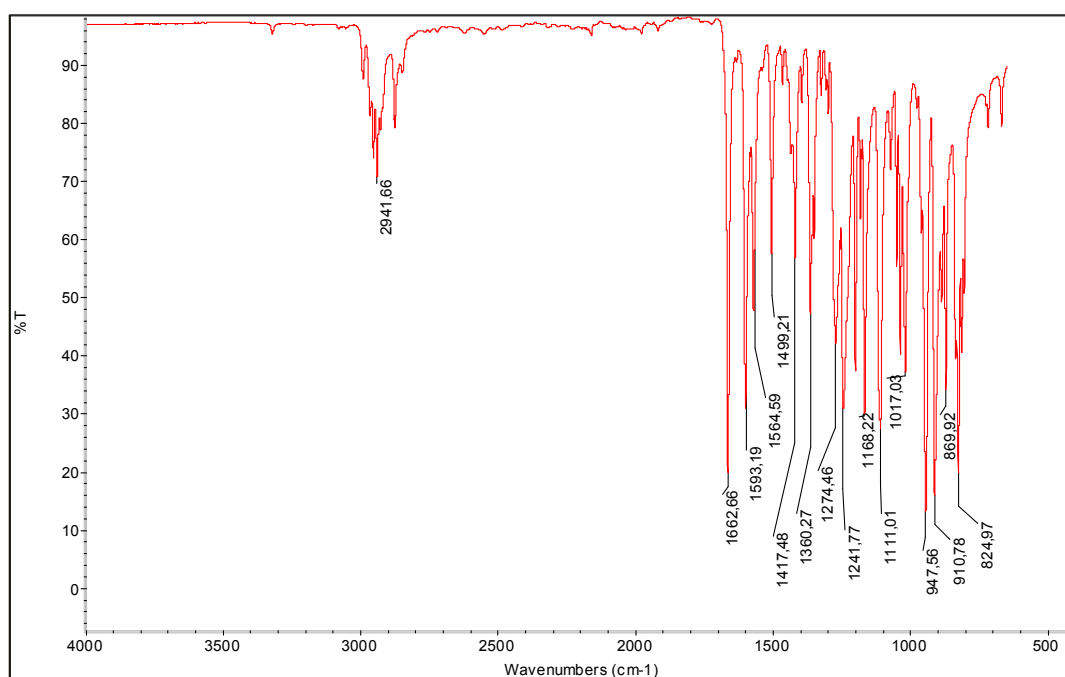


**Figure 3.12:** Synthesis of 4-tetrahydropyran-2-yloxy acetophenone

The FT-IR spectrum of 4-tetrahydropyran-2-yloxy acetophenone in Figure 4.3. shows that, the characteristic broad band peak of  $-\text{OH}$  group at  $3301\text{ cm}^{-1}$  disappears. The  $-\text{CH}_2$  peaks and the  $-\text{C-O-C}-$  peaks of the 4-tetrahydropyran-2-yloxy acetophenone occur at  $2941\text{ cm}^{-1}$  and  $1111\text{ cm}^{-1}$  respectively. The FT-IR spectrum of 4-hydroxyacetophenone is shown in Figure 3.13.



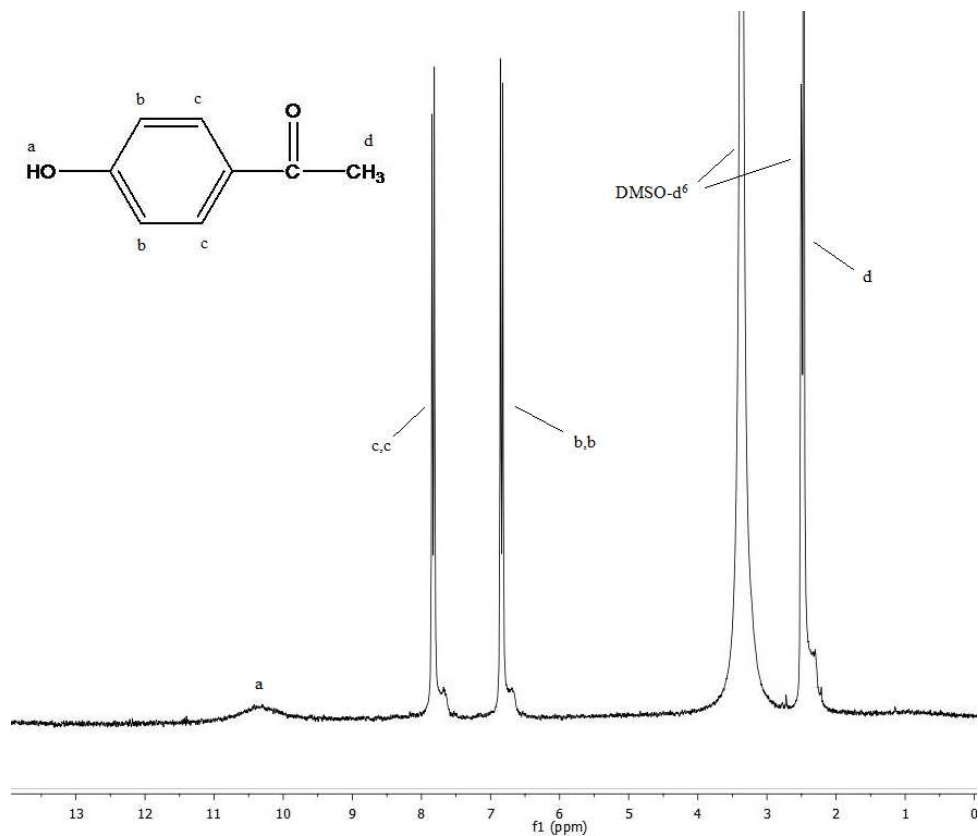
**Figure 3.13** IR Spectra of 4-hydroxyacetophenone



**Figure 3.14** IR Spectra of 4-tetrahydropyran-2-yl oxyl acetophenone

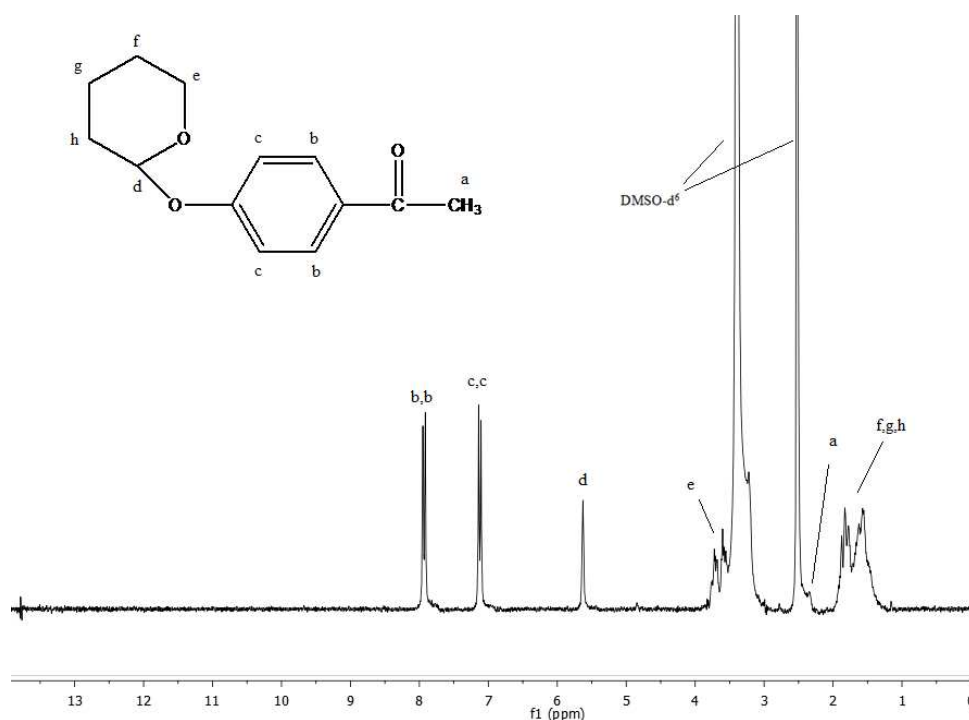
As a result of FT-IR analysis, we can clearly see that the protection of –OH group was satisfied via the formation of tetrahydropyranyl ether of the molecule. In

characterization of the molecule, NMR analysis was also applied.  $^1\text{H-NMR}$  spectrums of 4-hydroxyacetophenone and 4-tetrahydropyran-2-yloxy acetophenone (in  $\text{DMSO-d}^6$ ) are shown in Figure 3.15 and Figure 3.16 respectively.



**Figure 3.15.**  $^1\text{H-NMR}$  spectrum of 4-hydroxy acetophenone

According to the spectrum in figure 4.4, the  $-\text{OH}$  group of the 4-hydroxy acetophenone has a broad signal at 10.3 ppm.

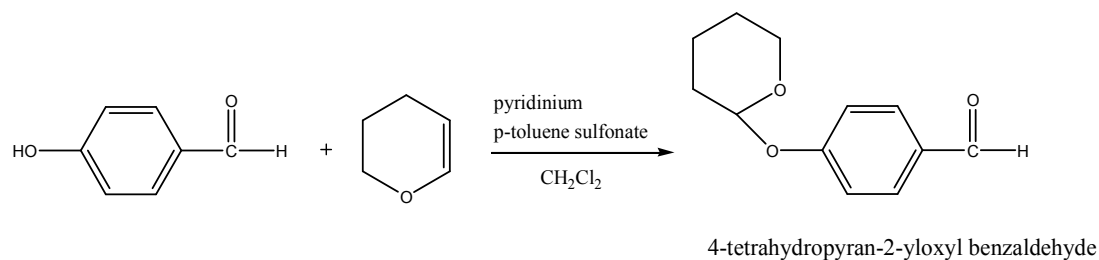


**Figure 3.16.**  $^1\text{H-NMR}$  spectrum of 4-tetrahydropyran-2-yloxy acetophenone

The spectrum shown in Figure 4.5 proves the expected structure of 4-tetrahydropyran-2-yloxy acetophenone. The broad signal of  $-\text{OH}$  group has disappeared and signals originating from etheric protons of the molecule occurred at 1.57-1.87, 3.60-3.72 and 5.62 ppm.

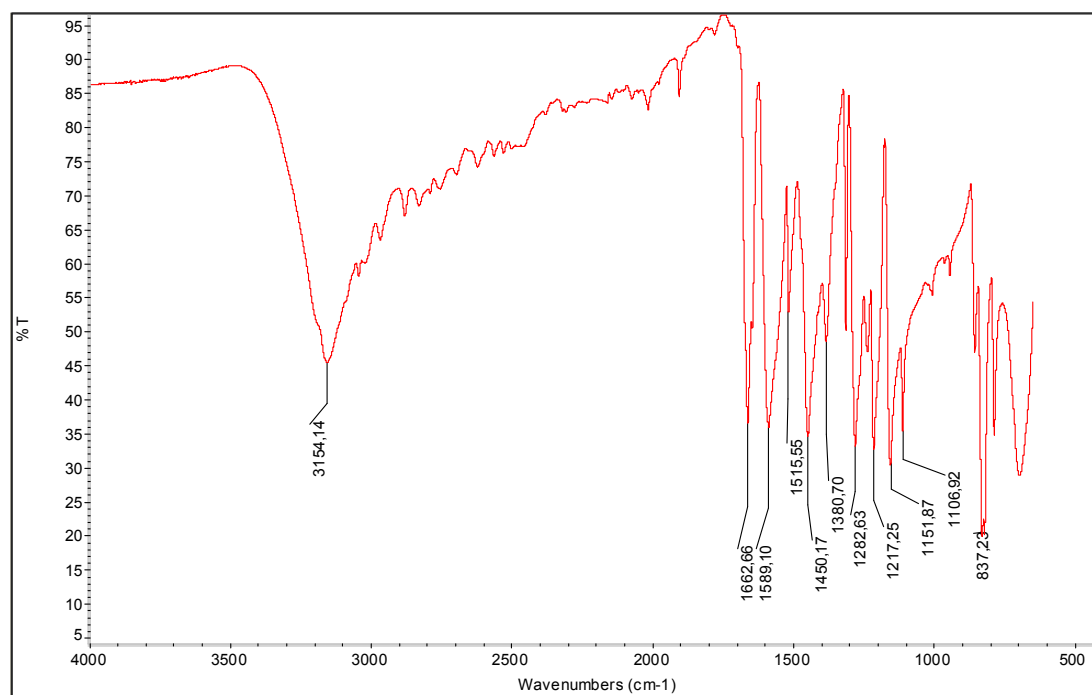
### 3.3.1.2 Synthesis of 4-tetrahydropyran-2-yloxy benzaldehyde

The reaction was carried out in a three-necked 500 ml round bottom flask equipped with a magnetic stirrer. 81.9 mmol (10 g) 4-hydroxybenzaldehyde and 3.28 mmol (0.82 g) pyridinium p-toluenesulfonate (PPTS) were dissolved in 200 ml of  $\text{CH}_2\text{Cl}_2$  and stirred for 30 minutes. After that 164 mmol (14.9 ml) 3,4-dihydro-2H-pyran was added dropwise into the mixture. Then the reaction mixture was stirred for 4 hours at room temperature. Finally, the mixture was washed with distilled water for 2 times and once with a saturated  $\text{NaCl}$  aqueous solution. The solvent was evaporated and the product was dried in vacuum evaporator. Yield of the reaction is 80 % [88-89]. The yielding molecule is 4-tetrahydropyran-2-yloxy benzaldehyde. Completion of reaction was checked by both FT-IR and  $^1\text{H-NMR}$  spectroscopy techniques.

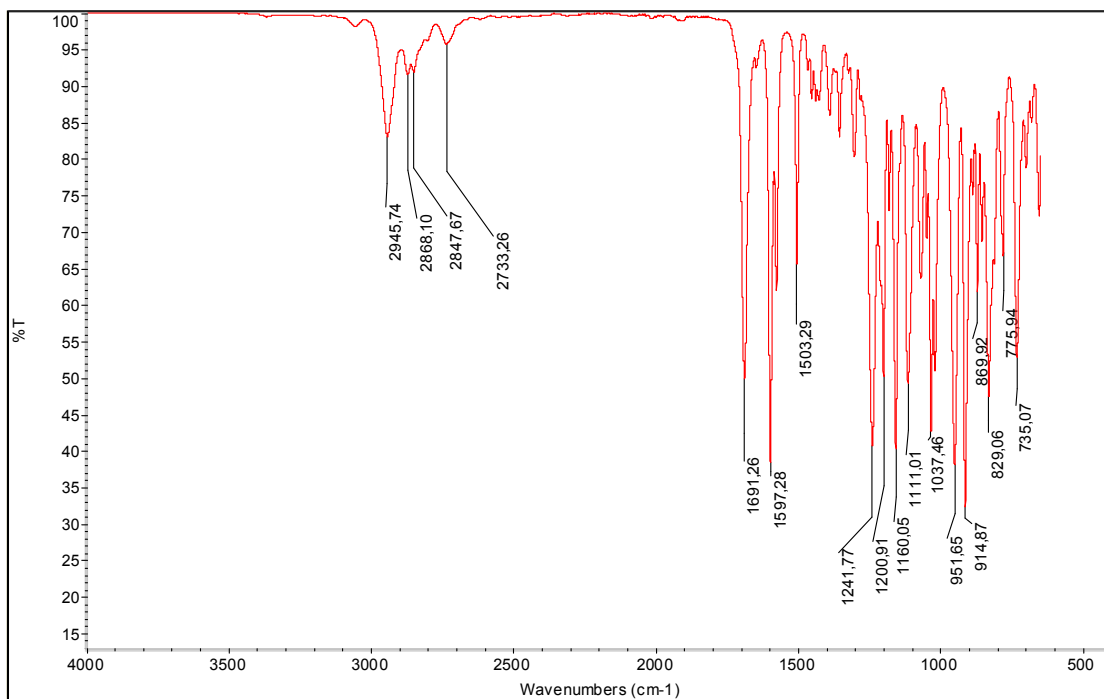


**Figure 3.17.** Synthesis of 4-tetrahydropyran-2-yloxy benzaldehyde

The FT-IR spectrum of 4-tetrahydropyran-2-yloxy benzaldehyde in Figure 4.8. shows that, the characteristic broad band peak of  $\text{-OH}$  group at  $3154\text{ cm}^{-1}$  disappears. The  $\text{-CH}_2$  peaks and the  $\text{-C-O-C-}$  peaks of the 4-tetrahydropyran-2-yloxy benzaldehyde occur at  $2945\text{ cm}^{-1}$  and  $1111\text{ cm}^{-1}$  respectively. The FT-IR spectrum of 4-hydroxybenzaldehyde is shown in Figure 3.18.

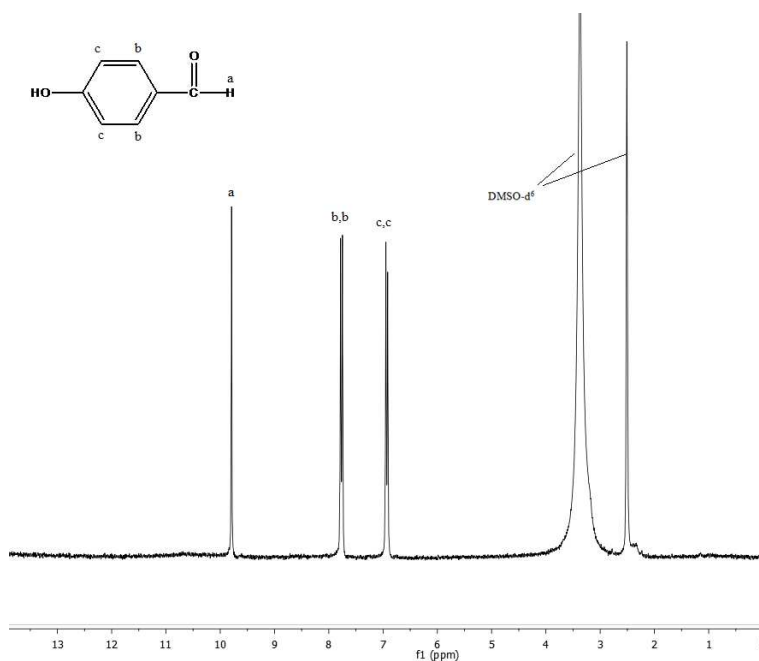


**Figure 3.18** IR Spectra of 4-hydroxybenzaldehyde



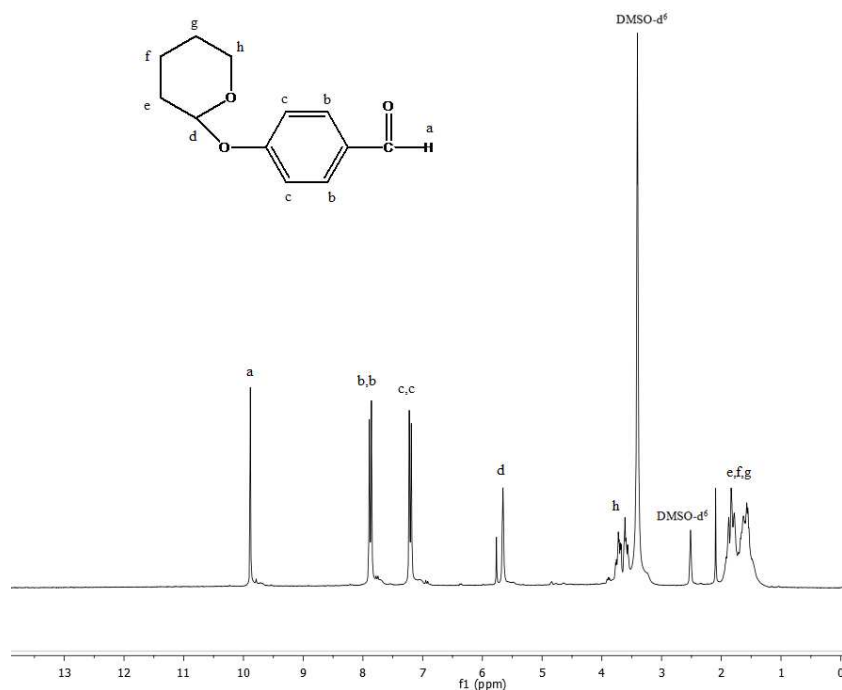
**Figure 3.19** IR Spectra of 4-tetrahydropyran-2-yloxy benzaldehyde

As a result of FT-IR analysis, we can clearly see that the protection of –OH group was satisfied via the formation of tetrahydropyranyl ether of the molecule. In characterization of the molecule, NMR analysis was also applied.  $^1\text{H-NMR}$  spectrums of 4-hydroxybenzaldehyde and 4-tetrahydropyran-2-yloxy benzaldehyde (in  $\text{DMSO-d}^6$ ) are shown in Figure 3.20 and Figure 3.21 respectively.



**Figure 3.20.**  $^1\text{H-NMR}$  spectrum of 4-hydroxy benzaldehyde

According to the spectrum in figure 4.9, signals originating from the aldehyde proton and the aromatic protons occur at 9.79, 7.78, 7.74, 6.94 and 6.91 ppm respectively.



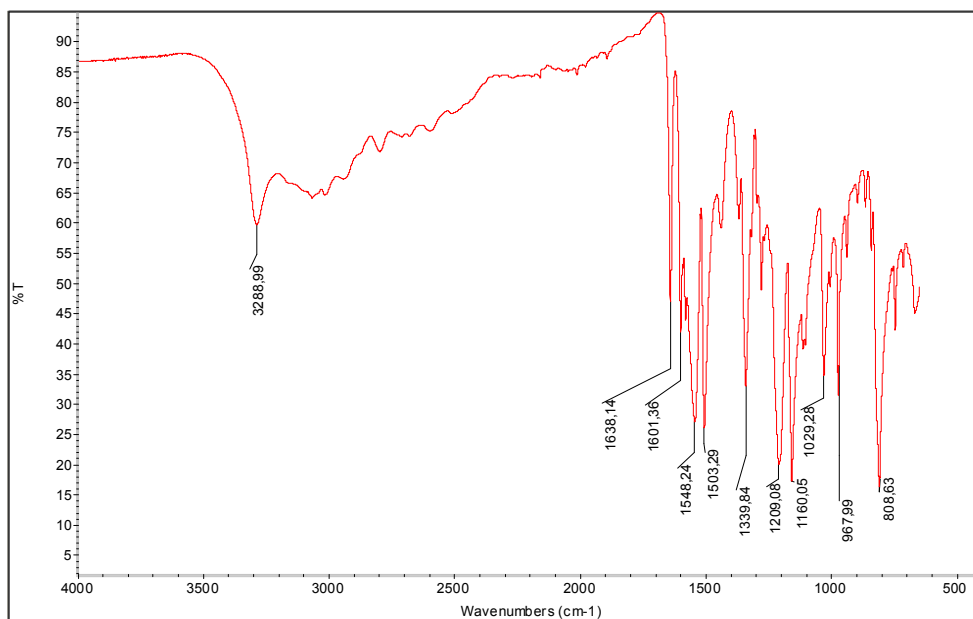
**Figure 3.21**  $^1\text{H-NMR}$  spectrum of 4-tetrahydropyran-2-yl benzaldehyde

The spectrum shown in Figure 4.10 proves the expected structure of 4-tetrahydropyran-2-yl benzaldehyde. The signals originating from etheric protons of the molecule occurred at 1.53-1.91, 3.56-3.77 and 5.65 ppm respectively.

### 3.3.1.3 Synthesis of 4,4'-dihydrochalcone

The reaction was carried out in a three-necked 500 ml round bottom flask equipped with a magnetic stirrer. 74.7 mmol (16.44 g) 4-tetrahydropyran-2-yl acetophenone was dissolved in 200 ml ethanol at 45°C. Then 74.7 mmol (15.39 g) 4-tetrahydropyran-2-yl benzaldehyde was added into the mixture. After that 40 % NaOH aqueous solution (7.47 g) was added dropwise into the solution with constant stirring. The mixture was stirred at room temperature for 12 h. The product was filtered and dried in vacuum evaporator. Yield 70 %.

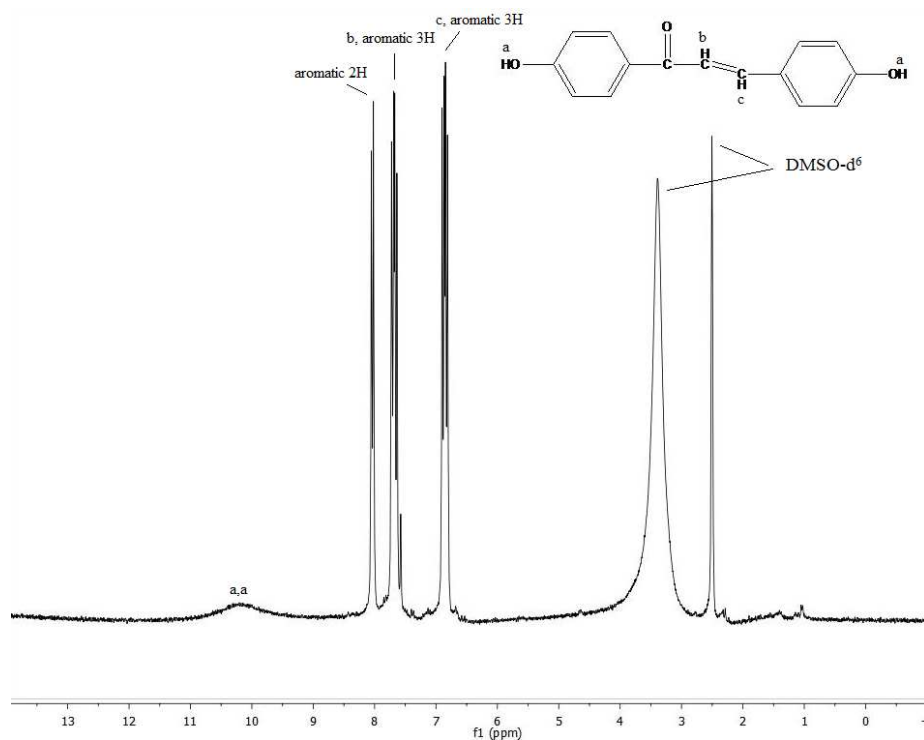




**Figure 3.23.** IR spectrum of 4,4'-dihydroxy chalcone

As a result of FT-IR analysis, we can clearly see that the deprotection of –OH group was satisfied via the p-toluenesulfonic acid and 4,4'-dihydroxychalcone was obtained. In characterization of the molecule, NMR analysis was also applied.

$^1\text{H-NMR}$  spectrum of 4,4'-dihydroxychalcone which was taken in  $\text{DMSO-d}^6$  is shown in Figure 3.24.



**Figure 3.24.**  $^1\text{H-NMR}$  spectrum of 4,4'-dihydroxy chalcone

The spectrum shown in Figure 3.24 proves the expected structure of 4,4'-dihydroxychalcone. The broad signal of –OH groups occurred at 10.30 ppm. Signals originating from ethylenic protons and aromatic protons occurred at 6.84-6.90, 7.63-7.72 and 8.01-8.05 ppm respectively.

### **3.3.4 Synthesis of urethane acrylate**

The reaction was carried out in a 100 ml round-bottom, three-necked flask equipped with a magnetic stirrer, thermocouple, spiral condenser, nitrogen inlet, and an outlet. All glassware was kept in the oven overnight and reaction system was cooled under nitrogen to remove humidity. The equivalent ratio of NCO/OH was 2.00. 8.33 mmol (7.91g) PEG 1000 was dissolved in 10 ml acetone at 40 °C. Secondly, a mixture of 16.66 mmol (3.70 g) IPDI and 10 ml of acetone was added dropwise into the flask at room temperature under nitrogen atmosphere. After that a specific amount of DBTL catalyst (0.1wt% based on the total weight of IPDI and polyol) was added into the solution at room temperature. Then the temperature of the system was set to 50°C in an oil bath. At the point that the –NCO peak remained constant, the conversion of NCO was determined by a standard dibutylamine back titration method. After this determination, the temperature of the system was set to room temperature. 0.01 g. hydroquinone was added into the reaction mixture and the mixture was stirred for 15 minutes. Then 16.66 mmol (2.166 g.) HEMA was dissolved in 5 ml of acetone and added dropwise into the system at room temperature. Lastly, a specific amount of DBTL catalyst (0.1wt % based on the total weight of IPDI and polyol) was added into the mixture at room temperature and the temperature of the system was set to 50°C. Disappearance of the characteristic -NCO peak at 2275 cm<sup>-1</sup> in the FT-IR spectrum confirmed that the reaction was completed.

### **3.3.5 Synthesis of chalcone modified urethane acrylate**

Preparation of UA-C25 is given as an example. UA-C50 and UA-C75 were synthesized by the same procedure described for UA-C25. The reaction was carried out in a 100 ml round-bottom, three-necked flask equipped with a magnetic stirrer, thermocouple, spiral condenser, nitrogen inlet, and an outlet. All glassware was kept in the oven overnight and reaction system was cooled under nitrogen to remove humidity. The equivalent ratio of chalcone/PEG 1000 was 1:3. 12.5 mmol (11.875 g)

PEG 1000 and 4.166 mmol (1.00 g) chalcone was dissolved in 15 ml acetone at 40°C. Secondly, a mixture of 33.3 mmol (7.41g) IPDI and 10 ml of acetone was added dropwise into the flask at room temperature under nitrogen atmosphere. After that a specific amount of DBTL catalyst (0.1wt% based on the total weight of IPDI and polyol) was added into the solution at room temperature. Then the temperature of the system was set to 50°C in an oil bath. At the point that the –NCO peak remained constant, the conversion of NCO was determined by a standard dibutylamine back titration method. After this determination, the temperature of the system was set to room temperature. 0.01 g. hydroquinone was added into the reaction mixture and the mixture was stirred for 15 minutes. Then 33.3 mmol (4.334 g.) HEMA was dissolved in 5 ml of acetone and added dropwise into the system at room temperature. Lastly, a specific amount of DBTL catalyst (0.1wt% based on the total weight of IPDI and polyol) was added into the mixture at room temperature and the temperature of the system was set to 50°C. Disappearance of the characteristic -NCO peak at 2275 cm<sup>-1</sup> in the FT-IR spectrum confirmed that the reaction was completed.

### 3.4 Preparation of formulations

Formulations were prepared for film formation via UV curing. The composition of the formulations are given in table.3.1.

**Table 3.1:** UV curing formulations

sample code	chalcone modification ratio of UA-C formulations (%)	modified resin (wt. %)	DPGDA (wt. %)	HDDA (wt.%)	photoinitiator (wt. %)
UA-C0	0	50	37	10	3
UA-C25	25	50	37	10	3
UA-C50	50	50	37	10	3
UA-C75	75	50	37	10	3

#### 3.4.1 Preparation of test samples

##### I. Free Films

To prepare free films, teflon mould having 10mm x 50mm x 1mm spaces was used. Free film formulations were prepared according to the table 3.1. Solutions were kept under vacuum approximately 30 minutes to remove bubbles, then poured into the spaces on the teflon mould. The mould was then placed under UV lamp and

irradiated for 300 seconds. The films were kept waiting for a couple of days before further tests. After that thermal and characterization analysis, chemical resistance and strain-stress tests were applied on these free films.

## II. Coated plexiglass plates

Firstly, temporary polyethylene coating films were pulled away by force from plexiglass plates surface. 1g of film solution for each plates was prepared. The plexiglass plates were put on smooth surface and coated with a film by pulling a glass rod from one side to another. Wet films were cured under UV lamp for 300 seconds and kept waiting for a couple of days before further tests. Cross-cut, pencil hardness, gloss, contact angle and pendulum hardness tests were applied on these plates.

### 3.5 Analyses

Following tests; Infrared Analysis (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA), Pendulum Hardness, Contact Angle Measurement, Gloss and Tensile tests, Pencil Hardness, Solvent Resistance and Gel Content were performed to monitor thermal, morphological and film properties of UA-C films.

#### 3.5.1 Infrared analysis

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification. Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10  $\text{cm}^{-1}$ , or wavelengths from 0.78 to 1000  $\mu\text{m}$ . It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies. IR absorption positions are generally presented as either wavenumbers ( $\tilde{\nu}$ ) or wavelengths ( $\lambda$ ). Wavenumber defines the number of

waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. The wavenumber unit ( $\text{cm}^{-1}$ , reciprocal centimeter) is more commonly used in modern IR instruments that are linear in the  $\text{cm}^{-1}$  scale. In the contrast, wavelengths are inversely proportional to frequencies and their associated energy. At present, the recommended unit of wavelength is  $\mu\text{m}$  (micrometers), but  $\mu$  (micron) is used in some older literature [90].

### 3.5.2 Nuclear magnetic resonance analysis

Nuclear magnetic resonance (NMR) is a property that magnetic nuclei have in a magnetic field and applied electromagnetic (EM) pulse or pulses, which cause the nuclei to absorb energy from the EM pulse and radiate this energy back out. The energy radiated back out is at a specific resonance frequency which depends on the strength of the magnetic field and other factors. This allows the observation of specific quantum mechanical magnetic properties of an atomic nucleus. Many types of information can be obtained from an NMR spectrum. Much like using IR to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR. All stable nuclides that contain an odd number of protons and/or of neutrons have an intrinsic magnetic moment and angular momentum, in other words a nonzero spin, while all nuclides with even numbers of both have spin 0. The most commonly studied nuclei are  $^1\text{H}$  (the most NMR-sensitive isotope after the radioactive  $^3\text{H}$ ) and  $^{13}\text{C}$ , although nuclei from isotopes of many other elements (e.g.  $^2\text{H}$ ,  $^{10}\text{B}$ ,  $^{11}\text{B}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{19}\text{F}$ ,  $^{23}\text{Na}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{35}\text{Cl}$ ,  $^{113}\text{Cd}$ ,  $^{129}\text{Xe}$ ,  $^{195}\text{Pt}$ ) are studied by high-field NMR spectroscopy as well. When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field. The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction  $\sigma$ .

The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical shift phenomenon. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and

given the symbol delta,  $\delta$ . In NMR spectroscopy, this standard is often tetramethylsilane,  $\text{Si}(\text{CH}_3)_4$ , abbreviated TMS. The chemical shift is a very precise metric of the chemical environment around a nucleus.

In this study, NMR analysis were used to support characterization of materials beside IR analysis.

### **3.5.3 UV spectroscopy analysis**

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state [91]. UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve. The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward-Fieser rules, for instance, are a set of empirical observations used to predict  $\lambda_{\text{max}}$ , the wavelength of the most intense UV/Vis absorption, for conjugated organic compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. Experimental variations such as the slit width (effective bandwidth) of the spectrophotometer will also alter the spectrum. To apply UV/Vis spectroscopy to

analysis, these variables must be controlled or accounted for in order to identify the substances present. The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law

where  $A$  is the measured absorbance,  $I_0$  is the intensity of the incident light at a given wavelength,  $I$  is the transmitted intensity,  $L$  the pathlength through the sample, and  $c$  the concentration of the absorbing species. For each species and wavelength,  $\epsilon$  is a constant known as the molar absorptivity or extinction coefficient. This constant is a fundamental molecular property in a given solvent, at a particular temperature and pressure, and has units of  $l / M * cm$  or often  $AU / M * cm$ .

The absorbance and extinction  $\epsilon$  are sometimes defined in terms of the natural logarithm instead of the base-10 logarithm. The Beer-Lambert Law is useful for characterizing many compounds but does not hold as a universal relationship for the concentration and absorption of all substances. A 2nd order polynomial relationship between absorption and concentration is sometimes encountered for very large, complex molecules such as organic dyes (Xylenol Orange or Neutral Red, for example).

In this study, chalcone modified urethane acrylates are examined by UV spectroscopy to check the photocrosslinking ability due to the existence of chalcone groups. In-situ UV-Vis absorption spectra recorded as a function of UV exposure time. Results are given in Figure 4.7.

#### **3.5.4 Thermogravimetric analysis**

Thermogravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere [92]. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking [93].

In this study, thermal stability was evaluated using a Q50 TGA from TA Instruments. Film samples of 5–10 mg were placed in the sample pan and heated from 25 °C to 900°C under N<sub>2</sub> (flow rate: 90 mL/min) at an applied heating rate of 20°C /min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature. The results are given in Figure 4.9.

### **3.5.5 Gel content measurement**

A cured film sample ( $m_1$ ) was accurately weighted, and then added to the Soxhlet extractor with acetone as extraction agent for 6 hrs. The cured film was dried until its weight was constant ( $m_2$ ). Gel content of the cured film was calculated by equation, Gel content (%) =  $(m_2/m_1) \times 100\%$

Where  $m_1$  is the weight of the cured film sample;  $m_2$  is the residual weight of the cured film sample. The results are shown on the Table 4.2.

### **3.5.6 Solvent resistance**

The solvent resistance of the cured films was determined by immersing in various solvents ( $m_1$ , 0.005-0.03g g/10 ml) for one day. After than cured films were dried until its weight were constant. After drying, the films were reweighted ( $m_2$ ) and weight loss was calculated.

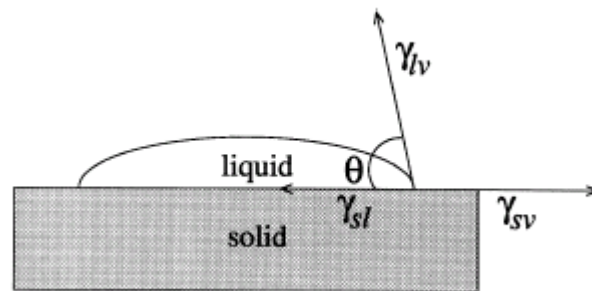
$$\text{Weight loss (\%)} = (m_1 - m_2) / m_1 \times 100$$

Solvents used in this test and results are shown in the Table 4.3-4.6.

### **3.5.7 Contact angle measurement**

The determination of solid-vapor  $\gamma_{SV}$  and solid-liquid  $\gamma_{SL}$  interfacial tensions is of importance in a wide range of problems in pure and applied science. Because of the difficulties involved in measuring directly the surface tension involving a solid phase, indirect approaches are called for: Several independent approaches have been used to estimate solid surface tensions, including direct force measurements; contact angles; capillary penetration into columns of particle powder; sedimentation of particles; solidification front interaction with particles; film flotation; gradient theory; Lifshitz theory of van der Waals forces; and theory of molecular interactions. Among these methods, contact angle measurements are believed to be the simplest [94]. Contact angle measurement is easily performed by establishing the tangent (angle) of a liquid drop with a solid surface at the base. The attractiveness of using

contact angles  $\theta$  to estimate the solid-vapor and solid-liquid interfacial tensions is due to the relative ease with which contact angles can be measured on suitably prepared solid surfaces. It will become apparent later that this seeming simplicity is, however, very misleading. The possibility of estimating solid surface tensions from contact angles relies on a relation which has been recognized by Young in 1805 [95]. The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: solid-vapor,  $\gamma_{SV}$ , solid-liquid,  $\gamma_{SL}$ , and liquid-vapor,  $\gamma_{LV}$  (Fig.3.26). This equilibrium relation is known as Young's equation where  $\theta$  is the Young contact angle, i.e. a contact angle which can be inserted into Young's equation. It will become apparent later that the experimentally accessible contact angles may or may not be equal to  $\theta_Y$ .



**Figure 3.25:** Scheme of a sessile-drop contact angle system

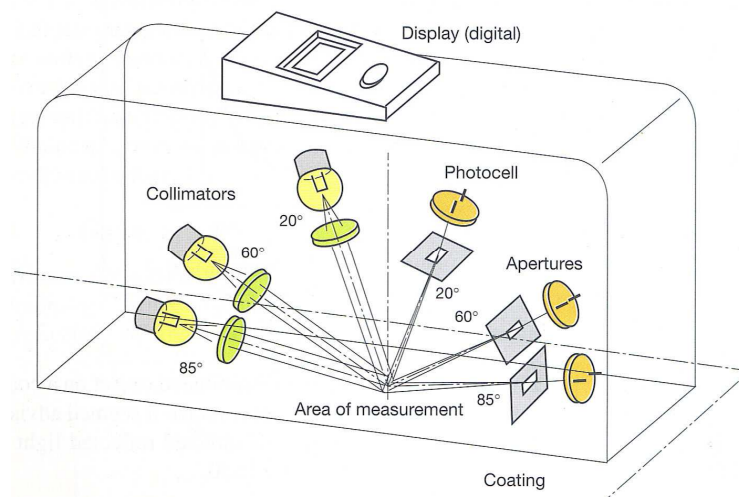
Contact angle is a well-known technique for investigating and controlling adhesion, surface treatments and cleaning, and polymer film modification. The wetting of solid substrates is a basic feature of many natural and industrial processes and contact angle is a simple, rapid, and sensitive method of characterizing the wettability of a solid surface [94]. The wettability of the film surfaces was measured using a contact angle KSV CAM100 system at ambient temperature. The equilibrium contact angles of  $5\mu\text{L}$  water droplets were measured by the sessile drop method. The contact angles were measured as follows: a  $5\mu\text{L}$  water droplet was placed on the sample using a syringe, and contact angle was recorded.

The water contact angle of UA-C films prepared in our experiments are listed in Table 4.7.

### 3.5.8 Gloss test

The traditional definition of gloss considers the light reflected at the surface of coatings. The reflection of light varies depending on the smoothness of the surface so the illuminated environment is reproduced more or less efficiently. The sensory impression perceived by the eye is recognized as gloss.

To increase the measuring accuracy and improve the reproducibility of the measurements it has become reliable procedure with samples manifesting different gloss to also set various angles of incidence and reflection for the measuring beam. Owing to the higher proportion of reflection light with larger angles of incidence matt surfaces are measured with a large angle of incoming light ( $85^{\circ}$ ), semi-gloss ones are measured with a medium angle ( $60^{\circ}$ ) and high-gloss ones with only a very small angle ( $20^{\circ}$ ). Modern devices contain all 3 measuring geometries and can be used universally by switching to the various ranges.



**Figure 3.26:** Scheme of a measurement device for gloss at different angles

The test was applied to the cured UA-C films coated on plexiglass plates to measure their gloss properties. The test results are shown at Table 4.8.

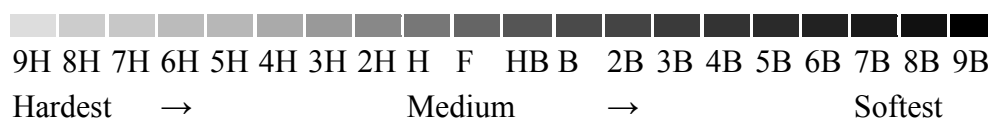
### 3.5.9 Pendulum hardness test

König pendulum hardness method which is frequently encountered in practice is used for measuring the hardness of the samples. The device itself consist of a pendulum, to the support of which two agate balls are attached. The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds which elapses until the amplitude of the pendulum has dropped from 6° to 3° [96].

Pendulum hardness of the cured film was measured to determine the film hardness. The test results are shown at Table 4.9.

### 3.5.10 Pencil hardness test

Non-standard but well-accepted measure of the hardness of pencil leads (made of different proportions of graphite and clay), commonly ranging from 6B (maximum graphite, hence softest) to 6H (least amount of graphite, hence the hardest) with HB (roughly equal amounts of graphite and clay, hence medium soft/hard) in the middle. Pencil hardness is used in indicating the toughness of surface coatings by testing which number pencil-lead can scratch it.



**Figure 3.27:** Pencil hardness and properties

Pencil Hardness (ASTM D-3363) was performed to check the through cure of coatings. Pencil hardness property of coating was determined using pencils ranging from H to 8H and the pencil that will not scratch the coating reported as pencil scratch hardness. The results are given in Table 4.10.

### 3.5.11 Tensile test

Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and

the elongation of the specimen over some distance. Tensile tests are used to determine the modulus of elasticity, elastic limit, elongation, proportional limit, reduction in area, tensile strength, yield point, yield strength and other tensile properties. The main product of a tensile test is a load versus elongation curve which is then converted into a stress versus strain curve. Since both the engineering stress and the engineering strain are obtained by dividing the load and elongation by constant values (specimen geometry information), the load-elongation curve will have the same shape as the engineering stress-strain curve. The stress-strain curve relates the applied stress to the resulting strain and each material has its own unique stress-strain curve. If the true stress, based on the actual cross-sectional area of the specimen, is used, it is found that the stress-strain curve increases continuously up to fracture. The linear-elastic region of the curve indicates that no plastic deformation has occurred. In this region, when the stress is reduced, the material will return to its original shape. In this linear region, the line obeys the relationship defined as Hooke's Law where the ratio of stress to strain is a constant. The slope of the line in this region where stress is proportional to strain and is called the modulus of elasticity or Young's modulus. The modulus of elasticity ( $E$ ) defines the properties of a material as it undergoes stress, deforms, and then returns to its original shape after the stress is removed. It is a measure of the stiffness of a given material. To compute the modulus of elastic, simply divide the stress by the strain in the material. Since strain is unitless, the modulus will have the same units as the stress, such as kpi or MPa. The modulus of elasticity applies specifically to the situation of a component being stretched with a tensile force. This modulus is of interest when it is necessary to compute how much a rod or wire stretches under a tensile load. Axial strain is always accompanied by lateral strains of opposite sign in the two directions mutually perpendicular to the axial strain. Strains that result from an increase in length are designated as positive (+) and those that result in a decrease in length are designated as negative (-). Poisson's ratio is defined as the negative of the ratio of the lateral strain to the axial strain for a uniaxial stress state. Poisson's ratio is sometimes also defined as the ratio of the absolute values of lateral and axial strain. This ratio, like strain, is unitless since both strains are unitless. For stresses within the elastic range, this ratio is approximately constant. For a perfectly isotropic elastic material, Poisson's Ratio is 0.25, but for most materials the value lies in the range of 0.28 to 0.33. Generally for steels, Poisson's ratio will have a value of approximately

0.3. This means that if there is one inch per inch of deformation in the direction that stress is applied, there will be 0.3 inches per inch of deformation perpendicular to the direction that force is applied.

In this study, tensile tests were applied to 10mm x 50mm x 1mm urethaneacrylate free films. The results are shown on Table 4.11.

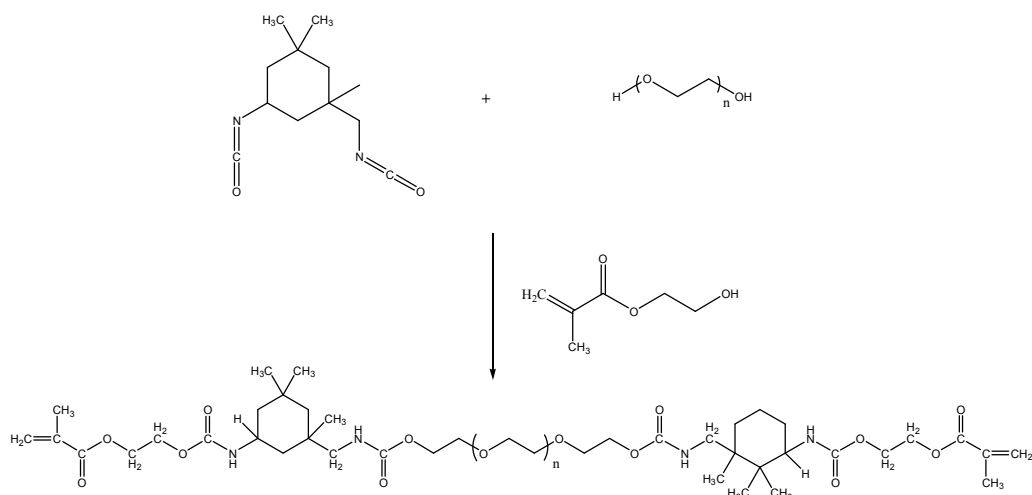
## **4. RESULTS AND DISCUSSION**

In this thesis, chalcone modified urethane acrylate resins at different modification ratios were synthesized and employed in various formulations for preparation of UV-cured coatings. For this purpose 4,4'-dihydroxychalcone was synthesized and employed in the synthesis of chalcone modified urethane acrylates.

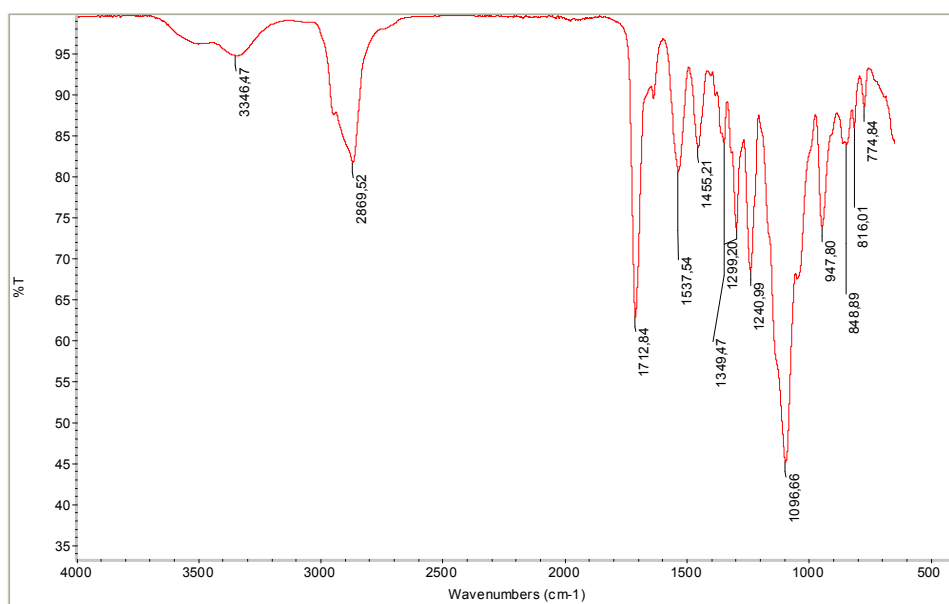
Chalcone modified urethane acrylates were incorporated into the formulations containing diacrylates, photoinitiator and coated on plexiglass plates and cured by UV light. Also, free films of all formulations are prepared and cured by the same way. Cured films were analysed for chemical, thermal and mechanical properties. For comparison, urethane acrylates which do not contain chalcone groups were also synthesized.

### **4.1 Synthesis of Urethane Acrylate**

Urethane acrylate was synthesized according to the procedure (Figure 4.1) mentioned in section 3.3.4. Isophorone diisocyanate was reacted with polyethyleneglycol 1000 and 2-hydroxyethylmethacrylate to yield urethane acrylate. Completion of reaction was checked by both FT-IR and <sup>1</sup>H-NMR spectroscopy techniques.

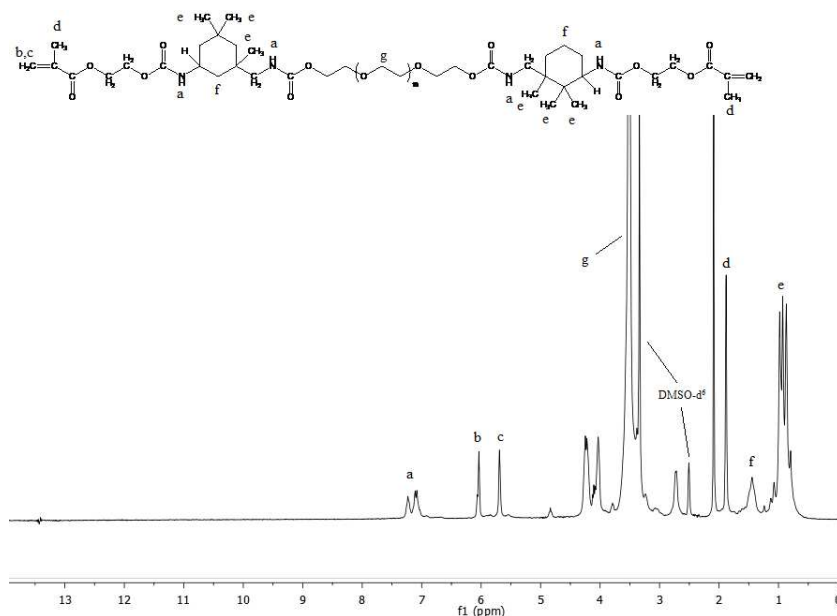


**Figure 4.1.** Synthesis of Unmodified Urethane Acrylate



**Figure 4.2:** IR spectrum of urethane acrylate

The FT-IR spectrum in Figure 4.2. contains characteristic peaks of N-H (3346 cm<sup>-1</sup>), and C=O (1712cm<sup>-1</sup>), -C-N- stretching bands 1544 cm<sup>-1</sup>, C-H aliphatic stretching band (2859 cm<sup>-1</sup>) are also observed. The disappearance of the absorption bands of the NCO group (2270 cm<sup>-1</sup>) of IPDI also proves the synthesis of the urethane acrylate. The absorption band at 1093 cm<sup>-1</sup> originates from C-O-C group. There are phenyl absorption bands at 1537 cm<sup>-1</sup>. <sup>1</sup>H-NMR spectrum of urethane acrylate which was taken in DMSO-d<sup>6</sup> is shown in Figure 4.16.

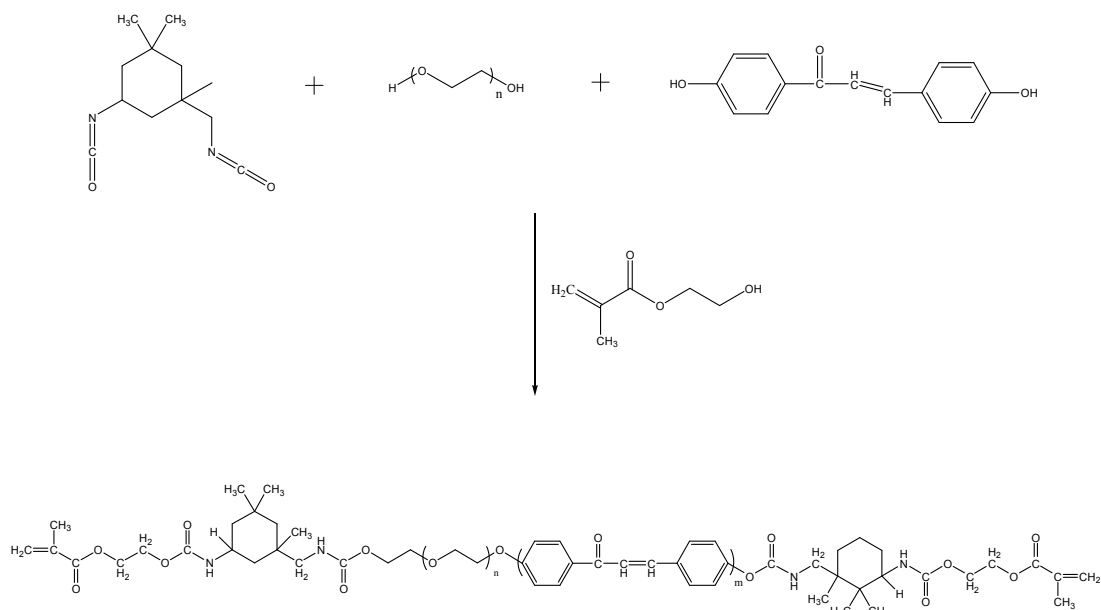


**Figure 4.3:**  $^1\text{H-NMR}$  spectrum of urethane acrylate

The spectrum proves the expected structure of urethane acrylate. According to the spectrum, the protons originating from urethane group show signal at 7.1 ppm,  $-\text{CH}_2$  protons of the polyethyleneglycol show signal at 3.51 ppm and the  $=\text{CH}_2$  protons of the HEMA show signals at 5.84 and 6.03 ppm respectively.

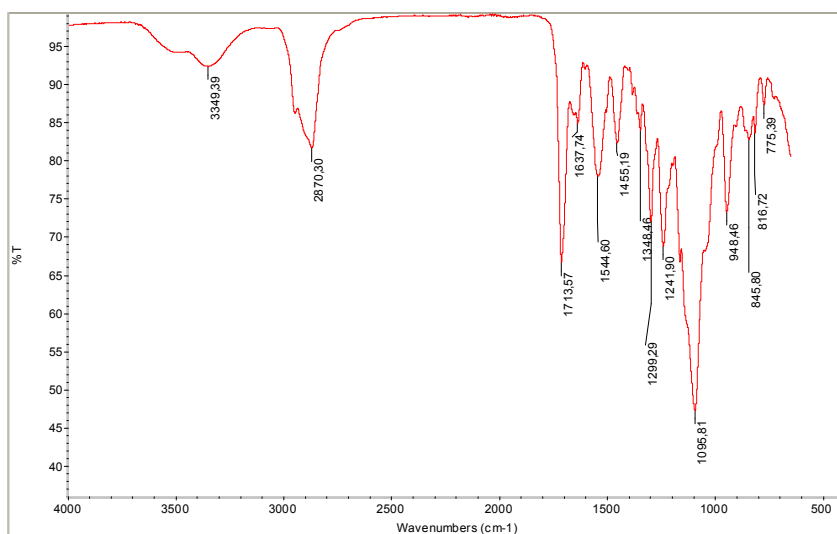
#### 4.2 Synthesis of Chalcone Modified Urethane Acrylate

Chalcone modified urethane acrylates were synthesized according to the procedure (Figure 4.4) mentioned in section 3.3.5. 4,4'-dihydroxy chalcone and isophorone diisocyanate at different ratios were reacted with polyethyleneglycol 1000 and 2-hydroxyethylmethacrylate to yield chalcone modified urethane acrylates. Completion of reaction was checked by both FT-IR and  $^1\text{H-NMR}$  spectroscopy techniques.



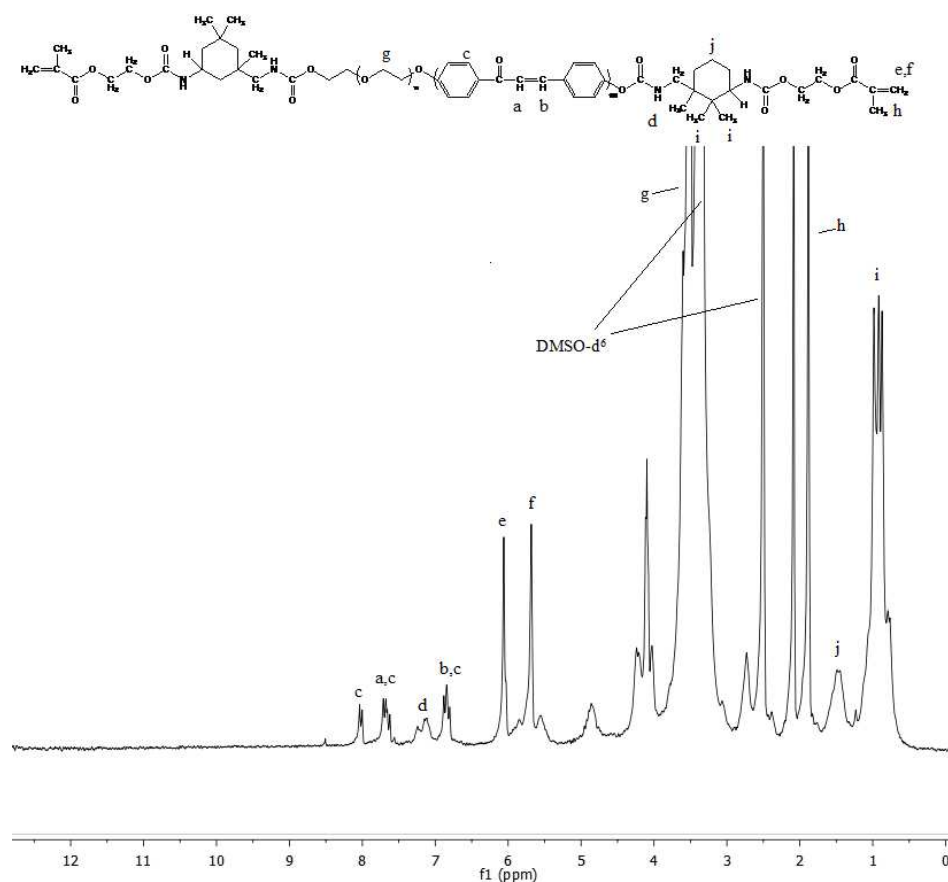
**Figure 4.4:** Synthesis of chalcone modified urethane acrylate

FT-IR spectrum of 25% chalcone modified epoxy acrylate (UA-C25) is given in Figure 4.4. In the spectrum, there are characteristic peaks of N-H ( $3349\text{ cm}^{-1}$ ), and C=O ( $1713\text{ cm}^{-1}$ ), -C-N- stretching band ( $1544\text{ cm}^{-1}$ ), C-H aliphatic stretching band ( $2870\text{ cm}^{-1}$ ) are also observed. The disappearance of the absorption bands of the NCO group ( $2270\text{ cm}^{-1}$ ) of IPDI also proves the synthesis of the UA-C25. The characteristic peak of acrylate group  $\text{-C=C-}$  is at  $1637\text{ cm}^{-1}$ . The absorption band at  $1095\text{ cm}^{-1}$  originates from C-O-C group. There is phenyl absorption band at  $1544\text{ cm}^{-1}$ .



**Figure 4.5:** IR spectrum of UA-C25

The characterization of the reaction was supported by  $^1\text{H}$ -NMR analysis.



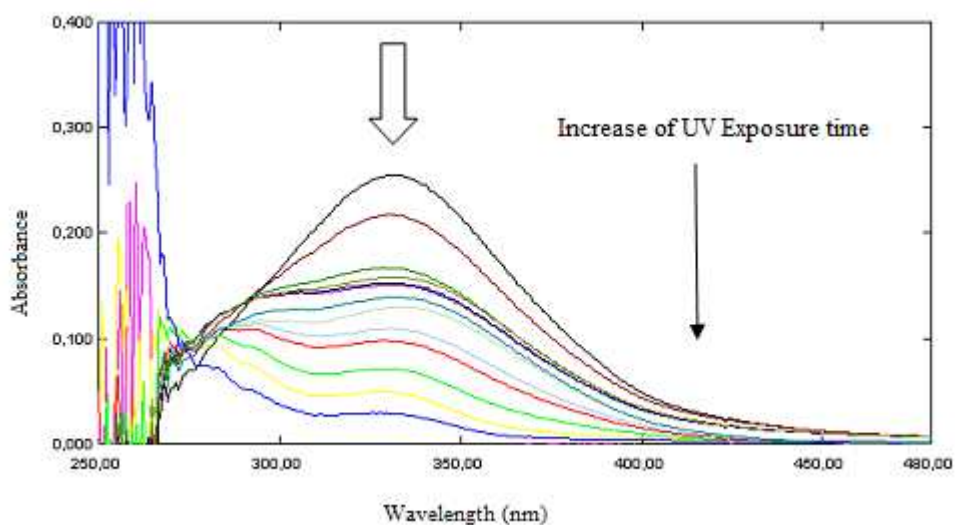
**Figure 4.6:**  $^1\text{H}$ -NMR spectrum of UA-C25

The  $^1\text{H}$ -NMR spectrum (Figure 4.6) proves the expected structure of UA-C25. According to the spectrum, the protons originating from urethane group show signal at 7.1 ppm,  $-\text{CH}_2$  protons of the polyethyleneglycol show signal at 3.50 ppm and the  $=\text{CH}_2$  protons of the HEMA show signals at 5.68 and 6.05 ppm. Also, signals originating from ethylenic ( $-\text{CH}=\text{CH}-$ ) and aromatic protons of the chalcone unit observed at 6.80-6.88, 7.62-7.71 and 8.0-8.03 ppm respectively.

### 4.3 Photocrosslinking Behaviour of Chalcone Units

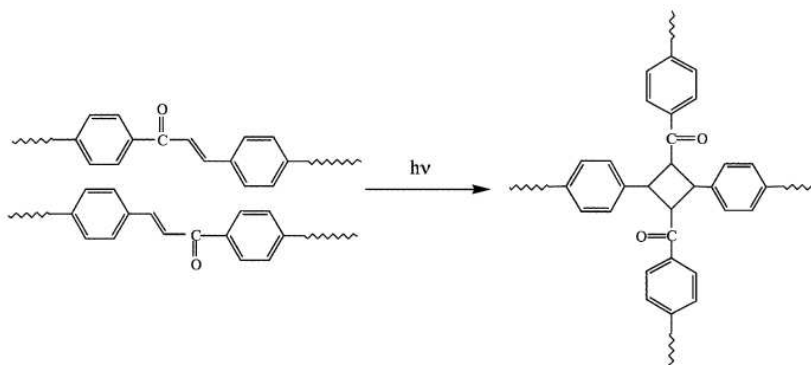
The UV absorption changes in the chalcone modified urethane acrylate (UA-C25) were investigated during UV irradiation from 0 second to 4 hours. The absorbance change at 332 nm was monitored during UV irradiation. The decrease in the absorption band at 332 nm was evident, which is attributed to the formation of

cyclobutane rings through [2+2] cycloaddition of the carbon-carbon double bond in the chalcone units (Figure 4.7).



**Figure 4.7:** In-situ UV-Vis absorption spectra as a function of UV exposure time

The expected photocrosslinked structure of the chalcone modified urethane acrylates after UV irradiation is shown in Figure 4.8. Cyclobutane rings are formed from chalcone groups.



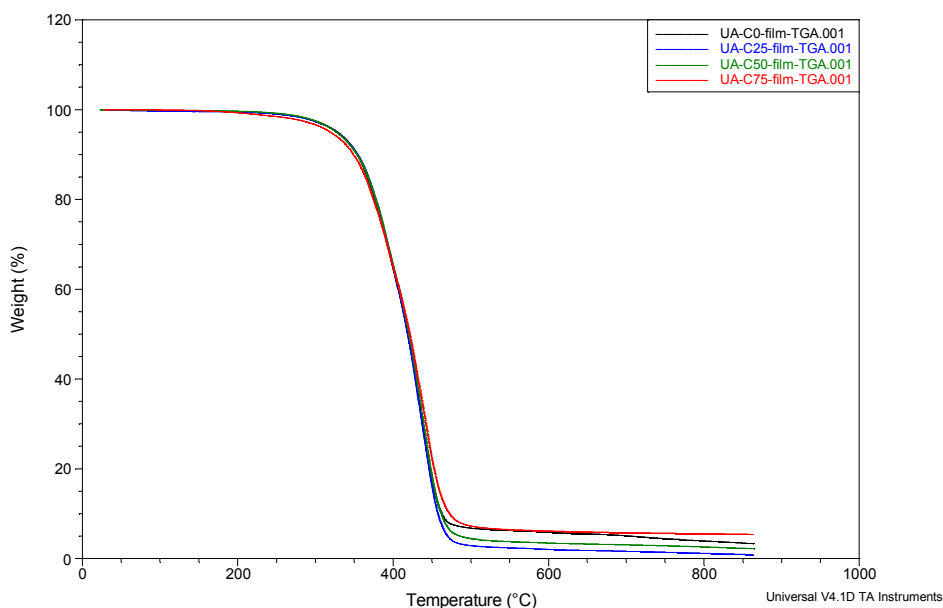
**Figure 4.8** Photocrosslinked chalcone groups

#### 4.4 Film Formation

Films were prepared according to procedure mentioned in section 3.4. After curing obtained samples are subjected to further tests.

#### 4.4.1 Thermogravimetric analysis

TGA analysis were carried out in a nitrogen atmosphere at a heating rate of 20°C/min between 30°C and 900°C for analysing thermal stabilities of the urethane acrylate films. Results are shown in Figure 4.20 and Table 4.1.



**Figure 4.9:** TGA thermogram of urethane acrylate films

Thermogravimetric analyses in Figure 4.9 and table 4.1 shows that because of the aromatic structure of the chalcone groups on the backbone and photocrosslinking ability that brought to the system, urethane acrylates show lower thermal stability and higher char yield as the chalcone content increases.

**Table 4.1 :** TGA analysis values of urethane acrylate films

Sample	5% weight loss temperature (C)	50% weight loss temperature (C)	Char yield (%)
UA-C0	328.11	418.43	0.344
UA-C25	327.02	418.56	0.844
UA-C50	326.73	420.07	2.199
UA-C75	319.22	421.24	5.368

#### 4.4.2 Gel content

This test was applied to measure the polymerization degree of the system. This procedure was proceeded as mentioned in section 3.5.10 and gel content values are listed in Table 4.4.

**Table 4.2** Gel content of cured films

Sample	Gel Content (wt %)
UA-0	96,67
UA-25	96,83
UA-50	97,14
UA-75	97,47

This results show us that unreacted part of cured materials are mostly under wt. 4%. As the chalcone content increases, gel content values of the films increase due to the increasing photocrosslinking.

#### 4.4.3 Solvent resistance

This test was applied according to section 3.5.6. the solvents and the results were listed in tables.

**Table 4.3** Solvent resistance of UA-C0

UA-C0	
Solvents	Weight loss (%) / Appearance
Xylene	<2 / good
CHCl <sub>3</sub>	<1 / brittle
CH <sub>3</sub> COOH	- / good
Methanol	<3 / good
NaOH	<3 / good
HCl %10	<1 / good

**Table 4.4** Solvent resistance of UA-C25

UA-C25	
Solvents	Weight loss (%) /Appearance
Xylene	- / good
CHCl <sub>3</sub>	<2 / brittle
CH <sub>3</sub> COOH	- / good
Methanol	- / good
NaOH	<3 / good
HCl %10	<1 / good

**Table 4.5** Solvent resistance of UA-C50

UA-C50	
Solvents	Weight loss (%) /Appearance
Xylene	- / good
CHCl <sub>3</sub>	<3 / brittle
CH <sub>3</sub> COOH	<3 / good
Methanol	<3 / good
NaOH	<3 / good
HCl %10	<1 / good

**Table 4.6** Solvent resistance of UA-C75

UA-C75	
Solvents	Weight loss (%) /Appearance
Xylene	- / good
CHCl <sub>3</sub>	<3 / brittle
CH <sub>3</sub> COOH	<3 / good
Methanol	<1 / good
NaOH	<2 / good
HCl %10	<1 / good

#### 4.4.4 Contact angle measurement

The contact angle value of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on plexiglass plates coated with four different urethane acrylate films. For each measurement one drop of water was tested on the surfaces and results are shown in Table 4.7

**Table 4.7** Contact angle results

Sample	Water Contact Angle (°)
UA-C0	83.65
UA-C25	87.48
UA-C50	88.86
UA-C75	91.15

As it can be seen in Table 4.7, urethane acrylate coating with no modification (UA-C0) has a hydrophobic, apolar surface and shows a water contact angle of 83.65°. Upon 75% modification with 4,4'-dihydroxychalcone, the contact angle value shifts to 91.15°. This is an expected behaviour assuming that aromatic chalcone moiety makes the surface more hydrophobic.

#### 4.4.5 Gloss tests

Gloss of the coated plates were measured at the angles of 20°, 60° and 85°. For gloss test, plexiglass plates were coated as mentioned in section 3.5.8. and results are given in table 4.8.

**Table 4.8:** Gloss test values of coated films

Sample	Gloss	
	20°	60°
UA-C0	145	147
UA-C25	152	148
UA-C50	154	150
UA-C75	157	152

The measurement at 85° is for matt surface, so these values were neglected. It is actually the ability of a surface to reflect light into the specular direction. The factors that affect gloss are the refractive index of the material, the angle of incident light and the surface topography. Materials with smooth surfaces appear glossy, while very rough surfaces reflect no specular light and therefore appear matt. In table 4.8 we can see the increase in gloss with increasing content of chalcone. Photocrosslinked structure of chalcone groups makes the surface smoother. As a result, gloss is increasing with the increasing chalcone chalcone modification.

#### 4.4.6 Pendulum hardness test

König pendulum hardness test is applied after all formulations coated plexiglass plates.

**Table 4.9 :** Pendulum hardness results

Sample	Pendulum Hardness
UA-C0	58
UA-C25	74
UA-C50	88
UA-C75	93

The hardness of the coating is the most important factor affecting the abrasion and scratch resistance. Hard coatings give better scratch resistance, whereas abrasion resistance is also affected by surface friction . Chain flexibility and crosslinking degree of the network play a major role in the value of hardness. As the chalcone content increases, pendulum hardness values of the films increase due to increased photocrosslinking.

#### 4.4.7 Pencil hardness

Pencil hardness test was applied on plexiglass plates mentioned in section 3.5.10. This test is applied to understand hardness of the surface in addition to pendulum hardness. In table 4.4. results are listed. As the chalcone content increases, pencil hardness values of the films increase due to increased photocrosslinking.

**Table 4.10 :** Pencil hardness results

Sample	Pencil Hardness
UA-C0	>5H
UA-C25	>6H
UA-C50	>7H
UA-C75	>7H

#### 4.4.8 Tensile test

The mechanical specification of free films, prepared at 50x10x1mm dimensions, made clearly with measurement of stress-strain values. Stress-strain values for urethane acrylate system are given in Table 4.5

**Table 4.11** : Stress-Strain Analysis of Polyurethane Acrylates

Sample	E-Modulus (N/mm)	Tensile Strength (MPa)	Elongation at Break (%)
UA-C0	154	11	15
UA-C25	212	13	12
UA-C50	258	15	9
UA-C75	394	23	7

As it can be seen in Table 4.5, Young's modulus and tensile strength of urethane acrylate increases with the increasing chalcone content because of increased photocrosslinking ability of the system. Thus, films become more rigid and elongation values decrease with the increasing chalcone content.

## 5. CONCLUSIONS

In this study, photocrosslinkable 4,4'-dihydroxychalcone compound and novel chalcone modified urethane acrylates at different chalcone ratios were synthesized. Urethane acrylates were added into a suitable formulation which is based on a bifunctional oligomer bearing diacrylate functionalities and UV curable coatings were prepared. Coatings were analyzed for their chemical, thermal and mechanical properties.

The thermal properties were elucidated by thermogravimetric analysis (TGA). Incorporation of aromatic chalcone groups to the backbone decreases the thermal stability.

An increase in crosslinking degree has important effect on improving film properties. In analysis results, chalcone groups increase photocrosslinking ability of the system, thus, increasing chalcone content enhances the gel content results. Solvent resistance test proves the high chemical stability of coatings against lots of solvents. The results of contact angle test also support that aromatic chalcone groups make film surface more hydrophobic when compared with unmodified urethane acrylate. On the contrary, gloss test values show increase by the help of smooth surface that chalcone groups brought to the system via photocrosslinking.

Hardness of the cured films are also improved with increasing modification ratio of chalcone units through photocrosslinking. Tensile test, pendulum hardness and pencil hardness tests prove this estimation.

As a result, it can be said that chalcone modification makes the urethane acrylate coatings mechanically more durable and enhances their gloss.



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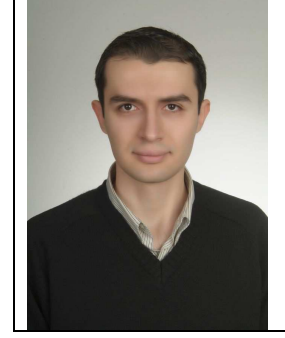
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