ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE OXIDE AND SULFONE CONTAINING POLYURETHANES

Ph. D. THESIS

Betül TÜREL

Department of Polymer Science and Technology

Polymer Science and Technology Programme

JULY 2013

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE OXIDE AND SULFONE CONTAINING POLYURETHANES

Ph. D. THESIS

Betül TÜREL
(515052001)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. I Ersin SERHATLI

JULY 2013

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FOSFİN OKSİT VE SÜLFON İÇEREN POLİÜRETANLARIN SENTEZİ VE KARAKTERİZASYONU

DOKTORA TEZİ

Betül TÜREL
(515052001)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. I. Ersin SERHATLI

TEMMUZ 2013

BETÜL TÜREL, **a Ph.D.** student of ITU **Graduate School of Science Engineering and Technology** student ID **515052001**, successfully defended the **thesis** entitled "**SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE OXIDE AND SULFONE CONTAINING POLYURETHANES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. I. Ersin SERHATLI** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. A. Sezai SARAÇ** İstanbul Technical University	.....
	Prof. Dr. Atilla GÜNGÖR Marmara University	.....
	Prof. Dr. Ayşen ÖNEN İstanbul Technical University	.....
	Prof. Dr. Yusuf Menceloğlu Sabancı University	.....

Date of Submission : 30 May 2013
Date of Defense : 05 July 2013

To my family and lovely housband,

FOREWORD

For working on the Ph.D. has been a wonderful and often overwhelming experience.It is hard to say whether is has been grappling with the topic itself which has been the real learning experience.

First of all, I am deeply grateful to my supervisor Professor I. Ersin Serhatlı. To work with you and to be a member at your research group has been a real pleasure to me. You have been a steady influence througout my Ph.D. career: you have oriented and supported me with promptness and care, and have always been patient and encouraging in times of new ideas. Through your direction and leadership I have been able to expand my knowledge in many areas of polymer science.

I would also like to give my sincere thanks to my doctoral committee member, Prof. Dr. Atilla Güngör and his group at the University of Marmara for their invaluable assistance for my analysis and test measurements.I am very grateful for his support, and for many motivating discussions. It is a pleasure for me to meet a really valuable person in my life. I would also like to thank one of my doctoral committe member Professor A. Sezai Saraç for his comments, suggestions and constant support. It was a chance for me to work with you. I would like to extend my gratitude to Prof.Dr. Ayşen Önen for her time and valuable instruction. I will never forget her good suggestions and invaluable help during my MSc. and Ph.D. Many thanks for her guidance, support, encouragement and advice throughout my work.

In addition, I have been very privileged to get to know and to collaborate withmany other great people who became friends over the last several years. I would like to extend my thanks to my dear friends Res. Asst. Dr. Tuba Çakır Çanak, Dr. Sümeyye Demirhan Şabani. It is really a chance for me to know you and work with you and share all the good and the bad things in our lifes. Thank you for sharing these years with me. My best friend M. Cenap Çetintaş has been a pleasure to be a friend with you since 1996. Thank you for your suggestions to start master and doctorate in İTÜ.

I am also indebted to the students I had the pleasure to work with. You have been an invaluable support day in, day out, during all these years. Specail thanks to Res. Asst. Müfide Karahasanoğlu, Ömer Faruk Vurur, Bahadır Güler, Dalida Erişsever, Kübra Kaya, Elif Rafiye Bahar, Thanks to all of you! This thesis would not have happened without your smile.

Much thanks is due to my husband Davut for accepting my long hours in laboratories, thank you for your help during my experiments and your great patience. Many thanks is due to my sister Oya, and my father Safa for their encourage, support, patience. This enables me to pursue my career, while at the same time enjoying a lifetime of supporting with them.

May 2013

Betül TÜREL
(Chemical Engineer, M. Sc.)

TABLE OF CONTENTS

Page

ABBREVIATIONS

PUA : Polyurethane Acrylate
BHEPS : Bis[4-hydroxyethoxy]phenylsulfone
IPDI : Isophorone diisocyanate
HEMA : 2-Hydroxyethyl methacrylate
DPGDA : Dipropyleneglycol diacrylate
HDDA : 1,6-Hexanediol diacrylate
FT-IR : Fourier Transform Infrared
^{1}H-NMR : Hydrogen Nuclear Magnetic Resonance
$PSCl_3$: Thiophosphorus Trichloride
TDI : Toluene Diisocyanate
MDI : Diphenylmethane diisocyanate
HDI : Hexamethylene diisocyanate
H_{12}MDI : 4,4-Disocyanatodicyclohexylmethane
TMXDI : m-tetramethylxylylene diisocyanate
DBTL : Dibutyltin dilaurate
HEA : 2-Hydroxyethyl acrylate
HPA : 2-Hydroxypropyl acrylate
TPGDA : Tripropylene glycol diacrylate
TMPTA : Trimethylolpropane triacrylate
GPTA : Propoxylated glycerol triacrylate
DPHA : Dipentaerythritol hexaacrylate
PTA : Pentaerythritol tetraacrylate
UV : Ultra-violet
BHPS : Bis(4-hydroxyphenyl)sulfone
NVP : N-vinyl pyrrolidone
Irgacure 184 : 1-hydroxy-cyclohexyl-phenyl-ketone
DMSO-d_6 : Deuterated dimethyl sulfoxide
$CDCl_3$-d_1 : Deuterated chloroform
TGA : Thermogravimetrical Analysis
BFPPO : Bis(4-fluorophenyl)phenyl phosphine oxide
BHPPO : Bis(4-hydroxyphenyl)phenyl phosphine oxide
BHEPPO : Bis[(4-hydroxyethoxy)phenyl]phenyl phosphine oxide
PPG : Polypropylene glycol
PC : Polycarbonatediol
PES : Polyester polyol
SUA : Difunctional sulfone containing urethane acrylate

LIST OF TABLES

Page

LIST OF FIGURES

Page

SYNTHESIS AND CHARACTERIZATION OF PHOSPHINE OXIDE AND SULFONE CONTAINING POLYURETHANES

SUMMARY

Polyurethanes have extensive range of applications, due to their flexibility on tailoring component functionality. UV-curing system has an increasing importance and could be used in many applications such as organic coatings, adhesives, varnishes, printing inks, biomedical materials, electronics, dentistry, leather industry, wood coatings, etc. Besides, UV-curing technology has some advantages such as less environmental pollution, easily adaptability, high speed of drying at ambient temperature, excellent film forming quality, high production efficiency and low consumption of energy.

In general, UV-curable systems contain four main components: reactive oligomers, monomers (reactive diluents), photoinitiators and various additives. The main types of acrylate oligomers are; epoxy, polyester, polyether, silicone, polyurethane, etc. Acrylic resins can be polymerized by heat activation, chemical activation, and light activation. In this study light activation is chosen for curing the acrylic resin. The reactive diluents are acrylic monomers that are added to reduce viscosity and modify the properties. Typical acrylic monomers are 1,6-hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA), trimethylolpropane triacrylate (TMPTA) etc. The photoinitiators are responsible for absorbing UV-radiation. Polyurethane acrylate (PUA) precursors are synthesized by the reaction of a polyol with an excess of a diisocyanate (e.g.NCO/OH:2/1). Then hydroxyl acrylate is added to the resulting product (i.e. prepolymer) to react with the remaining isocyanate groups, and this brings acrylate function to the terminal groups. Polyurethane acrylates exhibit chemical resistance, weathering resistance, adhesion, and flexibility of the coatings.

Sulfone containing polymers are well known for their high glass-transition temperatures, stiffness, outstanding thermal and oxidative resistance and mechanical strength. Besides, some examples of sulfone containing polymers such as polyethers, polyesters, polyarylates, epoxy resins show good mechanical, physical and thermal properties. This is related to their polar sulfone groups that increases intermolecular forces between polymer chains and brings advantages of thermal deformation resistance, higher T_g and thermal stability. Branched and linear sulfonated poly(ether ketone sulfone) and sulfonated multiblock copoly(ether sulfone) proton exchange membranes for fuel cell applications, highly branched sulfonated poly(arylene ether sulfone) for proton exchange membranes have been previously reported about sulfone in literature. Additionally sulfone containing polyimides were synthesized from sulfonated diamines and dianhydrides. Sulfone containing polyamides were synthesized from diamines and sulfone containing diacids. Also poly(urethane-imide) copolymers were prepared through the reaction of isocyanated polyurethane prepolymer containing imide function with sulfone containing glycols and diacids.

Phosphorus containing polymers are generally flame retardant. Other interesting characteristics of phosphorus polymers are metal ion binding, increased polarity and good adhesion. The general types of phosphorus moieties have been incorporated into different polymeric backbones such as poly(arylene ether)s, polyimides, polyamides, polyesters, polycarbonates, epoxy resins, etc. The polymers which contain phosphine oxide moieties have major advantages such as flame retardance, high thermal and oxidative stability, solubility in organic solvents, good adhesion to other compounds and miscibility.

This thesis is separated to three sections. Bis[(4-hydroxyethoxy)phenyl]sulfone (BHEPS) and bis[(4-hydroxyethoxy)phenyl]phenylphosphine oxide (BHEPPO) were synthesized as mentioned in literature. All sections modified PUA's were synthesized and prepared to improve the gloss, hardness and mechanical properties. In the first (Chapter 4) and second (Chapter 5) section; The objective of this study was to directly synthesize different proportions of sulfone and phosphine oxide containing polyurethane acrylates, to investigate curing behavior under UV light and to compare their physical, mechanical, thermal properties after applied as coating material. Three different types of polyols [polyester polyol (PES), polypropylene glycol (PPG), and polycarbonatediol (PC)] and a diol bis[(4-hydroxyethoxy)phenyl]sulfone with different percentages (0, 40%, 60%) as the soft segment, isophorone diisocyanate (IPDI) and toluene 2,4-diisocyanate (TDI) as hard segment, 2-hydroxyethyl methacrylate (HEMA) as blocking agent were used to synthesize nine different reactive urethane acrylates. Final structures of the PUAs were characterized with FT-IR and ^{1}H-NMR. The films of PUA were prepared by using reactive diluents and photoinitiator. The prepared coatings were investigated in detail for their surface properties, mechanical properties such as tensile strength, elongation, e-modulus, pencil and pendulum hardness results.

In the third section (Chapter 6); bis[(4-hydroxyethoxy)phenyl]sulfone was synthesized as mentioned in section one. Then we synthesized sulfone containing difuctional acrylate with the addition of isophorone diisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA). We used polyetherpolyol, as the soft segment, IPDI and as hard segment, HEMA as the blocking agent to synthesize reactive polyurethane acrylate. We added sulfone containing bifunctional initiator with different ratios to the polyetherpolyol based urethane acrylate. Coating performance of the urethane acrylates on plexiglass substrates was determined by the analysis technique, such as hardness, gloss. Also stress-strain tests were enhanced. The thermal behavior of the coatings was investigated by thermogravimetric analysis.

FOSFİN OKSİT VE SÜLFON İÇEREN POLİÜRETANLARIN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Poliüretan karbamat bağlantıları ile birleştirilen organik üniteler zincirinden oluşan bir polimerdir. Ticari poliüretanlar iki yada daha fazla izosiyanat grubu içeren moleküllerin iki yada daha fazla hidroksi grubu içeren poliol ile ekzotermik reaksiyonu ile üretilir. Genel olarak reaksiyon sırasında kullanılan izosiyanatın cinsi, poliolllerin molekül ağırlığı ve fonksiyonaliteleri çok değişik çeşitlerde poliüretan elde edilmesini sağlar. Daha hızlı çevrim zamanı elde edilebilmesi ve daha yüksek hacimli ürün elde edilebilmesi için etkim polimer reaksiyonuna katalizör eklenebilir. Poliüretanlar malzeme foksiyonelliğini uygun hale getirme esnekliği sebebiyle çok geniş bir kullanım alanına sahiptirler. Yoğunluklarının 6 - 1.220 kg/mt3 aralığında olması malzeme sertliğinin esnek elastomer yapısında, sert ve rijit plastic üretilmesine olanak verir. Poliüretanlar otomotiv, mobilya, konstrüksiyon, termal izolasyon, ayakkabı, kaplama gibi değişik endüstriyel alanlarda kullanılabilir. Poliüretan sert, parlak, çözücülere dayanıklı kaplamalardan, aşınma ve çözücülere dayanıklı lastiklere, esnek veya sert köpüklere kadar çok çeşitli şekilde üretilir. Poliüretan köpükler, ısı ve ses izolasyon maddesi olarak, mobilyaların, kırılacak maddelerin taşınmasında ve döşemelerde kullanılır. Sert poliüretan köpükler ince yapıya sahip uçak kanatlarının içine yerleştirilerek kullanılır.

İyi özellikleri sebebiyle üretan zincirleri UV (ultraviolet) kürlenme formatına dönüştürülmeye başlanmıştır. Akrilat grupları içeren polimerler radyasyona duyarlı katı polimerlerdir ve akrilat grupları UV ışığı ile uygun koşullar altında kürleşme reaksiyonu meydana getirirler. Poliüretan akrilatlar UV-kürlenme formülasyonlarında hem esnek hem de aşınma direnci sağlayan kaplamaların üretiminde sıkça kullanılırlar.

Bu sebeple UV-kürleme sistemi artan bir öneme sahiptir ve organik kaplamalar, yapıştırıcılar, vernikler, baskı mürekkepleri, biomedikal malzemeler, elektronik malzemeler, diş hekimliği, deri sanayi, ahşap kaplamalar, koruyucu kaplamalar vb. gibi birçok uygulamada kullanılabilmektedir. Bununla birlikte UV-kürleme teknolojisi daha az çevre kirliliği, kolayca uygulanabilme, ortam sıcaklığında yüksek hızda kuruma, mükemmel film oluşturma, yüksek üretim verimliliği ve düşük enerji tüketimi gibi pek çok avantajı vardır. UV radyasyon ile ıslak kaplama kompozisyonlarının çevre sıcaklığında ve uçucu madde emisyonu olmadan hızlı şekilde kürlenme sağlanır.

Genel olarak, UV-kürleme sistemleri dört ana bileşen içerir: reaktif oligomerler (üretan akrilat), monomerler (reaktif seyrelticiler), fotobaşlatıcılar ve çeşitli katkı maddeleri. Akrilat oligomerlerin ana tipleri: epoksi, poliester, polieter, silikon, poliüretan vb. Akrilik reçineler ısı aktivasyonu, kimyasal aktivasyon ve ışık aktivasyonu ile polimerize edilebilir. Bu çalışmada ışık aktivasyonu akrilik reçinelerin kürlenmesi için seçilmiştir. Poliüretan akrilat sentezinde: poliolün

miktarca fazla diizosiyanat ile senteziyle once prepolimer elde edilir. Sonrasında hidroksil akrilat eklenerek kalan izosiyanat ile reaksiyona girmesi sağlanır. Böylece izosiyanat grupları akrilat foksiyonu kazanmış olur.

Reaktif seyrelticiler viskoziteyi azaltmak ve özelliklerini değiştirmek için ilave edilir. 1,6-hekzandiol diakrilat (HDDA), dipropilen glikol diakrilat (DPGDA), trimetilolpropan triakrilat (TMPTA) vb. tipik akrilat monomerleridir. Fotobaşlatıcılar UV-radyasyonu absoplamaktan sorumludurlar. Poliüretan akrilatlar, öncelikle poliol ve diizosiyanatın fazlasının reaksiyona girmesi ile sentezlenirler (ör. NCO/OH:2/1). Sonra, hidroksil akrilat geri kalan izosiyanat grupları ile reaksiyona girmesi için ilave edilir ve uç gruplarda akrilat fonksiyonu elde edilmesini sağlar. Poliüretan akrilatlar, kaplamalarda kimyasal direnç, iklimlendirme direnci, adezyon ve esneklik özelliği sergiler.

Sülfon içeren polimerler yüksek camsı geçiş sıcaklığı, sertlik, üstün termal ve oksidatif dayanım ve mekanik mukavemetleri ile bilinirler. Bunun yanı sıra, polieterler, poliesterler, poliarilatlar, epoksi reçineler gibi bazı sülfon içeren polimerler iyi mekanik, fiziksel ve termal özellik gösterirler. Polar sülfon grupları, polimer zincirleri arasında moleküller arası kuvvetlerin artmasını sağlar ve termal deformasyon direnci, yüksek T_g ve termal stabilite gibi avantajlar getirir. Yakıt pillerinde kullanılan proton değiştirme membranları: Dallanmış ve lineer sülfonlu poli(eter keton sülfon) ve sülfonlu multiblok kopoli(eter sülfon), proton değiştirme membranları: yüksek dallanmış sülfonlu poli(arilen ether sülfon) daha önce literatürde raporlanmıştır. İlave olarak, sülfonlu diaminler ve dianhidritlerden sülfon içeren polimitler sentezlenmiştir. Diamin ve sülfon içeren diasitlerden sülfon içeren poliamitler sentezlenmiştir. Ayrıca, sülfon içeren glikoller ve diasitlerden sentezlenen imit ile izosiyanatlandırılmış poliüretan prepolimeri reaksiyonu neticesinde poli(üretan-imit) kopolimerleri hazırlanmıştır.

Fosfor içeren polimerler genellikle yanmayı geciktiricidir. Fosfor içeren polimerlerin diğer ilginç karaktersitik özellikleri iyon bağlama, arttırılmış polarite ve iyi adezyondur. Ana zincirinde genel tiplerde fosforlu kısım içeren polimerler poliarilen eterler, poliimidler, poliamitler, poliesterler, polykarbonatlar, vb. Fosfin oksit içeren polimerlerin yanma geciktirme, yüksek termal ve oksidatif stabilite, organik solventlerde çözünebilirlik, diğer malzemelerle iyi adezyon ve karışabilirlik gibi özel avantajları bulunmaktadır.

Bu tez üç bölümden oluşmaktadır. Birer diol olan Bis[[4-hidroksietoksi)fenil]sülfon (BHEPS) ve Bis[[4-hidroksietoksi)fenil]fenilfosfin oksit (BHEPPO) daha once literatürde anlatıldığı şekilde sentezlenmiştir. Bu dioller kullanılarak sülfon ve fosfin oksit içeren poliüretan akrilatlar ve sülfon içeren diakrilat sentezlenmiş ve film formları hazırlanmıştır. Tüm bu filmlerin parlaklık, sertlik, mekanik ve termal özellikleri incelenmiştir ve özellikle bu özelliklerinin geliştirilmesine çalışılmıştır.

Birinci (Bölüm 4) ve ikinci (Bölüm 5) bölümlerde; değişik oranlarda sülfon ve fosfin oksit ilaveli poliüretan akrilatların direkt olarak sentezlenmesini, UV ışığı ile kürleşme davranışının incelenmesini, kaplama yapıldıktan sonra fiziksel, mekanik, termal özelliklerinin karşılaştırılmasını içermektedir. Bu çalışmada yumuşak segment olarak üç çeşit poliol [poliester poliol (PES), polipropilen glikol (PPG), polikarbonatdiol (PC)] ve değişik yüzdelerde (0, 40%, 60%) iki çeşit diol [bis[(4-hidroksietoksi)fenil]sülfon ve bis[[4-hidroksietoksi)fenil]fenilfosfin oksit] kullanılmıştır. Toluene 2,4-diizosiyanat (TDI) ve izoforon diizosiyanat (IPDI) sert segment olarak, 2-hidroksietil metakrilat (HEMA) bloklaşma ajanı olarak, Irgacure

184 fotobaşlatıcı olarak on sekiz ayrı poliüretan akrilatın sentezlenmesi için kullanışmıştır. Sentezlenen poliüretan akrilatların yapıları FT-IR ve ^{1}H-NMR ile karakterize edilmiştir. Poliüretan akrilat filmler, sentezlenen üretan akrilatlar, reaktif seyrelticiler ve fotobaşlatıcı kullanılarak hazırlanmıştır. Hazırlanan kaplamaların özellikle detaylı şekilde parlaklık ve kontak açı gibi yüzey özellikleri, kimyasal ve solvent dayanımları, kürlenme oranları, su absorplama özellikleri, çekme mukavemeti, uzama, elastik modül bazında mekanik özellikleri, kalem ve pendulum sertlik değerleri ve termal özellikleri incelenmiştir. Hem sülfonlu hem de fosfin oksit içeren poliüretan akrilat kaplamalarda referans numunelere göre parlaklık değerinin arttığı, pendulum ve kalem sertlik değerlerini arttığı, çekme-kopma mukavemet, e-modulus değerlerinde iyileşme gösterdiği tespit edilmiştir. Su absorplama, kimyasal ve solvent dirençlerinin uygun olduğu görülmüştür. Filmlerin kürlenme miktarları jel içeriği testi ile tespit edilmiş ve formülasyonların uygun olduğu sonucuna varılmıştır. Sülfon ve fosfin oksit yapısının hidrofil olmasından ötürü kontak açı değerlerinin sülfon ve fosfin oksit miktarı arttığında düştüğü görülmüştür. Termal özelliklerde ise minimal bir iyileşme gözlenmiştir.

Üçüncü (Bölüm 6) bölümde bis[(4-hidroksietoksi)fenil]sülfon Bölüm 4'de belirtildiği gibi sentezlenmiştir. İzoforon diizosiyanat ve 2-hidroksietil metakrilat kullanılarak sülfon içeren iki fonksiyonlu sülfon içeren akrilat (SUA) sentezlenmiştir. Poliüretan akrilat sentezi sırasında yumuşak segment olarak polipropilen glikol, sert segment olarak izoforon diizosiyanat ve uç kapatma ajanı olarak HEMA kullanılmıştır. Sülfon içeren iki fonksiyonlu akrilat, hazırlanan poliüretan akrilatın içerisine değişik oranlarda ilave edilmiştir. Modifiye edilen üretan akrilatın kaplama performansı sertlik, parlaklık ve mekanik özellikler açısından incelenmiştir. Ayrıca termal özellikleri termogravimetrik analiz cihazı ile test edilmiştir. Yapılan testler sonucunda sülfon içeren iki fonksiyonlu akrilatın katkı maddesi gibi poliüretan akrilat içerisine eklenmesi pendulum ve kalem sertliği, çekme-kopma mukavemeti ve e-modulus gibi mekanik özelliklerde yüksek oranda iyileşme sağlamıştır.

1. INTRODUCTION

Polyurethanes give excellent performance properties such as toughness, flexibility, elongation, etc. Because of these inherently good qualities, it made sense to use urethane backbone by adapting as UV-curing format. UV-curing system is an attractive technology whereby use in industrial coatings such as adhesives, printing inks, varnishes, paints, packaging overcoat films, photoresist materials, biomaterials, finishing materials for leather industry and dry toners, etc. [1-7].

UV-curing technology is a well-accepted technology due to their advantages such as less environmental pollution, low VOC, easily adaptable, lower process cost, low viscosity, excellent film quality, high chemical stability, energy conservation, fast curing speeds at ambient temperature, and high production efficiency [2,8-15].

Conventional UV-curable formulations mainly composed of reactive acrylate oligomer, reactive diluents, multifunctional monomers, photoinitiators, pigments, and additives. Acrylic resin (acrylate oligomers) is generally preferred to use for protective coatings because of its performance such as weatherability, solvent resistance, anticorrosion, etc. Acrylic resins can be polymerized by heat activation, chemical activation, or light activation. Polyether acrylates, urethane acrylates, polyether urethane acrylates, polyester acrylates, epoxy acrylates and silicone acrylates are well known types of acrylate oligomers [16-18]. PUA is synthesized by the reaction of a polyol with an excess of a diisocyanate to obtain a prepolymer. A hydroxyl acrylate is then added to the resulting product to react with the remaining isocyanate (NCO) groups and NCO groups were replaced by terminal acrylate functionality. The reactive diluents are acrylic monomers that are added to modify the properties and reduce the viscosity. The photoinitiators are main components for the formulation and responsible for absorbing UV-radiation, become reactive and changing to highly reactive free radicals and then croslinking the resins [15,19-21].

Sulfone containing polymers are characterized by high glass-transition temperatures, good mechanical strength, stiffness, outstanding thermal and oxidative resistance

[22]. A number of investigations confirmed that sulfone containing polymers such as polyethers, epoxy resins, polyesters and polyarylates, display good physical, mechanical and thermal properties. Since polymer having a polar sulfone group, has a larger intermolecular force between polymer chains, it has the advantage of resistance to thermal deformation, higher Tg, and thermal stability [23,24]. Matsuyama et al. [25], Li et al. [26], reported the synthesis of highly branched sulfonated poly(arylene ether sulfone) for proton exchange membranes. The results showed newly synthesized materials exhibited higher conductivity, better dimensional and oxidative stability. Additionally branched and linear sulfonated poly(ether ketone sulfone) [27] and sulfonated multiblock copoly(ether sulfone) [28] proton exchange membranes for fuel cell applications were studied. Also sulfone containing polyimides were synthesized from dianhydrides and sulfonated diamines [29-32]. Diamines and sulfone containing diacids were used to synthesize polyamides previously [33,34].

Phosphine oxide containing polymers are characterized by flame resistant, thermal stability, electron withdrawing characteristics, excellent adhesion properties, enhanced solubility in organic solvents, and improved miscibility [34-42]. A wide variety of phosphorus moieties have been incorporated into different polymers has also been prepared by a number of research groups. For example, poly(arylene ethers)s [34, 37, 41, 43-46], epoxy acrylate [47], hyperbranched poly(arylene ether)s [32, 40], polyimides [38, 42], polyamides [36, 48], acrylates [49, 50], poly(ether ether ketones)s [39], poly(ester amide)s [35] and others.

1.1 Purpose of Thesis

This thesis is separated to three sections. In the first section (Chapter 4): In this chapter bis[4-hydroxyethoxy]phenylsulfone (BHEPS) was synthesized as mentioned in the literature [51,52]. Liaw et. al previously reported the synthesis of BHEPS and they used to synthesize BHEPS containing polycarbonates by melt transesterification [53], polyamides [54] and polyesters by direct polycondensation [52], and polyurethanes (photolysis investigation) [55], polyimides [56] in the literature. Also amorphous copolyesters [57-60], and poly(ethylene terephathalate) copolymers [61], polyurethane-ureas [62] which contain BHEPS were synthesized and presented

previously. BHEPS containing polyurethane acrylates was not provided in the literature before.

This thesis reported synthesis and characterizations of a series of UV-curable sulfone-containing urethane acrylates. The urethane acrylates were synthesized via two steps. Hydroxyl functionalized sulfone-containing precursor bis[4-hydroxyethoxyphenyl]sulfone, (BHEPS) and a polyol were first reacted with isophorone diisocyanate (IPDI) or 2,4 toluene diisocyanate (TDI); the obtained precursor (a prepolymer) were then endcapped with 2-hydroxyethyl methacrylate (HEMA). According to BHEPS percentage (0, 40%, and 60%) and types of polyol (polyester polyol, polycarbonatediol, and polypropylene glycol), nine different urethane acrylates were prepared. The resultant urethane acrylate resins were characterized by FT-IR, ^{1}H-NMR. To study the effects of sulfone group and properties of cured film, a series of acrylic resins containing sulfone were formulated based on reactive diluents, DPGDA, HDDA and photoinitiator, I-184. Various properties of the UV-cured films such as gloss and gel content measurement, chemical and solvent resistance, water absorption and contact angle measurement, pendulum and pencil hardness measurements, TGA, and mechanical measurements (tensile strength, modulus, elongation at break, and stress-strain) were investigated in detail.

In the second section (Chapter 5): In this chapter BHEPPO was synthesized as mentioned in the literature. Güngör et. al. previously reported the synthesis of BHEPPO and they used to synthesize BHEPPO containing flame retarding UV-curable organic-inorganic hybrid coatings [12], and UV-curable phosphorus containing hybrid materials prepared by sol-gel technique [10]. Also phosphine oxide moiety containing flame retardant poly(urethane-imide)s [63], and phosphine oxide containing polymers via ATRP [64] which contain BHEPPO were synthesized and presented previously. BHEPPO containing polyurethane acrylates was not provided in the literature before.

Section five reported synthesis and characterizations of a series of UV-curable phosphine oxide-containing urethane acrylates. Monomer BHEPPO was synthesized as mentioned in the literature. The urethane acrylates were synthesized via two steps. Hydroxyl functionalized phosphine oxide-containing precursor bis[4-hydroxyethoxyphenyl]sulfone, and a polyol were first reacted with isophorone

diisocyanate or toluene 2,4-diisocyanate; the obtained precursor (a prepolymer) were then endcapped with 2-hydroxyethyl methacrylate. According to BHEPPO percentage (0, 40%, and 60%) and types of polyol [polyester polyol (PES), polycarbonatediol (PC), and polypropylene glycol (PPG)], nine different urethane acrylates were prepared. The resultant urethane acrylate resins were characterized by FT-IR, ^{1}H-NMR. To study the effects of sulfone group and properties of cured film, a series of acrylic resins containing sulfone were formulated based on reactive diluents, dipropyleneglycol diacrylate, 1,6-hexanediol diacrylate and photoinitiator, I-184. Various properties of the UV-cured films such as gloss and gel content measurement, chemical and solvent resistance, water absorption and contact angle measurement, pendulum and pencil hardness measurements, TGA, and mechanical measurements (tensile strength, modulus, elongation at break, and stress-strain) were investigated in detail.

In section three (Chapter 6): In this chapter (bis[(4-hydroxyethoxy)phenyl]sulfone was synthesized as mentioned in chapter four. Then we synthesized sulfone containing difuctional acrylate with the addition of isophorone diisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA). We used polyetherpolyol, as the soft segment, IPDI and as hard segment, HEMA as the blocking agent to synthesize reactive polyurethane acrylate. We added sulfone containing bifunctional initiator with different ratios to the polyetherpolyol based urethane acrylate. Coating performance of the urethane acrylates on plexiglass substrates was determined by the analysis technique, such as hardness, gloss. Also stress-strain test were enhanced. The thermal behavior of the coatings was investigated by thermogravimetric analysis.

2. THEORETICAL PART

2.1 Overview of Sulfone Chemistry

Even -S- bridges introduce certain flexibility, but -SO_2- units introduce stiffness and enhanced stability toward oxidation. Sulfone containing polymers are characterized by high glass-transition temperatures, good mechanical strength, stiffness, outstanding thermal and oxidative resistance [22]. A number of investigations confirmed that sulfone containing polymers such as polyethers, epoxy resins, polyesters and polyarylates, display good physical, mechanical and thermal properties. Since polymer having a polar sulfone group, has a larger intermolecular force between polymer chains, it has the advantage of resistance to thermal deformation, higher Tg, and thermal stability [23,24]. Matsuyama et al. [25], Li et al. [26], reported the synthesis of highly branched sulfonated poly(arylene ether sulfone) for proton exchange membranes. The results showed newly synthesized materials exhibited higher conductivity, better dimensional and oxidative stability. Additionally branched and linear sulfonated poly(ether ketone sulfone) [27] and sulfonated multiblock copoly(ether sulfone) [28] proton exchange membranes for fuel cell applications were studied. Also sulfone containing polyimides were synthesized from dianhydrides and sulfonated diamines [29-32]. Diamines and sulfone containing diacids were used to synthesize polyamides previously [33,34].

2.2 Overview of Phosphorus Chemistry

Phosphorus compounds have found many important commercial applications such as fire retardants, animal feed, detergants, pharmaceutical industry, etc. Various classes of organophosphorus compounds are shown in Figure 2.1 [66-68].

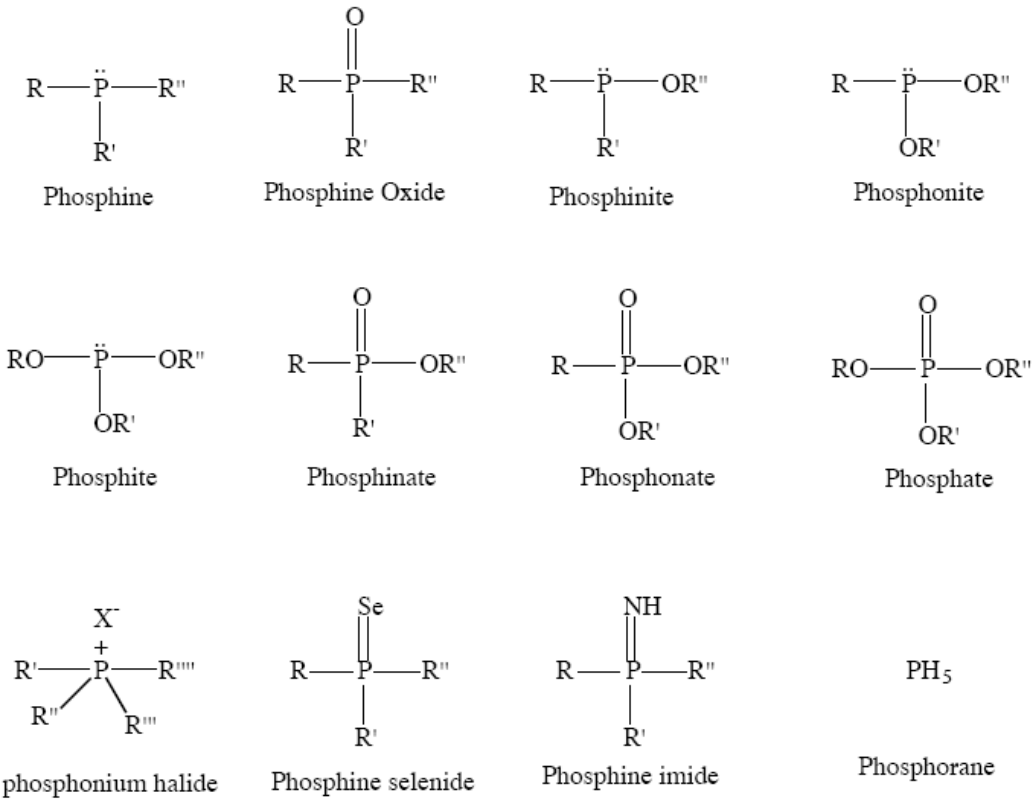


Figure 2.1 : Nomenclature for selected classes of phosphorus compounds [66].

2.2.1 Synthetic routes for the synthesis of phosphine and phosphine oxides

Phosphines can be synthesized using different techniques including Grignard and organolithium reagents. The synthesis with Grignard chemistry starts with phosphorus trichloride following the equation below (2.1) [67]:

$$PCl_3 + 3\ RMgX \longrightarrow R_3P + 3\ MgXCl \qquad \textbf{(2.1)}$$

After hydrolysis the product is separated using base, ether and then purified [69, 70]. Non-sterically hindered phosphines and primary or aryl Grignard reagents are obtained by Grignard synthesis with high yields [66, 70, 71]. When steric hindrance is so important organolithium compounds are preferred. Secondary and tertiary halides produce low yields of tertiary phosphine [70]. The synthesis of phosphine oxides can also be prepared by Grignard synthesis. Dialkylaryl and alkylaryl phosphine oxides can be synthesized by Grignard reagents as mentioned by Kormachex et.al [72]. The equations are illustrated in Figure 2.2 [66].

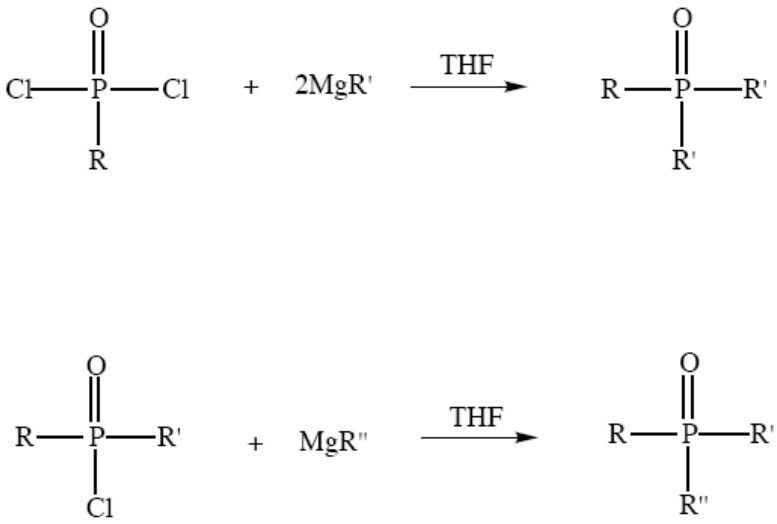


Figure 2.2 : Nomenclature for selected classes of phosphorus compounds [66].

A wide variety of phosphines and phosphine oxides have been synthesized utilizing Grignard chemistry and only a selected few are shown in Figure 2.3 [66].

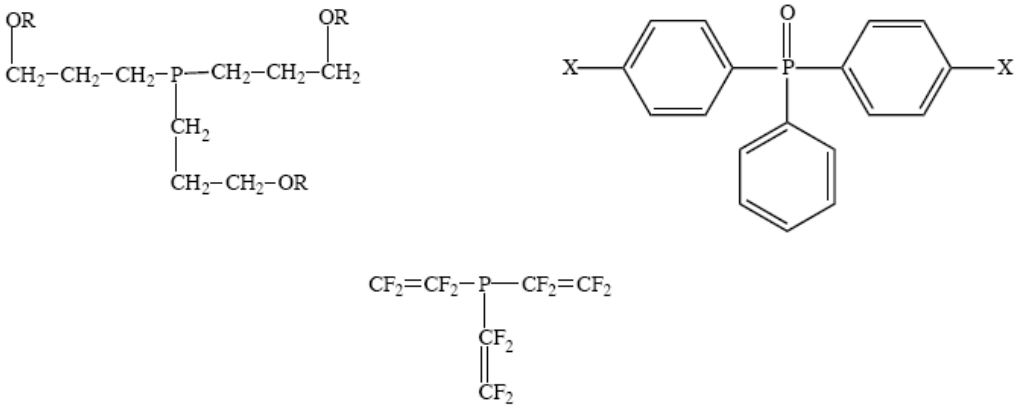


Figure 2.3 : Examples of phosphorus containing compounds synthesized via Grignard chemistry [66].

Phophines may also be synthesized using organolithium reagents [73, 74]. The synthesis of phosphines using organolithium reagents follows the form of the equation below (2.2):

$$3RLi + PCl_3 \longrightarrow R_3P + LiCl \qquad \textbf{(2.2)}$$

Organolithium compounds undergo similar reactions like Grignard reagents;they are much more reactive since the carbanion derived from a C-Li bond is more basic than of the C-Mg bond [74]. The sterically hindered phosphines such as tri-tert-butylphosphine is preferred to synthesize by organolithium route[75]. A wide variety

of sterically hindered phosphines have been synthesized using organolithium chemistry and as shown in Figure 2.4 [66].

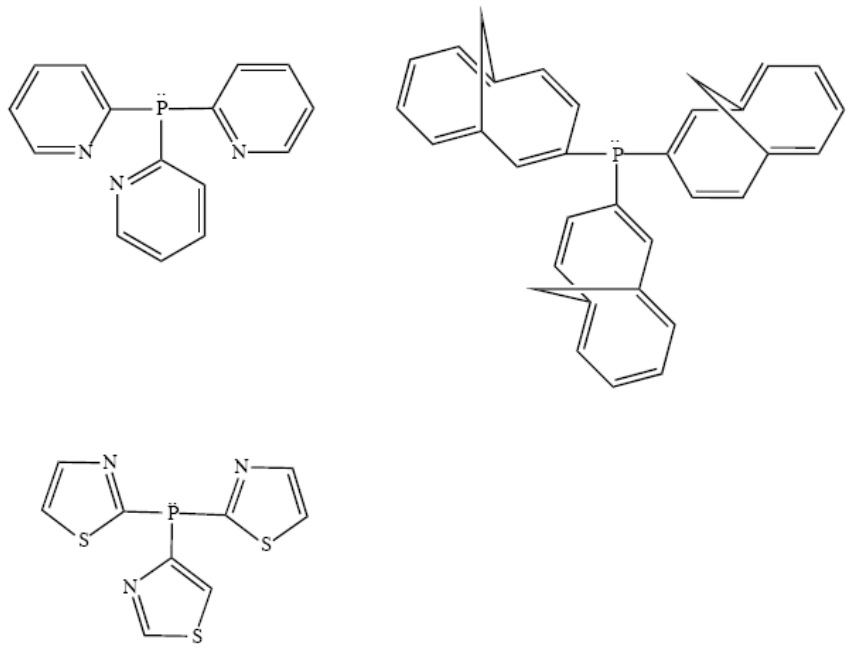


Figure 2.4 : Selected sterically hindered phosphines snthesized using organolithium reagents [66].

In addition, various phosphines and phosphine sulfides may be synthesized via electrophilic substitution using Friedel-Crafts chemistry.

In this electrophilic synthesis, the starting material is generally a mono-di-or tri-halophosphine or phosphine sulfide. In the case of thiophosphorus trichloride ($PSCl_3$) it is possible to perform sequential additions of benzene or substituted benzene reagents to prepare compounds of the structure bis(R)R'phosphine sulfide [76, 77]. Therefore, it is possible to prepare such a compound from thiophosphorus trichloride by first reacting $P(S)Cl_3$ with a slight excess of R and then subsequently with excess R'. This reaction has been studied in detail by Weiss and Kliener as shown in Figure 2.5. Similar work has also been carried out by Wescott in our group for involving the synthesis of 4,4'-bis(fluorophenyl)phenylphosphine sulfide using analogous chemistry [78].

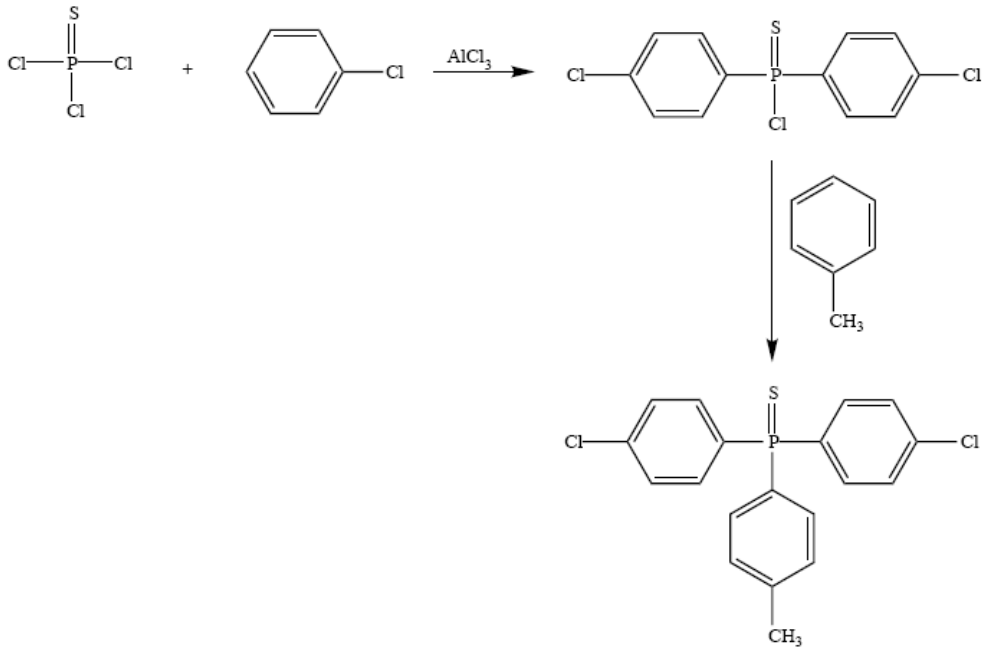


Figure 2.5 : Illustration of the synthesis of a trisubstituted phosphine oxide via subsequent addition of reagents [66].

Attempted synthesis using secondary or tertiary halides produce only low yields of tertiary phosphine [66]. This Grignard chemistry can also be applied to the synthesis of phosphine oxides;for example, Kormachev et al.[66] showed that dialkylaryl and alkylaryl phosphine oxides could be synthesized using alkyl Grignard reagents, as illustrated by the equations below.

2.3 Overview of Urethane Chemistry

Polyurethanes consist of two main components, an isocyanate component and a diol component [79].

2.3.1 Diisocyanates

The basic synthesis of isocyanate starts with an amine, aliphatic or aromatic and phosgene as shown in Figure 2.6. The isocyanate is formed by the elimination of two molecules of HCl [79].

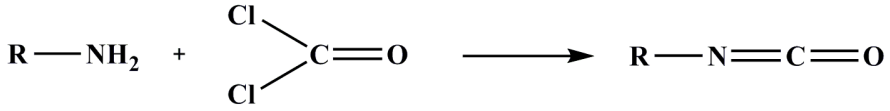


Figure 2.6 : Synthesis of isocyanates.

There are two ways to synthesize isocyanates: phosgene route and phosgene-free route.

route.

a) Phosgene Route: Isocyanates had been discovered in 1848 by Wurtz and the synthesis route via phosgene was invented in 1884 by Hentschel. There are two basic steps of this reaction as shown in Figure 2.7 [79].

   1) Formation of the carbamic chloride,

   2) Elimination of hydrochloric acid.

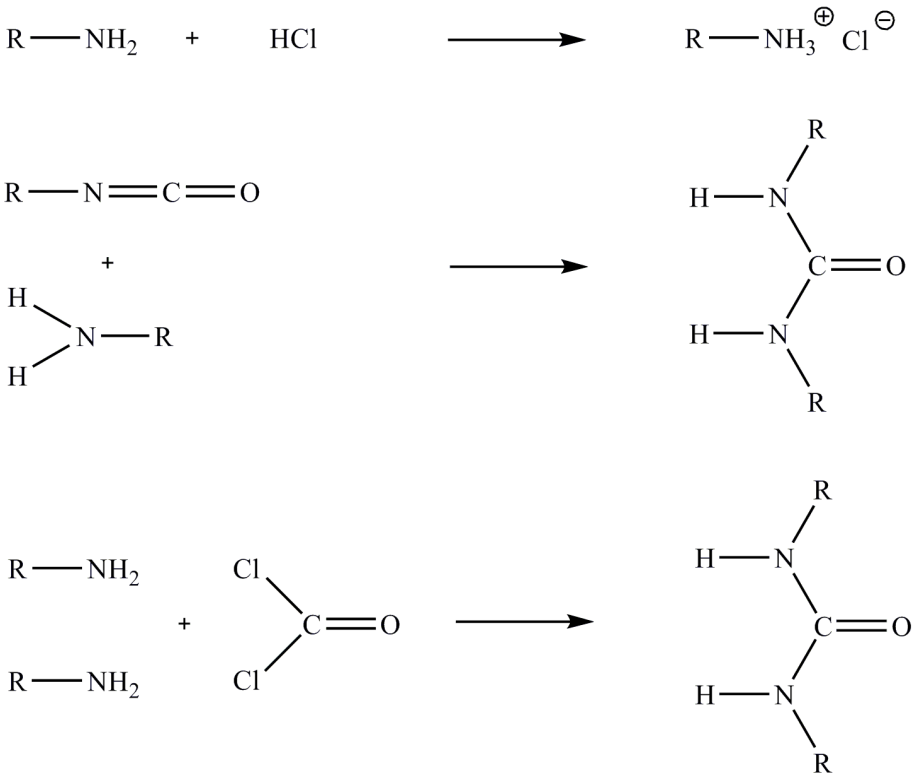


Figure 2.7 : Side reaction in isocyanate synthesis: Salt formation with HCL generated, formation of urea from amine and isocyanate, formation of urea from amine and phosgene [66].

b) Phosgene-free Route: The synthesis starts with nitrobenzene. The ethyl urethane is formed with carbon monoxide and ethanol directly. The urethane is dimerized by carbonylation reaction. Then isocyanate and alcohol is formed by the heating of urethane. The route is shown in Figure 2.8 [79].

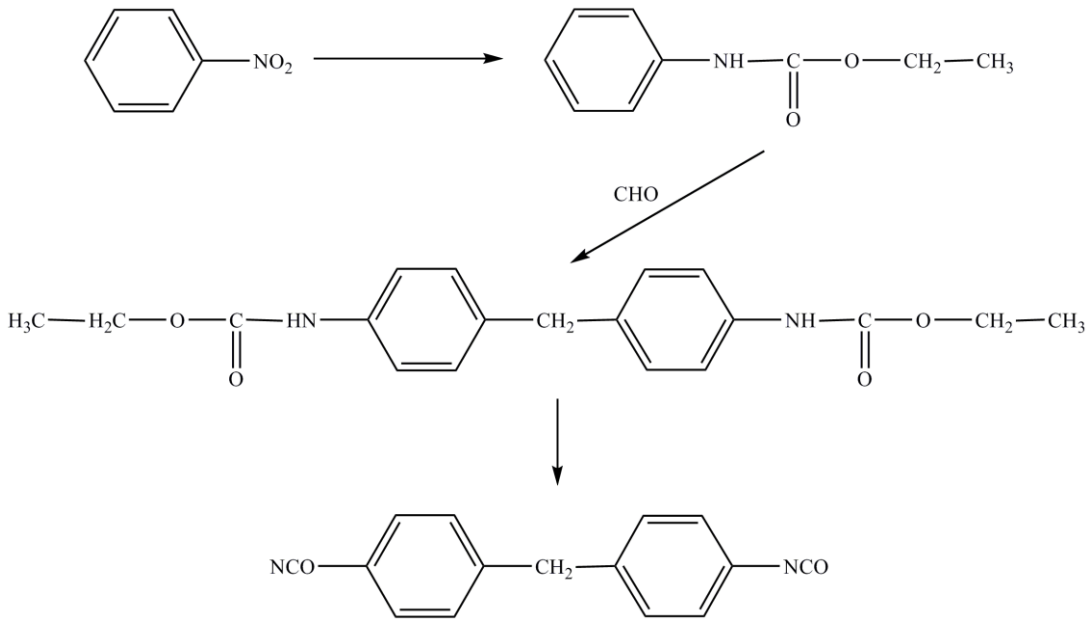


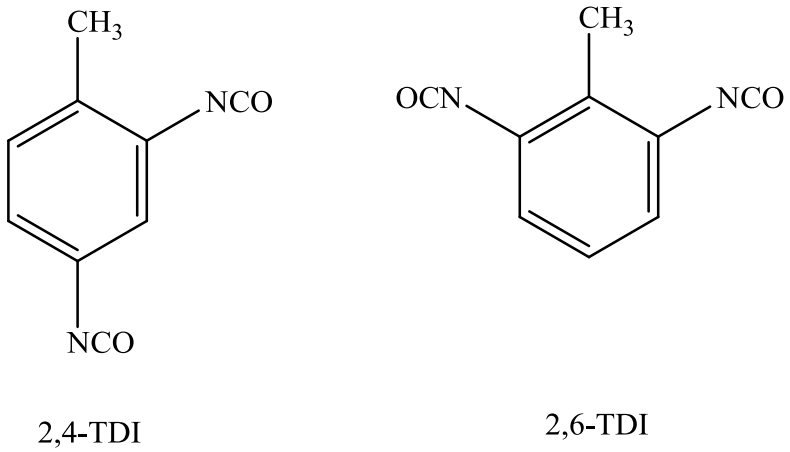
Figure 2.8 : Phosgene-free synthesis of diisocayanates [66].

There are two types of diisocyanates: aromatic and aliphatic.

2.3.1.1 Aromatic diisocyanates

A. Diisocyanatotoluene, toluene diisocyanate (TDI)

It is normally used in the form of an isomer mixture of 80% 2,4-toluene diisocyanate and 20% 2,6-toluene diisocyanate (TDI 80) for technical applications as shown in Figure 2.9. Other isomer mixtures such as 65:35 and virtually pure 2,4-TDI are also used for special applications in industry. At temperatures below 100 ^{o}C, the NCO group in the para position is far more reactive than the NCO groups in the 2,6 position [79, 80].

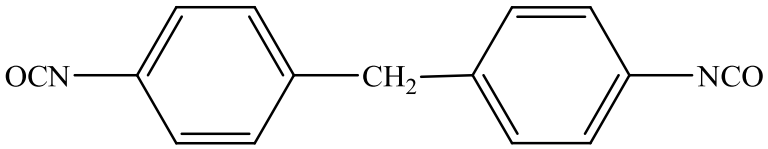


2,4-TDI 2,6-TDI

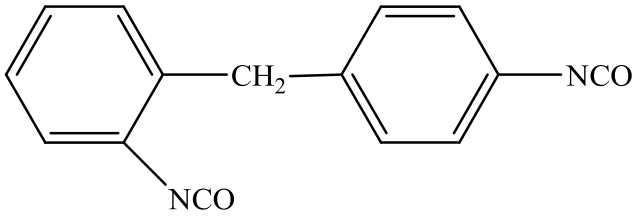
Figure 2.9 : 2,4-toluene diisocyanate and 2,6-toluene diisocyanate.

B. Diisocyanatodiphenylmethane, diphenylmethane diisocyanate (MDI)

The second most important aromatic diisocyanate is 4,4'-diphenylmethane diisocyanate. Isomer mixtures such as 60% 2,4'-MDI and 40% 4,4'-MDI are of less significance in coating applications as shown in Figure 2.10. Because of its low vapour pressure which allows the safe handling of the substance at ambient temperature and less toxic than TDI [79, 80].



4,4'-MDI



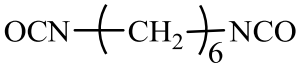
2,4'-MDI

Figure 2.10 : 4,4'-diphenylmethane diisocyanate and 2,4'-diphenylmethane diisocyanate.

2.3.1.2 Aliphatic diisocyanates

A. 1,6-Diisocyanatohexane, hecamethylene diisocyanate (HDI)

It is first introduction to coatings industry was early 1960s. It is the most important aliphatic derivative in coatings industry as shown in Figure 2.11 [79, 80].



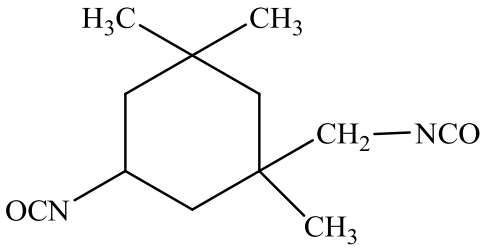
HDI

Figure 2.11 : Hexamethylene diisocyanate.

B. 3,5,5-Trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane, isophorone diisocyanate (IPDI)

This aliphatic diisocyanate is usually a mixture of approximately 75% cis and 25% trans isomers as shown in Figure 2.12. IPDI has two isocyanate groups of differing reactivity, perhaps, from sterical reasons, the secondary cycloaliphatic NCO group

being many times more than the primary aliphatic NCO group. The reactivity of both the primary and secondary NCO groups can be increased with the selection of the catalyst [79, 80].

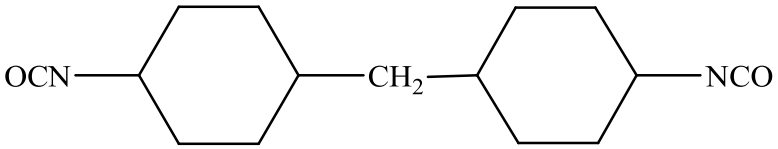


IPDI

Figure 2.12 : Isophorone diisocyanate.

C. 4,4'-Diisocyanatodicyclohexylmethane (H_{12}MDI)

H_{12}MDI is equivalent in formula to perhydrated MDI as shown in Figure 2.13. This cycloaliphatic diisocyanate is supplied as an isomer mixture (approx. 30% cis/cis, approx. 50% cis/trans, approx. 20% trans/trans) [79, 80].

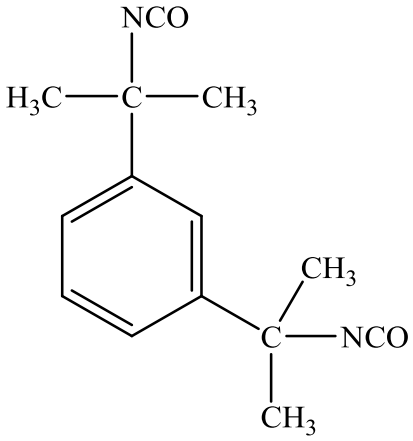


H_{12}MDI

Figure 2.13 : 4,4'-Diisocyanatodicyclohexylmethane.

D. m-Tetramethylxylylene diisocyanate (TMXDI)

This substance has an aromatic ring, but the NCO groups ar not bonded directly to this ring as shown in Figure 2.14 [79,80].



TMXDI

Figure 2.14 : m-Tetramethylxylylene diisocyanate.

2.3.2 Coreactants (Polyols)

The properties of polyurethene is also affected with hydroxy functional coreactant, polyol. The selection of polyols and isocyanates can change the characteristics of coatings and films. Drying, gloss, solid content, elasticty, hardness, resistance to chemicals and solvents, hydrolysis are some examples. The most importants polyols are hydroxyl functionalized polymers such as polyacrylate, polyester, polyether, polycarbonate, polycaprolactone and polyurethane polyols [81].

2.3.2.1 Polyacrylate polyols

The polyacrylate polyols covers copolymers of acrylic and/or methacrylic acid esters- ethyl acrylate, butyl acrylate and methyl methacrylate which contain hydroxyl groups. Different types of monomers are presented in Table 2.1. Polyacrylate polyols are performed by thermally initiated radical polymerization in organic solvents or in substance for industrial production. The molecular weight of the polyacrylate can be changed by the temperature, the type and the amount of the initiator. Polyacrylates ensure good weather stability and improve the initial physical drying of coatings. Polyacrylic resins are copolymers of various monomers, some of which contain hydroxyfunctional acrylate groups. These are often combined with other polymerizable compounds, e.g. styrene [80, 81].

Table 2.1 : Monomeric base products for polyacrylate polyols [80].

Building Block	For the control of
Methyl methacrylate	Hardness
Butyl acrylate	Flexibility
Ethylhexyl acrylate	Flexibility
Hydroxyethyl acrylate	OH functionality
Hydroxyethyl methacrylate	OH functionality
Hydroxypropyl methacrylate	OH functionality
Acrylic acid	COOH functionality
Styrene	Hardness

2.3.2.2 Polyester polyols

The polyester polyols are produced by the polycondensation of di- and polycarboxylic acids with an excess of polyfunctional alcohols (polyols). Building blocks for polyester polyols are presented in Table 2.2. The most important polycarboxylic acids and their anhydrides which are available in industry contain aromatic acids (phthalic acid and isophthalic acid), aliphatic acids (adipic acid and maleic acid), cycloaliphatic acids (tetrahydrophthalic acid and hexahydrophthalic acid).

Ethane diol, 1,2-propanediol, 1,6-hexanediol, neopentyl glycol, glycerol and trimethylolpropane, cycloaliphatic alcohols such as 1,4-cyclohexanedimethanol are aliphatic alcohols which are used as polyols.

Polyester polyols are synthesized by a polycondensation reaction of polycarboxylic acids with polyols, splitting of water. There are two ways to synthesize; The first one is azeotropic esterification performed in an azeotropic organic solvent. Azeotropic solvent acts as the carrier to remove the water from the reaction medium. The second one is melt condensation process in which the coreactants are reacted in melt at temperatures at approximately 160-260 ^{o}C. The reaction can be performed either in vacuum and a stream of inert gas to remove the water from the medium.

The saturated polyester polyols have good pigmentability, weather stability, high gloss. The aliphatic product gives good UV stability but the aromatic ones tend to yellow on exposure to light. The polyester polyols are suitable for broad range applications from vehicle finishing to general industrial coatings. Commercial polyester products have a molecular weight of 500 to 5000 g/mol. They canbe liquid or solid, hard and soft resins depending on the chemical structure [80, 81].

Table 2.2 : Building blocks for polyester polyols [80].

Diol / triol	Dicarboxylic acid / anhydride	Modifying components
Ethylene glycol	Adipic acid	Fatty acids (saturated)
1,2-Propane diol	Maleic acid	
1,4-Butane diol	Phthalic acid	
1,6-Hexane diol	Hexahydrophthalic acid	
Neopentyl glycol	Isophthalic acid	
Diethylene glycol*		
Glycerol		
Trimethylol propane		

*Yields ether esters

2.3.2.3 Polyether polyols

Polyether polyols are synthesized by the addition of ethylene oxide and/or propylene oxide to polyfunctional starter molecules (Figure 2.15). Polyether are mainly used for solvent-free formulations due to their low viscosity. Polyethers used in coatings applications have a molecular weight of between 500 and 2000 g/mol. The main properties of polyether polyols are melting point, viscosity, compatibility and hydrophilicty [80, 81].

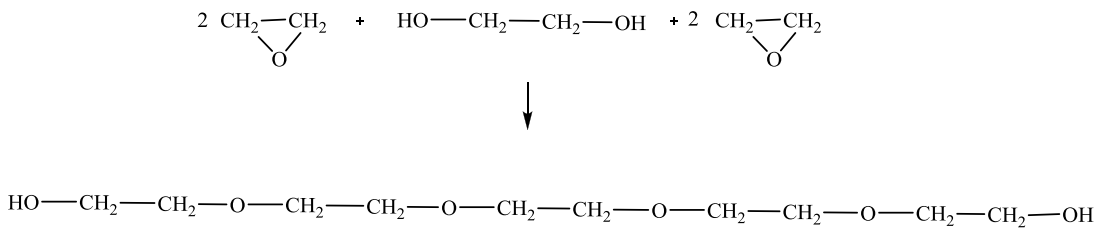


Figure 2.15 : Polyether acrylate.

2.3.2.4 Polycarbonate polyols

Polycarbonate polyols are esterification products formed by the reaction of carbonic acid with polyols (Figure 2.16). Polycarbonates are recommended for use in solvent-free formulations. Their major properties are low viscosity, good weather stability and good hydrolysis. Aliphatic polycarbonate polyols show low viscosity, good weather stability and good resistance to hydrolysis [80, 81].

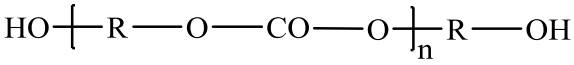


Figure 2.16 : Polycarbonate polyol.

2.3.2.5 Polycaprolactone polyols

Polycaprolactone polyols are synthesized by the ring-opening polymerization of ε-caprolactone (Figure 2.17). The ring-opening polymerization takes place at temperatures between 120-200 ^{o}C. The polylactones are manufactured by the polyaddition of caprolactone to diols and are available as uniform low-viscosity products with a defined functionality and a molecular weight of between 500 to 2000 g/mol. The advantages of polycaprolactones are flexibility, weather stability and low viscosity.Two-component polyurethane coatings for plastics and in solvent-free coatings for construction applications are major applications of polycaprolactones [80, 81].

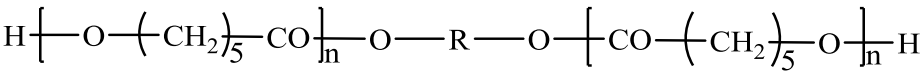


Figure 2.17 : Polycaprolactone polyol.

2.3.2.6 Polyurethane polyols

The polyacrylate polyols covers copolymers of acrylic and/or methacrylic acid esters- ethyl acrylate, butyl acrylate and methyl methacrylate which contain hydroxyl

groups. Because of their high viscosity, these products have less importance in the field of solventborne coating systems [80, 81].

2.3.3 Catalyst

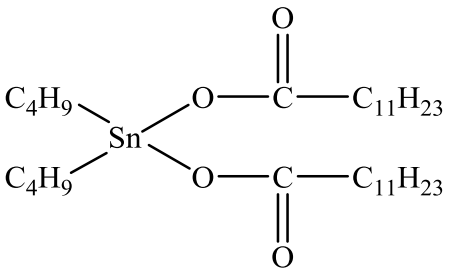
A variety of substances, for example, tertiary amines, organometallic compounds, metal salts (polyaddition), phosphines (dimerization), quaternary ammonium slats and phenols (trimerization) are used for acceleration of different reactions of isocyanate groups and thermal reverse processes catalytically.

In polyurethane coatings, aliphatic isocyanates are normally used with catalysts in order to compensate for their lower reactivity compared with aromatic isocyanates and thus satisfy the requirements for coating applications. There are two group catalysts are of key interest. Metal catalyst and amine catalyst.

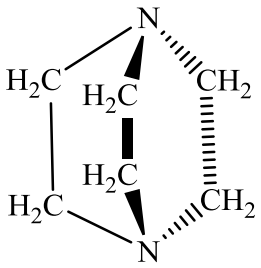
Metal catalysts activate the isocyanate group and accelerate the urethane reaction. Dibutyltin dilaurate (DBTL) is often used as is zinc octoate which is also used as a drier for binders which cure by oxidation as shown in Figure 2.18.

Amine catalysts, accelerate the urethane reaction primarily by activating the hydroxyl group. 1,4-diazobicyclo[2.2.2]octane is widely used and named as DABCO.

The combination of both types of catalyst can produce synergistic effect [79, 80, 82].



DBTL



DAPCO

Figure 2.18 : DBTL and DAPCO.

2.3.4 Acrylates

Radically polymerizable oligomers usually contain acrylate groups. Some main types of acrylates are shown in Figure 2.19.

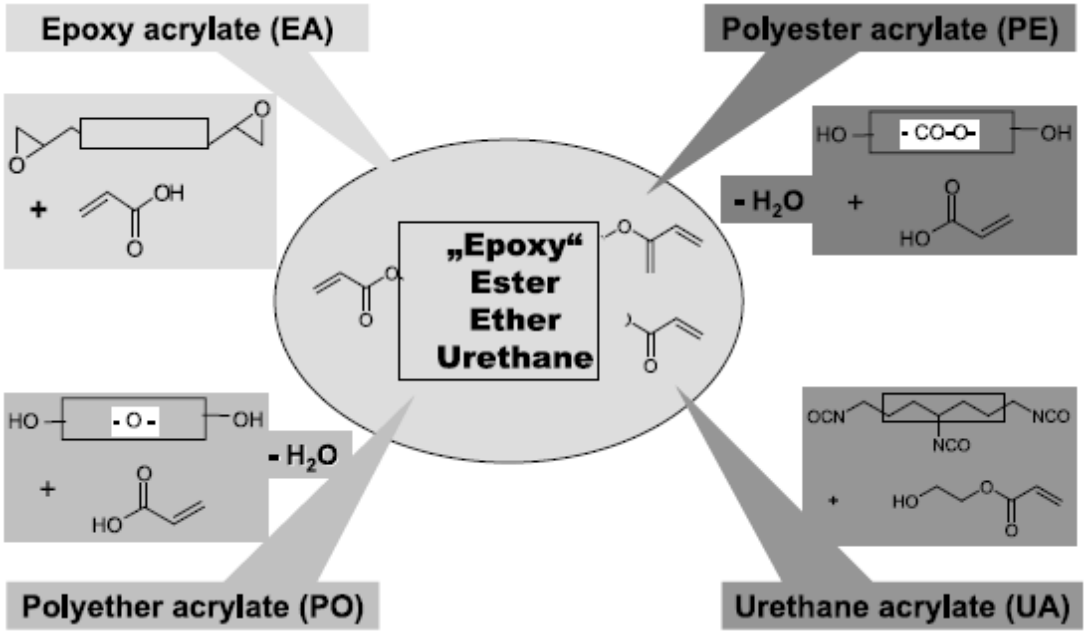


Figure 2.19 : Schematic chemical structure of main acrylate resin types for acrylate based radically curing UV coatings [83].

2.3.4.1 Epoxy acrylate

Epoxy acrylates are widely used in radiation curable formulations because of their low price and high reactivity. Bisphenol A epoxides, epoxy novolacs, and epoxidized oils are main compounds of this class. Bisphenol A diglycidyl ethers type oligomers are mostly used. When the curing is performed under air the reactivity is high molecules of HCl [79].

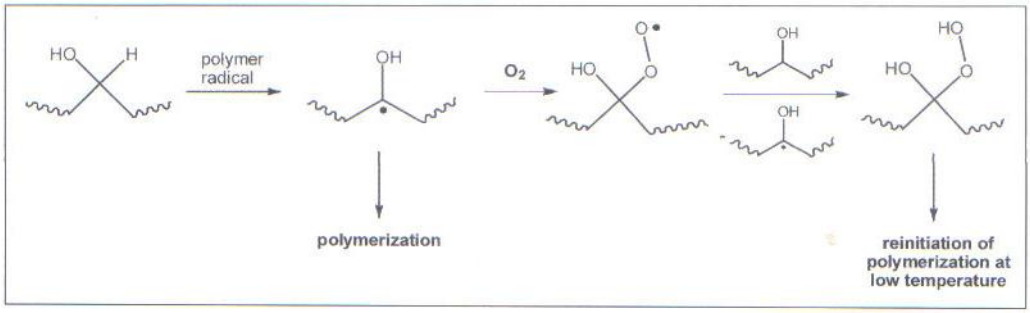


Figure 2.20 : Epoxy acrylate radicals can be formed by abstraction of hydrogen atoms [83].

A. Bisphenol A epoxy acrylates

Epoxy functional oligomers react with acrylic acid in a ring-opening addition reaction under mild conditions to obtain Bisphenol A epoxy acrylate as shown in Figure 2.21. The variation of the molecular weights of starting bisphenol A epoxy resins to achieve different properties. The viscosity of bisphenol A epoxy acrylate is high. The molecular weight is set to low level to obtain good flow behavior and better application. The reactive diluents are generally used to reduce the viscosity level. The resulting film generally shows high gloss, high hardness, good chemical and corrosion resistance. But yellowing and weathering resistance of the aromatic systems are relatively poor [83].

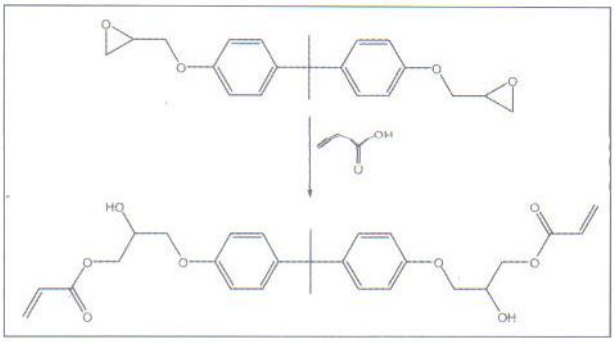


Figure 2.21 : Difunctional bisphenol A epoxy acrylate oligomers can be prepared from bisphenol A diglycidyl ether and acrylic acid [83].

B. Epoxy novolac acrylates

Bisphenol A epoxy acrylates react with the epoxide ring with acrylic acid to obtain epoxy novolac acrylates as shown in Figure 2.22. Reactivity and functionality are usually high because the resulting films have high crosslinking level. The films are hard and resistant to chemicals and heat [83].

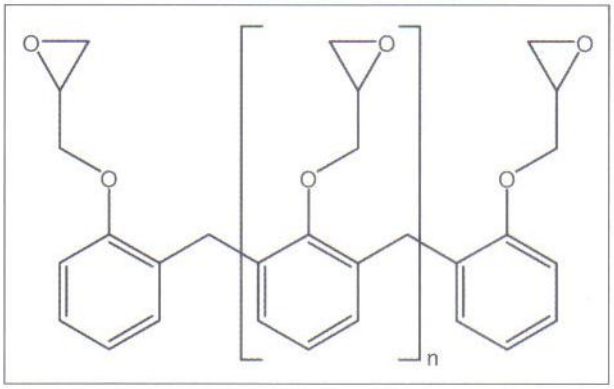


Figure 2.22 : Chemical structure of an epoxy novolac [83].

C. Acrylates of epoxidized oils

Epoxidized oils mainly derived from soy oils. They have low viscosity, low reactivity, and good pigment wetting properties. The mechanical properties are low [83].

2.3.4.2 Urethane acrylate

Urethane oligomers possess the best balance between hardness, toughness, and chemical and abrasion resistance on the one hand, and flexibility on the other hand, so they have the outstanding properties.Due to this large variation hard, abrasion resistant and soft, elastic films can be produced. This property is related with the intermolecular hydrogen bonds which increases the viscosity of the formulation as shown in Figure 2.23 [83].

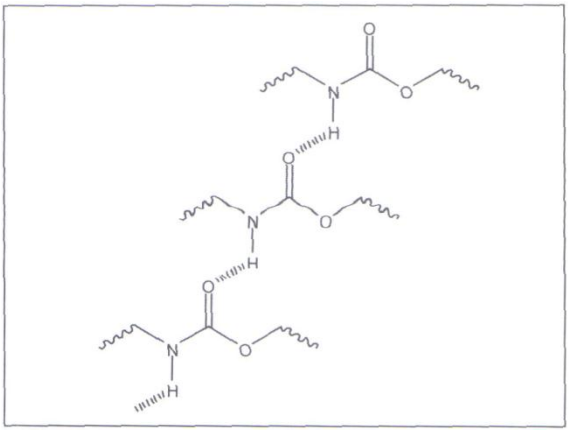


Figure 2.23 : Formation of intermolecular hydrogen bonds increases the viscosity [83].

Urethane acrylates can be obtained by the synthesis of di- or polyfunctional isocyanates with hydroxyalkyl acrylate components. There are two different ways to prepare urethane acrylates:

Diisocyanate is first reacted with the hydroxalkyl acrylate to remain one isocyanate group intact; this adduct is then reacted with the polyol to form an urethane acrylate as shown in Figure 2.24 [83].

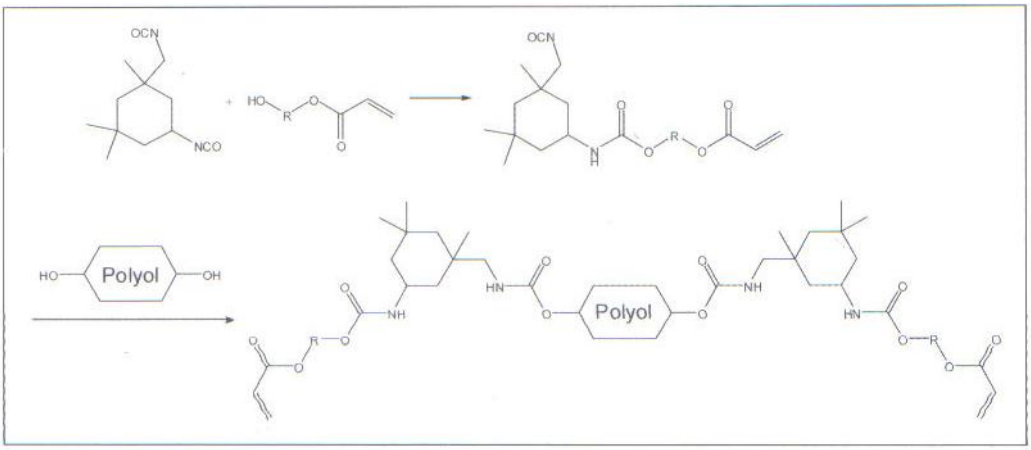


Figure 2.24 : Preparation of an urethane acrylate by route 1 from isophorone diisocyanate, a hydroxyalkyl acrylate (*where R is, e.g., C_2H_4 or C_3H_6*), and a polyol (*e.g., polyester polyol*) leads to well defined products and only small residues of free hydroxyalkyl acrylate [83].

Diisocyanate is reacted with the polyol to form an isocyanate-containing prepolymer. In the second step, the prepolymer is reacted with the hydroxyalkyl acrylate to form an urethane acrylate. Higher molecular weight products can be obtained by this formation.

2-hydroxyethyl acrylate (HEA) and 2-hydroxypropyl acrylate (HPA) are generally used as hydroxyalkyl acrylate.

Polyols can be simple diolas such as 1,6-hexanediol and oligoester, oligoether polyols. Oligoester-based urethane acrylates have higher reactivity, hardness, and solvent resistance, and lower tendency to yellowing compared to oligoether-based urethane acrylates [83].

2.3.4.3 Polyester acrylate

Polyester acrylates are prepared by esterification of OH-groups of polyester polyols with acrylic acid or its derivatives as shown in Figure 2.25. Diols, dicarboxylic acids, and polyester polyols are used for synthesis trimethylol propane is used to have branched [83].

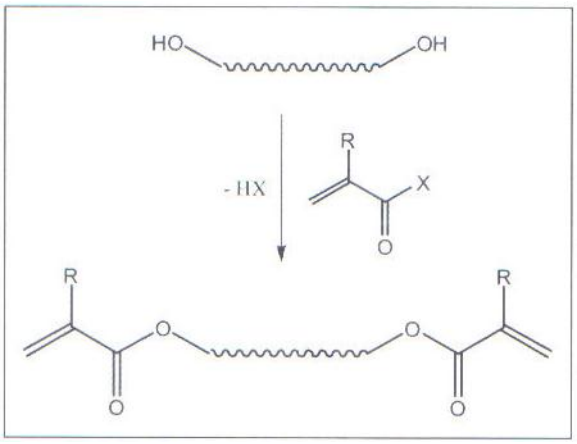


Figure 2.25 : Preparation of a (meth)acrylate-containing monomer/oligomer with two polymerizable groups; R=H, CH_3; chain: (cyclo)aliphatic, oligo- or polyether, epoxy resin, polyurethane, or polyester, etc; X=OH, OCH_3, $OCOCH=CH_2$ [83].

2.3.4.4 Polyether acrylate

The variation possibilities with polyether acrylates are less than polyester acrylates due to the limited number of raw materials. Generally ethylene oxide and propylene oxide based monomers are used. Polyether acrylates are highly flexible due to their low Tg. They have low viscosity compared to other oligomers so they are used to lower the viscosity when needed. The resistance to water and some chemicals is low because some of the polyether type oligomers are water-soluble. They are reactive so this have a possitive effect on curing [79].

2.3.5 Reactive Diluents

Monomers, oligomeric acrylates or vinyl ethers are reactive diluents and used to adjust the viscosity as shown in Figures 2.26. Monomers like styrene, N-vinyl pyrrolidone and monofunctional esters of acrylic acid monomers are best diluents but they have high volatility, strong odour, flammability, and skin irritation. Mono functional isobornyl acrylate or trimethylol propane formal monoacrylate have been developed which have high molecular weight between crosslink's or lower crosslink density. This property results with better flexibility, low odour and low volatility. Tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), propoxylated glycerol triacrylate (GPTA, like OTA480), and hexanediol diacrylate (HDDA) are some types of multifunctional monomers and synthesized by esterification reactions of acrylic acid with polyols. The other mentioned multifunctional acrylates have only small market share. Pentaerythritol tetraacrylate

(PTA) or dipentaerythritol hexaacrylate (DPHA) are higher funtional acrylates and used as minor ingredients. Small portion can change the crosslinking density and show hard but brittle films. Mono- or difunctional epoxides and vinyl ethers mainly used as reactive diluents in cationic polymerization [79].

Acrylates	Methacrylates	Others
Monofunctional acrylates	Hydroxypropyl-MA	Styrene
Isobornyl acrylate (IBOA)	Isobornyl-MA	N-Vinyl caprolactam
Trimethylolpropane-formal-mono-acrylate	Dicyclopentenyl-oxy-ethyl-MA	N-Vinyl pyrrolidone
Phenoxyethyl acrylate (POEA)	Hydroxyethyl-MA	N-Vinyl formamid
Difunctional acrylates		Acrylamidomorpholine
Tripropylene glycol diacrylate (TPGDA)		**Silanes**
Dipropylene glycol diacrylate (DPGDA)		**Vinyl ethers**
Hexandiol diacrylate (HDDA)		Divinylether of Tripropylenglycol
Neopentylglycol diacrylate (NPGDA)		Divinylether of cyclohexane-dimethanol
Multifunctional acrylates		Vinylether capped urethanes
Trimethylolpropane triacrylate (TMPTA)		
(Ethoxylated/propoxylated) TMPTA		
Propoxylated glycerole triacrylate		
Pentaerythritol triacrylate (PETIA)		
Pentaerythritol tetraacrylate (PT_4A)		
Dipentaerythritol penta/hexa acrylate		
Cationic: Mono-epoxides, Vinyl ethers, allyl ethers, oxetanes		

Figure 2.26 : Reactive diluent types for UV-curing systems.

2.3.6 Radical Photoinitiators

A photoinitiator is any chemical compound that decomposes into free radicals when exposed to light and form reactive species from their excited state, which initiate sequential reactions as shown in Figure xx. Radicals, cations or anions are the initiating species. Large number from companies like Ciba Specialties (trade names Irgacure® and Darocure®), Lamberti (Esacure®), BASF (Lucirin®), and many others represents 90% of commercial radical initiators. Union Carbide (Cyracure®), Degussa (Degacure®) are main companies for cationic photoinitiaors which is generally sulfonium salts and as well as iodonium salts from General Electric and iron complexes from Ciba [79].

Radical photoinitiators, which represent more than 90% of commercially used initiators, are available in large number from companies like Ciba Specialties (trade names Irgacure® and Darocure®), Lamberti (Esacure®), BASF (Lucirin®), and many others. Available in smaller number are cationic photoinitiators, mainly sulfonium salts, from Union Carbide (Cyracure®), Degussa (Degacure®) as well as iodonium salts from General Electric and iron complexes from Ciba. Almost all radical photoinitiators contain benzoyl(phenyl-CO-) structure. There ara two main classes for that: α-clevable (Norrish I type) and the non-clevable (hydrogen abstraction type II) as shown in Figure 2.27 [79].

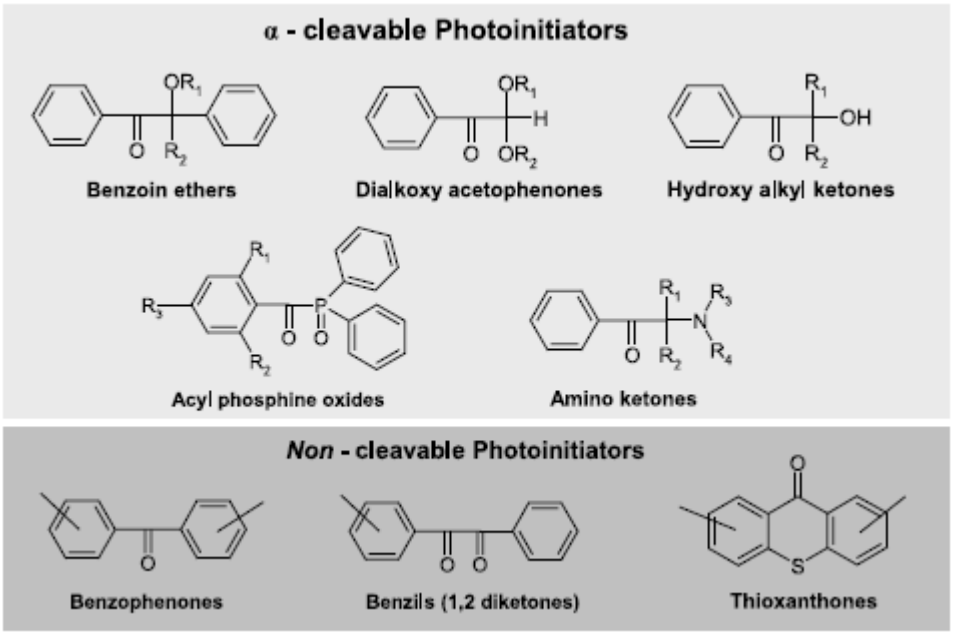


Figure 2.27 : Examples of "alpha-cleavage type" and non-cleavable "electron transfer-hydrogen abstraction type" photoinitiators.

2.4 UV-Curing Process

Radiation curing coatings and inks contain reactive groups which can react with each other after exposure of energy-rich radiation. Conventional coatings dry by evaporation of the solvents. Generally this process takes place at room temperature, at elevated temperatures below 100 ^{o}C or above 100 ^{o}C.

When the solvent evaporates from the coatings and no chemical reaction occurs, this is mentioned as physical drying. Similar principles apply to waterborne coatings, this time the solvent is water instead of organic solvents. In radiation curing formulations, the curing process occurs without any solvent. All components in a radiation curing formulation stay within the film. The components become the part of the final polymer network and affect on the final film properties. Figure 2.28 shows the differences between radiation curing process and the conventional coatings [83].

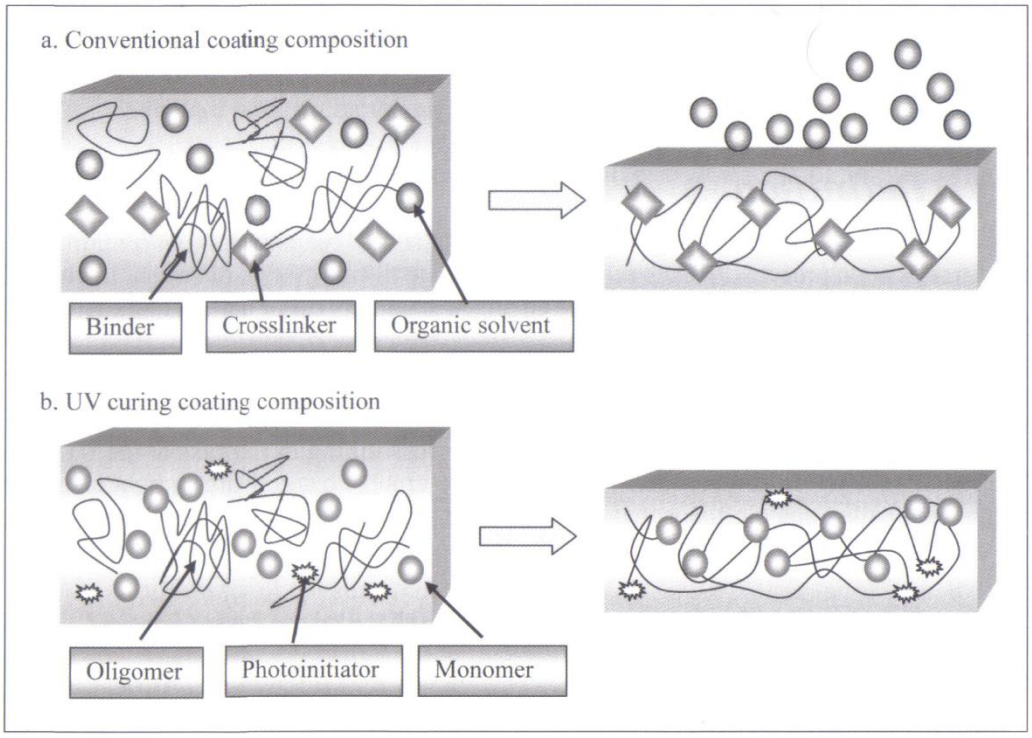


Figure 2.28 : a) In case of conventional coatings organic solvents leave the film during drying and crosslinking; b) UV curing formulations crosslink without emitting any organic solvents [83].

Radiation curing is distinctly different to conventional coatings technologies. The nearly intermediate cure and the absence of solvents allow obtaining a dry and fully cured film in just a few seconds. There is no need for long flass-off time- and energy-consuming drying tunnels in application lines. Cured surfaces can immediately be processed. Printed goods can be coated, cuy, embossed, etc. right away; coated surfaces ban be sanded, recoated, glued and assembled without waiting time. Radiation curing is ideal technology for curing coatings on flat (two-dimensional) substrates. Especially when the substrate is fed from a web like in graphic arts applications or flat substrates moved on a conveyor belt through the application line like in wood coatings applications a radiation curing unit is easy to install and operate. Figure 2.29 shows the principle of a web-fed UV coating unit. The most important advantages and disadvantages of radiation curing over conventional coating technology are summarized in Table 2.3 [83].

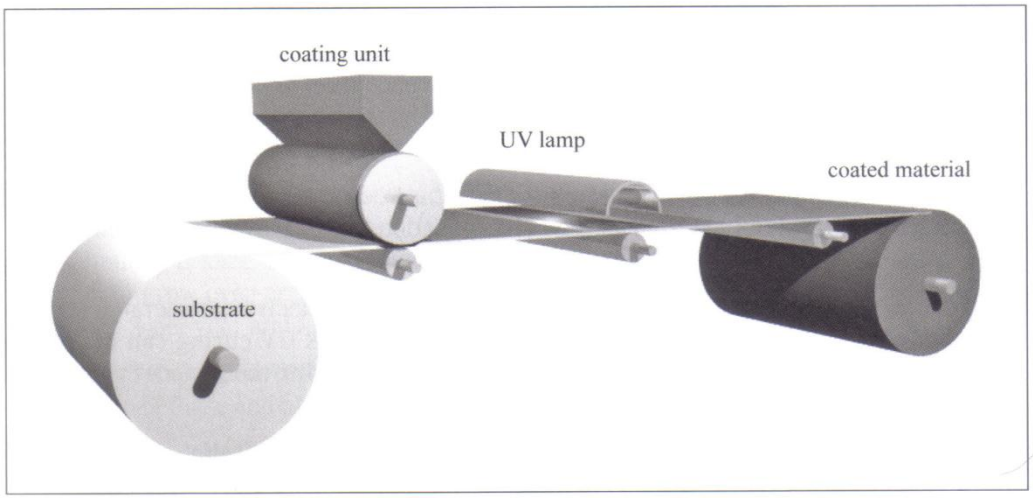


Figure 2.29 : a) In case of conventional coatings organic solvents leave the film during drying and crosslinking; b) UV curing formulations crosslink without emitting any organic solvents [83].

Table 2.3 : Main advantages and disadvantages of radiation curing over conventional coating technology [83].

Advantages	Disadvantages
Very fast cure speed	Cure of three-dimensional objectives requires complex curing units (shadow areas)
Time and cost savings	Skin irritation in case of some raw materials
Absence of volatile solvents (VOC), zero to low emissions of VOC	Very matte finishes difficult to obtain
Cured films display outstanding resistance properties and gloss	High pigmentation levels at high film thicknesses can create cure problems
Reduced energy consumption for cure (environmental and cost)	Inherent viscosity of radition curing formulations makes certain application methods impossible at room temperature
Relatively small capital investment in case of UV unit	Running and maintaining the curing unit requires qualified personnel
Little space requirements (especially in case of UV units)	Partly high raw material costs
Application on heat-sensitive substrates possible	Relatively high investment costs in case of EB
No pot-life = coating/ink does not dry before irradiation (no problems in case of machine stop; easy to clean and easy recycling)	Adhesion especially to metal or some plastic substrates
	Odor of formulations

2.4.1 The UV-curing process

Conventional linear polymers which is prepared by a step like process, as used in polyaddition and polycondensation reactions or by a chain process occurring in polymerization reactions as presents in Figure 2.30.

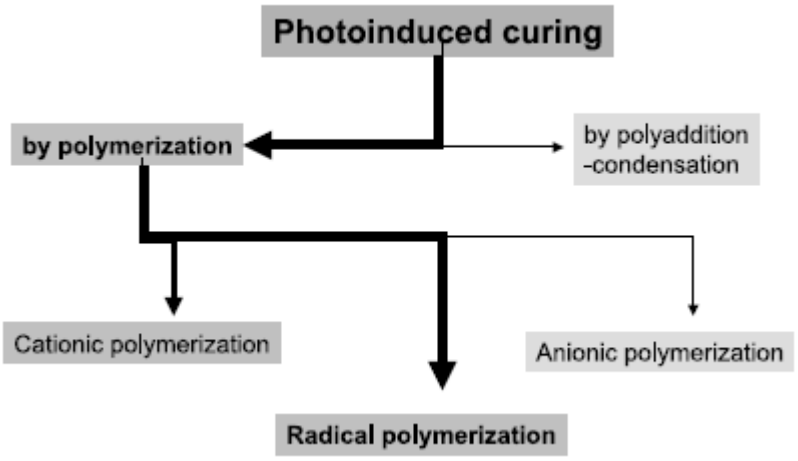


Figure 2.30 : Possibilities of photoinduced curing.

The UV curing technology is a transformation of reactive liquid formulation into a solid coating film with photoinitiation. Cation, anion or radical are the initiating species. Radical producing photoinitiators are majorly used in UVcurable coatings. The main components of such formulations based on radical polymerization:

- Reactive resins, contain polymerizable double bonds, give the main properties to the final coating
- Copolymerizable monomeric diluents, helps to adjust and decrease the level of viscosity,
- Photoinitiators,
- Other coating additives.

Radical initiated UV induced crosslinking can be divided into three steps: initiation, propagation and termination.

2.4.2 UV exposure and initiation

UV-light activates the photoinitiator to generate free radical to start the curing process as presented in Figure 2.31. The name of this step is photolysis. The radicals add to the double bonds of oligomers or monomers. In the initiation step of the

radical polymerization, they form a carbon centered radical. The photoinitiator has to be capable of absorbing light which is generated bu the lamp to start the initiation process. The absorption spectrum of the photoinitiator has to mesh with the emission spectrum of the lamp as shown in Figure 2.32.

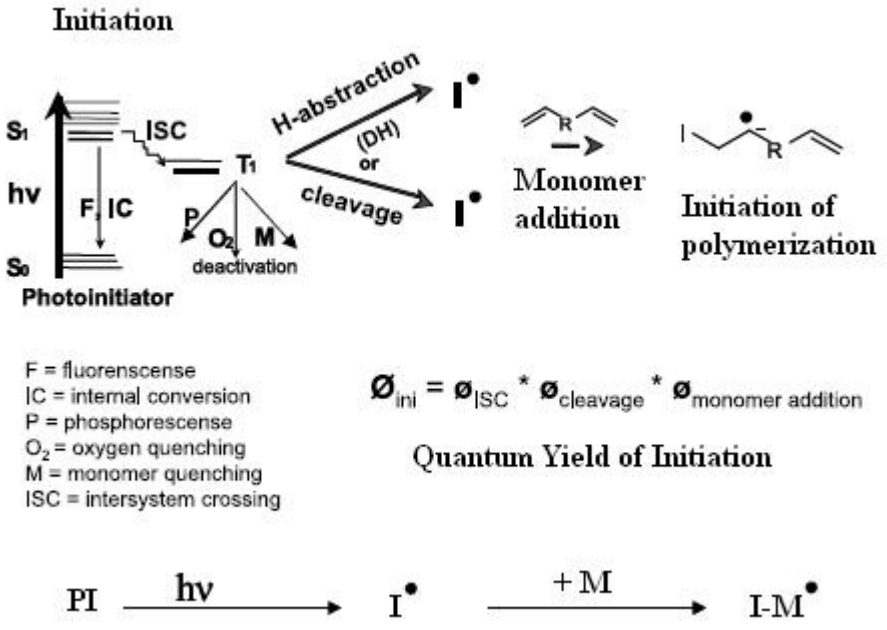


Figure 2.31 : Jablonsky-type diagram for photoinduced radical photoinitiation.

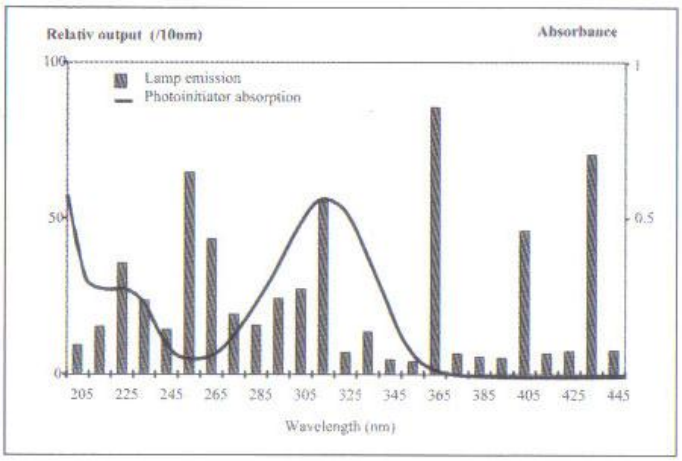


Figure 2.32 : Absorption spectrum of a photoinitiator and emission spectrum of a medium pressure mercury lamp.

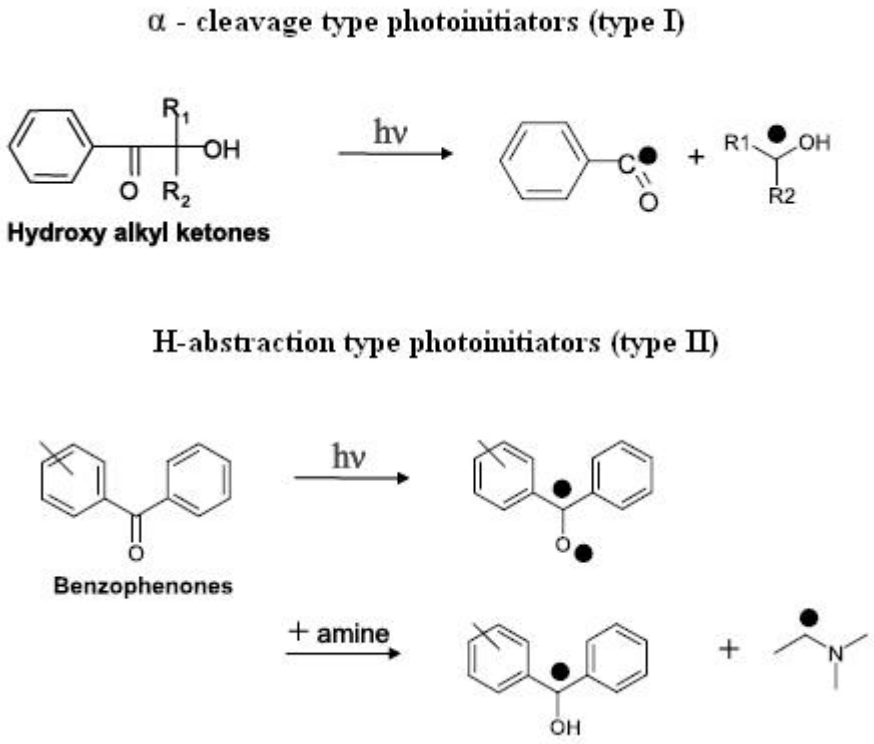


Figure 2.33 : Photoinitiator types.

If the photoinitiator does not satify this requirement, the curing reaction can not initiated. The appropriate absorption of commercial photoinitiators usually enlarges from 380 to 400 nm for UV-A, and around 230 nm for UV-C. For special applications some photoinitiators absorbing nearly in the visible range, slightly above 400 nm. The spectrum can be seen in Figure 2.34.

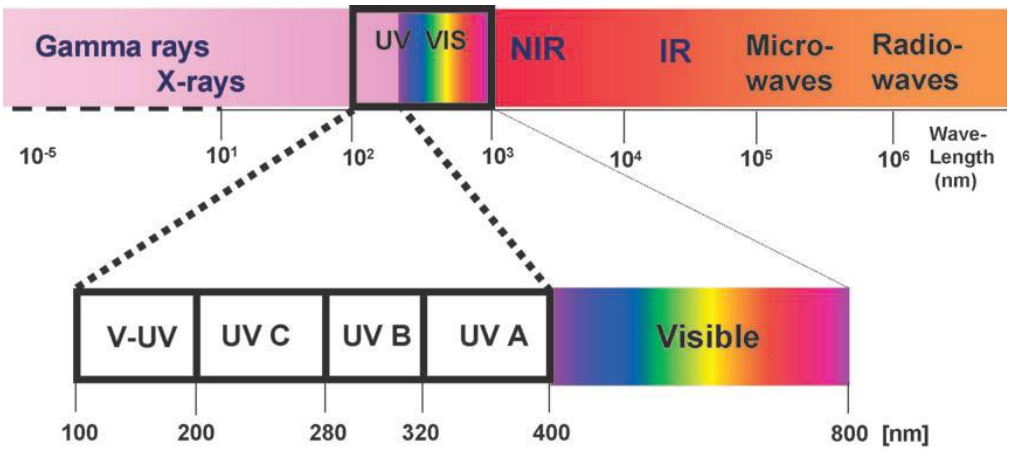


Figure 2.34 : Electromagnetic spectrum [16].

2.4.3 Propagation and curing mechanism

The radicals are forms in the initiation step. The propagation rate is depending on the initiation rate and oligomer reactivity. The temperature is increasing the propagation

rate but not the reactivity. The high temperature increases the chain mobility during gelation process and this property helps to have a fast and extensive curing. The heat generated by the lamp and the exothermicity of the reaction can increase the local temperature (Figure 2.35).

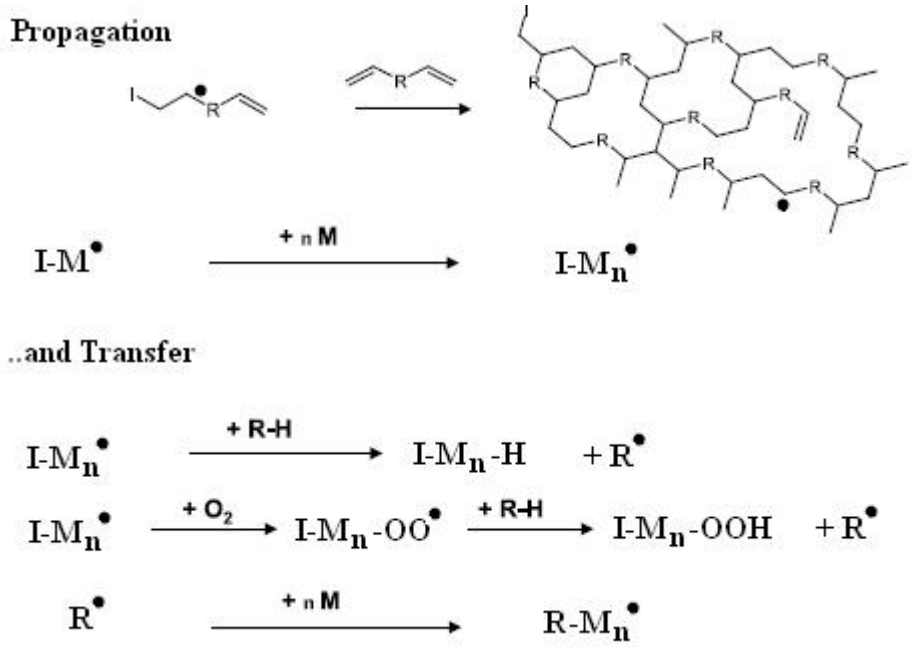


Figure 2.35 : Propagation reaction.

2.4.4 Chain Termination

The termination process is controlled by reaction diffusion: radicals either undergo a recombination reaction or a disproportionation or remain trapped due to the highly crosslinked network. Sometimes there can be unreacted molecules in the network (Figure 2.36).

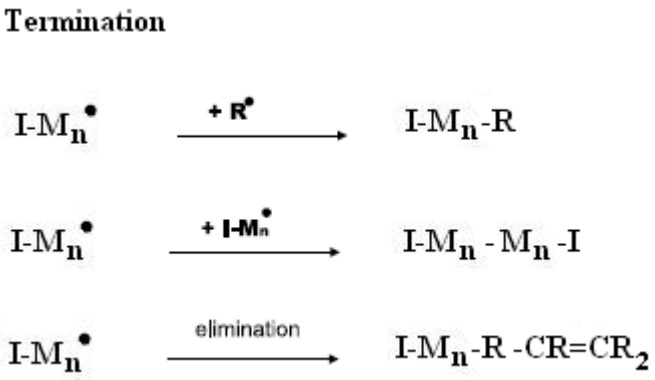


Figure 2.36 : Termination reaction.

2.4.5 Advantages of UV-curing

Low energy consumption

Reaction is easily controlled.

No volatile solvents

Formulations are stable

Ultra-rapid hardening

Reactions at room temperature.

3. EXPERIMENTAL WORK

3.1 Materials

Dibutyltin dilaurate (DBTDL) was purchased from Air Products Co., isophorone diisocyanate (Desmodur I) was purchased from Bayer. Toluene 2, 4-diisocyanate was purchased from Sigma-Aldrich. Linear polyester polyol (Hoopol S-1015-35)(*Mw*= 2000 g/mol) was purchased from Synthesia Internacional. Polypropylene glycol (Lupranol 1100)(*Mw*= 1100 g/mol) was purchased from Elastogran, BASF. Linear polycarbonatediol (Nippollan 980 R) (*Mw*= 2000 g/mol) was purchased from Nippon Polyurethane Industry. Ethylene carbonate, sodium carbonate, acetone, 1-bromo-4-fluorobenzene, Mg turnings, dichlorophenyl phosphine oxide, tetrahydrofuran, sulfuric acid, diethyl ether, sodium bicarbonate, magnesium sulphate, hexane, dimethyl sulphoxide, potassium hydroxide, bis(4-hydroxyphenyl)sulfone (BHPS), N-vinyl pyrrolidone (NVP), and methanol were purchased from Merck. Also 2-hydroxyethyl methacrylate (HEMA) from Laporte Performance Chemicals, dipropyleneglycol diacrylate (DPGDA) from CYTEC Chemicals, Irgacure 184 (1-hydroxy-cyclohexyl-phenyl-ketone) from Ciba Chemicals, 1,6-hexanediol diacrylate (HDDA) from Sartomer Chemicals were used for preparing films. All the products were used without further purification. Plexiglass panels provided from Polimercam Kimya San. were used as substrates in all coating applications.

3.2 Characterization

3.2.1 FT-IR analysis

Room temperature infrared spectra of the uncured PUA's was taken using a Nicolet FT-IR iS10 spectrometer with a detector at a resolution rate of 4 cm^{-1} in the range of 4000-400 cm^{-1} at room temperature. A total of 16 scans were used for signal averaging.

3.2.2 ^{1}H-NMR analysis

^{1}H-NMR spectra in deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$-d_1) were recorded on a Bruker Spectrometer at 250 MHz to characterize the chemical composition of the materials.

3.2.3 Gel content

A cured film sample (m_1) was accurately weighed, and then added to the Soxhlet extractor with acetone as extraction agent for 6 h. The UV-curable film was dried until its weight was constant (m_2). Gel content of the UV-cured film was calculated by the (3.1);

$$\text{Gel content (\%)} = (m_2 / m_1) \times 100 \qquad \textbf{(3.1)}$$

where m_1 is the weight of the cured film sample; m_2 is the residual weight of the cured film sample.

3.2.4 Chemical and solvent resistance

The UV-cured films were immersed into various chemicals and solvents at 25 ^{o}C. Weighed samples were kept in various solvents for at least 24 h and the values were calculated by (3.2)

$$\text{Weight loss: } ((m_s - m_d) / m_d) \times 100 \qquad \textbf{(3.2)}$$

where m_s and m_d are weights of a swollen and dry sample, respectively.

Materials used for chemical resistance: 10 % NaOH, 10 % Acetic acid, and 10 % HCl,

Materials used for solvent resistance: Chloroform, methanol, and xylene.

3.2.5 Water absorption

UV-cured samples were immersed in distilled water at 25 ^{o}C according to ASTM D 570 for predetermined period, and then they were taken out and the water was removed by filter paper. The water absorption value was calculated according to (3.3).

Water absorption (%) = $((w_{ht}-w_d) / w_d) \times 100$ **(3.3)**

where w_d is the initial weight of dry sample, and wht is the weight of humid sample at time t.

3.2.6 Contact angle

Contact angle measurements were carried out with a Krüss FM 41 instrument, equipped with camera. Analysis was conducted at room temperature by means of the sessile drop technique. Young's equation is used for calculations (Figure 3.1).For each sample, at least three measurements were made and the average was taken. The measuring liquid was distilled water. Initial drops (5-6μL) were deposited on the film surface from an airtight 1000 μL syringe, which was positioned 0.5 mm above the film surface.The tests were applied onto plexiglass substrate.

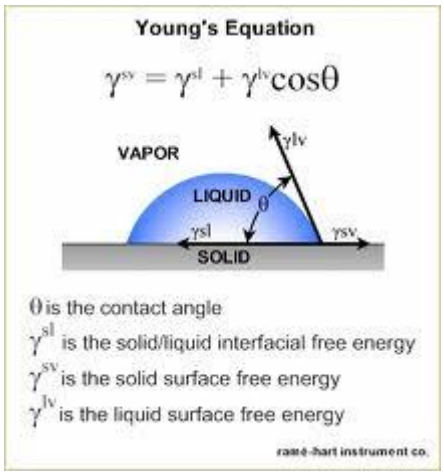


Figure 3.1 : Young's equation.

3.2.7 Gloss

Gloss of the UV-cured films was determined with a micro-tri-glossmeter (BYK-Gardner) according to ASTM D 523 (Figure 3.2). Gloss of the coated plates was measured at an angle of 20^o, 60^o and 85^o. For gloss test, plexiglass plates were coated substrate.

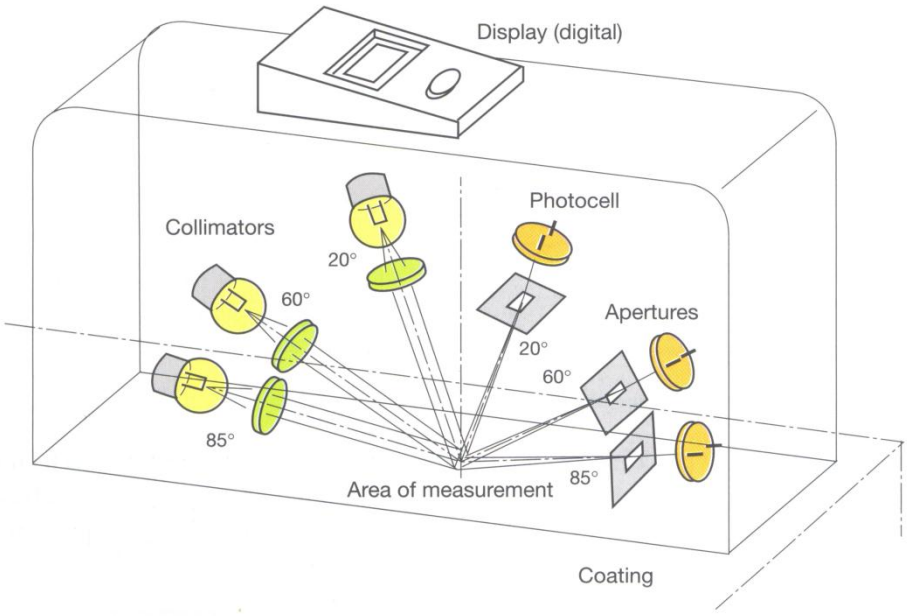


Figure 3.2 : Scheme of a measurement device for a gloss at different angles [85].

3.2.8 Pendulum hardness

The pendulum hardness of the UV-cured films was determined with a pendulum hardness tester (BYK-Gardner) according to ASTM D 4366 (pendulum weight = 200 ± 0.2g, amplitude limitation angle (deflection) = 6-3^{o}, osscillation period = 1.4 s) (Figure 3.3). König pendulum hardness tests are applied after all formulations onto coated plexiglass plates. Three points were tested with the values averaged for each specimen.

Figure 3.3 : Pendulum hardness tester [86-Gardner].

3.2.9 Pencil hardness

The pencil hardness of the UV-cured PUA films was determined by ASTM D 3363. Pencil hardness test was applied on plexiglass plates.

3.2.10 Cross-cut adhesion

The cross-cut adhesion test was determined by ISO 2409. Cross-cut test was applied on plexiglass plates.

3.2.11 Thermogravimetrical analysis

The decomposition profile of the UV-cured PUA's was thermogravimetrically analyzed (TGA) with a TA instrument Q50 model. Film samples ranging from 10-15 mg were placed in a platinium sample pan and heated from 30 to 700 ^{o}C under a N_2 atmosphere at a heating rate 20 ^{o}C/min, and the weight loss, residue was recorded as a function of temperature. Calibration was achieved with indium as reference material.

3.2.12 Stress-strain analysis

Mechanical properties of the films were determined by standard tensile stress-strain tests in order to measure the tensile strength, the modulus, and elongation at break. Stress-strain measurements were carried out at room temperature by using an universal testing machine (Zwick Roell Z010, extension rate of 500 mm/min.) The mechanical specification of free films, prepared at 50x10x1mm dimensions, made clearly with measurement of stress-strain values and three samples were tested for each film and the values were averaged.

To assess the coating performance of the materials, each formulation was applied to plexiglass panels using an applicator and cured in a bench type UV processor (EMA Group, 120 W/cm^2 medium pressure mercury UV lamps) were used.

4. SYNTHESIS OF SULFONE CONTAINING POLYURETHANE ACRYLATES

4.1 Experimetal Procedure

4.1.1 Synthesis of bis[(4-hydroxyethoxy)phenyl]sulfone (BHEPS)

A spherical flask (250 ml), equipped with a reflux condenser, magnetic stirrer, thermometer, and nitrogen inlet, was charged with 5 g bis(4-hydroxyphenyl)sulfone (0.016 mol), 2.8 g ethylene carbonate (0.032 mol), and 0.016 g sodium carbonate as catalyst. The mixture was heated to 175-180 ^{o}C under nitrogen for 2 h. The crude product was washed with water several times to remove unreacted ethylene carbonate and recrystallized from methanol. White crystalline product, m.p. 182 ^{o}C was obtained. The yield of the reaction was 90% after purification. The reaction takes place according to Figure 4.1 [51, 52].

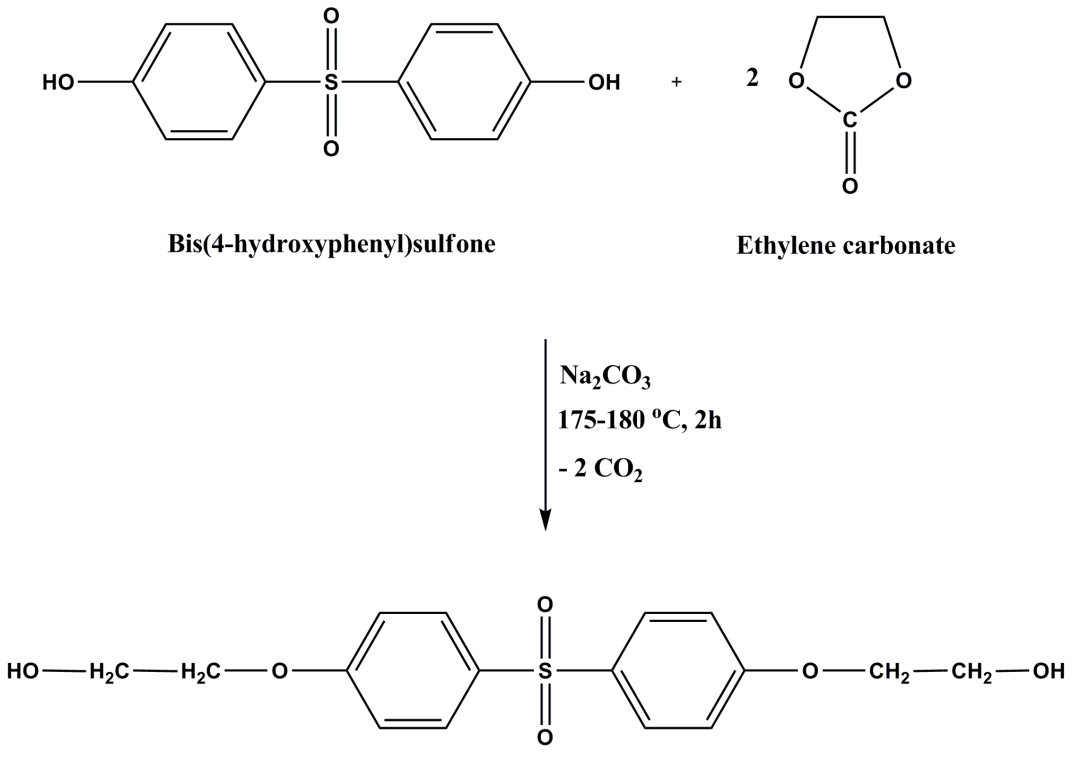


Figure 4.1 : Synthesis of bis[(4-hydroxyethoxy)phenyl]sulfone (BHEPS).

4.1.2 Synthesis of polyurethane acrylates (PUA's)

PUA's were prepared by a two-step solution polymerization method. The polyol/BHEPS was dissolved in acetone and placed into a round-bottom three-necked reaction flask equipped with a magnetic stirrer, heating mantle, reflux condenser, dropping funnel and nitrogen inlet and $CaCl_2$ tube. The mole ratios of the materials can be seen on Table 4.1. The diisocyanate dissolved in acetone was dropped into the reactor. The DBTDL added as catalyst, the temperature was increased to 55 ^{o}C. The reaction was continued till the isocyanate (NCO) content reached the theoretical value as determined by dibutylamine titration. In the second step HEMA dissolved in acetone was added dropwise through the dropping funnel for over a period of 30 min and mixed. The temperature was kept at about 50 ^{o}C to allow the termination to take place. The reaction was continued until NCO peak at 2270 cm^{-1} dissappeared totally in the FT-IR spectra of samples taken from the reaction medium every 0.5 h. The final product was vacuum dried at ambient temperature. The whole reaction process is depicted in Figure 4.2 and 4.3 [87].

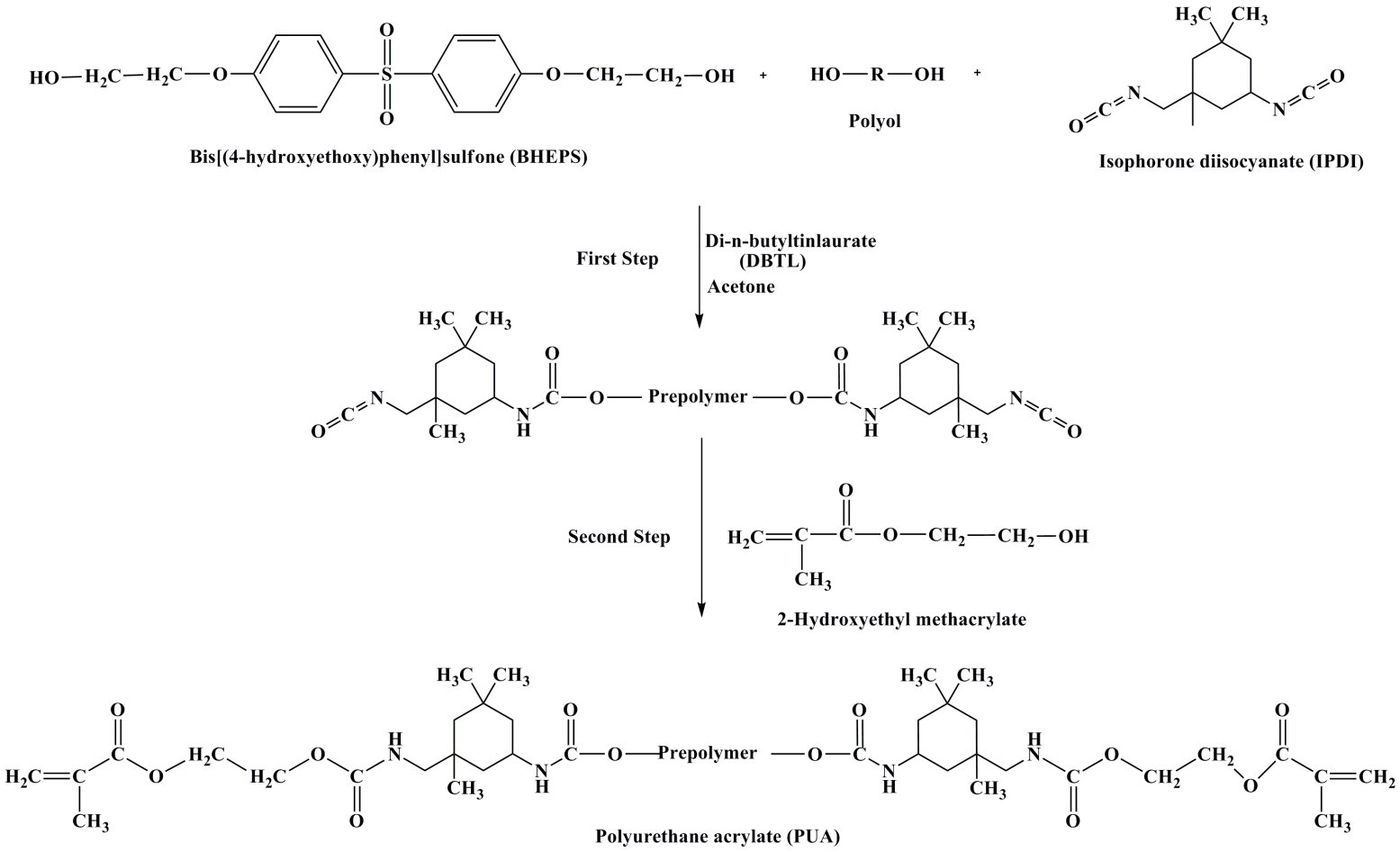


Figure 4.2 : Synthesis of IPDI containing PUA.

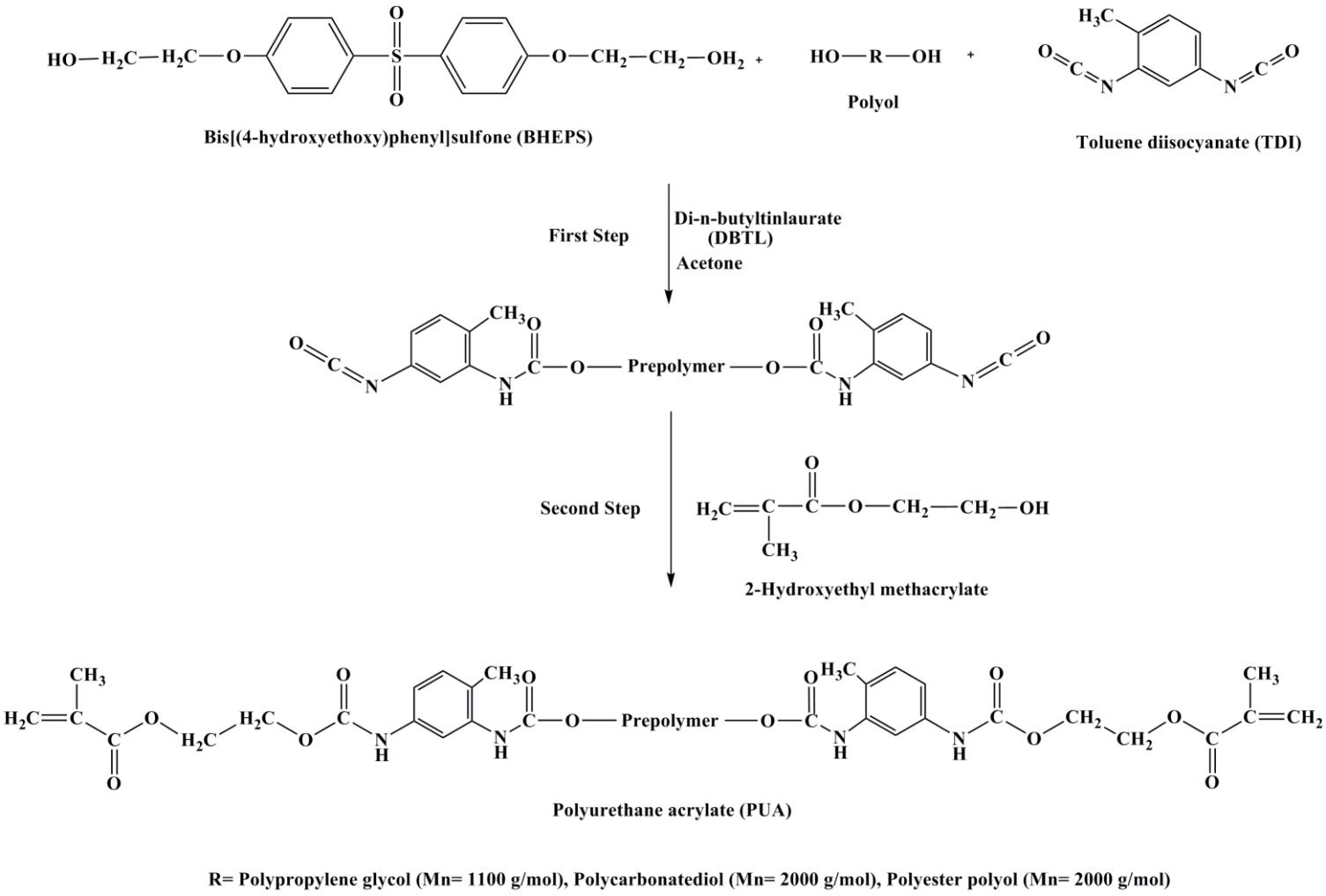


Figure 4.3 : Synthesis of TDI containing PUA.

Table 4.1 : Ratios and variations of PUA's.

Sample Code	PES	PC	PPG	BHEPS	IPDI	TDI	HEMA
S-PUA-1	1	-	-	-	2	-	2
S-PUA-2	0.6	-	-	0.4	2	-	2
S-PUA-3	0.4	-	-	0.6	2	-	2
S-PUA-4	-	1	-	-	2	-	2
S-PUA-5	-	0.6	-	0.4	2	-	2
S-PUA-6	-	0.4	-	0.6	2	-	2
S-PUA-7	-	-	1	-	2	-	2
S-PUA-8	-	-	0.6	0.4	2	-	2
S-PUA-9	-	-	0.4	0.6	2	-	2
S-PUA-10	1	-	-	-	-	2	2
S-PUA-11	0.6	-	-	0.4	-	2	2
S-PUA-12	0.4	-	-	0.6	-	2	2
S-PUA-13	-	1	-	-	-	2	2
S-PUA-14	-	0.6	-	0.4	-	2	2
S-PUA-15	-	0.4	-	0.6	-	2	2
S-PUA-16	-	-	1	-	-	2	2
S-PUA-17	-	-	0.6	0.4	-	2	2
S-PUA-18	-	-	0.4	0.6	-	2	2

4.1.3 Sample preparation

The coating formulations were mixed of PUA, HDDA, DPGDA, and NVP are used as reactive diluents and Irgacure 184 as photoinitiator. The formulation can be seen on Table 4.2. The formula was prepared separately for each formulation. FS symbol was added in front of the UV-cured PUA's to distinguish from uncured PUA's. Formulation 1 is applied to IPDI containing PUA's and formulation 2 is applied to TDI containing PUA's. NVP is used to dissolve TDI based PUA's.

Table 4.2 : Polyurethane acrylate formulations.

Components	Formulation 1 (%)	Formulation 2 (%)
PUA	50	50
DPGDA	37	22
HDDA	10	10
NVP	0	15
I-184	3	3

PUA: Polyurethane acrylate

DPGDA: Dipropyleneglycol diacrylate

HDDA: 1,6-Hexanediol diacrylate

NVP: N-vinyl pyrrolidone

I-184: Photoinitiator

4.1.4 Applications of the coating formulations

The coating formulations were applied on to plexiglass substrates at room temperature by a wire-gauged applicator to obtain a homogeneous thickened coating layer. The applied coatings were hardened by a UV processor with a medium pressure mercury lamp (120 W/cm_2, λ_{max}: 365 nm, total lamp power=3.24 kW) situated 15 cm above the moving belt after 10 pass. The speed of the processor was 2 m/min. and UV-cured.

Also free films were prepared by pouring the viscous material onto a TeflonTM mold (10 mm x 5 mm x 1 mm). A polyester film was also placed over Teflon to smooth surface and homogeneous cured film thickness as well. The films were cured by application of UV-lamp (OSRAM, 300 W) irradiation onto the free films for 180 sec. Mechanical, thermal, gel content, water absorption, chemical and solvent resistance tests were examined to free films.

4.2 Results and Discussion

4.2.1 Characterization

4.2.1.1 FT-IR spectrum of BHEPS

Synthetic route of BHEPS is given Figure 4.4. The FT-IR spectrum of BHEPS is shown in Figure 4.4. In the spectrum BHEPS showed characteristic bonds of hydroxyl and CH groups at 3416-2950 cm^{-1}, 1592 and 1455 cm^{-1} (C=C stretching of benzene rings), sulfone groups at 1319 cm^{-1}(SO_2 stretching). Etheric group related

with CH_2 protons, and etheric group related with phenyl groups were at 1141, 1253cm^{-1}, respectively.

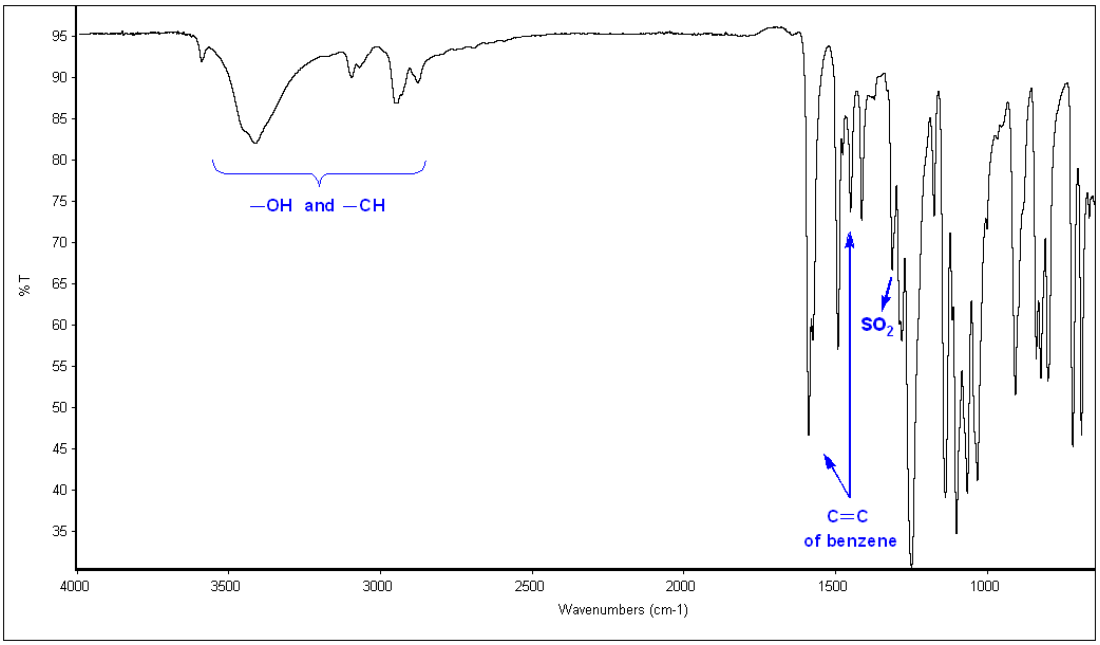


Figure 4.4 : FT-IR spectrum of BHEPS.

4.2.1.2 ^{1}H-NMR spectrum of BHEPS

Figure 4.5 shows ^{1}H-NMR spectra of BHEPS. The peak at 3.70 ppm was due to CH_2 protons near to hydroxyl group and 4.05 ppm was due to CH_2 protons near to etheric oxygen atom. The hydroxyl groups were observed at 4.94 ppm. The aromatic protons of BHEPS near to etheric oxygen atom appeared at δ = 7.65-7.89 ppm, and near to sulfone group appeared at δ= 6.84-7.17 ppm.

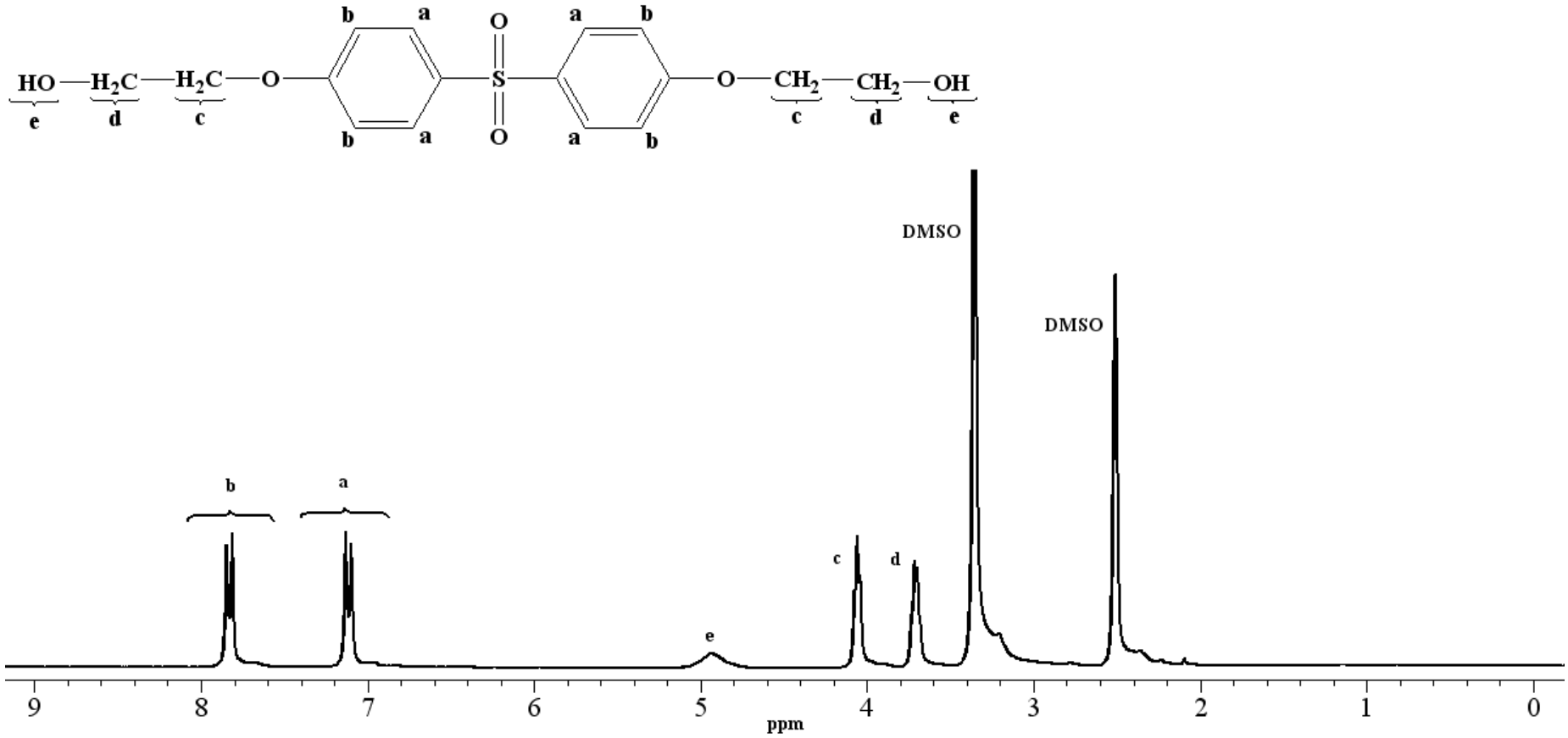


Figure 4.5 : ^{1}H-NMR spectrum of BHEPS.

4.2.1.3 FT-IR spectrum of PUA's.

The synthetic routes of PUA's are given in Figure 4.6 - 4.11. The FT-IR spectrums IPDI containing PUA's are shown in Figures 4.6 - 4.8, and spectrums of TDI containing PUA's are shown in Figures 4.9-4.11. In the spectrum, there are characteristic peaks of N-H (3300 cm^{-1}), and C=O (1700 - 1730 cm^{-1}), -C-N- stretching bands 1532 cm^{-1}, C-H aliphatic stretching bands (2945, 2858 cm^{-1}) are also observed. The dissappearence of the absorption bands of the NCO group (2270 cm^{-1}) of IPDI and TDI, and the OH group also proves successful synthesis of the PUA's. The characteristic peak of acrylate –C=C– is detected at 1638 cm^{-1}. The spectrum of PUA's with BHEPS contains ether and phenyl groups in the backbone. The absorption band at 1108 cm^{-1} originates from C-O-C group. There are phenyl absorption bands at 1594, 1508, and 814 cm^{-1}. The intensity of phenyl groups increased with addition of BHEPS in to the polymers. The characteristic peaks of S=O asymmetrical stretching bands 1330 - 1380 cm^{-1} and symmetrical bands 1135-1160 cm^{-1} are observed, the intensity of the S=O peaks increase due to the increase of sulfone content in PUA's.

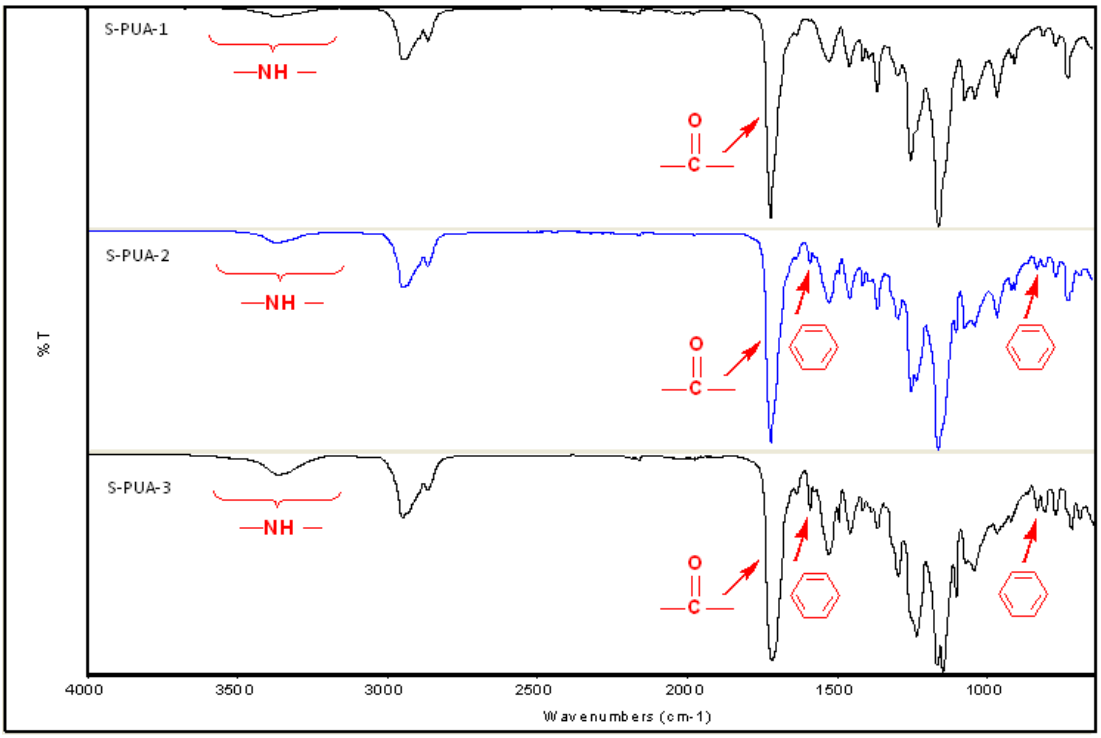


Figure 4.6 : FT-IR spectrum of IPDI and polyester polyol containing PUA's.

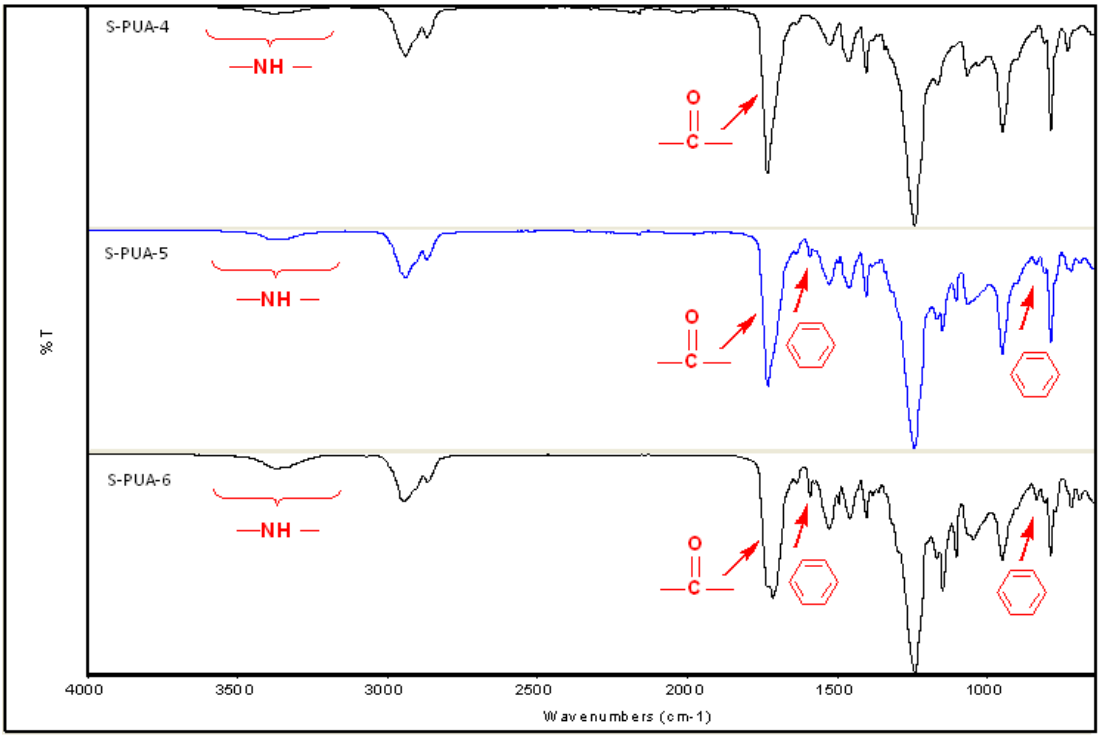


Figure 4.7 : FT-IR spectrum of IPDI and polycarbonatediol containing PUA's.

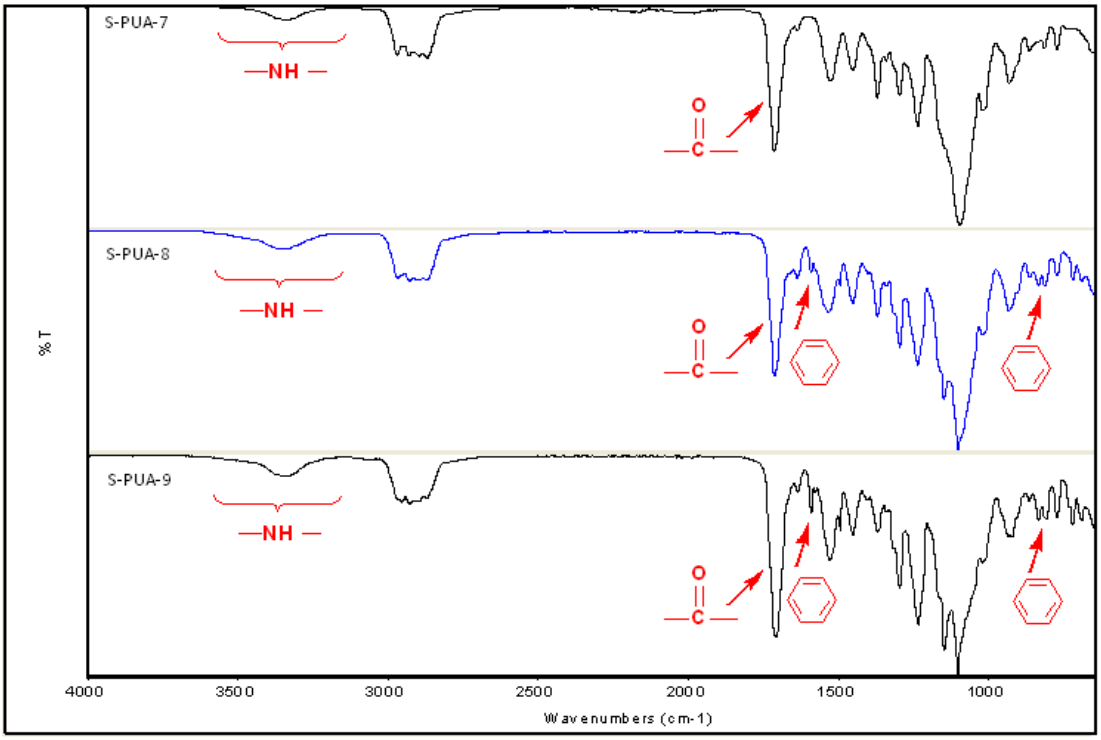


Figure 4.8 : FT-IR spectrum of IPDI and polypropylene glycol containing PUA's.

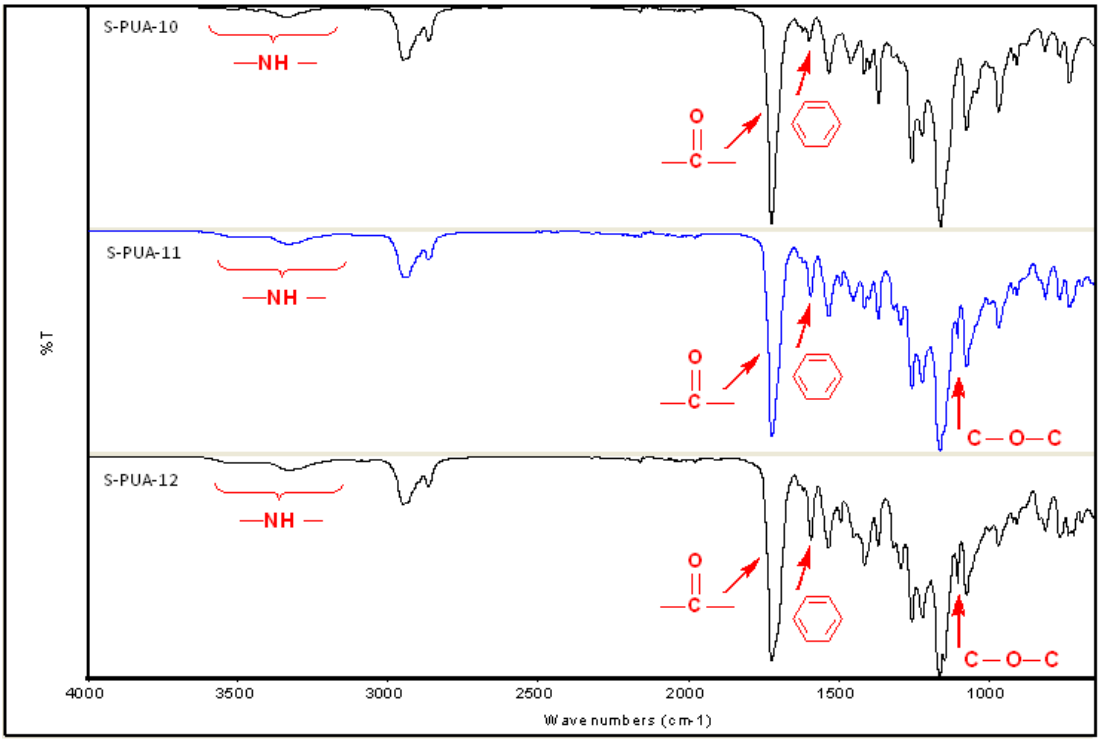


Figure 4.9 : FT-IR spectrum of TDI and polyester polyol containing PUA's.

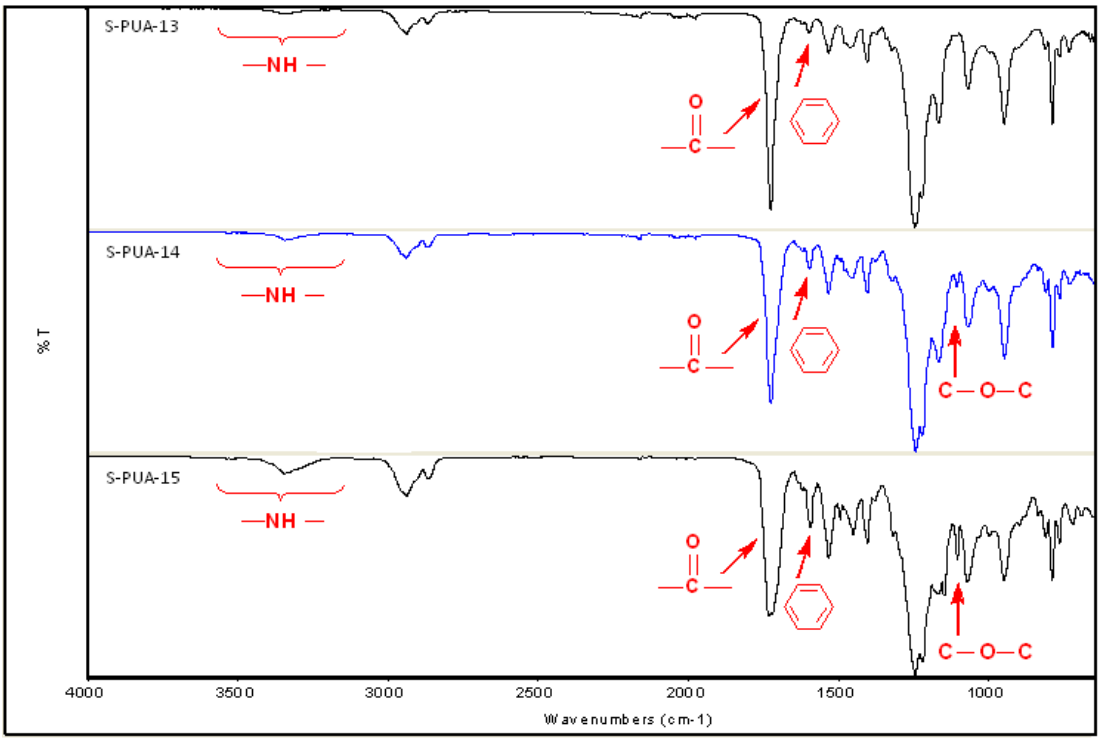


Figure 4.10 : FT-IR spectrum of TDI and polycarbonatediol containing PUA's.

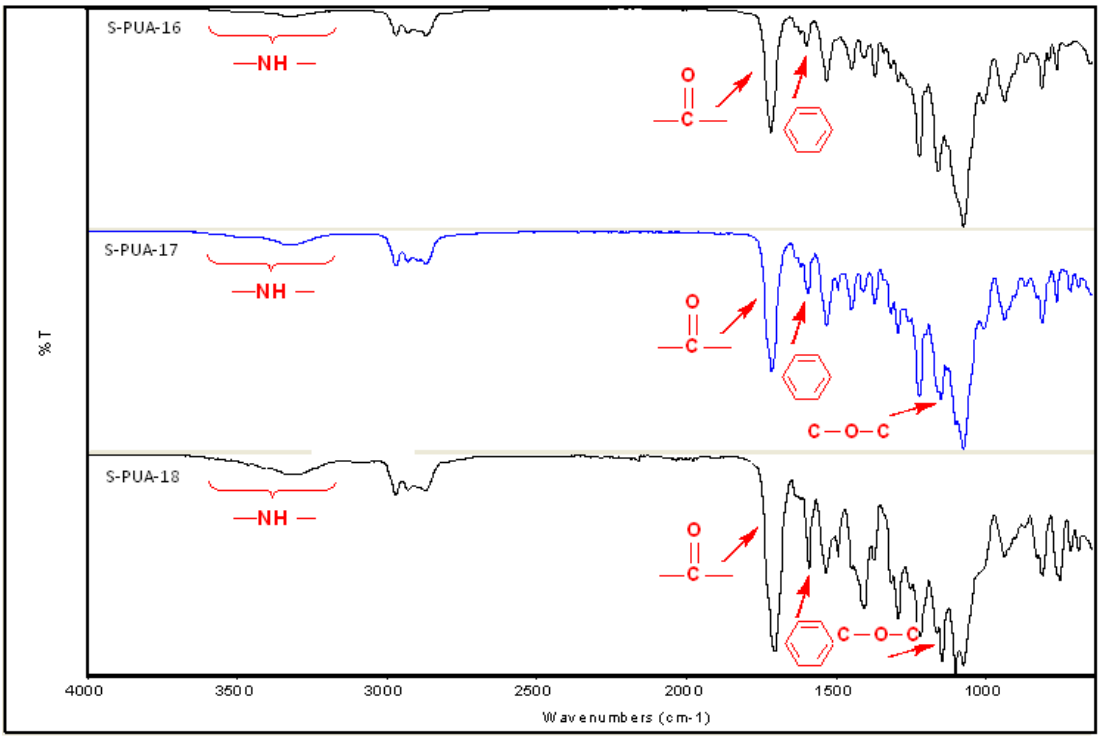


Figure 4.11 : FT-IR spectrum of TDI and polypropylene glycol containing PUA's.

4.2.1.4 ^{1}H-NMR spectrum of PUA's.

Figures 4.12 - 4.14 show ^{1}H-NMR spectra of IPDI containing PUA's in DMSO-d_6, and Figures 4.15 - 4.17 show ^{1}H-NMR spectra of TDI containing PUA's in DMSO-d_6. The peaks at 0.7-1.20 ppm are ascribed to the methyl (CH_3) protons and CH_2 protons of IPDI and CH_3 protons of neopenthyl moiety of PES. The central CH_2 protons of PES and PC and CH_2 protons in the cyclic ring of IPDI were at δ = 1.20-1.78 ppm. The peaks in the range of 1.81-2.00 ppm are methyl protons of HEMA and CH_2 protons of PES. Methylene groups attached to the carbonyl carbon of esteric groups (CH_2COO) were observed at 2.20-2.46 ppm. The methyl proton of TDI was assigned to the peak at δ = 2.5 ppm. Methylene groups attached to the urethane nitrogen atom were detected at 2.65-2.90 ppm for all PUA's. The peaks at 2.90-3.22 are ascribed to the CH_2 protons of IPDI. The peak at 3.22-3.81 ppm was due to the CH and CH_2 protons of IPDI (NCOCH and $NCOCH_2$), CH_2 protons of HEMA (CH_2OCONH), and CH_2 protons of BHEPS (CH_2OCONH). The CH_2 groups attached to the ester group oxygen atom of PES ($OCH_2C(CH_3)_2$), CH_2 protons attached to the etheric group of BHEPS (OCH_2CH_2), and CH_2 protons attached to the ester group oxygen atom of HEMA ($COOCH_2CH_2$) were detected at 3.81-4.45 ppm. The peaks in the range of 5.67-5.68 ppm and 6.02-6.05 ppm are obviously observed in both spectra, which prove the existence of acrylic group in PUA molecular

structure related with HEMA. The aromatic protons of BHEPS near to etheric oxygen atom appeared at δ = 7.7-7.8 ppm. The peaks at 6.9-7.2 ppm are ascribed to the protons of –NH- groups in urethane unit and aromatic protons of near to sulfone of BHEPS for IPDI based PUA's. The peaks at 6.9-7.2 ppm are aromatic protons of near to sulfone of BHEPS and the aromatic protons from TDI appeared at δ = 7-7.6 ppm. The urethane protons were observed at δ = 8.9-9.7 ppm for TDI based PUA's.

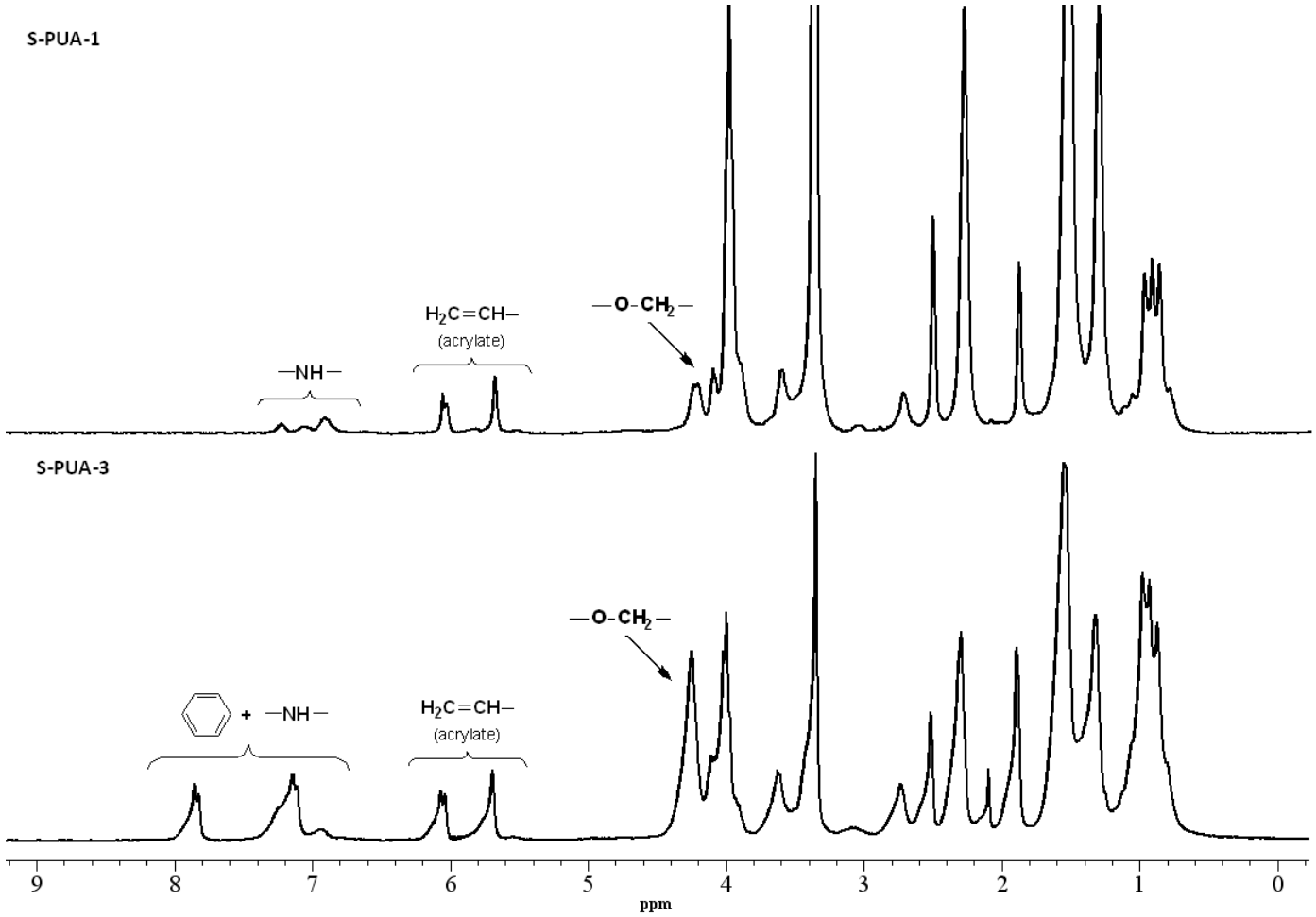


Figure 4.12 : ^{1}H-NMR spectrum of IPDI and polyester polyol containing PUA's.

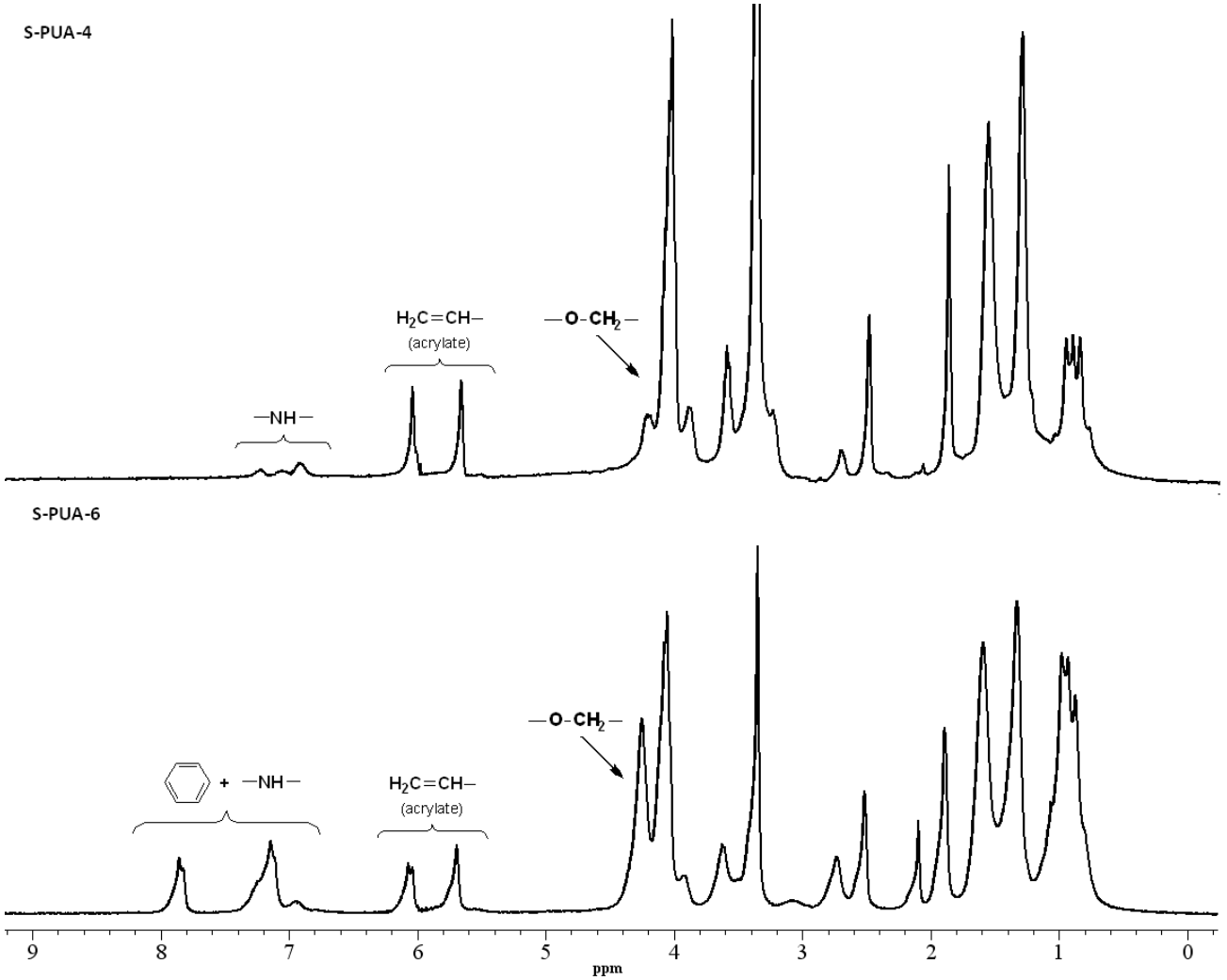


Figure 4.13 : ^{1}H-NMR spectrum of IPDI and polycarbonatediol containing PUA's.

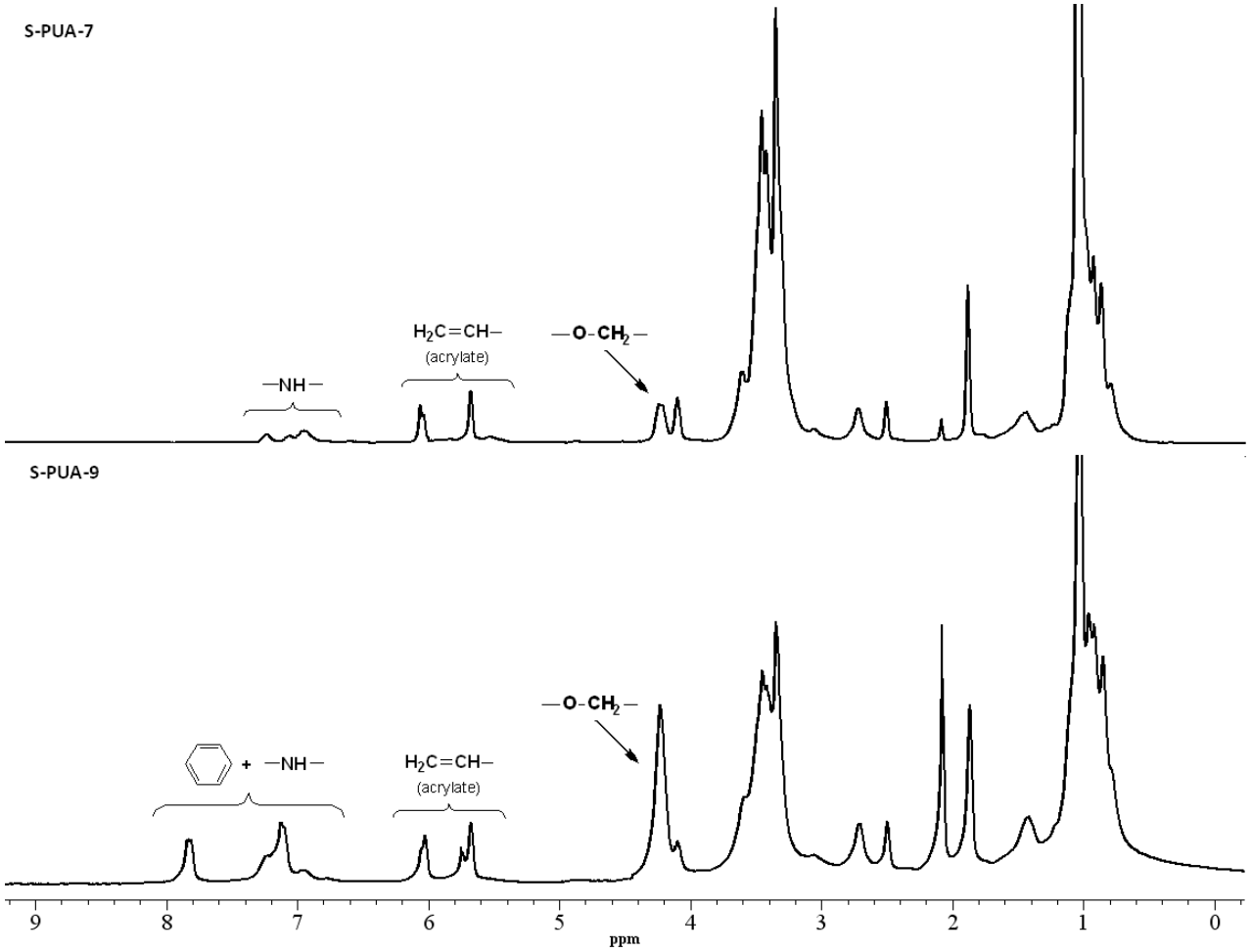


Figure 4.14 : ^{1}H-NMR spectrum of IPDI and polypropylene glycol containing PUA's.

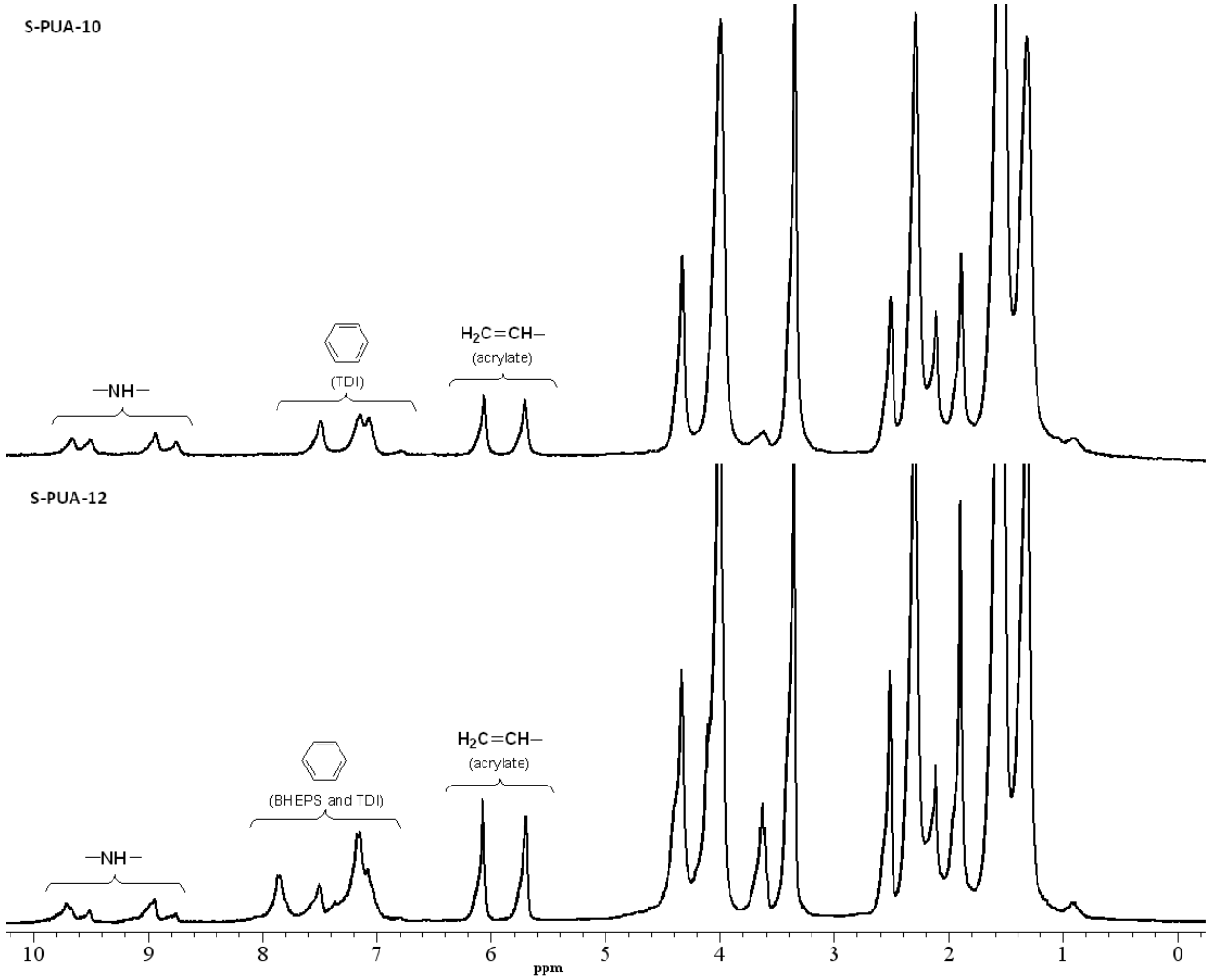


Figure 4.15 : ^{1}H-NMR spectrum of TDI and polyester polyol containing PUA's.

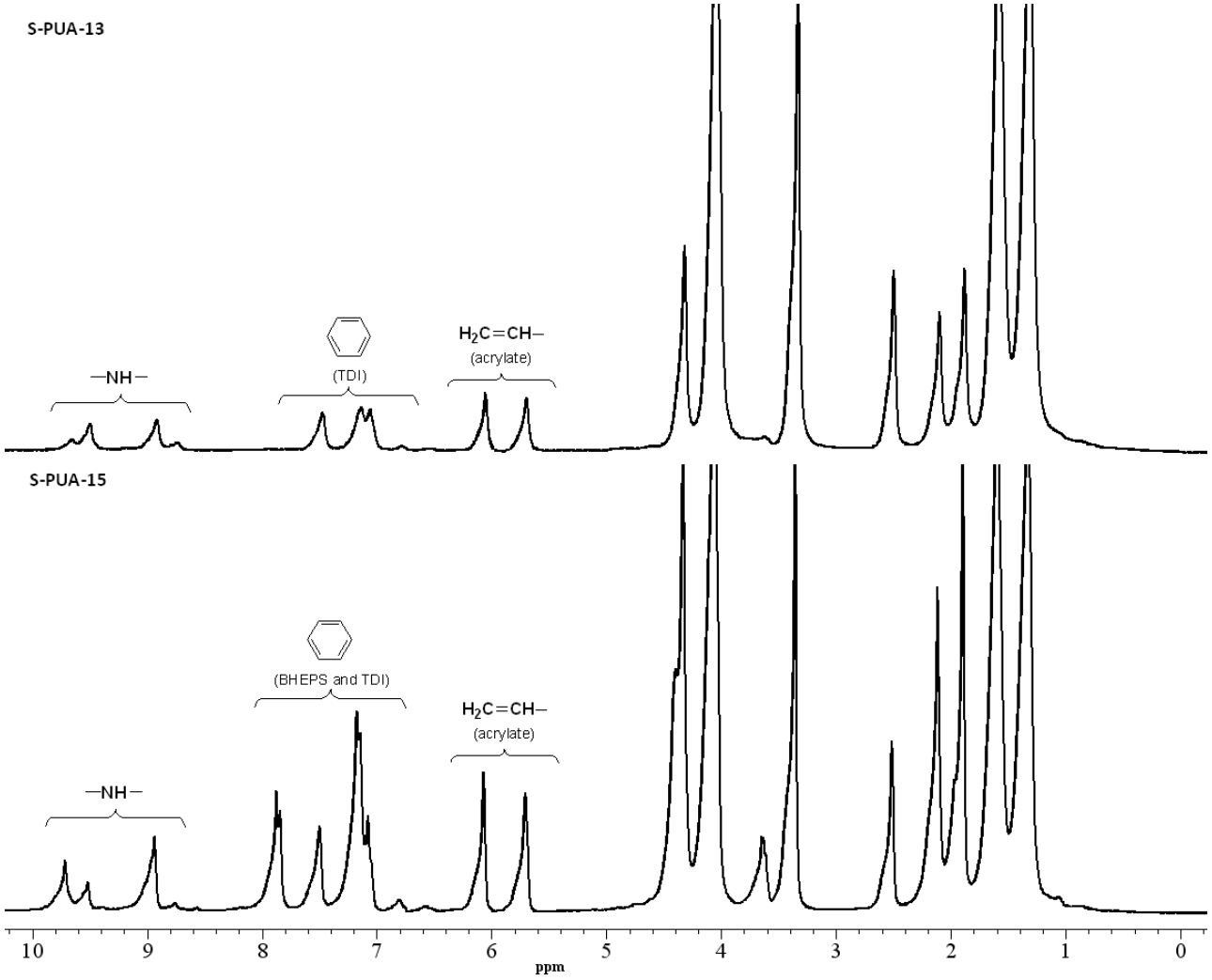


Figure 4.16 : ^{1}H-NMR spectrum of TDI and polycarbonatediol containing PUA's.

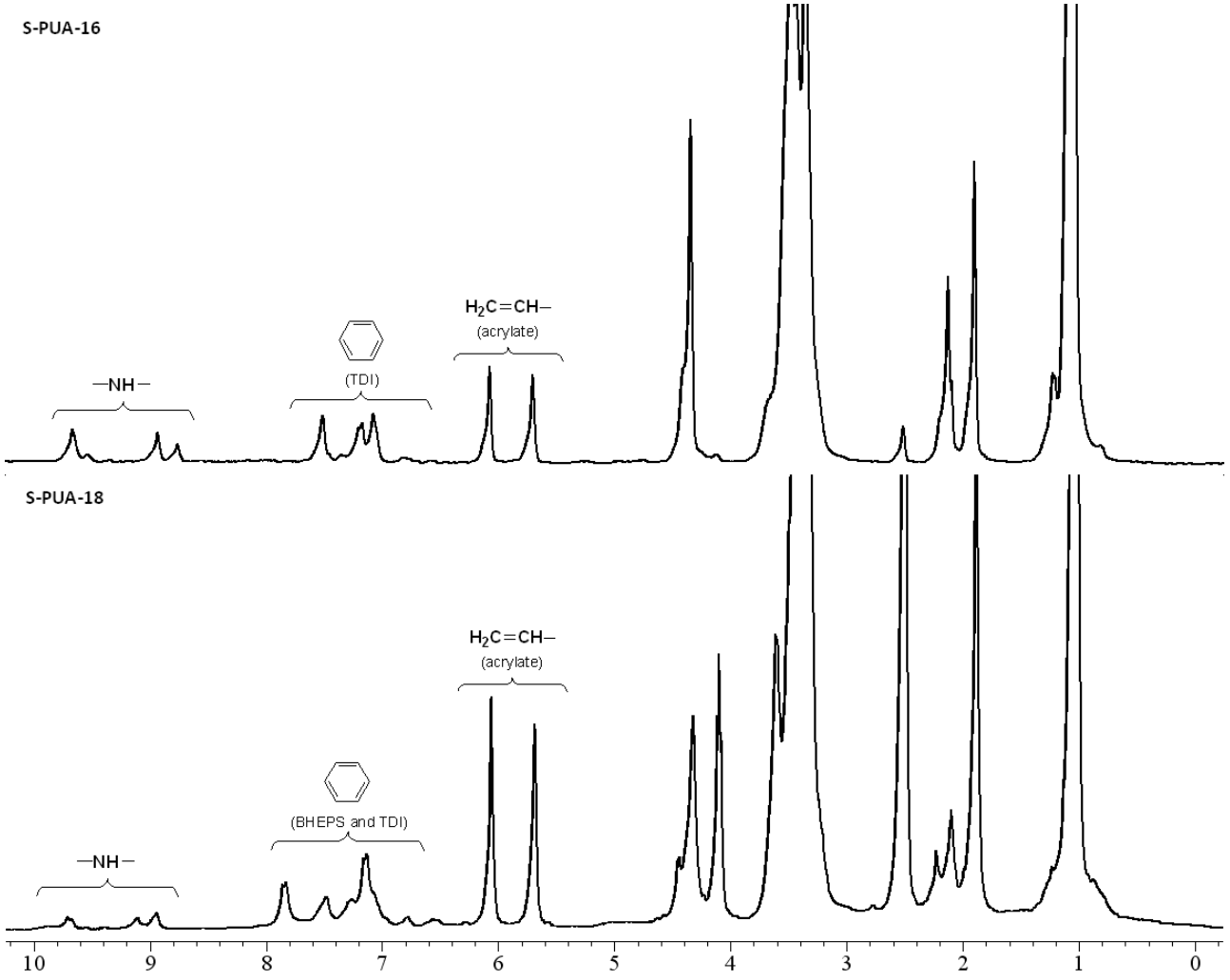


Figure 4.17 : ^{1}H-NMR spectrum of TDI and polypropylene glycol containing PUA's.

4.2.2 Gloss properties

The plexiglass plates were coated for the gloss test. Gloss of the coated plates was measured at an angle of 20^o, 60^o and 85^o. The measurement at 85^o 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. The gloss measurement results of UV-cured PUA's are shown in Figure 4.18 - 4.21 for 20^o and 60^o. Black side of Leneta Test Chart was used to measure the gloss values.

The gloss value is increased when the content of BHEPS increased in the PUA's. The average gloss (20^o) values of the sulfone containing UV-cured PUA's were between 67 - 155 for IPDI containing PUA's, 136 – 158 for TDI containing PUA's. The average gloss (60^o) values of the sulfone containing UV-cured PUA's were between 97 - 151 for IPDI containing PUA's, 133 – 155 for TDI containing PUA's. This was high value for coated materials. The values of PC and PPG containing PUA's are higher than PES containing PUA's due to the amorphous structure of the polyols which could make the polymers transparent. The PES could be amorphous but contain semi-crystalline structure. This could be the reason that gloss values of PES containing PUA's was less than the other ones. Also the presence of polar sulfone groups in BHEPS could effect on the amorphous structure and with addition of sulfone to the system, the gloss values increased simultaneously [88]. Additionally the materials used for coating formulation were homogeneously mixed and produce smooth and glossy surface. The polarity and free volume of sulfone and phenyl groups tend to give better surface properties.

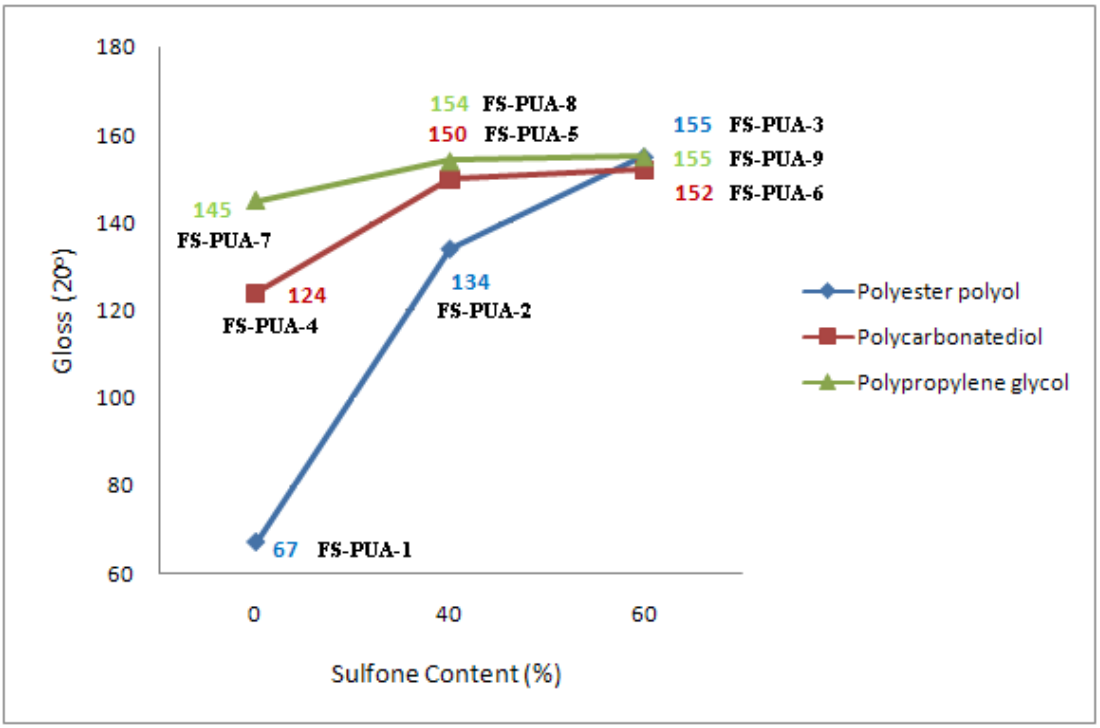


Figure 4.18 : 20° Gloss value of IPDI containing UV-cured PUA's.

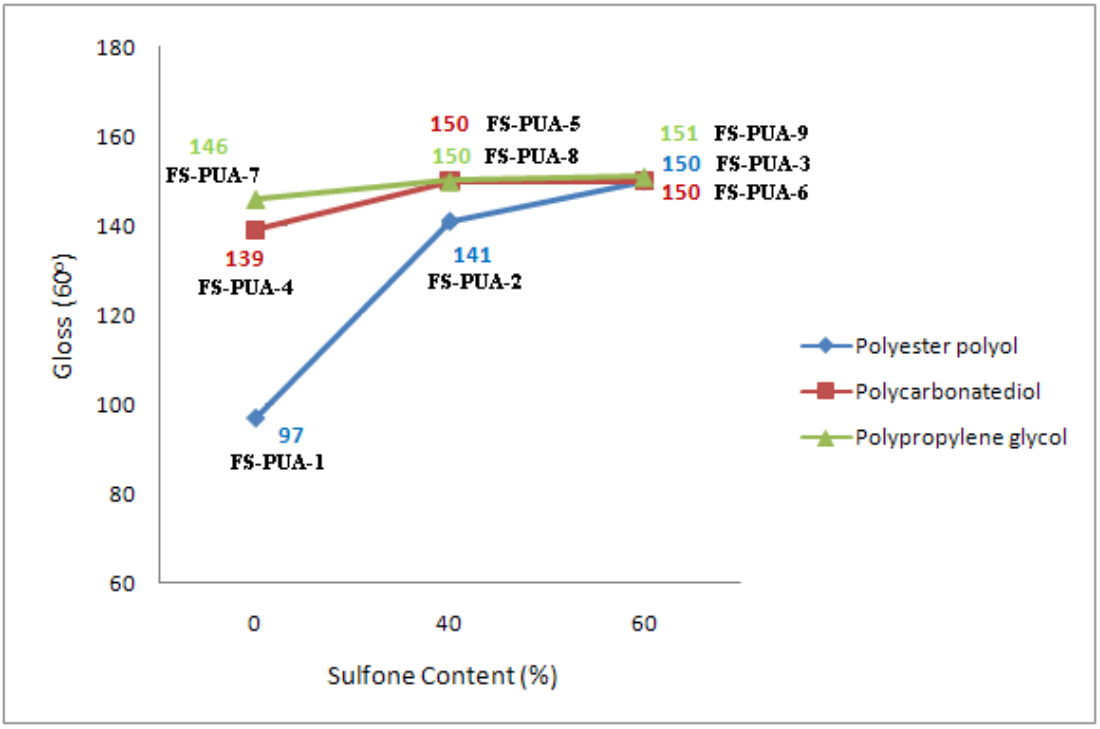


Figure 4.19 : 60° Gloss value of IPDI containing UV-cured PUA's.

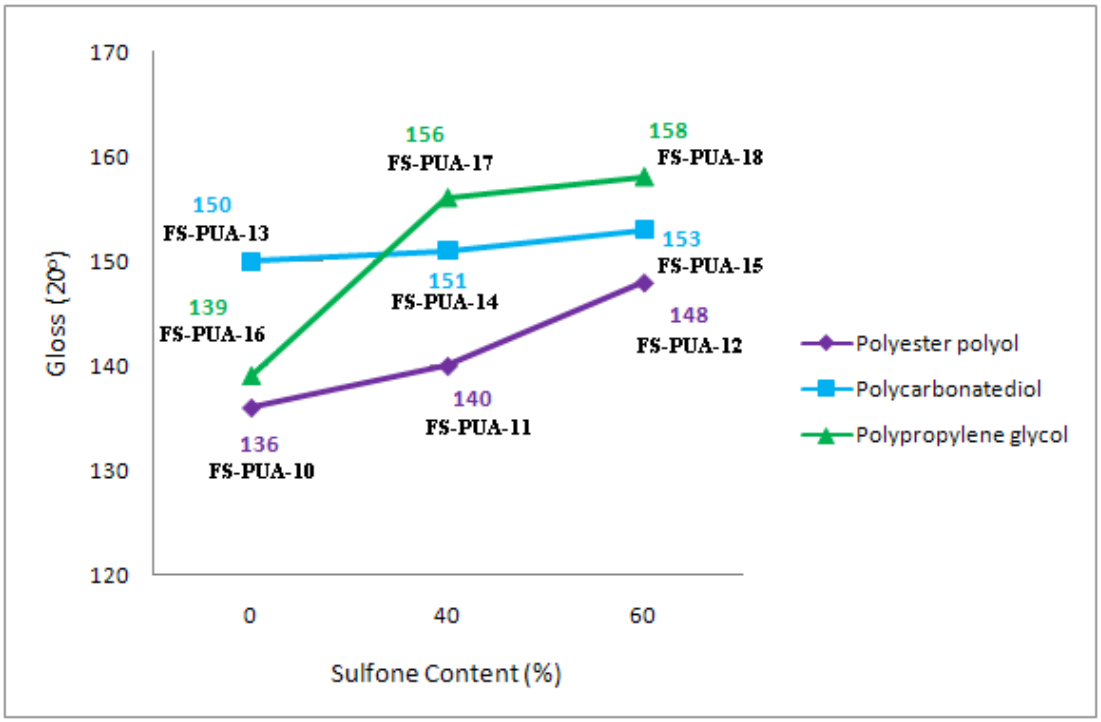


Figure 4.20 : 20^{o} Gloss value of TDI containing UV-cured PUA's.

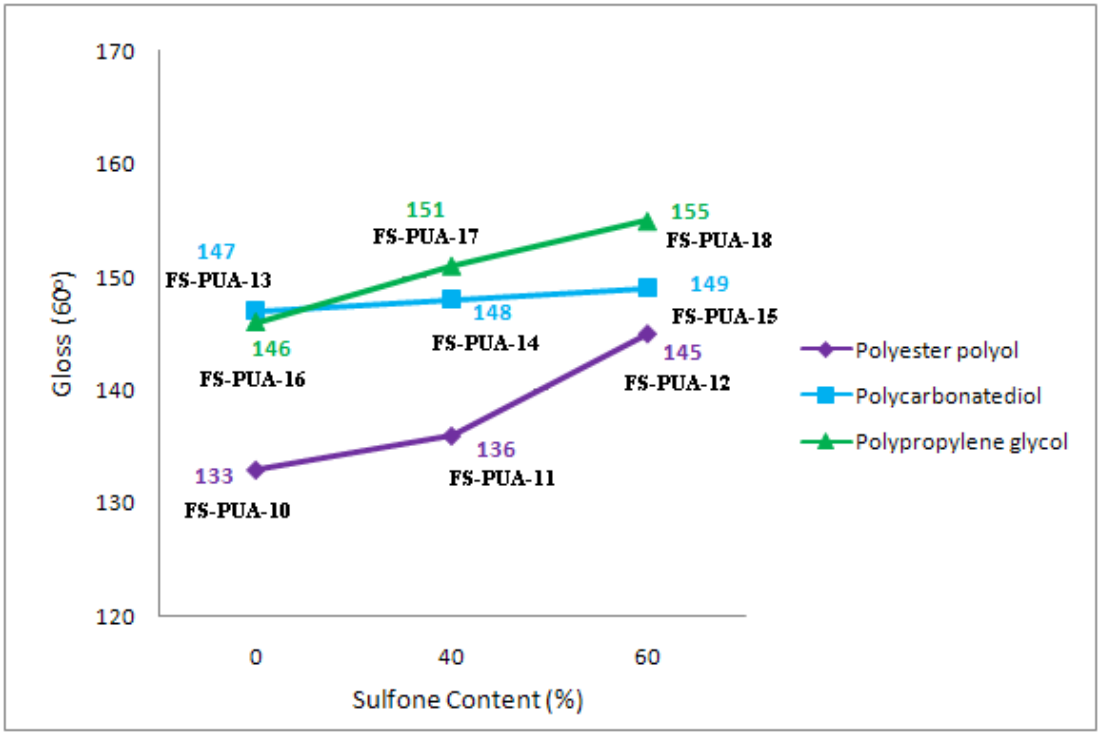


Figure 4.21 : 60^{o} Gloss value of TDI containing UV-cured PUA's.

4.2.3 Contact angle measurement

The surface hydrophilicity of the various samples, as characterized by static water contact angle, is summarized in Table 4.3 and 4.4. The value of the contact angle of a liquid on a film is a direct reflection of the surface wettability. Contact angles of

water were measured on plexiglass plate coated with different urethane acrylate films. The water contact angle was in the range of 95-67^{o} for IPDI containing films and 85-55^{o} for TDI containing films. When the content of BHEPS was increasing the contact angle value is decreasing. This was an expected behavior assuming that phenyl sulfone (BHEPS) groups make the surface more hydrophilic [23]. The presence of polar functional groups such as sulfone groups increases the hydrogen bonding interactions and therefore the contact angle decreases. Hydrophilicity is increasing from polyester polyol to polypropylene glycol (PES<PC<PPG) according to results. The contact angles results can be seen in Figure 4.22.

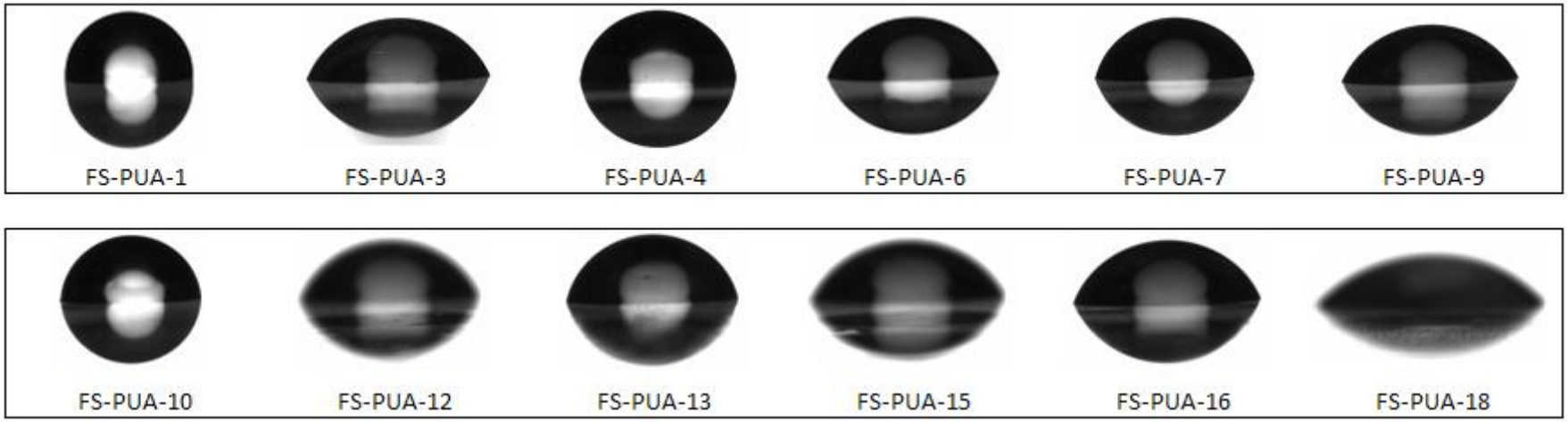


Figure 4.22 : Contact angle figures of UV-cured PUA's.

4.2.4 Water absorption

Water absorption values are collected in Table 4.3 and 4.4. There was no considerable difference in the amount of absorbed water. The PPG content was the main factor that can control the amount of absorbed water. The results presented clearly showed that water absorption of the samples increased with increasing the PPG content.

4.2.5 Gel content

Gel content of a film is related to the crosslinking density in the film. Gel content degree is related with the UV-curing time, selectivity of the initiator and acrylate oligomers. Unreacted part of the cured materials was under wt. 5%, so the polymerization systems and formulations were suitable for PUA's. Gel contents of the UV-cured films are represented in Table 4.3 and 4.4.

Table 4.3 : Contact angle, water absorption, gel content, and pencil hardness analysis of IPDI containing UV-cured PUA's.

Composition Code	Contact Angle (^{o})	Water Absorption (%)	Gel Content (%)	Pencil Hardness
FS-PUA-1	95	99	95	4 H
FS-PUA-2	93	98	95	4 H
FS-PUA-3	68	98	97	5 H
FS-PUA-4	84	98	97	5 H
FS-PUA-5	72	98	97	7 H
FS-PUA-6	70	98	95	7 H
FS-PUA-7	75	96	95	4 H
FS-PUA-8	73	97	97	6 H
FS-PUA-9	67	97	99	6 H

Table 4.4 : Contact angle, water absorption, gel content, and pencil hardness analysis of TDI containing UV-cured PUA's.

Composition Code	Contact Angle (^{o})	Water Absorption (%)	Gel Content (%)	Pencil Hardness
FS-PUA-10	85	94	95	4 H
FS-PUA-11	76	94	95	7 H
FS-PUA-12	69	94	95	7 H
FS-PUA-13	78	95	97	5 H
FS-PUA-14	68	95	96	7 H
FS-PUA-15	66	96	99	7 H
FS-PUA-16	68	95	95	3 H
FS-PUA-17	58	94	95	4 H
FS-PUA-18	55	94	96	6 H

4.2.6 Chemical and solvent resistance

In addition, to test the chemical and solvent resistance, cured films were immersed in chloroform, xylene, methanol, 10% HCl, 10% acetic acid, 10% NaOH, respectively, for 24 h at room temperature and experimental results show that PUA films has good solvent and chemical resistance performance. The results of chemical and solvent resistance are listed in Table 4.5 and 4.6. The weight loss values for each compound were less than 2 for chemical resistance and less than 6 for solvent resistance. This shows that resistance of PUA's to different type of chemicals were really high. The appearance of the samples was good except chloroform. The samples got broken with the existence of chloroform.

Table 4.5 : Solvent resistance of UV-cured PUA's.

Comp. Code	Chloroform		Xylene		Methanol	
	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance
FS-PUA-1	< 1	Broken	< 5	Good	< 5	Good
FS-PUA-2	< 1	Broken	< 6	Good	< 5	Good
FS-PUA-3	< 1	Broken	< 2	Good	< 5	Good
FS-PUA-4	< 1	Broken	< 5	Good	< 4	Good
FS-PUA-5	< 1	Broken	< 4	Good	< 4	Good
FS-PUA-6	< 1	Broken	< 5	Good	< 5	Good
FS-PUA-7	< 1	Broken	< 5	Good	< 6	Good
FS-PUA-8	< 1	Broken	< 2	Good	< 5	Good
FS-PUA-9	< 1	Broken	< 2	Good	< 5	Good
FS-PUA-10	< 1	Broken	< 5	Good	< 5	Good
FS-PUA-11	< 1	Broken	< 6	Good	< 6	Good
FS-PUA-12	< 1	Broken	< 4	Good	< 5	Good
FS-PUA-13	< 1	Broken	< 4	Good	< 3	Good
FS-PUA-14	< 1	Broken	< 4	Good	< 5	Good
FS-PUA-15	< 1	Broken	< 3	Good	< 4	Good
FS-PUA-16	< 1	Broken	< 3	Good	< 4	Good
FS-PUA-17	< 1	Broken	< 3	Good	< 5	Good
FS-PUA-18	< 1	Broken	< 3	Good	< 4	Good

Table 4.6 : Chemical resistance of UV-cured PUA's.

Comp. Code	HCl (10%)		Acetic Acid (10%)		NaOH (10%)	
	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance
FS-PUA-1	< 1	Good	< 2	Good	< 1	Good
FS-PUA-2	< 1	Good	< 2	Good	< 2	Good
FS-PUA-3	< 1	Good	< 2	Good	< 1	Good
FS-PUA-4	< 1	Good	< 1	Good	< 1	Good
FS-PUA-5	< 1	Good	< 2	Good	< 1	Good
FS-PUA-6	< 1	Good	< 1	Good	< 2	Good
FS-PUA-7	< 1	Good	< 2	Good	< 2	Good
FS-PUA-8	< 1	Good	< 2	Good	< 2	Good
FS-PUA-9	< 1	Good	< 2	Good	< 3	Good
FS-PUA-10	< 1	Good	0	Good	< 1	Good
FS-PUA-11	< 1	Good	0	Good	0	Good
FS-PUA-12	< 2	Good	< 2	Good	< 2	Good
FS-PUA-13	< 1	Good	< 2	Good	< 2	Good
FS-PUA-14	< 2	Good	0	Good	< 1	Good
FS-PUA-15	< 1	Good	< 1	Good	< 1	Good
FS-PUA-16	< 1	Good	< 2	Good	< 2	Good
FS-PUA-17	< 1	Good	< 1	Good	< 1	Good
FS-PUA-18	< 1	Good	< 1	Good	< 1	Good

4.2.7 Mechanical properties (Pendulum hardness, pencil hardness and tensile tests)

The hardness of the coating is important to affect 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. König pendulum hardness tests are applied to all coated plexiglass plates. The pendulum hardness values of the PUA's are shown in Figures 4.23 and 4.24. When the BHEPS content was 60% in the PUA's, the average pendulum hardness values were between 81-84 and the reference values were between 42-44 for IPDI containing films and the average pendulum hardness values were between 76-80 and the reference values were between 47-71 for TDI containing films. The improvement was really high. The pendulum hardness increased with increase in concentration of phenyl sulfone groups (BHEPS) in the PUA's backbone.

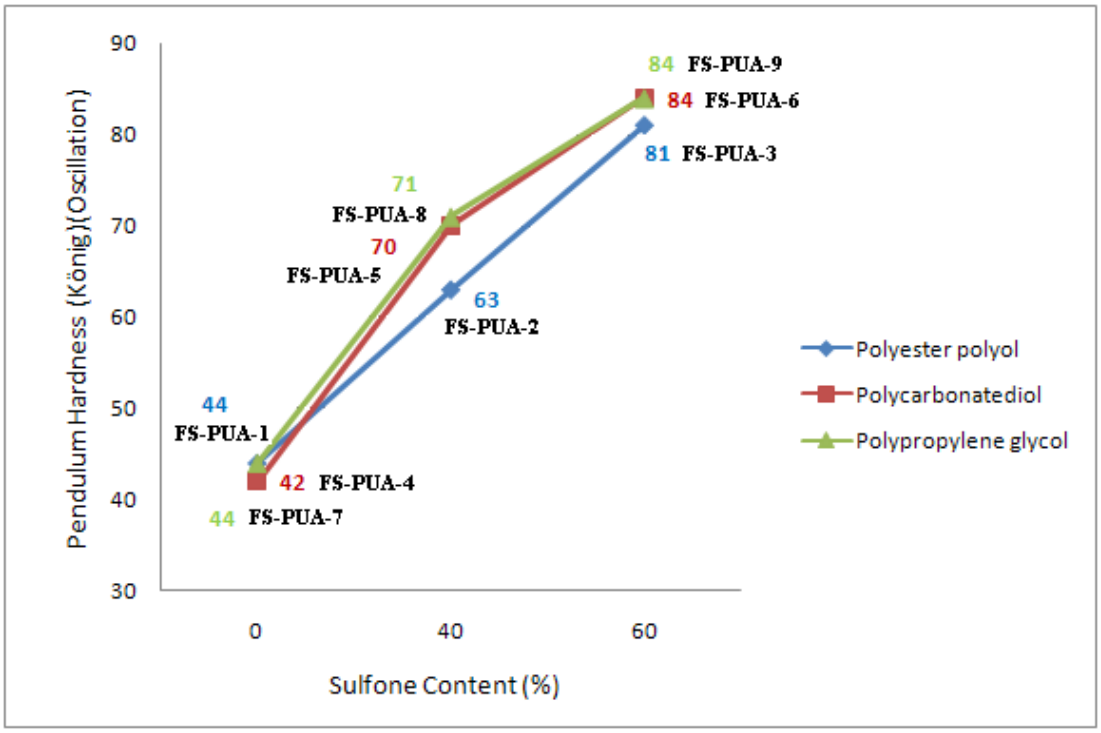


Figure 4.23 : Pendulum hardness values of IPDI containing UV-cured PUA's.

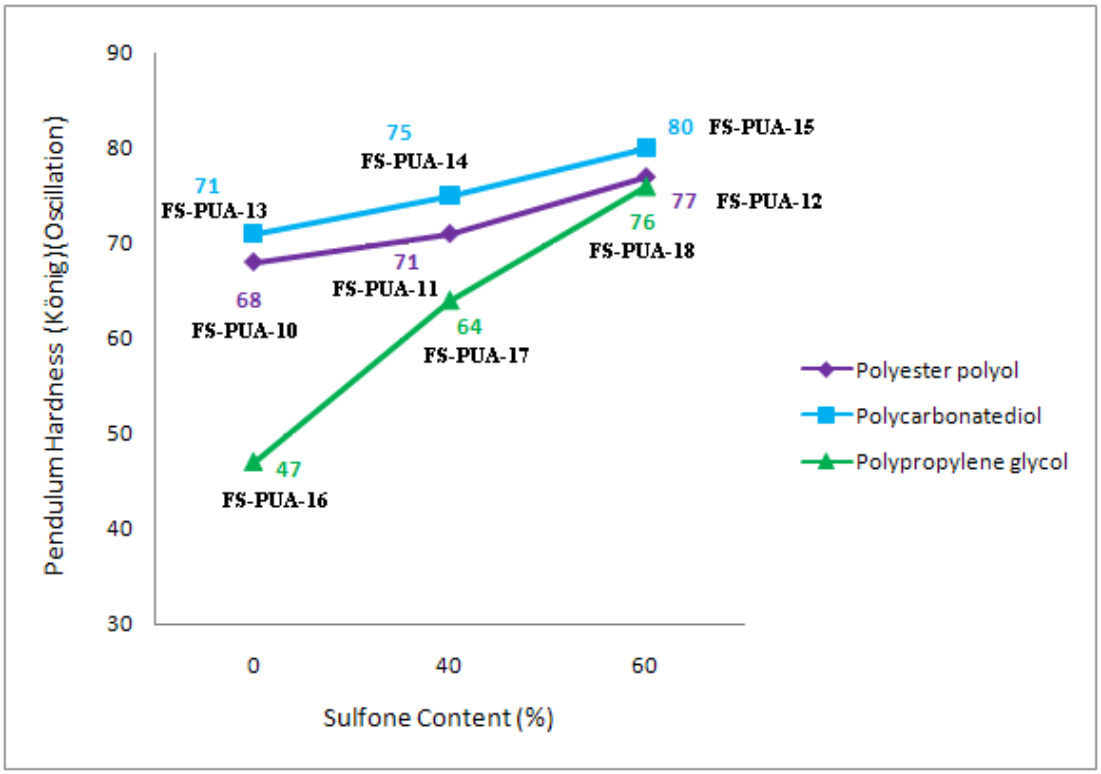


Figure 4.24 : Pendulum hardness values of TDI containing UV-cured PUA's.

Pencil hardness test was applied on plexiglass plates. This test is applied to understand hardness of the surface in addition to pendulum hardness. The pencil hardness results are presented in Table 4.3 and 4.4. When the content of BHEPS was

increased in PUA's, the pencil hardness values also increased. The values of polycarbonatediol containing PUA's were higher than the other PUA's.

The mechanical properties are very important for materials. With the variations of the polyol and sulfone percentage, polyurethane acrylate structure would change tensile strength and modulus values. The mechanical specification of free films, prepared at 50x10x1mm dimensions, made clearly with measurement of stress-strain values. The tensile strength at yield, tensile strength at break, elongation at break, e-modulus values of the PUA's are shown and listed in Figures 4.25-4.32. Generally with increasing BHEPS content in both PES, PC, PPG containing PUA's, the elongation at break decreases progressively, whereas the tensile strength and e-modulus increases slightly. This may be explained by the presence of rigid pendant phenyl sulfone groups in the resins, which makes the formed polymeric backbone more rigid. The biggest mechanical improvement was seen on the PUA's which contain polycarbonetediol, because of the high performance character of polycarbonates. The main difference between the reference and BHEPS added PUA's was seen on PUA's which contain PPG. Also there was a relation between tensile strength and e-modulus values, they were increased proportionally.

The strength of the attractive forces between polymer chains and particles can affect the properties of the polymers and substances. The intermolecular forces between polar molecules are dipole-dipole and H bonding. These forces could make the bonds very strong in binding different polymer chains together. Intermolecular forces affect polymers just like small molecules. But with polymers, these forces are greatly compounded. Because polymer chains are so long, these interchain forces are enlarged far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to ionic bonding and hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength [89-91].

The intermolecular forces in polymers can be affected by dipoles in the monomer units. Polymers containing amide or carbonyl groups can form hydrogen bonds between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one chain are strongly attracted to the partially negatively charged oxygen atoms in C=O groups on another [92]. These strong hydrogen bonds, for example, result in high tensile strength and melting point of polymers containing urethane or

urea linkages. If the soft segments are short the polyurethanes higher the hardness values. This assume could be related with the increase in cohesive energy density and polar groups in the polymer chain [93, 94]. The polar groups (sulfone, phenyl, urethane, ester, ether) which have high cohesive force participate in intermolecular hydrogen bonding and restrict the rotation of the polymer segments. This restriction is resulted with higher hardness and smaller elongation values [92, 95]. The reference PUA's contain long soft segment groups (PES>PC>PPG). Due to these long polymer chains, the mechanical properties of the reference PUA's may be lower than BHEPS added ones. But with the addition of BHEPS into the PUA's, the ratio of polyols are used less than the reference ones. BHEPS is a soft segment and it is shorter than polyols. The presence of phenyl and urethane linkages in PUA's, make the hardness values higher. The improvement of pendulum harness, pencil hardness, tensile strength and e-modulus can be explained by the presence of rigid polar pendant sulfone groups in the backbone. The polar groups can participate in intermolecular interaction and balance the polymer symmetry thereby resulting in higher strength values which could form the polymeric backbone more rigid compared to the reference samples.

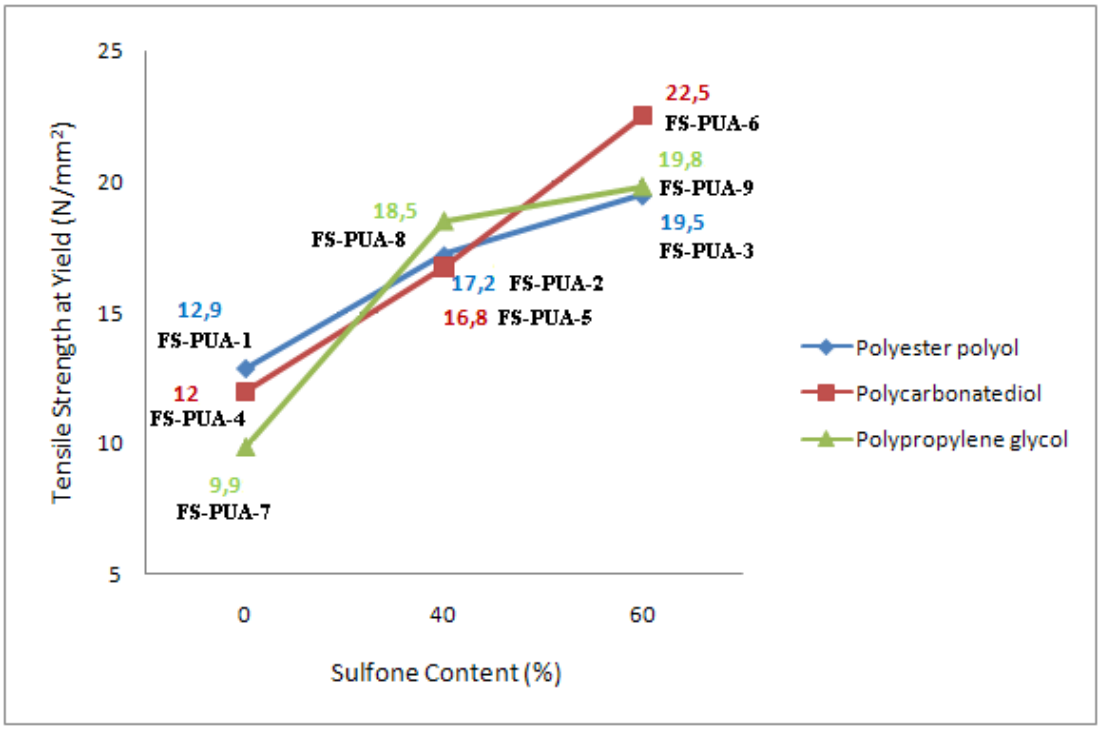


Figure 4.25 : Tensile strength at yield values of IPDI containing UV-cured PUA's.

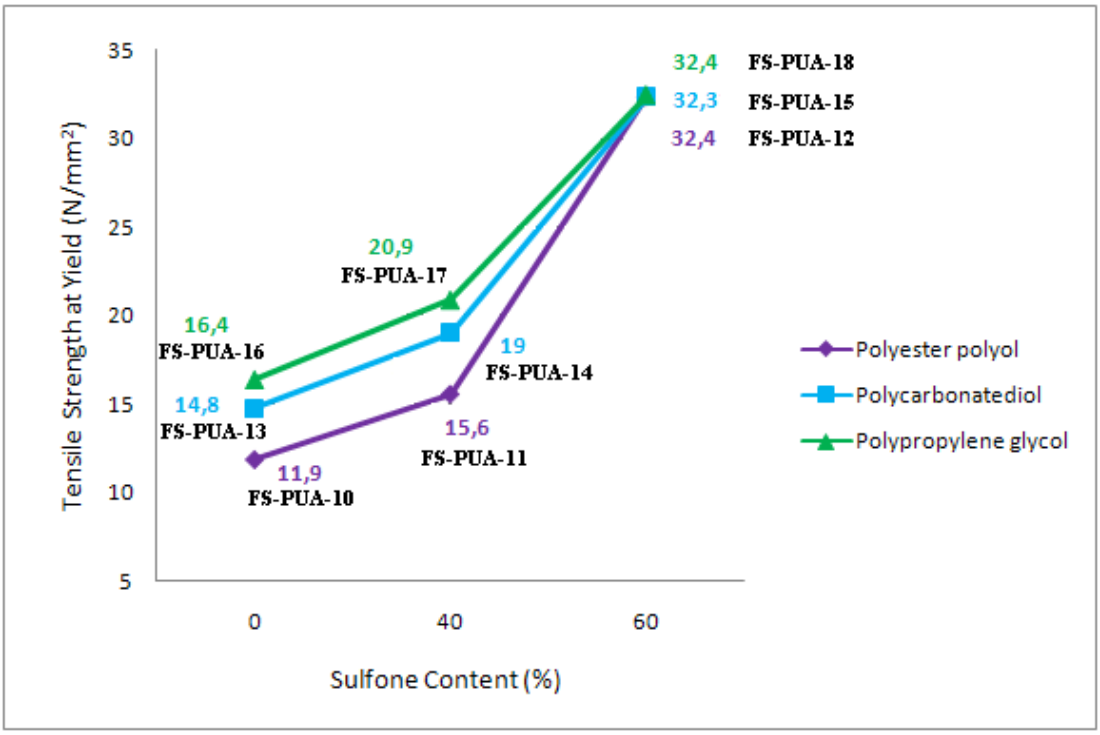


Figure 4.26 : Tensile strength at yield values of TDI containing UV-cured PUA's.

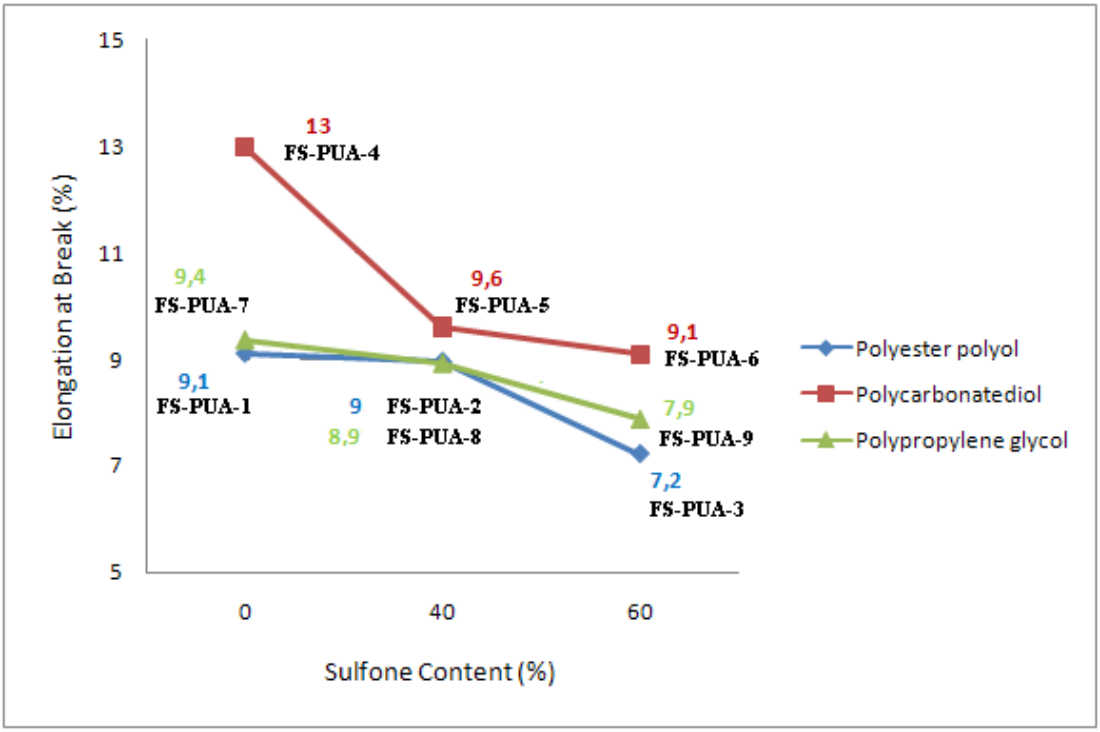


Figure 4.27 : Elongation at break values of IPDI containing UV-cured PUA's.

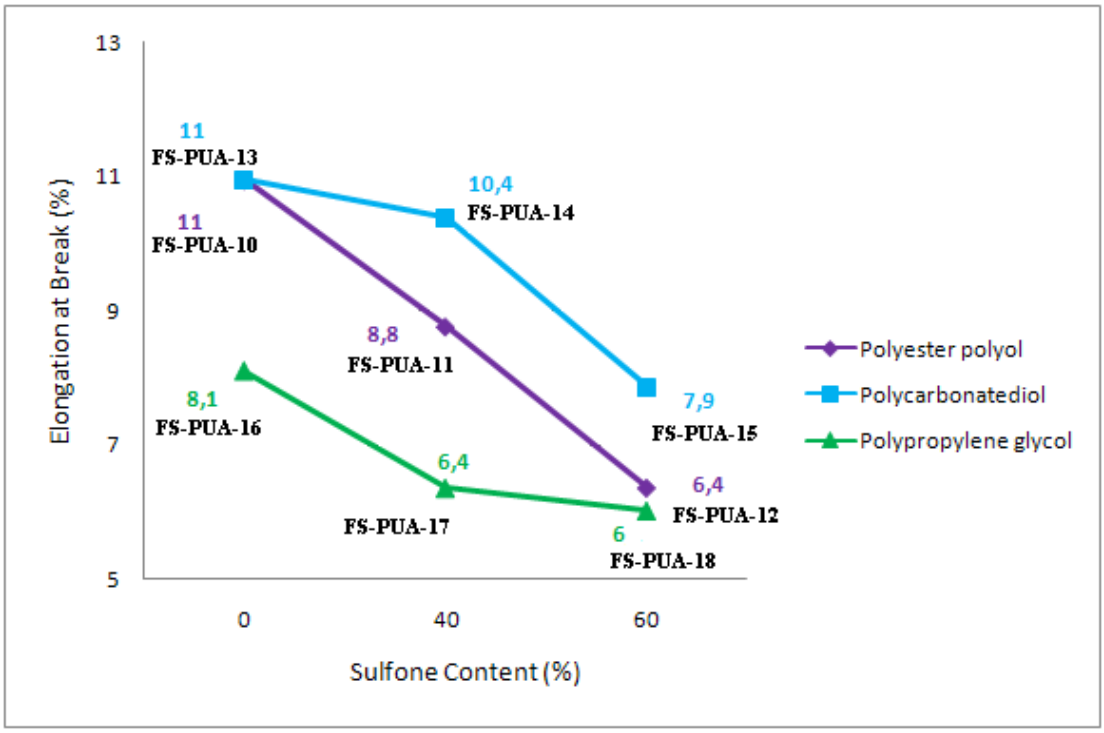


Figure 4.28 : Elongation at break values of TDI containing UV-cured PUA's.

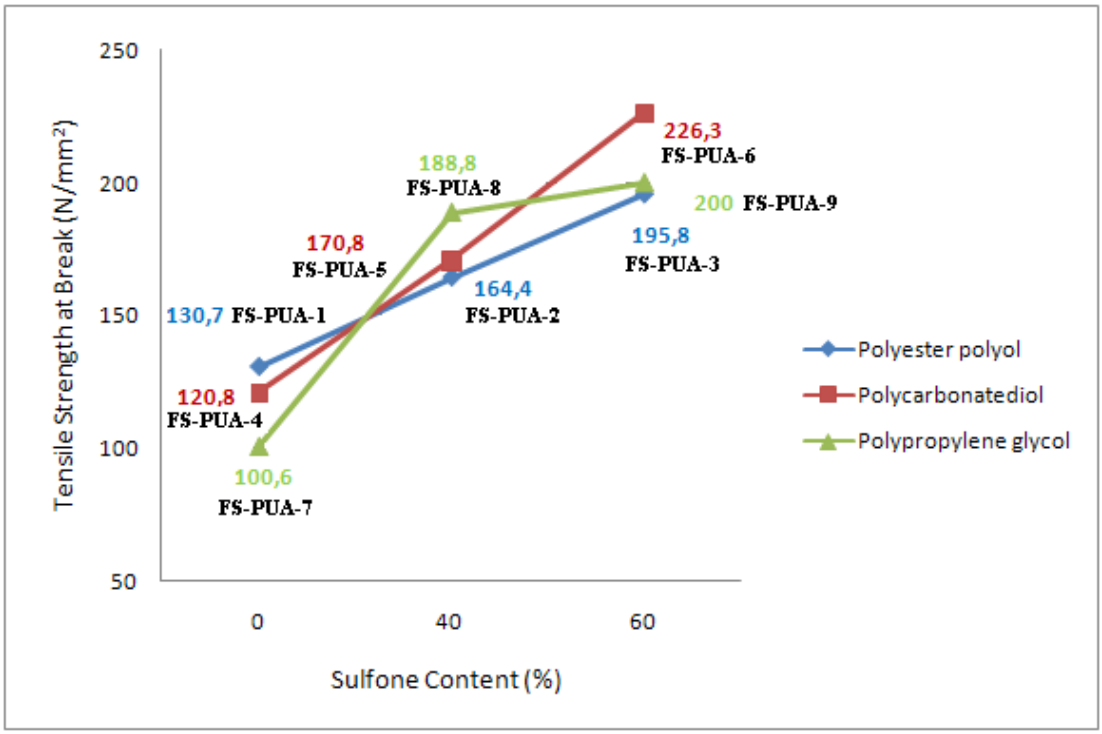


Figure 4.29 : Tensile strength at break values of IPDI containing PUA's.

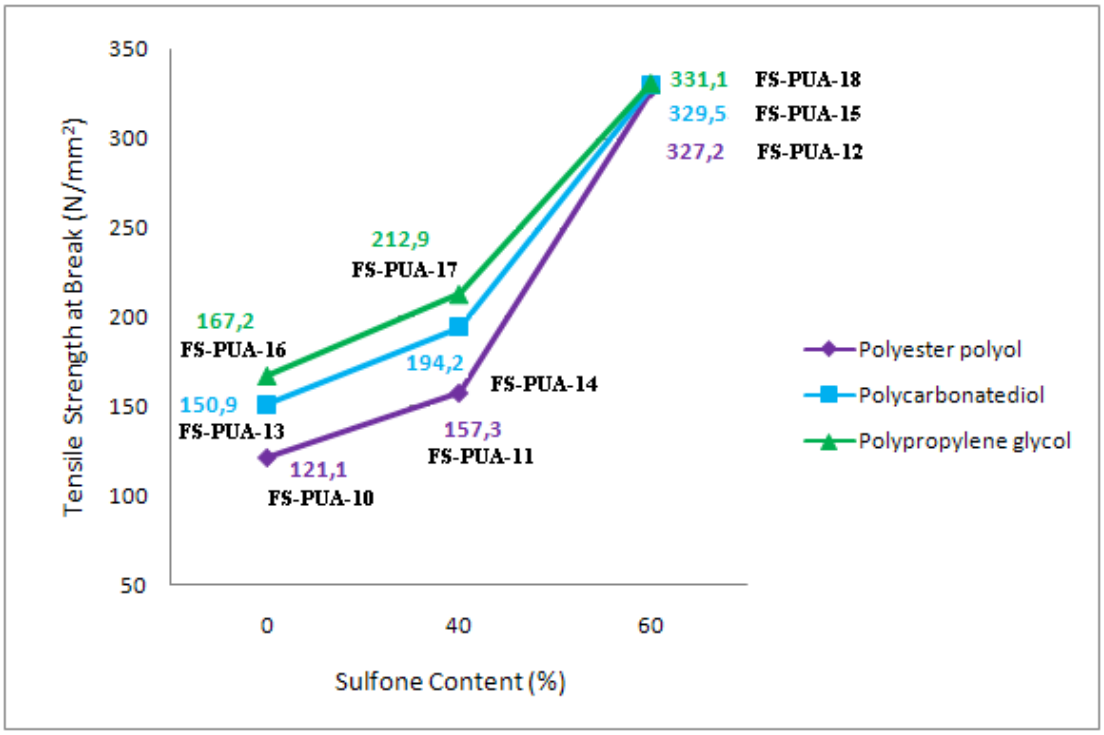


Figure 4.30 : Tensile strength at break values of TDI containing PUA's.

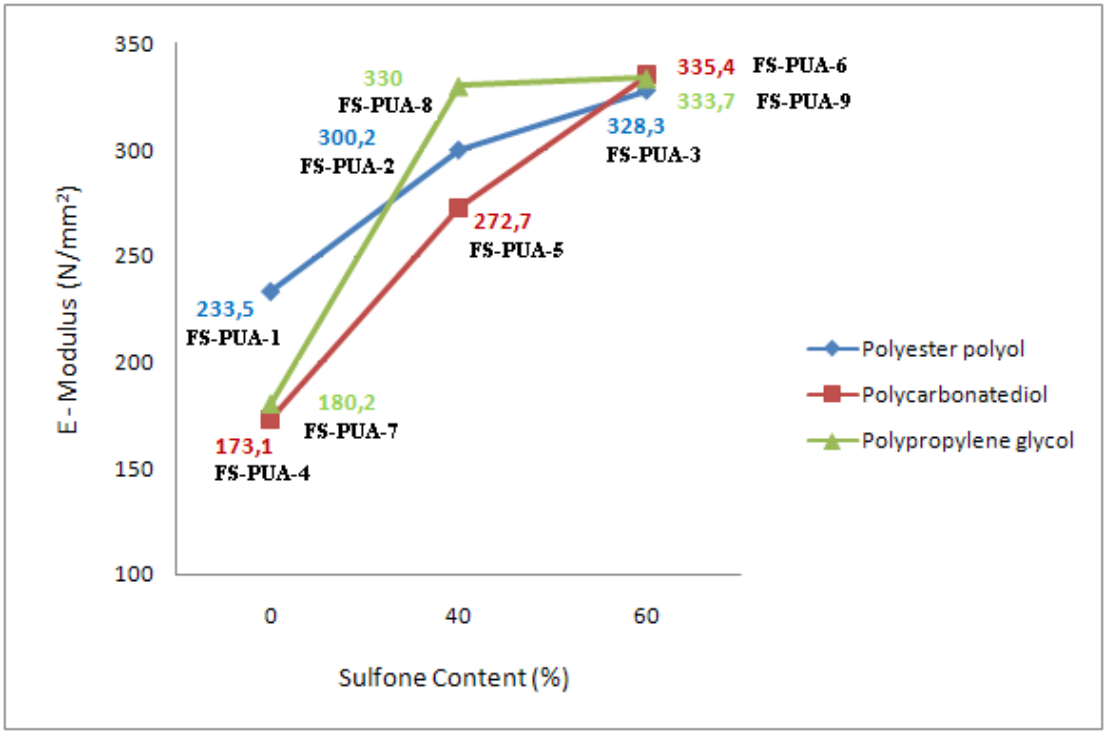


Figure 4.31 : E-modulus values of IPDI containing PUA's.

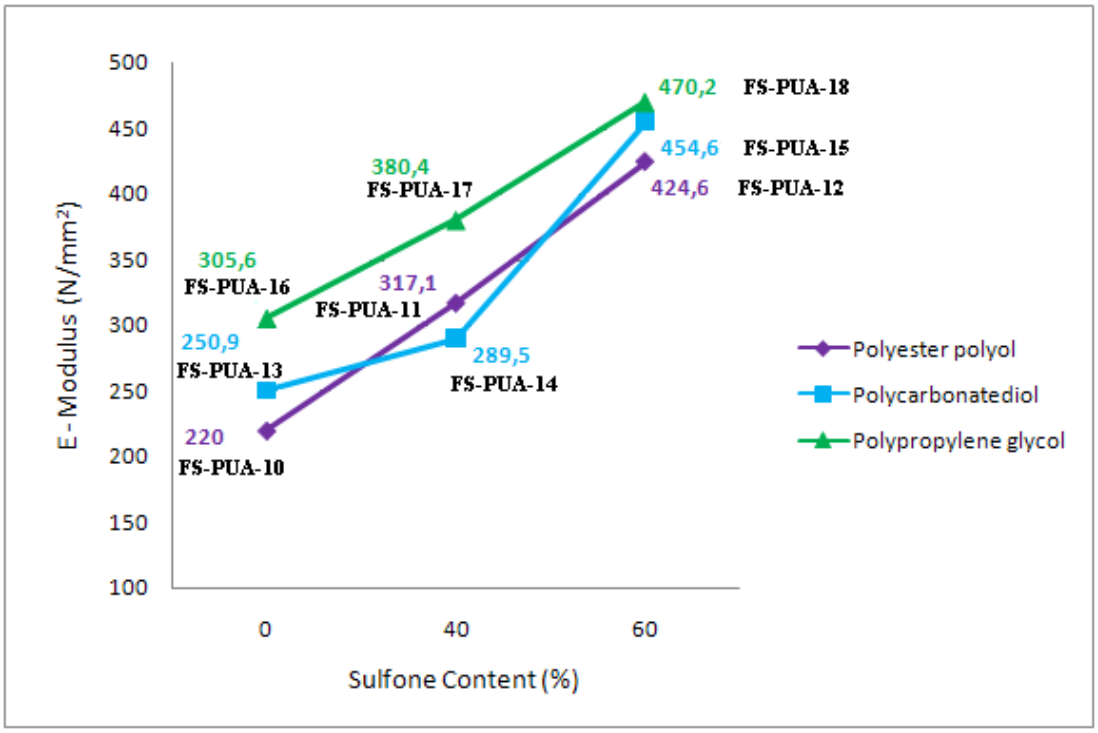


Figure 4.32 : E-modulus values of TDI containing PUA's.

4.2.8 Thermal properties

The thermal properties of the PUA's were performed by TGA. The thermal stability measurements were evaluated from 30 to 700 ^{o}C by TGA under nitrogen at a heating rate of 20 ^{o}C/min. The influence degree of sulfone content on both 5% weight loss (5WL) temperature, first maximum weight loss (FWL) temperature and the residual char yield (RCY) at 700 ^{o}C are summarized in Tables 4.7 and 4.8. As observed from TGA, 5WL begins at around 309-331 ^{o}C, and FWL begins at around 396-418 ^{o}C, and gives one stage weight loss for IPDI containing films and 5WL begins at around 281-334 ^{o}C, and FWL begins at around 396-426 ^{o}C, and gives one stage weight loss for TDI containing films. Due to the degradation process, breaking of urethane bonds, first weight loss started between 0%-5%. The degradation rate of PUA's is maximum between 310-470 ^{o}C. The degradation process which the first weight loss starts between 0 %-5 % corresponded due to the breaking of urethane bond breakages.

With the addition of phenyl sulfone group changes the values of the 5WL and FWL and the RCY of the coatings. When the sulfone content was increased in PUA's, the 5WL, FWL and RCY was increased. The results show that incorporating BHEPS units slightly increases the thermal stability of PUA's, this is due to the stability of BHEPS units [96]. The polycarbonatediol containing PUA's (FS-PUA-7-FS-PUA-9

and FS-PUA-16-FS-PUA-18) which contain oxyethylene units is expected to induce earlier decomposition related with the ether linkages rather than PES and PPG containing PUA's [53].

Table 4.7 : Thermal characteristics of UV-cured IPDI containing PUA's.

Composition Code	5% Weight Loss (^{o}C)	First Max. Weight Loss (^{o}C)	Residue (%)
FS-PUA-1	309	417	2.3
FS-PUA-2	328	418	3.7
FS-PUA-3	331	418	6.8
FS-PUA-4	325	396	1.9
FS-PUA-5	326	403	4.0
FS-PUA-6	326	403	6.1
FS-PUA-7	310	404	2.0
FS-PUA-8	312	404	2.6
FS-PUA-9	321	408	4.5

Table 4.8 : Thermal characteristics of UV-cured TDI containing PUA'.

Composition Code	5% Weight Loss (^{o}C)	First Max. Weight Loss (^{o}C)	Residue (%)
FS-PUA-10	329	424	5.4
FS-PUA-11	330	425	5.5
FS-PUA-12	334	426	5.7
FS-PUA-13	281	396	3.5
FS-PUA-14	320	406	4.6
FS-PUA-15	323	408	4.7
FS-PUA-16	317	410	5.4
FS-PUA-17	319	416	6.5
FS-PUA-18	321	417	6.6

4.3 Conclusions

A series of UV-curable sulfone containing PUA's have been synthesized. Three different polyols (polyester polyol, polycarbonatediol, polypropylene glycol) and BHEPS with different ratios (0, 40%, and 60%) were used for the synthesis of PUA's. Coating formulations were prepared with DPGDA and HDDA as the reactive diluents and I-184 as the photoinitiator. It was found that the concentration of BHEPS plays an important role in the properties such as gloss, pendulum and pencil hardness, tensile strength, and modulus values. The water wettability, gel content, chemical and solvent resistance tests were performed to check the crosslinking density and resistance to various chemicals.

The contact angle values were between 95 to 67 and decrease with the increase of BHEPS content [23]. This decrease is due to the hydrophilic structure of BHEPS. The gloss values of all the films were good due to the amorphous structure of PES, PC, PPG, BHEPS and polar structure of BHEPS [88]. Pendulum hardness, pencil hardness, tensile strength and e-modulus values increase as the BHEPS content increase. BHEPS contains polar sulfone and phenyl groups in the backbone. This structure gives good intermolecular forces between the polymer chains, and these forces result in higher mechanical properties [89-91]. The observed mechanical improvements could be explained by intermolecular forces, cohesive forces of monomer (BHEPS, TDI and polyols) and polymer chains as reported in the literature [92-95]. Homogeneous formulations of BHEPS, TDI, NVP combination improved the surface properties of PUA's. The BHEPS containing PUA's showed improvement both 5% weight loss temperature, first maximum weight loss temperature and residue results [53, 96].

5. SYNTHESIS OF PHOSPHINE OXIDE CONTAINING POLYURETHANE ACRYLATES

5.1 Experimental Part

5.1.1 Synthesis of bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO)

Bis(4-fluorophenyl) phenyl phosphine oxide (BFPPO) was synthesized by Grignard technique BFPPO was prepared by a variation of known Grignard techniques as shown in Figure 5.1 A flame dried 2l 3-neck round bottom flask fitted with an overhead mechanical stirrer, an addition funnel and a nitrogen inlet were added 13.44 g (0.56 mol) magnesium and 600 ml dry THF. This solution was cooled with an ice water bath. To this stirred solution was added dropwise at or below 5 ^{o}C 98 g (0.56 mol, 61.51 ml) *p*-bromofluorobenzene over 2 hours. This mixture was stirred at room temperature overnight to give a gray slightly cloudy solution. Next, 40 ml (55.2 g, 0.28 mol) dichlorophenyl phosphine oxide was added dropwise at 5 ^{o}C over 2 hours and this solution was allowed to stir at room temperature overnight to give a yellow clear solution. Enough 10% aqueous sulfuric acid was added to make the solution acidic and water was added, yielding a homogeneous golden yellow mixture. Ether was added in order to seperate the solution into organic and aqueous phases. The aqueous layer was washed well with ether and all organic layers were combined. This organic solution was washed well with 10% sodium bicarbonate, followed by water washings. Then sodium sulphate was added to stir at room temperature overnight to clearing the cloudy ether phase. After filtering from the blue banded filter paper, THF and ether was distilled by rotary evaporator. Proportion of (30/70) of THF/hexane solution was used for crystallization. The crystals typically giving overall yields around 65% of monomer grade material with melting point of 126-127 ^{o}C [34, 66].

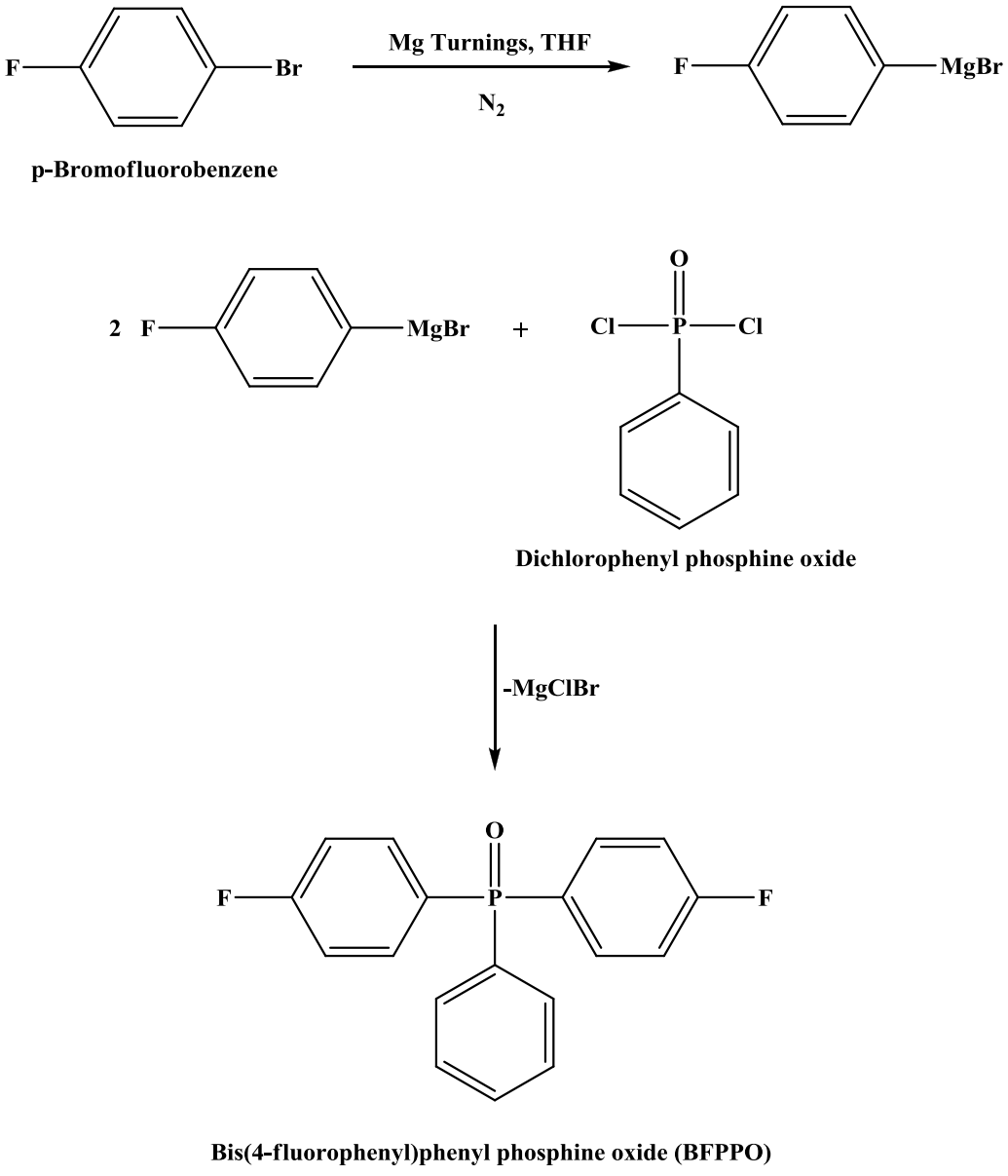


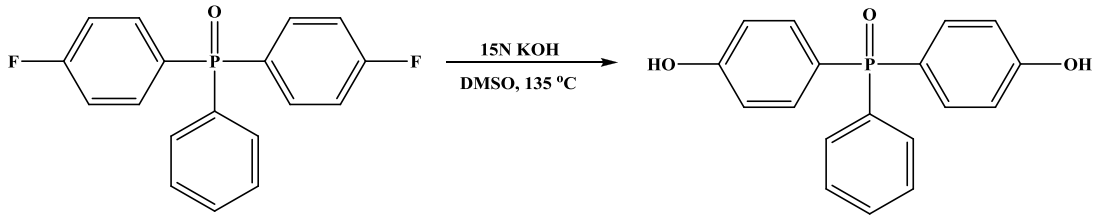
Figure 5.1 : Synthesis of bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO).

5.1.2 Synthesis of bis(4-hydroxyphenyl)phenyl phosphine oxide (BHPPO)

BHPPO was synthesized by hydrolyzing BFPPO using potassium hydroxide in DMSO as shown in Figure 5.2. 20 g (0.064 mol) BFPPO and 80 ml of DMSO were added to a 2 l 3-neck flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a condenser. To the solution was added a 15 N (21.3 ml) solution of 17.92g (0.32 mol) of potassium hydroxide in water. The solution was then raised to reflux (approximately 135 ^{o}C) and allowed to react for 8 hours. The solution was acidified well with 10% HCl and DMSO removed using a rotovap to afford a pale yellow solid. Water was then added to solid to remove remaining salt. The product was filtered, dried in vacum oven at 150 ^{o}C overnight, and then purified using

fractional recrystallization from 1:5 v/v ratio of methanol/water. Then resulting material was considered to be monomer grade with a melting point of 236-237 ^{o}C. The yield of the reaction was 65% after purification [34, 66].

BHPPO was prepared via a slight modification of the literature modification [34, 44, 66]. BHPPO was synthesized by hydrolyzing BFPPO using 15 N potassium hydroxide in DMSO. 0.032 mol BFPPO and 40 ml DMSO were added to a 250 ml 3-neck flask equipped with a mechanical stirrer, nitrogen inlet, and a condenser. To the solution was added a 15 N solution of potassium hydroxide in water. The solution was then raised to reflux (approximately 135 ^{o}C) and allowed to react for 18 hours. The solution was acidified with 10% HCl and then change to white. Water was then added to the solid to remove remaining salt. The product is filtered from filter paper and dried in a vacuum oven at 130 ^{o}C, and then purified using fractional recrystallisation from a 1:5 v/v ratio of methanol/water. The melting point is 257-258 ^{o}C, and the yield of the reaction was 95% after purification.



Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO) Bis(4-hydroxyphenyl)phenyl phosphine oxide (BHPPO)

Figure 5.2 : Synthesis of bis(4-hydroxyphenyl)phenyl phosphine oxide (BHPPO).

5.1.3 Synthesis of bis[(4-hydroxyethoxy)phenyl]phenyl phosphine oxide (BHEPPO)

Finally BHEPPO was synthesized according to the procedure [12, 51, 52]. A spherical flask (250 ml), equipped with a reflux condenser, magnetic stirrer, thermometer, and nitrogen inlet, was charged with 5 g BHPPO (0.016 mol), 2.816 g ethylene carbonate (0.032 mol), and 0.016 g sodium carbonate as catalyst. The mixture was heated to 165-170 ^{o}C under nitrogen for 2 h. The crude product was washed with water several times to remove unreacted ethylene carbonate and recrystallized from methanol. A light yellow-brown viscose liquid was obtained. The yield of the reaction was 90% after purification. The reaction takes place according to Figure 5.3

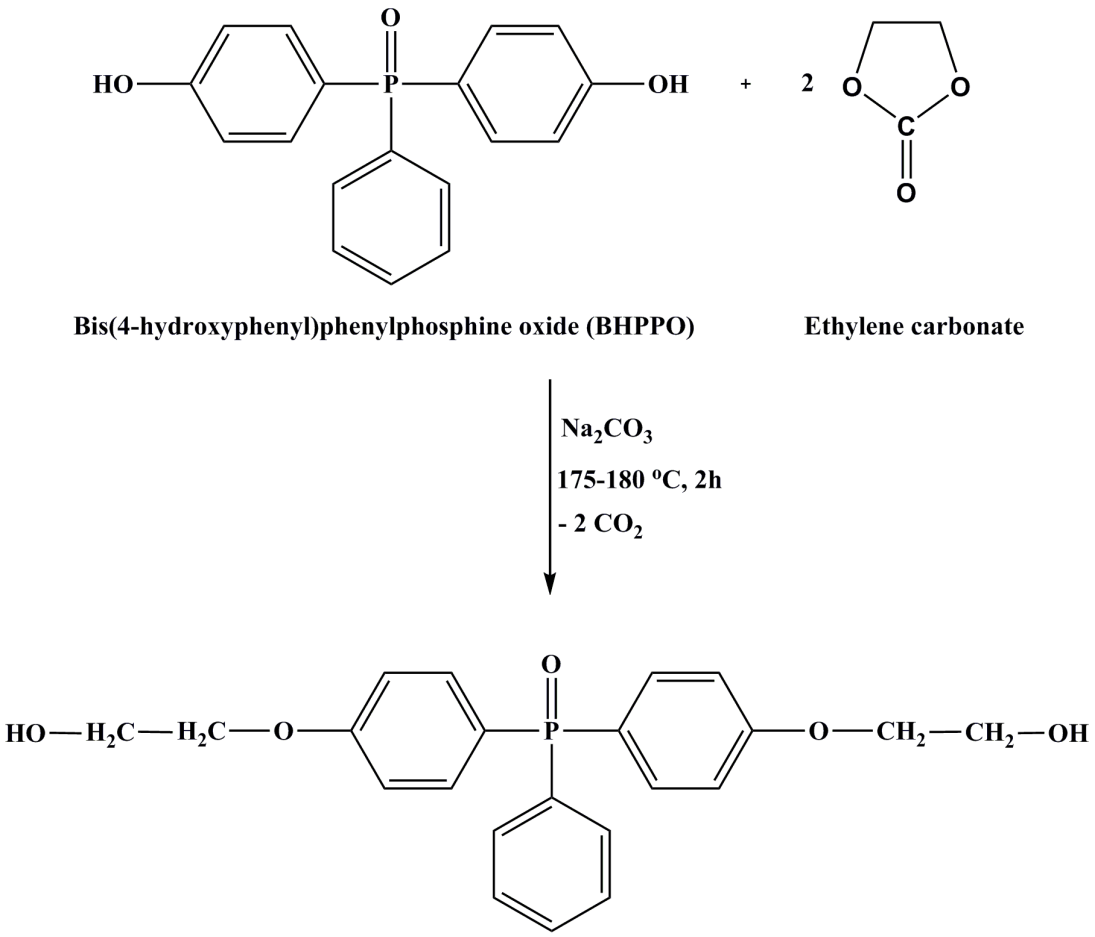


Figure 5.3 : Synthesis of bis[(4-hydroxyethoxy)phenyl]phenyl phosphine oxide (BHEPPO).

5.1.4 Synthesis of polyurethane acrylates (PUA's)

PUA's were prepared by a two-step solution polymerization method. The polyol/BHEPPO was dissolved in dichloromethane (CH_2Cl_2) and placed into a three-necked reaction kettle equipped with a magnetic stirrer, heating mantle, reflux condenser, dropping funnel and nitrogen inlet and $CaCl_2$ tube. The ratios of the materials can be seen on Table 5.1. The diisocyanate dissolved in dichloromethane was dropped into the reactor. The DBTDL added as catalyst, the temperature was increased to 40 ^oC. The reaction was continued till the isocyanate (NCO) content reached the theoretical value as determined by dibutylamine titration. Then HEMA dissolved in dichloromethane was added dropwise through the dropping funnel for over a period of 30 min and mixed. The temperature was kept at about 40 ^oC to allow the termination to take place. The reaction was continued until NCO peak at 2270 cm^{-1} dissappeared totally in the FT-IR spectra of samples taken from the reaction

medium every 0.5 h. The final product was vacuum dried at ambient temperature. The whole reaction process is depicted in Figure 5.4 and 5.5 [87].

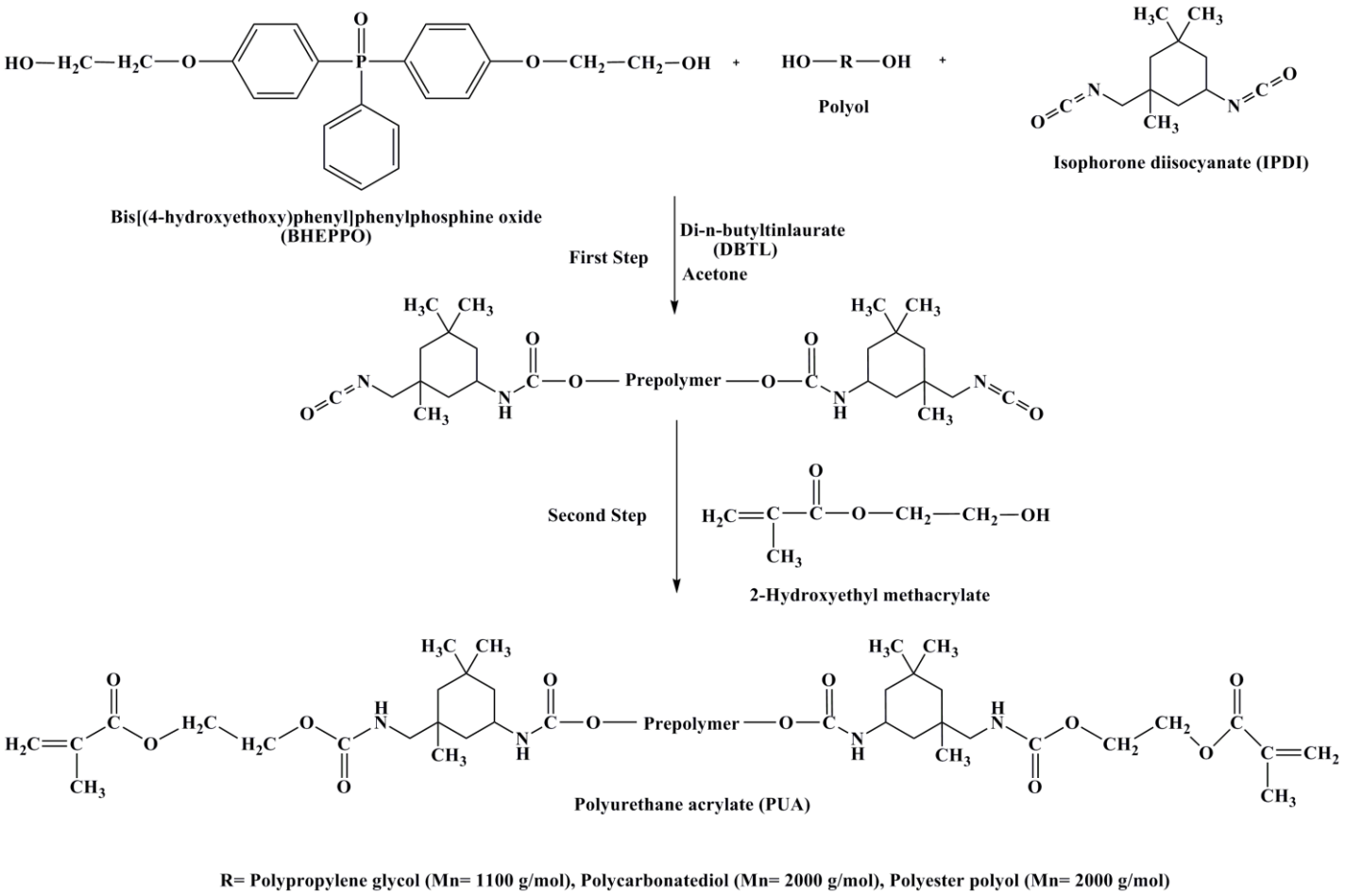


Figure 5.4 : Synthesis of IPDI containing PUA's.

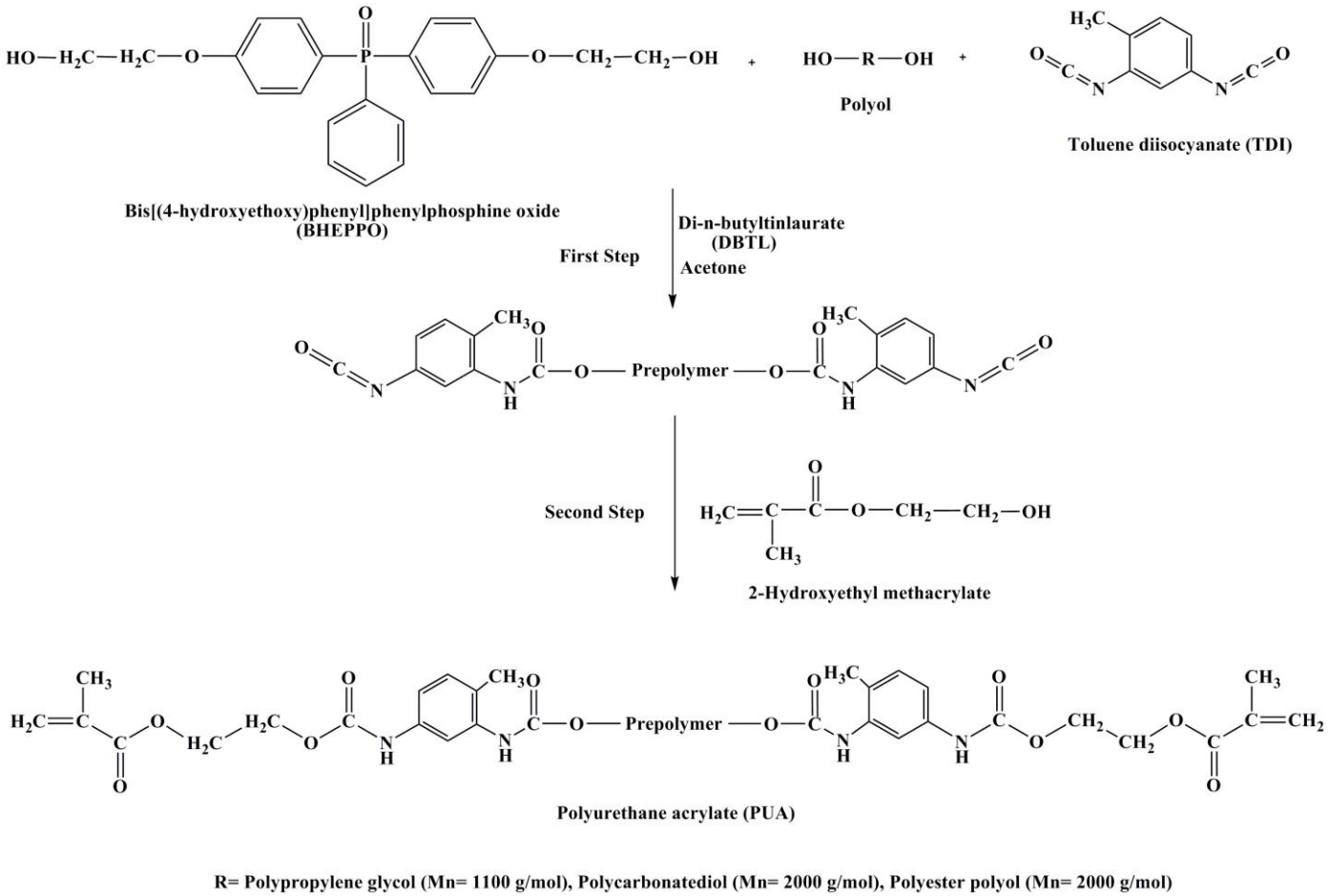


Figure 5.5 : Synthesis of TDI containing PUA's.

Table 5.1 : Ratio and variations of PUA's.

Sample Code	PES	PC	PPG	BHEPPO	IPDI	TDI	HEMA
P-PUA-1	1	-	-	-	2	-	2
P-PUA-2	0.6	-	-	0.4	2	-	2
P-PUA-3	0.4	-	-	0.6	2	-	2
P-PUA-4	-	1	-	-	2	-	2
P-PUA-5	-	0.6	-	0.4	2	-	2
P-PUA-6	-	0.4	-	0.6	2	-	2
P-PUA-7	-	-	1	-	2	-	2
P-PUA-8	-	-	0.6	0.4	2	-	2
P-PUA-9	-	-	0.4	0.6	2	-	2
P-PUA-10	1	-	-	-	-	2	2
P-PUA-11	0.6	-	-	0.4	-	2	2
P-PUA-12	0.4	-	-	0.6	-	2	2
P-PUA-13	-	1	-	-	-	2	2
P-PUA-14	-	0.6	-	0.4	-	2	2
P-PUA-15	-	0.4	-	0.6	-	2	2
P-PUA-16	-	-	1	-	-	2	2
P-PUA-17	-	-	0.6	0.4	-	2	2
P-PUA-18	-	-	0.4	0.6	-	2	2

5.1.5 Sample preparation

The coating formulations were mixed of PUA, HDDA, DPGDA are used as reactive diluents and Irgacure 184 as photoinitiator. The formulation can be seen on Table 5.2. The formula was prepared separately for each formulation. F symbol was added in front of the UV-cured PUA's to distinguish from uncured PUA's.

Table 5.2 : Polyurethane acrylate formulation.

Components	Formulation 1 (%)
PUA	50
DPGDA	37
HDDA	10
I-184	3

PUA: Polyurethane acrylate

DPGDA: Dipropyleneglycol diacrylate

HDDA: 1, 6-Hexanediol diacrylate

I-184: Photoinitiator

5.1.6 Application of the coating formulation

The coating formulations were applied on to plexiglass substrates at room temperature by a wire-gauged applicator to obtain a homogeneous thickened coating layer. The applied coatings were hardened by a UV processor with a medium pressure mercury lamp (120 W/cm^2, λ_{max}: 365 nm, total lamp power=3.24 kW) situated 15 cm above the moving belt after 10 pass. The speed of the processor was 2 m/min. and UV-cured.

Also free films were prepared by pouring the viscous material onto a TeflonTM mold (10 mm x 5 mm x 1 mm). A polyester film was also placed over Teflon to smooth surface and homogeneous cured film thickness as well. The films were cured by application of UV-lamp (OSRAM, 300 W) irradiation onto the free films for 180 sec. Mechanical, thermal, gel content, water absorption, chemical and solvent resistance tests were examined to free films.

5.2 Results and Discussion

5.2.1 Characterization

5.2.1.1 FT-IR spectrum of BFPPO

The FT-IR spectrum of BFPPO in Figure 5.6 contains the characteristic broad band (P=O) ν = 1394 cm^{-1}, (P-Ph) ν = 1434 cm^{-1}, (C-F) ν = 1220 cm^{-1}, (-CH) ν = 3057 cm^{-1}, and (C=C) ν = 1434-1589 cm^{-1}.

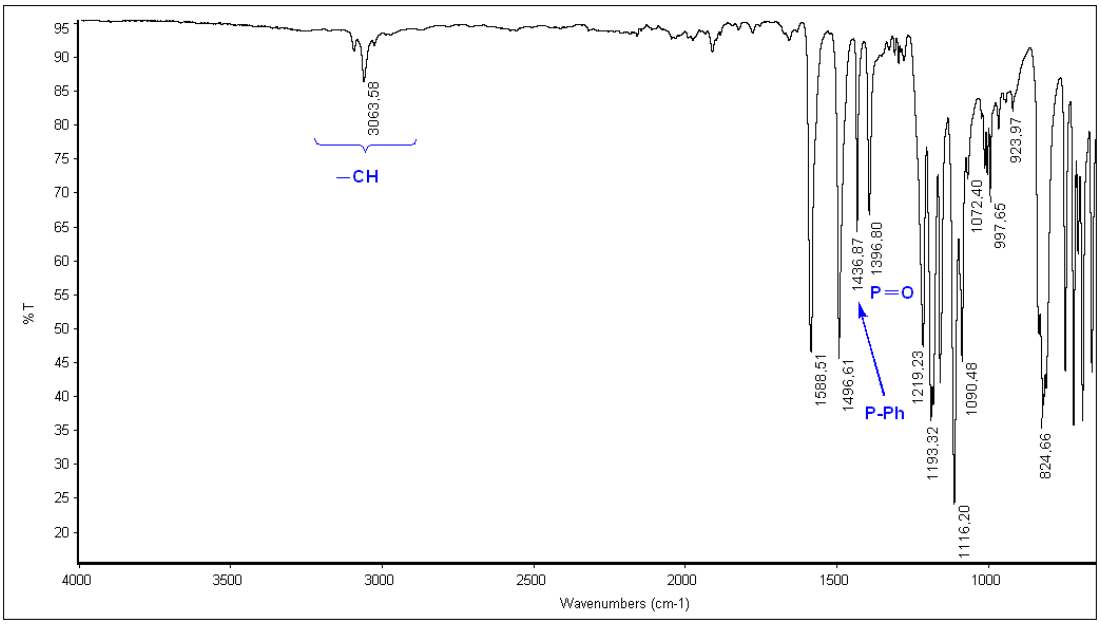


Figure 5.6 : FT-IR spectrum of BFPPO.

5.2.1.2 ^{1}H-NMR spectrum of BFPPO

There are four different aromatic protons are shown as Ha (7.65 ppm), Hb (7.56 ppm), Hc (7.48 ppm), Hd (7.16 ppm).

5.2.1.3 FT-IR spectrum of BHPPO

In this part, BFPPO was synthesized according to the procedure and presented in Figure 5.2. The chemical structures of the resulting material (BHPPO) was characterized by FT-IR (Figure 5.7). The characteristic absorption peak of the functional group (Ph-OH) 3138 $cm^{-1}$was detected for BHPPO. Peaks at 1278 cm^{-1} (-P=O), 1436 cm^{-1} (-P-Ph), 1122 cm^{-1} (C-O), and 1583-1600 cm^{-1} (C=C) proved the existence of phenyl phosphine oxide and hydroxy structure.

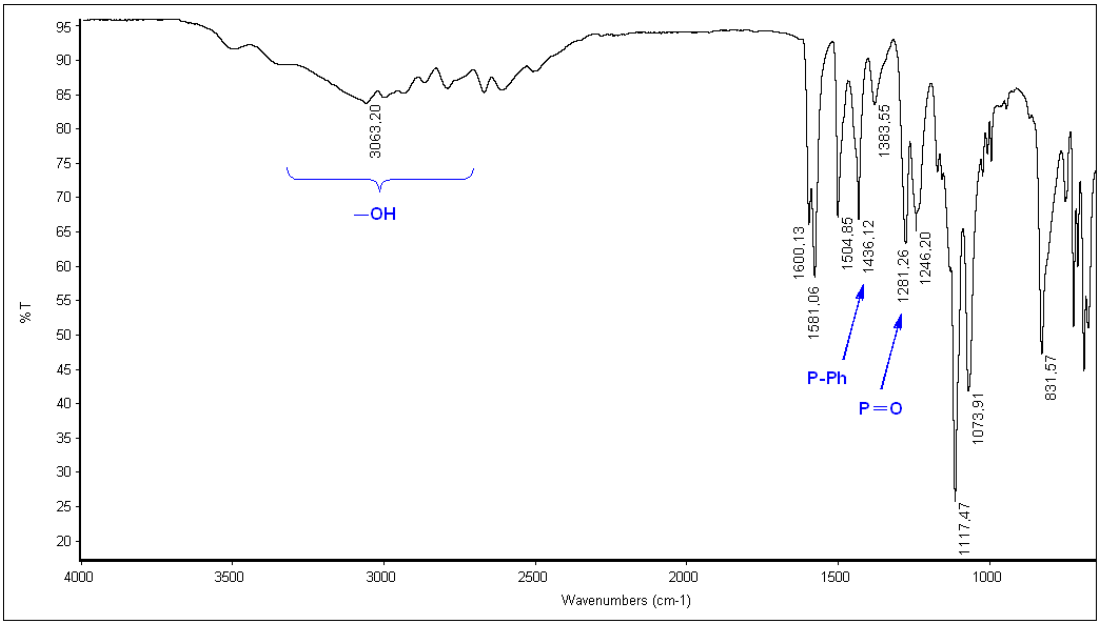


Figure 5.7 : FT-IR spectrum of BHPPO.

5.2.1.4 ^{1}H-NMR spectrum of BHPPO

The structure of this material was confirmed using ^{1}H-NMR in DMSO-d_6 as shown in Figure 5.8.

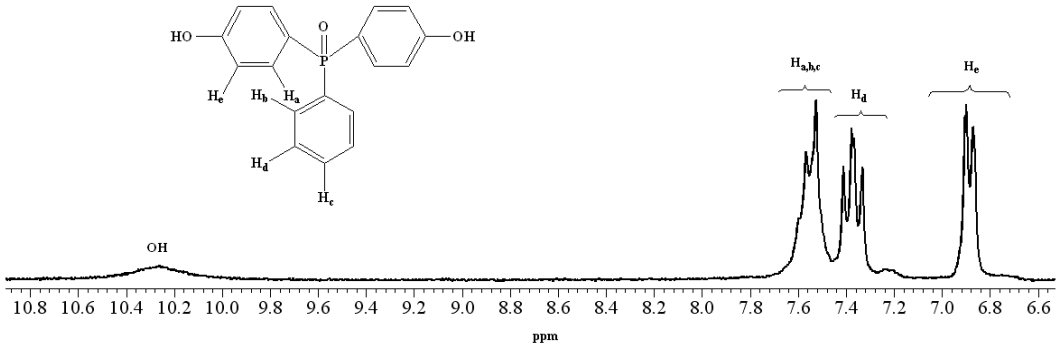


Figure 5.8 : ^{1}H-NMR spectrum of BHPPO in DMSO.

5.2.1.5 FT-IR spectrum of BHEPPO

Synthetic routes of BHEPPO and PUA's are given in Figure 5.3. Figure 5.9 displays the FT-IR spectra of the BHEPPO. The FT-IR spectra of BHEPPO absorptions due to hydroxyl groups was observed at 3302 cm^{-1} (CH_2—OH), 1162-1045 cm^{-1} (C—O), 3000-2872 cm^{-1} (C—H), 1594-1500 cm^{-1} (C=C). An absorption based on phenyl phosphine appear in the ranges (P—Ph) 1436 cm^{-1}, and phosphine oxide (P=O) 1345-1180 cm^{-1}.

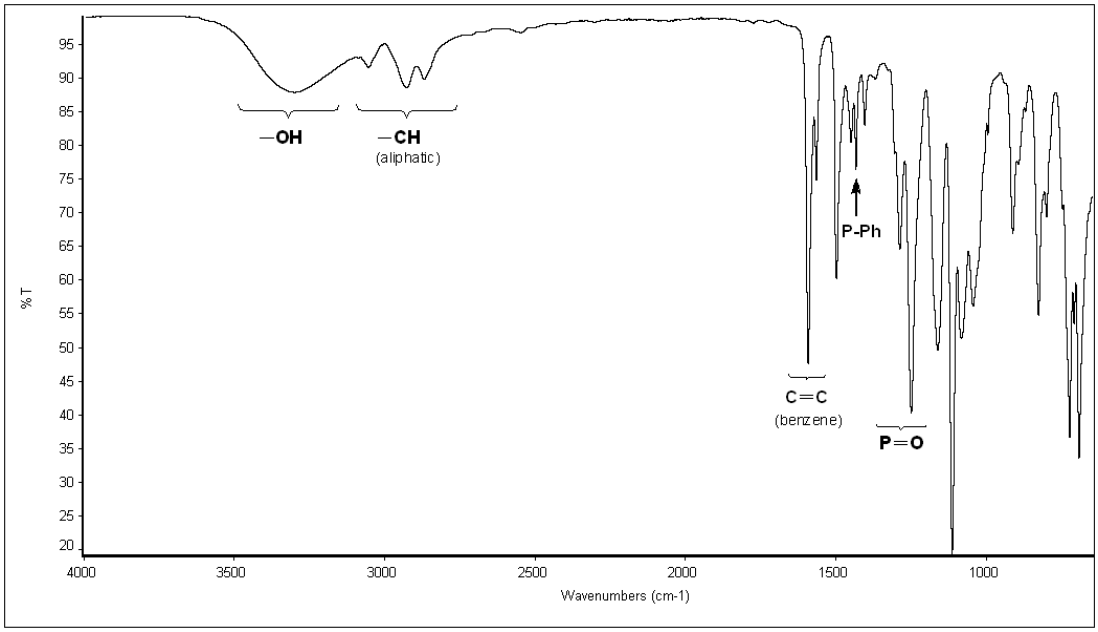


Figure 5.9 : FT-IR spectrum of BHEPPO.

5.2.1.6 ^{1}H-NMR spectrum of BHEPPO

Figure 5.10 shows ^{1}H-NMR spectra of BHEPPO. The peak at 3.92 ppm was due to CH_2 protons near to hydroxyl group and 4.05 ppm was due to CH_2 protons near to etheric oxygen atom. The hydroxyl groups were observed at 3.06 ppm. The aromatic protons of BHEPPO near to etheric oxygen atom appeared at δ = 6.6-7 ppm, and the other aromatic protons bonded to phosphine oxide group appeared at δ= 7-7.7 ppm.

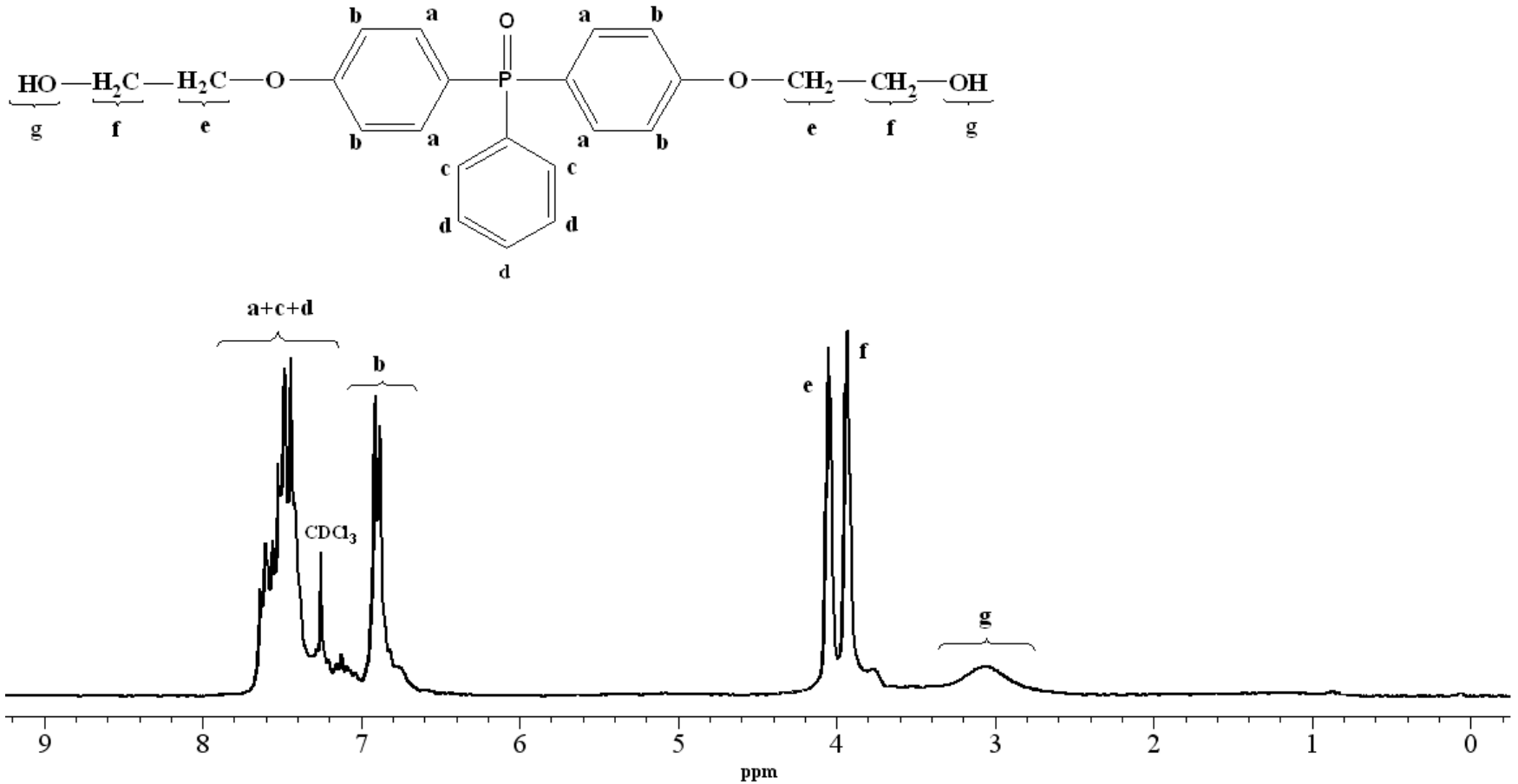


Figure 5.10 : ^{1}H-NMR spectrum of BHEPPO.

5.2.1.7 FT-IR spectrum of PUA

The synthetic routes of PUA's are given in Figures 5.4 and 5.5. The FT-IR spectrum of IPDI containing PUA's is shown in Figure 5.11 - 5.13, and spectrums of TDI containing PUA's are shown in Figures 5.14 - 5.16. In the spectrum, there are characteristic peaks of N-H (3300 cm^{-1}), and C=O (1700 - 1730 cm^{-1}), -C-N- stretching bands 1532 cm^{-1}, C-H aliphatic stretching bands (2945, 2858 cm^{-1}) are also observed. The dissappearence of the absorption bands of the NCO group (2270 cm^{-1}) of IPDI and TDI and the OH group also proves the synthesis of the PUA's. The characteristic peak of acrylate CH_2=C- is detected at 1638 cm^{-1}. The spectrum of PUA's with BHEPPO contains ether and phenyl groups in the backbone. The absorption band at 1108 cm^{-1} originates from C-O-C group. As expected, the intensity of the phenyl absorption peaks depended on the concentration of C=C atoms at 1594, 1508, and 814 cm^{-1}. Other peaks at 1165 (P=O) and 1437 cm^{-1} (P-Ph) confirm the presence of phosphine oxide moiety in PUA's. The intensity of the P=O peaks increase due to the increase of phosphine oxide content in PUA's.

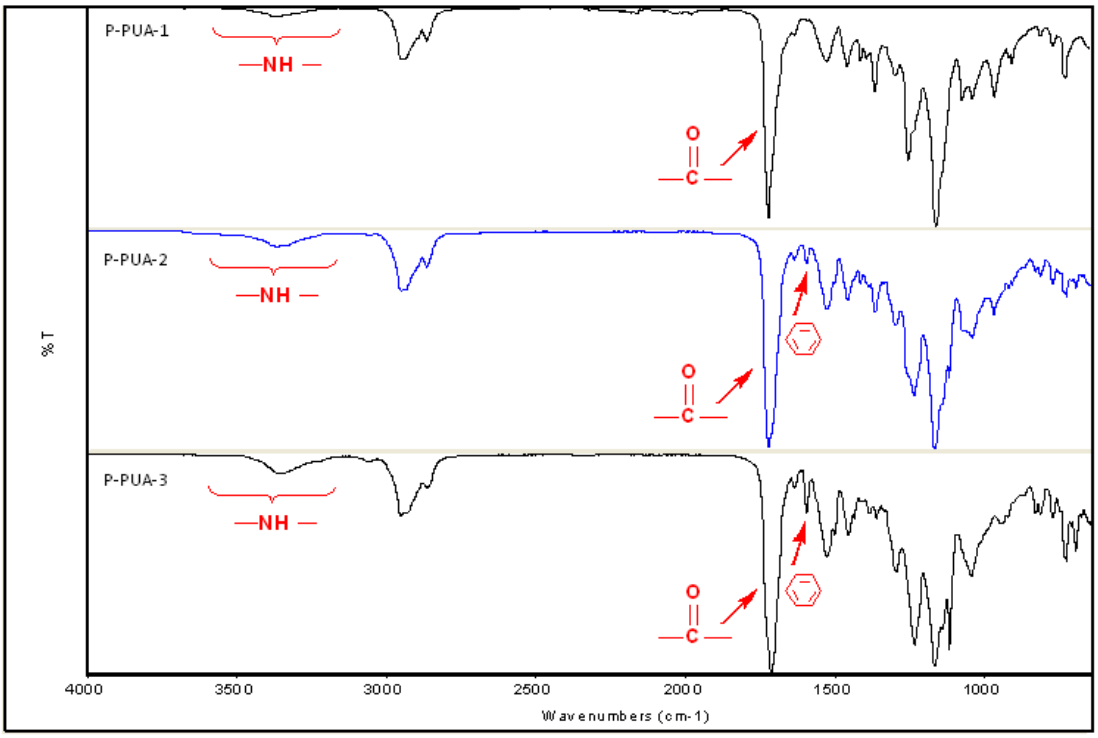


Figure 5.11 : FT-IR spectrum of IPDI and polyester polyol containing PUA's.

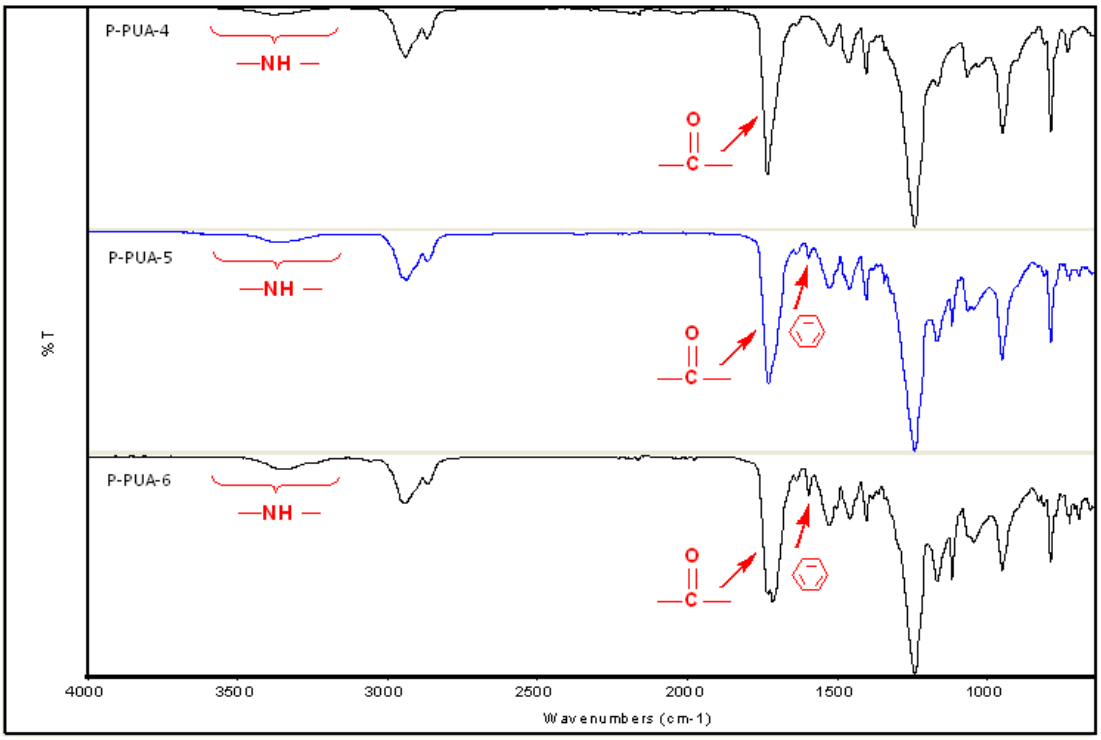


Figure 5.12 : FT-IR spectrum of IPDI and polycarbonatediol containing PUA's.

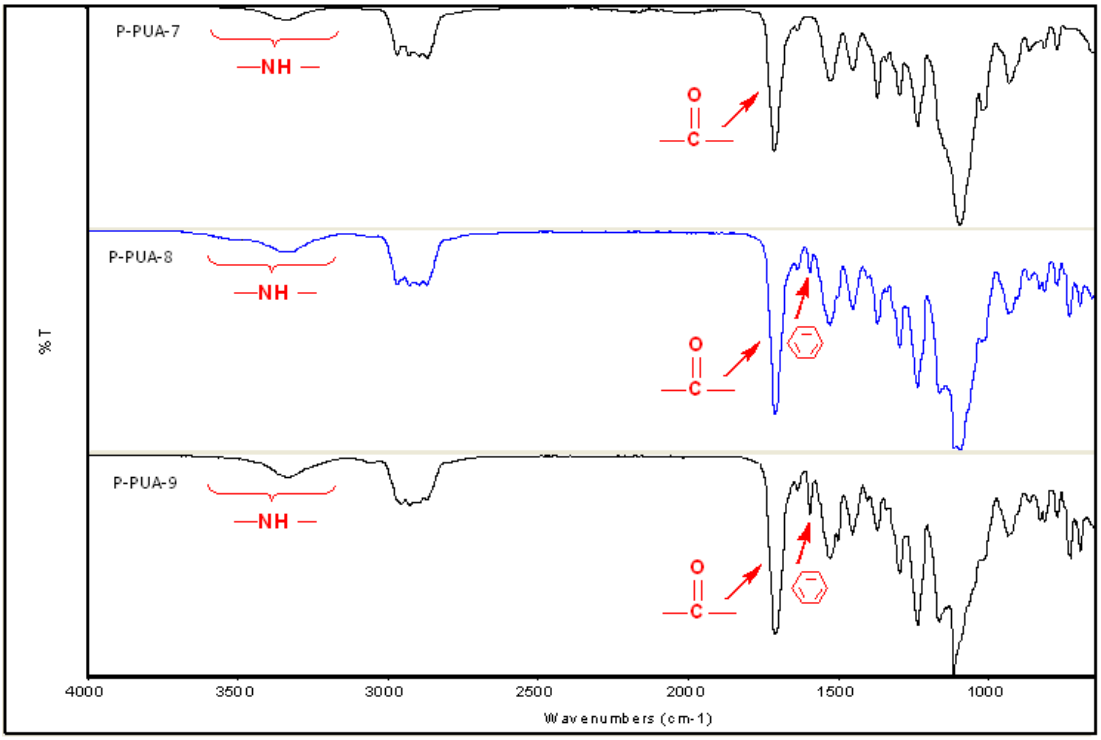


Figure 5.13 : FT-IR spectrum of IPDI and polypropylene glycol containing PUA's.

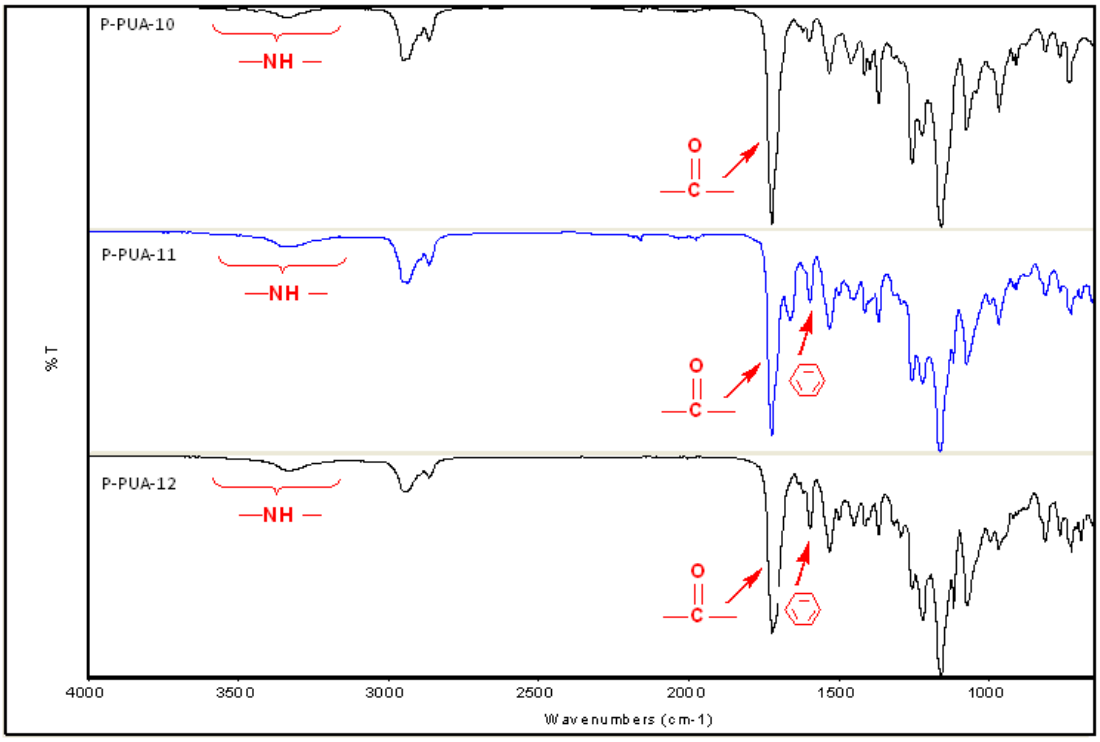


Figure 5.14 : FT-IR spectrum of TDI and polyester polyol containing PUA's.

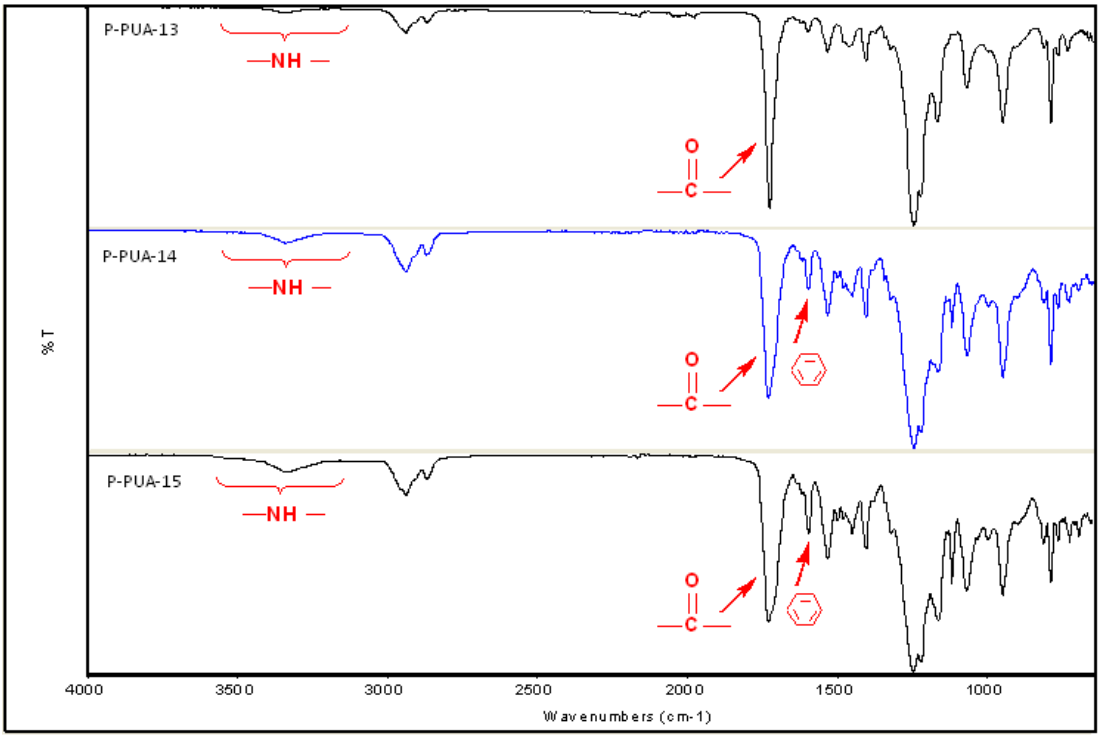


Figure 5.15 : FT-IR spectrum of TDI and polycarbonatediol containing PUA's.

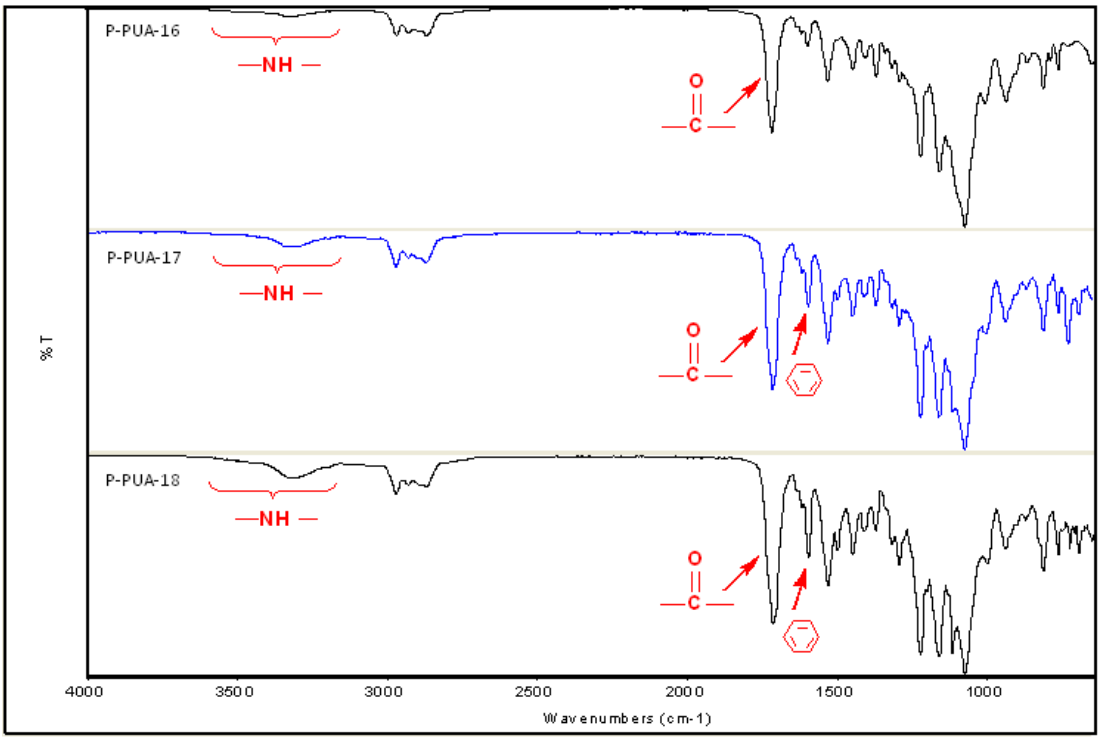


Figure 5.16 : FT-IR spectrum of TDI and polypropylene glycol containing PUA's.

5.2.1.8 ^{1}H-NMR spectrum of BHEPPO

Figures 5.17-5.19 show IPDI containing^{1}H-NMR spectra of PUA's in DMSO-d_6, and Figures 5.20-5.22 show TDI containing ^{1}H-NMR spectra of PUA's in DMSO-d_6. The peaks at 0.7-1.20 ppm are attributed to the protons of methyl (CH_3) and CH_2 protons of IPDI and CH_3 protons of neopenthyl moiety of PES. The central CH_2 protons of PES and PC and CH_2 protons in the cyclic ring of IPDI were at δ = 1.20-1.78 ppm. The peaks in the range of 1.81-2.00 ppm are methyl protons of HEMA and CH2 protons of PES. Methylene groups attached to the carbonyl carbon of esteric groups (CH_2COO) were observed at 2.20-2.46 ppm. The methyl proton of TDI was assigned to the peak at δ = 2.5 ppm. Methylene groups attached to the urethane nitrogen atom were detected at 2.65-2.90 ppm for all PUA's. The peaks at 2.90-3.22 are ascribed to the CH_2 protons of IPDI. The peak at 3.22-3.81 ppm was due to the CH and CH_2 protons of IPDI and TDI (NCOCH and $NCOCH_2$), CH_2 protons of HEMA (CH_2OCONH), and CH_2 protons of BHEPPO (CH_2OCONH). The CH_2 groups attached to the ester group oxygen atom of PES ($OCH_2C(CH_3)_2$), CH_2 protons attached to the etheric group of BHEPPO (OCH_2CH_2), and CH_2 protons attached to the ester group oxygen atom of HEMA ($COOCH_2CH_2$) were detected at 3.81-4.45 ppm. The peaks in the range of 5.67-5.68 ppm and 6.02-6.05 ppm are obviously observed in both spectra, which prove the existence of acrylic group in PUA

molecular structure related with HEMA. The aromatic protons of BHEPPO near to etheric oxygen atom appeared at δ = 7.7-7.8 ppm. The peaks at 6.9-7.2 ppm are ascribed to the protons of –NH- groups in urethane unit and aromatic protons of near to phosphine oxide of BHEPPO. The aromatic protons of BHEPPO near to etheric oxygen atom appeared at δ = 6.6-7 ppm, and the other aromatic protons bonded to phosphine oxide group appeared at δ= 7-7.7 ppm. The aromatic protons of TDI appeared at δ = 7-7.6 ppm. The urethane protons which contain TDI in the backbone were observed at δ = 8.9-9.7 ppm.

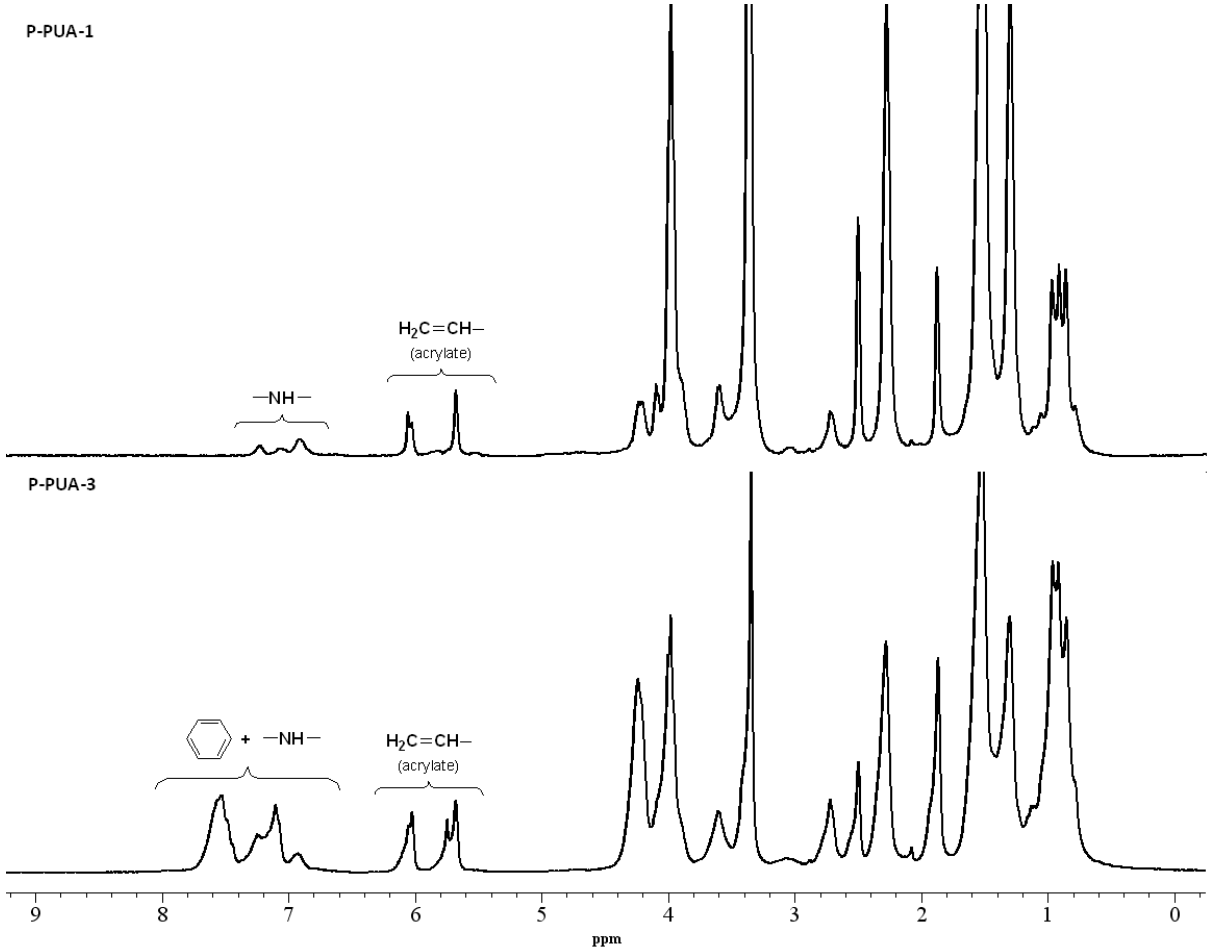


Figure 5.17 : ^{1}H-NMR spectrum of IPDI and polyester polyol containing PUA's.

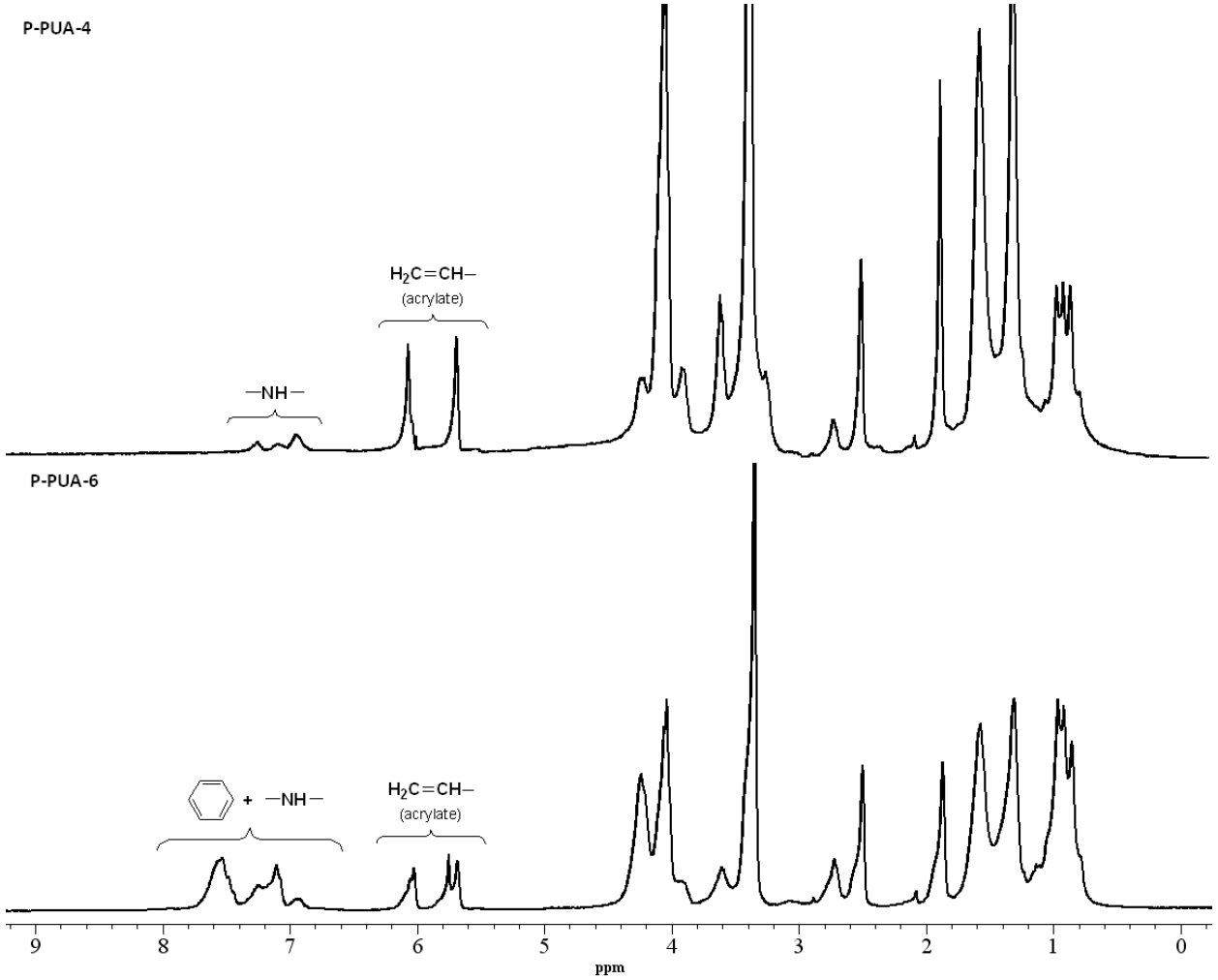


Figure 5.18 : ^{1}H-NMR spectrum of IPDI and polycarbonatediol containing PUA's.

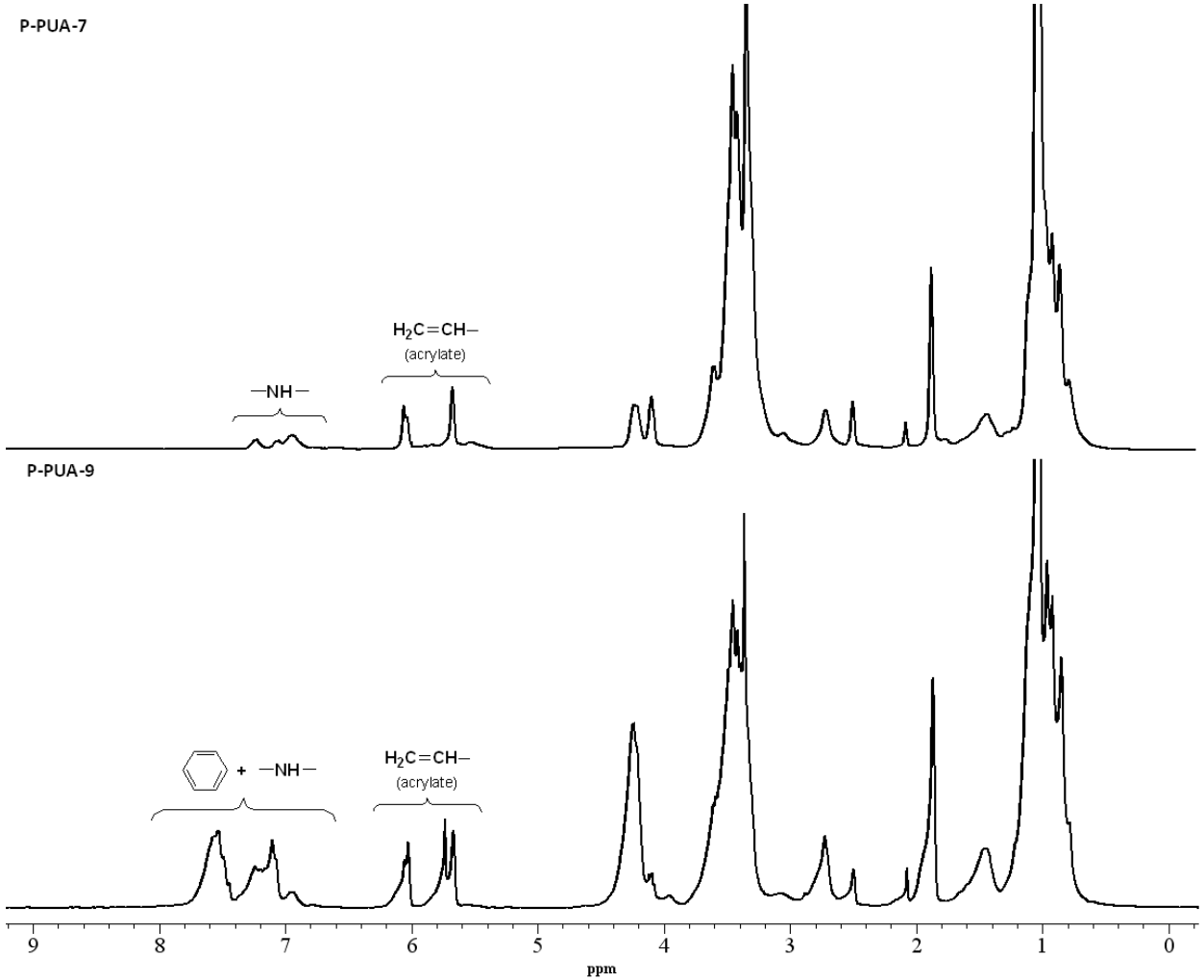


Figure 5.19 : ^{1}H-NMR spectrum of IPDI and polypropylene glycol containing PUA's.

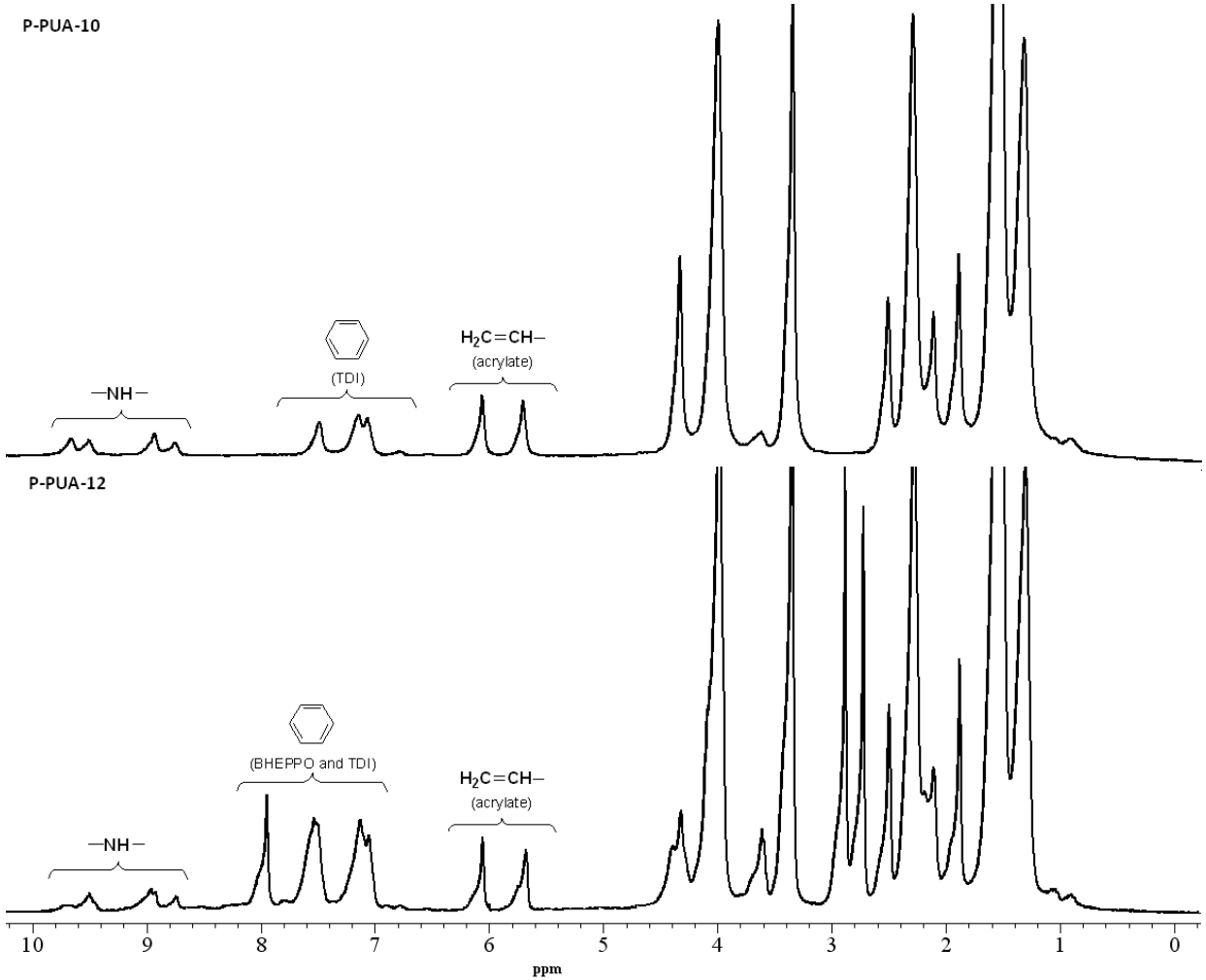


Figure 5.20 : ^{1}H-NMR spectrum of TDI and polyesterpolyol containing PUA's.

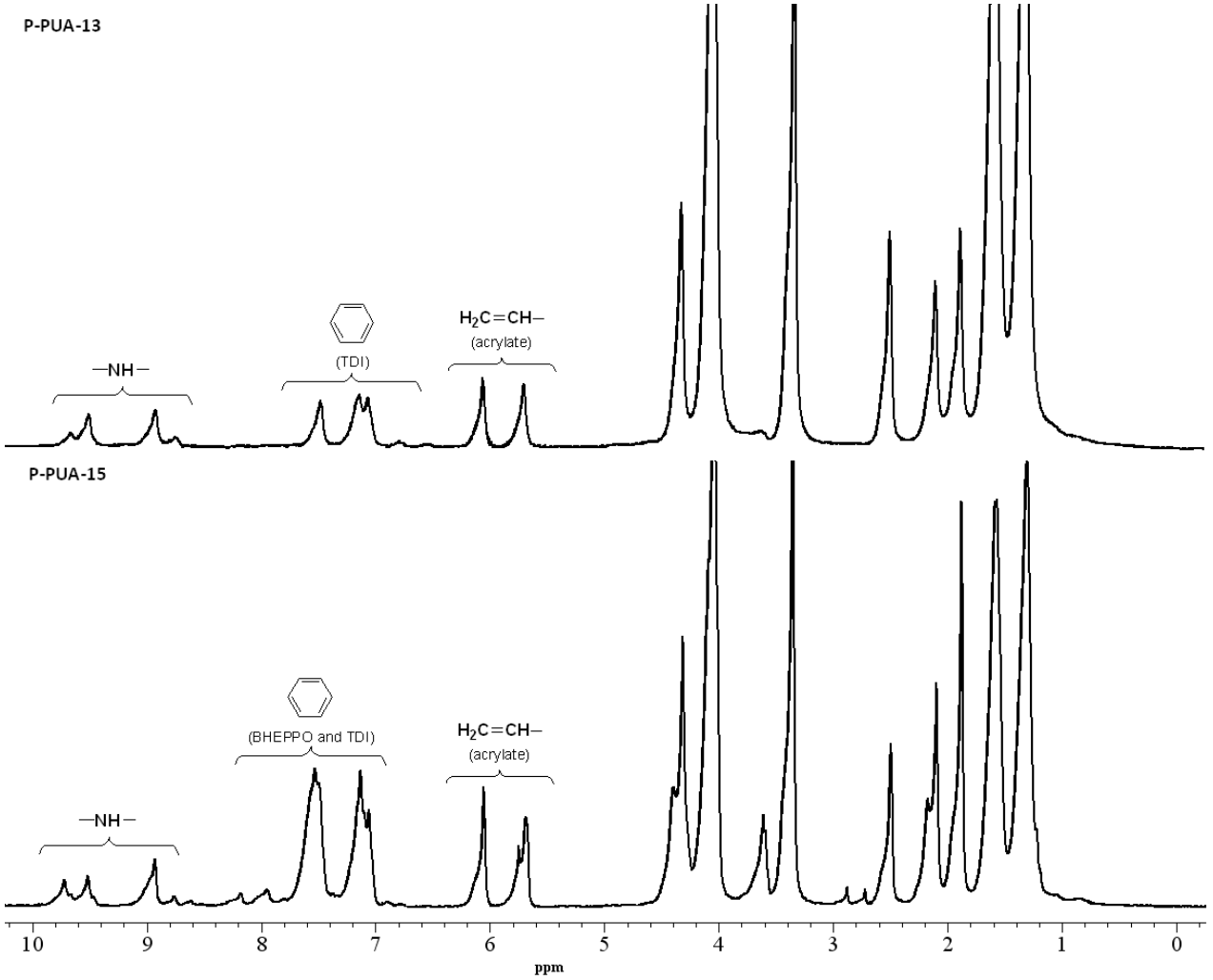


Figure 5.21 : ^{1}H-NMR spectrum of TDI and polycarbonatediol containing PUA's.

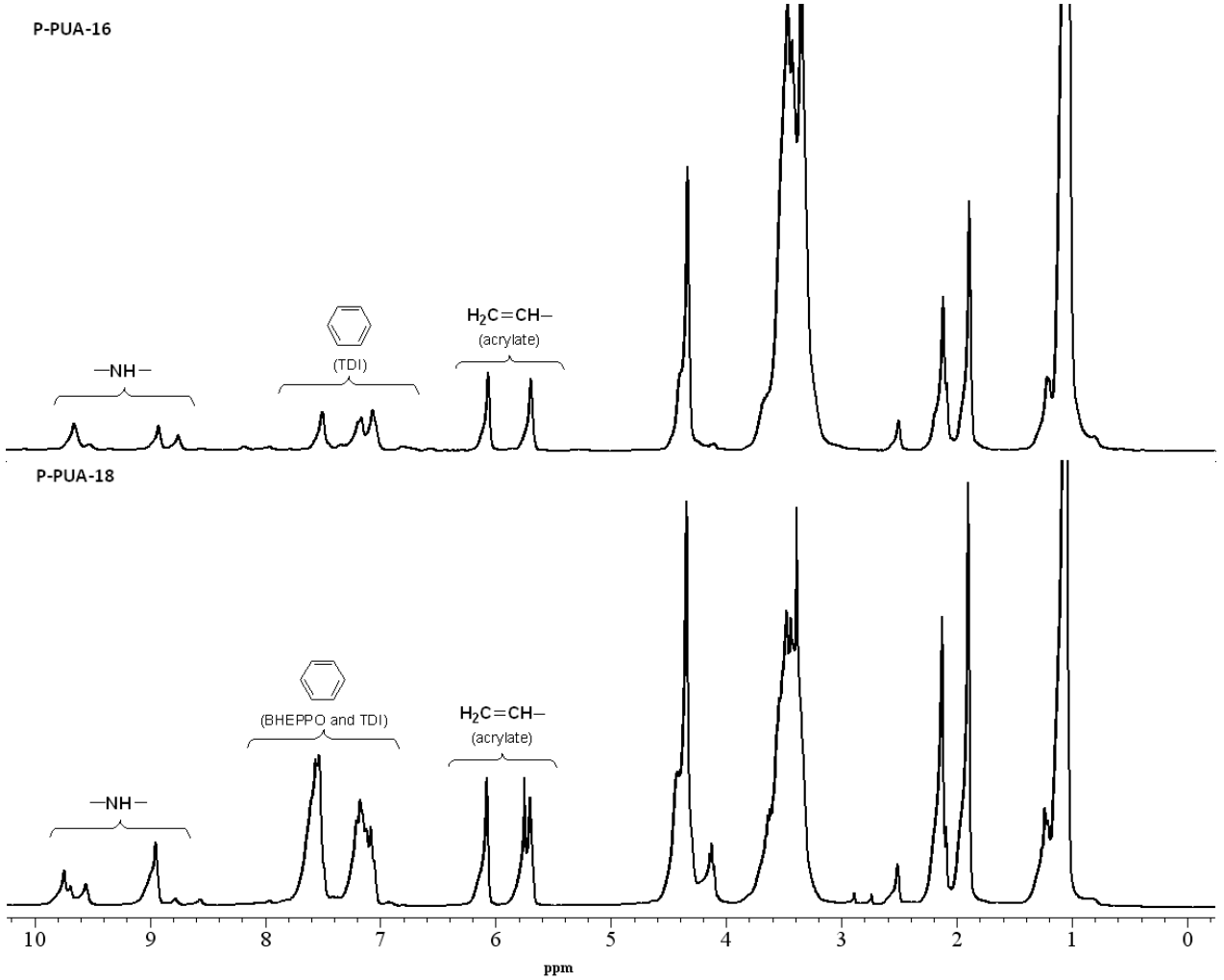


Figure 5.22 : ^{1}H-NMR spectrum of TDI and polypropylene containing PUA's.

5.2.2 Gloss properties

Gloss analysis of coated plates was measured at an angle of 20^o, 60^o, and 85^o. The measurement at 85^o is for matt surface, so these values were neglected. Specular angle is the angle of reflected light equal to the angle of the incident light beam. A high gloss surface reflects a large fraction of the light that is reflected from the surface at the specular angle. A larger fraction at nonspecular angles is reflected when the surface have lower gloss characteristics. The factors that affect gloss properties are refractive index of the material, angle of incident light and surface topography [82]. The results of gloss measurements of UV-cured PUA's are shown in Figures 5.23 – 5.26. The Leneta test card was put under the coated plates and black side of card was used to measure the gloss values.

As BHEPPO content in PUA's increase, the gloss values were also increased. The average gloss (20^o) values of the phosphine oxide containing UV-cured PUA's were between 67 - 155 for IPDI containing PUA's, 121 – 156 for TDI containing PUA's. The average gloss (60^o) values of the sulfone containing UV-cured PUA's were between 97 - 152 for IPDI containing PUA's, 138 – 153 for TDI containing PUA's.

The gloss values of PPG and PC containing PUA's were higher than PES containing PUA's. Polyols which have amorphous structure gives transparency property to the coating like PPG and PC. But PES could have amorphous and semi-crystalline structure. Due to the less transparency of semi-crystalline structure, the values of PES containing PUA's could be less than the others. BHEPPO containing PCs have the highest gloss value because PCs have high optical clarity to visible light.

Additionally BHEPPO which contain polar phosphine oxide groups could affect on the amorphous structure and this can increase the gloss values [57]. The value change of PPG containing PUA's is higher than the other PUA's due to the molecular weight of PPG. BHEPPO content is more efficient with PPG containing PUA's.

Also materials with smooth surfaces appear glossy, while rough surfaces reflect no specular light and appear matte. Depending on this theory consistency of the components in the formulation, homogeneous mixing and coating produce smooth and glossy surface [82].

In conclusion, amorphous structure, polarity, preparation of the mixture, application of the coating can effect on gloss properties.

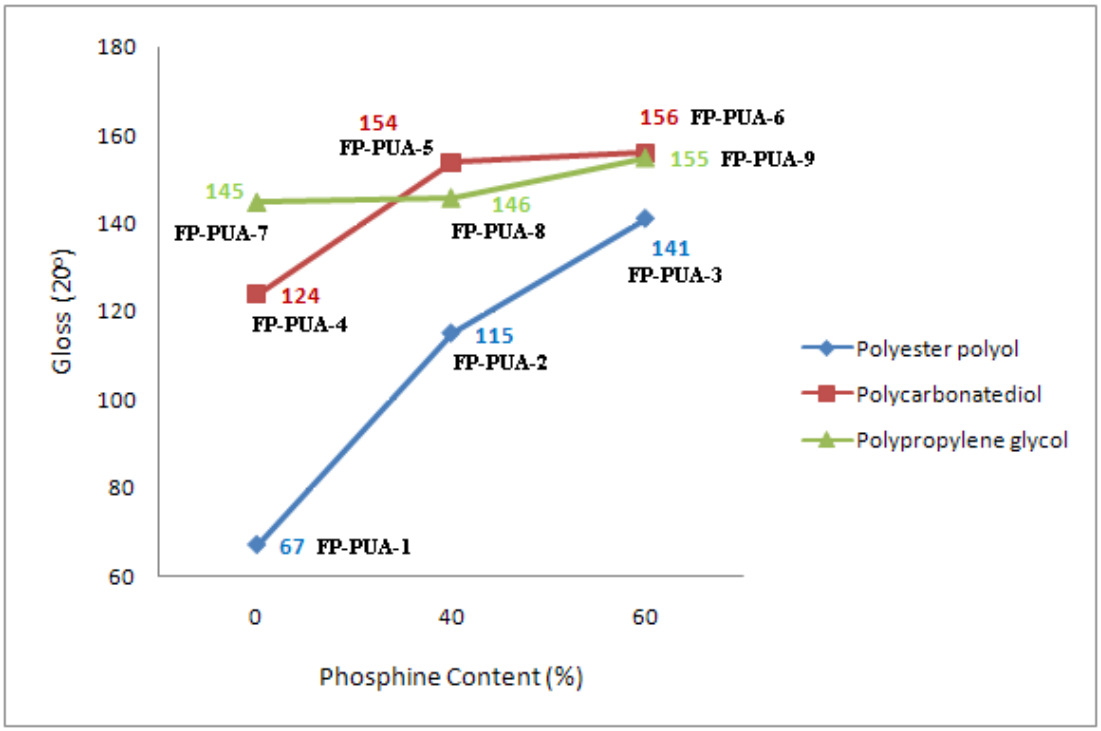


Figure 5.23 : 20° Gloss value of IPDI containing UV-cured PUA's.

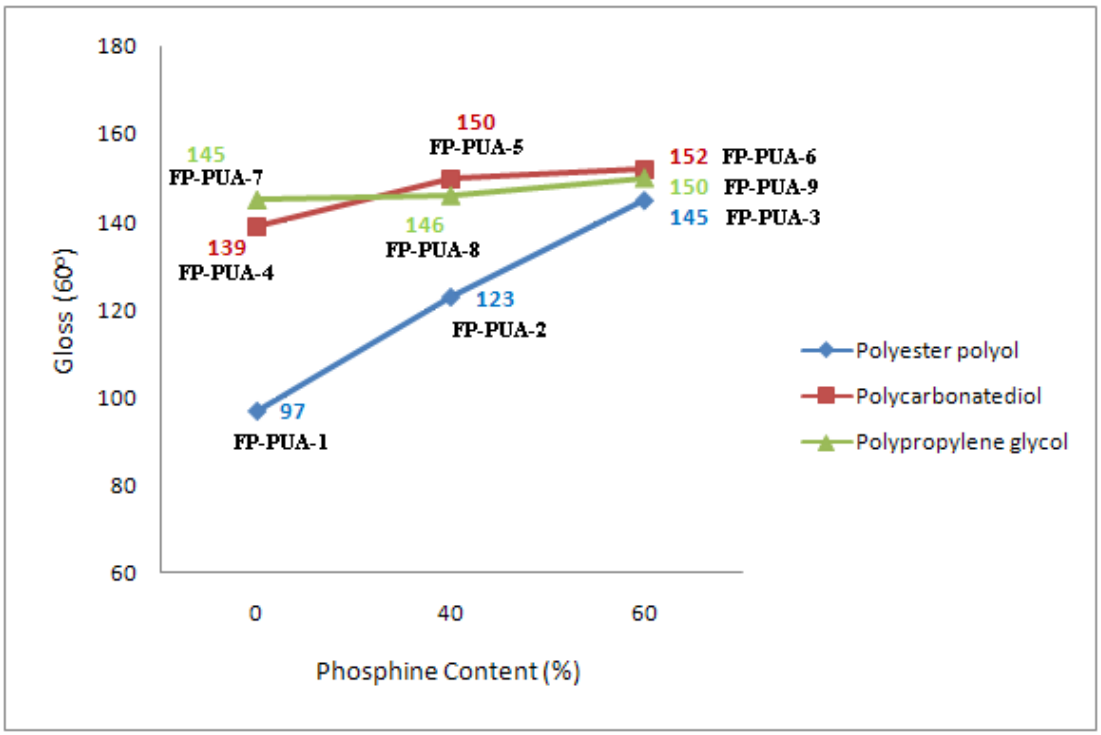


Figure 5.24 : 60° Gloss value of IPDI containing UV-cured PUA's.

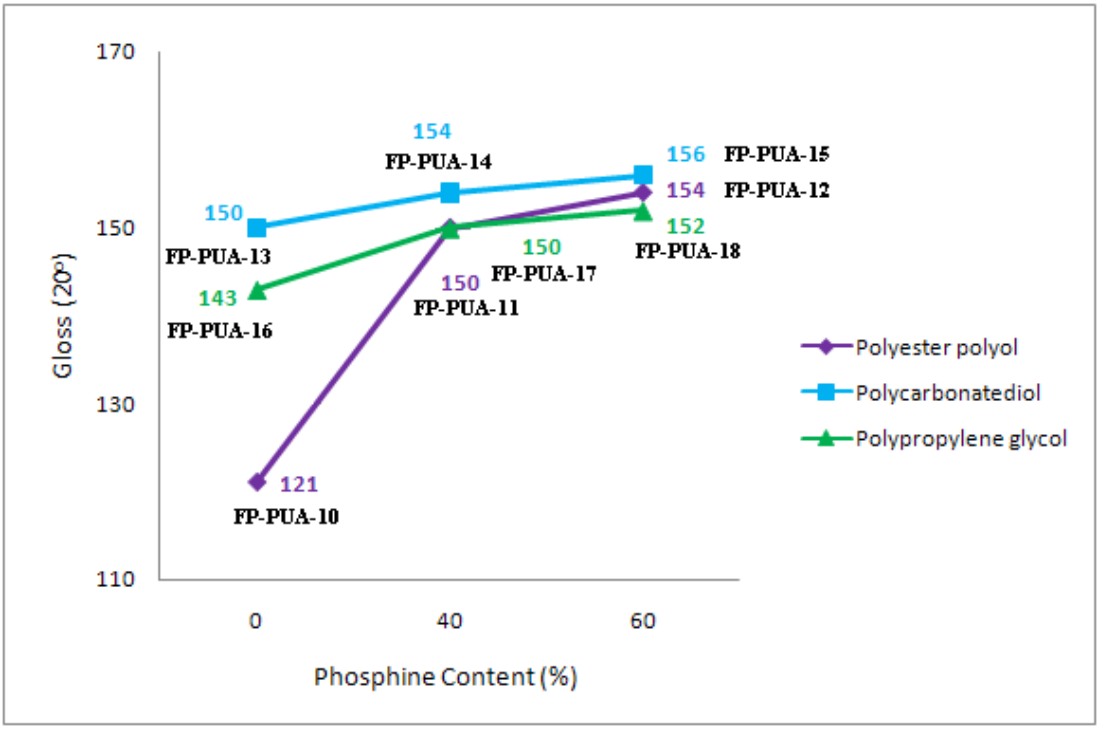


Figure 5.25 : 20° Gloss value of TDI containing UV-cured PUA's.

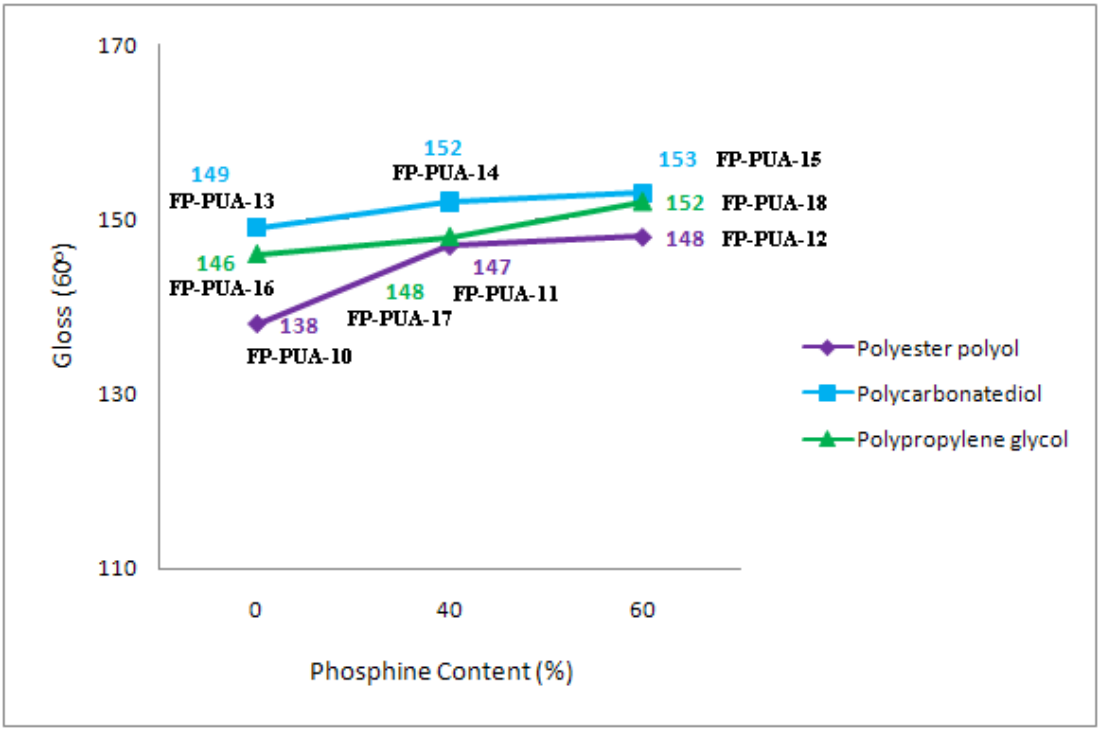


Figure 5.26 : 60° Gloss value of TDI containing UV-cured PUA's.

5.2.3 Contact angle measurement

The tests were applied onto polymer coated plexiglass substrates. Surface hydrophilicity of the various samples, as characterized by static water contact angle, is summarized in Tables 5.3 and 5.4. The water contact angle was in the range of 95-73^{o} for IPDI containing films and 74-65^{o} for TDI containing films. As the content of BHEPPO was increasing water contact angle value was decreasing. This was an expected behavior assuming that phenyl phosphine oxide (BHEPPO) groups make the surface more hydrophilic [22]. The presence of polar functional groups such as phosphine oxide groups increase the hydrogen bonding interactions and therefore contact angle decreases. Hydrophilicity of the coatings was increased from polyester polyol to polypropylene glycol (PES<PC<PPG). The contact angles can be seen in Figure 5.27.

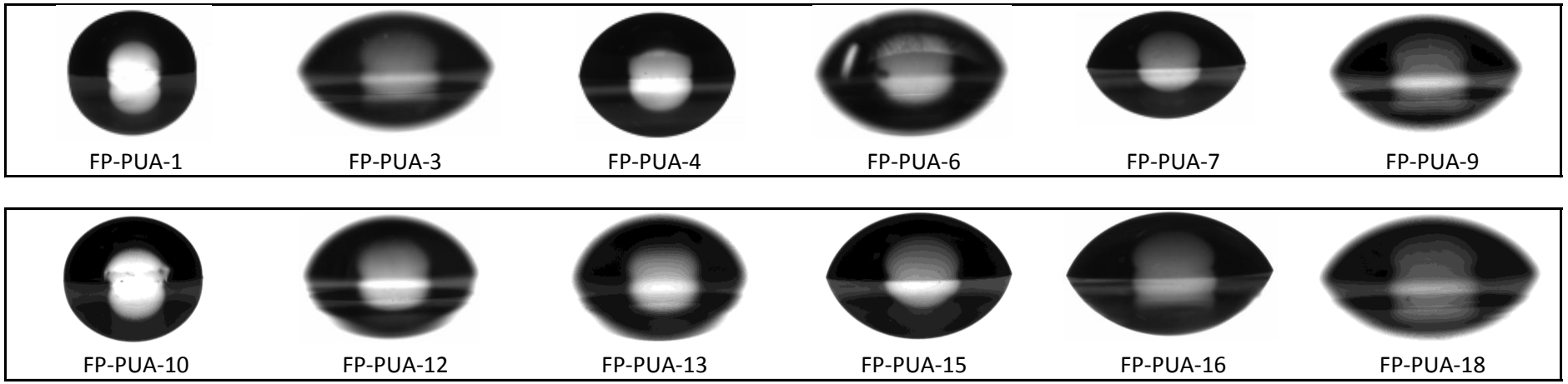


Figure 5.27 : Contact angle figures of UV-cured PUA's.

5.2.4 Water absorption

Water absorption measurements of UV-cured samples were carried out in distilled water at 25 ^{o}C according to ASTM D 570 standard. These values are tabulated in Table 5.3 and 5.4. There was no considerable difference in the amount of absorbed water. Experimental results showed that PPG content was the main factor that can control amount of absorbed water. The results clearly revealed that water absorption of the samples increased with increasing the PPG content.

5.2.5 Gel content

This test was applied to measure polymerization degree of UV-curing system. Gel content degree is related with UV-curing time, selectivity of the initiator and acrylate oligomers. Unreacted part of the cured materials was under 5 wt. % high gel content was associated with high crosslinking. Experimental studies showed that initiator used in this work yields high gel content value at chosen irradiation time (5 min) according to the results. Gel content values are also listed in Table 5.3 and 5.4.

Table 5.3 : Contact angle, water absorption, gel content, and pencil hardness analysis of IPDI containing UV-cured PUA's.

Composition Code	Contact Angle (^{o})	Water Absorption (%)	Gel Content (%)	Pencil Hardness
FP-PUA-1	95	99	95	4 H
FP-PUA-2	84	97	97	5 H
FP-PUA-3	70	97	97	6 H
FP-PUA-4	89	98	95	4 H
FP-PUA-5	76	98	95	5 H
FP-PUA-6	65	97	98	6 H
FP-PUA-7	84	98	97	5 H
FP-PUA-8	74	97	96	6 H
FP-PUA-9	73	97	98	6 H

Table 5.4 : Contact angle, water absorption, gel content, and pencil hardness analysis of TDI containing UV-cured PUA's.

Composition Code	Contact Angle (^{o})	Water Absorption (%)	Gel Content (%)	Pencil Hardness
FP-PUA-10	74	98	96	5 H
FP-PUA-11	80	98	95	7 H
FP-PUA-12	78	98	97	7 H
FP-PUA-13	75	96	95	4 H
FP-PUA-14	70	96	95	7 H
FP-PUA-15	66	97	97	7 H
FP-PUA-16	67	96	95	5 H
FP-PUA-17	66	96	96	6 H
FP-PUA-18	65	97	97	7 H

5.2.6 Chemical and solvent resistance

To estimate the performance of the PUA coatings, the UV-cured PUA films were tested to alkali and acidic action. Cured films were immersed in chloroform, xylene, methanol, 10% HCl, 10% acetic acid, 10% NaOH, respectively, for 24 h at room temperature to test the chemical and solvent resistance and experimental results show that PUA films has good solvent and chemical resistance performance. The results of chemical and solvent resistance are listed in Table 5.5 and 5.6. The weight loss values for each compound were less than 2 for chemical resistance and less than 6 for solvent resistance. This shows that resistance of PUA's to different type of chemicals were really high. The appearance of the samples was good except chloroform. The samples got broken with the existence of chloroform.

Table 5.5 : Solvent resistance of UV-cured PUA's.

Comp. Code	Chloroform		Xylene		Methanol	
	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance
FP-PUA-1	< 1	Broken	< 5	Good	< 5	Good
FP-PUA-2	< 1	Broken	< 3	Good	< 3	Good
FP-PUA-3	< 1	Broken	< 1	Good	< 3	Good
FP-PUA-4	< 1	Broken	< 5	Good	< 5	Good
FP-PUA-5	< 1	Broken	< 3	Good	< 4	Good
FP-PUA-6	< 1	Broken	< 2	Good	< 2	Good
FP-PUA-7	< 1	Broken	< 5	Good	< 4	Good
FP-PUA-8	< 1	Broken	< 2	Good	< 4	Good
FP-PUA-9	< 1	Broken	< 1	Good	< 3	Good
FP-PUA-10	< 1	Broken	< 4	Good	< 3	Good
FP-PUA-11	< 1	Broken	< 2	Good	< 1	Good
FP-PUA-12	< 1	Broken	< 1	Good	< 2	Good
FP-PUA-13	< 1	Broken	< 5	Good	< 6	Good
FP-PUA-14	< 1	Broken	< 1	Good	< 3	Good
FP-PUA-15	< 2	Broken	< 2	Good	< 2	Good
FP-PUA-16	< 1	Broken	< 3	Good	< 4	Good
FP-PUA-17	< 1	Broken	< 3	Good	< 3	Good
FP-PUA-18	< 2	Broken	< 1	Good	< 3	Good

Table 5.6 : Chemical resistance of UV-cured PUA's.

Comp. Code	HCl (10%)		Acetic Acid (10%)		NaOH (10%)	
	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance	Weight Loss (%)	Appearance
FP-PUA-1	< 1	Good	< 2	Good	< 1	Good
FP-PUA-2	< 2	Good	0	Good	0	Good
FP-PUA-3	< 2	Good	0	Good	< 2	Good
FP-PUA-4	< 1	Good	< 1	Good	< 1	Good
FP-PUA-5	< 2	Good	0	Good	0	Good
FP-PUA-6	< 1	Good	< 1	Good	0	Good
FP-PUA-7	< 1	Good	< 1	Good	< 1	Good
FP-PUA-8	< 1	Good	0	Good	0	Good
FP-PUA-9	< 2	Good	< 2	Good	0	Good
FP-PUA-10	< 1	Good	0	Good	< 1	Good
FP-PUA-11	< 1	Good	0	Good	0	Good
FP-PUA-12	< 3	Good	< 2	Good	< 3	Good
FP-PUA-13	< 1	Good	< 2	Good	< 2	Good
FP-PUA-14	< 2	Good	0	Good	< 1	Good
FP-PUA-15	< 1	Good	< 1	Good	< 1	Good
FP-PUA-16	< 1	Good	< 2	Good	< 2	Good
FP-PUA-17	< 1	Good	< 1	Good	< 1	Good
FP-PUA-18	< 1	Good	< 1	Good	< 1	Good

5.2.7 Mechanical properties (Pendulum hardness, pencil hardness, and tensile tests)

Hardness of a coating is an important factor affecting abrasion and scratch resistance of coatings. Hard coatings give better scratch resistance. Chain flexibility and crosslinking degree of the network play a major role in the value of hardness. The pendulum hardness results of the PUA's are shown in Figure 5.28 and 5.29. The pendulum hardness is increased with increase in concentration of phenyl phosphine oxide groups (BHEPPO) in the polyurethane acrylates. When the BHEPPO content was 60% in the PUA's, the average pendulum hardness values were between 80-83 and the reference values were between 44-57 for IPDI containing films and the average pendulum hardness values were between 69-83 and the reference values were between 41-62 for TDI containing films. The observed improvement is quite high.

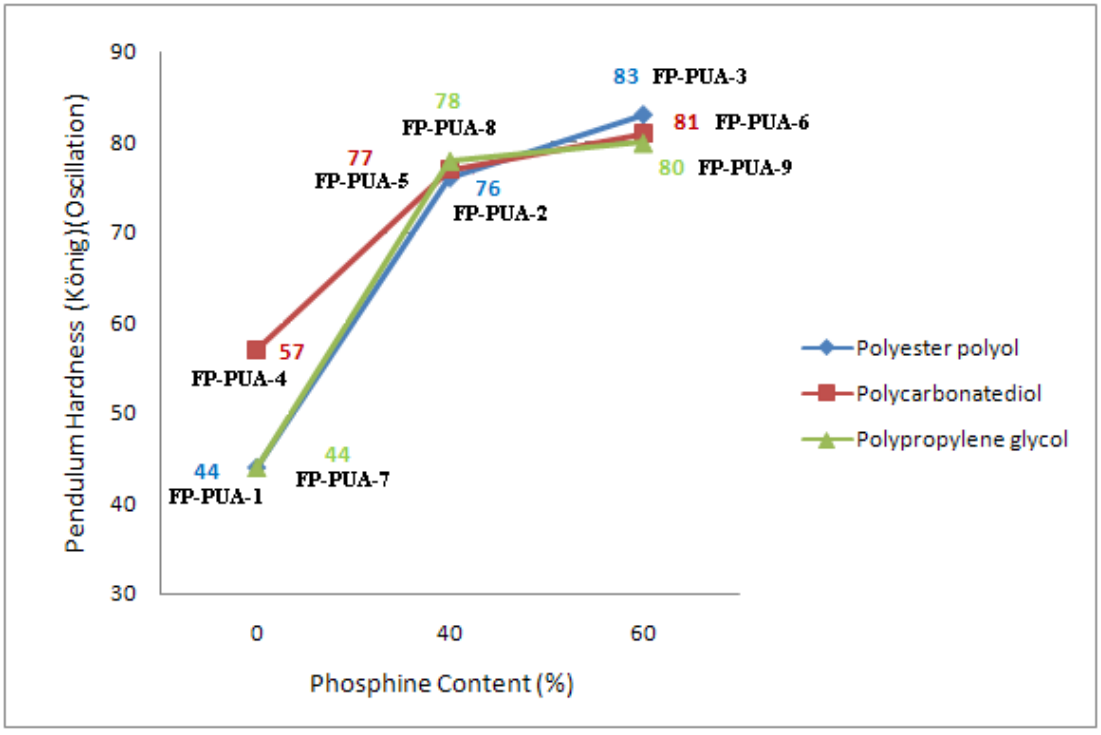


Figure 5.28 : Pendulum hardness values of IPDI containing UV-cured PUA's.

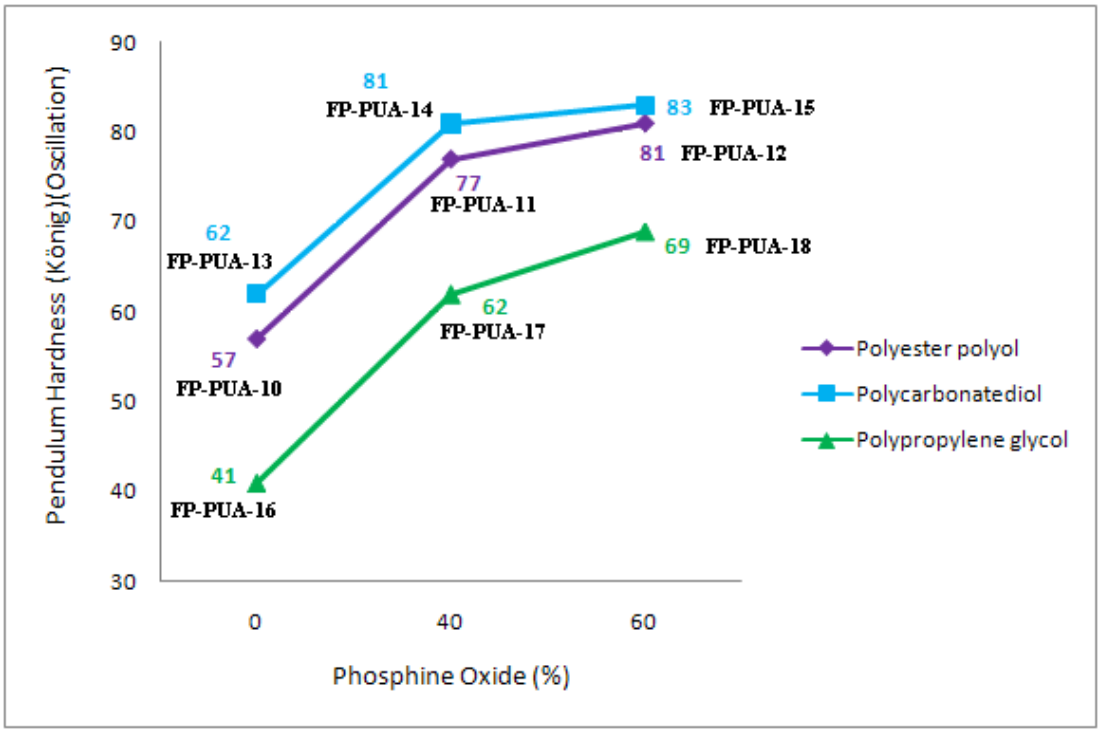


Figure 5.29 : Pendulum hardness values of TDI containing UV-cured PUA's.

Pencil hardness test was applied on plexiglass plates. This test is applied to understand hardness of the surface in addition to pendulum hardness. The pencil hardness results are presented in Tables 5.3 and 5.4. When the content of BHEPPOwas increased in PUA's, the pencil hardness values also increased. The values of polycarbonatediol containing PUA's were higher than the other PUA's.

Mechanical properties of the films were determined by standard tensile stress-strain tests in order to measure tensile strength, modulus, and elongation at breakvalues. The tensile behavior of with and without phosphine oxide containing PUA's were compared and presented in figures 5.3 - 5.4. When the content of BHEPPO in PUA was increased, the tensile strength and e-modulus of PUA's increased. Generally with increasing BHEPPO content in polyester polyol, polycarbonatediol, polypropylene glycol containing PUA's, elongation at break decreases progressively, whereas the tensile strength and elastic-modulus increases slightly. This could be explained by the presence of rigid and polar pendant phenyl phosphine oxide groups in the resins.

The strength of the attractive forces between polymer chains and particles can affect the properties of the polymers and substances. The intermolecular forces between polar molecules are dipole-dipole and H bonding. These intermolecular forces could make the bonds very strong in binding different polymer chains together.

Intermolecular forces could affect the polymers like small molecules. Polymer chains are long and the attractions between polymer chains enlarge these interchain forces. These stronger forces typically result in higher tensile strength [89-91].

Intermolecular forces in polymers can be affected by dipoles in constituting monomer units. Amide or carbonyl groups in polymers can form hydrogen bonds between adjacent chains, the partially positively charged hydrogen atoms in N-H groups of one chain are strongly attracted to partially negatively charged oxygen atoms in C=O groups on another [92]. These hydrogen bonds result in high elastic-modulus and tensile strength and melting point of polymers containing urethane or urea linkages. If the soft segments areshort polyurethanes higher the hardness values. This is because of the cohesive energy density increase and the presence of polar groups in the polymer chain [93, 94]. The polar groups which have high cohesive force participate in intermolecular hydrogen bonding and restrict the rotation of the polymer segments. This restriction is resulted with higher hardness and smaller elongation values [46]. Due to the strong polarity of the P=O group can increase the hydrogen bonding ability of the polymer. Incorporation of the rigid triphenylphosphine oxide group into the polymer chain resulted with enhanced chain stiffness of the polymer chain [97]. Polar groups such as sulfone, phenyl, urethane, ester, ether, all which have high cohesive force participate intermolecular hydrogen bonding and restrict the rotation of the polymer segmentsdue to steric hindrance. This restriction is resulted with higher hardness and smaller elongation values [92, 95].

Additionally, mechanical properties reproduced from TDI are also high. This is due to the phenyl group in TDI structure and with the effect of the cohesive forces, tensile strength and elastic-modulus values increase. In conclusion, rotation of the polymer segments hindered and as a result of this increase in tensile strength and decreases in elongationvalues were observed. The elastic-modulus values were high because of the rigid BHEPPO and TDI groups in the main polymer chains. This combination made the PUA’s stronger as expected.

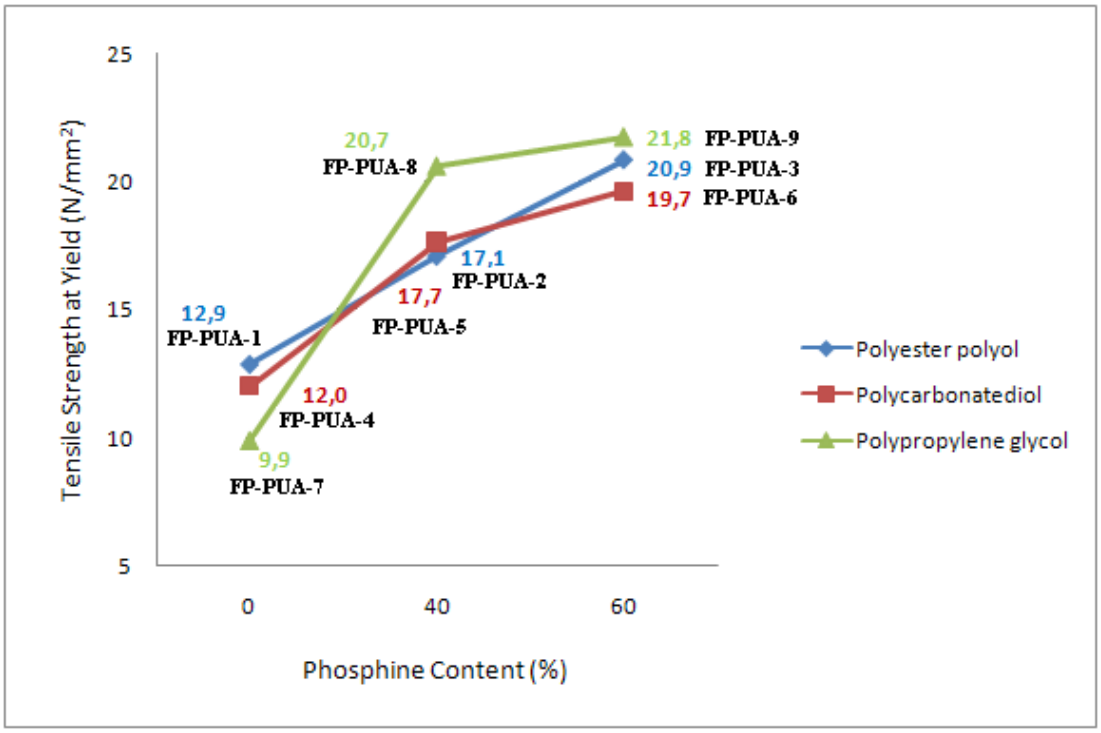


Figure 5.30 : Tensile strength at yield of IPDI containing PUA's.

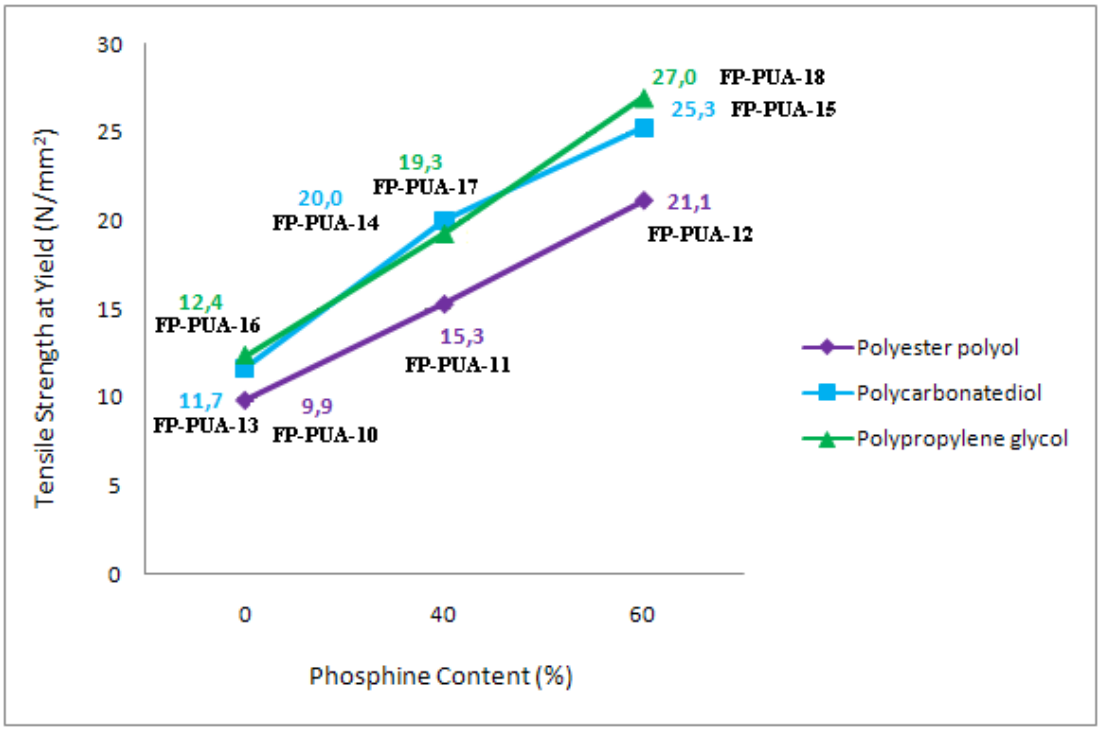


Figure 5.31 : Tensile strength at yield of TDI containing PUA's.

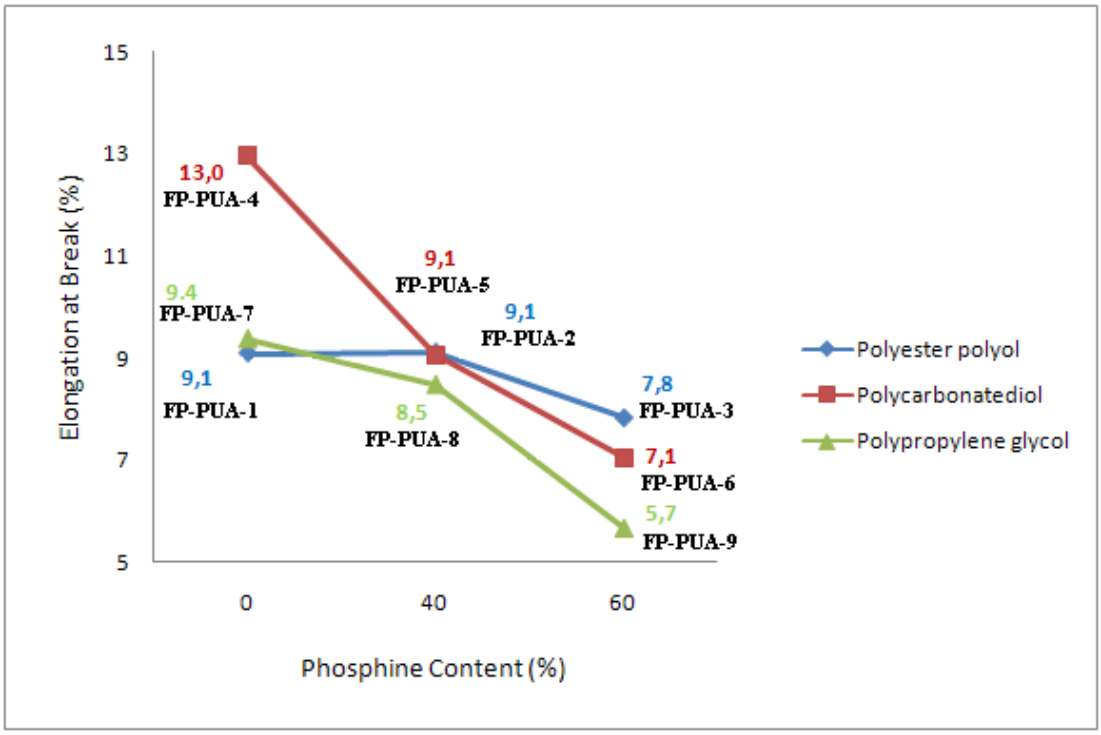


Figure 5.32 : Elongation at break results of IPDI containing UV-cured PUA's.

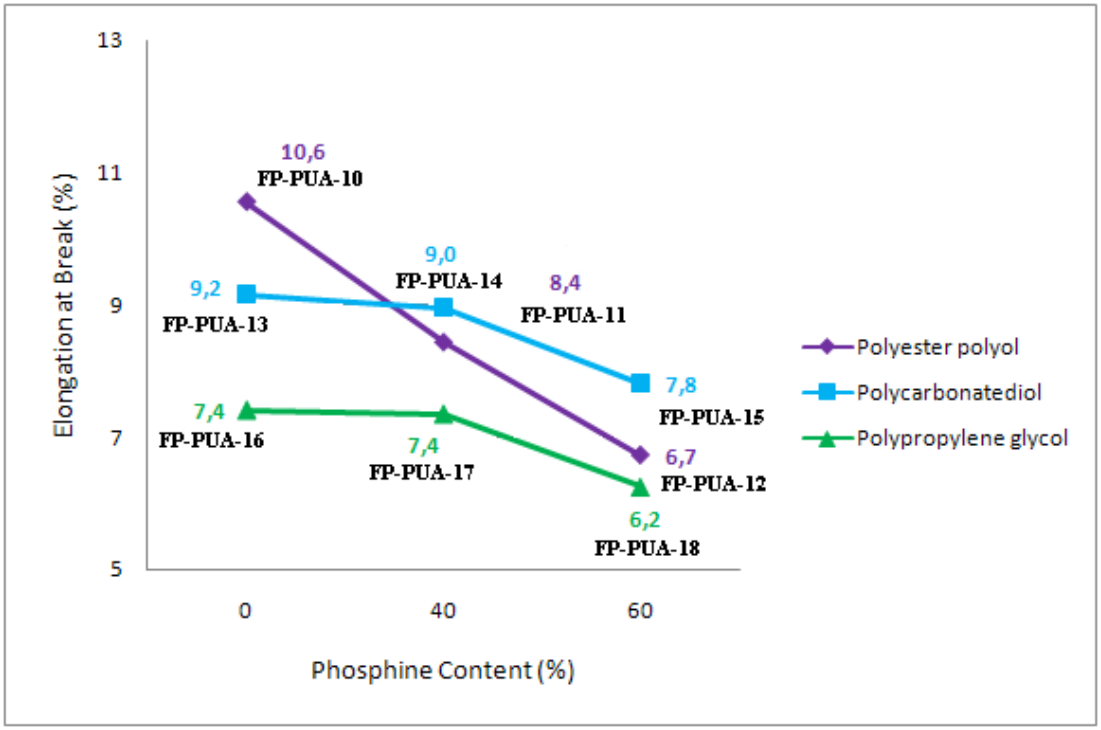


Figure 5.33 : Elongation at break results of TDI containing UV-cured PUA's.

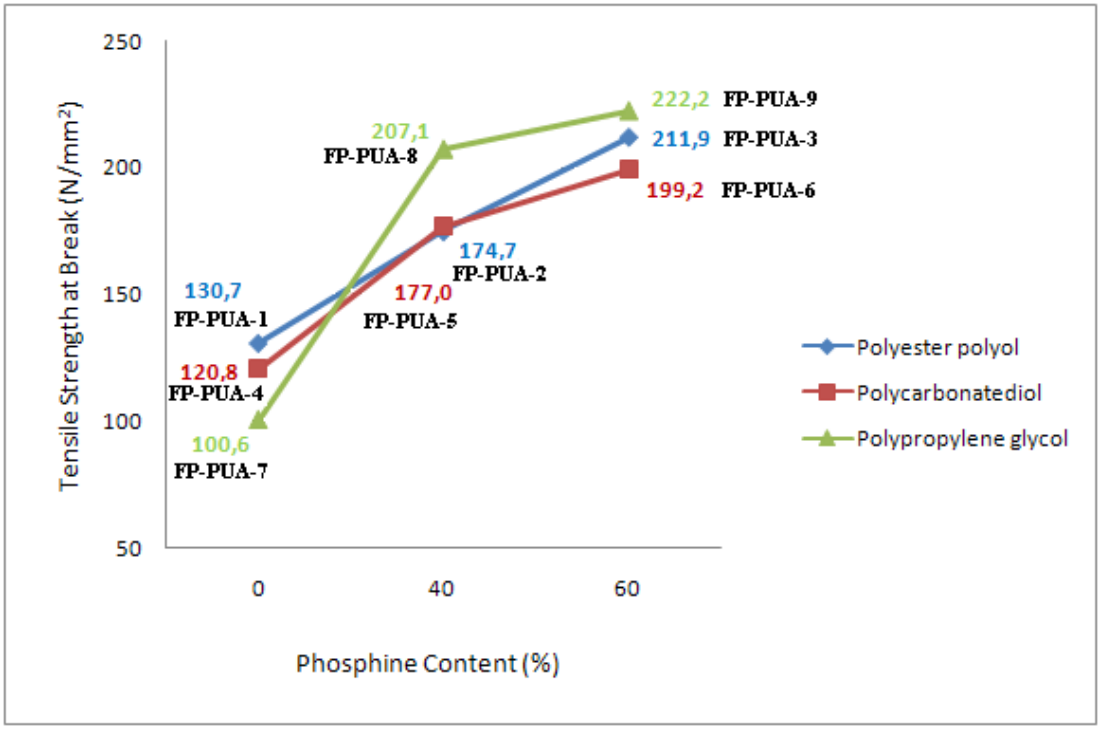


Figure 5.34 : Tensile strength at break results of IPDI containing UV-cured PUA's.

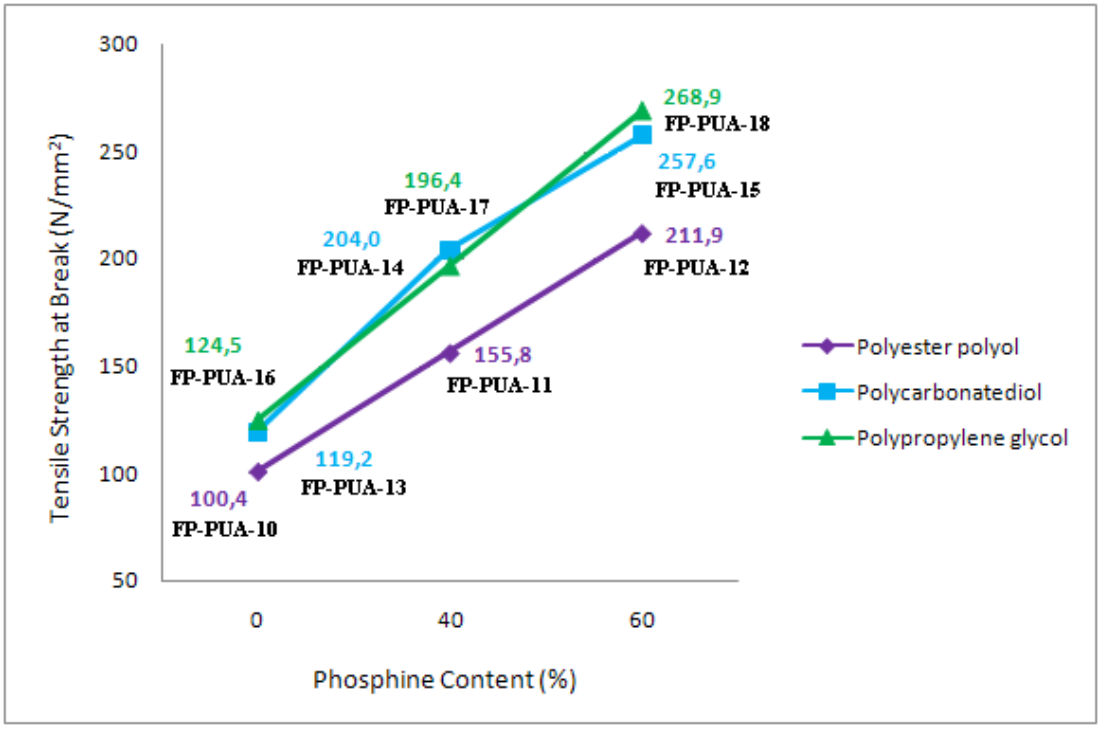


Figure 5.35 : Tensile strength at break results of TDI containing UV-cured PUA's.

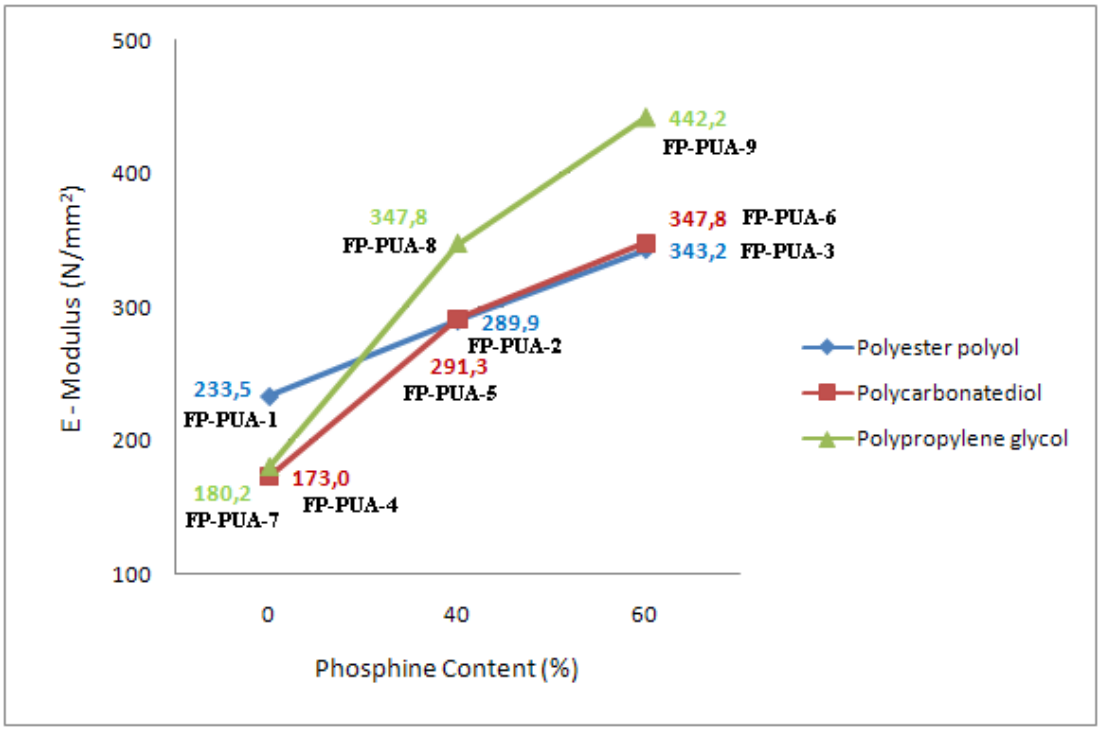


Figure 5.36 : E-modulus results of IPDI containing UV-cured PUA's.

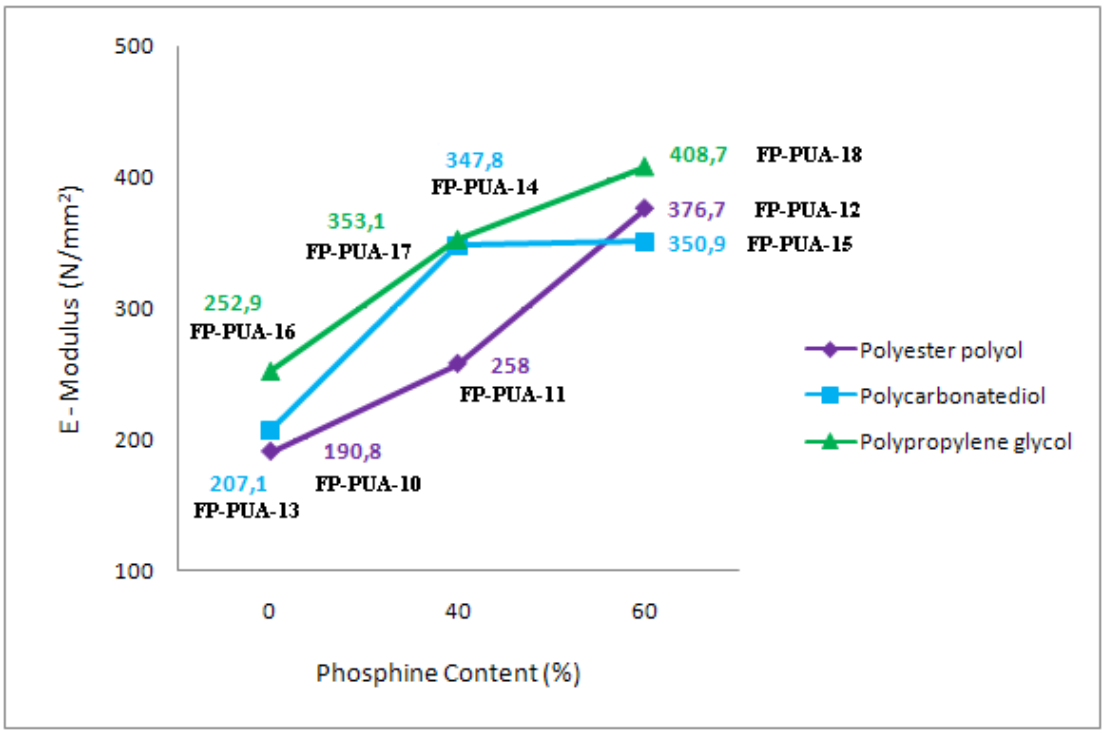


Figure 5.37 : E-modulus results of TDI containing UV-cured PUA's.

5.2.8 Thermal properties

Thermal gravimetrical analysis was performed on a TA-Q50 instrument to UV-cured samples under the nitrogen atmosphere at a heating rate 20 ^{o}C/min. The temperature range was 30-700 ^{o}C. The 5 % weight loss temperatures (5WL), first maximum weight loss (FWL) and residue char yield (RCY) in a nitrogen atmosphere are given in Table 5.7 and 5.8. As observed from TGA, 5WL begins at around 309-331 ^{o}C, and FWL begins at around 396-426 ^{o}C, and gives one stage weight loss for IPDI containing films and 5WL begins at around 314-332 ^{o}C, and FWL begins at around 394-414 ^{o}C, and gives one stage weight loss for TDI containing films. Addition of phenyl phosphine oxide group changes the values of the 5WL, FWL and RCY of the coatings. The degradation process which the first weight loss starts between 0 %-5 % corresponded due to the breaking of urethane bond breakages. When the phosphine oxide content increased in the PUA's, the 5WL, FWL, and RCY were increased. When phosphine oxide added to the polymer chains, it gives increased thermal resistance to the final product. The polycarbonatediol containing PUA's with oxyethylene units is expected to induce earlier decomposition of the ether linkages of backbone. When BHEPPO units incorporated into the backbone of PUA's, it slightly increases the thermal stability of PUA's because of its inherit thermal stability.

Table 5.7 : Thermal characteristics of UV-cured IPDI containing PUA's.

Composition Code	5% Weight Loss (^{o}C)	First Max. Weight Loss (^{o}C)	Residue (%)
FP-PUA-1	309	418	2.2
FP-PUA-2	321	420	2.6
FP-PUA-3	329	420	6.8
FP-PUA-4	331	419	2.6
FP-PUA-5	322	422	3.8
FP-PUA-6	325	426	6.1
FP-PUA-7	320	396	1.9
FP-PUA-8	326	410	3.1
FP-PUA-9	326	410	6.8

Table 5.8 : Thermal characteristics of UV-cured TDI containing PUA's.

Composition Code	5% Weight Loss (^{o}C)	First Max. Weight Loss (^{o}C)	Residue (%)
FP-PUA-10	317	394	3.2
FP-PUA-11	319	403	3.9
FP-PUA-12	332	410	5.8
FP-PUA-13	313	404	2.8
FP-PUA-14	315	411	3.2
FP-PUA-15	321	411	4.5
FP-PUA-16	314	408	4.9
FP-PUA-17	317	413	6.0
FP-PUA-18	325	414	6.1

5.3 Conclusions

In this study, different types of PUA's have been synthesized. Three different polyols were used: polyester polyol, polycarbonate diol, polypropylene glycol and BHEPPO was used as a diol. BHEPPO was added with different ratios to the PUA's. Polyol and diol containing urethane prepolymers was synthesized and acrylated by using HEMA. Polyurethane acrylates were coated onto substrates for coating applications and cured by UV light at room temperature. Uncured materials were characterized with FT-IR and ^{1}H-NMR. The effects of soft segment types (different polyols and BHEPPO) on their physical and thermal properties have been investigated.

The good mechanical properties such as pendulum hardness, pencil hardness, cross-cut adhesion, tensile strength, e-modulus of the PUA's were observed by the incorporation of BHEPPO to the PUA's backbone. The pendulum hardness, pencil hardness, tensile strength and e-modulus values increased with the increasing content of BHEPPO in the PUA's [89-92]. The gloss values of all the PUA films were good. BHEPPO contains polar phosphine oxide and phenyl group. This structure gives good intermolecular forces between the polymer chains, so the mechanical properties of PUA's which contain BHEPPO increased with the increase of the BHEPPO content in the polymer chain [97]. The BHEPPO containing PUA's showed improvement both 5% weight loss temperature and residue results. The polycarbonatediol containing polymers which contain oxyethylene units is expected to induce earlier decomposition related with the ether linkages rather than PES and PPG containing PUA's.

6. SYNTHESIS AND CHARACTERIZATION OF DIFUNCTIONAL SULFONE CONTAINING URETHANE ACRYLATE AND ITS APPLICATIONS

6.1 Experimental Procedure

6.1.1 Synthesis of bis[(4-hydroxyethoxy)phenyl]sulfone (BHEPS)

The synthesis and the schematic presentation have been previously mentioned in section 4.1.1.

6.1.2 Synthesis of difunctional sulfone containing urethane acrylate (SUA)

2 mol of IPDI and acetone were placed into a three-necked reaction kettle equipped with a magnetic stirrer, heating mantle, reflux condenser, dropping funnel and nitrogen inlet and $CaCl_2$ tube. 2 mol of HEMA dissolved in acetone was dropped into the reactor at a rate that the reaction temperature would not surpass 35 ^oC. The dibutyltinlaurate added as catalys, the temperature was increased to 45 ^oC. The reaction was continued till the NCO content reached the theoretical value as determined by dibutylamine titration. Then 1 mol of BHEPS dissolved in acetone was added dropwise through the dropping funnel for over a period of 30 min and mixed. The temperature was maintained at about 40 ^oC to allow the termination to take place. The reaction was continued until NCO peak at 2270 cm^{-1} dissappeared totally in the FT-IR spectra of samples taken from the reaction medium every 0.5 h. The final product was vacum dried at ambient temperature. The reactions take place according to Scheme 2.

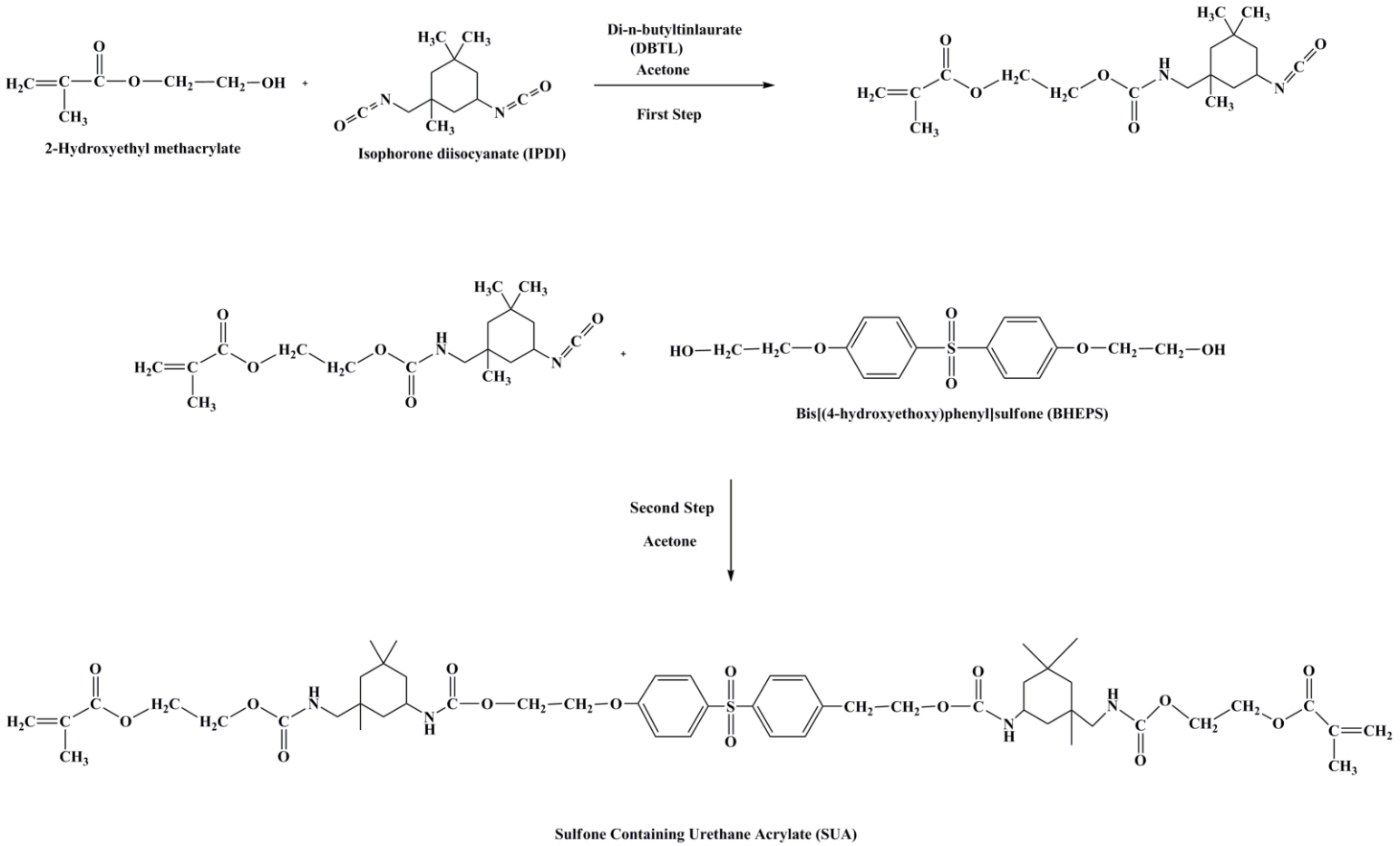


Figure 6.1 : Synthesis of difunctional urethane acrylate.

6.1.3 Synthesis of polyurethane acrylate (PUA)

PUA were prepared by a two-step solution polymerization method. The polypropylene glycol was dissolved in acetone and placed into a three-necked reaction kettle equipped with a magnetic stirrer, heating mantle, reflux condenser, dropping funnel and nitrogen inlet and $CaCl_2$ tube. The ratios of the materials can be seen on Table 5.1. IPDI dissolved in acetone was dropped into the reactor. The DBTDL added as catalyst, the temperature was increased to 55 ^oC. The reaction was continued till the isocyanate (NCO) content reached the theoretical value as determined by dibutylamine titration. Then HEMA dissolved in acetone was added dropwise through the dropping funnel for over a period of 30 min and mixed. The temperature was kept at about 50 ^oC to allow the termination to take place. The reaction was continued until NCO peak at 2270 cm^{-1} dissappeared totally in the FT-IR spectra of samples taken from the reaction medium every 0.5 h. The final product was vacuum dried at ambient temperature. The whole reaction process is depicted in Figure 5.4 and 5.5 [87].

6.1.4 Preparation of the coating formulation

PUAThe coating formulations were mixed of SUA, PUA, hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA), N-vinyl pyrrolidone (NVP) were used as reactive diluents and Irgacure 184 as photoinitiator. The ratios can be seen on Table 6.1.

Table 6.1 : Polyurethane acrylate formulation.

Sample Code	SUA	PUA	NVP	DPGDA	HDDA	I-184
F-SUA-0	0	50	10	17	10	3
F-SUA-5	5	45	10	17	10	3
F-SUA-10	10	40	10	17	10	3
F-SUA-15	15	35	10	17	10	3
F-SUA-20	20	30	10	17	10	3

6.1.5 Applications of the coating formulation

The coating formulations were applied on to plexiglass substrates at room temperature and UV-cured. Mechanical and optical tests were applied. Also free films were prepared by casting the formulations on Teflon mold and UV-cured. Mechanical and thermal tests were examined to free films.

6.2 Results and Discussion

6.2.1 Characterization

6.2.1.1 FT-IR spectrum of BHEPS

The FT-IR result of BHEPS can be seen in section 4.2.1.1.

6.2.1.2 ^{1}H-NMR spectrum of BHEPS

The 1H-NMR results of BHEPS can be seen in section 4.2.1.2.

6.2.1.3 FT-IR spectrum of SUA

The FT-IR spectrum of SUA is shown in Figure 6.2. In the spectrum, SUA showed characteristic bonds of hydroxyl and CH groups at 3100-2950 cm^{-1}, sulfone groups at 1297 and 1150 cm^{-1}(SO_2 stretching). In the spectrum, there are characteristic peaks of N-H (3300 cm^{-1}), and C=O (1700-1710 cm^{-1}). The characteristic peak of acrylate –C=C- is detected at 1642 cm^{-1}.

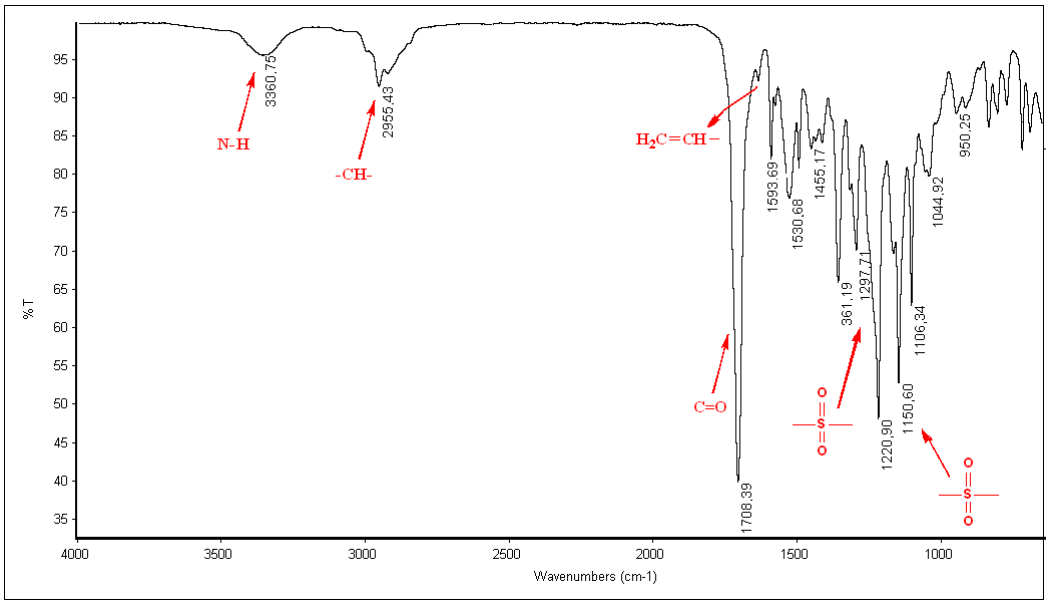


Figure 6.2 : FT-IR spectrum of SUA.

6.2.1.4 ^{1}H-NMR spectrum of SUA

Figure 6.3 shows ^{1}H-NMR spectra of SUA in DMSO-d_6. The peak at 4.05 ppm was due to CH_2 protons near to etheric oxygen atom. The aromatic protons of SUA near to etheric oxygen atom appeared at δ = 7.70-8.10 ppm, and near to sulfone group appeared at δ= 6.80-7.50 ppm. The peaks at 0.78-1.20 ppm are ascribed to the methyl (CH_3) protons and CH_2 protons of IPDI. CH_2 protons in the cyclic ring of IPDI were

at δ = 1.20-1.7 ppm. The peaks in the range of 1.80-2.00 ppm are methyl protons of HEMA. The peaks at 2.90-4.20 ppm are ascribed to the CH and CH_2 protons of IPDI (NCOCH and $NCOCH_2$), CH_2 protons of HEMA ($O(CH_2)_2OCO$). The peaks in the range of 5.50-5.70 ppm and 5.50-6.20 ppm are obviously observed which prove the existence of acrylic group in UA structure related with HEMA. The peaks at 7.60-8.20 ppm are ascribed to the protons of –NH- groups in urethane unit.

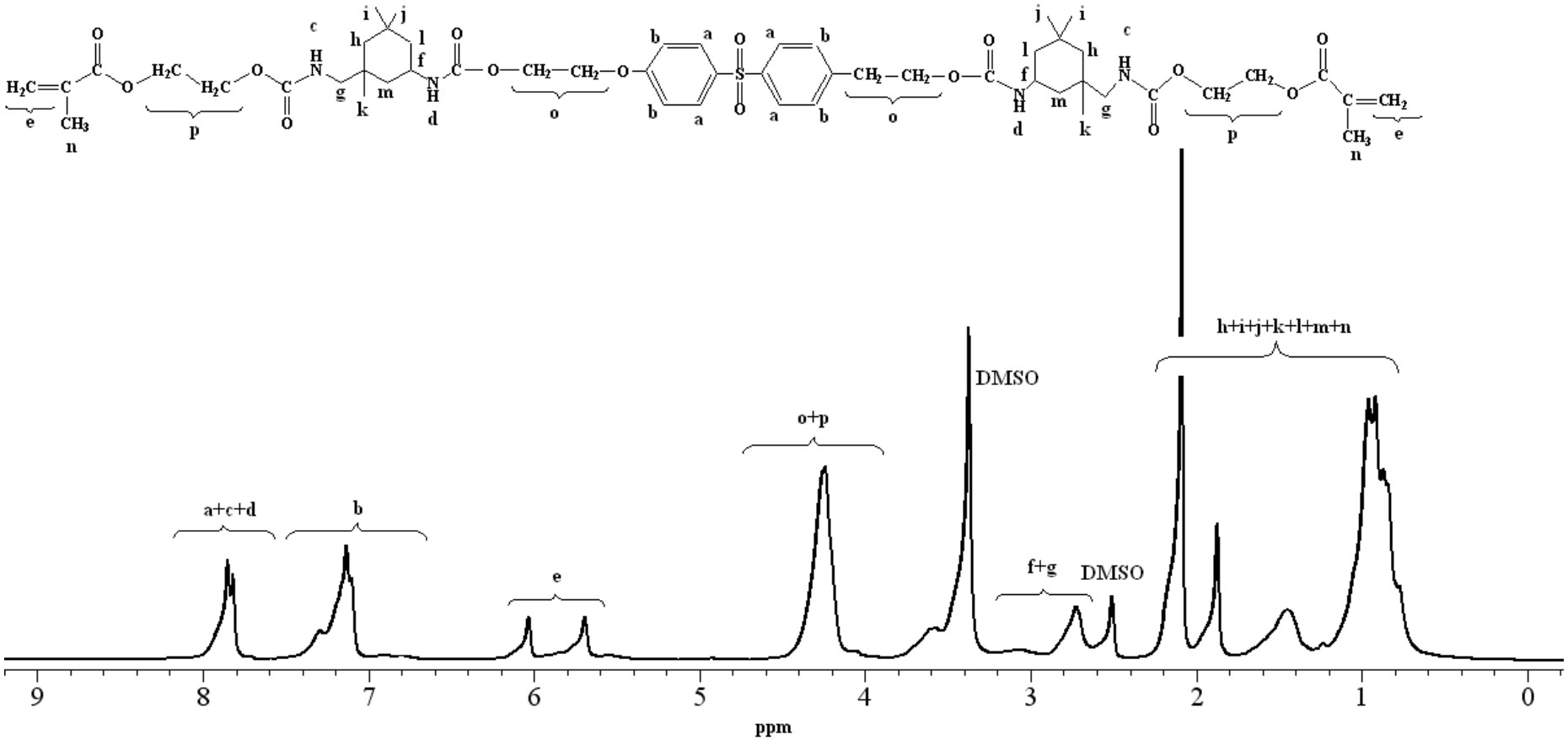


Figure 6.3 : ^{1}H-NMR spectrum of SUA.

6.2.1.5 FT-IR spectrum of PUA.

The FT-IR spectrum of urethane acrylates are shown in Figure 6.4. In the spectrum, there are characteristic peaks of N-H (3300 cm^{-1}), and C=O (1700-1730 cm^{-1}), -C-N- stretching bands 1532 cm^{-1}, C-H aliphatic stretching bands (2945, 2858 cm^{-1}) are also observed. The dissappearence of the absorption bands of the NCO group (2270 cm^{-1}) of IPDI and the OH group also proves the synthesis of the urethane acrylates. The characteristic peak of acrylate –C=C- is detected at 1638 cm^{-1}.

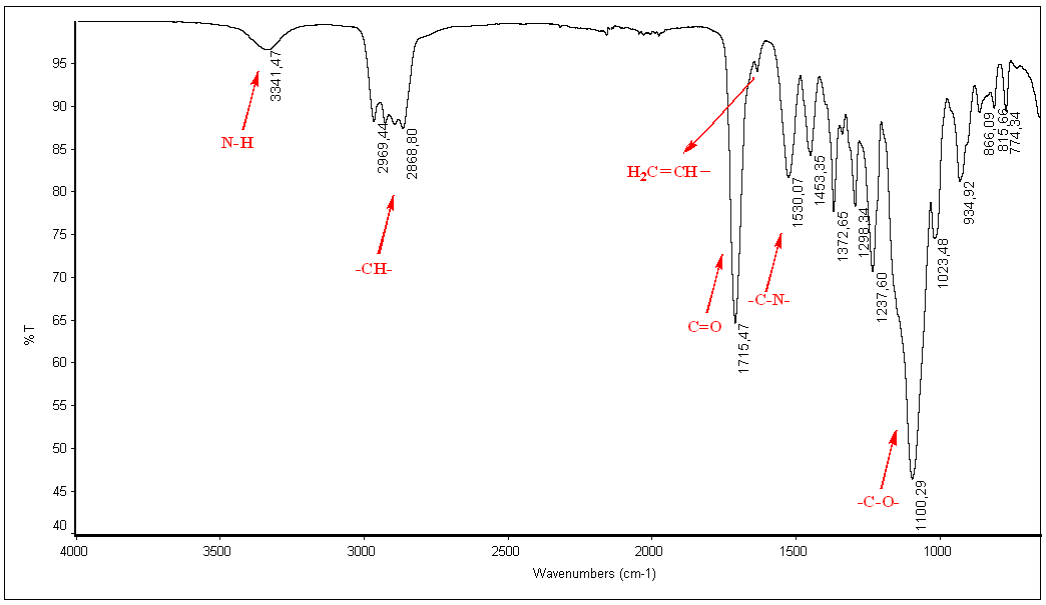


Figure 6.4 : FT-IR spectrum of PUA.

6.2.1.6 ^{1}H-NMR spectrum of PUA.

Figure 6.5 shows ^{1}H-NMR spectra of UA in DMSO-d_6. The peaks at 0.78-1.20 ppm are ascribed to the methyl (CH_3) protons and CH_2 protons of IPDI and methyl protons of PPG. CH_2 protons in the cyclic ring of IPDI were at δ = 1.20-1.7 ppm. The peaks in the range of 1.80-2.00 ppm are methyl protons of HEMA. The peaks at 2.90-4.20 ppm are ascribed to the CH and CH_2 protons of IPDI (NCOCH and $NCOCH_2$), CH_2 protons of HEMA ($O(CH_2)_2OCO$). The peaks in the range of 5.50-5.70 ppm and 5.90-6.10 ppm are obviously observed which prove the existence of acrylic group in UA structure related with HEMA. The peaks at 6.9-7.3 ppm are ascribed to the protons of –NH- groups in urethane unit.

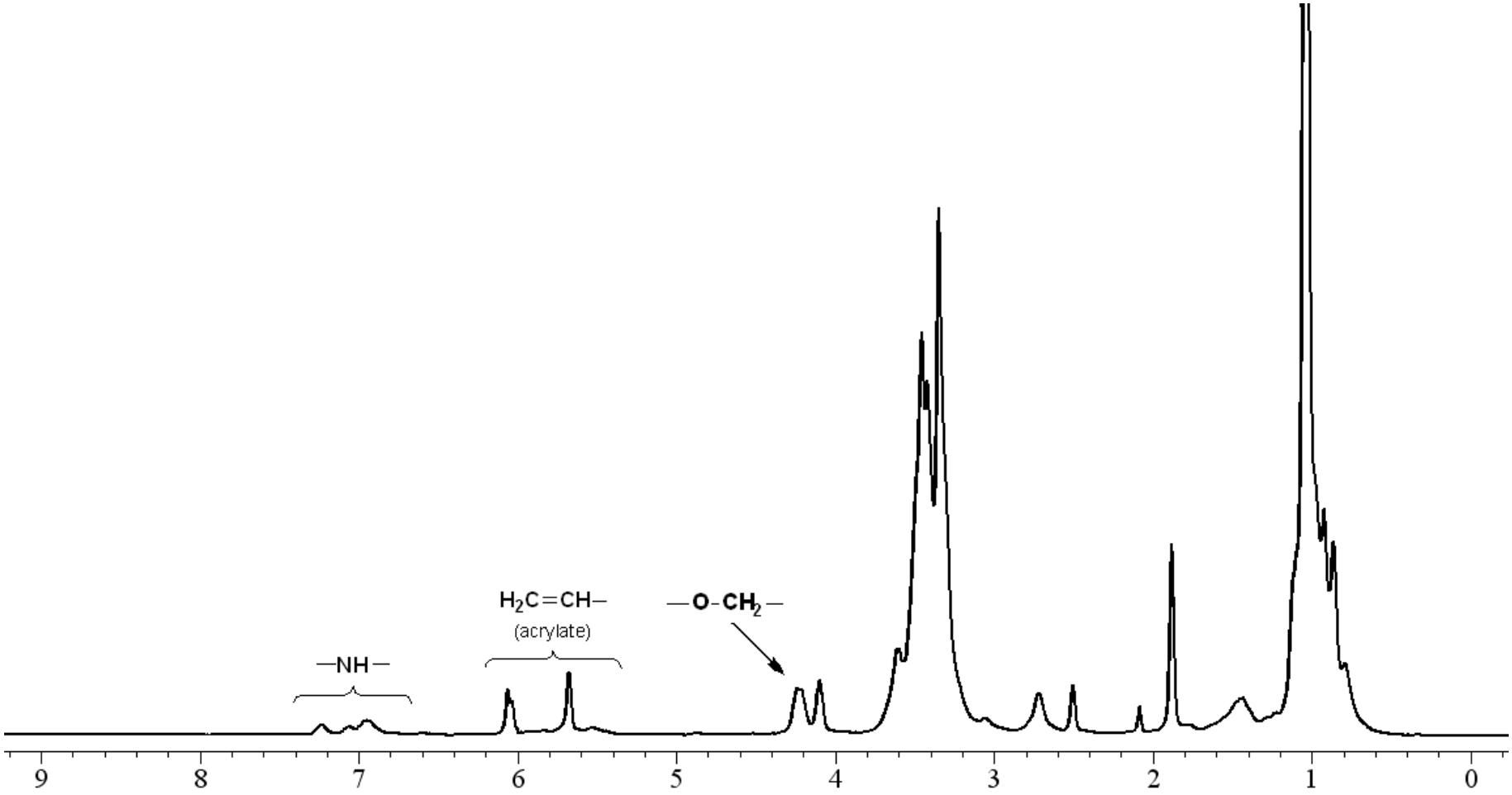


Figure 6.5 : ^{1}H-NMR spectrum of PUA.

6.2.2 Gloss properties

Gloss of the UV-cured films was determined with a micro-tri-glossmeter (BYK-Gardner) according to ASTM D 523. Gloss of the coated plates was measured at an angle of 20^o, 60^o and 85^o. For gloss test, glass plates were coated.

The measurement at 85^o 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. The gloss value is increased when the content of sulfone increased in the PUA's as shown in Table 2. The average gloss values (20^o) of the sulfone containing PUA's were between 150 and 154. The value of PPG containing PUA is 148. The amorphous structure of both PPG and sulfone, the gloss values were really high. Also the presence of polar sulfone groups increased the gloss property.

6.2.3 Contact angle measurement

Contact angle measurements were carried out with a Krüss FM 41 instrument, equipped with a camera. Analysis was conducted at room temperature by means of the sessile drop technique. For each sample, at least three measurements were made and the average was taken. The measuring liquid was distilled water. The tests were applied onto coated plexiglass substrate. The results are shown in Table 6.2.

The value of the contact angle of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on plexiglass plate coated with different urethane acrylate films which were cured. For each measurement one drops of water was tested on the surfaces.

The water contact angle was in the range of 80-65 for sulfone containing PUA's, even the PUA without sulfone was 83. When the content of sulfone was increasing the contact angle value is decreasing. This is because the sulfone groups make the surface more hydrophilic. The figures can be seen in Figure 6.6.

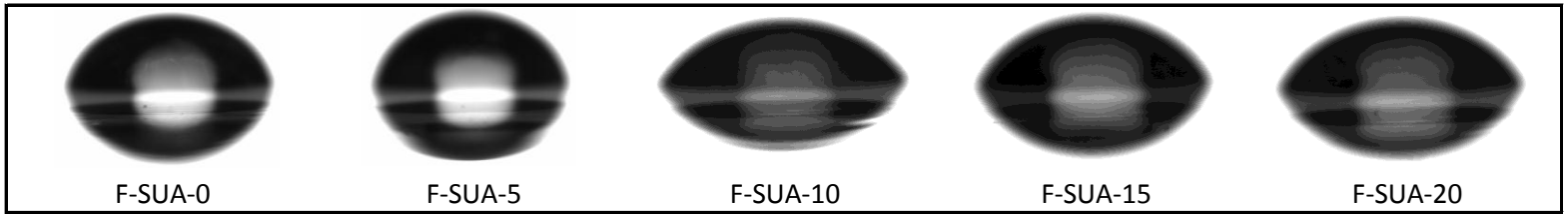


Figure 6.6 : Contact angle figures of UV-cured SUA's.

6.2.4 Mechanical properties

The pendulum hardness of the UV-cured films was determined with a pendulum hardness tester (BYK-Gardner) according to ASTM D 4366 (pendulum weight = 200 ± 0.2g, amplitude limitation angle (deflection) = 6-3^o, oscillation period = 1.4 s). König pendulum hardness tests are applied after all formulations to coated glass plates.

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. The results can be seen in Table 6.2.

The urethane acrylates with sulfone, contains hard phenyl groups so the hardness values of these films are higher than the urethane acrylates without sulfone.

The pencil hardness of the UV-cured PUA films was determined by ASTM D 3363. Pencil hardness test was applied on coated plexiglass plates. This test is applied to understand hardness of the surface in addition to pendulum hardness. In Table 6.2, results are listed. A small increase in pencil hardness value with the increasing sulfone content was observed.

Table 6.2 : Gloss, contact angle, pendulum hardness and pencil hardness analysis of polyurethane acrylate.

Sample Code	Gloss		Contact Angle	Pendulum Hardness	Pencil Hardness
	20^o	60^o			
F-SUA-0	148	148	83	70	5H
F-SUA-5	150	148	80	78	6H
F-SUA-10	150	146	70	80	6H
F-SUA-15	152	144	68	81	7H
F-SUA-20	154	148	65	83	7H

Mechanical properties of the films were determined by standard tensile stress-strain tests in order to measure the tensile strength, the modulus, and elongation at break. Stress-strain measurements were carried out at room temperature by using an universal testing machine (Zwick Roell Z010, extension rate of 500 mm/min.). 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 6.3. Young's modulus values of urethane acrylate

with sulfone are higher than the urethane acrylate without sulfone. When we increase the content of sulfone, modulus is increasing. The increase in value of tensile strength at yield point is also related with the pendant phenyl groups. On the other hand elongation is decreasing with the increasing amount of phenyl groups.

The hardness values increase due to the cohesive energy density and polar groups in the polymer chain. The polar groups (sulfone, phenyl, urethane, ester, ether, etc.) which have high cohesive force participate in intermolecular hydrogen bonding and restrict the rotation of the polymer segment. This restriction is resulted with higher hardness and smaller elongation values [92-96].

Table 6.3 : Stress-strain analysis of polyurethane acrylate.

Sample Code	Tensile Strength at Yield (N/mm^2)	Elongation at Break (%)	Tensile Strength at Break (N/mm^2)	E-Modulus (N/mm^2)
F-SUA-0	18	12.6	180.4	256.7
F-SUA-5	19.4	11.1	196.2	301.1
F-SUA-10	21.8	10.2	221.9	353.0
F-SUA-15	29.5	10.1	300.5	357.2
F-SUA-20	32.7	10.0	330.4	466.8

6.2.5 Thermal analysis

Thermal gravimetrical analysis was performed on a TA TGA Q50 instrument to UV-cured samples under the nitrogen atmosphere at a heating rate 20 ^oC/min in the temperature range of 30-700 ^oC. The weights of samples are 6-10 mg in all cases. Calibration was achieved with indium as reference material. The thermogram results are collected in Table 6.4.

Addition of phenyl sulfone group changes the values of the 5% weight loss and first-max weight loss and the char yield of the coatings. The results show that incorporating sulfone units slightly increases the thermal stability of PUA's, this is due to the stability of sulfone units [96].

Table 6.4 : Thermal characteristics of polyurethane acrylate.

Sample Code	%5 Weight Loss (^{o}C)	First Max. Weight Loss (^{o}C)	Residue (%)
F-SUA-0	321	403	2.3
F-SUA-5	321	403	3.0
F-SUA-10	321	406	4.3
F-SUA-15	323	408	5.2
F-SUA-20	322	412	6.8

6.3 Conclusions

Photo curable, sulfone containing difunctional urethane acrylate were synthesized. Newly synthesized difunctional urethane acrylate was used to increase mechanical properties of polyurethane acrylate. The structure of BHEPS, SUA and PUA were proved by FT-IR and ^{1}H-NMR. Increasing amount of sulfone containing difunctional urethane acrylate incorporation into the formulations improve pendulum hardness, pencil hardness. Tensile strength and e-modulus values improved with the addition of SUA in the coating formulations [92-96]. The obtained results beneficial for developing applications of UV-curable sulfone containing urethane acrylates, polyurethane acrylates in areas such as coatings, packaging and adhesives.

7. GENERAL CONCLUSION

This chapter is the general conclusion part for the comparison of three main chapters.

The processability of sulfone containing PUAs is harder than phosphine oxide containing PUAs and SUAs. Because it is solid but the others were liquid.

Phosphine oxide containing PUAs dissolved in other acrylates which was mentioned in the coating formulation, but NVP is needed for the solubility of sulfone containing PUAs.

The gloss properties of IPDI containing PUAs between chapter 4 and 5; the effect of sulfone is much higher than phosphine oxide.

The contact angle results of polyester polyol and IPDI containing PUAs between chapter 4 and 5 were nearly the same.

The contact angle results of polycarbonatediol and phosphine oxide containing PUAs were higher than sulfone containing PUAs except FP-PUA-6.

The contact angle results of polypropylene glycol and phospine oxide containing PUAs were higher than sulfone containing PUAs.

According to the results hydrophilicity of sulfone containing PUA coatings were higher than phosphine oxide containing coatings.

Generally phosphine oxide and TDI containing PUAs have higher contact angle values than sulfone containing PUAs. PPG have the lowest contact angle value than all of others. This is due to the NVP, TDI and hydrophlic sulfone content.

Water absorption and gel content results were nearly the same. 94-99 % range for water absorption, 95-99 % range for gel content.

The sulphone containing PUAs pencil hardness values were higher than phosphine oxide containing PUAs, NVP, Sulfone and TDI containing PUAs have the highest pencil hardness values. This is because of pendant sulfone and aromatic groups.

Solvent and chemical resistance results were nearly the same, and in the range of 0-6 %.

The pendulum hardness values of 40% phosphine oxide containing PUAs were higher than sulfone containing PUAs, but it has opposite structure when the content reaches to 60%.

Thermal properties of both sulfone and phosphine oxide containing PUAs are nearly the same. Polypropylene glycol and containing sulfone PUAs have the highest improvement.

REFERENCES

[1] **Fang, S., Gao, L., Zhou, L., Zheng, Z., Guo, B., and Zhang, C.** (2009). Synthesis and Characterization of Excellent Transparency Poly(urethane-methacrylate). *Journal of Applied Polymer Science*, *111*, 724-729.

[2] **Lee, J. M., Kim, D. S.** (2007). Effect of Clay Content on the Ultra-violet Curing and Physical Properties of Urethane-Acrylate/Clay Nanocomposites. *Polymer Composites*, *28*, 325-330.

[3] **Zhang, J., Xiao, S., Shi, S., Nie, J.** (2009). Synthesis and Photopolymerization Kinetics of Multifunctional Aromatic Urethane Acrylates Containing Tertiary Amine Group. *Polymers for Advanced Technologies*, *20*, 16-20.

[4] **Oprea, S.** (2007). Synthesis and Characterization of Polyurethane Urea Acrylates: Effects of the Hard Segments Structure. *Journal of Applied Polymer Science*, *105*, 2509-2515.

[5] **Xiao, X., Hao, C.** (2010). Preparation of Waterborne Epoxy Acrylate/Silica Sol Hybrid Materials and Study of Their UV Curing Behavior. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *359*, 82-87.

[6] **Lin, Y. H., Liao, K. H., Huang, C. K., Chou, N. K., Wang, S. S., Chu, S. H., Hsieh, K. H.** (2010). Superhydrophobic Films of UV-Curable Florinated Epoxy Acrylate Resins. *Polymer International*, *59*, 1205-1211.

[7] **Seo, J., Jang, E. S., Song, J. H., Choi, S., Khan, S. B. Han, H.** (2010). Preparation and Properties of Poly(Urethane-acrylate) films for Ultraviolet-Curable Coatings. *Journal of Applied Polymer Science*, *118*, 2454-2460.

[8] **Xing, W., Jie, G., Song, L., Wang, X., Lv, X., Hu, Y.** (2011). Flame Retardancy and Thermal Properties of Epoxy Acrylate Resin/Alpha-Zirconium Phosphate Nanocomposites used for UV-Curing Flame Retardant Films. *Materials Chemistry and Physics*, *125*, 196-201.

[9] **Chang, C. W., Lu, K. T.** (2010). Epoxy Acrylate UV/PU Dual-Cured WOOD Coaitngs. *Journal of Applied Polymer Science*, *115*, 2197-2202.

[10] **Karataş, S., Kayaman-Apohan, N., Turunç, O., Güngör, A.** (2011). Synthesis and Characterization of UV-Curable Phophorus Containing Hybrıd Materials Prepared by Sol-Gel Technique. *Polymers for Advanced Technologies*, *22*, 567-576.

[11] **Karataş, S., Hoşgör, Z., Kayaman-Apohan, N., Güngör, A.** (2009). Preparation and Characterization of Phosphine Oxide Containing

Organosilica Hybrid Coatings by Photopolymerization and Sol-Gel Process. *Progress in Organic Coatings*, *65*, 49-55.

[12] **Karataş, S., Hoşgör, Z., Menceloğlu, Y., Kayaman-Apohan, N., Güngör, A.** (2006). Synthesis and Characterization of Flame Retarding UV-Curable Organic-Inorganic Hybrid Coatings. *Journal of Applied Polymer Science, 102*, 1906-1914.

[13] **Zhang, Y., Zhan, F., Shi, W.** (2011). Photopolymerization Behavior and Properties of Highly Branched Poly(Thioether-Urethane) Acrylates used for UV-Curing Coatings. *Progress in Organic Coatings, 71*, 399-405.

[14] **Gao, Q., Li, H., Zeng, X.** (2011). Preparation and Characterization of UV-Curable Hyperbranched Polyurethane Acrylate. *Journal of Coatings Technology and Research*, *8*, 61-66.

[15] **Lee, B. H., Choi, J. H., Kim, H. J.** (2006). Coating Performance and Characteristics for UV-Curable Aliphatic Urethane Acrylate Coatings Containing Norrish Type I Photoinitiators. *Journal of Coatings Technology and Research*, 3, 221-229.

[16] **Schwalm, R.** (2007). UV Coatings: Basics, Recent Developments and New Applications. Amsterdam: Elsevier.

[17] **Nebioğlu, A., Soucek, M. D.** (2006). Optimization of UV Curable Acrylated Polyester-Polyurethane/Polysiloxane Ceramer Coatings Using a Response Surface Methodology. *Journal of Coatings Technology and Research, 3*, 61-68.

[18] **Meier-Westhues, U.** (2007). Polyurethanes: Coatings, Adhesives and Sealants. Hannover: Vincentz Network.

[19] **Kim, B. K., Paik, S. H.** (1999). UV-Curable Poly(ethylene-glycol) based Polyurethane Acrylate Hydrogel. *Journal of Polymer Science and Technology Part:A Polymer Chemistry*, *37*, 2703-2709.

[20] **Barbeau, P. H., Gerard, J. F., Magny, B., Pascault, J. P.** (2000). Effect of the Diisocyanate on the Structure and Properties of Polyurethane Acrylate Prepolymers. *Journal of Polymer Science and Technology Part:A Polymer Chemistry*, *38*, 2750-2768.

[21] **Allen, N. S.** (Ed.), (2010). Photochemistry and Photophysics of Polymer Materials Canada: Wiley International

[22] **Liaw, D. J., Huang, C. C., Liaw, B. Y.** (1998). Synthesis and Properties of Polyurethanes Based on Bisphenol-S Derivatives. *Polymer*, *39*, 3529-3535.

[23] **Qin, X., Xiong, J., Yang, X., Wang, X., Zheng, Z.** (2007). Preparation, morphology, and Properties of Polyurethane-Urea Elastomers Derived From Sulphone-Containing Aromatic Diamine. *Journal of Applied Polymer Science*, *104*, 3554-3561.

[24] **Liang, C., Maruyama, T., Ohmukai, Y., Sotomi, T., Matsuyama, H.** (2009). Characterization of Random and Multiblock Copolymers of Highly Sulfonated Poly(arylene ether sulfone) for a Proton Exchange Membrane. *Journal of Applied Polymer Science*, *114*, 1793-1802.

[25] **Wang, L., Wang, D., Zhu, G., Li, J.** (2011). Synthesis and Properties of Highly Branched Sulfonated Poly(arylene ether)s as Proton Exchange Membranes. *European Polymer Journal*, *47*, 1985-1993.

[26] **Park, H. S., Seo, D. W., Choi, S. W., Jeong, Y. G., Lee, J. H., Kim, D. I., Kim, W. G.** (2008). Preparation and Characterization of Branched and Linear Sulfonated Poly(ether ketone sulfone) Proton Exchange Membranes for Fuel Cell Applications. *Journal of Polymer Science Part A: Polymer Science*, *46*, 1792-1799.

[27] **Nakabayashi, K., Matsumoto, K., Higashirara, T., Ueda, M.** (2008). Influence of Adjusted Hydrophilic-Hydrophobic Lengths in Sulfonated Multiblock Copoly(ether-sulfone) Membranes for Fuel Cell Application. *Journal of Polymer Science Part A: Polymer Science*, *46*, 7332-7341.

[28] **Liaw, D. J., Liaw, B. Y.** (1997). Synthesis and Properties of Polyimides Derived from 3,3',5,5'-tetramethyl-bis[4-[4-aminophenoxy)phenyl] sulfone. *European Polymer Journal*, *33*, 1423-1431.

[29] **Yılmaz, T., Güçlü, H., Özarslan, Ö., Yıldız, E., Kuyulu, A., Ekinci, E., Güngör, A.** (1997). Kinetic Investigations of Formation of Polyimides Containing Arylene Sulfone Ether Linkages by Potentiometric Titration and Their Characterization. *Journal of Polymer Science Part A: Polymer Science*, *35*, 2981-2990.

[30] **Einsla, B. R., Kim, Y. S., Hickner, M. A., Hong, Y. T., Hill, M. L., Pivovar, B. S., McGrath, J. E.** (2005). Sulfonated Naphthlane Dianhydride Based Polyimide Copolymers for Proton-Exchange-Membrane Fuel Cells: II. Membrane Properties and Fuel Cell Performance. *Journal of Membrane Science*, *255*, 141-148.

[31] **Einsla, B. R., Hong, Y. T., Kim, Y. S., Hickner, Wang, F., Gunduz, N., McGrath, J. E.** (2004). Sulfonated Naphthlane Dianhydride Based Polyimide Copolymers for Proton-Exchange-Membrane Fuel Cells: I. Monomer and Copolymer Synthesis. *Journal of Polymer Science Part A: Polymer Science*, *42*, 862-874.

[32] **Zhang, Y., Tebby, J. C., Wheeler, J. W.** (1997). Polyamides Incorporating Phosphine Oxide Groups.II. Aromatic Polymers Containing Sulfone Functionality. *Journal of Polymer Science Part A: Polymer Science*, *35*, 493-497.

[33] **Hsiao, S. H., Huang, P. C.** (1997). Preparation and Characterization of Aromatic Polyamides Based on Ether-Sulfone-Dicarboxylic Acids.*Journal of Polymer Science Part A: Polymer Science*, *35*, 2421-2429.

[34] **Riley, D. J., Güngör, A., Srinivasan, S. A., Sankarapandian, M., Tchatchoua, C., Muggli, M. W., Ward, T. C., McGrath, J. E.** (1997). Synthesis and Characterization of Flame Resistant Poly(Arylene Ether)s. *Polymer Engineering and Science*, *37*, 1501-1511.

[35] **Liou, G. S., Hsiao, S. H.** (2002). Synthesis and Properties of Aromatic Poly(Ester Amide)s with Pendant Phosphorus Groups. *Journal of Polymer Science Part A: Polymer Science, 40,* 459-470.

[36] **Faghihi, K., Hagibeygi, M.** (2007). New Aromatic Polyamide with Azo and Phosphine Oxide Groups in the Main Chain. Turkish Journal of Chemistry, *31,* 65-73.

[37] **Kaiti, Sridevi, Fossum, E.** (2006). Effect of Reaction Conditions on the Molecular Weight and Polydispersity of Linear Poly(Arylene Ether Phosphine Oxide)s Prepared From an AB Monomer. *Journal of Polymer Science Part A: Polymer Science, 44,* 2099-2106.

[38] **Jeong, K. U., Jo, Y. J., Yoon, T. H.** (2001). Adhesion Property of Novel Polyimides Containing Fluorine and Phosphine Oxide Moities.*Journal of Adhesion Science and Technology, 15,* 1787-1803.

[39] **Chen, X. T., Sun, H., Tang, X. D., Wang, C. Y.** (2008). Synthesis and Properties of Novel Phosphorus-Containing Poly(Ether Ether Ketone Ketone)s. *Journal of Applied Polymer Science, 110,* 1304-1309.

[40] **Czupik, M., Fossum, E.** (2003). Manipulation of the Molecular Weight and Branching Structure of the Hyperbranched Poly(Arylene Ether Phosphine Oxide)s Prepared via an $A_2 + B_3$ Approach. *Journal of Polymer Science Part A: Polymer Science, 41,* 3871-3881.

[41] **Jeong, K. U., Park, I. Y., Kim, I. C., Yoon, T. H.** (2001). Adhesive and Flame Resistance Behavior of Poly(Arylene Ether Phosphine Oxide) (PEPO) and PEPO-Modified Epoxy Resins. *Journal of Applied Polymer Science, 80,* 1198-1205.

[42] **Çakir, M., Karataş, S., Menceloğlu, Y., Kayaman-Apohan, N., Güngör, A.** (2008). Phosphorus-Containing Sulfonated Polyimides for Proton Exchange Membranes. *Macromolecular Chemistry and Physics, 209,* 919-929.

[43] **Dang, T. D., Dalton, M. J., Venkatasubramanian, N., Johnson, J. A., Cerbus, C. A., Feld, W. A.** (2004). Synthesis and Characterization of Polyaryleneetherketone Triphenylphosphine Oxides Incorporating Cycloaliphatic/ Cage Hydrocarbon Structural Units. *Journal of Polymer Science Part A: Polymer Science, 42,* 6134-6142.

[44] **Smith, C. D., Grubbs, H., Webster, H. F., Güngör, A., Wightman, J. P., McGrath, J. E.** (1991). Unique Characteristics Derived From Poly(Arylene Ether Phosphine Oxide)s. *High Performance Polymers, 3,* 211-229.

[45] **Kim, J. P., Kang, J. W., Kim, J. J., Lee, J. S.** (2003). Synthesis and Optical Properties of Fluorinated Poly(Arylene Ether Phosphine Oxide)s. *Journal of Polymer Science: Part A: Polymer Chemistry, 41,* 1497-1503.

[46] **Smith, J. G., Thompson, C. M., Watson, K. A., Connell, J. W.** (2002). Poly(Arylene Ether)s Containing Phenylphosphine Oxide Groups. *High Performance Polymers, 14,* 225-239.

[47] **Liu, W., Varley, R. J., Simon, G. P.** (2004). A Phosphorus-Containing Diamine for Flame-Retardant, High-Functionality Epoxy Resins.I. Synthesis, Reactivity, and Thermal Degradation Properties. *Journal of Applied Polymer Science*, *92*, 2093-2100.

[48] **Zhang, Y., Tebby, J. C., Wheeler, J. W.** (1996). Polyamides Incorporating Phosphine Oxide Groups.I. Wholly Aromatic Polymers. *Journal of Polymer Science Part A: Polymer Science*, *34*, 1561-1566.

[49] **Chen, X., Hu, Y., Jiao, C., Song, L.** (2007). Thermal and UV-Curing Behavior of Phosphate Diacrylate Used for Flame Retardant Coatings. *Progress in Organic Coatings*, *59*, 318-323.

[50] **Miao, H., Huang, Z., Cheng, L., Shi, W.** (2009). Syntheses and Properties of Fluorinated Phosphate Acrylates Used for UV-Curing Coatings. *Progress in Organic Coatings*, *64*, 365-370.

[51] **Liaw, D. J., Shen, W. C.** (1992). Synthesis of Epoxy Resins Based on Bisphenol-S and Its Derivatives. *Die Angewandte Makromolokulare Chemie*, *199*, 171-190.

[52] **Liaw, D. J., Chen, P. S. (**1996). Preparation and Properties of Polyesters Derived from 4,4'-sulfonyl dibenzoyl chloride by Solution Polycondensation. *Journal of Polymer Science Part A: Polymer Science*, *34*, 885-891.

[53] **Liaw, D. J., Chang, P.** (1997). Synthesis and Characterization of Polycarbonate Based on Bisphenol S by Melt Transesterification. *Journal of Polymer Science Part A: Polymer Science*, *35*, 2453-2460.

[54] **Liaw, D. J., Liaw, B. Y., Su, K. L.** (1999). Synthesis and Properties of New Polyamides Derived from 2,2-Bis[4-[2-[aminophenoxy) ethoxy]phenyl]sulfone by Direct Polycondensation. *Polymers for Advanced Technologies*, *10*, 329-335.

[55] **Liaw, D. J., Lin, S. P., Liaw, B. Y.** (1999). Photolysis of Bisphenol-Based Polyurethanes in Solution. *Journal of Polymer Science Part A: Polymer Science*, *37*, 1331-1339.

[56] **Liaw, D. J., Liaw, B. Y.** (1999). Preparation and Characterization of New Polyimides Derived from 2,2-bis[4-[2-(4-aminophenoxy) ethoxy]phenyl]sulfone. *Polymers for Advanced Technologies*, *10*, 13-19.

[57] **Turner, S. R., King, B., Ponasik, J., Adams, V., Connell, G.** (2005). Amorphous Copolyester Containing Monomers Derived from Bisphenols. *High Performance Polymers*, *17*, 361-376.

[58] **Qin, X. M., Xiong, J. W., Yang, X. H., Wang, X. L., Zheng, Z.** (2007). Preparation, Morphology, and Properties of Polyurethane-Urea Elastomers Derived from Sulphone-Containing Aromatic Diamine. *Journal of Applied Polymer Science*, *104*, 3529-3535.

[59] **Turner, S. R.** (2004). Development of Amorphous Copolyesters Based on 1,4-cyclohexanedimethanol. *Journal of Polymer Science Part A: Polymer Science*, *42*, 5847-5852.

[60] **Liu, Y., Turner, S. R., Wilkes, G.** (2011). Melt-Phase Synthesis and Properties of Triptycene-Containing Copolyesters. *Macromolecules*, *44*, 4049-4056.

[61] **Tsai, Y., Fan, C. H., Hung, C. Y., Tsai, F. J.** (2009). Synthesis and Characterization of Amorphous Poly(ethylene terephthalate) Copolymers Containing Bis [4-[2-hydroxyethoxy)phenyl]sulfone. *European Polymer Journal*, *45*, 115-122.

[62] **Mark, H. F.** (Ed.) (2004). Encyclopedia of Polymer Science and Technology. New York: Wiley.

[63] **Özarslan, Ö., Bayazıt, M. K., Çatıker, E.** (2009). Preparation and Properties of Flame Retardant Poly(Urethane-Imide)s Containing Phosphine Oxide Moiety. *Journal of Applied Polymer Science, 114*, 1329-1338.

[64] **Türel, B., Karataş, S., Güngör, A., Serhatlı, I. E.** (2013). Synthesis of Triphenyl Phosphine Oxide Containing Polymers via ATRP. *Journal of Applied Polymer Science, 128*, 888-898.

[65] **Fink, J.** (2008). High Performance Polymers. New York: William Andrew.

[66] **Riley, D. J.** (1997). Synthesis and Characterization of Phosphorus Containing Poly(Arylene Ether)s, *PhD Thesis, Virginia Polytechnic Institute, Blacksburg, Virginia.*

[67] **Hartley, F. R.** (Ed.) (1990). The Chemistry of Organophosphorus Compounds Vol. 1. New York: John Wiley and Sons.

[68] **Hartley, F. R.** (Ed.) (1990). The Chemistry of Organophosphorus Compounds Vol. 2. New York: John Wiley and Sons.

[69] **Davies, W. C., Jones, W. J.** (1929). Tertiary Phosphines Containing the n-butyl radical. *Journal of the Chemical Society*, 33-35.

[70] **Davies, W. C., Pearse, P. L., Jones, W. J.** (1929). Tertiary Phosphines Containing the Higher Alkyl Radicals. *Journal of the Chemical Society*, 1262-1268.

[71] **Grim, S. O, McFarlane, W., Davidoff, E. F.** (1967). Group Contributions to Phosphorus-31 Chemical Shifts of Tertiary Phosphines. *Journal of Organic Chemistry, 32*,781-784.

[72] **Metzger, S. H., Basedow, O. H., Isbell, A. F.** (1964). Highly Branched Alkylphosphorus Compounds. II. Synthesis of 1,1,2-Trimethylpropylphosphonyl Chloride. *Journal of Organic Chemistry, 29*,627-630.

[73] **Morrison, R. T., Boyd, R. N.** (1987). Organic Chemistry, 5th ed. Allyn and Bacon.

[74] **Srivastava, R. C.** (1985). Journal of Chemical Research, 330.

[75] **Hoffmann, H., Schellenbeck, P.** (1967). Notiz über die Darstellung von Tri-tert.-butylphosphin. *Chemiche Berichte., 100*, 692-693.

[76] **Kleiner, H. J., Weiss, E.** (1986). Chemical Abstract, 105, 115206a.

[77] **Weiss, E., Kleiner, H. J.** (1987). Chemical Abstract, 107, 134489c.

[78] **Wescott, J. M.** (1993). PhD thesis, Virginia Polytechnic Institute, Blacksburg, Virginia.

[79] **Fink, J. K.** (2005). Reactive Polymers Fundamentals and Applications. USA: William Andrew.

[80] **Stoye, D., Freitag, W.** (1996). Resins for Coatings-Chemistry, Properties and Applications. New York: Hanser Publishers.

[81] **Meier-Westhues, U.** (2007). Polyurethanes-Coatings, Adhesives and Sealants. Germany: Vincentz Network.

[82] **Oldring, P. K. T., Hayward, G.** (1987). A Manual for Resins for Surface Coatings. England: Sita Technology.

[83] **Glöckner, P., Jung, T., Struck, S., Studer, K.** (2008). Radiation Curing-Coatings and Printing Inks-Technical Basics, Applications and Trouble Shooting. Germany: Vincentz Network.

[84] **Wicks, Z. W., Jones, F. N., Pappas, S. P., Wicks, D. A.** (2007). Organic Coatings-Science and Technology. USA: Wiley Interscience.

[85] **Goldschmidt, A., Streitberger, H. J.** (2003). BASF Handbook on Basics of Coating Technology. Germany: Vincentz Network.

[86] **Url-1 <** http://www.byk.com >, alındığı tarih: 10.05.2013.

[87] **Türel Erbay, B., Serhatlı, I. E.** (2013). Synthesis of Bis[(4-hydroxyethoxy)phenyl]sulfone Containing Urethane Acrylates and Their Applications. *Progress in Organic Coatings*, *76*, 1-10.

[88] **Turner, S. R., King, B., Ponasik, J., Adams, V., Connell, G.** (2005). Amorphous Copolyesters Containing Monomers Derived from Bisphenols. *High Performance Polymers, 17*, 361-376.

[89] **Israelachvili, J. N.** (2011). Intermolecular and Surface Forces, USA: Elsevier.

[90] **Turro, N. J., Ramamurthy, V., Scaiano, J. C.** (2010). Modern Molecular Photochemistry of Organic Molecules. USA: University Science Books.

[91] **Kotz, J. C., Treichel, P. M., Townsend, J. R.** (2012). Chemistry-Chemical Reactivity. China: Brooks/Cole-Cengage Learning.

[92] **Liaw, D. J.** (1997). The relative physical and thermal properties of polyurethane elastomers: Effect of chain extenders of bisphenols, diisocyanate, and polyol structures. *Journal of Applied Polymer Science, 66*, 1251.

[93] **Minoura, Y., Yamashita, S., Okamoto, H., Matsuo, T., Izawa, M, Kohmoto, S.** (1978). Crosslinking and Mechanical Property of Liquid Rubber.I. Curative Effect of Aliphatic Diols. *Journal of Applied Polymer Science, 22*, 1817.

[94] **Minoura, Y., Yamashita, S., Okamoto, H., Matsuo, T., Izawa, M, Kohmoto, S.** (1978). Crosslinking and Mechanical Property of Liquid Rubber.I. Curative Effect of Aliphatic Diols. *Journal of Applied Polymer Science, 22*, 3101.

[95] **Oprea, S., Vlad, S., Stanciu, A., Macoveanu, M.** (2000). Epoxy Urethane Acrylate. *European Polymer Journal, 36*, 373.

[96] **Tsai, Y., Fan, C. H., Hung, C. Y., Tsai, F. J.** (2009). Synthesis and Characterization of Amorphous Poly(Ethylene terephthalate) Copolymers Containing Bis[4-(2-hydroxyethoxy)phenyl]sulfone. *European Polymer Journal, 45*, 115.

[97] **Hoffmann, T., Pospiech, D., Haussler, L., Komber, H., Voigt, D., Harnisch, C., Kollann, C., Ciesielski, M., Döring, M., Perez-Graterol, R., Sandler, J., Altstadt, V.** (2005). Novel Phosphorous-Containing Aromatic Polyethers-Synthesis and Characterization. *Macromolecular Chemistry and Physics*, *206*, 423-431.

CURRICULUM VITAE

Name Surname: Betül TÜREL

Place and Date of Birth: İstanbul, 28.06.1976

E-Mail: betul_turel@yahoo.com

B.Sc.: Yıldız Technical University, Department of Chemical Engineering, 2000

B.Sc.: Anadolu University, Business Administration, 2005

M.Sc. : Istanbul Technical University, Polymer Science and Technology, 2005

Professional Experience and Rewards:

Elif Plastic Packaging and Manufacturing and Trading Inc., Istanbul
Printing Department Manager (2011-)
Printing Department Chief (2010-2011)
Color and Ink Management Department Chief (2007-2009)

Telka Manufacturing and Trading Unlimited Company, Istanbul
Quality Control and Process Engineer (2000-2006)

Internship
KORDSA Sabancı Dupont Industrial Yarn and Tire Cord Fabric Manufacturing and Trading Inc., Kocaeli (1998 & 1999)

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Türel Erbay, B.,** and Serhatlı, I. E., 2013. Synthesis of Bis[(4-hydroethoxy)phenyl]sulfone Containing Urethane Acrylates and Their Applications. Progress in Organic Coatings, 76, (1), 1-10.

- **Türel Erbay, B.,** and Serhatlı, I. E., 2013. Synthesis, Characterization and Coating Application of Bis[(4-hydroethoxy)phenyl]sulfone Containing Urethane Acrylates. Progress in Organic Coatings, submitted.

- **Türel, B.,** and Serhatlı, I. E., Synthesis and Application of Sulfone Containing Urethane Acrylates. Paint Istanbul-Paint Industry and Auxiliary Products Congress and Exhibition-BOSAD (24/09-25/09/2010), Istanbul, Turkey. Oral presentation

- **Türel Erbay, B.,** and Serhatlı, I. E., Synthesis and Characterization of Sulfone Containing Polyurethane Acrylate Coatings.European Coatings Congress, Vincents

and European Coatings Journal (28/03-30/03/2011), Nürnberg, Germany. Poster presentation

- **Türel Erbay, B.,** and Serhatlı, I. E., Synthesis of Phenylphosphine Oxide Containing Urethane Acrylates and Their Applications. European Polymer Congress, European Polymer Federation (26/06-01/07/2011) Oral presentation

List of Publications and Patents:

- **Türel, B.,** Karataş, S., Güngör, A., and Serhatlı, I. E., 2013. Synthesis of Triphenyl Phosphine Oxide Containing Polymers via ATRP. Journal of Applied Polymer Science, 128, (1), 888-898.

- Yanılmaz, M., **Türel Erbay, B.,** Serhatlı, I. E., Karakaş, H., and Saraç, A. S., 2013. Synthesis of Polyurethane Acrylate based Electromagnetic Interference Shielding Materials. Journal of Applied Polymer Science, 127, (6), 4957-4966.

- **Türel, B.,** Karataş, S., Güngör, A., and Serhatlı, I. E., Synthesis of Triphenyl Phosphine Oxide Containing Polymers via ATRP. XIX. National Chemistry Congree, Ege University, (30/09- 04/09/2005) , Kuşadası-Aydın ,Türkiye. poster presentation

- **Türel Erbay, B.,** Serhatlı, I. E., Synthesis and Characterization of Bifunctional Sulfone Containing Urethane Acrylate and Its Applications. Paint Istanbul-Paint Industry and Auxiliary Products Congress and Exhibition-BOSAD (13/09-15/09/2012), Istanbul, Turkey. Poster presentation