ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

THE FUNCTIONAL POLYMERS BY RING OPENING POLYMERIZATION OF CAPROLACTONE AND THEIR FURTHER MODIFICATIONS FOR COATING PURPOSES

Ph.D. THESIS

Çiğdem TAŞDELEN YÜCEDAĞ

Department of Chemical Engineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KAPROLAKTONUN HALKA AÇILMASI POLİMERİZASYONU İLE FONKSİYONEL POLİMERLERİN SENTEZİ VE BAĞLAYICI OLARAK KULLANIMLARI İÇİN MODİFİKASYONLARI

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Çiğdem TAŞDELEN YÜCEDAĞ, **a Ph.D.** student of ITU Graduate School of Science, Engineering and Technology student ID **506062001**, successfully defended the **thesis/dissertation** entitled "**THE FUNCTIONAL POLYMERS BY RING OPENING POLYMERIZATION OF CAPROLACTONE AND THEIR FURTHER MODIFICATIONS FOR COATING PURPOSES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my lovely family,

FOREWORD

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ABBREVIATIONS

St	**:** Styrene
ROP	**:** Ring opening polymerization
PCL	**:** Polycaprolactone
ε-CL	**:** ε-caprolactone
SFO	**:** Sunflower oil
SFOPG	**:** Sunflower oil partial glycerides
SOMPE	**:** Sunflower oil-modified polyester
PBZ	**:** Polybenbenzoxazine
HFB-a	**:** Hydroxy-functional benzoxazine monomer
HPCL	**:** Vinyl functional polyester
VTMS	**:** Vinyl trimethoxysilane
HEMA	**:** 2-hydroxyethyl methacrylate
SO	**:** Stannous octoate or tin (II) 2-ethylhexanoate
TDI	**:** 2,4-toluene diisocyanate
BPO	**:** Benzoyl peroxide
^{1}H-NMR	**:** Hydrogen Nuclear Magnetic Resonance spectroscopy
FT-IR	**:** Fourier Transfrom Infrared spectrocopy
GPC	**:** Gel Permeation Chromatography
DSC	**:** Differential Scanning Calorimetry
TGA	**:** Thermal Gravimetric Analysis
SEM	**:** Scanning Electron Microscopy

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THE FUNCTIONAL POLYMERS BY RING OPENING POLYMERIZATION OF CAPROLACTONE AND THEIR FURTHER MODIFICATIONS FOR COATING PURPOSES

SUMMARY

Polymeric binders are widely used in organic coatings as an integrating material of the other components in the formulation. Since they have great influence on the main characteristics of the coating, their molecular structure can be designed according to the specific applications. Synthetic polymers are mostly produced by using petrochemical raw materials. The renewable resources for the production of polymeric materials have been drawn great attention due to being cheap and environmentally friendly alternatives to fossil sources.

Triglyceride oils are one of the most widely used renewable resources and the oldest binders for paints. When triglycerides are applied on a surface, they can form solid films by oxidative polymerization and crosslinking through the double bonds of the fatty acid chains. Since triglycerides form a film with insufficient properties such as drying speed, adhesion, hardness and durability, they are used in coating formulations together with other synthetic polymers in order to improve their performance.

The aim of this study is to develop new polymeric coatings by combining high potential of triglycerides with other polymerization techniques. One of the techniques used in this study is the ring opening polymerization (ROP). ROP is a versatile method of producing polyesters with tailored material properties such as high molecular weight, low polydispersity and other characteristics as required according to the specific application. In this regard, polycaprolactone (PCL) based functional polymer samples were prepared by the ROP of ε-caprolactone (CL). Then, these polymers were further modified to develop new polymeric binders. These modifications were conducted by using two strategies.

The first strategy was to use benzoxazine monomer for the modification. Benzoxazine monomers have several desirable properties such as high thermal and chemical stability, high char yield, near-zero volume changes and no by-products during curing, low flammability and rich molecular design flexibility. Besides their good properties, they have some disadvantages including brittleness, high curing temperature, and difficulty in processing.

In the first part of this thesis, for the ROP of CL, sunflower oil partial glycerides (SFOPG) were used as the initiator in the presence of stannous octoate (SO) catalyst. In addition to being initiator, SFOPGs participate in the drying process of the film sample for coating purposes. The structure of the sample was characterized by gel permeation chromatography (GPC), fourier transform infrared spectroscopy (FT-IR) and hydrogen nuclear magnetic resonance spectroscopy (^{1}H-NMR) analyses.

The film of sunflower oil-modified polyester (SOMPE) cannot reach a fully dried state as a result of its less oil moiety content. By increasing the oil fraction, the chain length of polycaprolactone (PCL) decreased by changing the [monomer]/[initiator] mol ratio and shortening the reaction time. Even with these precautions, the molecular weight of SOMPE could not be reduced below 5000 g/mol, and this caused the film to become soft. Therefore, hydroxy-functional benzoxazine monomer (HFB-a) was prepared and used in a further modification of SOMPE. HFB-a was chemically combined with SOMPE via the urethane linkage formed from the reaction of 2,4-toluene diisocyanate, yielding SOMPE-HFB-a. Because the SOMPE-HFB-a sample also had a soft film, additional HFB-a was used to prepare the SOMPE-HFB-a/HFB-a blend. The cured blend prepared with SOMPE-HFB-a and HFB-a in a weight ratio of 1/8, [SOMPE-HFB-a/HFB-a:1/8], had good film properties such as adhesion, flexibility, and alkali, acid and water resistances. The cured film was examined by FT-IR and differential scanning calorimetry (DSC) after the curing process. After our modifications were applied, PCL and polybenzoxazine lost their softness and brittleness, respectively. Moreover, the thermal gravimetric analysis (TGA) results exhibited improvements in thermal properties.

The second strategy was based on sol-gel process. Sol-gel process is an organic polycondensation reaction, which polymeric structures form by the combination of small molecules. The production of three dimensional cross-linked network structure by the reaction of small molecules has several advantages such as a high control of the purity and composition of the final materials and easy processability. Additionally, sol-gel reactions are favorable in comparison with other inorganic network forming methods, due to having mild reaction conditions and a broad solvent compatibility.

In the second part of the thesis, first a vinyl functional polyester based macromonomer (HPCL) was prepared by ROP of CL using 2-hydroxyethyl methacrylate (HEMA) as the initiator. Then, this macromonomer was copolymerized with styrene (St) and vinyl trimethoxysilane (VTMS), yielding a terpolymer (HPCL-St-VTMS). The characterization of the polymer samples were done by using FT-IR, GPC and ^{1}H-NMR. Since, the cured film of HPCL-St-VTMS showed a tacky property, SFOPG was used as a modifier for HPCL-St-VTMS to enhance crosslinking as well as the flexibility to obtain a product which is applicable in terms of organic coatings. For this purpose, SFOPG was mixed with HPCL-St-VTMS terpolymer and sunflower oil-modified terpolymer (SFOM-HPCL-St-VTMS) was obtained through the sol-gel reaction between methoxy silane moieties of terpolymer and hydroxyl groups of SFOPG. After this modification softness was disappeared. Nanosize inorganic domains were seen in the scanning electron microscopy (SEM) image. The thermal analyses of resulting crosslinked film of SFOM-HPCL-St-VTMS were done by DSC and TGA. SFOM-HPCL-St-VTMS, having no melting behavior, gave a higher char yield and decomposition temperature at 5% weight loss, compared to the unmodified film of HPCL-St-VTMS. In the end, the film properties showed that SFOM-HPCL-St-VTMS could be used as a coating material.

KAPROLAKTONUN HALKA AÇILMASI POLİMERİZASYONU İLE FONKSİYONEL POLİMERLERİN SENTEZİ VE BAĞLAYICI OLARAK KULLANIMLARI İÇİN MODİFİKASYONLARI

ÖZET

Polimerik bağlayıcıların, organik kaplama formülasyonlarında diğer komponentleri birleştiren bir malzeme olarak kullanımları yaygındır. Kaplamanın ana karakteristikleri üzerinde önemli bir etkileri olduğundan dolayı, polimerik bağlayıcıların molekül yapıları korozyona karşı koruma, aşınmaya ve mikrobiyal kirliliğe karşı direnç gibi spesifik uygulamalara uygun olarak tasarlanabilir. Poliesterler, epoksiler, poliüretanlar, poliüreler, akrilikler, vinil asetatlar, silikonlar, silikatlar, polivinil klorürler, fenolikler ve vinil dien florürler gibi çok sayıda sentetik polimer organik kaplamalarda bağlayıcı olarak kullanılmaktadır.

Sentetik polimerler çoğunlukla petrokimyasal hammaddeler kullanılarak üretilir. Fosil kaynakların sürekli tükeniyor olmaları, karbon dioksit emisyonu kaynaklı sera etkisine yol açmaları, bozunabilirlik ve geri dönüştürülebilirlik özelliklerine sahip olmamaları gibi ana sebeplerden ötürü, yenilenebilir hammaddeler petkokimyasallara alternatif olarak kullanılmaktadır. Son yıllarda, yenilenebilir kaynakların enerji ve malzeme üretiminde kullanılmaları endüstri ve akademide dikkat çekmektedir. Doğal yağlar, selüloz ve nişasta gibi polisakkaritler ve proteinler kimya endüstrisinde en çok kullanılan yenilenebilir hammaddelerdir.

Trigliserit yağlar, yenilenebilir kaynakların en önemlilerinden biridir ve boyalar için bilinen en eski bağlayıcılardır. Trigliserit yağlar bir yüzeye uygulandıklarında, oksidatif polimerizasyon ve yağ asidi zincirlerinin çift bağlarıyla gerçekleşen çapraz bağlanma sayesinde katı filmler oluşturabilirler. Oluşturdukları film, kuruma süresi, yapışma, sertlik ve dayanıklılık açısından yeterli özelliklere sahip olmadığı için, performanslarını artırmak amacıyla trigliserit yağlar kaplama formülasyonlarında diğer sentetik polimerlerle birlikte kullanılırlar.

Bu çalışmanın amacı, trigliserit yağların yüksek potansiyelleriyle diğer polimerizasyon tekniklerini birleştirerek yeni polimerik kaplamalar geliştirmektir. Bu çalışmada kullanılan tekniklerden biri halka açılması polimerizasyonudur (ring opening polymerization, ROP). ROP, yüksek molekül ağırlığı, düşük polidispersite ve spesifik uygulamalara yönelik diğer karakteristikler gibi uygun hale getirilmiş malzeme özelliklerine sahip poliesterlerin üretilmeleri açısından çok yönlü bir metotdur. Örneğin, yüksek mekanik mukavemet, biyouyumluluk ve biyobozunabilirlik gibi dikkat çekici özelliklere sahip polikaprolakton (PCL) polimeri, halka açılması polimerizasyonu ile üretilebilen alifatik bir poliesterdir.

Bu bağlamda, polikaprolakton (PCL) temelli fonksiyonel polimer numuneleri, kalay oktoat (stannous octoate, SO) katalizörü varlığında ε-kaprolakton (CL) monomerinin halka açılması polimerizasyonu ile hazırlanmıştır. Daha sonra, bu fonksiyonel

polimerler, polimerik bağlayıcı geliştirmek amacıyla modifiye edilmişlerdir. Bu modifikasyonlar iki strateji izlenerek gerçekleştirilmiştir.

İlk stratejide, sentezlenen fonksiyonel polimerin modifikasyonu için benzokzazin monomeri kullanılmıştır. Benzokzazin, bir benzen molekülüne bağlanmış halde bulunan okzazin halkasından oluşur. Okzazin, bir oksijen ve bir azot atomu içeren altı üyeli heterosiklik bir bileşiktir. Son yıllarda gelişmiş termoset fenolik reçineler olan benzokzazinler, çok sayıda araştırmacı tarafından kapsamlı şekilde çalışılmıştır. Benzokzazin monomerleri, ısı uygulandığında ortamda herhangi bir katalizör olmaksızın halka açılması polimerizasyonu ile polimerize olabilirler. Böylece polibenzokzazinler oluşur. Okzazin halkasının oksijen ve azot atomlarının kuvvetli bazlığı katyonik polimerizasyonun başlamasını tetikler. Benzokzazin monomerleri, yüksek termal ve kimyasal kararlılık, yüksek yanma ürünü yüzdesi, kürlenme esnasında sıfıra yakın hacim değişimi ve yan ürün oluşturmama, düşük tutuşabilirlik ve moleküler tasarım esnekliği gibi özelliklere sahiplerdir. Bu iyi özelliklerinin yanısıra, kırılganlık, yüksek kürlenme sıcaklığı ve işlenme zorluğu gibi dezavantajları da mevcuttur.

Bu tezin ilk bölümünde, CL monomerinin kalay oktoat (stannous octoate, SO) varlığında ROP'u için, ayçiçek yağı kısmı gliseritleri (sunflower oil partial glycerides, SFOPG), başlatıcı olarak kullanılmıştır. Başlatıcı olmalarının yanısıra, SFOPG'ler kaplama amaçlı film numunelerinin kuruma prosesine katılmaktalardır. Numune yapısı, jel geçirgenlik kromatografisi (gel permeation chromatography, GPC), fourier transform infrared spektroskopisi (FT-IR) ve hidrojen nükleer manyetik rezonans spektroskopisi (^{1}H-NMR) analizleri ile karakterize edilmiştir.

Ayçiçek yağı ile modifiye edilmiş poliesterin (sunflower oil-modified polyester, SOMPE) filmi, düşük yağ içeriği sebebiyle tam bir kuruma gösterememiştir. PCL'nin zincir uzunluğu yağ fraksiyonunu artırmak yoluyla, [monomer]/[başlatıcı] mol oranını değiştirerek ve reaksiyon süresini kısaltarak düşürülmüştür. Bu önlemlere rağmen, SOMPE'nin molekül ağırlığı 5000 g/mol'ün altına düşmemiştir ve bu durum da filmin yumuşak olmasına yol açmıştır. Bunun için, hidroksi fonksiyonel benzokzazin monomeri (hydroxy-functional benzoxazine monomeri, HFB-a) hazırlanmış ve SOMPE'nin daha ileri modikasyonunda kullanılmıştır. HFB-a ile SOMPE birbirilerine üretan bağlarıyla kimyasal olarak bağlanmıştır. Böylece SOMPE-HFB-a bileşiği elde edilmiştir. SOMPE-HFB-a yine yumuşak bir film verdiği için, SOMPE-HFB-a/HFB-a karışımı hazırlamak amacıyla ilave HFB-a kullanılmıştır. 1/8 ağırlık oranıyla hazırlanan [SOMPE-HFB-a/HFB-a:1/8] karışım, kürlendikten sonra yapışma, esneklik, baza, aside ve suya dayanıklılık açısından iyi film özellikleri göstermiştir. Kürlenme prosesi, FT-IR ve diferensiyel taramalı kalorimetre (differential scanning calorimetry, DSC) ile incelenmiştir. Yapılan modifikasyonlar sonucunda, PCL yumuşaklığını, benzokzazin ise kırılganlığını kaybetmiştir. Ayrıca termal gravimetrik analiz (thermal gravimetric analysis, TGA) sonuçları termal özelliklerde iyileşme olduğunu göstermiştir.

İkinci strateji sol-jel prosesi temel alınarak uygulanmıştır. Sol-jel prosesi, küçük moleküllerin birleşmeleriyle polimerik yapıların oluştuğu bir polikondenzasyon reaksiyonudur. Bu şekilde oluşan çapraz bağlanmış ağ yapılarının, nihai ürünlerin saflığında ve bileşiminde yüksek kontrol ve kolay işlenebilirlik gibi avantajları mevcuttur. Sol-jel prosesinde, alkoksisilana ait alkoksi grubu su ile reaksiyona girebilir. Böylece, bir alkolün de açığa çıkmasıyla silanol grupları oluşur. Daha sonra, bu silanol grupları kondenzasyon reaksiyonu ile birleşir ve siloksan köprüleri

meydana gelir. Bu esnada, reaksiyondan yan ürün olarak su veya alkol açığa çıkar. Ek olarak, ılımlı reaksiyon koşulları ve çok sayıda çözücüye uyumu nedeniyle, sol-jel tekniği diğer inorganik ağ yapısı oluşturma metotlarına kıyasla tercih edilmektedir.

Bu tezin ikinci bölümünde ise, ilk olarak bir vinil fonksiyonel poliester sentezlenmiştir. Bunun için, CL monomerinin halka açılması polimerizasyonunda katalizör olarak kalay oktoat ve başlatıcı olarak ise 2-hidroksietil metakrilat (HEMA) kullanılmıştır. Böylece vinil fonksiyonel poliester temelli bir makromonomer (HPCL) hazırlanmıştır. Daha sonra, bu makromonomer, stiren (St) ve vinil trimetoksisilan (VTMS) ile serbest radikal polimerizasyonu uygulanarak benzoil peroksit (benzoyl peroxide, BPO) katalizörü varlığında kopolimerize edilmiştir. Böylece, gerçekleştirilen reaksiyon sonucunda HPCL-St-VTMS terpolimeri elde edilmiştir.

Polimer numunelerinin karakterizasyonları FT-IR, GPC ve ^{1}H-NMR teknikleri kullanılarak yapılmıştır. HPCL-St-VTMS terpolimerinin kürlenmiş filmi yapışkan özellik gösterdiğinden dolayı, SFOPG çapraz bağlanmanın ve esnekliğin artırılması için modifiye edici madde olarak kullanılmıştır. SFOPG ve HPCL-St-VTMS'nin karıştırılmasıyla ayçiçek yağı ile modifiye edilmiş terpolimer (SFOM-HPCL-St-VTMS), SFOPG'nin hidroksil grupları ile terpolimerin methoksisilan grupları arasındaki sol-jel reaksiyonu ile hazırlanmıştır. Böylece, çapraz bağlanma yoğunluğu artmış, fakat bir kaplama malzemesi olmaya uygun esnekliğe sahip bir ağ yapısı elde edilmiştir. Bu modifikasyondan sonra, taramalı elektron (scanning electron microscopy, SEM) mikroskobu görüntüsünde çoğunluğu nano boyutta olan inorganik kısımlar tespit edilmiştir. SFOM-HPCL-St-VTMS'ye ait filmin termal özellikleri DSC ve TGA ile incelenmiştir. Erime davranışı göstermeyen SFOM-HPCL-St-VTMS, modifiye edilmemiş HPCL-St-VTMS filmine kıyasla, daha yüksek yanma ürünü yüzdesi ve bozunma sıcaklığı (%5 kütle kaybının gerçekleştiği sıcaklık) göstermiştir. Film özelliği testleri ile de SFOM-HPCL-St-VTMS'nin bir kaplama malzemesi olarak kullanılabileceği belirlenmiştir.

Sonuç olarak, yukarıda bahsedilen her iki strateji izlenerek elde edilen yağ-temelli bağlayıcılar, yapışma ve esneklik, baz, asit ve su direnci açısından iyi film özellikleri göstermiştir. Buna ek olarak, termal karakterizasyon çalışmaları, yapıya benzokzazin monomerinin katılmasının ve poliester zincirleri arasında siloksan köprülerinin kurulmasının termal kararlılığı artırdığını göstermiştir. Elde edilen tüm bulgular ışığında, bu bağlayıcıların kaplama malzemesi olarak kullanılabilecekleri anlaşılmıştır.

1. INTRODUCTION

Polymeric binders are one of the most vital components of organic coatings since they serve as an integrating material of the other components in the formulation. In this context, molecular structure of polymeric binders should be designed to fulfill the utilization of the coatings for specific purposes, such as protection against corrosion, abrasion and microbial fouling [1-4].

A broad range of polymers including polyesters, epoxides, polyurethanes, polyureas, acrylics, vinyl acetates, silicones, silicates, polyvinyl chlorides, phenolics and vinylidiene fluorides are used as binders for organic coating materials [5]. These polymers are mostly produced from petrochemical raw materials. Because of the detrimental influences of fossil sources on environmental and economic issues, renewable resources have gained considerable importance by virtue of their benefits such as inexpensiveness, abundancy, biodegradability, low toxicity and high purity [2, 6-11]. As a renewable resource, beside the nutrition purpose, triglyceride oils have been widely used for technical purposes such as in the manufacture of soap, surface active materials and oleoresinous binders. In their direct use as a binder, they form a film with insufficient properties like drying speed, hardness, adhesion and durability. Due to this fact, in order to improve their performance, triglyceride oils are used in coating formulations together with alkyds, epoxy esters, uralkyd resins and other synthetic polymers [2, 6, 10-11].

A further progress for converting triglycerides into more useful state in terms of coating performance is the preparation of copolymers with vinyl monomers. In this sense, a number of studies were previously performed in our laboratory to enhance the film properties [12-17]. For this purpose, two strategies namely, macromonomer (macromer) and macroinitiator methods were developed. In macromer method, vinyl functionality was inserted into the oil structure and the resulting oil-based vinyl macromers were copolymerized with styrene (St) to obtain styrenated oil [15-20]. In this way, the formation of homopolystyrene, which causes opacity on the films, was minimized. On the other hand, in case of macroinitiator method, partial glyceride

was priorly reacted with 4,4'-azobis(4-cyanopentanoyl chloride) to generate azo functionalities on the oil structure [12-14]. For the preparation of styrenated oil, this macroinitiator was heated in the presence of St monomer, and styrenated oil without homopolymer formation was gained.

Besides the free radical polymerization, controlled free radical living polymerizations such as nitroxide mediated radical polymerization (NMRP) in the presence of 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO) and reversible addition-fragmentation chain transfer polymerization (RAFT) were studied in our laboratory. The obtained copolymers with low polydispersity resulted in good film properties [21-22]. In addition to these studies, nonvinly monomers of 3-aminopropyltriethoxysilane [23], diisocyanates [24] and methylolated abietic acid [25] were also used for the triglyceride oil modification. 3-aminopropyltriethoxysilane causes crosslinking due to the sol-gel reaction producing a film with nano hybrid composite structure [23].

In this thesis, functional polymer samples were prepared by ring opening polymerization (ROP), which is an easy and featured method of producing polyesters. ROP allows one to generate new polymers with tailored material properties such as high molecular weight, low polydispersity and other characteristics as required according to the specific application. For example, polycaprolactone (PCL) is an aliphatic polyester with remarkable features such as good mechanical strength, biocompatibility and biodegradability [26].

One procedure for producing PCL is the ROP of ε-caprolactone (CL) in the presence of a stannous octoate catalyst. Activated stannous alkoxide is formed in the presence of alcohol groups and promotes polymerization [26-27]. By predetermining the alcohol/monomer molar ratio, the molecular weight can be controlled and a wide variety of polyester products can be generated by adjusting the alcohol content. For instance, polymeric alcohols such as polyvinyl alcohol [28], polyethylene glycol [29-30], chitin [31], and starch [32] can be utilized to generate grafted PCL. Additionally, PCL allows one to design molecules that have functional groups such as naphthoxazine functional PCL [33].

In the first part of this thesis, sunflower oil partial glycerides (SFOPG) were used as an alcohol component to initiate the ROP of CL in the presence of stannous octoate

and to take advantage of the oxidative polymerization potential, which causes the film to become dry. However, because long PCL chains were formed, the fraction of the oil moiety was not sufficient to convert the film to a hard state (although some degree of crosslinking did occur through the fatty acid chains). To solve this problem, sunflower oil-modified polyester (SOMPE) was further modified with benzoxazine.

Polybenzoxazines (PBZs), a class of thermosetting phenolic resins, have gained more attention recently, in light of their intriguing characteristics, such as high thermal stability, good flame retardance, high glass transition temperature, low moisture absorption, rich molecular design flexibility, good mechanical properties, small shrinkage after processing and the absence of by-products during curing [34-37]. Despite these outstanding properties, pure polybenzoxazines are not favorable for coating applications due to their brittleness, low degree of polymerization and high curing temperatures [38-39]. To overcome these drawbacks, different strategies such as the preparation of benzoxazine monomers with additional functionalities [33], the synthesis of benzoxazine-based composites and alloys [36, 40] and the incorporation of benzoxazine in polymer chains [39, 41] have been utilized. To improve the flexural and impact properties of tough PBZ, blending with PCL of low T_g is recommended in the literature [38-39, 41-43].

In the second part of the thesis, sunflower oil partial glycerides were used as a modifier for a synthetic resin prepared in the laboratory by copolymerization of vinyl functional polyester (HPCL) with styrene (St) and vinyl trimethoxysilane (VTMS), yielding terpolymer (HPCL-St-VTMS). Vinyl functional polyester based macromonomer was prepared by ROP of CL using 2-hydroxyethyl methacrylate (HEMA) as the initiator. Since, cured film of HPCL-St-VTMS was slightly soft, to overcome this deficiency, SFOPG was used as a modifier. Sunflower oil-modified HPCL-St-VTMS (SFOM-HPCL-St-VTMS) showed good film properties due to the counter balance effect of the excess crosslinking and flexibility coming from the inserted oil moiety.

2. THEORETICAL PART

2.1 Ring Opening Polymerization

Ring opening polymerization (ROP) is a significant process for formation of polymers. In this type of reactions, polymerization propagates via the addition of opened structures to the polymer chain, in the same manner as in chain-growth mechanism (Figure 2.1) [44].

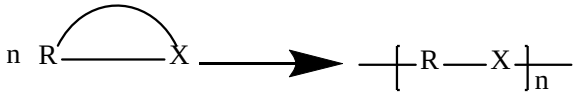

Figure 2.1 : General mechanism of ROP [44].

A wide range of structures can be synthesized by ROP such as, alkanes, alkenes, ethers, acetals, lactones, lactides, carbonates, phosphates, phosphonates, phosphites, phosphines, phosphazenes, anhydrides, polysulfur, polysulfides, lactams, siloxanes, silaethers, carbosilanes, silanes, imides, *N*-carboxyanhydres, 1,3-oxaza derivatives [45].

ROP is known as an easy and featured method of producing macromolecules. ROP allows one to generate new polymers with tailored material properties such as high molecular weight, low polydispersity and other characteristics as required according to the specific application. ROP enables the preparation of complex structures such as stars, brushes, cyclics and crosslinked materials which need controlled synthesis conditions [26, 46-48].

From the point of the production of aliphatic polyesters, with these beneficial features ROP is preferable in comparison to step growth polymerization. As known, the step growth polymerization, based on the polycondensation of hydroxycarboxylic acids or of a diol with dicarboxylic acid [48], has some disadvantages such as difficulties in controlling the molecular weight and polydispersity of the polymer, necessity the removal of water from the reaction medium to increase the conversion, high temperatures and long reaction times with accompanying side reactions. Moreover, the aliphatic polyesters of lactones and lactides synthesized by ROP have

good mechanical properties, hydrolyzability, biodegradability and biocompatibility. Therefore, these polyesters are versatile for biomedical and pharmaceutical industries in applications such as prosthetics, artificial skin and drug delivery. Also, polycaprolactone is utilized in agricultural applications as mulch films, ropes or cups. The production of polycaprolactone and polylactic acid in large volumes is realized for using as packaging materials and commodity plastics [45].

In ROP, the nature of active species, in other words the initiator type determines the polymerization mechanism. There are three major mechanisms for the ROP as cationic, anionic and coordination-insertion [46].

2.1.1 Mechanisms of ROP

2.1.1.1 Cationic polymerization

In cationic ROP, the carbonyl oxygen of monomer attacks the electrophilic reagents and cationic species form. The initiators of cationic ROP are Brønsted acids, Lewis acids and alkyl esters of strong organic acids [44-45, 49].

A general mechanism is given in Figure 2.2. Y-X represents the polarized bonds, where Y, X and E^+ denotes an atom or a functional group, cationic center and electrophilic initiator, respectively. Y behaves like Lewis base to react with electrophiles because of its unpaired electron. The nucleophilic attack of Y towards E^+ induces the ring opening reaction of monomer, and then X becomes a cationic center. These resulting cationic species can be attacked by another Y to undergo ring opening reaction (S_N2 mechanism), or they can undergo a ring opening reaction to form an acylic cationic species which will be attacked by the monomer (S_N1 mechanism) [45].

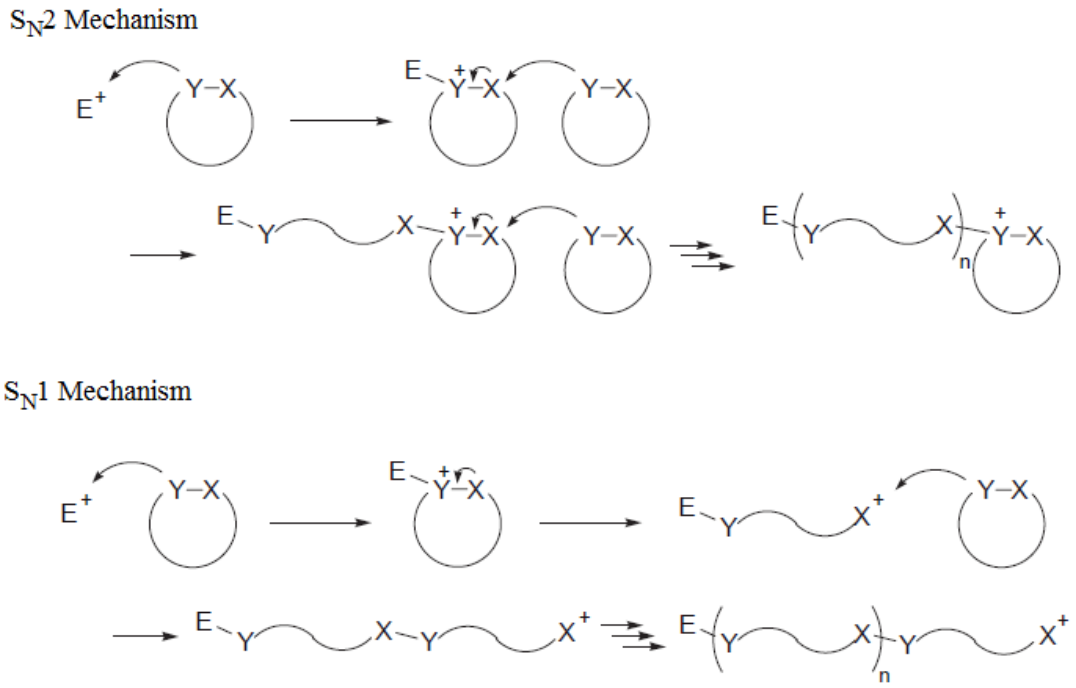

Figure 2.2 : General mechanism for cationic ROP [45].

2.1.1.2 Anionic polymerization

Anionic ROP is based on nucleophilic attack of propagating chain end to monomer. The initiators for this type of mechanism are organometals such as alkyl lithium, alkyl magnesium bromide, alkyl aluminum, and metal amides, alkoxides, phosphines, amines, alcohols and water. A general reaction mechanism is given in Figure 2.3. X-Y, X and Y ascribes to the functional group in cyclic monomers, electron-deficient atom usually carbon atom and an electron-withdrawing atom such as oxygen, nitrogen and sulfur, respectively [45].

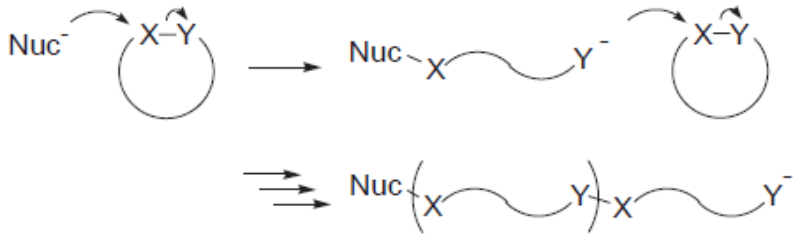

Figure 2.3 : General mechanism for anionic ROP [45].

By the nucleophilic attack of negatively charged initiator to the atom X, the ring of the monomer opens and Y releases. This formed anionic species attack again the atom X belonging to another monomer molecule. Thus, polymer chain propagates and linear polyester forms [45].

In the case of anionic ROP of ε-caprolactone (CL) monomer, which is depicted in Figure 2.4, polymerization is initiated by an alkoxide function (RO^-). The ring opening reaction is triggered by the nucleophilic attack of alkoxide initiator to the carbon atom of the carbonyl group of CL. This newly formed alkoxide which is at the end of the chain reacts with another lactone molecule, and polymerization reaction proceeds through the addition of new monomers [45-46].

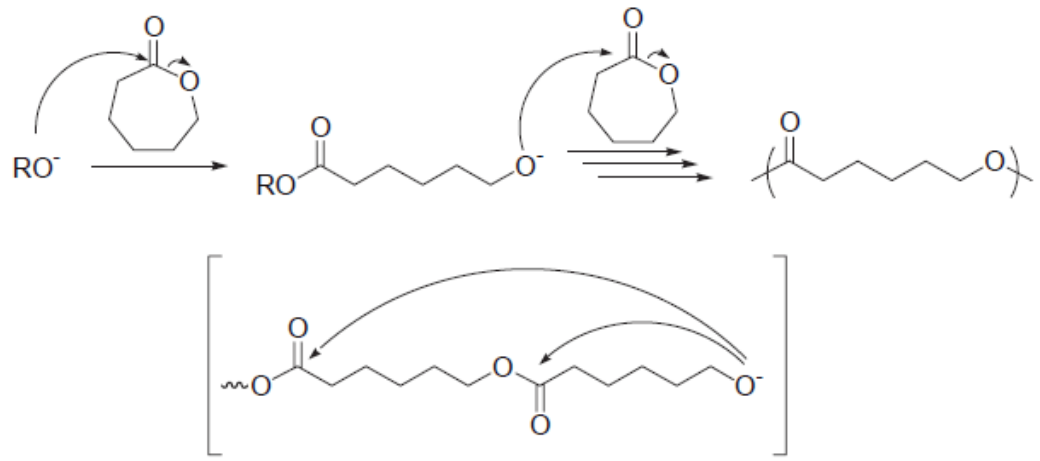

Figure 2.4 : Anionic ROP of ε-caprolactone monomer [45].

2.1.1.3 Coordination-insertion polymerization

The synthesis of aliphatic polyesters with well defined structure via coordination-insertion polymerization mechanism has been widely studied. Common initiators used for the coordination-insertion mechanism are various aluminum and tin alkoxides and carboxylates. The wide range of initiators enable the preparation of polymers with well defined architecture, controlled molecular weight, narrow molecular weight distribution and desired end groups [46].

In coordination-insertion polymerization mechanism, by the coordination of exocyclic oxygen to the metal atom, the carbonyl carbon of the monomer becomes more polarized and susceptible for nucleophilic attack. The initiation mechanism is given in Figure 2.5. The propagation proceeds through the cleavage of acyl-oxygen bond of the monomer and simultaneous insertion into the metal-oxygen bond [46, 49]. The polymerization mechanism is depicted in Figure 2.6.

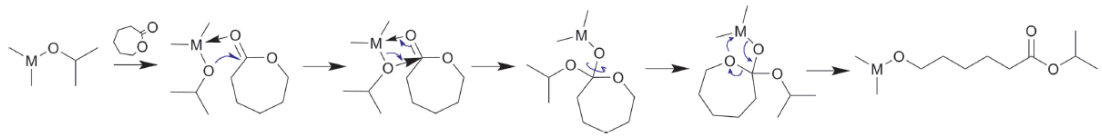

Figure 2.5 : Initiation mechanism of coordination-insertion ROP [49].

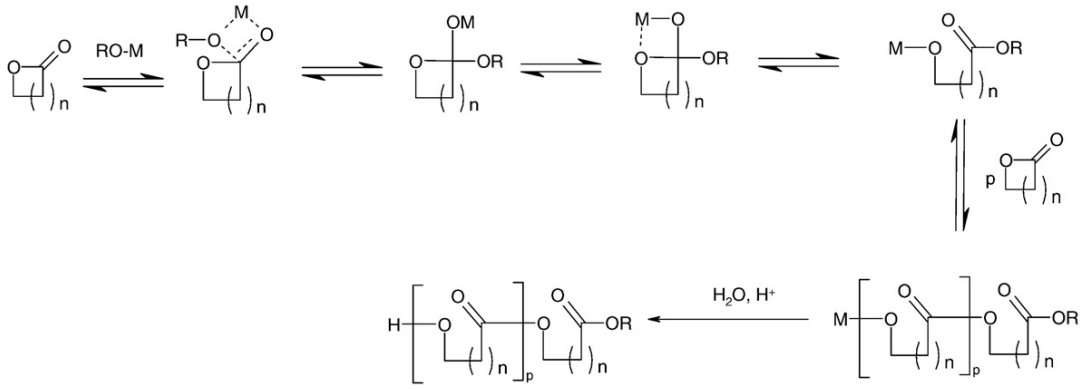

Figure 2.6 : ROP of lactones through the coordination-insertion mechanism [48].

2.1.2 Metal catalysts for ROP

2.1.2.1 Aluminum alkoxides

Aluminum-based catalysts are widely used for the ROP of lactones due to having ability of good control over the reaction. Initiation of ROP of lactones and lactides has been realized by using aluminum trialkoxides and aluminum alkyl dialkoxides (Figure 2.7) as catalysts. Aluminum alkoxide initiated ROP of lactones progresses through the coordination-insertion mechanism. Since the initiation reaction is faster in comparison to propagation reaction, polymers can be obtained with narrow molecular weight distribution. Additionally, by using aluminum alkoxides catalysts, aliphatic (co)polyesters such as comb-like, star-shaped, graft and hyperbranched can be obtained [46, 48].

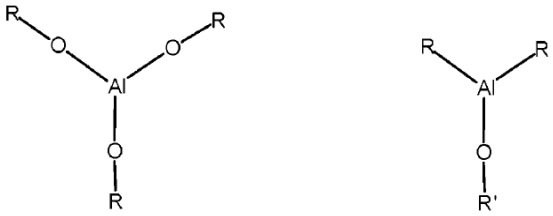

Figure 2.7 : Structure of aluminum alkoxides [46].

2.1.2.2 Lanthanide alkoxides

Yttrium isopropoxide and yttrium 3-oxapentoxide are two examples of lanthanide alkoxides, which are used for the ROP of CL and lactides. Ligands and oxidation state of these rare earth metals affect the polymerization yield, molecular weight, polydispersity and stereoregularity of the resulting polymer [46].

2.1.2.3 Tin-based catalysts

Tin (II) carboxylates, oxides and tin (IV) alkoxides are the organometallic compounds for the ROP of lactones and lactides. Tin (II) 2-ethylhexanoate or stannous octoate (SO) is the most widely used catalyst for ROP of aliphatic polyesters. SO has low toxicity, low cost and high efficiency. Additionally, it is commercially available, easy to handle and soluble in common organic solvents and lactones. Since, it has been approved as a food additive by US Food and Drug Agency, production process does not require an additional catalyst removal step [46, 48-49].

For ROP in the presence of SO, several mechanisms have been proposed in the literature. In case of coordination-insertion polymerization mechanism, firstly SO reacts with a nucleophilic compound, generally alcohol or hydrogen compounds, thus tin alkoxide forms and initiates the polymerization (Figure 2.8) [46, 48].

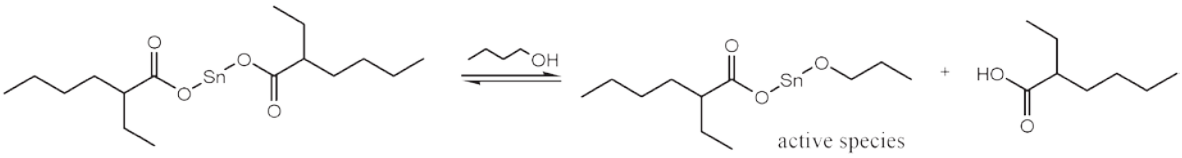

Figure 2.8 : Formation of tin alkoxide complex [49].

The type and amount of the alcohol is very important due to acting as initiator. Because, the nucleophilic attack of the formed alkoxides on the carbonyl carbon of the monomer is the rate-determining step in the ROP. Determining the amount of alcohol which will be purposely added into the reaction medium is an effective way of controlling the molecular weight of the resulting polymer.

When compared to aluminum isopropoxide, SO has higher activity in terms of reaction times. A polymerization reaction can take a few days in the presence of aluminum isopropoxide, while it can take only a few hours with SO. Additionally, as

mentioned before SO is generally utilized together with an alcohol in order to obtain high molecular weight polymers (up to 10^5-10^6 g/mol) and to decrease the reaction time [45].

The bulk polymerization of CL catalyzed by SO at 130^{o}C temperature was performed and the initiation mechanism of polymerization was explained [50]. As given in Figure 2.9a, in the beginning of polymerization, hydroxyfunctional compounds (such as water) or deliberately added alcohol react with SO and tin alkoxide species form while 2-ethylhexanoic acid releases. In Figure 2.9b, the formed tin alkoxide reacts again with another alcohol molecule. Tin dialkoxide initiator forms with the second equivalent 2-ethylhexanoic acid. If there is adventitious water in the reaction medium, it can react with tin alkoxide and unwanted tin alkoxide derivative may form, which is shown in Figure 2.9c. This tin alkoxide derivative is less efficient as an initiator because of being more thermodynamically stable. Through the coordination-insertion mechanism, tin dialkoxide initiator attacks a lactone monomer and the first actively propagating chain end generates (Figure 2.9d). This active chain end may propagate by the addition of other monomers. On the other hand, it may interact with hydroxyl groups of remaining initiator or another hydroxy chain ends generated in situ (Figure 2.9e) [50].

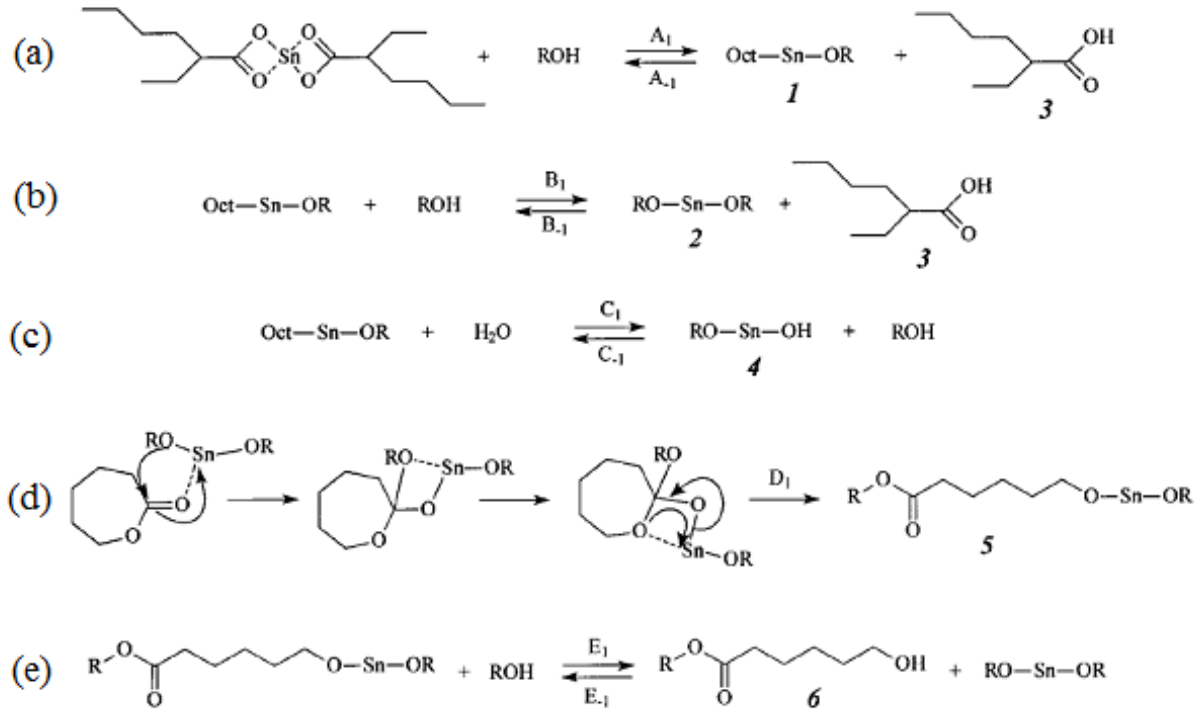

Figure 2.9 : Mechanism of initiation of CL polymerization catalyzed by SO, (a, b) formation of tin alkoxide, (c) deactivation of catalyst with reaction by water, (d) coordination-insertion of monomer into the tin alkoxide bond and (e) chain transfer from polymerizing center to unreacted alcohol [50].

2.1.3 Polycaprolactone

Polycaprolactone (PCL), which was first synthesized by ROP in the early 1930s, is an aliphatic polyester with advantageous features such as good mechanical strength, biocompatibility, biodegradability and non-toxicity. It is a semi-crystalline, hydrophobic and rubbery polymer with a very low glass transition temperature (T_g) of -60^oC and a low melting point (T_m) between 59-64^oC [26-28, 31, 51]. PCL can dissolve in chloroform, dichloromethane, carbon tetrachloride, benzene, toluene, cyclohexanone and 2-nitropropane at room temperature. Also, it is poorly soluble in acetone, 2-butanone, ethyl acetate, dimethylformamide and acetonitrile and is insoluble in alcohol, petroleum ether and diethyl ether [26].

PCL is synthesized by ROP of cyclic CL monomer in the presence of SO catalyst and an initiator having an active hydrogen atom. The structure of PCL is shown in Figure 2.10. PCL polymers can be liquids to hard waxes having different molecular

weights in a range from 200 to 100,000 g/mol. Also their crystallinity decreases, as the molecular weight increases.

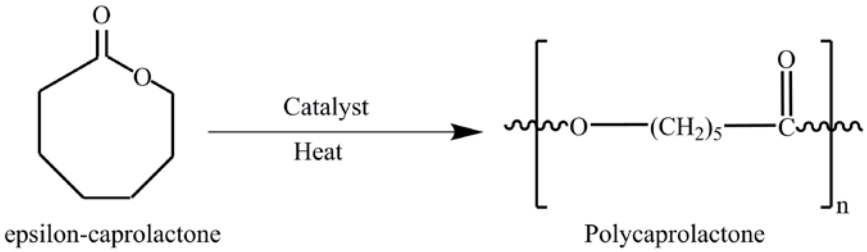

Figure 2.10 : Structure of polycaprolactone.

PCL is flexible at room temperature because of its low T_g value, and miscible with a range of polymers and organic materials. They are utilized as a plasticizer in the preparation of the blends of brittle polymers to improve stress crack resistance, dyeability and adhesion [52].

PCL can be prepared as blends with other polymers or as block and random copolymers. It is generally blended with other polymers benefiting from its good compatibility, especially to enhance the permeability of the drug delivery systems. For the copolymerization of PCL, a wide range of monomers such as ethyleneoxide, vinylchloride, chloroprene, ethylene glycol, styrene, diisocyanates, tetrahydrofuran, diglycolide, dilactide, δ-valerolactone, substituted caprolactones, 4-vinyl anisole, methyl methacrylate and vinly acetate can be used [26].

PCL has been drawn attention in drug delivery applications due to possessing benefits of tailorable degradation kinetics and mechanical properties, ease of shaping and manufacture and the controlled delivery [26].

As a conclusion, they have been investigated and used in multiple biomedical and environmental applications such as prostheses, dental implants, bandages, degradable sutures, drugs, pesticides and surgery repair materials [31, 51].

2.2 Free Radical Polymerization

Among the others, vinyl polymers are the most important industrial polymers. Polystyrene, polyethylene (high and low density), polyvinyl chloride, and polypropylene are just some of them (Table 2.1).

Table 2.1 : Some of industrially important vinyl polymers [53].

Polymer	Major uses
Polystyrene	Packaging, foam insulation, appliances, housewares, toys
Polyethylene, low density	Packaging film, wire and cable insulation, toys, flexible bottles, housewares, coatings
Polyvinyl chloride	Construction, rigid pipe, flooring, wire and cable insulation, film and sheet
Polypropylene	Packaging, textiles, stationery, containers, laboratory equipment, automotive parts

From this point of view, vinyl polymers have been studied extensively in polymer technology. These polymers are prepared by free radical polymerization mechanism. Free radical polymerization has three steps:

- Initiation: radical generation from nonradical species.
- Propagation: radical addition to substituted alkene.
- Termination: atom abstraction or radical-radical recombination reactions.

Propagations are usually chain reactions. As the reaction proceeds, double bonds of vinyl monomers are consumed. Some monomers such as styrene and methyl methacrylate can polymerize by heating. But, most monomers need initiators. These initiators are peroxides or hydroxyperoxides, azo compounds, redox initiators and photoinitiators [53].

The copolymerization of vinyl monomers is similar to that of homopolymerization, but the reactivities of monomers are different from each other. Thus, the overall rate, molecular weight distribution, copolymer composition and microstructure depend on the propagation kinetics of copolymerization [54].

2.3 Triglyceride Oils in Production of Polymers

The continuous depletion of fossil sources, green house effects due to CO_2 emission, non-degradability and non-recyclability are the main reasons for preferability of renewable raw materials instead of petrochemical derivatives by the industrial

manufacturers. In recent years, the utilization of renewable resources for the energy and material production has been drawn great attention in both industry and academy. With this background, it is vital to develop polymeric materials from renewable resources due to the detrimental influences of fossil sources on environmental and economic issues. Natural oils, polysaccharides such as cellulose and starch, wood and proteins are the most widely used raw materials in the chemical industry [6-10, 55-56].

Triglyceride oils, which have benefits of inexpensiveness, abundancy, biodegradability, low toxicity and high purity, are the most important renewable resources among the others. They have a widespread usage as raw materials for the production of cosmetic products, lubricants, surfactants, inks, plasticizers, resins, coatings and agrochemicals in addition to their applications in food industry. Additionally, plant oils are also used for the production of biorenewable fuels [6, 8, 56-57].

The history of drying oils has started in prehistoric times. They are the oldest binders for paints that can form solid films. The double bonds of the fatty acid chains present in the molecular structure of drying oils react with the oxygen of the atmosphere, thus polymerized and crosslinked films can be obtained. The applications of triglycerides in polymer science were reviewed in view of coating and resin preparations and it was concluded that they are promising renewable resources to synthesize polymers during the 21st century [2, 56].

2.3.1 Structure and composition of triglyceride oils

“Oil” means, trigylcerides that are in liquid state at room temperature. Natural oils are triglyceride esters of fatty acids. Triglycerides contain three fatty acids attached to a glycerol molecule, which is shown in Figure 2.11. Fatty acids comprise almost entirely straight chain aliphatic carboxylic acids [11, 58].

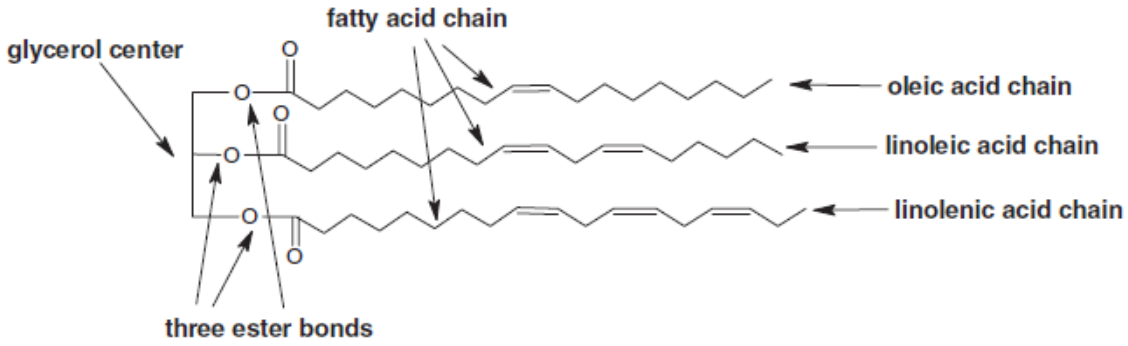

Figure 2.11 : Structure of triglycerides [58].

Their chain length differs from 14 to 22 carbons, but most of them have 18 carbons, with 1-3 double bonds. The stereochemistry of the double bonds of the fatty acids, length of carbon chains and their degree of unsaturation are the most important features which affect their physical and chemical structures. Actually, more than 1000 fatty acid types exist in the nature, nearly 20 of them are of commercial interest. The main fatty acids are palmitic, oleic and linoleic, sometimes accompanied by stearic acid and by linolenic acid. Myristic, lauric, erucic, hexadecenoic, petroselinic, γ-linolenic acid, eleostearic and isomers, ricinoleic and vernolic acid exist only in specialty oils [11, 56]. Some examples of fatty acids are given in Figure 2.12.

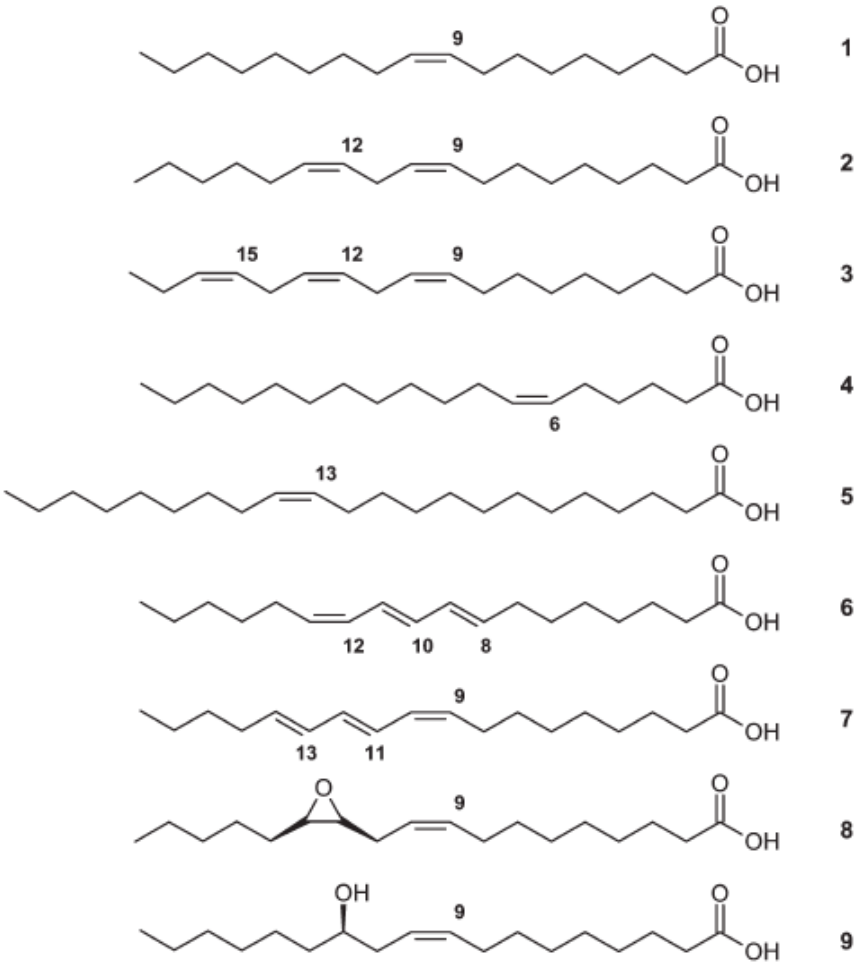

Figure 2.12 : Some examples of fatty acids (1) oleic acid, (2) linoleic acid, (3) linolenic acid, (4) petroselinic acid, (5) erucic acid, (6) calendic acid, (7) α-eleostearic acid, (8) vernolic acid, (9) ricinoleic acid [56].

According to the unsaturation degree, in other words iodine value (amount of iodine in grams that can react with double bonds present in 100 g of sample under specified conditions) oils can be categorized as three classes:

- Drying oils (iodine value >170)
- Semi-drying oils (iodine value, 100-170)
- Non-drying oils (iodine value < 100).

The fatty acid content of triglyceride oils depends on the plant, the crop, the season and the growing conditions. Typical fatty acid compositions of some oils are given in Table 2.2.

Table 2.2 : Fatty acid composition of some oils [18].

Fatty acid	Castor oil (%)	Linseed oil (%)	Oiticica oil (%)	Palm oil (%)	Rapeseed oil (%)	Refined tall oil (%)	Soybean oil (%)	Sunflower oil (%)
Palmitic acid	1.5	5	6	39	4	4	12	6
Stearic acid	0.5	4	4	5	2	3	4	4
Oleic acid	5	22	8	45	56	46	24	42
Linoleic acid	4	17	8	9	26	35	53	47
Linolenic acid	0.5	52	—	—	10	12	7	1
Ricinoleic acid	87.5	—	—	—	—	—	—	—
Licanic acid	—	—	74	—	—	—	—	—
Other	—	—	—	2	2	—	—	—

2.3.2 Sunflower oil

Sunflower oil is extracted from *Helianthus annus* plant. Sunflower oil comprises of mainly linoleic acid (65%), at a lesser amount of oleic acid (24%) and palmitic acid (6%) [11, 57, 59]. Sunflower oil is one of the commonly used triglyceride oils for the preparation of oil-modified polymers. Since it is a semi-drying oil, the paint formulations, which they are added, give good film properties [18].

2.3.3 Relationship of triglycerides to the chemical industry

Since triglycerides have a widespread utilization in chemical industry, a lot of modification and synthesis reactions exist in order to manufacture the desired products for the specific applications. Some examples for these reactions are hydrolysis, esterification, ester exchange, oxidation, reduction and the other types of modifications of oils.

The most important reactions from the point of fatty acid and lipid chemistry are converting acids to esters or esters to acids and the exchange of ester groups. Through these reactions, which are shown in Figure 2.13, a wide variety of processes are applicable from preparation of methyl esters for gas chromatography analysis to industrial productions of oleochemicals and biodiesel.

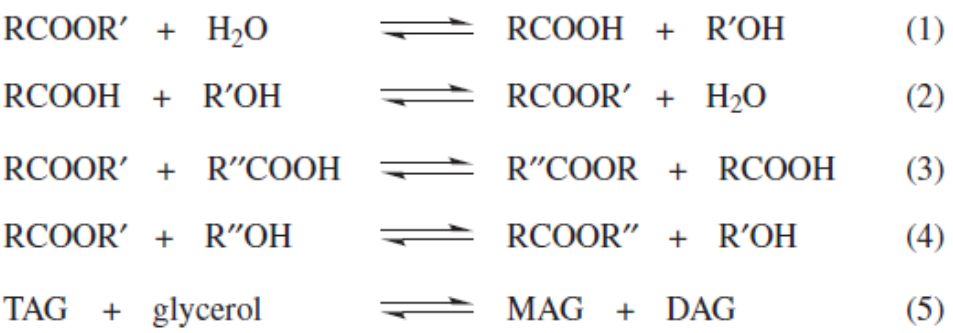

Figure 2.13 : Exchange reactions at the carboxyl group (1) hydrolysis, (2) esterification, (3) acidolysis, (4) alcoholysis, and (5) glycerolysis. The starting esrer RCOOR' will often be a triacylglycerol. MAG: monoacylglycerol, DAG: diacylglycerol, TAG: triacylglycerol. [11].

Glycerolysis is one of the important reaction of triglycerides in view of coating technology. Glycerolysis is an ester exchange reaction conducted by the reaction of triglyceride with glycerol in the presence of a catalyst such as sodium hydroxide, sodium methoxide and calcium hydroxide. By this reaction, partial glycerides with modified composition and properties are obtained [11].

2.3.4 Film drying of oil-based coatings

As mentioned before, triglycerides can undergo polymerization due to susceptibility of their double bonds and adjacent allylic carbons to oxidation. While the oxidation of unsaturated oils reduces the nutritional quality in food industry, it is a vital reaction from the point of paint industry.

When the double bonds of the fatty acids in drying oils are oxidized, they form a film on the applied surface and a crosslinked polymer structure is obtained. This oxidative radical chain reaction, or in other words, drying occurs in five steps [11, 56]:

- Beginning of reaction is induction period, physical or chemical changes are not observed and antioxidant compounds are consumed.
- The second step involves the formation of hydroperoxides through the attack of oxygen to bisallylic hydrogen atoms.
- In third step, the conjugation takes place by the isomerization of double bonds (from cis to trans).
- By decomposition of peroxides, free radicals form in the medium and the process turns into autocatalytic reaction.

- In the last step, polymerization takes place through the recombination reactions between the formed radicals, and also scission reactions start. During this step high molecular weight crosslinked products form with accompanying increase in viscosity. Additionally, low molecular weight carbonyl and hydroxyl groups, carbon dioxide, water and some volatile products release.

A brief summary of the crosslinking reactions of drying oils is depicted in Figure 2.14. The importance of the unmodified oils and fats in view of coating technology is displayed by means of these reactions [56].

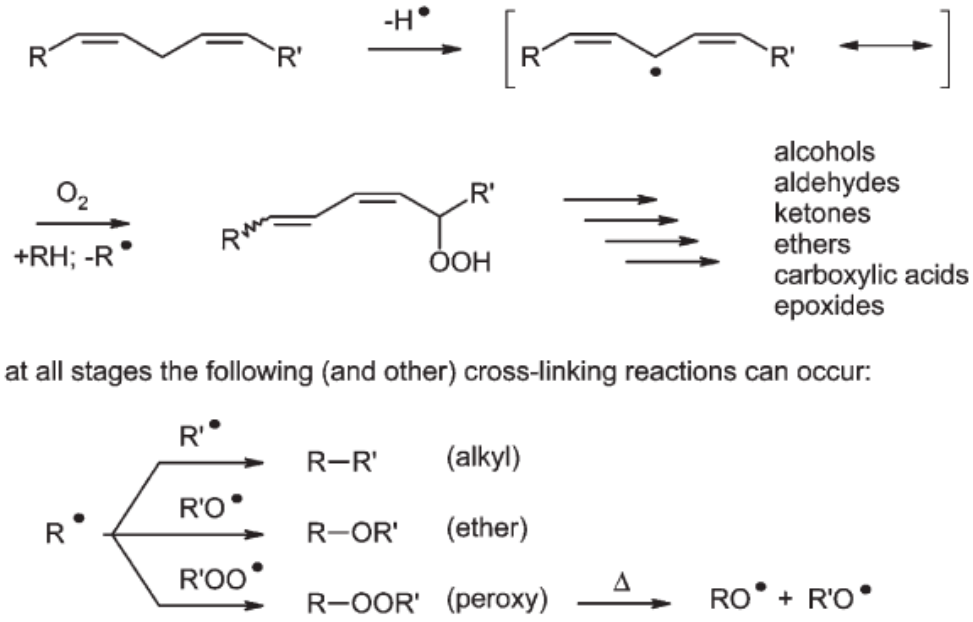

Figure 2.14 : A simplified scheme of the overall crosslinking reactions of drying oils [56].

From the point of reaction kinetics, it is thought that the beginning, i.e. the induction period is slow, but the reaction rate increases after reaching to autocatalytic state. There are a lot of parameters that the rate depends on such as temperature, light and the content (traces of heavy metal or inhibitors) of oil or coating. The drying reaction of 9,12-octadecadienoic, in other words linoleic acid takes place as shown in Figure 2.15.

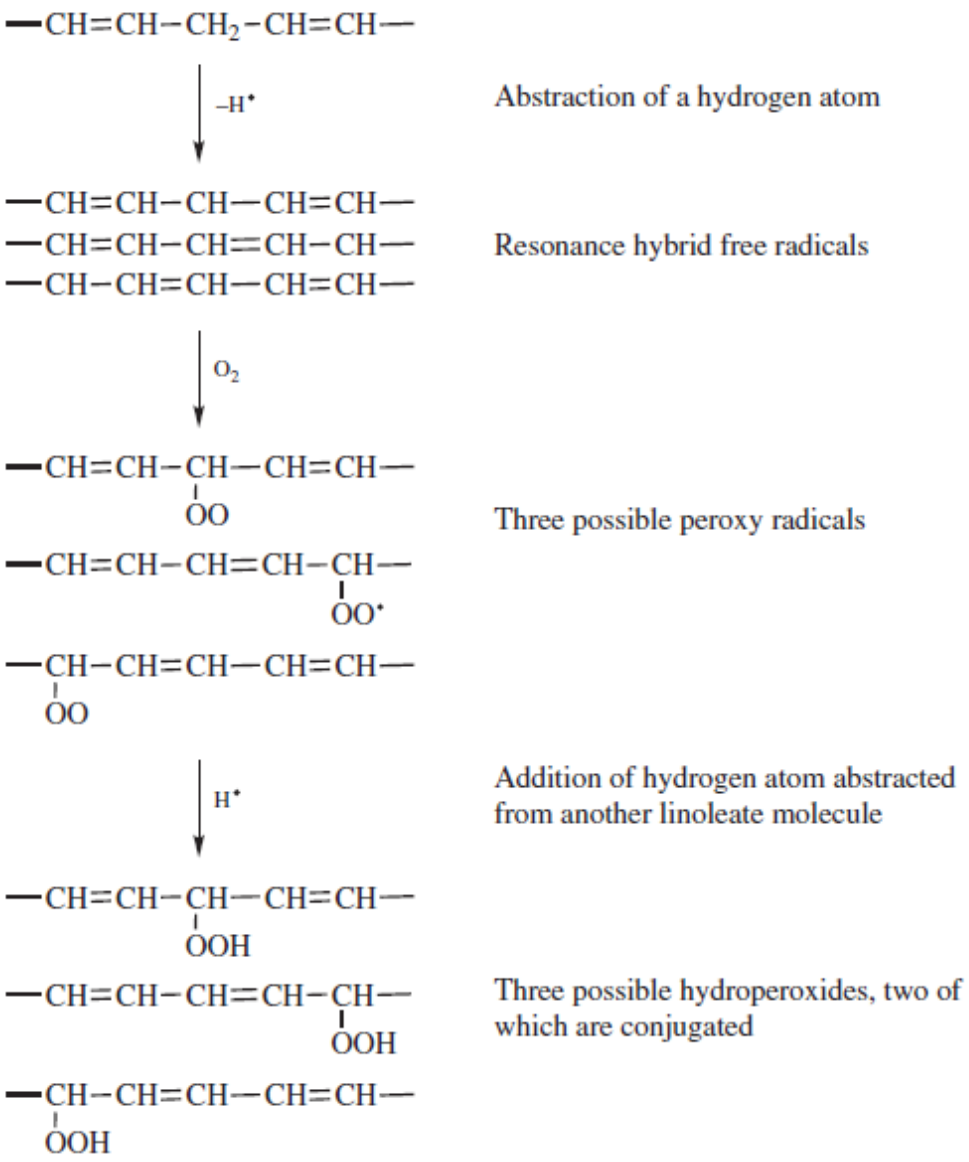

Figure 2.15 : Drying mechanism of linoleic acid [11].

In order to explain the drying of linoleic acid in more detail, it can be said that the dehydrogenation from the α-methylene group to generate a radical is postulated as the initial step. The proposal of the removal of hydrogen atom via free radical reaction is supported by the fact that this process needs a considerable amount of energy. The $R^{\bullet}$ radical forms by the hydrogen abstraction of radical $A^{\bullet}$ from RH molecule (2.1).

$$RH + A^{\bullet} \rightarrow R^{\bullet} + AH \qquad \textbf{(2.1)}$$

Resonance hybrid free radicals are formed and double bonds shift to a conjugated position due to being allylic of radical to the double bonds. This is followed by (2.2), (2.3):

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad \textbf{(2.2)}$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad \textbf{(2.3)}$$

The reaction in brief is formation of hydroperoxide (2.4):

$$RH + O_2 \rightarrow ROOH \quad \textbf{(2.4)}$$

This mechanism explained above belonging to the autooxidation of linoleate represents the properties of free radical chain reaction. A small amount of substance can initiate the reaction by forming free radicals via decomposition.

There is a common assumption on the mechanism of chain propagation reaction, but the chain initiation reaction is a debated topic. In the beginning, hydroperoxides are proposed as the initial products of autoxidation. Several authors agreed that initiation reaction is triggered by the attack of oxygen to the double bonds, not the α-methylenic carbon-hydrogen bond. Because, the cleavage of this bond requires high amount of energy. But, some other authors proposed that the oxidative attack to the double bonds is limited, so that sufficient amount of radicals cannot be produced. It is suggested that a cyclic transition state forms by the attack of oxygen to the double bonds and then, this cyclic substance cleaves and hydroperoxides yield.

Since it is claimed that direct attack of oxygen is difficult from the thermodynamic point of view, it has been thought that trace metal contaminants can catalyze the initiation by producing free radicals via electron transfer. By the addition of cobalt to the medium, the initiation reaction is accelerated [11, 56, 60]. This reaction takes place according to the following steps (2.5)-(2.8):

- Trace hydroperoxides yield free radicals by reduction.

$$Co^{2+} + ROOH \rightarrow Co^{3+} + OH^{-} + RO^{\bullet} \quad \textbf{(2.5)}$$

- Metal ion reacts with oxygen directly. The formed oxygen radical ion can initiate the chain reaction of oxidation.

$$Co^{2+} + O_2 \rightarrow Co^{3+} + O_2^{-\bullet} \quad \textbf{(2.6)}$$

- The complex reaction takes place between the metal compounds and oxygen.

$$Co^{2+} + O_2^{-} \rightarrow Co^{3+\bullet}O_2 \quad \textbf{(2.7a)}$$

$$Co^{3+}{}^{\bullet}O_2 + XH \rightarrow Co^{3+} + X^- + HO_2^{\bullet} \quad \textbf{(2.7b)}$$

- Oxidation occurs by the metal ion and radical forms.

$$Co^{3+} + RH \rightarrow Co^{2+} + H^+ + R^{\bullet} \quad \textbf{(2.8)}$$

2.3.5 Polymers from triglyceride oils

From the point of coating applications, direct use of triglycerides as binders gives films with insufficient properties such as drying speed, hardness, adhesion and durability. With this background, they are used in the preparation of binders together with alkyds, epoxy esters, uralkyd resins and other synthetic polymers [2, 6, 10-11].

2.3.5.1 Alkyd resins

Among the organic binders, alkyd resins are the most important polyesters with their economical benefits and ease of application [18, 61-64]. Two methods exist for the production of alkyd resins: monoglyceride (alcoholysis) and fatty acid. In the monoglyceride method (Figure 2.16), triglycerides are first reacted with polyol by the alcoholysis reaction. After this step, obtained free hydroxyl groups are used for the further esterification with polyacid or acid anhydride.

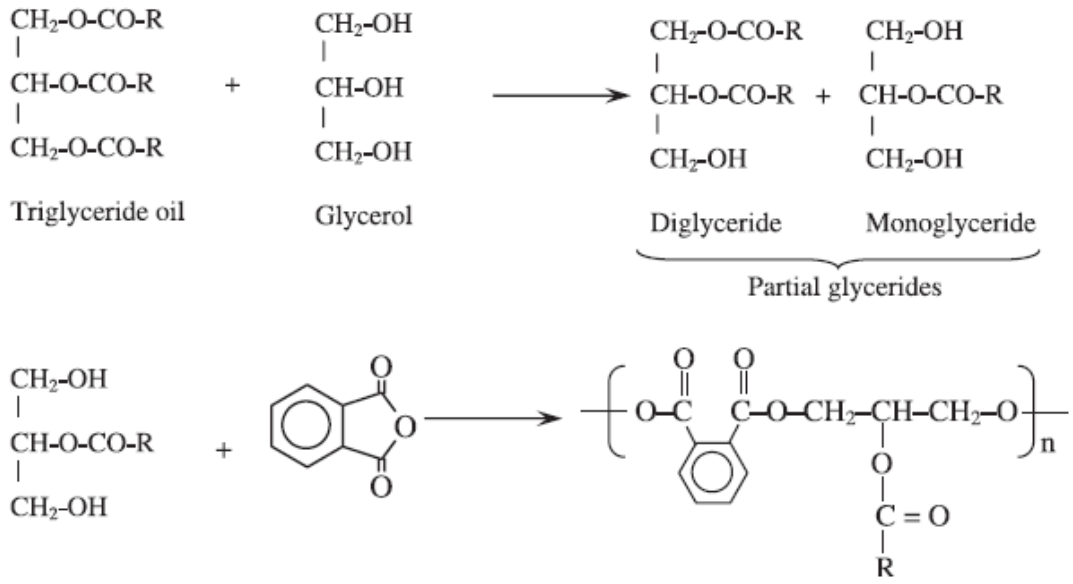

Figure 2.16 : Preparation of alkyd resin [18].

In the fatty acid method, polyacid, polyalcohol and fatty acid are added together at the beginning of the reaction. Since free fatty acids are used instead of oils as the starting component, this method is more preferable because of avoiding the

alcoholysis step. The resulting resins from this method involve more linear backbone chain structure, higher molecular weight, higher viscosity, good drying and hardness properties in comparison with the resins prepared by conventional process [11, 18].

2.3.5.2 Urethane oils

The importance of triglycerides for the polyurethanes arises from the polyols used in urethane reaction, since polyurethanes are synthesized by reaction of diisocyanates with hydroxyl containing compounds [18, 65]. Triglycerides are used in the polyurethane formulations after generating functional groups by the reactions such as epoxidation, ring opening, ozonolysis, alcoholysis and hydration [26, 66-68].

Erciyes et al. studied solvent-soluble urethane oils for coating applications. Sunflower oil-based urethane oils were synthesized by using three different isocyanate compounds: toluene diisocyanate, hexamethylene diisocyanate and poly(1,4-butandiol) toluene 2, 4 isocyanate terminated prepolymer. The effects of amount and type of diisocyanate component on the film properties were investigated. Aromatic diisocyanate based polymers gave good water resistance. Also, it was observed that when the amounts of diisocyanate compounds increased, shorter drying times were achieved. Urethane oils showed good alkali and water resistances in comparison with alkyd resins [24].

In another study of Erciyes et al., urethane oils were prepared by using some seed oils, *Ecballium elaterium* and *P. mahaleb* as the oil component. Since these oils included conjugated trienoic acids, the resulting polymers showed good film properties such as short drying time, good water, alkali and acid resistances [69].

However, castor oil was added directly to the urethane reaction without modification due to including high amount of recinoleic acid, which is a hydroxyl containing fatty acid. The synthesis of epoxy-terminated polyurethane prepolymer is given in Figure 2.17.

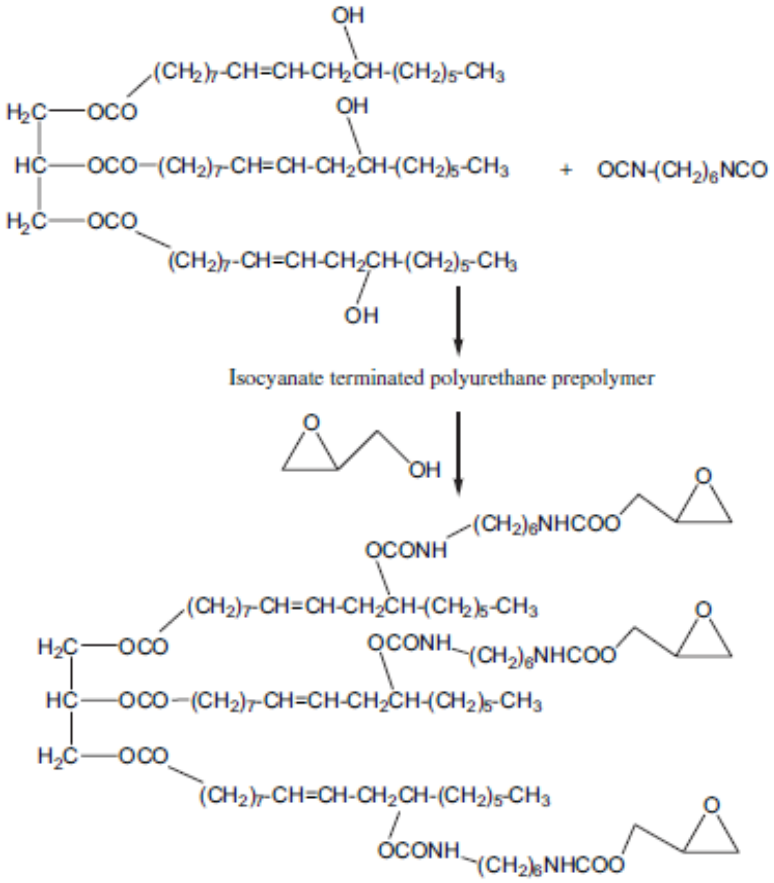

Figure 2.17 : Synthesis of epoxy-terminates polyurethane prepolymer [66].

2.3.5.3 Modification of oils with vinyl monomers

The copolymerization of triglyceride oils with vinyl monomers such as styrene, α-methylstyrene, cyclopentadiene and divinyl benzene is one of the oldest methods for modification of oils [18]. It has been investigated by several researchers [67, 70-73].

Erciyes et al. suggested an alternative method, namely macroinitiator, for the styrenation of oils [12]. The macroinitiator method is based on the attachment of styrene monomers to the oil via a low molecular azo initator. First, azo functionalities are generated on the oil, then oil-styrene copolymers are obtained by the thermal decomposition of these azo groups without pretreatment (Figure 2.18).

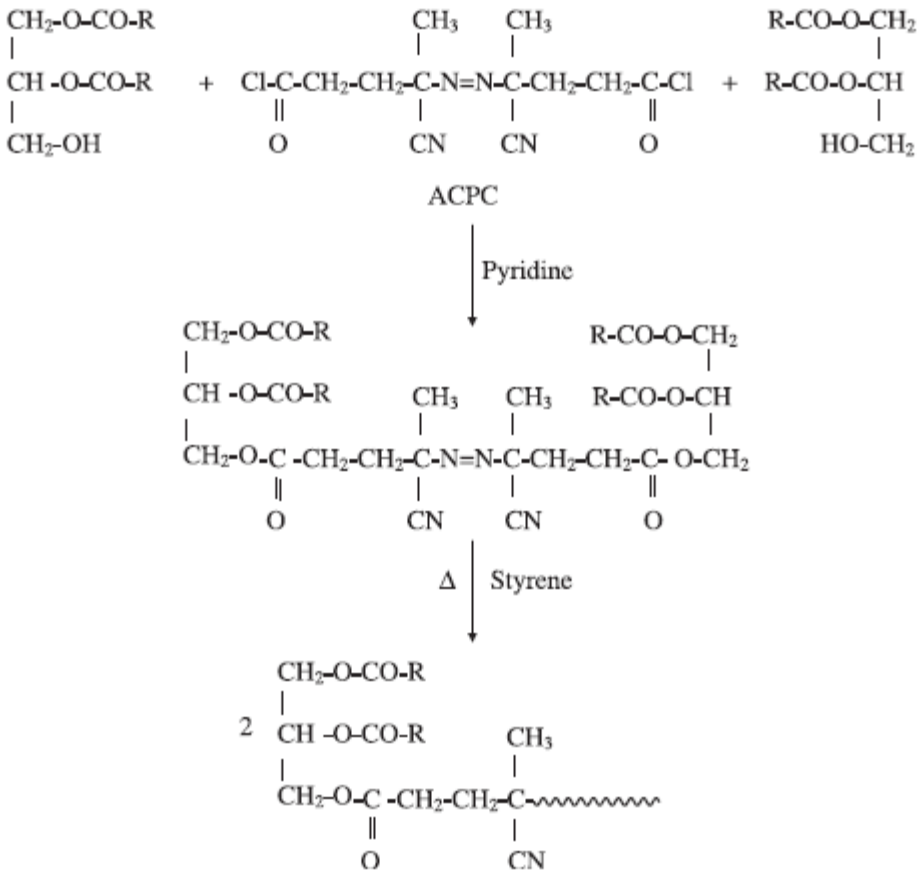

Figure 2.18 : Styrenation of triglyceride by macroinitiator method, ACPC: 4,4'-azobis(4-cyanopentanoyl chloride) [18].

Homopolystyrene formation as a by-product did not observed due to generation of active radical sites directly on the oil backbone. With the aid of this method, polymer coatings were synthesized using thermally splitted secondary esters of castor oil (Figure 2.19) and interesterification product of linseed and castor oils (Figure 2.20) [13-14]. The styrenated oils prepared by macroinitiator method gave good film properties.

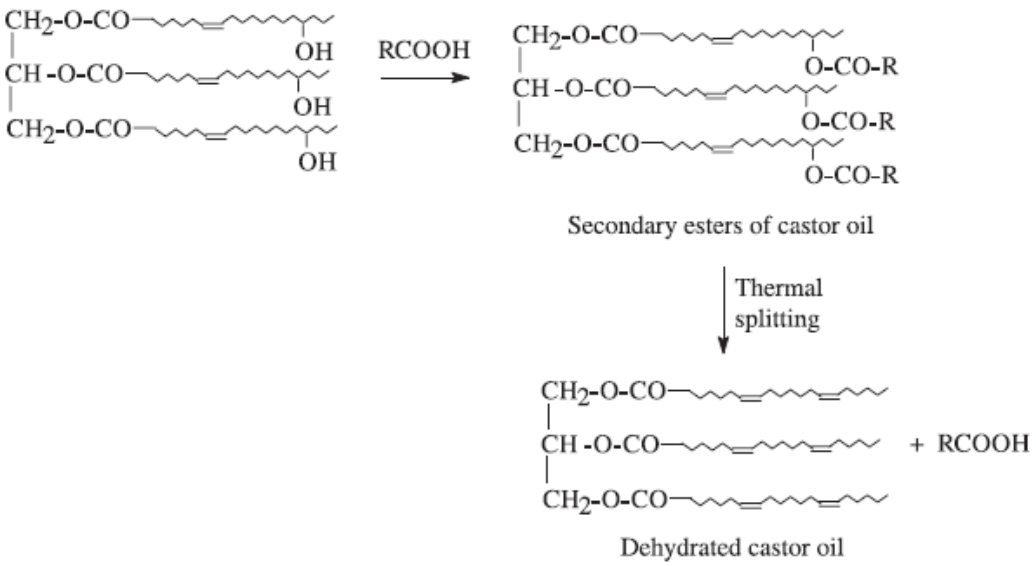

Figure 2.19 : Modification of castor oil [18].

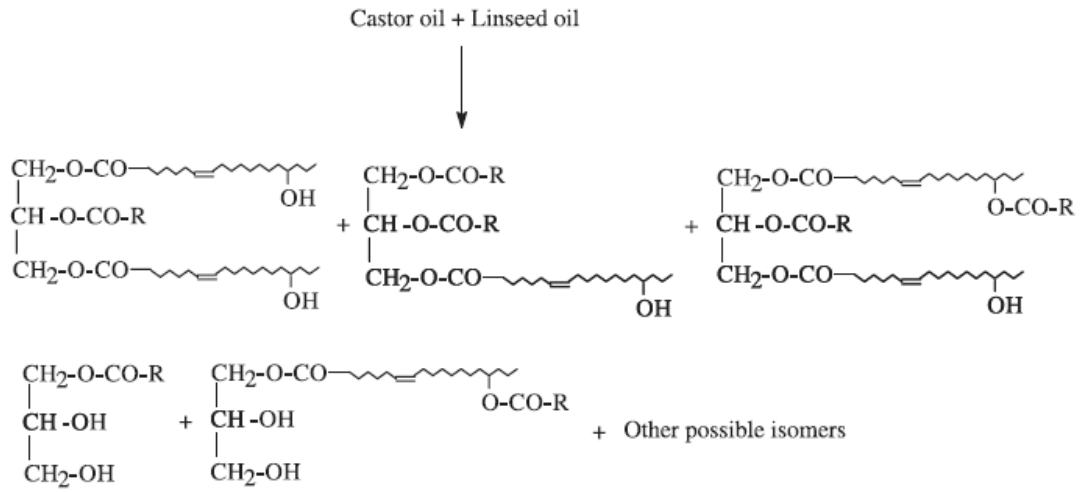

Figure 2.20 : Interesterification of castor oil and linseed oil [18].

Another method reported by Erciyes et al., was macromonomer (macromer) technique. In macromonomer method, first a macromer is synthesized by the reaction between hydroxyl containing oils with a vinyl monomer such as acrylic acid or methyl methacrylate, and then obtained product is homopolymerized and copolymerized with styrene (Figure 2.21).

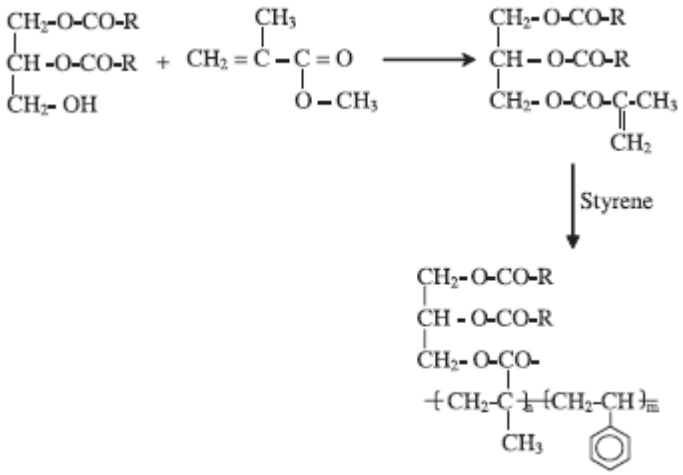

Figure 2.21 : Styrenation of triglyceride by macromonomer method [18].

In another study, transesterification product of linseed oil and castor oil is used to obtain a macromonomer. For this purpose, the transesterification product was esterified with acrylic acid to obtain vinyl groups on the acid molecules. Then, macromonomer was subjected to homopolymerization and copolymerization reactions by following the same route (Figure 2.22) [16].

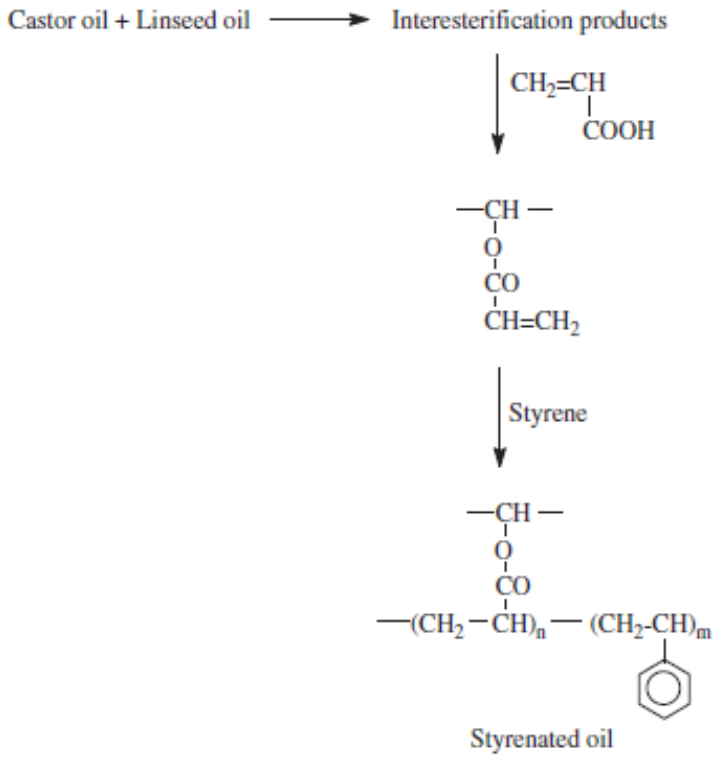

Figure 2.22 : Styrenation of castor oil and linseed oil mixture by macromonomer method [18].

Erciyes et al. applied nitroxide mediated radical polymerization (NMRP) method as a controlled free radical living polymerization, for the preparation of styrenated oil to obtain a narrow molecular weight distribution. For this purpose, firstly an oil-based macroinitiator was synthesized by reacting partial glycerides with 4, 4-azobis-4-cyanopentanoyl chloride (ACPC). Then, this macroinitiator was polymerized with styrene in the presence of 2,2',6,6'-tetramethylpiperidinyl-1-oxy (TEMPO). The resulting polymer had narrow polydispersity and good film properties except flexibility and adhesion. These properties were improved by further polymerization of final product with oil-based macromonomer (Figure 2.23) [21].

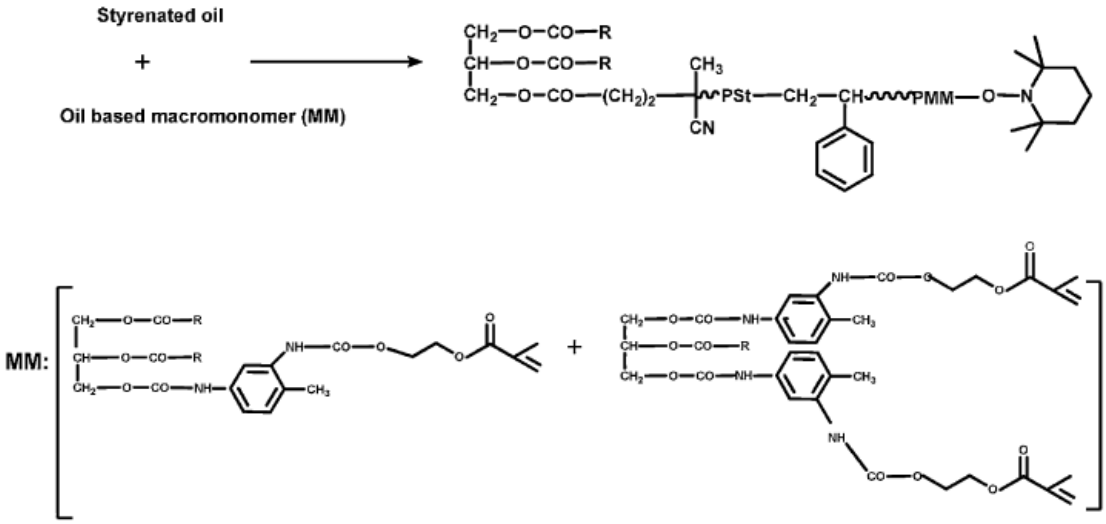

Figure 2.23 : The reaction of styrenated oil with oil-based macromonomer [21].

Erciyes et al. proposed a novel approach involving a combination of air blowing and NMRP processes for the styrenation of linseed oil. Hydroperoxide groups were obtained on the fatty acid chains during air blowing and used as a macroinitiator in NMRP of styrene with TEMPO. Styrenated oil samples showed good film properties (Figure 2.24) [22].

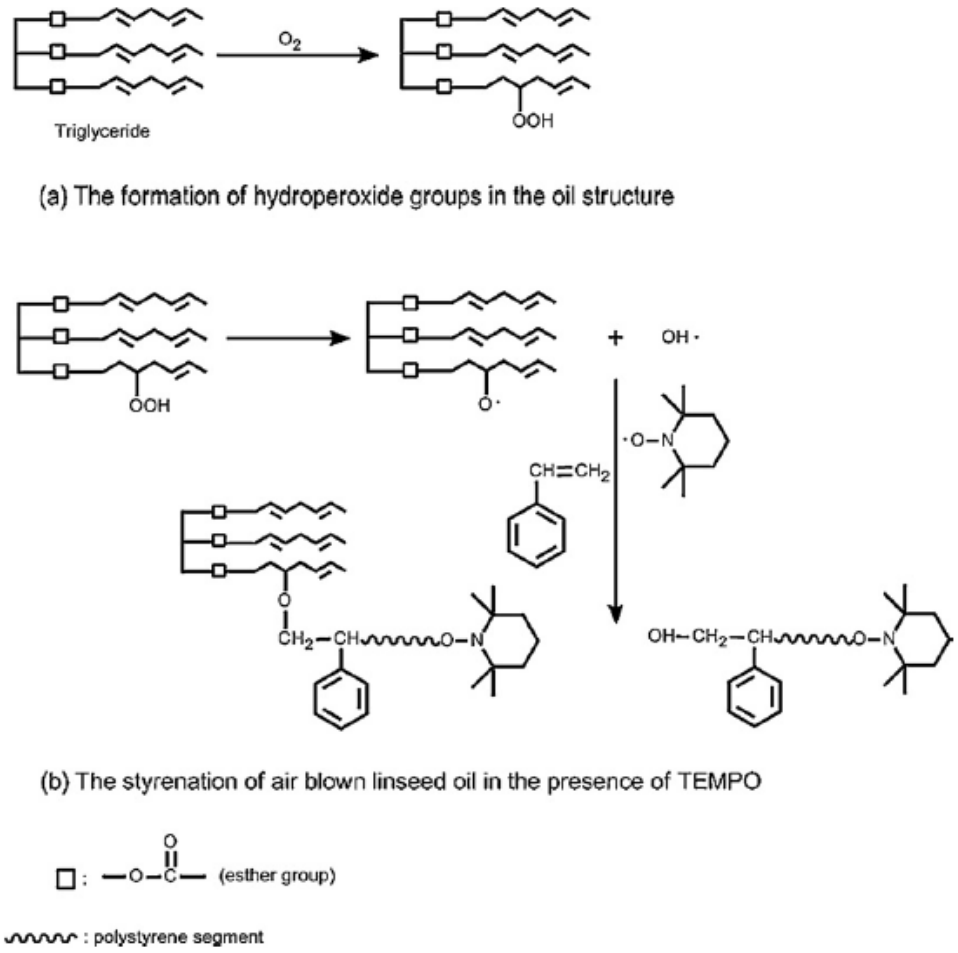

Figure 2.24 : (a) The formation of hydroperoxide groups in the oil structure , (b) and styrenation of air-blown linseed oil in the presence of TEMPO [22].

2.3.5.4 Modification of oils with nonvinyl monomers

Erciyes at al. also reported the modification of triglycerides with nonvinyl monomers of 3-aminopropyltriethoxysilane [23], benzoxazine [74], and methylolated abietic acid [25].

2.4 Benzoxazines

Benzoxazine comprises of an oxazine ring attached to a benzene molecule. Oxazine is a heterocyclic six-membered compound containing one oxygen and one nitrogen atom. Although the first report on the synthesis of benzoxazine was published in 1944 (by Holly and Cope), properties of polybenzoxazine were first reported in 1994 (by Ning and Ishida) [75].

Benzoxazines, as recently developed thermosetting phenolic resins, have been studied extensively by many researchers. The reason for having great interest is their unique properties. These can be listed as follows: near-zero volume changes, low water absorption, relatively high T_g, high char yield (between 160-400^oC), no strong acid catalysts or additives required for curing, no by-products during curing, fast development of properties at low conversions, thermal and chemical stability, low flammability, stable dielectric constant, and molecular design flexibility [75-81]. Moreover, their molecular design flexibility allows synthesis of materials with tailored properties for the various specific applications. The possible hydrogen bond interactions such as inter and intramolecular OH...OH, intramolecular OH...N six-membered hydrogen bonds and OH...π interactions are thought as the reasons for possessing these interesting properties explained above [75].

Besides these intriguing features, neat polybenzoxazines have some disadvantages including high curing temperature, difficulty in processing, and brittleness. To overcome these drawbacks, a lot of methods have been used, such as synthesis of benzoxazine monomers with additional functionality [33, 81-85], incorporation of benzoxazine into the polymer structure [39, 41] and preparing benzoxazine-based composites and alloys [35, 37-38, 42-43, 76, 86-94].

2.4.1 Synthesis of benzoxazine monomers

Benzoxazine monomers are prepared using primary amines, formaldehyde and phenol via Mannich condensation reaction (Figure 2.25) by employing solution or solventless methods. From the point of structure-property relationship, the choice of raw materials is very critical due to having a direct effect on the resulting monomers.

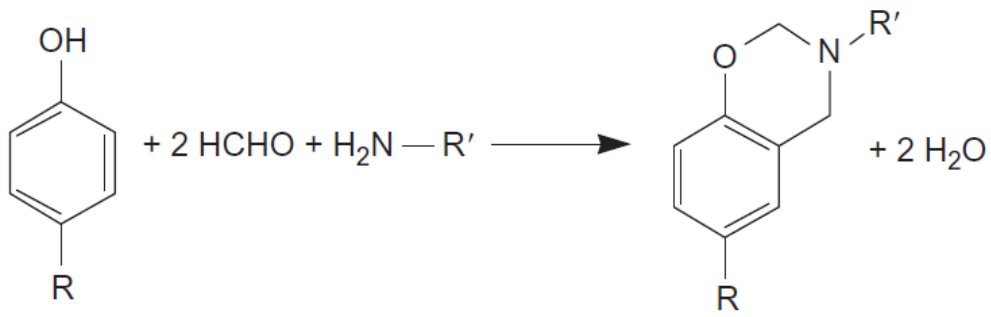

Figure 2.25 : Synthesis of benzoxazine monomers [75].

Monofunctional, difunctional (bisphenol, diamine), with polymerizable group such as acetylene, allyl, epoxy, glycidyl, maleimide, methacrylate, nitrile, norbornone, oxazoline, phthalonitrile, propargyl and vinyl ester itself, with potentially polymerizable group with a suitable compound (phenol, carboxyl, methylol, ethylol, etc.) benzoxazine monomers and reactive polybenzoxazines (main-chain, side chain and telechelic type) were reported in the literature [75].

2.4.2 Ring opening polymerization of benzoxazines

The six-membered heterocycle structure of oxazine ring provides the driving force for ROP, under specific conditions. High basicity (by Lewis deifinition) of oxygen and nitrogen atoms of the oxazine ring triggers the initiation of cationic polymerization and supports opening of the ring. Two mechanisms have been proposed for the curing of benzoxazines.

2.4.2.1 Cationic polymerization of benzoxazines

a) Acid catalyzed polymerization

It was reported that the usage of catalysts for the curing of benzoxazines can reduce the induction time and accelerate the reaction rate. In the presence of acid catalysts, benzoxazine can protonated via displacement of the proton of nitrogen atom to the oxygen atom. Thus, iminium ions form in the chain structure. After the protonation of oxygen atom to form an iminium ion, electrophilic aromatic substitution takes place (Figure 2.26).

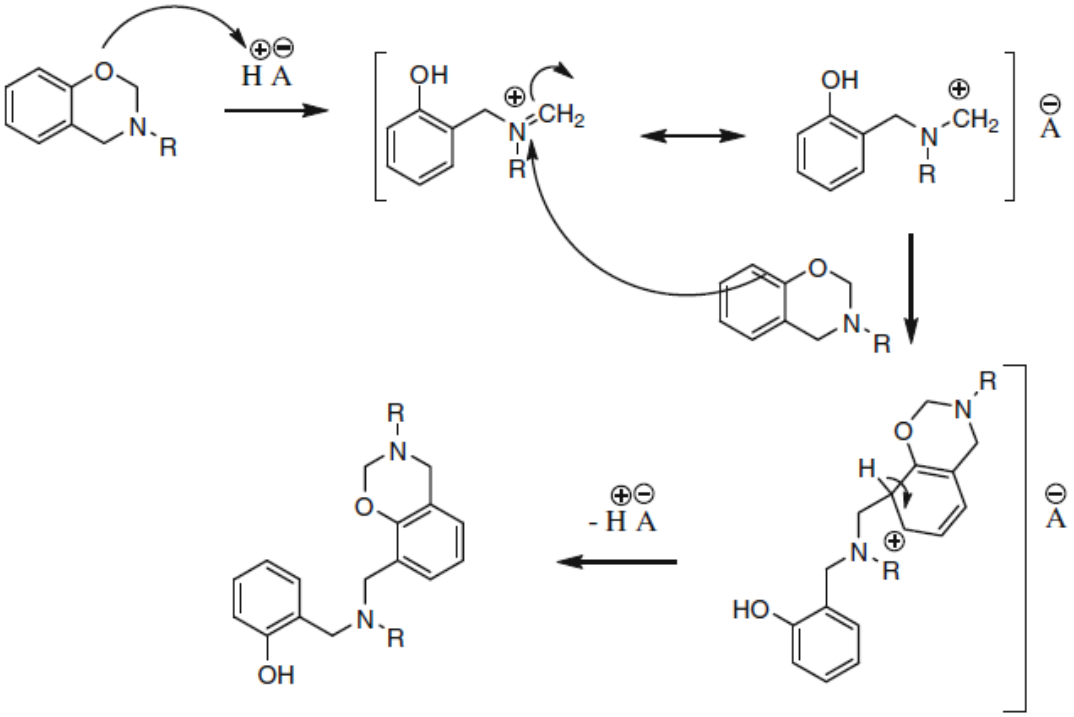

Figure 2.26 : Acid catalyzed ROP of benzoxazine monomer [95].

When there was no catalyst in the reaction medium, benzoxazine can cure by the catalytic effect of phenols formed by the ring opening from trace impurities, at 160 and 170°C temperatures. When one benzoxazine ring opens, one trisubstituted benzene ring forms, simultaneously, since the ring opening and Mannich base bridge formation are the successive reactions. By the attack of cationic initiator, the protonated oxygen atom initiates the reaction. The polymerization reaction progresses via the addition of monomers through the reaction between the intermediate and the oxygen of another oxazine ring. The formation of Mannich bridges takes place and polybenzoxazine structure is obtained [77, 96-98].

Some compounds used for cationic polymerization are boron trifluoride, phosphorus pentachloride, mineral acids such as sulphuric acid, organic acids such as phenol and substituted phenols and carboxylic acids such as trifluoroacetic acid, formic acid, acetic acid, adipic acid and sebacic acid [95].

Additionally, cationic polymerization has a drawback that the resulting polymer network may have low thermal stability and brittleness because of the residual catalyst trapped in the network [95].

b) Photo-initiated polymerization

In this type of polymerization, simultaneous ring opening reaction of the protonated monomer takes place either at the oxygen or nitrogen atoms in the presence of radical sources and photosensitizers [77].

2.4.2.2 Thermal polymerization of benzoxazines

As already mentioned, benzoxazines can be thermally polymerized without adding a curing agent (Figure 2.27).

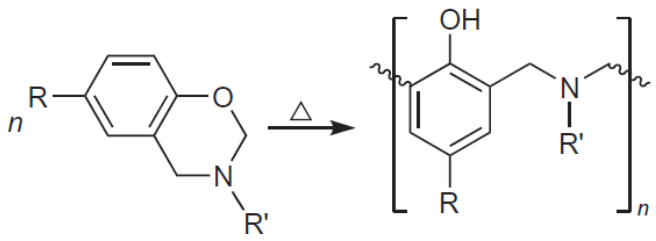

Figure 2.27 : Thermal polymerization of benzoxazine monomer [75].

By simple heating, polymerization can occur due to a small amount of cationic initiator, such as phenolic compounds and benzoxazine olimers, as an impurity. Heating simply increases the rate of polymerization. It is reported that, during the synthesis of a difunctional benzoxazine monomer, some dimers and oligomers also form by the subsequent reactions between the rings and *ortho* position of hydroxyl groups of phenolic compound. The polymerization is initiated by these free phenolic hydroxy structures including dimers and oligomers, and then crosslinking reactions occur. Through the investigations on the cure mechanism and kinetics of the thermal curing of mono and difunctional benzoxazines, it was explained that after the initiation of ring opening, a carbocation and an iminium ion release. The reaction progresses through the electrophilic substitution by carbocation to the benzene ring. The initiation reaction is given Figure 2.28 [75, 77].

The basicity of amine determines the reactivity. As the basicity of amine increases, the stability of the iminium ion increases, thus the equilibrium shifts toward it and propagation rate decreases. If the iminium ion is unstable, equilibrium shifts toward the carbocation and propagation rate increases [77].

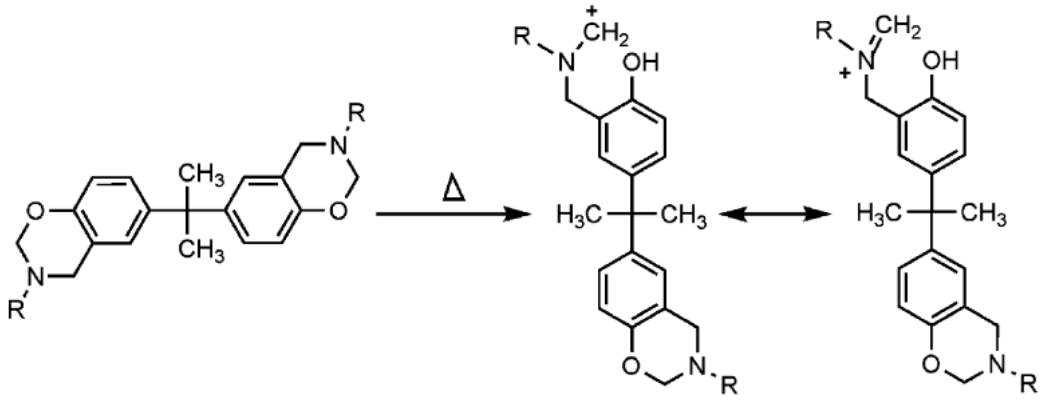

Figure 2.28 : Initiation of ROP of benzoxazines [77].

The polymerization rate, especially the propagation rate, is affected by temperature. Additionally, also the purity of the benzoxazine monomer has influence on the polymerization rate. As the purity of monomer increases, the required temperature for polymerization increases, too.

The conversion of monomer can be monitored as a function of polymerization time and temperature by using differential scanning calorimetric (DSC) analysis. The amount of heat released from the polymerization reaction and the reaction rate are proportional to the heat flow measured in DSC. It was proved that for several benzoxazine monomers, the polymerization mechanism is autocatalytic. In addition, steric hindrance and electronic properties of the surrounding groups have also effect on the rate of ring opening polymerization [75].

2.4.3 Polybenzoxazine and polycaprolactone blends

The blends of polybenzoxazine with polycaprolactone have been studied extensively. It was reported that hydrogen bonding is established between the hydroxyl groups of polybenzoxazines and carbonyl groups of polycaprolactone. Also, by the detailed investigations with the aid of FT-IR analysis, three types of hydrogen bonding were proposed. These are intermolecular hydrogen bonding between two hydroxyl groups of polybenzoxazine (Figure 2.29a), intramolecular hydrogen bonding between hydroxyl groups and nitrogen atoms of Mannich bridge (Figure 2.29b), intermolecular hydrogen bonding between the carbonyl groups of polycaprolactone and hydroxyl groups of polybenzoxazine (Figure 2.29c) [42].

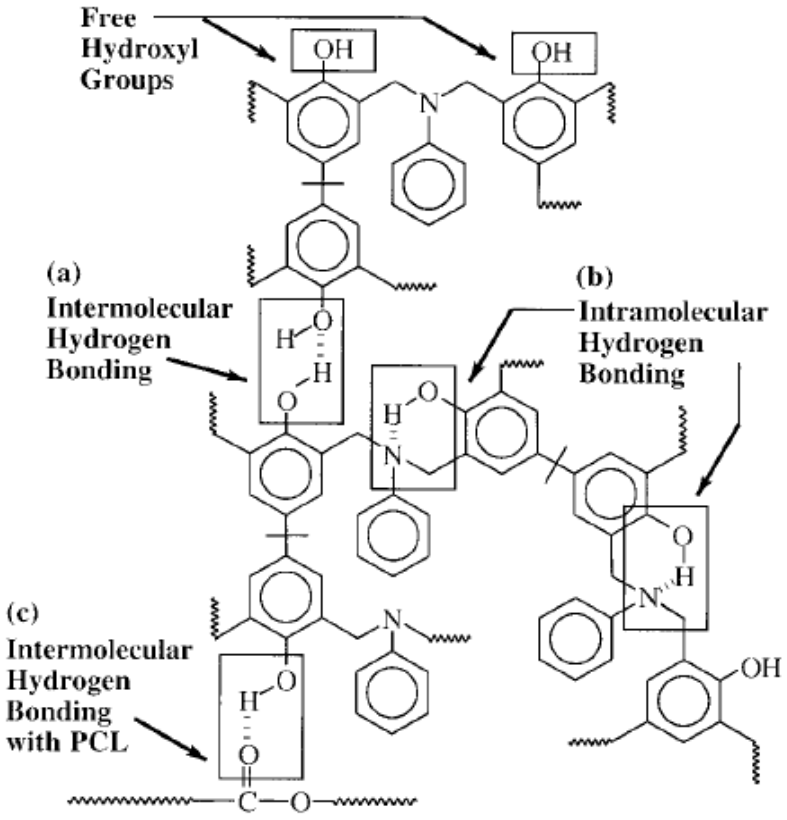

Figure 2.29 : Three types of hydrogen bonding that may possibly occur in the polybenzoxazine/polycaprolactone blends [42].

2.5 Hybrid Materials by the Sol-Gel Process

First hybrid material was prepared thousands years ago, by mixing of dyes or inorganic pigments and other inorganic and organic compounds in order to obtain bright and colorful paints. Despite their very long history, hybrid materials were realized by researchers at the end of the 20th century with the aid of novel physico-chemical characterization methods. Designing hybrid materials with novel properties became possible by the combination of different analytical techniques [5].

The first sol-gel process was the production of silica by using silicon alkoxides as precursors in the 1930s. The development of silicon based sol-gel process promoted the production of organic-inorganic hybrid materials. The stability of the Si-C bond in the course of silica network formation and good processability of silicon allow the production of organic modified inorganic network in one step [5].

Sol-gel process is an organic polycondensation reaction, which polymeric structures form by the combination of small molecules. The production of three dimensional cross-linked network structures by using small molecules has several advantages such as a high control of the purity and composition of the final materials and easy processability due to solvent-based chemistry [5].

In the sol-gel process, the alkoxy group of alkoxysilane may react with water, thus a silanol forms with the release of an alcohol. Then, by the condensation of these silanol groups, siloxane bridges form with the elimination of water or alcohol. These reactions take place as follows:

$$\equiv Si - OR + H_2O \rightarrow \equiv Si - OH + ROH \qquad \textbf{(2.9)}$$

$$\equiv Si - OH + \equiv Si - OH \rightarrow \equiv Si - O - Si \equiv + H_2O \qquad \textbf{(2.10)}$$

$$\equiv Si - OR + \equiv Si - OH \rightarrow \equiv Si - O - Si \equiv + ROH \qquad \textbf{(2.11)}$$

For instance, sol-gel process of tetrialkoxysilanes is depicted in Figure 2.30. Si-O-Si bonds are produced by the hydrolysis of Si-X bonds of $R_{4-n}SiX_n$ compounds. In this reaction, oligomers, polymers and cyclic compounds are first formed (the sol) and then reaction goes on by the crosslinking of solid particles (the gel).

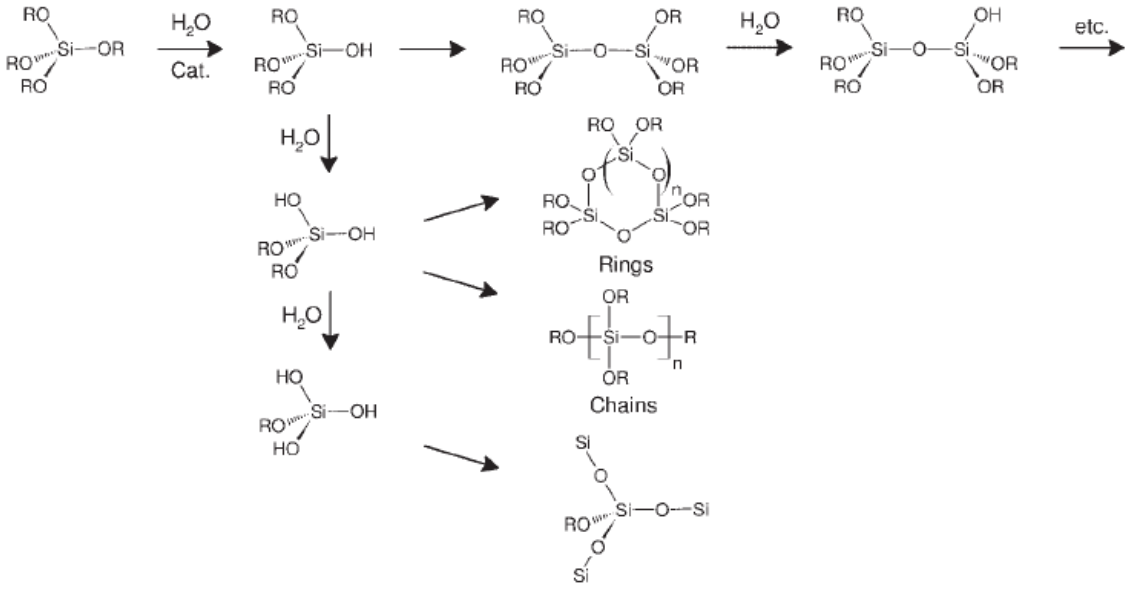

Figure 2.30 : Fundamental reaction steps in the sol-gel process based on tetrialkoxysilanes [5].

The sol-gel process can be catalyzed by acids (HCl) or bases (NaOH, NH_4OH) by various reaction mechanisms with changing condensation reaction rates. The structures of precursors have influence on the reaction kinetics as well as pH and other reaction conditions. The gelation point can be defined as the transition from a sol to gel. After reaching to gel point, condensation reactions take place for a long time and final network is obtained. During this crosslinking, in other words drying process, phase separations of organic and inorganic species in the materials or between the network and unreacted compounds may occur. These undesired reactions, which have a visible effect on the product as opacity, can weaken the properties of hybrid materials.

Sol-gel reactions are favorable in comparison with other inorganic network forming methods, due to having mild reaction conditions and a broad solvent compatibility. Thus, inorganic network can be produced in the presence of a preformed organic polymer or polymerization can be carried out before, during or after the sol-gel reaction. In the synthesis of an organic-inorganic hybrid material, the phase morphology and the interfacial region between the two components must be taken into consideration in view of final properties.

In order to avoid the phase separation problems of hybrid materials, two precautions can be applied such as selection of a solvent which is immiscible with organic polymers and simultaneously compatible with sol-gel reactions and using polymers with functional groups which are compatible with the reaction conditions of the sol-gel process. For instance, if the polymers with hydroxyl functionalities are used, these hydroxyl groups can interact with the hydroxyl groups formed during the sol-gel process.

The coupling agents serve as molecular bridges at the interface of polymeric binder and fillers through the covalent bonds. In industry, for the development of polymeric structural materials, the utilization of coupling agents has been an important method from the point of improving the adhesion and compatibility of different materials [99-100].

In coating applications, the use of silane coupling agents to support the bonding of organic polymers to mineral surfaces was suggested by several studies. The main reasons for using silane coupling agents can be listed as follows:

- They are commercially available widespread chemicals.
- Since they possess alkoxy silane groups in the chain end, they can react with hydroxyl functional surfaces (like glass).
- They have a wide variety of functional groups which can be used to design appropriately for the matrix.

In this connection, the sol-gel process is an easy and economical method in order to synthesize hybrid coatings. Since sol-gel process promotes the establishment of chemical bonds between the soft organic and the hard inorganic species, mechanical toughness, flexibility, hardness and thermal stability properties can be combined in one material. The obtained hybrid material have attractive properties such as high optical transparency, superior weathering and corrosion resistance, excellent abrasion and impact resistance as well as better adhesive properties than traditional polyurethanes or epoxy-amine coatings [101].

These benefits of sol-gel process allowed the development of organic-inorganic coatings called “ormocers” (organically modified ceramerics), which have a high inorganic content (95-40 wt%) and a low organic content (5-60 wt%). Ormocers possess both the characteristics of ceramic and polymeric materials. They are accepted as high performance materials due to the ability of withstanding high temperature applications [5]. The applications of ormocers include scratch and abrasion resistant coating for plastics, functional coatings on glass, corrosion protection layers for metals, barrier layers on polymer for food packaging applications and gas sensitive layers [102].

The coating formulations prepared by mixing of the silane-functionalized isocyanurate and unfunctionalized 1,6-hexamethylene diisocyanate (HDI isocyanurate) were studied in terms of general coating properties. It was suggested that with this formulation, adhesion, crosslink density and glass transition temperature increased [103]. Also, it was reported that by the addition of tetraethylorthosilicate (TEOS) oligomers into the HDI isocyanurate and monofunctionalized isocyanurate (as a coupling agent), the adhesion on aluminum was enhanced [104].

A novel siliconized epoxy interpenetrating coating system was studied using epoxy resin as base, hydroxyl-terminated polydimethylsiloxane as modifier, γ-

aminopropyltriethoyxsilane as crosslinking agent, butyltindilaurate as catalyst and also polyamidoamine and aromatic polyamine compounds as curing agents. It was concluded that siliconized epoxy coating systems could be used as thermal barrier coatings in comparison to epoxy coating systems [105].

A large number of reports exist in the literature explaining that the properties of coating materials enhanced by the incorporation of silanes into the polymer structures. For instance, the addition of tri(3, 4-epoxycyclohexylmethyloxy) phenyl silane into a commercial epoxide improved the flame retardancy [106], and corrosion protection of magnesium alloys was enhanced by the synthesis of epoxy-silane coatings with added functionalities [107].

The hybrid coating formulation based on a UV-curable epoxy acrylate resin and methacryloxypropyl trimethoxysilane was prepared and it was concluded that pendulum hardness, cross-cut adhesion, gloss and the impact strength properties increased by the increment of the silane compounds [108].

Ceramer coatings based on seed oils (such as linseed, safflower, soybean, and sunflower oil) as the organic phase and metal alkoxides as the inorganic phase were developed by Soucek et al. [109-111]. Mechanical and physical properties were improved via the incorporation of metal alkoxides in the oil based coatings in comparison to parent oil based coatings. Also, it was reported that metal-oxo clusters can catalyze the autoxidative reactions of the drying oil by acting as a drier.

Erciyes et al. reported the synthesis of alkoxysilane-functionalized urethane oil/titania hybrid films by sol-gel method. First, alkoxysilane-functionalized urethane oil was synthesized by the reaction of 3-aminopropyltriethoxysilane with partial glycerides in the presence of toluene diisocyanate. Then, the obtained product was further reacted with titanium isopropoxide by sol-gel process. The resulting crosslinked structure (Figure 2.31) was better than classical urethane oil in view of film properties [23].

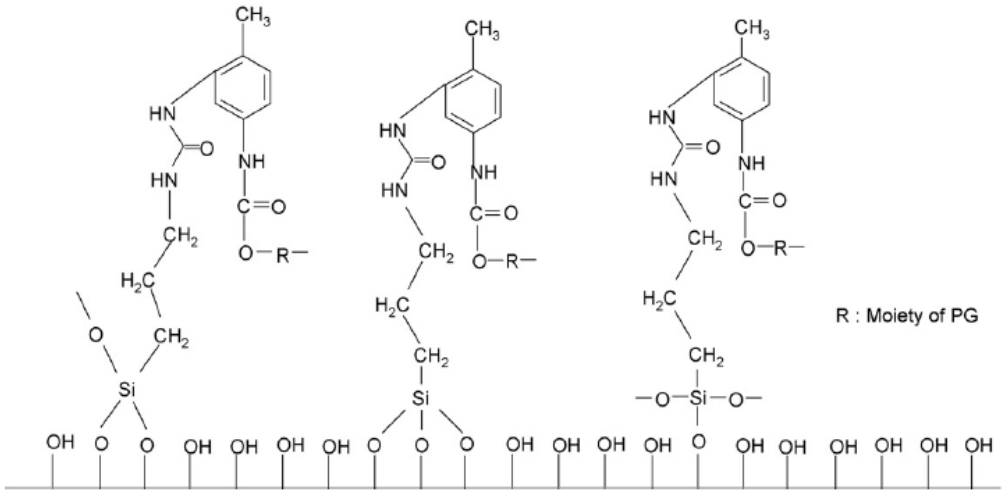

Figure 2.31 : Representative interaction between coating film and glass substrate [23].

As a continuation, Erciyes et al. prepared the alkoxysilane-functionlized oil based polyester hybrid coatings. First, oil-based polyester was synthesized by the esterification of partial glycerides with maleic anhydride. Then, the obtained polyester was copolymerized with both styrene and vinyl trimethoxysilane. It was concluded that the resulting network structure could be used as a coating material due to its good film properties and higher thermal stability [20].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

ε-Caprolactone (CL, 99%, Alfa Aesar):

It was dried over calcium hydride for 48 h at room temperature and distilled under vacuum.

Styrene (St, 99%, Aldrich):

It was passed through a basic alumina column to purify from the inhibitor.

2-hydroxyethyl methacrylate (HEMA, 99%, Fluka):

It was used as received.

Vinyl trimethoxysilane (VTMS, 98%, Sigma-Aldrich):

It was used as received.

3.1.2 Solvents

Ethanol (≥ 99.5%, Sigma-Aldrich):

It was used as received.

Methanol (≥ 99.8%, VWR):

It was used as received for the precipitation of polymers.

Toluene (≥ 99.9%, Merck):

It was used as received.

Diethyl ether (≥ 99.0%, Sigma-Aldrich):

It was used as received.

1,4-dioxane (≥ 99.5%, Sigma-Aldrich):

It was used as received.

Chloroform (99-99.4%, Sigma-Aldrich):

It was used as received.

Tetrahydrofuran (THF, 99.7%, VWR):

It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

3.1.3 Other chemicals

Sunflower oil (SFO):

It was purchased from the market and used as received.

Glycerol (≥ 99.5%, Merck)

It was used as received.

Tin (II) 2- ethylhexanoate (Stannous octoate, SO, 95%, Aldrich):

It was used as received.

Phenol (≥ 99.0%, Sigma-Aldrich):

It was used as received.

6-amino-1-hexanol (94%, Acros Organics):

It was used as received.

Paraformaldehyde (95%, Merck):

It was used as received.

2,4-toluene diisocyanate (TDI, 98%, Sigma-Aldrich):

It was used as received.

Benzoyl peroxide (BPO, Sigma-Aldrich):

It was used as received.

Hydroquinone (98%, Fluka):

Hydroquinone was used to inhibit the polymerization of vinyl functionality during ROP.

Sulfuric acid (95-98%, Merck):

It was used as received.

Calcium hydroxide (≥ 96.0%, Merck):

It was used as received.

Calcium hydride (95%, Sigma-Aldrich):

It was used as received.

Sodium hydroxide (96-100.5%, Merck):

It was used as received.

Sodium sulfate (≥ 99.0%, Merck):

It was used as received.

3.2 Equipment

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) spectra were recorded in deuterated chloroform with tetramethylsilane as an internal standard using a Varian Unity INOVA instrument at a proton frequency of 500 MHz.

3.2.2 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded using a Perkin Elmer FT-IR Spectrum One B spectrometer.

3.2.3 Gel permeation chromatography (GPC)

a) Gel permeation chromatography analyses were measured on a Viscotek GPCmax autosampler system consisting of a pump as well as a Viscotek differential refractive index (RI) detector with THF as eluent at a flow rate of 1.0 mL/min at 35^{o}C. Three ViscoGEL GPC columns (G2000HHR, G3000HHR, and G4000HHR, 7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456-42800 g/mol, 1050-107000 g/mol and 10200-2890000 g/mol, respectively. Data were analyzed using Viscotek OmniSEC Omni-01 software.

b) Molecular weights of polymer samples were measured against a polystyrene standard employing Agilent 1100 consisting of a isocratic pump and refractive index (RI) detector with THF as eluent at a flow rate of 1.0 mL/min at 30^{o}C. Two Agilent PLgel GPC columns (5 μm MIXED-C) were used connected in series. The effective molecular weight range was 200-2,000,000 g/mol. Data were analyzed using Agilent ChemStation software.

3.2.4 Differential scanning calorimetry (DSC)

DSC thermograms were determined using a Perkin Elmer (DSC 4000) instrument with a heating rate of 10^{o}C/min under nitrogen flow (20 mL/min).

3.2.5 Thermal gravimetric analysis (TGA)

Thermal analysis was performed on a Perkin Elmer Diamond TG/DTA with a heating rate of 10^{o}C/min under nitrogen flow (200 mL/min).

3.2.6 Scanning electron microscopy (SEM)

Morphology of the resulting coating was examined by SEM using a SEM JEOL JSM 6390 LV operated at 15 kV accelerating voltage.

3.3 Preparation Methods

3.3.1 Synthesis of partial glycerides of sunflower oil (SFOPG)

Sunflower oil partial glyceride was prepared through a glycerolysis reaction between triglyceride oil and glycerol in a three-necked round-bottomed flask equipped with a dry nitrogen flow through an inlet and a reflux condenser. A total of 120 g of oil and 10.4 g of glycerol [112] were placed into the reaction flask and heated. When the temperature reached 218^{o}C, $Ca(OH)_2$ was added as catalyst, constituting 0.1% by weight of the oil portion. Then, the temperature was adjusted to 230^{o}C, and the reaction continued for 1 h under nitrogen atmosphere. At predetermined time intervals, samples were taken from the reaction mixture and poured into a three-fold amount of ethanol. When the alcohol solution became clear, transesterification was terminated. After cooling, the contents of the flask were dissolved in diethyl ether, washed with dilute sulfuric acid and then distilled water to remove the catalyst and free glycerol, respectively. The etheral solution was dried over anhydrous Na_2SO_4,

and the solvent was then removed. The hydroxyl and acid values of dry SFOPGs were determined [113].

3.3.2 Synthesis of sunflower oil-modified polyester (SOMPE)

SOMPE was synthesized by a ring opening polymerization of ε-caprolactone (CL) initiated with sunflower oil partial glycerides (SFOPG) in the presence of a stannous octoate (SO) catalyst in a toluene medium according to a previously reported procedure [114]. SFOPG, SO, CL and dried toluene were added into a 50 mL four-necked flask. SFOPG and CL were charged according to the given mol ratio of [CL]/[SFOPG]. The amount of SO was set to a [SO]/[SFOPG] mol ratio of 0.012. The reaction flask was equipped with a dry nitrogen inlet tube, a reflux condenser, a thermometer, and a magnetic stirrer and was placed in a temperature-controlled oil bath at 130^{o}C. To understand the influence of the reaction time, the reaction was conducted for different lengths of time. The reaction mixture was precipitated into methanol and then washed with methanol several times. The obtained polymer sample was filtered off and dried in a vacuum oven at 30^{o}C for 24 h.

3.3.3 Synthesis of hydroxyl-functional benzoxazine monomer (HFB-a)

6-Amino-1-hexanol (51.7 mmol, 6.05 g), phenol (51.7 mmol, 4.86 g), and paraformaldehyde (103.5 mmol, 3.1 g) were fed into a three-necked round-bottom flask. The contents of the flask were dissolved in 150 mL of 1,4-dioxane and refluxed for 5 h. Then, 1,4-dioxane was evaporated under vacuum. The crude product was dissolved in chloroform and washed with distilled water, the chloroform solution was dried with anhydrous sodium sulfate and filtered, and the solvent was evaporated (Yield: 63%) [115].

3.3.4 Synthesis of oil and benzoxazine modified polycaprolactone (SOMPE-HFB-a)

For the preparation of SOMPE-HFB-a, SOMPE and HFB-a were linked through their hydroxyl groups by a reaction with 2,4-toluene diisocyanate (TDI) under nitrogen atmosphere. HFB-a and a equimolar amount of TDI were placed into the reaction flask in a temperature-controlled oil bath at 45^{o}C. A 24% solution of lead naphthenate in white spirit was added in an amount that constituted 0.03% of the oil portion. After 50 min, SOMPE was added, the temperature was raised to 95^{o}C and

the reaction was allowed to continue until the NCO peak around 2270 cm^{-1} disappeared (FT-IR).

3.3.5 Thermal curing of SOMPE-HFB-a samples

SOMPE-HFB-a samples were thinned with toluene to 70% of the solid content and then applied on substrates according to standard procedures. After the solvent was evaporated, samples were cured sequentially in an air-circulating oven at 150^{o}C for 1 h, 170^{o}C for 1 h and 190^{o}C for 2 h to ensure complete curing [88].

3.3.6 Synthesis of vinyl functional macromonomer (HPCL)

Vinyl functional macromer (HPCL) was prepared by the ROP of CL initiated by HEMA using SO catalyst. HEMA (8.7 mmol, 1.15 g), CL (108.3 mmol, 12.36 g), SO (0.274 mmol, 0.11 g) and dried toluene (5 mL) were added into a 50 mL four-necked flask. The reaction flask was equipped with a dry nitrogen inlet tube, a reflux condenser, a thermometer, and a magnetic stirrer and was placed in a temperature-controlled oil bath at 120^{o}C. Hydroquinone was added into the reaction medium to inhibit the polymerization of vinyl functionality during the ROP of CL. After 3 h reaction time, polymerization was stopped immediately by cooling the flask in the ice bath. Then, flask mixture was precipitated into refrigerated methanol and washed with methanol repeatedly to remove the unreacted monomers. The product was filtered off and dried in a vacuum oven at 40^{o}C for 24 h.

3.3.7 Synthesis of HPCL-St-VTMS terpolymer

The graft polymer was prepared by free radical polymerization using wt. % (based on total amount of St and VTMS) amount of benzoyl peroxide (BPO) as catalyst. HPCL (0.1175 mol, 0.4384 g), predetermined amount styrene, vinyl trimethoxysilane, benzoyl peroxide (according to Table 3.1) and dried toluene (3 g) were charged into the reaction flask. The flask content was deoxygenated by bubbling with dry nitrogen for 30 min and heated to 100^{o}C, simultaneously. After 4 h of reaction time, the flask was cooled to the room temperature. Then, reaction mixture was precipitated into refrigerated methanol and washed with methanol several times. The product was filtered off and dried in a vacuum oven at 35^{o}C for 24 h.

Table 3.1 : $HPCL_x$-St_x-$VTMS_x$-BPO-x synthesis conditions.

Sample	Mole ratio [VTMS/St]	BPO wt%
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-5.0*	0.5	5.00
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-3.0	0.5	3.00
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5	0.5	1.50
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.0	0.5	1.00
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.5	0.5	0.50
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.27	0.5	0.27
$HPCL_1$-St_{50}-$VTMS_{50}$-BPO-5.0	1.0	5.0
$HPCL_1$-St_{50}-$VTMS_{50}$-BPO-3.0	1.0	3.0
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5	1.0	1.5
$HPCL_1$-St_{50}-$VTMS_{75}$-BPO-5.0	1.5	5.0
$HPCL_1$-St_{50}-$VTMS_{75}$-BPO-3.0	1.5	3.0
$HPCL_1$-St_{50}-$VTMS_{75}$-BPO-1.50	1.5	1.50

*The subscripts denote the moles of relevant monomer. BPO-x abbreviation states the wt% of BPO used in the reaction. For example, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-5.0 was synthesized with 1 mol of HPCL, 50 moles of St and 25 moles of VTMS in the presence of 5.0 wt% of BPO. BPO percentages were calculated based on total amount of St and VTMS.

3.3.8 Preparation and curing of oil modified $HPCL_x$-St_x-$VTMS_x$-BPO-x film samples

$HPCL_x$-St_x-$VTMS_x$-BPO-x sample was mixed with SFOPG (20 % of polymer) and thinned with toluene to 50% of the solid content. Oxidative polymerization catalysts, 0.5% lead naphthenate and 0.05% cobalt naphthenate as metal based on solid content was added to the mixture. The obtained mixture was applied on substrates according to standard procedures. The prepared film samples were exposed to moisture in a closed box of 95 % humidity at 30^oC for 48 h. Then, they were placed into a closed oven at 180^oC for 48 h to complete the crosslinking.

3.3.9 Preparation of model compound

VTMS and SFOPG (20 % of monomer) were well mixed and employed on watch glass. This mixture was exposed to moisture in a placed in closed box of 95 % humidity at 30^oC for 48 h. Then, it was placed into a closed oven at 180^oC for 2.5 h.

3.3.10 Determination of film properties

To determine film properties such as flexibility [116], adhesion [117], acid resistance [118], alkali resistance [118] and water resistance [118], cured film samples prepared as described above were used directly in tests. For adhesion, polymer films were applied on both glass plates and tin plates with a Bird film applicator of size 60 μm. In the flexibility, water resistance and adhesion tests, tin plate panels were used as a substrate. For all other tests (alkali and acid resistance), a dipping method was employed and glass tubes were used, as explained in related procedures.

4. RESULTS AND DISCUSSION

The aim of this thesis was to develop new polymeric binders by using triglyceride oils as renewable resources. For this purpose, functional polyester samples were prepared by ROP and further modified for coating purposes. These studies will be presented as two parts.

First, sunflower oil partial gylceride (SFOPG) was prepared by the glycerolysis reaction according to the procedure given in experimental part as shown in Figure 4.1.

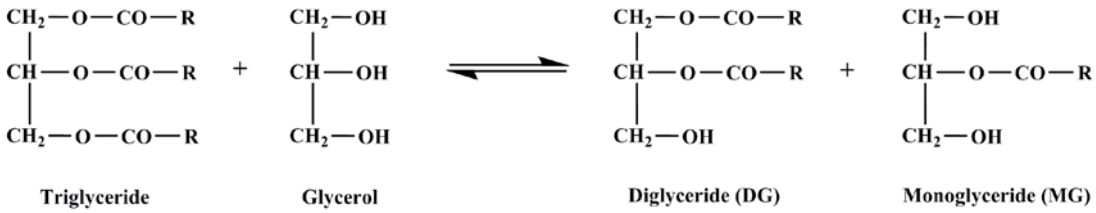

Figure 4.1 : Synthesis of SFOPGs.

The hydroxyl and acid values of SFOPG were determined to be 107 and 1.74, respectively.

4.1 Preparation of Oil-Modified Polycaprolactone and its Further Modification with Benzoxazine

The objective of the first part of this thesis is to synthesize a surface coating material with good film properties that utilizes the advantages of both sunflower oil-modified polyester (SOMPE) and polybenzoxazine (PBZ). As stated previously, SOMPE was prepared by the ROP of CL initiated by SFOPGs in the presence of stannous octoate (SO).

Inserting the oil moiety into the polyester structure was achieved directly using SFOPG as an alcohol component during the ring opening polymerization, without any additional steps. The formation of SOMPE is shown in Figure 4.2.

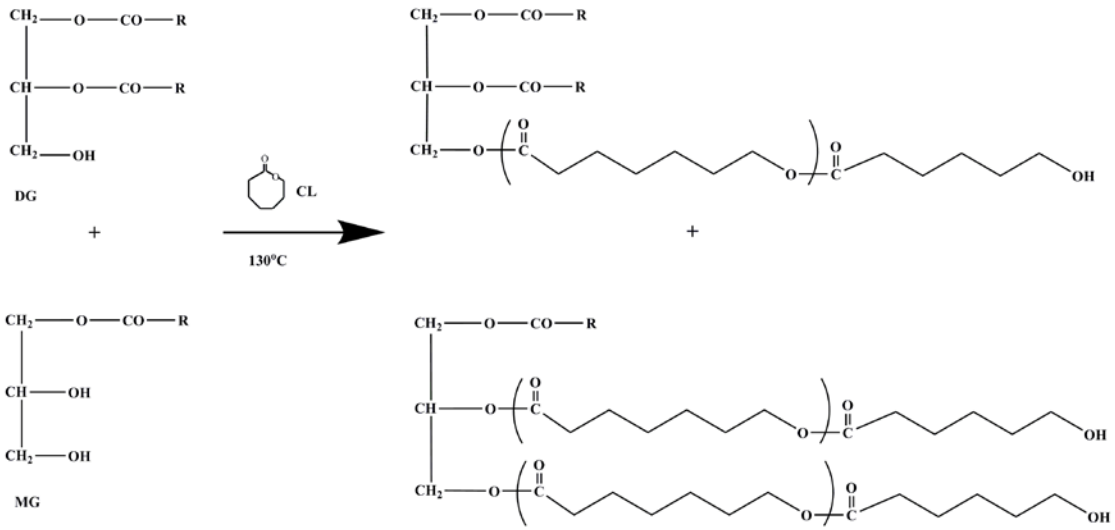

Figure 4.2 : The ROP of CL initiated by SFOPGs.

Figure 4.3 represents the FT-IR spectrum of SOMPE. The wide peak at 3430-3560 cm^{-1} corresponds to the absorption of hydroxyl groups. The sharp peak at 1729 cm^{-1} represents the characteristic carbonyl band of the ester groups [119-121].

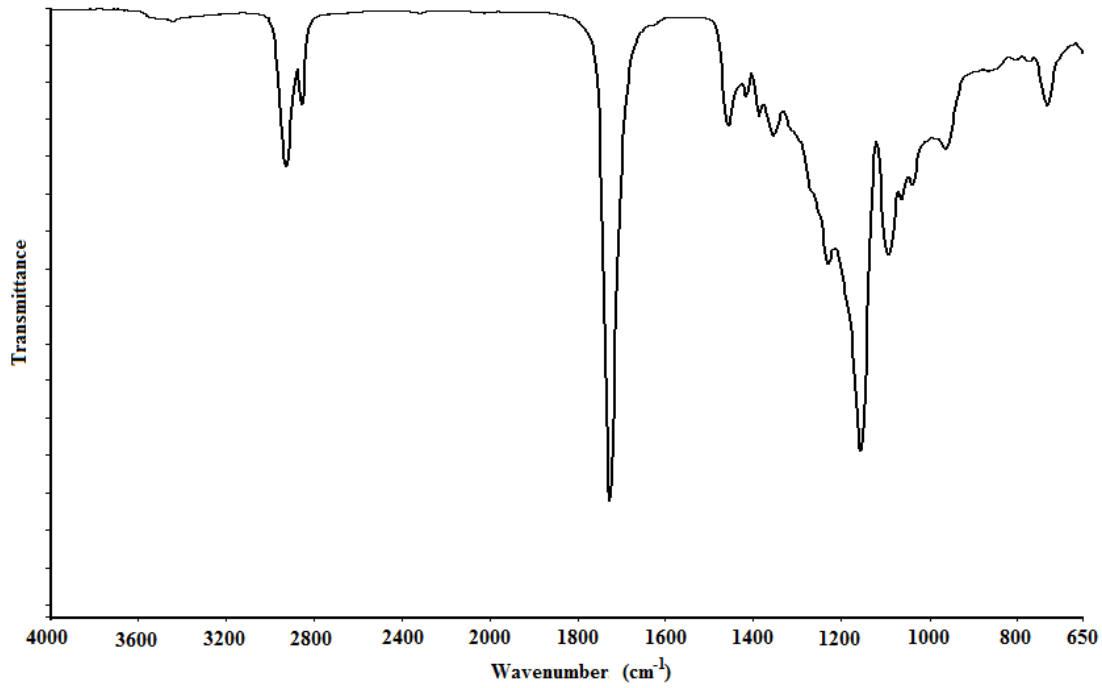

Figure 4.3 : FT-IR spectrum of SOMPE.

The chemical structure of SOMPE was also examined by recording ^{1}H-NMR spectra. To confirm that SFOPG functioned as an initiator, the ^{1}H-NMR spectrum of the reference homopolyester that was prepared by water-initiated ROP was evaluated together with that of SOMPE. As shown in Figure 4.4a and 4.4b, peaks at 1.31 and 1.58 ppm, respectively, are assigned to the aliphatic methylene protons of PCL. The

peaks at 2.23, 3.57, 3.84 and 3.99 ppm are attributed to –$OCOCH_2$–, –CH_2OH, –OH and –CH_2O–, respectively. The weak signals at 4.21 and 5.27 ppm in Figure 4.4a represent –CH_2OCO– and –CHOCO–, respectively, in the oil moieties of polyester. These last two peaks disappear in the ^{1}H-NMR spectrum of the homopolyester, as shown in Figure 4.4b. These findings imply that SFOPG molecules were successfully combined with polyester segments by serving as an initiator of ROP [28, 119].

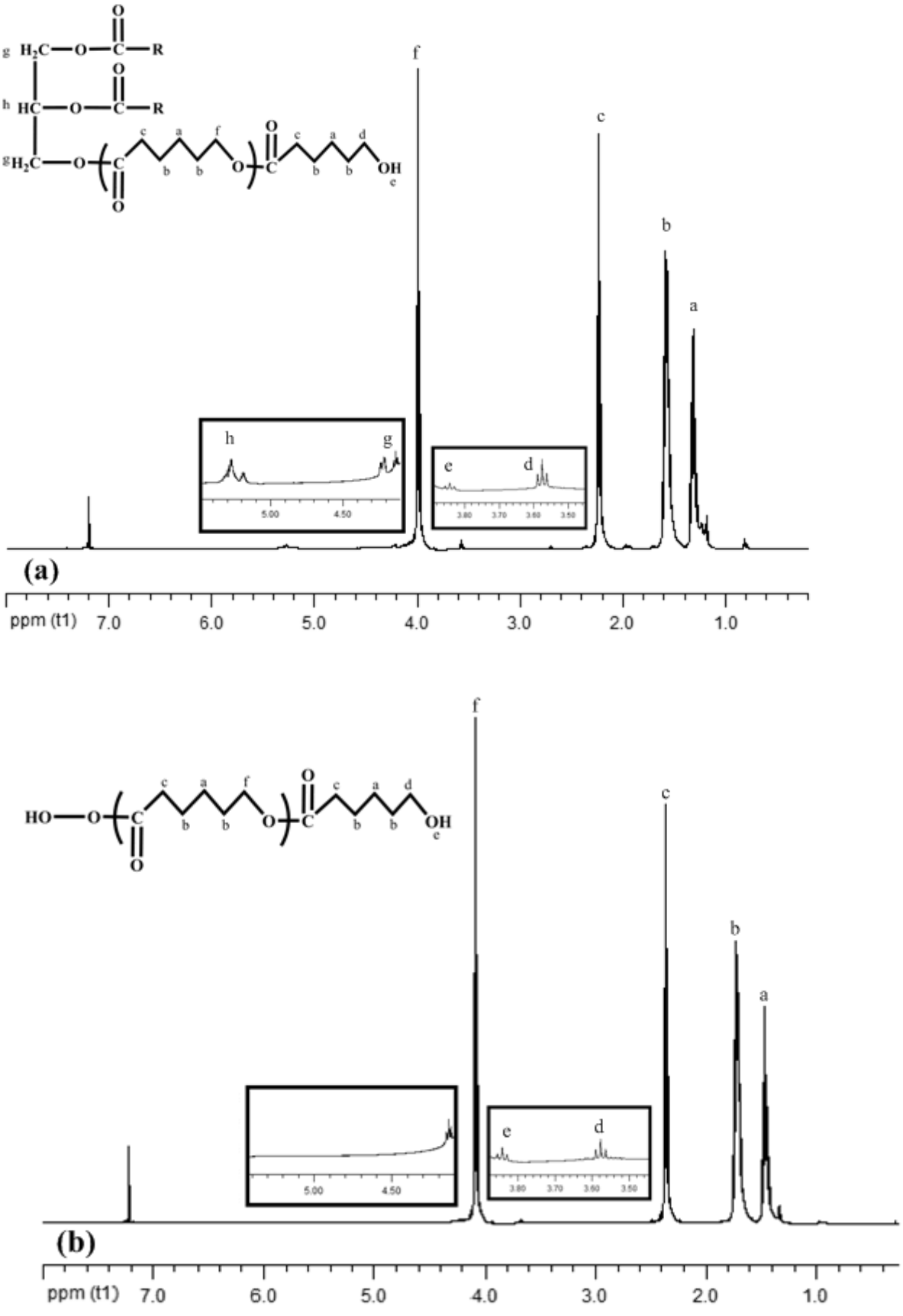

Figure 4.4 : H-NMR spectra of (a) SOMPE and (b) the homopolyester.

In order to determine the drying capability of SOMPE, as prepared with a ([CL]/[SFOPG]) mol ratio of 40, the film sample with 0.5 % lead naphthenate and 0.05 cobalt naphthenate as metal based on solid content was allowed to dry by oxidative polymerization at 25^{o}C and 70 % relative humidity. It was observed that the film sample remained soft, even after 24 h. To increase the oil portion for a higher degree of crosslinking through autoxidation, the reaction was forced to yield a low-molecular-weight SOMPE by decreasing the polymerization time and changing the ([CL]/[SFOPG]) mol ratio. The results of these studies are shown in Table 4.1. These results show that even at the end of 5 h, with a ([CL]/[SFOPG]) mol ratio of 40, the molecular weight was still greater than 10,000. In the following experiments, a molecular weight of 5335 could be reached after 1.5 h with an initial ([CL]/[SFOPG]) mol ratio of 10. This result is consistent with the literature indicating that the molecular weight can be reduced by lowering the ([monomer]/[initiator]) ratio [122-123]. To obtain a SOMPE sample with the smallest possible molecular weight, the samples were successively taken from the reaction medium and precipitated into methanol. The first precipitable fraction was obtained after 1 h with a molecular weight of 5011. Even with this reduced molecular weight, the SOMPE film was still soft. To overcome such deficiencies, SOMPE was chemically modified with HFB-a to obtain a hard film. Thus, the HFB-a monomer was synthesized by the reaction depicted in Figure 4.5. The formation of PBZ by ROP is also included in this figure.

Table 4.1 : Molecular weights of SOMPE samples.

[CL/SFOPG]	Polymerization time (h)	M_n GPC
40	24	16832
40	5	10376
10	24	7581
10	1	5011
10	1.5	5335
10	2.5	5472

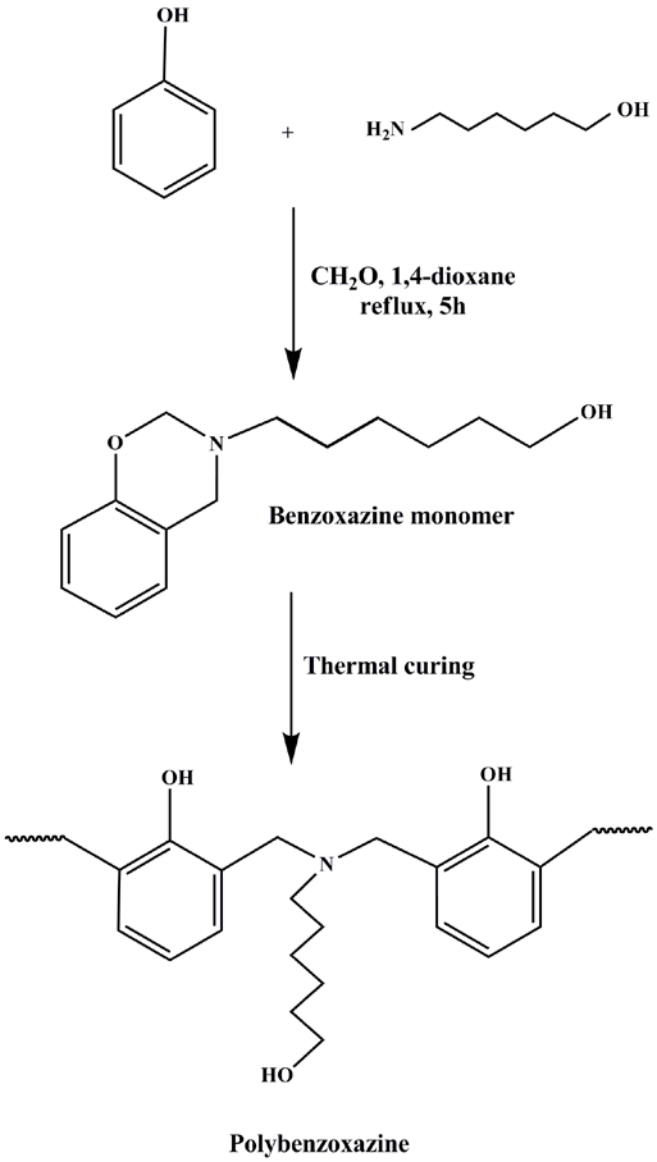

Figure 4.5 : Preparation of the HFB-a monomer and PBZ.

The chemical structure of the prepared HFB-a monomer was also confirmed using FT-IR and ^{1}H-NMR. Figure 4.6 and Figure 4.7 represent the FT-IR and ^{1}H-NMR spectra, respectively, of the HFB-a monomer. In Figure 4.6, the band at 922 cm^{-1} demonstrates the out-of-plane CH vibration of the benzene ring to which an oxazine ring is attached. Furthermore, the asymmetric and symmetric stretching vibrations of C-O-C appear at 1222 and 1034 cm^{-1}, respectively. The peaks at 1131 and 863 cm^{-1} represent the asymmetric and symmetric, respectively, stretching vibrations of C-N-C. Furthermore, the peaks at 1608, 1585, 1488, 1456 and 751 cm^{-1} are characteristic absorption bands of HFB-a [37, 124-125].

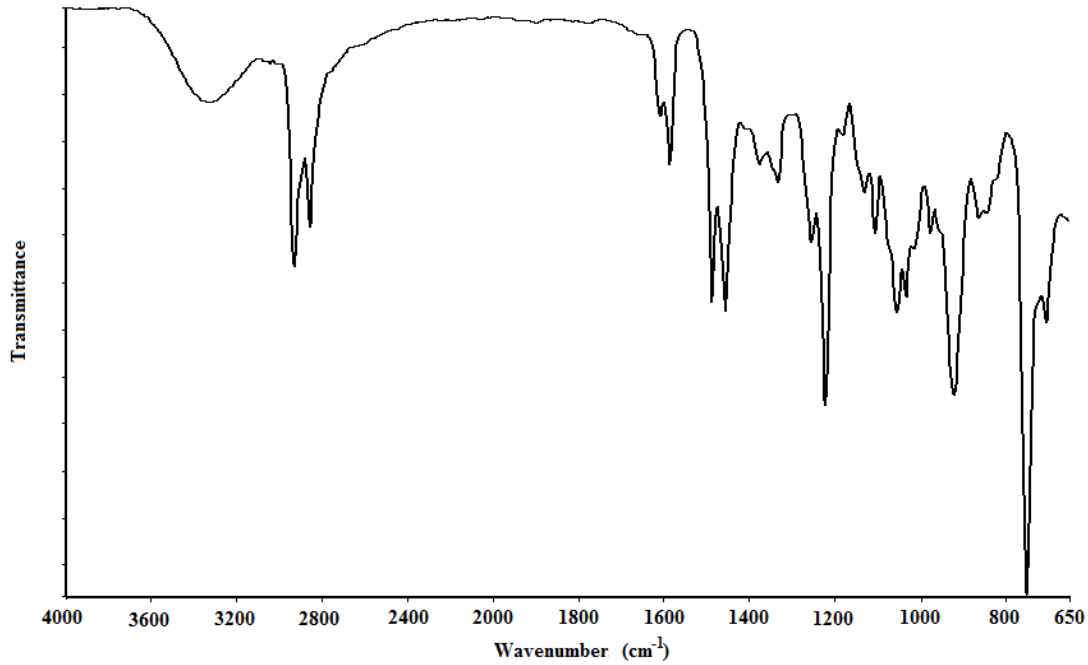

Figure 4.6 : FT-IR spectrum of HFB-a.

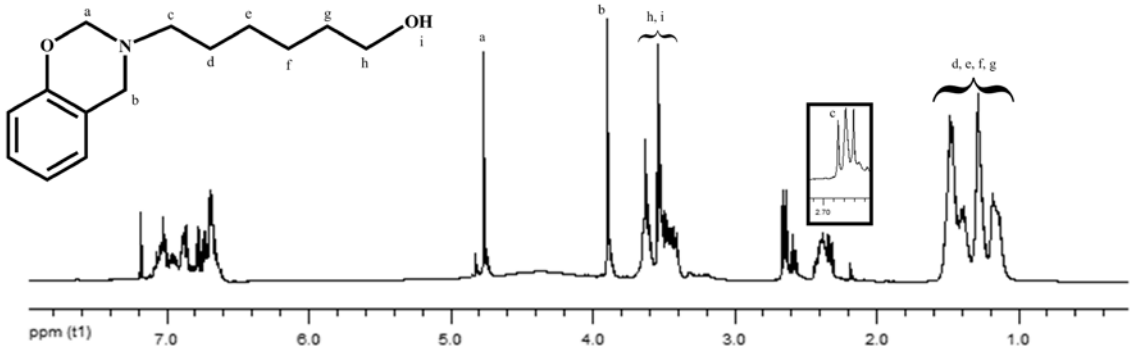

Figure 4.7 : ^{1}H-NMR spectrum of HFB-a.

As seen in Figure 4.7, the peaks at 3.89 and 4.76 ppm are assigned to Ar-CH_2-N- and –O-CH_2-N-, respectively, which are the characteristic proton resonances of the oxazine ring of HFB-a. The multiplet in the range 6.60-7.18 ppm is attributed to protons of the aromatic ring. All of these results are in agreement with the literature [37, 124-125].

Figure 4.8 illustrates the further modification of SOMPE with HFB-a. As shown, SOMPE and HFB-a were combined with each other through the urethane linkage formed from the reaction of TDI. In order to avoid the combination of TDI with only HFB-a or only with SOMPE, HFB-a was first reacted with TDI at 45^{o}C, as shown in Figure 4.8a. Thus, the more reactive N=C=O groups were reacted with HFB-a, and the less reactive N=C=O groups remained free to react with SOMPE by the reaction

shown in Figure 4.8b at an elevated temperature of 95^{o}C. Figure 4.9 represents FT-IR spectra of SOMPE-HFB-a. In Figure 4.9a, the free N=C=O peak at 2266 cm^{-1} became less intense compared to the initial scan due to the consumption of more reactive N=C=O groups (Figure 4.9b), and the peak disappeared completely by the end of the reaction at 95^{o}C (Figure 4.9c). Additionally, the peak at 1737 cm^{-1} belonging to the C=O stretching was intensified at the end of the reaction due to the contribution of the formed urethane groups (Figure 4.9c) [37].

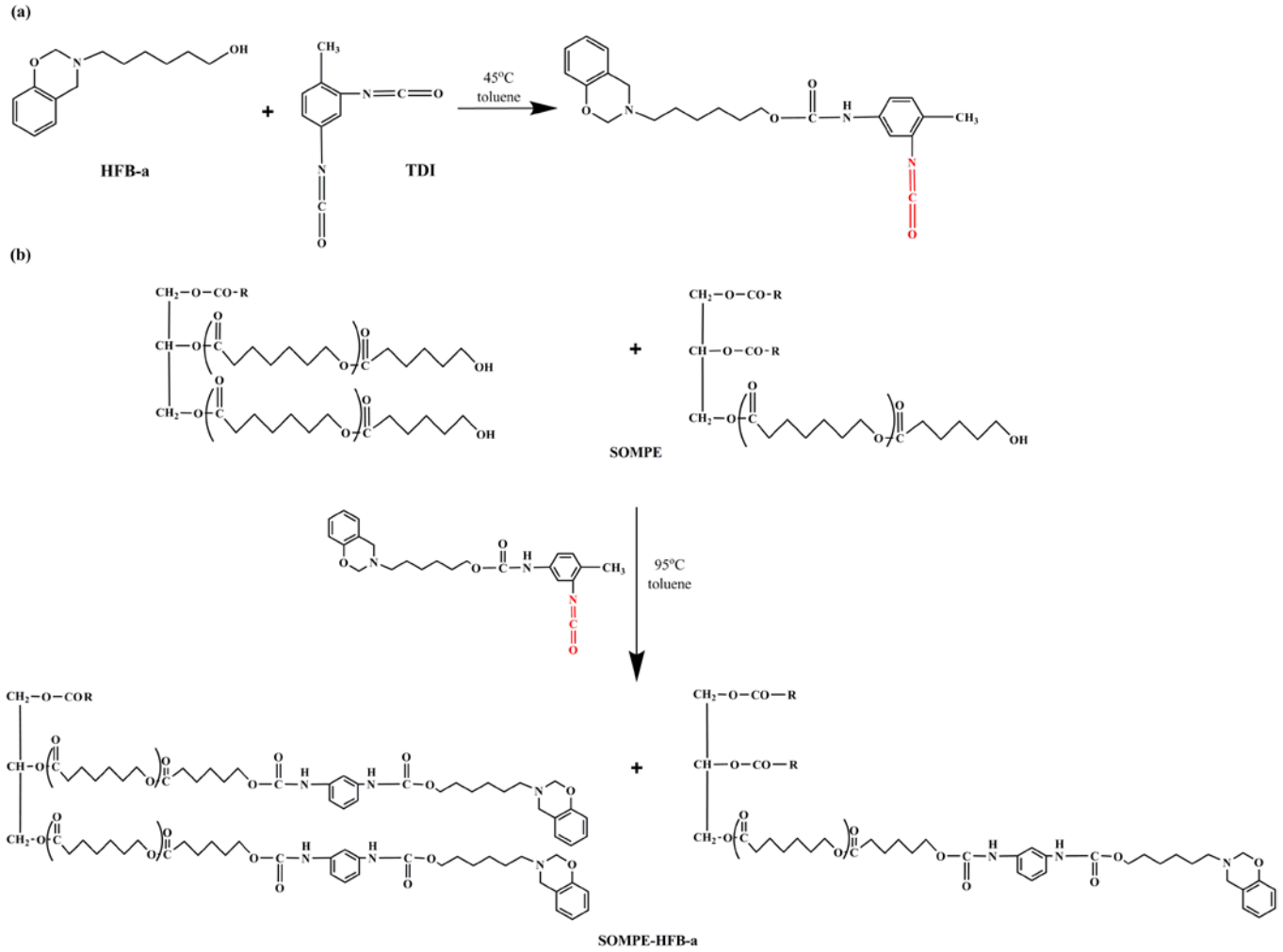

Figure 4.8 : Representative reaction scheme of SOMPE-HFB-a.

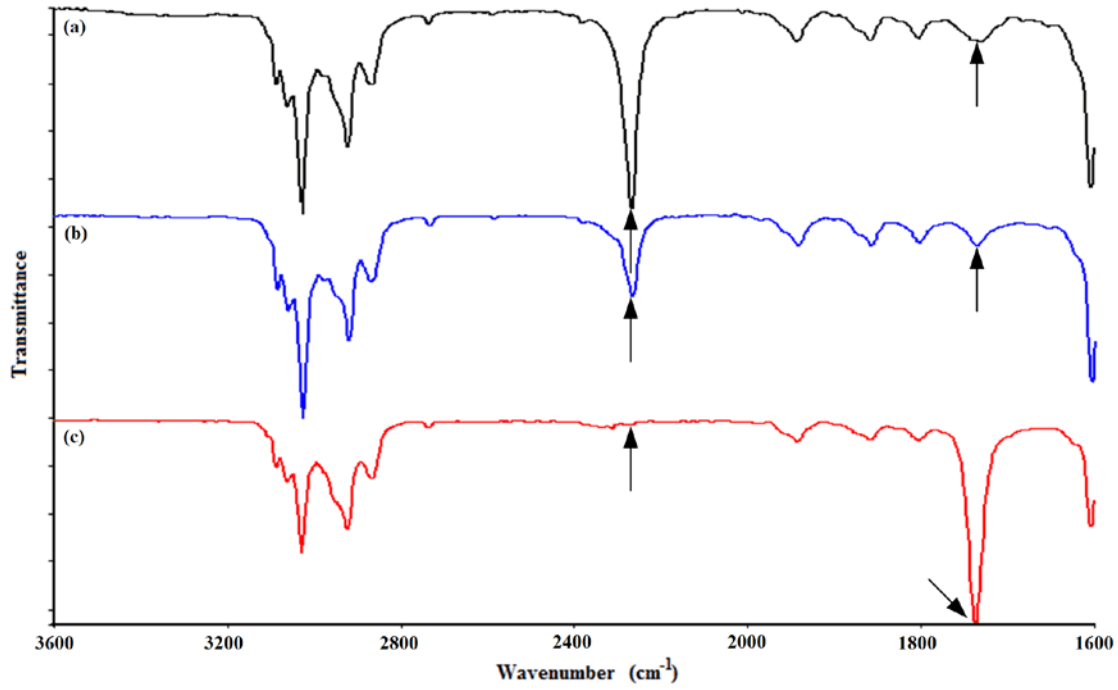

Figure 4.9 : FT-IR spectra of SOMPE-HFB-a: (a) at the beginning of the reaction, (b) 50 min later at 45°C, and (c) at the end of reaction at 95°C.

Thus, it was understood that HFB-a was successfully combined with SOMPE through urethane linkages and that SOMPE-HFB-a was obtained. The SOMPE-HFB-a sample was applied as a thin film and cured according to the procedure explained in experimental part. It is well known that curing proceeds via the ring opening polymerization of the cyclic structure without a catalyst and without by-products [40, 42].

The cured film was still tacky, implying that more HFB-a should be used. Thus, SOMPE-HFB-a was blended with additional HFB-a monomer at different weight ratios (these samples were assigned as [SOMPE-HFB-a/HFB-a:1/6], [SOMPE-HFB-a/HFB-a:1/8], [SOMPE-HFB-a/HFB-a:1/10]) and cured (Figure 4.10). By applying this measure, the film lost its soft material property, as in the cases of [SOMPE-HFB-a/HFB-a:1/8] and [SOMPE-HFB-a/HFB-a:1/10]. The film properties were determined in detail. However, before discussing these results, confirmation studies that verify the completeness of the curing should be mentioned. To this end, the cured and uncured samples were investigated by FT-IR and DSC.

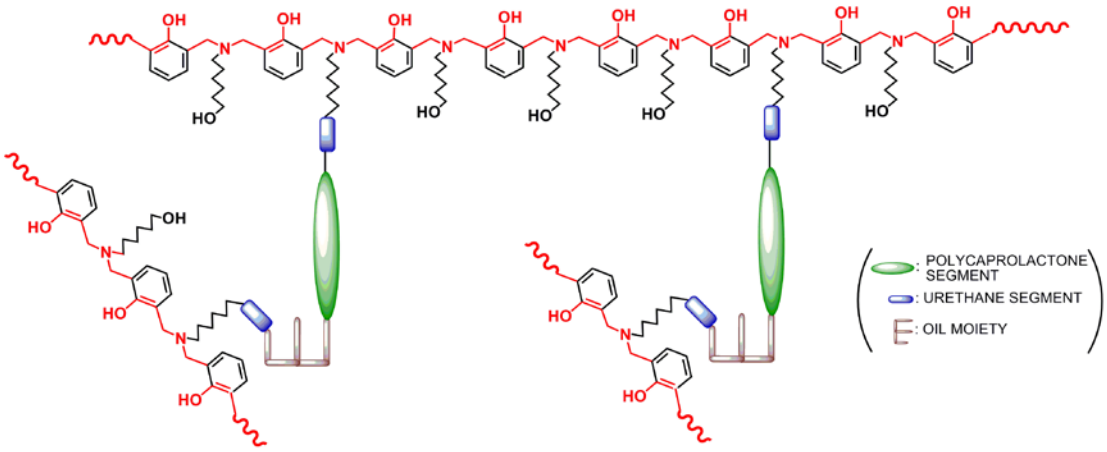

Figure 4.10 : Representative structure of SOMPE-HFB-a/HFB-a blends after thermal curing.

FT-IR spectra of SOMPE-HFB-a/HFB-a blends before and after curing are given in Figure 4.11. The vibration mode of the benzene ring is at 922 cm^{-1}, the stretching modes of aromatic ether are at 1034 and 1222 cm^{-1}, the vibrational modes of C-N-C are at 1134 and 864 cm^{-1}, and the other peaks at 1608, 1584, 1488 cm^{-1} are the characteristic absorption bands of the closed oxazine ring. Because these peaks were absent in the treated sample, we concluded that curing was realized (Figure 4.11b). Additionally, the stretching vibration of O-H of HFB-a at 3340 cm^{-1} disappears after the curing reaction. These results demonstrate the ring opening and curing [37, 124-126]. The obtained network structure is shown in Figure 4.10.

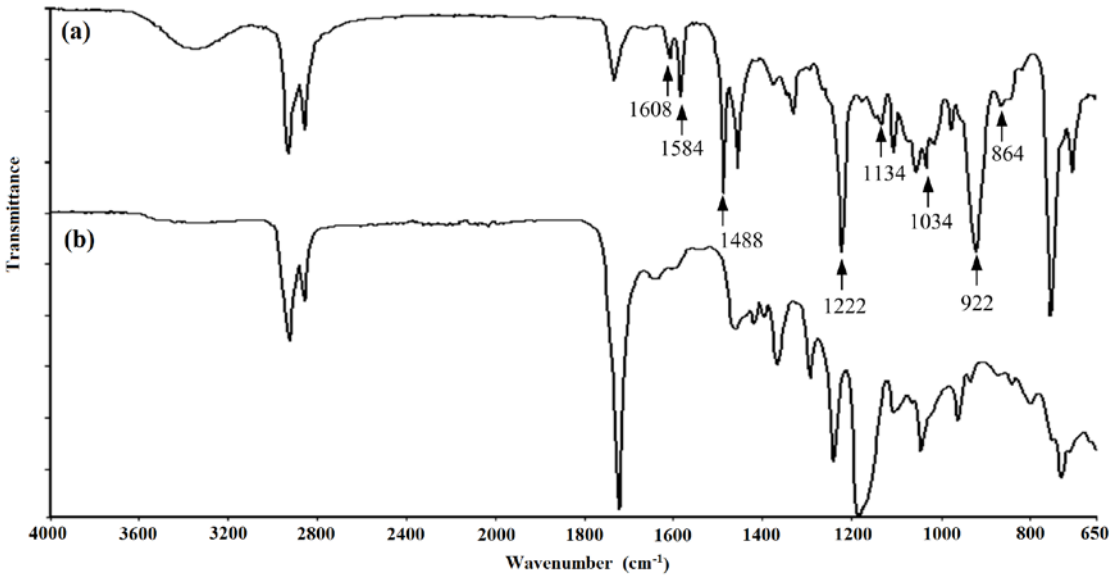

Figure 4.11 : FT-IR spectra of SOMPE-HFB-a/HFB-a blends: (a) before and (b) after thermal curing.

In order to clarify the degree of curing, the cured and uncured samples were subjected to thermal analysis. In Figure 4.12, the DSC thermograms of uncured samples of HFB-a and SOMPE-HFB-a/HFB-a are given. As seen in Figure 4.12a, the HFB-a thermogram has a single exotherm with onset and maximum temperatures of 175°C and 202°C, respectively. The total heat of ring opening polymerization for HFB-a is 126 J/g. As shown in Figure 4.12b, an exothermic peak of ring opening polymerization of SOMPE-HFB-a/HFB-a was detected with an onset temperature at 204°C and a maximum at 220°C. The total heat of polymerization was found to be 132 J/g. The onset and maximum temperatures of SOMPE-HFB-a/HFB-a were higher in comparison to cured HFB-a. Such a shift of the exothermic peak arises from the retarding effect of PCL segments of SOMPE-HFB-a. This finding is also observed and explained in the literature [38-39, 41-43].

To examine the level of unpolymerized HFB-a, the cured samples were also studied by DSC. The thermograms of cured samples of HFB-a and SOMPE-HFB-a/HFB-a are given in Figure 4.13. These results, which are explained in Figure 4.13, show that under the applied curing conditions, ring opening was achieved to 94% for HFB-a and 97% for SOMPE-HFB-a/HFB-a, implying that the curing practically reached completion [37].

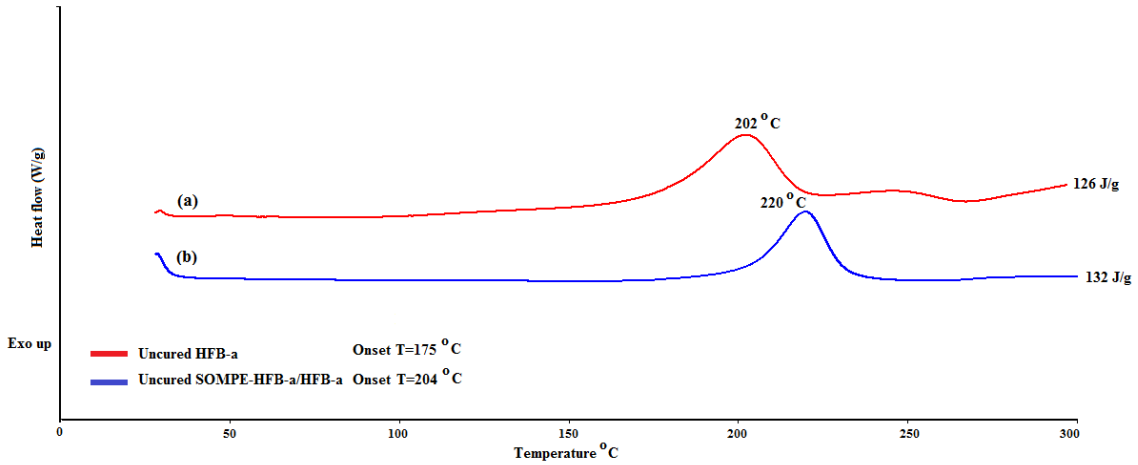

Figure 4.12 : DSC thermograms of (a) uncured HFB-a and (b) the uncured SOMPE-HFB-a/HFB-a blend.

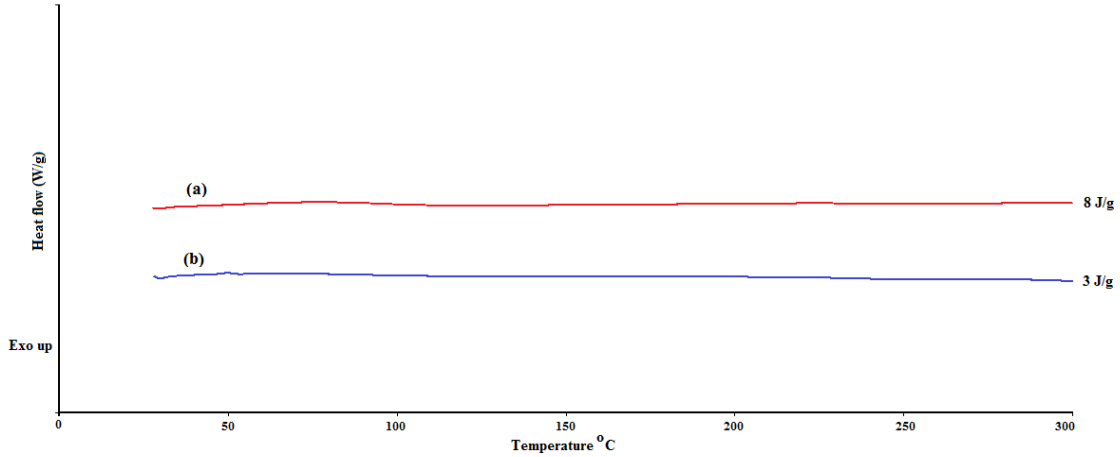

Figure 4.13 : DSC thermograms of (a) cured HFB-a and (b) the cured SOMPE-HFB-a/HFB-a blend.

The film properties of [SOMPE-HFB-a/HFB-a:1/8], [SOMPE-HFB-a/HFB-a:1/10] and pure HFB-a were determined using the cured film samples. The applied tests and results are collected in Table 4.2. As seen, [SOMPE-HFB-a/HFB-a:1/8] and [SOMPE-HFB-a/HFB-a:1/10] yielded excellent film properties, except for adhesion on a tin plate. However, the adhesion of [SOMPE-HFB-a/HFB-a:1/8] on a tin plate was enhanced, at least to some extent, compared to [SOMPE-HFB-a/HFB-a:1/10] . The samples [SOMPE-HFB-a/HFB-a:1/8] and [SOMPE-HFB-a/HFB-a:1/10] could be bent, without cracking, over the cylinder with diameters of 8 mm and 12 mm, respectively. As seen, adhesion on the glass surface was excellent, being 5B. There was no change in the films subjected to acid and water resistance tests, even after 48 h. In the case of exposure to alkali, a partial peeling in the films was observed after more than 5 h. In our previous study, the film samples of the dehydrated castor oil and linseed oil based urethane oils showed partial peeling after 20 min and 30 min, respectively [69]. In fact, the urethane oil is considered to be a coating material with good film properties. By comparison, the film properties of [SOMPE-HFB-a/HFB-a:1/8] and [SOMPE-HFB-a/HFB-a:1/10] are better than those of the urethane oils. Considering this observation, SOMPE-HFB-a/HFB-a should be considered a good binder for coating purposes.

Table 4.2 : Film properties of polymer samples at different weight ratios cured at 150^{o}C for 1 h, 170^{o}C for 1 h and 190^{o}C for 2 h.

	Applied test					
Sample	Flexibility[a]	Adhesion on a glass surface[b]	Adhesion on a tin plate[b]	Acid resistance[c]	Alkali resistance[d]	Water resistance[e]
[SOMPE-HFB-a/HFB-a :1/6]	----------Film is tacky----------					
[SOMPE-HFB-a/HFB-a :1/8]	8 mm	5B	2B	no change	303 min pp	no change
[SOMPE-HFB-a/HFB-a:1/10]	12 mm	5B	0B	no change	333 min pp	no change
Pure HFB-a	16 mm	4B	0B	no change	no change	no change

[a] The diameter of the cylinder that did not cause a crack on the film.
[b] Test method B was applied.
[c] Test was performed at 25^{o}C with 9% H_2SO_4 solution for 48 h.
[d] Test was performed at 25^{o}C with 3% NaOH solution. pp = partial peeling.
[e] Test was performed at 25^{o}C for 48 h.

Thermogravimetric analysis (TGA) was also performed, and the obtained thermograms of the cured films are illustrated in Figure 4.14. As seen from Table 4.3, the temperatures corresponding to a 5% weight loss are 304, 291, 274, and 270^{o}C, whereas char yields at 538^{o}C are 1.1, 26.6, 26.4 and 28.8% for cured samples SOMPE-HFB-a, [SOMPE-HFB-a/HFB-a:1/8], [SOMPE-HFB-a/HFB-a:1/10] and HFB-a, respectively. Although cured HFB-a is known to be a good heat-resistant material, its decomposition temperature was found to be lower than that of cured SOMPE-HFB-a. This result is reasonable due to the highly cleavable Mannich bridges of HFB-a. However, after removal of this volatile fraction, the surface of the bulky mass of cured HFB-a degraded in regard to the volatile portion and inherently became rich in terms of char, and enhancing the heat-resistance capability of the material. Thus, as the temperature increases, the weight loss of SOMPE-HFB-a increases compared to that of HFB-a. The char yields given in Table 4.3 are consistent with this explanation [38-39, 77, 92, 127-129].

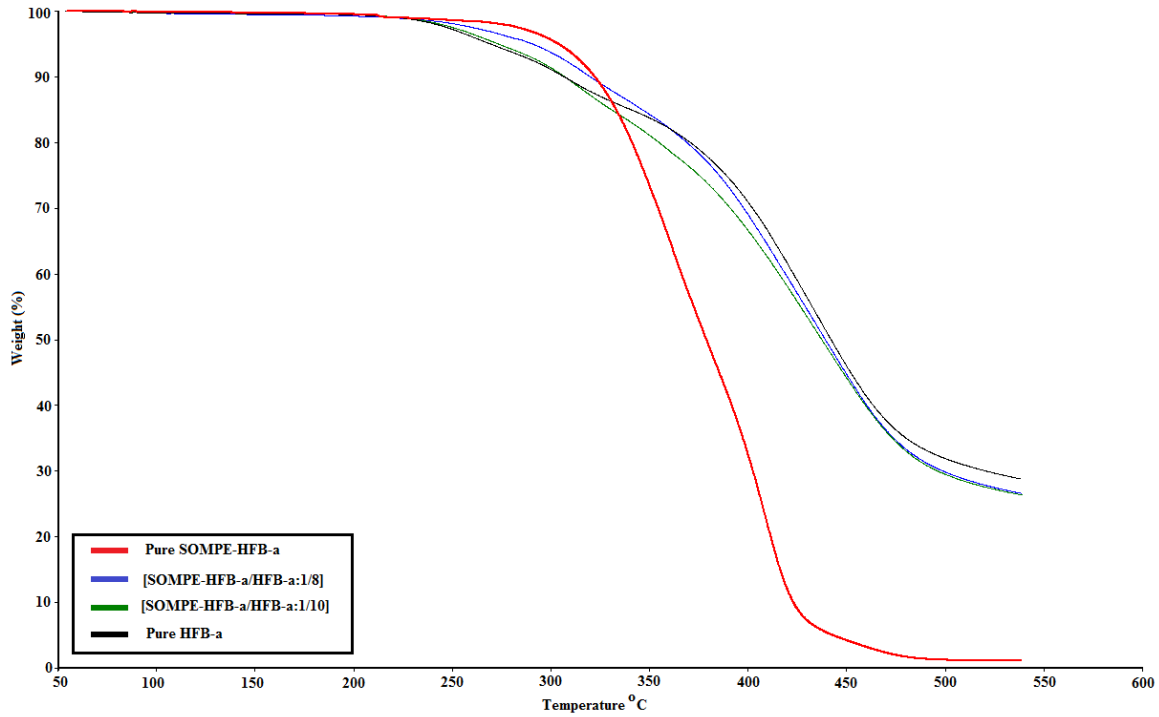

Figure 4.14 : TGA thermograms of cured samples.

Table 4.3 : Thermal properties of the cured samples.

Sample	$T_{5\%}$ (^oC)	Char Yield (%)
Pure SOMPE-HFB-a	304	1.1
[SOMPE-HFB-a/HFB-a:1/8]	291	26.6
[SOMPE-HFB-a/HFB-a:1/10]	274	26.4
Pure HFB-a	270	28.8

4.2 Modification of polycaprolactone-styrene-vinyl trimethoxysilane terpolymer with sunflower oil

In the second part of this thesis, a vinyl functional polyester based macromonomer was synthesized and further modified with SFOPG by sol-gel method to utilize as polymeric binder.

For this purpose, first vinyl functional macromonomer (HPCL) was prepared by ROP of CL using 2-hydroxyethyl methacrylate (HEMA) as initiator, and then copolymerized with styrene (St) and vinyl trimethoxysilane (VTMS), yielding a terpolymer (HPCL-St-VTMS). Since the film of HPCL-St-VTMS showed a tacky property, SFOPG was used as a modifier for HPCL-St-VTMS to enhance crosslinking as well as the flexibility to obtain a product which is applicable in terms of organic coatings.

The route of macromer synthesis by ROP of CL in the presence of HEMA initiator is shown in Figure 4.15. The FT-IR spectrum of HPCL can be seen in Figure 4.16. The existence of carbonyl band at 1721 cm^{-1} indicates the formation of polyester structure. The peaks at 2944 and 2865 cm^{-1} correspond to asymmetric and symmetric CH_2 stretching [130]. Additionally, the peak at 1638, and the broad peak between 3437 and 3549 cm^{-1} are attributed to C=C double bond of HEMA moiety and hydroxyl functionalities, respectively [131].

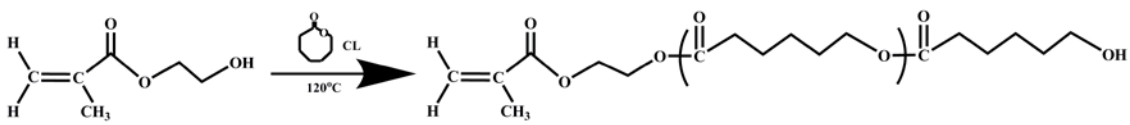

Figure 4.15 : Synthesis of HPCL by ROP.

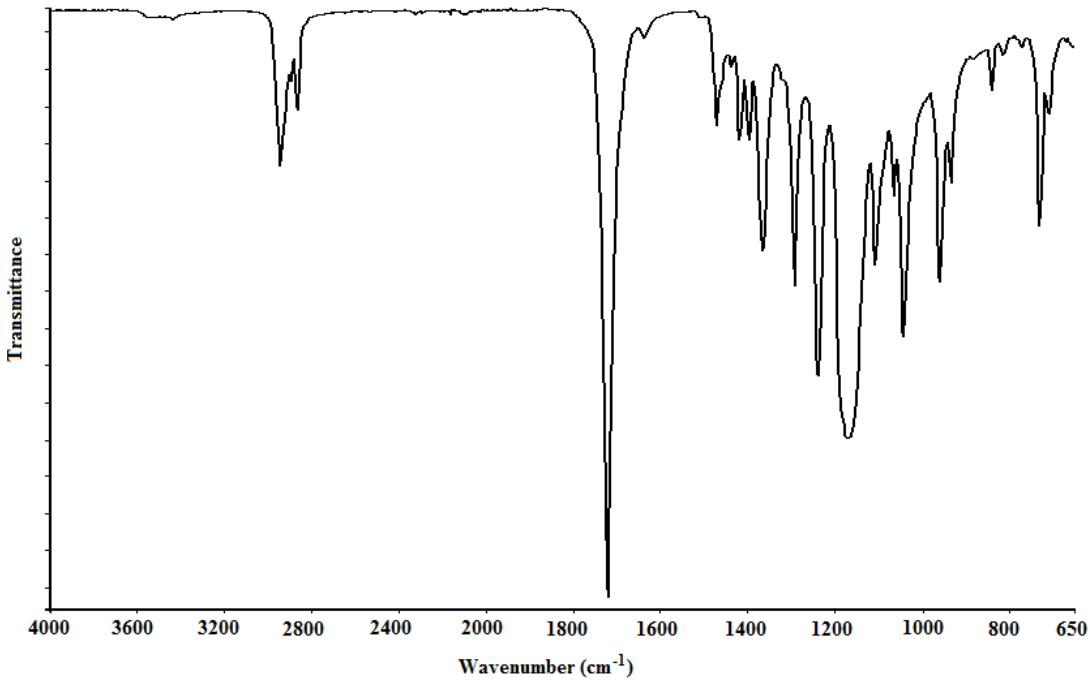

Figure 4.16 : FT-IR spectrum of HPCL.

Besides the FT-IR analysis, ^{1}H NMR spectrum was also recorded for the structural examination of HPCL. Figure 4.17 represents the ^{1}H NMR spectrum of HPCL. The signals at 5.52 and 6.05 ppm indicate that the olefinic protons of HEMA were preserved during the ROP of CL. The signals of main chain protons of PCL are located at 1.31, 1.57, and 2.24 ppm. The most intense multiplet at 3.98 ppm, the triplets at 3.84 and 3.56 ppm show the protons of $–CH_2–O$, –OH and $–CH_2OH$, respectively. The other peaks centered at 1.88 and 4.28 ppm belong to $–CH_3$ and $–CH_2–CH_2–$ bonds of HEMA moiety, respectively [131]. All of these results confirmed that the macromer has the same structure as that of given in Figure 4.15.

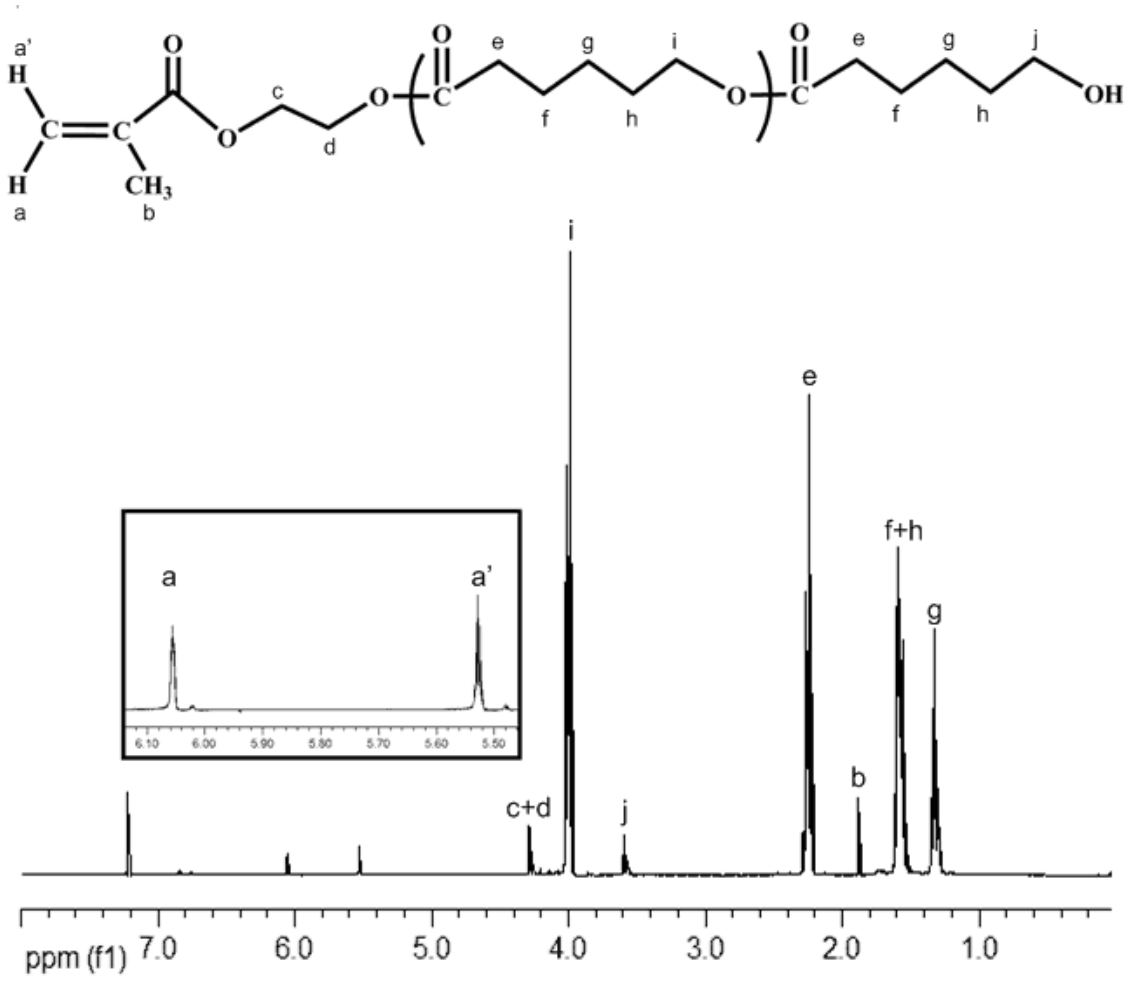

Figure 4.17 : ^{1}H NMR spectrum of HPCL.

The obtained HPCL was copolymerized with St and VTMS (HPCL-St-VTMS) (Figure 4.18) by free radical polymerization with the [VTMS/St] mol ratio of 0.5, 1.0 and 1.5 in the presence of various benzoyl peroxide amounts (Table 3.1). Reaction mixture (for each run) was precipitated into methanol and dried under vacuum, then investigated by using FT-IR. The absorption band at 3026 cm^{-1} given in Figure 4.19, represents the aromatic C-H stretching of benzene ring. The other characteristic peaks belonging to styrene are located at 1601, 1493, 1453, 759 and 698 cm^{-1} wavenumbers [132-134]. The ester carbonyl appears at 1722 cm^{-1} as a strong peak. The Si-O-CH_3, methoxy groups of silane moiety are observed at 1187, 1086 and 815 cm^{-1}. The overlapped condition of the peak at 1187 cm^{-1} is due to containing of C-O-C stretching of HPCL which appears at 1170 cm^{-1} [130]. The structure of HPCL-St-VTMS was also confirmed by ^{1}H NMR analysis. The ^{1}H NMR spectrum of HPCL-St-VTMS is given in Figure 4.20. It was observed that the new signals arised between 6.30-7.16 ppm imply the St attachment to the structure. The other vital

indicative peak centered at 3.49 ppm representing the protons of –Si–OCH_3 group confirms the VTMS attachment to the polymer chain.

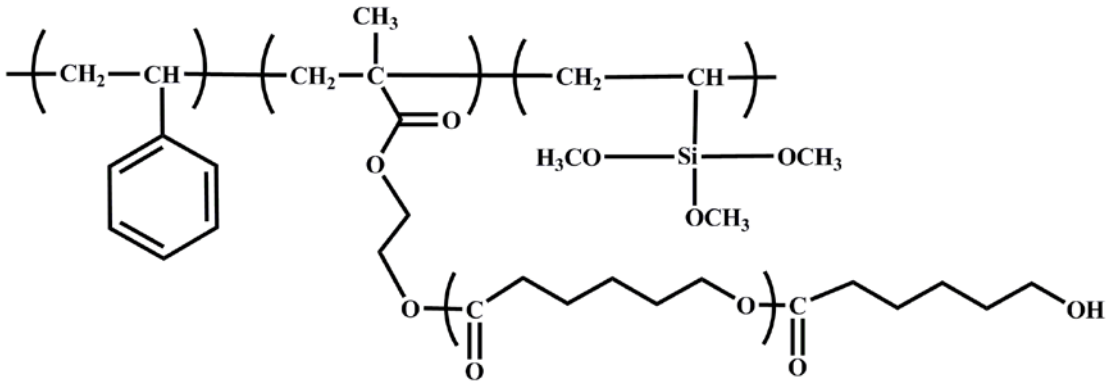

Figure 4.18 : Structure of HPCL-St-VTMS synthesized by free radical polymerization.

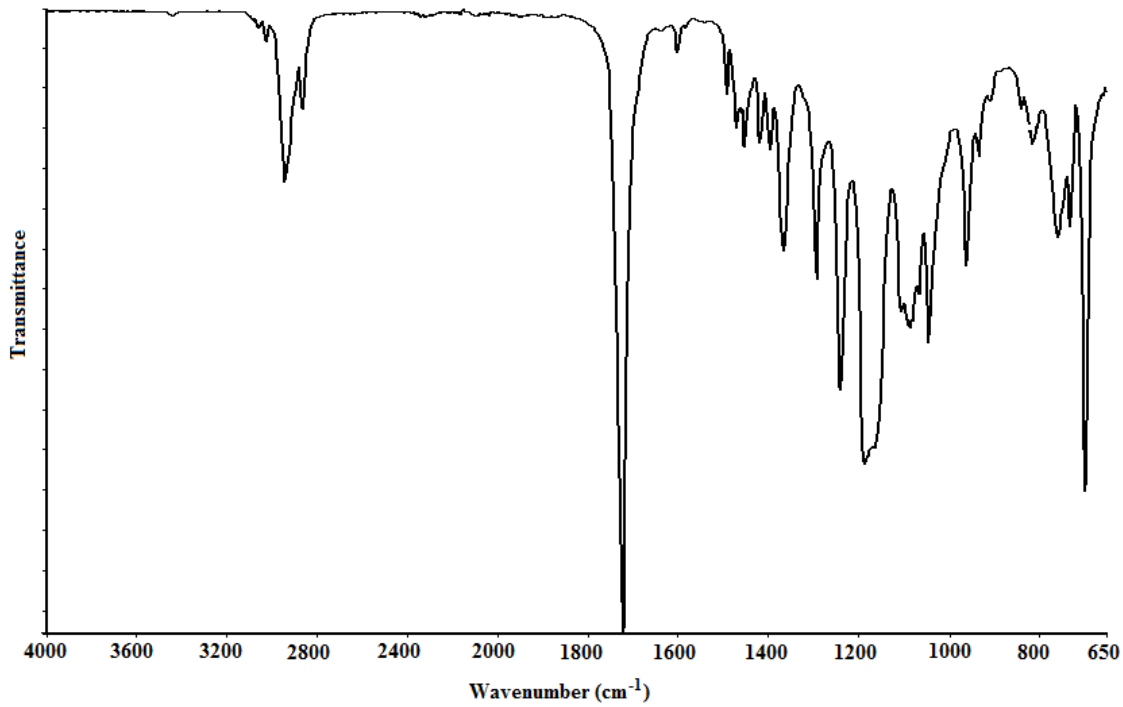

Figure 4.19 : FT-IR spectrum of HPCL-St-VTMS.

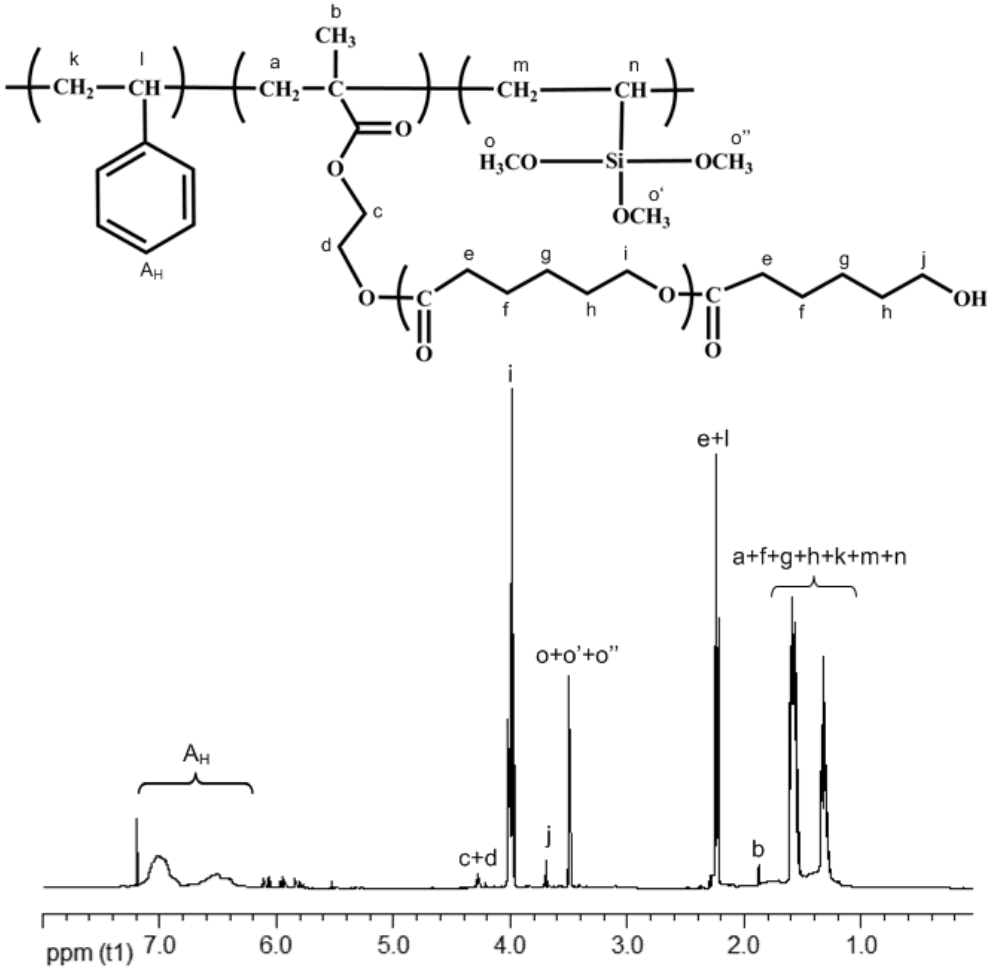

Figure 4.20 : ^{1}H NMR spectrum of HPCL-St-VTMS.

The polymer samples, prepared with different amounts of BPO and VTMS monomer feed were elaborated in view of attached VTMS via ^{1}H NMR data. Relative VTMS percentages were roughly estimated in order to make a comparison between the terpolymer samples by using the integration ratio of o+o'+o'' signal to all signals [135]. VTMS percentages found in this way were tabulated in Table 4.4. As seen, the increase of VTMS in the feed did not change VTMS amount attached to the polymer chain, considerably. This behavior is most probably due to steric hindrance of substituent group in VTMS and stabilization effect of the methoxy oxygen atom in the molecule [136-137]. However, the highest VTMS percentage has been obtained, when BPO amount and the [VTMS/St] mol ratio was 1.5 wt% and 0.5, respectively.

Molecular weights of $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-5.00, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-3.00, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.50, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.00, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.50, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.27, $HPCL_1$-St_{50}-$VTMS_{50}$-BPO-

1.48, $HPCL_1$-St_{50}-$VTMS_{75}$-BPO-1.50 samples which obtained at different initiator amounts, were determined also given in Table 4.4. It is apparent that the number average molecular weight (M_n) values are close to each other.

Table 4.4 : The results of terpolymer samples.

Sample	BPO wt%[a]	Mole ratio [VTMS/St]	VTMS%[b]	M_n[c]
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-5.00	5.0	0.5	1.35	11,328
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-3.00	3.0	0.5	1.59	12,561
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.50	1.5	0.5	1.65	12,281
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.00	1.0	0.5	1.51	12,511
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.50	0.5	0.5	1.35	11,916
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.27	0.27	0.5	1.33	13,209
$HPCL_1$-St_{50}-$VTMS_{50}$-BPO-1.48	1.48	1.0	1.05	11,500
$HPCL_1$-St_{50}-$VTMS_{75}$-BPO-1.50	1.50	1.5	1.11	10,930

[a]BPO wt% was based on total amount of St and VTMS.
[b]Percentage of VTMS in terpolymer was calculated from ^{1}H-NMR.
[c]Determined by GPC against polystyrene standards.

All terpolymer samples given in Table 3.1 were applied as thin films on glass substrates and cured by the following the procedure given in experimental part. As it is well known, the silane crosslinking occurs in two stages. In the first stage, the methoxy groups of VTMS are hydrolyzed and silanols are produced. Then, these silanol groups combine with each other through the condensation reaction with leaving of alcohol or water. In the course of condensation reaction, silanol groups can react with other hydroxyl groups belonging to other kind of compound present in the medium, as well [103, 138-139].

The obtained film samples showed tacky and sticky properties, therefore they required additional modification. For this purpose, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 sample was subjected to further modification with SFOPG (Figure 4.1). Possessing free hydroxyl groups, SFOPG was chemically combined with the terpolymer chain through the sol-gel reaction during the curing process. Through these modifications the obtained film sample gave good film properties due to the counter balance effect of the excess crosslinking and flexibility coming from the inserted oil moiety.

For this purpose, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 and SFOPG 20 wt% (based on $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5) were mixed together and applied on the glass substrate, and then the film was cured as explained in experimental part. The representative structure of the cured film product (SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5) is illustrated in Figure 4.21. Cured film sample of SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 was examined by FT-IR to reveal both the crosslinking reaction and whether the silanols were reacted with the hydroxyl groups of SFOPG. As evident from Figure 4.22, the methoxy bands at 1187, 1086 and 815 cm^{-1} disappered after the curing reaction in the presence of SFOPG (Figure 4.22a). New peaks arised resulting from the formation of Si–O–Si linkages by the sol-gel reaction (Figure 4.22b).

Additionally, in order to clarify, whether the SFOPG hydroxyls can give the same kind of condensation reaction, a model mixture of VTMS monomer and SFOPG was prepared and subjected to curing reaction. The curing reaction was terminated before reaching a fully cured state to obtain a sample soluble in $CDCl_3$ for ^1H NMR analysis. ^1H NMR spectra of VTMS-SFOPG mixture before and after sol-gel reaction were recorded, given in Figure 4.23. The resulting product was depicted in Figure 4.24.

As shown in Figure 4.23a, the signals between 5.76-6.12 ppm include the protons of CH_2=CH– moiety of VTMS. The other vital peak of VTMS, which belongs to –Si–OCH_3 is located at 3.51 ppm. In Figure 4.23a, the proton spectra between 0-3.0 ppm contains the methyl and methylene chain protons of SFOPG. Moreover, the signals at 4.06 and 4.21, 5.19 and 5.27 are attributed to protons of CH_2–OCOR, CH–OCOR and –CH=CH–, respectively. The –OH group of SFOPG which was expected to react with methoxy group of VTMS via sol-gel reaction is located at 3.65 ppm.

Comparing Figures 4.23a and 4.23b shows that SFOPG participated in condensation reaction throughout the hydrolysis of methoxy moieties. It was observed from Figure 4.23b that the signal of –OH group of SFOPG disappeared while new chemical shifts developed at 4.33, 4.35 and 4.57 representing –Si–OCH_2– and –Si–OCH– linkages. Thus, ^1H NMR data confirm that SFOPG molecules were successfully combined with methoxy groups of VTMS [140-142]. These results demonstrate the occurence of hydrolysis and condensation reactions, thus building up the film structure via crosslinking.

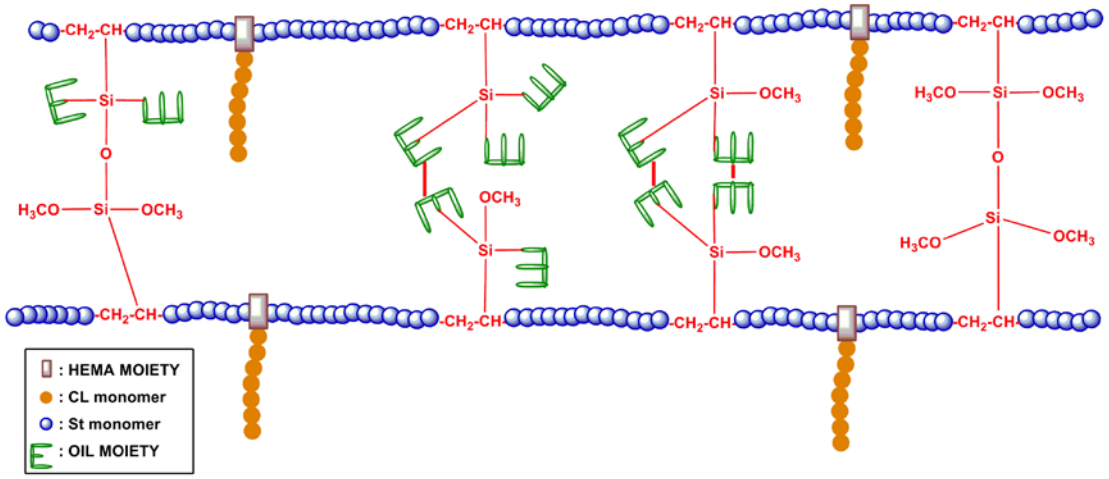

Figure 4.21 : Representative structure of SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5 after crosslinking.

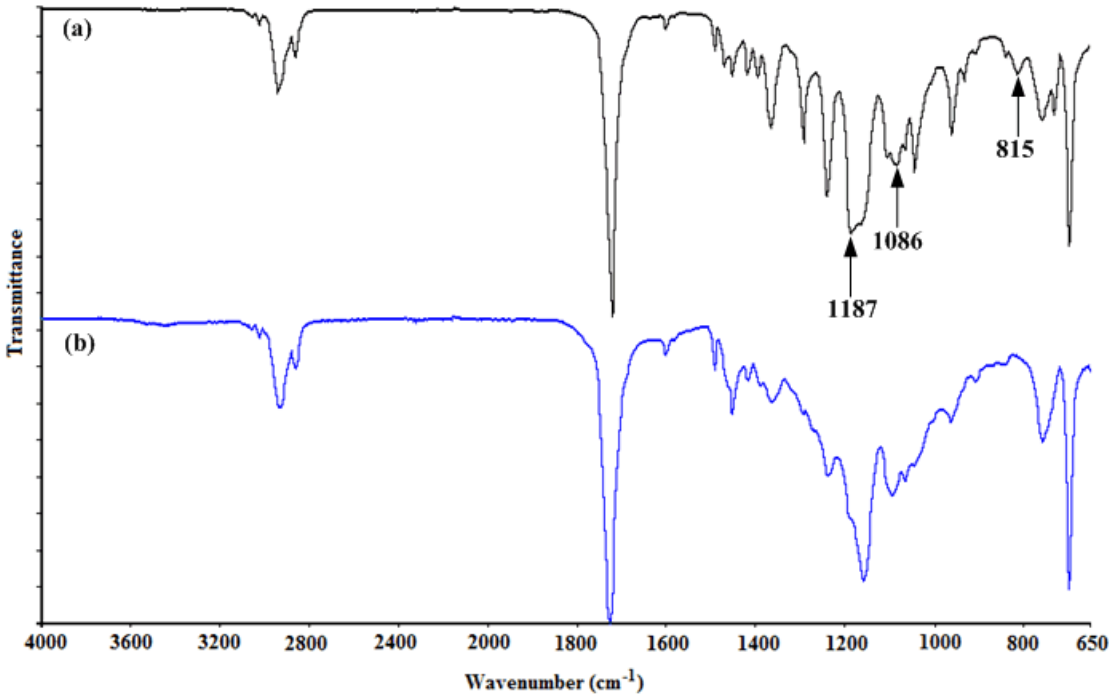

Figure 4.22 : FT-IR spectra of (a) HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5 and (b) cured SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5.

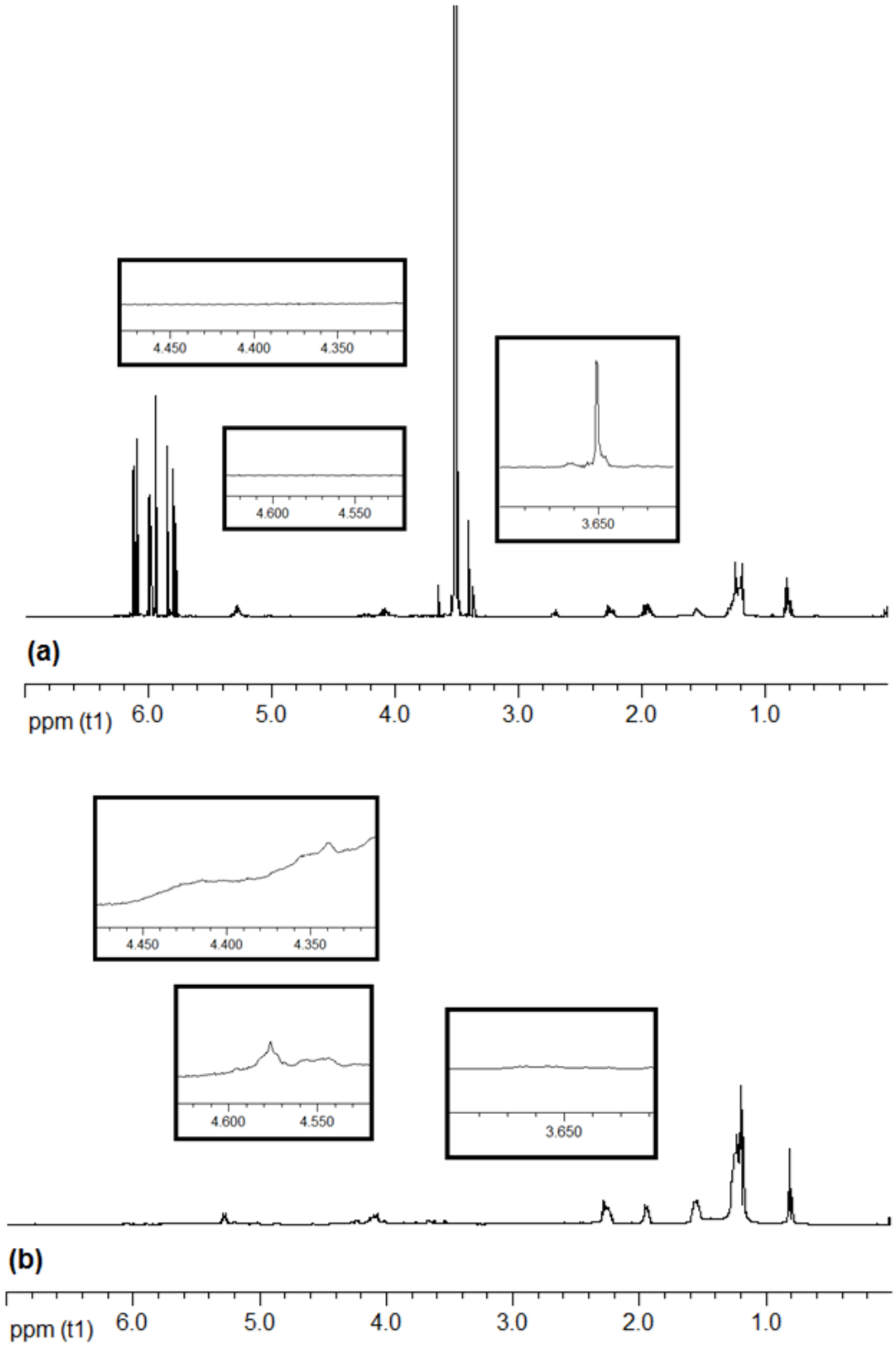

Figure 4.23 : ^{1}H NMR spectra of VTMS-SFOPG mixture (a) before and (b) after crosslinking.

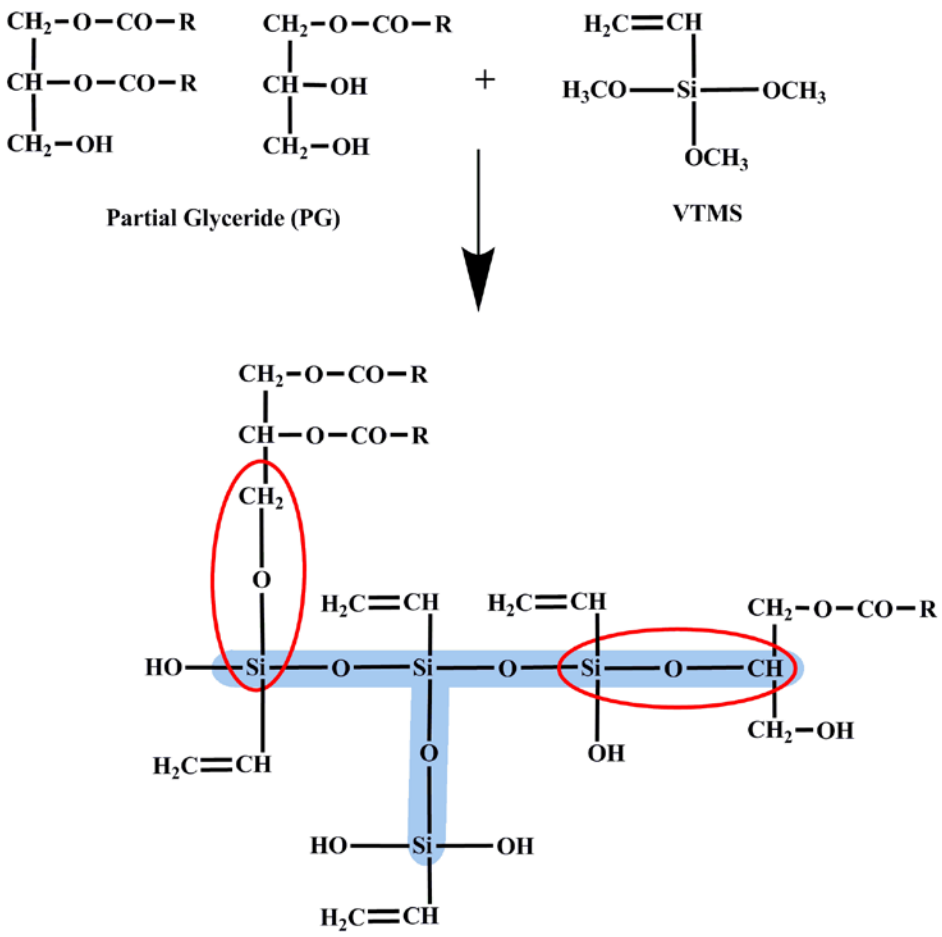

Figure 4.24 : Representative structure of crosslinked VTMS-SFOPG mixture.

Concerning the thermal characterization, the cured and uncured polymer samples were studied to analyze the melting behavior using DSC with nitrogen as a purge gas. Figure 4.25 displays the DSC thermograms of the samples. The melting points (determined as the peak temperatures, T_m) and melting enthalpies (ΔH_m) of HPCL, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5, cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 and cured SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 samples are summarized in Table 4.5. As seen, the melting enthalpies of HPCL, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 and cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 are 107.0, 38.9 and 7.6 J/g, and the corresponding melting points are 58.5, 50.7 and 45.9^{o}C, respectively.

Through the participation of silane units into the polymer backbone and subsequent crosslinking caused a decrease in the crystalline content, the melting temperatures of the crosslinked samples were lower than those of uncrosslinked ones, which is consistent with the findings in the literature [136, 143-144].

On the other hand, the sample of cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 film has a very low melting enthalpy of 7.6 J/g. This small endothermic peak implies that the achieved crosslinking degree still allows the molecular motion of the chains to some extent.

Besides the added cobalt and lead naphthenate, metal-oxo clusters in the matrix resulting from the sol-gel reaction can promote the oxidative polymerization through the fatty acid chains, similar to the conventional metal driers [5]. Therefore, the sample of cured SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 showed no melting behavior. These findings indicate that sol-gel reaction between SFOPG and methoxy silane groups occured and yielded a high crosslink degree preventing the molecular motion in the polymer matrix.

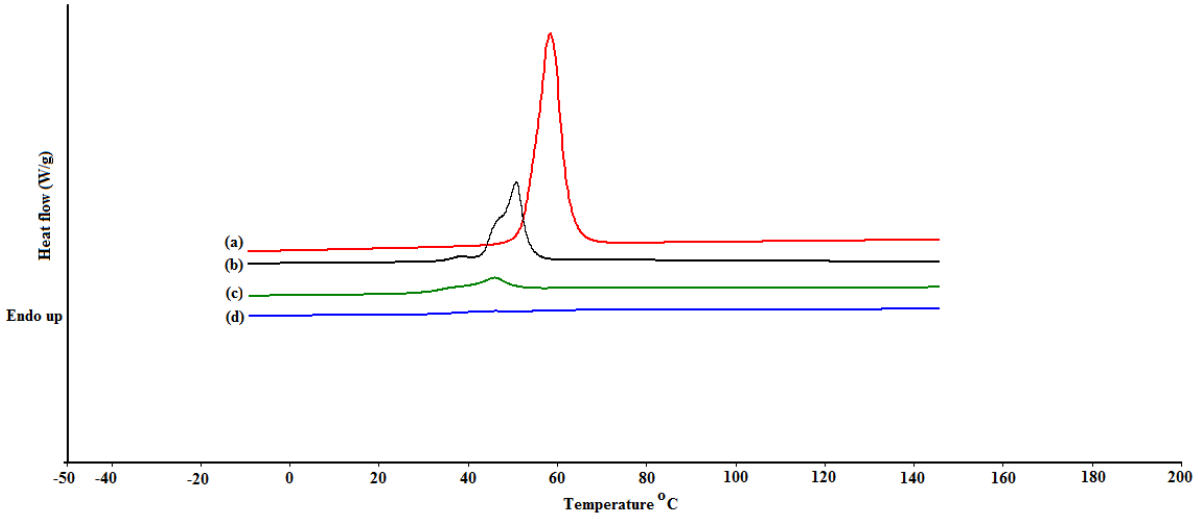

Figure 4.25 : DSC thermograms of (a) HPCL, (b) $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5, (c) cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 and (d) cured SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5.

Table 4.5 : Melting points and enthalpies of the samples.

Sample	**T_m (^oC)**	**ΔH_m (J/g)**
HPCL	58.5	107.0
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5	50.7	38.9
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 (cured)	45.9	7.6
SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5(cured)	-	-

TGA was also applied for the thermal characterization of the synthesized polymer samples. Figure 4.26 illustrates the thermograms recorded in nitrogen atmosphere. As seen in Table 4.6, the decomposition temperatures referring to 5% weight loss

($T_{5\%}$) are 262, 312 and 312°C for HPCL, cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 and cured SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5, respectively.

It is evident that $T_{5\%}$ value increased due to retarding effect of siloxane bridges resulting from the incorporation of inorganic silane domains into the polymer structure [145-146]. Since dissociation energy of –Si–O– bond is higher than those of –C–O– and –C–C– bonds, –Si–O– bonds show more resistance to thermal degradation and decomposition temperature shifted to a higher value.

The char yields of HPCL, cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 and cured SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 at 555°C are 0.6 wt%, 6.0 wt% and 9.3 wt%, respectively. The cured SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 gave the higher char yield in comparison with cured $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5. This is an expected result due to the strong covalent bonds of –Si–OCH_2– and –Si–OCH–, builded between the Si–OH groups and –OH functionalities of SFOPG [147].

Table 4.6 : Thermal properties of polymer samples.

Sample	$T_{5\%}$ (°C)	Char Yield (wt %)
HPCL	262	0.6
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 (cured)	312	6.0
SFOM-$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5 (cured)	312	9.3

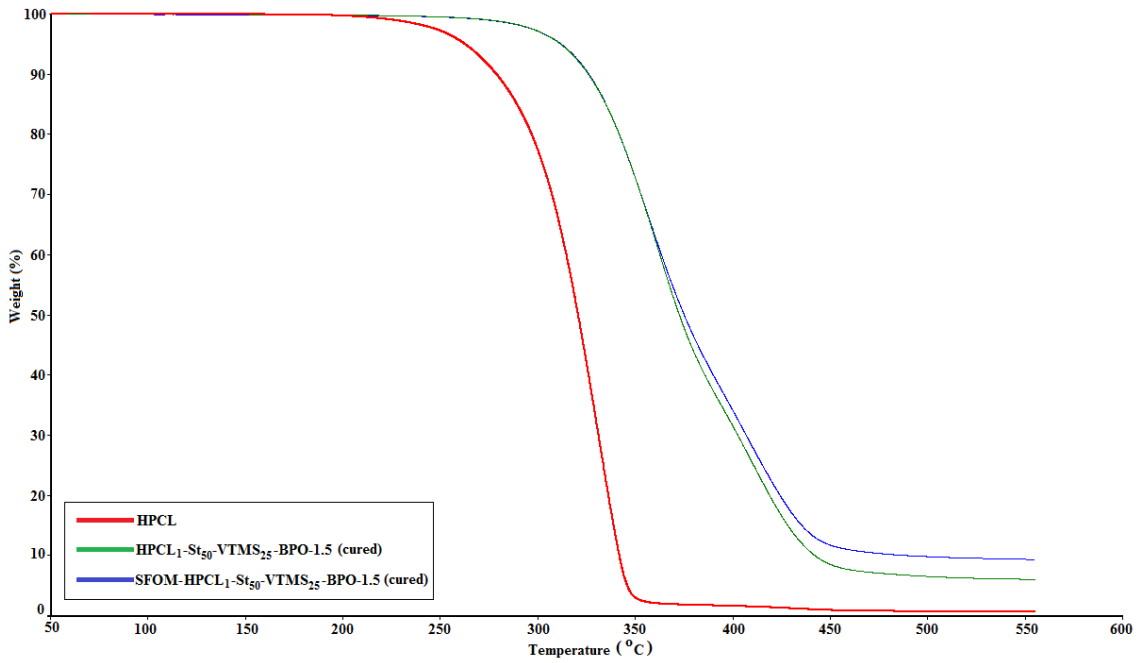

Figure 4.26 : TGA thermograms of polymer samples.

The SEM image of cured SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5 coating is given in Figure 4.27. As seen inorganic domains contain mainly nano particles and less amount of agglomerated structures, as encountered by others [20, 108, 148-149].

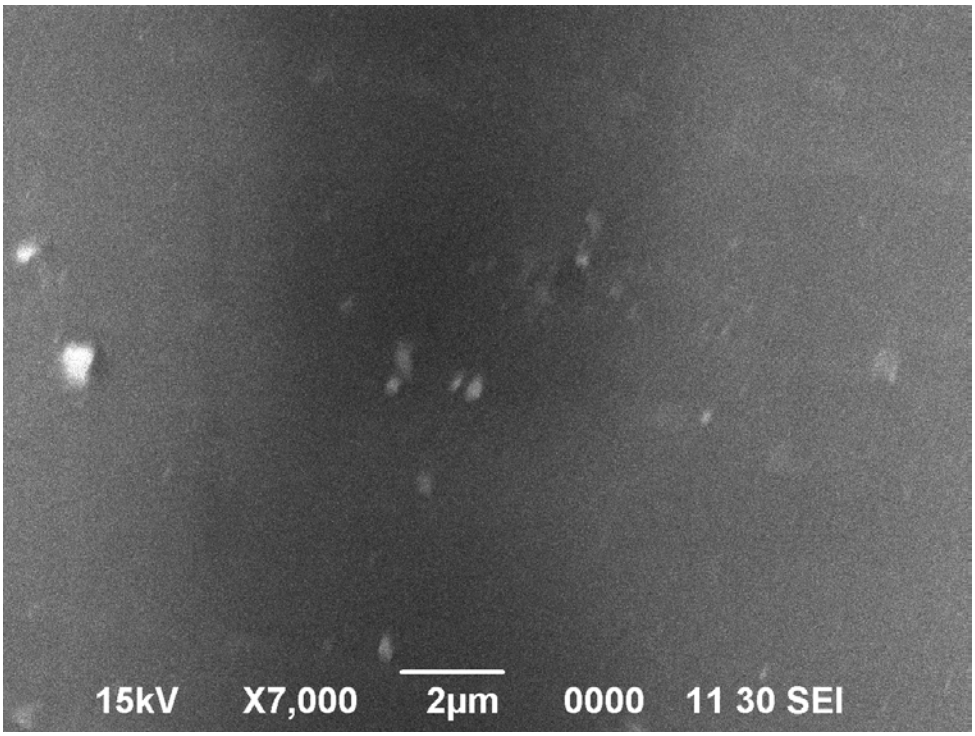

Figure 4.27 : SEM micrograph of cured SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5 coating.

The film properties of SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5 sample were also determined to evaluate its potential use in terms of organic coatings. The results are summarized in Table 4.7. The film showed good adhesion both on glass and metal surfaces, while it could be bent without cracking over the cylinder with diameter of 2 mm. Also, no change was observed both in the acid and in the water resistance tests. In case of exposure to alkali, the film was partially peeled after 176 min. In our previous study, the urethane oils showed partial peeling after 20 and 30 min later [69]. In comparison with these results, SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5 film can be considered a better alkali resistant material, which can be used as an oil-based binder.

Table 4.7 : Film properties of cured SFOM-HPCL$_1$-St$_{50}$-VTMS$_{25}$-BPO-1.5.

Applied test	Flexibility[a]	Adhesion on a glass surface[b]	Adhesion on a tin plate[b]	Acid resistance[c]	Alkali resistance[d]	Water resistance[e]
Film sample	2 mm	5B	5B	No change	176 min pp	No change

[a] The diameter of the cylinder that did not cause a crack on the film.
[b] Test method B was applied.
[c] Test was performed at 25^{o}C with 9% H_2SO_4 solution for 48 h.
[d] Test was performed at 25^{o}C with 3% NaOH solution. pp = partial peeling.
[e] Test was performed at 25^{o}C for 48 h.

5. CONCLUSION

In this dissertation, we have investigated the functional polymers by ring opening polymerization of ε-caprolactone and their further modifications for the coating applications. For the modification, two strategies were used:

- preparation of oil-modified polycaprolactone and its further modification with benzoxazine,
- modification of polycaprolactone-styrene-vinyl trimethoxysilane terpolymer with sunflower oil.

In the first strategy, SFOPG was used as an initiator in the ROP of CL. The resulting polymer (SOMPE) that was obtained in this manner demonstrated soft film properties due to its low oil moiety content. In order to avoid the soft property, oil-modified PCL was further modified with benzoxazine (HFB-a). First, HFB-a was chemically combined with SOMPE by a urethane linkage through the reaction of TDI with the hydroxyls of SOMPE and HFB-a (SOMPE-HFB-a). SOMPE-HFB-a also showed tacky film properties because the soft segments of the molecular structure were still dominant. To reduce such dominance, additional HFB-a was blended with SOMPE-HFB-a. For this purpose, HFB-a was mixed in different weight ratios, and the properties of the resulting film were determined. The sample [SOMPE-HFB-a/HFB-a:1/8] had good film properties. By applying this modification, deficiencies arising from the softness of polyester and brittleness of polybenzoxazine were eliminated, and a product with good film properties was achieved.

In the second strategy, vinyl functional polyester (HPCL) was prepared by the ROP of CL in the presence of HEMA, as the initiator. This obtained macromonomer was copolymerized with St and VTMS monomers by free radical polymerization to obtain HPCL-St-VTMS terpolymer. Since the crosslinking degree of terpolymer was not sufficient in terms of film properties, it was further modified with SFOPG. A

network structure with high crosslinking density in accompanying with flexibility still appropriate for coating was achieved.

The obtained oil-based binders by using these two strategies gave good film properties such as adhesion, flexibility, alkali, acid and water resistances. Additionally, the thermal characterization studies revealed that the incorporation of benzoxazine monomer into the structure and siloxane bridges formed between the polyester chains enhanced the thermal stability. In the end, it was understood that these binders could be used as coating materials.

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Publications:

- **Taşdelen-Yücedağ, Ç.,** Erciyes, A.T., "Preparation of oil-modified polycaprolactone and its further modification with benzoxazine for coating purposes", *Progress in Organic Coatings*, 76, 137-146 (2013).
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- Artun, G., Özkan, E., Omay, D., **Taşdelen-Yücedağ, Ç.,** Güvenilir, Y., "Biodegradation of Polyurethanes with Protease", *European Polymer Congress (EPF 2009)*, pp. 142, July 12-17 2009, Graz, Austria.
- Omay, D., **Taşdelen, Ç.**, Guvenilir, Y., "Enzymatic Degradation of Freezer Bags with Protease Enzyme", *13th International IUPAC Conference*, pp. 202, July 5-8 2009, Montreal, Canada.
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PUBLICATIONS/PRESENTATIONS ON THE THESIS

Publications:

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- **Taşdelen-Yücedağ, Ç.,** Erciyes, A.T., "Modification of polycaprolactone-styrene-vinyl trimethoxysilane terpolymer with sunflower oil for coating purposes" (2013) (in preparation).

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