ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

THE PREPARATION OF LINSEED OIL FATTY ACID MODIFIED POLYSTYRENE

M.Sc. THESIS

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Department of Chemical Engineering

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KETEN YAĞI ASİTİ İLE MODİFİYE EDİLMİŞ POLİSTİREN ELDESİ

YÜKSEK LİSANS TEZİ

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Kimya Mühendisliği Programı

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HAZİRAN 2017

Özgün Uçak, a M.Sc student of İTU Graduate School of Science Engineering and Technology student ID 506131027, successfully defended the thesis/dissertation entitled “THE PREPARATION OF LINSEED OIL FATTY ACID MODIFIED POLYSTYRENE”, which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 05.05.2017
Date of Defense : 08.06.2017

To my mother,

FOREWORD

I would like to thank to my precious supervisor, Prof. Dr. Ahmet Tuncer ERCIYES, who always support and guide me during the research process.

May 2017

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ABBREVIATIONS

St : Styrene
NMRP : Nitroxide Mediated Radical Polymerization
FA : Linseed Oil Faaty Acid
CMS : 4-Chloromethyl styrene
FRP : Free Radical Polymerization
TEMPO : 2,2,6,6-tetramethyl piperidinyl-1-oxy
BPO : Benzoyl Peroxide
GPC : Gel Permeation Chromatography
FT-IR : Fourier Transform Infrared
^{1}H-NMR : Nuclear Magnetic Resonance
DMF : N,N- Dimethylformamide
PCMS : Poly(4-chloromethyl styrene)
P(St-co-CMS) :Styrene and 4-chloromethyl styrene copolymer
VBC : Vinylbenzyl chloride

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THE PREPARATION OF LINSEED OIL FATTY ACID MODIFIED POLYSTYRENE

SUMMARY

Vegetable oils are raw material resources that enable to synthesize polymers in oil based organic coating industry. However, oils could not be used without modification for coating purposes. Linseed oil has an iodine value in the 185-190 region that is a good choice for modification of polystyrene polymers because of its naturally drying capacity. Because of brittle characteristic of polystyrenes, they could not be used in coating applications. However they could form adhesive, tough films when modificated with vegetable oils [1-2]. On the other hand, benzyl chloride bonds of 4-chloromethyl styrene (CMS) are made nucleophilic substitutions possible. In this thesis, the aim is to eliminate the fragility character of polystyrene by the way of modification via linseed oil fatty acid for being used as a coating material in industry.

For this purpose, first of all, linseed oil fatty acid (FA) mixture was prepared by saponification reaction. Linseed oil was boiled with 10% KOH solution then, obtained soap mixture was turned into fatty acid mixture by acidulation with sulfate acid solution.

In the next step, polymer of Styrene-co-4-Chloromethyl Styrene [P(St-co-CMS)] was synthesized by using Nitroxide Mediated Radical Polymerization (NMRP) method to control polymerization process and to obtain narrow molecular weight distributions. The molecular weights and polydispersities of the copolymers were identified by Gel Permeation Chromatography (GPC). The number of functional chloromethyl groups (CH_2-Cl) were calculated by using the results of Nuclear Resonance Spectroscopy (^{1}H-NMR) and GPC. According to results of the characterization studies (^{1}H-NMR, GPC), number of 4-CMS units in each copolymer chain were calculated as 1.373 mole and 2.3946 mole for P(St-co-CMS)1 and P(St-co-CMS)2, respectively.

In the step of modification with FA, nucleophilic substitution reaction was achieved having regard to the number of functional CH_2-Cl groups in 1 mole P(St-co-CMS)2 chain. FA attached to the P(St-co-CMS)2 backbone by substitution reaction. The reaction was achieved between chloro group and acid group in the presence of K_2CO_3. For the characterization studies GPC, ^{1}H-NMR and Fourier Transform Infrared Spectroscopy (FT-IR) were applied. The film properties of the samples were specified according to ASTM standarts.

Although P(St-co-CMS)2-FA appears to be a feebleness material for coating, to decrease the fragility, polymer of CMS (PCMS) was synthesized. But, modification products with PCMS was not formed since gelation occurred due to the high molecular weight and high chlorine group numbers.

KETEN YAĞI ASİTİ İLE MODİFİYE EDİLMİŞ POLİSTİREN ELDESİ

ÖZET

Bitkisel yağlar uzun süredir düşük maliyetli olması, kolay ulaşılabilir olması, yenilenebilir olması gibi pek çok nedenden dolayı polimer üretiminde kullanılmaktadır. Yağların, polimer modifikasyonlarında kullanılmasıyla ilgili pek çok çalışma yapılmaktadır. En çok kullanılan yağlar; ayçiçek, hindistan cevizi, pamuk, keten ve soyadır. Trigliserit yağlar; kuruyan, kurumayan ve yarı kuruyan olarak sınıflandırılırlar. Kuruma özelliği yağ asiti içeriğiyle ilgilidir.

Sabunlaşma reaksiyonu sonucu oluşan sabun çözeltisinin sülfat asiti ile muamele edilmesi sonucu yağ asitleri elde edilir. Yüzey kaplama malzemesi olarak kullanılmaları için modifikasyonlara ihtiyaç duyulmaktadır. Pek çok makalede yağ asitleriyle yapılmış çalışmalar yer almaktadır [3].

Polistirenler; transparan, sert, hafif, suya dayanıklı, alkali kimyasallara ve asite karşı dayanıklı olmasının yanı sıra oldukça kırılgandırlar. Polistirenler kırılgan özellikte olmaları dolayısıyla modifikasyona uğramadıkları sürece kaplama malzemesi olarak kullanılamamaktadırlar. Bu nedenle, kırılganlık özelliklerinin giderilmesi ve kaplama malzemesi olarak kullanılabilmeleri için polistiren zincirine yağ asiti takılması hedeflenmiştir.

Bu çalışmada, öncelikle kuruma özelliğine sahip yüksek iyot değerli (185-190) keten yağından, sabunlaşma reaksiyonu sabun çözeltisi elde edilmiştir. Daha sonra elde edilen bu sabun çözeltisi, sülfat asiti varlığında asite dönüştürülmüş ve keten yağı asitleri elde edilmiştir.

Bir sonraki aşamada, CMS ve St monomerleri kullanılarak BPO ve TEMPO varlığında NMRP yöntemi ile P(St-co-CMS)1 ve P(St-co-CMS)2 kopolimerleri sentezlenmiştir. Elde edilen P(St-co-4-CMS)1 ve P(St-co-CMS)2 kopolimerlerinin molekül ağırlıkları sırasıyla 2207 g/mol ve 3931 g/mol, polidispersiteleri ise 1.35 ve 1.16 olarak GPC vasıtasıyla tayin edilmiştir. ^{1}H-NMR spektrumu ile kopolimer zincirindeki CMS ve St aromatik protonlarına ait olan 6.3 ve 7.5 ppm arasındaki toplam pik alanı ile 4.5 ppm deki CH_2-Cl grup protonlarına ait olan pikin alanları hesaplanmıştır. 1 mol polimer zincirinin içerdiği CH_2-Cl grup sayısı; GPC, Denklem 4.1,4.2,4.3 ve ^{1}H-NMR analiz sonucları kullanılarak P(St-co-CMS)1 ve P(St-co-CMS)2 için sırasıyla 1.373 mol ve 2.3946 mol olarak hesaplanmıştır. Reaksiyon başlangıcında ve bitişinde FT-IR analizleri yapılmış ve karakteristik pikler teyit edilmiştir.

Çalışmanın sonraki adımında, P(St-co-CMS)2 kopolimerinin keten yağı asitiyle modifikasyonu gerçekleştirilmiştir. 1 mol kopolimer zinciri üzerindeki 2.3946 mol klorometil fonksiyonel grubunun tamamını asit grubu ile bağlamak için reaksiyona girecek yağ asiti ve potasyum karbonat ekivalent miktarları hesaplanmış olup nitrojen atmosferi altında 70°C’ de modifikasyon reaksiyonu gerçekleştirilmiştir. Oluşan ürünün esneklik[4] ve kuruma süresi[5] ASTM standartlarına göre tayin edilmiştir.

P(St-co-CMS)2-FA kaplama endüstrisi için gelecek vaadeden malzeme olmasına rağmen elde edilen ürün yeterli esneklik özelliği gösterememiştir. Dolayısıyla, film özelliklerinin iyileştirilmesi için esneklik özelliği kazandıran birimlerin arttırılması gerektiği sonucuna varılmıştır. Bu amaçla, serbest radikal polimerizasyonu ve nitroksit ortamlı radikal polimerizasyonu yöntemleri ile farklı molekül ağırlıklarında ve farklı polidispersite değerlerine sahip PCMS1, PCMS2, PCMS3, PCMS4 homopolimerleri sentezlenmiştir. Serbest radikal polimerizasyonu ile elde edilen PCMS1 ve PCMS2 polimerlerinin molekül ağırlıkları 6.5 saat sonunda 34483 g/mol ve 4 saat sonunda 25559 g/mol olarak, polidispersiteleri ise 4.63 ve 5.28 olarak GPC ile tayin edilmiştir. Ayrıca 1 mol polimer zincirindeki klorometil fonksiyonel grubu sayıları da 225 mol ve 167 mol olarak hesaplanmıştır. Üretilen yüksek molekül ağırlıklı bu polimerlerin klorometil fonksiyonel gruplarının yalnızca %40'ına ve %20'sine keten yağı asiti bağlanılması denenmiş olup, modifikasyon reaksiyonunda jelleşme gözlendiği için ürün elde edilememiştir. Sonuçta; büyük molekül ağırlıklı ve çok miktarda klorometil fonksiyonel gruplarına sahip olan polimerler kullanıldığında jelleşme kaçınılmaz olmuştur. Bundan dolayı, yoğun oluşan çapraz bağlanmayı engellemek amacıyla molekül ağırlığı kontrolünün sağlanamadığı serbest radikal polimerizasyonu yerine; düşük molekül ağırlıklı, düşük polidispersiteli polimer üretimine olanak veren nitroksit ortamlı radikal polimerizasyonu yöntemi kullanılarak PCMS3 ve PCMS4 polimerleri sentezlenmiştir. Oluşan PCMS3 ve PCMS4 polimerlerinin molekül ağırlıkları 9276 g/mol ve 7141 g/mol olarak GPC ile saptanmıştır. 1 mol polimer zincirinin içerdiği CMS birim sayısı 60 mol ve 44 mol olarak hesaplanmıştır. FRP yöntemi ile üretilen polimerlerin molekül ağırlıklarına kıyasla NMRP ile sentezlenen polimerlerin molekül ağırlıkları düşük olmasına rağmen, yağ asiti ile substitution reaksiyonu sonucu ürün yine oluşamamış ve çapraz bağlanma oluşumu gözlenmiştir.

1. INTRODUCTION

Polymers are materials that consist of covalently bonded long molecules. They could be obtained from natural or synthetic sources[6]. Polymers are commonly used for different technical aims because of their diversified properties. A functional variation and their impacts has made them useful in a very diversity of application areas. The monomer and the design of polymer molecule define the major properties of synthesized polymers[7].

Vegetable or plant oils are renewable resources that could be used as primary starting substance to create novel products in a diversified amount of structural , useful and practicable variety. The abundant accessibility and comparatively being low cost make plant oils an industrially interesting essential component for polymer industry. Vegetable oils and their derivatives have been used in chemistry industry due to their low cost, renewable characteristic ,world–wide accessibility and wide application potentiality over the years. During the recent years, vegetable oils have been demanded in large quantities as an raw material for producing additive to a variety of industries such as coating, adhesive, polymer, nanocomposite [8-12]. Due to the excessive resource consumption , industrially applicable and alternative raw materials require to be searched. For this reason, huge demand for plant oils have come into existence. Under this circumstances, vegetable oils enable lots of advantages in not only accessibility but olso prices. The largest plant oil resources are linseed, soybean, cottonsead, peanut, coconut, olive, sunflower, corn [13].

In chemical industry, the most important raw materials are plant oils and their fatty acid derivatives which could be processed to form functional polymers, coating materials and additives [14-17]. The main component of vegetable oil is triglyceride. Fatty acids constitute 95% of them. The contents of fatty acids change with regard to vegetable oil types, which means all fatty acids have different characteristics. The industrial potential of fatty acids and their derivatives with polymers are growing day by day. Fatty acids can be obtained easily from triglyceride oils.

Plant oils having high viscosity indices and low volatility have been used in lots of implementations such as additives in coating and polymer industry [14].

Fatty acids have been taken advantage of widely to procure coatings. Usage as toughening factors were published in literature. Fatty acids from drying oils are significant raw material for coating purposes as they can be modified to present different types of functionalities. However, it is known that drying oils are more efficient when they alter their natural state for polymerization and to form tough, adherent, waterproof films [1-2].

CMS is a significant functional monomer because of its benzylic chlorine which could make lots of nucleophilic substitutions [18-20]. Moreover, CMS monomer could be copolymerized easily with different initiators and the reaction product (polymer/copolymer) can able to react with nucleophilic reagents [21-23]. Living free radical polymerization provide the preparation of polymers with controlled molecular weight and narrow polydispersity [24-26]. The polymer with controlled molecular weight and narrow polydispersity was synthesized by using TEMPO as a chain-end counter-radical to mediate the polymerization of styrene [27]. Nitroxide mediated polymerization enables synthesis of controlled molecular weight copolymers under light conditions by using of a classic initiator BPO in the presence of stable nitroxide radical TEMPO.

Modern earth understood the important of natural resources usage in place of synthetic ones. While material science especially coating technology is evolving, lots of natural resources are included to organic coating production process by scientists. Thataway, many experiments, researches were achieved and numerous research papers have been issued which indicate the worldwide study for using triglyceride oils to produce functional polymers for coating purposes [28-36]. Also many research papers were published to show functionality attachment via nucleophilic substitution of CMS units [37-58] but none of them have attached fatty acids into PCMS and P(St-co-CMS) by using FRP and NMRP techniques.

In this thesis, our motivation is to develop a point of view on how linseed oil fatty acid based copolymers are used in coating implementations. For that purpose, benzylic chlorine characteristic of CMS was taken advantage of for nucleophilic subtitution. In this study, fatty acids were prepared from linseed oil. P(St-co-CMS) was synthesized in the present of BPO and TEMPO by using NMRP technique. Then, immediately after drying of copolymers, fatty acids were attached to polymer scaffold. End product was obtained and successful organic coating properties were observed. The structure was characterized by ^{1}H-NMR and FT-IR. Film properties of P(St-co-CMS)-FA were examined. Drying time [5], flexibility [4] were determined according to standarts. To improve film properties, soft segments of the molecules should be increased. Therefore PCMS which has high molecular weight was synthesized by using FRP in the presence of BPO. Fatty acids were tried to be attached to the 40% and 20% of the chloro groups in the presence of K_2CO_3 under nitrogen atmosphere. But the desired product could not be acquired due to the intense crosslinking occurrence. For this reason PCMS was synthesized by NMRP method to get low molecular weight. However, final product could not be obtained again in the substitution reaction.

2. THEORETICAL PART

2.1 Triglyceride Oil

Triglyceride oils are naturally occuring oils in liquid form at common temperatures. They have three molecules of fatty acids and glycerol [58]. They are produced from plants.

On the other hand, with the reaction between glycerol and fatty acids, triglyceride oils could be synthesized. The general structure of triglyceride oil is represented as follows:

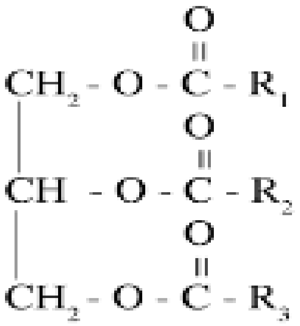


Figure 2.1 : Structure of triglyceride oil [58].

R_1, R_2, R_3 symbolize fatty acid residues. The fatty acid chain length vary from C_8 to C_{22}, but in vegetable oils; C_{18} is the most common fatty acids. The triglyceride molecules generally comprise different fatty acids [60]. These molecules are entitled according to fatty acid components; for example tristearin (Figure 2.2) molecule which contains three molecules of stearic acid [58].

% 90-95 weight of triglyceride oils comprise of fatty acids. For each triglyceride oils, fatty acid content becomes different. Chemical and physical properties of oils depend on their fatty acid compositions.

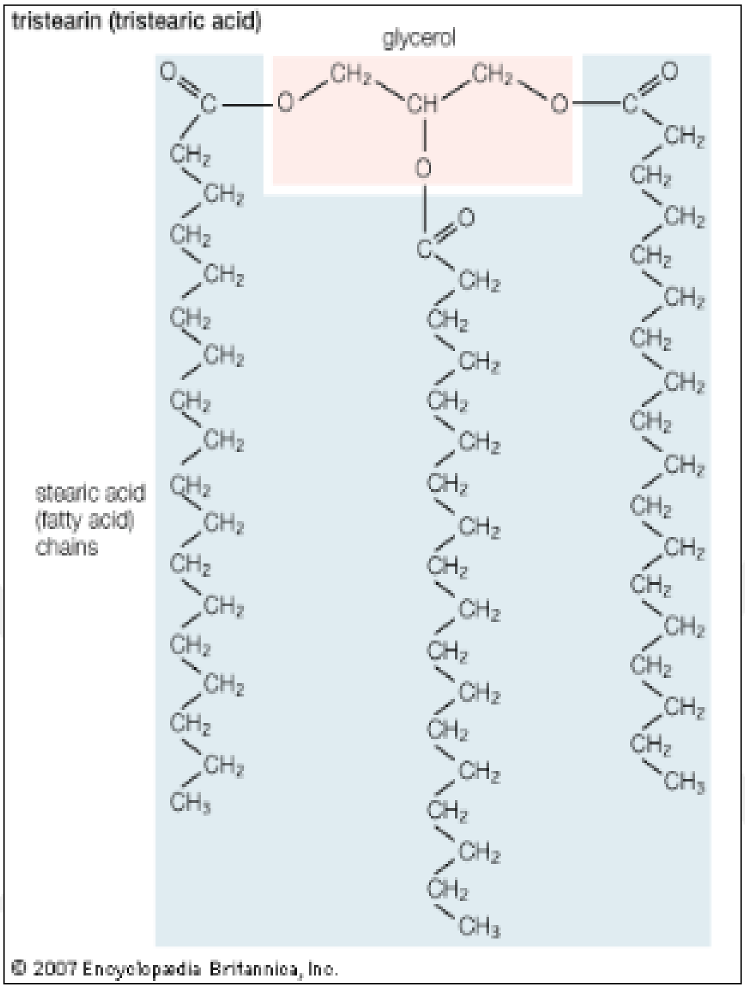


Figure 2.2 : Tristearin [58].

The most common fatty acids used for coating industry are [60]:

- $CH_3 – (CH_2)_6 – COOH$ Caprylic
- $CH_3 – (CH_2)_8 – COOH$ Capric
- $CH_3 – (CH_2)_{10} – COOH$ Lauric
- $CH_3 – (CH_2)_{12} – COOH$ Myristic
- $CH_3 – (CH_2)_{14} – COOH$ Palmitic
- $CH_3 – (CH_2)_{16} – COOH$ Stearic

The different fatty acid structures; oleic acid, linoleic acid, linolenic acid, erucic acid, petroselinic acid, riciloneic acid, vernolic acid and 10-undecenoic acid are given in Figure 2.3.

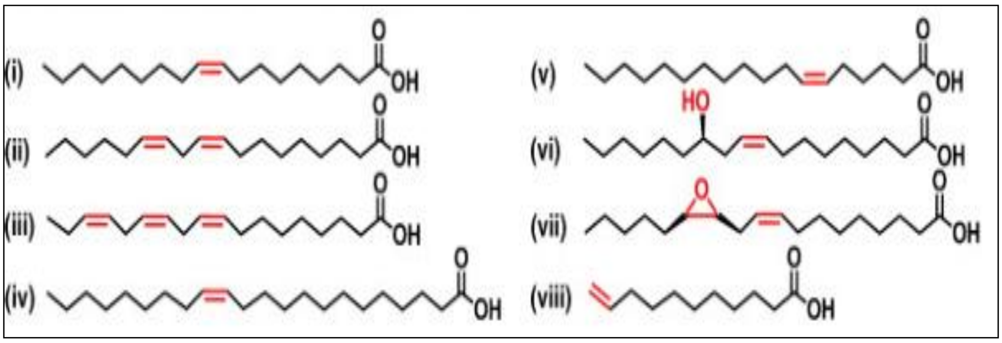


Figure 2.3 : Structure of different fatty acids [61].

(i) oleic acid, (ii) linoleic acid, (iii) linolenic acid, (iv) erucic acid, (v) petroselinic acid, (vi) riciloneic acid, (vii) vernolic acid, (viii) 10-undecenoic acid.

Fatty acid percentages of some triglyceride oils were given in Figure 2.4.

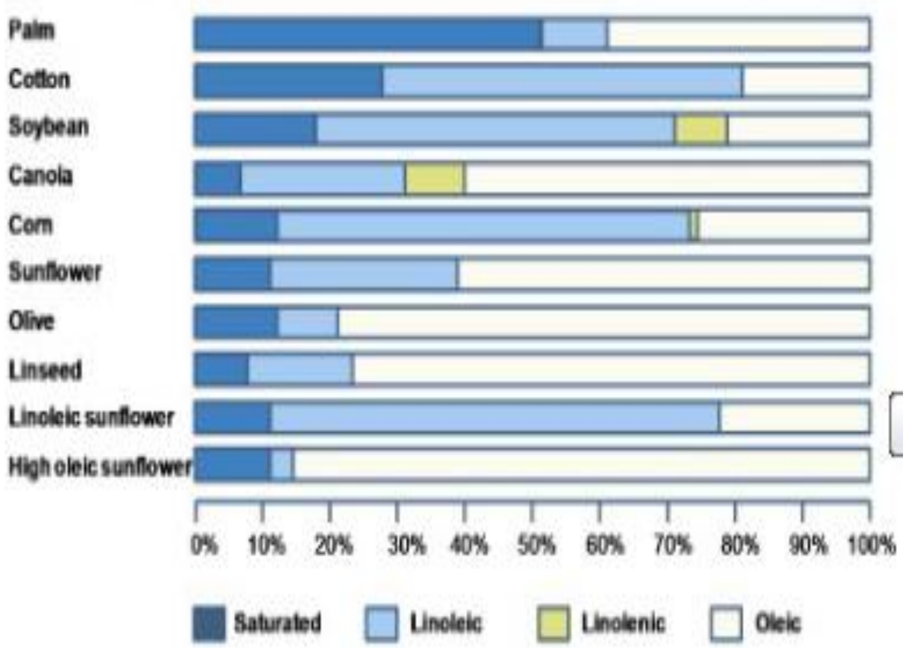


Figure 2.4 : Fatty acid composition of triglyceride oils [61].

As shown in Figure 2.4, linseed oil have approximately 75% oleic acid. Fatty acid ingredient changes with regard to grow condition, season and purification process.

2.2 Fatty Acids and Their Characteristics

Fatty acids are carbon chains with a carboxyl group and methyl group. The acid property of that molecule comes from carboxyl group (-COOH) which makes it carboxylic acid. Almost all fatty acids possess even-numbered carbon atoms. The fatty acids of triglyceride oils show an alteration in carbon numbers and bond locations.

2.2.1 Saturated

Saturated fatty acids have single carbon-to-carbon bonds and no double bonds. Their general formula is known as $C_nH_{2n}O_2$. The physical properties of fatty acids could be different due to chain lengths. While the acids with long chains are solid, the others are liquid at room temperature [62]. Various fatty acids and their molecular weights, saponication values were given in Table 2.1.

Table 2.1 : Various saturated fatty acid types [62].

Common Name	n	Molecular Weight	Saponification Value
Caproic	6	116	483
Caprylic	8	144	389
Capric	10	172	325.7
Lauric	12	200	280.1
Myristic	14	228	245.7
Palmitic	16	256	218.8
Stearic	18	284	197.2
Arachidic	20	312	179.5
Behenic	22	340	164.7
Lignoceric	24	368	152.2

2.2.2 Unsaturated

The unsaturated fatty acids have double or triple bonds. Because of its unsaturation, the fatty acid molecule is more reactive. According to double bonds location, number, geometry and number of carbon atoms in chain, fatty acids differ from each other. Generally, most of them are liquid at room conditions.

2.2.2.1 Monoethenoid fatty acids

Unsaturated fatty acids with one double bonds are named as monoethenoid acids. Their general molecular formula is symbolized as $C_nH(_{2n-2})O_2$. The double bond could be anywhere between two carbon atoms excluding first two. But some exemptions might be possible in earth. The most common one double-bonded fatty acids were indicated in Table 2.2.

Table 2.2 : Common fatty acids with one double bond [62].

Common Name	n	Position of double	Molecular weight	Saponification value	Iodine value
Palmitoleic	16	Δ9,10	254	220.5	99.8
Petrosclinic	18	6,7	282	198.6	89.9
Oleic	18	9,10	282	198.6	89.9
Vaccenic	18	11,12	282	198.6	89.9
Gadoleic	20	9,10	310	180.7	81.8
Cetoleic	22	11,12	339	165.7	75
Erucic	22	13,14	339	165.7	75
Selacholeic	4	15,16	367	153	69.2

Furthermore, one double bonded fatty acids could have geometric isomers which are known as cis and trans such as oleic and elaidic acids in Figure 2.5.

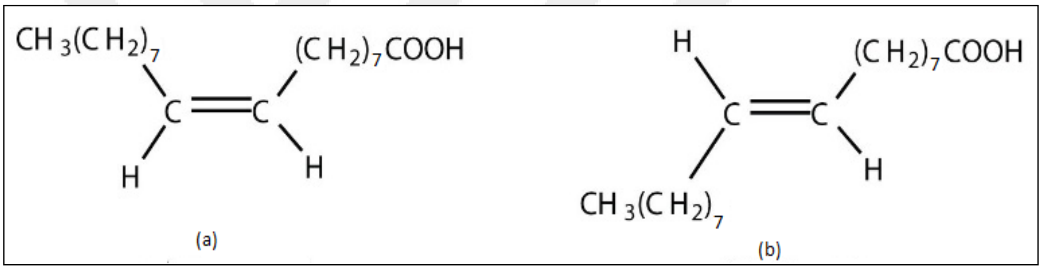


Figure 2.5 : Geometric isomerism; (a) Oleic acid (cis-octadecenoic acid) and (b) Elaidic acid (trans-octadecenoic acid) [62].

As shown in the Figure 2.5, oleic and elaidic acids are cis and trans geometric isomers of each other, respectively. One double bonded fatty acids could not show drying characteristics even if they have high percentage of oleic acid. Olive oil is such a good example that has lack of drying when be exposed to atmospheric oxygen [62].

2.2.2.2 Polyethenoid fatty acids

Unsaturated fatty acids are named as polyethenoid when they have two or more double bonds. In carbon chain, double bonds could possess none or many carbon atoms. If the double bonds are divided by none of carbon atoms, the double bonds are named as conjugated; however, if they are separated by at least two carbon atoms then the double bonds are called as nonconjugated or isolated. Table 2.3 shows the common di and poly-unsaturated fatty acids.

Table 2.3 : Di and poly-unsaturated fatty acids [62].

Common Name	n	Double Bonds		Molecular Weight	Saponification Value	Iodine Value
		No	Position			
Linoleic	18	2	Δ9,12	280	200.1	181
Linolenic	18	3	9-12-15	278	201.5	273
Elaeostearic	18	3	9-11-13	278	201.5	273
Parinaric	18	4	9-11-13-15	276	203	367
Arachidonic	20	4	5-8-11-14	305	184.3	333
Clupanodonic	22	5	4-8-12-15-19	330	169.8	384
Nisinic	24	6	4-8-12-15-18-21	337	157.4	427

Di and poly unsaturated fatty acids have an important place in formation of films as conjugation promotes the reactivity of fatty acids. Fatty acids and oils are effected mainly by unsaturation degree which is measured by iodine value. This value is estimated by taking into account the quantity of iodine which is consumed by the reaction with double bonds for sample of 100g under stated circumstances [14]. High iodine values in fatty acids cause increment in drying rate and also it enables to obtain hardness in coating production.

As shown in Table 2.3 linoleic acid has high iodine value and it is a distinctiveness of linseed oil. Due to the existence of polyunsaturated bonds in linoleic acids, linseed oil could dry very quickly when be exposured to atmospheric oxygen. Even if with a minute quantity of linoleic acid, drying capability rises very much. Furthermore, as understood from the Table 2.3, physical and chemical properties are changing due to the distinctive double bonds structure [62].

2.2.2.3 Substituted fatty acids

Fatty acids which have hydroxyl, epoxy, oxo, keto groups or triple bonds are defined as substituted acids. All these distinctness give rise to diversity in physical and chemical properties of fatty acids [63]. Table 2.4 shows the unsual structured fatty acids.

Table 2.4 : Unsual Structured Fatty Acids [62].

Common Name	n	Double Bonds		Sunstituent		Molecular Weight	Saponification Value	Iodine Value
		No	Position	Type	Position			
Ricinoleic	18	1	Δ9	OH	Δ12	299	188	85.1
Kamlolenic	18	3	9-11-13	OH	18	294	190.5	259.2
Licanic	18	3	9-11-13	CO	4	292	191.9	260.4

As indicated Table 2.4, ricinoleic acid has hydroxyl group on the carbon atom of twelft. On the other hand, licanic acid has ketone group and conjugated double bonds. These substituted fatty acids enable to gain extra reactivity to the unsaturation structure [62].

2.3 Classification of Triglyceride Oils

Triglyceride oils are categorized according to their film creating / drying capabilities as non-drying, semi-drying, drying as shown in Table 2.5. Drying of an oil is capability to form a tough, resistant film when be exposed to air. This ability depends on fatty acid structure, ethylene group number and existence of functional groups like OH etc [64]. Iodine value represents the average value of unsaturation. To understand the drying ability of an oil, iodine value is measured.

Table 2.5 : Triglyceride oil classification according to iodine value [65].

Triglyceride oil	Iodine Value
Drying	>140
Semidrying	125-140
Nondrying	<125

The drying rate is controlled by the double bond’s degree of unsaturation. Due to the high iodine values, the triglyceride oils and fatty acids demonstrate fast drying as well as giving much better hardness and gloss in coatings. Moreover, double bond placement is also significant because the conjugated bonds are more capable to autoxidation [65].

2.3.1 Drying

Drying oils have fatty acids that are rich in unsaturated bonds. By this way, they could easily oligamerize, polymerize and create films when are exposed to atmospheric oxygen [64]. They are used in protective coating area because of their capability for polymerizing and drying when have been implemented to a surface. After application on a surface they form tough, cohesive, waterproof, and corrosion resistant films. Film-forming property depends on their unsaturation degree. Owing to the fact that, polymerization come about in unsaturated centers [66].

Myristic, palmitic, stearic, oleic, linoleic, linolenic, pinolenic, ricinoleic, and α-eleostearic acids are general fatty acids which exist in drying oils.

Table 2.6 : Common fatty acids in drying oils [67].

Common Name	Formula
Myristic Acid	$CH_3(CH_2)_{12}CO_2H$
Palmitic Acid	$CH_3(CH_2)_{14}CO_2H$
Stearic Acid	$CH_3(CH_2)_{16}CO_2H$
Oleic Acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$
Linoleic Acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$
Linolenic Acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$
Pinolenic Acid	$CH_3(CH_2)_4CH{=}CHCH_2C{=}CHCH_2CH{=}CH(CH_2)_3CO_2H$
Riciloneic Acid	$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7CO_2H$
AEleostearic	$CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7CO_2H$

Especially; linoleic, linolenic, pinolenic, dehydrated ricinoleic and α-eleostearic fatty acids are completely drying triglyceride oils. These triglyceride oils have two or more unsaturation parts which are divided by maximum one methylene group per molecule [68]. The methylene group is the active group which starts drying process. Therefore, drying is relevant with diallylic group average number. If this number is greater than 2.2, a triglyceride oil have drying character [69].

2.3.2 Semi-drying

Semi-drying oils are between drying and non-drying oils. They form mild film instead of tough one like in drying oils even after a long exposure. Unlike drying oils, semi-drying oil take up air slowly. They do not include linolenic acid, just contain linoleic and saturated acids [70]. Iodine value of semidrying oils are between 125 and 140. Free fatty acids which are obtained from them have less reactive characteristic [71]. Some samples for semi-drying oils are cotton seed oil, sesame oil, mustard oil and sunflower oil [70].

2.3.3 Non-drying

Non-drying oils could not compose flexible films when are exposed to air even after long exposure. They have abundance of saturated acid and oleic acid. Moreover, non-drying oils contain saturated carbon chain. Therefore, they are stable at mild temperatures [72]. Some examples to non-drying oils are caster oil and olive oil [70]. Additionally, their iodine value are low. For this reason, there is not a site for oxidative cross-linking. Drying index, saturated percentages and iodine numbers of typical oils are shown in Table 2.7.

Table 2.7 : Iodine values, drying index, partial composition for typical oils [70].

Oils	Iodine number	Drying index	%Saturated
Drying			
Soybean	130	66	14
Linseed	185	123	10
Sunflower	139	66	8
Tung	165	>172	5
Semidrying			
Corn	124	54	17
Nondrying			
Coconut	8	2	92

2.4 Linseed Oil

Linseed oil is outstanding drying oil which has great amount of α-linolenic acids. Generally, linseed oil has the following fatty acid types:

- Tri-unsaturated α-linolenic acid, 51.9-55.2 %
- Saturated palmitic, 7% and stearic acids, 3.4-4.6 %
- Monosaturated oleic acid, 18.5-22.6 %
- Di-unsaturated linoleic acid, 14.2-17 %

Due to the high ingredient of di and tri-unsaturated fatty acids, linseed oil is prone to polymerization reactions under atmospheric oxygen which results in stiffening of the endproduct.

Linseed oil fatty acid structure is extremely influenced by temperature and climatical circumstances [73]. 35 different linseed genotypes were grown [74]. However, the typical demonstration is shown as in Figure 2.6.

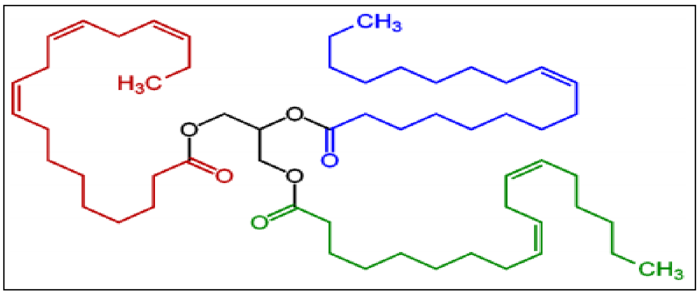


Figure 2.6 : Triglyceride in linseed oil [75].

Linseed oil comprises at least about 60% percent of polyunsaturated linoleic and linolenic acids. And they could be conjugated or nonconjugated [76].

2.5 Drying Process of Vegetable Oils

Drying is a process where film formation happens. This is occurred because of physical and chemical alterations like oxidation and polymerisation. As is known, vegetable oils include saturated and unsaturated fatty acids and they could form film when exposed to atmospheric oxygen. The formation of film or in other words the drying of oils are occurred by oxidation of unsaturated units of fatty acids under oxygen. For drying process, unsaturation degree is very significant factor. It should be also noted that while drying oils do not need heat treatment to dry, nondrying and semidrying oils need heat treatment. Mechanism of drying process consists such certainities;

- Through the drying process so much oxygen intake occurs.
- Number of conjugated double bond affect drying ability.
- Amount of absorbed oxygen does not change with distinctive unsaturation degree up to the gel point.

The mechanism of drying process for vegetable oils are distinct in conjugated and nonconjugated systems [77].

Additionaly, as is known, oxidation happens naturally but its reaction rate is so slow that to diminish drying period organometallic catalysts and dryers are added.

2.6 Chain growth (addition) polymerisation

Chain growth or addition polymerisation is a process that polymers consist through the consecutive addition of unsaturated monomers [65]. In this polimerisation process, unsaturated monomers joined to active centers (in the end of the growing chain) by way of rapid sequence. Addition rate of monomers to active sites which relates with the monomer to polymer overall conversion is considerably fast. This means that high molecular weight polymers could be produced even while lots of monomers have not consumed yet. In addition, polymers generated at the beginning step of the reaction are slightly influenced by the extent of the reaction. High molecular weight polymers and unreacted monomer mixture are present in partly polymerized mixture [66].

In addition, the active centers could be free radical, coordination complexes, carbonium ions which exist mostly in low concentrations. According to the characters of the active center, polymerizations are categorized as free radical, ionic (anionic or cationic) and coordination polymerization.

2.6.1 Free radical chain growth polymerization

Free radical polymerization is mostly used chemical process for making polymers. The first papers related to free radical polymerization were issued in 1940s and

1950s. Conventional free radical polymerization has many advantegeous such as it

enables to use a diverse range of vinylic monomers and it is simple to implement. Besides, FRP necessitates normal circumstances [80]. They could be implemented to solution, emulsion and bulk polymerization. On the other hand, radical growth species are resistant extremely to functional groups. Consequently, radical polymerization could be taken place with functional monomers. FRP is implemented at mediate temperatures which changes from room temperature to 140°C. This temperature range rely on monomer type and utilised initiating system. Fundamental processes of conventional free radical polymerization are initiation, propagation, transfer and termination [81].

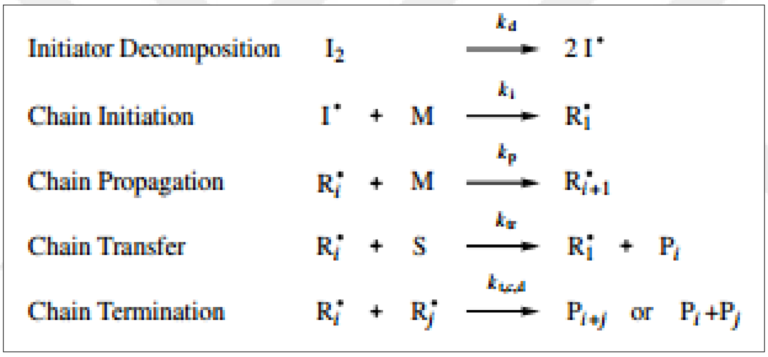
- Initiation: In initiation stage, primary initiating radicals are generated from nonradical species [82]. After decomposition, these radicals react with monomers. Generation reaction of radicals is slower than reaction of radical with monomer. Generally; peroxides, redox systems and diazo derivatives are utilized at low concentrations such as 1-0.01% [84].

- Propagation: Propagation take place after activation of the polymerization. Monomer molecules are added one by one to the active chain end. The reactive region regenerates after each addition. It is believed that this reaction is irrespective of chain length. Propagating free radical concentration depends on rates of initiation and termination reactions [84].

- Transfer: Transfer reaction take place when an active region is transmitted to monomer, polymer or transfer agent. The transfer process concludes terminated molecule and a new active region. The transfer reaction has an impression over kinetics due to the reinitiation is rapid. On the other hand, in the case of gradual reinitiation, retardent could take place. In FRP, due to the low conversions and coupling termination, low polydispersities such as 1.5 could be obtained. Nevertheless, for the most part of the systems polydispersities are obtained more than 2.

- Termination: Termination reaction takes place via combination (coupling reaction of two active centers) or disproportionation (atomic transfer between active chains). In this step, rate constant is contingent upon chain length and conversion. In the case of dominated coupling, high molecular weights and low polydispersities could be seen [84].

FRP is shown schematically in Figure 2.7.



Initiator Decomposition	$I_2 \xrightarrow{k_d} 2\,I^\bullet$
Chain Initiation	$I^\bullet + M \xrightarrow{k_i} R_1^\bullet$
Chain Propagation	$R_i^\bullet + M \xrightarrow{k_p} R_{i+1}^\bullet$
Chain Transfer	$R_i^\bullet + S \xrightarrow{k_{tr}} R_1^\bullet + P_i$
Chain Termination	$R_i^\bullet + R_j^\bullet \xrightarrow{k_{t,c,d}} P_{i+j}$ or $P_i + P_j$

Figure 2.7 : Common representation of free radical polymerization [85].

R_i^* denotes a radical of chain length; I_2 represents the initiator; M is the monomer; S denotes a transfer agent and P shows polymer.

The effect of chain transfer both on the average degree of polymerization and polydispersity matters as chain transfer take place for all radical. Moreover, the significant feature of FRP is that the partly polymerized mixture comprise ofhigh molecular weight polymers and unreacted monomers. However, some limitations of FRP are existent such as there is no control over the polymer tacticity and there is a little control over molar mass distribution because of the diffusion controlled terminated reactions between growth radicals.

2.6.1.1 Controlled/Living free radical polymerization

Conventional Free Radical Polymerization were started to be changed in 1994 and new technique which is named as Controlled Living Free Radical Polymerization was developed [85-86]. CRP could enable to generate polymers with absolutely controlled structure and constitution such as block, gradient and copolymers [87-88]. All these polymers could not be generated through conventional free radical polymerization. CRP entegrates optimum characterisics of FRP.

The word of living denotes extension capability of a chain through monomer addition. CRP is very significant polymerization technique when considered effectivity and a wide range of polymer production. CRP process depends on completely pure reactions. By this way, no termination is resulted in by impurities. This polymerization process stop only when all monomer consumed. The CRP could carry on with monomer addition and could be stopped and renewed at any moment. The CRP mechanism relies on a dynamic balance among propagating radicals and inactive subspecies [88-89]. The fundamentals of CRP process are;

- Initiation stage is fast when compared to propagation because whole chains should begin to grow simultaneously and retain functionality.
- The exchange between active and dormant species is fast. By this way, the greater part of the growing chains are in dormant form and just small part is existing as propagating free radicals.

Even if FRP and CRP proceed by virtue of the same radical mechanism, many significant progresses of CRP are existent. In FRP, initiation is slow and free radical initiator is often existed unreacted,but in CRP, initiation is fast. In FRP almost all chains are dead, however the ratio of dead chains is generally under 10% in CRP. In FRP, termination generally takes place between long chains and newly generated chains, whereas in CRP all chains are short at initial stages of the reaction due to the persistent radical effect. CRP are categorized according to techniques. In this thesis, just stable free radical(SFR) or in other words nitroxide mediated radical polymerization will be mentioned (NMRP) [85,86,90].

Nitroxide mediated free radical polymerization

Nitroxide mediated living radical polymerization is the leading advanced technique for controlling the polymerization. The main point of this process is reversible termination of the growth chain by way of nitroxide radical. Characteristically, NMRP which is conducted in the presence of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) was restricted with polymerization of styrene [91-92]. The most common used nitroxide radical is TEMPO [94]. However, it has some disadvantages in usage such as high polymerization temperature and its unconformity to numerous significant monomers. NMRP process make polymers possible to be obtained with narrow molecular weight distributions. At high molecular weight values such as more than 200000 g/mol, termination reactions matter due to control deficiency and living nature of NMRP process [93].

2.7 Polymers from Triglyceride Oils

Vegetable oils have importance for polymer development because of some reasons. First of all, the global warming is threat for our world and this danger is getting bigger and bigger day by day. Secondly, consuming of petroleum reserves problem. And thirdly, the desire of getting low overall costs. And the final reason is desire of a pollution free environment. The whole reasons lead to the development of renewable sources. Therefore linseed, castor, soybean, sunflower, corn, canola, palm, safflower have a usage in the synthesis of varied polymers such as polyesters, polyurethanes, epoxies, polyamides, polyolefins, poly(esteramide)s and others [95]. Vegetable oils and their fatty acids were used in polyamide synthesis. They achieve FRP [96-99]. FRP is achieved with vinyl monomers like styrene in the presence of initiator, BPO.

Furthermore, fatty acid based polyanhydrides were synthesized by melt polycondensation technique [100]. To modify coating characteristics, triglyceride oil can be heated with vinyl monomers. Copolymerization of vinyl monomers with triglyceride oils is very old technique for modification. But this old process make better film properties possible [101]. Generally, modification of triglyceride oils such as linseed, tung, soybean, sunflower with styrene are practiced by using free radical polymerization [102-106].

Another polymer which was synthesized by using triglyceride oil and fatty acid mixture is poly(ester amide)s. Linseed, safflower, sunflower, soybean, castor and coconut have been used in these synthesizes [107-114].

2.8 Chloromethylstyrene (CMS) or Vinylbenzylchloride (VBC) Monomers

Chloromethylstyrene monomer is one of the most significant functional monomers. The earliest synthesis dates back to 1957 [115] however it was not implemented too much until 1972. Lots of articles and patents have been published about synthesized polymers and copolymers at the present time. CMS monomer has benzylic chlorine which enables to make nucleophilic substitution and also has polymerizable double bond. This characteristic properties enable to polymerize and copolymerize in the case of suitable experimental conditions [116-118]. PCMS and also P(St-co-CMS) could react with diversified nucleophilic reagents [119].

2.8.1 Polymerization and copolymerization of CMS

CMS has been easily polymerized with initiators of radical or cationic. Reactions could be implemented in bulk, solution, suspension and emulsion circumstances when radical initiators are used. Polymers of CMS are produced via living radical polymerizations. They could be synthesized through cationically with mixture of tin tetrachloride and tetrabuthylammonium chloride [120] or by way of radically in the presence of BPO and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [108].

On the other hand, copolymerization could be achieved by CRP method so that synthesized polymers could react with varied nucleophilic reagents [122-123]. Copolymerization have been implemented with numerous comonomers such as styrene in the presence of nitroxide initiators [124].

2.8.2 Chemical modification of polymer and copolymer of CMS

Modification of polymer and copolymer of CMS are accomplished through chlorine nucleophilic substitutions [125]. Commonly, PCMS and P(St-co-CMS) are produced to obtain beads and microspheres [126-128].

3. EXPERIMENTAL WORK

3.1 Materials

CMS monomer (90%, Aldrich), TEMPO (98%, Aldrich), BPO (≥98%, Aldrich), Aluminum oxide, Alumina (99.9%, Aldrich), Potassium carbonate (≥99%, Aldrich), Methanol (99%, Aldrich), Xylene, DMF (≥99%, Aldrich), Ethanol (≥99.5%, Aldrich) and linseed oil were used.

3.2 Equipments

Products of molecular weights and polydispersities were determined by Gel Permeation Chromatography (Agillent 1100 Series) with the flow rate of 0.3 ml/min and Tetrahydrofuran was used as solvent. The structures of products was characterized by Fourier Transform Infrared Spectroscopy (Perkin- Elmer FT-IR Spectrum One B Spectrometer) and Nuclear Magnetic Resonance Spectroscopy (Bruker AC250, 250.133 Mhz). Film properties were investigating according to ASTM standards.

3.3 Preparation Methods

3.3.1 Purification of CMS monomer

Potassium carbonate was dried overnight at 110°C before used. The glass column was filled with alumina and potassium carbonate. CMS monomer was passed through the column to remove the polymerization inhibitor.

3.3.2 PCMS synthesis by FRP method

0.06 mole (9.1675 g.) 4CMS and 5 ml xylene were placed into the reaction flask. And the reaction mixture was immediately purged with nitrogen gas for 15 minutes. Then, 0.000231 mole (0.056g.) BPO was added and stirred. Temperature was increased to 135°C and reaction continued for 6.5 hours. Reaction time can be optimized to get low molecular weight polymer. During this time period, the flask kept closed. After cooling the reaction mixture was added to methanol dropwise in order to precipitate the polymer. The product is filtered off, washed and dried under vacuum at 45°C for 24 hours. The molecular weight and polydispersities of product were determined by GPC analysis.

3.3.3 Preparation linseed oil fatty acid mixture

50 g linseed oil and 200 cm^3 of 10% KOH solution was mixed in reaction flask and boiled for 1 hour. Then boiling soap solution was taken into glass beaker. 2 N sulfiric acid was added to soap solution. By this step, soaps turned into acids. The upper face of mixture which is fatty acid was separated and taken into another separatory funnel and washed with water until it becomes neutral. After washing process diethyl ether was added and dried overnight with sodium sulfate. Then mixture was filtered and diethyl ether was removed by rotary evaporator. Acid value was determined.

To calculate acid value of linseed oil fatty acid; 10 g fatty acid was taken in a 250 ml conical flask. 50 ml equal volume of ethanol- diethyl ether mixture was added to the fatty acid. 3 drops of phenolphthalein was added. Then titrated with 0.1 N NaOH with ethanol solution from the burette until to obtain pink color. Consumed amount of NaOH solution was determined.

3.3.4 Preparation of P(St-co-CMS) copolymer by NMRP method

St and CMS monomers were passed through columns which filled with basic alumina and dry potassium carbonate to remove the polymerization inhibitor. 0.17398 mole (18.12g.) styrene and 0.0142 mole (2.166g.) CMS and 10 ml xylene were placed into reaction flask. The reaction mixture was immediately purged with nitrogen gas for 15 minutes. Then 0.005926 mole (0.9259 g.) TEMPO and 0.0047 mole (1.14g.) BPO were added and stirred. Temperature was increased to 135°C and polymerization reaction was continued for 48 hours. After cooling the reaction mixture was added to methanol dropwise in order to precipitate the copolymer. The product was filtered off and washed and dried under vacuum oven at 45°C for 24 hours. FT-IR, H-NMR and GPC analysis were applied for molecular weight and structure determination.

3.3.5 Modification of PCMS via fatty acid

In a typical functionalization reaction, the polymer (1.0 CMS equivalent), linseed oil fatty acid (1.1 equivalent), and potassium carbonate (1.5 equivalent) should be taken [115]. Because of one mole polymer chain has 226 mole chlorine, to bind 40% of this chlorine which equals 90.4 mole chlorine, 99.44 mole fatty acid and 135.6 mole potassium carbonate are necessary. According to this mole proportions, samples of different weight proportions were prepared. 3.20 g PCMS, 2.6065 g fatty acid and 1.739 g dry potassium carbonate were dissolved in 7.0322 g. DMF and reaction was carried out at 70°C under nitrogen atmosphere. The product results were mentioned in Results and Discussion section.

3.3.6 Modification of P(St-co-CMS)2 via fatty acid

By using GPC and 1H-NMR results, number of CMS unit in each P(St-co-CMS)2 was calculated according to Equation (4.2) and (4.3). The mole number of chlorine functional group in one mole copolymer was found as 2.3946 mole. Then, equivalent amounts were calculated for the modification reaction to bond 100% of chlorine group; 1 mole copolymer, 2.634 mole fatty acid and 3.5919 mole potassium carbonate were reacted in the presence of 10 ml DMF. The substitution reaction was carried out at 70°C for 48 hours under nitrogen atmosphere. The obtained product's characterization was done by using GPC, FT-IR and ^{1}H-NMR. The results were given in Discussion Section.

4. RESULTS AND DISCUSSION

In the present study, P(St-co-CMS) copolymer was modified with linseed oil fatty acid. The P(St-co-CMS) was obtained by NMRP and FRP methods. Linseed oil fatty acid was prepared from linseed oil in the laboratory by saponification method. The acid value of the obtained fatty acid mixture was 196. The overall process is shown in Figure 4.1.

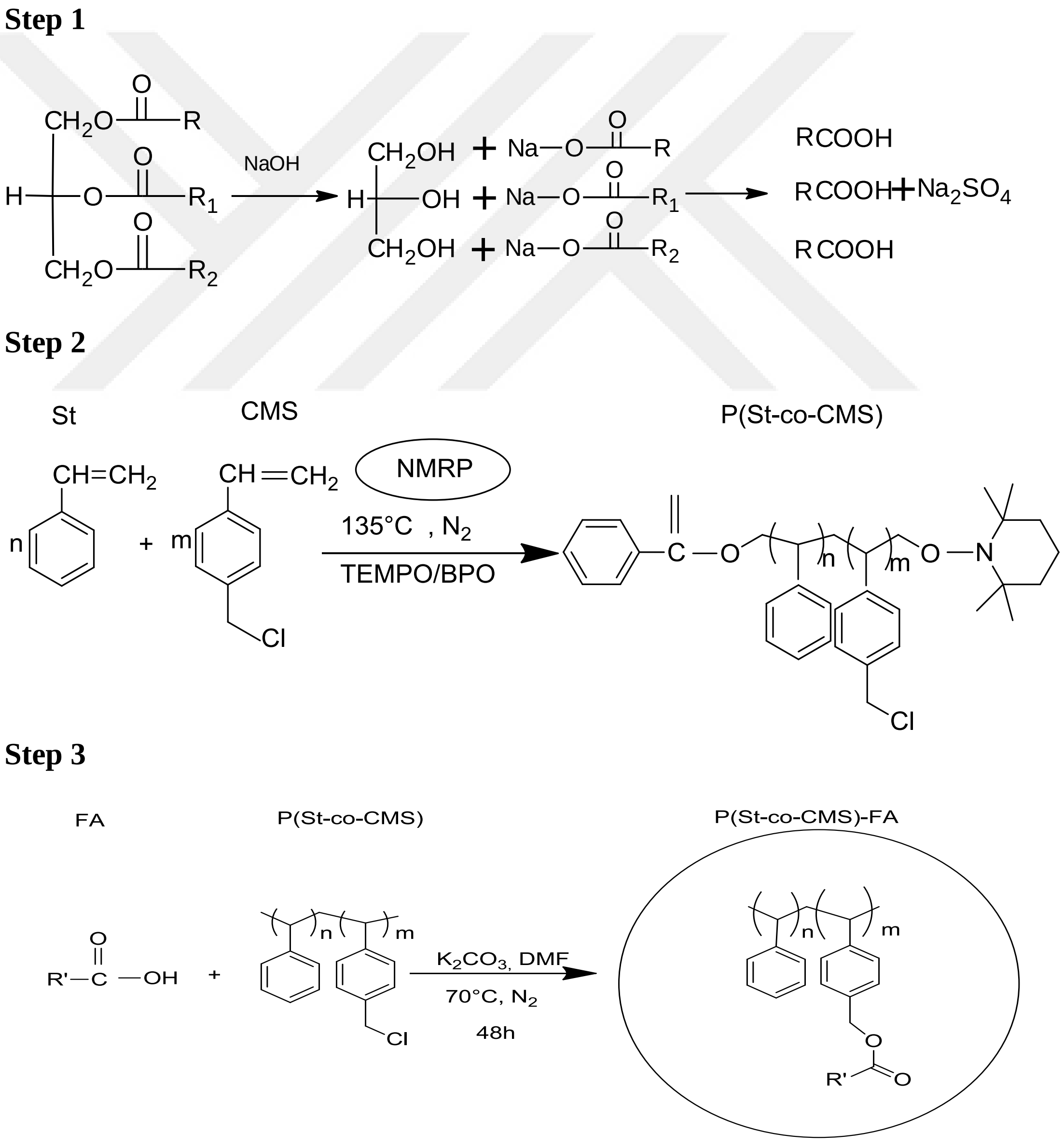
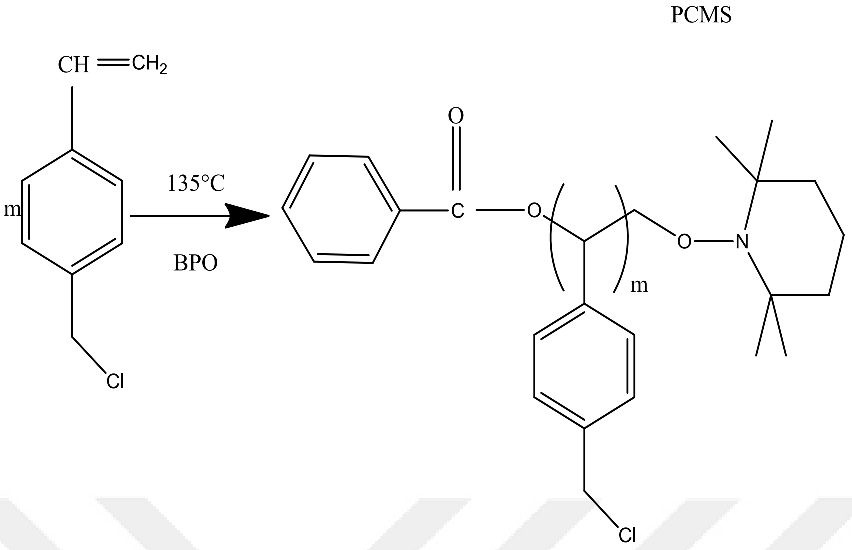


Figure 4.1 : Overall process.

Step 4



Step 5

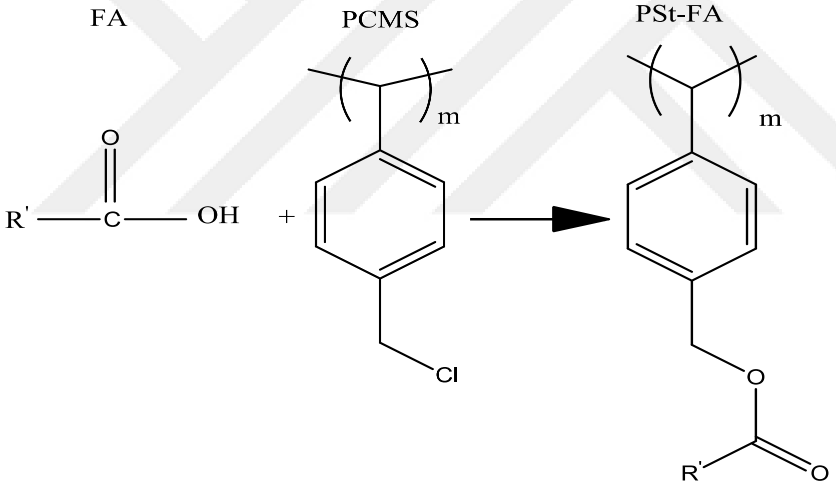


Figure 4.1 (Continue): Overall process.

4.1 Synthesis of P(St-co-CMS) Copolymer and Modification with Fatty Acid

P(St-co-CMS) samples were prepared by using styrene and CMS monomers by NMRP method as mentioned in Section 3.3.4. The used monomer ratios, molecular weights of products, polydispersities and number of chloromethyl functional groups (CH_2-Cl) in one polymer chain (mol/mol) were given in Table 4.1. The number of CH_2-Cl group in each polymer chain was calculated by using CMS:St (mol/mol) ratio and molecular weights of products.

Table 4.1 : Properties of P(St-co-CMS) synthesized by NMRP.

Sample	CMS:St (mol:mol)	Molecular Weight[a] (M_n)	Polydispersity[c] (M_w/M_n)	CH_2-Cl group/Polymer[b] (mol/mol)
P(St-co-CMS)1	1:9.53	2207	1.35	1.373
P(St-co-CMS)2	1:9.75	3931	1.16	2.3946

[a,c] Molecular weight and polydispersities were determined by GPC.
[b] CH_2-Cl functional group number in one polymer chain was determined by using ^{1}H-NMR and GPC results..

The FT-IR spectrum of the copolymer sample obtained after 48 hours is given in Figure 4.2.

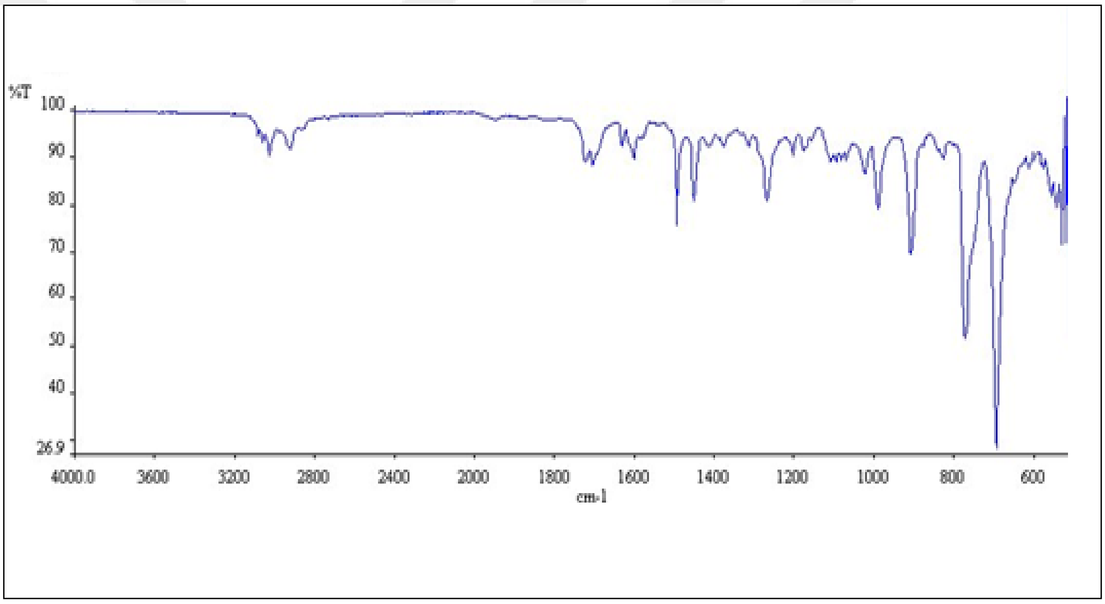


Figure 4.2 : FT-IR spectrum of P(St-co-CMS)2 after 48 hours.

Absorbances at 3027.01 cm^{-1} and 2923.97 cm^{-1} are assigned to the stretching vibration of C-H bonds. The characteristic absorbance of aromatic overtones are seemed at 1600-2000 cm^{-1} region. Moreover, the absorption at 1493.90 and 1602.01 cm^{-1} are attributed to aromatic C=C stretching vibrations. CH_2 bending vibrations are appeared at 1376.67 cm^{-1} and 1450.23 cm^{-1} [129]. Furthermore, the peak at 1268.13 cm^{-1} is attributed to Cl atom of benzyl group [130]. The characteristic absorbances between 600-800 cm^{-1} illustrates the C-Cl bond [131].

The ^{1}H-NMR spectra of P(St-co-CMS)2 was shown in Figure 4.3.

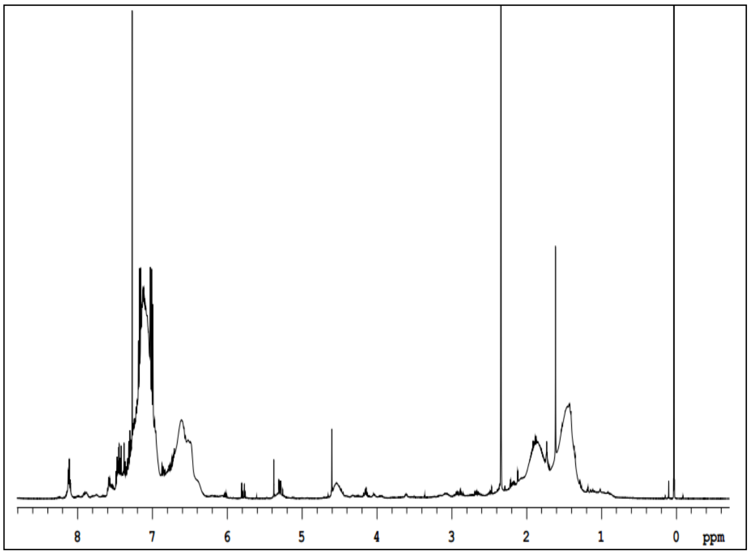


Figure 4.3 : ^{1}H-NMR spectrum of P(St-co-CMS)2.

The ^{1}H-NMR spectra illustrates that the resonance at 6.3-7.5 ppm are assigned to the aromatic protons of styrene and 4-chloromethyl styrene on the copolymer [132]. Moreover, the resonance at 4.5 ppm is attributed to the CH_2Cl group protons with regard to CMS units [133]. Also, the groups of $–CH_2$ and –CH on the copolymer chain are seen at 1.6-2.5 ppm [134].

The mole fractions of St and CMS in the copolymer chain were determined by using integrated intensities of the peaks at 4.5 ppm and 6.3-7.5 ppm (determined from ^{1}H-NMR). The CMS mole fraction in the copolymer chain (F_{CMS}), number of CMS unit in each P(St-co-CMS) (n_{Cl}) were calculated as shown in Equation 4.1, 4.2 and 4.3 [122-124].

$$F_{CMS} + F_{St} = 1 \tag{4.1}$$

$$F_{CMS} = [5/(2*I_{6.3\text{-}7.5}/I_{4.5}+1)] \tag{4.2}$$

$$n_{Cl} = F_{CMS}*M_n/M_{CMS} \tag{4.3}$$

The total peak area between 6.3 and 7.5 ppm regarding to the aromatic protons of CMS and St units on the copolymer chain is denoted as ($I_{6.3\text{-}7.5}$) and the peak area for the $–CH_2Cl$ protons with respect to the CMS units is indicated as ($I_{4.5}$) in Equation 4.2. Also (F_{St}), (M_{CMS}) and (M_n) demonstrates the St mole fraction in the copolymer chain, the molecular weight of CMS, the molecular weight of copolymer respectively in Equation 4.1 and 4.3. The mole fraction of CMS and St were calculated as 0.093

and 0.907, respectively. Also number of CMS unit in each P(St-co-CMS)2 chain was estimated as 2.3946 mol/mol copolymer.

4.2 Modification of P(St-co-CMS)2 with Linseed Oil Fatty Acid Mixture

The copolymer P(St-co-CMS)2 was modified by incorporation of linseed oil fatty acids. The fatty acid attachment to the copolymer backbone was achieved by the nucleophilic substitution reaction between chloro (CH_2-Cl) groups and acid (COOH) groups in the presence of K_2CO_3 [137]. The copolymer was reacted with equivalent amounts of linseed oil fatty acids and K_2CO_3 to bind 100% of chloro groups [137]. The obtained product [P(St-co-CMS)2-YA], was characterized by ^{1}H-NMR and FT-IR and results were given in Figure 4.4 and Figure 4.5.

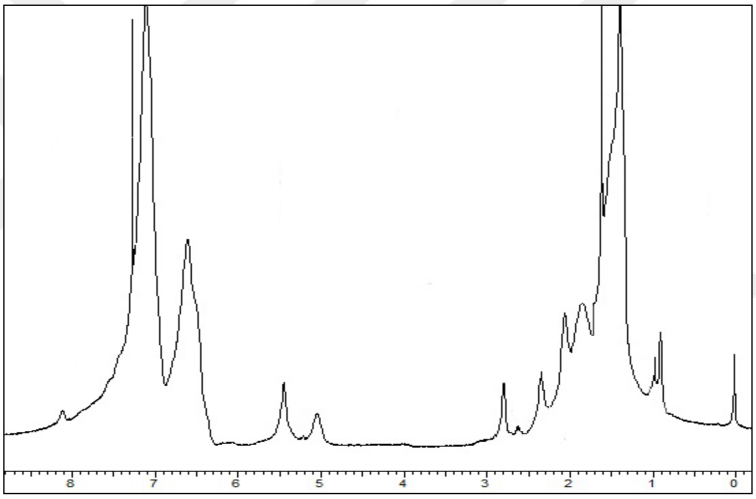


Figure 4.4 : H-NMR of P(St-co-CMS)3-FA.

As shown in Figure 4.4, the ^{1}H-NMR spectrum illustrates that the resonance at 5.5 ppm corresponds to (-CH=CH-) group protons of linseed oil fatty acid unsaturations. Besides, the peak corresponding to the (-CH_2-CH=CH-) group is observed at 2.06 ppm. The hyrogens of the ending methyl groups of linolenic acid (CH_3-CH_2-CH=CH-) is seen at 1.0 ppm. The signal is indicated at 0.90 ppm due to hyrogens of the ending methyl groups of all acids except linolenic acid and the resonance at 2.8 ppm due to (-CH=CH-CH_2-CH=CH-) group of linolenic and linoleic fatty acids. The resonance at 2.3-2.4 ppm corresponds to the methylene hydrogens attached to carbonyl groups (-CH_2-C(O)-O-) [138]. However, (-CH_2-Cl) group signal is disappeared [134] and the characteristic peak at 5.1 ppm is shown up due to the -

CH_2- between benzene ring on one side and oxygen atom on another [130] because of the substitution reaction.

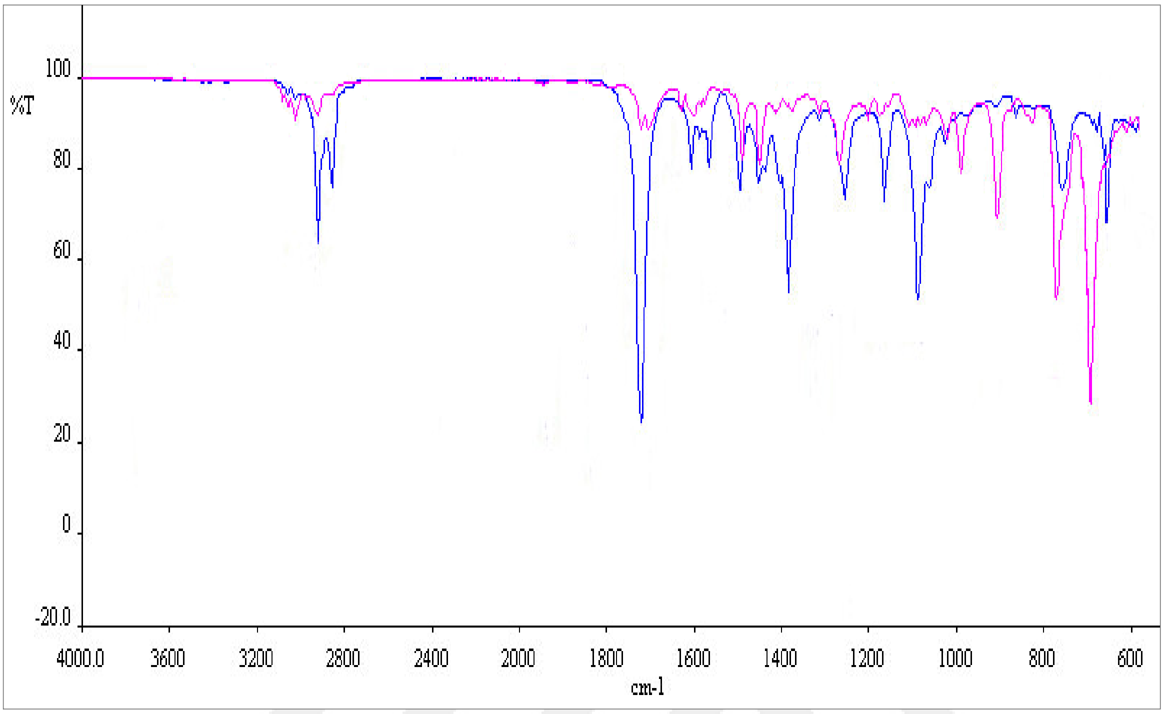


Figure 4.5 : FTIR of P(St-co-CMS)2-FA.

As shown in Figure 4.5, the characteristic absorbance at 1268.13 cm^{-1} corresponds to Cl atom of benzyl group [130] and the peaks between 600-800 cm^{-1} due to (-C-Cl) group [131] were disappeared because of the linseed oil fatty acid attachment. Besides signals between 2950-2850 cm^{-1} corresponds to stretching of aliphatic C-H [131]. Also the O-H bend of carboxylic acid at 936 cm^{-1} [131] was disappeared due to the nucleophilic substitution reaction between chloro group of copolymer. Carbonyl (C=O) group stretch gives a peak at 1725 cm^{-1}. The signal at 1176 cm^{-1} which corresponds to (C-O-C) group and the (O-C-O) group peak at 1089 cm^{-1} [131] shows the substitution reaction was achieved successfully.

4.3 Synthesis of PCMS and Modification with Fatty Acids

PCMS was synthesized by using FRP method and high molecular weighted polymers were obtained. The polydispersities (M_w/M_n), molecular weights (M_n), number of CMS unit in each PCMS (n_{Cl}), and mole fraction of CMS in the feed were given in Table 4.2.

Table 4.2 : Properties of PCMS synthesized by FRP.

Sample	CMS:St (mol/mol)	Polydispersity (M_w/M_n)	M_n[a] (g/mol)	n_{Cl}[b] (mol/mol)	t (h)
PCMS-1	1/0	4.63	34483	225	6.5
PCMS-2	1/0	5.28	25559	167	4

(a) Molecular weights were determined by GPC.
(b) Number of CMS unit in each chain.

As shown in Table 4.2, molecular weights are very high. The polydispersity index results show that molecular weight distribution is broad due to the FRP technique.

In next step, for modification of PCMS molecules with linseed oil fatty acid; the amounts of fatty acids were decided to be correspond to 40 percent of total CH_2-Cl groups in the polymer backbone. Even under this condition gelation could not be avoided. Because of occurring of gelation, whether a saponification occurs or not, some control were done with HCl. But changes in gel structure could not be observed. This result indicates that there is a high crosslinking degree. To prevent crosslinking some processes were tried. Firstly, fatty acid was reacted with dry K_2CO_3 in the presence of 15% ethanol-water solution as solvent for 3 hours.

$$RCOOH + K_2CO_3 \xrightarrow{\qquad\qquad} RCOOK + H_2O + CO_2 \qquad (4.1)$$

Then, solvent was removed. After that, PCMS was reacted with this product. But gelation occurred and crosslinking was observed again. Therefore, it was decided that molecular weight of the polymer and number of CH_2 – Cl group should be decreased to prevent crosslinking. Additionally, polymerization was carried out under controlled condition by method of nitroxide mediated radical polymerization (NMRP).

With the same CMS monomer feed ratio, polymerization was carried out under nitroxide medium in the presence of BPO and TEMPO at 135°C. The results belong to PCMS were given in Table 4.3.

Table 4.3 : Properties of PCMS synthesized by NMRP.

Sample	CMS:St (mol/mol)	TEMPO:BPO (mol/mol)	M_n (g/mol)	n_{Cl} (mol/mol)	t (h)
PCMS-3	1/0	1.32/1	9271	60	3
PCMS-4	1/0	1.32/1	7147	44	2

As can be seen in Tables 4.2 and Table 4.3, in the case of NMRP technique, a polymer product with low molecular weight and less $CH_2 – Cl$ content could be obtained. Even with this homopolymer case, gelation occurring could not be eliminated. Upon this the use of P(St-co-CMS) was taken into account. And the prepared samples as explained in Section 4.2 were used in the film properties determination.

4.4 Film properties

The film properties of P(St-co-CMS)2-FA were investigated according to ASTM standarts.

Table 4.4 : The film properties of P(St-co-CMS)2-FA.

Film Properties	P(St-co-CMS)2-FA
Drying Time (a)	40s
Flexibility (b)	2mm

(a) The test was carried out at 25°C and 60% humidity.
(b) The diameter of the cylinder that caused no crack on the film.

The test results regarding to film properties were determined and it is understood that modificated P(St-co-CMS) with linseed oil fatty acid seems to be a promising material for the coating purposes. Therefore, soft segments of the molecules should be increased for the improvement of the film properties.

5. CONCLUSIONS AND RECOMMENDATIONS

In this study,the preparation of P(St-co-CMS) and its modification with linseed oil fatty acids were performed successfully. Homopolymer of CMS was also prepared and modified with fatty acids. In the characterization studies FT-IR and ^{1}H NMR analysis were applied. The modified products were evaluated in view of organic coating purposes. The film preparation of PCMS polymer showed gelation properties during fatty acid modification. P(St-co-CMS) was found to be encouraging material in coating industry. However it should be developed to obtain a product with improved film properties.

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