ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF METHYL ETHYL KETONE FORMALDEHYDE RESINS INCLUDING BORON

M.Sc. THESIS

Hatay CÖCEN

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BOR İÇEREN METİL ETİL KETON FORMALDEHİT REÇİNELERİNİN SENTEZİ VE KARAKTERİZASYONU

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ARALIK 2015

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To my brother,

FOREWORD

I would like to send my special thanks to my advisor, *Prof. Dr. Nilgün KIZILCAN*, for her very valuable support, her patience, her friendly and helpful approach and *TÜBİTAK* for 2210-A Graduate Education Scholarship Programme.

December 2015

Hatay CÖCEN
Chemical Engineer

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ABBREVIATIONS

DCM	**:** Dichloromethane
DMS	**:** Dimethyl sulfoxide
DSC	**:** Differential Scanning Calorimetry
FTIR	**:**Fourier Transform Infrared Spectroscopy
MEKFR	**:** Methyl ethyl ketone formaldehyde resin
MEKFR-AA	**:** Methyl ethyl ketone formaldehyde resin modified with alendronic acid
MEKFR-CUAA	**:** Methyl ethyl ketone formaldehyde resin modified with cyclic urea containing alendronic acid
MEKFR-DEA	**:** Methyl ethyl ketone formaldehyde resin modified with diethanolamine
MEKFR- DEA-BA	**:** Methyl ethyl ketone formaldehyde resin modified with boric acid after the modification with diethanolamine
NMR	**:** Nuclear Magnetic Resonance Spectroscopy
TGA	**:** Thermogravimetric Analysis
THF	**:** Tetrahydrofuran

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SYNTHESIS AND CHARACTERIZATION OF METHYL ETHYL KETONE FORMALDEHYDE RESINS INCLUDING BORON

SUMMARY

Methyl ethyl ketone formaldehyde resins are modified in situ and after the polymerization with different modifiers to increase their physical and chemical performances by changing their chemical structures.

In this thesis study, methyl ethyl ketone formaldehyde resins including nitrogen and/or boron are synthesized and their phycical and chemical properties are analyzed in a comperative way.

The resins are prepared by alkaline-catalysed condensation of methyl ethyl ketone and formalde in a molar ratio of 1: 2 in a batch process. NaOH is used as catalyst for this reaction. During all of the reaction pH value should been kept around 10-11. The medium is kept at 80-90^{o}C. After 4h, the reaction is completed, and yellow resin is formed. For in sitı modifications, the modifer is added to the reaction medium in the beginning of the reaction. For boric acid modification, of resin sample is dissolved in toluene, and boric acid is added. Using deanstag systam, the medium is heated to 150^{o}C, refluxed for about 2h until no water is collected any more.

Ten different types of methyl ethyl ketone formaldehyde resins are synthesized for this study, five of which include nitrogen, one includes boron and three include both nitrogen and boron: methyl ethyl ketone formaldehyde resin (MEKFR), MEKFR modified with alendronic acid at a ratio of 5wt% (MEKFR-AA), MEKFR modified with cyclic urea which is synthesized from alendronic acid at a ratio of 5wt% (MEKFR-CUAA), MEKFR modified with diethanolamine at ratios of 5wt%, 10wt% and 20wt% (MEKFR-DEA), MEKFR and three MEKFR-DEA modified with boric acid (MEKFR-BA and MEKFR-DEA-BA, respectively).

After the synthesis and modifications of resins, their chemical structures are analyzed, and Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (NMR) are used for this purpose. When the spectums of resins obtained are looked through the characteristics peaks and their corresponding functional groups, it is concluded that the estimated chemical structures as the product of synthesis and modification reactions match with the results obtained.

In the terms of physical properties, solubility analyses are carried out in five different solvents, namely ethanol, acetone, dichloromethane (DCM), tetrahydrofuran (THF) and dimethylsulfoxide (DMS), and it is seen that depending on the modifier type and ratio, the solubility of resins change, as a result of the changes in the chemical structures.

Lastly, in order to get information about thermal behaviour of the resins and effects of modifications on thermal degradation of them, thermogravimetric analyses (TGA) and

differential scanning calorimetry (DSC) analyses are carried out for each of resins. T_{50} values and residue amounts of them obtained from TGA curves as well as glass transition and melting temperatures obtained from DSC curves are the crucial parameters used during the evaluation of thermal properties of the resins.

BOR İÇEREN METİL ETİL KETON FORMALDEHİT REÇİNELERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Reçine, yapışkanlar, kaplamalar, döküm, kalıp ve depolama malzemeleri dahil olmak üzere geniş uygulama yelpazesine sahip olan bir organic maddedir. Reçineler mükemmel kimyasal direnci, iyi yapışma özelliklerine, ısı direnci, oksidatif stabilite ve mükemmel elektriksel özellikleri ile plastik, tekstil, elektrik ve elektronik, kağıt, boya, inşaat alanında hayati rol oynamaktadır.

Genel olarak, reçineler, doğal reçineler ve sentetik reçineler olmak üzere iki grupta sınıflandırılır. Doğal reçineler, kabukları kesildiğinde, dışarı viskoz sıvı veren ağaçlardan elde edilir. Sakız, kolofan, balmumu bu reçinelere örnek verilebilir. Doğal reçinelerin parfüm üretimi, keman ve çello gibi enstrümanların yaylarının işlenmesi gibi kullanım alanları vardır.

Sentetik reçineler ise basit moleküller veya monomerlerden inşa edilen polimerlerdir. Kullanılan monomerlerin tipine göre, katılma polimerizasonu veya yoğuşma polimerizasyonu ile üretilirler. Alkid reçineler, epoksi reçineler, poliamit reçineler, poliüretan reçineler, vinil reçineler, polistiren reçineler, akrilik reçineler, fenolik reçineler ve ketonik reçineler en çok kullanılan sentetik reçinelerdir.

Ketonik reçineler α-hidrojeni içeren ketonlar ve formaldehit gibi reaktif aldehitleri nreaksiyonundan elde edilir. En çok kullanılan ketonik reçineler siklohekzanon formaldehit, asetofenonformaldehit, metil etil keton formaldehit gibi termoplastik reçinelerdir. Ticari bakımdan ilgi gören reçineler, çoğunlukla düşük molekül ağırlıklı, kolayca ufalanabilen katı termoplastiklerdir. Tek başlarına kullanılamazlar. Çoğu kez nitro selüloz, alkid reçinesi gibi diğer polimerik maddelerle karıştırılarak yüzey kaplama sanayinde kullanılır. Kullanım alanı olarak yüzey kaplamadan başka, vernik, mürekkep, tekstil, kağıt sektörleri en önemli alanlar olarak söylenebilir. Ayrıca çeşitli alanlarda yapışmayı artırıcı, parlaklık verici ve ışığa dayanımı artırıcı özelliklerinin gelişmesini sağlamak için ketonik reçineler kullanılır.

Son yıllarda ketonik reçinelerin polipirol ve polikarbazol ile kopolimerleri sentezlenerek çözünür ve iletken malzemeler elde edilmiştir. Ketonik reçinelerin uygulamaları çok sayıda yerde kullanılmaktadır. Kaplama sektöründe, çoğu diğer uygulamalarda olduğu gibi, ürünlerin diğer bağlayıcılar, yumuşatıcılar, pigmentler ve yardımcıları ile kombine olarak kullanılır. Son formülasyonları, deniz boyaları, metal primerler ve yıkama primerler, toz boya ve yol çizgi boyaları içerir. Baskı mürekkepleri ve diğer amaçlar arasında, sadece selüloz nitrat dayalı köklü flekso ve gravür baskı mürekkepleri söz değil, aynı zamanda transfer baskı mürekkepleri, radyasyon tedavi edilebilen sistemler ve mürekkep püskürtmeli mürekkepler yapılabilir Diğer önemli uygulamalar, kayıt ve kopyalama teknolojisi (toner), baskılı devreler, yapıştırıcılar, oluklu mukavva için bağlayıcı, döküm döküm kumları ve laminatlardır.

Lineer alifatik ketonlar, metil etil keton ve aseton gibi ketonlar reçine oluşturmak için formaldehit ile reaksiyona girerler. Aynı yöntemle, metil izobütil ketondan yapıştırıcı olarak kullanılmak üzere reçine elde edilir. Yüksek alifatik ketonlar uzun süreli reçineler oluşturmazlar. Siklopentanon, sikloheptanone ve halkalı ketonların yanı sıra, sikloalifatik ketonlar, siklohekzanon ve metil siklohekzanon çok önemlidir. Çünkü, zincirlerin uzun kısımları reçinler için hammadde olarak tanımlanır.

Metil etil keton reçineleri kaplamalarda ve yapıştırıcılarda kullanılır. Metil etil keton reçineleri, siklo alifatik, alifatik-aromatik ketonların çözünürlüğü ve uygunluğundan farklıdırlar. Onların özellikleri ketonların polaritesi ve alkali kataliz reaksiyonu boyunca özel davranışlarda bulanmasından kaynaklanır. Meti letil keton-formaldehit reçineleri hafif bir içsel renklenmeye sahiptirler ve alkoller, esterler, ketonlar ve glikol eterler gibi polar çözücülerde çözünürler. Molar kütlesi 3000 ve 5000 g/mol arasındadır ve 80 ve 125^{o}C arasında yumuşama gösterir.

Bu tez çalışmasında, metil etil keton ile formaldehitin bazik ortamda polimerizasyonu ile metil etil keton formaldehit reçinesi sentezlenmiştir. Ayrıca, metil etil keton formaldehit reçinesinin, ağırlıkça %5 oranında alendronikasit, %5 oranında sikloüre ve %5, %10 ve %20 oranlarında dietanolamin bileşikleri ile in situ modifikasyonları gerçekleştirilmiştir. Daha sonra hem metil etil keton formaldehit reçinesi hem de dietanolamin ile modifiye reçineler hidroksil grupları üzerinden boric asit ile sonradan modifiye edilmişlerdir.

Bu çalışmanın ilk adımı metil etil keton formaldehit reçinesinin sentezidir. Metil etil keton ve formaldehit karıştırılarak üç boyunlu bir balona konulmuştur. Reaksiyonun katalizörü sodyum hidroksittir, bu sebeple reaksiyonu başlatmadan önce %20'lik sodyum hidroksit çözeltisi hazırlanmıştır. Üç boyunlu balon altında ısıtıcı olan bir yağ banyosuna oturtturulmuş, mekanik karıştırıcı balona bağlanmış ve balon standa sabitlenmiştir. Boyunlardan birine geri soğutucu bağlanmıştır. Diğer boyun ise cam kapakla kapatılmış ve reaksiyon için sistem hazır hale getirilmiştir. Sistem ısınmaya başlayınca, karışıma hazırlanan %20'lik sodyum hidroksit çözeltisi damla damla eklenmiş ve sistemin pH'ı 10-11 arasına sabitlenmiştir. Reaksiyon başladığından dolayı pH zamanla düşme eğilimindedir, bu sebeple kısa aralıklarla pH kontrol edilmiştir. Düşen pH tekrar %20'lik sodyum hidroksit ile tekrar ayarlanmıştır. Sıcaklık ise 80°C'ye sabitlenir. Reçinenin reaksiyon süresi 4 saattir. Bu süre sonunda reaksiyon ısıtıcı ve karıştırıcıyı kapatarak sonlandırılmış ve reçine su ile yıkanmıştır. Öncelikle etüvde 80°C'de beş saat kurutulan reçine, vakum etüvünde tekrar kurutulmuştur. Kuruyan reçine toz haline getirilmiştir.

Aynı proses metil etil keton formaldehit reçinesinin in situ modifikasyonları için de geçerlidir. Reçinein modifiye edilceği kimyasal, reaksiyon başında, modifikasyonun oranına göre gerekli miktarda reaksiyon ortamına eklenir ve aynı proses gerçekleştirilir. Borik asit ile gerçekleştirilen sonradan modifikasyon için ise izlenen prosedür şu şekildedir: Kurutulup toz haline getirilmiş reçine toluen içinde çözünür ve bu çözeltiye gerekli miktarda borik asit eklenir. Deanstag sistemi ile reaksiyon ortamı 150^{o}C'ye kadar ısıtılır ve yaklaşık iki saat boyunca rifluks gerçekleştirilir. Elde edilen modifiye reçine kurutulur ve toz haline getirilir.

Halojen içeren alev geciktiricilere alternatif olarak fosfor içerikli bileşikler önerilir. Düşük toksisite, daha az zehirli gaz salınımı ve alevlenme durumunda daha yavaş duman oluşumu sebepleriyle halojen içeren alev geciktircilerden daha çok tercih

edilirler. Fosfor alev geciktirici olarak yoğunlaşan fazda rol alır. Isıya maruz kaldıkça fosfor bileşikleri parçalanır. Reaksiyon ürünleri olarak fosforik ve polifosforik asitler oluşur ve fosfor bakımından zengin yanmış maddenin yoğunlaşan fazda oluşmasını katalize ederler.

Azotun organofosfor kimyasalları ile sinerjistik etki yaratarak maddelerin alev geciktirici özelliklerini iyileştirdiği bilinmektedir. Azot alev geciktirmeye olan etkisi azot kayanağına bağlı olarak değişir. Bu nedenle amin grubunu temsilen alendronic asit, amit grubunu temsilen de alendronic asitten sentezlenen siklo üre ile metil etil keton formaldehit reçinelerinin in situ modifikasyonları gerçekleştirilmiştir.

Borik asit ve borat tuzları 1800'lerin başından beri alev geciktirici katkı maddeleri olarak kullanılmıştır, ancak fosfor, halojen, ve diğer bileşiklerden daha az incelenmiştir. Çinko borat (ZnB), boraks, boric asit gibi bor bileşiklerinin çok düşük oranda olsa bile geleneksel alev geciktricilere eklenmesi alev geciktirici etkisini arttırmaktadır.

Bu nedenle boric asitin metil etil keton formaldehit reçinesine bağlanması ile ısısal davranış ve çözünürlük gibi fiziksel özelliklerindeki etkisini görmek için sentezlenen reçine sonradan boric asit ile modifiye edilmiştir. Ayrıca boric asitin geleneksel alev geciktiricilerle olan sinerjistik etkisini incelemek amacıyla da metil etil keton formaldehit reçinesi öncelikle dietanolamin ile ağırlıkça %5, %10 ve %20 olmak üzere üç farklı oranda in situ modifikasyonu gerçekleştirilmiş, daha sonar ise elde edilen bu modifiye reçineler boric asit ile tekrar modifiye edilmişlerdir.

Sentezlenen ve sonradan modifiye edilen bu 10 farklı metil etil keton formaldehit reçinesinin FTIR ve proton NMR ile spektroskopik olarak karakterizasyonu yapılmıştır. Fouier transform infrared spektroskopi ve nükleer magnetik resonans spektroskopi spektrumlarından elde edilen sonuçlardan yararlanılarak, sentezler ve modifikasyonlar sırasında gerçekleşen reaksiyonların sonucu eldee dilen son ürünlerin kimyasal yapıları konusunda öneride bulunulmuştur.

Reçinelerin fiziksel özelliklerindeki değişimler ise farklı solventlerdeki (tetrahidrofuran, diklorometan, etanol, aseton ve dimetilsülfoksit) çözünürlük analizleri ile gözlenlenmiştir. Yapılan modifikasyonlar sonucu reçinelerin çözünürlüklerinde meydana gelen değişimler karşılaştırmalı olarak yorumlanmıştır.

Tüm bunlara ek olarak, reçinelerin termal özellikleri termogravimetrikanaliz (TGA) ve diferansiyel tarama kalorimetrisi (DSC) yöntemleriyle analiz edilmiştir. Termogravimetrik analizlerden elde edilen madde kaybının başladığı sıcaklık ve kalan kül miktarı, diferansiyel tarama kalorimetrisi analizlerinden elde edilen camsı geçiş sıcaklığı ve erime noktaları, metil etil keton formaldehit ve modifiye reçinelerinin termal özelliklerinin değerlendirmesinde kullandığımız önemli parametreler olmuştur.

Specktroskopik metodlar, çözünürlük analizleri ve termal analizlerden elde edilen sonuçlar, sentezlenen reçinelerin, öngörülen reaksiyon mekanizmaları ile tahmin edilen kimyasal yapılarını ve değişen kimyasal yapılarına bağlı olarak beklenen fiziksel ve kimyasal özelliklerini destekler niteliktedir. Bor ve azot içeren yeni modifiye metil etil keton formaldehit reçineleri endüstride reçinelerin kullanım alanlarını genişletecektir.

1. THEORETICAL PART

1.1 Introduction to Resins

Resin is an organic substance which has wide range of applicationsincluding consolidants, adhesives, coatings, casting, molding, and storage materials. Resins play a vital role like excellent chemical resistance, good adhesion properties, heat resistance, oxidative stability, and excellent electrical properties in the field of plastic, textile, electrical and electronics, paper, paint, construction, etc. In coating technology, resins are mainly used to provide gloss and elasticity, for suspension of pigments, to provide resistance to water and chemical, besides acting as a dispersant [1-2].

Broadly, resins are classified as natural resins and synthetic resins based on their occurrence. Natural resins are obtained from trees which exude a viscous liquid when the bark is damaged. Commonly available natural resins are Dammar, Mastic, Rosin, Shellac and Beeswax etc. Natural resins are used for a wide range of applications like production of perfumes, treatment of bows for instruments such as violins and cellos [1,3].

Synthetic resins are essentially polymers, which are built up from simple molecules or monomers. There are two general methods for the production of polymers, namely, addition polymerization and condensation polymerization, and which method to be employed depends on the type of monomer. Common synthetic resins are: alkyd resins, epoxy resins, polyamide resins, polyurethane resins, vinyl resins, polystyrene resins, acrylic resins, phenolic resins, and ketonic resins, etc [1,3]. They can be seen with their precursors and applications in Table 1.1.

1.2 Ketone-Aldehyde Resins

Ketone-aldehyde (KA) resin, an important resins synthesizedwith ketone and aldehyde, is well known as multifunctional additives in coatings and inks [5-7].Owing to the existence of carbonyl and hydroxyl groups, in the molecular structure, KA resin has good compatibility with coating or ink resins, and can be used as dispersant for pigments in the coatings and inks [8–10]. Meanwhile, KA resin can endow the products with high hardness

Table 1.1: Types of synthetic resins, their precursor and applications [4].

Resin	Precursor	Applications
Phenolic resin	Phenol and formaldehyde	Wood adhesive, moulding compounds, foundry binders, laminate mouldings, electrical laminates, ablative coating casting and fibre composites for household appliances, automotive, aircraft construction and accessories, electrical and lighting industries
Unsaturated polyester	Dicarboxylic acids, diols and reactive diluents e.g.,, styrene	Surface coating, fibre composites for mechanical equipment and building construction, electrical and lighting industries
Epoxy	Epichlorohydrin and bisphenols	Engineering adhesives, paints and surface coating, electrical laminates, fibre composites for automotive, marine construction and aerospace applications.
Vinyl ester	Epoxy resin and acrylic or methacrylic acid	Fibre composites for mechanical equipment and building construction, marine construction, electrical industries
Melamine	Melamine and formaldehyde	Coatings, moulding compounds, wood materials processing, friction linings, textile auxiliaries
Urea	Urea and formaldehyde	Moulding compounds, textile auxiliaries, wood materials, foundry binder, foams
Furan	Furfuryl alcohol	Refractory materials processing, fibre composites, moulding compounds, grinding wheels, acid-resistant cements
Polyurethane (PU)	Diisocyanate and hydroxylfunctionalised oligomer (polyol)	Coating, adhesive, encapsulating materials, acid-resistant cements, foams, adhesives
Polyimide	Diamines and dianhydride	Coating and composite for hightemperature applications
Cyanate ester	Cyanogen halide and alcohol or phenol	Fibre composites for aircraft, rocket, missiles and re-entry vehicles
Bismaleimide	Bismaleic acid and amine	Fibre composites for aircraft, rockets, missiles and re-entry vehicles

and good adhesion to various substrates. In addition, the saturated chain in KA resin made contributions to the high gloss of the coating film [11-12]. Therefore, the preparation of KA resin and its application in coatings and inks have been paid more and more attentions [13–15].

Most of the natural resins are quickly affected by caustic potash or caustic soda. Many synthetic resins (e.g. phenolformaldehyde resin) are also affected by strong alkali. Ketonic resins (obtained from ketone monomer) have the ability to resist caustic alkali and even on boiling the resin with alkali [1, 16]. Ketonic resins can be used in combination with high molecular weight film formers (e.g. cellulose derivatives, chlorinated rubber, vinyl esters, vinyl ethers, vinyl chloride, vinyl aromatics etc.) or chemically drying binders (e.g. alkyd resins) for production of surface coatings and also for making adhesives, printing inks, toner, pigments, varnishes for surface treatment of wood, metal etc. [1, 17-18]

Ketone-aldehyde resins are obtained by self-condensation or more frequently by co-condensation with formaldehyde from aliphatic, cycloaliphatic or aliphatic-aromatic ketones and aldehydes. The condensation of monomers can be accelerated by means of basic, acidic or neutral catalysts. [19-20]

To produce such additional resins are suitable

a) ketones (such as acetone, methyl ethyl ketone, cyclohexanone, acetophenone in Figure 1.1) and/or

b) aldehydes (such as formaldehyde and isobutyraldehyde in Figure 2.1) and / or

c) alkylated aromatics (such as m-xylene in Figure 3.1) [19-20]

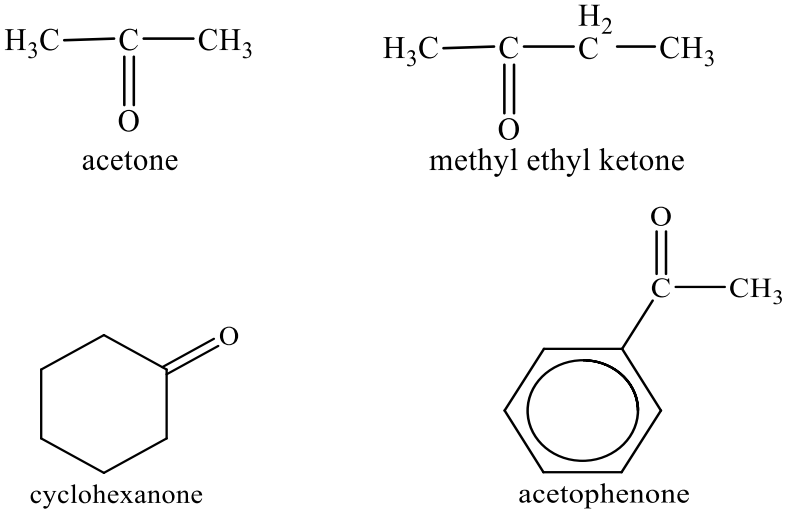

Figure 1.1 : Chemical structures of ketones.

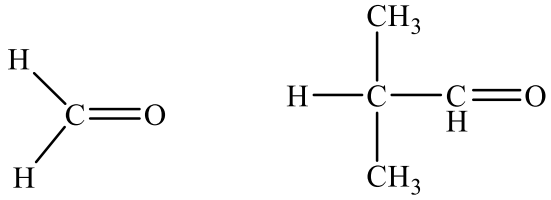

Figure 1.2 : Chemical structures of aldehydes.

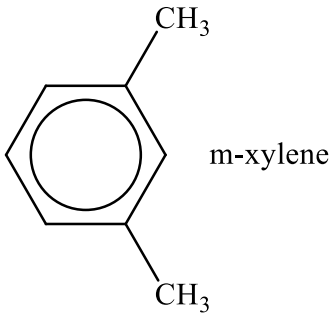

Figure 1.3 : Chemical structure of alkylated aromatic.

In the co-condensation of the ketones with formaldehyde, basic catalyst play the major role. The reaction follows the mechanism of the aldol condensation, and leads to aldol-type products and, after elimination of water, to unsaturated compounds. As seen in Figure 1.4, in the first step of the reaction, formaldehyde is added to form the ketone alcohol. [21-22]

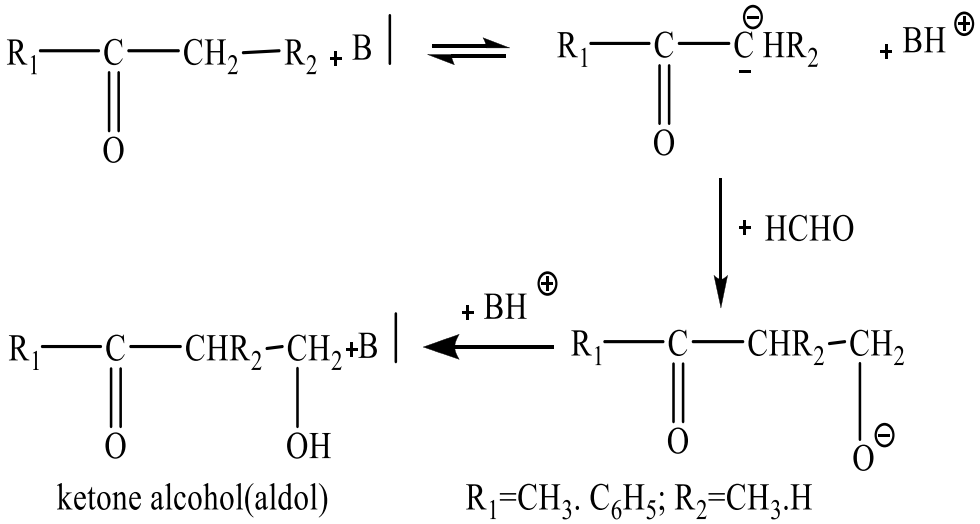

Figure 1.4 : Formation of enolate anion and methylol of ketone.

Subsequently, depending on the molar ratio of ketone to formaldehyde and on the other reaction conditions (temperature, pH, concentration), ketone alcohol can either undergo

dehydration to form polymerizable vinyl ketones, or with further formaldehyde can form highly reactive methylol compounds (see Figure 1.5).

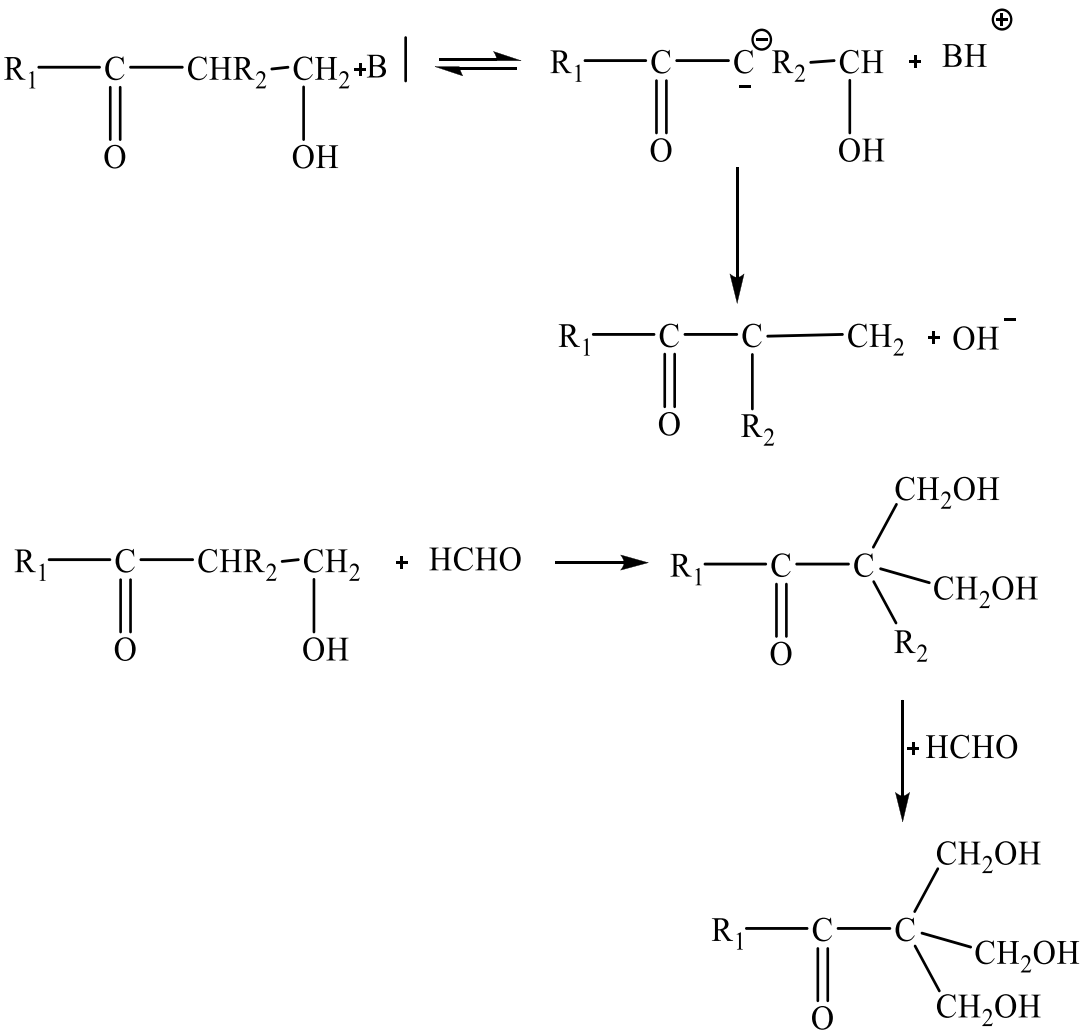

Figure 1.5 : Formation of three methylol of ketone.

1.3 Methyl Ethyl Ketone-Formaldehyde Resins (MEKFR)

The methyl ethyl ketone-formaldehyde resins possess a slight inherent coloration and are soluble in polar solvents such as alcohols, esters, ketones and glycol ethers. The hydroxyl numbers are in the range from 80 to 190mg of KOH/g. The resins are strongly polar, hygroscopic and have an oxygen content of from 21 to 29 per cent by mass. The polar masses are between 3000 and 5000 g/mol, the softening range between 80 and 125ºC. Other physical properties have been described. The resins cannot be hydrolysed, and possess not only keto and hydroxyl groups but also C-C double bonds. Their chemical reactivity is exploited in industry: the OH groups react with carboxylic acids and anhydrides or with isocyanates, while the double bonds can be hydrogenated. [23]

The resins are prepared by alkaline-catalysed condensation of methyl ethyl ketone and formalde in a molar ratio of from 1: 2 to 1:2.5 in a batch process. Without purification beforehand, the ketone is reacted with formaldehyde in the presence of water. NaOH and KOH have proven to be the best catalyst for this reaction. The increase in the melting point from 80 to 120ºC can be achieved by raising the excess of formaldehyde. High softening points are also obtained by phase transfer catalysis. [23]

The structure shown in Figure 1.6 is greatly simplified, since hydroxyl groups and double bonds are also found in the resins.

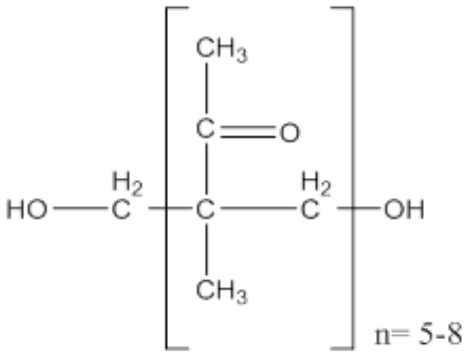

Figure 1.6 : Chemical structure of methyl ethyl ketone formaldehyde resin.

More recently it has also proved possible to obtain high molecular weight methyl ethyl ketone-formaldehyde and acetone-formaldehyde resins by specipic vinyl polymerization (molar masses 40 000 to1000 000 g/mol) [24]. In this process seen in Figure 1.7, the ketone alcohol is first prepared under alkaline conditions and seperated off by fractional distillation. Then, pound which is then subjected to free-radical polymerization.

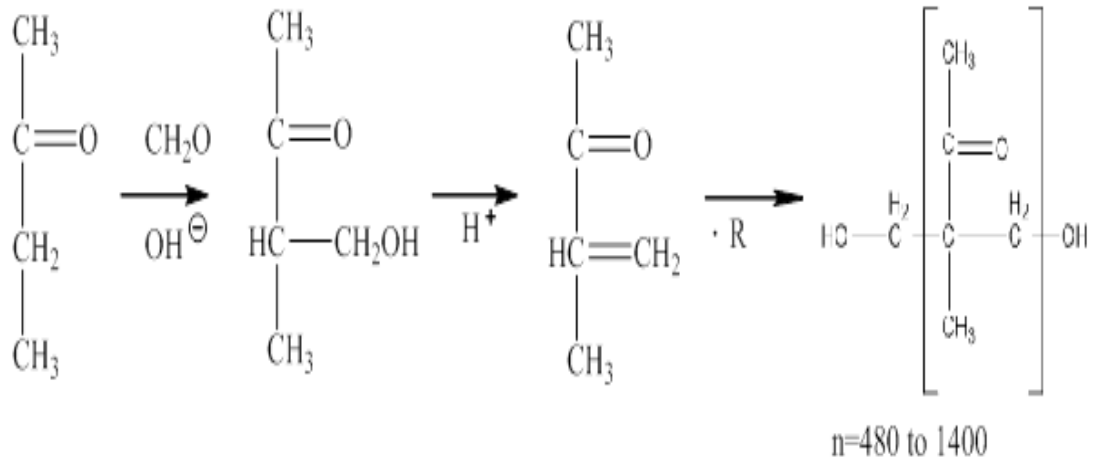

Figure 1.7 : Synthesis of methyl ethyl ketone formaldehyde resin.

1.4 Modification with Alendronic Acid

Alendronic acid (see Figure 1.8) can be used for flame retardancy properties. Bromine containing flame-retardants, such as brominated diphenyl oxide flame-retardants, was being used as flame-retardants until they are banned due to toxicity. As an alternative, phosphorus-containing flame-retardants are proposed. They are more preferable than halogen containing flame-retardants due to low toxicity, less release of toxic gases and slow formation of smoke in the case of fire. Phosphorus begins to act as a fire retardant in the condensed phase. Phosphorus compounds decompose as the heat exposure occurs. As the product of the reaction, phosphoric or polyphosphoric acids forms and they catalyzes the formation of phosphorus-rich char in the condensed phase. [25]

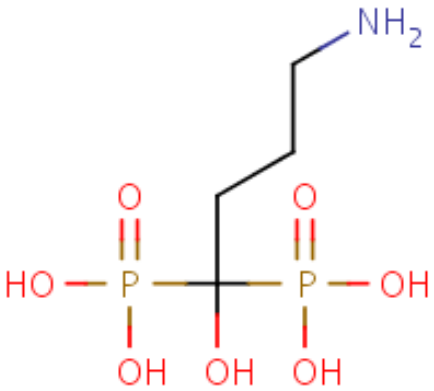

Figure 1.8 : Chemical structure of alendronic acid [26].

1.5 Modification with Cyclic Urea Synthesized From Alendronic Acid

The synergistic role of nitrogen in enhancing the flame retardant characteristics of substrates with organophosphorus chemicals has been reported in several publications. The contribution of nitrogen to the flame-retarding efficiency of organophoshorus chemicals depends on the source of nitrogen.

While the amido and amino nitrogen enhance, the nitrile nitrogen adversely affects the flame-retarding properties. Among the amide nitrogens, melamine and melamine derivatives have been found to the most effective in enhancing flame-retardent properties. [27]

For this reason, a cyclic urea is synthesized from alendronic acid in order to get an organophosphorus compound with amide group (see Figure 1.9).

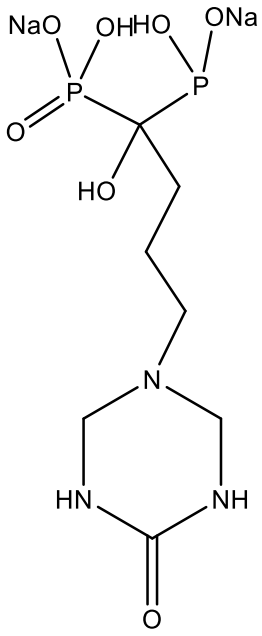

Figure 1.9 : Chemical structure of cyclic urea synthesized from alendronic acid.

1.6 Modifications with Amines

Nitrogen compounds are a small but rapidly growing group of flame retardants which are in the focus of public interest concerning environmentally friendly flame retardants. Today their main applications are melamine for polyurethane flexible foams, melamine cyanurate in nylons, melamine phosphates in polyolefines, melamine and melamine phosphates or dicyandiamide in intumescent paints, guanidine phosphates for textiles and guanidine sulfamate for wallpapers. [28]

Their main common advantages are their low toxicity, their solid state and, in case of fire, the absence of dioxin and halogen acids as well as their low evolution of smoke. Their efficiency lies between that of halogen compounds and that of aluminumtrihydrate and magnesium hydroxide. The metallic hydroxides split off water and are environmentally friendly, but their low activity requires high concentrations which change the mechanical properties of the matrix that they are applied to. In contrast to many halogen compounds, flame retardants based on nitrogen do not interfere with the set of stabilizers added to every plastic material. [28]

Recycleability has become important as many plastics are recycled. Flame retarded materials based on nitrogen compounds are suitable for recycling as the nitrogen flame

retardants have high decomposition temperatures. In the field of cable jacketing they evolve less corrosive gases during combustion and do not damage the electrical installations. [28]

Flame retardants based on nitrogen are environmentally friendly because they do not add any new element to those already present in the polymers such as polyurethanes, nylons and ABS. In regard to waste disposal they are comparable with fertilizers as they possess the same elements of importance, namely nitrogen and phosphorous. [28]

In comparison with metallic hydroxides they are more efficient and deteriorate the mechanical properties of the plastic material less. [28]

1.7 Modification with Boric Acid

Boric acid and borate salts have been used as flame retardant additives since early 1800s but they have been less studied than phosphorous, halogen and other compounds [29].

The use of borates for enhancing the flame retardancy of polymericmaterials wasreported in 20th century. The affectivityof borates as flame retardants in various materials has beenexplained by their formation of nonpenetrable glass coatings,which exclude oxygen and prevent the further propagation ofcombustion. Boric acid and hydrated inorganic borates havelow melting temperatures (Tm) and fit nicely into this schemeof forming glass coatings. When it is slowly heated, boric acid (mp 171^{o}C) loses water and changes first into metaboric acid,then to HBO_2, and finally to boric oxide (B_2O_3). Above 325^{o}C,B_2O_3 softens to into glass and becomes pourable only at 500^{o}C.The flame-retardant action of the boron-containing compoundson polymeric materials is chemical and physical. It was foundthat these inorganic boron compounds promote char formation in the burning process. The borate esters formed were furtherdehydrated, probably by carbocation mechanisms. [30-32]

The addition of percentage of boron compounds such as zinc borate (ZnB), boraz and boric acis, etc. with conventional flame retardants seemed to enhance the flame-retardant action [33-35].

2. EXPERIMENTAL PART

2.1 Materials Used During Synthesis and Analyses

The materials used during synthesis and analyses and their supplier companies can be seen in Table 2.1.

Table 2.1: Materials used during synthesis and analyses.

Material	**Manufacturer**
Methyl ethyl ketone	Tekkim
Formaldehyde (37%)	Merck
Sodium hydroxide	Riedel de Haen
Hydrochloric acid (37%)	Merck
Cyclic urea synthesized from alendronic acid	Ready to use (synthesized by Yusuf Yivlik, Chemist)
Diethanolamine	Merck
Boric acid	Merck
THF	Merck
Dichloromethane	Merck
Dimethyl sulfoxide	VWR BDH Prolab
Ethanol	J. T. Baker
Acetone	J. T. Baker

2.2 Equipments Used During Synthesis and Analyses

The equipments used during synthesis and analyses and their supplier companies can be seen in Table 2.2.

Table 2.2: Equipments used during synthesis and analyses.

Equipment	**Brand**
Mechanical stirrer	Heidoplh RZR 2020
Heater	Heidolph MR 301 K
Oven	Binder
Oven with vacuum	MMM Medcenter
FTIR	Bruker
NMR	Variant 500 MHz
TGA	Mettler Toledo
DSC	Mettler Toledo

2.3 Characterization Methods

2.3.1 Infrared spectroscopy

In Fourier Transfer Infrared Spectrometer (FTIR), electromagnetic spectrum goes through the sample. Sample absorbs specific wavelengths and is excited to higher energy level. The molecules have specific frequencies that they absorb the spectra and they vibrate or rotate. There are four kinds of energy types of molecules: electronic, vibrational, rotational and

translational. All vibrations and rotations of molecules are not infrared active. Dipole moment of the molecule must change for FTIR analysis of sample. By using FTIR, presence of chemical groups can be determined. It is also can be used for determination of certain functional groups, structure of polymer, polymer degradation process and to examine polymerization processes. [36-37]

FT-IR spectra was measured using model recorded Bruker Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, directly from the sample without help of the KBr discs.

2.3.2 ^{1}H Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) is a spectrometric technique to determine chemical structures of materials. The theory behind NMR is the allignment of the nucleus in the direction of applied magnetic field. Energy is required to reverse the allignment, which depends on appllies magnetic field and nature of nucleus. The reversal is a resonant process and specific to components. By determining energy level transitions for all of the atoms in the molecule, properties of components can be revealed. The most common nuclei that is examined are H and C; therefore, ^{1}H NMR and ^{13}C NMR the most used NMR systems and ^{1}H NMR is more sensitive than ^{13}C NMR. [36]

All ^{1}H-NMRdata were obtained from a Varian (AC 500 MHz, Germany) spectrometer, using $CDCl_3$ as solvent and TMS as internal reference.

2.3.3 Thermogravimetric analysis (TGA)

Thermogravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function temperature or time in a controlled atmosphere. [38] Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000^{o}C. The technique can characterize materials that exhibit weigt loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking. [38]

TGA was carried out in nitrogen atmosphere with a heating rate 40°C/min up to 900°C temperature by Mettler Toledo instrument. Weight loss (%) of samples was calculated within temperature range 20-900°C.

2.3.4 Differential scanning calorimetry (DSC)

With differential scanning calorimetry (DSC), a sample and a reference are heated separately in a measurement cell in metal boats. The heating rate for the reference is kept constant. By means of a control unit, the temperature of the sample is regulated

such that there is no temperature difference between sample and reference. In transformation phenomena, such as, for example, melting, boiling, crystallization or solidification, endothermic or exothermic heat effects ocur. The change in the heating energy required maintain the sample boat at the same temperatures is recorded. A recorder plots in differential thermal energy as heat flux. In the case of resins for coatings, which are prodominantly amorphous, DSC is used primarily to determine the glass transition temperature (Tg). The glass transition is a second-order transition which appears in the thermogram as a step in the spesific heat, Cp. The glass transition stage is defined by the centre of the cp step. If the sample undergoes defined heating from a low to a higher temperature, then in the glass transition the sample changes from a brittle, glass-like state to a rubber-like viscoelastic. [38-39]

DSC curves were obtained by using Mettler Toledo instrument; the heating rate was 10°C/min under a nitrogen atmosphere.

2.4 Procedures

2.4.1 Synthesis of methyl ethyl ketone formaldehyde resin

90 ml MEK and 150 ml formaldehyde are poured into the in a three necked round-bottom flask which is inserted into a silicone-oil bath (see Figure 2.1). 4,8 g of andhyrous NaOH pellets are dissolved in 30 mL of water and this NaOH solution is added dropwise in 15-20 minutes to the flask. The reagents are mixed for 1.5h at 80^{o}C. Then, as the second time, NaOH solution (1,2g/30ml) is added dropwise, and the temperatuse is increased to 90^{o}C. The mixture is stirred at this temperature for 2,5h. During all of the reaction pH value should be around 10-11. After 4h, the reaction is completed, and yellow resin is formed.

The medium is cooled to the 60ºC, and neutralized with HCl solution (37%). Then the resin is washed with warm water several times until it is free from excess formaldehyde and dried in the vacuum oven at 80C.

Figure 2.1: Resin synthesis set-up.

2.4.2 Synthesis of methyl ethyl ketone formaldehyde resin modified with alendronic acid (MEKFR-AA-5wt%)

For the synthesis of MEKFR-AA, 3,6g alendronic acid, which is equal to the 5wt% of MEK, is added to the flask in the beginning of the reaction, and same procedure in 2.3.1 is followed.

2.4.3 Synthesis of methyl ethyl ketone formaldehyde resin modified with cyclic urea synthesized from alendronic acid (MEKFR-CU-5wt%)

For the synthesis of this resin, firstly, cyclic urea is synthesized following this procedure: Into the 0,05 mole urea, 0,2 mole formaldehyde and 0,05 mole amine (alendronic acid) mixtue, KOH is added until the alendronic acid is completely dissolved. After that, pH is adjusted to 8, and cyclic urea is synthesized at 90ºC for 3h.The product obtained is the mixture of 0,05 mole cyclic urea and 0,1 mole formaldehyde.

With a 5wt% ratio of MEK, cyclic urea is added into the polymerization flask, and the same procedure in 2.3.1 is followed.

2.4.4 Synthesis of methyl ethyl ketone formaldehyde resin modified with diethanolamine (MEKFR-DEA-5wt%, 10wt%, 15wt%)

3,6g, 7,2g and 10,8g diethanolamine is added to the medium in the beginning of the reaction, and the same procedure in 2.3.1 is followed in order to obtain 5, 10 and 15wt% diethanolamine modified MEKFR resins, respectively.

2.4.5 Boric acid modification of MEKFR and MEKFR-DEA resins

In order to modify MEKFR and MEKFR-DEA resins with excess boric acid, 15g of resin sample is dissolved in 100ml of toluene in a round bottom flask which is inserted into the silicone-oil bath, and 1,25g of boric acid is added to the flask. Using deanstag systam, the medium is heated to 150^{o}C, refluxed for about 2h until no water is collected any more.

3. RESULTS & DISCUSSION

3.1 Methyl Ethyl Ketone Formaldehyde Resin (MEKFR)

Formation of methyl ethyl ketone formaldehyde resins (MEKFR) starts with an aldol-like reaction following a base-catalyzed elimination reaction of water from methylol derivatives of methyl ethyl ketone (Figure 3.1).

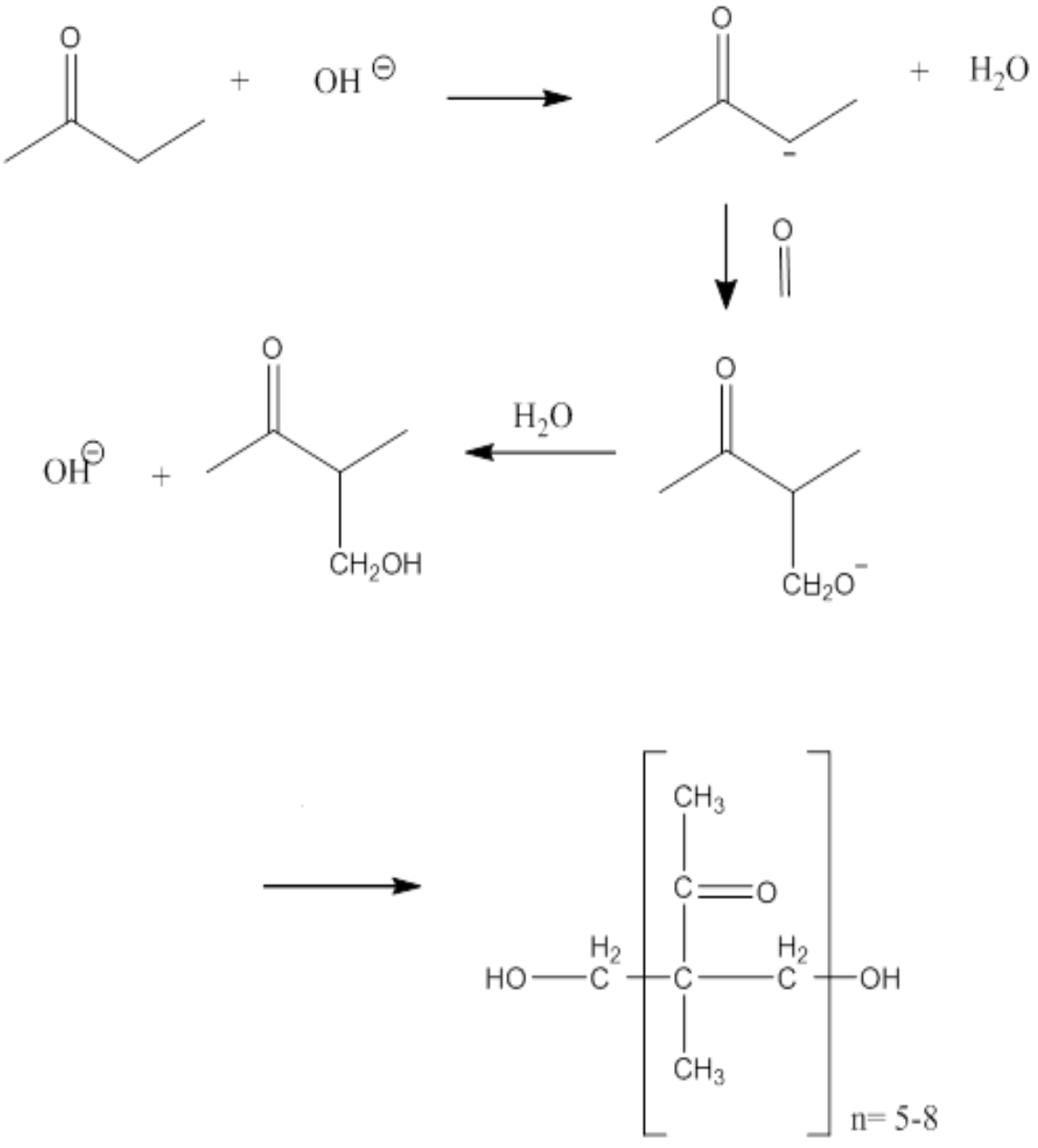

Figure 3.1: Formation of MEKFR.

FTIR spectrum of the MEKFR synthesized can be seen in Figure 3.2. The characteristic structures of this products are ketone -C=O group and –O-H groups. If we look at the left side of the 1500cm-1, we see there are three characteristic peaks. The broad one at 3436cm^{-1} belongs the –O-H group whereas the ones in the region of 2800-3000 cm^{-1}are for the –C-H strecthes of alkyl groups in the structure. In the terms of -C=O bond, we observe a stong peak at 1702 cm^{-1} representing the ketonic carbonyl group of our product, MEKFR.

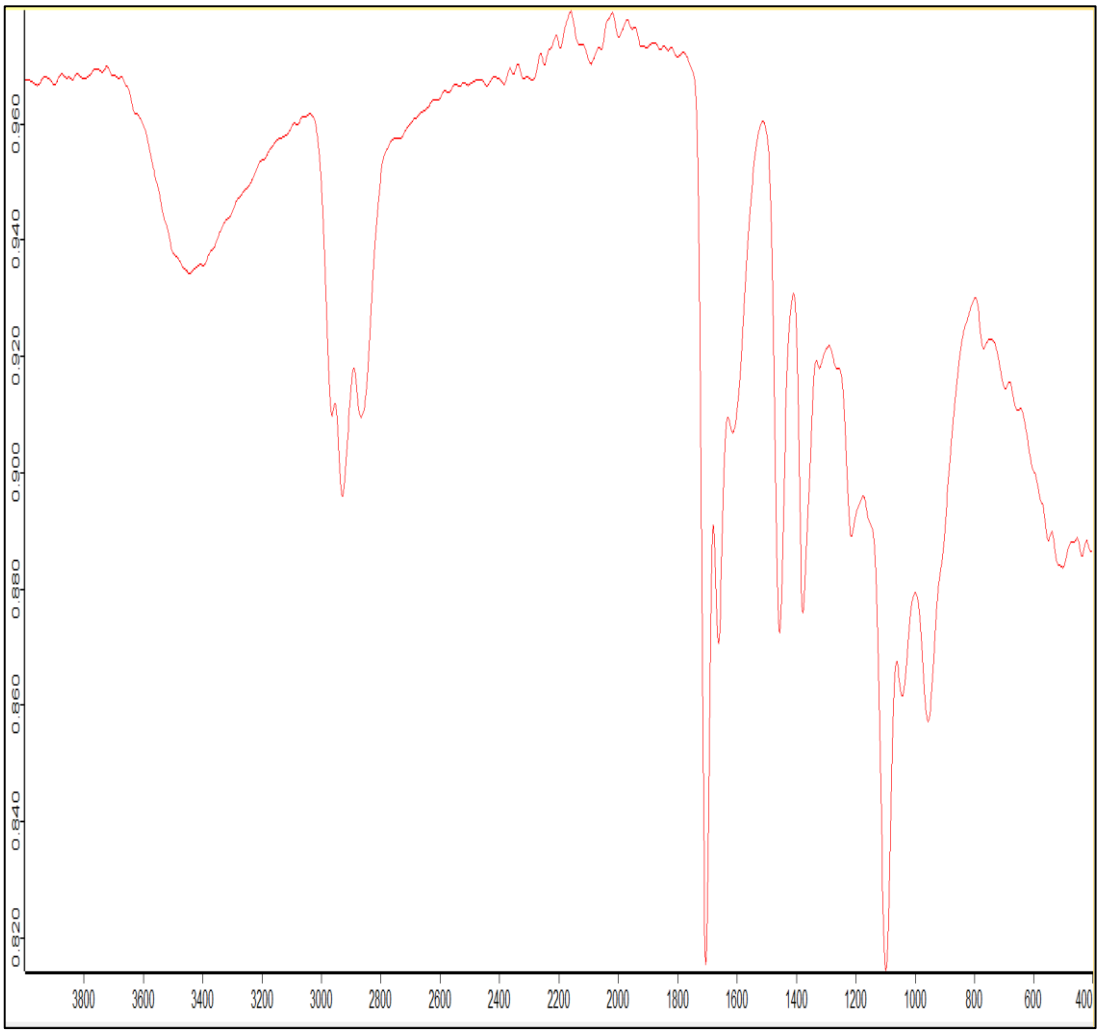

Figure 3.2: FTIR spectrum of MEKFR.

When we analyze the NMR spectrum of MEKFR seen Figure 3.3, we see that hydrogens in the methyl groups next to the alkane carbon and carbonyl carbon atom give peaks near 1 and 3 ppm, respectively whereas the peaks of OH hydrogens in the structure are observed near 5 ppm. In addition, methylene hydrogens next to the hydoxyl group give peak near 6 ppm. Another important point is the low intensity of hydrxyl hydrogen and methylene hydrogens next to the hydroxyl group since they are only in the end groups of the polymer chain.

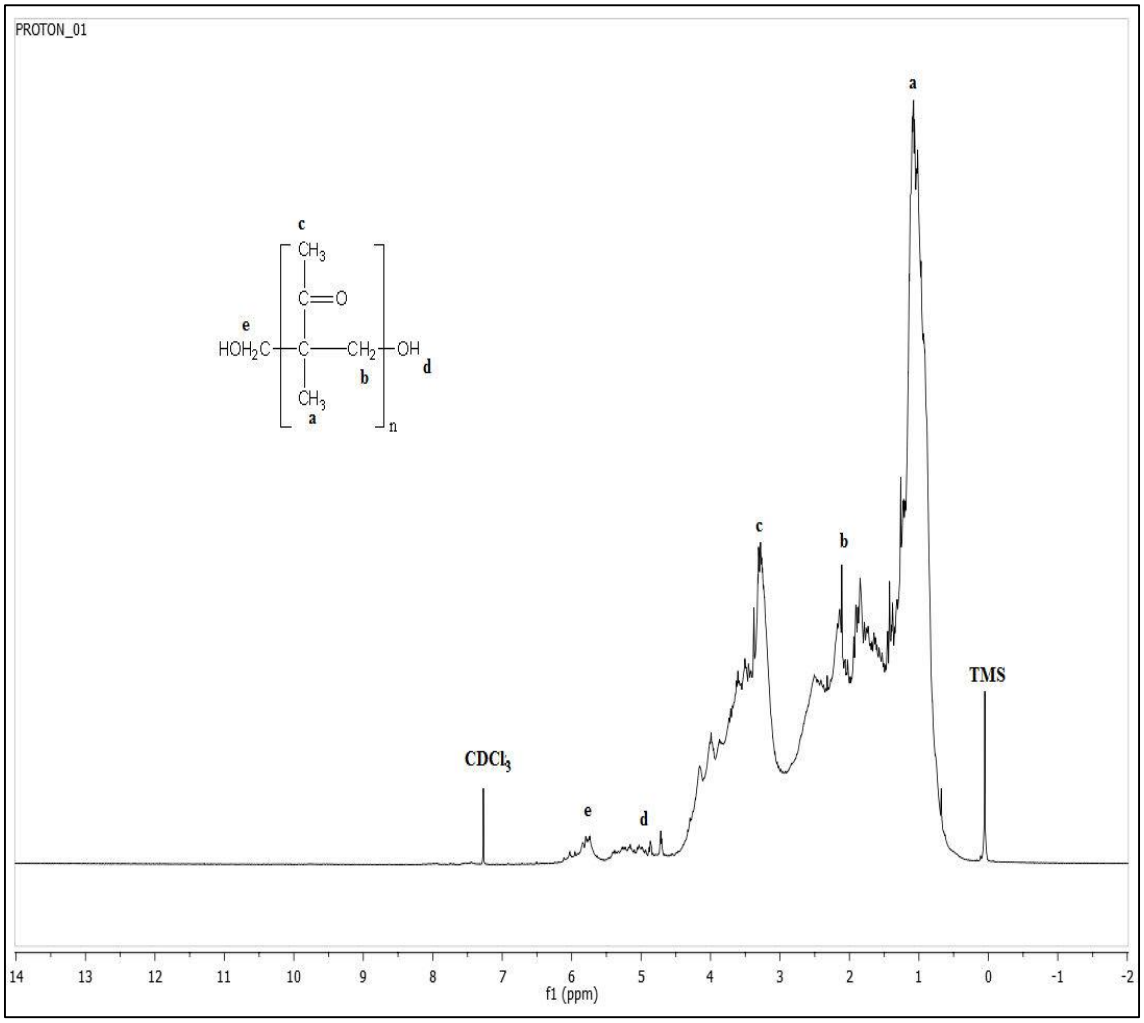

Figure 3.3: NMR spectrum of MEKFR.

In order to get an insight about physical properties of resins synthesized, their solubilities are analyzed in different solvents, namely, tetrahyrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMS), ethanol and acetone.The solubilities of MEKFR can be seen in Table 3.1.

TGA and DSC curves of MEKFR can be seen in figures 3.4 and 3.5, respectively. The onset of degradation is measured as 119^{o}C and glass transtion temperature as 52^{o}C. In addition, the ash amount is determined as 0,34%.

Table 3.1: Solubility of MEKFR in diffrerent solvents.

	THF	**DCM**	**DMS**	**Ethanol**	**Acetone**
MEKFR	**s**	**s**	**sl**	**s**	**s**

"s" means soluble, **"sl"** means slightly soluble.

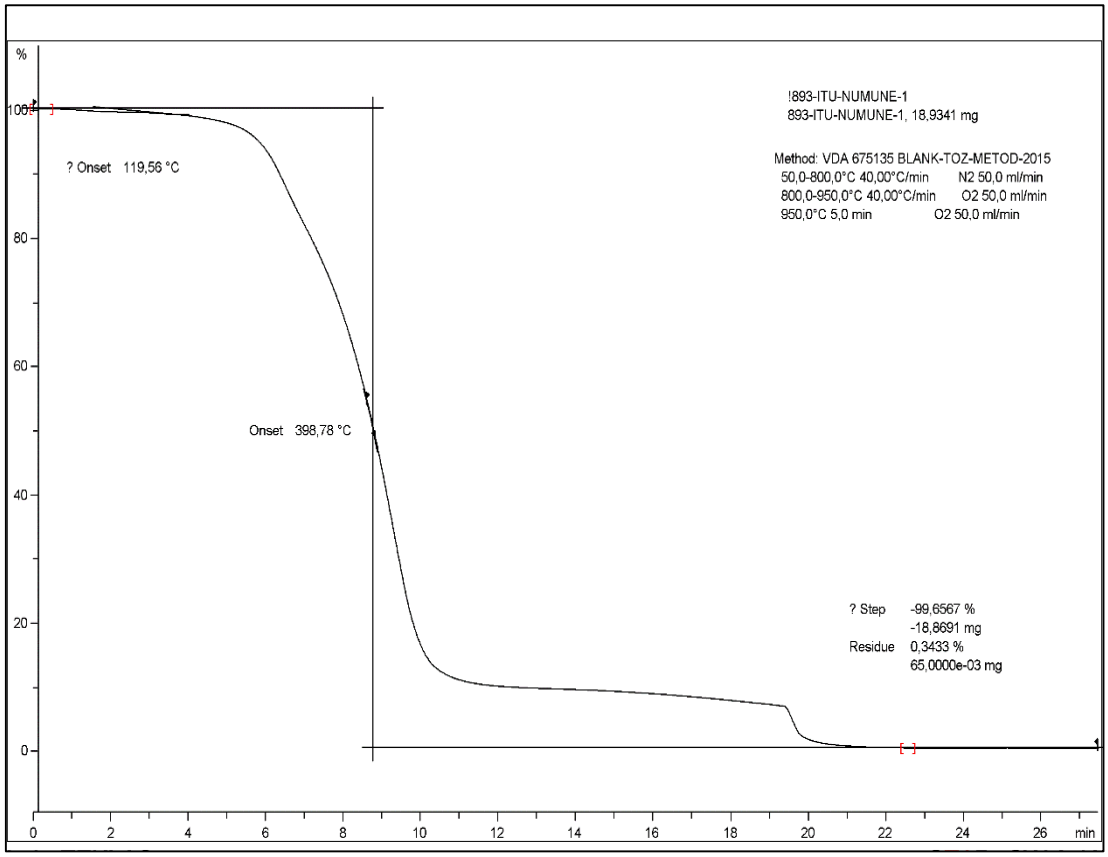

Figure 3.4: TGA curve of MEKFR.

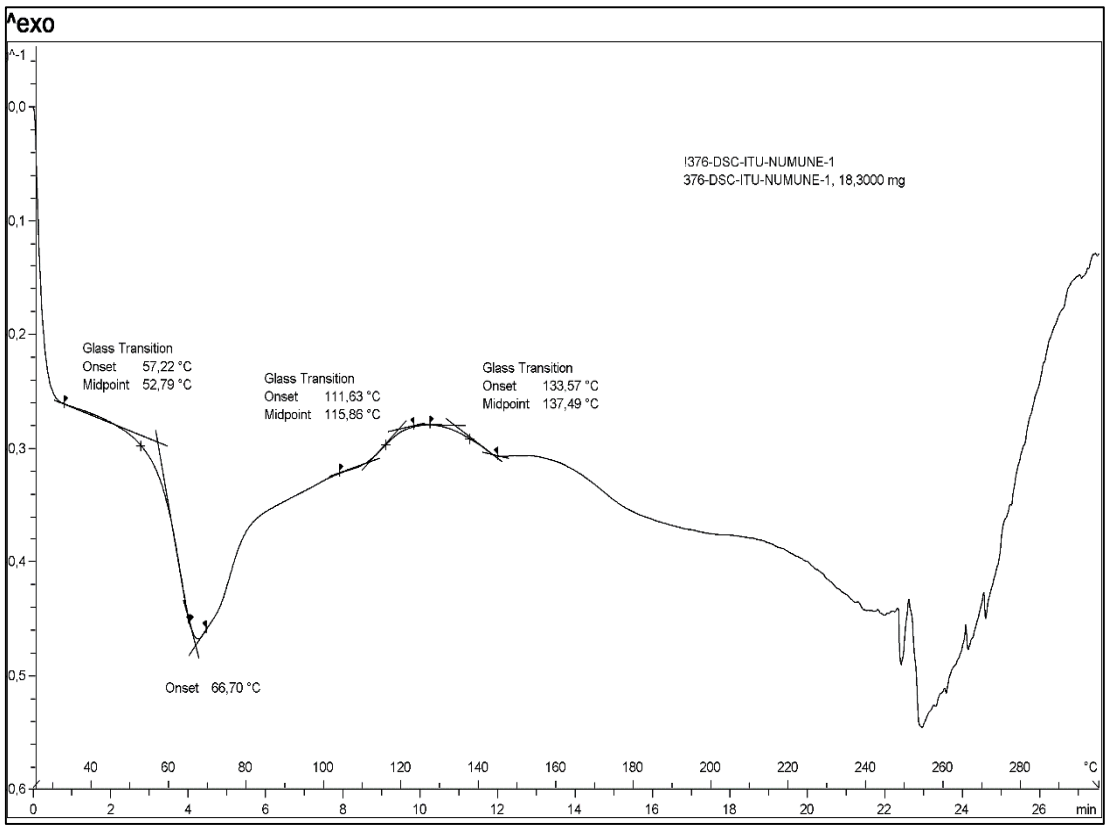

Figure 3.5: DSC curve of MEKFR.

3.2 Methyl Ethyl Ketone Resin Modified with Alendronic Acid (MEKFR-AA)

Both methyl ethyl ketone and alendronic acid probably react with formaldehyde at the beginning of polymerization in the presence of NaOH solution. They form their methylol derivatives such as monomethylols and dimethylols. Condensation reaction between methyl ethyl ketone, alendronic acid, monomethylols and dimethylols present in the reaction media results modified methyl ethyl ketone-formaldehyde resin. (see figure 3.6)

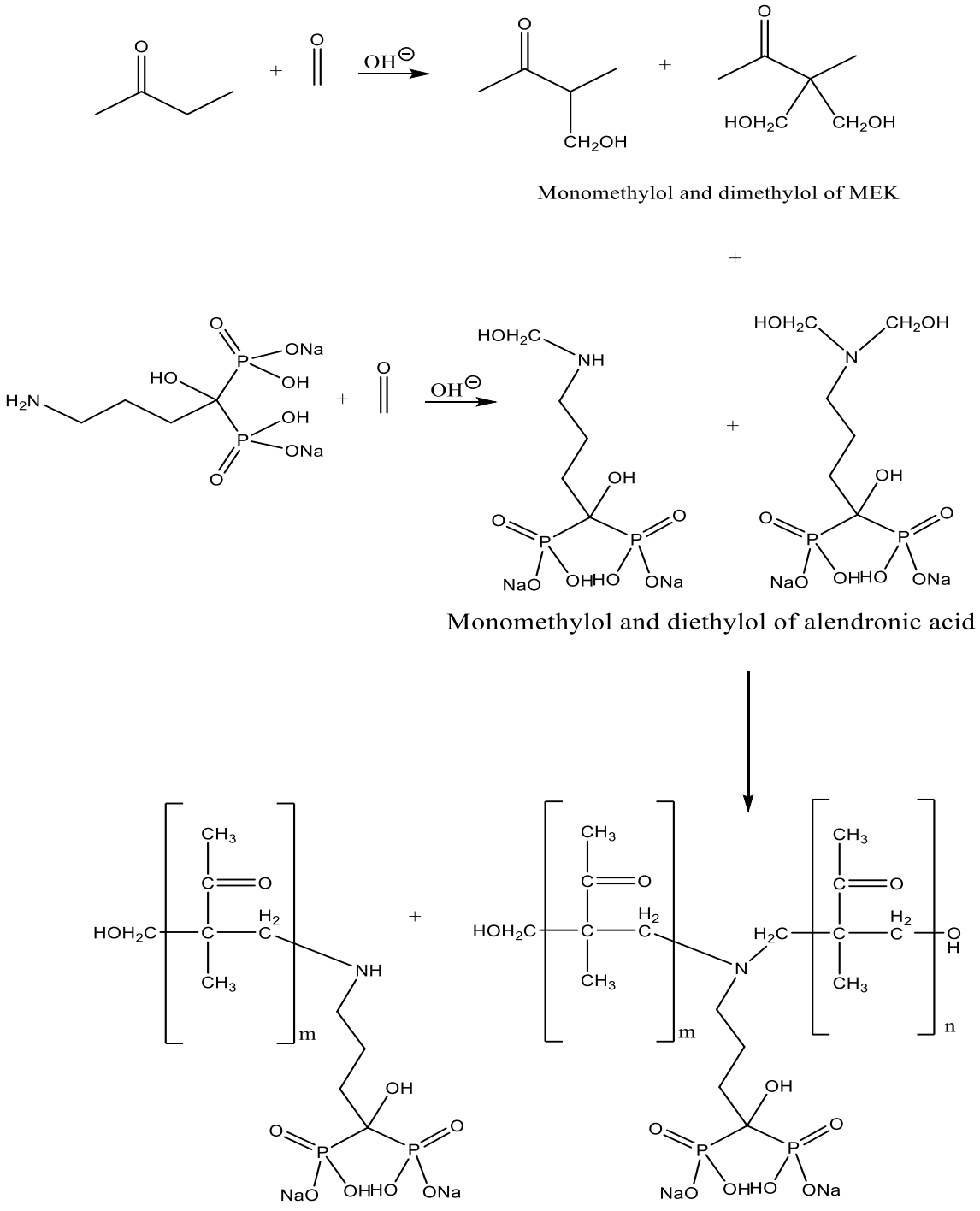

Figure 3.6: Formation of MEKFR-AA.

If we look at the IR spectrum of MEKFR-AA in Figure 3.7, we notice an additional peak in fingerprint region, to be more precise at 753 cm^{-1} band which belongs to –N-H wag signing the presence of secondary amines which means monomethylol of alendronic acid reacts with methyl ethyl ketone formaldehyde resin.However, the peaks related with –N-H strech, which should be observed in 3250-3400 cm^{-1} region can not be observed as an additional peak due to overlap of them with –O-H peak.

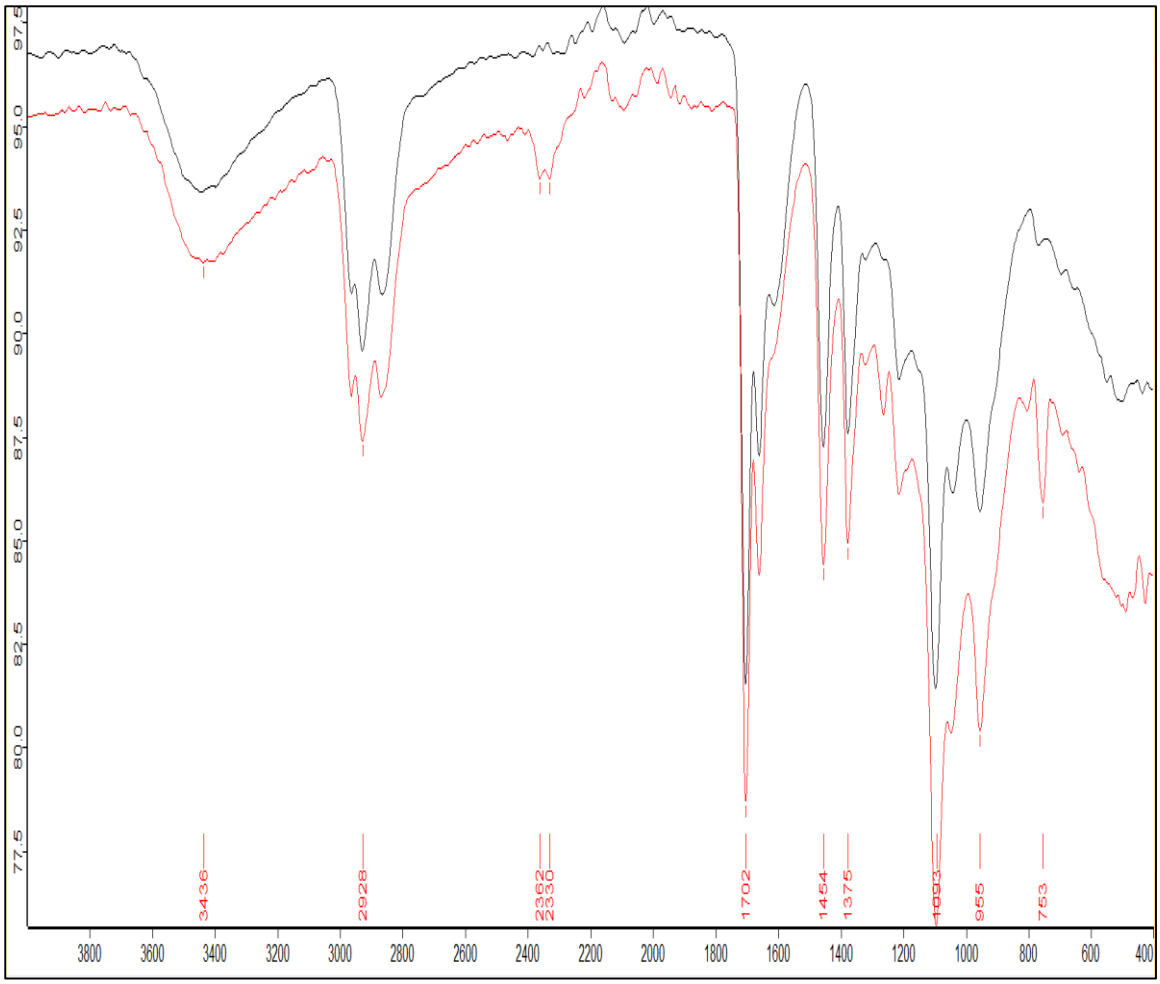

Figure 3.7: FTIR spectra of MEKFR-AA and MEKFR.

When the NMR spectrum of MEKFR-AA is analyzed (see Figure 3.8), two important peaks are observed in addition to the ones in MEKFR spectrum. The first one is for the hydrogen in secondary amine near 2 ppm which complies with the result we derived from FTIR spectrum. The second one is for hydrogen in hydroxyl group next to the phosphorus which is observed near 7 ppm, and it also approves the presence of alenronic acid and modification of MEKFR with it.

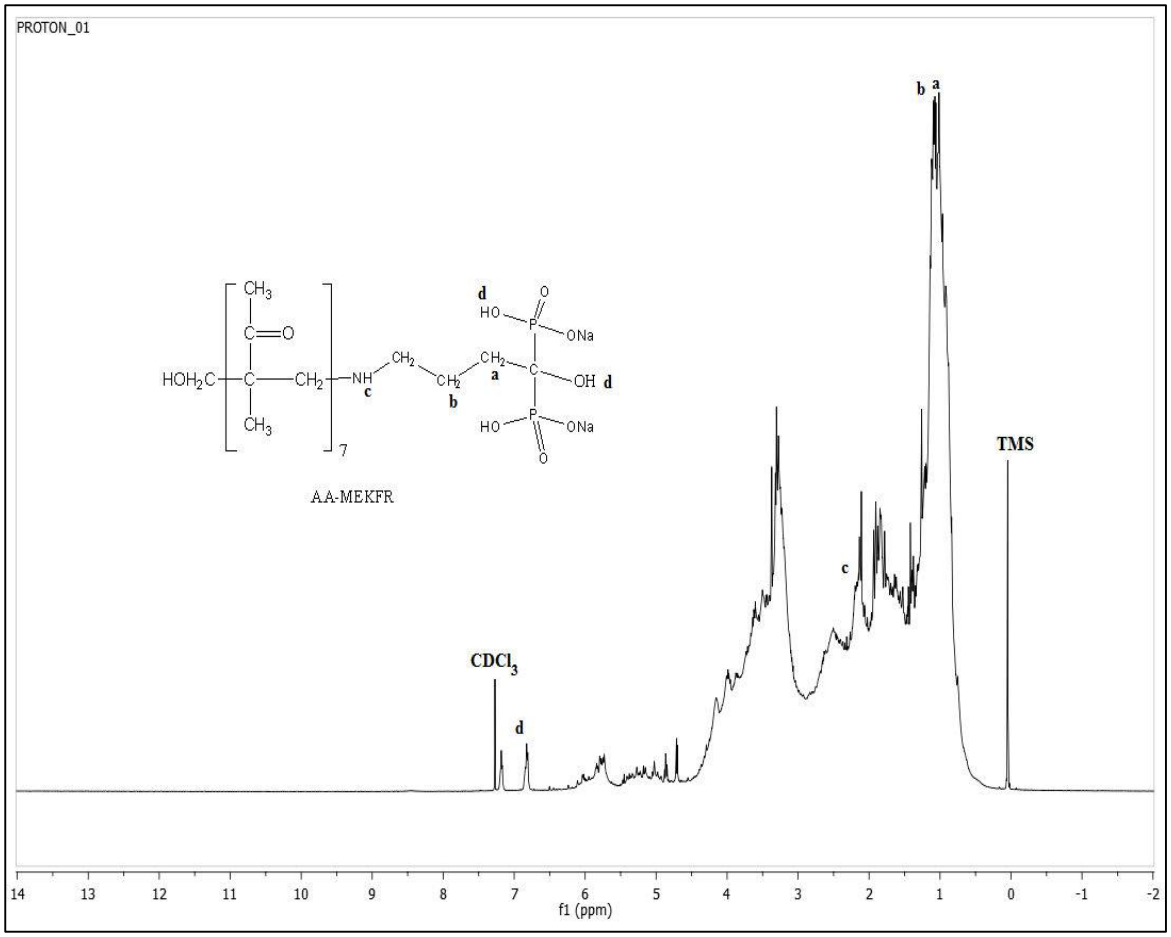

Figure 3.8: NMR spectrum of MEKFR-AA.

The solubility of MEKFR-AA resin in different solvents caan be seen in Table 3.2. If the results are compared with the ones for MEKFR, it can be realized that the solubilities of alendronic acid modified resin in ethanol and acetone decreases.

TGA and DSC curves of MEKFR-AA can be seen in Figure 3.9 and Figure 3.10, respectively. The onset of degradation is measured as 113^{o}C and glass transtion temperature as 52^{o}C. In addition, the ash amount is determined as 2,22%.

Table 3.2: Solubility of MEKFR-AA in diffrerent solvents.

	THF	**DCM**	**DMS**	**Ethanol**	**Acetone**
MEKFR	**s**	**s**	**sl**	**s**	**s**
MEKFR-AA	**s**	**s**	**s**	**i**	**i**

"s" means soluble, **"sl"** means slightly soluble.

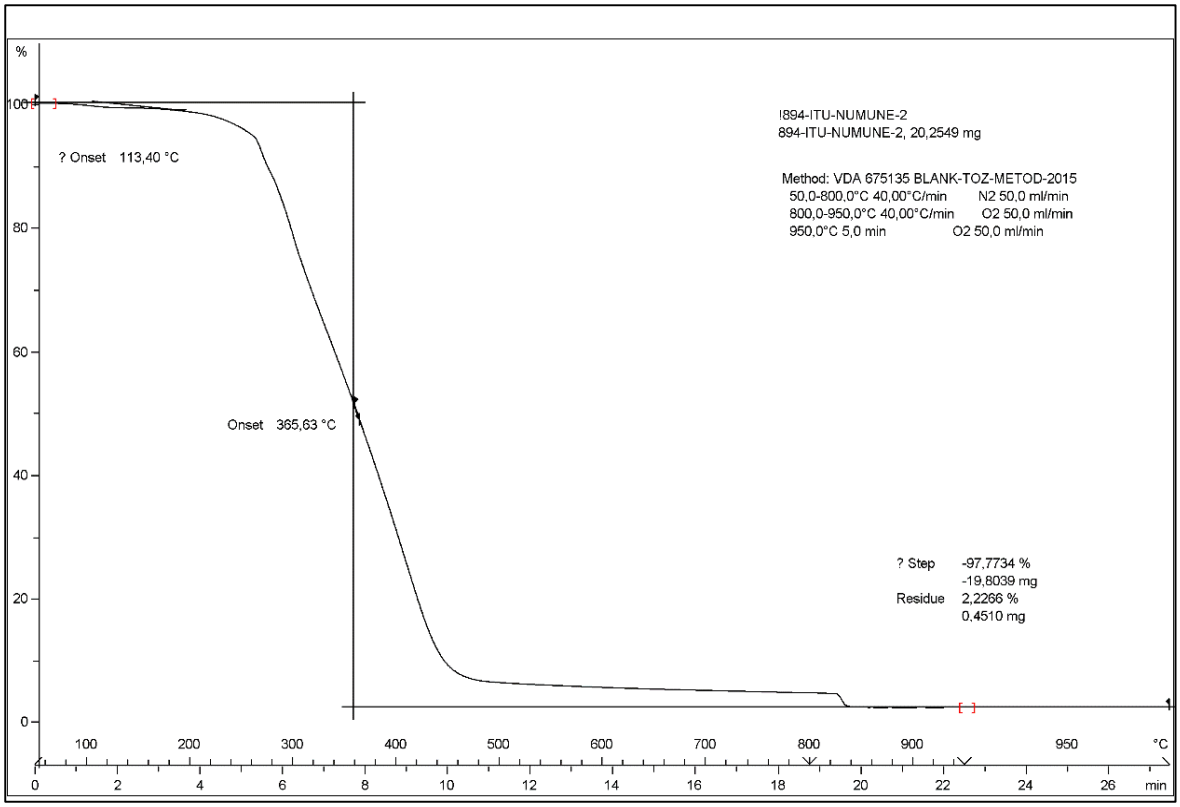

Figure 3.9: TGA curve of MEKFR-AA.

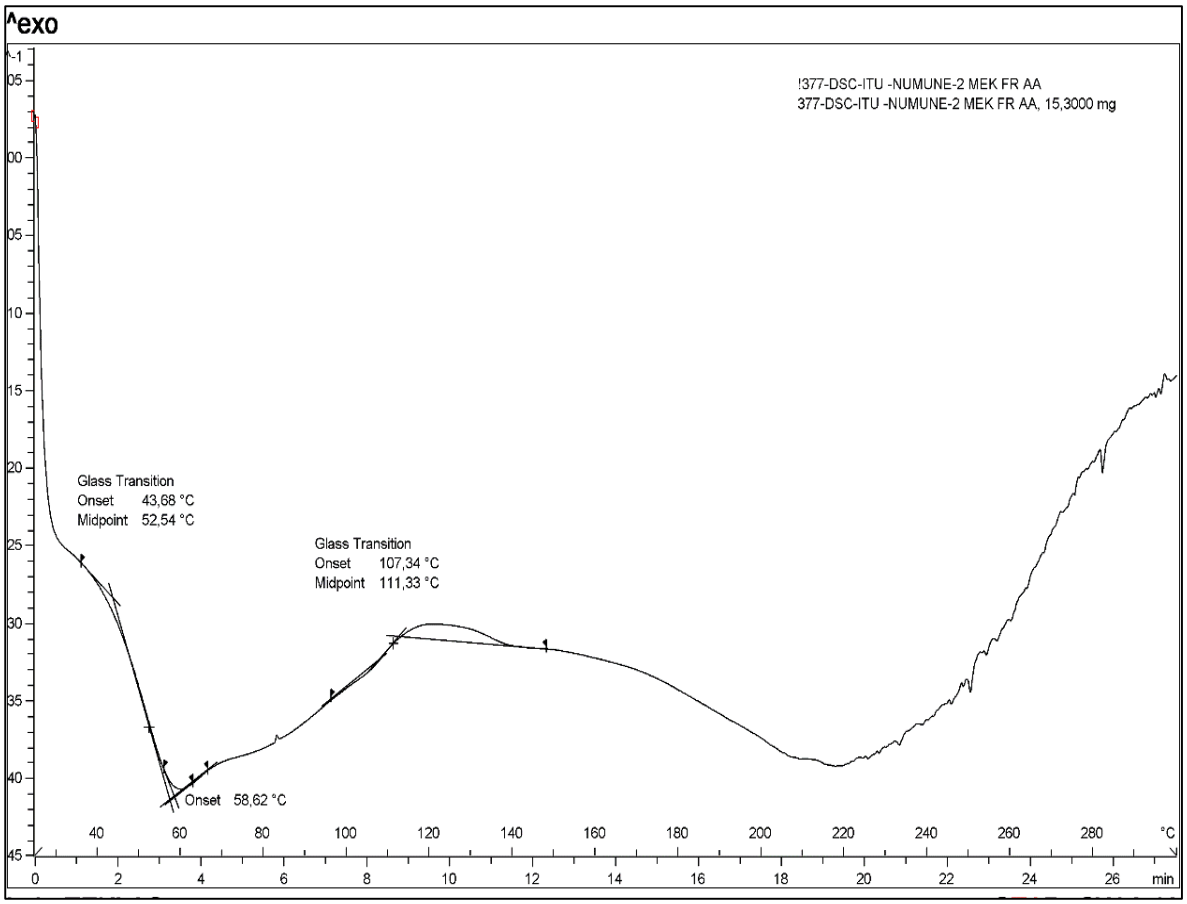

Figure 3.10: DSC curve of MEKFR-AA.

3.3 Methyl Ethyl Ketone Resin Modified with Cyclic Urea Synthesized From Alendronic Acid (MEKFR-CUAA)

A cyclic urea is synthesized from alendronic acid in order to get an organophosphorus compound with amide group, as seen in Figure 3.11. FTIR and NMR spectrum of cyclic urea can be seen in Figure 3.12 and Figure 3.13, respectively.

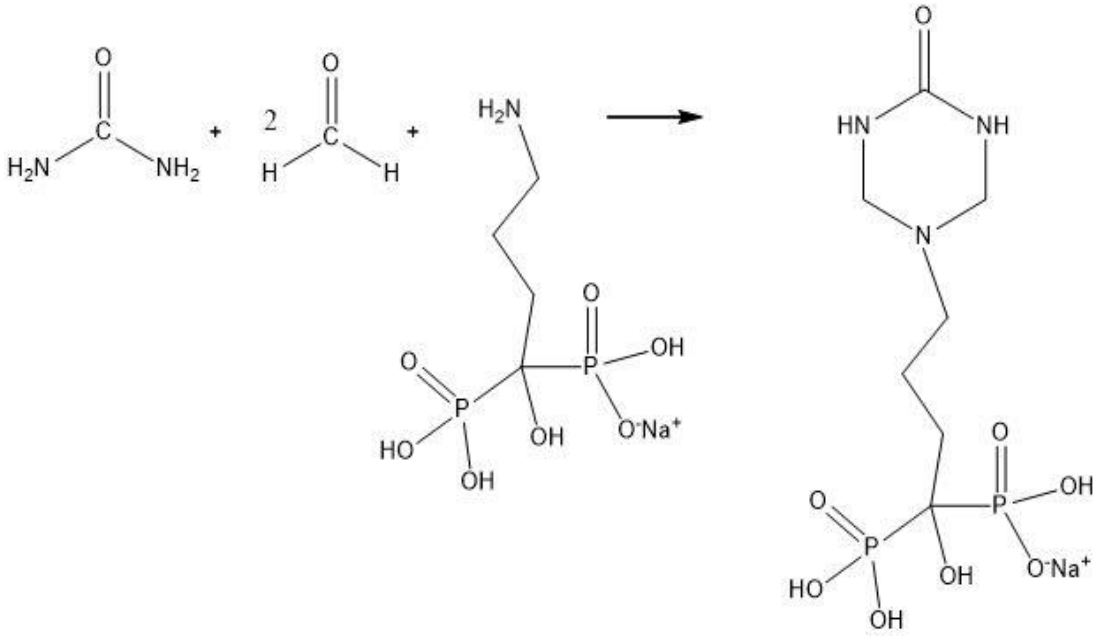

Figure 3.11: Formation of cyclic urea from alendronic acid.

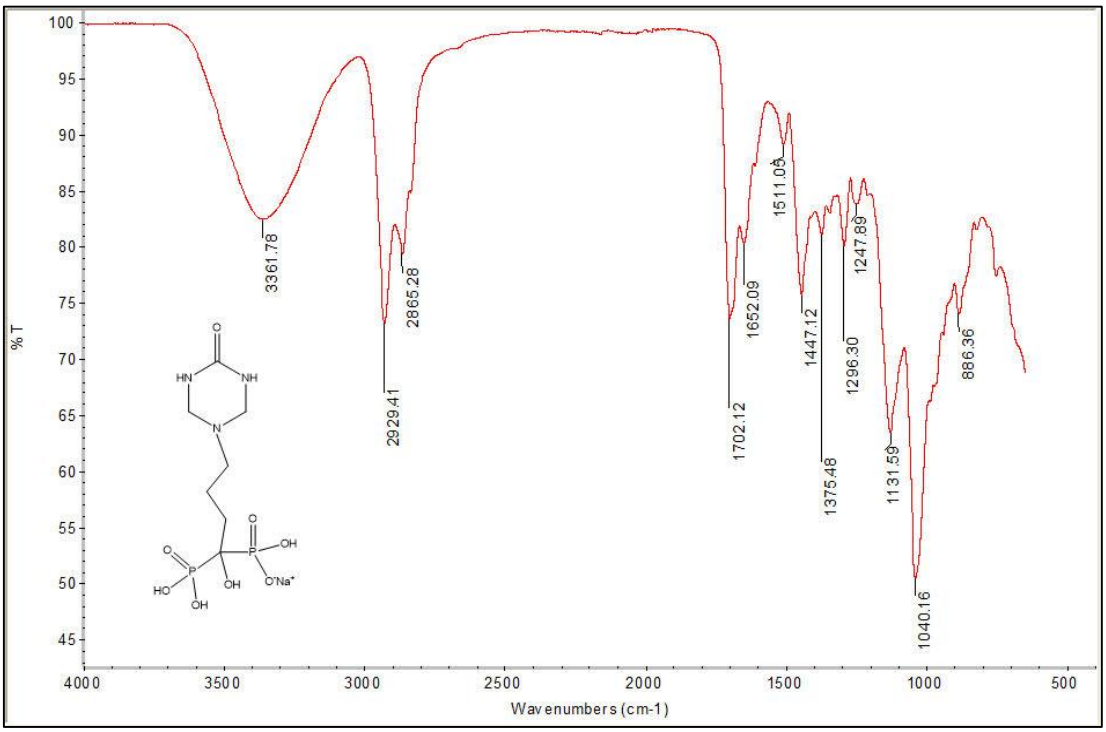

Figure 3.12: FTIR spectrum of cyclic urea synthesized from alendronic acid.

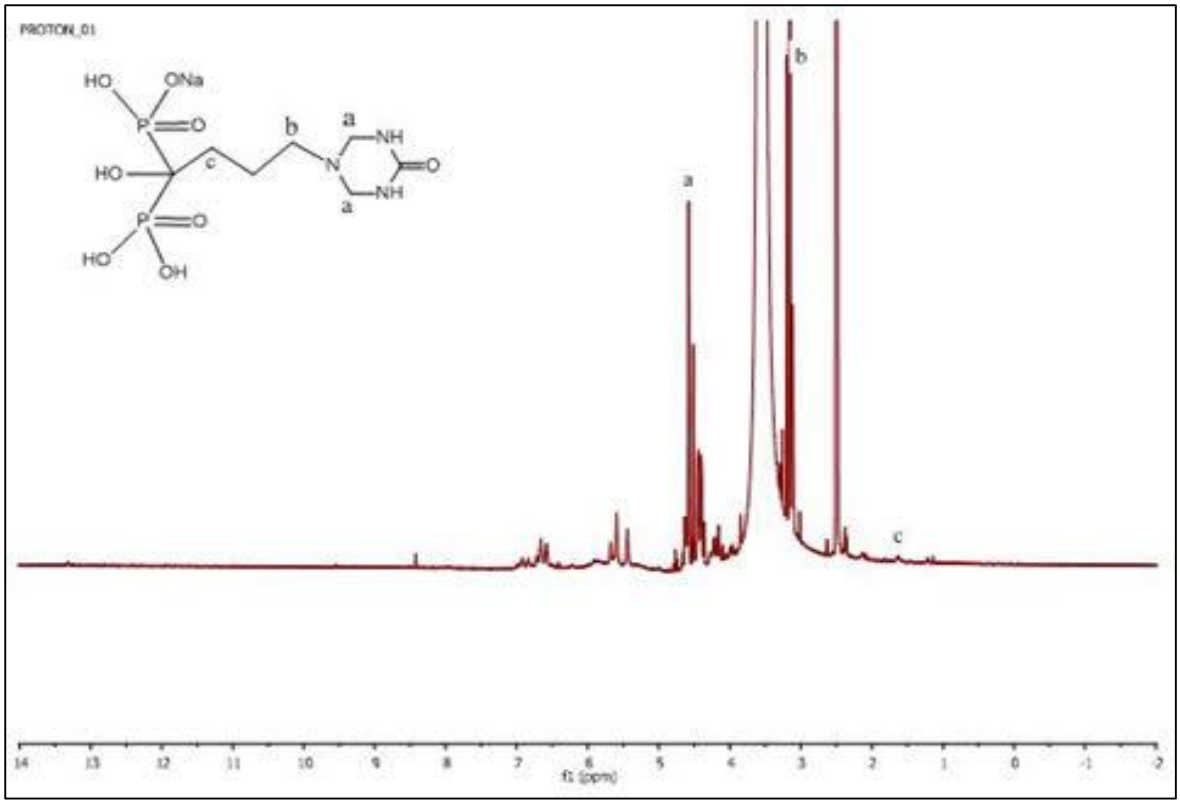

Figure 3.13: NMR spectrum of cyclic urea synthesized from alendronic acid.

After the polymerization reaction of methyl ethyl ketone and formaldehyde with cyclic urea in Figure 3.11, a product seen in Figure 3.14 is synthesized.

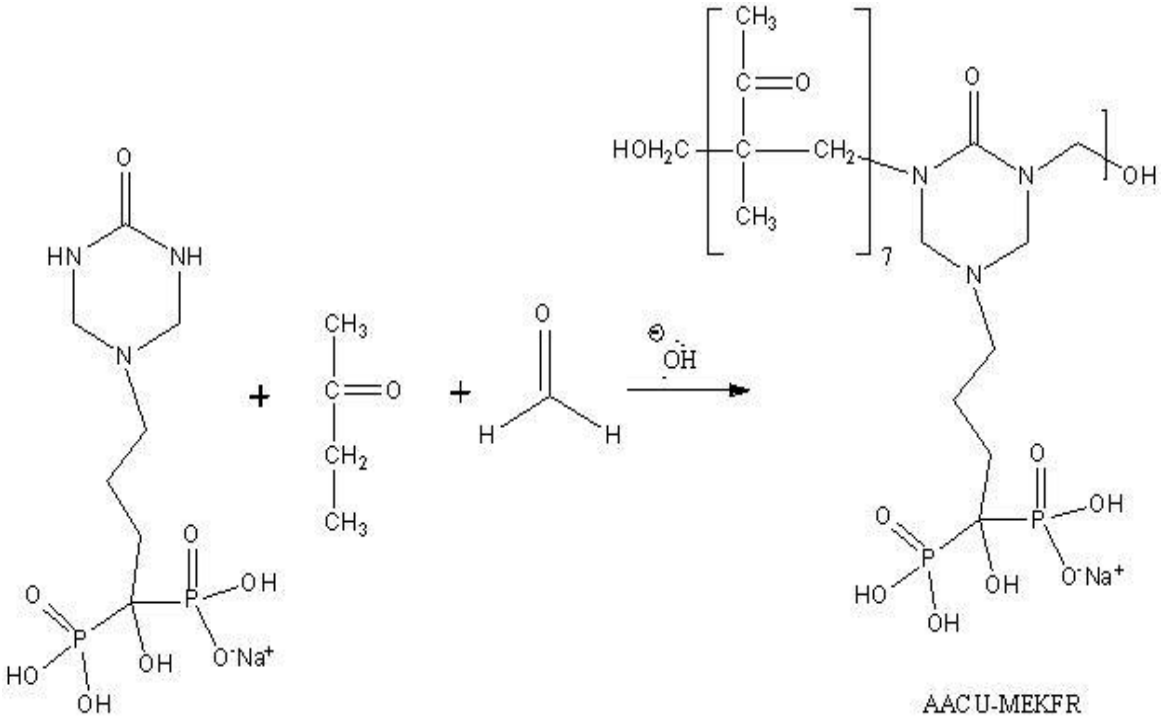

Figure 3.14: Formation of MEKFR-CUAA.

In Figure 3.15, FTIR spectrum of MEKFR-CU can be seen. Altough much difference from MEKFR spectrum can not be observed, the case is not same for the NMR spectrum in Figure 3.16, where we can see the amine peaks of the cyclic structure easily in the region of 4,5-5 ppm.

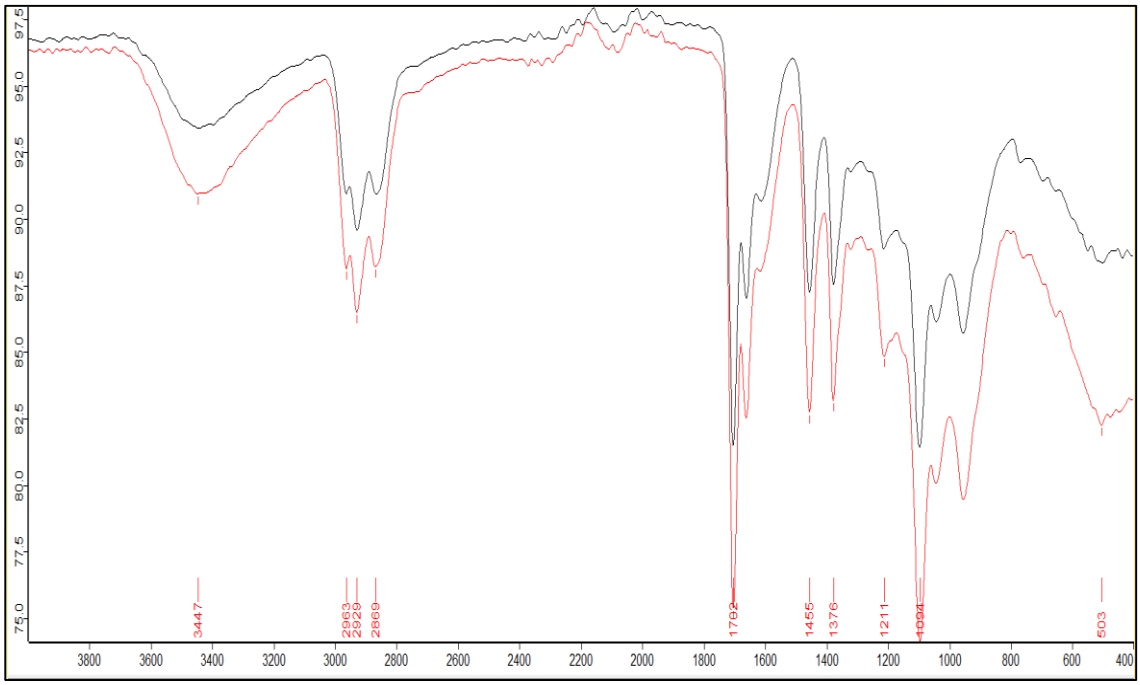

Figure 3.15: FTIR spectra of MEKFR-CUAA and MEKFR.

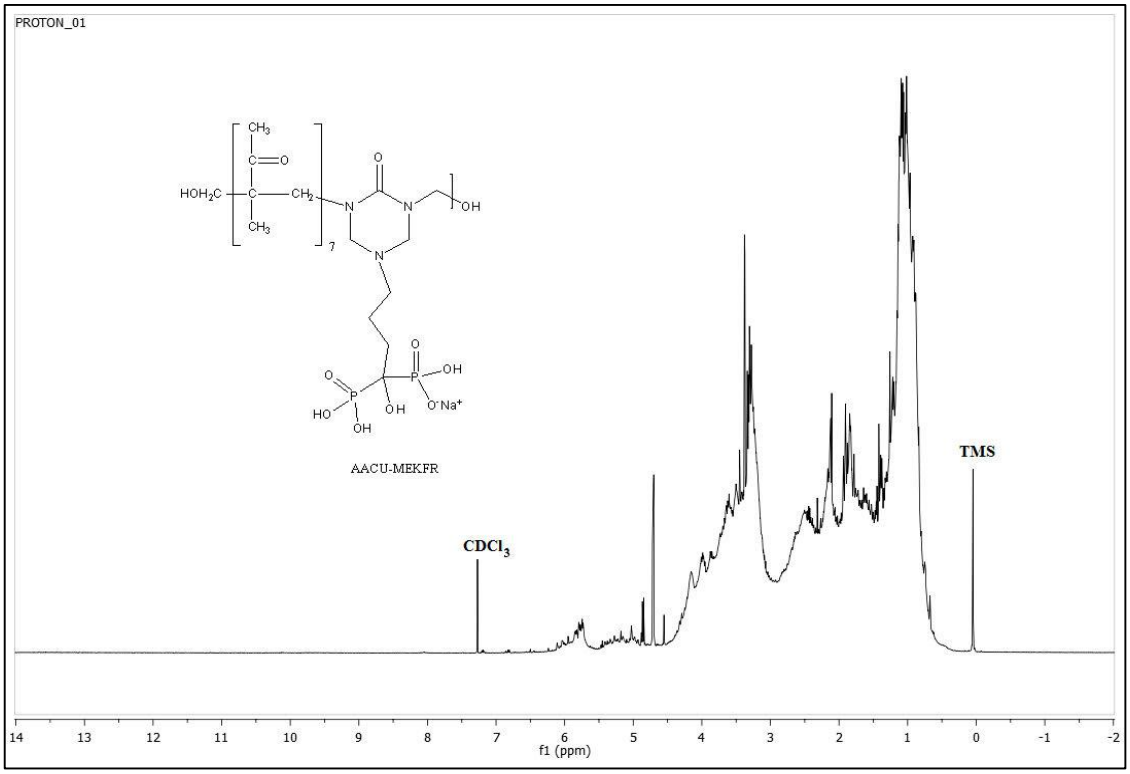

Figure 3.16: NMR spectrum of MEKFR-CUAA.

As seen in Table 3.3, there is not much difference between the solubilities of MEKFR and MEKFR-CU resins.

TGA and DSC curves of MEKFR-CUAA can be seen in Figure 3.17 and Figure 3.18, respectively. The onset of degradation is measured as 149^{o}C and glass transtion temperature as 52^{o}C. In addition, the ash amount is determined as 0,54%.

Table 3.3: Solubility of MEKFR-CUAA in diffrerent solvents.

	THF	**DCM**	**DMS**	**Ethanol**	**Acetone**
MEKFR	**s**	**s**	**sl**	**s**	**s**
MEKFR-CU	**s**	**s**	**s**	**sl**	**s**

"s" means soluble, **"sl"** means slightly soluble.

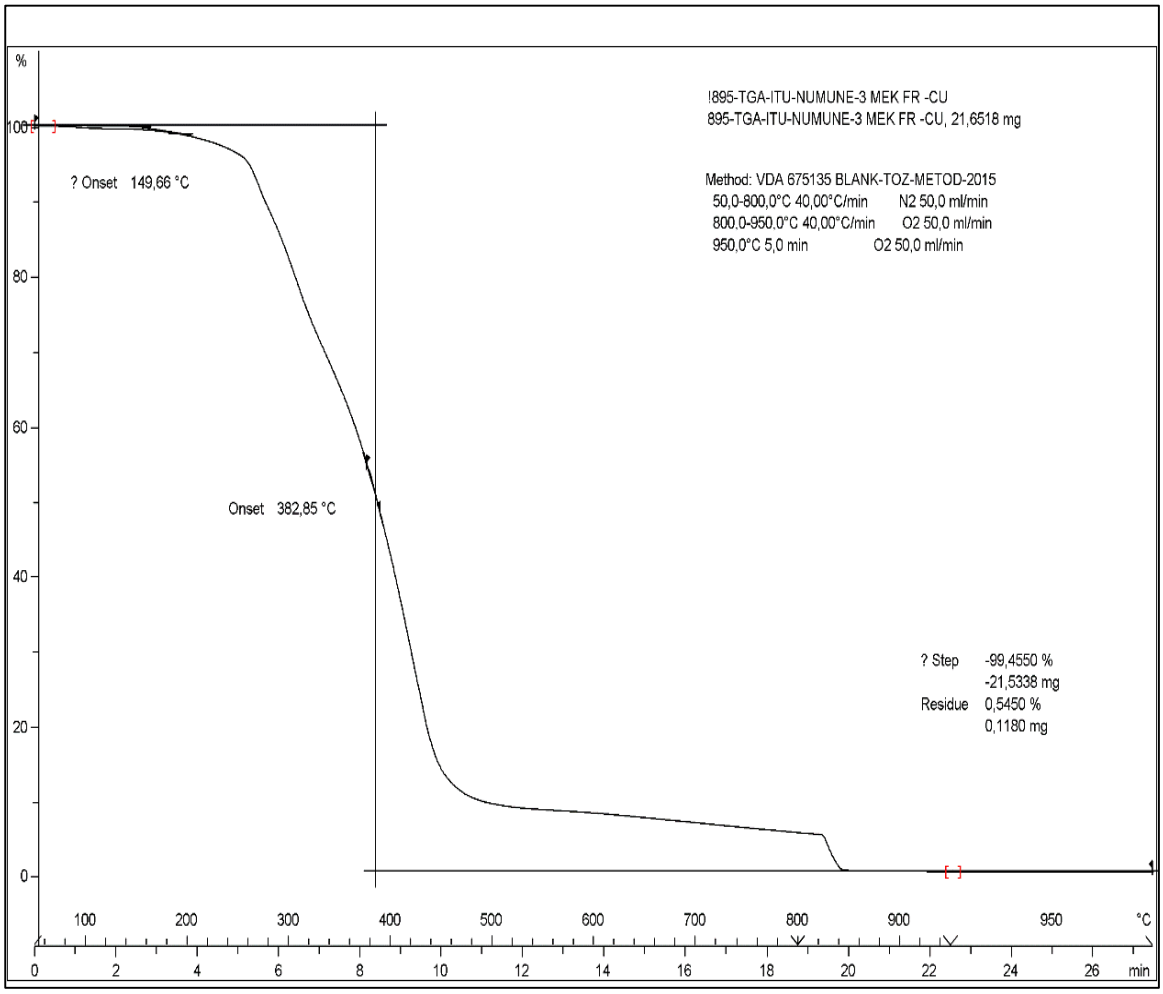

Figure 3.17: TGA curve of MEKFR-CUAA.

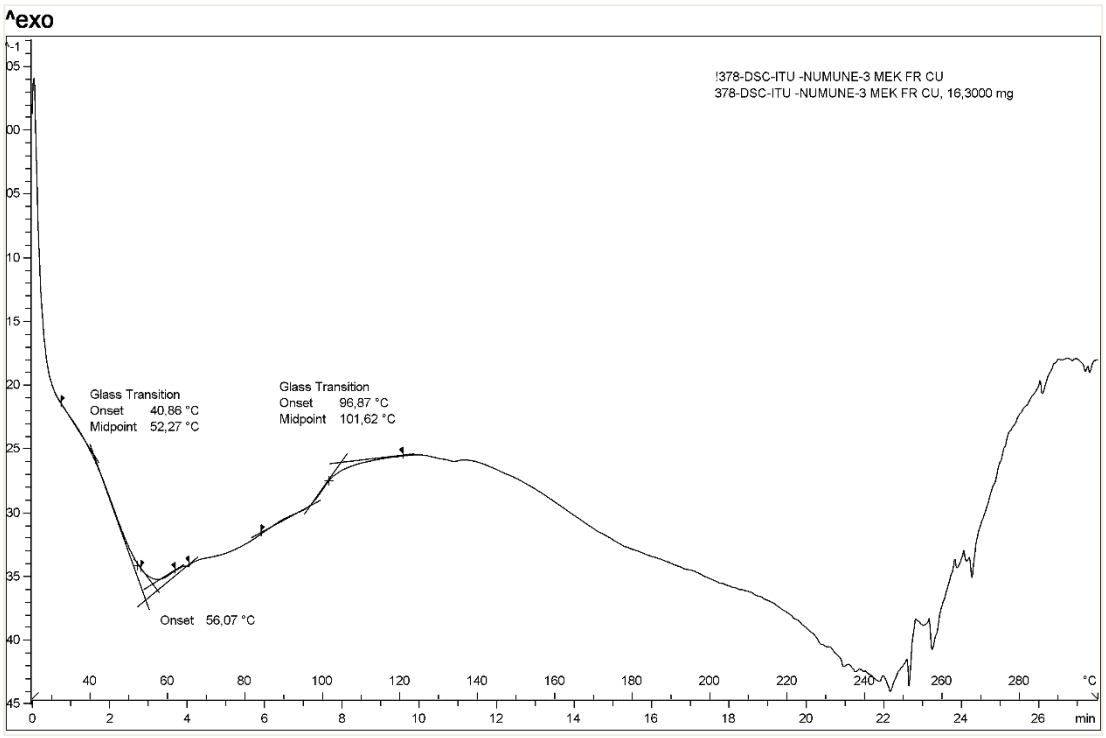

Figure 3.18: DSC curve of MEKFR-CUAA.

3.4 Methyl Ethyl Ketone Formaldehyde Resins Modified with Diethanolamine (MEKFR-DEA)

Methyl ethyl ketone formaldehyde resin modified with diethanolamine is obtained according to the reaction in Figure 3.19.

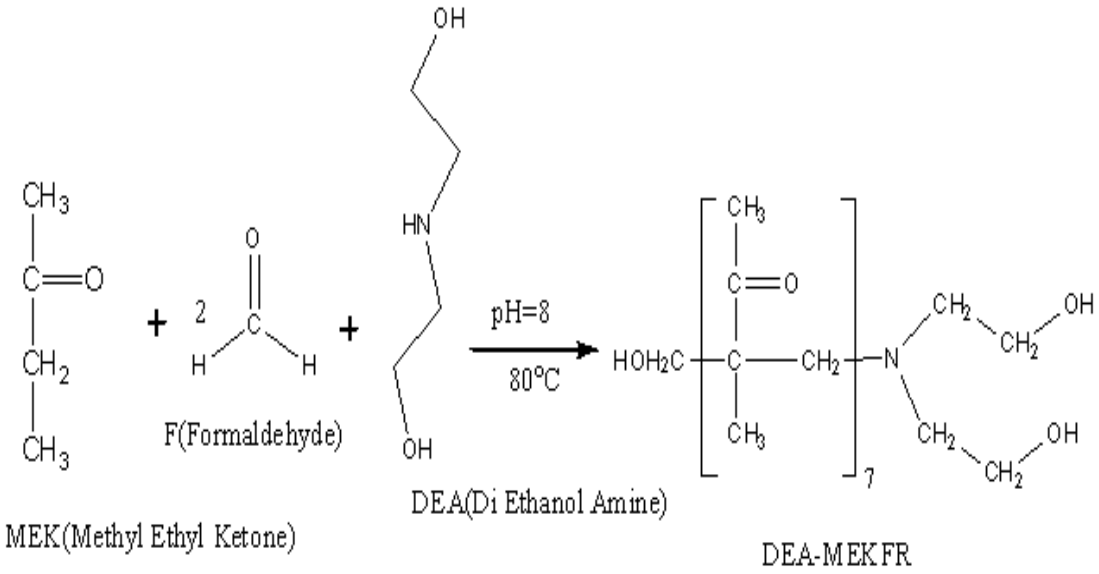

Figure 3.19: Formation of MEKFR-DEA.

If FTIR spectra of MEKFR-DEAs in Figure 3.20 are analyzed (blue: 5wt%, red: 10wt%, green: 20wt%), it is observed that all of them have similar chemical structures which shows the reaction is independent of modifier ratio. It is also noticed that as the modifier ratio increases, the intensity of peaks also increases.

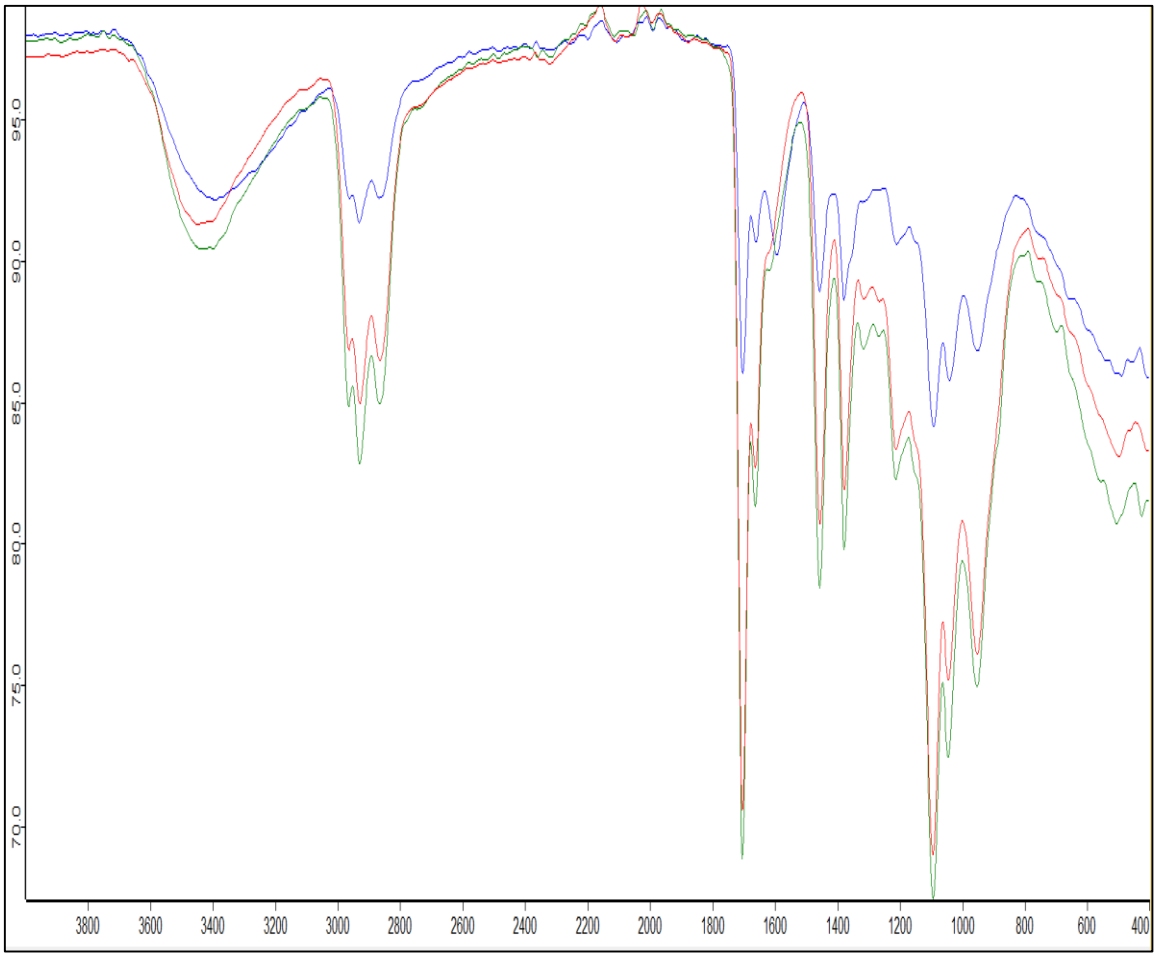

Figure 3.20: FTIR spectra of MEKFR-DEA.

When we compare the FTIR spectrum of MEKFR-DEA5 with MEKFR's (see Figure 3.21), we can not see any significant change because of the fact there is only one difference in functional groups which is the exchange of –C-O- bond with –C-N- and unfortunately these functional groups give peaks in similar regions. The most apparent change is increase in the intensity of –O-H peak since 2 moles of alcohol group form in MEKFR-DEA instead of 1 mole in the MEKFR.

This change is also observed in NMR spectrum in Figure 3.22, in which it is realized that the peak between 4.5 and 5 ppm respresenting the hydroxyl hydrogen coming from diethanolamine increases.

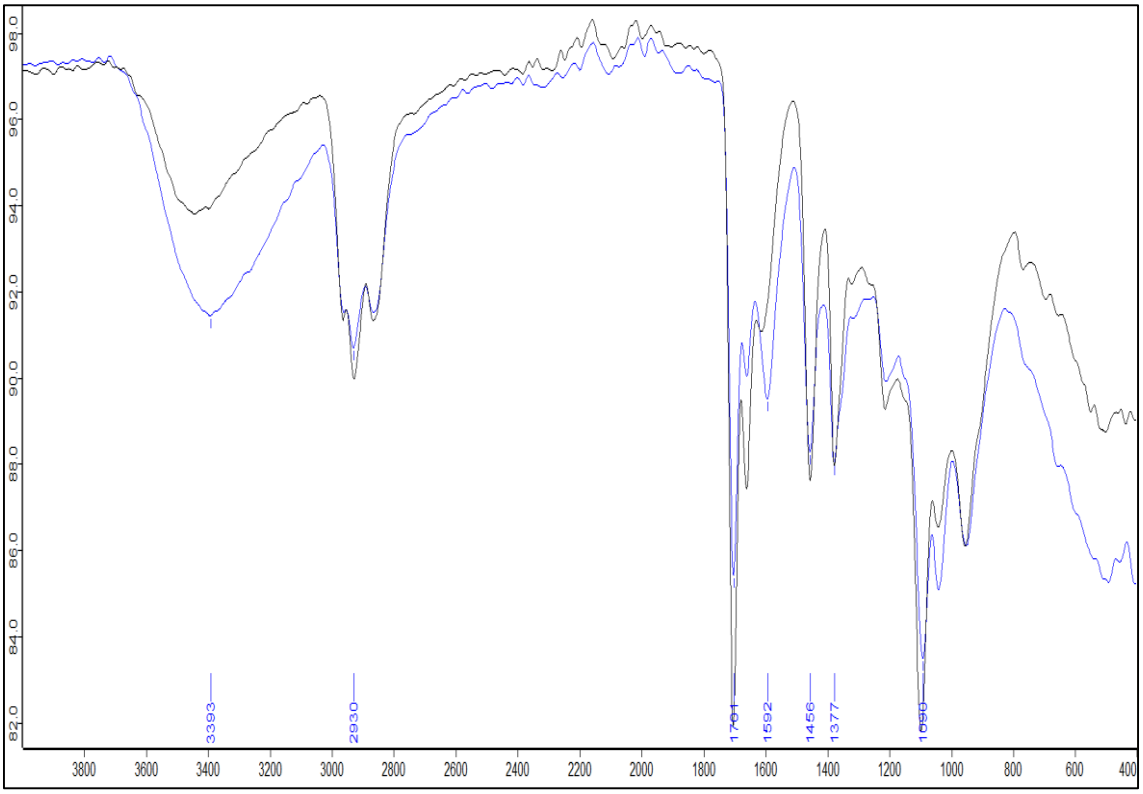

Figure 3.21: FTIR specta of MEKFR-DEA5 and MEKFR.

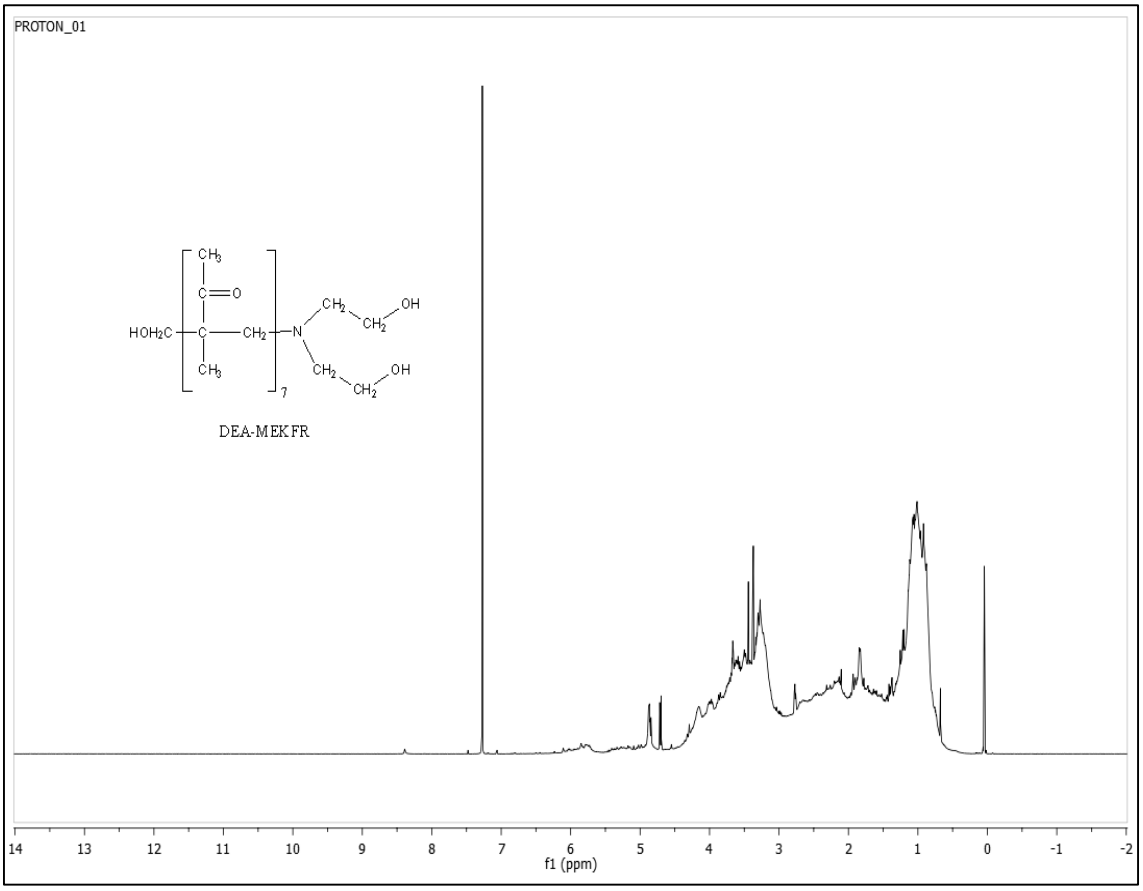

Figure 3.22: NMR specta of MEKFR-DEA5.

The cases are same for the MEKFR-DEA10 and MEKFR-DEA20 whose spectra are seen in figures 3.23, 3.24, 3.25 and 3.26. While there is not much change in FTIR spectra, hydroxyl hydrogen peaks coming from diethanolamine are observed in NMR spectra with increasing intensity as a results of increasing modifier ratio.

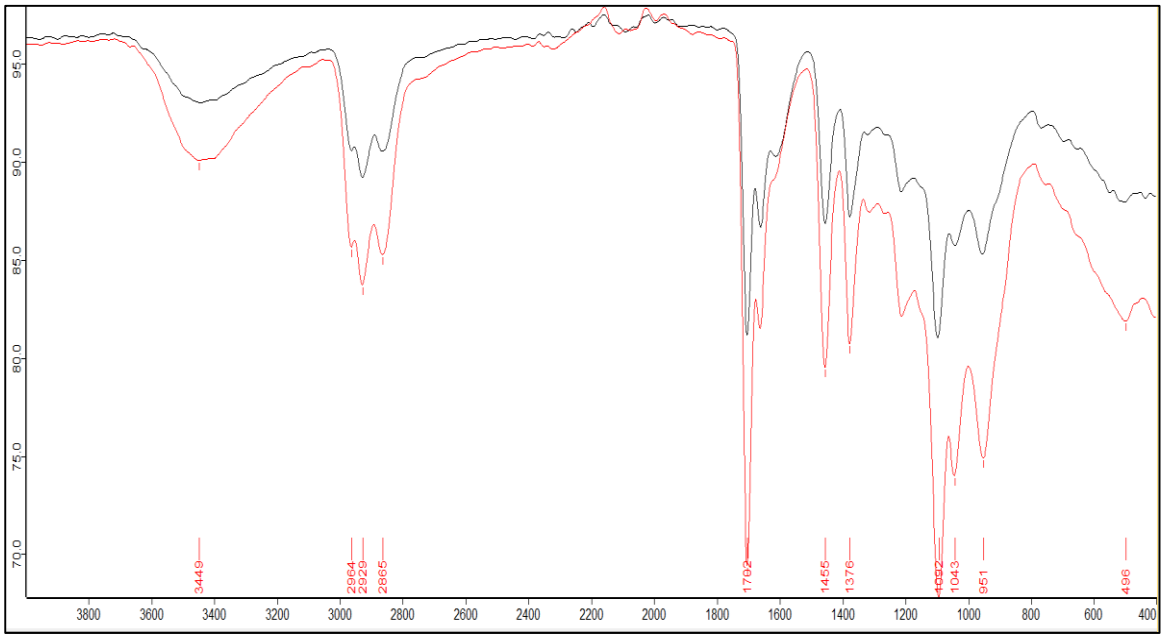

Figure 3.23: FTIR spectra of MEKFR-DEA10 and MEKFR.

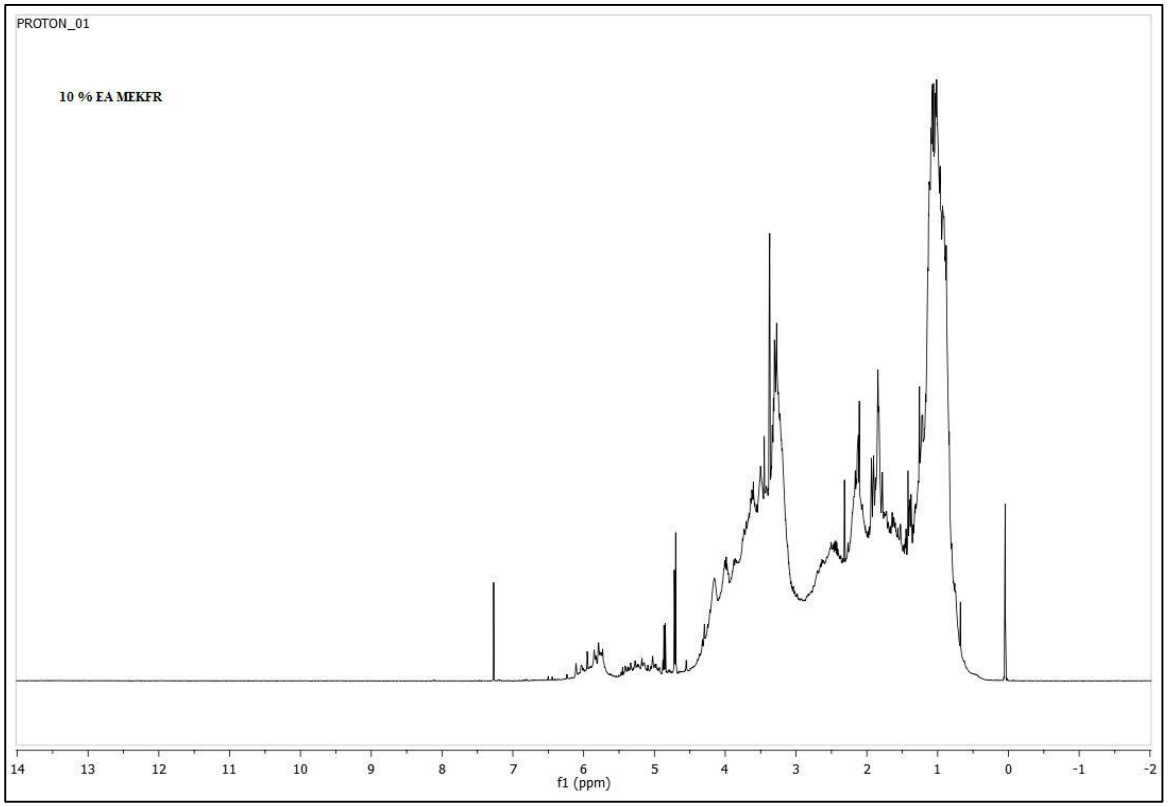

Figure 3.24: NMR spectrum of MEKFR-DEA10.

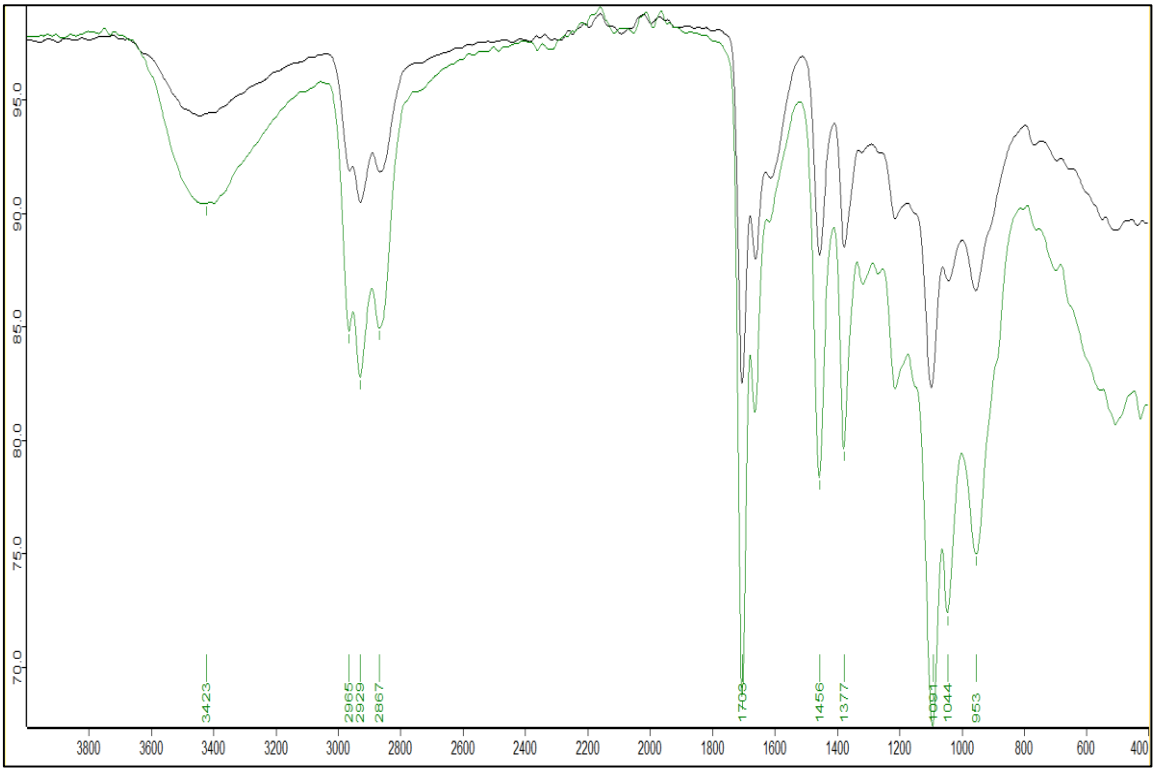

Figure 3.25: FTIR spectra of MEKFR-DEA20 and MEKFR.

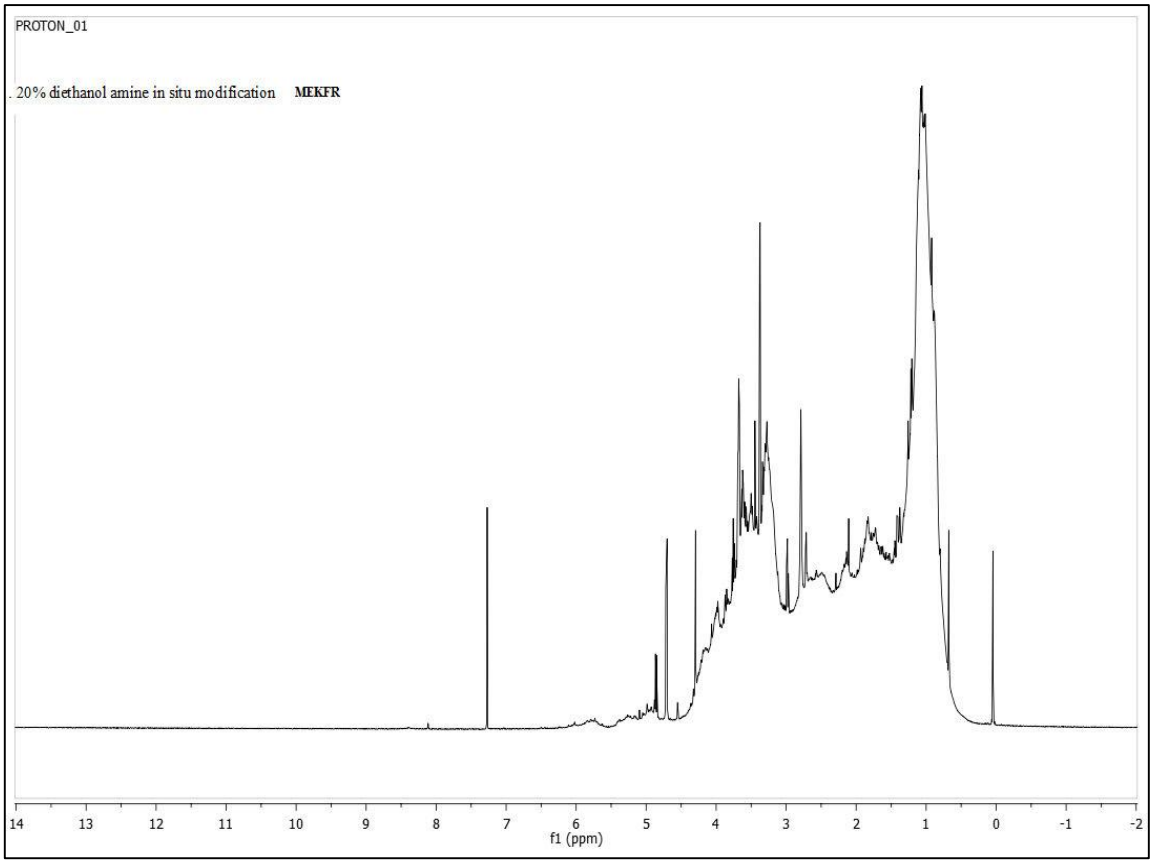

Figure 3.26: NMR spectrum of MEKFR-DEA20.

The solubility of MEKFR-DEA resin in different solvents can be seen in Table 3.4. If the results are compared, it can be realized that the solubilities of MEKFR-DEA decreases in solvents as amine ratio increases. This situation can be explained with the formation of network structure between hydrogen bonds.

TGA and DSC curves of MEKFR-DEA5 can be seen in Figure 3.27 and Figure 3.28, respectively. The onset of degradation is measured as 49^{o}C and glass transtion temperature as 62^{o}C. In addition, the ash amount is determined as 0,56%.

Table 3.4: Solubility of MEKFR-DEA in diffrerent solvents.

	THF	**DCM**	**DMS**	**Ethanol**	**Acetone**
MEKFR	**s**	**s**	**sl**	**s**	**s**
MEKFR-DEA5	**s**	**s**	**s**	**sl**	**s**
MEKFR-DEA10	**s**	**s**	**s**	**sl**	**s**
MEKFR-DEA20	**sl**	**sl**	**i**	**i**	**sl**

"s" means soluble, **"sl"** means slightly soluble.

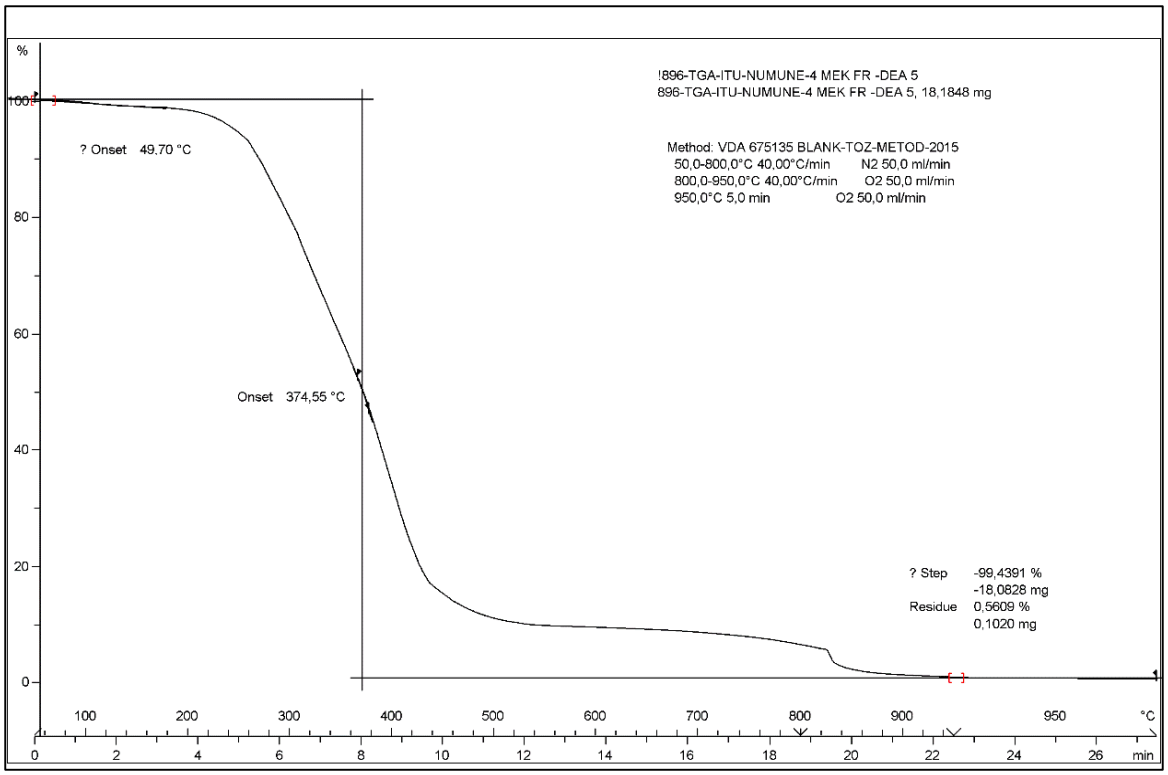

Figure 3.27: TGA curve of MEKFR-DEA5.

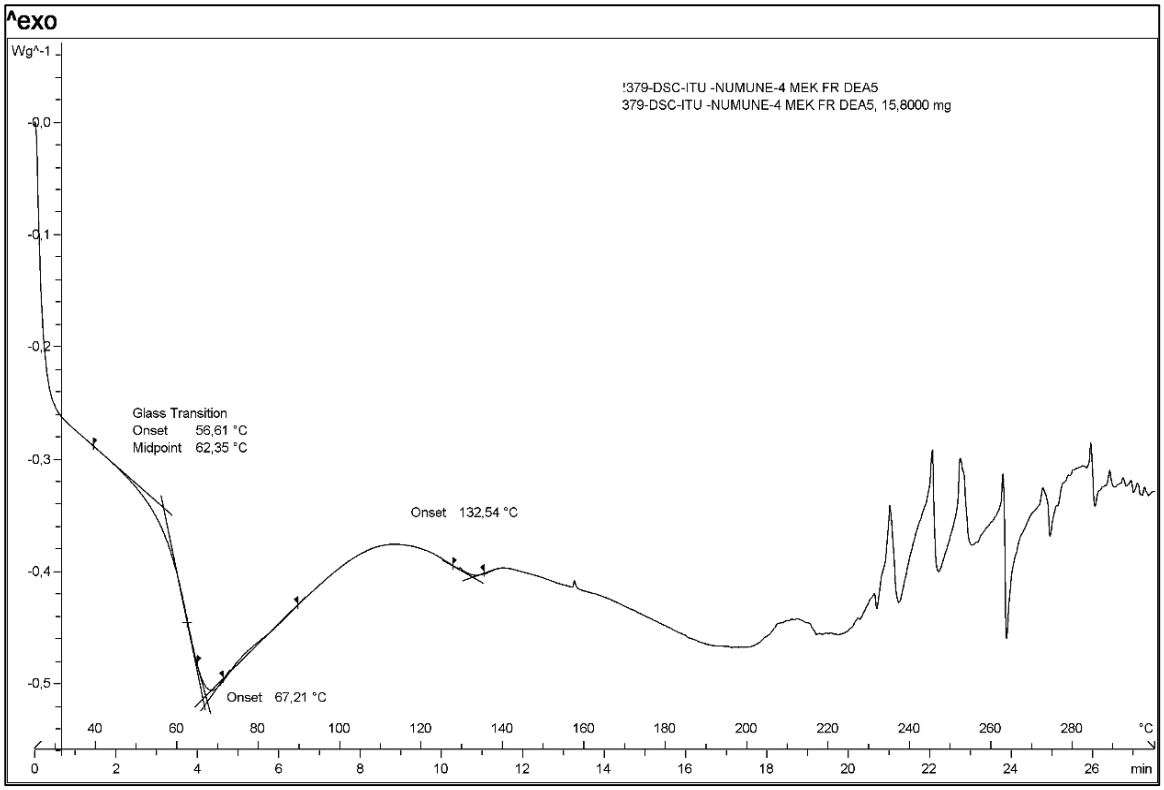

Figure 3.28: DSC curve of MEKFR-DEA5.

TGA and DSC curves of MEKFR-DEA10 can be seen in figures 3.29 and 3.30, respectively. The onset of degradation is measured as 48^{o}C and glass transtion temperature as 54^{o}C.

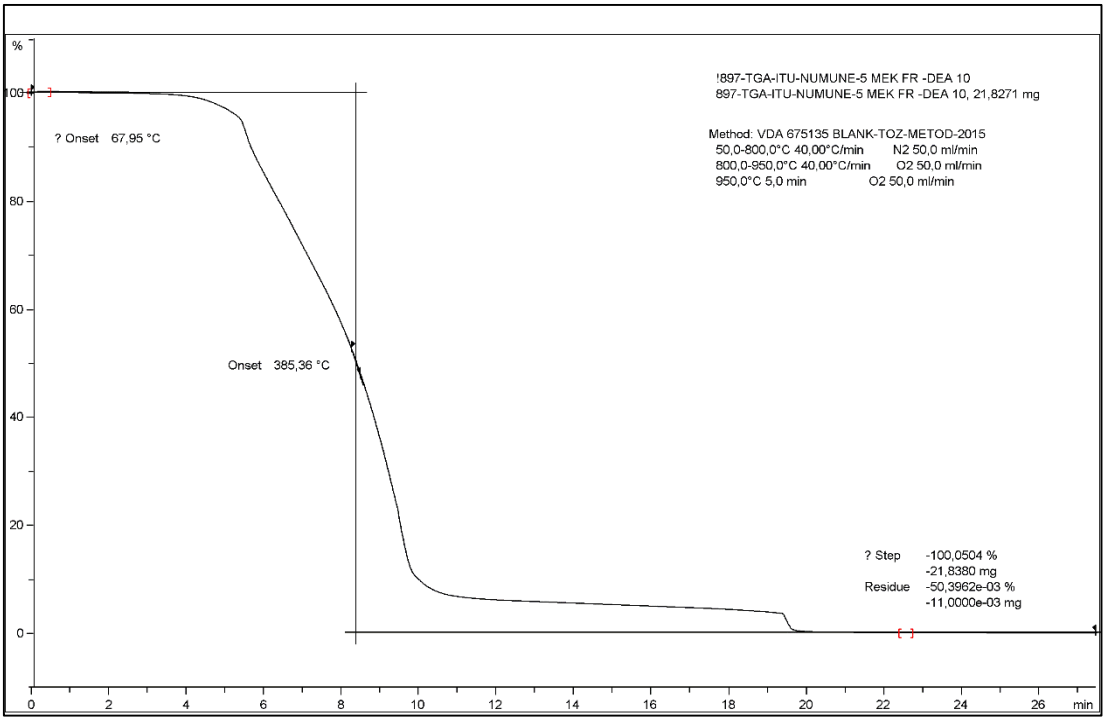

Figure 3.29: TGA curve of MEKFR-DEA10.

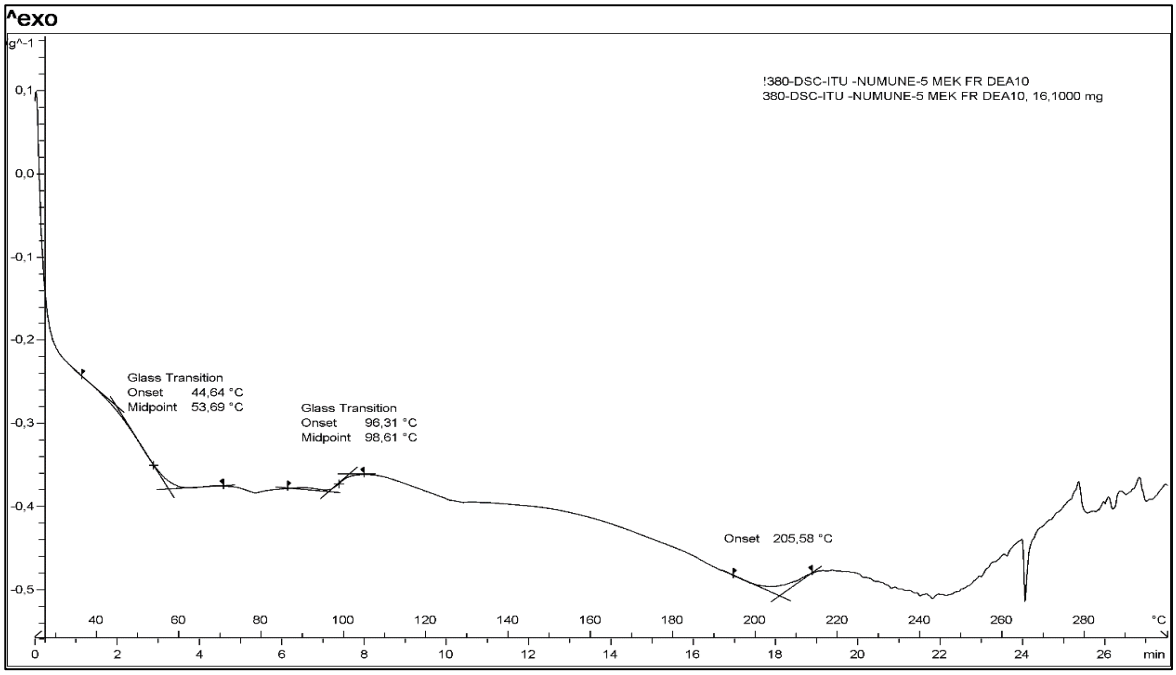

Figure 3.30: DSC curve of MEKFR-DEA10.

3.5 Boric Acid Modification

After the synthesis of MEKFR, its boric acid modifications is carried out through the reactions in Figure 3.31.

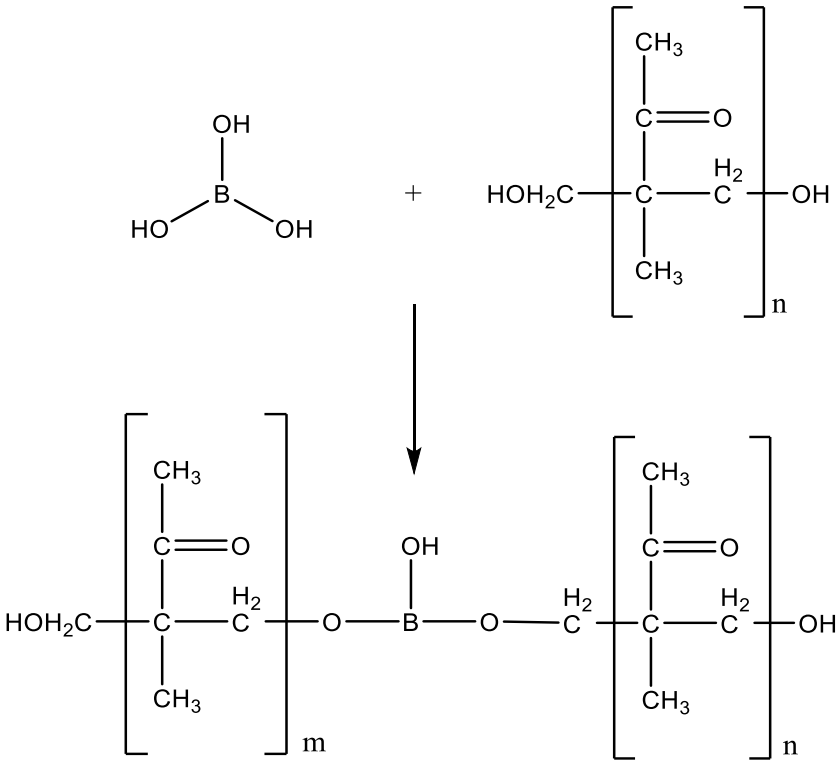

Figure 3.31: Boric acid modification of MEKFR

When the FTIR spectrum of boric acid modified resin is analyzed (see Figure 3.32), formation of new peaks in the region of 600-800cm^{-1}, which are the sign of -O-B-O- bonds, and decrease in the intensity of –O-H- peak, which is at 3000-3500cm^{-1} are observed, and these changes prove us the modification of resins with boric acid.

NMR spectrum complies with FTIR spectrum since it is observed that the peaks of hydroxyl groups coming from diethanolamine, which are in between 5-5,5 ppm, disappears (see Figure 3.33).

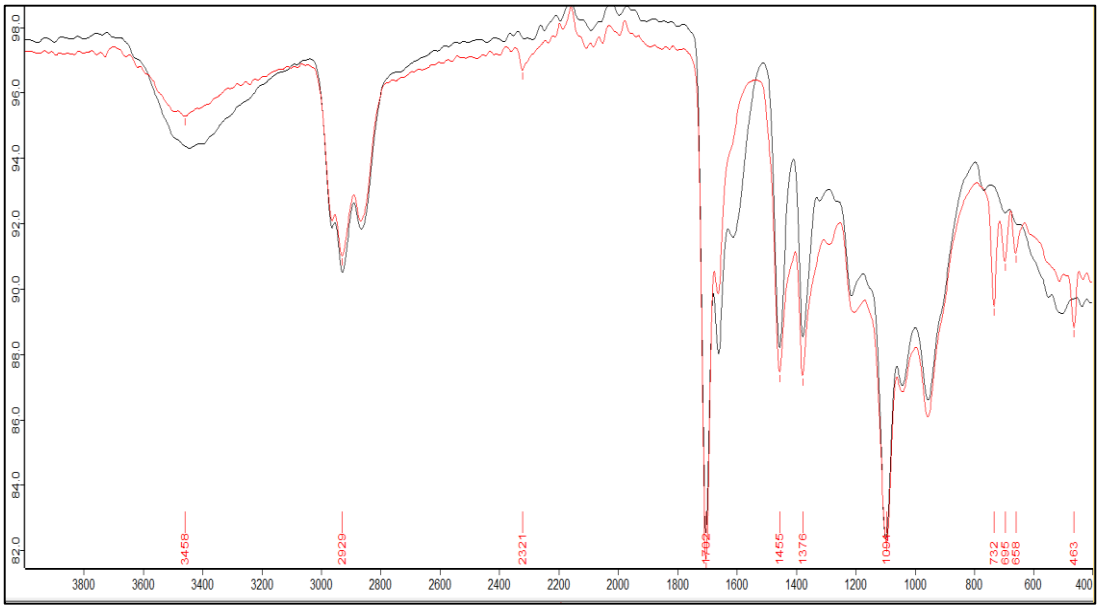

Figure 3.32: FTIR spectra of MEKFR-BA and MEKFR.

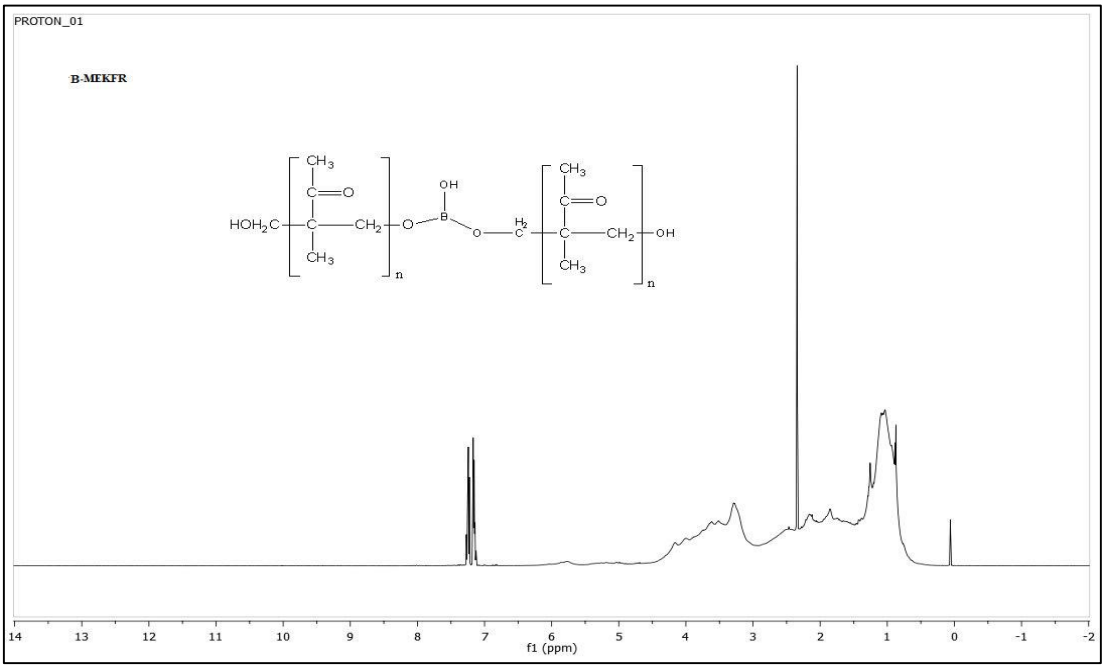

Figure 3.33: NMR spectrum of MEKFR-BA.

TGA curve of MEKFR-BA can be seen in Figure 3.34. The onset of degradation is measured as 48ºC and the ash amount is determined as 0,65%. In Figure 3.35, it is seen that T_g of MEFFR-BA is measured as 69,3ºC in DSC analysis.

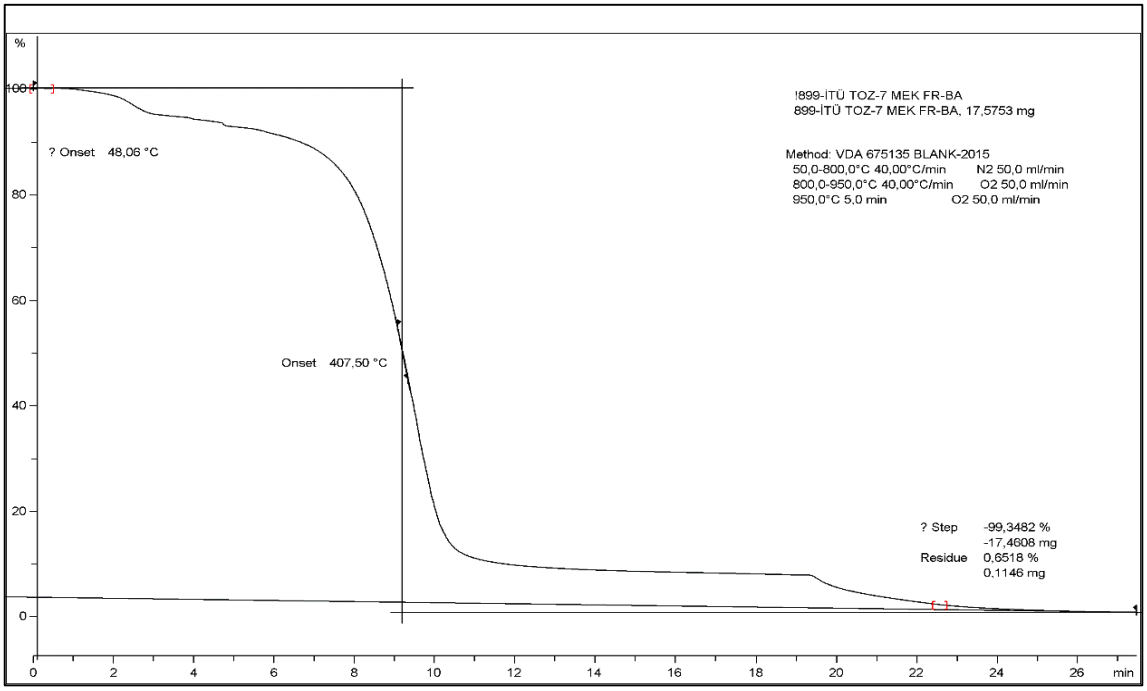

Figure 3.34: TGA curve of MEKFR-BA.

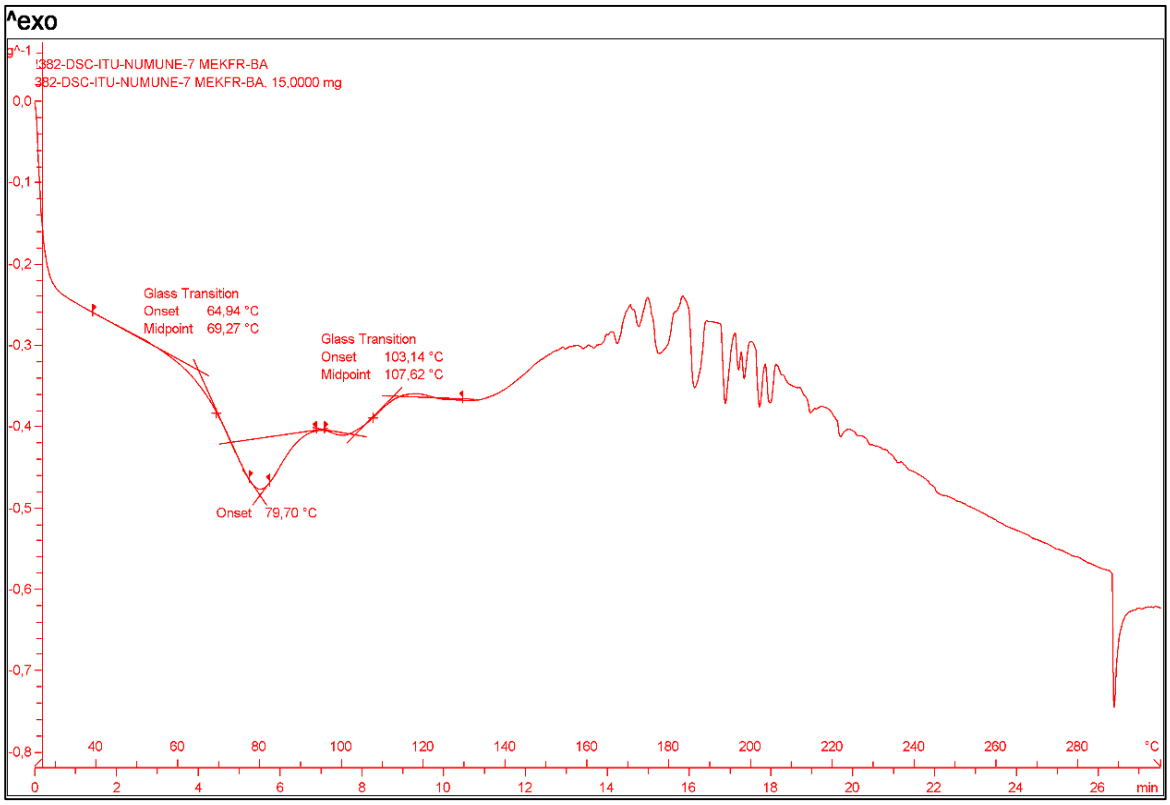

Figure 3.35: DSC curve of MEKFR-BA.

When we compare the TGA and DSC curves of boric acid modified MEKFR with the non-modifed one, the improvement in thermal resistance is seen apparently since the curves shift to the right (see figures 3.36 and 3.37).

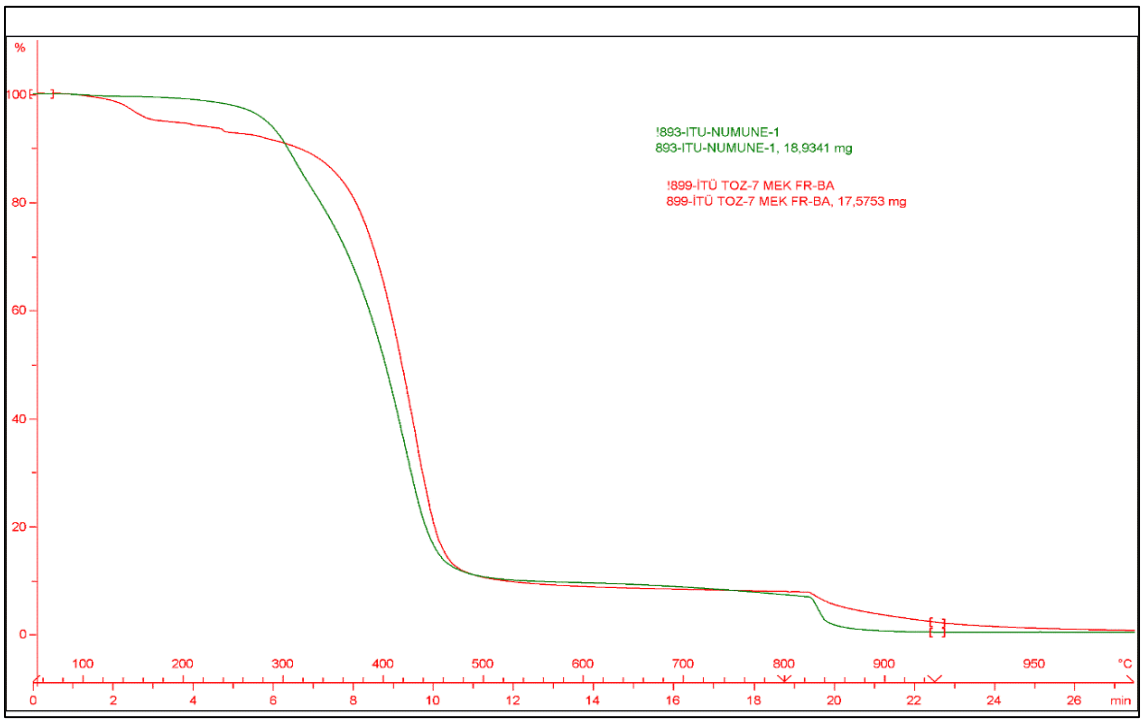

Figure 3.36: Compararison of TGA curves of MEKFR-BA and MEKFR.

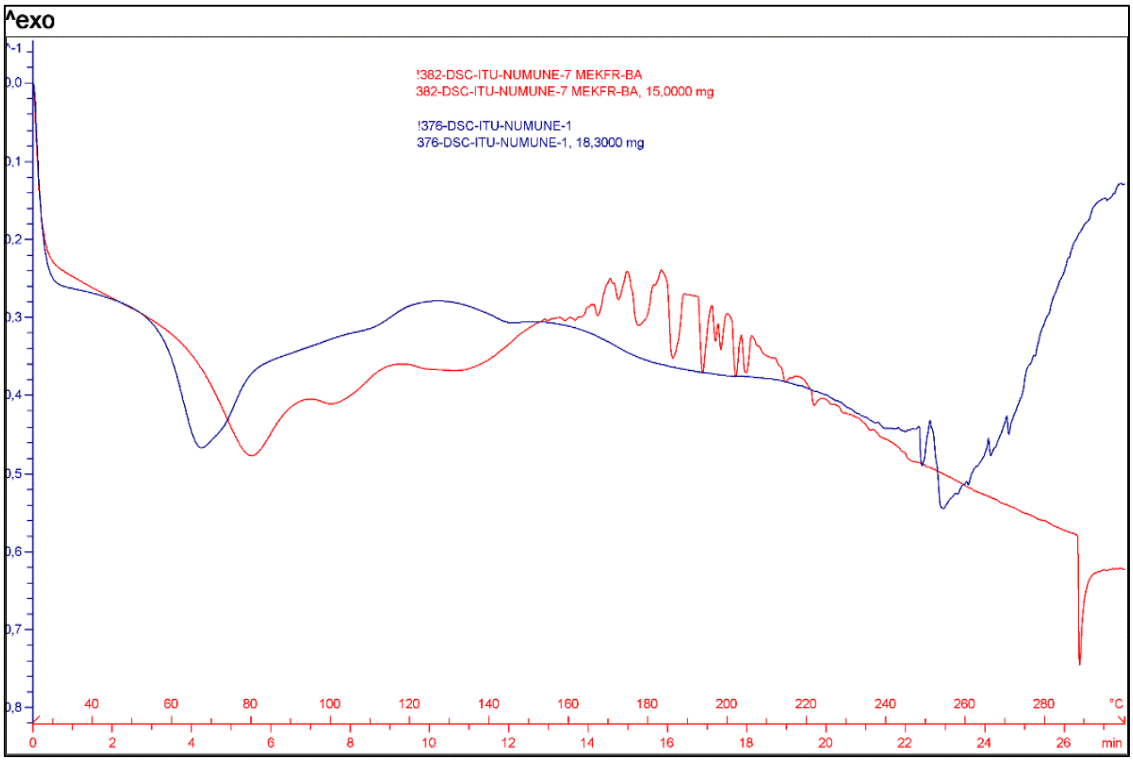

Figure 3.37: Compararison of DSC curves of MEKFR-BA and MEKFR.

MEKFR-DEAs are also modified boric acid and this modification reaction can be seen in Figure 3.38.

When we look at the FTIR spectra of MEKFR-DEA-BA in Figure 3.39 (blue: MEKFR-DEA5-BA, red: MEKFR-DEA10-BA, green: MEKFR-DEA20-BA), we notice similar -O-B-O- peaks with in MEKFR-BA case which are in between 600-800 cm^{-1} range.

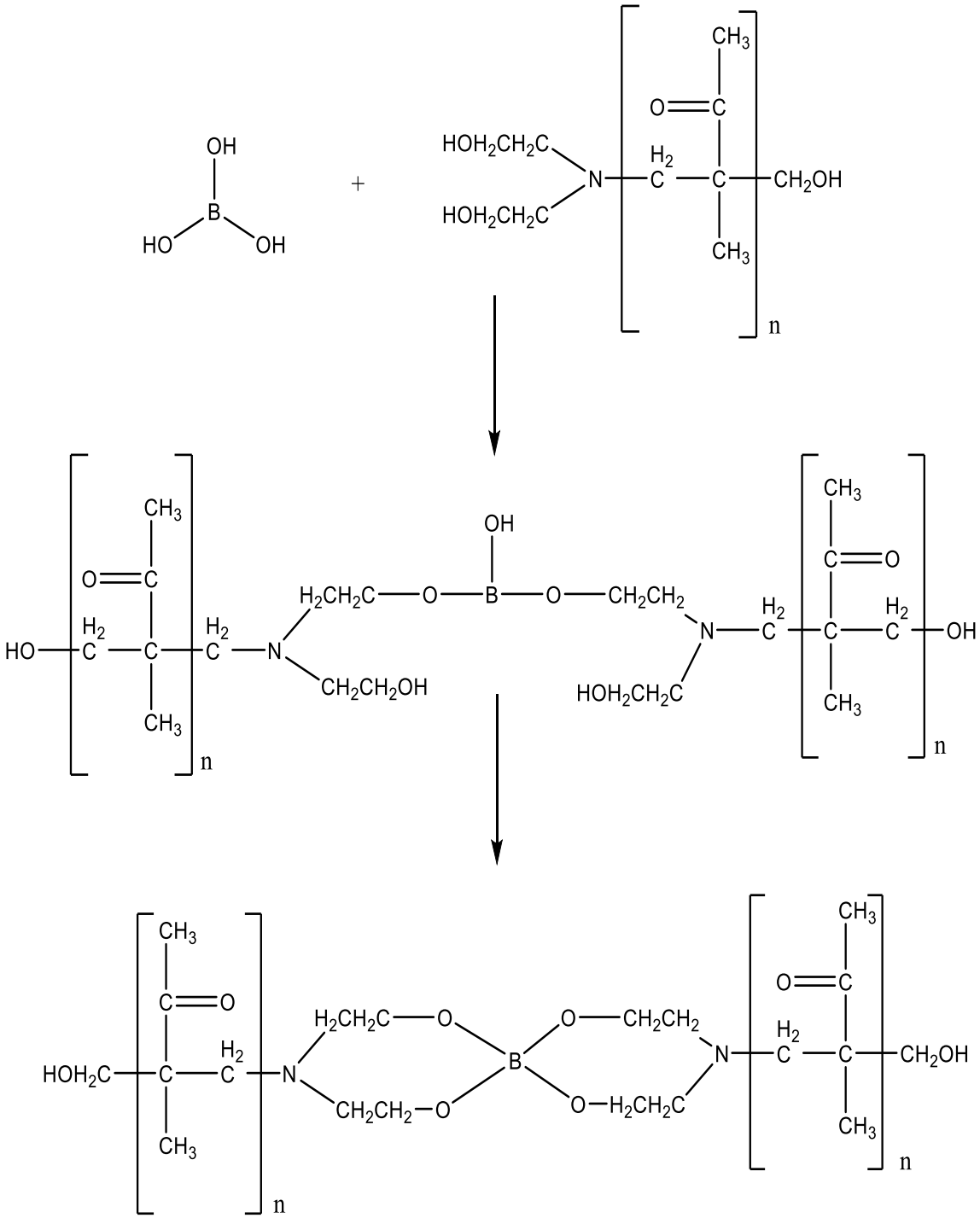

Figure 3.38: Boric acid modification reaction of MEKFR-DEA.

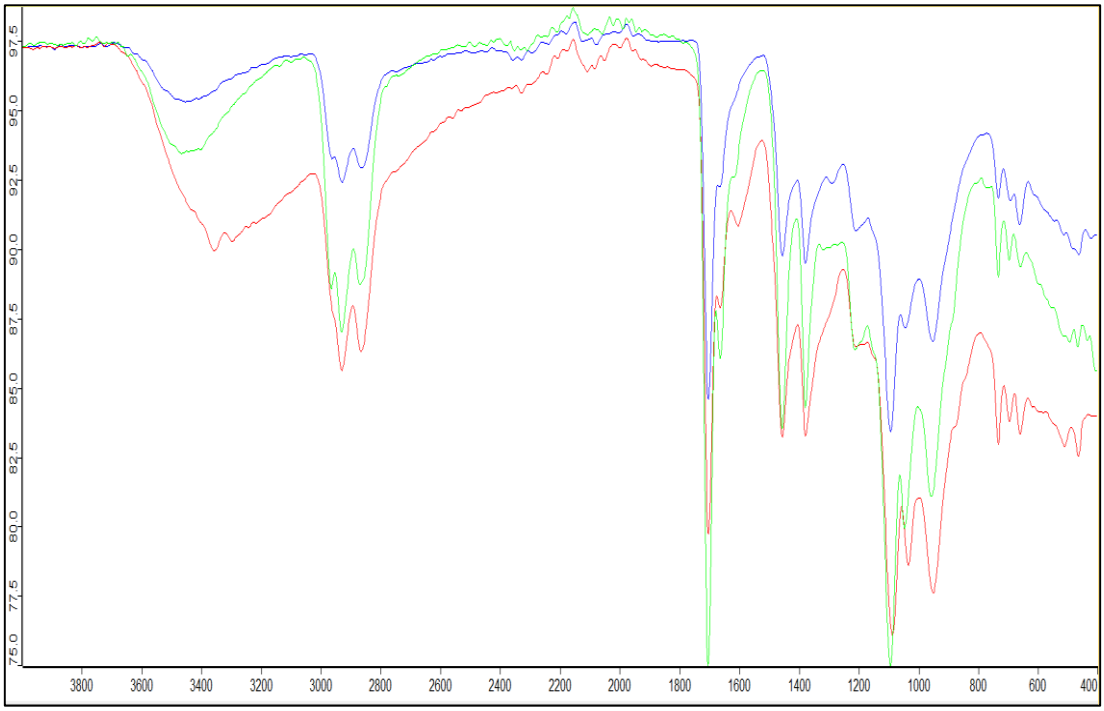

Figure 3.39: FTIR spectra of MEKFR-DEA-BA.

If we further analayze the FTIR spectra comperatively with MEKFR-DEAs, in additon of formation of -O-B-O- bonds, a drastic dercerase in –O-H bond also is realized in all of three cases (see figures 3.40 and 3.41).

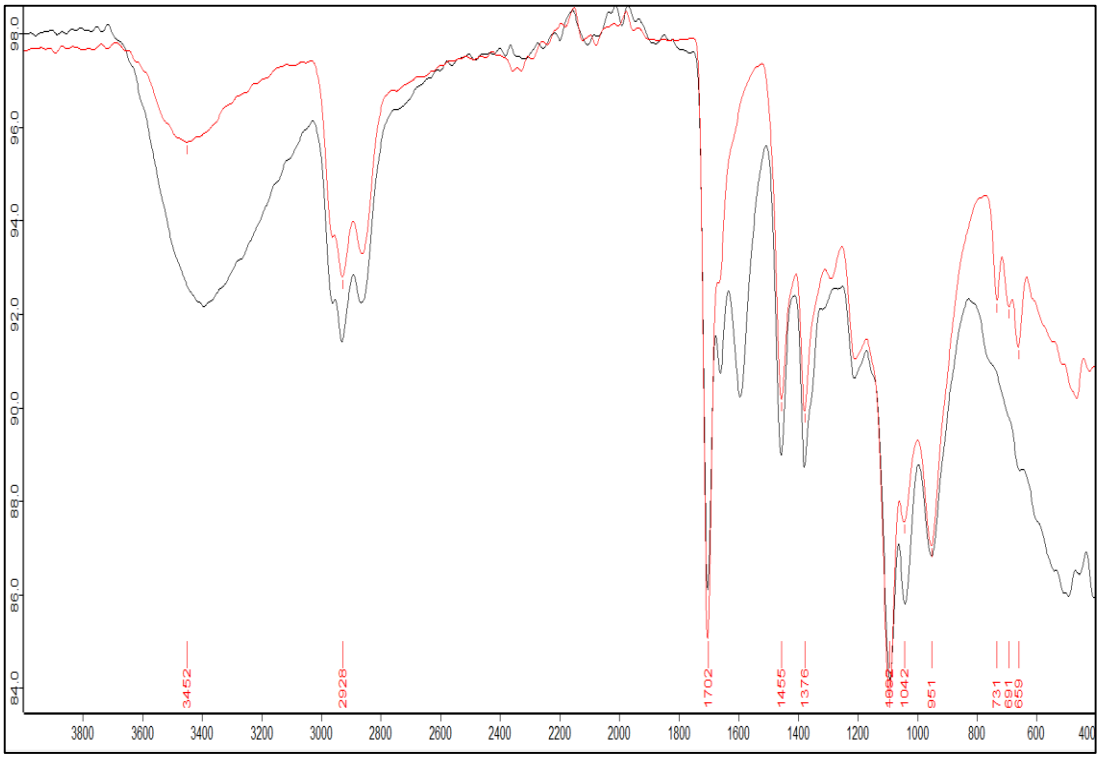

Figure 3.40: FTIR spectra of MEKFR-DEA5-BA and MEKFR-DEA5.

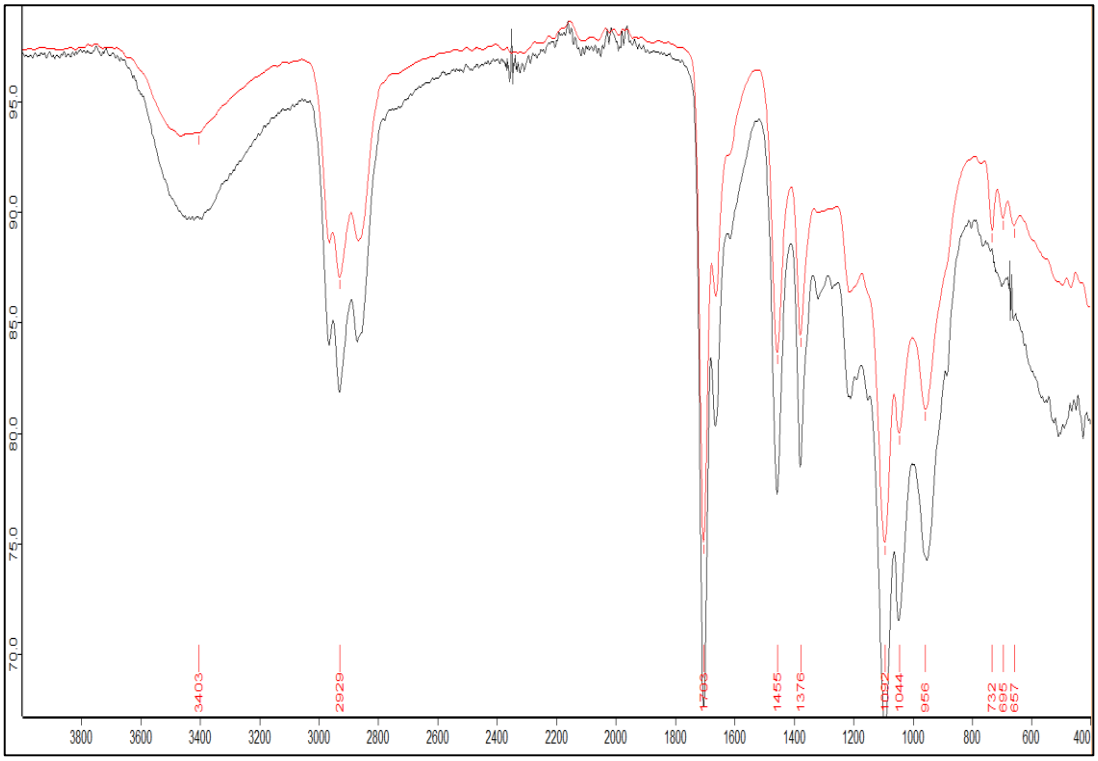

Figure 3.41: FTIR spectra of MEKFR-DEA20-BA and MEKFR-DEA20.

In figures 3.42 and 3.43, NMR spectra of MEKFR-DEA5-BA and MEKFR-DEA20-BA, respectively. In both them, decrease in the intensities of hyrdoxyl hyrogen are observed as a result of boric acid modification.

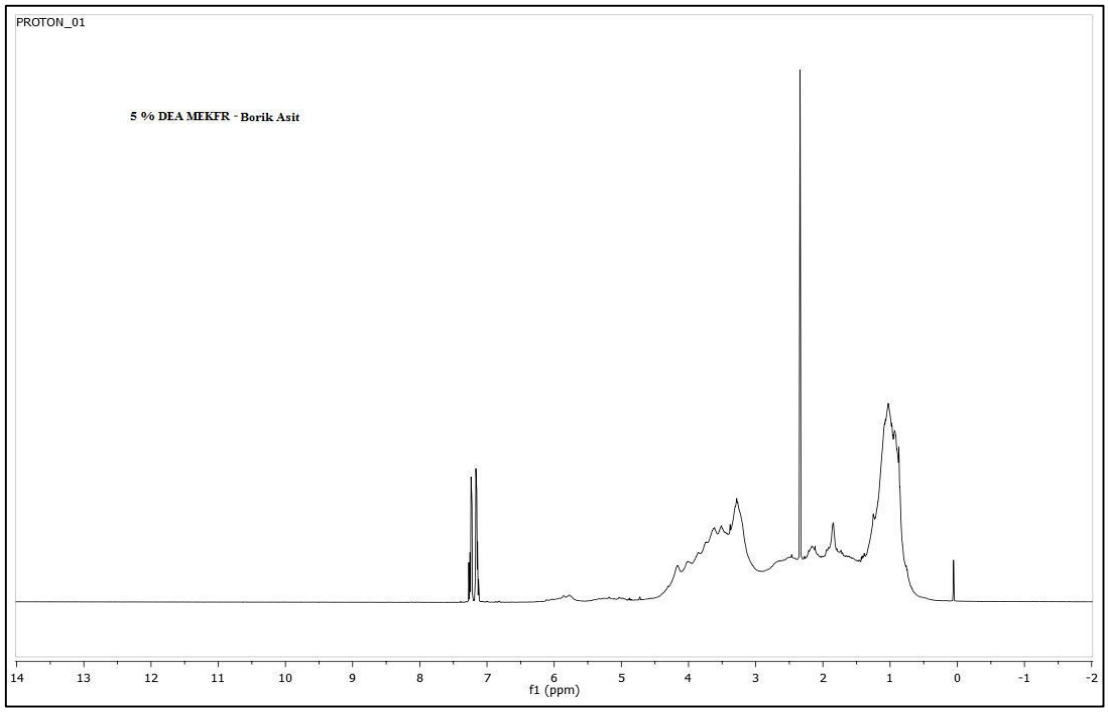

Figure 3.42: NMR spectrum of MEKFR-DEA5-BA

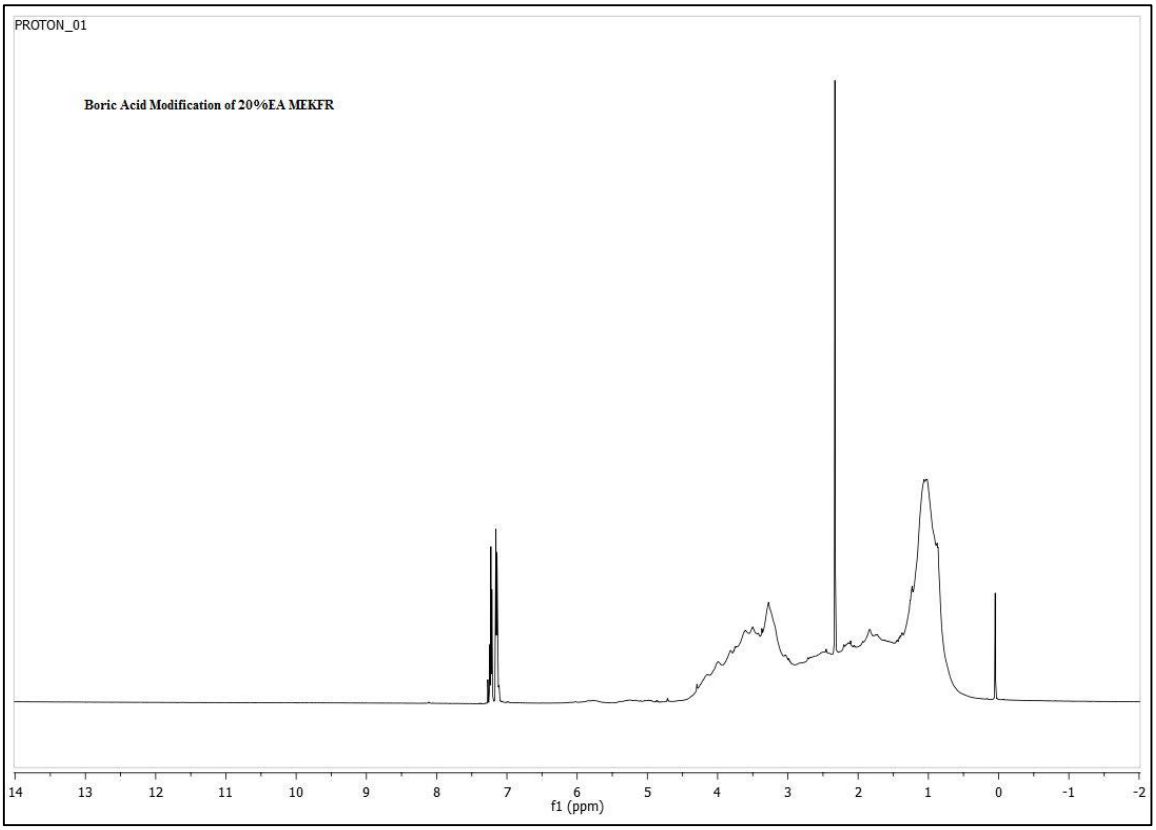

Figure 3.43: NMR spectrum of MEKFR-DEA20-BA

As seen in Table 3.5, boric acid modification increases the solubilities of MEKFR-DEA resins.

Table 3.5: Solubility of MEKFR-DEA-BA in diffrerent solvents.

	THF	**DCM**	**DMS**	**Ethanol**	**Acetone**
MEKFR-DEA5	**s**	**s**	**s**	**sl**	**s**
MEKFR-DEA5-BA	**s**	**s**	**s**	**s**	**s**
MEKFR-DEA10	**s**	**s**	**s**	**sl**	**s**
MEKFR-DEA10-BA	**s**	**s**	**s**	**s**	**s**
MEKFR-DEA20	**sl**	**sl**	**sl**	**i**	**sl**
MEKFR-DEA20-BA	**s**	**s**	**s**	**i**	**s**

"s" means soluble, **"sl"** means slightly soluble.

TGA curve of MEKFR-DEA5-BA and MEKFR-DEA10-BA can be seen in figures 3.44 and 3.45, respectively. The onset of degradation is measured as 48ºC for both. The ash amount is determined as 0,38 and 1,55%.

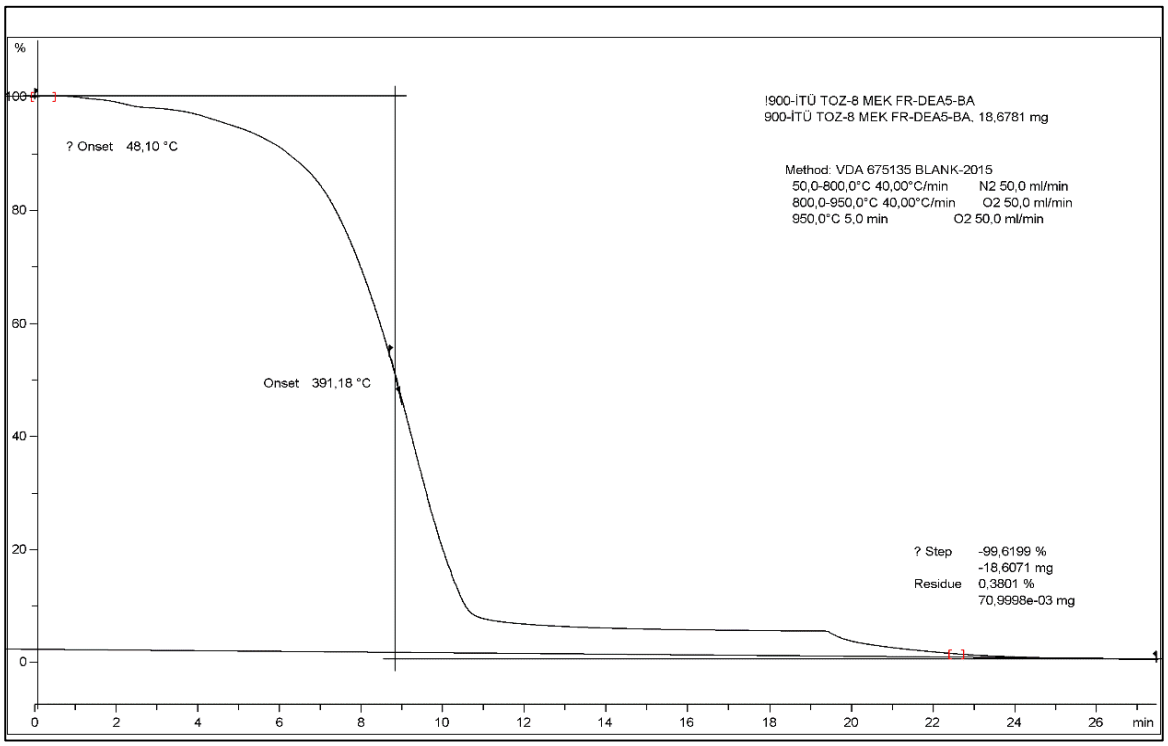

Figure 3.44: TGA curve of MEKFR-DEA5-BA

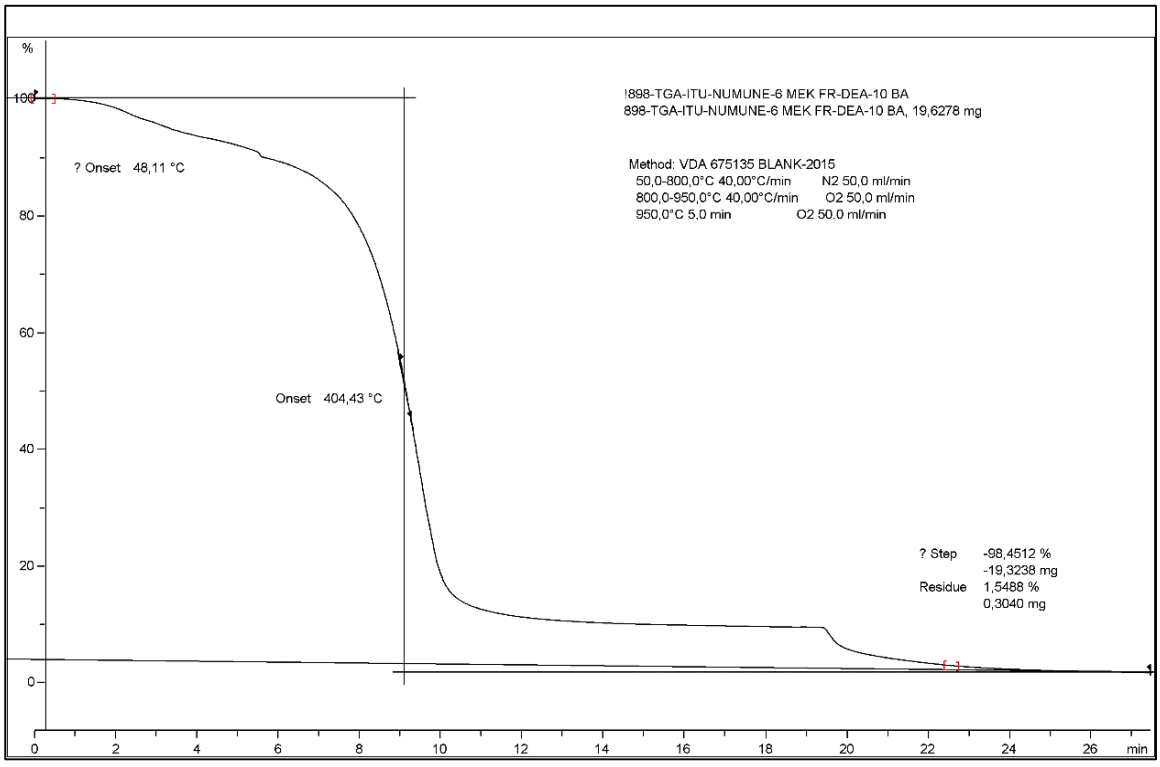

Figure 3.45: TGA curve of MEKFR-DEA10-BA

DSC curve of MEKFR-DEA5-BA and MEKFR-DEA10-BA can be seen in figures 3.46 and 3.47, respectively. It is observed that glass transition disappears as the diethanol amine and so boric acid modification through the hydroxyl groups, increases.

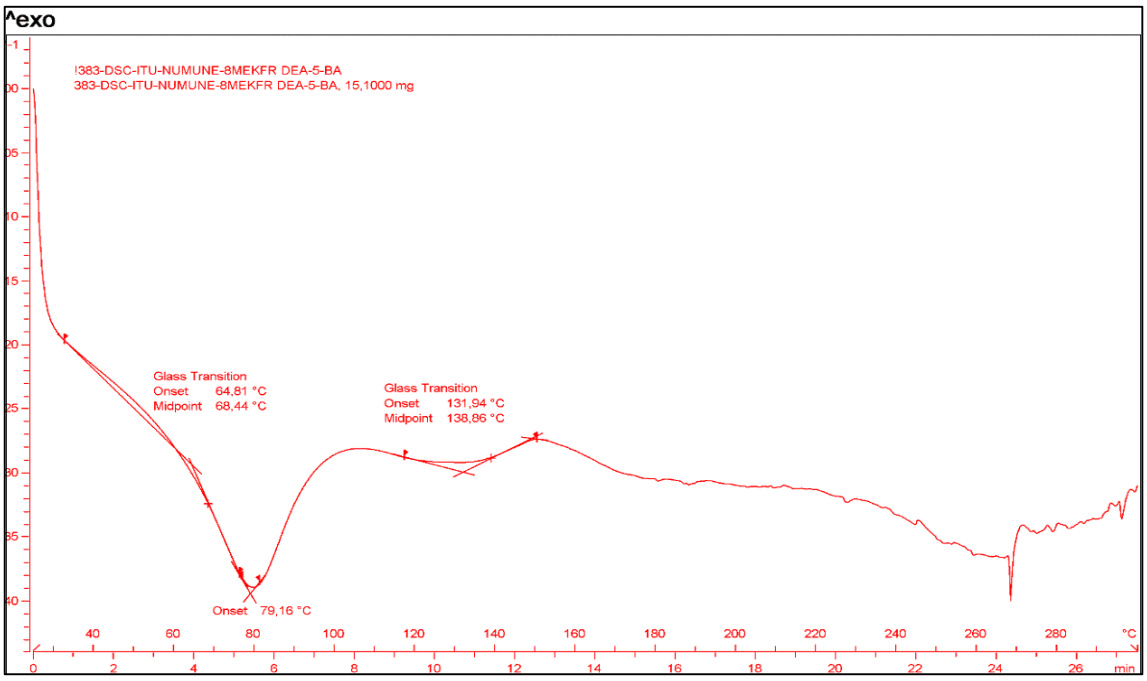

Figure 3.46: DSC curve of MEKFR-DEA5-BA

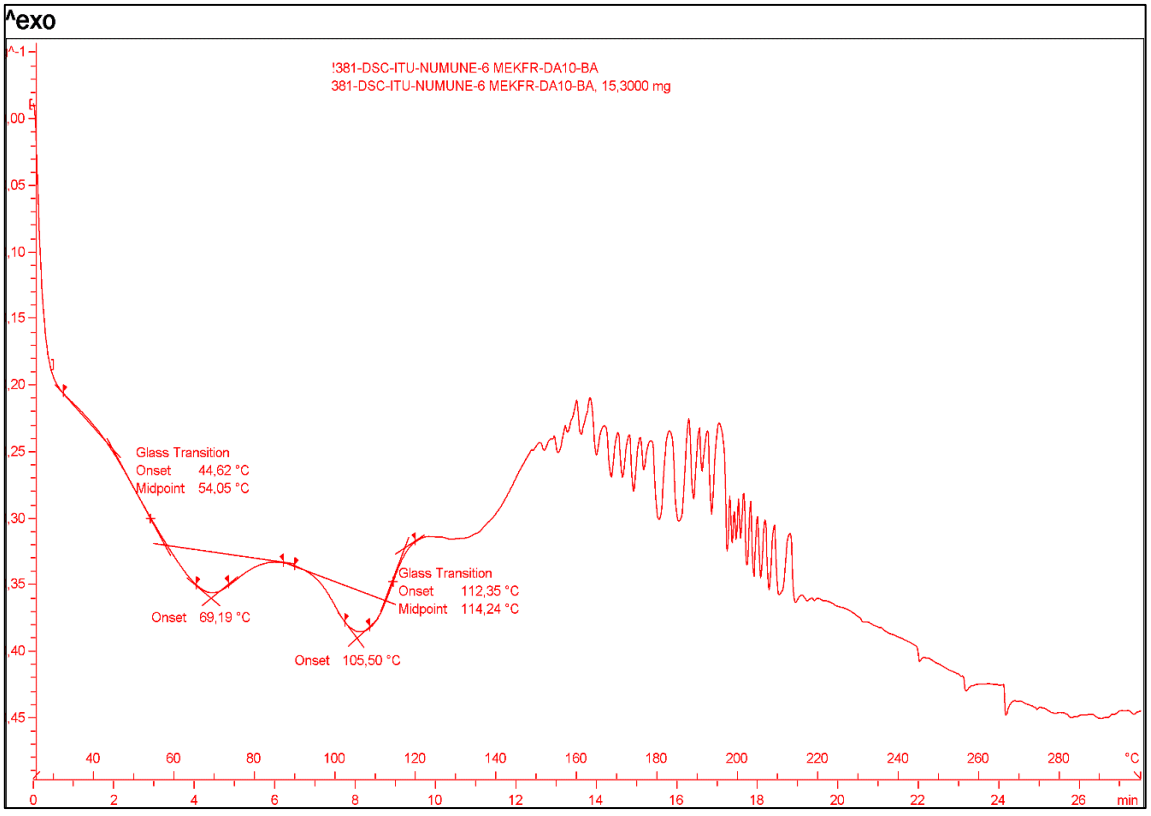

Figure 3.47: DSC curve of MEKFR-DEA10-BA

When we compare the TGA curves of boric acid modified MEKFR-DEA with the non-modifed one, the improvement in thermal resistance is seen apparently since the curves shift to the right (see figures 3.48 and 3.49).

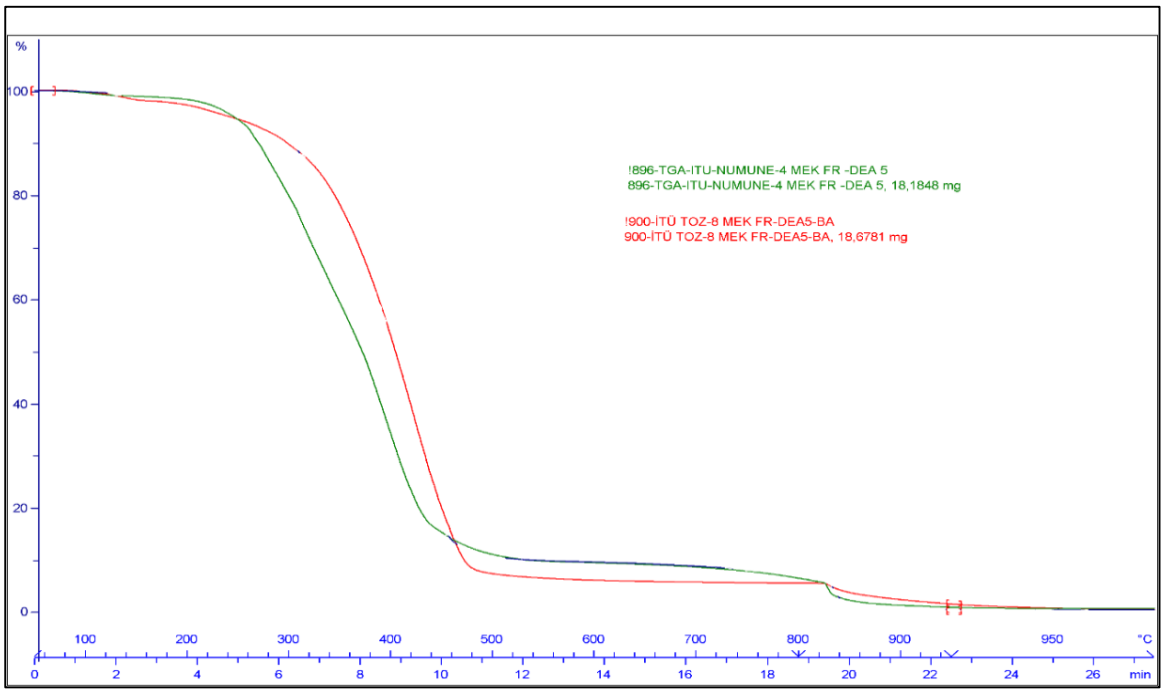

Figure 3.48: Compararison of MEKFR-DEA5-BA and MEKFR-DEA5

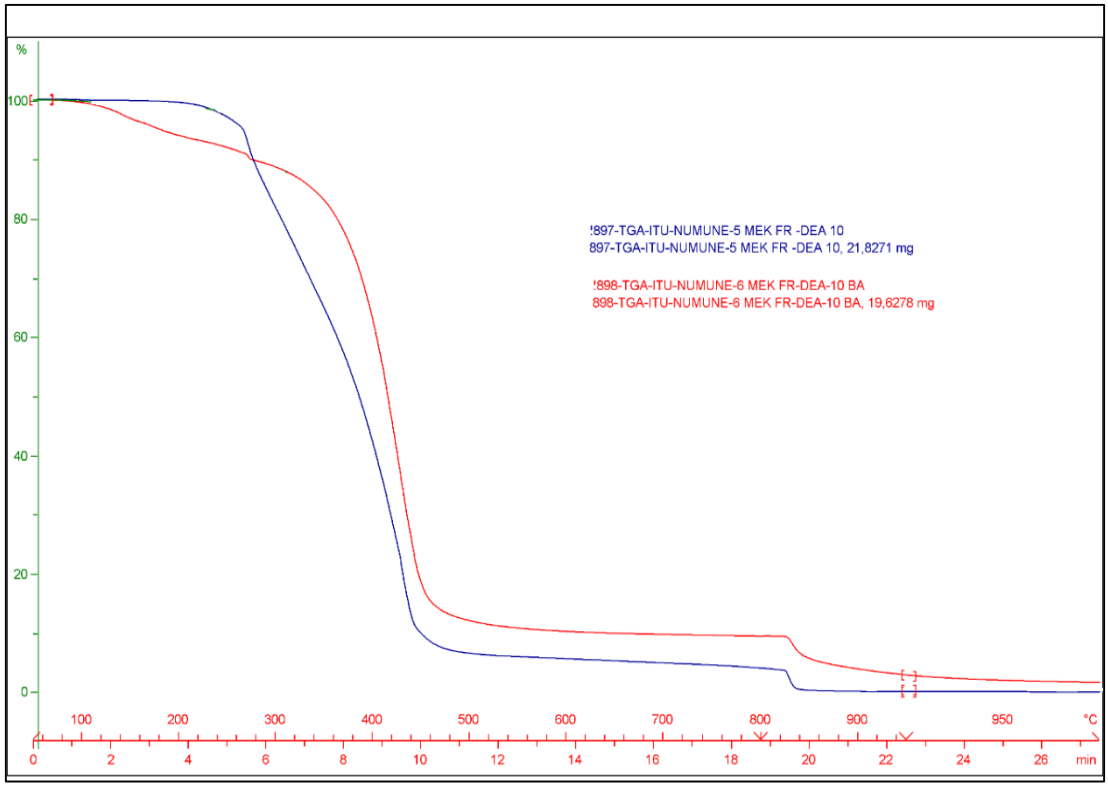

Figure 3.49: Compararison of MEKFR-DEA10-BA and MEKFR-DEA10

T_g, T_{onset}, T_{50} and ash content of resins obtained from TGA and DSC analyses can be seen in Table 3.6.

Table 3.6: T_g, T_{onset}, T_{50} and ash content of all resins.

	T_g (°C)	**T_{onset} (°C)**	**T_{50} (°C)**	**Ash (%)**
MEKFR	52	119	398	0,34
MEKFR-AA	52	113	365	2,23
MEKFR-CUAA	52	150	383	0,55
MEKFR-DEA5	62	50	375	0,56
MEKFR-DEA10	54	68	385	0,005
MEKFR-BA	69,3	48	408	0,65
MEKFR-DEA5-BA	-	48	391	0,38
MEKFR-DEA10-BA	-	48	404	1,55

4. CONCLUSION

To increase their physical and chemical performances by changing their chemical structures, methyl ethyl ketone formaldehyde resins are modified in situand after the polymerization with different modifiers which are alendronic acid, cyclic urea, diethanolamine and boric acid.

After the synthesis and modifications of resins, in order to get information about the chemical structures of the final products, they are analyzed using IR and NMR . In the terms of physical properties, solubility analyses are carried out in five different solvents, namely ethanol, acetone, dichloromethane, tetrahydrofuran and dimethyl sulfoxide. Lastly, regarding the thermal behavioır of the resins and the effects of modifications on the thermal degradation of them, TGA and DCS analyses are carried out for each one.

At the end of these analyses carried out, it is concluded that, after modifications, physical and chemical properties of the methyl ethyl ketone formaldehyde resin are changed as a result of the changes in the chemical structure. Boric acid nodification results in improvement of thermal resitance and increase in resin solubilities.

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