

SYNTHESIS AND CHARACTERIZATION OF HYDROGELS FROM ALLYL  
METHACRYLATE AND ACRYLAMIDE COPOLYMER

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**SYNTHESIS AND CHARACTERIZATION OF HYDROGELS FROM ALLYL  
METHACRYLATE AND ACRYLAMIDE COPOLYMER**

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## ABSTRACT

### SYNTHESIS AND CHARACTERIZATION OF HYDROGELS FROM ALLYL METHACRYLATE AND ACRYLAMIDE COPOLYMER

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Acrylamide based hydrogels were synthesized through copolymerization reaction of allyl methacrylate with acrylamide. Copolymerization reactions were carried out with solution polymerization in tetrahydrofuran by using  $\alpha$ - $\alpha$ -azoisobutyronitrile as an initiator at 60 °C. Three copolymer compositions were studied having 5, 15, 25 molar percentage of allyl methacrylate as feed concentrations. The synthesized copolymers were characterized by FTIR, NMR, DSC, TGA and GPC. <sup>1</sup>H-NMR spectra were used to confirm the chemical structures of the copolymers and to determine the comonomer compositions of the copolymers. DSC and TGA analysis were conducted to determine the thermal properties of the copolymers and TGA results showed that copolymers have two step degradation behavior. Molecular weights of the copolymers were determined by GPC. Swelling capacities of the obtained hydrogels were investigated and swelling capacity of the gels reached to 77% as maximum value.

Keywords: Acrylamide, Hydrogel, Allyl methacrylate, Swelling Capacity.

## ÖZ

### ALİL METAKRİLAT VE AKRİLAMİD KOPOLİMERİNDEN HİDROJEL SENTEZİ VE KARAKTERİZASYONU

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Akrilamid tabanlı hidrojeller alil metakrilat ile akrilamid kopolimerleştirilerek sentezlendi. Monomerler, başlatıcı olarak  $\alpha$ - $\alpha$ -azoisobütronitril kullanılarak 60 °C' de tetrahidrofuranda çözelti polimerleşmesi yöntemiyle kopolimerleştirildi. Üç kopolimer kompozisyonu alil metakrilatın molar yüzdesi 5, 15 ve 25 olacak şekilde çalışıldı. Sentezlenen kopolimerler FTIR, NMR, DSC, TGA ve GPC ile karakterize edildi. <sup>1</sup>H-NMR yöntemi kopolimerlerin kimyasal yapılarını ve kopolimerlerdeki komonomer kompozisyonlarını belirlemek için kullanıldı. DSC ve TGA karakterizasyon yöntemleri kopolimerlerin termal özelliklerini gözlemlemek için uygulandı ve TGA sonuçları kopolimerlerin iki basamaklı bozunma özelliğine sahip olduklarını gösterdi. Kopolimerlerin moleküler ağırlıkları GPC yöntemi ile tespit edildi. Elde edilen hidrojellerin şişme kapasiteleri araştırıldı ve jellerin şişme kapasitelerinin en yüksek değer olarak %77 ye ulaştığı görüldü.

Anahtar Kelimeler: Akrilamid, Hidrojel, Alil metakrilat, Şişme Kapasitesi

*To my dear mother*

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Allyl Methacrylate

Allyl methacrylate (AMA) is an unsymmetrical difunctional compound containing two types of vinyl groups which have quite different reactivities.

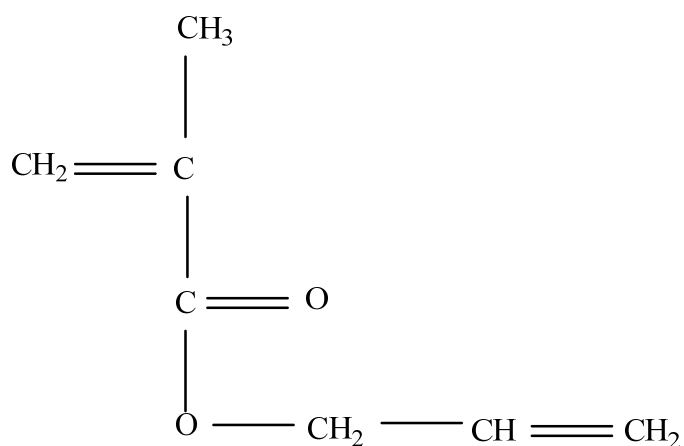


Figure 1.1 Chemical structure of allyl methacrylate

It is a colorless, toxic and flammable liquid. It is inhibited with monomethyl ether hydroquinone since it can polymerize by sunlight and heat.

Table 1.1 Physical properties of allyl methacrylate

Property	Value
Molecular Weight	126.16 g/mol
Boiling Point	140 °C
Freezing Point	-65 °C
Density (at 20 °C)	0.945 g/mL
Flash Point	35 °C

## 1.2 Acrylamide

Acrylamide (AAm) is a highly reactive monomer that can polymerize vigorously when heated above its melting point and evaluate heat.

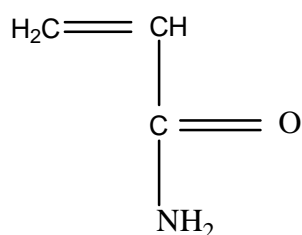


Figure 1.2 Chemical structure of acrylamide

It is a crystalline, white solid which has a long shelf life due to its thermal stability [1].

Table 1.2 Physical properties of acrylamide

Property	Value
Molecular Weight	71.08 g/mol
Boiling Point	- (polymerization)
Melting Point	84.5 °C
Density (at 30 °C)	1.122 g/mL
Flash Point	138 °C

### 1.3 Hydrogel Systems

Hydrophilic gels called hydrogels are three-dimensional polymer networks that can behave like a matrix to hold water inside the network by filling the available free volumes if there is enough interstitial space, so that large amount of water is absorbed by hydrogel without being dissolved [2].

Hydrogels can be categorized by four different ways; by origin, water content, processing and chemical stability. According to their origin, they are named natural and synthetic. There are four types of hydrogels according to their water content; low swelling (20-50%), medium swelling (50-90%), high swelling (90-99.5%), superabsorbent (>99.5%). By their processing, hydrogels are divided into two groups; thermoset (chemically crosslinked) and thermoplastic (physically crosslinked). Hydrogels are called biodegradable or nondegradable according to their chemical stability [3].

Chemical crosslinks are created by forming covalent bonds between chains and physical crosslinks are formed by physical interactions between the chains. There are many methods to form both chemically crosslinked and physically crosslinked hydrogels. Chemically crosslinked hydrogels can be synthesized by radicalic polymerization, chemical reaction of complementary groups which are aldehydes, addition reactions and condensation reactions, high energy irradiation and using enzymes. Physically crosslinked hydrogels are formed by ionic interactions, crystallization, from amphiphilic block and graft copolymers, hydrogen bonding and protein interactions [4].

There are three main methods to prepare hydrogels; from monomers, from prepolymers and from existing hydrophilic polymers. First method involves copolymerization of hydrophilic monomers with polyfunctional comonomers



which can act as crosslinkers. Hydrophilic acrylates, methacrylates, acrylamides and methacrylamides are generally preferred as monomers. In the second method, hydrogels are synthesized by crosslinking of oligomers and low molecular weight hydrophilic polymers. Last method is basically synthesizing hydrogels by chemical crosslinking of hydrophilic polymers [2].

Hydrogels which can show sensitive response to small external stimuli changes such as temperature, pH, ionic strength, electric field, etc. are called stimuli-responsive or intelligent hydrogels. They are used in biomedical and bioengineering applications such as drug delivery, chemical separations, tissue engineering and enzyme immobilization due to their fast response rate to external changes [5, 6].

Another important class of hydrogels is superabsorbent hydrogels due to their high water absorbency capacity. High water capacity makes hydrogels similar to natural tissue; as a result they are useful in biomedical and pharmaceutical applications. In addition to high swelling capacity their other important properties such as hydrophilicity, lack of toxicity and biocompatibility make them available for many applications like, soil conditioners for agriculture, disposable diapers, water blocking tapes, absorbent pads, gel actuators, extraction of precious metals, release of agrochemicals, etc [7].

Natural-based superabsorbent hydrogels has recently gained importance due to their biocompatibility and biodegradability. They are formed by graft polymerization of vinyl monomers onto polysaccharide backbone and crosslinking of the chains. Polysaccharides are mainly chosen in natural-based superabsorbent hydrogels because of their renewability, biocompatibility and nontoxicity [8].

Most important properties of the hydrogels are swelling capacity and elastic modulus of the gel which both depend on the nature of the gel. Factors affecting the properties of the gel strongly depend on the network structure of the gel that also depends on the polymerization conditions like monomer concentration or control of the temperature [9, 10].

Generally hydrogels have mechanical strength problem for some applications such as drug delivery, thus to overcome the problems and make hydrogels more useful for any kind of applications one should aim to design the gel with desired properties.

To improve the mechanical strength of hydrogel best way is to introduce a hydrophobic monomer to the network although it causes a decrease in water content of the gel. Copolymerization, grafting and forming interpenetrating networks are the mostly used methods for introducing hydrophobic monomers into hydrogels. Among these methods copolymerization is the easiest one to achieve the goal [11].

Designing a hydrogel with desired swelling ratio or mechanical strength both requires correlation with the structure and property of the gel which can be done by controlling the conditions of the polymerization.

## 1.4 Acrylamide Based Hydrogels

Acrylamide is a very important monomer for hydrogel systems due to its hydrophilicity; as a result it is commonly chosen in hydrogel synthesis. Many researchers used acrylamide as a monomer and comonomer in hydrogel preparations.

Zhou, Yao and Kurth prepared superabsorbent copolymers from acrylamide, sodium methallylsulfonate and sodium acrylate. They investigated the water absorbency of the copolymers and found out that water-absorbency increased when copolymers were crosslinked with sodium acrylate. They also investigated the effects of polymerization conditions on the water-absorbency of the hydrogels [9, 12].

Poly(ethylene glycol dimethacrylate-co-acrylamide) hydrogel beads were synthesized by suspension polymerization with and without using toluene as diluent by Kesenci and Pişkin. Without toluene nonswellable, nonporous beads were formed having low acrylamide incorporation and with toluene, microporous beads were formed and acrylamide incorporation was higher [13].

Rosa, Bordado and Casquilho synthesized copolymer of acrylamide and 2-acrylamido-2-methylpropanosulfonic acid by inverse emulsion technique. They performed experimental design to obtain the optimum values of polymerization conditions which are concentration of organic solvent, concentration of emulsifier, reaction temperature and studied their effects on the swelling [14].

In another study, poly(acrylamide-1-allyl-2-thiourea) hydrogels were synthesized by gamma irradiation with different irradiation doses and different 1-allyl-2-thiourea amounts. Rigid hydrogels were formed at high irradiation doses and high 1-allyl-2-thiourea amount by Salih and his coworkers [15].

Caykara and his coworkers synthesized series of acrylamide copolymers. They synthesized thermo responsive poly(N-isopropylacrylamide-co-acrylamide) hydrogels by free-radicalic polymerization. N,N-Methylenebisacrylamide was used as crosslinker and they observed that swelling behavior of the hydrogel could be controlled by the amount of the crosslinker. With the same method, ionic hydrogels based on acrylamide, itaconic acid and N,N-dimethylacrylamide were synthesized. Swelling property of the hydrogels was investigated in buffer solutions having different pH values. Macroporous poly(N-3-dimethylaminopropyl methacrylate-co-acrylamide) hydrogels were synthesized with different pore-forming agents which are hydroxypropyl cellulose and poly(ethylene glycol) and their effect on swelling property of the hydrogels were studied. Magnetic field-sensitive gel was prepared from poly(N-tert-butylacrylamide-co-acrylamide) synthesis and forming Fe<sub>3</sub>O<sub>4</sub> particles in the hydrogel. Magnetic response of the gel was investigated by applying magnetic field to the gel [10, 16, 17, 18].

Poly(acrylic acid-co-acrylamide) were synthesized by many researchers and used for different purposes. Shukla and Bajpai synthesized networks of poly(vinyl alcohol) grafted by acrylic acid and acrylamide copolymer which resulted highly swelling smart hydrogels [19].

Copolymeric hydrogels of acrylic acid and acrylamide were synthesized by crosslinking with trimethylolpropane by Chauhan and Kumar. They used these hydrogels for uranyl ion uptake from solution having 5% NaCl and it was

observed that uptake property of the hydrogel was affected by structural property of the hydrogel [20].

Superabsorbent polymers of acrylic acid and acrylamide copolymer were synthesized by using different crosslinkers which are glutaraldehyde, poly(ethylene glycol) diacrylate, N,N-methylene bisacrylamide and divinylbenzene by Xie and his coworkers. They investigated the absorbency property of these superabsorbent polymers and observed that when poly(ethylene glycol) diacrylate used as crosslinker highest absorbency obtained whereas divinylbenzene as crosslinker resulted the lowest absorbency [21].

Another research group synthesized superabsorbent gels based on acrylic acid and acrylamide by free radical polymerization. They used three functional monomers (anionic, cationic and zwitterionic) to have different charged groups on the gels and investigated the water absorbency of the gels in distilled water, 0.9 wt% NaCl solution and mixed solution having 60mg/L  $\text{CaCl}_2$  and 30 mg/L  $\text{MgCl}_2$  [22].

Poly(acrylic acid-co-acrylamide) hydrogels and hydrogel nanoparticles were synthesized by Ray and his coworkers. They loaded the hydrogels with a colon-specific drug and tested the swelling of the gels in rat caecal medium. Results showed that drug entrapment increased by increasing the acrylamide content in the feed [23].

## 1.5 Allyl Methacrylate Polymerization and Copolymerization

Allyl methacrylate was homopolymerized by many methods. In our research group it was polymerized by solution polymerization in  $\text{CCl}_4$  (solvent) with AIBN (initiator), by gamma radiation and by atom transfer radical polymerization. Polymer was characterized by FTIR, NMR, DSC and TGA. Results showed that only 1-2% of the allyl groups changed during the polymerization causing limited crosslinking [24, 25].

Allyl methacrylate was also copolymerized by many researchers. Liu and his coworkers synthesized a triblock copolymer by anionic polymerization; poly(solketal methacrylate)-block-poly(2-cinnamoyloxyethyl methacrylate)-block-poly(allyl methacrylate). Polymer was characterized by GPC, NMR and light scattering [26].

Another research group synthesized methacrylic acid-ethyl acrylate-allyl methacrylate terpolymer by precipitation polymerization in toluene with AIBN (initiator). Viscosity measurements were done and it was observed that when crosslinking agent (allyl methacrylate) concentration increased viscosity increased [27].

Paris and Fuente synthesized series copolymers of allyl methacrylate by atom transfer radical polymerization method. They prepared poly(allyl methacrylate-co-butyl acrylate) in different solvents at different temperatures; in toluene at  $100^\circ\text{C}$  and in benzonitrile at  $70^\circ\text{C}$ . In benzonitrile solution and at  $70^\circ\text{C}$  gelation-free polymerization was observed [28, 29].

Same research group synthesized another copolymer of allyl methacrylate with glycidyl methacrylate having two different functional pendant groups which cause possibility of crosslinking and modification that could also result in new polymeric materials [30].

Allyl methacrylate was also used in hydrogel preparation. Yin and Stöver synthesized poly(N,N-dimethylacrylamide-co-allyl methacrylate) by free radical polymerization. Copolymer resulted having pendant allyl groups along the chains. Aqueous solutions of the copolymer showed liquid-liquid phase transitions at different temperatures depending on allyl methacrylate content [31].

## **1.6 Aim**

In this study, it was aimed to synthesize copolymeric hydrogels from a hydrophilic (acrylamide) and a hydrophobic (allyl methacrylate) monomer by free radical copolymerization.

Allyl methacrylate was intended for use both as a comonomer and crosslinking agent due to its difunctional property.

Swelling capacity of the hydrogels were measured to investigate the effects of hydrophilic comonomer content and hydrophobic comonomer content on water absorbancy of the gels having different monomer compositions.

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 Polymer Synthesis

##### 2.1.1 Materials

Acrylamide (AAm, anhydrous) was supplied by Sigma Chemical Company and used as received. Allyl methacrylate (AMA, Merck) was purified by vacuum distillation prior to use.  $\alpha$ - $\alpha$ -Azobisisobutyronitrile (AIBN, Merck) and tetrahydrofuran (THF, Merck, extra pure) were used as received. n-Pentane and methanol were directly used to precipitate the polymers. Double distilled water was used after all the copolymerization reactions as well as for swelling studies.



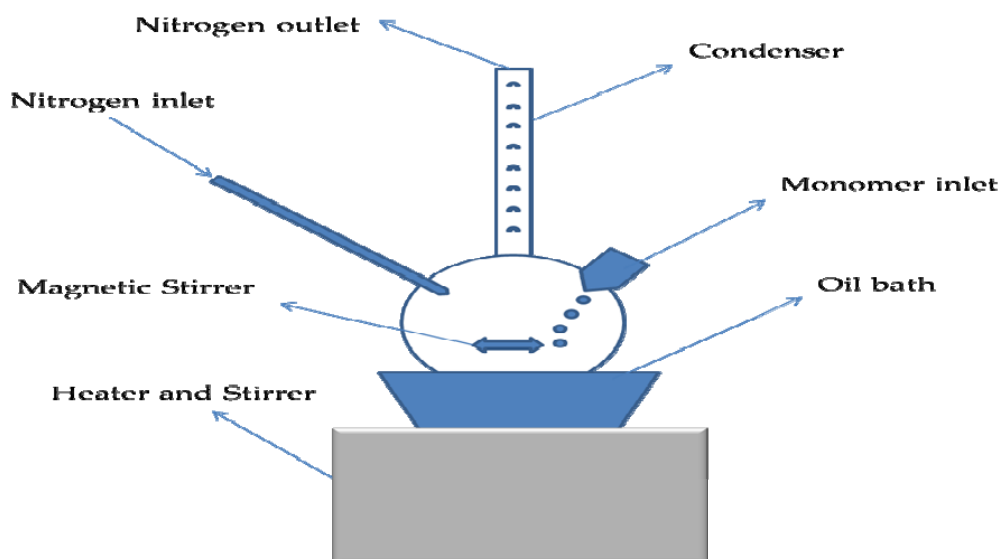


Figure 2.1 Schematic representation of experimental apparatus

### 2.1.2 Method for Synthesis

The homopolymerization and copolymerization reactions were carried out in a three-neck round-bottomed flask fitted with a condenser, nitrogen gas inlet and magnetic stirrer by solution polymerization method.

For homopolymerization reactions, both monomers (0.025 mol) were polymerized in THF (50 mL) with AIBN (0.25 mmol) at 60 °C. Polyallyl methacrylate was precipitated into 150 mL n-pentane, filtered and dried in vacuum oven at 40 °C. Polyacrylamide was precipitated into n-pentane, filtered, dissolved in distilled water and precipitated into methanol before being dried in vacuum oven at 40 °C.

For copolymerization reactions, various comonomer ratios were added to THF to prepare 100 mL of 1 molar solution (total monomer concentration). For the first 30 minutes AMA was mixed with AIBN (0.041g) in 10 mL THF, then AAm (dissolved in 90 mL THF with 0.123g AIBN) was added for one and a half hour. (30 mL every 30 minutes)

The product was precipitated into n-pentane, filtered and washed with distilled water for several times. Finally, copolymers were dried in vacuum oven at 40 °C overnight.

Table 2.1 Recipe for homopolymer and copolymer amounts

Polymer	AAm	AMA	AIBN	THF	[Monomer] mol/L	[Initiator] mol/L
PAAm	1.78g 0.025mol	-	0.041g 0.25 mmol	50 mL	0.5	0.005
PAMA	-	3.15g 0.025mol	0.041g 0.25 mmol	50 mL	0.5	0.005
PAAm(75)- co- PAMA(25)	5.33g 0.075mol	3.15g 0.025mol	0.164g 1 mmol	100 mL	1	0.01
PAAm(85)- co- PAMA(15)	6.04g 0.085mol	1.89g 0.015mol	0.164g 1 mmol	100 mL	1	0.01
PAAm(95)- co- PAMA(5)	6.75g 0.095mol	0.63g 0.005mol	0.164g 1 mmol	100 mL	1	0.01

## **2.2 Polymer Characterization Methods**

### **2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)**

Infrared spectra of the samples were obtained on a Nicolet IS 10 Thermo Scientific ATR-FTIR spectrometer.

### **2.2.2 Nuclear Magnetic Spectroscopy (NMR)**

<sup>1</sup>H NMR spectra of polymers were recorded on a Avance III Bruker 400 MHz NMR spectrometer (BioSpin, Ettlingen, Germany ) in deuterated chloroform (CDCl<sub>3</sub>) with respect to tetramethylsilane (TMS) as the internal reference.

### **2.2.3 Differential Scanning Calorimetry (DSC)**

The glass transition temperature (T<sub>g</sub>) of the polymers were evaluated by Scinco DSC-N-650. Measurements in the temperature range from 25 to 300°C at a heating rate of 10°C/min under a nitrogen atmosphere were performed. Standard 40-μL aluminum pans with perforated lids were used.

### **2.2.4 Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis (TGA) of the obtained polymers was carried out on a PerkinElmer Pyris TGA-FTIR spectrometer. Thermograms were recorded in the temperature range 25–500 °C with a heating rate of 10 °C/min under a 20-ml/min nitrogen atmosphere.

### **2.2.5 Gel Permeation Chromatography (GPC)**

PL-GPC 220 (Polymer Laboratories Ltd., Church Stretton, UK) gel permeation chromatograph was used to determine the molecular weight distribution of the polymers with the use of polystyrene standards. The samples were dissolved in THF (1% w/v solutions), which was used also as a carrier solvent at a flowing rate of 1 ml/min.

### **2.2.6 Swelling Capacity Measurement**

Polymers were weighted to determine the dry gel weight after they were immersed into 100 mL distilled water at room temperature for one week and weighted again to find out the swollen gel weight.

Water absorbency ratio was calculated by using the following equation:

$$SC (\%) = [ ( W_s - W_d ) / W_d ] \times 100$$

$W_s$  and  $W_d$  were weights of the swollen and the dry gels, respectively.

## CHAPTER 3

### RESULTS AND DISCUSSION

Polyacrylamide-co-poly(allyl methacrylate) copolymers (PAAm-coPAMA) at three different compositions (95:5, 85:15 and 75:25 as AAm:AMA molar percentage ratio in the feed) and their homopolymers were synthesized by solution polymerization.

In this chapter, chemical structures and compositions were evaluated by FTIR and  $^1\text{H-NMR}$ , molecular weights were measured by GPC. The thermal properties were investigated by DSC and TGA and swelling capacities were calculated.

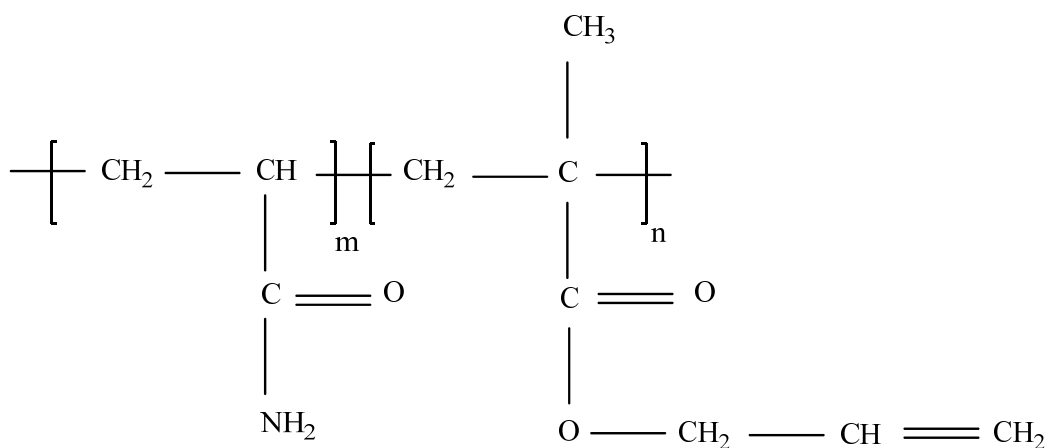


Figure 3.1 Chemical structure of poly(acrylamide)-co-poly(allyl methacrylate) PAAm-co-PAMA copolymer

### 3.1. Fourier Transform Infrared Spectroscopy (FTIR) Results

FTIR spectra of the acrylamide and poly(acrylamide) were given in Fig. 3.2 and the peak assignments were tabulated in Table 3.1. The complete disappearance of C=C peaks, which were seen at 815  $\text{cm}^{-1}$ , 840  $\text{cm}^{-1}$  and 985  $\text{cm}^{-1}$  in the spectrum of acrylamide, were the evidence of the formation of polyacrylamide. C-H stretching peaks were seen at 2812  $\text{cm}^{-1}$  and 2929  $\text{cm}^{-1}$  in the spectra of acrylamide and polyacrylamide, respectively. C=O peak at 1668  $\text{cm}^{-1}$  in acrylamide spectrum shifted to 1650  $\text{cm}^{-1}$  in polyacrylamide spectrum and -NH<sub>2</sub> (stretching band) peak shifted from 3341  $\text{cm}^{-1}$  to 3336  $\text{cm}^{-1}$ . Other amide group peaks were observed at 1610  $\text{cm}^{-1}$  (NH<sub>2</sub> absorption band) and 3168  $\text{cm}^{-1}$  (N-H vibration band) in the acrylamide spectrum whereas in the spectrum of polyacrylamide they appeared at 1604  $\text{cm}^{-1}$  and 3188  $\text{cm}^{-1}$ .

Table 3.1 The peak assignments for the FTIR spectra of acrylamide and poly(acrylamide)

Functional Group	Wavenumber ( $\text{cm}^{-1}$ )	
	AAm	PAAm
C=C	815, 840, 985	-
C-H	2812	2929
C=O	1668	1650
-NH <sub>2</sub>	3341	3336
-CH <sub>2</sub> - , -CH-	1424, 1350	1411, 1318
-CONH <sub>2</sub>	1610, 3168	1604, 3188

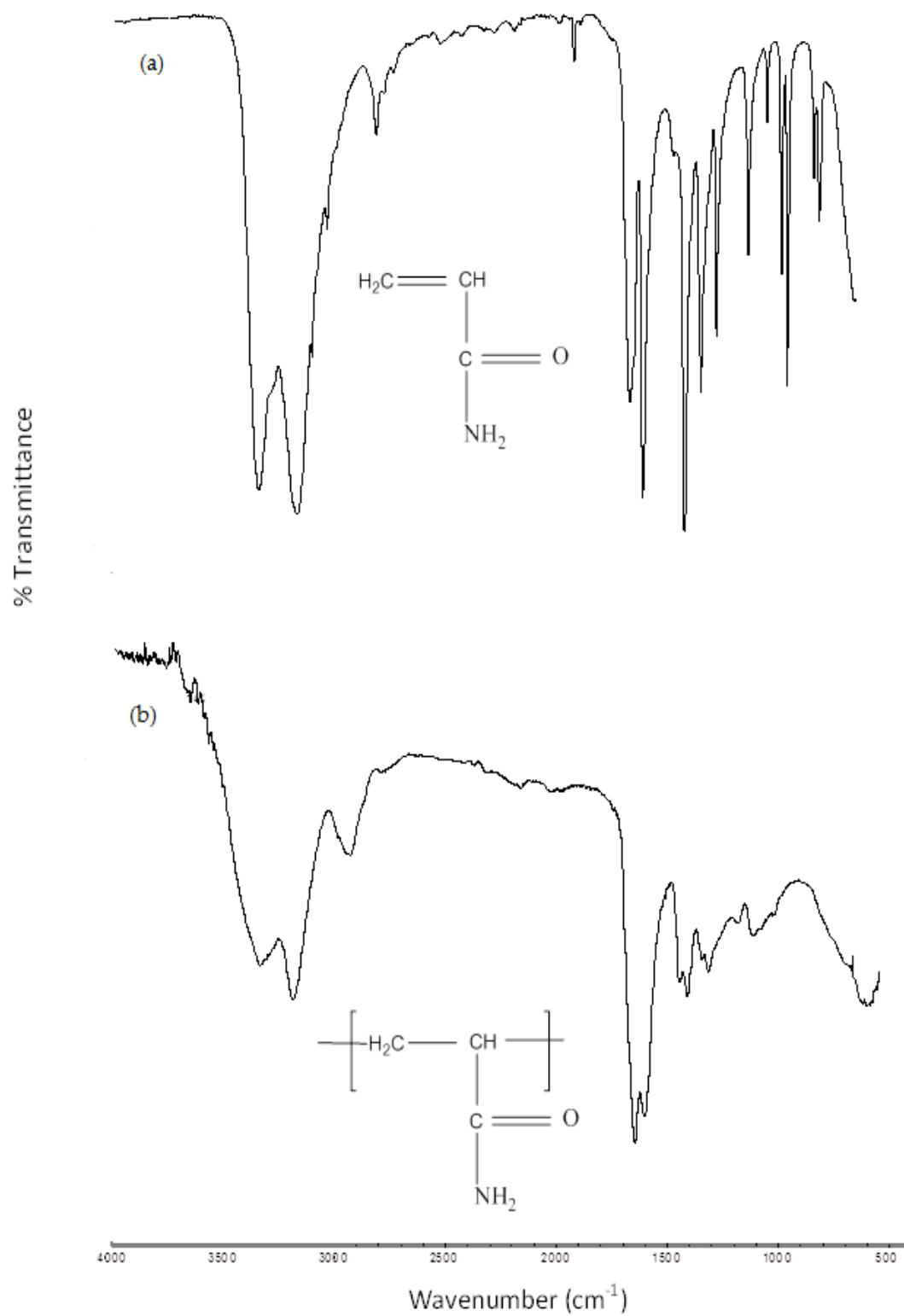


Figure 3.2 FTIR spectra of (a) acrylamide and (b) poly(acrylamide)

In Fig. 3.3 the IR spectra of allyl methacrylate and poly(allyl methacrylate) were given and characteristic vibrational bands are tabulated in Table 3.2. C=O peaks were seen at 1718 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> for allyl methacrylate and polyallyl methacrylate, respectively. Ester peak was observed at 1154 cm<sup>-1</sup> for monomer and at 1138 cm<sup>-1</sup> for the homopolymer. C-H stretching peaks were at 2930 cm<sup>-1</sup> and 2984 cm<sup>-1</sup> in the allyl methacrylate spectrum and at 2937 cm<sup>-1</sup> and 2988 cm<sup>-1</sup> in the poly(allyl methacrylate) spectrum. The allyl group vibrational bands appeared at 3087 cm<sup>-1</sup>, 935 cm<sup>-1</sup>, 984 cm<sup>-1</sup> in the spectrum of allyl methacrylate and at 3083 cm<sup>-1</sup>, 926 cm<sup>-1</sup> and 981 cm<sup>-1</sup> in the polyallyl methacrylate spectrum. Vinyl group peak observed at 813 cm<sup>-1</sup> in the monomer spectrum, disappeared in the polyallyl methacrylate spectrum, indicating that the polymerization carried throughout the vinyl groups and allyl groups mainly remained as pendant groups.

Table 3.2 The peak assignments for the FTIR spectra of allyl methacrylate and poly(allyl methacrylate)

Functional Group	Wavenumber ( cm <sup>-1</sup> ) AMA	Wavenumber ( cm <sup>-1</sup> ) PAMA
C=C (vinyl)	813	-
C=C (allyl)	935, 984, 3087	926, 981, 3083
C-H	2930, 2984	2988, 2937
C=O	1718	1720
-O-C=O	1154	1138
-CH <sub>2</sub> -, -CH <sub>3</sub>	1452, 1317, 1296	1448, 1387, 1231



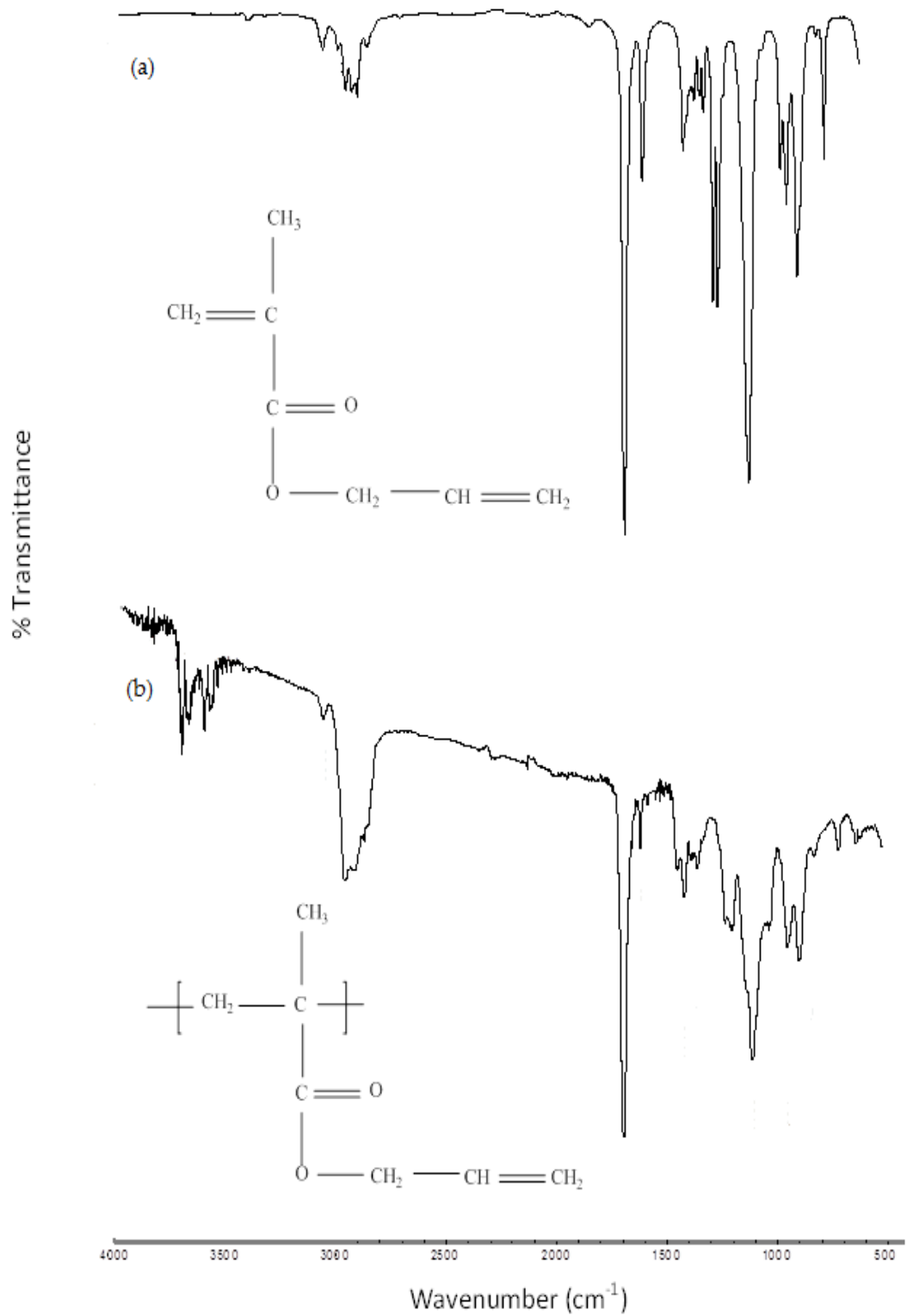


Figure 3.3 FTIR spectra of (a) allyl methacrylate and (b) poly(allyl methacrylate)

Copolymer spectra were evaluated in accordance with the homopolymer FTIR spectra (Fig. 3.4). In the copolymer spectra,  $\text{-NH}_2$  stretching peak was observed at  $3351\text{ cm}^{-1}$ . The peak was quite broad due to hydrogen bonding capability of acrylamide (between N-H and between N-H and oxygen of C=O groups). The other vibrational bands appeared at  $1720$ ,  $2985\text{-}2938$  and  $1138\text{ cm}^{-1}$  for C=O, C-H and  $\text{-O-C=O}$  stretching, respectively (Table 3.3). Allyl group peaks were seen at  $3083\text{ cm}^{-1}$  and  $927\text{ cm}^{-1}$ ,  $981\text{ cm}^{-1}$ .

Table 3.3 The peak assignments of the FTIR spectra of the (PAAm-co-PAMA) copolymers

Functional Group	Wavenumber ( $\text{cm}^{-1}$ ) PAAm(75)-co-PAMA(25)	Wavenumber ( $\text{cm}^{-1}$ ) PAAm(85)-co-PAMA(15)	Wavenumber ( $\text{cm}^{-1}$ ) PAAm(95)-co-PAMA(5)
C=C (allyl)	981, 927, 3083	981, 928, 3081	981, 927, 3084
C-H	2985, 2938	2987	2988, 2943
C=O	1720	1719	1720
$\text{-O-C=O}$	1138	1139	1138
$\text{-NH}_2$	3351	3338	3343
$\text{-CONH}_2$	1685, 3186	1685, 3185	1664, 3192
$\text{-CH}_2\text{-}$ , $\text{-CH}_3\text{-}$ , $\text{-CH-}$	1448, 1388, 1266	1449, 1388, 1261	1448, 1420, 1265

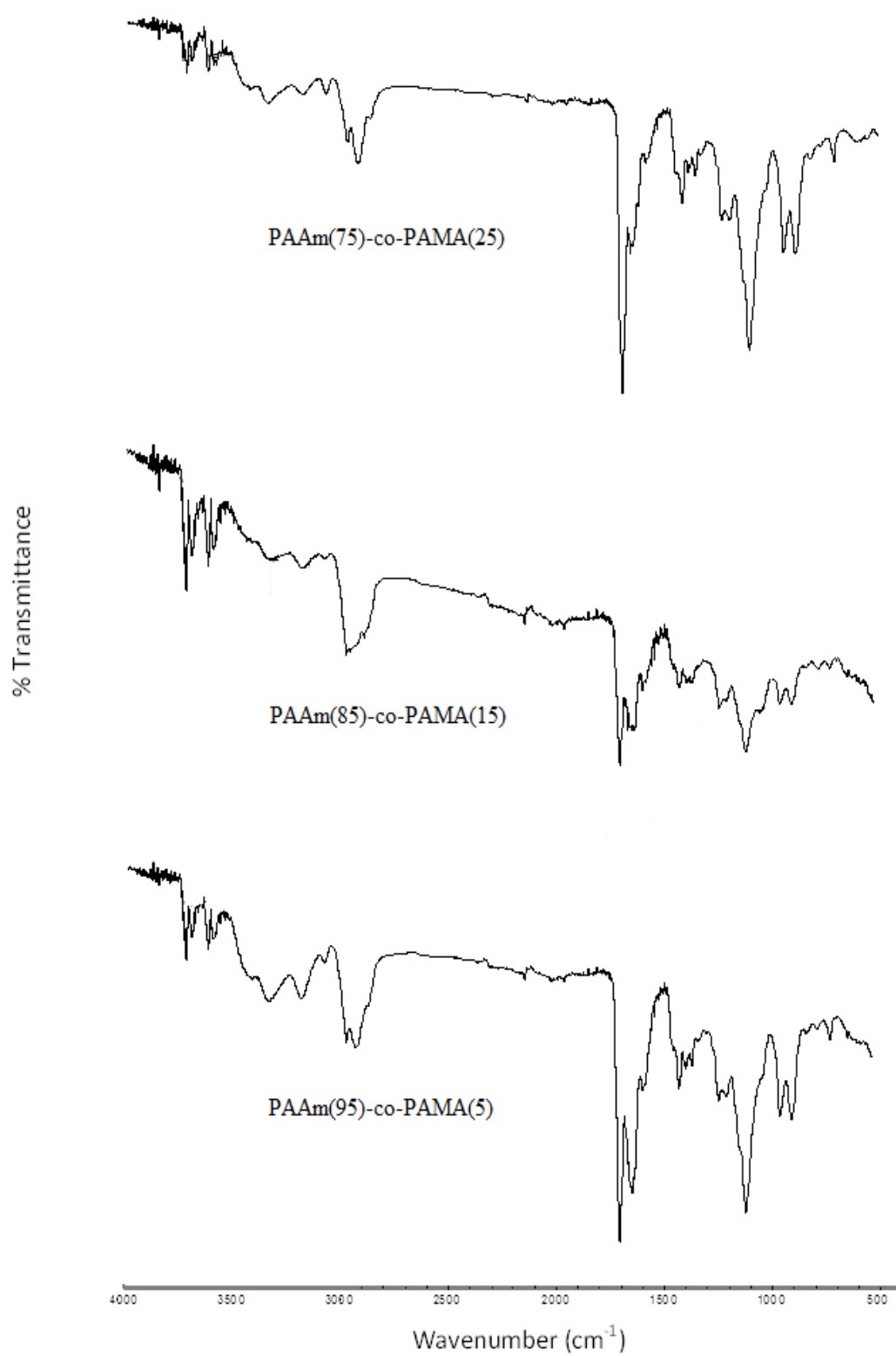


Figure 3.4 FTIR spectra of the (PAAm-co-PAMA) copolymers

### 3.2 Nuclear Magnetic Resonance Spectroscopy (NMR) Results

The  $^1\text{H}$ -NMR spectra of acrylamide and poly(acrylamide) were given in Fig. 3.5. In the  $^1\text{H}$ -NMR spectrum of acrylamide, the vinyl hydrogen peaks of acrylamide were observed at 5.7 ppm and 6.2 ppm for  $\text{CH}_2$  and 6.3 ppm for  $\text{CH}$  (Table 3.4).  $\text{NH}_2$  protons were observed at 5.8 ppm. In the polyacrylamide spectrum vinyl group protons disappeared and peaks shifted to 1-1.6 ppm by opening up the double bonds.  $\text{NH}_2$  peak shifted to 6.45 ppm.

Table 3.4 The peak assignments of the  $^1\text{H}$ -NMR spectra of acrylamide and poly(acrylamide)

Proton Type	Chemical Shift (ppm)	
	AAm	PAAm
$\text{CHH}=\text{CH}-$	5.7	-
$\text{CHH}=\text{CH}-$	6.2	-
$\text{CH}_2=\text{CH}-$	6.3	-
$-\text{NH}_2$	5.8	6.45
$-\text{CH}_2-\text{CH}-$	-	1.2-1.4
$-\text{CH}_2-\text{CH}-$	-	1.6-2.1
$\text{CDCl}_3$	7.2	7.2

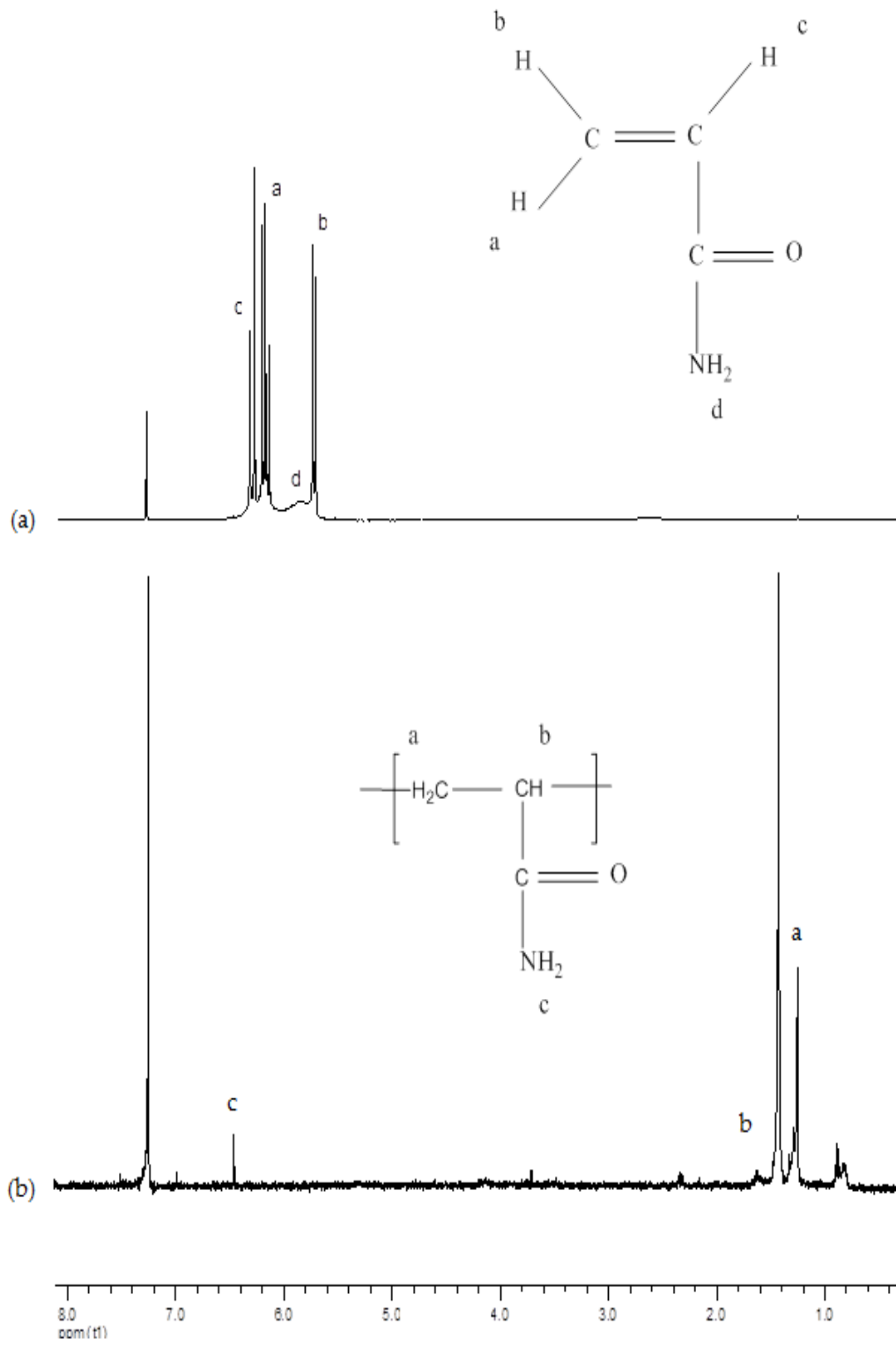


Figure 3.5  $^1\text{H-NMR}$  spectra of (a) acrylamide and (b) poly(acrylamide)

In the allyl methacrylate NMR spectrum vinyl group hydrogen protons were seen at 5.5 ppm and 6.1 ppm for CH<sub>2</sub> and peak of CH<sub>3</sub> hydrogens appeared at 1.9 ppm. The peak at 4.6 ppm belongs to –OCH<sub>2</sub> protons. CH<sub>2</sub> protons of allyl group appeared at 5.1-5.3 ppm and CH peak of allyl group was seen at 5.8-5.95 ppm. In the poly(allyl methacrylate) spectrum by opening up the double bond of vinyl group CH<sub>2</sub> peaks shifted to 1.4-2.2 ppm. The peaks of CH<sub>3</sub> hydrogens were seen between 0.8 ppm and 1.1 ppm and –OCH<sub>2</sub> hydrogen peaks were observed at 4.4-4.6 ppm in the homopolymer spectrum. Allyl group protons, on the other hand were observed at 5.2-5.5 ppm for CH<sub>2</sub> and 5.85-5.95 ppm for CH. But the peak at 3.8 ppm belongs to –OCH<sub>2</sub>CH<sub>2</sub> which indicates that although allyl groups were clearly observed as pendant groups in the homopolymer chains, some of them opened up and also contributed to the polymerization which resulted in crosslinking.

Table 3.5 The peak assignments of the <sup>1</sup>H-NMR spectra of allyl methacrylate and poly(allyl methacrylate)

Proton Type	Chemical Shift (ppm) AMA	Chemical Shift (ppm) PAMA
CHH=C(CH <sub>3</sub> )-	5.5	-
CHH=C(CH <sub>3</sub> )-	6.1	-
-CH <sub>2</sub> -	-	1.4-2.0
-CH <sub>3</sub>	1.9	0.8-1.1
-OCH <sub>2</sub> -	4.6	4.4-4.6
-OCH <sub>2</sub> CH=CH <sub>2</sub>	5.8-5.95	5.85-5.95
-OCH <sub>2</sub> CH=CH <sub>2</sub>	5.1-5.3	5.2-5.5
-OCH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> -	-	3.75
-OCH <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> -	-	1.3-1.4
CDCl <sub>3</sub>	7.2	7.2

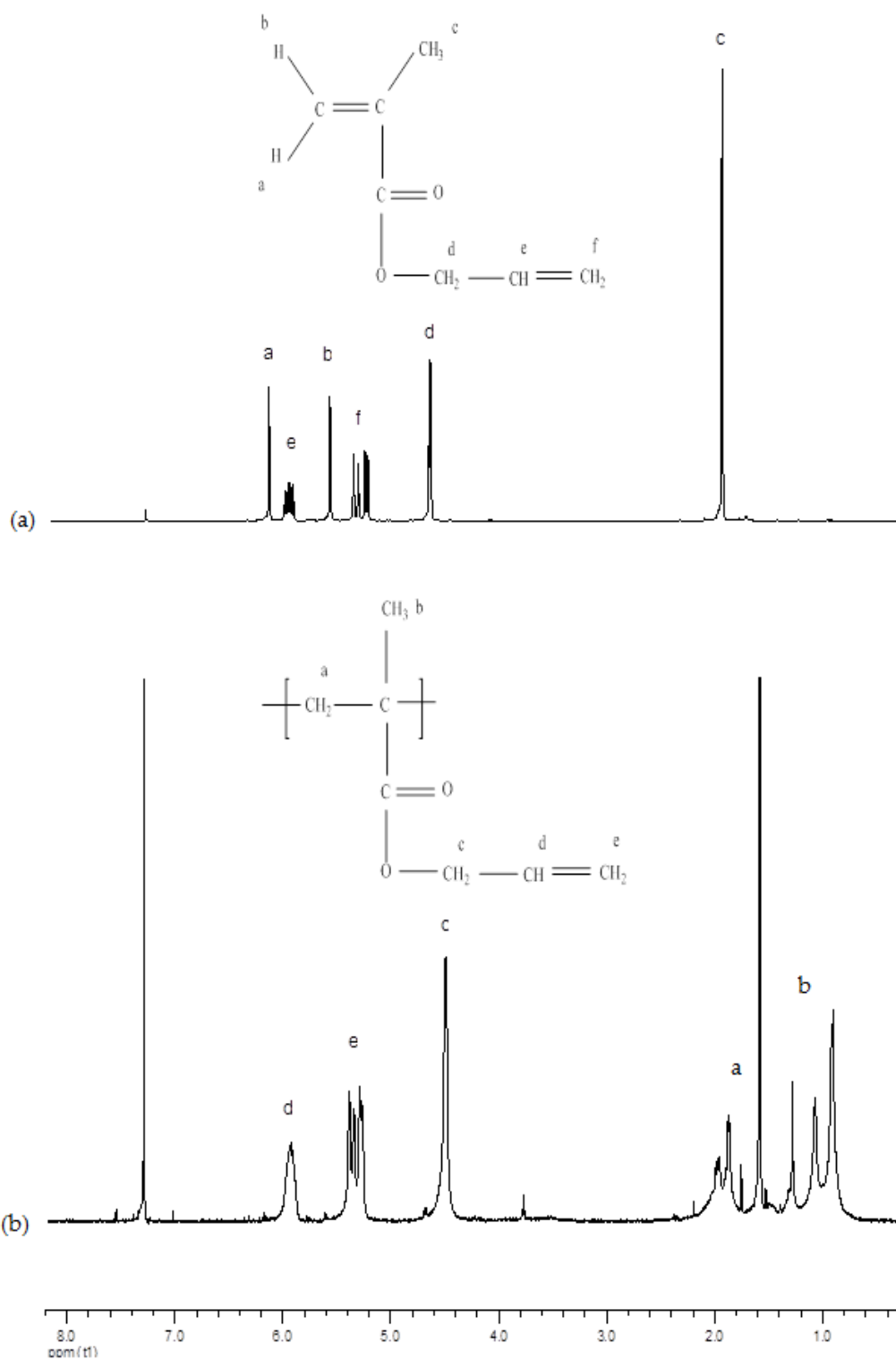


Figure 3.6  $^1\text{H-NMR}$  spectra of (a) allyl methacrylate and (b) poly(allyl methacrylate)

In the copolymer spectra shown in Fig. 3.7, CH<sub>3</sub> peaks were observed between 0.8-1.1 ppm and CH<sub>2</sub> proton peaks were at 1.5-2.1 ppm (Table 3.6). The peak at 6.45 ppm belongs to NH<sub>2</sub> and the peak between 4.4 ppm and 4.65 ppm belongs to -OCH<sub>2</sub> hydrogens. The peaks for CH<sub>2</sub> hydrogens of allyl group were seen at 5.2-5.45 ppm and CH hydrogen of the allyl group was between 5.8 ppm and 6.0 ppm. On the other hand, the peaks at 3.7 ppm belongs to -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> of allyl group showing that a small amount of the double bond of allyl group also opened up and contributed to the polymerization resulting with crosslinking.

Table 3.6 The peak assignments of the <sup>1</sup>H-NMR spectra of (PAAm-co-PAMA) copolymers

Proton Type	Chemical Shift (ppm) PAAm(75)-co-PAMA(25)	Chemical Shift (ppm) PAAm(85)-co-PAMA(15)	Chemical Shift (ppm) PAAm(95)-co-PAMA(5)
-CH <sub>2</sub> -CH-	1.5-2.1	1.4-2.1	1.6-2.1
-CH <sub>2</sub> -CH-	1.2-1.4	1.2-1.4	1.2-1.4
-NH <sub>2</sub>	6.45	6.45	6.45
-CH <sub>2</sub> -C(CH <sub>3</sub> )-	1.5-2.1	1.4-2.1	1.4-1.7
-CH <sub>3</sub>	0.8-1.1	0.75-1.1	0.75-1.1
-OCH <sub>2</sub> -	4.4-4.65	4.4-4.6	4.4-4.55
-OCH <sub>2</sub> CH=CH <sub>2</sub>	5.8-6.0	5.8-6.0	5.8-6.0
-OCH <sub>2</sub> CH=CH <sub>2</sub>	5.2-5.45	5.2-5.4	5.2-5.4
-OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	3.7	3.7	3.7
-OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	1.3-1.4	1.3-1.4	1.3-1.4



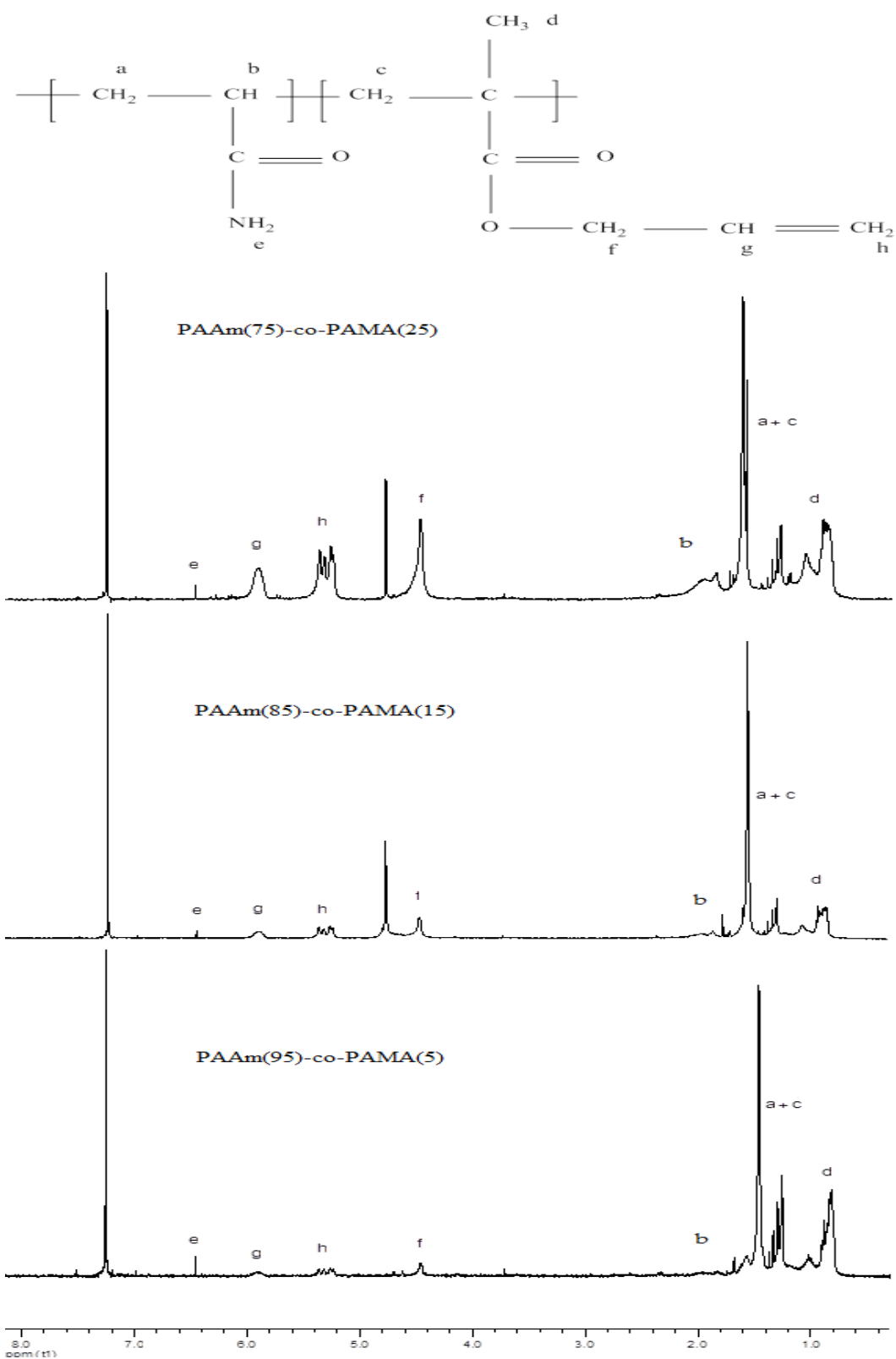


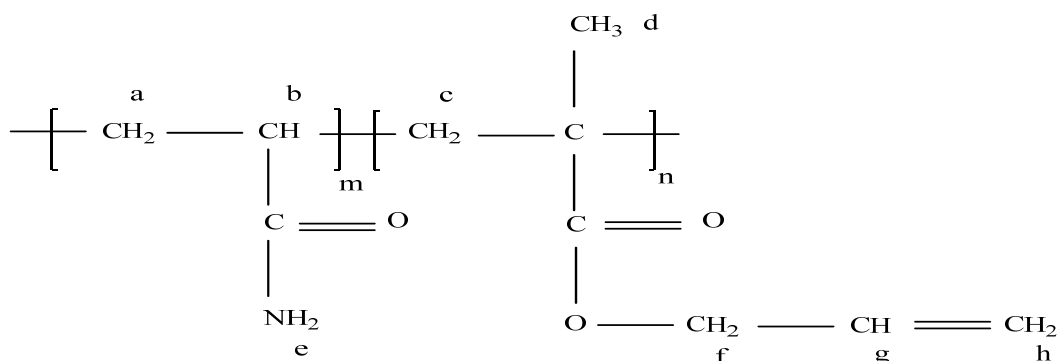
Figure 3.7 <sup>1</sup>H-NMR spectra of (PAAm-co-PAMA) copolymers

The percent of incorporated monomer into the copolymer was calculated from the following equations:

$$\% \text{ AAm} = (m/m+n) \times 100$$

$$\% \text{ AMA} = 100 - \% \text{ AAm}$$

$$\% \text{ AMA} = (n/n+m) \times 100$$



m and n values were calculated by using the following integral values obtained from the NMR spectra shown in Figure 3.8:

$$I(f) = I(-\text{OCH}_2) = 2n$$

$$I(c) + I(d) = I(-\text{CH}_2\text{CCH}_3) + I(-\text{CH}_3) = 5n$$

$$I(a) + I(b) = I(-\text{CH}_2\text{CH}) + I(-\text{CH}_2\text{CH}-) = 3m$$

Table 3.7.1 Calculation of the copolymer compositions

PAAm(75)-co-PAMA(25)	PAAm(85)-co-PAMA(15)	PAAm(95)-co-PAMA(5)
2n = 1 n = 0.5	2n = 1 n = 0.5	2n = 1 n = 0.5
5n+3m = 6.49 2.5+3m = 6.49 3m = 3.99 m = 1.33	5n+3m = 11.42 2.5+3m = 11.42 3m = 8.92 m = 2.97	5n+3m = 39.67 2.5+3m = 39.67 3m = 37.17 m = 12.39
%AAm = (m/m+n) x 100 = (1.33/1.83) x 100 = 72.7	%AAm = (m/m+n) x 100 = (2.97/3.47) x 100 = 85.6	%AAm = (m/m+n) x 100 = (12.39/12.89) x 100 = 96.1
%AMA = 100 - %AAm = 27.3	%AMA = 100 - %AAm = 14.4	%AMA = 100 - %AAm = 3.9

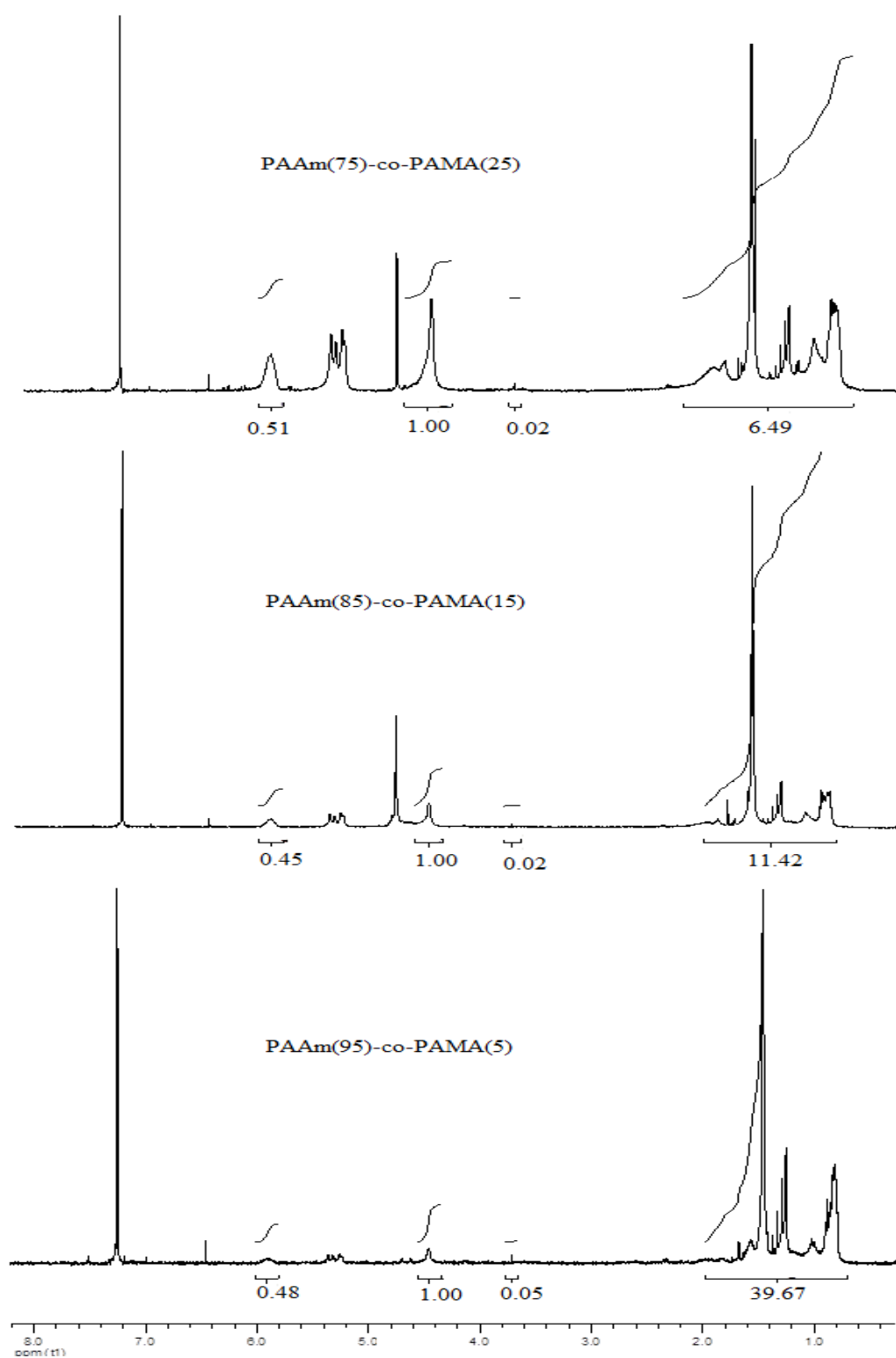
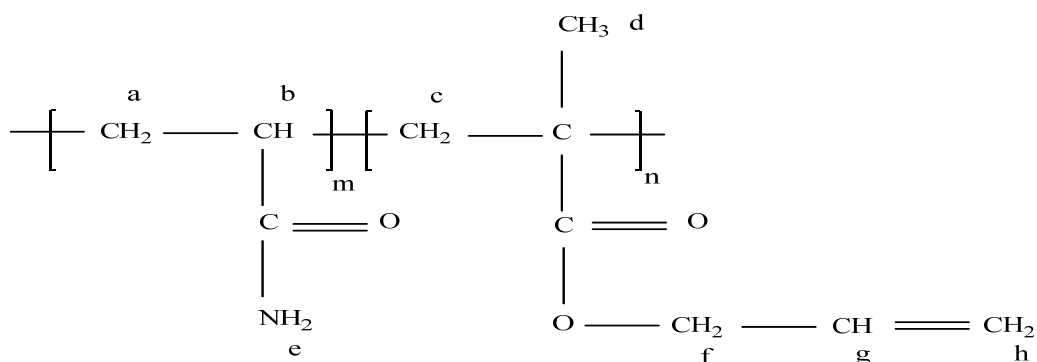


Figure 3.8.1  $^1\text{H-NMR}$  spectra of (PAAm-co-PAMA) copolymers with integral areas

m and n values were also calculated by using only integral values of the CH<sub>2</sub> peaks obtained from the NMR spectra shown in Figure 3.8.2:



$$I(c) = I(-\text{CH}_2\text{CCH}_3) = 2n$$

$$I(a) = I(-\text{CH}_2\text{CH}) = 2m$$

Table 3.7.2 Calculation of the copolymer compositions

PAAm(75)-co-PAMA(25)	PAAm(85)-co-PAMA(15)	PAAm(95)-co-PAMA(5)
$2n = 1$ $n = 0.5$	$2n = 1$ $n = 0.5$	$2n = 1$ $n = 0.5$
$2n+2m = 3.40$ $1+2m = 3.40$ $2m = 2.40$ $m = 1.20$	$2n+2m = 8.31$ $1+2m = 8.31$ $2m = 7.31$ $m = 3.66$	$2n+2m = 29.96$ $1+2m = 29.96$ $2m = 28.96$ $m = 14.48$
$\%A\text{Am} = (m/m+n) \times 100$ $= (1.20/1.70) \times 100$ $= 70.6$	$\%A\text{Am} = (m/m+n) \times 100$ $= (3.66/4.16) \times 100$ $= 87.9$	$\%A\text{Am} = (m/m+n) \times 100$ $= (14.48/14.98) \times 100$ $= 96.7$
$\%A\text{MA} = 100 - \%A\text{Am}$ $= 29.4$	$\%A\text{MA} = 100 - \%A\text{Am}$ $= 12.1$	$\%A\text{MA} = 100 - \%A\text{Am}$ $= 3.3$

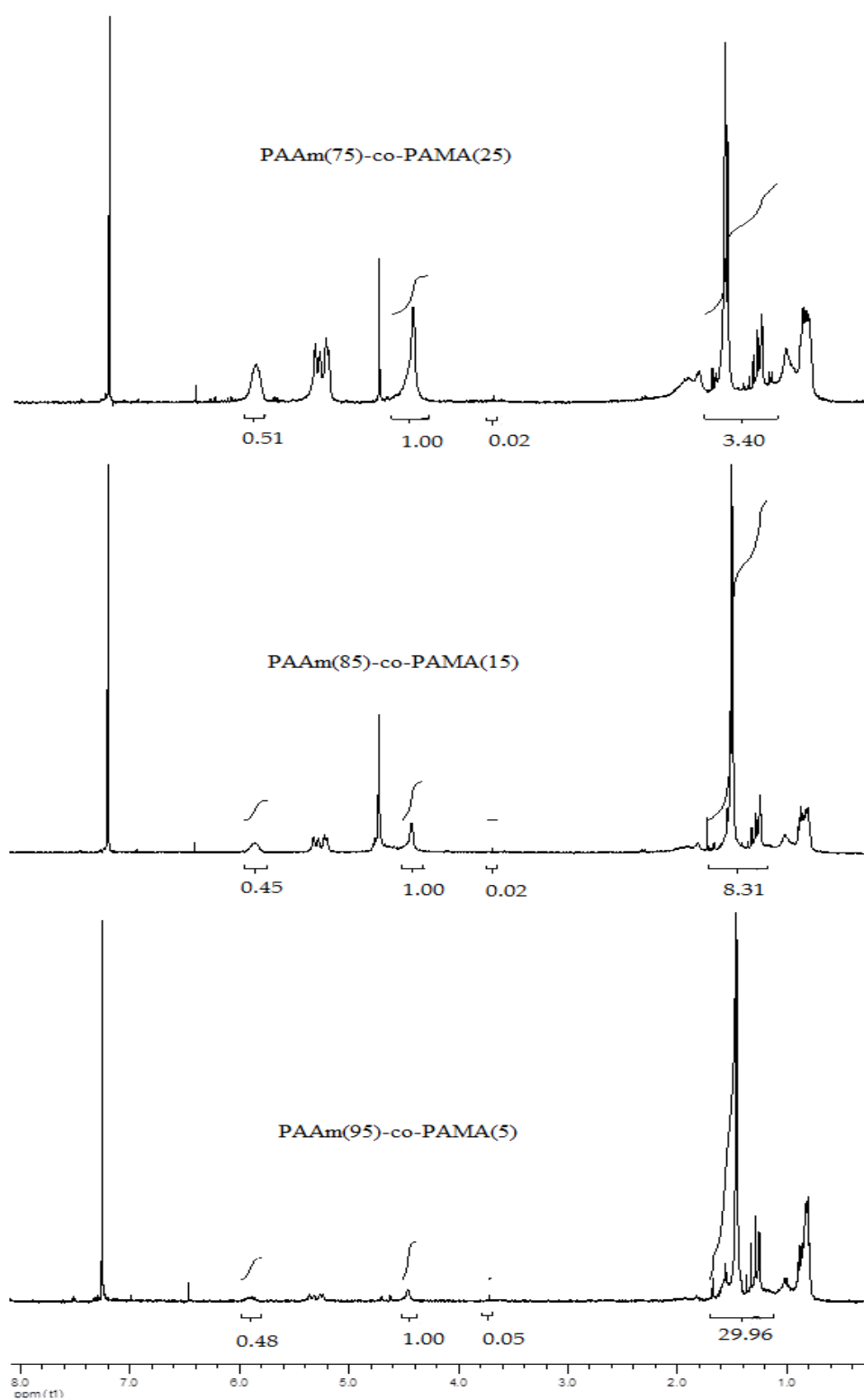


Figure 3.8.2  $^1\text{H-NMR}$  spectra of (PAAm-co-PAMA) copolymers with integral areas

The allyl groups which caused crosslinking were not taken into account in the composition calculations since intensity of the peak at 3.7 ppm were too low in each copolymer composition. When it is assumed all of the corresponding allyl groups resulted in crosslinking, the percentages of the crosslinking were calculated and given in Table 3.8.

Table 3.8 Calculation of the crosslinking percentage

PAAm(75)-co-PAMA(25)	PAAm(85)-co-PAMA(15)	PAAm(95)-co-PAMA(5)
$\frac{I(3.7\text{ppm})}{I(g)+I(3.7\text{ppm})} \times 100$ $\frac{[0.02/0.53] \times 100}{\%3.8}$	$\frac{I(3.7\text{ppm})}{I(g)+I(3.7\text{ppm})} \times 100$ $\frac{[0.02/0.47] \times 100}{\%4.3}$	$\frac{I(3.7\text{ppm})}{I(g)+I(3.7\text{ppm})} \times 100$ $\frac{[0.05/0.53] \times 100}{\%9.4}$

It can be seen that the percent crosslinking in the copolymers increases as the molar concentration of AMA decreases.

### 3.3 Differential Scanning Calorimetry (DSC) Results

The glass transition temperature ( $T_g$ ) of the copolymers and homopolymers were determined by DSC and shown in Fig. 3.9. The determined  $T_g$  values of the copolymers were lower than the determined  $T_g$  values of the homopolymers which could be explained by the mixed nature of the final polymers and impurities present in the reaction medium.

Table 3.9  $T_g$  values of the homopolymers and copolymers

Polymer	$T_g$ (°C)
PAAm	99.97
PAMA	84.83
PAAm(75)-co-PAMA(25)	48.50
PAAm(85)-co-PAMA(15)	53.48
PAAm(95)-co-PAMA(5)	77.18

In addition to experimental values,  $T_g$  of copolymers were also calculated theoretically according to Fox equation:

$$1/T_g^{AB} = (w_A/T_g^A) + (w_B/T_g^B) \quad (1)$$

where  $w_A$  and  $w_B$  are the mass fraction of comonomers [32]. The theoretical  $T_g$  values of the copolymers were in between the  $T_g$  values of the corresponding homopolymers, as expected and were given in Table 3.10.

Table 3.10 Calculated  $T_g$  values of copolymers

Copolymer	$w_A$	$w_B$	$T_g^{AB}$ (°C)
PAAm(75)-co-PAMA(25)	0.63	0.37	93.5
PAAm(85)-co-PAMA(15)	0.76	0.24	96.2
PAAm(95)-co-PAMA(5)	0.91	0.09	98.0

The  $T_g$  values of the copolymers were found to increase with the increase of acrylamide content. As the acrylamide amount increased in the copolymers, polymer-polymer interactions increased since acrylamide groups were smaller than allyl methacrylate groups and that caused a decrease in mobility of the chains which caused the increase in  $T_g$  [33].

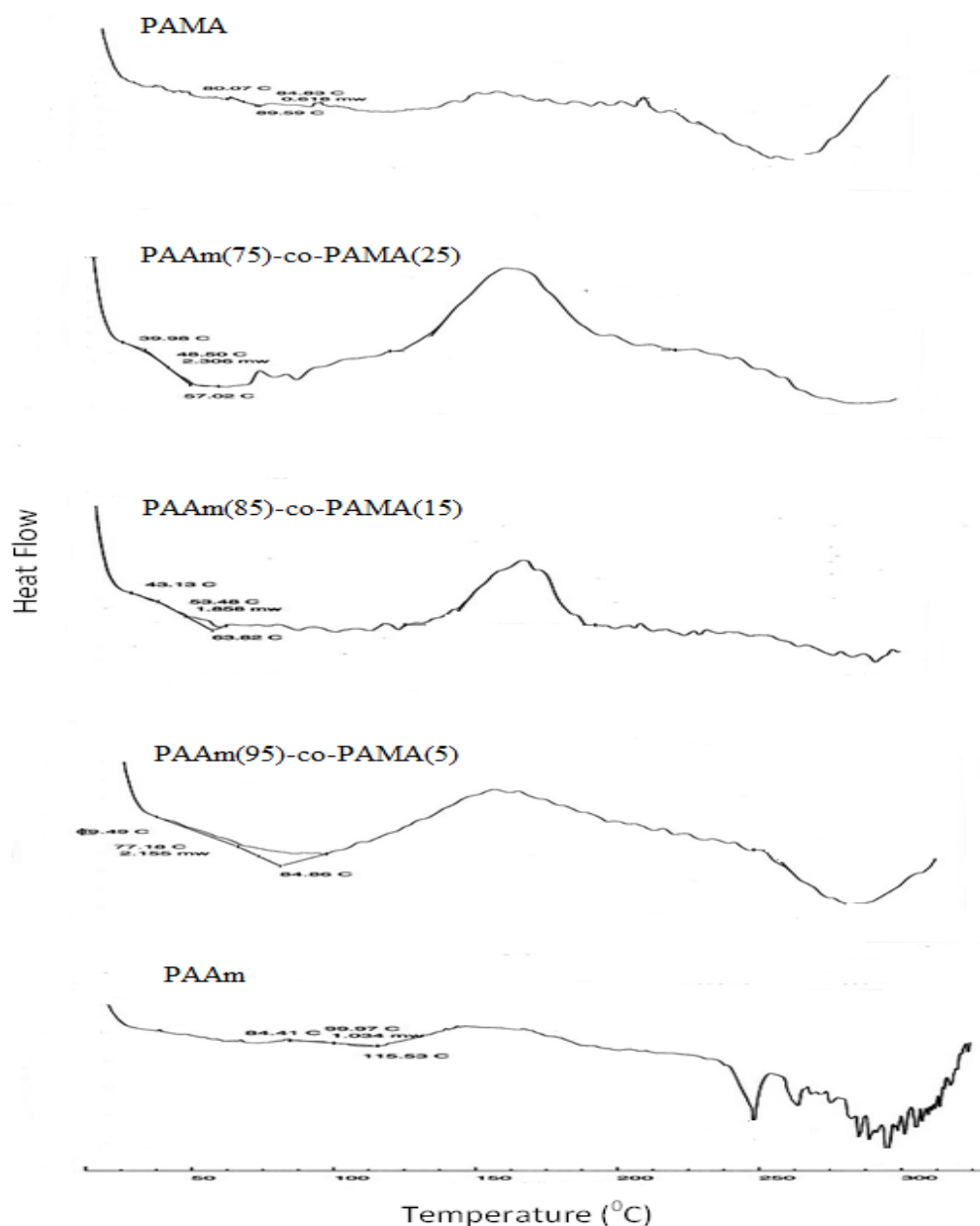


Figure 3.9 DSC thermograms of homopolymers and copolymers



### 3.4 Thermogravimetric Analysis (TGA) Results

Thermogravimetric analysis was carried out to determine degradation behavior of the copolymers. The weight loss behavior of homopolymers involves two steps as shown in Figure 3.10.

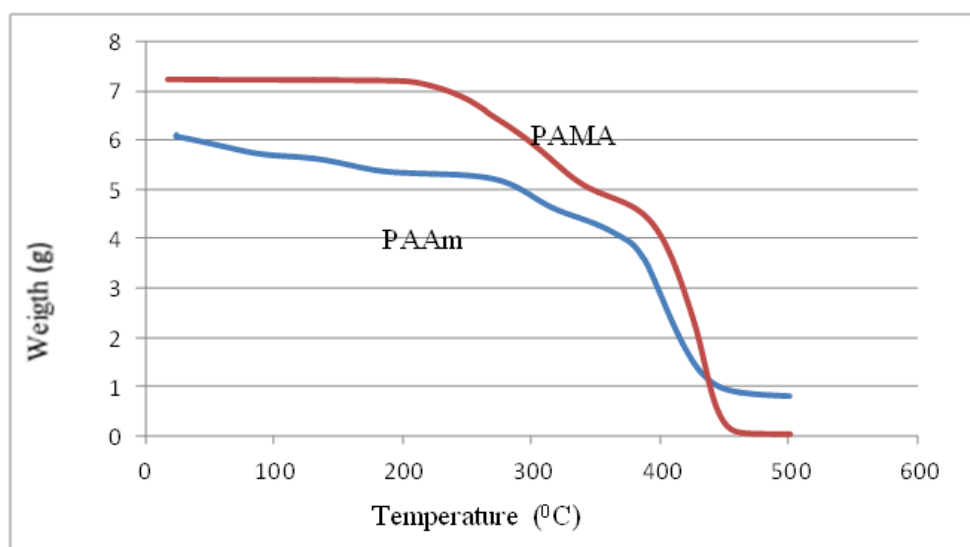


Figure 3.10 Weight loss vs temperature curves of homopolymers

The degradation process of copolymers also involved two steps. First step having weight loss about 5-10 % was assigned to the volatilization of volatile matter in the copolymers. In the second stage higher weight loss was observed due to depolymerization mechanism which includes side groups and main chains degradation and possible secondary decomposition reactions such as cracking and gasification processes [34, 35].

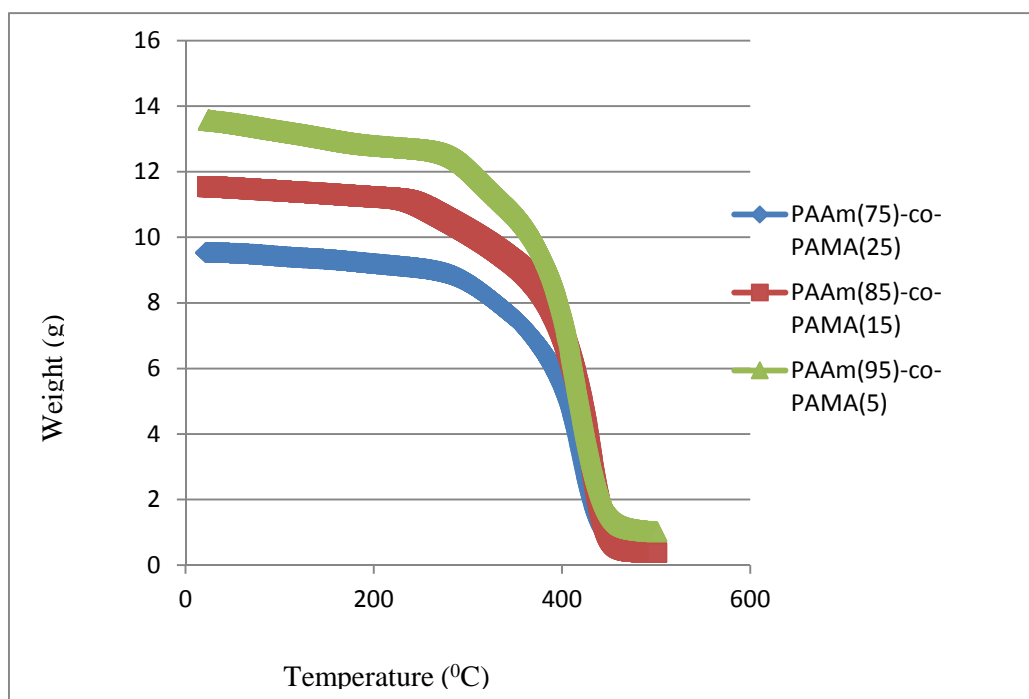


Figure 3.11 Weight loss vs temperature curves of copolymers

Table 3.11 Thermal decomposition properties of homopolymers and copolymers  
( $T_{10}$  = Temperature for 10% decomposition)

Polymer	$T_{10}$ (°C)
PAAm	158
PAAm(95)-co-PAMA(5)	297
PAAm(85)-co-PAMA(15)	287
PAAm(75)-co-PAMA(25)	301
PAMA	268

It is shown in Table 3.11 that PAMA has a higher main decomposition temperature than PAAm and same behavior is also observed for the corresponding copolymers.

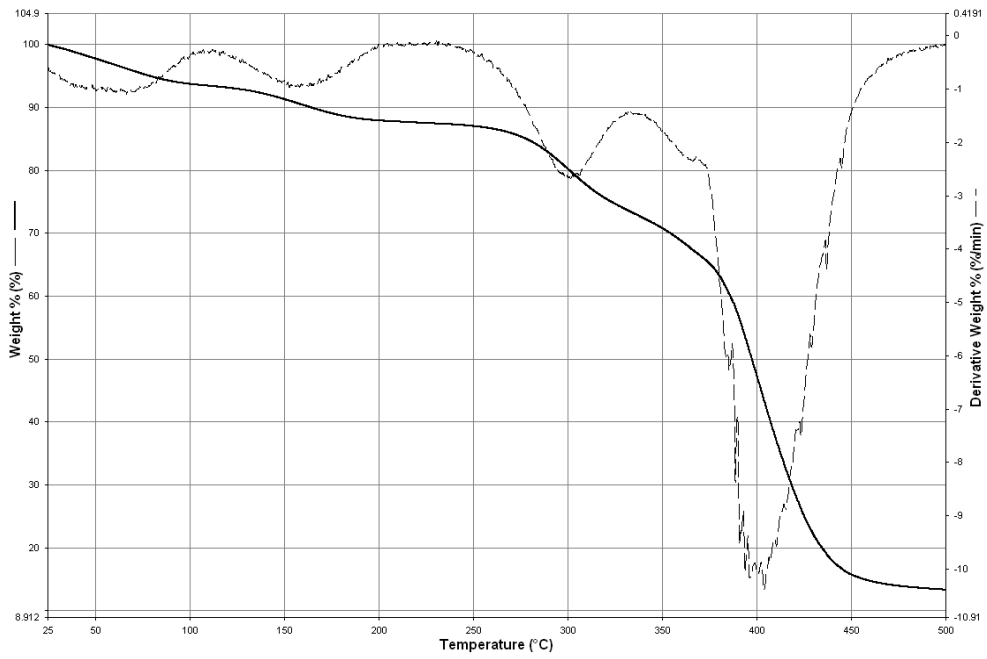


Figure 3.12 TGA thermogram of PAAm

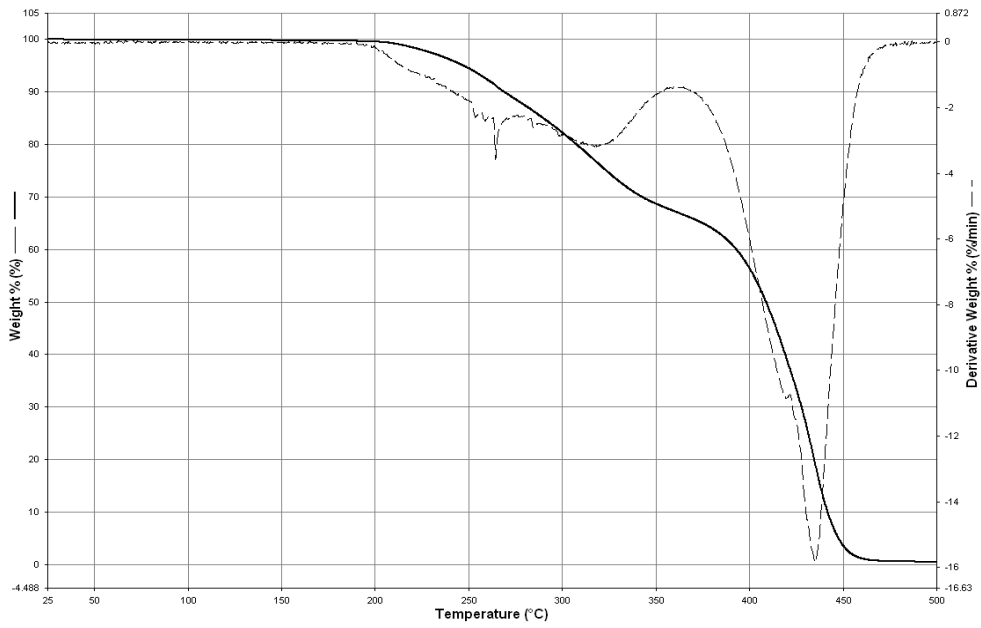


Figure 3.13 TGA thermogram of PAMA

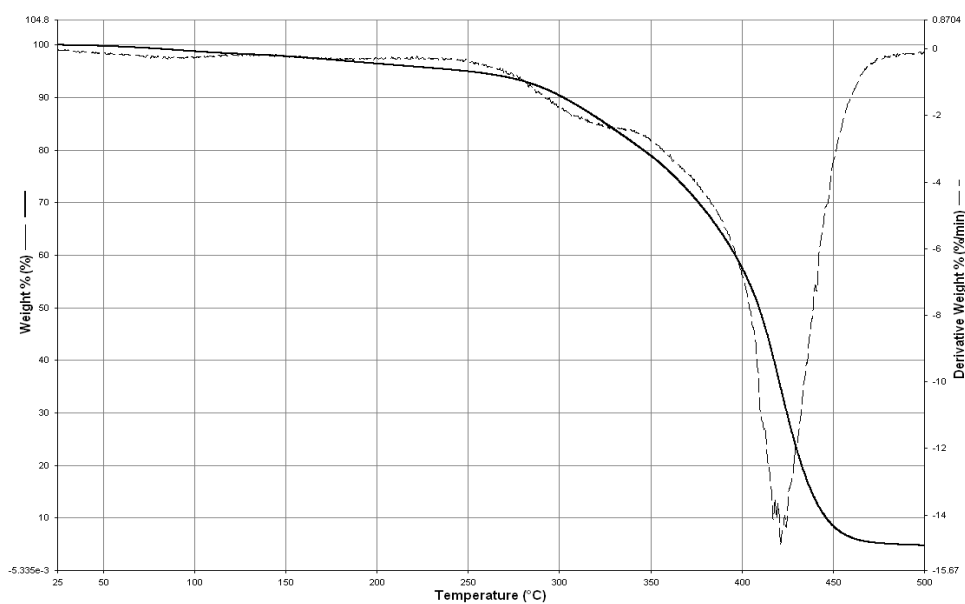


Figure 3.14 TGA thermogram of PAAm(75)-co-PAMA(25)

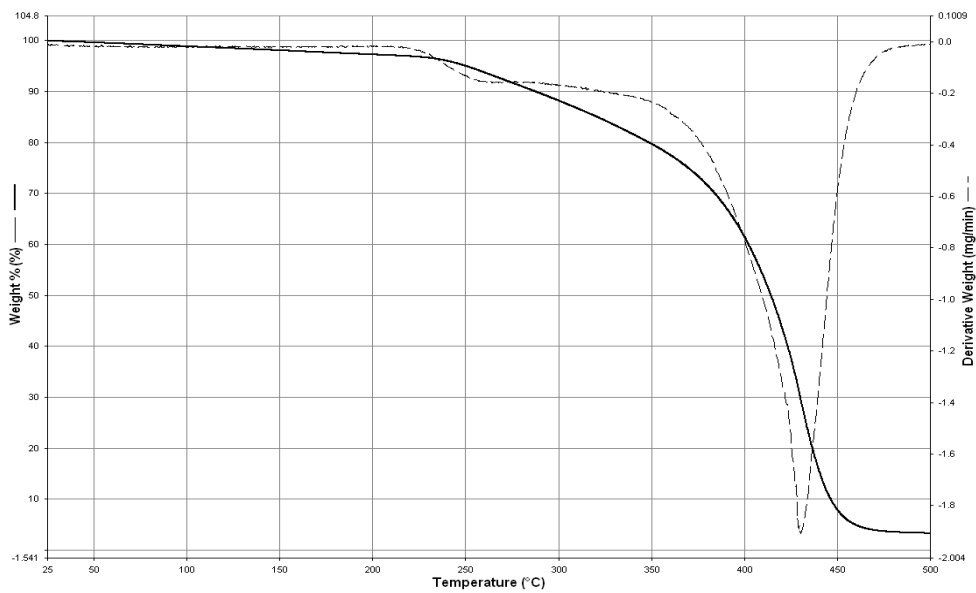


Figure 3.15 TGA thermogram of PAAm(85)-co-PAMA(15)

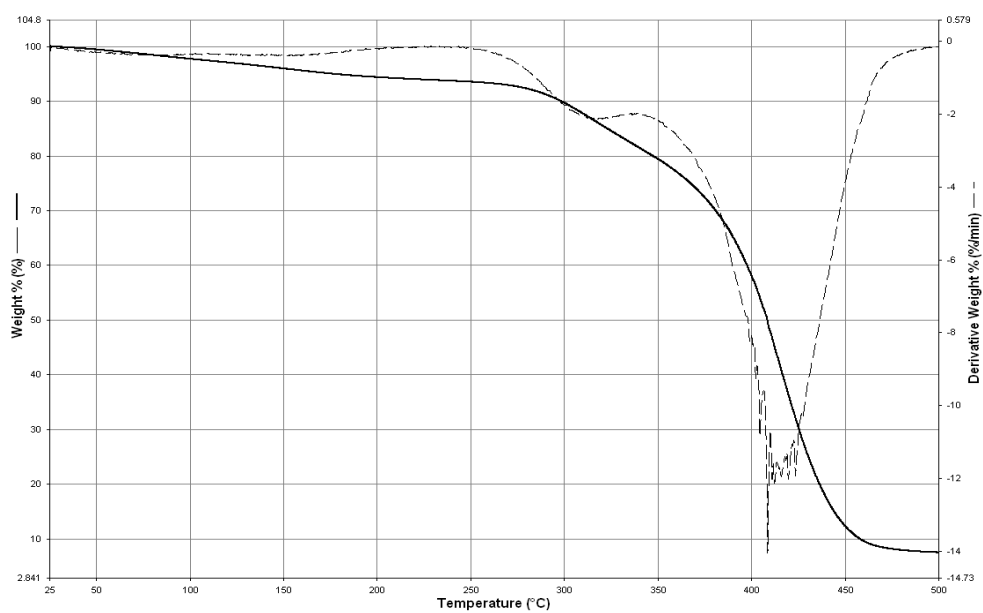


Figure 3.16 TGA thermogram of PAAm(95)-co-PAMA(5)

### 3.5 Swelling Behavior Analysis

Copolymers were dried in vacuum oven at 40 °C for one day and weighted to determine the dry gel weight. 0.1g of each were immersed in 100 mL distilled water at room temperature for one week and weighted again to find out the swollen gel weight. Swelling capacity was calculated by using the following equation:

$$SC (\%) = [ (W_s - W_d) / (W_d) ] \times 100 \quad (2)$$

where  $W_s$  and  $W_d$  are weights of the swollen and dry gel, respectively.

Table 3.12 Swelling capacities of the copolymers

Polymer	Swelling Capacity (%)
PAAm	dissolved
PAMA	5.4
PAAm(75)-co-PAMA(25)	24.5
PAAm(85)-co-PAMA(15)	66.9
PAAm(95)-co-PAMA(5)	77.3

Hydrophilicity is the most important parameter in water absorbency. It is expected that as the hydrophilicity increases, water absorbency should also increase. By looking at the results, it is clear that as the acrylamide ratio increases in the copolymer composition, swelling capacity of the copolymer also increases. Since acrylamide is the hydrophilic component in the copolymer, results are consistent with this theory.

### 3.6 Gel Permeation Chromatography (GPC) Results

Molecular weights of the homopolymers and copolymers were measured by GPC and given in Table 3.13.

Table 3.13 GPC results of the homopolymers and copolymers

<b>Polymer</b>	<b>M<sub>n</sub></b>	<b>M<sub>w</sub></b>	<b>PDI</b>
PAAm	1.6x10 <sup>4</sup>	9.3x10 <sup>4</sup>	5.8
PAMA	6.2x10 <sup>4</sup>	2.1x10 <sup>5</sup>	3.4
PAAm(75)-co-PAMA(25)	6.98x10 <sup>4</sup>	5.92x10 <sup>5</sup>	8.5
PAAm(85)-co-PAMA(15)	8.5x10 <sup>4</sup>	1.6x10 <sup>6</sup>	18.8
PAAm(95)-co-PAMA(5)	5.5x10 <sup>5</sup>	8.2x10 <sup>5</sup>	1.5

It was seen that M<sub>n</sub> values of the copolymers increased as the acrylamide content in copolymers increases. Results belong to the soluble fraction of the copolymers since they were not completely soluble in the GPC solvent.

## CHAPTER 4

### CONCLUSIONS

From the results of the experimental and characterization investigations, following conclusions can be achieved:

FTIR and NMR confirmed that comonomers were incorporated into copolymer backbone.

Polymerization carried out through vinyl double bonds and allyl groups mostly stayed as pendant groups in the copolymer chains.

Although most of the allyl groups stayed as pendant, a small percentage of them caused crosslinking and crosslinking percentage increased as the allyl methacrylate content decreased in the copolymer compositions.

DSC results showed that  $T_g$  values of the copolymers increased as the acrylamide content increased in the copolymers due to the decrease in mobility.

Swelling capacity measurements showed that as the acrylamide content increased water absorbency of the gels increased due to the high hydrophilicity of acrylamide. On the other hand, as the allyl methacrylate content decreased



crosslinking percentage increased in the copolymeric gels and that also could cause an increase in the swelling capacity.

TGA thermograms showed that copolymers had two step degradation behavior; volatilization of volatile matter and depolymerization mechanism with secondary decomposition reactions.

GPC results showed that copolymers had quite high molecular weights. Different copolymer compositions will be synthesized in future study.

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