2-ACRYLAMIDO-2-METHYL-1-PROPANESULFONIC ACID - METHACRYLIC ACID COPOLYMER AND ITS POLYETHYLENE GLYCOL METHYL ETHER DERIVATIVES AS SUPERPLASTICIZERS IN CONCRETE

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ABSTRACT

2-ACRYLAMIDO-2-METHYL-1-PROPANESULFONIC ACID - METHACRYLIC ACID COPOLYMER AND ITS POLY (ETHYLENE GLYCOL) METHYL ETHER DERIVATIVES AS SUPERPLASTICIZER IN CONCRETE

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Polymers in concrete have received considerable attention over the past 30 years. Superplasticizers are one of the admixtures which have polymeric structure. In this study, polycarboxylate type slump-releasing dispersant, which is a copolymer of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and methacrylic acid (MAA), was synthesized in different feed compositions. The synthesis procedure of this copolymer was retrieved from literature. The derivatives of this water-soluble copolymer (AMPS-MAA) were synthesized by a macromonomer which was synthesized by the esterification of poly(ethylene glycol) methyl ether (PEG) with MAA (PEGMA) and then copolymerizing this macromonomer with AMPS monomer, the resulting copolymer is AMPS-PEGMA. In order to study the methyl group effect on fluidity, the other type of macromonomer (PEGA), composed of PEG and acrylic acid (AA), was synthesized and copolymerized with AMPS monomer, giving AMPS-PEGA. The structures of synthesized polymers were verified by NMR and FT-IR analysis. The slump-releasing effect of the synthesized copolymers was studied in terms of reaction pH, composition, molecular weight, amount of PEG side chains, and molecular weight of PEG side chains. The AMPS-MAA copolymer with 40% AMPS content was the most effective in promoting the fluidity of cement pastes. In scope of reaction pH, the AMPS-MAA copolymer, synthesized at a pH of 11, gave the most effective result on fluidity of the cement pastes. In copolymers of PEG acrylate macromonomers and AMPS monomers, copolymers with 5% PEG acrylate content showed the highest fluidity both in copolymers of PEGA and PEGMA. In copolymers with PEG side chains, the 15% AMPS-PEGA copolymer synthesized at pH of 6 gave the most effective result on fluidity of cement pastes. In the study of mechanical properties of the mortar samples prepared by the copolymers selected, AMPS-PEGA copolymer with 25% PEG content showed the highest flexural strength, and AMPS-MAA copolymer with 60% AMPS content and a reaction pH of 11 gave the highest compressive strength. In this study, zeta potential measurements were also performed to analyze the fluidity behavior of the copolymers.

Keywords: polyelectrolyte, superplasticizer, concrete, fluidity, grafting.

ÖZ

BETON İÇİN SÜPERAKIŞKANLAŞTIRICI OLARAK 2-AKRİLAMİDO–2-METİL–1-PROPANSÜLFONİK ASİT – METAKRİLİK ASİT KOPOLİMERİ VE POLİ(ETİLEN GLİKOL) METİL ETER TÜREVLERİ

Tuzcu, Gözde
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Betonda polimer kullanımı, son 30 yılda hatırı sayılır bir dikkat topladı. Süperakışkanlaştırıcılar da betonda kullanılan polimer yapılı katkılardan bir tanesidir. Polikarboksilat tipi yayılma artırıcı bir kopolimer olan 2-akrilamido–2-metil–1-propansülfonik asit (AMPS) ve metakrilik asidin (MAA) kopolimeri farklı besleme oranları ile sentezlenmiştir. Bu kopolimerin sentez yöntemi literatürden alınmıştır. Suda çözünebilen bir kopolimer olan AMPS-MAA kopolimerinin farlı türevleri, poli(etilen glikol) metil eter (PEG) ve metakrilik asidin (MAA) esterifikasyonu ile bir makromonomer sentezlenmesi (PEGMA) ve bu makromonomerin AMPS monomeriyle kopolimerizasyonu ile sentezlenmiştir (AMPS-PEGMA). Ayrıca, metil grubunun akışkanlık ve kompozisyon üzerine etkilerini incelemek için, PEG ve akrilik asidin (AA) esterifikasyonu ile elde edilen makromonomerin AMPS ile kopolimerizasyonu sonucunda oluşan kopolimer (AMPS-PEGA) sentezlenmiştir. Sentezlenen kopolimerlerin yapıları FT-IR ve NMR spektrumları ile tasdik edilmiştir. Sentezlenen kopolimerlerin çimento pastasının akışkanlığı üzerinde olan etkisi, reaksiyon pH’ı, kompozisyon, moleküler ağılık, PEG yan zincir miktarı ve PEG yan zincirinin moleküler ağırlığı açısından incelenmiştir. %40 AMPS içeren AMPS-MAA kopolimeri çimento pastasının akışkanlığı üzerinde en çok etkiye sahip olmuştur. Reaksiyon pH’ı açısından, pH 11’de sentezlenen AMPS-MAA kopolimeri en yüksek akışkanlığı göstermiştir. PEG Akrilat ve AMPS monomerlerinin oluşturduğu kopolimerler arasında, %5 PEG akrilat içeren kopolimerler (akrilat ve metakrilat) çimento pastasının yayılmasında en yüksek etkiyi göstermiştir. PEG akrilatlı kopolimerler arasında pH 6’ da sentezlenen 15% AMPS-PEGA kopolimeri en yüksek yayılmayı göstermiştir. Mekanik özellikleri bakımından, 25% PEGMA ihtiva eden AMPS-PEGMA kopolimeri en yüksek bükülme dayanımını, pH 11’ de sentezlenen % 60 AMPS ihtiva eden AMPS-MAA kopolimeri en yüksek basınç dayanımını göstermiştir. Bu çalışmada, ayrıca, kopolimerlerin akışkanlık davranışlarını analiz edebilmek için, zeta potansiyel ölçümleri gerçekleştirilmiştir.

Anahtar Kelimeler: polielektrolit, süperakışkanlaştırıcı, beton, akışkanlık, aşılama.

To my family

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LIST OF ABBREVIATIONS

AMPS: 2-acrylamido-2-methyl-1-propanesulfonic acid
MAA: methacrylic acid
AA: acrylic acid
PEG: Poly (ethylene glycol) methyl ether
AMPS-MAA: 2-acrylamido-2-methyl-1-propanesulfonic acid / methacrylic acid copolymer
AMPS-PEGMA: 2-acrylamido-2-methyl-1-propanesulfonic acid / poly (ethylene glycol) methyl ether methacrylate copolymer
AMPS-PEGA: 2-acrylamido-2-methyl-1-propanesulfonic acid / poly (ethylene glycol) methyl ether acrylate copolymer
NMR: Nuclear Magnetic Resonance
FT-IR: Fourier Transform Infrared Spectroscopy
ASTM: American Society for Testing and Materials
SNF: Sulfonated naphthalene formaldehyde
SMF: Sulfonated melamine formaldehyde
TS: Turkish Standards
BS: British Standards
EN: European Standards in English

CHAPTER 1

INTRODUCTION

1.1 Concrete

Concrete is a construction material which was firstly used in early 1840s. Communities around the world rely on concrete as a safe, strong and simple building material. It is used in all types of construction; from simple houses to skyscrapers, from tunnels to bridges.

Concrete is composed of four main material groups;

- Water
- Aggregates
- Cement
- Admixtures

Water, used in concrete, shall be free from sewage, oil, acid, strong alkalis or vegetable matter, and also shall be free from clay and loam [1]. Generally, if the water which will be used for concrete is potable, it is generally satisfactory for use in concrete.

Aggregates have generally two basic types; coarse aggregates that are crushed rock, and gravel or screenings; and fine aggregates that are fine and coarse sands and crusher fines. Aggregate is the filler of the concrete, but the mechanical property is mainly given by the aggregates in concrete. Although aggregates make up three fourths of the volume of concrete, the active constituent of concrete is cement paste, and the properties and the performance of concrete are largely determined by the properties of cement paste [2].

When cement is mixed with water it becomes a paste, and this paste acts like glue for adhesion of the aggregates [3]. Cement consists of a mixture of oxides of calcium, silicon and aluminum, and it is made by heating limestone with small quantities of other materials (such as clay) to 1450°C in a kiln. The resulting hard substance, called ‘clinker’, is then ground with a small amount of gypsum into a powder to make ‘Ordinary Portland Cement’, the most commonly used type of cement. According to ASTM C-150, Portland cement is hydraulic cement produced by pulverizing clinker consisting essentially of hydraulic calcium silicates, usually containing one or more types of calcium sulfate as an interground addition [2]. Normal Portland cement consists of at least two-thirds by mass of calcium silicates ($3CaO.SiO_2$ and $2CaO.SiO_2$), the remainder consisting of aluminum- and iron-containing clinker phases and other compounds. The ratio of CaO to SiO_2 is not less than 2.0 (EN 197-1). Chemical admixtures are materials in the form of powder or fluids that are added to the concrete to give it certain characteristics not obtainable with plain concrete mixes. In general use, admixture dosages are less than 5% by mass of cement, and are added to the concrete at the time of batching or mixing. The most common types of admixtures are [4]:

- Accelerators: They speed up the hydration (hardening) of the concrete. Without accelerants, concrete may take years to cure.
- Retarders: They decrease the rate of the hydration of concrete, and are used in large or difficult pours. In this situation, partial setting before the pour may be completed is undesirable.
- Air-entrainers: They entrain and distribute tiny air bubbles in the concrete, which will reduce damage during freeze-thaw cycles thereby increasing the concrete's durability. However, entrained air must be very carefully controlled as each 1% of air may result in 5% decrease in compressive strength.

- Plasticizers (water-reducing admixtures): They increase the workability of plastic or "fresh" concrete, allowing it to be placed more easily, with less consolidating effort.
- Superplasticizers (high-range water-reducing admixtures): They are a class of plasticizers which have fewer deleterious effects when used to significantly increase workability. Alternatively, plasticizers can be used to reduce the water content of a concrete (and have been called water reducers due to this application) while maintaining workability. This improves its strength and durability characteristics.
- Pigments: They can be used to change the color of concrete, for aesthetics.
- Corrosion inhibitors: They are used to minimize the corrosion of steel and steel bars in concrete.
- Bonding agents: They are used to create a bond between old and new concrete.
- Pumping aids: They improve pumpability, thicken the paste, and reduce dewatering of the paste.

1.1.1 Superplasticizers used in Concrete

Superplasticizers or water reducers are chemical admixtures that can be added to concrete mixtures to improve workability. Strength of concrete is inversely proportional to the amount of water added or water-cement (w/c) ratio. In order to produce stronger concrete, less water should be added, which makes the concrete mixture very unworkable and difficult to mix, necessitating the use of plasticizers and superplasticizers [5].

The superplasticizers can also have some additional functions like accelerating or retarding cement hydration, and air entraining. The accelerating water-reducing admixtures, while possessing the water-reducing capability, give higher strengths during the earlier hydration period and faster setting time which allow finishing operations to be carried out in a timely manner, particularly at lower temperatures. The retarding water-reducing admixtures behave in similar manner and have similar chemical composition with the normal superplasticizers. However, using at a higher dosage level of superplasticizer extends the period of plastic state of the concrete. This means that the time available for transport, handling, placing and finishing is lengthened. The air-entraining water-reducing agents possess the ability to entrain microscopic air bubbles into the cement paste therefore allowing a reduction in the water-cement ratio greater than that which would be obtained by the air entrainment itself [6].

Primarily, as a water reducer, Ca, Na or NH_4 salts of lignosulfonic acid, Na, NH_4 or triethanolamine salts of hydrocarboxylic acids, and carbohydrates are used. Lignosulfonates containing -OH, -COOH, and $–SO_3H$ groups are more widely used than others. Gluconic acid-based admixtures are also used extensively. The role of water reducers in terms of their effect on the hydration of cement is similar to that of accelerators and retarders. Superplasticizers belong to a class of water reducers chemically different from the primary water reducers. Primary water reducers decrease the water requirements of concrete by about 10-15%, whereas superplasticizers are capable of reducing the water requirements by about 20-40%. [2]

There are three generations of superplasticizers in concrete. The first generation, namely plasticizers, is commonly manufactured from lignosulfonates, a by-product from the paper industry. The second generation superplasticizers have generally been manufactured from sulfonated naphthalene formaldehyde or sulfonated melamine formaldehyde, although the third, new generation products based on polycarboxylic ethers are recently generated and now developing. Traditional lignosulfonate based plasticizers and naphthalene and melamine based superplasticizers disperse the flocculated cement particles through a mechanism of electrostatic repulsion. In normal plasticizers, the active substances are adsorbed on to the cement particles, giving them a negative charge, which leads to repulsion between particles. Naphthalene and melamine superplasticizers are organic polymers. The long molecules wrap themselves around the cement particles, giving them a highly negative charge so that they repel each other. Polycarboxylate ether based superplasticizers, the new generation of superplasticizers are not only chemically different from the older sulfonated melamine and naphthalene based products but their action mechanism is also different, giving cement dispersion by steric stabilization. This form of dispersion is more powerful in its effect and gives improved workability retention to the cementitious mix [5].

1.1.1.1 Lignosulfonates

Lignosulfonates, or sulfonated lignin, are water-soluble anionic polyelectrolyte polymers; they are by-products from the production of wood pulp using sulfite pulping.

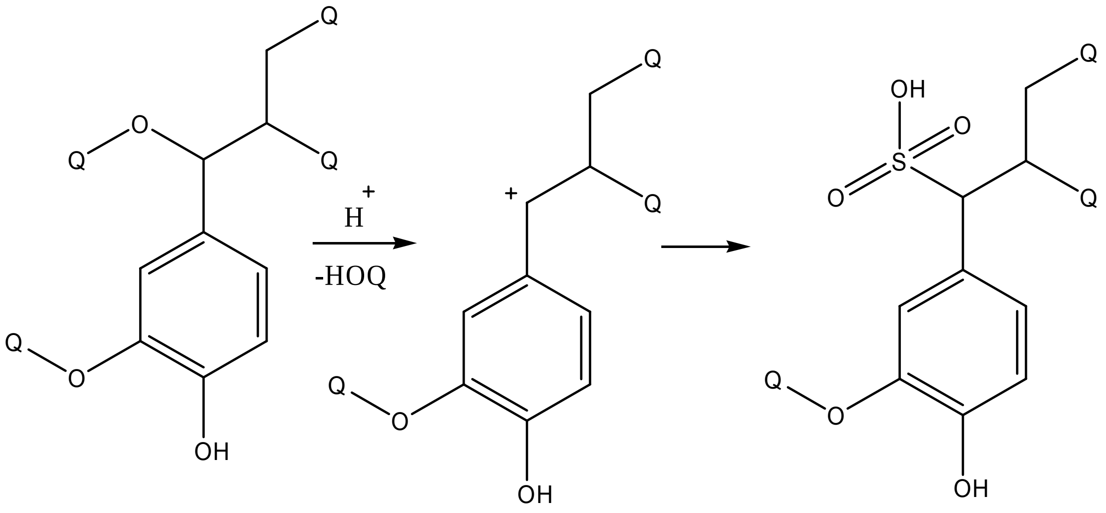

Figure 1.1 The structures of lignin and lignosulfonate

Lignin is a complex material which makes up approximately 20% of the composition of wood. The lignosulfonate molecule is a substituted phenyl propane unit containing hydroxyl, carboxyl, methoxy and sulfonic acid groups. In Fig. 1.1 the groups labeled by Q may be wide variety of groups found in the structure of lignin. The lignosulfonate monomer will be polymerized from the phenolic OH and methylol group, as it can be seen from the Fig. 1.2.

During the process for production of paper-making pulp from wood, waste liquor is formed as a by-product containing a complex mixture of substances, including decomposition products of lignin and cellulose, sulfonation products of lignin, various carbohydrates (sugars) and free sulfurous acid or sulfates. Subsequent neutralization, precipitation and fermentation processes [7] produce a range of lignosulfonates of varying purity and composition.

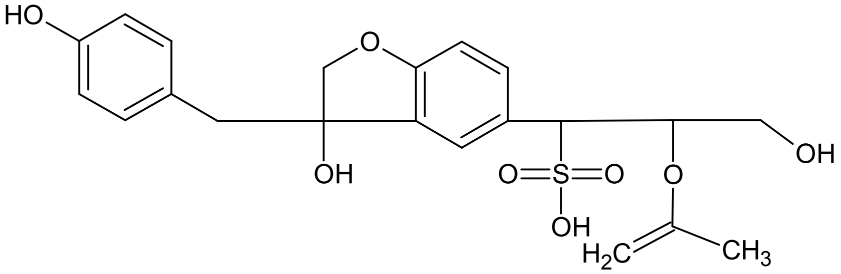

Figure 1.2 Repeating unit of a lignosulfonate molecule

The Lignosulfonates formed the basis of almost all the available water-reducing admixtures until 1950s, when the hydrocarboxylic acid salts were developed.

It has been found [8] that the lignosulfonate polymer is not a simple linear flexible coiled chain, but forms spherical microgels. Thus the charges are predominantly on the outside of the spheroid with the internal carboxyl groups and sulfonate group being non-ionized [6]. These ionic groups outside the microgel is adsorbed to the cement particle and gives it a negative charge, and by the electrostatic repulsion, cement particles are dispersed in aqueous solution.

Lignosulfonate admixtures are used widely as normal water reducers. At a dosage of 0.05-0.1% of cement weight, they reduce the water requirement by 6 to 10%. At higher dosages, excessive retardation of set and entrainment of air occurs and hence they cannot be used as high range water-reducing admixtures. Although, the naphthalene and melamine sulfonates have a water reducing ratio about 20-30%, and do not affect the setting and air entraining properties adversely, lignosulfonates are still in use because of their low cost. [2]

Rixom and Waddicor [9] prepared various types of lignosulfonates and studied their effect on concrete slump and water requirement. The significance of molecular weight, cationic species, degree of sulfonation and carbohydrate contents on initial set, workability and strength characteristics of concrete was studied. It was concluded that increase in molecular weight of lignosulfonate resulted in a more workable concrete, and retardation of initial set, but a slight reduction in compressive strength at the end of 24 hours. On the other hand, increase of sulfonation did not affect the workability or entrained air but it reduced the setting time. It was also found that sodium lignosulfonate was a more effective plasticizer than calcium lignosulfonate. Generally, increased amounts of sugar in lignosulfonate resulted in longer setting times.

1.1.1.2 Melamine and Naphthalene Sulfonates

Sulfonated melamine formaldehyde condensates and sulfonated naphthalene formaldehyde condensates are classified as superplasticizers of the first generation.

These admixtures, after being absorbed on cement particles, create electrostatic repulsions and overcome attractive forces. This results in the dissociation of the cement agglomerates into primary particles with significant decrease in the viscosity of the mixes and a great improvement in the workability of fresh concrete without segregation or bleeding [10].

1.1.1.2.1 Sulfonated Naphthalene Formaldehyde (SNF)

This raw material was one of the first materials referred to in the literature as a water-reducing agent.

The material is produced from naphthalene by oleum (sulfur trioxide in sulfuric acid) or sulfur trioxide sulfonation under conditions conductive to the formation of the β sulfonate. Subsequent reaction with formaldehyde leads to polymerization and the sulfonic acid is neutralized with sodium hydroxide [11]. Formaldehyde causes methylolation and from these methylol groups, polymerization occurs by condensation, which is illustrated in Fig. 1.3.

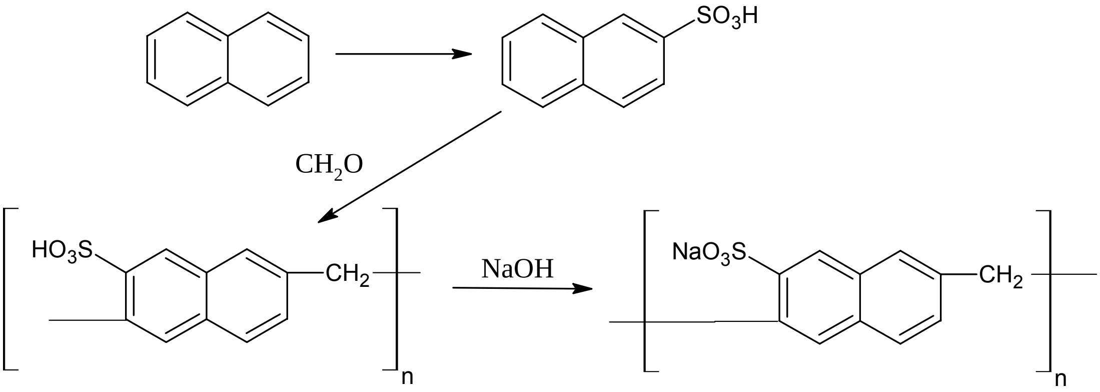

Figure 1.3 Formation of sulfonated naphthalene formaldehyde from naphthalene

1.1.1.2.2 Sulfonated Melamine Formaldehyde (SMF)

This type of chemical product was originally developed in 1950s as a dispersant for a wide variety of industries, but it was not until some 10 years later that the possibilities for its use in concrete were recognized. It is manufactured by normal resinification techniques as it is shown in Fig. 1.4; a novel four-step process has been developed for the synthesis of SMF. The four steps included hydroxymethylation, sulfonation, low pH condensation and high pH rearrangement. [2] The length of the polymerization time will influence the molecular weight of the product, the most useful average molecular weight being about 30,000. This material is normally used alone or in combination with SNF. When used alone it is typified by having minimal effect on air entrainment or setting time.

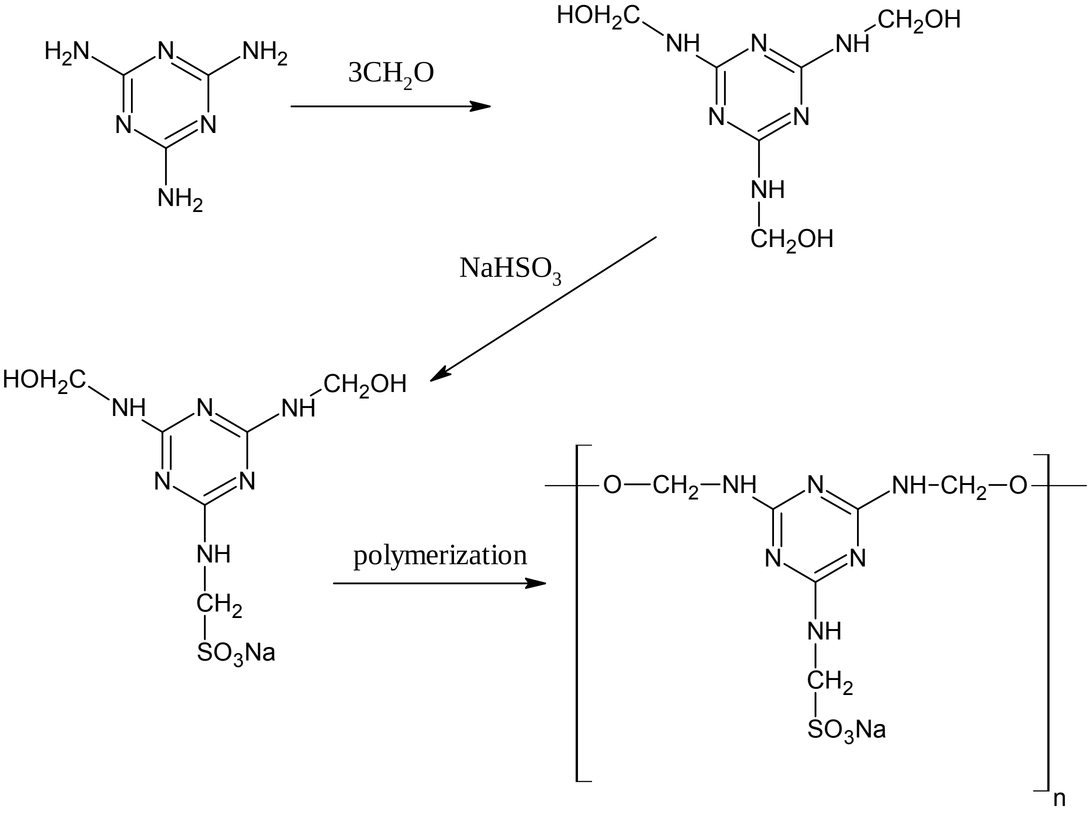

Figure 1.4 Formation of sulfonated melamine formaldehyde resin from melamine.

The general structure of melamine and naphthalene sulfonate resin is network structure. This structure can be controlled by the amount of formaldehyde which causes methylolation and further polymerization.

The most important property of superplasticizers is its ability of dispersing the cement particles. Electron microscopic examination reveals that in water suspensions of cement, large irregular agglomerates of cement are dispersed into small particles. Portland cement, in contact with water, has a tendency to flocculate due to van der Walls' forces, electrostatic interactions between the opposite charges and surface chemical interactions between the hydrating particles. This will cause the formation of an agglomeration of particles with open structure with spaces that entrain water molecules. These water molecules are not immediately available for hydration and do not have a lubricating effect. In the presence of superplasticizer, deflocculation or dispersion of cement particles occurs due to adsorption and electrostatic repulsion. This process does not allow the formation of entrapped water and discourages surface interaction of the particles. Some steric hindrance is possible especially when high molecular weight superplasticizers are used [2]. Steric hindrance effect is seen more predominantly in new generation superplasticizers.

1.1.1.3 Polycarboxylate Ethers

The various types of polyacrylate polymers are manufactured from the relevant monomers by a free radical mechanism using peroxide or persulfate initiators and can be 'block' or 'random' polymers depending on the degree of prepolymerization of the monomers used. [6] Depending on the composition of the monomer feed and the polymerization procedure, different types of heterogeneities may become important.[12] Heterogeneities in the system are some homopolymers of the monomers, and polymer chains with different composition ratios of the monomers like long monomer blocks.

The polycarboxylates used in concrete as a superplasticizer, generally have ionic pendant groups and long polyethylene glycol (PEG) grafted chains. The pendant groups are possibly sulfonic acid, carboxylic acid and carboxylic esters. The ionic character of sulfonic acid or carboxylic acid groups can be changed by the pH of the solution; as pH increases the sulfonic acid will turn to sulfonates, and carboxylic acid will turn to carboxylates.

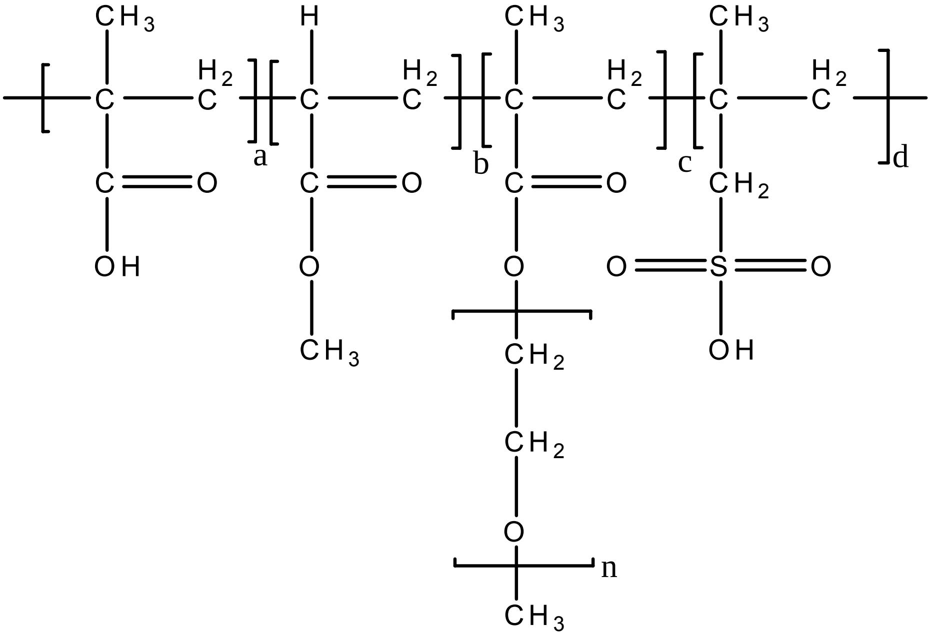

Figure 1.5 General structure of polycarboxlate ether type superplasticizer

The ionic pendant groups form an electrostatic layer between the main chain and cement particle, it is called "stern layer". This layer gives a negative charge to the cement particle, and makes the cement particles repel each other. The stern layer and the zeta potential of a charged particle are illustrated in Fig. 1.6.

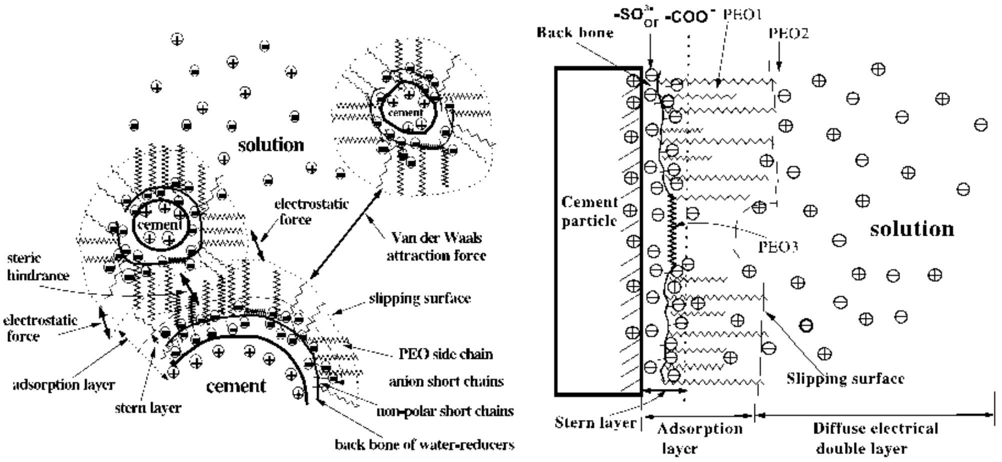

Figure 1.6 Working principle of polycarboxylate based superplasticizers in concrete [6].

This repulsion behavior is generally determined by zeta potential measurements. The potential difference on the slipping layer illustrated in Fig. 1.6 is the zeta potential. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential, then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta potential values, then there is no force to prevent particles from coming together and flocculating. [13]

Zeta potential measurement is performed by determining the electrophoretic mobility by applying a potential difference to the chamber filled with the solution and then applying Henry equation to the mobility values. The Henry equation is below:

$$U_E = \frac{2\varepsilon z f(ka)}{3\eta} \tag{1}$$

where,

z : Zeta potential

U_E : Electrophoretic mobility

ε : Dielectric constant

η : Viscosity

f(ka) : Henry's function

The charge of the main chain of the polycarboxylate ether type copolymers is negative because of negative charge of the oxygen atoms in carboxylic acid groups. Thus, the magnitude of zeta potential of the polymers is negative. Though, for the carboxylated ether type superplasticizers, the electrostatic properties, like zeta potential and mobility of the ions, are not the dominant factor affecting the fluidity of the cement paste, the dominant factor is the steric hindrance of PEG side chains, when a copolymer consists of a long hydrocarbon-like PEG side chains.

The main function of PEG chains is to cause steric hindrance, prevent the cement particles from approaching to each other. This effect is more dominant than the electrostatic interactions in polycarboxylate ether type superplasticizers [6].

The long, grafted PEG chains are generally between molecular weight 500 and 2000. The end group of the PEG chain is generally a methyl group in order to prevent esterification of PEG from both two end groups.

Comb-type PEG grafted polycarboxlate ethers were developed as a cement superplasticizer in 1990s in Japan. [14] These copolymers have structural characteristics that provide more fluid concrete, which was more resistant to segregation and exutation than any prepared concrete with the superplasticizers known previously. For these reasons, nowadays polycarboxylate admixtures have been rather used in the cement systems as superplasticizers than admixtures based on melamine and naphthalene. [15]

In the study of Heon-Young Cho et.al[16], the dispersion ability of PEG grafted polycarboxylate ethers in cement paste is studied. They found that the dispersion ability and dispersion stability of PEG grafted polycarboxylate in cement paste are strongly affected by the reaction temperature and reaction time but weakly affected by the amount of ammonium persulfate used as a radical polymerization initiator in the polymer synthesis and these properties are more affected by the heavier molecules than by the lighter ones in the polymer. Hence, the dispersibilities of the polymers are increased by the heterogeneity in that polymer system.

The effect of molecular weight of carboxylated acrylic esters on the workability of concrete has still been a study subject. In the study of Winnefeld and his friends [17], it is found that a decreasing density of the PEG side chains enhances workability. However, the lengths of the side chains and the molecular weight of the polymers have only a minor influence on fluidity. The minor effect of side chain lengths is probably due to the conformation of the PEG chains, which is not stretched but more mushroom-like structure (see Fig. 1.7) especially in aqueous solutions with high ionic strengths.

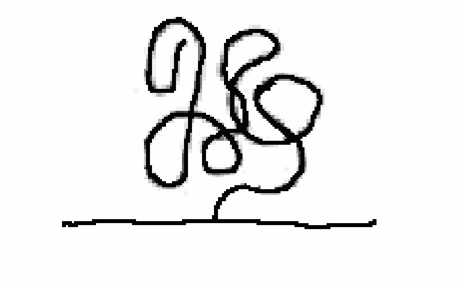

Figure 1.7 “Mushroom-like” conformation type of PEG side chains [17]

1.2 Concrete Properties

1.2.1 Workability

The quality of fresh concrete is determined by the ease and homogeneity with which it can be mixed, transported, compacted and finished. Workability includes properties such as flowability, moldability, cohesiveness, and compactibility. One of the main factors affecting workability is the water content in the concrete mix. A harsh concrete becomes workable by addition of water. However, excess water causes excess bleeding and affects mechanical properties of concrete negatively, so workability is also improved by the addition of plasticizers and air entraining agents.

Although several methods have been suggested to determine workability, none is capable of measuring this property directly. It is therefore usual to measure some type of consistency as an index of workability. The most extensively used test is the slump test. This method is described by ASTM C143-78. The slump test uses a frustum of cone 30 cm high. Concrete is filled in this cone and the cone is lifted slowly and the decrease in the height of the center or the increase in the diameter of the slumped concrete is measured [2]. The schematic representation of slump-flow test is shown in Fig. 1.8. When this measurement is done with only the cement paste, it is called mini-slump test, the conical mold is smaller than the one used with concrete.

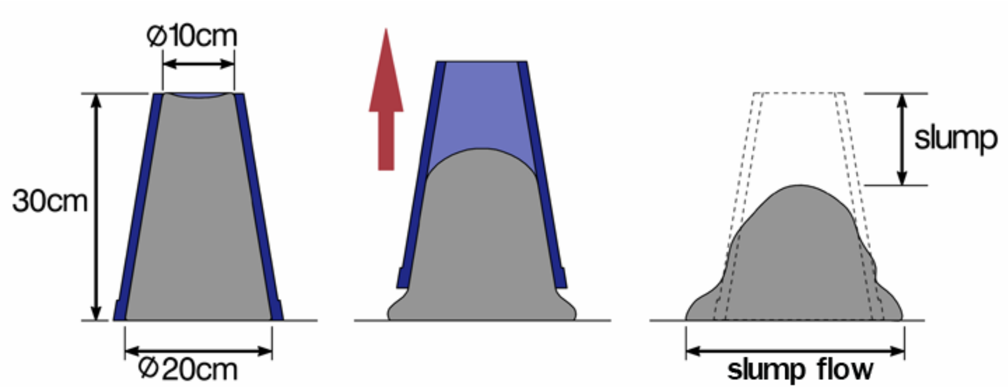

Figure 1.8 Schematic representation of slump-flow test *

There are other methods such as the *Compacting Factor Test* based on the measurement of the density ratio (the ratio of the weight of concrete without compaction with additional force and the fully compacted concrete) (BS 1881), the *Ball Penetration Test* based on measuring the penetration of 150

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[*] (Wikipedia, retrieved February 5, 2008, from http://en.wikipedia.org/wiki/Abrams_cone)

mm diameter steel cylinder with a hemispherically shaped bottom weighing 13.6 kg (ASTM C 360-82), the *Remoulding Test* with a basis of the effort required in changing the shape of the concrete (BS 1881). [18] All these tests attempt to measure workability and they are not comparable. [2]

1.2.2 Setting

The setting of concrete is determined by using the mortar contained in it (ASTM C 191). A penetrometer is used for determining the initial and final setting times of mortar. A needle of appropriate size has to be used. The force required to penetrate one inch depth is noted. The force divided by the area of the bearing surface of the needle yields the penetration resistance. The initial setting time is the elapsed time after the initial contact of cement and water required for the mortar sieved form the concrete to reach a penetration resistance of 3.5 MPa (500 lbs/in^2). The corresponding resistance for the final setting time is 27.6 MPa (4000 lbs/in^2). [2] The apparatus used for measuring the setting time is shown in Fig. 1.9.

Figure 1.9 Vicat apparatus for setting time test [*]

1.2.3 Bleeding and Segregation

In a freshly placed concrete which is still plastic, settlement of solids is followed by the formation of a layer of water on the surface. This is called bleeding or water gain. Bleeding may give rise to *laitance*, a layer of weak, nondurable material containing diluted cement paste and fines from the aggregate. If bleeding occurs by uniform seepage of water, and no undesirable effects result, then this bleeding is called “normal bleeding”. Bleeding is not necessarily harmful. If undisturbed, the water evaporates so that the effective water cement ratio is lowered with a resultant increase in strength.

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[*] (ELE International, http://www.ele.co.uk/pdfs/106-108.pdf, retrieved February 5, 2008)

Bleeding characteristics are measured by bleeding rate or bleeding capacity applying the ASTM C232 standard. In this method, the relative amount of mix water that appears on the surface of concrete placed in a cylindrical container is measured. At specific intervals the water accumulating on the surface is determined until bleeding ceases. The top surface of concrete subsides during bleeding causing plastic shrinkage, which is shown in Fig. 1.10.

Figure 1.10 Plastic shrinkage because of bleeding *

The separation of coarse aggregates from the mixture resulting in a nonuniform concrete mass is called segregation. Segregation may cause flaws in the final product and honeycombing may occur in some instances, as shown in Fig. 1.11. The primary cause of segregation is the differences in the size of the particles and specific gravity of the mix. By proper grading of the constituents and handling, this problem can be controlled. [2]

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* (U.S. Department of Transportation, Federal Highway Administration, http://www.tfhrc.gov/pavement/pccp/pubs/04122/03.htm, retrieved February 6, 2008)

Figure 1.11 Honeycombing in a concrete [*]

1.2.4 Mechanical Properties

The hardened concrete has to conform to certain requirements for mechanical properties. They include compressive strength, splitting tensile strength, flexural strength, static modulus of elasticity, Poisson’s ratio, mechanical properties under triaxial loads, creep under compression, abrasion resistance, bond development with steel, penetration resistance, pullout strength, etc.

Concrete is a composite material, a composite material is a three dimensional combination of at least two chemically and mechanically distinct materials with a definite interface separating the components. This multiphase material will have different properties from the original components.

The factors that is influencing the mechanical behavior of concrete are shape, size, distribution of constituents, concentration and orientation of the

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[*] (Syracuse University Library, http://library.syr.edu/digital/collections/c/Ceraldi/D3-4.htm, retrieved February 6, 2008)

particles, topology, composition of disperse and continuous phases. The strength of concrete depends on the strength of the paste, coarse aggregate, and the paste aggregate interface. This interface is the weakest region of concrete and this weakness is due to weak bonding and development of cracks. They may develop due to bleeding and segregation and volume changes of the cement paste during setting and hydration.

1.3 Aim of the Study

In this project, the aim was to design, synthesize and characterize a novel water-soluble polycarboxylate ether copolymer that can be used as a superplasticizer in concrete, to study the effects of changing the reaction pH and time on the flow properties and the mechanical strength of the copolymers in concrete, to study the effects of content and molecular weight of PEG side chains on the flow properties and mechanical strength of the copolymers containing PEG side chains, and to analyze the flow properties and mechanical strength results in terms of zeta potential values of the samples.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

The chemicals used in this study are 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Aldrich), methacrylic acid (MAA) (Aldrich), acrylic acid (AA) (Acros), polyethylene glycol 2000 monomethyl ether (PEG 2000) (Fluka), polyethylene glycol 1100 monomethyl ether (PEG 1100) (Fluka), ammonium persulfate (Riedel-de Haen), methane sulfonic acid (MSA) (Merck), hydroquinone (Sigma), sodium hydroxide (NaOH)(Riedel-de Haen), hydrochloric acid (HCl) (Riedel-de Haen), ethanol (EtOH) (Riedel-de Haen), toluene (Merck),and hexane (J.T. Baker).

2.2 Instrumentation

2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the polymers were recorded on a Nicolet 510 FT-IR spectrophotometer in METU Chemistry Department. The polymer samples are pounded into powder in mortar and mixed with KBr, and pressed into pellets.

2.2.2 Nuclear Magnetic Resonance (NMR)

Both ^{1}H and ^{13}C NMR spectra of the polymers were recorded in Bruker-Spectrospin Avance DPX 400 high performance digital FT-NMR spectrometer at METU Chemistry Department NMR Laboratory. D_2O was used as NMR solvent, tetramethylsilane was used as the internal standard and ppm scale was used to designate the chemical shifts δ.

2.2.3 Dilute Solution Viscosimetry

Viscosity measurements were performed by Ubbelohde viscometers in distilled water at 35°C, the flow time was measured with a stopwatch.

In dilute solution viscosimetry experiments, 25 ml solutions having 0,5 g/dl concentration were prepared. The Ubbelohde viscometer was filled with 15 ml of these solutions. The concentration of the samples changed by the addition of 3 ml solvent, repeated for four different concentrations, and for each diluted solution, the flow times were measured. Finally, η_{sp}/C versus C graphs were plotted with the 5 data obtained for each sample.

2.2.4 Mini Slump-Flow Test

The polymer samples were dissolved in water at a ratio of 1.2:240 by weight. These solutions were mixed with 600 g cement with the help of ELE International Automatic/Manual Mortar Mixer in Civil Engineering Department Material Testing Laboratory. The cement used in these tests is Portland cement CEM I 42.5R as defined by TS EN 197-1. A conical mold which is a standard for the slump-flow test was filled with these prepared cement pastes. When the mold is lifted up, the cement paste flows. After waiting for 30 seconds the diameter of the expanded cement paste was measured according to ASTM C 143, the standard for test method for slump of hydraulic cement concrete. The schematic representation of this measurement is shown in Fig. 1.8. The difference between the slump test and the mini-slump test is the dimensions of the mold filled up with the cement paste or concrete. In concrete, a conical mold is used with a height of 30 cm, upper diameter of 10 cm and bottom diameter of 20 cm, however in mini- slump test; the mold has a height of 6 cm, upper diameter of 7 cm and, bottom diameter of 10 cm.

The relative fluidity effect of the polymers was measured by the mini-slump-flow test. To measure the relative fluidity of the polymers, firstly the fluidity of blank cement paste was measured for comparison. This blank cement paste is composed of only water and cement in a ratio of 4:10 by weight. The relative fluidity was calculated with the equation below [19]. The result is relative fluidity of the sample.

$$\Gamma_m = \left(d/d_0\right)^2 - 1 \quad (2)$$

Γ_m is the relative fluidity of the samples, d is the flow diameter of the sample, d_o is the diameter of the mold.

2.2.5 Mechanical Measurements of Mortars Prepared with the Polymer Samples

2.2.5.1 Flexural Strength Measurements

The same solutions which have been prepared for the mini-slump tests were prepared for the flexural strength measurements of the samples. 225 grams of these solutions were taken and mixed with 1350 g standard sand mixture and 450 g Portland cement. The mixture is called mortar. The molds with dimensions 4x4x16 were filled with these mixtures. From the mixture, it is possible to fill three molds. These mortar mixtures were prepared and the flexural strength tests were performed according to TS EN 196-1.

The machine used for determining the flexural strength is Losen Hausen Loading Frame. It has a capacity of 1,000 kilogram force (kgf) for flexural strength tests.

After removing the mortar samples from the mold, they were put in the loading frame as it is shown in Fig. 2.1. The total length of the bar is 16 cm, however, the length of the support span is 12 cm, the height and the width of the bar is 4 cm.

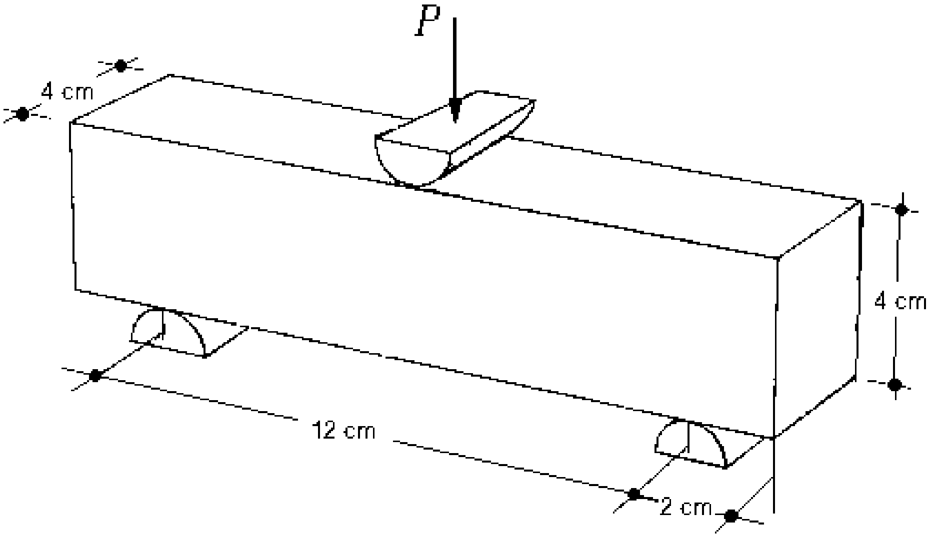

Figure 2.1 Schematic representation of flexural strength measurement test

The length of the bar on which the force was applied is 12 cm. The cross-sectional area of the bar is 4x4=16 cm^2.

The flexural strength of a material is:

$$\sigma_{flex} = \frac{\mu \cdot c}{I} \tag{3}$$

where;

μ = moment occurred by the applied force

c = the distance from the neutral axis to the bottom fiber for the x-section.

I = moment of inertia of square prism $= \frac{1}{12} bd^3$

If we let c = d/2,

$$\sigma_{flex} = \frac{\mu \cdot \frac{d}{2}}{\frac{1}{12} \cdot bd^3} \tag{4}$$

Where,

$$\mu = \frac{P \cdot L}{4} \tag{5}$$

P = the load (force) at the fracture point (flexural stress)

L = the length of the support span

b = width of the bar

d = height of the bar

Then,

$$\sigma_{flex} = \frac{\frac{P \cdot L}{4} \cdot \frac{d}{2}}{\frac{1}{12} \cdot bd^3} \tag{6}$$

Since b=d;

$$\sigma_{flex} = \frac{\frac{P \cdot L}{4} \cdot \frac{d}{2}}{\frac{1}{12} \cdot d^4} \tag{7}$$

When the equation is simplified,

$$\sigma_{flex} = \frac{3}{2} \cdot \frac{P \cdot L}{d^3} \tag{8}$$

This equation was used for calculating the flexural strength of the samples [20].

The unit of the load applied is kgf, so the unit of the flexural strength in terms of N/mm^2 will be:

$$\sigma_{flex} = \left[\frac{kgf \cdot cm}{cm^3}\right] = \left[\frac{kgf}{cm^2}\right] = \frac{9,8}{100} \cdot \left[\frac{N}{mm^2}\right] \tag{9}$$

2.2.5.2 Compressive Strength Measurements

The compressive strength tests were performed on the broken pieces of the mortar samples according to the TS EN 196-1.
The machine used for the determination of the compressive strength is ELE universal compressive testing machine with a capacity of 300,000 kgf.

4x4x4 cubic mortar samples, which were the samples from the flexural strength tests, were put in compressive test machine as shown in Fig. 2.2.

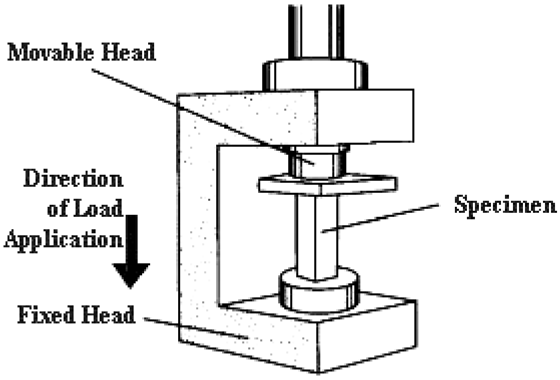

Figure 2.2 Schematic representation of compressive strength test

The compressive strength of the mortar samples was calculated by the equation below:

$$\sigma = \frac{F}{A_0} \tag{10}$$

While inserting the data for the calculation of σ and σ_{flex}, TS EN 196-1 standard is also used.

2.2.6 Zeta Potential Measurements

The zeta potential measurements were performed by Malvern Nano ZS90 zeta potential and mobility measurement device in the Central Laboratory in METU.

A slurry mixture was prepared by mixing water, cement and superplasticizer polymers. The plasticizer/cement ratio has been used in slump-flow tests was also used for the zeta potential measurements (1.2:600); however, the samples were diluted more for the measurements. After mixing, the slurry samples were let to settle down for one night, the clear solution over the sediment was taken with the help of a pipette, and filtered through a Gooch crucible with a porosity of 10-16 µm.

2.3 Synthesis

2.3.1 Synthesis of 2-Acrylamido-2-methyl-1-propanesulfonic acid / Methacrylic acid copolymer (AMPS-MAA)

Synthesis of AMPS-MAA was carried out according to the following procedure [10]. AMPS and MAA were copolymerized in water with the molar ratios shown in Table 2.1, by refluxing in water bath, under N_2 atmosphere, at 60ºC, for 4 hours, at a pH of 8. The polymerization reaction is illustrated in Fig. 2.3.

Table 2.1 Feed compositions of AMPS-MAA copolymer

copolymer	feed composition (mol fraction)
80% AMPS-MAA (80% AMPS)	AMPS: 10 g, 0.0483 mol MAA: 0.797 g, 0.01207 mol
60% AMPS-MAA (60% AMPS)	AMPS: 9 g, 0.04347 mol MAA: 1.91 g, 0.02898 mol
40% AMPS-MAA (40% AMPS)	AMPS: 7 g, 0.0338 mol MAA: 3.34 g, 0.0507 mol
20% AMPS-MAA (20% AMPS)	AMPS: 5 g, 0.0483 mol MAA: 6.38 g, 0.0966 mol

60% AMPS-MAA was synthesized for four more times with the same procedure by changing the reaction pH as; 6, 9, 10, 11.

After polymerization, the polymer solution was precipitated in ethanol, distilled by vacuum vaporization with the help of Heidolph Rotary Evaporator Laborota 4002 and dried in oven at 45ºC till constant weight.

The scheme for the synthesis of the AMPS-MAA copolymers is given in Fig. 2.4.

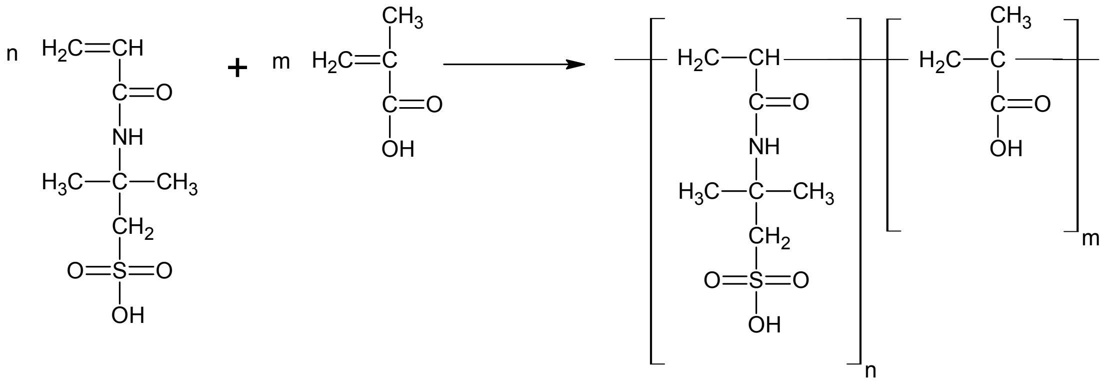

Figure 2.3 The radicalic copolymerization between the AMPS and MAA monomers

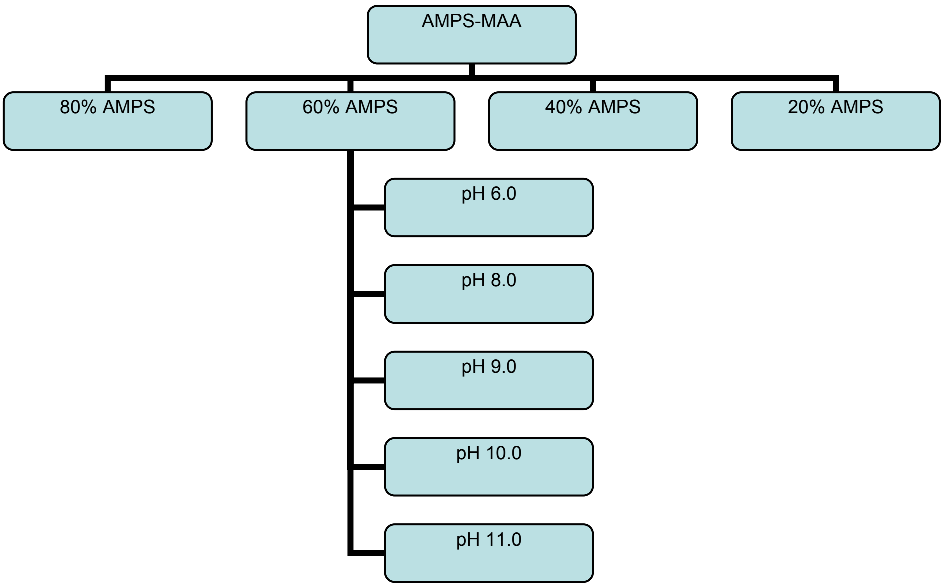

Figure 2.4 Schematic representation of the synthesis of AMPS-MAA copolymers

2.3.2 Synthesis of Acrylamido-2-methyl-1-propanesulfonic acid / poly (ethylene glycol) methyl ether methacrylate copolymer (AMPS-PEGMA)

Poly(ethylene glycol) methyl ether (PEG) was condensed with MAA according to the following procedure [21]. PEG and MAA were refluxed in toluene, with methane sulfonic acid (MSA) as a catalyst and hydroquinone as a radicalic polymerization inhibitor to avoid the polymerization of the double bonds, at 90ºC, for 7 hours, in oil bath. The macromonomer poly(ethylene glycol) methyl ether methacrylate (PEGMA) was obtained. The structure of the macromonomer is given in Fig. 2.5.

This esterification procedure was performed for different PEGs with molecular weights 1100 and 2000.

The macromonomers were precipitated in hexane, filtered by vacuum filtration and dried in oven at 45ºC till constant weight.

The AMPS-PEGMA copolymers were synthesized by the same procedure used for the synthesis of AMPS-MAA. The feed compositions of the reactions are shown in Table 2.2.

Table 2.2 Feed compositions of AMPS-PEGMA copolymers.

copolymer	feed composition (w/w)
5% AMPS-PEGMA	PEGMA: 0.6 g, 0.000293 mol AMPS : 11.4 g, 0.055 mol
15% AMPS-PEGMA	PEGMA: 1.8 g, 0.000879 mol AMPS : 10.2 g, 0.049 mol
25% AMPS-PEGMA	PEGMA: 3 g, 0.001465 mol AMPS : 9 g, 0.043 mol

The scheme for the synthesis of AMPS-PEGMA copolymers is given in Fig. 2.6.

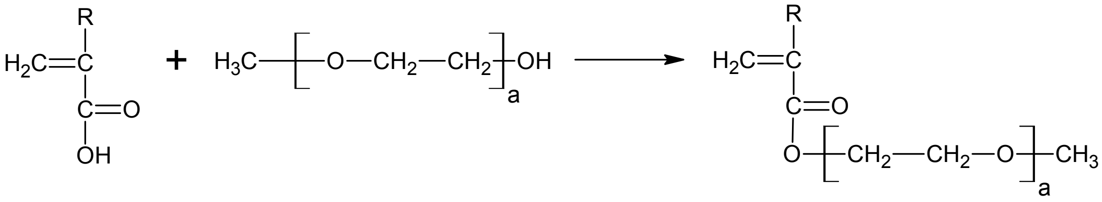

Figure 2.5 The synthesis of PEGMA or PEGA macromonomer (* R = H or CH3)

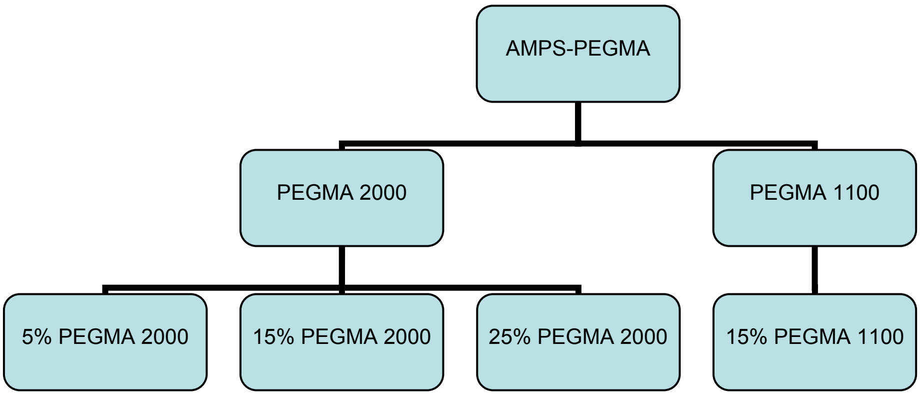

Figure 2.6 Schematic representation of the sythesis of AMPS-PEGMA copolymers

2.3.3 Synthesis of Acrylamido-2-methyl-1-propanesulfonic acid / poly (ethylene glycol) methyl ether acrylate copolymer (AMPS-PEGA)

AA and PEG were condensed by the same procedure used in condensation of MAA with PEG. The produced polyethylene glycol methyl ether acrylate (PEGA) macromonomer was copolymerized with AMP monomer with the same procedure of AMPS-MAA synthesis. The feed compositions and the reaction conditions were the same with the synthesis of AMPS-PEGMA. The structure of copolymer is shown in Fig. 2.7

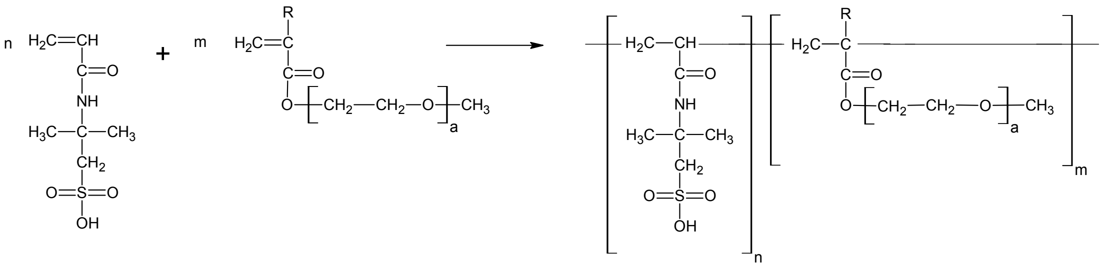

Figure 2.7 Radicalic copolymerization between AMPS and PEGA or PEGMA monomers (* R = H or CH_3)

The schematic representation of the synthesis of AMPS-PEGA copolymers is given in Fig. 2.8.

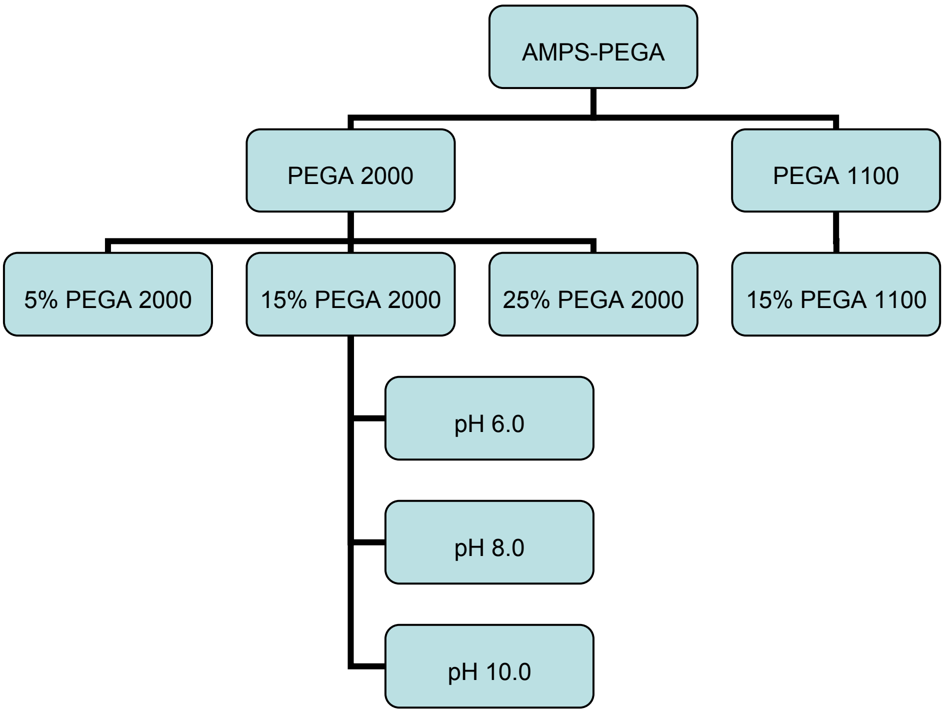

Figure 2.8 Schematic representation of the synthesis of AMPS-PEGA copolymers

CHAPTER 3

RESULTS AND DISCUSSION

The new generation superplasticizers, carboxylated polymers or copolymers, have so much additional advantages in concrete industry. Improving the fluidity of the concrete about 40-50% without additional water is very important for the high performance concretes in high-tech architecture [22]. In this study, a series of novel polymers was synthesized to improve the fluidity of concrete and their effect in mechanical strength of concrete was studied.

3.1 Characterization of the Polymers

3.1.1 Characterization of AMPS-MAA by FT-IR and NMR Analysis

In Fig. 3.1, the FT-IR spectrum of 60% AMPS-MAA is given, FT-IR spectra of AMPS-MAA copolymers with 20%, 40% and 80% AMPS content are given in the Fig. A.1 in the appendix.

FT-IR spectrum of AMPS-MAA copolymer showed the following absorption bands: 3447.64 cm^{-1} (acid O-H and amide N-H stretching), 2987.19 cm^{-1} (C-H stretching), 1457.00 cm^{-1} (C-H bending), 1558.17 cm^{-1} (N-H bending), 1399.82 cm^{-1} (S=O stretching), 1653.14 cm^{-1} (acid C=O and amide C=O stretching), 1226.35 (acid C-O stretching), 1051.89 cm^{-1} (amide C-N stretching). There is no C=C stretching band which should have been observed at a frequency of 1620 cm^{-1}.

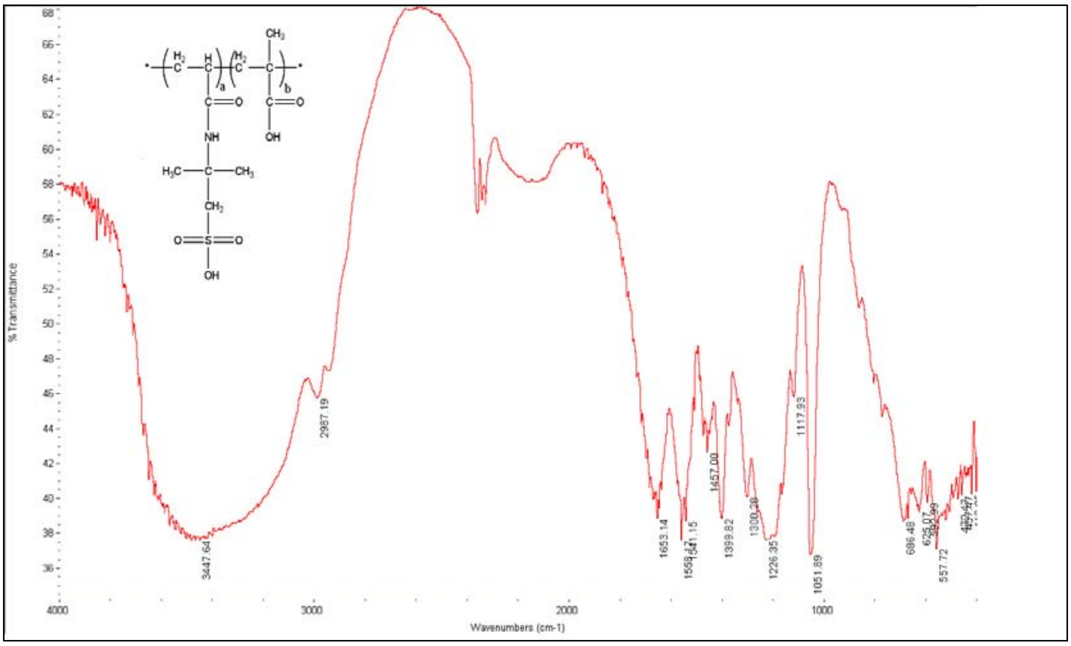

Figure 3.1 FT-IR Spectra of 60% AMPS-MAA

The ^{1}H NMR of AMPS monomer is shown in Fig. 3.2. (400 MHz, D_2O) The chemical shifts (δ) in ppm are as follows: δ 6.75 (1H) (3), 5.15 (1H) (2), 4.95 (1H) (6), 4.6 (1H) (1), 2.25 (2H) (5), and 0.35 (6H) (4). ^{13}C NMR of AMPS monomer is in the Fig. A.2 in the appendix. The chemical shifts (δ) in ppm are as follows: δ 26.8, 52.5, 56.5, 126.5, 130, and 167.

^{1}H NMR spectrum of AMPS-MAA copolymer is shown in Fig. 3.3. According to the NMR spectrum of AMPS-MAA copolymer, since there is no H peaks belonging to C=C bonds, it is proved that the copolymerization is successful. The chemical shifts (δ) in ppm are as follows: δ 7.25 (1H) (6), 3.3 (2H) (1), 1.9 (1H) (2), 1.4 (11H) (3, 4, 5).

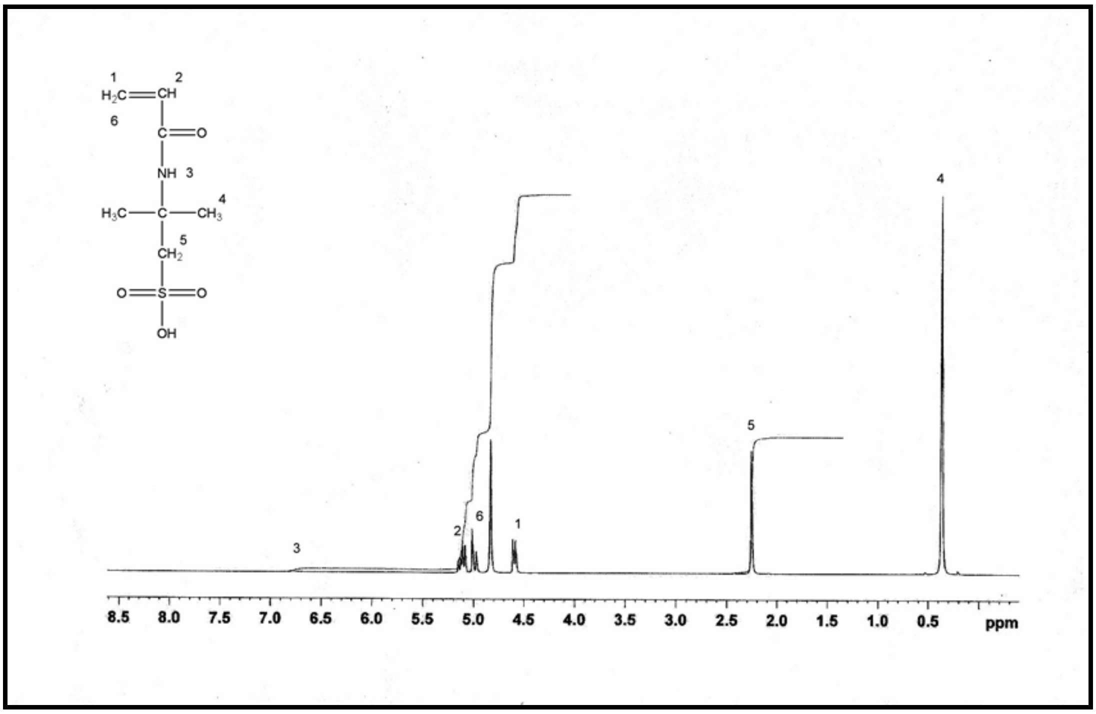

Figure 3.2 ^{1}H NMR spectrum of AMPS monomer

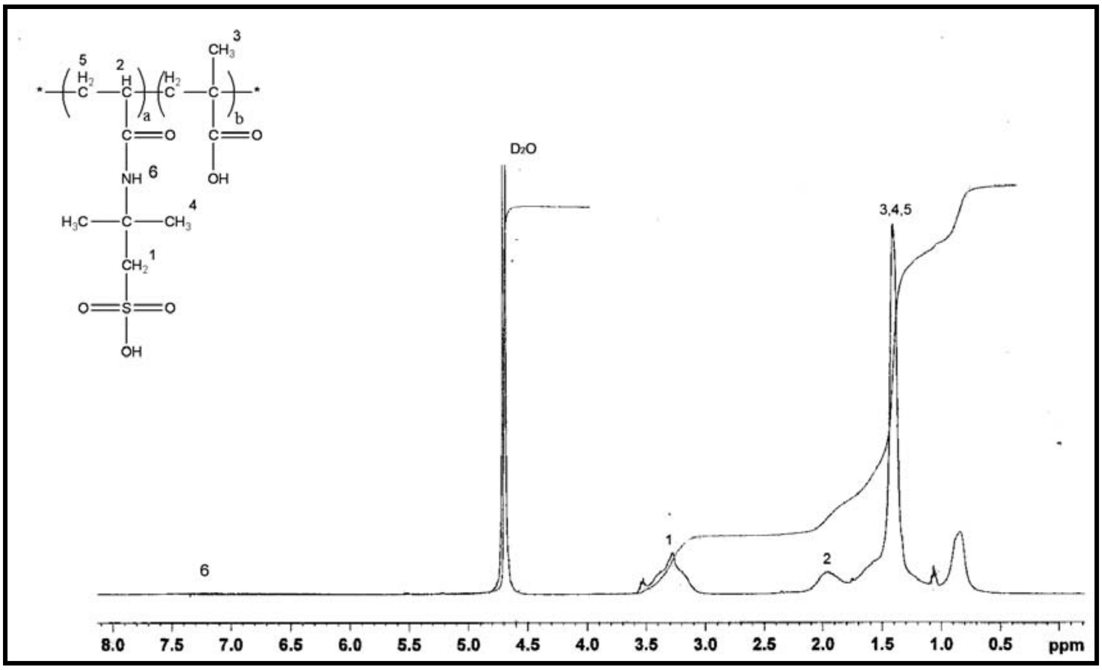

Figure 3.3 ^{1}H NMR spectrum of AMPS-MAA copolymer

3.1.2 Characterization of PEGA and PEGMA macromonomers by FT-IR and NMR Analysis

FT-IR spectrum of PEGA macromonomer is shown in Fig. 3.4. The FT-IR spectrum showed the following absorption bands: 1732.24 cm^{-1} (ester C=O stretching) 1281.38 cm^{-1} and 1242.23 cm^{-1} (ester C-O stretching, two bands). 2885.55 cm^{-1} (C-H stretching band of PEG), 1469.11 cm^{-1} (C-H bending of PEG), 1112.53 cm^{-1} (C-O ether stretching of PEG), 1649.50 cm^{-1} (C=C stretching), C=C stretching band proves that there is no radical polymerization in the reaction, since we used hydroquinone as a radical polymerization inhibitor in the synthesis of these macromonomers.

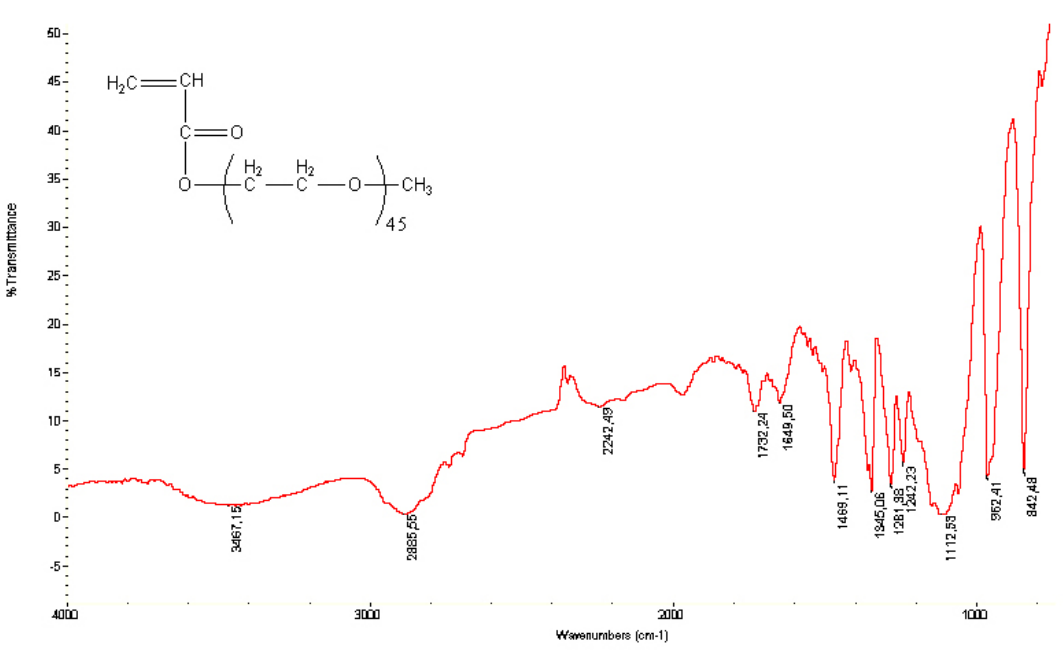

Figure 3.4 FT-IR Spectrum of PEGA macromonomer

^{1}H NMR spectrum of PEGMA macromonomer is shown in Fig. 3.5. The chemical shifts are: δ 6.18 and 5.78 (2H) (1), 3.63 (2H) (3), 3.55 (3H) (4), 1.96 (3H) (2). The hydrogen shifts belonging to C=C are displayed in 5.78 and 6.18 ppm. This proves that the double bonds are preserved.

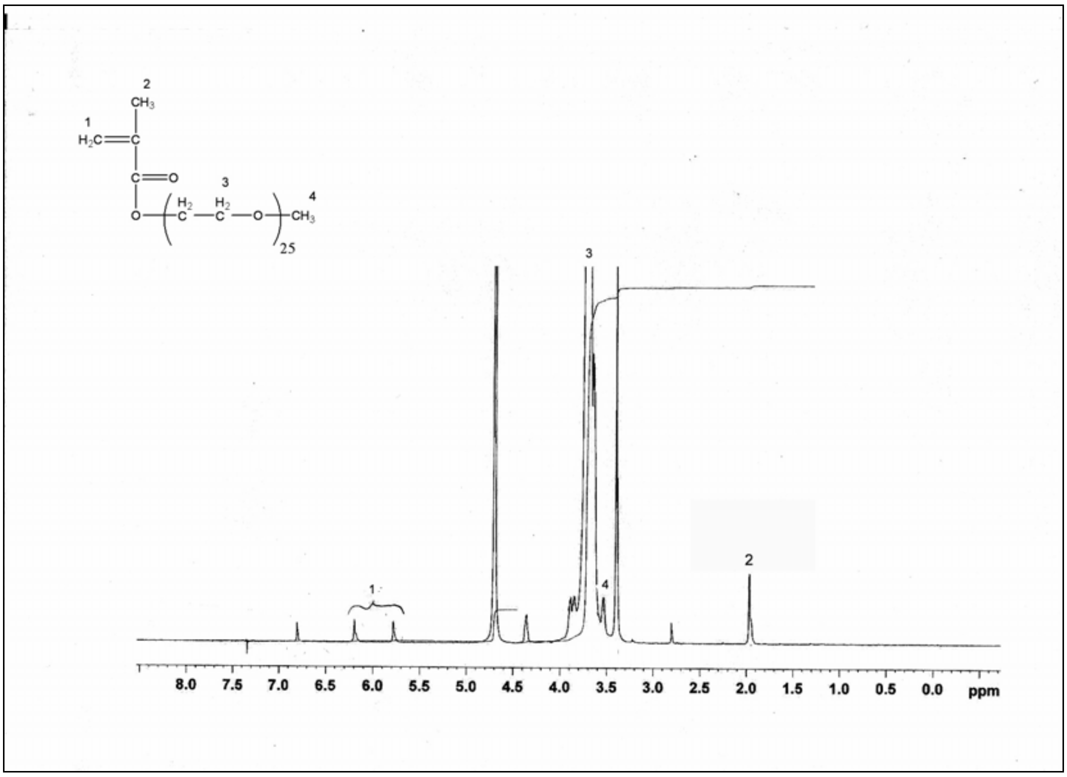

Figure 3.5 ^{1}H NMR spectrum of PEGMA macromonomer

^{1}H NMR of PEGA macromonomer and ^{13}C NMR of both PEGMA and PEGA macromonomer are in Fig. A.3, A.4, and A.5, respectively in the appendix.

The comparable FT-IR spectra of PEGA 1100 and PEGMA 1100 are in the Fig. A.6 in the appendix.

3.1.3 Characterization of AMPS-PEGMA and AMPS-PEGA copolymers by FT-IR and NMR analysis

In the FT-IR spectrum of AMPS-PEGMA copolymer in Fig. 3.6, showed the following absorption bands: 3507.55 (amide N-H stretching), 1669.89 cm^{-1} (the stretching band of carbonyl of amide group and ester group are overlapped), 1043.05 cm^{-1} (ester C-O stretching), 2934.66 cm^{-1} (C-H stretching of PEG), 3080.76 cm^{-1} (C-H stretching of the main chain), 1458.29

cm^{-1} (C-H bending), 1188.88 cm^{-1} (C-O ether stretching), 1555.09 cm^{-1} (amide N-H bending), 1390.58 cm^{-1} (S=O stretching), 1043.05 cm^{-1} (amide C-N stretching).

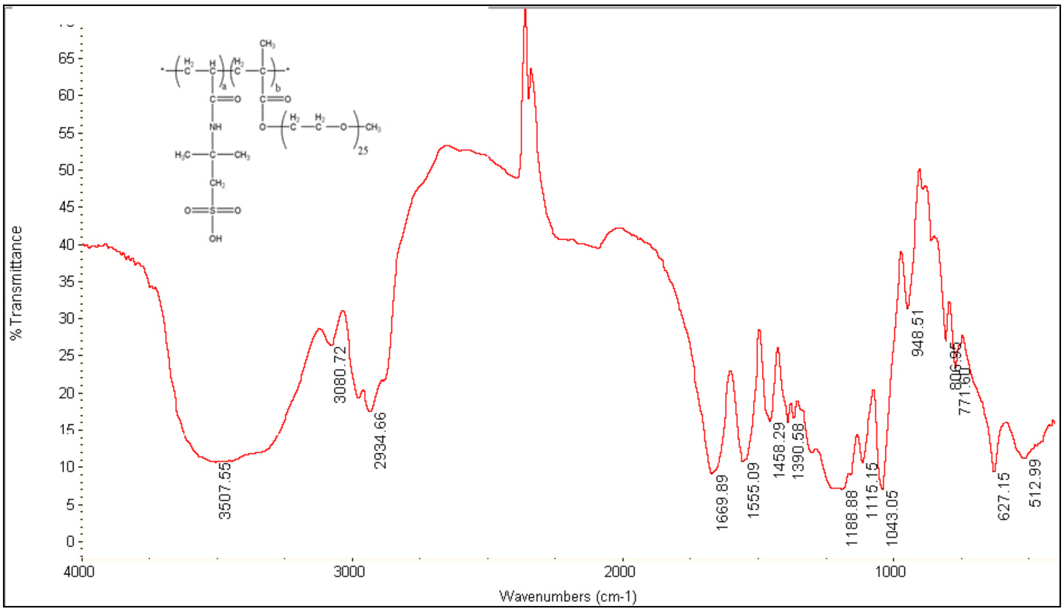

Figure 3.6 FT-IR spectrum of 25% AMPS-PEGMA copolymer

In all AMPS-PEGA and AMPS-PEGMA copolymers, similar infrared absorption trends are observed. The peak intensities vary due to the difference in the compositions of the copolymers and these FT-IR spectra of AMPS-PEGMA copolymers with different PEG contents are given in Fig. A.7 in the appendix.

The comparison of FT-IR spectra of AMPS-PEGA and AMPS-PEGMA copolymers with the 25% PEG content is in Fig. 3.7. The bending peak of N-H in the copolymer with the methyl group has higher intensity than the copolymer without a methyl group at 1555.09 cm^{-1} and the C-H stretch peak has a less intensity in the copolymer with methyl group which can be seen at the frequency of 1188.88 cm^{-1}. This spectrometric result shows that PEGMA macromonomer has a different reactivity then PEGA macromonomer with AMPS monomer.

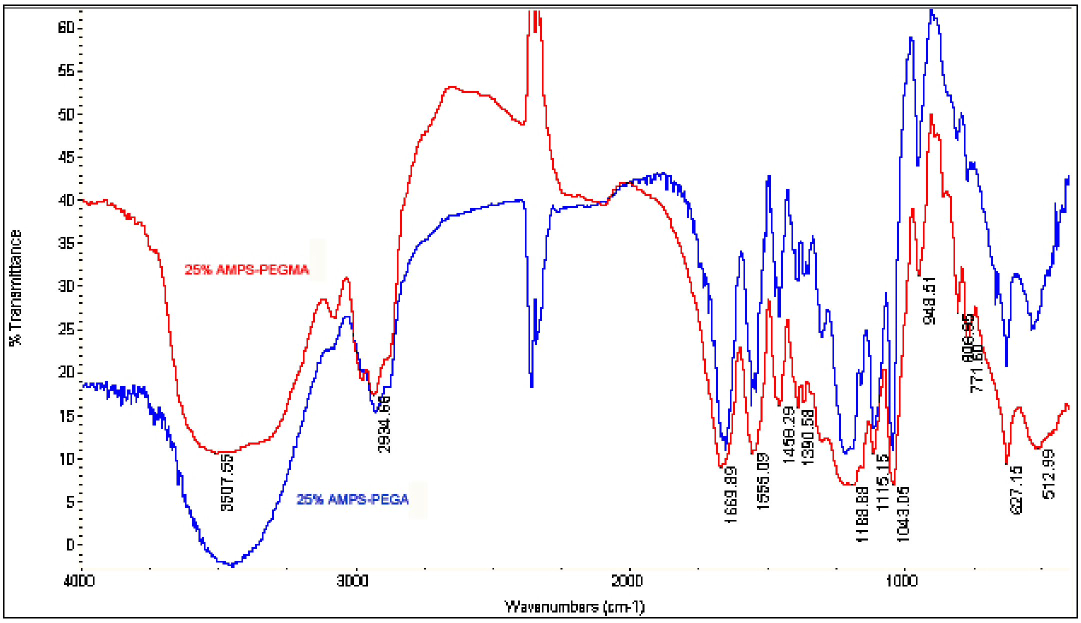

Figure 3.7 Comparison of FT-IR Spectra of 25% AMPS-PEGMA and 25% AMPS-PEGA

The ^{1}H NMR Spectra of copolymers with PEGA and PEGMA are shown in Fig. 3.8 and 3.9, respectively. The chemical shifts of PEGA macromonomer are as follows: δ 3.58 (2H) (1), 3.26 (2H) (2), 1.96 (1H) (3), 1.37 (8H) (4, 5). The chemical shifts of PEGMA macromonomer are: δ 3.43 (2H) (1), 3.13 (2H) (2), 1.80 (1H) (3), 1.26 (11H) (4, 5, 6).

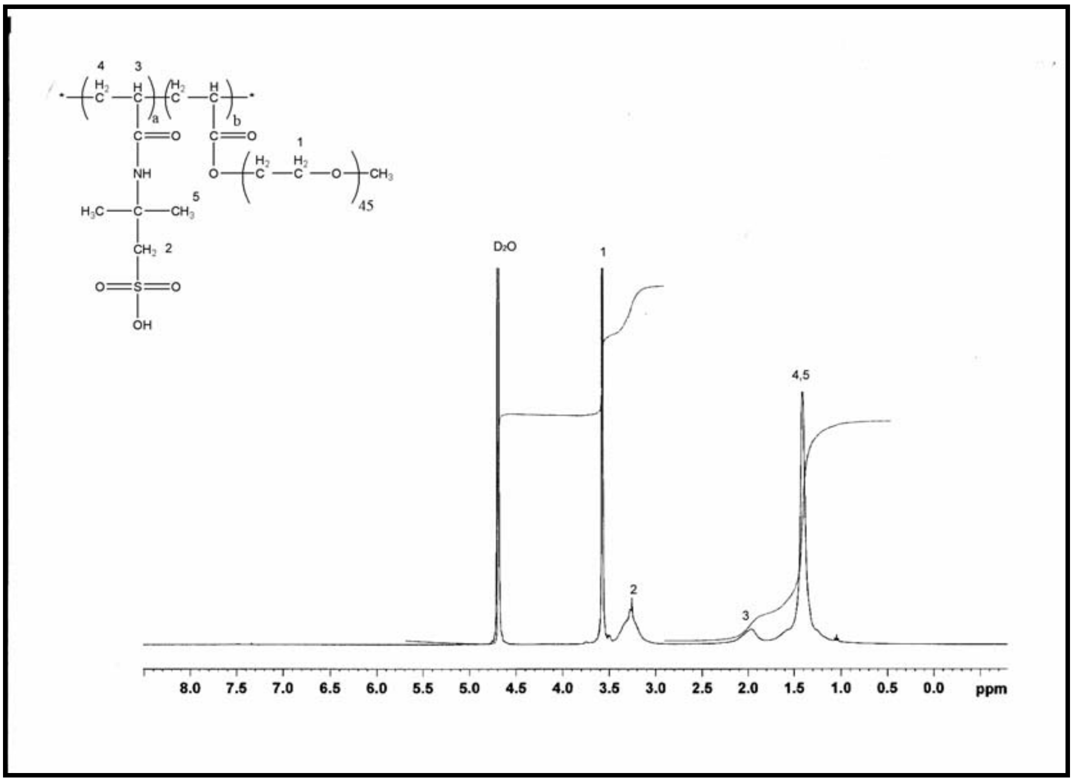

Figure 3.8 ^{1}H NMR of 15% AMPS-PEGA copolymer with reaction pH of 6

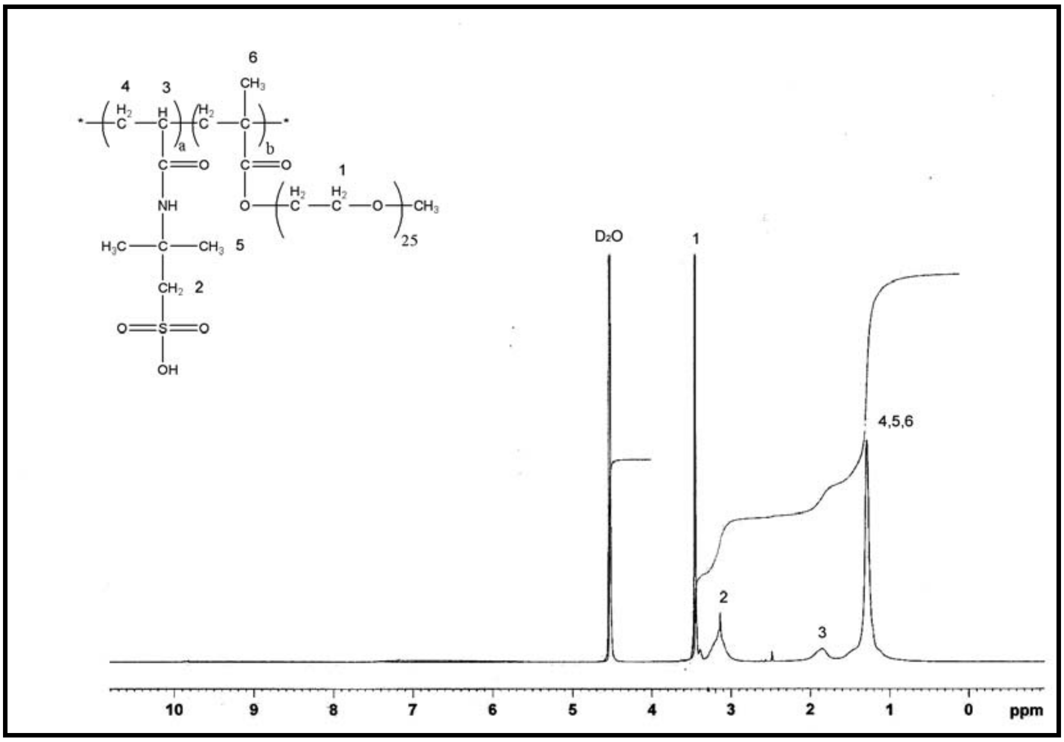

Figure 3.9 ^{1}H NMR of 15% AMPS-PEGMA copolymer with PEG molecular weight of 1100

^{13}C NMR spectra of 15% AMPS-PEGA copolymer with PEG 2000 (pH=6), and 15% AMPS-PEGMA copolymer with PEG 1100 are in Fig. A.8 and A.9 respectively in the appendix.

FT-IR spectrum of 15% AMPS-PEGA synthesized at pH 6 is in the Fig. A.10 in the appendix.

3.2 Mini Slump-flow Test Results

In the mini slump-flow tests, the effects of the composition, reaction pH and time, pH of the sample solutions prepared for mini slump-flow tests and the amount of PEG acrylates and their molecular weight in the copolymers were studied.

3.2.1 Mini Slump-flow Test Results of AMPS-MAA Copolymers

3.2.1.1 Effect of Composition

The mini slump-flow test results for AMPS-MAA copolymer having various compositions are represented in Fig. 3.10. The highest relative slump value was observed in the AMPS-MAA copolymer with 40% AMPS content and the lowest relative slump value leads to AMPS-MAA copolymer with 80% AMPS content. In addition to the different feed compositions, the different amounts of homopolymers of AMPS or MAA that may have formed during the synthesis have affected these results in slump-flow tests.

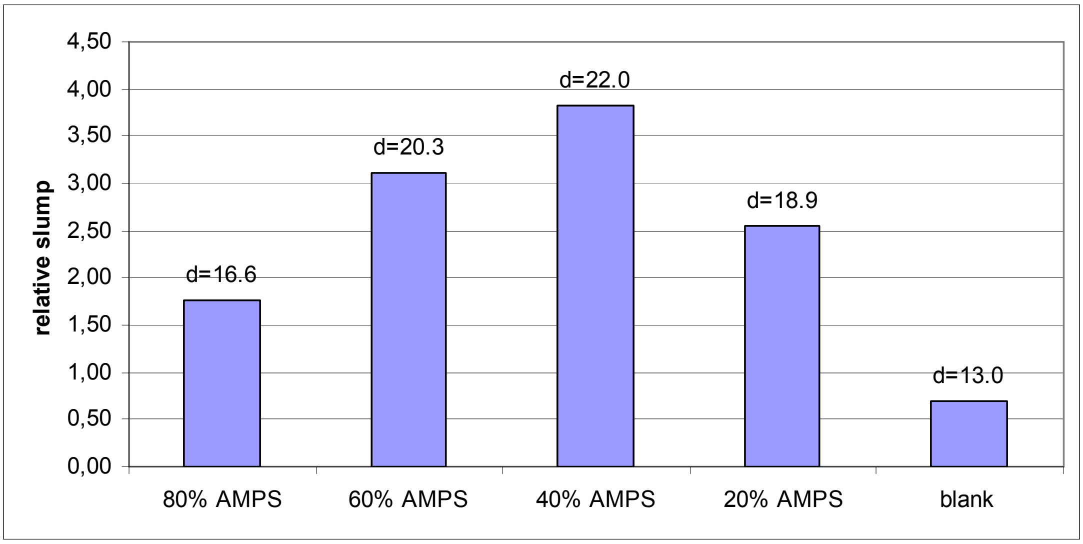

Figure 3.10 Fluidity test results of AMPS-MAA copolymers with different feed ratio at pH 8.

3.2.1.2 Effect of Reaction pH

In the mini slump-flow test studies, the effect of pH of the reaction to the fluidity is also examined. It is recognized that the ionic content of the medium is highly effective on fluidity. As it is shown in the Fig. 3.11, the highest relative slump value was observed in the copolymer with a reaction pH of 11. This result may be due to the increase in ionic strength of the medium, thus the ionic interactions between the cement particle and the copolymer increases, more electrostatic interactions are expected to cause an increase in fluidity.

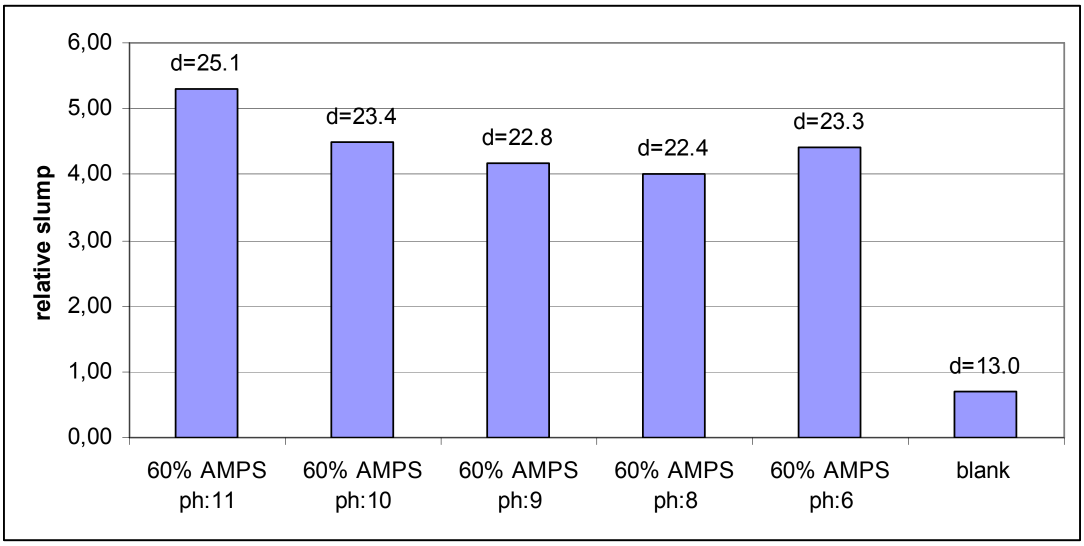

Figure 3.11 Slump test results of 60% AMPS-MAA with different reaction pH’s

3.2.1.3 Effect of Sample Solution pH

The effect of direct pH change before the mini slump-flow test was also examined. For this purpose, the fluidity trend was examined from pH 8.5 to pH 4.0 (Fig. 3.12). It is found that in both acidic and alkaline media, the fluidity is enhanced. At pH 7, the AMPS-MAA copolymer shows the minimum fluidity, since the concentration of H^+ ions is equal to the concentration of OH^- ions and Na^+ ion content is limited. When acidity increases, there is a slight increase in the fluidity, however, when the alkalinity increases, the increase in the fluidity is more significant, and its results are given in Fig. 3.12.

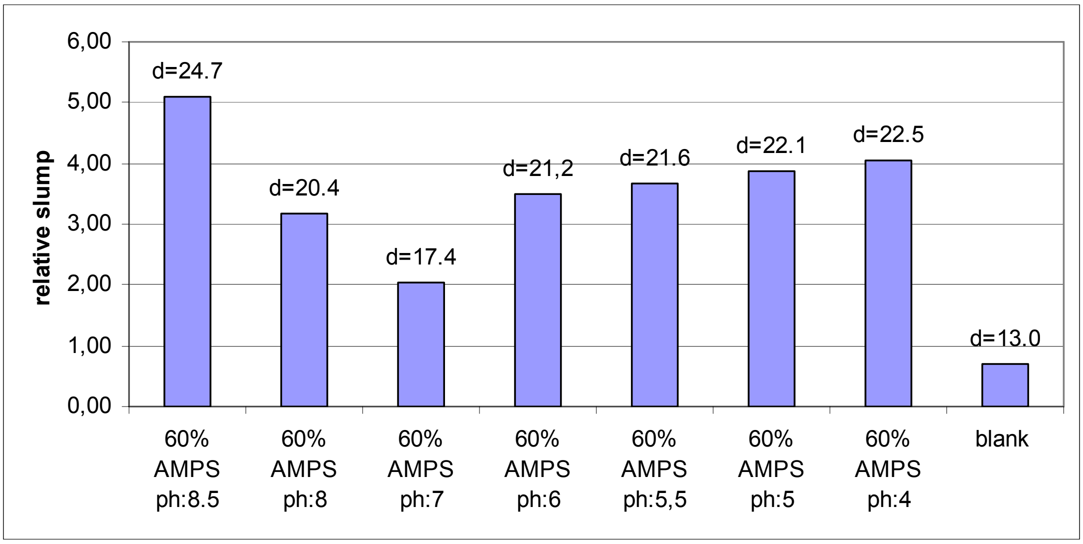

Figure 3.12 Slump-flow test results of 60% AMPS-MAA with different solution pH's.

3.2.2 Mini Slump-flow Test Results of AMPS-PEGMA and AMPS-PEGA

3.2.2.1 Effect of PEG Content

In the graph of fluidity results of AMPS-PEGMA with different feed composition (Fig. 3.13), the highest fluidity was observed in the AMPS-PEGMA copolymer with a feed ratio of 5% PEGMA. The same trend can be observed in the copolymers with PEGA (Fig. 3.14). It is interesting that the both two copolymers with 5% and 25% PEGMA gave higher fluidity than the copolymer with 15% PEGMA. This result is possibly related to the different feed ratios which may be responsible for the formation of some homopolymers, and change in molecular weight which will be discussed in dilute solution viscosimetry results.

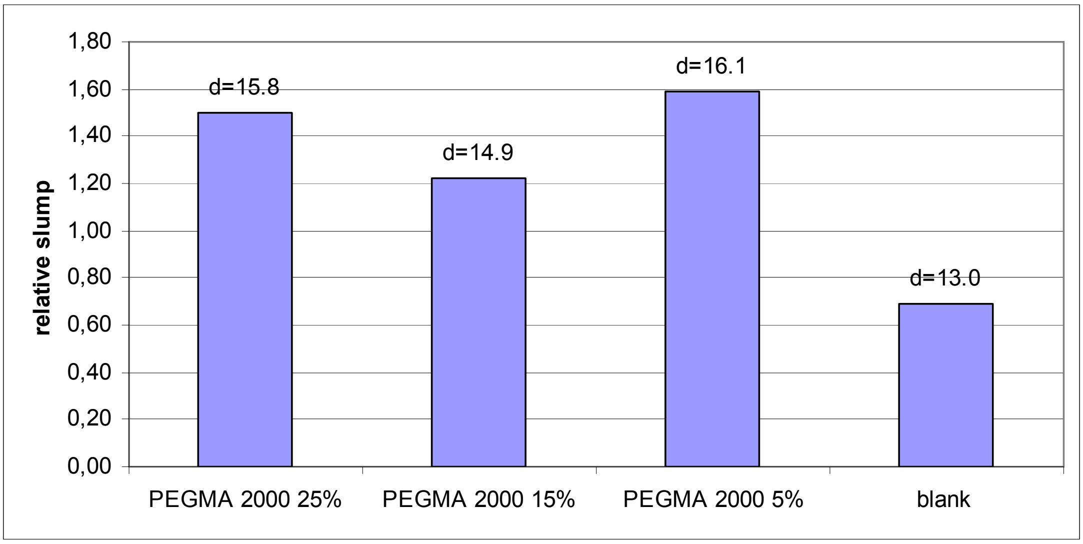

Figure 3.13 Slump-flow test results of AMPS-PEGMA with different feed compositions.

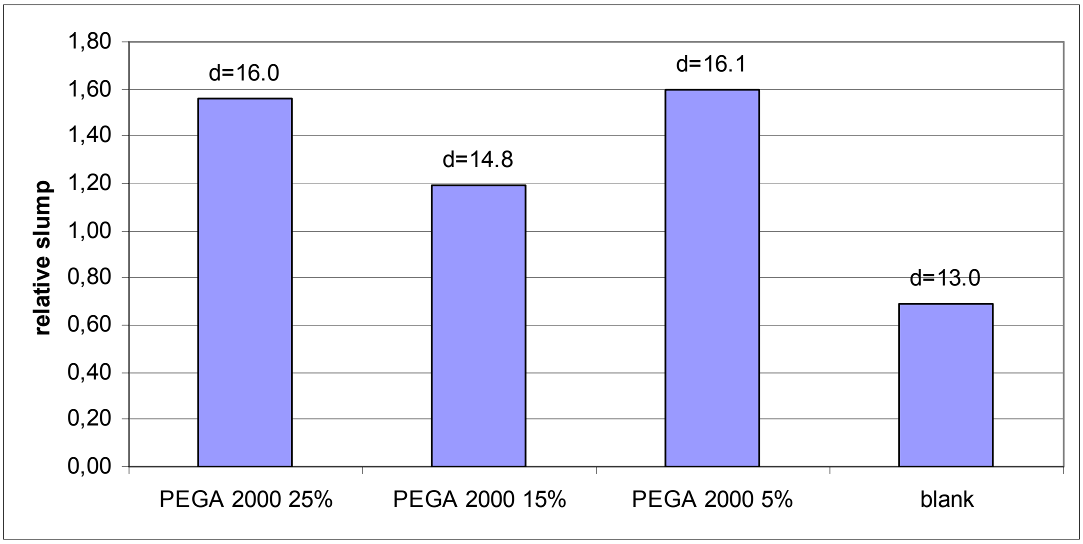

Figure 3.14 Slump-flow test results of AMPS-PEGA with different feed compositions.

3.2.2.2 Effect of Reaction pH

AMPS-PEGA copolymers, synthesized at low pH, gave higher fluidity in mini slump-flow tests. Possible explanation of this behavior is the non-ionic end of grafted PEG chains. –OCH_3 group is a hydrophobic end group, and it tends to attach the hydrophobic ethyl parts of PEG chains in aqueous medium, this causes a clustering “gel”, a network-like structure [23].Thus, the PEG chains cannot work as a comb-like structure which causes steric hindrance in the aqueous media. Hydrochloric acid which was used for adjusting the pH of the synthesis generally increases the solubility of PEG chains in aqueous media [24]. This means that in acidic media, the PEG chains tend to extend and the interactions decrease between each other, and they work as a comb-like structure in the solution. Thus, the fluidity is increasing in acidic medium for the copolymers with PEG. In Fig. 3.15, fluidity results of samples with different reaction pH are shown.

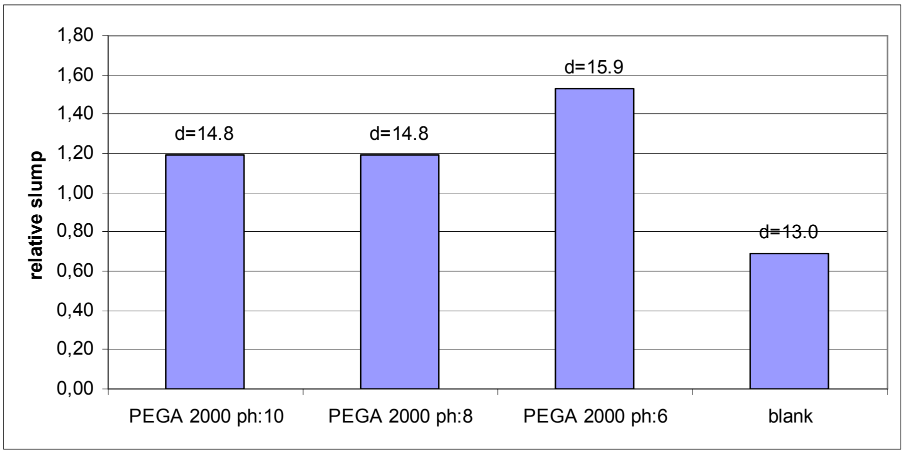

Figure 3.15 Slump-flow test results of 15% AMPS-PEGA with different reaction pH’s

3.2.2.3 Effect of Methyl Group

From the Fig. 3.16, the effect of the methyl group on the composition of the copolymers is observable. It is known that there is an optimum molecular weight giving the highest fluidity. In the study of Ye and his friends [8], the optimum molecular weight of the copolymers that gives the highest fluidity is 50,000 g/mol. So as mentioned previously, the methyl side group changes the reactivity of AMPS with the PEG acrylates, as a result, the molecular weight will be different in copolymers PEGMA and the copolymers with PEGA, thus the different molecular weight of AMPS-PEGA and AMPS-PEGMA leads to different relative slump values.

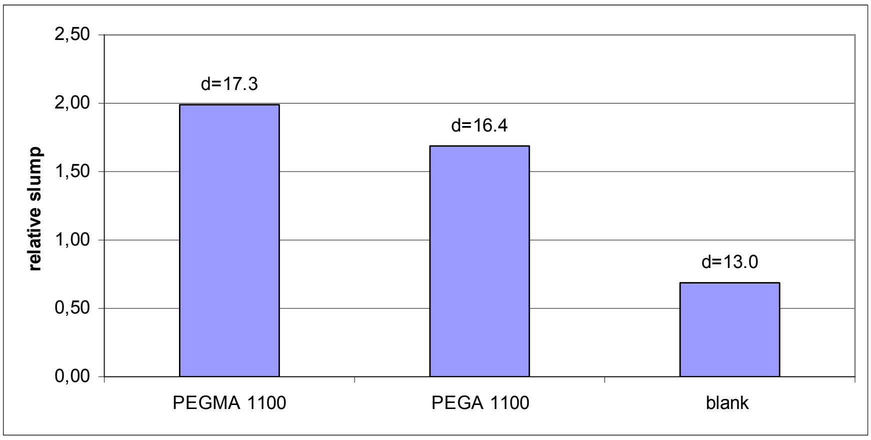

Figure 3.16 Slump-flow test results of AMPS-PEGMA and AMPS-PEGA with 15% PEG acrylate ratio

3.2.2.4 Effect of Molecular Weight of PEG

As mentioned previously, the length of PEG side chains has a minor influence on relative slump, since the conformation of the long side chains are generally “mushroom-like”. In the comparison of relative slump values of AMPS-PEGMA copolymers with different molecular weight of PEG, which are shown in Fig. 3.17, the relative slump value of AMPS-PEGMA with PEG 1100 is higher than one with PEG 2000. In Fig. 3.18, the same comparison is represented for AMPS-PEGA copolymers.

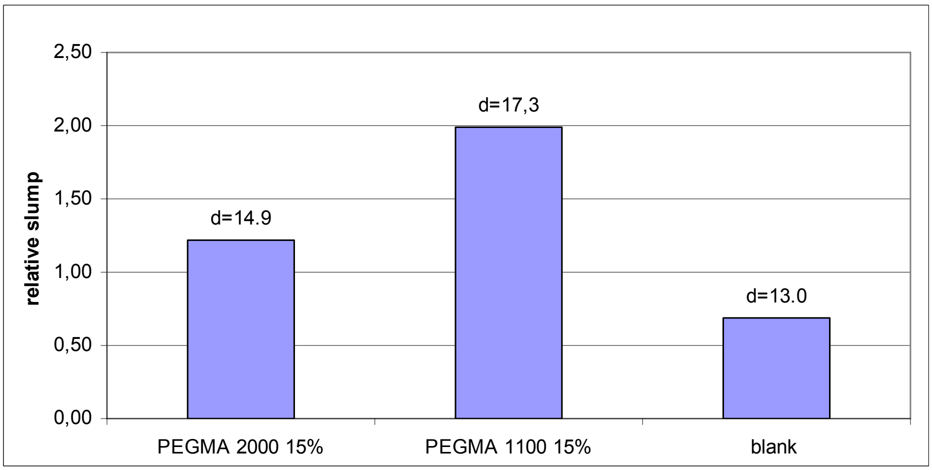

Figure 3.17 Comparison of relative slump values of AMPS-PEGMA with different molecular weight of PEG

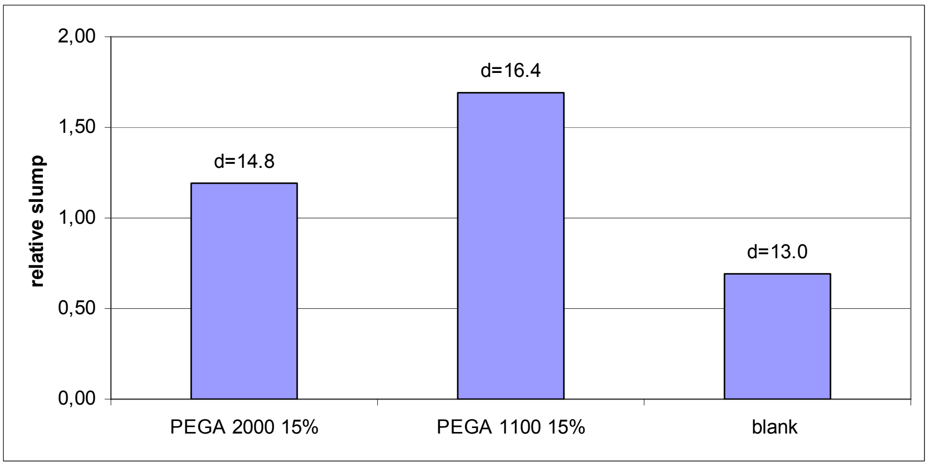

Figure 3.18 Comparison of relative slump values of AMPS-PEGA with different molecular weight of PEG.

3.3 Dilute Solution Viscosimetry Results

Dilute solution viscosimetry measurements are performed in order to study the effect of molecular weight on mini slump-flow tests. As given from literature [10], molecular weight is also an important parameter which affects fluidity. Since the samples show polyelectrolyte behavior, their intrinsic viscosities cannot be determined. Yet, η_{sp}/C vs C plots give some comparative information about the sizes of the molecules.

3.3.1 Dilute Solution Viscosimetry Results of AMPS-MAA

3.3.1.1 Effect of Composition

In Fig. 3.19, the η_{sp}/C vs C results for 60%, 40% and 20% AMPS-MAA copolymers are given. As seen from the figure, viscosity average molecular weights of the samples are having very slight difference, and when the fluidity results are considered, it is observed that 40% AMPS-MAA copolymer has the highest fluidity and comparatively the highest molecular weight.

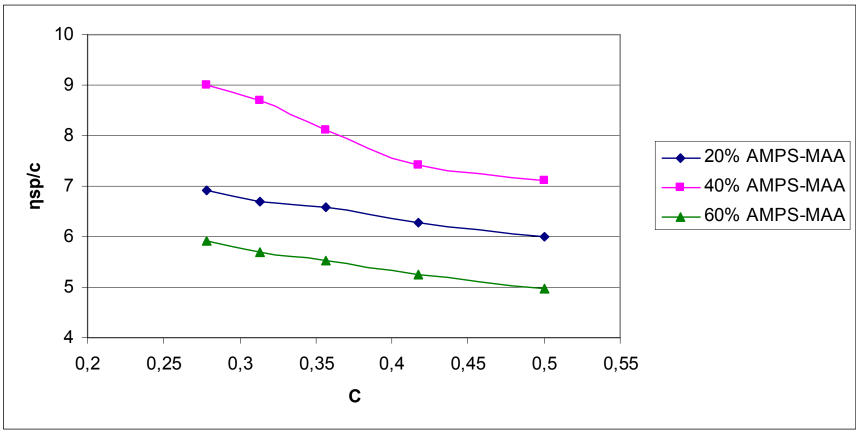

Figure 3.19 Dilute solution viscosimetry results of AMPS-MAA copolymers with different feed ratio

3.3.1.2 Effect of Reaction pH

When the reaction pH of the AMPS-MAA copolymers changes, the differences in the results of the solution viscosity measurements become observable. In the Fig. 3.20, the polyelectrolytic effect can be easily observed. Additional to having the highest molecular weight, AMPS-MAA synthesized with a pH 11 shows the highest fluidity in mini-slump-flow tests.

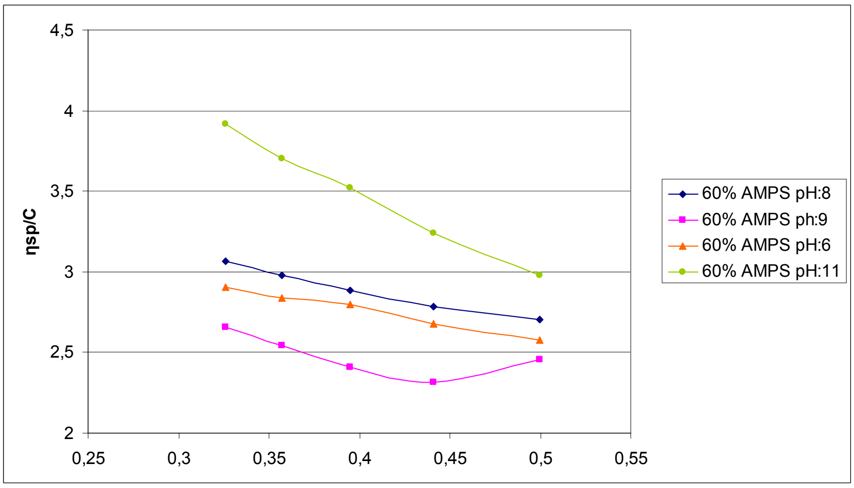

Figure 3.20 Dilute solution viscosimetry results of AMPS-MAA copolymers with different reaction pH’s

3.3.2 Dilute Solution Viscosimetry Results of AMPS-PEGMA and AMPS-PEGA

3.3.2.1 Effect of PEG Content

The AMPS-PEGMA 2000 copolymers which have different PEG contents are compared in terms of dilute solution viscosimetry in Fig. 3.21. From this comparison, it is observed that higher PEG content decreases the polyelectrolytic behavior of the samples; furthermore, in 25% AMPS-PEGMA copolymer, polyelectrolytic behavior is hardly observed. When the mini slump-flow test results are considered, 5% AMPS-PEGMA copolymer has the highest fluidity and relatively the highest molecular weight.

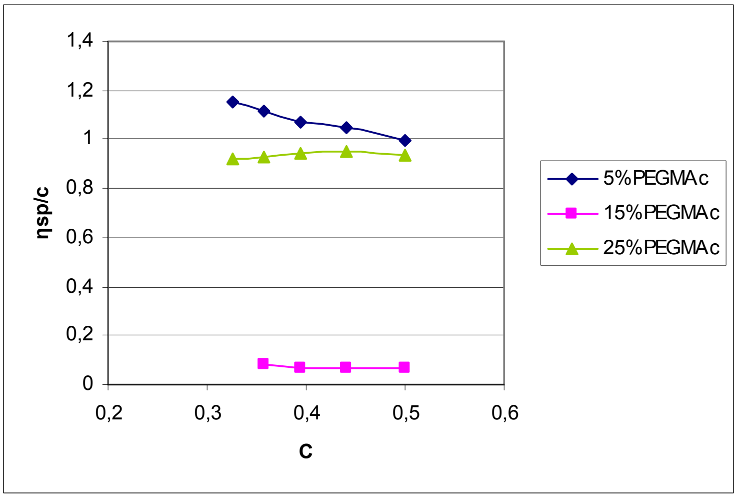

Figure 3.21 Dilute solution viscosimetry results of AMPS- PEGMA with different feed composition

3.3.2.2 Effect of Reaction pH

Dilute solution viscosity measurement results of AMPS-PEGA copolymers synthesized at different reaction pH are shown in Fig. 3.22. The AMPS-PEGA copolymer synthesized at acidic media, pH 6, shows the highest polyelectrolytic effect, with respect to synthesis pH 8 and 10. When the viscosity average molecular weights of the samples are considered, the sample is a candidate for highest molecular weight and it has the highest fluidity in mini slump-flow tests.

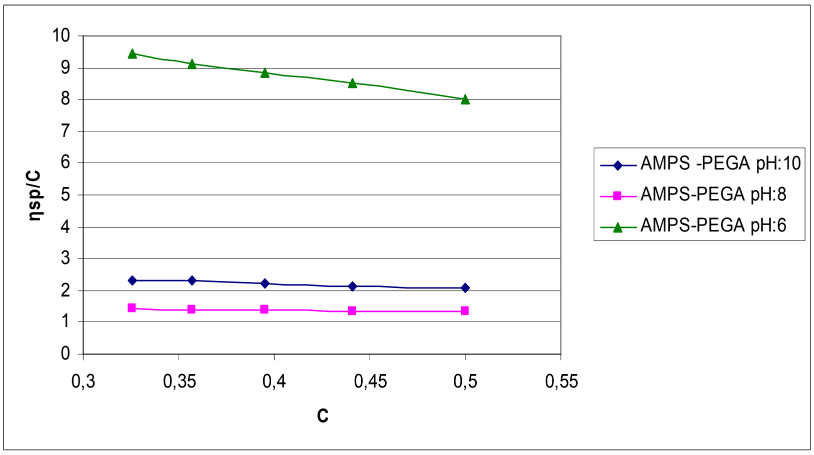

Figure 3.22 Dilute solution viscosimetry results of AMPS-PEGA with different reaction pH

3.3.2.3 Effect of Methyl Group

In Fig. 3.23, the comparison of dilute solution viscosimetry results of AMPS-PEGMA 1100 and AMPS-PEGA 1100 is represented. AMPS-PEGMA has higher molecular weight, higher polyelectrolytic effect, and also in mini slump-flow tests, it has higher fluidity than AMPS-PEGA.

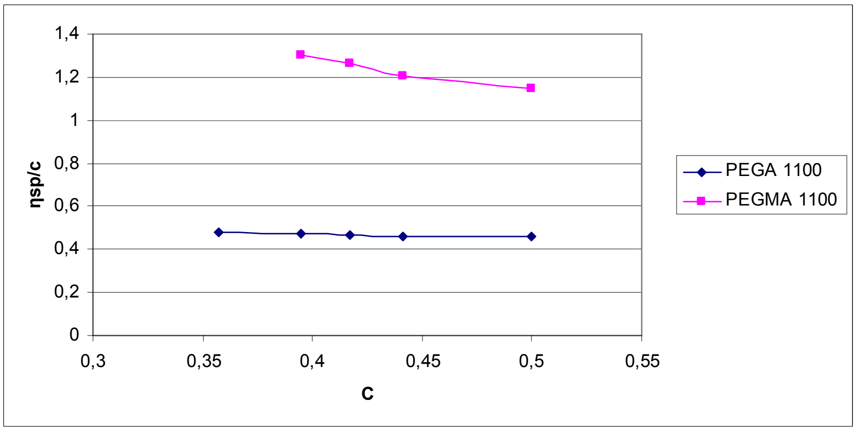

Figure 3.23 Dilute solution viscosimetry results of AMPS-PEGMA and AMPS-PEGA copolymers with PEG having molecular weight 1100.

3.3.2.4 Effect of Molecular Weight of PEG

The effect of long PEG side chains on the molecular weight of copolymers is observed in comparison of dilute solution viscosimetry results of AMPS-PEGMA copolymers with PEG 1100 and PEG 2000 which are represented in Fig. 3.24. as seen from the figure, longer the PEG chain lower the molecular weight which proves an indirect relation between PEG length and the molecular weight of the copolymer. When the slump-flow test results are considered, AMPS-PEGMA 1100 having higher molecular weight has higher fluidity.

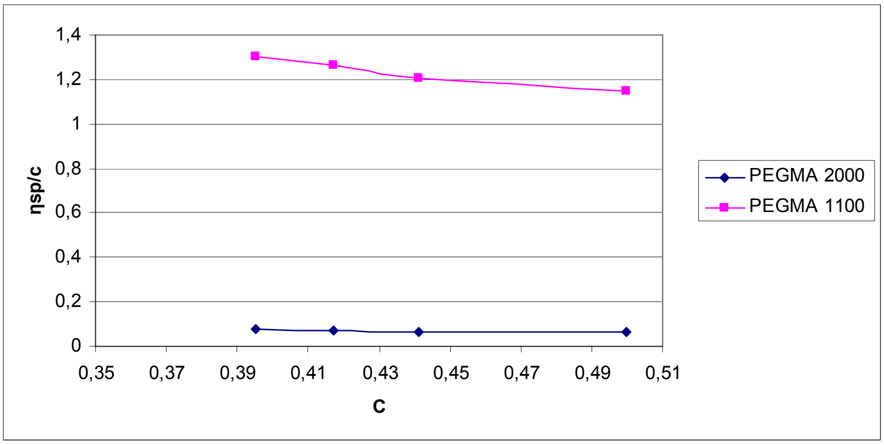

Figure 3.24 Comparison of dilute solution viscosimetry results of AMPS-PEGMA copolymers with PEG 1100 and PEG 2000.

3.4 Mechanical Strength Test Results

3.4.1 Flexural Strength Test Results

Maximum flexural stresses experienced by the mortar samples at their moment of rupture are given in Table 3.1.

Table 3.1 Maximum flexural stresses experienced by the mortar samples

		Force (kgf)			Force (kgf)
A	sample 1	250	D	sample 1	230
	sample 2	235		sample 2	275
	sample 3	240		sample 3	240
B	sample 1	190	E	sample 1	225
	sample 2	205		sample 2	260
	sample 3	175		sample 3	225
C	sample 1	120	F	sample 1	250
	sample 2	115		sample 2	270
	sample 3	130		sample 3	235

Samples illustrated with the letters in the Table 3.1 are defined as:

- A: The blank mortar (with no admixture)
- B: AMPS-PEGMA with 15% PEG of molecular weight of 1100 and reaction pH 8.
- C: AMPS-PEGA with 15% PEG of molecular weight of 2000 and reaction pH 6.
- D: AMPS-PEGMA with 25% PEG of molecular weight of 2000 and synthesis pH of 8.
- E: AMPS-MAA copolymer with 60% AMPS and reaction pH 11.
- F: AMPS-PEGA with 25% PEG of molecular weight of 2000 and synthesis pH of 8.

The stress data obtained from the flexural strength test is inserted into the equation 8 and the units are converted according to the conversion labeled as equation 9, the average flexural strength results of the mortar samples in kgf/cm^2 and N/mm^2 are represented in Table 3.2.

Table 3.2 Flexural strengths of mortar samples

	A	B	C	D	E	F
kgf/cm²	67,97	53,44	34,22	69,84	66,56	70,78
N/mm²	6,66	5,24	3,35	6,84	6,52	6,94
std.dev.	35,52	26,04	17,05	33,36	32,17	34,92

The discussion for the flexural strength results and the compressive strength results will be done together.

3.4.2 Compressive Strength Test Results

Maximum compressive stresses experienced by the mortar samples at the moment at which the samples are crashed are given in Table 3.3.

Table 3.3 Maximum compressive stresses experienced by the mortar samples

		Force (kgf)			Force (kgf)
A	sample 1	8870	D	sample 1	6370
	sample 2	7080		sample 2	6130
	sample 3	6940		sample 3	6350
B	sample 1	5280	E	sample 1	7990
	sample 2	5240		sample 2	6760
	sample 3	5020		sample 3	7170
C	sample 1	2790	F	sample 1	6260
	sample 2	2360		sample 2	6580
	sample 3	2480		sample 3	6290

The average compressive strength data calculated in kgf/cm^2 and N/mm^2 from equation 10 are given in Table 3.4.

Table 3.4 Compressive strengths of the mortar samples

	A	B	C	D	E	F
kgf/cm²	438,125	323,75	158,9583	392,7083	473,75	398,5417
N/mm²	42,93625	31,7275	15,57792	38,48542	46,4275	39,05708
std.dev.	220,7648	150,5336	89,88111	187,5508	230,526	184,8172

The water content of all mortar samples are the same, thus, their mechanical properties are also expected to be similar with the blank mortar, however, the samples showed higher fluidity than the blank mortar in slump-flow tests. Except the sample C, all the other four samples give approximately the same mechanical strength with the blank mortar.

Since the copolymers which are water-reducing agents, will reduce the water content of the concrete, their mechanical strengths are expected to improve to a noticeable values [25].

As it is shown in Fig. 3.22, the molecular weight of the sample C, AMPS-PEGA copolymer having reaction pH of 6, is significantly higher than the AMPS-PEGMA copolymers with reaction pH 8 and 10. This higher molecular weight of the polymer will prevent the interaction of cement particles with each other and with water. This is an advantage for fluidity and workability of mortar, however, for hardening, the cement particles should interact with water, get hydrated and form a network structure with the other cement particles and work as glue for the aggregates. For the sample C, the high molecular weight of this superplasticizer induces an inhibition on the interaction of the cement particles and this inhibition causes a decrease in mechanical strength in the mortar samples. The same situation is valid for the sample B, AMPS-PEGMA with 15% PEG 1100.

3.5 Zeta Potential (ζ) Measurement Results

The zeta potential and mobility values of the selected copolymers are given as a graph in Fig. 3.25.

Although, the highest fluidity is observed for the AMPS-MAA copolymer with 60% AMPS content among all the species tested in this work, it does not show the higher zeta potential value.

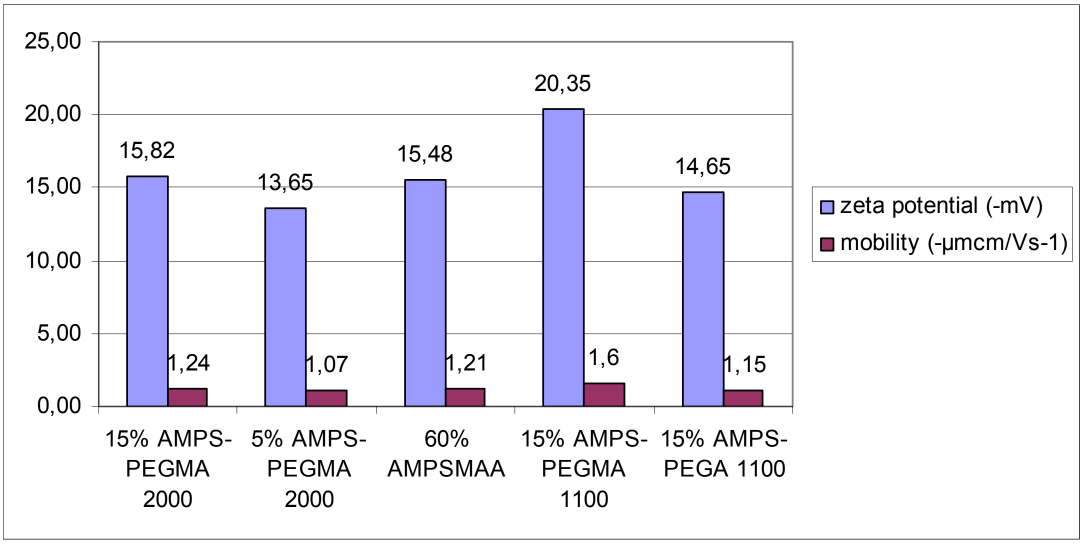

Figure 3.25 Zeta potential and electrophoretic mobility values of the samples

The most important factor that has an effect on zeta potential is pH. A zeta potential value on its own without a quoted pH does not indicate a property for the samples [13]. In the zeta potential measurements, pH of all samples are adjusted to the same value, thus the pH effect on the zeta potential value can be neglected. The pHs of all samples are adjusted to 13.20.

It is reported that [26], |ζ| (absolute zeta potential value) is proportional to the amount of adsorbed carboxylate and sulfonate groups. Furthermore, there is an inverse proportionality between the molecular weight of the superplasticizer and adsorption of the copolymers to the cement particles.

The adsorption mechanism is also affected from the adsorption conformation [27]. Thus, different trend of zeta potential measurements from fluidity tests may possibly be due to the relatively lower molecular weight of AMPS-PEGMA copolymers with respect to the AMPS-MAA copolymer, as it can be seen from the dilute solution viscosimetry results. Furthermore, the long PEG side chains cause different adsorption conformation from AMPS-MAA copolymer having no long side chains.

It is also reported that, more negative zeta potential values indicate that electrostatic repulsion is responsible for dispersion, and less negative zeta potential values indicate that steric hindrance of side chains is responsible for the dispersion [27]. Thus, in spite of the significantly higher molecular weight of 60% AMPS-MAA copolymer, the zeta potential of this sample is not very low when compared to the copolymers with PEG side chains whose molecular weights are significantly low.

CHAPTER 4

CONCLUSION

In this study, a series of concrete superplasticizer, AMPS-MAA, was synthesized in various compositions and pHs according to the procedure from the study of Ye et.al [10]. With the similar procedure, two novel carboxylate type copolymers AMPS-PEGMA and AMPS-PEGA were designed and synthesized in various compositions and pHs, as a superplasticizer in concrete. The effect of these polymers to the fluidity of concrete is studied in terms of polymer compositions, reaction pH and pH of the fluidity test sample solutions, molecular weight of the copolymers, content and molecular weight of PEG side chains. As a result, it can be concluded that;

- In a scope of composition in AMPS-MAA copolymers, AMPS-MAA copolymer with 40% AMPS content gave the highest positive fluidity.

- The pH of the reactions and the solutions prepared for fluidity tests also affects the fluidity. In both situations, increase in the amount of ions caused an increase in fluidity, furthermore, basic media gave higher fluidity to the cement paste samples than the acidic media. AMPS-MAA copolymer with 60% AMPS content and synthesized at a pH of 11 has given the highest fluidity in slump-flow tests. In PEG-grafted samples, compared to reaction pH, molecular weight of the samples had a more significant effect on fluidity. AMPS-PEGA copolymer synthesized at a pH of 6 has given the highest fluidity result.

- The variation in the PEG content of copolymers produced a change in polyelectrolytic behavior of the copolymers, increasing PEG content decreased the polyelectrolytic behavior, however the fluidities of the samples were affected more from viscosity average molecular weights.

- As a result of change in the composition and molecular weight of the copolymers, AMPS-PEGMA copolymers showed higher viscosity average molecular weight and fluidity values than AMPS-PEGA copolymers.

- Copolymers with PEG side chains with a molecular weight 1100 gave higher fluidity and viscosity average molecular weight values than copolymers with PEG 2000 side chains.

- For all the samples tested in this research, increase in molecular weight caused an increase in fluidity, however, a decrease in mechanical properties due to the retardation of hydration of the cement particles.

- The samples, except C, showed similar mechanical strengths with respect to the blank mortar. It is well known that reducing water content results in better mechanical properties, therefore the water reducing agents will reduce the water content of the concrete thus, improve the mechanical properties.

- Zeta potential measurement results showed that a slipping surface has formed between colloids formed from the cement particles and the copolymers adsorbed to them, consequently provided the dispersion of the cement particles in the aqueous medium.

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APPENDIX

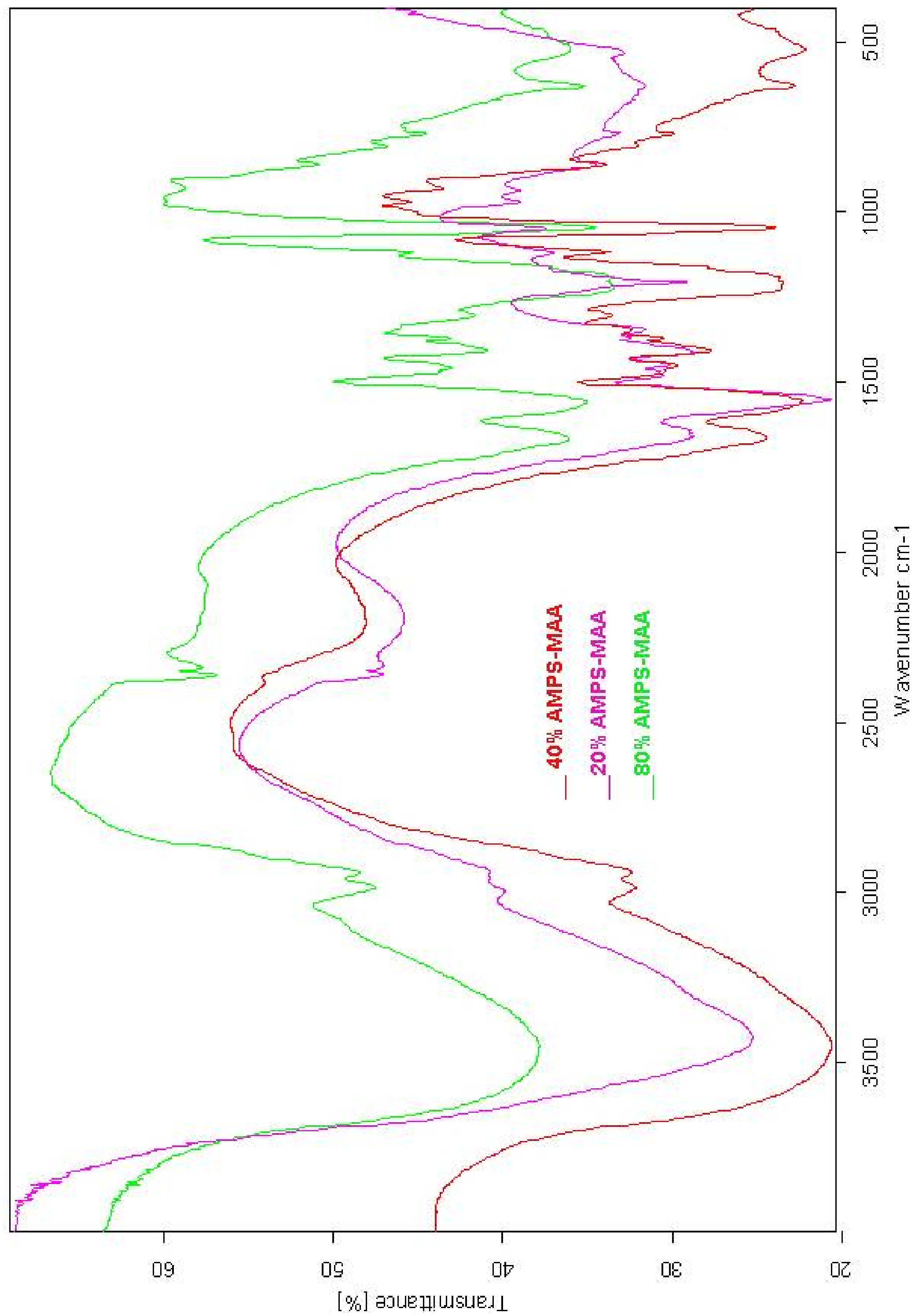

Figure A.1 FT-IR Spectra of 20%, 40% and 80% AMPS-MAA copolymers

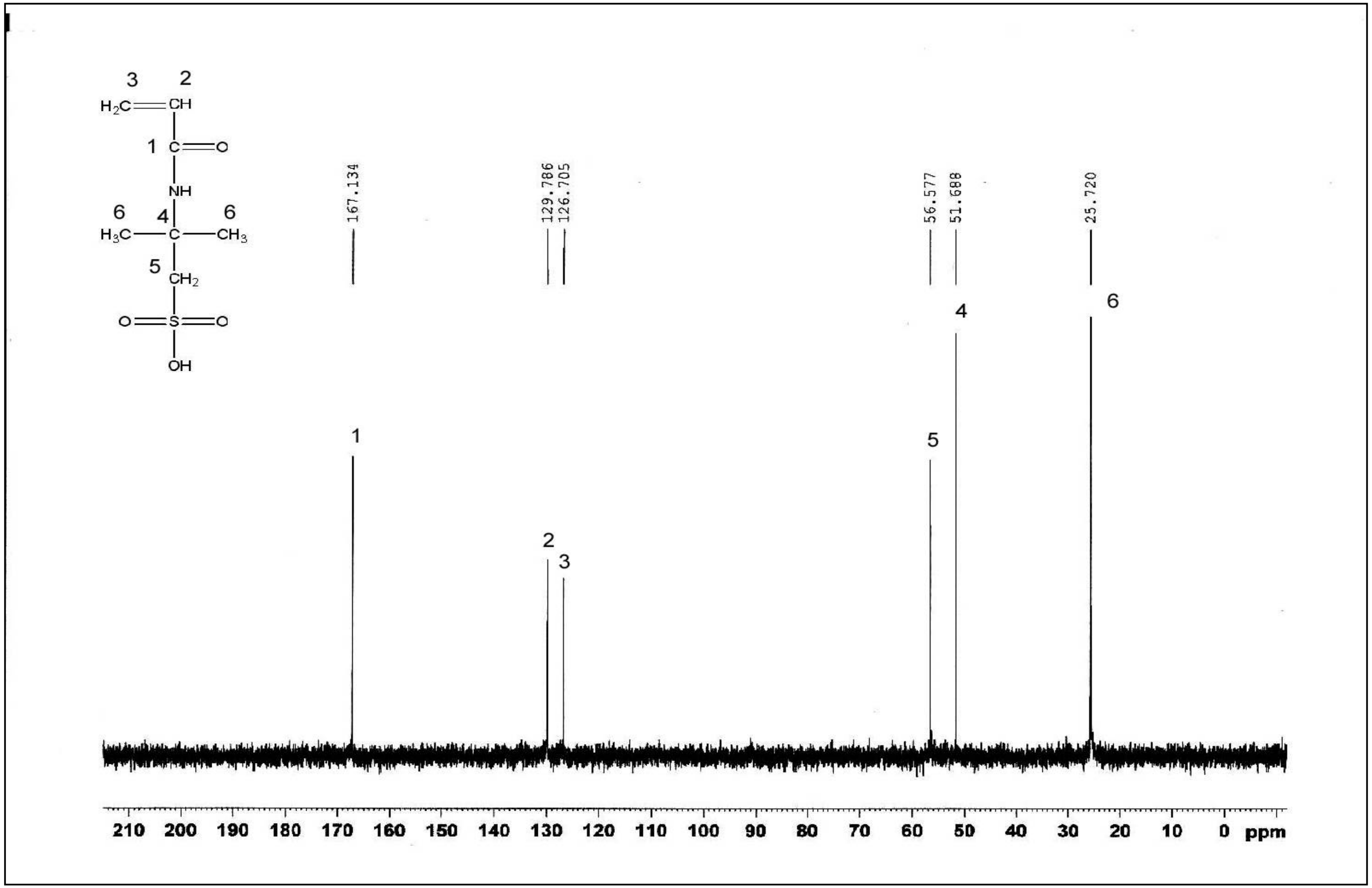

Figure A.2 ^{13}C NMR of AMPS monomer

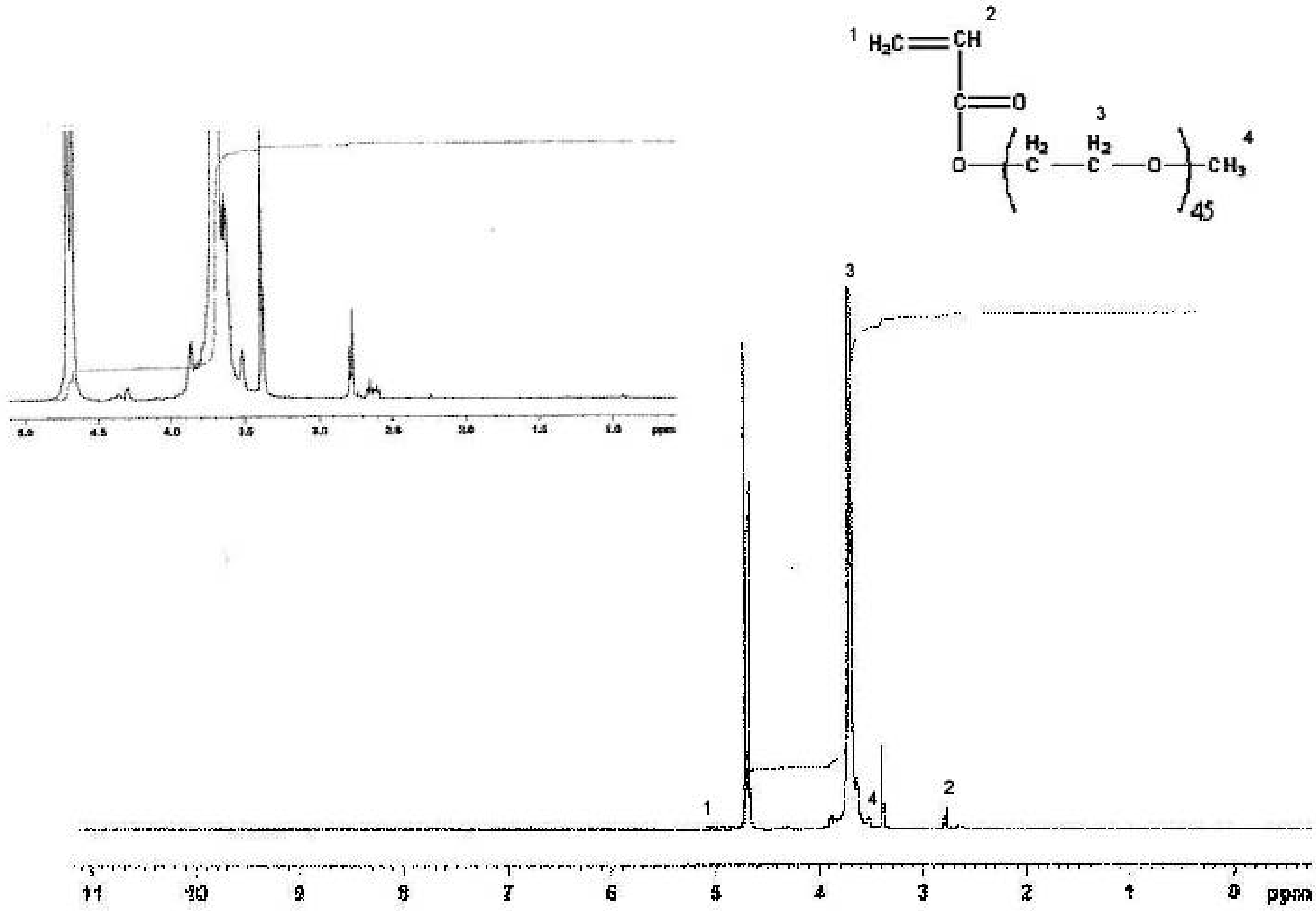

Figure A.3 ^{1}H NMR of PEGA 2000 macromonomer

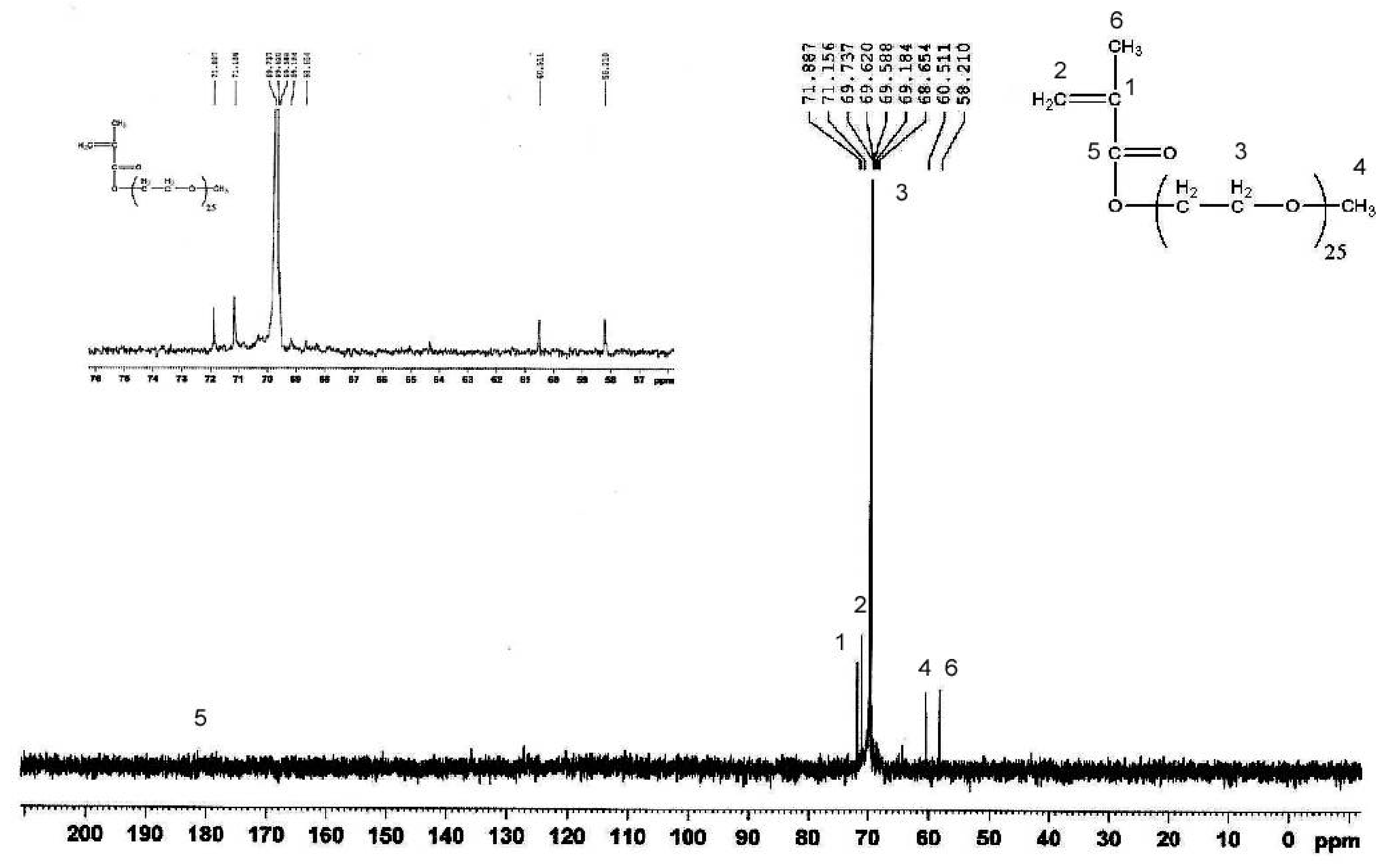

Figure A.4 ^{13}C NMR of PEGMA macromonomer

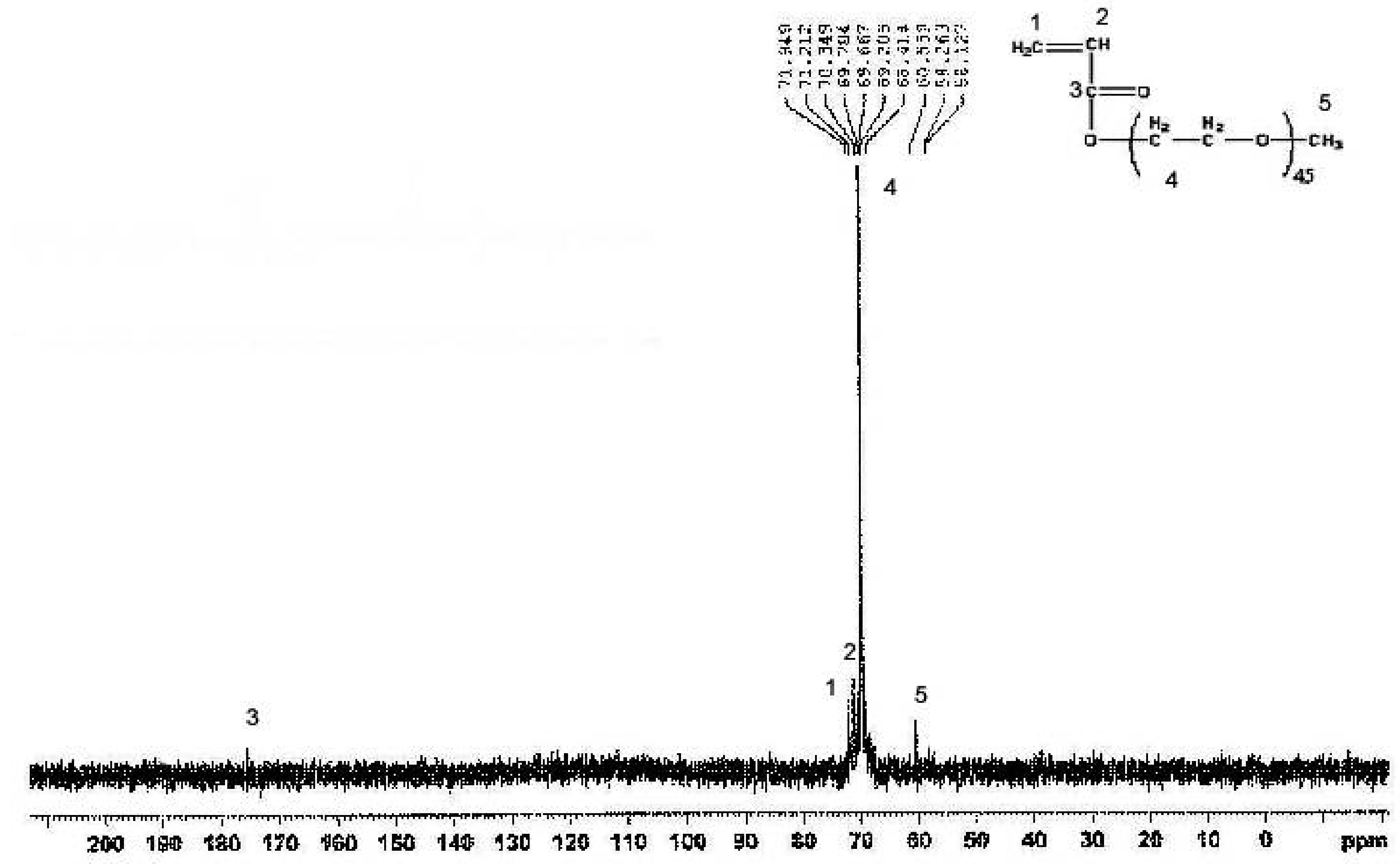

Figure A.5 ^{13}C NMR of PEGA 2000 macromonomer

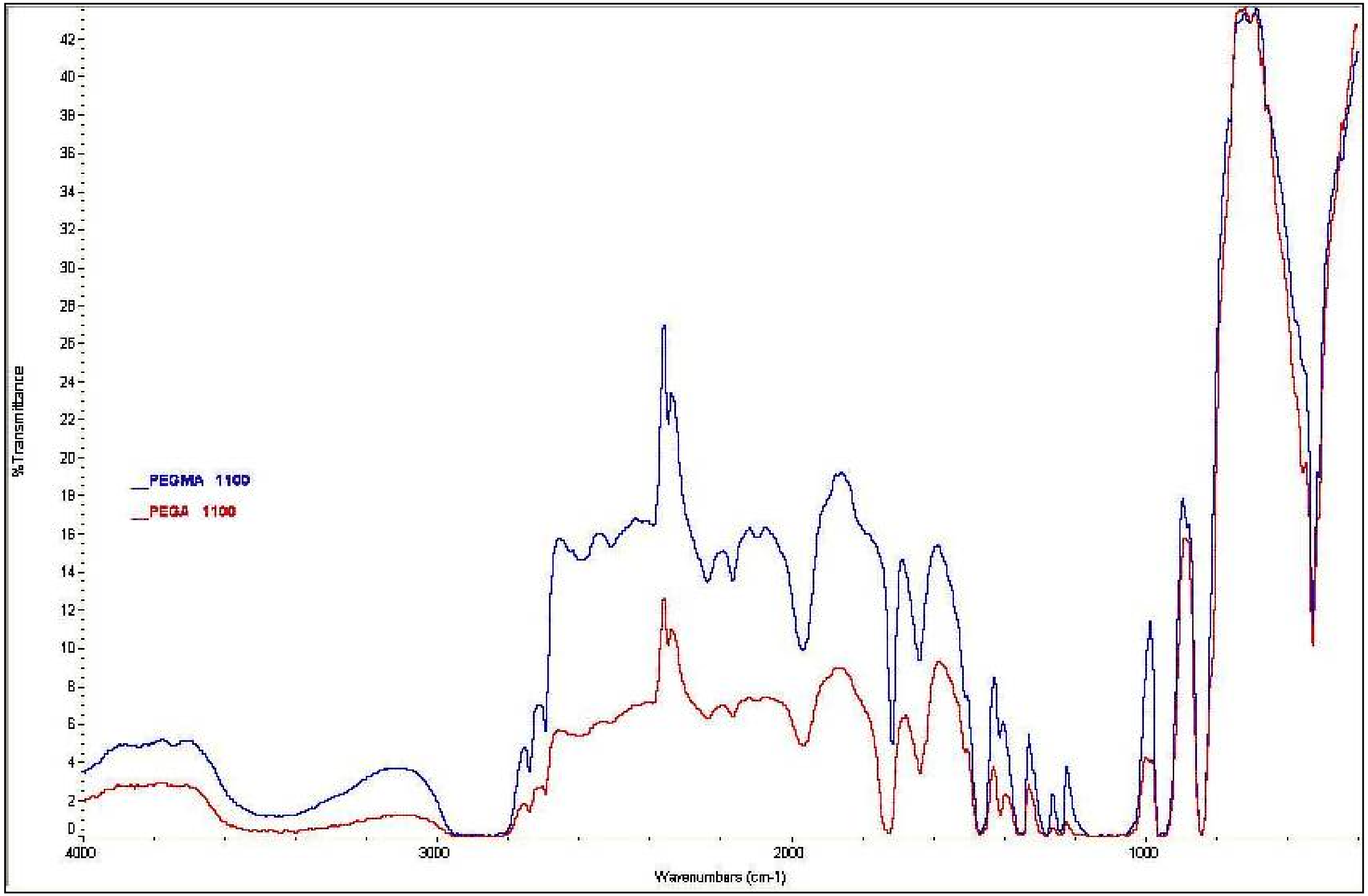

Figure A.6 Comparable FT-IR spectra of PEGMA 1100 and PEGA 1100.

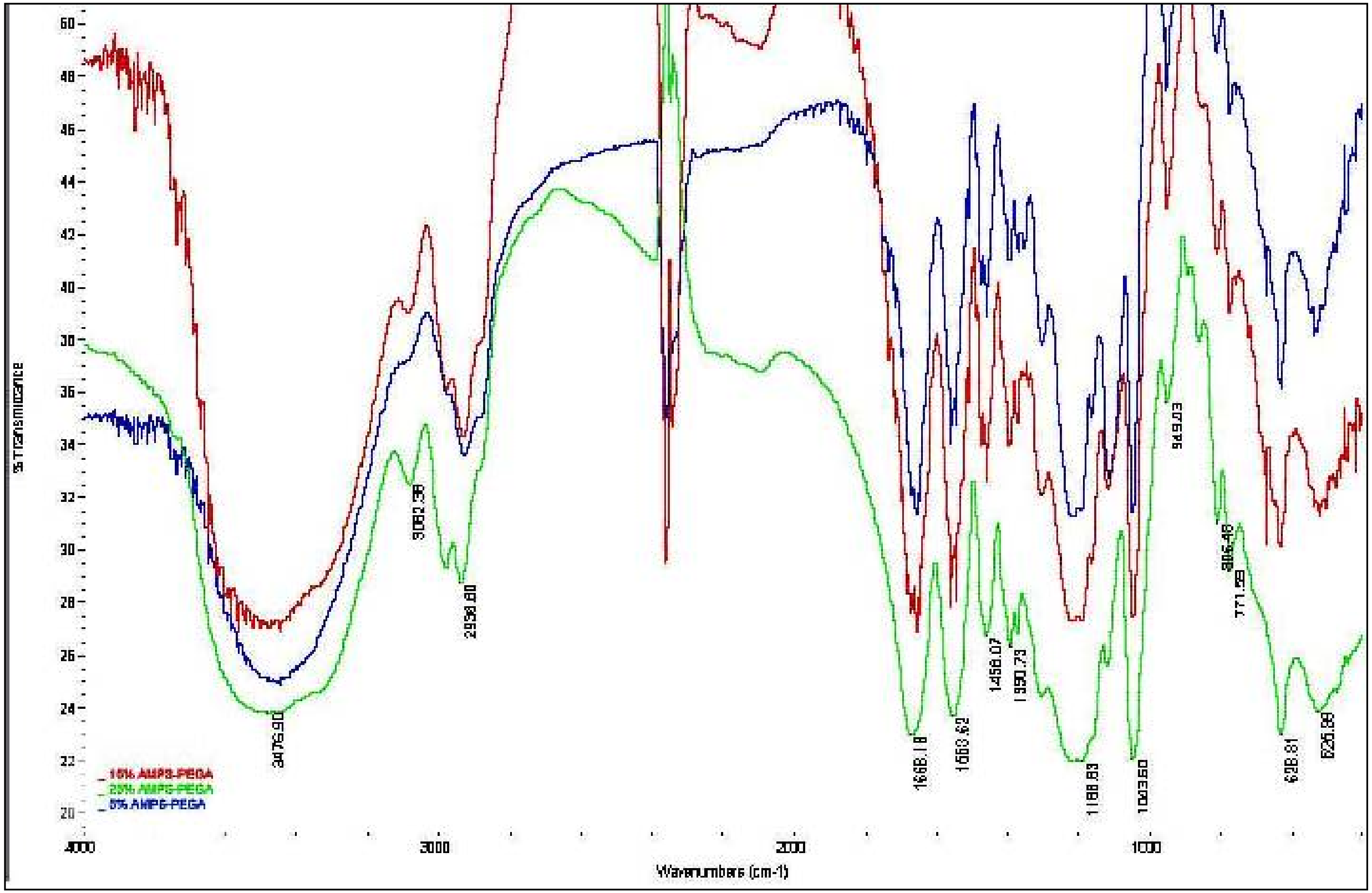

Figure A.7 FT-IR Spectra of AMPS-PEGA copolymers with different compositions

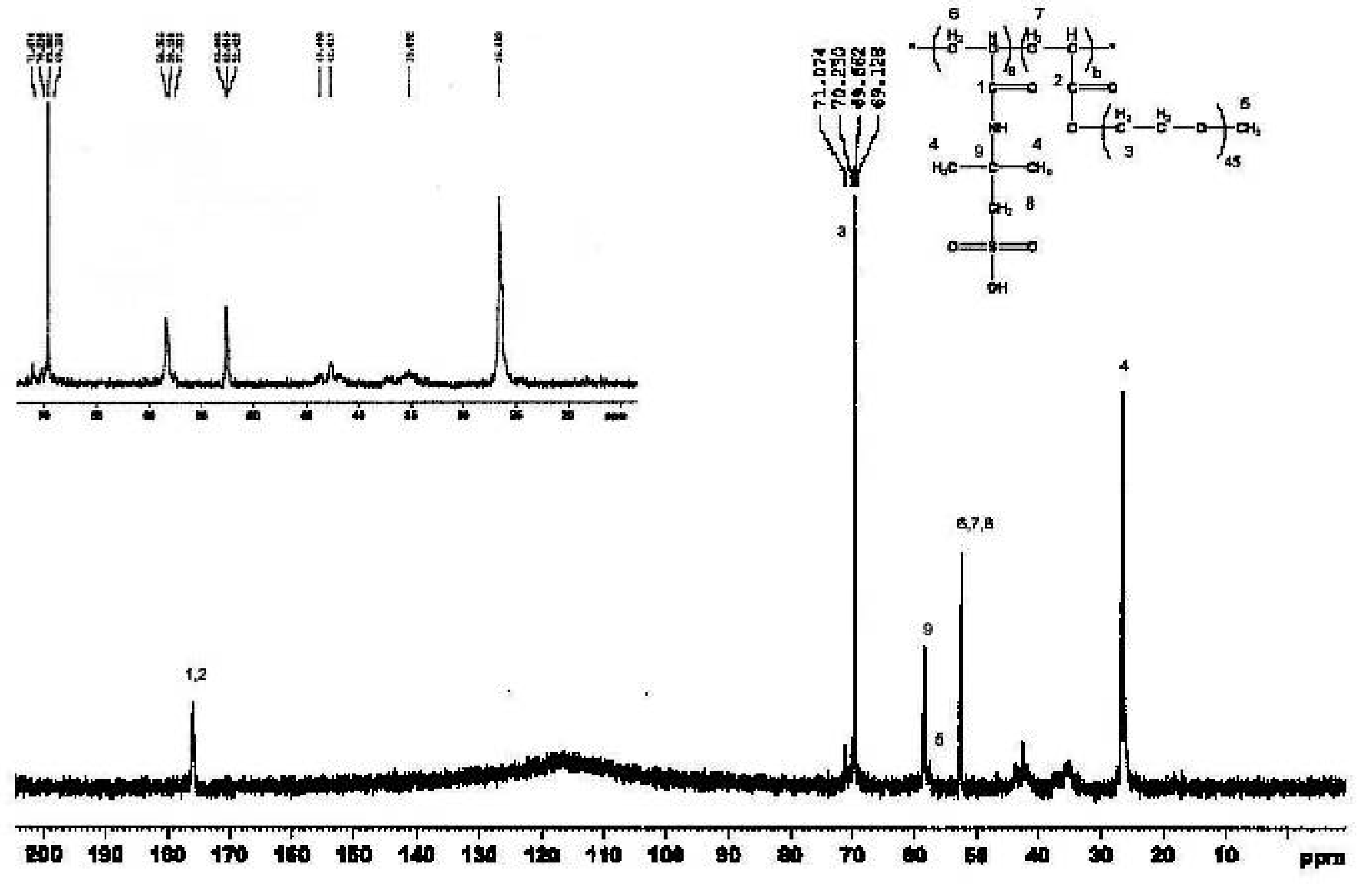

Figure A.8 ^{13}C NMR of 15% AMPS-PEGA copolymer with reaction pH 6.

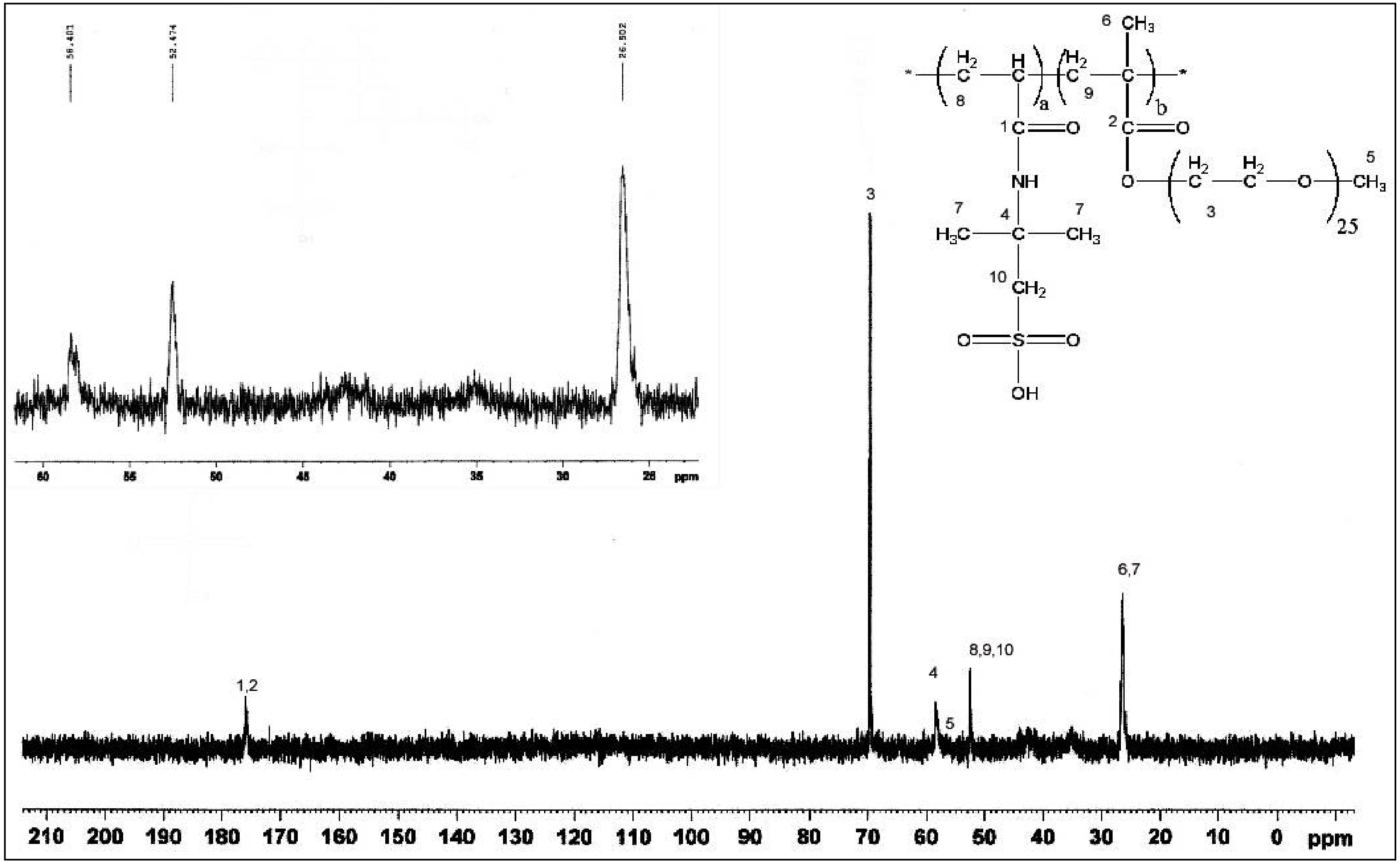

Figure A.9 ^{13}C NMR of 15% AMPS-PEGMA copolymer with PEG molecular weight of 1100

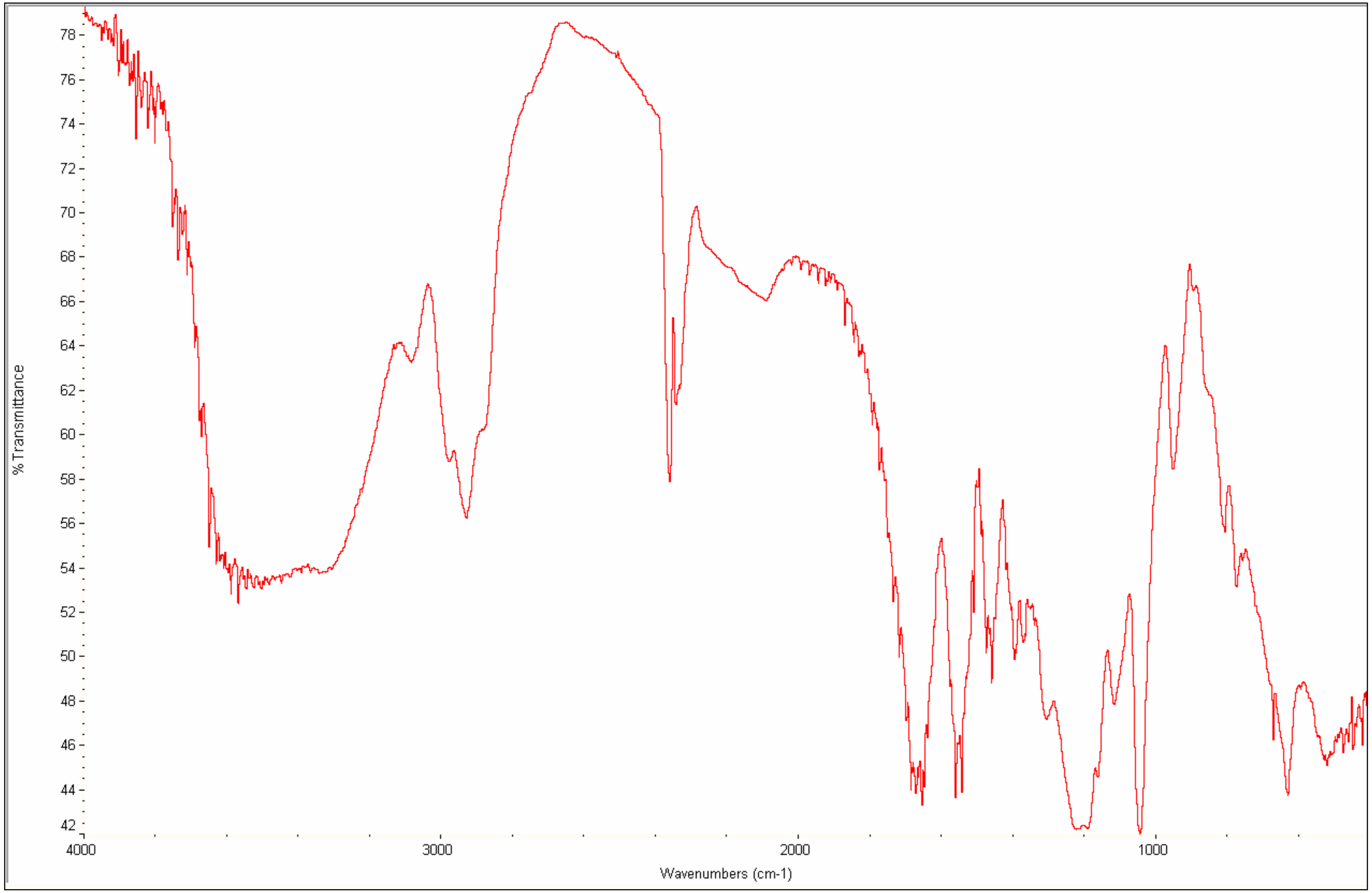

Figure A.11 FT-IR spectrum of 15% AMPS-PEGA copolymer with reaction pH of 6