FORMALDEHYDE-FREE CROSSLINKER SYNTHESIS IN WATERBORNE BINDER DISPERSIONS FOR TEXTILE INDUSTRY

by

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ABSTRACT

FORMALDEHYDE-FREE CROSSLINKER SYNTHESIS IN WATERBORNE BINDER DISPERSIONS FORTEXTILE INDUSTRY

In textile industry, the binders used are mostly water based acrylic dispersions. These binders provide strength, elastic recovery, soft hand, flexibility, color retention and also resistance to washing and aging to the textile and nonwoven. Nevertheless, binders having no reactive functional monomers are not very successful in imparting these properties. Self crosslinking monomers are used to improve the properties of textile and non woven end products. *N*-methylolacrylamide (NMA) is one of these monomers having functional groups for self-crosslinking. However, *N*-methylol acrylamide used in textile binders emit formaldehyde during crosslinking at high temperatures. This formaldehyde either remains in the end product or is liberated into the air. The U.S. Department of Health and Human Services published the 12th Report on Carcinogens and formaldehyde is listed in the category of *known to be a human carcinogen.* Researchers on textile sector are focud on the subject of formaldehyde emission due to the harmfull effects on both people and environment. In this study, a novel monomer that emmits no formaldehyde and have ability to self-crosslink was investigated for replacement of NMA and the performance results are compared with that of NMA.

ÖZET

TEKSTİL ENDÜSTRİSİNDEKİ SU BAZLI BAĞLAYICI DİSPERSİYONLARI İÇİN FORMALDEHİT SALIMI YAPMAYAN YENİ BİR ÇAPRAZ BAĞLAYICININ SENTEZİ

Tekstil sektöründe yaygın bir şekilde kullanılan bağlayıcılar, kullanıldıkları dokumalı ve dokumasız kumaşlara sağlamlık, dayanıklılık ve bütünlük veren emülsiyon polimerleridir. Ancak, bu tür özellikleri sağlamak için kullanılan bağlayıcılar yapılarında reaktif fonksiyonel monomerler içermediğinde yeteri kadar verimli çalışmazlar.Kendi kendine çapraz bağlanma özelliği olan monomerler kullanmak, bağlayıcı sistemlerin daha iyi çalışmasını sağlamak ve dokumalı ve dokumasız kumaşların son ürün kalitesini arttırmak için kullanılan yöntemlerden biridir. Günümüzde yaygın olarak yüksek sıcaklıklarda reaksiyona giren çapraz bağlayıcılar kullanılmaktadır ve bunlardan biri de n-metilolakrilamittir(NMA). Bunlar tekstil üzerinde film oluştururken polimerin hem kendi kendine hem de tekstile daha iyi bağlanmasını sağlarlar. Bu sayede tekstilin elastikiyeti düşmeden su ve farklı kimyasallara dayanımı artar.Ancak NMA çapraz bağlanma işleminin gerçekleştiği kürlenme aşamasında yan ürün olarak formaldehit açığa çıkarmaktadır. NMA çapraz bağlayıcı monomeri içeren bağlayıcıların kullanıldığı ürünlerde kürlenme sırasında ortaya çıkan formaldehit ya üründe kalır ya da çevreye salınır. Formaldehit toksik etkisi bulunan ve kanserojen bir maddedir. Bu durum Birleşik Devletler Sağlık ve İnsan Hizmetleri Departmanı tarafından yayınlanmış olan 12. Kanserojen Maddeler raporunda "Formaldehit, insanlarda kansere neden olduğu bilinen bir maddedir" şeklinde belirtilmiştir. Formaldehitin insan sağlığına ve çevreye zararlarından dolayı tekstil sektöründe formaldehit salınımı ya da azaltılması önemli çalışmalardan biridir. Bu gelişmeler doğrultusunda bu çalışmada formaldehit salınımı yapmayan ve NMA kullanımına alternatif olabilecek yeni bir çapraz bağlayıcı monomeri üzerinde çalışılmıştır. Sentezlenen monomerin performansı NMA ile karşılaştırılıp sonuçlar değerlendirilmiştir.

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LIST OF ACRONYMS/ABBREVIATIONS

AA	Acrylic Acid
AATCC	American Association of Textile Chemists and Colourists
AM	Acrylamide
BA	Butyl Acrylate
$CDCl_3$	Deuterated chloroform
CH_2Cl_2	Dichloromethane
CMC	Critical Micelle Concentration
CTAs	Chain Transfer Agents
DHP	2,3-Dihydro-*2H*-pyran
DiW	Deionized Water
E	Emulsion
EtOAc	Ethyl Acetate
EVAs	Ethylene-Vinylacetate Copolymers
FT-IR	Fourier Transform Infrared Spectroscopy
HCHO	Formaldehyde
MFT	Minimum Film Formation Temperature
MMA	Methyl Methacrylate
NaPS	Sodium Persulfate
NMA	N-Methylolacrylamide
NMR	Nuclear Magnetic Resonance
SBRs	Styrene-Butadiene Copolymers
SDS	Sodium Dodecyl Sulfate
t-BHP	tert-Butyl Hydroperoxide
T_g	Glass Transion Temperature
TLC	Thin Layer Chromatography
UV	Ultra Violet
VOCs	Volatile Organic Compounds

1. INTRODUCTION

1.1. Binders

Binders are any materials which bonds materials together mechanically, chemically or as an adhesive. Water based binders are simply the products of emulsion polymerization process. Emulsion polymerization is basically expressed as a free radical polymerization of monomers in aqueous medium stabilized by appropriate surfactants. A binder is also expressed as "colloidal dispersion of polymer particles in aqueous medium". The terms latex, polymer dispersions, polymer colloids and also polymer emulsions are the synonyms of binders, especially in the textile industry [1, 2].

Binders work as bonding agents and hold fibers of the nonwoven together like glue and strengthens the web.This is one of the basic techniques in the production of nonwoven fabric. During the process, the latex binder is applied to a nonwoven web and the final composition is dried and cured at appropriate temperatures. The latex binds to the web of the textile fibers sticks them to each other like an adhesive. The maximum strength of nonwoven is gained when all the intersecting points of fiber web is chemically bonded to each other. The stiffness and the integrity of nonwoven is improved by the additional binder material found at the intersecting points [3, 4].

In view of the improving performance and demand of nonwovens in various applications, properties of binders are imporant. Binder efficiency is the indicative factor in fabrics for nonwoven performance. If a nonwoven performance does not satisfy the needs, the main reason is the binder choice. The use of inadequate binder results in deficiencies in the nonwoven product.Possible deficiencies are listed below:

- Strength and integrity is not enough
- Low washing fastness
- Inadequate tear and abrasion strength
- Not soft hand

To maintain the desired performance of nonwoven products, new chemical binders were introduced over the years [5].

Natural resins and glues instead of latex binders were employed in the early stages of the nonwoven development. Although such binders are successfull to provide some strength and integrity to nonwoven web, they come short on other properties such as soft hand, firmness, solvent resistance, flame retardence, wash and aging resistance. The ideal binder used for nonwoven should have these properties as much as possible [5, 6].

Throughout history of binders, different polymer families of latexes were employed according to application area. These are butadiene-styrene copolymers(for synthetic rubber, paints, paper coatings and nonwoven fabrics), poly(vinyl acetate) copolymers (for adhesives and paints), acrylate ester copolymers(for nonwoven fabrics and exterior paints), poly(vinyl chloride) and vinyl chloride copolymers (for coatings and plastisols), polyethelene and ethylene copolymers(for coatings and plastisols).Among these, first successful binder was polyvinyl acetate. In terms of adhesion, this material had superior properties than the early natural products. Polyvinyl acetate is also very flexible. To provide stifness to the end product, there was a need to increase the amount of resin. However, adding more resin resulted in over stiffness. To achive the stiffness together with soft-hand, acrylic based binders were introduced to nonwoven sector [7].

In paralel to the demands of customers, there were huge improvements in the technology of synthetic latex binders. Superior performance expectations for the end use of nonwoven has brought new chemical components to the latex binders. By the introduction of cross-linkable and or self crosslinkable binders, there was a high flexibility in terms of binder strength, durability, and also washing fastness and dry cleanability [5].

Binders for nonwoven web application area is very large. The properties of binder used varries according to the end use. Nonwoven web application area includes hygiene (disposable tissues, towels, nappies), automotive (car interiors), consumer products, apperal, filtration, medical/surgical products, packaging, furnishings, electronics and wipes and the like. Latex binders can be used in various applications depending on the desired properties [4, 8].



Figure 1.1. Examples of nonwoven products that contain binders.

1.1.1. The Desired Properties of a Binder

The desired properties of a binder used in nonwoven goods depends on the end uses. The characteristics of nonwoven web can be altered by changing the composition of the monomer mixture used in the synthesis of the binder.The desired properties of binders are listed below [9, 10]:

- Strength and integrity: The strength and integrity of a nonwoven web is directly related with the strength of the applied binder.
- Flexibility: For the soft materials, the nonwoven substrate should have flexibility and easy handling.
- Washing / Dry Cleaning Resistance:Some nonwoven goods needs resistance to washing and dry cleaning.
- Adhesion: Depending on the end uses, binder-to-fiber bond has to be considered.
- Aging resistance:In the nonwoven web, the latex binder should be stable and there should not be any degradation on storage.
- Good Color: In nonwoven industry, there are wide ranges of colors used. The binder should be resistant to discoloration and yellowing problems should be prevented.

- Other Special Requirements:Resistance to craze, chemicals, light, oxygen, weathering, heat, flat abrasion etc. is also important [3].

1.1.2. Why Binders?

The fibers of the nonwoven should be bonded to acquire a stiff and durable nonwoven web. There are some ways to get bonded fiber of nonwoven such as melt diffusion of fibers during the formation of the web. An other technique is post-fusion of heat sensitive fibers which is mixed with non-heat sensitive fibers. The last but the most frequent technique is latex binder application to the fiber for bonding nonwoven together. In this way, loosely assembled web of nonwoven fibers are chemically bonded together. The requirements to obtain a desired nonwoven web are satisfied with the binder usage. The superiority or popularity of latex binder can be explained by four important characteristics [9]:

- Low viscosity – to ease the applications
- High molecular weight – for strength and toughness
- The variety and versatility of latex binders
- Economical reasons; low cost

1.2. Raw Materials

Each latex polymer class has a variety of properties which depends on the chemical composition. When the property of nonwoven change between hydorphilic to hydrophobic or soft to firm, there is a need to use co-monomers to obtain the desired properties. Typical monomers for emulsion polymerization are mostly acrylates but often they are polymerized with non-acrylate ones to meet the specific requirements [9, 11].

1.2.1. Acrylics

Acrylics are the most preferable polymers for nonwoven industry. The main advantage of acrylics is their versatility. Acrylics are soft hand, have high light stability, good washing/shrinkage, heat and oxidation resistance which are all very crucial for

durable and disposable applications. Acrylics range from very soft to very hard depending on the monomer choices. There is no need for external modification like adding a plasticizer. Arcylics are also resistant to insect larvae and microbiological attacks which makes them suitable for babywearings. Acrylics are used widely in apperal thanks to the soft hand, washing resistance and dry-cleaning properties [9,10].

1.2.2. Styrene-Butadiene Copolymers (SBRs)

Styrene-butadiene copolymers were the first latex polymers for coating applications. They were used for synthetic rubber production during WW II and were widely used in tire industry. They provide the desired hydrophobicity when used with crosslinking resins and supply soft hand and solvent resistance. The ratio of styrene-butadiene affects the tensile strength, elasticity and oil/solvent resistance. For nonwoven binders, Styrene monomers provide hydrophobicity, tensile strength, oil and solvent resistance while butadiene monomers give elasticity, resiliance and toughness. Styrene ratio of styrene-butadiene copolymers can be changed from 45% to 90% depending on the desired stiffness. The disadvantage of styrene-butadiene copolymers are the vulnerablity of residual double bonds in the polymer chains to oxidation and discoloration. Styrene-butadiene copolymers are used in filtration equipments, wet wipes and industrial wipers [1, 3,13].

1.2.3. Ethylene-Vinylacetate Copolymers (EVAs)

Polyvinyl acetate alone is not a widely used nonwoven binder due to its stiffness. However vinyl acetate-ethylene copolymers are used in disposable applications and, less likely, in durables. They are more vulnerable to moisture and solvents than acrylics and styrene-butadiene resins. The advantages of EVAs are excellent liquid absorbancy and high wet tensile strength.Other usage of the ethylene-vinyl acetate copolymers are wire or cable coatings, coverstock, air-laid pulp and molding applications. Vinyl acetate has the role of giving stiffness and firmness to the binder and is generally added around 70% to 90% as co monomer [5, 10, 14].

1.2.4. Vinylacetate-Acrylate Copolymers

Vinyl acetate monomer itself is too water soluble and also quite reactive. To improve the mechanical properties and to prevent the low glass transition temperature and thus too low softness, acrylics or methacrylics can be used as comonomers by semicontinuous addition. Vinyl acetate binders can be plasticized by water and this helps the film formation process. However, hydrophobic monomers have a role of reducing the water sensitivity of the film. Poly vinyl acetate-acrylates are used for both disposable and durable applications [13].

1.2.5. Polyvinyl Acetate Homopolymer

Polyvinyl acetate homopolymers are highly hydrophilic and they have moisture sensitivity. They are used in shoddy, highloft products and some interfacings. Polyvynil acetate homopolymers are relatively inexpensive binders and due to their low Tg, they are not that stiff. They are hydrophilic and have enough dry strength [4, 10].

1.2.6. Acrylonitrile Butadiene Copolymers

Butadiene is copolymerized with acrylonitrile to produce oil and solvent resistant binders with good elasticity. These superior properties, however, come with the higher cost. Although they have convenient resilience and softness, acrylonitrile-butadiene copolymers have limited light fastness and heat resistance and also low UV resistance [9, 10].

1.3. Factors that Influence Binder Properties

Researches on nonwoven fabrics have been carried out to understand the factors influencing theperformances and esthetics. Effects of variations of polymer composition, functional groups and reactivity determines the fabric properties [6].

1.3.1. Polymer Composition

The latex polymer is produced from monomers *via* free radical emulsion polymerization. For binder production, the monomers and co-monomers used are described generally with vinyl monomer as the basic monomer and "R" represents different co-monomers that can be seen in Figure 1.2 [10].

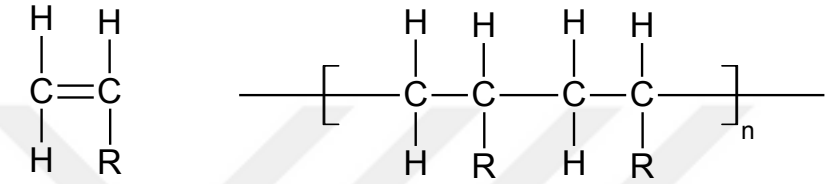


Figure 1.2. General structure of vinyl monomer and vinyl polymer [15].

To obtain correct polymer construction, different kinds of co-monomers are used which substantially affect the emulsion polymerization process and the end product and it is shown in Table 1.1 [10].

The end product properties differ with the choice of composition of the co-monomer. The basic properties related with co-monomers are glass transition temperature and hydrophilicity/hydrophobicity. For the glass transition temperature, T_g,when it is lower, the softer the nonwoven product. T_g values of homopolymers of widely used monomers in binder applications are shown in Table 1.2 [2,16].

Table 1.1. Examples of vinyl monomers [15].

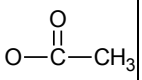
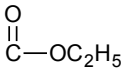
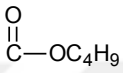
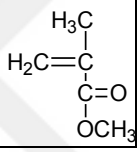
Name	**R**
Ethylene	H
Styrene	C_6H_5
Vinyl Acetate	
Vinyl Chloride	Cl
Ethyl Acrylate	
Butyl Acrylate	
Acrylonitrile	CN
Methyl Methacrylate	

Table 1.2. Glass transition temperatures of common emulsion homopoylmers [17].

Homopolymers	***T_g (^oC)***
Poly(methacrylic acid)	228
Polyacrylonitrile	125
Poly(methyl methacrylate)	106
Polystyrene	100
Poly(vinyl chloride)	82
Poly(vinyl acetate)	30
Poly(ethyl acrylate)	-22
Poly(butyl acrylate)	-54

Hydrophilic/hydrophobic ratio of the co-monomer composition also affects the nonwoven property. When the desired property is high wet strength, co-monomer is chosen among more hydrophobic monomers like styrene which should be selected over vinyl acetate. Instead, for the high solvent resistance, hydrophilic co-monomers such as

acrylonitrile should be selected. Examples of relative hydrophobicity of monomers can be seen in Table 1.3 [5, 10].

Table 1.3. Hydrophilicity and hydrophobicity of monomers *versus* hardness [17].

Monomer	***Nature***	***Tg (^oC)***
Styrene	*Most Hydrophobic*	+100
2-Ethyl hexyl acrylate		-85
Butyl acrylate		-52
Methyl methacrylate		+105
Ethyl acrylate		-21
Methyl acrylate		+8
Acrylonitrile		+125
Vinyl acetate	*Most Hydrophilic*	+30

1.3.2. Functional Groups

The preperation of latex needs addition of other functional groups. The latex copolymers usually contain 4 to 5 comonomers of which some contains reactive functional groups. High value polymer latices with appropriate morphology need reactive functional groups because they improve the performance of the nonwoven binder by assisting crosslinking, increasing polarity and adhesion, improving colloidal stability and altering alkali solubility and swellability. Moreover, the functionality of polymer affects wet and solvent tensile strength while dry strength of a latex binder is influenced by the polymer backbone. Functional groups that are commonly found in the monomers are as follows. [1, 9]:

- Carboxyl functionality
- Amide functionality
- *N*-Methylol functionality

Carboxyl functionality is directly related to colloidal stability, adhesion, self-thickening and hydrophilicity of the nonwoven binder. It also provides reaction sites for crosslinking resins [9].

Copolymerization of acrylamide derivatives produces crosslinking sites on the polymer backbone. Monomers containing amide and aldehyde functional groups are able to self crosslink at high temperatures. Self condensation of alcohol functional group on the acrylamide monomer results in crosslinking. This reaction can be seen in urea/formaldehyde or melamine/formaldehyde resins. N-methylol acrylamide monomer contains these groups and there are many other commercial examples like isobutoxy methylacrylamide (IBMA) or acrylamidoglycolic acid monohydrate (Highlink AG). These monomers are used in emulsion polymerization to increase crosslinking density of the polymer [18].

In acrylic latex products, *N*-methylol acrylamide is a widely usedself-crosslinking agent; it is self-crosslinking at sufficiently high temperatures. It is synthesized from the reaction of acrylamide with formaldehyde. N-methylol acrylamide is added to the emulsion polymerization as co-monomer and it provides self-crosslinking property to the binder to which it is added. Self crosslinking takes place when sufficient heat and appropriate acid catalyst are applied to the acrylic latex [8, 11].

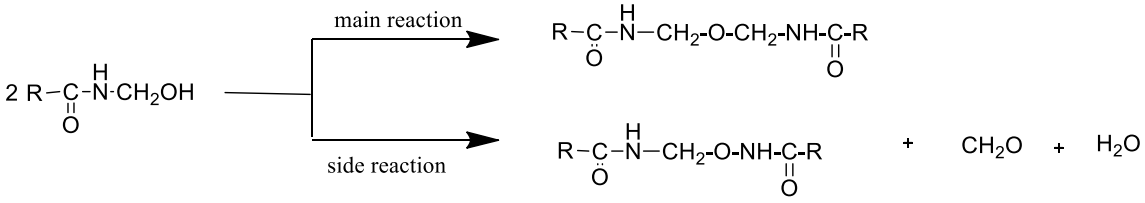


Figure 1.3. Main and side rections of NMA during crosslinking.

1.3.3. Reactivity

The acrylic binders can be classified according to their reactivity. For the nonwoven industry, there are three types of polymers and they are non-crosslinking, crosslinkable, and self-crosslinking.

The non-crosslinking term describes polymer that have no monomers having reactive functional groups and accordingly does not react with itself or any added curing resin by means of crosslinking [9].

The polymers with reactive functional groups such as carboxyl (carboxylic acid) or amide are called crosslinkable polymers. The crosslinkable means that binder has monomers with carboxyl or amide functionalities and the polymer does react with external curing resin but does not crosslink with itself [9, 12].

The curing resin addition increases the crosslinking density but do not lower the crosslinking temperature. A widely used example is the melamine-formaldehyde condensate resin and it is shown in Figure 1.4. This curing resin has capability of reacting with carboxyl, hydroxyl, amide and an methylol amide groups . The added curing resin can also react with itself. Other curing resins include urea formaldehyde, phenolic, epoxy and metal ion complexes (with carboxyl).

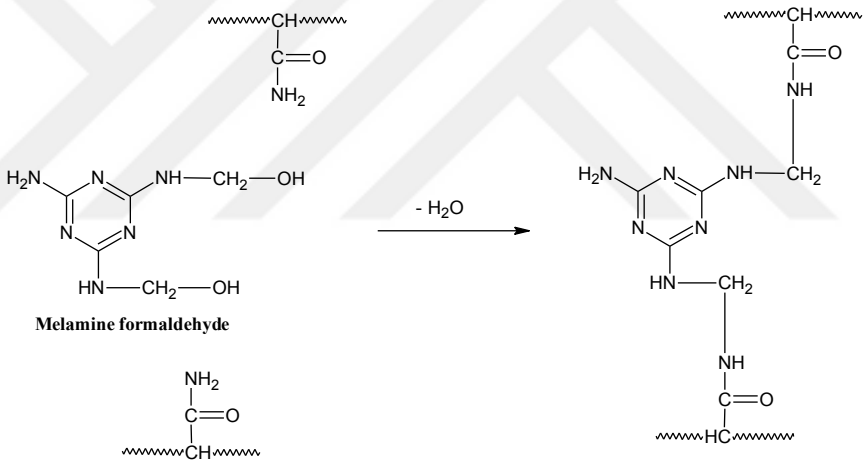


Figure 1.4. External crosslinking with melamine formaldehyde [16].

Self-crosslinking aqueous polymer latex compositions can crosslink with themselves. They do not need any additional crosslinker but can be used together with added curing resin if needed. The self crosslinking polymers allow easier preparation of the end product by eliminating extra components such as additional catalyst or crosslinking agents prior to the application process. In addition, by eliminating external crosslinker or catalyst addition, the possibility of migration of undesired monomeric catalysts or ureacted crosslinking agents into latex environment is decreased. This kind of polymers also ease the manufacturing process by providing post-curable sites. They allow the preperation of

partly-cured articals or stock materials which can come across with additional processing steps before post curing [4, 9].

For self-crosslinking latex poylmer, n-methylol acrylamide is one of the most common crosslinking agents. The curing process of *N*-methylol acrylamide takes place at high temperatures [10].

1.4. N-Methylolacrylamide

N-methylol acrylamide is widely used as a reactive functional monomer in latex polymer recipes in nonwovens, paper and fabric coatings, textile finishes and adhesives applications. NMA acts as a crosslinker agent and provides chemical and water resistance, mechanical strength and heat resistance [9].

The NMA containing polymer crosslinks upon heating starting from 150 ^{o}C and curing reaction can be seen in Figure 1.5. The temperature and the time for crosslinking can be shortened with the addition of acid catalysts such as phosphonic acid [12].

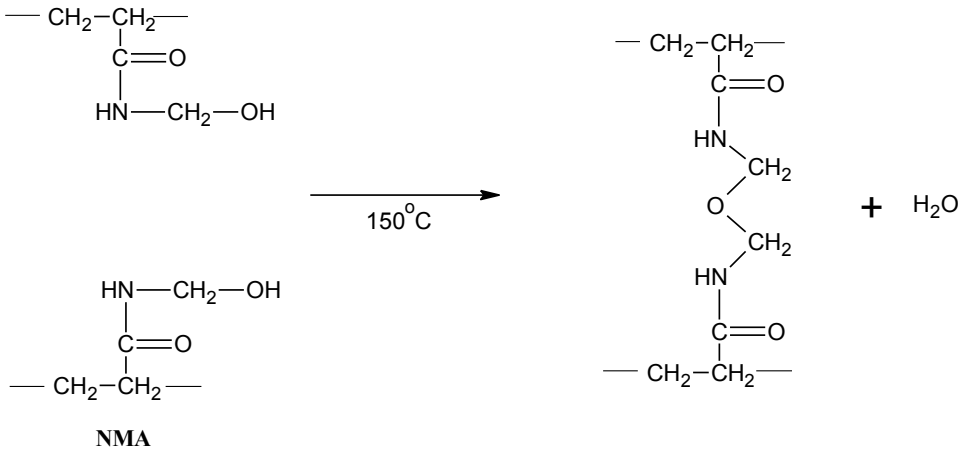


Figure 1.5. Crosslinking mechanism of NMA [17].

However, NMA containing emulsions have a side reaction and the *by*-product formaldehyde limits the use of this crosslinker due to healt considerations. The reaction of formaldehyde release during curing is shown in Figure 1.6. This generated formaldehyde is released into the environment or retained in the substrates. Disadvantages of incorporating

NMA to the binder system are the generation of formaldehyde during the curing step and emission of free formaldehyde in the finished product.

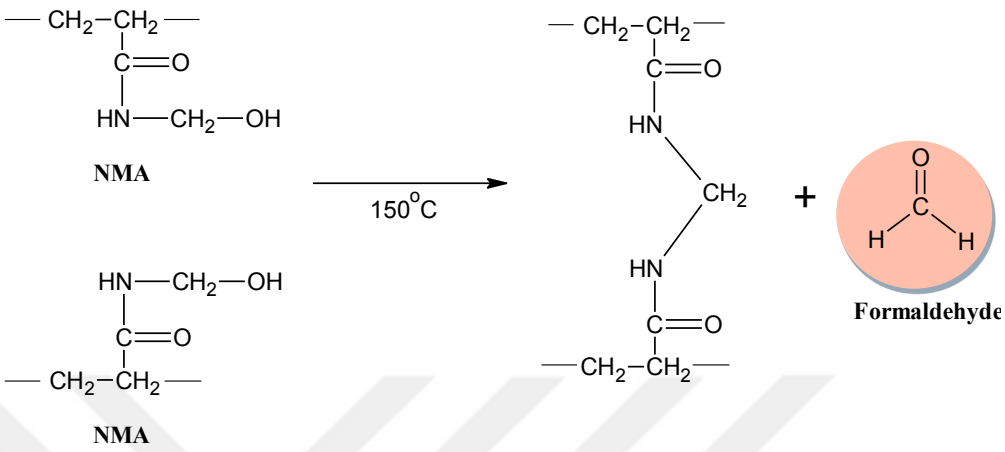


Figure 1.6. Side reaction of NMA during curing step [17].

Due to the formaldehyde emission which is a suspected human carcinogen, from NMA suppliers search for alternatives of NMA for ultra low or no formaldehyde releasing crosslinkers for textile and nonwoven industry [19].

1.5. Formaldehyde in Textiles

Formaldehyde is a colorless flammable and pungent-smelling chemical. It is synthesized by the oxidation of methane or methanol with the addition of catalyst. The compound is soluble in water, diethyl ether, ethanol and acetone and it is a strong electrophile. Formaldehyde is widely used in resins for wood products and in products such ascosmetics, glues and adhesives, clothing(e.g. winkle resistance) and other textiles. Other basic uses of formaldehyde include use as fungicide or bactericide and as intermediates in the synthesis of other chemicals [19, 20].

Formaldehyde is accepted as a gaseous pollutant liberated from human activity and natural sources. While small amount of formaldehyde is a natural *by*-product of combustion processes of plants, humans and animals, large amounts are generated by the industrial processes. Formaldehyde release to the outdoor air comes from power plants,

manufacturing facilities and also aoutomobile exhausts. Emisson of formaldehyde to the indoor air comes from consumer products, building blocks and also tobacco smoke. However, in indoor spaces, exposure to formaldehyde is much higher than in outdoor environment. Possible formaldehyde sources can be seen in Figure 1.7 [21].

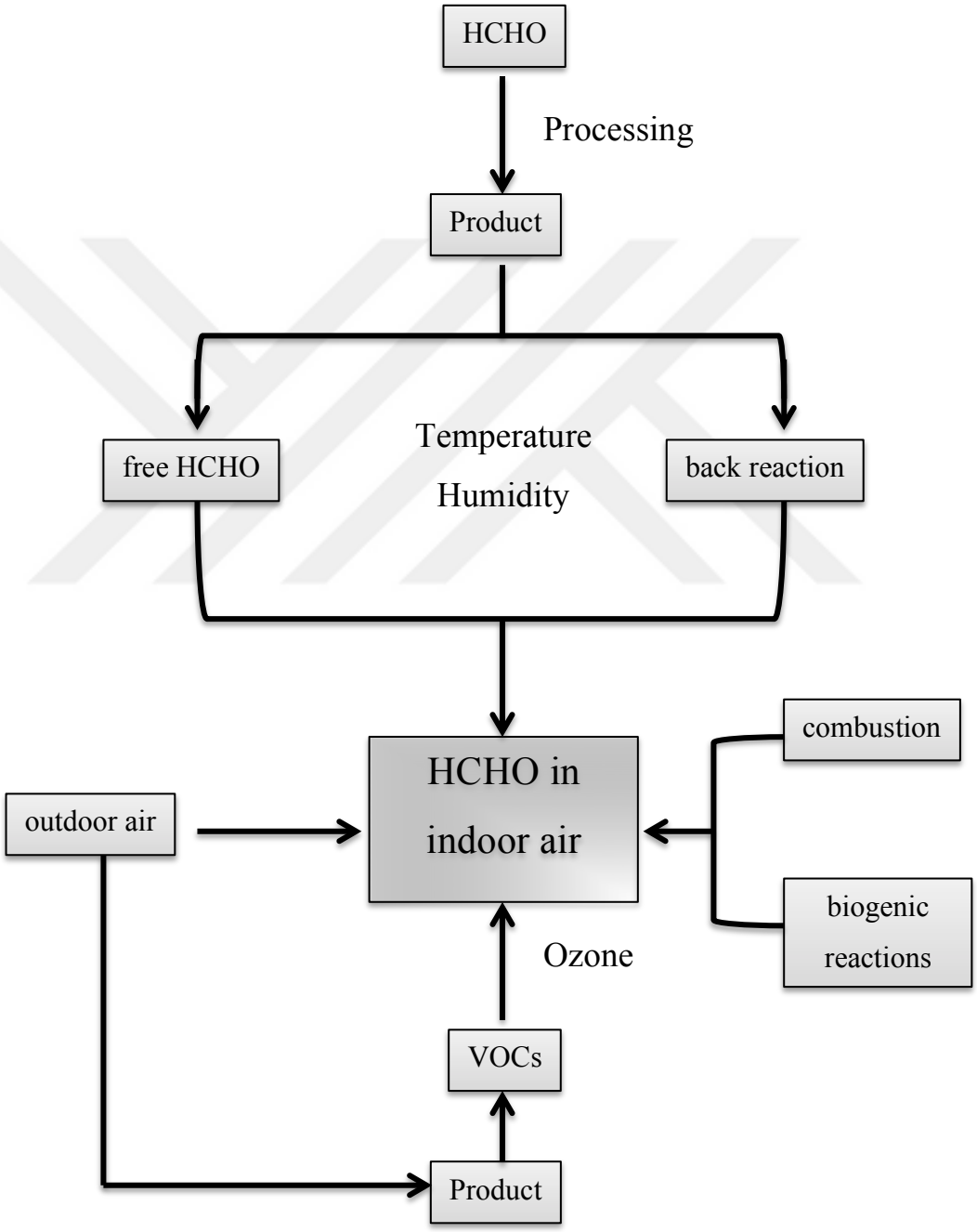


Figure 1.7. Possible formaldehyde sources [20].

Since mid-1920s, formaldehyde-containing polymers have been used in clothing and other textile applications because they provide durable press characteristics and also easy-care benefits. Formaldehyde containing resins became more widely used materials after the introduction of synthetic fabrics such as nonwoven. The formaldehyde-containing resins may degrade and liberate free formaldehyde when exposed to humidity and high temperatures. The prevalent binders have three sources of formaldehyde release and these are emulsifiers, biocides, and crosslinking agents such as NMA or urea- formaldehyde [19].

1.5.1. Toxicity of Formaldehyde

The high water solubility of formaldehyde results in fast absorption in the respiratory and gastrointestinal tracts. In these tracts, formaldehyde might be oxidized to produce formate and it is exhaled as carbon dioxide or integrated in biological matrices. Due to the electrophilic property of formaldehyde, it can easily react with nucleophilic biologic compounds. The formaldehyde toxicity is attained at specific levels like many other reactive compounds but the main problem is the extensive use and abondent emmission of formaldehyde. It is one of the main ingredients in many manufacturing processes and it is found in most indoor or outdoor products. There is a constant formaldehyde emmision from synthetic binders and their end-use products [19].

The primary affects of formaldehyde exposure are irritation of eyes and mucosa of the upper respiratory tract. Other adverse affects of formaldehyde are headaches, vomiting, fatigue and nosebleeds. Long and large amount of exposure to formaldehyde gaseous causes damage to liver and central nervous system, and dizziness [19].

In the textile industry, major effect of skin contact toformaldehyde is dermatitis which is a well-known health problem. There are two types of dermatitis as irritant and allergic dermatitis [19].

In the 12threport on carcinogens, published by U.S. Department of Health and Human Services, formaldehyde is classified as human carcinogen. According to the report there is a direct relationship between formaldehyde exposure and cancer in humans. People

exposed to high level of formaldehyde have a high risk of having lymphohematopoietic cancer, lung cancer, nasopharyngeal cancer, sinonasal cancer, and myeloid leukemia [22].

The high toxic characteristics of formaldehyde has brougth the limitation of formaldehyde release by the OEKO-TEX® Standard 100, which is an independent foundation for testing and certification of textile materials. In Table 1.4, the established limiting values can be seen for the release of formaldehyde in different classes of textile products [23].

Table 1.4. Limit values for formaldehyde [23].

Product Class	**I Baby**	**II in direct contact with skin**	**III with no direct contact with skin**	**IV Decoration material**
Formaldehyde(mg/kg)	n.d.*	75	300	300

*n.d. corresponds to an absorbance unit less than 0.05 resp. <16 mg/kg according to “Japanese Law 112” test method.

1.5.2. Measuring Formaldehyde in Textiles

There are several historical methods to obtain accurate determination of formaldehyde levels in clothing and other textiles. The more prevelant and valid analytical test methods preferred in textile industry for formaldehyde determination are American Association of Textile Chemists and Colourists Methods 112 (AATCC method 112) and Japanese Law Method 112 [24].

AATC Method 112 includes the process of putting the weighed sample of fabric in a sealed jar full with water. After then, the sealed jar is put into an oven with a given temperature and time. The formaldehyde released changes the color of the solution by derivatization. In this way, the released formaldehyde is detected by colorometric method *via* spectrophotometer [19].

In the Japanese Law 112 Method, test sample is treated with a cold aqueous solution of sodium sulfite first. Free formaldehyde is extracted from the test sample into aqueous solution and then it is derivatized to a colored complex. So free formaldehyde is detected in terms of color change and measured by visible spectrophotometer as same as the AATC Method 112 [19]. The reactions of free formaldehyde detection is shown in Figure 1.8.

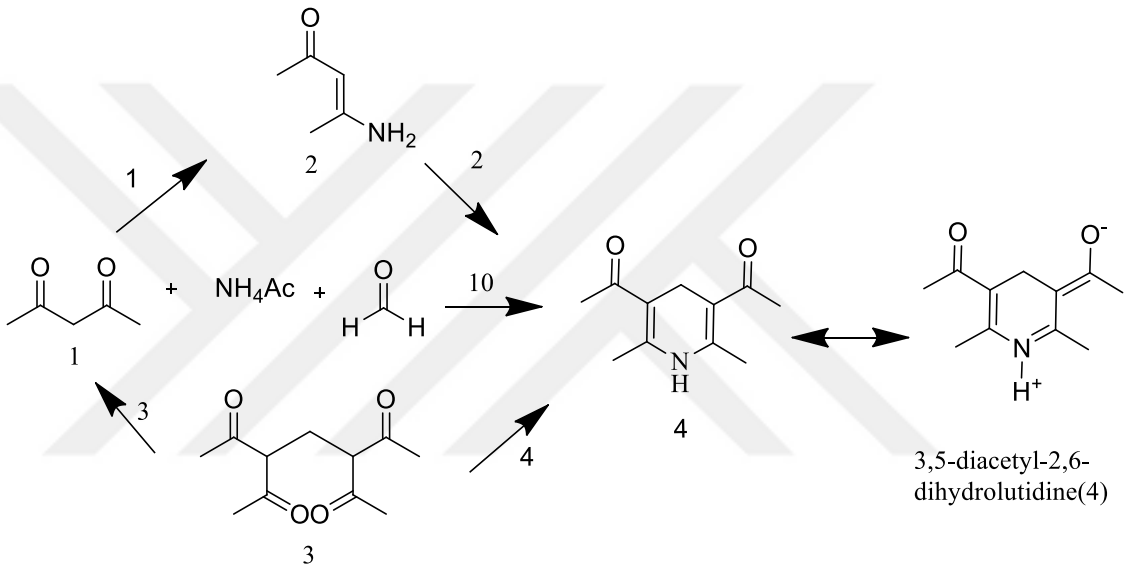


Figure 1.8. Reaction of derivitized colored complex for formaldehyde detection.

The level of formaldehyde is stated as micrograms of formaldehyde per gram of textile in both methods [19].

1.6. Emulsion Polymerization

Emulsion polymerization is a process of free radical polymerization in heterogeneous medium by a suitable emulsifier. The formulation of emulsion polymerization includes [15].

- Monomer (water or oil soluble)
- Emulsifier

- Initiator and
- Dispersion medium.

In emulsion polymerization process, emulsification takes place in water with an appropriate emulsifier. Polymerization is started by the free radical initiator which is oil or water soluble. The monomer mixture polymerizes at a given temperature. The final product of emulsion polymerization is a milky fluid called “latex”, “polymer dispersions” or “synthetic latex”. Latex is a colloidal dispersion of polymer particles in water [2].

1.6.1. Mechanism of Emulsion Polymerization

Emulsion polymerization mechanism includes three distinctive steps called intervals according to Harkins model. The schematic representation of emulsion polymerization mechanism is shown in Figure 1.9. Interval I is called as the nucleation stage and consists of nucleation of monomers that stay as free droplets in aqueous solutions. The nucleation of monomers or polymer particle generation starts with very few amounts of monomers covered by a layer of anionic surfactant and dispersed in the aqueous phase. New particles are formed by the entrance of radicals into the micelles and also by homogenous nucleation. While particle formation happens, both number of polymer particles and polymerization rate increases. Surfactant is adsorbed on monomer droplets and also on polymer particles, and it stabilizes them. Therefore free surfactant concentration drops below the critical micelle concentration(CMC). This occurs at the end of the nucleation process and then the number of particles stays constant [24].

Particles formed in interval I continues to polymerize and uses up monomers that stay as large droplets in interval II. Monomers move from large droplets to the growing polymerization due to the concentration gradient. At the end of Interval II there is no monomer droplets left [25, 26].

During interval III, all monomers are in the polymer growing micelles and continue to polymerize until the full conversion to the polymer is complete. At the end of this stage the monomer concentration in polymer particles is zero [27].

The main ingredients for emulsion polymerization are monomers, initators, surfactants. There is also other ingredients necessary for emulsion polymerization recipe [13].

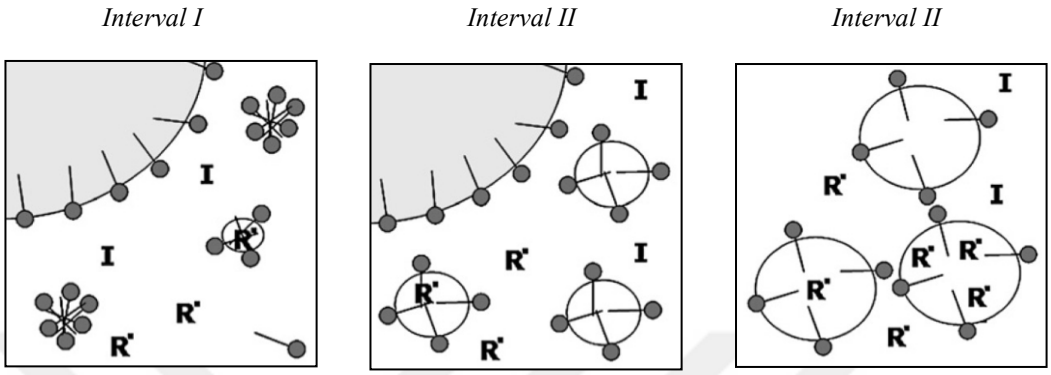


Figure 1.9. Schematic representation for mechanism of emulsion polymerization [27].

1.6.2. Major Monomers

Major monomers make up the large part of the final polymer chains. They are generally used greater than five percent of the final composition of polymer. Major monomers might be polymerized with themselves to obtain homopolymers containing repeating units of the same type. However, more frequently, they are used to polymerize as mixtures of co-monomers to give copolymers. Generally, the choice of monomer is decided according to desired property of the end-product. One of the important determinating factor is the glass transition temperature [13].

T_g is not the only determining factor for the monomer choice, there are other desired properties such as solvent resistance, toughness, rigidity, heat and light aging which also alter the monomer choices. The major monomers used in emulsion polymerization process are listed in Table 1.5 [13].

Table 1.5. Examples of major monomers used in emulsion polymerization.

Monomer	Structure	Normal b.p. (^oC)	Tg of Homopolymer(^oC)
n-Butyl acrylate	CH_2=CH-C(O)-O-$(CH_2)_3$-CH_3	148	-54
Methyl acrylate	CH_2=CH-C(O)-CH_3	80	10
Vinyl acetate	CH_2=CH-O-C(O)-CH_3	73	32

The general characteristics for controlling the polymer property are basic chemical composition, temperature, glass transition temperature, molecular weight and molecular weight distribution,crystallinity, gel and crosslinking. Although there are vast numbers of polymer combinations, Table 1.6 shows some examples of monomer combination to obtain desired binder product [13].

Table 1.6. Possible monomer combinations to get special characteristics of polymer[13].

Desired Property	**Possible Polymer Combination**
Stifness	Methacrylates, acrylonitrile, styrene
Soft hand	*N*-butyl acrylate, ethyl acrylate, butadiene
tackiness	2-ethylhexyl or hexyl acrylate
Water resistance	Crosslinking monomers NMA, n-butyl acrylate or styrene
High tensile strength	High Tg monomers, acrylonitrile, styrene, methyl methacrylate

1.6.3. Functional Monomers

Functional monomers are used less than five percent of total latex polymer composition, generally 2-5%, and they provide certain special characteristics to the latex polymer and the colloidal system. Examples of common functional monomers are shown in Table 1.7 [16].

Most prevalent functional monomers are methacrylic acids and acrylic acids which are monobasic carboxylic acids. For dibasic acids more common functional monomers are fumaric and itaconic acids. Through their highly polar carboxyl groups, they usually stay at the surface of the polymer particle. The acid group ionizes in water and negative charge provides colloidal stability because polymer particles repell each other due to like charges.

Table 1.7. Examples of functional monomers.

Functional Monomers	**Structure**
Acrylic acid	CH_2=CH-C(O)-OH
Methacrylic acid	CH_2=C(CH_3)-C(O)-O-H
Hydroxyethyl acrylate	CH_2=CH-C(O)-O-CH_2-C(OH)H_2
Acrylamide	CH_2=CH-C(O)-NH_2
N-methylol acrylamide	CH_2=CH-C(O)-NH-CH_2-O-H

The presence of the functional carboxyl groups also assists crosslinking of urea-formaldehyde, phenol-formaldehyde, melamine-formaldehyde and similar systems.

1.6.4. Initiators

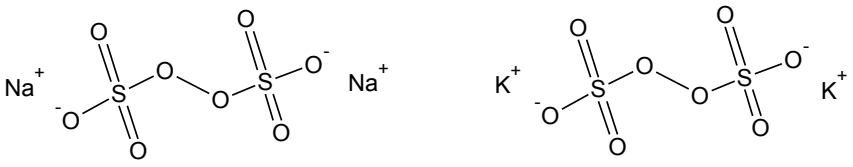
Initiators are the source of free radicals which start the propagation of polymer chains. Initiators in emulsion polymerization are mainly divided into two types;

- thermally decomposable
- decomposing with the help of redox system

Initiators can be soluble in water or soluble in organic solvents. Former is used for latex systems but oil soluble initiators are preffered in solution polymerizations [27].

Initiators generally used for emulsion polymerization mechanism are water soluble peroxide salts. Examples of these salts are ammonium and sodium peroxydisulfate. The initiation type can be thermal or redox type. For thermal systems, peroxy compounds are

widely used and sodium-, ammonium-, potasium disulphates, tert-butyl hydroperoxides and peroxydisulfates are examples of them [28].



sodium persulfate

potassium persulfate

tert-butyl hydroperoxide

Figure 1.10. Examples of initiators [15].

In thermal initiation mechanism, peroxydisulfate dissociates into two $SO_4^{-\cdot}$ radicals.

$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow 2SO_4^{-\cdot}$

peroxydisulfate — sulfate radical

Figure 1.11. Structure of thermal initiaton of peroxy disulfate ion.

For redox systems, peroxydisulfate dissociates into a sulfate radical and sulfate ion by obtaining one electron from a reducing agent especially Fe^{2+} or Ag^{+1} [29].

$Fe^{2+} + {}^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow Fe^{3+} + SO_4^{-\cdot} + SO_4^{2-}$

peroxydisulfate — sulfate radical

Figure 1.12. Redox dissociation mechanism of peroxydisulfate ion.

1.6.5. Surfactants

Surfactant is one of the main ingredient of the emulsion polymerization process and is selected based on several considerations. Surfactants are also called as emulsifiers, dispersing agents, detergent and soap. The amphiphilic characteristics of the surfactants, lower the interfacial tension between aqeous and the monomer phase. They are also micelle generating substances. If they are used above critical micelle concentration(CMC), the clusters of emulsifiers, micelles, are formed. The appropriate surfactant controls the latex particle size and provides stabilization of growing particles. Surfactants assist micellar solubilization of monomers and help nucleation process by forming the primary sites [1, 2, 13].

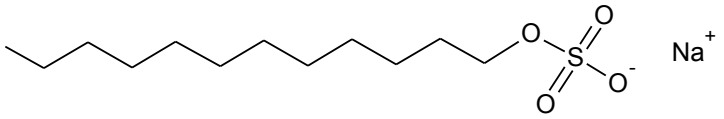
Surfactants contain two main groups, a hydrophilic(water-soluble) head and hydrophobic(oil-soluble) tail. Generally, the nature of the water soluble head group determines the classification of surfactant as being anionic, cationic and or non-ionic [2, 30].

Anionic surfactants are the most prevalent surfactants used in emulsion polymerization. Anionic surfactants have negatively charged hydrophilic head such as carboxylate groups with sodium, potasium and ammonium counter ions. This negatively charged head group may also be sulfonated derivatives of aliphatic, arylaliphatic and naphtenic substances. As anionic emulsifiers, sodium lauryl(dodecyl) sulfate, sodium dodecyl benzene sulfonate are very common. Hydrophilic head determines electrostatic stabilization and pH dependant behavior while hydrophobic tail is responsible for critical micelle concentration(CMC), steric stabilization and adsorption property of the latex and interfacial tension [31].

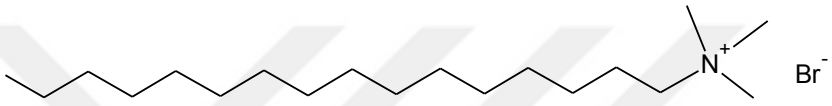
Dodecyltrimethylammonium bromide, acetyl dimethyl benzyl ammonium chloride, hexadecyl trimethyl ammonium bromide quaternary salts are some of the examples for the cationic surfactants and one example representing cationic surfactant is shown in Figure 1.13 [2].

Non-ionic surfactants are also widely used in emulsion polymerization. They include polyoxyethyleneated alkylphenols and straigth chain alcohols at which the moles

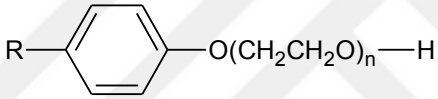
of ethylene oxide and alkyl group length might differ. The nonionoic surfactants provide additional electrolyte tolerance and mechanical shear stability to the emulsion. However, they have a tendency to coagulate. For this reason, non-ionic and anionic surfactants are often used together in emulsion polymerization recipes and the examples of these surfactants can be seen in Figure 1.13 [1, 2].



sodium dodecyl sulfate (anionic surfactant)



hexadecyl trimethyl ammonium bromide (cationic surfactant)



polyoxyethylenated alkylphenols (non-ionic surfactant)
R - Nonyl and n - 5, 10, 15

Figure 1.13. Structure of commonly used surfactants [15].

1.6.6. Other Ingredients

The latex formulation recipes often include a wide variety of other ingredients.

Chain transfer agents are used for regulating the molar mass and molar mass distribution of latex. Examples of chain transfer agents are mercaptans which rea the most used ones, carbon tetrachloride and or chloroform. Also transfurs which are surface active transfer agents are used in latex systems [2, 32].

In emulsion polymerization systems, a buffer such as sodium bicarbonate is used to regulate the pH [32].

The surfactant usage brings the need of antifoaming agents addition. This addition keep away the polymer from too much entrapment of air in the latex sytem. They can be silicon based or non silicon based. General addition of defoarmer is 0.01 to 0.05% (on aqueous solution) [32].

The addition of catalysts supports the crosslinking in latex systems by decreasing crosslinking temperature and the curing time. The added catalysts concentrations range between 0.1% and 2% [9].

In latex recipes there are other additives suc as plasticizers, thickening agents, antioxidants, UV-absorbers, fillers, flame retardants, salts, pigments, optical brighteners and water repellents. The addition of these may be changed regarding to desired performance of latex product [5].

1.6.7. Film Formation

In emulsion polymerization, the shelf life of the latex, stabilization of the particles are so important. The choice of the right stablizer is the main part of the latex product to prevent flocculation of particles. However, when a dispersion is applied on a surface, the polymer particles must overcome stabilizing forces(electrostatic and static) to form a coalesed film upon evopartion of water (the continuous phase). This complex process is explained in several stages [32]. In many industrial applications, latex is spread on a substrate for coating, painting or decorating purposes. In the fist stage, water evoprates from the surface making polymer particles touch one another. This is the longest stage of film formation and it continuous until the volume fraction of the polymer reaches 60-70 %. In the second stage of the film formation, particle deformation occurs. In the third stage interdiffusion of polymer chains across boundaries takes place.In this stage polymer film acquires its full mechanical strength. Schematic representation of film formation is shown in Figure 1.14 [1].

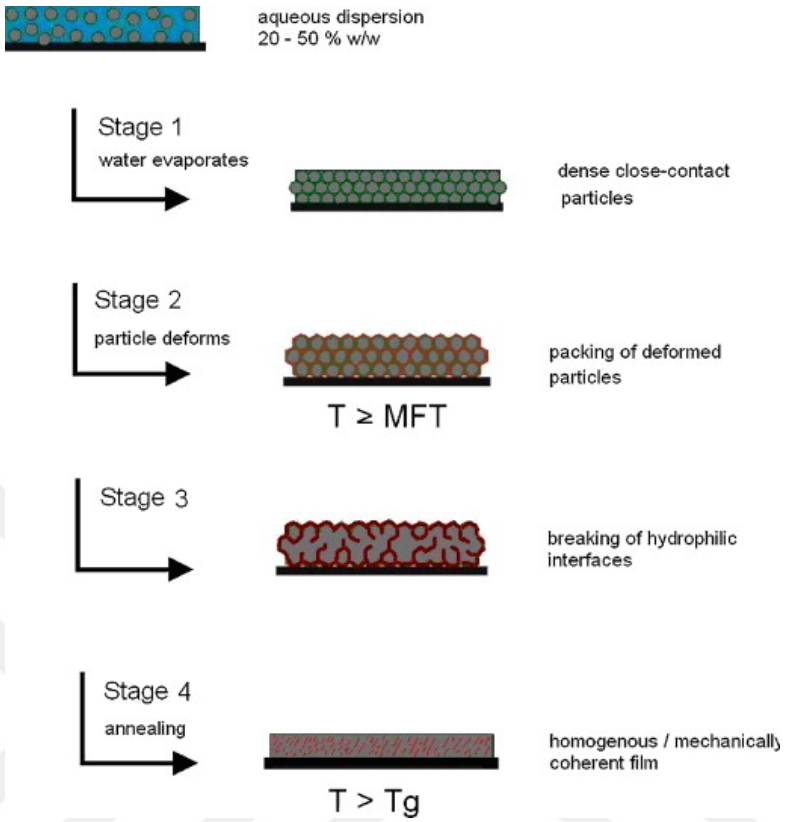


Figure 1.14. Schematic representation of film formation stages [31].

2. AIM OF THE STUDY

In the binder technology, incorporation of a self crosslinking monomer is a common method which provides durability to nonwoven, textile and paper. In textile industry *N*-methylol acrylamide is a widely used self-crosslinking monomer. However, during the curing conditions(generally 150^{o}C) liberation of formaldehyde has been observed as a by-product which is known as a toxic and carcinogenic substance.

In this study, the main goal was first to synthesize novel crosslinking agents which do not generate formaldehyde and then introduce these monomers into acrylic emulsion recipes and measure their performanced. The active site of the novel self-crosslinking agent was expected to react with funtional groups of the polymer when baked at high temperatures with the help of acid catalyst. This reactive monomer was also expected to react with the hydroxyl group of cellulose to improve the textile performance (Figure 2.1). The performance of dispersions containing the new crosslinker was expected to be close to N-methylol acrylamide based self crosslinking acrylic emulsions.

Throughout this study, there were synthesized three different crosslinkers. First one is N-(2-tetrahydropyranyl)acrylamide (Xlink A) monomer which is synthesized by Sezgin Bayrak. The α-hydroxymethylation reaction of Xlink A was carried on to increase the hydrophilicity of this monomer. Hence, 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide (Xlink B) was synthesized by Bayliss Hilman reaction method. Third monomer that is of 2-(2-tetrahydropyranyloxy) ethyl methacrylate (Hema-modified) was included in expired patent of PPG company [33].This monomer was named as crosslinker but it is not performed to the emulsion polymerization recipe for nonwoven binder.

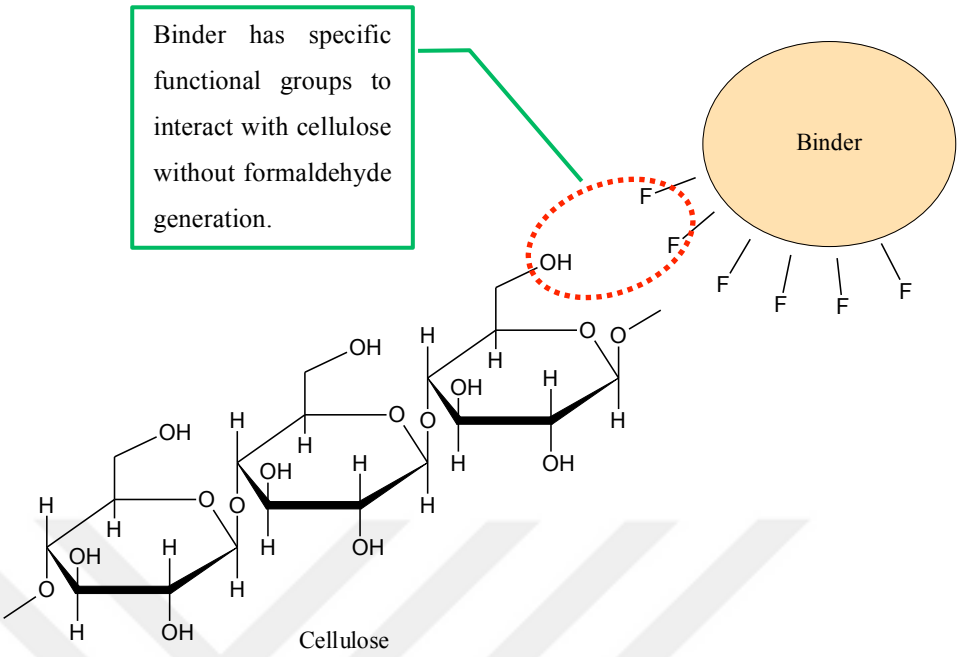


Figure 2.1. Schematic representation of binder interaction with cellulose.

3. EXPERIMENTAL

3.1. Methods and Materials

All chemicals used during crosslinking reactions were obtained from the manufacturer (Merck, Aldrich). In emulsion polymerization process, all the chemicals were obtained from Organik Kimya A.Ş. (Industrial Grade),and were used as received without further purification. The residues thus obtained were purified by column chromatography using silicagel-60 (43-60 nm). Thin layer chromatography was used using silica gel plates (Kiesel gel 60 F254, 0,2mm, Merck).

3.2. Instrumentation

Thin layer chromatography (TLC) plates were viewed under 254 nm UV lamp. ^{1}H-NMR, ^{13}C-NMR spectra were measured with a Varian Gemini 400 MHz spectrometer (Varian Associates, Palo Alto, CA) in $CDCl_3$ as solvent at the Advanced Technologies Research and Development Center at Bogazici University. FT-IR spectra was recorded on Thermo Scientific Nicolet 380 FT-IR spectrometer.

3.3. Synthesis of the Crosslinker

In this study, N-(2-tetrahydropyranyl)acrylamide was synthesized with the addition of dihydropyran ring according to literature search [34].After then, this product was reacted with formaldehyde by Baylis Hillman reaction method and the desired crosslinking monomer 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide was obtained. In addition, to observe the crosslinking behavior, 2-(2-tetrahydropyranyloxy)ethyl methacrylate was synthesized to compare the curing temperature results with NMA.

3.3.1. Synthesis of N-(2-tetrahydropyranyl)acrylamide (Xlink A)

The pyranylation of acrylamide reaction for the crosslinker synthesis which is performed by Sezgin Bayrak was done according to literature search [34].

To a stirred solution of acrylamide (74 g, 1 mol) in sulphiric acid solution(2%, 1,96 g, 50 % by weight water), 2,3-dihydropyran was added slowly with an additional funnel. BHT is added to the vessel to avoid polymerization. When the biphasic mixture turned to one phase, temperature was set to 50^0C and stirred 5 hours by controlling the reaction with thin layer column chromatography(TLC). The crude product was purified by column chromatography using silica gel and hexane/ethyl acetate (EtOAc)(3:2) as eluent phase. The purified product was obtained as white solid with 50% yield. **^{1}H NMR** (400 MHz, $CDCl_3$), *δ*: 6.28 (dd, 1H,CH_2=C*H*), 6.09 (d, 1H,CH=CH*H*), 6.07 (d, 1H,CH=C*H*H), 5,63 (s,1H,N*H*), 5.16 (m,1H,C*H*-CH), 3.96 (s, 1H, O-C*H*H), 3.60 (s,1H, O-CH*H*), 1.96 (s, 1H, CH-CH*H*), 1.84(m, 1H, CH-C*H*H), 1,72 (m, 1H, CH-CH_2-CH*H*), 1,55-130 (m, 3H, O-CH_2-CH*H*, O-CH_2-C*H*H, CH-CH_2-C*H*H) ppm.

^{13}C NMR (101 MHz, cdcl$_3$), *δ* 164.78 (*C*=O), 130.65 (*C*H=CH_2), 127.43 (*C*H2=CH), 77.90 (NH-*C*H-O), 67.41 (O-*C*H_2), 31.53 (O-CH_2-*C*H_2), 25.06 (NH-CH-*C*H_2), 22.79 (0-CH_2-CH_2-*C*H_2) ppm.

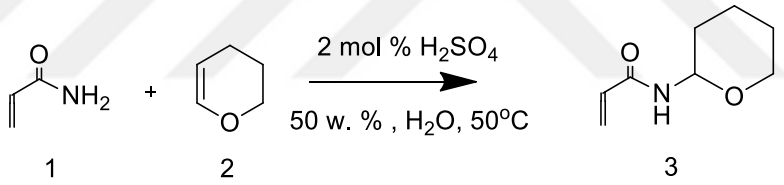


Figure 3.1. Synthesis of N-(2-tetrahydropyranyl)acrylamide (Xlink A) (3).

3.3.2. Synthesis of 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide (Xlink B)

The α–hydroxymethylation reaction of Xlink A was performed according to the literature [35-38]. 30% aqeous formaldehyde (10.67 g, 0.1067mol) was mixed with 100 mol % of 1,4-diazabicyclo[2.2.2]octane (DABCO) (10.88 g, 0,1067 mol) in H_2O:1,4-dioxane solvent mixture. Then Xlink A was charged into reaction medium. One phase reaction mixture was stirred at ambient temperature for 3 days. The progress of the reaction was controlled by TLC. After completion of reaction, mixture was portioned with ethyl acetate (750 ml) and brine (60 ml). The aqeous layer was extracted with chloroform (3 x 180 ml). Anydrous magnesium sulfate was added to dry the combined organic layer.

The crude product was purified by column chromatography using silica gel with Hexane/EtOAC (5/2) as eluent phase. The desired product was obtained with 51 % yield as a white solid. The reaction is shown in Figure 3.2. **^{1}H NMR** ($CDCl_3$), δ: 7.23 (s, 1H,N*H*), 5.88 (s, 1H, C=CH*H*), 5.50 (s, 1H, C=C*H*H), 5.10 (m, 1H, NH-C*H*), 4.25 (s ,2H, HO-CH*H*, HO-C*H*H), 3.89 (m, 1H, CH-O-CH*H*), 3.59 (m, 1H,CH-O-C*H*H), 3.50 (b, 1H, O*H*), 1.80 (m, 2H, CH-CH*H*, CH-C*H*H), 1.47 (m, 4H, CH-CH_2-CH*H*, O-CH_2-CH*H*, O-CH_2-C*H*H, CH-CH_2-C*H*H) ppm. **^{13}C NMR** ($CDCl_3$), δ:166.85 (C=O), 141.87 (*C*=CH_2), 122.53 (*C*H_2=C), 77.86 (*C*H-O), 67.27 (O-CH_2), 63.31 (CH_2=C-*C*H_2), 31.25 (O-CH-*C*H_2), 25.01 (O-CH_2-*C*H_2), 22.68 (CH-CH_2-*C*H_2) ppm.

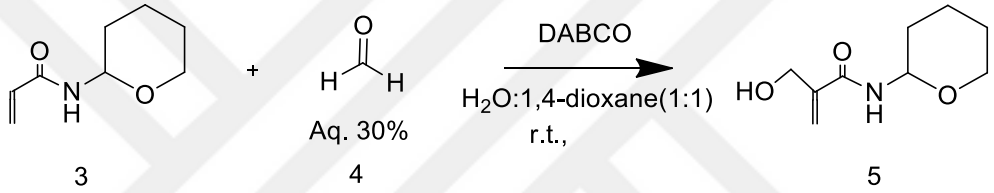
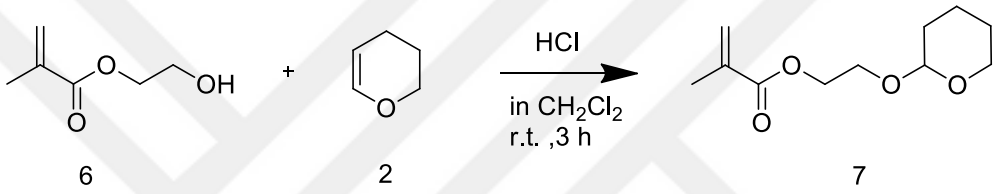


Figure 3.2. Synthesis of 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide (5).

3.3.3. Synthesis of 2-(2-tetrahydropyranyloxy) ethyl methacrylate (Hema-modified)

Pyranylation reaction of hyroxyethyl methacrylate was performed according to literature[33]. In Figure 3.3, the reaction of the synthesis is shown. Hydroxyethyl methacrylate (HEMA) (32.54 g, 250mmol) was weighed in a 3 necked 250 ml round botttom flask. Hydroquinone (0.063 g, 2.27mmol) and hydrochlorid acid solution (0.057 g, 37%, 0.1N) were added and 42 ml CH_2Cl_2 was used as a solvent. Reaction was continued in an ice bath and by continuous stirring. 2,3-dihydropyran (23.72 ml) was added slowly to the reaction mixture with the help of volumetric flask. After the addition of 2,3-dihydropyran reaction was kept at room temperature. Reaction progress was controlled by thin layer chromatography and CH_2Cl_2 as the diluting agent and EtOAc/Hex (2/3) was used as eluting agent. For work up process, Na_2CO_3(1.25g, 14.8mol) was dissolved in H_2O (12.5 ml) and reaction mixture was extracted once with Na_2CO_3solution to neutralize HCl. And then the mixture was stirred and seperated. The combined organic layer was distilled after the addition of hydroquinone (0.0315 g, 2.27 mol).

The yieldof 2-(2-tetrahydropyranyloxy) ethyl methacrylate is about 97% conversion.**^{1}H NMR** ($CDCl_3$), δ: 6.03 (s, 1H, C=CH*H*), 5.47 (s, C=C*H*H), 4.58 (t, 1H,O-C*H*), 4.23 (m, 2H ,C=O-CH*H*, C=O-C*H*H), 3.84 (m, 1H, CH_2-CH_2-CH*H*), 3.76 (m, 1H, CH_2-CH-O-CH*H*), 3.59 (m, 1H, CH_2CH_2C*H*H), 3.42 (m, 1H, CH_2-CH-O-C*H*H), 1.85 (s, 3H, C-CH_3), 1.72 (m, 1H, CH-CH*H*), 1.60 (m, 1H, CH-C*H*H), 1.47 (m, 4H, CH-CH_2-CH_2-CH*H*, CH-CH_2-CH_2-CH*H*, CH-CH_2-CH*H*, CH-CH_2-C*H*H) ppm. **^{13}C NMR** ($CDCl_3$), δ: 167.13 (*C*=O), 136.13 (*C*=CH_2), 125.41 (*C*H_2=C), 98.49 (O-*C*H-O), 64.95 (*C*H_2-O-CH-O), 63.75 (O-*C*H_2), 61.73 (O=C-*C*H_2), 30.33 (O-CH-*C*H_2), 25.31 (O-CH_2-*C*H_2-CH_2), 19.07 (CH-CH_2-*C*H_2), 18.15 (*C*H_3-C=O) ppm.



6 2 7

Figure 3.3. Synthesis of 2-(2-tetrahydropyranyloxy) ethyl methacrylate (7).

3.3.4. Synthesis of Binders

The synthesis of latex binders was carried out with respect to the recipes shown in Table 3.1 and 3.2.

During emulsion polymerization process, an automatic reactor equipped with 2000 mL glass container, steel strirrer and also peristaltic feeding pumps was used. First of all, water was precharged into the glass reactor and the reactor was heated to 60˚C. Then, pre-emulsion solution which was 5 % of emulsion by mass was added in to reactor. The APS (4 %) and MBS (4 %) initiators were charged respectively as shot which allows starting of the reaction. The reaction was allowed to proceed 10 minutes. After then, parallel feeding of the emulsion and initiators (APS, MBS solutions) was started by using peristaltic feeding pumps which lasted 3 hours. At the end of the feeding, the reaction continued to progress for an additional 30 minutes by continuous stirring to decrease the free monomer amount. To eliminate all radicals and radicalic polymer chains, redox process was performed by the addition of t-BHP and MBS solutions with parallel flow and this process

is called redox. In the last stage of emulsion polymerization process, reaction vessel was cooled to room temperature and aqueous ammonia was added for pH arrangement and emulsion was discharged from the reactor. The emulsion polymerization recipe is shown in Table 3.1. The emulsion was filtered by using 250 mesh nylon to remove coagulum. The solid content of the resultant emulsion was around 40 %.

To observe the effect of acid catalyst on crosslinking mechanism, two types of emulsions were prepared as with and without p-toluene sulfonic acid. For reference solution, S-1, p-toluene sulfonic acid was not added The recipe of paratoluene sulfonic acid added emulsion is shown in Table 3.2.

Table 3.1. Recipes of binders that containdifferent self-crosllinking monomers.

	Recipe	S-1	S-2	S-3	S-4	S-5
Precharge	DiW	190 g				
Emulsion	DiW	170				
	Sodium Lauryl Sulfate (15%)	21				
	Tridecyl alcohol 40-ethoxylate (70%)	8.5				
	BA	194				
	MMA	104				
	AA	3				
	Reference	-	-	-	-	-
	NMA (101 g/mol)	-	5	-	-	-
	Xlink-A (155 g/mol)	-	-	7.75	-	-
	Xlink-B (185 g/mol)	-	-	-	9.25	-
	HEMA-modified (214 g/mol)	-	-	-	-	10.7
Pre-emulsion		5 % of Emulsion				
Initiation(shot)	APS (4%)	4				
	MBS(5%)	4				
Initiation(feeding)	APS(%4)	20				
	MBS(%5)	24				
Post-polymerization Redox(feding)	t-BHP (3%)	10				
	MBS(5%)	10				
Neutralization	NH_4OH (25%)	3,2				

Table 3.2. Recipes of binders that contain different crosslinker and p-tsa as catalyst.

	Recipe	S-1	S-2P*	S-3P	S-4P	S-5P
Precharge	DiW	190 g				
Emulsion	DiW	170				
	Sodium Lauryl Sulfate (15%)	21				
	Tridecyl alcohol 40-ethoxylate (70%)	8.5				
	BA	194				
	MMA	104				
	AA	3				
	Reference	-	-	-	-	-
	NMA (101 g/mol)	-	5	-	-	-
	Xlink-A (155 g/mol)	-	-	7.75	-	-
	Xlink-B (185 g/mol)	-	-	-	9.25	-
	HEMA-modified (214 g/mol)	-	-	-	-	10.7
Pre-emulsion		5 % of Emulsion				
Initiation(shot)	APS (4%)	4				
	MBS(5%)	4				
Initiation(feeding)	APS(%4)	20				
	MBS(%5)	24				
Post-polymerization Redox(feding)	t-BHP (3%)	10				
	MBS(5%)	10				
Neutralization	NH_4OH (25%)	3,2				
	p-Toluenesulfonic acid (g)	1% of solid content				

* P means paratolunesulfonic acid catalyzed solution (1% of solid content)

3.3.5. Film Formation

In order to obtain polymer films, silicon molds of 10x10 cm^2were covered with 24 gr of the dispersions and left to dry at laboratory conditions at 23^0C and 50% relative humidity for 5 days. The polymer films became transparent within 3 days and two additional days were introduced for complete water evaporation and drying.

3.3.6. Percent Solubles and Swell Index Calculations on Polymer Films

After film formation and drying process, shaped samples of 1cm × 1cm were prepared where the thicknesses of the films ranged between 0.1-0.15 cm and weighed between 50-80 mg. There were prepeared three samples of each polymer film and average weighings are recorded. For curing process, firstly, the polymer samples were cured in an oven at 160^0C for 3 and 10 minutes. After the crosslinking of polymers, all samples were weighed and were soaked in a jar full with 100 ml acetone for 24 hours. After incubation of cured polymer samples, swelled polymers were filtered fast and swollen weights are recorded. Then, swollen films were dried at room temperature for 3 hours and redried at 150^0C. Totally dried polymer films after swelling were weighed again.

In accordance with the following equations (3.1) and (3.2), "Percent Solubles" and "Swell Index" ratios of cured polymers were calculated:

$$\%\, Solubles = 100\times\left[1-\left(\frac{\frac{weight\ of\ dry\ film}{after\ acetone\ swell}}{original\ dry\ film\ weight}\right)\right] \tag{3.1}$$

$$Swelling\ Index = \frac{sample\ weight\ swollen\ in\ acetone}{original\ sample\ weight} \tag{3.2}$$

The curing process and swelling studies were done at various temperatures (180, 200, 220^{o}C) and curing times (3 and 10 minutes) and then percent solubles and swell index values were measured.

3.3.7. Free Formaldehyde Determination

The determination of free formaldehyde of binders containing NMA, Xlink A, Xlink B and Hema-modified was done by applying the standart method of ISO 15373:2001 Plastics-Polymer dispersions-Determination of free formaldehyde.

4. RESULTS AND DISCUSSION

The aim of this study was first to synthesize three different formaldehyde free self crosslinking agents alternative to NMA which is known to generate formaldehyde during the curing process. Novel self-crosslinking monomers were synthesized which contained N-O and O-O acetal group bonded to a ring and general structure of these monomers can be seen in Figure 4.1. Then, monomers were polymerized *via* emulsion polymerization to obtain binder polymer emulsions. Finally, performance tests of these binder emulsions containing the novel crosslinkers were done and compared against the NMA containing ones.

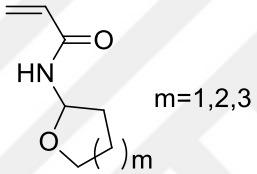


Figure 4.1. General structure of crosslinkers containing N-O acetal groups bonded to a ring.

For two of the novel N-O acetal containing crosslinkers synthesized in this work, the m value was 2 which means N-O acetal group is bonded to a six membered tetrahydropyran ring. N-O acetal group containing monomers are XLink A and Xlink B in this study. The crosslinking process is heat induced and was expected to be achieved through a transacetalization reaction of the N-O acetal group. The polymer film containing self-crosslinking agents was cured at high temperatures in acidic medium. The cyclic N-O acetal should in principle eliminate or decrease the possibility of formaldehyde release during and after the crosslinking.

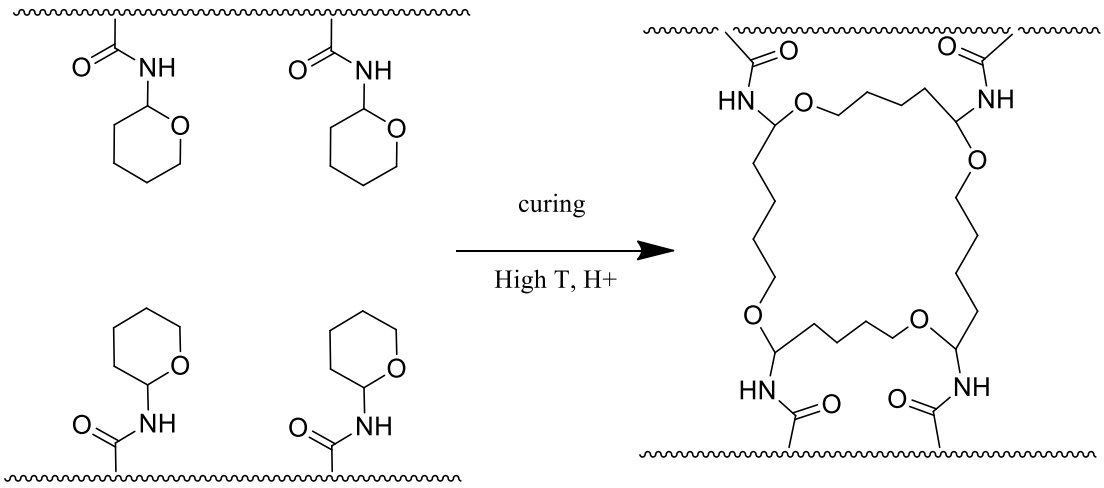


Figure 4.2. Crosslinking mechanism of polymer containing self-crosslinking agents Xlink A and Xlink B.

The possible reaction mechanism of this type of monomer with the hydroxyl group of cellulose is shown in Figure 4.3.

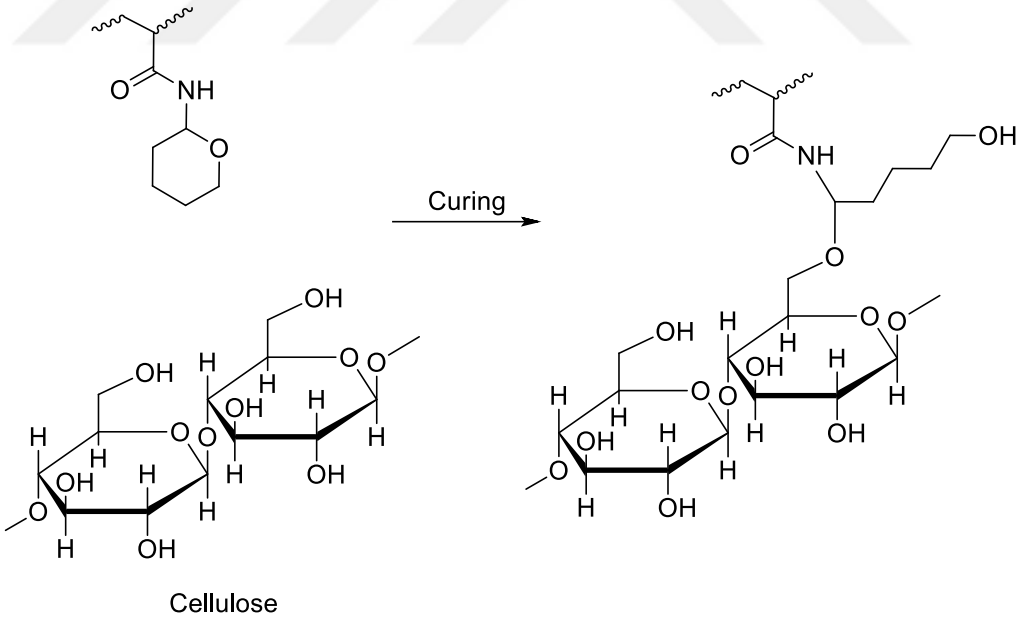


Figure 4.3. Possible reaction mechanism of monomers containing N-O acetal group bonded to tetrahydropyranyl ring.

The third monomer, 2-(2-tetrahydropyranyloxy) ethyl methacrylate (Hema-modified), contains O-O acetal groups. Hema-modified monomer also undergoes heat

induced ring opening reaction. The possible reaction during crosslinking is shown in Figure 4.4.

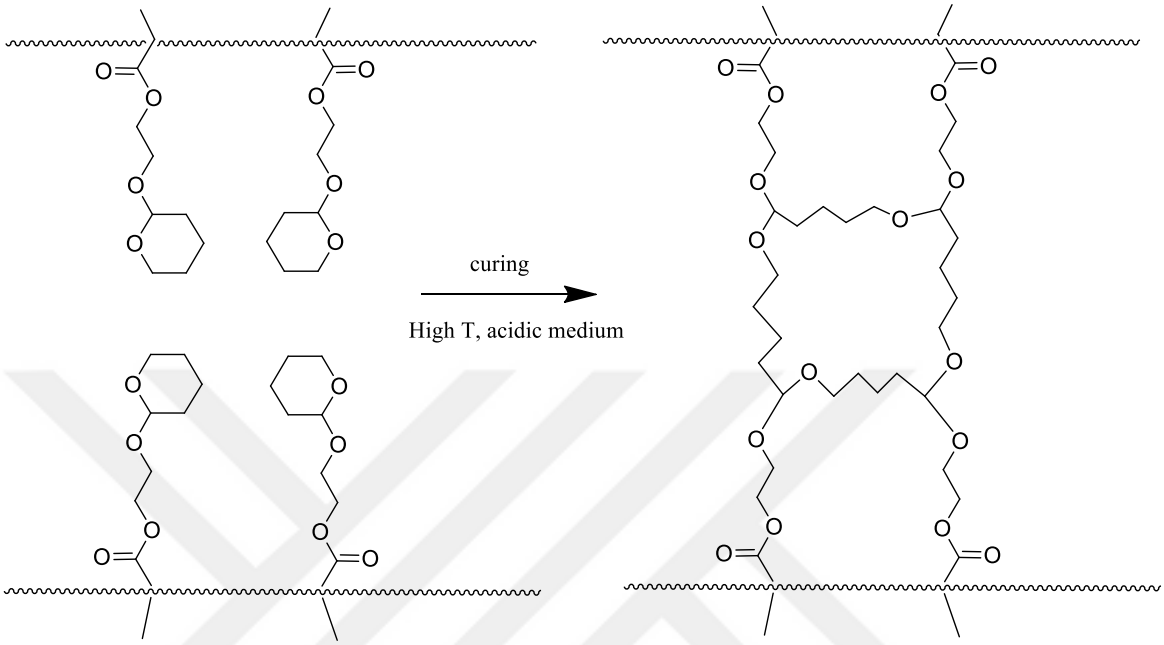


Figure 4.4. Crosslinking reaction of polymers containing O-O acetal group bonded to tetrahydropyranyl ring.

In the case of crosslinking, addition of acrylamide to the emulsion polymerization recipe, there can be enhancement on the temperature of crosslinking. The industrial grade *N*-methylol acrylamide (NMA) aqueous solution contains 25-50% of free acrylamide. It is well known that the acrylamide groups provide the crosslinking reactions by reacting with N-O hemiaminal group of NMA. This reaction is shown in Figure 4.5.

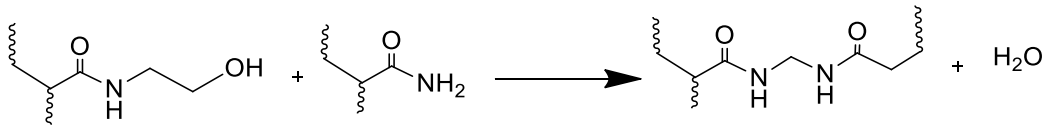


Figure 4.5. Condensation reaction of *N*-methylol acrylamide and acrylamide.

Therefore, theoretically the unreacted acrylamide can be allowed to stay in the solution. However, in the present study, the Xlink A, Xlink B and Hema was used as a purified monomer and the acrylamide was not added externally. The reason was to see full transacetilization ability of these monomers.

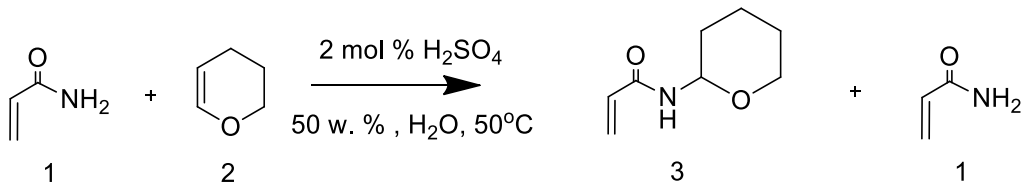


Figure 4.6. Synthesis of XLINK A without purification.

In the presence of acrylamide in emulsion polymerization medium, acrylamide groups should then react with the N-O hemiaminal group of the novel self-crosslinking agent in presence of acid catalyst and high temperatures and this reaction is shown in Figure 4.7. The resulting crosslinked polymer chains will contain N-N aminal group which are known to be thermodynamically more stable than N-O hemiacetal group. In other words the reaction is thermodynamically driven towards the formation of a more stable product.

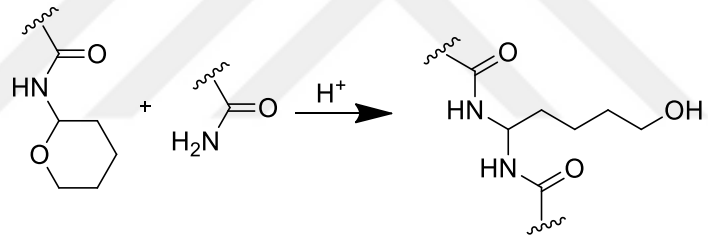


Figure 4.7. Crosslinking mechanism of polymers contining Xlink A type monomers.

The first stage of this project was the synthesis of three potential self-crosslinking monomers. Then the emulsion polymerizations of these potential crosslinkers with other acrylic monomers to form latex binders was done. Finally, the curing and performance tests of the new binders were carried out. In the following sections the results will be discussed in this order.

4.1. The Synthesis of the Crosslinkers

The self crosslinking monomer (Xlink A) was obtained from the pyranylation reaction of acrylamide which is shown in Figure 4.8. The starting material acrylamide was reacted with 2,3-dihydropyran in the presence of an acid catalyst, sulphuric acid. This

reaction was performed at 50 ^{0}C and reaction time was 5 hours with 50% conversion of acrylamide to Xlink A.

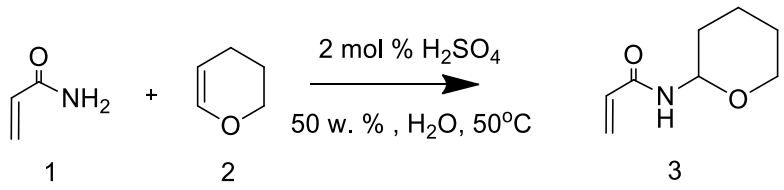


Figure 4.8. The Synthesis of XLINK A.

X link B (4) was synthesized from α-hydroxymethylation of Xlink A using the Baylis-Hillman Reaction that can be seen in Figure 4.9. The aim was to increase the hydrophilicity of X link A. The hydrophilicity of the monomer is known to alter the emulsion polymerization process. The X-linkA, once synthesized was found to be more hydrophobic than the commercially used NMA. In order to use the same polymerization conditions and additives as the NMA polymerizations, there was a need to increase the hydrophilicity of the X-link-A. Thus, we believed that the introduction of an extra hydroxyl group would allow to achieve the desired hydrophilicity. In this reaction, Xlink A (3) was reacted with aqeous formaldehyde catalyzed by 1,4-diazabicyclo[2,2,2]octane (DABCO) in THF:H_2O(1:1). This reaction was performed in 48% yield.

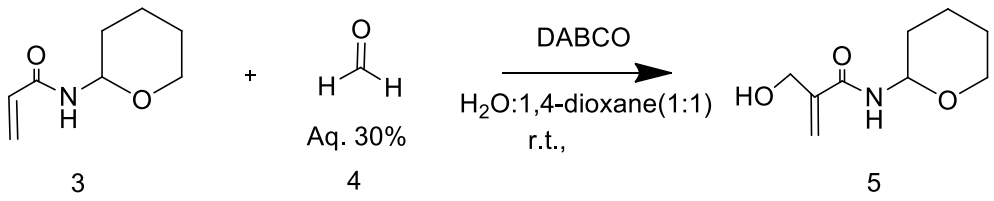


Figure 4.9. The Synthesis of Xlink B by the Baylis-Hillman Reaction.

The third monomer synthesized in this study was the HEMA-modified monomer and the reaction is shown in Figure 4.10. This monomer was different than the previous ones, in the sense that it contained O-O acetal instead of N-O acetal. The O-O acetal was synthesized by the pyranylation of HEMA with DHP in the presence of an acid catalyst, aqueous HCl (0.057g, 0.1N). This crosslinker has been previously mentioned in the patent

literature, as a crosslinker, however it has never been used in non-woven binders [38]. Therefore, its potential as non-woven binder was questioned. The main aim of synthesizing this monomer, however, was to compare its results with Xlink A and NMA containing binders. This would also allow us to compare the efficiency of N-O and O-O acetals in crosslinking the non-woven materials. The desired monomer was synthesized in 97% yield.

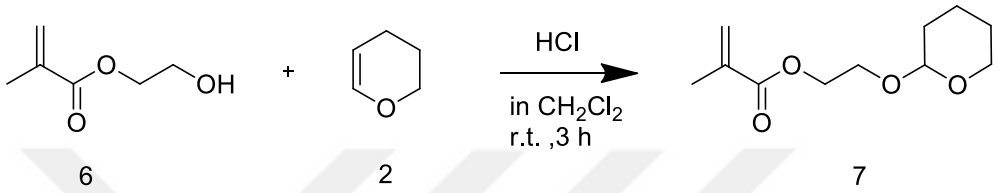


Figure 4.10. Synthesis of Hema-modified monomer.

4.2. The Emulsion Polymerizations of the Novel Crosslinkers

During the second stage of this study, the aim was to incorporate novel self crosslinking monomers into emulsion polymerization and then prepare the corresponding films and compare the film performance results against NMA. Therefore, film formation process was carried out, swelling index and percent soluble results were calculated.

Acrylic binder emulsions were prepared *via* emulsion polymerization containing various acrylate monomers such as butyl acrylate, methyl acrylate and acrylic acid. Five different emulsions were prepared. S-1 was reference polymer that did not contain any crosslinker. S-2 was NMA containing polymer which was used as an industrial standart for further comparing the novel crosslinkers. S-3, S-4 and S-5 emulsions contained Xlink A, Xlink B and Hema-modified self-crosslinking agents respectively. The crosslinker amount for emulsions was set to 50 mmol (1,7 mol % with respect to other monomers). The solid content, particle size, viscosity and pH of acrylic emulsions are shown in Table 4.1.

Table 4.1. General properties of the synthesized polymer emulsions.

	Emulsions				
	S-1	**S-2**	**S-3**	**S-4**	**S-5**
XL*	-	NMA	Xlink A	Xlink B	Hema-modified
XL amount, mole	0.05	0.05	0.05	0.05	0.05
Solid Content,%	40	40	40	40	40
Particle Size(nm)	140	135	132	130	142
Viscosity(cps)	45	55	45	55	50
pH	7	7	7	7	7

* XL means Crosslinker.

4.3. Determination of the Crosslinking Temperature

To obtain the performance results of binders, swell index and percent soluble tests were carried out. The ability of binders to crosslink at different temperatures was determined and the measured data were compared with that of NMA.

The calculations of percent solubles and swell index were done by using Eq. 3.1 and Eq. 3.2. at various temperatures. The list of percent solubles and swell index results at different curing temperature and curing times are shown in the Table 4.2. The graphs of solvent temperature *versus* temperature and swell index *versus* temperature for 3 min and 10 min curing time are shown in the Figure 4.11 to Figure 4.14.

The crosslinking of the polymers containing three different novel crosslinking groups are successful only at 200°C and 220°C. The good results of percent soluble and swell index at 160°C and 180°C were obtained only for NMA containing emulsions as S-2 and S-2P and results can be seen in Figure 4.11-4.14. Other polymer emulsions containing Xlink A, Xlink B and Hema-modified monomers were all soluble after curing and waiting in acetone, so percent soluble results were 100 for all of them and swell index results can

not be recorded. However, it can be said that, according to the graphs, 10 minutes cure gives better results than 3 minutes at all temperatures. This can be clearly seen in Figure 4.13 and 4.14.

The extent of rosslinking can be determined by performing swelling experiments in organic solvents. The solvent was acetone for swelling tests. Crosslinking decreases the swelling values. According to the results, the most successful crosslinking belongs to the S-2 emulsions containing 0.005 mol NMA and it can bee seen in the Figure 4.13 and 4.14. For novel crosslinkers, S-5P and S-5 which contain Hema-modified crosslinker had better swelling index among others. This means hema-modified monomer had better self crosslinking ability than Xlink A and Xlink B. This may be attributed to the higher stability of the N, O acetals compared to O,O acetals towars the transacetalization reactions. In the NMA case, this process is fast because the structure contains a reactive and relatively less stable hemi aminal group.

The percent solubles calculation of different emulsions were related to the extent of crossliknking. Again, the NMA containing S-2 gave the best results. The percent soluble results of S-3 and S-4 polymer films could be recorded at only 200°C and 220°C which is shown in Figure 4.11 and 4.12. Among polymers containing Xlink A, Xlink B and Hema-modified crosslinkers, S-5 and S-5P which contain Hema-modified crosslinker had lower percent soluble results which means higher crosslinking.

The effect of acid addition was also checked since it is well known that trans acetalization reactions are acid catalyzed. When the results from the percent solubles and swell index are checked, a slight improvement is observed in the p-toluene sulfonic acid catalyzed S-2P, S-3P, S-4P and S-5P polymers. Thus acid addition seems to enhance slightly the crosslinking behavior of the novel crosslinkers as expected.

The time for curing was very important. In all polymer emulsions, 10 minutes cure gave better results than 3 minutes. Most of the results showed that percent soluble and swelling ratio decrased when polymers were cured for 10 minutes. However, while swell index values decreases as temperature rises for 3 minutes curing, it is almost steady for 10 minutes curing and it is seen in Figure 4.13 and 4.14.

From these results, it can be said that novel crosslinkers did not work well for these binder emulsions. They have the ability to crosslink only above 200°C. This temperature is higher than the typical crosslinking temperature (150 °C) of NMA. Moreover, the percent soluble and swelling index results of novel monomers are lower than NMA even at 200°C. This means that crosslinking density and crosslinking amount are not close to NMA even at high temperatures. It can be stated that new crosslinkers function at higher temperatures than 200°C.

Table 4.2. Percent solubles and swell index values.

Emulsions	**% Solubles**		**Swelling Index**	
	3 min	10 min	3 min	10 min
160 °C				
S-1	100	100	∞	∞
S-2	10.82	11.23	8.45	9.51
S-2P	10.50	10.26	7.69	8.96
S-3	100	100	∞	∞
S-3P	100	100	∞	∞
S-4	100	100	∞	∞
S-4P	100	100	∞	∞
S-5	100	100	∞	∞
S-5P	100	100	∞	∞
180 °C				
S-1	100	100	∞	∞
S-2	8.21	9.25	10.16	9.83
S-2P	7.25	8.67	9.21	8.04
S-3	100	100	∞	∞
S-3P	100	100	∞	∞
S-4	100	100	∞	∞
S-4P	100	100	∞	∞
S-5	100	100	∞	∞
S-5P	100	100	∞	∞
200 °C				
S-1	100	100	∞	∞
S-2	13.57	15.25	10.66	7.23
S-2P	12.55	14.86	9.75	6.19
S-3	100	70.00	∞	36.14
S-3P	100	80.89	∞	16.54
S-4	100	82.69	∞	12.56
S-4P	100	79.05	∞	19.05
S-5	100	83.38	∞	12.74
S-5P	100	92.52	∞	9.23

Table 4.2. Percent solubles and swell index values (contd.)

220 °C				
S-1	100	100	∞	∞
S-2	19.91	20.63	8.97	6.75
S-2P	14.50	19.23	7.31	5.27
S-3	80.04	41.59	15.68	34.10
S-3P	68.76	32.83	26.47	15,12
S-4	63.48	63.09	27.00	11.05
S-4P	71.52	46.87	22.14	20.46
S-5	18.05	23.57	8.26	11.82
S-5P	12.36	17.46	6.51	10.54

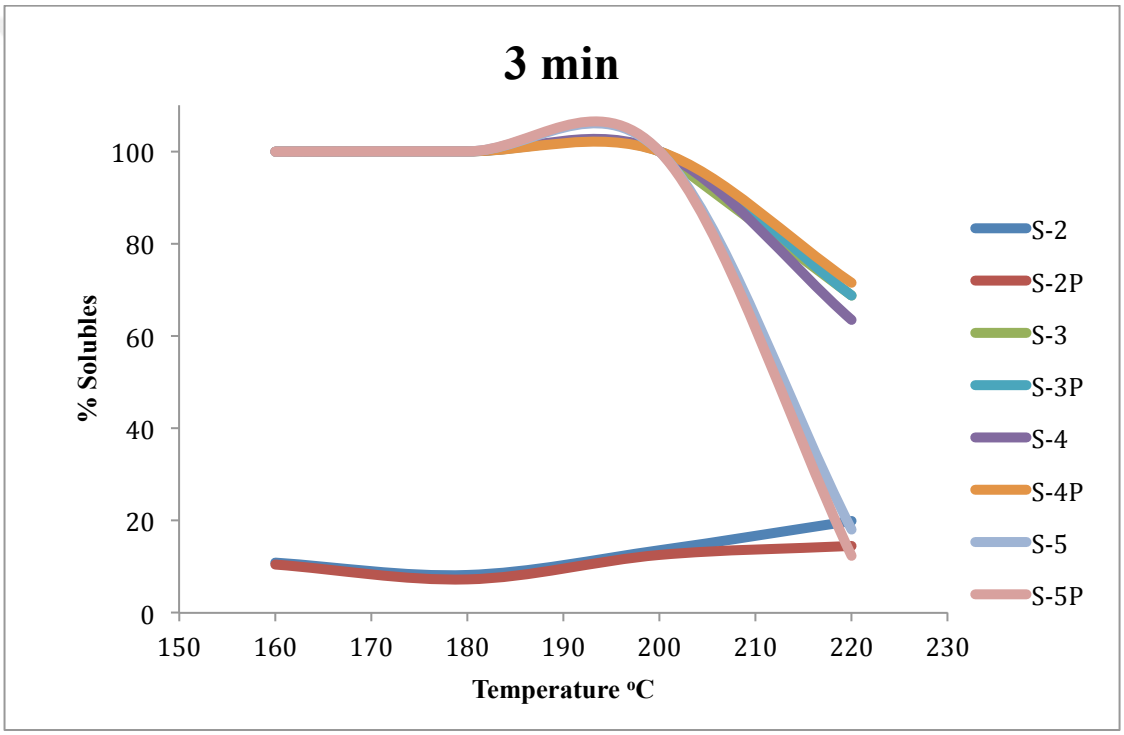


Figure 4.11. Percent solubles graphs for 3 minutes curing.

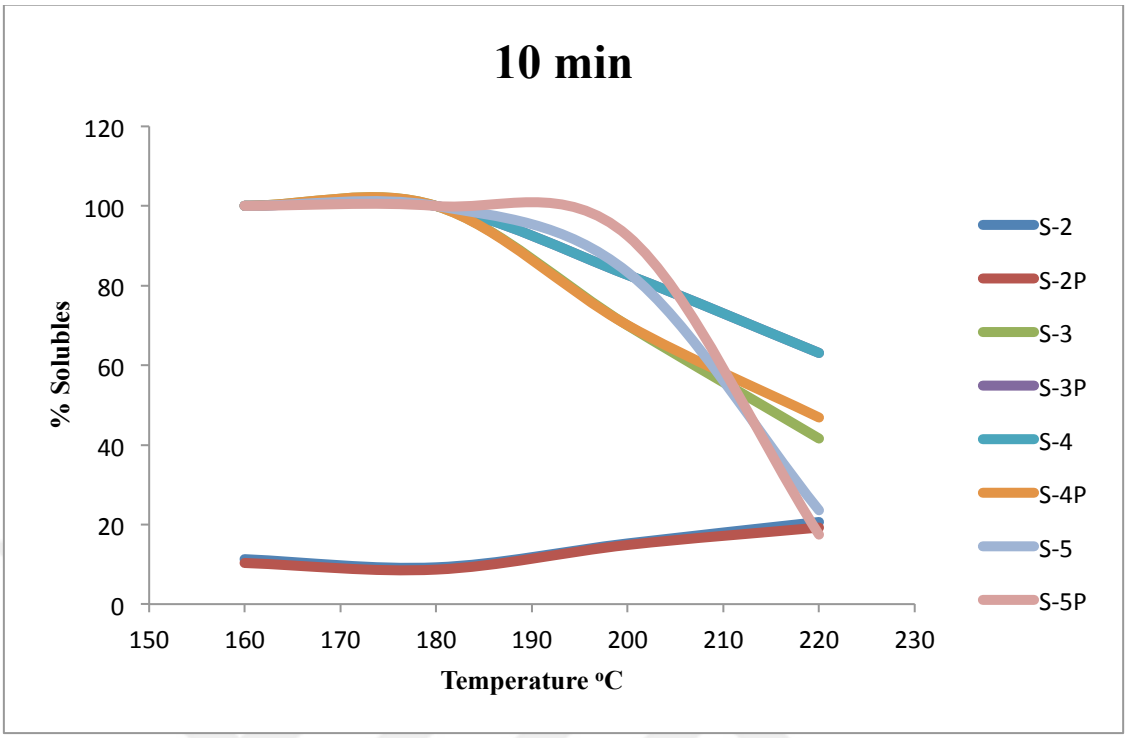


Figure 4.12. Percent solubles graphs for 10 minutes curing.

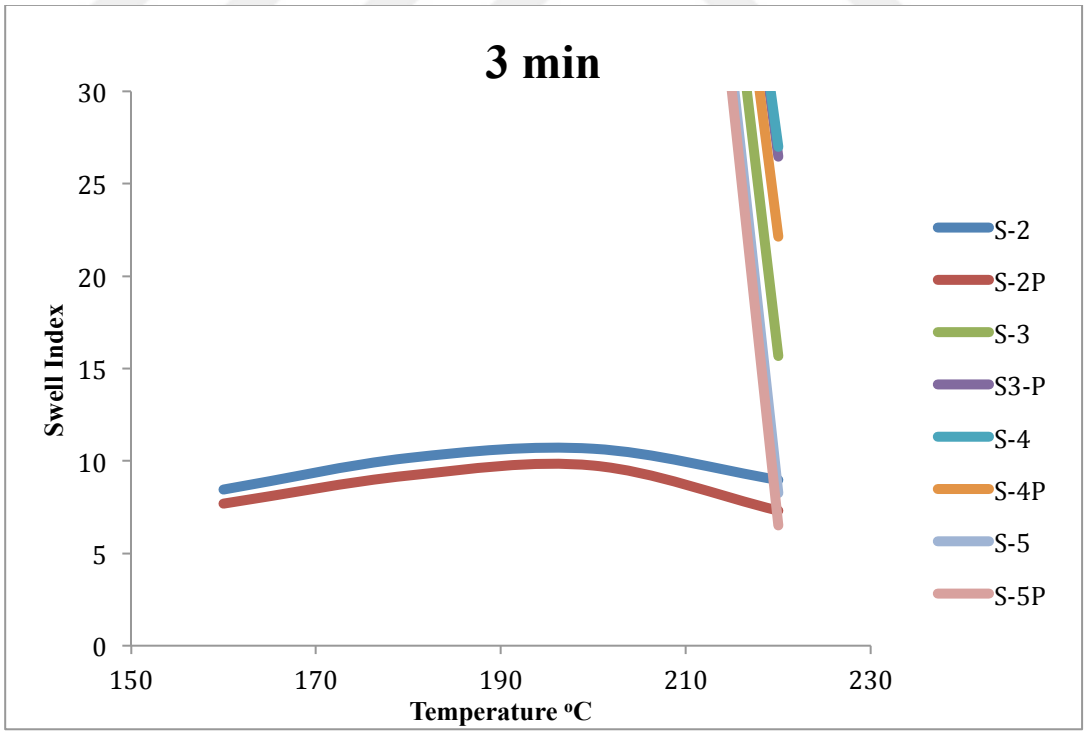


Figure 4.13. Swelling index graphs for 3 minutes curing.

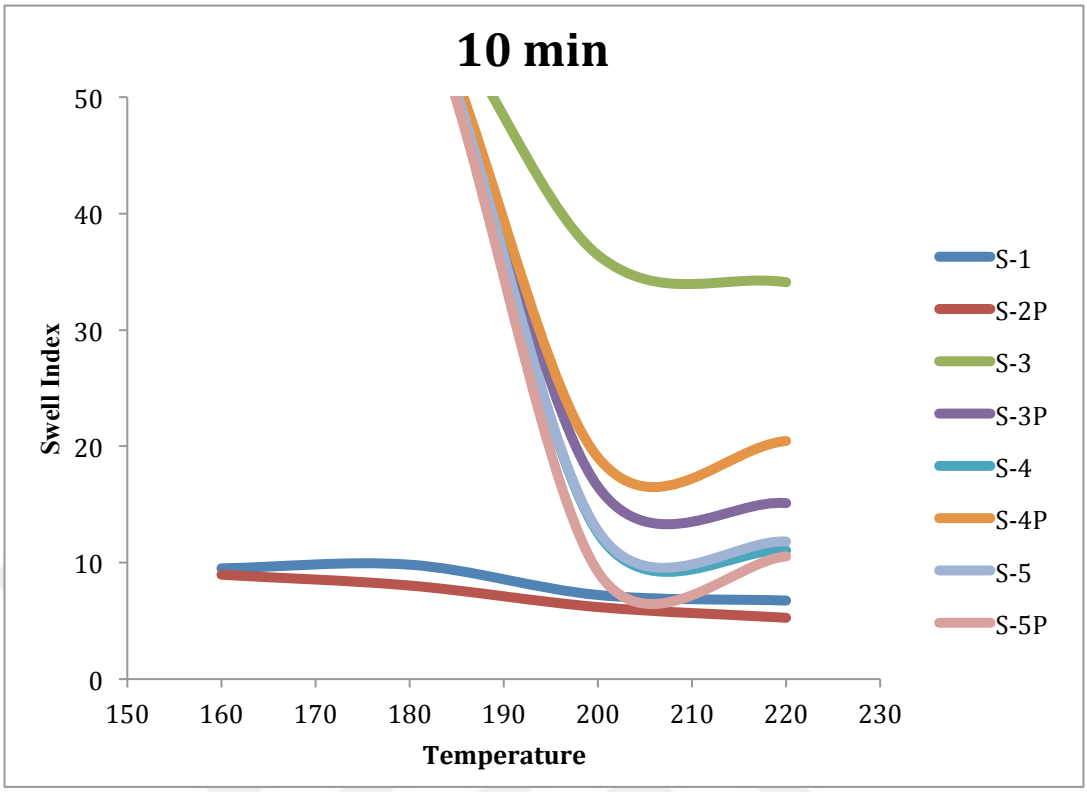


Figure 4.14. Swelling index graphs for 10 minutes curing.

4.4. Determination of Free Formaldehyde in Binders.

Determination of free formaldehyde was done for the binders containing crosslinkers NMA, Xlink A and Xlink B which were used in the emulsions S-2, S-3, S-4 and S-5 respectively using "ISO 15373:2001 Plastics-Polymer dispersions-Determination of free formaldehyde" standart technique. As can be seen from Table 4.3, no free formaldehyde was observed in the binders containing the novel crosslinkers. As stated before the industrially used NMA crosslinker releases formaldehyde. It is important to state that these tests are carried out at room temperature samples.

Table 4.3. Formaldehyde levels in binders.

Emulsions	**S-2**	**S-3**	**S-4**	**S-5**
Formaldehyde(ppm)	265	n.d*	n.d	n.d

* n.d. corresponds to a value under 16 ppm which is the detection limit.

5. FUTURE WORK

As a future work, elemental analysis of synthesized crosslinker will be applied. Also, acrylamide will be added to the emulsion polymerization recipe to enhance the crosslinking ability of the monomer. In addition, application of the binder on the cellulosic and nonwoven substrates and performance evaluation will be performed. Lastly, the synthesis of crosslinkers containing N-O acetal groups bonded to 5 membered furanyl ring will be tried. In this way, the stability of the ring will be lowered and ring opening reaction will be performed at low temperatures.

6. CONCLUSION

Throughout this study, novel formaldeyde free self-crosslinking monomers were synthesized and adopted into the emulsion polymerization recipes for potential replacement of NMA. The crosslinking abilities of binders were evaluated by comparing with NMA containing polymers.

In the first stage of this study, three different formaldehyde-free self-crosslinking monomers were successfully synthesized. In the second stage, polymer emulsions were synthesized containing the new crosslinkers. Finally, percent solubles and swell index tests of binders were performed after the curing process and crosslinking results were compared with NMA containing binders.

As a result, synthesized crosslinkers works higher temperatures than NMA. The crosslinking temperature of novel crosslinkers are 200^{o}C and above. The use of acid catalyst has affected crosslinking temperature slightly but it is not enough to replace NMA. Among three novel monomers, best results were recorded for Hema-modified monomers. This indicates that the N-O acetals are significantly more difficult to react than O-O acetals and hemi-aminals.

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APPENDIX A: SPECTROSCOPY DATA

FT-IR, ^{1}H and ^{13}C NMR spectrums of the synthesized products are included. Necessary expansions were made on the spectroscopy data.

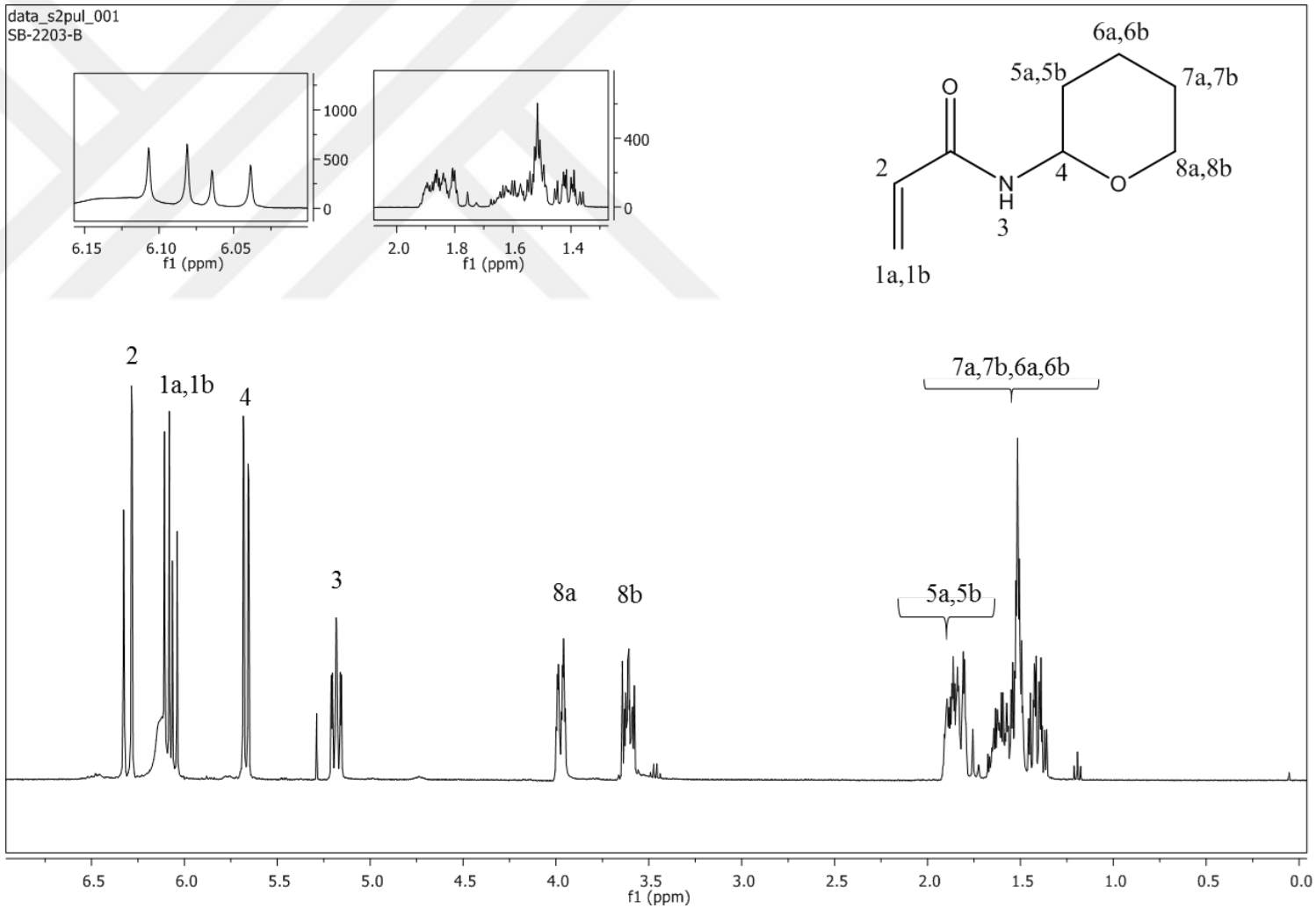


Figure A.1. ^{1}H-NMR Spectrum of N-(2-tetrahydropyranyl)acrylamide .

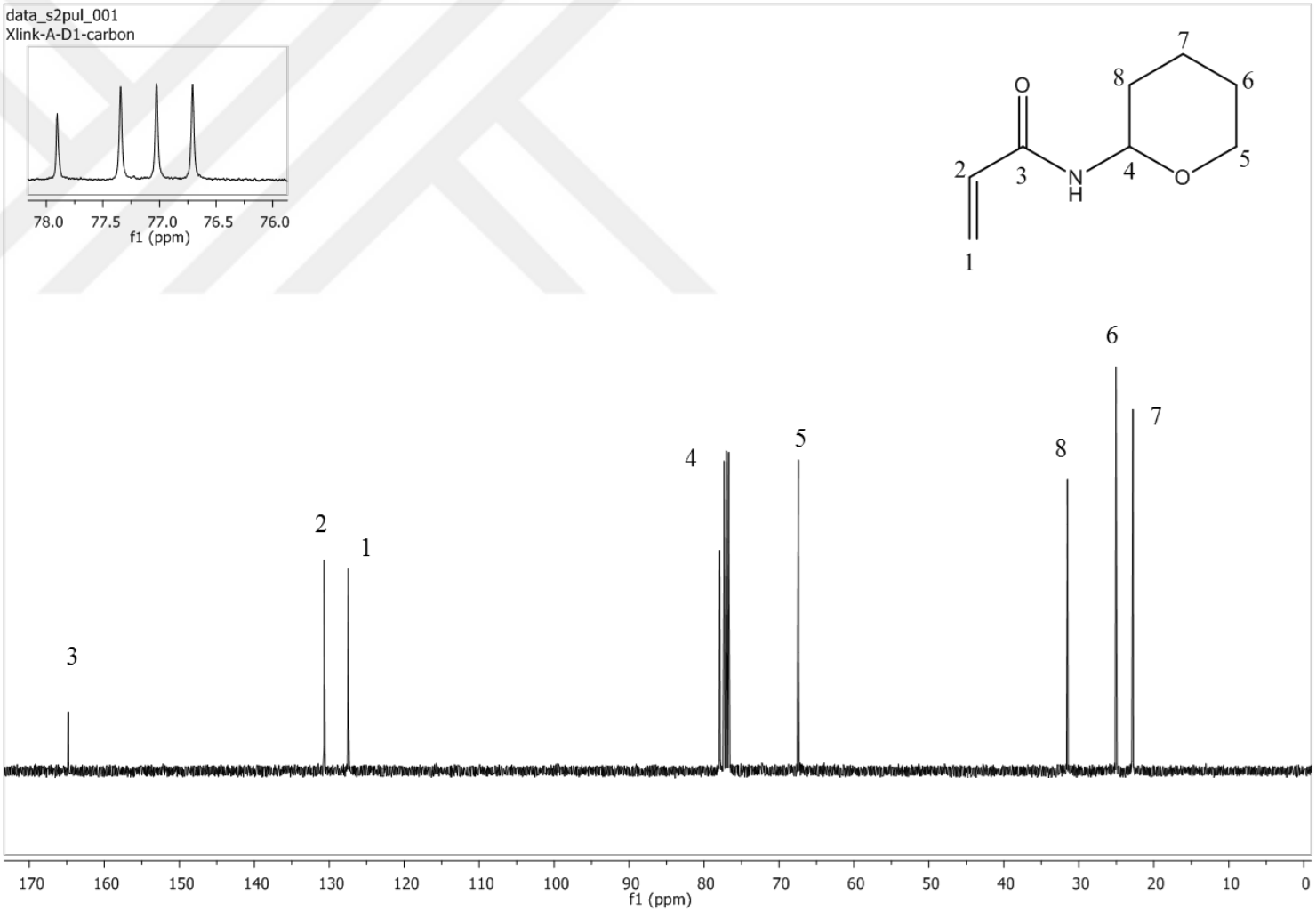


Figure A.2.^{13}C NMR of N-(2-tetrahydropyranyl)acrylamide.

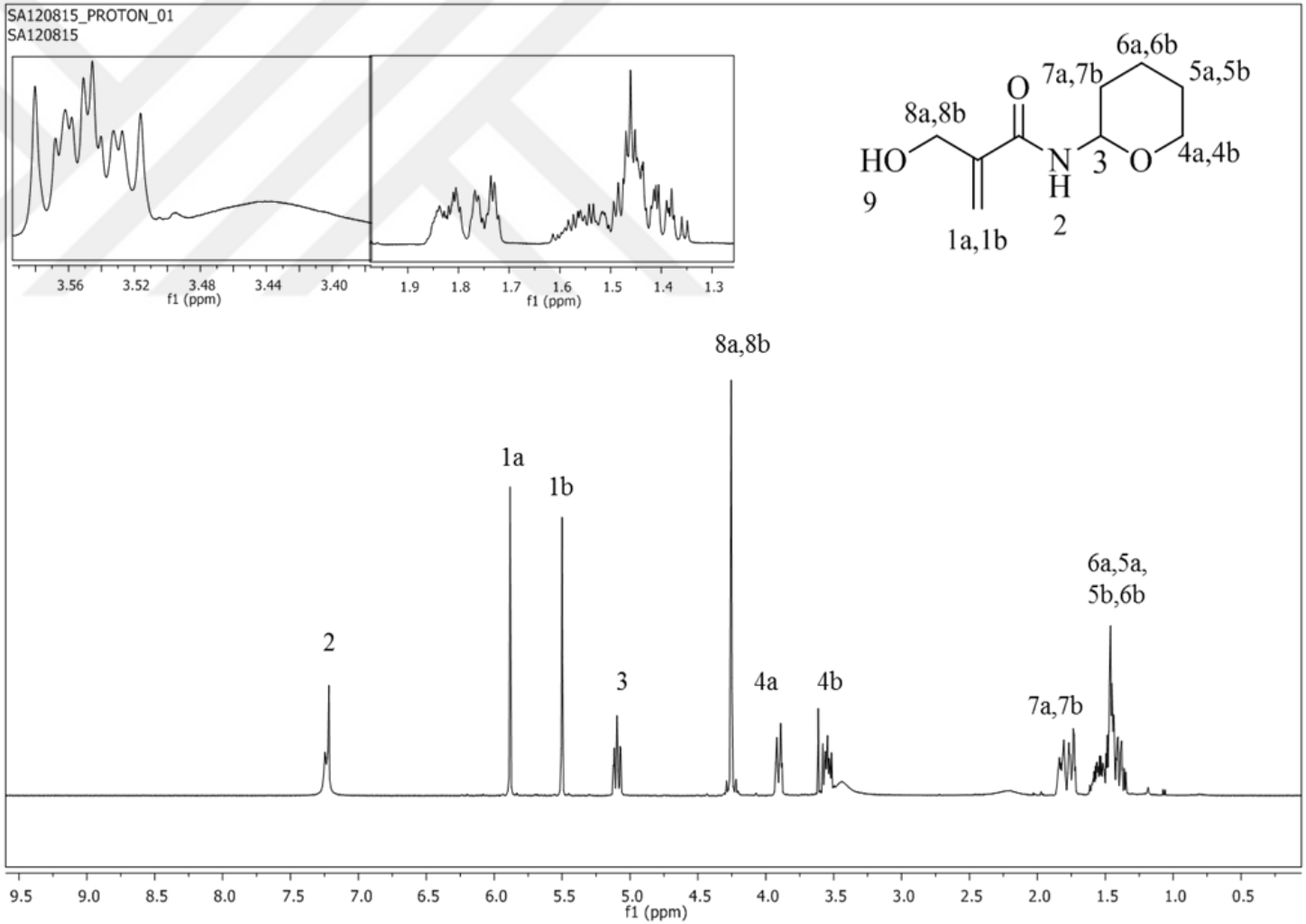


Figure A.3. ^{1}H-NMR Spectrum of Synthesis of 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide (Xlink B)

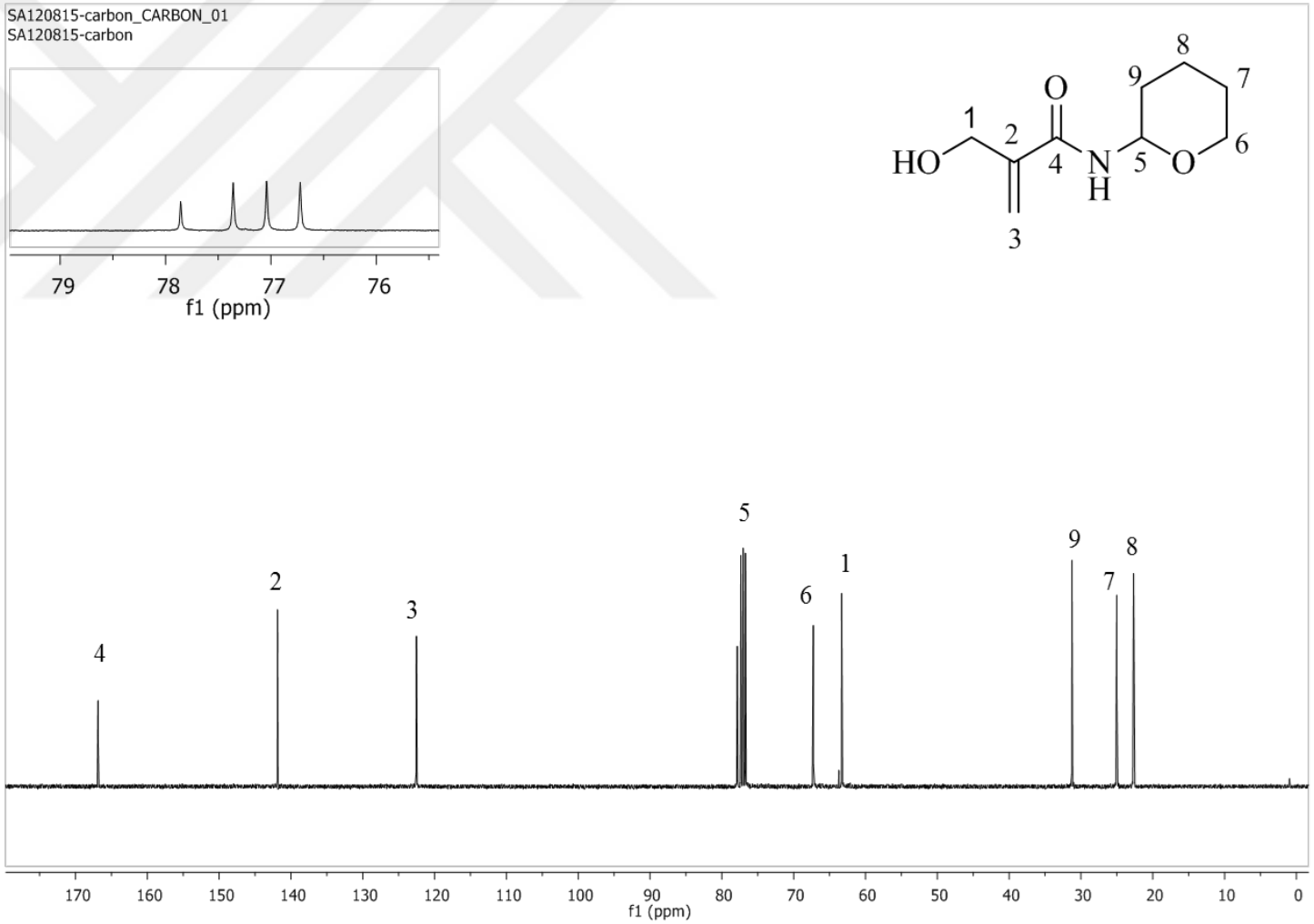


Figure A.4. ^{13}C NMR of Spectrum of 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide(Xlink B)

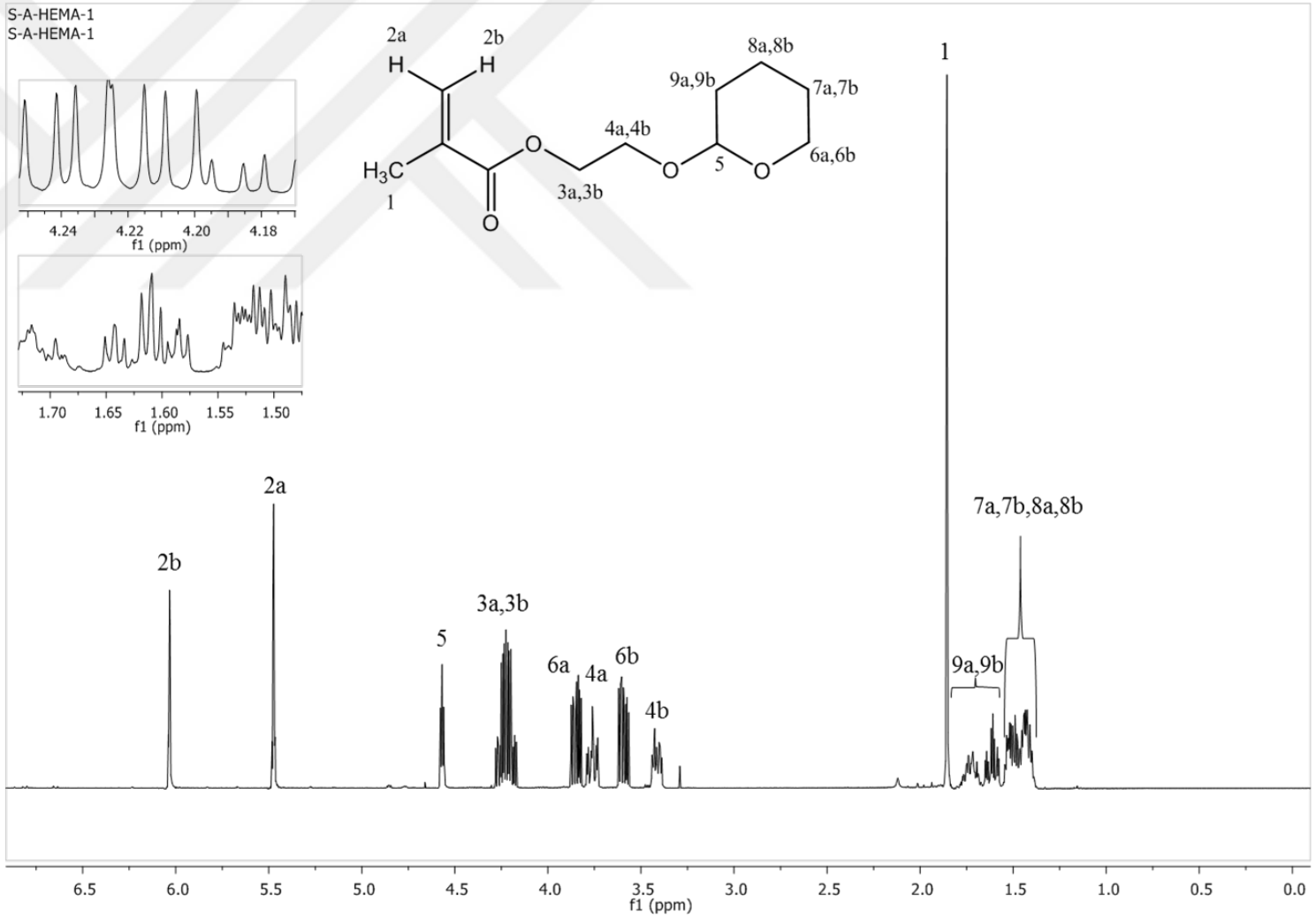


Figure A.5. ^{1}H-NMR Spectrum of2-(2-tetrahydropyranyloxy) ethyl methacrylate (Hema-modified)

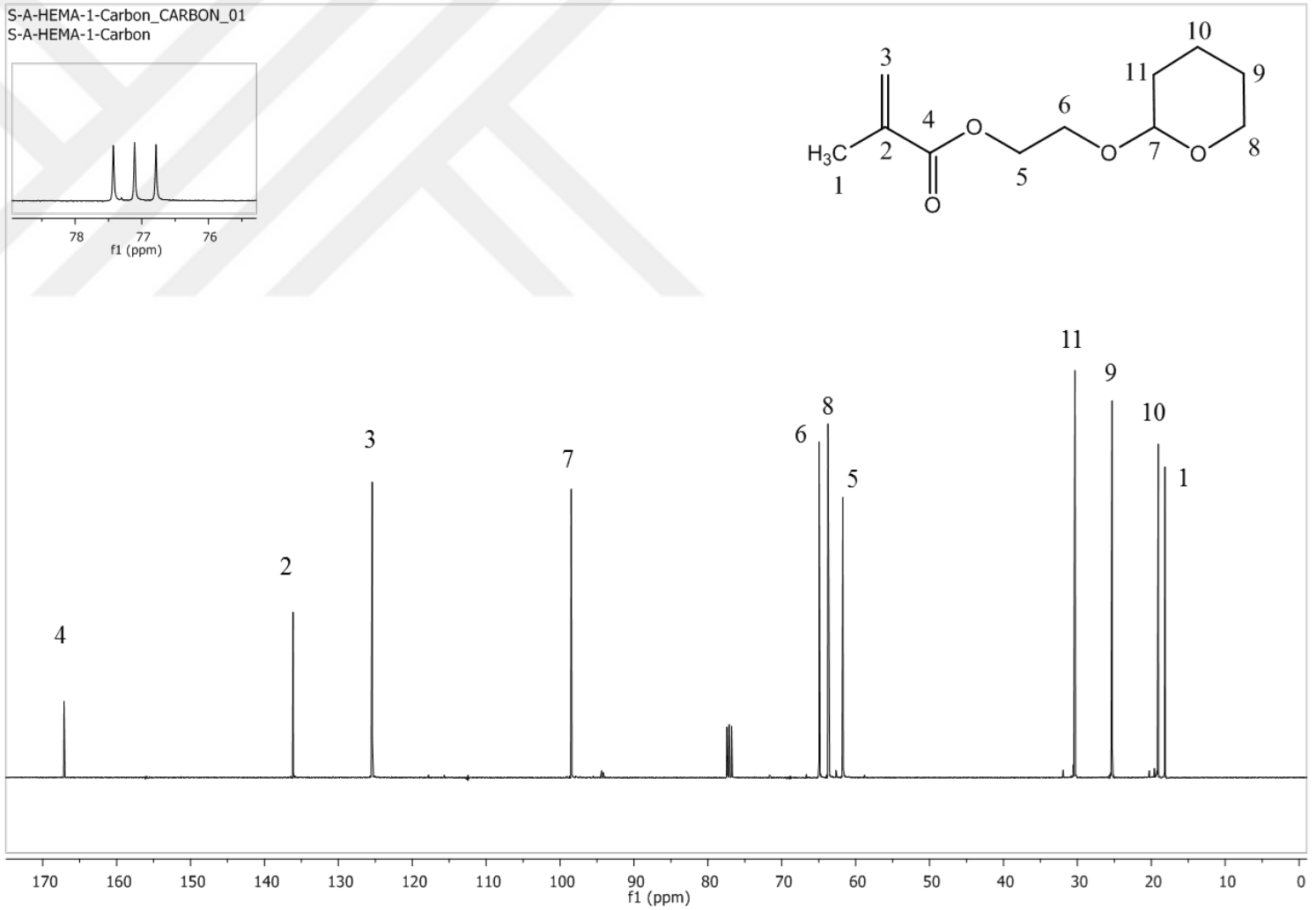


Figure A.6. ^{13}C NMRSpectrum of 2-(2-tetrahydropyranyloxy) ethyl methacrylate (Hema-modified)

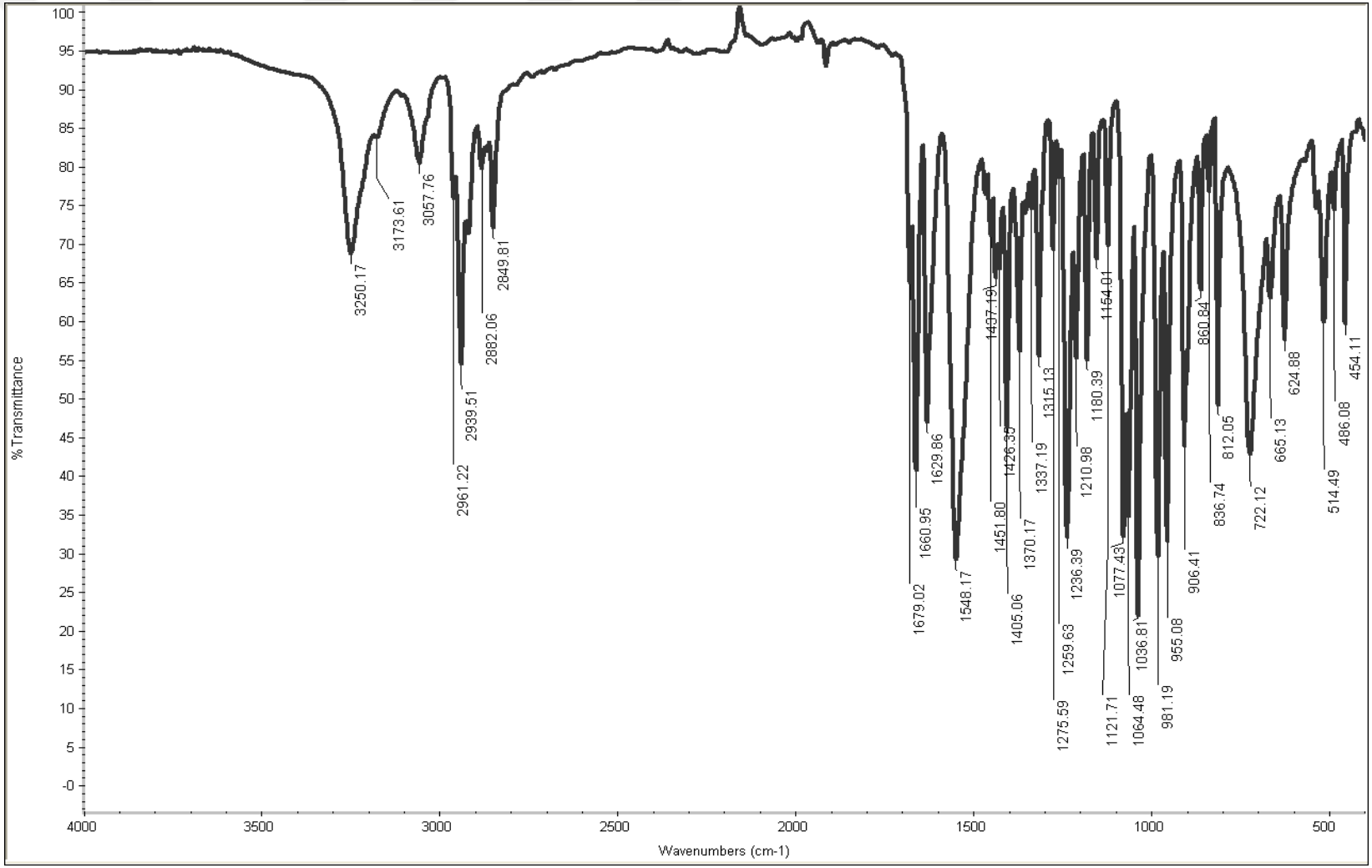


Figure A.7. FTIR Spectrum of N-(2-tetrahydropyranyl)acrylamide.

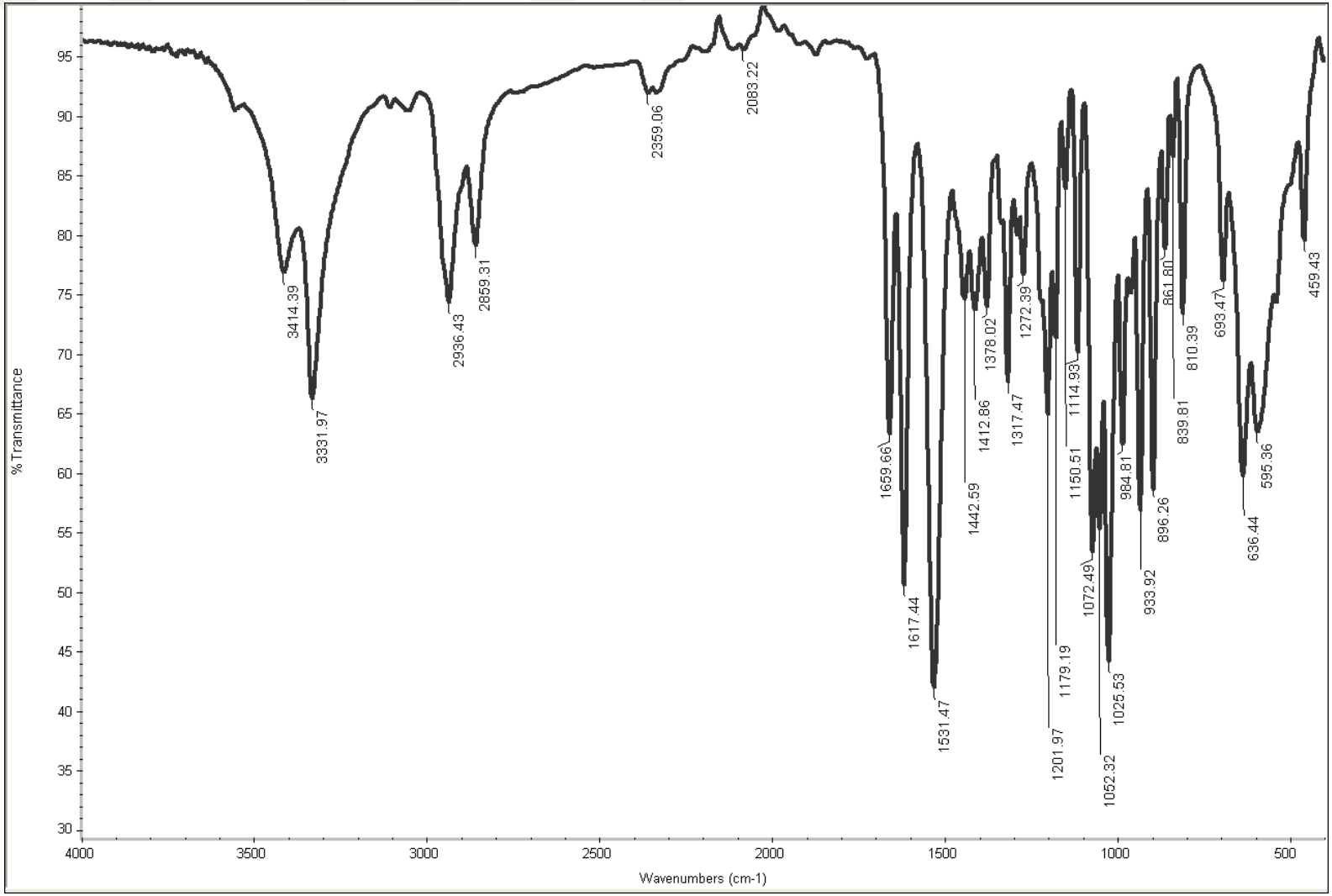


Figure A.8. FTIR Spectrum of 2-(hydroxymethyl)-*N*-(tetrahydro-*2H*-pyran-2-yl)acrylamide

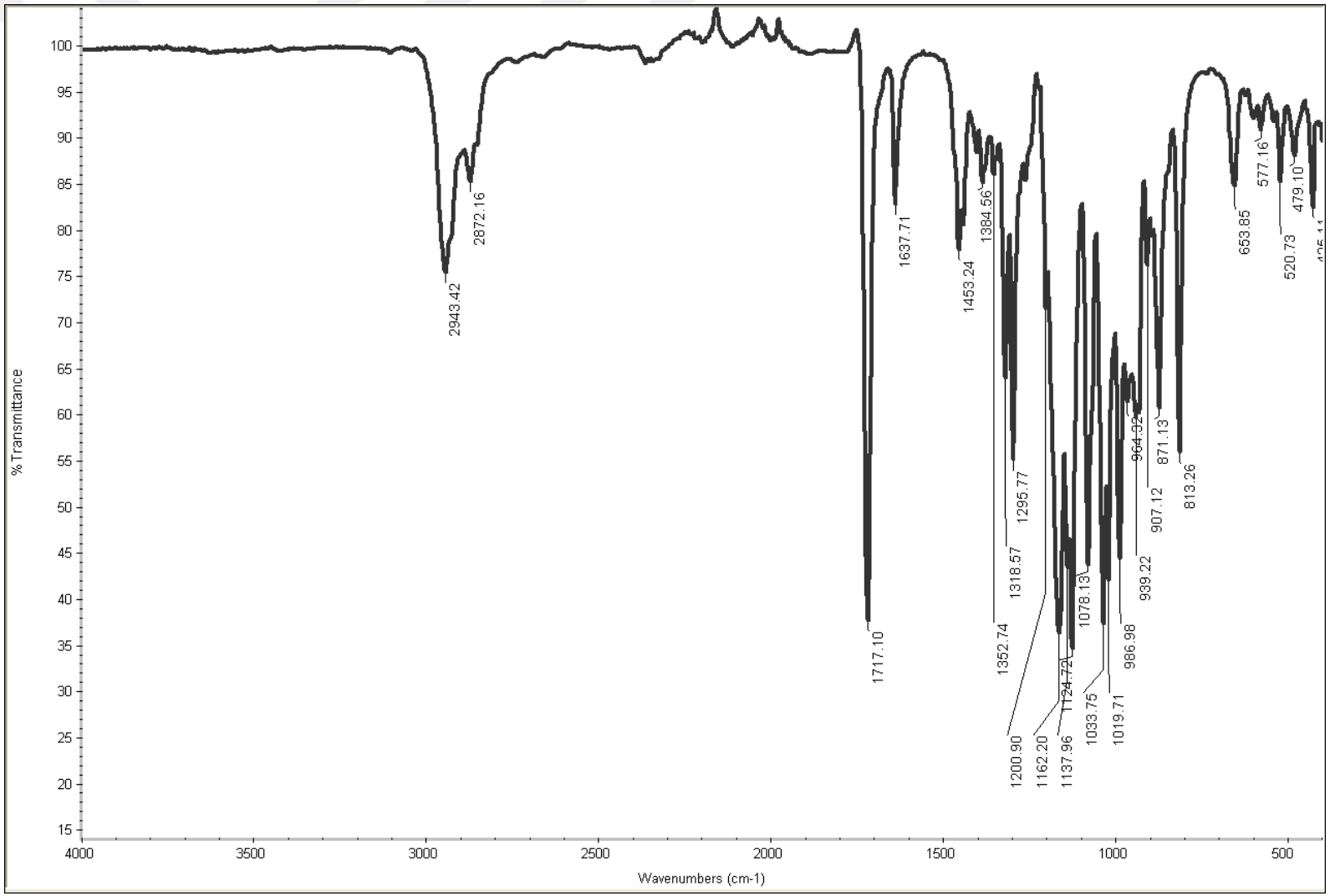


Figure A.9. FTIR Spectrum of 2-(2-tetrahydropyranyloxy) ethyl methacrylate (Hema-modified)