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

by

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B.S., Chemistry, Dokuz Eylul University, 2010

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Chemistry

Boğaziçi University

2014

Anneme…

ACKNOWLEDGEMENTS

I would like to begin my thanks with my supervisor Assoc. Prof Ersin Acar. It is a pleasure for me to express my sincerest gratitude to him for his endless support and wise guidance all along this study.

I also would like to thank my thesis committee members Prof. Selim Kusefoğlu and Assoc. Prof Funda Yağcı Acar for spending their time and reviewing my dissertation.

It would be unfair if I forget to thank my lab friends. Ahmet, Duygu, Ayşenur, thank you so much for your help and friendship during my study. Cem, thank you so much for funny times we had in lab and everything. Seda and Elif, I gained two good friends like you through my master education. Thank you for everything. And İlknur, you never spared your support and help from me when you are here and even far away. Your friendship is very important for me, thank you for everything. And finally Sezgin, thank you so much for making my emulsion polymers, generosity when sharing your knowledge with me, and your friendship.

I also want to thank my little budgie "Vecihi" for taking all my boredom and cheering me up with his tweets during writing this thesis.

Finally, I want to thank my family, and especially my mother. She is the one who made my life bearable when I had hard times during my master period. Without her support and encouregement, nothing would have been possible.

Thank y'all!!

This project has been funded by Organik Kimya A.Ş. and Ministry of Science, Industry and Technology with 0819.STZ.2011-1 SAN-TEZ project number.

ABSTRACT

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

Binders are emulsion polymers used in textile and nonwoven production to impart integrity, strength and durability. However, binders that do not have reactive functional monomers in their formulations are not efficient enough to provide these properties. Addition of self-crosslinking monomers to the binder system is a common method to improve the properties of textile and nonwoven products. Textile industry has used monomers such as n-methylolacrylamide (NMA) as functional group to crosslink upon curing. But, this crosslinking mechanism has a by-product. NMA generates formaldehyde when it is heated to crosslink. Formaldehyde remains in the products in which binders are used or is released into the environment. According to the 12th Report on Carcinogens published by the U.S. Department of Health and Human Services, formaldehyde is a substance listed in the category of *known to be a human carcinogen.* Because of its toxicity, reduction or elimination of formaldehyde emission is one of the focal points of development in textile industry. In this study, a novel formaldehyde-free crosslinking monomer was synthesized for waterborne binder dispersions and its performance was evaluated in comparison with NMA.

ÖZET

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

Bağlayıcılar dokumalı ve dokumasız kumaş üretiminde bütünlük, dayanıklılık ve sağlamlık vermek için kullanılan emülsiyon polimerleridir. Ancak, yapılarında reaktif fonksiyonel monomerler bulundurmayan bağlayıcılar bu özellikleri sağlamada yeteri kadar etkili değillerdir. Bağlayıcı sistemlere kendi kendine çapraz bağlanabilen monomerlerin katılması, dokumalı ve dokumasız kumaş ürünlerinin özelliklerini geliştirmede kullanılan yaygın bir yöntemdir. Tekstil endüstrisi, kürlenme ile çapraz bağlanması için fonksiyonel grup olarak n-metilolakrilamit (NMA) gibi monomerler kullanmaktadır. Fakat bu çapraz bağlanma mekanizmasının bir yan ürünü vardır. NMA çapraz bağlanması için ısıtıldığında formaldehit oluşturmaktadır. Formaldehit, bağlayıcıların kullanıldığı ürünlerde kalır ya da çevreye salınır. Birleşik Devletler Sağlık ve İnsan Hizmetleri Departmanı tarafından yayınlanan 12. Kanserojen Maddeler Raporu'na göre, formaldehit, *insanlarda kansere neden olduğu bilinen* olarak listelenen bir maddedir. Toksisitesinden dolayı, formaldehit salınımının azaltılması ya da yok edilmesi tekstil endüstrisinde gelişimin odak noktalarından biridir. Bu çalışmada, su bazlı bağlayıcı dispersiyonları için formaldehit salınımı yapmayan yeni bir çapraz bağlayıcı monomer sentezlenmiştir ve performansı NMA ile karşılaştırmalı olarak 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
CMC	Critical Micelle Concentration
CTAs	Chain Transfer Agents
DiW	Deionized Water
E	Emulsion
EVAs	Ethylene-Vinylacetate Copolymers
FT-IR	Fourier Transform Infrared Spectroscopy
HCHO	Formaldehyde
MFT	Minimum Film Formation Temperature
MMA	Methyl Methacrylate
NaPS	Sodium Persulfate
NBRs	Acrylonitrile-Butadiene Copolymers
NMA	N-Methylolacrylamide
NMR	Nuclear Magnetic Resonance
NS	Nonionic Surfactant
SBRs	Styrene-Butadiene Copolymers
SDS	Sodium Dodecyl Sulfate
SLS	Sodium Lauryl Sulfate
t-BHP	tert-Butyl Hydroperoxide
T_g	Glass Transition Temperature
TLC	Thin Layer Chromatography
UV	Ultra Violet
VOCs	Volatile Organic Compounds

1. INTRODUCTION

1.1. Binders

A binder is simply the product of free radical polymerization of monomers, which is stabilized in water via surfactants. The term “binder” is synonym with all the espressions like adhesive, latex, polymer dispersion, and emulsion polymer [1,2].

Binder usage is one of the basic techniques used to strenthen the webs in the production of nonwoven fabrics. They bind the fibres in a web to each other like an adhesive. Generally, a nonwoven has its maximum strength when all the fibre intersecting points in a web are completely bonded. A binder material, which is placed between the intersecting points, has a stiffening role in the nonwoven production [2].

First binders were used to bond the fibres to each other in nonwovens to gain strength and integrity in the web. Although this is still their main function, binders are now expected to be more than just adhesives. They provide additional functions and aesthetics like flame retardency, softness, stretch, and recovery [3].

During the nonwoven development period, binders were the primary issue to work on, since, generally, nonwoven fabric performance is determined primeraly by binders. Deficiencies of nonwovens are consequence of inadequate binders. Some of the shortcomings of nonwovens are as follows:

- Low strength
- Poor laundering ability
- Inadequate dry cleaning ability
- Lack of a sense of textile

Therefore, all efforts to produce desired nonwovens has focused on the development and improvement of chemical binders [4].

In the early stages of the nonwoven development, various natural resins and glues were used as binders. Although they provided some integrity and durability, they also had so many inabilities which limited their use. Consequently, synthetic binders were developed to satisfy the demand of the desired nonwoven fabrics [4].

Polyvinyl acetate was the first succesful synthetic binder used in the nonwovens. However, the great improvements came with the introduction of acrylic-based binders in terms of strength and softness. By the use of proper co-monomer, it is possible to achieve binder properties with improved softness and sufficient strength [4].

As the synthetic binder technology improved, a great variety of chemical building blocks took part in the binder production. Introduction of crosslinkable and self-crosslinking monomers to the binder system provided much more flexible binders with very good strength, durability and other properties. This was very important for nonwovens where durability features such as washability and dry cleanability are must. Consequently, these binder systems have been used in nonwoven industry very widely [4].

Figure 1.1. Examples of nonwoven products that contains binders.

The market for binders used in nonwoven production is very large. It includes materials such as cleaning cloths, roofing, hand towels, medical/surgical products, interlinings, filters, nappies, car interiors, nonwoven carpets, clothing, and etc. Binders are used in so many applications because their properties can be purposely adapted according to the desired characteristics of the end use product [2].

1.1.1. Desired Properties of a Binder

Binders in the production of nonwovens are used to achive certain desired properties such as strength, softness, adhesion, firmness, durability, fire retardence, hydrophilicity, hydrophobicity, and solvent, wash, and acid resistance. The required properties can be varied according to the end-uses. When the issue is an ideal binder, followings are the main required considerations [5]:

- *Strength:* The strength of the nonwoven fabrics depends on the strength of binder.
- *Flexibility:* Some of the movements of fibres must be enabled after binder application, especially if a soft material is needed.
- *Adhesion:* Adhesion strength between binder and fibre is very important.
- *Washing / Dry Cleaning Resistance:* Nonwoven products must be durable towards cleaning processes according to their end-uses.
- *Resistance to Aging:* The binder in the fabric must not degrade throughout storage and use.
- *Good Color:* Many colors are needed, therefore colorfastness and yellowing problems must be eliminated.
- *Other Special Requirements:* Resistance to chemicals, light, oxygen, heat, etc is also important [4].

1.1.2. Why Binders?

There are so many requirements to obtain improved nonwoven products. Binders used to impart the required properties to the nonwovens have four important characteristics [1]:

- Low viscosity – to ease the applications
- High molecular weighy – for strength
- Binder versatility
- Low cost

1.2. Raw Materials

Each polymer class has a range of properties based on its chemical structure. Copolymers can also be designed, where their properties range from soft to firm, hyrophobic to hyrophilic, solvent resistant to redispersable. The binder selection depends on the desired nonwoven properties and the cost [3].

1.2.1. Acrylics

Acrylic copolymers are the most prevalent polymers used in the nonwoven industry, although they are more expensive than the other types. They are used very widely because they have good properties like light-stability, heat resistance, resistance to oxidation, washability, and shrink resistance which are very important for both durable and disposable applications. Acrylics are used in apparel interfacings because of their durability in washing and dry-cleaning and capability to retain color over the lifetime of the clothing. They are also used in medical materials because their properties are not reduced with sterilization [2,3].

1.2.2. Styrene-Butadiene Copolymers (SBRs)

Styrene-butadiene copolymers are less expensive than acrylics. They have excellent hydophobicity when used with crosslinking resins and provide very good balance of hand and solvent resistance. The styrene/butadiene ratio effects copolymer properties, including elastic recovery and firmness. Styrene level in the copolymer can be changed from 45% to 90% according to the desired stiffness. Styrene-butadiene copolymers are used in industrial wipers, wet wipes, and filtration [2,3].

1.2.3. Ethylene-Vinylacetate Copolymers (EVAs)

Vinylacetate-ethylene copolymers are used in disposable applications and, less likely, in durables.

Because they are less resistant to moisture and solvents than acrylics and SBRs, they have advantageous liquid absorption and high wet strength. Vinylacetate monomer provides excellent adhesion to many synthetic fibers. It also determines the firmness of copolymer, where it is generraly added about 70% to 90% [2,3].

1.2.4. Vinylacetate-Acrylate Copolymers

The properties of vinylacetate-acrylate copolymer are very similar to the EVAs. Acrylic monomer increases the moisture and solvent resistance and adhesion properties of the copolymer. In addition to the disposable applications, vinylacetate acrylates can be made suitable for durable applications by using crosslinking resins. The vinylacetate monomer decreases the cost of polymer compared to acrylics and is used up to 90% [3].

1.2.5. Polyvinyl Acetate Homopolymer

Polyvynil acetate homopolymers are very low-cost binders which are used in highloft products, shoddy and some interfacings. They are hydrophilic and have enough dry strength. Due to their sensitivity to moisture, they are generally modified with methacrylic acid and self-crosslinking functionality [2,3].

1.2.6. Acrylonitrile Butadiene Copolymers (NBRs)

Binders containing acrylonitrile monomer are used in materials that must have resistancy to solvents, oil, and grease. They are expensive due to these enhanced properties. NBRs have limited heat resistance and light fastness and low ultraviolet resistance. However, they also have convenient softness and resilience, and abrasion resistance [2,3].

1.3. Factors that Influence Binder Properties

Diversity is very important in nonwoven production. As indicated, the nonwoven fabrics are used in many different applications. Each application requires a binder that has specific functional properties. Therefore, there are many types of binders. To understand why there are so many binders used to bond nonwoven fabrics, factors that influence the binder properties must be considered. These factors are polymer composition, functional groups, and reactivity.

1.3.1. Polymer Composition

Binders are produced from monomers with emulsion polymerization. The monomers and co-monomers used for binder production are described with vinyl monomer as basic monomer and "R" representing different co-monomers (Figure 1.2 and Table 1.1) [2].

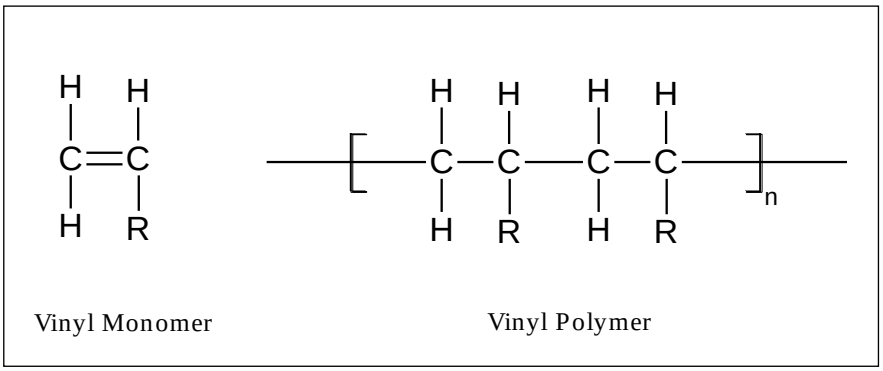

Figure 1.2. Structure of vinyl monomer and vinyl polymer.

To reach the desired polymer composition, different types of co-monomers are used, which results in wide range of binder classes [2].

Table 1.1. Different vinyl monomers.

Name	**R**
Ethylene	H
Styrene	C_6H_5
Vinyl Acetate	$O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$
Vinyl Chloride	Cl
Ethyl Acrylate	$\overset{\overset{O}{\|}}{C}{-}OC_2H_5$
Butyl Acrylate	$\overset{\overset{O}{\|}}{C}{-}OC_4H_9$
Acrylonitrile	CN
Methyl Methacrylate	$H_2C{=}\overset{\overset{CH_3}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$

The selection of co-monomers influences the properties of binders. One of these properties is the glass transition temperature, T_g. Simply, the lower the glass transition temperature, the softer the polymer. T_gs of homopolymers of commonly used monomers in binders are shown in Table 1.2 [2].

Table 1.2. Glass transition temperature of the homopolymers.

Monomer	***T_g (^oC)***
Ethylene	-125
Butadiene	-78
Butyl acrylate	-52
Ethyl acrylate	-22
Vinyl acetate	+30
Vinyl chloride	+80
Methyl methacrylate	+105
Styrene	+105
Acrylonitrile	+130

Another property that is effected by the co-monomer selection is hyrophilic-hyrophobic balance of the binders. Wet strength of a binder can be adjusted according to hyrophilic-hyrophobic nature of the co-monomers (Table 1.3.). If the desired property is high wet strength, hyrophobic co-monomers like styrene must be selected over vinyl acetate in the design. However, if solvent resistance is desired, hydrophilic co-monomers such as acrylonitrile would be a better choice [2,4].

Table 1.3. Hydrophilic-Hydrophobic nature versus hardness.

Monomer	***Nature***	***Tg (^{o}C)***
Styrene	*Most Hydrophobic*	+105
2-Ethyl hexyl acrylate		-85
Butyl acrylate		-52
Methyl methacrylate		+105
Ethyl acrylate		-21
Methyl acrylate		+8
Acrylonitrile		+130
Vinyl acetate	*Most Hydrophilic*	+30

1.3.2. Functional Groups

Functional groups are added to the binder system in addition to the co-monomers. They are incorporated via copolymerization of small amount of special functionality monomers. Functional groups influence the properties of binders, and therefore of the nonwoven. They can enhance the performance by improving the mechanical properties, emulsion stability, solvent resistance, and adhesion. Some of the functional groups used commonly in binder systems are as follows [1,2]:

- Carboxyl functionality
- Amide functionality
- n-Methylol amide functionality

Carboxyl functionality is incorporated to the binders in order to improve mechanical and emulsion stability, adhesion, and hydrophilicity. It also provides a reaction site to crosslink with added resins [1].

Amide functionality is related to binders that are copolymerized with acrylamide. This functionality provides reactive sites for added crosslinking resins [1].

n-Methylol amide functionality is added to binders via copolymerization of n-methylol acrylamide monomer. Binders containing this functionality are self-crosslinkable. When exposed to sufficient heat, this functionality is crosslinked and forms a three dimensional structure.

1.3.3. Reactivity

The term “reactivity” is related to the polymers’ ability to crosslink. There are non-crosslinking, crosslinkable, and self-crosslinking binders which differenciate in their reactivity.

The non-crosslinking means that the binder does not contain any monomer with reactive functional groups. Therefore, it can not crosslink with itself or external curing resins [1].

The crosslinkable means that binder has monomers with carboxyl or amide functionalities which facilitate the crosslinking reaction with external curing resins, but the binder can not crosslink with itself [1].

The most commonly used external curing resin in crosslinkable binder systems is melamine formaldehyde. This curing resin has ability to react with hydroxyl, carboxyl, amide, and n-methylol amide functional groups (Figure 1.3.). Binders containing these functional groups are reacted with curing resins to improve the durability and toughness. Other curing resins used less in nonwovens are urea formaldehyde, epoxy, phenolic, and metal ion complexes.

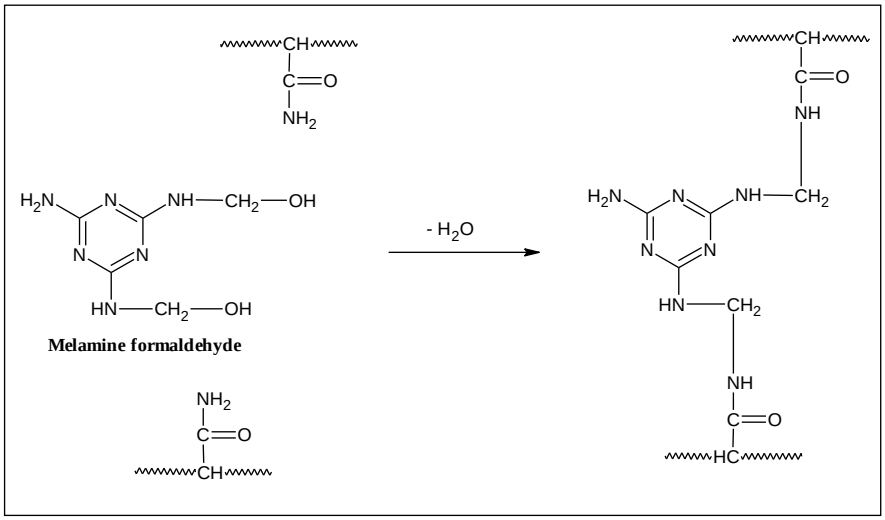

Figure 1.3. External crosslinking with melamine formaldehyde.

Lastly, self-crosslinking binders have ability to crosslink with themselves to increase the crosslinking density. They can be also used with external crosslinking resins. The self-crosslinking polymers make easy the preparation of the end-use composition by decreasing the number of components, eliminating the mixing of an additional catalyst or crosslinking agent prior to the application. By using self-crosslinking polymers, partly-cured, preformed articals or stock materials can be prepared, which can be exposed to additional processing steps before curing, enabling a flexible manufacturing process. In addition, use of self-crosslinking polymer latexes decreases the probability of migration of undesired monomeric catalysts or unreacted crosslinking agents into the environment from the end-use product [1,6].

In self-crosslinking binders, *n*-methylol acrylamide monomer is utilized to enable the crosslinking. This monomer is self-crosslinking at high temperatures [2].

1.4. N-Methylolacrylamide

NMA is a functional monomer that is added to binder systems to increase the reactivity. It is commonly used as a crosslinking agent in emulsions. It is utilized to increase the resistance of binders in the final application [2].

NMA is produced by the reaction of acrylamide with formaldehyde. Its crosslinking starts at 150 ^{o}C forming bridges between polymer chains (Figure 1.4). This temperature can be lowered significantly with the presence of acid catalysts such as phosphonic acid [7].

This crosslinking mechanism occurs during last step of nonwoven production. Latex binder "dried" films are exposed to the heat needed for crosslinking. This step is called the curing step.

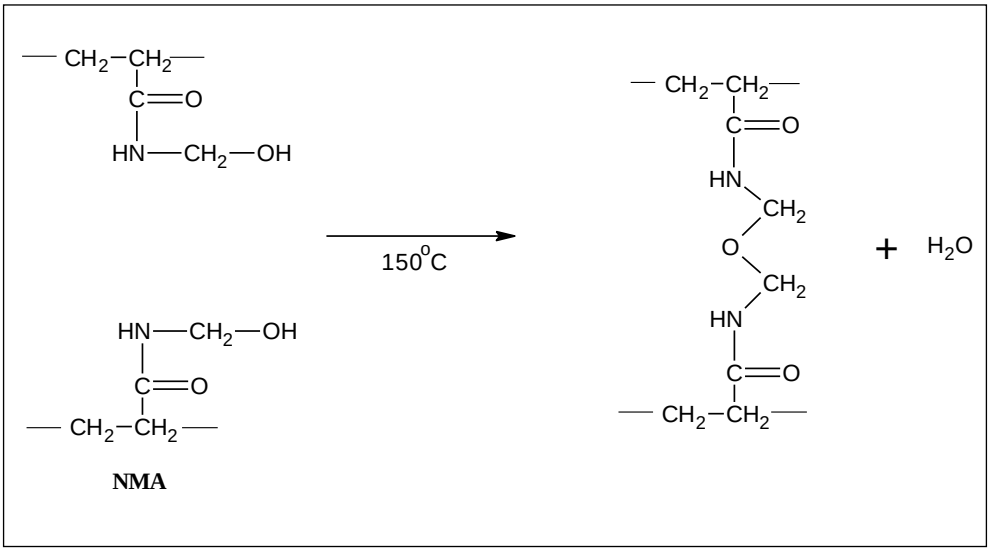

Figure 1.4. Crosslinking mechanism of NMA.

Unfortunately, NMA has a side reaction which limits its use as a crosslinker(Figure 1.5). 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 [2].

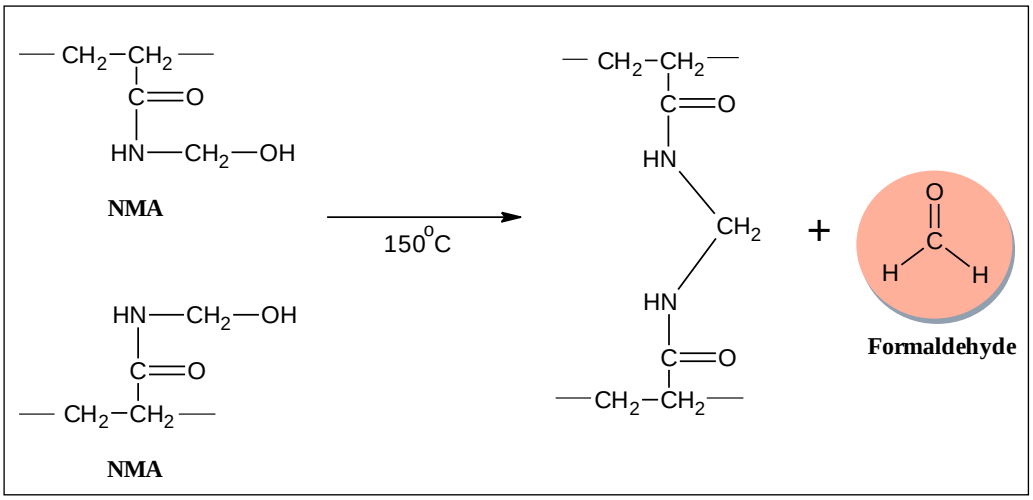

Figure 1.5. Side reaction of NMA during curing step.

This crosslinking agent by enviromentalists is considered as toxic because of the generation and the release of formaldehyde, which is a potential carcinogen. Therefore, researchers focused on other alternative chemistries with lower levels of free formaldehyde for textile and nonwoven industry [2].

1.5. Formaldehyde in Textiles

Formaldehyde is a colorless flammable organic compound with a characteristic irritating odor. It is produced by the oxidation of methane or methanol with the help of a catalyst. Formaldehyde is an important starting material used in the production of many other materials and chemical compounds. Without formaldehyde, the performance of products that use its chemistry would not be as sufficient as they are now. Some of the sectors that would be affected from the lack of formaldehyde are personal care products, automotive materials and textile products [8,9].

Formaldehyde is a pollutant generated from both human activity and natural sources. Small amount of formaldehyde is produced as a result of metabolism of plants, animals and humans. However, most of the formaldehyde comes from manufacturing and combustion processes [10].

The air in the cities includes formaldehyde generated and released from power plants, automobile exhausts and manufacturing, whereas the indoor air formaldehyde releases comes from building materials, tobacco smoke, and consumer products (Figure 1.6.) [10].

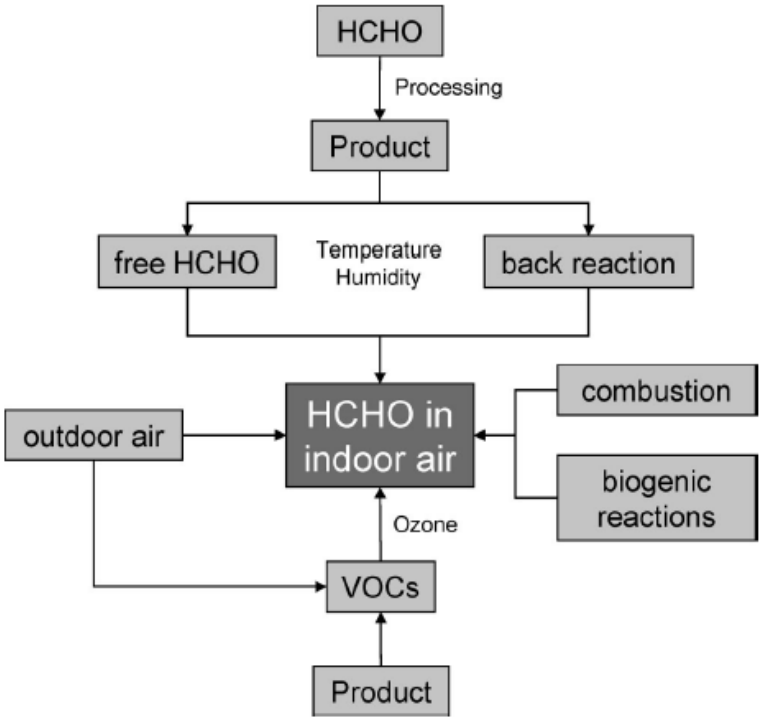

Figure 1.6. Possible formaldehyde sources [8].

One of the end-use applications where formaldehyde release is observed is in textile chemistry more specifically in nonwoven applications. This comes from the binder systems used in the manufacturing. The current binders have three sources of formaldehyde: emulsifiers, biocides, and crosslinking agents like NMA or urea-formaldehyde [2].

1.5.1. Toxicity of Formaldehyde

Formaldehyde is toxic at specific levels similar to many other reactive compounds. Although its toxicity is lower than many, the problem comes from some particular characteristics. First is the presence of formaldehyde all around the work and living spaces since it is in the gas form. Second point is the potential constant formaldehyde release from synthetic binders and their end-use products. Skin contact and inhalation are the two ways of exposure [9].

Irritation of eyes, nose, and throat are the general health problems observed in the people exposed to formaldehyde. Some other symptoms that is reported upon formaldehyde exposure are fatigue, vomiting, nosebleeds, nausea, headaches, and dizziness. Large amounts of formaldehyde exposure is also declared to induce fluid aggregation in the lungs, damage to liver, central nervous system, and kidneys [9].

In the textile industry, dermatitis is a well-known health problem after a skin contact with formaldehyde. It is also documented as sensitizer which causes a person to react to even small amounts of formaldehyde after years of exposure [9].

According to the 12th report on carcinogens published by U.S. Department of Health and Human Services, formaldehyde is listed as *known to be a human carcinogen.* Studies have shown a reasonable relationship between formaldehyde exposure and cancer in humans. The relationship comes from the strong findings of high risks of nasopharyngeal cancer, lymphohematopoietic cancer, sinonasal cancer, and myeloid leukemia in the individuals exposed to high levels of formaldehyde [11].

Because formaldehyde is a toxic substance to the human body, the OEKO-TEX® Standard 100, which is an independent testing and certification system for textile materials, has established limit values for formaldehyde in the different class of textile products (Table 1.4) [12].

Table 1.4. Limit values for formaldehyde [13].

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. non-detectable corresponding to an absorbance value less than 0.05 resp. <16 mg/kg by "Japanese Law 112" test method.

1.5.2. Measuring Formaldehyde in Textiles

Although there are several ways to measure free formaldehyde levels in clothing and other textiles, the two analytical test methods are presently used in textile industry. One of these is American Association of Textile Chemists and Colourists Method 112 (AATCC method 112) and the other is Japanese Law Method 112 [14].

In the AATCC Method 112, a weighed sample of fabric is placed in a sealed jar full with an aqueous solution. The jar is put into an oven at a specific temperature for a specific length of time. Formaldehyde released from the sample is derivatized in the solution resulting a change in the color. So, the amount of formaldehyde absorbed by water is determined colorimetrically with a visible spectrophotometer [9].

In the Japanese Law 112 Method, test sample is treated with a cold aqueous solution of sodium sulfite. Free formaldehyde extracted from test sample into aqueous solution is derivatized to a colored complex. This color change in the solution is measured by the visible spectrophotometer same as the AATCC Method 112 [9].

The level of formaldehyde is represented as micrograms of formaldehyde per gram of textile in both methods [9].

1.6. Emulsion Polymerization

Emulsion polymerization is a process in which radical polymerization reaction progress in a heterogenous medium. This process includes the emulsification of hyrophobic monomer in water with the help of an oil-in-water emulsifier and initiation with water-soluble or oil-soluble free radical initiator. As a result of polymerization reaction, a milky fluid is attained, which is generally called as “latex”, “synthetic latex” or “polymer dispersions”. Latex is the definition of a colloidal dispersion of polymer particles in an aqueous medium [15].

1.6.1. Mechanism of Emulsion Polymerization

According to the Harkins model, a batch reaction process has been proposed with three stages. The polymer particle generation occurs in the micells formed by the very small amount of monomer, which is covered by a layer of anionic surfactant and dissolved in the continuous aqueous phase. Generally, a water-soluble initiator is utilized. Polymerization process starts with the entrance of free radical initiator into the monomer swollen micelle. The monomer swollen micelles, which have a size of 10-20 nm, have larger surface area according to monomer droplets of size 1-10 μm, so, the posibility of free radical capture by a monomer droplet is small. While the monomer concentration is decreased upon growing particle, monomer diffusion starts from reservoir of monomer droplets to the particle. The particles are presumed to grow until another free radical enters into micelle to terminate the polymerizaiton reaction. This particle nucleation process, called first stage, is supposed to be complete when there is no longer uninitiated micelles and new micelle generation is stopped. Generally, conversion of monomers to polymers is about 10-15% at this stage [16].

After the particle nucleation process is over, the number of latex particles stays constant till the end of the polymerization. In the second stage, monomer swollen particles are the primary locations for the propagation reaction. Monomer droplets are only the reservoirs of monomer and surfactant for the growing particles.

The major monomer to polymer conversion happens at this stage (up to 60%). The particle growth stage (second stage) terminates when all the monomer droplets has been used [17].

Emulsion polymerization progresses from second stage to third stage when all the monomer droplets disappear. In this stage, monomers in the latex particles are converted to polymer and the concentration of the monomer continues to diminish. Therefore, polymerization rate drops off at the third stage (Figure 1.7) [17].

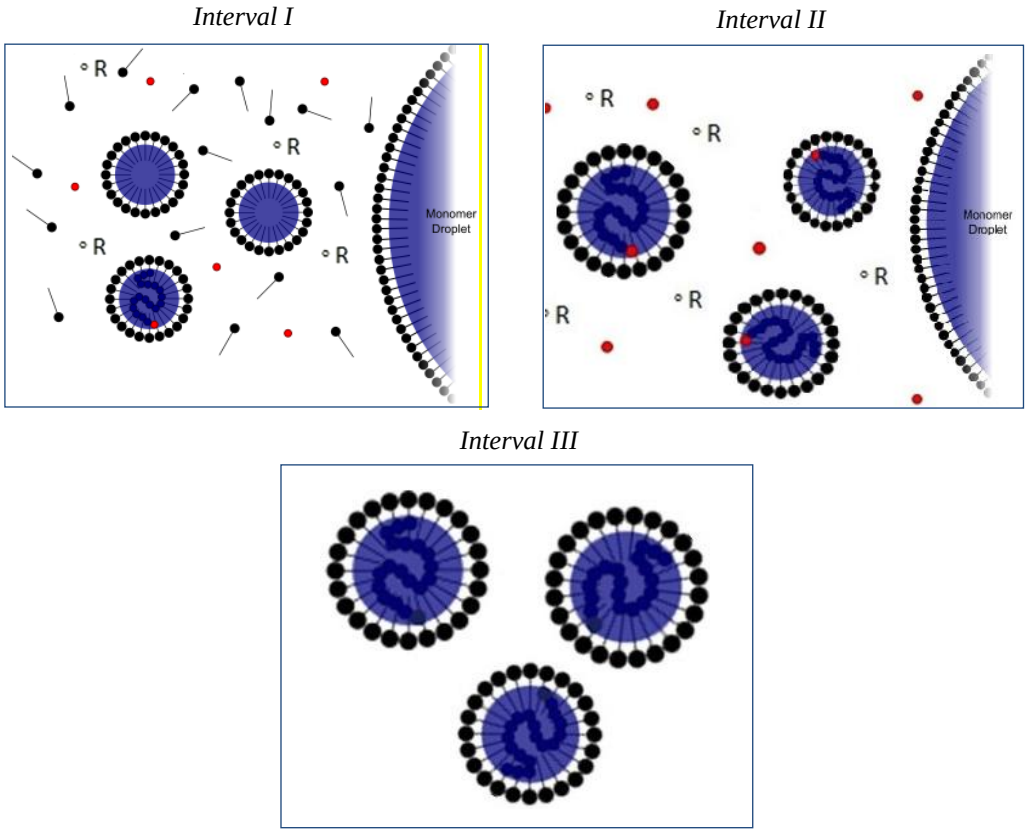

Figure 1.7. Schematic representation for mechanism of emulsion polymerization.

In the emulsion polymerization, there is a need for additional components as compared to solution polymerization. Beside water, stabilizers, chain transfer agents (CTAs), and buffers are a additional components [18].

1.6.2. Initiators

Radical mechanism constitutes the primary basis for the emulsion polymerization. The initiator is used for the generation of free radicals to lead the propagation of polymer molecules. There are two main ways to generate free radicals: thermal decomposition or redox reactions. Initiators can be water or oil-soluble. Water-soluble initiators are used in emulsion polymerizations whereas oil-soluble initiators generally are employed in organic solvent polymerizations. Sodium-, ammonium-, potassium-persulfates are the most used water soluble initiators (Figure 1.8). Persulfate ion gives two sulfate radical anions by the thermal decomposition, which are able to start polymerization. Hydrogen peroxide and other organic peroxides are other types of initiators that decompose thermally. The second type of initiators are redox initiators such as the persulfate-bisulfite system. Redox initiators generates free radicals through the reduction-oxidation reactions at low temperatures [15].

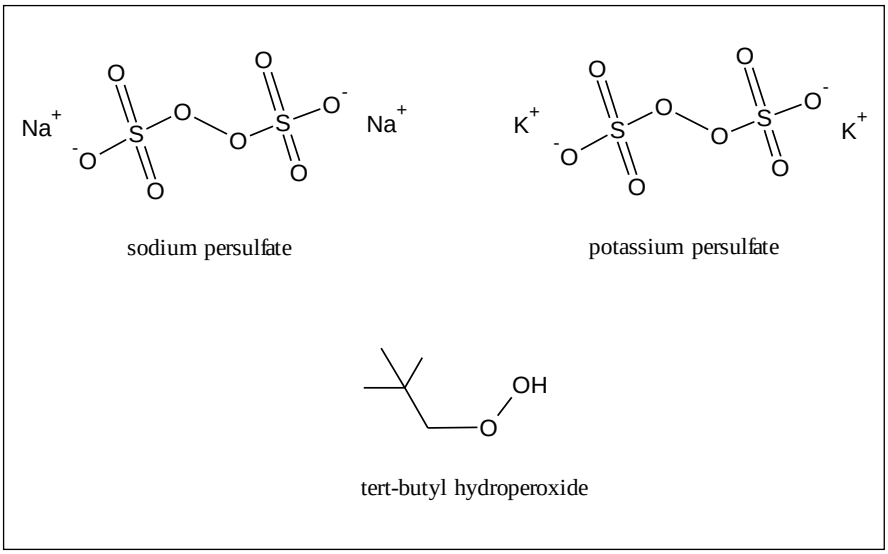

Figure 1.8. Structures of initiators [19].

1.6.3. Surfactants

Surfactants in emulsion polymerizations are employed because of their many important functions. They decrease the tension at the monomer-water interface, generate micelles, stabilize monomer droplets in water, solubilize monomer in micelles, enabling nucleation of particles, stabilize both the growing and final latex particles in water [15].

Surface activity is the main feature of surfactants which are also referred as emulsifiers, dispersing agents, soap, and detergents. These materials have two main parts one of which is a long chain hyrophobic group, and the other is a hyrophilic head group. Surfactants are generally categorized according to the water-soluble head group. They can be anionic, cationic, or non-ionic [15].

Anionic surfactants are the most prefered surfactants in emulsion polymerizations. They are sodium, ammonium, and potassium salts of fatty acids and sulfonated derivatives of aliphatic, arylaliphatic, or naphtenic compounds. Sodium dodecyl sulfate (SDS) is one of the most frequently used anionic surfactants (Figure 1.9). While the hydrophilic head group is responsible of pH dependant behavior and electrostatic stabilization, hyrophobic group is responsible of adsorption characteristics and steric stabilization of latex particle, critical micelle concentration (CMC) and interfacial tension [15,20].

Acetyl dimethyl benzyl ammonium chloride, hexadecyl trimethyl ammonium bromide quaternary salts can be given as examples for the cationic surfactants (Figure 1.9) [15].

Non-ionic surfactants have no charge on them and a head group of generally ethylene oxide units. Polyoxiethylenated alkylphenols, polyoxyethylenated polyoxypropylene glycols are some of the classes of nonionic surfactants (Figure 1.9). At high temperatures, these non-ionic surfactants have a tendency to aggregate. For this reason, they are not very efficient when used alone if the polymerization temperature is high. However they can be used effectively in combination with anionic surfactants [15,17].

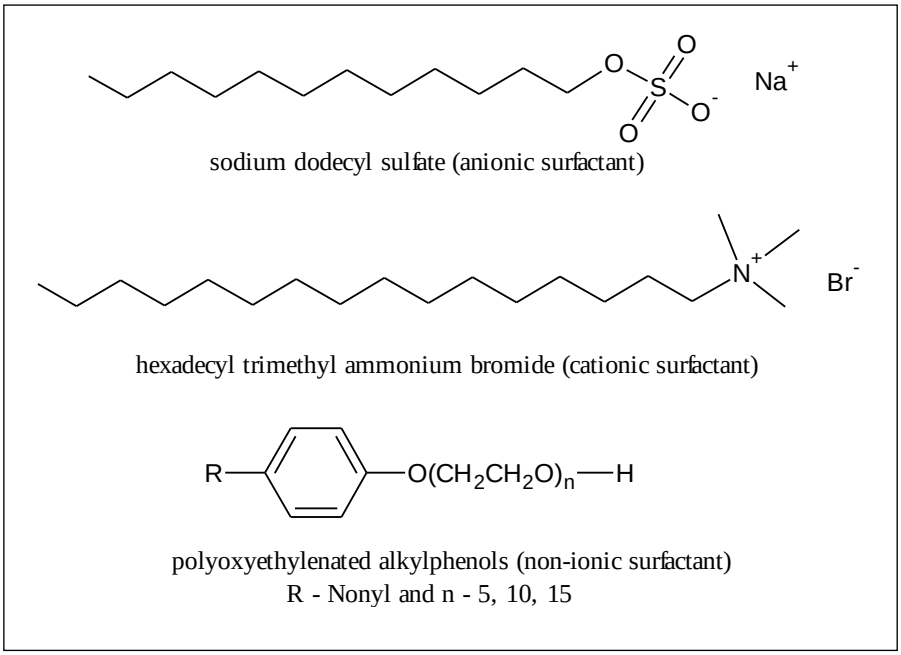

Figure 1.9. Structure of commonly used surfactants [19].

1.6.4. Other Ingredients

Emulsion polymerization formulations may contain a wide variety of additional ingredients.

One of these is chain transfer agents. These materials are added to the latex formulations to aid the adjustment of molar mass and molar mass distribution of latex polymer. Mercaptans such as dodecyl mercaptan are the most known type of CTAs. Also, surface active transfer agents called transurfs, are known to be used in emulsion polymerization formulations as CTAs [15].

Becides the components used during emulsion polymerization there are also other additives used as chemical finishings to tune the binder properties for a specific end-use. One component is buffers. The pH of the polymerization system is set by the addition of buffers to the formulation. Sodium bicarbonate is frequently used to form a buffer [15].

Defoamer is another additive. These materials are water dispersible and generally classified as silicone and non-silicone based. Defoamers can be added from %0.05 to %0.3 [1].

Catalysts are also utilized as chemical finishings. The primary function of catalysts is to assist the crosslinking in binder systems. They also decrease the crosslinking temperature and the curing time. So, they increase the performance of both binder and end-use product. Textile industry mostly uses acids and acid salts as catalysts. They are added to the binder system at concentrations ranging from 0.1% to 2% [1].

Other additives such as thickeners, flame reterdant salts, dyes, pigments, fillers, optical brighteners, and water repellents may also be included in the binder formulation. These can be added according to the desired performance of the finished product.

1.6.5. Film Formation

Emulsion polymers or latex dispersions are exposed to a drying process in applications such as paints, adhesives, textiles and nonwovens. The properties of dispersions are therefore important for the processing. It is the polymer film's properties that is significant for the final product and the polymer itself identifies these properties [5].

When a dispersion is placed on a flat substrate and evaporation process is allowed to take place, a continuous, coherent polymer film is generated. This operation is named as film formation. Film formation process involves three main stages: evaporation, deformation and coalescence. In the first stage, water evaporation takes place leading to particle packing. In the second stage, particles distort by generating a polyhedron structure. The polymer film becomes transparent at the end of this stage. However, film formation process is not finalized. Polymer film must proceed to third stage so that it can gain full mechanical strength. In this stage, membranes of surfactant between the particles are broken down and polymer particles diffuse into each other exceeding the borders (Figure 1.10) [21,22].

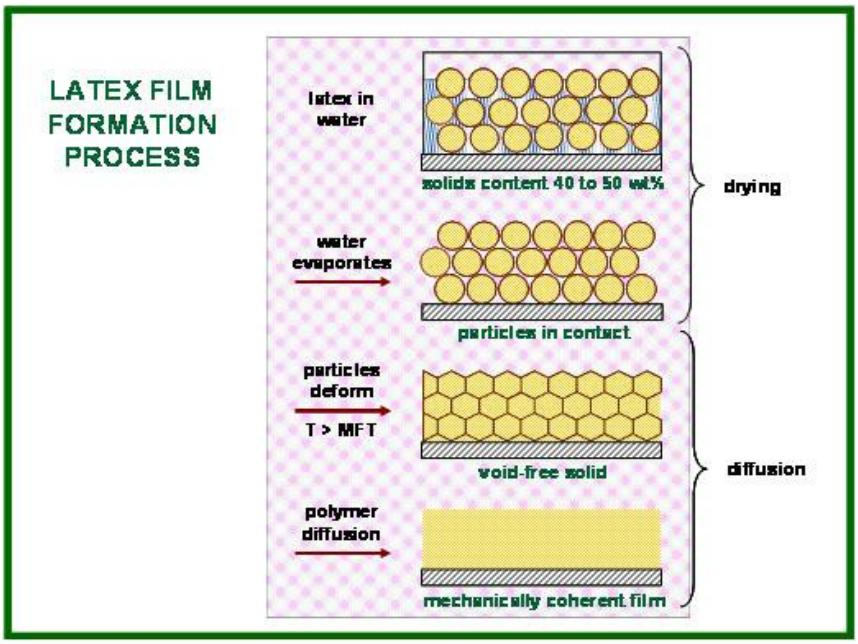

Figure 1.10. Schematic representation of film formation stages [23].

2. AIM OF THE STUDY

Binder manufacturers prefers to use self-crosslinking functionality in the emulsion polymers to produce durable textile products. One monomer used in textile industry for this purpose is *n*-methylol acrylamide (NMA). When NMA is exposed to heat for the crosslinking step, however, it generates formaldehyde which is a well-known toxic substance.

The aim of this study is to synthesize a novel crosslinking monomer for binder dispersions which will not emmit formaldehyde upon curing. This functional monomer will enhance the performance of textile products by reacting with the hydroxyl group of cellulose and by self-crosslinking without generation of formaldehyde (Figure 2.1). The toxicity of binder caused from formaldehyde will be eliminated by this way.

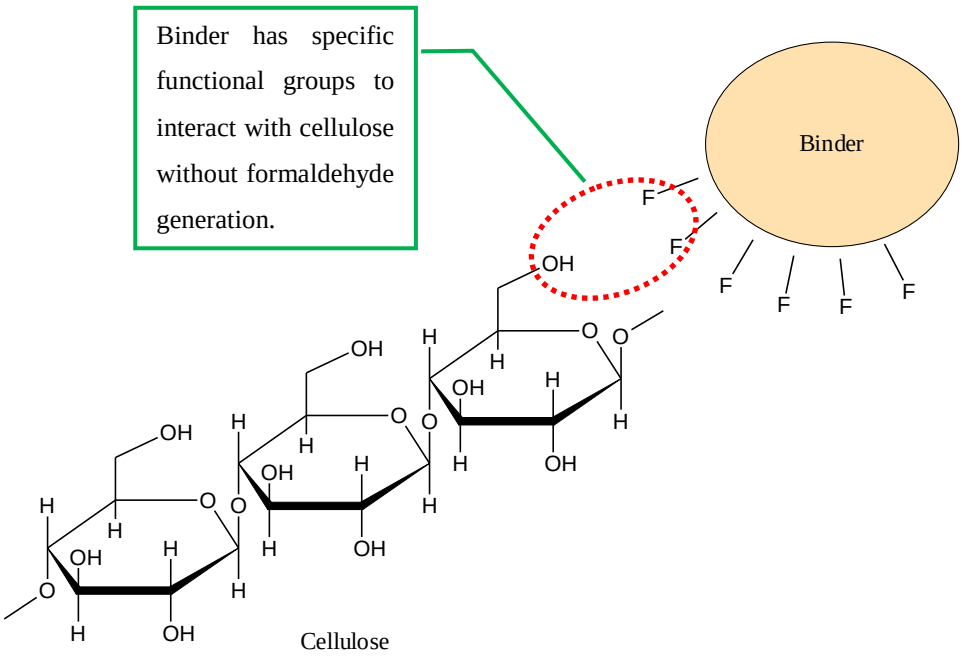

Figure 2.1. Schematic representation of binder interaction with cellulose.

3. EXPERIMENTAL

3.1. Methods and Materials

All chemicals used to synthesize the crosslinking monomer were used as received from the manufacturer (Merck, Aldrich). All chemicals used in the emulsion polymerization (Organik Kimya, Industrial Grade) were used without purification. Column chromatography was performed using silicagel-60 (43-60 nm). Thin layer chromatography was performed 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 recorded by using 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 spectras were recorded by Thermo Scientific Nicolet 380 FT-IR spectrometer.

3.2.1. Synthesis of Binders

Binder synthesis was carried out according to the recipes showed in the Table 3.1., Table 3.2., Table 3.3., and Table 3.4.

An automatic reactor which is equipped with a 2000 ml glass reaction container, a steel stirrer, and peristaltic feeding pumps was used in the synthesis. In the first stage, precharge was added into the glass reactor and heat was increased up to 82˚C. Then, pre-emulsion solution, which was prepared by separating 5% of E, and the initiation solution were put into the reactor respectively. The reaction was allowed to proceed about 10-15 minutes. After the preparation of white-yellowish pre-emulsions, E flow was started to feed the reaction for 2 hours with the help of peristaltic feeding pumps.

After feed was finalized, the reaction was let to progress for an additional 1 hour with stirring to raise the monomer conversion. In the last stage, polymerization reaction was finished with the addition of redox solution into the reaction medium to eliminate all remaining radicals and radicalic polymer chains.

After emulsion polymers were prepared, p-toluene sulfonic acid was added to the dispersions as its aqueous solution to evaluate the effect of acid catalyst on crosslinking.

Table 3.1. Recipes of binders that contain new crosslinking monomer as crosslinker.

	Recipe	Emulsion G0	Emulsion G2.5	Emulsion G5
Precharge	DiW (g)	120		
	SLS (%30) (g)	1.5		
	NS (%70) (g)	8		
	Na_2CO_3 (g)	0.8		
E*	DiW (g)	75		
	SLS (%30) (g)	4.3		
	NS (%70) (g)	24		
	BA (g)	120		
	MMA (g)	80		
	AA (g)	2		
	New Crosslinker (g)	-	5	10
Pre-emulsion		%5 of E		
Initiation	NaPS (g)	0.8		
	DiW (g)	10		
Redox	t-BHP (%70) (g)	0.3		
	DiW (g)	2.5		
	Bruggolite (g)	0.25		
	DiW (g)	2.5		

* E stands for Emulsion.

Table 3.2. Recipes of binders that contain new crosslinking monomer as crosslinker and p-toluenesulfonic acid as catalyst.

	Recipe	Emulsion G0P	Emulsion G2.5P	Emulsion G5P
Precharge	DiW (g)	120		
	SLS (%30) (g)	1.5		
	NS (%70) (g)	8		
	Na_2CO_3 (g)	0.8		
E*	DiW (g)	75		
	SLS (%30) (g)	4.3		
	NS (%70) (g)	24		
	BA (g)	120		
	MMA (g)	80		
	AA (g)	2		
	New Crosslinker (g)	-	5	10
Pre-emulsion		%5 of E		
Initiation	NaPS (g)	0.8		
	DiW (g)	10		
Redox	t-BHP (%70) (g)	0.3		
	DiW (g)	2.5		
	Bruggolite (g)	0.25		
	DiW (g)	2.5		
	p-Toluenesulfonic acid (g)	1% of solid content		

* E stands for Emulsion.

Table 3.3. Recipes of binders that contain NMA as crosslinker.

	Recipe	Emulsion N0	Emulsion N2.5	Emulsion N5
Precharge	DiW (g)	120		
	SLS (%30) (g)	1.5		
	NS (%70) (g)	8		
	Na_2CO_3 (g)	0.8		
E*	DiW (g)	75	60	45
	SLS (%30) (g)	4.3		
	NS (%70) (g)	24		
	BA (g)	120		
	MMA (g)	80		
	AA (g)	2		
	NMA (%25) (g)	-	10	20
Pre-emulsion		%5 of E		
Initiation	NaPS (g)	0.8		
	DiW (g)	10		
Redox	t-BHP (%70) (g)	0.3		
	DiW (g)	2.5		
	Bruggolite (g)	0.25		
	DiW (g)	2.5		

* E stands for Emulsion.

Table 3.4. Recipes of binders that contain NMA as crosslinker and p-toluenesulfonic acid as catalyst.

	Recipe	Emulsion N0P	Emulsion N2.5P	Emulsion N5P
Precharge	DiW (g)	120		
	SLS (%30) (g)	1.5		
	NS (%70) (g)	8		
	Na_2CO_3 (g)	0.8		
E*	DiW (g)	75	60	45
	SLS (%30) (g)	4.3		
	NS (%70) (g)	24		
	BA (g)	120		
	MMA (g)	80		
	AA (g)	2		
	NMA (%25) (g)	-	10	20
Pre-emulsion		%5 of E		
Initiation	NaPS (g)	0.8		
	DiW (g)	10		
Redox	t-BHP (%70) (g)	0.3		
	DiW (g)	2.5		
	Bruggolite (g)	0.25		
	DiW (g)	2.5		
	p-Toluenesulfonic acid (g)	1% of solid content		

* E stands for Emulsion.

3.2.2. Film Formation

After emulsion polymers were synthesized, film formation process was performed. Emulsion solutions were firstly diluted to 35% solid content. Then, diluted emulsions were poured into a mold as a thin layer. Polymer films were allowed to dry at room temperature for one week. In the first five days, films became all transparent, but they were allowed to dry for additional two days so that film formation was completed.

3.2.3. Percent Solubles and Swell Index Calculations on Polymer Films

1cm × 1cm shaped film samples were cut from dried films in changing amounts between 50 - 100 mg. These polymer samples were first cured in an oven at 160^{o}C for 3 and 10 minutes. After the curing step, all samples were weighed and then put into a jar. 100 ml acetone was added onto the samples and the cap of the jar was closed to prevent the solvent evaporation. Samples were incubated in acetone for 1 day. After 1 day, polymers soaked in acetone were briefly filtered and swollen weights were measured. These swollen polymer samples were allowed to stay at room temperature for a while and then redried in an oven at 150^{o}C for 10 minutes. Dried weights of polymer films after swell were also measured.

"Percent Solubles" and "Swell Index" values were calculated by placing all the recorded weights of polymers properly into the following equations:

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

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

All these film preparation, curing, swelling, and measurement steps were repeated as well at 180, 200, 220^{o}C and percent solubles and swell index values were calculated for all temperature values.

3.2.4. Free Formaldehyde Determination

Free formaldehyde determination of binder dispersions that contain crosslinker either NMA or new crosslinking monomer were done according to the ISO 15373:2001 Plastics-Polymer dispersions-Determination of free formaldehyde standard method.

4. RESULTS AND DISCUSSION

The purpose of this project was first to synthesize a novel crosslinker for textile binder dispersions which would not generate and emit formaldehyde during the curing process and then to investigate its performance in the binder polymers.

In the first stage of the study, synthesis of new formaldehyde-free crosslinker was performed. In order to verify the synthesis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy experiment data have been used.

In the second stage of the study, the use of synthesized new crosslinker in the binder dispersions and its performance evaluation was targeted. Therefore, emulsion polymerization of synthesized crosslinker in the presence of acrylic monomers, film formation, and performance test studies have been done.

Here, binder production with emulsion polymerization of acrylic monomers with synthesized new crosslinker, and the performance analysis of binder polymers will be discussed.

4.1. General Procedure for Synthesis of Binders

Polymer latexes were synthesized *via* emulsion polymerization of various acrylate monomers such as acrylic acid, methyl methacrylate, and butyl acrylate. Emulsions were synthesized including no crosslinker, new crosslinking monomer as crosslinker, and NMA respectively. Crosslinker containing emulsions were prepared including 1.4mole% and 2.7mole% NMA and 1.1mole% and 2.1mole% new crosslinker. Amount of monomers were chosen to obtain polymer latexes with desired physical and chemical properties. Solid content which is the weight ratio of monomers to the obtained polymer emulsions, particle size, free monomer, viscosity, and pH of emulsion polymers are shown in Table 4.1.

Table 4.1. General properties of synthesized emulsion polymers.

Emulsions	XL*	XL amount, mole%**	XL amount, mmol	Solid Content, wt%	Particle Size (nm)	Viscosity (cps)	pH
N2.5	NMA	1.4	25	47.1	133	680 (LVT3/60)	4.49
N5	NMA	2.7	50	47.4	210	6750(LVT3/60)	4.6
N2.5P* **	NMA	1.4	25	47.6	133	680 (LVT3/60)	~ 3
N5P* **	NMA	2.7	50	47.9	210	6750(LVT3/60)	~ 3
N0	-	0	0	46.1	103	45 (LVT2/60)	5.52
N0P* **	-	0	0	46.6	103	45 (LVT2/60)	~ 3
G2.5	New crosslinker	1.1	20	47.2	108	55 (LVT2/60)	5.44
G5	New crosslinker	2.1	40	48.1	113	60 (LVT2/60)	5.4
G2.5P* **	New crosslinker	1.1	20	47.7	108	55 (LVT2/60)	~ 3
G5P* **	New crosslinker	2.1	40	48.6	113	60 (LVT2/60)	~ 3

* XL stands for Crosslinker.

** Mole percent values were calculated according to the total monomer moles, other ingredients are not included.

*** The letter “P” stands for the emulsions that contain p-toluenesulfonic acid as the catalyst.

4.2. Determination of the Crosslinking Temperature

Percent solubles and swell index tests are done to measure a binder’s ability to crosslink. Crosslinking behavior of binders at different temperatures are examined with the help of these tests and from the results, crosslinking temperature of a crosslinker to be used in textile industry is determined.

Percent solubles and swell index values which are calculated by using Equation 3.1 and Equation 3.2 at various temperatures, curing temperatures and cure times are listed in the Table 4.2. Percent solubles *versus* temperature and swell index *versus* temperature graphs were drawn to better see the crosslinking behavior of binders.

According to the graphs, 10 minute cures give better results than 3 minute for the binders containing 1.1mole% new crosslinking monomer as crosslinker (Figure 4.1 and 4.2). Percent solubles value of emulsion G2.5P is better than G2.5's. This indicates that acid catalyzes the crosslinking reaction. Although percent solubles value decreases as temperature increases, which shows better crosslinking, it is not as good as the one with NMA (Figure 4.1). Similar observations were made for the swell index values (Figure 4.2).

For the binders containing 2.1mole% new crosslinking monomer as crosslinker, the results are better. Because the acid catalyst eases the crosslinking reaction, G5P has lower percent solubles and swell index values than G5. In the case of percent solubles, 10 minute cure is better than 3 minute. For the 3 minute cure, G5P reaches a good value of percent solubles after 180°C. But for the 10 minute cure, G5P reaches a very good value at 160°C and shows similar results for higher temperatures (Figure 4.3). Swell index value shows a decrease as temperature rises for 3 minute cures while it is steady for 10 minute cures (Figure 4.4).

From these results, it can be said that synthesized new crosslinking monomer shows very similar properties to the NMA's when it is used 2.1mole% in the presence of an acid catalyst and is cured for 10 minutes. Therefore, crosslinking temperature of new crosslinker can be stated as 160°C under these conditions.

Table 4.2. Percent solubles and swell index values.

Emulsions	% Solubles		Swell Index	
	3 min	10 min	3 min	10 min
160°C				
N5P	10.66	12.19	4.10	3.87
N5	15.88	14.27	4.87	4.50
N2.5P	16.61	14.84	5.88	6.29
N2.5	20.27	18.04	7.27	6.82
N0P	100	100	∞	∞
N0	44.34	43.61	21.02	19.90
G5P	28.22	15.53	12.52	8.72
G5	100	100	∞	∞
G2.5P	63.58	28.51	∞	13.52
G2.5	65.33	55.44	∞	30.77
180°C				
N5P	10.11	11.53	3.70	3.70
N5	13.83	15.75	4.48	4.57
N2.5P	14.03	14.39	5.50	5.79
N2.5	18.38	18.53	7.02	7.03
N0P	100	60.64	∞	∞
N0	43.49	41.30	18.90	17.53
G5P	14.98	11.39	8.53	7.37
G5	89.5	51.98	∞	31.94
G2.5P	36.89	24.10	19.01	14.04
G2.5	61.29	38.57	∞	29.49
200°C				
N5P	12.80	16.64	4.00	4.46
N5	16.86	19.83	4.56	4.93
N2.5P	21.76	22.39	6.85	7.44
N2.5	20.18	20.17	7.46	7.93
N0P	100	67.59	∞	∞
N0	48.43	46.66	37.45	46.66
G5P	15.20	12.94	8.93	8.51
G5	69.39	45.93	∞	24.70
G2.5P	34.32	21.75	15.94	12.76
G2.5	61.17	34.43	∞	26.00
220°C				
N5P	14.51	19.61	3.87	4.64
N5	19.81	20.44	4.61	4.89
N2.5P	25.24	26.40	7.37	7.88
N2.5	24.59	25.11	7.46	7.37
N0P	100	100	∞	∞
N0	69.71	71.63	∞	∞
G5P	17.19	9.49	9.53	7.02
G5	62.85	32.47	20.69	19.87
G2.5P	32.24	18.67	18.48	11.85
G2.5	58.81	33.94	21.11	22.65

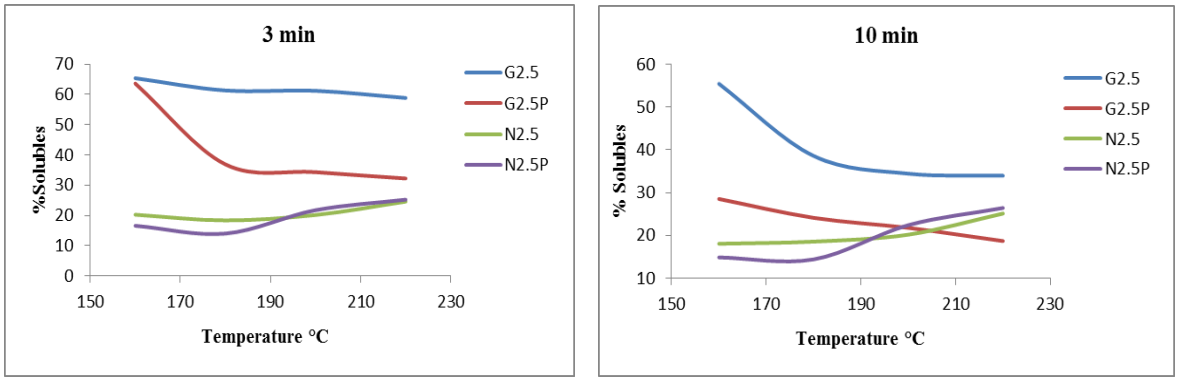

Figure 4.1 Percent solubles *versus* temperature graphs.

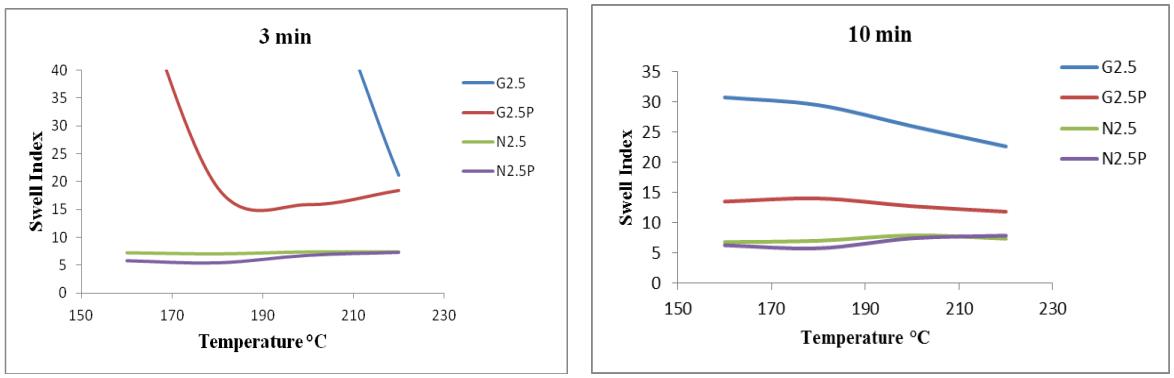

Figure 4.2 Swell index *versus* temperature graphs.

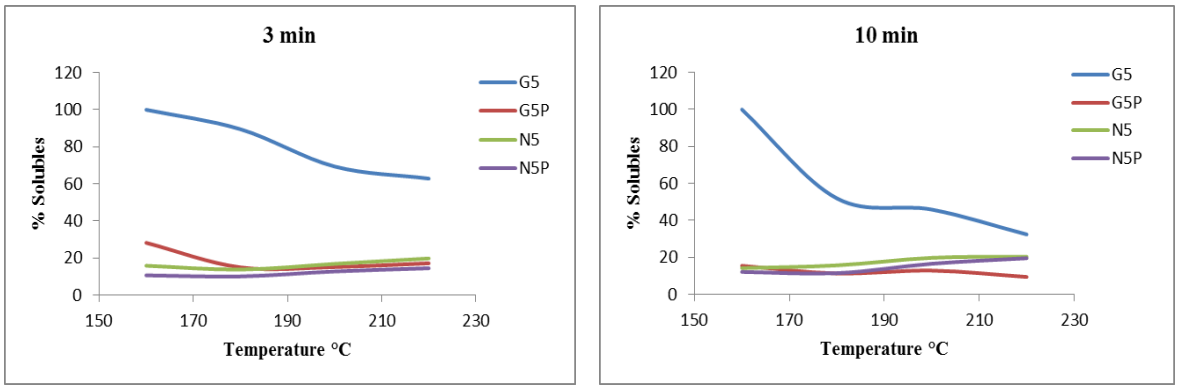

Figure 4.3 Percent solubles *versus* temperature graphs.

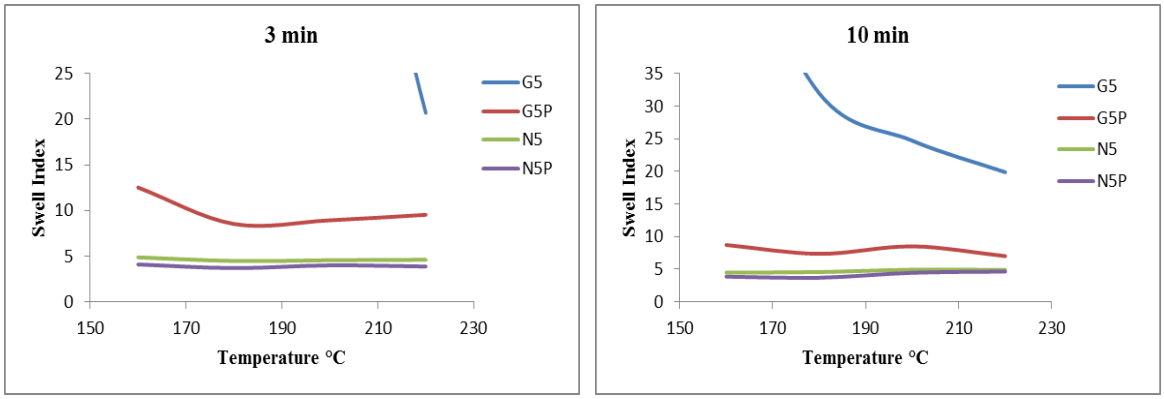

Figure 4.4 Swell index versus temperature graphs.

4.3. Determination of Free Formaldehyde in Binders.

Determination of free formaldehyde was done for the binders containing crosslinkers NMA and compound 5. As can be seen from Table 4.3, no free formaldehyde was observed in the binders containing new crosslinker.

Table 4.3. Formaldehyde levels in binders.

Emulsions	**N2.5**	**N5**	**G2.5**	**G5**
Formaldehyde(ppm)	265	405	n.d*	n.d

* n.d. non-detectable corresponds to a value less than 16 ppm which is the detection limit.

5. FUTURE WORK

As a future work, elemental analysis of synthesized crosslinker will be done. Also, application of the binder on the cellulosic and nonwoven substrates and performance evaluation with dry and wet strength tests will be performed.

6. CONCLUSIONS

In this study, a formaldehyde-free crosslinker that can be used instead of NMA in textile industry was synthesized and its performance evaluation was done in comparison with NMA.

In the first step of this study, formaldehyde-free crosslinker was successfully synthesized and transformations were verified with FT-IR and NMR spectrums. In the second step, binder dispersions were synthesized *via* emulsion polymerization in the presence of the synthesized new crosslinker. Percent solubles and swell index test were carried out after the curing process and results were compared with the NMA's.

As a result, it is observed that the synthesized crosslinker shows similar properties to NMA containing systems when used with an acid catalyst and the curing time is set to 10 minutes. Moreover, free formaldehyde determination test showed that binders containing the synthesized new crosslinker do not release any formaldehyde unlike NMA.

REFERENCES

1. Turbak, A. F., T. L. Vigo, *Nonwovens An Advanced Tutorial*, Tappi Press, Atlanta, 1989.

2. Albrecht, W., H. Fuchs, W. Kittelmann, *Nonwoven Fabrics*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.

3. Batra, S. K., F. L. Cook, B. Goswami, E. Vaughn, L. G. Wadsworth, W. K. Walsh, *Nonwoven Fabrics Handbook*, INDA Association of the Nonwoven Fabrics Industry, North Carolina, 1999.

4. Kamath, M. G., A. Dahiya, R. R. Hegde, *Chemical Bonding*, 2004, http://www.engr.utk.edu/mse/Textiles/Chemical%20Bonding.htm, accessed at January 2014.

5. Urban, D., K. Takamura, *Polymer Dispersions and Their Industrial Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2002.

6. Hutton, T. W. and R. W. Novak, "Low-Formaldehyde, Self-Crosslinking Polymer Latex Composition", US Patent, 5,143,954, 1992.

7. Guillaume, T., B. Boutevin, B. Ameduri, "Chemical Reactions of Polymer Crosslinking and Post-Crosslinking at Room and Medium Temperature", *Progress in Polymer Science*, Vol. 36, pp 191-217, 2011.

8. Salthammer, T., S. Mentese, R. Marutzky, "Formaldehyde in the Indoor Environment", *Chemical Reviews*, Vol. 110, pp 2536-2572, 2010.

9. *Formaldehyde in Textiles,* Cotton Incorporated, North Carolina, 2007.

10. *Public Health Statement for Formaldehyde,* 2008, http://www.atsdr.cdc.gov/ToxProfiles/tp111-c1-b.pdf, accessed at January 2014.

11. *Report on Carcinogens,* 2011, http://ntp.niehs.nih.gov/ntp/roc/twelfth/profiles/Formaldehyde.pdf, accessed at January 2014.

12. *OEKO-TEX® Standard 100*, https://www.oeko-tex.com/en/manufacturers/concept/oeko_tex_standard_100/oeko_tex_standard_100.xhtml, accessed at January 2014.

13. *Limit values and fastness,* https://www.oeko-tex.com/en/manufacturers/test_criteria/limit_values/limit_values.html, accessed at January 2014.

14. Basant, T., A. Rani, *Eco Analysis of Textiles to Determine Formaldehyde*, 2013, http://www.indiantextilejournal.com/articles/FAdetails.asp?id=5181, accessed at January 2014.

15. Yamak, H. B., *Emulsion Polymerization: Effects of Polymerization Variables on the Properties of Vinyl Acetate Based Emulsion Polymers*, 2013, http://www.intechopen.com/books/polymer-science/emulsion-polymerization-effects-of-polymerization-variables-on-the-properties-of-vinyl-acetate-based, accessed at January 2014.

16. Chern, C., *Principles and Applications of Emulsion Polymerization*, 1st edition, John Wiley & Sons, Inc., New Jersey, 2008.

17. Chern, C. S., “Emulsion Polymerization Mechanism and Kinetics”, *Progress in Polymer Science*, Vol. 31, pp 443-486, 2006.

18. Herk, A., *Chemistry and Technlogy of Emulsion Polymerization*, 1st edition, Blackwell Publishing Ltd., UK, 2005.

19. Yıldırım, İ., *Synthesis of Novel Pressure Sensitive Adhesives by Emulsion Polymerization Technique*, M.S. Thesis, Boğaziçi University, 2013.

20. Wang, Q., S. Fu, T. Yu, “Emulsion Polymerization”, *Progress in Polymer Science*, Vol. 19, pp 703-753, 1994.

21. Keddie, J. L., “Film Formation of Latex”, *Material Science and Engineering*, Vol. 21, pp 101-170, 1997.

22. Turshatov, A., J. Adams, D. Johannsmann, “Interparticle Contact in Drying Polymer Dispersions Probed by Time Resolved Fluorescence”, *Macromolecules*, Vol. 41, pp 5365-5372, 2008.

23. *Latex Films: Film Formation from Polymer Nanoparticles,* http://www.chem.utoronto.ca/staff/MAW/research_past.htm, accessed at January 2014.