SYNTHESES OF NOVEL ACETAL-BASED FORMALDEHYDE-FREE CROSSLINKERS

by

Şule Nihal Öz

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APPROVED BY:

Assoc. Prof. A. Ersin Acar …….
(Thesis Supervisor)

Assist. Prof. Fırat İlker …….

Assist. Prof. Safacan Kölemen …….

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Anneme ve Babama ...

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ABSTRACT

SYNTHESES OF NOVEL ACETAL-BASED FORMALDEHYDE-FREE CROSSLINKERS

Crosslinking of polymers is a fundamental process applied in industry to enhance mechanical and physical properties of polymeric materials. Wide variety of crosslinkers are available to be used for this purpose whose structures depend on functionalities of the polymers and desired characteristics of the products.

Crosslinkers can be in the form of polymeric or small molecule. As polymeric crosslinkers, formaldehyde based resins and latex binders may be given as examples of commonly used ones in coatings, adhesives and textile. *N*-Methylol acrylamide is one of the most commonly used monomer in latex binder composition to have crosslinkable system since it has good chemical, physical properties and self-crosslinking ability. However, it emits formaldehyde to the environment during the handling and crosslinking reaction as a side product. Formaldehyde based resins also release formaldehyde by degradation or during condensation as a side product. Formaldehyde is known as a human carcinogen compound and is harmful to the human health and the environment. Therefore there is a general tendency to limit or completely eliminate formaldehyde based chemical goods.

Previous studies performed in our research group involved the syntheses of novel formaldehyde-free crosslinkers that are free radically polymerizable and their incorporation into latex binders by incorporating them into the polymer chains. This manuscript focuses on the synthesis of new formaldehyde-free crosslinkers in the form of small molecules. New crosslinkers will contain cyclic acetals as functional groups and have *tetra*- or *tri*- functional analogues. They will be used to crosslink $–NH_2$ and -OH containing polymer chains through trans-acetalization reactions, and their crosslinking ability at different temperatures will be investigated.

ÖZET

FORMALDEHİT İÇERMEYEN, ASETAL BAZLI ÇAPRAZ BAĞLAYICI SENTEZİ

Polimer zincirlerinin çapraz bağlanması, endüstride polimerlerin mekanik ve fiziksel özelliklerini güçlendirmek amacıyla uygulanan önemli bir işlemdir. Polimer zincirleri üzerindeki fonksiyonel gruplara, ve bitmiş ürünün istenen özelliklerine göre değişecek şekilde çok sayıda çeşitli çapraz bağlayıcı kullanılmaktadır.

Çapraz bağlayıcılar büyük, polimerik yapılar veya küçük moleküller şeklinde bulunabilir. Formaldehit bazlı reçineler ve lateks, kaplama, yapıştırıcı ve tekstilde yaygın olarak kullanılan polimerik yapıdaki çapraz bağlayıcılara örnek olarak verilebilir. *N*-metilolakrilamit (NMA) molekülü, yüksek kimyasal ve fiziksel özellikleri ve kendi kendine çapraz bağlama özelliğinden dolayı, lateks bağlayıcılarda en yaygın olarak kullanılan monomerdir. Fakat NMA molekülü bağlama reaksiyonu sonucunda veya ürünün işlenmesi sırasında etrafa yan ürün olarak formaldehit salınımı yapar. Formaldehit, kanserojen olarak bilinen, hem insan sağlığı hem de çevre için zararlı olan bir maddedir. Bu sebeple, formaldehit bazlı kimyasal ürünlerin kullanımını azaltmak veya bitirmek üzere genel bir yönelim oluşmuş durumdadır.

Araştırma grubumuzda önceden yürütülmüş olan projelerde, serbest radikal polimerleşmesi ile polimerleşebilir, yeni, formaldehit içermeyen çapraz bağlayıcıların sentezi, ve bu çapraz bağlayıcıları polimer zincirlerine ekleyerek lateks bağlayıcı sisteminin hazırlanması üzerine çalışmalar yapılmıştır. Bu çalışmada da formaldehit içermeyen yeni çapraz bağlayıcı sentezi üzerine çalışılmıştır, fakat öncekilerden farklı olarak, çapraz bağlayıcılar küçük moleküllerdir. Bu moleküller, üç veya dört fonksiyonel grupludur ve fonksiyonel grup olarak halkalı asetaller içerir. Sentezlenen çapraz bağlayıcılar -NH_2 ve -OH gruplarını içeren polimer zincirlerini transasetalizasyon reaksiyonu ile bağlamak amacıyla kullanılacak, ve farklı sıcaklıklardaki bağlama güçleri kıyaslanacaktır.

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LIST OF ACRONYMS/ABBREVIATIONS

$CDCl_3$	Deuterated Chloroform
C	Carbon
DHP	Dihydropyran
DCC	Dicyclohexylcarbodiimide
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
DMF	Dimethyl formamide
DSC	Differential Scanning Calorimetry
H	Hydrogen
Et_3N	Triethylamine
EtOAc	Ethyl Acetate
EtOH	Ethanol
HMM	Hexamethylol Melamine
HEMA	Hydroxyethylmethacrylate
IR	Infrared
K_2CO_3	Potassium Carbonate
MDI	Methylene Diphenyl Diisocyanate
MF	Melamine-Formaldehyde
NMR	Nuclear Magnetic Resonance

NMA	*N*-methylol acrylamide
$NaBH_4$	Sodium Borohydride
NaOH	Sodium Hydroxide
p-TsOH	Para-Toluene Sulfonic Acid
polyHEMA	Poly(hydroxyethylmethacrylate)
RT	Room Temperature
TEA	Triethyl amine
T_g	Glass Transition Temperature
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TGIC	Triglycidil Isocyanurate
Xlinker	Crosslinker
HSQC	Heteronuclear Single Quantum Coherence
ΔG	Gibbs Free Energy

1. INTRODUCTION

1.1. Crosslinking of Polymers

1.1.1. General Definition of Crosslinking

Crosslinking is making a polymer network in which polymer chains are connected to each other from several intersection points. This improves some of the polymer's mechanical and physical properties such as stiffness, impact resistance, solvent and heat resistance, and tensile strength. Basic representation of uncrosslinked polymer chains and crosslinked polymer network is shown in Figure 1.1 [1].

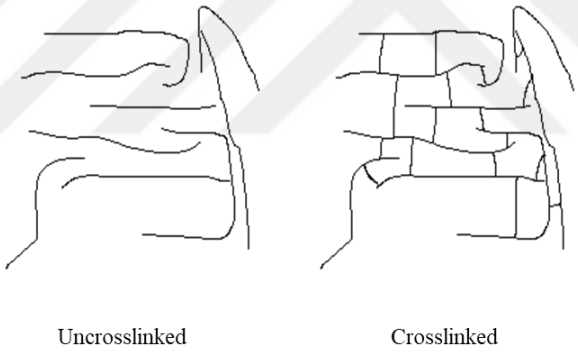


Figure 1.1. Schematic representation of uncrosslinked and crosslinked polymer chains [2].

Crosslinking of a polymer network can be analysed by observing the changes in some physical properties of the polymer such as tensile strength, hardness, solubility and swelling property and glass transition temperatures (T_g) [3]. This study will include observation of the change in glass transition temperature and calculation of swelling index in order to analyse crosslinking efficiency.

Glass transition temperature is the temperature where the mobility of amorphous part of the polymer changes. Below the glass transition temperature, amorphous polymer chains will lose their mobility and the polymer will be in a solid, glassy state. When the polymer is

heated and the glass transition temperature is reached, amorphous polymer chains will start to move and over this temperature the polymer will be softer and in a rubber-like state [4]. Since crosslinking restrict the free motion of the polymer chains by connecting them together, the T_g will be higher for the crosslinked polymer. As the crosslinking density increase in the polymer network, T_g will also increase. However, this phenomena may change after a point because when the crosslinker ratio is too much, it starts to change the structure of the polymer as it copolymerized with the polymer chain. Beside the increasing effect of crosslinking on T_g, copolymerizing may both increase or decrease the T_g depending on the structure. [5].

Swelling index is a parameter which indicates the amount of solvent that a crosslinked polymer absorbed. While a polymer can dissolve in a solvent, it may not be soluble in that solvent when it is crosslinked, instead, it will behave as hydrogel and will swell by absorbing the solvent. As the crosslinking density increases, the amount of absorbed solvent decreases [5].

1.1.2. Methods for Crosslinking

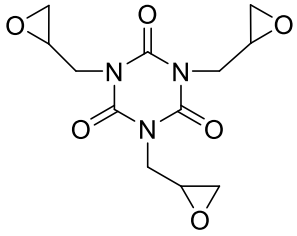
Crosslinking may occur during chain growth or step growth polymerization, or after the polymerization is completed. In chain growth polymerization, linear polymers are generally formed from monomers having one vinyl group. When a small amount of monomers having two polymerizable vinyl groups are added to the reaction, crosslinked polymer network may be formed [1]. In step-growth polymerization, polymers are formed by condensation reactions of difunctional monomers. Addition of small amount of *tri-* or *multi-* functional monomers produces crosslinked polymer network. The process where polymer chains are crosslinked once the polymerization is complete is called post-crosslinking. In post-crosslinking of polymers, either functional groups on chains can be reacted with each other, or an external crosslinker having two or more functionality is reacted with the functional groups present on the chains to form a crosslinked network [1][6].

1.2. Types of Crosslinkers

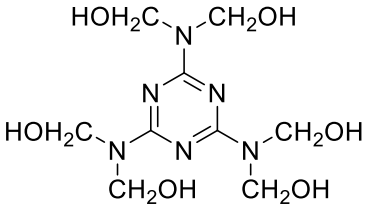
Although there are different ways of classifying crosslinkers we will divide them into two subgroups; crosslinkers can be small molecules or polymer based molecules. Polymer chains that will be crosslinked should have reactive functional groups such as hydroxyl, amine, carboxylic acid, epoxy, isocyanate, etc., that are capable of giving reactions with the crosslinker [7]. Triglycidyl isocyanate (TGIC) and hexamethylol melamine (HMM) may be given as examples of small crosslinker molecules [8]. Polymer based crosslinkers are bigger molecules having crosslinkable functional groups and polyaziridines, polyisocyanates, melamine-formaldehyde and urea-formaldehyde resins, and latex binders maybe given as examples [9][10].

1.2.1. Small Molecule Crosslinkers

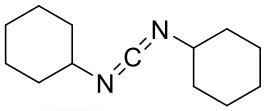
Polymers that contain functional groups such as hydroxyl, carboxyl, epoxy or amide are crosslinkable with a crosslinker molecule having two or more functional groups. Crosslinking reaction between polymer chains and crosslinkers occurs upon heating, or by using a suitable catalyst [1]. Commonly used crosslinkers generally have isocyanate, epoxy, carbodiimide, aldehyde, methylol functionalities [8]. They may be used in different applications such as coatings, films, textile finishings, self-healing polymers, and also in peptide synthesis and crosslinking of polymers. Figure 1.2 shows some examples of the most common crosslinkers for various applications,triglycidyl isocyanate (TGIC) commonly used in polyester crosslinking, hexamethylol melamine (HMM), bis(4-isocyanatophenyl)methane (MDI) which are used in crosslinking of polyols, and dicyclohexylcarbodiimide (DCC) commonly used in crosslinking of carboxylic acids. [11][12].



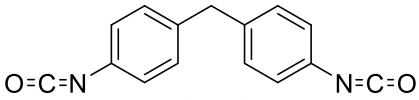
TGIC (epoxy functionality)



HMM (methylol functionality)



DCC (carbodiimide functionality)



MDI (isocyanate functionality)

Figure 1.2. Structures of crosslinkers with different functionalities.

1.2.2. Polymer Based Crosslinkers

There are large variety of polymer based crosslinkers for different applications, but in this part, formaldehyde containing or releasing crosslinkers will be addressed. This type of crosslinkers are polymeric resins such as melamine-formaldehyde, urea formaldehyde, phenol-formaldehyde, and *N*-methylol functional latex binders. Formaldehyde based resins are able to crosslink with a polymer chain having carboxylic acid, hydroxyl or amine functionality. The crosslinking reaction of melamine-formaldehyde resin with an amide functional polymer is shown in Figure 1.3. These resins are commonly used in adhesives, coatings and chemical binders [13][14].

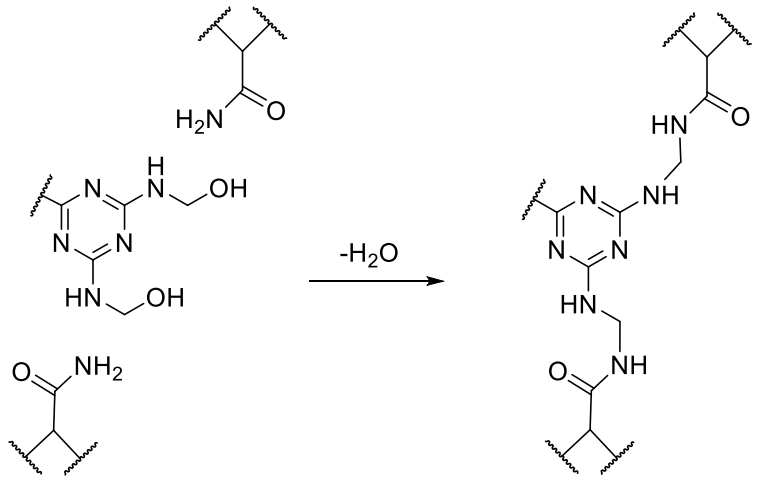


Figure 1.3. Crosslinking reaction mechanism of the amide functional polymer chains with melamine-formaldehyde resin [10].

The problem with using these resins as crosslinkers is the unwanted release of formaldehyde. During the processing of these resins, formaldehyde may be released because of the degradation of the resins, or condensation reaction between the methylol groups. Representative emission mechanism of formaldehyde from melamine-formaldehyde resin is given in Figure 1.4 [13][14].

Polymeric crosslinkers may also be in the form of emulsion in which organic phase of the emulsion is the crosslinking polymer in which at least one monomer with crosslinkable functional groups is present. Such systems are often called latex binders [15].

Latex binders are commonly used in coatings, adhesives and textile binders. It is an aqueous dispersion media formed by emulsion polymerization, in which binder polymer particles exist as surface active agent stabilized particles [15]. Latex binders are commonly preferred for chemical bonding because of their essential advantages. They can be easily applied since it is in aqueous media and the viscosity is very close to water. Other advantage is that it is possible to reach high molecular weight and give the material toughness. They are also economical, and lastly they are versatile materials [16].

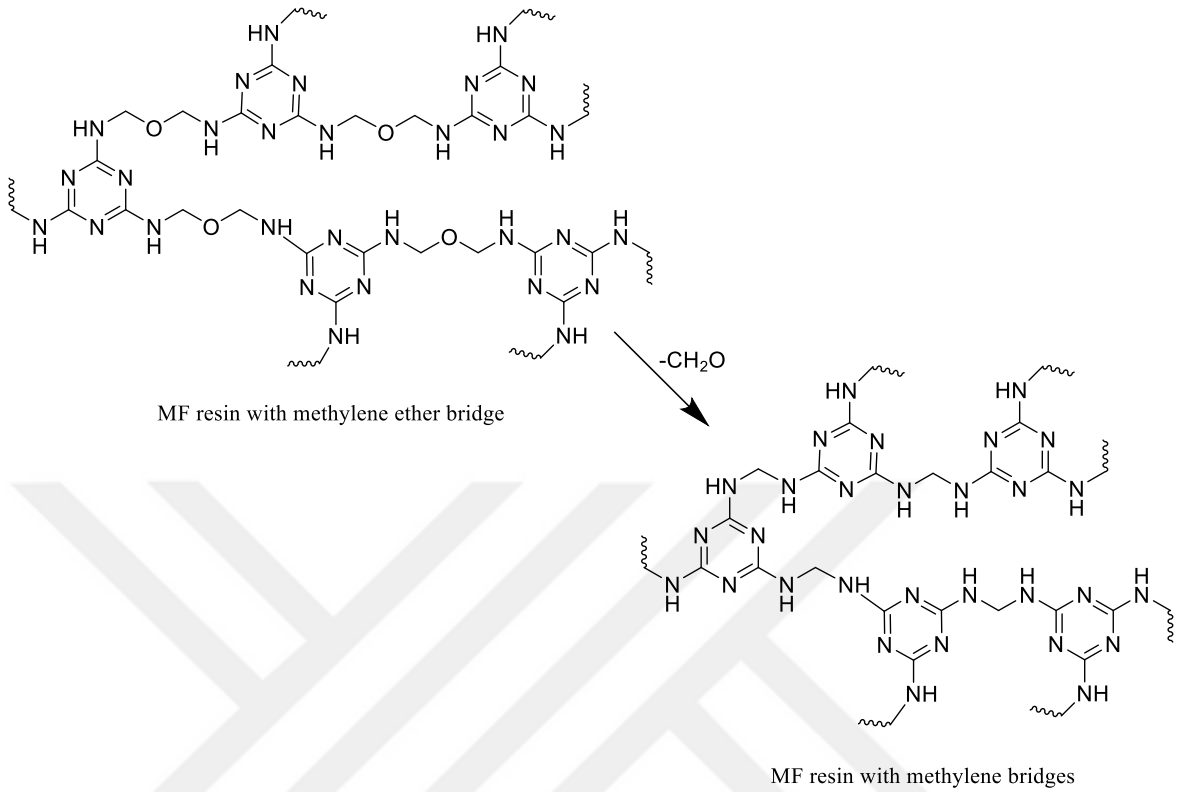


Figure 1.4. Formaldehyde emission of melamine-formaldehyde resin [14].

Versatility of the latex binders comes from their flexible composition. They can have several properties depending on three main factors; monomer type –vinyl acetate, styrene, acrylic, butadiene, etc.- that is used in polymer chain, functional groups –acrylamide, acrylic acid, *N*-methylol acrylamide, etc.- of polymer and other additives added to the latex formulation. Characteristics of the monomer used in polymer backbone affects durability, elasticity and strength of the material. The functional groups present determine the crosslinking, adhesion and solvent resistance. Other additives are added to the composition such as lubricants, dyestuff, water repellents etc.., to increase the performance and versatility [10][17].

Latex polymers may contain crosslinkable functional groups such as carboxylic acid, amide, hydroxyl or epoxy, and crosslinking occur by the reaction with an external crosslinker. On the other hand, they may have *N*-methylol functionality which has self-crosslinking ability, and crosslinking occurs upon heating. One of the most commonly used

molecule that is incorporated in latex polymer is *N*-methylol acrylamide [18] which often contains equimolar of free acrylamide monomer when commercially supplied.

N-methylolacrylamide is a well-known functional monomer which can be incorporated into a polymer chain by its ethylenically unsaturated carbons. It has self-crosslinking ability when it is heated to high temperatures (>140 ^{o}C). Addition of an acid catalyst such as paratoluene sulfonic acid can decrease the temperature needed for crosslinking [8]. Besides its self-crosslinking ability, *N*-methylolacrylamide increase the tensile strength, chemical and solvent resistance, peel strength and abrasion strength of the binder. Therefore it is commonly used in binder composition to achieve a self-crosslinking system. The crosslinking mechanism of *N*-methylol acrylamide incorporated polymers is shown in Figure 1.5. However, a side reaction may occur during the self-crosslinking reaction of *N*-methylol acrylamide and this side reaction results with the release of formaldehyde, a toxic chemical. The side reaction is given in Figure 1.6 [19].

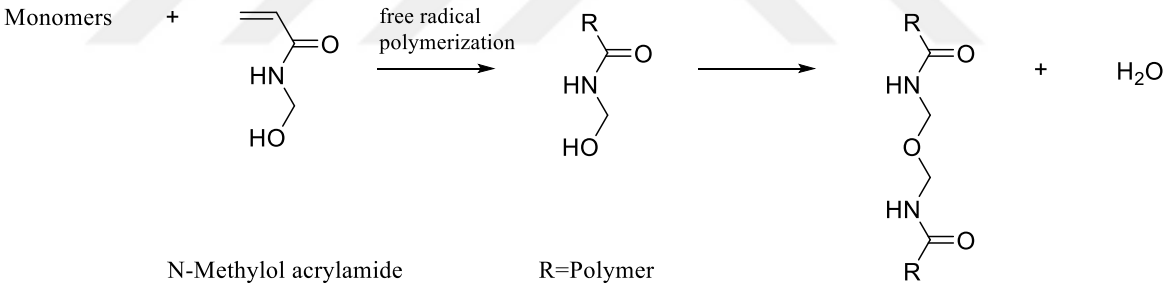


Figure 1.5. The mechanism of self-crosslinking reaction of *N*-methylol acrylamide incorporated polymers [20].

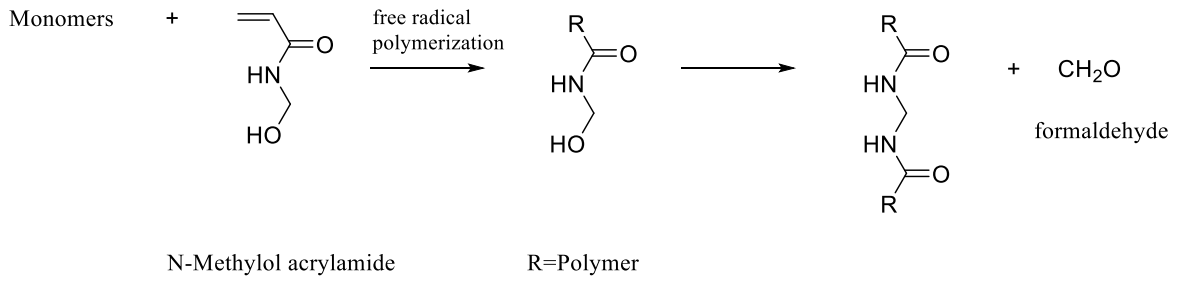


Figure 1.6. Side reaction during the crosslinking of *N*-methylol acrylamide incorporated polymers [20].

1.3. Formaldehyde Emission upon Crosslinking

Release of formaldehyde is a general result of employing *N*-methylol acrylamide functional latex binders or formaldehyde based resins for crosslinking. In formaldehyde based resins, methylene ether bridges (forming *N*,*O*-acetal groups in the structure) exist as seen in the Figure 1.4. Likewise, same bridges exist in the crosslinked network of *N*-methylol acrylamide containing polymers. These methylene ether linkages are unstable at high temperatures and they are transformed into methylene bridges (forming *N*,*N*-acetal groups), which are stable up to 350 ^{o}C, by eliminating formaldehyde [21][22].

Formaldehyde is a volatile chemical that one can be exposed to it by inhalation or skin contact, and this may cause damages to skin or to the respiratory system. According to U.S. Department of Health and Human Services, the World Health Organization and Environmental Protection Agency, long time inhalation of formaldehyde may also cause cancer. Because of these negative effects of formaldehyde on human health, many researches have been done to reduce or eliminate the formaldehyde emission during or after crosslinking [23][24].

One way that companies employed to reduce the formaldehyde level was using formaldehyde scavenging molecules in the binder composition (US5160503, US5112652, EP0488605). Enzymes were used to reduce the formaldehyde level (EP2239322). Many other studies discloses the preparation of alternative binder systems and crosslinking molecules to eliminate or reduce the formaldehyde emission. US4449978 discloses the synthesis of a new binder copolymer for nonwoven fiber bonding by replacing some of the

N-methylol acrylamide groups by acrylamide groups, so that the amount of *N*-methylol groups which are capable of releasing formaldehyde by condensation will decrease and free formaldehyde level will also decrease correspondingly. US5021529 describes the method to decrease formaldehyde emission by incorporating self-crosslinkable monomers into polymer chain such as *N*-ethylol acrylamide, *N*-propylol acrylamide, *N*-benzylol acrylamide groups, whose formaldehyde release are much lower than *N*-methylol acrylamide. US5258477 involves the use of acetal and aldehyde functional polymers as binders. Various other researches and experiments were done and still continues in this field [25][26].

1.4. Previous Studies in Our Research Laboratory

Our research group worked on the synthesis of novel crosslinkers that may be incorporated into polymer chains and will not release formaldehyde upon crosslinking. These monomers have unsaturated groups to incorporate into polymers, and a cyclic acetal or cyclic *N,O*-acetal as crosslinkable groups. General structures of the synthesized crosslinkers are given in Figure 1.7 and Figure 1.8.

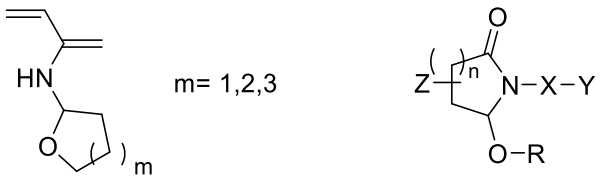
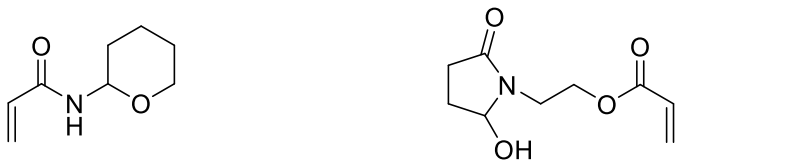


Figure 1.7. General structures of previously synthesized formaldehyde-free crosslinkers containing *N,O*-acetal groups [27] [28].



N-(2-tetrahydropyranyl)acrylamide

2-(2-hydroxy-5-oxopyrrolidin-1-yl)ethyl acrylate

Figure 1.8. Examples of previously synthesized formaldehyde-free crosslinkers.

Upon heating, or by addition of an acid catalyst, crosslinking occurs through the acetal ring opening. Representation of the crosslinking reaction between the acetal containing polymer chain and a hydroxyl containing surface is given in Figure 1.9.

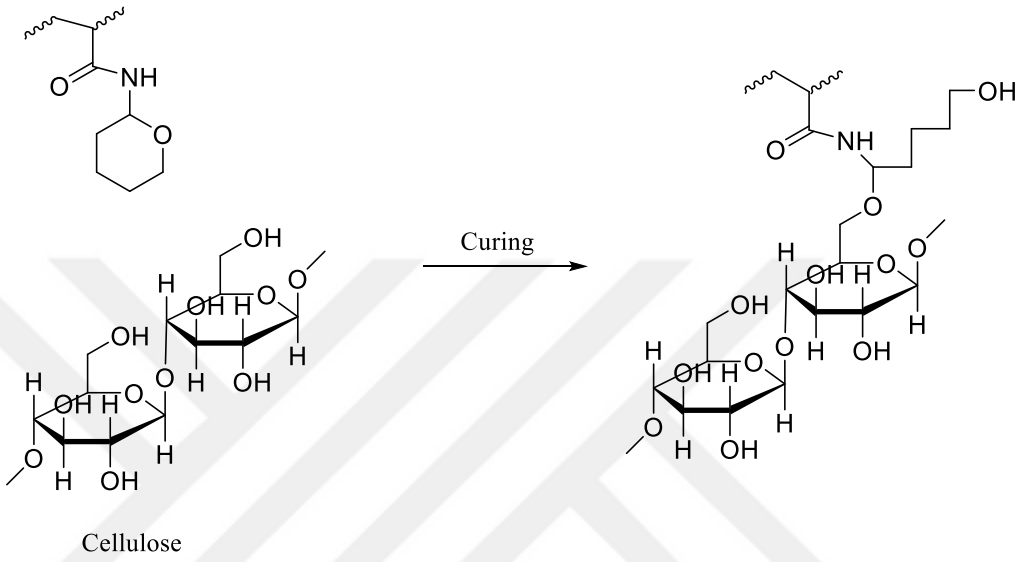


Figure 1.9. Possible curing reaction of monomers containing *N,O*-acetal group bonded to tetrahydropyranyl ring [28].

In that point, it would be helpful to consider acetal stability for better understanding the formaldehyde release of polymeric crosslinkers and also the crosslinking mechanism of these cyclic acetal based crosslinkers.

1.5. Stability of Acetals

Acetals are compounds with a carbon atom substituted with two –OR groups (*O,O*-acetal), or one –OR and one $–NR_2$ group (*N,O*-acetal), or two $–NR_2$ groups (aminal). Among these compounds, aminal derivatives are the most stable ones, followed by *N,O*-acetals then *O,O*-acetals. Cyclic form of these acetals are also more stable than their acyclic derivatives [29][30]. Representation of the acetal compounds in the order of increasing stability is given in Figure 1.10.

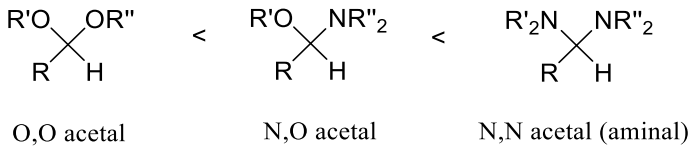


Figure 1.10. Increasing order of acetal stability.

Acetals may undergo transacetalization to form a more stable acetal when a suitable compound exist in the media. For instance, an *O,O*-acetal undergoes transacetalization if a bulkier alcohol exist, since the acetal stability increases as the size of R groups increase [31]. Basic representation of transacetalization of acetal is given in Figure 1.11.

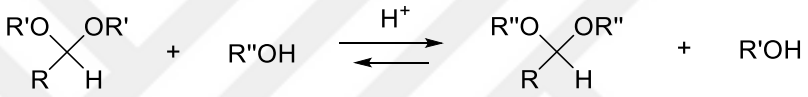


Figure 1.11. Representation of transacetalization reaction.

When the mechanisms of formaldehyde release from melamine-formaldehyde resin or *N*-Methylol acrylamide containing crosslinked polymers are considered, it can be seen that before the formaldehyde release, compounds have *N,O*-acetal groups, and formaldehyde is released by the formation of *N,N*-acetal, which is more stable. Similarly, the efficiency of the crosslinking of previously synthesized crosslinkers shown in Figure 1.8 is based on the acetal stability. As shown in Figure 1.9., cyclic *N,O*-acetal containing crosslinker forms an *N,O*-acetal with a much bulkier group at the end of the reaction, which favors the crosslinking.

This study also focuses on the synthesis of novel crosslinkers which will not release formaldehyde upon crosslinking or after crosslinking.

2. AIM OF THE STUDY

In the industry, polymer crosslinking is essential since it provides to the polymeric material important features as strength, durability and resistance. In this study, the aim was to synthesize novel small molecule crosslinkers which contain cyclic acetal as functional group. The crosslinking is expected to occur through the ring opening/transacetalization mechanism where no formaldehyde will be released during the process.

Previous researches in our group focused on the synthesis of free radically polymerizable formaldehyde free crosslinkers. In those studies, cyclic acetal containing monomers were synthesized and they were incorporated into polymer chains. Polymeric crosslinkers were used for crosslinking. In this study, synthesized compounds will have *tri-* or *tetra-* functional small molecules and will be used for crosslinking of polymers, through the formation of a more stable acetal at the end.

The synthesized molecules will be tested for their crosslinking abilities upon reactions with various –OH and $–NH_2$ functional polymers. The extent of crosslinking will be analyzed by swelling tests and by glass transition temperature measurements.

The target crosslinkers and their potential crosslinking mechanism is given in Figures 2.1-2.4.

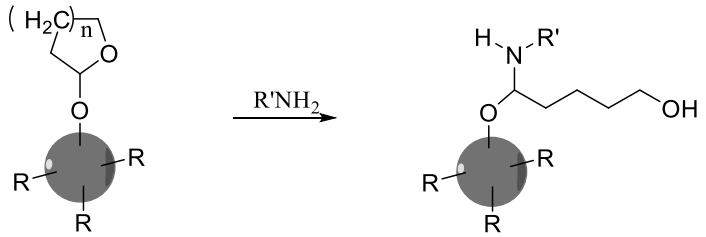


Figure 2.1. Schematic representation of crosslinking of cyclic acetal through the ring opening.

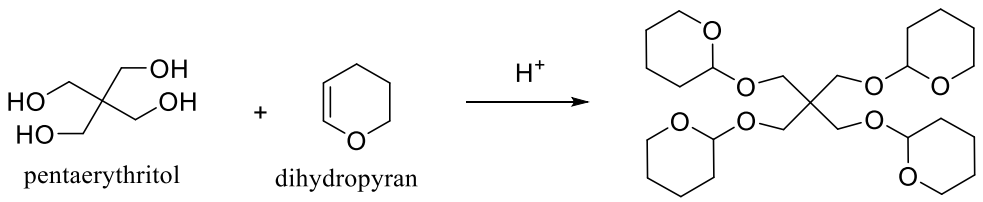


Figure 2.2. The reaction scheme of pentaerythritol with dihydropyran.

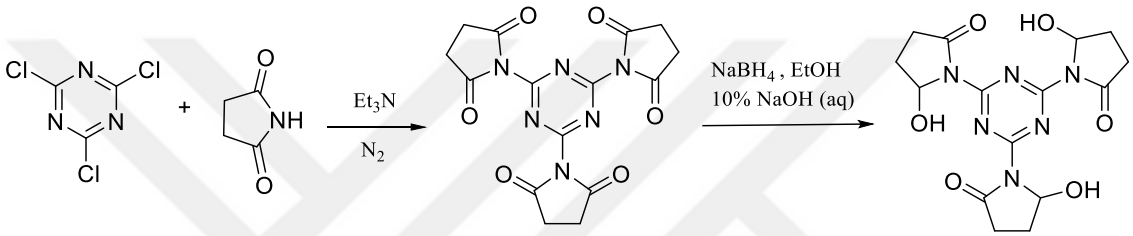


Figure 2.3. The reaction scheme of synthesis and reduction of 2,4,6-tris(succinimido)-1,3,5-triazine.

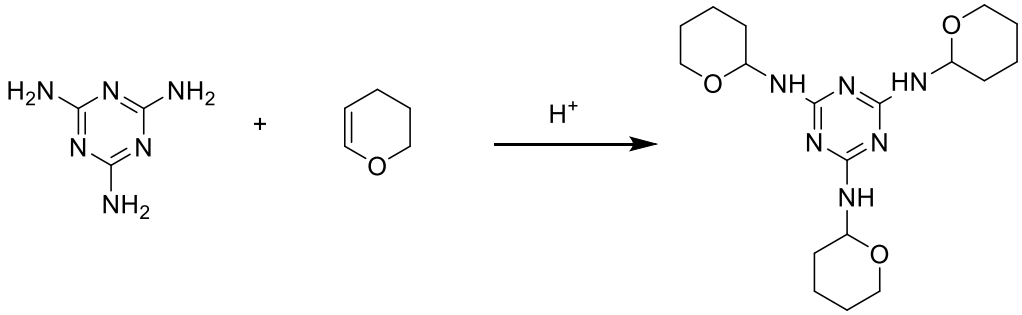


Figure 2.4. The reaction scheme of melamine with dihydropyran.

3. EXPERIMENTAL

3.1. Methods and Materials

Chemicals used for the crosslinker synthesis were purchased from Merck, Aldrich, Fluka and Acros Organics. Polymers used for crosslinking were obtained from Uras Kimya and Akkim. Column chromatography for purification were done by using aluminium oxide 90 active basic (0.063-0.200 mm). Thin layer chromatography were performed by using TLC plates with Silica gel 60 F_{254} and aluminium oxide 60 F_{254}.

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 at the Advanced Technologies Research and Development Center at Boğaziçi University and Bruker 400 MHz Ultrashiet spectrometer at Chemistry Department at Boğaziçi University. Mass analysis were performed with Shimadzu UFCL system. Glass transition temperature measurements were done with Exstar DSC 7020.

3.3. Synthesis of the Crosslinkers

3.3.1. Tetrahydropyranylation of Pentaerythritol

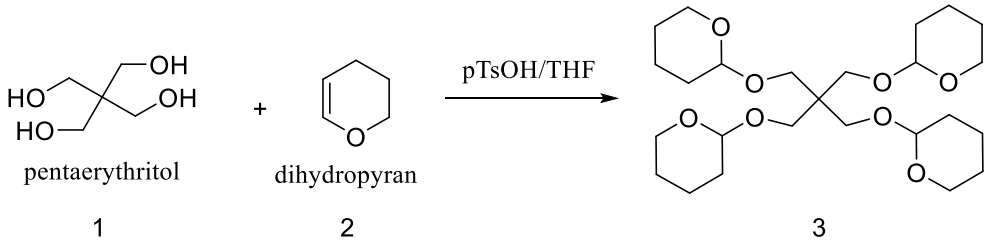


Figure 3.1. Synthesis of 2,2,2-tetrakis(2'-tetrahydropyranyloxymethyl)methane.

Pentaerythritol (2.00 gr, 14.7 mmol) in 40 mL dry THF was heated to 35° C. Then the suspension was cooled to room temperature and excess dihydropyran (5.26 gr, 62.5 mmol) was added to the suspension with stirring. Once the addition of dihydropyran was complete, p-toluenesulfonic acid monohydrate (0.025 gr, 0.131 mmol) was added as catalyst. Suspension was stirred at room temperature for 72 hours and a clear viscous solution was obtained at the end. The reaction was completed by the neutralization of the acid with triethylamine (0.25 mL). After neutralization was complete, THF was evaporated and the product was extracted with DCM (70 mL x 3) and distilled water (70 mL). Organic layer was collected and dried over anhydrous K_2CO_3, filtered, and DCM was evaporated. Purification of the product was performed in basic aluminium oxide eluting with 9,5:05 hexane:ethyl acetate mixture at the beginning and continuing with 9:1 hexane:ethyl acetate ratio. *Tetra*- functional product was obtained separately at the end of the column, proved by ^{1}H NMR and ^{13}C NMR spectrums. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.42–1.86 (m, 24H), 3.40 (ddd, 8H), 3.74–3.92 (m, 2H), 4.59 (dt, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$), δ: 98.81 (O-<u>C</u>H-O), 66.68 (O-<u>C</u>H_2-C), 61.29 (CH_2-<u>C</u>H_2-O), 44.45-44.10 (CH_2-<u>C</u>-CH_2), 30.52 (CH_2-<u>C</u>H_2-CH), 25.58 (CH_2-<u>C</u>H_2-CH_2), 19.05 (CH_2-<u>C</u>H_2-CH_2).

3.3.2. Synthesis and Reduction of 2,4,6-tris(succinimido)-1,3,5-triazine

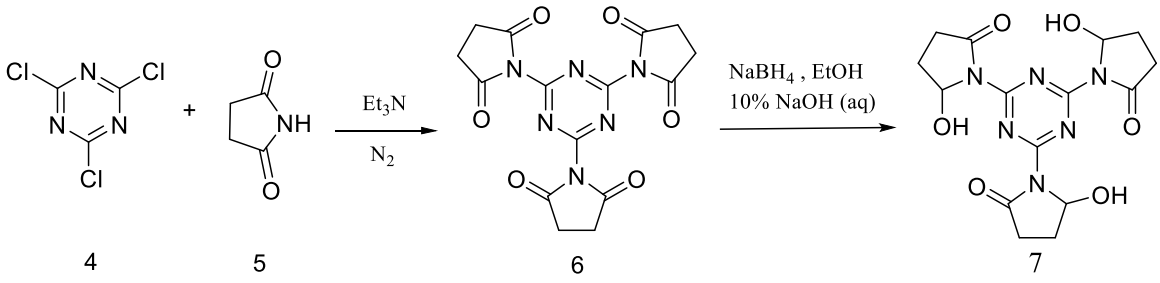
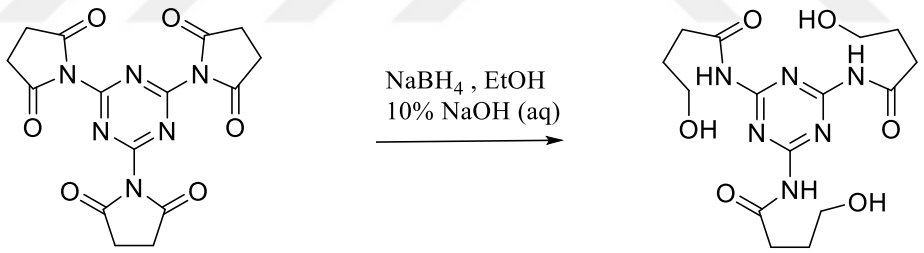


Figure 3.2. Synthesis and proposed reduction scheme of 2,4,6-tris(succinimido)-1,3,5-triazine.

Synthesis of 2,4,6-tris(succinimido)-1,3,5-triazine **(6)** were done according to the literature (US5807929). After synthesis of compound **6**, it was reduced by using $NaBH_4$. Compound **6** in 25mL ethanol was cooled to -10°C with an ice bath. $NaBH_4$ in 10 mL ethanol was added dropwise. After the addition was complete, the reaction mixture was allowed to

stir overnight at room temperature. When a completely clear viscous liquid formed, reaction mixture was quenched with 10% aqueous NaOH solution. Then solvent was evaporated and the solid was washed with water, ethanol and ethyl acetate. Synthesis of 2,4,6-tris(succinimido)-1,3,5-triazine and expected reduction reaction of it is shown in Figure 3.2.

However, according to NMR analysis, ring cleavage occurred at the end of the reduction, as shown in Figure 3.3. The product is highly polar, and insoluble in organic solvents. The product and impurities are both water soluble. Therefore, it was hard to purify the crude compound. Organic soluble impurities were removed by extraction with EtOAc many times, but highly polar impurities could not be totally removed. Complete purification of the compound could not be achieved. Synthesis of the compound was proven by the consistent NMR peaks. **^{1}H NMR** (400 MHz, CD_3OD, ppm) δ: 4.54 (3H, OH, s), 3.57 (t, CH_2-C$\underline{H_2}$-OH, 6H), 2.26-2.21 (t, CH_2-C$\underline{H_2}$-CO, 6H), 1.84-1.77 (m, CH_2-C$\underline{H_2}$-CH_2, 6H). **^{13}C NMR** (400 MHz, CD_3OH, ppm), δ: 181.24 (NH-$\underline{C}$O-CH_2), 159.92 (N=$\underline{C}$), 61.84 (CH_2-$\underline{C}H_2$-OH), 34.51 (CO-$\underline{C}H_2$-CH_2), 29.02 (CH_2-$\underline{C}H_2$-CH_2).



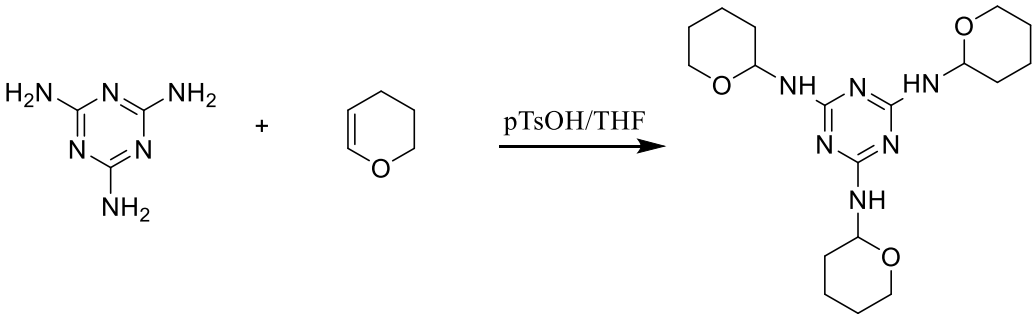
6 8

Figure 3.3. Observed reaction mechanism for the reduction of compound **6**.

3.3.3. Tetrahydropyranylation of Melamine

Tetrahydropyranylation reaction of melamine were performed in the same way with tetrahydropyranylation of pentaerythritol, and were repeated at RT, 40^{o} C and 60^{o} C separately. After 72 hr stirring, reaction medium was neutralized with TEA and then THF was evaporated. Crude material was poured into water and extracted with DCM 3 times. DCM phases were collected and solvent was evaporated. NMR analysis were done without further purification to see if acetal was formed or not. ^{1}H NMR results proved the acetal

formation for all three cases. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ: 5.56 – 5.45 (m, 1H), 4.06 – 3.86 (m, 2H), 2.12 – 1.57 (m, 6H).



9 2 10

Figure 3.4. Proposed reaction for tetrahydropyranylation of melamine.

3.4. Film Formation

Three different polymers were used to obtain films for swelling tests. These polymers had mainly acrylate functionality on the chains. Additionaly, one of them had 3% acrylamide groups, the other one had 3% hema groups, and the last one had no acrylamide and hema groups.

Polymers was in the form 45% aqueous solutions, and solutions was mixed with the crosslinker **(3)** with 50% ratio according to amount of hema and acrylamide functional groups, and with p-TsOH as catalyst. For the blank polymer, same amount of crosslinker **(3)** was used with the one for hema functional polymer. Polymers were also mixed with teraphtalaldehyde in order to compare the result with a known crosslinker. Mixtures was poured into aluminium plates by arranging the thickness of the film to 1mm after drying, by taking 7 gr into an aluminium plate of diameter 6 cm. Then, they were dried at room temperature during 5 days and dried films were cut into small squares with 1 cm side length.

3.5. Curing and Swelling of Polymer Films

Polymer films were cured at 110 ºC, 120 ºC, 150 ºC, 180 ºC and 200 ºC separately for 5 and 10 minutes. After curing, the weight of dry films were measured. Then, films were allowed to wait in 50 mL acetone for 24 hours, and the weight of swollen films were measured. Swelling indexes of the polymer films were calculated according to the equation 3.1.

$$Swelling\ Index = \frac{sample\ weight\ swollen\ in\ acetone}{original\ sample\ weight} \qquad (3.1)$$

3.6. Glass Transition Temperature (T_g) Analysis

In order to observe the shifts in glass transition temperature upon crosslinking, a polymer with 100% acrylamide functionality was used. Polymer was in the form of 40% aqueous solution. The solution was mixed with crosslinker in the amount of 30% with respect to the mole of acrylamide functional groups and with p-TsOH as catalyst. Polymer mixtures with no crosslinker and with crosslinker were cured at 120 ºC, 150 ºC and 190 ºC for 5, 10 and 30 min. separately. Samples were put in vacuum oven for complete removal of water. T_g analysis were done by using differential scanning calorimety (DSC) by using approximately 4 mg samples placed into small aluminium pans. The tests were performed under nitrogen atmosphere by applying the following method; first heated at a rate of 10 ºC/min from -20 ºC to 200 ºC, waited for 1 min at 200 ºC, then cooled at a rate of 10 ºC/min from 200 ºC to -20 ºC, waited for 2 min at -20 ºC, finally heated at a rate of 10 ºC/min from -20 ºC to 200 ºC.

4. RESULTS AND DISCUSSION

In this study, the aim was to synthesize small molecule crosslinkers which will have cyclic *N,O*- or *O,O*-acetal groups with at least three functionality. Polymeric form of this type of crosslinkers were synthesized previously in our research group [27][28][32] . The idea behind the current study is to investigate whether or not the small molecule forms of cyclic acetal based crosslinkers are efficient in crosslinking $–NH_2$ and -OH functional polymers. Hema containing polymer was used for –OH functionality and acrylamide containing polymers were used for $-NH_2$ functionality.

During this study, three different syntheses were performed to obtain three different crosslinkers, two of them were triazine based molecules which contains *N,O*-acetals, and one of them was pentaerythritol based molecule which contains *O,O*-acetals. The idea was to use *N,O*-acetal containing molecules to build a crosslinked polymer network through the formation of *N,N*-acetals, which is a more stable acetal, similarly, using *O,O*-acetal containing molecule to form a network through the formation of *N,O*-acetal.

In this section, firstly, the synthesis of pentaerythritol based cyclic *O,O*-acetal containing crosslinker, and its curing processes with different polymer solutions at different temperatures will be presented. Then, crosslinking analysis will be discussed in detail with the results of swelling tests and T_g measurements. In the last part, the syntheses of triazine based crosslinkers will be discussed.

4.1. Synthesis and Curing Studies of Cyclic *O,O*-Acetal Containing Crosslinker

4.1.1. Synthesis of 2,2,2,2-tetrakis(2'-Tetrahydropyranyloxymethyl)methane

Tetra-functional crosslinker **(3)** was synthesized successfully (Figure 4.1) by the reaction of DHP with pentaerythritol and obtained purely as confirmed by ^{1}H-NMR, ^{13}C-NMR and mass spectrometry (Data given in section 3.3.1.). *Tri-* , *di-* and *mono-* substituted

products may also be formed at the end of the reaction, however, only tetrafunctional product was isolated and used for crosslinking. The pure product was obtained in 32.4% yield.

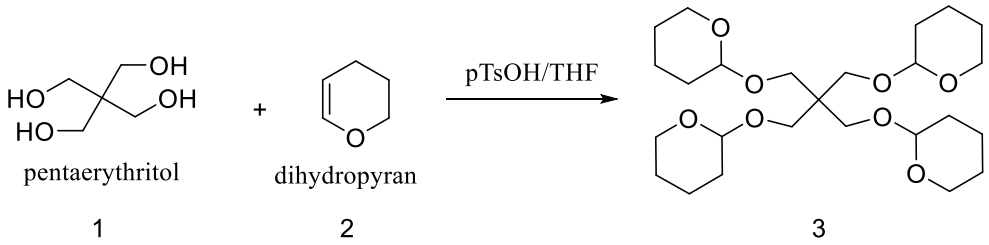


Figure 4.1. Synthesis of 2,2,2,2-tetrakis(2'-Tetrahydropyranyloxymethyl)methane.

4.1.2. Formation of Crosslinked Polymer Network

The formation of crosslinked network with the polymers depends on the stability of acetals that will be formed at the end of the crosslinking reaction. The idea is that if the acetals that are formed upon crosslinking reaction are thermodynamically more stable than the initial acetal, the crosslinking will be favored and a stable network will be formed. In the present case, cyclic *O,O*-acetal containing crosslinker was employed to cure polyacrylamide and poly(HEMA). In principle, with the former, *N,O*-acetals should be formed at the end of the reaction, which are known to be more stable than the *O,O*-acetal. Therefore, a stable crosslinking network upon curing with the amide containing polymers was expected. The target structure of the crosslinked network of polyacrylamide with tetra-functional crosslinker is given in Figure 4.2.

On the other hand, the crosslinking with poly(HEMA) is questionable since the stability of acetals are not easily comparable. With poly(HEMA), *O,O*-acetal will be formed at the end. It is not more stable than the cyclic *O,O*-acetal when acetal stability is considered. However, it will be bonded to a bulkier group, which can make the acetal more stable sterically. In order to see if this factor will be efficient enough for crosslinking, crosslinking experiments were also done by using poly(HEMA). The results are discussed in the next section.

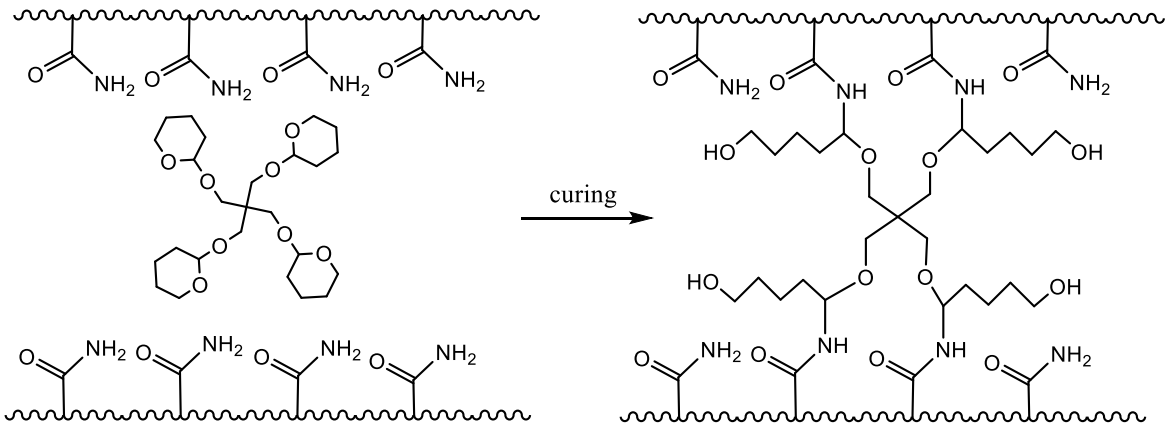


Figure 4.2. Proposed crosslinked network formed by the reaction of polyacrylamide with the *O,O*-acetal containing crosslinker.

4.1.3. Preparation and Curing of Polymers Films for Swelling Tests

In order to analyze the efficiency of the crosslinking, swelling tests were performed on comparative three polymer films. First was a blank polymer solution (contains no –OH or $–NH_2$ functionality), the second one was a polymer solution containing hydroxyethylmethacrylate (hema) functional groups, and the last one was a polymer solution containing acrylamide as functional groups.

By using these polymers, 3 different types of polymers films for each one were prepared. Films were prepared without adding any crosslinker, by adding the synthesized crosslinker (50% acetal functional groups with respect to the mole of acrylamide and hema functional groups), and by adding terephtalaldehyde which is a known small molecule crosslinker, in the same mole ratio with the former one, for comparative purpose. The compositions of polymer solutions and the films are shown in Table 4.1.

Table 4.1. The compositions of polymers and polymer films used for crosslinking.

Polymer Solution	Polymer Composition	Prepared Films
Blank polymer (B)	Mainly acrylate functionality on polymer chain. No OH or NH_2 groups exist.	**B0 -** B (no crosslinker) **B1 -** B + crosslinker **B2 -** B + terephtalaldehyde
Poly(HEMA) (H)	Mainly acrylate functionality on polymer chain. Additionally, 3% HEMA groups exist.	**H0 -** H (no crosslinker) **H1 -** H + crosslinker **H2 -** H + terephtalaldehyde
Polyacrylamide (A)	Mainly acrylate functionality on polymer chain. Additionaly 3% acrylamide groups exist.	**A0 -** A (no crosslinker) **A1 -** A + crosslinker **A2 -** A + terephtalaldehyde

Films were cured at 110 ^{o}C, 120 ^{o}C, 150 ^{o}C, 180 ^{o}C and 200 ^{o}C in order to see the effect of temperature on crosslinking. Each film was cured for 5 and 10 minutes to see whether the length of curing is effective on crosslinking. The curing times were kept short to be consistant with the industrial applications. After curing of the films, their acetone swellings were calculated.

No crosslinking was observed in blank polymer films B0, B1 and B2 as expected, since they did not have any functional group that can give a reaction with the acetal ring or aldehyde and form a network. Similarly, only partial networking was observed with the poly(HEMA) films H0, H1 and H2. They turned into a jellyfish like state but split easily into pieces mechanically. The reason for this may be that the crosslinker has cyclic *O,O*-acetals,

and at the end of the reaction of Poly(HEMA)'s -OH groups, *O,O*-acetal should be formed again. In other words, almost no significant stability gain can be achieved with respect to the bonds broken and formed. The only driving force may be that if crosslinked network is formed, the initial acetals will be replaced by bulkier groups, which is expected to be a more stable acetal. However, entropy change of this reaction is also unfavorable since one big molecule will be formed by connecting two molecules. By considering these entropic and enthalpic factors and the result of swelling tests, we may conclude that stability gain is not big enough to overcome the entropy loss. That's why the crosslinker was not efficient to form a network with –OH functional polymers.

On the other hand, polyacrylamide polymer films did not split into pieces in acetone, they swelled instead. This was the case for all the polyacrylamide films cured at different temperatures. Swelling results of the polymer films are given in Table 4.2 and 4.3, and their comparative graphs are given in Figure 4.3 and 4.4. Polymer films were labeled as A0, A1, A2 for the films containing no crosslinker, films containing the synthesized crosslinker, and films containing terephalaldehyde, respectively, as given in the Table 4.1.

Table 4.2. Swelling indexes of polyacrylamide films for 5 min curing.

Films	**Swelling Index (5 min curing)**				
	110°C	**120°C**	**150°C**	**180°C**	**200°C**
A0	5,70	6,12	7,20	9,13	10,74
A1	5,44	5,69	6,78	8,78	9,81
A2	5,70	5,98	6,38	6,04	6,14

Table 4.3. Swelling indexes of polyacrylamide films with 10 min curing.

Films	**Swelling Index (10 min curing)**				
	110°C	**120°C**	**150°C**	**180°C**	**200°C**
A0	5,79	6,07	7,38	9,76	11,48
A1	5,52	5,71	7,32	9,02	9,74
A2	5,58	6,09	4,93	5,40	6,16

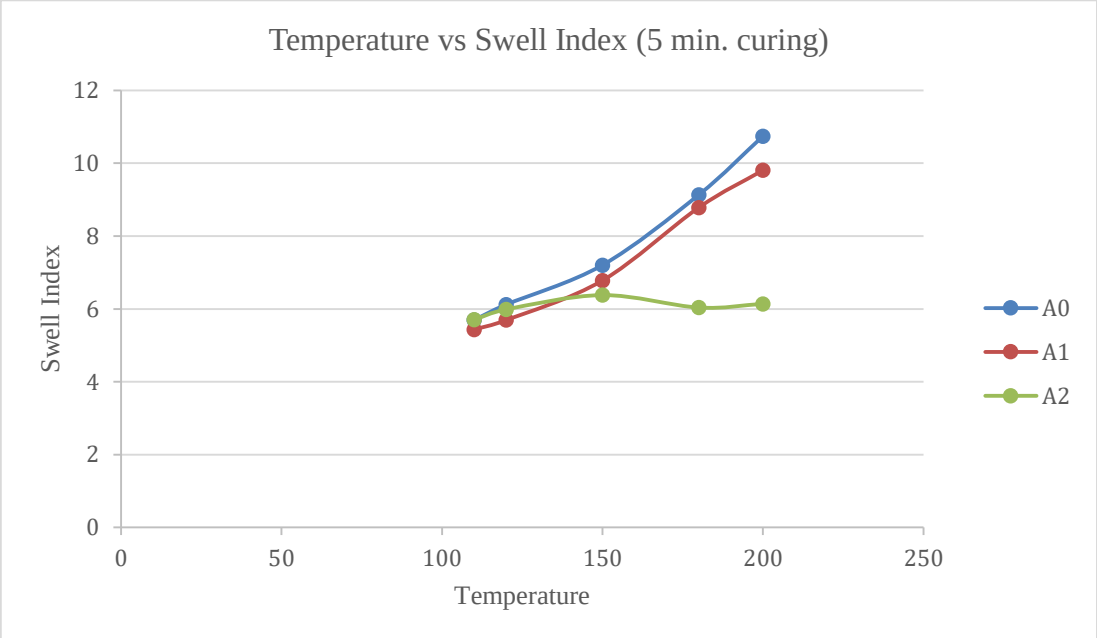


Figure 4.3. Temperature vs. Swell Index graph of polymer films for 5 min. curing.

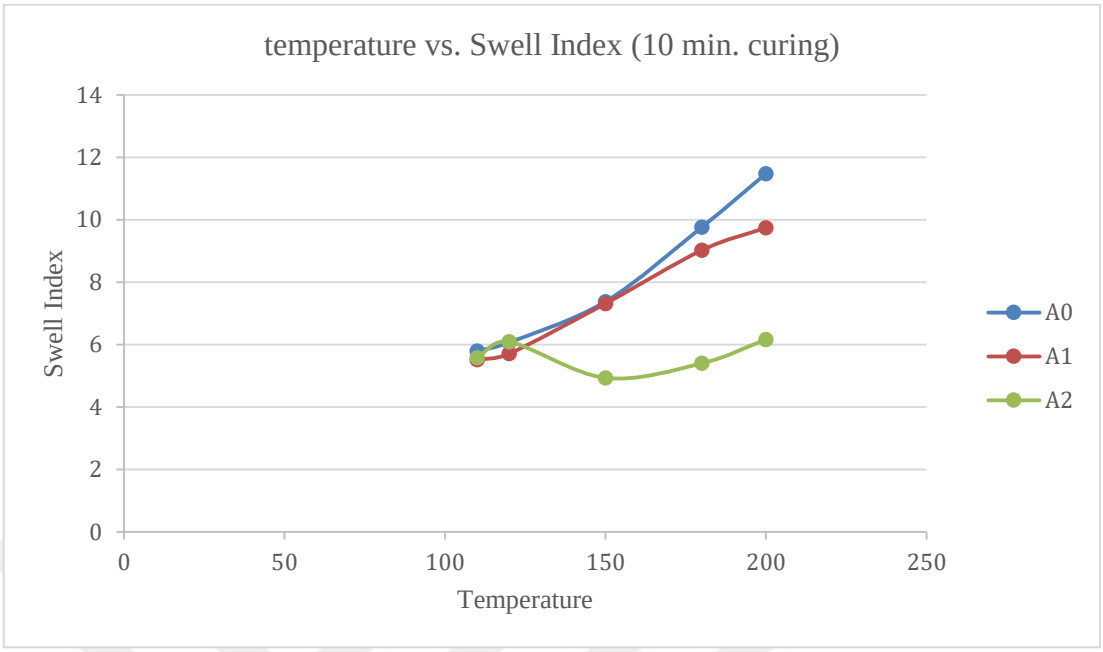


Figure 4.4. Temperature vs. Swell Index graph of polymer films for 10 min. curing.

In the acetone swelling test, one should remember that better crosslinking gives less swelling. When swelling results of acrylamide films are evaluated, it can be seen from the graphs that acrylamide films with the crosslinker (A1) gave smaller swelling values than films with no crosslinker (A0), however, when numerical values are considered, the difference is too small to prove an efficient crosslinking. The polymer itself gave good results when it has no crosslinker. This means that the polymer is self-crosslinkable. It may be because of imide formation by the reaction between amide and acrylate groups, or it may be due to strong hydrogen bonding between amide groups and acid groups of acrylic acid that may remain in polymer composition from the emulsion polymerization [33].

The swelling of A0, acrylamide polymer film without crosslinker, increased as the crosslinking was performed at higher temperatures. Higher swelling comes from decrease in crosslinking or structural changes such as degradation (i.e. hydrolysis). The crosslinker containing A1 films followed a similar pattern with the A0. However, the terephtalaldehyde containing A2 films gave better crosslinking at higher temperatures. At 150 ^{o}C, 180 ^{o}C, and 200 ^{o}C, A2 films are better crosslinked than A0. The crosslinking ability of teraphtalaldehyde is clearly seen from these results, and it is efficient in high temperatures,

however, the current data indicates that the synthesized molecule has poor crosslinking ability.

Curing for 5 min. or 10 min. did not make a significant change on swelling results, except for A2 at 150^{o} C and 180^{o} C. For these films longer curing time gave lower swelling values. Since the crosslinking efficiency of the polymer with teraphtalaldehyde is better than its self-crosslinking efficiency at high temperatures, the temperature effect on crosslinking of the polymer with the externally added crosslinker can be better observed, and it can be concluded that longer crosslinking time gives better crosslinking.

Since this method did not gave satisfactory results to conclude that the synthesized crosslinker is efficient to give a reaction with the amide containing polymers, further analysis were done by using 100 % acrylamide containing polymer in order to eliminate the self-crosslinking through the imide formation between acrylate and amide groups or through hydrogen bonding between acid and acrylamide groups. Crosslinking were analysed by observing the shifts in T_g, which will be discussed in the following section.

4.1.4. Glass Transition Temperature (T_g) Analysis

The polymer used for T_g analysis was in the form of clear aqueous solution at the beginning where then water was evaporated. T_g of polyacrylamide is too high, therefore it did not form a soft polymer film upon drying, instead, it turned into a white brittle solid. Curing of the polymers were done by mixing the polymer solution with the synthesized crosslinker (30% acetal functional groups with respect to the mole of acrylamide functional groups) and without the crosslinker, and waiting for one day for the evaporation of water, then curing at an oven at 120 ˚C, 150 ˚C and 190 ˚C for 5, 10 and 30 min. , separately. After waiting at vacuum oven for complete removal of moisture, T_g measurement were performed. T_g results of the cured polymers are given in Table 4.4;

Table 4.4. T_g results of polymers cured at different temperatures.

	T_g Measurements		
120 ˚C	**5 min.**	**10 min.**	**30 min.**
No Xlinker	170.4	171.7	170.2
With Xlinker	159.8	160.6	165.4
150 ˚C	**5 min.**	**10 min.**	**30 min.**
Without Xlinker	170.2	172.1	174.2
With Xlinker	165.9	166.9	167.5
190 ˚C	**5 min.**	**10 min.**	**30 min.**
Without Xlinker	174.0	175.0	178.4
With Xlinker	170.4	170.6	174.7

Figure 4.5 includes the comparison of polymers cured at different temperatures without crosslinker. The polymers that were cured at different temperatures without crosslinker gave different T_g values. As curing temperature increased, T_g values also increased even if they contained no crosslinker. This might be due to the self-crosslinking property of the polymer by imide formation [33].

The T_g results of polymers cured with crosslinker are compared in Figure 4.6. T_g of crosslinker containing polymer increases as curing temperature increases. However, since polymer itself has already a higher T_g at higher curing temperatures, these T_g increase of crosslinker containing polymers with temperature does not indicate an efficient crosslinking.

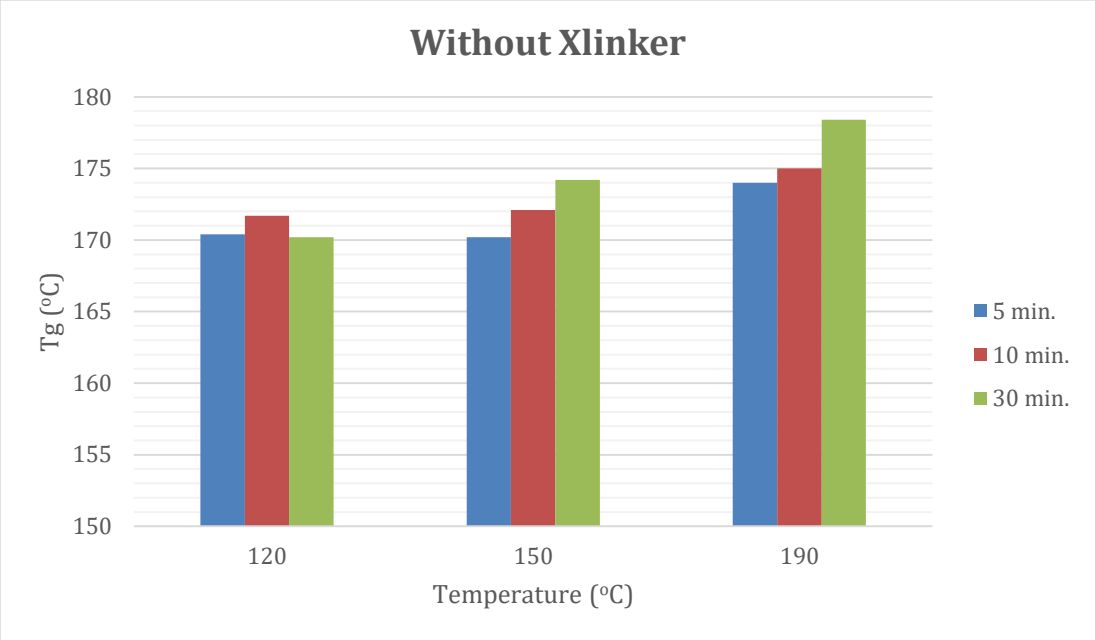


Figure 4.5. Temperature vs. T_g graph of polymers without crosslinker.

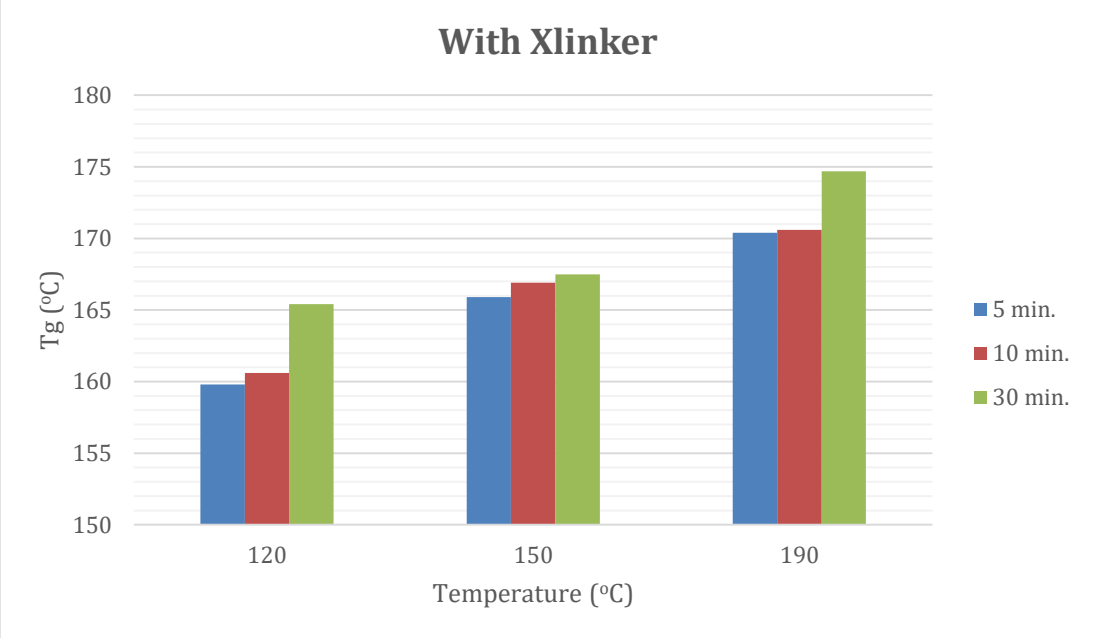


Figure 4.6. Temperature vs. T_g graph of polymers containing crosslinker.

Figure 4.8, Figure 4.9 and Figure 4.10 show the comparison of T_g results of polymers cured at same temperature with and without crosslinker for 5 min., 10 min. and 30 min. curing, respectively. The results show that T_g of the final polymers decreased when they were cured with crosslinker compared to T_g of polymer cured without crosslinker under the same conditions. However, T_g was expected to increase as the polymer was getting crosslinked. On the other hand, at 120 °C, polymer without the crosslinker did not show an increase in T_g as the curing time increased, however, T_g of polymer with crosslinker did. This result indicates a slight crosslinking at 120 °C. At 150 °C and 190 °C, T_g of polymers both with and without crosslinker increased, therefore, it is not possible to claim that a crosslinking occurred at these temperatures. .In order to be certain, ^{1}H-NMR was taken to especially see the change in acetal peaks upon curing.

In ^{1}H-NMR results of cured polymers, *N,O*-acetal peak at 4.86 ppm became apparent which did not exist prior to curing (Figures 4.10, 4.11 and 4.12).

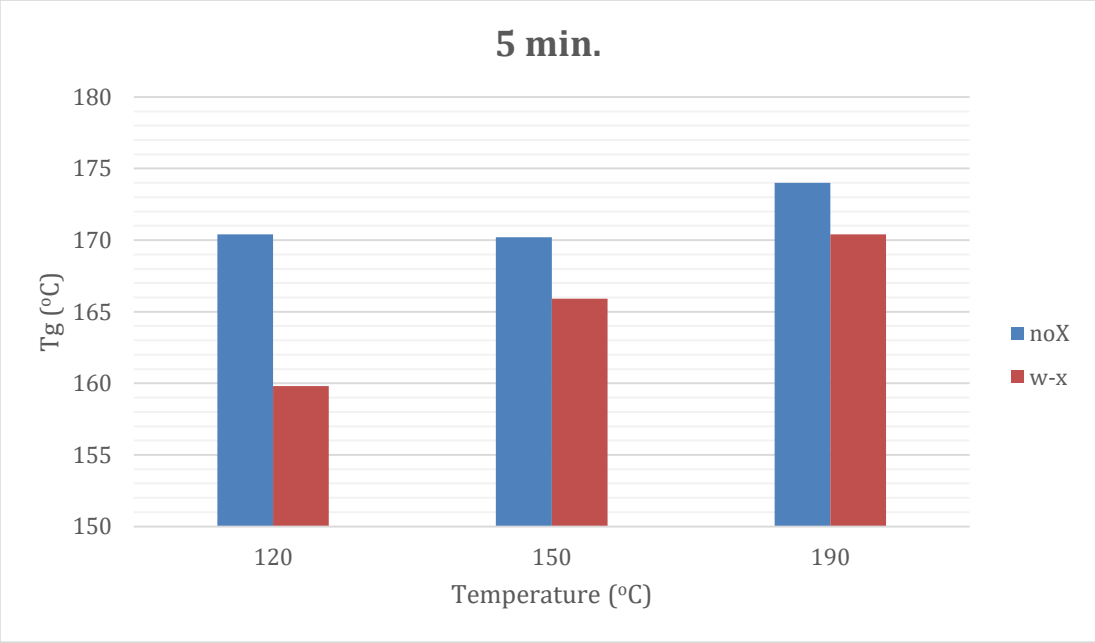


Figure 4.7. Temperature vs. T_g graph of polymers for 5 min. curing.

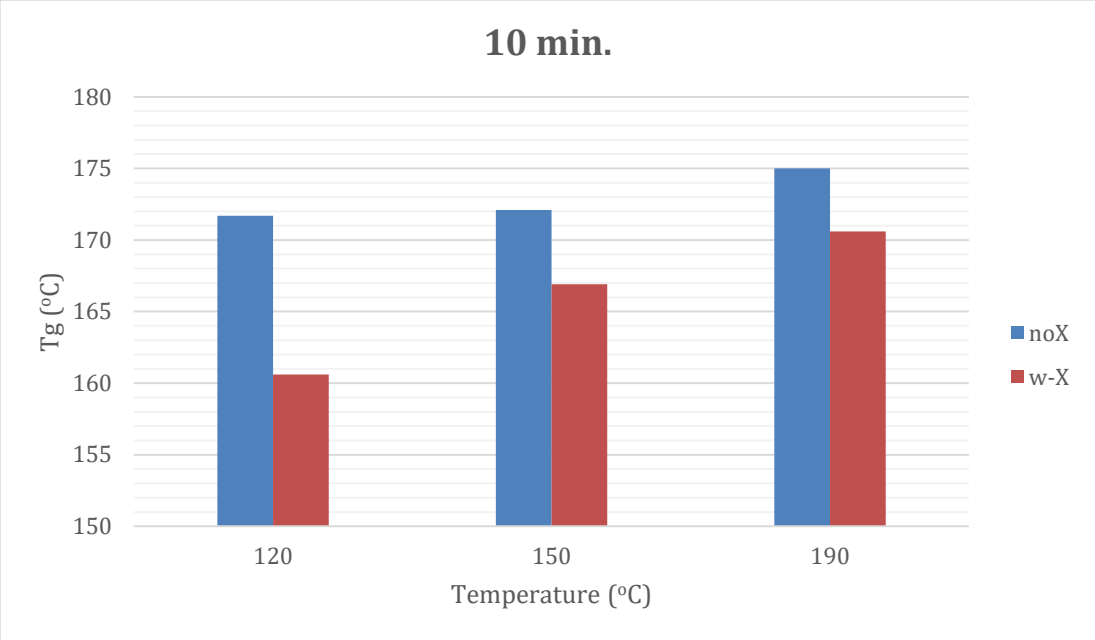


Figure 4.8. Temperature vs. T_g graph of polymers for 10 min. curing.

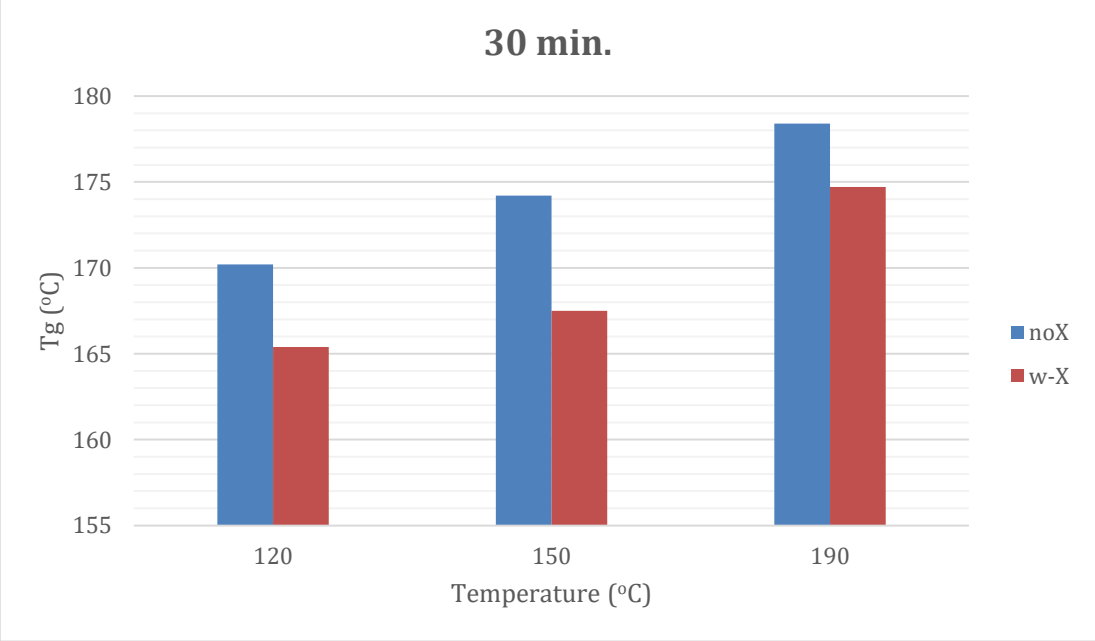


Figure 4.9. Temperature vs. T_g graph of polymers for 30 min. curing.

In ^{1}H-NMR spectrum of polymer cured at 120 °C for 5 min., almost no *N,O*-acetal peak is observable, the *O,O*-acetal peak of crosslinker is clearly seen. For all other spectra,

N,O-acetal peak is observed showing that crosslinking reaction occurred through transacetalization reaction and more stable acetal was formed. However, in all results, *O,O*-acetal peak is also observed showing that not all *O,O*-acetals gave reaction with the polymer. This might be the reason why T_g decreased upon curing while it was expected to increase. It is possible that the unreacted crosslinker molecules acted as plasticizer and caused a T_g decrease.

Figures 4.10, 4.11 and 4.12 show a part of the ^{1}H-NMR spectra of cured polymers that are zoomed to the region where acetal peaks exist (full spectra of polymers are given in Appendix A). *N,O*-acetal peak appears at 4.86 ppm and *O,O*-acetal peak appear 4.3-4.4 ppm In some of the spectra, *N,O*-acetal peak overlap with the D_2O peak, therefore, integral analysis could not be properly done to calculate the ratio of *O,O*-acetal and *N,O*-acetal hydrogens. However, even if the acetal peaks cannot be quantified, the presence and relative intensities can be interpreted from the ^{1}H-NMR spectra.

In Figure 4.10a, the spectrum for 5 min. curing at 120 ^{o}C, the intensity of *N,O*-acetal peak is very low . As the curing time increases, the *N,O*-acetal peak is becoming more intense as can be seen in Figures 4.10b and 4.10c. When these three spectra were compared, it can be concluded that longer curing time gives better crosslinking at 120 ^{o}C.

At 150 ^{o}C, 5 min. curing gives more intense *N,O*-acetal peak than 5 min. curing at 120 ^{o}C when Figure 4.10a and 4.11a were compared. This shows that the crosslinking is more efficient at 150 ^{o}C than 120 ^{o}C. As curing time increased at 150 ^{o}C, the intensity of *N,O*-acetal peaks increase. Additionally, the decrease in the intensity of *O,O*-acetal peak can clearly be observed in Figure 4.11c. At 150 ^{o}C, longer curing times gives better crosslinking.

In Figures 4.12a and 4.12b, spectra for 5 min. and 10 min. curing at 190 ^{o}C, *N,O*-acetal peaks are very intense and *O,O*-acetal peaks almost disappear. However, *O,O*-acetal peak become more apparent for 30 min. curing as seen in Figure 4.12c. When these three spectra are compared, it is seem as the crosslinking efficiency decrease as curing time increases at 190 ^{o}C. The reason for this might be that as the reaction time increase at very high temperatures, reverse reaction may be favourable since entropy gain and high temperature would make ΔG of the reverse reaction negative.

Considering these predictions, the conclusion might be that the crosslinker is more efficient at moderately high temperatures, but the curing time has to be tuned so that the extent of the reverse reaction is controlled.

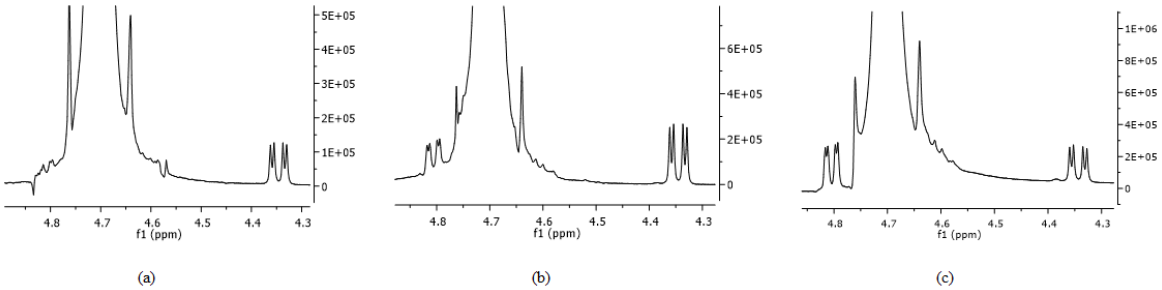


Figure 4.10. Zoomed ^{1}H-NMR spectra of polyacrylamide cured with crosslinker at 120 ^{o}C a) for 5 min. b)for 10 min. c) for 30 min.

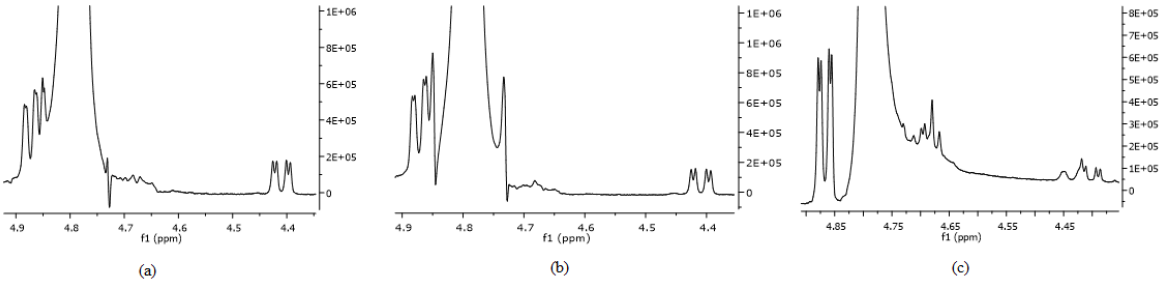


Figure 4.11. Zoomed ^{1}H-NMR spectra of polyacrylamide cured with crosslinker at 150 ^{o}C a) for 5 min. b)for 10 min. c) for 30 min.

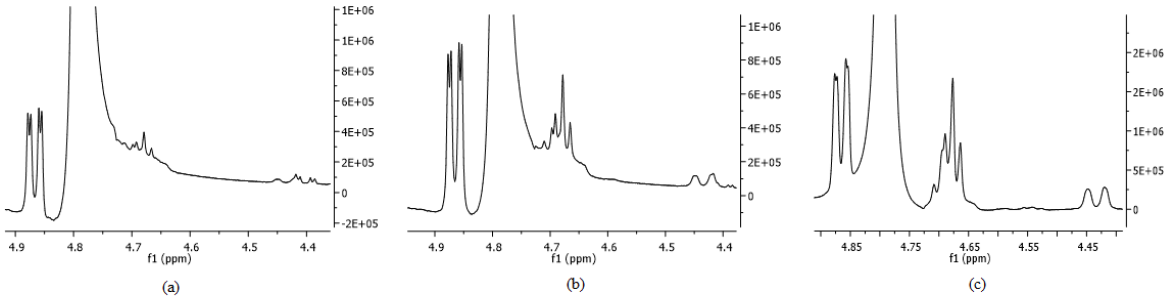


Figure 4.12. Zoomed ^{1}H-NMR spectra of polyacrylamide cured with crosslinker at 190 ^{o}C a) for 5 min. b)for 10 min. c) for 30 min.

Generally, forming a crosslinked network makes the polymer insoluble in solvents, and when it does not dissolved, it does not give peaks in NMR spectra. In this case, beside intermolecular crosslinking, intramolecular reaction of polymer chains with the crosslinker might also be occurred. This might be the reason that the cured polymer was soluble in water to some extent and it was possible to obtain an ^{1}H-NMR spectrum.

4.2. Synthesis of Triazine Based Crosslinkers

4.2.1. Synthesis and Reduction of 2,4,6-tris(succinimido)-1,3,5-triazine

Synthesis and purification of 2,4,6-tris(succinimido)-1,3,5-triazine were done according to the literature (US5807929). The reaction was performed at room temperature, and THF was used instead of the acetone as the solvent for cyanuric chloride. Pure product was obtained in 52.5 % yield. The reduction of the compound was done by using $NaBH_4$ in ethanol added at -10 ^{o}C and the reaction mixture was stirred at room temperature overnight. The crude product was purified by washing it with water, ethanol and ethyl acetate, and pure product in 44.5 % yield. The proposed reaction scheme for the synthesis and reduction of compound 6 is given in Figure 4.13.

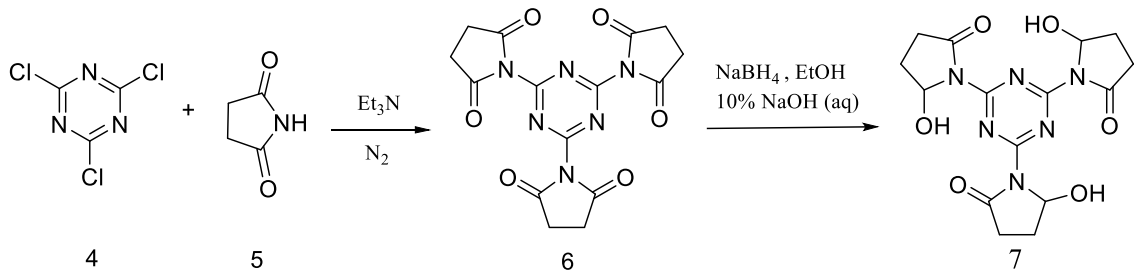


Figure 4.13. Synthesis of 2,4,6-tris(succinimido)-1,3,5-triazine and proposed reduction mechanism.

$NaBH_4$ could reduce one of the carbonyl groups of a cyclic imide to hydroxyl or alkoxy depending on solvent system of the reaction and work up method [34]. However, during the reduction, ring cleavage may also be observed and amide alcohol is formed at the end of the reaction [35]. Proposed mechanism for the ring cleavage is given in Figure 4.14. In this study, reduction of 2,4,6-tris(succinimido)-1,3,5-triazine **(6)** was aimed to reduce one of its carbonyl groups on the imide ring to hydroxyl in order to have *N,O*-acetal on the ring, yet the amide alcohol adduct was formed instead. The formation of amide alcohol was proven by ^{1}H-NMR, ^{13}C-NMR and HSQC analysis.

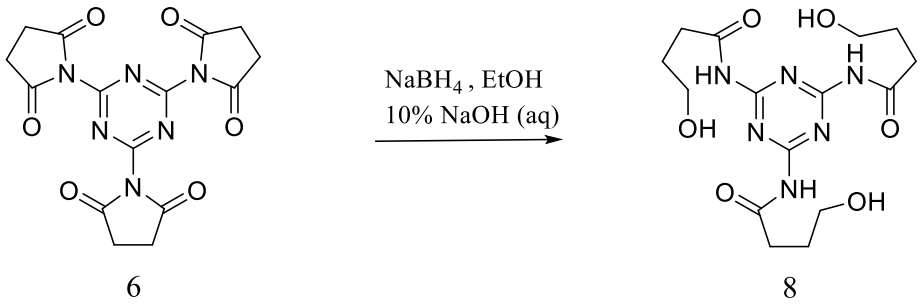


Figure 4.14. Observed reduction mechanism of 2,4,6-tris(succinimido)-1,3,5-triazine.

Interestingly, in one of the studies done by our research group, the reduction of one carbonyl of an imide group was achieved and no ring opening was observed [27]. The reason for this may be the difference of the groups that the cyclic imide was bond to. In the previous case, it was bonded to an alkyl group but in this case it is bonded to a triazine ring.

Figure 4.15 shows the ring opening mechanism of imides through the reduction with $NaBH_4$. The nature of R group is effective in whether ring cleavage is favored or not. If R group is able to delocalize the minus charge on transition state B, then ring cleavage will be favored. If it is not, then formation of cyclic *N,O*-acetal on ring by the protonation of A is more likely. [35].

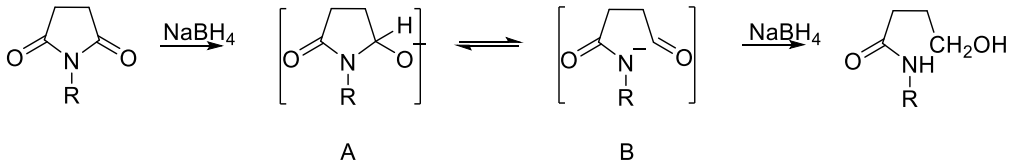


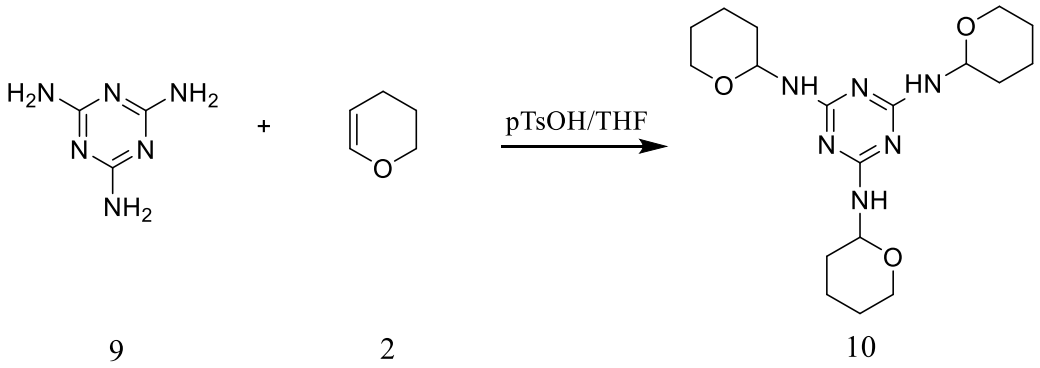
Figure 4.15. Proposed reductive ring opening mechanism of substituted imines by sodium borohydride [35].

In the present case, R group is a triazine ring bonded two other succinimide, which is expected to increase the resonance on transition state in a large extend. Therefore, ring cleavage is highly favored in this case.

4.2.2. Tetrahydropyranylation of Melamine

In melamine reactions, solubility of melamine has been an important challenge. It has poor solubility in water and it is insoluble in most of the organic solvents. Therefore, melamine reactions are generally performed in solvents like DMSO or DMF and high temperatures are needed for complete solubility.

Firstly, reaction of melamine with DHP in DMSO was performed at high temperatures. However, complete removal of DMSO was hard to achieve. The reaction mixture was extracted with DCM and H_2O with the ratio of 1:10 DCM:H_2O and extraction were done 10 times to collect DMSO in aqueous phase. However in that case, a considerable amount of organic phase remained in aqueous phase with DMSO. The obtained yield of the reaction was too low for purification and further analysis.



9 2 10

Figure 4.16. Tetrahydropyranylation reaction of melamine.

Since DMSO was not efficient enough for the reaction, dry THF was used instead of DMSO, but melamine is not soluble in THF at room temperature or at high temperatures, but we decided to start with a heterogeneous mixture. The reaction scheme is given in Figure 4.16. First, the reaction was run at room temperature for 3 days. The product was analyzed by ^{1}H-NMR. The peak at 5.53 in ^{1}H-NMR for acetal hydrogen proves the formation of acetal, however, the compound has complete symmetry, therefore it was not possible to detect the functionality of the product by ^{1}H-NMR. Mass spectrometry analysis were done to observe functionality of the compounds formed at the end of the reaction. The potential *mono- di-* and *tri-* functional products are shown in Figure 4.17. Product of the reaction performed at room temperature gave an m/z peak at 318 which is consistent with [M_2 + Na] (M_2 represent the molecular weight of di-functional product shown in Figure 4.9). In order to increase the reactivity, reaction was repeated at 40 ^{o}C and 60 ^{o}C separately. Similarly, ^{1}H-NMR and ^{13}C-NMR results conformed the formation of acetal. Product of the reaction performed at 40 ^{o}C gave an m/z peak at 378 for M_3 and also at 401 for [M_3 + Na] (M_3 represent the molecular weight of tri-functional product shown in Figure 4.17). Product of the reaction performed at 60 ^{o}C gave an m/z peak 318 for [M_2 + Na]. According to these results, we can assume that desired product was formed at 40^{o}C. The crude product was obtained in 14% yield.

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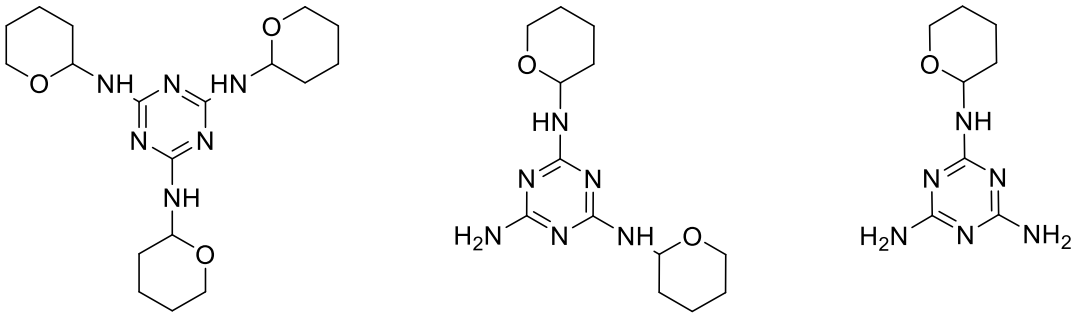

Figure 4.17. Products that are possible to form at the end of the reaction of melamine with DHP.

The reason for these inefficient reactions may be the irreversible nature of the pyranylation reaction. The reaction of melamine with DHP with an acid catalyst is a reversible reaction since acetal may hydrolize with the acid and water. Reaction was run at high temperature because of the low solubility of melamine, and high temperature may change the extent of the reverse reaction. So, even if melamine and DHP reacts and the desired product is formed, the amount of the product that was obtained at the end of the reaction was not enough to be purified and applied for crosslinking, therefore further studies was not performed with this compound.

In mass spectra of crude products, there are also peaks which correspond the trifunctional product and additional presence of one or two more melamine molecules, peak at 504 is for [M_3 + Melamine] , 528 is for [M_3 + Na + Melamine + 1], 544 for [M_3 + K + Melamine + 1], and at 631 for [M_3 + 2 Melamine + 1], 595 for [M_3 – 2 H_2O + 1], 619 for [M_3 – 2 H_2O + Na +2]. These peaks probably come from the side product formed by the attack of free melamine molecules to the *N,O*-acetal center resulting in *N,N*-acetal formation, which is a favorable reaction path since *N,N*-acetal is more stable. The predicted products are given in Figure 4.18.

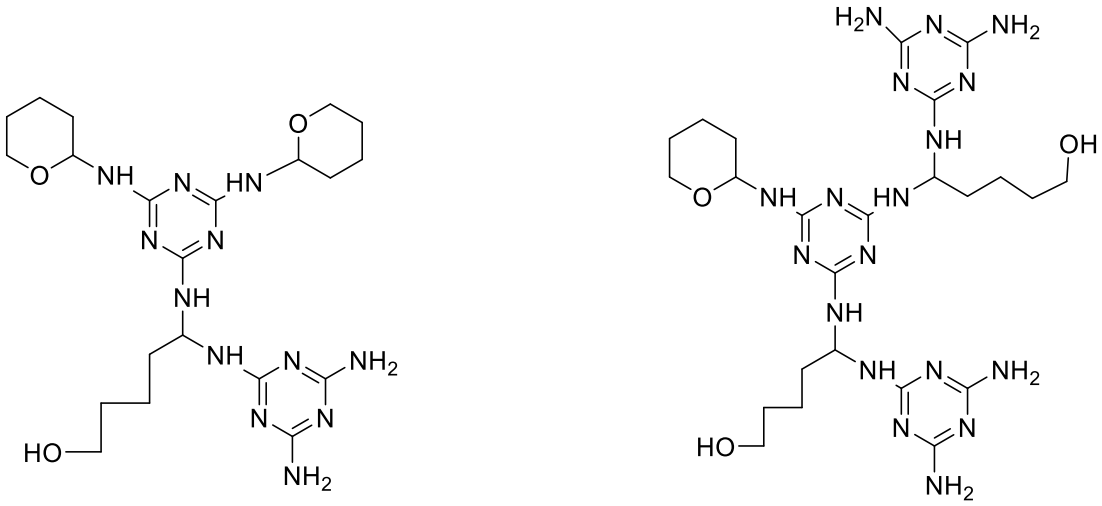

Figure 4.18. Predicted Side Products of Melamine – DHP Reaction.

5. CONCLUSIONS

In this study, mainly three synthesis were carried out and crosslinking tests with the efficiently synthesized crosslinker were performed.

The first synthesis was the reaction of pentaerythritol with dihydropyran to obtain a tetrafunctional *O,O*-acetal containing crosslinker. The desired product was obtained successfully and used for crosslinking tests with polyacrylamide and poly(HEMA). According the swelling results, it was clearly seen that the crosslinker was not efficient to form a crosslinked network with -OH containing polymer. According to swelling, T_g and ^{1}H-NMR results of the cured polyacrylamide, it can be concluded that the synthesized crosslinker gave the expected crosslinking reaction with acrylamide through the formation of more stable acetal, and the best result was seen in moderately high temperatures when ^{1}H-NMR results are considered, however, the crosslinking was not efficient enough to increase the physical properties of the polymer like swelling and glass transition temperature.

The second synthesis was a two-step reaction. In the first step 2,4,6-tris(succinimido)-1,3,5-triazine was synthesized according to the literature and in the second step it was reduced with $NaBH_4$. The obtained product was not the one that is expected in the first place, but was the ring opened and further reduced adduct. So the syntheses of such crosslinkers were abandoned.

The third synthesis was the reaction of melamine with dihydropyran to obtain a triazine based *N,O*-acetal containing three functional crosslinker. The synthesis of the desired molecule was successful, however the reaction was not very efficient due to the very low solubility of melamine in organic solvents and the yield of the crude product was too low to purify and use for industrial crosslinking applications.

6. FUTURE WORK

As a future work, crosslinking tests will be performed by using amine containing polymers. Additionally, new type of cyclic *N,O*-acetal containing crosslinkers will be synthesized, characterized and used to crosslink amine -NH_2 rather than amide containing polymers through the formation of *N,N*-acetal.

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APPENDIX A: SPECTROSCOPY DATA

This section includes ^{1}H-NMR Spectroscopy, ^{13}C-NMR Spectroscopy, Mass Spectroscopy and DSC Analysis of synthesized molecules. Necessary expansions were made on the data for easy interpretation.

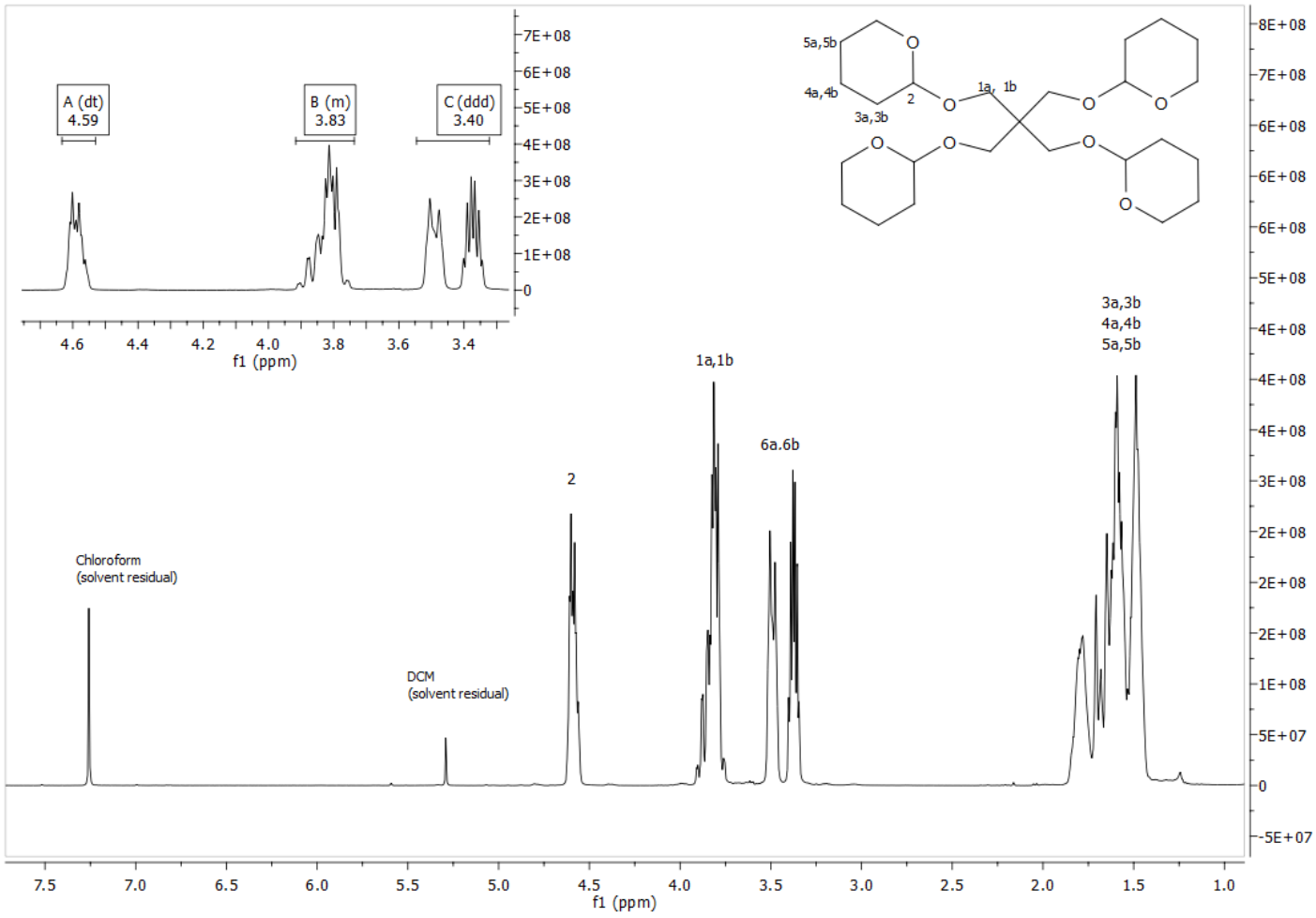

Figure A. 1. ^{1}H-NMR Spectrum of *O,O*-acetal Based Tetra-functional Crosslinker.

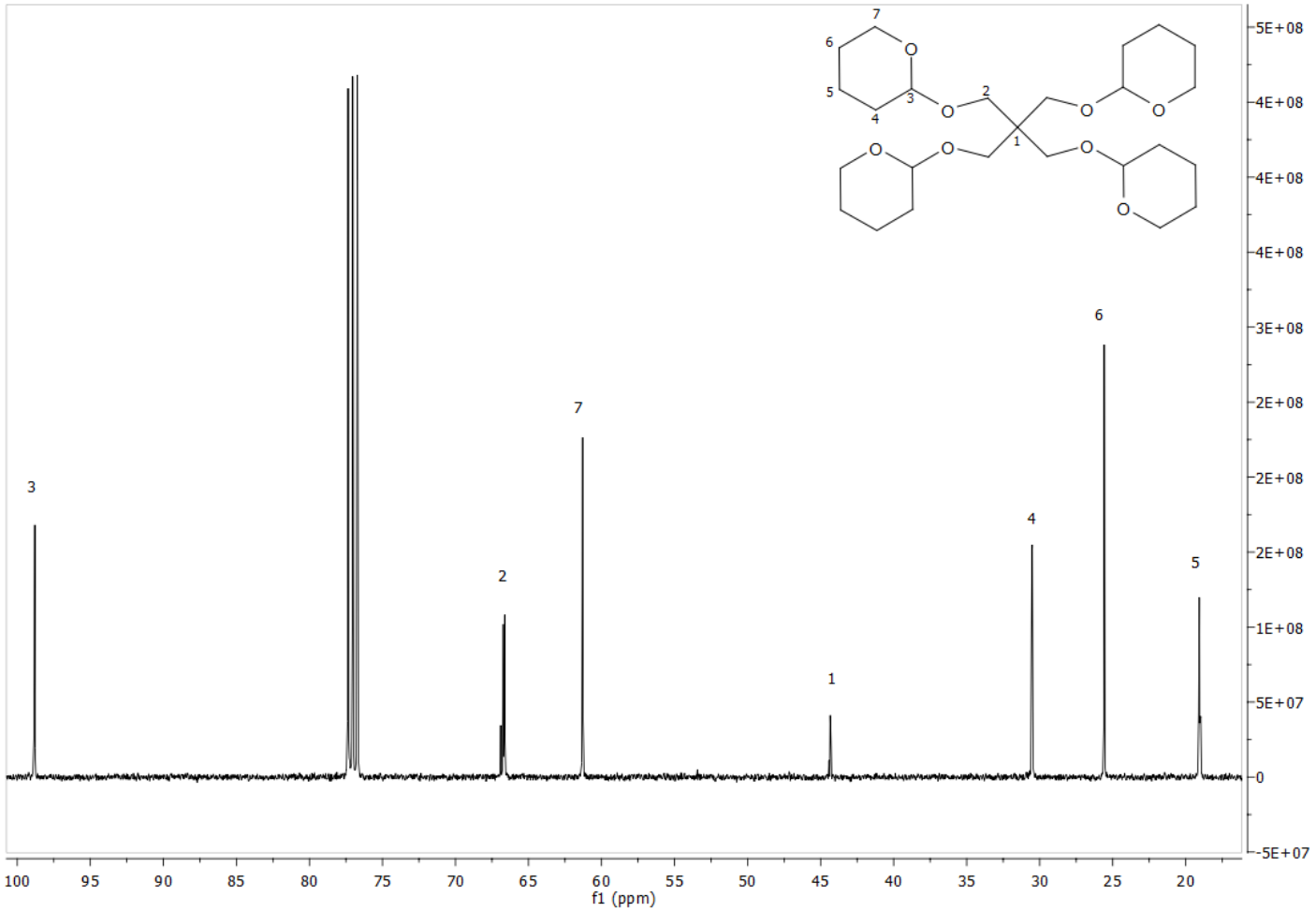

Figure A. 2. ^{13}C-NMR Spectrum of *O,O*-acetal Based Tetra-functional Crosslinker.

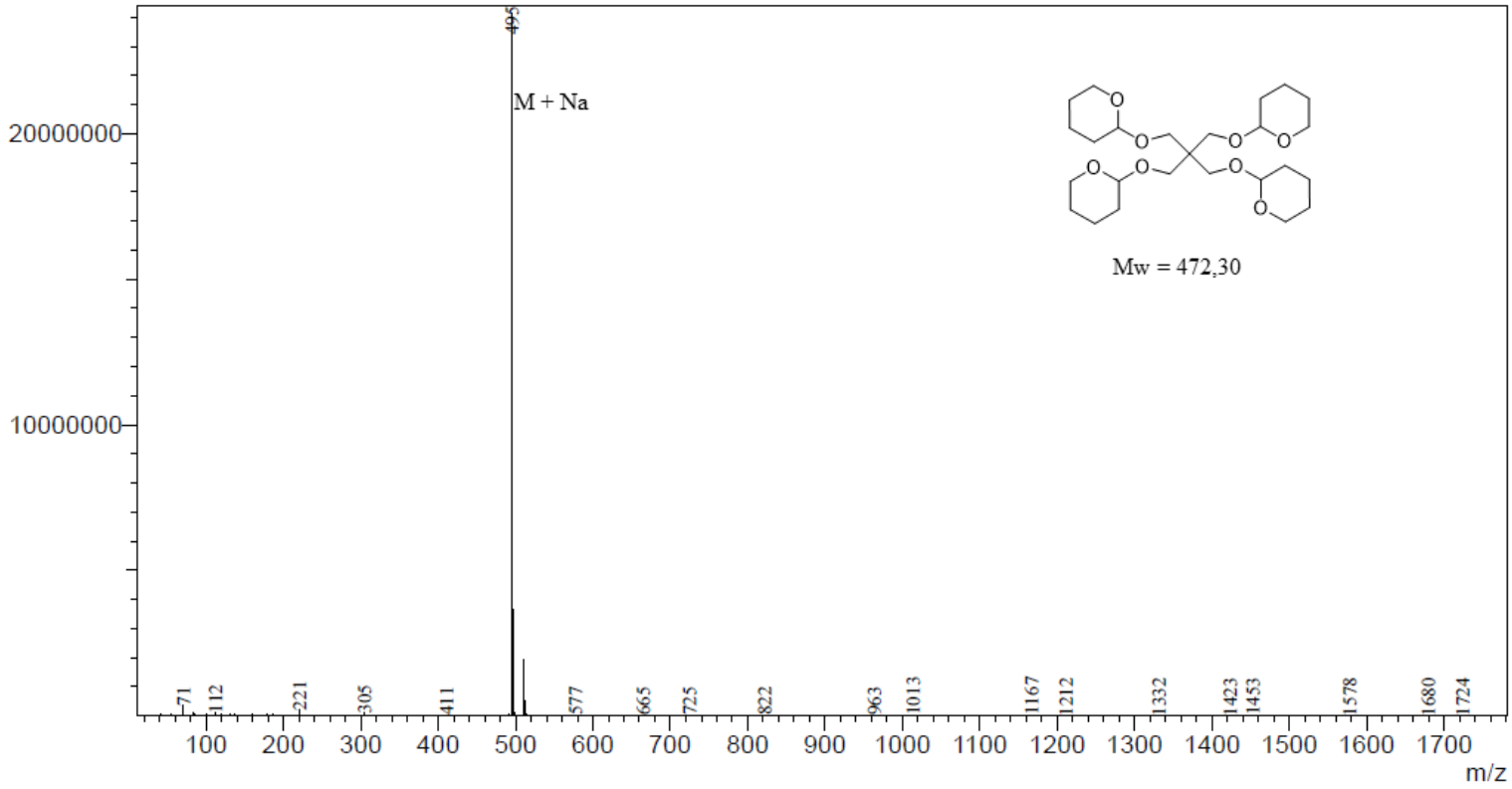

Figure A. 3. Mass Spectrum of *O,O*-acetal Based Tetra-functional Crosslinker.

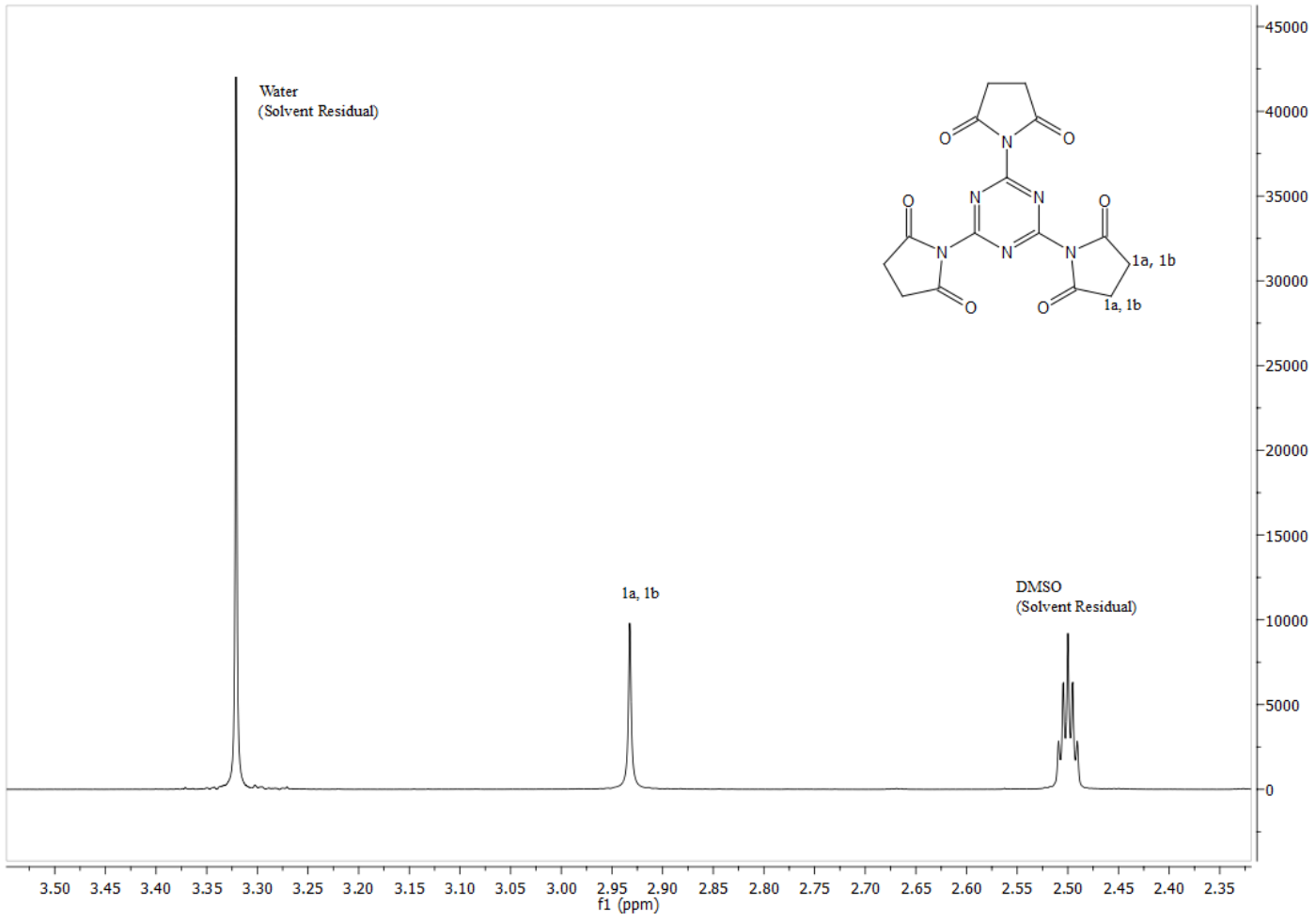

Figure A. 4. ^{1}H-NMR Spectrum of 2,4,6-tris(succinimido)-1,3,5-triazine.

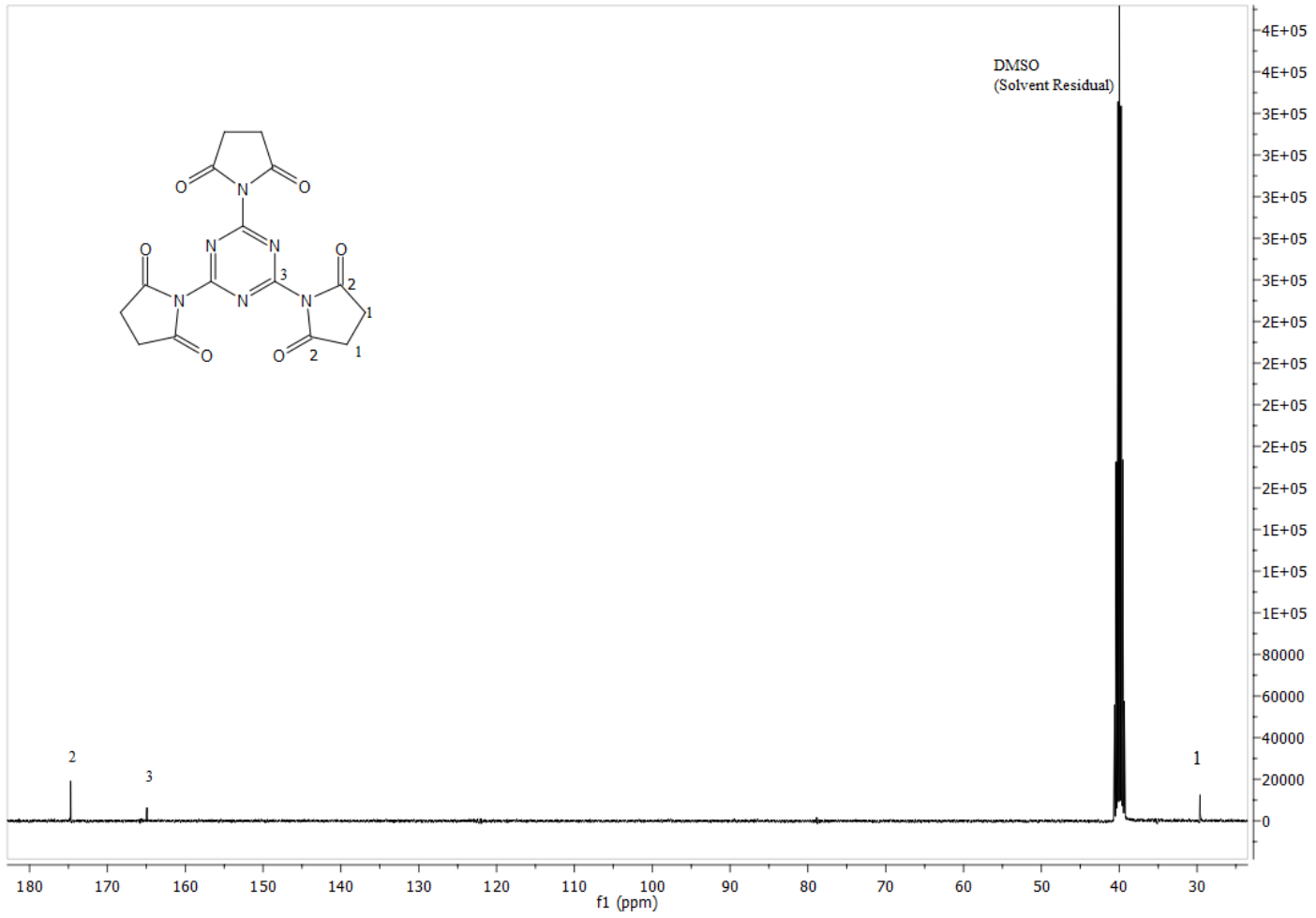

Figure A. 5. ^{13}C-NMR Spectrum of 2,4,6-tris(succinimido)-1,3,5-triazine.

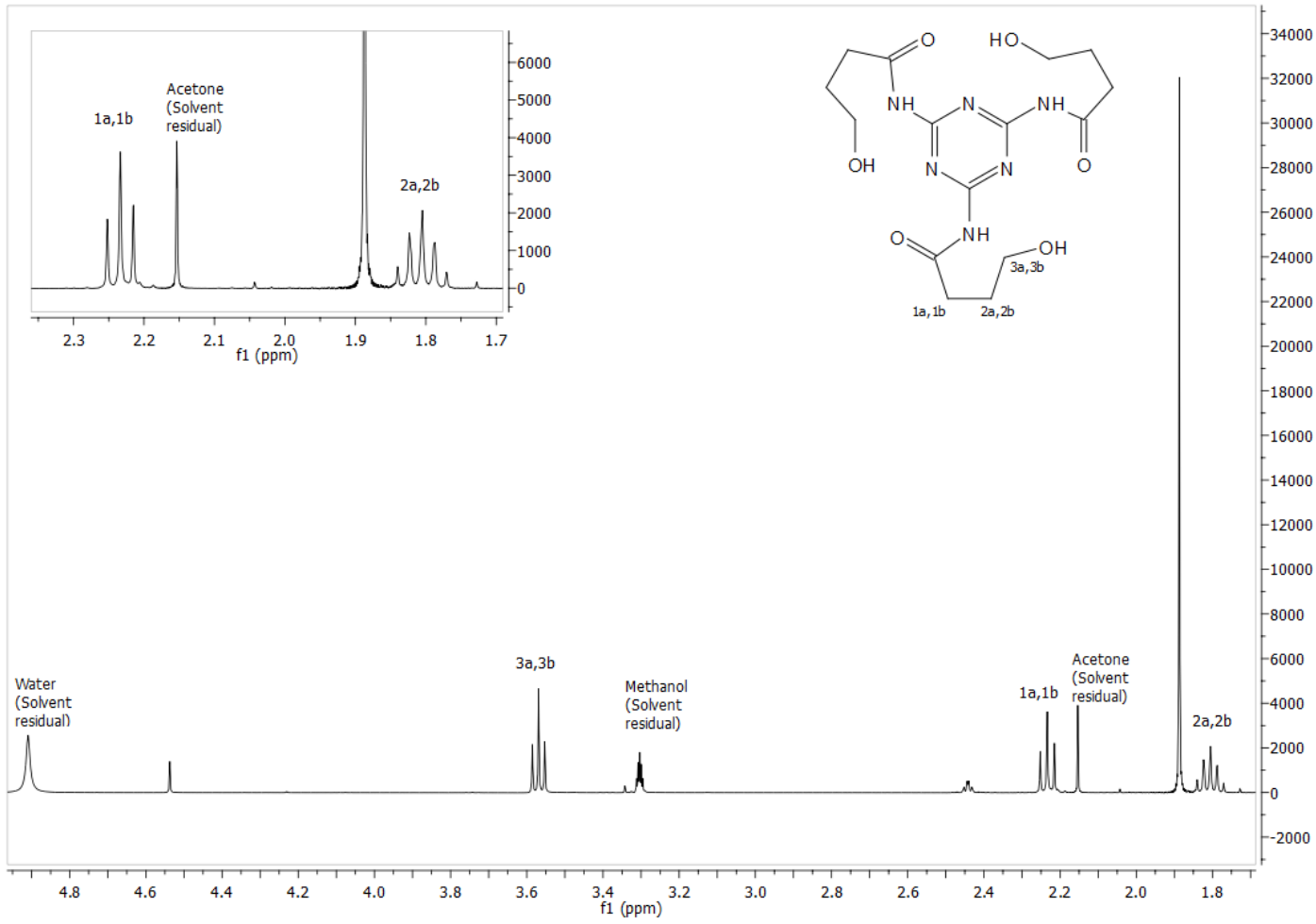

Figure A. 6. ^{1}H-NMR Spectrum of Reduction Product of 2,4,6-tris(succinimido)-1,3,5-triazine.

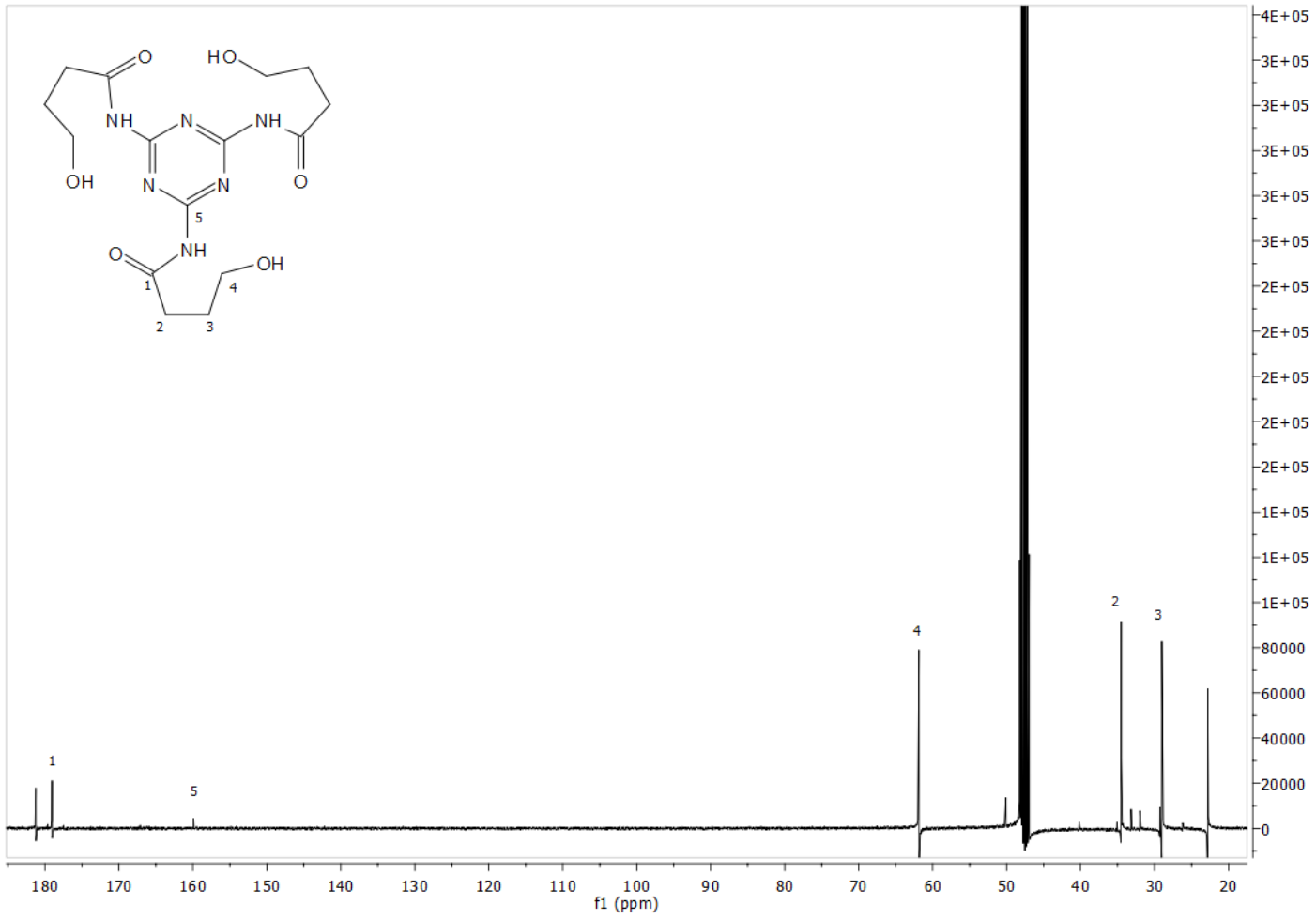

Figure A. 7. ^{13}C-NMR Spectrum of Reduction Product of 2,4,6-tris(succinimido)-1,3,5-triazine.

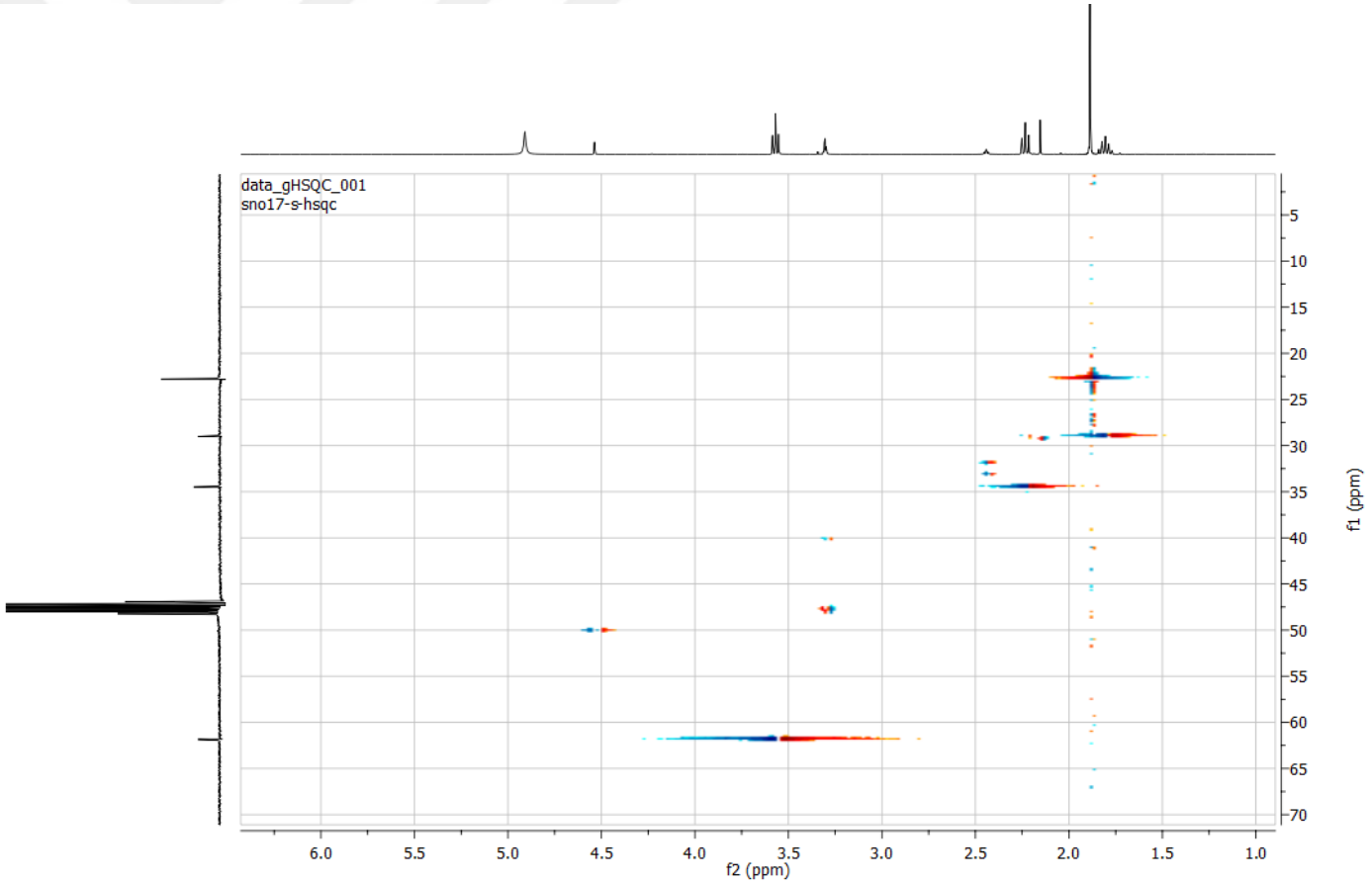

Figure A. 8. HSQC NMR Spectrum of Reduction Product of 2,4,6-tris(succinimido)-1,3,5-triazine.

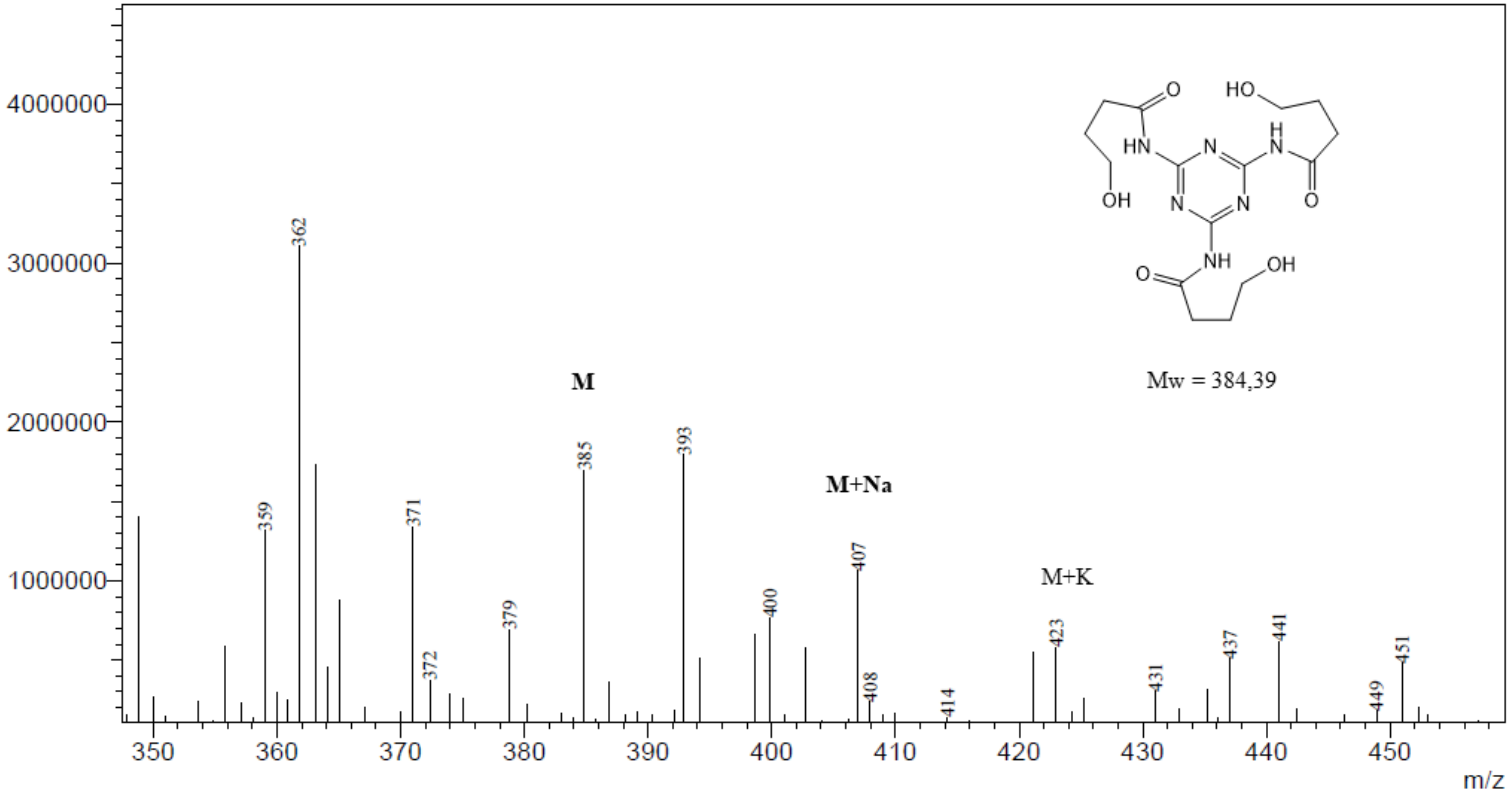

Figure A. 9. Mass Spectrum of Reduction Product of 2,4,6-tris(succinimido)-1,3,5-triazine.

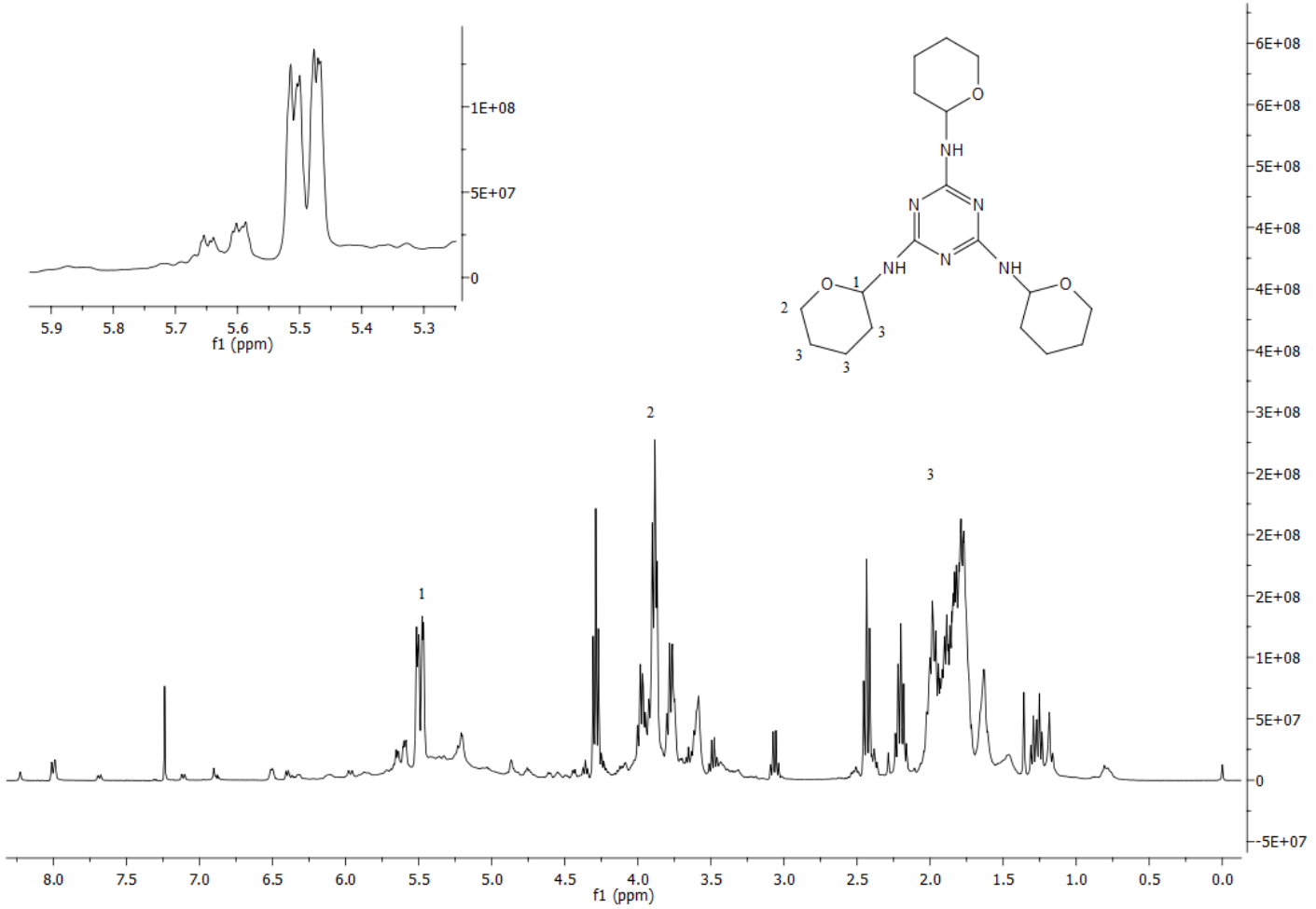

Figure A. 10. ^{1}H-NMR Spectrum of Crude Product of the Melamine – DHP Reaction at 40 ^{o}C.

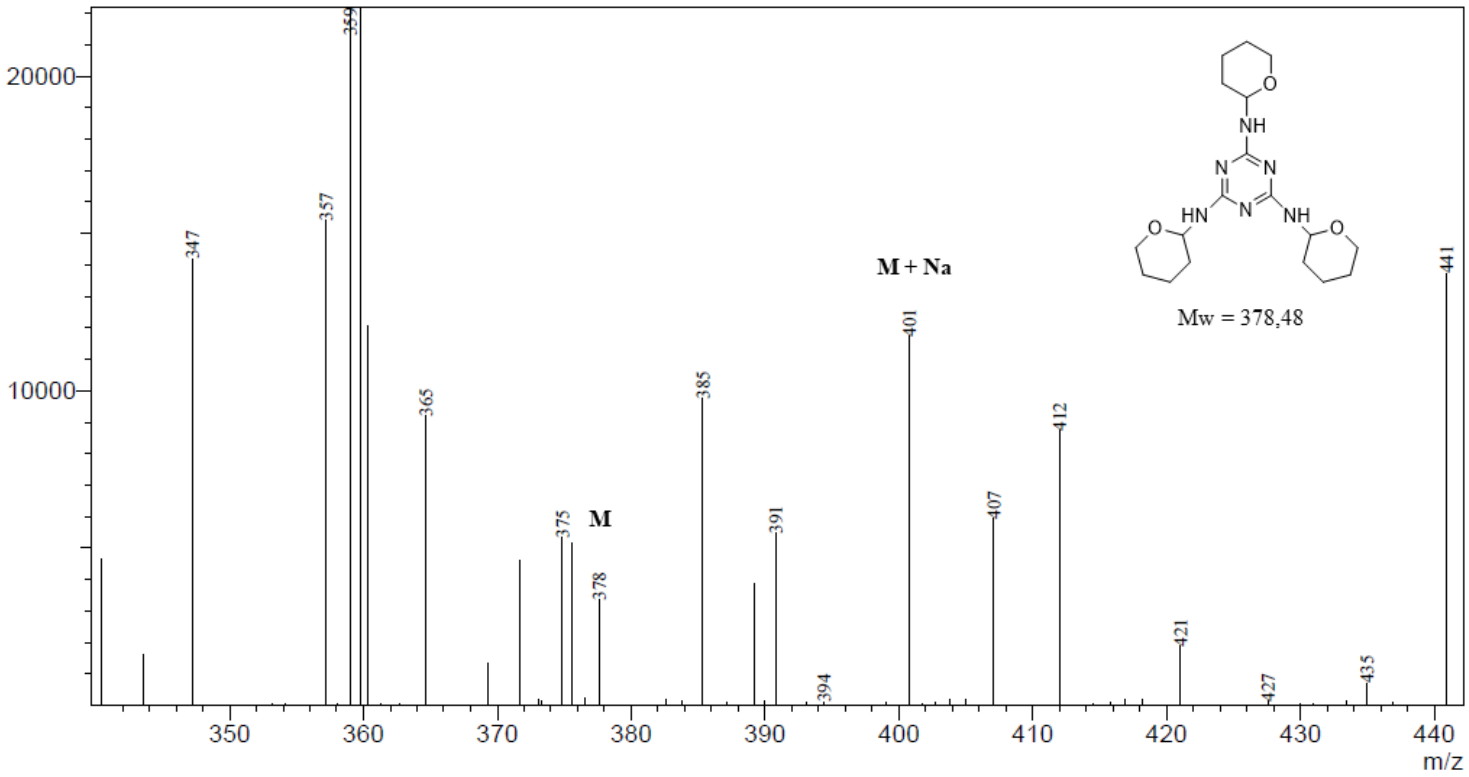

Figure A. 11. Mass Spectrum of Crude Product of the Melamine – DHP Reaction at 40 ºC.

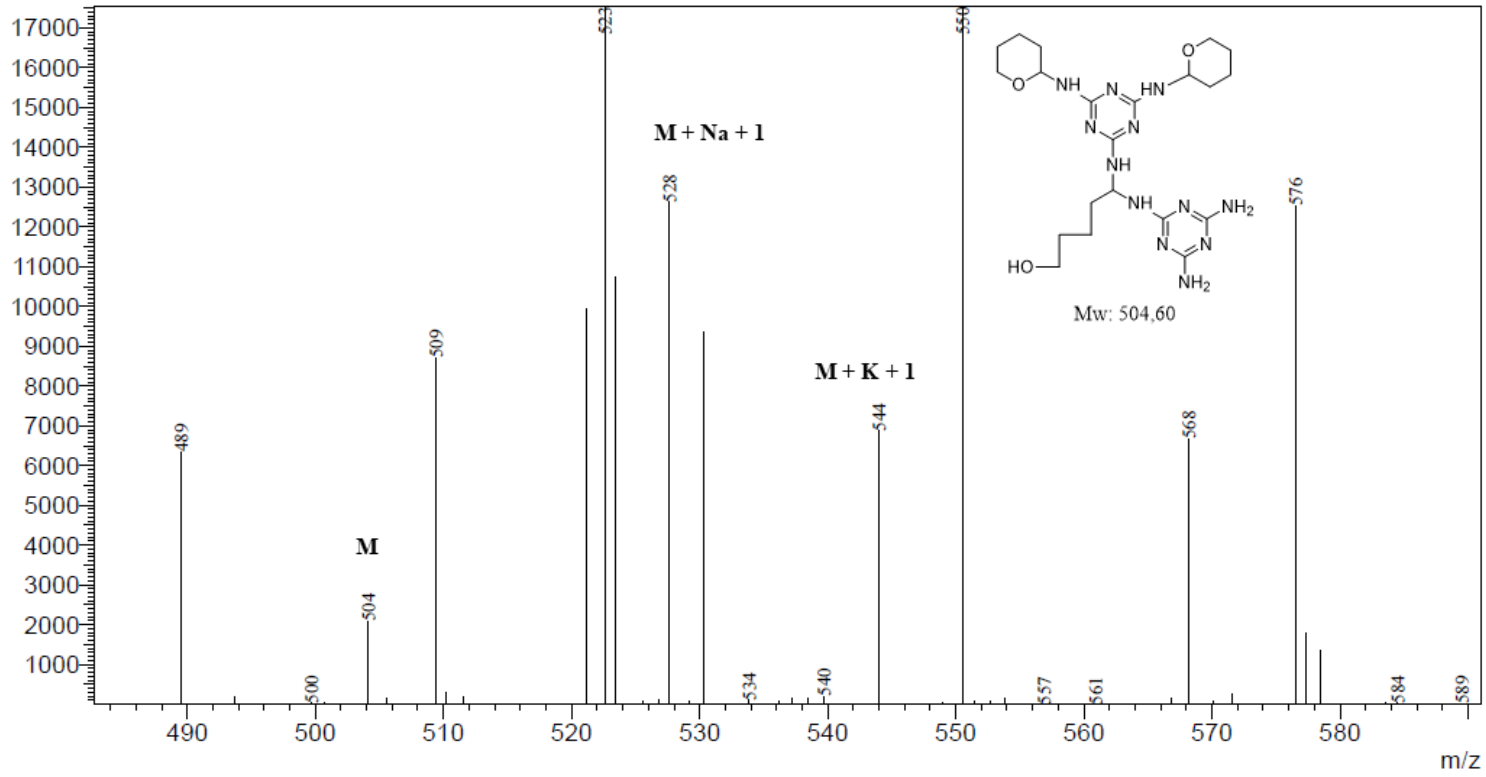

Figure A. 12. Zoomed Mass Spectrum of Crude Product of the Melamine – DHP Reaction at 40 ºC.

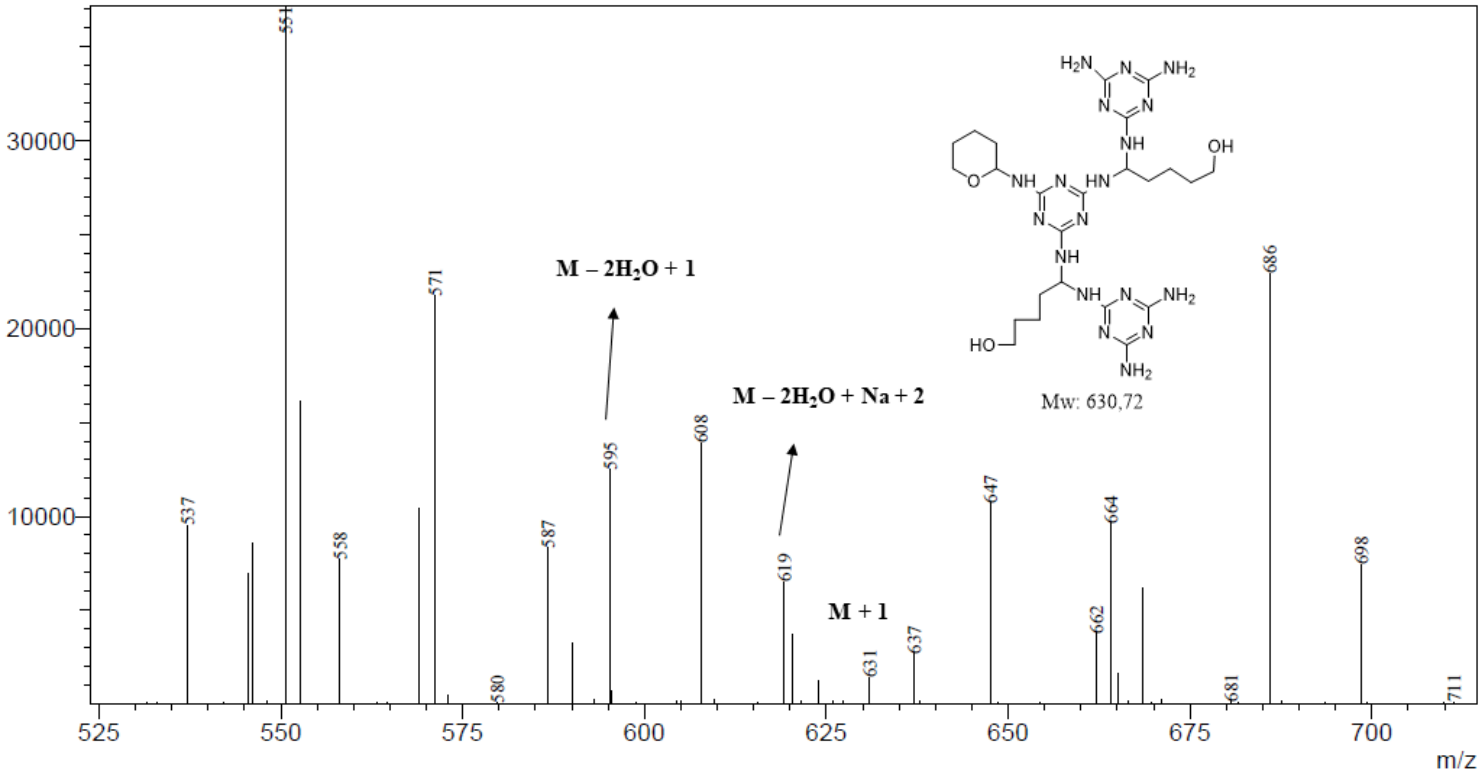

Figure A. 13. Zoomed Mass Spectrum of Crude Product of the Melamine – DHP Reaction at 40 ºC.

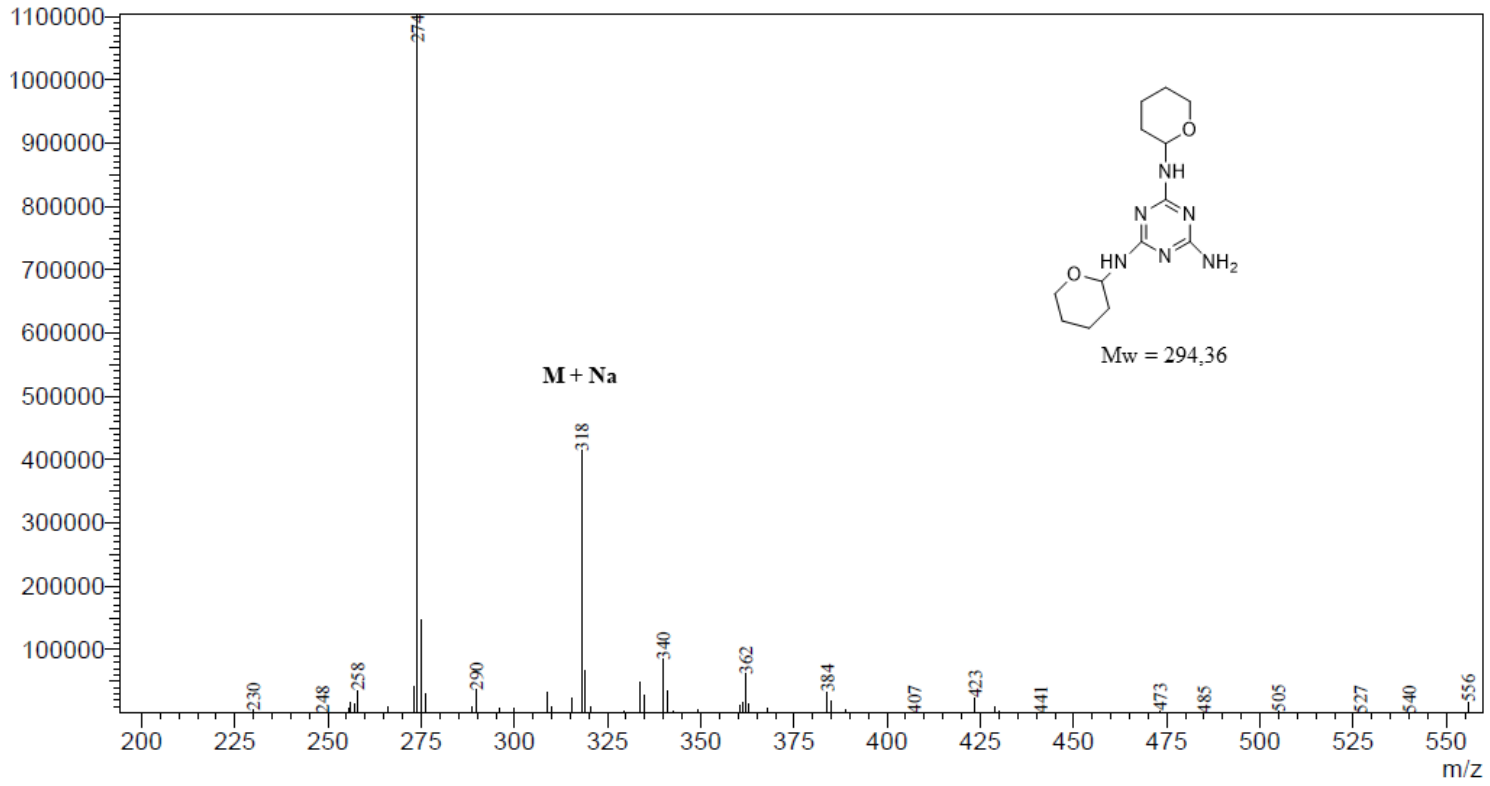

Figure A. 14. Mass Spectrum of Crude Product of the Melamine – DHP Reaction at 60 ºC.

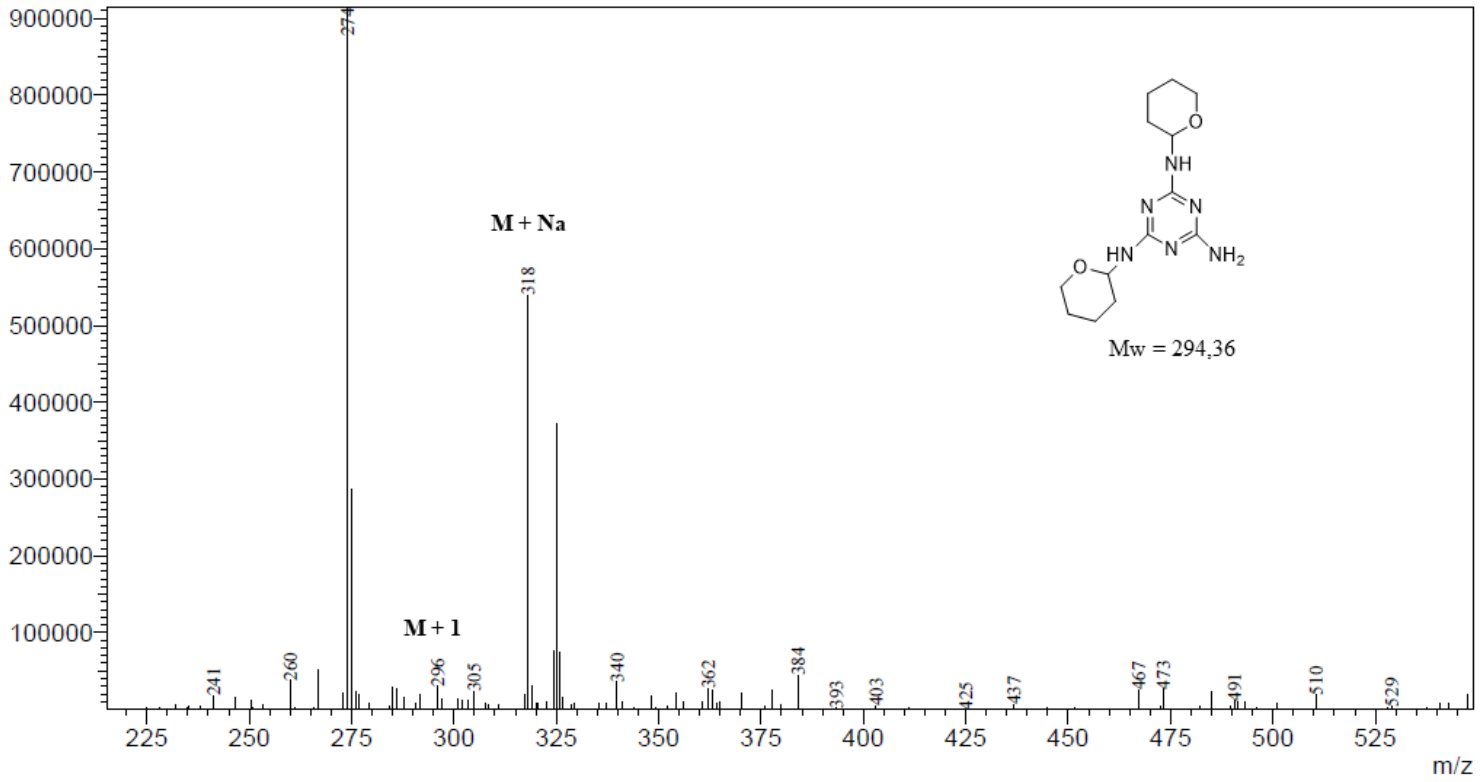

Figure A. 15. Mass Spectrum of Crude Product of the Melamine – DHP Reaction at RT.

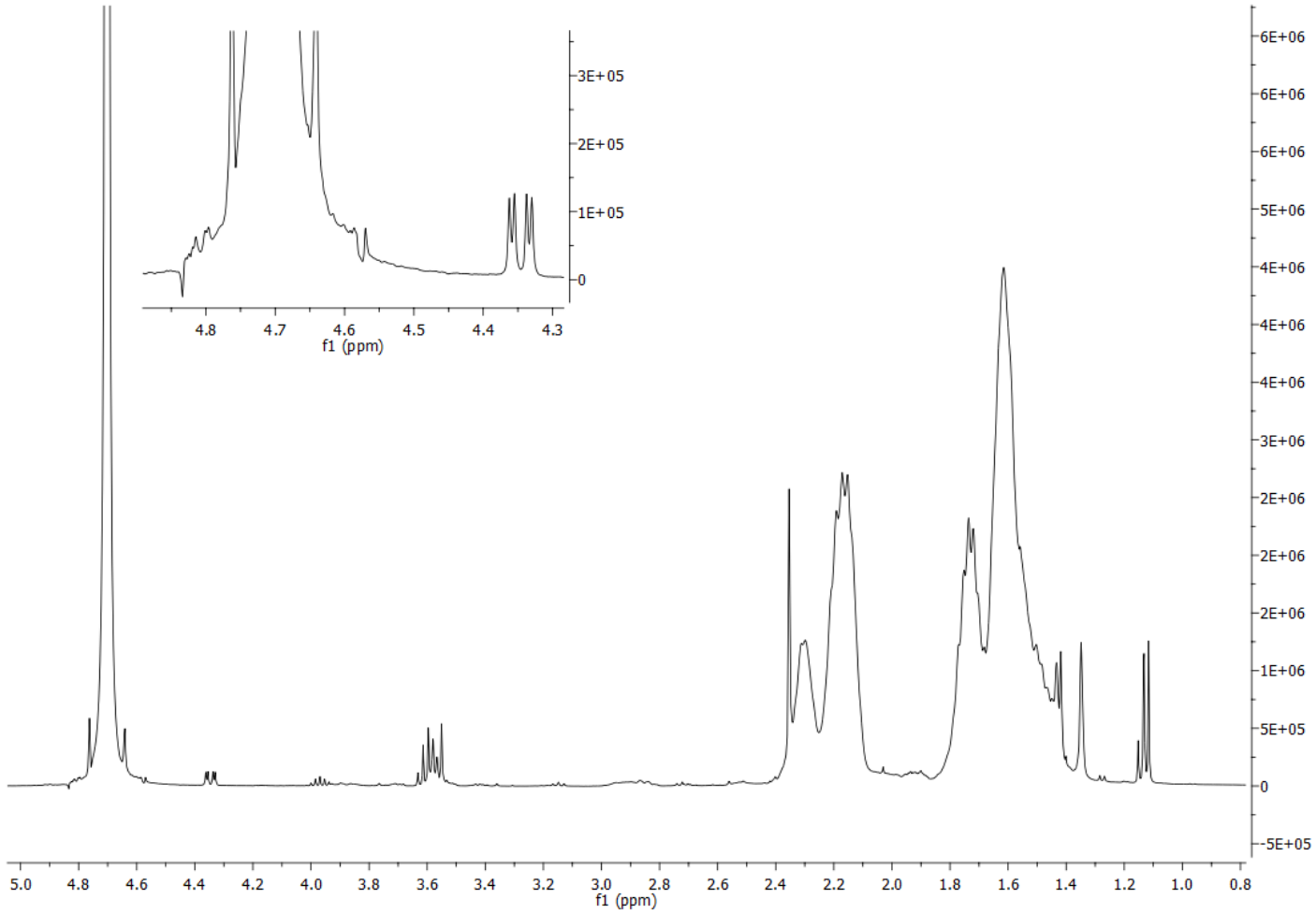

Figure A. 16. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 120 ^{o}C for 5 min. with Crosslinker.

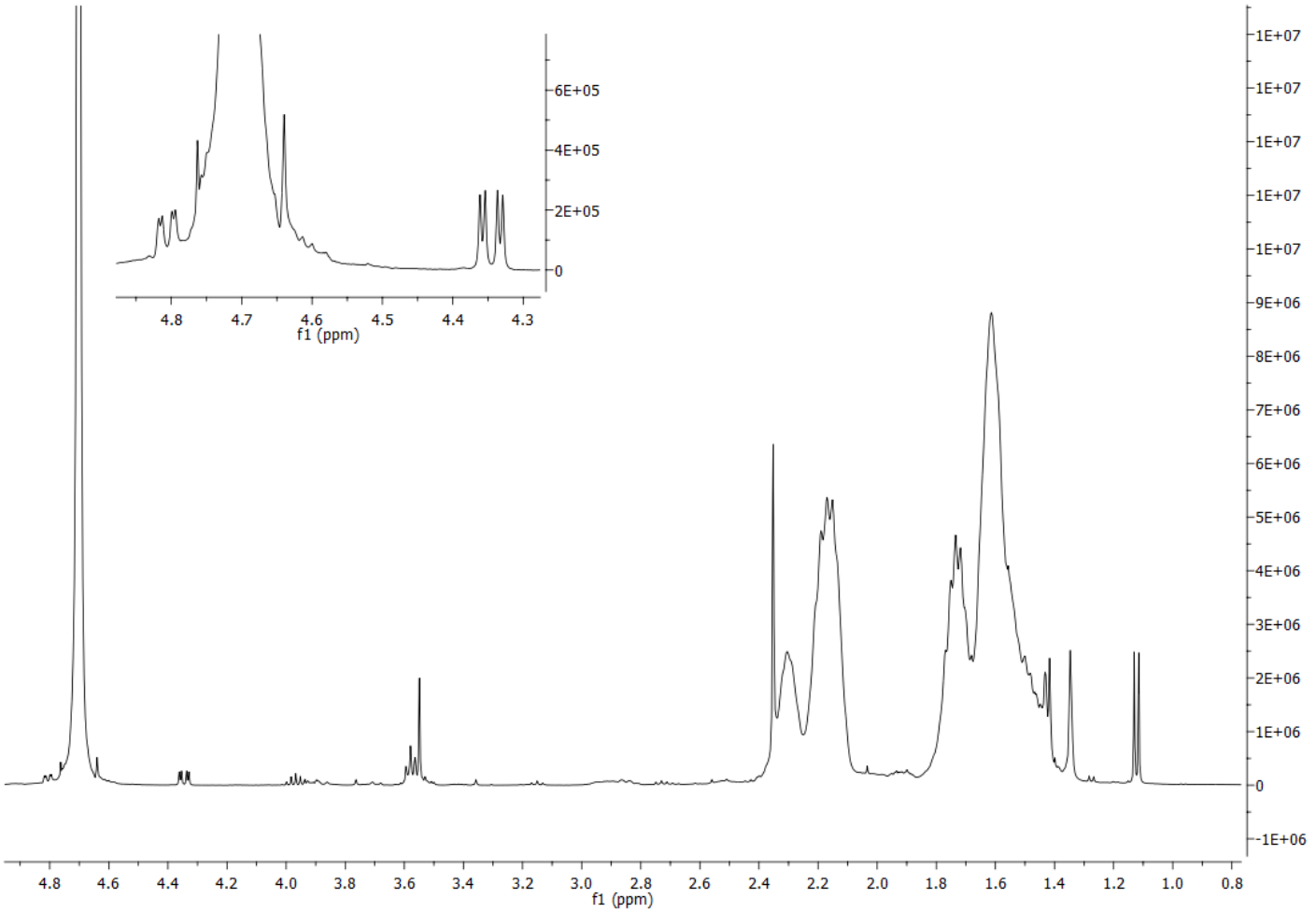

Figure A. 17. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 120 ^{o}C for 10 min. with Crosslinker.

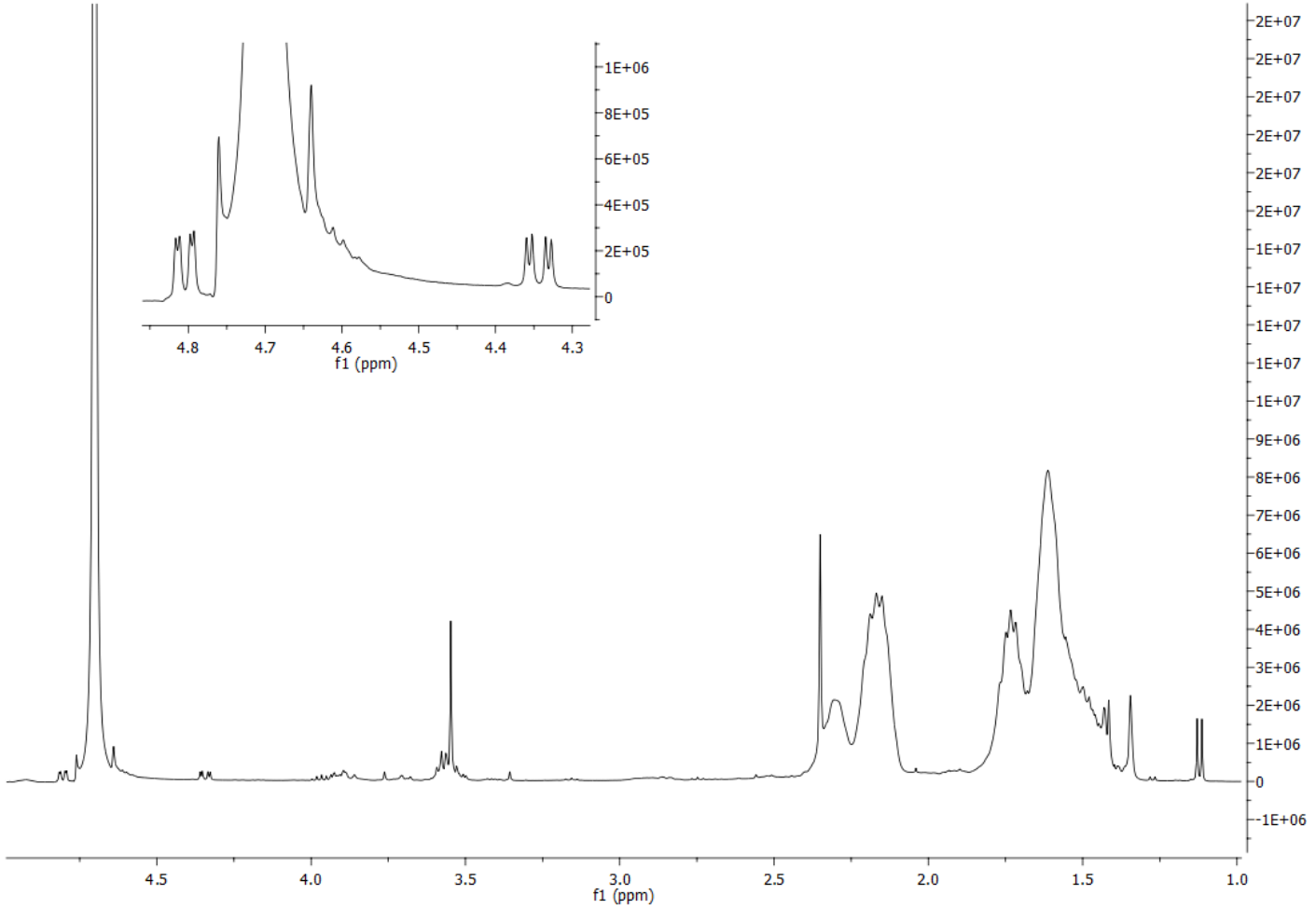

Figure A. 18. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 120 ^{o}C for 30 min. with Crosslinker.

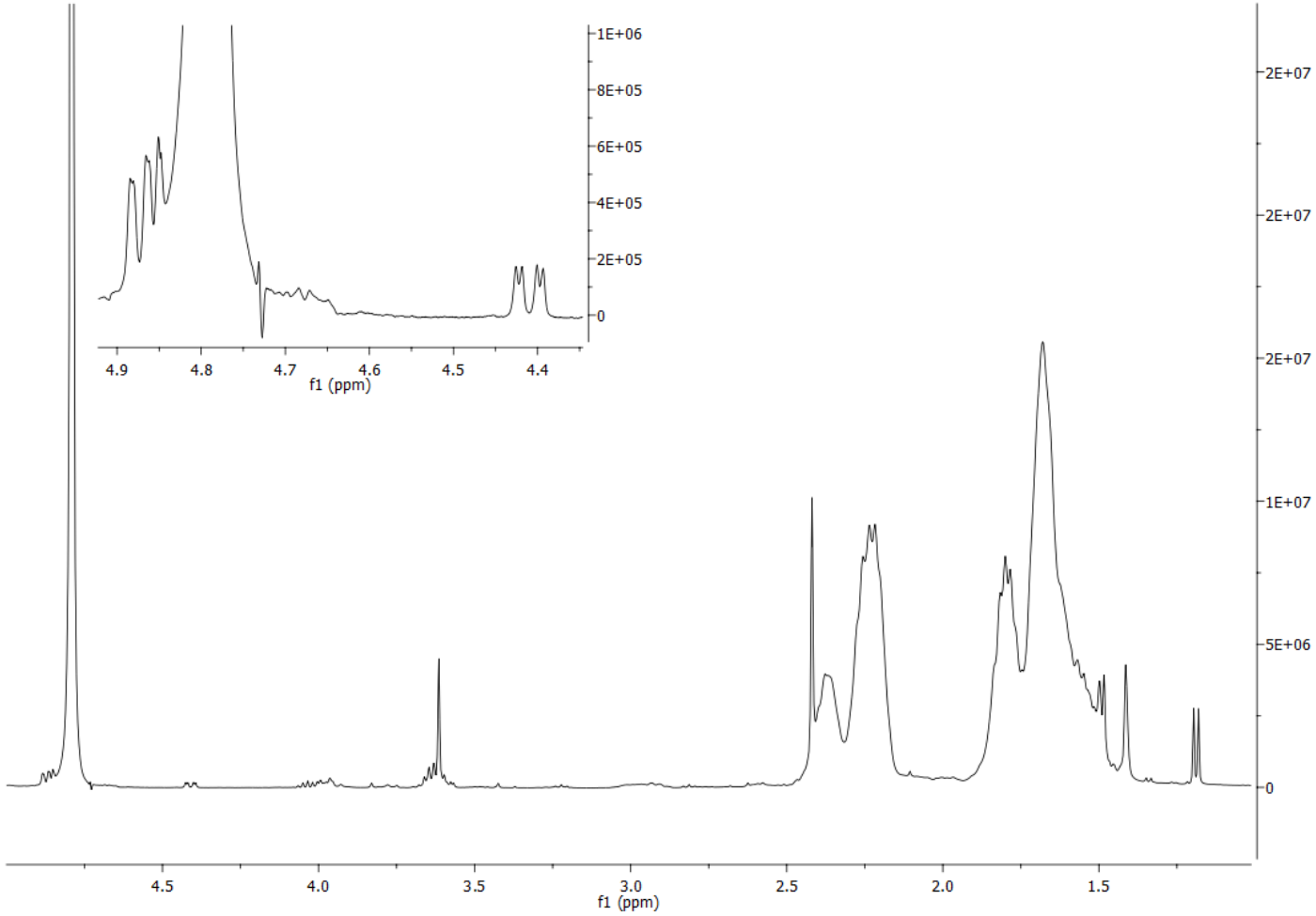

Figure A. 19. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 150 ^{o}C for 5 min. with Crosslinker.

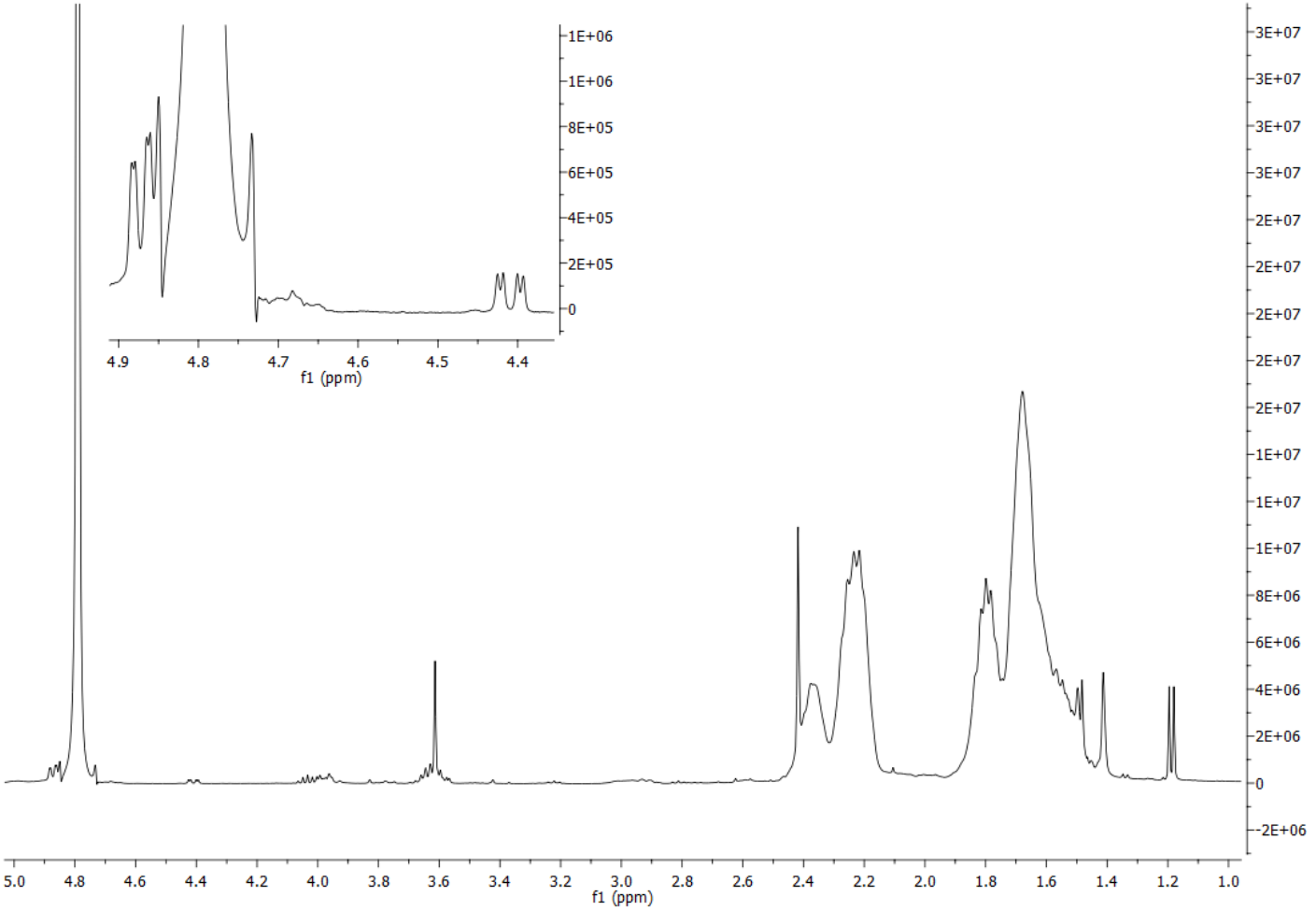

Figure A. 20. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 150 ^{o}C for 10 min. with Crosslinker.

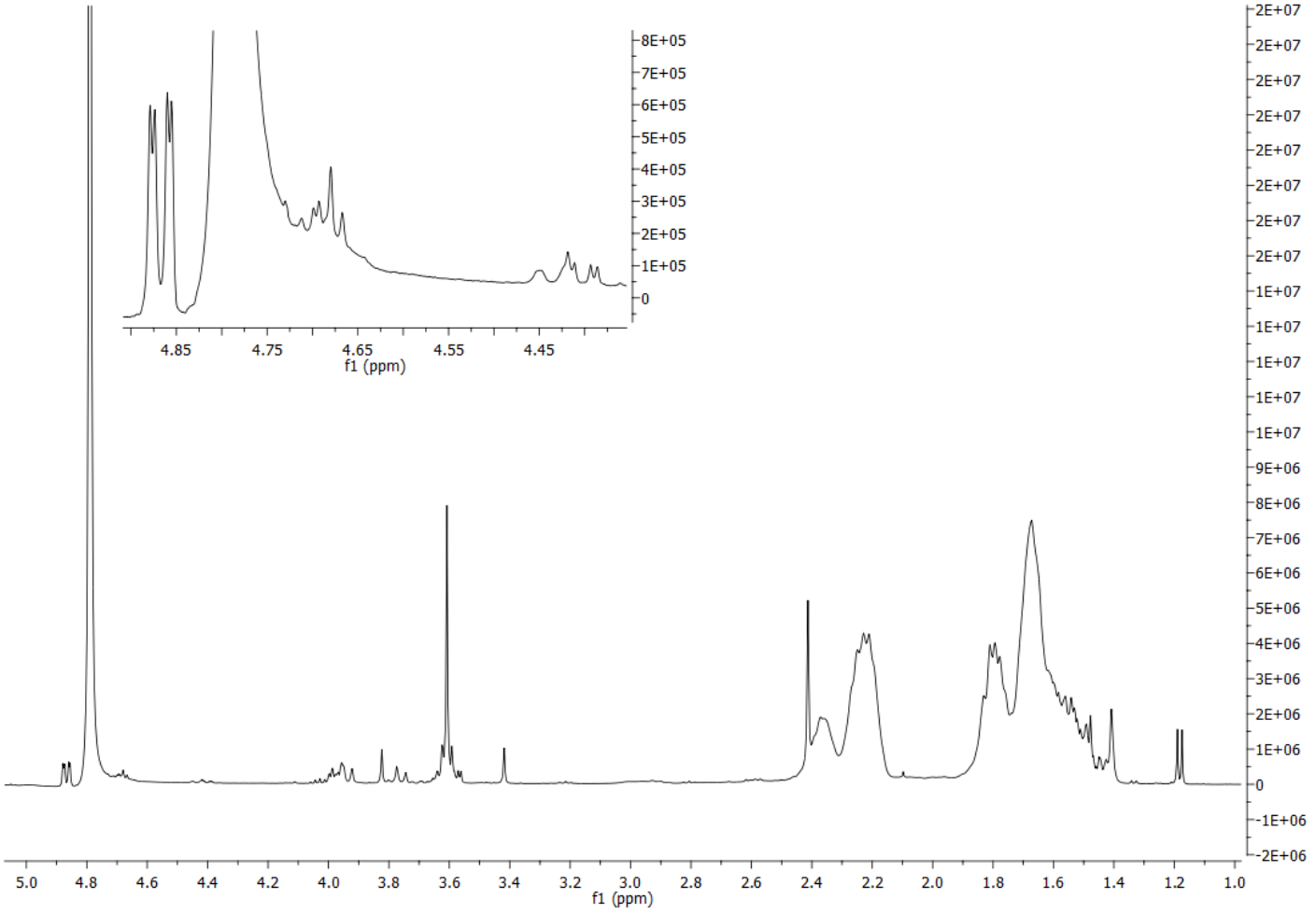

Figure A. 21. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 150 ^{o}C for 30 min. with Crosslinker.

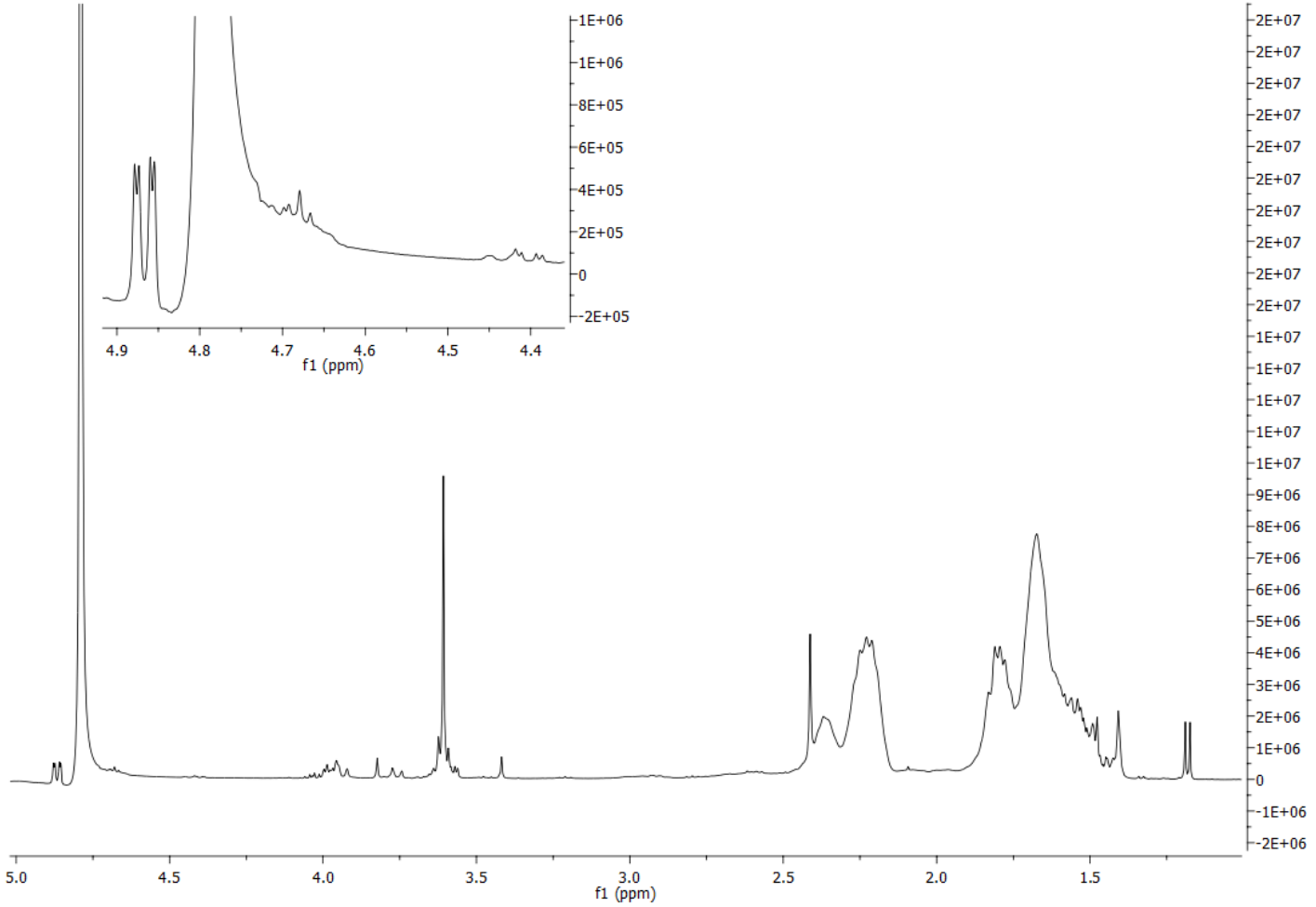

Figure A. 22. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 190 ^{o}C for 5 min. with Crosslinker.

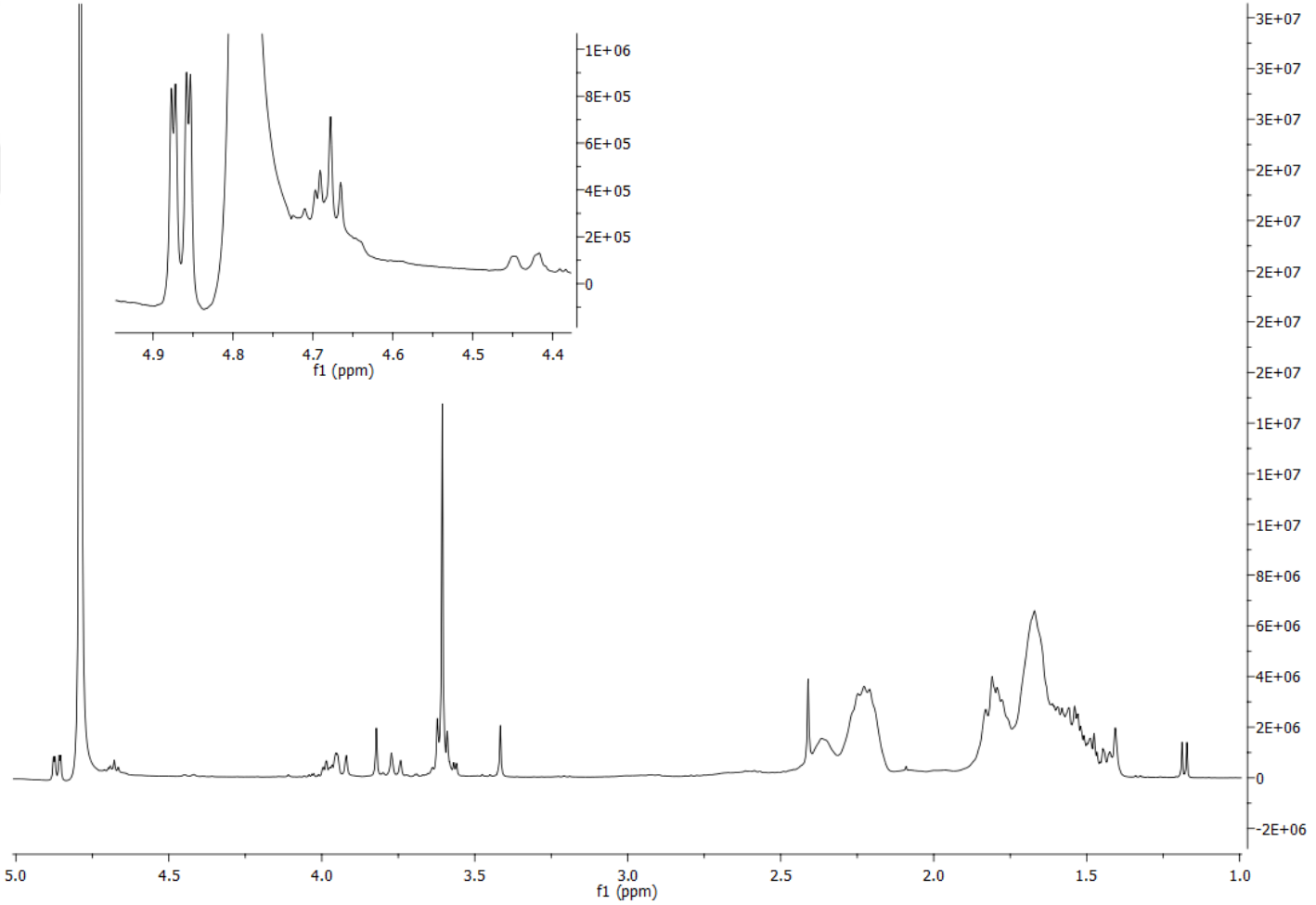

Figure A. 23. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 190 ^{o}C for 10 min. with Crosslinker.

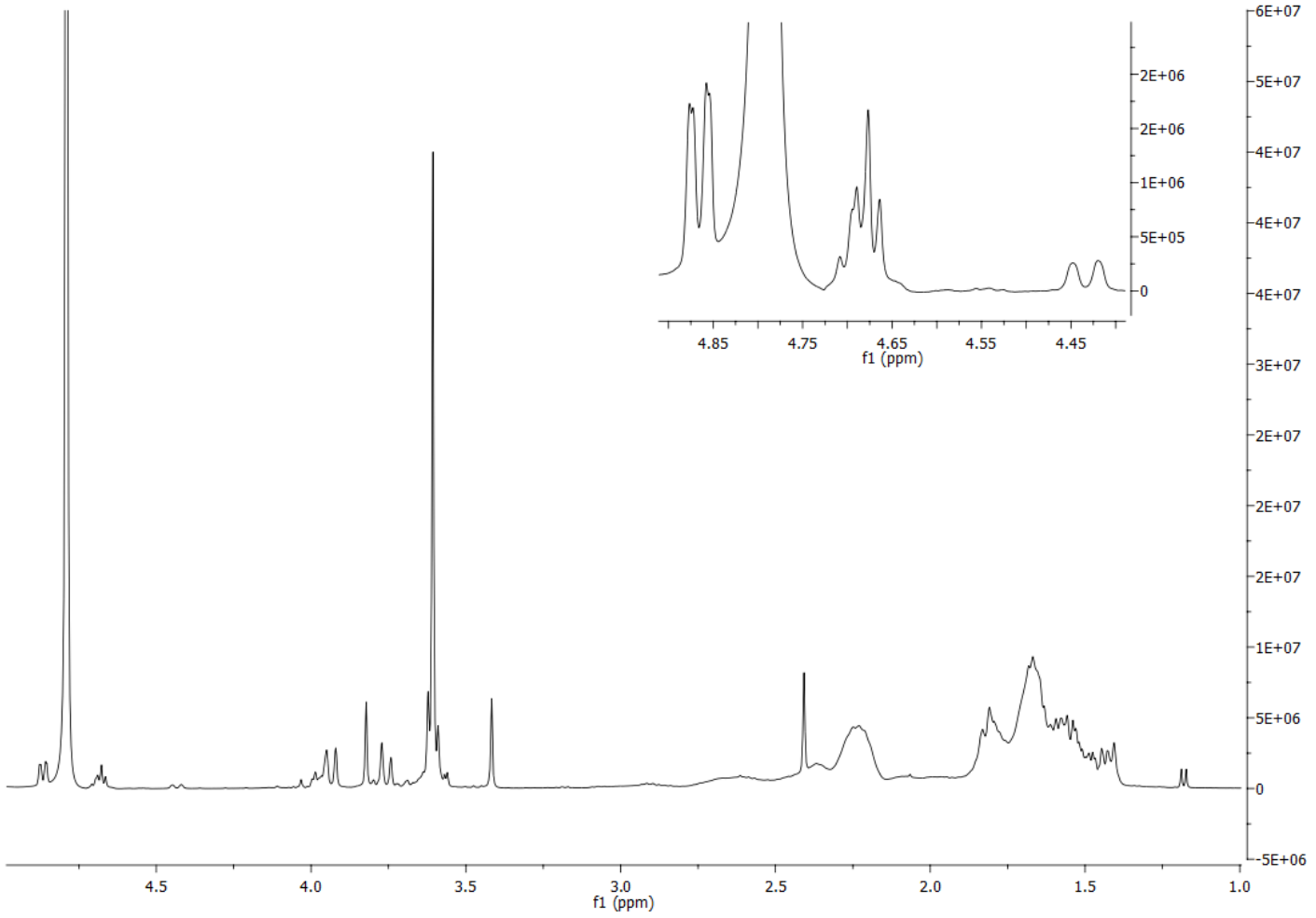

Figure A. 24. ^{1}H-NMR Spectrum of Polyacrylamide Cured at 190 ^{o}C for 30 min. with Crosslinker.

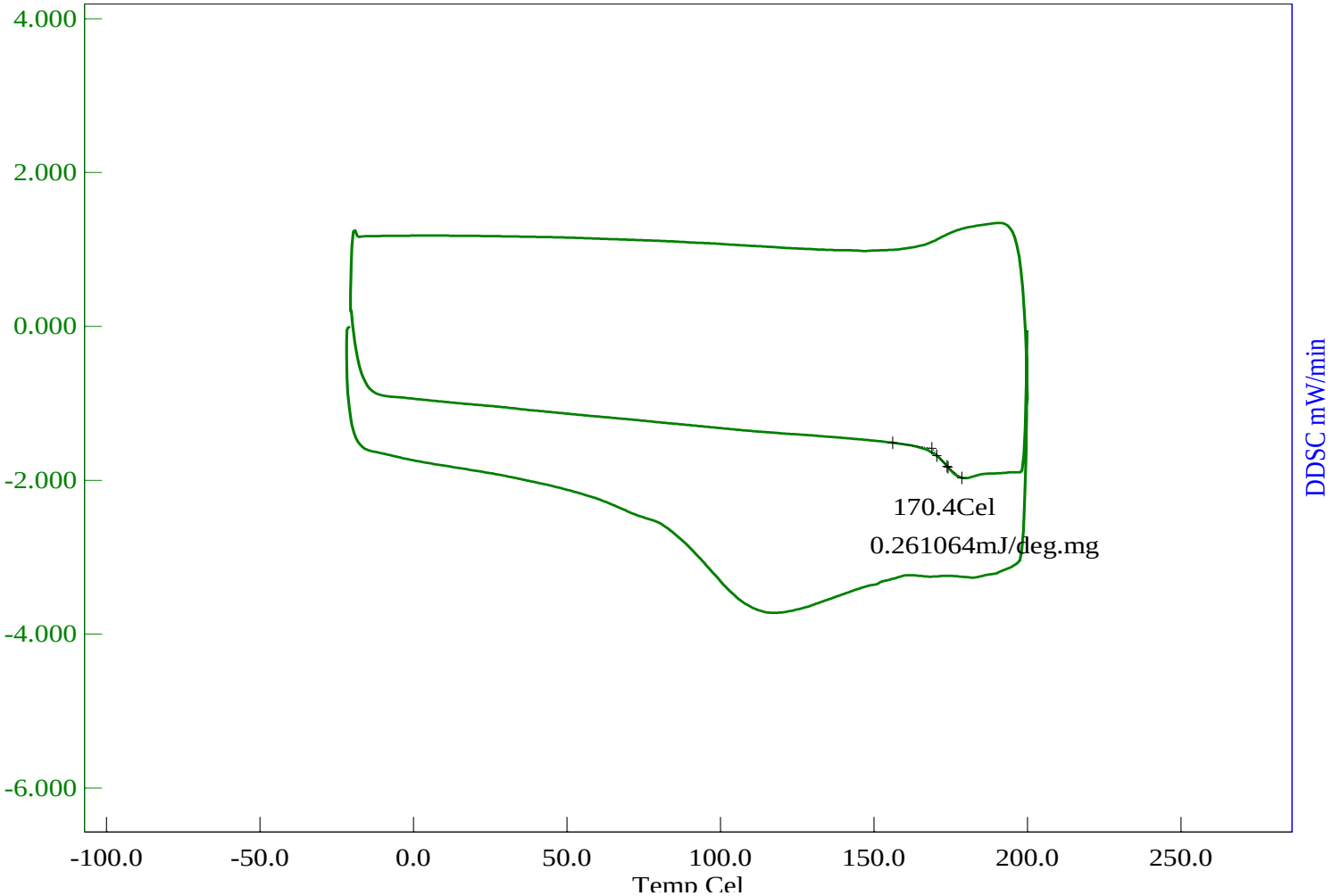

Figure A. 25. T_g Measurement of Polyacrylamide Cured at 120 ^oC for 5 min. Without Crosslinker.

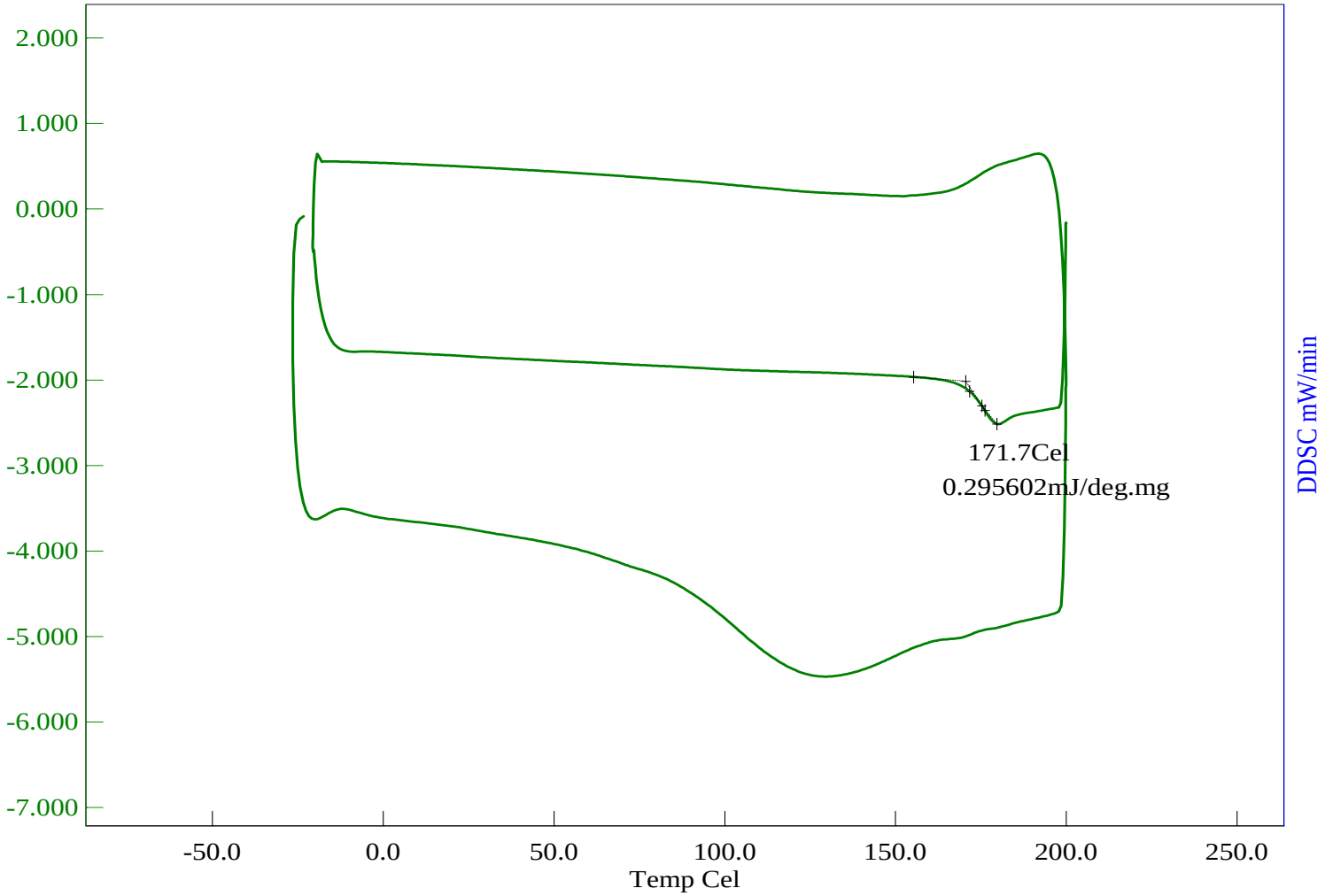

Figure A. 26. T_g Measurement of Polyacrylamide Cured at 120 ºC for 10 min. Without Crosslinker.

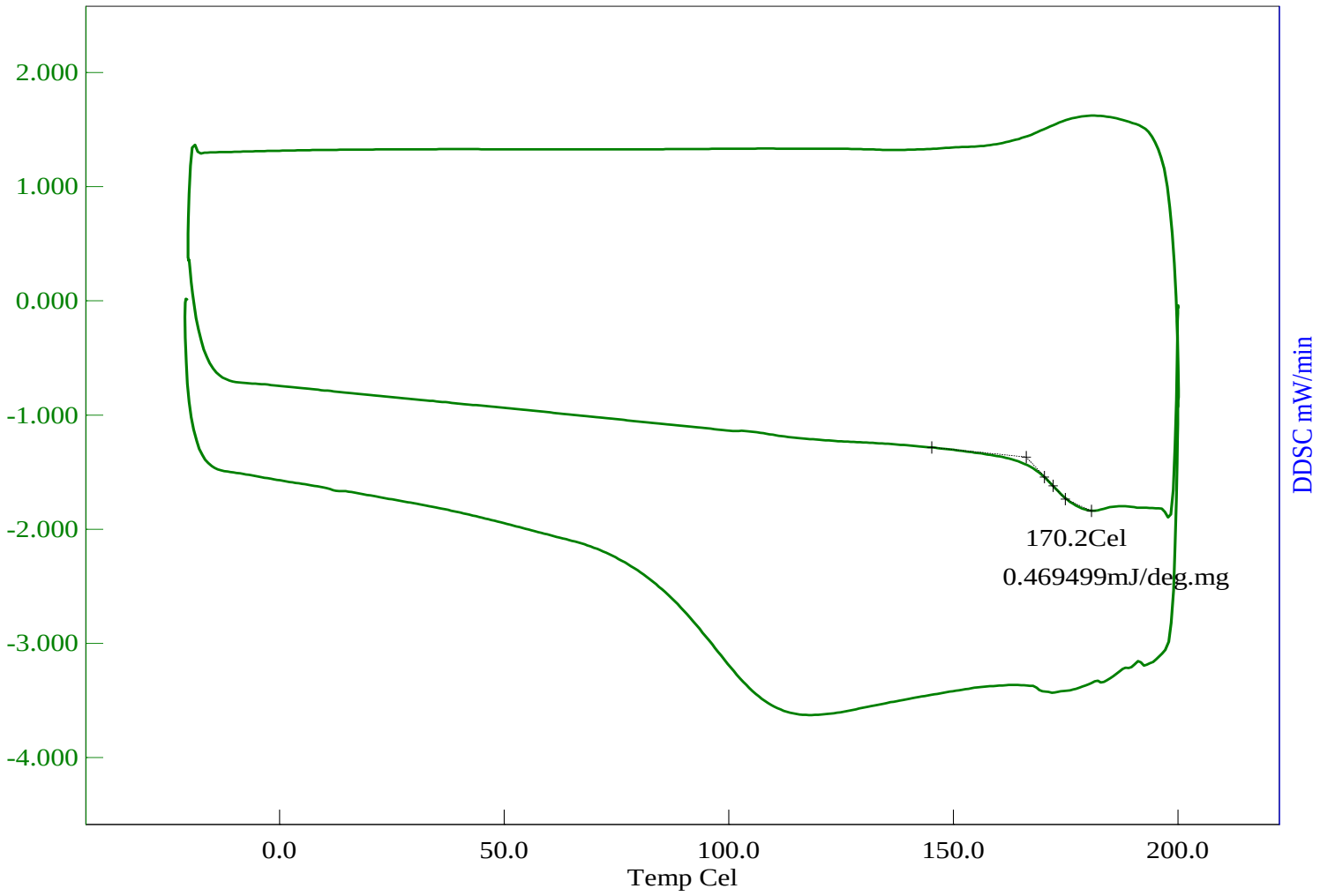

Figure A. 27. T_g Measurement of Polyacrylamide Cured at 120 ^oC for 30 min. Without Crosslinker.

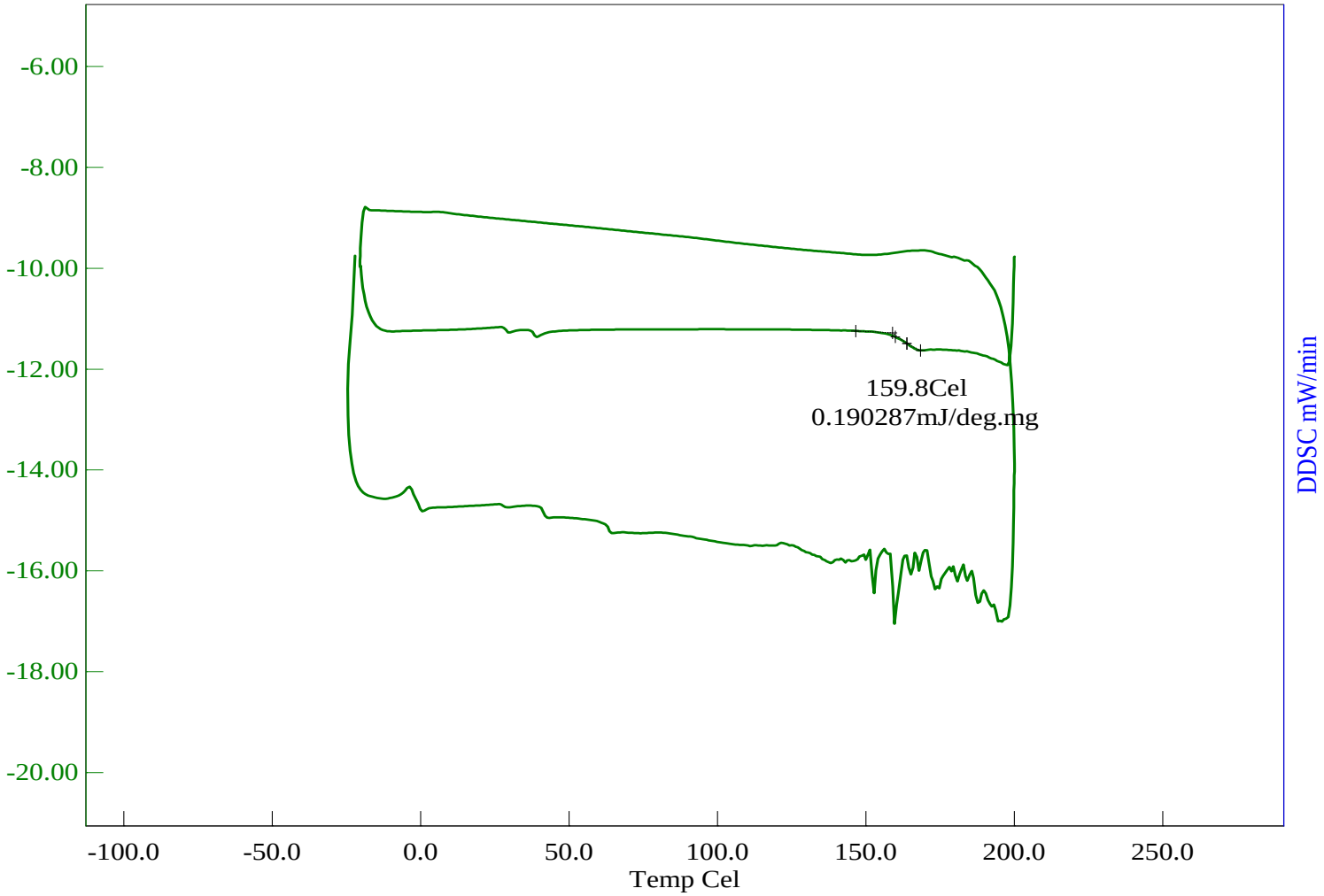

Figure A. 28. T_g Measurement of Polyacrylamide Cured at 120 ^oC for 5 min. With Crosslinker.

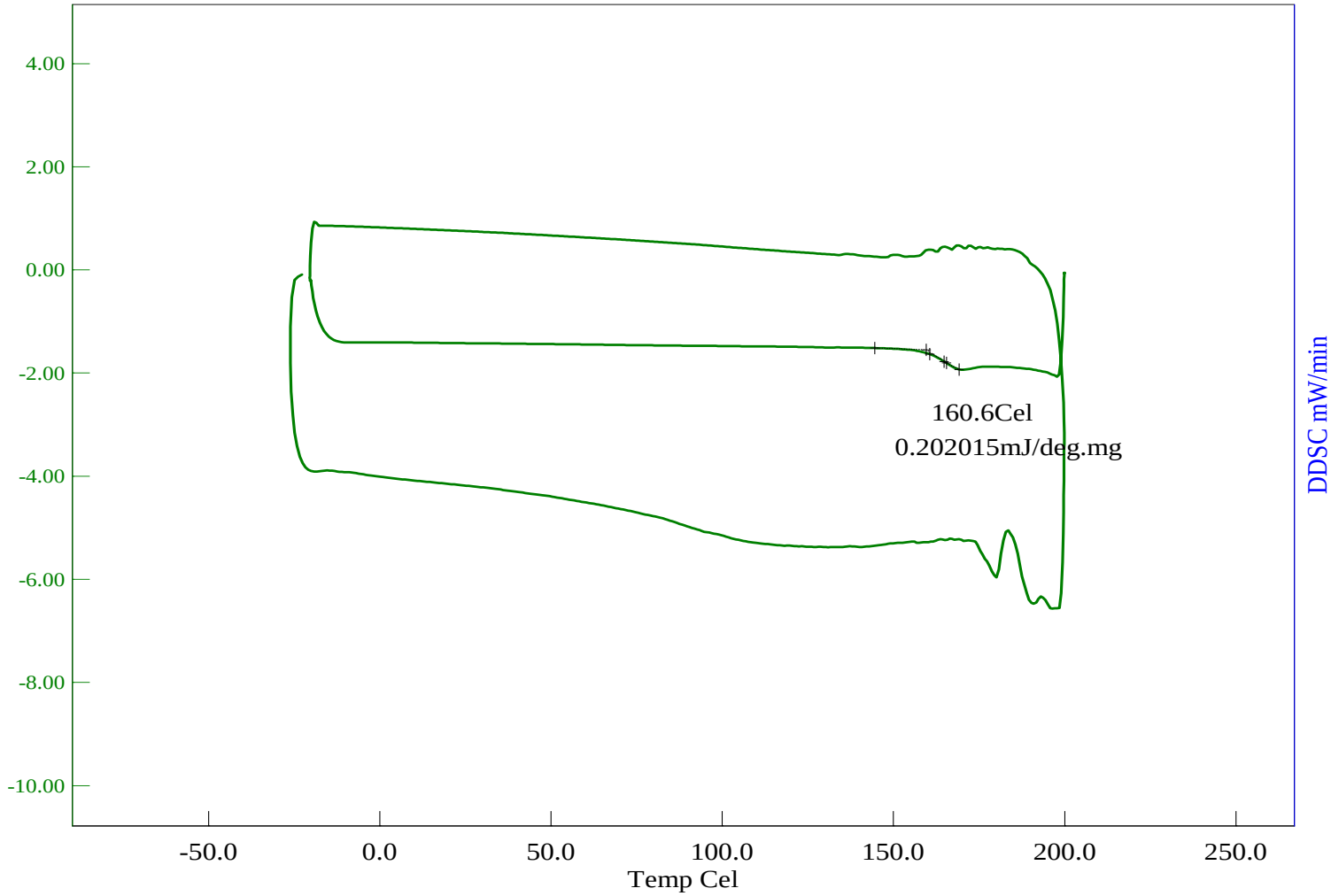

Figure A. 29. T_g Measurement of Polyacrylamide Cured at 120 ^oC for 10 min. With Crosslinker.

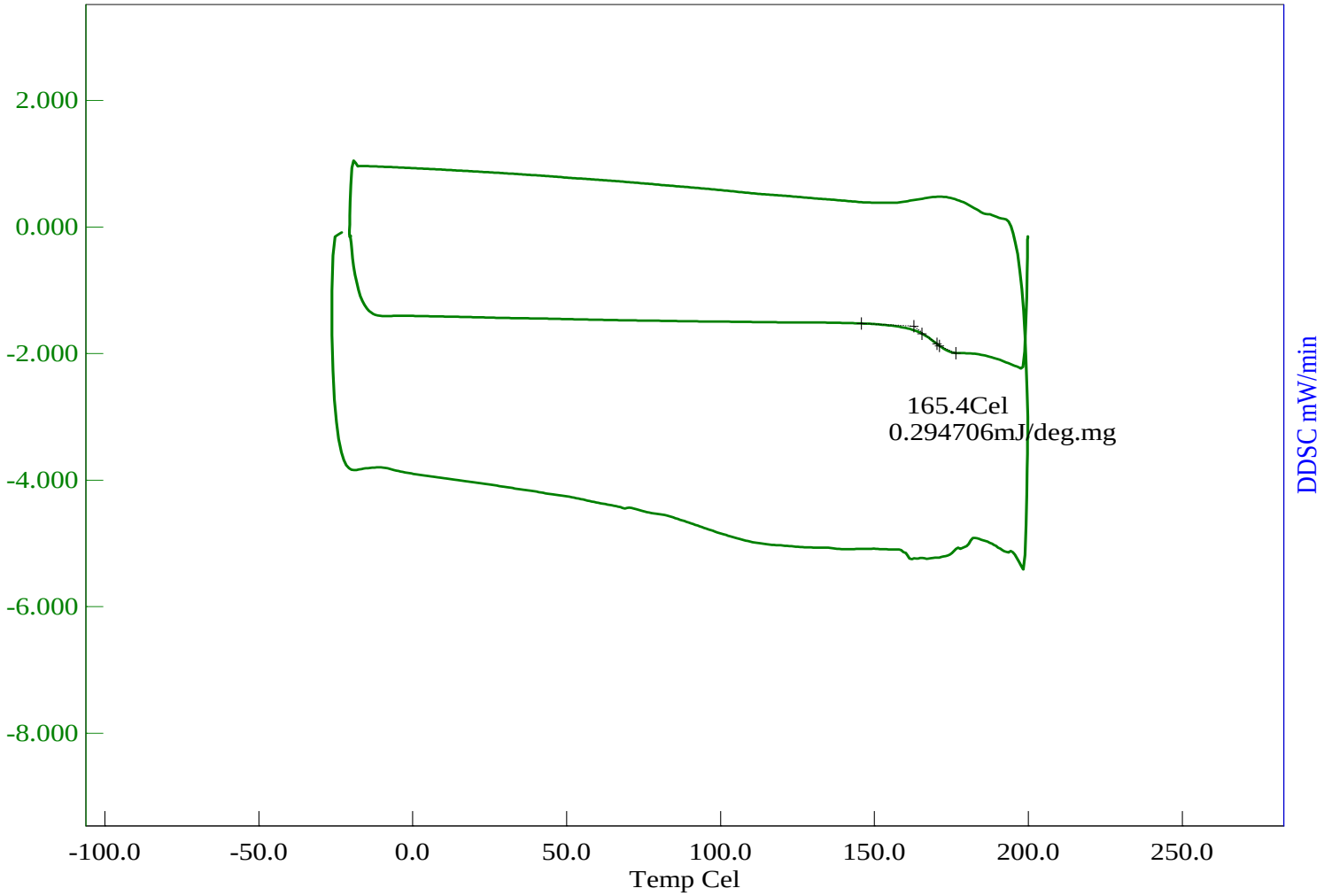

Figure A. 30. T_g Measurement of Polyacrylamide Cured at 120 ^oC for 30 min. With Crosslinker.

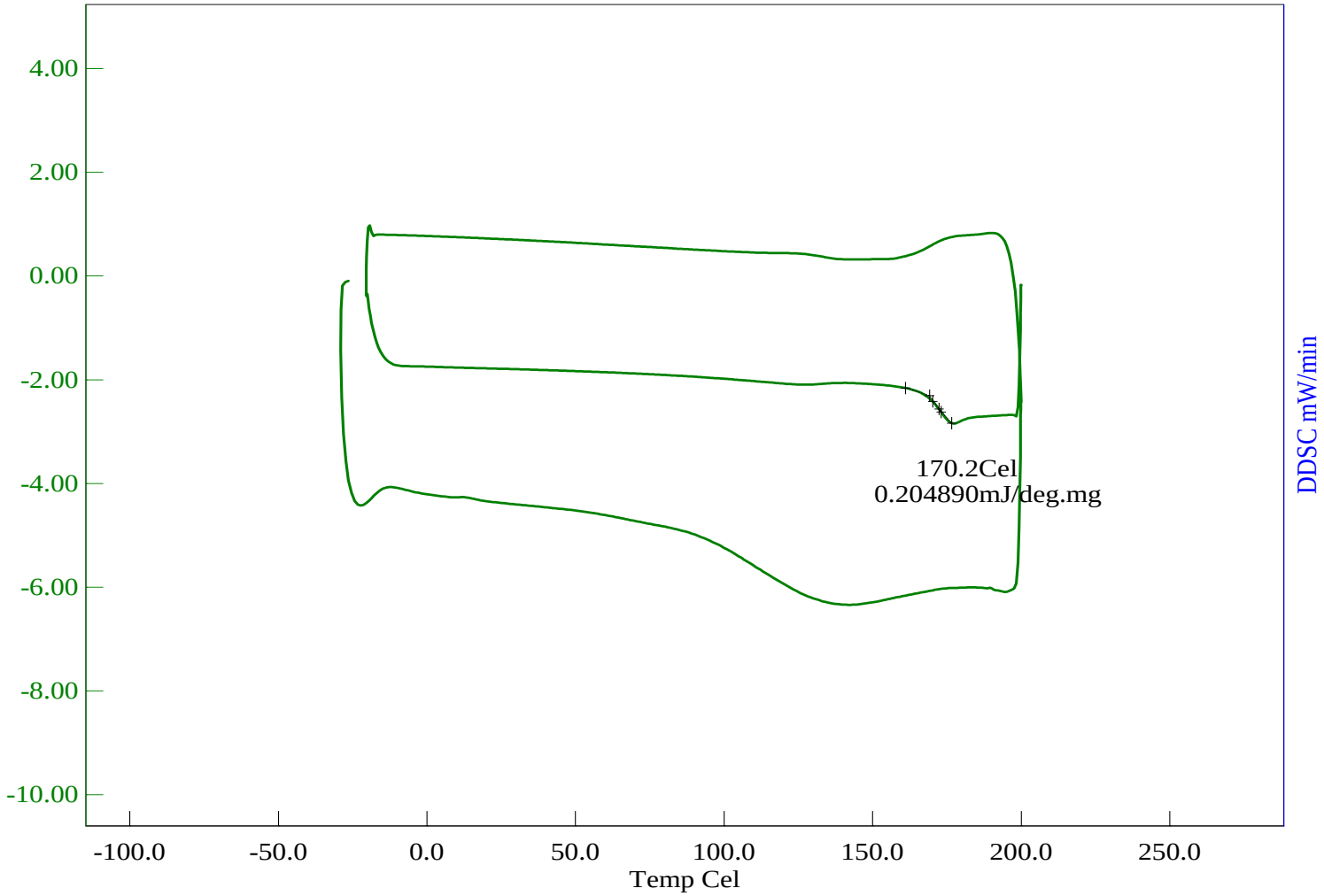

Figure A. 31. T_g Measurement of Polyacrylamide Cured at 150 ºC for 5 min. Without Crosslinker.

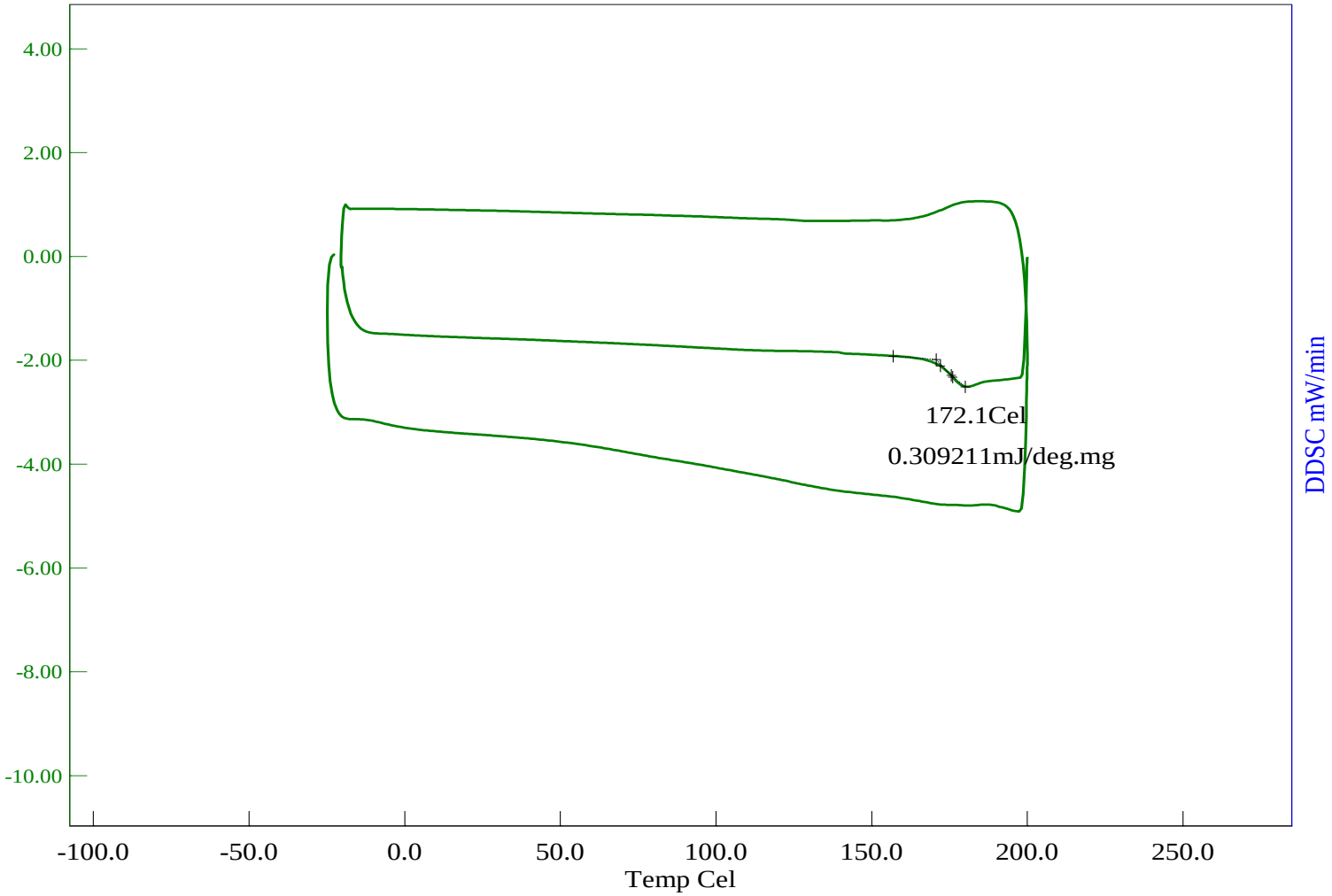

Figure A. 32. T_g Measurement of Polyacrylamide Cured at 150 ºC for 10 min. Without Crosslinker.

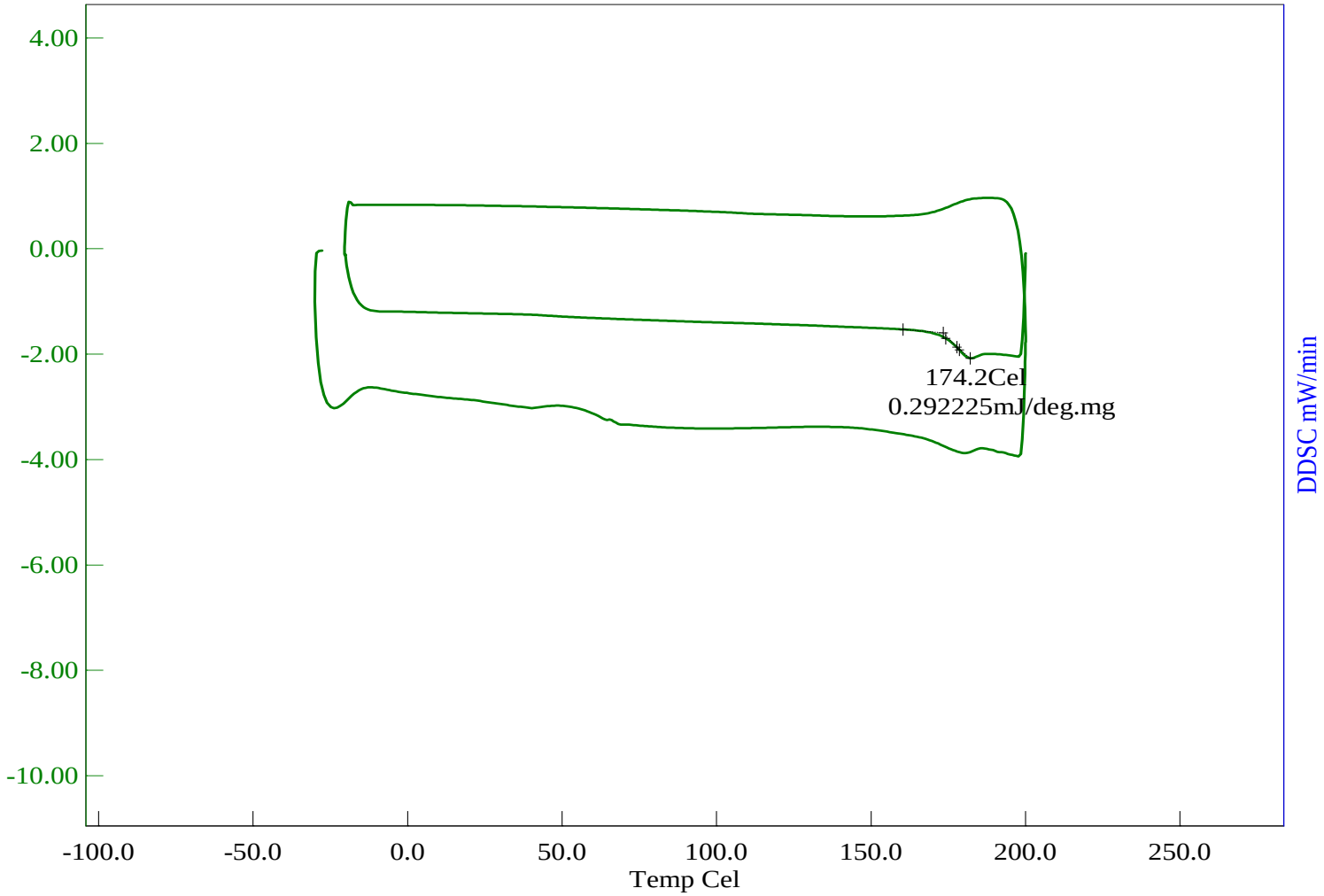

Figure A. 33. T_g Measurement of Polyacrylamide Cured at 150 ºC for 30 min. Without Crosslinker.

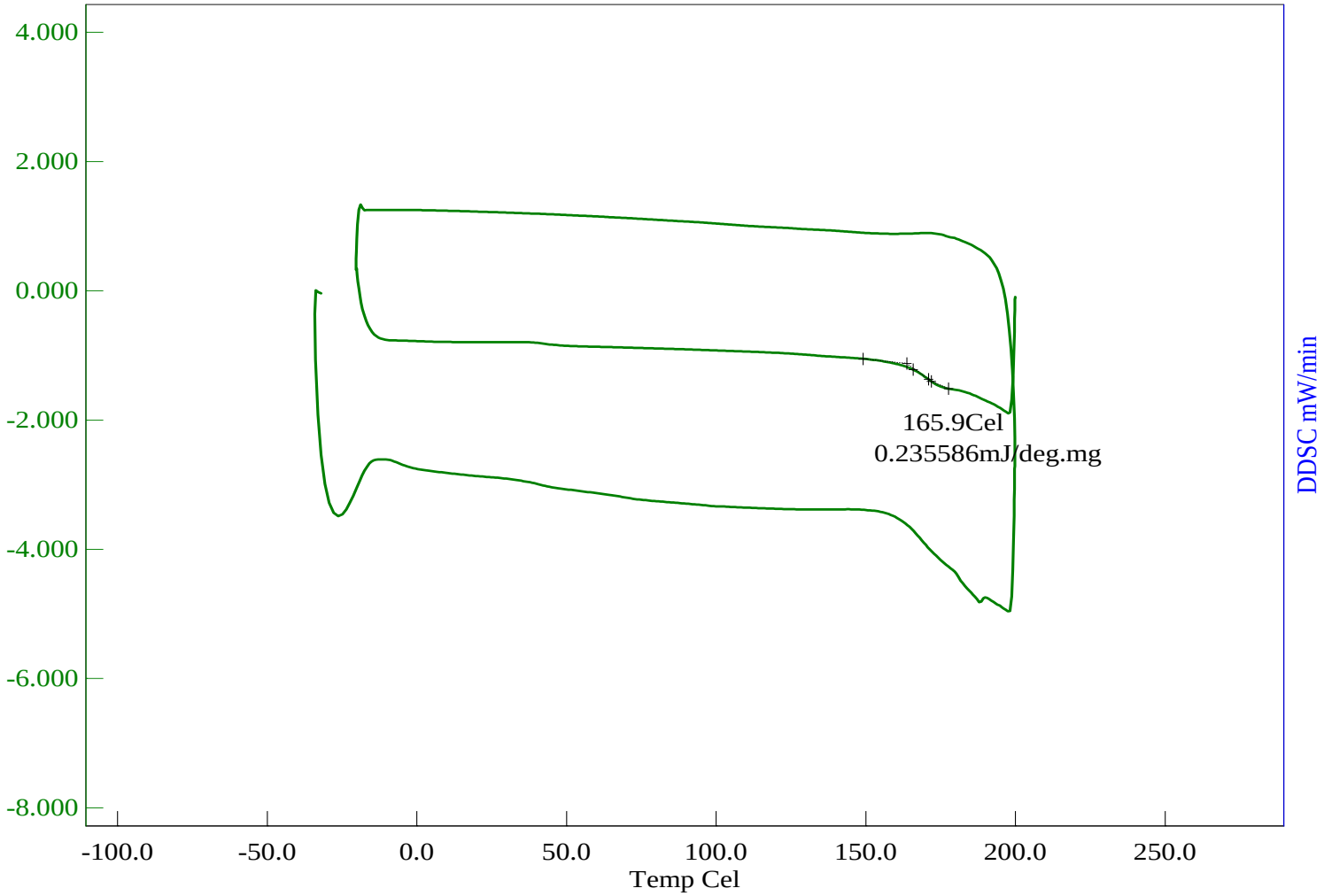

Figure A. 34. T_g Measurement of Polyacrylamide Cured at 150 ^oC for 5 min. With Crosslinker.

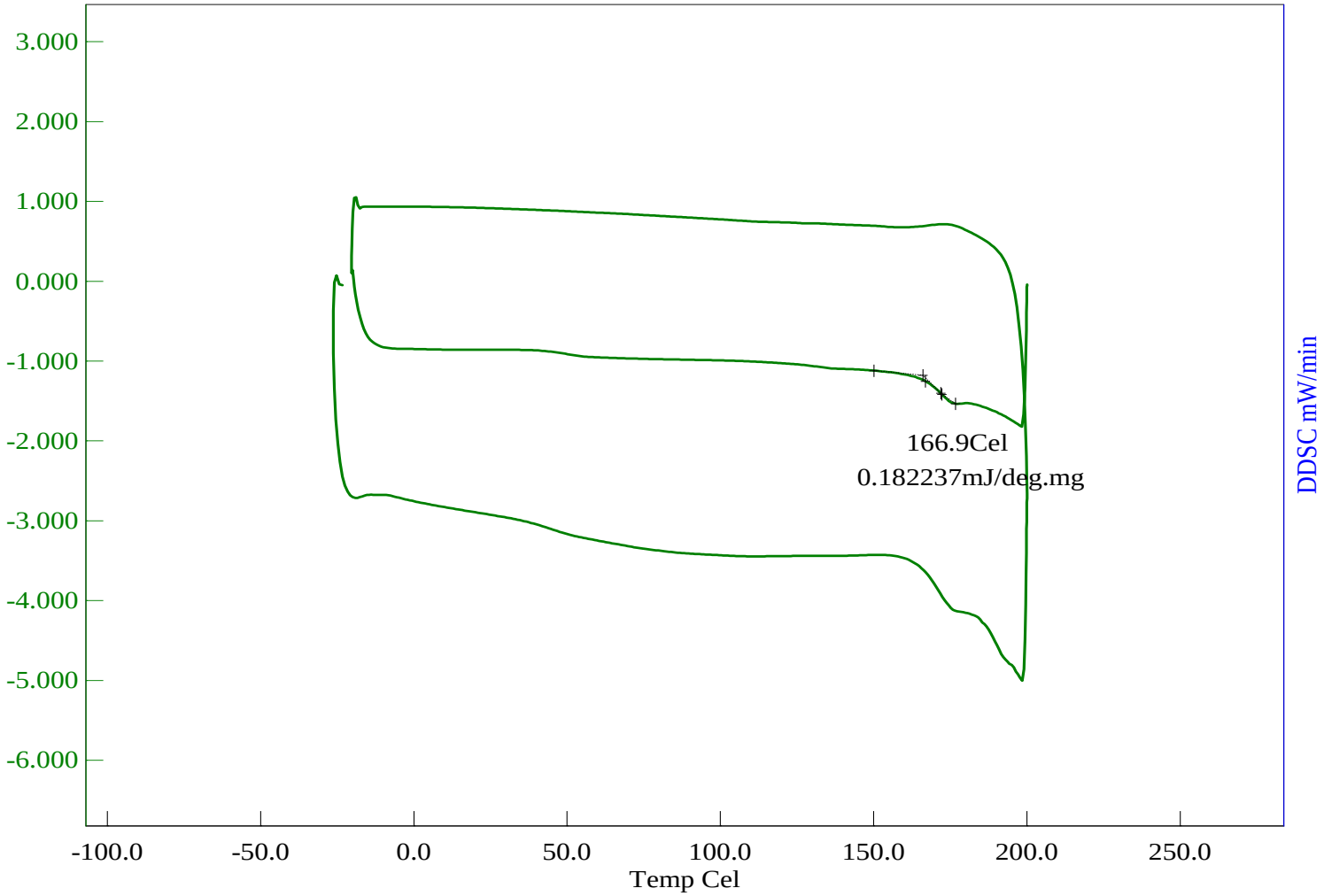

Figure A. 35. T_g Measurement of Polyacrylamide Cured at 150 ^oC for 10 min. With Crosslinker.

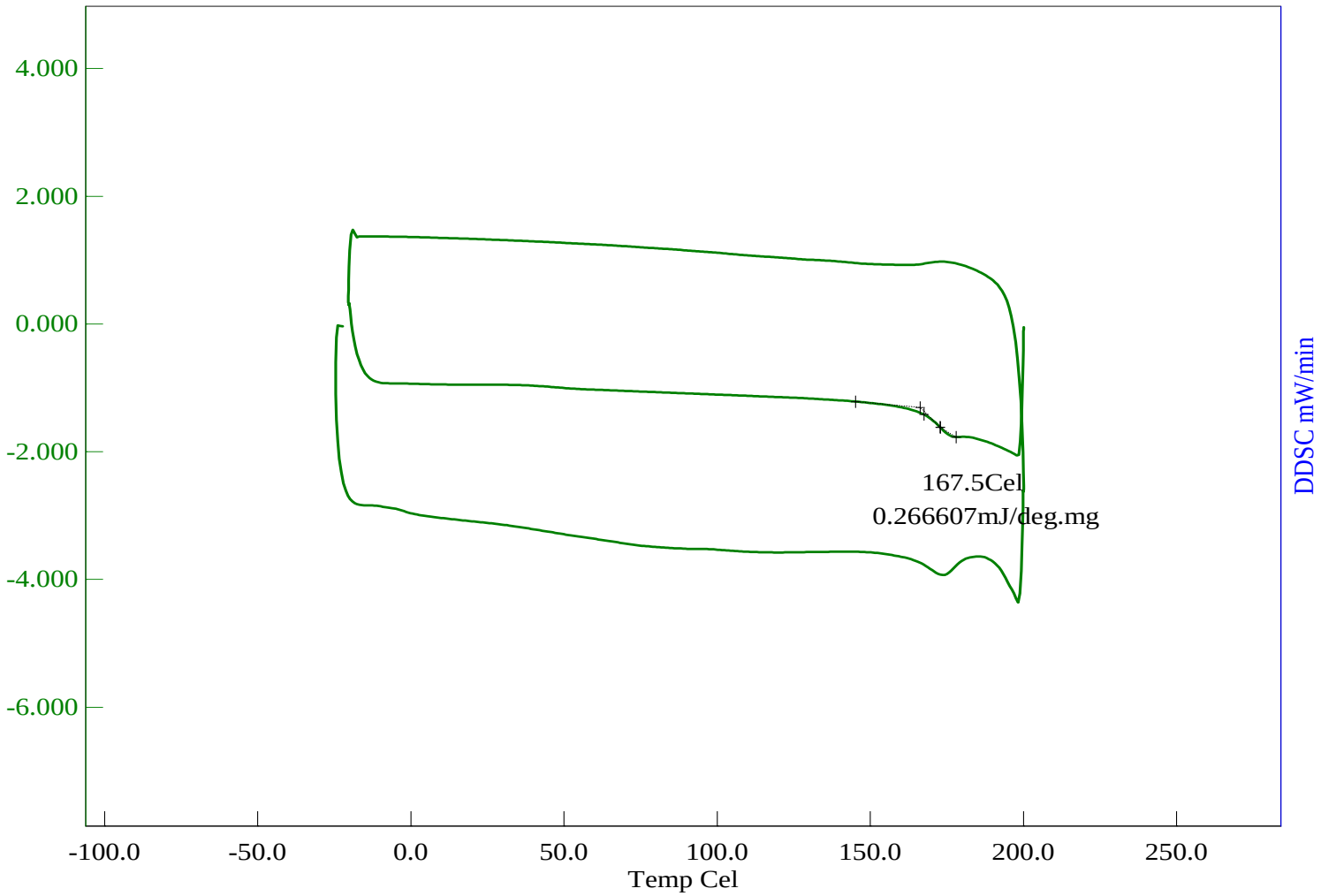

Figure A. 36. T_g Measurement of Polyacrylamide Cured at 150 ^oC for 30 min. With Crosslinker.

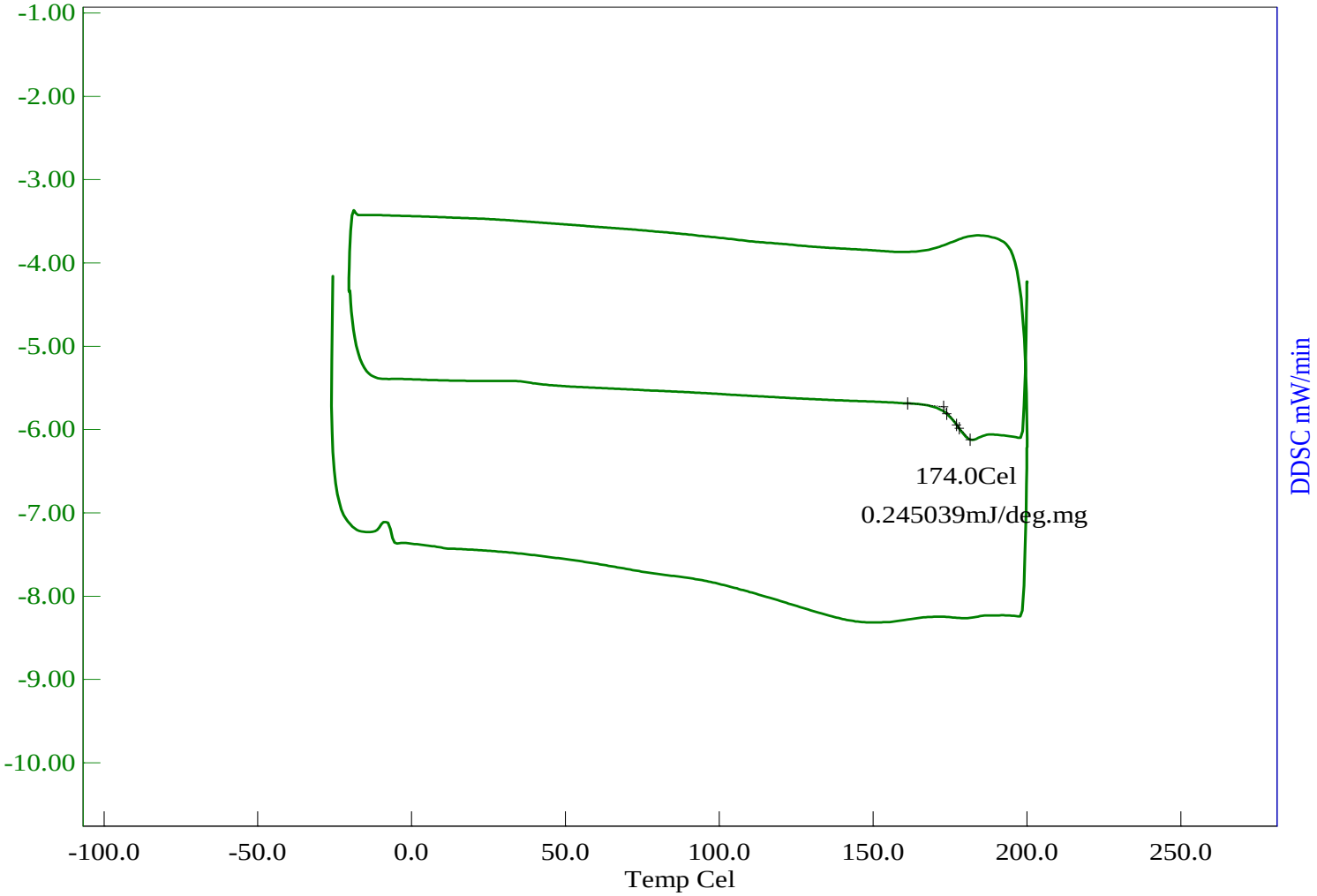

Figure A. 37. T_g Measurement of Polyacrylamide Cured at 190 ºC for 5 min. Without Crosslinker.

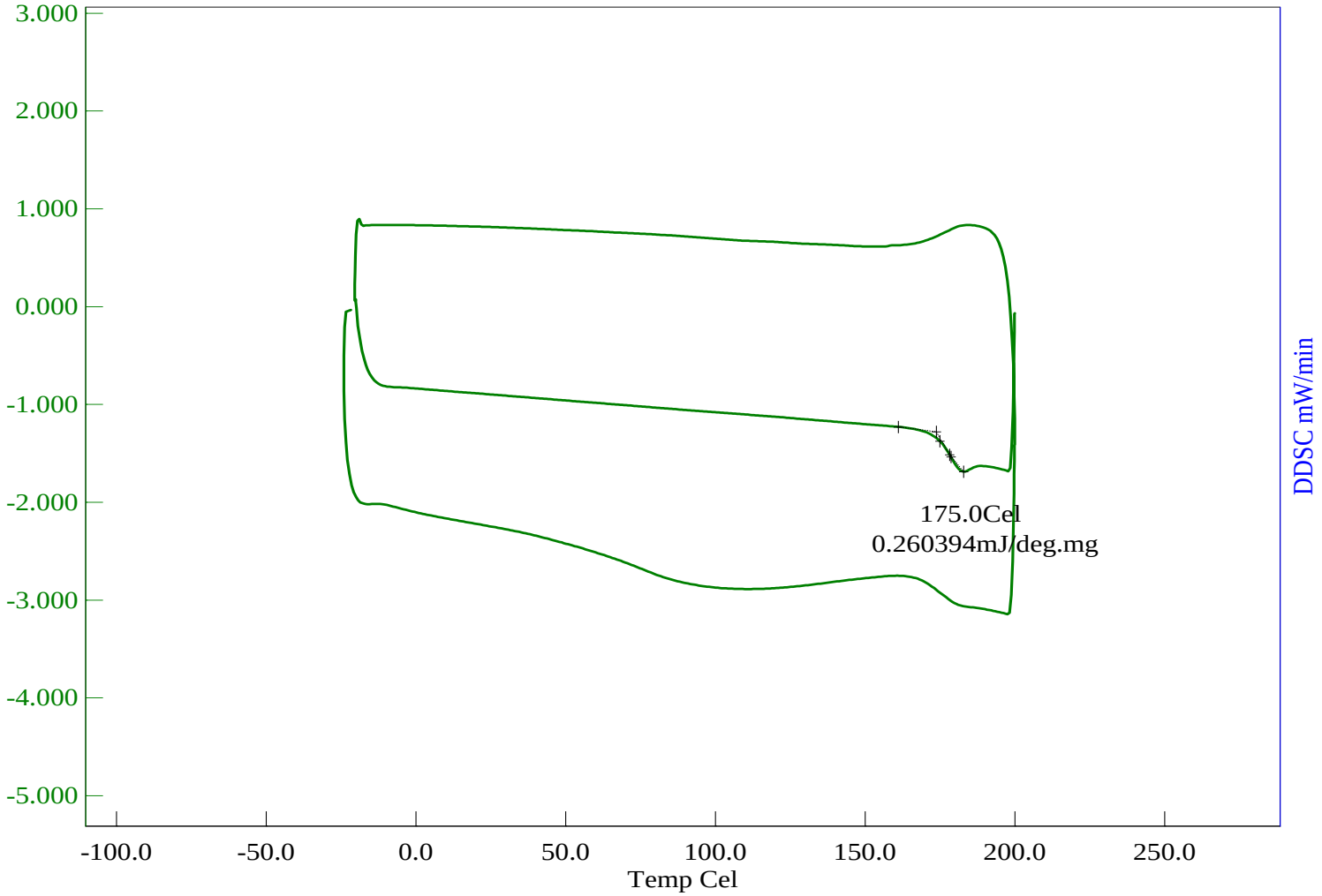

Figure A. 38. T_g Measurement of Polyacrylamide Cured at 190 ºC for 10 min. Without Crosslinker.

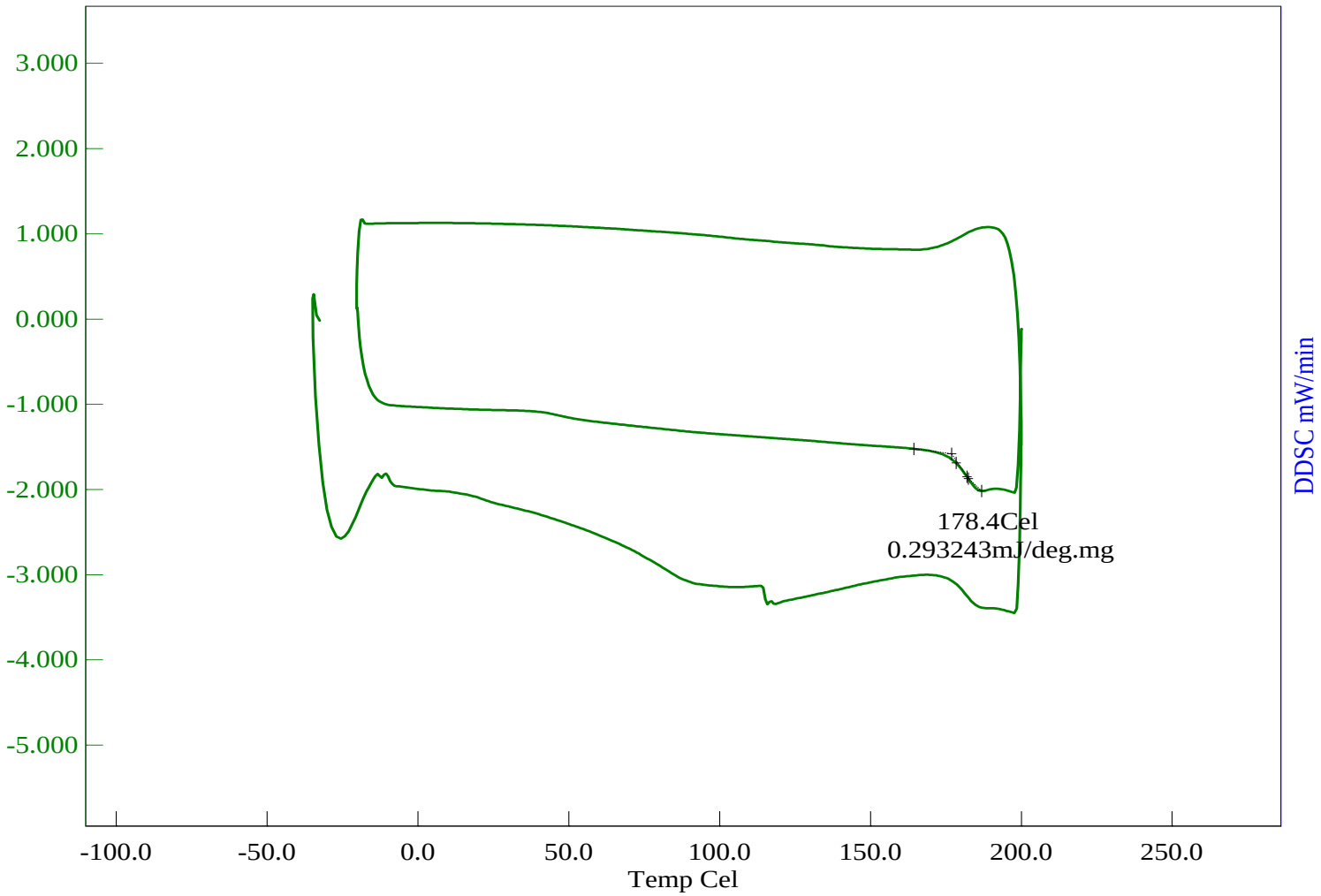

Figure A. 39. T_g Measurement of Polyacrylamide Cured at 190 ºC for 30 min. Without Crosslinker.

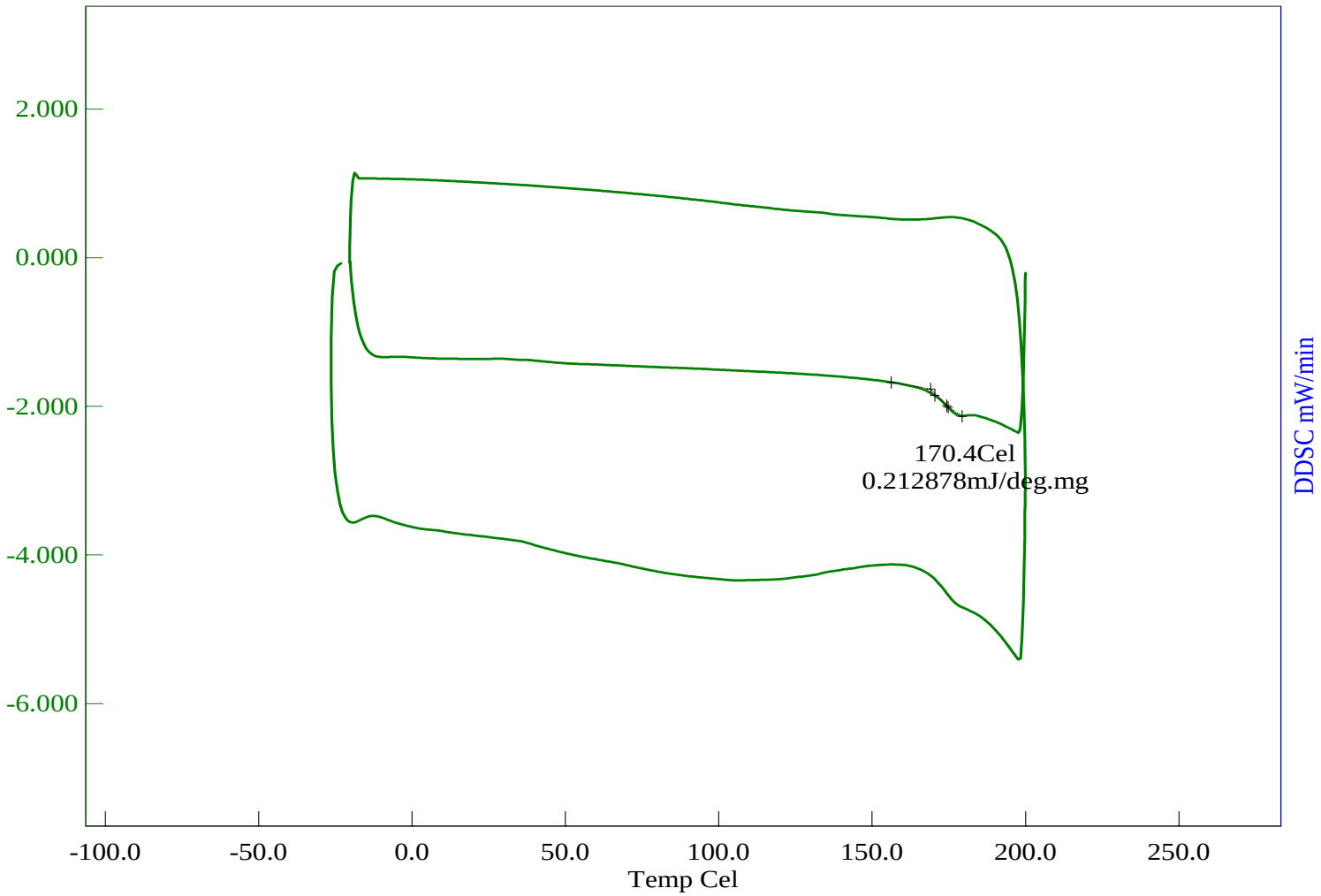

Figure A. 40. T_g Measurement of Polyacrylamide Cured at 190 ^oC for 5 min. With Crosslinker.

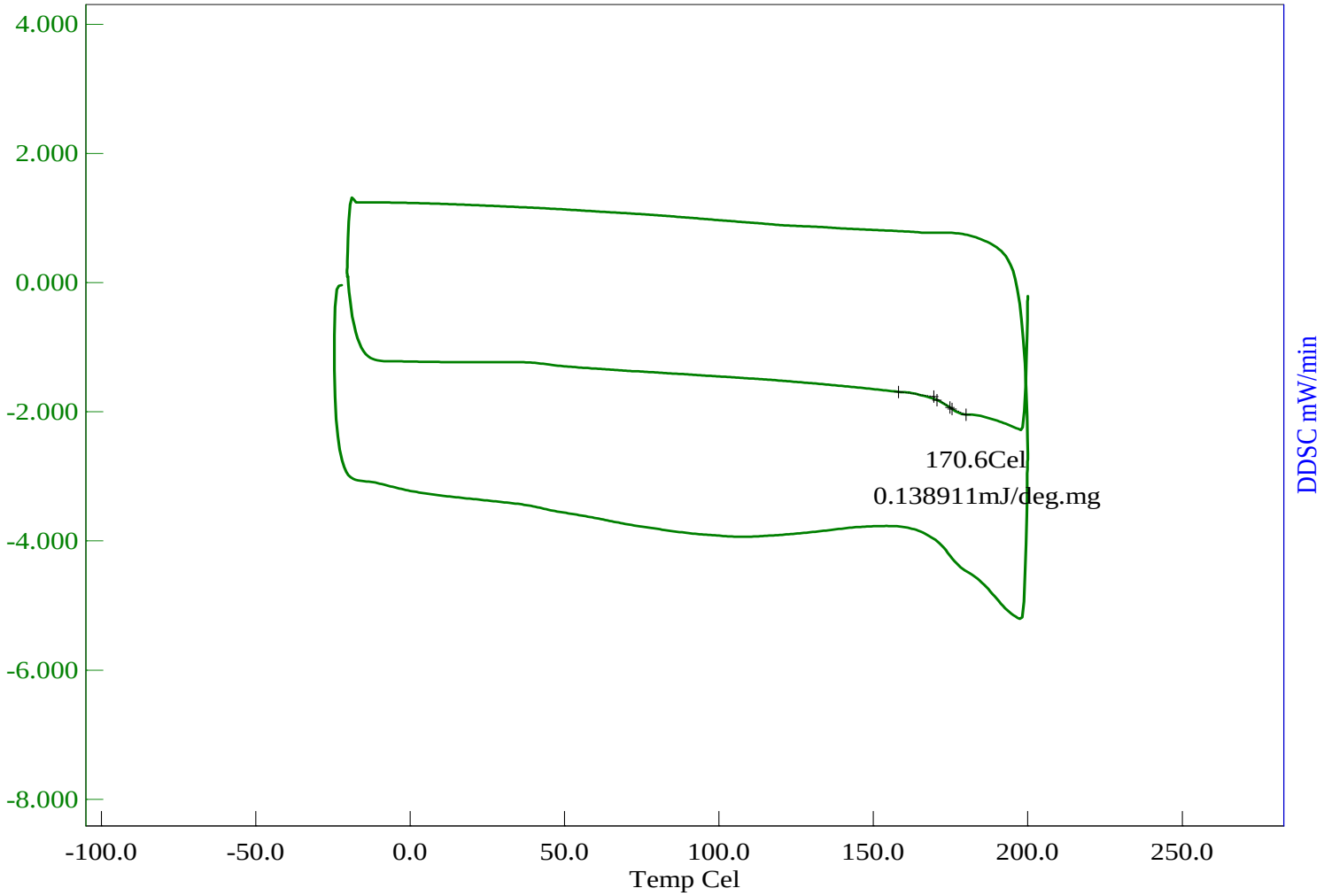

Figure A. 41. T_g Measurement of Polyacrylamide Cured at 190 ^oC for 10 min. With Crosslinker.

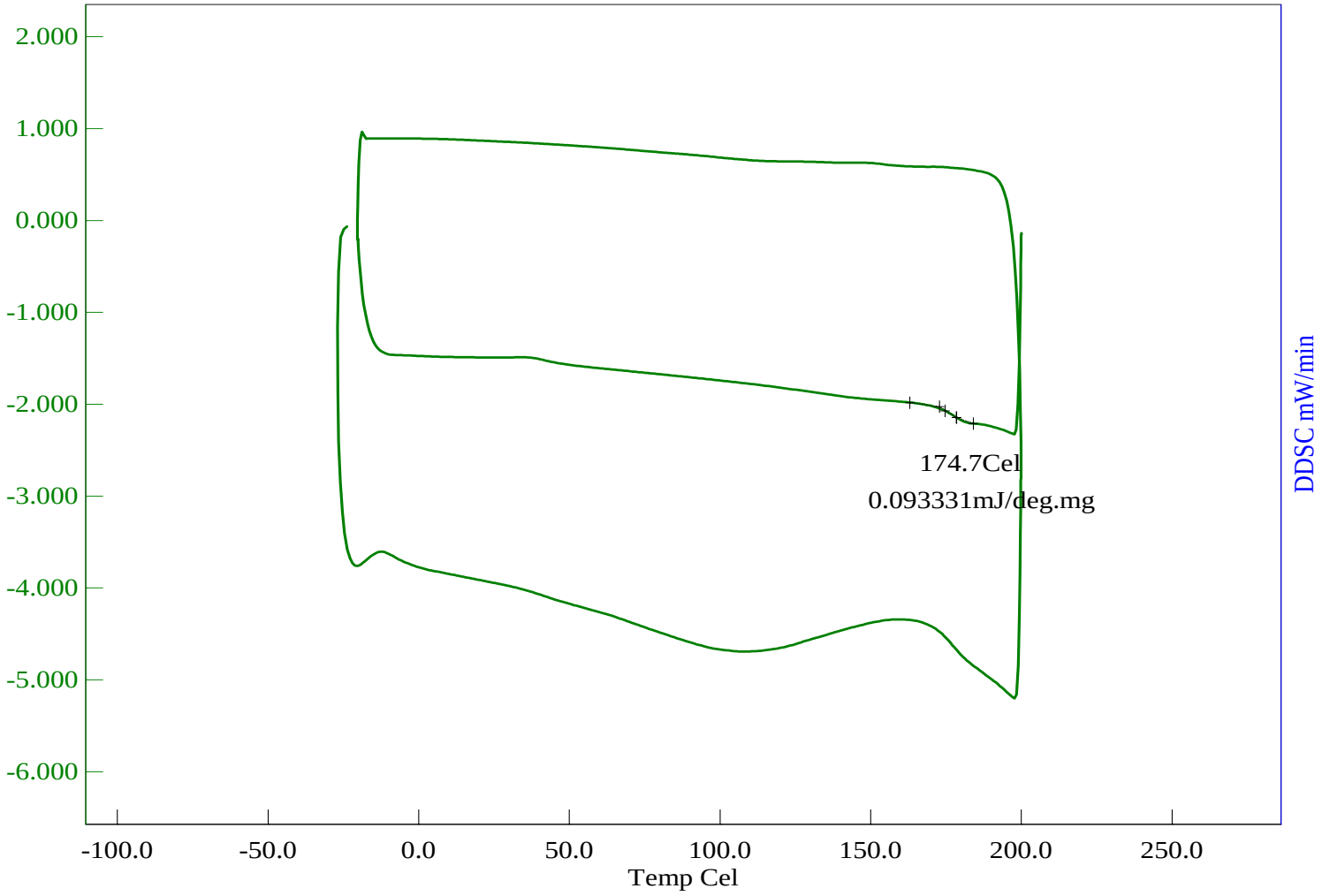

Figure A. 42. T_g Measurement of Polyacrylamide Cured at 190 ^oC for 30 min. With Crosslinker.