

POLYMERS FOR NEXT GENERATION

LITHOGRAPHY

THESIS

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by

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## **ABSTRACT**

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**SUPERVISING PROFESSOR: PATRICK E. CASSIDY**

Since the invention of microlithography there has been an exponential increase in the speed and performance of electronic devices with smaller and smaller arrays. Since then, the semiconductor industry has relied on electron beam lithography for sub-micron patterning of integrated circuits. Materials with unique properties are required to meet the needs of the lithography industry. Scientists are modifying the properties of resist materials by synthesizing new polymers to enhance lithographic performance. PMMA is one of the best e-beam resists, but suffers from fundamental drawback of poor radiation

sensitivity, brittle film formation and poor resistance to plasma etching, making it a bad choice for the process of lithography. This can be partially offset by functionalizing with more stable pendant groups. We have selected substituted *N*-methacryloyloxy phthalimide, containing cycloimido group as a pendant, which is strong enough to give sufficient thermal stability, at the same time expected to be sensitive to electron beam exposure because of the labile N – O bond. Electronic substituents on the cycloimido group aid in the cleavage of this bond. Electron withdrawing chloro and nitro groups weakens the N – O bond and copolymers of these monomers with methyl methacrylate showed sufficiently high mechanical properties which allow them to survive the semiconductor processing, yet are sensitive to degradation. The GPC results showed that most of the polymers had molecular weight  $\sim 18,000$  g/mol with a PDI of  $\sim 2.0$ . The electron beam lithography studies of polymer with nitro substitution on the pendant group showed the least line width of  $0.54 \mu\text{m}$  among the four selected polymers. Least dosage ( $251 \mu\text{C}/\text{cm}^2$ ) with fastest writing speed ( $1000 \mu\text{sec}/\text{mil}$ ) was observed for the polymer with methyl substitution. These two polymers were observed to be the promising materials as positive photoresists and can be studied for further evaluation of lithographic properties.

## CHAPTER I

### INTRODUCTION

#### History

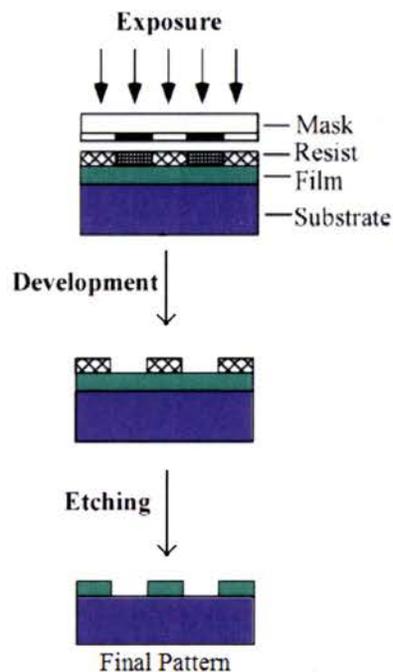
The word lithography has its origin from the Greek words “lithos” meaning stone and “graphein” to write<sup>1</sup>. Alois Senefelder from Germany, in the year 1798 invented the process of lithography. He used this process to reproduce artistic images based on the principle of repulsion between grease and water. When a drawing is made on a flat piece of limestone using greasy crayons, wetted with water, and dipped in greasy ink, only the crayon lines will hold the oily ink; leaving the other portions of the stone. The stone, when pressed against a suitable paper, reproduces the impression of the image on the paper. Over decades, this technological breakthrough has indeed become source for many new inventions related to lithography and each of them took their own way of creating indigenous technologies. Microlithography which is one among these modern technologies, has dominated the world of semiconductor industry over the past four decades.

#### Microlithography

Since the invention of integrated circuits there has been an exponential increase in the speed and performance of electronic devices with smaller and smaller arrays. It was predicted by Gordon Moore that the number of devices on a transistor doubles every 18

months, referred to as Moore's law and this extensive growth would not be possible without the process of microlithography

Microlithography is a modern lithography process in which minute dimensional patterns are transferred to a very thin layer of a radiation-sensitive material coated on a semiconductor wafer. A viscous solution of radiation-sensitive polymer called a photoresist is coated on the surface of the semiconductor wafer and then exposed to radiation through the mask. The radiation is transmitted through the clear parts of the mask and the image is projected on to the thin photoresist layer as shown in Figure 1<sup>2</sup>.



**Figure 1:** Process of photolithography<sup>2</sup>.

The exposed regions of photoresist undergo radiation-sensitive chemical reactions which, on development, transfer the pattern onto the photoresist. The process of selective etching removes the underlying layer of the semiconductor wafer. The photoresist layer is

then removed by washing, with a solvent which leaves a fine image of mask on the surface of the wafer. Depending on the application, the silicon wafers are then subjected to a series of metal deposition and etching processes to obtain the fabricated silicon chips.

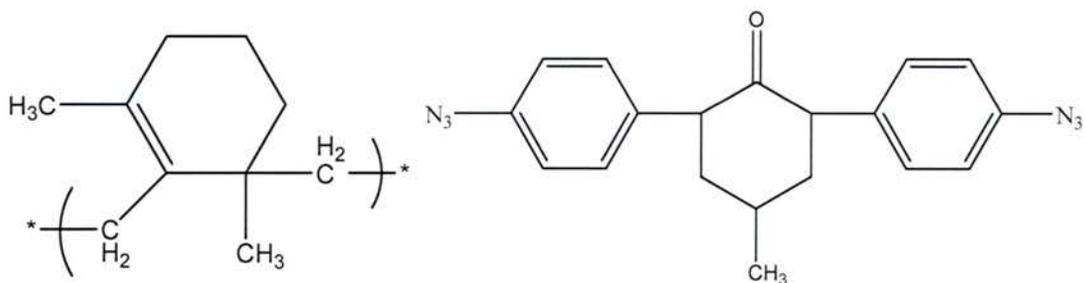
### Photoresists

A photoresist is a radiation-sensitive material that when exposed to radiation becomes either more soluble or insoluble in the developing solvents. Depending on the nature of the photoresist material used, they are classified into two types:

- Negative photoresist – becomes insoluble upon irradiation
- Positive photoresist – becomes soluble upon irradiation

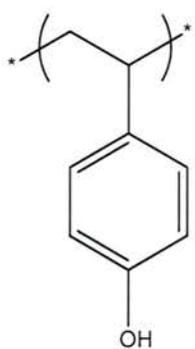
#### *Negative Photoresists*

The first resist used to fabricate solid-state devices was a negative photoresist<sup>3</sup>. These materials are easily soluble in the organic solvents before irradiation. Upon exposure to radiation, a negative photoresist absorbs energy and utilizes it to initiate a chain reaction which leads to crosslinking of the polymer which is insoluble in the developer solution. Finally, the developed photoresist is a negative tone of the mask, i.e. the unexposed portions of photoresist are removed, as shown in Figure 2<sup>4</sup>. A major drawback of negative photoresists is that they swell in the developing solvents; thereby limiting the resolution<sup>3</sup>. Cyclized poly(*cis*-isoprene) (Structure 1) crosslinked with bis(aryl azide) (Structure 2) as a photoactive crosslinking agent was the first example of a negative photoresist<sup>3</sup>. Poly(*p*-vinylphenol) (Structure 3) and poly(*p*-chloromethylstyrene) (Structure 4) are other examples of negative photoresists.

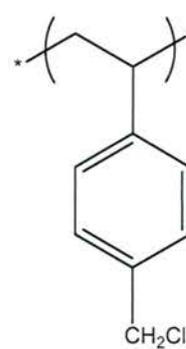


**Structure 1:** Cyclized poly(*cis*-isoprene)

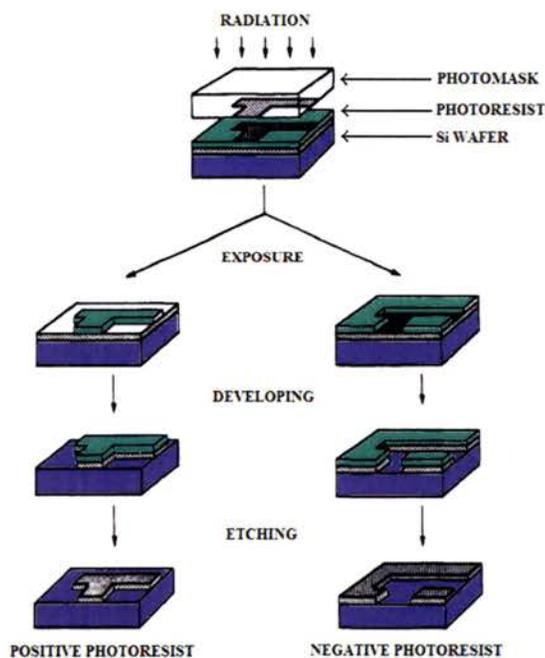
**Structure 2:** Bis(aryl azide)



**Structure 3:** Poly(*p*-vinylphenol)



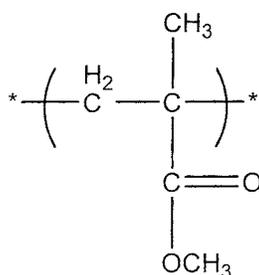
**Structure 4:** Poly(*p*-chloromethylstyrene)



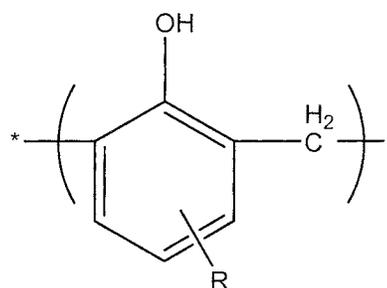
**Figure 2:** Photolithography process for positive and negative photoresists<sup>4</sup>.

### Positive Photoresists

A positive photoresist, prior to exposure, is insoluble in the organic solvents. Upon irradiation, the photoresist will absorb energy and undergo radiation-sensitive changes in its chemical structure. This will transform the irradiated pattern of photoresist into a species which is more soluble in the developing solution. A classic example of a positive photoresist is poly(methyl methacrylate) (PMMA) (Structure 5) which undergoes chain scission upon irradiation due to the presence of the photochemically labile ester linkages<sup>5</sup>. Other examples of positive photoresists include novolac (Structure 6) matrix resin with a base-insoluble sensitizer and various co-polymers of PMMA.



**Structure 5.** Poly(methyl methacrylate) [PMMA]



**Structure 6.** Novolac

### Types of Microlithography

Radiation-sensitive changes can be made to a photoresist by making use of different high energy sources. There are a number of such sources available for the process of lithography. These include UV light, electron beams, X-rays, light weight ions, to name a few. Each process of lithography is named for the source of irradiation used to expose the resist. Some of the most widely used lithography techniques are:

- Optical lithography (UV light)
- Electron beam lithography

- X-Ray lithography
- Ion projection lithography

Each technique has its own advantages and disadvantages. Based on the fact that electron beam lithography (EBL) is the technology used for production of high resolution images and the need for the photoresist materials to sustain the field in the market, this thesis will focus on EBL.

### Electron Beam Lithography

Electron beam lithography is a technique used for computer-aided sub-micron patterning of integrated circuits. This specialized technique uses a beam of high energy electrons to create extremely fine patterns on the substrate. Short wavelengths of electrons offer high resolution capability in EBL. One advantage of EBL, over optical lithography, is that optical lithography suffers from the optical diffraction of light. This makes it difficult to produce patterns of sub-micron resolution. Because of the small wavelength of electrons and the negligible diffraction at the resist surface, EBL overcomes this limitation.

Performance (higher speed, lower power and heat generation) of an integrated circuit can be increased by raising the number of circuits accommodated in a given area of the semiconductor wafer. This can be accomplished by reducing the size of the active circuit element<sup>6</sup> which in turn depends on resolution. Resolution is defined as the smallest possible feature on a photoresist that can be resolved clearly and distinctly. Resolution is directly proportional to the wavelength of radiation. Hence, using a shorter wavelength enables manufacturing of integrated circuits with smaller transistors<sup>7</sup>. The higher the

circuit density on a wafer, the smaller is the size of the device and the greater the performance.

Resolution can be increased by decreasing the wavelength of radiation<sup>7</sup> as discussed earlier. This explains the trend of migration from 436nm to 157 nm to EUV radiation. This can also be achieved by increasing the numerical aperture of the projection lens<sup>7</sup>. Numerical aperture is a measure of visualizing minute details on the wafer, which on increasing increases the critical angle of diffraction through the pattern of the mask and increases the possibility of recollecting the diffracted rays onto the wafer to form an image. Equation 1 explains this behavior in terms of wavelength and numerical aperture<sup>2</sup>.

$$Resolution = k\lambda / NA \quad (1)$$

In Equation 1,  $\lambda$  is the wavelength of radiation, NA is the numerical aperture and  $k$  is the proportionality constant, which depends on various parameters of photoresists such as thickness of the film, molecular weight *etc*

#### Requirements for Electron Beam Resists

Since the invention of EBL, the semiconductor industry has relied on resist chemistry for the development of new resist materials. Materials with unique properties are required to meet the needs of the lithography industry. Each process of lithography requires different resist materials, depending on the radiation source used. Some of the most basic requirements for electron beam resists are given below.

- Radiation sensitivity
- Etch resistance
- Contrast & Sensitivity

- Film formation
- Adhesion to semiconductor substrate

Resist materials are most commonly made from polymers. The chemical structure and molecular properties of these polymers define the usability of the polymer for a particular lithography process. These properties can be tailored depending on the source of radiation.

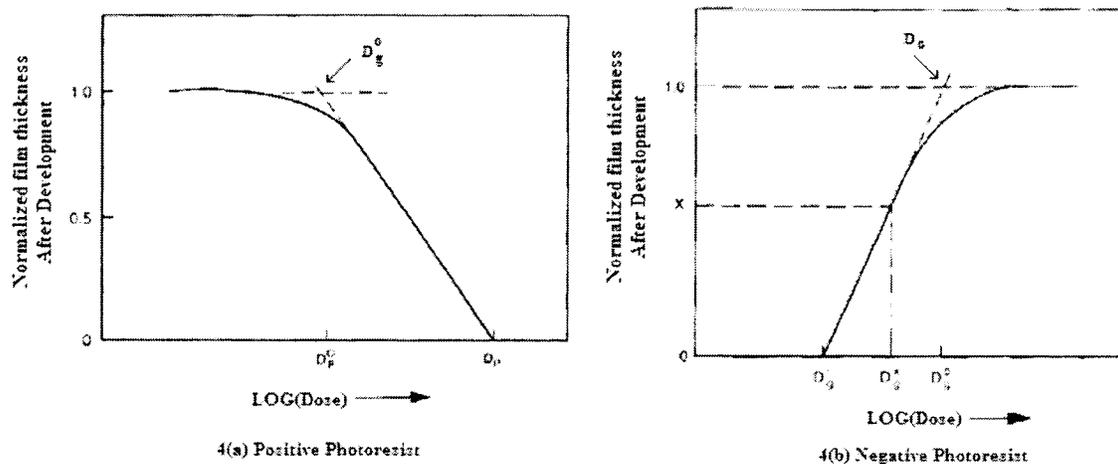
As mentioned above, the polymer resists must have the primary characteristic of radiation sensitivity. When exposed to radiation the polymer undergoes a chemical reaction altering the chemical structure, making it either more or less soluble in the developing solution. A polymer which forms a more soluble product is a positive resist while the one forming less soluble product is a negative resist.

Contrast of a resist is a measure of solubility changes as a function of the radiation dose on the polymer resist. This can be calculated from the slope of the linear portion of sensitivity curve (Figure 3). A sensitivity curve is a plot of normalized film thickness of photoresist after developing vs. logarithm of radiation dose. The contrasts for positive ( $\gamma_p$ ) and negative ( $\gamma_n$ ) photoresists are given by the equations (2) and (3)<sup>3</sup>.

$$\gamma_p = \left[ \text{LOG} \frac{D_p}{D_o} \right]^{-1} \quad (2)$$

$$\gamma_n = \left[ \text{LOG} \frac{D_g^o}{D_g^i} \right]^{-1} \quad (3)$$

Sensitivity, which is also a measure of the solubility change as a function of radiation dose, can be obtained from the sensitivity curve. In Figure 3, the sensitivity of positive photoresist is  $D_p$  and for negative photoresist it is  $D_g^x$ <sup>3</sup>.



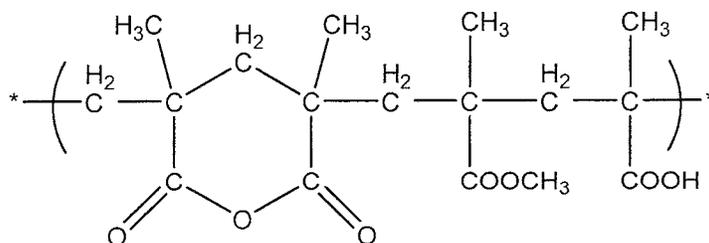
**Figure 3:** Sensitivity curve for positive and negative photoresist systems<sup>8</sup>.

Etch resistance is another important property of a resist. Etching removes selected layers of metals using dry gases or concentrated solutions. A process called plasma etching utilizes ionized gas called plasma to etch the layers of the substrate. Resists must be resistant to these actions in order to sustain the process of fabrication. The plasma etching properties of a polymer are typically related to the atomic components of the polymer repeat unit<sup>9</sup>. Plasma etching capabilities of resists can be improved by increasing the carbon content of the polymer<sup>10</sup>. An increase in the number of acyclic units, either in the polymer backbone or as pendant moieties, increases the plasma resistance of the photoresists<sup>10</sup>; but this also increases the brittleness of the films and the polymers display poor adhesion to the semiconductor substrate. Scientists are trying to offset the tradeoff between etch resistance and lithographic performance by synthesizing new polymers and co-polymers in an attempt to modify the properties.

## Background – Resist Materials

PMMA is a classic example of a positive photoresist. Hatzahis, in 1969, first reported the use of PMMA as a positive resist material for e-beam radiation<sup>11</sup>. On exposure to radiation PMMA undergoes chain scission of the backbone and forms low molecular weight compounds, which are soluble in the developer solution. Because of the low sensitivity of PMMA to radiation-induced degradation, brittle film formation and poor resistance to plasma etching<sup>12</sup>, does however, make it a bad choice for the process of lithography. Due to its high resolution many researchers have focused on PMMA in an attempt to improve its lithographic characteristics.

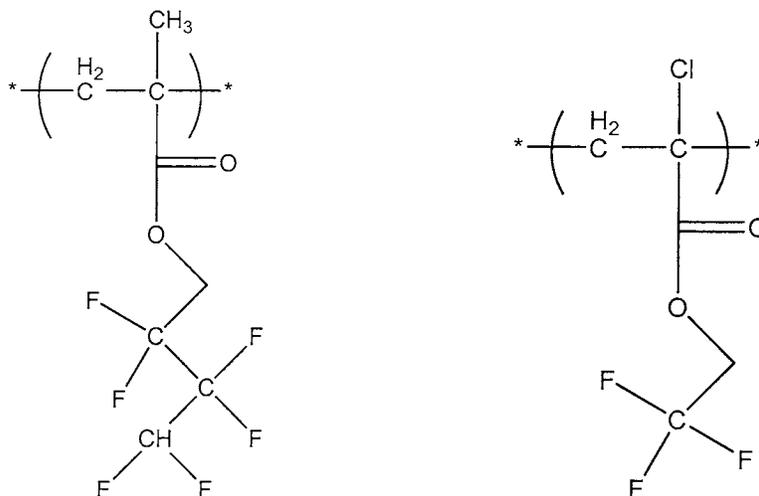
Moreau *et al.*<sup>13</sup> at IBM synthesized a Terpolymer (Structure 7) to demonstrate the improvement in sensitivity. A co-polymer of methyl methacrylate and methacrylic acid was made and subsequently heated to introduce the anhydride linkages. The final polymer, with three monomer units, displayed better sensitivity over PMMA and was manufactured as an electron beam resist at IBM in 1970's.



**Structure 7:** IBM Terpolymer

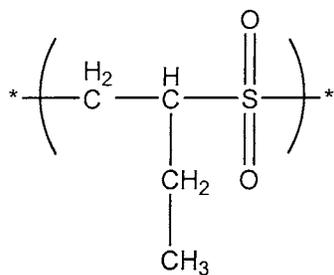
Backbone degradation in PMMA can also be enhanced by substituting the  $\alpha$ -methyl group with electronegative groups such as Cl and CN<sup>14</sup>. Another approach to improve the sensitivity is the incorporation of fluorine into the pendant ester group of PMMA. Poly(2,2,3,3,4,4-hexafluorobutyl methacrylate)<sup>15</sup> (Structure 8) and poly(2,2,2-trifluoroethyl-2-chloroacrylate)<sup>16</sup> (Structure 9) are some of the examples that belong to

this class of polymers. Substitution of electronegative groups on these polymers tremendously improves the sensitivity to radiation induced degradation.



**Structure 8:** Poly(2,2,3,3,4,4-hexafluorobutyl methacrylate)    **Structure 9:** Poly(2,2,2-trifluoroethyl-2-chloroacrylate)

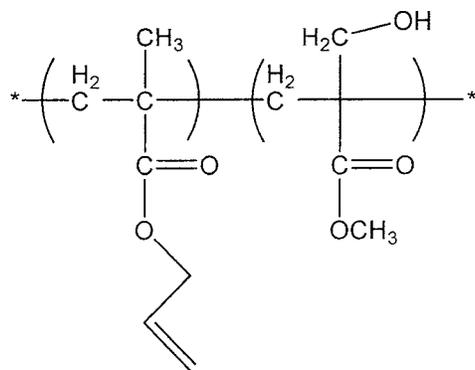
Poly(olefin sulfones) is another class of polymers of interest to resist chemists because of their thermal instability and low cost. Bowden *et al.*<sup>17</sup> developed poly(1-butene sulfone) (Structure 10) resists and utilized the relatively weak C-S bond to expose to e-beam radiation. These materials are extremely sensitive to e-beam radiation however, poor plasma and reactive ion etching stability have led scientists to look for better e-beam resists.



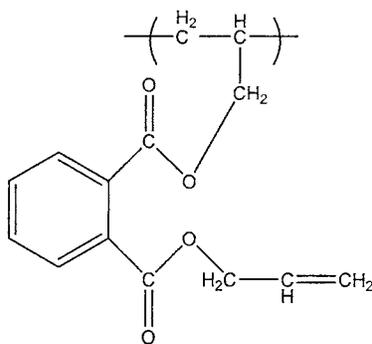
**Structure 10:** Poly(1-butene sulfone)

In order to circumvent the problem of low etch resistance, a two component positive resist system of novolac resin and poly(olefin sulfone) was developed by workers at Bell Laboratories<sup>18</sup>. Poly(olefin sulfone) is used as a dissolution inhibitor in the novolac matrix resin system. The resulting two component system expresses excellent film forming property and etch resistance from novolac resin and high sensitivity from the poly(olefin sulfone). The major difficulty in the resist manufacture is the blending of the two incompatible polymers into a homogeneous solution. A wide range of research has been done on substituted novolac-based photoresists in an attempt to solve the issue and emerge with a successful solution.

Polymers with various pendant groups, like epoxy and vinyl, which are capable of radiation-induced crosslinking are used as negative resists for high energy lithographic techniques. Crosslinking from unsaturated pendant groups was studied by Tan *et al* in 1981<sup>19</sup>. Examples of polymers with such chemistry are poly(allyl methacrylate-*co*-2-hydroxymethyl methacrylate) (Structure 11) and poly(diallyl *o*-phthalate)<sup>20</sup> (Structure 12). Because of their low contrast and resolution these polymers were not investigated in more detail.

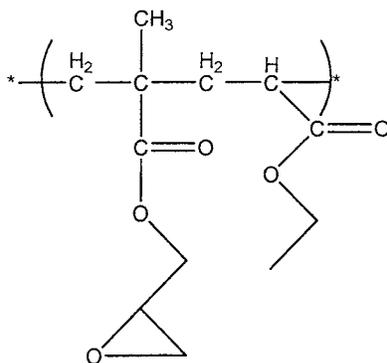


**Structure 11:** Poly(allyl methacrylate-*co*-2-hydroxymethyl methacrylate)



**Structure 12:** Poly(diallyl *o*-phthalate)

Epoxy side groups are sources for efficient cross-linking. Work done by Feit *et al*<sup>21</sup> on polymers with epoxy moieties confirmed the high sensitivity and high cross-link efficiencies. Unfortunately, these polymers also show low contrast and resolution in films with thicknesses greater than 0.4  $\mu\text{m}$ . Advances in epoxy-containing polymers have led to the development of methacrylate-based copolymers which showed good lithographic properties<sup>22</sup>. A copolymer of glycidyl methacrylate with ethyl acrylate (Structure 13) showed improved characteristics. These include good contrast and resolution in addition to better adhesion, shelf-life and wet-etch resistance<sup>22</sup>. These polymers, however, are not viable because of the need for photoresists with sub-micron resolution and better plasma-etch resistance.



**Structure 13:** Poly(glycidyl methacrylate-*co*-ethyl acrylate)

Another approach examined to improve these properties was carried out by Taylor *et al*<sup>23</sup>. They incorporated halogen groups into acrylate- and styrene-based polymers<sup>24</sup>. Radicals are formed from the cleavage of polarized carbon-halogen bonds. This is followed by various rearrangement reactions which lead to crosslinking of polymer chains. High sensitivity to radiation-induced crosslinking is observed in these polymers due to the electronegative effect of halogens. Another advantage is that the localized crosslinking mechanism of these polymers does not require a curing step; which is most common in epoxy and vinyl polymers. However, in the process of developing, the crosslinked polymer swells and results in image distortion.

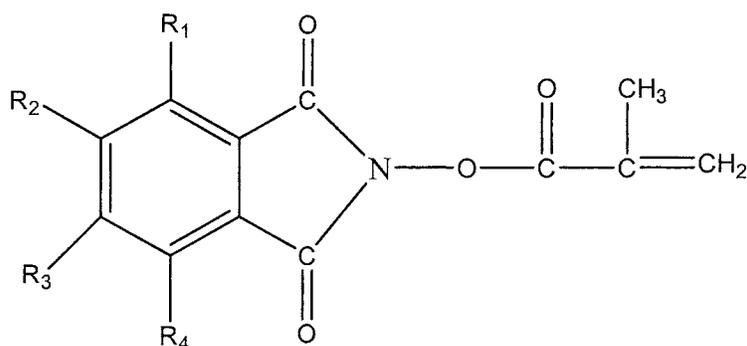
Various combinations of acrylic, alicyclic and aromatic systems have been evaluated for lithographic applications. Many photoresists have been developed successfully but were used only for several years in the semiconductor industry because of the limitations on contrast and etch resistance. In spite of the in-depth research for development of electron beam resists, no clear solution has emerged. Increasing demands for semiconductor devices have posed challenges for researchers to develop new strategies for synthesizing better electron beam resist materials.

#### Approach

One fundamental challenge in development of resist materials for EBL process is the selection of side groups. The pendant groups must be strong enough to give sufficient thermal stability, etch resistance, and other mechanical properties compatible to microelectronic applications. At the same time they must be sensitive to electron beam exposure and lose the side group readily in order to make the polymer more soluble after exposure. As seen in the literature, recent workers seem to favor methyl methacrylate-

based polymers as the promising materials for solving this problem<sup>25</sup>. But PMMA does suffer from the fundamental drawback of poor sensitivity and poor plasma etching stability. This can be partially offset by functionalizing with more stable pendant groups.

The work discussed here focuses on the cycloimido group. This group can be easily attached to methacrylic acid to form a radiation-sensitive resist material for use in EBL. The labile N–O bond of the cycloimido group, upon exposure to radiation, cleaves and forms a radical on the main chain of the polymer. This aids in further degradation of the polymer backbone to form low molecular weight material, which can be removed by the solvent. The ease of cleavage of this bond can be varied by attaching different substituents on the cycloimido group.



**Structure 14:** Substituted *N*-methacryloyloxy phthalimide

**Table 1:** Compounds with various substitutions on *N*-methacryloyloxy phthalimide.

Compound No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
1	H	Cl	Cl	H
2	H	CH <sub>3</sub>	H	H
3	H	H	H	H
4	H	NO <sub>2</sub>	H	H

We have developed various *N*-methacryloyloxy phthalimide monomers with different substitutions of electron withdrawing and electron donating groups on it to study the affect of electronic groups on the sensitivity of the photoresists. Monomer structure and the substitutions on the monomer are shown above (Structure 14 and Table 1).

The goal of the project was to design new positive resist materials to aid the semiconductor industry in its success in producing devices with smaller geometries. We report the syntheses of polymers that are radiation-sensitive have good resolution, good mechanical strength, and other beneficial lithographic properties.

## **CHAPTER II**

### **EXPERIMENTAL**

#### Instrumentation and Chemicals

#### NMR Spectroscopy

Proton nuclear magnetic resonance analyses of the samples were done with a VARIAN INOVA 400 MHz FT-NMR spectrometer with deuterated chloroform or DMSO being the preferred solvents.

#### IR Spectroscopy

IR spectra of synthesized monomers and polymers were measured as KBr pellets, using a Perkin-Elmer SPECTRUM ONE spectrophotometer. The instrument was used in the frequency range of 4000 to 200  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

#### Thermogravimetric Analysis (TGA)

TG thermograms were obtained from 20 °C to 800 °C at a heating rate of 5 °C per minute using a TGA Q50 module from TA Instruments Inc. A sample size of ~10 mg was weighed in each case. The decomposition temperature at 10% and maximum weight losses were determined and reported.

#### Differential Scanning Calorimetry (DSC)

Glass transition temperatures ( $T_g$ ) of all the polymers were determined using a 2920 MODULATED DSC from TA instruments Inc. The samples of 10-15 mg were

heated in an aluminum sample holder in a silver cell from 0 °C to 250 °C at a rate of 20 °C per minute. The step transition during the second heating cycle was considered as the  $T_g$  of the polymer.

#### Gel Permeation Chromatography (GPC)

Molecular weights of all the co-polymers synthesized in the lab were determined using a GPC with a WATERS 600 controller and a WATERS 2410 differential refractometer as the detector. The eluting solvent in the GPC column was chloroform and all the polymer solutions were made with HPLC grade chloroform. The packing material used in the GPC column was polystyrene-divinylbenzene and the molecular weights were calibrated using polystyrene as the standard.

#### Melting Point

Melting points of all the substituted *N*-methacryloyloxy phthalimides were determined using a MEL-TEMP-II hot block melting point apparatus using a 400 °C thermometer with out calibration.

#### Spin Coating

A spin coating instrument from Laurell Technologies corporation (model: WS-400A-6NPP/LITE/IND) with a 4 inch (100 mm) wafer aligner was used for spin coating polymer solutions on the silicon wafer. The digital speed controller programs the speed (in rpm) and time (in seconds) of rotation of the chunk.

#### Electron Beam Lithography

An electron beam lithography instrument assembled at University of Texas, Dallas, from various Texas Instruments products, was used to expose the photoresist

coated wafer. An Leica INM200 optical microscope was used to obtain the images of the patterns

### Chemicals

All the substituted phthalimide compounds, 4-dimethylaminopyridine (DMAP), hydroxylamine solution, di-tertiarybutyldicarbonate (BoC<sub>2</sub>O), *N,N'*-dicyclohexyl carbodiimide (DCC), tetrachloro ethylene, trichloroethylene, methacrylic acid, azobis(isobutyronitrile) (AIBN) and methylmethacrylate (MMA) were purchased from Sigma-Aldrich. 4-nitro-*N*-hydroxyphthalimide was purchased from TCI America. Reagent grade solvents were purified and dried by standard methods before being used in the reactions.

### Experimental Procedure

#### Monomer Synthesis

A one-pot synthetic procedure, developed by Einhorn *et al*<sup>26</sup> was used to synthesize a series of substituted *N*-hydroxyphthalimides. A general procedure explaining the synthesis of *N*-methacryloyloxy phthalimide is given below. Masses and volumes vary according to the specific compounds (see Tables 3 and 4).

#### *N*-(*tert*-Butoxycarbonyl)-phthalimides

A 500 mL, clean, dry, three-neck round-bottom flask with a magnetic stirrer was connected to an argon source. The flask was purged with argon for one minute. Acetonitrile (75 mL), dried under 5 Å molecular sieves, was measured into the flask followed by the addition of commercially obtained phthalimide (22.1 g, 150 mmol). The suspension was made homogeneous by stirring the solution for five minutes at room temperature. 4-Dimethylaminopyridine (18.32 g, 150 mmol) was added to the suspension

and allowed to stir for two minutes. An appropriate quantity (see Table 2) of di-tertiarybutyldicarbonate (stored at 5 °C) was weighed (36.1 g, 150 mmol) and added to the suspension immediately after weighing. The suspension turned into an orange-colored homogeneous solution with rapid evolution of CO<sub>2</sub> and dissolution of phthalimide. The solution was stirred for 30 minutes at room temperature until no suspended particles were observed in the bottom of the flask. After the reaction, a homogeneous solution of *N*-(tert-butoxycarbonyl)-phthalimide was obtained. This product was not isolated but the same reaction setup was continued for the next step of synthesis.

**Table 2:** Quantity of di-tertiarybutyldicarbonate used in the synthesis.

<b>Substitution on Phthalimide</b>	<b>BoC<sub>2</sub>O (eq)</b>
4,5-Dichloro	1.5
4-Methyl	1.1
-	1.1

*Hydroxylammonium salt of phthalimides*

After the starting material was converted to the *N*-BoC derivative of phthalimide, 150 mmol (9.15 ml) of aqueous hydroxyl amine solution (50 wt% solution) was added

drop wise to the well stirred reaction mixture at room temperature. An immediate change in color from a pale orange to a dark brown solution with slow formation of orange precipitate was observed. The reaction was run for 20 hours at room temperature and then 100 mL of ether was added to precipitate the orange-colored hydroxyl ammonium salt of phthalimide. The precipitate was separated by vacuum filtration and washed twice with 20 mL of ether. All unreacted starting materials and byproducts of the reaction were washed using ether to obtain the pure hydroxyl ammonium salt of phthalimide. The salt was then air-dried to get the fine crystalline, orange-colored product. This material was used in the next step of synthesis with no further purification.

#### *N-Hydroxyphthalimides*

The fine powder of hydroxyl ammonium salt of phthalimide obtained in the previous step was dispersed in 250 mL of water. The solution was made homogeneous by stirring the reactants for 5 minutes. While stirring, the dispersion was acidified by adding 1.0 M hydrochloric acid dropwise until the pH of solution was 1.0 (monitored with a digital pH meter). The orange-colored dispersion turned pale-yellow on acidification. The pale-yellow-colored solid of *N*-hydroxyphthalimide was separated by vacuum filtration, washed with 50 mL of water and dried under vacuum. The product so obtained was used as-is for the final step of monomer synthesis.

#### *N-Methacryloyloxy phthalimides*

A 500 mL, three-neck, round-bottomed flask with a magnetic stirrer and argon inlet was fitted to a stand and purged with argon for one minute. *N*-Hydroxyphthalimide (65 mmol) obtained from the previous step was added to the flask and suspended with 100 mL of dry methylene chloride<sup>27</sup>. Methacrylic acid (10.6 g, 65 mmol) was added

dropwise to the suspension and stirred to make the suspension homogeneous. *N-N'*-Dicyclohexyl carbodiimide (13.4 g, 65 mmol), was weighed as solid and melted at 60 °C prior to addition. The melt was added dropwise to the well stirred cold suspension of the flask at room temperature. Formation of the white-colored urea derivative with condensation of water on the walls of the flask was observed. The reaction was continued with stirring for 20 hours at room temperature. The urea derivative, dicyclohexyl urea, formed as a byproduct was removed by vacuum filtration and the residue was washed with 20 mL of dry methylene chloride to remove any trapped product in the urea derivative. The filtrate was evaporated under vacuum to dryness at 30 °C. The residue was recrystallized from 95% ethanol to obtain purified *N*-methacryloyloxy phthalimide. Quantities of the starting materials used, yield and melting points of all the substituted *N*-methacryloyloxy phthalimides were determined and tabulated in Table 3.

#### 4,5-dichloro *N*- methacryloyloxy phthalimide

Melting point 117-118 °C; IR(KBr)  $\text{Cm}^{-1}$  3098 (s), 3027 (s), 2923 (s), 1731-1775 (b), 1607 (s), 1360-1385 (b), 1196 (s);  $^1\text{H NMR}$  (*d*-DMSO)  $\delta$  8.35 (s, 2H, Cl-*Ar*), 6.43 (s, 1H, -HC=CH<sub>2</sub>), 6.17 (s, 1H, -HC=CH<sub>2</sub>), 2.04 (s, 3H, -CH<sub>3</sub>)

#### 4-methyl *N*- methacryloyloxy phthalimide

Melting point 135-136 °C; IR(KBr)  $\text{Cm}^{-1}$  3098 (s), 2989 (s), 2923 (s), 1733-1769 (b), 1607 (s), 1366 (s), 1220 (s);  $^1\text{H NMR}$  (*d*-DMSO)  $\delta$  7.75-7.87 (m, 3H, *Ar*), 6.42 (s, 1H, -HC=CH<sub>2</sub>), 6.14 (s, 1H, -HC=CH<sub>2</sub>), 3.36 (s, 3H, CH<sub>3</sub>-*Ar*), 2.02 (s, 3H, -CH<sub>3</sub>)

#### 4-nitro *N*- methacryloyloxy phthalimide

Melting point 166-167 °C; IR(KBr)  $\text{Cm}^{-1}$  3109 (s), 2961 (s), 2868 (s), 1742-1802 (b), 1632 (s), 1539 (s), 1360-1385 (b), 1193 (s);  $^1\text{H NMR}$  (*d*-DMSO)  $\delta$  8.62-8.72 (m, 2H,

NO<sub>2</sub>-*Ar*), 8.27-8.25 (m, 1H, NO<sub>2</sub>-*Ar*), 6.45 (s, 1H, -HC=CH<sub>2</sub>), 6.18 (s, 1H, -HC=CH<sub>2</sub>),  
2.05 (s, 3H, -CH<sub>3</sub>)

*N*-methacryloyloxy phthalimide

Melting point 104-105 °C; IR(KBr) Cm<sup>-1</sup> 3098 (s), 3027 (s), 2967 (s), 1744 (b), 1604 (s),  
1355 (s), 1185 (s); <sup>1</sup>H NMR (*d*-DMSO) δ 8.00-7.94 (m, 4H, *Ar*), 6.43 (s, 1H, -HC=CH<sub>2</sub>),  
6.15 (s, 1H, -HC=CH<sub>2</sub>), 2.04 (s, 3H, -CH<sub>3</sub>)

**Table 3:** Data for synthesis of *N*-methacryloyloxy phthalimide.

Substitution	Starting Materials			Yield (g) / (%)	Melting Point (°C)
	<i>N</i> -hydroxy phthalimide (g) / (mmol)	Methacrylic acid (g)	DCC (mL)		
4,5-Dichloro	8.45 / 36.4	3.13	7.51	7.49 / 65	117-118
4-Methyl	9.3 / 52.5	4.25	10.84	6.3 / 46	135-136
4-Nitro	10.38 / 49.9	4.296	10.296	9.2 / 63	166-167
None	10.6 / 65	5.598	13.417	10.45 / 65	104-105

## Polymer Synthesis

### *Synthesis of Poly(N-methacryloyloxy phthalimide-co-methylmethacrylate)'s*

The above mentioned series of *N*-methacryloyloxy phthalimides were polymerized at various compositions with methylmethacrylate (MMA) by free radical solution polymerization. Predetermined amounts of MMA and/or substituted *N*-methacryloyloxy phthalimide(s) (Tables 4-7) were weighed into a Schlenk flask equipped with a magnetic stirrer. Sufficient DMF was added to make a one molar solution<sup>28</sup> AIBN (Tables 4-7) was added as a free radical initiator and the solution was made homogeneous by stirring for 5-10 minutes. The solution was degassed using three continuous freeze-pump-thaw cycles. After the reaction mixture was degassed, it was heated using an oil bath for 20 hours and a temperature of 65 °C was maintained throughout the reaction. The resulting solutions were precipitated into 10 times of the total reaction volume of methanol. The product was filtered under vacuum, washed twice with 250 ml portions of water and dried under vacuum for 24 h. Tables 8-11 give the weight and mol percentages of substituted *N*-methacryloyloxy phthalimide in the feed and the product.

Poly(4,5-dichloro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9802

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2939 (s), 2840 (s), 1736 (b), 1629 (s), 1445 (s), 1198 (b);  $^1\text{H}$

NMR (*d*-DMSO)  $\delta$  8.25 (s, 2H, Cl-*Ar*), 3.55 (s, 3H, OCH<sub>3</sub>), 1.85-1.76 (m, 6H, -CH<sub>3</sub>),

1.15-0.73 (m, 4H, -CH<sub>2</sub>-)

Poly(4,5-dichloro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9707

IR (KBr)  $\text{Cm}^{-1}$  3000 (s), 2950 (s), 1736 (b), 1613 (s), 1448 (b), 1193 (b);  $^1\text{H}$  NMR (*d*-

DMSO)  $\delta$  8.27 (s, 2H, Cl-*Ar*), 3.55 (s, 3H, OCH<sub>3</sub>), 2.10-1.46 (m, 6H, -CH<sub>3</sub>), 1.30-0.54

(m, 4H, -CH<sub>2</sub>-)

IR (KBr)  $\text{Cm}^{-1}$  3000 (s), 2950 (s), 1736 (b), 1613 (s), 1448 (b), 1193 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.27 (s, 2H, Cl-*Ar*), 3.55 (s, 3H, OCH<sub>3</sub>), 2.10-1.46 (m, 6H, -CH<sub>3</sub>), 1.30-0.54 (m, 4H, -CH<sub>2</sub>-)

Poly(4,5-dichloro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-7624

IR (KBr)  $\text{Cm}^{-1}$  3093 (w), 2994 (s), 2950 (s), 1736 (b), 1610 (s), 1448 (b), 1349(b), 1193 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.24 (s, 2H, Cl-*Ar*), 3.54 (s, 3H, OCH<sub>3</sub>), 2.19-1.44 (m, 6H, -CH<sub>3</sub>), 1.28-0.72 (m, 4H, -CH<sub>2</sub>-)

Poly(4,5-dichloro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)- 4852

IR (KBr)  $\text{Cm}^{-1}$  3093 (w), 2994 (s), 2945 (s), 1761 (b), 1607 (s), 1454 (b), 1352(b), 1193 (b)

Poly(4,5-dichloro *N*-methacryloyloxy phthalimide)

IR (KBr)  $\text{Cm}^{-1}$  3087 (s), 2994 (s), 2934 (s), 1747 (b), 1604 (s), 1454 (b), 1347(b), 1193 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.27-7.97 (s, 2H, Cl-*Ar*), 3.54 (s, 3H, OCH<sub>3</sub>), 2.06-1.18 (m, 5H, -CH<sub>3</sub>, -CH<sub>2</sub>-)

Poly(4-methyl *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9901

IR (KBr)  $\text{Cm}^{-1}$  3000 (s), 2950 (s), 1733 (b), 1679 (s), 1481 (b), 1390 (b), 1193 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  7.88 (m, 4H, CH<sub>3</sub>-*Ar*), 3.55 (s, 3H, OCH<sub>3</sub>), 3.34 (s, 3H, CH<sub>3</sub>-Ar), 2.03-1.62 (m, 6H, -CH<sub>3</sub>), 1.16-0.60 (m, 4H, -CH<sub>2</sub>-)

Poly(4-methyl *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9406

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2945 (s), 1731 (s), 1615 (s), 1478 (b), 1390 (b), 1190 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  7.97-7.76 (m, 4H, CH<sub>3</sub>-*Ar*), 3.55 (s, 3H, OCH<sub>3</sub>), 3.36 (s, 3H, CH<sub>3</sub>-Ar), 1.90-1.746 (m, 6H, -CH<sub>3</sub>), 0.92-0.72 (m, 4H, -CH<sub>2</sub>-)

Poly(4-methyl *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-7921

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2945 (s), 1733 (b), 1613 (s), 1478 (b), 1352 (b), 1193 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  7.89-7.35 (m, 4H,  $\text{CH}_3$ -Ar), 3.55 (s, 3H,  $\text{OCH}_3$ ), 3.36 (s, 3H,  $\text{CH}_3$ -Ar), 2.3-1.3 (m, 6H,  $-\text{CH}_3$ ), 1.06-0.92 (m, 4H,  $-\text{CH}_2$ -)

Poly(4-methyl *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-4852

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2945 (s), 1742 (b), 1613 (s), 1451 (b), 1358 (s), 1185 (s)

Poly(4-methyl *N*-methacryloyloxy phthalimide)

IR (KBr)  $\text{Cm}^{-1}$  2989 (s), 2928 (s), 1744 (b), 1613 (s), 1484 (b), 1355 (s), 1182 (s)

Poly(4-nitro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9901

IR (KBr)  $\text{Cm}^{-1}$  3104 (w), 2994 (s), 2945 (s), 1731 (s), 1613 (s), 1541 (s), 1448 (b), 1190 (b);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.83-8.53 (m, 2H,  $\text{NO}_2$ -Ar), 8.33-8.1 (s, 1H,  $\text{NO}_2$ -Ar), 3.55 (s, 3H,  $\text{OCH}_3$ ), 2.23-1.52 (m, 6H,  $-\text{CH}_3$ ), 1.17-0.73 (m, 4H,  $-\text{CH}_2$ -)

Poly(4-nitro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9208

IR (KBr)  $\text{Cm}^{-1}$  3104 (w), 2989 (s), 2950 (s), 1728 (b), 1621 (w), 1541 (s), 1445 (s), 1344 (s), 1193 (s);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.71-8.602 (m, 2H,  $\text{NO}_2$ -Ar), 8.33-8.07 (s, 1H,  $\text{NO}_2$ -Ar), 3.59-3.54 (s, 3H,  $\text{OCH}_3$ ), 2.19-1.52 (m, 6H,  $-\text{CH}_3$ ), 1.21-0.54 (m, 4H,  $-\text{CH}_2$ -)

Poly(4-nitro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-7228

IR (KBr)  $\text{Cm}^{-1}$  3104 (w), 3000 (s), 2950 (s), 1728 (b), 1621 (w), 1539 (s), 1347 (s), 1190 (s);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.69-8.59 (m, 2H,  $\text{NO}_2$ -Ar), 8.33-8.0 (s, 1H,  $\text{NO}_2$ -Ar), 3.65-3.54 (s, 3H,  $\text{OCH}_3$ ), 2.31-1.52 (m, 6H,  $-\text{CH}_3$ ), 1.45-0.73 (m, 4H,  $-\text{CH}_2$ -)

Poly(4-nitro *N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-4852

IR (KBr)  $\text{Cm}^{-1}$  3104 (s), 2994 (s), 2945 (s), 1750 (b), 1621 (w), 1544 (s), 1344 (s), 1193 (s);  $^1\text{H}$  NMR (*d*-DMSO)  $\delta$  8.60-8.50 (m, 2H,  $\text{NO}_2$ -Ar), 8.18-8.15 (s, 1H,  $\text{NO}_2$ -Ar), 3.65-3.61 (s, 3H,  $\text{OCH}_3$ ), 2.28-1.61 (m, 6H,  $-\text{CH}_3$ ), 1.60-0.78 (m, 4H,  $-\text{CH}_2$ -)

Poly(4-nitro *N*-methacryloyloxy phthalimide)

IR (KBr)  $\text{Cm}^{-1}$  3098 (s), 2989 (s), 2923 (s), 1750 (b), 1618 (w), 1539 (s), 1344 (s), 1193 (s);  $^1\text{H NMR}$  (*d*-DMSO)  $\delta$  8.83-8.07 (m, 3H,  $\text{NO}_2\text{-Ar}$ ), 1.75-1.46 (m, 5H,  $\text{-CH}_3$ ,  $\text{-CH}_2\text{-}$ )

Poly(*N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9901

IR (KBr)  $\text{Cm}^{-1}$  3000 (s), 2950 (s), 1731 (s), 1443 (b), 1190 (b);  $^1\text{H NMR}$  (*d*-DMSO)  $\delta$  7.90 (m, 4H,  $\text{Ar}$ ), 3.55 (s, 3H,  $\text{OCH}_3$ ), 2.08 (m, 6H,  $\text{-CH}_3$ ), 1.17-0.73 (m, 4H,  $\text{-CH}_2\text{-}$ )

Poly(*N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-9208

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2950 (s), 1744 (b), 1467 (s), 1371 (s), 1187 (s);  $^1\text{H NMR}$  (*d*-DMSO)  $\delta$  7.90 (m, 4H,  $\text{Ar}$ ), 3.59-3.54 (s, 3H,  $\text{OCH}_3$ ), 2.08 (m, 6H,  $\text{-CH}_3$ ), 1.30- 0.94 (m, 4H,  $\text{-CH}_2\text{-}$ )

Poly(*N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-7228

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2950 (s), 1736 (b), 1467 (s), 1363 (s), 1185 (s)

Poly(*N*-methacryloyloxy phthalimide-*co*-methylmethacrylate)-4852

IR (KBr)  $\text{Cm}^{-1}$  2989 (s), 2945 (s), 1736 (b), 1462 (s), 1369 (s), 1185 (s)

Poly(*N*-methacryloyloxy phthalimide)

IR (KBr)  $\text{Cm}^{-1}$  2994 (s), 2934(s), 1739 (b), 1467 (s), 1368 (s), 1182 (s)

**Table 4:** Data for co-polymers of 4,5-dichloro-*N*-methacryloyloxy phthalimide and MMA.

Ratio (mol %)	Monomers (g / mmol)		DMF (mL)	AIBN (mg)	Yield (g) / (%)
	Methyl Methacrylate	4,5-dichloro- <i>N</i> - methacryloyloxy Phthalimide			
98:2	4.5 / 44.94	0.5 / 1.66	46.61	76.54	4.5 / 90
93:7	3.75 / 37.45	1.25 / 4.16	41.6	68.34	4.5 / 90
76:24	2.5 / 24.97	2.5 / 9.05	33.3	54.68	4.4 / 88
52:48	1.25 / 12.48	3.75 / 12.5	24.98	41.02	4.3 / 86
0:100	0 / 0	5 / 16.66	16.66	27.35	4.2 / 84

**Table 5:** Data for co-polymers of 4-Methyl-N-methacryloyloxy phthalimide and MMA.

Ratio (mol %)	Monomers (g / mmol)		DMF (mL)	AIBN (mg)	Yield (g) / (%)
	Methyl Methacrylate	4-Methyl-N- methacryloyloxy phthalimide			
99:1	4.5 / 44.94	0.5 / 2.04	46.98	77.15	4.4 / 88
94:6	3.75 / 37.45	1.25 / 5.10	42.55	69.88	4.5 / 90
79:21	2.5 / 24.97	2.5 / 10.2	35.17	57.76	4.6 / 92
48:52	1.25 / 12.48	3.75 / 15.3	27.79	45.63	4.4 / 88
0:100	0 / 0	5 / 20.4	20.4	33.51	4.4 / 88

**Table 6:** Data for co-polymers of 4-nitro-N-methacryloyloxy phthalimide and MMA.

Ratio (mol %)	Monomers (g / mmol)		DMF (mL)	AIBN (mg)	Yield (g) / (%)
	Methyl Methacrylate	4-nitro- <i>N</i> - methacryloyloxy phthalimide			
99:1	4.5 / 44.96	0.5 / 1.81	46.75	68.94	4.4 / 88
93:7	3.75 / 37.45	1.25 / 4.52	41.98	68.94	4.4 / 88
80:20	2.5 / 24.97	2.5 / 9.05	34.02	55.87	4.3 / 86
50:50	1.25 / 12.4	3.75 / 13.5	26.07	42.8	4.5 / 90
0:100	0 / 0	5 / 18.1	18.11	29.75	4.6 / 92

**Table 7:** Data for co-polymers of *N*-methacryloyloxy phthalimide and MMA.

Ratio (mol %)	Monomers (g / mmol)		DMF (mL)	AIBN (mg)	Yield (g) / (%)
	Methyl Methacrylate	<i>N</i> - methacryloyloxy phthalimide			
99:1	4.5 / 44.94	0.5 / 2.16	47.11	77.36	4.4 / 88
92:8	3.75 / 37.45	1.25 / 3.74	42.86	70.39	4.6 / 92
72:28	2.5 / 24.97	2.5 / 10.82	35.79	58.78	4.5 / 90
48:52	1.25 / 12.48	3.75 / 16.23	28.72	47.16	4.3 / 86
0:100	0 / 0	5 / 21.64	21.64	35.54	4.4 / 88

**Table 8:** Data for incorporation 4,5-dichloro*N*-methacryloyloxy phthalimide.

<b>Feed (Wt%)</b>	<b>Feed (mol %)</b>	<b>Incorporation (mol %)</b>
10	4	2
25	10	7
50	25	24
75	50	48

**Table 9:** Data for incorporation 4-methyl *N*-methacryloyloxy phthalimide.

<b>Feed (Wt%)</b>	<b>Feed (mol %)</b>	<b>Incorporation (mol %)</b>
10	4	>1
25	12	6
50	29	21
75	55	52

**Table 10:** Data for incorporation 4-nitro *N*-methacryloyloxy phthalimide.

<b>Feed (Wt%)</b>	<b>Feed (mol %)</b>	<b>Incorporation (mol %)</b>
10	4	>1
25	11	7
50	27	20
75	52	51

**Table 11:** Data for incorporation *N*-methacryloyloxy phthalimide.

<b>Feed (Wt%)</b>	<b>Feed (mol %)</b>	<b>Incorporation (mol %)</b>
10	5	>1
25	13	8
50	30	28
75	57	52

## Spin Coating

### Polymer Sample Preparation

Four polymer samples, one from each series of polymers were used to coat the silicon wafer. The polymers used contains 20-28 mol % of substituted *N*-methacryloyloxy phthalimides. Solutions of 10 % (w/v) polymers were made using 1,1,2,2-tetrachloroethylene as solvent and the resulting solutions were filtered using 0.5  $\mu\text{m}$  teflon filters.

### Coating the Wafer

The silicon wafer was placed on the wafer chuck with the polished surface facing up. A 4 inch wafer aligner tool was used to center the wafer. Vacuum was turned on to mount wafer at the center of the chuck. The wafer aligner was removed and the lid was closed. A digital controller was used to program the speed and time (Table 12) of rotation of the wafer. The program has been used to spin coat the rest of the wafers.

**Table 12:** Spinning program for coating the wafer.

Step No.	Speed (rpm)	Time (sec)
1	1000	10
2	2000	8
3	3500	30
4	1500	10
5	0	8

Approximately 3 mL of the polymer photoresists solution prepared was applied to the center of the wafer using a clean and dry syringe. Same method was used to coat the rest of the wafers using the remaining polymer samples.

#### Soft Baking

Immediately after spin coating the wafer, the solvent traces were removed by soft baking the wafer. The wafer was placed on the hotplate, preset at 110 °C for 300 seconds. After soft baking, the wafer was removed and placed on a ceramic plate to cool to room temperature. The wafers are covered with aluminum foil and placed in the wafer holder to avoid further exposure to radiation.

#### Electron Beam Lithography

All wafers were exposed to electron beam radiation using a 0.5  $\mu\text{m}$  electron gun. A constant current of  $\sim 40$  nanoamperes was applied over an array of patterns with line width varying from 0.06  $\mu\text{m}$  to 1.5  $\mu\text{m}$  and writing speed varying from 5000  $\mu\text{sec}/\text{mil}$  to 1  $\mu\text{sec}/\text{mil}$  (APPENDIX V). A spread sheet obtained with varying line width and writing speed gives the dosage of each of the patterns formed on the silicon wafer.

The exposed radiations are developed in 70:30 solvent mixture of isopropyl alcohol and trichloroethylene for 60 seconds followed by rinsing in isopropyl alcohol for 60 seconds. The images of the array of patterns were obtained using an optical microscope.

## CHAPTER III

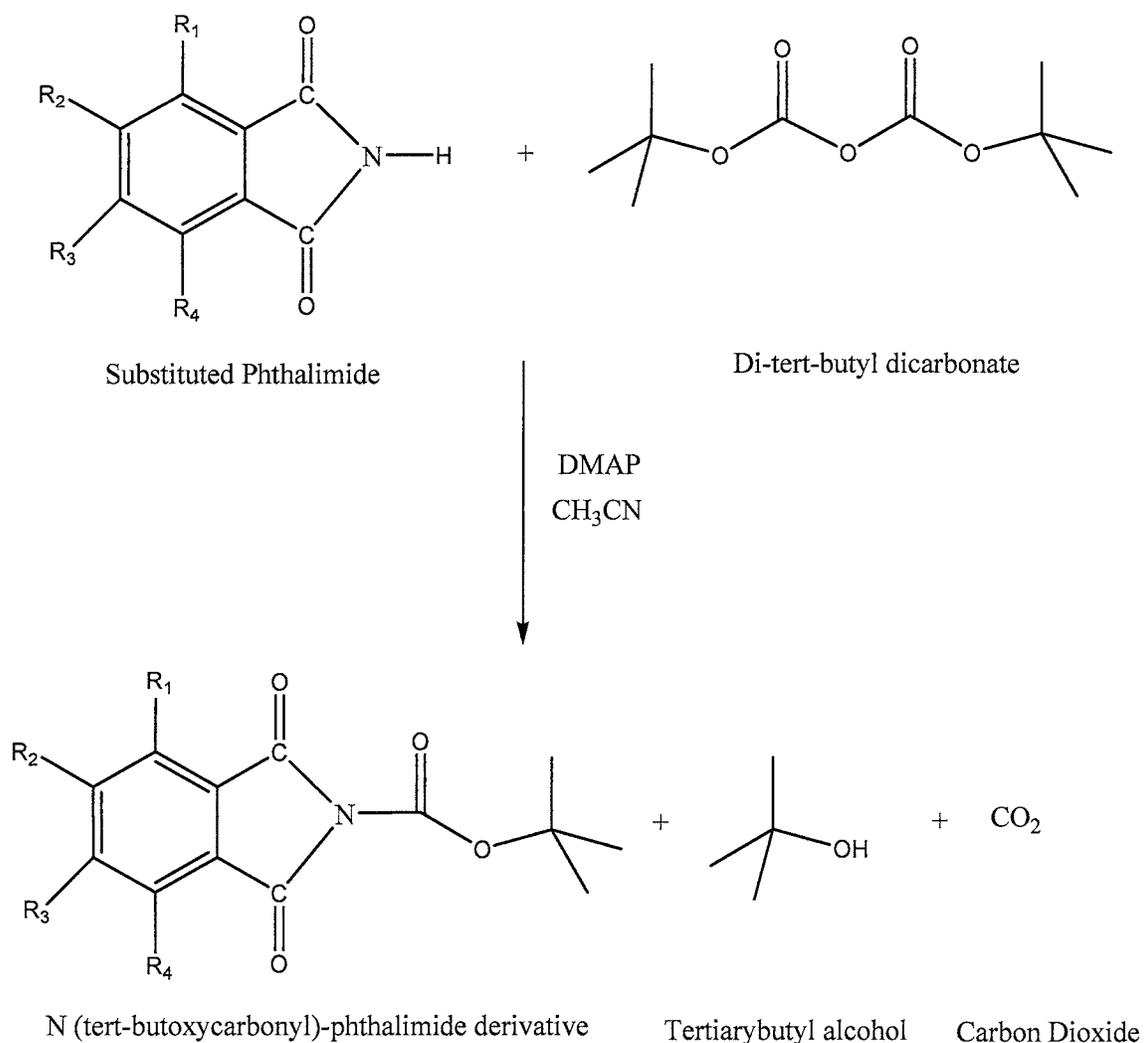
### RESULTS AND DISCUSSION

#### Monomer Synthesis

A series of *N*-methacryloyloxy phthalimides (Structure 14, Table 1) with different substituents were used for polymer synthesis. Since the monomers were not commercially available; their syntheses was required. A two-step procedure was used to synthesize all monomers except 4-nitro-*N*-methacryloyloxy phthalimide, for which a single step esterification reaction (Scheme 4) was performed.

#### *N*-(*tert*-Butoxycarbonyl)-phthalimides

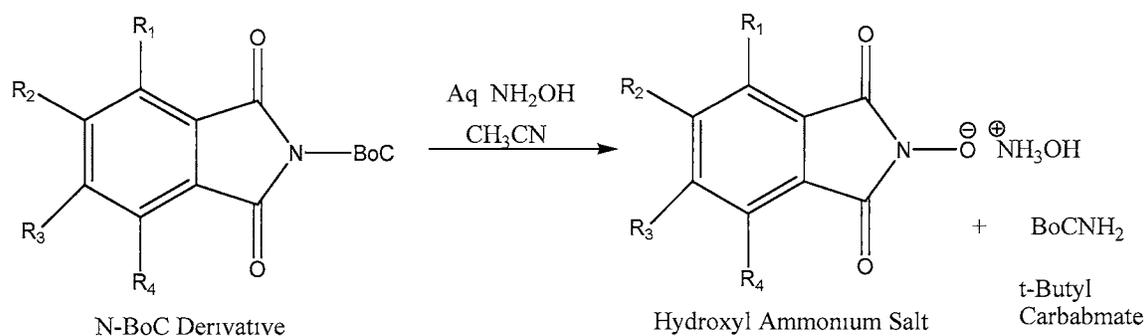
*N*-Unsubstituted phthalimides cannot be oxidized to *N*-hydroxyimides<sup>26</sup>; hence, they could not be used as precursors for synthesis of *N*-hydroxyphthalimides. Di-*tert*-butyl dicarbonate is a carbonate ester which reacts readily with the phthalimides (Table 1) in the presence of a catalyst such as DMAP, at room temperature, and forms the *N*-(*tert*-butoxycarbonyl) derivative (*N*-BoC derivative) of the compound (Scheme 1). The byproducts of this reaction are *t*-butyl alcohol and CO<sub>2</sub>. *t*-Butyl alcohol is soluble in the reaction medium and CO<sub>2</sub> was released from the reaction vessel through one of the necks of the round bottom flask. This reaction is fairly simple, highly efficient and gives good yields of *N*-Boc derivatives. The product was not isolated, but continued with the next step of synthesis.



**Scheme 1:** Synthesis of N-Boc derivatives from phthalimides

#### Hydroxylammonium salt of phthalimides

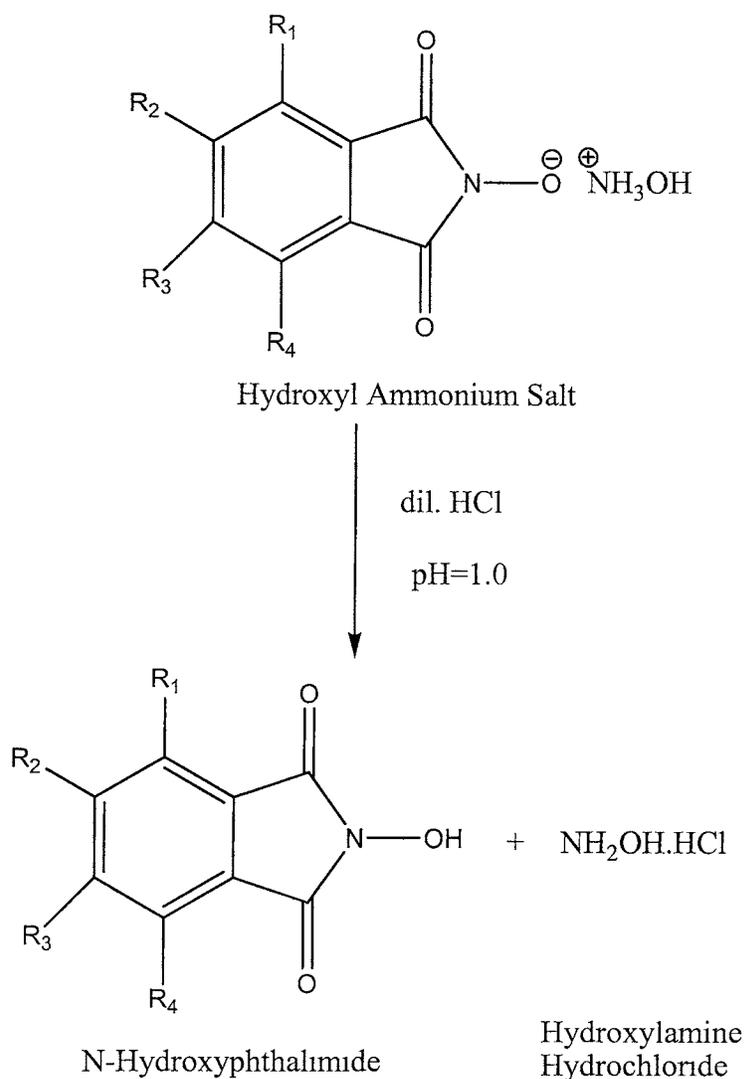
After the starting material was converted to the *N*-Boc derivative of phthalimide, addition of aqueous hydroxyl amine solution formed an orange precipitate which was probably the hydroxylammonium salt of *N*-hydroxyphthalimide (Scheme 2). *tert*-Butylcarbamate and *tert*-butyl alcohol, the byproducts of these reactions were completely soluble in the organic solution of the reaction medium.



**Scheme 2:** Synthesis of hydroxylammonium salt of phthalimides

### *N*-Hydroxyphthalimides

This reaction medium was basic because of the presence of hydroxylammonium ion. At higher pH (>7), hydroxylammonium ion dissociates into  $\text{NH}_2^+$  and  $\text{OH}^-$  ions which explains the basic nature of the solution. On addition of hydrochloric acid, protons from HCl are transferred onto the hydroxylammonium ion and a salt of hydroxylamine hydrochloride,  $\text{Cl}^- \text{NH}_3^+ \text{OH}$ , was formed which was soluble in the aqueous medium. This increases the acidity of the solution and a sudden drop in pH was observed. Under highly acidic conditions, pH=1.0, all hydroxylammonium ions are converted into the hydroxylamine hydrochloride favoring the formation of *N*-hydroxyphthalimides (Scheme 3). The product obtained was filtered under vacuum to separate the *N*-hydroxy compound from the aqueous solution of hydroxylamine hydrochloride. The residue was washed twice with water to ensure complete removal of salt solution and dried to get sufficiently pure *N*-hydroxyphthalimides which were used in the final step of monomer synthesis.

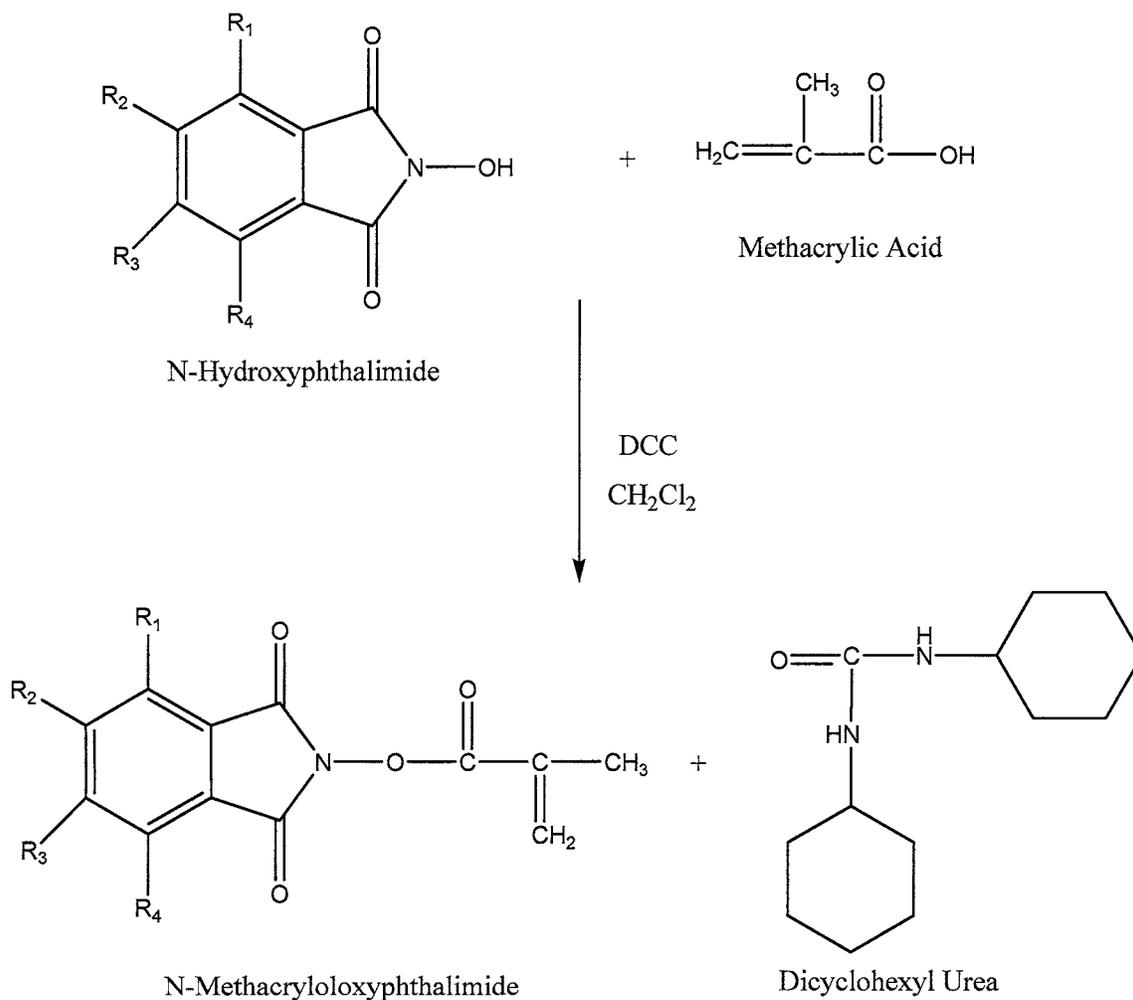


**Scheme 3:** Synthesis of substituted *N*-hydroxyphthalimide

#### *N*-Methacryloyloxy phthalimides

The Steglich esterification reaction<sup>29</sup> was performed using *N*-hydroxyphthalimide and methacrylic acid to synthesize *N*-methacryloyloxy phthalimide compounds (Scheme 4). *N,N*-dicyclohexyl carbodiimide reacts with methacrylic acid to form an activated carboxylic acid, an *O*-acylisourea intermediate which reacts with *N*-hydroxyphthalimide and forms a stable dicyclohexyl urea and the ester. The urea derivative was removed by

filtration under vacuum. Phthalimide was present in the homogeneous organic phase and was isolated by evaporating the filtrate under vacuum. The monomer was purified by recrystallization of the residue from 95% ethanol.



**Scheme 4:** Synthesis of substituted *N*-methacryloyloxy phthalimide

Monomer Characterization

NMR Studies

The <sup>1</sup>H-NMR spectra of all the monomers were taken in deuterated DMSO and presented in APPENDIX I. A solvent peak was present at 2.50 ppm in all the spectra

recorded in DMSO. In addition to this, a broad peak at 3.35 ppm due to the dissolved water in DMSO was also observed in each of these spectra.

In *N*-methacryloyloxy phthalimide the aliphatic protons from CH<sub>3</sub> are seen at  $\delta$  2.04 ppm (s, 3H). The hydrogen's of CH<sub>2</sub> are shifted downfield due to unsaturation and also because of the presence of electron withdrawing carbonyl group attached to its adjacent carbon (APPENDIX I, No. 4). Two peaks at  $\delta$  6.16 and 6.44 ppm correspond to the singlets of CH<sub>2</sub> protons. A multiplet for four aromatic protons was observed between 7.94 and 8.00 ppm. The deshielding effect of electron withdrawing substituents on the aromatic ring was observed from the spectrum of both 4,5-dichloro- and 4-nitro-*N*-methacryloyloxy phthalimides (APPENDIX I, No. 1, No. 3). An electron donating methyl group shifted the unsaturated CH<sub>2</sub> and aromatic protons to upfield which can be noticed in APPENDIX II, No. 2.

The presence of the nitro group on the aromatic ring shifted the peaks for aromatic protons from  $\sim$ 8.0 ppm to  $\sim$ 8.70 ppm. The splitting pattern was also different, as expected from the non-equivalent aromatic protons. Three separate peaks were observed for each aromatic proton. The multiple splitting of each peak can be explained from the long range coupling between these protons. A similar splitting pattern was observed for 4-methyl-*N*-methacryloyloxy phthalimide which confirms the position of both the methyl and nitro groups on the aromatic ring. A peak at 2.50 ppm was seen for the methyl group substituted on the aromatic ring of 4-methyl-*N*-methacryloyloxy phthalimide. The presence of chemically and magnetically equivalent protons on the aromatic ring of 4,5-dichloro-*N*-methacryloyloxy phthalimide showed a singlet at 8.35 ppm.

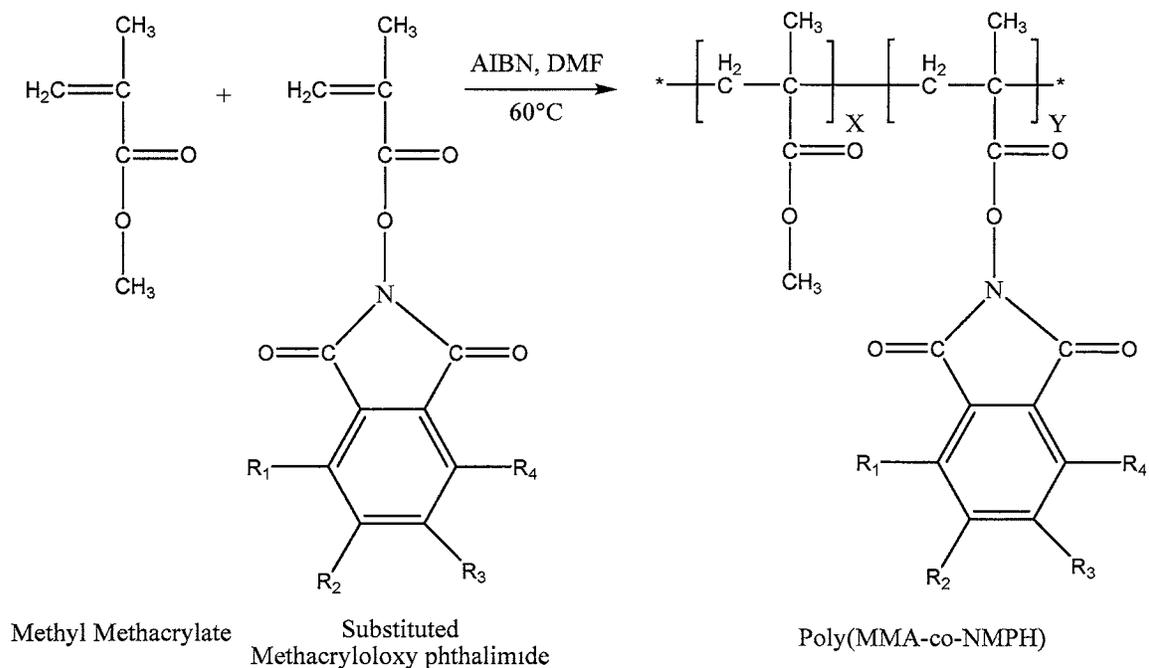
## IR Studies

IR spectra for all monomers were taken as KBr pellets and reported in APPENDIX II. Olefinic and aromatic C-H stretching, symmetric and asymmetric C-H stretching vibrations from the CH<sub>3</sub> group can be observed in the region of 2840 – 3150 cm<sup>-1</sup>. Two bands from C=C stretching vibrations around 1640 cm<sup>-1</sup> confirms the presence of aromatic character in the compounds. The presence of ester groups in the compounds can be seen from the strong C=O band around 1750 cm<sup>-1</sup> and the band at ~1200 cm<sup>-1</sup> from the C–O stretching vibrations. The ring strain from the five-membered cyclic structure shifts the absorption to higher frequencies<sup>30</sup>. Two strong bands around ~1800 cm<sup>-1</sup> corresponds to the C=O(s) from (C=O)–N–(C=O). In 4-nitro-N-methacryloyloxy phthalimide, a strong band at 1540 cm<sup>-1</sup> was from the N=O stretching vibrations.

## Polymer Synthesis

Synthesis of Poly (*N*-methacryloyloxy phthalimide(s)–co–methylmethacrylate)'s

Methylmethacrylate was polymerized at various compositions with the above mentioned series of *N*-methacryloyloxy phthalimides by free radical solution polymerization (Tables 4-7). Solutions of one molar concentration of DMF of monomer(s) were prepared in a Schlenk flask and AIBN (1 mol %) was added as a free radical initiator. The solution was degassed using three continuous freeze-pump-thaw cycles in order to eliminate quenching of the polymerization reaction with oxygen. After the reaction was complete polymer was precipitated into a non-solvent, methanol.



**Scheme 5:** Co-polymerization of methyl methacrylate and *N*-methacryloyloxy phthalimide(s)

## Polymer Characterization

### NMR Studies

$^1\text{H}$  NMR studies of all the synthesized polymers were taken in deuterated DMSO solvent. The aliphatic region of the polymers extended between 0.73 and 2.23 ppm. Three significant broad peaks are observed in this region. Two methyl groups each from methylmethacrylate and substituted *N*-methacryloyloxy phthalimide correspond to the two peaks around 1.0 ppm. A peak for methylene protons was observed around 1.9 ppm. The presence of two electron-withdrawing ester groups on each side of methylene explains the shifting of this peak upfield. The breadth of the peaks may be due to the presence of these protons under the influence of the random environment of ester groups. Another broad peak at  $\sim 3.55$  ppm corresponds to the protons from the methoxy group in

the co-polymers and was not seen in the homopolymers of substituted *N*-methacryloyloxy phthalimides.

The aromatic region extended between 7.70 and 8.80 ppm. The copolymers of 4,5-dichloro-*N*-methacryloyloxy phthalimide gave a single sharp peak at  $\sim 7.9$  ppm. Broad peaks between 7.6 to 7.8 ppm were observed for aromatic protons from the co-polymers of 4-methyl-*N*-methacryloyloxy phthalimide and *N*-methacryloyloxy phthalimide. The nitro-substituted polymers showed three peaks at 8.21, 8.69 and 8.59 ppm, one for each non-equivalent proton. The integration values for the aromatic protons increased with increase in the incorporation of the *N*-methacryloyloxy phthalimide monomer into the co-polymer. Investigation about the percentage incorporation of these monomers into the polymer and their reactivity ratios should be studied in future.

#### IR Studies

All the polymers showed C-H stretching from saturated methyl and methylene groups as discussed earlier (Section 3.2.2) in the IR studies of monomers. The aromatic hydrogens from pendant phthalimide groups showed bands around  $3094\text{ cm}^{-1}$ . A band around  $1600\text{ cm}^{-1}$  from stretching C=C bond was noticed in the spectrum from all the polymers. The broad band around  $1800\text{ cm}^{-1}$  due to carbonyl stretching was observed from both acrylic and the methacryloyloxy groups. A band with a split around  $1200\text{ cm}^{-1}$  was seen from the asymmetrical C–O–C stretching of methoxy group. Splitting of that band may be because of the C–O–N stretching vibrations of methacryloyloxy phthalimide group.

## Gel Permeation Chromatography

GPC was carried out for the polymers which were soluble in chloroform to determine the number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) (Tables 13-16). The molecular weight of the polymers was estimated on calibration with polystyrene standards. Most of the polymers are soluble in chloroform with exception of homopolymers of 4-nitro-, 4-methyl- and unsubstituted *N*-methacryloyloxy phthalimides. Most of the polymers had molecular weight of  $\sim 18000$  g/mol with a PDI of  $\sim 2.0$ . The tables below give the number and weight average molecular weight of the polymers along with their poly dispersity index (PDI).

**Table 13:** Molecular weight data for polymers from *N*-methacryloyloxy phthalimide.

Percentage		$M_n$ (g/mol)	$M_w$ (g/mol)	PDI (g/mol)
MMA	NMPH			
<99	<1	22300	43000	1.931
92	8	10600	22000	2.095
72	28	20700	53300	2.577
48	52	17900	90500	5.063

**Table 14:** Molecular weight data for polymers from 4-nitro-N-methacryloyloxy phthalimide.

Percentage Ratio (mol %)		Mn (g/mol)	Mw (g/mol)	PDI (g/mol)
MMA	4-nitro NMPH			
<99	>1	19300	39900	2.063
93	7	18000	37000	2.065
80	20	19100	41300	2.157
50	50	8100	13800	1.704

**Table 15:** Molecular weight data for polymers from 4-methyl-N-methacryloyloxy phthalimide.

<b>Percentage Ratio (mol %)</b>		<b>Mn (g/mol)</b>	<b>Mw (g/mol)</b>	<b>PDI (g/mol)</b>
<b>MMA</b>	<b>4-methyl NMPH</b>			
<99	>1	23100	43000	1.863
94	6	24500	52700	2.150
79	21	18000	52900	2.940
48	52	17900	131700	7.335

**Table 16:** Molecular weight data for polymers from 4,5-dichloro-*N*-methacryloyloxy phthalimide.

Percentage Ratio (mol %)		Mn (g/mol)	Mw (g/mol)	PDI (g/mol)
MMA	4,5-dichloro-NMPH			
98	2	16100	25800	1.601
93	7	19700	50300	2.554
76	24	23700	72700	3.074
52	48	23600	88600	3.750
0	100	2970	6270	2.109

#### Thermogravimetric Analysis

Weight loss at ~95 °C in the thermograms were from the traces of solvent (DMF) present in the polymer. The polymer degradation mechanism was expected to start either from the double bonded chain ends or from the labile N–O bond on the pendant group of backbone. The decomposition temperature at maximum weight loss for the polymers ranged between 260 °C and 310 °C. This sudden weight loss may be attributed to the formation of radicals on the backbone leading to the fragmentation of polymer. Small

percentages of degradation were also observed in the thermograms. This might be from the loss of smaller molecules (or radicals) like CO<sub>2</sub>, CO, OCH<sub>3</sub> or other pendant groups on the polymer backbone. Ultimate residues at 800 °C of less than 10% indicate that most of the polymers were of limited thermal stability.

#### Differential Scanning Calorimetry

Glass transition temperatures were measured for all the polymers. The T<sub>g</sub> of PMMA was found to be 88 °C and the T<sub>g</sub>'s of the copolymers ranged between 106 °C and 140 °C. Incorporation of NMPH into the polymer increased the glass transition temperature as expected. It was observed that there is only one glass transition temperature for each polymer; *i.e.* the polymerization did not result in a block copolymer. This implies that the monomer reactivity was random and that there was no phase separation.

The  $\pi$ -stacking and ring structure of the aromatic groups increases the rigidity of the polymer. This reduces the flexibility of polymer chains and hence more energy has to be induced in order to overcome the interactions. The presence of a number of carbonyl groups also adds to the rigidity of the polymer. As the bulky group is present as a pendant and not as a part of the polymer backbone, the rise in T<sub>g</sub> is not extensive; however, it is important that T<sub>g</sub>'s of the polymers are high enough to withstand semiconductor processing.

The T<sub>g</sub>'s of homopolymers are less compared to those copolymers which could be explained based on the length of the pendant groups. Longer pendant groups increase the distance between the polymer backbones. This affects dense packing of the polymer

chains and results in large voids, thus allowing free motion of the chains at lower energies.

### Electron Beam Lithography

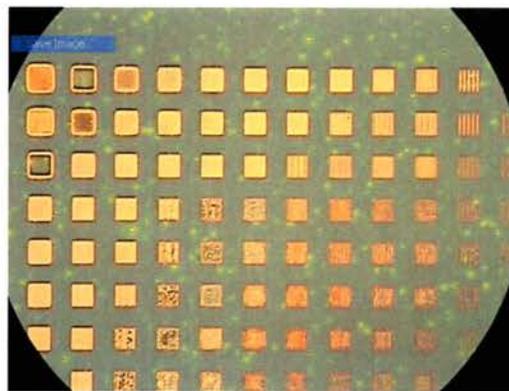
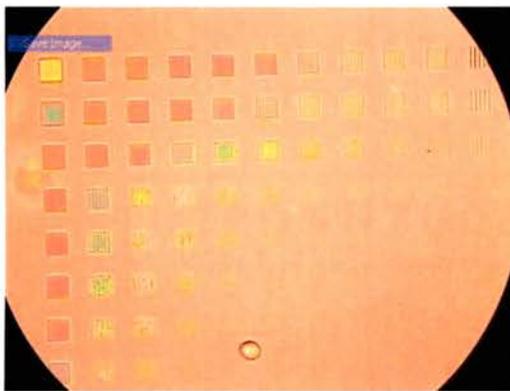
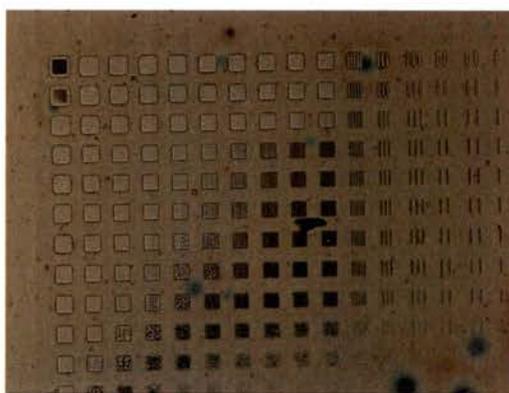
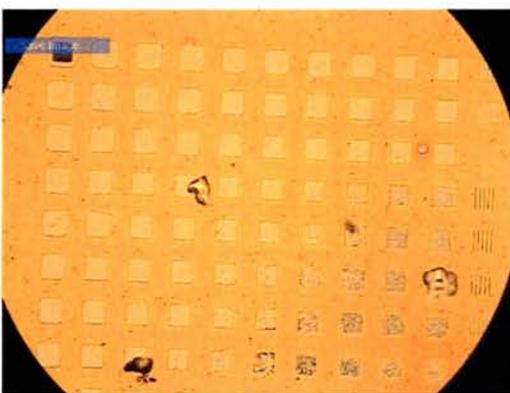
The process of electron beam lithography was done on four silicon wafers with a polymer photoresist (20-28 mol % of NMPH) on each silicon wafer, selected from each series of co-polymers of methyl methacrylate and *N*-methacryloyloxy phthalimide. Each wafer shows 32 X 25 (rows X columns) patterns on it and each pattern composed of 12.7  $\mu\text{m}$  lines arrayed to form squares of 12.7  $\mu\text{m}^2$ . The spreadsheet for each wafer exposed gives information about the line width, writing speed and dosage of each of the patterns.

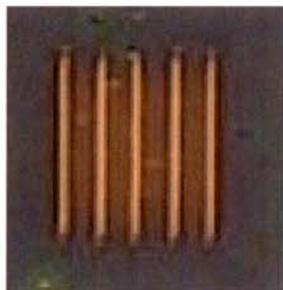
Some of the patterns are over dosed and some are under dosed. Dark colors inside the patterns indicate that the dosage is too high and resulted in either burning or crosslinking of the resist material. At lower dosage and higher speeds, all the patterns are not visible. Increasing writing speed gives less time for radiation-sensitive reaction and leads to inferior pattern quality. At some point of process the resist is no longer exposed enough to form the patterns. If the sensitivity of the resist material is high, exposures even with faster writing speed give better patterns on the wafer.

One best pattern from each wafer was selected and the dosage, writing speed, line width and density of that pattern was reported in the Table 17.

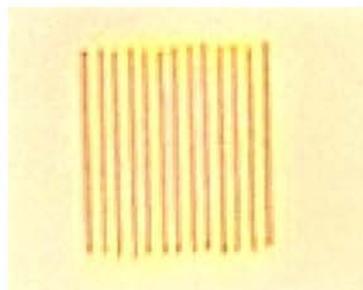
**Table 17:** e-Beam lithography data for polymer resists.

Sample Name	Line width ( $\mu\text{m}$ )	Dosage $\mu\text{C}/\text{cm}^2$	Writing Speed ( $\mu\text{sec}/\text{mil}$ )	Density (lines/mil)
Poly(MMA-N.NMPH)-8020	0.54	1342	5000	44
Poly(MMA-C.NMPH)-7624	0.66	878	4000	36
Poly(MMA-NMPH)-7228	0.66	659	3000	36
Poly(MMA-M.NMPH)-7921	0.6	251	1000	40

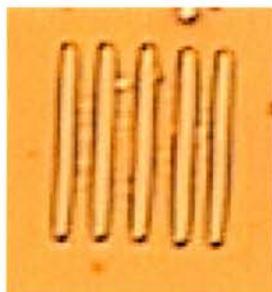
**Figure 4:** Full-Poly(MMA-N.NMPH)-8020. **Figure 5:** Full Poly(MMA-C.NMPH)-7624.**Figure 6:** Full Poly(MMA-NMPH)-7228. **Figure 7:** Full Poly(MMA-M.NMPH)-7921.



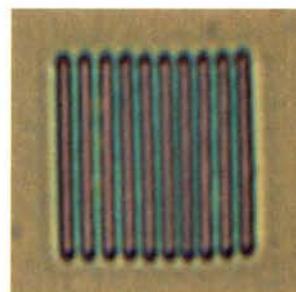
**Figure 8:** Poly(MMA-C.NMPH)-7624.



**Figure 9:** Poly(MMA-N.NMPH)-8020.



**Figure 10:** Poly(MMA-NMPH)-7228.



**Figure 11:** Poly(MMA-M.NMPH)-7921.

Figures 4-7 are the optical images of the array of best possible patterns formed after developing the wafers. Figures 8-11 shows the best images selected from each resist.

The presence of electronic groups on the chemical structure of the resist greatly influenced the lithographic properties. The polymers used as resists differ in the nature of the group attached to the *N*-methacryloyloxy phthalimide. Co-polymers substituted with nitro groups gave the smallest line width but with highest dose and lowest speed. Smallest dosage and fastest writing speed with comparable line width was obtained from the polymer resist substituted with methyl group.

## CHAPTER IV

### SUMMARY AND CONCLUSIONS

In summary, a series of *N*-methacryloyloxy phthalimide compounds (Table 1) were synthesized starting from the respective phthalimides. Each of these monomers was co-polymerized with methyl methacrylate at various compositions. The relative incorporation of substituted NMPH in the polymer was less than MMA. The monomers and polymers synthesized were characterized using techniques such as <sup>1</sup>H-NMR, and IR spectroscopy. These results confirmed the structures of the monomers and the polymers. It was observed that the compounds made were in high purity. The molecular weight of the polymers was determined using GPC. The molecular weight for most of the copolymers was ~18,000 g/mol. Low molecular weight of the polymers might be because of the experimental error of addition of initiator before degassing the flask. The molecular weight distribution was narrow in most cases with a PDI of ~2.0.

Thermal properties of the polymers were determined using DSC and TGA. The glass transition temperature of PMMA increased from 86 °C to ~130 °C with the incorporation of substituted *N*-methacryloyloxy phthalimide into the copolymer. Homopolymers showed lower  $T_g$ 's compared to the copolymers which could be because of the larger voids between the rigid cycloimido pendant group structures. The decomposition temperatures for the polymers ranged between 260 °C to 310 °C. The

thermal properties shown for the polymers are high enough to withstand the semiconductor processing.

Electron beam lithography studies were done on four polymer samples with 20-28% composition of substituted *N*-methacryloyloxy phthalimide. A 0.5  $\mu\text{m}$  e-beam gun was used for exposure and it was observed that the least line width on the patterns was  $\sim 0.54 \mu\text{m}$ . The polymer with nitro substitution on the pendant group showed the least line width but had highest dosage and least speed among the samples selected for EBL. Least dosage and fastest writing speed was observed for the polymer with methyl substitution. These two polymers were observed to be the promising materials as positive photoresist out of the four selected polymers.

## CHAPTER V

### FUTURE RESEARCH

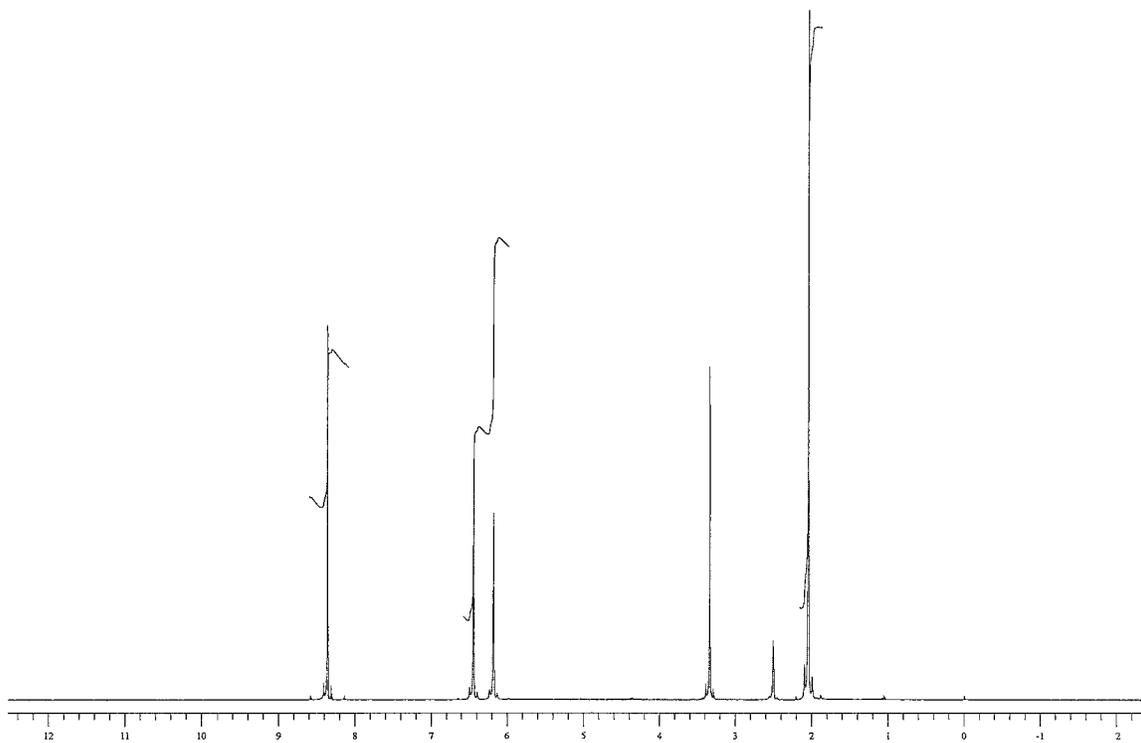
As an extension of this work, the reactivity ratios of the polymers can be determined. The molecular weight of the polymers was limited to ~20,000 g/mol. These polymers can be synthesized by varying the initiator concentration to improve the molecular weight. A detailed study of degradation mechanism of these polymers can be investigated from mass spectral studies using instruments like MALDI-TOF or MS-CI.

Polymers of tetrahydro *N*-methacryloyloxy phthalimide with various substituents on cyclohexyl group can be synthesized and their properties can be compared to the properties of polymers made from substituted *N*-methacryloyloxy phthalimide.

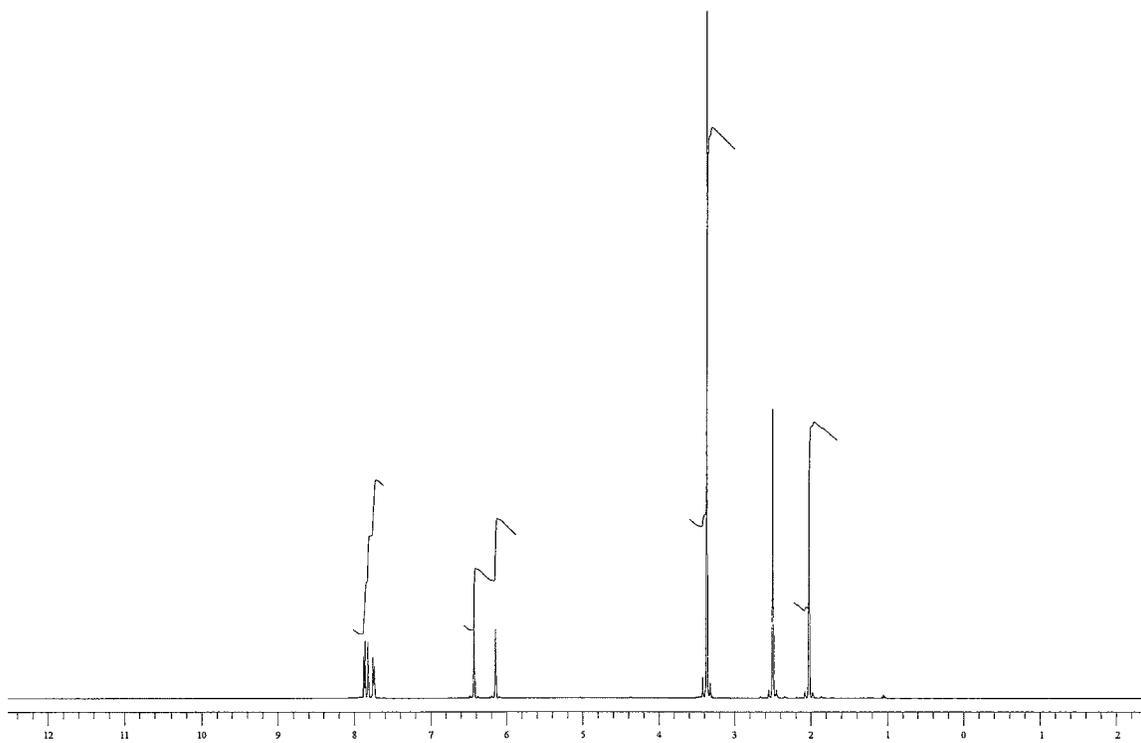
This thesis compared only few lithographic properties of four of the polymers made from various combinations of compositions and compounds. Properties like contrast, sensitivity, resolution and etch resistance were not studied. This work can be extended to evaluate the lithographic properties of the rest of the polymers including contrast, sensitivity, etch resistance and resolution. These properties can be compared to the properties of PMMA and the best performing materials can be selected for complete lithographic studies.

## **APPENDIX I**

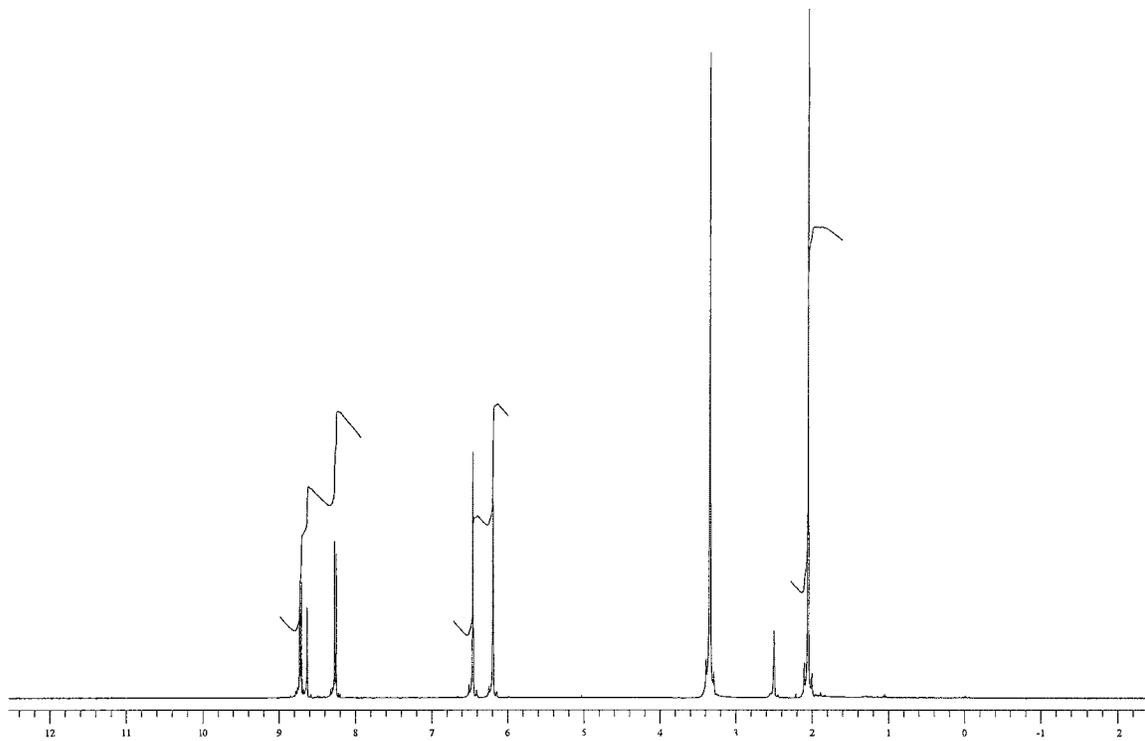
### **NMR**



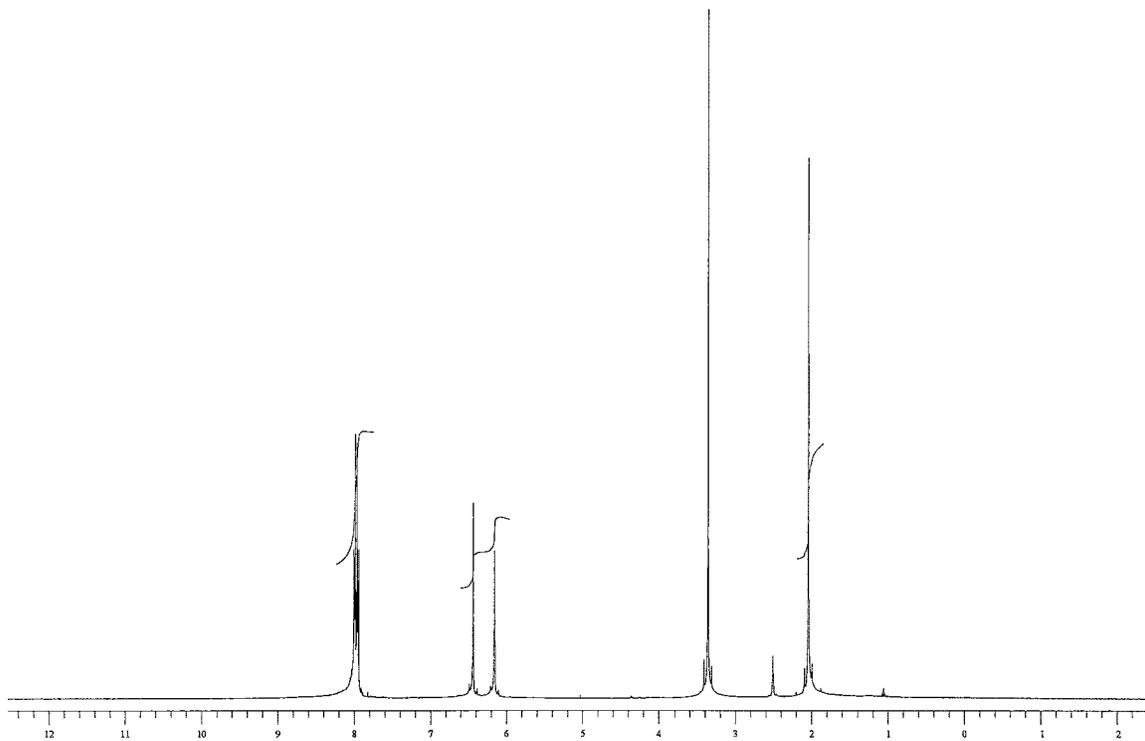
1. 4,5-dichloro-*N*-methacryloyloxy phthalimide



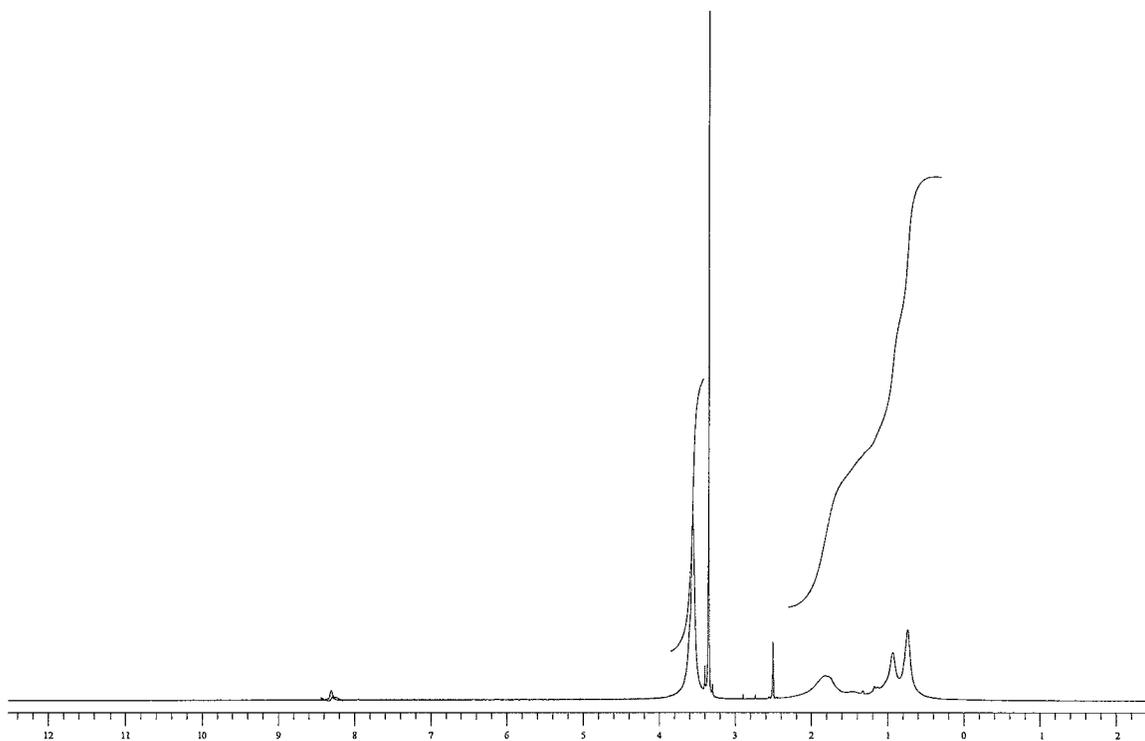
2. 4-Methyl-*N*-methacryloyloxy phthalimide



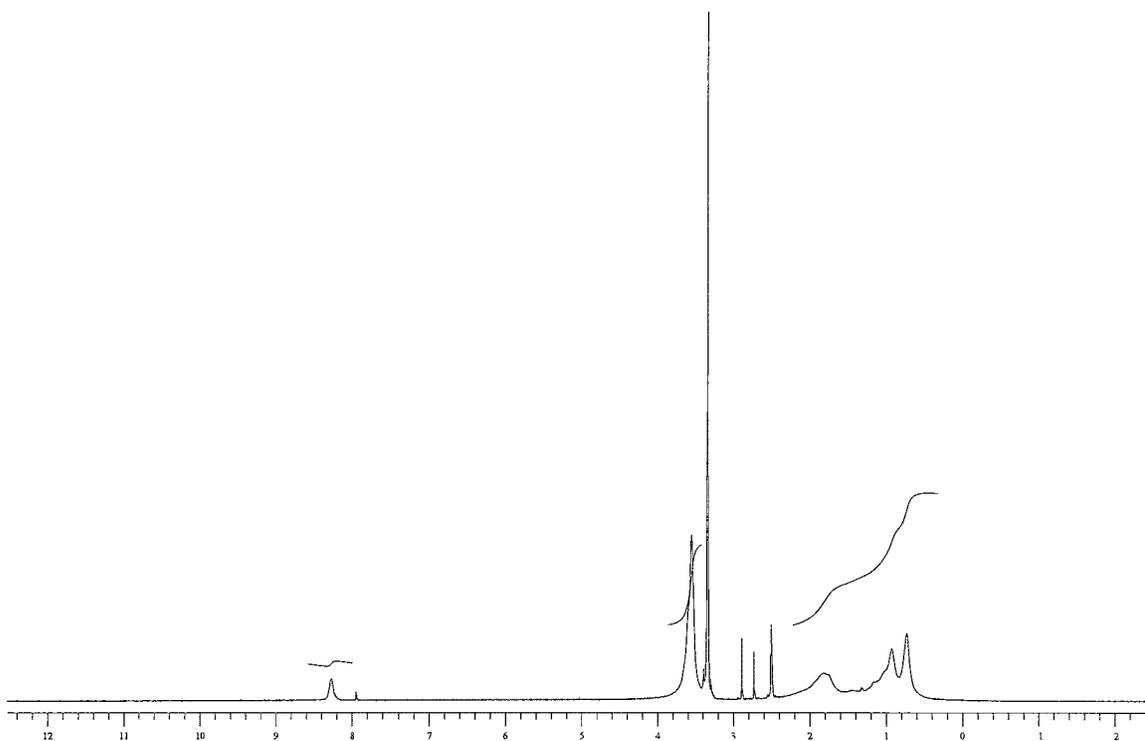
3. 4-nitro-*N*-methacryloyloxy phthalimide



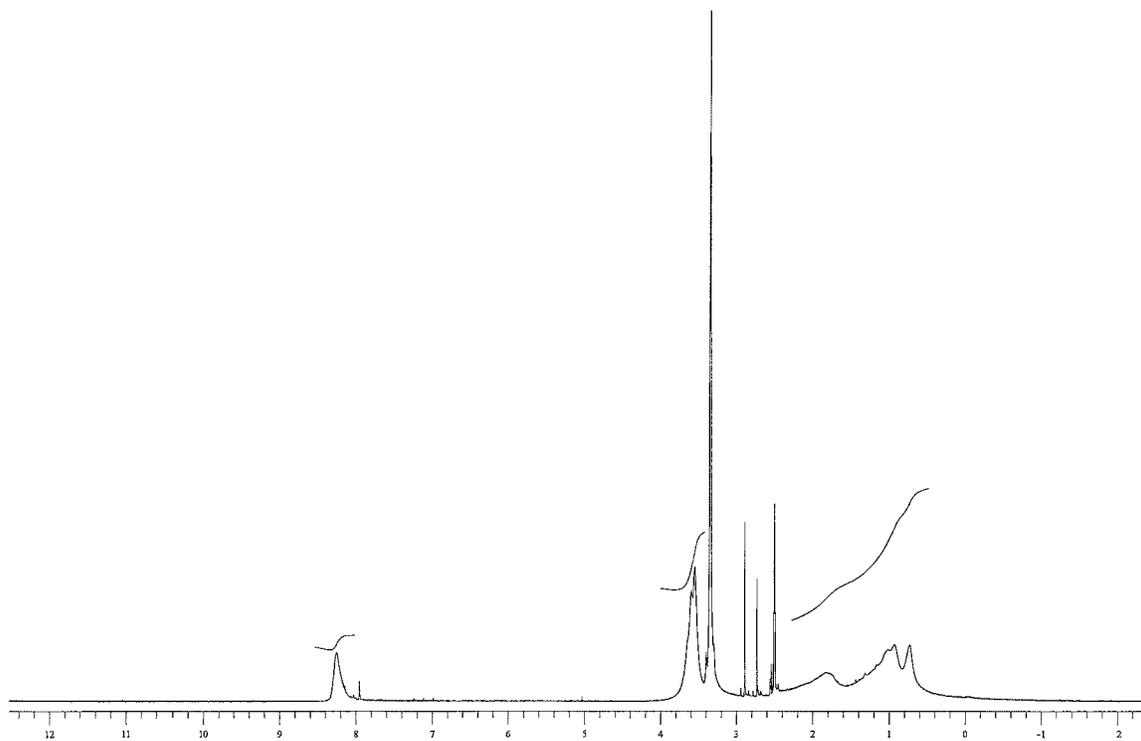
4 *N*-methacryloyloxy phthalimide



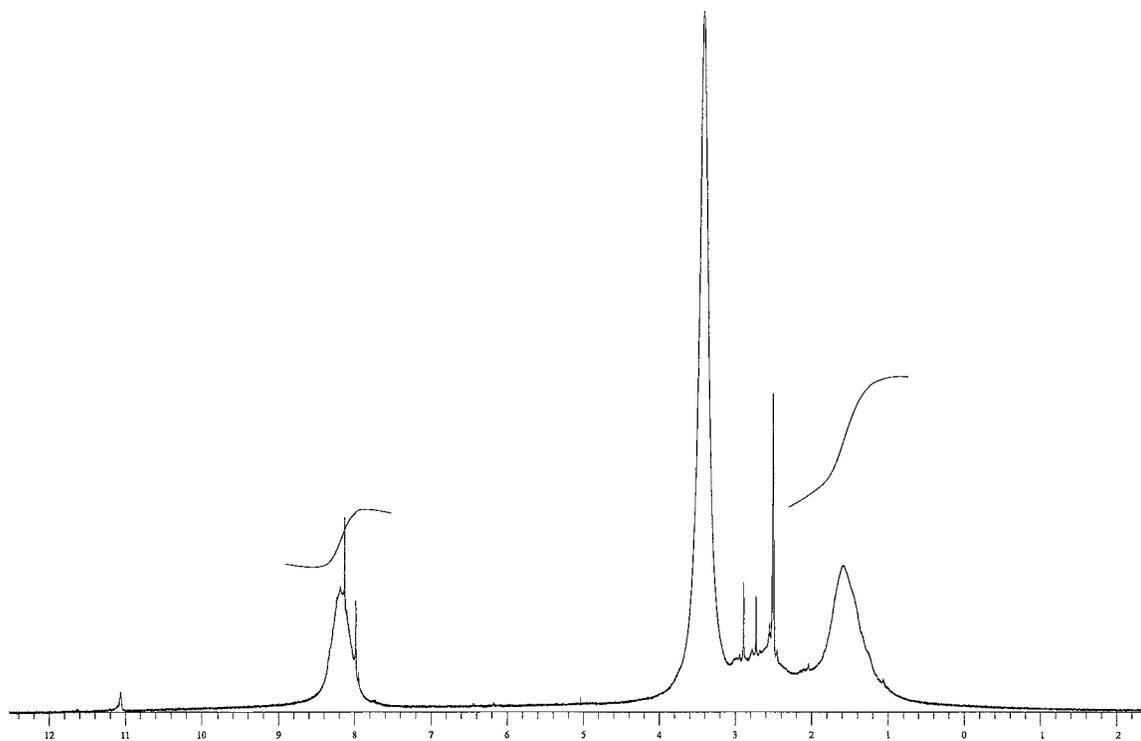
5. Poly(MMA-co-Cl.NMPH) - 9802



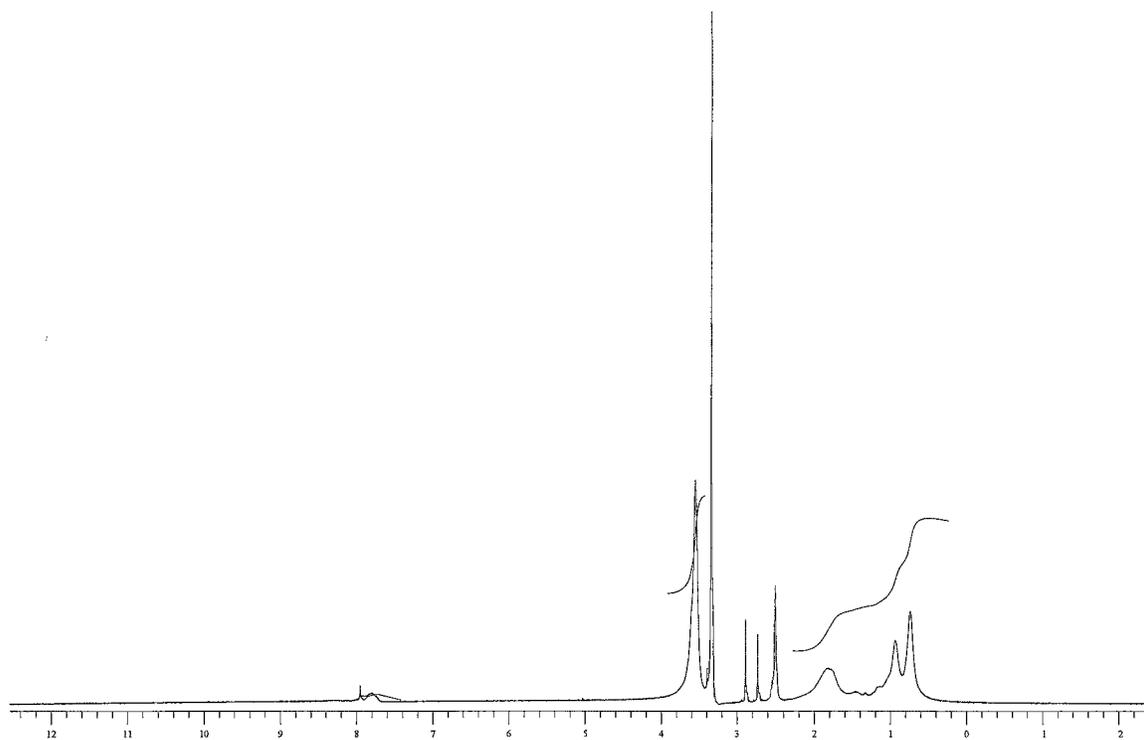
6. Poly(MMA-co-Cl.NMPH) - 9307



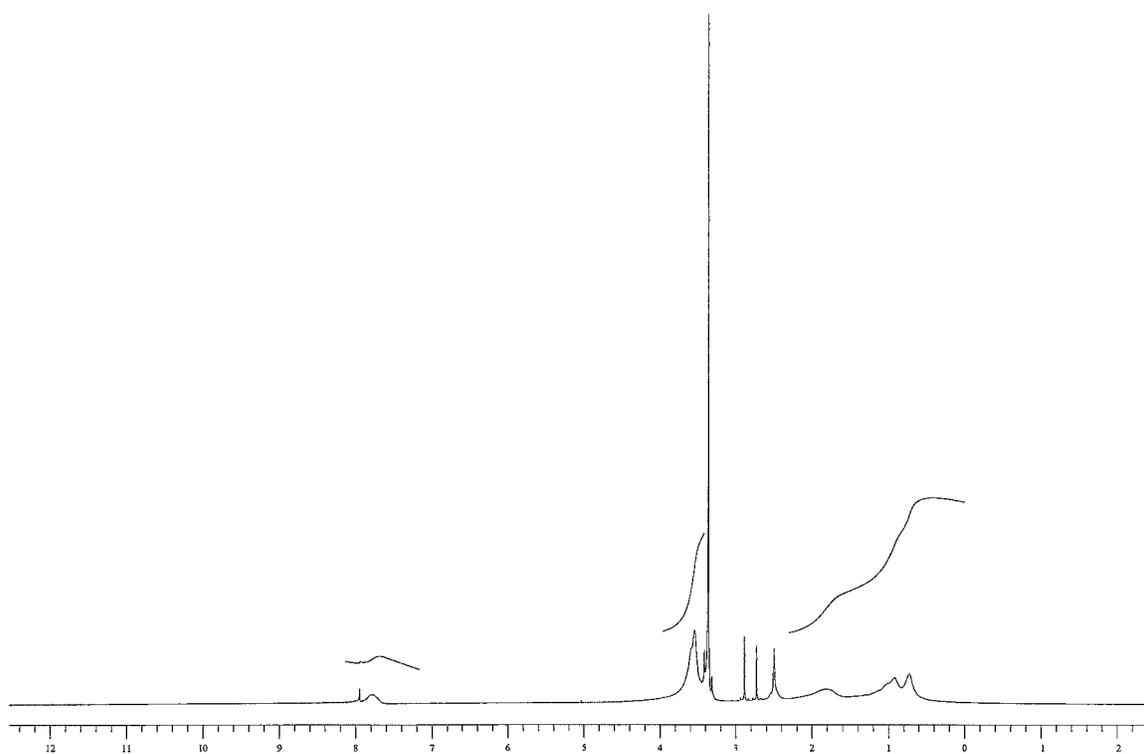
7. Poly(MMA-co-Cl.NMPH) - 7624



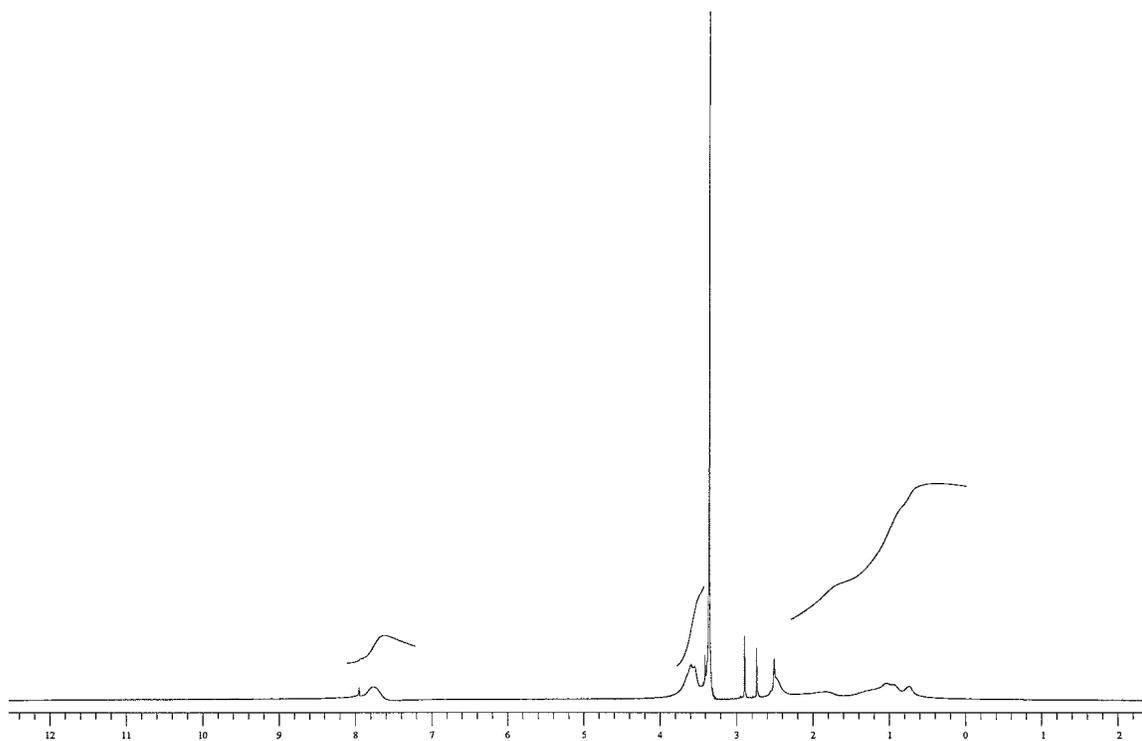
8. Poly(4,5-dichloro-N-methacryloyloxy phthalimide)



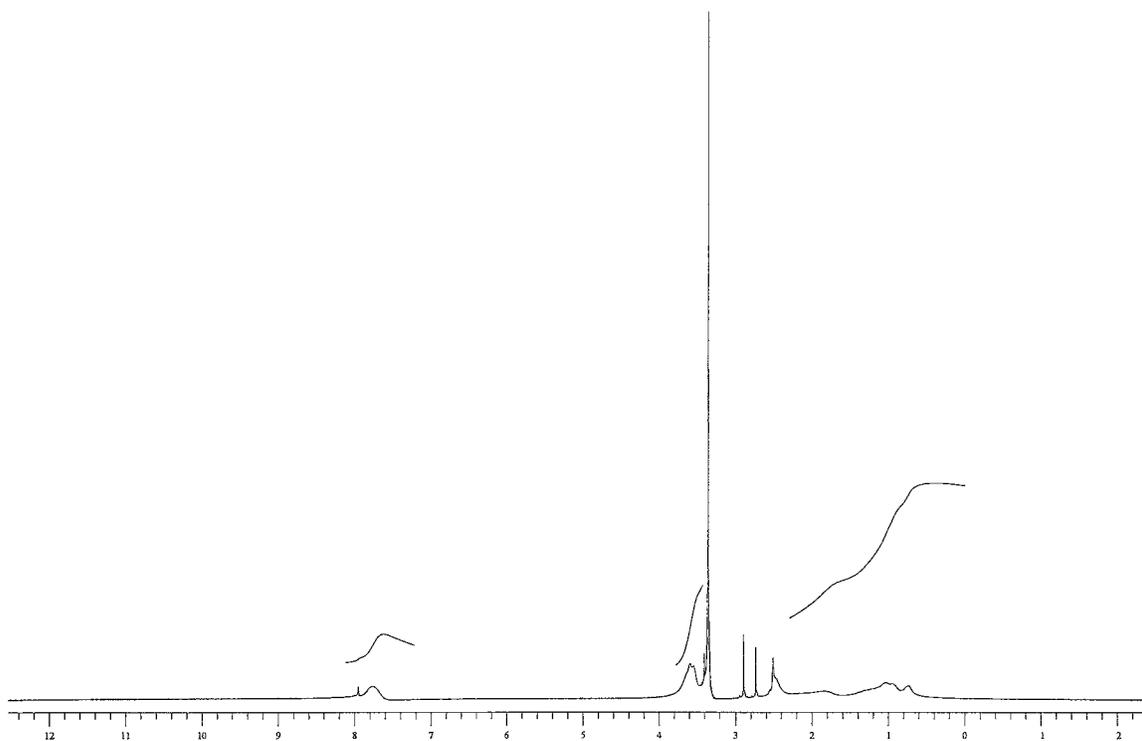
9. Poly(MMA-co-M.NMPH) -9901



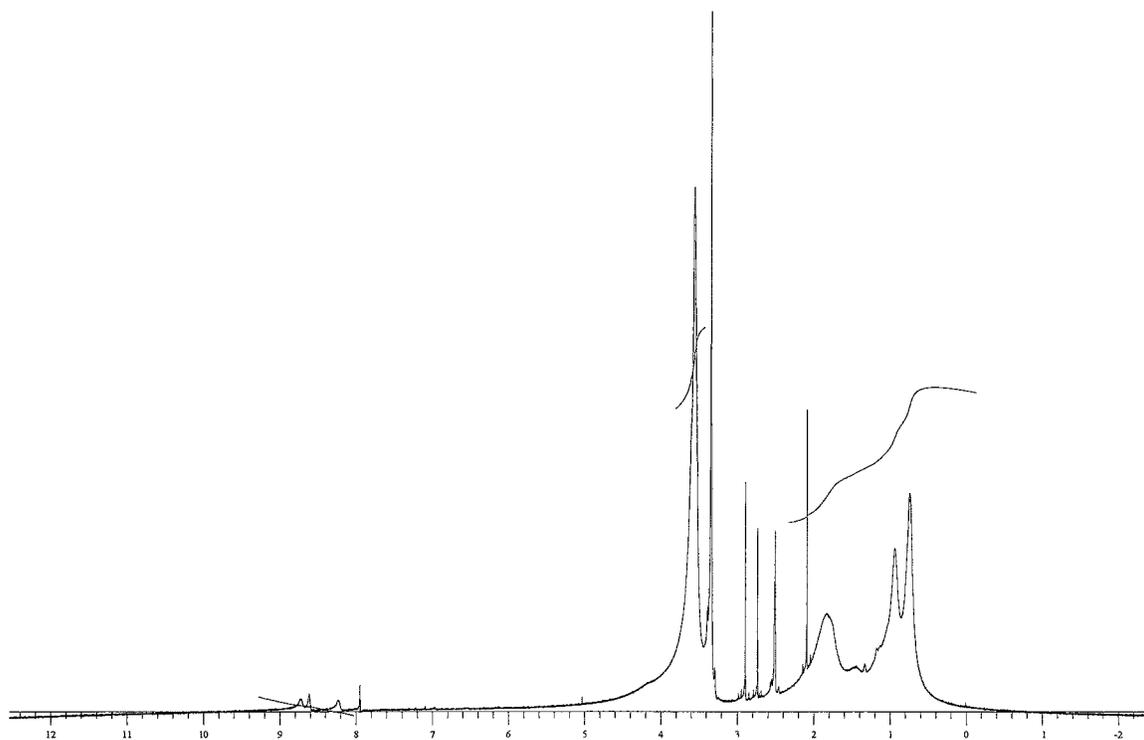
10. Poly(MMA-co-M.NMPH) - 9406



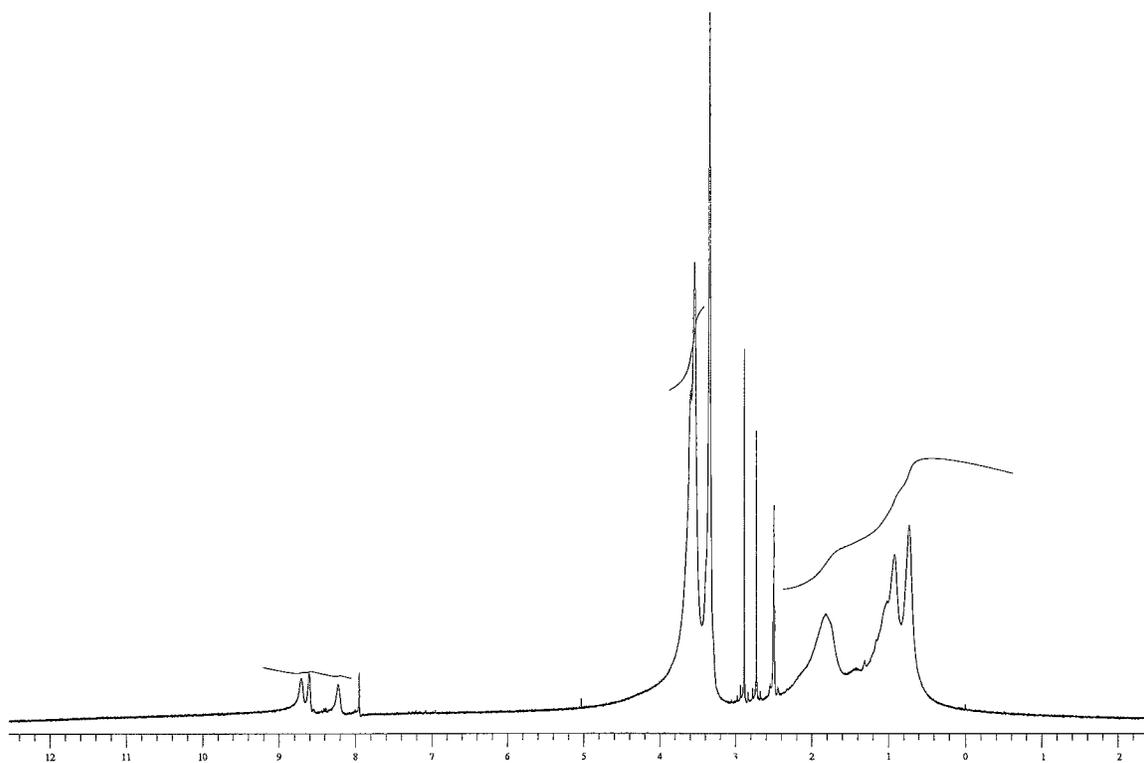
11. Poly(MMA-co-M.NMPH) - 7921



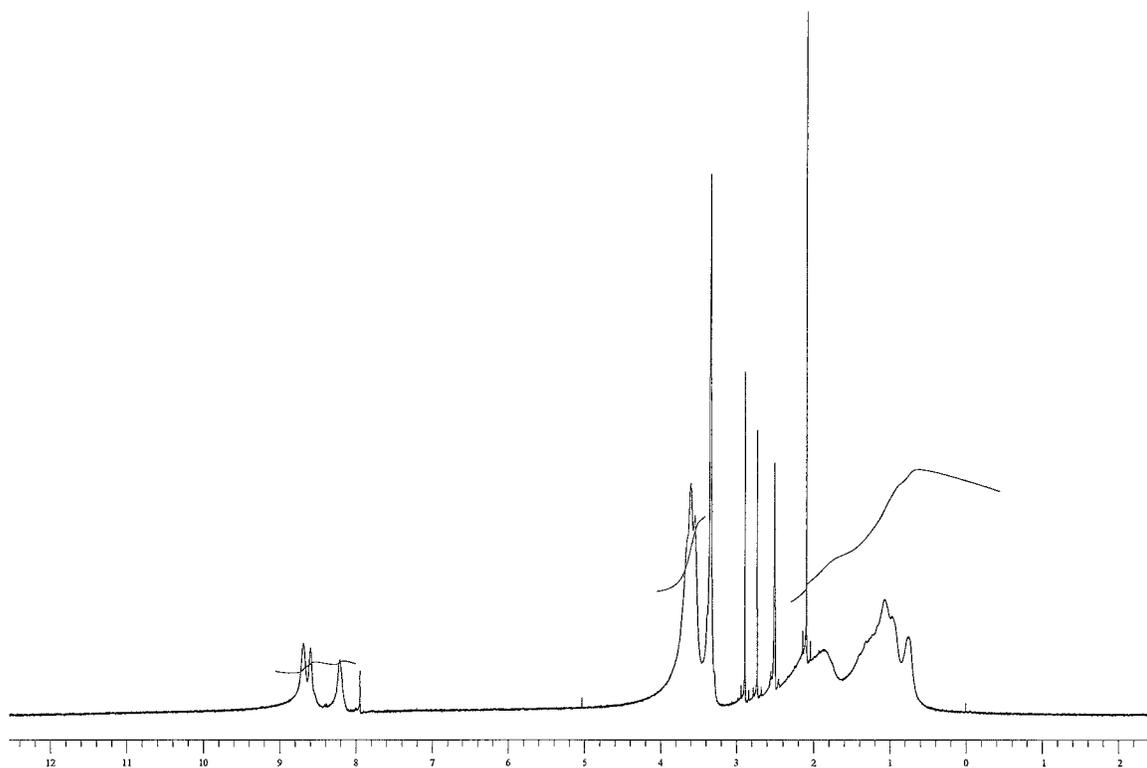
12. Poly(MMA-co-M.NMPH) - 4852



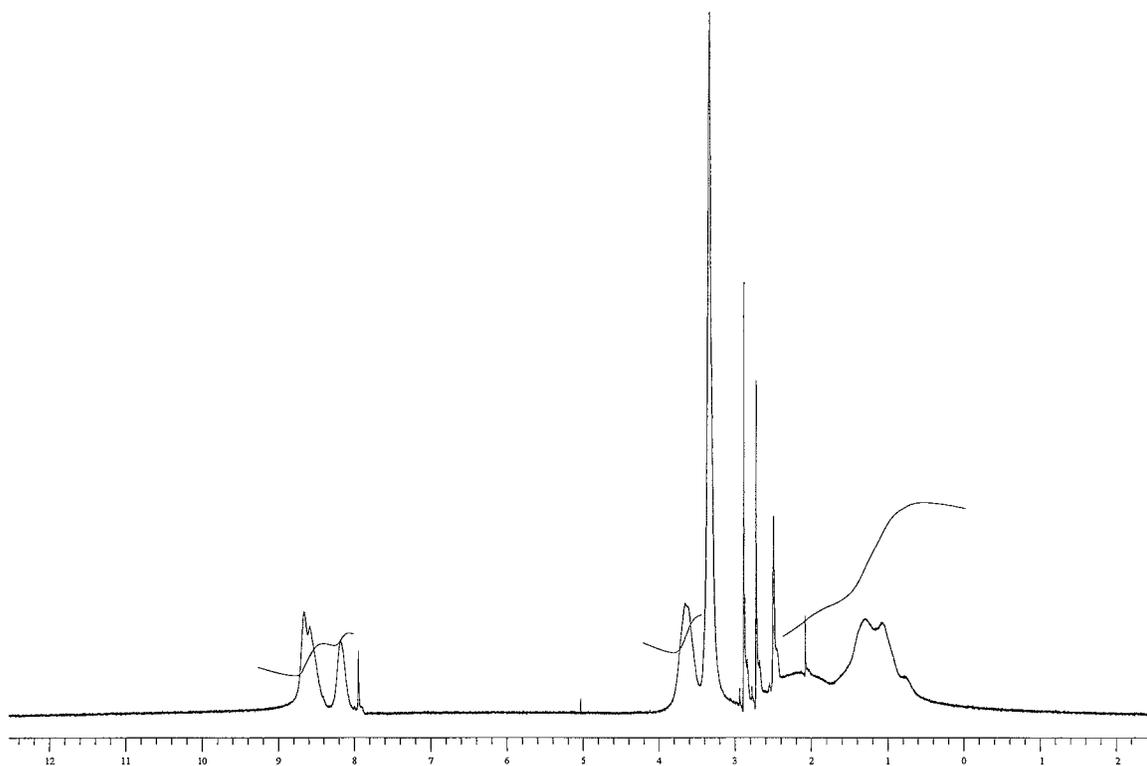
13. Poly(MMA-co-N.NMPH)-9901



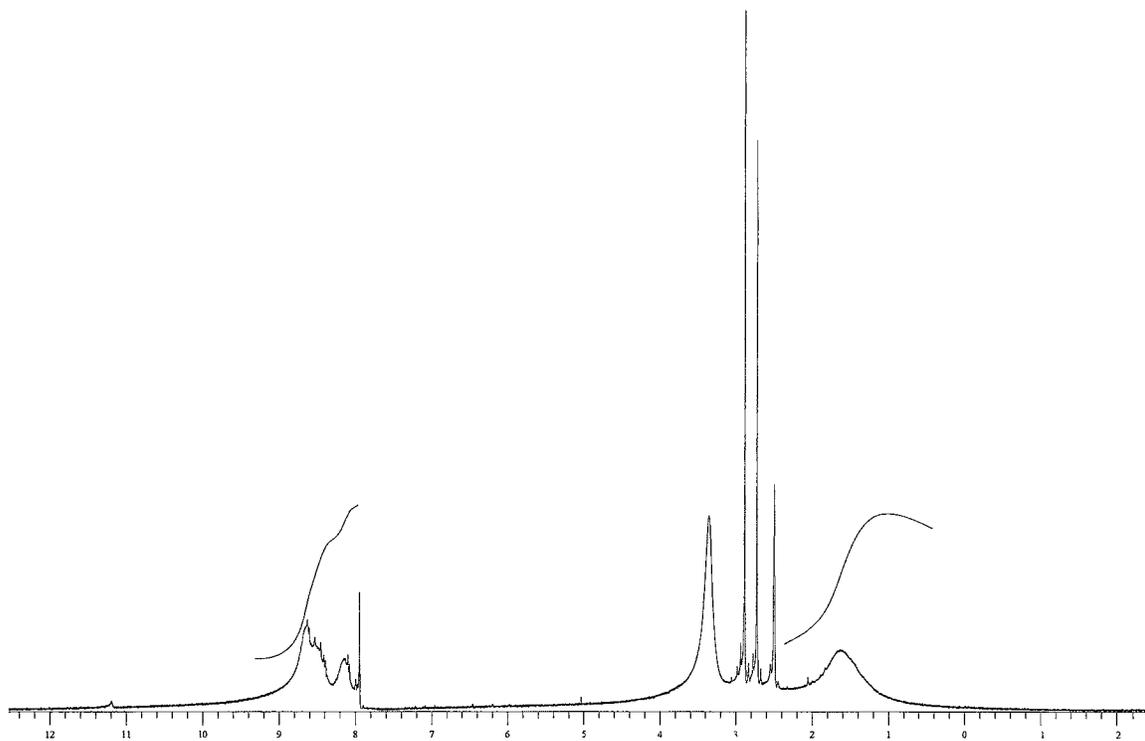
14. Poly(MMA-co-N.NMPH)-9307



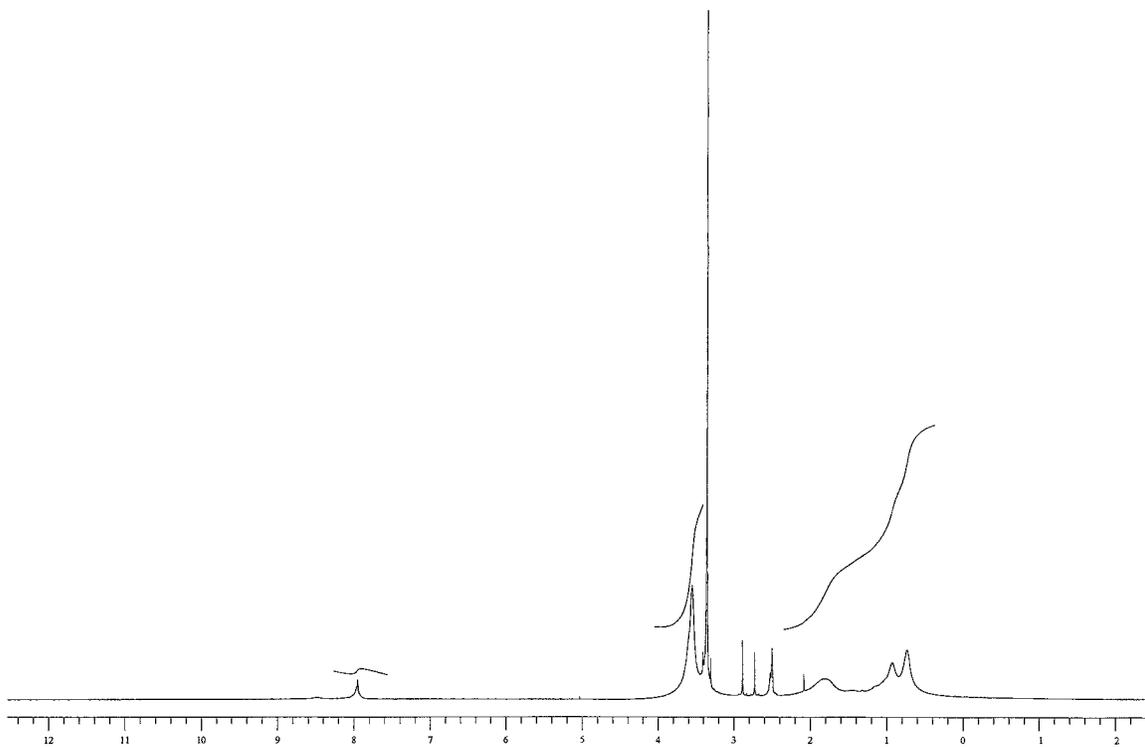
15. Poly(MMA-co-N.NMPH)- 8020



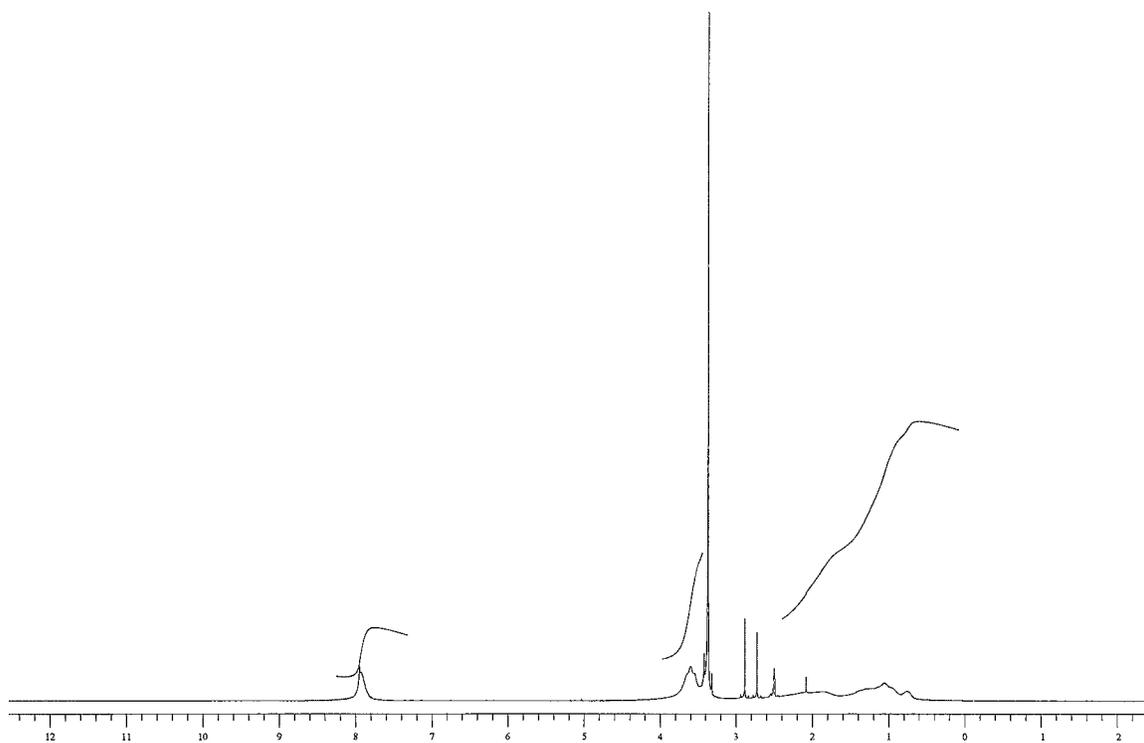
16. Poly(MMA-co-N.NMPH)- 5050



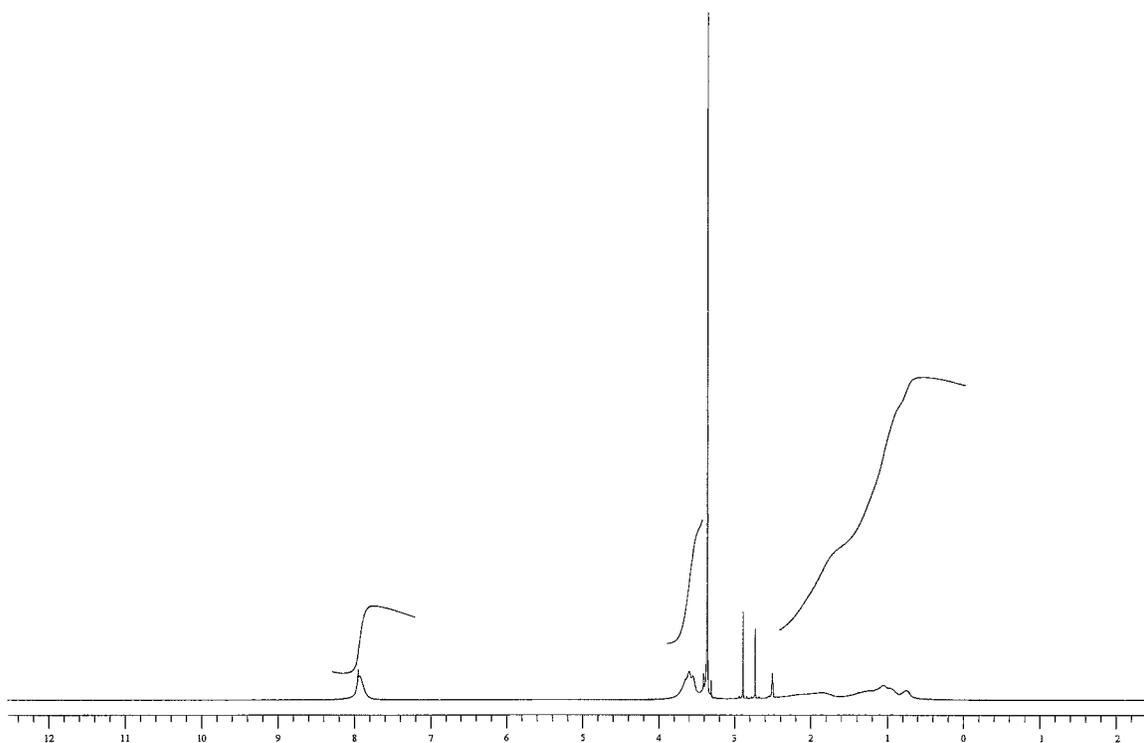
17. Poly(4 nitro-N-methacryloyloxy phthalimide)



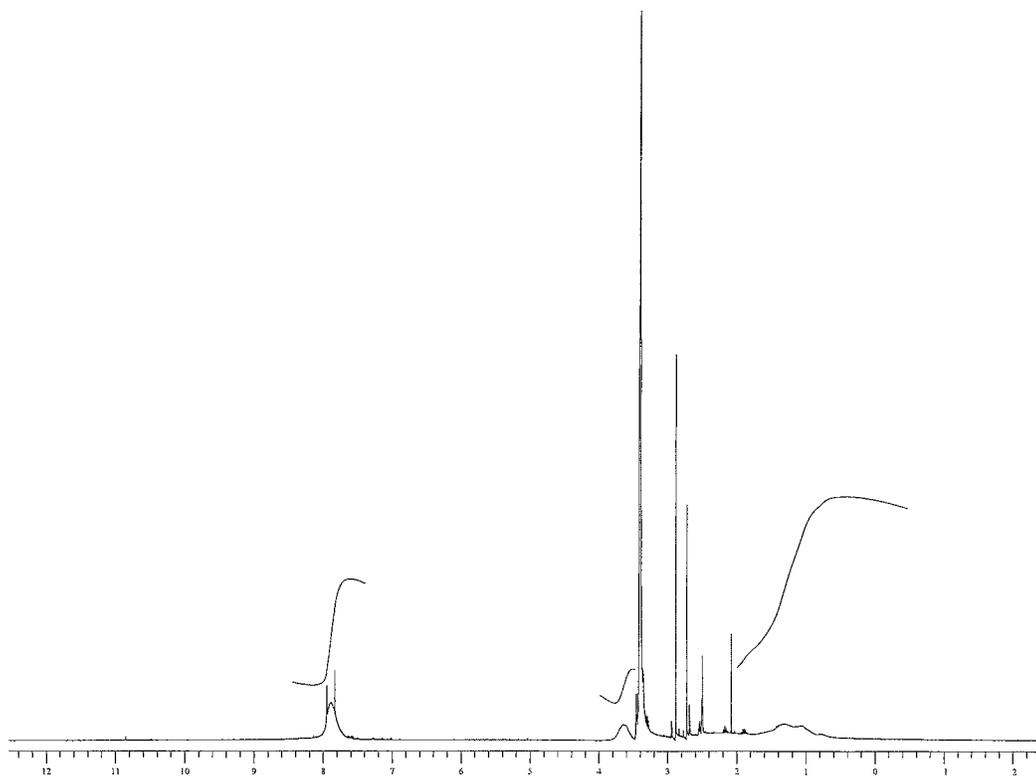
18. Poly(MMA-co-NMPH)-9901



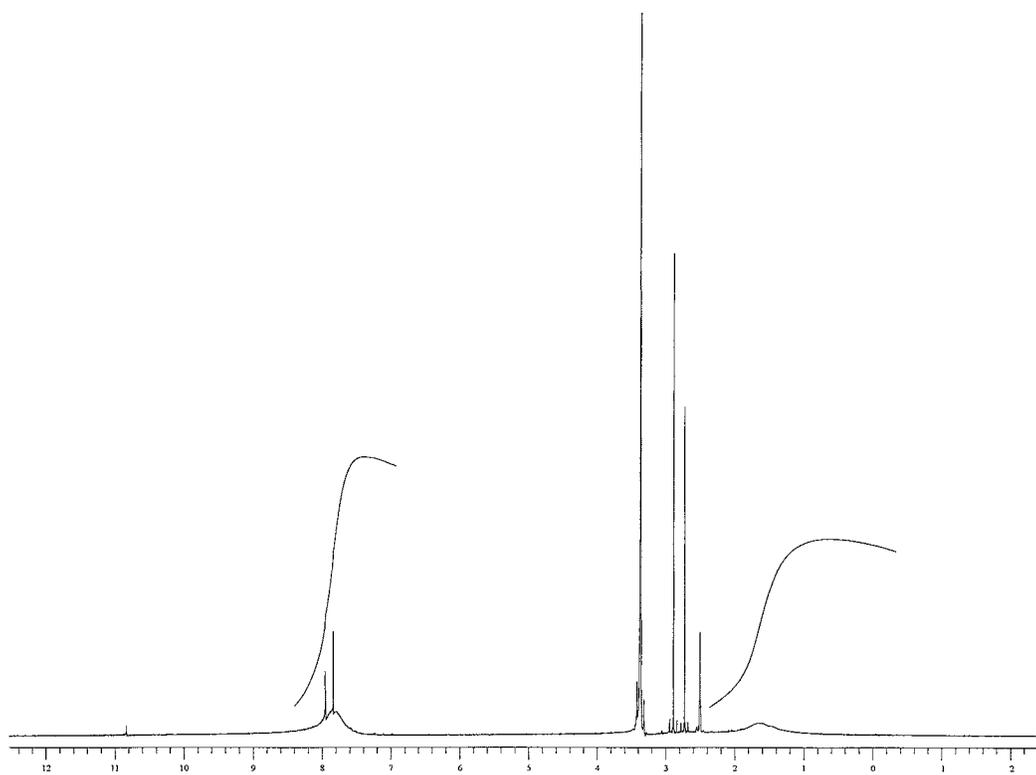
19. Poly(MMA-co-NMPPH)-9208



20. Poly(MMA-co-NMPPH)-7228

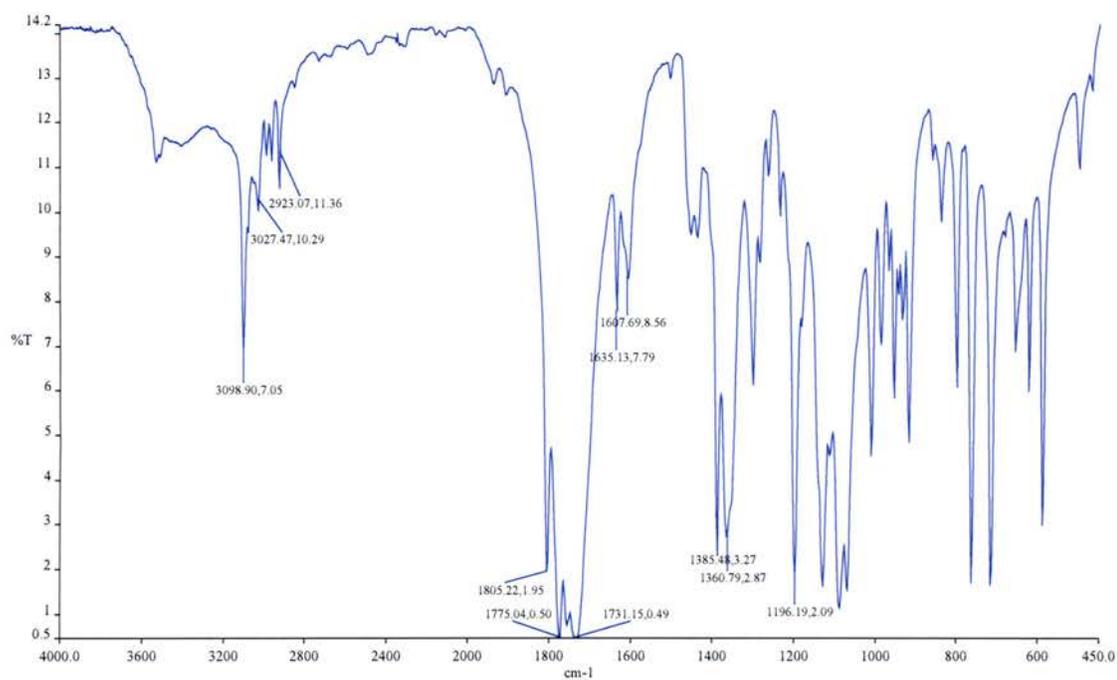


21. Poly(MMA-co-NMPH)- 4852

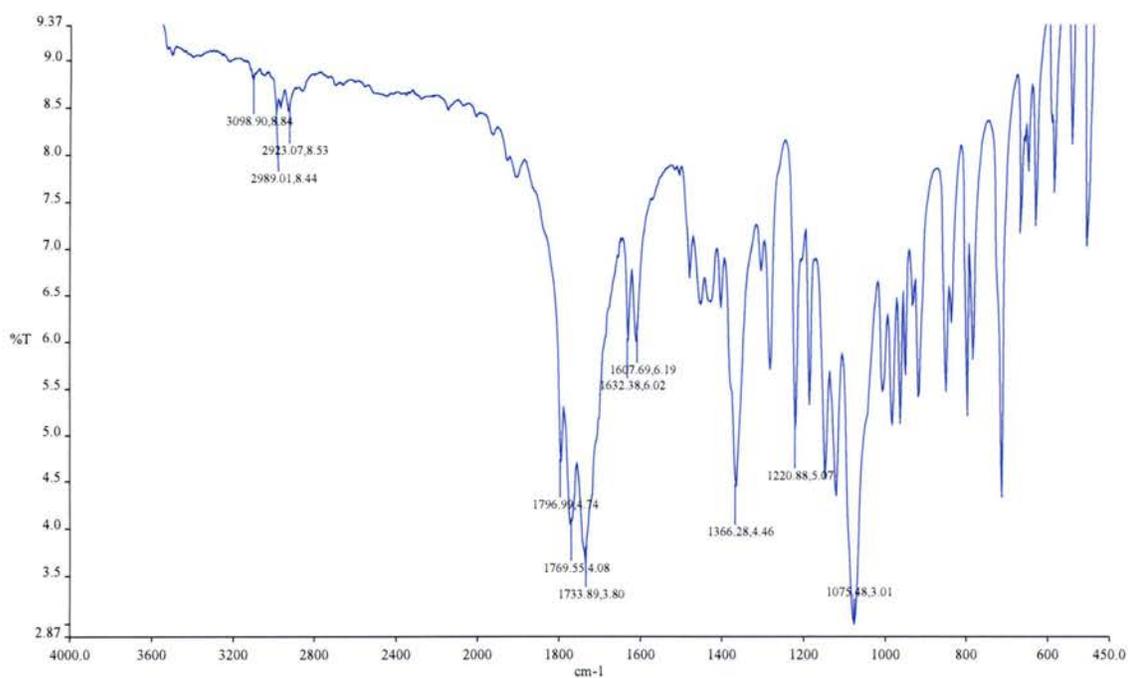
22. Poly(*N*-methacryloyloxy phthalimide)

**APPENDIX II**

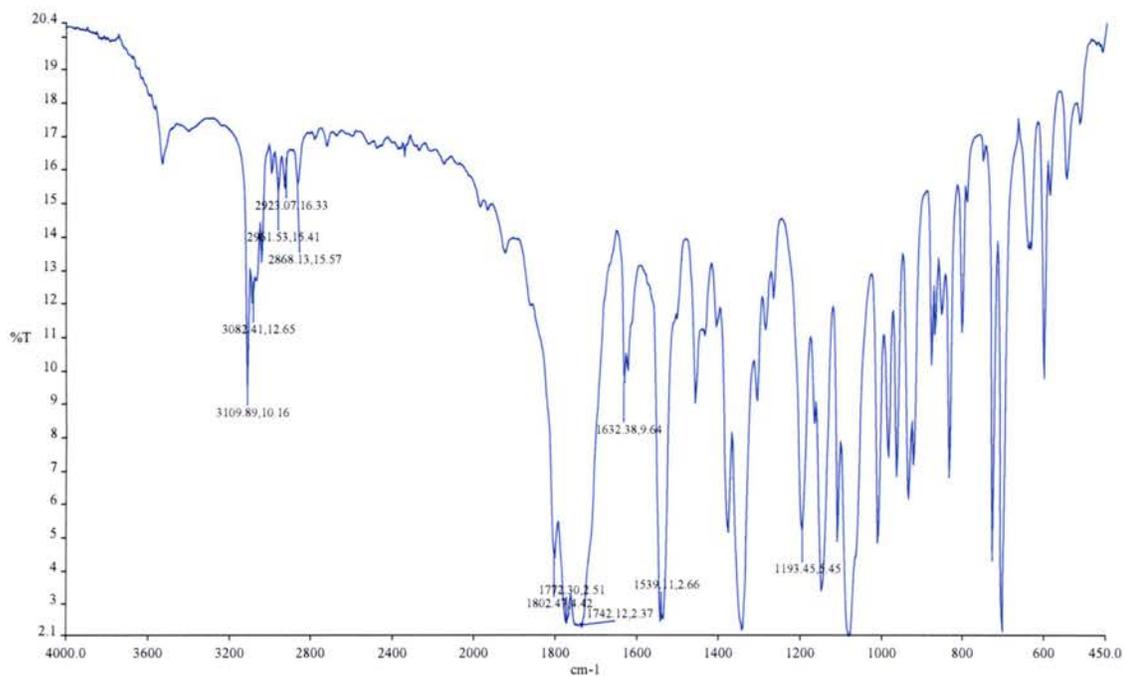
**IR**



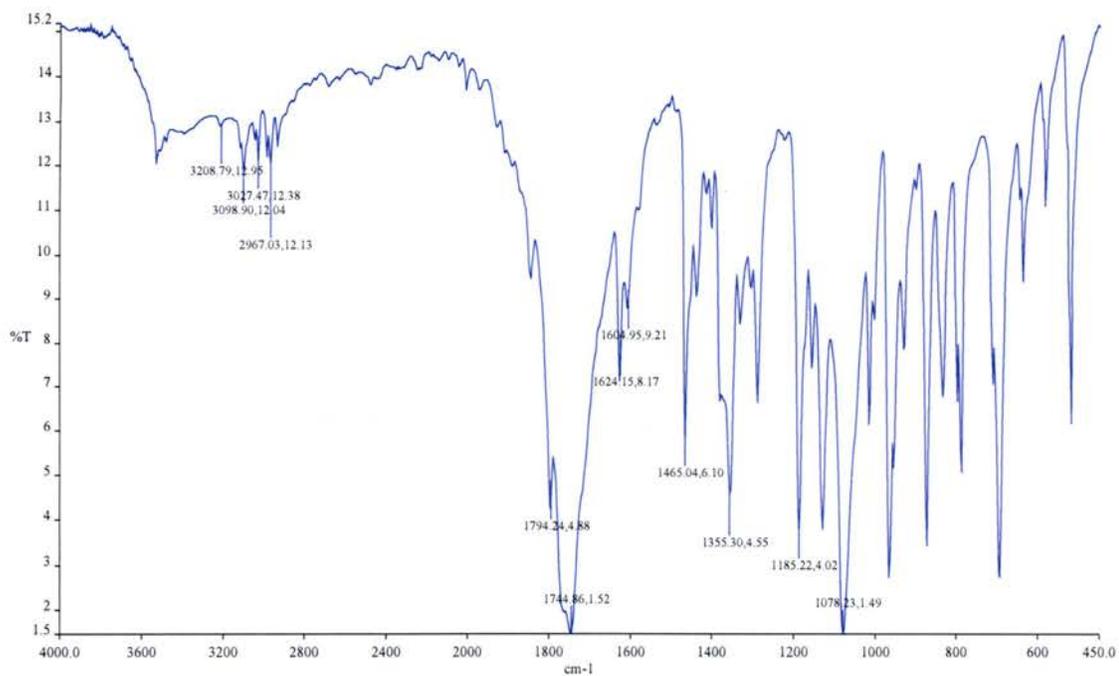
1. 4,5-dichloro-N-methacryloyloxy phthalimide



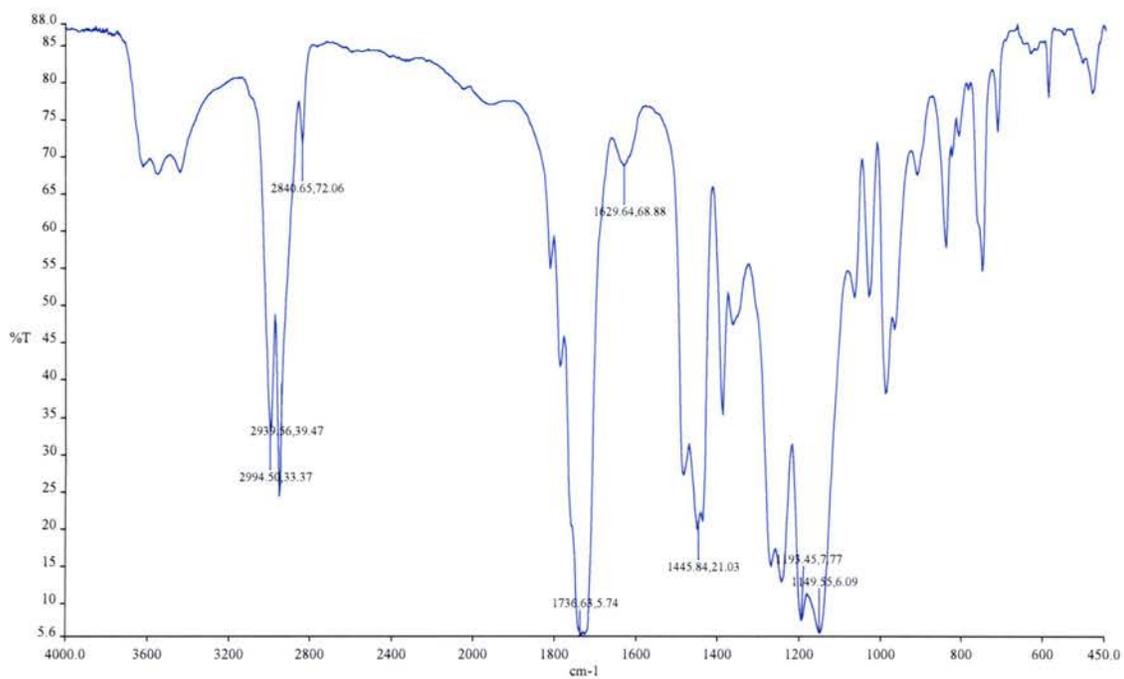
2. 4-methyl-N-methacryloyloxy phthalimide



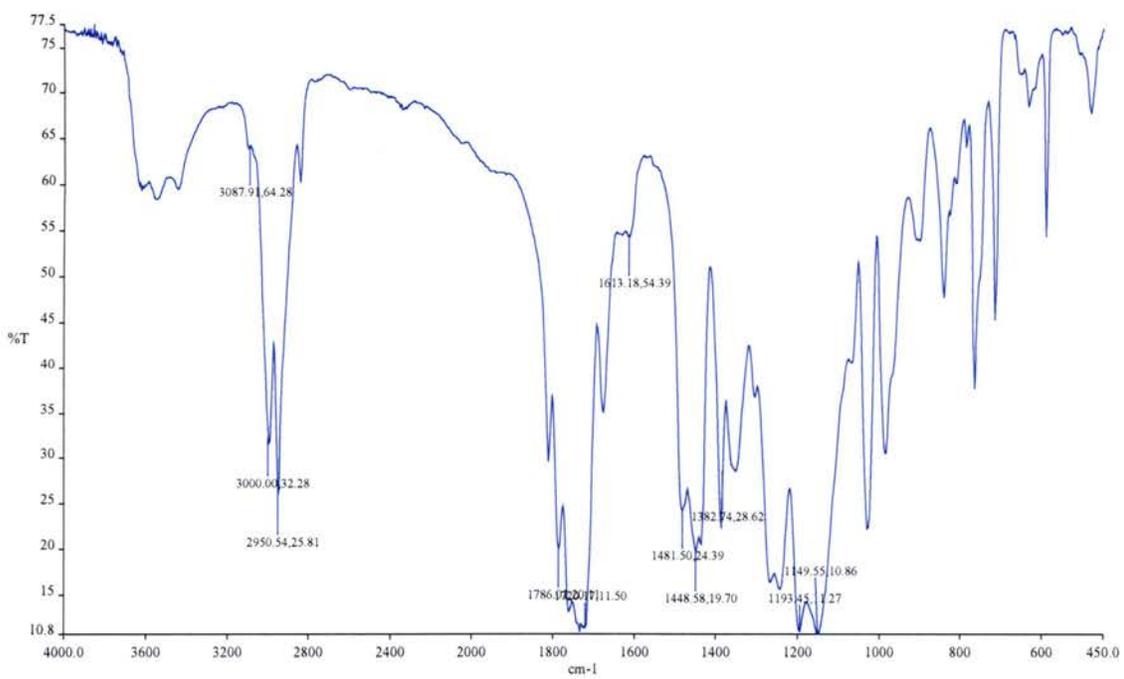
3. 4-nitro-N-methacryloyloxy phthalimide



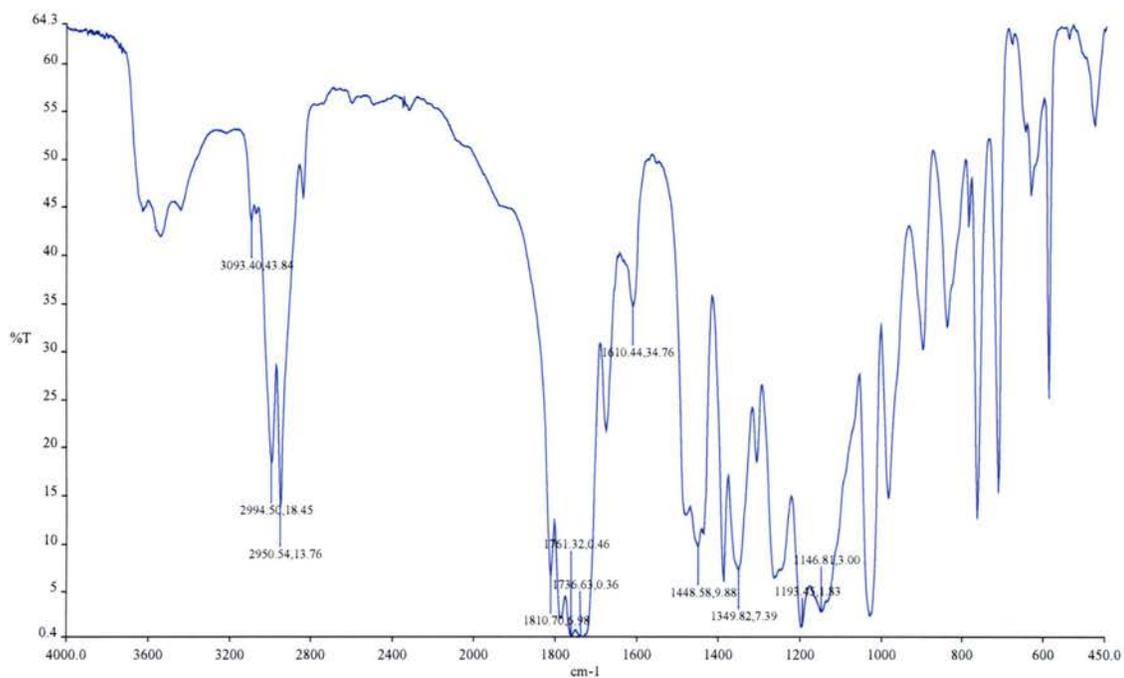
4. N-methacryloyloxy phthalimide



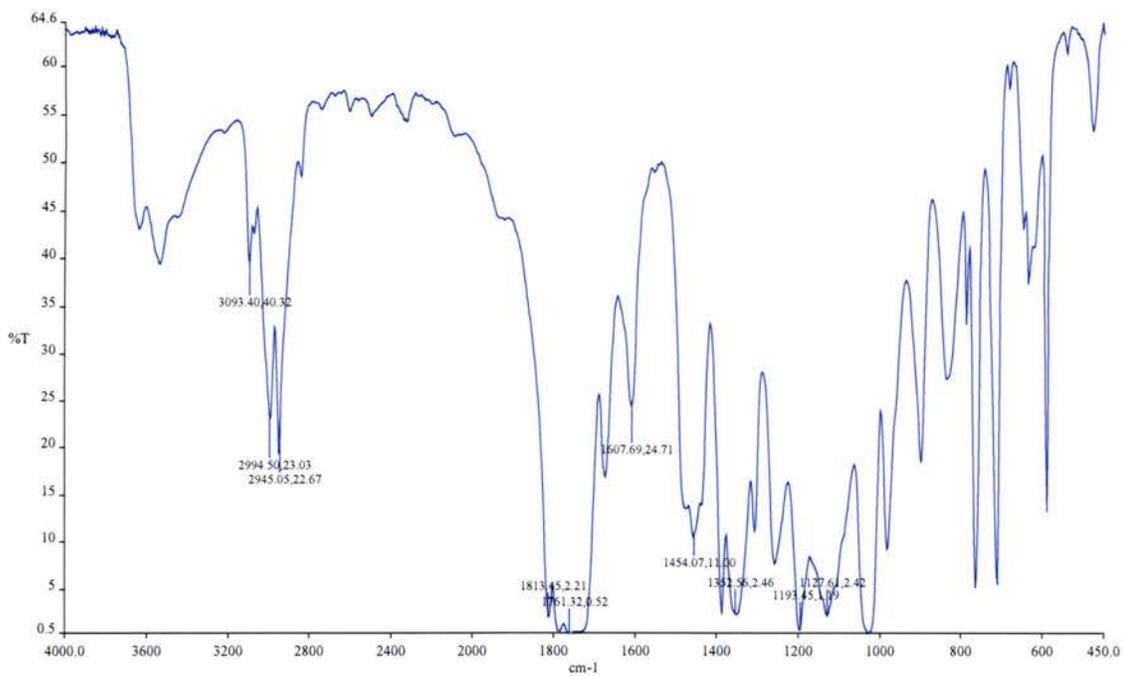
5. Poly(MMA-co-Cl.NMPH) – 9802



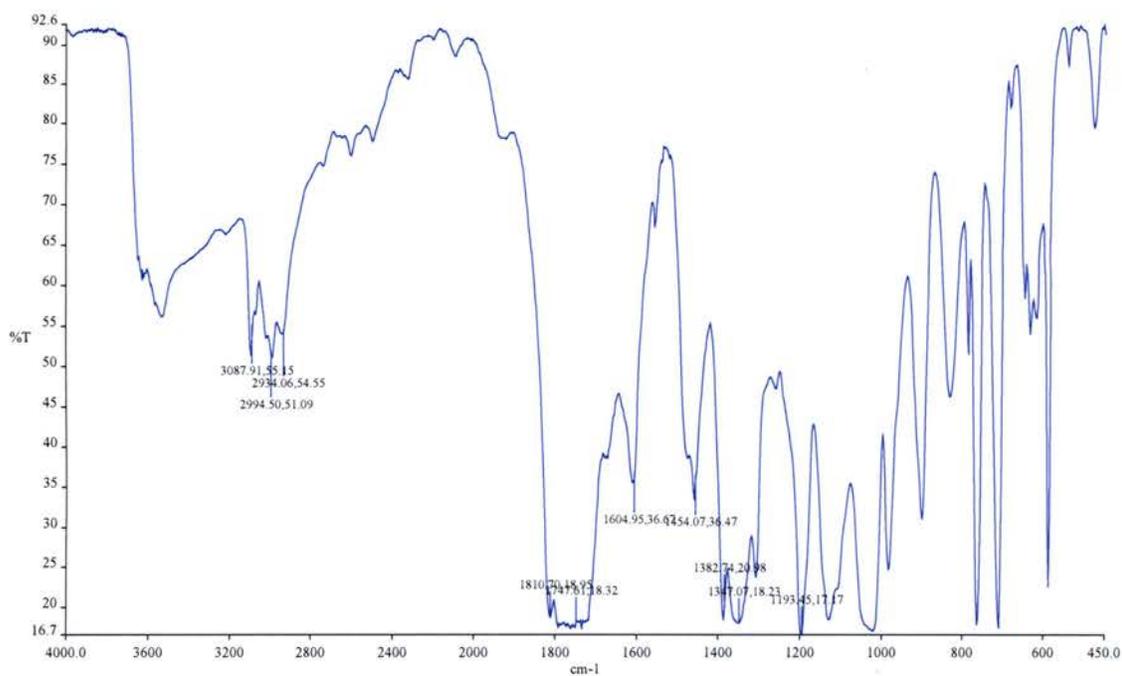
6. Poly(MMA-co-Cl.NMPH)- 9307



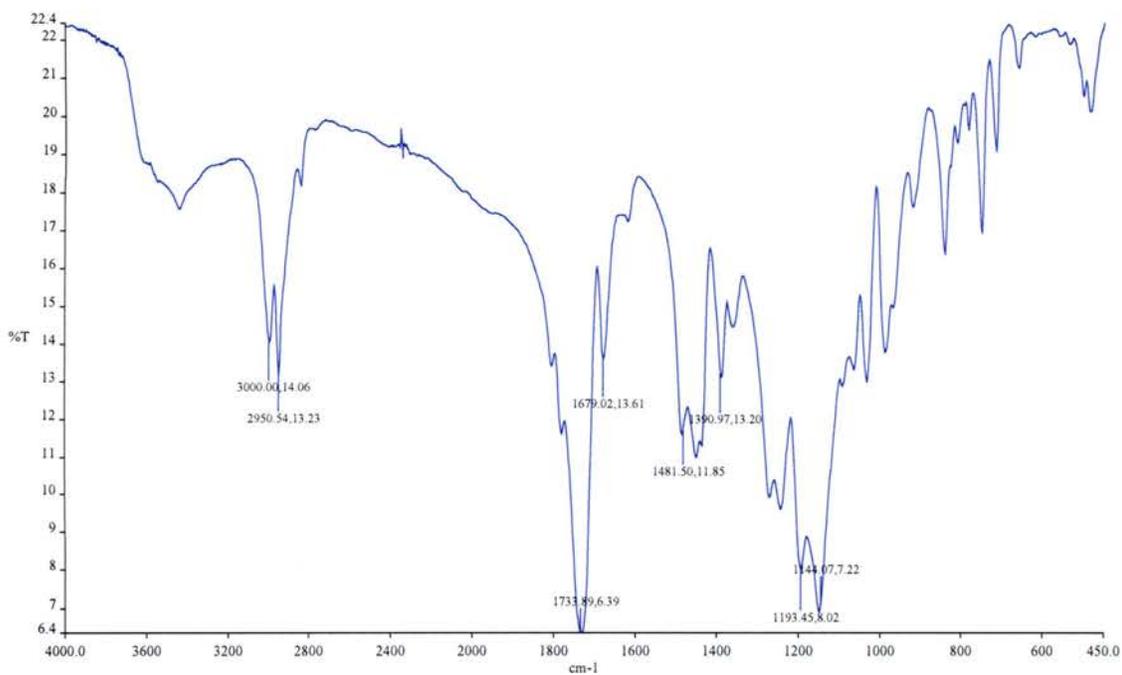
7. Poly(MMA-co-Cl.NMPH) – 7624



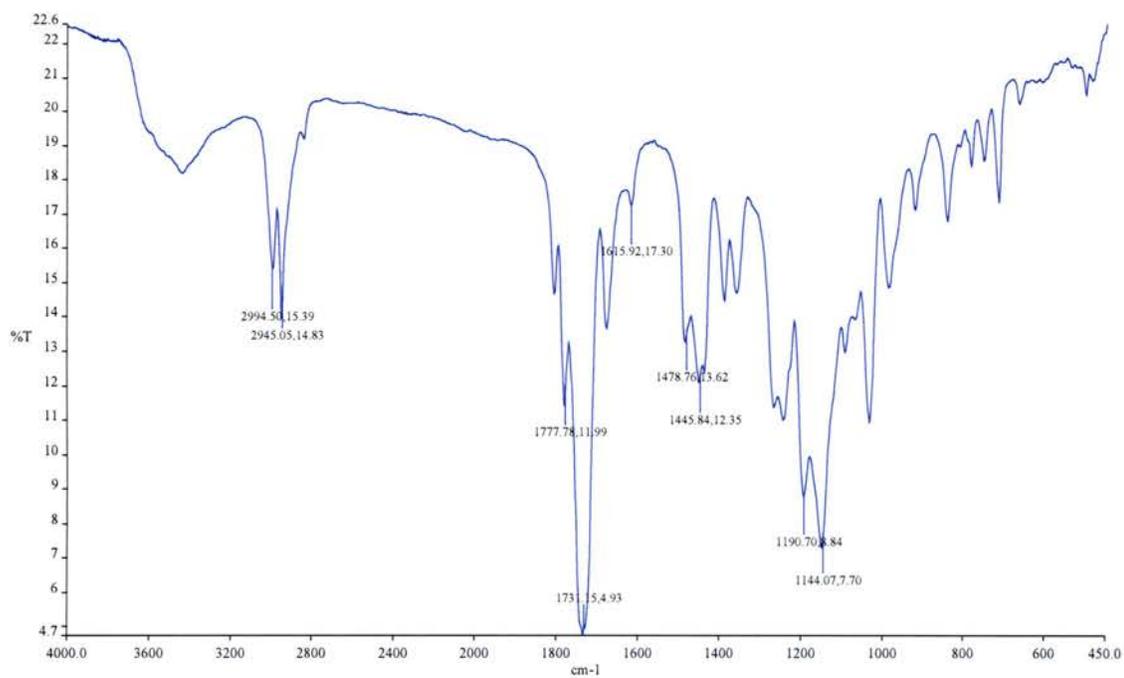
8. Poly(MMA-co-Cl.NMPH) – 5248



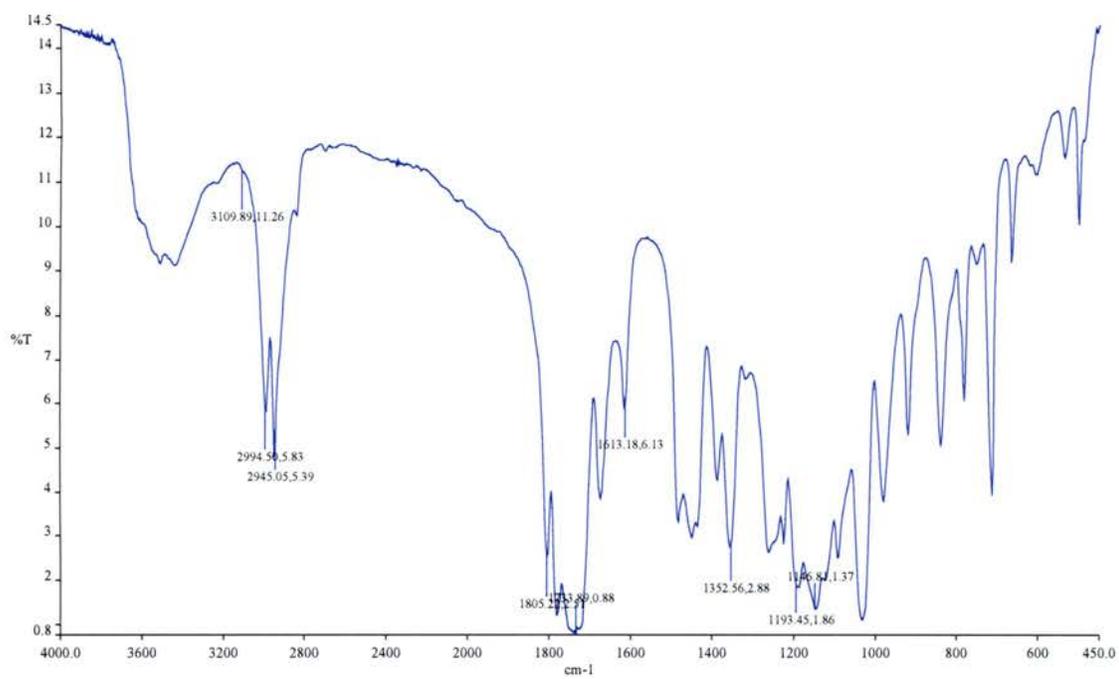
9. Poly(4,5-dichloro-N-methacryloyloxy phthalimide)



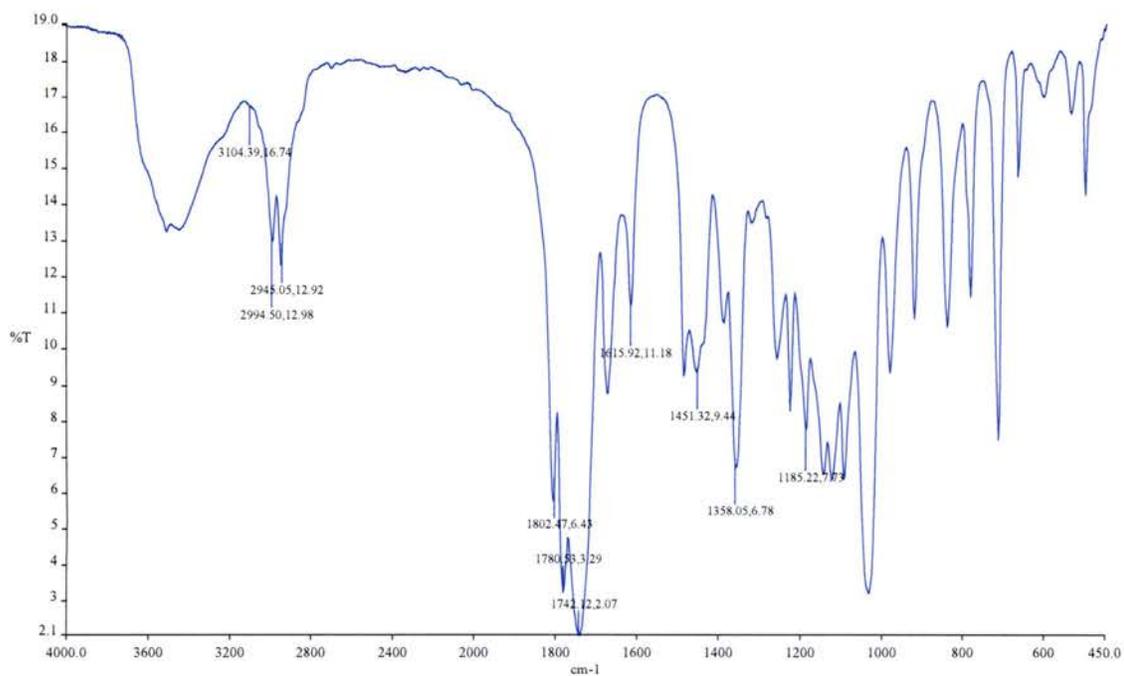
10. Poly(MMA-co-M.NMPH) -9901



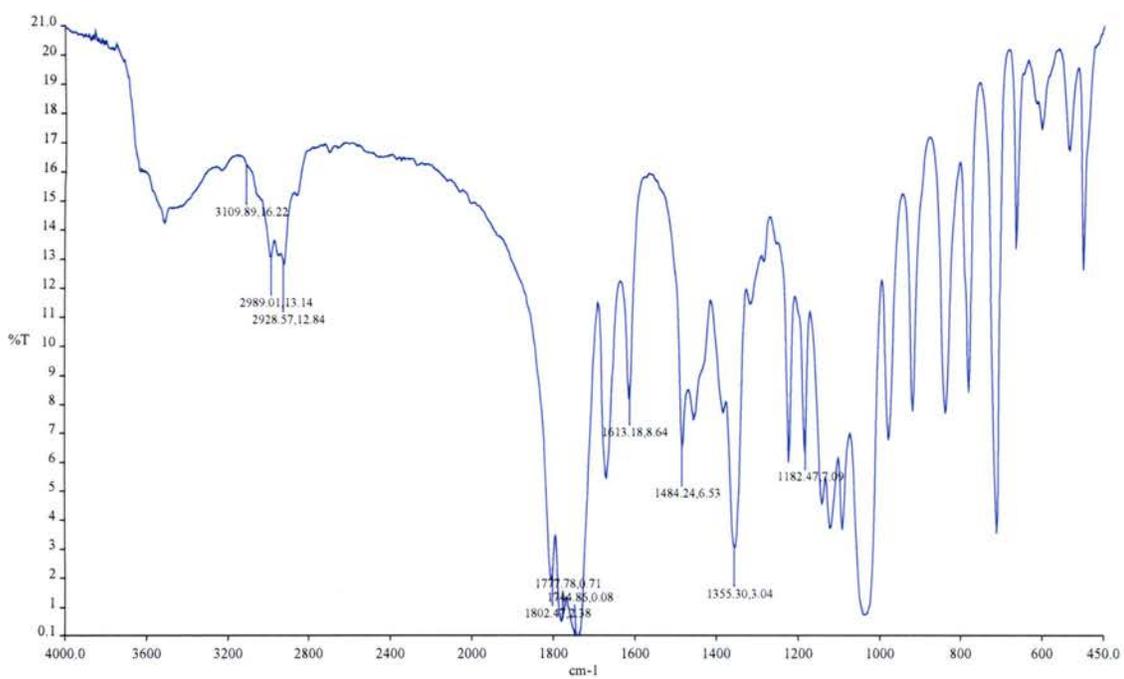
11. Poly(MMA-co-M.NMPH) – 9406



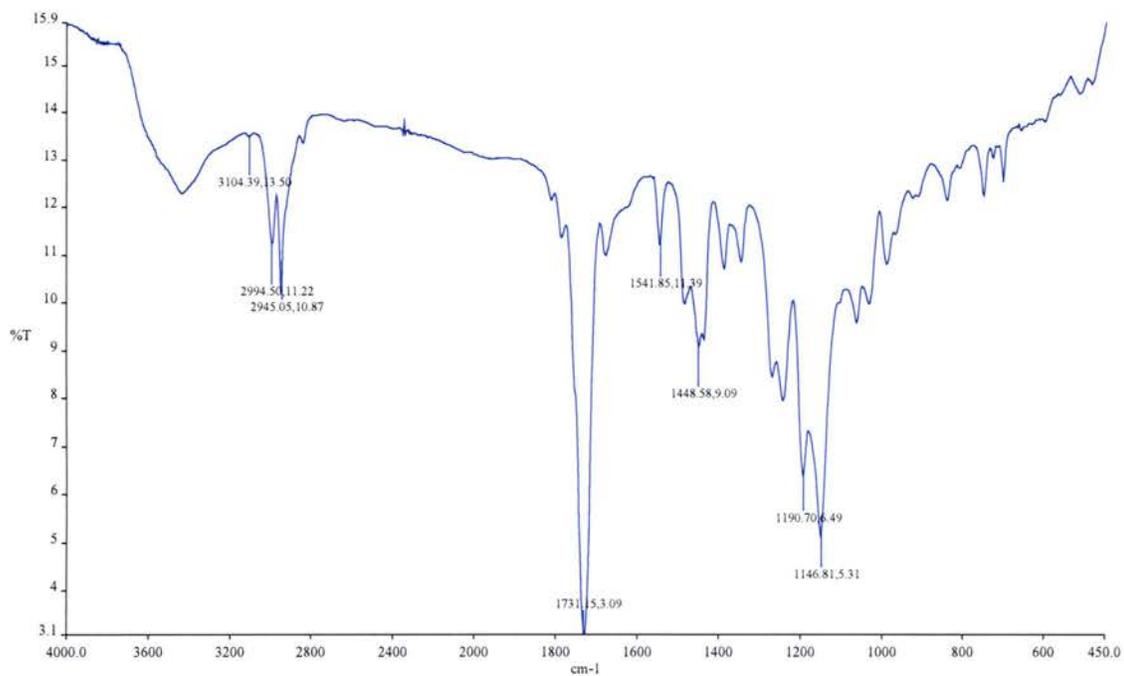
12. Poly(MMA-co-M.NMPH) – 7921



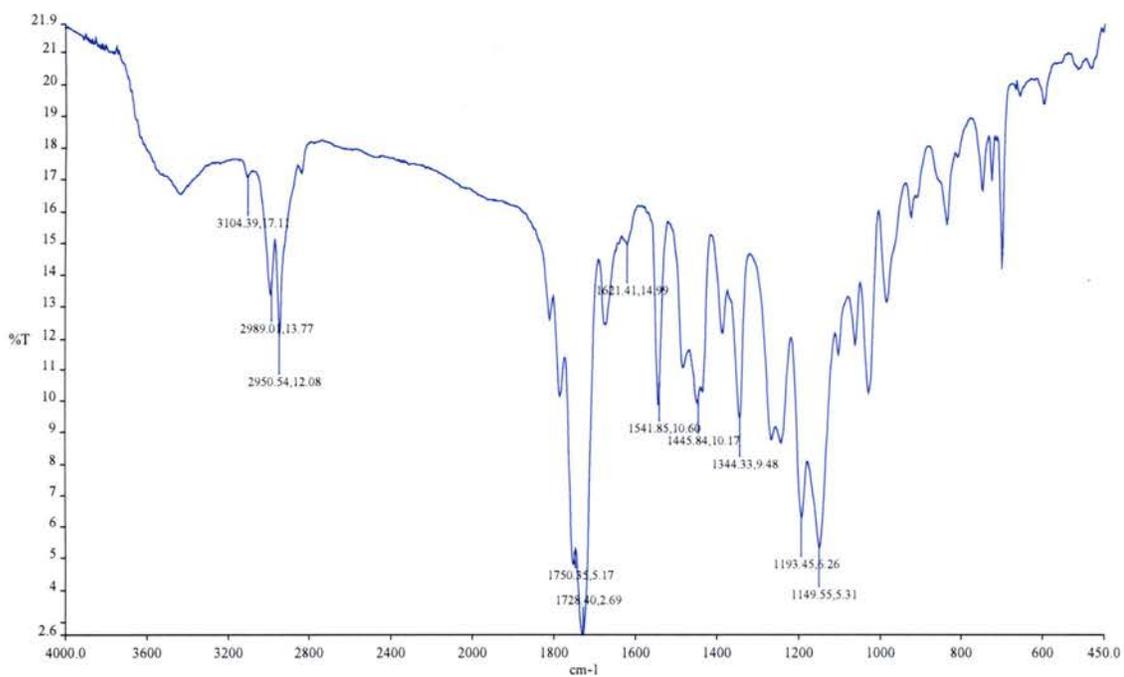
13. Poly(MMA-co-M.NMPH) – 4852



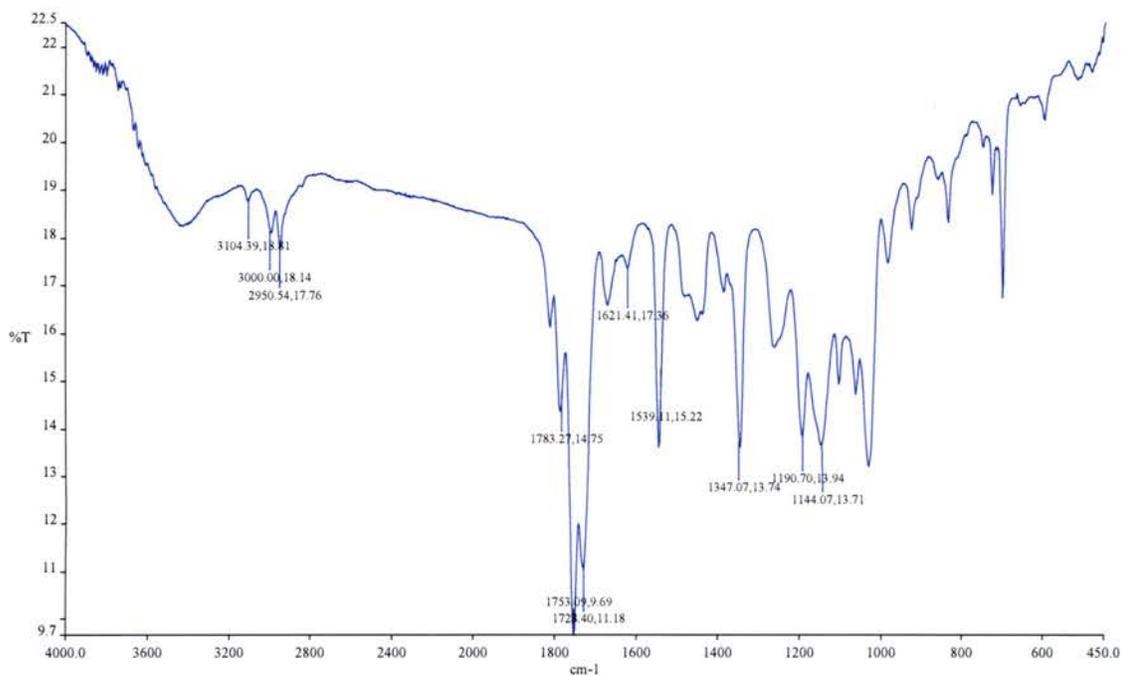
14. Poly(4-methyl-N-methacryloyloxy phthalimide)



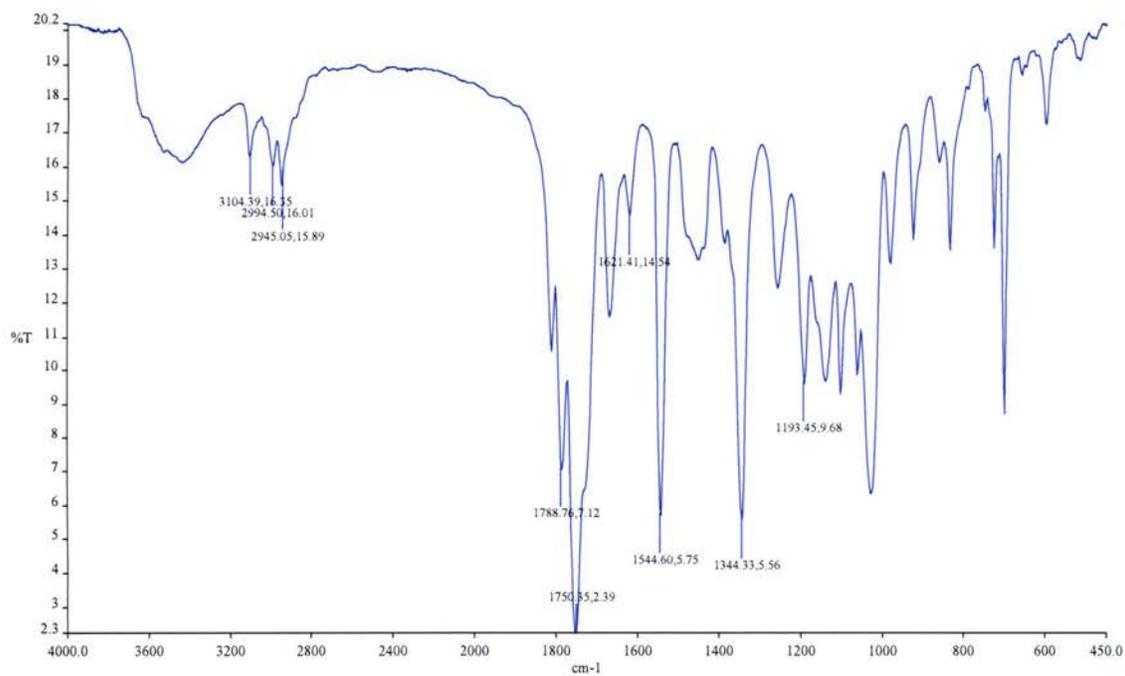
15. Poly(MMA-co-N.NMPH)-9901



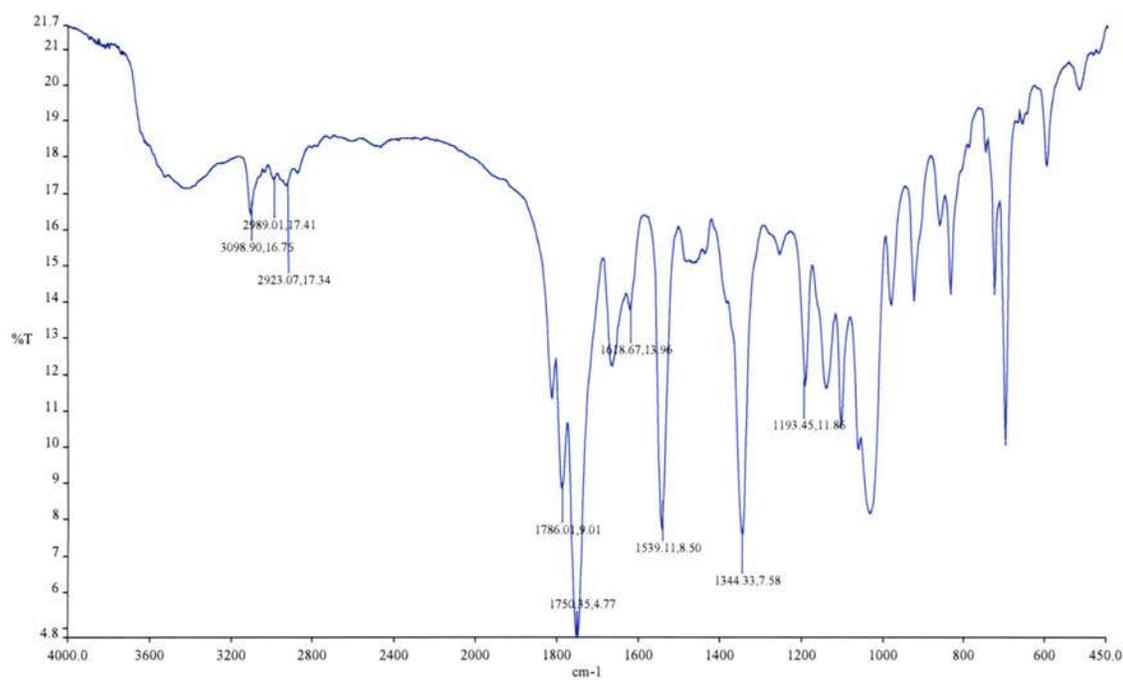
16. Poly(MMA-co-N.NMPH)- 9307



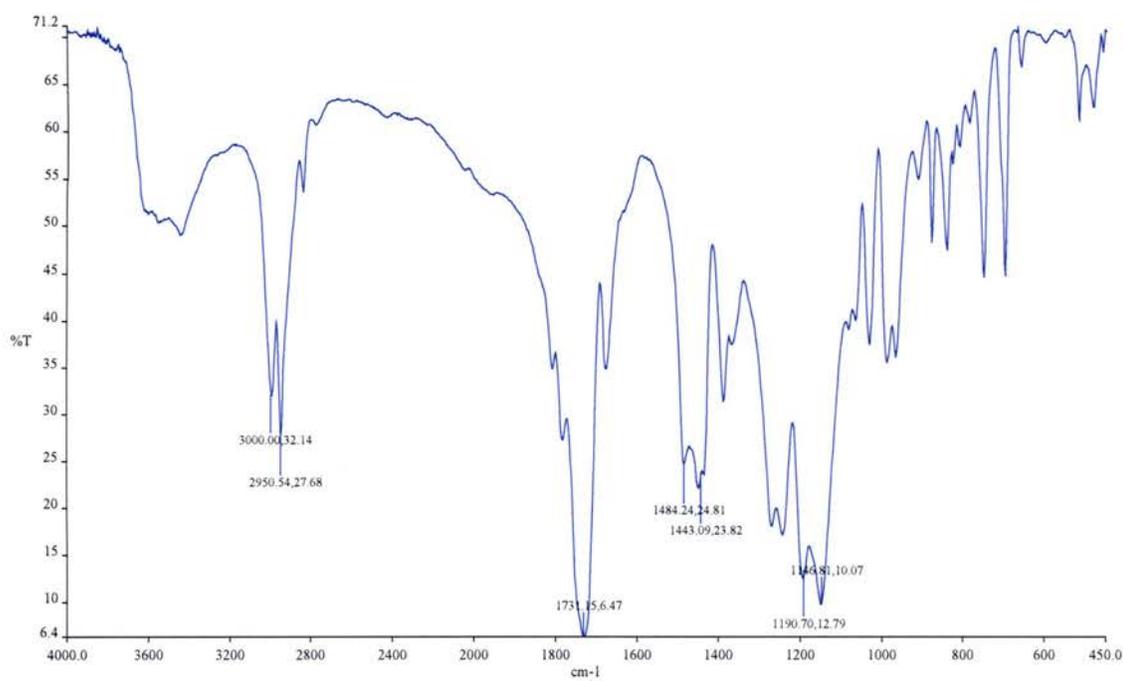
17. Poly(MMA-co-N.NMPH) - 8020



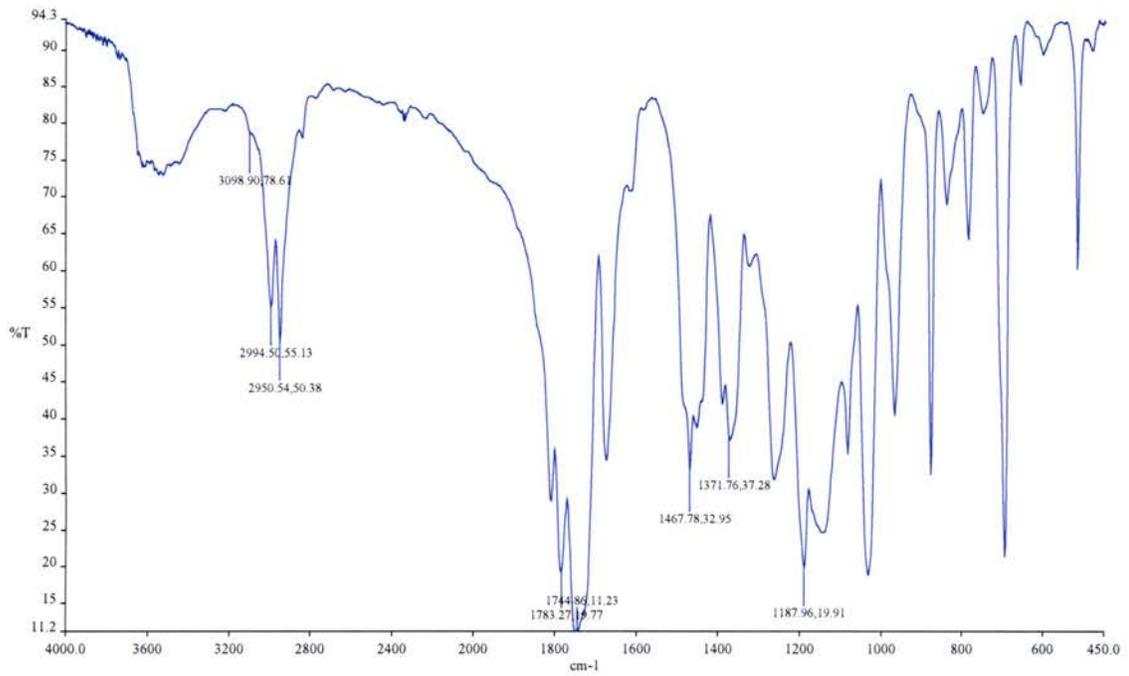
18. Poly(MMA-co-N.NMPH) - 5050



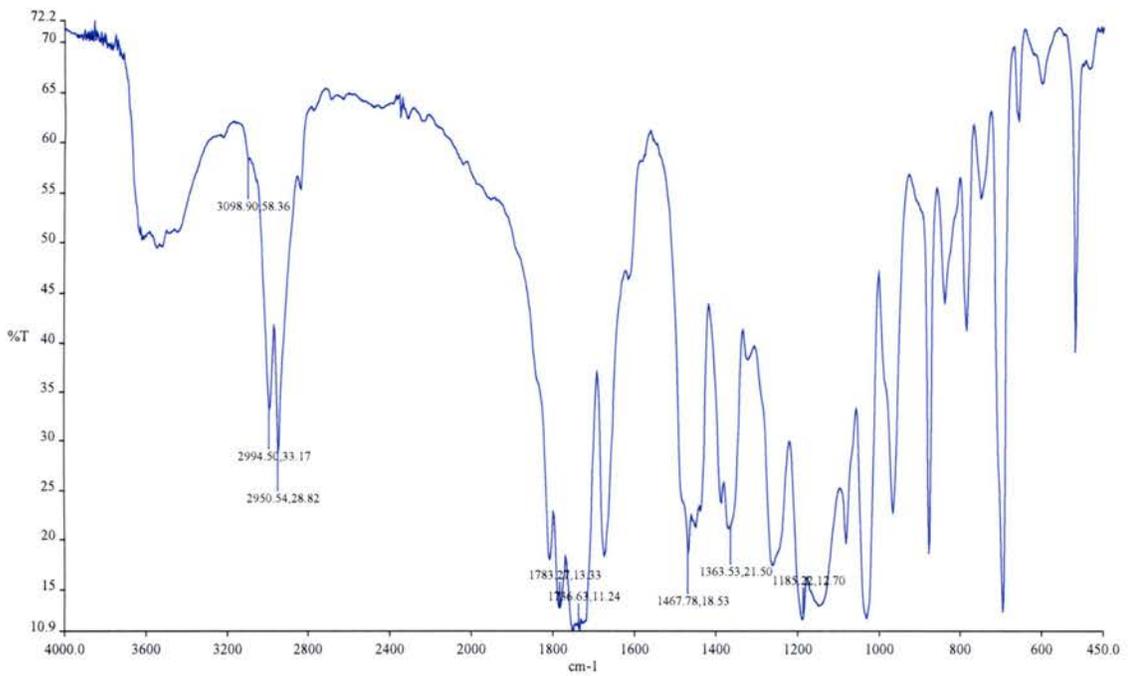
19. Poly(4-nitro-N-methacryloyloxy phthalimide)



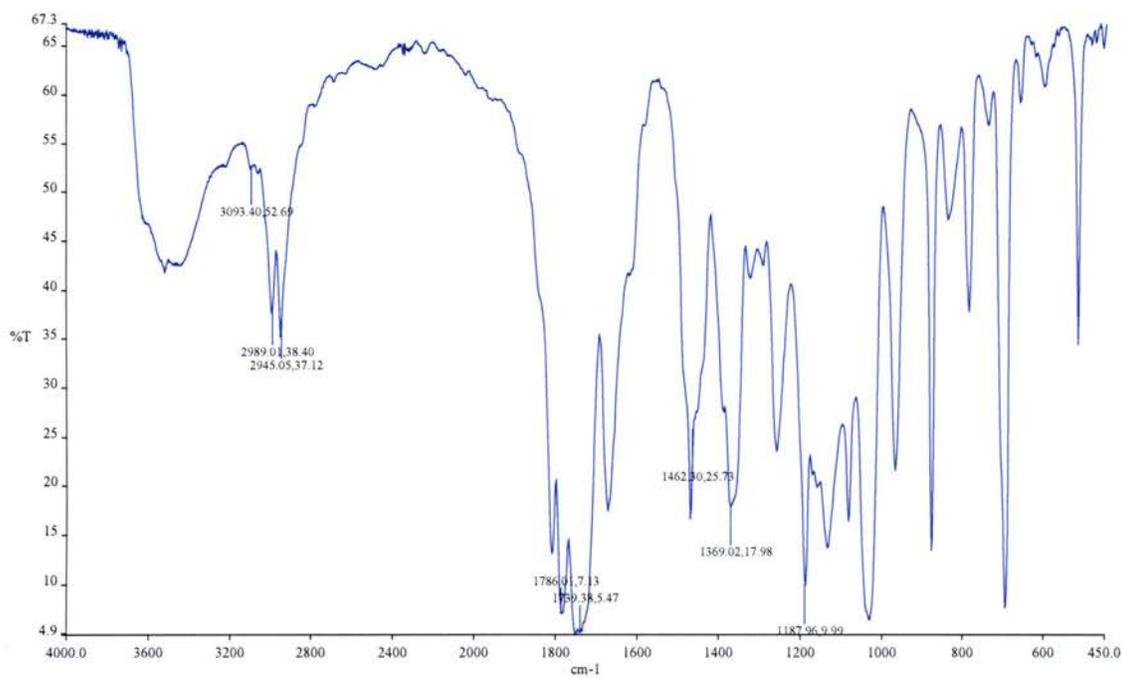
20. Poly(MMA-co-NMPH)-9901



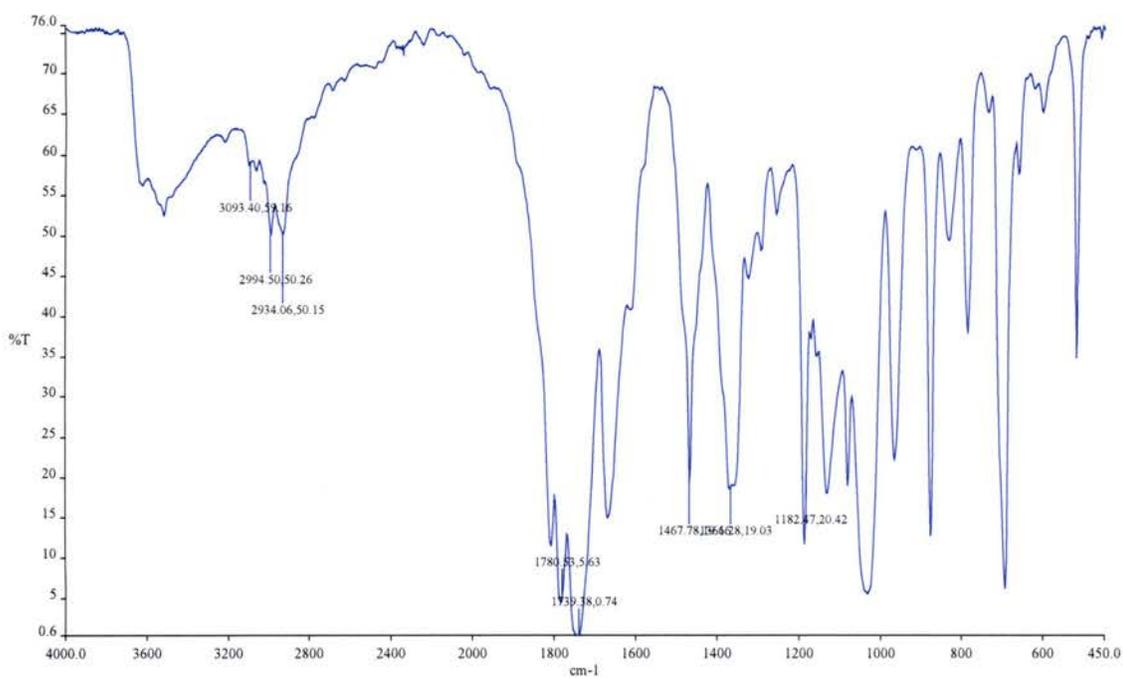
21. Poly(MMA-co-NMPH)- 9208



22. Poly(MMA-co-NMPH)- 7228



23. Poly(MMA-co-NMPH)- 4852

24. Poly(*N*-methacryloyloxy phthalimide)

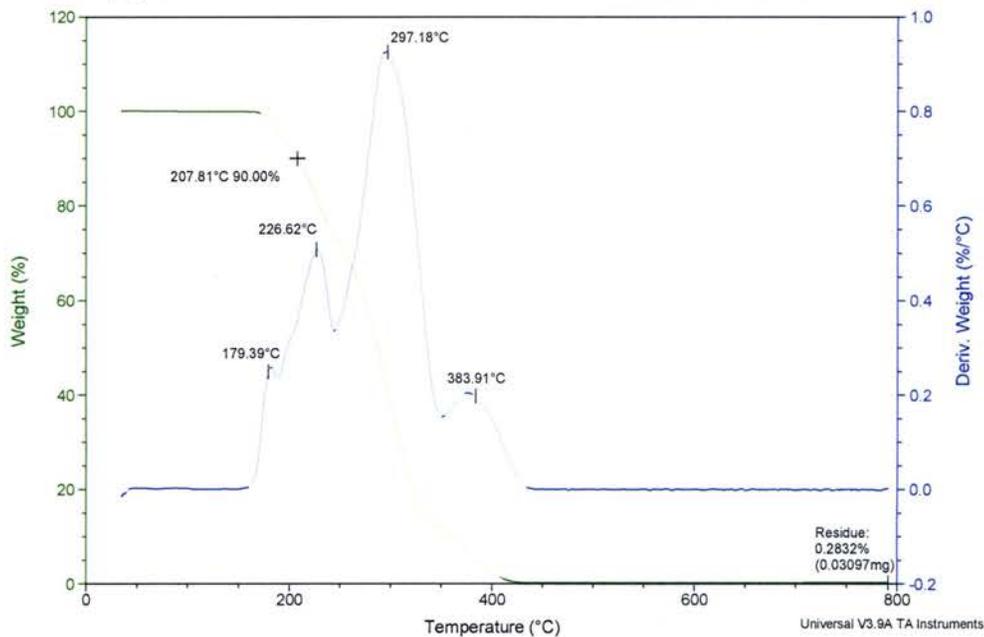
APPENDIX III

TGA

Sample: Poly(Cl-NMPH-MMA)-19  
Size: 10.9350 mg  
Method: Ramp  
Comment: copolymer

TGA

File: C:\...poly(Cl-NMPH-MMA)-19.001  
Operator: Mike  
Run Date: 15-Nov-05 13:14  
Instrument: TGA Q50 V6.4 Build 193

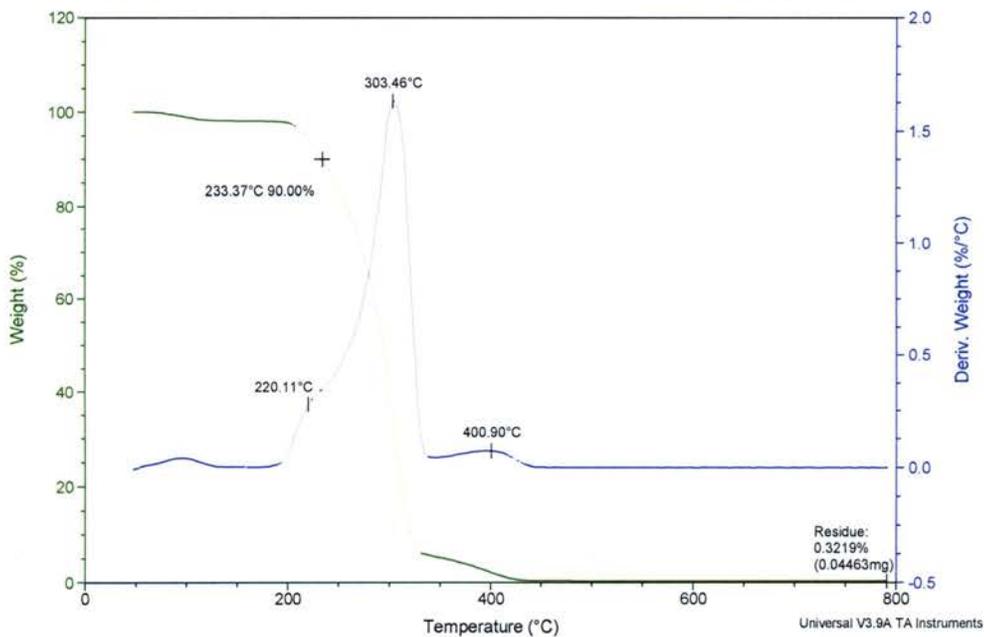


### 1. Poly(MMA-co-Cl.NMPH)- 9802

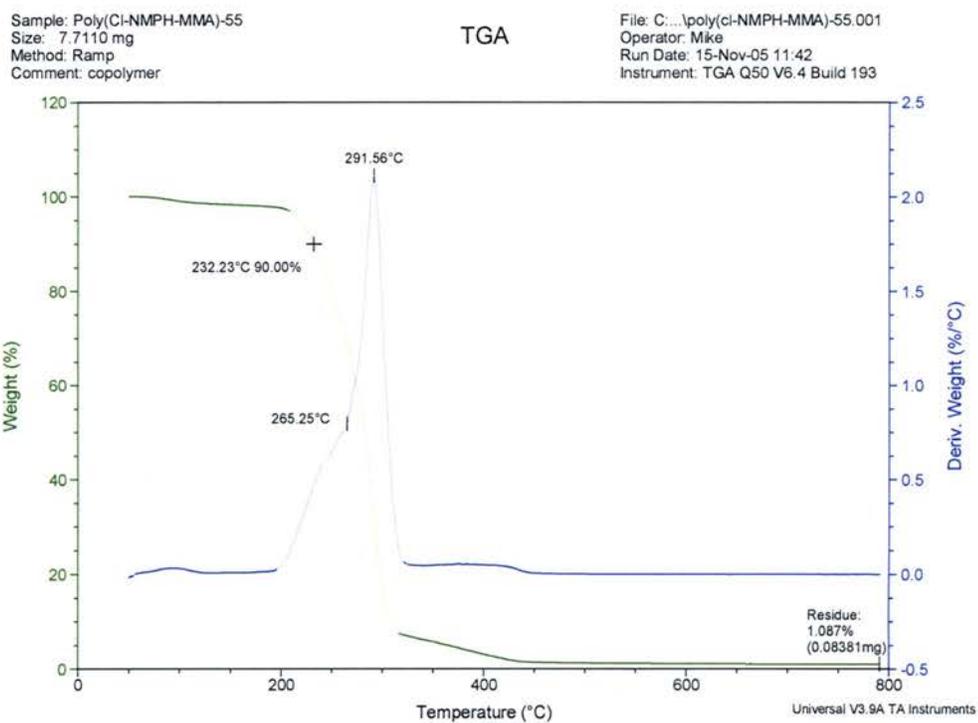
Sample: Poly(Cl-NMPH-MMA)-2575  
Size: 13.8670 mg  
Method: Ramp  
Comment: copolymer

TGA

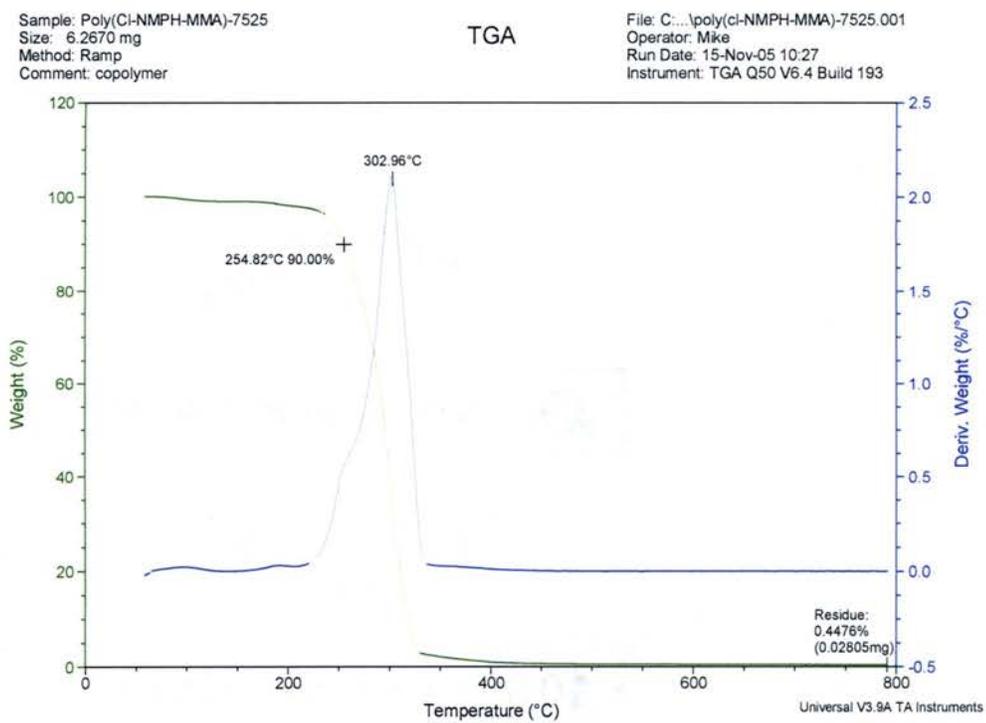
File: C:\...poly(Cl-NMPH-MMA)-2575.001  
Operator: Mike  
Run Date: 15-Nov-05 14:31  
Instrument: TGA Q50 V6.4 Build 193



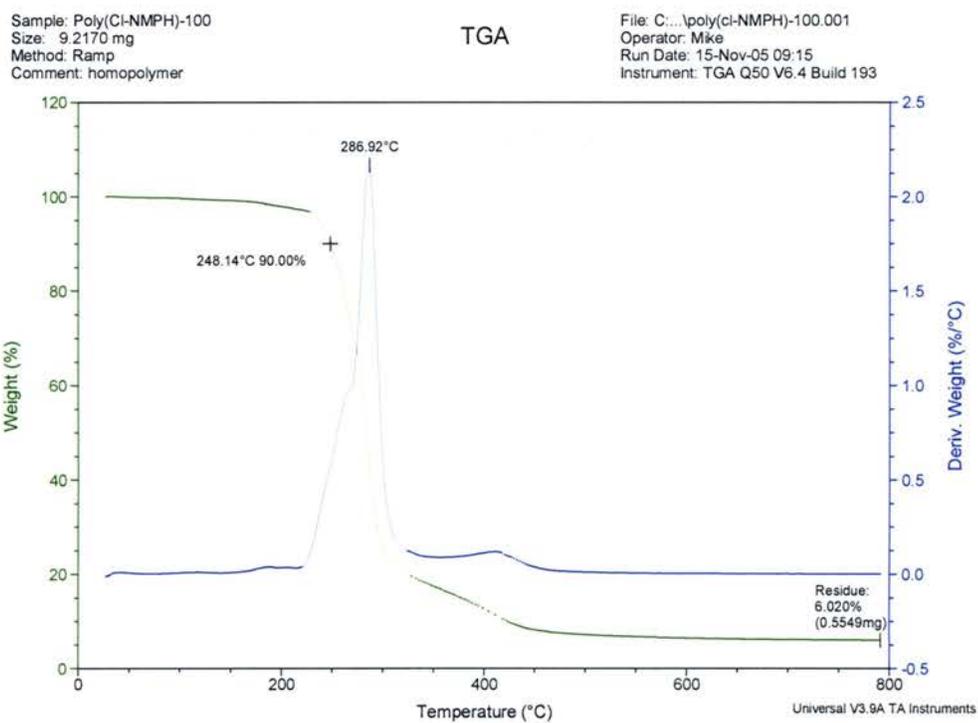
### 2. Poly(MMA-co-Cl.NMPH)- 9307



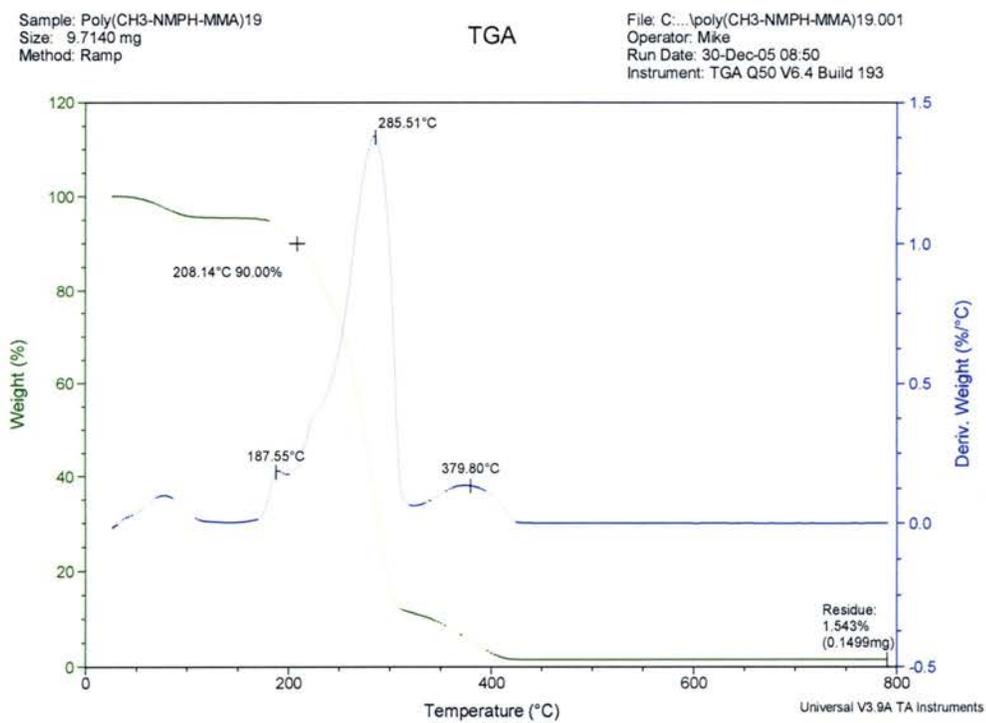
### 3. Poly(MMA-co-Cl.NMPH)- 7624



### 4. Poly(MMA-co-Cl.NMPH)- 5248



### 5. Poly(4,5-dichloro *N*-methacryloyloxy phthalimide)

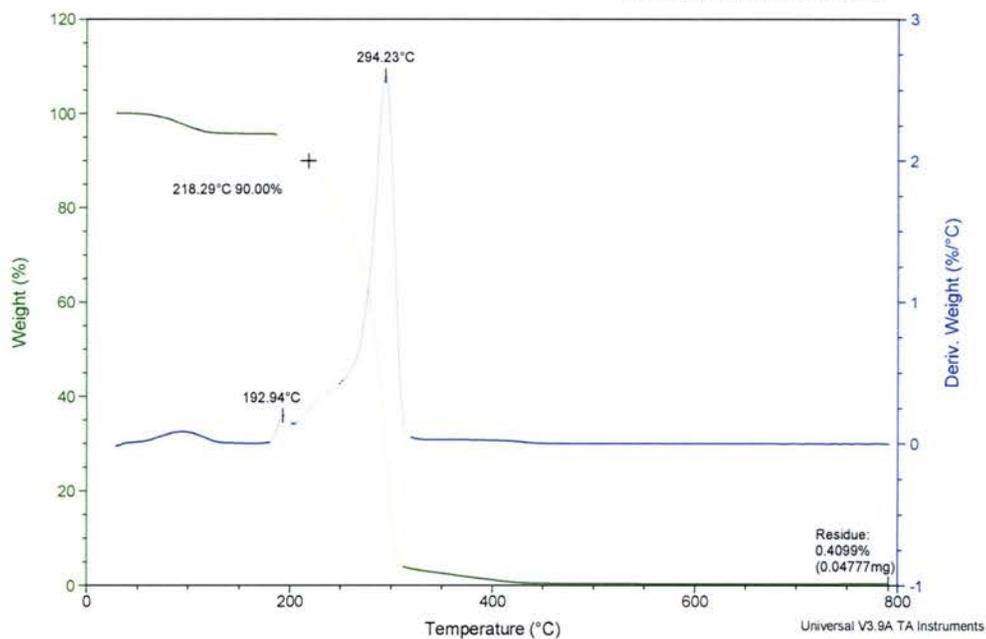


### 6. Poly(MMA-co-M.NMPH) -9901

Sample: Poly(CH3-NMPH-MMA)2575  
 Size: 11.6540 mg  
 Method: Ramp

TGA

File: C:\...poly(CH3-NMPH-MMA)2575.001  
 Operator: Mike  
 Run Date: 30-Dec-05 10:43  
 Instrument: TGA Q50 V6.4 Build 193

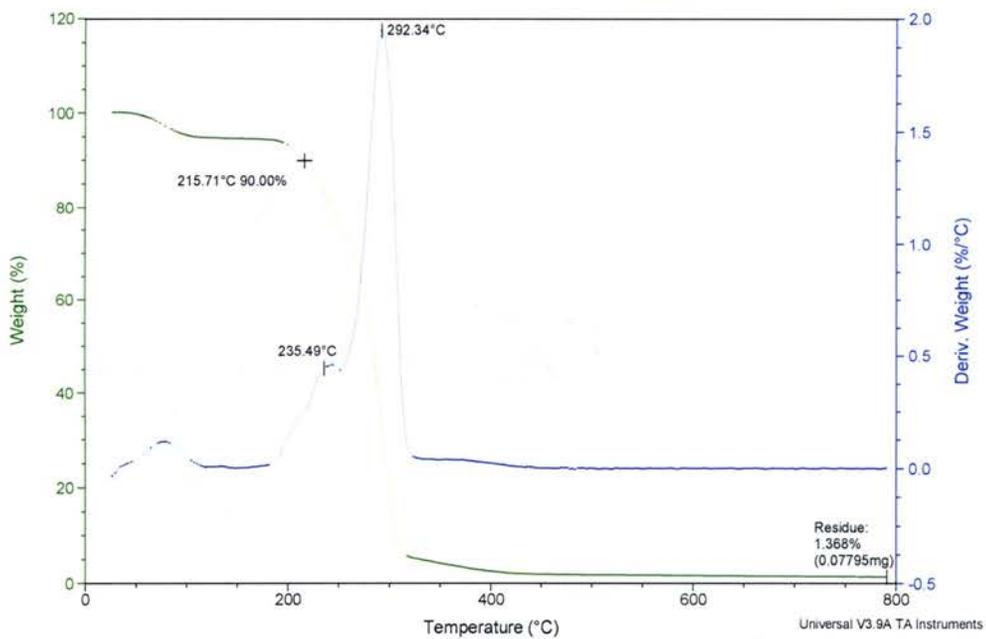


## 7. Poly(MMA-co-M.NMPH) - 9406

Sample: Poly(CH3.NMPH.MMA) - 55  
 Size: 5.6960 mg  
 Method: Ramp

TGA

File: C:\...Poly(CH3-NMPH-MMA)-55  
 Operator: Mike  
 Run Date: 05-Jan-06 11:19  
 Instrument: TGA Q50 V6.4 Build 193

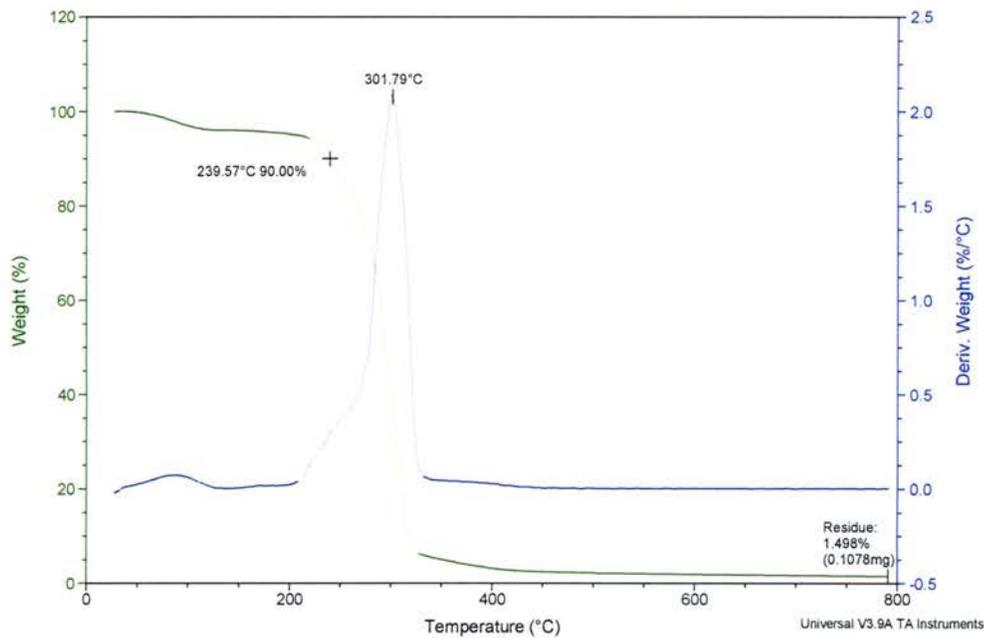


## 8. Poly(MMA-co-M.NMPH) - 7921

Sample: Poly(CH3-NMPH-MMA) - 7525  
Size: 7.1940 mg  
Method: Ramp

TGA

File: C:\...\Poly(CH3-NMPH-MMA)-7525.001  
Operator: Mike  
Run Date: 05-Jan-06 13:13  
Instrument: TGA Q50 V6.4 Build 193

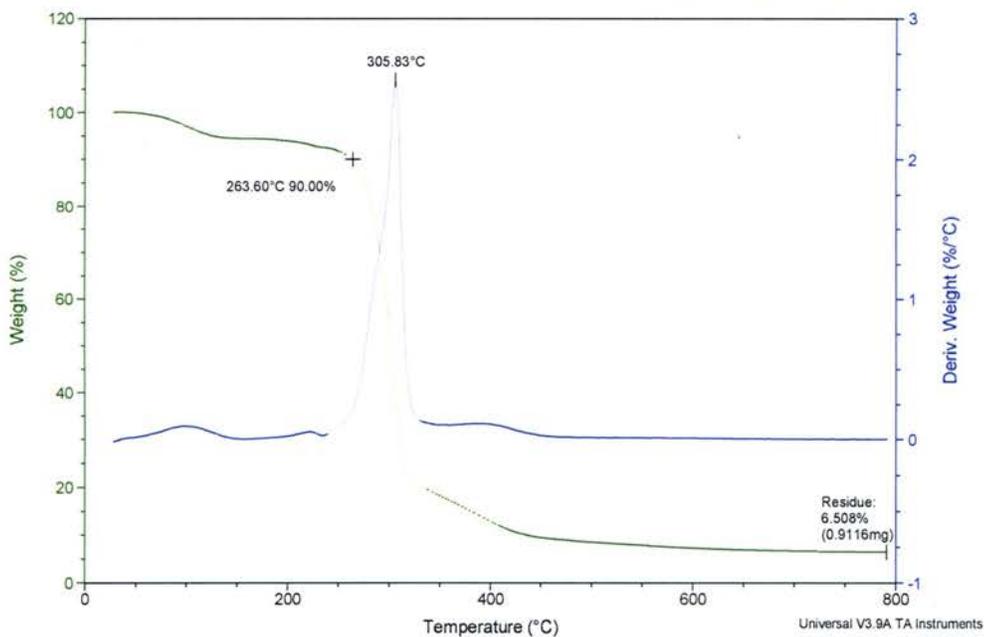


### 9. Poly(MMA-co-M.NMPH) - 4852

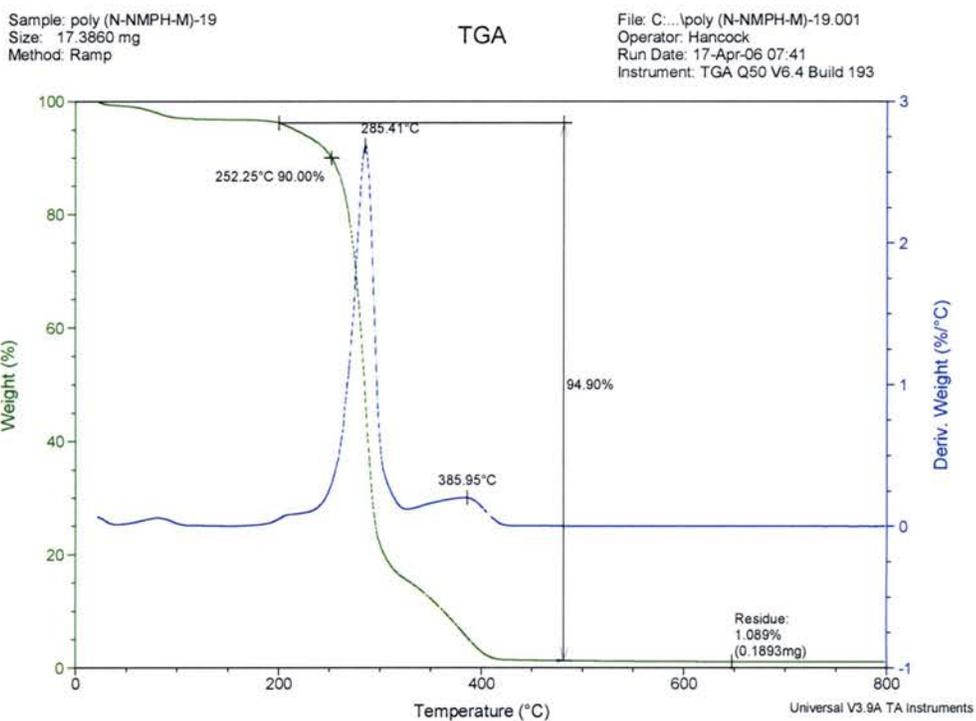
Sample: Poly(CH3-NMPH) - 100  
Size: 14.0080 mg  
Method: Ramp

TGA

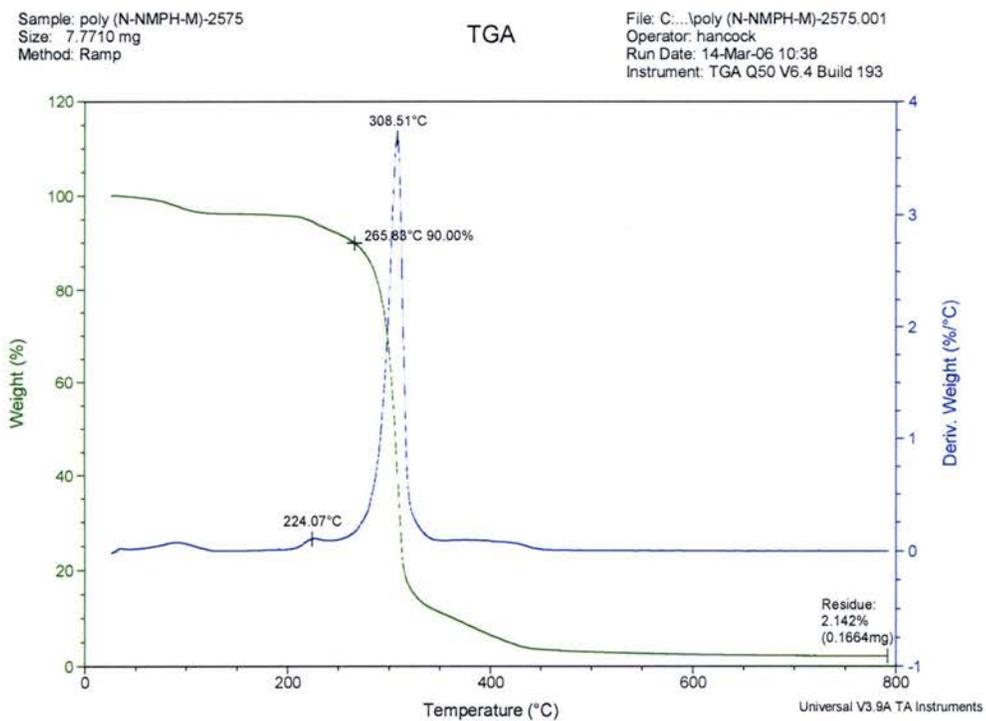
File: C:\...\Poly(CH3-NMPH)-100.001  
Operator: Mike  
Run Date: 05-Jan-06 15:06  
Instrument: TGA Q50 V6.4 Build 193



### 10. Poly(4-methyl-N-methacryloyloxy phthalimide)



## 11. Poly(MMA-co-N.NMPH) -9901

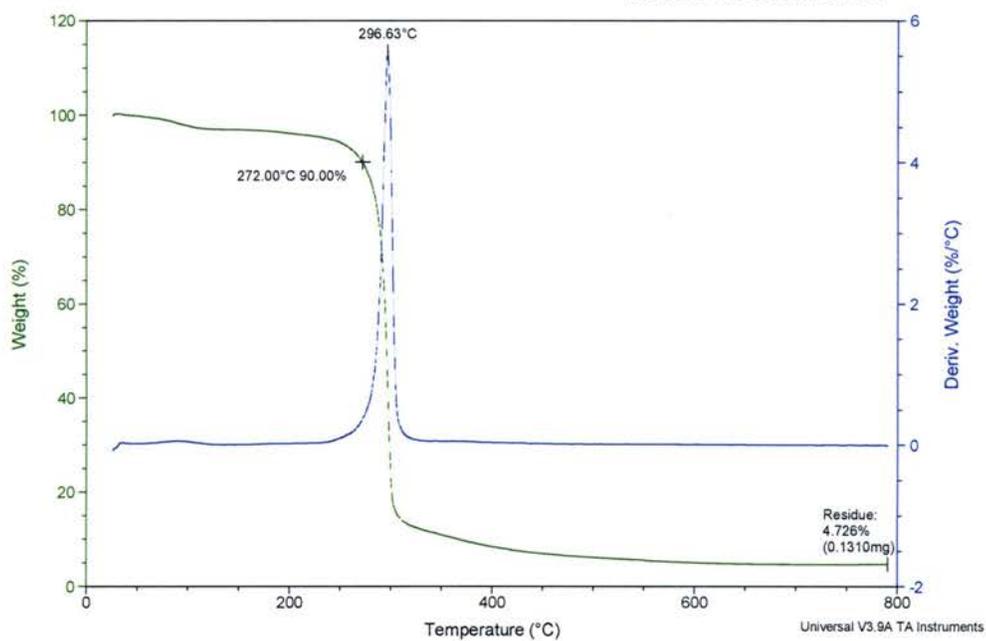


## 12. Poly(MMA-co-N.NMPH) - 9307

Sample: poly (N-NMPH-M)-55  
Size: 2.7710 mg  
Method: Ramp

TGA

File: C:\...poly (N-NMPH-M)-55.001  
Operator: Goodman  
Run Date: 15-Mar-06 15:21  
Instrument: TGA Q50 V6.4 Build 193

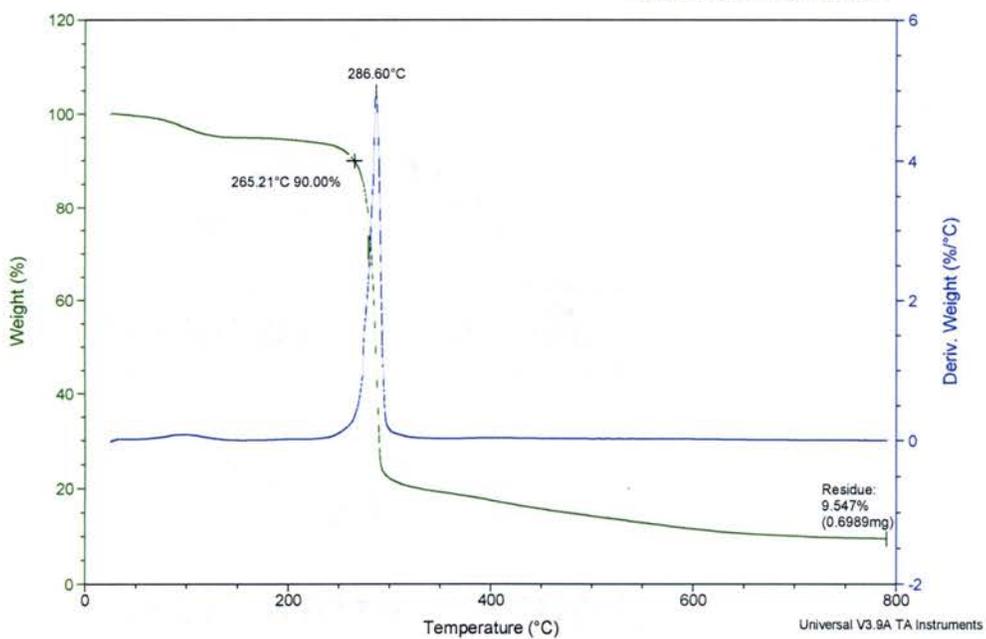


## 13. Poly(MMA-co-N.NMPH) - 8020

Sample: poly (N-NMPH-M)-7525  
Size: 7.3210 mg  
Method: Ramp

TGA

File: C:\...poly (N-NMPH-M)-7525.001  
Operator: Goodman  
Run Date: 16-Mar-06 10:41  
Instrument: TGA Q50 V6.4 Build 193

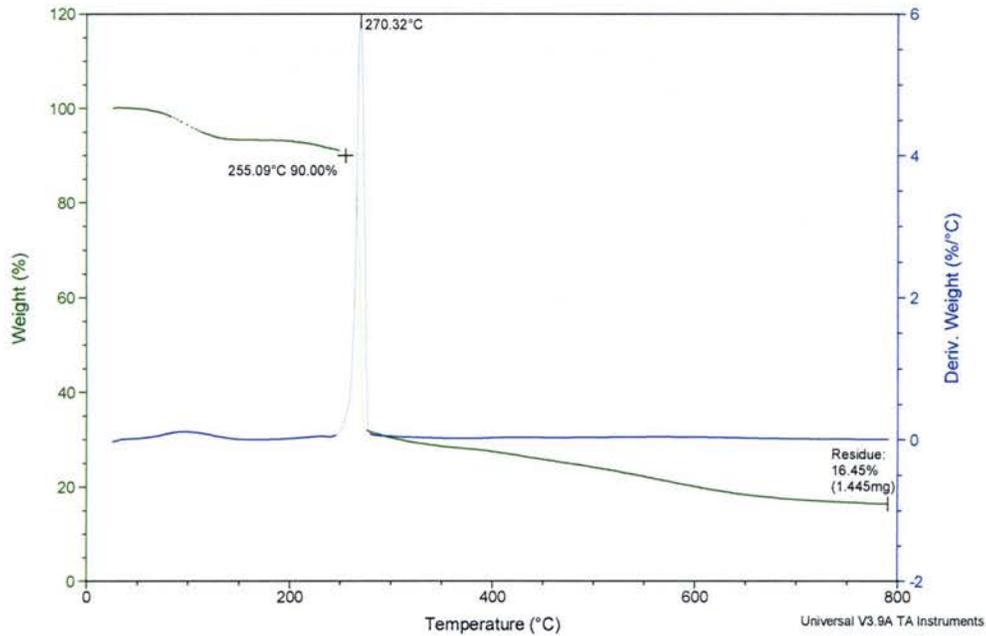


## 14. Poly(MMA-co-N.NMPH) - 5050

Sample: Poly(NO2-NMPH)-100  
 Size: 8.7870 mg  
 Method: Ramp

TGA

File: C:\...\Poly(NO2-NMPH)-100.001  
 Operator: Mike  
 Run Date: 21-Jan-06 10:16  
 Instrument: TGA Q50 V6.4 Build 193

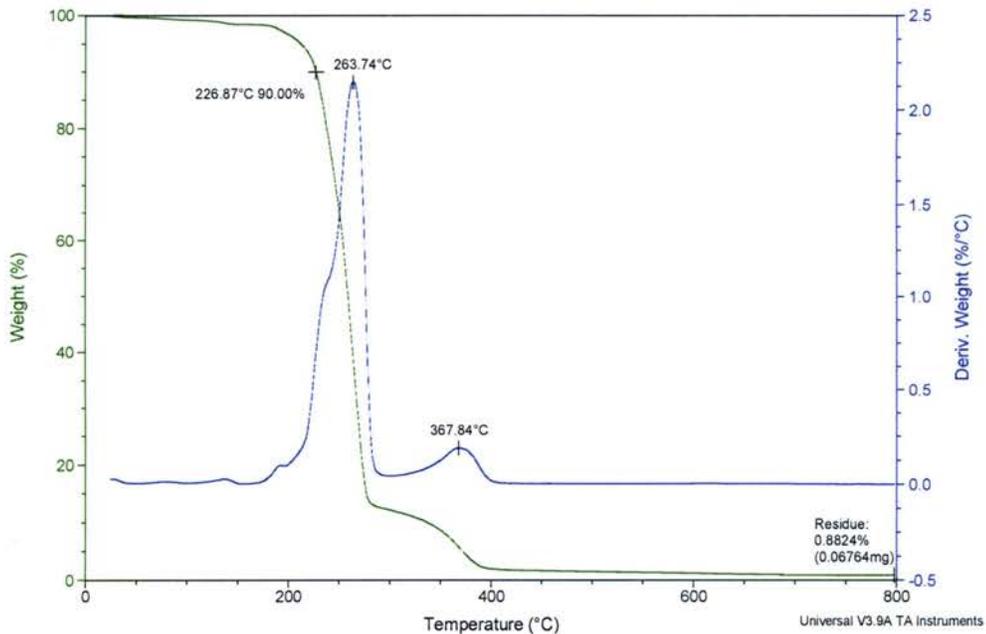


### 15. Poly(4-nitro-N-methacryloyloxy phthalimide)

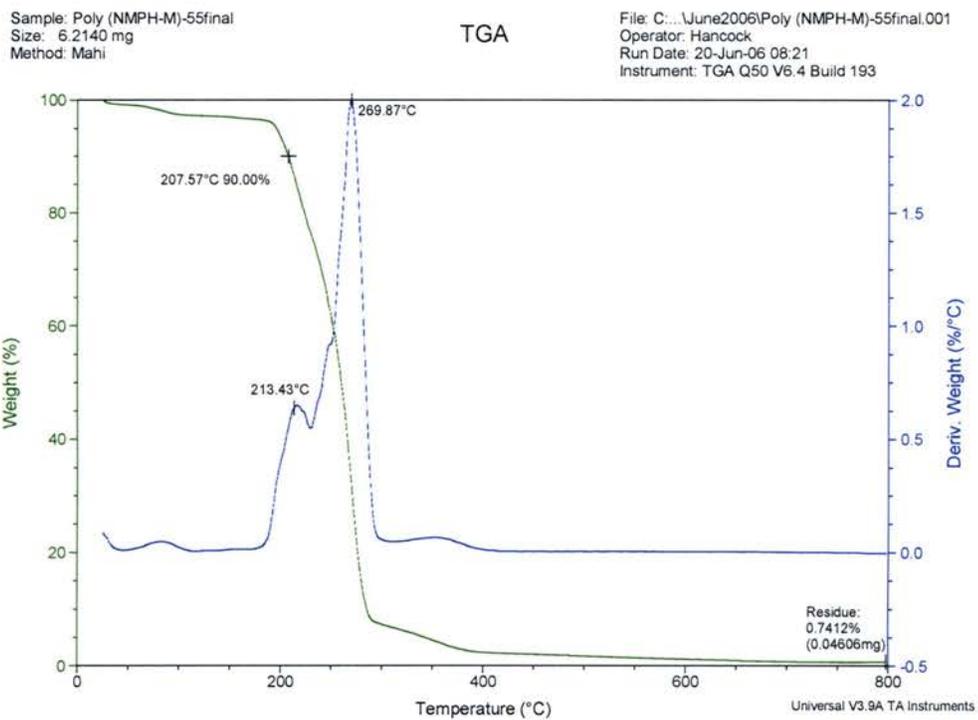
Sample: Poly (NMPH-M)-19final  
 Size: 7.6660 mg  
 Method: Mahi

TGA

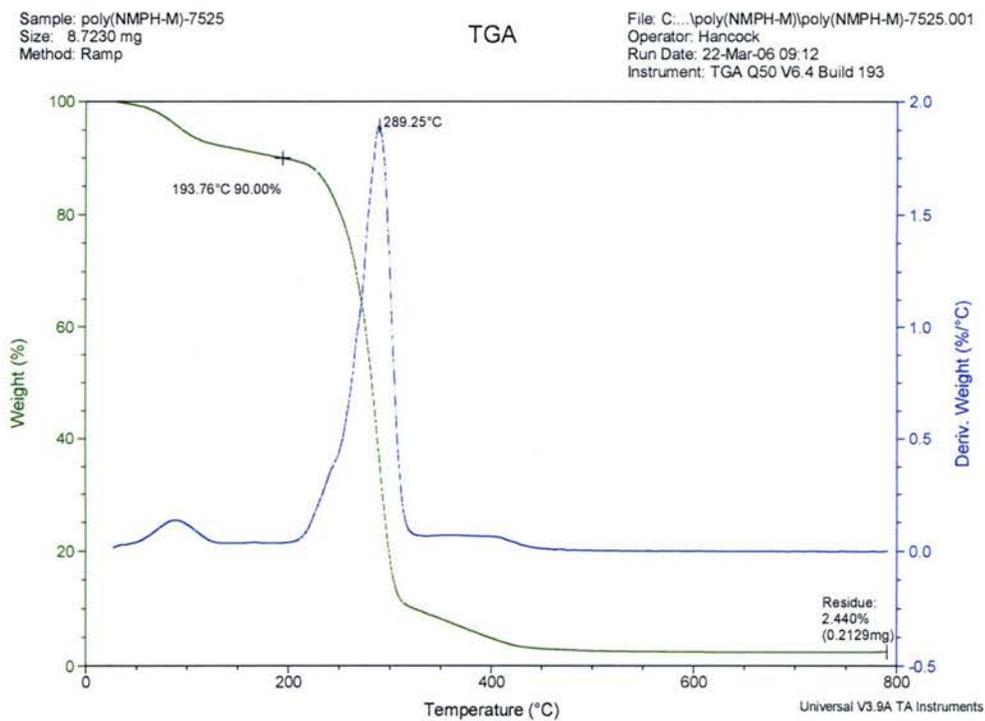
File: C:\...\June2006\Poly (NMPH-M)-19final.001  
 Operator: Hancock  
 Run Date: 16-Jun-06 17:17  
 Instrument: TGA Q50 V6.4 Build 193



### 16. Poly(MMA-co-NMPH)-9901



## 17. Poly(MMA-co-NMPH)- 7228

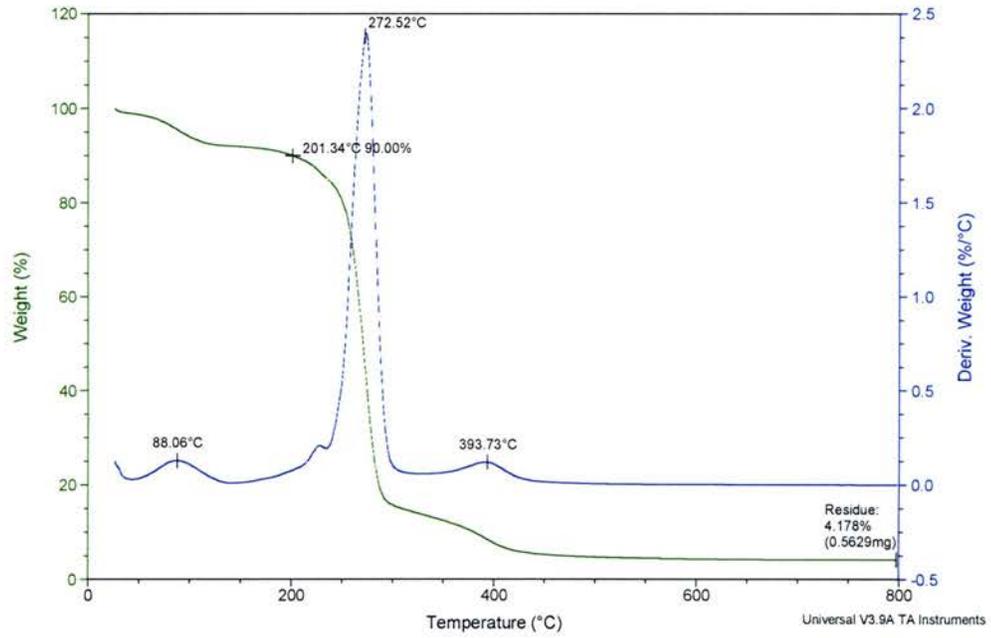


## 18. Poly(MMA-co-NMPH)- 4852

Sample: Poly(NMPH)-100  
Size: 13.4750 mg  
Method: Ramp

TGA

File: C:\...\(NMPH-M)5perMin\Poly(NMPH)-100.001  
Operator: Hancock  
Run Date: 18-Apr-06 11:16  
Instrument: TGA Q50 V6.4 Build 193



### 19. Poly(*N*-methacryloyloxy phthalimide)

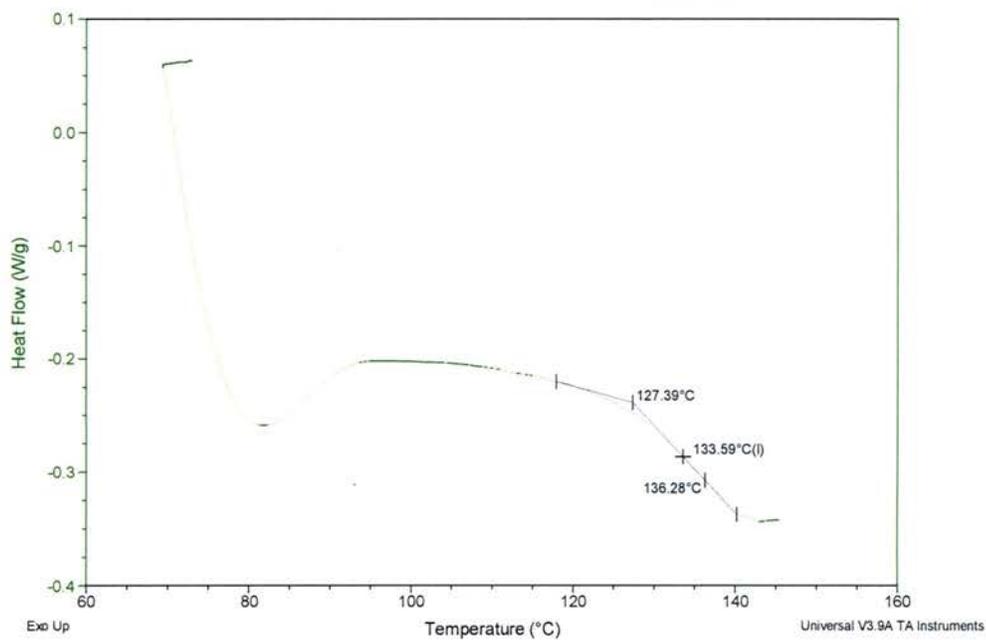
APPENDIX IV

DSC

Sample: Poly (C-NMPH-M)-19  
Size: 13.4000 mg  
Method: Mah's Loop

DSC

File: C:\Poly (C-NMPH-M)-19.001  
Operator: Hancock  
Run Date: 11-May-06 12:31  
Instrument: 2920 MDSC V2.6A

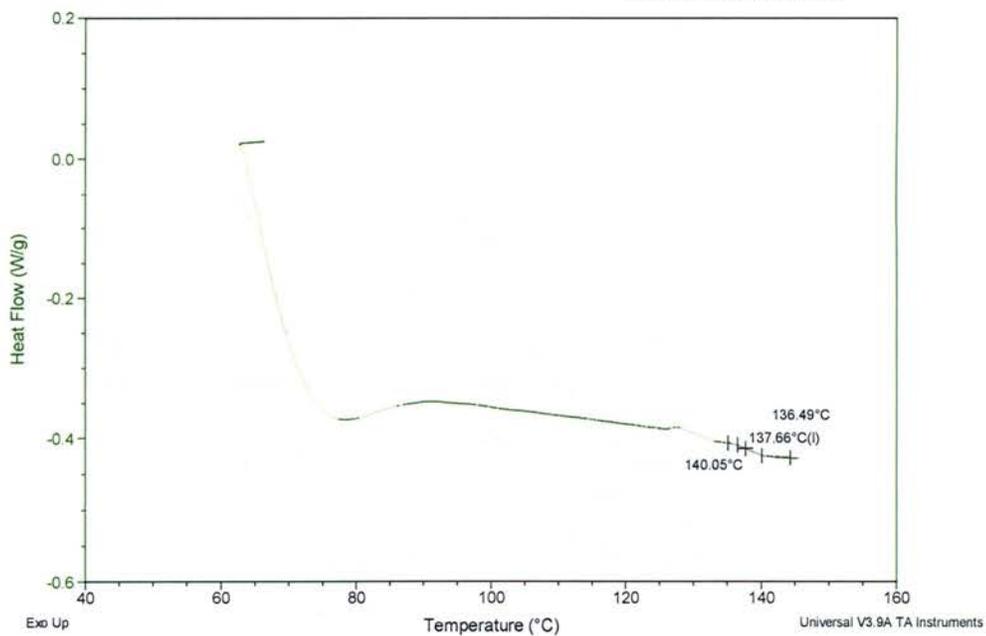


### 1. Poly(MMA-co-Cl.NMPH) - 9802

Sample: Poly (C-NMPH-M)-2575  
Size: 17.1000 mg  
Method: Mah's Loop

DSC

File: C:\Poly (C-NMPH-M)-2575.001  
Operator: Hancock  
Run Date: 11-May-06 15:31  
Instrument: 2920 MDSC V2.6A

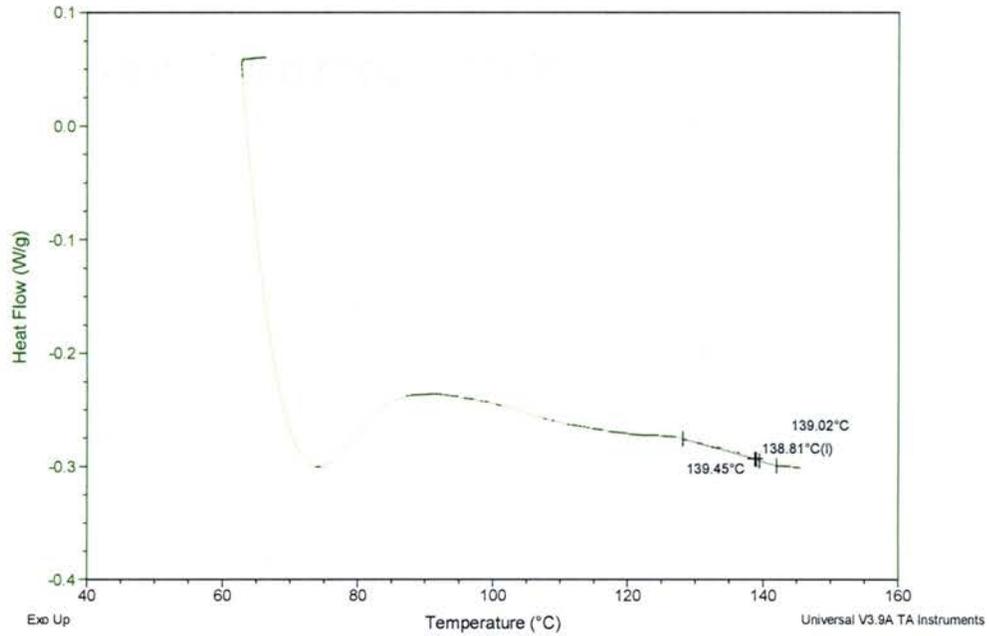


### 2. Poly(MMA-co-Cl.NMPH) - 9307

Sample: Poly (C-NMPH-M)-55  
Size: 13.2000 mg  
Method: Mahi's Loop

DSC

File: C:\Poly (C-NMPH-M)-55.001  
Operator: Hancock  
Run Date: 11-May-06 15:31  
Instrument: 2920 MDSC V2.6A

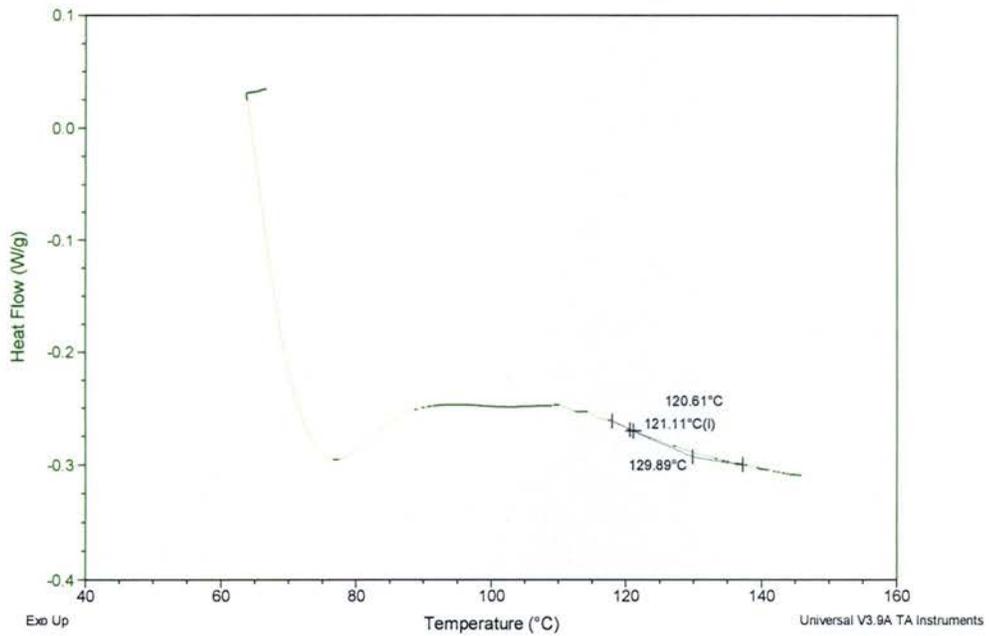


### 3. Poly(MMA-co-Cl.NMPH) – 7624

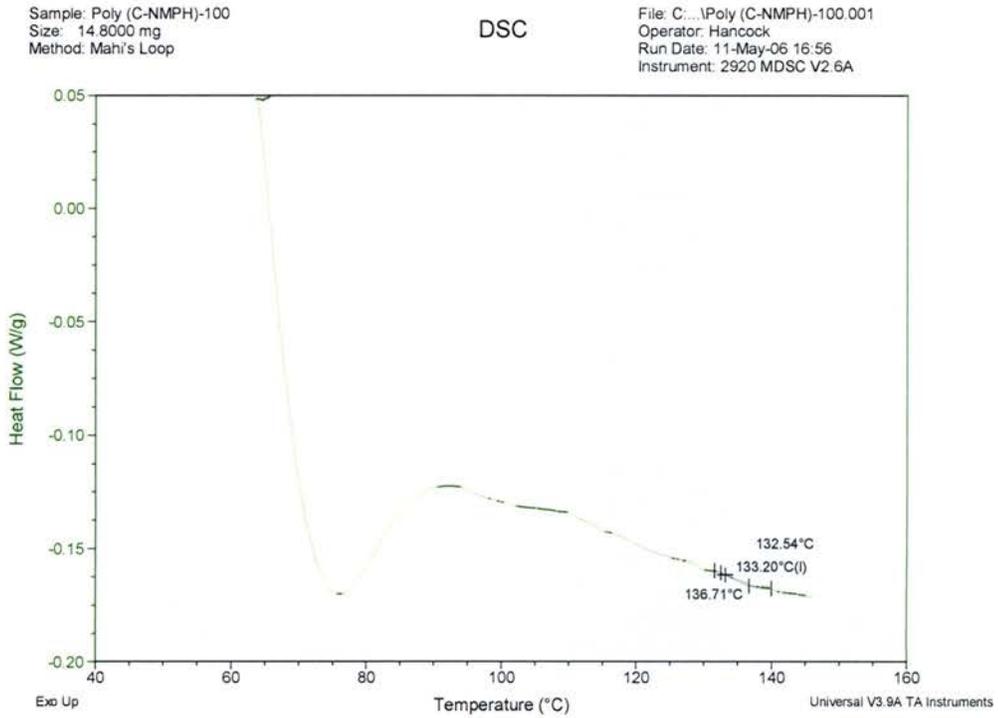
Sample: Poly (C-NMPH-M)-7525  
Size: 15.6000 mg  
Method: Mahi's Loop

DSC

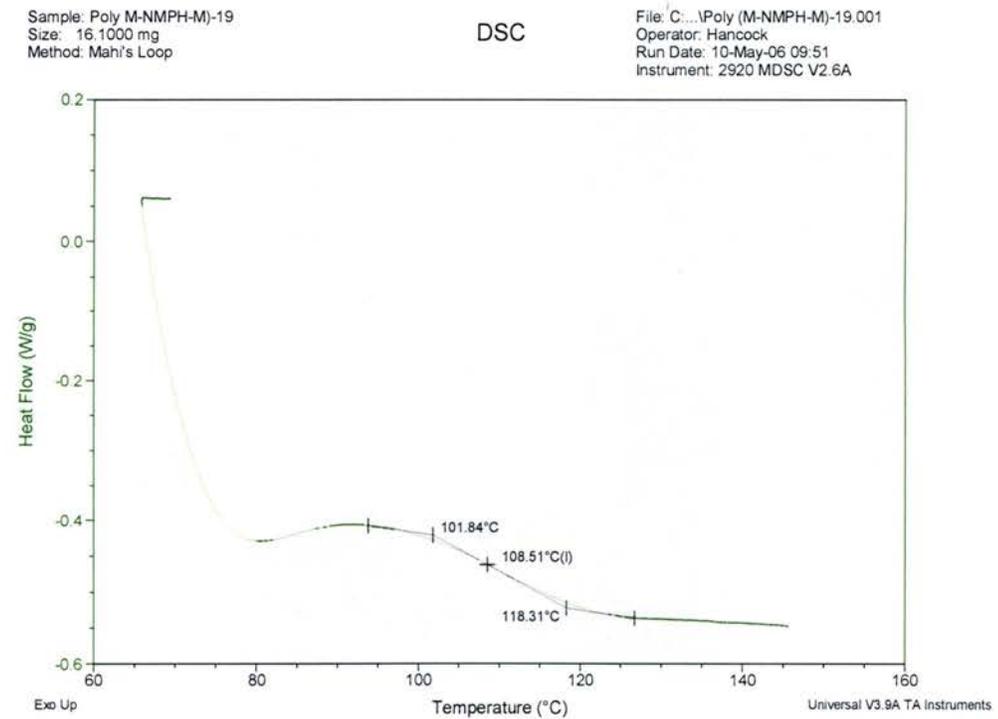
File: C:\Poly (C-NMPH-M)-7525.001  
Operator: Hancock  
Run Date: 11-May-06 16:56  
Instrument: 2920 MDSC V2.6A



### 4. Poly(MMA-co-Cl.NMPH) – 5248



### 5. Poly(4,5-dichloro-N-methacryloyloxy phthalimide)

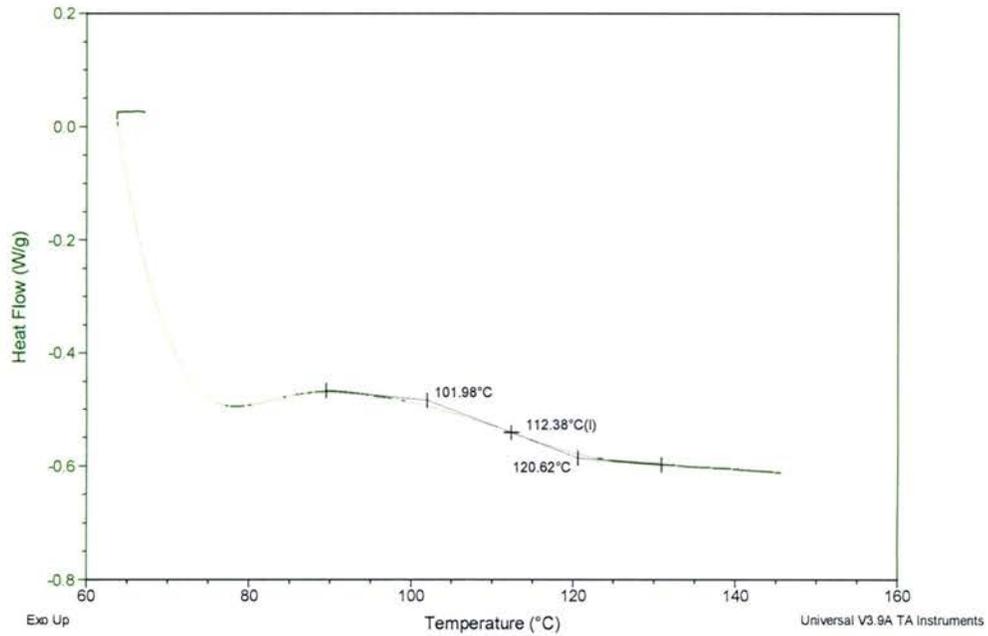


### 6. Poly(MMA-co-M.NMPH) -9901

Sample: Poly (M-NMPH-M)-2575  
Size: 14.1000 mg  
Method: Mah's Loop

DSC

File: C:\Poly (M-NMPH-M)-2575.001  
Operator: Hancock  
Run Date: 10-May-06 12:36  
Instrument: 2920 MDSC V2.6A

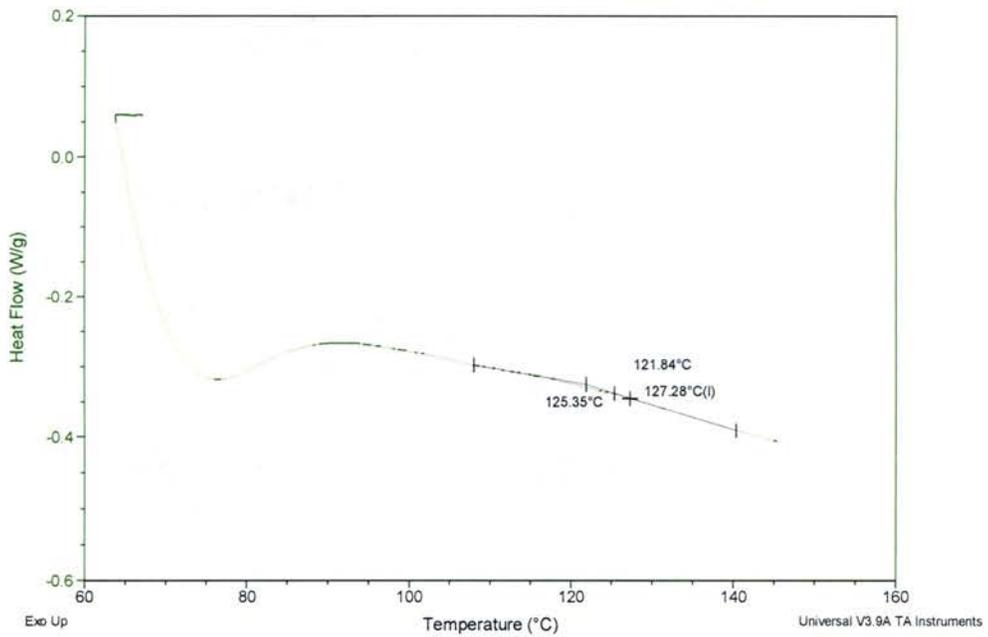


### 7. Poly(MMA-co-M.NMPH) - 9406

Sample: Poly (M-NMPH-M)-55  
Size: 11.3000 mg  
Method: Mah's Loop

DSC

File: C:\Poly (M-NMPH-M)-55.001  
Operator: Hancock  
Run Date: 10-May-06 12:36  
Instrument: 2920 MDSC V2.6A

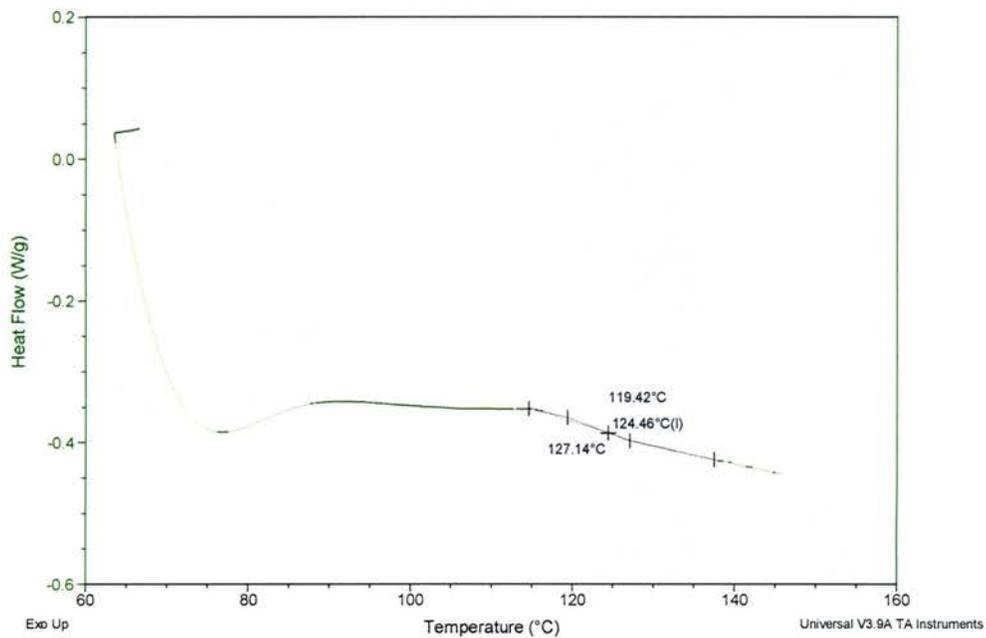


### 8. Poly(MMA-co-M.NMPH) - 7921

Sample: Poly (M-NMPH-M)-7525  
Size: 14.9000 mg  
Method: Mahi's Loop

DSC

File: C:\Poly (M-NMPH-M)-7525.001  
Operator: Hancock  
Run Date: 10-May-06 15:00  
Instrument: 2920 MDSC V2.6A

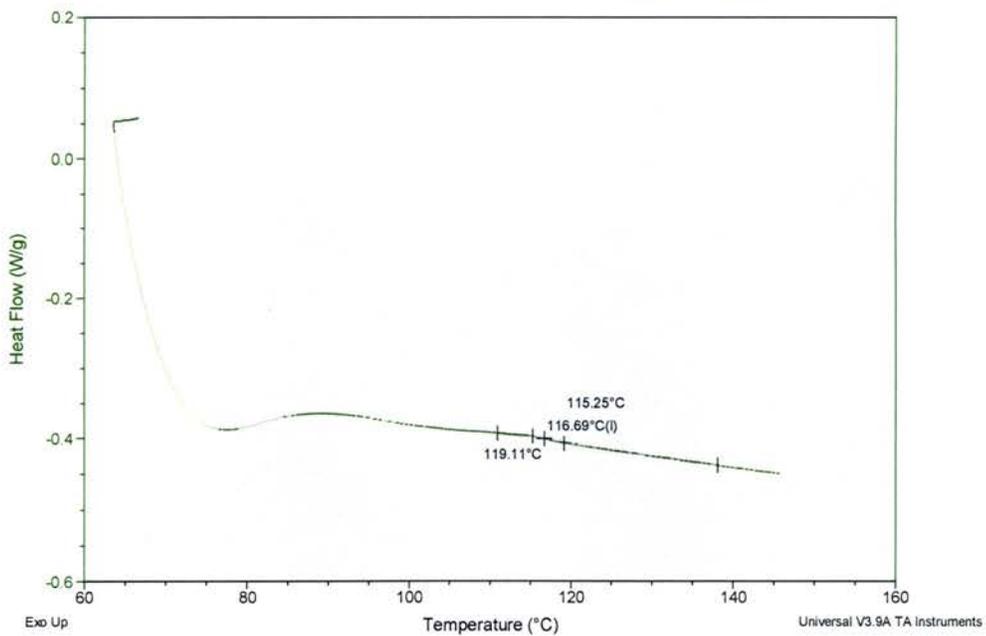


### 9. Poly(MMA-co-M.NMPH) - 4852

Sample: Poly (M-NMPH-M)-100  
Size: 18.9000 mg  
Method: Mahi's Loop

DSC

File: C:\Poly (M-NMPH)-100.001  
Operator: Hancock  
Run Date: 10-May-06 15:00  
Instrument: 2920 MDSC V2.6A

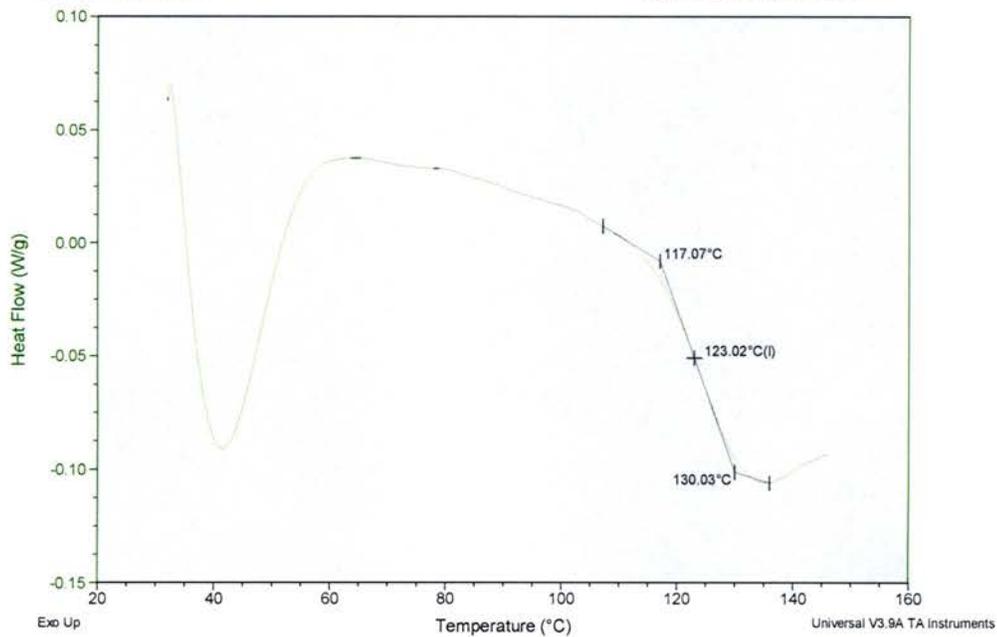


### 10. Poly(4-methyl-N-methacryloyloxy phthalimide)

Sample: Poly(N-NMPH-M)-19  
 Size: 6.6000 mg  
 Method: Mahi's Loop  
 Comment: Deep well pan

DSC

File: C:\Poly(N-NMPH-M)-19run3.003  
 Operator: Hancock  
 Run Date: 20-Apr-06 16:59  
 Instrument: 2920 MDSC V2.6A

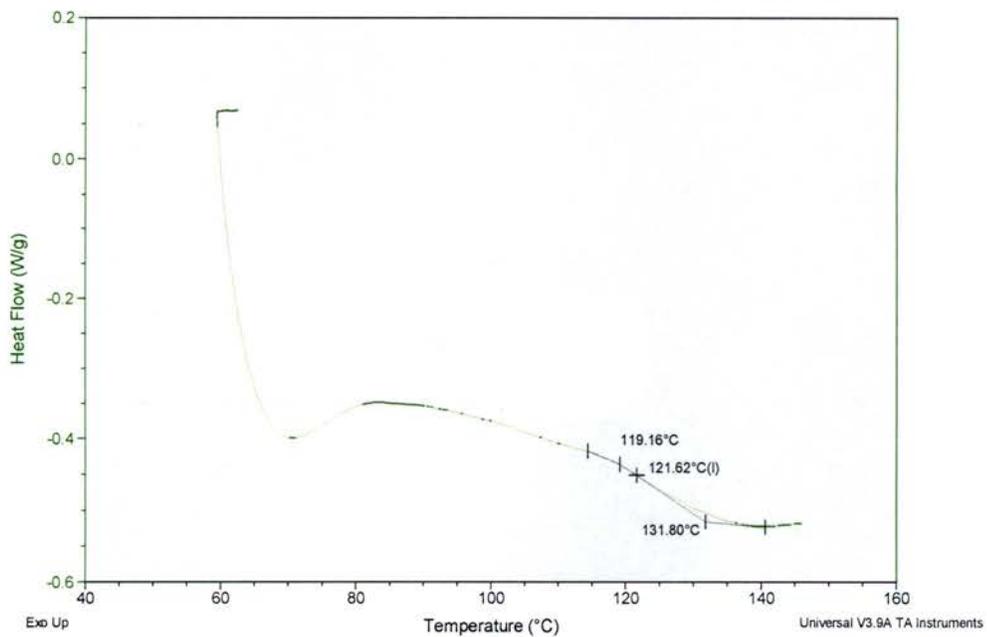


### 11. Poly(MMA-co-N.NMPH) -9901

Sample: Poly (N-NMPH-M)-2575  
 Size: 11.1000 mg  
 Method: Mahi's Loop

DSC

File: C:\Poly (N-NMPH-M)-2575  
 Operator: Hancock  
 Run Date: 9-May-06 13:56  
 Instrument: 2920 MDSC V2.6A

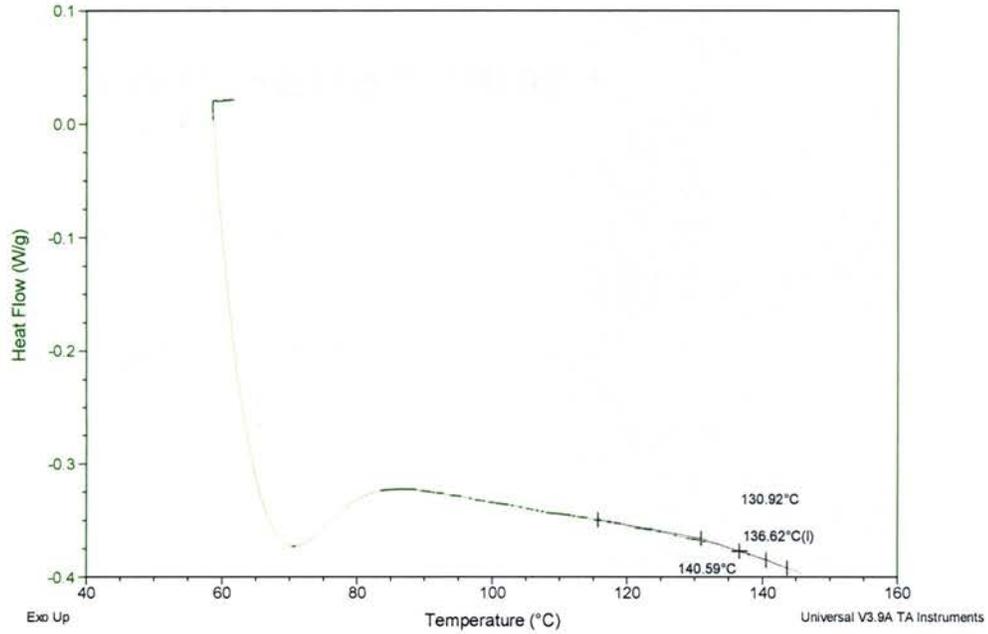


### 12. Poly(MMA-co-N.NMPH) - 9307

Sample: Poly (N-NMPH-M)-55  
Size: 16.0000 mg  
Method: Mah's Loop

DSC

File: C:\Poly (N-NMPH-M)-55.001  
Operator: Hancock  
Run Date: 10-May-06 08:11  
Instrument: 2920 MDSC V2.6A

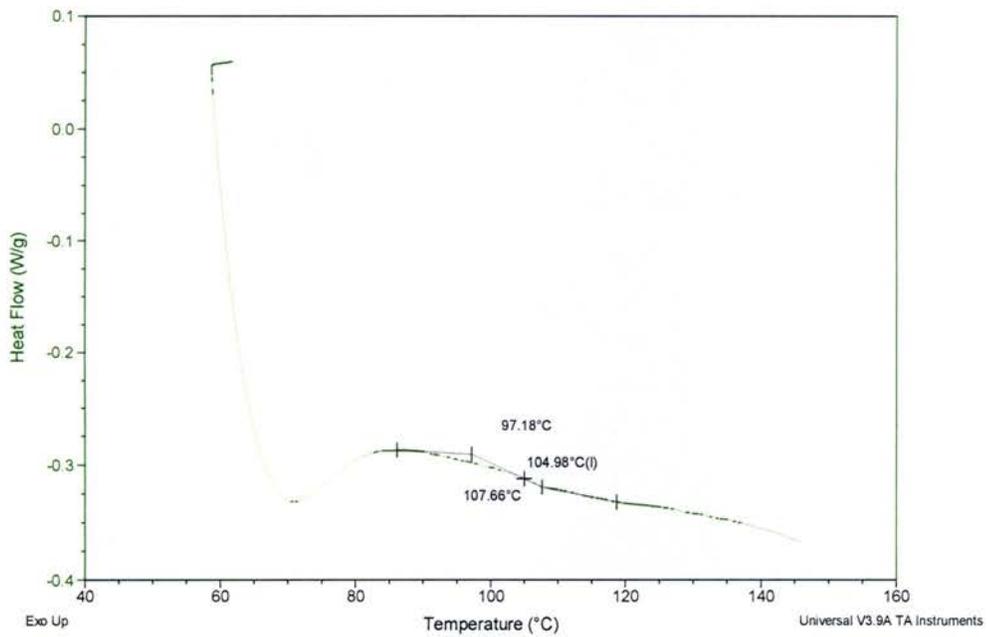


### 13. Poly(MMA-co-N.NMPH) - 8020

Sample: Poly (N-NMPH-M)-7525  
Size: 15.2000 mg  
Method: Mah's Loop

DSC

File: C:\Poly (N-NMPH-M)-7525.001  
Operator: Hancock  
Run Date: 10-May-06 08:11  
Instrument: 2920 MDSC V2.6A

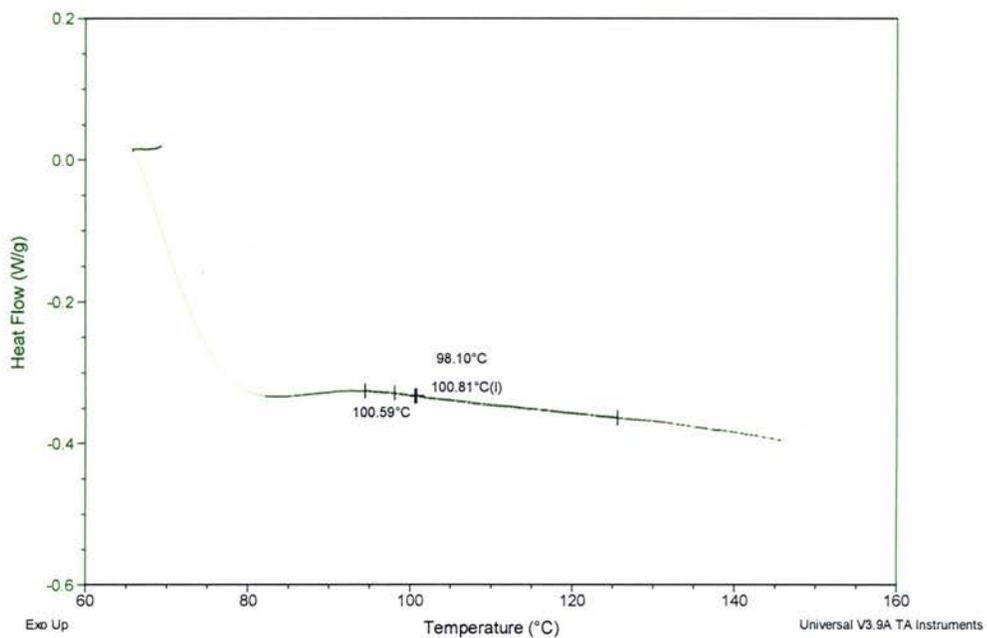


### 14. Poly(MMA-co-N.NMPH) - 5050

Sample: Poly (N-NMPH-M)-100  
 Size: 17.0000 mg  
 Method: Mahi's Loop

DSC

File: C:\...\Poly (N-NMPH)-100.001  
 Operator: Hancock  
 Run Date: 10-May-06 09:51  
 Instrument: 2920 MDSC V2.6A

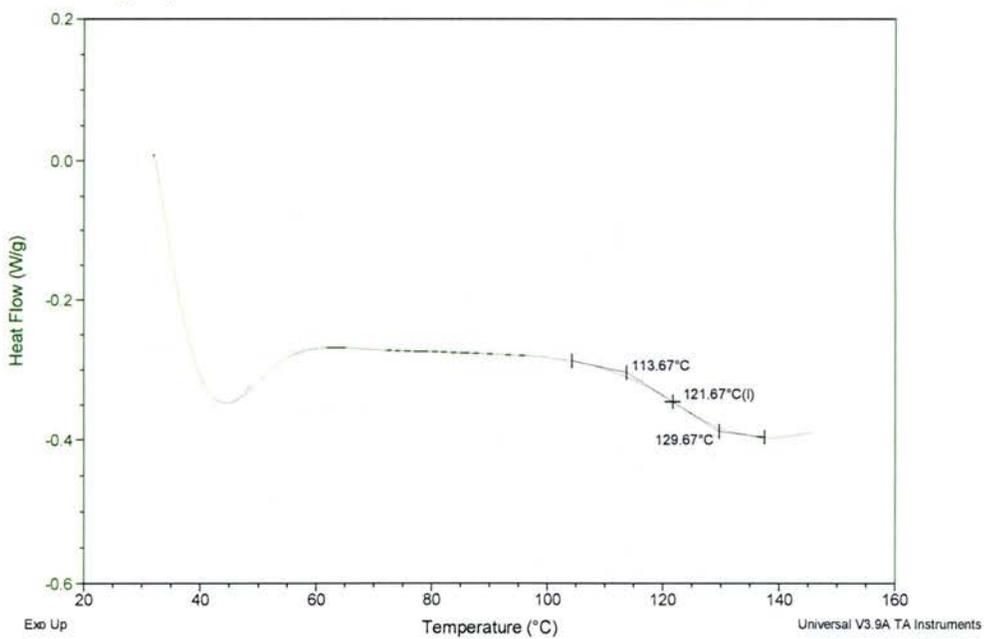


### 15. Poly(4-nitro-N-methacryloyloxy phthalimide)

Sample: Poly(NMPH-M)-19  
 Size: 10.0000 mg  
 Method: Mahi's Loop  
 Comment: Deep well pan

DSC

File: C:\...\Poly(NMPH-M)-19run3.003  
 Operator: Hancock  
 Run Date: 20-Apr-06 16:59  
 Instrument: 2920 MDSC V2.6A

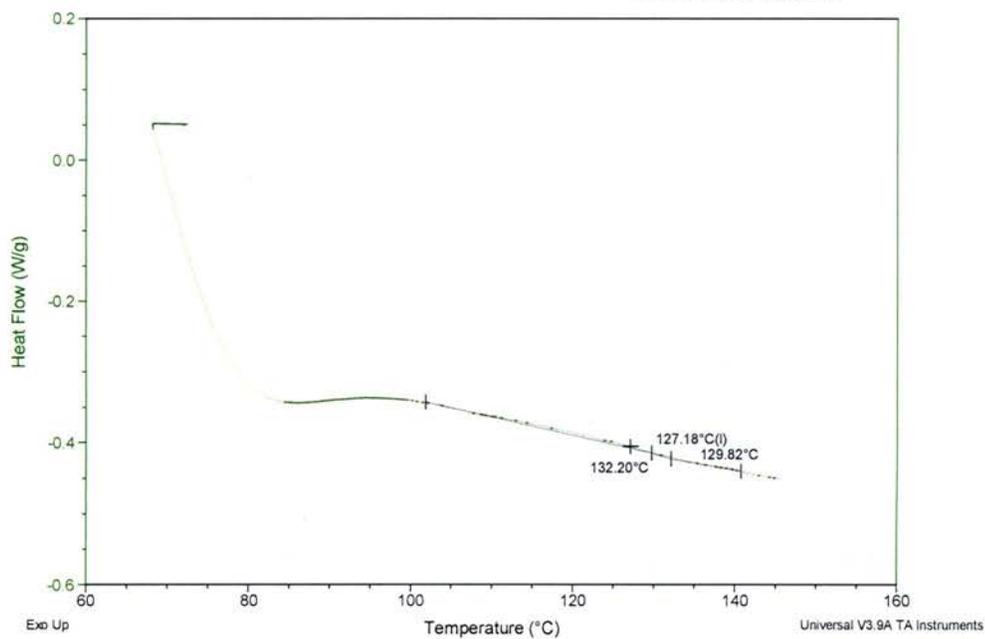


### 16. Poly(MMA-co-NMPH)-9901

Sample: Poly (NMPH-M)-2575  
Size: 20.7000 mg  
Method: Mahi's Loop

DSC

File: C:\Poly (NMPH-M)-2575.001  
Operator: Hancock  
Run Date: 11-May-06 07:40  
Instrument: 2920 MDSC V2.6A

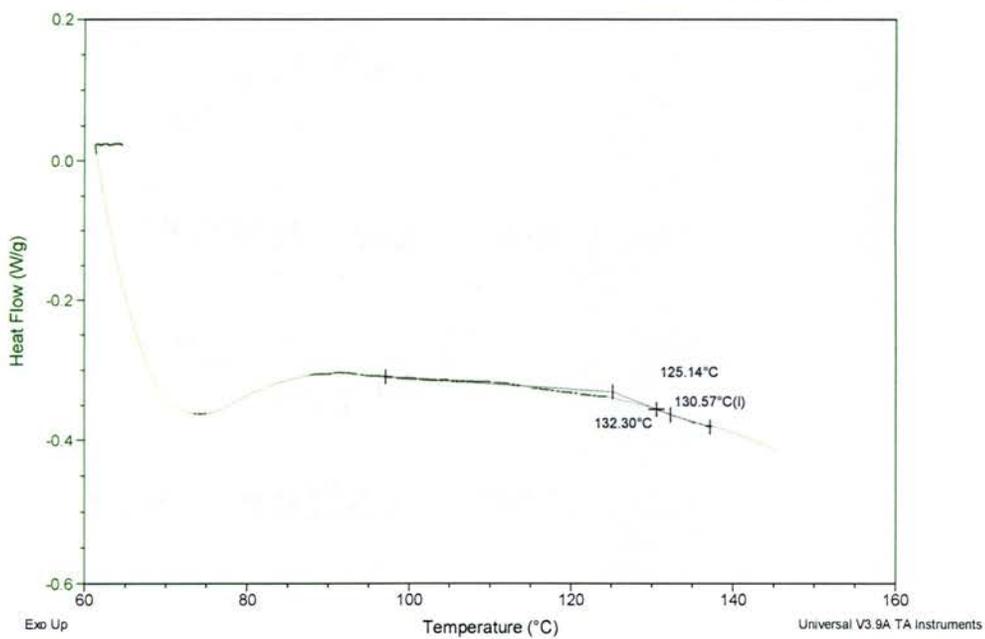


## 17. Poly(MMA-co-NMPH)- 9208

Sample: Poly (NMPH-M)-55  
Size: 15.5000 mg  
Method: Mahi's Loop

DSC

File: C:\Poly(NMPH-M)\Poly (NMPH-M)-55.001  
Operator: Hancock  
Run Date: 11-May-06 10:57  
Instrument: 2920 MDSC V2.6A

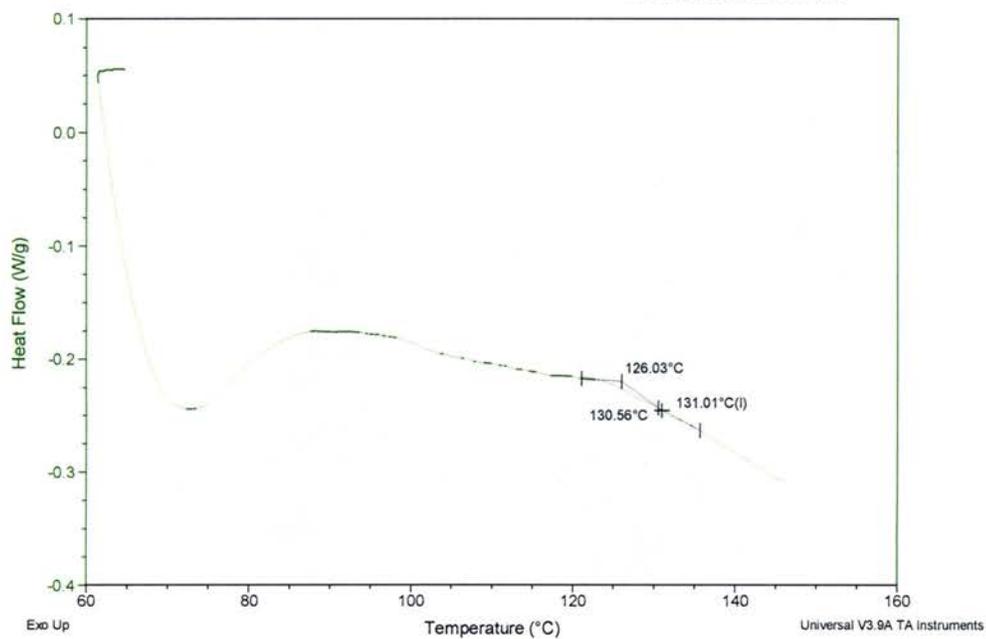


## 18. Poly(MMA-co-NMPH)- 7228

Sample: Poly (NMPH-M)-7525  
Size: 12.3000 mg  
Method: Mahi's Loop

DSC

File: C:\...\Poly (NMPH-M)-7525.001  
Operator: Hancock  
Run Date: 11-May-06 10:57  
Instrument: 2920 MDSC V2.6A

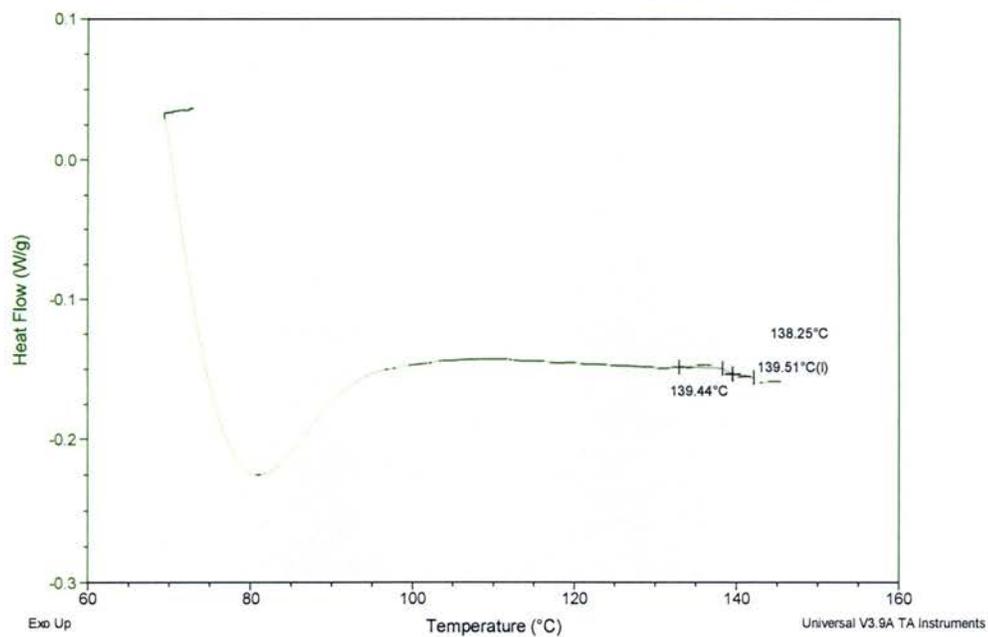


## 19. Poly(MMA-co-NMPH)- 4852

Sample: Poly (NMPH)-100  
Size: 14.0000 mg  
Method: Mahi's Loop

DSC

File: C:\...\Poly(NMPH-M)\Poly (NMPH)-100.001  
Operator: Hancock  
Run Date: 11-May-06 12:31  
Instrument: 2920 MDSC V2.6A

20. Poly(*N*-methacryloyloxy phthalimide)

**APPENDIX V**  
**ELECTRON BEAM LITHOGRAPHY DATA**

2003Graph.pdl		####																CURRENT= 41 nAmps															
Line	0.06	0.12	0.18	0.24	0.3	0.36	0.42	0.48	0.54	0.6	0.66	0.72	0.78	0.84	0.9	0.96	1.02	1.08	1.14	1.2	1.26	1.32	1.38	1.44	1.5								
	400	200	133	100	80	66	59	50	44	40	36	34	30	28	26	26	24	22	22	20	20	18	18	16	16								
5000	12535	6268	4168	3134	2507	2068	1849	1567	1379	1254	1128	1065	940	877	815	815	752	689	689	627	627	564	564	501	501								
4000	10028	5014	3334	2507	2006	1655	1479	1254	1103	1003	903	852	752	702	652	602	552	552	501	501	451	451	401	401	401								
3000	7521	3761	2501	1880	1504	1241	1109	940	827	752	677	639	564	526	489	489	451	414	414	376	376	338	338	301	301								
2000	5014	2507	1667	1254	1003	827	740	627	552	501	451	426	376	351	326	326	301	276	276	251	251	226	226	201	201								
1000	2507	1254	834	627	501	414	370	313	276	251	226	213	188	175	163	163	150	138	138	125	125	113	113	100	100								
900	2256	1128	750	564	451	372	333	282	248	226	203	192	169	158	147	147	135	124	124	113	113	102	102	90.3	90.3								
800	2006	1003	667	501	401	331	296	251	221	201	181	170	150	140	130	130	120	110	110	100	100	90.3	90.3	80.2	80.2								
700	1755	877	584	439	351	290	259	219	193	175	158	149	132	123	114	114	105	96.5	96.5	87.7	87.7	79	79	70.2	70.2								
600	1504	752	500	376	301	248	222	188	165	150	135	128	113	105	97.8	97.8	90.3	82.7	82.7	75.2	75.2	67.7	67.7	60.2	60.2								
500	1254	627	417	313	251	207	185	157	138	125	113	107	94	87.7	81.5	81.5	75.2	68.9	68.9	62.7	62.7	56.4	56.4	50.1	50.1								
400	1003	501	333	251	201	165	148	125	110	100	90.3	85.2	75.2	70.2	65.2	65.2	60.2	55.2	55.2	50.1	50.1	45.1	45.1	40.1	40.1								
300	752.1	376	250	188	150	124	111	94	82.7	75.2	67.7	63.9	56.4	52.6	48.9	48.9	45.1	41.4	41.4	37.6	37.6	33.8	33.8	30.1	30.1								
200	501.4	251	167	125	100	82.7	74	62.7	55.2	50.1	45.1	42.6	37.6	35.1	32.6	32.6	30.1	27.6	27.6	25.1	25.1	22.6	22.6	20.1	20.1								
100	250.7	125	83.4	62.7	50.1	41.4	37	31.3	27.6	25.1	22.6	21.3	18.8	17.5	16.3	16.3	15	13.8	13.8	12.5	12.5	11.3	11.3	10	10								
90	225.6	113	75	56.4	45.1	37.2	33.3	28.2	24.8	22.6	20.3	19.2	16.9	15.8	14.7	14.7	13.5	12.4	12.4	11.3	11.3	10.2	10.2	9.03	9.03								
80	200.6	100	66.7	50.1	40.1	33.1	29.6	25.1	22.1	20.1	18.1	17	15	14	13	13	12	11	11	10	10	9.03	9.03	8.02	8.02								
70	175.5	87.7	58.4	43.9	35.1	29	25.9	21.9	19.3	17.5	15.8	14.9	13.2	12.3	11.4	11.4	10.5	9.65	9.65	8.77	8.77	7.9	7.9	7.02	7.02								
60	150.4	75.2	50	37.6	30.1	24.8	22.2	18.8	16.5	15	13.5	12.8	11.3	10.5	9.78	9.78	9.03	8.27	8.27	7.52	7.52	6.77	6.77	6.02	6.02								
50	125.4	62.7	41.7	31.3	25.1	20.7	18.5	15.7	13.8	12.5	11.3	10.7	9.4	8.77	8.15	8.15	7.52	6.89	6.89	6.27	6.27	5.64	5.64	5.01	5.01								
40	100.3	50.1	33.3	25.1	20.1	16.5	14.8	12.5	11	10	9.03	8.52	7.52	7.02	6.52	6.52	6.02	5.52	5.52	5.01	5.01	4.51	4.51	4.01	4.01								
30	75.21	37.6	25	18.8	15	12.4	11.1	9.4	8.27	7.52	6.77	6.39	5.64	5.26	4.89	4.89	4.51	4.14	4.14	3.76	3.76	3.38	3.38	3.01	3.01								
20	50.14	25.1	16.7	12.5	10	8.27	7.4	6.27	5.52	5.01	4.51	4.26	3.76	3.51	3.26	3.26	3.01	2.76	2.76	2.51	2.51	2.26	2.26	2.01	2.01								
10	25.07	12.5	8.34	6.27	5.01	4.14	3.7	3.13	2.76	2.51	2.26	2.13	1.88	1.75	1.63	1.63	1.5	1.38	1.38	1.25	1.25	1.13	1.13	1	1								
9	22.56	11.3	7.5	5.64	4.51	3.72	3.33	2.82	2.48	2.26	2.03	1.92	1.69	1.58	1.47	1.47	1.35	1.24	1.24	1.13	1.13	1.02	1.02	0.9	0.9								
8	20.06	10	6.67	5.01	4.01	3.31	2.96	2.51	2.21	2.01	1.81	1.7	1.5	1.4	1.3	1.3	1.2	1.1	1.1	1	1	0.9	0.9	0.8	0.8								
7	17.55	8.77	5.84	4.39	3.51	2.9	2.59	2.19	1.93	1.75	1.58	1.49	1.32	1.23	1.14	1.14	1.05	0.97	0.97	0.88	0.88	0.79	0.79	0.7	0.7								
6	15.04	7.52	5	3.76	3.01	2.48	2.22	1.88	1.65	1.5	1.35	1.28	1.13	1.05	0.98	0.98	0.9	0.83	0.83	0.75	0.75	0.68	0.68	0.6	0.6								
5	12.54	6.27	4.17	3.13	2.51	2.07	1.85	1.57	1.38	1.25	1.13	1.07	0.94	0.88	0.81	0.81	0.75	0.69	0.69	0.63	0.63	0.56	0.56	0.5	0.5								
4	10.03	5.01	3.33	2.51	2.01	1.65	1.48	1.25	1.1	1	0.9	0.85	0.75	0.7	0.65	0.65	0.6	0.55	0.55	0.5	0.5	0.45	0.45	0.4	0.4								
3	7.521	3.76	2.5	1.88	1.5	1.24	1.11	0.94	0.83	0.75	0.68	0.64	0.56	0.53	0.49	0.49	0.45	0.41	0.41	0.38	0.38	0.34	0.34	0.3	0.3								
2	5.014	2.51	1.67	1.25	1	0.83	0.74	0.63	0.55	0.5	0.45	0.43	0.38	0.35	0.33	0.33	0.3	0.28	0.28	0.25	0.25	0.23	0.23	0.2	0.2								
1	2.507	1.25	0.83	0.63	0.5	0.41	0.37	0.31	0.28	0.25	0.23	0.21	0.19	0.18	0.16	0.16	0.15	0.14	0.14	0.13	0.13	0.11	0.11	0.1	0.1								
Dens	400	200	133	100	80	66	59	50	44	40	36	34	30	28	26	26	24	22	22	20	20	18	18	16	16								

## 1. Data for methyl substituted polymers with a current of 41 namps

2003Graph.pdl		####																CURRENT= 39.9 nAmps															
Line	0.06	0.12	0.18	0.24	0.3	0.36	0.42	0.48	0.54	0.6	0.66	0.72	0.78	0.84	0.9	0.96	1.02	1.08	1.14	1.2	1.26	1.32	1.38	1.44	1.5								
	400	200	133	100	80	66	59	50	44	40	36	34	30	28	26	26	24	22	22	20	20	18	18	16	16								
5000	12199	6099	4056	3050	2440	2013	1799	1525	1342	1220	1098	1037	915	854	793	793	732	671	671	610	610	549	549	488	488								
4000	9759	4880	3245	2440	1952	1610	1439	1220	1073	976	878	830	732	683	634	634	586	537	537	488	488	439	439	390	390								
3000	7319	3660	2434	1830	1464	1208	1080	915	805	732	659	622	549	512	476	476	439	403	403	366	366	329	329	293	293								
2000	4880	2440	1622	1220	976	805	720	610	537	488	439	415	366	342	317	317	293	268	268	244	244	220	220	195	195								
1000	2440	1220	811	610	488	403	360	305	268	244	220	207	183	171	159	159	146	134	134	122	122	110	110	97.6	97.6								
900	2196	1098	730	549	439	362	324	274	242	220	198	187	165	154	143	143	132	121	121	110	110	98.8	98.8	87.8	87.8								
800	1952	976	649	488	390	322	288	244	215	195	176	166	146	137	127	127	117	107	107	97.6	97.6	87.8	87.8	78.1	78.1								
700	1708	854	568	427	342	282	252	213	188	171	154	145	128	120	111	111	102	93.9	93.9	85.4	85.4	76.9	76.9	68.3	68.3								
600	1464	732	487	366	293	242	216	183	161	146	132	124	110	102	95.2	95.2	87.8	80.5	80.5	73.2	73.2	65.9	65.9	58.6	58.6								
500	1220	610	406	305	244	201	180	152	134	122	110	104	91.5	85.4	79.3	79.3	73.2	67.1	67.1	61	61	54.9	54.9	48.8	48.8								
400	975.9	488	324	244	195	161	144	122	107	97.6	87.8	83	73.2	68.3	63.4	63.4	58.6	53.7	53.7	48.8	48.8	43.9	43.9	39	39								
300	731.9	366	243	183	146	121	108	91.5	80.5	73.2	65.9	62.2	54.9	51.2	47.6	47.6	43.9	40.3	40.3	36.6	36.6	32.9	32.9	29.3	29.3								
200	488	244	162	122	97.6	80.5	72	61	53.7	48.8	43.9	41.5	36.6	34.2	31.7	31.7	29.3	26.8	26.8	24.4	24.4	22	22	19.5	19.5								
100	244	122	81.1	61	48.8	40.3	36	30.5	26.8	24.4	22	20.7	18.3	17.1	15.9	15.9	14.6	13.4	13.4	12.2	12.2	11	11	9.76	9.76								
90	219.6	110	73	54.9	43.9	36.2	32.4	27.4	24.2	22	19.8	18.7	16.5	15.4	14.3	14.3	13.2	12.1	12.1	11	11	9.88	9.88	8.78	8.78								
80	195.2	97.6	64.9	48.8	39	32.2	28.8	24.4	21.5	19.5	17.6	16.6	14.6	13.7	12.7	12.7	11.7	10.7	10.7	9.76	9.76	8.78	8.78	7.81	7.81								
70</																																	

**APPENDIX VI**  
**ABBREVIATIONS**

**ABBREVIATIONS**

PMMA – Poly(methyl methacrylate)

NMPH - *N*-methacryloyloxy phthalimide

DCC - *N,N'*-dicyclohexyl carbodiimide

*N*-Boc - *N*-(*tert*-butoxycarbonyl)

Cl.NMPH – 4,5-dichloro *N*-methacryloyloxy phthalimide

N.NMPH – 4-Nitro *N*-methacryloyloxy phthalimide

M.NMPH – 4-methyl *N*-methacryloyloxy phthalimide

Poly(MMA-N.NMPH)-8020 – Copolymer with incorporation of 80 mol % MMA and 20 mol % N.NMPH

Poly(MMA-C.NMPH)-7624 – Copolymer with incorporation of 76 mol % MMA and 24 mol % Cl.NMPH

Poly(MMA-NMPH)-7228 – Copolymer with incorporation of 72 mol % MMA and 28 mol % NMPH

Poly(MMA-M.NMPH)-7921 - Copolymer with incorporation of 79 mol % MMA and 21 mol % M.NMPH

## REFERENCES

- 1) [http://www.historychannel.com/thcsearch/thc\\_resourcedetail.do?encyc\\_id=21491](http://www.historychannel.com/thcsearch/thc_resourcedetail.do?encyc_id=21491)  
1
- 2) Modified from [www.physics.ucdavis.edu/~kliu/Phy250/Lithography1.pdf](http://www.physics.ucdavis.edu/~kliu/Phy250/Lithography1.pdf)
- 3) Reichmanis, E.; Thompson, L. F. *Chem. Rev.* **1989**, 89, 1273.
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