

## 4.2 Polymerization of Novel Carbazole Based Methacrylates, Dimethacrylates, and Acrylates

The functionalized carbazole based monomers were readily polymerized using a variety of free radical techniques. UV photopolymerization, using the photo-initiator 1-hydroxycyclohexyl phenyl ketone (Irgacure 184™), was used to polymerize the carbazole-phenoxy based methacrylate, the carbazole-bisphenol A based dimethacrylate, and copolymers of these two functionalized monomers. Solution polymerization, using the thermal initiator AIBN, was used to form linear polymers from the carbazole-phenoxy based methacrylate and from the carbazole-phenoxy based acrylate. Copolymers, using methyl methacrylate as a reactive diluent, were also produced using free radical solution polymerization. Polymerization in the melt, using the thermal initiator t-butyl peroxide, was used to polymerize the carbazole-phenoxy based methacrylate, neat. Finally, a modified suspension polymerization, using the free radical initiator benzoyl peroxide, was investigated using the carbazole-phenoxy based methacrylate.

Thermosets were produced with the functionalized carbazole based dimethacrylates. Linear polymers, which could potentially be used as thermoplastics, were produced with the functionalized carbazole based methacrylates and acrylates. Table 4.3 summarizes the various polymerizations explored, and the molecular weights and polydispersities obtained, for the carbazole-phenoxy based methacrylates. Solution polymerization produced medium to high molecular weight polymer with a reasonable polydispersity, ranging from 3.16 to 3.32, which indicated that linear polymer was probably produced. The photopolymerizations and melt polymerization produced insoluble, probably cross-linked polymers, possibly due to side group reactions. The modified suspension polymerization produced very high molecular weight polymer, with a high polydispersity, perhaps suggesting a branched polymer. At the higher temperatures and more reactive reaction conditions for the photopolymerizations, melt polymerization, and suspension polymerization, chain transfer likely occurred at the methine group, and perhaps at the methylene groups as well. A probable mechanism for this is shown in

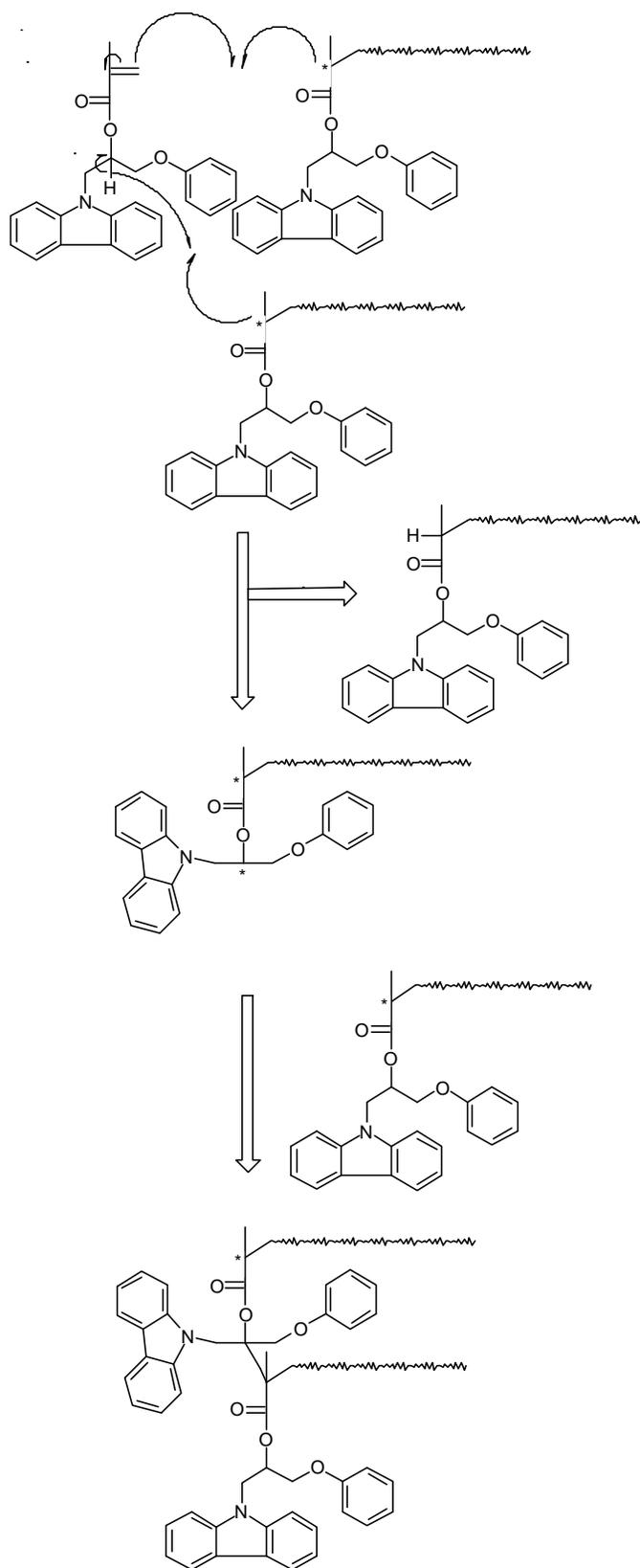
Scheme 4.1. The carbazole-phenoxy based methacrylate, in effect, was multi-functional at higher temperatures.

**Table 4.3** GPC Results for Free Radical Polymerizations of the Carbazole-Phenoxy Based Methacrylate

<b>Polymerization Method</b>	<b><math>\langle M_n \rangle</math></b> <b>(g/mole)</b>	<b><math>\langle M_w \rangle</math></b>	<b><math>\langle M_w \rangle / \langle M_n \rangle</math></b>
Solution Polymerization AIBN, 2 mole %	<b>14,900</b>	<b>47,100</b>	<b>3.16</b>
AIBN, 1 mole % 90°C	<b>58,900</b>	<b>195,300</b>	<b>3.32</b>
UV Photopolymerization Irgacure 184™, 2 mole % Very high temperatures	<b>Insoluble<sup>†</sup></b>		<b>N/A</b>
Melt polymerization t-Butyl peroxide, 2 mole % 118°C	<b>Insoluble<sup>†</sup></b>		<b>N/A</b>
Modified Suspension Polymerization Benzoyl peroxide, 1 mole % 90 to 98°C	<b>158,500</b>	<b>1,289,000</b>	<b>8.13<sup>‡</sup></b>

<sup>†</sup> Insoluble in methylene chloride, NMP (60°), and all other organic solvents.

<sup>‡</sup> Two large, overlapping bimodal peaks.



**Scheme 4.1** Possible Free Radical Cross-linking Reactions at Methine Position

#### 4.2.1 UV Photopolymerization of Carbazole Based Monomers

Transparent, amber, polymer films of the novel carbazole based methacrylates and dimethacrylates were synthesized directly using photopolymerization. Medium UV radiation, broadly centered between 300 to 450 nm, was used, with a suitable photo-initiator, such as 1-hydroxycyclohexyl phenyl ketone (Irgacure 184<sup>TM</sup>). 2 mole % of the Irgacure 184<sup>TM</sup> was mixed with 1 to 3 g of the monomer, dissolved in DMF or DMAC, and then UV irradiated in a custom built photo-curing oven.

In addition to irradiating the monomer with UV light, the mercury UV lamps in the photo-curing oven also produced a substantial amount of heat. A high boiling solvent, such as DMF, was needed to keep the carbazole based monomers in solution during photopolymerization. All of the carbazole based monomers were powdery when dry. After 60 minutes of UV irradiation, along with the associated heat, even the DMF was evaporated, leaving behind transparent polymer films in the photo-curing oven.

Homopolymer films of the carbazole-phenoxy based methacrylate and of the carbazole-bisphenol A based dimethacrylate were produced using photopolymerization. The carbazole-bisphenol A based dimethacrylate polymer film was highly cross-linked and very brittle. The 50/50 weight/weight copolymer of the carbazole-phenoxy based methacrylate and the carbazole-bisphenol A based dimethacrylate produced a transparent, slightly amber film, which was easier to handle than either of the homopolymer films. Of all the polymer films produced throughout this research, this 50/50 copolymer film was the least brittle and the least fragile.

Photopolymerization was also attempted on the carbazole-sulfur containing methacrylate and dimethacrylate. The sulfur containing monomers did not dissolve in DMF or DMAC (or other organic solvents), even when subjected to the associated heat produced in the photo-curing oven. Methyl methacrylate (MMA) was also used as a reactive diluent, but with poor results. All of the materials obtained from these sulfur

containing monomers, following UV irradiation, were white and very opaque, including the copolymers with MMA.

Transparent copolymer films of carbazole-phenoxy based methacrylate and methyl methacrylate were also produced using photopolymerization. These copolymerizations served as a model system for the carbazole based acrylates, which would use smaller acrylates as reactive diluents, in an analogous fashion to the copolymerizations where methyl methacrylate was used as a reactive diluent for the carbazole-phenoxy based methacrylate.

All of the photopolymerized films, unfortunately, were insoluble in any organic solvent. Although it was not possible to fully characterize these films due to probable cross-linking at the methine position, the transparent photopolymerized films were easily analyzed in terms of refractive index. The transparent polymer and copolymer films produced by photopolymerization were less fragile, and easier to handle, than films made by solution free radical polymerization. This cross-linking appears to have had advantageous effects in terms of strength and toughness. The cross-linking may also have prevented large scale phase separation in these films, where the separated phases were below the size that leads to excessive light scattering. Combined with the ease of producing good films using this method, photopolymerization of these carbazole based monomers may prove of further interest.

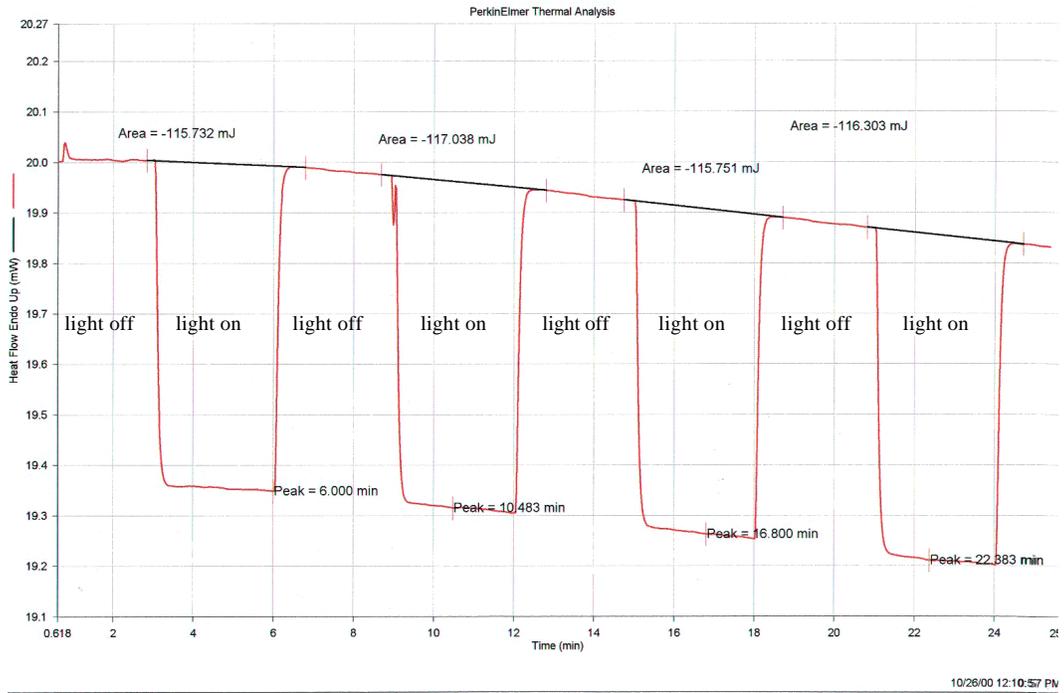
#### 4.2.1.1 Photo-DSC Analysis for the Carbazole-Phenoxy Based Methacrylate

Photo-differential scanning calorimeter (photo-DSC) was used to monitor the rapid exothermic heat of polymerization release for the carbazole-phenoxy based methacrylate. A Perkin Elmer DSC 7, which was equipped with a double beam photocalorimetric accessory (DPA) and a short-arc xenon lamp of 450 Watts, was used (Figure 2.7). A shutter, which was manually controlled, allowed light to radiate the sample when opened. A wavelength of 350 nm was chosen on the monochromator. The photopolymerizations were performed in modified aluminum pans (Figure 2.8). In order to reduce drift from the evaporation of the solvent DMF during the photo-DSC experiments, small quartz windows 7.0 mm in diameter were made, which fit directly over the modified sample pans of 6.5 mm in diameter.

Before performing the experiment on the monomer, the light intensity at 350 nm was determined using this photo-DSC apparatus. Graphite discs, which absorbed the UV radiation, were inserted into the sample holder. Figure 4.15 shows the DSC energy absorption rate profile for this measurement. The difference of the heat flow (mW) between the light on (shutter open) and the light off (shutter closed), divided by the area, gave the light intensity at the sample surface (equation 4.1). The light intensity for the photo-DSC at 350 nm was calculated to be 1.63 mW/cm<sup>2</sup>.

Unlike the UV photo-curing oven, the reaction conditions during the photo-DSC experiments were very controlled. A distinct wavelength of 350 nm UV light, rather than a broad UV range of radiation, was used for the analysis. Additionally, the temperature for the photo-DSC samples was isothermally maintained at 30°C throughout the photo-DSC experiments.

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 Operator ID: lr  
 Sample ID: Intensity measurements, 350nm  
 Sample Weight: 0.000 mg  
 Comment: C vs.C



1) Hold for 30.0 min at 30.00°C

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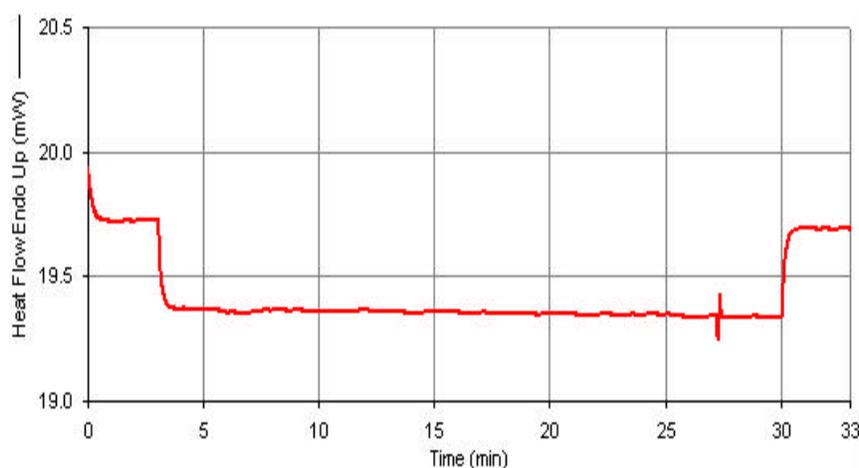
$$\text{Light Intensity} = \frac{mW_{(\text{light on})} - mW_{(\text{light off})}}{\text{light area in sample pan (cm}^2\text{)}} \quad \text{Equation 4.1}$$

$$\text{Light Intensity} = \frac{0.65 \text{ mW}}{0.40 \text{ cm}^2} = 1.63 \text{ mW/cm}^2$$

**Figure 4.15** Measurement of Light Intensity for the Photo-DSC at 350 nm

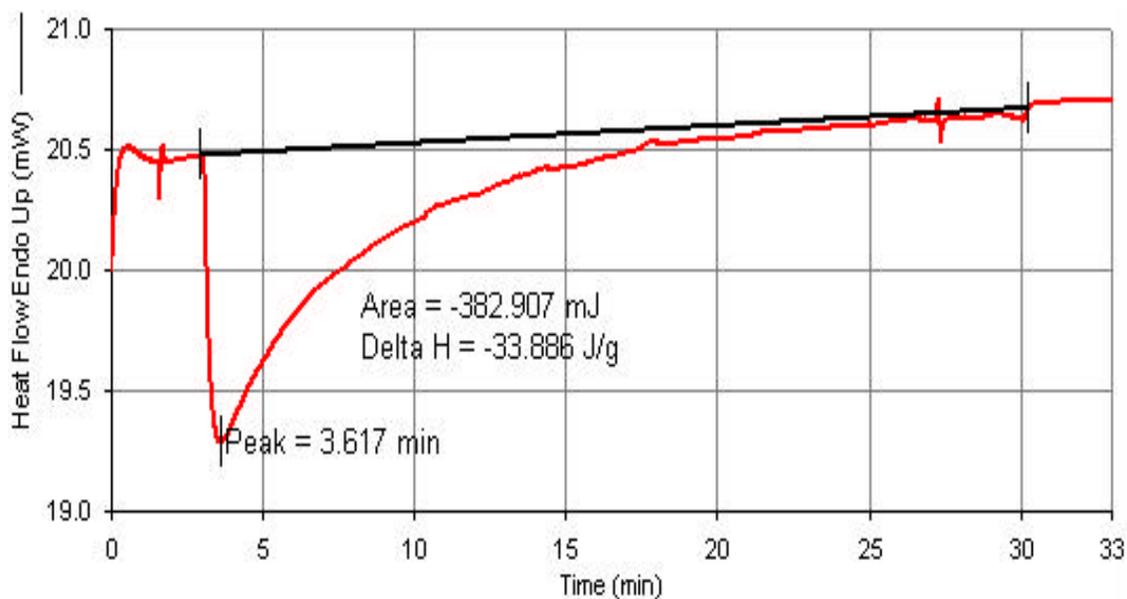
For the photo-DSC experiment, 20  $\mu\text{L}$  of the sample solution was placed in the modified sample pan, using a micropipette. An empty modified pan, also fitted with a quartz window, was placed in the reference cell. The sample solution contained 0.826 M carbazole-phenoxy based methacrylate in DMF, with 2 mole % Irgacure 184<sup>TM</sup>. At the beginning of the experiment, the shutter was closed (light off) to establish a baseline. After 3 minutes, the shutter was opened, and the sample was irradiated for 27 minutes. The shutter was closed again from 30 minutes to 33 minutes to reestablish the baseline.

The baseline after the large exothermic curve was lower than the baseline for the initial light-off position. This was caused from the absorbency of the carbazole and phenoxy substituents in the monomer, and from some drift due to slight evaporation of DMF during the photo-DSC experiment. Even with the small quartz windows on the modified sample pans, there was still some evaporation of DMF. To take these artifacts into account, the photo-DSC experiment was repeated using a solution of the (already) polymerized carbazole-phenoxy based methacrylate, in the same concentration with respect to repeat units, in DMF (Figure 4.16). The DSC profile of the carbazole-phenoxy based methacrylate polymer was subtracted from the DSC profile of the monomer, to produce an accurate measurement of the exotherm for the photopolymerization (Figure 4.17).



0.826 M (with respect to repeat units) in DMF,  $\lambda = 350 \text{ nm}$

**Figure 4.16** Photo-DSC of Polymer of Carbazole-Phenol Based Methacrylate



0.826 M Monomer in DMF, 2 mole % Irgacure 184,  $\lambda = 350$  nm

### Calculation of Enthalpy Conversions

$$[\text{Exp. } \Delta H_p \text{ (J/g sample)}] \times (\text{wt. total sample/wt. monomer}) \times (\text{molecular wt. monomer}) \\ = \Delta H_p \text{ (J/mole)} \quad \text{(Equation 4.2)}$$

$$-33.886 \text{ J/g sample} \times (1.163 \text{ g sample}/0.385 \text{ g monomer}) \times (385 \text{ g/mole}) \\ = -39,409 \text{ J/mole (monomer)} = -39.4 \text{ kJ/mole (monomer)}$$

**Figure 4.17** Corrected Photo-DSC for the Carbazole-Phenoxy Based Methacrylate

The enthalpy, or heat, of polymerization ( $\Delta H_p$ ) was calculated from the area of the exotherm, relative to the baseline (light off), and converted to kJ/mole (equation 4.2 in Figure 4.18). The  $\Delta H_p$  for the carbazole-phenoxy based methacrylate was  $-39.4$  kJ/mole, which compared to  $-54.8$  kJ/mole for methyl methacrylate.<sup>250</sup>

The extent of the reaction ( $E_p$ ) was determined by the percentage ratio of the  $\Delta H_p$  of the methacrylate and the  $\Delta H_p$  of methyl methacrylate, as shown in equation 4.3. The extent of the photopolymerization reaction was 71.9 % for the carbazole-phenoxy based methacrylate.

$$E_p = \frac{\Delta H_{p(\text{methacrylate})}}{\Delta H_{p(\text{methyl methacrylate})}} \times 100 \% \quad \text{Equation 4.3}$$

$$E_p = \frac{-39.4 \text{ kJ/mole}}{-54.8 \text{ kJ/mole}} \times 100 \% = 71.9 \%$$

Photo-DSC provided for an excellent method to capture, in real time, the rapid photopolymerization exotherm of the carbazole-phenoxy based methacrylate. The results of the photo-DSC experiment in terms of the heat of the photopolymerization reaction and the extent of reaction  $\Delta H_p$  and  $E_p$  are summarized in Table 4.4.

**Table 4.4** Heat of Polymerization and Extent of Polymerization for the Carbazole-Phenoxy Based Methacrylate

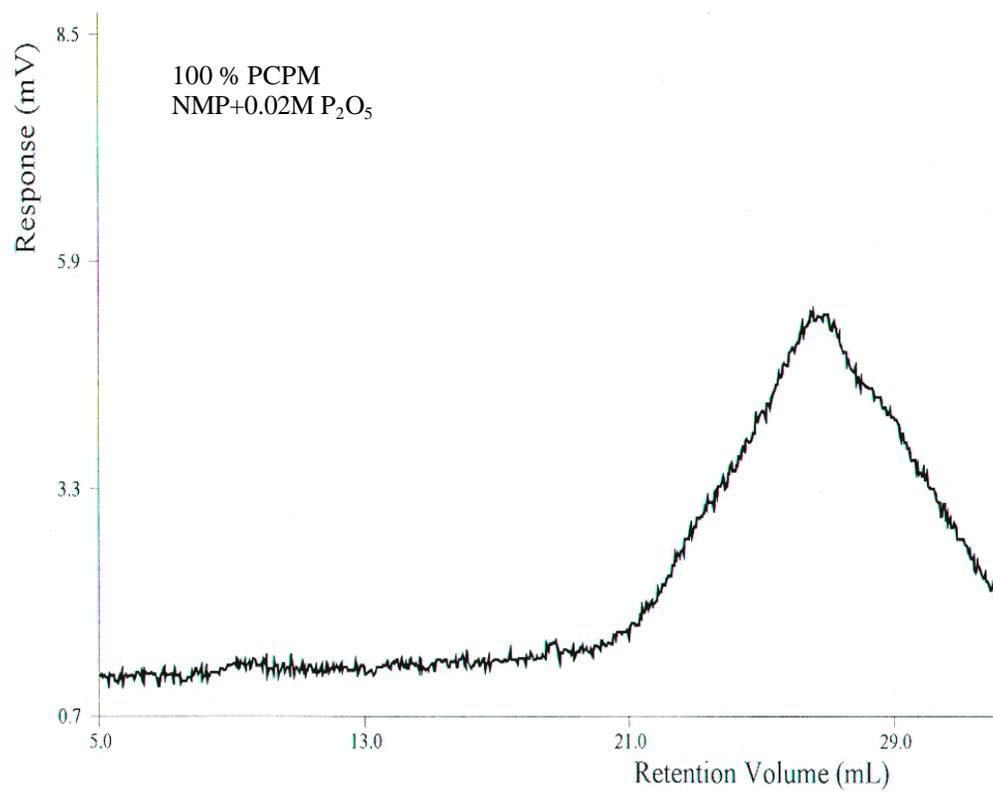
Monomer	$\Delta H_p$ (kJ/mole)	$E_p$
Carbazole-Phenoxy Based Methacrylate	-39.4	71.9 %

<sup>250</sup> Horie, K, Mita, I., *J. Radiat. Curing*, **1980**, 7(2), 20.

#### 4.2.2 Free Radical Solution Polymerization

Linear polymers derived from carbazole-phenoxy based methacrylate were readily polymerized by dissolving the monomer in nitrogen purged DMAC, and using 1 to 2 mole % AIBN as the thermal free radical initiator. Half-lives of AIBN are discussed on page 34 of Chapter 2 (Section 2.3.1.2). The polymerization was conducted under nitrogen in order to exclude oxygen (oxygen is a free radical scavenger). Reaction temperatures were between 85° and 95°C in a preheated oil or hot water bath for approximately 2 hours. The polymerizations were allowed to cool slowly to room temperature. The polymers were precipitated into chilled methanol, filtered, and vacuum dried. The carbazole-phenoxy based methacrylate was also polymerized in DMF under the same reaction conditions, with good results as well. For the carbazole-phenoxy based methacrylate polymerized in DMAC, with 2 mole % AIBN, the number average molecular weight ( $\langle M_n \rangle$ ) was 38,900 g/mole, with a polydispersity ( $\langle M_w \rangle / \langle M_n \rangle$ ) of 5.7. For a similar reaction in DMF, the number average molecular weight was 14,900 g/mole, with a polydispersity of 3.2, possibly suggesting chain transfer in DMF.

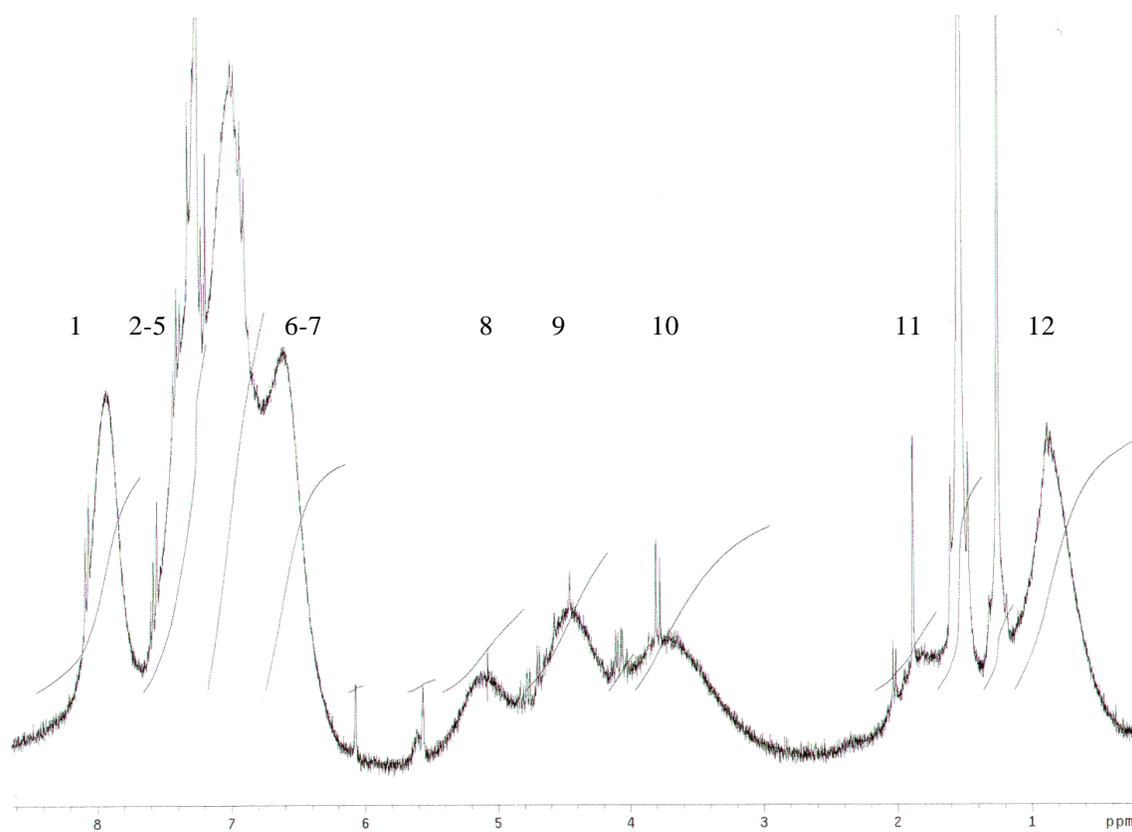
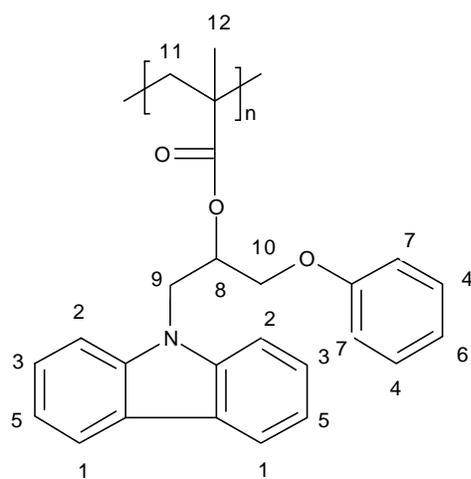
In order to produce good films, higher molecular weight polymer was needed. For subsequent solution polymerizations, the amount of initiator was reduced to 1 mole % AIBN. For the carbazole-phenoxy based methacrylate polymerized in DMAC, with 1 mole % AIBN, the  $\langle M_n \rangle$  was 58,900 g/mole, with a polydispersity of 3.3. The GPC chromatogram of this polymer is shown in Figure 4.18. This higher molecular weight polymer produced good transparent films, with a slight amber color, which were used to measure the refractive index. Polymer films were solvent cast from chloroform or methylene chloride, with a 30 weight % polymer to solvent ratio.



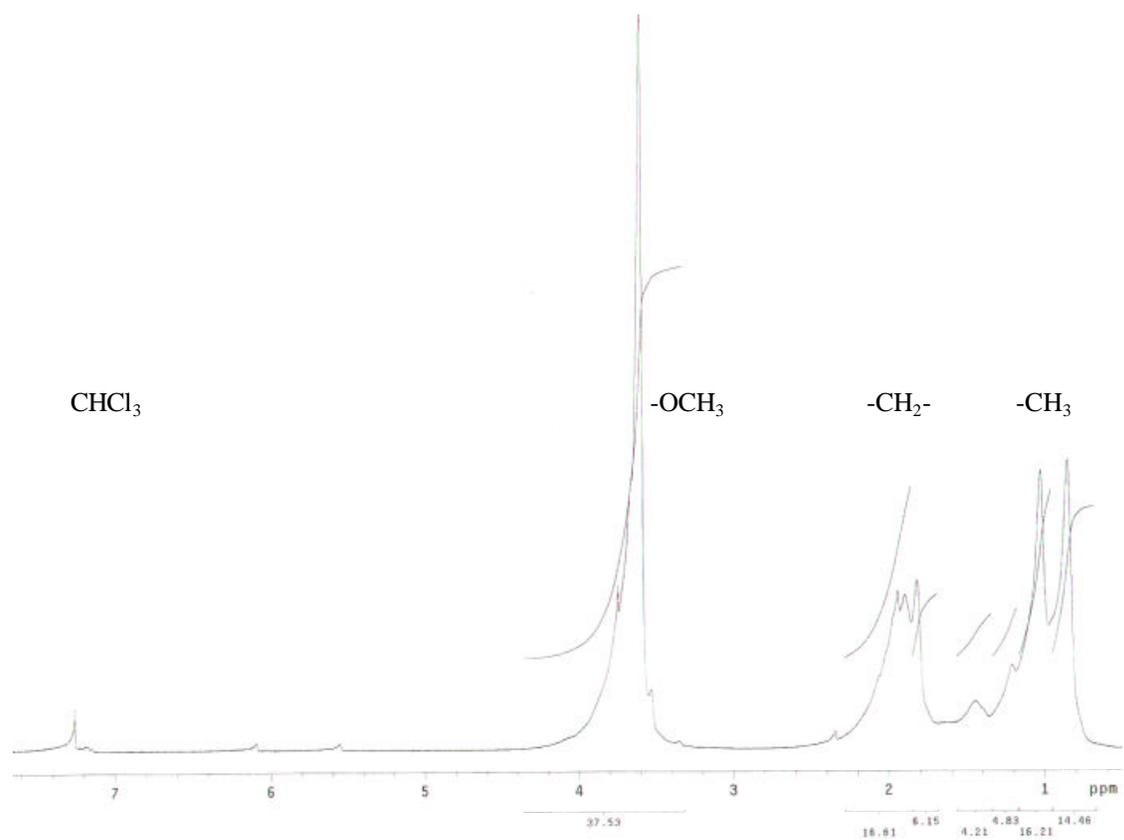
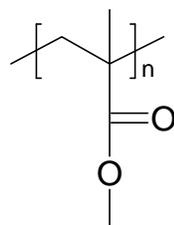
**Figure 4.18** GPC Chromatogram for the Carbazole-Phenoxy Based Methacrylate Polymer

Copolymers of carbazole-phenoxy based methacrylate and methyl methacrylate were produced in DMAC. For each copolymerization, 1 mole % of AIBN was used. Copolymers were produced in 25/75, 50/50, and 75/25 weight % ratios, and in 25/75, 50/50, and 75/25 mole % ratios. The homopolymer of methyl methacrylate was also produced, as a control, using 1 mole % AIBN. Polymers and copolymers were precipitated into chilled methanol, filtered, vacuum dried, and weighed. The free radical polymerizations were essentially quantitative. Table 4.5 describes the molecular weights and polydispersities for both the weight % and mole % copolymer series.

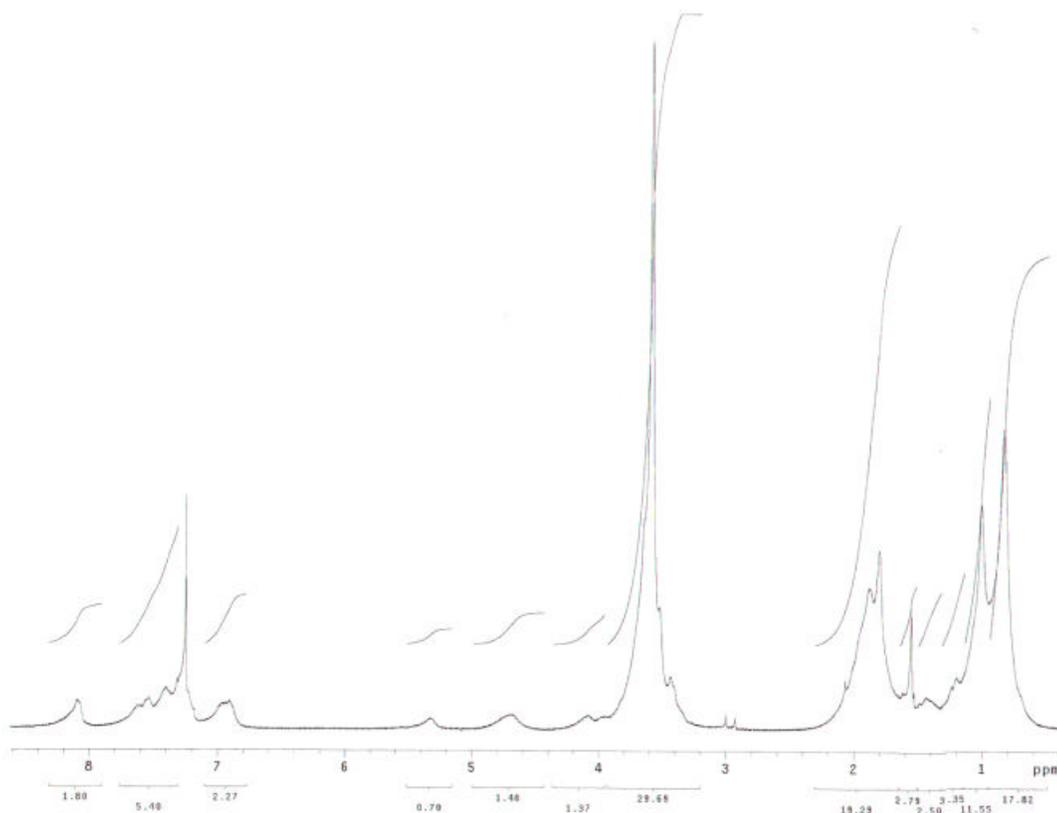
In order to confirm copolymer composition,  $^1\text{H}$  NMR spectroscopy was used. Figure 4.19 shows the  $^1\text{H}$  NMR spectrum of the carbazole-phenoxy based methacrylate homopolymer (PCPM), and Figure 4.20 shows the  $^1\text{H}$  NMR spectrum for the poly(methyl methacrylate) homopolymer (PMMA). Figure 4.21 depicts the  $^1\text{H}$  NMR of the 25 weight % PCPM/75 weight % PMMA copolymer, which converts to 8 mole % PCPM and 92 mole % PMMA. Using the two aromatic protons of the PCPM at 8.1 ppm and the three methoxy protons of the PMMA at 3.6 ppm, a ratio of 1 to 17 was expected from integration. The actual ratio of these two peaks was 1.0 to 16.5. For the copolymers that had more than 50 mole percent PMMA, the integration ratios between the two components were very close to expected values. For copolymers with a large mole percent of PCPM, the broad methylene peak adjacent to the phenoxy group of the PCPM overlapped into the methoxy peak of the PMMA, which increased the integration value for the methoxy peak (Figure 4.22). For copolymers with a large mole percent of PCPM, the integration ratios were erroneously high for the PMMA component using  $^1\text{H}$  NMR. The free radical homopolymerizations and copolymerizations of PCPM and PMMA were quantitative (98+ percent yields), however, so the final materials had virtually the same molecular composition ratios as the CPM/MMA monomer ratios added to the initial polymerization mixtures.



**Figure 4.19**  $^1\text{H NMR}$  Spectrum of the Carbazole-Phenoxy Based Polymer



**Figure 4.20** <sup>1</sup>H NMR Spectrum of Poly(methyl methacrylate)

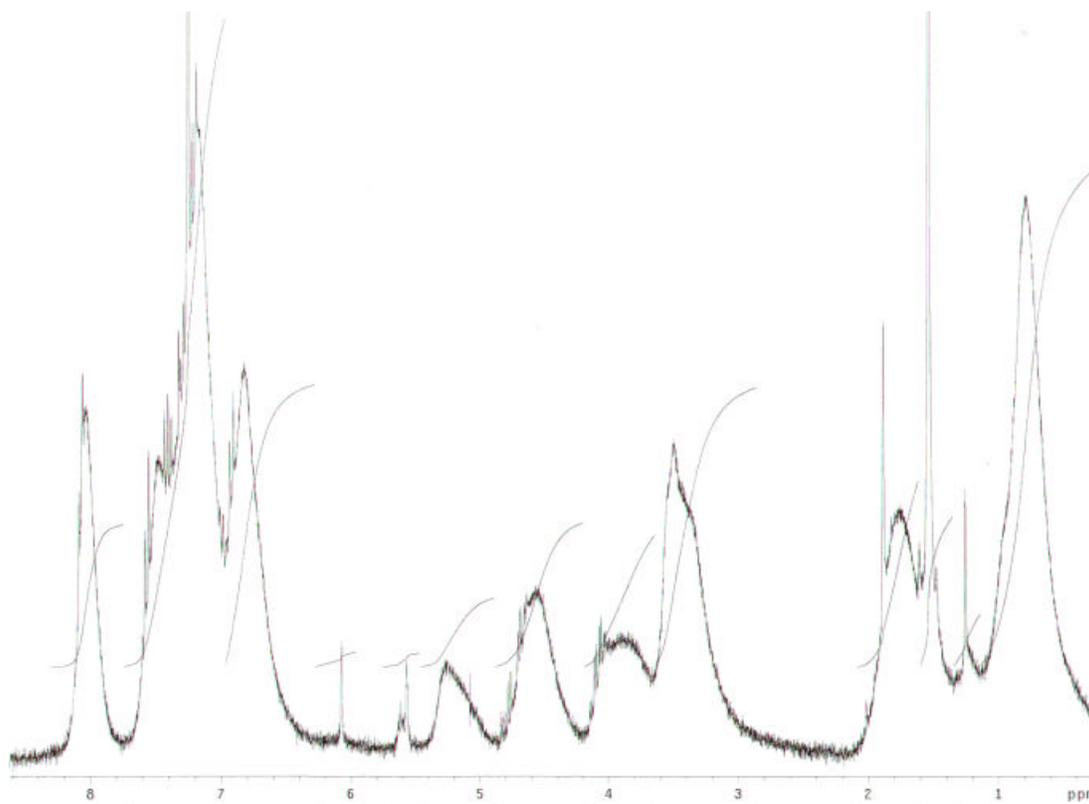


2 Carbazole H's at 8.1 ppm  
PCPM  
Expected: 1.0 : 17.0  
Observed: 1.0 : 16.5

3 OCH<sub>3</sub> H's at 3.6 ppm  
PMMA

**Calculation:** 25 weight % PCPM/75 weight % PMMA = 8 mole % PCPM/92 mole % PMMA  
 $8 \times 2 \text{ H's (at 8.1 ppm)} = 16$        $92 \times 3 \text{ H's (at 3.6 ppm)} = 276$       Total = 292  
 Theoretical Integration Ratio:  $16/292 = 0.0548$        $276/292 = 0.945$   
 $0.0548 : 0.945 = 1 : 17$

**Figure 4.21** <sup>1</sup>H NMR of 25 Weight % PCPM/75 Weight % PMMA



5.45  
 2 Carbazole H's at 8.1 ppm  
 PCPM  
 Expected: 2.0 : 3.0  
 Observed: 2.0 : 2.9

10.68  
 3 OCH<sub>3</sub> H's at 3.6 ppm  
 PMMA

**Calculation:** 50 mole % PCPM / 50 mole % PMMA  
 50 x 2 H's (at 8.1 ppm) = 100      50 x 3H's (at 3.6 ppm) = 150      Total = 250  
 Theoretical Integration Ratio: 100/250 = 0.40      150/250 = 0.60  
 0.40 : 0.60 = 2 : 3

**Figure 4.22** <sup>1</sup>H NMR Spectrum of 50 Mole % PCPM / 50 Mole % PMMA

Transparent polymer and copolymer films were solvent cast from methylene chloride, using a 30 weight % solution, dried slowly at room temperature, then vacuum dried slightly above their respective glass transition temperatures.

The carbazole-phenoxy based methacrylate/methyl methacrylate copolymer series were very useful in showing trends in terms of refractive index and thermal degradation behavior. These copolymerizations served as a model system for the carbazole based acrylates, which use alkyl acrylates as reactive diluents.

The carbazole-phenoxy based acrylate was also polymerized in DMAC, with 1 mole % AIBN. The resulting polymer was not as easily precipitated into chilled methanol (some dissolution), and was precipitated into chilled water instead, filtered, and vacuum dried slightly above 100°C. The final polymer was a slightly amber, slightly gummy material. The carbazole-phenoxy based acrylate polymer was difficult to dissolve in common organic solvents, so was probably cross-linked or very highly branched.

Solution free radical polymerization was the best method explored for producing good, linear polymers and copolymers from the carbazole-phenoxy based methacrylate. The polymers and copolymers produced using this method had quantitative yields, and for the most part, high molecular weights with relatively low polydispersities. These polymers were analyzed for thermal properties, such as degradation temperatures and glass transition temperatures. Solvent cast films were easily produced, which could then be analyzed for physical properties such as refractive index and birefringence.

**Table 4.5** GPC Results of the Free Radical Solution Homo- and Copolymerizations of the Carbazole-Phenoxy Based Methacrylate (CPM) with Methyl Methacrylate (MMA)

<b>Polymer Composition</b>	<b><math>\langle M_n \rangle</math></b>	<b><math>\langle M_w \rangle</math></b>	<b><math>\langle M_w \rangle / \langle M_n \rangle</math></b>
100 % PCPM	58,900	195,300	3.32
75/25 mole % PCPM/PMMA	211,800	622,700	2.94
50/50 mole % PCPM/PMMA	131,200	165,100	1.26
25/75 mole % PCPM/PMMA	87,100	89,500	1.03
100 % PMMA	39,700	47,800	1.20
72/25 wt % PCPM/PMMA	165,000	186,300	1.13
50/50 wt % PCPM/PMMA	30,700	67,500	2.20
25/75 wt % PCPM/PMMA	16,800	28,500	1.70

#### 4.2.2.1 *In situ* FTIR Spectroscopy Monitoring Solution Polymerization

The free radical solution polymerizations were allowed to progress for about two hours, but from observing changes in viscosity within the polymerization flask, the polymerizations appeared to be finished much sooner. *In situ* Fourier transform infrared (FTIR) spectroscopy was then used to follow the rate of the solution free radical polymerization, at 90°C, under nitrogen, with 2 mole % AIBN, in DMAC.

Before the *in situ* FTIR experiment was performed, however, FTIR spectra was obtained for both the carbazole-phenoxy based methacrylate monomer and polymer, and for the solvent, DMAC, used in the solution polymerization. Figure 4.23 shows the FTIR spectra for these three components. A window of low absorbance in the solvent spectrum in either the 3200 to 2800  $\text{cm}^{-1}$  range, or around 817  $\text{cm}^{-1}$  was necessary in order to follow the reaction. The peak close to 2900  $\text{cm}^{-1}$  corresponds to the aliphatic C-H stretch, while the peak close to 3100  $\text{cm}^{-1}$  corresponds to the vinyl C-H stretch.<sup>251</sup> Unfortunately, the absorbance from the solvent absorbed highly in this area of the spectrum, so it was not able to be monitored during the *in situ* FTIR experiment. The area around 817  $\text{cm}^{-1}$  corresponds to the C-H wag.<sup>252</sup> Fortunately, around 817  $\text{cm}^{-1}$ , the solvent had very low absorbance. The C-H wag around 817  $\text{cm}^{-1}$  reduced in intensity as the double bonds of the methacrylate were converted to the single bonds of the polymer. This peak was used to dynamically monitor the polymerization of the carbazole-phenoxy based methacrylate. *In situ* FTIR spectroscopy allowed for the solution free radical polymerization of the carbazole-phenoxy based methacrylate to be closely monitored in real time.

The *in situ* FTIR experiment used a relatively large scale polymerization. Following the C-H acrylate wag at 817  $\text{cm}^{-1}$ , the polymerization was essentially complete, under these reaction conditions, after 35 minutes. The polymerization reaction was quantitative

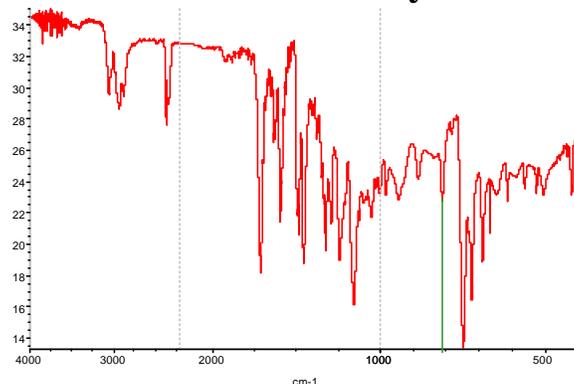
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<sup>251</sup> Pavia, D.L., Lampman, G.M., Kriz, G.S., *Introduction to Spectroscopy*, Saunders: Philadelphia, **1979**, 29.

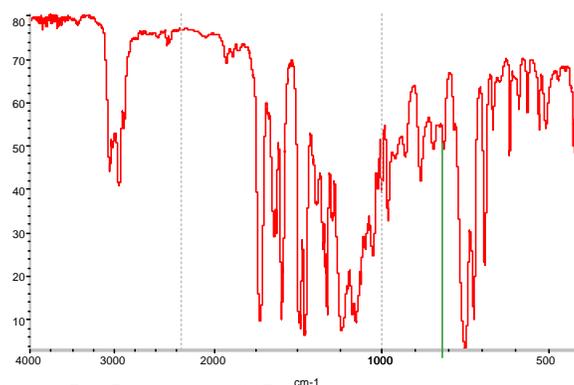
<sup>252</sup> Pavia, D.L., Lampman, G.M., Kriz, *ibid.*

(99+ % yield). Figure 4.24 shows the “waterfall” depiction, expanded around  $817\text{ cm}^{-1}$ , and Figure 4.25 follows the absorbance at  $817\text{ cm}^{-1}$  as a function of time. Figure 4.26 shows the full spectra. Using *in situ* FTIR spectroscopy, the polymerization reaction of the carbazole-phenoxy based methacrylate was unequivocally determined to be complete within a short amount of time, well within 40 minutes.

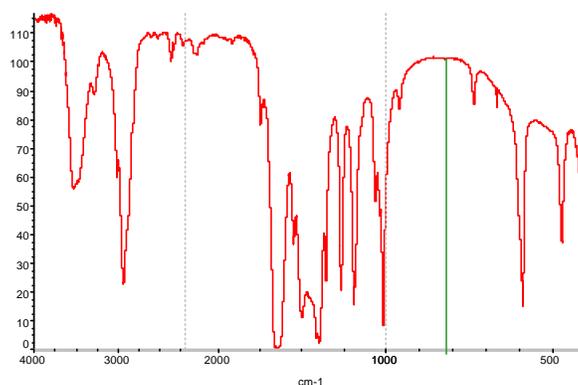
### Carbazole-Phenol Based Methacrylate



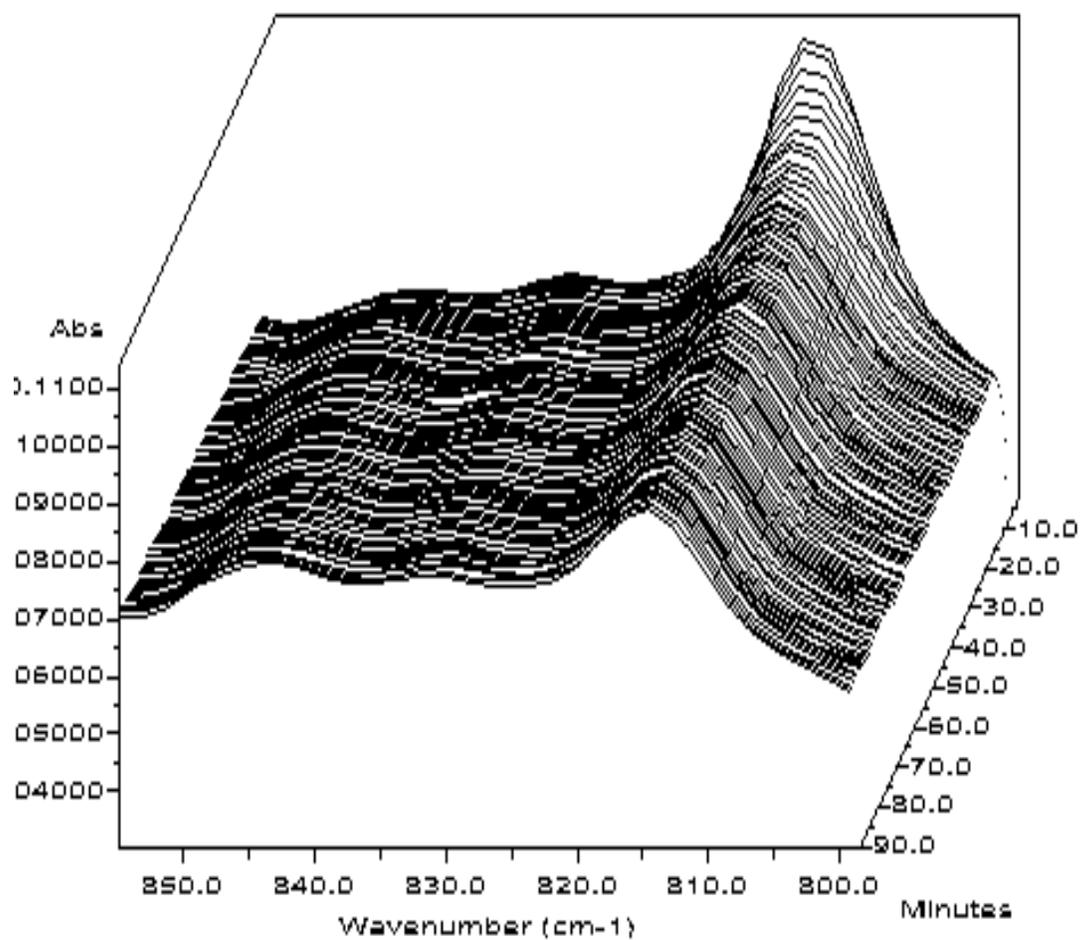
### Homopolymer of Carbazole-Phenol Based Methacrylate



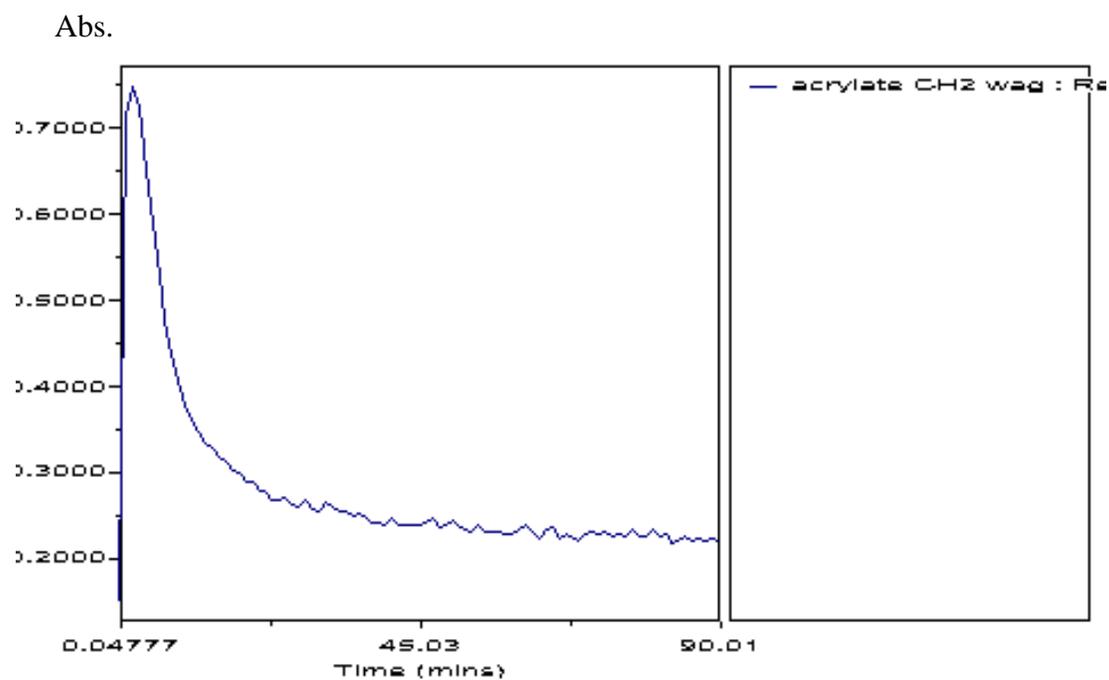
### N,N-Dimethylacetamide



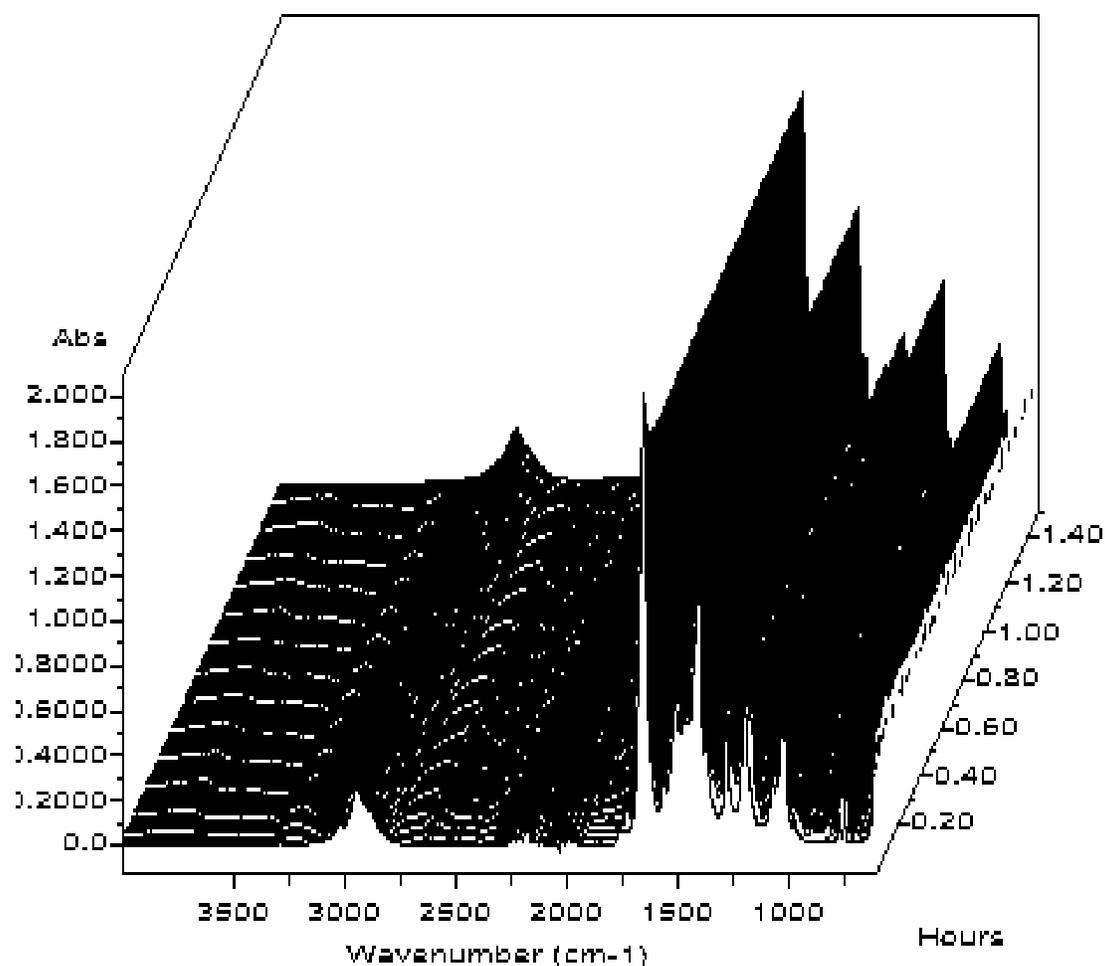
**Figure 4.23** FTIR Spectra for the Carbazole-Phenoxy Based Methacrylate Polymer, Monomer, and the Solvent DMAC



**Figure 4.24** *In situ* FTIR Experiment Following Free Radical Solution Polymerization of Carbazole-Phenoxy Based Methacrylate, Expanded around 817 (cm<sup>-1</sup>)



**Figure 4.25** *In situ* FTIR Experiment for Carbazole-Phenoxy Based Methacrylate, Following FTIR Peak at  $817\text{ (cm}^{-1}\text{)}$



**Figure 4.26** *In situ* FTIR Experiment Following Free Radical Solution Polymerization of Carbazole-Phenoxy Based Methacrylate, Full Spectra