

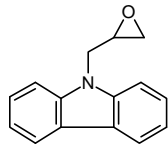
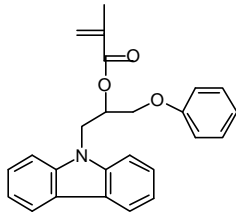
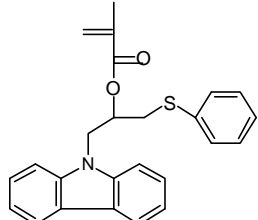
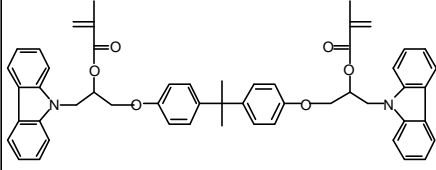
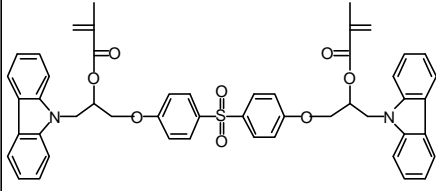
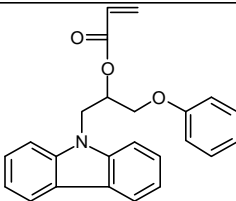
# Chapter 4

## Results and Discussion

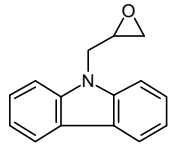
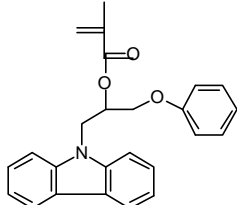
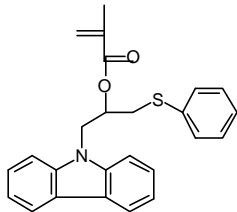
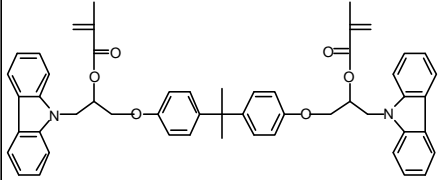
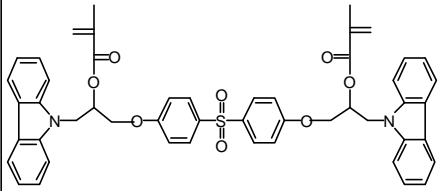
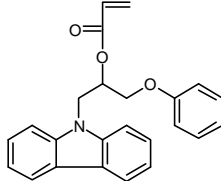
### 4.1 Monomer Syntheses

The syntheses of a family of novel, carbazole based methacrylate, dimethacrylate, and acrylate monomers, and subsequent purifications, were successful. The first intermediate, carbazole epoxide, was also included as a monomer because the 3-membered ring could potentially be ring opened to produce a linear polymer. To the carbazole epoxide, various phenols, diphenols, and thiols were reacted, followed by methacrylate or acrylate reactions. Table 4.1 summarizes the novel carbazole based monomers and their percent yields, purity HPLC or TLC, and melting point by DSC. Table 4.2 summarizes the novel carbazole based monomers and results from elemental analyses.

Of all the novel monomers synthesized, the carbazole-phenoxy based methacrylate was of most interest for several reasons. Foremost, it formed transparent films, from both solvent casting and photo-curing. Both of the carbazole-sulfur based monomers did not form transparent films. Second, under mild polymerization conditions, the carbazole-phenoxy based methacrylate produced a linear polymer, e.g., a thermoplastic rather than a cross-linked thermoset like the dimethacrylates.

Compound	Percent Yield	Purity	M.P. (°C) (DSC)
 Carbazole epoxide	85.0 %	98.7 % (HPLC)	111
 Carbazole-phenoxy methacrylate	85.2 %	98.2 % (HPLC)	92
 Carbazole-benzene thiol methacrylate	68.3 %	100 % (TLC)	114
 Carbazole-bisphenol A dimethacrylate	72.7 %	100 % (HPLC)	65
 Carbazole-sulfonyl diphenol dimethacrylate	85.2 %	100 % (TLC)	81
 Carbazole-phenoxy acrylate	56.0 %	100 % (TLC)	78

**Table 4.1** Table of Percent Yields, Purities, and Melting Points for Carbazole Based Monomers

Compound	Elemental Analysis	
	Actual	Theoretical
 Carbazole epoxide	80.12 % C 5.91 % H 6.22 % N 7.54 % O	80.72 % C 5.83 % H 6.28 % N 7.17 % O
 Carbazole-phenoxy methacrylate	77.31 % C 6.07 % H 3.57 % N 12.75 % O	77.92 % C 5.97 % H 3.65 % N 12.47 % O
 Carbazole-benzene thiol methacrylate	58.14 % C 7.27 % H 0.53 % N 31.09 % O 3.35 % S	74.81 % C 5.74 % H 3.49 % N 7.98 % O 7.98 % S
 Carbazole-bisphenol A dimethacrylate	77.86 % C 6.26 % H 3.20 % N 12.71 % O	78.52 % C 6.17 % H 3.46 % N 11.85 % O
 Carbazole-sulfonyl diphenol dimethacrylate	63.53 % C 5.26 % H 2.87 % N 16.89 % O 3.10 % S	72.11 % C 5.29 % H 3.37 % N 15.38 % O 3.85 % S
 Carbazole-phenoxy acrylate	70.92 % C 5.68 % H 3.14 % N 15.67 % O	77.62 % C 5.66 % H 3.77 % N 12.94 % O

**Table 4.2** Table of Elemental Analysis for Carbazole Based Monomers

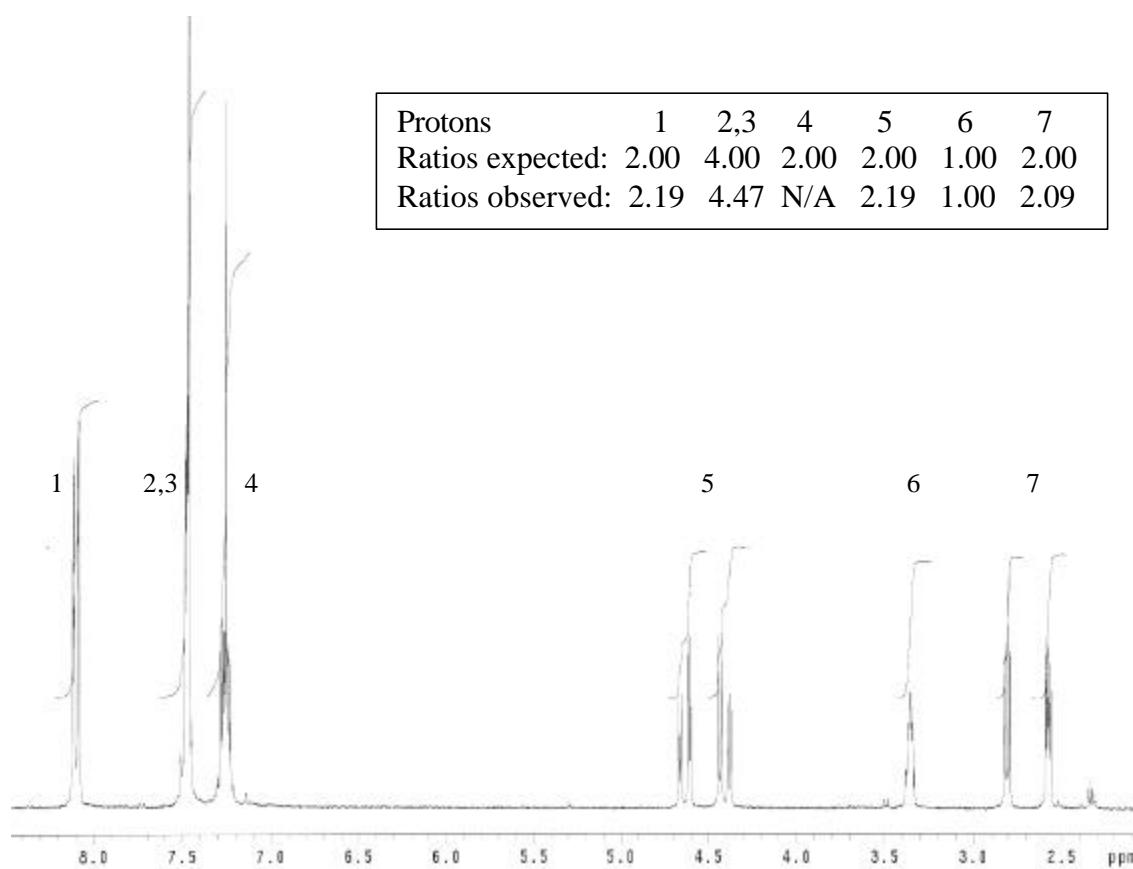
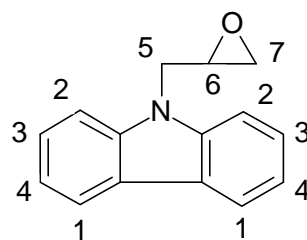
#### 4.1.1 Carbazole Epoxide

9-(2,3-epoxypropyl)-carbazole, also called carbazole epoxide, was the precursor for all the subsequent monomer syntheses. The carbazole epoxide was classified as a monomer because the 3-membered epoxy ring could potentially be used in ring-opening polymerizations.

To synthesize carbazole epoxide, carbazole was reacted with a 7-fold molar excess of epichlorohydrin, in the presence of a 2.5-fold molar excess of base, such as KOH, solvated in THF, and reacted under mild conditions (80°C, nitrogen), for 10 to 12 hours. The base acted as an acid trap for the hydrogen ions released from the reaction, forming water and the KCl salt. Completion of the reaction was easily monitored by TLC (25 % ether in hexane). Carbazole had an  $R_f$  of 0.47; carbazole epoxide had an  $R_f$  of 0.32. The carbazole epoxide was easily dissolved in many common organic solvents, such as acetone, ether, and methylene chloride.

$^1\text{H}$  NMR spectroscopy gave expected peaks with expected integration ratios (Figure 4.1). The peaks at 8.10, 7.49, and 7.23 ppm corresponded to the aromatic peaks of the carbazole group. The peaks between 2.5 and 5.0 ppm were from the aliphatic protons, with the protons on the strained 3-membered ring being shifted the most upfield. Figure 4.2 shows the full  $^1\text{H}$  NMR spectrum of the carbazole epoxide, and Figure 4.3 shows the  $^1\text{H}$  NMR spectrum for the spectrum of carbazole. Noteworthy was an absence of a peak in the 10 to 12 ppm region in Figure 4.2, which clearly demonstrated the loss of the proton on the carbazole nitrogen after the reaction with epichlorohydrin.

Melting point was determined using DSC at 10°C/minute from 30°C to 130°C. The carbazole epoxide had a sharp melting point of 111°C. The percent yield of the reaction was 85.0 %, with a purity of 99.7 % determined by HPLC (Figure 4.4). Elemental analysis gave excellent agreement to expected elemental ratios (Table 4.2).



**Figure 4.1**  $^1\text{H}$  NMR Spectrum of Carbazole Epoxide

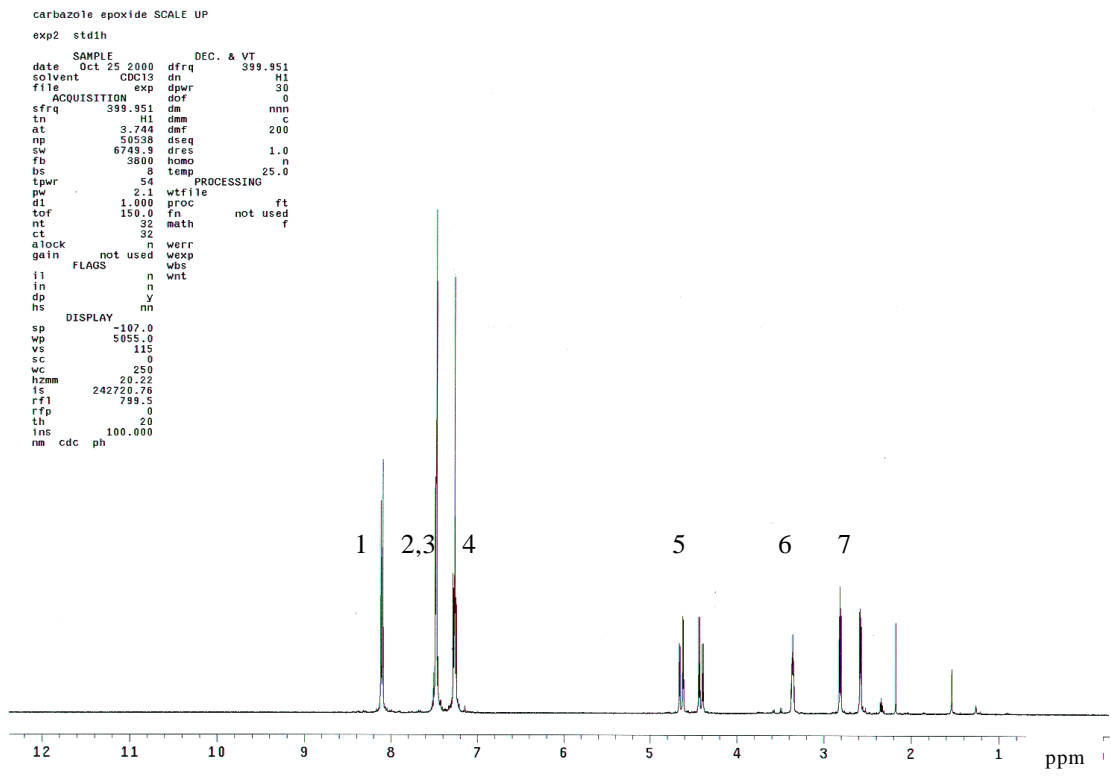
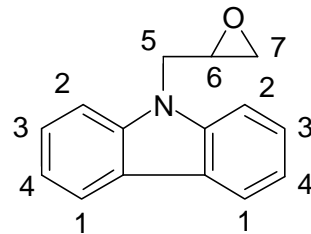


Figure 4.2 Full <sup>1</sup>H NMR Spectrum of Carbazole Epoxide

15,083-5  
Carbazole, zone refined, 99.9+%, GOLD LABEL  
M.W. 167.21 m.p. 245.74-246° b.p. 355°  
Boil. 20,433 IR 1,926G 2,1097G

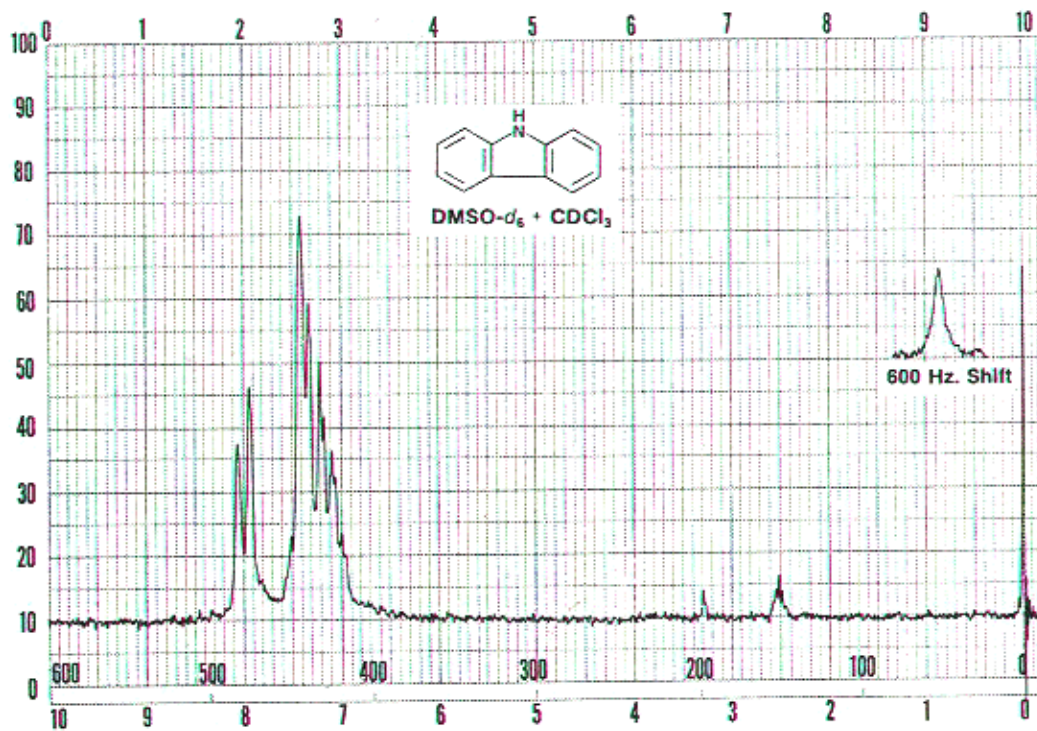
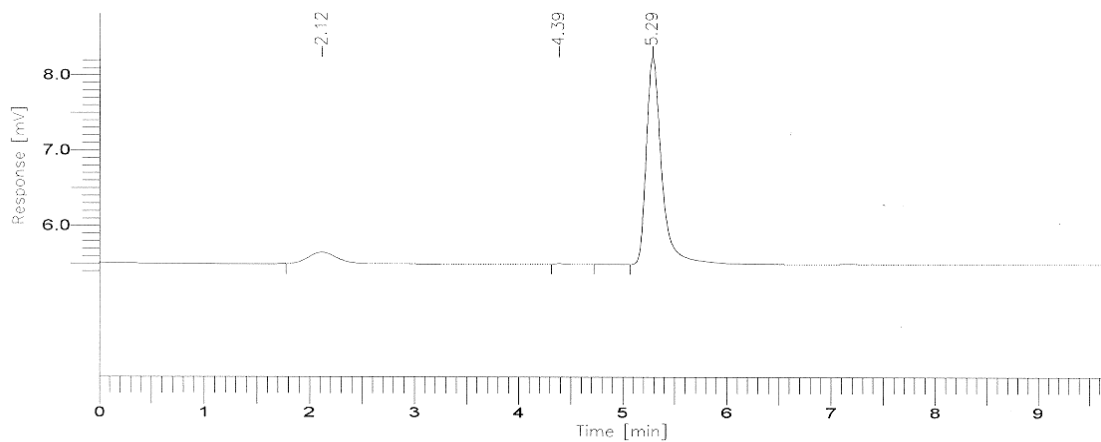


Figure 4.3 <sup>1</sup>H NMR Spectrum of Carbazole<sup>247</sup>

<sup>247</sup> Pouchert, C. J., *The Aldrich Library of NMR Spectra, Vol. 2*, Aldrich Chemical: Milwaukee, 1983, 548.

Peak #	Time [min]	Component Name	Area [ $\mu\text{V}\cdot\text{s}$ ]	Height [ $\mu\text{V}$ ]	Area [%]	Adjusted Amount
1	2.117		2929.90	154.70	9.23	0.0029
2	4.387		90.50	11.42	0.29	0.0001
3	5.288		28726.00	2751.72	90.49	0.0287
			31746.40	2917.84	100.00	0.0317



Disregarding solvent front, 0.32 % carbazole (peak #2), 99.68 % carbazole epoxide (peak #3)  
 Elution solvent = 60/40 acetonitrile/water  $\lambda_{\text{detector}} = 255 \text{ nm}$

**Figure 4.4** HPLC Chromatogram for Carbazole Epoxide

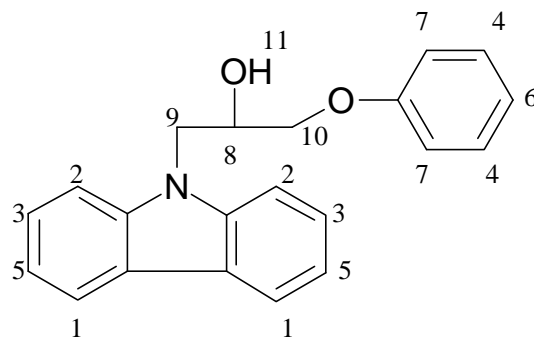


#### 4.1.2 Carbazole-Phenoxy Based Intermediate

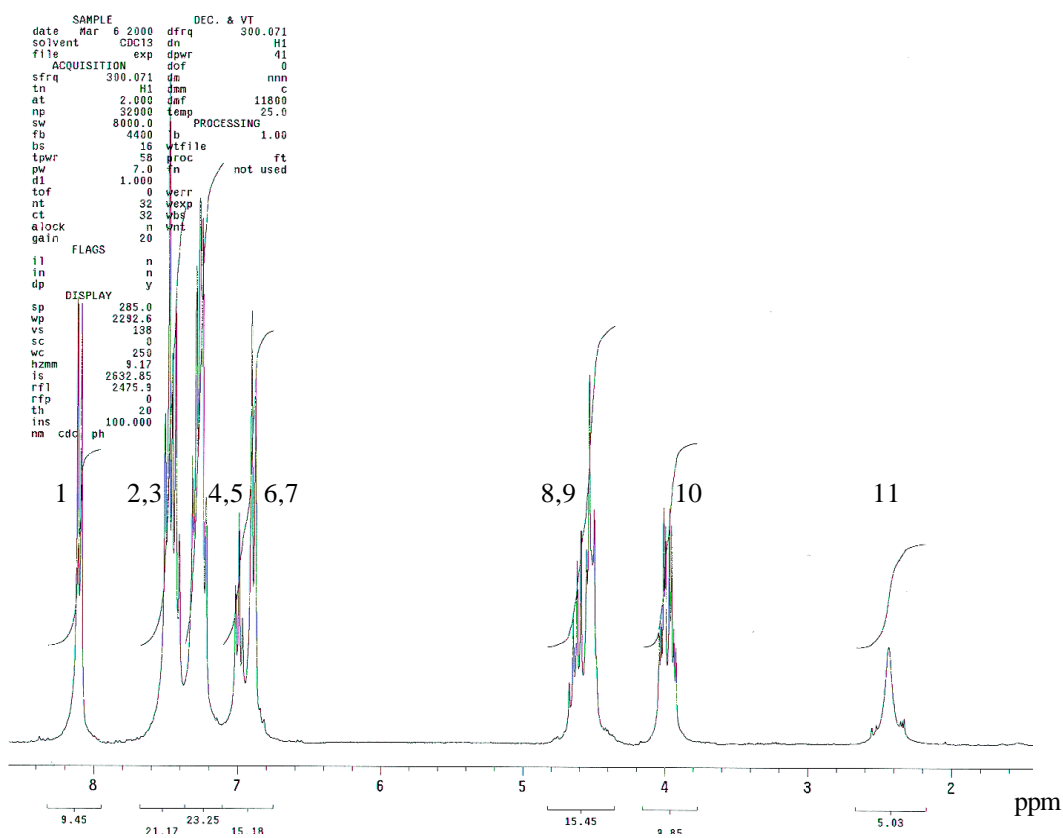
The carbazole-phenoxy based intermediate was synthesized from the carbazole epoxide. A large molar excess of phenol was reacted with the carbazole epoxide, in the presence of a catalytic amount of triphenylphosphine, neat, under nitrogen, with moderately high heating (120°C), overnight. Completion of the reaction was monitored by TLC (25 % ether in hexane). Carbazole epoxide had an  $R_f$  of 0.32, and the carbazole-phenoxy based intermediate had an  $R_f$  of 0.48.

Because phenol readily sublimates, purification was straightforward. Good vacuum with slight heating removed excess phenol. The percent yield of the reaction was high, with a 90.7 % yield. The carbazole-phenoxy intermediate, in subsequent reactions, was used to produce both the carbazole-phenoxy based methacrylate and the carbazole-phenoxy based acrylate.

$^1\text{H}$  NMR spectroscopy gave expected peaks with expected integration ratios (Figure 4.5). The peaks between 7.1 and 6.8 ppm corresponded to the aromatic phenoxy substituent. The peaks between 8.2 and 7.4 ppm corresponded to the aromatic carbazole substituent. The peak at 7.25 ppm was overlapped between both aromatic substituents. The peak at 2.44 ppm corresponded to the hydroxyl peak.



Protons	1	2,3	4,5	6,7	8,9	10	11
Ratios Expected	2 :	4 :	4 :	3 :	3 :	2 :	1
Ratios Observed	1.92:	4.30:	4.72:	3.08:	3.13:	2.00:	1.02



**Figure 4.5**  $^1\text{H}$  NMR of Carbazole-Phenoxy Based Intermediate

### 4.1.3 Carbazole-Phenoxy Based Methacrylate

The carbazole-phenoxy based methacrylate was synthesized by the methacrylate reaction with the carbazole-phenoxy based intermediate. A molar excess of either methacrylic anhydride or methacryloyl chloride was added, slowly, to the chilled, methylene chloride solution containing the carbazole-phenoxy based intermediate and triethylamine (TEA). A catalytic amount of dimethylaminopyridine (DMAP) was then added. TEA was used as an acid trap. DMAP is a well known hyper, or super, acylation catalyst.<sup>248</sup> The methacrylate reaction, particularly using methacryloyl chloride, was very exothermic. Low temperature, using an ice/NaCl salt bath, and slow addition of the methacrylating agent reduced the possibility of forming acylation by-products. The reaction was completed relatively quickly, within 3 to 4 hours. Completion of the reaction was monitored by TLC (25 % ether in hexane). The carbazole-phenoxy based methacrylate had an  $R_f$  of 0.77, which was higher than the 0.48  $R_f$  of the carbazole-phenoxy based intermediate. The enhanced mobility of the methacrylate final product compared to the intermediate product was due to the enhanced polarity of the methacrylate group, which offset the relatively small gain in molecular weight. The carbazole-phenoxy based monomer was easily dissolved in many common organic solvents, such as acetone, ether, and methylene chloride.

<sup>1</sup>H NMR spectroscopy gave expected peaks with expected integration ratios (Figure 4.6). The peaks between 8.2 and 6.8 ppm corresponded to the aromatic peaks of the carbazole and phenoxy groups. Three additional peaks at 6.08, 5.48, and 1.88 ppm corresponded to protons on the methyl methacrylate substituent. Noteworthy was the absence of a peak at 2.44 ppm, which clearly demonstrated the loss of the hydroxyl proton after the methacrylate reaction.

The pentad (peak 9) corresponded to the methine proton. The methylene protons adjacent to the carbazole group (peak 10) and adjacent to the phenoxy group (peak 11) were split, as were the doublet peaks for the vinylic protons (peaks 8,8'). The double

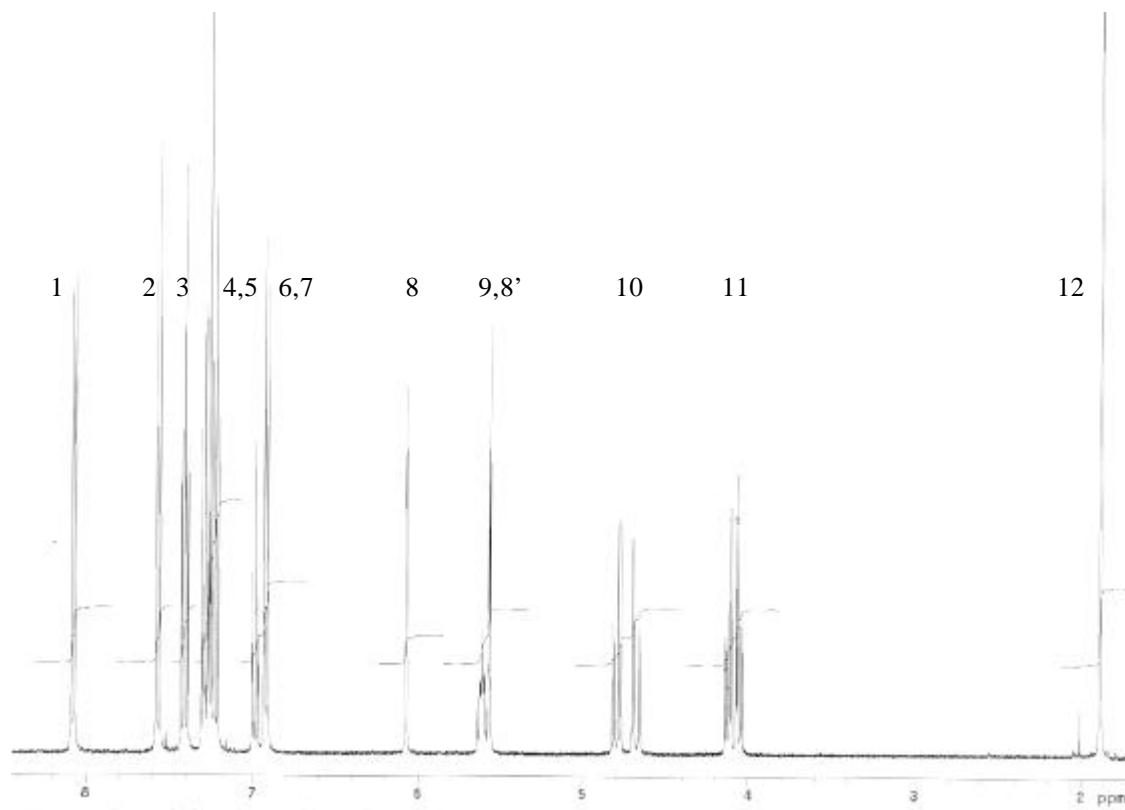
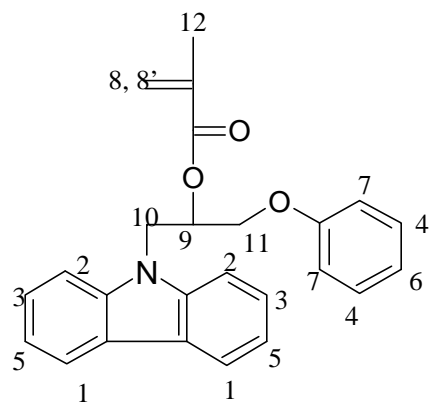
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<sup>248</sup> Scriven, E.F.V., *Chem. Soc. Rev.*, **1983**, 12(2), 129.

bond fixed the positions of the vinylic protons, thus the electronic environment for each proton was not equivalent. For the methylene protons, the steric hindrance from the two large aromatic substituents constrained the molecule, thus the electronic environment for each proton in the methylene groups was not equivalent, and signal splitting was observed.

Of interest was the spatial structure of the carbazole-phenoxy based methacrylate. Molecular modeling was explored, and discussed in section 4.5, to determine the theoretical structure of this large, aromatic, sterically hindered, constrained monomer. Spatial order of the aromatic groups within the final polymer could lead to interesting physical, electronic, and photo-electronic properties.

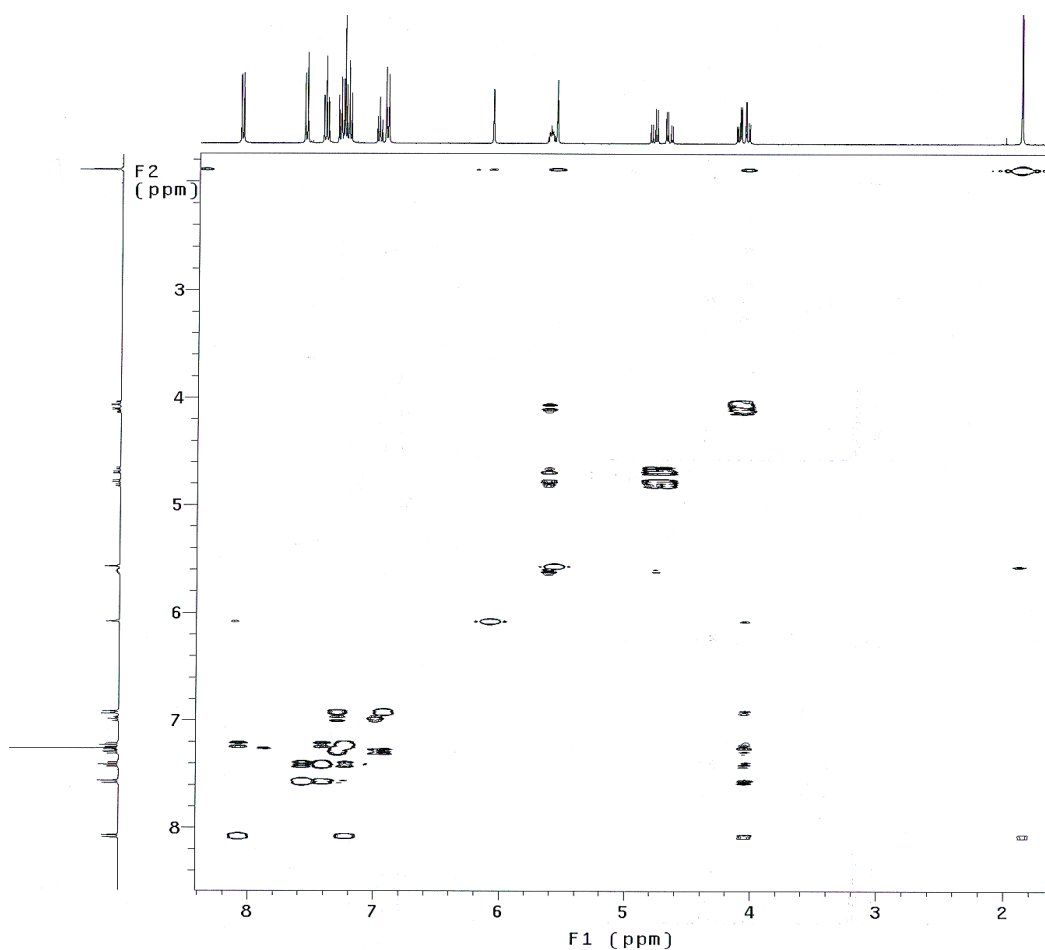
Two dimensional  $^1\text{H}$  NMR correlated spectroscopy (2D  $^1\text{H}$  NMR COSY) was used to resolve peaks in the crowded aromatic region. The 2D  $^1\text{H}$  NMR COSY spectrum is shown in Figure 4.7. An expansion of the aromatic region is shown in Figure 4.8. Using 2D  $^1\text{H}$  NMR COSY, the peaks at 8.08, 7.60, 7.42, and 7.25 ppm were definitively determined to correspond to the carbazole substituent. The peak at 7.60 ppm corresponded to the aromatic protons beta from the carbazole nitrogen, the peaks at 8.08 and 7.42 ppm corresponded to the aromatic protons delta from the nitrogen, and the peak at 7.25 ppm corresponded to the aromatic protons gamma from the carbazole nitrogen. Likewise, the peaks at 7.30, 6.94, and 6.89 ppm were definitively determined to correspond to the phenoxy substituent. The peak at 7.30 ppm corresponded to the meta protons, the peak at 6.94 ppm corresponded to the para proton, and the peak at 6.89 ppm corresponded to the ortho protons of the phenoxy substituent. Two dimensional correlated NMR spectroscopy was extremely useful for determining peak assignments from the complicated  $^1\text{H}$  NMR spectrum of the carbazole-phenoxy based methacrylate.



Ratios observed:	2.10	2.03	2.03	5.86	2.95	1.00	2.00	1.99	1.98	2.80
Ratios expected:	2.00	2.00	2.00	4.00	3.00	1.00	2.00	2.00	2.00	3.00

**Figure 4.6**  $^1\text{H}$  NMR Spectrum of the Carbazole-Phenoxy Based Methacrylate

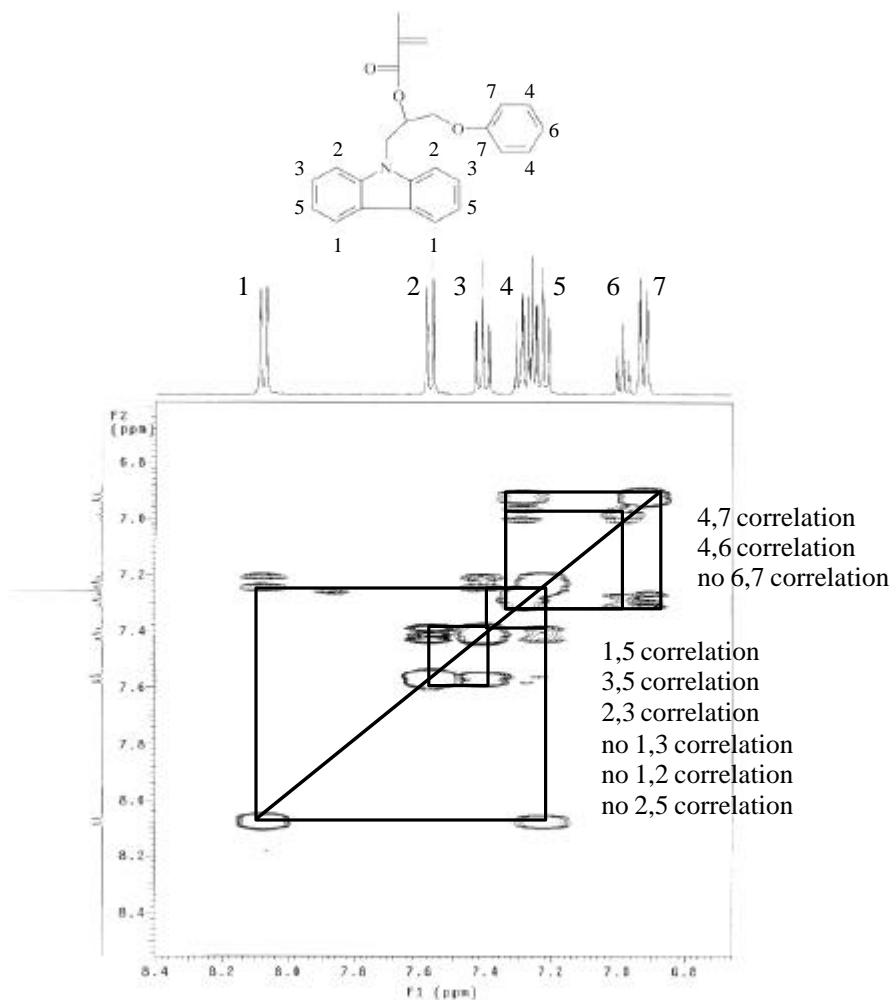
The peaks in Figure 4.8 were also clarified using the “ $n + 1$  rule”, where  $n$  is the number of equivalent protons on the carbon atoms next to the one to which it is bonded, and its resonance peak is split into  $(n + 1)$  components.<sup>249</sup> The peak at 8.08 ppm (peak 1) was a doublet; it had only one proton an adjacent carbon. The same was true for the doublet peak at 7.60 ppm (peak 2). The peak at 7.42 ppm (peak 3) was a triplet; it had two protons on adjacent carbons. The same was true for peak 4, of the phenoxy group, peak 5, of the carbazole group, and peak 6, of the phenoxy group. The peak at 6.89 ppm (peak 7) was a doublet; the equivalent ortho protons of the phenoxy group each had only one proton on the adjacent meta carbon.



**Figure 4.7** 2D  $^1\text{H}$  NMR COSY Spectrum of the Carbazole-Phenoxy Based Methacrylate

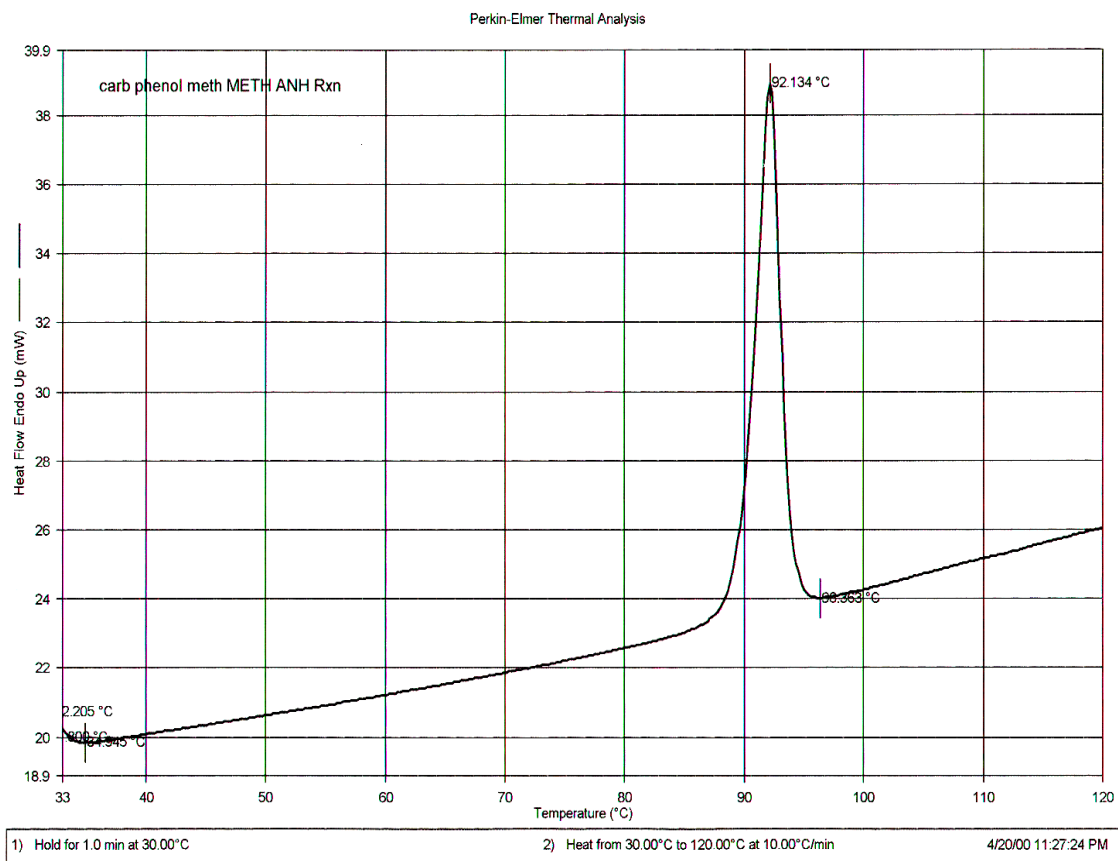
<sup>249</sup> Pavia, D.L., Lampman, G.M., Kriz, G.S., *Introduction to Spectroscopy*, Saunders: Philadelphia, 1979, 100.

## Expanded 2-D COSY $^1\text{H}$ NMR of Carbazole-Phenol Based Methacrylate



**Figure 4.8** 2D  $^1\text{H}$  NMR COSY Spectrum of the Carbazole-Phenoxy Based Methacrylate, Expansion of the Aromatic Region

Melting point was determined using DSC at 10°C/minute from 30°C to 120°C. The carbazole-phenoxy based methacrylate had a sharp melting point of 92°C (Figure 4.9). The monomer was a white, powdery solid (no tack) that was easy to pour, weigh, and manipulate. This ease of handling may prove useful commercially.



**Figure 4.9** DSC Melting Behavior of the Carbazole-Phenoxy Based Methacrylate