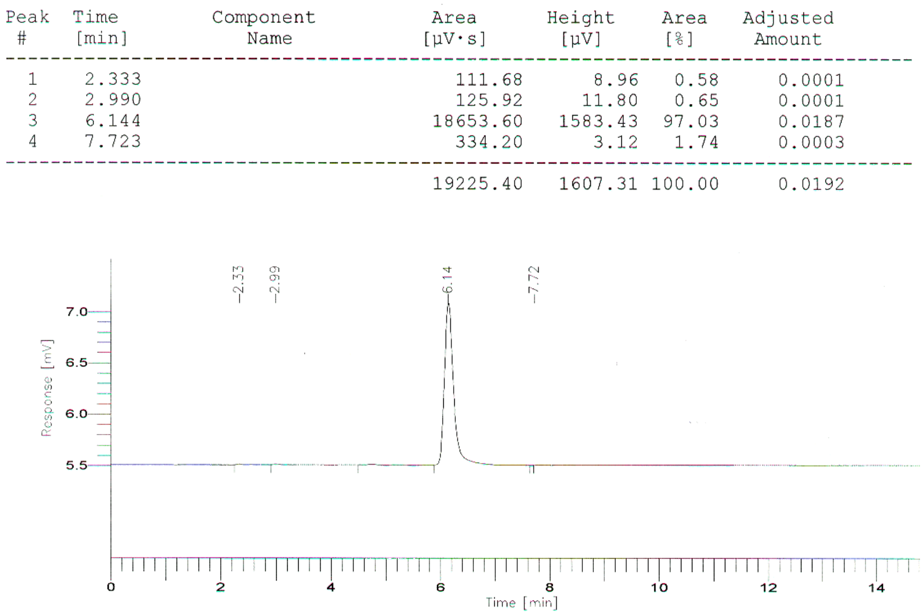
The percent yield of the methacrylation was 85.2 %, with a purity of 98.2 % determined by HPLC (Figure 4.10). Elemental analysis gave excellent agreement to expected elemental ratios (Table 4.2).



```
Peak  Time          Component          Area       Height    Area   Adjusted
 #    [min]           Name            [µV·s]      [µV]      [%]     Amount
----------------------------------------------------------------------------
  1    2.333                           111.68       8.96    0.58     0.0001
  2    2.990                           125.92      11.80    0.65     0.0001
  3    6.144                         18653.60    1583.43   97.03     0.0187
  4    7.723                           334.20       3.12    1.74     0.0003
----------------------------------------------------------------------------
                                     19225.40    1607.31  100.00     0.0192
```

Disregarding solvent front, 98.24 % peak # 3, 1.76 % peak #4
Elution solvent = 80/20 acetonitrile/water $\lambda_{detector}$ = 255 nm

Figure 4.10 HPLC Chromatogram of the Carbazole-Phenoxy Based Methacrylate

The ultraviolet (UV) spectrum between 200 and 400 nm for the carbazole-phenoxy based methacrylate in shown in Figure 4.11. Of concern in any photo-polymerization is whether the material itself absorbs light energy, which would in effect block the polymerization. This type of phenomena often produces an undesirable “skin” type effect, where the topmost layer of a material is photo-cured, and underlying layers remain uncured. Photo-polymerization of the novel carbazole based monomers used a medium wavelength Xenon UV light source, broadly centered around 305 nm. Fortuitously, above 300 nm, the carbazole-phenoxy based methacrylate had a very low absorbance. The absorbance at lower UV wavelengths, however, was substantial. For this monomer, photo-polymerizations conducted at UV wavelengths below 300 nm would be problematic.

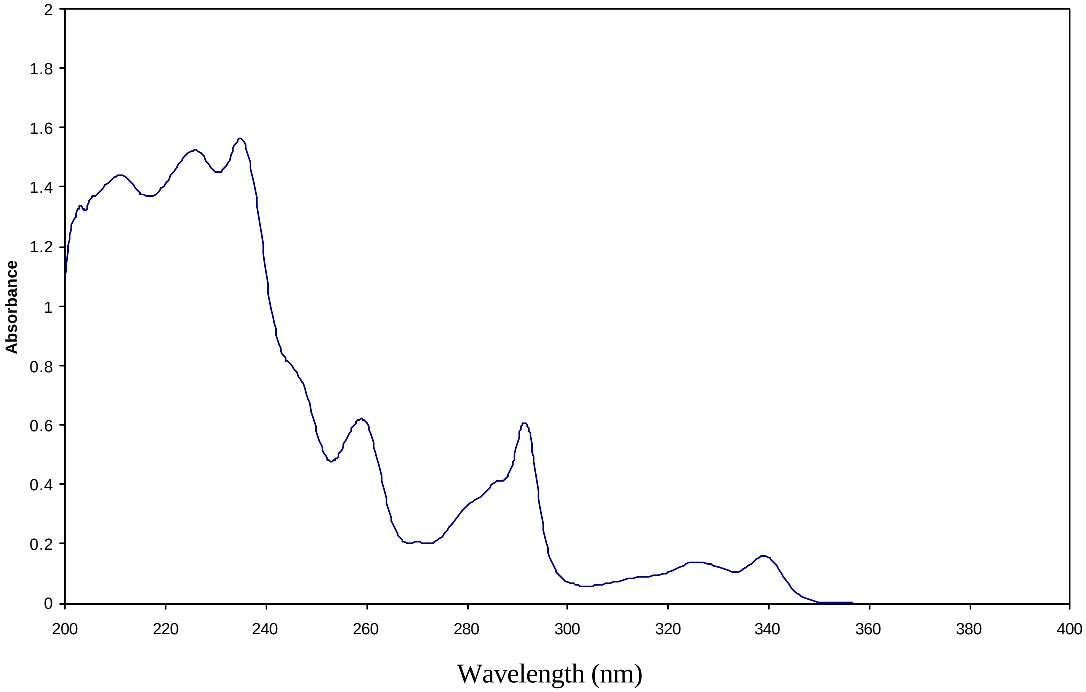


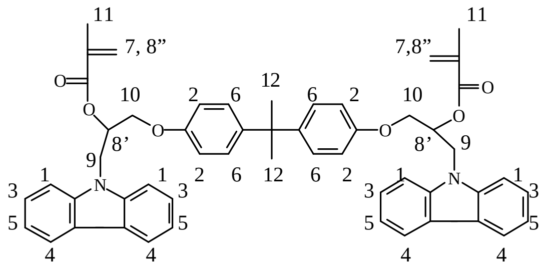
Figure 4.11 UV Spectrum of the Carbazole-Phenoxy Based Methacrylate

The carbazole-phenoxy based methacrylate was studied the most extensively, primarily because it could be polymerized to form a linear polymer. It could also be used as a reactive diluent when copolymerized with novel dimethacrylates. By copolymerizing with methyl methacrylate (as a reactive diluent), the carbazole-phenoxy based methacrylate served as a model for functionalized acrylate type polymerizations where reactive acrylates are used as diluents. The carbazole-phenoxy based methacrylate was polymerized and copolymerized using a wide variety of polymerization techniques.

4.1.4 Carbazole-Bisphenol A Based Dimethacrylate

The carbazole-bisphenol A based dimethacrylate was used to produce cross-linked networks. To form the intermediate, an exact molar ratio of 2 moles carbazole epoxide to 1 mole bisphenol A was reacted, neat, in the presence of a catalytic amount of triphenylphosphine. A 94.9 % yield was obtained for the intermediate. The intermediate was reacted with a 3-fold molar excess of methacrylic anhydride and TEA, with a catalytic amount of DMAP. Completion of the reaction was monitored using TLC (25 % ether in hexane). The carbazole –bisphenol based intermediate had an R_f of 0.09; the carbazole-bisphenol A based dimethacrylate had an R_f of 0.31. The percent yield for the methacrylation reaction was 72.7 %. The carbazole-bisphenol A based dimethacrylate was soluble in many common organic solvents, such as acetone, ether, and methylene chloride, though it was not as readily soluble as the analogous methacrylate.

^{1}H NMR spectroscopy gave expected peaks with expected integration ratios for the carbazole-bisphenol A based dimethacrylate (Figure 4.12). The peaks at 8.08, 7.39, 7.22, and 7.12 ppm corresponded to the aromatic carbazole substituents. The peaks at 7.55, 6.81, and 1.62 ppm corresponded to the bisphenol A substituent. The peaks at 6.05, 5.52 and 1.88 ppm corresponded to the methyl methacrylate substituents. The absence of a peak from 2.5 to 3.5 ppm demonstrated the loss of the hydroxyl proton of the intermediate after the methacrylation reaction.



Protons:	1	2	3	4	5	6	7	8	9	10	11	12
Ratios expected:	2.00	2.00	2.00	2.00	2.00	2.00	1.00	2.00	2.00	2.00	3.00	3.00
Ratios observed:	1.75	1.65	1.95	N/A	2.11	2.15	1.00	2.00	2.06	1.88	2.76	3.51

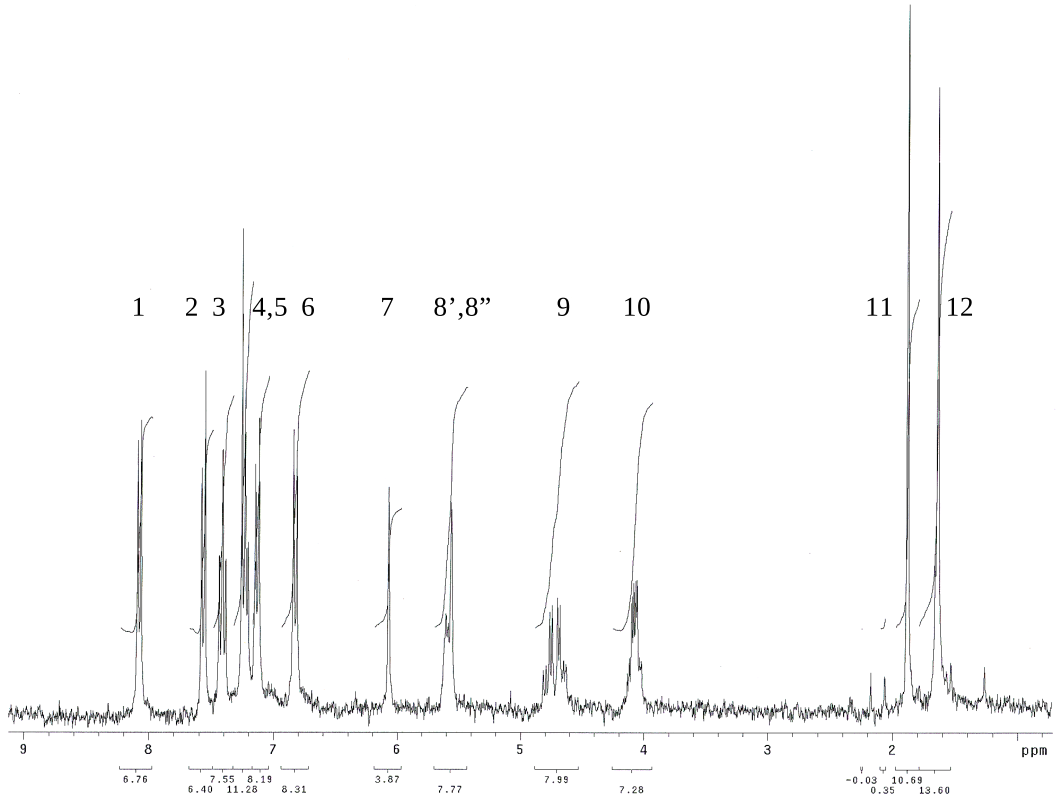


Figure 4.12 ^{1}H NMR Spectrum of the Carbazole-Bisphenol A Based Dimethacrylate

The purity was 100 % determined by HPLC. Elemental analysis gave excellent agreement to expected elemental ratios (Table 4.2). Melting point was determined using DSC at 10°C/minute from 30°C to 150°C (Figure 4.13). The carbazole-bisphenol A based dimethacrylate had a sharp melting point of 65°C. All of the novel dimethacrylates had lower melting points than their analogous methacrylate.

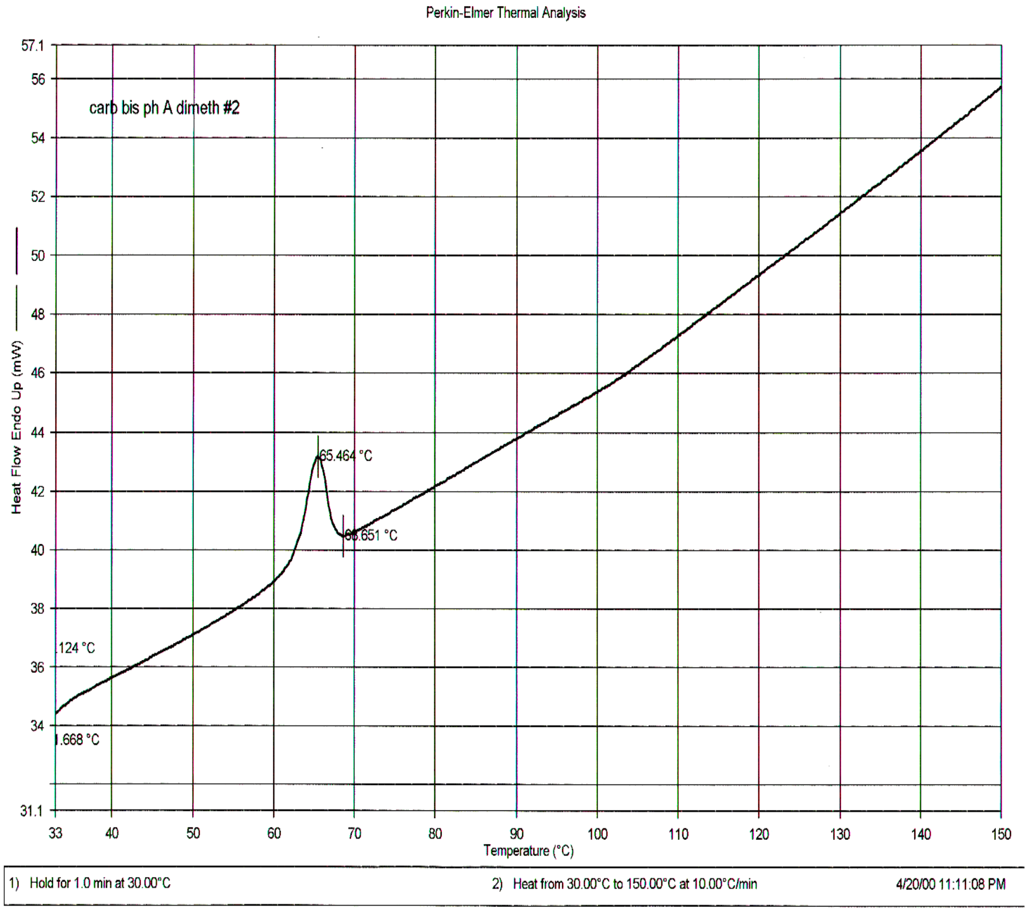


Figure 4.13 DSC Melting Behavior of Carbazole-Bisphenol A Based Dimethacrylate

The carbazole-bisphenol A based dimethacrylate had a functionality of four ($f = 4$), while the carbazole-phenoxy based methacrylate had a functionality of two ($f = 2$). The carbazole-bisphenol A based dimethacrylate was used to produce highly cross-linked networks as a homopolymer. Less cross-linked materials were obtained by copolymerizing the carbazole-bisphenol based dimethacrylate with the carbazole-phenoxy based methacrylate.

4.1.5 Carbazole-Benzene Thiol Based Methacrylate

The carbazole-benzene thiol based methacrylate was produced using synthetic methods similar to carbazole-phenoxy based methacrylate, with careful consideration and handling due to the volatility and stench of the benzene thiol. Completion of the reactions was monitored using TLC (25 % acetone in hexane). The intermediate had an R_f of 0.47; the carbazole-benzene thiol based methacrylate had an R_f of 0.55. The percent yield for the methacrylation reaction was 68.5 %.

The carbazole-benzene thiol based methacrylate was a white, powdery material that was insoluble in all common solvents. Because of lack of solubility, the monomer was not able to be recrystallized, so was precipitated into methanol instead. Neither HPLC nor NMR spectroscopy were able to be used.

Melting point was determined using DSC at 10°C/minute from 30°C to 200°C. The carbazole-benzene thiol based methacrylate had a melting point of 114°C. The melting point was much higher for the carbazole-benzene thiol based methacrylate than for the analogous carbazole-phenoxy based methacrylate. This was due to the much larger sulfur in the benzene thiol group compared to the analogous oxygen in the phenoxy group. Elemental analysis gave good agreement to the expected elemental ratios (Table 4.2).

The carbazole-benzene thiol based methacrylate, when polymerized, formed opaque white films. Copolymerization with methyl methacrylate also produced opaque white films.

4.1.6 Carbazole-4,4'-Sulfonyldiphenol Based Dimethacrylate

The carbazole-4,4'-sulfonyldiphenol based dimethacrylate was produced using synthetic methods similar to the carbazole-bisphenol A based dimethacrylate. Completion of the reactions was monitored by TLC (25 % acetone in hexane). The intermediate had a R_f of 0.16; the carbazole-sulfonyldiphenol based dimethacrylate had an R_f of 0.31. The percent yield for the methacrylation reaction was 85.2 %.

Like the carbazole-benzene thiol based methacrylate, the carbazole-sulfonyldiphenol based dimethacrylate was a white, powdery material that was insoluble in all common solvents. This monomer was not able to be recrystallized, so was precipitated into methanol instead. Neither HPLC nor NMR spectroscopy was able to be used.

Melting point was determined using DSC at 10°C/minute from 30°C to 200°C. The carbazole-sulfonyldiphenol based dimethacrylate had a melting point of 81°C. The melting point of the carbazole-sulfonyldiphenol based dimethacrylate was higher than the melting point of the analogous carbazole-bisphenol A based dimethacrylate. This was due to the rigid sulfur and oxygen containing sulfonyl group at the central position rather than the aliphatic dimethyl group of the bisphenol A. Elemental analysis gave good agreement to expected elemental ratios (Table 4.2).

The carbazole-sulfonyl diphenol based dimethacrylate, when polymerized, formed opaque white films.

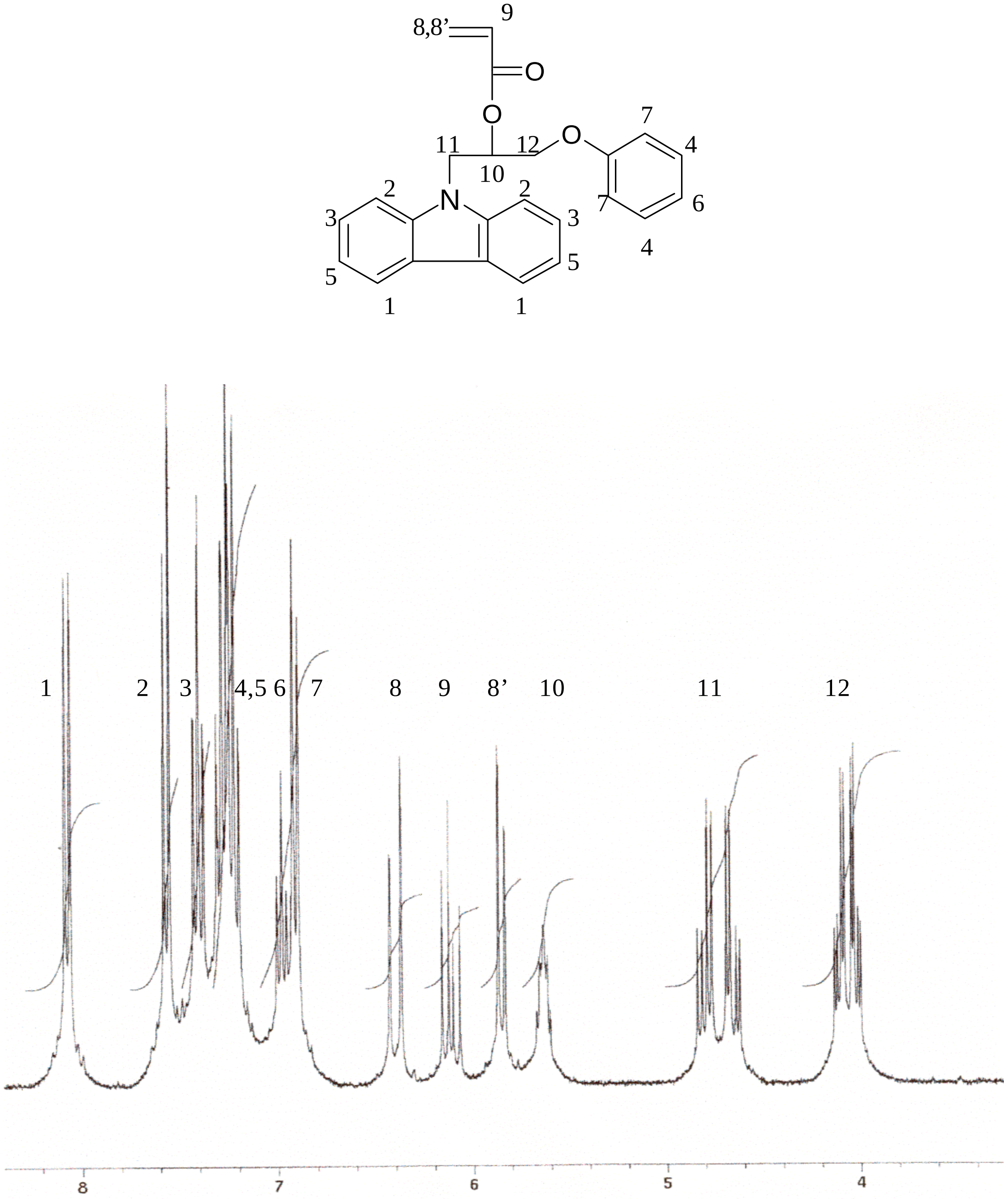
4.1.7 Carbazole-Phenoxy Based Acrylate

Acryloyl chloride was reacted with the carbazole-phenoxy based intermediate to synthesize the carbazole-phenoxy based acrylate, using the same ratios and reaction conditions as the analogous reaction with methacyloyl chloride or methacrylic anhydride. Completion of the reaction was monitored using TLC (25 % ether in hexane). The carbazole-phenoxy based acrylate had an R_f of 0.86, compared to the intermediate with an R_f of 0.48. The enhanced mobility of the acrylated final product, compared to the intermediate product, was due to the enhanced polarity of the acrylate group, which offset the relatively small gain in molecular weight. As expected, the mobility was greater for the acrylate than for the analogous methacrylate. The carbazole-phenoxy based acrylate was soluble in many common organic solvents, such as acetone, ether, and methylene chloride.

The percent yield for the acrylation product was 56.0 %. Purification involved recrystallization from methanol/water (50/50). This monomer was more soluble in methanol than the carbazole-phenoxy based methacrylate, which accounted for loss and lower yield. Elemental analysis gave good agreement to expected elemental ratios (Table 4.2).

^{1}H NMR spectroscopy afforded expected peaks with expected integration ratios for the carbazole-phenoxy based acrylate (Figure 4.14). For example, the peaks at 8.08, 7.57, 7.40, and 7.23 ppm corresponded to the aromatic carbazole substituent, and the peaks at 7.33, 6.99, and 6.86 ppm corresponded to the phenoxy substituent. The peaks between 5.7 and 6.6 ppm corresponded to the acrylate substituent. The pentad at 5.62 ppm corresponded to the methine proton. The methylene protons adjacent to the carbazole group (peak 11) and adjacent to the phenoxy group (peak 12) were split, as were the doublet peaks for the vinylic protons (peaks 8,8’). In the case of the vinylic protons, the double bond constrained these protons, thus the electronic environment for each proton was not equivalent. For the methylene protons, 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.

Melting point was determined using DSC at 10°C/minute from 30°C to 120°C. The carbazole-phenoxy based acrylate had a melting point of 78°C, which was lower than the 92°C melting point of the carbazole-phenoxy based methacrylate. The acrylate monomer was a white, slightly gummy solid. Due to its tack, it was more difficult to manipulate than the analogous methacrylate. The carbazole-phenoxy based acrylate, like the carbazole-phenoxy based methacrylate, also had a functionality of two ($f = 2$), and was able to form linear polymers.



Ratios expected:
2.00 2.00 2.00 4.00 3.00 1.00 1.00 1.00 1.00 2.00 2.00
Ratios observed:
1.84 2.09 2.45 N/A 3.32 0.93 0.78 1.07 1.07 2.27 2.30

Figure 4.14 ^{1}H NMR Spectrum of the Carbazole-Phenoxy Based Acrylate