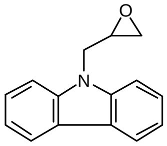
Chapter 5

Conclusions and Future Studies

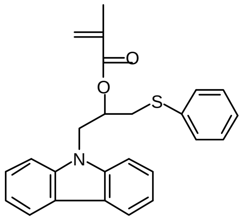
A family of novel, highly aromatic, carbazole based methacrylates, dimethacrylates, and acrylates was readily synthesized using a three step reaction mechanism. First carbazole epoxide (9-(2,3-epoxypropyl)-carbazole), the precursor for all of the subsequent reactions, was synthesized by reacting carbazole with an excess of epichlorohydrin in the presence of base, such as potassium hydroxide. The nitrogen of the carbazole nucleophilically attacked and ring-opened the epichlorohydrin. The alkoxide oxygen of the epichlorohydrin subsequently attacked, via a S_N2 reaction, the adjacent carbon atom, reforming the 3-membered epoxy ring. The base served as an acid trap for the reaction, forming water and the potassium chloride salt.

In the second step, the carbazole epoxide was reacted with a phenol, aromatic diol, or aromatic thiol. The oxygen or sulfur of the alcohol or thiol nucleophilically attacked and ring-opened the epoxy ring, producing a secondary alcohol or thiol. In the final step, the carbazole based intermediate was reacted with methacryloyl chloride or preferentially, methacrylic anhydride, to produce highly functionalized carbazole based methacrylates and dimethacrylates. For an acrylate product, the carbazole-phenoxy based intermediate was reacted with acryloyl chloride, to produce a novel carbazole based acrylate.

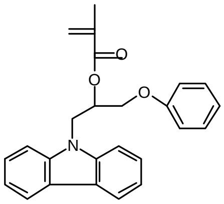
The structures of all the synthesized carbazole based monomers and their melting points are shown in Figure 5.1. The carbazole epoxide itself was considered a monomer because the 3-membered epoxy ring could conceivably be ring-opened to form polymer. Molecular modeling was used to explore the theoretical three dimensional structure of ring-opened carbazole epoxide. DSC was used to determine the melting point of each monomer. ^{1}H NMR was performed on all of the monomers and selected intermediates, with expected peaks and integration ratios. Two dimensional ^{1}H NMR was performed on the carbazole-phenoxy based methacrylate, which was extremely useful for determining peak assignments, particularly in the crowded aromatic region. HPLC was performed on the carbazole epoxide (98.7 % pure), the carbazole-phenoxy based methacrylate (98.2 % pure), and the carbazole-bisphenol A based dimethacrylate (100 % pure). Elemental analysis was performed on all of the novel carbazole based monomers, with good to excellent agreement with atomic composition.



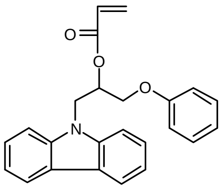
Carbazole Epoxide
m.p. = 111°C



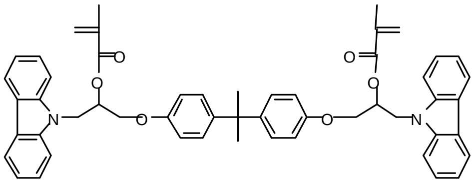
Carbazole-Benzene Thiol Based Methacrylate
m.p. = 114°C



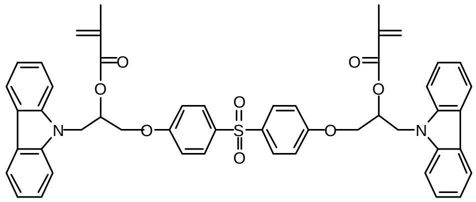
Carbazole-Phenoxy Based Methacrylate
m.p. = 92°C



Carbazole-Phenoxy Based Acrylate
m.p. = 78°C



Carbazole-bisphenol A Based Dimethacrylate m.p. = 65°C



Carbazole-Sulfonyl Diphenol Based Dimethacrylate m.p. = 81°C

Figure 5.1 Novel Carbazole Based Monomers and Melting Points

Transparent films were produced from homopolymers and copolymers of the carbazole-phenoxy based methacrylate and the carbazole-bisphenol A based dimethacrylate using photopolymerization. Transparent films of homopolymers and copolymers of the carbazole-phenoxy based methacrylate and methyl methacrylate were produced using both photopolymerization and solution polymerization. These copolymerizations served as a model system for the carbazole based acrylates, which use smaller acrylates as reactive diluents, in an analogous fashion as the methyl methacrylate was used for the carbazole-phenoxy based methacrylate. Opaque, rather than transparent films, were produced from both of the carbazole-sulfur based monomers. Lack of solubility, or solvent resistance, was an issue with the sulfur containing monomers.

The carbazole-phenoxy based methacrylate was investigated the most, because of its ability to form linear polymers, and its ability to readily produce good transparent films from both photocuring and from solvent casting. This monomer was polymerized using photopolymerization, free radical solution polymerization, free radical polymerization in the melt, and modified suspension polymerization. Photopolymerization and melt polymerization produced insoluble materials. The modified suspension polymerization produced a material with a very high molecular weight, $<M_n>$ = 158,500 g/mole, and a high polydispersity of 8.13. When polymerized under vigorous reaction conditions, cross-linking and branching apparently occurred. Free radicals probably occurred at the methine position of the carbazole-phenoxy based methacrylate, which in effect, gave this monomer a functionality of four at higher temperatures, leading to branching and cross-linking. Under the milder reaction conditions of the solution polymerization, carbazole-phenoxy based methacrylate polymers were produced with number average molecular weights, in the range of 14,900 g/mole to 58,900 g/mole, and low polydispersities, in the range of 3.16 to 3.32.

The heat of photopolymerization (ΔH_p) for the carbazole-phenoxy based methacrylate was determined using photoDSC. This rapid exotherm was monitored using a DSC equipped with a xenon UV lamp and an double beam photocalorimetric accessory. The ΔH_p was determined to be –39.4 kJ/mole, after correcting for the absorbence from the carbazole functionality. This compared to a ΔH_p of -54.8 kJ/mole for PMMA The extent of polymerization, E_p, for the carbazole-phenoxy based methacrylate was 72 %.

The free radical solution polymerization of the carbazole-phenoxy based methacrylate was monitored at 90°C using an ASI-FTIR ReactIR™. The acrylate C-H wag at 817cm-1 was followed as a function of time, for a relatively large scale polymerization of the carbazole-phenoxy based methacrylate: 9 g (23 mmole) carbazole-phenoxy based methacrylate, 30 mL DMAC (30 weight % monomer), and 2 mole % AIBN. The free radical solution polymerization was complete at 35 minutes. *In situ* FTIR spectroscopy allowed for the free radical solution polymerization of the carbazole-phenoxy based methacrylate to be closely monitored in real time. This polymerization was unequivocally determined to be complete within a short period of time, well within 40 minutes.

Differential scanning calorimetry was performed on homopolymers and copolymers of the carbazole-phenoxy based methacrylate and methyl methacrylate. The thermal glass transition temperature of the carbazole-phenoxy based methacrylate was 123°C, which compared to a thermal glass transition temperature of 106°C for PMMA prepared under the same conditions. The T_g of the carbazole-phenoxy based methacrylate was well above the 100°C research goal that was needed for this material to be considered for optical applications.

Thermal gravimetric analysis was performed on the homopolymers and copolymers of the carbazole-phenoxy based methacrylate and methyl methacrylate. The carbazole-phenoxy based methacrylate homopolymer had remarkably high decomposition temperatures. The onset of thermal degradation for this polymer was 316°C, with 5 % weight loss at 359°C. This compared to an onset thermal degradation of 218°, with a 5 % weight loss at 303°C, for the PMMA prepared under the same conditions. This thermal resistance was hypothesized to be due to the lack of head-to-head linkages in the final polymer. The large steric hindrance effects from the carbazole and phenoxy substituents would be prohibitive to forming head-to-head linkages during the polymerization. This hypothesis was tested using ^{13}C NMR spectroscopy on the polymer and molecular modeling experiments.

^{13}C noise decoupled NMR spectroscopy was used to explore the structure of the carbazole-phenoxy based methacrylate polymer in comparison to PMMA. The commercial grade PMMA was found to contain 1.1 % head-to-head linkages, while the PMMA prepared in the laboratory contained 6.3 % head-to-head linkages. From the ^{13}C NMR spectrum of the carbazole-phenoxy based methacrylate polymer, no detectable head-to head linkages were observed, however, the peaks were fairly broad in this spectrum, and the signal to noise level was fairly low, which decreased the sensitivity.

To explore the structure of the carbazole-phenoxy based methacrylate more thoroughly, molecular modeling was investigated using Gaussian 98 software. Lowest ground state energy configurations were determined for head-to-tail and head-to-head linkages of the carbazole-phenoxy based methacrylate polymer. Head-to-head configurations had a much higher nuclear repulsion energy than the head-to-tail linkages. Theoretically, the head-to-head linkage for the carbazole-phenoxy based methacrylate was very unlikely, after taking into account steric hindrance, bond lengths, nuclear repulsions, and other factors. The phenoxy groups and, especially, the carbazole groups were very restricted in their spatial orientation, with little free rotation, and theoretically had a stacked configuration along the main polymer chain. This restriction in rotation of the aromatic groups is also evident from the signal splitting apparent in the ^{1}H NMR spectra of the monomer. Each methylene proton in both the methylene adjacent to the carbazole nitrogen and the methylene adjacent to the phenoxy oxygen has a different electronic environment. At the molecular level, ^{1}H NMR spectroscopy clearly showed that these aromatic functionalities are extremely restricted in terms of free rotation. The carbazole-phenoxy based methacrylate polymer, composed of only head-to-tail linkages and no head-to-head linkages, would explain why the onset of thermal degradation was so high. These polymers may also be useful in non-linear optics, electronic, and photo-electronic applications due to ring current effects from the highly ordered and oriented carbazole and phenoxy groups.

The refractive indices of the novel carbazole based methacrylates, dimethacrylates, and acrylate polymers were very high, with many of the novel polymers having refractive indices above the refractive index of 1.58 for state-of-the-art bisphenol A based poly(carbonate), and well above the refractive index of 1.49 for poly(methyl methacrylate). The refractive index of the carbazole-phenoxy based methacrylate polymer had a refractive index of 1.63. The copolymers of the carbazole-phenoxy based methacrylate and methyl methacrylate had linear trends in terms of refractive index and percent weight composition. The refractive index of the carbazole-phenoxy based acrylate polymer had a refractive index of 1.64, which was even higher than for the carbazole-phenoxy based methacrylate polymer. A higher refractive index was expected for the acrylate due to the higher carbon to hydrogen ratio compared to the methacrylate.

The carbazole-bisphenol A based dimethacrylate had a refractive index of only 1.53, which was below the refractive index of bisphenol A based poly(carbonate). The 50/50 weight percent copolymer of carbazole-bisphenol A based dimethacrylate and the carbazole-phenoxy based methacrylate had a refractive index of 1.56, which was still too low for the intended application. This 50/50 copolymer, however, was the least brittle film produced, and was difficult to manually bend or break.

Overall, these carbazole based polymers are very suited for optical applications in terms of T_g and refractive index. The thermal resistance of the carbazole-phenoxy based methacrylate polymer would be advantageous for any processing or post-processing steps.

There has been a renewed interest in poly(vinyl carbazole) for non-linear optics and holographic applications.[262,263] Poly(methyl methacrylate), among its myriad applications, is also used as a substrate in lithography[264] and microlithography.[265] The

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optical properties of the carbazole-phenoxy based methacrylate polymer, coupled with the high degradation temperatures of this material, may allow for this material to be considered in electronic, photo-electronic, lithographic, and non-linear optic applications, such as holography. A profound advantage of the carbazole-phenoxy based methacrylate compared to vinyl carbazole is the ease with which it copolymerizes with methyl methacrylate.

In conclusion, the research in developing and characterizing a new family of carbazole based methacrylate, dimethacrylate and acrylate polymers produced a fascinating class of materials. The research goals of producing novel polymers with suitably high thermal glass transition temperatures and refractive indices were accomplished. The carbazole-phenoxy based methacrylate copolymerized readily with methyl methacrylate. In addition, selected polymers were found to have very high thermal stabilities. These carbazole based materials may be used in a variety of commercial applications, including both traditional optics and non-linear optics.