Chapter 1

Introduction

1.1 Optical Spectacle Lens

Polymers and copolymers produced from aromatic based methacrylates, acrylates, and dimethacrylates are excellent materials with a wide variety of applications, such as in dentistry and optical eye wear,[1,2,3,4,5,6,7,8,9,10,11] and in fiber optics, holography, and microelectronics.[12,13] The objective of this research was to design, synthesize, and characterize high refractive (RI or *n*) index polymers and copolymers for use in the optical spectacle lenses of eyeglasses. Modern spectacle lenses are typically multi-layer composites, composed of a wide variety of materials with different properties. Figure 1.1 depicts a cut-out view of a modern multi-layer spectacle lens composite.

Layer 1, closest to the eye, is a thin coating, often anti-reflective and somewhat anti-abrasive. Layer 2, which may or may not be present, and layer 4 are composed of high

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[1] Gunduz, N., *Synthesis and Photopolymerization of Novel Dimethacrylates, M.S. Thesis*, Virginia Tech, Blacksburg, VA, **1998**.
[2] Allam, C.; Kuo, J.L.; McGrath, J.E.; Mohanty, D.K., *Macromol. Chem. Phys*., **1999**, *200(8)*, 1854.
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[10] Clarke, R.L.; Braden, M., *Biomaterials*, **1989**, *10*, 349.
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refractive index materials used for focusing power. For support, layer 3, also called the preform, is composed of a strong and ductile, yet lightweight, material such as bisphenol A polycarbonate. Layers 5 and 6 are thin coatings which provide the lens with scratch resistance, anti-reflection, and (optional) tint. The focus of this research was to synthesize and investigate improved high refractive index materials for the second and fourth layers of the depicted lens.

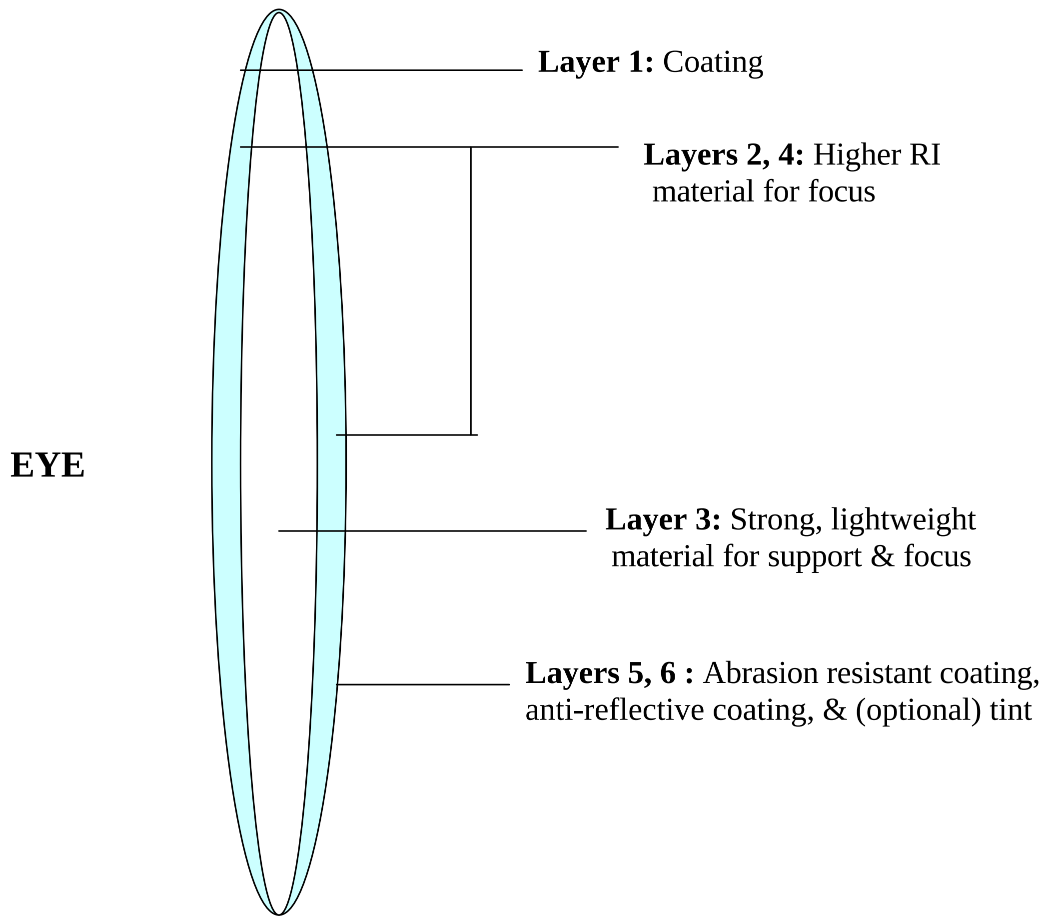

Figure 1.1 Optical Spectacle Lens Multiple-layer Composite

1.2 Polymeric Advantages for High Refractive Index Materials

Polymers offer profound advantages over traditional inorganic glass in terms of lighter weight, impact and shatter resistance, and greater focal control through higher refractive indices. Refractive index is the ratio of the speed of light in a vacuum, c_o, to the speed of light through a given medium, c. (Equation 1.1).[14] Improved polymers to be used as high refractive index materials for optical spectacle lenses should have a refractive index higher than 1.58, since that is the refractive index of state of the art bisphenol A polycarbonate.[15] The higher the refractive index attained, the more light is refracted through the lens, which increases the focusing power. Less material is needed, allowing for lighter, less expensive optical spectacles. Another desirable quality in the polymer is low chromatic aberration, which is measured in terms of the Abbe number.[16] Chromatic aberration leads to a "rainbow" effect, which is undesirable in eyeglasses. The equation for the Abbe number is shown in equation 1.2. Additionally, for a polymer to be used in an optical spectacle, the glass transition temperature (T_g) should be above 100°C. Refractive index and Abbe number are discussed further in Chapter 2.

$$n = c_o/c \qquad \textbf{Equation 1.1}$$

$$\text{Abbe Number} = \nu_e = \frac{n_e - 1}{n_{F'} - n_{C'}} \qquad \textbf{Equation 1.2}$$

where n_e = refractive index at λ_e of 546.1nm
$n_{F'}$ = refractive index at $\lambda_{F'}$ of 480.0 nm
$n_{C'}$ = refractive index at $\lambda_{C'}$ of 643.8 nm

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[14] Hofmann, C.; Zeiss, C., "Optical Materials" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1991**, *A18*, 193.
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Refractive indices are determined by the polarizabilities of the combined groups in a molecule. Contributions to the refractive indices are higher for carbon atoms than for hydrogen atoms. Since carbon atoms dominate the structure of most polymers, most common polymers have a refractive index near 1.5. Polymers with strongly electronegative substituents, such as fluorine and oxygen, will have lower refractive indices. Substituents with a high polarizability over a large atomic area, such as sulfur, phosphorus, bromine, and iodine, tend to have higher refractive indices.[17,18] Bulky conjugated or aromatic substituents, particularly hetero-aromatic substituents, such as carbazole, have high refractive indices.[19]

Carbazole based polymers have demonstrated good optical properties,[20,21] combined with ease of processing.[22,23] Polymethacrylates and polyacrylates are used commercially for many optical applications, and are easily polymerized and processed.[24,25,26] In this research, a family of novel methacrylates, acrylates, and dimethacrylates were synthesized by incorporating carbazole, along with other aromatic substituents. Subsequent polymerization provided for high refractive index materials well suited for lightweight optical spectacles.

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[17] Seferis, J.C., "Refractive Indices of Polymers" in *Polymer Handbook*, 4th ed., Brandrup, J.; Immergut, E.H.; Grulke, E.A. Eds, Wiley: New York, **1999**, *VI*, 571.
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[23] Ito, S.; Ohmori, S.; Yamamoto, M., *Macromolecules*, **1992**, *25*, 185.
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[25] Stickler, M.; Rhein, T., "Polymethacrylates" in *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., Elvers, B.; Hawkins, S.; Schultz, G. Eds., VHS: New York, **1992**, *A21*, 473.
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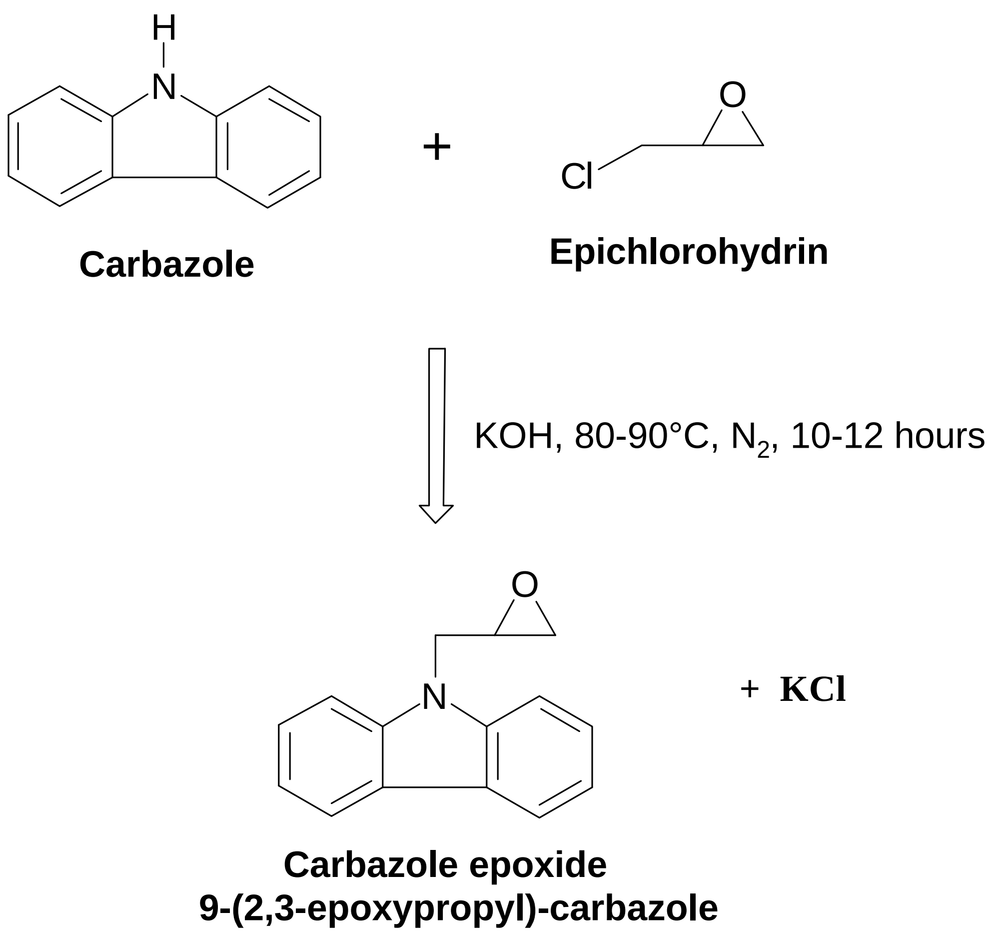
Carbazole Based Methacrylates, Acrylates, and Dimethacrylates

9-(2,3-Epoxypropyl)-carbazole, also called carbazole epoxide, was the precursor for all of the syntheses of the novel methacrylates, acrylates, and dimethacrylates. To synthesize carbazole epoxide, carbazole is reacted with a molar excess of epichlorohydrin, in the presence of a base, such as potassium hydroxide, and with moderate heat (Scheme 1.1). The nucleophilic nitrogen of the carbazole attacks and opens the ring of the epichlorohydrin. The oxygen of the epichlorohydrin subsequently attacks, via a S_N2 reaction, the adjacent chlorinated carbon atom, reforming the 3-membered epoxy ring. Chlorine is a good leaving group, and is released as a chloride anion.



Scheme 1.1 Synthesis of 9-(2,3-epoxypropyl)-Carbazole

The syntheses of novel, carbazole based methacrylates are shown in Scheme 1.2. Analogous reactions were used to produce carbazole based dimethacrylates. To produce the carbazole-phenoxy based methacrylate, an excess of phenol was added to the carbazole epoxide, and stirred, neat, with heating, in the presence of the catalyst triphenylphosphine. The nucleophilic oxygen of the phenol attacks and opens the ring of the epoxide, forming a secondary alcohol as an intermediate product. The intermediate is then reacted slowly with an excess of methacrylic anhydride or methacryloyl chloride at low temperatures, while solvated in methylene chloride, in the presence of triethylamine (TEA), and a catalytic amount of 4-dimethylaminopyridine (DMAP). DMAP is widely used as a hypernucleophilic acylation catalyst.[27]

By increasing the polarizability of substituent groups, the refractive index of the resulting polymer can be increased. By incorporating oxygen, sulfur, or sulfoxide at the X (or Y position), polymers with high refractive indices have been produced.[28,29] Incorporating carbazole into the final methacrylates and dimethacrylates was expected to increase the refractive index further.

The reaction of the intermediate alcohol with methacrylic anhydride or methacryloyl chloride eliminated any hydroxy groups in the final dimethacrylate. Hydroxy groups undergo intermolecular hydrogen bonding, which increase viscosity. The absence of hydroxy groups in the final dimethacrylate reduces viscosity, which is desirable for processing.

An analogous reaction has been performed using an excess of benzene thiol rather than phenol, to produce a novel carbazole based methacrylate with a sulfonated aromatic group (Scheme 1.2). Another analogous reaction, used to produce the carbazole based acrylate, is shown in Scheme 1.3. The carbazole based methacrylates and acrylates, with

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[28] Allam, C.; Kuo, J.L.; McGrath, J.E.; Mohanty, D.K., *Macromol. Chem. Phys.*, **1999**, *200(8)*, 1854.
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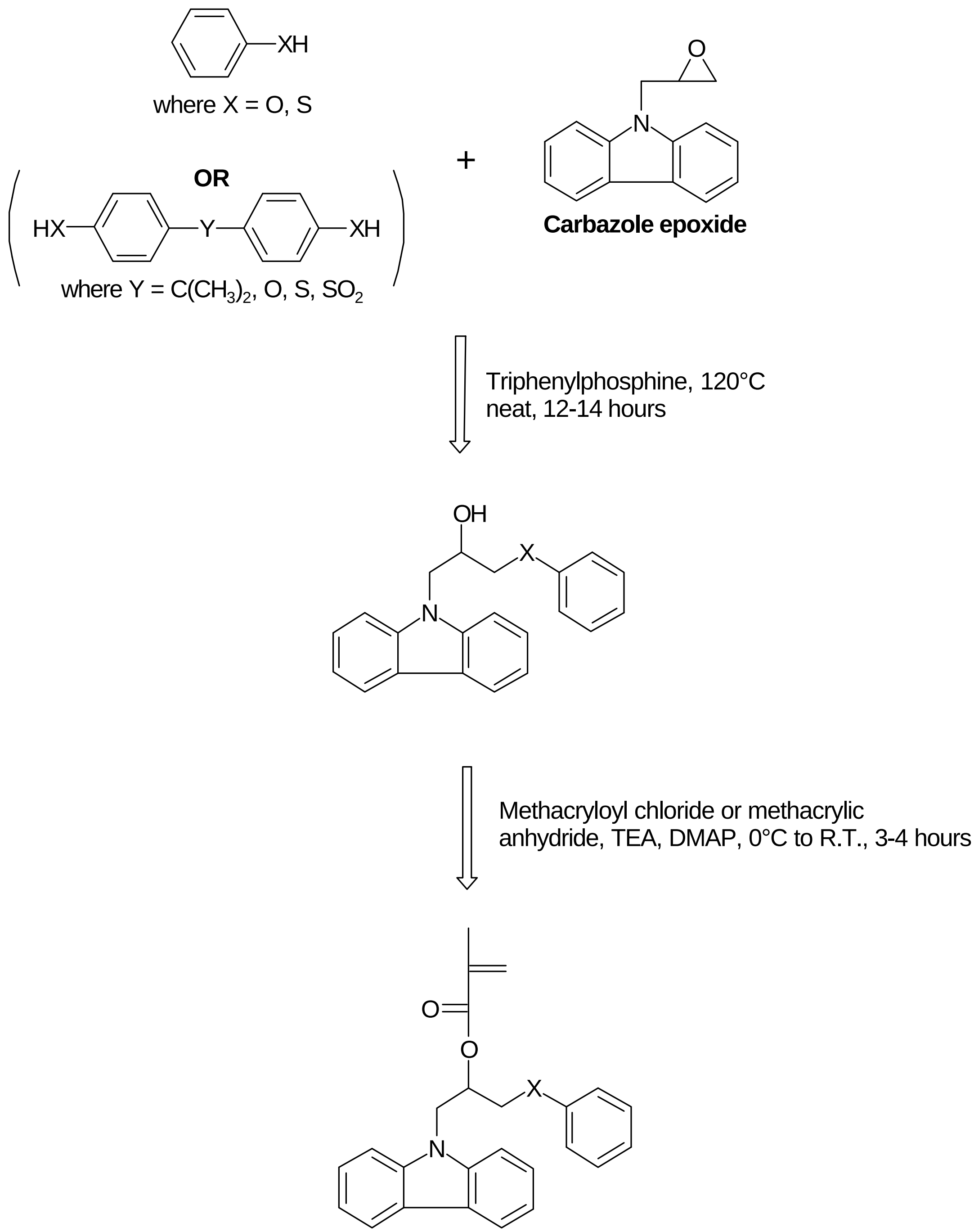
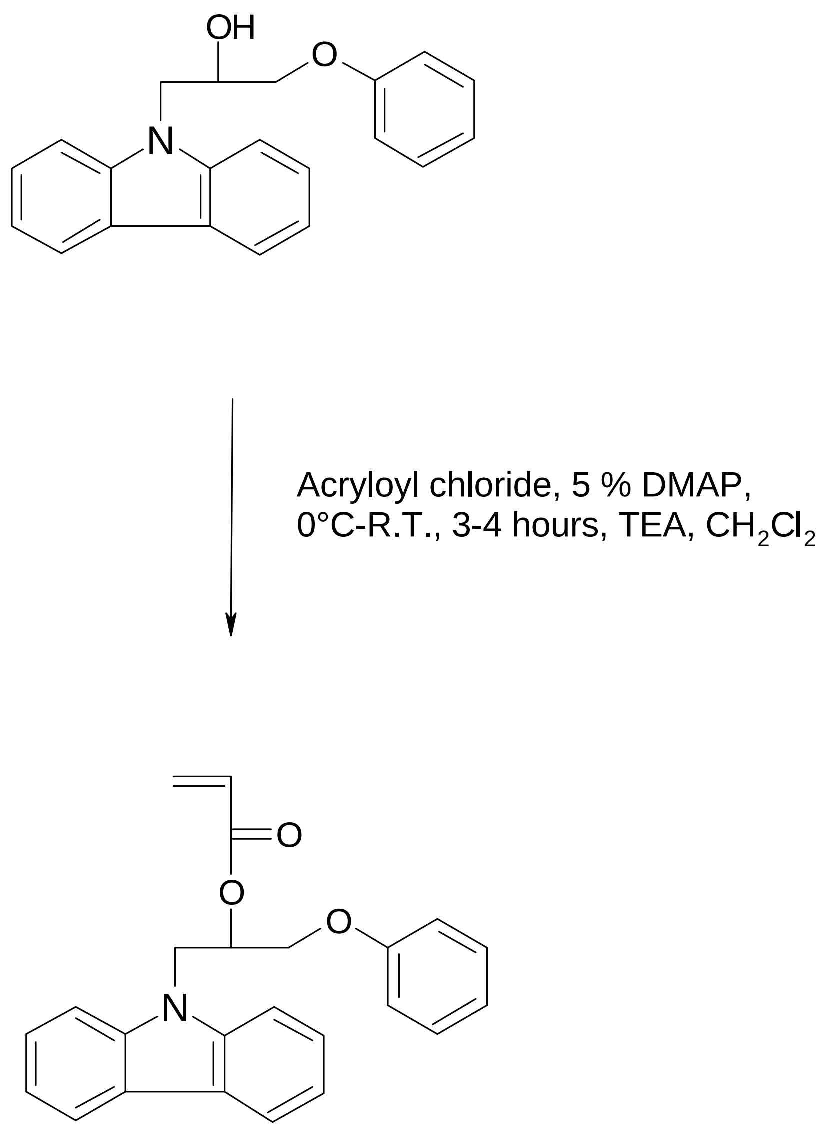
a functionality of two, were polymerized to produce linear polymers. The carbazole-phenoxy based methacrylate was also used as a reactive, high refractive index diluent for monomers of higher functionality.

To produce novel, carbazole based dimethacrylates, the carbazole epoxide and diol or dithiol were reacted together in an exact two to one molar ratio. The syntheses of the dimethacrylates used similar reaction conditions as for the methacrylates. The free radical polymerizations of novel dimethacrylates produced cross-linked polymer networks with high refractive indices.

The monomers were characterized, and synthetic reactions followed, by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC). One and two dimensional nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared spectroscopy (FTIR), elemental analysis, and differential scanning calorimetry (DSC) (for melting point determinations) were used to characterize the monomers. Ultraviolet-visible (UV-VIS) spectroscopy was used to determine the absorption profile of the carbazole-phenoxy based methacrylate monomer in the ultraviolet region.



Scheme 1.2 Syntheses of Carbazole Based Methacrylates (and Dimethacrylates)



Scheme 1.3 Synthesis of Carbazole-phenoxy Based Acrylate

Several free radical polymerizations were investigated: 1) solution polymerization using the thermal initiator 2,2'-azobisisobutyronitrile (AIBN) in *N*,*N*-dimethylacetamide (DMAC); 2) UV photopolymerization using the photoinitiator 1-hydroxycyclohexyl phenyl ketone (Irgacure 184™); 3) melt polymerization using the thermal initiator t-butyl peroxide; and 4) a modified suspension polymerization using the initiator benzoyl peroxide. Statistical copolymers of carbazole based methacrylates with methyl methacrylate (MMA) were also produced using free radical solution polymerizations and photopolymerizations. Cross-linked networks were obtained by photopolymerizations using the carbazole based dimethacrylates.

Gel permeation chromatography (GPC), NMR spectroscopy, FTIR spectroscopy, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA) were used to characterize the novel carbazole based polymers and copolymers. An *in-situ* FTIR experiment followed the free radical solution polymerization of the carbazole-phenoxy based methacrylate. Photo-DSC was used to determine the heat of polymerization in terms of change in enthalpy (ΔH_p) for the carbazole-phenoxy based methacrylate. One and two dimensional ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and molecular modeling were used for structure determination. Finally, refractive index was determined on selected carbazole based polymers and copolymers.

1.4 Thesis Statement

Aromatic dimethacrylates are excellent materials with many applications in dentistry, electronics, and optics, including optical eye wear, fiber optics, and non-linear optics, such as holography. Carbazole based polymers have demonstrated good photo-refractive, optical, and charge-transporting properties, combined with ease of processing. The objective of this research was to design, synthesize, and characterize high refractive index polymers and copolymers for use in the optical spectacle lenses of eyeglasses. This was achieved by incorporating carbazole substituents into novel aromatic methacrylates, acrylates, and dimethacrylates (Schemes 1.2 and 1.3).

Materials with enhanced optical properties, compared to PMMA and bisphenol A polycarbonate, were produced by the free radical polymerizations of these novel carbazole based methacrylates, acrylates, and dimethacrylates. Monomers and polymers were characterized in terms of molecular composition, melting point, glass transition temperature, thermal decomposition, and in terms of optical properties, such as refractive index. The reaction profile of the AIBN initiated carbazole-phenoxy based methacrylate polymerization was followed using *in-situ* FTIR. Photo-DSC was used to determine the heat of polymerization in terms of change in enthalpy (ΔH_p) for the carbazole-phenoxy based methacrylate.

The refractive index of materials can be increased by increasing the polarizability of substituent groups. By incorporating oxygen, sulfur, or sulfoxide at the X or Y position, high refractive index polymers have been attained. By reacting the phenol, aromatic diol, or aromatic thiol with carbazole epoxide, the refractive index was further increased (Scheme 1.2). The reaction of the carbazole based intermediate with methacryloyl chloride or methacrylic anhydride eliminated any hydroxyl groups in the final methacrylate or dimethacrylate. Hydroxyl groups undergo intermolecular hydrogen bonding, which increases viscosity. The absence of hydrogen bonding in the final methacrylated monomer reduces viscosity, which is desirable for processing.

Homopolymers and copolymers of the carbazole based methacrylates, acrylates, and dimethacrylates provided for high refractive index materials well suited for lightweight optical spectacles. Copolymers of carbazole based methacrylates with methyl methacrylate were also been produced and characterized in terms of molecular composition, refractive index, and glass transition temperature. These novel carbazole based monomers, by containing methacrylate or acrylate substituents, were readily polymerized and copolymerized using established free radical polymerization techniques. Overall, this research provided for a system of carbazole based chemistries to produced controlled linear and cross-linked materials with good optical properties.

Additionally, other interesting attributes were observed for selected carbazole based polymers, such as high thermal stability. ^{13}C NMR spectroscopy and molecular modeling experiments were used to explore the configuration of the polymerized carbazole-phenol based methacrylate. The lack of head-to-head linkages due to steric considerations could explain the high thermal stability observed for the carbazole-phenoxy based methacrylate polymer. Because of the high thermal stability coupled with good optical properties, these novel carbazole based materials may be well suited for non-linear optics and electronic data storage.