# Novel Carbazole Based Methacrylates, Acrylates, and Dimethacrylates to Produce High Refractive Index Polymers

W. Lenore Carman Rasmussen

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Prof. James E. McGrath, Chair
Prof. Timothy E. Long
Prof. Garth L. Wilkes
Prof. Judy Riffle
Prof. Harry Dorn

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## (ABSTRACT)

Homopolymers and copolymers produced from aromatic based methacrylates, acrylates, and dimethacrylates are excellent materials with many applications in dentistry, microelectronics, and optics, including optical eye wear, fiber optics, and non-linear optics, such as holography. Carbazole based polymers have demonstrated good optical, photo-refractive, 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 optical spectacle lenses of eyeglasses. Additionally, other interesting attributes were observed for selected carbazole based polymers, such as high thermal stability and birefringence, which could lend these materials to other uses, such as non-linear optics and electronic data storage. A family of novel, high refractive index homopolymers and copolymers were synthesized by incorporating carbazole, along with other aromatic substituents, into methacrylates, acrylates, and dimethacrylates. Subsequent free radical polymerizations provided for high refractive index materials well suited for lightweight optical spectacles and other applications.

The refractive index of materials can be increased by increasing the polarizability of substituent groups. By incorporating oxygen, sulfur, or sulfoxide groups into polymers, high refractive index polymers have been attained. By reacting the phenol, aromatic diols, or aromatic thiols with 9-(2,3-epoxypropyl)-carbazole, the refractive index of the final polymer can be increased further. 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 monomers reduces viscosity, which is desirable for processing.

Novel carbazole based monomers and polymers were characterized in terms of molecular composition and molecular weight, thermal properties, such as melting point, glass transition temperature, and decomposition, and in terms of optical properties, such as refractive index. The AIBN initiated carbazole-phenoxy based methacrylate polymerization was followed using *in-situ* FTIR, which showed the reaction to be completed within 40 minutes in DMAC at 90°C. Photo-DSC was used to determine the heat of polymerization ($\Delta H_p$) for the carbazole-phenoxy based methacrylate, which was found to be –39.4 kJ/mole. One and two dimensional $^1H$ NMR was used to characterize the molecular structure of the carbazole-phenoxy based methacrylate monomer. The carbazole-phenoxy based methacrylate homopolymer had a surprisingly high decomposition temperature. $^{13}C$ NMR spectroscopy experiments and molecular modeling were employed to explore the configuration of the polymerized carbazole-phenoxy based methacrylate. The lack of head-to-head linkages due to steric considerations could explain the higher thermal stability observed for the carbazole-phenoxy based methacrylate polymer.

Refractive indices of these carbazole based methacrylates, acrylates, and dimethacrylate polymers ranged from 1.53 to 1.63. Statistical copolymers of carbazole based methacrylates with methyl methacrylate were also produced by solution polymerization in DMAC, and characterized. Using free radical polymerization techniques, homopolymers and copolymers of the carbazole functionalized methacrylates, acrylates, and dimethacrylates were readily obtained. This research demonstrated a variety of carbazole based chemistries which could produce controlled linear and cross-linked materials with high refractive index values and other interesting features.

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