4.4 Refractive Index of Novel Carbazole Based Methacrylates, Acrylates, and Dimethacrylates

Refractive index (RI or *n*) is the ratio of the speed of light in a vacuum (c_o = 3.00 x 10^9 m/s) to the speed of light through a given medium (c); $n = c_o/c$. All refractive indices are greater than one. High refractive index materials are extremely useful for optical applications, particularly where focusing is required. The higher the refractive index, the more the material refracts (bends) the light, which increases the focusing power, so less material is needed. A high refractive index material provides greater focusing power, lower expense, and less weight for a given optical design.

Refractive index determination using the Metricon 2010 Prism Coupler Instrument is an extremely precise technique, with a refractive index accuracy of $\pm$ 0.001.[260] An improvement of refractive index in the third decimal place is considered noteworthy, while an improvement in the second decimal place is considered significant. An improvement of refractive index in the first decimal place is considered remarkable.

The carbazole-phenoxy based methacrylate homopolymer and copolymers with methyl methacrylate were analyzed for refractive index using a Metricon 2010 Prism Coupler Instrument. Cross-linked networks composed of the carbazole-bisphenol A based dimethacrylate, and copolymers of the carbazole-bisphenol A based dimethacrylate and the carbazole-phenoxy based methacrylate were also analyzed for refractive index, as well as the carbazole-phenoxy based acrylate polymer. The carbazole-phenoxy based methacrylate homopolymer and the carbazole-phenoxy based acrylate homopolymer were also tested for birefringence using the Metricon 2010 Prism Coupler Instrument.

The carbazole-phenoxy based methacrylate homopolymer had a refractive index of 1.63, which was much higher than the refractive index of 1.58 for bisphenol A based

[260] Model 2010 Prism Coupler, *Features and Specifications Guide*, Metricon: Pennington, NJ, **2000**.

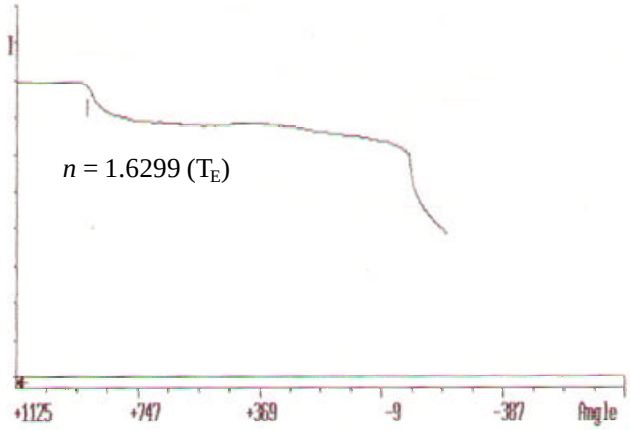
poly(carbonate). PMMA, in comparison, has a refractive index of only 1.49.[261] The refractive index for the carbazole-phenoxy based acrylate homopolymer was 1.64, which was higher than the refractive index of the carbazole-phenoxy based methacrylate homopolymer. This was an expected result due to the lower aliphatic content of the functionalized acrylate polymer compared to the functionalized methacrylate polymer. Figure 4.54 shows the refractive index trace for the carbazole-phenoxy based methacrylate homopolymer in the transverse electric field (T_E) (xy plane) and the transverse magnetic field (T_M) (z direction). Figure 4.55 shows the refractive index trace for the carbazole-phenoxy based acrylate homopolymer in the T_E and T_M fields. For comparison, Figure 4.56 shows the refractive index determination for PMMA. All of the polymer films were solvent cast from methylene chloride (30 weight % polymer to solvent), dried slowly, then vacuum dried above their glass transition temperatures.

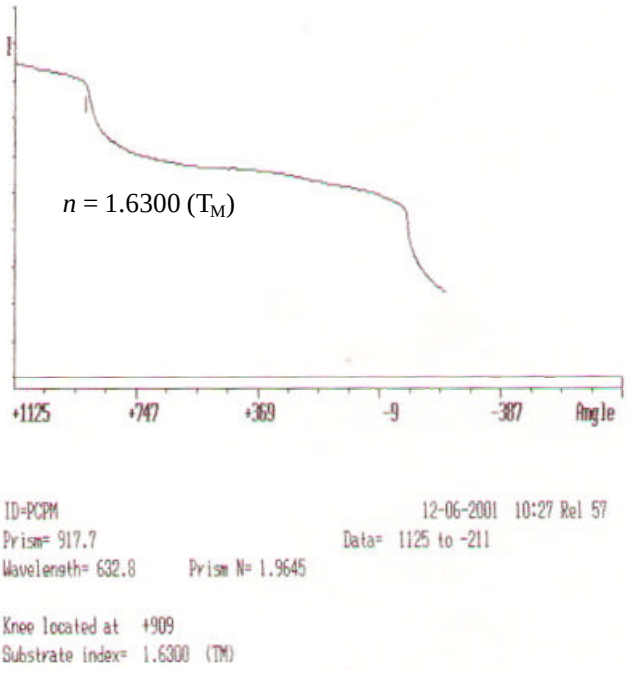
The 25/75, 50/50, and 75/25 weight percent compositions and mole percent compositions of copolymers of carbazole-phenoxy based methacrylate and methyl methacrylate were analyzed for refractive index (Table 4.8). Figure 4.57 shows a graph of refractive index as a function of percent PCPM composition. The refractive index of each copolymer was measured two or three times. Because the prism coupler was such a precise technique, the standard deviation was less than 0.001 for all the copolymer samples. The carbazole-phenoxy based methacrylate homopolymer was measured repeatedly on films from AIBN polymerized samples and photopolymerized samples, using the Metricon 2010 Prism Coupler Instrument at Virginia Tech, and also using the Metricon 2010 Prism Coupler Instrument at the home office of Metricon, Inc., in Pennington, New Jersey. Each and every refractive index measurement taken for the carbazole-phenoxy based methacrylate homopolymer was 1.63. The weight percent composition series had a more linear trend than the mole percent composition series. Because of the large molecular weight difference between the two monomers, it was expected that weight to weight (or mass to mass) compositions would correlate more than mole to mole compositions for optical properties such as refractive index.

[261] Seferis, J.C., "Refractive Indices of Polymers" in *Polymer Handbook*, 4th ed., Brandrup, J.; Immergut, E.H.; Grulke, E.S., Eds., Wiley: New York, **1999**, VI/571.

Table 4.8 Refractive Index for Homopolymers and Copolymers of Carbazole-Phenoxy Based Methacrylate and Methyl Methacrylate

% PCPM	RI (wt. %)	RI (mole %)
100 % PMMA	1.4916	1.4916
25/75 PCPM/PMMA	1.5176	1.5734
50/50 PCPM/PMMA	1.5606	1.5876
75/25 PCPM/PMMA	1.5885	1.6106
100 % PCPM	1.6306	1.6306





Note: Second drop in intensity is from mounting tape (artifact)

Figure 4.54 Refractive Index Trace for the Carbazole-Phenoxy Based Methacrylate Polymer

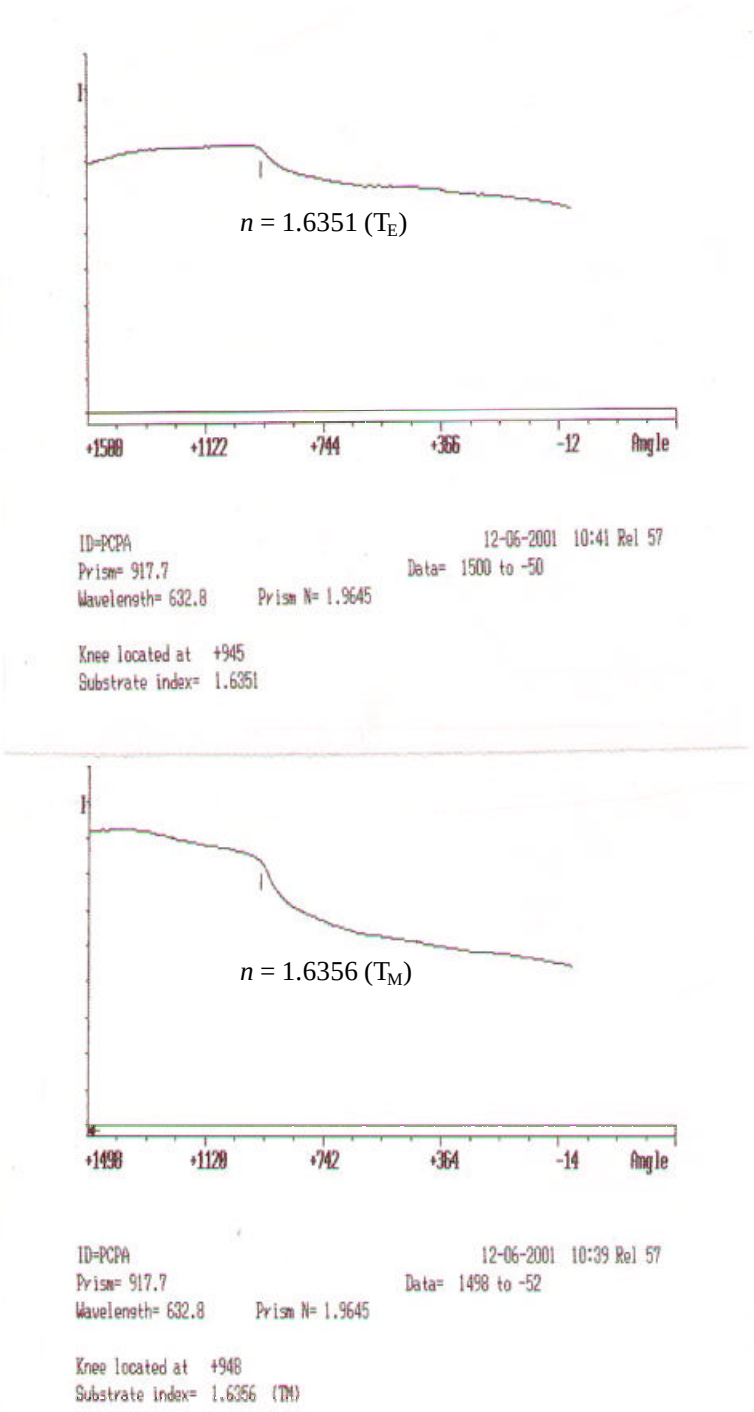


Figure 4.55 Refractive Index Trace for the Carbazole-Phenoxy Based Acrylate Polymer

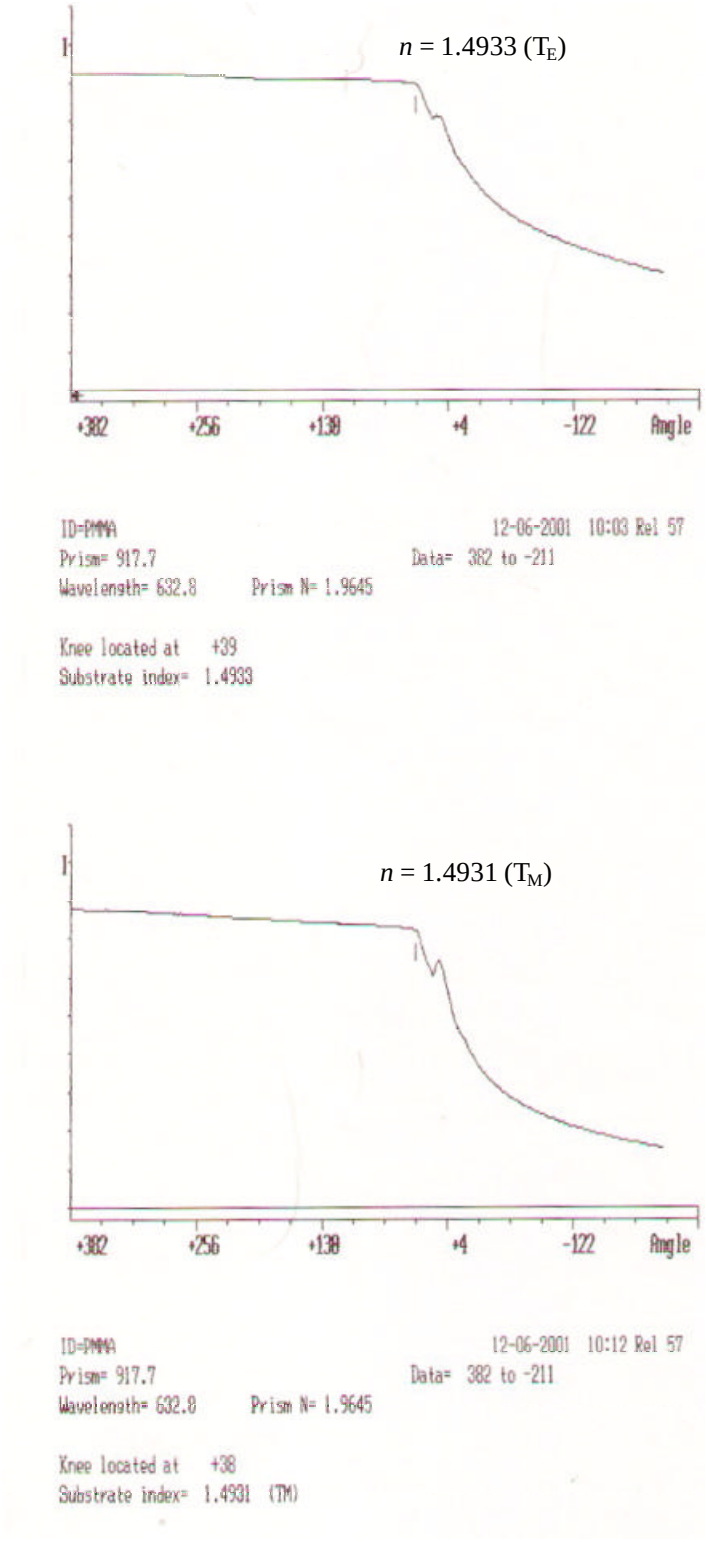


Figure 4.56 Refractive Index Trace for PMMA

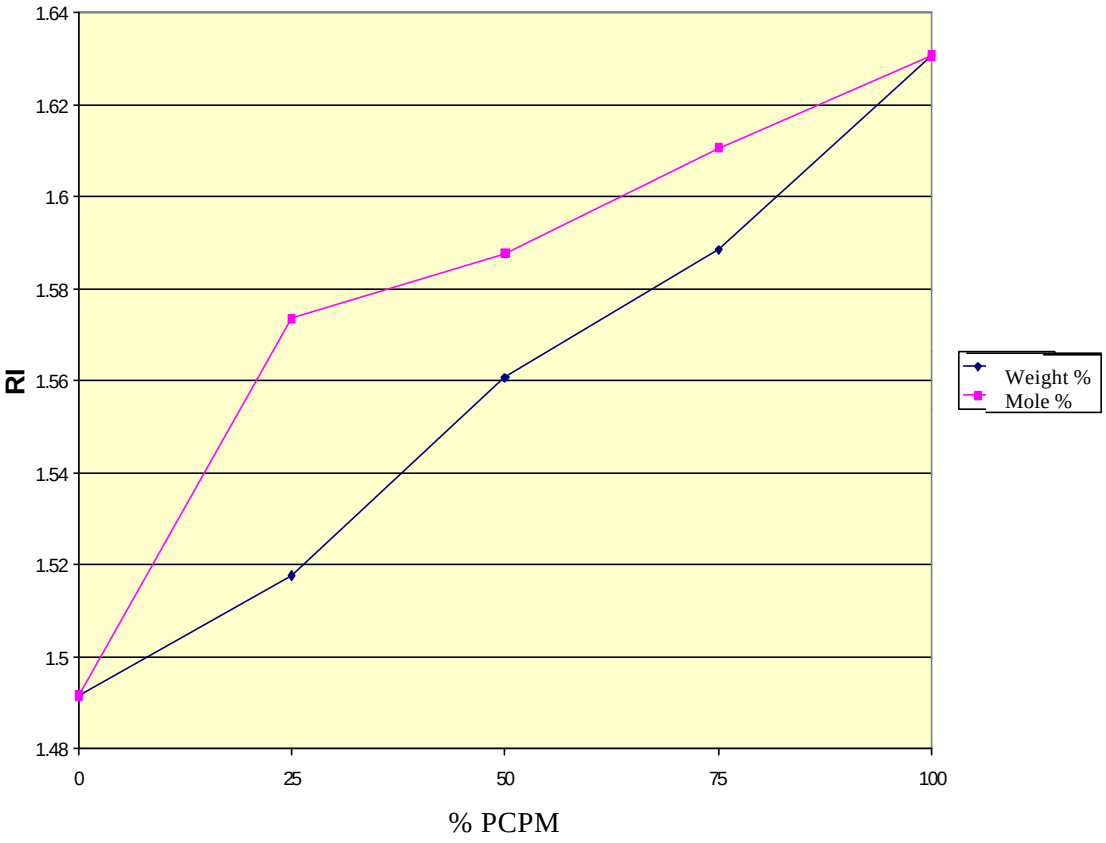


Figure 4.57 Graph of Refractive Index Versus Percent Composition of PCPCM/PMMA Polymers

The refractive indices were determined for cross-linked networks composed of the carbazole-bisphenol A based dimethacrylate, and copolymers of the carbazole-bisphenol A based dimethacrylate and the carbazole-phenoxy based methacrylate. The carbazole-bisphenol A based dimethacrylate polymer (PCBADM) had a refractive index of 1.53, which compared to a refractive index of 1.63 for the carbazole-phenoxy based methacrylate polymer. The 50/50 (mole percent) copolymer of the carbazole-bisphenol A based dimethacrylate and the carbazole-phenoxy based methacrylate had a refractive index of 1.56. These results are shown in Table 4.9 and graphically in Figure 4.58. The aliphatic character from the dimethyl groups in the bisphenol A substituent lowered the refractive index quite significantly. The dimethacrylate containing cross-linked networks were infusible, insoluble, amber colored, transparent materials. The 50/50 copolymer was fairly strong and less brittle than either homopolymer.

Table 4.9 Refractive Indices for Polymers of Carbazole-Bisphenol A Based Dimethacrylates and Carbazole-Phenoxy Based Methacrylates

Composition	**RI**
100 % PCBADM	**1.53**
50/50 % PCPM/PCBADM	**1.56**
100 % PCPM	**1.63**

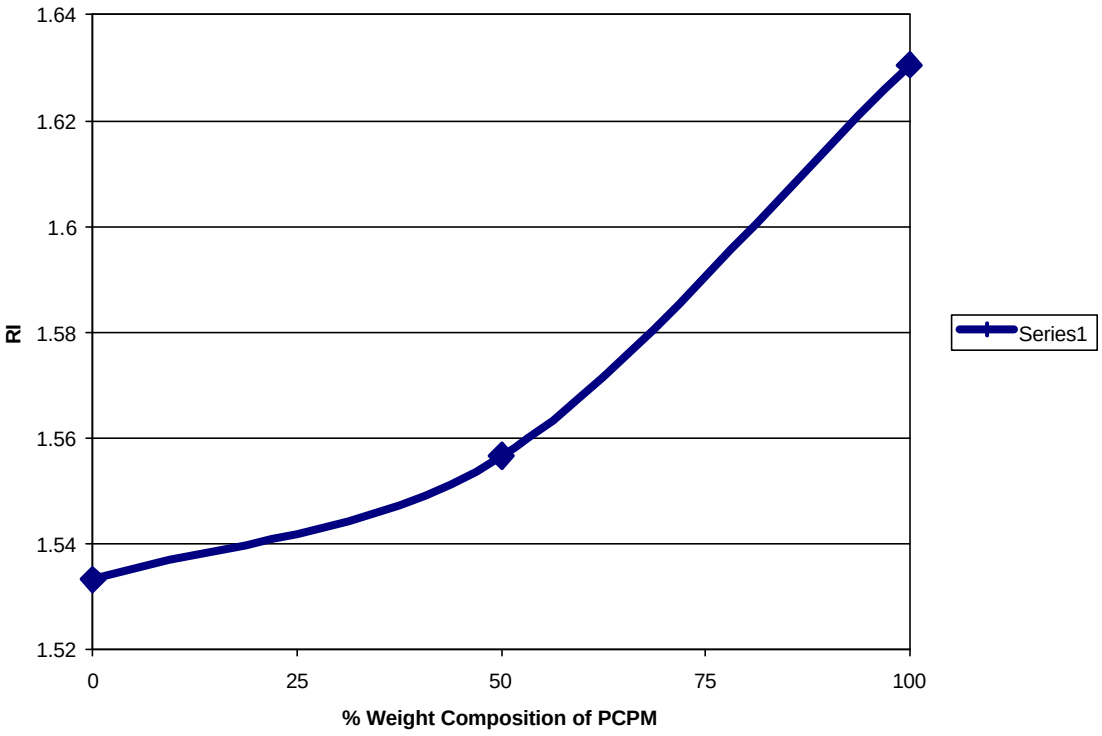


Figure 4.58 Graph of Refractive Index Versus Mole Percent PCBADM/PCPM

Birefringence could also be determined using the Metricon 2010 Prism Coupler Instrument by subtracting the refractive index taken in the T_M field from the refractive index taken in the T_E field. Birefringence, as expected, was not observed in the PMMA film (Figure 4.56). Birefringence was not observed in either the carbazole-phenoxy based methacrylate polymer or the carbazole-phenoxy based acrylate polymer (Figures 4.54 and 4.55).

The carbazole-phenoxy based methacrylate, acrylate and dimethacrylate materials formed good transparent films, with refractive indices well above the refractive index of PMMA. The carbazole-phenoxy based methacrylate homopolymer had a high refractive index of 1.63, and the carbazole-phenoxy based acrylate had a higher refractive index of 1.64, which were well above the refractive index of state-of-the-art bisphenol A based poly(carbonate). The carbazole-phenoxy based methacrylate and acrylate, when polymerized under mild conditions, formed linear polymers, which were solvent cast into films and conceivably could be processed into films and other shapes. The carbazole-bisphenol A based dimethacrylate readily formed infusible cross-linked networks. These materials, particularly the carbazole-phenoxy based methacrylate and acrylate polymers with their very high refractive indices, could find commercial use as high refractive index materials for optical applications. A profound advantage of the carbazole-phenoxy based methacrylate compared to vinyl carbazole is the ease with which it copolymerizes with methyl methacrylate.