2.4 Aromatic Dimethacrylates

Aromatic dimethacrylates, particularly 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (BisGMA), have been used extensively in dentistry for photocurable fillings.[202] BisGMA, shown below in Figure 2.15, can be formed by the reaction of bisphenol A with glycidyl methacrylate. In dentistry, large concentrations of fillers are mixed in with BisGMA to provide color, to control the exotherm, to allow for pre-cure molding (in the form of a paste), to provide post-cure strength, and to reduce post-cure shrinkage by reducing the coefficient of expansion (CTE). BisGMA is extremely viscous and difficult to work with due to intermolecular hydrogen bonding between the hydroxyl groups, and is usually diluted with triethylene glycol dimethacrylate.[203]

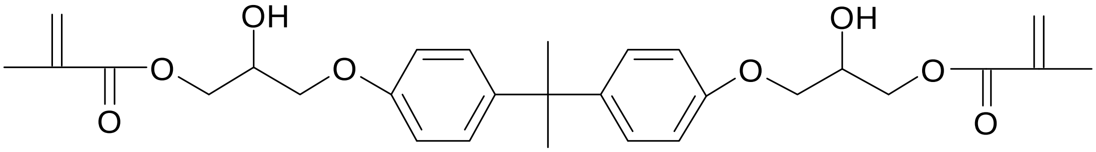

Figure 2.15 2,2-Bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (BisGMA)

McGrath, *et al.*, produced an extensive class of novel aromatic dimethacrylates with no pendant hydroxyl groups, examples of which are shown in Figure 2.16. These novel dimethacrylates were less viscous, thus easier to work with. Additionally, they exhibited less post-cure shrinkage, which is an extremely desirable property for any polymerization. For both of these reasons, less filler was required in dental applications, and potentially, in bone cement applications. Many of these polymers produced from the

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[202] Schmitt, W.; Purrmann, R.; Jochum, P.; Zahler, W.D., (ESPE) *US Patent*, **1975**, 3,923,740.
[203] Schmitt, W.; Purrmann, R.; Jochum, P.; Zahler, W.D., *ibid.*

aromatic dimethacrylates also had high refractive indices, and had the potential to be used for near optical applications.[204,205,206,207,208,209,210,211]

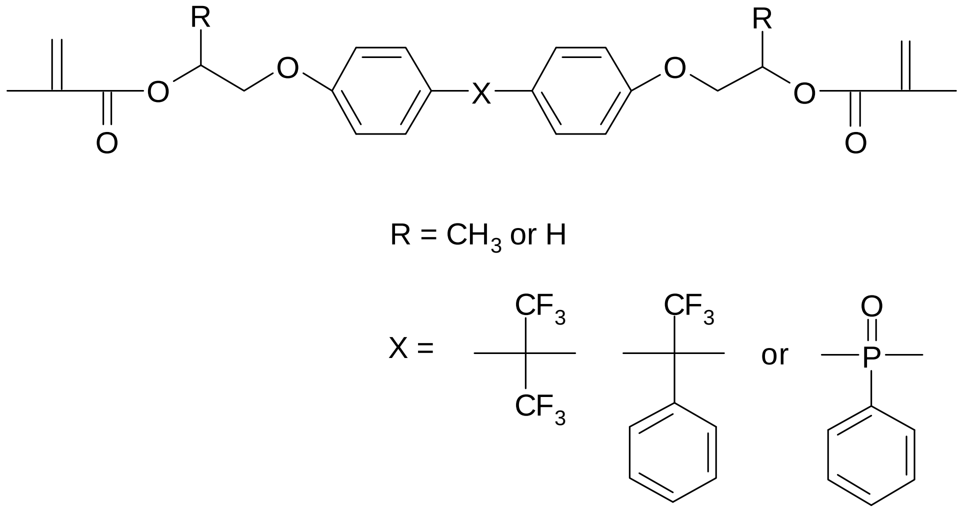

Figure 2.16 Examples of Aromatic Dimethacrylates with No Pendant Hydroxy Groups

McGrath, *et al.*, then synthesized a family of aromatic, thio dimethacrylates (Figure 2.17). The polymers produced from these aromatic sulfur containing dimethacrylates had refractive indices as high as 1.67.[212] The research for this thesis has further explored the

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[204] Gunduz, N., *Synthesis and Photopolymerization of Novel Dimethacrylates, M.S. Thesis*, Virginia Tech, Blacksburg, VA, **1998**.

[205] Allam, C.; Kuo, J.L.; McGrath, J.E.; Mohanty, D.K., *Macromol. Chem. Phys.*, **1999**, *200(8)*, 1854.

[206] Gunduz, N.; Shultz, A.R.; Shobha, H.K.; Sankarapandian, M.; McGrath, J.E., *Polym.Prepr.*, **1998**, *39(2)*, 647.

[207] Shobha, H.K.; Sankarapandian, M.; Kalachandra, S.; Taylor, D.F.; McGrath, J.E., *J. Sci.: Mater. Med.*, **1997**, 8(6), 385.

[208] Sankarapandian, M.; Xu, Q.; McGrath, J.E.; Taylor, D.F.; Kalachandra, S., *J. Adv. Mater.*, **1996**, *10*, 59.

[209] Shobha, H.K.; Sankarapandian, M.; Shultz, A.R.; McGrath, J.E.; Kalachandra, S.; Taylor, D.F., *Macromol. Symp.*, **1996**, *III*, 73.

[210] Kalachandra, S.; Taylor, D.F.; DePorter, C.D.; Grubbs, H.J.; McGrath, J.E., *Polymer*, **1993**, *34(4)*, 778.

[211] Kalachandra, S.; Taylor, D.F.; DePorter, C.D.; Grubbs, H.J.; McGrath, J.E., *Polym. Prepr.*, **1992**, *33(1)*, 467.

[212] Shobha, H., “Synthesis and Characterization of New Dimethacrylate Monomers for Optical Applications,” Group Presentation, Virginia Tech, Blacksburg, VA, March 27, **1999**.

incorporation of the hetero-aromatic group carbazole into novel methacrylates, acrylates, and dimethacrylates (Schemes 1.2 and 1.3, Chapter 1, p.5, p.8) to produce polymers with high refractive indices and other desirable properties.[213]

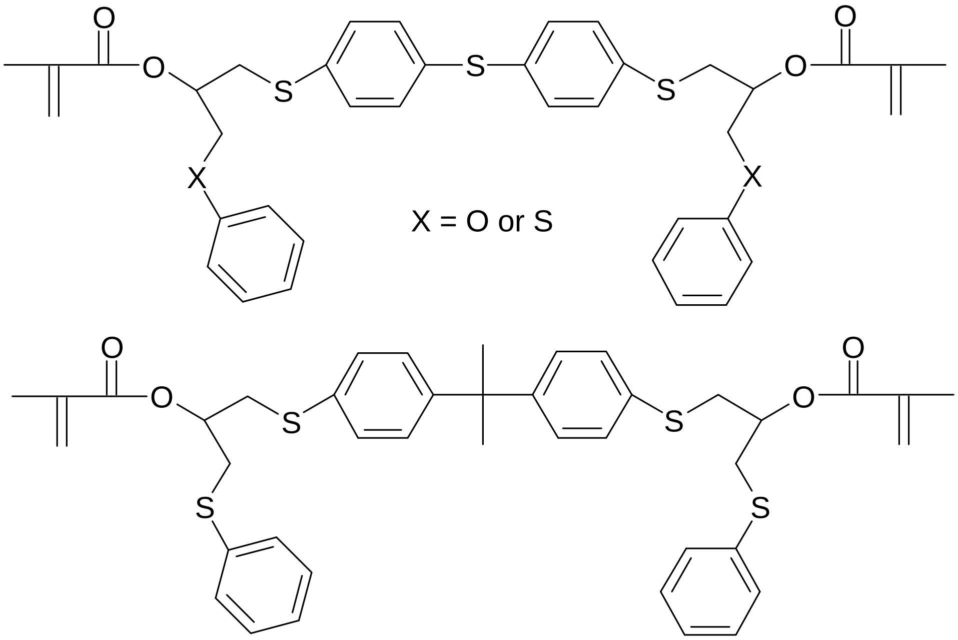

Figure 2.17 Examples of Sulfur Containing Dimethacrylates[214]

2.5 Heat of Polymerization Using Photo-DSC

Gunduz and McGrath, *et al.*, monitored the rapid exothermic heat of photopolymerization for four novel dimethacrylates, which were analogues of BisGMA.[215,216] A Perkin Elmer DSC 7 equipped with a double beam

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[213] McGrath, J.E.; Rasmussen, L.; Shobha, H.; Sankarapandian, M.; Uhrich, K.E., *Polym. Prepr.*, **2000**, *41(2)*, 1363.

[214] Shobha, H., "Synthesis and Characterization of New Dimethacrylate Monomers for Optical Applications," Group Presentation, Virginia Tech, Blacksburg, VA, March 27, **1999**.

[215] Gunduz, N., *Synthesis and Photopolymerization of Novel Dimethacrylates, M.S. Thesis*, Virginia Tech, Blacksburg, VA, **1998**.

[216] Gunduz, N.; Shultz, A.R.; Shobha, H.K.; Sankarapandian, M.; McGrath, J.E., *Polym.Prepr.*, **1998**, *39(2)*, 647.

photocalorimetric accessory (DPA) was used for these experiments (Figure 2.18). A short-arc xenon lamp of 450 Watts was used as the light source. A shutter, which was manually controlled, allowed light to irradiate the pans when opened. Desired wavelengths were chosen using the monochromator. Neutral density filters modulated the light intensity.[217]

Photo-polymerizations were performed in modified aluminum pans (Figure 2.19). Meniscus formation was prevented or greatly minimized due to the step configuration of the pan. Standard aluminum sample pans were pressed into this shape with a retrofitted press.[218]

The heat of polymerization (ΔH_p) was calculated from the area of the exotherm curve relative to the baseline (shutter closed). The extent of polymerization (E_p %) was determined by comparing the ΔH_p of the dimethacrylate to the ΔH_p of completely polymerized methyl methacrylate (-54.8 kJ/mole),[219] as shown in equation 2.10. The E_p was as high as 79 % for triethyleneglycol dimethacrylate.[220]

$$E_p\,\% = \frac{\Delta H_{p(\text{dimethacrylate})}}{\Delta H_{p(\text{methyl methacrylate})} \times 2} \times 100$$

Equation 2.10

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[217] Gunduz, N., *Synthesis and Photopolymerization of Novel Dimethacrylates, M.S. Thesis*, Virginia Tech, Blacksburg, VA, **1998**.

[218] Gunduz, N., *ibid.*

[219] Horie, K., *J. Radiat. Curing*, **1980**, *7(2)*, 20.

[220] Gunduz, N., *Op. Cit.*

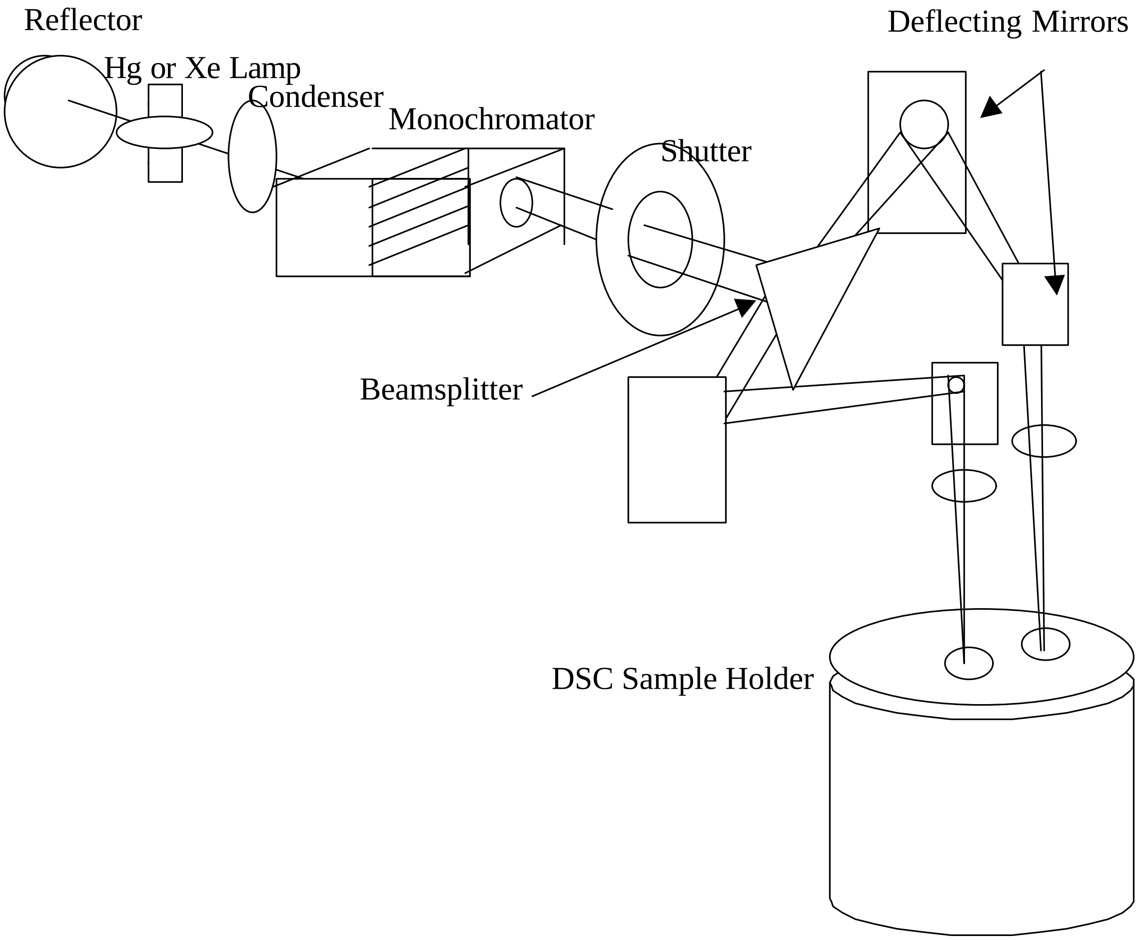

Figure 2.18 Photopolymerization Apparatus of DSC 7 Equipped with DPA[221]

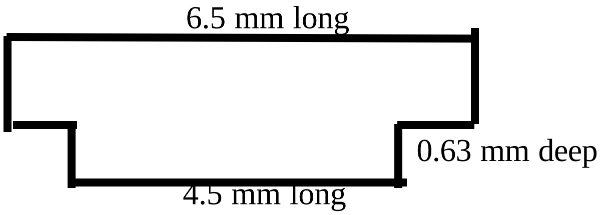

Figure 2.19 Cross Section of Modified Aluminum DSC Sample Pan for Photo-DSC Experiments[222]

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[221] Gunduz, N., *Synthesis and Photopolymerization of Novel Dimethacrylates, M.S. Thesis*, Virginia Tech, Blacksburg, VA, **1998**.

[222] Gunduz, N., *ibid.*

2.6 *In Situ* FTIR to Monitor Polymerizations

Using *in situ* FTIR, Long, *et al.*, investigated the polymerizations of 1,3-cyclohexadiene based star polymers,[223] maleic anhydride and norbornane based alternating copolymers,[224] and isocyanate prepolymers.[225] A probe, connected to the ASI-FTIR ReactIR™, was inserted into the polymerization flask at the onset of the experiment. Data points were taken, where the (equally spaced) time intervals could be varied between data points for different experiments. Using *in situ* FTIR, faster reactions, such as the 1,3-cyclohexadiene polymerization, and slower reactions such as the maleic anhydride and norbornane copolymerization, were readily monitored in real time.[226,227]

2.7 Carbazole Based Methacrylates and Acrylates

Some researchers have synthesized methacrylates and acrylates with pendant carbazole functionalities. Strohriegl has worked extensively with the amidation of polymethacrylates and polyacrylates, including the incorporation of pendant carbazole groups.[228,229,230,231] He used two different methods to synthesize polymethacrylates (and polyacrylates) with pendant carbazole groups (Scheme 2.2).[232]

In the first method, alkenylcarbazoles were prepared from the corresponding bromoalkenes. Hydroboration with 9-borabicyclo[3.3.1]nonane (9-BBN) produced the corresponding hydroxyalkylcarbazoles. Esterification with methacryloyl chloride

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[223] Williamson, D.; Brazhnik, K.; Elman, J.; Pasquale, A.J.; Long, T., *Polym. Prepr.*, **2000**, *41(2)*, 1544.

[224] Pasquale, A.J.; Karro, R.; Allen, R.; Long, T., *Polym. Prepr.* **2000**, *41(2)*, 1931.

[225] Pasquale, A.J.; Allen, R.; Long, T., *Proc. Annu. Meet. Adhes. Soc.*, **2000**, *23rd*, 232.

[226] Williamson, D.; Brazhnik, K.; Elman, J.; Pasquale, A.J.; Long, T., *Op. Cit.*

[227] Pasquale, A.J.; Karro, R.; Allen, R.; Long, T., *Op. Cit.*

[228] Strohriegl, P. *Makrol. Chem.*, **1993**, *194*, 393.

[229] Strohriegl, P. *Mol. Cryst. Liq. Cryst.*, **1990**, *183*, 261.

[230] Strohriegl, P. *Makrol. Mol. Chem., Rapid Commun.*, **1986**, *183*, 261.

[231] Reinhold, R.; Strohriegl, P.; Lauke, H.; Nick, B.; Haarer, D., (BASF) *US Patent*, **1993**, 5,176,962.

[232] Strohriegl, P., *Makrol. Chem., ibid.*

produced the carbazole based methacrylates, which were then polymerized in toluene with AIBN (Scheme 2.2). Molecular weights obtained using this method were low, with broad polydispersities. The reason was attributed to low solubility of the polymers in toluene. The polymerization was performed in more polar solvents, such as tetrahydrofuran (THF) and 1,4-dioxane, but still, only low molecular weight, oligomeric products were obtained. The reason was attributed to chain transfer with the solvent.[233]

The second method used by Strohriegl was successful in producing high molecular weight polymethacrylates with pendant carbazole groups. In the second method, the hydroxyalkylcarbazoles were reacted with butyllithium to form the corresponding alcoholates, which were then reacted with poly(methacryloyl chloride) in the solvent THF (Scheme 2.2). This method produced polymers with number average molecular weights of 50,000 g/mole or higher. The degree of substitution was at least 95 % for the entire series of carbazole based polymethacrylates. High quality films suitable for photoconductivity experiments were cast from these carbazole based polymethacrylates.[234]

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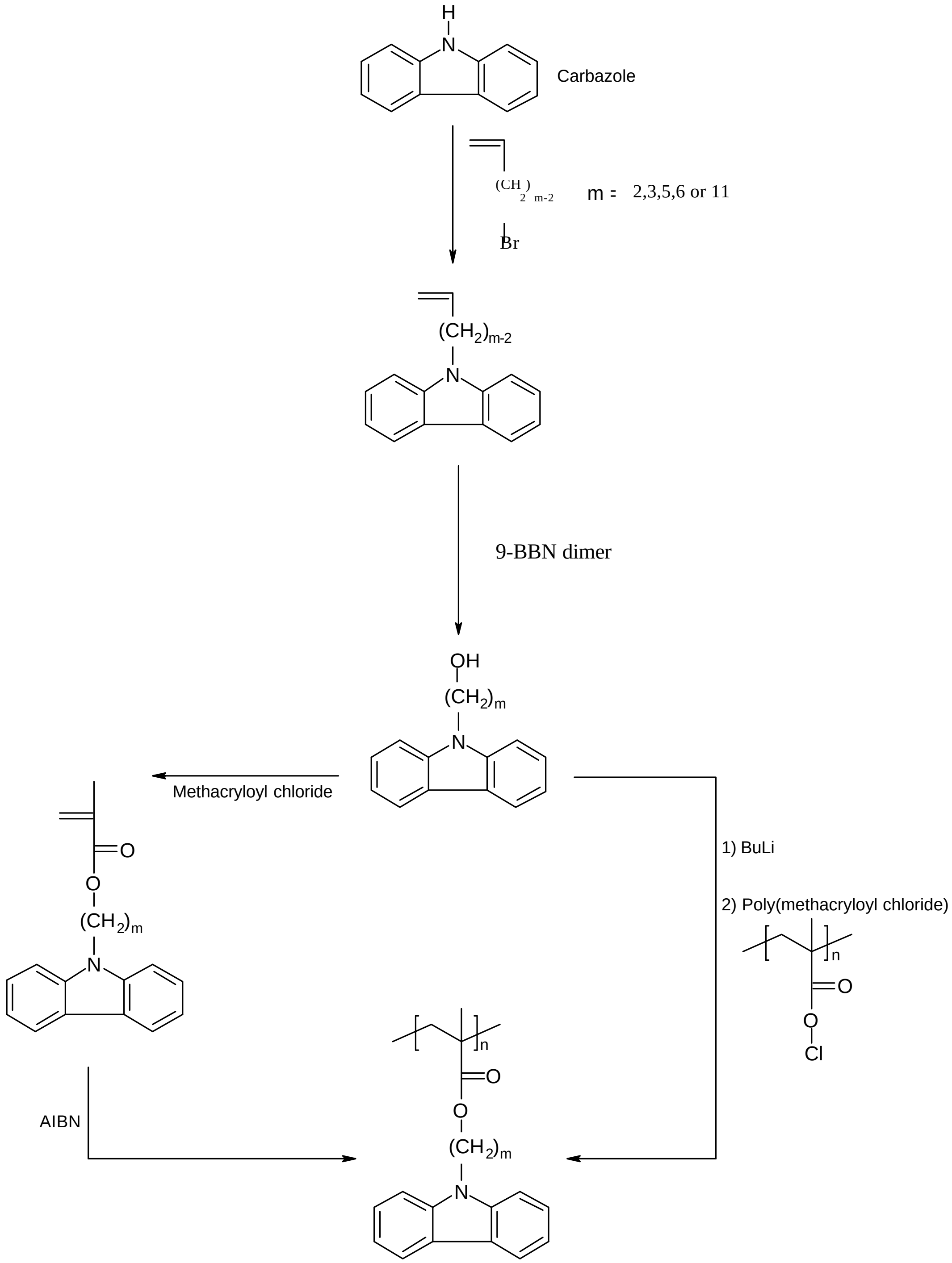
[233] Strohriegl, P. *Makrol. Chem.*, **1993**, *194*, 393.
[234] Strohriegl, P. *ibid.*



Scheme 2.2 Two Methods to Produce Carbazole Based Polymethacrylates[235]

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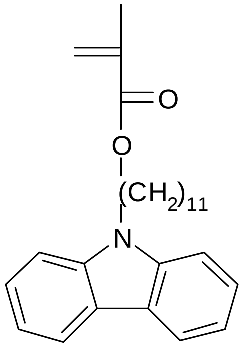
[235] Strohriegl, P. *Makrol. Chem.*, **1993**, *194*, 393.

DuBois was successfully able to polymerize the 11-(N-carbazolyl)undecylmethacrylate monomer (shown below). Dimethylformamide, instead of toluene, was used as the polymerization solvent, which increased the solubility of both the monomer and the polymer. Copolymers of 11-(N-carbazolyl)undecylmethacrylate were synthesized and investigated for holographic electro-optical applications.[236]



Prasad, *et al.*, produced copolymers containing poly(2-N-carbazolylethylmethacrylate),[237] where the poly(2-N-carbazolylethylmethacrylate) portion performed well as hole transporting agents for holography.[238,239] As a hole transporting agent, isotactic poly(2-N-carbazolylacrylate) has demonstrated very high hole transporting mobilities.[240,241] LeBarny also successfully synthesized a family of carbazole based methacrylates for promising holographic applications.[242] Urya and Yozo used carbazole-phenoxy based methacrylates and acrylates to produce copolymers that were used as photoconductive materials capable of inducing a smectic phase in liquid

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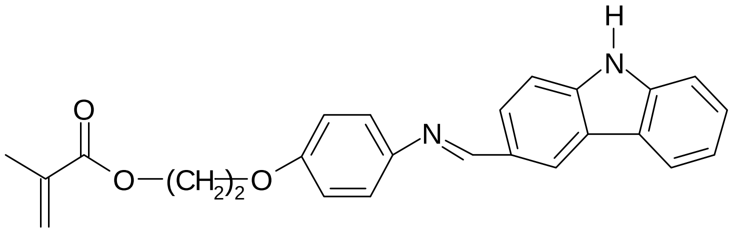
[236] DuBois, P., *J. Polym., Sci., Part B; Polym. Phys.*, **2000**, *38*, 205.
[237] Zhao, C.; Park, C.; Prasad, P.N.; Zhang, Y.; Ghosal, S.; Burzynski, R., *Chem. Mater.*, **1995**, *7*, 1237.
[238] Zhao, C.; Park, C.; Prasad, P.N.; Zhang, Y.; Ghosal, S.; Burzynski, R., *ibid.*
[239] Oshima, Y., *J. Polym., Sci., Polym. Let.*, **1985**, *23(5)*, 151.
[240] Urya, T.; Yozo, K., *Macromolecules*, **1987**, *20(4)*, 651.
[241] Urya, T.: Yozo, K., *Macromolecules*, **1985**, *18*, 1043.
[242] LeBarny, P.; Soyer, F.; Facoetti, H., (Thomson-CSF) *EP Patent*, **1998**, 850960.

crystals. An example of one of these carbazole-phenoxy methacrylates is shown below.[243]



Gaudiana, *et al.*, produced high refractive index carbazole based methacrylates and acrylates for optical applications, where the pendant carbazole groups were halogenated (Figure 2.20). Refractive indices ranged from 1.67 to 1.77.[244] Copolymers of carbazole based methacrylates and acrylates have also found potential use in contact lens and intraocular lens applications.[245]

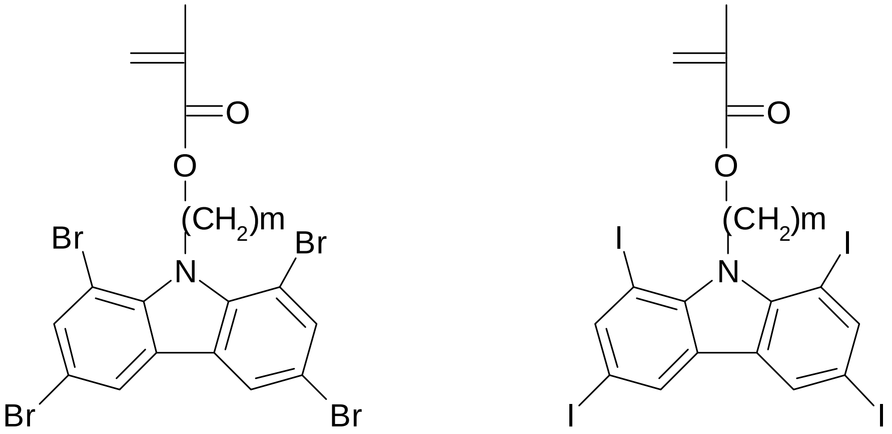


Figure 2.20 Examples of Methacrylates with Halogenated Carbazole Groups[246]

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[243] Urya, T.; Yozo, K., (Nippon) *JP Patent*, **1996**, 8092324.
[244] Gaudiana, R.; Minns, R.; Rogers, H., (Polaroid) *US Patent*, **1992**, 5,132,430.
[245] Makker, H.; Liao, X.; Weinschenk, J., (Allergan) *WO Patent*, **2000**, 00/26698.
[246] Gaudiana, R.; Minns, R.; Rogers, H., *Op. Cit.*

The syntheses of new and exciting carbazole based methacrylates and acrylates has provided for a variety of easily photocurable and thermally curable compounds. Homopolymers and copolymers designed from these novel methacrylates and acrylates have found applications in traditional optics, as well as holography, electro-optics, non-linear optics, liquid crystals, and electronic data storage. Our interest in novel carbazole based methacrylates, dimethacrylates, and acrylates was to produce high refractive index polymers for optical spectacle lenses in eyeglasses. These novel materials, however, may also prove very useful for other applications, such as holography and electronic data storage.