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Novel carbazole phenoxy-based methacrylates to produce high-refractive index polymers

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Abstract

A novel, high-refractive index homopolymer was produced by incorporating carbazole and phenol into the methacrylate monomer structure. The reaction of phenol with 9-(2,3-epoxypropyl)-carbazole, followed by the reaction of the carbazole phenoxy-based intermediate with methacryloyl chloride or methacrylic anhydride, and recrystallization from methanol, produced a good yield of highly pure carbazole phenoxy functionalized methacrylate monomer. Subsequent free radical polymerization or UV photopolymerization of the functionalized methacrylate monomer, in addition to copolymerizations with methyl methacrylate, provided for high-refractive index materials well suited for lightweight optical applications. Unlike *N*-vinyl carbazole, the novel carbazole phenoxy-based methacrylate readily copolymerized with methyl methacrylate. Statistical copolymers of carbazole based methacrylates with methyl methacrylate were produced by free radical solution polymerization in DMAC or by photopolymerization in DMF. The carbazole phenoxy-based methacrylate monomer was characterized for molecular weight using gel permeation chromatography (GPC), for melting point and glass transition temperature using differential scanning calorimetry (DSC), for decomposition using thermal gravimetric analysis (TGA), and for chemical composition by one- and two-dimensional ^{1}H nuclear magnetic resonance (NMR) spectroscopy and by elemental analysis. The AIBN initiated carbazole phenoxy-based methacrylate polymerization was followed using in situ FTIR, which showed the reaction to be complete within 40 min in DMAC at 90 °C. Refractive indices of the carbazole based methacrylate homopolymers and copolymers ranged from 1.52 to 1.63. PhotoDSC was used to determine the heat of polymerization (ΔH_p) for the carbazole phenoxy-based methacrylate ($\Delta H_p = -39.4$ kJ/mol). The carbazole phenoxy-based methacrylate homopolymer had a surprisingly high onset of decomposition temperature ($T_{onset} = 316$ °C). ^{13}C NMR spectroscopy experiments and molecular modeling were used to explore the configuration of the polymerized carbazole phenoxy-based methacrylate. The lack of head-to-head linkages due to steric considerations reasonably explains the high thermal stability observed for the carbazole phenoxy-based methacrylate polymer.

Keywords: Carbazole functionalized methacrylate; Nuclear magnetic spectroscopy; Ultraviolet photo-differential scanning calorimetry

1. Introduction

Polymers and copolymers produced from aromatic based methacrylates, acrylates, and dimethacrylates have a wide variety of applications in dentistry, optical eyewear, fiber optics, holography, and microelectronics. Recently, novel high-refractive index polymers and copolymers were designed, synthesized, and characterized for optical applications. A refractive index higher than 1.58, which is the refractive index of state-of-the-art bisphenol A polycarbonate [1], was required. Poly(*N*-vinyl carbazole) (PVK) has a high refractive index of 1.69 [1,2], however, it suffers from poor mechanical strength, and the monomer *N*-vinylcarbazole can be challenging to copolymerize with other monomers. PVK has good charge transporting properties, however, because of its highly conjugated carbazole pendant groups. High-performance photorefractive effects in holography were observed for composite materials based on PVK [3,4]. Dais et al., used conformational calculations to molecularly model syndiotactic pentad sequences and isotactic heptad sequences in order to understand how neighboring pendant carbazole units in PVK may be influencing one another. The syndiotactic pentad assumed a helical configuration. This was similar to the 2/1 helix observed for the syndiotactic sequence from the crystal structure [5,6]. The isotactic heptad approached a 3/1 helix [5–7]. The helical configurations, particularly the 'stacking' of the carbazole pendant groups in the syndiotactic polymer, would allow for many of the interesting electronic and photoconductive properties associated with PVK [5].

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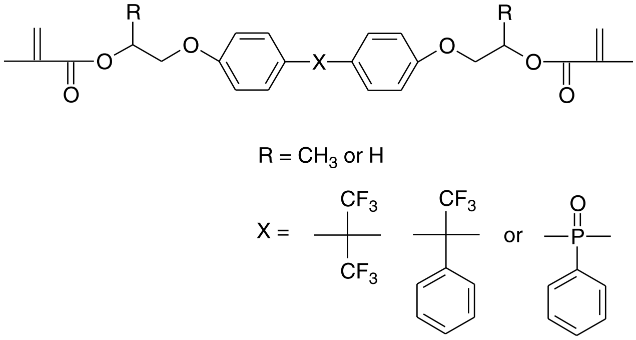
Strohriegl worked extensively with the amidation of polymethacrylates and polyacrylates, including the incorporation of pendant carbazole groups [8–10]. His recent work investigated a novel synthesis for *N*-alkylated 2,7-dibromocarbazoles, using Suzuki cross coupling to produce 2,7-linked carbazole trimers [11]. DuBois was successfully able to polymerize the 11-(*N*-carbazolyl)undecylmethacrylate monomer and investigate the polymers for holographic electro-optical applications [12]. Gaudiana et al., produced high refractive index carbazole based methacrylates and acrylates for optical applications, where the pendant carbazole groups were halogenated. Refractive indices ranged from 1.67 to 1.77 [13]. Carbazole compounds are also efficient electron-transfer photosensitizers for a wide variety of onium salt photoinitiated cationic polymerizations, and polymers containing carbazole compounds are generally very good photosensitizers. Crivello et al., found that the inclusion of even a small amount of a carbazole photosensitizer, such as PVK, was effective in markedly accelerating the photopolymerizations of epoxide and vinyl ether monomers [14,15]. The broadening of the spectral response through the use of these carbazole-based photosensitizers accounted for the rate enhancement of the polymerization reactions. Copolymers of *N*-vinylcarbazole with two vinyl monomers and a dimeric photosensitizer were synthesized and also shown to be efficient photosensitizers [15]. By incorporating tetramethyldisiloxane and vinylcyclohexene oxide, monomer bound carbazole based photosensitizers were prepared with outstanding reactivity in photointiated cationic polymerizations [16].

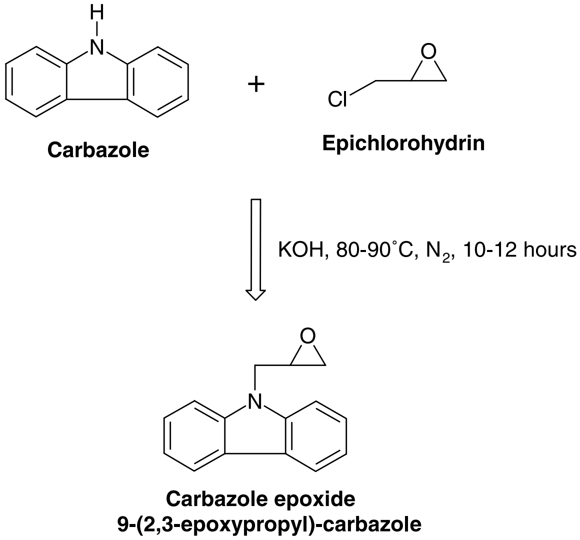
Aromatic dimethacrylates, particularly 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (BisGMA), have been used extensively in dentistry for photocurable fillings [17]. McGrath et al., produced a class of novel aromatic dimethacrylates with no pendant hydroxyl groups, examples of which are shown in Scheme 1 [18–23]. These novel dimethacrylates were much less viscous than BisGMA, making them easier to work with. Additionally, they exhibited less post-cure shrinkage. Many of these polymers produced from the aromatic dimethacrylates also had high refractive indices, so had the potential to be used for near optical applications [18–25].

The incorporation of the hetero-aromatic group carbazole into the methacrylate monomer structure provided for polymers with high refractive indices and other desirable properties [26]. The precursor for the novel methacrylate was 9-(2,3-epoxypropyl)-carbazole, also called carbazole epoxide. Carbazole epoxide was synthesized by the reaction of carbazole with a molar excess of base and epichlorohydrin (Scheme 2). To synthesize the carbazole phenoxy-based methacrylate intermediate, an excess of phenol was added to the carbazole epoxide, neat, in the presence of a catalytic amount of triphenylphosphine (Scheme 3). The intermediate was then reacted slowly with an excess of methacrylic anhydride or methacryloyl chloride at low temperatures, in the presence of triethylamine (TEA) and a catalytic amount of 4-dimethylaminopyridine (DMAP). DMAP is widely used as a hypernucleophilic acylation catalyst [27]. The reaction of the intermediate alcohol with methacrylic anhydride or methacryloyl chloride eliminated any hydroxy groups in the final methacrylate (Scheme 3). The monomer was characterized by high-performance liquid chromatography (HPLC), one- and two-dimensional ^{1}H NMR spectroscopy, Fourier-transform infrared spectroscopy (FTIR), elemental analysis, and DSC for melting point determinations. Ultraviolet–visible (UV–vis) spectroscopy was used to determine the absorption profile of the carbazole phenoxy-based methacrylate monomer in the ultraviolet region.

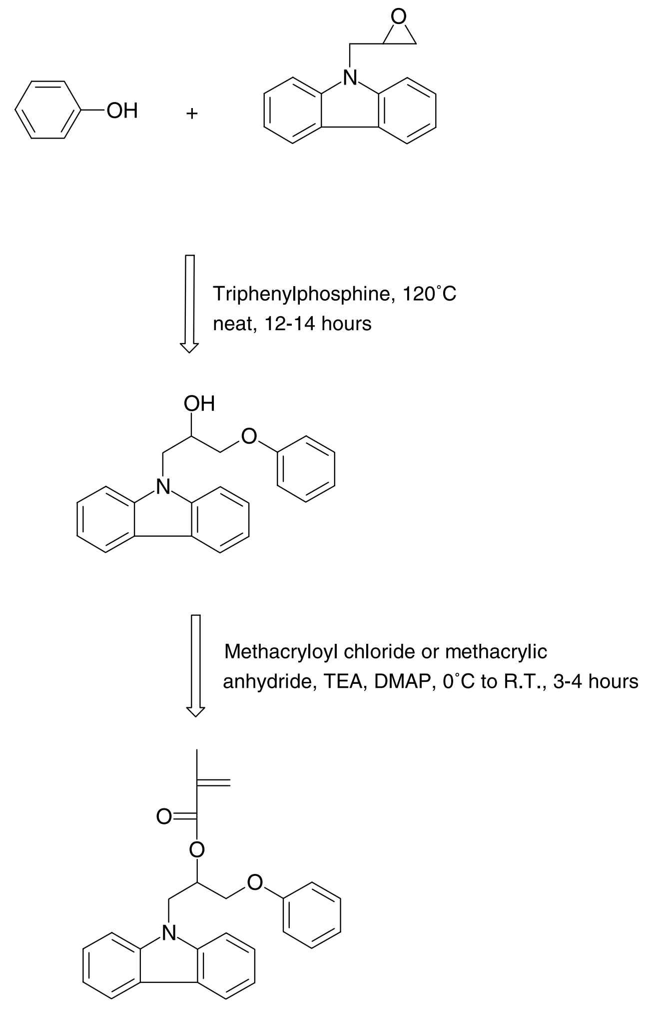
Solution free radical polymerizations were investigated using the thermal initiator 2,2′-azobisisobutyronitrile (AIBN) in *N*,*N*-dimethylacetamide (DMAC). UV photopolymerization polymerizations were investigated using the photoinitiator 1-hydroxycyclohexyl phenyl ketone (Irgacure 184™) in *N*,*N*-dimethylformamide (DMF). Statistical copolymers of carbazole based methacrylates with methyl methacrylate (MMA) were produced using free radical solution polymerizations and photopolymerizations. Refractive index, GPC, NMR spectroscopy, FTIR spectroscopy, DSC, and thermal gravimetric analysis (TGA) were used to characterize the carbazole based homopolymers and copolymers. PhotoDSC was used to determine the heat of polymerization in terms of change in



Scheme 1. Examples of aromatic dimethacrylates with no pendant hydroxy groups.



Scheme 2. Synthesis of 9-(2,3-epoxypropyl)-carbazole.



Scheme 3. Synthesis of the carbazole phenoxy-based methacrylate monomer from phenol and carbazole epoxide.

enthalpy (ΔH_p) for the carbazole phenoxy-based methacrylate. An in situ FTIR experiment followed the free radical solution polymerization of the carbazole phenoxy-based methacrylate. ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and molecular modeling experiments were used to determine the structure and explore the configuration of the carbazole phenoxy-based methacrylate homopolymer.

The incorporation of carbazole and phenol substituents into a novel methacrylate monomer, with subsequent polymerization and copolymerizations, produced high refractive index materials with enhanced optical properties compared to PMMA and bisphenol A polycarbonate. Overall, a system of carbazole based chemistries produced controlled linear materials with high thermal stabilities and good optical properties.

2. Experimental

2.1. Instrumentation

Melting points of the monomers, and glass transitions of the polymers, were determined using a Perkin–Elmer Pyrus 1 differential scanning calorimeter. High-performance liquid chromatography was used to determine monomer purity, with a Perkin–Elmer HPLC, Model 410. UV–vis spectroscopy was performed using a Lambda 40 UV/vis spectrometer. Monomer samples were submitted to Galbraith Laboratories for elemental analysis.

One- and two-dimensional ^{1}H NMR spectra of the intermediates and monomers were obtained on Varian 300 and 400 MHz spectrometers using 5 mm o.d. tubes. ^{13}C noise decoupled NMR spectroscopy was performed on a Varian 400 MHz spectrometer using 10 mm o.d. tubes. Commercial PMMA was obtained from Aldrich ($M_w \sim 120{,}000$ g/mol). Samples were analyzed in $CDCl_3$.

FTIR spectra were obtained using a Nicolet FTIR spectrometer. In situ FTIR experiments were performed using an ASI-FTIR ReactIR™, Model 1000. PhotoDSC experiments were performed using a Perkin–Elmer Pyrus 7 DSC coupled with a double beam photocalorimetric accessory (DPA) and a xenon lamp as the irradiation source. Additional 7.0 mm diameter quartz windows were fitted directly on top of the sample pans to reduce solvent evaporation.

Gel permeation chromatography (GPC) was used to analyze linear polymers using a Perkin–Elmer GPC, Model 200, with a HT 2+4+5 column, and 0.02 M P_2O_5 in *N*-methyl pyrrolidinone (NMP) as solvent. Thermal gravimetric analysis (TGA) of the polymers under nitrogen was determined using a Perkin–Elmer TGA 7. Ground state minimum energy configurations were determined using molecular modeling software. Molecular structures were first drawn in ChemDraw 3D, then imported, and energy minimization performed with the semiempirical PM3 method of the Gaussian 98 molecular modeling program. Refractive indices of the solvent cast polymer films were measured using a Metricon Prism Coupler Instrument, Model 2010.

2.2. Synthesis of the carbazole phenoxy-based methacrylate monomer

2.2.1. Carbazole epoxide

Carbazole epoxide (or 9-(2,3-epoxypropyl)-carbazole) was prepared by first dissolving 40 g carbazole (239 mmol) (Aldrich, purified by dilute HCl wash, followed by recrystallization in methanol) with 500 ml dry, distilled THF, in a 1 l of 3 neck round bottom flask equipped with mechanical stirrer, nitrogen inlet, condenser, and addition funnel. Next, 131 ml epichlorohydrin (1.67 mol; 7-fold molar excess) (Aldrich, used as received) was added to the reaction flask slowly by addition funnel, with rapid stirring. KOH (34 g, 598 mmol; 2.5-fold molar excess) (Fisher, used as received) was then added slowly. After the addition of KOH, the reaction solution changed from clear to turbid. The reaction was allowed to proceed under nitrogen, at 80–90 °C (oil bath), for 12–14 h. Completion of reaction was monitored by TLC (25% ether in hexane). Carbazole had an R_f of 0.47; carbazole epoxide had an R_f of 0.32. The turbid reaction mixture was passed through a Büchner funnel to remove salts, and the salt mass was rinsed with THF and acetone. Solvent was removed from the filtered solution, producing a yellowish white mass. The solid was dissolved in methylene chloride, washed with water, dried again, and recrystallized from methanol. White, pure carbazole epoxide was obtained in 45 g (85.0% yield), with a sharp melting point of 111 °C, which was determined by DSC (30–120 °C at 10 °C/min). By HPLC (C-18 reverse phase column, 60/40 acetonitrile/water), the carbazole epoxide was 98.7% pure. The ^{1}H NMR spectrum had peaks at 2.57, 2.81, 3.34, 4.40, 4.62, 7.23, 7.49, and 8.10 ppm, with expected integration ratios. The results of elemental analysis were 80.12% carbon, 5.91% hydrogen, 6.22% nitrogen, and 7.54% oxygen, which compared well with theoretical values 80.72% carbon, 5.83% hydrogen, 6.28% nitrogen, and 7.17% oxygen. The carbazole epoxide was easily dissolved in many common organic solvents, such as acetone, ether, and methylene chloride. The molar ratio for this reaction was 1 mol carbazole:7 mol epichlorohydrin:2.5 mol KOH. These ratios were maintained for both small and scaled up reactions.

2.2.2. Carbazole phenoxy intermediate

The carbazole phenoxy-based intermediate was produced by reacting 16.6 g (74.5 mmol) carbazole epoxide with 21 g phenol (224 mmol; 3-fold molar excess) (Aldrich, used as received), and 98 mg triphenylphosphine (372 μmol) (Aldrich, used as received), neat, under nitrogen, at 120 °C for 14–19 h. Completion of reaction was monitored by TLC (25% ether in hexane). Carbazole epoxide had an R_f of 0.32, and the carbazole–phenol intermediate had an R_f of 0.48. The excess phenol was removed with good vacuum and mild heat. The final product was a slightly tan solid, which was pulverized into small pieces and vacuum dried further. The carbazole–phenol intermediate was obtained in 21.4 g (90.7% yield). The ^{1}H NMR spectrum had peaks at 2.42, 3.98, 4.52, 4.61, 6.85, 6.99, 7.28, 7.49, and 8.10 ppm, with expected integration ratios. The molar ratio for this reaction was 1 mol carbazole epoxide:2.5 mol phenol:0.005 mol triphenylphosphine. These ratios were maintained for small and scaled up reactions.

2.2.3. Carbazole phenoxy-based methacrylate

The carbazole phenoxy-based methacrylate was produced by dissolving 11.8 g (37.3 mmol) of the carbazole–phenol intermediate in 100 ml dry, distilled methylene chloride, in a two-neck 250 ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and rubber septum. The reaction flask was cooled in an ice/NaCl salt bath under nitrogen. Triethylamine (TEA) (10.4 ml, 74.6 mmol, 2-fold molar excess) (Aldrich, used as received) was added by syringe. Methacrylic anhydride (11.12 ml, l74.6 mmol, 2-fold molar excess) (Aldrich, used as received) was added slowly, drop wise, maintaining temperature below 30 °C throughout the addition. Methacryloyl chloride may also be used rather than methacrylic anhydride. Dimethylaminopyridine (DMAP) (1.86 mmol) (228 mg, Aldrich, used as received) was then added to catalyze the reaction. The reaction proceeded at room temperature for 3–4 h, gradually warming to room temperature as the ice bath melted. Completion of reaction was monitored by TLC (25% ether in hexane). The carbazole–phenol intermediate had an R_f of 0.48, and the carbazole phenoxy-based methacrylate had an R_f of 0.77. The contents of the reaction flask were washed using separatory funnel extraction with distilled, deionized (DD) water, dilute HCL, dilute $NaHCO_3$, and then DD water. The solvent was removed from the organic layer, leaving a very viscous orange liquid. The product was recrystallized with methanol to afford 12.23 g of the carbazole phenoxy functionalized methacrylate (85.2% yield). The final product was white, powdery material with no detectable odor. The carbazole phenoxy-based methacrylate was 98.2% pure by HPLC (C-18 reverse phase column, 80/20 acetonitrile/water). The ^{1}H NMR spectrum had peaks at 1.89, 4.08, 4.65, 4.79, 5.61, 6.08, 6.92, 7.42, 7.58, and 8.08 ppm, with expected integration ratios. Two-dimensional noise decoupled ^{1}H correlated spectroscopy (COSY) was used to help resolve peak assignments. A sharp melting point of 92 °C was determined by DSC (30–120 °C at 10 °C/min). The results of elemental analysis were 77.31% carbon, 6.07% hydrogen, 3.57% nitrogen, and 12.75% oxygen, which compared well to theoretical values of 77.92% carbon, 5.97% hydrogen, 3.64% nitrogen, and 12.47% oxygen. The carbazole phenoxy-based monomer was easily dissolved in many common organic solvents, such as acetone, ether, and methylene chloride. The molar ratio for this reaction was 1 mol carbazole–phenol intermediate:2 mol methacrylic anhydride:2 mol TEA:0.05 mol DMAP. These ratios were maintained for small and scaled up reactions.

2.3. Novel carbazole containing homopolymers and copolymers

2.3.1. General polymerization considerations

The carbazole phenoxy-based methacrylate polymerization was investigated using UV photopolymerization and solution free radical polymerization. All polymerization solvents were vacuum purged, then well purged with nitrogen, several times, or distilled under nitrogen. Copolymers of carbazole phenoxy-based methacrylate and methyl methacrylate were also produced by solution polymerization and photopolymerization. Refractive index, GPC, FTIR, ^{1}H NMR, ^{13}C NMR, DSC, and TGA were used to analyze the polymers.

2.3.2. UV photopolymerization and photoDSC

Carbazole based methacrylate polymer films were produced by photo-induced polymerizations using UV irradiation (300–450 nm) with a suitable photoinitiator, such as 1-hydroxycyclohexyl phenyl ketone (Irgacure 184™, Ciba Specialty Chemicals, used as received). Typically, 2 mol% of photoinitiator was mixed with 1–3 g of methacrylated monomer, or mixtures of monomers, then dissolved in 2–5 ml of nitrogen purged DMF or DMAC. Films were photopolymerized in a custom built, mercury bulb, UV oven in air for 60 min. Copolymers of carbazole phenoxy-based methacrylate and methyl methacrylate were also produced using photopolymerization. Methyl methacrylate (Aldrich) was prepared by passing through either a basic alumina column or an inhibitor removal column (Aldrich).

Modified crimped DSC pans were used for all photoDSC experiments, without lids. To prevent volatiles from escaping, small quartz windows with a diameter of 7.0 mm, which was slightly larger than the pans yet smaller than the diameter of the sample holder for the pans, were placed on top of the sample and reference pans. The photoDSC experiments were performed isothermally at 30 °C, using a UV wavelength of 350 nm. A small quantity, 10 μl of 0.826 M carbazole phenoxy-based methacrylate in DMF, with 2 mol% Irgacure 184™, was placed in the sample using a micropipette. The shutter was closed for the first 3 min of the experiment. After 3 min, the shutter was opened, irradiating both the sample pan and empty reference pan with 350 nm UV light. The shutter was closed again at 30 min (so irradiation time was for 27 min). A background sample was needed to take into account the absorption of the carbazole and phenoxy substituents. The experiment was repeated with 10 μl of 0.826 M, with respect to repeat units, of polymerized carbazole phenoxy-based methacrylate in DMF. The DSC thermogram of the polymer was subtracted from the analogous DSC thermogram of the monomer. The corrected ΔH for the carbazole phenoxy-based methacrylate obtained was -39.4 kJ/mol.

2.3.3. Solution free radical polymerization and in situ FTIR solution polymerization

Polymers of carbazole phenoxy-based methacrylate were polymerized in nitrogen purged DMAC. Typically, several grams of monomer were mixed with 1 or 2 mol% of AIBN. Enough DMAC was added to dissolve the monomer, typically 5–10 ml of nitrogen purged DMAC. The polymerization was performed with rapid stirring in a round bottom flask equipped with a nitrogen inlet between 85–95 °C (hot water bath), for 2 h. The polymerization was allowed to cool slowly to room temperature. Free radical solution polymerizations were also performed in nitrogen purged DMF, with similar results.

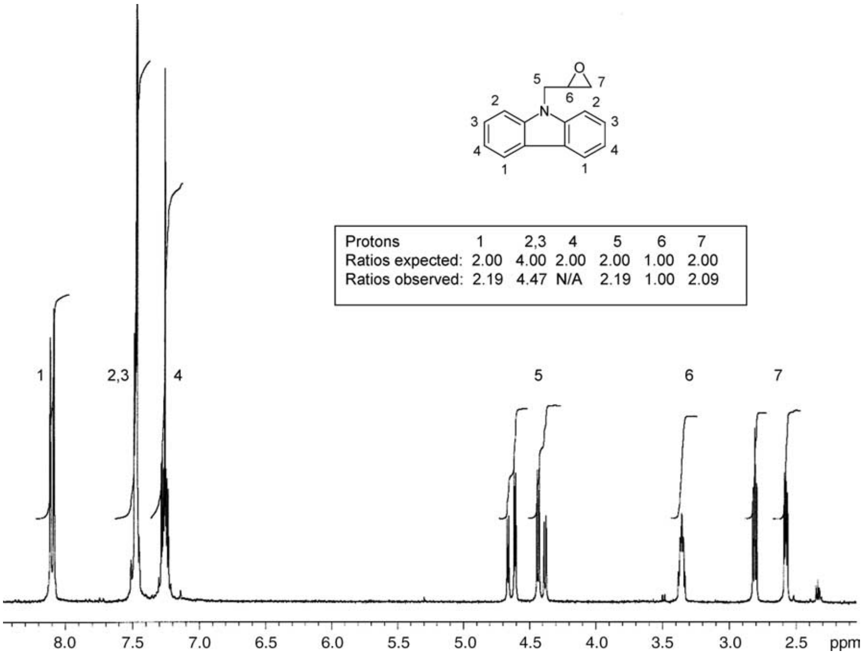
Copolymers of carbazole phenoxy-based methacrylate and methyl methacrylate were produced, in 25/75, 50/50, 72/25 mole percent and weight percent ratios. Polymer films were produced by solvent casting from chloroform or methylene chloride, with a 30 wt% polymer to solvent ratio. Films were dried slowly, then vacuum dried at temperatures slightly above their respective glass transition temperatures.

In situ FTIR was used to follow the free radical, solution polymerization of the carbazole phenoxy-based methacrylate. To the reaction flask, 9 g of carbazole phenoxy-based methacrylate (23.4 mmol) was mixed with 76.8 mg AIBN (468 μmol, 2 mol%), and dissolved in 30 ml nitrogen purged DMAC (30 wt% solids). The reaction was performed at 90–91 °C (hot oil bath), under nitrogen, for 90 min. From the in situ FTIR experiment, the solution free radical polymerization was completed within 40 min.

3. Results and discussion

3.1. Monomer synthesis and characterization

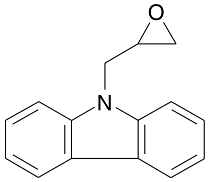
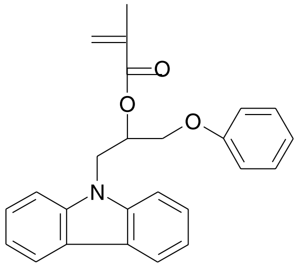
9-(2,3-Epoxypropyl)-carbazole, also called carbazole epoxide, was the precursor for the carbazole phenoxy-based methacrylate. To synthesize carbazole epoxide, carbazole was reacted with a 7-fold molar excess of epichlorohydrin, in the presence of a 2.5-fold molar excess of base, such as KOH, solvated in THF, and reacted under mild conditions (80 °C, nitrogen), for 10–12 h. The base acted as an acid trap, forming water and the KCl salt. Completion of the reaction was easily monitored by TLC. ^{1}H NMR spectroscopy gave expected peaks with expected integration ratios (Fig. 1). The carbazole epoxide had a sharp melting point of 111 °C determined by DSC. The percent yield of the reaction was 85.0%, with a



Protons	1	2,3	4	5	6	7
Ratios expected:	2.00	4.00	2.00	2.00	1.00	2.00
Ratios observed:	2.19	4.47	N/A	2.19	1.00	2.09

Fig. 1. ^{1}H NMR spectrum of carbazole epoxide.

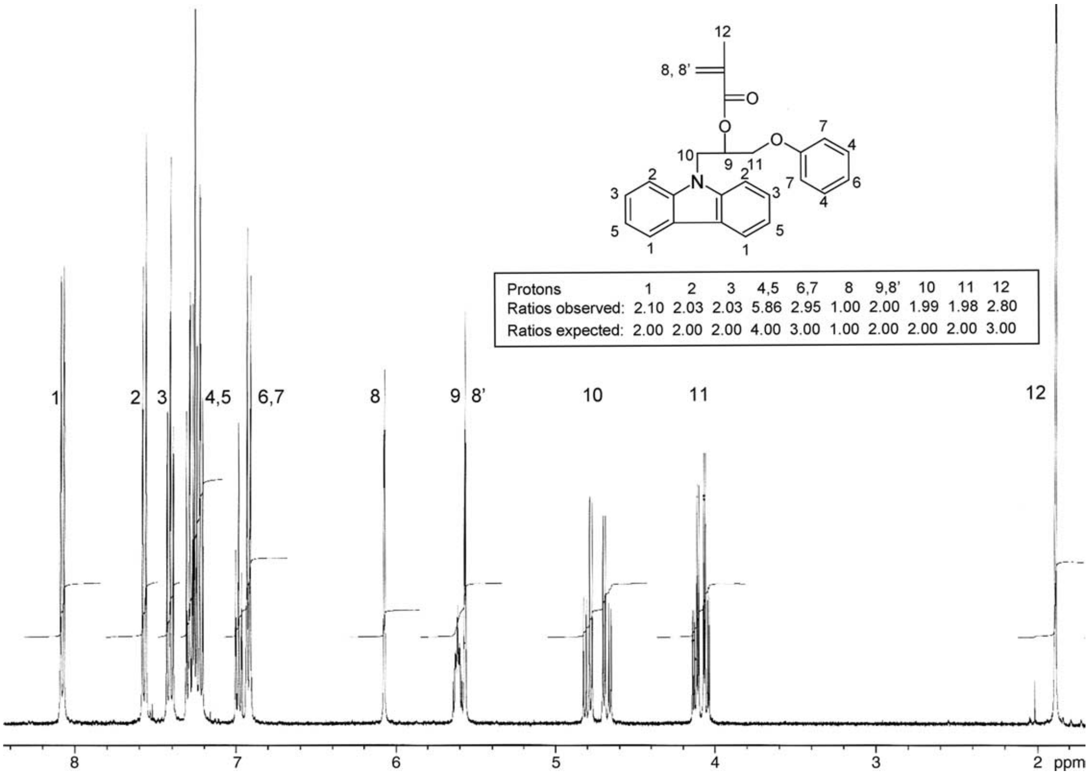
Table 1
Elemental analysis for the carbazole based precursor and carbazole phenoxy functionalized methacrylate

Compound	Element analysis	
	Actual	Theoretical
 Carbazole epoxide	80.12% C 5.91% H 6.22% N 7.54% O	80.72% C 5.83% H 6.28% N 7.17% O
 Carbazole phenoxy methacrylate	77.31% C 6.07% H 3.57% N 12.75% O	77.92% C 5.97% H 3.65% N 12.47% O

purity of 98.7% determined by HPLC. Elemental analysis gave excellent agreement to expected elemental ratios (Table 1).

To synthesize the carbazole phenoxy-based intermediate from the carbazole epoxide, first a large molar excess of phenol was reacted with the carbazole epoxide, in the presence of a catalytic amount of triphenylphosphine, neat, under nitrogen, with moderately high heat (120 °C), overnight. Completion of the reaction was monitored by TLC (25% ether in hexane). Because phenol readily sublimes, purification was straightforward. Good vacuum with slight heat removed excess phenol. The percent yield of the reaction was high, with a 90.7% yield. ^{1}H NMR spectroscopy gave expected peaks with expected integration ratios.

The carbazole phenoxy-based methacrylate was synthesized by the methacrylate reaction with the carbazole phenoxy-based intermediate. A molar excess of either methacrylic anhydride or methacryloyl chloride was added, slowly, to the chilled, methylene chloride solution containing the carbazole phenoxy-based intermediate and TEA. A catalytic amount of DMAP was then added. DMAP is a well known hyper, or super, acylation catalyst [27]. TEA was used as an acid trap. The methacrylate reaction, particularly using methacryloyl chloride, was very exothermic. Low temperature, using an ice/NaCl salt bath, and slow addition of the methacrylating agent reduced the possibility of forming acylation by-products. The reaction was completed relatively quickly, within 3–4 h. Completion of the reaction was monitored by TLC (25% ether in hexane). The carbazole phenoxy-based methacrylate had an R_f of 0.77, which was higher than the 0.48 R_f of the carbazole phenoxy-based intermediate. The enhanced mobility of the methacrylate final product compared to the intermediate product was due to the enhanced polarity of the methacrylate group, which offset the relatively small gain in molecular weight. ^{1}H NMR spectroscopy gave expected peaks with expected integration ratios (Fig. 2). Noteworthy was the absence of a peak at 2.44 ppm due to the loss of the hydroxyl proton after the methacrylate reaction. The methylene protons



Protons	1	2	3	4,5	6,7	8	9,8'	10	11	12
Ratios observed:	2.10	2.03	2.03	5.86	2.95	1.00	2.00	1.99	1.98	2.80
Ratios expected:	2.00	2.00	2.00	4.00	3.00	1.00	2.00	2.00	2.00	3.00

Fig. 2. ^{1}H NMR spectrum of the carbazole phenoxy-based methacrylate.

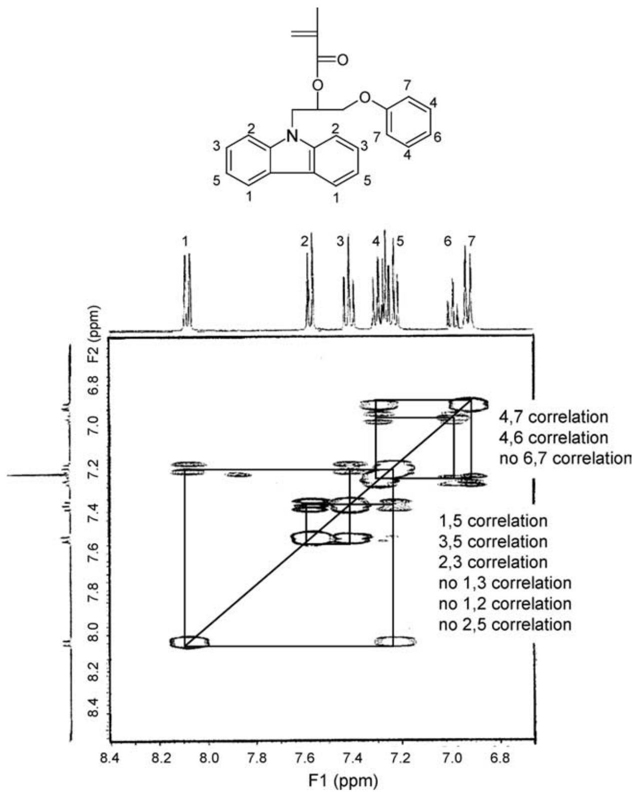


Fig. 3. 2D ^{1}H NMR COSY spectrum of the carbazole phenoxy-based methacrylate, expansion of the aromatic region.

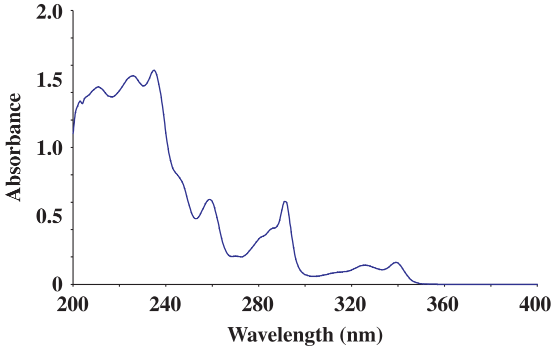


Fig. 4. UV spectrum of the carbazole phenoxy-based methacrylate.

adjacent to the carbazole group (peak 10) and adjacent to the phenoxy group (peak 11) were split, as were the doublet peaks for the vinylic protons (peaks 8,8′). The double bond fixed the positions of the vinylic protons, thus the electronic environment for each proton was not equivalent. For the methylene protons, the steric hindrance from the two large aromatic substituents constrained the molecule, thus the electronic environments for each methylene proton in the methylene adjacent to the carbazole nitrogen and the methylene adjacent to the phenoxy oxygen were not equivalent, and signal splitting was observed. Two-dimensional ^{1}H NMR correlated spectroscopy (2D ^{1}H NMR COSY) was used to resolve peaks in the crowded aromatic region between 8.2 and 6.8 ppm (Fig. 3). The peaks at 8.08, 7.60, 7.42, and 7.25 ppm were definitively determined to correspond to the carbazole substituents. Likewise, the peaks at 7.30, 6.94, and 6.89 ppm corresponded to the phenoxy substituent. The carbazole phenoxy-based methacrylate had a sharp melting point of 92 °C determined by DSC. The monomer was a white, powdery solid (no tack) that was easy to pour, weigh, and manipulate. The percent yield of the methacrylate reaction was 85.2%, with a purity of 98.2% determined by HPLC. Elemental analysis gave excellent agreement to expected elemental ratios (Table 1).

The ultraviolet (UV) spectrum between 200 and 400 nm for the carbazole phenoxy-based methacrylate in shown in Fig. 4. Of concern in any photopolymerization is whether the material itself absorbs light energy, which would in effect block the polymerization. This type of phenomena often produces an undesirable 'skin' type effect, where the topmost layer of a material is photo-cured, and underlying layers remain uncured. Photopolymerization of the novel carbazole based monomers used a medium wavelength mercury UV light source, broadly centered around 305 nm. Fortuitously, above 300 nm, the carbazole phenoxy-based methacrylate had a very low absorbance. The absorbance at lower UV wavelengths, however, was substantial. For this monomer, photopolymerizations conducted at UV wavelengths below 300 nm would be difficult.

3.2. Polymerization of the carbazole phenoxy-based methacrylate

The functionalized carbazole based methacrylate monomer was readily polymerized using photopolymerization and free radical techniques, producing transparent, amber polymer films. The amber color was most likely due to the high concentration of carbazole functionalities in the polymer. Carbazole has a yellow color and is used industrially as a colorant. UV photopolymerization was performed using the photoinitiator 1-hydroxycyclohexyl phenyl ketone (Irgacure 184™). Free radical solution polymerization, using the thermal initiator AIBN, was used to form linear polymers from the carbazole phenoxy-based methacrylate. Copolymers, using methyl methacrylate as a reactive diluent, were also produced using free radical solution polymerization.

3.2.1. UV photopolymerization and photoDSC

Transparent, amber, polymer films of the novel carbazole based methacrylate were synthesized directly using photopolymerization. Medium UV radiation, broadly centered between 300 and 450 nm, was used, with a suitable photoinitiator (Irgacure 184™). To 1–3 g of the monomer was mixed 2 mol% of the Irgacure 184™, dissolved in DMF or DMAC, and then UV irradiated in air in a custom built photo-curing oven. In addition to irradiating the monomer with UV light, the mercury UV lamps in the photo-curing oven also produced a substantial amount of heat. A high boiling solvent, such as DMF, was needed to keep the carbazole based monomers in solution during photopolymerization. After 60 min of UV irradiation, along with the associated heat, the DMF was evaporated, leaving behind transparent polymer films in the photo-curing oven.

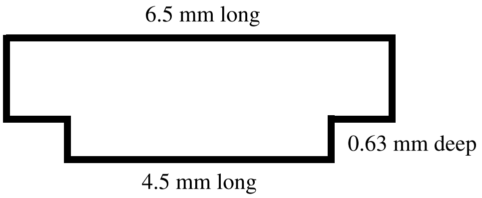


Fig. 5. Cross section of modified aluminum DSC sample pan for photoDSC experiments.

Photodifferential scanning calorimetry (photoDSC) was used to monitor the rapid exothermic heat of polymerization release for the carbazole phenoxy-based methacrylate. A Perkin–Elmer DSC 7 was used, which was equipped with a double beam photocalorimetric accessory (DPA) and a short-arc xenon lamp of 450 W. A shutter, which was manually controlled, allowed light to radiate the sample when opened. A wavelength of 350 nm was chosen on the monochrometer. The photopolymerizations were performed in modified aluminum pans (Fig. 5). In order to reduce drift from the evaporation of the solvent DMF during the photoDSC experiments, small quartz windows 7.0 mm in diameter were made, which fit directly over the modified sample pans of 6.5 mm in diameter. Before performing the experiment on the monomer, the light intensity at 350 nm was determined using this photoDSC apparatus. Graphite discs, which absorbed UV radiation, were inserted into the sample holder. The difference of the heat flow (mW) between the light on (shutter open) and the light off (shutter closed), divided by the area, gave the light intensity at the sample surface (Eq. (1)). The light intensity for the photoDSC at 350 nm was calculated to be 1.63 mW/cm^2. Unlike the UV photo-curing oven, the reaction conditions during the photoDSC experiments were very controlled. A distinct wavelength of 350 nm UV light, rather than a broad UV range of radiation, was used for the analysis. Additionally, the temperature for the photoDSC samples was isothermally maintained at 30 °C throughout the photoDSC experiments.

Calculation of light intensity

$$\text{Light intensity} = \frac{\text{mW}_{(\text{light on})} - \text{mW}_{(\text{light off})}}{\text{light area in sample pan (cm}^2)} \tag{1}$$

$$\text{Light intensity} = \frac{0.65\ \text{mW}}{0.40\ \text{cm}^2} = 1.63\ \text{mW/cm}^2$$

For the photoDSC experiment, 20 µl of the sample solution was placed in the modified sample pan, using a micropipette. An empty modified pan, also fitted with a quartz window, was placed in the reference cell. The sample solution contained 0.826 M carbazole phenoxy-based methacrylate in DMF, with 2 mol% Irgacure 184™. At the beginning of the experiment, the shutter was closed (light off) to establish a baseline. After 3 min, the shutter was opened, and the sample was irradiated for 27 min. The shutter was closed again from 30 to 33 min to reestablish the baseline. The baseline after the large exothermic curve was lower than the baseline for the initial light-off position. This was caused from the absorbency of the carbazole and phenoxy substituents in the monomer, and from some drift due to slight evaporation of DMF during the photoDSC experiment. Even with the retrofitted quartz windows on the modified sample pans, there was still some evaporation of DMF. To take these artifacts into account, the photoDSC experiment was repeated using a solution of the (already) polymerized carbazole phenoxy-based methacrylate, in the same concentration with respect to repeat units, in DMF (Fig. 6). The DSC profile of the carbazole phenoxy-based methacrylate polymer was subtracted from the DSC profile of the monomer, to produce an accurate measurement of the exotherm for the photopolymerization (Fig. 7).

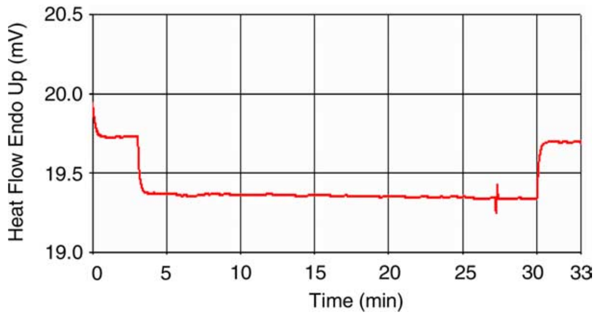


Fig. 6. PhotoDSC thermogram of polymer of carbazole phenoxy-based methacrylate.

The enthalpy, or heat, of polymerization (ΔH_p) was calculated from the area of the exotherm, relative to the baseline (light off), and converted to kJ/mol (Eq. (2)). The ΔH_p for the carbazole phenoxy-based methacrylate was −39.4 kJ/mol, which compared to −54.8 kJ/mol for methyl methacrylate [28]. The extent of the reaction (E_p) was determined by the percentage ratio of the ΔH_p of the methacrylate to the ΔH_p of methyl methacrylate (Eq. (3)). The extent of the photopolymerization reaction was 71.9% for the carbazole phenoxy-based methacrylate. PhotoDSC provided for an excellent method to capture, in real time, the rapid photopolymerization exotherm of the carbazole phenoxy-based methacrylate.

Calculation of enthalpy conversions

$$\begin{aligned}&[\text{Exp. } \Delta H_p \text{ (J/g sample)}](\text{wt. total sample/wt. monomer})\\ &\quad(\text{molecular wt. monomer}) = \Delta H_p(\text{J/mol})\end{aligned} \tag{2}$$

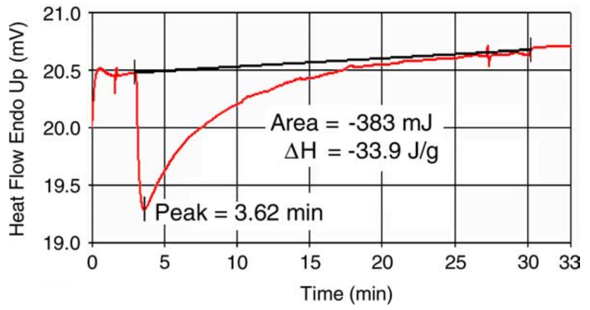


Fig. 7. Corrected photoDSC thermogram for the carbazole phenoxy-based methacrylate.

$$-33.886\ \text{J/g sample}\ (1.163\ \text{g sample}/0.385\ \text{g monomer})$$

$$(385\ \text{g/mol})$$

$$= -39,409\ \text{J/mol (monomer)} = -39.4\ \text{kJ/mol (monomer)}$$

Calculation of extent of reaction

$$E_{\mathrm{p}} = \frac{\Delta H_{\mathrm{p(methacrylate)}}}{\Delta H_{\mathrm{p(methyl\ methacrylate)}}} \times 100\% \tag{3}$$

$$E_{\mathrm{p}} = \frac{-39.4\ \text{kJ/mol}}{-54.8\ \text{kJ/mol}} \times 100\% = 71.9\%$$

3.2.2. Free radical solution polymerization and in situ FTIR

Linear polymers derived from carbazole phenoxy-based methacrylate were readily polymerized by dissolving the monomer in nitrogen purged DMAC, and using 1–2 mol% AIBN as the thermal free radical initiator. Polymerizations were conducted under nitrogen in order to exclude oxygen. Reaction temperatures were between 85 and 95 °C in a preheated oil or hot water bath for approximately 2 h. The polymerizations were allowed to cool slowly to room temperature. The polymers were precipitated into chilled methanol, filtered, and vacuum dried. For the carbazole phenoxy-based methacrylate polymerized in DMAC, with 1 mol% AIBN, the ⟨Mn⟩ was 58,900 g/mol, with a polydispersity of 3.3. The polymer produced good transparent films, with a slight amber color, which were used to measure the refractive index. Polymer films were solvent cast from chloroform or methylene chloride, with a 30 wt% polymer to solvent ratio, dried slowly at room temperature, then vacuum dried slightly above respective glass transition temperatures.

Solution free radical polymerization was the best method for producing good, linear polymers and statistical copolymers from the carbazole phenoxy-based methacrylate. The polymers and copolymers produced using this method had quantitative yields, and for the most part, high molecular weights with relatively low polydispersities. These polymers were analyzed for thermal properties, such as degradation temperatures and glass transition temperatures. Solvent cast films were easily produced, which could then be analyzed for physical properties such as refractive index. The carbazole phenoxy-based methacrylate/methyl methacrylate (PCPM/PMMA) copolymer series were very useful in showing trends in terms of refractive index and thermal degradation behavior.

The free radical solution polymerizations were allowed to progress for about 2 h, but from observing changes in viscosity within the polymerization flask, the polymerizations appeared to be finished much sooner. In situ Fourier transform infrared (FTIR) spectroscopy was then used to follow the rate at 90 °C, under nitrogen, for a relatively large scale free radical polymerization of the carbazole phenoxy-based methacrylate:9 g (23 mmol) carbazole phenoxy-based methacrylate with 2 mol% AIBN in 30 ml DMAC (30 wt% monomer). Before the in situ FTIR experiment was performed, however, FTIR spectra were obtained for both the carbazole phenoxy-based methacrylate monomer and polymer, and for the solvent, DMAC, used in the solution polymerization. Fig. 8 shows the FTIR spectra for these three components. A window of low absorbance in the solvent spectrum in either the 3200–2800 $\mathrm{cm^{-1}}$ range, or around 817 $\mathrm{cm^{-1}}$ was necessary in order to follow the reaction. The peak close to 2900 $\mathrm{cm^{-1}}$ corresponds to the aliphatic C–H stretch, while the peak close to 3100 $\mathrm{cm^{-1}}$ corresponds to the vinyl C–H stretch [29]. Unfortunately, the absorbance from the solvent absorbed highly in this area of the spectrum, so it could not be monitored during the in situ FTIR experiment. The area around 817 $\mathrm{cm^{-1}}$

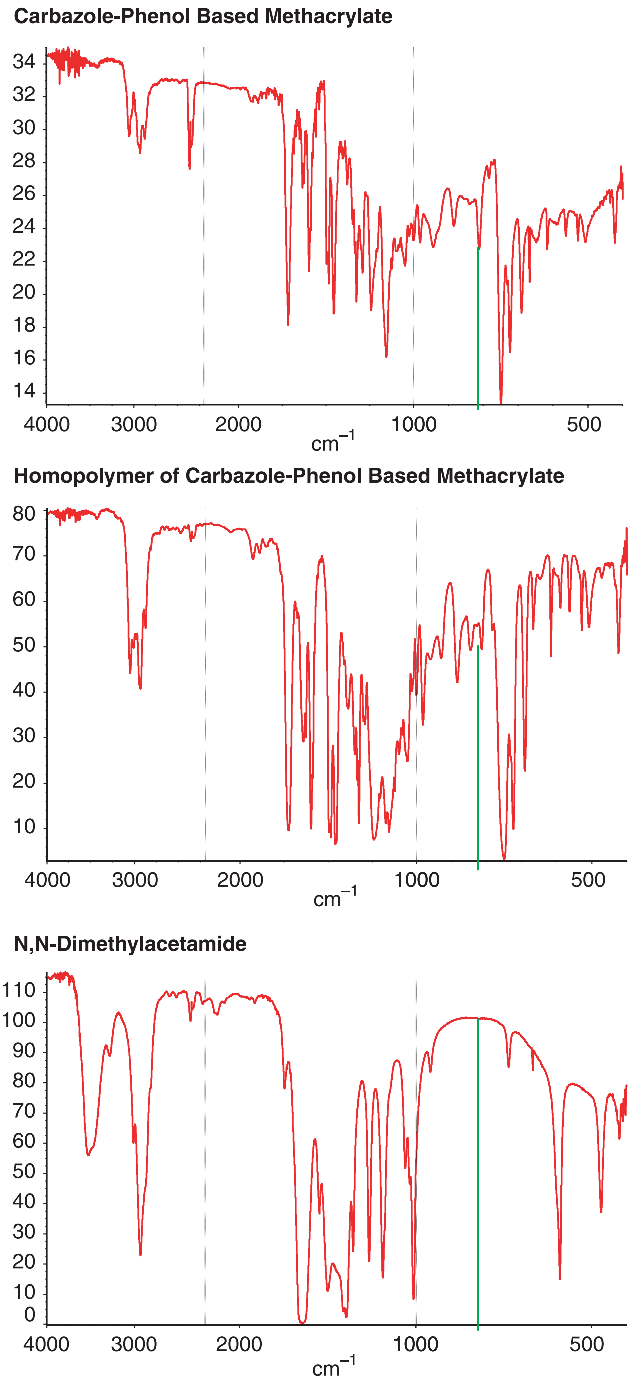


Fig. 8. FTIR spectra for the carbazole phenoxy-based methacrylate polymer, monomer, and the solvent DMAC.

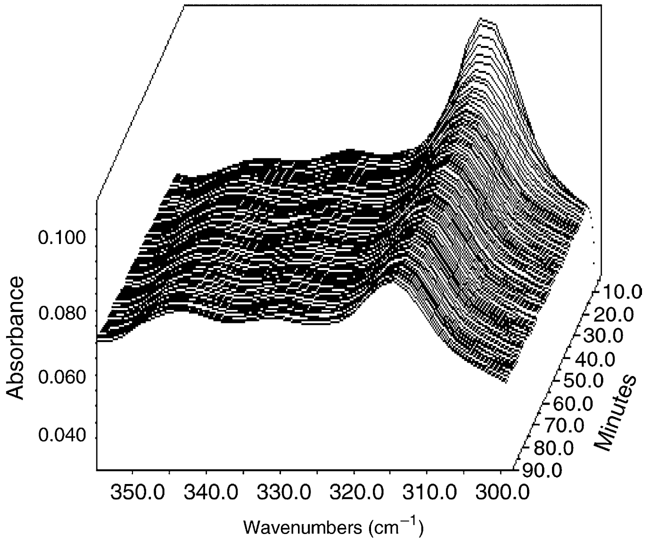


Fig. 9. In situ FTIR experiment following free radical solution polymerization of carbazole phenoxy-based methacrylate, expanded around 817 (cm^{-1}).

corresponds to the C–H wag [29]. Fortuitously, around 817 cm^{-1}, the solvent had very low absorbance. The C–H wag around 817 cm^{-1} reduced in intensity as the double bonds of the methacrylate were converted to the single bonds of the polymer. This peak was used to dynamically monitor the polymerization of the carbazole phenoxy-based methacrylate. In situ FTIR spectroscopy allowed for the solution free radical polymerization of the carbazole phenoxy-based methacrylate to be closely monitored in real time. Following the C–H acrylate wag at 817 cm^{-1}, the polymerization was essentially complete, under these reaction conditions, after 35 min. The polymerization reaction was quantitative (99+% yield). Fig. 9 shows the 'waterfall' depiction, expanded around 817 cm^{-1}, and Fig. 10 follows the absorbance at 817 cm^{-1} as a function of time. Using in situ FTIR spectroscopy, the polymerization reaction of the carbazole phenoxy-based methacrylate was unequivocally determined to be complete within a short amount of time, well within 40 min.

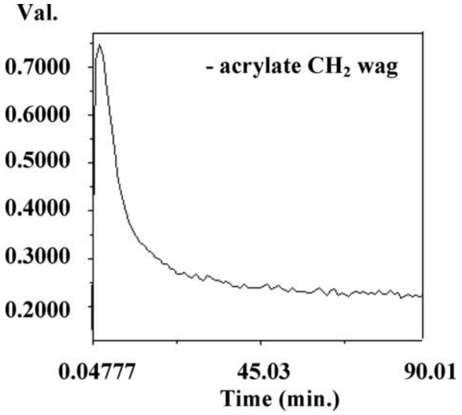


Fig. 10. In situ FTIR experiment for carbazole phenoxy-based methacrylate, following FTIR peak at 817 (cm^{-1}).

3.3. Refractive index of homopolymers and copolymers of PCPM and PMMA

The carbazole phenoxy-based methacrylate homopolymer and copolymers with methyl methacrylate were analyzed for refractive index using a Metricon 2010 Prism Coupler Instrument. Refractive index determination using the Metricon 2010 Prism Coupler Instrument is an extremely precise technique, with a refractive index accuracy of +0.001 [30]. All of the polymer films were solvent cast from methylene chloride (30 wt% polymer to solvent), dried slowly, and then vacuum dried above their glass transition temperatures. 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 poly(carbonate) [1]. PMMA, in comparison, has a refractive index of only 1.49 [1]. The 25/75, 50/50, and 75/25 wt % compositions and mole percent compositions of copolymers of carbazole phenoxy-based methacrylate and methyl methacrylate were also analyzed for refractive index (Table 2). Refractive index determinations were performed in triplicate, and standard deviations were less than 0.001 on all polymer samples tested. The refractive index of the carbazole phenoxy-based methacrylate homopolymer was measured on films from both 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, NJ, USA. 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, weight to weight compositions correlated more than mole to mole compositions for optical properties such as refractive index.

3.4. Thermal characterization

Differential scanning calorimetry was used to determine glass transition temperatures (T_g) of the linear carbazole phenoxy-based methacrylate polymers and copolymers with methyl methacrylate. Thermal gravimetric analysis was used to determine degradation temperatures based on weight loss for the carbazole phenoxy-based methacrylate polymers and copolymers. These polymers, particularly the homopolymer of the carbazole phenoxy-based methacrylate, had remarkably high degradation temperatures. ^{13}C NMR spectroscopy was

Table 2
Refractive index for homopolymers and copolymers of PCPM and PMMA

% PCPM	RI (wt%)	RI (mol%)
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

Table 3
Thermal glass transition temperatures for weight and mole percent homopolymers and copolymers of PCPM and PMMA

Composition	T_g (°C)	
	Wt%	Mol%
100% PMMA	106	106
25/75 PCPM/PMMA	117	102
50/50 PCPM/PMMA	94	117
75/25 PCPM/PMMA	114	117
100% PCPM	123	123

used to explore, structurally, the reason for these high degradation temperatures. Molecular modeling was also used to investigate the structure of the carbazole phenoxy-based methacrylate polymer.

Using DSC, the carbazole phenoxy-based methacrylate had a T_g of 123 °C, which compared to a T_g of 106 °C for the lab-scale PMMA that was made under the same solution polymerization conditions. Table 3 summarizes the thermal glass transition temperatures for both the weight percent series and mole percent series of the PCPM/PMMA homopolymers and copolymers. In terms of T_g, no linear trends were apparent with respect to composition for either copolymer series, due to probable fluctuations in molecular weight. Because of the small scale of each polymerization (typically 2–3 g batch sizes) a very slight difference in the amount of initiator would create a variance in the final molecular weights of the polymers and copolymers. The films were vacuum dried above 125 °C overnight, removing any residual solvent. Noteworthy was the presence of a single glass transition temperature in each of the PCPM/PMMA copolymers, which indicated that these materials were statistical copolymers.

TGA was performed between 50 and 700 °C under nitrogen. The TGA thermogram for the carbazole phenoxy-based methacrylate homopolymer is shown in Fig. 11. The onset of degradation for the homopolymer of carbazole phenoxy-methacrylate was 316 °C, with 5% weight loss at 359 °C. In comparison, the onset of degradation for the homopolymer of methyl methacrylate was 218 °C, with 5% weight loss at 303 °C. Both the weight percent and the mole percent copolymer series were analyzed. Table 4 displays the TGA results with respect to onset of degradation and with respect to 5% weight loss. The weight percent copolymer series, particularly with respect to onset of degradation, produced a more linear correlation between percent composition and decomposition temperatures than the mole percent copolymer series. Because of the large molecular weight difference between the two monomers, weight-to-weight compositions correlated more than mole to mole compositions for physical properties such as thermal degradation. The onset of thermal degradation for the carbazole phenoxy-based methacrylate homopolymer was well above 300 °C. The thermal stability of this polymer may prove very useful commercially, not only for processing and for optical applications, but also for applications such as electronics, where heat stability is a fundamental requirement.

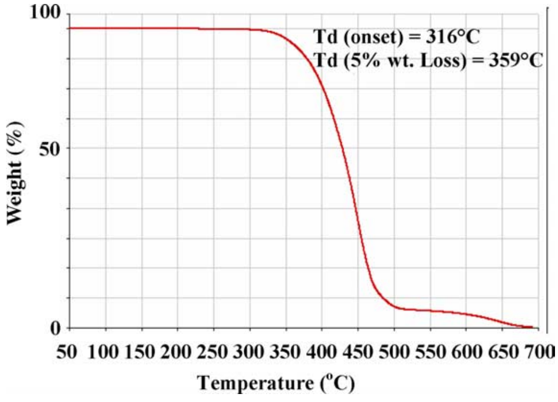


Fig. 11. TGA for the carbazole phenoxy-based methacrylate polymer.

Table 4
Thermal decomposition temperatures for homopolymers and copolymers of PCPM and PMMA

Composition	Thermal degradation temperatures			
	T_{onset} (°C)		$T_{5\%wt.\ loss}$ (°C)	
	Wt%	Mol%	Wt%	Mol%
100% PMMA	218	218	303	303
25/75 PCPM/PMMA	233	239	317	334
50/50 PCPM/PMMA	289	306	350	360
75/25 PCPM/PMMA	274	324	356	381
100% PCPM	316	316	359	359

3.5. ^{13}C NMR spectroscopy and molecular modeling

The particularly high degradation temperature of the carbazole phenoxy-based methacrylate was a surprising phenomenon, particularly compared to PMMA. For methacrylate polymerizations, the majority of additions to the polymer chain are a head-to-tail placement, also called a 1,3-placement of monomer units. A small portion of the additions, however, results in a head-to-head placement, also called 1,2-placement of monomer units. The head-to-tail propagation predominates in chain polymerizations, comprising about 95+% of the repeat unit structure for PMMA [31]. The small amount of head-to-head linkages typically contributes to the onset of thermal degradation. In effect, the head-to-head linkages, and the subsequent tail-to-tail linkages, are the weak links within the polymer chains, which undergo scission. This scission leads to rapid chain degradation. Because the carbazole phenoxy-based methacrylate is so sterically hindered, head-to-head addition should be virtually impossible. The polymer composition of only head-to-tail linkages could explain why the thermal degradation was so high. Noise decoupled ^{13}C NMR spectroscopy was used to explore this hypothesis with the carbazole phenoxy-based methacrylate polymer.

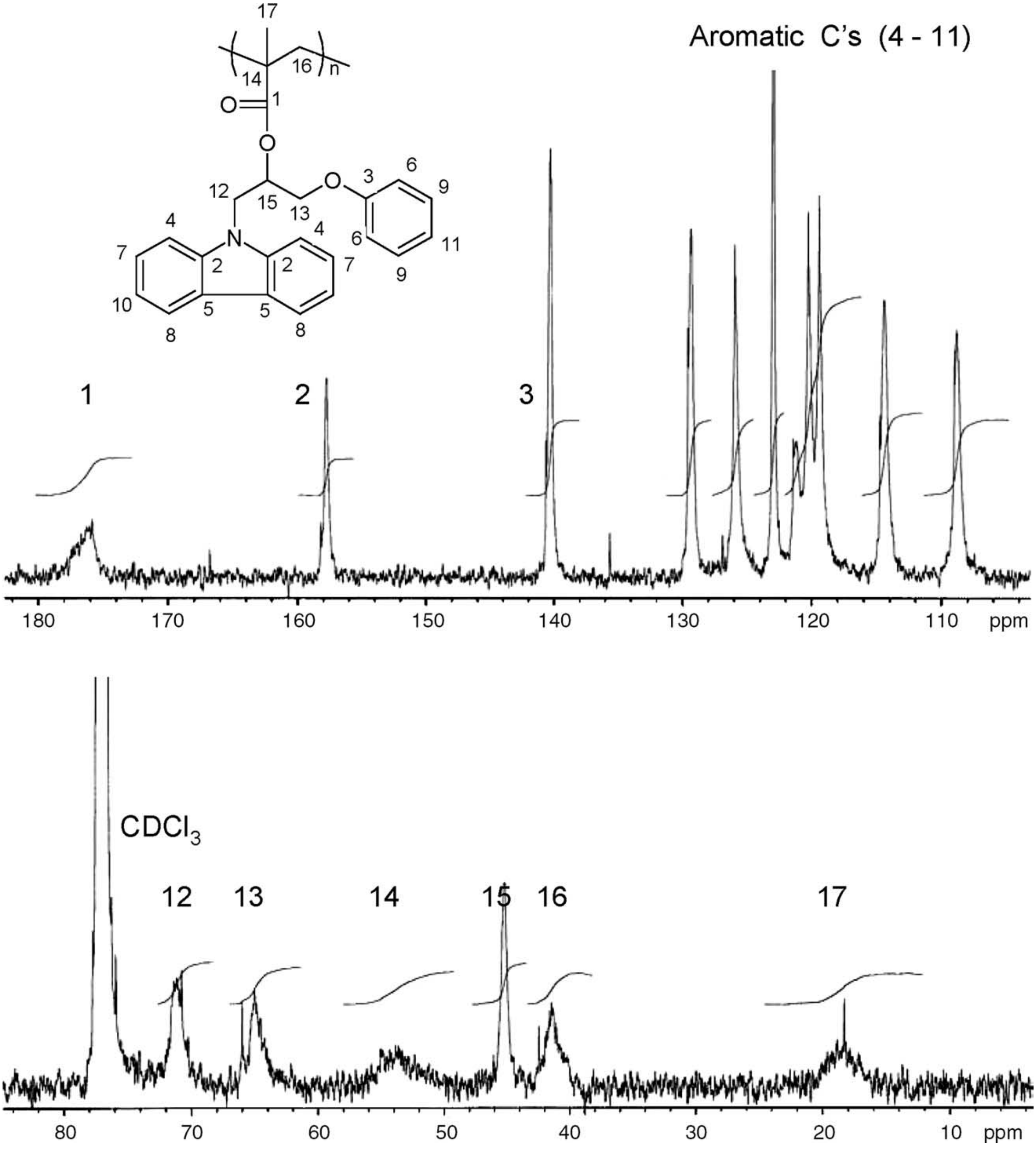
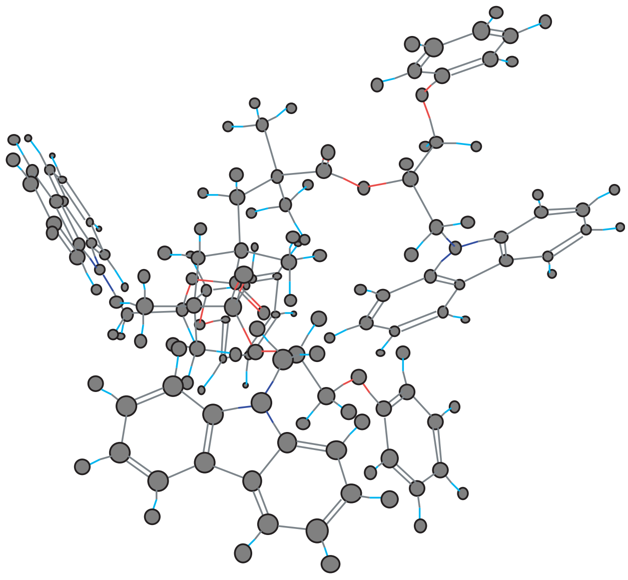


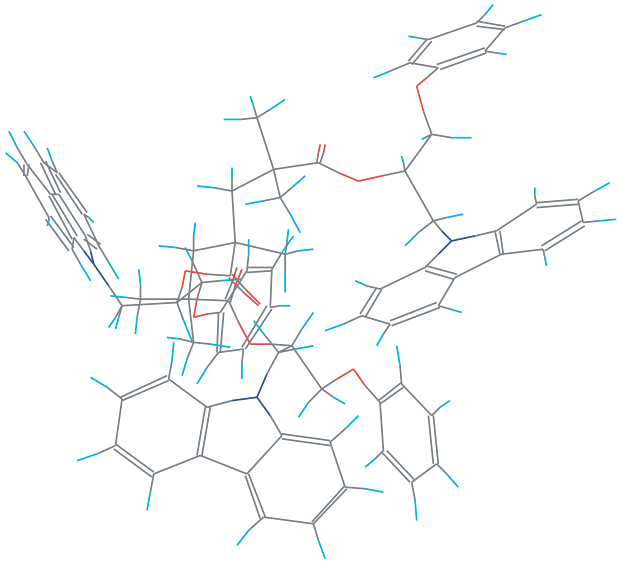
Fig. 12. ^{13}C NMR spectrum of the carbazole phenoxy-based methacrylate polymer.

Fig. 12 shows the ^{13}C NMR spectrum for the carbazole phenoxy-based methacrylate homopolymer. Noteworthy was the absence of peaks between 20 and 22 ppm. No peaks could be found for the isotactic triad stereoisomerization (mm) or for the head-to-head placement using this NMR technique. The carbazole phenoxy-based methacrylate polymer did not dissolve well into the deuterated chloroform, however, so the signal-to-noise ratio was low and the peaks were broad, which decreased sensitivity. This experiment was not unequivocal proof, but nonetheless, was limited evidence that the carbazole phenoxy-based methacrylate contained no detectable isotactic triad configurations or head-to-head linkages within the polymer chains. The absence of head-to-head linkages would provide for a methacrylate with high degradation temperatures, as was observed with the carbazole phenoxy-based methacrylate homopolymer.

^{13}C NMR analysis of the carbazole phenoxy-based methacrylate polymer did provide additional evidence as to



Ball-and-stick Depiction

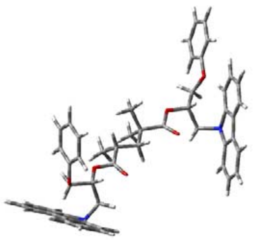


Stick-only Depiction

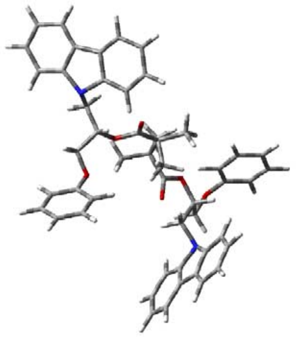
Fig. 13. Minimum energy configurations using molecular modeling (Gaussian 98) of three repeat units of the carbazole phenoxy-based methacrylate polymer.

the structure of this highly functionalized polymer. The peak at 176 ppm corresponded to the carbonyl carbon. Ten aromatic carbon peaks between 80 and 160 ppm corresponded to the 10 equivalent carbon atoms from both the carbazole and phenoxy substituents. The peak at 71.5 ppm corresponded to the methylene carbon adjacent to the carbazole group. The peak at 65 ppm corresponded to the methylene carbon adjacent to the phenoxy group. The peak at 53.5 ppm corresponded to the methylene carbon of the methacrylate group. The sharp peak at 45 ppm corresponded to the methine carbon. The peak at 41 ppm corresponded to the quaternary carbon of the methacrylate group. The peak at 18.5 ppm corresponded to the methyl group of the methacrylate group. The methyl peak was very broad, so tacticity was not able to be reliably determined using this analytical method. Because of the large size of the aromatic carbazole and phenoxy substituents, the carbazole phenoxy-based methacrylate polymer was probably configured with a syndiotactic tacticity. Molecular modeling was used to explore the structure of the carbazole phenoxy-based methacrylate polymer further.

Molecular modeling using Gaussian 98 software was employed to investigate the ground state minimum energy configurations for three repeat units of the carbazole phenoxy-based methacrylate polymer. Molecular structures were first drawn in ChemDraw 3D, then imported, and energy minimization performed with the semiempirical PM3 method of the Gaussian 98 molecular modeling program. Molecular modeling provided some insight into the structures of these compounds, from a Maxwell demon point of view. Fig. 13 shows the three-dimensional, minimum energy configuration of three repeat units of the carbazole phenoxy-based methacrylate polymer. Of interest was how the carbazole and phenoxy rings were arranged around the polymer chain, in a stacked, somewhat helical fashion. Due to the bulkiness and steric hindrance of these large, aromatic substituents, the aromatic groups in the final rod-like polymer should be very ordered. This helical structure, due theoretically to high order from lack of space for the aromatic groups to freely rotate, may provide the final polymer with ring current effects, which could



H-T Linkage, 2 Repeat Units
E(RHF) = -2465.09663844 A.U.
$E_{\text{Nuclear Repulsion}}$ = 7723.79 Hartrees



H-H Linkage, 2 Repeat Units
E(RHF) = -2464.99550886 A.U.
$E_{\text{Nuclear Repulsion}}$ = 8019.26 Hartrees

Δ E(RHF)$_{\text{H-T – H-H}}$ = -0.10113 A.U.
Δ E$_{\text{Nuclear Repulsion (H-T – H-H)}}$ = -296 Hartrees

Fig. 14. Molecular modeling for two repeat units of the carbazole phenoxy functionalized methacrylate polymer.

prove useful in electronic applications and in non-linear optics. This is somewhat analogous to the structure of PVK investigated by Dais et al. [5], so this polymer would be expected to have properties similar to PVK. Molecular modeling provided for a fascinating, three-dimensional glimpse into the hypothetical structure of this highly functionalized polymer.

The head-to-head and head-to-tail linkages of the carbazole phenoxy-based methacrylate were investigated using energy minimization with the semiempirical PM3 method of the Gaussian 98 molecular modeling program (Fig. 14). As a control, analogous molecular modeling was also performed for the head-to-head and head-to-tail linkages for PMMA (Fig. 15). For both polymers, the difference between head-to-head and head-to-tail linkages of the ground state minimum energy configuration was minimal, however, the difference between head-to-head linkages for the minimum energy configurations in terms of nuclear repulsion energy was quite significant. The head-to-tail polymerization of PMMA predominates, with about 95+% its structure composed of head-to-tail linkages, and this is with the theoretical nuclear repulsion energy of the head-to-tail structure 82 Hartrees less than the head-to-head structure. The head-to-tail structure of the carbazole phenoxy-based methacrylate polymer was determined to be 296 Hartrees less than the head-to-head structure, in terms of nuclear repulsion energy. One Hartree equals 627.5095 kcal/mol. This is very strong theoretical evidence that the formation of head-to-head linkages in the carbazole phenoxy-based methacrylate polymer would be very unlikely due to nuclear repulsion from steric hindrance. The absence of head-to-head linkages would explain the remarkably high decomposition temperatures observed for the carbazole phenoxy-based methacrylate polymer.

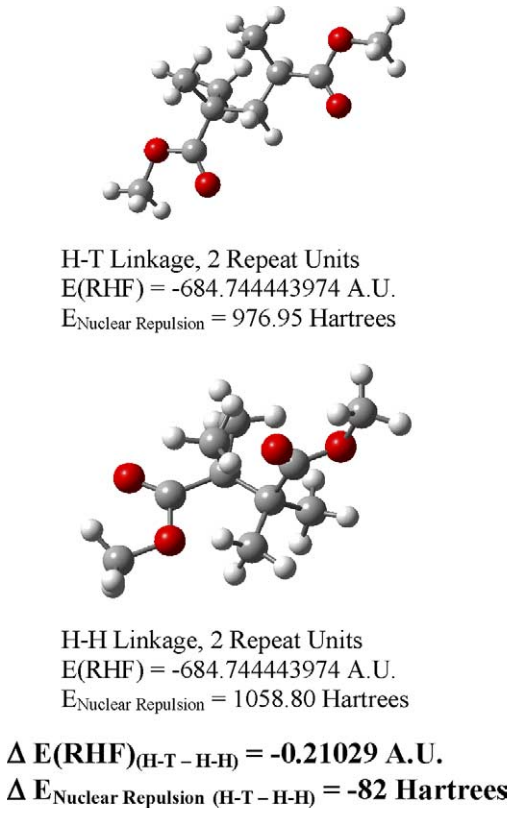


Fig. 15. Molecular modeling for two repeat units of PMMA.

The carbazole phenoxy-based methacrylate materials formed good transparent films. The carbazole phenoxy-based methacrylate homopolymer had a high refractive index of 1.63, which was well above the refractive index of PMMA and state-of-the-art bisphenol A polycarbonate. When polymerized under mild conditions, the carbazole phenoxy-based methacrylate formed linear polymers, which were solvent cast into films and conceivably could be processed into many other shapes. These materials could find commercial use as high refractive index materials for optical applications. An advantage of the carbazole phenoxy-based methacrylate compared to vinyl carbazole was the ease with which it copolymerized with methyl methacrylate.

4. Conclusions

A novel, highly aromatic, carbazole based methacrylate was readily synthesized using a three step reaction mechanism. First, the precursor, carbazole epoxide, was synthesized by reacting carbazole with an excess of epichlorohydrin in the presence of base, such as KOH. In the second step, the carbazole epoxide was reacted with an excess of phenol. In the final step, the carbazole based intermediate was reacted with methacryloyl chloride or preferentially, methacrylic anhydride, to produce the highly functionalized carbazole based methacrylate monomer.

DSC was used to determine the melting point of the carbazole phenoxy-based methacrylate monomer, ^{1}H NMR was performed on the monomer and intermediates, with expected peaks and integration ratios, and 2D COSY ^{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) and the carbazole phenoxy-based methacrylate (98.2% pure). In addition, elemental analysis was performed on carbazole epoxide and the novel carbazole based monomer, with excellent agreement with respect to atomic composition.

Transparent films of homopolymers and copolymers of the carbazole phenoxy-based methacrylate and methyl methacrylate were produced using both photopolymerization and free radical solution polymerization techniques. Under the milder reaction conditions of solution polymerization, linear carbazole phenoxy-based methacrylate polymers were produced, which could be fully characterized. The ΔH_p for the carbazole phenoxy-based methacrylate was determined using photoDSC. The ΔH_p was determined to be -39.4 kJ/mol, after correcting for the absorbance from the carbazole functionality. This compared to a ΔH_p of -54.8 kJ/mol 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™ by following the acrylate

C–H wag at 817 cm^{-1} as a function of time. 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 min.

The refractive index of the novel carbazole based methacrylate was 1.63, which was above the refractive index of 1.58 for bisphenol A based poly(carbonate), and well above the refractive index of 1.49 for poly(methyl methacrylate). The copolymers of the carbazole phenoxy-based methacrylate and methyl methacrylate had linear trends in terms of refractive index and percent weight composition.

Using differential scanning calorimetry, the T_g 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. Using thermal gravimetric analysis, the carbazole phenoxy-based methacrylate homopolymer had a remarkably high decomposition temperature. 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 °C, with a 5% weight loss at 303 °C, for PMMA. This thermal stability was determined to be due to the lack of head-to-head linkages in the final carbazole based 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. Head-to-head configurations were determined, using molecular modeling, to have a much higher nuclear repulsion energy than the head-to-tail linkages. The molecular structure of the carbazole phenoxy-based methacrylate polymer, composed of only head-to-tail linkages and no head-to-head linkages, would explain the high thermal stability. The phenoxy groups and 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 was also evident from the signal splitting observed in the ^{1}H NMR spectrum of the monomer. NMR spectroscopy and molecular modeling clearly showed that these aromatic functionalities are extremely restricted in terms of free rotation. 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 pendant to the polymer chain.

Overall, these carbazole based homopolymers and copolymers are very well suited for optical applications. 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 PVK for non-linear optics and holographic applications. Poly(methyl methacrylate), among its myriad applications [32], is also used as a substrate in lithography [33], microlithography [34], and microcontact printing [35]. A profound advantage of the carbazole phenoxy-based methacrylate compared to vinyl carbazole is the ease with which it copolymerizes with methyl methacrylate. The optical properties of the carbazole phenoxy-based methacrylate polymer, coupled with the high degradation temperatures, may allow for these carbazole based materials to be used in a variety of commercial applications, including both traditional optics and non-linear optics.

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