

## Moderately High Refractive Index, Low Optical Dispersion Polymers with Pendant Diamondoids

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**ABSTRACT:** Soluble, colorless polymers containing pendant diamondoid moieties (adamantane and diamantane) were synthesized and characterized. The materials exhibited an unusual combination of moderately high refractive index with low optical dispersion. These properties may make the polymers valuable as specialty optical plastics. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** optical plastics; monomer and polymer synthesis; refractive index; optical dispersion; Abbe number; diamondoid moieties; adamantane; diamantane; vinyl free radical polymerization; vinyl cationic polymerization; chain transfer; ATRP; ellipsometry; variable angle spectroscopic ellipsometry; VASE

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### INTRODUCTION

Optical plastics are widely used to produce lenses, viewfinders, windows, data storage media, light-diffusing elements etc. The field is dominated by commodity polymers such as poly(methyl methacrylate) (PMMA), polycarbonate (PC), and polystyrene (PS). However, no one material is ideal for all applications, leading to numerous efforts to produce optical polymers with customized properties. For example, cyclic olefin copolymers<sup>1,2</sup> (COCs, based on norbornene or similar polycyclic aliphatic monomers) have become important specialty materials in optical applications such as DVD substrates, despite being significantly more expensive than commodity polymers. In addition to such valuable properties as high transparency and low moisture absorption, COCs also have unusually high refractive indexes for simple plastics, presumably because of their relatively high carbon-to-hydrogen content arising from their polycyclic structures.

Along these lines, one can consider diamond as the ultimate polycyclic carbon compound. It has an extraordinarily high refractive index ( $n_d = 2.387$ ),<sup>3</sup> considering that it lacks heavy elements and unsaturation. In the context of polycyclic carbon compounds, diamond's high index is a consequence of its large (essentially infinite) carbon-to-hydrogen ratio and its relatively high density (approximately  $3.5 \text{ g/cm}^3$ ).

Another important parameter for optical polymers is dispersion, the variance of refractive index with wavelength. Low dispersion

in the visible region is desirable for optical plastics because of reduced chromatic aberration. Dispersion is often characterized by the Abbe number,<sup>4</sup> which is approximately inversely proportional to optical dispersion. Generally, organic materials containing conjugation (e.g., PS, PC, etc.) have relatively low Abbe numbers (high dispersion), while mostly saturated materials (e.g., PMMA, COCs) have higher values (lower dispersion). Diamond also falls into the latter category. This combination of high index and low dispersion is at least partly responsible for diamond's visual appeal. However, of course, diamonds are difficult to process into arbitrary shapes for applications as optical materials.

Comparison of COCs and the diamond structure led us to consider whether polymers containing small polycyclic units of diamond ("diamondoids")<sup>5,6</sup> might possess valuable optical properties. In particular, polymers other than COCs with relatively high refractive index and relatively low dispersion are rare. Incorporation of structural subsets of the diamond structure into polymers might be a path to this desirable combination of properties. One might hope to gain increased refractive index from the relatively high carbon-to-hydrogen ratio (and therefore high density) of diamondoids, but avoid high optical dispersion that is associated with UV absorption bands from unsaturated moieties such as aromatic rings. Along the same lines, saturated polycyclic hydrocarbons such as the diamondoids have very low absorption in the visible, obviously crucial for many optical applications.

The simplest molecules containing the diamond structure are adamantane (**1**) and diamantane (**2**). The latter was used as a logo for the 1963 International Congress of Pure and Applied Chemistry (IUPAC). It was not a known compound at that time, and its synthesis was presented as a challenge to the congress participants, leading to its alternative name, “congressane.”<sup>7</sup> Apparently, this challenge was immediately undertaken, in that the synthesis and crystal structure of **2** were reported the following year.<sup>8,9</sup> Later, more convenient synthetic routes were disclosed.<sup>10–13</sup> A number of publications describing the synthesis of substituted dimantanes have since appeared.<sup>14–21</sup>

Higher fused polycyclic compounds that are likewise superimposable on the diamond structure are also known. Triamantane<sup>22</sup> and one of the four possible isomeric tetramantanes<sup>23</sup> have been successfully synthesized, although with great difficulty. More recently, Dahl et al. disclosed that a great variety of even larger diamondoids (4- to 11-mers) were present at low concentration in certain petroleum distillates, and could be extracted, individually isolated, and characterized.<sup>24</sup>

Polymers containing adamantane are very well known. A number of examples have been reported with this diamondoid within the polymer backbone,<sup>25</sup> including polyamides,<sup>26</sup> polyimides,<sup>27</sup> and poly(enaminonitriles).<sup>28</sup> Fluorescent polymers for OLED that contained an adamantyl unit within the backbone were disclosed by Zheng et al.<sup>29</sup> Malik et al. prepared and polymerized diethynyladamantane.<sup>30</sup> Many side-chain polymers containing adamantane have been prepared. In an early example, a US Patent in 1972 disclosed polymers based on adamantyl acrylate (**Aa**) and methacrylate (**Am**).<sup>31</sup> Otsu and coworkers made a comprehensive study of the free radical polymerization of **Am**, discovering that its overall rate of polymerization was unusually high because termination was inhibited by the bulky side-groups.<sup>32</sup> Another US Patent discloses diacrylates of adamantane as cross-linkers.<sup>33</sup> There are abundant examples of adamantane-containing acrylic polymers used in photoresist technology, especially in the patent literature.<sup>34–37</sup> The diamondoid is key to this technology because it imparts etch resistance while maintaining deep-UV transparency. Finally, there is one report of the polymerization of 1-vinyladamantane (**Va**) via a cationic mechanism.<sup>38</sup>

Regarding polymers containing higher diamondoids, various condensation polymers based on diamantane were prepared by Chern et al. during the 1990s.<sup>39–46</sup> In these studies, the very high thermal stability of the diamondoid repeat unit was of prime importance. Similarly, Malik et al. produced thermally stable materials by polymerizing mixed isomers of diethynyldiamantane.<sup>47</sup> Several examples of side-chain diamantane-containing polymers have appeared. A Japanese patent application disclosed the synthesis of 1-diamantyl acrylate monomer (**Da**),<sup>48</sup> and a preprint mentioned the synthesis of 1-diamantyl methacrylate monomer (**Dm**).<sup>49</sup> Related acrylic diamantane polymers have been studied for photoresist applications,<sup>50,51</sup> and one recent article reports a relatively high refractive index (1.56) for a polymer of this type.<sup>52</sup>

Polymers based on even higher diamondoids have not been reported, presumably because of the scarcity of these com-

pounds and the complexity of their chemistry. One patent lists a variety of triamantane-containing acrylic polymers as photoresist materials, but no actual examples or data on such polymers was presented.<sup>51</sup>

Despite the considerable literature on these materials, very little information about the optical properties of diamondoid-containing polymers has been disclosed. The possibility of developing new optical plastics led us to investigate simple polymers with side-chain diamondoids. We report herein the synthesis and characterization of these polymers, and their optical properties.

## EXPERIMENTAL

### Materials

Adamantan-1-ol, 2-hydroxyethyl-1-adamantane, and norbornadiene were obtained from Sigma Aldrich. 1-Hydroxydiamantane (**7**) was prepared via the sequence 1-bromoadamantane (**6**) => diamantane (**2**) => tetrahydrobinor S (**5**) => Binor S (**4**) => norbornadiene, according to the literature.<sup>10–21</sup> The synthesis of **7** is described below because the literature procedure<sup>19</sup> was modified.

### Instrumental

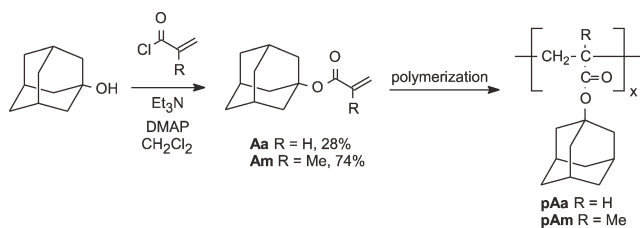
NMR spectra were obtained on a Varian VXR-300S spectrometer (300 MHz for <sup>1</sup>H, 75 MHz for <sup>13</sup>C). Polymer molar mass distributions were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF). Results were calibrated using narrow molar mass distribution PS standards, or reported as absolute molar masses via viscometric detection, as noted. Glass transition temperatures (*T<sub>g</sub>*) were measured by differential scanning calorimetry (DSC) under nitrogen at 10°C/min heating rate. The reported values are the midpoint of the change in heat capacity.

### Synthesis of 1-Adamantyl Acrylate (**Aa**)

A stirred mixture of adamantane-1-ol (54.6 g, 0.359 mol), triethylamine (54.4 g, 0.538 mol), 4-dimethylaminopyridine (4.38 g, 0.036 mol), and 250 mL of dry dichloromethane was cooled in an ice bath and treated with acryloyl chloride (48.7 g, 0.538 mol) under a nitrogen atmosphere. The reaction mixture was allowed to warm slowly to ambient temperature overnight, then washed successively with water, 5% aqueous NaHCO<sub>3</sub>, and again with water. The organic layer was dried (MgSO<sub>4</sub>) and concentrated to deposit an orange oil that gradually crystallized. The product was purified by distillation at reduced pressure (bp = 70–90°C/0.05 mm) followed by recrystallization from 75% ethanol/25% water. A white solid was obtained, mass 20.9 g (28%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 1.65 (br s, 6H), 2.13 (br s, 9H), 5.69 (dd, 1H), 5.9–6.1 (m, 1 H), 6.26 (dd, 1H).

### Synthesis of 1-Adamantyl Methacrylate (**Am**)

A stirred mixture of adamantane-1-ol (25.55 g, 0.168 mol), triethylamine (20.4 g, 0.193 mol), 4-dimethylaminopyridine (DMAP) (1.03 g, 0.084 mol), a trace of methyl-*t*-butyl-hydroxyphenylsulfide (inhibitor), and 100 mL of dry dichloromethane was cooled in an ice bath and treated with a solution of methacryloyl chloride (48.7 g, 0.538 mol) in 20 mL of dichloromethane under an argon atmosphere. The reaction mixture was allowed to warm slowly to ambient temperature overnight, then



**Scheme 1.** Synthesis of acrylic adamantane-containing polymers.

100 mL each of 10% aqueous HCl and dichloromethane were added. The organic layer was washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated to deposit a yellow oil. The product was distilled at reduced pressure, collecting the fraction bp 81–100°C (0.2 mm). A colorless oil was obtained, 27.31 g (74%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 1.65 (br m, 6H), 1.87 (s, 3H), 2.13 (br s, 9H), 5.45 (s, 1H), 5.98 (s, 1H).

### Synthesis of Vinyl Adamantane (Va)

A mixture of 2-hydroxyethyl-1-adamantane (24.9 g, 0.138 mol), carbon tetrachloride (42.5 g, 0.28 mol), triphenyl phosphine (27.45 g, 0.166 mol), and 200 mL of dry THF was stirred mechanically at reflux for 18 h, then cooled to ambient temperature. The precipitated triphenylphosphine oxide was removed by filtration. The filtrate was partially concentrated, then mixed with 700 mL of hexanes to precipitate more triphenylphosphine oxide. After a second filtration, the filtrate was concentrated to deposit an oil that crystallized on standing. 2-Chloroethyladamantane was purified by recrystallization from methanol to provide 18.4 g (67%) of a white solid, mp 48–50°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 1.51 (m, 6H), 1.5–1.7 (m, 8H), 1.96 (br s, 3H), 3.53 (t, 2H). A heterogeneous mixture of 2-chloroethyladamantane (7, 19.3 g, 0.097 mol), potassium *tert*-butoxide (21.8 g, 0.194 mol), 18-crown-6 (50 mg), and 100 mL toluene was heated at reflux for 18 h, then cooled to ambient temperature. Water was added to break up the resulting gel, and the organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and con-

centrated to deposit an oil. The product was purified by distillation at reduced pressure, bp 28–30°C (0.03 mm). A colorless oil was obtained, 13.0 g (82%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 1.58 (m, 6H), 1.6–1.8 (m, 6H), 1.98 (br s, 3H), 4.85 (m, 2H), 5.7 (m, 1H).

### Synthesis of 1-Hydroxydiamantane (7).<sup>19</sup>

A round-bottomed flask was charged with 23.71 g (0.089 mol) of 1-bromoadamantane (6). The flask was swept with nitrogen, and the outgas was bubbled through a solution of 10% aqueous sodium bisulfate. Concentrated nitric acid (112 g) was added slowly, and the mixture was stirred magnetically while warming with a 50°C oil bath. Once the evolution of elemental bromine stopped (5 h), the mixture was cooled to ambient temperature and diluted with water. The precipitated crude product was collected, washed thoroughly with water, and air-dried. After recrystallization from heptane, 8.57 g (47%) of light yellow needles was obtained. Additional 7 was obtained as follows. The mother liquor of recrystallization (containing 8) was concentrated and then treated with 4 g of NaHS in EtOH at 60°C for 4 h. The mixture was cooled to ambient and added to 200 mL water. The precipitated product (7) was washed with water, air-dried, and recrystallized from heptane. Off-white needles were obtained, 3.36 g (19%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 1.4–1.481 (m, 3H), 1.58–1.68 (m, 10H), 1.73 (m, 1H), 1.95 (s, 2H), 2.05 (m, 1H), 2.14 (s, 1H), 2.18 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 25.3, 30.4, 32.5, 36.7, 37.5, 38.0, 39.9, 43.4, 46.4, 70.7.

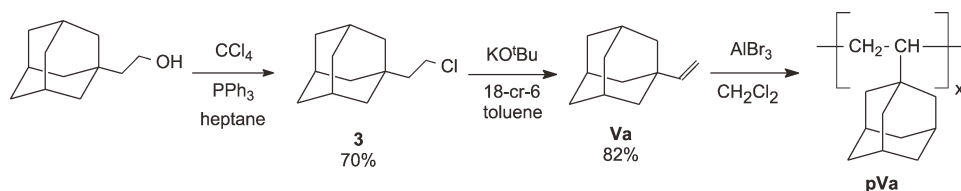
### Synthesis of 1-Diamantyl Acrylate (Da)

A solution diamantane-1-ol (7, 3.36 g, 16 mmol), triethyl amine (3.33 g, 33 mmol), DMAP (0.2 g, 1.6 mmol), a trace of methyl-*t*-butyl-hydroxyphenylsulfide (inhibitor), and 30 mL of dry toluene was cooled in an ice bath and treated with a solution of methacryloyl chloride (2.98 g, 33 mmol) under an argon atmosphere. The ice bath was removed, and the reaction mixture was heated in 60°C oil bath for 3 h. Methanol (5 mL) was added to decompose the excess acryloyl chloride, and heating was continued for 20 min. The reaction mixture was cooled to ambient temperature, filtered, washed successively with 10% aqueous

**Table I.** Synthesis and Properties of Adamantane-Containing Acrylic Polymers

Monomers	Initiating system	Solvent	Time (h)	$T$ (°C)	Yield	$M_n^a$ (g/mol)	$M_w^a$ (g/mol)	PDI <sup>a</sup>	$T_g^b$ (°C)
<b>Aa</b>	AIBN <sup>c</sup>	PhCl	24	60	96%	55,000	568,000	10.2	160
<b>Am</b>	AIBN <sup>d</sup>	PhCl	16	60	89% (gel)	-	-	-	-
<b>Am</b>	AIVN/DDT <sup>d</sup>	PhCl	17	60	86%	10 200	25,900	1.77	-
<b>Am</b>	AIVN/DDT <sup>e</sup>	PhCl	17	60	92%	19,300	104,000	5.39	-
<b>Am</b>	EBIB/CuBr/HMTETA <sup>f</sup>	PhOMe	16	70	22%	6300	10,500	1.66	240
<b>Am</b>	EBIB/CuBr/HMTETA <sup>f</sup>	PhOMe	52	70	21%	7200	12,600	1.75	-
<b>Am (25%)</b>	AIBN <sup>d</sup>	PhCl	15	70	-	14 700	29,500	2.01	105
<b>Mma<sup>h</sup> (75%)</b>									
<b>Am (50%)</b>	AIBN <sup>d</sup>	PhCl	21	70	-	1300	257,000	19.8	128
<b>Mma<sup>h</sup> (50%)</b>									
<b>Am (75%)</b>	AIBN <sup>d</sup>	PhCl	21	70	(gel)	-	-	-	156
<b>Mma<sup>h</sup> (25%)</b>									

<sup>a</sup>Molar mass by size exclusion chromatography, polystyrene equivalents. <sup>b</sup>Glass transition temperature by differential scanning calorimetry. <sup>c</sup>Azobisisobutyronitrile (0.1 mol %). <sup>d</sup>Azobisisobutyronitrile (2 mol %). <sup>e</sup>Azobisisobutyronitrile (1.0 mol %)/dodecane-1-thiol (1.2%). <sup>f</sup>Azobisisobutyronitrile (1.0 mol %)/dodecane-1-thiol (0.5%). <sup>g</sup>Ethyl bromoisobutyrate (0.6 mol %)/CuBr (0.6 mol %)/hexamethyltriethylenetetraamine (1.3 mol %). <sup>h</sup>Methyl methacrylate.



**Scheme 2.** Synthesis of poly(1-vinyladamantane).

HCl, 10% aqueous NaHCO<sub>3</sub>, and brine, dried, and concentrated to deposit a yellow oil. Bulb-to-bulb distillation (Kugelrohr apparatus) provided **Da** as a semi-crystalline white solid, melting near 25°C. 3.42 g (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 1.4–1.5 (br d, 2H), 1.5–1.8. (m, 8H), 2.0–2.1 (m, 5H), 2.2 (d, 2H), 2.38 (br s, 2H), 5.74 (dd, 1H), 6.17 (m, 1H), 6.32 (dd, 1H).

#### Synthesis of 1-Diamantyl Methacrylate (**Dm**)

A stirred mixture of diamantane-1-ol (**7**, 2.33 g, 11 mmol), triethyl amine (1.38 g, 14 mmol), DMAP (0.07 g, 0.6 mmol), a trace of methyl-*t*-butyl-hydroxyphenylsulfide (inhibitor), and 30 mL of dry THF was cooled in an ice bath and treated with a solution of methacryloyl chloride (1.43 g, 14 mmol) under an argon atmosphere. The reaction mixture was allowed to warm slowly to ambient temperature, then heated at reflux for 24 h. Additional portions of methacryloyl chloride (2.0 g, 19 mmol) and DMAP (0.1 g, 0.8 mmol) were added, and refluxing was continued 3 d. The reaction mixture was cooled to ambient temperature, and 50 mL each of water and dichloromethane were added. The organic layer was washed successively with 10% aqueous HCl, with 10% aqueous NaHCO<sub>3</sub>, and with brine, dried, and concentrated to deposit a tan oil that partially solidified. The product was purified by flash column chromatography on silica gel (heptane/dichloromethane eluate) followed by recrystallization from acetonitrile. A colorless solid was obtained, 1.63 g (52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 1.46 (br d, 2H), 1.5–1.8. (m, 8H), 1.93 (m, 3H), 2.0–2.1 (m, 5H), 2.2 (d, 2H), 2.38 (br s, 2H), 5.49 (m, 1H), 6.05 (m, 1H).

#### Free Radical Polymerization of Acrylic Monomers

**Typical Procedure.** A round-bottomed flask was charged with 6.80 g (0.031 mol) of 1-adamantyl methacrylate (**Am**), 0.059 g

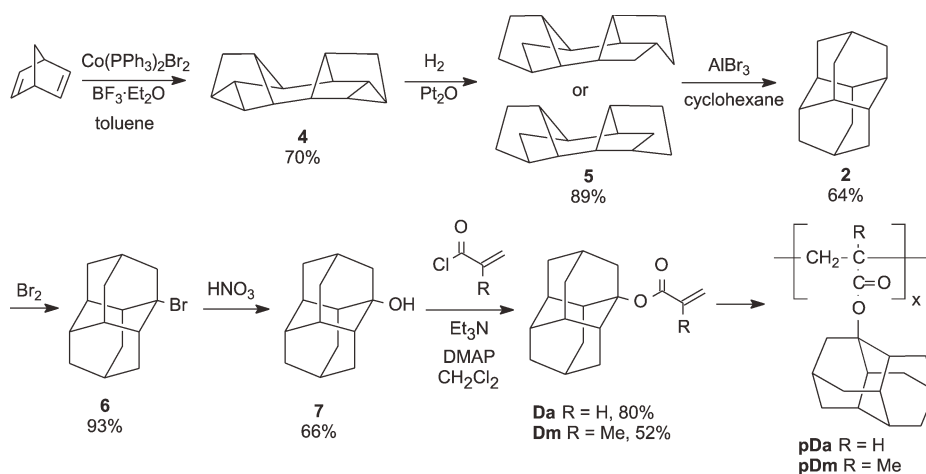
(0.31 mmol) of azobis(isovaleronitrile), 0.031 g (0.15 mmol) of dodecane-1-thiol, and 15 mL chlorobenzene. The flask was sealed with a septum, and the contents were deoxygenated by sparging with argon for 15 min. The mixture was heated in a 60°C oil bath for 17 h, and then cooled to ambient temperature. The polymer was precipitated in excess methanol, collected, washed with methanol, and dried in a vacuum oven at 65°C for 24 h. A white solid was obtained, 6.26 g (92%).

#### Atom Transfer Radical Polymerization of 1-Adamantyl Methacrylate (**Am**)

**Typical Procedure.** A round-bottomed flask was charged with 5.00 g (0.023 mol) of 1-adamantyl methacrylate (**Am**), 0.028 g (0.14 mmol) of ethyl bromoisobutyrate, 0.021 g (0.14 mmol) of copper (I) bromide, 0.066 g (0.029 mmol) of hexamethyltriethylenetetraamine, and 5 mL anisole. The flask was sealed with a septum, and the contents were deoxygenated by sparging with argon for 15 min. The mixture was heated in a 70°C oil bath for 16 h with magnetic stirring, and then cooled to ambient temperature. The polymer was precipitated in excess methanol, collected, washed with methanol, and air-dried. The polymer was redissolved in 15 mL of THF and stirred 1 h with ~3 g Dowex Marathon acidic ion exchange beads to remove residual copper catalyst. After filtration and reprecipitation in excess methanol, the polymer was washed with methanol and dried in a vacuum oven for 24 h at 65°C. A white powder was obtained, 1.07 g (22%).

#### Poly(1-Vinyladamantane)

To a solution of 7.00 g (0.043 mol) of freshly distilled (from P<sub>2</sub>O<sub>5</sub>) 1-vinyladamantane (**Va**) and 35 mL of dry dichloromethane was added 0.45 mL of a 1.0M solution (0.43 mmol) of aluminum bromide at 0°C. The reaction mixture was held 2 h



**Scheme 3.** Synthesis of acrylic diamantane-containing polymers.

**Table II.** Synthesis and Properties of Poly(1-Vinyladamantane)

Monomer	Initiating system	Solvent	Time (h)	T (°C)	Yield	M <sub>n</sub> <sup>a</sup> (g/mol)	M <sub>w</sub> <sup>a</sup> (g/mol)	PDI <sup>a</sup>	T <sub>g</sub> <sup>b</sup> (°C)
<b>Va</b>	AlBr <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	2	0	55%	390	550	1.40	67
<b>Va</b>	AlBr <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	2	-78	78%	400	610	1.50	62

<sup>a</sup>Absolute molar mass by size exclusion chromatography with viscometric detection. <sup>b</sup>Glass transition temperature by differential scanning calorimetry.

at 0°C, then gradually warmed to ambient temperature overnight. Water (20 mL) was added to decompose the catalyst, and the polymer was precipitated into a mixture of 400 mL of methanol and 1.5 mL concentrated hydrochloric acid. The polymer was collected, washed with methanol, and air-dried. The polymer was redissolved in dichloromethane, filtered through a pad of Celite to remove a small amount of insoluble material, and reprecipitated in 400 mL of methanol and 1.5 mL concentrated hydrochloric acid. The polymer was collected, washed with methanol, and dried in a vacuum oven at 40°C for 24 h to produce 3.9 g (55%) of a cream-colored solid. The polymerization was repeated at -78°C to provide 4.9 g (71%) of the polymer after an identical workup.

## RESULTS AND DISCUSSION

### Synthesis of Adamantane-Containing Polymers

1-Adamantyl acrylate (**Aa**) and 1-adamantyl methacrylate (**Am**) were prepared by standard acylation of the commercially available alcohols with the corresponding acid chlorides (Scheme 1).

**Aa** was a low-melting solid, and could be recrystallized from aqueous ethanol, although the recovery was rather poor. **Am** was obtained as an oil, and was purified by vacuum distillation. Solution polymerization of these monomers under standard conditions (azo initiator in chlorobenzene) provided a soluble white solid with **Aa** (albeit with a very broad molecular weight distribution), but an insoluble gel with **Am**, indicating possible cross-linking. As there is no obvious mechanism by which **Am** will cross-link by itself, especially considering that **Aa** does not cross-link, we assume that this problem is caused by polyfunctional impurities in the monomer that were not removed by distillation. However, the addition of small amounts of 1-dodecanethiol as chain transfer during the polymerization of **Am** led to soluble polymer. Similarly, atom transfer radical polymerization (ATRP) of **Am** also produced soluble material. Copolymers of **Am** with methyl methacrylate (**Mma**) were also soluble; however, SEC of the 75: 25 copolymer contained a substantial fraction of high molar mass material, consistent

with incipient cross-linking. Results of these polymerizations are shown in Table I.

1-Vinyladamantane (**Va**) was synthesized from commercially available 2-hydroxyethyl-1-adamantane by substituting first chlorine for hydroxyl to form **3**, followed by base-promoted elimination (Scheme 2). Attempts to prepare **Va** by pyrolysis of the borate ester of 2-hydroxyethyl-1-adamantane according to the analogous literature procedure<sup>53</sup> (which used 1-hydroxyethyl-1-adamantane) failed. Cationic polymerization of **Va** initiated by aluminum bromide provided the polymer (Scheme 2); however, the molar mass was very low (Table II).

### Synthesis of Diamantane-Containing Polymers

Acrylic polymers containing diamantane were synthesized via a multi-step route, as shown in Scheme 3. Unsubstituted diamantane (**2**) was an intermediate in this synthesis, and was prepared following the literature procedure.<sup>10-13</sup> Direct reaction of elemental bromine with **2** gave exclusively the 1- ("belt") monobromide (**6**), as reported.<sup>14-16</sup> Oxidative hydrolysis of **6** using nitric acid<sup>19</sup> provided 1-hydroxydiamantane (**7**) in moderate yield. The literature yield<sup>19</sup> was reported to be much higher, but in our hands, the reaction produced at least two significant by-products, one of which was tentatively identified as diamantane-1-nitrate (**8**). The desired product **7** could be isolated easily by recrystallization. The nitrated by-product was reduced to **7** by treatment of the mother liquor of crystallization with NaSH in ethanol, thereby providing additional **7** after further recrystallization.

Treatment of **7** with acryloyl chloride in toluene at 60°C for 3 h, catalyzed by triethylamine and DMAP provided the acrylic monomer **Da**. This monomer was purified by bulb-to-bulb distillation at reduced pressure to produce a semi-crystalline material with a melting point near room temperature. Similar reaction of **7** with methacryloyl chloride in THF or toluene proceeded much more slowly. A moderate yield of monomer **Dm** as a white solid was obtained after purification by chromatography and recrystallization.

**Table III.** Synthesis and Properties of Diamantane-Containing Acrylic Polymers

Monomer	Initiating system	Solvent	Time (h)	T (°C)	Yield	M <sub>n</sub> <sup>a</sup> (g/mol)	M <sub>w</sub> <sup>a</sup> (g/mol)	PDI <sup>a</sup>	T <sub>g</sub> <sup>b</sup> (°C)
<b>Da</b>	AIVN <sup>c</sup>	PhCl	18	60	79%	7 160	20,100	2.81	173
<b>Dm</b>	AIVN <sup>c</sup>	PhCl	18	60	75%	6 290	17,700	2.81	nd <sup>d</sup>

<sup>a</sup>Molar mass by size exclusion chromatography, polystyrene equivalents. <sup>b</sup>Glass transition temperature by differential scanning calorimetry. <sup>c</sup>Azobisisobutyronitrile (1 mol %). <sup>d</sup>T<sub>g</sub> was detected below 250°C.

**Table IV.** Refractive Index Measurements of Diamondoid-Containing Polymers by Variable Angle Spectroscopic Ellipsometry

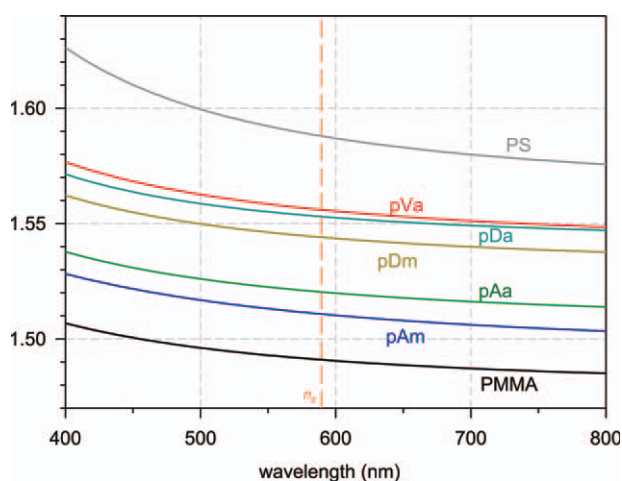
Polymer	$n_d^a$	$n_F^b$	$n_C^c$	$v^d$
<b>Poly(Aa)</b>	1.5165	1.5232	1.5138	54.8
<b>Poly(Mma/Am)75/25</b>	1.4996	1.5059	1.4970	56.3
<b>Poly(Mma/Am) 50/50</b>	1.5044	1.5107	1.5018	56.4
<b>Poly(Am)</b>	1.5108	1.5181	1.5077	49.3
<b>Poly(Va)</b>	1.5560	1.5640	1.5528	49.5
<b>Poly(Da)</b>	1.5530	1.5599	1.5505	58.9
<b>Poly(Dm)</b>	1.5441	1.5511	1.5413	55.5
<b>PMMA</b>	1.4910	1.4972	1.4885	56.1
<b>PS</b>	1.5881	1.6022	1.5827	30.1

<sup>a</sup>Refractive index at 589.26 nm. <sup>b</sup>Refractive index at 486.13 nm. <sup>c</sup>Refractive index at 656.28 nm. <sup>d</sup>Abbe number.<sup>3</sup>

Standard solution polymerization of monomers **Da** and **Dm** as before provided soluble white solids in good yields (Table II). Molar masses were surprisingly low, considering that the adamantane-containing monomers **Aa** and **Am** led to very large polymers. The  $T_g$  of **Da** homopolymer was only slightly higher than that of the corresponding adamantane polymer (173 vs. 160°C). As might have been expected, the  $T_g$  of **Dm** homopolymer was too high to measure.

### Optical Properties

Thin films of the title polymers were prepared by spin-coating on silicon wafers. Refractive indexes as a function of wavelength for the polymer films were determined by variable angle spectroscopic ellipsometry (VASE). As expected, the diamondoid-containing polymers were found to have significantly higher refractive indexes than PMMA, but comparable dispersion (Table III and Figure 1). Polyacrylates had slightly higher refractive indexes than the corresponding polymethacrylates, and poly(1-vinyladamantane) had the highest refractive index



**Figure 1.** Refractive index vs. wavelength for diamondoid-containing polymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

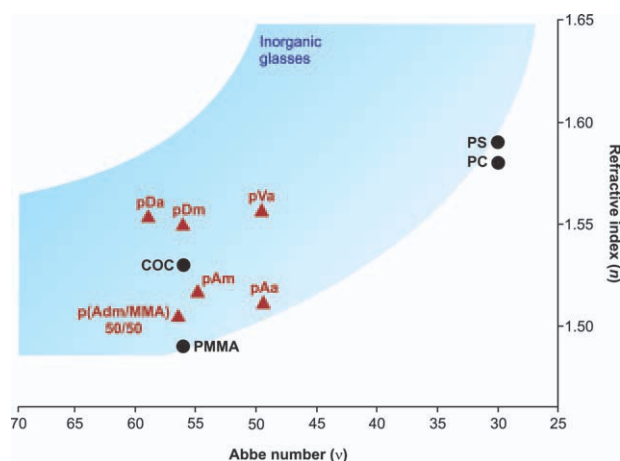
of the polymers studied. For additional comparison, the refractive index of PS was higher still, but its dispersion was significantly greater.

The relatively high refractive index and low dispersion of the title polymers place them in an unusual position in the “glass map”<sup>54</sup> (Figure 2) compared with many common optical plastics, in a region that is occupied by certain inorganic glasses such as the borosilicate crown glasses. COCs are the only polymers that also fall into this region, as might be expected because of their structural similarity to the title polymers.

### CONCLUSIONS

Soluble, colorless polymers containing diamondoid moieties were successfully synthesized and characterized. Thin films of these polymers could be prepared easily by spin-coating; molding processes should be equally facile (except for **pDm**, where the  $T_g$  is above the polymer’s decomposition point). These materials exhibited significantly larger refractive indexes than PMMA, but similarly low dispersion, an unusual combination among optical plastics. Poly(1-vinyl adamantane) possessed the highest refractive index among the polymers studied, but its molar mass was very low (essentially oligomers). In addition, the <sup>1</sup>H NMR of **pVa** showed small signals corresponding to ethylenic protons, possibly derived from unsaturated end-groups. Therefore, its optical dispersion might be decreased somewhat by hydrogenation of these groups, or simply by preparing higher molar mass material (which would dilute the effects of unsaturation). Future experiments should be aimed at improving the cationic polymerization, or developing alternative polymerization methods for this monomer, with the goal of providing high molar mass.

There are many polymers with high refractive index or high Abbe numbers, but very few with at least moderately high values of both simultaneously. Polymers containing diamondoids seem to fulfill these specifications. This combination of optical properties along with high transparency in the visible may make



**Figure 2.** Refractive index vs. Abbe number “glass map.” [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

the title polymers valuable as specialty optical plastics despite their undoubtedly high cost. In particular, polymers based on diamantane seem promising because there may be a natural source of this polycyclic hydrocarbon; at the very least, its synthesis can be accomplished in three catalytic steps from an inexpensive starting material.

It seems likely that even larger refractive indices could be obtained from polymers containing higher diamondoids; however, development of such materials awaits a ready supply of the diamondoids and the discovery of suitable functionalization chemistry.

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