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## Design and Synthesis of High Refractive Index Polymers. II

Richard A. Minns<sup>a</sup>; Russell A. Gaudiana<sup>a</sup>

<sup>a</sup> Materials Research Laboratory Polaroid Corporation, Cambridge, Massachusetts

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## DESIGN AND SYNTHESIS OF HIGH REFRACTIVE INDEX POLYMERS. II

RICHARD A. MINNS\* and RUSSELL A. GAUDIANA

Materials Research Laboratory  
Polaroid Corporation  
Cambridge, Massachusetts 02139

### ABSTRACT

The synthesis, physical and optical properties of a series of high molecular weight, colorless, nonbirefringent, amorphous polymethacrylates (and acrylates) comprising brominated and iodinated carbazole rings that are connected to the backbone by short hydrocarbon spacers are described. The refractive indices exhibited by these homopolymers are in the range of 1.67 to 1.77. A ternary mixture of brominated monomers has a low melting point ( $< 50^{\circ}\text{C}$ ); the refractive index of the corresponding polymer = 1.72.

### INTRODUCTION

In a series of papers [1–5] spanning the last several years, we have reported the development of melt or solution-processable, rodlike polymers that have a unique combination of properties. The optical properties of these polymers, for example, are particularly unusual in that they are colorless, noncrystalline, and hence non-scattering. The latter attributes, when combined with high refractive index and high birefringence in oriented films and fibers, make them very useful in certain optical applications [1, Refs. 1–3 therein].

Wholly-aromatic, rodlike polyamides with repeat units composed of groups with high  $\pi$ -electron density directly on the backbone, such as linearly conjugated double bonds and aromatic heterocyclic rings, exhibit isotropic refractive indices that may be as high as 1.8–2.0. Birefringence values for oriented films of polyamides far exceed 0.5 and several are as high as 0.85; the corresponding parallel and

perpendicular indices for these polymers are in the ranges 2.2–2.4 and 1.5–1.7, respectively, depending on the molecular structure and degree of orientation [5].

In order to make optical devices utilizing these highly birefringent films, it may be necessary to bond them to fibers, films, or glass with index-matching, optical quality bonding agents. For this purpose we have synthesized a series of colorless, nonbirefringent, amorphous polyacrylates (and methacrylates) that contain brominated and iodinated carbazole rings connected to the polymer backbone with short hydrocarbon ( $\leq 6$  methylenes) spacers [6]. The refractive indices exhibited by these homopolymers are extremely high for nonrodlike polymers.

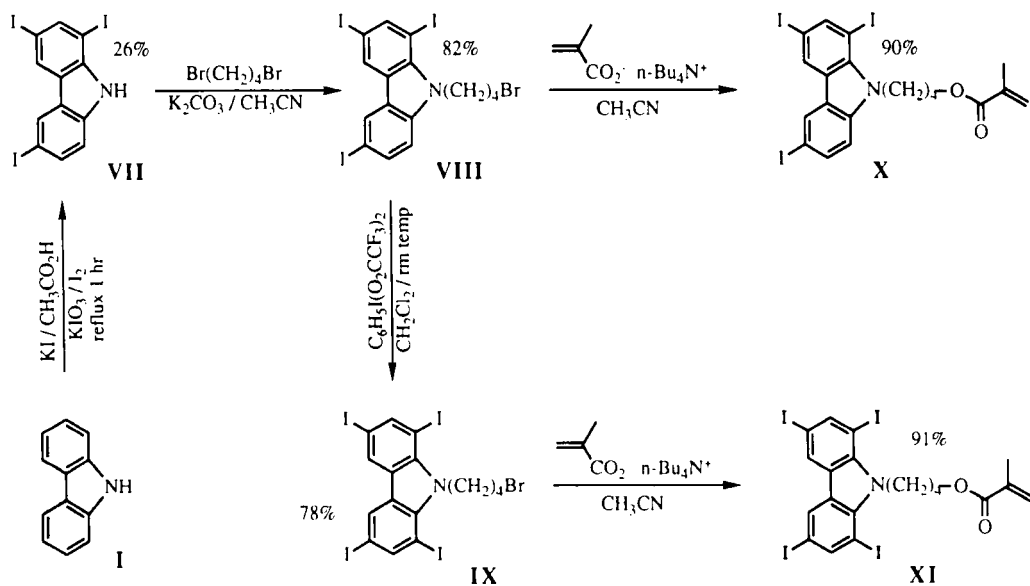
From an applications standpoint, liquid bonding agents are of much greater utility than solids. Unfortunately, carbazole-containing acrylic polymers are glasses with high softening temperatures, and their monomeric precursors are high-melting crystalline solids. These properties necessitated the investigation of monomer mixtures. A ternary mixture of brominated carbazole monomers was found to have a sufficiently low melting temperature to be liquefied and copolymerized between two optical components (glass plates or prisms).

## EXPERIMENTAL

### Monomer Preparation

#### 1,3,6,8-Tetrabromocarbazole [7] (II, Scheme 1)

Into a 250-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a thermometer, an addition funnel, and a condenser topped by a calcium chloride drying tube leading to a water trap to remove the evolved HBr were placed carbazole I (3.4 g, 20 mmol) and glacial acetic acid (50 mL). With stirring at room



SCHEME 1.

temperature, a solution of bromine (4.5 mL, 88 mmol) in acetic acid (50 mL) was added. The mixture was then stirred and heated in a 90°C oil bath for 8 h. After standing overnight at room temperature, the product was collected by filtration and recrystallized from toluene/acetic acid to yield light yellow crystals of **II** (7.6 g, 77%), mp 228–231°C (lit. [7], mp 233–235°C).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 7.85 (d, 2H, *J* = 2 Hz, H2, H7), 8.51 (d, 2H, *J* = 2 Hz, H4, H5), 11.51 (s, 1H, NH). MS (EI) *m/z*: 479 (M<sup>+</sup>, 4 Br's).

#### 9-(4-Bromobutyl)-1,3,6,8-tetrabromocarbazole (**IIIc**, *n* = 4)

Into a 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a thermometer, and a condenser connected to a nitrogen bubbler were placed **II** (1.0 g, 2.1 mmol), 1,4-dibromobutane (5 mL, 42 mmol), powdered anhydrous potassium carbonate (3 g, 22 mmol), and anhydrous acetonitrile (20 mL). The mixture was stirred and heated under reflux in a 100°C oil bath for 18 h. Most of the acetonitrile was then distilled, water and dichloromethane were added, and the two phases were separated. The aqueous phase was extracted twice with dichloromethane, and the combined organic phase was dried over anhydrous sodium sulfate and filtered through a pad of Celite to give a light-yellow clear solution. Dichloromethane and most of the excess 1,4-dibromobutane were evaporated on a steam bath in a stream of nitrogen. The resulting oil was dissolved in boiling dichloromethane (100 mL), and methanol was added until crystals appeared. After cooling in an ice-water bath, the light yellow crystals were filtered and dried to yield **III** (1.02 g, 80%); mp 142–144°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.93 (m, 4H), 3.41 (t, 2H, CH<sub>2</sub>Br), 5.12 (t, 2H, CH<sub>2</sub>N), 7.76 (d, 2H), 8.00 (d, 2H). MS (EI) *m/z*: 613 (M<sup>+</sup>, 5 Br's), 492 (M – (CH<sub>2</sub>)<sub>3</sub>Br).

The following homologs of **III** were similarly prepared:

**IIIa**, *n* = 2, 92% yield, mp 191–194°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 3.65 (t, 2H, *J* = 8 Hz, CH<sub>2</sub>Br), 5.32 (t, 2H, *J* = 8 Hz, CH<sub>2</sub>N), 7.72 (d, 2H), 7.95 (d, 2H).

**IIIb**, *n* = 3, 93% yield, mp 157–159°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 2.33 (m, 2H), 3.34 (t, 2H, CH<sub>2</sub>Br), 5.15 (t, 2H, CH<sub>2</sub>N), 7.68 (d, 2H), 7.91 (d, 2H). Elemental analysis (%). Calculated for C<sub>15</sub>H<sub>10</sub>Br<sub>5</sub>N: C, 29.84; H, 1.67; N, 2.32; Br, 66.17. Found: C, 29.90, 29.75; H, 1.70, 1.67; N, 2.25, 2.29; Br, 66.09, 66.26.

**IIIc**, *n* = 4, 93% yield, mp 136–138°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.51 (m, 2H), 1.85 (m, 4H), 3.33 (t, 2H, CH<sub>2</sub>Br), 5.03 (t, 2H, CH<sub>2</sub>N), 7.72 (d, 2H), 7.94 (d, 2H). MS (EI) *m/z*: 627 (M<sup>+</sup>, 5 Br's), 492 (M<sup>+</sup> – (CH<sub>2</sub>)<sub>4</sub>Br).

**IIIe**, *n* = 6, 90% yield, mp 122–123°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.40 (m, 4H), 1.82 (m, 4H), 3.30 (t, 2H, CH<sub>2</sub>Br), 5.06 (t, 2H, CH<sub>2</sub>N), 7.73 (d, 2H), 8.00 (d, 2H). MS (EI) *m/z*: 641 (M<sup>+</sup> 5 Br's), 492 (M<sup>+</sup> – (CH<sub>2</sub>)<sub>5</sub>Br).

#### 4-(1,3,6,8-Tetrabromo-9-carbazolyl)-1-butyl methacrylate (**IVb**)

A solution of tetrabutylammonium methacrylate was prepared in a 50-mL round-bottomed flask by titrating methacrylic acid (0.1 mL, 1.2 mmol) in methanol (10 mL) with approximately 1.2 mL of a 1-*M* solution of tetrabutylammonium hydroxide in methanol until the solution was just basic to wet pH paper. The solution was acidified with several drops of methacrylic acid, and the solvents were removed on a rotary evaporator at 30°C. Acetonitrile was then added and evapo-

rated to remove the remaining water and methanol. The resulting oil was dissolved in acetonitrile (10 mL), and **IIIc** (0.68 g, 1.1 mmol) along with benzene (10 mL) were added. The mixture was warmed briefly to effect solution, and the resulting solution was stirred overnight at room temperature under nitrogen. The solvents were then evaporated with the temperature maintained below 40°C, water was added, and the mixture was extracted with benzene. The organic phase was dried and evaporated, and the crude product was purified by flash chromatography on silica gel with 1:1 dichloromethane/hexanes to yield white crystals of **IVb** (0.60 g, 86%); mp 155–156.5°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 1.77 (m, 4H), 1.88 (s, 3H, CH<sub>3</sub>), 4.10 (t, 2H, CH<sub>2</sub>O), 5.05 (t, 2H, CH<sub>2</sub>N), 5.47 (m, 1H, vinyl), 5.98 (m, 1H, vinyl), 7.68 (d, 2H), 7.92 (d, 2H). MS (EI) *m/z*: 619 (M<sup>+</sup>, 4 Br's), 492.

The following homologues of **IV** were also prepared:

**IVa**, *n* = 3, mp 177–178°C. MS (EI) *m/z*: 605 (M<sup>+</sup>, 4 Br's), 492.

**IVc**, *n* = 5, 72% yield, mp 146–148°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.3–1.8 (m, 6H), 1.84 (m, 3H, CH<sub>3</sub>), 4.00 (t, 2H, CH<sub>2</sub>O), 5.02 (t, 2H, CH<sub>2</sub>N), 5.40 (m, 1H, vinyl), 5.90 (m, 1H, vinyl), 7.68 (d, 2H), 7.91 (d, 2H). MS (EI) *m/z*: 633 (M<sup>+</sup>, 4 Br's), 492.

**IVd**, *n* = 6, 94% yield, mp 124–126°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.3–1.8 (m, 8H), 1.80 (m, 3H, CH<sub>3</sub>), 4.05 (t, 2H, CH<sub>2</sub>O), 5.07 (t, 2H, CH<sub>2</sub>N), 5.47 (m, 1H, vinyl), 6.00 (m, 1H, vinyl), 7.76 (d, 2H), 8.02 (d, 2H). MS (EI) *m/z*: 647 (M<sup>+</sup>, 4 Br's), 492. Elemental analysis (%). Calculated for C<sub>22</sub>H<sub>21</sub>Br<sub>4</sub>NO<sub>2</sub>: C, 40.59; H, 3.25; N, 2.15; Br, 49.09. Found: C, 40.49; H, 3.30; N, 2.10; Br, 49.56.

### 9-(6-Bromohexyl)-1,2,3,4,6,7,8-heptabromocarbazole (**Vc**, *n* = 6)

Into a 250-mL round-bottomed flask equipped with a magnetic stirrer and a condenser, topped by a calcium chloride drying tube leading to a water-filled trap to remove evolving HBr, were placed **IIIe** (5.0 g, 7.74 mmol), bromine (50 mL), and tetrachloromethane (50 mL). The solution was heated in an oil bath and stirred overnight under reflux. Excess bromine and tetrachloromethane were then recovered by simple distillation for use in another run, and the resulting solid was dried in a stream of nitrogen. Recrystallization from carbon disulfide/ethanol yielded **Vc** (6.23 g, 91%) as a white solid; mp 161–162°C.

<sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.3 (m, 6H), 1.67 (m, 2H), 3.23 (t, 2H, CH<sub>2</sub>Br), 4.98 (t, 2H, CH<sub>2</sub>N), 9.02 (s, 1H). MS (EI) *m/z*: 875 (M<sup>+</sup>, 8 Br's).

The following homologues of **V** were similarly prepared:

**Va**, *n* = 4, mp 189–191°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.57 (m, 4H), 3.17 (t, 2H, CH<sub>2</sub>Br), 5.09 (t, 2H, CH<sub>2</sub>N), 9.08 (s, 1H). MS (EI) *m/z*: 847 (M<sup>+</sup>, 8 Br's). Elemental analysis (%). Calculated for C<sub>16</sub>H<sub>9</sub>Br<sub>8</sub>N: C, 22.49; H, 1.06; N, 1.64; Br, 74.81. Found: C, 22.68, 22.80; H, 1.13, 1.09; N, 1.64, 1.65; Br, 74.79, 74.82.

**Vb**, *n* = 5, 84% yield, mp 165–167°C. <sup>1</sup>H NMR (CS<sub>2</sub>) δ: 1.3 (m, 4H), 1.67 (m, 2H), 3.14 (t, 2H, CH<sub>2</sub>Br), 4.98 (t, 2H, CH<sub>2</sub>N), 8.97 (s, 1H). MS (EI) *m/z*: 861 (M<sup>+</sup>, 8 Br's).

### ω-(1,2,3,4,6,7,8-Heptabromo-9-carbazolyl)-α-alkyl (meth)acrylates (**VI**)

These monomers were prepared from the alkyl bromides and the tetrabutylammonium (meth)acrylates by a procedure analogous to that described in the preparation of **IV** above. The structures **VI** were confirmed by NMR and mass spectral analyses.

**VIa**,  $n = 4$ ,  $R = H$ , 66% yield, mp 164–166°C.  $^1H$  NMR ( $CDCl_3 + CS_2$ )  $\delta$ : 1.41 (m, 4H), 4.01 (t, 2H,  $CH_2O$ ), 5.12 (t, 2H,  $CH_2N$ ), 5.6–6.5 (m, 3H, vinyl), 9.14 (s, 1H). MS (EI)  $m/z$ : 839 ( $M^+$ , 7 Br's).

**VIb**,  $n = 4$ ,  $R = Me$ , 77% yield, mp 170–172°C.  $^1H$  NMR ( $CS_2$ )  $\delta$ : 1.40 (m, 4H), 1.82 (m, 3H,  $CH_3$ ), 3.91 (t, 2H,  $CH_2O$ ), 5.07 (t, 2H,  $CH_2N$ ), 5.40 (m, 1H, vinyl), 5.84 (m, 1H, vinyl), 9.05 (s, 1H). MS (EI)  $m/z$ : 853 ( $M^+$ , 7 Br's). Elemental analysis (%). Calculated for  $C_{20}H_{14}Br_7NO_2$ : C, 27.94; H, 1.64; N, 1.63; Br, 65.06. Found: C, 28.05; H, 1.61; N, 1.79; Br, 65.30, 65.14.

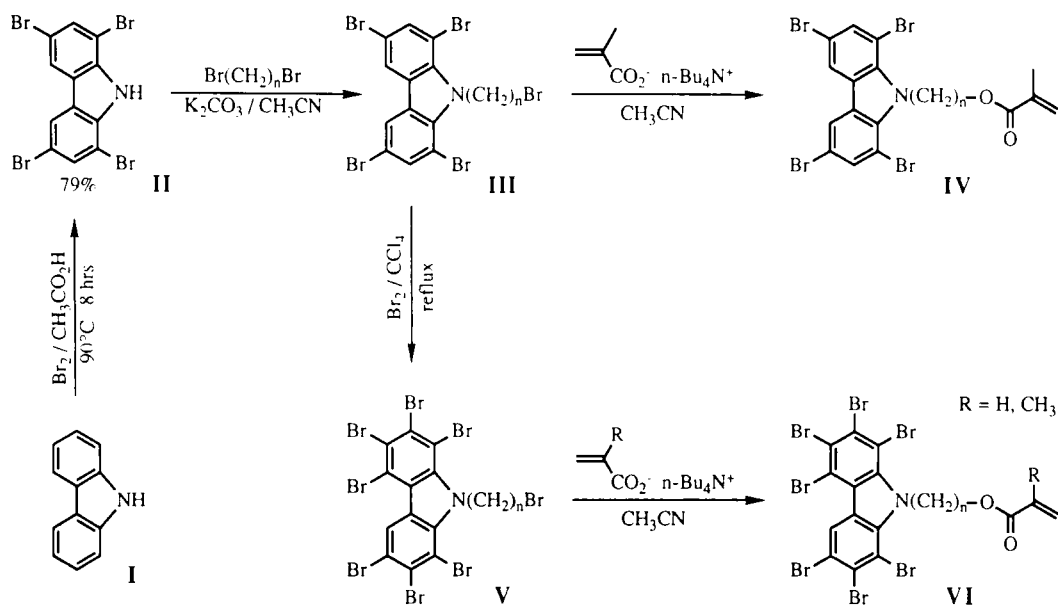
**VIc**,  $n = 5$ ,  $R = Me$ , 91% yield, mp 145–146°C.  $^1H$  NMR ( $CS_2$ )  $\delta$ : 1.10 (m, 2H), 1.47 (m, 4H), 1.82 (m, 3H,  $CH_3$ ), 3.91 (t, 2H,  $CH_2O$ ), 5.04 (t, 2H,  $CH_2N$ ), 5.40 (m, 1H, vinyl), 5.85 (m, 1H, vinyl), 9.05 (s, 1H). MS (EI)  $m/z$ : 867 ( $M^+$ , 7 Br's).

**VI d**,  $n = 6$ ,  $R = Me$ , 88% yield, mp 120–121°C.  $^1H$  NMR ( $CS_2$ )  $\delta$ : 1.12 (m, 4H), 1.37 (m, 4H), 1.82 (m, 3H,  $CH_3$ ), 3.88 (t, 2H,  $CH_2O$ ), 4.99 (t, 2H,  $CH_2N$ ), 5.35 (m, 1H, vinyl), 5.85 (m, 1H, vinyl), 8.98 (s, 1H). MS (EI)  $m/z$ : 881 ( $M^+$ , 7 Br's).

### 1,3,6-Triiodocarbazole (VII, Scheme 2)

This preparation is a modification of the preparation of 3,6-diiodocarbazole as described by Tucker [8].

Into a 250-mL, three-necked, round-bottomed flask equipped with a heating mantle, a magnetic stirrer, and a condenser were placed carbazole I (8.35 g, 50 mmol), potassium iodide (11 g, 66 mmol), and glacial acetic acid (125 mL). The mixture was heated to reflux with stirring, the resulting solution was cooled slightly, and potassium iodate (16 g, 75 mmol) was cautiously added with continued stirring. After heating for an additional 15 min under reflux, the iodine color faded. Iodine



SCHEME 2.

(5 g, 20 mmol) was added and the reaction mixture was stirred under reflux for 1 h. It was then poured into an aqueous solution of sodium bisulfite; the precipitated solid was collected by filtration and extracted with acetone in a Soxhlet extractor. Fractional crystallization from acetone yielded two products with  $R_f$  values of 0.33 and 0.64 as determined by thin layer chromatographic analysis on silica gel with 20% dichloromethane in hexanes. The lower  $R_f$  product was an off-white solid **VII** (7.0 g, 26%); mp 228–238°C.

A sample of **VII** that was purified by flash chromatography on silica gel with carbon disulfide followed by recrystallization from carbon disulfide/hexanes had a melting point of 237–238°C.

$^1\text{H NMR}$  (DMSO- $d_6$ )  $\delta$ : 7.37 (d, 1H,  $J = 8$  Hz, H8), 7.66 (dd, 1H,  $J = 2, 8$  Hz, H7), 7.98 (d, 1H,  $J = 2$  Hz, H2), 8.53 (m, 2H, H4, H5), 11.37 (s, 1H, NH). MS (EI)  $m/z$ : 545 ( $M^+$ ), 418 ( $M^+ - I$ ), 291 ( $M^+ - 2I$ ), 164 ( $M^+ - 3I$ ).

#### 9-(4-Bromobutyl)-1,3,6-triiodocarbazole (**VIII**)

This compound was prepared from **VII** by an alkylation procedure analogous to that described for the preparation of **III**. Off-white crystals were obtained in 82% yield; mp 143–145°C.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.97 (m, 4H), 3.43 (t, 2H,  $\text{CH}_2\text{Br}$ ), 4.64 (t, 2H,  $\text{CH}_2\text{N}$ ), 7.17 (d, 1H,  $J = 8$  Hz, H8), 7.75 (dd, 1H,  $J_s = 2, 8$  Hz, H7), 8.17 (d, 1H,  $J = 2$  Hz, H2), 8.27 (m, 2H, H4, H5). MS (EI)  $m/z$ : 679 ( $M^+$ , 1 Br), 552 ( $M^+ - I$ ), 473 ( $M^+ - \text{Br}$ ), 346 ( $M^+ - \text{I}_2\text{Br}$ ).

#### 9-(4-Bromobutyl)-1,3,6,8-tetraiodocarbazole (**IX**)

Into a 100 mL round-bottomed flask equipped with a magnetic stirrer were added **VIII** (1.0 g, 1.47 mmol), iodine (0.20 g, 0.79 mmol), [bis(trifluoroacetoxy)iodo]benzene (0.35 g, 0.81 mmol), and dichloromethane (50 mL). After stirring the dark purple solution at room temperature for 5 h, a white solid began to precipitate. Stirring was continued at room temperature for 2 days, then the mixture was allowed to stand at room temperature for an additional 4 days. The white solid was collected by filtration and washed with a small volume of dichloromethane to yield **IX** (0.93 g, 78%); mp 211–214°C.

$^1\text{H NMR}$  ( $\text{CS}_2$ )  $\delta$ : 1.82 (m, 4H), 3.30 (t, 2H,  $\text{CH}_2\text{Br}$ ), 5.08 (t, 2H,  $\text{CH}_2\text{N}$ ), 8.18 (m, 4H, small  $J$ 's). MS (EI)  $m/z$ : 805 ( $M^+$ , 1 Br), 599 ( $M^+ - \text{Br}$ ).

#### 4-(1,3,6-Triiodo-9-carbazolyl)-1-butyl Methacrylate (**X**) and 4-(1,3,6,8-Tetraiodo-9-carbazolyl)-1-butyl Methacrylate (**XI**)

These compounds were prepared from the alkyl bromides by a procedure analogous to that described in the preparation of **IV** above.

**X**, 90% yield, mp 157–159°C.  $^1\text{H NMR}$  ( $\text{CS}_2$ )  $\delta$ : 1.90 (m, 7H, 2  $\text{CH}_2$ 's,  $\text{CH}_3$ ), 4.13 (t, 2H,  $\text{CH}_2\text{O}$ ), 4.61 (t, 2H,  $\text{CH}_2\text{N}$ ), 5.49 (m, 1H, vinyl), 6.01 (m, 1H, vinyl), 7.11 (d, 1H,  $J = 8$  Hz, H8), 7.66 (dd, 1H,  $J_s = 2, 8$  Hz, H7), 8.12 (d, 1H,  $J = 2$  Hz, H2), 8.20 (m, 2H, H4, H5). MS (EI)  $m/z$ : 685 ( $M^+$ ), 558 ( $M^+ - I$ ). Elemental analysis (%). Calculated for  $\text{C}_{20}\text{H}_{18}\text{I}_3\text{NO}_2$ : C, 35.06; H, 2.65; N, 2.04; I, 55.57. Found: C, 35.02; H, 2.61; N, 2.08; I, 55.58.

**XI**, 91% yield, mp ~210°C.  $^1\text{H NMR}$  ( $\text{CS}_2$ )  $\delta$ : 1.73 (m, 4H), 1.87 (m, 3H,

CH<sub>3</sub>), 4.09 (t, 2H, CH<sub>2</sub>O), 5.12 (t, 2H, CH<sub>2</sub>N), 5.48 (m, 1H, vinyl), 5.99 (m, 1H, vinyl), 8.24 (m, 4H). MS (EI) *m/z*: 811 (M<sup>+</sup>), 684 (M<sup>+</sup> - I), 557 (M<sup>+</sup> - 2I).

### Polymer Synthesis and Characterization

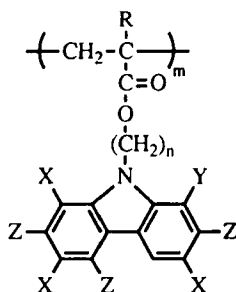
This example illustrates the thermal, bulk polymerization of these monomers. Into a 10-mL, round-bottomed flask was placed **IVb** (0.28 g). Polymerization was effected by continuously evacuating the flask with a mechanical vacuum pump while heating it at 160°C for 2 h. The resulting polymer was dissolved by stirring in 1-chloronaphthalene (3 mL) at 150°C. The viscous solution was then filtered, and the polymer was isolated by precipitation into dichloromethane (70 mL). The precipitate was filtered, washed thrice with dichloromethane, and dried to yield a white polymer (0.21 g, 74%);  $\eta_{inh} = 0.68$  dL/g (1-chloronaphthalene),  $T_g = 160^\circ\text{C}$  as determined by differential scanning calorimetry,  $n_D = 1.68$  as determined by microscopy using Becke line analysis.

Table 1 summarizes the structure and properties of similarly prepared polymers.

The acrylate monomers described in this paper (**IV**, **VI**, **X**, **XI**) can also be

TABLE 1. Thermal and Optical Properties of Halogenated Carbazole Monomers and Polymers

X	Y	Z	<i>n</i>	R	Monomer		Polymer			
					No.	mp, °C	$\eta_{inh}$	$T_g$ , °C	$T_{dec}$ , °C	$n_D$
Br	Br	H	3	Me	IVa	177-178	—	—	—	—
Br	Br	H	4	Me	IVb	155-177	0.68	160	335	1.68
Br	Br	H	5	Me	IVc	146-148	0.27	132	387	—
Br	Br	H	6	Me	IVd	124-126	0.28	112	400	1.67
Br	Br	Br	4	H	VIa	164-166	0.07	176	—	—
Br	Br	Br	4	Me	VIb	170-172	0.17	198	382	1.74
Br	Br	Br	5	Me	VIc	145-146	0.21	185	385	—
Br	Br	Br	6	Me	VI d	120-121	0.10	163	377	1.72
Br	Br	Br	4,5,6	Me	VIe	< 50	0.19	175	390	1.72
I	H	H	4	Me	X	157-159	0.10	—	—	1.74
I	I	H	4	Me	XI	~210	—	—	—	1.77





polymerized by melting them between two glass circles on a Fisher-Johns melting point apparatus and holding the liquids at a temperature above their melting points for several minutes. The glass circles lock together as the polymer is formed, resulting in an optically clear, colorless sandwich. For example, maintaining **IVb** at 170°C for several minutes yields the polymer which softens at approximately 200°C, and it can be made to flow at 250°C without discoloration. Upon cooling, the glass can be pried apart with a razor blade or dissolved in hydrofluoric acid to isolate the brittle polymer.

A low-melting mixture (mp < 50°C) of the three heptabromo monomers **VI** with  $n = 4, 5,$  and  $6$  was prepared by dissolving 20 mg each of **VIb**, **VIc**, and **VI d** in dichloromethane (2 mL), filtering the solution, and evaporating the solvent in a stream of nitrogen. Application of a vacuum to remove final traces of solvent yielded a taffy-like foam. A sample that was placed between two glass circles on a Fisher-Johns melting point apparatus melted below 50°C to a clear liquid and polymerized at approximately 100°C to a clear film.

## RESULTS AND DISCUSSION

The goal of this research was the design and synthesis of polymers that were expected to be useful as optical adhesives having high refractive indices and no birefringence. The application we specifically had in mind for these polymers was the bonding of two glass prisms to a highly birefringent polymer film for the fabrication of a polarizing beam splitter. In the bonding process, heating the optical components to high temperatures could not be tolerated. Since an adhesive must flow and wet the substrates to be joined, and since polymers having both a high refractive index and a low softening point are unknown, we anticipated that the most likely solution to this dilemma would be the use of monomers or mixtures of monomers that exhibit low melting points. After laminating and bonding, polymerization would be expected via thermal or photochemical means.

The specific requirements of the monomers or monomer mixtures are: 1) they should be liquids at room temperature or low melting solids; 2) they must not dissolve or swell the polymer film; and 3) they must polymerize rapidly by thermal or photochemical initiation.

The most important requirements for the polymers themselves are: 1) the polymer formed from these monomers must bond polymer films to glass or other polymer films; 2) they must be optically transparent, i.e., colorless and nonscattering; 3) they cannot be too brittle; and 4) they must have a high refractive index, e.g.,  $> 1.70$ .

Both the liquid monomer, 1-vinylnaphthalene, and the low-melting monomer, 9-vinylcarbazole (mp 64–66°C), yield polymers having a refractive index of 1.68. However, these polymers have high glass transition temperatures ( $T_g$ 's of 160 and 227°C [9], respectively) and are quite brittle. Substitution of chlorine, bromine, or iodine onto the rings of either of these polymers would raise their refractive indices, but also would likely increase the melting points of the monomers and the  $T_g$ 's of the polymers.

Previous experience in this laboratory with polyacrylates containing bulky halogenated side chains has shown that softening temperatures can be lowered by inserting a flexible spacer between the bulky group and the polymer backbone [10].

Polyacrylates with a carbazole group connected to the backbone by a hydrocarbon spacer also exhibit lower  $T_g$ 's as the length of the spacer increases [11]. Although the incorporation of spacers would be expected to lower the refractive index of a carbazole-containing polymer, it was hoped that halogenation of the carbazole ring with bromine or iodine would more than compensate for this effect and result in polymers with enhanced refractive indices and useful  $T_g$ 's. Furthermore, by varying the spacer lengths, a series of homologous monomers could readily be prepared which should form compatible mixtures with lower melting points.

Accordingly, we synthesized a series of acrylic esters in which the halogenated carbazole group is separated from a reactive (meth)acrylate group by a flexible spacer (**IV**, **VI**, **X**, **XI**). These monomers undergo facile free radical polymerization, generating acrylic polymers with good thermal stability, moderate glass transition temperatures, and good optical properties including uniquely high refractive indices.

### Synthesis of Monomers

The synthesis of the monomers used in this study was accomplished with three relatively simple reactions, i.e., halogenation, alkylation, and esterification, from commercially available carbazole **I**. References 11 and 12 give additional information on the synthesis of nonhalogenated carbazole-containing acrylates.

Carbazole **I** may be readily tetrabrominated by bromine in acetic acid to give a good yield of **II** (Scheme 1). However, iodination under similarly mild conditions yielded a mixture of products from which the triiodo compound **VII** was isolated in 26% yield (Scheme 2).

Placement of the spacer on the nitrogen atom of the tetrabrominated or triiodinated carbazole was accomplished by reaction with large excesses of an  $\alpha,\omega$ -dibromoalkane and potassium carbonate in refluxing acetonitrile. This rather straightforward reaction gave the desired product in high yield in every case (see Experimental Section).

Higher levels of bromination on the rings of **III** were readily achieved by reaction with equal volumes of bromine and tetrachloromethane under reflux to yield **V**. Interestingly, only one aromatic ring could be perbrominated. Bromine could be added to the second ring only at the C-7 position; the C-5 position is completely unreactive probably due to steric hindrance by the bromine atom on the C-4 position of the first ring.

Further iodination of the C ring of **VIII** to produce **IX** was accomplished by reaction with iodine and [bis(trifluoroacetoxy)iodo]benzene for several days at room temperature. Perhaps because of steric effects, attempts to obtain higher levels of iodination were unsuccessful.

From the *N*-( $\omega$ -bromoalkyl) halogenated carbazoles, acrylate or methacrylate monomers were prepared in high yield by reaction with the tetrabutylammonium salt of the desired acid anion. In the bromocarbazole series, the yields of **IV** and **VI** ranged from 66 to 94%; for the two iodinated methacrylates **X** and **XI**, the yields were 90 and 91%, respectively.

### Monomer Melting Points

As mentioned earlier, low-melting monomers would be easier to apply as bonding agents than their respective polymers. As expected, the melting points of

the tetrabromocarbazole methacrylates **IV** decrease from 178°C for the monomer containing the propylene spacer to 126°C for the monomer with the hexylene spacer (Table 1). A similar trend was previously reported for analogous nonhalogenated carbazole-containing acrylates [11]. Coincidentally, the triiodocarbazole methacrylate **X** with a butylene spacer has a melting point very close to that of the tetrabromo derivative **IVb**, but the addition of one more iodine raises the melting point of **XI** to ~210°C.

The same trend of longer spacers generating lower melting points was also observed in the heptabromo series of methacrylates. One might anticipate that the latter monomers would exhibit higher melting points due to their significantly higher mass. As expected, the heptabromocarbazole methacrylate with a butylene spacer **VIb** melts about 15°C higher than its tetrabromo analog **IVb**. Interestingly however, **VIc** with a pentylene spacer exhibits a melting point that is about 1°C lower than its tetrabromo analog **IVc**, and **VIId** melts approximately 4°C lower than **IVd**.

Although the melting point results of the individual monomers were encouraging, particularly those of the heptabromocarbazole series **VI**, the melting points of all of these compounds were still too high to be practical for our application. Consequently, we prepared a ternary mixture (**VIe**), composed of equal weights of heptabromocarbazole methacrylates with butylene (**VIb**), pentylene (**VIc**), and hexylene spacers (**VIId**). Although the melting temperature of this composition is very broad (it is a soft, taffy-like solid at room temperature), it converts completely to an isotropic liquid at 50°C.

### Polymer Properties

Since it was not our intent to optimize the polymerization procedure in order to generate the highest polymer molecular weight, the halogenated monomers were polymerized in bulk without initiator. Many of these polymers were thermally polymerized between glass slides in order to closely simulate the conditions under which they would be utilized. Most of the resulting polymers bonded the plates so well that they could only be isolated for characterization by dissolving the glass in hydrofluoric acid or by prying the plates apart. In every example, the colorless monomers generated colorless, nonscattering, optically isotropic polymers. An indication of good thermal stability is the observation that these optical properties were maintained even when the polymers were heated at 160–170°C for several hours. In addition, all of the brominated polymers synthesized have glass transitions below 200°C (Table 1), and when heated to 50–100°C above this temperature, they soften significantly and flow readily without discoloration. The decomposition temperatures (TGA) for the brominated polymers range from 335 to 400°C with no apparent correlation between thermal stability and the degree of bromination.

The glass transition temperatures of the tetrabrominated and heptabrominated methacrylate polymers decrease as the spacer length increases. Although only one example of an acrylate was synthesized, it has a lower  $T_g$  than the analogous methacrylate.

The polymers were insoluble in common polymer solvents such as dichloromethane, 1,1,2,2-tetrachloroethane, benzene, chlorobenzene, tetrahydrofuran, dimethylformamide, and dimethylsulfoxide. However, it was found that they are soluble at room temperature in liquids such as 1-methyl; 1-chloro; and 1-bromo-

naphthalene. This discovery permitted the determination of inherent viscosities (0.5 g/dL) in 1-chloronaphthalene.

The refractive indices of these polymers are shown in Table 1. One can see that the expected index-lowering effect caused by the incorporation of hydrocarbon spacers between the polymer backbone and the highly polarizable carbazole group may be compensated by halogenation of the carbazole ring. For example, the refractive index of poly(vinylcarbazole) (no spacer) and poly[4-(1,3,6,8-tetrabromo-9-carbazolyl)-1-butyl methacrylate] (**IVb** polymer) are both 1.68. Lengthening the carbon spacer by two methylene groups, e.g., a hexylene spacer, in the homologous brominated carbazole polymer **IVd** decreases the index by 0.01. For a two-methylene increase in spacer length, a decrease of 0.02 is observed in the heptabromo-containing polymers **VI**, but in these examples the refractive index is 1.74 and 1.72, respectively. Hence, the addition of three more bromine atoms to the carbazole ring results in a significant increase in refractive index.

As expected, the iodinated polymers **X** and **XI** have even higher refractive indices, 1.74 and 1.77. These polymers were not extensively investigated due to their potential photolytic reactivity.

The most extensively investigated polymer of this study is that derived from the ternary mixture of the heptabromocarbazole methacrylates with butylene, pentylene, and hexylene spacers **VIe**. The interest in this particular polymer derives predominantly from the low liquefaction temperature exhibited by the monomer mixture. The polymer was prepared by melting **VIe** between glass plates at a temperature slightly above 50°C to form a clear, transparent liquid. Upon raising the temperature to 100°C, the clear, transparent polymer formed within 30 min. The  $T_g$  of this glassy material is 175°C, and the refractive index, as measured by Becke line analysis, is 1.72.

## CONCLUSION

A series of acrylic-based polymers containing halogenated carbazole rings connected to the main chain by flexible spacer groups was investigated. The monomers are crystalline solids with melting points above 100°C. Bulk polymerization was accomplished at temperatures slightly above the melting points. The resulting polymers are glassy, colorless, and nonscattering, and they possess high isotropic refractive indices between 1.67 and 1.77.

Monomer melting points below 100°C were obtained by the use of mixtures. A useful three-component mixture was found to melt below 50°C, and its polymer exhibits a refractive index of 1.72. This mixture was found to be an effective adhesive for bonding glass prisms and birefringent polymer films.

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