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Poly(*N*-acylethylenimines) with Pendant Carbazole Derivatives. 2. Synthesis of 3,6-Dimethoxy-, 3,6-Dihydroxy-, and 2,7-Dihydroxycarbazole-Containing Polymers

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ABSTRACT: The synthesis and polymerization of 2-[2-(9-(3,6-dimethoxycarbazolyl))ethyl]-2-oxazoline and 2-[4-(9-(3,6-dimethoxycarbazolyl))butyl]-2-oxazoline are described. The former gave a polymer with a high percentage of cross-linking; the latter gave an amorphous polymer in 100% yield. Demethylation of the second polymer and a 2,7-dimethoxycarbazole-containing polymer with boron tribromide gave amorphous 3,6-dihydroxycarbazole and 2,7-dihydroxycarbazole polymers, respectively, in quantitative yields. These polymers showed higher T_g's than those of methoxycarbazole polymers and were insoluble in most organic solvents; strong hydrogen bonding may cause the insolubility.

Introduction

Modification of electrical properties of pendant group polymers through formation of charge-transfer complexes has been studied extensively, especially for carbazole-containing polymers such as poly(*N*-vinylcarbazole) (PVK).[1] Although many complexes of PVK showed semiconducting behavior and EPR signals, the conductivity (σ) remained very low, even at very high dopant concentrations. A more promising approach to improve the conductivities of PVK-based materials was reported in 1977 by Block et al.[2] They introduced unpaired electrons into PVK: partial oxidation of PVK with tris(*p*-bromophenyl)ammonium hexachloroantimonate gave cross-linked material containing 3,3′-dicarbazylium cation radicals having $\sigma_{RT} = 10^{-5}$ $(\Omega\ cm)^{-1}$. These authors also estimated $\sigma_{RT} = 10^{-2}$ $(\Omega\ cm)^{-1}$ for the fully oxidized material. However, this material is undoubtedly highly cross-linked and impossible to process. To avoid the necessity of processing, cross-linked films were recently made by electrochemical oxidation of various carbazole polymers in situ.[3] For example, electrooxidation of PVK gave 50% oxidized films having $\sigma_{RT} = 6 \times 10^{-4}$ $(\Omega\ cm)^{-1}$.

Another way of solving the processing problem is to develop polymers that will not cross-link when oxidized, in other words, to produce redox-reversible carbazole polymers by blocking the reactive 3,6-positions of the carbazole ring.[4] The major objective of this work was to synthesize redox-reversible poly(*N*-acylethylenimines) with pendant carbazole derivatives which could form stable ion radical salts.

In the first paper of this series, we reported the synthesis of poly(*N*-acylethylenimines) with 2,7-dimethoxycarbazole as the side groups from properly substituted oxazoline monomers.[5] Here, we describe the preparation of similar polymers with 3,6-dimethoxycarbazole on the side chain. One important reason for selecting the methoxylated carbazoles as the side groups is the ease of hydrolysis of the methoxy groups to form corresponding hydroxylated carbazole polymers, which are our major interest and which may show reversible electrochemical behavior. The oxazoline ring, however, is relatively basic and can be protonated by a phenoxy proton to a slight extent, if there are any present. The protonated oxazoline is very vulnerable to nucleophilic attack and ends up as an amide ether. Therefore, the methoxys serve as protecting groups, which prevent chain transfer of the phenolic protons on oxazoline rings and make the polymerization possible.

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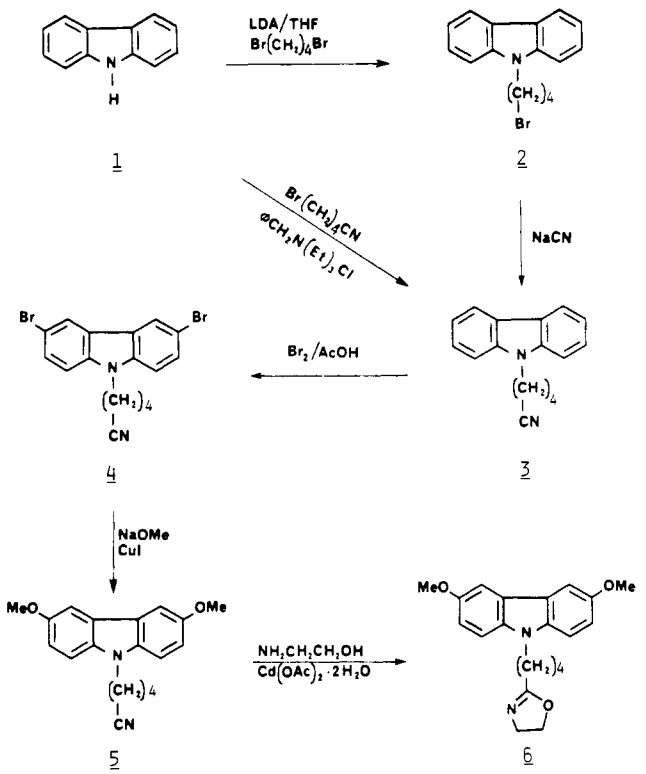
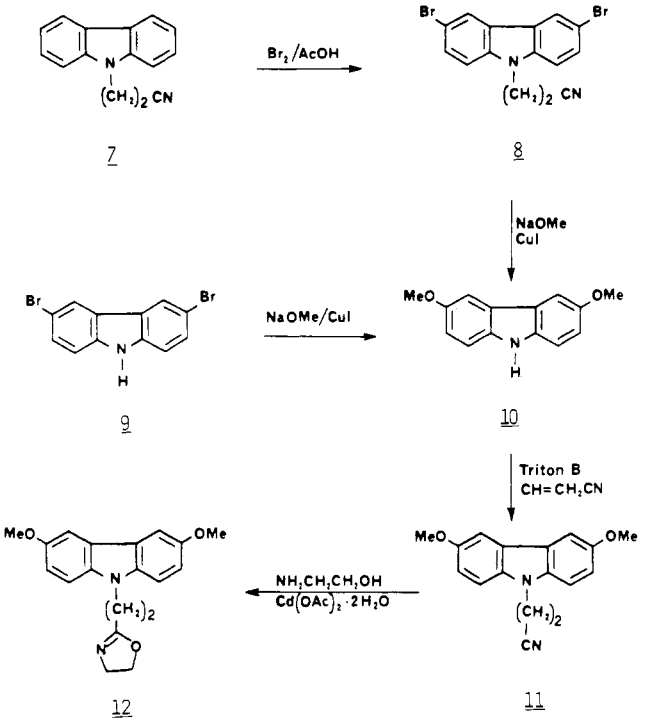
Scheme I



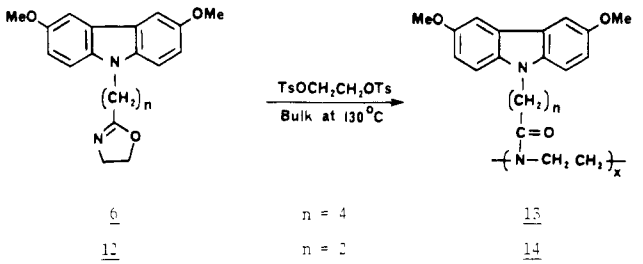
Scheme II



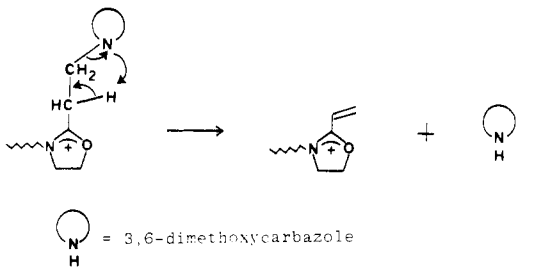
Results and Discussion

In our earlier paper,[5] **3** was synthesized in two steps from **1** via **2** (Scheme I). More conveniently, **3** was prepared in one step by reacting **1** with 1-bromo-4-cyanobutane in the presence of benzyltriethyl ammonium chloride in caustic solution, a method reported by Nishi et al.[6] Bromination of **3** with 2 equiv of bromine in acetic acid gave a 91% yield of 3,6-dibrominated **4**. This was treated with a large excess of sodium methoxide in the presence of copper(I) iodide, a procedure developed by Staito et al.,[7] to give **5** in 48% yield. Compound **5** was reacted further with ethanolamine, with cadmium acetate dihydrate as the catalyst,[8] to give **6** in 65% yield.

Scheme III



Scheme IV

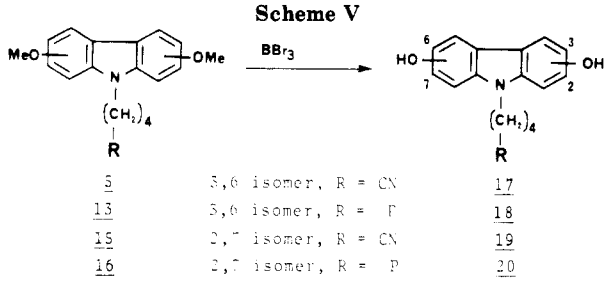


A similar route did not work, however, for the preparation of **12**. As shown in Scheme II, **8** was obtained in 90% yield from **7**, which was prepared from **1** and acrylonitrile with a catalytic amount of Triton B according to a known procedure.[9] Reaction of **8** with excess sodium methoxide and copper(I) iodide yielded dealkylated **10** instead of **11**. The fact that dealkylation occurred only for **8** and not for **4** indicates that deprotonation of the proton adjacent to the nitrile group followed by elimination to form acrylonitrile was taking place in the base treatment of **8**. Clearly, the dealkylation made this route inappropriate and another approach was thus undertaken. Bromination of **1** in a similar fashion gave **9** (90%), which was transformed to **10** (52%) with excess sodium methoxide and copper(I) iodide. Reaction of **10** with acrylonitrile and a catalytic amount of Triton B gave **11** in 92% yield. Reacting with ethanolamine and cadmium acetate dihydrate, **11** gave **12** in 63% yield.

Monomers **6** and **12** were purified by the same procedure described in the earlier paper[5] and then polymerized (Scheme III) in bulk under high vacuum (ca. 10^{-4} mmHg) in sealed tubes with ethylene glycol ditosylate as the initiator. Polymers **13** and **14** having almost identical appearance right after polymerization, light yellow and transparent, were obtained in 100% yields. These two polymers showed very similar IR spectra, with the amide bands at 1645 cm^{-1} in both cases. The intrinsic viscosities of **13** (dL/g, in $CHCl_3$ at 30.00 ± 0.02 °C) were 0.42, 0.77, 0.85, and 0.95 respectively when monomer-ω-initiator ratios of 1000, 3200, 5000, and 10 000 were used. In contrast to **13**, which was readily soluble in many organic solvents, especially chlorinated ones such as chloroform, dichloromethane, and *o*-dichlorobenzene, **14** was not soluble in any organic solvent tested. There was no obvious swelling when **14** was placed in the organic solvents; this suggests a relatively high degree of cross-linking. In addition there was no obvious softening or flowing when **14** was examined under a hot-stage optical microscope at 280 °C, far above its T_g (130 °C; see below).

The cross-linking was unexpected and its mechanism is difficult to understand completely. However, side reactions such as that given in Scheme IV may initiate the cross-linking process. It is possible that an oxazolinium ion chain end may eliminate 3,6-dimethoxycarbazole

Scheme V



5	5,6 isomer, R = CN	17
13	5,6 isomer, R = P	18
15	2,7 isomer, R = CN	19
16	2,7 isomer, R = P	20

P = poly(N-acylethylenimine) backbone

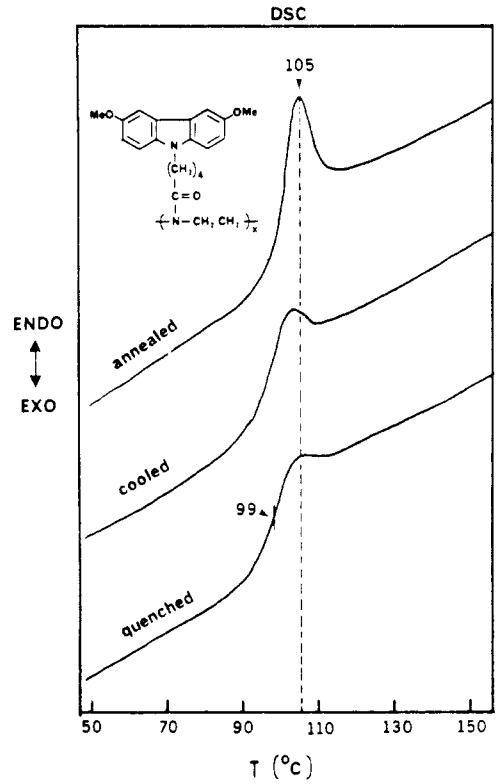


Figure 1. DSC curves of **13** at 20 °C/min heating rate.

through a four-center rearrangement, generating a 2-vinyl-2-oxazolinium ion. This species has many reaction modes,[10] which could result in cross-linking.

We reported earlier[5] that poly[*N*-((9-2,7-dimethoxycarbazolyl))-5-pentanyl)ethylenimine], a polymer with four methylene units on the side chain, compound **16** in Scheme V, crystallized during the polymerization. Similar polymers with three and five methylene units on the side chains did not. This seemed to suggest that polymers with even numbers of methylene units have a better chance to be crystalline and thus led us to prepare **13** and **14**. However, **13** is amorphous; its DSC thermograms are given in Figure 1. A small endothermic peak can be seen in the quenched **13** (curve C). When the sample was cooled and reheated at 20 °C/min, the endothermic peak was relatively large (curve B). The endothermic peak became very large upon prolonged annealing and the T_g's rose (curve A). This type of thermal behavior has been discussed in greater detail elsewhere.[5,11] The as-obtained cross-linked **14** was also examined by DSC and a T_g was observed at 130 °C. Its general DSC behavior was similar to that of **13**.

Demethylation of some methoxy compounds, **5**, **13**, **15**, and **16**, with boron tribromide (BBr_3) to the corresponding hydroxy products, **17**, **18**, **19**, and **20**, is shown in Scheme V. (The synthesis of **15** and **16** has been described.[5]) The amount of BBr_3 used was determined by the number of heteroatoms, nitrogen and oxygen, present in the molecule or in a repeat unit for the polymers.[12] There are two oxygen and two nitrogen atoms in **5** and **15**; therefore 4 equiv of BBr_3 was used for 1 equiv of **5** and **15** to give **17** and **19**, respectively, in about 80% yields. Similarly, 5 equiv of BBr_3 was used for 1 equiv of the polymer repeat in **13** or **16** to give **18** or **20**, respectively, in quantitative yields.

Table I
Characterization Data for the Polymers

polymer	T_g,[a] °C	IR (cm^{-1}, KBr) C=O (amide)	elem anal.[b] % C	% H	% N	% O
13	99	1645	71.34 (71.59)	6.97 (6.82)	7.84 (7.95)	13.36 (13.64)
14	130	1645				
18	185	1624	70.11 (70.37)	6.26 (6.17)	8.40 (8.64)	14.98 (14.81)
20	169	1611	70.13 (70.37)	6.32 (6.17)	8.75 (8.64)	14.67 (14.81)

[a] Based on quenched sample, at 20 °C/min heating rate. [b] Calculated values in parentheses.

The characterization data for all the polymers in terms of T_g, amide I absorption band in the IR, and elemental analysis are given in Table I. The results of the elemental analysis fit well with the calculated values. Both **18** and **20** are amorphous with higher T_g's than those of the corresponding methoxylated analogues. This may be due to strong hydrogen bonding between the phenoxy hydrogens and the amide carbonyl groups of the polymer backbones, as suggested by their IR spectra. The stretching bands due to the amide carbonyls of **18** and **20** appear respectively at 1624 and 1611 cm^{-1}, which are much lower than those (1645 cm^{-1}) of the methoxylated polymers where no hydrogen bonding can occur. The strong hydrogen bonding may be responsible for the very small solubility of **18** and **20** in many common organic solvents. So far DMF is the best solvent found, able to dissolve the freshly prepared **18** and **20** to a small extent at room temperature and a larger extent at temperatures close to its boiling point. These polymers become insoluble even in boiling DMF after storing for a few days. The aged polymers were still amorphous according to X-ray diffraction and showed DSC and IR spectra similar to those of freshly prepared samples. These indicate that there was no chemical reaction such as cross-linking taking place. It is possible, therefore, that the hydrogen bonding is creating some local order, which is not significant enough to be detected or to crystallize the polymers. Due to the potential insolubility, the newly prepared polymers **18** and **20** were dissolved immediately in hot DMF for further study.

Conclusions

This paper is concerned with the synthesis of dimethoxy- and dihydroxy-carbazole polymers and model compounds. As these were desired as the starting materials for the electrochemical studies reported in the next paper, rather than as ends in themselves, there are a few conclusions. The cross-linking of polymer **14** was not expected. We postulate the loss of carbazole, regenerating a double bond for two reasons. First, such a reaction is base catalyzed, as shown in the attempted synthesis of (dimethoxycarbazolyl)propionitrile (**11**) from **8**. Also, when four CH_2's are present, cross-linking does not occur, showing that the carbazole ring is not attacked during polymerization. The structure shown in Scheme IV will generate a branch which can lead to cross-linking.

The lack of solubility of the dihydroxycarbazole polymers is not too surprising. They can interact strongly via H bonding with the other dihydroxycarbazole units as well as with the backbone. It is difficult to find a solvent with the correct solubility parameter for the whole molecule which can also solvate the phenoxy groups well. If the molecules are kept apart in solution, they stay soluble. However, if they are precipitated, intermolecular interactions gradually form and strengthen until the polymer can no longer be dissolved in DMF.

Experimental Section

All melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Digilab FTS-14 Fourier transform spectrometer and are given in cm^{-1}. ^1H NMR spectra were taken at 60 MHz with a Varian EM-360 instrument in chloroform with Me_4Si as reference, unless indicated otherwise, and are reported in δ values. Mass spectra and exact mass measurements were taken on a AEI Kratos MS-30 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The viscosities of the polymer solutions were determined with a Cannon-Ubbelohde viscometer. T_g's and T_m's of polymers were determined with a Perkin-Elmer DSC II. Wide-angle X-ray patterns were recorded with a flat-plate camera using a Philips XRG 3100 X-ray generator with Ni-filtered Cu Kα radiation.

Neutral aluminum oxide and silica gel were from Fisher Scientific Co. Toluene, *n*-heptane, and hexanes were distilled before use for chromatography and recrystallization of all oxazoline monomers. All glassware used in purification and polymerization of the monomers was soaked overnight in Nochromix cleaning solution, rinsed with water, 10% ammonium hydroxide, and water, and soaked in distilled water and dried in a hot-air oven.

9-(4-Cyanobutyl)carbazole (3). A mixture of carbazole (5 g, 0.03 mol), 50% aqueous NaOH (20 mL), benzene (3 mL), and benzyltriethyl ammonium chloride (200 mg) was stirred magnetically in a 125-mL Erlenmeyer flask. To the mixture was added 1-bromo-4-cyanobutane (5 mL) dropwise. The resulting mixture was stirred for 2 h and then poured into hot water (20 mL). After cooling, precipitate was collected, washed with water until neutral, air-dried, and recrystallized from ethanol to give **3** (6.5 g, 88%) as white crystals: mp 118–120 °C (lit.[5] mp 118–120 °C).

9-(4-Cyanobutyl)-3,6-dibromocarbazole (4). To a water-cooled mixture of **3** (25 g, 0.1 mol), acetic acid (100 mL), and sodium acetate (16.5 g), Br_2 (11.5 mL, 0.22 mol) in 50 mL of acetic acid was added dropwise through an additional funnel. After addition was completed, the mixture was stirred for 2 h and poured into 500 mL of 1% stannous chloride aqueous solution to give crude **4** as white powder (39 g, 96%). This was used directly for the next step or recrystallized from chloroform to give **4** (37 g, 91%) as white crystals: mp 135–137 °C; IR (KBr) 2960 (w), 2940 (w), 2870 (w), 2248 (w), 1593 (w), 1476 (s), 1435 (s), 1381 (w), 1357 (w), 1289 (m), 1236 (m), 1183 (w), 1150 (w), 1055 (w), 1022 (w), 878 (m), 828 (m), 803 (m); NMR 8.1 (d, J = 2 Hz, 2 H), 7.3 (center of an AB, J = 10 Hz, $\Delta\nu$ = 22 Hz, with downfield peaks split further with J = 2 Hz, 4 H), 4.2 (t, J = 6 Hz, 2 H), 2.2 (t, J = 6 Hz, 2 H), 2.0–1.3 (m, br, 4 H); mass for $C_{17}H_{14}Br_2N_2$, m/e 406.

9-(4-Cyanobutyl)-3,6-dimethoxycarbazole (5). Into a three-necked flask fitted with a condenser, N_2 inlet, addition funnel, and magnetic stirrer was added 350 mL of dry methanol. The entire solution was cooled to 0 °C with ice water before sodium (31.5 g, 1.37 mol) was added gradually. The ice water bath was removed and the mixture was stirred until all the sodium had reacted. To this sodium methoxide solution was added DMF (170 mL), copper(I) iodide (52 g, 0.27 mol), **4** (27.5 g, 0.068 mol), and another 170 mL of DMF. The resulting mixture was heated to reflux for 4 h under a N_2 atmosphere. The precipitate was filtered while hot and the filtrate was diluted with 500 mL of water and extracted with chloroform (300 mL × 3). The combined organic layers were neutralized with 5% HCl, followed by washing with water and brine, drying by passing through sodium sulfate, and concentrating in vacuo. The residue was crystallized from methanol to give fine gray needles and then sublimed in vacuo (180 °C (0.02 mmHg)). The sublimate was recrystallized from methanol to give **5** (10 g, 48%) as fine needles: mp 98–100 °C; IR (KBr) 2940 (w), 2836 (w), 2246 (w), 1610 (w), 1580 (w), 1494 (s), 1483 (s), 1335 (m), 1308 (w), 1290 (w), 1204 (s), 1160 (s), 1068 (m), 1028 (m), 833 (w), 807 (m), 777 (m); NMR 7.5 (m, 2 H), 7.2 (m, 4 H), 4.2 (t, J = 6 Hz, 2 H), 3.9 (s, 6 H), 2.2 (t, J = 6 Hz, 2 H), 2.0–1.2 (m, br, 4 H); mass for $C_{19}H_{20}N_2O_2$, m/e 308.

2-[4-(9-(3,6-Dimethoxycarbazolyl))butyl]-2-oxazoline (6). To a 25-mL flask equipped with a condenser and magnetic stirrer were added **5** (6.2 g, 0.02 mol), cadmium acetate dihydrate (0.25 g), and ethanolamine (2 mL). The resulting mixture was heated at 140–145 °C under N_2 for 24 h. The hot melt was poured into 500 mL of boiling hexanes and heated on a hot plate with magnetic stirring for 5 min. The hot hexane layer was decanted into a round-bottom flask and concentrated in vacuo to give a pale solid. This was dissolved in 100 mL of toluene and then passed quickly through a short alumina column 20 g, activity III, slurry packed with toluene). Elution was continued until **6** had been collected completely, monitored by TLC. The toluene was evaporated and the residual solid was recrystallized from hexanes to give **6** as white crystals: mp 92–94 °C; IR (KBr) 2955 (w), 2900 (w), 2835 (w), 1670 (m), 1609 (w), 1485 (s), 1338 (w), 1211 (s), 1173 (s), 1073 (m), 1030 (m), 952 (w), 808 (m), 780 (m); NMR 7.50 (d, J = 4 Hz, 2 H), 7.3–6.9 (m, 4 H), 4.3–3.7 (m, 12 H, OCH_3 peak at 3.9 ppm), 2.25 (t, 2 H), 2.0–1.5 (m, 4 H); mass for $C_{12}H_{24}N_2O_3$, m/e 352.

9-(2-Cyanoethyl)-3,6-dibromocarbazole (8) was prepared according to the procedure for the preparation of **4**. **7** (4.4 g, 0.2 mol) and Br_2 (21 mL) were reacted and **8** was obtained as a white powder (72 g, 95%). The recrystallized **8** (acetone) showed the following: mp 196–199 °C; IR 2251 (w), 1594 (w), 1471 (s), 1435 (s), 1377 (m), 1350 (m), 1282 (s), 1228 (m), 1199 (m), 1145 (w), 800 (s), 650 (w); NMR 8.1 (d, J = 2 Hz, 2 H), 7.4 (center of an AB, 4 H), 4.5 (t, J = 7 Hz, 2 H), 2.8 (t, J = 7 Hz, 2 H).

3,6-Dibromocarbazole (9) was prepared according to the procedure for the preparation of **4**. **1** (50 g, 0.3 mol) and Br_2 (32 mL) were reacted and **9** was obtained as a white powder (92 g, 95%). The recrystallized **9** (ethanol) showed the following: mp 210–212 °C (lit.[13] 211–213 °C); NMR (acetone-d_6) 9.7–8.9 (br, 1 H), 8.1 (s, 2 H), 7.4 (m, 4 H).

3,6-Dimethoxycarbazole (10) was prepared from **9** (16.5 g, 0.05 mol) and copper(I) iodide (38 g) in DMF/MeOH containing sodium methoxide, which was prepared from sodium (23 g, 1.0 mol) in methanol (250 mL) according to the procedure for the preparation of **5**. After workup, the solid residue was sublimed in vacuo (170 °C (0.02 mmHg)) to give **10** (6.1 g, 54%) as white needles: mp 102–104 °C (lit.[4a] mp 178–180 °C); IR (KBr) 3406 (m), 3005 (w), 2833 (w), 1612 (w), 1579 (m), 1497 (s), 1468 (s), 1438 (m), 1335 (w), 1297 (s), 1264 (w), 1210 (s), 1153 (s), 1024 (m), 805 (m), 778 (m); NMR (acetone-d_6) 9.1–8.7 (br, 1 H), 7.6 (d, J = 2.5 Hz, 2 H), 7.2 (AB, J = 9 Hz, $\Delta\nu$ = 22 Hz, with higher field peaks split further having J = 2.5 Hz, 4 H), 3.9 (s, 6 H). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74.01; H, 5.73; N, 6.16; O, 14.10. Found: C, 73.79; H, 5.83; N, 6.17; O, 13.95. Compound **10** obtained from base treatment of **8** showed the same physical properties.

9-(2-Cyanoethyl)-3,6-dimethoxycarbazole (11). Into a 150-mL Erlenmeyer flask equipped with a magnetic stirrer were added **9** (11.5 g, 0.05 mol) and acrylonitrile (50 mL). The mixture was cooled to ca. 0 °C with an ice water bath, and 40% Triton B (0.12 mL) was added dropwise via syringe. The resulting mixture was removed from the bath and stirred until it reached room temperature. The precipitated product was filtered and the filtrate was concentrated in vacuo to give additional product. The combined products were sublimed in vacuo (180 °C (0.1 mmHg)) to give **11** (13 g, 92%) as white crystals: mp 148–149 °C; IR 2950 (w), 2834 (w), 2250 (w), 1610 (w), 1579 (w), 1486 (s), 1480 (s), 1330 (m), 1220 (m), 1200 (s), 1160 (s), 1066 (m), 1025 (m), 830 (m), 810 (m), 780 (m); NMR 7.5 (d, 2 H), 7.3–6.9 (m, 4 H), 4.5 (t, J = 7 Hz, 2 H), 3.9 (s, 6 H), 2.7 (t, J = 7 Hz, 2 H). Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.86; H, 5.71; O, 11.43; N, 10.0. Found: C, 72.59; H, 5.68; O, 11.58; N, 10.10.

2-[2-(9-(3,6-Dimethoxycarbazolyl))ethyl]-2-oxazoline (12) was prepared following the procedure for **6** from **11** (7.0 g, 0.025 mol) and ethanolamine (1.7 mL) with $Cd(OAc)_2 \cdot 2H_2O$ (0.15 g) as catalyst. Pure **12** (5.5 g, 68%) showed the following: mp 125–126 °C (hexanes); IR (KBr) 2940 (w), 2831 (w), 1664 (m), 1483 (s), 1203 (s), 962 (s); NMR 7.50 (d, J = 4 Hz, 2 H), 7.3–6.9 (m, 4 H), 4.3–3.7 (m, 12 H), 2.3 (t, 2 H); mass for $C_{19}H_{20}N_2O_3$, m/e 324.

Polymerization. A polymerization tube containing **6** (4.0 g, 10.3 mmol) and ethylene glycol ditosylate (0.4 mg, 1.08×10^{-6} mol) was degassed under high vacuum (ca. 10^{-4} mm) overnight and sealed. The sealed tube was heated in a thermal bath at 130 °C for 6 h, at 140 °C for 3 h, and finally at 160 °C for 3 h. The mixture slowly thickened and solidified to a pale yellow mass. The product was dissolved in CH_2Cl_2, precipitated by adding slowly to excess methanol, and vacuum-dried at 100 °C overnight to give **6** in 100% yield. Polymerization of **12** was done by the same procedure and under the same conditions.

9-(4-Cyanobutyl)-2,7-dihydroxycarbazole (19). Into a 100-mL three-necked flask equipped with a magnetic stirrer, addition funnel, and septum inlet adaptor was placed **15** (1.5 g, 5 mmol). This system was dried under vacuum and then purged with nitrogen before CH_2Cl_2 (20 mL) was added. After **15** was dissolved completely, 1 M BBr_3 in CH_2Cl_2 (20 mL, 20 mmol) was placed in the funnel via syringe and then added dropwise to the ice water cooled **15**/CH_2Cl_2. The mixture was stirred at room temperature for 3 h and then poured into 100 mL of water, followed by extraction with ethyl acetate (50 mL × 2). After workup, the organic layer was concentrated in vacuo and the solid residue was sublimed in vacuo (160 °C/0.01 mmHg)) to give **19** (1.0 g, 75%) as a pale white powder: 160–162 °C; IR 3600–3000 (br, peak at 3310), 2250 (w), 1610 (s), 1570 (s), 1360 (m), 1323 (m), 1205 (s), 1155 (s), 1130 (s), 980 (m), 825 (m), 797 (m); NMR (acetone-d_6) 9.0–8.0 (br, 2 H), 7.8 (downfield peaks of an AB, J = 8 Hz, 2 H), 6.9 (d, J = 2 Hz, 2 H), 6.8 (high-field peaks of the AB, J = 8 Hz; these peaks split further due to β coupling having J = 2 Hz, 2 H), 4.2 (t, J = 6 Hz, 2 H), 2.4 (t, J = 6 Hz, 2 H), 1.4–2.1 (m, 4 H); mass for $C_{17}H_{16}N_2O_2$, m/e 280.

9-(4-Cyanobutyl)-3,6-dihydroxycarbazole (17) was prepared, according to the procedure for the preparation of **19**, from **5** (1 g, 3.25 mmol) in CH_2Cl_2 (20 mL) and 1 M BBr_3 in CH_2Cl_2 (13.2 mL, 13.2 mmol). The crude **17** was sublimed under vacuum (230 °C (0.05 mmHg)) to give **17** (0.71 g, 78%) as a white powder: mp 172–175 °C; IR 3394 (s), 2935 (w), 2251 (w), 1580 (m), 1504 (s), 1479 (s), 1440 (m), 1345 (s), 1312 (m), 1197 (s), 1174 (m), 1155 (m), 1140 (m), 940 (m), 863 (m), 800 (s); NMR (acetone-d_6) 8.2–7.6 (br, 2 H), 7.5 (d, J = 3 Hz, 2 H), 7.1 (center of an AB, J = 9 Hz, $\Delta\nu$ = 18 Hz; the high-field peaks were split further due to β coupling having J = 3 Hz, 4 H), 4.2 (t, J = 6 Hz, 2 H), 2.3 (t, J = 6 Hz, 2 H), 1.9–1.3 (m, 4 H); mass for $C_{17}H_{16}N_2O_2$, m/e 280.

Poly[*N*-((9-(2,7-dihydroxycarbazolyl))-5-pentanoyl)-ethylenimine] (20). The reaction setup was similar to that for preparation of **19**. 1 M BBr_3 (5 mL, 5 mmol) was added to ice water cooled **16** (0.35 g, 1 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 3 h and then poured into MeOH (150 mL). The precipitate was filtered and dried in a vacuum oven overnight to give **20** (0.33 g, 100%) as a white powder. Anal. Calcd for $(C_{19}H_{20}N_2O_3)_x$: C, 70.37; H, 6.17; N, 8.64; O, 14.81. Found: C, 70.13; H, 6.32; N, 8.75; O, 14.67.

Poly[*N*-((9-(3,6-dihydroxycarbazolyl))-5-pentanoyl)-ethylenimine] (18). Polymer **18** was prepared as described for **20** from **19** by using the same quantities of reactants. The yield for **18** was 100%. Anal. Calcd for $(C_{19}H_{20}N_2O_3)_x$: C, 70.37; H, 6.17; N, 8.64; O, 14.81. Found: C, 70.11; H, 6.26; N, 8.40; O, 14.98.

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