Poly(*N*-acylethylenimines) with Pendant Carbazole Derivatives. 1. Synthesis

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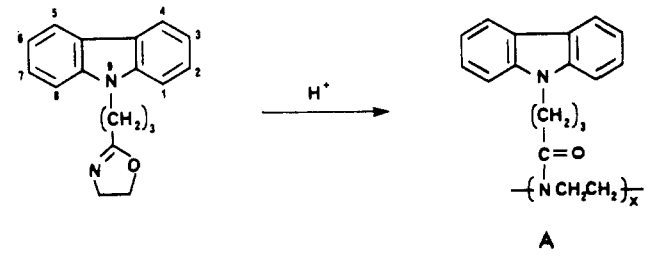
ABSTRACT: The synthesis and polymerization of 2-[3-(2,7-dimethoxycarbazol-9-yl)propyl]-2-oxazoline (**8a**), 2-[4-(2,7-dimethoxycarbazol-9-yl)butyl]-2-oxazoline (**8b**), 2-[5-(2,7-dimethoxycarbazol-9-yl)pentyl]-2-oxazoline (**8c**), 2-(3-carbazol-9-ylpropyl)-2-oxazoline (**8d**), 2-(4-carbazol-9-ylbutyl)-2-oxazoline (**8e**), and 2-(5-carbazol-9-ylpentyl)-2-oxazoline (**8f**) are described. The polymers were characterized by intrinsic viscosity, elemental analysis, glass transition temperature, and melting temperature. The polymer derived from **8b** is the only polymer which crystallized during polymerization and shows T_m = 232 °C.

Introduction

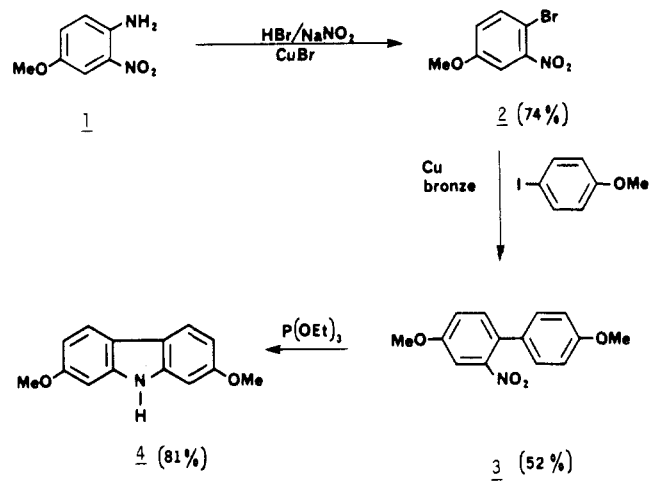
Carbazole-containing polymers, especially those having carbazole derivatives on the side chains, are important because of their interesting electrical and photoelectrical properties.[1] These properties, in many cases, can be enhanced through chemical modification of the side-chain groups and/or formation of charge-transfer (CT) complexes with molecular electron acceptors,[1,2] such as tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), and 2,4,7-trinitrofluorenone (TNF). A more promising method of producing conducting polymers based on the side-chain carbazole groups was introduced by Block et al.:[3] poly(*N*-vinylcarbazole) (PVK) was partially oxidized with a small amount of tri(*p*-bromophenyl)ammoniumyl hexachloroantimonate to form dicarbazolyl cation radicals having a conductivity of 10^{-5} Ω^{-1} cm^{-1} at room temperature. They also predicted a conductivity of 10^{-2} Ω^{-1} cm^{-1} for the fully oxidized material. Since then, many electrochemical oxidation of various carbazole polymers to prepare radical-containing films which cannot be obtained through the chemical method have been reported.[4] In this paper we describe the synthesis of carbazole-containing poly(*N*-acylethylenimines). The studies of their TCNQ complexes[5] and electrochemical oxidation[6] will be presented later.

Poly(*N*-acylethylenimines) have tertiary amide backbones with the side chains attached to the nitrogen. It is therefore impossible to have the stereoirregularity found in vinyl, epoxy, etc., polymers. Because of this, most of these polymers can be crystallized easily to highly crystalline materials.[7a] However, great difficulty was encountered in trying to crystallize A,[7b,c] synthesized in our research group from its corresponding oxazoline monomer (Scheme I). To study the factors determining the ease of crystallization of carbazole-containing polymers, two modifications were investigated. First, the spacing between the pendant groups and the main chain was adjusted by varying the number of methylene groups. Although the analogues of A with one[8a] or two[8] methylene units between the carbazole and the polymer backbone were synthesized as oligomer or low molecular weight polymers, their properties were not reported. It is possible that the low molecular weight resulted from steric hindrance of the bulky carbazole ring close to the oxazoline ring. The larger spacers could reduce the steric effect and hence make it easier to produce high molecular weight polymers. Therefore, polymers having longer side chains were synthesized. Second, 2,7-dimethoxycarbazole, a more polar and electron-rich molecule than carbazole, was chosen as the side-chain substituent. It was hoped that the polarity of 2,7-dimethoxycarbazole could induce easier crystallization of the polymers.

Scheme I



Scheme II



Results and Discussion

The synthesis of 2,7-dimethoxycarbazole (**4**) was carried out according to Scheme II. Commercially available **1** was diazotized with sodium nitrite and then added to a boiling solution of cuprous bromide in hydrobromic acid to give a 74% yield of **2**. This compound was reacted with *p*-iodoanisole in the presence of activated copper bronze in bulk at 200 °C to give **3** in 52% yield. This procedure is more convenient that that reported,[9] in which nitrobenzene was used as solvent. (When this coupling reaction was run in DMF, a mixture of **3** (15%) and the symmetrically coupled product of **2**, i.e., 2,2′-dinitro-4,4′-dimethoxybiphenyl (34%) was obtained.) Reductive cyclization of **3** with triethyl phosphite, the Cadogan carbazole synthesis,[10] gave **4** in 81% yield. Although all the steps involved in making **4** have been described earlier,[9,11,12] the modified procedures are given in detail in the Experimental Section.

Efforts to N-alkylate carbazole (**5**) by reacting sodium carbazole with appropriate alkylating agents, a widely used method for the preparation of *N*-alkylcarbazole,[8a,13] were quickly abandoned because of two major problems. First, incomplete formation of the sodium carbazole created

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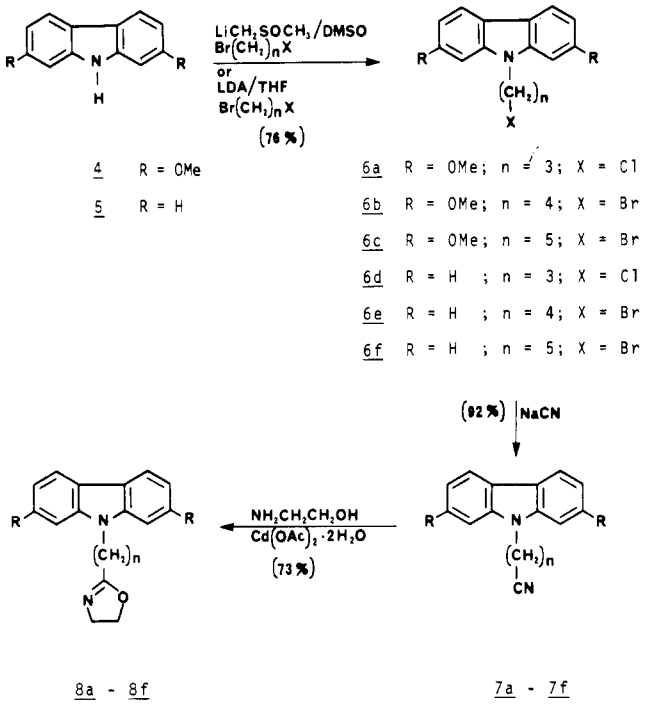
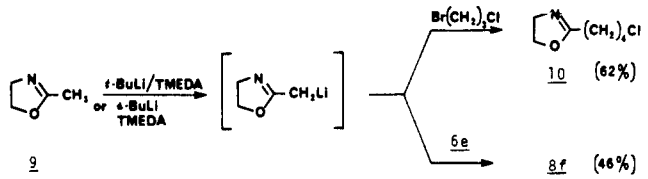
Scheme III



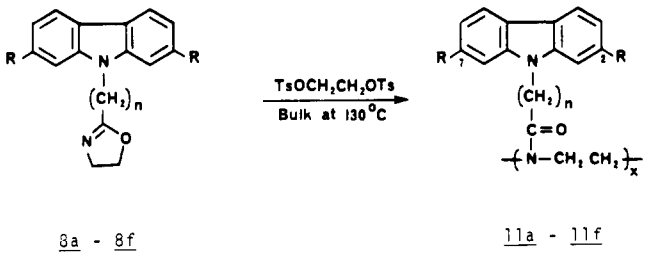
Scheme IV



difficulty in purification and low yields of the alkylated products were obtained. Second, the reaction procedure was tedious, e.g., refluxing the reaction mixture for a long period of time to form sodium carbazole is generally necessary. Therefore, two alternative mild methods for preparation of carbazole anions were developed and are shown in Scheme III: N-alkylation of **4** and **5** was achieved by generating the respective nitrogen anions with lithium dimethyl sulfoxide or, more conveniently, with lithium diisopropylamide (LDA) in the THF at room temperature. The anion was reacted with a large excess of 1-bromo-3-chloropropane, 1,4-dibromobutane, or 1,5-dibromopentane to give 45% yields of **6a** and **6d** and 75% average yields of **6b**, **6c**, **6e**, and **6f**. The lower yields in the first two cases were due to a competing side reaction, namely dehydrobromination of 1-bromo-3-chloropropane, since large amounts of starting carbazoles, **4** and **5**, were detected by NMR and TLC. (Dehydrobromination was the exclusive reaction when 1,2-dibromoethane or 1-bromo-2-chloroethane was reacted with the anion of **5**. No alkylated product could be found and **5** was recovered.) The alkylated products were reacted with sodium cyanide to give **7a–f** in higher than 91% isolated yields. When the crude alkyl halides (**6a–f**) were reacted directly with sodium cyanide, **7a** and **7d** were isolated in about 60% yields and **7b**, **7c**, **7e**, and **7f** were isolated in about 80% yields from **4** and **5** correspondingly. Reaction of the nitrile compounds with ethanolamine in the presence of a catalytic amount of cadmium acetate dihydrate, a procedure developed by Witte et al.,[14] gave the corresponding oxazolines, **8a–f**, in about 70% yield.

Alternatively, **8f** was prepared (Scheme IV) in 46% yield by reacting **6e** with the anion of **9**, which was generated

Scheme V



a R = OMe; n = 3
b R = OMe; n = 4
c R = OMe; n = 5
d R = H ; n = 3
e R = H ; n = 4
f R = H ; n = 5

slowly with *n*-butyllithium, or more readily with *sec*-butyllithium or *tert*-butyllithium and 1 equiv of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) at −78 °C. As also shown in Scheme IV, a 62% yield of **10** was isolated when the anion of **9** was quenched with 1-bromo-3-chloropentane. This one-step synthesis, however, was not used in the large-scale preparation of **8c** and **8f** because of its low yield and the highly restrictive reaction conditions required.

Normal monomer purification techniques such as distillation, sublimation, multiple recrystallization, etc., all failed to give ultrapure monomer which could be polymerized to high molecular weight polymer. This suggested that traces of hydroxamide and/or other polar impurities, which could retard or inhibit the polymerization, remained in the monomer. The use of column chromatography as a means of purification also has problems: the oxazoline ring is highly reactive and was hydrolyzed. Only a small amount of oxazoline monomer was obtained if enough alumina was used to attempt a true chromatographic separation. A successful purification procedure was developed to eliminate all the polar impurities by recognition of these facts. The oxazoline was purified by passing a toluene solution of the crude product mixture quickly through 5 times its weight of neutral alumina (activity III). All the polar impurities were adsorbed on the column while the oxazoline saturated the column and passed through. The monomer was recrystallized from hexanes or *n*-heptane. Thus purified, the monomers readily polymerized with monomer–initiator ratios as high as or higher than 10000. This simple method greatly improved the practical value of the oxazoline ring opening polymerization, since monomer purification has always been a major problem.

All the monomers were polymerized (Scheme V) in bulk in sealed tubes at 130 °C for 6 h and 140 °C for 3 h and finished by heating at 160 °C for 3 h. Ethylene glycol ditosylate was used as the initiator. The poly(*N*-acylethylenimines) (**11a–f**) were obtained in almost quantitative yields.

Polymerizations with different monomer–initiator ratios are summarized in Table I. The intrinsic viscosity for each polymer increases gradually with the increase of the monomer–initiator ratio and approaches a limiting value of 1 dL/g. Polymers **11a**, **11c–e**, and **11f** are more or less transparent immediately after polymerization and are soluble in many organic solvents such as dichloromethane, chloroform, *o*-dichlorobenzene, DMF, THF, and Me_2SO. Interestingly, **11b** becomes white during polymerization

Table I
Polymerization with Various Monomer-to-Initiator Ratios

polymer	M/I[a]	$[\eta]$,[b] dL/g
11a	3400	0.68
	9500	0.88
11b	1000	0.44[c]
	3900	0.82[c]
	5200	0.96[c]
	10500	1.08[c]
11c	2000	0.41
	3800	0.68
	4900	0.73
	10000	0.84
11d	2000	0.67[d]
	5000	0.77
11e	500	0.31
	2000	0.56
	5000	0.72
	9300	0.83
11f	1000	0.46
	2000	0.58
	5200	0.80
	10000	0.98

[a] Monomer-to-initiator molar ratio. [b] In $CHCl_3$ at 30.00 ± 0.02 °C. [c] In CH_2Cl_2 at 25.00 ± 0.02 °C. [d] See ref 8.

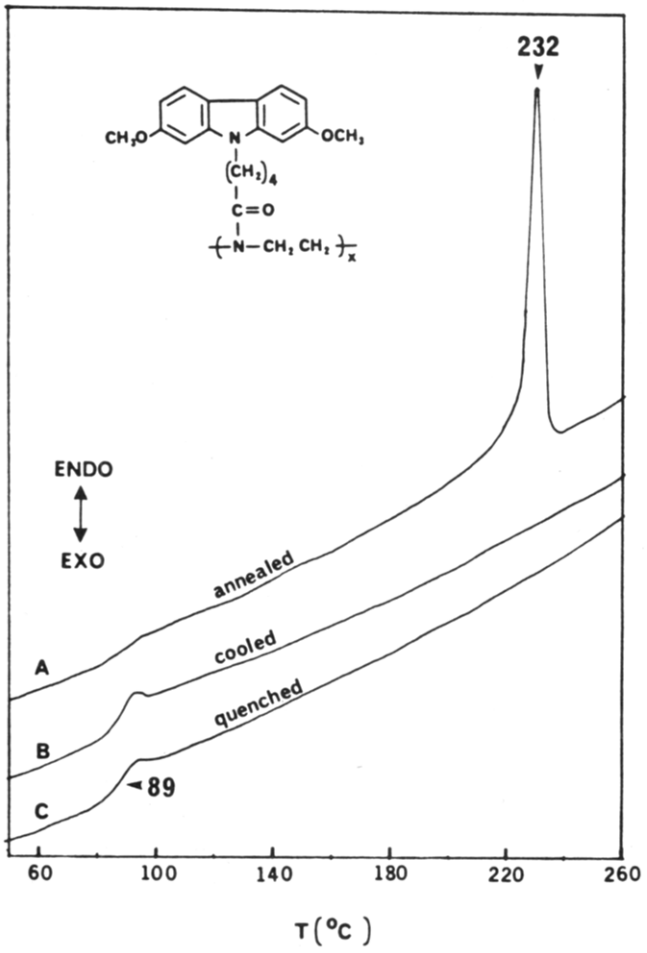


Figure 1. DSC curves of **11b** under different treatments (heating rate 20 °C/min): (A) annealed sample (160 °C for 24 h); (B) the sample heated to 260 °C and cooled at 20 °C/min to 30 °C; (C) sample heated to 260 °C and cooled very quickly to 30 °C.

and is soluble at room temperature only in dichloromethane among the many common organic solvents.

It was established in earlier studies[15] that the crystallization behavior of poly(*N*-acylethylenimines) having linear alkyl side-chain groups was highly influenced by the length of the side chains. In light of this and the difficulty in crystallization of **11d**, which has three methylene groups

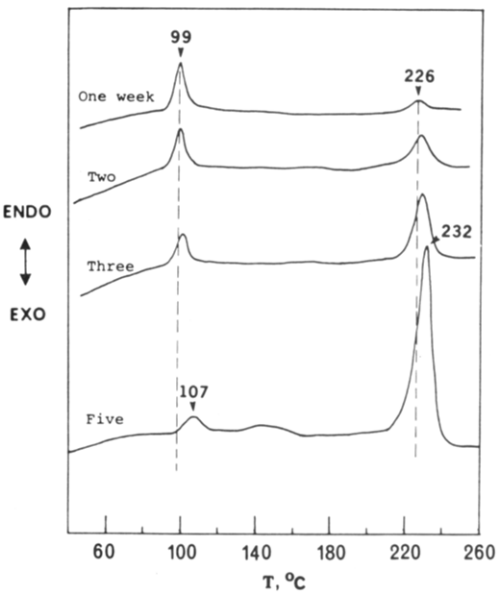


Figure 2. DSC curves of **11b** after various annealing periods at 90 °C.

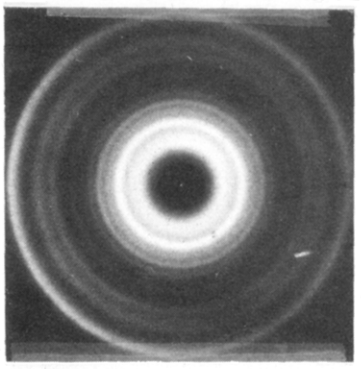


Figure 3. WAXD pattern of **11b**.

on the side chain, we postulated that a polymer having an even number of methylene groups might crystallize more easily. The synthesis of the polymers having different side-chain lengths was thus undertaken. As it turned out, **11b** was the only polymer which crystallized during the polymerization. The DSC traces (Figure 1) of annealed **11b** at 160 °C for 24 h displayed a sharp and intense melting peak at 232 °c and a barely seen glass transition temperature (curve A). The T_g at 89 °C become prominent in the quenched sample (curve C). The fact that **11d** did not crystallize on cooling after being heated above T_m (curve B) suggests that the crystallization rate is slow. The large side groups probably restrict the mobility of the polymer chains and make packing difficult. However, **11b** can still be crystallized at temperatures much lower than its T_m as illustrated in Figure 2. After **11b** was annealed at 90 °C for 1 week, a small melting peak at 226 °C as well as a large endothermic peak at 99 °C, corresponding to a T_g of 94 °C, can be seen. These peaks shifted toward higher temperatures as the annealing period increased and finally reached a T_m of 232 °C and a T_g of 102 °C, which is higher than that of the quenched sample by 13 °C. The melting peak area increased gradually while the lower temperature peak decreased. This indicates that the amorphous portion is crystallizing during the annealing. The crystallized **11b** had a high degree of crystallinity as reflected by its X-ray powder diffraction pattern (Figure 3); many sharp rings are observed. Other than **11b**, all the polymers were amorphous and gave no X-ray diffraction pattern. The amorphous polymers showed similar DSC

Table II
Characterization Data of the Polymers

polymer	T_g,[a] °C	$IR_{C=O(amide)}$ (KBr), cm^{-1}	elemental anal.[b] %C	%H	%N	%O
11a	114	1645	71.30 (71.01)	6.62 (6.51)	8.39 (8.28)	14.25 (14.20)
11b	89 (T_m = 232 °C)	1645	71.68 (71.59)	6.68 (6.82)	7.91 (7.95)	13.49 (13.64)
11c	67	1645	71.93 (72.13)	7.05 (7.10)	7.72 (7.65)	13.22 (13.11)
11d	112	1645	77.47 (77.70)	6.81 (6.47)	10.02 (10.07)	5.93 (5.76)
11e	90	1645	77.76 (78.08)	7.00 (6.85)	9.46 (9.45)	6.05 (5.48)
11f	78	1645	78.29 (78.43)	7.37 (7.19)	9.02 (9.15)	5.42 (5.23)

[a] Heating rate of 20 °C/min. [b] Calculated values in parentheses.

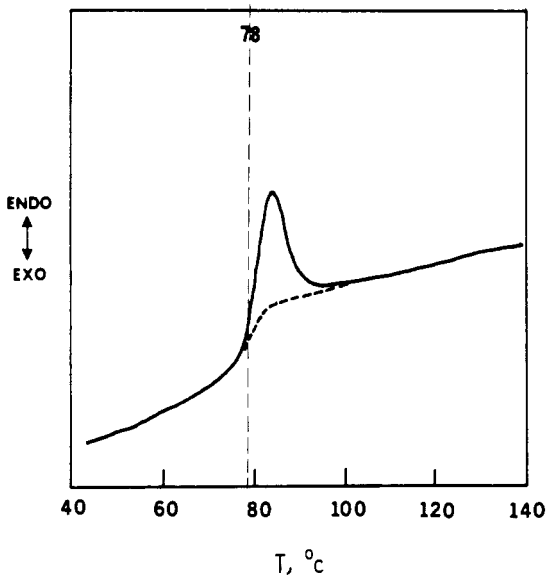


Figure 4. DSC curves of **11f** (heating rate = 20 °C/min): scans for material annealed at 70 °C for 24 h (—) and quenched (---).

characteristics; those are the increase in T_g's upon annealing and the appearing of endothermic peaks at temperatures close to the T_g's. See Figure 4, in which the DSC scans for annealed and unannealed **11f** are superimposed.

For most of these polymers, the situation shown in Figure 2 is more typical.[16] Even when the sample is quenched (curve C) there is a slight endothermic peak. When the sample is cooled and reheated at 20 °C/min (curve B), the endothermic peak at T_g is relatively large. This has been described for **11d** in greater detail elsewhere.[7b,c] This is in contrast to the behavior of most glassy polymers which show an endotherm only after annealing.[17]

For **11d**, an endotherm of 1.22 cal/g at 125 °C was found after annealing, even though the sample was not crystalline. Annealing of **11d** in the presence of anisole vapor slowly caused the polymer to crystallize. However, the melting peak was still at 125 °C and the endotherm was only 3.49 cal/g.

Such behavior for a class of crystallizable polymers is unusual. One speculation is that the molecular can organize readily locally, but that close, regular packing with neighboring molecules is very difficult, because of the bulkiness of the aromatic group. However, on long annealing, regular packing can take place to generate crystallinity. This may require reorganization within the molecule to a slightly higher energy conformer. On this reasoning, **11b** crystallizes well because its internal conformation allows the packing of neighboring molecules to occur easily with no local rearrangement. The lack of methoxy groups in **11d** could change the energies of the various conformers and thus inhibit spontaneous crystallization. Similarly, changing the number of CH_2 groups from even to odd will change the conformation necessary for good local packing. On this hypothesis, polymers with two or six CH_2 groups should crystallize.

As one might expect, this problem intrigued us. If the packing of the molecules could be studied, these questions might be answered. We tried many times to orient films of **11b** by standard methods. However, the X-ray pattern was far from a typical fiber diagram; there was little orientation and no obvious *c* axis repeat. We suspect that lamellae may be orienting with little disruption, leading to a pattern with much texture.

The characterization data for the polymers in terms of glass transition temperature, amide I absorption band in IR, and elemental analysis are summarized in Table II. It is to be noted that the T_g's given in Table II were based on the T_g's of the quenched samples. A comparison of the T_g's reveals that the T_g's of the polymers having given side-chain substituents decrease as the side-chain length increases.

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 Varian EM-360 instruments 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. Analytical samples were determined by Galbraith Laboratories, Knoxville, TN. The viscosities of polymer solutions were determined with a Cannon-Ubbelohde viscometer. T_g 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. Tetrahydrofuran was distilled from benzophenone over sodium. *n*-Butyllithium–hexane solution was titrated at −78 °C in THF with HMPA–Ph_3CH as indicator.

Reactions run in an inert atmosphere used a three-way stopcock which allowed the flask to be flame dried under vacuum and filled with purified nitrogen. Workup refers to (1) extraction with dichloromethane, (2) washing the organic layers with 5% sodium bicarbonate and saturated brine, (3) drying the solution by filtering through anhydrous sodium sulfate, and (4) concentrating in vacuo. 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 overnight. The glassware was then rinsed many times with distilled water and dried at 110 °C in a hot air oven.

3-Nitro-4-bromoanisole (2). Finely powdered **1** (168 g, 1.0 mol) was added gradually to a 1-L Erlenmeyer flask containing 300 mL of 48% hydrobromic acid while stirring magnetically. The mixture was stirred until homogeneous and then cooled to 0 °C. A solution of sodium nitrite (80 g in 110 mL of water) was then added dropwise through a separatory funnel. Addition of small pieces of ice during the reaction was necessary to keep the temperature below 10 °C. The resulting dark brown solution was

stirred at room temperature for 2 h and then added to a boiling mixture of cuprous bromide (80 g) in 48% hydrobromic acid (80 mL), heated with a flame in a 2-L round-bottom flask, at such a rate that the mixture boiled vigorously. Heating was continued for 3–5 min after addition was completed. The final black mixture was transferred to a 2-L separatory funnel and the lower organic layer was collected and distilled through a Vigreux column (1 × 13 cm) at 102–108 °C/0.4 mm to give **2** as a yellow oil which mostly crystallized upon standing: mp 32–33 °C (lit.[11] mp 32 °C); IR (KBr) 1540 (s), 1350 (s) cm^{-1}; NMR (CCl_4) δ 7.5 (d, J = 10 Hz, 1 H), 7.25 (d, J = 3 Hz, 1 H), 6.9 (d of d, J = 10 Hz, J = 3 Hz, 1 H), 3.85 (s, 3 H).

2-Nitro-4,4′-dimethoxybiphenyl (3). A mixture of **2** (46 g, 0.2 mol) and *p*-iodoanisole (60 g, 0.25 mol) in a 500-mL three-necked flask, equipped with a thermometer and a solid addition funnel, was stirred mechanically and heated to 190 °C in an oil bath. Activated copper bronze (30 g) was then added gradually through the funnel. The mixture was kept at 200–220 °C for 2 h and then another 15 g of copper bronze was added. After 2 h more heating, a small amount of *N*-methylpyrrolidone (30 mL) was added so that the reaction mixture solidified to a slush when cooled. The resulting mixture was transferred into a Soxhlet extraction apparatus and extracted with acetone to separate the product from copper bronze. Yellow crystals precipitated upon cooling and **3** (27 g, 52%) was isolated as chunky crystals in several crops: mp 136–138 °C (lit.[9] mp 138 °C); IR (KBr) 1530 (s), 1495 (s), 1360 (m), 1245 (s) cm^{-1}; NMR δ 7.4–6.8 (m, 7 H), 3.9 (s, 3 H), 3.85 (s, 3 H).

2,7-Dimethoxycarbazole (4). A mixture of **3** (52 g, 0.2 mol) in triethyl phosphite (150 mL) was heated to reflux under nitrogen atmosphere for 4 h. During that time white crystals separated. After cooling, the product was collected by suction filtration, washed thoroughly with methanol, and vacuum dried at 100 °C to give **4** (37 g, 81%) as white crystals: mp 272–274 °C (lit.[12] mp 272 °C); IR (KBr) 3390 (s), 1460 (s), 1270 (s), 1236 (s), 1170 (s), 1155 (s) cm^{-1}; NMR (Me_2SO-d_6) δ 11–10.8 (br, 1 H), 7.8 (d, J = 8 Hz, 2 H), 6.95 (d, J = 2 Hz, 2 H), 6.75 (d of d, J = 8, 2 Hz, 2 H), 3.85 (s, 6 H).

9-(4-Bromobutyl)-2,7-dimethoxycarbazole (6b). This is a general procedure using LDA as base. Into a 500-mL three-necked flask equipped with magnetic stirrer, an addition funnel, and a septum inlet adapter was placed **4** (17 g, 0.075 mL). This system was then flame dried under vacuum and purged with N_2, before diisopropylamine (12 mL, 0.086 mol) and THF (150 mL) were added through the septum via syringe. The addition funnel was charged with 2.5 M *n*-butyllithium in hexane (36 mL, 0.09 mol) which was then added dropwise to the stirred suspension. During the addition the lithium salt of **4** precipitated. After addition was completed, the mixture was stirred for 30 min and cooled to −78 °C. The septum inlet adaptor was quickly replaced by a funnel through which 1,4-dibromobutane (100 mL, 0.8 mol) was added all at once. The flask was recapped and the dry ice bath was removed. The mixture was stirred overnight, then transferred into a separatory funnel, and extracted sequentially with 5% hydrochloric acid, water, and brine. The organic layer was dried by passing through sodium sulfate and concentrated in vacuo. The excess dibromobutane was distilled off under vacuum through a short Vigreux column at 55–60 °C/6 mm. The residual oil was triturated with 50 mL of methanol to give a gray solid which was collected and vacuum dried to remove traces of the alkylating agent, 1,4-dibromobutane in this case. The dried crude product (24 g) was recrystallized from methanol to give **6b** (21 g, 76%) as white needles: mp 81–83 °C; IR (KBr) 3010 (w), 2940 (w), 2840 (w), 1608 (s), 1488 (s), 1461 (s), 1363 (m), 1333 (w), 1251 (s), 1203 (s), 1475 (m), 1144 (m), 1120 (s), 1060 (m), 1041 (m), 1031 (m), 820 (s) cm^{-1}; NMR δ 7.9–7.7 (m, 2 H), 6.9–6.6 (m, 4 H), 4.2 (t, J = 6 Hz, 2 H), 3.9 (s, 6 H), 3.3 (t, J = 6 Hz, 2 H), 2.1–1.8 (m, 4 H); mass spectrum for $C_{18}H_{20}BrNO_2$ m/e 361.

9-(3-Chloropropyl)-2,7-dimethoxycarbazole (6a). **6a** was prepared in a similar fashion as **6b** from **4** (17 g) and 1-bromo-3-chloropropane (20 mL, 0.2 mol). The crude product was extracted in a Soxhlet apparatus with ethanol to separate **6a** from recovered **4**. Upon cooling, **6a** (9.8 g, 43%) crystallized as white crystals: mp 102–104 °C; IR (KBr) 2994 (w), 2963 (w), 2930 (w), 2834 (w), 1605 (s), 1192 (w), 1161 (s), 1122 (s), 1055 (m), 1031 (m), 828 (m), 807 (m) cm^{-1}; NMR δ 7.9–7.65 (m, 2 H), 6.9–6.6 (m, 4 H), 4.25 (t, J = 6 Hz, 2 H), 3.85 (s, 6 H), 3.4 (t, J = 6 Hz, 2 H), 2.2 (quint, J = 6 Hz, 2 H); mass spectrum for $C_{17}H_{18}ClNO_2$ m/e 303.

9-(5-Bromopentyl)-2,7-dimethoxycarbazole (6c). A general procedure used lithium dimethyl sulfoxide as base. The apparatus setup was similar to that for preparation of **6b**. An ice water cooled mixture of **4** (17 g) and Me_2SO (150 mL) was stirred magnetically and 1.4 M methyllithium ethereal solution (59 mL, 0.08 mol) was added dropwise. The resulting solution was transferred into a 250-mL addition funnel under N_2 pressure via a two-ended needle and then added to 1,5-dibromopentane (150 mL) with stirring. The organic layer was separated and dried, and excess 1,5-dibromopentane was distilled off. The residue was triturated with methanol to give a pale yellow solid which was used for the next step. The crude material was recrystallized from ethanol to give **6c** (20 g, 72%) as white needles: mp 84–85 °C; IR (KBr) 3010 (w), 2940 (m), 2908 (m), 2833 (m), 1608 (s), 1486 (s), 1467 (s), 1460 (s), 1437 (s), 1362 (m), 1331 (w), 1245 (m), 1239 (s), 1199 (s), 1173 (s), 1140 (m), 1114 (s), 1040 (s), 985 (w), 960 (w), 813 (s), 790 (s) cm^{-1}; NMR δ 7.9–7.7 (m, 2 H), 6.9–6.6 (m, 4 H), 4.05 (t, J = 6 Hz, 2 H), 3.9 (s, 6 H), 3.2 (t, J = 6 Hz, 2 H), 2.1–1.2 (m, 6 H); mass spectrum for $C_{19}H_{22}BrNO_2$ m/e 375.

9-(3-Chloropropyl)carbazole (6d). **6d** was prepared in a similar manner as **6b** by using the following quantities: **5** (10 g, 0.060 mol); diisopropylamine (12 mL); THF (50 mL); 2.5 M *n*-butyllithium in hexane (15 mL); 1-bromo-3-chloropropane (20 mL). The crude oil was chromatographed on silica gel column (2 × 15 cm, slurry packed with 10% ether/hexane). Pure **6d** (7 g, 48%) was isolated as a colorless oil after evaporating the first fraction of eluent (1200 mL). The oil was crystallized by triturating with ethanol to give **6d** (6.5 g, 45%) as white needles: mp 32–33 °C; IR (KBr) 3050 (w), 2967 (w), 2941 (w), 1627 (w), 1597 (m), 1485 (s), 1464 (s), 1473 (s), 1381 (m), 1358 (m), 1326 (s), 1300 (m), 1281 (m), 1237 (s), 1205 (m), 1120 (w), 1063 (w), 1020 (w), 980 (w), 845 (w), 756 (s), 733 (s) cm^{-1}; NMR δ 8.2–7.9 (m, 2 H), 7.5–7.0 (m, 6 H), 4.2 (t, J = 6 Hz, 2 H), 3.3 (t, J = 6 Hz, 2 H), 2.2 (quint, J = 6 Hz, 2 H); mass spectrum for $C_{15}H_{14}ClN$ m/e 243.

9-(4-Bromobutyl)carbazole (6e). **6e** was prepared similarly by using the following quantities: **5** (30 g, 0.18 mol); diisopropylamine (30 mL); THF (350 mL); 81 mL (0.2 mol) of 2.5 M *n*-butyllithium in hexane; 210 mL of 1,4-dibromobutane. The crude product was sublimed at 150 °C/0.1 mm and the sublimate was recrystallized from chloroform to give **6e** (41 g, 76%) as white needles: mp 106–107 °C (lit.[13b] mp 106 °C); IR (KBr) 3056 (w), 2960 (w), 2930 (w), 2876 (w), 1629 (w), 1595 (m), 1485 (s), 1466 (s), 1456 (s), 1357 (m), 1332 (s), 1151 (m), 1231 (m), 1200 (m), 1153 (m), 1124 (w), 756 (s), 726 (m) cm^{-1}; NMR δ 8.2–7.9 (m, 2 H), 7.5–7.0 (m, 6 H), 4.2 (t, J = 6 Hz, 2 H), 3.2 (t, J = 6 Hz, 2 H), 2.2–1.5 (m, 4 H).

9-(5-Bromopentyl)carbazole (6f). **6f** was prepared similarly by using **5** (30 g, 0.18 mol) and 1,5-dibromopentane (250 mL). The crude product was sublimed at 160–170 °C/0.05 mm and the sublimate was recrystallized from ethanol as white crystals: mp 56–58 °C; IR (KBr) 3060 (m), 2937 (m), 2855 (w), 1627 (w), 1600 (m), 1484 (s), 1462 (s), 1348 (m), 1333 (s), 1261 (m), 1223 (s), 1195 (m), 1157 (m), 1125 (m), 925 (w), 832 (w), 752 (s), 723 (s) cm^{-1}; NMR δ 8.2–7.9 (m, 2 H), 7.5–7.0 (m, 6 H), 4.2 (t, J = 6 Hz, 2 H), 3.25 (t, J = 6 Hz, 2 H), 2.0–1.9 (m, 6 H); mass spectrum for $C_{17}H_{18}BrN$ m/e 315.

9-(3-Cyanopropyl)-2,7-dimethoxycarbazole (7a). A General Procedure. A mixture of **6a** (9.5 g, 0.03 mol), sodium cyanide (2 g, 0.04 mol), and Me_2SO (30 mL) was heated at 80 °C for 10 h. The resulting solution was poured into 5% sodium bicarbonate with stirring and the precipitate was collected, air-dried, and recrystallized from acetone to give **7a** (8.2 g, 95%) as white crystals: mp 150–152 °C; IR (KBr) 3010 (w), 2940 (w), 2841 (w), 2252 (w), 1613 (s), 1490 (m), 1477 (s), 1458 (s), 1437 (m), 1372 (w), 1334 (w), 1392 (w), 1243 (s), 1212 (s), 1183 (w), 1163 (s), 1132 (w), 1117 (m), 1084 (w), 1061 (w), 1042 (w), 822 (m), 800 (m) cm^{-1}; NMR δ 7.9–7.7 (m, 2 H), 6.9–6.65 (m, 4 H),4.2 t, br, 2 H), 3.9 (s, 6 H), 2.25–2.0 (m, 4 H); mass spectrum for $C_{18}H_{18}N_2O_2$ m/e 294.

9-(4-Cyanobutyl)-2,7-dimethoxycarbazole (7b). **7b** was prepared by heating 24 g of crude **6b**, 4.0 g of sodium cyanide, and 70 mL of Me_2SO at 80 °C for 5 h. The resulting solution was poured into 300 mL of 5% sodium bicarbonate and the precipitate was collected, air-dried, and recrystallized from ethanol to give

7b (19 g, 82% from **6b**) as white crystals: mp 111–113 °C; IR (KBr) 3013 (w), 2960 (w), 2939 (w), 2838 (w), 1608 (s), 1491 (m), 1475 (s), 1461 (s), 1438 (s), 1368 (m), 1335 (w), 1270 (m), 1254 (s), 1225 (s), 1203 (s), 1160 (s), 1120 (m), 1061 (m), 1036 (m), 900 (w), 832 (w), 811 (m) cm^{-1}; NMR δ 7.9–7.7 (m, 2 H), 6.9–6.6 (m, 4 H), 4.2 (t, J = 6 Hz, 2 H), 3.9 (s, 6 H), 2.2 (t, J = 6 Hz, 2 H), 2.1–1.4 (br, 4 H); mass spectrum for $C_{19}H_{20}N_2O_2$ m/e 308.

9-(5-Cyanopentyl)-2,7-dimethoxycarbazole (7c). The crude **6c** (25.5 g) was treated with sodium cyanide (4.0 g) in 90 mL of Me_2SO as above to give **7c** (20.5 g, 83% from **6c**) as white crystals: mp 108–110 °C; (ethanol); IR (KBr) 3018 (w), 2961 (m), 2939 (m), 2839 (w), 2253 (w), 1613 (s), 1490 (s), 1478 (s), 1461 (s), 1438 (m), 1360 (m), 1332 (w), 1290 (w), 1253 (s), 1218 (s), 1201 (s), 1197 (m), 1158 (m), 1122 (s), 1062 (m), 1041 (m), 833 (m), 821 (m), 792 (s) cm^{-1}; NMR δ 7.9–7.7 (m, 2 H), 6.9–6.7 (m, 4 H), 4.1 (t, J = 6 Hz, 2 H), 3.9 (s, 6 H), 2.1 (t, J = 6 Hz, 2 H), 2.0–1.3 (m, br, 6 H); mass spectrum for $C_{20}H_{22}N_2O_2$ m/e 322.

9-(3-Cyanopropyl)carbazole (7d). **7d** was prepared from **6d** (5.0 g) and sodium cyanide (1.5 g) in 20 mL of Me_2SO (4.5 g, 93%). The recrystallized product showed the following: mp 84–85 °C (ethanol); IR (KBr) 3050 (w), 2940 (w), 2250 (w), 1624 (w), 1598 (m), 1490 (s), 1461 (s), 1388 (w), 1330 (s), 1250 (m), 1221 (m), 1193 (m), 1160 (m), 1131 (w), 1070 (w), 756 (s), 731 (s) cm^{-1}; NMR δ 8.25–8.0 (m, 2 H), 7.65–7.05 (m, 6 H), 4.20 (t, J = 6 Hz, 2 H), 2.15–1.85 (m, 4 H); mass spectrum for $C_{16}H_{14}N_2$ m/e 234.

9-(4-Cyanobutyl)carbazole (7e). **7e** was prepared as above from **6e** (36.3 g, 0.12 mol) and sodium cyanide (6 g) in 100 mL of Me_2SO (28 g, 92%). The product was obtained as white crystals: mp 118–120 °C (acetone); IR (KBr) 3060 (w), 2940 (w), 2880 (w), 2251 (w), 1625 (w), 1599 (m), 1485 (s), 1464 (s), 1458 (s), 1423 (w), 1350 (m), 1332 (s), 1243 (m), 1220 (s), 1180 (w), 1157 (w), 1121 (w), 1063 (w), 1020 (w), 1000 (w), 857 (w), 760 (s), 732 (m) cm^{-1}; NMR δ 8.2–8.0 (m, 2 H), 7.5–7.0 (m, 6 H), 4.3 (t, J = 6 Hz, 2 H), 2.4–1.4 (m, 6 H); mass spectrum for $C_{17}H_{16}N_2$ m/e 248.

9-(5-Cyanopentyl)carbazole (7f). **7f** was prepared as above from **6f** (31.6 g, 0.1 mol) and sodium cyanide (5.5 g) in 100 mL of Me_2SO (23.5 g, 92%). The recrystallized product was obtained as white crystals: mp 71–73 °C (ethanol); IR (KBr) 3060 (w), 2942 (m), 2860 (w), 2250 (w), (w), 1629 (w), 1600 (m), 1488 (s), 1463 (s), 1423 (w), 1347 (m), 1333 (s), 1241 (m), 1214 (m), 1161 (w), 1135 (w), 752 (s) cm^{-1}; NMR δ 8.25–8.0 (m, 2 H), 7.5–7.0 (m, 6 H), 4.2 (t, J = 6 Hz, 2 H), 2.2–1.2 (m, 8 H); mass spectrum for $C_{18}H_{18}N_2$ m/e 262.

2-[4-(2,7-Dimethoxycarbazol-9-yl)butyl]-2-oxazoline (8b). A General Procedure. To a 50-mL flask equipped with condenser and magnetic stirrer was added **7b** (18.5 g, 0.06 mol) and cadmium acetate dihydrate (0.35 g, 1.5 mmol). The system was heated to 130 °C under N_2 atmosphere, and ethanolamine (4.2 mL, 0.066 mol) was added dropwise with syringe through a septum at the top of the condenser. The resulting mixture was heated at 130–140 °C for 25 h. The hot melt was poured into 500 mL of boiling n-heptane and heated on a hot plate in a 1-L Erlenmeyer flask with magnetic stirring. After 5 min of heating, the heptane layer was decanted into a round-bottom flask and concentrated in vacuo to give a yellow oil. This was diluted with 30 mL of toluene and then quickly passed through a short alumina column (100 g, activity III, slurry packed with toluene). The complete collection of **8b** was determined by TLC. The toluene was evaporated and the colorless residue was crystallized from n-heptane to give **8b** (15.5 g, 72%) as white needles: mp 101–103 °C; IR (KBr) 2940 (m), 2836 (w), 1673 (s), 1607 (s), 1486 (m), 1465 (s), 1440 (m), 1363 (m), 1278 (m), 1242 (s), 1204 (s), 1161 (s), 1152 (s), 1121 (m), 1044 (m), 984 (m), 975 (m), 914 (w), 816 (m) cm^{-1}; NMR δ 7.85–7.60 (m, 2 H), 6.8–6.5 (m, 4 H), 4.2–3.5 (m, 12 H, with methoxy methyl peak at 3.85 ppm), 2.2 (t, br, 2 H), 2.0–1.5 (m, br, 4 H); mass spectrum for $C_{21}H_{24}N_2O_3$ m/e 352.

2-[3-(2,7-Dimethoxycarbazol-9-yl)propyl]-2-oxazoline (8a). A mixture of **7a** (6.5 g, 0.022 mol) and cadmium acetate dihydrate was heated to 155 °C due to the high melting point of **7a**. The temperature was descreased to 140 °C after **7a** had melted completely. Ethanolamine (1.5 mL) was added dropwise through a syringe and the resulting mixture was heated for 24 h at 140 °C. The final mixture was extracted with boiling heptane and the residue, after concentration of the heptane solution, was purified by passing through a short alumina (40 g) column and eluting with toluene. After evaporation of the toluene, the residual white solid was recrystallized from heptane to give **8a** (4.5 g, 60%) as fine needles: mp 95–96 °C; IR (KBr) 3008 (w), 2943 (w), 2841 (w), 1671 (m), 1608 (s), 1464 (s), 1435 (m), 1395 (w), 1357 (w), 1324 (w), 1290 (w), 1243 (m), 1230 (m), 1215 (m), 1177 (m), 1160 (s), 1120 (m), 1037 (m), 994 (w), 997 (w), 743 (w), 842 (w), 804 (m) cm^{-1}; NMR δ 7.95–7.7 (m, 2 H), 6.90–6.65 (m, 4 H), 4.40–3.65 (m, 12 H, with methoxy methyl peak at 3.90 ppm), 2.3–2.0 (m, 4 H); mass spectrum for $C_{20}H_{22}N_2O_3$ m/e 338.

2-[5-(2,7-Dimethoxycarbazol-9-yl)pentyl]-2-oxazoline (8c). **8c** was prepared as above from **7c** (10 g, 0.03 mol), cadmium acetate dihydrate (0.2 g), and ethanolamine (3.0 mL) and obtained as white crystals (8.5 g, 74%): mp 103–105 °C (heptane); IR (KBr) 2940 (m), 1666 (m), 1602 (s), 1473 (s), 1461 (s), 1436 (m), 1362 (m), 1336 (w), 1248 (m), 1230 (s), 1200 (s), 1173 (s), 1145 (m), 1066 (w), 1038 (m), 990 (m), 957 (w), 860 (m) cm^{-1}; NMR δ 7.85–7.60 (m, 2 H), 6.9–6.6 (m, 4 H), 4.3–3.5 (m, 12 H, with OCH_3 peak at 3.9 ppm), 2.2 (t, br, 2 H), 2.0–1.1 (m, br, 6 H); mass spectrum for $C_{22}H_{26}N_2O_3$ m/e 366.

2-(3-Carbazol-9-ylpropyl)-2-oxazoline (8d). **8d** was prepared as shown above from **7d** (1.7 g, 7.3 mmol), cadmium acetate dihydrate (0.03 g), and ethanolamine (0.5 mL) after purifying by passing its toluene solution through alumina (10 g) with toluene. The recrystallized **8d** (1.5 g, 71%) showed the following: mp 52–53 °C (hexanes, lit.[3] mp 53 °C); IR (KBr) 3054 (2), 2936 (m), 1667 (s), 1626 (w), 1596 (m), 1484 (s), 1457 (s), 1426 (w), 1383 (m), 1352 (m), 1327 (s), 1246 (m), 1224 (w), 1203 (m), 1167 (s), 1063 (w), 1023 (m), 980 (m), 956 (m), 916 (w), 754 (s), 725 (s) cm^{-1}; NMR δ 8.10–7.85 (m, 2 H), 7.40–6.90 (m, 6 H), 4.35–3.30 (m, 6 H), 2.20–1.90 (m, 4 H).

2-(4-Carbazol-9-ylbutyl)-2-oxazoline (8e). **8e** was obtained as above from **7e** (12.5 g, 0.05 mol), cadmium acetate dihydrate (0.3 g), and ethanolamine as white needles after passing through neutral alumina (50 g) and recrystallization from hexanes (11 g, 76%). Pure **8e** showed the following: mp 74–76 °C; IR (KBr) 3055 (w), 2940 (m), 1665 (s), 1626 (m), 1594 (m), 1486 (s), 1467 (s), 1457 (s), 1387 (m), 1356 (m), 1331 (m), 1270 (w), 1220 (m), 1186 (m), 1161 (m), 1126 (w), 1023 (m), 979 (w), 946 (m), 908 (w), 752 (s), 727 (s) cm^{-1}; NMR δ 8.2–8.0 (m, 2 H), 7.5–7.0 (m, 6 H), 4.4–3.5 (m, 6 H), 2.2 (t, br, 2 H), 2.2–1.5 (m, br, 4 H); mass spectrum for $C_{19}H_{20}N_2O$ m/e 292.

2-(5-Carbazol-9-ylpentyl)-2-oxazoline (8f). **8f** was prepared as above from **7f** (13 g, 0.05 mol), cadmium acetate dihdyrate (0.3 g), and ethanolamine and obtained as white crystals (10.5 g, 70%): mp 56–58 °C (hexane); IR (KBr) 3044 (w), 2940 (m), 1665 (s), 1625 (w), 1596 (m), 1584 (s), 1461 (s), 1381 (w), 1334 (s), 1232 (s), 1160 (s), 1129 (w), 1062 (w), 990 (m), 956 (m), 917 (w), 762 (s) 734 (m) cm^{-1}; NMR δ 8.1–7.9 (m, 2 H), 7.5–6.9 (m, 6 H), 4.3–3.4 (m, 6 H), 2.3–1.0 (m, 8 H); mass spectrum for $C_{20}H_{22}N_2O$ m/e 306. Alternatively **8f** was prepared from **6e** according to the following procedure: into a 50-mL three-necked flask equipped with magnetic stirrer, addition funnel, and septum was added **9** (0.5 g, 5.87 mmol), TMEDA (1.0 mL, 6.6 mmol), and 5 mL of THF. The entire solution was cooled to −78 °C with an acetone–dry ice bath; then 2.2 M *tert*-butyllithium (3 mL, 6.5 mmol) in pentane was added dropwise via syringe. The solution turned yellow when the first drop of *tert*-butyllithium was added. The solution was stirred for 15 min before **6e** (1.5 g, 5 mmol) in 7 mL of THF was added all at once through the addition funnel. The dry ice bath was removed and the solution was stirred for 1 h as it warmed up to room temperature. After concentration in vacuo, the residue was purified by passing its toluene solution through an alumina (20 g) column with toluene and crystallizing from hexane to give **8f** (0.7 g, 46%) having the same physical properties given above.

2-(4-Chlorobutyl)-2-oxazoline (10). To a dry ice–acetone cooled solution of **9** (2.0 mL, 24 mmol) and TMEDA (4.0 mL, 26.4 mmol) in 20 mL of THF was added 2.4 M n-butyllithium (11 mL, 26.4 mmol) through an addition funnel. The solution turned yellow slowly after the addition was completed. The yellow solution was stirred for another 30 min and 1-bromo-3-chloropropane (2.7 mL, 24 mmol) was added all at once via syringe. The dry ice bath was removed and the solution was stirred for 2 h and poured into 30 mL of ice water. Workup as usual (ether was used as the extracting solvent) gave a pale yellow oil which was purified by molecular distillation (65 °C/0.2 mm). The distilled **10** (2.4 g, 62%) showed the following: IR (neat) 1664 (s), 1210 (s), 1022 (s) cm^{-1}; NMR (CCl_4) δ 4.5–3.4 (m, 6 H), 2.3 (t, br, 2 H), 2.0–1.6

(m, 4 H); mass spectrum for $C_7H_{12}ClNO$ m/e 161.

General Procedure for Polymerization. Since all the polymerizations were carried out under the same conditions, only the polymerization of **8b** is described here as an example. A polymerization tube containing **8b** (2.0 g, 5.68 mmol) and ethylene glycol ditosylate (0.2 mg, 5.4×10^{-7} mol) was degassed under high vacuum (ca. 10^{-5} mm) overnight and then 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 pure white mass in the first period of heating. The product was dissolved in dichloromethane, precipitated by adding to excess methanol, and vacuum dried at 100 °C overnight to give **11b** in quantitative yield.

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Modification of Low-Density Polyethylene Film Using Polymerizable Surfactants[1]

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ABSTRACT: Ultraviolet-induced polymerization (254 nm) of aqueous dispersions comprised of 1,2-bis[11-(methacryloyloxy)undecyl]-*sn*-glycero-3-phosphocholine (**1**), 1,2-bis(heptadeca-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (**2a**), 1,2-bis(heneicosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (**2b**), 1,2-bis(hexacosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine (**2c**), bis[10-(methacryloyloxy)decyl] hydrogen phosphate (**4**), or bis[11-(methacryloyloxy)undecyl]dimethylammonium dimethyl phosphate (**5**) in the presence of low-density polyethylene film (PE) provides a simple and effective means for producing hydrophilic polyethylene surfaces. These modified films show excellent stability toward 1:1 $CHCl_3$–CH_3OH at room temperature, maintaining their hydrophilicity and surfactant content. On the basis of (1) the similarity between the expected loading for monolayer coverage (estimated from collisional areas that have been calculated from pressure–area isotherms for monomeric monolayers constructed at the air–water interface) and the measured surfactant content for each film, (2) the requirement that **2a–c** be properly aligned for effective topotactic polymerization, and (3) the apparent film thickness of polymerized **2b** deposited onto a siliconized silicon oxide surface and its resulting hydrophilicity, it is proposed that each surface bears an ordered polymerized surfactant coating, approaching monolayer coverage. Attempted modification of PE with 1-palmitoyl-2-[11-(methacryloyloxy)undecyl]-*sn*-glycero-3-phosphocholine (**3**) and dimethylhexadecyl[11-(methacryloyloxy)undecyl]ammonium dimethyl phosphate (**6**) failed to alter the film's surface.

Introduction

Surface structure and composition play a major role in defining many of the physical properties and ultimate uses of solid organic polymers. In particular, features such as wetting,[3] weathering,[4] adhesion,[5] dye adsorption,[5] friction,[5] electrostatic charging,[6] permeation,[7] and biocompatibility,[8,9] which are important for engineering and biotechnological applications, are largely influenced by surface characteristics. Despite this fact, current methods available for modifying polymer surfaces in a well-defined manner remain limited.[10]

In this paper we described a new method for modifying the surface of low-density polyethylene film.[10,11] Our *rationale* behind this new approach is summarized in Scheme

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