Synthesis and Oxidative Cross-Linking of Fluorene-Containing Polymers To Form Conjugated Network Polyfluorenes: Poly(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl)

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Introduction. The use of fluorene and its derivatives as laser-generating[1] or photoactive fluorescent materials is well-known.[2] In particular, recent interest in the synthesis of π-conjugated fluorene polymer materials with fluoren-2,7-diyl units synthesized by either palladium-[3] or nickel-catalyzed[4] coupling of 2,7-dibromofluorenes has found applications in the fabrication of blue polymer light-emitting diode (PLED) devices.[5] Suzuki coupling between 2,7-dibromofluorene and 2,7-dioxaborolanyl fluorene derivatives,[6] chemical oxidation of fluorenes with FeCl₃,[7] or electrochemical oxidation of fluorenes has also been reported.[8] Intractability and insolubility are a common problem with stiff conjugated polymers with increasing conjugation efficiencies. For the polymers derived from fluorenyl units, substitution at the 9-fluorenyl positions enhances the solubility and processability of the resulting polymers.[9] The two acidic hydrogens on the 9-position are available for lithiation, and 9,9-dilithiofluorenes have been found to react readily with monobromoalkanes resulting in carbon−carbon bond formation.[4−6]

In an effort to prepare polymer materials with *tethered* fluorene units, we have prepared a series of polymers containing fluorene units directly attached to the polymer main chain and separated by a series of alkylene spacer units.[10] The goal is to utilize this "precursor polymer"[11] toward the synthesis of conjugated polyfluorene *network* species via a cross-linking reaction.[12] This poly(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl) polymers as we describe in this paper were obtained from a modified nucleophilic substitution reaction derived from a stoichiometric 1:1 combination of 9,9-dilithiofluorene and α,ω-dibromoalkane.[10,13] Cross-linking at the 2,7-positions produced a network conjugated polymer (or oligomer) derivative achieved by chemical oxidation. The procedure involved the use of the FeCl₃ system as reported by Yoshino and co-workers.[7] To our knowledge this is the first reported systematic procedure for the synthesis of π-conjugated poly(fluorene) derivative via cross-linking of a homologous series of precursor fluorene-containing polymers.[14]

Experimental Section. a. Polymerization and Characterization.[10,15,16] A typical procedure is described as follows: The initial step involves activation of the fluorene ring by lithiation. 9,9-Dilithiofluorene was prepared by the dropwise addition of *n*-butyllithium (9.8 mL of a 2.5 M solution, 24 mmol) to a solution of fluorene (2 g, 12 mmol) in ether (50 mL) at 0 °C, followed by stirring for 45 min. Polymerization was carried out by the addition of α,ω-dibromoalkane (12 mmol) to the above solution at 0 °C. The mixture was stirred for another 24 h at room temperature, and the polymer was precipitated by the addition of methanol to a mixture. The polymers were labeled as **1a**−**e** (Figure 1).

b. Oxidation.[7] A typical procedure for chemical oxidation (cross-linking) involves the following: To a solution of a polymer (0.5 g) in chloroform (100 mL), iron(III) chloride (ca. 5 equiv) was added at room temperature. Upon the addition of iron(III) chloride, the color of the mixture changed to dark purple or dark blue. The mixture was kept stirring for 24 h, and the polymer was precipitated by the addition of methanol (100 mL). The formed polymer was isolated by filtration, and the polymer was rinsed with methanol for a few times and placed under reduced pressure to remove remaining solvents.

Results and Discussion. a. Polymerization. From a series of five different dibromoalkane units, polymers of various molecular weights (MW's) and molecular weight distribution (MWD) were obtained. A systematic comparison of the different spectral and photoluminescence properties was carried out. A range of MW and MWD values were obtained by SEC (using polystyrene calibration) with MW from 7620 to 10 700 (M_n) and MWDs from 2.37 to 6.0.[16] However, MALDI-TOF-MS confirmed values of up to 6000−7000 or corresponding to the degree of polymerization (DP) of 20−30 units.[16] Clearly, the discrepancy lies with the appropriateness of using polystyrene calibration methods. From the broad MWD and the propagation reaction involved, it is evident that a step-growth reaction polymerization is involved.[17] These S_N2 type of polymerizations are not known to give high-MW polymers.[10,13] Similar observations have been made with condensation reactions of malonic esters with α,ω-dibromoloalkanes to give poly(alkylene malonic esters), giving MW's of the order of 800−20 000 g/mol.[13,18] We are currently exploring various methods, including stoichiometric titration methods to increase the MW of these polymers. Important possibilities with the polymer growth mechanism needs to be addressed, which include attachment of a single dibromoalkane to the 9-position followed by successive activation of another fluorene unit or the simultaneous reaction of two dibromoalkane units at the 9,9-position of the activated fluorene.[17] During chain growth, it is not known how equilibrium is shifted between chemical species. The possibility of cyclization vs linear chain growth polymerization needs to be addressed.[16] Nevertheless, the change in the polymer microstructure with different alkyl main chain spacers is observed with trends in the NMR chemical shifts. These values are summarized in Table 1.

Compared with the chemical shifts of the protons of the 9,9-dialkylfluorene,[6] all the chemical shifts derived from the structure are shifted progressively toward the upfield region, especially for polymers with shorter alkyl spacers (i.e., $n = 4, 6$). This result is a good evidence for the changing polymer microstructure in a homologous alkylene series. Not only are the main-chain proton resonances shifted, but also the aromatic protons of fluorene which are presumably shielded by the neighboring fluorene groups, when the spacer is shorter. Differential scanning calorimetry (DSC) measurements

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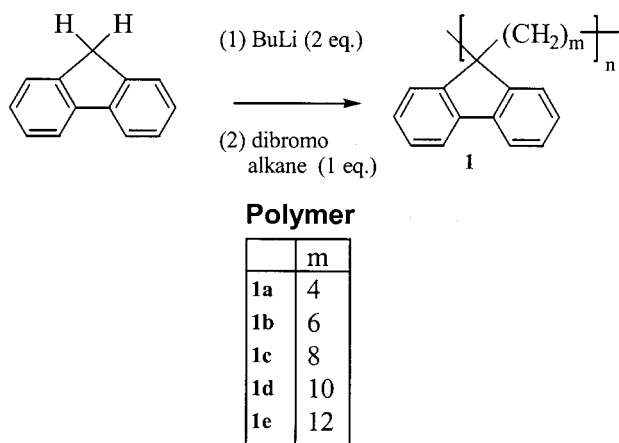‡ Agilent Technologies Research Laboratories.

Figure 1. Synthetic scheme for the polymerization of the precursor polyfluorenes using a dilithiation reaction at the 9,9-position followed by a substitution reaction with a series of α,ω-dibromoalkanes.
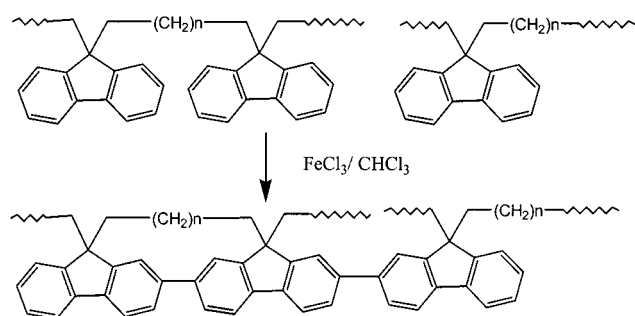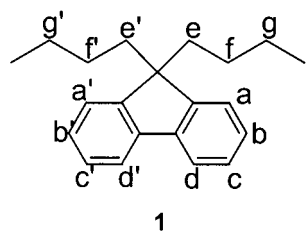
Polymer	m
1a	4
1b	6
1c	8
1d	10
1e	12

Figure 2. Cross-linking reaction scheme of poly(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl) using $FeCl_3$.

Table 1. Chemical Shift of Protons in Polymers 1a–e

polymer **1-m**	$\delta_{f,f'}$	$\delta_{g,g'}$	$\delta_{e,e'}$	$\delta_{a,a',b,b',c'c'}$	$\delta_{d,d'}$
4	0.21	*n*/a	1.45	6.95–7.25	7.55
6	0.37	0.74	1.70	7.1–7.3	7.62
8	0.48	0.7–1.0	1.83	7.2–7.3	7.65
10	0.54	0.85–1.05	1.89	7.23–7.33	7.66
12	0.57	0.9–1.1	1.92	7.25–7.35	7.67
reference 9,9-dioctylfluorene	0.79	1.24–1.35	2.12	7.42	7.82

also reveal a decrease in glass transition (T_g) values with increasing alkyl methylene spacer length: C-4, 71.5 °C; C-6, 65.6 °C; C-8, 48.4 °C; C-10, 26.5 °C; C-12, 17.5 °C. The values were obtained after the second heating cycle to avoid the previous thermal history.[16]

Initial absorbance and photoluminescence characterization was made with the following results:[15] Polymers **1a** through **1e** have similar spectra with λ_{max} of 266 nm and two significant shoulders at 293 and 304 nm (Figure 3). Those shoulders are slightly moved from those of fluorene (λ_{max} at 266 nm, shoulders at 290 and 301 nm),[19] showing a slightly lower band gap of the resulting fluorene-containing polymers. Photoluminescence of the polymers at 320 nm excitation reveals that polymers **1a** through **1e** exhibit photoluminescence with the
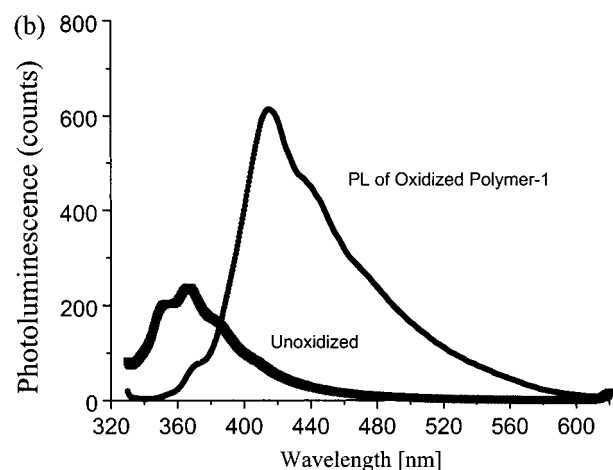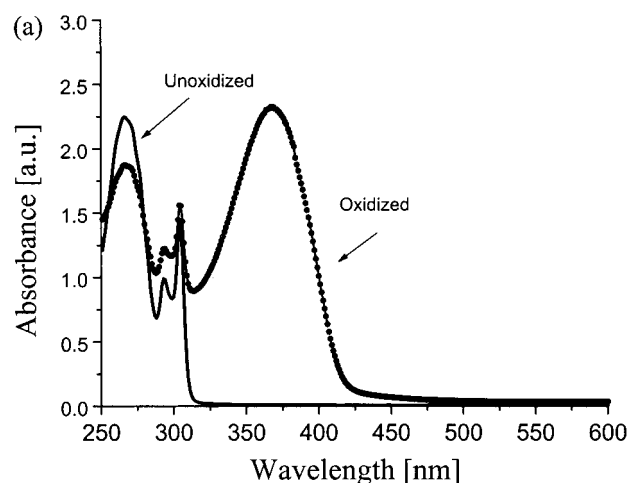
Figure 3. Absorbance and PL spectra in solution of poly-(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl) before and after cross-linking.

maxima at 370 nm and a shoulder extending from 390 to 500 nm. These peaks and shoulders are shifted from that of fluorene molecules (peaks at 382, 404, and 428 nm), implying a different aggregation behavior where fluorene units are connected by alkylene spacer groups.[19]

b. Cross-Linking of Fluorene Units To Form π-Conjugated Networks. Cross-linking at the 2,7-positions to produce π-conjugated network derivatives was achieved initially by chemical oxidation of these polymers. The procedure involved the use of the $FeCl_3$ system as reported by Yoshino.[7] For our initial investigation, we attempted to oxidize a short and longer member of the homologous series. Polymers **1b** and **1e** were readily oxidized with $FeCl_3$. Oxidation of polymers **1b** and **1c** gave insoluble yellow powdery materials, while oxidation of polymers **1d** and **1e** gave a yellow-green polymer, which is partly soluble in $CHCl_3$ and THF and can be spin-coated from solution. From the above results, we can only infer that the differences in solubility indicate that for polymers **1b** and **1c** intramolecular oligomerization of fluorene was inhibited.[16] This is due to the connection of fluorene units by shorter alkyl groups (intermolecular cross-linking would be preferred). In the case of polymers **1d** and **1e**, a less sterically restricted structure enabled intramolecular oligomerization of fluorene units, resulting in a tractable polymer. In this case, the design of the poly(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl) polymer, i.e., specifically the length of the alkyl chain spacer, determined the degree

of network polymerization to form a distribution of π-conjugated species. This was evident in the spectroscopic properties of the network polymer.

Initial absorbance and photoluminescence characterization of the oxidized polymers was made. Oxidized polymer **1e** exhibits a strong absorbance at 365 nm in contrast to the un-cross-linked polymer (Figure 3). This λ_{max} is slightly shorter than λ_{max} for polyfluorenes with controlled molecular weight (λ_{max} = 380 nm is expected).[4] Polymer **1e** also showed absorbances at 266, 294, and 304 nm, which implies that the resulting polymer still has the characteristics of the fluorene group from the unoxidized parts of the polymer. Thus, the above results suggest that the oxidation of the polymer gave partially oligomerized fluorene units in the network. The oxidized polymer **1e** also exhibited strong fluorescence at 420 nm (320 nm excitation). The intensity of fluorescence is ca. 10−50 times stronger than that of unoxidized polymer. These fluorescence characteristics are more similar to that of conjugated poly(2,7-fluorene) solutions.[4,12] Further work is needed to control the extent of cross-linking toward more conjugated oligomers or polymer species. Applications are being investigated toward cross-linking at electrode surfaces and PLED devices.[10,14]

Conclusion. We have demonstrated that, by a novel polymerization method of fluorene and α,ω-dibromoalkanes, fluorene-containing polymers are obtained. The procedure resulted in a homologous series of a precursor polymer, which has similar spectral and fluorescent properties as fluorene. Chemical oxidation of these polymers gave cross-linked conjugated materials with oligofluorene or polyfluorene units in the structure. The degree of cross-linking is primarily dependent on the chain length. Applications for polymer LEDs as either electroluminescent or hole injecting materials should be explored.

Supporting Information Available: Table of molecular weight analysis of polymers **1**, MALDI-TOF-MS analysis of polymer **1b**, syntheses of polymers **1a**−**e**, and table of strain energy on oxidized polymers **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Materials: fluorene, *n*-butyllithium (2.5 M solution in hexane), 1,4-dibromobutane, 1,6-dibromohexane, 1,8-dibromooctane, 1,10-dibromodecane, 1,12-dibromododecane, and anhydrous iron(III) chloride were purchased from the Aldrich Chemical Co. and used as received. Diethyl ether (Fisher) was purified by distillation over sodium benzophenone ketyl. Chloroform (Fisher) was purified by washing with water, followed by drying over Na_2SO_4. Methanol, methylene chloride, and tetrahydrofuran (Fisher) were used as received. All of the reactions were carried out under nitrogen atmosphere. Instrumentation: NMR (Bruker 400 MHz), IR (Bruker Vector 22), UV−vis (Perkin-Elmer Lambda 20), SEC (Waters Chromatography), MALDI-TOF-MS (Perseptive Biosystems Voyager Elite DE), DSC (Mettler DSC30), TGA (Mettler TG50), PL (Perkin-Elmer LS50B). Products: The polymer products formed are named: poly(fluoren-9,9-diyl-*alt*-alkan-α,ω-diyl) where alkan = (C-4) butan, (C-6) hexan, (C-8)octan, (C-10) decan, and (C-12) dodecan.
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MA011466K