

Polyfluorene Derivatives: Effective Conjugation Lengths from Well-Defined Oligomers

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Efficient, thermally stable blue light emitting materials are needed both to complete the color spectrum and to serve as energy transfer media for incorporated fluorophores. The extended delocalization lengths of most fully conjugated polymers, however, result in small electronic band gaps and red-shifted emissions. Poly(*p*-phenylene) derivatives (PPP) show large band gaps since the aromatic rings are twisted to relieve unfavorable steric interactions in the backbone, which limits the effective conjugation length.¹ The dihedral angle between the aromatic rings in unsubstituted PPP is $\sim 23^\circ$.² Unsubstituted PPP is, however, highly insoluble, limiting the molecular weights and processability, and films are often generated via soluble precursor polymers.³ Large, solubilizing substituents may also be incorporated, resulting in improved processability, but this usually exacerbates the steric interactions in the polymer main chain.⁴

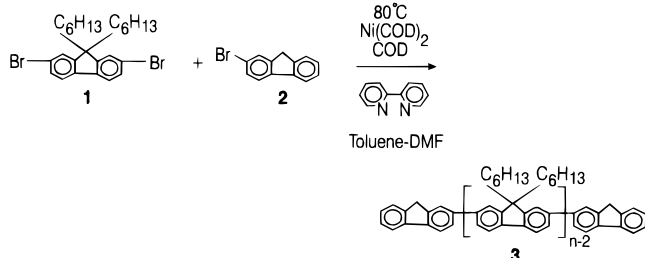
Fluorene derivatives are interesting since they contain a rigidly planar biphenyl unit and the facile substitution at the remote C₉ site provides the possibility of improving the solubility and processability of polymers without significantly increasing the steric interactions in the polymer backbone. Remote substitution also offers the possibility of controlling interchain interactions, which can lead to excimer formation in the excited state.⁵ Polyfluorene derivatives also have extremely high luminescence efficiencies in solution (rivaling those of many laser dyes), which are largely maintained in the polymer films.^{6c,d,7} As a result, polyfluorenes have been intensively studied recently as blue light emitting materials.^{6,7} Despite this, the effective conjugation length, which determines such important electronic properties as band gaps, absorption coefficients, emission quantum yields, etc., has not been reported for these polymers. The effective conjugation length may be defined as the minimum number of bonded aromatic rings necessary to produce saturation of the optical and electronic properties.⁸

Substituted polyfluorene derivatives were first prepared by oxidative polymerization of 9-alkyl-substituted monomers.⁹ These polymers, however, were of low molecular weight^{9c} and gave poor quality films. It is also difficult to remove residual metallic impurities; a potential problem for electroluminescent devices. Recently, however, we⁷ and others^{6c} have described the successful preparation of high molecular weight polyfluorene homo- and copolymers by the nickel(0)-mediated polymerization of 9,9-disubstituted-2,7-dibromofluorene monomers (Yamamoto polymerization).¹⁰ We have used this procedure in concert with polymer end capping to prepare well-defined fluorene oligomers and have used these to estimate the effective con-

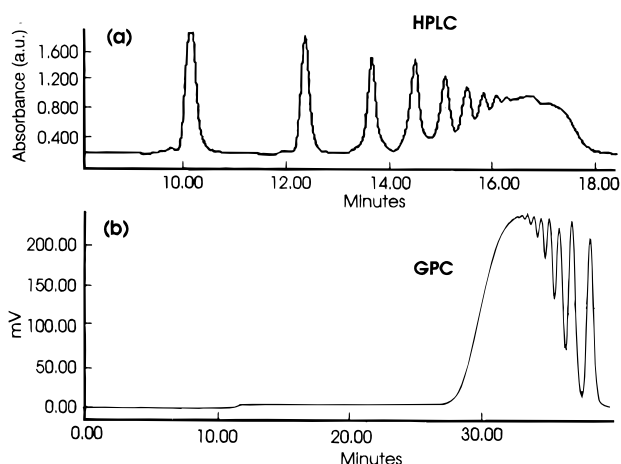
jugation length¹¹ for poly(9,9-di-*n*-hexylfluorene-2,7-diyl) (**3**).

The synthetic procedure is illustrated in Scheme 1. We have used the nonintrusive end-capping reagent 2-bromofluorene to control molecular weights and to generate well-defined oligomers that can subsequently be separated and characterized. A typical procedure is described below. Into a Schlenk tube was placed 2.6 mmol of bis(1,5-cyclooctadiene)nickel(0), 2.6 mmol of 2,2'-bipyridyl, 0.2 mL of 1,5-cyclooctadiene, 4 mL of DMF, and 8 mL of toluene, and the mixture was stirred at 80 °C (0.5 h). The 2,7-dibromo-9,9-di-*n*-hexylfluorene (1.125 mmol) and 2-bromofluorene (0.375 mmol) in 6 mL of toluene were added to the blue solution, and the mixture was heated at 80 °C for 3 days. The capped oligomers were precipitated into an equivolume mixture of concentrated HCl, methanol, and acetone. The solid was redissolved in chloroform and precipitated from acetone/methanol.

The addition of **2** at the onset of the reaction leads to the formation of both soluble oligomers and low molecular weight linear polymer. Higher molar ratios of **2/1** lead to lower molecular weight polymer and an enhancement of the oligomeric fraction. These data are reported in Table 1. End group analysis of the unfractionated low molecular weight materials isolated by precipitation after 3 days by ¹H NMR (integration of the C₉ methylene protons of the end groups at $\delta \sim 4.00$ relative to the methylene signals of the *n*-hexyl substituents at $\delta \sim 2.0$) provides a value for M_n to be compared with that determined by GPC analysis. The latter value, based on polystyrene standards, is always somewhat greater than that determined by ¹H NMR. The crude reaction product is composed of a mixture of oligomers and low molecular weight polymer, as determined by GPC analysis. Better separation of the oligomers from the polymer fraction was achieved by HPLC on Kromasil C₁₈-10 μm using a gradient elution with acetonitrile/chloroform (Figure 1), and the constituents of the oligomeric fraction were separated in this manner. Using this technique, oligomers ranging from $n = 3$ to $n = 10$ were separated and characterized. The spectroscopic properties of these isolated materials are reported in Table 2. The parent masses for each of the oligomers, as determined by field desorption mass spectroscopy, are also included in the table. It is significant that the observed parent masses are consistent with the presence of a fluorene capping unit at *each* end of the oligomeric chain. Although the spectral absorption maxima continue to move to the red through $n = 10$, the emission maxima remain virtually unchanged beyond $n = 6$. This would suggest that the backbone geometry changes significantly in going from the ground state (S_0) to the vibronically relaxed excited-state (S_1). For reference, the absorption maximum of high molecular weight poly(di-*n*-hexylfluorene-2,7-diyl)-(**3**) (PDHF) prepared by nickel-mediated coupling in the absence of the end-capping reagent occurs at 388 nm for material with a degree of polymerization of 54 (M_n determined by GPC analysis using polystyrene standards).⁷ This value is very close to that reported by Fukuda et al.^{9c} (387 nm) for the polymer where $n = 14$. Figure 2 shows the absorption spectra of the separated oligomers ($n = 3$ –10) together with that of

Scheme 1. Preparation of Oligomeric Poly(9,9-di-*n*-hexylfluorenes)**Table 1. Polymer Properties of End-Capped Oligomeric 9,9-Di-*n*-hexylfluorenes**

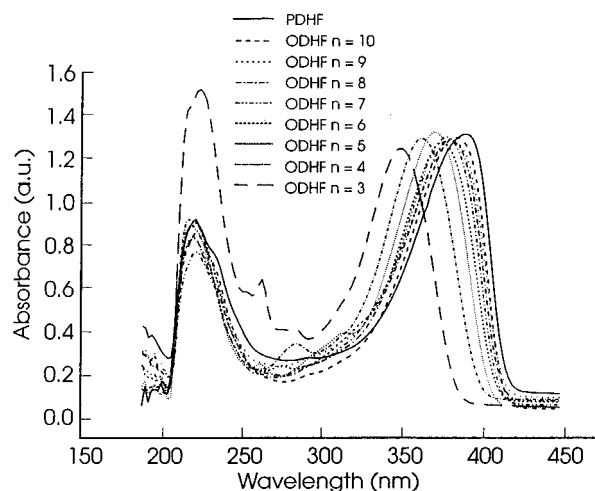
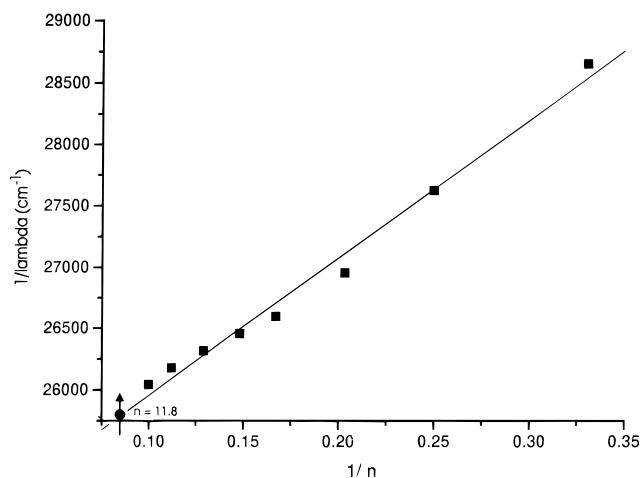
monomer ratio 1:2	isolated yield (%)	M_n^a	M_w^a
75:25	89	1800	2600
50:50	76	1200	1900

^a Measured by GPC using polystyrene standards.**Figure 1.** Separation of low molecular weight polymers and oligomers obtained from reaction of **1** and **2** in a 1:1 ratio. (a) HPLC separation on a Kromasil C8–10 μm column using an acetonitrile/chloroform gradient elution, detection wavelength 327.5 nm. (b) GPC separation (Waters Styragel column package, 7.8×300 mm, HR5c/HR4/HR3/HR1) using THF as an eluent, flow rate 1 mL/min.**Table 2. Spectral Properties of Oligomeric 9,9-di-*n*-hexylfluorenes**

oligomer n	λ_{max} (nm) ^a	λ_{em} (nm) ^a	M^+ (Da) ^b
3	348	413	668.2
4	362	425	994.6
5	370	434	1327.8
6	376	445	1665.4
7	378	445	1992.5
8	380	445	2325.6
9	382	445	2657.6
10	384	445	2990.4
PDHF ^c	388	445	

^a Absorption and emission studies were conducted in tetrahydrofuran solvent. ^b Measured by field desorption mass spectroscopy. ^c High molecular weight poly(9,9-di-*n*-hexylfluorene-2,7-diyl) (**3**) with a degree of polymerization = 54 based on the number average molecular weight (M_n) measured by GPC analysis.

the high molecular weight homopolymer. The emission spectra of oligomeric and polymeric 9,9-dialkylfluorene derivatives in nonpolar solvents consist of a vibronically structured band with three primary maxima. The vibronic spacing is about 1400 cm^{-1} . Since the longest wavelength component is weak, we have arbitrarily chosen to report the position of the

**Figure 2.** UV-visible spectra of the end-capped 9,9-di-*n*-hexylfluorene oligomers and high molecular weight homopolymer in tetrahydrofuran. The degree of polymerization of the high molecular weight polymer (PDHF) derived from the GPC-determined number average molecular weight was 54.**Figure 3.** Plot of $1/\lambda_{\text{max}}$ versus $1/n$. (a) The λ_{max} were determined in tetrahydrofuran, and n is equal to the number of fluorene units in the oligomers as determined by field absorption mass spectroscopy. The absorption maximum for high molecular weight (degree of polymerization = 54) poly(9,9-di-*n*-hexylfluorene-2,7-diyl) (**3**) was 388 nm.

second longest maxima. The analysis here is independent of the specific vibronic band chosen for reference as long as the choice is consistent throughout the series. The relevant emission component of the high molecular weight homopolymer in solution appears at 445 nm.

It is often possible to determine the limiting conjugation length of oligomeric materials by examination of the plot of the absorption energy (or some proportional quantity) versus the quantity $1/n$, where n represents the oligomeric length, as long as soluble high molecular weight materials are available for comparison (see Figure 3).¹¹ In this study, we have chosen n to equal the number of bonded fluorene units including the end caps. The number of bonded aromatic rings in this case would be equal to $2n$. With the limiting absorption maximum of 388 nm determined for the high molecular weight polyfluorene homopolymer ($n \approx 54$), linear extrapolation of the plot in Figure 3 would suggest an effective conjugation length of approximately 12 bonded fluorene units or a total of 24 aromatic rings. The plot

using the data points obtained for the oligomers is reasonably linear (correlation coefficient = 0.994). However, linear extrapolation to $1/n = 0$ yields a value of $24\,835\text{ cm}^{-1}$ (403 nm) for $\bar{\nu}_{\infty}$. This should be compared with the value of $25\,773\text{ cm}^{-1}$ (388 nm) measured for the high molecular weight polymer. This observation suggests that a linear fit is not appropriate over the entire molecular weight range. This result is consistent with the study of Meier et al.,¹² who find that an exponential function is more appropriate for oligomers of substituted poly(*p*-phenylenevinylene) (PPV) oligomers. In this case, the use of a linear extrapolation to determine the effective conjugation length introduces relatively little error since the absorption maxima are practically converged by $n = 10$. The measurement accuracy for the diode array absorption spectrometer is estimated to be $\pm 2\text{ nm}$. The effective conjugation length determined for poly(9,9-di-*n*-hexylfluorene-2,7-diyl) (**3**) may be compared with that obtained for soluble alkyl-substituted poly(tetrahydropyrene) derivatives (PTHP), where the effective conjugation length has been estimated to comprise ~ 20 benzene rings.¹³ In the case of the tetrahydropyrene derivatives, the dihedral angle between the aromatic rings is estimated to be approximately 20° . The fluorene monomers are somewhat more rigid with a dihedral angle between the two aromatic rings close to 0° .¹⁴ Despite this difference, the effective conjugation length for the polyfluorenes is quite close to that of the PTHP polymers and is substantially longer than that measured for a fully conjugated and presumably planar soluble ladder polymer produced by polymer analogous cyclization techniques.¹³

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