Macromolecules **2000,** *33,* 3961−3963 **3961**

Poly(fluorenyleneethynylene)s by Alkyne Metathesis: Optical Properties and Aggregation Behavior

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Received February 23, 2000
Revised Manuscript Received April 13, 2000

We report here the aggregation behavior and the synthesis of poly[(9,9-dialkyl)fluoren-2,7-yleneethynylene]s (PFE, **4**) made by alkyne metathesis. Conjugated organic polymers are semiconductors[1] and, as such, important in the fabrication of optoelectronic devices including light-emitting diodes,[2] thin-film transistors,[3] lasers,[4] and light-emitting electrochemical cells.[5] While poly(*p*-phenylenevinylene)s (PPV)[2,6] have been the most frequently utilized hydrocarbon polymers for these purposes,[7] the polyfluorenes[8] have become more important in recent years. The popularity of the polyfluorenes is due to their efficient blue photo- and electroluminescence coupled with their high chemical stability.[8]

We have optimized a simple catalyst system formed in situ from $Mo(CO)_6$ and a phenol[9] and used it to synthesize high molecular weight poly(*p*-phenyleneethynylene)s (PPE) by alkyne metathesis. This simple and powerful synthetic method bodes for the extension to other alkyne-bridged polymers.[10] It was thus of interest as to whether the sparsely described[11] but attractive PFE **4** could be obtained by alkyne metathesis.

Starting from diiodofluorene[12] (**1**), phase transfer alkylation furnished a series of 9,9-dialkyl-2,7-diiodofluorenes (**2**) in multigram quantities (see Scheme 1). Propynylation according to the previously published procedure gave the desired monomers **3a**−**e** in good-to-excellent yields after chromatography.[13] While **3b**−**e** are colorless oils, **3a** is crystalline. Alkyne metathesis of **3a** ($Mo(CO)_6$/4-chlorophenol/1,2-dichlorobenzene, 140 °C) furnished a yellow, highly fluorescent powder after precipitation of the reaction solution into methanol, as well as some gel-like material that was only slightly soluble even under our reaction conditions, suggesting that hexyl groups are not effective to impart solubility to **4**. To obtain better soluble PFEs **4**, longer and branched side chains were introduced into **3**. Upon metathesis of **3b**−**e** under standard conditions[14] (Table 1), the soluble yellow PFEs **4b**−**e** were obtained. The yield of **4** is variable due to the formation of some insoluble, high molecular weight material, which was filtered off. Gel permeation chromatography revealed that these PFEs **4a**−**e** show substantial molecular weights (see Table 1). Their solubility in chlorinated organics is sufficient to perform spectroscopic (^{13}C NMR, UV/vis, and fluorescence) characterization but is significantly less than that of similarly substituted PPEs.[15a] This is not too surprising, because the concentration of solubilizing side chains is lower in PFEs **4** than in the PPEs. In the solid state, PFEs **4** are yellow and have a powdery, brittle quality, suggesting that we do not have a lamellar but an interdigitated structure.[15b] Spin-cast and solution-cast (chloroform) films of **4a**−**e** are free-standing and clear. They appear black when examined under crossed polarizers, suggesting that no long-range order exists in the as-spun films. A lyotropic nematic phase, however, was evidenced by a Schlieren texture when solutions of **4a** were slowly evaporated on a glass slide.

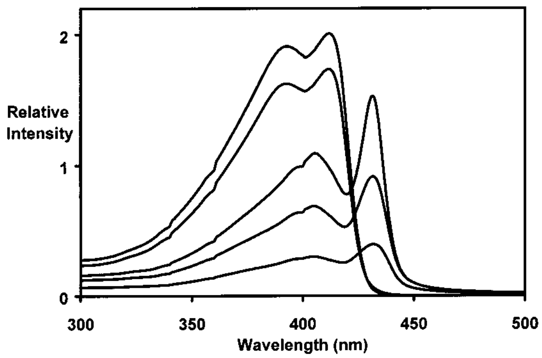

Figure 1. Absorption spectrum of **4e** ($CHCl_3$) upon the addition of MeOH (0, 17, 38, 50, 74% top to bottom).

UV/vis spectra of **4a**−**e** in solution (chloroform) are identical and show two absorptions at 392 and 412 nm. We investigated the solvatochromic behavior of **4e**. An aggregate band appears at 432 nm when to a chloroform solution of **4e** methanol is added. At about 38 vol % methanol, the aggregate band is completely developed (see Figure 1). The behavior of **4e** (and of the other polymers **4**) has an analogy in that of the dialkyl-PPEs,[16] the polythiophenes,[17a] and the polydiacetylenes[17b,c] where similar aggregate bands are described. In PPEs, polythiophenes, and the ladder-type polyphenylenes,[17d] this band is due to planarization of the backbone through enhancement of the conjugation.[18] We propose that planarization of the backbone likewise leads to the observed red shift in the solid state of the PFEs. Spin-cast films are amorphous and show UV spectra similar to those obtained in $CHCl_3$ solution without the pronounced aggregate band. Only **4e** shows a slight bathochromic shift of 12 nm.[19] The difference between the solid-state and $CHCl_3$−MeOH spectra is striking and probably a consequence of a higher order in the latter case. Equilibration of the methanol-induced aggregates under Ostwald ripening is probably responsible.

The fluorescence spectrum of PFE **4e** (and that of the other representatives of **4**) in chloroform shows emission at 427 and 447 nm (see Figure 2a). In comparison to the poly(dialkylfluorene)s, there is a slight red shift observed in the PFEs. This may be explained by the improved π-overlap due to the accommodating nature of the acetylene unit.[20] Emission spectra (Figure 2a) taken in chloroform−methanol mixtures show that the two bands split into four, one of which is hypsochromically shifted to 412 nm. Thin clear films of **4b** strongly emit in the blue with a red shift of 1−7 nm of the emission maxima, when compared to spectra taken in $CHCl_3$. The reason for the solid-state intense fluorescence is under examination at the moment. Closely packed chains of **4b** must show an alignment of the transition dipole moment, leading to highly emissive

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10.1021/ma0003250 CCC: $19.00

Scheme 1

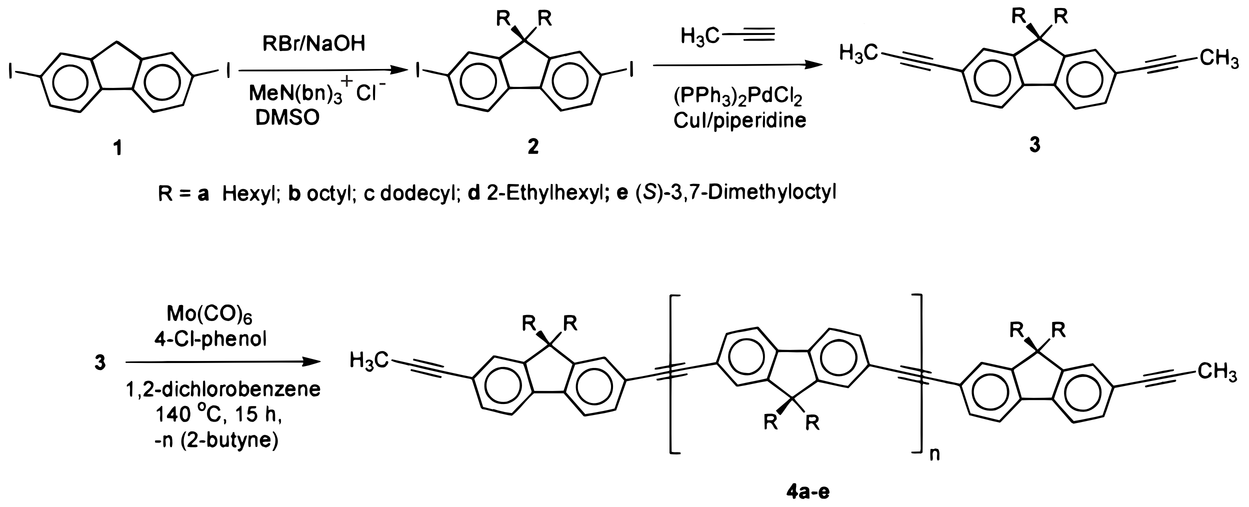

Table 1. Characterization of PFEs 4a–e

			GPC				absorbance/nm		emission/nm[b]	
polymer	time (h)	yield (%)	M_n[a]	M_w[a]	P_n[a]	P_{di}[a]	$CHCl_3$	thin film	$CHCl_3$	thin film
4a	14.5	23[c]	14 100	59 900	40	4.2	392, 413	396, 415	427, 447	428
4b	14.5	74	11 600	67 000	28	5.8	392, 412	394, 416	426, 447	429
4c	25	69	9 800	42 800	19	4.4	390, 410	387, 413	426, 447	429
4d	19.5	34	17 000	61 000	41	3.6	394, 412	392, 416	426, 446	434
4e	18	65	9 500	51 100	20	5.4	392, 412	396, 424	427, 447	434

[a] Gel permeation chromatography results based on polystyrene standards, P_n(calc) from M_n. [b] Excitation was at 393 nm. [c] All data given for **4a** pertain to the soluble fraction.

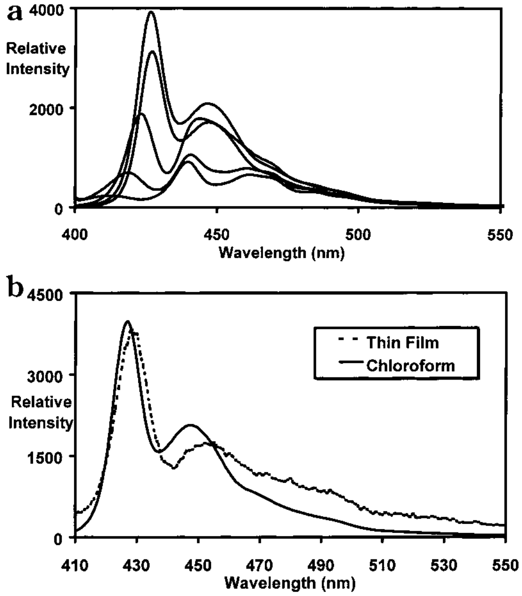

Figure 2. (a) Emission spectrum of **4e** ($CHCl_3$) upon the addition of MeOH (0, 17, 29, 50, 69% top to bottom). (b) Comparison of emission spectra of **4a** in solution versus as thin film.

states.[21] Structural investigations and determination of the solid-state fluorescence quantum yields, including the examination of oligomeric models, are under way.

In conclusion, we have been able to make a series of PFE's **4** by alkyne metathesis of dipropynylfluorenes **3**. The aggregation behavior of **4** was examined by UV/vis and fluorescence spectroscopy. The absorption spectra of **4** resemble that of the PPEs, with the well-developed aggregation band, while the emission spectra (comparison of solution vs solid state) are more reminiscent of that of the polydialkylfluorenes.[8] The remarkable aggregation-induced behavior (UV/vis) puts the PFE's in a class with the dialkyl-PPE's, the alkylpolythiophenes, the polydiacetylenes, and the ladder-polyphenylenes.[17d] The solid-state structure, phase behavior, and use of **4** in LEDs are under examination.

Acknowledgment. We thank Mary E. Vaughn for the measurement of several UV/vis spectra, Katie Stitzer for powder diffraction data, and Professors M. L. Myrick (USC) and M. D. Curtis (Ann Arbor) for stimulating discussions. We thank the Commission of Higher Education of the State of South Carolina, the National Science Foundation (Grant CHE 9814118), and the Research Corporation for generous support for this work. U.H.F.B. is an NSF CAREER awardee (CHE 9981765, 2000–2003).

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(13) Propynylation of **2c** was performed using a controlled amount of propyne gas (see ref 10), resulting in **3c** (89%) as a clear oil. Selected data for **3c**: ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 2H, $J = 8.2$ Hz), 7.37−7.35 (m, 4H), 2.09 (s, 6H), 1.94−1.90 (m, 4H), 1.28−1.03 (m, 36H), 0, 87 (t, 6H, $J = 7.0$), 0.58 (bs, 4H); ^{13}C NMR ($CDCl_3$) δ 150.7, 140.0, 130.3, 125.7, 122.4, 119.5, 85.8, 80.6, 55.1, 40.4, 32.0, 30.1, 29.7, 29.6, 29.4, 23.8, 22.8, 14.2, 4.5.

(14) Sample polymerization: **3c** (0.500 g, 0.860 mmol), $Mo(CO)_6$ (0.021 g, 0.086 mmol), 4-chlorophenol (0.111 g, 0.860 mmol), and *o*-dichlorobenzene (20 mL) were held at 140 °C for 25 h under a steady stream of N_2. The cooled reaction mixture was dissolved in 75 mL of CH_2Cl_2, washed with diluted base, acid, and H_2O, and then poured into MeOH for precipitation. The resulting yellow solid **4c** (69%) was filtered using a #4 frit. ^{1}H NMR (CD_2Cl_4) δ 7.74−7.62 (m), 2.08 (bs), 1.19 (m), 0.91 (m); ^{13}C NMR (CD_2Cl_4) δ 151.4, 140.8, 131.0, 126.1, 122.3, 119.9, 91.9, 81.0, 55.4, 55.3, 40.2, 31.7, 30.0, 29.2, 29.1, 23.9, 22.5, 13.9, 4.3. IR $\nu_{\max}$ (KBr)/cm^{-1} 2925, 2852, 2360, 1472, 889, 820 Selected data for **4e**: ^{1}H NMR ($CDCl_3$) δ 7.69−7.67 (m), 7.57−7.52 (m), 7.38−7.35 (m), 2.09 (s), 2.09−2.06 (bm), 1.52−1.43 (m), 1.24−1.02 (m), 0.87−0.47 (m); ^{13}C NMR ($CDCl_3$) δ 151.1, 140.8, 130.9, 125.8, 122.1, 199.7, 90.8, 55.1, 39.2, 37.7, 36.6, 32.9, 30.4, 27.9, 24.5, 22.7, 22.6, 19.5. IR $\lambda_{\max}$ (KBr)/cm^{-1} 2954, 2925, 2860, 2360, 1642, 1474, 888, 826.

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