Macromolecules **1997,** *30,* 7391−7396 **7391**

Synthesis and Photophysical Characterization of Group Transfer Polymers with Pendent Aryl Chromophores

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Received June 24, 1997; Revised Manuscript Received September 13, 1997⊗

ABSTRACT: Naphthalene- and pyrene-labeled polymers (poly-**3**−**5**) prepared by group transfer polymerization of methyl 2-(2-naphthyl)acrylate, methyl 2-(1-pyrenyl)acrylate, and ethyl 5-(2-naphthyl)-pentadienoate and ethyl 5-(2-naphthyl)hexadienoate, respectively, were studied as probes for backbone conformational rigidity. Excimer formation was observed in the steady-state fluorescence spectra, and the observation of biexponential decay of time-resolved fluorescence indicates two distinct environments for excimer formation. These, in turn, point to substantial conformational flexibility in the polymer backbone.

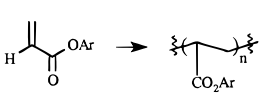
Introduction

Polymers with appended chromophores have been used as models for vectorial energy migration in new optoelectronic materials and in biologically relevant light collection assemblies.[1−6] In most vinyl polymers investigated so far, energy migration is suppressed because excimer traps localize and dissipate the excitation energy.[6−9] These observations thus indicate insufficient separation of the pendent groups, random orientation of the chromophores, and/or unrestricted mobility of the polymer backbone.

Group transfer polymerization (GTP), a living polymerization technique,[10,11] is unusual among possible polymerization methods in having a high tolerance for several functional groups and in producing a living polymer capable of extension to block copolymers in subsequent steps.[10−13] Although variation of the composition of GTP block copolymers is known to produce remarkable changes in their physical properties, few polymers bearing absorptive or emissive groups have been prepared. Among those that have been prepared, none have been examined for optoelectronic applications.

By characterizing the relevant excited-state interactions in such macromolecules, valuable structural information concerning backbone rigidity and intramolecular interactions between pendent groups is likely to be attained. For example, in several families of norbornene-derived homopolymers, excimer emission can be suppressed when the interacting chromophores are sterically isolated, i.e., separated from the nearest neighbor by more than one monomer residue.[1c,d,14]

In principle, chromophoric groups (e.g., an aryl group, Ar) could be appended as either an ester attachment **1** or on the carbon backbone, e.g., **2**. However, homopolymers **1** derived from acrylate esters (Ar = 9-anthryl, benzyl, and 2-naphthyl) have been shown earlier to suffer cleavage of the ester linkage upon excitation.[7b,15−17] We have focused therefore on the preparation of homopolymers **2** that bear the chromophore probe as a covalent attachment to the polymer backbone.



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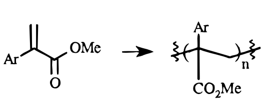

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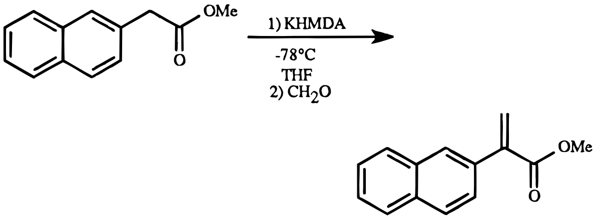
We describe here the GTP synthesis and photophysical characterization of polymers derived from methyl 2-(2-naphthyl)acrylate **3**, methyl 2-(1-pyrenyl)acrylate **4**, and a family of ethyl 5-(2-naphthyl)pentadienoates and -hexadienoates **5**. The latter family was examined to define the effect caused by the introduction of a double bond into the resulting polymer backbone. We hoped to establish whether this structural feature might restrict conformational freedom and better spatially separate the appended aryl groups, resulting in a lower level of excimer formation. The photophysical characteristics of these poly(arylacrylates) (poly-**3** and poly-**4**) and poly(pentadienoates) (poly-**5**) illustrate the effect of polymer structure on singlet energy migration and excimer formation.

Results

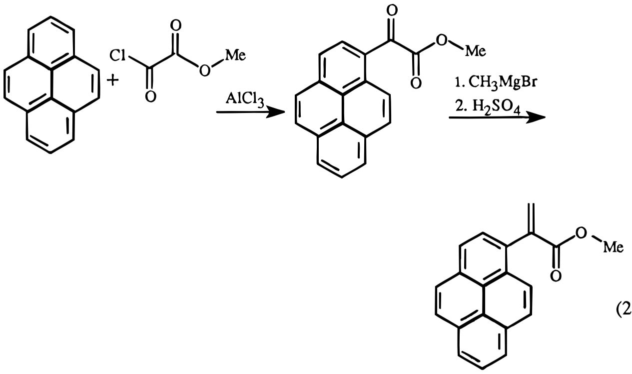
Synthesis of Monomers. Methyl 2-(2-naphthyl)-acrylate **3** was prepared in 65% yield from the reaction of formaldehyde with the enolate anion of methyl 2-naphthylacetate, which had been formed by deprotonation with potassium hexamethyldisilazide (KHMDA), a non-nucleophilic base (eq 1).



(1)

3

Friedel−Crafts acylation of pyrene with methyl oxalyl chloride gave an α-ketoester (78%), methylation and dehydration of which gave methyl 2-(1-pyrenyl)acrylate **4** in a 45% overall yield (eq 2). The ethyl 5-(2-napthyl)-



(2)

4

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1997.

S0024-9297(97)00928-5 CCC: $14.00

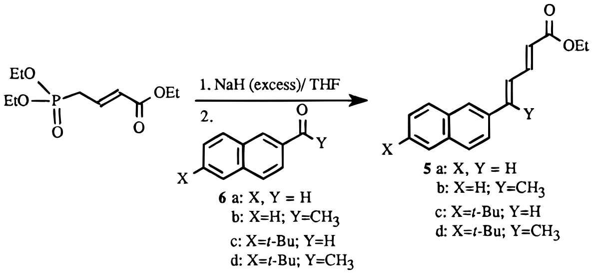
Table 1. Yields and Polydispersities of Poly-3 and Poly-4

	poly-**3**	poly-**3** (entry 2)	poly-**4**
M_n	3380	4950	4740
$M_{n\ calc}$	3195	5325	4305
PDI	1.06	1.08	1.10
yield (%)	74	70	65

Table 2. Molecular Weights and Polydispersities for Poly-5a and Poly-5c

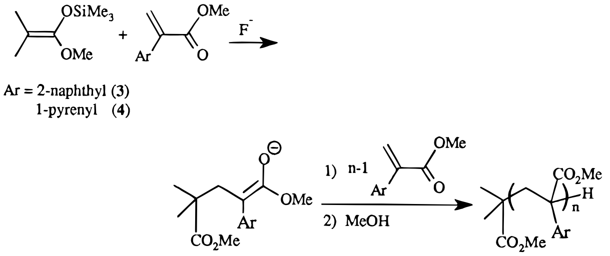
	poly-**5a**	poly-**5c**
M_n	5200	5600
$M_{n\ calc}$	6350	6220
n	25	20
PDI	1.22	1.11
yield (%)	80	81

pentadienoate and -hexadienoate monomers **5** were synthesized through a modified Horner–Emmons reaction between diethylphosphonocrotonate and an appropriate aldehyde or ketone **6** (eq 3).



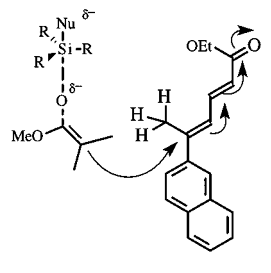
(3)

Polymerization of 3 and 4. The polymerizations of **3** and **4** were undertaken under standard GTP conditions:[10–13] as solutions in THF under Ar with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene as the initiator and tetra-*n*-butylammonium fluoride as the catalyst (eq 4). The molecular weights of the resulting poly(acrylates) could be controlled by selecting a desired monomer-to-initiator ratio. Because GTP is a living method, a homopolymer of the desired molecular weight range could be attained by addition of a second aliquot of monomer or the procedure could be adapted to the preparation of a block copolymer by adding a different monomer. Upon complete consumption of the monomer (as monitored by ^{1}H NMR), the propagating polymer was allowed to continue chain growth by addition of a second aliquot of monomer. When the desired molecular weight had been attained, the elongated chain was terminated by treatment with methanol.



(4)

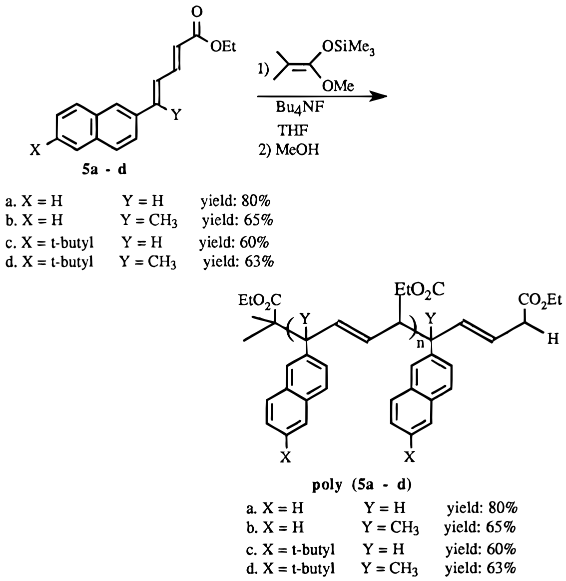
The number-average molecular weight and polydispersity index of these homopolymers, determined by gel permeation chromatography against a polystyrene standard, are listed, together with isolated yields, in Table 1. Low polydispersities were observed, such that the calculated number-average molecular weights ($M_{n\ calc}$: from the monomer-to-initiator ratio, assuming quantitative conversion) compared well with the experimentally observed M_n values obtained from GPC analysis. The polydispersity indices (PDI) for poly-**3** and poly-**4** agree well with published data for nonarylated poly(acrylates) or poly(methacrylates) produced under the same conditions (PDI: 1.1–1.4).[10a–d,18] Consistent with a living polymerization,[18,19] the addition of more monomer did produce the expected increase in molecular weight (Table 1, entry 2).



5b

Figure 1. Proposed attack of the initiator–catalyst complex on the sterically crowded γ,δ-double bond of **5b** inhibited by the methyl group in the δ-position.

An analogous polymerization[10c] of **5** was performed by GTP in THF under Ar with the same initiator and catalyst (eq 5). The yields and polydispersities of poly-**5a** and poly-**5c** are summarized in Table 2. As with **3** and **4**, stepwise addition of subsequent aliquots led predictably to higher molecular weight oligomers with reasonably low polydispersities. Although a soluble polymer was obtained in good yield for **5a** and **5c**, the molecular weights and polydispersities of these polymers were somewhat better than those typically observed with the acrylates (PDI range of 1.3–1.8).[10] Possibly, competing side reactions, such as polymer cross-linking and chain-transfer reactions observed with the parent pentadienoates, are minimized with these substituted monomers.[10d]



(5)

Monomers with a δ-disubstituted γ,δ-double bond (**5b** and **5d**) did not polymerize under standard GTP conditions or even at higher temperatures (60 °C). To our knowledge, this was the first attempt to use δ-disubstituted dienoate esters as monomers for GTP. It is probable that transition state crowding (Figure 1) caused by the δ-methyl group inhibited these polymerizations.

Steady-State Fluorescence. An important factor to consider in judging whether a polymer is suitable for

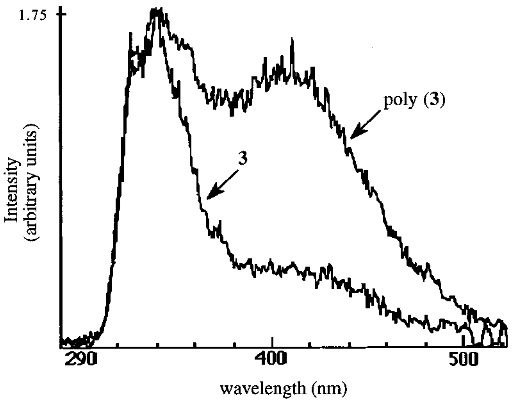


Figure 2. Steady-state fluorescence spectra of 1 × 10^{-4} M solutions of **3** and poly-**3** in degassed CH_2Cl_2.

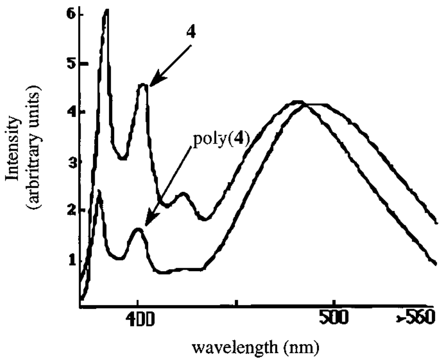


Figure 3. Steady-state fluorescence spectra of 1 × 10^{-4} M solutions of **4** and poly-**4** in degassed CH_2Cl_2.

promoting unidirectional energy or electron transfer is the fraction of excimer emission in the steady-state fluorescence spectra of these compounds. The emission spectra of the monomer and the corresponding polymer (**3**, poly-**3**, **4**, and poly-**4**) showed emission from isolated monomer units at 340 nm and excimer fluorescence at 420 nm in **3** (weak) and poly-**3** (strong) (Figure 2). The same emissions are observed in **4** and poly-**4** in the region of 380−430 nm and at 490−500 nm, respectively, with comparably strong excimer emission being observed in **4** and poly-**4** (Figure 3). The observation of significant excimer is consistent with data reported for poly(vinylnaphthalenes) with similar skeletons.[5,8b,18] Apparently, a flexible polymer backbone, together with a chromophore that is unrestricted in its rotational freedom and sterically accessible to an adjacent aryl group, permits excimer formation in poly-**3** and poly-**4**, even in dilute solution.

The emission spectra of monomers **5a** and **5c** and the corresponding polymers poly-**5a** and poly-**5c** show strong excimer emission in the monomer and polymer, with the emission maximum being shifted to longer wavelength in the polymer (Figure 4 and Table 3). The presence of the additional methyl group in **5c** and poly-**5c** did not substantially affect the emission profile. Nor did the polymerization affect the quantum yield of fluorescence for these substrates. When the concentration of monomer **5a** in CH_2Cl_2 was decreased (Figure 5), the ratio of monomer-to-excimer emission increased, as would be consistent with an intermolecular origin for excimer formation. However, when the concentration of poly-**5a** in CH_2Cl_2 was similarly varied, the ratio of monomer-to-excimer emission was unchanged (Figure 6).

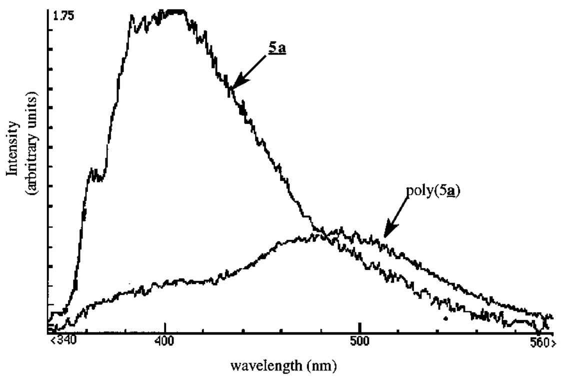


Figure 4. Fluorescence spectra of 1 × 10^{-4} M solutions of **5a** and poly-**5a** in degassed CH_2Cl_2.

Biexponential decay was observed in the time-resolved fluorescence spectra of the excimer of poly-**5a** but not in dilute solutions of the monomer **5a** (Table 3 and Figure 7), where monoexponential decay was observed. We assigned these two decays in poly-**5a** to two distinct excimers formed in quite different environments along the polymeric chain.[21,22] There is no evidence for ground-state $\pi-\pi$ stacking in the absorption spectra, but because such interactions are often difficult to observe spectroscopically, their possible contribution to intramolecular interactions responsible for excimer formation cannot be ruled out from the available data.

The similar intensities of excimer emission in poly-**5a** and poly-**5c** imply that variation in the steric bulk of the aryl group does not influence appreciably the approach of these chromophores to a geometry required for excimer formation. This observation is unlike that reported for the acrylate polymers, where aryl steric bulk was more important.

Conclusions

Even though polymerization of aryl-substituted acrylates of low polydispersity can be achieved by group transfer polymerization, excimer emission dominates the fluorescence spectra of the naphthyl and pyrenyl derivatives of methyl acrylate, respectively, poly-**3** and poly-**4**. Chromophore-appended pentadienoates **5** polymerize smoothly if the δ-position of the conjugated ester is substituted only by a single δ-aryl group but fail with δ-disubstitution in the corresponding hexadienoates. Like the polyacrylates, however, the polymers show emission dominated by excimer, even in dilute solution.

A double bond introduced into the polymer backbone does not provide sufficient conformational rigidity to obviate excimer formation (cf. poly-**5** vs poly-**3**). Thus, each of these polymers has insufficient conformational restriction, with or without an additional C=C double bond, to suppress excimer emission, and the introduction of additional steric bulk on the aryl substituent (as a 6-*tert*-butyl substituent) is insufficient to obviate such interactions. We can infer that the chromophores situated along the polymer chain are not geometrically isolated and that normal conformational flexing permits stable intramolecular excimer formation. An alternate explanation involving ground-state $\pi-\pi$ stacking may also contribute to these observations. The biexponential decay in the time-resolved fluorescence spectra of poly-**5a** and poly-**5c** suggests that excimer emissions from two different environments contribute to the excited-state decay of poly-**5**.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out with standard

Table 3. Absorbance and Emission of Methyl Pentadienoate Monomers 5a and 5c and Their Polymers[a]

compound	λ_{max} (nm)	ϵ ($M^{-1} cm^{-1}$)	λ_{em} (nm)	Φ_{fl} (emission)	τ_1, τ_2 (ns) at $\lambda = 420$ nm
5a	284, 278	15 000, 7600	350, 410	0.15	27
poly-**5a**	284, 274	14 800, 7400	400, 480	0.15	33, 4
5c	278, 284	13 000, 8700	340, 420	0.12	21
poly-**5c**	278, 284	21 400, 8400	390, 480	0.12	28, 7

[a] In CH_2Cl_2 at an OD = 0.08 (≈1 × 10^{-5} M).

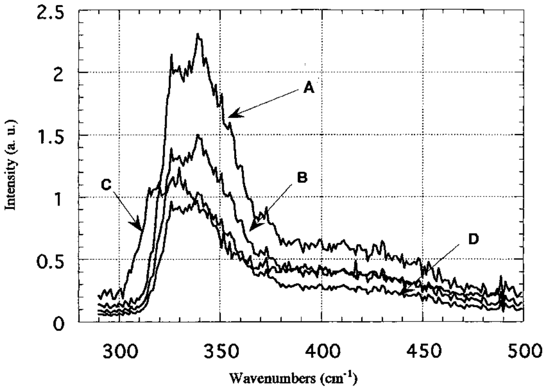


Figure 5. Effect of dilution on the fluorescence spectra of degassed solutions of **5a** in degassed CH_2Cl_2: (A) 1 × 10^{-4} M, (B) 5 × 10^{-5} M, (C) 1 × 10^{-5} M, (D) 5 × 10^{-6} M. λ_{exc} = 284 nm.

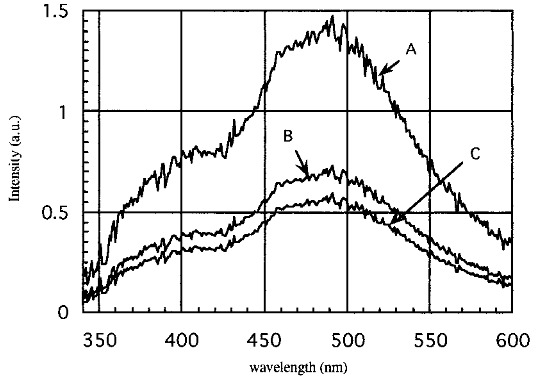


Figure 6. Effect of dilution on the fluorescence spectra of degassed solutions of poly-**5a** in CH_2Cl_2: (A) 1 × 10^{-4} M, (B) 1 × 10^{-5} M, (C) 5 × 10^{-6} M. λ_{exc} = 284 nm.

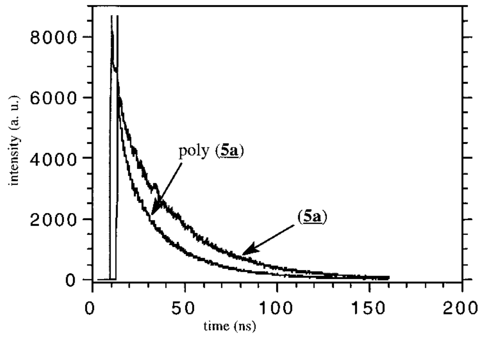


Figure 7. Time-resolved fluorescence spectra of **5a** and poly-**5a**.

Schlenk-line techniques. All glassware was dried in the oven at 200 °C overnight or flame-dried prior to use.

Dichloromethane was spectral grade and was distilled from CaH_2 and benzene, and tetrahydrofuran was distilled from sodium–benzophenone under N_2 prior to use. Commercially available reagents were used without further purification: 2-naphthaldehyde; sodium hydride; triethylphosphonocrotonate; 2-acetonaphthone; aluminum chloride; *tert*-butyl chloride; 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene; tetra-*n*-butylammonium fluoride; and naphthalene. 6-*tert*-butyl-2-acetonaphthone[1] and 6-*tert*-butyl-2-naphthaldehyde[1] were prepared by literature procedures.[20a,22,23]

All melting points (uncorrected) were determined using a Melt-Temp apparatus. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a General Electric QE 300 or a Nicolett 360 MHz spectrometer and are reported in parts per million from an internal TMS standard. The coupling constants are reported in hertz. Gel permeation chromatography was carried out in CH_2Cl_2 using a Waters 550 HPLC pump, a Waters 410 differential refractometer, and a Waters 745 data module with Ultrastyragel 10^4, 10^3, and 500 Å columns connected in series and calibrated with a polystyrene standard. Polydispersity indices and average molecular weights of the polymers were obtained using GPC (gel permeation chromatography) analysis referenced to the polystyrene standard. Absorbance spectra were obtained on a Hewlett-Packard 8451A diode array spectrophotometer. Emission spectra were obtained on a SLM Aminco SPF-500C spectrofluorometer. High-resolution mass spectral analyses were carried out at The University of Texas at Austin Spectral Facility using a Finnigan TSQ70 or a Fisons TS270 mass spectrometer.

Synthesis of Methyl 2-(2-Naphthyl)propenoate (3). A dry, Ar-flushed, three-neck, 50 mL, round-bottomed flask was charged with THF (15 mL). Potassium hexamethyldisilazide (1.2 g, 6 mmol) in THF (5 mL) was added. Methyl 2-naphthylacetate (2 mmol, 0.4 g) was slowly added to the stirred solution via a syringe, and the mixture was allowed to stir at −78 °C for 30 min after the addition was complete. Paraformaldehyde (1.0 g) in THF (5 mL) was then slowly added. The color of the solution turned from orange to white when the reaction was complete. The reaction mixture was poured onto ice and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over anhydrous Na_2SO_4 for 1 h. The solvent was removed under reduced pressure and a white solid was obtained in 65% yield. Mp: 88−92 °C. ^1H NMR ($CDCl_3$): δ 7.79 (m, 3 H), 7.40 (m, 3 H), 7.30 (s, 1 H), 6.69 (d, 1 H, J = 2.6 Hz), 5.85 (d, 1 H, J = 2.6 Hz), 3.52 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 167.2, 143.6, 134.9, 132.8, 132.5, 128.6, 128.2, 127.5, 126.5, 126.3, 122.7, 122.7 122.3, 51.9. UV (CH_2Cl_2): λ_{max} = 276 nm (ϵ = 16 000 $M^{-1} cm^{-1}$), 284 nm (ϵ = 8000 $M^{-1} cm^{-1}$). Fluorescence (CH_2Cl_2): λ_{max} = 310 nm (Φ_{fl} = 0.16 for λ_{ex} = 284 nm). HRMS (*m*/*e*): calcd for $C_{14}H_{12}O_2$, 212.091; found, 212.096.

Polymerization of Methyl 2-(2-Naphthyl)propenoate (Poly-3). 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (28 mg, 0.2 mmol) and tetra-*n*-butylammonium fluoride (9.0 mg, 10 mol %) were dissolved in 1 mL of THF under Ar on the Schlenk line. The monomer (0.6 g, 4.0 mmol) was dissolved in THF (1 mL) and was added to the solution of catalyst and initiator. After 8 h, methanol (1 mL) was added to quench the polymerization. The solution was added dropwise to stirring hexanes (100 mL) to precipitate the polymer as a yellow solid. The polymer was characterized by GPC and NMR. ^1H NMR ($CDCl_3$): δ 7.8−7.2 (br), 3.52 (br), 1.94 (br). ^{13}C NMR ($CDCl_3$): δ 172.2, 134.1, 133.8, 132.5, 128.3, 127.8, 126.9, 126.5, 126.4, 124.7, 124.3, 50.6, 43.4, 41.8. UV (CH_2Cl_2): λ_{max} = 260 nm (ϵ = 40 700 $M^{-1} cm^{-1}$), 308 nm (ϵ = 3100 $M^{-1} cm^{-1}$). Fluorescence (CH_2Cl_2): λ_{max} = 335 nm (Φ_{fl} = 0.17 for λ_{ex} = 284 nm), 400 nm (broad excimer band). MW = 3400. PDI = 1.3.

Synthesis of Methyl 2-(1-Pyrenyl)propenoate (4). $AlCl_3$ (0.15 g, 1.1 mmol) was added to a dry 50 mL, round-bottomed flask under Ar. THF (10 mL) and pyrene (1.0 mmol, 0.25 g) in THF (5 mL) were added via a syringe. Methyl oxalyl chloride (1.1 mmol, 0.14 g) in THF (15 mL) was added via a dropping funnel over 30 min, and the reaction mixture was stirred for 3 h. It was then poured onto ice and extracted with ether (3 × 30 mL). Methyl 1-pyrenoylformate was dissolved in ether (10 mL) and converted to the α-hydroxyl ester using methylmagnesium bromide in THF (2 mL of a 1.0 M solution) by heating at reflux for 30 min. The α-hydroxyl ester was characterized by an IR spectrum (solution cell) (cm^{-1}): 3500 (OH peak), 1730 (C═O). Subsequent dehydration with concentrated H_2SO_4 (1 mL) or HCl gas gave the desired product in 45% yield as a yellow solid. Mp: 145−149 °C. ^1H NMR ($CDCl_3$): δ 8.40−7.90 (m, 9 H), 6.90 (d, 1 H, 2.9 Hz), 6.00 (d, 1 H, 2.9 Hz), 3.70 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 192.8, 148.2, 134.4, 131.3, 131.2, 130.8, 130.7, 130.6, 130.3, 128.7, 127.3, 127.1, 126.9, 126.7, 126.5, 124.6, 124.4, 123.8, 122.9, 31.3. UV (CH_2Cl_2): $\lambda_{max} = 314$ nm ($\epsilon = 32\,600$ M^{-1} cm^{-1}), 328 nm ($\epsilon = 11\,400$ M^{-1} cm^{-1}), 344 nm ($\epsilon = 21\,400$ M^{-1} cm^{-1}), 424 nm ($\epsilon = 9800$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 375$ nm ($\Phi_{fl} = 0.09$ for $\lambda_{ex} = 352$ nm), 482 nm (broad excimer band). HRMS (*m/e*): calcd for $C_{20}H_{14}O_2$, 286.130; found, 286.131.

Polymerization of Methyl 2-(1-Pyrenyl)propenoate (Poly-4). 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (28 mg, 0.2 mmol) and tetra-*n*-butylammonium flouride (9.0 mg, 10 mol %) were dissolved in THF (1 mL) on the Schlenk line. Monomer (1.1 g, 4.0 mmol) was dissolved in THF (1 mL) and was added to the solution of catalyst and initiator. After 8 h, methanol (1 mL) was added to quench the polymerization. The solution was added dropwise to stirring hexanes (100 mL) to precipitate the polymer as a yellow solid. The polymer was characterized by NMR and GPC. ^1H NMR ($CDCl_3$): δ 8.40−7.90 (br), 3.60 (br), 1.90 (br). ^{13}C NMR ($CDCl_3$): δ 192.8, 135.4, 131.3, 130.9, 130.8, 130.7, 130.6, 130.3, 127.3, 127.1, 126.9, 126.7, 125.5, 124.6, 123.8, 123.4, 122.9, 58.2, 47.7, 31.3. UV (CH_2Cl_2): $\lambda_{max} = 314$ nm ($\epsilon = 67\,600$ M^{-1} cm^{-1}), 328 nm ($\epsilon = 15\,000$ M^{-1} cm^{-1}), 344 nm ($\epsilon = 11\,400$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 375$ nm ($\Phi_{fl} = 0.04$ for $\lambda_{ex} = 352$ nm), 500 nm (broad excimer band). MW = 4700. PDI = 1.5.

General Procedure for the Preparation of Naphthyl-Substituted Pentadienoate and Hexadienoate Esters (5). Mineral oil was removed from excess NaH (80% dispersion in mineral oil) by washing repeatedly with petroleum ether (3 × 15 mL). THF (15 mL) was added to the NaH in a 100 mL, round-bottomed flask at 0 °C. Diethylphosphonocrotonate (10 mmol, 2.2 mL) in THF (10 mL) was added slowly via a syringe to the flask. The orange mixture was stirred at room temperature for 1 h. It was filtered under Ar to remove any unreacted NaH, resulting in a clear orange solution. The substituted naphthalene derivative (2-acetonaphthone or 2-naphthaldehyde, with or without a 6-*tert*-butyl group, 10 mmol) in THF (10 mL) was added slowly. The reaction mixture was heated at reflux for 4 h and quenched by pouring onto ice and extracting with ether (3 × 30 mL). The solvent was removed under reduced pressure, yielding the desired product **5**.

Ethyl 5-(2-Naphthyl)-2,4-pentadienoate (5a). Compound **5a** (2.1 g, 80%) was obtained by the general procedure from 2-naphthaldehyde (10 mmol, 1.6 g). Mp: 88−90 °C. ^1H NMR ($CDCl_3$): δ 7.80 (m, 3 H), 7.61 (s, 1 H), 7.42 (m, 3 H), 7.01 (d, 1 H, $J = 13.9$ Hz), 6.99 (d, 1 H, $J = 13.9$ Hz), 6.01 (d, 1 H, $J = 15.3$ Hz), 5.99 (d, 1 H, $J = 15.3$ Hz), 4.11 (quart, 2 H, $J = 1.9$ Hz), 1.32 (t, 3 H, $J = 1.9$ Hz). ^{13}C NMR ($CDCl_3$): δ 174.8, 147.6, 147.4, 137.1, 136.2, 132.9, 131.5, 129.1, 128.8, 127.2, 125.6, 124.5, 123.3, 122.4, 122.1, 62.1, 29.4. UV (CH_2Cl_2): $\lambda_{max} = 276$ nm ($\epsilon = 15\,700$ M^{-1} cm^{-1}), 284 nm ($\epsilon = 7600$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 335$ nm ($\Phi_{fl} = 0.15$ for $\lambda_{ex} = 284$ nm), 410 nm (broad structureless band). HRMS (*m/z*): calcd for $C_{17}H_{16}O_2$, 252.124; found, 252.124.

Ethyl 5-(2-Naphthyl)-2,4-hexadienoate (5b). Compound **5b** (1.8 g, 65%) was obtained from 2-acetonaphthone as a yellow solid. Mp: 95−98 °C. ^1H NMR ($CDCl_3$): δ 7.80 (m, 3 H), 7.60 (s, 1 H), 7.40 (m, 3 H), 7.01 (d, 1 H, $J = 13.6$ Hz), 6.01 (d, 1 H, $J = 14.8$ Hz), 5.99 (d, 1 H, $J = 14.8$ Hz), 5.61 (s, 3 H), 4.10 (quart, 2 H, $J = 1.7$ Hz), 1.30 (t, 3 H, $J = 1.7$ Hz). ^{13}C NMR ($CDCl_3$): δ 174.8, 147.6, 147.4, 137.3, 136.8, 134.2, 131.5, 129.1, 128.8, 127.2, 125.6, 124.5, 123.3, 122.4, 122.1, 62.1, 48.4, 29.4. UV (CH_2Cl_2): $\lambda_{max} = 260$ nm ($\epsilon = 40\,700$ M^{-1} cm^{-1}), 308 nm ($\epsilon = 3100$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 335$ nm ($\Phi_{fl} = 0.15$ for $\lambda_{ex} = 284$ nm), 410 nm (broad structureless band). HRMS (*m/z*): calcd for $C_{18}H_{18}O_2$, 266.132; found, 266.136.

Ethyl 5-(6-*tert*-Butyl-2-naphthyl)pentadienoate (5c). Compound **5c** was obtained from 6-*tert*-butyl-2-naphthaldehyde[8] (10 mmol, 1.9 g) as a yellowish solid (2.6 g, 60%). Mp: 94−97 °C. ^1H NMR ($CDCl_3$): δ 8.32 (s, 1 H), 8.14 (s, 1 H), 7.82 (m, 2 H), 7.41 (m, 2 H), 7.01 (d, 1 H, $J = 13.9$ Hz), 6.99 (d, 1 H, $J = 13.9$ Hz), 6.01 (d, 1 H, $J = 15.3$ Hz), 5.99 (d, 1 H, $J = 15.3$ Hz), 4.1 (quart, 2 H, $J = 1.9$ Hz), 1.4 (s, 9 H), 1.3 (t, 3 H, $J = 1.9$ Hz). ^{13}C NMR ($CDCl_3$): δ 174.8, 147.6, 147.4, 137.1, 136.2, 134.2, 131.5, 129.1, 128.8, 127.2, 125.6, 124.5, 123.3, 122.4, 122.1, 84.3, 65.6, 62.1, 31.2. UV (CH_2Cl_2): $\lambda_{max} = 278$ nm ($\epsilon = 14\,800$ M^{-1} cm^{-1}), 284 nm ($\epsilon = 8700$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 335$ nm ($\Phi_{fl} = 0.12$ for $\lambda_{ex} = 284$ nm), 410 nm (broad structureless band). HRMS (*m/z*): calcd for $C_{21}H_{24}O_2$, 308.234; found, 308.235.

Ethyl 5-(6-*tert*-butylnaphthyl)-2,4-hexadienoate (5d). Compound **5d** (2.4 g, 63%) was obtained as a yellow oil from 6-*tert*-butyl-2-acetonaphthone. ^1H NMR ($CDCl_3$): δ 8.14 (s, 1 H), 7.80 (m, 2 H), 7.60 (s, 1 H), 7.40 (m, 2 H), 7.01 (d, 1 H, $J = 13.8$ Hz), 6.01 (d, 1 H, $J = 14.3$ Hz), 5.99 (d, 1 H, $J = 14.3$ Hz), 5.6 (s, 3 H), 4.1 (quart, 2 H, $J = 1.8$ Hz), 1.4 (s, 9 H), 1.3 (t, 3 H, $J = 1.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 174.8, 147.6, 147.4, 137.1, 136.2, 134.2, 131.5, 129.1, 128.8, 127.2, 125.6, 124.5, 123.3, 122.4, 122.1, 82.7, 65.6, 64.8, 62.1, 29.4. UV (CH_2Cl_2): $\lambda_{max} = 276$ nm ($\epsilon = 4700$ M^{-1} cm^{-1}), 284 nm ($\epsilon = 3100$ M^{-1} cm^{-1}), 410 nm (broad structureless band). Fluorescence (CH_2Cl_2): $\lambda_{max} = 335$ nm ($\Phi_{fl} = 0.12$ for $\lambda_{ex} = 284$ nm). HRMS (*m/z*): calcd for $C_{22}\ H_{26}\ O_2$, 322.124; found, 322.126.

General Procedure for the Polymerization of 5. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (0.2 mmol, 28 mg) and tetra-*n*-butylammonium fluoride (9.0 mg, 10 mol %) were dissolved in THF (1 mL). Monomer (10 mmol) was dissolved in THF (1 mL) and was added to the solution of catalyst and initiator. After 8 h, methanol (1 mL) was added to quench the polymerization. The reaction mixture was poured into 50 mL of vigorously stirred hexanes and precipitated. The polymer was collected by filtration and washed with hexanes.

Poly-5a. Poly-**5a** was prepared by polymerization of **5a** (10 mmol, 0.25 g) and was obtained as a white solid (0.22 g, 80%). ^1H NMR ($CDCl_3$): δ 7.80−7.40 (m, 7 H), 6.01 (br, 2 H), 4.1 (br, 2 H), 2.7 (br, 1 H), 2.5 (br, 1 H), 1.3 (br, 3 H). ^{13}C NMR ($CDCl_3$): δ 174.8, 147.6, 146.4, 134.2, 131.5, 129.1, 128.8, 127.2, 125.6, 124.5, 123.3, 122.4, 122.1, 62.1, 43.4, 41.8, 29.4. UV (CH_2Cl_2): $\lambda_{max} = 278$ nm ($\epsilon = 14\,700$ M^{-1} cm^{-1}), 284 nm ($\epsilon = 7400$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 335$ nm ($\Phi_{fl} = 0.15$ for $\lambda_{ex} = 284$ nm). MW = 5200. PDI = 2.12.

Poly-5c. Poly-**5c** was prepared from **5c** (10 mmol, 0.31 g) as a yellow−white solid (0.27, 80%). ^1H NMR ($CDCl_3$): δ 8.32−7.4 (m, 6 H, br), 5.99 (br, 2 H), 3.9 (br, 2 H), 2.8 (br, 1 H), 2.5 (br, 1 H), 1.4 (s, 9 H), 1.2 (br, 3 H). ^{13}C NMR ($CDCl_3$): δ 174.8, 146.4, 134.2, 131.5, 129.1, 128.8, 127.4, 125.6, 124.5, 123.3, 122.6, 122.1, 84.3, 65.6, 62.1, 43.4, 41.8, 31.2. UV (CH_2Cl_2): $\lambda_{max} = 276$ nm ($\epsilon = 21\,400$ M^{-1} cm^{-1}), 284 nm ($\epsilon = 8400$ M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): $\lambda_{max} = 335$ nm ($\Phi_{fl} = 0.17$ for $\lambda_{ex} = 284$ nm). MW = 5600. PDI = 2.26.

Attempts To Prepare Poly-5b and Poly-5d. No polymer was obtained from the general procedure, even at higher temperatures and with variation of the catalyst. Only starting material was recovered.

Photophysical Measurements. Emission and excitation spectra were recorded at 25 °C in spectral-grade CH_2Cl_2 or THF using a SLM Aminco SPF 500 spectrofluorimeter. All solutions had an optical density (OD) < 0.10 in a 1-cm cuvette. The emission spectra were recorded in the ratio mode (to correct for variations in lamp intensity with time) with excitation at $\lambda_{ex} = 284$ nm. The quantum yields for fluorescence were determined according to literature procedure[24] using naphthalene in cyclohexane as reference (OD = 0.2). The steady-state fluorescence efficiency was measured in solutions with optical densities of ∼0.1 at the excitation wavelength ($\lambda_{ex} = 284$ nm). Transient absorption experiments were made with a Q-switched, frequency-tripled ($\lambda = 355$ nm, 30 mJ) Quantel YG481 Nd:YAG laser (pulse width 12 ns). A right angle geometry was used to obtain transient absorption signals from a 1-cm cell with solutions of OD = 0.2−0.4. An averaging procedure was used to increase the signal-to-noise ratio in which the signals from 30 laser pulses were averaged for each absorption decay measurement. Transient species were monitored by optical absorption spectroscopy, with spectra being recorded point by point, using a pulsed high-intensity Xe arc lamp (150 W probe). The spectra were obtained by recording the absorbance changes at 5 or 10 nm increments, with 5−7 laser pulses being averaged at each wavelength on in-house software at the Center for Fast Kinetics Research at The University of Texas at Austin.

Acknowledgment. This work was supported by the Texas Advanced Research Program, the Robert A. Welch Foundation, and the Office of Basic Energy Sciences of the U.S. Department of Energy.

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MA970928K