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Fluorescence and Singlet Energy Migration in Conformationally Restrained Acrylate Polymers Bearing Pendant Chromophores

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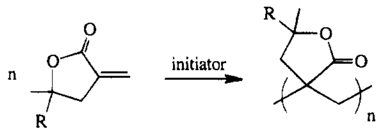
ABSTRACT: Fluorescence and singlet energy migration can be studied in chromophore-appended polyacrylates in which conformationally restricted ring structures in the polymer backbone prevent excimer formation. Specifically, two substituted α-methylene-γ-butyrolactones (**1a** bearing a naphthyl group and **1b** bearing a phenanthryl group) and a naphthyl-substituted diethyl 2,6-dimethyleneheptanedioate (**2**) yield linear polymers with five-membered rings fixed perpendicular to the main chain (poly(**1**)) or cyclopolymers with six-membered rings in the main chain (poly(**2**)) upon radical or group transfer polymerization. 4-Methyl-4-(2-naphthyl)butyrolactone (**3a**), 4-methyl-4-(3-phenanthryl)butyrolactone (**3b**), and 1-(1-naphthylmethoxycarbonyl)-1-(ethoxycarbonyl)cyclohexane (**4**) were prepared as spectroscopic models for these polymers. No evidence for excimer emission could be seen in poly(**1a**) or poly(**1b**), but poly(**2**) exhibited weak excimer emission. Defects in the polymer structure of poly(**2**) correlate with observed sites for excimer formation. Steady-state fluorescence quenching experiments by CCl$_4$ demonstrate that singlet energy migration occurs intramolecularly along these polymer chains.

Introduction

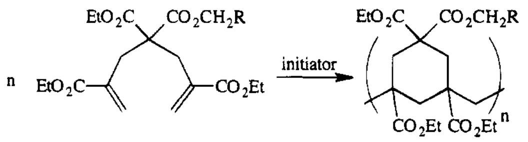
Studies of directional energy transport in polymers can contribute to a fundamental understanding of electronic interactions in macromolecular and supramolecular arrays such as that found in the reaction center of photosynthetic bacteria.[1−5] Electron and energy transfer in polymers is complicated, however, by the flexibility of the polymer chain. Although this flexibility permits energy migration, it also allows for the formation of excimer traps,[5] leading to undesirable energy loss. Excimer formation plagues most known homopolymers derivatized with naphthyl groups[5−15] and is a particular problem in polyacrylates.[5−10] One method frequently employed to circumvent excimer formation is the introduction of bulky substituents (e.g., *tert*-butyl groups) on the chromophore, sterically blocking interchromophore interactions.[12,16] Another method employs polymers with restricted main-chain flexibility induced by the presence of conformationally constrained rings in the polymer chain. Functionalized polymers obtained by ring-opening metathesis polymerization of substituted norbornenes are rigid on the time scale of excited-state lifetimes, and those bearing pendant naphthyl and phenanthryl groups do not exhibit excimer.[17] Thus, the structures of these polymers per se diminish the amount of excimer formed. Block copolymers incorporating these same groups exhibit substantial quenching and exciplex formation at the block interfaces, indicating that desirable energy and electron transfer occurs.[18] Continued studies of electron and energy transfer in synthetic, chromophore-functionalized polymers are necessary for the development of new electron transfer models and of new materials.

In this work, the synthesis and study of polyacrylates containing various chromophores have been undertaken to define the design features that inhibit excimer formation while permitting energy migration along the polymer chain. In particular, we wish to examine the influence of polymer structure on the efficiency of excimer formation in functionalized polyacrylates. The polymerization of substituted α-methylene-γ-butyrolactones (**1**; eq 1)[19−21] and the cyclopolymerization of substituted diethyl 2,6-dimethyleneheptanedioates (**2**; eq 2)[22,23] have been chosen for this study in order to explore the effects of the conformationally restricted ring structures on the branching ratio for energy migration and intramolecular excimer formation. Poly(**1**) contains five-membered rings perpendicular to the polymer chain, whereas poly(**2**) has six-membered rings in the plane of the polymer chain (assuming exclusive head-to-tail polymerization of component acrylate units). The main chains of these polymers should be less flexible than the less highly substituted polyacrylates studied so far, at least on the time scale of excited-state lifetimes, because conformational restriction by the rings should diminish the importance of competing energy loss pathways while simultaneously enhancing energy and electron transfer between appended groups.



(1)

1a R = 2-naphthyl poly(1a)
1b R = 3-phenanthryl poly(1b)



(2)

2 R = 1-naphthyl poly(2)

Experimental Section

General Procedures. All manipulations were carried out under air unless otherwise noted. Syntheses under an inert atmosphere follow standard Schlenk or drybox (N$_2$-filled, Vacuum Atmospheres) procedures. Commercial grade THF was dried with sodium benzophenone under N$_2$ and was freshly distilled prior to use. Other solvents were used as received. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ on a Bruker AC-250 spectrometer (250 MHz) (or a General Electric GN-500 (500 MHz) spectrometer when noted) and are

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reported in parts per million relative to an external Me_4Si standard (0 ppm). Melting points were corrected. Gel permeation chromatography (GPC) 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 in series, calibrated with polystyrene standards. Absorbance spectra were obtained on a Hewlett-Packard 8451A diode array spectrophotometer. Emission spectra were obtained on a SLM Aminco SPF-500C spectrofluorometer. Singlet-state lifetimes were determined by single-photon-counting[24] experiments carried out at the Center for Fast Kinetics Research at the University of Texas at Austin. High-resolution mass spectral analysis was carried out at the University of Texas at Austin Mass Spectral Facility using a Finnigan TSQ70 or a Fisons TS270 spectrometer.

Reagents obtained from Aldrich were used as received. Ethyl α-(bromomethyl)acrylate,[25] tetra-*n*-butylammonium bibenzoate,[26] potassium ethyl malonate,[27] and $SmI_2(THF)_2$[28,29] were prepared by literature methods.

2-Methylene-4-methyl-4-(2-naphthyl)butyrolactone (1a). 2-Acetylnaphthalene (2.56 g, 15.6 mmol) and Zn (1.20 g, 18.7 mmol) were combined in a 100 mL three-neck flask under an Ar atmosphere. Dry THF (40 mL) was added. Finally, ethyl α-(bromomethyl)acrylate (3.00 g, 15.6 mmol) was added slowly via syringe, and the resulting solution was heated to reflux for 2 h. The solution was then cooled to room temperature, poured into 50 mL of 3% aqueous HCl, and extracted with CH_2Cl_2 (3 × 30 mL). The organic fractions were combined and dried over $MgSO_4$ before the solvent was removed in vacuo. The oil was dissolved in Et_2O (50 mL) and was chilled to −10 °C overnight. White crystals of product were obtained (3.74 g, 73%). MP = 98−100 °C. ^{1}H NMR ($CDCl_3$): δ 7.85 (m, 3 H, Nap), 7.49 (m, 3 H, Nap), 7.41 (m, 1 H, Nap), 6.27 (t, 1 H, J = 2.8 Hz, olefin), 5.63 (t, 1 H, J = 2.8 Hz, olefin), 3.22 (t, 2 H, J = 2.8 Hz, CH_aH_b), 3.21 (m, 2 H, CH_aH_b), 1.80 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 169.4 (CO), 141.6 ($C{=}CH_2$); 134.9, 132.8, 132.5, 128.6, 128.2, 127.5, 126.5, 126.3, 122.7, 122.3 (C_{Nap}); 122.7 ($C{=}CH_2$), 84.0 (C_{quat}), 42.4 (CH_2), 29.8 (Me). HRMS (*m/z*): (M + H) calcd for $C_{16}H_{15}O_2$, 239.1062; found, 239.1072.

2-Methylene-4-methyl-4-(3-phenanthryl)butyrolactone (1b). 3-Acetylphenanthrene (1.71 g, 7.70 mmol) and Zn (510 mg, 7.70 mmol) were combined in a 100 mL Schlenk flask under an Ar atmosphere. Dry THF (30 mL) was added and ethyl α-(bromomethyl)acrylate (1.50 g, 7.70 mmol) was added slowly via syringe. The resulting solution was heated to reflux for 2 h. The solution was cooled to room temperature and poured into 100 mL of 3% aqueous HCl. The mixture was extracted with CH_2Cl_2 (3 × 40 mL). The organic fractions were combined and dried over $MgSO_4$. The solvent was removed in vacuo. The oil was dissolved in Et_2O (50 mL) and was chilled to −10 °C overnight. A white microcrystalline material was obtained (1.42 g, 67%). (This compound must be used immediately because it is easily polymerized under ambient conditions). ^{1}H NMR ($CDCl_3$): δ 8.71 (m, 2 H, Phen), 7.82 (m, 2 H, Phen), 7.67 (m, 4 H, Phen), 7.44 (dd, 1 H, J = 8.4, 1.7 Hz, Phen), 6.27 (t, 1 H, J = 2.8 Hz, olefin), 5.55 (t, 1 H, J = 2.8 Hz, olefin), 3.13 (m, 2 H, CH_2), 1.77 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 166.8 (CO), 140.5 ($C{=}CH_2$); 133.1, 130.4, 129.4, 128.4, 128.2, 127.4, 126.9, 125.9, 125.2, 125.1, 124.6, 121.2, 121.1, 116.3 (C_{Phen}); 121.2 ($C{=}CH_2$), 83.8 (C_{quat}), 43.2 (CH_2), 31.3 (Me). HRMS (*m/z*): (M + H) calcd for $C_{20}H_{17}O_2$, 289.1229; found, 289.1235.

Ethyl 1-Naphthylmethyl Malonate. Potassium ethyl malonate (15.0 g, 88.3 mmol) was suspended in DMF (100 mL). 1-(Chloromethyl)naphthalene (15.6 g, 88.3 mmol) was added and the mixture was stirred for 6 days. The mixture was poured into water (100 mL), and diethyl ether (100 mL) was added. The ether layer was separated and washed with water (3 × 50 mL) and dried over $MgSO_4$. The solvent was removed in vacuo. The resulting oil was purified by column chromatography (SiO_2, CH_2Cl_2 eluent) (23.8 g, 99%). ^{1}H NMR ($CDCl_3$): δ 8.01 (d, 1 H, J = 7.6 Hz, Nap), 7.87 (d, 1 H, J = 7.6 Hz, Nap), 7.84 (d, 1 H, J = 7.6 Hz, Nap), 7.56−7.40 (m, 4 H, Nap), 5.63 (s, 2 H, CH_2Ar), 4.13 (q, 2 H, J = 7.1 Hz, CH_2CH_3), 3.42 (s, 2 H, CH_2), 1.17 (t, 3 H, J = 7.1 Hz, Me). ^{13}C NMR ($CDCl_3$): δ 166.3 (CO), 166.2 (CO); 133.5, 131.4, 130.6, 129.3, 128.5, 127.5, 126.4, 125.8, 125.0, 123.3 (C_{Nap}); 65.3 (CH_2), 61.3 (CH_2), 41.4 (CH_2), 13.7 (Me). HRMS (*m/z*): calcd for $C_{16}H_{16}O_4$, 272.1049; found, 272.1039.

Diethyl 4-(Ethoxycarbonyl)-4-(1-naphthylmethoxycarbonyl)-2,6-dimethyleneheptanedioate (2). Ethyl 1-naphthylmethyl malonate (2.00 g, 7.33 mmol) was added dropwise to a suspension of NaH (60% in mineral oil; 877 mg, 21.7 mmol) in THF (70 mL). After bubbling ceased, ethyl α-(bromomethyl)acrylate (2.88 g, 14.6 mmol) was added. The mixture was stirred under an inert atmosphere for 12 h as a white precipitate formed. Water (50 mL) was added and the mixture was extracted with diethyl ether (3 × 50 mL). The ether layers were combined and dried over Na_2SO_4. The ether was evaporated under reduced pressure, and the product was obtained directly as a colorless oil before being further purified by chromatography (SiO_2, hexanes/ethyl acetate 9/1 eluent) (3.12 g, 86%). ^{1}H NMR ($CDCl_3$) δ: 7.97 (d, 1 H, J = 7.6 Hz, Nap), 7.84 (d, 1 H, J = 7.6 Hz, Nap) 7.81 (d, 1 H, J = 7.6 Hz, Nap), 7.51−7.38 (m, 4 H, Nap), 6.20 (d, 2 H, J = 1.2 Hz, olefin), 5.62 (d, 2 H, J = 1.2 Hz, olefin), 5.53 (s, 2 H, CH_2Nap), 4.12 (q, 4 H, J = 7.1 Hz, CH_2CH_3), 3.81 (q, 2 H, J = 7.1 Hz, CH_2CH_3), 2.95 (s, 4 H, CH_2), 1.24 (t, 6 H, J = 7.2 Hz, Me), 0.84 (t, 3 H, J = 7.2 Hz, Me). ^{13}C NMR ($CDCl_3$): δ 169.9, 169.8, 167.7, (CO); 135.8 ($C{=}CH_2$); 133.4, 131.4, 130.7, 129.0, 128.5, 127.3, 126.2, 125.7, 124.9, 123.4 (C_{Nap}); 128.3 ($C{=}CH_2$), 65.1 (CH_2Nap), 61.1 (CH_2CH_3), 60.6 (CH_2CH_3), 57.2 (C_{quat}), 34.6 (CH_2), 13.9 (Me), 13.1 (Me). HRMS (*m/z*): calcd for $C_{28}H_{32}O_8$, 496.2097; found, 496.2083.

4-Methyl-4-(2-Naphthyl)butyrolactone (3a). Ethyl acrylate (200 mg, 2.00 mmol), 2-acetylnaphthalene (340 mg, 2.00 mmol), and *tert*-butyl alcohol (140 mg, 2.00 mmol) were dissolved in 4 mL of dry degassed THF in a N_2-filled drybox, and the resulting solution was added to a solution of $SmI_2(THF)_2$ (2.19 g, 4.00 mmol) in THF (4 mL). The solution turned from blue to yellow as a precipitate formed. The mixture was stirred for 30 min, after which it was removed from the drybox and poured into 3% aqueous HCl (50 mL). The mixture was extracted with diethyl ether (3 × 50 mL). The ether fractions were combined and dried over Na_2SO_4. The volatile components were removed in vacuo. Addition of dry ether to the orange oil produced an off-white precipitate, which was recrystallized from THF/diethyl ether as white needles (402 mg, 89%). Mp = 73 °C. ^{1}H NMR ($CDCl_3$): δ 7.83 (m, 4 H, Nap), 7.49 (m, 3 H, Nap), 2.56 (m, 4 H, CH_2CH_2), 1.79 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 176.4 (CO); 141.3, 132.8, 132.4, 128.5, 128.0, 127.4, 126.4, 126.1, 122.5, 122.3 (C_{Nap}); 86.9 (C_{quat}), 35.8 (CH_2), 29.1 (Me), 28.8 (CH_2). HRMS (*m/z*): calcd for $C_{15}H_{14}O_2$, 227.1072; found, 239.1070.

4-Methyl-4-(3-phenanthryl)butyrolactone (3b). Ethyl acrylate (200 mg, 2.00 mmol), 2-acetylphenanthrene (440 mg, 2.00 mmol), and *tert*-butyl alcohol (140 mg, 2.00 mmol) were dissolved in 4 mL of dry degassed THF in a N_2-filled drybox, and the resulting solution was added to a solution of $SmI_2(THF)_2$ (2.19 g, 4.00 mmol) in THF (4 mL). The solution turned from blue to yellow as a precipitate formed. The mixture was stirred for 30 min, when it was removed from the drybox and poured into aqueous HCl (3%, 50 mL). The mixture was extracted with diethyl ether (3 × 50 mL). The ether fractions were combined and dried over Na_2SO_4. The volatile components were removed in vacuo. Addition of dry ether to the orange oil produced an off-white precipitate, which was crystallized from THF/diethyl ether (531 mg, 95%). Mp = 150−151 °C. ^{1}H NMR ($CDCl_3$): δ 8.72 (d, 1 H, J = 8.0 Hz, Phen), 8.71 (s, 1 H, Phen), 7.88 (d, 2 H, J = 8.1 Hz, Phen), 7.67 (m, 2 H, Phen), 7.63 (dt, 2 H, J = 1.6, 8.3 Hz, Phen), 7.52 (dd, 1 H, J = 1.8, 8.3 Hz, Phen), 2.57 (m, 4 H, CH_2CH_2), 1.83 (s, 3 H, Me). ^{13}C NMR ($CDCl_3$): δ 176.5 (CO); 142.3, 132.2, 131.8, 130.1, 130.0, 129.0, 128.6, 127.3, 126.8, 126.7, 126.2, 122.7, 122.7, 117.7 (C_{Phen}); 87.3 (C_{quat}), 36.2 (CH_2), 29.6 (Me), 28.9 (CH_2). HRMS (*m/z*): (M + H) calcd for $C_{19}H_{17}O_2$, 277.1229; found, 277.1233.

1,1-Bis(ethoxycarbonyl)cyclohexane. The compound was prepared by modification of the literature method.[30] NaH (2.40 g, 60 wt % in mineral oil, 60.0 mmol) was suspended in dry THF (120 mL). A solution of diethyl malonate (2.94 g, 18.4 mmol) and 1,5-dibromopentane (4.23 g, 18.4 mmol) in

THF (20 mL) was added dropwise under a N_2 atmosphere. When the addition was complete, the mixture was heated to reflux for 12 h. Water (100 mL) was added to the mixture, which was then extracted with diethyl ether (3 × 60 mL). The organic fraction was dried over Na_2SO_4 and the volatile components were removed in vacuo, yielding a pale yellow oil. The product was purified by column chromatography (SiO_2, hexanes/ethyl acetate 9/1 eluent) (1.60 g, 38%). ^1H NMR ($CDCl_3$): δ 4.11 (q, 4 H, $J = 7.1$ Hz, CH_2), 1.91 (m, 4 H, CH_2), 1.46 (m, 6 H, CH_2), 1.18 (t, 6 H, $J = 7.1$ Hz, Me). ^{13}C NMR ($CDCl_3$): δ 171.8 (CO), 60.9 (CH_2O), 54.8 (C_{quat}), 31.2 (CH_2), 25.1 (CH_2), 22.6 (CH_2), 13.9 (Me). HRMS (*m/z*): (M + H) calcd for $C_{12}H_{21}O_4$, 229.1440; found, 229.1444.

1-(1-Naphthylmethoxycarbonyl)-1-(ethoxycarbonyl)-cyclohexane (4). 1,1-Bis(ethoxycarbonyl)cyclohexane (945 mg, 4.14 mmol) was dissolved in absolute ethanol (4 mL). A solution of KOH (231 mg, 4.14 mmol) dissolved in ethanol (6 mL) was added dropwise. After stirring for 24 h, the ethanol was removed in vacuo and the resulting solid was washed with diethyl ether. The solid was then suspended in DMF (10 mL), and 1-(chloromethyl)naphthalene was added. The mixture was stirred for 96 h. The suspension was diluted with diethyl ether (100 mL) and extracted with water (50 mL) and brine (3 × 50 mL). The ether layer was dried over Na_2SO_4, and the volatile components removed in vacuo. The product was purified by column chromatography (SiO_2, hexanes/ethyl acetate 9/1 eluent) (916 mg, 65%). ^1H NMR ($CDCl_3$): δ 7.97 (d, 1 H, $J = 9.0$ Hz, Nap), 7.83 (d, 1 H, $J = 7.3$ Hz, Nap), 7.80 (d, 1 H, $J = 7.5$ Hz, Nap), 7.49 (m, 2 H, Nap), 7.41 (d, 1 H, $J = 8.2$ Hz, Nap), 7.38 (d, 1 H, $J = 7.1$ Hz, Nap), 5.59 (s, 2 H, CH_2), 3.93 (q, 2 H, $J = 7.0$ Hz, CH_2), 1.98 (m, 4 H, CH_2), 1.49 (m, 4 H, CH_2), 1.40 (m, 2 H, CH_2), 0.97 (t, 3 H, $J = 7.0$ Hz, Me). ^{13}C NMR ($CDCl_3$): δ 171.6, 171.5 (CO); 133.5, 131.4, 131.0, 129.1, 128.5, 127.3, 126.3, 125.7, 125.0, 123.4 (C_{Nap}); 65.1 (CH_2), 60.9 (CH_2), 54.9 (C_{quat}), 31.2 (CH_2), 25.0 (CH_2), 22.5 (CH_2), 13.6 (Me). HRMS (*m/z*): calcd for $C_{21}H_{24}O_4$, 340.1675; found, 340.1682.

Poly(1a). Method A. **1a** (0.500 g, 2.1 mmol) was dissolved in freshly distilled THF (10 mL), and benzoyl peroxide (51 mg, 0.21 mmol) was added. The solution was heated to reflux for 12 h under an Ar atmosphere. The solution was added dropwise into hexanes (100 mL), precipitating the polymer as a white solid (0.460 g, 92%). The polymer was characterized by GPC ($M_n = 1550$, $M_w/M_n = 1.22$). ^1H NMR ($CDCl_3$): δ 7.90 (br, 3 H, Nap), 7.50 (br, 4 H, Nap), 3.60–0.80 (br, 9 H, alkyl). ^{13}C NMR ($CDCl_3$): δ 179.2, 178.1 (CO); 143.6, 143.3, 140.7, 132.9, 132.6, 128.1, 127.5, 126.4, 122.3, 122.3 (C_{Nap}); 84.7, 47.5, 44.4, 36.5, 33.8, 30.1. Some resonances are not resolved due to broadened peaks.

Method B. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (28 mg, 0.2 mmol) and tetra-*n*-butylammonium bibenzoate (9.0 mg, 10 mol %) were dissolved in THF (1 mL) in a nitrogen-filled drybox. **1a** (720 mg, 3.0 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 white solid (680 mg, 92%). The polymer was characterized by GPC ($M_n = 1500$, $M_w/M_n = 1.29$). The spectral properties were identical to those of the polymer produced by method A.

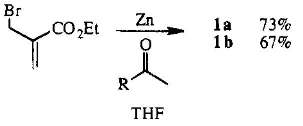
Poly(1b). This polymer was prepared in an identical manner to poly(**1a**), method A (85% yield). The polymer was characterized by GPC ($M_n = 13\,800$, $M_w/M_n = 2.80$). ^1H NMR ($CDCl_3$): δ 8.76 (br, 2 H, Phen), 7.55 (br, 7 H, Phen), 3.60–0.80 (br, 9 H, alkyl). ^{13}C NMR ($CDCl_3$): δ 178.6 (CO); 144.2, 143.3, 132.3, 131.6, 129.2, 129.1, 127.3, 123.3, 118.0 (C_{Phen}); 84.4, 48.2, 44.4, 32.8, 14.3. Some resonances are not resolved due to broadened peaks.

Poly(2). This polymer was prepared in an identical manner to poly(**1a**), method B (60% yield). The polymer was characterized by GPC ($M_n = 165\,000$, M_w/M_n, = 1.60). ^1H NMR ($CDCl_3$): δ 7.93 (br, 1 H, Nap), 7.78 (br, 2 H, Nap), 7.46 (br, 4 H, Nap); 5.62, 5.36 (br, 2 H, CH_2), 4.10 (br, 4 H, CH_2), 3.64 (br, 2 H, CH_2), 2.41 (br, 2 H, CH_2), 1.94 (br, 4 H, CH_2), 1.56 (br, 2 H, CH_2), 1.24 (br, 6 H, Me), 0.77 (br, 3 H, Me). ^{13}C NMR ($CDCl_3$; 125.7 MHz): δ 176.2, 174.6, 171.5, 133.5, 131.6, 131.2, 130.9, 129.7, 128.6, 128.4, 127.3, 126.4, 125.8, 125.1, 123.6, 65.3, 61.3, 60.8, 58.8, 57.5, 52.0, 43.2, 42.9, 34.7, 24.0, 19.7, 13.6, 13.4.

Photophysical Measurements. All solutions were bubble-degassed with solvent-saturated Ar before irradiation. Quantum yields for fluorescence were determined as described in the literature[31] using naphthalene ($\Phi_F = 0.23$)[31] and phenanthrene ($\Phi_F = 0.13$)[32] as reference compounds in cyclohexane. Naphthyl- and phenanthryl-substituted compounds were irradiated at 276 and 335 nm, respectively. Steady-state fluorescence quenching was examined in dilute CH_2Cl_2 solutions with optical densities ~ 0.05 at the excitation wavelength. Aliquots of deoxygenated quencher (CCl_4) were added sequentially. Fluorescence quenching was determined at the maximum intensity or by monitoring the integrated intensity of the peak. Single-photon-counting experiments were conducted in CH_2Cl_2, exciting naphthyl samples at 285 nm and phenanthryl samples at 340 nm.

Results

Monomer Synthesis. The syntheses of the lactone (**1**) and difunctional (**2**) monomers employ ethyl (α-bromomethyl)acrylate[25] as the basic building block. **1** is prepared in one step from ethyl (α-bromomethyl)-acrylate, zinc, and an aldehyde or ketone in good yield (eq 3)[33] as 2-naphthyl (**1a**) and 3-phenanthryl (**1b**) derivatives. The difunctional monomer **2** was synthesized in one pot by the dialkylation of ethyl (1-naphthylmethyl) malonate with ethyl (α-bromomethyl)acrylate (eq 4).



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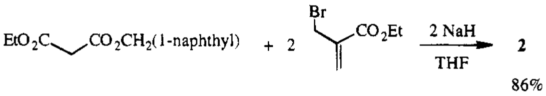

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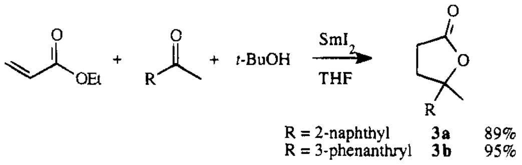
Synthesis of Model Compounds. Model compounds were prepared for photophysical comparison to the polymers. Model γ-butyrolactones were prepared using the SmI_2-induced reductive coupling of ethyl acrylate and a ketone (eq 5),[34] and the 2-naphthyl (**3a**) and 3-phenanthryl (**3b**) derivatives were obtained in high yield.



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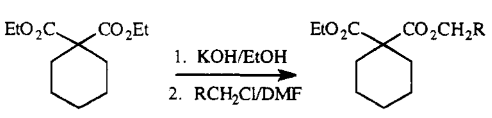
A model for the six-membered ring in poly(**2**) was prepared from 1,1-bis(ethoxycarbonyl)cyclohexane by saponification of one ester group, followed by alkylation with 1-(chloromethyl)naphthalene (eq 6).



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Polymerization. Polymers of **1a**, **1b**, and **2** have been prepared by group transfer or radical polymerization in THF. In each case, a soluble polymer was obtained in good yield. The results of the polymeriza-

Table 1. Molecular Weights and Polydispersities for Poly(1a), Poly(1b), and Poly(2)

monomer	polymerization method	M_n[a]	M_w/M_n[a]	yield (%)
1a	radical[b]	1550	1.22	92
1a	group transfer[c]	1500	1.20	92
1b	radical	13800	2.80	85
2	group transfer	165000	1.60	60

[a] Determined by GPC versus polystyrene standards. [b] $(PhCO_2)_2$ (10 mol %) was used as the initiator in THF (0.2 M in monomer). [c] 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (6.7 mol %) was used as the initiator and $[n\text{-}Bu_4N][PhCO_2]_2H$ (15 mol %) was used as the catalyst in THF (1.5 M in monomer).

Scheme 1. Proposed Mechanism of Cyclopolymerization of a Substituted Diethyl 2,6-Dimethyleneheptanedioate

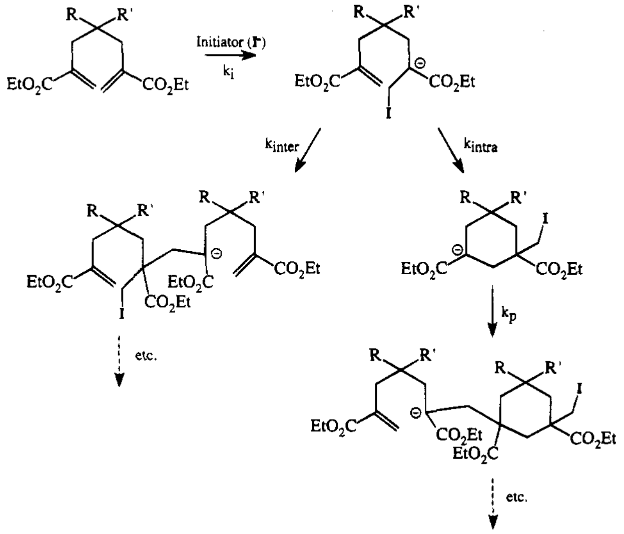

Table 2. Absorbance and Emission Data for Substituted Acrylates, Lactones, and Polymers[a]

compd	λ_{max} (nm)	ϵ ($M^{-1}\,cm^{-1}$)	λ_{em} (nm)[b]	Φ_F[c]	τ (ns)
1a	231	22000	336, 420	0.018	
	276	5200			
poly(**1a**)	231	24000	336	0.039	15
	276	4900			
3a	231	20000	336	0.041	12
	276	4900			
1b	258	39000	350, 368, 387, 409, 433	0.010	
	300	8300			
	334	590			
	350	460			
poly(**1b**)	256	43000	351, 369, 388, 409, 433	0.051	24
	300	9900			
	334	750			
	350	620			
3b	256	57000	350, 369, 387, 409, 433	0.051	18
	278	15000			
	298	12000			
	334	790			
	350	670			
2	232	8800	327, 337	0.14	
	274	5800			
	284	6800			
poly(**2**)	232	8600	327, 338	0.14	12, 3.4[d]
	274	5800			
	284	6800			
4	232	8700	327, 338	0.12	10
	274	5100			
	284	5900			

[a] All spectral data were obtained in CH_2Cl_2 solution. [b] Naphthyl derivatives were excited at 276 nm and phenanthryl derivatives were excited at 335 nm. [c] Quantum yields were obtained by comparison with naphthalene and phenanthrene standards in cyclohexane. [d] The preexponential factor for the 12 and 3.4 ns components were 0.76 and 0.24, respectively.

tions are summarized in Table 1. Polymers of **1a** prepared upon treatment with benzoyl peroxide in THF had a relatively narrow molecular weight distribution ($M_w/M_n = 1.22$), which may be attributed to low degree of polymerization ($M_n = 1550$). Poly(**1b**), prepared by this same method, had a higher molecular weight ($M_n = 13\,800$) versus polystyrene and a higher polydispersity ($M_w/M_n = 2.8$).

Previous workers have shown that polymers of α-methylene-γ-butyrolactones can be made by living, group transfer polymerization.[20,35] Poly(**1a**) synthesized by group transfer polymerization (GTP) with 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene as the initiator and tetra-*n*-butylammonium bibenzoate as the catalyst in THF produced a polymer whose characteristics were similar to those of the polymer prepared by the radical route (Table 1). **2** was successfully polymerized by GTP using the same catalyst and initiator. The molecular weight of the resulting poly(**2**) was substantially higher than expected and the molecular weight distribution was broad ($M_n = 168\,000$, $M_w/M_n = 1.60$).

The catalyst, solvent, and temperature, known to play important roles in cyclopolymerizations,[36] have not been optimized for this system. Unlike linear polymerizations in which the rate of initiation (k_i) and the rate of propagation (k_p) are important factors in determining molecular weight distributions, the rate of initiation (k_i), the rate of intermolecular propagation (k_{inter}), and the rate of intramolecular propagation (cyclization; k_{intra}) must be matched to give narrow-dispersity polymers (Scheme 1). It is most desirable to have $k_{intra} \gg k_{inter}$ in order to prevent formation of interchain links that lead to high molecular weight polymers with broad molecular weight distributions. In poly(**2**), a significant level of undesirable chain linking has occurred, leading to noncyclized defects and to high molecular weight. The ^{13}C NMR spectrum of poly(**2**) exhibits multiple resonances at 57.5 and 52.0 ppm for the quaternary carbon α to the two ester functionalities, most likely corresponding to noncyclized (57.2 ppm in **2**) and cyclized (54.9 ppm in **4**) portions of the polymer chains. Even so, the amount of excimer formation is diminished in poly(**2**) relative to the amount observed in ordinary substituted polyacrylates (see below).[10,37]

Photophysical Characterization. Photophysical data for the substituted acrylates, lactones, and polymers are summarized in Table 2. The absorption spectra of the monomers, polymers, and model compounds are essentially identical within each series. An important factor in determining whether these polymers are good candidates for promoting unidirectional electron transfer is the fraction of excimer emission in the steady-state fluorescence spectra of these compounds. The fluorescence spectra obtained here are nearly identical to those of the independent chromophores.[38] Figure 1 shows the emission spectra of **1a**, poly(**1a**), and the model compound **3a**. The emission at low energy observed for the monomer **1a** (Figure 1a) is lacking in **3a** (Figure 1c), indicating the operation of an excited-state interaction between the 2-naphthyl and acrylate moieties. This possibility is substantiated by the lower quantum yield (quenching) of fluorescence for **1a** ($\Phi_F = 0.018$) than for poly(**1a**) or **3a** ($\Phi_F = 0.039$ and 0.041, respectively). The lower energy emission band persists upon further dilution, indicating that this is an intramolecular interaction. The striking similarity be-

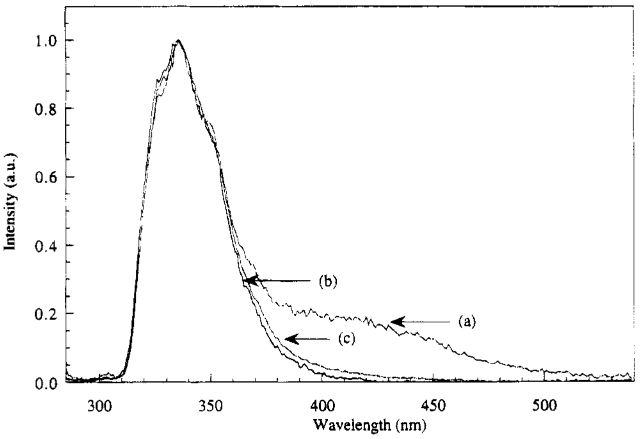

Figure 1. Steady-state emission spectra of (a) **1a** (2×10^{-5} M), (b) poly(**1a**) (2×10^{-5} M), and (c) **3a** (2×10^{-5} M) obtained in degassed CH_2Cl_2 (excitation at 276 nm; maxima are normalized).

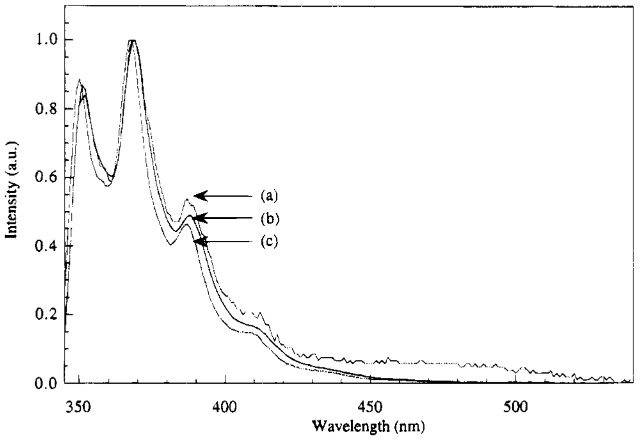

Figure 2. Steady-state emission spectra of (a) **1b** (1×10^{-4} M), (b) poly(**1b**) (8×10^{-5} M), and (c) **3b** (8×10^{-5} M) obtained in degassed CH_2Cl_2 (excitation at 335 nm; maxima are normalized).

tween the steady-state fluorescence spectra of poly(**1a**) (Figure 1b) and **3a** (Figure 1c) demonstrates the absence of excimer emission in CH_2Cl_2, even though the absorbance spectra of **1a**, poly(**1a**), and **3a** are nearly identical.

Similar behavior is observed in the steady-state emission spectra of the 3-phenanthryl series (Figure 2). As with **1a**, the fluorescence spectrum of **1b** (Figure 2a) and its decreased quantum yield of fluorescence indicate an excited-state interaction between the chromophore and the acrylate unit. Stern–Volmer quenching experiments between methyl methacrylate and the singlet excited state of **3b** demonstrate that significant quenching does not occur. Therefore, the constrained orientation of the two functional groups in the cyclic monomer is contributing strongly to the observed effect. The fluorescence spectra and quantum yields of fluorescence for poly(**1b**) (Figure 2b) and **3b** (Figure 2c) are identical, demonstrating the absence of excimer or other modes of quenching in this system as well. Thus, the rigid ring structure of the poly(α-methylene-γ-butyrolactone)s successfully prevents excimer formation by forming a configurationally restricted structure that must be rigid on the time scale of the emission (i.e., the lifetime of the singlet excited state).

The steady-state emission spectra of the difunctional monomer **2**, the cyclopolymer poly(**2**), and the model cyclohexane (**4**) are shown in Figure 3. The monomer

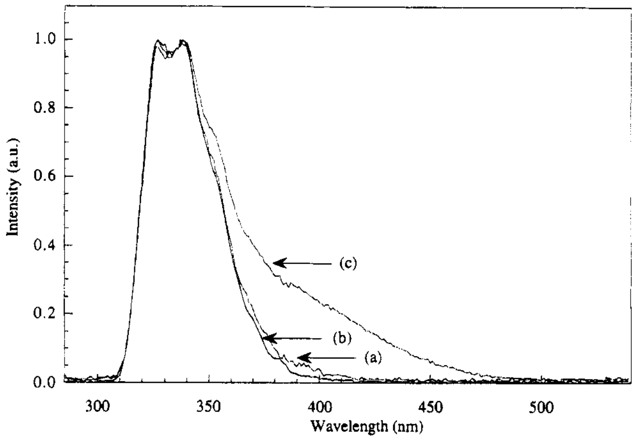

Figure 3. Steady-state emission spectra of (a) **2** (2×10^{-5} M), (b) **4** (8×10^{-6} M), and (c) poly(**2**) (1×10^{-5} M) obtained in degassed CH_2Cl_2 (excitation at 276 nm; maxima are normalized).

emission (Figure 3a) does not exhibit lower energy components, as was found above in the cyclic lactone monomers, and is identical to the fluorescence spectrum of **4** (Figure 3b), consistent with the flexible nature of **2** relative to monomers **1a** and **1b**. The emission spectrum of poly(**2**) (Figure 3c) shows the presence of a moderate amount of excimer (~30%). Since the polymer structure contains a large amount of chain linking caused by inefficient cyclization, the observation of excimer emission in this polymer is not discouraging. It is likely that the excimer-forming sites exist in the "floppy" sections of the polymer chain where linear polymerization has occurred instead of at the more rigid sites where cyclopolymerization gave six-membered rings.

In order to determine the efficiency of energy migration in poly(**1a**), poly(**1b**), and poly(**2**), the singlet energy migration constants (Λ_s) and the average diffusion lengths of the excitation energy (L_s) were measured by establishing the relative quenching efficiency of a contact quencher (CCl_4) for both the conformationally constrained polymer species and for the model compounds.[6,7,14] Bimolecular rate constants for quenching of the singlet states (k_q) were determined from the Stern–Volmer equation (eq 7), where I_0 is the intensity of the fluorescence in the absence of quencher, I is the intensity of the fluorescence in the presence of a known amount of quencher, τ_0 is the lifetime of the excited state in the absence of quencher, and [Q] is the concentration of quencher.

$$I_0/I = 1 + k_q\tau_0[Q] \qquad (7)$$

The quenching rate constant k_q having been determined for the polymer and the model compound, the singlet energy migration constant Λ_s/D was calculated from eq 8.[7,14] [$D = (D_q + D_e)/^2$, where D_q is the diffusion constant of the quencher (1.5×10^{-5} cm^2 s^{-1} for CCl_4)[39] and D_e is the diffusion constant of the excited-state species, and $D = D_q$ when $D_e = 0$.] As a starting point

$$\Lambda_s/D = \frac{k_q^{\text{polymer}} - 0.5k_q^{\text{model}}}{0.5k_q^{\text{model}}} \qquad (8)$$

for this model, it is assumed that $\Lambda_s = 0$ for the model compound and $D_e = 0$ for the polymer (diffusion of polymer segments during the lifetime of the excited state can be ignored).[7] The excitation diffusion length

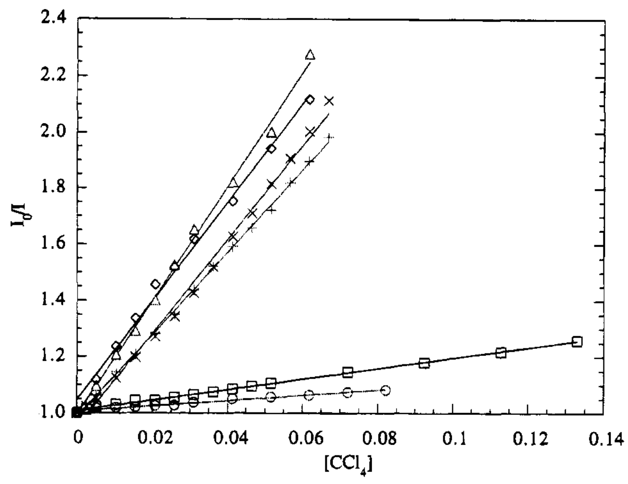

Figure 4. Stern–Volmer quenching of poly(**1a**) (×), **3a** (+), poly(**1b**) (□), **3b** (○), poly(**2**) (◇), and **4** (△) by CCl_4 in CH_2Cl_2.

Table 3. Stern–Volmer Quenching Constants and Singlet Energy Migration Parameters for Polyacrylates and Model Lactones

compd	K_{SV} (M^{-1})[a]	k_q ($\times 10^8$ M^{-1} s^{-1})[a]	Λ_s/D[b]	L_s (Å)[c]
poly(**1a**)	16.7	11.1	1.3	77
3a	11.3	9.7	0	0
poly(**1b**)	1.87	0.77	0.8	76
3b	1.58	0.87	0	0
poly(**2**)	20.4	16.3	0.92	59
4	17.6	16.9	0	0

[a] Determined from the slope of Stern–Volmer quenching plots in degassed CH_2Cl_2 solutions. [b] Calculated from eq 8. [c] Calculated from eq 9 ($D = 1.5 \times 10^{-5}$ cm^2 s^{-1}, ref 39).

(L_s) can then be calculated from eq 9, which is based on a one-dimensional random walk of the excited state along the polymer backbone.[7]

$$L_s = (2\Lambda_s\tau_0)^{1/2} \tag{9}$$

Stern–Volmer quenching constants (K_{SV}) were determined by monitoring fluorescence quenching in degassed CH_2Cl_2 solutions of poly(**1a**), poly(**1b**), poly(**2**), **3a**, **3b**, and **4** upon addition of known amounts of degassed CCl_4, with the relevant quenching plots shown in Figure 4. In each case, quenching was linear with quencher concentration. Notably, the polymers examined here do not show the negative deviation from linearity previously observed in other polymer systems.[6,14] K_{SV} was determined from the slope of the lines in Figure 4. The results of the quenching studies are summarized in Table 3. The fact that L_s is approximately the same for each of the polymers (within experimental error) suggests that the energy migration efficiency in each of the polymers is quite similar, as expected from the similarities in polymer structure in the series. The relatively small values of Λ_s/D limit the generality of conclusions that can be drawn; but, since Λ_s/D is positive for all of the polymers, we can conclude unambiguously that singlet energy migration is occurring with the exclusion of excimer formation.[14]

Conclusions

The structure and relative rigidity of the polymer chain are important design criteria for the preparation of polymers that favor energy migration over excimer emission. Substituted poly(α-methylene-γ-butyrolactones) and poly(diethyl 2,6-dimethyleneheptanedioates) are excellent candidates for directional electron and energy transport studies. The inclusion of rings perpendicular to the polymer chain and aligned with the polymer chain introduces enough structural rigidity to avoid excimer formation in the excited state while maintaining singlet energy migration along the polymer chain. A small amount of excimer emission observed in the case of the cyclopolymer derives from linear defects introduced during the polymerization, emphasizing the utility of rings for controlling the photophysical properties of these polymers. Energy loss pathways are diminished and energy transfer is enhanced by eliminating excimer formation, making these polymer structures interesting for future photoinduced electron transfer studies. Work continues in our laboratory toward the syntheses of the monomers containing quenchers to be incorporated into isostructural block copolymers containing a gradient of chromophores and redox quenchers.[1–3,5] Such copolymers will allow us to test less ambiguously the ideas described herein for achieving optimal unidirectional electron transfer along the polymer chain.[1–3,5]

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