

Intramolecular Complex Formation and Triplet Energy Transfer in Polynorbornenes Incorporating Benzophenone

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Abstract: The photophysical properties of homopolymers (**2**) and block copolymers (**3**) prepared by ring-opening metathesis polymerization of norbornenes substituted with benzophenone, naphthalene, and phenanthrene groups (**1**) have been investigated. When benzophenone is attached to this polynorbornene backbone, its excited state behavior differs from that observed for monomeric benzophenone. A new intramolecular excited state complex can be observed in the transient absorption and emission measurements of the benzophenone-substituted homopolymer. In copolymers bearing benzophenone and naphthalene or phenanthrene substituent blocks, triplet energy transfer from the sensitizer (benzophenone) to the arene is observed. This energy transfer dominates over the intramolecular complexation that characterizes group interactions in the homopolymer.

Introduction

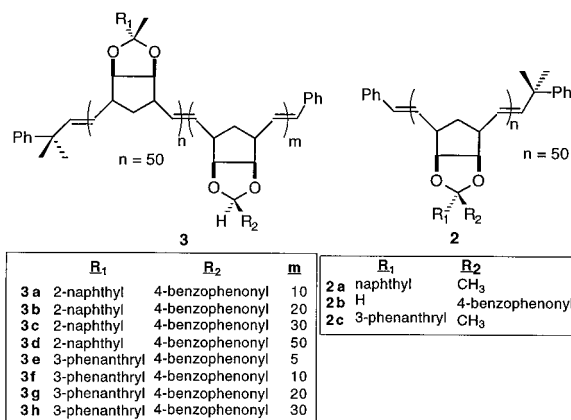
We are interested in preparing block copolymers (**3**) that permit photoinduced vectorial electron and energy transfer between attached donors and acceptors.^{1–3} Photoinduced energy transfer (sensitization) occurs when the excited state singlet or triplet energy of a donor lies above that of an acceptor such that the excited molecule can transfer its singlet or triplet energy to the acceptor to generate its excited state and regenerate the ground state of the donor.⁴ Photoinduced electron transfer occurs when the excited molecule transfers an electron from its HOMO to the LUMO of the acceptor to generate the radical cation of the donor and the radical anion of the acceptor, or, conversely, a donor in its ground state can transfer an electron from its HOMO to the excited state of the acceptor to generate the radical cation/anion pair.^{4,5}

Vectorial electron and energy transfer may be envisioned between blocks of chromophores attached to a polymer by arranging the chromophores such that transfer is only energetically favored in one direction. Such directional electron and energy transfer between appended blocks could lead, in principle, to long-lived charge separation and efficient light harvesting, which in turn can render these materials useful as photoconductive or other optical devices. Furthermore, the block copolymers described here are interesting because of the unique photophysical interactions such as intramolecular energy transfer and exciplex formation that arise as a consequence of attachment of chromophores to a conformationally rigid macromolecule.

We are interested in probing interactions on the triplet manifold since the attachment of a triplet sensitizer to a somewhat rigid backbone would allow phosphorescent species to persist over unusually long periods. Benzophenone has long been used as an effective triplet sensitizer because of its high intersystem crossing yield and long lifetime; it was therefore chosen as the sensitizer for our studies.⁴ With a triplet sensitizer,

triplet energy transfer between different species will likely occur according to the Dexter (exchange) mechanism over distances of 10–15 Å.⁴ Triplet energy can also migrate isoenergetically along the polymer by hopping through repeat units until an appropriate acceptor is reached to allow the energy transfer to take place intramolecularly.

Block copolymers (**3**) that contain benzophenone and an aryl triplet energy acceptor have been synthesized by ring-opening metathesis polymerization (ROMP) in order to study triplet energy migration to and across the interblock interface and have been compared to the corresponding homopolymers (**2**) (Scheme 1). Phosphorescence was typically observed at low temperatures in **2**, but time-resolved transient absorption and emission measurements reveal an unexpected interaction between the benzophenone ketyl radical and the benzophenone triplet in the benzophenone-substituted homopolymer **2b**. This interaction is suppressed in copolymers containing an arene block as in **3a–h** that can act as a triplet quencher. The synthesis and photophysical characterization of these interesting polymers are therefore discussed.



Experimental Section

Kinetic Methods. Absorption spectra were obtained on a Hewlett-Packard 8451A diode array spectrometer. Fluorescence and phosphorescence measurements were made on a SLM Aminco SPF 500 fluorometer. A phosphoroscope attachment equipped with light baffles and a variable speed chopper (0–10 000 rpm) was used to differentiate

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short and long lifetime species. Quantum yields were determined according to standard procedures.⁶ Transient absorption spectra were obtained with a Q-switched, frequency-tripled ($\lambda = 355$ nm, 8 mJ/pulse) Quantel YG481 Nd:YAG laser and a pulsed high-intensity Xe arc lamp in a 1 cm cell containing a solution with OD = 0.2–0.4 AU. The decay measurements reported were averages of 20 laser pulses, and transient spectra were obtained as the average of three laser pulses at 10 nm intervals.

Transient emission lifetimes were obtained at 77 K with a Q-switched, frequency-tripled ($\lambda = 355$ nm, 8 mJ/pulse) Quantel YG481 Nd:YAG laser. Transient emission spectra were obtained using a Continuum Surelite Q-switched Nd:YAG laser (6 ns pulsewidth, 10–20 mJ/pulse). Decay measurements and spectra were obtained as the average of 50 laser pulses at 10 nm intervals.

Structural Analysis of Polymers. Gel permeation chromatography (GPC) measurements were made in CH_2Cl_2 at an elution rate of 1 mL/min using a Waters 6000A solvent delivery system through 7.8×300 mm Styrogel columns (10^4 Å, 10^3 Å, 500 Å) with a Rainin Dynamax UV detector and a Waters 410 differential refractometer. Thermal gravimetric analysis (TGA) measurements were done on a Rheometrics Thermal Analyzer using ceramic pans. The temperature was increased from 25 to 600 °C at a rate of 10 °C/min under nitrogen.

Materials. Polymerizations were performed under N_2 in a Vacuum Atmospheres HE-493 drybox. Air- or moisture-sensitive reactions were performed under N_2 that had been passed through columns of Linde 4 Å molecular sieves, drierite, and oxygen-scavenging Ridox (Fisher). 4-Methylbenzophenone, 2-acetylnaphthalene (Aldrich), and 3-acetylphenanthrene (Lancaster) were used without further purification. Benzaldehyde was distilled from CaH_2 and was degassed through five freeze–pump–thaw cycles. 2,6-Diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (Strem) was stored in the drybox. 4-(Dimethylamino)pyridine (DMAP) was recrystallized twice with ether. Tetrahydrofuran (THF) was doubly distilled from Na/benzophenone ketyl radical, and toluene was distilled from Na. Before being taken into the glovebox, the dried solvents were degassed through five freeze–pump–thaw cycles. 2-Methyltetrahydrofuran (MTHF) used in the photophysical measurements was distilled from Na or LiAlH_4 . Thiophene-free benzene was used without further purification.

4-Benzoylbenzaldehyde was prepared from 4-methylbenzophenone using Thiel oxidation conditions.⁷ 2-Naphthyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene ketal (**1a**), 3-phenanthryl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene ketal (**1c**), and their corresponding homopolymers (**2a** and **2c**, respectively) were prepared as previously described.⁸ 4-Benzophenonyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene acetal (**1b**) was prepared similarly from *exo,cis*-2,3-bicyclo[2.2.1]hepta-2,5-ene diol.

4-Benzophenonyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene acetal (1b). *exo,cis*-2,3-Bicyclo[2.2.1]hepta-2,5-ene diol⁹ (0.3 g, 2.4 mmol) and 4-benzoylbenzaldehyde (0.5 g, 2.4 mmol) were taken up in CH_2Cl_2 (2.9 mL) and chlorotrimethylsilane (1.0 mL, 7.9 mmol) was added under N_2 . The solution was stirred in the dark for 24 h and was neutralized with 5% NaHCO_3 before the solvent was removed. The residue was taken up with water, and the aqueous solution was extracted several times with ether. The organic fractions were combined, washed with brine, and dried over anhydrous MgSO_4 . The solvent was removed *in vacuo*, and the product was recrystallized from ethyl acetate/hexanes to yield 0.28 g (37%) of **1b** as white needles, mp 85–87 °C; ^1H NMR (CDCl_3) δ 7.81 (m, 4 H), 7.63 (m, 2 H), 7.57 (m, 1 H), 7.48 (m, 2 H), 6.15 (d, 2 H, $J = 1.7$ Hz), 5.99 (s, 1 H), 4.32 (s, 2 H), 2.97 (br s, 2 H), 2.17 (d, 1 H, $J = 9.1$ Hz), 1.80 (d, 1 H, $J = 9.1$ Hz); ^{13}C NMR (CDCl_3) δ 196.3, 140.7, 138.5, 137.4, 137.0, 132.5, 130.1, 130.0, 128.7, 126.6, 106.4, 81.5, 45.1, 43.2; UV λ_{max} (MTHF): 248 nm ($\epsilon = 18\,000\ \text{M}^{-1}\ \text{cm}^{-1}$), 344 nm ($\epsilon = 170\ \text{M}^{-1}\ \text{cm}^{-1}$), 560 nm ($\epsilon = 30\ \text{M}^{-1}\ \text{cm}^{-1}$); HRMS (*m/e*): calc. for $\text{C}_{21}\text{H}_{18}\text{O}_3$, 319.1334; found, 319.1318.

General Procedure for the Preparation of Homopolymers (2). The polymerizations were accomplished according to reported methods,^{10,11} with minor modifications.

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Poly(4-benzophenonyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene acetal) (2b). To a vigorously stirred solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (3.5 mg, 6.4 μmol) in 1 mL of THF (or toluene) was added DMAP (8.8 mg, 72 μmol) followed by **1b** (0.11 g, 36 mmol) in 1 mL of solvent. After 15 min, the polymerization was quenched with 0.2 mL of benzaldehyde and precipitated onto MeOH. The polymer **2b** was filtered, washed with MeOH, and dried under vacuum (0.092 g, 80%). ^1H NMR (CDCl_3) δ 7.77 (m, 3 H), 7.68 (m, 1 H), 7.50 (m, 3 H), 7.42 (m, 2 H), 5.90 (s, 1 H), 5.83 (s, 1 H), 5.58 (br s, 2 H, 87% *trans* olefinic), 5.39 (br s, 2 H, 13% *cis* olefinic), 4.39 (br s, 2 H), 2.76 (br s, 2 H), 2.10 (m, 1 H), 1.49 (m, 1 H); ^{13}C NMR (CDCl_3) δ 196.2, 141.1, 138.6, 137.4, 132.5, 131.5, 131.4, 130.1, 128.3, 126.8, 126.7, 106.5, 106.4, 86.8, 86.7, 47.6, 38.7; UV λ_{max} (MTHF): 248 nm ($\epsilon = 203\,000\ \text{M}^{-1}\ \text{cm}^{-1}$), 344 nm ($\epsilon = 6600\ \text{M}^{-1}\ \text{cm}^{-1}$); $M_w = 25\,000$, $M_n = 19\,000$, PDI = 1.33; M_n (calc. on the basis of molar ratio of catalyst to monomer) = 15 000; TGA: 10% weight loss at 315 °C.

Preparation of Block Copolymers (3). **Poly(2-naphthyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene ketal)-block-poly(4-benzophenonyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene acetal) (3a).** A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (4.4 mg, 8.0 μmol) and **1a** (130 mg, 0.47 mmol) were allowed to react in toluene as in the general procedure for homopolymers **2**. DMAP (29 mg, 0.09 mmol) in toluene (1.0 mL), was added and the resulting solution was stirred for 15 min. Monomer **1b** (11 mg, 0.09 mmol) was then added, and the solution was stirred for an additional 30 min. The polymerization was quenched with benzaldehyde (0.20 mL), and the mixture was stirred for 20 min. The polymer was precipitated onto MeOH producing 0.13 g (92%) of white solid. ^1H NMR (CDCl_3) δ 7.95–7.80 (m, 3 H), 7.77 (m, 4 H), 7.56 (m, 5 H), 7.45 (m, 2 H), 5.91 (s, 1 H), 5.59 (s, 2 H, *trans* olefinic), 5.52 (s, 2 H, 75% *trans* olefinic), 5.28 (br s, 2 H, 25% *cis* olefinic), 4.40 (s, 2 H), 4.07 (s, 2 H), 2.83 (br s, 2 H), 2.74 (br s, 2 H), 2.11 (br s, 1 H), 2.03 (br s, 1 H), 1.73 (s, 3 H), 1.38 (m, 2 H); ^{13}C NMR (CDCl_3) δ 141.1, 140.1, 138.6, 137.4, 133.0, 132.6, 132.4, 131.4, 130.1, 130.0, 128.3, 128.2, 128.1, 127.6, 126.8, 126.1, 126.0, 124.0, 123.9, 123.8, 123.7, 113.0, 112.8, 112.6, 106.4, 86.9, 86.7, 85.7, 47.9, 47.8, 47.6, 47.5, 43.8, 39.1, 38.8, 29.7, 28.9, 28.8, 28.7; $M_w = 43\,000$, $M_n = 32\,000$, PDI = 1.3; M_n (calc.) = 16 000; TGA: 10% weight loss at 312 °C.

Polymers **3b–d** were prepared as in **3a**, where the only difference was the number of equivalents of **1b** added. The NMR appeared the same as **3b**, except that the integration for the block of benzophenonyl units was increased.

Polymer 3b. A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μmol) and **1a** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. DMAP (13 mg, 0.11 mmol) in toluene (1.0 mL) was added, and the resulting solution was stirred for 15 min. Monomer **1b** (56 mg, 0.18 mmol) was then added, and the solution was stirred for an additional 30 min. The polymer was precipitated onto MeOH producing 0.15 g (87%) of white solid. $M_w = 31\,000$, $M_n = 24\,000$, PDI = 1.3; M_n (calc.) = 20 000.

Polymer 3c. A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μmol) and **1a** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. DMAP (13 mg, 0.11 mmol) in toluene (1.0 mL) was added, and the resulting solution was stirred for 15 min. Monomer **1b** (84 mg, 0.26 mmol) was then added, and the solution was stirred for an additional 30 min. The polymer was precipitated onto MeOH producing 0.18 g (87%) of white solid. $M_w = 33\,000$, $M_n = 27\,000$, PDI = 1.2; M_n (calc.) = 24 000.

Polymer 3d. A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μmol) and **1a** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. DMAP (13 mg, 0.11 mmol) in toluene (1.0 mL) was added, and the resulting solution was stirred for 15 min. Monomer **1b** (140 mg, 0.42 mmol) was then added, and the solution was stirred for an additional 30 min. The polymer was precipitated onto MeOH producing 0.21 g (83%) of white solid. $M_w = 51\,000$, $M_n = 35\,000$, PDI = 1.3; M_n (calc.) = 29 000.

Poly(3-phenanthryl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene ketal)-block-poly(4-benzophenonyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene ac-

etal) (3f). A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μ mol) and **1c** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. DMAP (13 mg, 0.11 mmol) in toluene (1.0 mL) was added, and the resulting solution was stirred for 15 min. Monomer **1b** (34 mg, 0.11 mmol) was then added, and the solution was stirred for an additional 30 min. The polymerization was quenched with benzaldehyde (0.20 mL), and the mixture was stirred for 20 min. The polymer was precipitated onto MeOH producing 0.20 g (96%) of white solid, poly-(3-phenanthryl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene ketal)-*block*-poly-(4-benzophenonyl-*exo,cis*-2,3-bicyclo[2.2.1]hepta-5-ene acetal) (**3f**). ^1H NMR (CDCl_3) δ 8.73 (m, 2 H), 7.78 (br s, 5 H), 7.62 (m, 7 H), 7.59–7.45 (m, 4 H), 5.91 (s, 1 H), 5.60 (s, 2 H), 5.53 (s, 2 H, 86% *trans* olefinic), 5.25 (br s, 2 H, 14% *cis* olefinic), 4.40 (br s, 2 H), 4.10 (br s, 2 H), 2.76 (br s, 4 H), 2.11 (m, 1 H), 2.03 (br s, 2 H), 1.78 (s, 3 H), 1.40–1.31 (m, 2 H); ^{13}C NMR (CDCl_3) δ 142.0, 141.9, 141.1, 138.6, 137.4, 132.6, 132.4, 132.1, 131.6, 131.4, 130.7, 130.1, 130.0, 128.7, 128.5, 128.3, 128.0, 127.1, 126.8, 126.6, 126.5, 126.1, 126.0, 124.2, 124.1, 122.9, 119.2, 119.1, 113.2, 112.8, 106.4, 87.0, 86.7, 85.8, 47.9, 47.5, 43.8, 39.1, 38.8, 29.2, 29.1, 28.9; $M_w = 19\,000$, $M_n = 16\,000$, PDI = 1.2; $M_n(\text{calc.}) = 20\,000$; TGA: 10% weight loss at 321 $^\circ\text{C}$.

Polymers **3e** and **3g–h** were prepared as in **3f**, where the only difference was the number of equivalents of **1b** added. The NMR appeared the same as **3f**, except that the integration for the block of benzophenonyl units was increased.

Polymer 3e. A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μ mol) and **1c** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. Monomer **1b** (7.4 mg, 23 μ mol) was then added, and the solution was stirred for an additional 30 min. The polymer was precipitated onto MeOH producing 55 mg (65%) of white solid. $M_w = 18\,000$, $M_n = 15\,000$, PDI = 1.2; $M_n(\text{calc.}) = 18\,000$.

Polymer 3g. A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μ mol) and **1c** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. Monomer **1b** (30 mg, 93 μ mol) was then added, and the solution was stirred for an additional 30 min. The polymer was precipitated onto MeOH producing 89 mg (84%) of white solid. $M_w = 21\,000$, $M_n = 18\,000$, PDI = 1.2; $M_n(\text{calc.}) = 23\,000$.

Polymer 3h. A solution of 2,6-diisopropylphenylimidoneophylidene-molybdenum bis(*tert*-butoxide) (5.9 mg, 11 μ mol) and **1c** (180 mg, 0.53 mmol) were allowed to react in toluene as in the preparation of **3a**. Monomer **1b** (45 mg, 0.14 mmol) was then added, and the solution was stirred for an additional 30 min. The polymer was precipitated onto MeOH producing 0.10 g (84%) of white solid. $M_w = 21\,000$, $M_n = 18\,000$, PDI = 1.2; $M_n(\text{calc.}) = 26\,000$.

Laser-Induced Degradation of 2b in Solution. A sample of **2b** in benzene was irradiated with a laser power of 12.5 mJ/pulse at 3 pulses/min and aliquots removed at 5, 10, 15, and 30 min intervals were analyzed by GPC (Table 5), UV-vis, and IR.

Laser-Induced Degradation of 2b in the Solid State. A film of **2b** was prepared from a 10% solution of **2b** in THF by slow evaporation of the solvent. The film was then irradiated with a laser power of 12.5 mJ/pulse at 600 pulses/min. After 2 min of pulsing, the white film became brown in the area of the path of the laser beam. This area became increasingly dark, and after 10 min of pulsing, a hole was formed in the film.

Results

Synthesis. The polymerization of chromophore-appended norbornene acetals and ketals (**1**) has been described earlier, and the regiochemistry of **1** was assigned on the basis of NOE difference experiments.⁸ It was determined from these studies that when an acetal linkage is generated as in **1b**, the arene is *anti* to the *endo* hydrogens of the norbornene, whereas when a ketal linkage is generated as in **1a** and **1c**, the configuration is *syn*.⁸ The same general procedures were employed here: the catalyst used induces ring-opening metathesis polymerization of strained olefins to form a predominantly *trans*-polyolefin

Table 1. GPC Results of the Polymerization of **1b** with and without Added DMAP^a

conditions	M_n	M_w	$M_n(\text{calc.})$	PDI	yield (%)
no DMAP	67 000	200 000	18 000	3.0	58
0.1 eq DMAP	20 000	39 000	12 000	2.0	87
2.5 eq DMAP	19 000	25 000	15 000	1.3	65
10.0 eq DMAP	14 000	16 000	15 000	1.1	80

^a DMAP in 1.0 mL of THF (or toluene) was added to a stirring solution of catalyst in 1.0 mL of solvent. After stirring for 5 min with the base, **1b** in 1.0 mL of solvent was added and stirred for 15 min.

(Scheme 1).^{12,13} The chain end remains reactive until a quencher such as benzaldehyde or pivaldehyde is added, permitting formation of multiblock macromolecules. The catalyst reacts, however, with carbonyl compounds according to the normal sequence of reactivity of carbonyl compounds toward nucleophiles (aldehydes > ketones \gg esters).

The attempted polymerization of **1b** in the absence of base (typical ROMP conditions¹⁴) resulted in materials with broad polydispersities and molecular weights much higher than expected.¹⁵ Presumably, the ketone group in **1b** reacts slowly with the reactive chain-end to quench the polymerization and cross-link propagating chains. Addition of 4-(dimethylamino)pyridine (DMAP) to the reaction mixture alleviated this problem by acting as an external base that was reversibly bound to the catalyst, thus suppressing nucleophilic reaction with the carbonyl groups in the monomer while permitting the free activation of the olefinic group (Table 1).¹⁶ In practice, this simple modification produces a higher yield of narrowly dispersed polymer.

Photophysical Behavior. The benzophenone-containing monomer (**1b**) and homopolymer (**2b**) displayed strong phosphorescence upon steady-state excitation at 355 nm as glasses at low temperature in MTHF (λ_{max} 450 nm, Figure 1), and, as expected, no emission was observed at room temperature in the steady-state.⁴ In accordance with earlier studies of benzophenone, no evidence for excimer emission could be detected in the spectrum of **2b** under steady-state conditions (excitation at 266 nm and 355 nm, emission monitored 400 to 600 nm).⁴ The phosphorescence quantum yields (relative to benzophenone) and lifetimes for **1b** and **2b** were determined (Table 2). The shorter triplet lifetime observed in the polymer **2b** than in the monomer **1b** is ascribed to (1) nonradiative quenching or (2) decay processes induced by interchromophore interactions enhanced by close proximity of groups positioned along the polymer chain. Furthermore, the triplet in polymer **2b** decays biexponentially, which suggests that the decay is affected by the configuration and conformational preferences of the polymer backbone. However, the relative contributions of the two components does not correspond directly to the distribution of *cis* and *trans* olefinic linkages in the polymer (Table 2).

Time-resolved emission spectra of **1b** and **2b** were measured at room temperature in benzene/acetonitrile (Figures 2 and 3)

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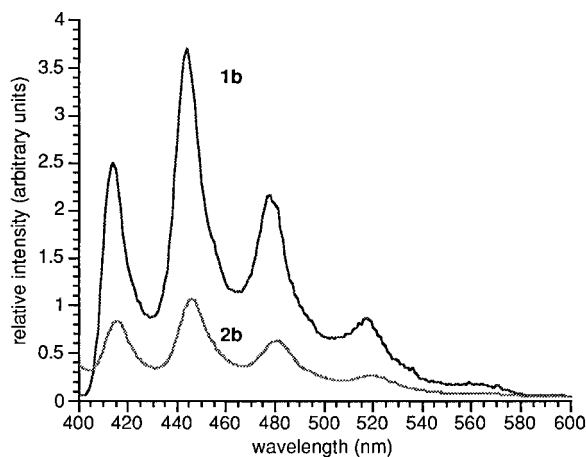


Figure 1. Steady-state emission spectra of **1b** (10^{-5} M) and **2b** (10^{-5} M) in degassed MTHF glasses at 77 K. Excitation occurred at 355 nm. The emission maxima at 415, 450, 480, and 520 nm are assigned to benzophenone phosphorescence.

Table 2. Phosphorescence Quantum Yields, Φ_p , and Lifetimes, τ_p , of Monomers and Polymers Containing Benzophenone

	quantum yield, Φ_p	contribution (%)	lifetime, τ_p (ms)	<i>trans</i> olefins in backbone (%)
1b	0.90 ± 0.01	100	4.8 ± 0.1	N/A
2b	0.35 ± 0.01	23 77	3.9 ± 0.1 0.6 ± 0.1	87

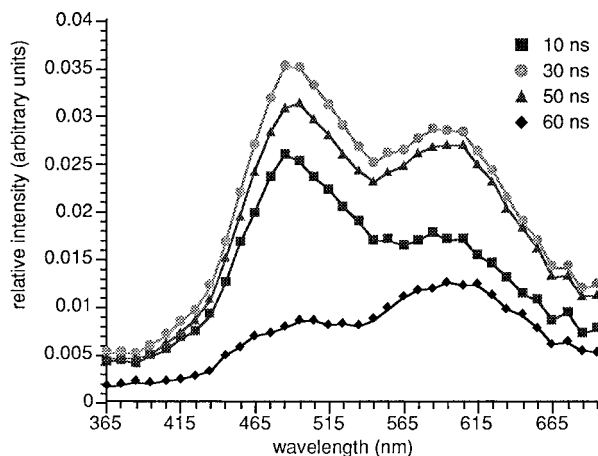


Figure 2. Time-resolved emission spectrum of **1b** (10^{-5} M) in 3:1 degassed benzene/acetonitrile at room temperature. Excitation occurred at 355 nm with a laser power of 12.5 mJ/pulse. The broad emission maximum at 485 nm is assigned to an exciplex between the benzophenone triplet and the ketyl radical. The emission maximum at 585 nm is assigned to ketyl radical emission.

and that of **2b** also in THF (Figure 4), however, detailed kinetics could not be obtained due to the resolution of our instrument. The polymer showed a maximum at 485 nm in both solvents, but in THF a second maxima was found at 585 nm. Both of these bands in the time-resolved spectra are red-shifted from the maximum observed in the low temperature phosphorescence spectrum (Figure 1, λ_{\max} 450 nm) and must derive from a different emissive transient. The spectrum of **2b** in THF (Figure 4) is nearly identical to that of the monomer in benzene/acetonitrile (Figure 2) which is expected since it has been well established that the triplet of benzophenone can abstract a hydrogen very efficiently from THF.¹⁷ In previous studies of benzophenone in Freon-113 and Freon-11 (1,1,2-trichloro-1,2,2-

Table 3. Singlet and Triplet Energies (E_S , E_T) of Benzophenone, Naphthalene, and Phenanthrene³⁷ and Doublet Energy (E_D) of the Ketyl Radical²²

	E_S (eV)	E_T (eV)	E_D (eV)
benzophenone	3.23	3.00	
naphthalene	3.99	2.64	
phenanthrene	3.59	2.69	
ketyl radical			2.27

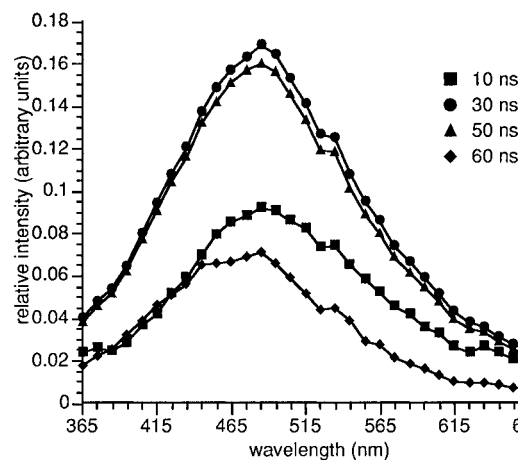


Figure 3. Time-resolved emission spectrum of **2b** (10^{-5} M) in 3:1 degassed benzene/acetonitrile at room temperature. Excitation occurred at 355 nm with a laser power of 12.5 mJ/pulse. The broad emission maximum at 485 nm is assigned to an exciplex between the benzophenone triplet and the ketyl radical.

trifluoroethane and chlorotrifluoromethane, respectively), the peak at 585 nm was attributed to ketyl radical emission,¹⁸ and studies in MTHF, benzene, and isooctane revealed ketyl radical emission at 577 nm.¹⁹

In all of the room temperature emission spectra, the intensities of the peaks increase over a period of 10 ns before decaying back to the ground state. Naqvi and Wild observed a similar growth in the decay profile in benzene and isooctane and assigned it to the triplet depletion of benzophenone due to ketyl radical sensitization.¹⁹ This suggests that the initially excited benzophenone triplet sensitizes the ketyl radical which then subsequently decays. The energies of the benzophenone triplet and ketyl radical are given in Table 3. In THF, the polymer displays only a broad emission maximum at 485 nm and upon increasing the laser power, this broad, structureless peak in **2b** shifted blue (to a maximum at 450 nm) which corresponds to the phosphorescence maximum of benzophenone, λ_{\max} 450 nm (Figure 5). An analogous blue-shift to the phosphorescence maxima at 450 nm was detected for monomer **1b** when the laser power was similarly varied. At higher laser powers, sufficiently high concentrations of the benzophenone triplet moieties are generated so that the sensitization to the ketyl radical is not observed. Alternatively, perhaps the ketyl radical is destroyed as it is formed since it absorbs at 355 nm.

The originally colorless samples of **1b** and **2b** became yellow after a few sequences of pulsed irradiation. This yellow color persisted for more than 10 min, but disappeared upon exposure to O₂. The ground-state absorption spectrum of the yellow irradiated solutions displayed a small hyperchromic shift, and the $n-\pi^*$ band became very broad. The absorption spectrum for the ketyl radical is similar to that of the ground state of benzophenone and could be the cause of the hyperchromic shift.

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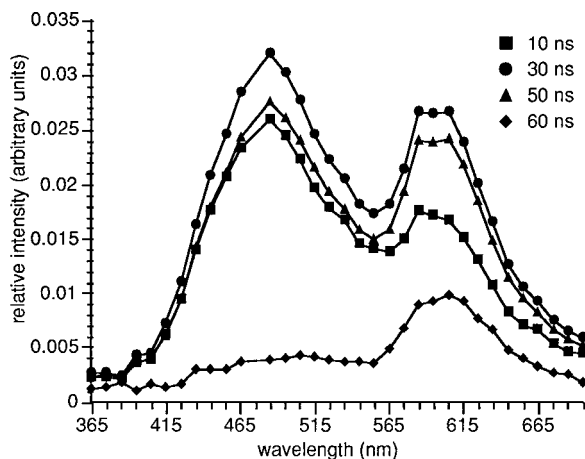


Figure 4. Time-resolved emission spectra of **2b** (10^{-5} M) in degassed THF at room temperature. Excitation occurred at 355 nm with a laser power of 12.5 mJ/pulse. Spectral assignments are the same as in Figure 2.

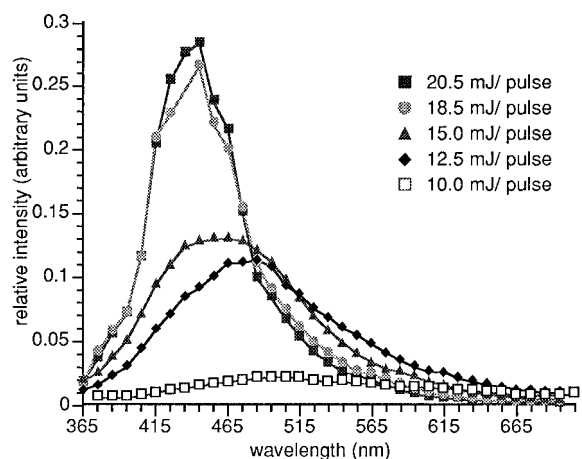


Figure 5. Time-resolved emission spectra of **2b** (10^{-5} M) at 30 ns after the laser pulse in 3:1 degassed benzene/acetonitrile. Excitation occurred at 355 nm at room temperature with variant laser power. Spectral assignments are the same as in Figures 1 and 3.

There is also a small band at 560 nm,²⁰ so it is likely that the yellow color observed is due to ketyl radical absorption.¹⁹

After laser irradiation at 355 nm, **1b** and **2b** exhibited steady-state emission at room temperature with λ_{max} at 480 nm for the polymer (which was similar to the time-resolved spectra) and at 450 nm for the monomer (Figure 6).²¹ The emission from the monomer is benzophenone phosphorescence, but we believe that the observed emission from the polymer derives from another species because it is red-shifted from the phosphorescence observed at low temperatures. Furthermore, excitation spectra monitored at 480 nm reveal two bands that differ from the ground-state absorbance spectrum of **2b**. Both **1b** and **2b** exhibit maxima at 400 nm. Monomer **1b** also has a second band at 290 nm which overlaps with the ground state absorbance for benzophenone. In **2b**, a second band at 320 nm may be the source for the observed steady-state emission. In **2b**, it is suggested that an excited-state complex is generated that is stable toward nonradiative decay at room temperature such that it can be measured in the steady-state.

Transient absorption measurements for **2b** in MTHF or THF at room temperature induced by excitation at 355 nm gave no evidence for the benzophenone triplet because H-abstraction

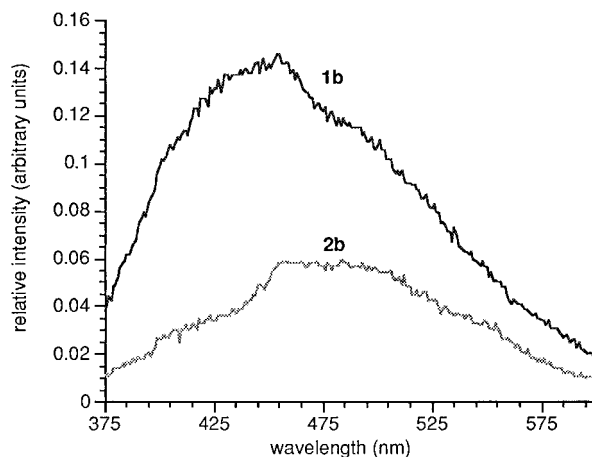


Figure 6. Steady-state emission spectra of **1b** (10^{-5} M) and **2b** (10^{-5} M) in 3:1 degassed benzene/acetonitrile at room temperature after irradiation on the laser. Excitation occurred at 355 nm. Spectral assignments are the same as in Figures 1 and 3.

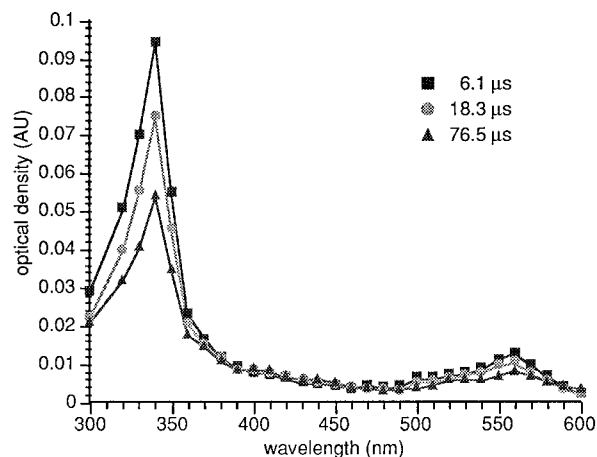


Figure 7. Transient absorption spectrum of **2b** (10^{-5} M) in degassed MTHF at room temperature. Excitation occurred at 355 nm with a laser power of 8 mJ/pulse. The maxima at 340 and 560 nm are assigned to ketyl radical absorption.

from the solvent took place very quickly and very efficiently.²² Instead, the benzophenone ketyl radical (with maxima at 340 and 560 nm) was observed (Figure 7),²⁰ even at the first transient spectra generated after flash excitation. Samples of **2b** in benzene also showed the ketyl radical absorption, along with an additional new peak at 400 nm whose intensity did not depend on ground-state concentration nor on laser pulse power (Figure 8). Under the same conditions, a dilute solution of benzophenone alone displays a triplet-triplet absorption (with maxima at 330 and 550 nm).²³ These bands have been assigned to the triplet by diluting the sample with benzhydrol and observing the consequent ketyl radical at 340 and 560 nm.²⁴ The peak at 400 nm observed in **2b** is in equilibrium with the ketyl radical and grows in as the ketyl radical decays (an isosbestic point is observed at 380 nm). This behavior is unique to **2b**. Under identical conditions, flash excitation of **1b** in degassed benzene shows the formation of ketyl radical (maximum at 330 nm) with a shoulder (maximum at 380 nm) that decays with the same time-profile as the other maxima (Figure 9). When observed in previous studies of benzophenone in water and in water/ethanol mixtures, this shoulder at 380 nm

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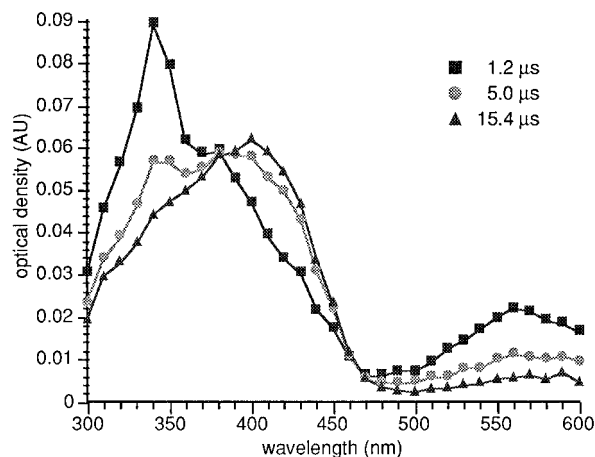


Figure 8. Transient absorption spectrum of **2b** (10^{-5} M) in degassed benzene at room temperature. Excitation occurred at 355 nm with a laser power 8 mJ/pulse. The absorption maxima at 340 and 560 nm are from the ketyl radical absorption and that at 400 nm is assigned to absorption of the excited-state complex between the benzophenone triplet and the ketyl radical.

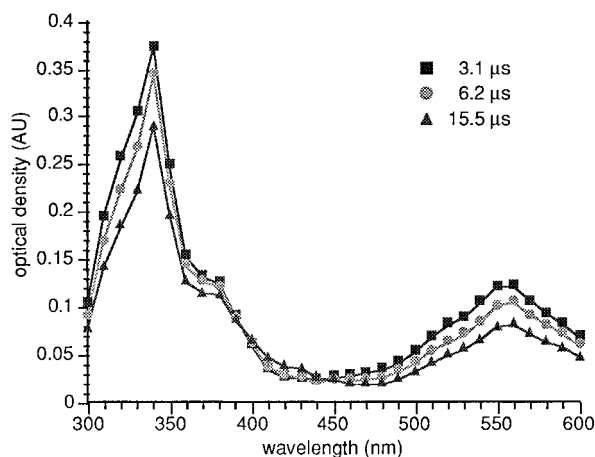


Figure 9. Transient absorption spectrum of **1b** (10^{-5} M) in degassed benzene at room temperature. Excitation occurred at 355 nm with a laser power of 8 mJ/pulse. The absorption maxima at 340 and 560 nm derive from the ketyl radical absorption, and that at 380 nm is from the absorption of the hydroxyl radical adduct of benzophenone.

has been attributed to the hydroxyl radical adduct of benzophenone.²⁵ We are confident that this shoulder is derived from a species different from that which is responsible for the peak at 400 nm because a rise time observed in the polymer **2b** is absent in either the monomer **1b** or benzophenone itself. The observed lifetimes for these transient absorptions are listed in Table 4.

To identify the new absorption at 400 nm, several possible decomposition products of benzophenone were investigated: benzhydrol, benzpinacol, triphenylacetophenone, 9-fluorenone, and 9-hydroxyfluorene.⁴ However, none produced an observable transient at 400 nm. A dilution study revealed that the peak at 400 nm decreased linearly with initial chromophore concentration, whereas the transient assigned to the ketyl radical did not. This led us to believe that the new absorption at 400 nm probably derives from an intramolecular excited state or a charge transfer complex in the polymer and that the ketyl radical is produced as a result of intra- or intermolecular H-abstraction from the backbone.

Because of the marginal solubility of the polymer in both polar and nonpolar solvents, the transient measurements can

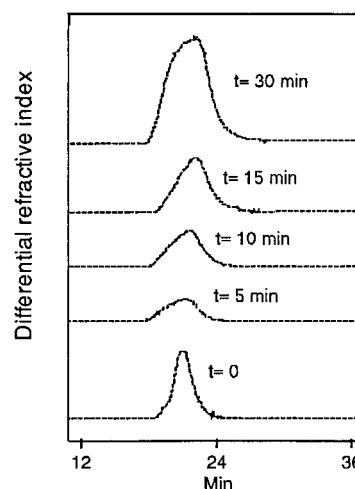


Figure 10. Gel permeation chromatography traces of samples of **2b** that were irradiated in benzene with a laser power of 12.5 mJ/pulse at 3 pulses/min. Aliquots were removed at 5, 10, 15, and 30 min intervals.

Table 4. Transient Absorption Lifetimes of **1b** and **2b** in Degassed Benzene Produced by Laser Pulse Excitation at 355 nm with a Laser Power of 8 mJ/pulse

	wavelength (nm)	contribution (%)	lifetime (μ s)
1b	340	45	19.6 ± 0.8
		55	98.3 ± 0.5
	380	100	21.4 ± 0.5
2b	560	53	15.8 ± 0.4
		47	93.5 ± 0.4
	400 (rise)	75	1.2 ± 0.1
2b	400 (rise)	28	9.5 ± 0.1
		25	1.3 ± 0.1
	560	75	8.7 ± 0.2
2b		25	1.1 ± 0.1
		25	7.9 ± 0.1

Table 5. Molecular Weight Changes Induced by Laser Pulsed Irradiation of **2b** (10^{-5} M) in Degassed Benzene at 355 nm^a

irradiation time (min)	M_n	M_w	M_w/M_n
0	14 000	16 000	1.1
5	14 000	22 000	1.6
10	11 000	15 000	1.4
15	10 000	14 000	1.4
30	11 000	19 000	1.7

^a The laser power was 12.5 mJ/pulse with 3 pulses/min.

be conducted in only a few solvents; this in turn makes it difficult to establish the polarity dependence of the peak at 400 nm. Although the polymer is not soluble in CH_3CN , a sample of **2b** in benzene diluted by one-third with CH_3CN did not affect the presence, structure, or lifetime of the new peak. This information also suggests intramolecular complex formation in **2b**.

The stability of polymer **2b** differs from polymers substituted with the other chromophores that do not participate in intermolecular hydrogen abstraction in the triplet state (**2a** or **2c**). Upon continued laser excitation, **2b** degrades. As observed from Figure 10 and Table 5, the molecular weight of a solution-phase sample of **2b** decreases and the polydispersity increases upon continued pulse excitation. After 5 min of irradiation, the clear solution became cloudy as a white precipitate formed. The absorption spectrum shows an initial hyperchromic shift after 5 min of irradiation, followed by a decrease back to the initial intensity, but with a substantial decrease in intensity of the $n-\pi^*$ band. The reasonable inference that the benzophenone carbonyl group is altered is confirmed by a substantial decrease of intensity of the IR carbonyl stretch at 1650 cm^{-1} , as would be

(25) Ledger, M. B.; Porter, G. *J. Chem. Soc., Faraday Trans. 1* **1972**, 68, 539.

expected if the benzophenone ketyl radical is converted to benzhydryl upon irradiation in benzene. In contrast, a sample of **2c** does not degrade at all under the same conditions.

A thin film of **2b** degrades as well upon laser pulsed irradiation, with that portion of the film in the pathlength of the beam being observed to ablate within 10 min. This decomposition behavior is interesting for the possible use of these materials as a negative photoresist.^{26,27} Benzophenone has been used in several photoresist systems for light-induced cross-linking and as a sensitizer.^{28–30}

Donor–Acceptor Interactions and Triplet Energy Transfer in Copolymers 3 Containing Benzophenone and an Arene Chromophore. Copolymers containing a block of **1a** or **1c** attached to a block of **1b** (**3a–d** and **3e–h**, respectively) were synthesized to determine if intramolecular energy transfer across the block interface could be observed. The triplet energies of benzophenone, naphthalene, and phenanthrene are given in Table 3. Polymers **2a** and **2c** had been prepared previously, and intramolecular energy migration was reported in the singlet excited state,³¹ but photophysical interactions on the triplet manifold have not been described before. Geometry optimization of *cis* and *trans*, isotactic and syndiotactic pentamers was obtained with an MM2 forcefield calculation. Adjacent chromophores were found to be separated by 8–12 Å in the isotactic pentamers and by 8–10 Å in the syndiotactic pentamers (some chromophores were as close as 3 Å in the syndiotactic pentamers, suggesting that most of the observed excimer derives from these linkages). Because triplet energy transfer by the Dexter mechanism can take place over separations of only less than 10–15 Å, transfer between a triplet benzophenone group and an aryl acceptor will most likely occur at the interface between adjacent chromophore blocks. Upon excitation of a randomly positioned benzophenone, triplet energy can migrate through the block until an acceptor is encountered. Energy transfer can then take place, and the energy of the sensitized arene can subsequently migrate through the second block.

To characterize triplet migration and triplet energy transfer, phosphorescence was monitored in the steady-state at 77 K in MTHF glasses. The emission spectra for homopolymers **2a** and **2c** at 77 K are compared with the emission of block copolymers **3a** and **3f** in Figures 11 and 12, respectively. The emission spectrum of **2a** (Figure 11) is a combination of the naphthalene group's fluorescence (λ_{max} at 350 nm), delayed fluorescence (λ_{max} at 400 nm), and phosphorescence (λ_{max} at 510 nm).³² The observed phosphorescence in the homopolymer is weak upon excitation at 300 nm. For comparison, phosphorescence of the copolymer **3a** is shown in the same figure. Both samples were prepared with a ground-state absorbance of 0.10 AU at the excitation wavelength of 300 nm. In the copolymer **3a**, the phosphorescence from the benzophenone block overlaps with that of the naphthalene and naphthalene delayed fluorescence, but an increase in the naphthalene phosphorescence is evident in the area of 460–600 nm (see inset, Figure 11). The phosphorescence quantum yields for **2a** and **3a–d** are shown in Table 6, and those of **3a–d** were corrected to remove emission caused by direct excitation of the benzophenone block,

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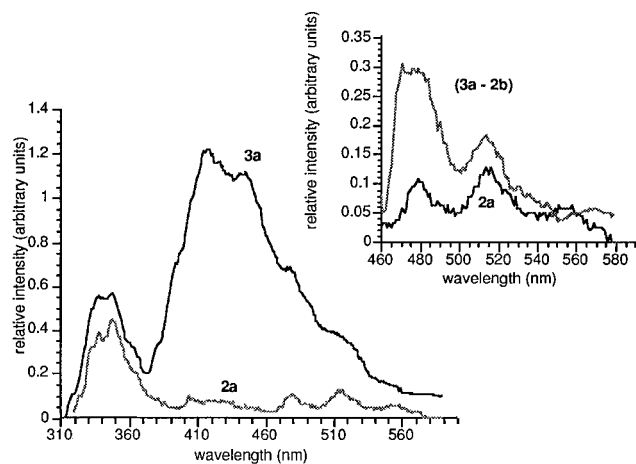


Figure 11. Steady-state emission spectra of **2a** (10^{-5} M) and **3a** (10^{-5} M) in degassed MTHF glasses at 77 K. Excitation occurred at 300 nm. Inset: Difference spectrum of the steady-state emission of **3a** after subtracting the steady-state emission spectrum of **2b** to correct for emission due to direct excitation of the benzophenone block. The emission maxima at 340 and 350 nm are assigned to naphthalene fluorescence, the maximum at 410 nm is assigned to naphthalene delayed fluorescence, and the maxima at 420, 450, and 480 nm are assigned to benzophenone phosphorescence.

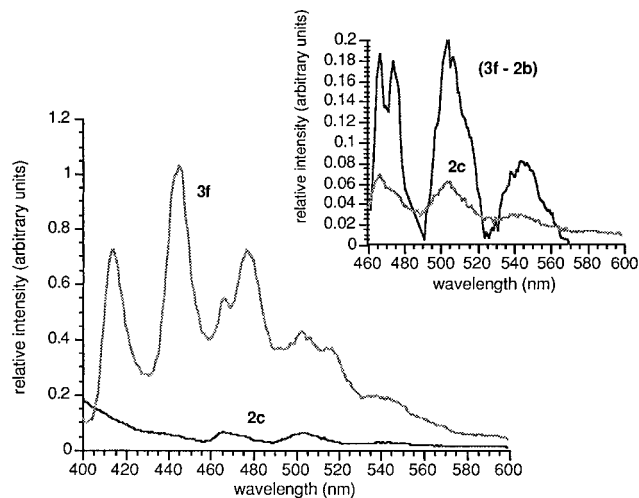


Figure 12. Steady-state emission spectra of **3f** (10^{-5} M), and **2c** (10^{-5} M) in degassed MTHF glasses at 77 K. Excitation occurred at 355 nm. Inset: Difference spectrum of the steady-state emission of **3f** after subtracting the steady-state emission spectrum of **2b** to correct for emission due to direct excitation of the benzophenone block. The maxima at 465, 505, and 540 nm are due to phenanthrene phosphorescence, and the maxima at 420, 450, 480, and 520 nm are due to benzophenone phosphorescence.

Table 2. Comparing the quantum yield for **2a** to the corrected value for **3a–d**, sensitization results in a 4-fold increase in the intensity of the naphthalene phosphorescence (see inset, Figure 11). In copolymers **3a–d**, triplet–triplet energy transfer occurs from benzophenone to naphthalene, most likely intramolecularly at the block interface. An increase in the naphthalene delayed fluorescence may also be present, however, since it overlaps strongly with the benzophenone phosphorescence, a quantitative increase could not be determined.

The steady-state phosphorescence spectra for **2c** and **3f** are shown in Figure 12. The homopolymer phosphorescence is also very weak upon excitation at 355 nm. Maxima at 465, 500, and 540 nm are due to phenanthrene phosphorescence in Figure 12. Excitation at this wavelength minimizes absorption of phenanthrene in the copolymer **3f**: thus, the homopolymer **2c** phosphorescence is shown for comparison. As in the naphtha-

Table 6. Phosphorescence Quantum Yields, Φ_P , Backbone Configuration and Transient Absorption Lifetimes for **2a**, **2c**, and **3a–h**

	quantum yield, Φ_P (± 0.001)	<i>trans</i> olefins in backbone (%)	contribution (%)	lifetime, τ_{T-T} (μ s)
2a	0.026	75	100	N/A ^b
2c	0.006	88	30	2.8 ± 0.1
			70	10.0 ± 0.1
3a	0.410	75	100	19.0 ± 0.3
	[0.100] ^a			
3b	0.461	72	100	17.4 ± 0.4
	[0.112] ^a			(rise) ^c
3c	0.468	79	100	20.5 ± 0.1
	[0.114] ^a			(rise 0.5 ± 0.1)
3d	0.440	78	100	25.4 ± 0.5
	[0.107] ^a			(rise 1.4 ± 0.1)
3e	0.188	79	45	1.0 ± 0.1
	[0.020] ^a		55	5.8 ± 0.1
3f	0.150	86	42	1.6 ± 0.1
	[0.016] ^a		58	8.7 ± 0.1
3g	0.344	86	38	1.9 ± 0.1
	[0.037] ^a		62	8.7 ± 0.1
3h	0.355	87	40	1.7 ± 0.1
	[0.038] ^a		60	7.5 ± 0.1

^a Quantum yield corrected for emission from benzophenone block.

^b Does not absorb at 355 nm. ^c A rise was visible in the decay trace; however, excessive noise precluded us from obtaining an accurate fit.

lene case described above, the benzophenone phosphorescence overlaps with that of phenanthrene, but qualitatively the efficiency of the expected sensitization is clear. Quantum yields were determined for **2c** and **3e–h**, Table 6. To make a direct comparison between the homopolymer and the copolymer, the observed emission was corrected for the phosphorescence of **2b** to reveal a three-fold increase in the efficiency of the phenanthrene phosphorescence in the copolymers **3e–f** and a 6-fold increase in **3g–h** (see inset, Figure 12).

To determine the effective quenching radius in the homopolymers and to provide insight as to whether energy migration was taking place intra- or intermolecularly, the Perrin model of active-sphere quenching was used.^{33,34} Since all of the phosphorescence measurements were obtained from frozen glasses, this model is appropriate because it has been shown previously to apply effectively to quenching in the solid state and to describe intramolecular energy migration in poly(acrylophenone).³⁵ This model assumes that diffusion is negligible and that bimolecular quenching is due to static interactions that occur within a defined radius around the excited molecule. The emissions of **2a–c** at 77 K were quenched with CCl₄ to determine the radius of the quenching-sphere according to eq 1^{33,34}

$$\ln(I_0/I) = VN[Q] \quad (1)$$

where I_0 is the emission without any quencher (Q), I is the emission at a concentration of CCl₄, V is the volume of the active sphere of quenching, and N is Avogadro's number. The volume is directly converted to an effective quenching radius, R ,

$$R = (3V/4\pi)^{1/3} \quad (2)$$

according to eq 2. The volume and radii of active sphere quenching for homopolymers **2a–c** are shown in Table 7. Polymers **2a–c** were found to have very similar quenching radii.

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Table 7. Determination of the Volume and the Radius of Active Sphere Quenching for Homopolymers **2**

	vol. of active sphere of quenching, V (10^{-25} m ³)	radius of quenching, R (\AA)
2a	4.6	48
2b	4.3	47
2c	1.8	35

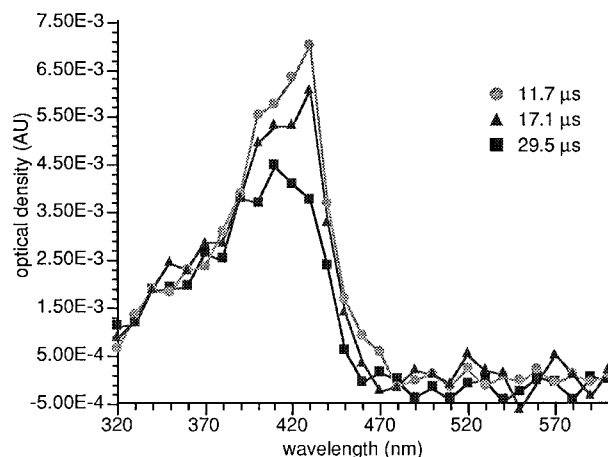


Figure 13. Transient absorption spectrum of **3a** (10^{-5} M) in degassed benzene at room temperature. Excitation occurred at 355 nm with a laser power of 12.5 mJ/pulse. The absorption maxima at 390, 410, and 430 nm are triplet–triplet absorptions of naphthalene.

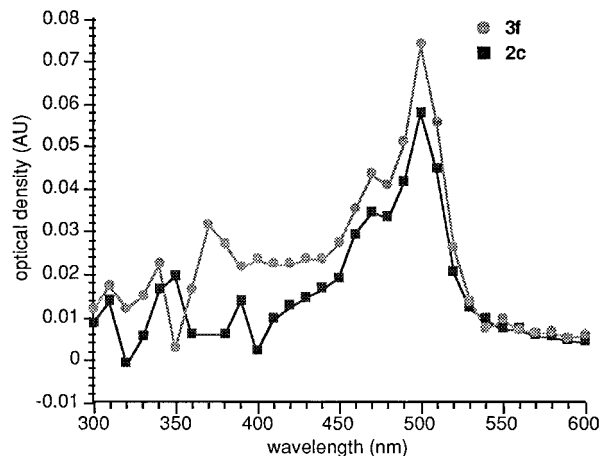
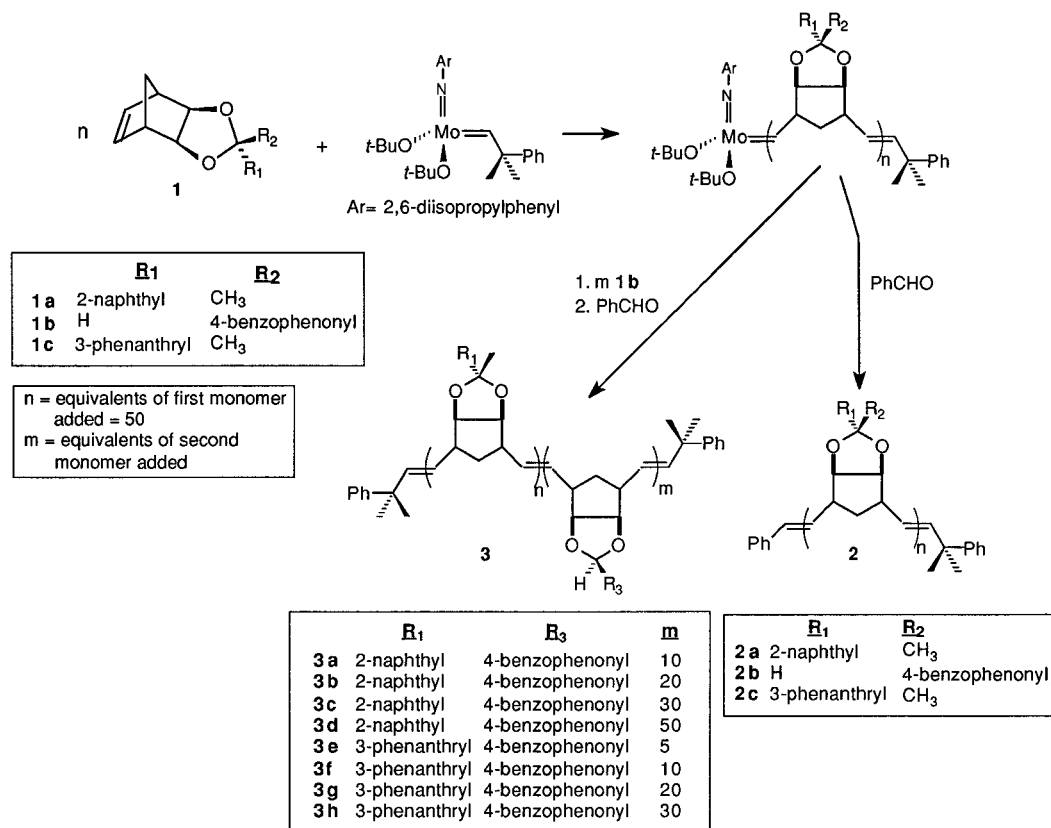


Figure 14. Transient absorption spectrum of **3f** (10^{-5} M) and **2c** (10^{-5} M) in degassed benzene at room temperature. Excitation occurred at 355 nm with a laser power of 12.5 mJ/pulse. The absorption maxima at 470 and 500 nm are triplet–triplet absorptions of phenanthrene.

From our calculations, we would expect an R of 8–12 \AA if no energy migration were occurring and if self-quenching were taking place intramolecularly between two chromophores. The experimentally determined radii are much larger and suggest that significant intramolecular energy migration is taking place between groups appended along the polymer backbone.³⁵

The transient absorption measurements of block copolymers **3a–d** reveal that upon excitation at 355 nm, appended benzophenone groups efficiently transfer their triplet energy to the pendant naphthyl groups, resulting in a triplet transient with a λ_{max} at 430 nm (Figure 13) and lifetimes shown in Table 6. As the number of benzophenonyl repeat units were increased, the observed lifetime of the triplet–triplet absorption of naphthalene did not increase, but in copolymers **3b–d**, triplet rise times were observed. Unfortunately, the rise component observed in **3b** was too noisy to be fit accurately, and the lifetimes for the rise components in **3c–d** were 0.5 and 1.4 μ s, respectively. The

Scheme 1. Preparation of Homo- and Copolymers Using Ring-Opening Metathesis Polymerization (ROMP)

inverse of these rise times should correspond to the rate of energy transfer from benzophenone to naphthalene. Since the rise times become longer as the number of benzophenone repeat units increases, the triplet energy must migrate over larger distances to reach a naphthalene acceptor.

The naphthalene groups in **3a–d** are not directly excited at 355 nm, and it is interesting to note that no excited state absorption is observed for the benzophenone groups (compare to Figure 8). Dilution of **3a** results in a decrease in the optical density of the triplet–triplet absorption observed at 430 nm (sensitized by benzophenone) relative to the initial chromophore concentration. In principle, the naphthalene triplet might also be sensitized by **2b** bimolecularly: however, a control experiment demonstrated that much higher concentrations of naphthalene were required to observe bimolecular sensitization than were required to easily observe sensitization in the copolymer. A solution of the homopolymer **2b** required a bimolecular naphthalene concentration of 10^{-2} M to observe sensitization, whereas in copolymer **3a**, sensitization from the benzophenone block to the naphthalene block could be observed at much lower concentrations (10^{-5} M), suggesting that the energy transfer sensitization is likely intramolecular in the copolymer.

The transient absorption spectrum for **3f** displays only the triplet–triplet absorption of phenanthrene (λ_{max} at 500 nm), and its decay was biexponential (Table 6). The lifetimes for **3e–h** are similar to those observed upon direct excitation of the homopolymer **2c**. Unfortunately, no rise times were found in the decay traces, so the energy transfer rates must be faster than can be measured on the nanosecond time scale. Although the phenanthryl block absorbs slightly upon excitation at 355 nm, the triplet–triplet absorption intensity was much higher in **3e–h** than in homopolymer **2c** (Figure 14).

Discussion and Conclusions

Pendant benzophenone groups can be incorporated into rigid polynorbornyl polymers prepared by the ROMP of substituted

norbornenes **1**. The behavior of the homopolymer **2b** in time-resolved transient measurements is unusual. As a dilute solution in a solvent containing an abstractable hydrogen, benzophenone is excited to the triplet and abstracts a hydrogen atom from the solvent to form benzhydrol within the solvent cage.³⁶ In our case, laser pulse excitation of **2b** generates the triplet of benzophenone, which can abstract a hydrogen from a hydrogen-donating solvent or from the polymer backbone when dissolved in a poor hydrogen-donating solvent such as benzene. Its component monomer **1b** likewise abstracts a hydrogen atom in non-hydrogen-donating solvents, either intra- or intermolecularly, to generate the ketyl radical. This abstraction ultimately disrupts the integrity of the polymer and constitutes a basis for application as a negative photoresist. These processes are summarized in Scheme 2.

In a solution of **2b** in benzene, a novel transient species that does not give an absorption spectrum corresponding with that expected for typical decomposition products was detected. One possibility for the origin of this transient is the result of energy transfer from the triplet of benzophenone (3.00 eV) to the ketyl radical (2.27 eV), and this is shown in Scheme 2.^{22,37} Exciplex formation in solutions of benzophenone has been suggested as a cause for a shorter observed triplet lifetime compared to that measured in Freon-113 and Freon-11, although no unambiguous spectroscopic evidence was reported.^{38–40} Another possible origin for this transient is triplet–triplet annihilation from the benzophenone groups in **2b**. This process has been documented with benzophenone in Freon-11, where a characteristic peak at 520 nm is observed in the emission studies. However, the spectrum observed here (Figures 2–4) displays a maximum at

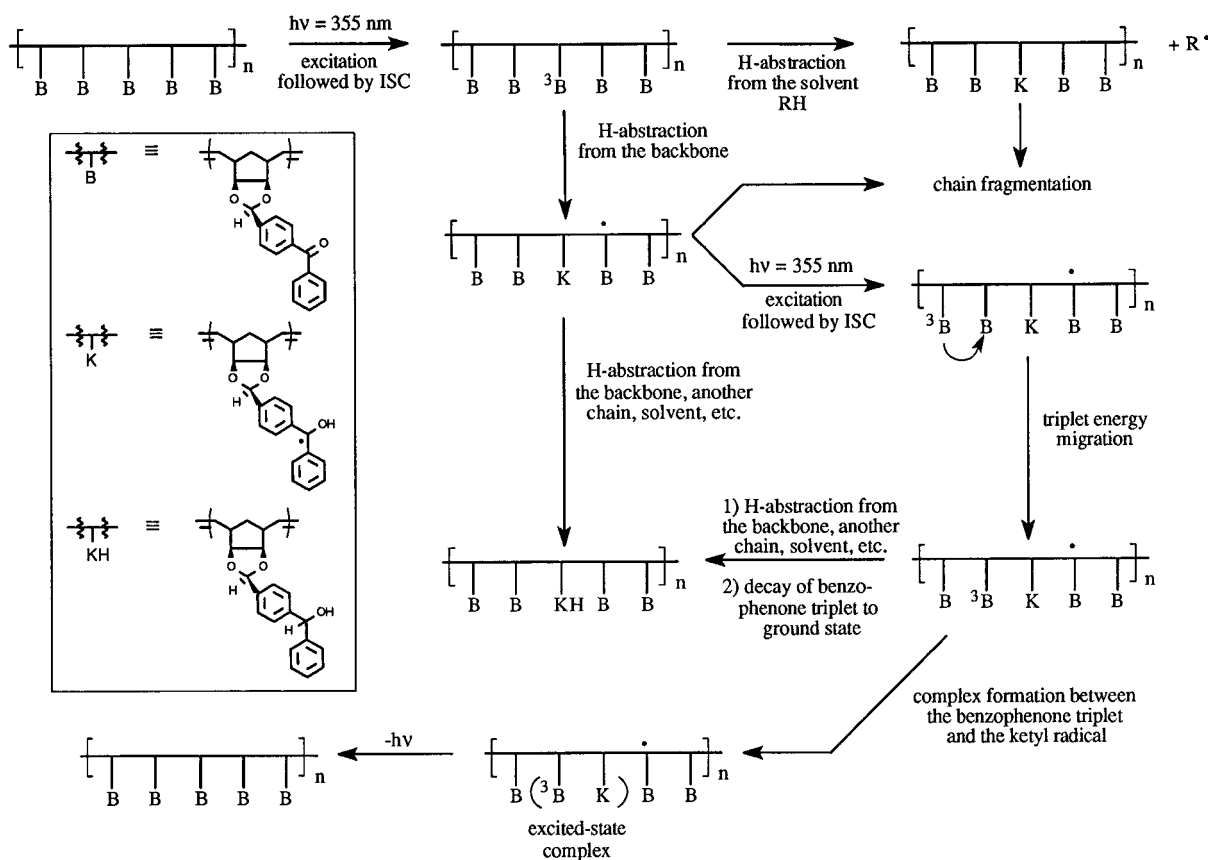
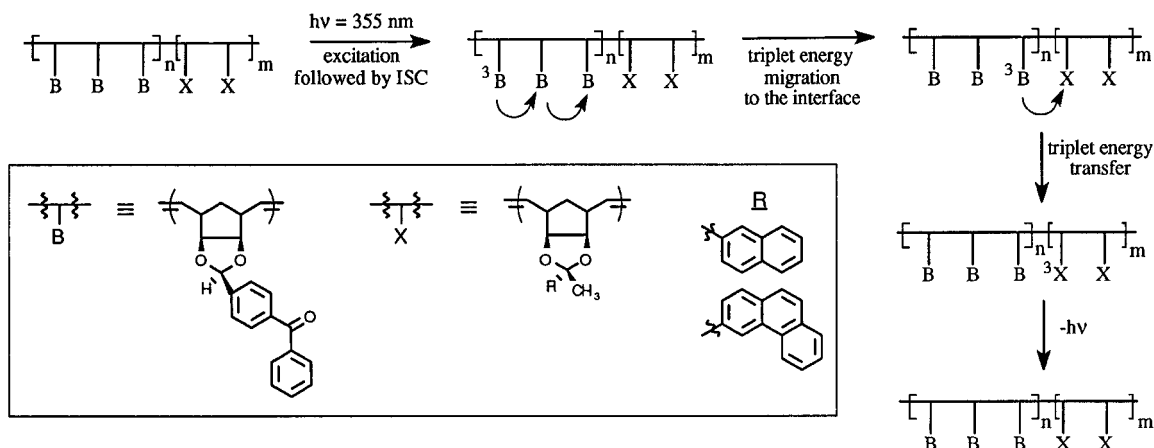
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Scheme 2. Proposed Photophysical Pathways in a Simplified Representation of Homopolymer **2b** Accounting for Chain Scissions**Scheme 3.** Proposed Photophysical Pathways in a Simplified Representation of Copolymers **3** Illustrating Directional Triplet Energy Transfer for Interblock Sensitization

485 nm.^{41,24} Furthermore, when the laser power is increased, the peak at 485 nm shifts to 450 nm, producing a transient whose maximum corresponds with that expected from the phosphorescence of benzophenone.

If triplet-triplet annihilation were taking place, the intensity of the band at 520 nm would increase linearly with the square of the incident light intensity, but that is not the case. The steady-state measurements after laser pulse irradiation lead us to believe that excimer or exciplex formation takes place by virtue of the red-shifted emission (compare with the phosphorescence observed at low temperature and the monomer emission shown in Figure 5). It is interesting that this behavior is not observed in monomer **1b** or in benzophenone itself: it therefore

must derive from the close proximity of the pendant groups in **2b** and from a polymer conformation that permits easy interaction between the benzophenone moieties on adjacent repeat units (Scheme 2).

Aggregation of the polymer chain was considered a probable cause for the observed complexation. Because of the limited solubility of the polymer and the ease of hydrogen abstraction from almost all solvents in which it was soluble (THF, MTHF, CHCl_3 , CH_2Cl_2), it was difficult to rule out excited state interactions. Measurements in bromobenzene gave the same transient absorption spectra as in benzene suggesting that the excited state complex is not affected by a more polar or viscous solvent. Exciplex was not observed in the emission spectrum of **2b** in bromobenzene: only benzophenone phosphorescence was detected. This does not confirm aggregation

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either since even bimolecular exciplexes are known to be more favored in nonpolar solvents.

The complexation behavior observed in **2b** is suppressed under conditions where triplet energy transfer is favorable (as in **3a–d** and **3e–h**). In these systems, the triplet of benzophenone produced by initial excitation transfers its energy to the adjacent arene block to generate the triplet of the triplet energy acceptor (Scheme 3). This energy transfer was detected by emission in the steady-state and by the transient triplet–triplet absorption of the attached chromophore. From the observed quantum yields, we can set a lower limit for the efficiency of triplet energy transfer in these block copolymers: the presence of a benzophenone block in the copolymers results in at least a 3- to 4-fold increase in the phosphorescence of the acceptor. We ascribe this increased emission to intramolecular energy transfer because bimolecular energy transfer between the benzophenone homopolymer **2b** and an external quencher requires much higher concentrations than required to observe sensitization in the block copolymers.

From the rise times observed in **3b–d**, triplet migration occurs through the benzophenone block until a naphthalene acceptor is reached. As is consistent with a Perrin model, we have also determined that intramolecular energy migration can occur in these homopolymers over distances of 35–48 Å. Finally, no complexation that was observed in **2b** in the transient absorption and emission studies was detected in the copolymers **2a** and **2c**. Thus, in the block copolymers, triplet energy transfer dominates over charge-transfer complexation or exciplex forma-

tion observed in the benzophenone polymer, as established by transient absorption and steady-state emission studies, respectively. This behavior would be expected if the energy transfer from the triplet of benzophenone to the ground state of the arene were to occur faster than the competing H-abstraction of the benzophenone triplet to give the ketyl radical. We have been unable to observe separate rise times for H-abstraction and energy transfer in **3a** and **3e–h**: therefore, we can only estimate that both processes occur on similarly fast timescales.

We have shown that polynorbornenes incorporating benzophenone generate a photoinduced excited state complex which we assign to an exciplex between the ketyl radical of benzophenone and the triplet of benzophenone. This behavior is not observed in benzophenone itself or in the monomer. Furthermore, this complexation is suppressed in the presence of a good triplet energy acceptor such as naphthalene or phenanthrene. This is particularly interesting because excimers and exciplexes generally act as energy minima and typically interfere with further electron or energy transfer processes.

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