Synthesis and Photophysical Characterization of Aryl-Substituted Polynorbornenediol Acetal and Ketal Multiblock Copolymers

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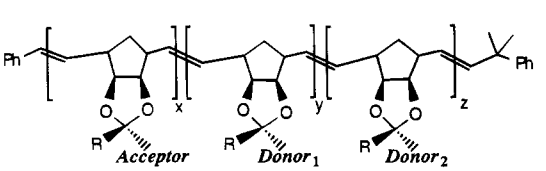
ABSTRACT: A series of homopolymers and di-, tri-, and tetrablock copolymers (MW = 3600–28 000) synthesized by ring-opening metathesis polymerization of *exo,cis*-norbornenediol monomer units bearing various aryl chromophores (naphthalene, phenanthrene, anthracene, pyrene, dimethylaniline, dicyanobenzene, and pentamethylbenzene) have been examined by steady-state emission. Ketal-appended naphthyl, phenanthryl, and anthryl homopolymers show unperturbed monomer emission indicative of a rigid polymer backbone (at least on the time scale of the excited-state lifetimes of the chromophores), whereas acetal-appended naphthyl, anthryl, and pyrenyl homopolymers show substantial excimer formation. Molecular modeling of four possible polymer conformations for both the acetal- and ketal-derived polymers qualitatively explains the differences in their fluorescence emissions. ^{1}H- and ^{13}C-NMR and absorption spectroscopy as well as retention behavior in gel permeation chromatography (polydispersity indices 1.1–1.4) show this family to exist as rigid, living, well-defined, narrow-polydispersity polymers.

Introduction

The synthesis and photophysical study of macromolecular and supramolecular assemblies designed to mimic light collection in photosynthetic arrays have been active research areas for many years.[1–5] Such studies have shown that a rigid and uniform backbone is desirable for the placement and orientation of photoactive electron and energy transfer relays. Low molecular weight model systems[6–9] are usually not large enough to maintain physical separation of the transient radical ions generated by photoexcitation, and the lack of structural rigidity in larger self-organizing systems, e.g., micelles[10] or polystyrene-based polymers,[11] makes it difficult or impossible to specify the exact position or relative orientation of participants in the desired electron transfer sequence. The use of polymers to attain long-lived charge separation over macroscopic distances, however, has been impeded by the lack of convenient and efficient preparative methods that allow for controlled positioning of chromophores and charge relays at specific locations along a rigid polymer backbone. In order to address uncertainties about distance and orientation in macromolecules bearing redox-active donors and acceptors, we have employed ring-opening metathesis polymerization (ROMP) to prepare multifunctional block copolymers of varying length with the following general structure.



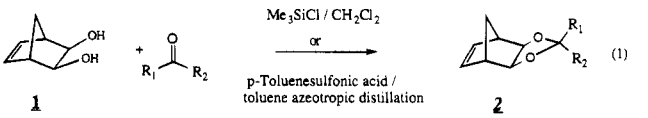
R = H, CH_3

In these narrow-polydispersity polymers, the relative positions of the emissive pendant groups can be inferred precisely from steady-state emission studies and gel permeation chromatographic analysis. Block lengths and the size of the appended chromophore are varied to probe the effect of spacing between the appended groups.

This paper describes the synthesis and characterization of the physical properties and photophysical behavior of a series of functionalized norbornenyl monomers and related polymers bearing one to four blocks of differing composition. The fluorescence spectra of a subset of these polymers (**3a** and **3b**) have been described in a preliminary communication.[12]

Results and Discussion

Design and Characterization of Aryl-Substituted Norbornene Monomers. Monomers **2** were prepared by linking *exo,cis*-norbornenediol **1**[13] with various aryl ketones or aldehydes by ketal or acetal linkages (eq 1). A norbornenyl skeleton was chosen as the unit on which to append the various aryl groups because a strained olefin is required for the irreversible addition of monomer units to a propagating ROMP polymer chain.[14] The attached chromophores were selected based on their appropriate redox and absorption properties, as the key components to attain directional electron or energy transfer.[10]



R_1	R_2
CH_3	Ar = phenyl
CH_3	Ar = 2-naphthyl
CH_3	Ar = 3-phenanthryl
CH_3	Ar = 2-anthryl
CH_3	Ar = 1-pyrenyl
CH_3	Ar = 3-(N,N-dimethylamino)phenyl
H	Ar = 2-naphthyl
H	Ar = 3-phenanthryl
H	Ar = 2-anthryl
H	Ar = 1-pyrenyl
H	Ar = 2,5-dicyanophenyl
H	Ar = pentamethylphenyl

2a: $R_1 = CH_3$; R_2 = phenyl
2b: $R_1 = CH_3$; R_2 = 2-naphthyl
2c: $R_1 = CH_3$; R_2 = 3-phenanthryl
2d: $R_1 = CH_3$; R_2 = 2-anthryl
2e: $R_1 = CH_3$; R_2 = 1-pyrenyl
2f: $R_1 = CH_3$; R_2 = 3-(N,N-dimethylamino)phenyl
2g: R_1 = 2-naphthyl; R_2 = H
2h: R_1 = 3-phenanthryl; R_2 = H
2i: R_1 = 2-anthryl; R_2 = H
2j: R_1 = 1-pyrenyl; R_2 = H
2k: R_1 = 2,5-dicyanophenyl; R_2 = H
2l: R_1 = pentamethylphenyl; R_2 = H

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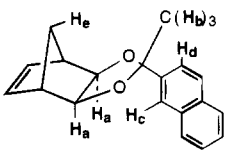
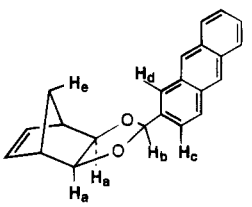
The acetal and ketal linkages offer several positive features: (1) they allow for facile functionalization of **1** with a variety of pendant groups; (2) they provide a rigid structure and orientation for the appended chromophore or quencher, as shown by NOE experiments discussed below; (3) they allow for the preparation of symmetrical monosubstituted monomers; and (4) the coupling of the diol and the corresponding aldehyde or ketone yields only a single configurational isomer (rather than a mixture of isomers). Because norbornenyl monomers bearing *exo* substituents react more ideally with ROMP catalysts than those that contain one or two *endo* substituents,[14] the family **2** is particularly well suited for controlled ROMP polymerization.[15]

The symmetry plane of monomer **2** is important because it reduces the number of possible stereoisomers in the polymeric product and hence, limits structural uncertainty to questions of *cis/trans* isomerism and tacticity. In addition, attachment of a single light-absorbing group in the monomer precludes intramolecular excimer formation in the monomers, making it possible to employ photophysical measurements to study intra- and interchain interactions in the derived polymers.[16-20] In contrast, two aryl chromophores attached to both the 1- and 2-positions of norbornene can approach to within 3–6 Å, a distance short enough for efficient intramolecular excimer formation.[16]

The structures of monomers **2** were assigned from nuclear Overhauser effect (NOE) experiments designed to determine the orientation of the aryl moieties relative to the apical protons. Monomers **2b** and **2i** employing



2b



2i

a ketal and acetal linkage, respectively, were examined, as representative of these classes. Careful irradiation of **2b** at 3.98 ppm (the resonance frequency of protons H_a) of the two norbornyl *endo* protons (assigned by comparison with the ^{1}H-NMR spectrum of the unsubstituted norbornenediol **1**)[13] induced a positive enhancement of the signal assigned to aromatic protons H_c and H_d. Likewise, irradiation of the ketal methyl protons H_b (1.75 ppm) induced a positive NOE signal of H_e but not of H_a. Thus, the 2-naphthyl group in **2b** is "syn" to the axial norbornyl protons (H_a), whereas the methyl group is "anti", as illustrated above.

Similarly, the irradiation of **2i** at 4.34 ppm (the resonance frequency of the *endo* protons H_a) induced a positive enhancement of the signal assigned to H_b, and irradiation of H_b showed a complementary positive enhancement of the signal assigned to H_a. Irradiation of H_e afforded a corresponding positive NOE for the signal assigned to aromatic protons H_c and H_d. Thus, the acetal **2i** exists with the aryl group "anti" and the proton H_b "syn" to the H_a bridgehead protons. The constitutional isomers of the other members of the series were similarly verified by ^{1}H-NMR spectroscopy (Table 1), in which the proton resonance of the *endo* protons for the ketal-derived monomers is approximately 0.3–0.5 ppm upfield from the analogous acetal-linked monomers. This follows from the assigned structures of **2b** and **2i**, for the *endo* protons in −2b are shielded by the ring currents of the "syn" aromatic group, whereas in **2i** these protons are relatively unperturbed.

Table 1. Comparison of ^{1}H-NMR Chemical Shifts of *Endo* Protons in Acetal- and Ketal-Derived Monomers

appended arene	ketal shifts (ppm)	acetal shifts (ppm)
phenyl	**2a:** 3.93	
2-naphthyl	**2b:** 3.98	**2g:** 4.31
3-phenanthryl	**2c:** 4.05	**2h:** 4.34
2-anthryl	**2d:** 4.03	**2i:** 4.32
1-pyrenyl	**2e:** 3.46	**2j:** 4.49
m-(dimethylamino)phenyl	**2f:** 4.35	
2,5-dicyanophenyl		**2k:** 4.40
pentamethylphenyl		**2l:** 4.49

Table 2. Gel Permeation Chromatographic Characterization of Average Molecular Weights and Polydispersities of Homopolymers and Di-, Tri-, and Tetrablock Copolymers[a]

polymer (no. of units)	M_w/M_n	M_n	M_n(calc)[b]	% *trans*
3a (50)	1.15	8200	9126	85
3b (100)	1.16	37000	27800	88
3c (20)	1.27	6300	6560	87
3d (20)	1.42	2500	2640	96
3e (10)	1.32	3600	3520	90
3f (25)	1.33	6500	5420	89
3g (15)	1.32	4800	5302	87
3h (10)	1.28	3000	3141	88
3j (10)	1.32	3600	3520	93
3k (10)	1.27	5100	6565	67
3l (20)	1.23	1000	8520	89
4a (10:10)	1.30	6700	5500	88
4b (20:20)	1.31	9300	10980	88
4c (10:10)	1.36	1100	5620	91
4d (10:10)	1.19	9400	5993	87
4e (20:20)	1.16	7000	11986	84
4f (50:5)	1.20	3600	3383	80
4g (10:10)	1.26	26000	5550	87
5a (50:5:5)	1.36	19000	14369	80
5b (50:10:5)	1.11	14000	14369	80
5c (50:10:10)	1.10	15000	17390	80
5d (10:10:10)	1.40	11000	8330	88
6 (50:5:10:5)	1.17	23000	22685	89

[a] Determined by GPC against commercial polystyrene standards. [b] Calculated from the ratio of monomer to catalyst based on quantitative conversion for a living system.

Living Nature of Substituted Norbornenediol-Derived Polymers and Block Copolymers. Ring-opening metathesis polymerization (ROMP) is unique among possible polymerization techniques in having a high tolerance of several functional groups and producing a living oligomer capable of extension to block copolymers in subsequent steps.[14] All homopolymers discussed herein were prepared by ROMP of **2**, using Schrock's Mo(CHCMe$_2$Ph))(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ complex as catalyst (eq 2).[14]

Polymerization was conducted by adding monomers **2** to a solution of catalyst in toluene. Following complete consumption (5–20 min) of the first monomer (verified by ^{1}H-NMR), either the propagating polymer (**P**) was cleaved from the metal catalyst by addition of benzaldehyde (15 μL) or subsequent monomers wee sequentially added to **P** to form an oligomeric block copolymer which was then cleaved by treatment with benzaldehyde. In the homopolymers (**3**) and di- (**4**), tri- (**5**), and tetrablock (**6**) copolymers (Chart 1), the attained molecular weights could be selected within a range of 3600–28000 by controlling the ratio of monomer to catalyst. Low polydispersities (1.1–1.4) were observed in each member of the series (Table 2), and the calculated number-average molecular weights (M_n) (column 3) compared within 10–20% to the experimentally observed M_n (column 2) from GPC analysis.

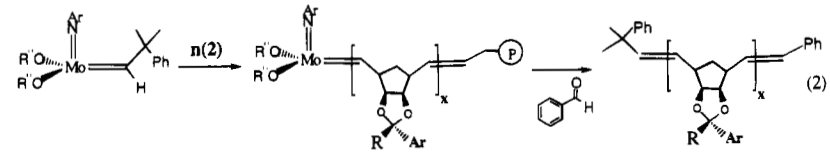
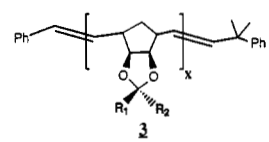


Chart 1

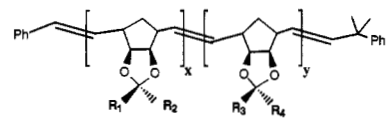
Homopolymers



3

3a: $R_1 = CH_3$, x = 50, R_2 = phenyl
3b: $R_1 = CH_3$, x = 100, R_2 = 2-naphthyl
3c: $R_1 = CH_3$, x = 20, R_2 = 3-phenanthryl
3d: $R_1 = CH_3$, x = 20, R_2 = 2-anthryl
3e: $R_1 = CH_3$, x = 10, R_2 = 1-pyrenyl
3f: $R_1 = CH_3$, x = 25, R_2 = 3-N,N-dimethylamino)phenyl
3g: R_1 = 2-naphthyl, R_2 = H, x = 15
3h: R_1 = 3-phenanthryl, R_2 = H, x = 10
3i: R_1 = 2-anthryl, R_2 = H, x = 10
3j: R_1 = 1-pyrenyl, R_2 = H, x = 10
3k: R_1 = (2,5-dicyanophenyl), R_2 = H, x = 10
3l: R_1 = pentamethylphenyl, R_2 = H, x = 30

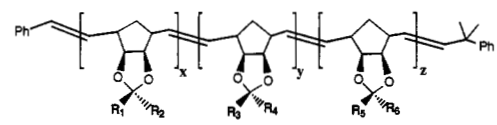
Diblock copolymers



4

4a: $R_1 = CH_3$, R_2 = 2-naphthyl, x = 10; $R_3 = CH_3$, R_4 = 3-(N,N-dimethylamino)phenyl, y = 10
4b: $R_1 = CH_3$, R_2 = 2-naphthyl, x = 20; $R_3 = CH_3$, R_4 = 3-(N,N-dimethylamino)phenyl, y = 20
4c: $R_1 = CH_3$, R_2 = 2-naphthyl, x = 10; R_3 = pentamethylphenyl, R_4 = H, y = 10
4d: $R_1 = CH_3$, R_2 = 3-phenanthryl, x = 10; $R_3 = CH_3$, R_4 = 3-(N,N-dimethylamino)phenyl, y = 10
4e: $R_1 = CH_3$, R_2 = 3-phenanthryl, x = 20; $R_3 = CH_3$, R_4 = 3-(N,N-dimethylamino)phenyl, y = 20
4f: $R_1 = CH_3$, R_2 = phenyl, x = 50; R_3 = 2-anthryl, R_4 = H, y = 5
4g: R_1 = pentamethylphenyl, R_2 = H, x = 10; $R_3 = CH_3$, R_4 = 3-(N,N-dimethylamino)phenyl, y = 10

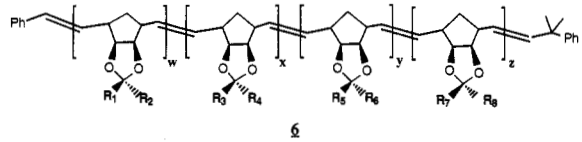
Triblock copolymers



5

5a: $R_1 = CH_3$, R_2 = phenyl, x = 50; $R_3 = CH_3$, R_4 = 2-naphthyl, y = 5; R_5 = 2-anthryl, R_6 = H, z = 5
5b: $R_1 = CH_3$, R_2 = phenyl, x = 50; $R_3 = CH_3$, R_4 = 3-phenanthryl, y = 5; R_5 = 2,5-dicyanophenyl, R_6 = H, z = 5
5c: $R_1 = CH_3$, R_2 = phenyl, x = 50; $R_3 = CH_3$, R_4 = 3-phenanthryl, y = 10; $R_5 = CH_3$, R_6 = 3-(N,N-dimethylamino)phenyl, z = 10
5d: $R_1 = CH_3$, R_2 = 3-N,N-dimethylamino)phenyl, x = 10; R_3 = 1-pentamethylphenyl, R_4 = H, y = 10; $R_5 = CH_3$, R_6 = 2-naphthyl, z = 10

Tetrablock copolymer



6

6: $R_1 = CH_3$, R_2 = phenyl, x = 50; $R_3 = CH_3$, R_4 = 3-N,N-dimethylamino)phenyl, x = 5; $R_5 = CH_3$, R_6 = 3-phenanthryl, z = 10; R_7 = 2,5-dicyanophenyl, R_8 = H, z = 5

The number of aryl groups incorporated within the homopolymers and block copolymers was also verified by comparing their extinction coefficients to those of the corresponding monomer units, i.e., the absorbing species at the wavelength of excitation (Table 3). For example, the ratio of extinction coefficients of **3b** to **2b** is 109: this agrees within 10% with the 100 units expected from the stoichiometry employed in the synthesis of the homopolymer. Similarly, the observed extinction coefficient in copolymer **4a** corresponds to eight naphthalene units in the 10:10 diblock, i.e., within 20% of that expected by the stoichiometric addition of monomers to the catalyst. Thus, the living nature of these polymers has been demonstrated by (1) irreversible addition of monomers to form polymers, (2) narrow PDIs in homopolymers and block copolymers, and (3) consumption of second monomer after the first is consumed (or third, etc.) to form well-defined block copolymers with additive molecular weights (as determined by GPC analysis).

Table 3. Comparison of Extinction Coefficients of Monomers, Homopolymers, and Block Copolymers

polymer	ϵ (M^{-1} cm^{-1}) (wavelength)	ratio[a] ($\epsilon_{pol}/\epsilon_{mon}$)	ratio[b] expected
2a	272 (335 nm), 10900 (300 nm)		
2b	44600 (344 nm)		
2c	50000 (344 nm)		
2d	4600 (284 nm)		
2e	2050 (296 nm), 1900 (286 nm)		
2f	5400 (378 nm)		
2g	400 (335 nm)		
2h	6600 (284 nm)		
2i	790 (288 nm)		
2j	13200 (260 nm), 2500 (308 nm)		
2k	5000 (378 nm), 2060 (388 nm)		
2l	220 (258 nm)		
3a	196900 (300 nm)	18	20
3b	296100 (344 nm)	8	10
3c	355000 (344 nm)	7	10
3d	66900 (284 nm)	15	15
3e	14700 (286 nm)	8	10
3f	108500 (378 nm)	20	20
3g	3200 (335 nm)	8	10
3h	718200 (284 nm)	109	100
3i	25800 (284 nm)	32	30
3j	64000 (308 nm)	26	25
3k			
3l	12300 (258 nm)	8	10
4a	50800 (284 nm)	8	10
4b	90800 (284 nm)	14	20
4c	4900 (335 nm)	18	20
4d	68700 (284 nm)	10	10
4e	2900 (335 nm)	10	10
4f	14150 (388 nm)	7	5
4g	18100 (308 nm)	7	10
5a	2880 (335 nm)	11	10
5b	3500 (350 nm)	13	10
5c	68700 (284 nm)	10	10
5d	17100 (378 nm)	3	5
6	2500 (335 nm)	9	10

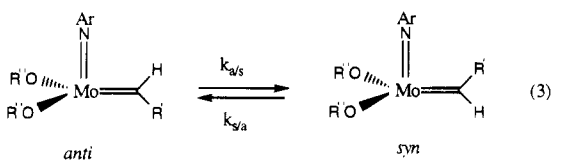
[a] Calculated from the extinction coefficient ratios of the polymer/monomer. [b] Calculated from the known molecular weight of the monomer which was multiplied by the stoichiometric equivalents of monomer added to form the respective homopolymer or diblock copolymer.

The physical characteristics of these polymers (solubility, emission, and absorption) were also examined. Homopolymers prepared from ketal-linked monomers remained soluble throughout the polymerization (20 min). In contrast, homopolymers derived from acetal-linked monomers began to precipitate from solution about 2–3 min after initiation of polymerization. Presumably, the additional methyl group in ketal-derived monomers and their *endo* configurations enhance the solubility of the growing polymer as it forms. Once polymerized, each of the homopolymers, except **3i**, was somewhat soluble in methylene chloride and tetrahydrofuran. The insolubility of **3i** presumably results from its regularity and rigidity, since very rigid polymers are known to be highly insoluble.[23] The homopolymer **3i** was insoluble in most solvents, although upon vigorous stirring for 30 min, it was sufficiently soluble in CH_2-

Cl_2, the solvent from which it had been polymerized, that a fluorescence spectrum could be obtained. X-ray diffraction studies of the homopolymer **3i** showed it to be noncrystalline; hence the insolubility does not result from any crystalline or semicrystalline property in the polymer. When **3i** was polymerized as a second block appended to a 50-block oligomer of **2a** as the first block, its solubility was much higher, making possible its complete characterization as a diblock polymer.

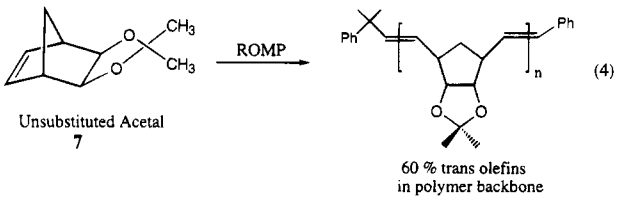
***Cis/Trans* Geometries of Olefins in the Polymer Backbones.** The morphology of ROMP polymers is largely defined by two stereochemical elements: (1) *cis* to *trans* ratio of the olefin linkages in their backbones and (2) tacticity, arising from the relative configurations between the two chiral bridgehead carbons in the norbornenyl monomer. Because the latter is not yet controllable using the Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)-(O-*t*-Bu)$_2$ catalyst, we have focused on defining the former as it pertains to our polymers.

The ^{1}H-NMR spectra of all polymers **3**, **4**, **5**, and **6**, except **3k**, show that 80−96% of the olefinic linkages in the polymer backbones exist in the *trans* geometry (Table 2) as determined by a comparison of the relative intensity of *cis* and *trans* ^{1}H-NMR resonance frequencies at ~5.6 and ~5.3 ppm, respectively.[15] Schrock and Oskam have shown that the *cis* to *trans* content in a norbornenyl polymer backbone is determined by the rate of interconversion between rotational isomers derived from the Mo(VI) alkylidene complex and the relative reactivity of an individual monomer with the more reactive rotamer (eq 3).[22] Because the rotational isomers of the Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ catalyst interconvert rapidly and the because the anti form reacts more rapidly than the syn, form, the resulting polymer conformations are predominantly *trans*.[22] For example, with Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ as catalyst, **7** polymerized to give a slight preference for *trans* linkages (60% *trans*) (eq 4).[21]



(3)

R' = R'' = (CHCMe$_2$Ph), Ar = 2,6-iPr$_2$-C$_6$H$_3$



(4)

The higher *trans* content (>80%) observed upon polymerization of **2** is an indication of its even higher selectively than with **7**. The slight differences in the *trans* content of the series of polymers derived from **2** are a result of the varying sizes of the appended aryl groups. For example, among the homopolymers **3**, the sterically larger 1-pyrenyl and 2-anthryl groups yield polymers with the highest *trans* content (93 and 96%, respectively), whereas the smaller phenyl group yields a polymer with a *trans* content of only 80%. The high fraction of *trans* linkages in the backbones of **3**, **4**, **5**, and **6** thus produces regular and uniform structures, as discussed below.

Molecular Modeling of Polynorbornenyl Chains Bearing Pendant Aryl Groups. The lowest energy conformations of the polynorbornenyl backbone (5 units long) bearing pendant aryl groups linked through ketal (Figure 1) or acetal (Figure 2) monomers have been modeled using the Hyperchem molecular modeling program. These models were used as a qualitative tool to explain the observed differences in the configurational isomers of the acetal- and ketal-linked polymers. The four possible configurational isomers for ROMP polymers are *trans*-syndiotactic, *trans*-isotactic, *cis*-syndiotactic, and *cis*-isotactic. These minimum energy structures for the ketal (Figure 1) and the acetal (Figure 2) allow us to view the interactions between pendant and/or adjacent chromophores as dictated by a balance between van der Waals forces, π-stacking, and steric interactions of the methyl group in the ketal-linked or of hydrogen in the acetal-linked monomer. A comparison of the structures shown in Figures 1 and 2 demonstrates a distinctive stereochemical difference in the *cis* forms of the ketal-derived (**3b**) and the acetal-derived (**3g**) polymers. Specifically, these figures show that $\pi-\pi$ stacking interactions exist between adjacent chromophores in the *cis*-isotactic and *cis*-syndiotactic forms of **3g**, whereas, in contrast, the corresponding *cis*-isotactic and *cis*-syndiotactic stereoisomers of ketal **3b** are not capable of this interaction because the intervening methyl groups limit the approach of adjacent chromophores. The distances between the planes of the aryl groups shown in Figure 2C,D (3.67 Å) are close enough to allow excimer formation between an excited-state chromophore and the adjacent ground-state chromophore.[16] Thus, the observed excimer emission presumably derives from the 12% *cis* content found in the backbone of **3g** (Table 2).

Symmetry requirements for aryl excimer formation in solution dictate that the two interacting arenes must be parallel such that the projection of one molecule on the plane of the other either partially or completely overlaps (eclipses) it.[25] From the eight conformations in Figures 1 and 2, it is clear that only the *cis*-syndiotactic form of the acetal-derived polymer displays the appropriate face-to-face geometric orientation to allow excimer emission to occur. The *cis* form of the ketal-derived polymer, while similar in overall conformation to the acetal-derived polymer, does not display any face-to-face interactions between adjacent chromophores. Such interactions are inhibited by the steric interference of the methyl groups between respective chromophore planes.

Polymer Rigidity and Structure As Defined by Steady-State Emission from Pendant Aryl Groups. The fluorescence spectra of chromophore-labeled polymers in dilute solution have been used to obtain information about their macroscopic conformations.[17] Polymers with flexible backbones show both weak monomer emission and intense excimer emission resulting from polymer folding.[24] Typical fluorescence emission spectra of acetal- and ketal-derived homopolymers **3**, in comparison to their component monomers, are shown in Figures 3−7. The homopolymers containing ketal linkages show no excimer at all, whereas the corresponding acetal-derived polymers show weak excimer emission. This is completely consistent with the molecular modeling results discussed above.

Thus, within the lifetime of the excited state, the backbone to which the ketal-linked chromophores are appended is sufficiently rigid to inhibit the approach necessary to produce excimers. In addition, the relative orientation of respective ketal-linked chromophores does

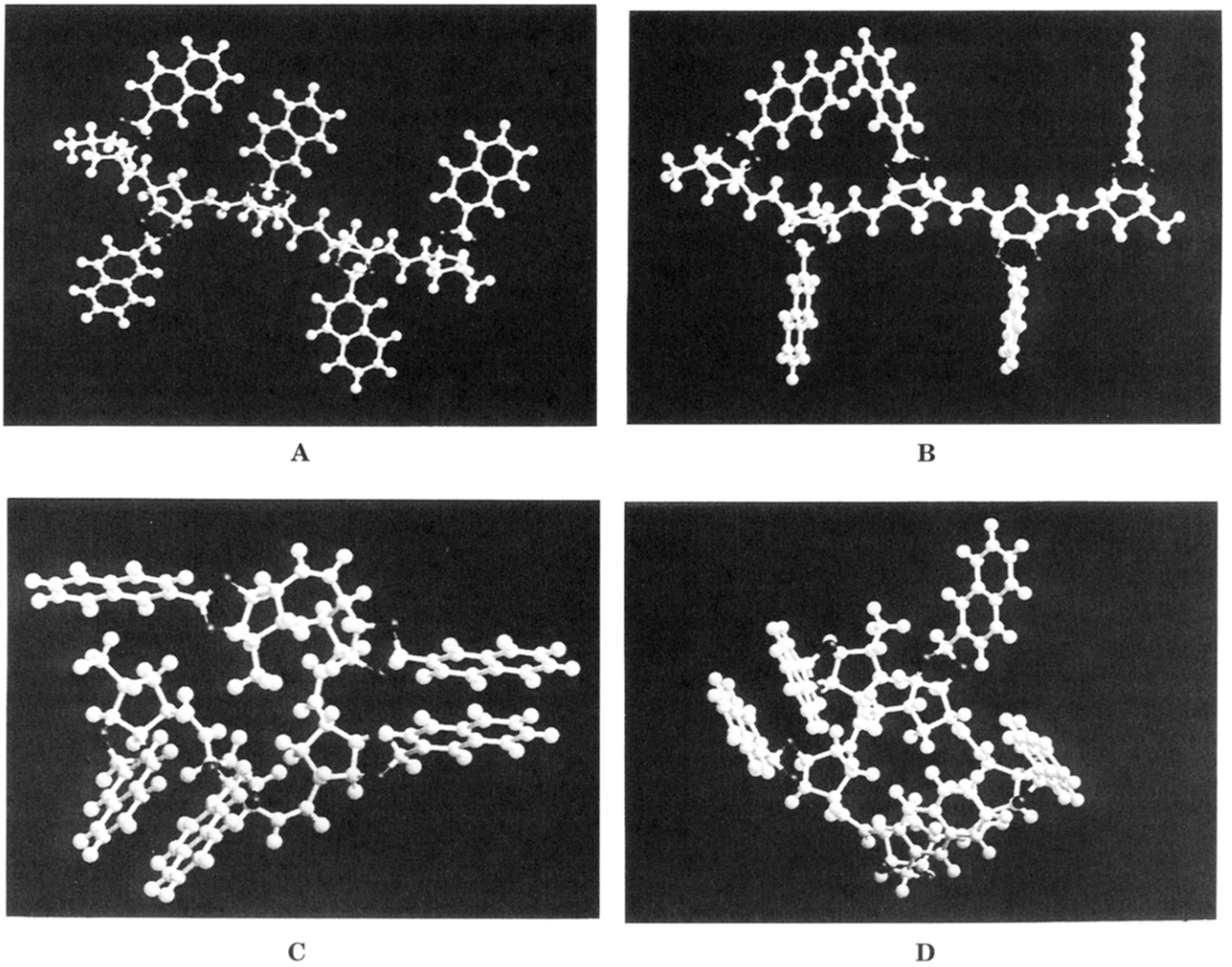


Figure 1. Molecular modeling of five-unit-long acetal-derived homopolymer segment of **3g** minimized in an MM+ force field with the Hyperchem molecular orbital program on a Silicon Graphics workstation. The four possible conformations are (A) *trans*-syndiotactic, (B) *trans*-isotactic, (C) *cis*-syndiotactic, and (D) *cis*-isotactic.

not permit face-to-face interactions because of the steric bulk of the methyl group. In contrast, the *cis* acetal-linked chromophores are oriented so that the approach necessary to form excimer is uninhibited.

Both the acetal- and ketal-derived 1-pyrenyl homopolymers show substantial excimer emission (Figure 6). Presumably, in **3j** and **3e**, the appended chromophores are sufficiently large that excimer formation between adjacent pyrenes can take place in both the *cis* and *trans* conformations.

The fluorescence spectra of each copolymer **4**, **5**, and **6** show a broad structureless long-wavelength band (exciplex) in addition to monomer emission (Figure 7) as is indicative of interaction between the excited-state chromophore and the adjacent ground-state donor at the diblock interface. Intermolecular exciplex formation as a source of the long-wavelength emission was eliminated, for the intensity of this band was invariant in concentrations ranging from 10^{-6} to 10^{-4} M. The spectral characteristics of the exciplex emissions of **4**, **5**, and **6** demonstrate that we have made phase-separated block copolymers rather than polydisperse, highly folded mixtures of the corresponding homopolymers of each monomer. Emission spectroscopy provides unique information about structural organization. Prior attempts at characterization of diblock copolymers have monitored changes in the PDI between diblocks and the corresponding homopolymers from which they were made, with the resulting diblock being confirmed by the observation of a narrow PDI when the second, third, or fourth blocks are linked together.[25] This method, while useful, does not provide information on the nature of the interface between block copolymer segments as do these fluorescence measurements.

Determination of the Relative Rates of Polymerization and Initiation for ROMP of Substituted Norbornenes. In the preparation of block copolymers, it is important to determine the number of monomer equivalents required to completely consume the initiator so that addition of a second monomer adds only to the initiated first block and that polydispersity of the first block is fixed and narrow. Otherwise, a polydisperse mixture of block copolymer and homopolymers of the first and second monomers may result.

Integrated ratios of ^{1}H-NMR signal intensities assigned to alkylidene and initiator resonances in the region from 11.1 to 11.6 ppm (eq 5) can be used to calculate a value for the relative rates of polymerization and initiation, k_p/k_i.[27] This experiment was performed on monomer **2a**, which was used in the initiation of the first block in several of the multiblock copolymers. The relative rates of polymerization and initiation, $r = k_p/$

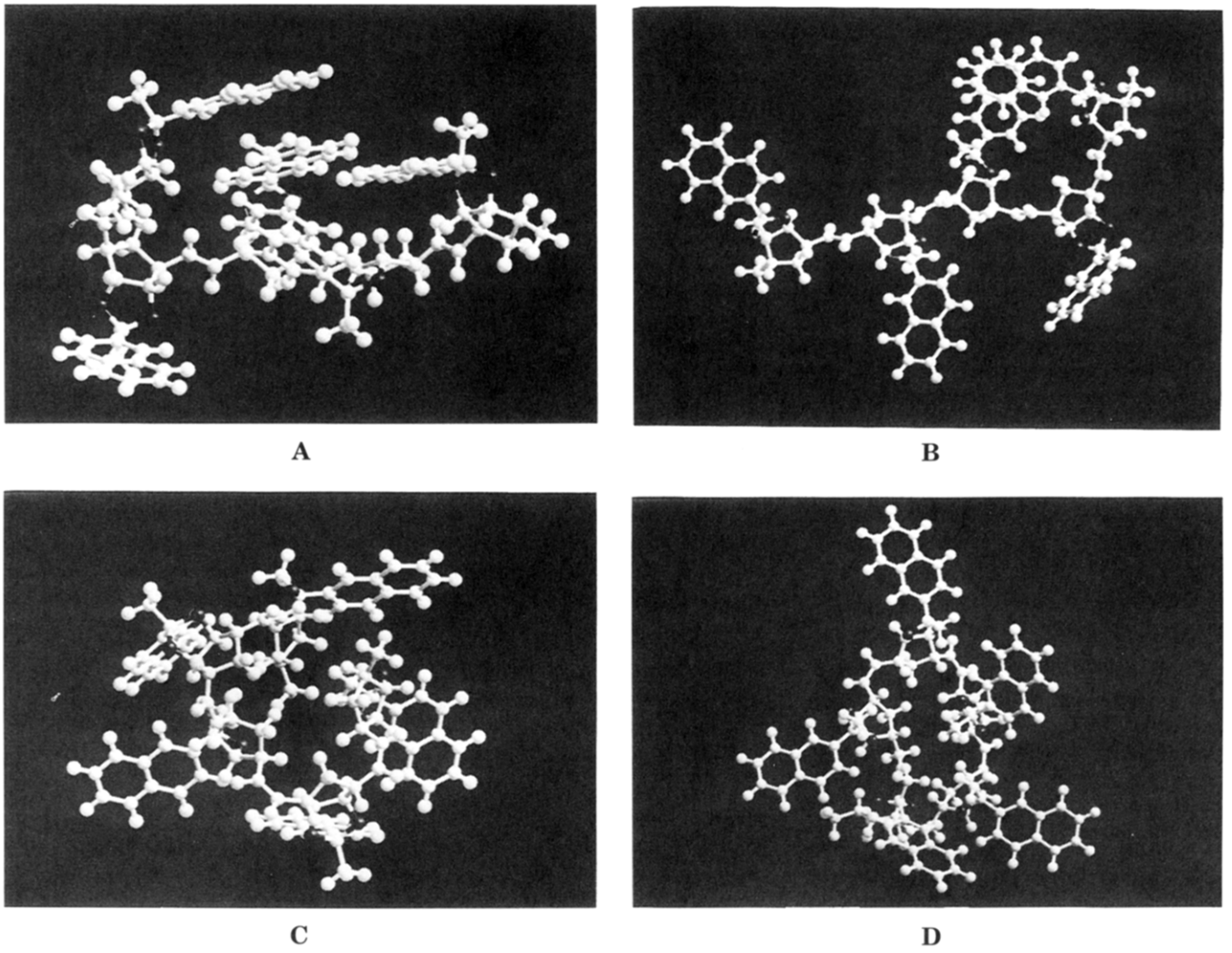
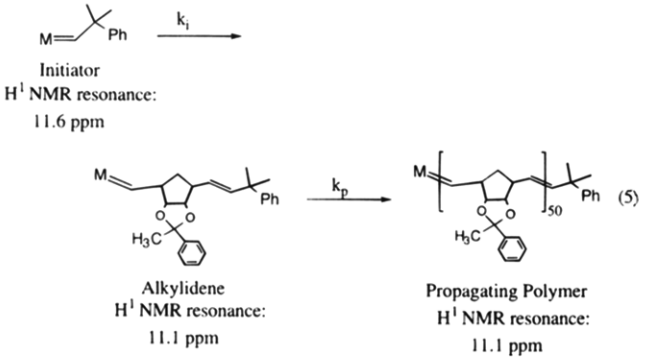


Figure 2. Molecular modeling of five-unit-long ketal-derived homopolymer segment of **3b** minimized in an MM+ force field with the Hyperchem molecular orbital program on a Silicon Graphics workstation. The four possible conformations are (A) *trans*-syndiotactic, (B) *trans*-isotactic, (C) *cis*-syndiotactic, and (D) *cis*-isotactic.



k_i, can be determined from eq 6.[24]

$$\frac{M_0}{I_0} + r\ln\left(\frac{I}{I_0}\right) + (1-r)\left(\frac{I}{I_0} - 1\right) = 0 \qquad (6)^{27}$$

The proton NMR intensities mentioned above were used to define I_0, the initial concentration of initiator, and I, the concentration of propagating polymer. Because the initial concentration of monomer is fixed, we can therefore determine r. A value of 42.5 for k_p/k_i was so determined for **2a**, which is comparable to the value reported earlier for ROMP of norbornene itself (k_p/k_i = 35–40).[14]

This analysis also allows us to determine the number of equivalents of monomer needed to consume all of the catalyst.[27] For example, with a monomer-to-catalyst molar ratio of 5:1, 55% of the catalyst remains unbound after 20 min of stirring under an inert atmosphere. This same experiment, when performed with monomer-to-catalyst ratios of 20, 40, or 50, shows the presence of 10, 4, and 0% uninitiated catalyst, respectively. Thus, with a monomer-to-catalyst molar ratio of 50, the first monomer completely consumes the catalyst, producing a propagating alkylidene capable of continuing the polymerization upon adding a second aliquot of monomer.

The polydispersities of short (10–30 units) block copolymers (Table 1) are somewhat larger than the corresponding polymers of longer length. Schrock and co-workers have similarly noted that shorter chain oligomers have broader molecular weight ranges than do longer chain polymers (~100 units or greater).[26] This problem was circumvented by starting with a 50-unit block of **2c** at the beginning of each copolymer chain, as in **5c**. In order to use these polymers for later photophysical studies, **2a** was chosen for this purpose because it is not photoactive in the region where the chromophores **2b**–**i** absorb light. Thus, polydispersity is improved from 1.19 in **4d** to 1.11 in **5c** upon first appending a photoinactive 50-unit initial block. This first block allows us to establish consumption of catalyst in the initiation step so that subsequent polymerization of homopolymers or block copolymers can take place with apparent unimolecular kinetics.

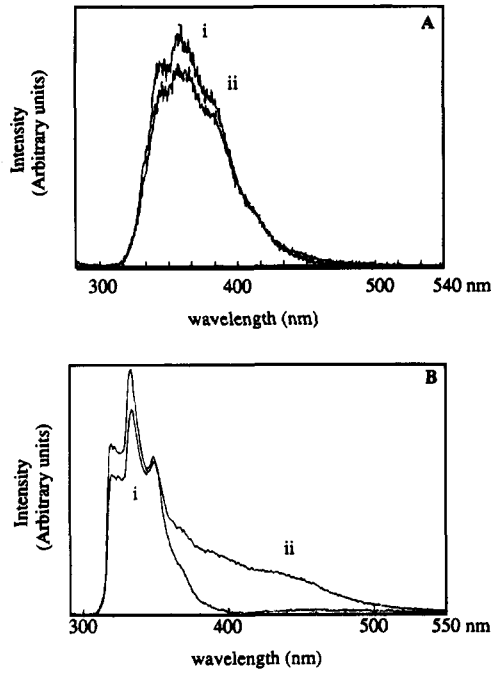


Figure 3. Fluorescence emission in CH_2Cl_2 of naphthyl-derived monomers and homopolymers: (A) ketal homopolymer **3b** (ii), overlaid with ketal monomer **2b** (i) (λ_{ex} = 284 nm); (B) acetal homopolymer **3g** (ii), overlaid with acetal monomer **2g** (i).

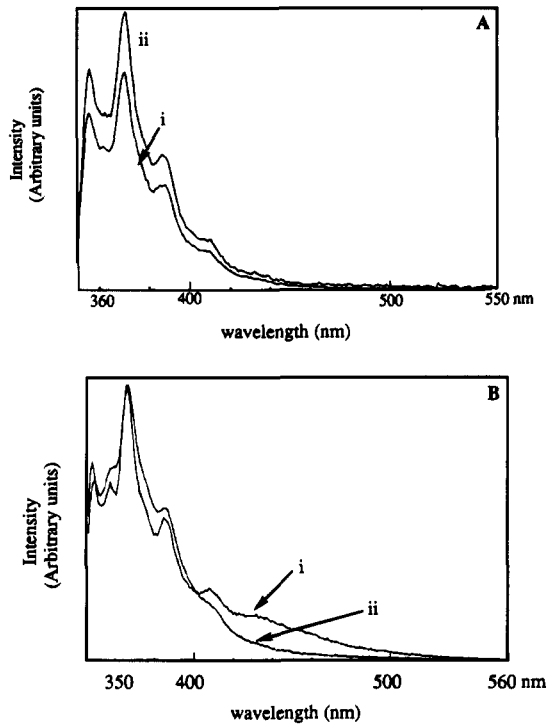


Figure 4. Fluorescence emission in CH_2Cl_2 of phenanthryl-derived monomers and homopolymers: (A) ketal homopolymer **3c** (ii), overlaid with ketal monomer **2c** (i) (λ_{ex} = 335 nm); (B) acetal homopolymer **3h** (ii), overlaid with acetal monomer **3h** (i).

Conclusion

Arene-appended acetals and ketals of *exo,cis*-norbornendiol can be polymerized using ROMP techniques. Both homopolymers and block polymers show relatively narrow polydispersity indices, indicating that regular, defined, rigid macromolecules have been prepared. Living polymerizations are still achieved with varying sizes of arene-appended norbornenyl monomers. Minimum energy polymer conformations determined by molecular modeling studies show key $\pi-\pi$ bonding interactions between adjacent chromophores in the acetal-derived polymers. Photophysical properties, such as excimer formation, can be controlled by using the appropriate ketal or acetal monomer.

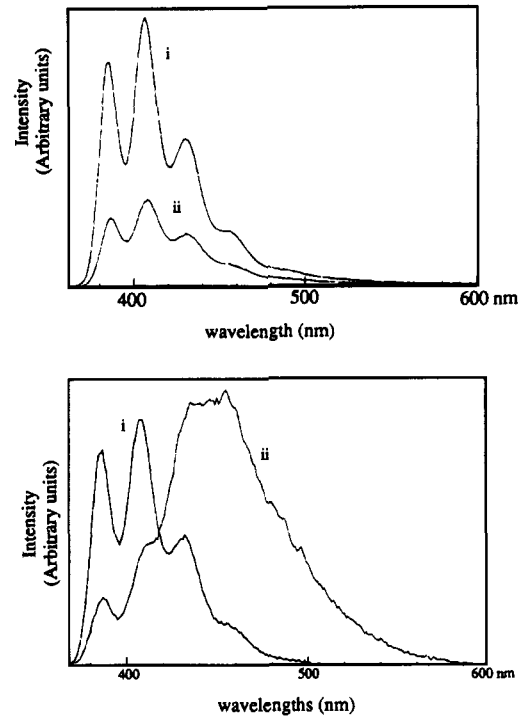


Figure 5. Fluorescence emission in CH_2Cl_2 of anthryl-derived monomers and homopolymers: (A) ketal homopolymer **3d** (ii), overlaid with ketal monomer **2d** (i) (λ_{ex} = 355 nm); (B) acetal homopolymer **3i** (ii), overlaid with acetal monomer **2i** (i).

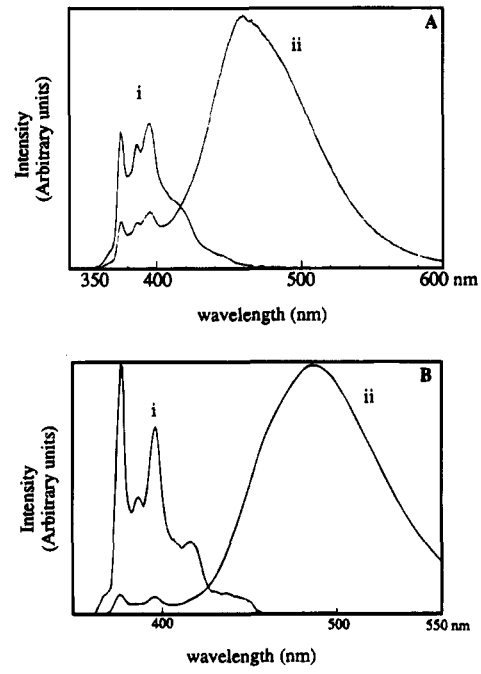


Figure 6. Fluorescence emission in CH_2Cl_2 of pyrenyl-derived monomers and homopolymers: (A) acetal homopolymer **3j** (ii), overlaid with ketal monomer **2j** (i) (λ_{ex} = 355 nm); (B) ketal homopolymer **3e** (ii), overlaid with ketal monomer **2e** (i).

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out with standard Schlenk line techniques or in a N_2-filled drybox. Nitrogen was purified by passage through columns of Linde 4 Å molecular

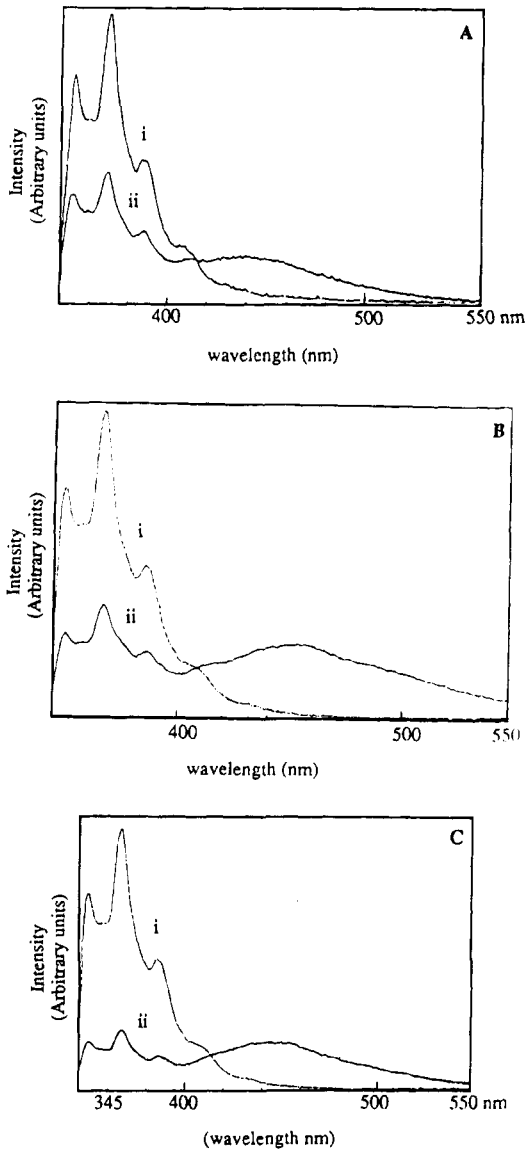


Figure 7. Fluorescence emission in CH_2Cl_2 of (A) homopolymer **3c** (i) and **3c** overlaid with diblock copolymer **4d** (ii) (λ_{ex} = 335 nm), (B) homopolymer **3c** (i) and **3c** overlaid with triblock copolymer **5b** (ii), and (C) homopolymer **3c** (i) and **3c** overlaid with tetrablock **6** (ii).

sieves, color-indicating Drierite, and oxygen scavenging Ridox. Nuclear magnetic resonance (NMR) spectra were recorded on a GE QE-300 (300 MHz) spectrometer. NOE experiments were carried out on a 500 MHz Varian NMR spectrometer. High-resolution mass spectrometry measurements were obtained on a VG ZAB2-E mass spectrometer (VG Analytical Ltd.). Preparative gas chromatography was performed on a Hewlett-Packard 5890A chromatograph equipped with a flame ionization detector (fid) and a 30 m capillary column, with He as carrier gas. Absorption spectra were recorded on a Hewlett-Packard 8451A diode array spectrometer. Fluorescence spectra were measured on an SLM-500C spectrofluorometer.

Polymers were synthesized under N_2 in a Vacuum Atmospheres HE-493 drybox. All solvents were degassed by five freeze–pump–thaw cycles prior to their introduction into the drybox. Dichloromethane was freshly distilled from sodium hydride. Benzene and toluene (Aldrich) were dried over sodium, with benzophenone ketyl being used as indicator. Methanol was dried over sodium. All monomers were dried under vacuum (0.1 μm) overnight before being polymerized. Catalysts were taken directly into the drybox for storage and were used without further purification. Wheaton glass bottles (Aldrich) were dried at 200 °C before transfer into the drybox.

Chemicals. Norebornadiene, pentamethylbenzene, bromine, *N*-methylmorpholine, formaldehyde, *n*-butyllithium, 1-naphthylmethanol, 2-acetylnaphthalene, 3-acetylphenanthrene, 9-anthraldehyde, 1-pyrenecarboxaldehyde, acetophenone, *p*-nitrosodimethylaniline, lithium aluminum hydride, sodium hydride, chlorotrimethylsilane, and sodium chloride (Aldrich), *N*,*N*-dicyclohexylcarbodiimide and dibromotoluene (Lancaster), benzoyl peroxide, pyridine, chloroform, ethyl acetate, tetrahydrofuran, toluene, dichloromethane, cyclohexane, carbon tetrachloride, and sodium sulfite (Mallinckrodt), sulfuric acid (EM Science), potassium permanganate and sodium hydroxide (Fisher), *m*-(dimethylamino)acetophenone (Tokyo Kasei), and Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ catalyst (Strem) were used without further purification. *N*-Bromosuccinimide (Aldrich) was recrystallized from water.

Photochemical Methods. Extinction coefficients were determined from Beer's law. Quantum yields for emission from the first excited singlet state were determined by comparison of integrated intensity with known standards: anthracene (ϕ_f = 0.27), naphthalene (ϕ_f = 0.21), phenanthrene (ϕ_f = 0.13) and pyrene (ϕ_f = 0.53).[28]

Experimental Determination of k_p (Rate of Polymerization)/k_i (Rate of Initiation). To a solution of Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ (10 mg, 0.02 mmol) in benzene-d_6 (0.5 mL) was added 50 equiv of 2-methyl-1-phenyl-2,3-dioxonorbornene (23 mg, 0.10 mmol) monomer in 0.5 mL of benzene-d_6. This yellow solution was allowed to stir for 2 min, after which it was transferred under nitrogen to an NMR tube. Integrated areas of the alkylidene signal at 11.40 ppm and the initiator signal at 11.25 ppm were determined to be 6.1 and 9.1, respectively. The ratio of the initiator area to the sum of the areas of the initiator and alkylidene signals (0.603) was inserted into eq 6, which was solved for r.

Molecular Modeling. Low-energy conformations of polymers were minimized in an MM+ force field on a Silicon Graphics workstation using the Hyperchem molecular modeling program.

Monomer Synthesis. The monomer precursor (*exo*,*cis*-5-norbornene-2,3-diol) was prepared by literature procedures.[13] Acetal linkages to aryl ketones and aldehydes were prepared by a modification of a previous literature procedure.[29]

General Methods. (A) The aryl methyl ketone or aryl aldehyde (7.9 mmol) was added portionwise to a solution of *exo*,*cis*-5-norbornene-2,3-diol[13] (7.9 mmol) in 10 mL of CH_2Cl_2 under N_2. To this mixture was added chlorotrimethylsilane (26 mmol), and the resulting mixture was stirred at room temperature for 24 h. A 5% solution of aqueous $NaHCO_3$ (10 mL) was added, and the resulting mixture was extracted with ether (2 × 50 mL) and washed with brine (2 × 40 mL) before the combined extracts were dried over anhydrous $MgSO_4$. The ether was removed under reduced pressure, and the resulting white solid was recrystallized from methanol and acetone to yield the purified monomer.

(B) A solution of the aryl aldehyde or aryl methyl ketone (4.0 mmol), *exo*,*cis*-5-norbornene-2,3-diol (4.0 mmol),[13] toluene (10 mL), and *p*-toluenesulfonic acid monohydrate (4.8 mol) was stirred and heated to reflux for 30 min. The water formed during the reaction was removed by azeotropic distillation (Dean–Stark trap) over a period of 0.5–1 h. The reaction mixture was poured into water (11 mL), made alkaline with 50% aqueous NaOH (2 mL), and extracted with toluene (2 × 50 mL). After drying and evaporation of the organic layer, the yellowish residue was placed in the freezer overnight to induce crystallization. The resulting crystals were filtered and washed with methanol to yield the purified monomer.

The syntheses of monomers **2b**, **2c**, **2f**, and **2i** were reported as supplementary material in a previous communication.[12]

Preparation of the Methyl Phenyl Ketal of *exo*,*cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2a). Monomer was prepared by method A using 0.48 g (3.9 mmol) of acetophenone. The crude product was recrystallized from hexanes and acetone to yield 0.71 g of white diamond-shaped crystals (78%), mp = 65–66 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.44 (2H, d, J = 6.8 Hz), 7.31 (3H, m), 5.96 (2H, s), 3.93 (2H, s), 2.83 (2H, s), 2.13 (1H, d, J = 8.9 Hz), 1.72 (1H, d, J = 8.9 Hz), 1.63 (3H, s). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.69, 28.76, 38.66, 47.71, 85.49, 112.77, 125.77, 125.18, 125.24, 127.67, 127.94, 128.07, 131.24, 143.52. UV (CH_2Cl_2): λ_{max} = 258 nm (ϵ = 200 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 300 nm (Φ_{fl} = 0.002 for

λ_{ex} = 284 nm). HRMS (*m/e*): calcd for $C_{15}H_{16}O_2$, 229.1228; found, 229.1240.

Preparation of 2-Acetylanthracene. To 2-cyanoanthracene[31] (5 g, 0.025 mol) in 400 mL of THF at 0 °C was added 16.4 mL of 3.0 M methylmagnesium bromide in diethyl ether. This yellow solution was allowed to stir under reflux for 3 h, followed by the addition of 12.4 mL of concentrated HCl and additional stirring under reflux for 12 h. The resulting dark red solution was allowed to cool to room temperature for 1 h, at which time a yellow solid precipitated. The entire mixture was diluted with THF and washed with 10% $NaHCO_3$, dried over $MgSO_4$, and filtered. The excess solvent was removed under vacuum to obtain 4.8 g (87% yield), mp = 139–141 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.56 (s, 1H), 8.42 (s, 1H), 8.04 (m, 4H), 7.53 (m, 2H), 2.75 (s, 3H). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 122.61, 125.87, 126.13, 126.58, 128.12, 128.32, 128.63, 128.88, 130.27, 131.56, 131.95, 132.56, 133.15, 133.92, 197.84. HRMS (*m/e*): calcd for $C_{16}H_{12}O$ 221.0966; found 221.0963.

Preparation of the Methyl 2-Anthryl Ketal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2d). Monomer was prepared by method A using 1.06 g (4.80 mmol) of 2-anthryl ketone. The crude product was recrystallized from hexanes to yield 0.53 g of a yellow-white crystalline solid (76.0% yield), mp = 234–236 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.38 (s, 1H), 8.06 (s, 1H), 7.96 (m, 2H), 7.47 (m, 4H), 5.98 (s, 2 H), 4.03 (s, 2H), 2.89 (s, 2H), 2.19 (d, 1H, J = 8.9, Hz), 1.79 (d, 1H, J = 8.9 Hz). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 43.15, 44.99, 80.84, 113.83, 123.67, 123.89, 125.32, 125.87, 126.52, 128.04, 128.43, 131.08, 131.73, 131.79, 136.55, 140.23. UV (CH_2Cl_2): λ_{max} = 342 (ϵ = 4800 M^{-1} cm^{-1}), 360 (ϵ = 6600 M^{-1} cm^{-1}), 378 nm (ϵ = 5400 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = nm (Φ_{fl} = 0.7154 for λ_{ex} = 352 nm). HRMS (*m/e*): calcd for $C_{23}H_{20}O_2$, 328.1478; found, 328.1463.

Preparation of the Methyl 1-Pyrenyl Ketal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2e). Monomer was prepared by method A using 0.59 g (2.4 mmol) of 1-pyrenecarboxaldehyde. The crude product was recrystallized from hexanes to yield 0.59 g of yellow-white needles (59% yield), mp = 145–147 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.90 (1H, d, J = 8.9 Hz), 8.27 (1H, d, J = 7.9 Hz), 8.10 (7H, m), 5.96 (2H, s), 3.46 (2H, d, J = 4.9 Hz), 2.93 (2H, s), 2.29 (1H, d, J = 8.7 Hz), 2.01 (3H, s), 1.82 (1H, d, J = 8.7 Hz). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.13, 43.26, 45.12, 80.68, 115.05, 124.29, 124.48, 124.82, 125.06, 125.12, 125.12, 125.26, 125.91, 127.18, 127.33, 127.54, 128.27, 130.56, 131.26, 131.26, 131.42, 136.64, 136.69. UV (CH_2Cl_2): λ_{max} = 314 (ϵ = 13900 M^{-1} cm^{-1}), 328 (ϵ = 33900 M^{-1} cm^{-1}), 344 nm (ϵ = 50000 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 375 nm (Φ_{fl} = 0.0214 for λ_{ex} = 352 nm). HRMS (*m/e*): calcd for $C_{25}H_{20}O_2$ 352.1463; found, 352.1469.

Preparation of the 2-Naphthyl Acetal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2g). Monomer was prepared by method A using 0.62 g (3.9 mmol) of 2-naphthaldehyde. The crude product was recrystallized from hexanes to yield 0.90 g of clear needles (86% yield) mp = 100–101 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.96 (1H, s), 7.82 (3H, m), 7.64 (1H, d, J = 7.3 Hz), 7.47 (2H, m), 6.13 (2H, s), 6.06 (1H, s), 4.31 (2H, s), 2.96 (2H, s), 2.26 (1H, d, J = 9.0 Hz), 1.79 (1H, d, J = 9.0 Hz). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 43.33, 45.18, 81.37, 107.40, 123.87, 126.13, 126.38, 126.44, 127.72, 128.33, 132.97, 133.98, 134.03, 137.03. UV (CH_2Cl_2): λ_{max} = 276 (ϵ = 5900 M^{-1} cm^{-1}), 284 nm (ϵ = 4600 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 335 nm (Φ_{fl} = 0.229 for λ_{ex} = 284 nm). HRMS (*m/e*): calcd for $C_{18}H_{16}O_2$ 265.1228; found, 265.1217.

Preparation of 3-Phenanthraldehyde. 3-Phenanthraldehyde was prepared by reduction and hydration of 3-cyanophenanthrene, which was attained by photocyclization of cyanostilbene.[34] The sequence begins with the Wittig reaction of benzaldehyde with (*p*-cyanobenzyl)triphenylphosphonium bromide as catalyzed by DBU to give a mixture of *cis*- and *trans*-4-cyanostilbene (mp = 112–114 °C).[34]

The mixture of geometric isomers of 4-cyanostilbene was photochemically cyclized and oxidized in the presence of oxygen and iodine to give 3-cyanophenanthrene (mp – 78–80 °C).[35] ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.72 (m, 4H), 7.86 (s, 1H), 7.90 (m, 3H), 8.61 (d, 1H, J = 8.1 Hz), 8.99 (s, 1H). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 109.84, 119.53, 122.56, 126.05, 127.73, 127.83, 127.97, 128.22, 128.90, 129.38, 129.50, 130.02, 130.36, 132.24, 134.29. HRMS (*m/e*): calcd for $C_{15}H_9N$, 204.0805; found, 204.0813.

The 3-cyanophenanthrene was converted to 3-phenanthraldehyde by reaction with diisobutylaluminum hydride (DIBAL) in benzene followed by hydrolysis with dilute acid and water. (76% yield), mp = 67–69 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.26 (s, 1H), 9.16 (s, 1H), 8.76 (1H, J = 8.1 Hz), 8.08–7.63 (m, 7H). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 122.69, 125.10, 126.36, 127.18, 127.40, 127.49, 128.87, 129.49, 130.09. 130.35, 130.48, 132.19, 134.24, 136.02, 192.35. HRMS (*m/e*): calcd for $C_{15}H_{10}O_2$, 207.0809; found, 207.0816.

Preparation of the 3-Phenanthryl Acetal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2h). Monomer was prepared by method A using 0.30 g (1.3 mmol) of 3-phenanthraldehyde. The crude product was recrystallized from hexanes to yield 0.32 g of white crystals (80% yield), mp = 145–147 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.80 (1H, s), 8.70 (1H, d, 5.6 Hz), 7.57 (7H, m), 6.17 (1H, s), 6.15 (2H, s), 4.34 (2H, s), 3.45 (2H, s), 2.32 (1H, d, J = 8.7 Hz), 1.82 (1H, d, J = 8.7 Hz). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 43.37, 45.22, 81.44, 107.64, 121.29, 122.78, 124.64, 126.60, 126.62, 126.68, 127.57, 128.57, 128.87, 130.04, 130.37, 132.13, 132.83, 134.66, 137.05. UV (CH_2Cl_2): λ_{max} = 300 (ϵ = 10100 M^{-1} cm^{-1}), 335 nm (ϵ = 400 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 367 nm (Φ_{fl} = 0.016 for λ_{ex} = 335 nm). HRMS (*m/e*): calcd for $C_{22}H_{18}O_2$, 315.1376; found, 315.1385.

Preparation of the 2-Anthryl Acetal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2i). Monomer was prepared by method A using 0.46 g (1.5 mmol) of 2-anthraldehyde.[31–33] The crude product was boiled with hot hexanes, and the yellow solution was filtered from the brown precipitate. The yellow solution was placed in the freezer overnight to form a yellow solid. The yellow solid was then recrystallized from methanol to yield 0.10 g of yellow flakes (14% yield), mp = 215–218 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.41 (2H, d, J = 9.3 Hz), 8.10 (1H, s), 8.02 (2H, m), 7.62 (1H, d, J = 8.8 Hz), 7.45 (2H, m), 6.14 (1H, s), 6.08 (2H, s), 4.32 (2H, s), 2.98 (2H, s), 2.29 (1H, d, J = 8.8 Hz), 1.83 (1H, d, J = 8.8 Hz). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 43.35, 45.20, 81.41, 107.53, 123.35, 125.46, 125.62, 126.16, 126.88, 126.98, 128.17, 128.20, 128.78, 131.02, 131.85, 132.02, 132.08, 133.37, 136.94, 137.06. UV (CH_2Cl_2): λ_{max} = 260 (ϵ = 31100 M^{-1} cm^{-1}), 360 (ϵ = 5700 M^{-1} cm^{-1}), 378 nm (ϵ = 5000 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 408 nm (Φ_{fl} = 0.0819 for λ_{ex} = 352 nm). HRMS (*m/e*): calcd for $C_{22}H_{18}O_2$, 314.1306; found, 314.1309.

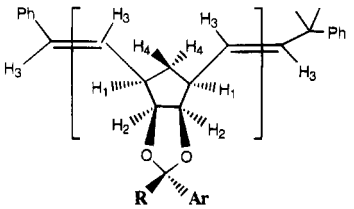
Preparation of the 1-Pyrenyl Acetal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2j). Monomer was prepared by method A using 1.82 g (7.9 mmol) of 1-pyrenecarboxaldehyde. The crude product was recrystallized from hexanes and acetone to yield 1.05 g of yellow-white needles (39% yield), mp = 149–151 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.47 (1H, d, J = 8.0 Hz), 8.35 (1H, d, J = 9.3 Hz), 8.14 (4H, m), 8.05 (2H, s), 7.96 (1H, t, J = 7.6 Hz), 7.23 (1H, s), 6.23 (2H, s), 4.49 (2H, s), 3.00 (2H, s), 2.23 (1H, d, J = 9.4 Hz), 1.79 (1H, d, J = 9.4 Hz). ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 43.44, 45.28, 81.55, 104.59, 122.67, 123.09, 124.67, 124.75, 125.33, 125.43, 125.91, 127.41, 127.78, 128.07, 128.69, 129.57, 130.62, 131.18, 131.94, 136.98. UV (CH_2Cl_2) λ_{max} = 278 (ϵ = 33200 M^{-1} cm^{-1}), 314 (ϵ = 11700 M^{-1} cm^{-1}), 328 (ϵ = 27900 M^{-1} cm^{-1}), 344 nm (ϵ = 44600 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 375 nm (Φ_{fl} = 0.0885 for λ_{ex} = 352 nm). HRMS (*m/e*): calcd for $C_{24}H_{18}O_2$, 338.1304; found, 338.1307.

Preparation of the (2,5-Dicyanophenyl Acetal of *exo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (2k). Monomer was prepared by method B using 0.18 (1.19 mmol) of *p*-dicyanobenzaldehyde.[31] The crude black product was recrystallized from hexanes and methanol to yield a crude brown solid. Recrystallization from ethanol yielded 70 mg (22%) of pure beige crystals, mp = 57–59 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.20 (1H, s), 7.80 (2H, s), 6.20 (1H, s), 6.15 (2H, s), 4.4 (2H, s), 2.95 (2H, s), 1.95 (1H, d, J = 9.4 Hz), 1.80 (1H, d, J = 9.4 Hz). ^{13}C-NMR (71 MHz, $CDCl_3$): δ 43.19, 44.95, 82.12, 102.82, 115.18, 115.65, 116.86, 116.99, 130.84, 132.91, 133.41, 136.87, 141.36. UV (CH_2Cl_2): λ_{max} = 296 (ϵ = 2.050 M^{-1} cm^{-1}), 286 nm (ϵ = 1900 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 417

nm (Φ_{fl} = 0.015 for λ_{ex} = 284 nm). HRMS (*m/e*): calcd for $C_{16}H_{12}N_2O_2$, 265.0977; found, 265.0970.

Synthesis of Homopolymers. General Method. To a solution of aryl-substituted monomeric acetal or ketal (2.05 mmol) in toluene (1.0 mL) under an inert drybox atmosphere was added dropwise a rapidly stirred solution of Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ (0.0205 mmol) in toluene (0.5 mL). The resulting solution was stirred for 30 min before the polymerization was quenched by the addition of 25 μL of benzaldehyde. After 20 min, the resulting solution was added to 250 mL of methanol, and the precipitated polymer was isolated by filtration before being reprecipitated from tetrahydrofuran into acetonitrile. The resulting white solid was filtered and placed under vacuum overnight to yield the purified polymer product.

The preparations of homopolymers **3b** and **3c** were reported as supplementary material in a previous communication.[12] Abbreviations for appended aryl groups in the ^{1}H-NMR of the homopolymers are defined as follows: naphthalene (nap), phenanthrene (phen), anthracene (anth), pyrene (pyr), pentamethylbenzene (pmb), *N*,*N*-dimethylaniline (dma), 2,5-dicyanobenzene (dcb), phenyl (phenyl). Standard segments of the polymer backbone described in the ^{1}H-NMR of the homopolymers and block polymers are used throughout and defined as follows:



H_1 = allylic CH
H_2 = CHO
H_3 = *cis* or *trans* CH=CH
H_4 = bridgehead CHH
R = H = acetal-H
R = CH_3 = ketal-CH_3

% transolefin for each homopolymer was calculated using the ratios of integration taken from the *trans*-CH=CH and *cis*-CH=CH resonance frequencies. Polydispersity indices (PDI) were obtained by gel permeation chromatography against polystyrene standards for all homopolymers.

Polymer 3a. Polymerization of **2a** (230 mg, 1.0 mmol) yielded 200 mg (88%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45−7.30 (br, phenyl), 5.50 (br, *trans*-CH=CH), 5.29 (br, *cis*-CH=CH), 4.10 (br, CHO), 3.2 (br, allylic CH), 2.7 (br, allylic CH), 2.1 (br, C*H*H bridgehead), 1.65 (br, ketal CH_3), 1.40 (br, CH*H* bridgehead). % trans olefin = 85. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.7, 28.8, 38.6, 47.7, 85.5, 112.8, 125.1, 125.2, 127.7, 127.9, 128.1, 131.2, 143.5. UV (CH_2Cl_2): λ_{max} = 258 nm (ϵ = 12300 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 300 nm (Φ_{fl} = 0.0467 for λ_{ex} = 284 nm). PDI = 1.15.

Polymer 3d. Polymerization of **2d** (130 mg, 0.41 mmol) yielded 120 mg (90%) of a yellow-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.40−7.20 (br, anth), 5.50 (br, *trans*-CH=CH), 5.48 (br, *cis*-CH=CH), 4.10 (br, CHO), 2.75 (br, allylic CH), 2.00 (br, allylic CH), 1.78 (br, CMe), 1.6−1.4 (br, CH*H* bridgehead). % trans olefin = 96. ^{13}C-NMR (90.8 MHz, $CDCl_3$): The polymer was not sufficiently soluble in any deuterated solvent to obtain a clean ^{13}C spectrum. Several attempts to obtain a spectrum of a dilute solution obtained from sonication of the polymer in chloroform-*d* only resulted in hydrolyzed polymer and cleaved anthracenyl ketone. UV (CH_2Cl_2): λ_{max} = 360 (ϵ = 137500 M^{-1} cm^{-1}), 342 (ϵ = 120370 M^{-1} cm^{-1}), 378 nm (ϵ = 108500 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 408 nm (Φ_{fl} = 0.2587 for λ_{ex} = 352). PDI = 1.42.

Polymer 3e. Polymerization of **2e** (140 mg, 0.41 mmol) yielded 120 mg (86%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.2−8.8 (br, pyr), 5.40 (br, *trans*-CH=CH), 4.85 (br, *cis*-CH=CH), 4.00 (br, CHO), 3.15 (br, allylic CH), 2.78 (br, allylic CH), 2.10 (br, C*H*H, bridgehead), 2.00 (br, ketal CH_3), 1.35 (br, CH*H* bridgehead). % trans olefin = 90. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.79, 28.88, 38.53, 43.55, 47.70, 47.85, 47.89, 85.32, 85.37, 85.45, 85.51, 85.61, 113.90, 124.00, 124.07, 124.09, 124.19, 124.41, 124.75, 125.04, 125.19, 125.29, 125.32, 125.46, 125.84, 126.04, 127.10, 127.18, 127.29, 127.47, 127.55, 127.93, 128.02, 128.45, 129.02, 130.46, 131.20, 131.34, 131.48, 131.51, 136.53, 136.58, 136.67, 136.72. UV (CH_2Cl_2): λ_{max} − 314 (ϵ = 110081 M^{-1} cm^{-1}), 328 (ϵ = 256500 M^{-1} cm^{-1}), 344 nm (ϵ = 355000 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 375 nm (Φ_{fl} = 0.0068 for λ_{ex} = 352 nm). PDI = 1.32.

Polymer 3f. Polymerization of **2f** (110 mg, 0.41 mmol) yielded 100 mg (90%) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32−6.55 (br, dma), 5.48 (br, *trans*-CH=CH), 5.32 (br, *cis*-CH=CH), 4.40 (br, CHO), 2.98 (br, NCH_3, *trans*), 2.85 (br, NCH_3, *cis*), 2.80 (br, allylic CH), 2.50 (br, allylic CH), 1.78 (br, CH*H* bridgehead), 1.60 (br, ketal CH_3), 1.20 (br, C*H*H bridgehead). % trans olefin = 89. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.82, 28.88, 29.20, 36.77, 36.83, 36.87, 36.91, 40.71, 43.02, 46.89, 47.01, 47.18, 86.59, 86.66, 87.47, 109.48, 109.64, 111.88, 112.79, 113.71, 113.91, 114.02, 126.11, 128.49, 128.66, 128.83, 131.33, 131.40, 131.55, 131.61, 132.49, 132.54, 145.60, 145.99, 150.13, 150.18. UV (CH_2Cl_2): λ_{max} = 260 (ϵ = 339700 M^{-1} cm^{-1}), 308 nm (ϵ = 64000 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 357 nm (Φ_{fl} = 0.91 for λ_{ex} = 284 nm). PDI = 1.33.

Polymer 3g. Polymerization of **2g** (110 mg, 0.41 mmol) yielded 100 mg (92%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ, 7.2−7.8 (br, nap), 5.98 (br, *trans*, acetal H), 5.85 (br, *cis*, acetal H), 5.55 (br, *trans*-CH=CH), 5.4 (br, *cis*-CH=CH), 4.40 (br, CHO), 3.25 (br, allylic CH), 2.80 (br, allylic CH), 1.51 (br, C*H*H bridgehead), 1.27 (br, CH*H* bridgehead). % trans olefin = 87. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 38.47, 47.48, 47.58, 76.75, 86.67, 86.73, 107.20, 107.32, 123.98, 126.02, 126.11, 126.15, 126.47, 126.68, 127.74, 128.29, 128.34, 131.36, 131.40, 131.49, 132.9, 134.03, 134.33. UV (CH_2Cl_2): λ_{max} = 276 (ϵ = 88350 M^{-1} cm^{-1}), 284 nm (ϵ = 66900 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 335 nm, (Φ_{fl} = 0.173 for λ_{ex} = 284 nm). PDI = 1.32.

Polymer 3h. Polymerization of **2h** (130 mg, 0.41 mmol) yielded 110 mg (85%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.2−8.7 (br, phenyl), 6.45 (br, *trans*, acetal H), 6.31 (br, *cis*, acetal H), 5.57 (br, *trans*-CH=CH), 5.4 (br, *cis*-CH=CH), 4.45 (br, CHO), 3.25 (br, allylic CH), 2.82 (br, allylic CH), 2.12 (br, C*H*H bridgehead), 1.51 (br, CH*H* bridgehead). % trans olefin = 88. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 38.46, 38.53, 47.31, 47.38, 53.40, 86.63, 104.59, 113.63, 122.51, 122.78, 123.01, 124.75, 124.97, 126.11, 126.36, 126.46, 126.71, 127.20, 129.02, 129.24, 129.30, 129.67, 130.64, 130.87, 130.97, 131.07, 131.44, 131.51, 131.58. UV (CH_2Cl_2): λ_{max} = 300 (ϵ = 95200 M^{-1} cm^{-1}), 335 (ϵ = 4500 M^{-1} cm^{-1}), 355 nm (ϵ = 3200 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 367 nm (Φ_{fl} = 0.020 for λ_{ex} = 335 nm). PDI = 1.28.

Polymer 3i. Polymerization of **2i** (130 mg, 0.41 mmol) yielded 120 mg (93%) of a yellow solid. The polymer was not soluble in any organic solvent. Therefore, ^{1}H-NMR, ^{13}C-NMR, and GPC characterization were not possible. The fluorescence spectrum in Figure 2 was obtained from a dilute solution (optical density 0.01) of the polymer which was sonicated in dichloromethane for ~2 h, followed by filtration from undissolved polymer.

Polymer 3i. Polymerization of **2j** (69 mg, 0.41 mmol) yielded 57 mg (83%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.30 (br, pyr), 8.10 (br, pyr), 8.05 (br, pyr), 6.71 (br, acetal H), 5.5 (br, *trans*-CH=CH), 5.30 (br, *cis*-CH=CH), 4.45 (br, CHO), 3.3 (br, allylic CH), 2.85 (br, allylic CH), 2.1 (br, C*H*H bridgehead), 1.32 (br, CH*H* bridgehead). % trans olefin = 88. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.87, 38.42, 38.45, 38.49, 47.43, 86.76, 86.87, 104.44, 104.54, 104.59, 122.86, 123.67, 124.58, 124.68, 125.16, 125.31, 125.39, 129.03, 129.69, 130.55, 131.12, 131.51, 131.57, 131.66, 131.98. UV (CH_2Cl_2): λ_{max} = 278 (ϵ = 267600 M^{-1} cm^{-1}), 330 (ϵ = 215000 M^{-1} cm^{-1}), 344 nm (ϵ = 296100 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 375 nm (Φ_{fl} = 0.0048 for λ_{ex} = 352 nm), 482 nm (large broad excimer band). PDI = 1.10.

Polymer 3k. Polymerization of **2k** (11 mg, 0.042 mmol) yielded 10 mg (91%) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.0−7.15 (br, dcb), 6.08 (br, *trans*, acetal H), 6.00 (br, *cis*, acetal H), 5.58 (br, *trans*-CH=CH), 5.40 (br, *cis*-CH=CH), 4.45 (br, CHO), 3.25 (br, allylic CH), 2.85 (br, allylic CH), 2.19 (br, C*H*H bridgehead), 1.20 (br, C*H*H bridgehead).

% trans olefin = 67. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 39.03, 42.66, 42.70, 43.32, 46.88, 47.03, 87.11, 87.17, 88.43, 88.58, 88.65, 103.38, 103.70, 115.46, 115.67, 115.70, 115.72, 115.77, 115.79, 115.88, 116.59, 116.72, 116.91, 116.99, 126.09, 128.21, 129.02, 131.30, 131.45, 131.51, 131.57, 131.61, 131.64, 131.78, 131.87, 131.89, 132.37, 132.40, 132.43, 132.47, 133.9, 133.86, 133.94, 134.01, 141.09, 141.17. UV (CH_2Cl_2): λ_{max} = 244 (ε = 135100 M^{-1} cm^{-1}), 286 (ε = 14700 M^{-1} cm^{-1}), 296 nm (ε = 14800 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 417 nm (Φ_{fl} = 0.10 for λ_{ex} = 284 nm). PDI = 1.27. **Polymer 3l.** Polymerization of **2l** (120 mg, 0.41 mmol) yielded 100 mg (90%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.35–7.10 (br, pmb), 6.25 (br, *trans*-CH=CH), 6.20 (br, acetal H), 5.63 (br, *trans*-CH=CH), 5.40 (br, *cis*-CH=CH), 4.40 (br, CHO), 2.95 (br, allylic CH), 2.55 (br, allylic CH), 2.3–1.9 (br, aryl Me_5), 1.5 (br, CH*H* bridgehead), 1.20 (br, C*H*H, bridgehead). % trans olefin = 89. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 15.95, 16.18, 16.26, 16.33, 16.40, 16.48, 16.53, 17.13, 17.17, 34.61, 34.67, 34.70, 46.63, 46.72, 46.79, 46.91, 84.69, 84.78, 85.91, 99.93, 100.14, 126.09, 126.12, 127.67, 131.43, 131.50, 131.58, 131.66, 131.70, 132.72, 132.79, 132.99, 133.76, 133.80, 136.02. UV (CH_2Cl_2): λ_{max} = 284 nm (ε = 25800 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 316 nm (Φ_{fl} = 0.073 for λ_{ex} = 284 nm). PDI = 1.23.

Synthesis of Diblock Copolymers. General Methods. To a solution of monomeric acetal or ketal (1.0 mmol) in toluene (1.0 mL) was added dropwise a rapidly stirred solution of Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ (0.02 mmol) in toluene (0.5 mL), and the resulting solution was stirred for 1 h. To this yellow viscous solution was added a second monomer (0.20 mmol) in toluene (1 mL), and the solution was stirred for an additional 30 min and then quenched by addition of 25 μL of benzaldehyde. After 20 min the resulting solution was added to 250 mL of methanol, and the precipitated polymer was isolated by filtration, before being reprecipitated from tetrahydrofuran into acetonitrile. The resulting white solid was filtered and placed under vacuum overnight to yield the purified polymer.

The preparations of diblock copolymers **4a**, **4b**, **4d**, and **4e** were reported as supplementary material in our previous communication.[12]

Polymer 4c. Polymerization of **2b** (67 mg, 0.20 mmol) with **2l** (56 mg, 0.20 mmol) yielded 98 mg (85%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.80 (br, nap), 7.50 (br, nap), 7.23 (br, pmb), 7.20 (br, nap), 7.19 (br, nap), 6.20 (br, acetal H, pmb), 5.66 (br, *trans*-CH=CH, pmb), 5.52 (br, *trans*-CH=CH, nap), 5.25 (br, *cis*-CH=CH, nap), 4.40 (br, *cis*-CH=CH, pmb), 4.10 (br, CHO, nap), 3.20 (br, allylic CH, nap), 2.7 (br, allylic CH, nap), 2.63 (br, allylic CH, pmb), 2.20 (br, aryl Me_5, pmb), 2.10 (br, C*H*H bridgehead, nap), 1.90 (br, allylic CH, pmb), 1.80 (br, C*H*H bridgehead, pmb), 1.80 (br, ketal CH_3, *trans*, nap), 1.75 (br, ketal CH_3, *cis*, nap), 1.42 (br, CH*H* bridgehead, pmb), 1.40 (br, CH*H* bridgehead, nap). % trans olefin = 88. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 15.97, 16.21, 16.29, 16.43, 17.19, 22.45, 28.82, 29.22, 40.78, 43.03, 46.19, 46.65, 46.91, 47.03, 47.20, 48.53, 48.93, 49.39, 84.71, 86.59, 86.67, 99.95, 109.61, 109.72, 109.85, 111.98, 112.19, 112.71, 112.78, 114.04, 127.68, 128.05, 128.70, 128.86, 131.41, 131.52, 131.63, 133.02, 133.77, 136.04, 146.03, 150.11. UV (CH_2Cl_2): λ_{max} (10:10 diblock) = 278 nm (ε = 58800 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 335 nm (Φ_{fl} = 0.042 for λ_{ex} = 284 nm). PDI = 1.36.

Polymer 4f. Polymerization of **2a** (230 mg, 1.0 mmol) with **2i** (64 mg, 0.20 mmol) yielded 250 mg (84%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.40 (br, anth), 7.90 (br, anth), 7.60 (br, m, anth), 7.40 (br, anth), 7.30 (br, phenyl), 5.90 (br, acetal H, anth), 5.60 (br, *trans*-CH=CH, anth), 5.50 (br, *trans*-CH=CH, phenyl), 5.30 (br, *cis*-CH=CH, phenyl), 4.40 (br, s, CHO, anth), 4.10 (br, CHO, *cis*, phenyl), 4.05 (br, allylic CH, phenyl), 3.10 (br, allylic CH, anth), 2.7 (br, allylic CH, anth), 2.10 (br, C*H*H bridgehead, phenyl), 1.80 (br, ketal CH_3, *trans*, phenyl), 1.70 (br, ketal CH_3, *cis*, phenyl), 1.20 (br, CH*H* bridgehead). % trans olefin = 80. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.79, 28.86, 31.01, 38.73, 43.89, 44.01, 47.81, 48.01, 85.61, 87.10, 112.46, 112.85, 125.27, 125.32, 126.08, 127.74, 128.16, 131.35, 131.35, 132.48, 143.65, 143.79. UV (CH_2Cl_2): λ_{max} = 256 (ε = 196300 M^{-1} cm^{-1}), 388 nm (ε = 14150 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 355 nm (Φ_{fl} = 0.028 for λ_{ex} = 352 nm). PDI = 1.20.

Polymer 4g. Polymerization of **2l** (58 mg, 0.20 mmol) with **2f** (56 mg, 0.20 mmol) yielded 100 mg (87%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.23 (br, m, pmb), 7.21 (br, m, dma), 6.90 (br, m, dma), 6.65 (br, m, dma), 6.20 (br, acetal H, pmb), 5.65 (br, *trans*-CH=CH, pmb), 5.51 (br, *trans*-CH=CH, dma), 4.40 (br, *cis*-CH=CH, pmb, dma), 4.40 (br, s, CHO, dma), 2.99 (br, NMe_3, *trans*), 2.90 (br, NMe_3, *cis*), 2.88 (br, allylic, dma), 2.65 (br, allylic, *trans*, pmb), 2.5 (br, allylic CH, dma), 2.20 (br, aryl Me_5, pmb), 1.90 (br, allylic CH, pmb), 1.80 (br, C*H*H bridgehead, pmb), 1.78 (br, CH*H* bridgehead, dma), 1.60 (br, ketal CH_3, *cis*, dma), 1.42 (br, CH*H* bridgehead, pmb), 1.41 (br, ketal CH_3, *trans*, dma), 1.20 (br, CH*H* bridgehead, dma). % trans olefin = 87. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 15.94, 16.18, 16.39, 17.16, 22.43, 25.50, 27.92, 28.79, 28.87, 29.19, 34.62, 34.70, 36.83, 36.91, 40.72, 43.02, 46.62, 46.89, 47.00, 47.18, 84.70, 86.59, 86.65, 87.47, 99.95, 109.54, 109.68, 111.92, 112.78, 112.87, 113.97, 114.11, 122.74, 126.11, 127.68, 128.03, 128.66, 128.83, 131.41, 131.49, 131.62, 132.51, 132.99, 133.77, 136.02, 146.01, 150.15. UV (CH_2Cl_2): λ_{max} (10:10 diblock) = 256 (ε = 58800 M^{-1} cm^{-1}), 308 nm (ε = 18080 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 357 nm (Φ_{fl} = 0.008 for λ_{ex} = 284 nm). PDI = 1.26.

Synthesis of Triblock Copolymers. General Method. To a solution of monomeric acetal or ketal (0.20 mmol) in toluene (1.0 mL) was added dropwise a rapidly stirred solution of Mo(CHCMe$_2$Ph)(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(O-*t*-Bu)$_2$ (0.02 mmol). The resulting solution was stirred for 30 min before a second monomer (0.20 mmol) in toluene (1 mL) was added, and the solution was stirred for an additional 30 min. Then a solution of a third monomer (0.20 mmol) in toluene (1 mL) was added, and the resulting solution was allowed to stir for an additional 30 min before the polymerization was quenched by the addition of 25 μL of benzaldehyde. After 20 min, the resulting solution was added to 250 mL of methanol, and the precipitated polymer was isolated by filtration before being reprecipitated from tetrahydrofuran into acetonitrile. The resulting white solid was filtered and placed under vacuum overnight to yield the purified polymer product.

The preparation of triblock copolymer **5d** was reported as supplementary material in our previous communication.[12]

Polymer 5a. Polymerization of **2a** (230 mg, 1.0 mmol) with **2b** (29 mg, 0.20 mmol) and **2i** (32 mg, 0.20 mmol) yielded 284 mg (96%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.60 (br, anth), 8.40 (br, anth), 8.20 (br, anth), 7.90 (br, anth, nap), 7.80 (br, nap), 7.50 (br, phenyl), 7.30 (br, phenyl), 5.90 (br, acetal H, anth), 5.60 (br, *trans*-CH=CH, anth), 5.50 (br, *trans*-CH=CH, phenyl), 5.25 (br, *cis*-CH=CH, phenyl), 4.40 (br, s, CHO, anth), 4.10 (br, s, CHO, nap), 4.09 (br, CHO, phenyl), 3.05 (br, allylic CH, anth), 3.2 (br, allylic CH, nap), 2.95 (br, NMe_3, *trans*), 2.8 (br, allylic CH, *trans*, nap), 2.70 (br, allylic CH, *trans*, phenyl), 2.20 (br, C*H*H bridgehead, anth and phenyl), 1.70 (br, ketal CH_3, phenyl), 1.60 (br, CH*H*, bridgehead, anth), 1.2 (br, C*H*H bridgehead, nap). % trans olefin = 80. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.81, 38.74, 43.72, 47.82, 85.62, 86.90, 112.45, 112.85, 125.27, 126.09, 127.739, 128.16, 131.35, 132.49, 132.97, 143.66, 143.82. UV (CH_2Cl_2): λ_{max} = 360 nm (ε = 508040 M^{-1} cm^{-1}), 378 nm (ε = 17100 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 460 nm (Φ_{fl} = 0.0122 for λ_{ex} = 284 nm). PDI = 1.36.

Polymer 5b. Polymerization of **2a** (230 mg, 1.025 mmol) with **2c** (28 mg, 0.20 mmol) and **2k** (27 mg, 0.20 mmol) yield 270 mg (95%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.70 (br, phen), 7.95 (br, phen), 7.90 (br, dcb, phen), 7.60 (br, phen), 7.50 (br, phenyl, phen), 7.20 (br, phenyl), 6.05 (br, acetal H, dcb), 5.50 (br, *trans*-CH=CH, phenyl, phen, dcb), 5.25 (br, *cis*-CH=CH, phenyl, phen, dcb), 4.40 (br, s, CHO, dcb), 4.10 (br, s, CHO, phen), 4.09 (br, CHO, phenyl), 3.70 (br, allylic, *cis*, dcb), 3.1 (br, allylic CH, phen), 2.70 (br, allylic CH, phenyl, phen), 2.20 (br, C*H*H bridgehead, phen, phenyl), 1.80 (br, ketal CH_3, phen), 1.70 (br, ketal CH_3, phenyl), 1.40 (br, CH*H* bridgehead, phen, phenyl, dcb), 1.2 (br, C*H*H bridgehead, phenyl). % trans olefin = 80. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.79, 28.86, 29.12, 38.72, 39.25, 43.81, 47.79, 47.99, 85.59, 85.74, 86.89, 112.44, 112.83, 125.25, 127.72, 128.13, 131.32, 132.46, 143.64, 143.78. UV (CH_2Cl_2): λ_{max} = 300 (ε = 71,150

M^{-1} cm^{-1}), 350 nm (ϵ = 3540 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 367 nm (Φ_{fl} = 0.0136 for λ_{ex} = 335 nm), 454 nm (broad exciplex band). PDI = 1.11.

Polymer 5c. Polymerization of **2a** (230 mg, 1.025 mmol) with **2c** (67 mg, 0.20 mmol) and **2f** (56 mg, 0.20 mmol) yielded 330 mg (93%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.70 (br, phen), 7.95 (br, phen), 7.90 (br, phen), 7.60 (br, phen), 7.50 (br, phenyl, phen), 7.20 (br, phenyl, dma), 6.90 (br, dma), 5.50 (br, *trans*-CH=CH, phenyl, phen, dma), 5.25 (br, *cis*-CH=CH, phenyl, phen, dma), 4.40 (br, CHO, dma), 4.10 (br, CHO, phen), 4.09 (br, CHO, phenyl), 3.1 (br, allylic CH, *cis*, phen), 2.95 (br, NMe_2), 2.90 (br, allylic CH, *cis*, dma), 2.70 (br, allylic CH, *trans*, phenyl, phen), 2.50 (br, allylic CH, *trans*, dma), 2.20 (br, C*H*H bridgehead, phen, phenyl), 1.80 (br, ketal CH_3, phen), 1.70 (br, ketal CH_3, phenyl), 1.40 (br, CH*H* bridgehead, phen, phenyl, dma), 1.2 (br, C*H*H bridgehead, phenyl). % trans olefin = 80. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.69, 28.70, 28.85, 29.20, 38.61, 40.68, 47.70, 47.99, 85.51, 109.48, 109.62, 111.87, 112.44, 112.76, 112.97, 113.90, 113.99, 123.90, 123.96, 125.22, 126.03, 127.71, 127.90, 128.03, 128.13, 128.66, 131.21, 131.38, 131.60, 132.93, 140.95, 143.51, 145.99, 150.15. UV (CH_2Cl_2): λ_{max} = 256 (ϵ = 58840 M^{-1} cm^{-1}); 300 (ϵ = 3600 M^{-1} cm^{-1}), 335 nm (ϵ = 2880 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 367 nm (Φ_{fl} = 0.0195 for λ_{ex} = 335 nm); 433 nm (broad exciplex band). PDI = 1.10.

Synthesis of Tetrablock Copolymers. General Method. To a solution of monomeric acetal or ketal (0.205 mmol) in toluene (1.0 mL) was added dropwise a rapidly stirred solution of $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(O\text{-}t\text{-}Bu)_2$ (0.02 mmol). The resulting solution was stirred for 30 min before the second monomer (0.20 mmol) in toluene (1 mL) was added, and the solution was stirred for an additional 30 min. Then a solution of the third monomer (0.20 mmol) in toluene (1 mL) was added, and the solution was stirred for 30 min. Finally, the fourth monomer (90 mmol) was added, and the resulting solution was allowed to stir for an additional 30 min before the polymerization was quenched by the addition of 25 μL of benzaldehyde. After 20 min, the resulting solution was added to 250 mL of methanol, and the precipitated polymer was isolated by filtration before being reprecipitated from tetrahydrofuran into acetonitrile. The resulting white solid was filtered and placed under vacuum overnight to yield the purified polymer product.

Polymer 6. Polymerization of **2a** (230 mg, 1.0 mmol) with **2f** (28 mg, 0.10 mmol), **2c** (67 mg, 0.20 mmol), and **2k** (27 mg, 0.10 mmol) yielded 130 mg (76%) of a white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.70 (br, phen), 7.95 (br, phen), 7.90 (br, dcb, phen), 7.60 (br, phen), 7.50 (br, phenyl, phen), 7.20 (br, phenyl, dma), 6.90 (br, dma), 6.65 (br, dma), 6.05 (br, acetal H, dcb), 5.50 (br, *trans*-CH=CH, phenyl, phen, dcb, dma), 5.25 (br, *cis*-CH=CH, phenyl, phen, dcb, dma), 4.40 (br, CHO, dcb, dma), 4.10 (br, CHO, phen), 4.09 (br, CHO, phenyl), 3.70 (br, allylic CH, *cis*, dcb), 3.1 (br, allylic CH, *cis*, phen, phenyl), 2.95 (br, NMe_2), 2.9 (br, allylic CH, *cis*, dma, dcb), 2.75 (br, allylic CH, *trans*, phen), 2.70 (br, allylic, CH, *trans*, phenyl), 2.50 (br, allylic CH, *trans*, dma, dcb), 2.10 (br, C*H*H bridgehead, phen, dcb, phenyl), 1.80 (br, ketal CH_3, phen), 1.70 (br, ketal CH_3, phenyl, phen, dcb), 1.40 (br, CH*H* bridgehead, phen, phenyl, dcb, dma), 1.2 (br, C*H*H bridgehead, phenyl). % trans olefin = 89. ^{13}C-NMR (90.8 MHz, $CDCl_3$): δ 28.79, 28.87, 28.96, 29.09, 29.21, 29.23, 38.63, 38.76, 38.93, 39.13, 40.70, 43.69, 43.88, 43.95, 46.89, 47.79, 47.92, 48.00, 85.59, 85.74, 86.58, 86.67, 86.89, 87.05, 87.12, 87.18, 109.64, 111.87, 112.47, 112.79, 112.86, 113.17, 113.89, 115.86, 119.125, 122.90, 124.07, 125.27, 125.34, 125.43, 126.11, 126.15, 126.50, 126.55, 126.61, 127.07, 127.71, 127.75, 127.86, 128.05, 128.17, 128.29, 128.51, 128.56, 128.60, 128.67, 129.98, 130.35, 131.33, 131.41, 131.51, 131.56, 131.75, 132.12, 132.48, 132.58, 133.96, 141.14, 141.86, 143.63, 143.78. UV (CH_2Cl_2): λ_{max} = 256 (ϵ = 106900 M^{-1} cm^{-1}), 300 (ϵ = 554500 M^{-1} cm^{-1}), 335 nm (ϵ = 2500 M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{max} = 368 nm (Φ_{fl} = 0.0098 for λ_{ex} = 335 nm), 445 nm (broad exciplex bands). PDI = 1.17.

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