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Dendrimer–Linear Polymer Hybrids through ROMP

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A dendritic, highly monodisperse hybrid polymer is produced by ring-opening metathesis polymerization of a norbornenediol ketal affixed to a second-generation dendron bearing multiple aromatic (naphthyl) chromophores. Substantial excimer emission observed in the hybrid polymer attests to significant polymer aggregation and interchromophore interaction, even in dilute solution.

Introduction

The synthesis of monodisperse linear polymers that bear dendritic side groups and therefore possess many of the desirable properties of dendrimers (e.g., high solubility, ease of industrial processibility, and low intrinsic viscosity) has become an increasingly attractive scientific goal.[1–7] Such macromolecules could be obtained, in principle, either by polymerization of an appropriately functionalized dendron or by appending dendrimer segments to an existing polymer. Ring-opening metathesis polymerization (ROMP) has been shown in the last several years to be a technique for achieving low polydispersities across a wide array of molecular weights, but so far no report has appeared in which ROMP has been adopted as a useful synthetic route to hybrid polymers bearing dendrimer or dendritic segments.

Preliminary descriptions of other approaches to related families of hybrid polymers have recently appeared. For example, the first polymerization of a monomer bearing a pendent hyperbranched group was prepared by Fréchet and co-workers.[8] Schlüter and co-workers have also sought to make hybrid dendrimer-containing rigid-rod polymers based on poly[1.1.1]-propellanes or poly(*p*-phenylene)s[9] in which a cylindrical morphology was envisioned as useful for vesicle and membrane applications.[10,11] Recently, this same group both prepared Fréchet-type second-generation dendrons with an isocyanate functionality at the focal point and attached dendrimers to styrene monomers in order to study the effect of backbone rigidity on the hybrid's packing,[11] although neither the structure nor the properties of these materials have yet been reported. Similarly, Tomalia has grown dendrimers from linear poly(ethylene imines),[12] and Percec has reported polymethacrylates with highly tapered side chains that organize into hexagonally packed cylindrical columns in the solid state.[13]

In our approach, we sought to append a chromophore-labeled dendrimer segment to a monomer that could be polymerized by ROMP in order to assemble, in only a few steps, high molecular weight molecules (such as **1**) heavily loaded with poly(aryl ether) dendrons, thus defining a new polymer architectural hybrid. Chromophore- and quencher-labeled ROMP homopolymers and block copolymers designed for photoinduced electron and energy transfer have been previously described by our research group, e.g., **2**,[14–16] and we wished to understand how the photophysical properties of such homopolymers might change when the simple chromophore of **2** is replaced by a chromophore-labeled dendrimer segment,[16] e.g., in **1** (Figure 1). This work seeks to test the possibility that molecular architecture may drive the insertion of new properties in such hybrids by taking advantage of "skeletal macromolecular isomerism".[17]

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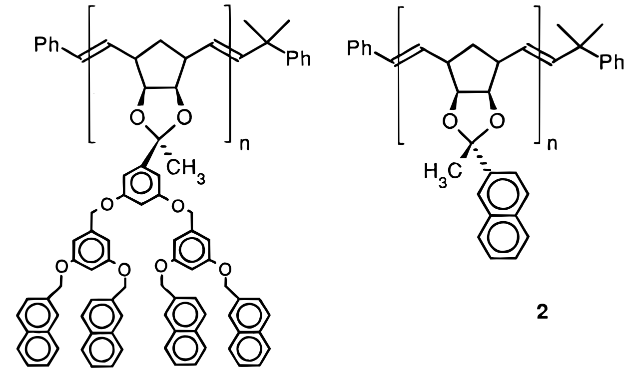

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Figure 1. ROMP homopolymers bearing a single chromophore **2** and an appended naphthyl-capped dendron **1** in each repeat unit.

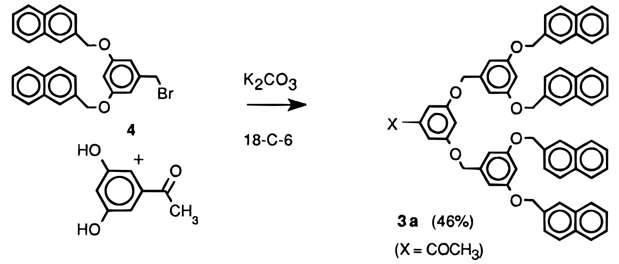


Figure 2. Synthesis of an acyl-terminated dendron **3a** from **4** and 3,5-dihydroxyacetophenone.

We describe here our results in preparing the ROMP polymer **1** heavily loaded with absorptive dendritic antenna segments. In this approach, chromophores were appended via an acetal or ketal linkage to *exo-cis*-norbornenediol.[18] The norbornenyl monomer was selected because it is known to add irreversibly to a living ROMP polymer chain,[14−16] permitting access to homopolymers and block copolymers of low polydispersity when the commercially available molybdenum amide [Mo(CH-*t*-Bu)(N-2,6-*i*-$Pr_2C_6H_3$)(O-*t*-$Bu)_2$][19] is used as polymerization initiator.

Monomer Synthesis

A dendron terminated as an aldehyde or ketone was required for attachment to the norbornenyl diol by an acetal or ketal linkage for the monomeric precursor to polymer **1**. The acyl-terminated dendron **3a** (X = $COCH_3$) was prepared by condensing 3,5-dihydroxyacetophenone with the naphthyl-capped first generation dendron **4**[16] (Figure 2). Many of the spectral features of **3a** are similar to those of **3b** (X = CH_2OH), whose synthesis has been described before.[17] Dendron **3a** was then attached to *exo-cis*-norbornenediol in the presence of trimethylsilyl chloride to give the monomer **5** (Figure 3).

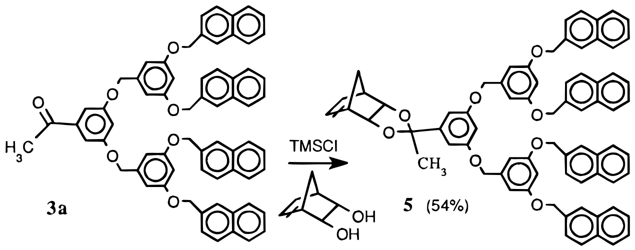
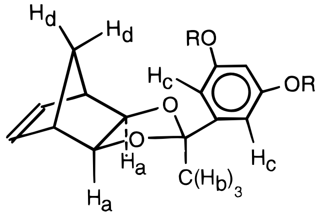


Figure 3. Synthesis of monomer **5** required for ROMP polymerization to **1**.

Nuclear Overhauser effect (NOE) experiments were used to assign the three-dimensional structure of monomer **5**. The orientation of the hydrogens (H_b) of the ketal methyl group and the dendrimer ortho hydrogens (H_c) relative to the norbornyl *endo* protons H_a was determined by selective irradiation at 4.38 ppm (the resonance frequency of protons H_a). A positive enhancement of the signal assigned to methyl protons H_b was observed, while no enhancement of H_c was detected. Selective irradiation of the apical protons H_d was not possible because of significant overlap of its resonance with that of the methyl protons H_b:



The spatial requirements of a second generation poly(benzyl ether) dendrimer segment[17] attached as a chromophore in homopolymer **1** is easily accommodated by the ROMP polymer chain. Molecular models by Hyperchem molecular modeling showed that the shortest distance between chromophores appended to adjacent monomer units was 3.7 Å for polymer repeat units joined by *cis*-isotactic or *cis*-syndiotactic linkages.[20] (The distance between repeat units joined by trans linkages was not reported.) Thus, the assembled ROMP polymer should easily provide enough space for second generation dendrons, which have been shown previously to exhibit effective electronic coupling between the peripheral light-absorbing units and the dendron focal point.[16]

Polymerization

Standard ROMP polymerization conditions were employed to convert monomer **5** into polymer **1**. Gel permeation chromatography showed excellent molecular weight control (from a defined initiator-to-monomer ratio), producing an apparent polydispersity of 1.3. Furthermore, spectroscopic data for **1** were fully consistent with structure **1**. Polymer **1** showed high solubility in tetrahydrofuran (THF), CH_2Cl_2, and $CHCl_3$.

Steady-State Fluorescence

Strong fluorescence is observed in monomer **5**, in its structural analogues **3a** and **3b**, and in polymer **1**, in both THF and CH_2Cl_2 (Table 1). More efficient emission is observed in polymer **1** in THF than in any of the structurally related monomers, although this difference disappears in dichloromethane. One possible explana-

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Table 1. Fluorescence Quantum Yields for 1 and Relevant Models[a]

compound	λ_{em} (nm)	Φ_f (THF) ±0.02	Φ_f^c (CH_2Cl_2) ±0.02
1	335, 400[b]	0.048	0.028
5	335	0.033	
3a	335	0.015	
3b	290, 335[c]	0.020[c]	0.028

[a] Measured as ~10^{-7} M degassed solutions; excited at 284 nm. [b] Shoulder. [c] Compound **3b** was not soluble in THF. As a result, this measurement was made in CH_3CN.

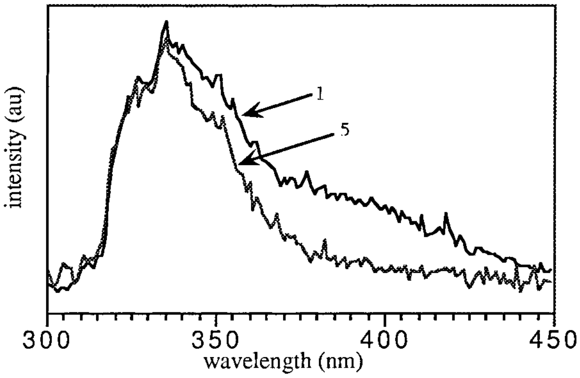

Figure 4. Fluorescence spectra of polymer **1** and monomer **5** in degassed THF, λ_{ex} = 284 nm.

tion is that intermolecular aggregation is less important in THF, so that excimer emission arising from interchain events is less pronounced, although Fréchet and co-workers have observed that dendritic macromolecules often have spherical shapes that would predict dense packing of the outer generation.[4,5,7]

The steady-state fluorescence spectrum of monomer **5** shows only contributions from the naphthalene singlet (centered at about 330 nm): no naphthalene excimer emission is observed (even when OD ~ 0.1). In contrast, in polymer **1**, both the naphthalene singlet (centered at about 335 nm) and excimer emissions (centered about 400 nm) can be observed in THF (Figure 4). A slight decrease in the relative magnitude of the excimer signal occurs when the solution is diluted, but even at very low concentrations (OD ≤ 0.01) weak excimer emission persists.

Thus, we infer that the dendritic repeat units in polymer **1** do not adopt the same conformation as in the isolated monomer **5** in dilute solution. Instead, the excimer signal in **1** probably arises from interchain interactions deriving from polymer aggregation, from intradendron events arising from the increased steric constraints on the dendrimer segment in the polymer, or from encounters by naphthyl groups attached to adjacent repeat units in the polymer (“nearest-neighbor dendron”). Our inability to suppress the excimer emission upon dilution argues for at least a partial contribution from one of the latter modes. However, the intensity of the excimer emission in **1** is slightly lower in THF than in CH_2Cl_2, suggesting that varying degrees of polymer aggregation or solvation induced by differences in solvent dielectric may also contribute to the observed effect.

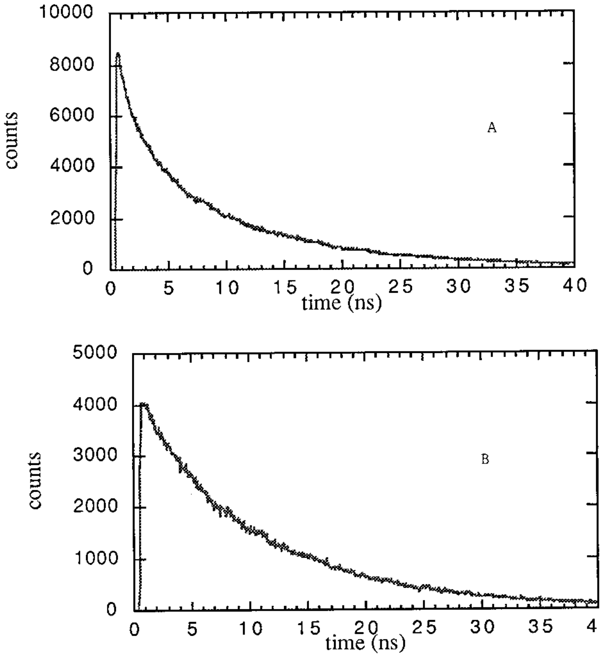

Figure 5. Decay traces for the transients produced by flash excitation of degassed solutions of (A) polymer **1** and (B) monomer **5** in THF, λ_{ex} = 284 nm, λ_{em} = 340 nm. Chromophore concentration: 10 mM.

Table 2. Fluorescence Lifetimes for Isolated Naphthalene Units and Excimer Emission in 1 and Relevant Models[a]

compound	τ_1 (ns) 340 nm	τ_2 (ns) 340 nm	τ_3 (ns) 400 nm growth
1	12 (0.53)	2.4 (0.47)	12
5	11 (1.0)		
3a	6.0 (0.16)	1.2 (0.84)	
3b	10 (1.0)		

[a] Dilute solutions in THF (~10^{-6} M) were bubble degassed with Ar; λ_{ex} = 284 nm.

Time-Resolved Fluorescence

Decay traces for **5** and **1** at 340 nm are shown in Figure 5. Monomer **5** and its structural analogue **3b**[17] exhibit clear single-exponential decays attributable to isolated naphthalene units, with lifetimes of about 10 ns (Table 2). The acyl-terminated dendron **3a** shows biexponential decay at this wavelength, presumably a result of facile intersystem crossing caused by the carbonyl group. Polymer **1** also shows biexponential decay, but in **1** this is most likely indicative of at least two distinct local environments in the heavily loaded polymer. In parallel to this observed fluorescence decay, the rise time for the excimer signal at 400 nm is easily detected in the polymer. The rise and decay lifetimes were obtained by single-photon counting, and good fit was attained (R = 0.9987).

Conclusions

A norbornenyl monomer bearing a second-generation naphthyl-capped dendron prepared under standard ROMP conditions has low polydispersity and high solubility in THF, CH_2Cl_2, and $CHCl_3$. The presence of an array of naphthyl groups at the periphery of the dendron serves as a fluorescent probe for the three-dimensional structure of this hybrid dendrimer–polymer. Whereas the previously reported ROMP polymer **2** (with one appended aryl chromophore per repeat unit) is rigid enough to prevent excimer formation,[14,15] the pendent dendrimer units are apparently sufficiently flexible to allow appreciable excimer formation in **1**. It is therefore unlikely that **1** will show substantial advantage over the more simply substituted analogue **2** as a medium for vectorial electron or energy transport. However, these hybrid materials may have other promising applications that depend on efficient light-harvesting properties or on this unique molecular architecture.

Experimental Section

Materials. *exo-cis*-Norbornenediol[18] was prepared by literature methods. 3,5-Dihydroxyacetophenone (Aldrich) was recrystallized from ethanol. Trimethylsilyl chloride and benzaldehyde (Aldrich) were distilled prior to use. Acetone was distilled from anhydrous K_2CO_3 that had been dried in a 130 °C oven prior to use.

Techniques. All manipulations or air- and/or water-sensitive compounds were carried out with standard Schlenk techniques or in a N_2-filled Vacuum Atmospheres HE-493 drybox. Nitrogen was purified by passage through columns of Linde 4 Å molecular sieves, drierite, and oxygen-scavenging Ridox. THF (B&J, spectroscopic grade) was distilled twice from sodium benzophenone ketyl and then degassed by three freeze−pump−thaw cycles. THF was stored over anhydrous Al_2O_3 in a drybox and was filtered immediately before use.

Polydispersity indices (PDI) were determined by gel permeation chromatography (GPC) in CH_2Cl_2 using a Waters 550 HPLC pump, a Waters 410 differential refractometer, Rainin Dynamax absorbance detector, and a Waters 745 data module with Ultrastyragel 10^4, 10^3, and 500 Å columns in series, calibrated with polystyrene standards. Absorption spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Fluorescence spectra were recorded on an Aminco SLM-500C spectrofluorometer; all solutions were studied at an OD of ∼0.03 to ∼0.10. Fluorescence quantum yields were determined by reference to naphthalene in cyclohexane.[21] Lifetime measurements were recorded at the University of Texas Center for Fast Kinetics Research using previously described single-photon-counting techniques.[22]

Preparation of 3,5-Bis[3,5-bis(2-naphthylmethyloxy)-benzyloxy]acetophenone [3a]. A suspension of 3,5-bis[3,5-bis(2-naphthylmethyloxy)benzyloxy]benzyl bromide[17] (1.1 g, 2.3 mmol), 3,5-dihydroxyacetophenone (16 mg, 1.1 mmol), anhydrous K_2CO_3 (360 mg, 2.6 mmol), and 18-crown-6 ether (56 mg, 0.20 mmol) in dry acetone (50 mL) was heated at reflux under Ar for 7 h. Acetone was removed in vacuo, and the remaining solid was taken up in CH_2Cl_2 (2 × 40 mL) and then washed with distilled water (2 × 100 mL). The organic layer was concentrated in vacuo. The product was purified by flash column chromatography in 50% CH_2Cl_2:50% hexanes increasing to 67% CH_2Cl_2:33% hexanes to give a white solid in 46% yield, mp 109−111 °C. ^{1}H NMR ($CDCl_3$) δ 7.86−7.80 (m, 16 H), 7.52−7.46 (m, 12 H), 7.15 (d, J = 2.2 Hz, 2 H), 6.76 (t, J = 2.0 Hz, 1 H), 6.73 (d, J = 1.9 Hz, 4 H), 6.67 (t, J = 2.1 Hz, 2 H), 5.21 (s, 8 H), 5.01 (s, 4 H), 2.53 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 197.6, 160.2, 159.8, 139.0, 138.6, 134.2, 133.3, 133.1, 128.4, 127.9, 127.7, 126.4, 126.2, 126.1, 125.3, 107.4, 106.7, 106.5, 101.8, 70.27, 70.16, 26.74. HRMS (*m*/*z*) calcd for $C_{66}H_{52}O_7$ 956.3713; found 956.3725.

Preparation of Dendron-Substituted Monomer [5]. Trimethylsilyl chloride (176 mg, 1.44 mmol) was added to a solution of **3a** (458 mg, 0.479 mmol) and *exo-cis*-norbornenediol (60.8 mg, 0.482 mmol) in CH_2Cl_2 (10 mL) under Ar. After 12 h, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (6 mL). This mixture was extracted with CH_2Cl_2 (20 mL), washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The solid white product (279 mg, 54% yield) and starting material **3** (160 mg, 35% recovery) were isolated by column chromatography on neutral alumina in 40% CH_2Cl_2: 60% hexanes, mp 149−150 °C. ^{1}H NMR ($CDCl_3$) δ 7.88−7.83 (m, 16 H), 7.54−7.46 (m, 12 H), 6.86 (d, J = 2.0 Hz, 2 H), 6.77 (s, 4 H), 6.67 (s, 2 H), 6.58 (s, 1 H), 6.08 (s, 2 H), 5.20 (s, 8 H), 5.00 (s, 4 H), 4.38 (s, 2 H), 2.89 (s, 2 H), 1.85 (d, J = 8.9 Hz, 1 H), 1.63 (s, 3 H), 1.60−1.57 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 160.2, 159.7, 144.8, 139.4, 136.8, 134.3, 133.3, 133.1, 128.4, 128.0, 127.7, 126.4, 126.2, 126.0, 125.3, 114.0, 106.6, 104.5, 101.7, 101.6, 80.81, 70.24, 70.00, 45.35, 43.15, 25.70. HRMS (*m*/*z*) calcd for $C_{73}H_{60}O_8$ 1064.4288; found 1064.4283.

Polymerization of Monomer 5. A solution of monomer **5** (37 mg, 035 mmol) in THF (1.0 mL) was added in one portion to a rapidly stirred solution of catalyst (2.0 mg, 0.0036 mmol) in THF (0.5 mL), and the resulting solution was stirred under Ar for 30 min. The polymerization was quenched by the addition of benzaldehyde (200 μL) in one portion. The polymer was isolated by precipitation into methanol (50 mL), then purified by further precipitation from dichloromethane into methanol (2×). The product, a fine white powder, was isolated in ∼90% yield, mp 115−116 °C. ^{1}H NMR signals ($CDCl_3$) were very broad. Assignments were made by comparison to monomer and to known norbornyl ketal polymers:[20] δ 7.8−7.4 (naphthyl), 7.4−7.2 (naphthyl), 6.9−6.3 (phenyl), 5.3−5.1 (*trans*-C*H*=CH), 5.1−4.9 (*cis*-C*H*=CH), 4.9−4.8 (naphthyl C*H₂*), 4.8−4.7 (benzyl C*H₂*), 4.2−4.0 (C*H*O), 2.4−2.2 (allylic C*H*), 1.7−1.5 (allylic C*H*), 1.4 (C*Me*), 1.2 (bridgehead C*H*H), 0.8 (bridgehead C*H*H). ^{13}C NMR ($CDCl_3$) δ 160.1, 159.6, 144.8, 139.3, 134.2, 133.2, 133.0, 131.4, 128.3, 127.9, 127.7, 126.3, 126.1, 126.0, 125.3, 106.5, 104.9, 101.6, 101.6, 70.04, 70.04, 59.53, 47.07, 38.15, 31.23, 29.69, 28.19. M_w 18 500, M_n 13 900, PDI = 1.33 (refractive index detector); M_w 18 400, M_n 13 600, PDI = 1.35 (absorption detector). Thermal gravimetric analysis revealed that the resulting polymer is stable to 250 °C.

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