Ruthenium Catalyzed Synthesis of Cross-Conjugated Polymers and Related Hyperbranched Materials. Copoly(arylene/1,1-vinylene)s

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ABSTRACT: Dihydridocarbonyltris(triphenylphosphine)ruthenium catalyzed copolymerization of acetophenone and 1,4-bis((trimethylsilyl)ethynyl)benzene yields a linear copolymer—copoly[2-acetyl-1,3-phenylene/α,α′-bis((trimethylsilyl)methylene)-1,4-xylenylene]. This reaction involves regioselective catalytic addition of the ortho C−H bonds of acetophenone across the C−C triple bonds of 1,4-bis-((trimethylsilyl)ethynyl)benzene such that the hydrogen becomes bonded to the carbon which bears the trimethylsilyl group. A similar ruthenium catalyzed reaction between 1,4-bis((trimethylsilyl)ethynyl)-benzene and 2-methylacetophenone has been used to prepare α,α′-1,4-bis-[β-(trimethylsilyl)-2-acetyl-3-methylstyrenyl]benzene, a monomeric compound which possesses the same type of chromophore as the linear polymer. Analogous ruthenium catalyzed reaction of 4-((trimethylsilyl)ethynyl)acetophenone yields a hyperbranched material. All three of these cross-conjugated unsaturated materials have regularly alternating arylene and 1,1-vinylene units. These materials have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and by IR, UV, and fluorescence spectroscopy. Polymer properties have been measured by GPC, DSC, and TGA.

Introduction

While there has been considerable synthetic, practical, and theoretical interest in conjugated copolymers which have a copoly(arylene/1,2-vinylene) backbone due to their potential utility in a number of applications such as light emitting diodes,[1,2] there have been only a few examples of unsaturated cross conjugated systems based on copoly(arylene/1,1-vinylene) backbones. Such systems have been previously prepared by a multistep synthetic sequence which involves stoichiometric rather than catalytic organometallic reactions. For example, treatment of poly[2-(trimethylsilyl)-1-dicyclopentadienylzirconium-3,6-indenylene] with hydrochloric acid results in protonolysis of the carbon−zirconium bonds to yield dicyclopentadienylzirconium dichloride and low molecular weight copoly[1,4-phenylene/2-(trimethylsilyl)-1,1-vinylene].[3]

By comparison, we should like to report the one-step ruthenium catalyzed synthesis of copoly[2-acetyl-1,3-phenylene/α,α′-bis((trimethylsilyl)methylene)-1,4-xylenylene]. Thus dihydridocarbonyltris(triphenylphosphine)-ruthenium catalyzed copolymerization of acetophenone and 1,4-bis((trimethylsilyl)ethynyl)benzene directly yields the desired cross conjugated system (eq 1). α,α′-1,4-Bis-[β-(trimethylsilyl)-2-acetyl-3-methylstyrenyl]benzene, a model compound which contains a similar cross conjugated chromophomore, has been prepared by ruthenium catalyzed reaction between 1,4-bis[(trimethylsilyl)ethynyl]benzene and 2-methylacetophenone (eq 2). Similarly, we have been able to prepare a hyperbranched material which has a cross-conjugated arylene/1,1-vinylene backbone by treatment of 4-[(trimethylsilyl)-ethynyl]acetophenone with the ruthenium catalyst (eq 3). The ruthenium catalyzed reaction between α-tetralone and internal acetylenes such as (phenylethynyl)-trimethylsilane to yield *E*/*Z*-α-(8-α-tetralonyl)-β-(trimethylsilyl)styrene has been reported.[4]

Previously, we have been interested in the dihydridocarbonyltris(triphenylphosphine)ruthenium catalyzed step-growth copolymerization of aromatic ketones with α,ω-dienes. This regioselective anti-Markovnikov addition of the ortho C−H bonds of aromatic ketones, such as acetophenone, across the C−C double bonds of α,ω-dienes such as 1,3-divinyltetramethyldisiloxane yields, for example, copoly(2-acetyl-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disilaheptanylene).[5,6] This polymerization reaction is closely related to a reaction first reported by Murai, who discovered the ruthenium catalyzed ortho-alkylation of acetophenone by trimethylvinylsilane.[7,8]

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-250 spectrometer operating in the Fourier transform mode. ^{29}Si NMR spectra were recorded on an IBM Bruker WP-270-SY spectrometer. Five percent w/v chloroform-*d* solutions were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad band decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20-s delay was used to acquire ^{29}Si NMR spectra.[9] These were externally referenced to TMS. Residual chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. IR spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. UV spectra of methylene chloride solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer.

Fluorescence spectra were performed on a PTI instrument, equipped with a model A1010 Xe/Hg lamp and a model 710 photomultiplier defraction detector. Spectra were obtained on methylene chloride, toluene, and dimethyl sulfoxide solutions which had been degassed by bubbling argon through them for 10 min. Fluorescence quantum yields were determined relative to that of 7-diethylamino-4-methylcoumarin.[10]

Gel permeation chromatography (GPC) analysis of the molecular weight distribution of these polymers was performed on a Waters system. Two 7.8 mm × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked polystyrene, HR4 and HR2, in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.3 mL/min. The retention times were calibrated against known monodisperse polystyrene standards (929 000; 212 400; 47 500; 13 700; 794).

The glass transition temperatures (T_gs) of the copolymers were determined on a Perkin-Elmer DSC-7 instrument. The

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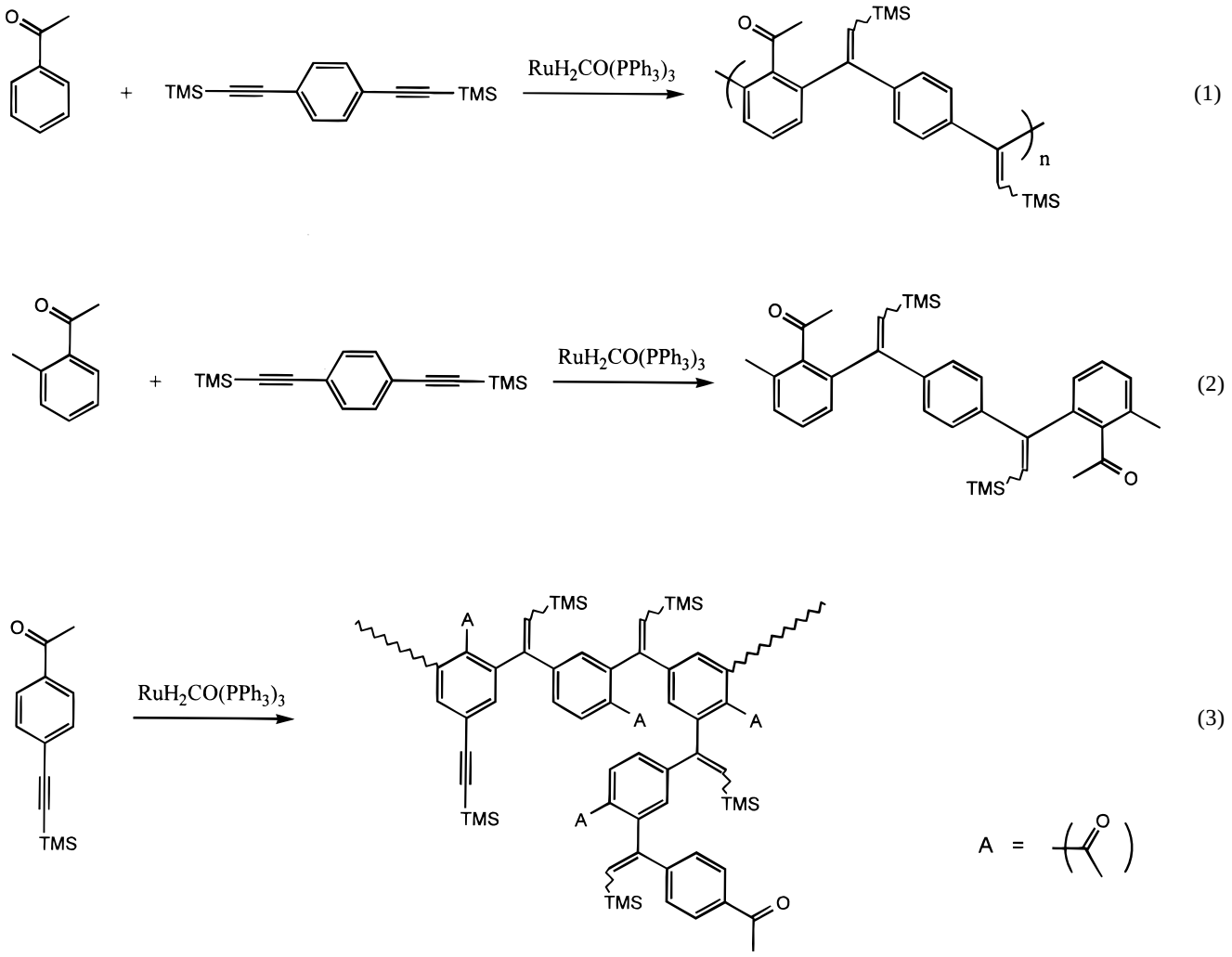


(1)

(2)

(3)

melting point of indium (156 °C) was used to calibrate the DSC. The analysis program was 10 °C/min from 25 to 200 °C.

TGA of the polymers was measured on a Shimadzu TGA-50 instrument. The temperature program was 5 °C/min from 25 to 750 °C. The temperature was held at 750 °C for an additional 5 min.

Elemental analyses were run by Oneida Research Services Inc., Whitesboro, NY.

High-resolution mass spectra were run at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF instrument. Ammonia was employed as the chemical ionization agent.

Predictions of ^{1}H NMR chemical shifts of arylene/1,1-vinylene and arylene/1,2-vinylene structures were generated by using ACD/HNMR 2.5 software from Advanced Chemistry Development, Inc., Toronto, Canada.

All reactions were carried out in flame-dried glassware under an atmosphere of purified argon. 4-Bromoacetophenone, styrene, tributylamine, acetophenone, 2-methylacetophenone, triphenylphosphine, and palladium acetate were obtained from Aldrich. 1,4-Bis((trimethylsilyl)ethynyl)benzene was acquired from Farchan. Dihydridocarbonyltris(triphenylphosphine)-ruthenium catalyst was prepared from ruthenium trichloride hydrate (Aldrich).[11]

4-(Trimethylsilylethynyl)acetophenone (75883-03-3). 4-((Trimethylsilyl)ethynyl)acetophenone was prepared by a palladium acetate catalyzed reaction between 4-bromoacetophenone and trimethylsilylacetylene.[12] ^{1}H NMR δ: 0.24 (s, 9 H), 2.56 (s, 3 H), 7.51 (d, 2 H, J = 8 Hz), 7.85 (d, 2 H, J = 8 Hz). ^{13}C NMR δ: −0.32, 26.38, 97.88, 103.89, 127.74, 127.94, 131.86, 136.19, 196.93. IR ν: 3004, 2961, 2901, 2160, 1686, 1601, 1560, 1405, 1359, 1265, 1251, 1220, 1179, 864, 842, 761 cm^{-1}. MS *m/e* (rel intensity): 216(49) M$^{\bullet+}$, 201(100) M − 15, 158(23), 143(7). High-resolution mass spectra (M$^{\bullet+}$) calcd for $C_{13}H_{16}OSi$: 216.0970. Found: 216.0975.

Hyperbranched Poly[4-((trimethylsilyl)ethynyl)acetophenone]. Dihydridocarbonyltris(triphenylphosphine)-ruthenium (14 mg, 0.014 mmol), 1 mL of toluene, styrene (1.6 μL, 0.014 mmol), and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube. The tube was purged with argon, capped, and heated at 135 °C for 3 min. The tube was cooled to room temperature, and a solution of 4-((trimethylsilyl)ethynyl)acetophenone (520 mg, 1.39 mmol) in 4 mL of toluene was added. Following a second argon purge, the tube was heated at 135 °C for 24 h. Solvent was removed from the hyperbranched material by evaporation under reduced pressure. The resulting crude material was taken up in a minimal amount of methylene chloride and was precipitated by addition of methanol. This process was repeated three times. In this way, 412 mg, 79% yield, M_w/M_n = 1550/1077, T_g = 113 °C, were obtained. ^{1}H NMR δ: −0.17 (s, 1.47 H), −0.11 (s, 2.51 H), −0.06 (s, 2.74 H), −0.01 (s, 1.25 H), 0.23 (br s, 0.55 H), 0.26 (br s, 0.48 H), 1.50−1.90 (br m, 0.76 H), 2.20−2.35 (br s, 1.19 H), 2.53 (s, 0.40 H), 2.58 (s, 0.65 H), 5.83−5.95 (br m, 0.38 H), 6.29−6.45 (br m, 0.28 H), 6.80−7.40 (br m, 2.74 H), 7.78−7.88 (br m, 0.60 H). ^{13}C NMR δ: −0.51, −0.21, −0.17, 0.0, 28.9, 29.6, 30.9, 31.4, 31.8, 103.3, 103.5, 126.6, 127.1, 127.3, 127.6, 127.8, 127.9, 128.1, 128.2, 128.5, 129.3, 129.5, 129.8, 129.9, 131.3, 131.9, 132.1, 132.6, 133.5, 134.2, 136.1, 137.3, 139.3, 140.8, 142.2, 144.2, 146.7, 153.1, 154.9, 156.0, 198.7, 202.2. ^{29}Si NMR δ: −8.59 (br s). IR ν: 2952, 2895, 2155, 1929, 1687, 1602, 1589, 1575, 1436, 1402, 1355, 1264, 1248, 1184, 1113, 1093, 1073, 1059, 1015, 957, 899, 861, 840, 772, 750, 694, 633, 621, 589 cm^{-1}. UV λ_{max} nm (ϵ): 230 (6621), 250 (7162), 284 (5676). When irradiated at 285 or 370

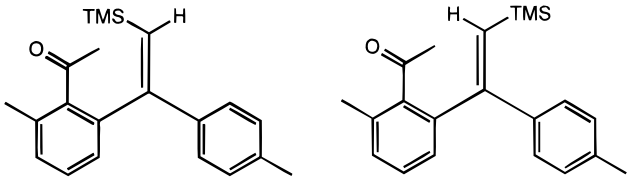
nm, fluorescence was observed at 450 ± 10 nm. The quantum yield (Φ) was equal to 0.001. The excitation scan had an adsorbance at 370 ± 5 nm. Elemental anal. Calcd for $C_{13}H_{16}OSi$: C, 72.22%, H, 7.41%. Found: C, 71.05%, H, 6.95%.

Copoly[2-acetyl-1,3-phenylene/α,α′-bis((trimethylsilyl)methylene)-1,4-xylenylene]. Dihydridocarbonyltris(triphenylphosphine)ruthenium (36 mg, 0.036 mmol), 1 mL of toluene, styrene (4 μL, 0.036 mmol), and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube. The tube was purged with argon, capped, and heated at 135 °C for 3 min. The tube was cooled to room temperature, and a solution of acetophenone (220 mg, 1.8 mmol) and 1,4-bis-((trimethylsilyl)ethynyl)benzene (500 mg, 1.8 mmol) in 4 mL of toluene was added. Following a second argon purge, the tube was heated at 135 °C for 24 h. Solvent was removed from the polymer by evaporation under reduced pressure. The resulting crude polymer was taken up in a minimal amount of CH_2Cl_2 and precipitated by addition of methanol. This process was repeated three times. In this way, 522 mg, 73% yield, M_w/M_n = 6560/5712, T_g = 173 °C, were obtained. ^{1}H NMR δ: −0.09 (s, 3.72 H), −0.065 (s, 5.12 H), −0.15 (s, 4.08 H), 0.40 (s, 5.07 H), 1.55−2.00 (br m, 2.85 H), 2.20−2.35 (br m, 0.15 H), 5.75−5.95 (br s, 0.88 H), 6.1−6.4 (br s, 0.84 H) 6.8−7.6 (br m, 7.28 H). ^{13}C NMR δ: −0.47, −0.15, 0.04, 24.7, 29.7, 31.0, 31.1, 31.5, 31.7, 31.9, 104.8, 126.5, 126.9, 127.5, 127.8, 128.4, 128.9, 129.1, 129.3, 129.7, 130.2, 131.0, 131.4, 131.6, 131.7, 135.8, 139.7, 140.9, 141.8, 143.1, 154.4, 155.9, 202.6, 204.7, 206.8. ^{29}Si NMR δ: −9.57(s), −9.08(s), −8.22-(s). The intensity ratio of these resonances is 1:2:1. IR ν: 3028, 3058, 2953, 2897, 2157, 1933, 1699, 1580, 1504, 1449, 1404, 1349, 1321, 1247, 1189, 1158, 1109, 1100, 1049, 1016, 983, 958, 900, 861, 841, 763, 728, 693, 671, 615, 600 cm^{-1}. UV λ_{max} nm (ε): 240 (49 180), 284 (36 486). When irradiated at 285 or 380 nm, fluoresence was observed at 420 ± 5 nm; Φ equal to 0.001. The excitation scan shows an adsorbance at 360 ± 10 nm. Elemental anal. Calcd for $C_{24}H_{30}OSi_2$: C, 73.85%, H, 7.69%. Found: C, 72.56%, H, 7.32%.

α,α′-1,4-Bis-[β-(trimethylsilyl)-2-acetyl-3-methylstyrenyl]benzene. Dihydridocarbonyltris(triphenylphosphine)-ruthenium (36 mg, 0.036 mmol), 1.5 mL of toluene, 2-methylacetophenone (490 mg, 3.6 mmol), and 1,4-bis((trimethylsilyl)ethylnyl)benzene (500 mg, 1.8 mmol) were placed in an Ace pressure tube. The tube was purged with argon, capped, and heated at 135 °C for 24 h. After workup, 619 mg, 62.5% yield, of α,α′-1,4-bis-[β-(trimethylsilyl)-2-acetyl-3-methylstyrenyl]benzene were isolated. ^{1}H NMR δ: −0.13 (s, 2.5 H), −0.06 (s, 2.5 H), −0.03 (s, 13 H), 2.04 (s, 0.4 H), 2.07 (s, 0.9 H), 2.23 (s, 1.4 H), 2.24 (s, 1.6 H), 2.26 (s, 3.4 H), 2.29 (s, 4.2 H), 5.86 (s, 0.3 H), 5.89 (s, 1.3 H), 6.35 (s, 0.1 H), 6.41 (s, 0.3 H), 6.86 (d, 1.7 H, J = 7.5 Hz), 7.08 (br s, 1 H), 7.10 (s, 1 H), 7.11 (s, 1.4 H), 7.13 (s, 0.5 H), 7.14 (s, 0.7 H), 7.16 (s, 0.4 H), 7.19 (s, 3 H), 7.22 (s, 0.3 H). ^{13}C NMR δ: −0.65, −0.13, −0.07, 19.6, 31.8, 32.1, 125.8, 126.4, 126.8, 127.1, 128.1, 128.3, 128.4, 129.2, 129.6, 1229.7, 129.9, 130.0, 131.5, 131.8, 131.9, 132.1, 132.4, 133.3, 133.5, 135.8, 136.0, 136.2, 136.4, 136.6, 136.8, 138.1, 141.6, 141.7, 141.9142.0, 142.2, 142.3, 143.0 153.5, 155.7, 205.7, 206.8, 206.9. ^{29}Si NMR δ: −9.61, −9.20, −8.59. UV λ_{max} nm (ε): 236 (18 100), 280 (11 760). When irradiated at 285 or 370 nm, fluorescence was observed at 410 ± 5 nm; Φ equal to 0.001. The excitation scan shows an adsorbance at 376 nm. High-resolution mass spectra ($M^{\bullet+}$) calcd for $C_{34}H_{42}Si_2O_2$: 538.2723. Found: 538.2731.

Results and Discussion

The ^{1}H NMR spectral data for the linear cross conjugated polymer copoly[2-acetyl-1,3-phenylene/α,α′-bis((trimethylsilyl)methylene)-1,4-xylenylene] is consistent with the structure proposed. The signals at 5.75−5.95 and 6.1−6.4 ppm, of equal intensity, are assigned to the protons of the terminal vinyl groups and are in agreement with the chemical shifts calculated for similar structures by the ACD/HNMR 2.5 program (Figure 1).



δ (ppm) vinylic H: 5.93 6.12

Figure 1. Calculated ^{1}H NMR chemical shifts by ACD/HNMR 2.5.

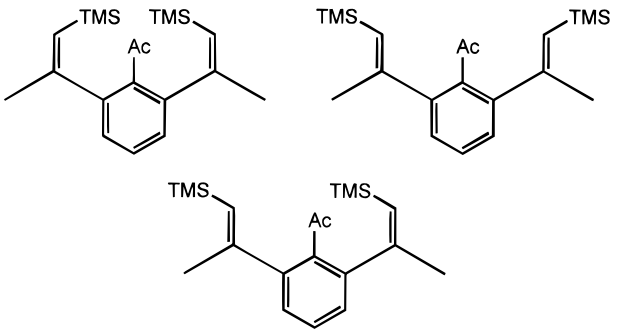


Figure 2. Diad microstructures of adjacent trimethylsilyl groups in copoly[2-acetyl-1,3-phenylene/α,α′-bis((trimethylsilyl)methylene)-1,4-xylenylene].

When both of the ortho positions are substituted, the resonances due to the acetyl methyl groups come between 1.55 and 2.00 ppm. On the other hand, when only one of the ortho positions is substituted, the resonance due to acetyl methyl group comes between 2.2 and 2.35 ppm. These are assigned to terminal groups. Integration of these two signals permits calculation of M_n by end group analysis. This is found to be equal to 7460, whereas by GPC a value for M_n of 5710 is observed. Considering that the GPC values are based on comparison to polystyrene standards, this seems to us to be in reasonably good agreement.

Three resonances which are in an intensity ratio of 1:2:1 are observed in the ^{29}Si NMR. These may result from the orientation of neighboring trimethylsilyl groups relative to the acetyl. Trimethylsilyl groups are sterically relatively large. Thus when two adjacent trimethylsilyl groups are both oriented toward the acetyl group, steric effects are expected to cause the acetyl group to twist out of coplanarity with the benzene ring changing the electronic nature of the acetyl unit. Similarly three carbonyl resonances are observed in the ^{13}C NMR spectrum (Figure 2).

The ^{1}H, ^{13}C, and ^{29}Si NMR of the monomer α,α′-1,4-bis-[β-(trimethylsilyl)-2-acetyl-3-methylstyrenyl]benzene, support the assignments made for the linear copolymer.

Careful analysis of the ^{1}H NMR of hyperbranched 4-((trimethylsilyl)ethynyl)acetophenone provides insight into the microstructure of the material. 4-((Trimethylsilyl)ethynyl)acetophenone is an AB_2 type monomer, in that it has two reactive ortho carbon−hydrogen bonds and a single (trimethylsilyl)ethynyl unit. Ruthenium catalyzed regioselective reaction occurs by addition of an ortho C−H bond across the carbon−carbon triple bond so that the hydrogen becomes bonded to the carbon which bears the trimethylsilyl group. According to Flory's analysis, each hyperbranched macromolecule possesses a single A unit (eq 3).[13] The ^{1}H NMR resonance for trimethylsilyl groups attached to an sp

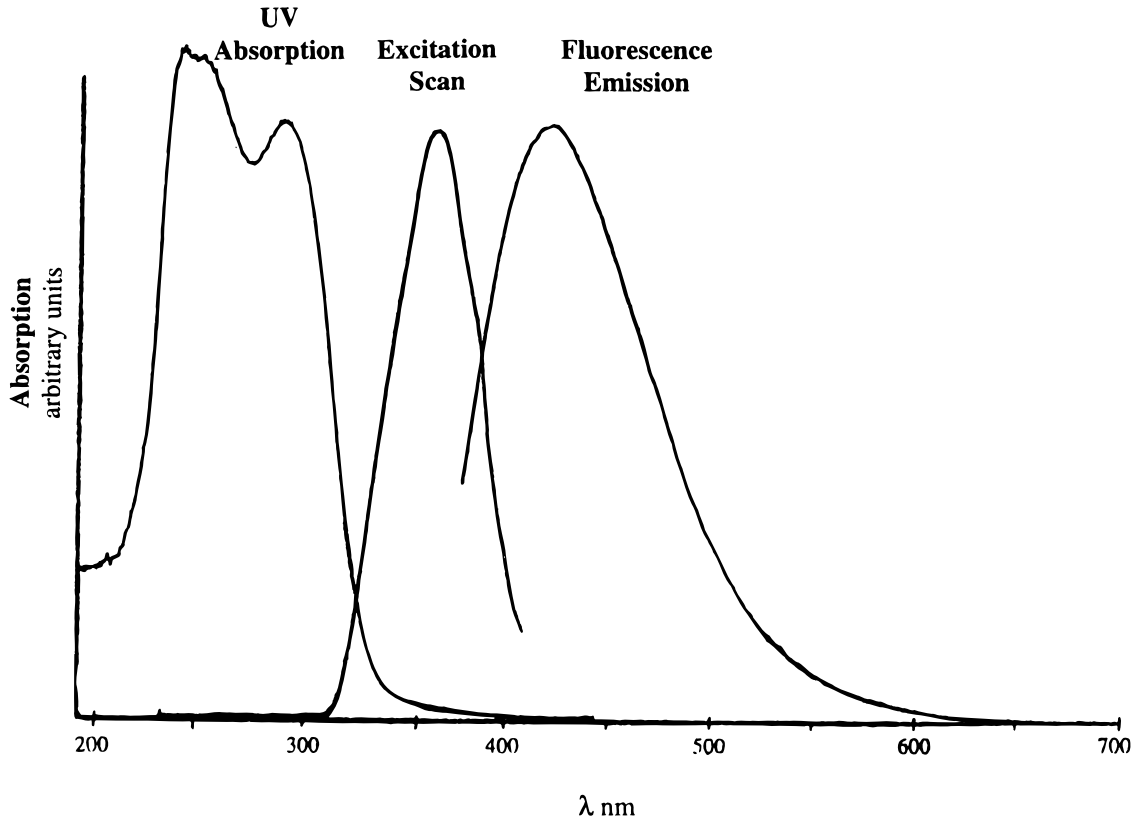


Figure 3. UV absorption, excitation scan, and fluorescence emission of copoly[2-acetyl-1,3-diphenylene/α,α′-bis((trimethylsilyl)-methylene)-1,4-xylenylene] (II).

hybridized carbon comes at 0.24 ppm, whereas those attached to an sp^2 hybridized carbon are found between −0.2 and 0.0 ppm. Integration of these proton signals permits us to determine that there are about 11 units of monomer in each hyperbranched macromolecule. Based on this end group analysis, the number average molecular weight (M_n) of the hyperbranched macromolecule should be approximately 2400. By GPC, M_w/M_n = 1550/1077. It has been previously found that the molecular weight obtained by GPC is often low for hyperbranched materials.[14]

The resonances due to the methyl group are particularly sensitive to substitution at the adjacent ortho positions. Specifically, sharp singlet resonances at 2.53 and 2.58 ppm are due to terminal units in which neither of the ortho C−H bonds is substituted. These assignments are based on the ^{1}H NMR of the starting material 4-((trimethylsilyl)ethynyl)acetophenone. Based on this assignment, there are ∼35% terminal units. The methyl resonances between 2.2 and 2.35 ppm correspond to methyl resonances from monosubstituted units ∼40%. Finally, the resonances between 1.55 and 1.90 ppm are due to signals from methyl which have both ortho positions substituted ∼25%. Branching occurs at each unit which is disubstituted. The resonance at 7.78−7.88 ppm is due to the ortho aromatic hydrogens of monosubstituted and terminal units. The resonances at 5.83−5.95 and at 6.29−6.45 ppm are assigned to the terminal protons of the vinylene units. The stereochemical assignments of these have been made by comparison to chemical shifts calculated for similar model structures by using ACD/HNMR 2.5 (Figure 1).

Both the linear and hyperbranched cross conjugated materials absorb at 284 nm, while the chromophore monomeric model compound, α,α′-1,4-bis-[β-(trimethylsilyl)-2-acetyl-3-methylstyrenyl]benzene, absorbs at 280 nm. The extinction coefficient for the linear material is larger (3.6×10^4) than that for either the hyperbranched (5.7×10^3) or the chromophore monomeric model (1.18×10^4). This difference may result from the increased length of the conjugated system in the linear material, which is of higher molecular weight than the hyperbranched material. The linear cross-conjugated polymer previously reported also has a strong absorption at 280 nm.[3] Irradiation of the linear cross conjugated material at either 285 or 380 nm results in a fluorescence emission which has a maximum at 420 ± 5 nm. The quantum yield for fluorescence is found to be $\Phi = 0.001$ (Figure 3). The large band gap in this polymer, along with its conjugated backbone, suggests that it may be useful as a carrier transporting material in organic LEDs and other optoelectronic applications. By comparison, irradiation of our hyperbranched material at 285 or 370 nm results in fluorescence at 450 ± 10 nm and $\Phi = 0.001$. Irradiation of the monomeric chromophore model compound at 285 or 370 nm results in a fluorescence emission at 410 ± 5 nm. Thus the wavelength of the fluorescence and the quantum yield for both the linear polymer and the monomeric chromophore model are quite similar. The fluorescence maximum observed for all three systems is only slightly affected by change of solvents from methylene chloride to toluene to dimethyl sulfoxide.

The linear polymer is thermally stable to 260 °C. Between 260 and 350 °C a few percent weight loss is observed. Above 350 °C rapid weight loss occurs. By 500 °C, a 35% weight loss is observed. Between 500 and 750 °C slower weight loss occurs. By 750 °C, 53% of the initial sample weight remains. The hyperbranched material is surprisingly thermally stable for

such a low molecular weight substance. It is thermally stable to 240 °C. Between 240 and 405 °C approximately 20% of the initial sample weight is lost. Above 405 °C a slower, almost linear, weight loss is observed. By 750 °C, 48% of the initial sample weight remains. By comparison, both the linear and the hyperbranched materials undergo a two stage thermal decomposition. The ultimate residue remaining at 750 °C in both is about 50%.

β-Styrenyltrimethylsilanes are well-known to be versatile synthetic building blocks which undergo a variety of electrophilic substitution reactions with loss of the trimethylsilyl group.[15,16] Thus it should be possible by use of a variety of electrophilic stoichiometric desilation reactions to chemically modify both copoly[2-acetyl-1,3-phenylene/α,α'-bis((trimethylsilyl)methylene)-1,4-xylenylene] and hyperbranched poly[4-((trimethylsilyl)-ethynyl)acetophenone]. This may permit the facile synthesis of a number of novel cross conjugated polymers which contain arylene/1,1-vinylene backbone units. In this regard it should be noted that there is considerable interest in the chemical modification of polymers.[17−20] Such modification may permit facile tuning of the fluorescence wavelength of these materials.

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