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Synthesis and Characterization of Wavelength-Shifting Monomers and Polymers Based on 3-Hydroxyflavone

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ABSTRACT: The synthesis of novel fluorescent polymers containing 3-hydroxyflavone (3HF) as a pendant group is described. Monomers prepared for radical bulk and solution polymerization include 3-hydroxy-4′-ethenylflavone (V3HF), 3-hydroxy-4′-(1-methylethenyl)flavone (MV3HF), and 3-hydroxy-4′-(1-phenylethenyl)flavone (ST3HF). All monomers were synthesized by a modification of the Algar–Flynn–Oyamada route generally used for flavonols. Homopolymers of V3HF and styrene copolymers of V3HF and MV3HF were characterized by molecular weight studies and DSC/TGA, which indicated higher glass transition temperatures and similar thermal stabilities compared to polystyrene. Both monomers and polymers exhibited spectral properties that were similar to 3HF proper, including a very large (>180 nm) red shift of absorbed light due to an intramolecular proton-transfer mechanism, making them suitable for use as radiation-hard intrinsic scintillators for the detection of high-energy radiation.

Introduction

Polymers containing photoactive moieties find applications as fluorescent labels, photon harvesters,[1-5] and scintillators.[6] Fluorescent labeling has been used to study water-soluble polymers, polyelectrolytes, and block copolymers, homopolymers, and random copolymers.[7-15] Water-soluble polymers with aromatic chromophores sensitize photochemical reactions.[16] Another innovation is the use of polymers in scintillating materials,[6] where a fluorescent molecule dispersed within a polymer matrix emits light on excitation by a high-energy particle.[17] These "plastic scintillators", which are conveniently processed into the form of plates or fibers, have faster response times than solid scintillators based on inorganic compounds and are thus useful in applications requiring high rates of energy analysis, such as particle accelerator facilities.

Plastic scintillators used in high-radiation fields are subject to damage,[18,19] which takes the form of radiation-induced color centers that severely attenuate light traveling through the medium. It was shown, however, that this radiation-induced damage can be circumvented, to some extent, with the use of a secondary dye that red shifts the emitted light to a region of the spectrum where self-absorption is minimized. A particularly effective wavelength shifter is 3-hydroxyflavone (3HF), first applied to plastic scintillator by Renschler and Harrah.[20] The large red shift was shown to be a consequence of an intramolecular excited-state proton transfer (ESPT). The ESPT mechanism has been studied extensively[21-26] and is shown in Figure 1. In the 3HF ESPT process the molecule absorbs a photon (λ_{max} = 340 nm) and a hydroxyl proton is transferred to a neighboring carbonyl group in the excited state. The resulting tautomer emits at a significantly lower energy (λ_{max} = 530 nm). There is very little contribution from the "normal" emission (410 nm) in nonpolar media, which, when combined with relatively high quantum efficiency (60% in polystyrene solid), fast decay (time constant of less than 7 ns), and radiation stability, presents a very attractive set of properties for the use of 3HF in scintillators. One of the major drawbacks is the photooxidative instability of 3HF.[27] A number of other compounds exhibiting proton-transfer emission have been reported. ESPT molecules commonly used for plastic scintillator molecules include 2-(2-hydroxyphenyl)benzoxazole, 2-(2-hydroxyphenyl)benzothioazole,[28,29] and 2,2′-bipyridyl-3-ol.[30] 10-Hydroxybenzo[*h*]quinoline[27] has one of the most red-shifted tautomer emissions, is more stable than 3HF to photooxidation, but suffers from low quantum efficiency.

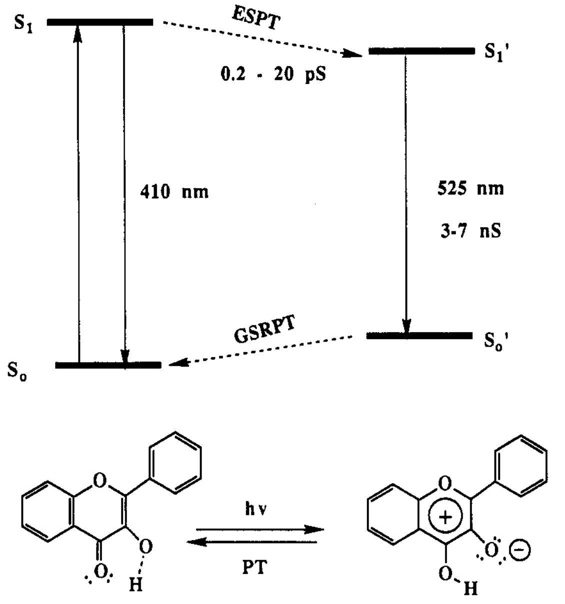

Figure 1. Energy-level diagram for 3-hydroxyflavone. UV excitation of 3HF leads to either blue fluorescence or excited-state proton transfer. The excited tautomer emits in the green and undergoes ground-state reverse proton transfer (GSRPT). Lifetimes and rates of proton transfer are solvent dependent.

The current method of dispersing the fluorescent dye within the polymer matrix usually entails dissolving the dye in the pure monomer and polymerizing the mixture under a slow temperature ramp. The dye is thus physically dispersed throughout the polymer. Solubility limitations constrain the concentration of 3HF to below 1 wt % in polystyrene. Any supersaturated concentration of dye is likely to result in migration and phase separation, particularly as the scintillator is cooled. Further, solution processing of scintillator is difficult and significant

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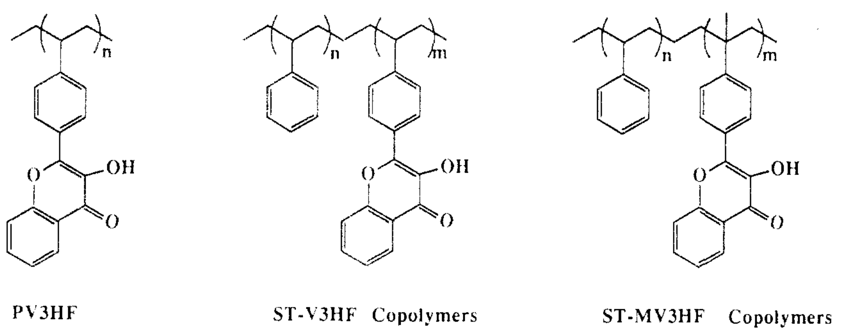
Chart 1. Structure of Homopolymers and Copolymers



Scheme 1. Synthesis of 3-Hydroxy-4′-ethenylflavones

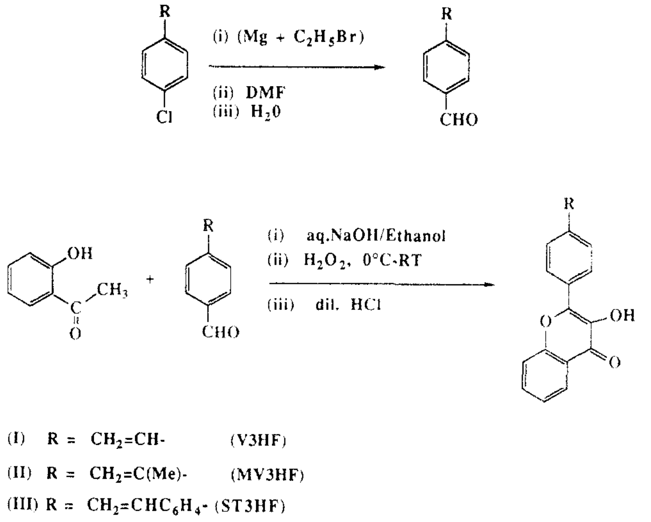


Table 1. Conditions of Polymerization

entry	solvent	T (°C)	yield (%)
PV3HF1	THF	60	40
PV3HF2	DMF	60	40
PMV3HF	THF	55	0
ST-V3HF2	DMF	55	<10
ST-V3HF3	DMF	55	<10
ST-MV3HF2	Bulk	55	20
ST-MV3HF3	THF	55	10
ST-MV3HF4	THF	55	10
ST + V3HF (0.1% w/v)	bulk[a]	60–140	>95
ST + MV3HF (0.1 % w/v)	bulk[a]	60–140	>95
ST + 3HF (0.1 % w/v)	bulk[a]	60–140	>95

[a] Thermal Initiation

quantities of dye may compromise the mechanical properties of fibers made from plastic. Making the fluorescent dye an integral part of the polymer through covalent binding is an important step in the rational design of polymeric scintillators. In this paper we present the first synthesis of polymers containing a proton-transfer species.

Results and Discussion

Monomer Synthesis. All three monomers containing 3HF groups were prepared by reaction of corresponding vinyl aldehydes with 1-hydroxyacetophenone as shown in Scheme 1. 4-Styrene- and α-methyl-4-styrenecarboxaldehydes were prepared in high yield from the commercially available corresponding 4-chloro derivatives using a Grignard reaction.[31-33] 4-Vinylbiphenylcarboxaldehyde was prepared by Pd-catalyzed coupling of 4-trimethyltin styrene with bromobenzaldehyde using a reaction reported by Gronowitz and Peters.[34] 4-Trimethyltin styrene is a bifunctional molecule. In the presence of a Pd(0) catalyst both the vinyl group (Heck's reaction)[35] and trimethyltin[36] can react with bromobenzaldehyde.

We obtained 4′-vinylbiphenylene-4-carboxaldehyde using Pd-catalyzed coupling, with no evidence of α,β-disubstituted styrene. However, we encountered some difficulty in reproducing the yield of the product. The reaction was repeated several times but the yield of purified material remained low, over the range 10–35%, using a variety of conditions. We also synthesized 4-vinylbiphenylcarboxaldehyde by coupling 4-styreneboronic acid with 4-bromobenzaldehyde in the presence of Pd(0) and $NaHCO_3$ in DME as solvent (Suzuki's reaction[37]) with similar results. No α,β-disubstituted styrenes were obtained. Recently, Hunt et al.[38] reported on the reaction of vinylboronic acid with aryl halides catalyzed by Pd(0). This reaction led to a mixture containing the products of Heck's reaction and coupling, with difficulties in reproducing the ratios and yields of the various products formed.

Vinyl-containing 3-hydroxyflavones were synthesized using a modified Algar–Flynn–Oymada (AFO) synthesis.[39-41] In the AFO reaction base and peroxide are usually added in one portion to yield flavone directly. The reaction is actually a two-step process. Acetophenone undergoes a Claisen–Schmidt-type reaction with the aldehyde to give a chalcone.[38-40] Then the chalcone undergoes ring closure and oxidation which finally, in the presence of hydrogen peroxide, gives 3-hydroxyflavone. Although these two steps can be separated by adding base first to yield the chalcone and then peroxide, we used a one-pot synthesis for convenience. The overall yield of the reaction is generally less than 50%. Styrene benzoic acids are formed as a side product. The solubility behavior of V3HF (**I**) is similar to that of 3HF. MV3HF is more soluble than 4V3HF in common organic solvents due to the presence of the methyl group. Both V3HF and MV3HF (**II**) are insoluble in pentane but sparingly soluble in methanol, ethanol, and hexane. Both V3HF and MV3HF are more soluble in THF, $CHCl_3$, and DMF. However, 4-styryl-3HF (**III**) is only slightly soluble in THF and in DMF.

Polymerization. Detailed conditions for homo- and copolymerization are given in Table 1. V3HF (**I**) was polymerized using AIBN as initiator in THF or DMF. The structure of the polymer (PV3HF) was confirmed by NMR spectroscopy. ^1H NMR showed the absence of vinyl protons and the appearance of a broad peak in the aliphatic region which indicated the formation of polymer. The structure of the polymer was confirmed by ^{13}C NMR, which exhibited sharp resonances, and showed the absence of vinyl carbons and the presence of an additional resonance in the aliphatic region. Homopolymer exhibited intense green fluorescence when exposed to UV light. Unsuccessful attempts were made to polymerize MV3HF using AIBN at 50 °C. It is known that α-methylstyrene and its derivatives are very difficult to homopolymerize using

Table 2. Copolymer Composition

polymer	solvent	infeed of M_1	M_1 in copolymer by UV	M_1 in copolymer by EA[a]
ST-V3HF2	DMF	0.0086	0.0314	0.0300
ST-V3HF3	DMF	0.0392	0.1495	0.1320
ST-MV3HF2	Bulk	0.0083	0.0190	0.0200
ST-MV3HF3	THF	0.0083	0.0252	0.0259
ST-MV3HF4	THF	0.0437	0.1030	0.0820

[a] EA, elemental analysis.

Table 3. GPC and Glass Transition Temperature of Polymers [a]

polymer	M_w	M_n	T_g
PV3HF (THF)	7 400	3 900	195
PV3HF(DMF)	13 000	9 300	
ST + V3HF	600 000	312 000	
ST-V3HF2	136 000	78 000	106
ST-V3HF3	162 000	82 000	132
ST + MV3HF	534 000	347 000	
ST-MV3HF2	207 000	104 000	
ST-MV3HF3	52 000	29 000	108
ST-MV3HF4	30 000	19 000	113
ST + 3HF	433 000	155 000	101

[a] Conditions: THF as solvent against polystyrene standards at 340 nm.

radical initiators due to their low ceiling temperature.[42,43] α-Methylstyrene, however, can be copolymerized with number of vinyl monomers using radical initiators under suitable polymerization conditions.[42-44] Generally, copolymers containing lower amounts of α-methylstyrene can be synthesized since these compositions are less susceptible to depolymerization.[42,43] Both V3HF and MV3HF were copolymerized with styrene in bulk and in solution. Copolymer conversions were less than 15% to avoid composition drift. A transparent film of copolymer could be cast from chloroform or THF.

Copolymer composition was determined by elemental analysis and by UV-vis absorption spectroscopy. The intensities of absorption maxima of V3HF copolymers were measured at 348 nm, and intensities were compared to a calibration curve constructed by measuring the absorbance maxima of PV3HF/THF standards. The copolymer flavone absorption maximum was close (±3 nm) to that of the homopolymer. Compositions of MV3HF copolymers were determined in a similar manner with PV3HF standards. Copolymer compositions obtained using this spectroscopic assay were in agreement with those from elemental analysis, as indicated in Table 2. Copolymers contain a higher mole fraction of V3HF and MV3HF than feed concentrations, suggesting both the monomers have higher reactivity than styrene under the conditions used here. Copolymer containing higher compositions of V3HF or MV3HF could not be synthesized because of their low solubility in THF and DMF.

Molecular weights of PV3HF and the copolymers were studied using GPC against polystyrene standards. GPC data are summarized in Table 3. PV3HF was synthesized in two different solvents, THF and DMF. The low solubility of the monomer resulted in polymer of low molecular weight for both, although PV3HF synthesized in the better solvent, DMF, had higher molecular weight. Copolymers of styrene and V3HF synthesized in DMF exhibited significantly higher molecular weights, which depended on the concentration of comonomer. Specifically, increasing the MV3HF concentration in copolymer lowered the molecular weight, which can be attributed to the tendency of MV3HF to depolymerize.

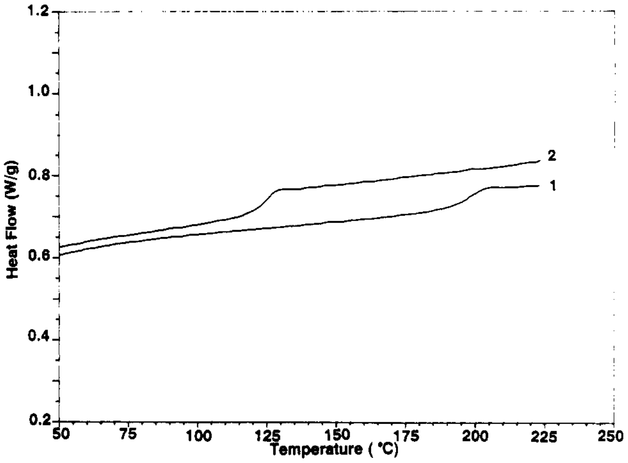


Figure 2. DSC of styrene-V3HF copolymers at 5 °C min^{-1} under nitrogen: (1) PV3HF and (2) ST-V3HF2.

Table 4. Spectral Data of Hydroxyflavones in THF

	λ_{max} (abs)	λ_{max} (em) (±2 nm)	quantum yield (o)[a]	ϵ (M^{-1} cm^{-1})
3HF	348	536	1.0	14 000
V3HF	355	551	1.5	23 000
MV3HF	353	551	1.5	23 000
PVHF	355	550	1.0	14 000
ST3HF	355	558	1.5	36 000

[a] Relative to 3HF.

Thermal bulk polymerization of styrene in the presence of 0.1% (w/v) V3HF or MV3HF to high conversion (>95%) yielded polymer with a molecular weight in the range of polymer obtained by simply dissolving 3HF in styrene (ST + 3HF). The molecular weight of these materials was reasonably high, indicating that the hydroxyl group of 3HF does not participate in chain-transfer reactions to any significant extent. Copolymers synthesized in bulk, which were of higher molecular weights compared to those synthesized in solution, are in the morphology that would be useful for scintillator applications.

Thermal Characterization

Glass transition temperatures were determined using DSC. PolyV3HF has a T_g at 190 °C, as shown in Figure 2. A higher T_g, in comparison to polystyrene, is expected due to the presence of a rigid group substituting at the para position. T_g's of all the homopolymers and copolymers are summarized in Table 3. DSC of V3HF and MV3HF copolymer shows that an increase in content of vinyl-3HF increases the T_g. All the homopolymers and copolymers have glass transition temperatures higher than that of polystyrene. A higher T_g could be advantageous if polymers are used in a fiber morphology, since there would be less likelihood that polymers would deform if exposed to higher temperatures.

The thermal stability of copolymers was determined in a nitrogen atmosphere using TGA. The data in Figure 3, showing a single weight loss at about 350 °C, suggest that polymers are stable up to a reasonably high temperature. Styrene-MV3HF copolymers also showed similar behavior. Interestingly, TGA gave no evidence for a tendency of the styrene-MV3HF copolymers to depolymerize. This suggests that MV3HF units are randomly distributed over the copolymer chain. If they were adjacent to each other unzipping of copolymer chains should have resulted at elevated temperature.

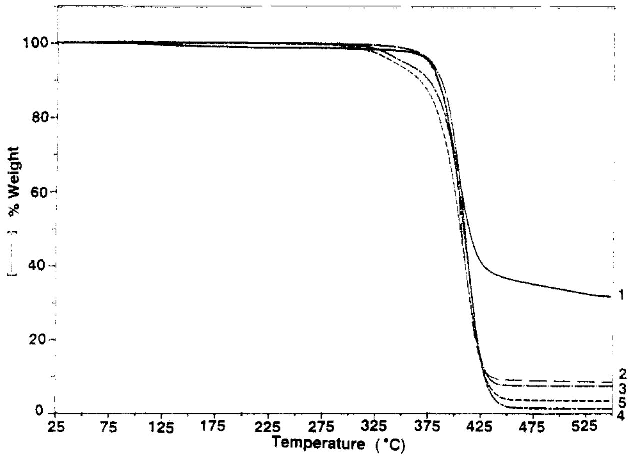


Figure 3. TGA of styrene–V3HF copolymers at a heating rate of 10 °C min^{-1}: (1) V3HF homopolymer, (2) ST-V3HF3, (3) ST-V3HF2, (4) ST-MV3HF3, and (5) ST-MV3HF4.

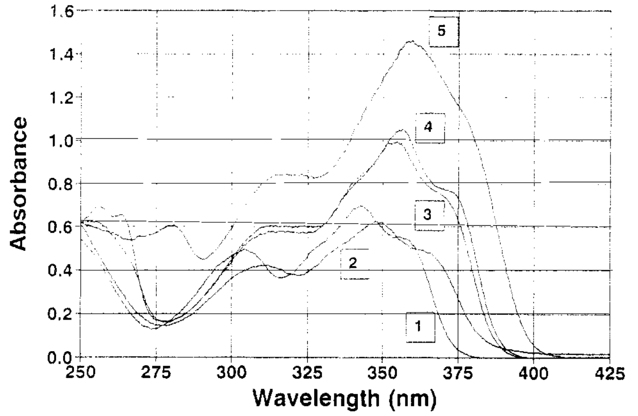


Figure 4. UV–vis absorption spectra of monomers and polymer in THF (conc 4 × 10^{-5} M): (1) 3HF, (2) PV3HF, (3) V3HF (I), (4) MV3HF (II), and (5) ST3HF (III).

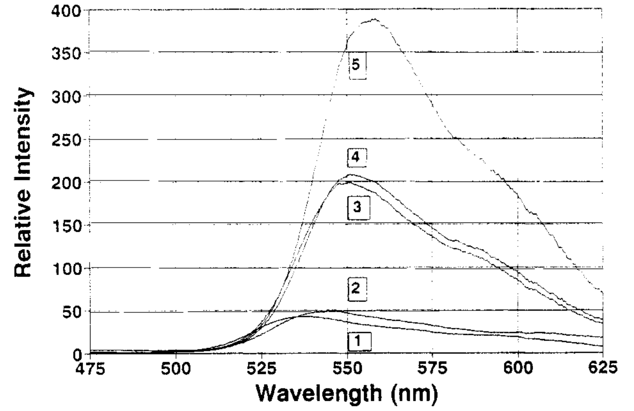


Figure 5. Corrected fluorescence spectra of compounds in Figure 4 (conc 4 × 10^{-5} M in THF). Excitation wavelength is in parentheses: (1) 3HF (299 nm), (2) PV3HF (308 nm), (3) V3HF (308 nm), (4) MV3HF (308 nm), and (5) ST3HF (307 nm).

Fluorescent Properties

Absorption spectra of **I**, **II**, **III**, PV3HF, and 3HF recorded in THF (0.04 mM) are shown in Figure 4, with corresponding emission spectra depicted in Figure 5. Spectral data, including quantum yields and molar extinction coefficients, are summarized in Table 4. In comparing the data, several points are noteworthy. First, substitution of a vinyl group at the 4′-position of the β phenyl ring in 3HF leads to higher extinction coefficients and quantum yields when compared to 3HF. It is interesting that only two extra conjugated π-electrons added to the 10 already present on the parent flavone and β-rings should enhance the extinction coefficient by almost a factor of 2. The increased quantum yield is perhaps due to the extra π-electrons stabilizing the proton-transferred pyrilium tautomer. A lower energy in the proton-transferred excited state may compete better with other states that result in nonradiative relaxation.

Enhanced efficiency and extinction coefficients have important practical implications, in that scintillators made with these fluorescent compounds are expected to have greater light output and longer attenuation lengths. Substitution at the 4′-position also leads to absorption and emission at slightly longer wavelengths, which is also advantageous for use in radiation-hard scintillators. Although substitution provides for distinct changes in extinction coefficients and quantum yields the effect on absorption and emission wavelengths is small.[45] The red shift caused by a vinyl group at the 4′-position, 15 nm, is approximately the same as noted by Pla-Dalmau for a phenyl group.[45,46] As expected, the extinction coefficient[46] for phenyl-3HF (35 000) is intermediate between vinyl and styryl.

The spectral properties of PV3HF are very close to those of 3HF, although the slight red shift due to the alkyl substitution at the 4′-position is retained. In particular, PV3HF is a very effective waveshifter, with a separation between absorption and emission maxima of about 190 nm. No intermediate features are observed, such as would be expected from "normal" (non-proton-transfer) emission.[22] Copolymers of **I** and styrene, and **II** and styrene, exhibited properties similar to those of **I** homopolymer. The fluorescence lifetime of copolymerized **I** in THF was somewhat longer (870 ps) than that of 3HF (580 ps). A detailed study on further 3HF derivatives and their lifetimes is in progress.[47]

All polymers and copolymers gave a bright green fluorescence when exposed to UV light and were found to scintillate strongly when bombarded with 3 MeV electrons from a van de Graaf generator.

Experimental Section

Materials. 4-Chlorostyrene (Fluka) and 4-chloro-α-methylstyrene (Aldrich) were dried over CaH_2 prior to use. 1-Hydroxyacetophenone (Aldrich) and Mg turnings (Fisher) were used as received. Ethyl alcohol was purified by standard procedures.[48] Anhydrous dimethyl formamide (DMF) (Aldrich) was used as received. Tetrahydrofuran (THF) was dried over sodium benzophenone and was distilled prior to use.

Monomer Synthesis. 3-Hydroxy-4′-ethenylflavone (V3HF) (I). 4-Vinylbenzaldehyde was synthesized according to literature procedures.[31-33] Polymeric impurities were removed by precipitating the product in pentane. The crude monomer obtained thus was used without further purification to avoid polymerization. **I** was synthesized according to the modified AFO synthesis of 3-hydroxyflavones.[40] 4-Vinylbenzaldehyde (13 g, 96 mmol) was added to a flask containing 13.9 g (0.102 mol) of 1-hydroxyacetophenone in 150 mL alcohol. NaOH (13 g) in 100 mL of aqueous alcohol (75%) was added to the reaction mixture. After allowing the solution to stand at room temperature overnight, 6 g of NaOH in 200 mL of aqueous ethyl alcohol (75%) was added, and the reaction mixture was stirred at 4 °C for 15 min. A solution of 50 mL of 30% hydrogen peroxide in 50 mL of aqueous ethyl alcohol (75%) was added to the reaction flask in one portion. The solution was slowly warmed to room temperature and was stirred for 6 h. The reaction mixture was neutralized with dilute HCl at 4 °C. The white precipitate was filtered and washed with distilled water and was recrystallized from THF/ethanol. Yield: 13.5 g (50%). Mp: 183–184 °C. ^1H NMR (270 MHz, DMSO-d_6): δ 5.37 (d, 1H, J = 10.8 Hz), 5.95 (d, 1H, J = 18.9 Hz) 6.81 (dd, —CH═, J = 10.8 and 18.9 Hz), 7.42–7.48 (m, 1H), 7.64 (d, 2H, J = 10.8 Hz), 7.72–7.82 (m, 2H), 8.10 (d, 1H, J = 8.1 Hz), 8.20 (d, 2H, J = 8.1 Hz), 9.65 (—OH, s broad). ^{13}C NMR(50) (68 MHz, DMSO-d_6): δ 115.9 (CH_2=), 135.9 (CH=), 172.7 (>C=O), 154.4 (>COH), 144.7 (>COC), 139.0, 138.3, 133.5, 130.6, 127.7, 126.1, 124.7, 124.4, 121.2, 118.2 (all ring carbons). IR (KBr): 3202, 1633, 1613, 1519, 1481, 1213, 1123 cm^{-1}. Elemental Analysis: Calculated for $C_{17}H_{12}O_3$; C, 76.91; H, 4.55. Found: C, 77.27; H, 4.54.

3-Hydroxy-4′-(1-methylethenyl)flavone (MV3HF) (II). α-Methylstyrene-4-carboxaldehyde was synthesized from 4-chloro-α-methylstyrene. It was used without further purification. α-Methylstyrene-4-carboxaldehyde (5.95 g, 0.04 mol) and 7 g (0.05 mol) of hydroxyacetophenone were combined in a similar way to the procedure described for **I**. The product was recrystallized from THF/ethanol. Yield: 5 g (52%). Mp: 162–163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 3H), 5.17 and 5.49 (s, 2H), 7.01 (s broad, —OH) 7.37 (m, 1H), 7.56–7.60, 7.68–7.71, and 8.23–8.25 (multiplets, ring protons). ^{13}C NMR (68 MHz, DMSO-d_6):(50) δ 115.9 (—CH_2=), 135.9 (=CH), 172.7 (>C=O), 154.4 (>COH), 144.8 (>COC), 139.0, 138.3, 133.5, 130.6, 127.7, 126.1, 124.7, 124.4, 121.2, and 118.2 (all ring carbons). IR (KBr): 3198, 1626, 1611, 1567, 1482, 1212, 1120 cm^{-1}. Mass Spectrum: *m/e* peak at 279.6 (M + 1). Elemental Analysis: Calculated for $C_{19}H_{16}O_3$: C, 77.69; H, 5.03. Found: C, 77.48; H, 5.23.

3-Hydroxy-4′-(1-phenylethenyl)flavone (ST3HF) (III). (i) 4-Vinyl-2,2′-biphenylene-4′-carboxaldehyde was synthesized by coupling 4-trimethyltin styrene with 4-bromobenzaldehyde in the presence of a Pd(0) catalyst.[34] 4-Trimethyltin styrene was synthesized by the reaction of trimethyltin chloride with the Grignard reagent of 4-chlorostyrene.[49] 4-Vinyl-2,2′-biphenylene-4′-carboxaldehyde was also synthesized by the coupling of 4-styreneboronic acid with 4-bromobenzaldehyde in the presence of tetrakis(triphenylphosphine)palladium. In a typical procedure, 2.77 g of bromobenzaldehyde was added to 877 mg of tetrakis(triphenylphosphine)palladium in a dry box followed by 50 mL of ethylene glycol dimethyl ether. The reaction mixture was refluxed under nitrogen atmosphere for 1 h. 4-Trimethyltin styrene (6 g, 22 mmol) was dissolved in 30 mL of ethylene glycol dimethyl ether and added to the reaction mixture under nitrogen. Saturated $NaHCO_3$ (2 mL) was added as a catalyst. The reaction mixture was heated at 65 °C for 72 h under nitrogen, poured into 50 mL of water, and extracted twice with 100 mL of methylene chloride. The organic layer was dried over anhydrous $MgSO_4$, concentrated, and poured into pentane. The white precipitate obtained was filtered, the filtrate was extracted with methanol and poured into water to yield the product. Mp: 108–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.30 (d, 1H, J = 10.8 Hz), 5.80 (d, 1H, J = 10.8 Hz), 5.80 (d, 1H, J = 17.7 Hz), 6.75 (dd, CH=, J = 10.8 and 17.7 Hz) 7.50 (d, 2H, J = 8.1 Hz), 7.60 (d, 2H, J = 8.1 Hz), 7.73 (d, 2H, J = 8.1 Hz), 7.93 (d, 2H, J = 8.4 Hz) (ring protons), and 10.03 (s, 1H).

(ii) 3-Hydroxy-4′-(1-phenylethenyl)flavone (ST3HF) (**III**) was synthesized in a similar way to V3HF (**I**). Yield: 40%. Mp: 250 °C (decomposes, varies with the heating rate). ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.31 (d, 1H, J = 10.8 Hz), 5.90 (1H, d, J = 17.7 Hz), 6.78 (dd, —CH=, J = 10.8 and 17.4 Hz), 7.45–8.34 (multiplets, ring protons), 9.73 (s broad, —OH). IR (KBR): 3141, 1682, 1613, 1483, 1566, 1213, 1123 cm^{-1}. Mass spectrum: *m/e* peak at 341 (M + 1). Elemental Analysis: Calculated for $C_{23}H_{16}O_3$: C, 81.17; H, 4.07. Found: C, 80.36; H, 4.86.

Polymerization. Poly(V3HF). Of V3HF (**I**) (500 mg) was transferred to a polymerization tube containing 25 mg of AIBN. This was followed by the addition of 7.5 mL of dry DMF. The polymerization tube was sealed under vacuum after repeated freeze–pump–thaw cycles. After the desired conversion (typically <15%) the reaction was stopped by breaking the seal and pouring the contents into ethyl alcohol. The yellow precipitate obtained was filtered and washed several times with hot ethyl alcohol. The polymer was purified by dissolving in DMF and reprecipitating in ethyl alcohol. ^{1}H NMR (270 MHz, DMSO-d_6): δ 1.5 (broad), 6.3–8.5 (broad), and 9.0 (boad). ^{13}C NMR (68 MHz, DMSO-d_6): δ 172.4 (>C=O), 154.0 (>COH), 144.8 (>COR), 146.4, 138.4, 137.6, 133.0, 128.9, 128.6, 127.4, 124.1, 120.7, 117.5 (all ring carbons). IR (KBr): 3321, 3070, 2921, 1614, 1569, 1483, 1204, 1188 cm^{-1}. Elemental Analysis: Calculated for $C_{17}H_{12}O_3$: C, 76.91; H, 4.55. Found: C, 75.85; H, 5.07.

Copolymerization. Copolymerization of V3HF. Copolymers containing different weight percentages of V3HF were synthesized using AIBN as initiator. In a typical procedure, 500 mg of V3HF was mixed with 5 mL of styrene and 10 mg of AIBN in 7.5 mL DMF. The polymerization tube was sealed under vacuum after repeated freeze–pump–thaw cycles. When a desired conversion (<15%) was reached, polymerization was stopped by breaking the seal and pouring the contents into ethyl alcohol. The yellow precipitate obtained was filtered and washed several times with hot ethyl alcohol. The polymer was purified by dissolving in THF and reprecipitating in hot ethyl alcohol twice. Finally, the polymer was filtered and dried under vacuum. Transparent and somewhat brittle films of copolymer could be cast from THF. Copolymer showed intense green fluorescence when exposed to UV light.

Solid polystyrene samples containing 0.1% (w/v) of V3HF or MV3HF were synthesized for studying their spectral properties in the solid state. Styrene and 0.1% of the flavone were charged in a polymerization tube containing no initiator or solvent, which was degassed and sealed under vacuum. Polymerization was initiated thermally using a temperature program of 60 °C for 48 h, 90 °C for 24 h, 125 °C for 24 h, and 140 °C for 48 h, and then slow cooling to 90 °C over 24 h so that complete conversion was obtained (>95%). Tubes were broken and a solid piece was cut into the dimensions of a 1-cm cuvette and polished.

Copolymerization of MV3HF(II). MV3HF was copolymerized with styrene in bulk and in solution as above. ST3HF (**III**) exhibits poor solubility in THF and DMF, therefore polymerization studies of **III** were not carried out.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on Brucker 250 and Varian 300-MHz FTNMR spectrometers. IR spectra were recorded on a Nicolet-520 FTIR spectrometer. UV–vis spectra were recorded on a Shimadzu UV-260 spectrometer. Excitation and emission spectra were recorded on a Perkin-Elmer LC-50 spectrofluorimeter. Excitation and emission spectra were run in optically dilute solutions (absorbance < 0.3 unit) to avoid any saturation of spectra. Al emission spectra reported were corrected against standard quinine sulfate solution in periodic acid. Elemental analysis was performed by Atlantic Microlab, Atlanta, GA. Melting points are uncorrected. DSC/TGA was conducted on a DuPont 9100 thermal analyzer. DSC thermograms were run by first preheating the samples to 180 °C for 3 min and rapidly cooling under a nitrogen atmosphere. Data were collected during second heating runs at a heating rate of 5 °C/min. For TGA, polymer samples were heated to 550 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The molecular weights and molecular weight distributions of polymers were determined by gel permeation chromatography on a Perkin-Elmer LC 250 solvent delivery system fitted with LC 290 UV detector. A Beckman 7.8 mm × 30 cm styrene–divinylbenzene cross-linked column was used for the analysis with THF at a flow rate of 1 mL/min. The retention times were calibrated against standard monodisperse polystyrene samples.

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