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Effects of the Hydrogen Bonding on the Fluorescence of Ketone-Substituted Poly(phenylene)s in Solutions and Solid State

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ABSTRACT: The fluorescence intensities of poly(2-benzoyl-1,4-phenylene) (PBP) and poly(2-trifluoroacetyl-1,4-phenylene) (PTFAP) in chloroform and dioxane solutions were found to decrease on addition of phenols. The fluorescence intensity diminishes in proportion to the acidity of phenols. Similar phenomena were observed on addition of acetic acid and a fluorinated alcohol. However, when the poly(*p*-vinylphenol) (PVPh) was added to these polymer solutions, the fluorescence intensity increased with an increasing amount of PVPh. These results suggest that hydrogen bonding between the carbonyl group of PBP or PTFAP and the OH group of phenols has opposite effects on fluorescence in the two cases. The strong hydrogen bonding with small phenol compounds in the excited state may increase the restriction of the bond rotation between the phenyl rings of the polymer and result in decreasing of π-electron conjugation and the fluorescence intensity. On PVPh addition to the polymer solution, the PVPh chain may wrap around PBP or PTFAP via hydrogen-bonding formation and reduce polymer chain associations, thereby mitigating the concentration quenching effect and conferring a large position contribution to the fluorescence intensity. PTFAP−PVPh blend films were prepared. Among these blends, 1 wt % of PTFAP in PVPh showed the highest fluorescence emission intensity 80 times larger than that of the pure PTFAP film. This suggests that the PTFAP chains are dispersed molecularly, or nearly so, in a matrix of PVPh in the 1 wt % blend; consequently, each polymer chain contributes additively to the emission intensity with a minimal deleterious impact due to aggregation.

Introduction

The photo- and electroluminescence of π-conjugated, rigid polymers have become subjects of widespread research activities recently.[1,2] Earlier we have studied the fluorescence of poly(2-benzoyl-1,4-phenylene), PBP (Figure 1a), and its application as the emission layer in blue electroluminescence devices.[3,4] Recently, we have also synthesized poly(2-trifluoroacetyl-1,4-phenylene) (PTFAP) (Figure 1b). The introduction of benzoyl and trifluoroacetyl groups to the otherwise insoluble and infusible poly(*p*-phenylene) backbone renders the polymers soluble in organic solvents such as THF, $CHCl_3$, and dioxane. The solutions of PBP and PTFAP show fluorescence in the region of 350−400 nm for PTFAP and 420−470 nm for PBP when they are excited at 310−315 and 370 nm, respectively. Fluorescence occurs from the electronic excitation of the conjugated polyphenylene; in general, the more coplanar the structure of the substituted polyphenylene, the higher the fluorescence intensity is obtained.[4] We have observed that when acidic small compounds such as phenols and acetic acid were added into the polymer solutions, the fluorescence intensities of the polymer solutions were decreased. This observation motivated us to investigate the effect of the addition of various substituted phenols and acids on the fluorescence properties in solution and solid state.

Experimental Section

Materials. 1,4-Dichloroiodobenzene, magnesium turning, trifluoroacetic anhydride, anhydrous dimethylformamide, bipyridine, and diethyl ether were purchased from Aldrich and used without further purification. Poly(vinylphenol), PVPh, was obtained from Hoechst Celanese Corp. The molecular weight of PVPh was 1.35×10^4 and T_g was 146 °C.

Characterization. ^1H and ^{13}C NMR spectra were recorded by using a Bruker 300 MHz spectrometer. UV spectra were recorded by a Shimazu 2000S spectrophotometer. The fluorescence spectra were obtained by using a Perkin-Elmer LS-50B luminescence spectrophotometer. The spectra were recorded using 0.1 and 1 cm quartz cells. The infrared spectra were recorded by a Perkin-Elmer 1600 FT-IR spectrophotometer.

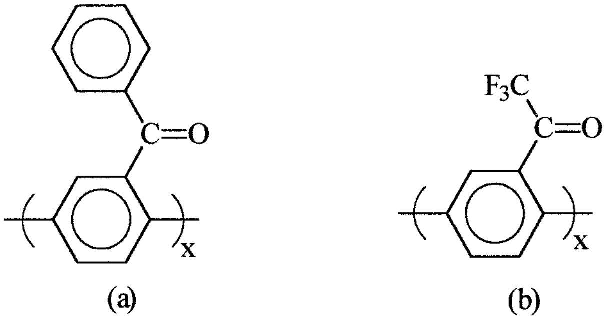

Figure 1. (a) Poly(2-benzyl-1,4-phenylene) and (b) poly(2-trifluoroacetyl-1,4-phenylene).

Poly(2-benzoyl-1,4-phenylene) (PBP). The preparation of PBP was reported in our previous paper.[3] ^1H and ^{13}C NMR analysis of the PBP obtained shows the benzoyl groups on the phenylene backbone were arranged primarily in a head-to-tail arrangement.

Poly(2-trifluoroacetyl-1,4-phenylene) (PTFAP).[5] This polymer was prepared by the route shown in Scheme 1.

Synthesis of 1,4′-Dichloro-2,2,2-trifluoroacetophenone (TFAP). Magnesium (13.2 g) in anhydrous ethyl ether (100 mL) was added to a 250 mL three-neck round-bottom flask equipped with a condenser. 1,4-Dichloroiodobenzene (14 g, 0.5 mol) in 10 mL of anhydrous ethyl ether was added dropwise into the ether solution in a period of 30 min. The solution was refluxed for 1 h and then cooled to room temperature with stirring for another hour. The reaction mixture was added slowly into a solution of trifluoroacetic anhydride (13 g, 0.05 5 mol) and 20 mL of anhydrous ethyl ether at −78 °C in 30 min. The reaction mixture was then allowed to warm to room temperature and stirred for 16 h.

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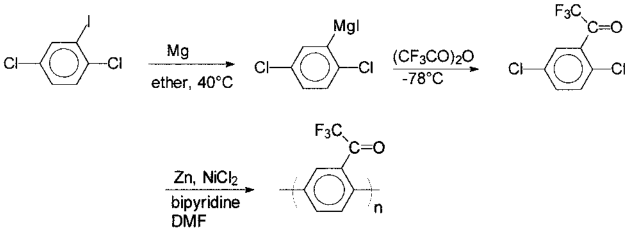
Scheme 1. Synthesis of PTFAP (Poly(2-trifluoroacetyl 1,4-phenylene))



The reaction mixture was poured into 300 mL of water and extracted with three 100 mL portions of ether. The ether layer was dried over magnesium sulfate. After ether was removed by evaporation, a dark brown liquid was obtained which after distillation under reduced pressure (0.01 mmHg) had a pale yellow color. The product yield was 61%, bp 65−67 °C (0.001 mmHg). ^{1}H NMR (300 Hz, d_6-acetone, ppm): δ 7.87−7.82 (s, 1-H, phenyl), δ 7.76−7.71 (dd, 1H, phenyl), δ 7.7−7.65 (d, 1H, phenyl). ^{13}C NMR (d_6-acetone): δ 185.1, 136.9, 135.7, 135.3, 134.8, 133.9, 132.2, 116.1.

Polymerization of 1,4′-Dichloro-2,2,2-trifluoroacetophenone. An anhydrous dimethylformamide (100 mL) solution containing TFAP (14 g, 0.05 mol), $NiCl_2$ (2.2 g, 0.02 mol), bipyridine (3.1 g, 0.02 mol), Zn (13 g), and 1,5-cyclopentadiene (5 mL) was added to a 250 mL round-bottom flask equipped with a condenser and kept at 75 °C for 48 h. The reaction mixture was then poured into 0.01 N HCl (200 mL) and stirred for 30 min to remove residual Zn. The precipitate was filtered and washed with 0.01 N HCl (200 mL) three times. The residue was redissolved in THF, precipitated in water, and dried under vacuum. ^{1}H NMR (300 Hz, d_6-acetone, ppm): δ 8.0−6.85 (m, 3H, phenyl).

The stereoregularity of PTFAP was investigated by measuring of NMR and showed that the polymer contained both regioregular (head-to-tail) and regioirregular (head-to-head and tail-to-tail) configuration.

The molecular weight of PTFAP was estimated from gel permeation chromatography (GPC), using polystyrene as standard, to be 2700 (M_n), which corresponds to about 16 repeating units. The polydispersity index (M_w/M_n) is about 1.6. Although the molecular weight obtained from GPC may not represent the true value, the polymer chain is sufficient length for studying the fluorescence properties in solution and the solid state.

Optical quality of thin films of PTFAP−PVPh blends was obtained by solvent casting from PTFAP−PVPh dioxane solutions on a Teflon plate. All the films were obtained at 75 °C for 48 h in a vacuum before measurement. Film thickness is in the range 25−40 μm.

Results and Discussion

The UV absorption of PBP in $CHCl_3$ shows a maximum at 373 nm with $\log \epsilon_{max} = 4.11$ M^{-1} cm^{-1}. In a dilute solution (−0.008 g/L), the fluorescence emission maximum is located at 450 nm (excited at 370 nm) (Figure 2, curve a), and the intensity increased with increasing concentration up to 0.033 g/L (curves b and c). Further increase to 0.13 g/L causes a large decrease in intensity (curve d). The diminished emission intensities may be due to the inner filter effect. PTFAP has UV absorption maximum at 312 nm with $\log \epsilon_{max} = 2.95$ M^{-1} cm^{-1}. The highest fluorescence intensity with emission maximum at 370 nm was obtained at the concentration 0.05 g/L, and the intensity again decreased at higher concentration also due to the inner filter effect (Figure 3).

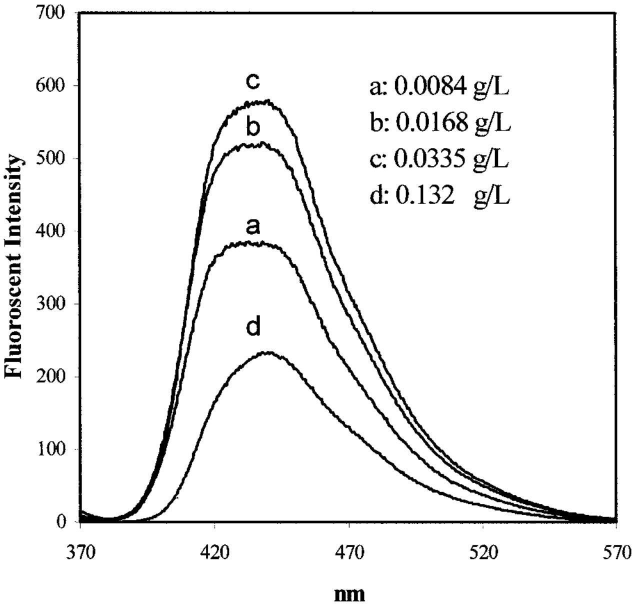


Figure 2. Fluorescence spectra of PBP in DMAc solutions, excited at 370 nm.

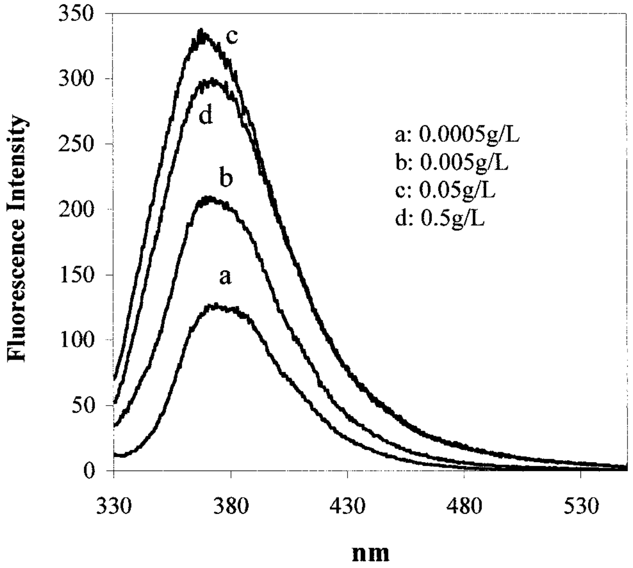


Figure 3. Flourescence spectra of PTFAP in 1,4-dioxane solutions excited at 312 nm.

The hydrogen-bonding interaction was revealed in the carbonyl-stretching region of the infrared spectra. For example, the carbonyl-stretching band of PBP in chloroform solution occurred at 1667 cm^{-1}. A clearly visible shoulder commonly observed in the mixtures containing phenols and carbonyl groups was also observed at 1660 cm^{-1} in the PBP chloroform solution upon the addition of 4-chlorophenol. This shoulder at lower wavenumber was ascribed to hydrogen bonding. Although the concentration of PBP chloroform solution used for the infrared measurements was 0.5 g/L, which was much higher than that of the solution used for the fluorescence measurement, it is reasonable to believe that hydrogen bonding of the carbonyl group of PBP and PTFAP with the hydroxyl group of phenols could be formed in a lower concentration. The UV absorption peak positions, however, did not change (or the changes were small and could not be detected using our present experimental technique). This indicates that the hydrogen bond formation at the ground state has a little effect on the electronic structure of the polymers. However, the fluorescence intensities decreased with increasing acidity of the phenols and the concentration (Figure 4).

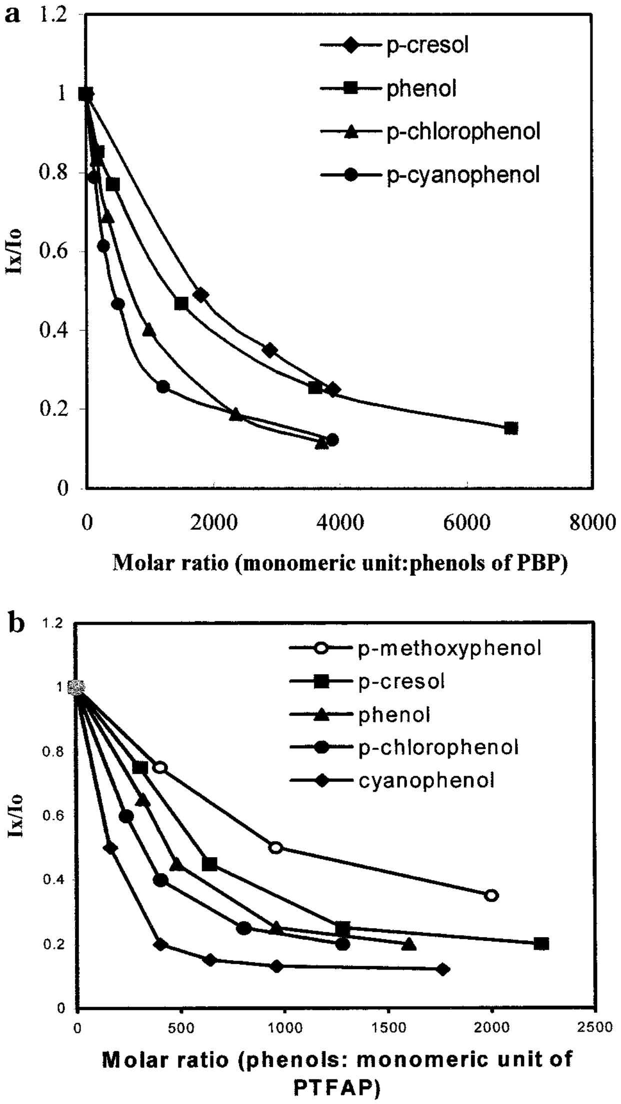


Figure 4. (a) Effects of para-substituted phenol in fluorescence intensity of PBP in $CHC1_3$ solution (0.02 g/L) (I_x: the fluorescence intensity of PBP/para-substituted phenol system; I_0: the fluorescence intensity of pure PBP. (b) Effects of para-substituted phenol in fluorescence intensity of PTFAP in $CHCl_3$ solution (0.05 g/L) (I_x: the fluorescence intensity of PTFAP/para-substituted phenol system; I_0: the fluorescence intensity of pure PTFAP system).

Webry and Rogers reported that the protolytic dissociation constants of phenols hold a linear relationship with the electrophilic substitution constant σ^+ rather than the Hammet constants σ[6]. Thus, we plotted the diminishing in the fluorescence intensity of the polymer–phenol systems against the σ^+ value[7] of the substituted phenols (Figure 5). These results show a good linear relationship for each polymer.

These phenomena were also observed by addition of other acidic compounds such as acetic acid and 1,1,1,-3,3,3-hexafluoro-2-propanol. In these cases, the UV absorption peak positions were also identical before and after addition of these acidic compounds into polymer solutions.

It was reported that when the carbonyl group of benzophenone (a monomeric unit of PBP) was protonated or hydrogen bonded with acidic OH, the fluorescence intensity was greatly increased.[8] Tamaki also found hydrogen-bonding formation of 2-acetylanthracene to increase the fluorescence intensity in the cyclohexane-methanol solution.[9] These results with small molecules are in contrast with the polyphenylene system such as PBP and PTFAP, in which hydrogen-bonding formation decreases the fluorescence intensity.

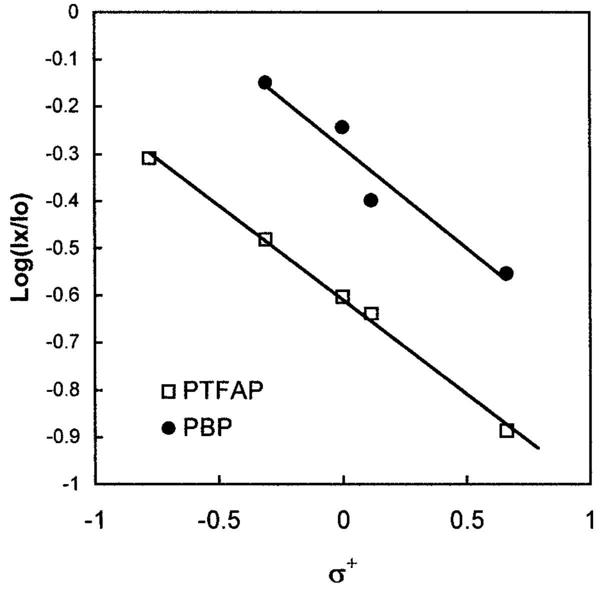


Figure 5. Hammet-type plot of fluorescence intensity vs σ^+ (I_x: fluorescence intensity containing para-substituted phenols (OCH_3, CH_3, Cl, CN, and NO_2; I_0: fluorescence intensity of polymer solution without phenols added). PTFAP: concentrated 0.05 g/L; PBP: concentrated 0.02 g/L in $CHCl_3$ (molar ratio of phenols to monomeric unit is 1000:1).

The source of the reduction in the fluorescence intensity by addition of acidic compounds to these polymeric solutions is not clear at the present moment, but one can speculate that the hydrogen bonding between the carbonyl groups of these polymers and acid added may form stronger hydrogen bonding at the excited state and then may increase restriction of the bond rotation between the backbone phenyl rings of the polymer, resulting in a decrease of seven-electron conjugation and hence the fluorescence intensity. The stronger the acidity of phenol formed, the stronger the hydrogen bonding between the carbonyl and hydroxyl group, and then the larger the intensity reduction was observed.

However, when a polymeric phenol PVPh was added into the PBP solution, the fluorescence intensity was first decreased when the concentration of PBP solution was ∼0.02 g/L, and at higher concentration (∼0.5 g/L), the intensity increased with increasing the amount of PVPH added. In the case of PTFAP, the fluorescence intensity increased by the addition of PVPh in the concentration at around 0.02–0.3 g/L (Figure 6).

These results suggest that there are two opposite mechanisms by addition of PVPh into PBP and PTFAP solutions. The interpolymer hydrogen bonding between PBP or PTFAP and PVPh is still expected to have a negative effect on fluorescence due to decrease of the π-electron conjugation on the poly(phenylene) system. However, in more concentrated solutions of the polymer, the polymer chains tend to aggregate, and the added PVPh molecules may wrap over PBP and PTFAP via interpolymer hydrogen-bonding association and thus reduce polymer chain aggregation, thereby mitigating the concentration quenching effect and conferring a large position contribution to fluorescence intensity. If the negative effect due to the interpolymer hydrogen

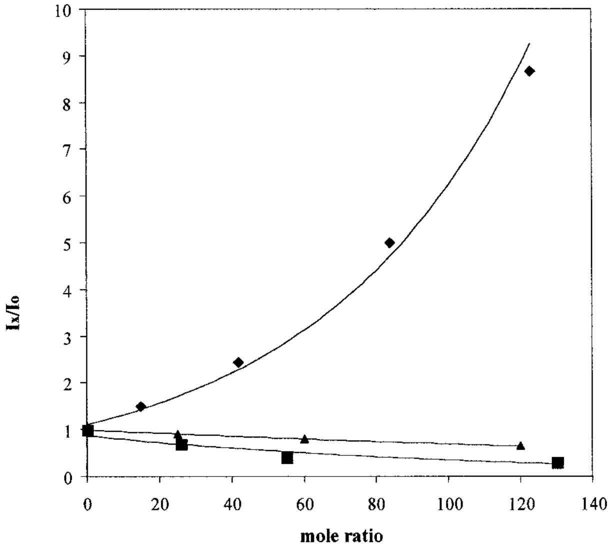


Figure 6. Effects of addition of para-substituted phenols and polymers in fluorescence intensity of PTFAP in dioxane solution (0.3 g/L) (I_x: the fluorescence intensity of PTFAP/para-substituted phenols (or polymers) systems; I_0: the fluorescence intensity of pure PTFAP system): ▲, *p*-cresol; ■, *p*-chlorophenol; ◆, PVPh.

bonding on intensity were comparable to that of *p*-cresol, the intensity increase due to the physical barrier effect of PVPh be even larger than observed.

Since hydrogen bonding between carbonyl and phenol groups has been known to enhance polymer miscibility in the solid state, we have extended our investigation to PTFAP/PVPh blend films to see whether the beneficial effect seen in solution is also present in the solid state. The emission intensity of the PTFAP film itself is too low due to large concentration quenching. Among the blends, the one containing 1 wt % PTFAP in PVPh showed the highest fluorescence emission intensity of the film studied when excited at 325 nm (Figure 7). The emission intensity at 380 nm was 80 times that of pure PTFAP film, and it was 20 times the value for the 50 wt % PTFAP blend and 4 times that of the 10 wt % blends. This phenomenon suggests that the PTFAP chains are dispersed molecularly, or nearly so, in a matrix of PVPh in the 1 wt % blend; consequently, each chain contributes additively to emission intensity with minimal deleterious impact from quenching effects.

Conclusion

The hydrogen bonding of the carbonyl groups of poly(2-benzoyl-1,4-phenylene) (PBP) and poly(2-trifluoroacetyl-1,4-phenylene) (PTFAP) with the OH groups of phenols and polymeric phenol has opposite effects on the fluorescence. The hydrogen bonding with small phenol compounds may increase the restriction of the bond rotation between the phenyl rings of the polymer back chain, resulting in decreasing of π-electron conjugation and fluorescence intensity. Upon the adding of poly(vinylphenol) (PVPh) to these polymer solutions, PVPh acts as a physical obstacle by wrapping itself around polyphenylenes so as to reduce the polymer aggregation/concentration quenching and confer a large positive contribution to the fluorescence intensity.

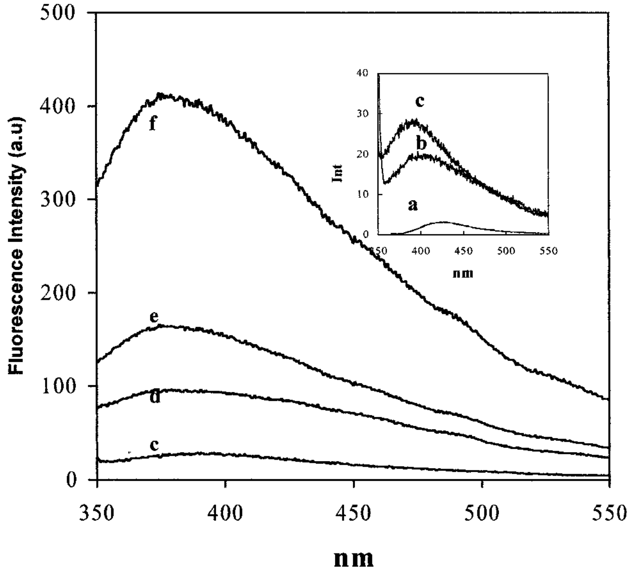


Figure 7. Flourescence spectra of (a) pure PTFAP, (b) 50 wt %, (c) 20 wt %, (d) 10 wt %, (e) 5 wt %, and (f)1 wt % of PTFAP in PTFAP/PVPh solid-state films.

PTFAP−PVPh blended films were prepared. Among the blends, the 1 wt % of PTFAP in PVPh showed the highest fluorescence emission intensity (80 times larger than the pure PTFAP film). The result suggests that PTFAP is dispersed in a matrix of PVPh blend. Consequently, each polymer chain contributes to the emission with a minimal deleterious impact from concentration/quenching.

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