

# Effect of polymer matrix on the performance of pressure-sensitive paint comprising 5,10,15,20-tetrakis(pentafluorophenyl)porphinato platinum(II) and poly(1,1,1,3,3,3-hexafluoroisopropyl-co-tert-butyl methacrylates)

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**ABSTRACT:** Copolymers of 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIPM) and *tert*-butyl methacrylate (TBM) were prepared by conventional radical copolymerization as a novel binders for pressure-sensitive paints (PSP). The monomer reactivity ratios  $r_{\text{HFIPM}}$  and  $r_{\text{TBM}}$  were determined as 0.45 and 0.67, respectively. The glass transition temperature of the copolymers increased from 77 to 126°C with increasing mole fraction of TBM units in the copolymer. The PSP were formed by combining the resulting copolymers and 5,10,15,20-tetrakis(pentafluorophenyl)porphinato platinum(II). The pressure and temperature sensitivities of the PSPs were measured at air pressures ranging from 5 to 120 kPa and at temperatures ranging from 0 to 60°C. Modified Stern–Volmer plots indicated slight increases in the pressure sensitivity, but significant decrease in the temperature sensitivity as the mole fraction of HFIPM units increased in the copolymer. Applying a theoretical model to our calibration data, we inferred that luminescence quenching is primarily responsible for increasing the temperature sensitivity in the resulting copolymers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43316.

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## INTRODUCTION

Pressure-sensitive paint (PSP) is an emerging technology for air pressure imaging in wind tunnel experiments.<sup>1–6</sup> PSPs are prepared from a luminescent dye and an oxygen-permeable polymer. Air pressure measurements by PSPs are based on luminescence quenching by oxygen molecules. The luminescence intensity or lifetime depends on the local concentration of oxygen molecules dissolved in the polymer matrix. If Henry's law holds, the local concentration of oxygen molecules is proportional to the local air pressure on the outer surface. Hence, the air pressure distribution can be obtained by capturing the luminescence intensity or lifetime image by a digital imaging device. Luminescent dyes for PSP measurements must meet several requirements such as being able to be excited and detected by visible light, having a high photochemical durability, having a long excited state lifetime, having a reasonable solubility in common organic solvents suitable for painting, and having an acceptable cost. 5,10,15,20-Tetrakis(pentafluorophenyl)porphi-

nato platinum(II) (PtTFPP) is one of the most preferred luminescent dyes for PSP applications. Because the analyte of PSP is the oxygen molecule, the permeability of oxygen molecules in the polymer matrix is essential for successful measurement. Typical oxygen-permeable polymers in PSP applications are polydimethylsiloxane,<sup>7–9</sup> fluorinated polymethacrylates<sup>4–6,10–13</sup> and poly(3-trimethylsilyl-1-propyne).<sup>14</sup>

One of the most serious problems in PSP-based air pressure measurements is the temperature dependence of the luminescent intensity or lifetime. The temperature effect is unavoidable, and it introduces serious errors in air pressure measurements. Hence, the reduction of the temperature sensitivity of the PSP coating is an important issue to be addressed. For a given luminescent dye, the temperature effect is significantly influenced by the polymer matrix. For example, Puklin *et al.* synthesized poly(1,1,1,3,3,3-hexafluoroisopropyl-co-2,2,3,3,4,4,4-heptafluorobutyl methacrylates) (FIB) for PSP applications using PtTFPP as the luminescent dye.<sup>4</sup> PSPs comprising PtTFPP and FIB exhibit a high dynamic range of pressure

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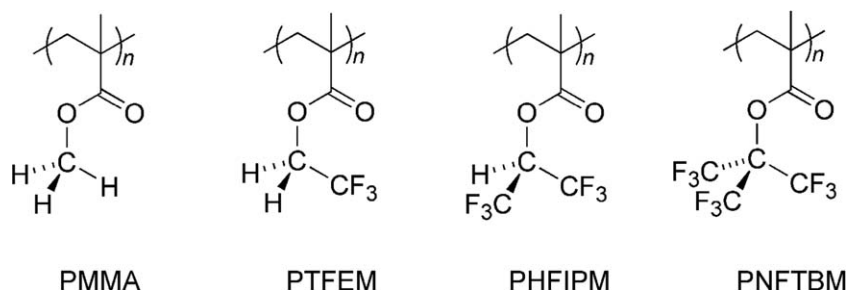


Chart 1. PMMA and its CF<sub>3</sub>-substituted derivatives.<sup>13</sup>

response, very short response time, and very low temperature sensitivity ( $-0.6\%/^{\circ}\text{C}$ ). By contrast, Amao *et al.* developed poly(isobutyl-*co*-2,2,2-trifluoroethyl methacrylates) (FEM)<sup>10</sup> and combined it with PtTFPP, affording a PSP with slightly higher temperature sensitivity ( $-1.2\%/^{\circ}\text{C}$ ).<sup>15</sup> These examples clearly highlight the importance of the polymer matrix in reducing the temperature sensitivity.

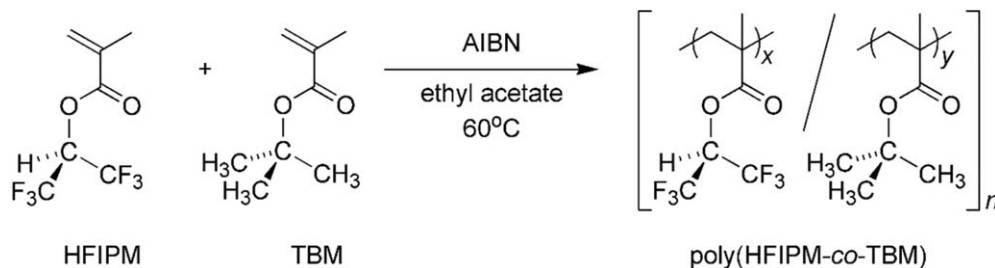
Recently, we reported the systematic study of PMMA and three derivatives with trifluoromethyl groups, namely poly(2,2,2-trifluoroethyl methacrylate) (PTFEM), poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHFIPM), and poly(nonafluoro-*tert*-butyl methacrylate) (PNFTBM), as binders and PtTFPP as the luminescent dye in a PSP (Chart 1).<sup>13</sup> In a detailed temperature sensitivity analysis of PSP coating comprising PtTFPP and these polymers, we identified two structural features that are crucial for reducing the temperature sensitivity. One is the high glass transition temperature ( $T_g$ ) of the polymer, which reduces the temperature sensitivity by a non-radiative deactivation process. The other is the fluorination degree of the polymer, which reduces the temperature sensitivity by luminescence quenching by oxygen molecules. We also found that the PSP comprising PtTFPP and PNFTBM was least sensitive to temperature. Unfortunately, PNFTBM does not readily dissolve in common organic solvents and requires costly fluorinated solvents, such as hexafluorobenzene. To develop a PSP with low temperature sensitivity, the polymer must have a high glass transition temperature and a high degree of fluorination. Changing the degree of fluorination requires the tedious and costly synthesis of a fluorinated monomer or the fluorination of the resulting polymer. However, the glass transition temperature of a polymer can be changed by stereospecific polymerization or by copolymerization with a miscible monomer having a high glass transition temperature. Hence, the radical copolymerization approach is a feasible and practical means of modulating the glass transition temperature of a polymer. The copolymerization of 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIPM) with a nonfluorinated monomer such as *tert*-butyl methacrylate

(TBM) should increase the glass transition temperature of the resulting polymer, resulting in a decrease the temperature sensitivity due to nonradiative deactivation. However, such copolymerization also coincidentally reduces the degree of fluorination, thereby increasing the temperature sensitivity due to luminescence quenching by oxygen molecules. Therefore, we expect that a tradeoff exists between the two temperature sensitivities. In this article, we synthesized copolymers of HFIPM and TBM, adopted them as binders in PSPs with PtTFPP as the luminescent dye, and examined the pressure and temperature sensitivities of the PSPs. We also derived a theoretical model of the overall temperature sensitivity, assuming an Arrhenius-type equation for the rate constants of the non-radiative deactivation process and the luminescence quenching by oxygen molecules. The theoretical model was validated in a calibration data analysis.

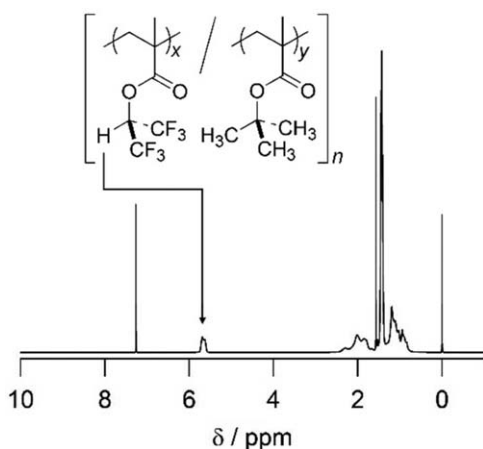
## EXPERIMENTAL

### Materials and Analytical Techniques

All chemicals were of analytical grade. HFIPM (Central Glass, Tokyo, Japan) and TBM (Wako Pure Chemical Industries, Osaka, Japan) were distilled under reduced pressure. <sup>1</sup>H NMR spectra were recorded using an AVANCE 400 instrument (400 MHz; Bruker Biospin K.K., Yokohama, Japan) and an AVANCE III HD (500 MHz; Bruker Biospin K.K., Yokohama, Japan). The glass transition temperatures ( $T_g$ s) of the polymers were determined using a DSC-60 Plus calorimeter (Shimadzu, Kyoto, Japan) with a scan rate of  $10^{\circ}\text{C min}^{-1}$ . Size exclusion chromatography (SEC) was performed on the HPLC instrument (pump, LC-20AT; refractive index detector, RID-10A, Shimadzu) using Styragel HR4 ( $7.8 \times 300 \text{ mm}^2$ ) (Waters, MA), Styragel HR3 ( $7.8 \times 300 \text{ mm}^2$ ), and Styragel HR1 ( $7.8 \times 300 \text{ mm}^2$ ) columns thermostated at  $40^{\circ}\text{C}$  as a stationary phase and tetrahydrofuran (THF) as a mobile phase at a flow rate of  $1 \text{ mL min}^{-1}$ . The SEC was calibrated with 11 polystyrene standards (Showa Denko, K.K., Tokyo, Japan) ranging in molecular mass from 1.31 to 3740



Scheme 1. Radical copolymerizations of 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIPM) with *tert*-butyl methacrylate (TBM) in ethyl acetate at  $60^{\circ}\text{C}$ .



**Figure 1.**  $^1\text{H}$  NMR spectrum of poly(HFIPM-*co*-TBM) ( $F_{\text{HFIPM}} = 0.44$ ) in  $\text{CDCl}_3$ .

$\text{kg mol}^{-1}$ . The number-average molar mass ( $M_n$ s) and the dispersities ( $M_w/M_n$ s) were calculated by polystyrene calibration.

### Radical Copolymerizations of HFIPM with TBM

In the typical copolymerization procedure, HFIPM (935.5 mg), TBM (569.0 mg), azobisisobutyronitrile (AIBN) (4.1 mg), and dry ethyl acetate (1.36 mL) were placed in a test tube, and the tube was tightly sealed with a rubber septum. Nitrogen gas was introduced into the solution for 15 min. The solution was heated at  $60^\circ\text{C}$  for 1 h, and then cooled to ambient temperature. After the solvent was evaporated under reduced pressure, the residue was poured into an excess amount of methanol. The resulting precipitate was collected in a glass filter and dried under vacuum to give poly(HFIPM-*co*-TBM) as a white solid (114.8 mg, 7.6%).  $M_n = 80,600$ .  $M_w/M_n = 2.12$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz,  $\text{Si}(\text{CH}_3)_4$ ):  $\delta$  (ppm): 5.8–5.5 ( $\text{CH}(\text{CF}_3)_2$ ), 2.7–0.5 ( $\alpha\text{-CH}_3$ ,  $\text{CH}_2$  and  $\text{C}(\text{CH}_3)_3$ ).

**Table I.** Radical Copolymerizations of 1,1,1,3,3,3-hexafluoroisopropyl Methacrylate (HFIPM) with *tert*-butyl Methacrylate (TBM) in Ethyl Acetate at  $60^\circ\text{C}$ , used for Constructing the Composition Curve<sup>a</sup>

$f_{\text{HFIPM}}^b$	Yield (%) <sup>c</sup>	$F_{\text{HFIPM}}^d$	$M_n$ ( $M_w/M_n$ ) <sup>e</sup>
0.1	6.5	0.14	127,600 (1.85)
0.2	7.0	0.26	102,600 (2.03)
0.3	7.4	0.28	99,900 (2.15)
0.4	6.7	0.40	74,000 (2.30)
0.5	7.6	0.46	80,600 (2.12)
0.6	5.0	0.51	83,600 (2.00)
0.7	4.0	0.64	75,800 (1.98)
0.8	3.4	0.70	79,200 (1.91)

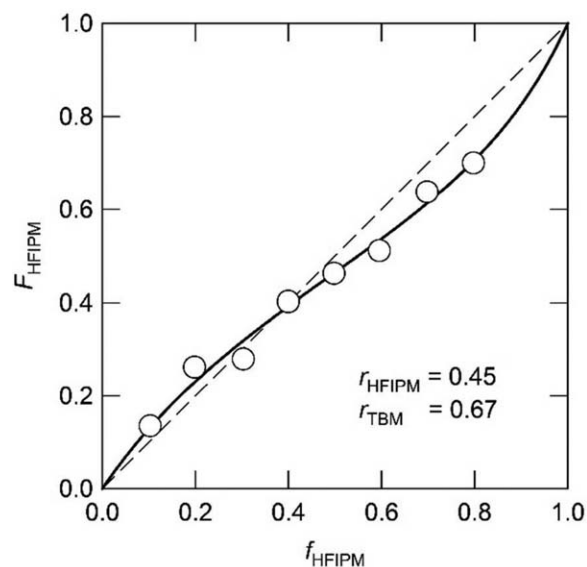
<sup>a</sup>  $[\text{monomer}]_0 = 50 \text{ vol } \%$ ;  $[\text{AIBN}]_0 = 1.5 \text{ mg mL}^{-1}$ ; time, 60 min.

<sup>b</sup> Mole fraction of HFIPM in the monomer feed.

<sup>c</sup> Isolated yield.

<sup>d</sup> Mole fraction of the HFIPM units in the copolymer determined by  $^1\text{H}$  NMR spectroscopy.

<sup>e</sup> The number-average molar mass ( $M_n$ ) and the dispersity ( $M_w/M_n$ ) were determined by SEC using polystyrene standards.



**Figure 2.** Copolymer composition curve for the radical copolymerizations of 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (HFIPM) with *tert*-butyl methacrylate (TBM) in ethyl acetate at  $60^\circ\text{C}$ .

### Tests of the Pressure- and Temperature-sensitivities of the PSP Coatings

PtTFPP and poly(HFIPM-*co*-TFEM) were dissolved in ethyl acetate. The concentrations of PtTFPP and the polymer were 0.5 and  $25 \text{ g L}^{-1}$ , respectively. The solution was sprayed onto an aluminum plate ( $15 \times 15 \text{ mm}^2$ ) using a conventional air brush. The plate was then mounted in a temperature-controlled pressure chamber. Excitation was provided by a 300 W Xe lamp (C4338, Hamamatsu Photonics) equipped with a 400–550 bandpass filter. The emission from the sample was detected by a cooled CCD camera (C4880-50-26W, Hamamatsu Photonics;  $1000 \times 1018$  pixels, 16-bit intensity resolution) with a 590–710 nm bandpass filter. The luminescence intensities  $I(T, P)$  were collected at air pressures ( $P$ ) ranging from 5 to 120 kPa and at temperatures ( $T$ ) ranging from 0 to  $60^\circ\text{C}$ .

The relative luminescence intensity at constant temperature is described by the Stern–Volmer equation:

$$\frac{I(T, 0)}{I(T, P)} = 1 + K_{\text{app}}(T)P \quad (2-1)$$

where  $K_{\text{app}}(T)$  is the apparent Stern–Volmer constant (in  $\text{kPa}^{-1}$ ) at temperature  $T$ , and  $I(T, 0)$  is the luminescence intensity in a vacuum. Because  $I(T, 0)$  is difficult to measure, eq. (2-1) is modified to eq. (2-2) by changing the reference state

$$\frac{I(T_{\text{ref}}, P_{\text{ref}})}{I(T, P)} = \frac{1}{g(T, T_{\text{ref}})} \left\{ \frac{1 + K_{\text{app}}(T)P}{1 + K_{\text{app}}(T_{\text{ref}})P_{\text{ref}}} \right\} \quad (2-2)$$

where  $T_{\text{ref}}$  and  $P_{\text{ref}}$  are the reference temperature (293 K) and air pressure (100 kPa), respectively, and  $g(T, T_{\text{ref}})$  is the relative luminescence intensity in a vacuum as defined in eq. (2-3) as follows:

$$g(T, T_{\text{ref}}) = \frac{I(T, 0)}{I(T_{\text{ref}}, 0)} \quad (2-3)$$

Because  $g(T, T)$  is unity, eq. (2-2) at constant temperature reduces to:

**Table II.** Radical Copolymerizations of 1,1,1,3,3,3-hexafluoroisopropyl Methacrylate (HFIPM) with *tert*-butyl methacrylate (TBM) in Ethyl Acetate at 60°C Used in Pressure and Temperature Sensitivity Tests<sup>a</sup>

$f_{\text{HFIPM}}^b$	Yield (%) <sup>c</sup>	$F_{\text{HFIPM}}^d$	$M_n$ ( $M_w/M_n$ ) <sup>e</sup>	$T_g$ (°C) <sup>f</sup>
0	97	0	191,200 (1.67)	126
0.16	92	0.14	188,400 (1.90)	118
0.32	87	0.34	131,500 (2.04)	111
0.50	81	0.44	103,900 (2.21)	105
0.66	78	0.63	107,100 (2.02)	99
0.80	71	0.69	200,000 (1.47)	92
1	56	1	76,800 (1.83)	77

<sup>a</sup>[monomer]<sub>0</sub> = 50 vol %; [AIBN]<sub>0</sub> = 1.5 mg mL<sup>-1</sup>; temp., 60°C; time, 21 h.

<sup>b</sup>Mole fraction of HFIPM in the monomer feed.

<sup>c</sup>Isolated yield.

<sup>d</sup>Mole fraction of the HFIPM units in the copolymer determined by <sup>1</sup>H NMR spectroscopy.

<sup>e</sup>The number-average molar mass ( $M_n$ ) and the dispersity ( $M_w/M_n$ ) were determined by SEC using polystyrene standards.

<sup>f</sup>The glass transition temperature ( $T_g$ ) was determined by DSC.

$$\frac{I(T, P_{\text{ref}})}{I(T, P)} = \{1 - C(T, P_{\text{ref}})\} + C(T, P_{\text{ref}}) \frac{P}{P_{\text{ref}}} \quad (2-4)$$

where  $C(T, P_{\text{ref}})$  is defined as follows:

$$C(T, P_{\text{ref}}) = \frac{K_{\text{app}}(T)P_{\text{ref}}}{1 + K_{\text{app}}(T)P_{\text{ref}}} \quad (2-5)$$

According to eq. (2-4),  $I(T, P_{\text{ref}})/I(T, P)$  is a linear function of  $P/P_{\text{ref}}$ . In reality, the plot frequently deviates from linearity and affords a slightly concave shape. Such data are well fitted by a two-site model containing a small fraction of oxygen-insensitive region, namely  $K_{\text{app}}(T) = 0$ , such as eq. (2-6):

$$\frac{I(T, P_{\text{ref}})}{I(T, P)} = \frac{f}{1 + K_{\text{app}}(T)P_{\text{ref}}} + (1-f) \quad (2-6)$$

where  $f$  is the fractional contribution of the oxygen-sensitive region to the total luminescence intensity in the absence of oxygen. The  $K_{\text{app}}(T)$  values were obtained by curve-fitting the experimental data to eq. (2-6).

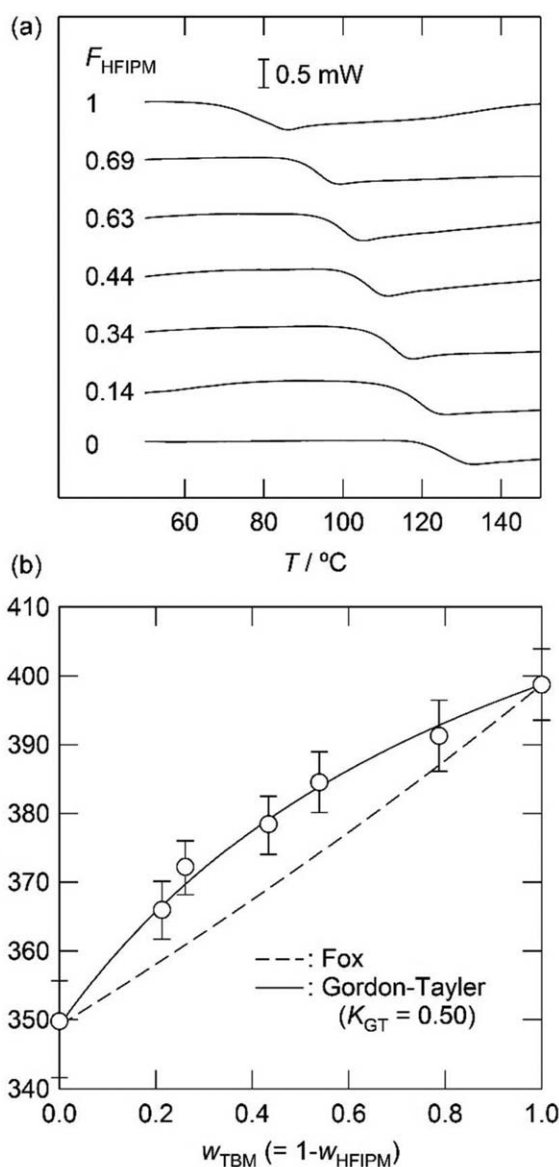
The temperature sensitivity under constant air pressure  $P$  was evaluated by plotting  $I(T, P)/I(T_{\text{ref}}, P)$  against the temperature  $T$ . The temperature sensitivity under vacuum  $g(T, T_{\text{ref}})$  was estimated as follows:

$$g(T, T_{\text{ref}}) = \frac{I(T, 0)}{I(T_{\text{ref}}, 0)} = \frac{I(T, 0)}{I(T, P_{\text{ref}})} \times \frac{I(T_{\text{ref}}, P_{\text{ref}})}{I(T_{\text{ref}}, 0)} \times \frac{I(T, P_{\text{ref}})}{I(T_{\text{ref}}, P_{\text{ref}})} \quad (2-7)$$

In eq. (2-7),  $I(T, 0)/I(T, P_{\text{ref}})$  and  $I(T_{\text{ref}}, P_{\text{ref}})/I(T_{\text{ref}}, 0)$  were estimated by extrapolating eq. (2-6).

### Theoretical Model of Luminescence Kinetics

The minimum set of photophysical processes in PSP includes radiative deactivation (rate constant  $k_r$ ), nonradiative deactivation (rate constant  $k_{\text{nr}}$ ), and luminescence quenching of an electronically excited luminescent dye molecule by an oxygen molecule



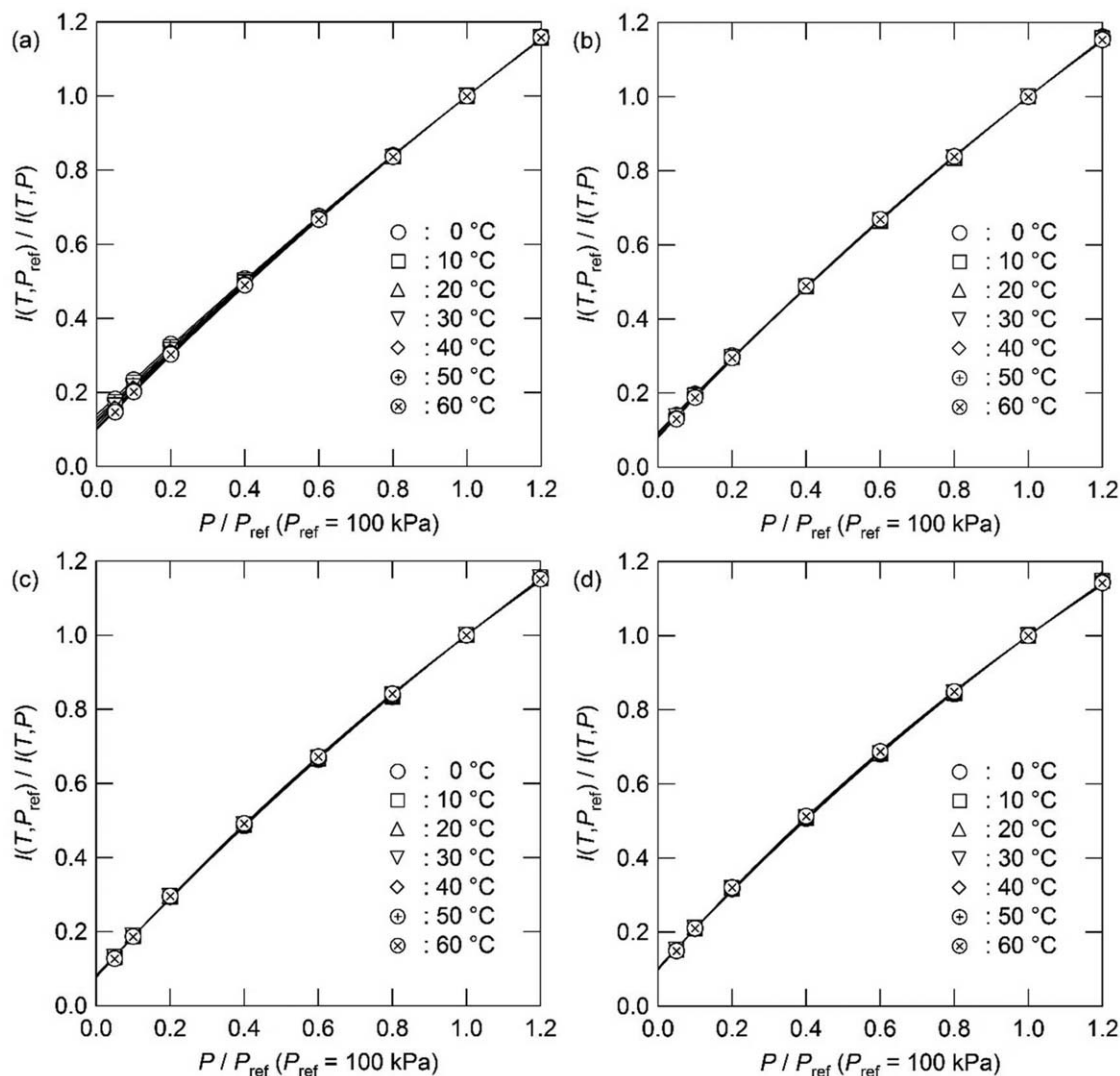
**Figure 3.** DSC traces of poly(HFIPM-co-TBM) (a) and the plots of the  $T_g$  versus the weight fraction of the TBM units in poly(HFIPM-co-TBM) ( $w_{\text{TBM}}$ ) (b). Broken and solid lines are the predictions of the Fox equation and the best-fit line of the Gordon-Taylor equation, respectively.

(rate constant  $k_q$ ). It should be noted that  $k_q$  describes the overall luminescence quenching process, which involves both dissolution and diffusion of the oxygen molecules. Here,  $k_r$  is assumed as temperature independent, and  $k_{\text{nr}}$  and  $k_q$  are described by the following temperature-dependent functions:

$$k_{\text{nr}} = k_{\text{nr}0} + A_{\text{nr}} \exp\left(-\frac{E_{\text{nr}}}{RT}\right) \quad (2-8)$$

$$k_q = A_q \exp\left(-\frac{E_q}{RT}\right) \quad (2-9)$$

In these expressions,  $k_{\text{nr}0}$  is a temperature-independent term,  $A_{\text{nr}}$  and  $A_q$  are pre-exponential factors,  $E_{\text{nr}}$  and  $E_q$  are the activation



**Figure 4.** Stern–Volmer plots of the PSP coatings comprising PtTFPP and poly(HFIPM-*co*-TBM) ( $F_{\text{HFIPM}} = 0$  (a), 0.34 (b), 0.63 (c), and 1 (d)). Solid lines are the best-fit curves to a two-site model.

energies of each process.<sup>1</sup> The Stern–Volmer equation is given as follows:

$$\frac{I(T, 0)}{I(T, P)} = 1 + \frac{k_q}{k_r + k_{nr}} P \quad (2-10)$$

Therefore, the  $K_{\text{app}}(T)$  is calculated as follows:

$$K_{\text{app}}(T) = \frac{k_q}{k_r + k_{nr}} = \frac{A_q \exp\left(-\frac{E_q}{RT}\right)}{k_r + k_{nr0} + A_{nr} \exp\left(-\frac{E_{nr}}{RT}\right)} \quad (2-11)$$

and  $g(T, T_{\text{ref}})$  is given by:

$$g(T, T_{\text{ref}}) = \frac{I(T, 0)}{I(T_{\text{ref}}, 0)} = \frac{k_r + k_{nr0} + A_{nr} \exp\left(-\frac{E_{nr}}{RT_{\text{ref}}}\right)}{k_r + k_{nr0} + A_{nr} \exp\left(-\frac{E_{nr}}{RT}\right)} \quad (2-12)$$

Using eq. (2-12), we can rewrite  $K_{\text{app}}(T)$  as follows:

$$K_{\text{app}}(T) = K_{\text{app}}(T_{\text{ref}}) g(T, T_{\text{ref}}) \exp\left\{-\frac{E_q}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right\} \quad (2-13)$$

Taking logarithms of both sides of eq. (2-13), we obtain the following linear equation:

$$\ln \frac{K_{\text{app}}(T)}{K_{\text{app}}(T_{\text{ref}}) g(T, T_{\text{ref}})} = -\frac{E_q}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right) \quad (2-14)$$

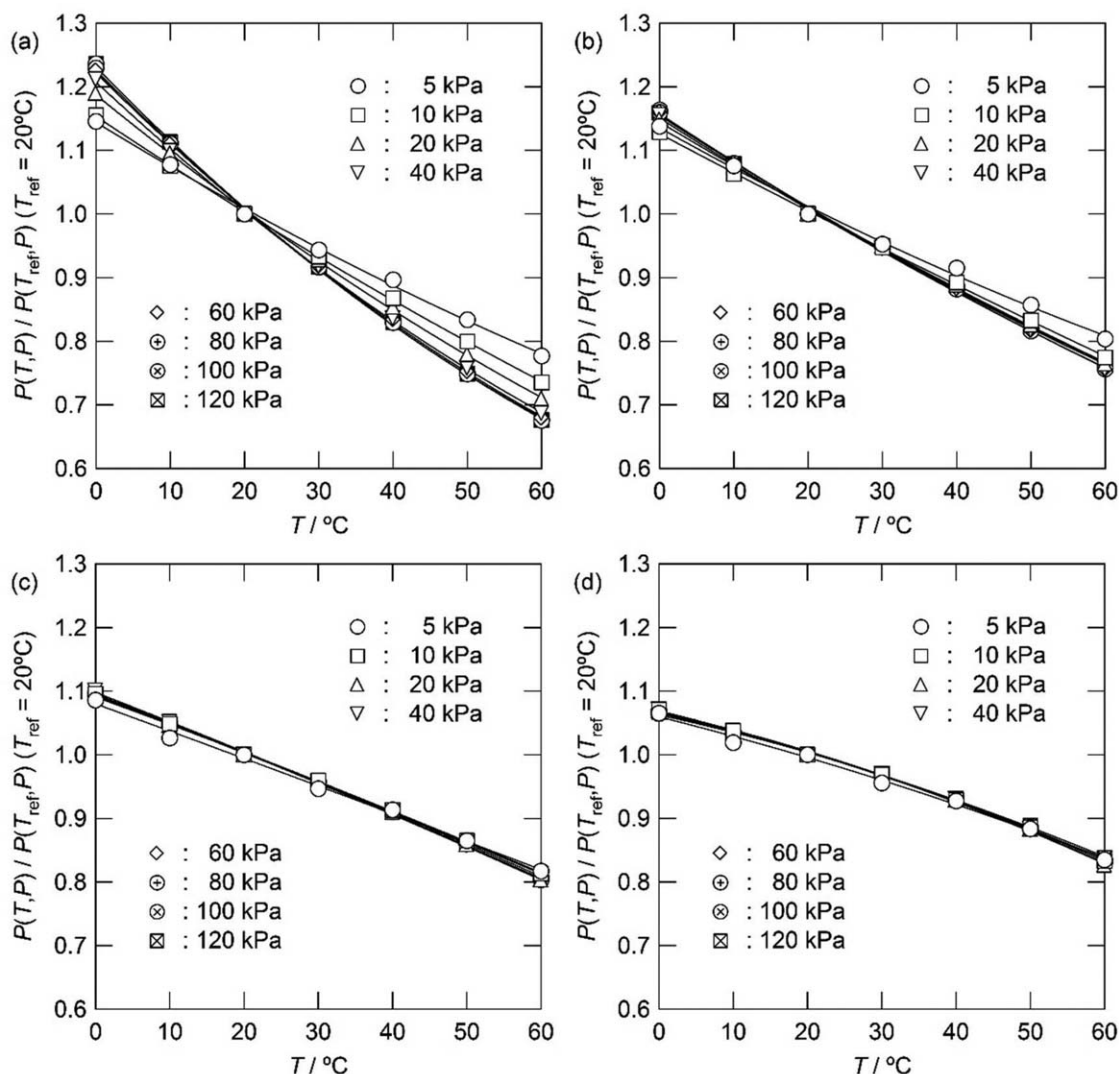
Thus, a plot of  $\ln\{K_{\text{app}}(T)/\{K_{\text{app}}(T_{\text{ref}})g(T, T_{\text{ref}})\}\}$  versus  $1/T - 1/T_{\text{ref}}$  affords a straight line with slope  $-E_q/R$ .

Using eqs. (2-2) and (2-13), the temperature sensitivity at the reference state ( $T_{\text{ref}}, P_{\text{ref}}$ ) is given as follows:

$$\left[\frac{d}{dT} \left[\frac{I(T, P_{\text{ref}})}{I(T_{\text{ref}}, P_{\text{ref}})}\right]\right]_{T=T_{\text{ref}}} = f_{nr} \left[\frac{dg(T, T_{\text{ref}})}{dT}\right]_{T=T_{\text{ref}}} + f_q \left(-\frac{E_q}{RT_{\text{ref}}^2}\right) \quad (2-15)$$

where  $f_{nr}$  and  $f_q$  are defined as follows:

$$f_{nr} = 1 - C(T_{\text{ref}}, P_{\text{ref}}) = 1 - \frac{K_{\text{app}}(T_{\text{ref}}) P_{\text{ref}}}{1 + K_{\text{app}}(T_{\text{ref}}) P_{\text{ref}}} \quad (2-16)$$



**Figure 5.** Relative luminescent intensities of the PSP coatings comprising PtTFPP and poly(HFIPM-*co*-TBM) ( $F_{\text{HFIPM}} = 0$  (a), 0.34 (b), 0.63 (c), and 1 (d)) as a function of temperature.

$$f_q = 1 - f_{nr} = C(T_{\text{ref}}, P_{\text{ref}}) = \frac{K_{\text{app}}(T_{\text{ref}})P_{\text{ref}}}{1 + K_{\text{app}}(T_{\text{ref}})P_{\text{ref}}} \quad (2-17)$$

Because  $g(T, T_{\text{ref}})$  defines the relative luminescence intensity in a vacuum (namely in the absence of oxygen),  $[dg(T, T_{\text{ref}})/dT]_{T=T_{\text{ref}}}$  defines the temperature sensitivity contributed by the nonradiative deactivation process. By contrast, the quantity  $-E_q/RT_{\text{ref}}^2$  is the temperature sensitivity contributed by luminescence quenching by oxygen molecules. Therefore, eq. (2-15) implies that the apparent temperature sensitivity can be fractionated into two distinct sensitivities, one due to nonradiative deactivation, and the other due to luminescence quenching by oxygen molecules.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Poly(HFIPM-*co*-TBM)

Radical copolymerizations of HFIPM and TBM were carried out in ethyl acetate at 60°C using AIBN as an initiator (Scheme 1). The polymerization mixture was purified by reprecipitation with methanol to give the copolymer as a white

solid. Figure 1 shows the  $^1\text{H}$  NMR spectrum of poly(HFIPM-*co*-TBM) ( $F_{\text{HFIPM}} = 0.44$ ) in  $\text{CDCl}_3$ . The peak at 5.5–5.8 ppm is assigned to the methine proton of the HFIPM unit, whereas the peaks at 0.5–2.5 ppm arise from the main chain and *tert*-butyl groups. The area ratio of these two regions gives the mole fraction of the HFIPM units in copolymer ( $F_{\text{HFIPM}}$ ). To determine the monomer reactivity ratios  $r_{\text{HFIPM}}$  and  $r_{\text{TBM}}$ , the polymerization was initially limited to 1 h to suppress monomer conversion (Table I). The composition of the resulting copolymer was determined by  $^1\text{H}$  NMR spectroscopy. Figure 2 shows the copolymer composition curve during the radical copolymerization of HFIPM with TBM. The data were fitted to the Mayo–Lewis equation (solid line), from which the  $r_{\text{HFIPM}}$  and  $r_{\text{TBM}}$  values were determined as 0.45 and 0.67, respectively. The slightly alternating tendency in the sequence of the resulting copolymer is attributed to the electron-withdrawing nature of the 1,1,1,3,3,3-hexafluoroisopropyl group and the electron-donating nature of the *tert*-butyl group. Otsu *et al.* reported the  $Q$  and  $e$  values of 0.78 and

**Table III.** Summary of Temperature Sensitivities at the Reference State

$F_{\text{HFIPM}}^{\text{b}}$	Overall (%/°C)	Nonradiative	Luminescence quenching by $\text{O}_2$		Calc <sup>a</sup> (%/°C)
		$dg(T, T_{\text{ref}})/dT$ ( $f_{\text{nr}}^{\text{c}}$ ) (%/°C)	$E_{\text{q}}^{\text{d}}$ (kJ mol <sup>-1</sup> )	$-E_{\text{q}}/RT_{\text{ref}}^2$ ( $f_{\text{q}}^{\text{e}}$ ) (%/°C)	
0	-1.01	-0.41 (0.11)	7.8	-1.10 (0.89)	-1.02
0.14	-0.84	-0.40 (0.09)	6.4	-0.90 (0.91)	-0.86
0.34	-0.69	-0.38 (0.08)	5.4	-0.76 (0.92)	-0.73
0.44	-0.58	-0.35 (0.07)	4.5	-0.64 (0.93)	-0.62
0.63	-0.45	-0.38 (0.07)	3.6	-0.50 (0.93)	-0.49
0.69	-0.40	-0.36 (0.07)	3.1	-0.43 (0.93)	-0.42
1	-0.34	-0.35 (0.08)	2.5	-0.35 (0.92)	-0.35

<sup>a</sup> Temperature sensitivity calculated by eq. (3-4).

<sup>b</sup> Mole fraction of the HFIPM units in the copolymer.

<sup>c</sup> Temperature sensitivity due to the non-radiative deactivation process; the values in the parenthesis are the fractional contributions to the overall temperature sensitivity.

<sup>d</sup> Activation energy of overall luminescence quenching by oxygen molecules.

<sup>e</sup> Temperature sensitivity due to the luminescence quenching by oxygen molecules; the values in the parenthesis are the fractional contributions to the overall temperature sensitivity.

0.17, respectively, for TBM in conventional bulk radical copolymerization with styrene at 60°C.<sup>16</sup> In our previous paper,<sup>13</sup> we determined the  $Q$  and  $e$  values of HFIPM as 1.21 and 1.19, respectively, in conventional radical copolymerization with styrene in ethyl acetate at 60°C. Subsequently, we calculated the  $r_{\text{HFIPM}}$  and  $r_{\text{TBM}}$  as 0.46 and 0.77, respectively, under Alfrey and Price's  $Q$ - $e$  framework. These calculated values reasonably agree with the experimental values, indicating no significant steric effect in the radical copolymerization. To examine the pressure and temperature sensitivities, we prepared poly(HFIPM-*co*-TBM) with high monomer conversion under the same conditions (Table II). The number-average molar mass ( $M_n$ ) was varied from 76,800 to 200,000, and the dispersity ( $M_w/M_n$ ) ranged from 1.47 to 2.21. The glass transition temperature ( $T_g$ ) was determined by differential scanning calorimetry (DSC). Panels (a) and (b) of Figure 3 show the DSC traces and the plots of  $T_g$  versus the weight fraction of the TBM units in the copolymers ( $w_{\text{TBM}}$ ). As expected, the  $T_g$  values monotonically increased from 77 to 126°C with an increase in the  $w_{\text{TBM}}$  values. The  $T_g$  values were significantly higher than those predicted by the Fox equation<sup>17</sup> [broken line in Figure 3(b)]. The Fox equation is given by

$$\frac{1}{T_g} = \frac{w_{\text{TBM}}}{T_{g,\text{PTBM}}} + \frac{w_{\text{HFIPM}}}{T_{g,\text{PHFIPM}}} \quad (3-1)$$

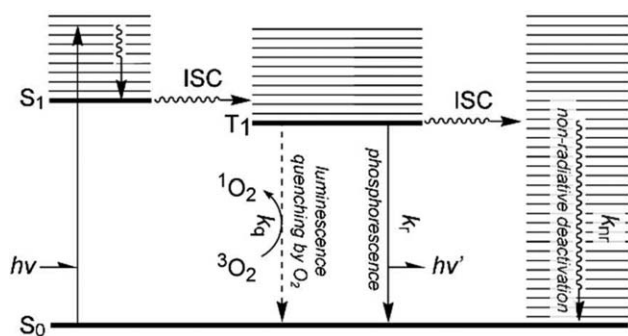
where  $T_{g,\text{PTBM}}$  and  $T_{g,\text{PHFIPM}}$  are the  $T_g$  values of TBM and HFIPM homopolymers, respectively, and  $w_{\text{TBM}}$  and  $w_{\text{HFIPM}}$  are the weight fractions of the TBM and HFIPM units, respectively, in the copolymer. Hence, we fitted the plots to the Gordon–Tayler equation<sup>18</sup>

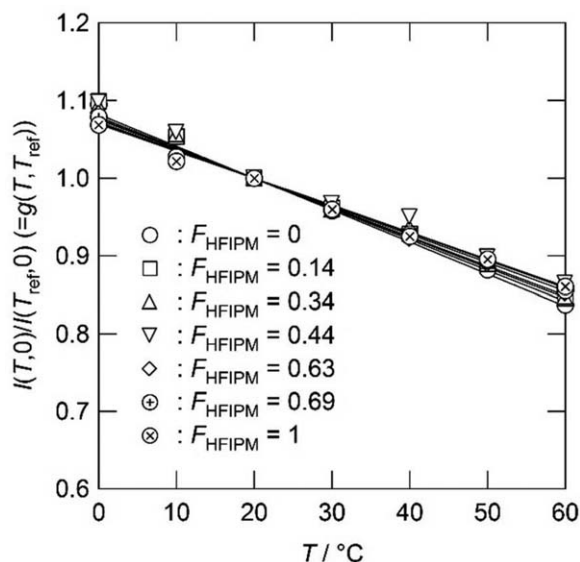
$$T_g = \frac{T_{g,\text{PTBM}} w_{\text{TBM}} + K_{\text{GT}} T_{g,\text{PHFIPM}} w_{\text{HFIPM}}}{w_{\text{TBM}} + K_{\text{GT}} w_{\text{HFIPM}}} \quad (3-2)$$

where  $K_{\text{GT}}$  is the fitting parameter. The best-fit Gordon–Tayler equation [solid line in Figure 3(b)] was obtained for  $K_{\text{GT}} = 0.50$ . Zhou *et al.* reported on conventional radical copolymerizations of HFIPM with methyl methacrylate (MMA) and the thermal properties of the resulting copolymers.<sup>19</sup> Interestingly, they found that the  $T_g$  value was higher in copolymer containing 30 wt % HFIPM units than in the homopolymers of HFIPM and MMA. Unlike poly(HFIPM-*co*-TBM), their plots of  $T_g$  versus weight fraction positively deviated from the Gordon–Tayler equation, hence, they fitted their  $T_g$  values to the Schneider equation<sup>20</sup>

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = (1 + K_1) w_{2c} - (K_1 + K_2) w_{2c}^2 + K_2 w_{2c}^3 \quad (3-3)$$

where  $w_{2c}$  is the weight fraction corrected by the  $K_{\text{GT}}$  value in the Gordon–Tayler equation, and  $K_1$  and  $K_2$  are fitting parameters. In poly(HFIPM-*co*-MMA), the best fit parameters  $K_{\text{GT}}$ ,  $K_1$  and  $K_2$  were determined as 0.36, 6.57, and 5.74, respectively. The large  $K_1$  and  $K_2$  values indicate significant enthalpic and entropic interactions between the HFIPM and MMA units. Because the Gordon–Tayler and Schneider equations are identical when both  $K_1$  and  $K_2$  values are zero, the  $K_1$  and  $K_2$  values of poly(HFIPM-*co*-TBM) are substantially zero and significantly lower than those of poly(HFIPM-*co*-MMA). This suggests that the bulky *tert*-butyl groups of TBM units interfere interactions with the HFIPM units in poly(HFIPM-*co*-TBM).

**Figure 6.** Jablonski diagram.



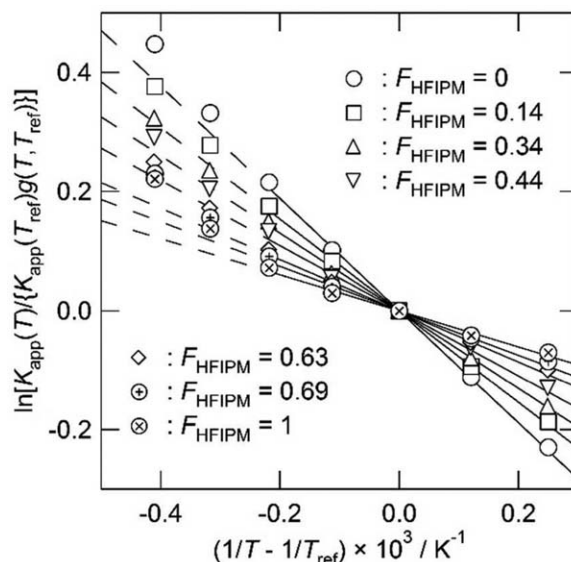
**Figure 7.** Relative luminescence intensities of the PSP coatings comprising PtTFPP and poly(HFIPM-co-TBM) in the absence of oxygen as a function of temperature.

#### Pressure and Temperature Sensitivities

The pressure and temperature sensitivities of the PSP coatings comprising the resulting copolymers were examined by using PtTFPP as the luminescent dye. The PSP coatings were formed on aluminum plates using a conventional air brush filled with an ethyl acetate solution of the copolymers and PtTFPP. The polymer and PtTFPP concentrations were 25 and 0.5 g L<sup>-1</sup>, respectively. The coatings were irradiated under a Xe lamp, and their luminescence intensities were collected as the air pressure and temperature was ranged from 5 to 120 kPa and from 0 to 60°C, respectively. Figure 4 shows representative examples of the modified Stern–Volmer plots, namely the plots of the  $I(T, P_{ref})/I(T, P)$  versus  $P/P_{ref}$  at a reference air pressure  $P_{ref}$  of 100 kPa. These plots were well fitted with the two-site model, with a small contribution by the nonresponsible components ( $K_{app} = 0$ ) [eq. (2–6)]. From the plots, we obtained the apparent Stern–Volmer constants,  $K_{app}(T)$  (in kPa<sup>-1</sup>) and the fractional contributions  $f$  (the best-fit parameters are listed in Tables SI–SVII in the Supporting Information). Figure 4 indicates that the pressure sensitivity, which can be evaluated by the slope of the plots, slightly increased with increasing  $F_{HFIPM}$ . Surprisingly, the TBM homopolymer showed excellent pressure sensitivity despite lacking fluorine atoms. Therefore, fluorine atoms are dispensable for achieving high pressure sensitivity. Figure 5 shows representative plots of  $I(T, P)/I(T_{ref}, P)$  as functions of the temperature  $T$  (where  $T_{ref} = 20^\circ\text{C}$ ). The temperature sensitivity, estimated by the slope of the plots, depended on the air pressure and apparently decreased with increasing  $F_{HFIPM}$ . Unfortunately, this indicates that the introduced TBM units did not reduce the temperature sensitivity of the PSP coating.

#### Theoretical Model of the PSP Luminescence Kinetics

Table III summarizes the temperature sensitivity of the luminescence intensity at the reference state ( $T_{ref}, P_{ref}$ ) (listed in the column titled



**Figure 8.** Plots of  $\ln\{K_{app}(T)/\{K_{app}(T_{ref})g(T, T_{ref})\}\}$  values as a function of  $(1/T - 1/T_{ref}) \times 10^3 / \text{K}^{-1}$ . The reference temperature ( $T_{ref}$ ) is 293 K.

“overall” in Table III). As the  $F_{HFIPM}$  increased, the temperature sensitivity decreased from  $-1.01$  to  $-0.34\%/^\circ\text{C}$ . Typically, a dye that is electronically excited by photoirradiation is deactivated via radiative or non-radiative deactivation processes or by energy transfer to an oxygen molecule (Figure 6). The temperature sensitivity of the luminescence intensity stems from the temperature dependency of the rate constants in the nonradiative deactivation process ( $k_{nr}$ ) and/or in the overall luminescence-quenching process ( $k_q$ ) by an oxygen molecules including the dissolution and diffusion processes of oxygen molecules. To analyze the temperature sensitivity, we assumed an Arrhenius-type equation for the rate constants  $k_{nr}$  and  $k_q$ . Under this assumption, the temperature sensitivity at the reference state can be divided into the two terms described as follows:

$$\left[ \frac{d}{dT} \left[ \frac{I(T, P_{ref})}{I(T_{ref}, P_{ref})} \right] \right]_{T=T_{ref}} = f_{nr} \left[ \frac{dg(T, T_{ref})}{dT} \right]_{T=T_{ref}} + f_q \left( -\frac{E_q}{RT_{ref}^2} \right) \quad (3-4)$$

In eq. (3-4),  $E_q$  denotes the overall activation energy of the luminescence-quenching by oxygen molecules, and  $g(T, T_{ref})$  is the relative luminescent intensity in a vacuum at temperature  $T$ , defined as follows:

$$g(T, T_{ref}) = \frac{I(T, 0)}{I(T_{ref}, 0)} = \frac{I(T, 0)}{I(T, P_{ref})} \times \frac{I(T_{ref}, P_{ref})}{I(T_{ref}, 0)} \times \frac{I(T, P_{ref})}{I(T_{ref}, P_{ref})} \quad (3-5)$$

The parameters  $f_{nr}$  and  $f_q$  are defined as follows:

$$f_{nr} = 1 - C(T_{ref}, P_{ref}) = 1 - \frac{K_{app}(T_{ref})P_{ref}}{1 + K_{app}(T_{ref})P_{ref}} \quad (3-6)$$

$$f_q = 1 - f_{nr} = C(T_{ref}, P_{ref}) = \frac{K_{app}(T_{ref})P_{ref}}{1 + K_{app}(T_{ref})P_{ref}} \quad (3-7)$$

Because  $g(T, T_{ref})$  is the relative luminescence intensity in the absence of oxygen, the first term in the right side of eq. (3-4)



represents the temperature sensitivity due to the nonradiative deactivation process. The second term in the right side of eq. (3-4) represents the temperature sensitivity due to the luminescence-quenching by oxygen molecules because this term only depends on the  $E_q$  value. Therefore,  $f_{nr}$  and  $f_q$  denote the fractional contributions of the nonradiative deactivation and the luminescence-quenching by oxygen molecules, respectively, to the overall temperature sensitivity. Figure 7 plots  $g(T, T_{ref})$  as a function of temperature. The temperature sensitivities of  $g(T, T_{ref})$  at the reference temperature  $T_{ref}$ , denoted  $[dg(T, T_{ref})/dT]_{T=T_{ref}}$ , fall in a relatively narrow range between  $-0.41$  and  $-0.35\%/^{\circ}\text{C}$  (Table III). This suggests that the TBM units had little effect on the temperature sensitivity contributed by the nonradiative deactivation process.

Under the above assumption, the apparent Stern–Volmer constant  $K_{app}(T)$  is given by eq. (3-8):

$$K_{app}(T) = K_{app}(T_{ref})g(T, T_{ref})\exp\left\{-\frac{E_q}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right\} \quad (3-8)$$

Therefore, the  $E_q$  value can be estimated by plotting  $\ln\{K_{app}(T)/\{K_{app}(T_{ref})g(T, T_{ref})\}\}$  as a function of  $(1/T - 1/T_{ref})$ . Figure 8 indicates the relatively good linearity of the plots of  $\ln\{K_{app}(T)/\{K_{app}(T_{ref})g(T, T_{ref})\}\}$  as a function of  $(1/T - 1/T_{ref})$ . The  $E_q$  values were determined by the linear regression of the plots around the reference temperature  $T_{ref}$ . As the  $F_{HFIPM}$  increased, the  $E_q$  values decreased from 7.8 to 2.5  $\text{kJ mol}^{-1}$  (Table III). These correspond to the temperature sensitivities of  $-1.10$  to  $-0.35\%/^{\circ}\text{C}$  at the reference temperature  $T_{ref}$ . In addition, the fractional contributions  $f_{nr}$  and  $f_q$  were calculated from the  $K_{app}(T_{ref})$  value. All variables in eq. (3-4) are listed in Table III. These values approximately satisfy eq. (3-4), indicating that this theoretical model properly describes the luminescence kinetics. Therefore, incorporating the TBM units into the HFIPM polymer slightly affects the temperature sensitivity contributed by nonradiative deactivation in the polymer but significantly increases that contributed by luminescence quenching by oxygen molecules. The  $f_q$  value is identical to the pressure sensitivity in the modified Stern–Volmer plot and is typically close to unity. Hence, eq. (3-4) suggests that the overall temperature sensitivity predominantly depends on the activation energy of the luminescence quenching process rather than on the nonradiative deactivation process. This is the reason why the introduced TBM units did not reduce the temperature-sensitivity, because the TBM units mainly affect the nonradiative deactivation process.

## CONCLUSIONS

The conventional radical copolymerizations of HFIPM and TBM afforded the poly(HFIPM-co-TBM)s with various compositions. The monomer reactivity ratios  $r_{HFIPM}$  and  $r_{TBM}$  suggest a small preference for alternating polymer characteristics. As expected, the glass transition temperature of the copolymer increased with increasing the mole fraction of the TBM units in the copolymer. The PSP coatings were prepared on an aluminum plate using PtTFPP as a luminescent dye and the resulting copolymer as a binder, and their luminescence intensities were collected under various air pres-

ures and temperatures. The modified Stern–Volmer plot was relatively insensitive to the polymer composition. Surprisingly, despite lacking any fluorine atoms, poly(TBM) showed a very high pressure sensitivity. Unfortunately, the introduced TBM units increased the temperature sensitivity of the copolymer, which is an undesired property. Assuming an Arrhenius-type equation for the rate constants  $k_{nr}$  and  $k_q$ , the temperature sensitivity at the reference state was theoretically divided into two contributions; one from nonradiative deactivation and the other from luminescence quenching by oxygen molecules. This theoretical model was validated by the calibration data of poly(HFIPM-co-TBM). According to the data analysis, the enhanced temperature sensitivity after introducing the TBM units only slightly affects the temperature sensitivity due to a nonradiative deactivation process, but significantly increases the temperature sensitivity due to luminescence quenching by oxygen molecules. The theoretical model derived in this study could assist in elucidating the origin of the temperature sensitivity and for developing novel binders for PSP.

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