Temperature-Dependent, Static, and Dynamic Fluorescence Properties of Disubstituted Acetylene Polymer Films

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The fluorescence thermosensing behavior of poly[1-(trimethylsilyl)phenyl-2-phenylacetylene] (PTMSDPA) as a thin film was investigated for the purpose of potential application of this polymer as a thermosensor. The fluorescence significantly decreased as the temperature increased in a wide range from 25 to 200 °C. Conversely, the fluorescence increased as the temperature decreased. This fluorescence−temperature relationship held for the repeated trials. In the IR spectra, new peaks gradually appeared in a range from 1300 to 1800 cm^{-1} surrounding the 1590 cm^{-1} peak due to C═C double bond. This was caused by increasing temperature, indicating an occurrence of a slight molecular perturbation in the main chain. In the time-resolved fluorescence spectroscopy, the fluorescence decayed as the temperature increased, indicating significant exciton deconfinement at high temperature. The quenching rates of PTMSDPA in solution and in film at 95 °C are approximately 0.80 and 0.45, respectively. The PTMSDPA quenched the fluorescence more quickly than other fluorescent disubstituted acetylene polymers tested in this study. The PTMSDPA has a low density (0.91) and a high fractional free volume (FFV, 0.26). Thus, we presumed that PTMSDPA may provide substantial space for molecular perturbation even in the solid film.

Introduction

A variety of molecular thermosensors based on thermochromic conjugated polymers,[1−5] fluorescent dye-labeled polymers,[6−8] metallophorphyrin-based supramolecules[9] as well as conventional coordination dynamics-based metal salts sensors[10] have been developed to date and have shown excellent performance in multicolor appearance, switching, and logic gate function, as well as high sensitivity and reproducibility. However, most molecular sensors work only in solution and hence their applications are limited to wet conditions. Meanwhile, fluorescent dye-dispersed polymers have been extensively used as temperature-sensitive paints (TSP) and pressure-sensitive paints (PSP), for aerodynamic testing, with such benefits as low cost, easy setup, high sensitivity, and real-time monitoring.[11−17] As a result of the intrinsic conjugation cooperativity, conjugated polymers can respond to minor changes in electronic structure.[18] In this respect, fluorescent conjugated polymers should be optimal as an optical output material of fine fluorescence (FL) imaging because there will be no significant phase separation and aggregation in the film unlike fluorescent dye-dispersed polymers. However, practical application is dependent upon the polymer's stability. Thus, if such conjugated polymers prove thermally, chemically, and mechanically stable in a wide temperature range, the sensory materials would be more appealing for practical applications.

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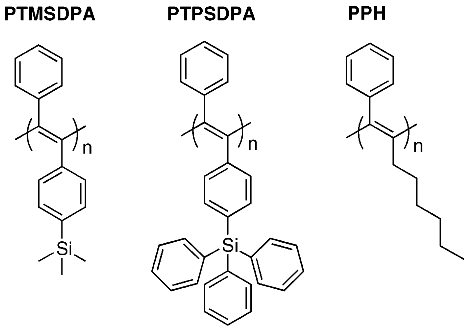
Chart 1. Chemical Structures of FL DAPs tested in This Study



Substituted acetylene polymers have attracted much attention as a result of their unusual functional properties derived from various substituents.[19] In particular, disubstituted acetylene polymers (DAPs) are intensively fluorescent in the blue and green regions, whereas the corresponding monosubstituted acetylene polymers and unsubstituted polyacetylene do not exhibit FL, or at most exhibit very weak FL, without the aid of an appropriate chromophoric pendant.[20−24] The exciton dynamics and electronic structures of DAPs have been explored theoretically and also documented by means of time-resolved FL spectroscopy and polarized Raman scattering studies.[22,25,26] The major reason for DAP high emission quantum efficiencies is now explained in terms of effective exciton confinement on the main chain due to the steric hindrance and/or intramolecular π electron interaction of such bulky aromatic substituents as the phenyl ring. This means that their FL efficiency can be controlled either by modification of the chemical/electronic structures of the side groups or by electronic perturbation and disorder induced by external stimuli within the conjugating main chain. Indeed, the effects that chemical structure of the side group have on their photophysical properties was clearly verified by Yoshino et al.[26] They showed that the exciton dynamics of the DAPs significantly depends on the substituents attached to the side chain. On the other hand, the influence of such external stimuli as heat on the FL efficiency has not been reported yet.

Among the DAPs, the aromatic polyacetylene, poly[1-(trimethylsilyl)phenyl-2-phenylacetylene] (PTMSDPA in Chart 1), has attracted much attention as photoluminescence and electroluminescence (PL/EL) (quantum yield, $\Phi = 0.25$ in film) device materials,[27,28] highly gas permeable membranes,[29] and optical sensors,[30] and it was recently developed as a photopolymer[31] for fluorescent image patterning by us. In addition, the same polymer with a high molecular weight up to 1.0×10^6 can be easily obtained by using $TaCl_5$−*n*-Bu_4Sn catalyst.[32] This polymer is quite soluble in organic solvents, such as chloroform and toluene, and then provides a mechanically very strong membrane.[33] Moreover, this polymer is thermally stable, even though it is a purely organic material, presumably because the main chain consisting of C=C double bonds is protected by the two bulky phenyl rings of the side chain. In fact, no weight loss of the polymer occurs below approximately 400 °C in thermogravimetric analysis (TGA). This satisfies the basic requirement for thermosensors: heat resistant in practical use. Therefore, if the photophysics of the PTMSDPA is sensitive to heat, the polymer and its derivatives may be applicable to such advanced materials as sensing paint for luminescence imaging.

On the basis of this idea, we investigated the thermooptical property and potential application of the PTMSDPA thin film as an optical thermosensor. This polymer was found to be suitable for FL thermosensing in a wide temperature range. The FL was directly related to temperature in the range from 25 to 200 °C. Temperature-variable, time-resolved FL spectroscopy and temperature-variable IR spectroscopy studies revealed that the thermally induced FL quenching is ascribed to exciton deconfinement related to molecular perturbation of the conjugating main chain.

Experimental Section

Synthesis. PTMSDPA, poly[1-(triphenylsilyl)phenyl-2-phenylacetylene] (PTPSDPA), and poly(1-phenyl-1-heptyne) (PPH) were synthesized according to the method used by Masuda et al.[32,33]

Preparation of Thin Films. Thin films were prepared by spin-coating the toluene solution on a glass slide (Matsunami) using a Mikasa 1H-D7 spin coater. The thickness of all films was adjusted for the absorbance at the λ_{max} to be approximately 1.

Measurements. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymer were evaluated using gel permeation chromatography (Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B [300 mm in length] as the column and HPLC-grade tetrahydrofuran as the eluent at 40 °C), based on a calibration with polystyrene standards. IR and emission spectra were measured on Horiba FT-730 spectrophotometer and JASCO FP-6500 spectrofluorometer, respectively. The time-resolved FL spectrum was measured on a streak camera using a femtosecond pulse-laser system (a Ti−sapphire mode-lock laser pumped by a continuous wave diode laser) and a second

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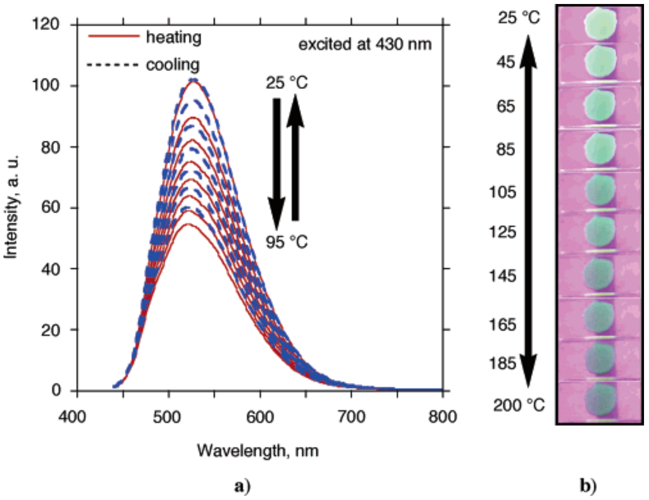

Figure 1. Changes in (a) florescence spectra and (b) appearance of the 1.0-μm-thick PTMSDPA film upon heating and cooling.

harmonic generator unit. The pulse width was approximately 100 fs, and the repetition rate was 76 MHz. The center wavelength of 400 nm was used as the excitation light source. All measurements were conducted in air. All temperature-variable measurements were carried out on a Mettler Toledo FP82HT hot stage equipped with a Mettler Toledo FP90 central processor. The density of each sample was determined using a Mettler Toledo AX205 analytic balance coupled with a Mettler Toledo density determination kit at room temperature. The density determinations were performed by Archimedes' principle, and methanol was used as an auxiliary liquid. The isothermal TGA was performed in air at 200 °C using a Seiko EXSTR6200 TG-DTA apparatus.

Results and Discussion

The PTMSDPA used in this study has a weight-average molecular weight (M_w) of 5.6×10^5 with a polydispersity of 5.3. For the absorbance of a film of PTMSDPA at the λ_{max} to be approximately 1, experimental conditions such as the concentration of polymer solution and spin-coating process were adjusted. Eventually, a thin film with thickness of approximately 1 μm was obtained on a slide glass.

Figure 1a shows the changes in FL spectra of the PTMSDPA film upon heating from 25 to 95 °C. The FL gradually decreased with increasing temperature and returned to the initial intensity after cooling. The change was also recognized by the naked eye in a wider range from 25 to 200 °C, as shown in Figure 1b. This FL-temperature relationship was consistent for repeated trials, as shown in Figure 2. This indicates neither degradation nor thermal oxidation in the film in the course of heating. Figure 3 shows the isothermal TGA curves at 200 °C. No weight loss occurs even after several hours of high heat, confirming the excellent heat resistance of PTMSDPA.

Figure 4 shows the temperature-variable IR spectra of the PTMSDPA film on a KBr pellet. The polymer exhibited several characteristic peaks at 2960 ($\delta_{\mathrm{s,C-H}}$), 1590 ($\delta_{\mathrm{s,C=C\ double\ bond}}$), 1250 ($\delta_{\mathrm{s,SiC-H}}$), 1119, 855 ($\nu_{\mathrm{as,Si-CH_3}}$), and 812 ($\nu_{\mathrm{s,Si-CH_3}}$) cm^{-1} at all temperatures tested in the range of 25–95 °C. Noticeably, new peaks gradually appeared in the range from 1300 to 1800 cm^{-1} on either side of the 1590 cm^{-1} peak due to the C=C double bond with increasing temperature, which indicates occurrence of other stretching vibrations with various energies within the main chain, whereas there were few changes around the 2960 cm^{-1}, 1250 cm^{-1}, 855 cm^{-1}, and 812 cm^{-1} peaks due to the C–H and C–Si bonds within the side chain. Conjugated polymers usually exhibit collective properties that are sensitive to such a minor electronic disorder.[18] Thus, we concluded that the thermally induced change in the photophysical properties of PTMSDPA is due to a slight molecular perturbation in the main chain.

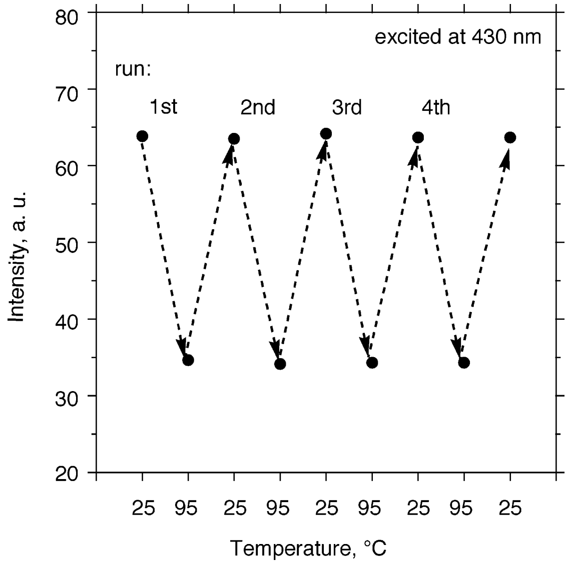

Figure 2. Dependence of FL intensity of the 1.0-μm-thick PTMSDPA film at 530 nm on the repeatedly changing temperature between 25 and 95 °C

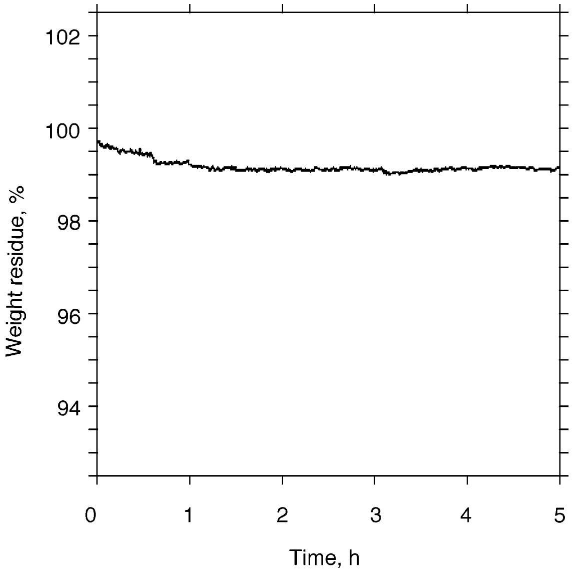

Figure 3. Isothermal TGA curve of PTMSDPA in air at 200 °C.

To understand the appreciable FL thermosensitivity of PTMSDPA in detail, we further investigated the exciton dynamics using temperature-variable, time-resolved FL spectroscopy. Figure 5 shows the change in FL decay curves as the temperature increases from 25 to 200 °C. The FL decays non-single exponentially at all emission wavelengths tested. As expected, the FL decays fast as the temperature increases, indicating significant exciton deconfinement at high temperature. Figure 6 shows the FL decays of PTMSDPA observed at different emission wavelengths. The FL decay is significantly dependent on the emission

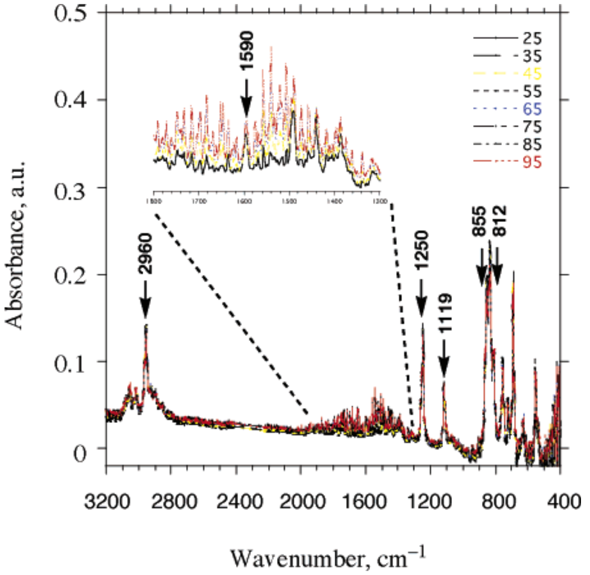

Figure 4. Change in IR spectra of PTMSDPA film upon heating.

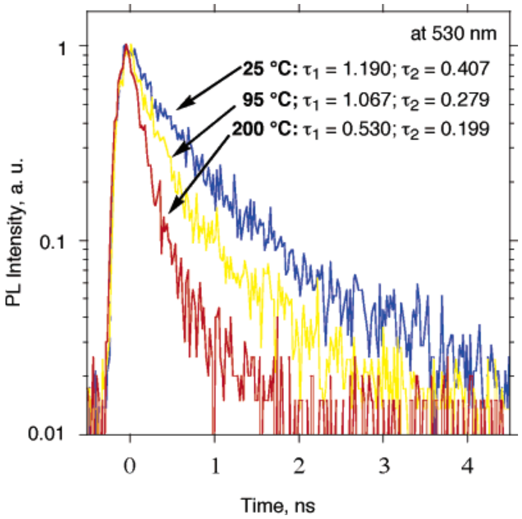

Figure 5. FL decay of the 1.0-μm-thick PTMSDPA film at different monitoring temperatures at 530 nm. The wavelength corresponds to the wavelength of the FL spectral peak. The FL decay dynamics are described by a two-term exponential function.

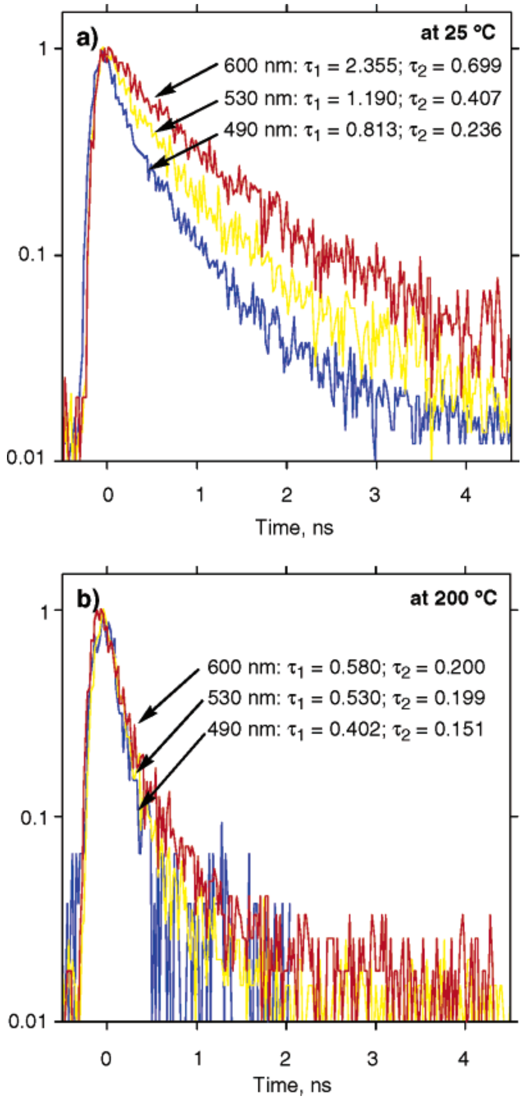

Figure 6. FL decays of the 1.0-μm-thick PTMSDPA film at three different emission wavelengths at (a) 25 °C and (b) 200 °C. The FL decay dynamics are described by a two-term exponential function.

wavelength at 25 °C. That is, the FL decays faster at short emission wavelengths than at long ones, suggesting an efficient energy migration or transfer from higher to lower energy levels at low temperature. However, such dependency of FL decay on emission wavelength was not observed at 200 °C. This strongly suggests that certain charge separation begins to occur as the temperature increases and then the charge transfer character with a non-radiative process overcomes an energy transfer character with a radiative process. In other words, the FL quenching is ascribed to a certain polar excited state, which results from an exciton deconfinement in the main chain. Accordingly, the thermally induced FL quenching of PTMSDPA is not explicable only in terms of molecular perturbation but also according to exciton dissociation in the main chain.

Figure 7 shows the FL quenching rates of PTMSDPA in a dilute solution and in a solid. The PTMSDPA exhibited a significant FL quenching in the solution. The degree of quenching in solution is greater than that in film. The quenching rates in solution and film at 95 °C are approximately 0.80 and 0.45, respectively. This suggests that FL quenching does not result only from intramolecular electronic disorder but also from intermolecular electron coupling which accompanies self-absorption. Thus, such intermolecular factors as local molecular mobility[36] and molecular packing would be very important for the solid-state thermo-sensitivity as related to molecular perturbation.

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(34) The fractional free volume is defined as follows: FFV = $(v_{sp} - v_0)/v_{sp} \approx (v_{sp} - 1.3v_W)/v_{sp}$ where v_{sp} is the specific volume of the polymer and v_0 is the occupied volume (or zero-point volume at 0 K) of the polymer. Typically, the occupied volume is estimated to be 1.3 times the van der Waals volume (v_W), which is calculated from group contribution methods (van Krevelen, D. W. *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, 3rd ed.; Elsevier Science: Amsterdam, 1990; pp 71−107). The factor of 1.3 is a universal packing parameter introduced by Bondi (Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; John Wiley and Sons: New York, 1968; pp 25−52, 53−97).

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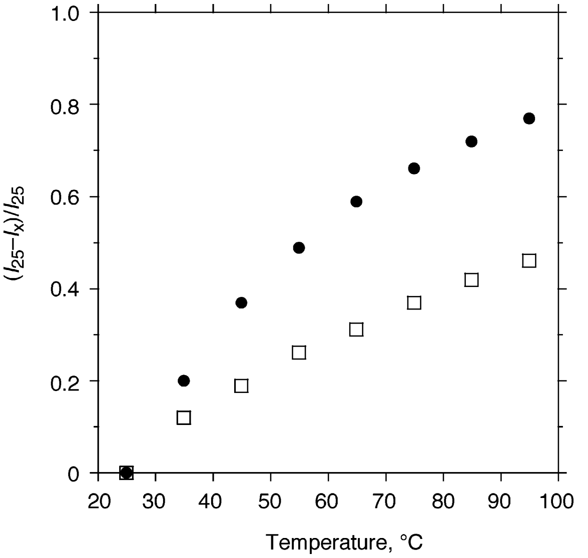

Figure 7. Plots of FL quenching of the PTMSDPA as a function of temperature (●, in solution, $c = 1.0 \times 10^{-6}$ M; □, in the 1.0-μm-thick film). The I_{25} and I_x are the intensities of FL at 25 and X °C, respectively.

Table 1. Molecular Weights and Physical Properties of DAPs

polymer	molecular weight (M_w, M_w/M_n)	$\nu_{em,max}$ (nm)	density (g/cm^3)	FFV[a]
PTMSDPA	5.6×10^5, 5.3	530	0.91[b]	0.26[b]
PTPSDPA	1.3×10^6, 5.8	540	1.16[c]	0.13[c]
PPH	2.8×10^5, 4.5	445	1.03	0.15

[a] Calculated using the equation shown in ref 34. [b] Reference 29. [c] Reference 35.

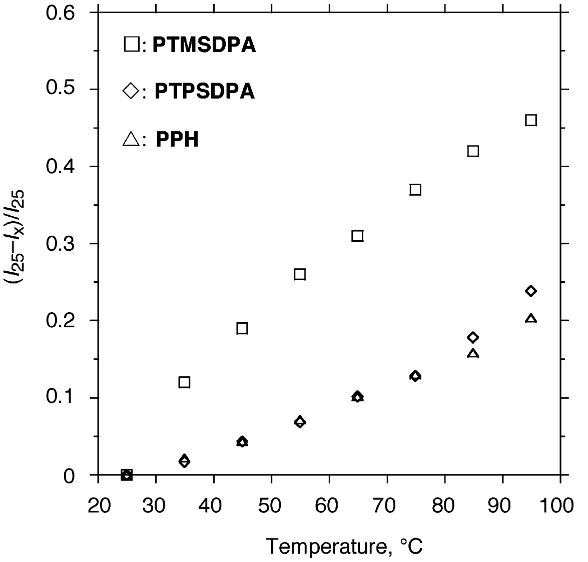

Figure 8. Plots of FL quenching of thin films from polymers listed in Table 1 as a function of temperature. The I_{25} and I_x are the intensities of FL at 25 and X °C, respectively.

To clarify this idea, we investigated FL quenching behaviors of some other fluorescent DAPs (PTPSDPA and PPH) in comparison with that of PTMSDPA. The chemical and physical properties of these glassy polymers are summarized in Table 1. The PTPSDPA has an extremely bulky, heavy substitutent in the side chain and shows an intense emission in the yellowish green region similar to that of PTMSDPA, while the PPH, which is a DAP with one alkyl side chain, emits blue light. Figure 8 shows the degrees of FL quenching of PTPSDPA and PPH compared to that of PTMSDPA. Both of them quench the FL more slowly as compared to PTMSDPA, although their chemical and electronic structures differ quite a bit from each other. The PTMSDPA has two very bulky phenyl rings and a trimethylsilyl group in the side chain. The steric bulkiness of these large substituents inhibits efficient, dense chain packing, leading to unusually high fractional free volume (FFV) in the polymer. In fact, the PTMSDPA has a low density (0.91) and a large FFV value of 0.26, as summarized in Table 1, while the other polymers have relatively small values of FFV, below 0.15. The free volume is closely correlated to microvoids, which are molecular-scale gaps, in the polymer. Thus, such a highly porous polymer as PTMSDPA may afford sufficiently large spaces for molecular perturbation in a solid film leading to quick response to temperature.

Such an idea on the porosity effect has been widely accepted in the field of chemosensory materials for the detection of nitroaromatic explosive TNT (2,4,6-trinitrotoluene).[37−40] Swager et al. have induced high porosity in solid films of fluorescent conjugated polymers based on poly(*p*-phenyleneethynylene)s[37,38,40] and poly(*p*-phenylenevinylene)s[39] by introducing an extremely bulky, rigid three-dimensional pentiptycene scaffold to the films. As a result, this facilitated rapid analyte diffusion into the polymer film to achieve quicker and larger amplitude responses to TNT. This tells us that the molecular design of a highly thermosensitive fluorescent polymer film would be basically the same as that of such TNT sensory polymers.

Conclusion

The fluorescent, porous, disubstituted aromatic acetylene polymer, PTMSDPA, exhibited great potential as a thermally stable, highly sensitive optical thermosensor. The FL intensity significantly changed in a wide range from 25 to 200 °C. The change was reversible, which was true for the repeated trials. Temperature-variable IR and time-resolved FL spectroscopy studies revealed that both molecular perturbation and exciton deconfinement within the main chain caused the thermally induced FL quenching of PTMSDPA. The faster FL quenching of PTMSDPA, compared to other acetylene polymers, was found to be ascribed to the high FFV. In addition, PTMSDPA is already known to have extremely high oxygen permeability, more than 1000 barrer.[29] We expect that this unusual property will make PTMSDPA as applicable as the PSP in aerodynamic testing of aircraft as well as TSP in thermal fatigue testing of the aircraft turboprop engine.[11−17]

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