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Stabilization of Excited 2,3-Bis(2-methyl[*b*]benzothiophen-3-yl)maleic Anhydride in a Poly(ethylene glycol)-*g*-Polysiloxane

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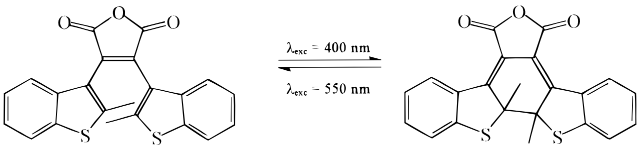
ABSTRACT: Fluorescence studies on 2,3-bis(2-methyl[*b*]benzothiophen-3-yl)maleic anhydride (BTMA)-doped polymer films were investigated. Poly(ethylene glycol) grafted polysiloxane (PEG-*g*-polysiloxane) films containing 5 wt % of BTMA were prepared by using a poly(ethylene glycol) modified sol−gel precursor and tetraethoxysilane (TEOS) in an acidic condition. The BTMA-doped film was transparent and showed a water contact angle of 40°. The fluorescence spectrum of BTMA in the PEG-*g*-polysiloxane film showed a large Stokes shift of 0.81 eV, compared to that of BTMA-doped polyethylene film at 0.65 eV. The Stokes shifts in the emission spectra of BTMA molecules in other polymeric hosts such as polystyrene, polycarbonate, and PMMA showed strong correlations with the solubility parameter and dielectric constant of the hosts and coincidentally the contact angle of the doped films. Thus it seems entirely plausible that there exist strong interactions between the excited BTMA molecules with a polar polymeric host. The more polar becomes the host, the stronger would be the interactions. The Stokes shift of 0.81 eV in PEG-*g*-polysiloxane is attributed to a stabilization of excited BTMA molecules in the polar PEG-*g*-polysiloxane system. From the plot of Stokes shift ($\nu_a - \nu_f$) against $[(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)]$ for different polymeric media, it is proposed that the excited state of BTMA molecules have a larger dipole moment than those of the ground state.

Introduction

Photochromic dyes, dispersed in or bound to polymer matrixes, are of significant interest for their potential application in optical memory, switches, and other optoelectronic devices.[1] Among those, bis(thiophen-3-yl)ethene (BTE) derivatives have attracted interest for their high photochromic efficiency and thermal stablility.[2,3] The photochromic properties of BTE arise from the photoinduced ring closure/opening process, as depicted below for 2,3-bis(2-methyl[*b*]benzothiophen-3-yl)-maleic anhydride (BTMA).

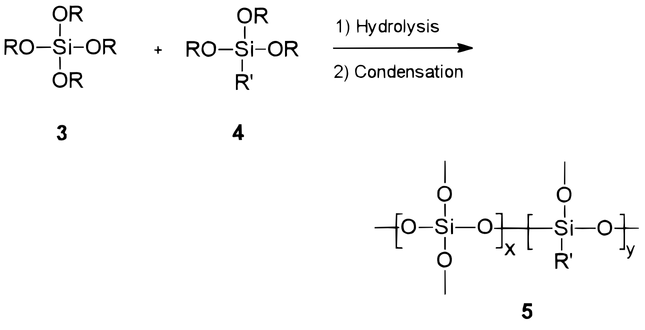


BTMA, 1 **2**

It is reported[4] that the ring closure/opening reaction and emission characteristics of the BTE molecules in solution are highly dependent on the solvent polarity. Thus, large Stokes shifts were found in polar solvents such as acetonitrile.

Attaining a large Stokes shift from a fluorescent dye is important for enhancing collection efficiency, i.e., for a high output of the incident light in the form of fluorescent light.[5] Such a large difference between the absorption and fluorescence bands can be obtained if there is optimum stabilization of the excited dye molecule by the medium. Stabilization of the excited state by interaction with the medium is much easier in a medium of low viscosity than in a highly viscous medium such as a solid polymer matrix. To induce lower frequencies for the fluorescence maximum in a polymer matrix, attempts have been made to dope a polymer matrix with low molecular weight compounds.[6] These low molecular weight dopants act as a plasticizer or interact directly with the fluorescent dye to stabilize the excited state of the dye. However, the doping method is often limited because of phase separation among the components. Thus, a method to reduce the phase separation would be to bind the plasticizing or interacting groups to the polymer backbone by covalent linking.

One of the methods to introduce a plasticizing group and/or polar substitutent into a polymer backbone is a sol−gel condensation of alkoxysilane with a sol−gel precursor substituted with a plasticizer group. Thus we have investigated a PEG-modified polysiloxane system that can be prepared from a PEG-modified triethoxysilane precursor and tetraethoxysilane (TEOS) via the sol−gel process.



3 **4** **5**

R' = Plasticizing and/or polar substituent

Particularly, such a modification of a polysiloxane network by a low molecular weight plasticizer or polar group is important for the development of the host matrix for trapping of optoelectronic molecules.[7] Furthermore, films prepared from polysiloxanes are reported to be optically transparent while exhibiting good mechanical properties.[8] There are several reports on the dye molecules dispersed in the polysiloxane matrix prepared from alkoxysilane; however, reports on a PEG-*g*-polysiloxane have not been found in the literature. Therefore, we embarked on the examination of a PEG-modified polysiloxane system, since the polar and flexible PEG side chain may confer an increased mobility to the polymer segments coupled with enhanced interactions with polar excited molecules, giving rise to further stabilization of the excited states of the chromophores.

We report here the preparation and characterization of a PEG-modified polysiloxane system and stabilization studies of excited-state BTMA molecules in this matrix.

Experimental Section

Materials. Tetraethoxysilane (TEOS) from Tokyo Kasei and 3-nitro-α,α,α-trifluorotoluene (Aldrich) were used as received. Pyrene (Aldrich) was recrystallized several times from ethanol. Toluene was distilled over sodium hydride. Polystyrene (LG, Korea), polycarbonate (Lexan 100), PMMA, and amorphous polyethylene (ZEONEX 480 R) were used as received. Tetrahydrofuran (THF) was distilled over metallic sodium. Dimethylformamide (DMF) was distilled over anhydrous magnesium sulfate under reduced pressure (40 mm) at 78 °C. Poly(ethylene glycol) monomethyl ether (PEGM, $M_n = 350$, Aldrich) was dried over molecular sieves before use. Polyurethane was prepared from 4,4′-diphenylmethane diisocyanate (MDI, Aldrich) and poly(tetramethylene glycol ether) (PTMG, $M_n = 1000$) with 1,4-butanediol as a chain extender in *N*,*N*-dimethylacetamide (HPLC grade, Aldrich). 2,3-Bis(2-methylbenzo[*b*]thiophen-3-yl)maleic anhydride (BTMA) was synthesized from benzothiophene over four steps according to the literature.[9] BTMA had the following characteristics: M_p, 240−244 °C; IR (KBr pellet, cm^{-1}) 1716, 1767, and 1828 (C=O stretching of maleic anhydride), 909 (asymmetric stretching of C−O−C of maleic anhydride); ^{1}H NMR ($CDCl_3$, ppm) δ 2.10 (s, 3H), 2.27 (s, 3H), 7.10 (d, 1H), 7.21−7.30 (m, 4H), 7.41 (d, 1H), 7.67 (dd, 2H). PEG-modified silane precursor, ω-methoxy poly(ethylene glycol) 3-(triethoxysilyl)propyl carbamate (MPTRS) was synthesized from (3-isocyanatopropyl)triethoxysilane (Aldrich) and PEGM using di-*n*-butyltin dilaurate (Aldrich) as a catalyst, following a procedure reported in the literature.[10] MPTRS was obtained as a transparent liquid after column chromatography. T_g: −68 °C. T_m: −8 °C. Anal. Cald For $(CH_3CH_2O)_3Si(CH_2)_3CONH(OCH_2CH_2)_{7.23}OCH_3$, $C_{25.46}H_{53.92}O_{12.23}NSi$; C (51.16%), H (9.03%), N (2.34%), O (32.76%). Found: C (51.70%), H (8.98%), N (2.28%), O (31.90%).

Preparation of Dye-Doped Polysiloxane Films. The method of preparing sol−gel glasses by the acidic hydrolysis of TEOS in ethanol was adopted from the literature[11] with minor modifications. MPTRS and TEOS was added to a solution of ethanol containing 10^{-5} M pyrene. The molar ratio of TEOS and MPTRS was 4:1. The solution was adjusted to a pH of 3.1 by HCl and stirred for 2 days at room temperature. The solution was stirred further for 1 day at 60 °C. The reaction mixture was then cooled to room temperature and concentrated by evaporation of solvent under reduced pressure until the weight loss of the mixture reached 85%. The resultant viscous solution was filtered with membranes of 0.45 μm pore size attached to a Teflon syringe, and the solution was coated on a slide glass by a spin-coater with a spin rate of 1000−2000 rpm. The coated slide glass was cured at 80 °C for 12 h. During the sol−gel process, the intensity ratio of the monomer band (F_m) at 395 nm to the excimer band (F_d) at 466 nm, F_m/F_d, was determined from emission spectra of pyrene-doped PEG-*g*-polysiloxane. In addition, the intensity ratio of the third vibronic band (I_3) at 385 nm to the 0−0 band (I_1) at 375 nm, was determined. The values of F_m/F_d, and I_3/I_1 were changed as follows. The F_m/F_d ratio of the starting mixture of MPTRS and TEOS in ethanol containing pyrene was 1.29 with the I_3/I_1 value of ∼2. The value of F_m/F_d was 1.35 with an I_3/I_1 value of ∼2 for the viscous solution obtained by microgellation and concentration. Thin films of the above viscous solution followed by curing at 80 °C for 15 min showed the F_m/F_d value as 14.6 with an I_3/I_1 value of 1.03. After curing at 80 °C for 3 h, the F_m/F_d value for the film was 15.3 with an I_3/I_1 value of 0.98. F_m/F_d values for the film cured at 80 °C for 1 day and 4 days were 21.3 and 21.6, respectively, with I_3/I_1 values of 0.97 and 0.92, respectively.

BTMA-doped PEG-*g*-polysiloxane film was prepared as follows. TEOS (7.91 wt % of the final mixture) and MPTRS (6.31 wt %) were added to a solution consisting of four components, 0.15 M HCl (16.2 wt %), ethanol (56.9 wt %), DMF (6.11 wt %), and 3-nitro-α,α,α-trifluorotoluene (6.11 wt %). The resultant homogeneous mixture was stirred for 1 day at room temperature, then BTMA (50 mg) was added to the above mixture. The resultant mixture was stirred for 2 days at room temperature and then was further stirred for 1 day at 60 °C. The reaction mixture was then cooled to room temperature and concentrated by evaporation under reduced pressure. The final weight loss was 85 wt %. The resultant viscous solution was filtered with membranes of 0.45 μm pore size attached to a Teflon syringe, and the solution was coated on a slide glass by a spin-coater with a spin rate of 1000−2000 rpm. The coated slide glass was cured at 80 °C for 12 h. The final dye content in the film was 5 wt %.

Preparation of Dye-Doped Polymer Films. Solutions for BTMA-doped polystyrene (PS), PMMA (PM), and polycarbonate (PC) films were prepared by adding BTMA (5 mg) to solutions of 100 mg of polymer dissolved in $CHCl_3$ (5 mL). A solution for BTMA-doped polyurethane film was prepared by adding BTMA (5 mg) to a solution of THF containing 100 mg of polyurethane. The solutions were filtered with membranes of 0.45 μm pore size attached to a Teflon syringe, and the solution was coated on a slide glass by a spin-coater with a spin rate of 1000−2000 rpm. The coated slide glass was dried at room temperature under a nitrogen atmosphere and then at 50 °C for 3 h in a vacuumed oven. Dye-doped polyethylene film (PE) was prepared by solution coating at 100 °C using a hot solution of 100 mg of amorphous polyethylene and BTMA (5 mg) in *p*-xylene (5 mL). The dye-doped polymer films were dried at 100 °C for 12 h under reduced pressure.

Instruments. ^{1}H and ^{13}C NMR spectra were determined on a Bruker ARX-300 spectrometer. FT-IR spectra were obtained from a Bio-Rad Digilab Division FTS-80. Film porosity was determined by a JSM-840A scanning microscope (JEOL). The number of pores and pore size were determined from the scanned image, and they were divided by total area to calculate the porosity of the film. UV spectra were obtained on a Guided Wave Model 260 (Guided Wave, Inc.) and fluorescence spectra were on a Fluoro Max-2 (Jobin Yvon-SPEX instruments S.A., Inc.). The excitation wavelength for the pyrene probe was 340 nm. The fluorescence efficiency of BTMA in different media was determined by the ratio of fluorescence intensity to absorbance, $\Phi_{FL} = I_{FL}/I_{abs}$. The relative fluorescence efficiency was calculated by dividing the fluorescence efficiency of the sample (Φ_{FL}) with that of BTMA in hexane, $\Phi_{FL}(rel) = \Phi_{FL}(sample)/\Phi_{FL}(HX)$. The contact angle was measured on an Olympus TGHM (lamp, Olympus Optical Co., Ltd.) with a NRL C.A. Goniometer (Rumé-hart, Inc.). The contact angles presented here are the advancing angles.

Results and Discussion

Preparation of PEG-Modified Polysiloxane Films. Polysiloxane film could be prepared from the sol−gel mixture of tetraethoxysilane (TEOS) and the PEG-graft precursor (MPTRS) with a mole ratio of 4:1 by a sol−gel-process. The sol−gel processed polysiloxane film is

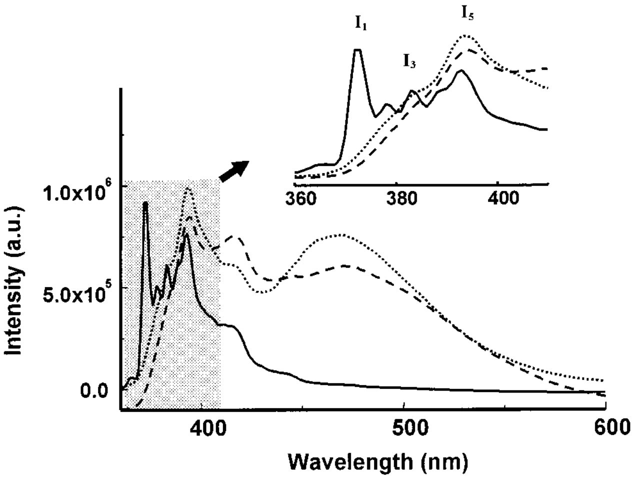
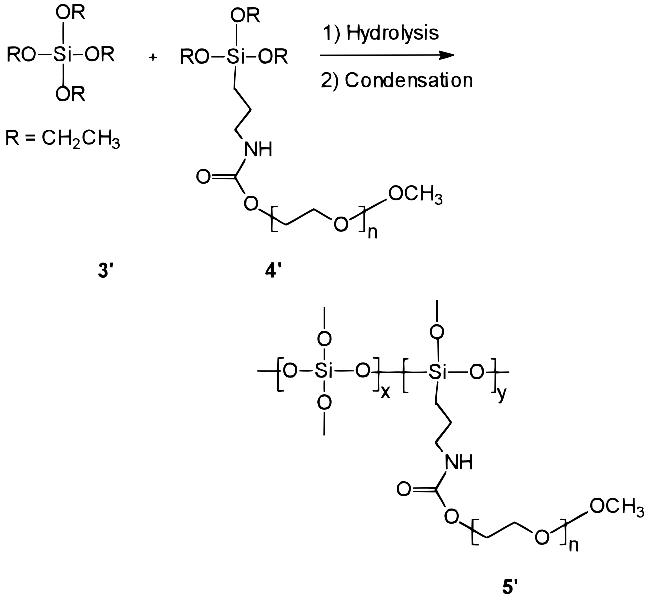


Figure 1. Fluorescence spectra of pyrene in the initial sol–gel mixture (···),viscous sol–gel mixture after solvent evaporation (- - -), cast film cured for 3 h at 80 °C under reduced pressure (—).

composed of a silica and poly(oxyethylene) graft silica block as described below.



To determine the reaction time and monitor the sol–gel process, we have used excimer and monomer fluorescence of pyrene as the monitoring probe. The viscosity changes during the sol–gel process could be inferred from the intensity ratio of excimer and monomer fluorescence at 395 and 466 nm, respectively, using the pyrene probe.[11,12] The fluorescence spectrum of the initial solution of MPTRS and TEOS containing pyrene in EtOH, showed a large excimer emission band (F_d) at 466 nm together with the monomer emission (F_m) at 395 nm (Figure 1). The ratio F_m/F_d for the initial solution was 1.2, indicating that the emission from the excimer is large in the initial low-viscosity solution. After aging and partial removal of solvent, the ratio increased to 1.3 and then further increased steeply to a value of 14–15 when the viscous sol–gel solution was cured at 80 °C under reduced pressure. Such a high F_m/F_d value indicates the sol–gel–xerogel transition since the excimer formation decreases with increasing host matrix viscosity. Further curing for 1 day at 80 °C resulted in a transparent solid film with the F_m/F_d ratio of 21, which remained the same up to 4 days. With this pyrene probe method, the sol–gel process time could be determined and the same method was applied for the preparation of BTMA-doped polysiloxane film.

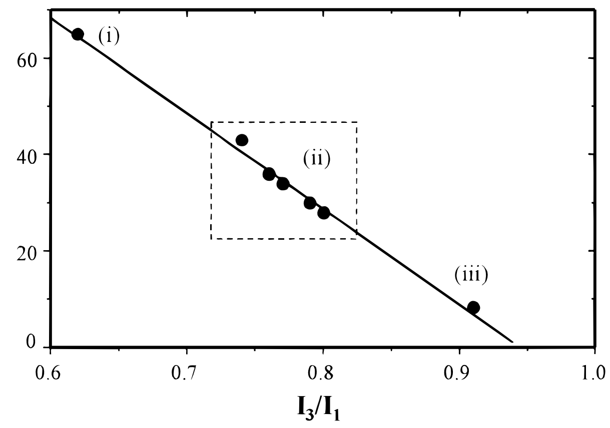


Figure 2. Plot of the I_3/I_1 ratio against the dielectric constant for the sol–gel process using the data reported in ref 11: (i) data for xerogel and vacuum-dried films; (ii) sol–gel solution; (iii) estimated value for the PEG-*g*-polysiloxane film in this study.

From the intensity ratio of the third vibronic band (I_3) to that of the 0–0 band (I_1), the polarity of the PEG-modified polysiloxane matrix could be determined as follows. Kaufman and Avnir showed that the changes in the polarity of the pyrene environment along the sol–gel process can be probed by using the intensity ratio of the vibronic structures.[12] Matsui et al. have also shown that fluorescence spectra of pyrene provide a reliable means of determining the environmental changes in the silica cage.[11] The intensities of the vibronic bands are strongly dependent on the solvent environment and the ratio I_3/I_1 decreases with increasing solvent polarity. Thus, I_3/I_1 of the pyrene in the vacuum-dried polysiloxane matrix was 0.56–0.62 when the molar ratio of water to TEOS was 1.2–4.7.[11] The corresponding dielectric constant was 73–62, and it depends on the water content.

In the initial mixture of MPTRS and TEOS containing pyrene in EtOH, the I_3/I_1 ratio was ~2, which decreased to 0.98 after the sol–gel process followed by curing for 3 h at 80 °C. The ratio decreased to 0.91 when the film was cured further, which is a signature for a polar film containing much less water than the film prepared from TEOS and water. The estimated dielectric constant (ϵ) for the PEG-*g*-polysiloxane was 8.3 by a graphical method for the correlation of the ratio I_3/I_1 and the dielectric constant of sol–gel medium as reported in ref 11. The plot shows a linear relationship of $\epsilon = -200(I_3/I_1) + 190$ with a correlation factor of 0.9969, as shown in Figure 2.

Preparation of BTMA-Doped Polymer Films. Transparent yellow films could be prepared using the same solution of PEG-modified sol–gel precursor and TEOS plus BTMA. The glass transition temperature of BTMA-doped PEG-*g*- polysiloxane film was −65 °C, as determined by DSC.

Figure 3 shows SEM photographs for the BTMA-doped sol–gel-processed film and BTMA-doped PC film. The porosity as determined by SEM was 3.4% for the BTMA-doped PEG-*g*-polysiloxane film. The film was quite adherent to glass and silicon wafers. The porosity of the BTMA-doped polystyrene film was larger (~20%)

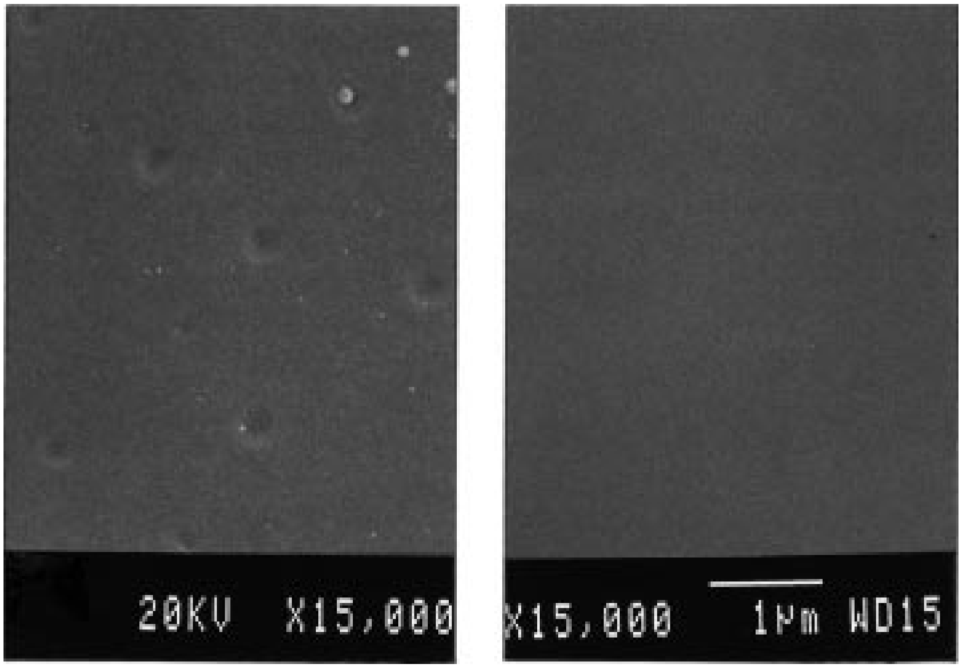


Figure 3. SEM photographs for BTMA-doped sol−gel processed film (left) and BTMA-doped PC film (right).

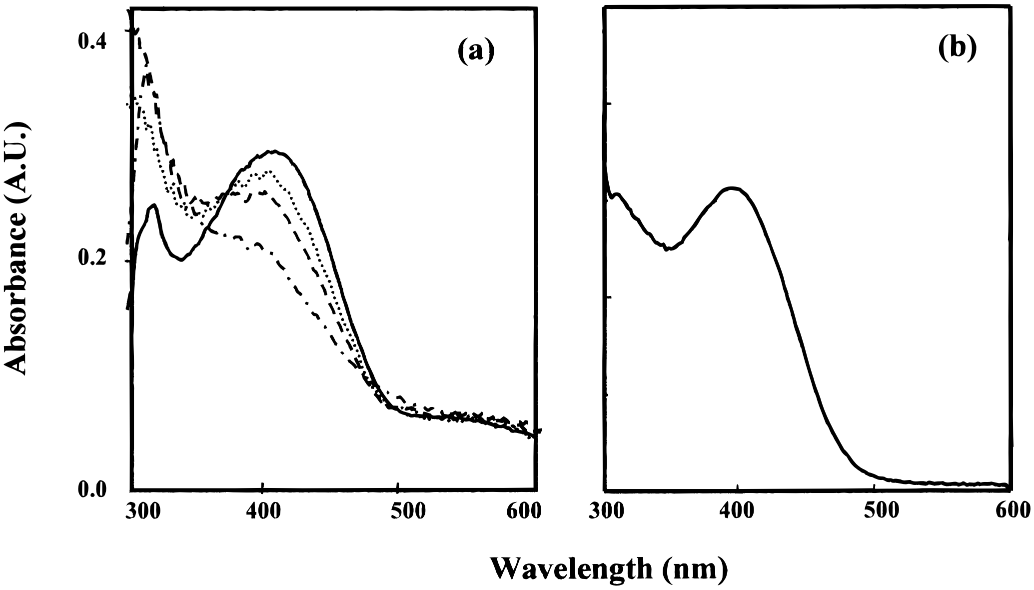


Figure 4. Absorption spectra of BTMA in (a) polystyrene (—), polycarbonate (···), polyurethane (— — —) and PEG-*g*-polysiloxane film (—·—), and (b) acetonitrile (1 × 10^{-4} M).

than those of the BTMA-doped PEG-*g*-polysiloxane film and BTMA-doped PC film.

Figure 4 shows absorption spectra of BTMA-doped polymer films. Interestingly, the absorption maxima, λ_{max}, of BTMA in polymeric media were centered at 400 (±5) nm, irrespective of the polymer medium. Furthermore, the absorption spectra were comparable to the that of BTMA in solution (Figure 4b). This indicates that the ground structure of BTMA was not much changed by the polymeric medium nor by the polarity of the medium. Thus any changes in the fluorescence band maximum has to be attributed exclusively to the change in the excited state. In other words, the Stokes shift relates to the ability of the polymer matrix to lower the energy of the excited state of BTMA molecules by particular reorientation and interactions.

Fluorescence Study of BTMA-Doped Polymer Films. Excitation of the BTMA-doped polysiloxane film with a monochromatic light of 405 nm showed emission maximum at 550 nm, as shown in Figure 5.

The emission band was shifted ~60 nm (0.87 eV) from the reported band of 488 nm in hexane.[4] The Stokes shift of BTMA was 0.81 eV in the PEG-*g*-polysiloxane matrix and comparable to that in a polyurethane film. The emission band of the BTMA-doped polyethylene film was centered at ~506 nm and showed much less shift compared to that in the PEG-*g*-polysiloxane film. Furthermore, the Stokes shifts of BTMA in PS, PC, and PMMA were larger than that in a polyethylene film (Table 1). Similarly, the emission energy of BTMA in different solvents showed a strong dependence on the solvent polarity, as summarized in Table 2. A larger Stokes shift observed in PEGM solution than in EtOH

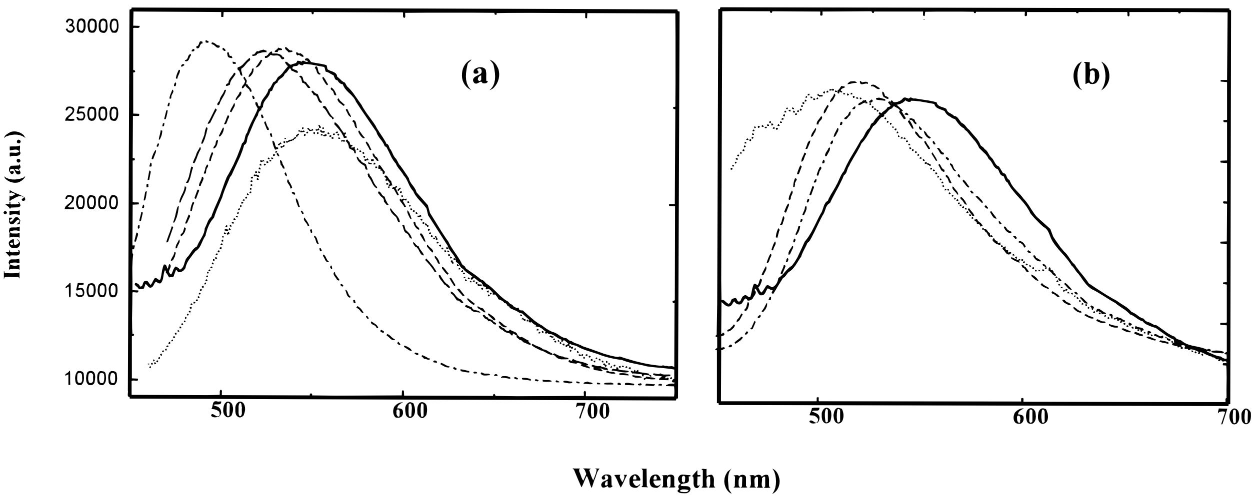


Figure 5. (a) Emission spectra of BTMA in PEG-*g*-polysiloxane film (—) in comparison with emission spectra in solution: acetonitrile (···), PEGM (- - -), EtOH (— — —) and hexane (—•—); emission spectra with excitation at 405 nm. (b) Emission spectra of BTMA in polymer films: PEG-*g*-polysiloxane film (—), polycarbonate (—•—), polystyrene (- - -), and polyethylene film (···).

Table 1. Spectral Data of BTMA in Different Polymeric Media[a]

sample code	polymer	thickness μm	λ_{abs}, nm	λ_{FL}, nm	Φ_{FL} (rel)[b]	Stokes shift, eV
PE	polyethylene	46	400	506	0.52	0.65
PS	polystyrene	23	404	520	0.43	0.68
PM	PMMA	7	402	522	0.38	0.71
PC	polycarbonate	8.5	398	529	0.18	0.77
PU	polyurethane	10	402	548	0.05	0.82
SG	PEG-*g*-polysiloxane	9	404	550	0.10	0.81

[a] Dye contents in these films were 5 wt %.[b]Relative fluorescence efficiency to HX in Table 2.

Table 2. Spectral Data of BTMA in Different Solution

sample code	medium	λ_{abs}, nm	λ_{FL}, nm	conc, M	Stokes shift, eV	Φ_{FL} (rel)[a]
HX	*n*-hexane	404	491	9.6×10^{-5}	0.54	1
HX1	*n*-hexane	400	492	1.3×10^{-4}	0.58	0.10
HX2	*n*-hexane	406	491	1.9×10^{-4}	0.53	0.009
AN	acetonitrile	399	554	1.0×10^{-4}	0.87	0.051
ET	EtOH	395	526	2.3×10^{-4}	0.78	0.25
PEGM	PEGM	390	537	2.57×10^{-4}	0.87	0.47

[a] Relative fluorescence efficiency to HX.

could be ascribed to the higher viscosity in the PEGM solution, in which both the ground and excited states could be stabilized due to the increased viscosity in the vicinity of BTMA molecules.

The fluorescence intensity in the PEG-*g*-polysiloxane matrix was 10% of that in hexane solution but higher than that in acetonitrile solution as summarized in Table 1. The maxima, λ_{FL}, in the emission spectra were not changed by the BTMA concentration in the polysiloxane matrix. However, the fluorescence efficiency was reduced as the concentration of BTMA was increased in the polymer film. Similarly, λ_{FL} was only slightly shifted toward longer wavelengths in a concentrated hexane solution, whereas the fluorescence efficiency was much reduced as the concentration was increased (Table 2). Such a decrease in fluorescence efficiency may be attributed to the excimer quenching in a highly concentrated solution or polymer film. Therefore, the origin of the Stokes shift of BTMA could be traced to the interactions of excited-state BTMA molecules with the medium.

To investigate the origin of the Stokes shifts in different polymeric media, we attempted to correlate the shift with the solubility parameter, polarity, porosity, contact angles, and thermal behavior of the polymer film. The physical properties of solvent and host polymers are summarized in Table 3.

Figure 6 shows the plot of emission energy against the physical properties of the polymer film. It is noteworthy that the emission energy of BTMA molecules in the film is increased as the solubility parameter and dielectric constants of the medium are decreased. On the other hand, there was no simple correlation with T_g of the polymer host. Since the solubility parameter or cohesive energy density is a measure of the strength of the interaction in a material, it seems that the emission energy of BTMA decreases as the interactions between the BTMA molecules and the media increase. Thus the interactions between the excited state BTMA and PEG-*g*-polysiloxane matrix are likely to be the strongest cause for the lowest emission energy. Furthermore, as the polarity of the medium increases, the emission energy shifts to lower energy as shown in the Figure 6 for dielectric constant plot. Thus the nature of the interactions between the excited-state BTMA molecules and polymer hosts seem to be polar in character.

It has been reported that the excited state of neutral molecules has a larger dipole moment than the ground state. The difference in energy ($\Delta\nu$, cm^{-1}) of absorption (ν_a) and emission (ν_f) for neutral molecules is generally given by[13]

$$\Delta\nu = \frac{2(\mu_e - \mu_g)^2}{hca^3}\left(\frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}\right) + \text{constant} \qquad (1)$$

where, μ_e and μ_g are the dipole moments of the excited and ground states, respectively, a is the Onsager's cavity radius, ε is the dielectric constant, and n is the refractive index of the medium. Thus, Stokes shifts of molecules capable of intra- and/or intermolecular electron transfer in their fluorescent state can be large in polar solvents. Since the chemical structure of the polymer, i.e., the polarity of the polymer repeat unit, affects the Stokes shift in the same way as for low molecular weight

Table 3. Physical Properties of Solvent and Host Polymers[a]

sample code	medium	solubility parameter, σ, cal/cm^3	dielectric constant, ε	refractive index, n_D	T_g (°C)
HX	*n*-hexane	7.3	1.89	1.372	
AN	acetonitrile	11.9	36.2	1.342	
ET	ethanol	12.7	24.5	1.361	
PEGM	PEGM	11.4[b]	15.4[b]	1.426	
PE	polyethylene	8.1[c]	2.28 (at 1 kHz)	1.51	−80 to −90
PS	polystyrene	9.1	2.49−2.55 (at 1kHz)	1.59	80−100 (90)[e]
PM	PMMA	9.1−9.4	3.0 (at 1 kHz)	1.492	105
PC	polycarbonate	9.3−9.9	2.97−3.17	1.585	144
PU	polyurethane	10.0[d]		1.499[d]	
SG	sol−gel film		8.3[e]	1.462[e]	−65[e]

[a] Physical data from ref 15. [b] Data for ethylene glycol monomethyl ether. [c] Data for LDPE. [d] Data for MDI−PTMG. [e] Measured in this work.

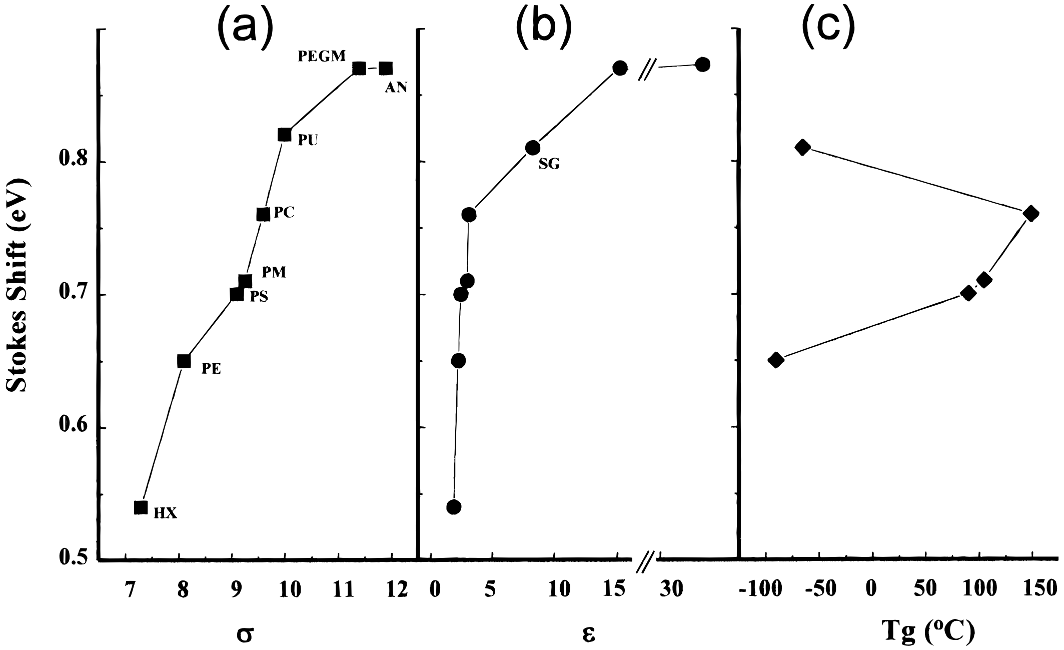


Figure 6. Plot of emission energy versus the physical property of the medium, (a) solubility parameters, (b) dielectric constant, and (c) T_g (°C), where BTMA in different media are denoted as AN (acetonitrile), HX (hexane), PU (polyurethane), SG (PEG-*g*-polysiloxane film), polycarbonate (PC), polystyrene (PS), and polyethylene film (PE).

solvents,[14] it can be concluded that the large Stokes shift (0.81 eV) in the PEG-*g*-polysiloxane matrix, of which the repeating units are polar PEG-*g*-silica, can be attributed to strong polar interactions between the excited BTMA molecules and the PEG units. Particularly, such polar interactions are thought to be important in BTMA molecules that are capable of electron transfer between the electron-accepting maleic anhydride and electron-donating benzothiophene rings in the fluorescent state.

Evaluation of the Excited-State Dipole Moment. Since the emission energy relates to the polarity of the medium, we have attempted to evaluate the excited-state dipole moment by applying the Lippert−Mataga equation.[4,13] The physical data for the dielectric constant and refractive indices of PE, PS, PC, and PMMA were obtained from ref 15. The dielectric constant for the PEG-*g*-polysiloxane film was estimated by using the pyrene probe method as described above, and the refractive index for PEG-*g*-polysiloxane film was determined by a prism coupler.[16] Figure 7a shows a Lippert−Mataga plot for BTMA in polymer films. The increase of $\Delta\nu$ with increasing $[(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)]$ indicates that the excited state has a larger dipole moment than the ground state. The dipole moment difference between the ground and excited state, $\mu_e - \mu_g$, could be calculated from the slope of Figure 7a as $5.74 \times 10^{10} a_o^{3/2}$. Using the value of Onsager's cavity radius[4] (a_o) as 6×10^{-8} cm, the dipole moment difference ($\Delta\mu$) between the ground and excited state in polymeric media was estimated as 8.4 D. It was noteworthy that the estimated $\Delta\mu$ value was smaller than that of the reported $\Delta\mu$ in solution (15 D).[4] Indeed, Figure 7b shows that the slope of the plot for BTMA in solution was larger than that in the polymer.

The energy of the excited state of BTMA molecules in polar solution could be lowered by reorientation of the polar solvent molecules around BTMA molecules, due to their increased dipole moment in the excited state. Similar but slower reorientation of PEG group in the PEG-*g*-polysiloxane matrix could occur around BTMA molecules in the excited state. If so, the stabilization of BTMA in PEG-*g*-polysiloxane film could be attributed to the strong interactions of BTMA molecules with polar PEG units, giving rise to such polar interactions by segmental motions. According to Irie et al.,[4] a twisted structure was suggested for the excited BTMA molecules in polar solvents. Since Stokes shift and dipole moment changes of BTMA molecules in polymeric media show a trend similar to that in solution, we postulate that PEG side chains in the PEG-*g*-polysiloxane film could interact in a way to stabilize the polar

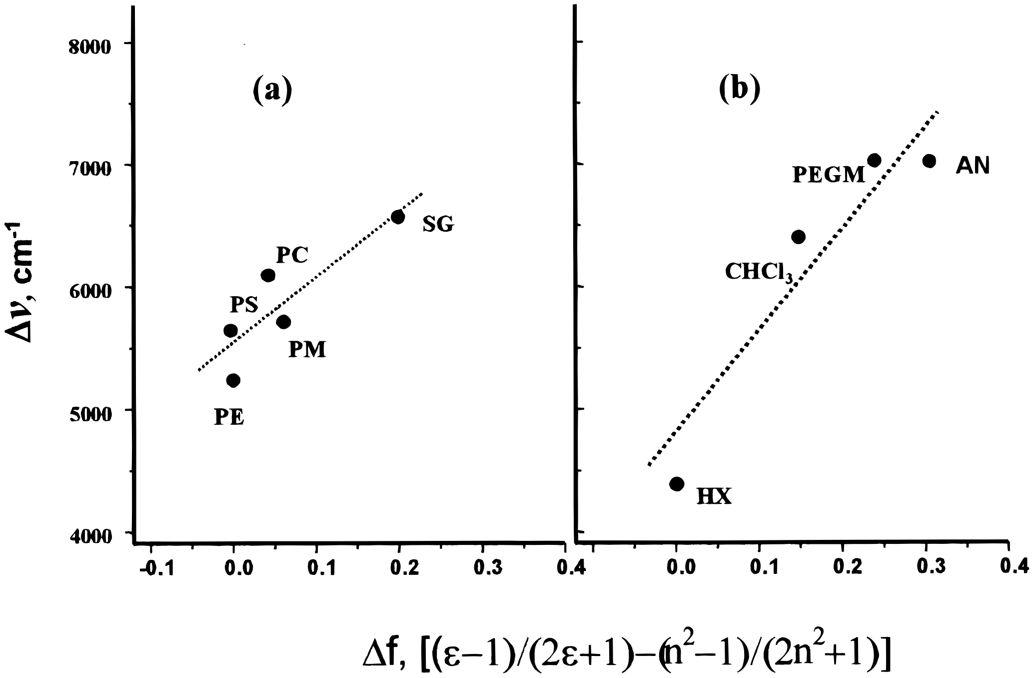
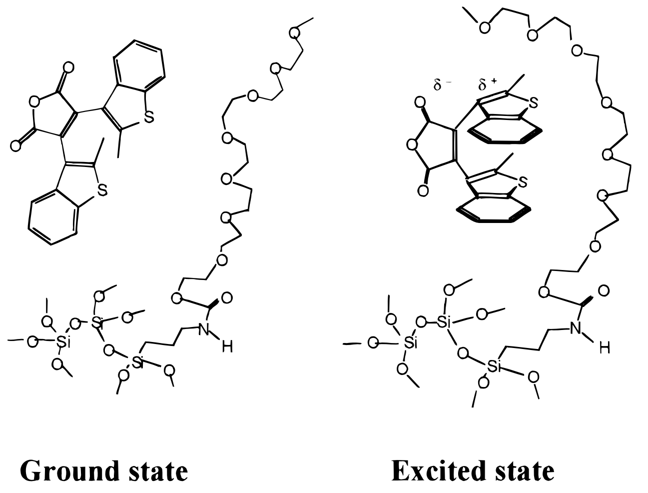


Figure 7. Plot of $\Delta\nu$ against Δf, $[(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)]$, for BTMA in (a) polymer films and (b) solution. Abbreviations are the same as in Figure 6.

twisted structure as depicted below.



Polarity Effect of the Polymer Host on BTMA Molecules. The degree of polar interactions between BTMA molecules and polymer could be determined by measuring contact angles of the film if we assume that the bulk properties of doped films are faithfully reflected in their surface properties. Although this is a drastic assumption, the consequence merits some credence. BTMA-doped PE film showed an average advancing contact angle of 95.5° over 8 runs. It was similar to the reported advancing contact angle of 96° in undoped PE.[17] BTMA-doped PEG-*g*-polysiloxane film was quite polar as estimated from its water contact angle of 40°. Contact angles of BTMA-doped polymer films were not very different from those without BTMA, and it can be inferred that the low concentration of neutral BTMA molecules in polymeric media does not affect the polarity of the film. Contact angles of the BTMA-doped films are summarized in Table 4.

Table 4. Contact Angles of BTMA-Doped Films

sample code	medium	contact angle (θ)[a]	$(1 + \cos\theta)^2$
PE	a-polyethylene	95.5 (96)[b]	0.82
PS	PS	91.2	0.96
PM	PMMA	75[b]	1.58
PC	PC	69.2	1.84
SG	PEG-*g*-polysiloxane	40	3.12

[a] Advancing contact angles at room temperature (25 °C) for the films containing 5 wt % of BTMA. [b] Data for undoped film from ref 18.

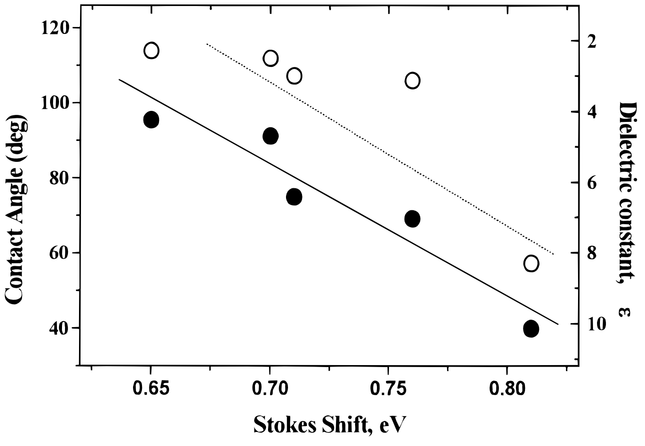


Figure 8. Correlation of the Stokes shift with contact angles (●) and dielectric constants (○) of BTMA in different polymer films.

We infer that the bulk polarity of the films is reflected in the water contact angle on the film surface. Thus polarity of the BTMA-doped film increases in the order PE < PS < PC < SG. Such a polarity trend was correlated to the emission energy of BTMA in different polymer films. Figure 8 shows the plot of the Stokes shift ($\Delta\nu$) against dielectric constant (ε) and contact angle (deg). It shows unambiguously the polarity effect of the host on BTMA while validating in part our starting assumption of the bulk vs surface properties.

Conclusion

BTMA-doped PEG-*g*-polysiloxane film was prepared through a sol−gel process using a PEG-modified sol−gel precursor and TEOS. A large Stokes shift was observed from the BTMA-doped PEG-*g*-polysiloxane film, which is clearly correlated with the polarity of the polymer film. Hence, the large Stokes shift in the PEG-*g*-polysiloxane matrix (0.81 eV), of which the repeating units are polar PEG-*g*-silica, is attributed to strong polar interactions between the BTMA molecules and the PEG units. From a Lippert−Mataga plot of the Stokes shift ($\Delta\nu$) against $[(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)]$ in different polymeric media, the dipole moment difference between the ground and excited state, $\mu_e - \mu_g$, is determined to be 8.4 D.

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