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NOTE

Enhancements in Emission and Chemical Resistance of Substituted Acetylene Polymer via in Situ Sol−Gel Reaction in Film

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Aromatic substituted acetylene polymers are thermally and (photo)chemically stable as compared to aliphatic substituted polyacetylenes.[1−3] Poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] (PTMSDPA in Chart 1), which is a highly soluble diphenylacetylene polymer derivative with an ultrahigh molecular weight (M_w) of $> 1.0 \times 10^6$, was for the first time synthesized by Masuda et al. in 1991.[4,5] As one of the most interesting features of PTMSDPA, this polymer emits an intense fluorescence (FL) in a visible region because of the effective exciton confinement within the main chain due to the steric hindrance and/or intramolecular electron interactions of bulky aromatic substituents such as phenyl rings.[6] On the basis of these unusual properties, we have recently developed various potential applications such as thermosensor,[7] VOC sensor,[8] imaging of latent fingerprint,[9] electrospun optic nanofiber,[10] highly polarized fluorescent film,[11] and fluorescence image patterning.[12] The PTMSDPA is not easily degradable, even though it is a purely organic material, because the main chain consisting of C═C double bonds is protected by the bulky aromatic rings of two phenyl groups in the side chain. Thus, this polymer avoids, as much as possible, fatal damages, such as a significant decrease in molecular weight and a change in characteristics upon degradation. On the other hand, the FL emission property of PTMSDPA is highly sensitive to external stimuli such as light and heat, as already described in our previous papers, because such a conjugated polymer usually exhibits collective properties that are sensitive to very minor electronic perturbation triggered by the external stimuli.[7,12] For example, when the polymer film was exposed to UV light with an appropriate power in air, the FL intensity significantly decreased. Also, the FL intensity of PTMSDPA in film significantly decreased as the temperature increased in a wide range from room temperature to 200 °C.

PTMSDPA is also well-known as a fluorescent conjugated polymer with an extremely large fractional free volume (FFV) of about 0.26 in film.[13] In previous studies, we found that this polymer makes for various kinds of liquid chemicals to easily diffuse into its film due to the high porosity at the molecular size level.[8,9] Also, the photophysical property significantly changed when the chemicals diffused into the film through the many microvoids. The diffusion of common organic solvents such as alcohols and liquid hydrocarbons into the PTMSDPA film led to chain entanglement relaxation in order to remarkably enhance the FL emission via the swelling-induced quenching sites degeneration,[8] whereas electron-deficient explosive chemicals such as nitroaromatic compounds immediately quenched the FL emission due to a polymer-to-analyte energy migration effect.[14]

Meanwhile, silane coupling agents (SCAs) have been widely used for surface modification. SCAs consist of two components, a trialkoxysilyl group and an organic functional group;[15−20] the former reacts with the surface hydroxyls of inorganic materials and hydrolyzes to be cross-linked with covalent Si−O−Si bond linkages while the latter has some interactions, such as an intermolecular weak interaction and a strong covalent bond, with organic materials. Thus, SCAs have the ability to form a durable bond between organic and inorganic materials. Especially, with utilizing a sol−gel reaction to prepare silica gel at a relatively low temperature, nano-ordered polymer−silica hybrid films have been successfully developed by casting a mixture solution of polymer and alkoxysilane in the presence of various types of SCAs.[21−24]

Although the molecular sizes of SCAs may be much larger than common organic solvents, these molecules are usually in liquid states at room temperature. Also, because the most of SCA molecules are nonexplosive and nonpolar chemicals, they will not act as FL quenching sources. Thus, we thought that if the SCA molecules diffuse into the PTMSDPA film through microvoids, the emission of the film may be enhanced by the swelling out of entangled polymer chains. Moreover, if the SCA molecules undergo a sol−gel reaction to transform to silica gel in situ in the PTMSDPA film, the polymer chains may be locked up with being left swollen out, and thus the enhanced emission will be retained. In this event, the chemical resistance of the PTMSDPA film is also expected to be enhanced due to the protecting effects of the silica gel incorporated in the polymer film.

The final goal of this study is to develop fluorescent conjugated polymer−silica hybrid film with enhanced emission and enhanced chemical resistance via a facile method. For this purpose, we tried to test sol−gel reactions of the simplest silane sols, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), in situ in PTMSDPA film. The polymer used in this study has a high weight-average molecular weights (M_w) of 5.2×10^6 g/mol and polydispersity index (PDI = M_w/M_n) of 3.2. Actually, when the PTMSDPA film was contacted to the TMOS or TEOS ethanol solution (40 vol % of alkoxysilane in ethanol) containing a little amount of water, the emission was significantly enhanced. Afterward, the enhanced emission was retained, even after the process of complete ethanol evaporation in the atmosphere, due to the alkoxysilane component remaining in the film. A little amount of water is essential for an effective hydrolysis reaction. However, the TMOS and TEOS are not mixed very well, even with the catalytic amount of water. Also, their boiling points (bp: 121 °C for TMOS and 168 °C for TEOS) are not high enough to avoid evaporation in the course of the in situ sol−gel reaction at a relatively high temperature of 100 °C in an open system of the cast film. Thus, despite several times trials, we could not obtain a well-constructed hybrid film after the thermal treatment. The thermally treated film rather became opaque and was cracked due to a phase separation of the polymer and partially formed silica (Figure S1 in Supporting Information).

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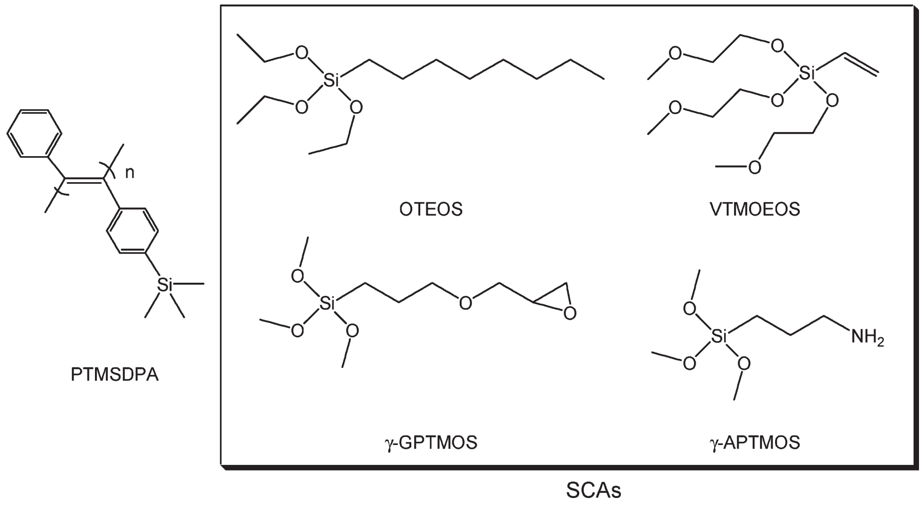
Chart 1. Chemical Structures of PTMSDPA and Silane Coupling Agents (SCAs)



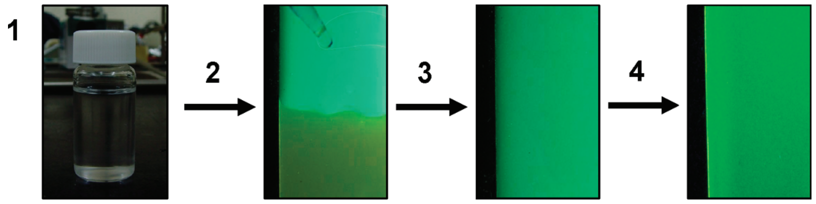


Figure 1. Preparation procedure of the PTMSDPA−SCA hybrid film: (1) preparation of deposition solution ((Et_2OH/H_2O 95/5 vol %):VTMOEOS = 60:40 vol %); (2) dropping the deposition solution onto the PTMSDPA film (thickness ≈10 μm); (3) evaporation of Et_2OH in air at room temperature for several minutes; (4) heating PTMSDPA film at 90 °C in air for 5 h. The photographs show the each step changes in fluorescence of the PTMSDPA film on glass slide (excited at 420 nm).

The phase separation is presumably due to the fact that neither the TMOS nor the TEOS has organic functional groups, and thus there is no interaction between PTMSDPA and the alkoxysilanes. Although these two alkoxysilane compounds did not meet with our purpose to prepare a transparent PTMSDPA−silica hybrid film, these results hinted that SCAs with a high boiling point, water solubility, and miscibility to PTMSDPA are better suitable for our purpose.

To satisfy such properties needed for the silane sol materials in the desired direction, we chose several SCA compounds as follows: octyltriethoxysilane (OTEOS, M_w 276.6, bp 250 °C), vinyl-tris(2-methoxyethoxy)silane(VTMOEOS, M_w 280.4, bp 285 °C), γ-glycidoxypropyltrimethoxysilane (γ-GPTMOS, M_w 236.1, bp 290 °C), and γ-aminopropyltrimethoxysilane (γ-APTMOS, M_w 179.3, bp 210 °C).[25] Chart 1 shows their chemical structures. These all have high boiling points of more than 200 °C and organic functional groups such as a long alkyl, vinyl, epoxy, and amino groups, respectively, to be potentially miscible with PTMSDPA polymer chains. Moreover, these all are readily hydrolyzed by the addition of a catalytic amount of water. Both VTMOEOS and γ-APTMOS dissolve especially well in water.[25]

In this study, the SCAs were used for hybridizing the PTMSDPA via an in situ sol−gel reaction in the polymer film but not for simply coating the PTMSDPA film. Thus, a typical silane coupling agent chemistry for the purpose of inorganic surface coating and surface modification was modified in this work. The preparation procedure of the PTMSDPA−SCA hybrid film is shown in Figure 1. The 40 vol % SCA was added to a 60 vol % ethanol/water (95/5 vol %) mixture under slightly acidic conditions in the presence of a catalytic amount of sulfuric acid. The amount of the added SCA was determined by a preliminary experiment: The emission of the PTMSDPA−SCA hybrid film after evaporation of ethanol and water increased with the increase in the SCA content in a concentration range of 5−40 vol %, whereas the SCA content of less than 5 vol % was not sufficient for a remarkable emission enhancement. Thus, the total SCA concentration of the deposition solution used in this study was fixed at a relatively high fraction of 40 vol %, which was enough to completely coat the surface of PTMSDPA film. The deposition solution of SCA/ethanol/water mixture was aged for 6 h before use.

When the PTMSDPA film was deposited by the SCA solutions, the film was slightly swollen and became more flexible. At the same time, the polymer film immediately responded to the chemical stimuli, resulting in a significant emission enhancement. For instance, Figure 2 shows the variations in fluorescence spectra of the PTMSDPA film in the process of the hybridization with VTMOEOS in situ in the film. After deposition of the VTMOEOS solution to the PTMSDPA film, the fluorescence intensity at 542 nm increased about 4.8 times, and simultaneously, the fluorescence maximum band shifted to a shorter wavelength by 22 nm to appear at 520 nm. The enhanced emission was retained even after the complete ethanol evaporation because a sufficient amount of VTMOEOS remained in the PTMSDPA film. This emission enhancement is ascribed to quenching sites degeneration by the swelling-induced chain entanglement relaxation. Such fluorescence response mechanism as swelling-induced emission enhancement (SIEE) has already been well explained in our previous paper.[8] Furthermore, in order to accelerate the sol−gel reaction of the SCA in situ in the film, the film was dried at room temperature in air for several minutes before heating at 90 °C in air for 5 h. Noticeably, the emission further increased and slightly shifted to red by 6 nm after the thermal treatment. Other SCAs also showed a same tendency (Figures S2−S4 in Supporting Information).

Figure 3 shows the IR spectra of the PTMSDPA−VTMOEOS hybrid film in comparison with the virgin PTMSDPA film. The

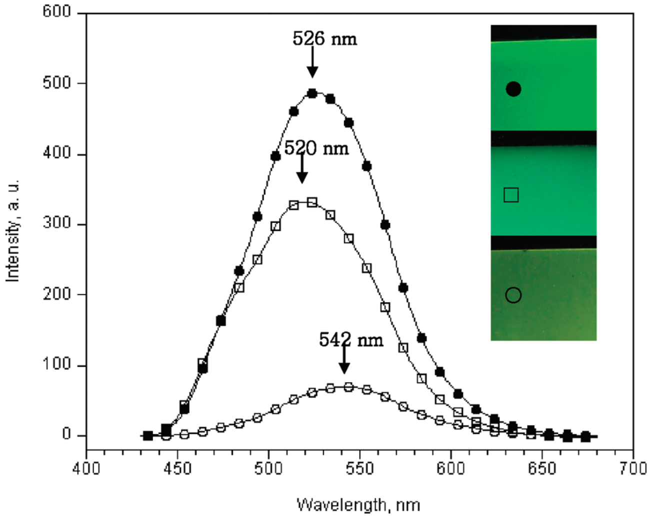


Figure 2. (a) Variation on fluorescence spectra of PTMSDPA film on glass slide (film thickness ≈10 μm) in a course of hybridization with VTMOEOS (excited at 420 nm, ○: virgin; □: after dropping deposition solution and subsequent evaporation of Et_2OH; ●: after heating at 90 °C in air for 5 h).

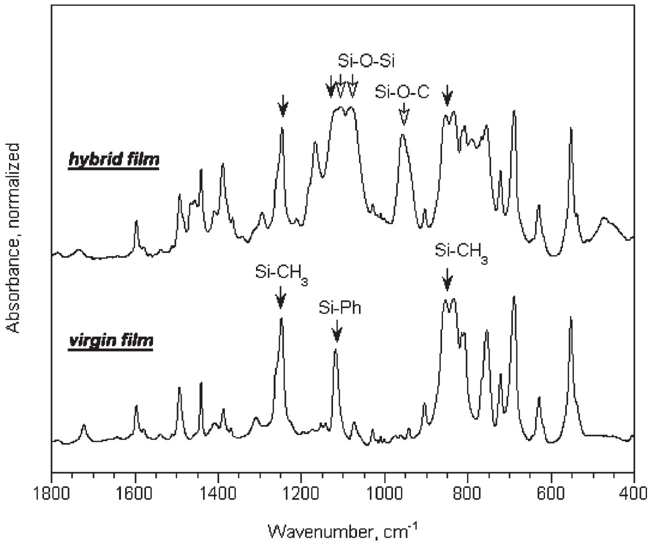


Figure 3. IR absorption spectra of PTMSDPA film (thickness ≈10 μm) before and after hybridization with VTMOEOS.

hybrid film shows absorption peaks characteristic to siloxane linkages (1081, 1105 cm^{-1} due to Si−O−Si; 957 cm^{-1} due to Si−O−C) in addition to absorption peaks due to $Si-CH_3$ (1248, 854 cm^{-1}) and Si−phenyl (1118 cm^{-1}). This indicates that SCA molecules are hydrolyzed to form silica gel in situ in PTMSDPA film to produce a nano-ordered polymer−silica hybrid film.

The solvent resistance of the hybrid film was estimated by means of solvent extraction experiments in comparison with that of virgin film. We measured the UV−vis absorption spectra of the extracts from the hybrid and virgin films while keeping them in toluene at room temperature. As shown in Figure 4, in contrast to the rapid extraction from the virgin film, the extract from the hybrid film shows a merely slight increase in the absorption band due to the PTMSDPA even after several time periods of 10 min. This indicates an enhanced solvent-resistance of the PTMSDPA−SCA hybrid film.

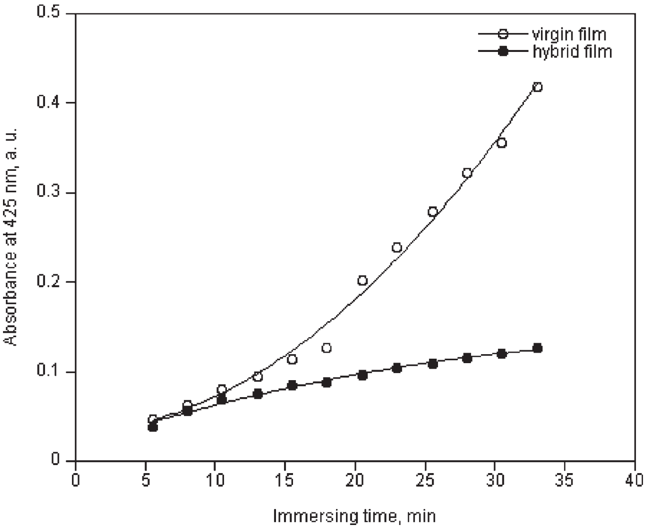


Figure 4. Plots of UV−vis absorbance of the extracts from the virgin (PTMSDPA) and the hybrid (PTMSDPA−VTMOEOS) films as a function of immersing time. Toluene was used as an extract solvent. The absorption band at 425 nm is due to PTMSDPA (film thickness ≈10 μm).

In summary, we successfully developed a PTMSDPA−silica hybrid film with an enhanced emission in addition to chemical resistance. In this study, it was a key point to cross-link SCA molecules in situ in the PTMSDPA film. As expected, the SCA molecules easily diffused into PTMSDPA film and simultaneously the emission of the film significantly increased. Subsequently, when the SCA-deposited film was thermally treated at an appropriate temperature, SCA molecules were readily hydrolyzed and condensed to transform to silica gel in situ in PTMSDPA film. The newly formed PTMSDPA−silica hybrid film hardly dissolved in organic solvents. The hybrid film semipermanently retained the enhanced emission due to the in situ organic−inorganic hybridization. The present SCA treatment technique is also expected to facilitate multilayer lamination on PTMSDPA film due to the enhanced chemical resistance.

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Supporting Information Available: Experimental methods; fluorescence photograph of PTMSDPA−TEOS hybrid film (Figure S1); variation on fluorescence spectra of PTMSDPA film in a course of hybridization with OTEOS, γ-GPTMOS, and γ-APTMOS (Figures S2−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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