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Poly(p-xylene tetrahydrothiophenium chloride) doped photoluminescent sol-gel composite

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Poly(p-xylene tetrahydrothiophenium chloride), a polyphenylene vinylene (PPV) precursor in water and sol-gel solution has been used to prepare photoluminescent glass and coatings. Lactic acid-tetramethoxysilane and lactic acid-aminopropyltriethoxysilane sol solutions were doped with 0.02–0.47 wt% PPV precursor solution (2.5 g/dm^3). The visible light emission from vacuum dried doped sol coating, at 365 nm excitation is about four times brighter than pure uncured PPV precursor film. A 23 mg of lactic acid-aminopropyltriethoxysilane sol containing 31 μg PPV precursor, coated on glass slide gave an emission of 286 Cd/m^2. The brightness increases with dopant concentration and is stable on heating to 130°C. The brightness decreases to 27 Cd/m^2 at 190°C due to coversion of poly(p-xylene tetrahydrothiophenium chloride) to PPV. The bright emission from doped composite is due to wave guiding of sol, transparency of the polymer in the matrix, and the morphology of the composite. The nonlinear optical properties of this material may be useful in display technology and optoelectronics and when coated on glass convert UV radiation to visible light. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

There has been great interest in potential applications of conjugated polymers due to their photonic and electro-optical properties. These polymers find diverse applications as efficient light emitting diodes [1–3], transistors [4–7], photovoltaics [8–10] and electrochromic [11] devices. Though a number of polymers are used in these applications, polyphenylene vinylene (PPV) and its derivatives are the most promising. PPV is thermally and chemically stable and a robust conducting polymer. Its effective conjugation length can be controlled [12] and its luminescence can be chemically tuned by copolymerization [13].

Sol-gel chemistry [14–16] facilitates an efficient way of trapping polymers in inorganic oxide glass. Added to a sol-gel solution, the polymer or an organic compound can be locked in a rigid cage to impart distinctive properties to the sol glass. For example addition of asymmetric silicate can generate nonlinear optical properties [17], spiropyrane/SiO$_2$ is a photochromic material [18] and laser dyes sol provide luminescent materials that have been used as laser cavities [19]. The materials that convert UV light of long-wavelength to visible light could replace the mercury in fluorescent lights with a less toxic material and better conversion efficiencies. In the present work, water soluble PPV precursor was added to sol-gel to study its luminescent behavior in a transparent composite glass matrix and its ability to convert UV to visible light.

2. Experimental

Tetramethoxysilane (TMOS), aminpropyltriethoxysilane (APTES) and lactic acid (LA) from Aldrich were used as received. PPV precursor, poly(p-xylene tetrahydrothiophenium chloride) was prepared by slight modifications to the method described by Wessling [20] and Lenz *et al.* [21]. A sulfonium salt, prepared earlier by the reaction of $\alpha'\alpha'$-dichloro-p-xylene with tetrahydrothiophene was used in PPV precursor preparation. Sulfonium salt solution in deionized water was cooled to 0°C in an ice salt bath and 0.1 M NaOH was added slowly under nitrogen to initiate polymerization. The polymerization was terminated by addition of enough 1.0 M HCl to make the viscous solution slightly acidic. The solution was dialysed in deionized water for 6–7 days. The concentration of dialysed PPV precursor was 2.5 g/dm^3. This precursor solution has density 1.01 at 20°C, pH1.67 and refractive index 1.3347.

To prepare sol-gel glass, 0.2×10^{-6} m^3 (1.3×10^{-3} mol) of TMOS was added slowly under nitrogen to 10^{-6} m^3 of lactic acid (1.3×10^{-2} mol) and stirred for a few minutes and the viscous solution was poured into a ceramic pan for gelation.

PPV precursor doped sol was prepared by addition of 0.25×10^{-6} m^3 (6.2×10^{-4} g) of precursor to 0.5×10^{-6} m^3 (6.7×10^{-3} mol) of lactic acid and stirred for a few minutes. To this, 0.5×10^{-6} m^3 (3.3×10^{-3} mol) of TMOS was added slowly under nitrogen while stirring. The viscous reaction mixture was transferred to a small dish to gel and allowed to dry in the glove

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box for two days, and then dried in open air at room temperature. A light green transparent monolith glass resulted on drying. A number of PPV precursor doped TMOS-lactic acid sol-gel glass pellets were prepared with varying concentrations of dopant to give pellets with 0.08, 0.19, 0.35, and 0.47 wt% PPV precursor.

TMOS was replaced with APTES to prepare PPV precursor doped sol coating material. For this purpose 0.5×10^{-6} m^3 lactic acid (6.7×10^{-3} mol) was placed in each flask and 0, 0.2, 0.5, 0.8, 1.2, and 1.5×10^{-6} m^3 of PPV precursor was added respectively. After stirring, 0.5×10^{-6} m^3 APTES (3.3×10^{-3} mol) was added to each reaction bottle, stirred and then applied on pre-weighed glass slides (22 × 22 × 0.3 mm). After standing in the glove box for two days, the samples were vacuum dried for another 48 h. To study thermal stability of the coatings, the samples were heated overnight under vacuum at 30°C, followed by heating at 50, 65, 110, 135, and 190°C. After each drying/heating cycle, light emission was measured under 365 nm excitation, and the weight changes and UV-Vis spectra were recorded.

The UV stability of the glass composite was examined by exposure to seven hours of continuous exposure at 365 nm. Measurements of the emission from the glass before and after UV "baking" showed no change.

3. Discussion

The sol-gel process was used to prepare poly(p-xylene tetrahydrothiophenium chloride) doped photoluminescent glass to enhance the photoluminescence character of the polymer, while providing chemical and thermal stability to the PPV precursor polymer.

A 2.5 g/dm^3 solution of poly(p-xylene tetrahydrothiophenium chloride) in water has been used with LA-TMOS and LA-APTES sol systems. This doped glass after drying, gives a very bright green emission when exposed to UV light. The observed photoluminescence is rather extraordinary given the tiny fraction of polymer present in the sol.

PPV precursor doped LA-TMOS sol-gel pellets with 17.8 mm diameter, 1.6 mm thickness, and 0.6–0.7 g weight were exposed to 365 nm λ, coming through a slit. The light source was a Spectroline Model ENF-280C. The manufacturer reports the active continuous light, 4.7 W/m^2 at 0.152 m from the source. Visible light emission from the samples was measured with an International Light Radiometer IL1700 and SHD033 detector. The light emission from the UV lamp itself, pure PPV precursor film, LA-TMOS sol-gel glass, and polymer doped sol-gel glasses was measured. Fig. 1 shows a regular increase in photoluminescence with increase in PPV precursor concentration in LA-TMOS sol-gel glass.

It is to be noted that the brightest visible light emission from the PPV doped samples is from its edges, while the measurements were made from the top, not the edges. The detector is positioned to measure light from a narrow 2° cone, 60 mm above the face of the sample. The calibrated radiometer measures less than 2% of the emitted light in its narrow 2° field of view.

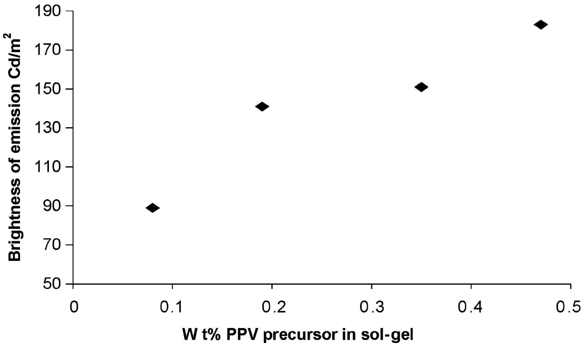

Figure 1 Light emission with increase in PPV precursor concentration in sol.

A sol-gel pellet with its sides curved upward was prepared to determine if some light guiding towards the detector significantly increases the measured light. The light from a sample prepared in a round bottom test tube with an upward edge, is much brighter at the detector. A 0.45 wt% polymer doped sol-gel pellet with a total sample mass of 0.24 g, gave an emission of 311 Cd/m^2. The light guiding toward the observer (detector) with a negative meniscus shows that light emission at the sample edges is brighter than from the face of the coating alone. Where this effect can be utilized, a brighter light can be fabricated. Since a radiant flux of 1 W is equal to 54 candela at this wavelength, an efficiency calculation gives 28.5 mW/68 mW, or 42% Stokes Shift Efficiency. The theoretical limit is $365/550 \text{ nm} = 66\%$.

APTES was used in place of TMOS to prepare sol solution for coating. This sol-gel solution containing varying concentrations of PPV precursor was coated on glass slides and the effect of polymer concentration and temperature on photoluminescence and stability of the system was studied. The samples were heated overnight under vacuum at 30, 50, 65, 110, 135, and 190°C. After each heating cycle, photoluminescence was measured with 365 nm excitation, and the weight changes and UV-Vis spectra were recorded.

No change in the physical appearance of samples was observed up to 130°C. Between 130 and 135°C, the samples developed a slight yellow tinge and at 185–190°C, the samples changed to a golden brown color, due to curing of polymer precursor to PPV and decomposition of APTES.

The weight of polymer doped sol-gel glass, coated on slides was in the range 23–42 mg, doped with small amounts of PPV precursor (8.0–32.8 μg). All the coatings were homogeneous except at the highest loading. The samples dried at 50°C showed 133–286 Cd/m^2 light emission when exposed to excitation light at 365 nm. This extremely bright emission is significant since PPV precursor is present in μg levels. The light emission from a reference sol-gel is negligible (0.78 Cd/m^2) while pure PPV precursor on a glass slide emitted 85 Cd/m^2. It is evident that it is the PPV precursor and not the sol-gel matrix responsible for the bright emission.

There is a gradual but significant increase in light emission with increase in dopant concentration (Fig. 2). The maximum face photoluminescence is 286 Cd/m^2 for 31.2 μg (0.12% loading of Polymer) flat coated

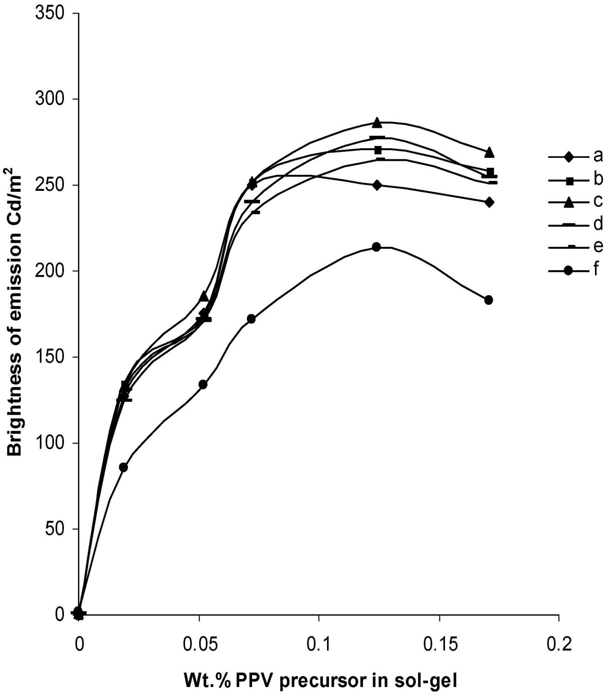

Figure 2 Photoluminescence in sol-gel composite as a function of PPV precursor concentration and process temperature, (a) 20°C (b) 30°C (c) 50°C (d) 65°C (e) 110°C (f) 135°C.

sample. Further increase in dopant concentration shows a slight decrease in photoluminescence, due to visible phase separation in the sample. It is anticipated that higher PPV concentration would enhance photoluminescence if phase separation within the sol-gel was eliminated. Fig. 2 also reflects the temperature stability of doped sol-gel glass. The samples having varying dopant concentration are stable at 110°C with respect to photoluminescence but as the temperature reaches 135°C, some decline is noticed. The samples start changing to light yellow color at 130–140°C.

The weight loss from doped sol-gel with increase in temperature reflects basic physical and chemical changes in the matrix. Any alcohol from condensation reaction or water from dopant solution trapped in the sol matrix is expelled from the system on heating and 15–16% weight loss is noticed at 110°C. When the same samples are heated to 190°C under vacuum, an additional 15% loss takes place due to conversion of PPV precursor to conjugated PPV polymer with elimination of tetrahydrothiophene and hydrochloric acid (Fig. 3) and decomposition of APTES. This phenomena has significant impact on light emission ability of the doped sol system.

Fig. 4 shows light emission (Cd/m^2) from polymer doped LA-APTES sol with respect to temperature changes. A sol sample, with 0.12 wt% PPV precursor shows significant decrease in light emission when the temperature is raised from room temperature to 190°C. Uncured or partially cured PPV precursor in sol matrix is more photoluminescent than fully cured PPV sol and the presence of tetrahydrothiophenium salt in precursor polymer contributes to luminescence.

The UV-Vis, spectra of pure sol-gel and the PPV precursor doped LA-APTES sol samples coated on 0.3 mm thick glass were recorded after heating at 110, 135, and 190°C (Fig. 5). The reference sol-gel does not absorb in the visible region while the composite does. The absorption spectrum of sample heated at 110°C shows all the characteristic bands of PPV precursor solution and the film (321, 340, 373, 396, 430 nm); however, when heated to 190°C, the nature of absorption bands change. The peaks at 373 and 396 nm tend to disappear and a broad band at 465 nm emerges due to increased conjugation in PPV polymer. It is concluded that sulfonium groups remain stable in the sol environment to 110°C and above this temperature are slowly eliminated to give cured PPV sol.

Fig. 6 shows the photoluminescence spectra of polymer doped LA-APTES coated slides and that of a lactic acid-TMOS pellet. The photoluminescence maximum is at 495 nm with a shoulder at 525 nm when excited at 365 nm. The peak positions in samples a, b, c and d are identical while the absolute intensities change due to variation in PPV content. The difference in emission intensities is most prominent at 525 nm, those with relatively higher polymer loading show greater intensities. The appearance of the luminescent composite is bright green, described best with International Commission on Illumination (CIE) color coordinates of (0.123, 0.508). The maximum in this sol composite is at a relatively lower wavelength compared to PPV film spectrum maxima 511 and 548 nm [22], which can be attributed to shortening of effective conjugation wavelength due to partial elimination of tetrahydrothiophene and hydrochloric acid. The stability of dopant precursor solution is dependent on its storage life [23] and with time it slowly converts to PPV through an elimination reaction. The dopant used has some short conjugated segments of PPV and tetrahydrothiophene salt pendent groups on the chains responsible for bright photoluminescence (Fig. 7). The macomolecular associations are retained in the sol matrix until heated above 130°C. The brightness of photoluminescence decreases above this temperature due to loss of sulfonium salt groups. It is reported that even a small change in the side groups of the polymer results in dramatic change in absorbance and photoluminescence [24].

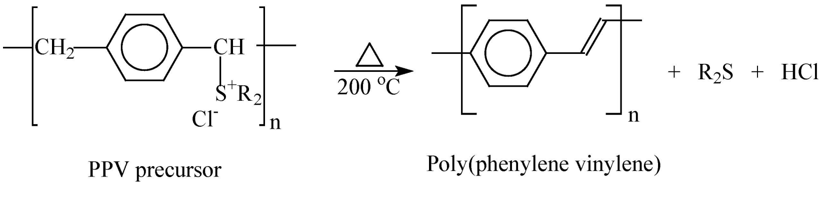

Figure 3 Thermal curing of PPV precursor.

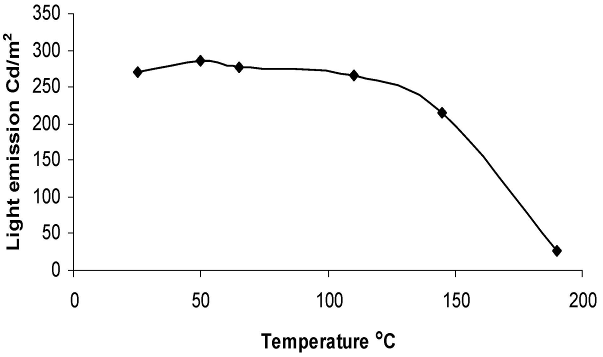

Figure 4 Light emission from 0.12 wt% PPV precursor in sol composite with respect to curing temperature.

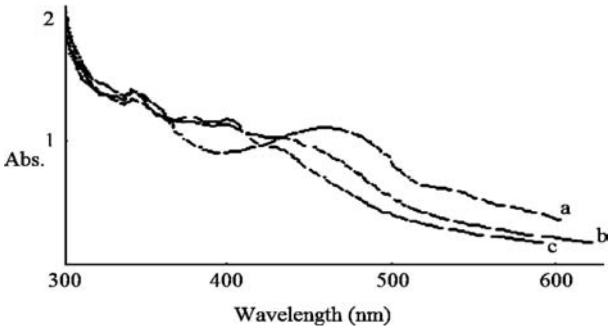

Figure 5 UV-Vis spectra of PPV precursor doped LA-APTES sol, cured at (a) 190°C (b) 135°C (c) 110°C.

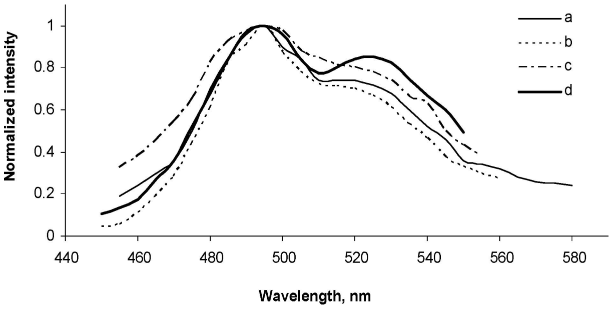

Figure 6 Photoluminescence spectra of PPV precursor-sol composite, LA-APTES sol system with different dopant concentrations (a, b, c), LA-TMOS sol (d).

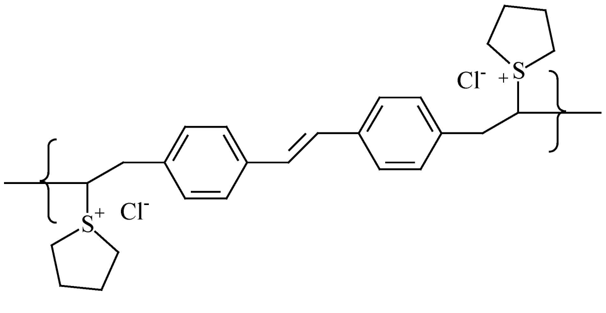

Figure 7 Photoluminescent polymer chain.

The precursor polymer is dispersed homogeneously in the sol matrix and forms a interpenetrating polymer network. The agglomeration of polymer is controlled by keeping a check on its concentration in sol. The sol matrix restricts the molecular rotation and vibration to some degree, which contributes to photoluminescence.

The PPV precursor doped sol-gel composite is stable to UV exposure at 365 nm. Seven hours of continuous exposure to this UV wavelength has no measurable effect on the emission intensity of the samples. This radiation does not appear to be energetic enough to expel leaving groups from the composite network.

It is concluded that excellent photoluminescence from doped sol-gel glass is due to the characteristic nature of the polymer chains (Fig. 7), wave guiding nature of the sol, transparency of the matrix and polymer islands and morphology of the composite. This composite material with nonlinear optical properties may be useful in display technology and optoelectronics and has a potential application on home and greenhouse windows to increase visible light throughput.

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