Characterization of sol–gel processed poly(*p*-phenylenevinylene) silica and V_2O_5 composites using waveguide Raman, Raman and *FT*i.r. spectroscopy

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A composite of poly(*p*-phenylenevinylene) (PPV) with V_2O_5 is prepared through sol–gel processing and compared with the corresponding composite with silica. The effective conjugation length as determined by the band gap remains the same when V_2O_5 is chosen as a dopant, whereas the effective conjugation length is reduced in the PPV/silica composite. These composites exhibit good optical quality and show promise for optical waveguiding. The waveguide Raman spectra of these composites can be easily obtained. The refractive index of the PPV/V_2O_5 composite is higher than that of the PPV/silica composite. Furthermore, the Raman spectra do not indicate any existence of chemical bonds between the vinyl group of PPV and the glassy matrix (silica oxide or V_2O_5). The sol–gel processed PPV/V_2O_5 composite also exhibits a larger $\chi^{(3)}$ value than that of the PPV/silica composite.

(Keywords: characterization; sol–gel processing; composites)

INTRODUCTION

For many years much attention has been focused on conjugate polymers as candidates for practical non-linear optical applications such as optical information processing, telecommunications and integrated optics[1–5]. Organic materials have certain distinct advantages over their inorganic counterparts, such as relatively large optical non-linearity, fast temporal response, high damage threshold and transparency over a large wavelength range. In particular, organic materials can be easily processed and offer the possibilty of designing molecules with desired physico-chemical properties through molecular engineering. One such tailoring procedure which can be used to fabricate high optical quality thin films of organic polymers is sol–gel processing[6–8].

The sol–gel method has been actively studied as a possibly superior alternative for the preparation of ceramics, glasses and composites[9–11] because of the potential advantages[12–15] of this process compared to conventional melt/sintering techniques. Since the sol–gel process involves the use of low viscosity solutions as the starting reagents, there are several clear advantages: high degree of homogeneity; better control of stoichiometry; low processing temperature; less contamination; and ease of preparation of thin films.

Most organic polymers have generally not been found to be good photonic media due to their high optical losses[16]. Inorganic glasses, on the other hand, are excellent photonic media because of their high optical quality and extremely low optical losses. Therefore, combining an inorganic glass and an organic polymer is one of the best ways to obtain materials with large non-linearity and low optical losses. The first sol–gel processed optical quality composite film made with the precursor technique was developed in our laboratory[17,18]. In order to obtain both high non-linear coefficient, $\chi^{(3)}$, and high optical quality composite, poly(*p*-phenylenevinylene) (PPV) with high $\chi^{(3)}$ and silica were mixed successfully without any phase separation or precipitation[19]. Although this composite has proven to produce good optical waveguiding[19–21], its structure and morphology have not been studied until now. In this paper, we report our investigation on the structure of the sol–gel processed PPV/silica and PPV/V_2O_5 composites using waveguide Raman, Raman and *FT*i.r. spectroscopy. We also compare the refractive indices and the $\chi^{(3)}$ values of the two composites.

EXPERIMENTAL

Preparation of the films

We have prepared the PPV film, PPV/silica and PPV/V_2O_5 composite films by the spin coating and doctor blading methods. Preparation of the PPV/silica and the PPV/V_2O_5 films involves solution mixing of the water soluble sulfonium salt precursor of PPV with a proper amount of tetramethyl orthosilicate or vanadic acid, respectively[17–19]. The solution is then spin coated on a 1 mm thick microscope slide and subsequently heat treated in a vacuum (~1.33 Pa) oven when the polymer precursor converts into the conjugated polymer. The compositions for both PPV/silica and PPV/V_2O_5 are, respectively, ~50:50 and ~30:70 by weight. The thicknesses of the composite films are in the range of 1–5 μm.

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Refractive index and thickness measurements

The refractive index and the thickness of the film were determined by a Prism Coupler (Metricon PC-2000). The basic theory of this instrument is based on the waveguide technique[22]. The sample to be measured is brought into contact with the base of a prism by means of a pneumatically operated coupling head, creating a small air gap between the film and the prism. A laser beam strikes the base of the prism and is normally totally reflected at the prism base onto a photodetector. However, at certain discrete values of the incident angle (θ), called mode angles, photons will tunnel across the air gap into the film and enter into a guided optical propagation mode, causing a sharp drop in the intensity of light reaching the detector.

Waveguide Raman spectroscopy

A planar optical waveguide structure consists of a substrate (refractive index n_s), a thin film (refractive index n_f) and a superstrate (refractive index n_c). When the thickness of the film is comparable to the excitation wavelength and the refractive index of the film is larger than that of both the substrate and the superstrate the electric field is constrained by the total internal reflection and will propagate through the film as a guided wave[23]. The guided waves are characterized by the internal reflection angle (θ), the effective refractive index $n_f \sin\theta$ and the effective wave vector $kn_f \sin\theta$. Based upon the theory of guided waves there are discrete allowed modes of transverse electric (TE) and transverse magnetic (TM) polarizations. The evanescent field associated with the guided modes extends several hundred angstroms into both the superstrate and the substrate. The shape of the electric field distribution inside the film depends on the order and polarization of the excited mode. It is usually desirable to select the zeroth-order mode since it has a maximum field distribution inside the film. However, if the investigating material is not guiding it can be used as the superstrate and probed by the evanescent field. If this is the case, the thickness of the superstrate should be taken into account. In the present work we excited all spectra with the TE_0 mode.

The input laser field can be coupled into the film using a variety of coupling techniques such as prism coupling, grating coupling and end-fire coupling. Whatever the coupling technique selected for introducing power into the film, the propagation equations are the same. In this work we employed a prism coupler. By means of a pressure applicable aluminium structure the coupling prism could be pressed against the film until a satisfactory optical contact was achieved. To obtain a Raman spectrum of the film or the superstrate, the input beam is focused onto the face of the prism that is in contact with the film by a 25 cm focal length lens. When a particular angle of incidence is chosen corresponding to an eigen value equation of the guided modes, the corresponding mode is driven. Raman scattering results from the interaction of the propagating field with the molecules of which the waveguide is made. Because of the beam confinement in the film, the optical field intensity is very high, and one can obtain Raman spectra with high signal-to-noise ratios.

The Raman spectra of pure PPV, PPV/silica and PPV/V_2O_5 composites were recorded via the planar optical waveguide geometry. In the case of V_2O_5, the crystalline material was held in a capillary tube and the spectrum was obtained with the conventional 90° scattering geometry. The spectrometer used in this investigation consists of a continuous wave Ar ion laser (Spectra Physics 2020) operating in the TEM_{00} mode. The output from the Ar ion laser pumps a tunable dye laser (Coherent 595-01) which has an average output power of ~500 mW at 670 nm. This output was used to excite the sample in order to avoid large emission from the samples in the 450–600 nm spectral range. The scattered light was collected with a 15 cm focal length lens and focused on the entrance slit of a Czerny–Turner double monochromator. The dispersed light was focused onto the photocathode of a thermoelectrically cooled photomultiplier (ITT model FW130). The signal from the photomultiplier was fed into a digital electrometer (Keithley 614) and the electrometer output was read by a microcomputer which also controls the monochromator. The data were recorded at a rate of $5\,cm^{-1}\,s^{-1}$.

RESULTS AND DISCUSSION

U.v.-visible and FTi.r. spectra

Figures 1a, b and *c* show the absorption spectra of the PPV, the PPV/silica and the PPV/V_2O_5 films, respectively, in the u.v.-visible range. The absorption maximum for the PPV/V_2O_5 gel shows no significant change compared to that of PPV. Therefore, one can infer that the effective conjugation length remains the same when V_2O_5 is chosen as the inorganic counterpart. This is in contrast to the PPV/silica composite in which the effective conjugation length is shorter than in pure polymer PPV, as deduced by the observed 40 nm shift in the absorption spectrum[18]. *Figures 2a, b* and *c* show the changes in the i.r. spectra of PPV, V_2O_5 gel and the PPV/V_2O_5 composite, respectively. These i.r. spectra were recorded on an *FT*i.r. spectrometer (The Alpha Centauri FT-IR) and the samples were prepared in KBr pellets. *Figure 2a* presents the spectrum of fully converted PPV – this spectrum is identical to the published result[24]. The absence of the *cis* C–H bending vibration (630 cm^{-1}) and the presence of the strong absorption corresponding to the *trans* C–H out-of-plane bending vibration (950 cm^{-1}) show that the elimination reaction results in *trans* PPV exclusively. Thus, it confirms the full elimination of the PPV film in our sample.

Abello *et al.* have shown[25] that the composition of the vanadium oxide gel, corresponding to the formula $V_2O_5 \cdot nH_2O$ with $n = 1.6$, 1.2, 0.6, 0.4 and 0.3, depends

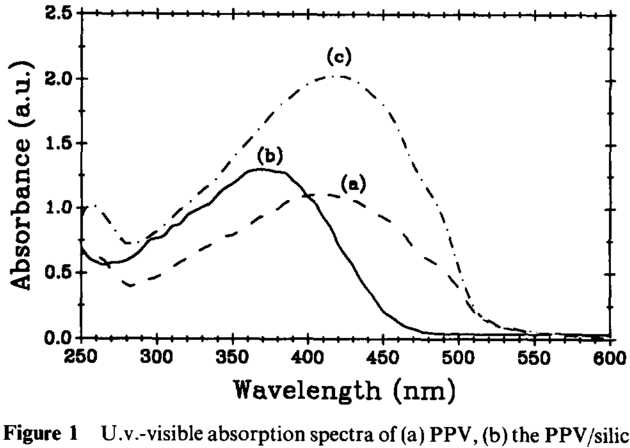

Figure 1 U.v.-visible absorption spectra of (a) PPV, (b) the PPV/silica composite and (c) the PPV/V_2O_5 composite

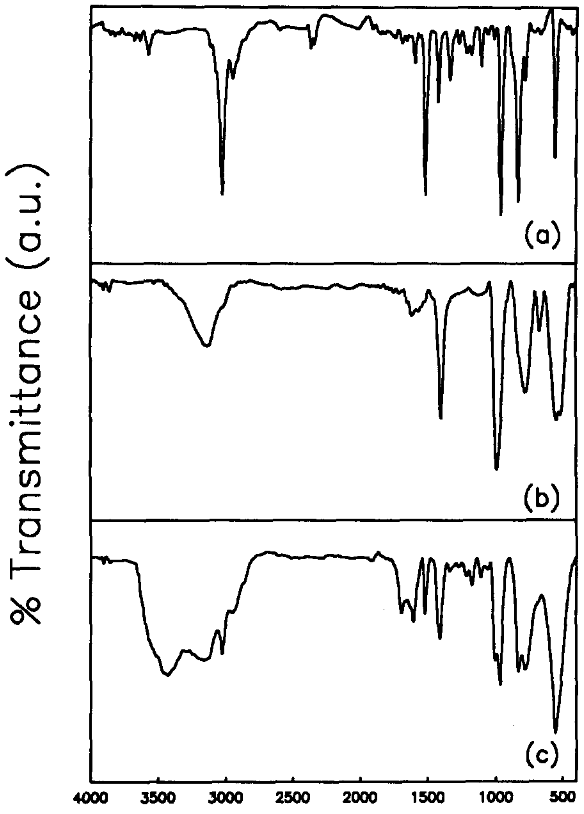

Figure 2 I.r. transmission spectra of (a) PPV, (b) the V_2O_5 gel and (c) the PPV/V_2O_5 composite

upon the elimination conditions. The i.r. spectrum of the V_2O_5 gel in *Figure 2b* shows that the water content in our sample is very small[26]. The stretching vibration of V=O gives rise to a narrow i.r. band at 997 cm^{-1}. The i.r. spectrum of the PPV/V_2O_5 composite is shown in *Figure 2c*. Clearly, the intensity of the vibration band at 963 cm^{-1} (*Figure 2a*), which is due to vinyl *trans* C–H out-of-plane bending, is decreased in *Figure 2c* because of the formation of the PPV/V_2O_5 composite. Furthermore, a broad absorption band was observed at 3480 cm^{-1} in *Figure 2c* which could be due to the trace of water in the composite.

Raman spectra

Vibrational spectra provide useful information on the morphology and structure of polymeric materials[26]. In particular, Raman spectroscopy has been utilized to elucidate conformational structure in oriented and doped polymers[27]. Unfortunately, in thin films ($<0.1\,\mu m$) the measurements are very difficult with conventional spontaneous Raman spectroscopy due to the smaller scattering volume. This difficulty can be overcome by incorporating integrated optical techniques such as waveguide Raman spectroscopy. Waveguide Raman spectroscopy has certain advantages over the conventional spontaneous Raman technique[23]. For example, bulk polymeric samples very often contain crystals or particles whose size is comparable to the excitation wavelength which can scramble the polarization of the incident beam, preventing any meaningful measurements of polarization dependence of spectra. In contrast, a thin film waveguide of the same material can be fabricated without any such crystals.

The waveguide raman spectrum of pure PPV film is shown in *Figure 3*. No Raman peak was observed in the case of the precursor. The Raman peaks observed in this spectrum can be categorized mainly into two groups, namely the peaks associated with the vibration of the vinyl moiety and the peaks associated with the vibration of the aromatic ring counterparts. The vibrational peaks at 1330 and 1628 cm^{-1} are characteristic of the vinyl group where the former is characteristic of the aromatic ring and the latter originates from the $\nu_{C=C}$ stretching vibration of the vinyl linkage[28]. The rest of the Raman peaks are associated with the benzene ring vibrations of PPV.

It is seen that, in the case of the PPV/silica composite, different excitation wavelengths (488 nm in *Figure 4a*, 670 nm in *Figures 4b* and *c*) generate Raman spectra that show no frequency dispersion as a function of the excitation wavelength. In this respect, the behaviour of the PPV/silica composite is very similar to that of pure PPV which also displays no frequency dispersion. However, in the case of PPV, the Raman spectrum obtained with the 488 nm excitation is dominated by the background fluorescence. In the case of pure V_2O_5 gel, the Raman spectrum largely depends on the amount of residual water content in the film. When the molar fraction of water in the gel is very low ($<0.3\,H_2O$) the Raman spectrum of the gel is essentially equal to that of crystalline V_2O_5 (*Figure 5a*). The Raman spectrum of the PPV/V_2O_5 composite obtained in the waveguide

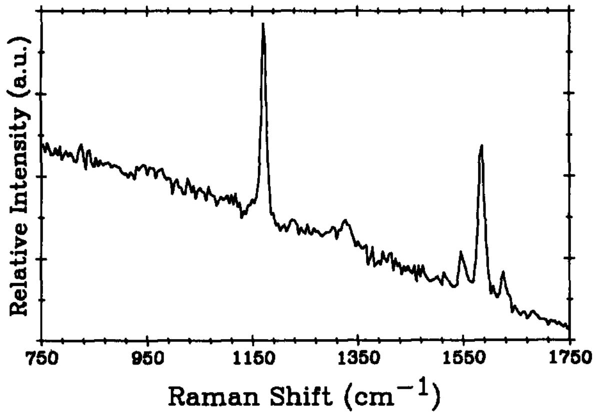

Figure 3 Raman spectra of PPV film (excitation wavelength: 670 nm)

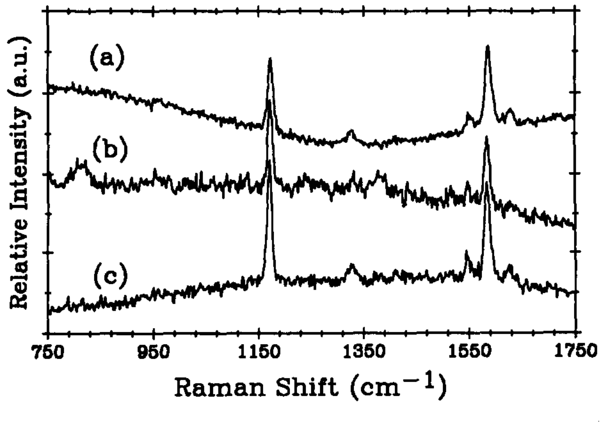

Figure 4 Raman spectra of (a) the PPV/silica composite (excitation wavelength: 488 nm), (b) PPV/silica thermally treated at 360°C and (c) PPV/silica thermally treated at 220°C [excitation wavelength: 670 nm for (b) and (c)]

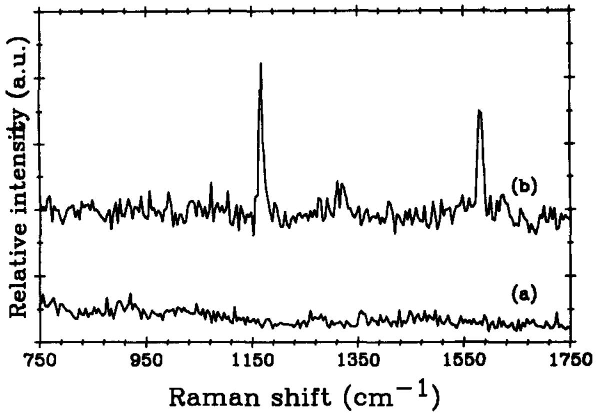

Figure 5 Raman spectra of (a) the V_2O_5 powder and (b) the PPV/V_2O_5 composite (excitation wavelength: 678 nm)

geometry is also shown in *Figure 5*. The characteristic vibrations of the aromatic ring and vinyl group appear at the same frequencies (1628 and 1330 cm^{-1}) as in the case of pure PPV.

There are no apparent differences between the Raman spectra of PPV incorporated into the silica matrix (*Figure 4*) and that of pure PPV polymer. It has been shown that the Raman spectrum of PPV doped with $FeCl_3$ is very different from that of the undoped sample[28]. The disappearance of well resolved Raman bands at 1552 and 1628 cm^{-1} indicates that the distortion of the vinyl linkage between the benzene groups is due to dopant. The shift of the $\nu_{C=C}$ stretching vibration of the vinyl linkage to a lower frequency suggests that the electron density of the –C=C– has been reduced in the doped material due to interaction with the dopant. However, in the Raman spectra of the sol–gel processed PPV/silica such electronic perturbations at the vinyl bridge are not apparent. Even after heating the sample to a temperature of 220°C the Raman spectrum of the sol–gel composite remains the same (*Figure 4*). Therefore, there are no chemical bonds between the glassy matrix and the vinyl bridge of the PPV in the sol–gel processed PPV/silica (or V_2O_5) composites.

Thermal analysis

Characterization of the elimination reaction of the pure polymer and the composites was performed by d.s.c. (Shimadzu DSC 50). These measurements were done at the same heating rate (10°C min^{-1}) under nitrogen atmosphere. The d.s.c. responses of the PPV precursor, the V_2O_5 precursor and the PPV/V_2O_5 precursor are shown in *Figures 6a, b* and *c*, respectively. These results are very similar to the d.s.c. responses of the PPV/silica composite reported in a previous paper[19]. Two endothermic responses are observed in the PPV precursor. In *Figure 6a*, the first peak centred at 110°C corresponds to the dehydration of the precursor, whereas the second response located at 230°C can be assigned to the E1cB elimination reaction producing the conjugated polymer. However, when V_2O_5 is introduced into the PPV polymer, a broadened response is observed instead of any significant shifting. The broadened effect is mainly due to the V_2O_5 gel.

Refractive index and third-order non-linear susceptibility $\chi^{(3)}$

Based on the refractive index measurement of a prism coupler, the PPV/silica composite shows a refractive index (TE mode) of 1.75 at 633 nm while the PPV/V_2O_5 composite has a value of 2.23. The $\chi^{(3)}$ value was evaluated by comparing the strength of the degenerate four-wave mixing signal at low incident photon flux with that of CS_2 according to the following relationship[1]:

$$(\chi^{(3)}{}_s/\chi^{(3)}{}_c) = (n_s/n_c)^2(l_c/l_s)(I_s/I_c)^{1/2}(\alpha l_s)/[\exp(-\alpha l_s/2)][1-\exp(-\alpha l_s)] \qquad (1)$$

where n is the refractive index, l is the interaction length and a is the linear absorption coefficient. The subscripts c and s refer to CS_2 and the sample, respectively. The CS_2 sample is non-absorbing at the wavelength used in our experiments (602 nm). A value of $\chi^{(3)} = 6.8 \times 10^{-13}$ esu was used[29] as the reference value for CS_2. However, in the case of the PPV/silica and the PPV/V_2O_5 composites the absorption term in equation (1) is ignored because the samples show negligible linear absorption at the wavelength of 602 nm. The measured effective $\chi^{(3)}$ values for PPV/silica and PPV/V_2O_5 are $\sim 3 \times 10^{-10}$ and $\sim 6 \times 10^{-10}$ esu, respectively. These values can be compared with $\sim 4 \times 10^{-10}$ reported by Singh *et al.*[30] for PPV at 602 nm. The $\chi^{(3)}$ values for the polymer/sol–gel silica composites are slightly smaller than for the corresponding pure polymer. Based on the number density consideration ($\sim$50% by weight of the polymer in the composite), one would expect to see a reduction in the $\chi^{(3)}$ value by a factor of 2. The observation that the composite film shows a $\chi^{(3)}$ value very close to that of the parent polymer film may be a consequence of the significantly improved optical quality of the composite

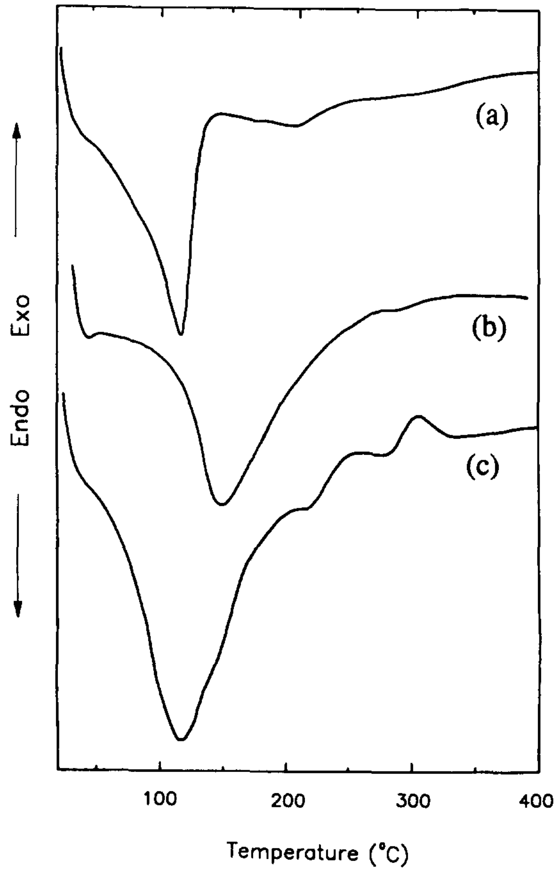

Figure 6 D.s.c. responses of (a) the PPV precursor, (b) the V_2O_5 precursor and (c) the PPV/V_2O_5 precursor (heating rate: 10°C min^{-1})

film, permitting a more realistic assessment of its intrinsic $\chi^{(3)}$ value. A similar situation has been found in another polymer composite of poly(*p*-phenylenebenzobisthiazole) and nylon (Zytel 330), where the improved optical quality of the film yielded a higher $\chi^{(3)}$ value[31]. The increase of the $\chi^{(3)}$ value of the PPV/V_2O_5 composite may be due to increased refractive index of the composite.

CONCLUSIONS

Novel composites of polymer doped silica (or V_2O_5) have been prepared by the sol–gel process. The effective conjugation length remained the same when V_2O_5 was chosen as the dopant, whereas the effective conjugation length appears to be reduced in the PPV/silica composite. These composites exhibit good optical quality, showing promise for optical waveguiding. The waveguide Raman spectra of these composites can be easily obtained. The refractive index of the PPV/V_2O_5 composite is higher than that of the PPV/silica composite. Furthermore, the Raman spectra do not indicate any chemical bond between PPV and the glassy matrix in either of these composites. However, the sol–gel processed PPV/V_2O_5 composites yield a higher refractive index and larger $\chi^{(3)}$ value than those of the PPV/silica composite.

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