Comparison of the Linear and Nonlinear Optical Properties of Poly(*p*-phenylenevinylene)/Sol−Gel Composites Derived from Tetramethoxysilane and Methyltrimethoxysilane

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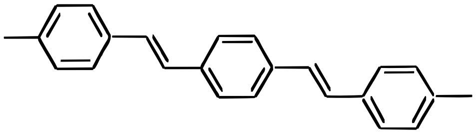
Poly(*p*-phenylenevinylene) (PPV) has been incorporated into sol−gel matrixes via its soluble precursor polymer, using tetramethoxysilane (TMOS) and methyltrimethoxysilane (MTMS) as the silane monomers. Linear absorption maximum (λ_{max}) and nonlinear refractive index n_2 of the PPV in the two composite systems were compared and studied. Compared to pristine PPV, a reduction was seen in λ_{max} and $|n_2|$ of the composite films. This paper addresses chemical and processing effects directed at minimising this matrix-induced reduction in λ_{max} and $|n_2|$. Of the parameters studied, the nature of the silane monomer has the greatest influence on the λ_{max} and $|n_2|$ values of the composites. The reduction of the λ_{max} and $|n_2|$ values in the composite films was much greater when TMOS was the matrix host. There is a smaller decrease in both $|n_2|$ and λ_{max} if acid catalysis is used during either the sol synthesis or during the thermal transformation process, but this effect is marginal for TMOS. A differential matrix effect on λ_{max} and $|n_2|$ is also seen in the temperature required for the conversion to PPV within the respective matrixes.

Introduction

Poly(*p*-phenylenevinylene) (PPV) is a one-dimensional conjugated polymer with the structure shown in **I**. The



(I)

polymer has a number of attributes associated with its possible use as a switching medium in photonics. It has a reasonably large nonresonant nonlinearity, with good thermal and environmental stability. The PPV itself is insoluble in organic solvents, but it can be readily processed via its soluble polyelectrolyte precursor polymer, thus allowing fabrication of the final PPV into various forms. Despite all these desirable properties, PPV in the pristine state cannot be used in photonics as the material has high optical losses arising from reflection, absorption, and scattering. The problem of optical losses in the PPV is particularly severe when film thickness is ≥1 μm. Thus, to use PPV as a nonlinear material, composites of PPV must be considered, with the matrix host providing the required optical transparency, mechanical integrity and protection of the dopant from the harmful environment. Sol−gel glass is a medium which can be used to improve on these properties of the PPV.

The use of sol−gel silica as a host matrix for PPV was first reported in 1991.[1] The resultant composite films showed a significant change in the position of the maximum linear absorption (λ_{max}) when compared with the pristine PPV. There was a reduction of λ_{max}, when PPV was in the matrix of TMOS glass, from 410 nm in the PPV to 370 nm in the composite.[1] The wavelength shift observed is indicative of shortening of the conjugation length in the PPV. This is undesirable in terms of the nonlinearity of PPV, as both theoretical and experimental work on one-dimensional conjugated polymers has shown a power-law dependence of the nonlinearity on conjugation length.[2−6] Recent work on PPV has also shown a chain-length-dependent nonlinearity.[7] Thus, to exploit the inherently large nonlinearity in PPV for all-optical switching, the extent of the λ_{max} reduction must be minimized.

Our preliminary work on the PPV/TMOS composite films not only confirmed the previously reported undesirable reduction in λ_{max} but also showed a tendency of the films to crack when film thickness approached 1 μm. There is therefore a need for an alternate gel matrix for PPV that will not only reduce the extent of the λ_{max} shift but also will allow good optical quality thick films of at least a few microns to be fabricated for use in

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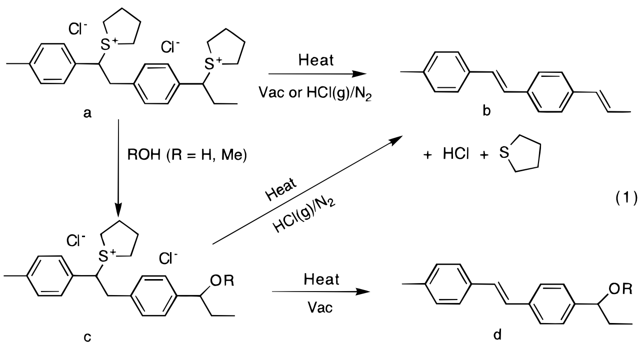

Figure 1. Synthetic pathways to PPV.

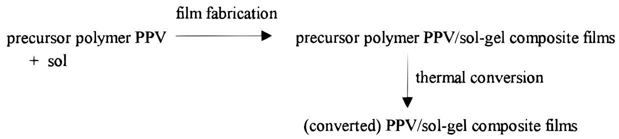

Figure 2. Schematic diagram showing the steps involved in the formation of PPV/sol−gel composite films from precursor polymer PPV and TMOS or MTMS sol solution.

photonics. Methyltrimethoxysilane (MTMS) is known to form thick films without the problem of cracking.[8] The reaction rates of alkyl-substituted alkoxysilanes are also known to be faster than those of the tetrafunctional counterparts.[9,10] The use of MTMS thus could lead to a gel with different properties and different matrix/dopant interaction. The reduced functionality in MTMS has an additional advantage in reducing the host index, thus allowing a greater level of the high index PPV (~2.2) to be incorporated into the matrix without excessively raising the composite index beyond that of glass. In this way, a larger nonlinearity of the composites may be achieved.

Apart from the nature of the gel matrix, we have also studied the effect of changing the sol chemistry on the optical properties of the gel-trapped PPV, by varying the water to silane and acid to silane ratios. Acid catalysis during the thermal conversion of the precursor polymer PPV to PPV in the sol−gel composites was also studied to see whether extension of the PPV conjugation length occurred, as has been found to be the case with pristine PPV,[11,12] and whether such a use of the acid affects the gel properties and the matrix/dopant interaction. Finally, the effects of conversion temperature and thermal cycling on $\lambda_{\max}$ and $|n_2|$ of the composite films are investigated. These two parameters are known to determine the conjugation length in the PPV[13] and affect the gel structures.[14]

Experimental Section

Chemical Preparation. α,α-Dichloro-*p*-xylene, tetrahydrothiophene, 1 M methanolic tetrabutylammonium hydroxide, tetramethoxysilane (TMOS), and methyltrimethoxysilane (MTMS) were purchased from Aldrich and used without further purification. Methanol was AR grade and used as received; water was deionized.

The precursor polymer to the PPV (structure a, Figure 1) was prepared following the standard polyelectrolyte route,[11,15] using α,α-dichloro-*p*-xylene and tetrahydrothiophene as the starting reactants. Polymerization was carried out in methanol, with tetrabutylammonium hydroxide as a base catalyst. At the end of the polymerization, the reaction was quenched by neutralizing the basic reaction mixture with dilute HCl(aq) (0.5 M), to a pH of ~4−6. The precursor polymer solution thus prepared was purified by dialysis against methanol (Spectra/Por 3, with a molecular weight cutoff of 3500) over a period of 3 days, with a daily change of fresh solvent. The dialysis process removed low molecular weight impurities such as the oligomers of the PPV precursor and the salt formed in the neutralization process (tetrabutylammonium chloride). The precursor polymer thus obtained is a colorless, viscous solution, whose viscosity may be adjusted by the temperature of polymerization (−5−0 °C was used in the present work) and the concentration of the reacting solutions (0.4 M used). The precursor polymer solution prepared has a typical weight content of the converted PPV of ~0.5%.

Sol solutions of TMOS and MTMS were prepared by reacting TMOS or MTMS in methanol (mole ratio of silane to methanol = 1:3.5) with the required amount of water (or acidified water using 0.01 N HCl) and heated at an internal temperature of ~60 °C for 1 h. After cooling to room temperature and dilution with equal volume of methanol, the sol solution was filtered (0.2 μm) and an appropriate amount of the sol solution was mixed with the PPV precursor polymer (room temperature, 2−4 h) and spin-coated for film formation. The films were then allowed to dry in covered Petri dishes at room temperature prior to being thermally converted to the PPV. Schematic diagram for the formation of the PPV/sol−gel composite films from the PPV precursor polymer and TMOS or MTMS sol solution is given in Figure 2. All the composite films used in this study have a 20−25% weight content of the converted PPV in SiO_2.

Sol solutions for the gelling study were prepared[16] by reacting MTMS or TMOS, methanol, water, and HCl in the mole ratio of $1:3:5:4.6 \times 10^{-4}$. Half the acidified water was added to the methanolic solution of the appropriate silane at the reaction temperature of ~60 °C and heated at this temperature for 90 min. The remaining half of the water and acid was then added, and the mixture was heated for an additional 60 min at the same temperature. Finally the sols were allowed to age in closed containers overnight at 50 °C, whereby the TMOS sol increased in sol viscosity and gelled within 24 h, while that of the MTMS sol turned turbid with no apparent increase in viscosity. Precipitation of the MTMS sol particles was observed over a period of a few months and finally settled to the bottom and formed a solid translucent gel (~6 months).

For BET surface area determination, the sols were prepared by one-step acid hydrolysis. The mole ratio of the silicon alkoxide:methanol:water:HCl used was $1:3.5:2:1.8 \times 10^{-4}$. The reaction was carried out at 60−65 °C for 1 h. After cooling to room temperature, the sols were aged in closed polyethylene vials at 40 °C overnight, and subsequently left to age at room temperature uncovered for 1 week prior to the BET surface area measurements.

Measurements. Measurements of the optical properties (linear absorption, nonlinear refractive index) were carried out using the thermally converted films of the PPV precursor polymer or of its composites with sol−gel (structure a → structure b, Figure 1). To prevent saturation of the optical absorption in the UV−vis measurements, the highly viscous solution of the PPV precursor polymer was first diluted with

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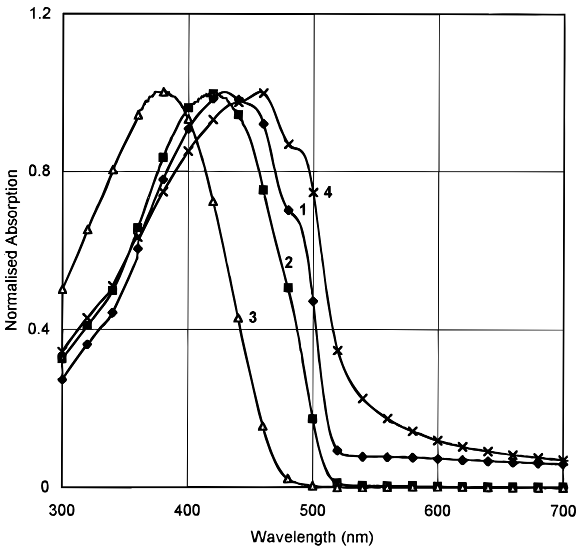

Figure 3. Comparison of UV−vis absorption spectra of pristine PPV and its sol−gel composites with TMOS and MTMS. 1 (solid line with diamonds) = pristine PPV. 2 (solid line with squares) = PPV/MTMS (prepared according to condition (1), Table 1). 3 (solid line with triangles) = PPV/TMOS (prepared according to condition (1), Table 1). 4 (solid line with crosses) = PPV/MTMS (prepared according to condition (4), Table 1). The films were converted at 200−220 °C under a pressure of 0.1 mmHg, 2 h. Composition of the composite films is 20−25% by weight of the converted PPV in SiO_2.

methanol prior to addition of the sol solution. Films were subsequently formed onto substrates by the spin-coating technique—glass substrates (Fisher) for UV−vis measurement and silica substrates (GM Associates, Inc.) for film thickness determination. The spin speed used varied from 200 to 3000 rpm, and the spin time was 60−120 s.

UV−vis absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. The spectra presented were normalised with respect to the maximum intensity in the visible region. Film thickness was determined using a Metricon prism coupler (Model 2010). Nonlinear refractive index values (n_2) were measured by the degenerate four-wave mixing method (DFWM), using an amplified system based on a Coherent Mira Ti sapphire laser having a pulse width of 100 fs. The wavelength of measurement was 800 nm. BET surface area measurements were carried out on blank TMOS and MTMS dried gels (grown as gel disks) and performed by the Advanced Mineral Products Research Centre, the University of Melbourne, Australia.

Thermal Conversion. Thermal consolidation of the precursor polymer of PPV to PPV was carried out in a programmable oven under a dynamic vacuum. A typical heating program consists of a slow heat increase to the required temperature (150 to 220 °C) over a period of 2 h, held at this temperature for 2 h for films with thickness $<1\ \mu$m and 6 h for films with thickness $>1\ \mu$m, and finally a slow cooling to room temperature. For heating above 220 °C, a glass oven with an external heating element was used. This setup allows both heating under vacuum and heating under a slow stream of $HCl(g)/N_2$ or N_2. HCl(g) was generated by passing N_2 through a solution of concentrated hydrochloric acid, followed by a solution of concentrated sulfuric acid and finally calcium chloride(s).

Results

Effects of Chemical Processing on λ_{max}. We first confirmed the literature finding that the use of TMOS as a matrix host for PPV caused a reduction of the λ_{max} from that of pristine PPV,[1] by approximately 40−50 nm (Figure 3, spectrum 3 compared to spectrum 1). The use of MTMS as a matrix resulted in an improvement of λ_{max} compared to that in TMOS, with a smaller reduction of the λ_{max} (spectrum 2). Worth noting is the loss of fine structure on the longer wavelength side of the absorption band spectra of the PPV/sol−gel films compared to that of pristine PPV. This is indicative of a decrease in chain order in the PPV[17] accompanying a reduction of its λ_{max} in the environment of a gel glass.

Table 1. Comparison of λ_{max} of PPV/TMOS and PPV/MTMS Composite Films Prepared under Different Sol Conditions

	λ_{max} (nm)[b]	
reaction conditions[a]	PPV/TMOS	PPV/MTMS
(1) $R_w = 2$, no acid	377	421
(2) $R_w = 1$, no acid	376	418
(3) $R_w = 1$, 0.01 N HCl	380	
(4) $R_w = 2$, 0.01 N HCl		456[c]
(5) $R_w = 4$, 0.01 N HCl	383	*d*
(6) $R_w = 5$, no acid	378	421

[a] $R_w = [H_2O]/[silane]$; [HCl]/[silane] varies from 1.8×10^{-4} for $R_w = 1$, to 7.3×10^{-4} for $R_w = 4$; [MeOH]/[silane] = 3.5. All reactions were carried out at 60 °C (1 h) except for (6) where the reaction temperature was 25 °C (1 h). [b] Determined on the composite films (20−25% by weight of the converted PPV in SiO_2) after thermal conversion at 200−220 °C under vacuum (0.1 mmHg, 2 h). The starting precursor polymer PPV was converted under the same condition as its composite films with sol−gel. The λ_{max} of the converted pristine PPV is at 429 nm. [c] Cloudy. [d] Experiment not carried out due to anticipated film cloudiness.

The amounts of water to silane and of acid to silane were varied to study the influence of these parameters on the λ_{max} of the gel-trapped PPV and how the change in λ_{max} depends on the type of the matrix used. Table 1 lists λ_{max} values of the PPV composite films in the TMOS and MTMS matrixes.

In all cases examined the λ_{max} values of the PPV/TMOS composites are smaller than those of the PPV/MTMS composites. The size of the difference depends on the acidity used for the sol reactions, varying from ~40 nm under a neutral sol pH to ~70 nm under an acidic sol pH. Under an acid-catalyzed condition for the sol synthesis of MTMS, the resultant λ_{max} of the converted PPVMTMS film is actually increased compared to the starting pristine PPV (spectrum 4, Figure 3). This increase, unfortunately, is accompanied by severe film cloudiness. It is also seen that the fine structure of the absorption profile—previously noted as disappearing when λ_{max} decreases—is restored when the λ_{max} of the PPV/MTMS composite film is increased to better than that of the pristine PPV. The higher background traces of spectra 1 and 4 in Figure 3 can be attributed to loss of the incident energy due to reflection (index of PPV ~2.2), scattering and absorption by the films.

Effects of Thermal Processing on λ_{max}. Thermal conversion of the PPV precursor polymer films and the composites of the precursor polymer PPV with sol−gel transforms the unconjugated precursor polymer PPV to the conjugated PPV. The effect of variation in selected parameters of the thermal conversion process on λ_{max} was examined. The parameters examined were temperature, thermal cycling, and presence of acid during the conversion process. Temperature variations and an acidic/moist environment can induce structural modi-

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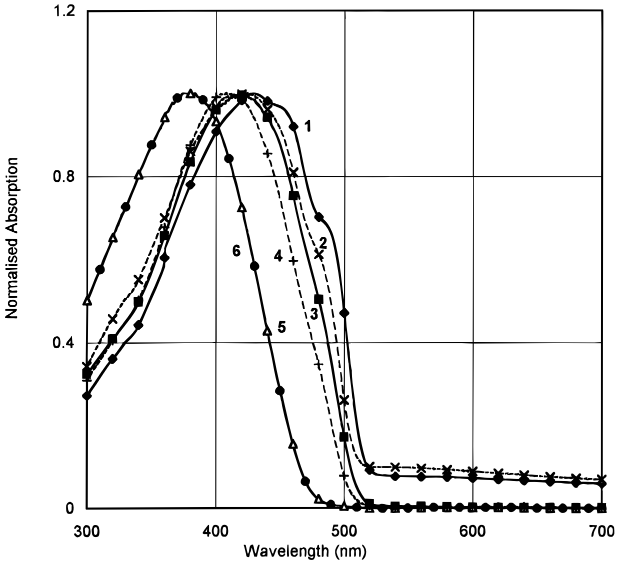

Figure 4. Dependence of UV−vis absorption spectra of pristine PPV and PPV/sol−gel composites on the temperature of conversion. 1 (solid with diamonds) = pristine PPV, 220 °C. 2 (dashed line with crosses) = pristine PPV, 150 °C. 3 (solid line with squares) = PPV/MTMS, 220 °C. 4 (dashed line with pluses) = PPV/MTMS, 150 °C. 5 (solid line with triangles) = PPV/TMOS, 220 °C. 6 (solid line with circles) = PPV/TMOS, 150 °C. All conversions were carried out under a pressure of 0.1 mmHg. The composite films were prepared according to condition (1) in Table 1 and have composition of 20−25% by weight of the converted PPV in SiO_2.

Table 2. Optical Stability[a] of Pristine PPV and PPV in TMOS and MTMS as a Function of Processing Temperatures

	λ_{max} (nm)		
heating conditions[b]	PPV/TMOS[c]	PPV/MTMS[c]	PPV
(1) 2 h, 200−220 °C (vacuum, 0.1 mmHg)	380	420	429
(2) 4 h, 200−220 °C (vacuum, 0.1 mmHg)	380	420	429
(3) 4 h, 300 °C (N_2)	380	414	429
(4) 4 h, 400 °C (N_2)	370	412	429

[a] As measured by the constancy of the λ_{max} in the UV−vis absorption spectrum. [b] Heating was carried out sequentially from (1) to (4) as shown in the table. After each heating cycle, the films were allowed to cool to room temperature under a slow stream of N_2, stored at room temperature for at least 24 h before the next heating cycle was applied. [c] Prepared according to condition (1) in Table 1. The composition is 20−25% by weight of the converted PPV in SiO_2.

fications of the matrix host,[14] and such modifications can alter the PPV/sol−gel interaction and hence affect the optical properties of the PPV. Results from this study are as follows:

1. *Temperature.* The temperature generally used for the thermal conversion of the precursor polymer PPV to PPV is ~220 °C, when the leaving group is tetrahydrothiophene with chloride as the counterion.[7,11] This is in agreement with the thermal gravimetric analysis (tga) result of pristine PPV,[1] where a temperature of 230 °C was recorded for the thermal transformation of PPV. In contrast, tga of the PPV/TMOS composite was noted as having a transition temperature as low as 140 °C.[1] A previous study has found that over the temperature range 80−300 °C, increasing the temperature of conversion of the precursor polymer PPV increased the conjugation length in the converted PPV and hence increased λ_{max}[13] (a temperature higher than 220 °C was needed due to a different and a more sluggish leaving group). These results together,[1,13] suggest that there is a relationship between the λ_{max} of a converted PPV and the temperature required for the transformation. In fact, the low temperature of conversion seen in the tga result (140 °C) is consistent with the 40 nm reduction in the λ_{max} of the PPV/TMOS composite films.[1]

We carried out the thermal conversion of both types of composite films at the two different temperatures of 150 and 220 °C in order to find out whether there is a relationship between λ_{max} and the temperature required for the complete conversion. Figure 4 shows the absorption spectra of the PPV, PPV/TMOS, and PPV/MTMS films obtained when the respective precursor polymer PPV films were heated at these two temperatures. The absorption spectra of the PPV/TMOS composite films are the same when the precursor polymer PPV/TMOS films were converted at 150 and 220 °C. Converting the precursor polymer PPV/MTMS film at 150 °C resulted in a shift of the absorption spectrum of the PPV/MTMS to lower wavelengths compared to when the heating was carried out at 220 °C. The absorption spectra of pristine PPV showed behavior similar to those of PPV in MTMS matrix. Results from Figure 4 thus lead us to conclude that there is a relationship between λ_{max} and the temperature required for its maximum conversion. A higher temperature of conversion does not lead to a longer conjugation if this length is predetermined by chain defects.

2. *Thermal Cycling.* We next examined the effect of thermal cycling on λ_{max} of the composite and pristine PPV films. Thermal cycling was performed in four-stages, with increasing temperature up to 400 °C. After each heating, the films were cooled to room temperature, spectra recorded, and the films reheated again using the next heating cycle. Table 2 shows the λ_{max} of the composites and that of pristine PPV after heating at various temperatures. A decrease in λ_{max} is observed in the two composite systems when reheated at 300 and 400 °C (7−10 nm), indicating a reduction of the conjugation length in PPV. The λ_{max} of pristine PPV remained constant throughout the temperature range tested. This is in agreement with the thermal analysis result that PPV is stable up to 550 °C in nitrogen.[15] It suggests therefore that the wavelength shifts in the PPV/sol−gel composite films when thermally cycled to 300 and 400 °C are due to changes that occurred in the sol−gel matrix and not due to the thermal degradation of the PPV.

3. *Presence of HCl(g).* Inclusion of HCl(g) during the thermal conversion of the PPV precursor polymer/sol−gel composite films leads to an increase in λ_{max} compared to when the films were heated under vacuum. This is seen in films A.1 compared to A.2, and B.1, B.2, and B.3 compared to B.5 in Table 3 (explanation for the difference in λ_{max} of B.1, B.2, and B.3 is given in the Discussion). Such a wavelength shift of the λ_{max} has also been reported for pristine PPV when its precursor polymer is thermally transformed under similar conditions.[18] The effect has been attributed to acid-assisted elimination of chemical defects in the PPV precursor polymer chains[11,12,18] (structure c → structure b, Figure 1).

Table 3. Reaction and Processing Conditions, and λ_{max} for the (Converted) PPV/Sol–Gel Composite Data Points in Figure 6

composite films[a]	λ_{max} (nm)	silane	reaction conditions (silane:MeOH:H_2O:HCl) (60 °C, 1 h)	thermal conversion[b]
A.1	415	MTMS	(1:3.5:2.5:0)	HCl(g)/N_2
A.2	407	MTMS	(1:3.5:2.5:0)	vacuum 1[c]
B.1	440[d,e]	MTMS	(1:3.5:1:1 × 10^{-2})	HCl(g)/N_2
B.2	430[d,e]	MTMS	(1:3.5:1:1 × 10^{-2})	HCl(g)/N_2
B.3	412[d]	MTMS	(1:3.5:1:1 × 10^{-2})	HCl(g)/N_2
B.4	410	MTMS	(1:3.5:1:0)	HCl(g)/N_2
B.5	395	MTMS	(1:3.5:1:1 × 10^{-2})	vacuum 1[c]
C.1	408	MTMS	(1:3.5:1:0)	HCl(g)/N_2
C.2	374	TMOS	(1:3.5:1:0)	HCl(g)N_2
C.3	415	MTMS	(1:3.5:2.5:1.7 × 10^{-4})	HCl(g)/N_2
C.4	383	TMOS	(1:3.5:2.5:1.7 × 10^{-4})	HCl(g)/N_2
C.5	412 → 396[f]	MTMS	(1:3.5:2.5:1.7 × 10^{-4})	HCl(g)/N_2
C.6	383 → 360[f]	TMOS	(1:3.5:2.5:1.7 × 10^{-4})	HCl(g)/N_2
D.1	423	MTMS	(1:3.5:2.5:2 × 10^{-4})	HCl(g)/N_2
D.2	390	TMOS	(1:3.5:2.5:2 × 10^{-4})	HCl(g)/N_2
E.1	421	MTMS	(1:3.5:2:0)	vacuum 2[c]
E.2	377	TMOS	(1:3.5:2:0)	vacuum 2[c]

[a] Composite films A.1 → E2 were prepared (20–25% by weight of the converted PPV in SiO_2) using different PPV precursor polymers A → E, which have the following λ_{max} values for the converted PPV (200–220 °C, 2 h): precursor A: λ_{max} = 415 nm (2 mm Hg), 430, 455 nm (HCl(g)/N_2); precursor B: λ_{max} = 392 nm (2 mmHg), 420 nm (HCl(g)/N_2); precursor C: λ_{max} = 406 nm (2 mmHg), 430 nm (HCl(g)/N_2); precursor D: λ_{max} = 400 nm (2 mmHg), 430 nm (HCl(g)/N_2); precursor E: λ_{max} = 429 nm (0.1 mmHg). [b] Thermal conversion of the PPV precursor polymer to the PPV in the composite films was carried out at 200–220 °C (2 h), under vacuum or in a slow stream of HCl(g)/N_2. The HCl(g) was generated by passing N_2 gas through concentrated hydrochloric acid, concentrated sulfuric acid, and finally calcium chloride(s). [c] Vacuum 1 = 10 mmHg; vacuum 2 = 0.1 mmHg. [d] Film thickness: B.1 = 0.1 μm, B.2 = 0.6 μm, B.3 = 0.8 μm. [e] Cloudy in films with thickness >1 μm. [f] The films were first heated at 200–220 °C under a stream of HCl(g)N_2/2 h, cooled to room temperature under N_2. The films were then left at room temperature for a few days before reheating under the same conditions. The λ_{max} values were shifted to lower values as indicated.

There is a significant reduction in λ_{max} of the PPV/sol–gel composite films when the films were reheated in the presence of HCl(g)/N_2 (~20 nm, films C.5 and C.6 in Table 3). No change in λ_{max} was observed if the reheating of the composite films was carried out in vacuum (compare entry (1) with entry (2) in Table 2). In the absence of a sol–gel matrix, heating of a previously converted PPV film in HCl(g) also leads to no change of the absorption spectrum.[18]

Optical Nonlinearity and the Relationship between λ_{max} and $|n_2|$ of the PPV/Sol–Gel Composites. Pristine PPV is known to have an ultrafast response time and to exhibit a power law relationship between the λ_{max} and $|n_2|$.[7] Measures were made of $|n_2|$ of the PPV in the sol–gel composites to determine whether these nonlinear properties of PPV were retained by the presence of the sol–gel hosts. Indeed they were, as Figures 5 and 6 show. The data points of the PPV/sol–gel composite films shown in Figure 6 are tabulated in Table 3, relating the λ_{max} values to the silane monomer and reaction and processing conditions.

The power law relationship between λ_{max} and $|n_2|$ seen in pristine PPV and in the gel-trapped PPV reinforces the idea that both the λ_{max} and $|n_2|$ are dependent on the same molecular property—namely, that of conjugation length. It is interesting to note that when the $|n_2|$ values of the composite films are scaled to 100% PPV, the new set of data points (triangles, Figure 6) now closely matches that of the pristine PPV (circles, Figure 6).

A λ_{max} reduction of ~40 nm is accompanied by a reduction of $|n_2|$ by a factor of ~20. The apparent discrepancy between this result and that reported on the PPV/TMOS composites[19]—that $|n_2|$ of the composite was only slightly smaller than that of pristine PPV despite a reduction of ~40 nm in λ_{max}—is addressed in the Discussion.

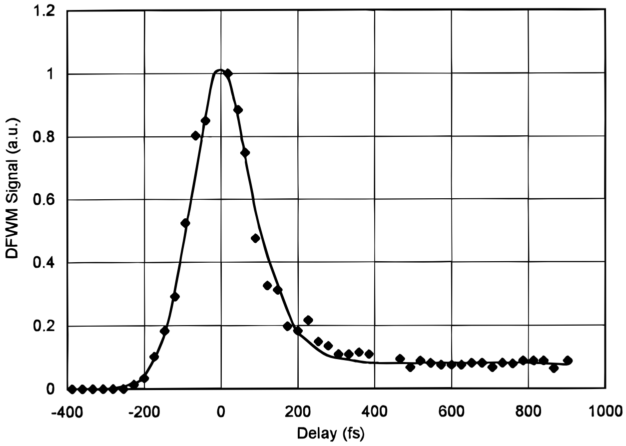

Figure 5. Time-resolved DFWM signal obtained from a PPV/sol–gel composite film. Circles denote experimental data, and the full line is the theoretical fit. The composite film is that of PPV/MTMS and was prepared according to condition (1) in Table 1. The thermal conversion of the film was carried out at 200–220 °C under a pressure of 0.1 mmHg, 6 h. Composition of the film is 20–25% by weight of the converted PPV in SiO_2.

Discussion

The difference in λ_{max} of the converted PPV (referred to as PPV) in the TMOS and MTMS gel hosts (Tables 1 and 3) indicates a difference in the PPV conjugation length. Since the same PPV precursor polymer was used as the starting material for the PPV/TMOS and PPV/MTMS composite films, the observed difference in λ_{max} of the PPV in the two gel hosts thus arises from a

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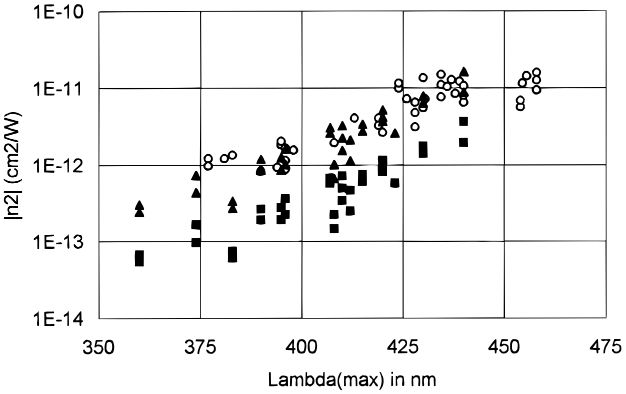


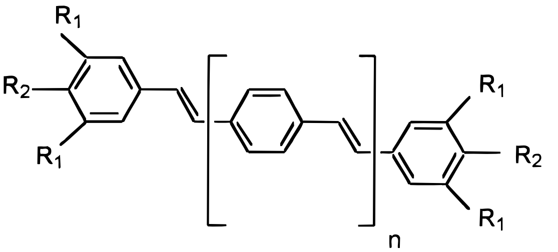
Figure 6. Relationship between λ_{max} and $|n_2|$ values of pristine PPV films[7] (circles), PPV/sol−gel composite films containing 20−25% converted PPV in SiO_2 (squares), and the composite films when scaled to 100% PPV (triangles). λ_{max} was determined by UV−vis absorption spectroscopy. $|n_2|$ was determined by degenerate four-wave mixing (DFWM) at a wavelength of 800 nm, and a pulse width of 100 fs. 100% PPV (triangles) was obtained by multiplying $|n_2|$ of the 20−25% by weight of PPV in SiO_2 composite films by a factor of 4.5. The λ_{max} and reaction and processing conditions of the composite films data points (squares) are given in Table 3. The scatter of data points at the same λ_{max} value is due to errors associated with measurements when the measurements are taken at different locations on the same film.

difference in the gel properties. The first part of this section discusses the importance of chain defects in limiting the extent of conjugation in PPV. This is then followed by a consideration of the variation of the λ_{max} and $|n_2|$ values as a function of the chemical and processing parameters. Finally, some gel properties are considered in relation to the observed difference in optical behavior of PPV in TMOS and MTMS matrixes.

Chain Length and Conjugation Length in Pristine and Gel-Trapped PPV. To provide insight into the importance of chain defects in limiting the conjugation length and the optical properties of the PPV, we report some literature values of the length of the PPV prepolymer chains and the actual effective conjugation length in the converted PPV. The use of the word "chain length" here means the number of repeat units in the chain and not the geometrical length of the chain.

Using the gel permeation chromatography technique, the average molecular weight of a typical PPV polyelectrolyte precursor polymer has been determined and found to correspond to ~750 repeat units.[20] This number of repeat units is likely to remain unchanged after the precursor polymer PPV is thermally transformed to PPV. For a PPV absorbing at 430 nm, the intramolecular coherence length is 50 Å,[17] which is ~8 repeat units (each repeat unit in PPV is ~6 Å). From these results it can be seen that the PPV polymer chain is made up of a large number of small conjugated segments punctuated by chain defects, which disrupt electron delocalization. Chain defects have been known to limit conjugation length in pristine PPV.[18] The defects can be chemical or conformational in origin.[18] The lower λ_{max} of the PPV in TMOS matrix compared to pristine PPV or to PPV in MTMS matrix is thus due to a greater number of defects in the PPV in the environment of the TMOS gel host.

It is informative to compare the λ_{max} of the (converted) PPV/sol−gel composite films with those of oligomeric PPV whose conjugation lengths are known. From this an estimate of the average conjugation length of the PPV in the sol−gel composites can be made. Sakamoto et al.[21] measured the UV−vis absorption of oligomers of PPV (**II**, R_1 = H, R_2 = CH_3)in solutions of THF and



(II) n = 0, 1,......5

found that for $n = 2$ the λ_{max} occurred at 386 nm, approximate in value to those obtained from the PPV/TMOS films. Similar results were obtained by Tian et al.[22] and Woo et al.[23] using oligomers with $n = 0, 1, ..., 5$, and R_1 = *tert*-butyl, R_2 = H. Comparison of the published λ_{max} of the oligomers with those of the PPV/sol−gel composite films in the present study, leads to the conclusion that the majority of the conjugation lengths of the PPV in TMOS matrix corresponds to ~3 repeat units (i.e., a structure similar to **II** with $n = 2$). For pristine PPV with an absorption maximum at ~430 nm, electron diffraction measurement gave an intrachain coherence of 50 Å[17] corresponding to ~8 repeat units. For oligomers of PPV with 6 repeat unit (**II**, $n = 5$) the λ_{max} is 419 nm.[22] Thus most of the conjugation lengths of the PPV in the MTMS matrix with λ_{max} of ~420−430 nm are 6−8 repeat units, which is approximately twice the length of the PPV in the TMOS matrix. The short conjugation length of the PPV of 3−8 repeat units in the gel matrixes is to be contrasted with the typical length of a PPV polymer chain, which is made up of ~750 repeat units.[20] This further highlights the critical role played by chain defects in limiting the conjugation length in PPV.

Dependence of λ_{max} and $|n_2|$ Values of the PPV/Sol−Gel Composite Films on the Reaction and Processing Parameters. Of all the parameters varied, the nature of the silane monomer exerts the greatest influence on the λ_{max} and $|n_2|$ values of the PPV in the composite films. The use of a gel matrix leads to a reduction in λ_{max} for the PPV, with the reduction being greater when TMOS is the host than when MTMS is the host (see Tables 1 and 3). The magnitude of the reduction depends on the chemical conditions of the sol−gel hosts. This includes the use of acid catalysis either during the sol synthesis or during the thermal conversion of the precursor polymer PPV to PPV. Varying the water content in the sols did not influence the λ_{max} of the composite films as much as when sol acidity was

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varied. Some variation in λ_{max} of the PPV/sol–gel composites occurred depending on the PPV precursor polymer used. As Table 3 shows, the conjugation length of the PPV in a gel host does not appear to depend on the quality of the solute PPV precursor polymer alone. It is possible that the solvent solution of the precursor polymer PPV also affect the conjugation length of the PPV in the sol–gel matrixes. Ionic salts are known to catalyze sol condensation.[14] The solution of the PPV precursor polymer contains residual salts that remain after the dialysis process. The differing amount of these salts in the PPV precursor polymer/sol solutions could thus lead to a different extent of sol condensation, resulting in gel matrixes of different structures and properties.

The reduction in λ_{max} of the PPV in the TMOS host indicates a shortening of the PPV conjugation length and a decrease in the extent of the electron delocalization. A corresponding decrease in the magnitude of $|n_2|$ follows (~20 times for a shift of ~40 nm, see Figure 6). Previous work on the nonlinear of the PPV/TMOS composite films showed, however, that its nonlinearity is only slightly smaller than that of the pristine PPV,[19] despite a difference of ~40 nm in the λ_{max} value. As noted by the authors,[19] this similarity in the nonlinearity of the PPV in the composites and of the pristine PPV could arise from the improved optical quality of the composite films, reducing the scattering loss, and hence increasing the signal strength in the nonlinear measurement and the final $|n_2|$ value. One possible explanation for the difference (in the relationship between the nonlinearity and the λ_{max}) between the previous work and this reported here is that the wavelength of 602 nm used[19] for the nonlinear measurement is much closer to the one-photon resonance of the PPV and the interplay between the influence of the one-photon and two-photon resonances on the value of the third-order nonlinearity may account for the similar values of the nonlinearity measured for the pristine PPV and the sol–gel composites with the lower λ_{max}.

A lower temperature of conversion was required for the transformation of the precursor polymer PPV to PPV when TMOS is the matrix host, compared to when MTMS is the matrix host (Figure 4). This indicates that the chain length over which the effective conjugation was to be created had been defined by chain defects prior to and/or during the thermal transformation process—that is, the matrix-induced defects formed in the PPV occurs in the precursor stage of the PPV rather than in the converted PPV. The precursor polymer PPV is unconjugated and the polymer chains are more flexible than the converted and conjugated PPV. The conformational change in response to its environment[24,25] thus occurs more readily in the precursor polymer. The importance of conformational defects in defining the conjugation length and hence the linear absorption behaviour of pristine PPV is seen in the increase of λ_{max} when the number of these defects is decreased through mechanical stretching of the PPV precursor polymer chains.[26] Another example illustrating the importance of conformational defects in determining the conjugation length of the PPV is seen in the use of HCl(g) to catalyze the thermal elimination of a previously converted pristine PPV (heated under vacuum). No change in the absorption spectrum occurred after the acid treatment, despite a decrease in the number of chemical chain defects as evident from the elemental analysis result.[18] Thus the use of HCl(g) to remove chemical defects[11,12] is effective in extending the conjugation length in the PPV only when HCl(g) is applied to the flexible precursor polymer, where conformational change is more likely.

The use of acid during the sol synthesis increased the λ_{max} and $|n_2|$ values of the composites films, when compared with those of the composite films prepared using a neutral sol. The increase is however matrix dependent. The TMOS host imposes a greater limitation on the PPV conjugation length than the MTMS host (Table 1), resulting in a considerably smaller increase in λ_{max} and $|n_2|$. The large increase in λ_{max} of the PPV/MTMS films prepared from an acid-catalyzed MTMS sol is however accompanied by film cloudiness (Tables 1 and 3). The corresponding acid-catalyzed composite films PPV/TMOS, on the other hand, remained clear irrespective of the amount of acid used in the sol synthesis. Cracks however occurred in the PPV/TMOS films as thickness approaches 1 μm. Composite films of PPV/MTMS with thickness up to 6 μm are crackfree.

The role of the acid used during the sol synthesis is to speed up the reaction kinetics of the sol.[14] The possibility that this acid-induced shift of the λ_{max} occurs through an acid-assisted thermal elimination process[11,12] (structure c → structure b, Figure 1) can be discounted as the λ_{max} of the PPV/TMOS film is at least 70 nm less than that of the PPV/MTMS films, despite a greater amount of acid being used in the TMOS sol (compare entry 4 in column 3 with entry 5 in column 2; Table 1).

Like pristine PPV,[18] the use of acid during the thermal conversion of the precursor polymer PPV/sol–gel composite films increased the λ_{max} of the converted PPV/sol–gel composite films (compare A.1 with A.2, and B.1, B.2, and B.3 with B.5, Table 3). Heating the composite films for a second time in the presence of HCl(g) (same temperature of 200–220 °C) resulted in a reduction of the λ_{max} by ~15–20 nm (films C.5 and C.6, Table 3). No observable change in the λ_{max} occurred if the double-heating of the composite films was carried out under vacuum (200–220 °C, Table 2). Heating a converted pristine PPV film for a second time in the presence of HCl(g) also resulted in no change of the absorption spectrum.[18] These results together show that the reduction in λ_{max} of the composite films C.5 and C.6 is due to a change in the gel matrix properties and not to the decomposition of the PPV by HCl(g) during the second heating. The HCl(g) used during the thermal conversion process thus not only reduced the number of chemical defects in the PPV precursor polymer and PPV chains but also interacted with the gel matrixes. These two types of interaction of HCl(g) with the composite films have opposing effects on the λ_{max} of the entrapped PPV—increased by the former and decreased by the latter. But the latter effect dominates once the conformational of the gel-trapped PPV has been substantially locked in by the initial heat treatment.[18]

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A small reduction of the composite films λ_{max} (~7−10 nm) was seen if the temperature of the second heating was raised to 300−400 °C (N_2 atmosphere). No change in the λ_{max} was observed when the same heating condition was applied to pristine PPV (Table 2). The reduction in λ_{max} of the PPV/TMOS and PPV/MTMS composite films when reheated at these higher temperatures is also due to a change to the matrix properties.

Composite films B.1, B.2, and B.3 in Table 3 were prepared using the same silane monomer, the same reaction and thermal conversion conditions, but with different spin speed during film fabrication. The λ_{max} of these films decreases with increasing film thickness, λ_{max}: B.1 = 440 nm, B.2 = 430 nm, and B.3 = 412 nm, for film thickness of 0.1, 0.6, and 0.8 μm respectively. In the conversion of these films to PPV, HCl(g) acts as a catalyst. Therefore the concentration of HCl(g) at the defect sites in the PPV precursor may affect the efficiency and extent of the conversion to PPV. Such concentration differences could arise from incomplete diffusion of HCl(g), which would require that the diffusion coefficient for HCl(g) into the films was sufficiently small (e.g., $\sim 10^{-12}$ cm^2 s^{-1} for film thickness ~1 μm, diffusion time $\sim 10^4$ s; derived using $x = (Dt)^{1/2}$, where x = film thickness, D = diffusion coefficient, and t = diffusion time).

It is known on the other hand that the spin speed used in the fabrication of polymeric thin films can cause a change in the optical and spectroscopic properties of the polymer due to shear-induced change in the polymer morphology, such as is seen in polysilicates.[14] It is therefore possible that the different λ_{max} seen in composite films B.1, B.2, and B.3 is due to a difference in shear alignment of the PPV precursor polymer (and possibly the polysilicate host). A higher spin speed (to give a thinner film) induces a greater shear alignment in the flexible PPV precursor polymer chains, causing a reduction in the number of conformational defects and hence a longer conjugation length in the converted PPV.

In either case, the extent of the conversion to PPV is more likely to be greater in the thinner films.

Gel Properties, λ_{max} and $|n_2|$ Values of the Entrapped PPV. The similarity of the correlation between the λ_{max} and $|n_2|$ values of the PPV in the pristine state and in the sol−gel composites (Figure 6, circles and squares respectively) indicates two things: first that the contribution of the nonlinear property of the gel host to the overall nonlinearity of the composite films is negligible, and second the gel host does not interfere with the nonlinear process of the PPV (which involves interaction of the electric field of the laser beam with the π-electron cloud of the PPV). The magnitude of $|n_2|$ at a particular λ_{max} value should thus depend only on the concentration of the PPV in the gel matrix. The good match between the data points of the PPV/sol−gel composites when scaled to 100% PPV and those of pristine PPV (Figure 6, triangles and circles, respectively) shows this to be the case. The gel hosts does, however, indirectly dictate the magnitude of $|n_2|$. This occurs through the gel-induced chain defects in the PPV precursor polymer discussed earlier, shortening the conjugation length in the converted PPV and reducing its nonlinear response. The gel host participates in the establishment of the NLO property of the PPV—thereafter, the NLO process is significant only for the PPV moiety.

The difference in the λ_{max} and $|n_2|$ values of the PPV in TMOS and MTMS matrix clearly point to a difference in the gel properties of the two host systems. Different gel properties have been used to explain changes in optical behavior of the entrapped molecules.[27−30] The particular gel property responsible for the change in the optical property depends on the identity of the dopant molecules.

The effects of alkyl substitution on the gel properties of TMOS have not been reported. However, the effects on the closely related TEOS have been reported. Changes in the gelling behavior and in the structures of the sol particles and of the gel matrixes of the related TEOS have been studied for when it is in the presence of its methyl- or dimethyl-substituted silane (methyltriethoxysilane, MTES, and dimethyldiethoxysilane, DMDES).[31,32] The increase in gel time or the failure to form gels in the TEOS/MTES or TEOS/DMDES systems has been explained to be due to a decrease in gel connectivity or formation of cyclic sol particles.[31,32] The shorter gel time of TMOS compared to TEOS sols has also been attributed to a difference in the structures of the sol particles—TMOS forms lightly branched linear chains which compact and form gel network more readily, whereas the slower gelling TEOS has a greater contribution from cyclic sol intermediates.[33] The gelling behavior of TMOS and MTMS sols carried out in the present work is very different. An increase in sol viscosity and formation of a clear gel was observed within 24 h in the TMOS sol (aged at 50 °C), but the MTMS sol (aged under the same condition) became turbid and did not gel over a period of a few months. The very different gelling behavior of TMOS and MTMS thus leads to the conclusion that the structure of the sol particles of TMOS and MTMS are different. It follows therefore that the resultant matrix structure in the two gels are also different from one another.[14,33]

To gain some idea whether TMOS and MTMS are fundamentally different in their gel structures, an attempt was made to determine the pore structures of the TMOS and MTMS blank gels. Results from BET surface area measurements by the N_2 adsorption method gave very low values for the surface area for both gels (<1 m^2/mg), making it impossible to compare the pore properties of the two gels. The results of Fahrenholtz and Smith on the pore structure change of TEOS as a function of methyl- and dimethyl-substituted alkoxysilane content (MTES, DMDES) is worth noting.[34] A larger pore volume and a greater surface area were obtained with increasing mole content of MTES and

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DMDES. If the MTMS gel matrix does indeed possess a larger pore volume than the TMOS gel, the implication is that the gel-trapped PPV precursor polymer can uncoil to a greater extent in the environment of the MTMS gel, reducing the number of conformational defects in the precursor polymer. The favorable increase in the λ_{max} value of the PPV/MTMS films prepared from an acid-catalyzed MTMS sol and the accompanying film cloudiness are indicative of extension of the conjugation length and of an increase in size of the scattering centers (e.g., sol particles, pore volume) in the gel matrix. The possibility that acidity within the gel matrix may assist in the elimination process and thus increases the conjugation length has previously been discussed but was considered unlikely. The control of the conjugation length, or of the frequency of chain defects, of the PPV in the gel matrix is therefore likely to be related to the physical rather than the chemical environment in the gels. The difference in the temperature requirement for the thermal conversion of the precursor polymer PPV in TMOS and MTMS matrixes, and the difference in the gel structures of TMOS and MTMS as inferred from the very different gel time, are both consistent with the idea that the matrix-induced defects in the PPV are due to conformational changes of the flexible PPV precursor polymer, imposed by the physical environment of the two matrix systems.

Compared to MTMS, the matrix of TMOS is more rigid and more polar due to an increased functionality in TMOS. The λ_{max} and $|n_2|$ values of the more rigid and more polar PPV/TMOS composite films are consistently smaller than those of the PPV/MTMS films. If matrix rigidity and polarity are the major causes for the observed difference in the optical properties of the gel-trapped PPV, increasing the matrix polarity and rigidity by increasing the water and acid contents in the sols should lead to a decrease in λ_{max} of the PPV/TMOS and PPV/MTMS films. But this was not the case; an increase in λ_{max} was observed instead (Table 1). It is thus unlikely that matrix rigidity and pore wall polarity are the determining factors for the optical behavior of the gel-trapped PPV. Acidity within the gel matrix has been discussed. The much smaller change in λ_{max} of the PPV/TMOS composite films (<7 nm, Table 1) compared to that seen in the PPV/MTMS films (~35 nm, Table 1) despite a higher acid content used in the former films, also makes this gel property an unlikely cause for differential matrix effects seen in the optical properties of the gel-trapped PPV.

Results from the present study have not conclusively proved, but do suggest, that pore structure in the TMOS and MTMS gels may be responsible for the observed difference in the λ_{max} and $|n_2|$ of the gel-trapped PPV. Further studies involving investigation of the molecular and pore structures of the TMOS and MTMS sols and gels, or measurements of the optical properties of the gel-trapped PPV in gel hosts of known differences in pore structures, should be carried out to verify the validity of the proposed explanation.

Conclusion

Poly(*p*-phenylenevinylene), PPV, has been incorporated into gel matrixes of TMOS and MTMS via its soluble precursor polymer. The nature of the sol–gel matrix exerts a dominating influence on the linear absorption and nonlinear refractive index n_2 of the entrapped PPV. Compared to the MTMS matrix, the matrix of TMOS induces in the entrapped PPV a larger reduction in value of the linear absorption maximum (λ_{max}) and a lower value of the nonlinear refractive index $|n_2|$. Such differential matrix effects are seen under all reaction and processing conditions investigated.

The difference in λ_{max} and $|n_2|$ of the PPV in the TMOS and MTMS matrixes have been explained in terms of a difference in the number of chain defects, caused by the gel matrixes. These matrix-induced chain effects were created in the PPV precursor polymer prior to and/or during the thermal transformation process. Results on the λ_{max} shifts of the composite films due to the use of acid-catalyzed sols and due to a second heating of the composite and pristine PPV films under different conditions lead to the conclusion that it is the physical rather than the chemical environment of the gel host which is responsible for the matrix-induced chain defects in the PPV. An important result is that the fundamental nonlinear process that gives rise to the nonlinear refractive index n_2 of the PPV is unchanged by the sol–gel matrixes. Rather, any changes in $|n_2|$ of the PPV when it is in the environment of a sol–gel host are due to the effect the sol–gel hosts have on the precursor polymer, from which PPV is derived.

Several factors—the observed gelling behavior of TMOS and MTMS, the optical and mechanical properties of the PPV/sol–gel composite films, the known difference in the pore structures of TEOS and its alkyl-substituted gels—all point to a relationship between the PPV conjugation length and the pore structure of its gel hosts. Further studies into the structures of the sols and gels of TMOS and MTMS are warranted to elucidate the nature of the matrix-induced changes in the optical properties of the gel-trapped PPV.

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