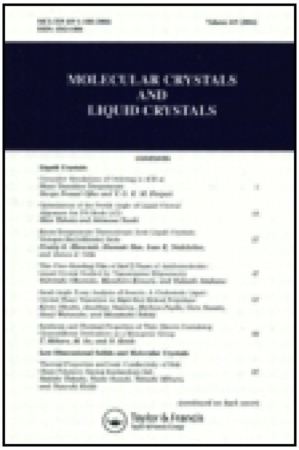


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Sol-Gel Processed Conjugated Polymers for Optical Waveguides

Kwang-Sup Lee [a] [e] , Chichang J. Wung [b] , Paras N. Prasad [b] , Jong-Chul Kim [c] , Chi Kyun Park [c] , Jung-Il Jin [c] & Hong-Ku Shim [d]

[a] Polymer Laboratory 2, Korea Research Institute of Chemical Technology, Taejon, Korea, 305-606

[b] Photonics Research Laboratory, Department of Chemistry, State University of New York, at Buffalo, Buffalo, New York, 14214

[c] Department of Chemistry, Korea University, Seoul, Korea, 136-701

[d] Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, Korea, 305-701

[e] Department of Macromolecules Science, Han Nam University, Taejon, Korea, 300-791

Version of record first published: 24 Sep 2006.

To cite this article: Kwang-Sup Lee , Chichang J. Wung , Paras N. Prasad , Jong-Chul Kim , Chi Kyun Park , Jung-Il Jin & Hong-Ku Shim (1993): Sol-Gel Processed Conjugated Polymers for Optical Waveguides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 224:1, 33-43

To link to this article: http://dx.doi.org/10.1080/10587259308032476

Mol. Cryst. Liq. Cryst., 1993, Vol. 224, pp. 33–43
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Sol-Gel Processed Conjugated Polymers for Optical Waveguides

KWANG-SUP LEE†‡
Polymer Laboratory 2, Korea Research Institute of Chemical Technology, Taejon, Korea 305-606

and

CHICHANG J. WUNG and PARAS N. PRASAD
Photonics Research Laboratory, Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

and

JONG-CHUL KIM, CHI KYUN PARK and JUNG-IL JIN
Department of Chemistry, Korea University, Seoul, Korea 136-701

and

HONG-KU SHIM
Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon, Korea 305-701

(Received January 29, 1992; in final form February 17, 1992)

Novel sol-gel processed poly(1,4-phenylene vinylene) (PPV) and poly(2,5-disubstituted-1,4-phenylene vinylene)/silica composites were prepared by a soluble precursor technique. The two PPV derivatives included in this study were poly(2-bromo-5-methoxy-1,4-phenylene vinylene) and poly(2-butoxy-5-methoxy-1,4-phenylene vinylene). The spectral characteristics of these materials have been investigated using UV-visible and FT-IR spectroscopy. The densification process was studied by differential scanning calorimetry and thermal gravimetric analyzer. The third-order nonlinear susceptibility $\chi^{(3)}$ have been investigated for the polymers themselves and their sol-gel composites at 602nm using degenerate four-wave mixing (DFWM) technique. Relatively large $\chi^{(3)}$ values ($4 \times 10^{-10} \sim 1 \times 10^{-9}$ esu) with a subpicosecond response were observed.

Keywords: sol-gel processing, derivatized PPV, precursor technique, densification, optical nonlinearity

---

†To whom all correspondence should be addressed.

‡Present address: Department of Macromolecules Science, Han Nam University, Taejon, Korea 300-791.

INTRODUCTION

Conjugated polymers having extensive π-electron delocalization have been considered as best candidates for third-order nonlinear optical materials because of the large π-electron contribution to the optical nonlinearity.[1-3] Most conjugated polymers, however, have generally not been found to good photonic media due to the high optical losses. In contrast, inorganic glasses like silica or vanadium oxide are excellent photonic media and can be made into high quality fibers and films with extremely low optical losses. Therefore, if conjugated polymers and inorganic glasses can be mixed homogeneously, this could be one of the better ways for obtaining materials with large optical nonlinearity and low optical losses.

The first conjugated polymer/silica composite made from precursor technique was developed by our group.[4] In order to obtain the composites having high nonlinear coefficient $\chi^{(3)}$ as well as the high optical quality, poly(1,4-phenylene vinylene) (PPV) and silica alkoxide were mixed successfully without any phase separation or precipitation at certain optimized conditions. This unusual composite by combining of organic and inorganic compound has shown a great advantage in the optical waveguiding and other photonic applications.[5,6] Since PPV and its two derivatives—poly(2-bromo-5-methoxy-1,4-phenylene vinylene) (BrMPPV) and poly(2-butoxy-5-methoxy-1,4-phenylene vinylene) (BuMPPV)—can be synthesized by the precursor technique,[7-9] preparation of the composites composed of an inorganic oxide and the π-conjugated organic polymers through precursor technique was possible. It should be noted that BrMPPV has two opposite substituents, i.e., one electron-withdrawing and the other electron-donating, whereas BuMPPV has two electron-donating substituents. Examination of the dependence of $\chi^{(3)}$ values on the nature of substituents is our major interest in this investigation. The preparation of these composites by sol-gel process, characterization and optical properties of these composites, and the $\chi^{(3)}$ evaluations by degenerate four-wave mixing (DFWM) technique will be reported in this paper.

EXPERIMENTAL

1. Synthesis of PPV, BrMPPV and BuMPPV

PPV, BrMPPV and BuMPPV were prepared by the precursor route as reported elsewhere.[7-9]

2. Sol-Gel Process

Since all of the composites were prepared by the same method, only the preparation of BrMPPV/silica composite is described in detail to present the representative experimental procedure: Equal amount by volumes of tetramethyl orthosilicate (TMOS), methanol and the sulfonium polyelectrolyte polymer precursor are mixed with stirring and added proper amount of 0.1N of HCl to adjust the pH = 3. For sol-formation, this mixture was heated at 60°C for about 30 min, cooled down to room temperature and diluted to be 10 times by volumes of TMOS in solution by addition of methanol. Consequently, equal volumes of above mixture and BrMPPV precursor solution (5% by weight) are mixed. After storing at room temperature for 24 hrs, the final BrMPPV precursor/silica sol-gel solution is casted on a suitable substrate (silica glass or quartz plate) using spin coater. The resulting film is then thermally treated with the temperature increased at a rate of 20°C/min in a vacuum oven ($\sim 10^{-2}$ torr) and held 210°C for 20 hrs. As a result, the BrMPPV precursor is converted into BrMPPV and an optical quality composite film is formed. The only difference in preparation of BuMPPV/silica sol-gel composite is that tetrahydrofuran was used as a solvent instead of methanol that was used in BrMPPV systems.

3. Measurements

IR spectra were obtained by an infra-red (Alpha Centauri FT-IR) spectrometer. In order to study the correlation between the third-order nonlinear susceptibilities $\chi^{(3)}$ and the band gaps for the polymers and composites, the UV-visible spectra for the polymers and silica sol-gel composites were obtained a Shimadzu spectrophotometer (model 3101 PC). The band gap energies were determined from the onsets of the bands in spectra. A prism coupler (Metricon PC-2000) was employed for the refractive indecies and film thickness measurements. Characterization of the thermal elimination reaction of the polymers and composites was conducted on a DuPont 9900 thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC). These measurements were performed at a heating rate of 20°C/min under a nitrogen atmosphere. The third-order optical nonlinearities of samples were measured by the DFWM technique using 400 femtosecond pulses at 602nm. The laser system consists of a Nd-YAG laser (Spectra Physics, model 3800 mode-locked) with a fiber optic pulse compressor (Spectra Physics, model 3690), a synchronously pumped dye laser (Spectra Physics, model 375B), and a three-stage amplifier (Qunta-Ray PDA-1) pumped at 30Hz with a Qunta-Ray DCR Nd-YAG laser. The beams in the forward wave geometry for DFWM were focused onto the film. The conjugate signal was detected by a photodiode and processed by a boxcar averager (EG&G, model 4200). A detailed experimental setup and procedure can be found in elsewhere.[10]

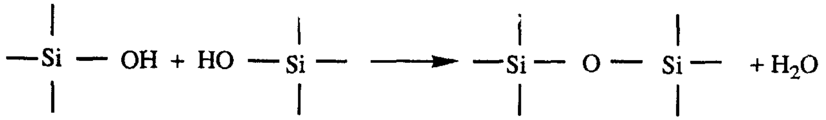
RESULTS AND DISCUSSION

1. Preparation and Characterization of the Composites

In general, the sol-gel composites can be made either by cogelation of monomers or oligomers with metal alkoxide or by their impregnation in porous gels. Nevertheless, not all the polymers can form sol-gel composite by cogelation or impregnation with alkoxide. We utilized a new method for preparing optical quality composites by mixing the precursor polymers with the silicate in common solvent and a conversion of the mixture to final polymer/silica composite by thermal treatment.

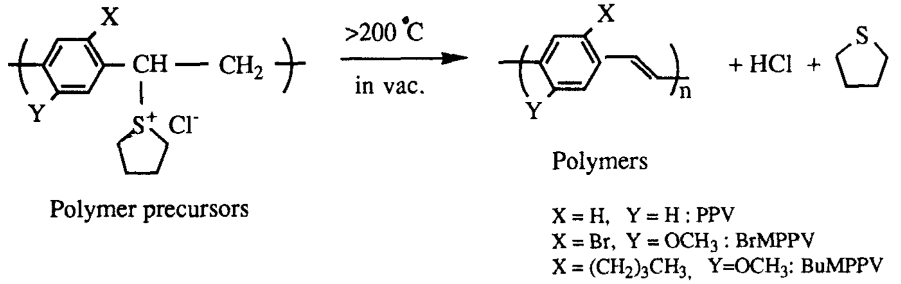
For the preparation of polymer/silica composites using sol-gel technique, several factors such as (i) the type of alkoxide used, (ii) the proper control of pH value, (iii) the amount of water in the system, (iv) the type of solvent used in precursor polymer, (v) a reaction and consolidating temperature, etc. should be considered. Due to the different properties of the polymer precursors and the alkoxides, the preparation of these composites is greatly affected by these factors and becomes more complicated than that for a pure sol-gel system. An improper control of any of preparation parameters can easily lead to phase separation or precipitation.

Essentially, four stages are involved in the formation of pure sol-gel system from the monomer TMOS: hydrolysis and polymerization of monomer to form small particles, increasing in the size of the particles, and then coalescing of these particles in the form three-dimensional networks. The polymerization reaction can be pictured as the condensation between silanol groups, i.e.,



$$-\underset{|}{\overset{|}{Si}}-OH + HO-\underset{|}{\overset{|}{Si}}- \longrightarrow -\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- + H_2O \qquad (1)$$

In the present approach, the precursors of BrMPPV and BuMPPV were introduced into the sol-gel system forming a homogenous mixture and then a thermal reaction above 200°C in a vacuum was followed converting the precursor polymers into the final polyconjugated polymers uniformly dispersed in the silicate matrix. This process involves the reaction (1) and the following elimination reaction (2).



(2)

Since the glass formed in the sol-gel process of TMOS is porous, the polymer is believed to be embedded within the inorganic oxide glass. It was reported earlier that the pore radii in the pure silica obtained via sol-gel process are much smaller (1,5-10 nm) than the near UV or visible radiation wavelength and, thus, pure sol-gel glass was transparent.[11] The present BrMPPV- and BuMPPV-silica composite films was not only homogenously transparent but also exhibited a smooth surface according to an initial study on interference patterns observed by the multiple beam interferometry. However, we do not have any evidence for molecularly mixing. Using the sol-gel technique, we can prepare polymer composites in which two components are mixed in large compositions up to 50% by weight without any phase separation.

Figure 1(a), (b), (c) and (d) show UV-visible spectra of BrMPPV precursor, BrMPPV/sol-gel precursor, polymer BrMPPV, and BrMPPV/sol-gel composite,

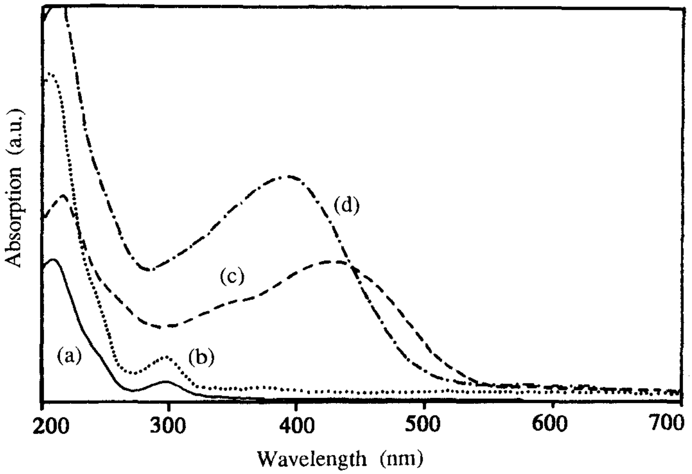


FIGURE 1 The UV-visible absorption spectra of (a) BrMPPV precursor, (b) BrMPPV/sol-gel precursor, (c) BrMPPV, and (d) BrMPPV/sol-gel composite.

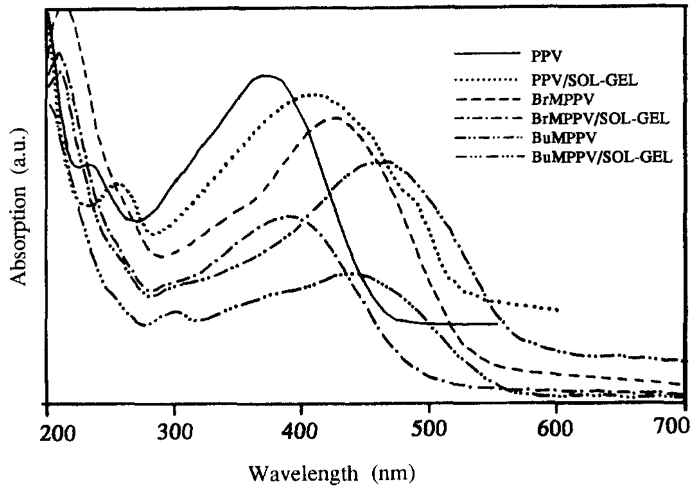


FIGURE 2 The UV-visible absorption spectra of thermally treated PPV, BrMPPV and BuMPPV, and their sol-gel composites.

respectively. The precursor polymer films showed very weak absorptions in the visible range indicating that they are very stable at room temperature and contain little conjugated units. Their UV spectra displayed three absorption bands with their absorption maximum at 210 (phenyl), 265 (sulfonium) and 298 nm (trans-stilbene structure). After the films were thermally treated, their spectra showed broad, continuous absorptions indicative of highly conjugated systems. The onset of the absorption which yields the optical band gap is 525 nm (2.37 eV) for BrMPPV, and that of the BrMPPV/sol-gel composite showed about 10 nm blue shift (510 nm). The absorption maximum for BrMPPV is 441 nm compared to 395 nm for the BrMPPV/sol-gel composite. As shown in Figure 2, such UV absorption pattern is also found between BuMPPV and BuMPPV/sol-gel composite; when the BuMPPV precursor polymer is mixed with silica glass and converted into BuMPPV/sol-gel composite, the absorption maximum shifts from 460 nm to 432 nm in the fully eliminated BuMPPV film. Namely, composite shows blue shift. This trend is similar to our previous result for PPV and PPV/sol-gel composite.[4] It is thus believed that polymer chains are indeed incorporated within the bulk of the glass and the effective conjugation length is shorter than in the pure polymers.

The IR transmission spectra of the silica sol-gel, BrMPPV, BrMPPV/sol-gel and, BuMPPV/sol-gel composite are shown in Figures 3(a), (b), (c), and (d), respectively. In the spectrum of silica sol-gel, three characteristic absorption bands of amorphous silica are observed between 400 and 1300 cm^{-1}. The strong band at 1080 cm^{-1} corresponds to the stretching vibration of the Si—O bond.[12] The one at 455 cm^{-1} is attributed to the vibrational modes of deformation of the O—Si—O and Si—O—Si bonds.[12,13] The band positioned at 820 cm^{-1} corresponds to the ring structure of the tetrahedral (SiO_4).[14] There are three other bands at 3500, 1620, and 950 cm^{-1}. The bands at 3500 and 1620 cm^{-1} correspond to the stretching and deformation modes for hydroxyl groups and water molecules.[15] The last absorption band at 950 cm^{-1} is generally attributed to the vibration of the Si—O bonds for the glasses containing non-bridging oxygens[16] or to the stretching mode of Si—O(OH) bonds.[17] This band disappears at higher temperature.[18]

In the case of fully converted BrMPPV, the trans-vinylene CH out-of-plane bending absorption band at 963 cm^{-1} and trans-vinylene CH stretching at 3054 cm^{-1} were observed in the IR spectrum (Figure 3(b)).[19] No absorbance was observed near 630 cm^{-1} where cis-CH bending mode would be expected. Finally, the IR transmission spectrum of BrMPPV/sol-gel (Figure 3(c)) has the features of those from both silica sol-gel and BrMPPV. This implies that the elimination reaction of BrMPPV was not hampered in the composite during the sol-gel process. Very similar spectral features in BuMPPV/sol-gel composite was also observed (Figure 3(d)).

2. Thermal Analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), were conducted to examine thermal behavior of the composites. Figure 4 shows the DSC curve of BrMPPV precursor, silica sol-gel, and BrMPPV precursor-silica gel which had been dried at room temperature in a desiccator for 3 months. In the case of BrMPPV precursor (Figure 4(a)), two endortherms appear at about 120°C and 150°C of which the former may mainly be related to the loss of residual volatiles and the latter to the elimination HCl and tetrahydrothiophene as shown in Equation 2. For the silica sol-gel (Figure 4(b)), we observe a very broad endothermic peak in the range of 50-210°C, for the loss of residual volatiles and dehydration reaction (Equation 1) are responsible. Figure 4(c) shows a broad doublet shaped endotherm between 50°C and 130°C and the peak maximum positions are slightly lower than those of BrMPPV precursor given in Figure 4(a). The shift of peak positions strongly implies the presence of interaction between two components (BrMPPV precursor and silica sol-gel) in the system.

The TGA results are consistent with the DSC data. Figure 5(a), (b), and (c)

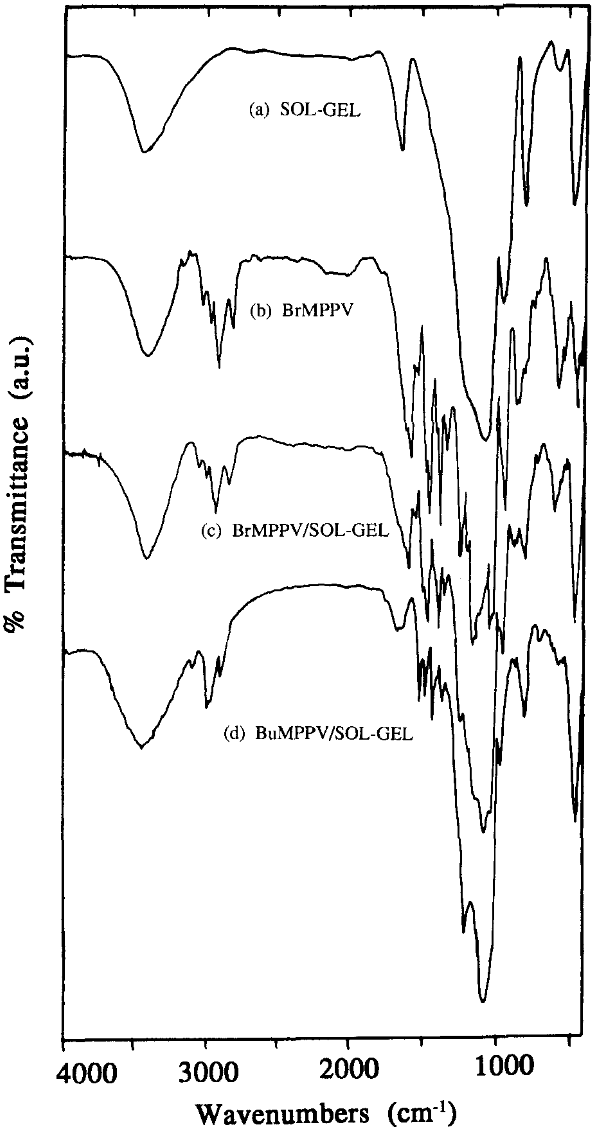


FIGURE 3 The IR transmission spectra of (a) sol-gel, (b) BrMPPV, (c) BrMPPV/sol-gel composite, and (d) BuMPPV/sol-gel composite.

show the TGA curves of BrMPPV precursor, the silica sol-gel and the BrMPPV precursor/silica sol-gel composite, respectively. According to Figure 5(a) the maximum rate of weight loss for BrMPPV precursor occurred around 130°C and 450°C. The first loss corresponds to the liberation of volatiles and thermolyzed products, HCl and tetrahydrothiophene. The second weight loss was due to degradation of BrMPPV to a black carbonaceous film. However, in the case of BrMPPV precursor/sol-gel silica composite, the above-mentioned two weight loss occurred at lower temperature (Figure 5(c)) and become broader than in pure polymer pre-

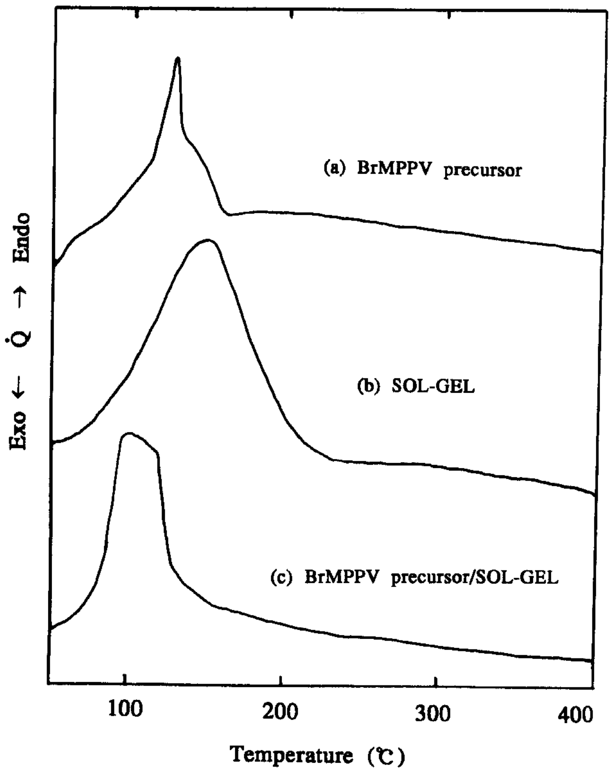


FIGURE 4 DSC curves for (a) BrMPPV precursor, (b) sol-gel, and (c) BrMPPV precursor/sol-gel composite.

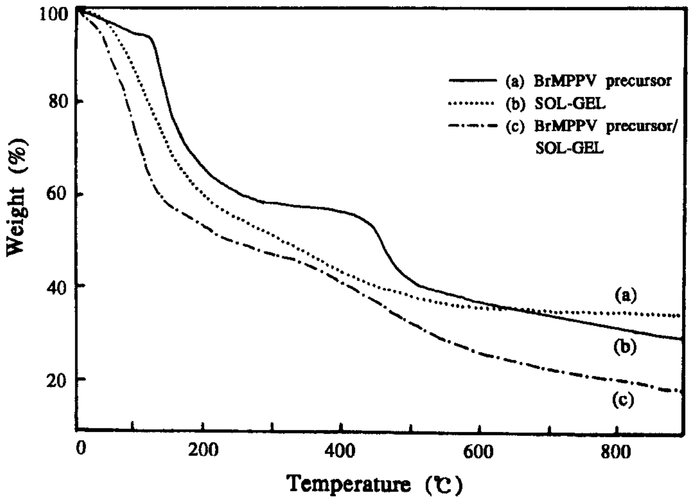


FIGURE 5 TGA curves of (a) BrMPPV precursor, (b) the sol-gel, and (c) BrMPPV precursor/sol-gel composite.

cursor. This could be due to the polymer which is trapped in the sol-gel matrix, and causing the occurrence of the elimination reaction over the broader range of temperature. Both DSC and TGA studies suggest that the BrMPPV precursor/silica sol-gel composite tends to accelerate the elimination and condensation reaction when compared with each component. Furthermore, the repeated scan showed that the process associated with the endothermic reaction was irreversible and no glass transition was detected for the final compositions. Thermal properties showed similar characteristics for BuMPPV/silica composite.

3. $\chi^{(3)}$ Evaluations by DFWM Technique

The $\chi^{(3)}$ value was evaluated by comparing the strength of the conjugate signal at low incident photon flux with that of CS_2 according to the following Equation (3):

$$\frac{\chi_s^{(3)}}{\chi_c^{(3)}} = \left(\frac{n_s}{n_c}\right)^2 \frac{l_c}{l_s} \left(\frac{I_s}{I_c}\right)^{1/2} \times \frac{\alpha \cdot l_s}{\exp(-\alpha \cdot l_s/2)[1 - \exp(-\alpha \cdot l_s)]} \qquad (3)$$

Where n is refractive index, l the interaction length, and α the linear absorption coefficient. The subscript c and s refer to CS_2 and the sample, respectively. The CS_2 sample is nonabsorbing at the wavelength (602 nm) used in our experiments. The value of $\chi^{(3)} = 6.8 \times 10^{-13}$ esu was used as the reference value for CS_2.[20] In all samples the absorption term in Equation (3) is ignored because the sample is nearly nonabsorbing at the wavelength of 602 nm (see Figure 2). Figure 6 represents a typical subpicosecond DFWM response of BrMPPV. The symmetrical signal shape indicates that this compound has nonresonant pattern. All investigated samples showed similar shapes with BrMPPV. The material forms, band gap energies and the third-order nonlinear susceptibilities $\chi^{(3)}$ are presented in Table I. The measured effective $\chi^{(3)}$ values for BrMPPV and BuMPPV are 9×10^{-10} and $2 \times$

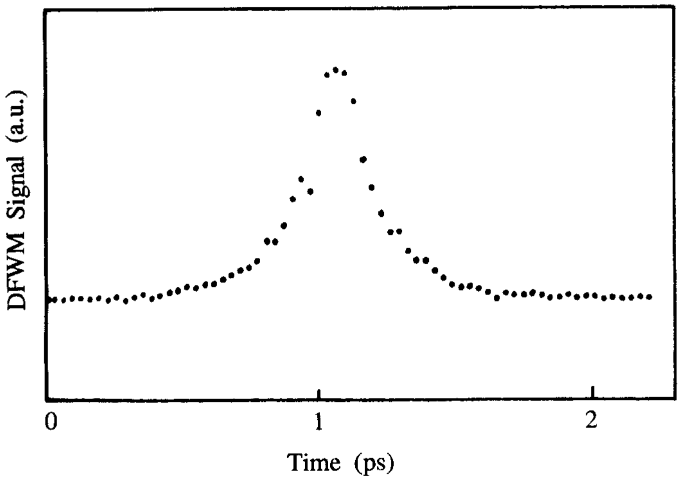


FIGURE 6 DFWM signal profile for BuMPPV obtained by delaying the forward beam (400 femtosecond pulses, 602 nm).

TABLE I

Band gap energies and the third-order nonlinear coefficients $\chi^{(3)}$ of PPV, BrMPPV, BuMPPV and their silica composites

Materials	Band gaps (eV)	$\chi^{(3)}$ (esu)
PPV film	2.46	4×10^{-10}
PPV/sol-gel composite	2.70	3×10^{-10}
BrMPPV film	2.37	9×10^{-10}
BrMPPV/sol-gel composite	2.52	8×10^{-10}
BuMPPPV film	2.19	2×10^{-9}
BuMPPV/sol-gel composite	2.23	1×10^{-9}

10^{-9} esu, respectively. These values are significantly enhanced when compared with the value of 4×10^{-10} reported by Singh *et al.* for PPV at 602 nm.[21] The $\chi^{(3)}$ values for the polymer/sol-gel composites show slightly smaller values than those for the corresponding pure polymers. This can be attributed to two reasons: (1) the onsets of the absorption spectra in the composites are shifted to shorter wavelength indicating a reduction in the effective configuration or conjugation length, (2) and the number density of the polymeric units responsible for $\chi^{(3)}$ is reduced in the composite. Since silica glass has relatively low $\chi^{(3)}$ value and behaves as a solid diluent in the polymer/silica composites.

Organic polymers with extended π-conjugation have a relatively large non-resonant third-order susceptibility $\chi^{(3)}$ due to their π-electron delocalization.[1] The results of our measurement of $\chi^{(3)}$ values reflect that there is a significant contribution for $\chi^{(3)}$ from the electron donor substituents at the 2, 5 positions of PPV phenylene rings. The butoxy and methoxy electron donor groups at 2, 5 positions enhance the π-electron density in the conjugated polymer BuMPPV. In fact, BuMPPV film exhibited maximum absorption at 460 nm, which is much longer wave length when compared with PPV's maximum absorption at about 410 nm. In contrast, the maximum absorption in the visible region occurs at 441 nm, for BrMPPV indicating a slight bathochromic shift when compared with absorption position of PPV. It is certain that the two substituents on the phenylene rings electronically influence the absorption character of the polymer opposite direction. Thus, the energy band gap is smallest and the effective $\chi^{(3)}$ value is the largest for BuMPPV.

CONCLUSION

Composite materials of PPV, BrMPPV and BuMPPV with silica were prepared using sol-gel processing technique. The blue shift in the UV-visible spectra and reaction endothermic appearance at lower temperature in the case of composites provide strong evidence for the interaction between the polymers and the silica components. Nonlinear optical coefficients $\chi^{(3)}$ of the pure polymers and the polymer/sol-gel silica composites had been determined by DFWM technique. The trend of increasing $\chi^{(3)}$ values for BrMPPV and BuMPPV reflects the contribution derived from the substitution of the electron donating groups at 2,5-position of

PPV. The $\chi^{(3)}$ values for the polymer/sol-gel silica composites are slightly lower than those for the corresponding pure polymers. This may originate from the shortening of effective conjugation length due to tight trapping in silica matrix, and the lower number of density of the polymeric units. Compared to the pure polymers, sol-gel processed polymer/silica films are of significantly improved optical quality.

Acknowledgment

This research was supported by the Air Force Office of Scientific Research through contract number F-4920-91-C0053. K.-S. Lee, J.-I. Jin and H.-K. Shim would like to express their appreciation to the Korea Science and Engineering Foundation (KOSEF) for the financial suport.

References

1. P. N. Prasad and D. J. Williams, "Introduction to Nonlinear Optical Effects in Molecules and Polymers," Wiley, New York, 1991.
2. K.-S. Lee, M. Samoc and P. N. Prasad, *Comprehensive Polymer Science*, Pergamon Press, in press.
3. K.-S. Lee and M. Samoc, *Polymer Commun.*, **32**, 361 (1991).
4. C. J. Wung, Y. Pang, P. N. Prasad and F. E. Karasz, *Polymer*, **32**, 605 (1991).
5. G. S. He, C. J. Wung, G. Xu and P. N. Prasad, *Applied Optics*, in press.
6. Y. Pang, M. Samoc and P. N. Prasad, *J. Chem. Phys.*, **94**, 5282 (1991).
7. D. R. Gagnon, J. D. Capistran, F. E. Karasz, R. W. Lenz and S. Antoun, *Polymer*, **28**, 567 (1987).
8. J.-I. Jin, C. K. Park, H. K. Shim, and Y. W. Park, *J. Chem. Soc., Chem Commun.*, **1989**, 1205.
9. J.-I. Jin, J.-C. Kim and H. K. Shim, *Macromolecules*, submitted for publication.
10. S. K. Ghosal, P. Chopra, B. P. Singh, J. Swiatkiewicz and P. N. Prasad, *J. Chem. Phys.*, **90**, 5078 (1989).
11. M. Yamane, S. Aso and T. Sakaino, *J. Mater. Sci.*, **13**, 865 (1978).
12. E. R. Lippencott, A. Van Valkenburg, C. E. Weir and E. N. Bunting, *J. Res. Nat. Bur. Stand.*, **61**, 61 (1958).
13. R. Hanna, *J. Am. Ceram. Soc.*, **48**, 595 (1965).
14. K. Kamiya and S. Sakka, *Res. Rep. Fac. Eng. Mie Univ.*, **2**, 87 (1977).
15. J. Fripiat and A. Jelli, Congre. Inter. du verre, Bruxelles, 1968, p. 14.
16. S. P. Mukherjee, *J. Non-Crystalline Solids*, **42**, 477 (1980).
17. J. Zarzycki and F. Naudin, *J. Chim. Phys.*, **58**, 830 (1961).
18. M. Decottignies, J. Phalippou and J. Zarzycki, *J. Mat. Sci.*, **13**, 2605 (1978).
19. S. Tokito, T. Momii, H. Murata, T. Tsutsui and S. Saito, *Polymer*, **31**, 1137 (1990).
20. N. P. Xuan, J. L. Ferrier, J. Gazengel and G. Rivorie, *Opt. Commun.*, **51**, 433 (1984).
21. B. P. Singh, P. N. Prasad and F. E. Karasz, *Polymer*, **29**, 1940 (1988).