Poly(*p*-phenylene vinylene)–silica composite: a novel sol–gel processed non-linear optical material for optical waveguides

C. J. Wung, Y. Pang and P. N. Prasad*
Photonics Research Laboratory, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA

and F. E. Karasz*
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

(Received 28 February 1990; revised 16 April 1990; accepted 19 April 1990)

We report here the first case (to our knowledge) of a compatible blend of an inorganic polymer, silica glass, and a π-conjugated non-linear optical polymer, poly(*p*-phenylene vinylene), homogeneously miscible over wide composition ranges. This composite material was prepared by combining sol–gel processing techniques applicable to the silica glass with those used for the synthesis of the organic polymer from a water/alcohol-soluble sulphonium salt precursor. In this preparation the organic polymer precursor and the inorganic sol were mixed in a common solvent and converted to the final composite material. The thermal conversion of the precursor polymer released HCl, which catalysed the gelation of the inorganic sol. The resulting composite material has been characterized by infra-red and ultra-violet/visible spectral analysis and thermogravimetric and differential scanning calorimetric analysis. The material can be cast into various forms. Thin films cast by the doctor-blading technique exhibit good optical quality and show promise for application as optical waveguides.

(Keywords: sol–gel; hybrid; poly(*p*-phenylene vinylene); tetramethyl orthosilicate)

INTRODUCTION

The sol–gel process for making inorganic glasses, thin films and porous solids has been widely studied for the past two decades[1,2]. This process possesses considerable advantages compared to melt fusion techniques. Since it involves the use of low-viscosity solutions of the reagents, compositional uniformity can be easily achieved at a molecular level. For example, amorphous silica doped with organic molecules, if the latter can be dissolved in the initial solutions, can be made with a high degree of homogeneity.

Mackenzie and coworkers[3] have prepared silica gel–poly(methyl methacrylate) composites by the impregnation of porous gels with organic monomer and polymerization *in situ*. Wilkes[4] and coworkers have reported the incorporation of poly(tetramethylene oxide)-based polyurethane oligomers with multiple triethoxysilane groups into a sol–gel process. In the present work we report the preparation of high-quality waveguide films consisting of silica glass containing relatively high proportions of poly(*p*-phenylene vinylene) (PPV), a conjugated organic polymer. Conjugated organic polymers constitute an important class of optical materials because they have shown large, non-resonant (non-absorptive), optical non-linearity with fast response time in the subpicosecond regime[5]. In common with most organic polymers, however, in their pure state these materials have generally not been found to form good photonic media because of typically high optical losses. Conversely, many inorganic glasses, including silica, form excellent photonic media because of the extremely low optical losses achievable. A major problem with such glasses is that their third-order non-linear optical coefficient $\chi^{(3)}$, fundamental to all optical switching, is extremely low. There thus exists a need for a material combining high non-linear optical coefficients with high optical quality. In this study PPV has been chosen as a dopant since it is known to possess a relatively high third-order non-linear optical coefficient $\chi^{(3)}$ with femtosecond response time[6]. The insolubility and infusibility of PPV makes processing and formation of optical device structures based on this polymer difficult. Even though a method has been developed[7] by which a soluble polymer precursor of PPV can be cast into various forms and subsequently converted by thermal or chemical means to yield high-molecular-weight PPV, the relatively low optical quality of the resultant PPV films presents an obstacle to potential applications in non-linear optics.

This report describes a process for preparing a composite material of PPV and silica employing the sol–gel technique, which confers some processability and yields materials of high optical quality. In this process, a water/alcohol-soluble PPV precursor was mixed with tetramethyl orthosilicate (TMOS, silicon tetramethoxide) to form a PPV precursor/sol solution from which films have been cast. After gelation and TMOS polymerization is completed, the film was heated to convert the dispersed PPV precursor to PPV. It has proved to be advantageous that the small amount of HCl released

---

* To either of whom correspondence should be addressed

0032-3861/91/040605-04

during the mixing of the PPV precursor (by spontaneous conversion to PPV) catalyses the sol formation from TMOS.

A combination of thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.), and ultra-violet/visible and infra-red (u.v.-vis., i.r.) spectroscopy have been used to characterize this new composite material.

EXPERIMENTAL

The PPV/sol–gel composite was produced by mixing the sulphonium polyelectrolyte polymer precursor for PPV[7] and tetramethyl orthosilicate (TMOS) (Aldrich) in a common solvent. Equal volumes of a 5% aqueous solution of the filtered PPV precursor, methanol and TMOS were mixed with stirring and constant agitation at 60°C for about 30 min until a sol formed. After cooling to ambient temperature, additional methanol was added until the total volume was 10 times that of the TMOS in solution. The resulting solution was kept in a 60°C water bath for a further 30 min and cooled to room temperature, forming solution I. Equal volumes of solution I and the PPV precursor solution (5% by weight) were mixed to form solution II. After storing at room temperature for 24 h, solution II was used to cast films on a suitable substrate (silicate glass or quartz) using either spin-coating or more simply by doctor-blading. The resulting films were consolidated and the PPV precursor was converted into PPV in a vacuum oven, where it was heated at a rate of 8°C $\min^{-1}$ and held at 220°C for upwards of 2 h. Characterization of the thermal elimination reaction of the composite was monitored by using t.g.a. (Perkin–Elmer TGS-2) and d.s.c. (Perkin–Elmmer DSC-2). These measurements were made at 20°C $\min^{-1}$ and under a nitrogen atmosphere. Further characterization of the films was obtained by u.v.-vis. (Shomadzu UV-260) and i.r. (The Alpha Centauri FT-IR) spectroscopy.

Further details are presented elsewhere[8].

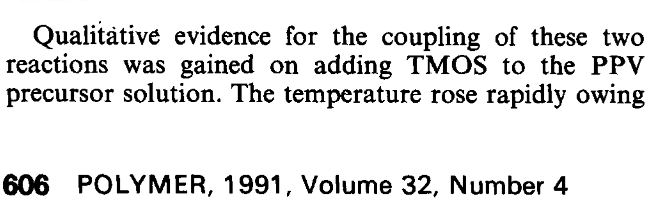
RESULTS AND DISCUSSION

Two separate reactions occur in the overall process: (a) a spontaneous polymerization of TMOS to form a silica sol–gel and (b) a thermolysis of the PPV precursor yielding PPV. The sol–gel process involves the following reactions:

$$n\,Si(OCH_3)_4 + 4n\,H_2O \overset{H^+}{\rightarrow} n\,Si(OH)_4 + 4n\,CH_3OH$$
$$n\,Si(OH)_4 \rightarrow (SiO_2)_n + 2n\,H_2O$$

Scheme 1

The PPV precursor undergoes the following ElcB elimination reaction[7] upon heating:



Scheme 2

Qualitative evidence for the coupling of these two reactions was gained on adding TMOS to the PPV precursor solution. The temperature rose rapidly owing to the polymerization of TMOS, although no catalyst was added to the system. It may be observed (*Scheme 2*) that one of the products of the elimination reaction is HCl, which serves as a catalyst for polymerization of TMOS. Although the optimum temperature for the PPV precursor thermolysis is higher, it is known that the reaction also occurs at room temperature to some extent. Measurement of the pH (value 4) indicated that the trace amount of HCl in the PPV precursor solution catalysed the sol formation process in the TMOS. This mild acidic condition also delays gelation, which was advantageous because the fluidity is crucial for high optical quality film casting.

The glass formed in the sol–gel process is porous, though the average pore diameters are typically much smaller (1.5–10 nm)[9] than the near-u.v. or visible radiation wavelength. The present composite also showed low scattering, from which we infer that the PPV is dispersed in the silica matrix in domains that must be of the order of 50 nm or less. In contrast to SiO_2 films produced in the normal sol–gel process, the PPV/sol–gel derived films described here can be formed in the thickness range from 0.5 μm up to tens of micrometres without cracking. The films exhibit a mechanically strong surface, and very good optical quality. Preliminary study on waveguiding through these films is encouraging. A propagation distance of $\geqslant 2$ cm has readily been accomplished at a wavelength of 1.06 μm. The waveguide losses for TE modes at 1.06 μm are at least 10 times less in the composite film compared to that in the pure PPV film.

In *Figure 1*, curves a, b, c, d and e show respectively the u.v.-vis. spectra of the undoped sol–gel, precursor PPV, heat-treated PPV, precursor PPV/sol–gel composite and the thermally treated PPV/sol–gel films after heating to 220°C. The precursor PPV and precursor PPV/sol–gel spectra are almost identical except for a 10 nm blue shift in the maxima in the latter (curves b and d). When the polymer is mixed with the silica glass and converted into PPV, the absorption maximum shifts to 370 nm, compared with the absorption maximum at 410 nm in the case of fully eliminated PPV films (spectra c and e). This may indicate that the tight trapping of PPV chains in the silica matrix changes the configuration of the polymer so that the effective conjugation length achieved in PPV conversion is shorter in the PPV/sol–gel composite system. We note that further heat treatment

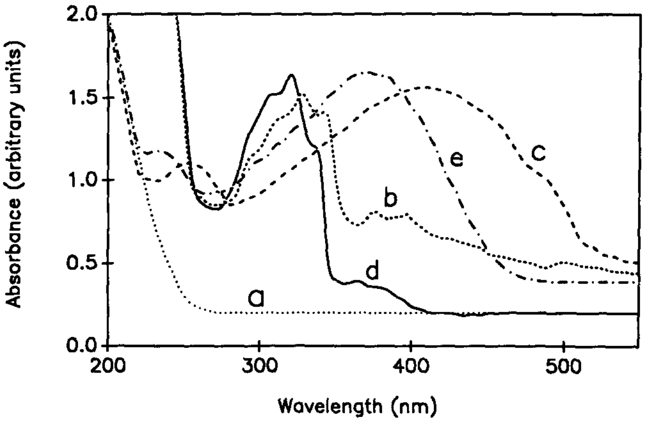


Figure 1 U.v.-vis. spectra of (a) pure sol–gel, (b) PPV precursor, (c) thermally treated PPV, (d) precursor PPV/sol–gel and (e) thermally treated (at 220°C) PPV/sol–gel films

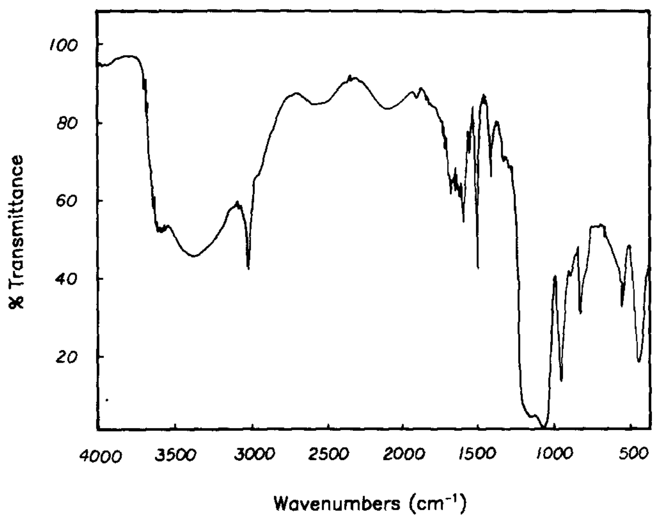


Figure 2 I.r. spectrum of PPV/sol–gel after thermal treatment at 220°C

of the film at 360°C produces no further change in the u.v.-vis. spectra.

The i.r. spectra of the fully converted PPV/sol–gel sample show characteristics of vitreous silica (*Figure 2*), with broad absorption bands due to the silica network located between 1100 and 800 cm^{-1}. The 448 cm^{-1} band corresponds to the deformation vibration of Si–O–Si–O[10,11]. In the frequency range 4800–3600 cm^{-1}, these bands are mainly due to overtones or combinations of vibrations of Si–OH or H_2O[12]. The broad absorption band between 3600 and 3000 cm^{-1} corresponds to the fundamental stretching vibration of different hydroxyl groups, comprising the 3590 cm^{-1} silanol groups linked to molecular water through hydrogen bonds, the 3750 cm^{-1} free Si–OH motion on the surface of the gel, and the 3660 cm^{-1} internal Si–OH mode[13]. The symmetric stretching mode of the Si–OCH_3 bond appears at 2958 cm^{-1}. The remaining bands in the spectrum can be identified with features observed in fully eliminated pure PPV[7]. No absorbance is observed in the vicinity of 630 cm^{-1} that can be associated with the *cis*-CH bending mode, though a strong absorbance at 959 cm^{-1} due to the *trans*-CH out-of-plane bending mode is observed. This shows that the sol–gel process occurring in the composite system does not change the nature of the elimination reaction, which yields *trans*-PPV exclusively[7].

Figure 3 shows the results of t.g.a. for the PPV precursor, the sol–gel and the PPV/sol–gel systems. *Figure 3a* reveals the reaction in the PPV precursor on heating. The transition at 230 °C is related to the thermal elimination reaction, which yields tetrahydrothiophene and HCl and converts the PPV precursor to PPV. The second thermal transition seen at 600°C is due to a degradation reaction of PPV[7]. In *Figure 3b* the transition observed at about 100°C represents the sol–gel polymerization, yielding a network formation. The second transition with a less well defined temperature range can be attributed to a reaction such as vaporization of any residual CH_3 groups. *Figure 3c* shows the t.g.a. results for the PPV precursor/sol–gel composite and appears not to be a simple superposition of *Figures 3a* and *3b*. The first broad transition band is possibly due to the overlap of the sol–gel polymerization and the PPV conversion reaction, with the latter now occurring at a lower temperature. By comparison of *Figures 3a* and *3c* one finds that the temperature for the conversion to PPV shifts from 230 to 140°C in the PPV precursor/sol–gel composite. This provides further evidence for the interaction of the two components in the system.

The d.s.c. results are consistent with the t.g.a. data. *Figure 4* shows the d.s.c. measurements for the same systems used in the t.g.a. measurement as displayed in *Figure 3*. The d.s.c. maxima in *Figure 4* correspond to endothermic responses. Each of the transitions corresponding to the observed peaks is accompanied by a weight loss as shown by the t.g.a. curve. The measured enthalpy changes are $\Delta H = 48.5\ \mathrm{J\,g^{-1}}$ for peak A and $\Delta H = 147.7\ \mathrm{J\,g^{-1}}$ for peak B. Peak A can be attributed to the elimination of physically absorbed water and peak B can be assigned to the E1cb elimination reaction. However, when PPV is introduced into the sol–gel system, the peak position shifts to lower temperature and overlaps with the sol–gel response (*Figure 4c*, peak maxima at 118 and 140°C, combined $\Delta H = 114\ \mathrm{J\,g^{-1}}$. An initial study shows that samples with different ratios

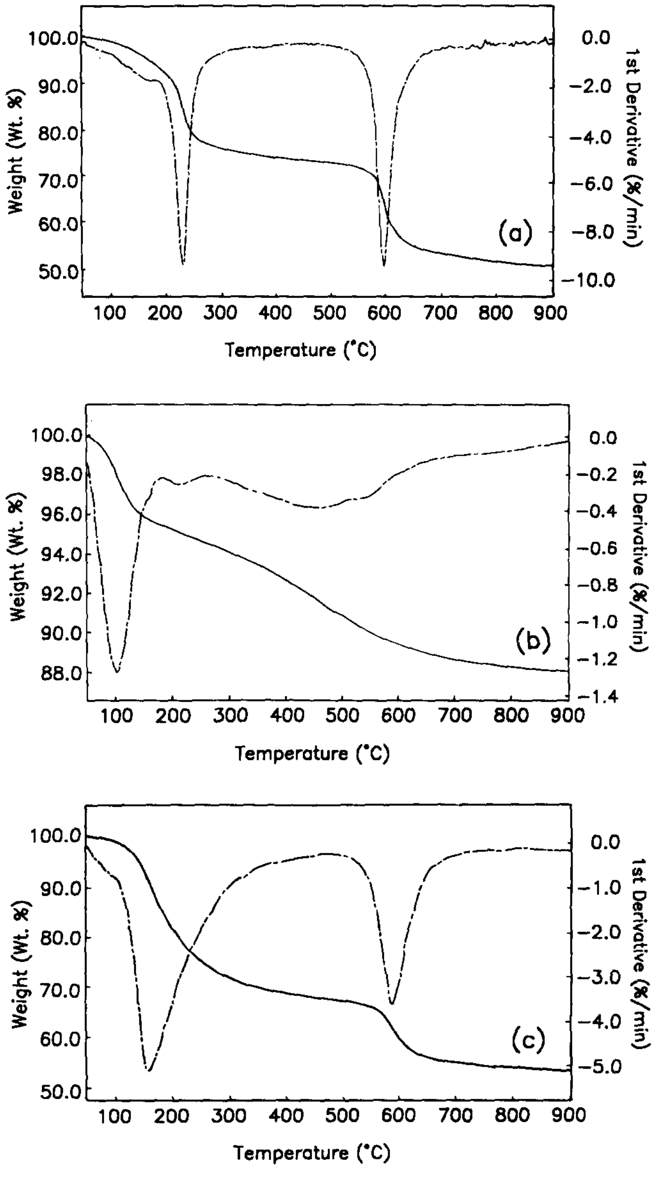


Figure 3 T.g.a. (full curve) and d.t.g.a. (chain curve) of (a) the PPV precursor, (b) the sol–gel and (c) the PPV precursor/sol–gel system

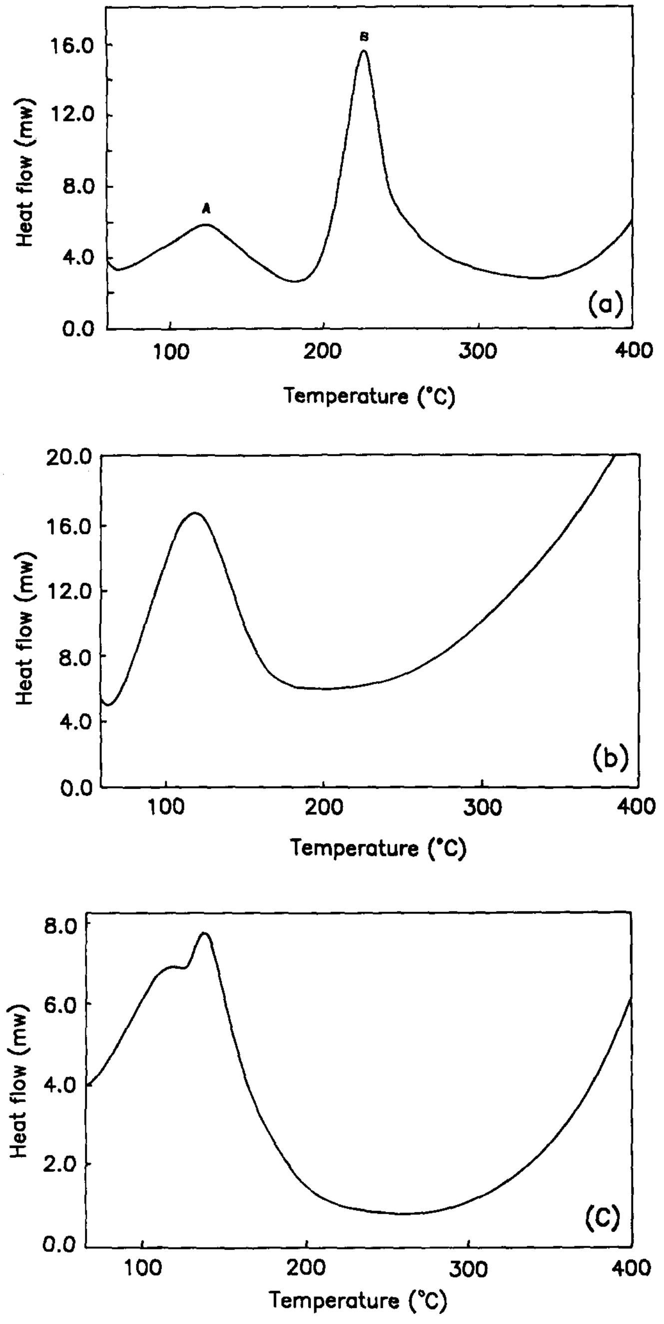


Figure 4 D.s.c. measurements of (a) the PPV precursor, (b) the sol–gel and (c) the PPV precursor/sol–gel system

of the PPV and TMOS show different peak positions. This is probably due to a lowering of the activation energy during the condensation polymerization and sintering of the PPV/sol–gel composite. We attribute this lowering of the conversion temperature for the PPV precursor to the presence of a porous structure, which facilitates the elimination reaction. We also noticed that a previously reported[7] peak at 360°C was not observed in our t.g.a. measurements.

CONCLUSIONS

A novel composite of polymer-doped glass has been developed through a sol–gel process. The new material is chemically and thermally stable. It exhibits good optical quality, showing promises for waveguiding. The active component for potential application in non-linear optics, the PPV polymer, obtained through E1cb reaction of its precursor polymer in the composite, has a structure similar to that in its pure state. However, a blue shift of the maxima in the u.v.-vis. spectrum suggests that the effective conjugation length in the composite is reduced. The polymerization of the sol–gel and the elimination reaction of the PPV precursor show some coupled interaction. The product, HCl, from PPV conversion provides a mild acidic environment and uniformly catalyses sol formation. The sol–gel process introduces a large surface area and decreases the energy barrier in the PPV conversion reaction. In the composite, the sol–gel glass gains mechanical strength while the optical quality is improved relative to pure PPV.

ACKNOWLEDGEMENTS

This research was sponsored by the Office of Innovative Science and Technology, Defense Initiative Organization, and the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under contract numbers: F4962087C0097 (SUNY at Buffalo), F4962087C0042 (SUNY at Buffalo), F4962087C0111 (University of Massachusetts) and F4962089C0027 (University of Massachusetts).

REFERENCES

1 Brinker, C. J. and Scherer, G. W. *J. Non-Cryst. Solids* 1985, **70**, 301
2 Dislich, H. *J. Non-Cryst. Solids* 1983, **57**, 371
3 Pope, E. J. A., Asami, M. and Mackenzie, J. D. *J. Mater. Res.* 1989, **4**, 1018
4 Huang, H., Wilkes, G. L. and Carlson, J. G. *Polymer* 1989, **30**, 2001
5 Prasad, P. N. and Ulrich, D. R. (Eds.) 'Nonlinear Optical and Electroactive Polymers', Plenum Press, New York, 1988
6 Singh, B. P., Prasad, P. N. and Karasz, F. E. *Polymer* 1988, **29**, 1940
7 Gagnon, D. R., Capistran, J. D., Karasz, F. E., Lenz, R. W. and Antoun, S. *Polymer* 1987, **28**, 567
8 Prasad, P. N., Karasz, F. E., Pang, Y. and Wung, C. J. US Patent filed on 17 February 1989 (application no. 312132)
9 Yamane, M., Aso, S. and Sacking, T. *J. Mater. Sci.* 1978, **13**, 865
10 Eitel, W. 'Silicate Science', Academic Press, New York, 1964, Vol. 1, p. 23
11 Simon, I. 'Modern Aspect of the Vitreous State' (Ed. J. D. Mackenzie), Butterworths, London, 1960, Vol. 1, p. 135
12 Woigniers, T. and Phalippou, J. *Riv. Staz. Sper. Vetro* 1984, **5**, 47
13 McDonald, R. S. *J. Phys. Chem.* 1958, **62**, 1168