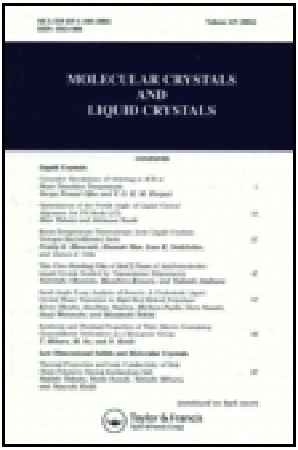

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INTERACTION OF ORGANIC COMPOUNDS WITH SILICA MATRIX PREPARED BY A SOL-GEL PROCESS FOR NLO APPLICATIONS

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ABSTRACT In this work, MNA (2-methyl-4-nitroaniline) and substituted carbazoles were incorporated into silica matrix to form composite thin films on the glass substrate by a sol-gel process for NLO applications. In the composite thin films, the thermal stability was dependent on the type of functional groups incorporated into the organic compounds. DR 1(disperse red 1) and carbazole-2 (5-nitro-9-hydroxyethyl-cabazole) which has a terminal -OH group showed enhanced thermal stability, whereas carbazole-1 (5-nitro-9-ethyl-carbazole) and MNA, which don't have a reactive functional group, showed rapid degradation upon thermal treatment. This strongthly suggests that the thermal stability of incorporated organic compounds can be enhanced by a reactive terminal group in organic compounds without severely damaging NLO property.

INTRODUCTION

The sol-gel transformation consists of several steps: preparation of homogeneous sol mixtures, gellation, drying and calcination. Many applications have been reported in the preparation of new glass composite materials and advanced ceramics.[1,2] Especially in optical application, some inorganic films, such as lithium tetra-borate and lithium-tantalate, have been sucessfully prepared from a homogeneous sol at a low processing temperature.[3,4]

Recently some new studies have been reported for making organic (polymer)

/inorganic composites for nonlinear optical (NLO) applications. In organic/inorganic composites, a large optical nonlinearity and a fast response can be expected due to the extensively delocalized-eletron configuration of the incorporated organic (polymer) compound. In addition, inorganic matrixes are expected to give processing flexibility, thermal stability and transparency to composite films. Several organic materials, such as P-NA(nitro-aniline), PPV{poly(*p*-phenylene vinylene)}, BrMPPV {poly(2-buthoxy-5-methoxy phenylene vinylene)}, have been used to give an optical nonlinearity to composite films.[5,6]

In this work, MNA(2-methyl-4-nitroaniline), DR 1(disperse red 1) and substituted carbazoles were incorporated into silica matrixes to form composite thin films by sol-gel process. The characteristics of the composite films were then evaluated.

EXPERIMENTAL PROCEDURES

The precursor solution was consisted of TEOS (tetra ethyl ortho-silicate), water, HCl and additives (hexylene glycol, hydroxypropyl cellulose and dimethyl formamide). The additives were used to prepare a clear mixture sol for spin coating. MNA, DR 1 and substituted carbazoles were purified by a recrystallization process to ensure optical grade purity. The molecular structure of these matrials are shown in Fig.1. Especially, for the NMR measurements the ethanol-D_6, D_2O, DCl and DR 1 were used in preparing a silica sol.

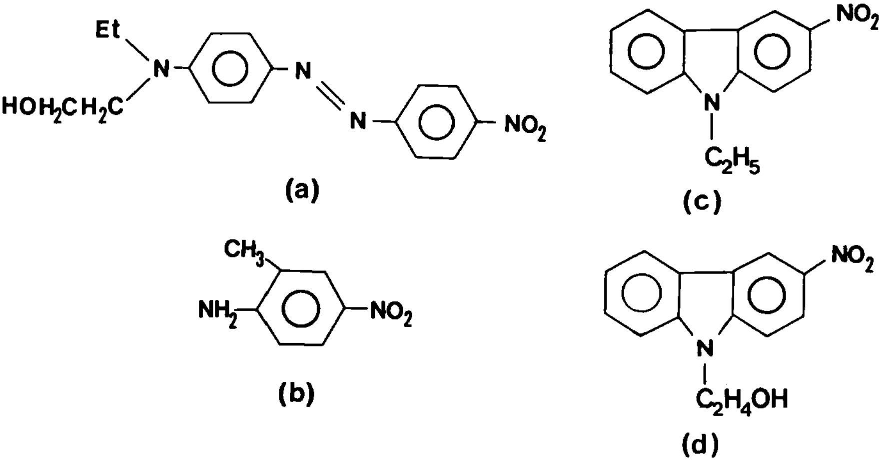

FIGURE 1 Molecular structure of NLO dye.
a) DR 1 b) MNA c) Carbazole 1 d) Carbazole 2

After preparing a partially hydrolyzed silica sol at room temperature, organic materials dissolved in organic solvent (DMF and additives) were added and stirred to form a homogeneous organic/inorganic composite solution. This solution was spin-coated on the glass substrate to get a composite thin film of 1-2μm. The wet film was dried in oven at 50℃ for 30 min. In order to polize the organic materials in the silica matrix, corona polarization was carried out with a 15 KV electric field. The polarized state and the degree of degradation of organic materials during the thermal process were measured by UV (Shimadzu-160A) spectrometer. A viscosity change with time was measured by concentric cylinder viscometer (Rotovisco RV 3) with the NV-ST type of sensor. The structure change of the organic/inorganic composite solution was analyzed by IR (Shimadzu-440) and NMR (Brucker ACF-200) spectrometer. The second harmony generation (SHG) was monitered by Nd : YAG Laser and the rotation angle of these samples were kept from -80° to 80° with 10 MW/cm^2 laser power.

RESULTS AND DISCUSSIONS

The structure change of the silica solution was monitered by IR spectrometer and the results are shown in Fig. 2. Two large bands at around 1100 and 1150cm^{-1} suggest C-O-C streching peaks of the ethoxy group attached to the tetraethoxy silane (TEOS) in a initial reaction time. The intensity of these peaks are reduced gradually as the reaction proceeds. As a results of forming silanol group with the reaction, a broad and strong -OH peak begins to appear at lower frequency region around 3400 cm^{-1}. A Si-O-Si network structure resulted from the condensation reaction make asymmetric stretching bands stronger and stronger around 1090-1160cm^{-1}. Also, the peaks at 830 and 600cm^{-1} seem to be remarkably increased because they become -si- network structure. From these results, it is safely argued that the growth of -si- structure is the straight network formation of the 4-fold ring. With change of the ratio of TEOS/EtOH, the time dependence of viscocity is shown in Fig. 3. The viscosity of silica sol was slowly increased at the early stage of reaction but rapidly at the gellation. The possible range of the coating time is shown as dot line. Eventhough the coating time becomes longer as amount of alcohol increases, the ratio of TEOS/EtOH was fixed to be 10 due to the limited reactivity of the organic NLO materials and the ineffectiveness on forming the silica network structure. When the hexylene glycol was added as a cosolvent, clean silica thin film was produced without a porus part.

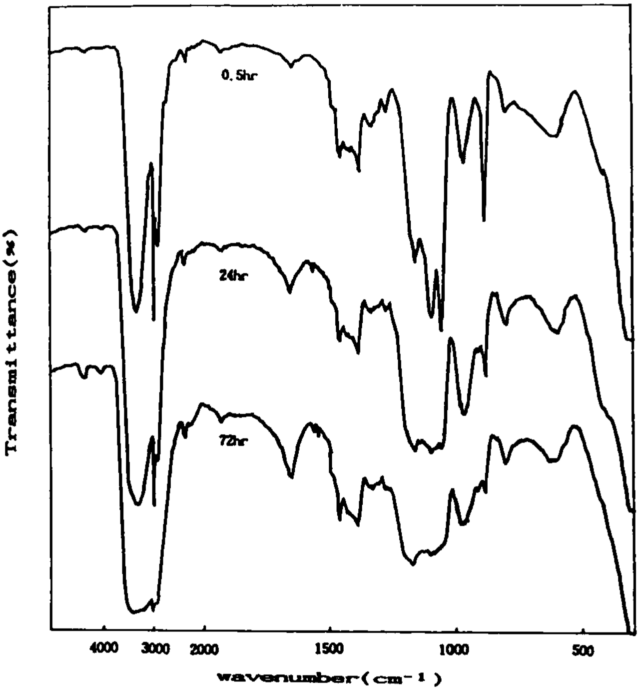

FIGURE 2 IR Spectra of silica sol during the sol-gel reaction.

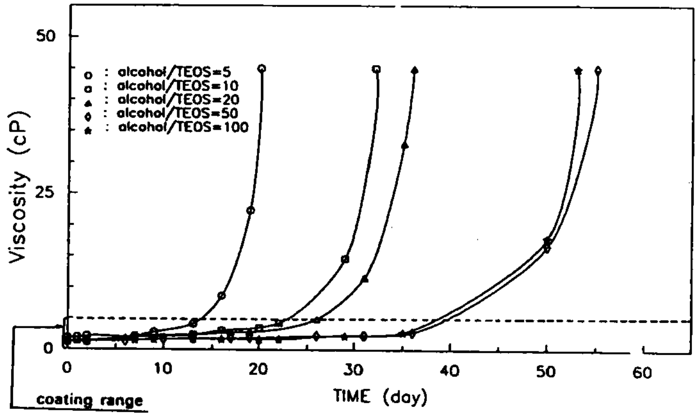

FIGURE 3 Viscosity change of silica sol with time.

The structure change of silica sol containing DR 1 as a organic material was monitered by ^{1}H NMR spectrometer. The spectra were compared each other changing time as shown in Fig.4 (a) and (b).

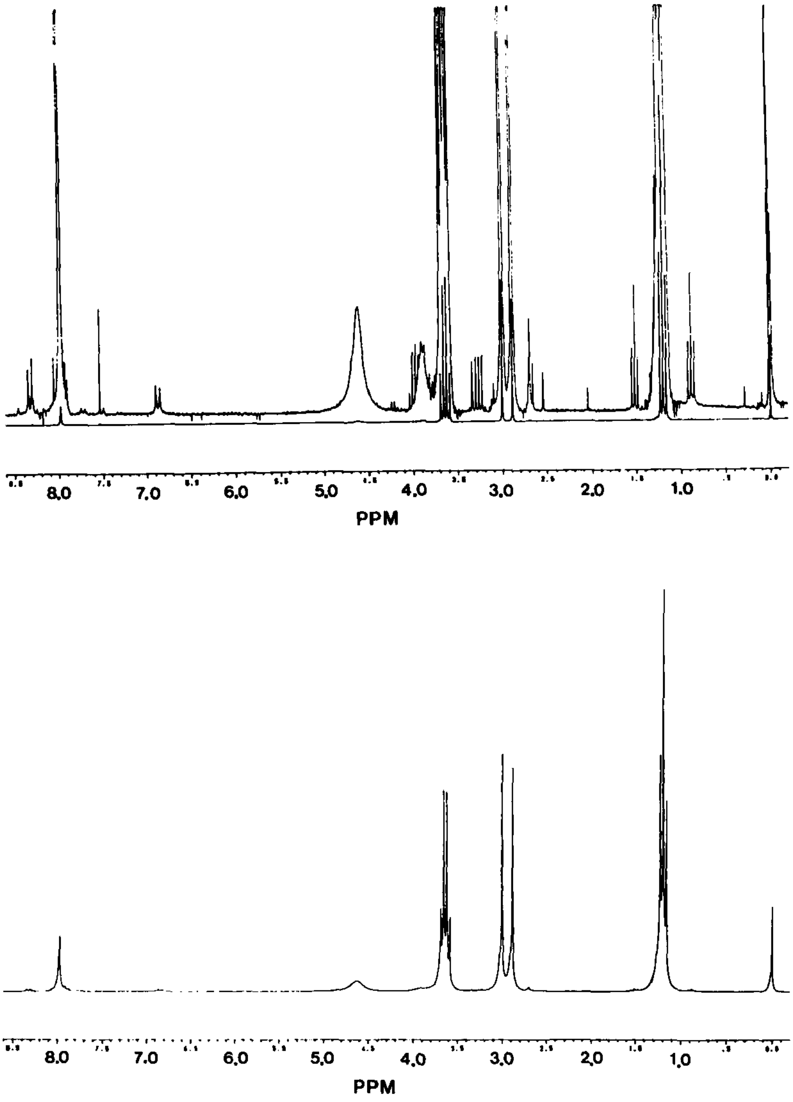

FIGURE 4 a) ^{1}H NMR spectra of silica solution with DR 1 at initial reaction time.

b) ^{1}H NMR spectra of silica solution with DR 1 before gellation time.

The strong multiplet peaks at 3.66 and 1.28 ppm are corresponded to the methylene and methyl signals of the TEOS, respectively. Other strong peaks at 8.00, 3.00 and 2.89 ppm can be easily assigned to the signals of DMF. The weak peaks in Fig. 4(a) can be assigned to the peaks for the DR 1; (1) the multiplet peaks at 8.30, 7.90, 7.40 and 6.81 ppm are assigned to the aromatic proton signals. (2) The broad peak at 3.9 ppm corresponds to -OH proton signal. (3) The signals in the upfilled region at 3.60, 2.10 ppm and a triplet signal at 1.05 ppm are assigned to the methylene and methyl proton of DR 1, respectively. In addition to these peaks, the signals of ethanol are observed on 4.61, 3.62 and 1.50 ppm as a side product. The ^{1}H NMR spectra of the reaction mixture before the formation of silica gel are shown in fig. 4(b). With the peaks of ethanol, the strong peaks for the DMF at 8.00, 3.00 and 2.89 ppm are still remained. The peaks corresponding to the TEOS are disappeared and trace peaks at 3.66 and 1.28 ppm can be observed. From these ^{1}H NMR spectra, it revealed that the TEOS reacts with DR 1 during the hydrolysis reaction to form a chemical bond with silica matrix. After that the polycondensation reaction occurs to form a -Si-O-Si- network structure before gellation process. The major solvent, EtOH, was easily eliminated by evaporation process and the remining DMF by thermal treatment. The thermal stability of the matrix prepared by sol-gel process is maintained and proved by the second harmonic generation (SHG) experiment.

Fig. 5 shows the UV spectra of the organic compounds which were incorporated into silica films. In absorbance spectra, the main peak seems to originate from the incorporated organic compound. The peak maximum of MNA incorporated film appeared at 383nm and those of carbazole-1 and carbazole-2 incorporated films appeared at 389nm and 420nm, respectively. The position of absorption which corresponds to carbazole-2 moved to longer wavelength. The maximum peak's shift in carbazole incorporated films could be attributed to the differences between functional groups of carbazole-2 ($-C_2H_4OH$) and carbazole-1 ($-C_2H_5$). Table I shows the absorbance changes due to the thermal degradation of the organic compounds incorporated into the silica films. The samples were treated at 100℃ in atmospheric air and the degradation degree of the organic compounds was monitored by the absorbance change of maximum peaks.

The decay rate of absorbance peak in the silica film was in the following order;

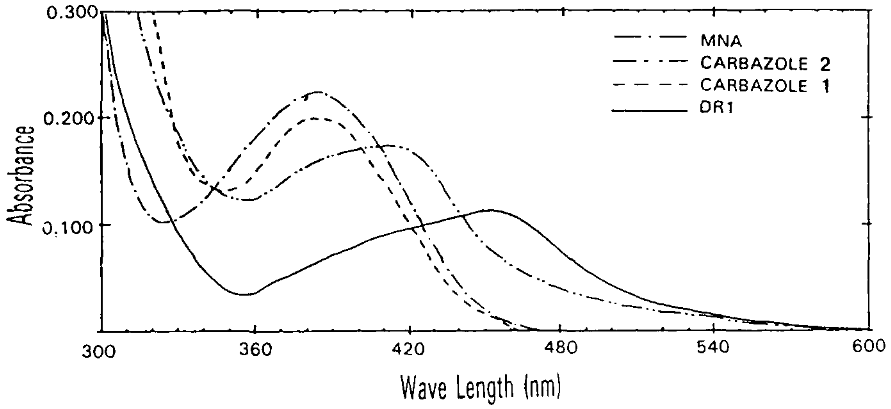

FIGURE 5 UV Spectra of organic compounds incorporated silica films.

Table I Absorbance changes of NLO dye incorporated silica films.

NLO dye	Absorbance Change(A/A0)
Carbazole 1	0.49
MNA	0.69
DR 1	1.15
Carbazole 2	1.20

carbazole-1 > MNA >> DR 1 > carbazole-2. The absorbance decay of MNA and carbazole-1 incorporated films maybe related to the thermal unstability of organic compounds due to sublimation and thermal degradation. It is notable that DR 1 and carbazole-2 incorporated silica films showed stable absorbance. A slight increase in absorbance could be explained by the increased optical transparency of the composite films corresponding to the densification of porous silica film during the thermal treatment.[2] The thermal stability of carbazole-2 incorporated films could not be attributed to the inherrent stability of carbazole-2 because carbazole-1, which had structural similarity with carbazole-2, showed very unstable behavior at the same condition. Therefore, the difference of the thermal stability must come from the difference of the functional groups: the group $-C_2H_4OH$ in carbazole-2 could chemcally interact with silica sol at the initial reaction time.

Fig. 6 shows the UV spectra variation of carbazole-2 incorporated silica film after polarizing and subsequent relaxation processes. Corona polarization was carried out under 15 KV at 100℃. With 5min. polarization, the sample showed a 10% decrease in absorbance due to the allignment of polar carbasol-2 in the silica matrix under the electric field. The relaxation process of alligned carbasol-2 was measured after cooling the sample to room temperature as shown in Fig. 6 (a)-(b)-(c). The sample showed a slight recovery of absorbance after 12h. with electric field removal due to the slow relaxation of the alligned carbazole-2 in the porous silica matrix.

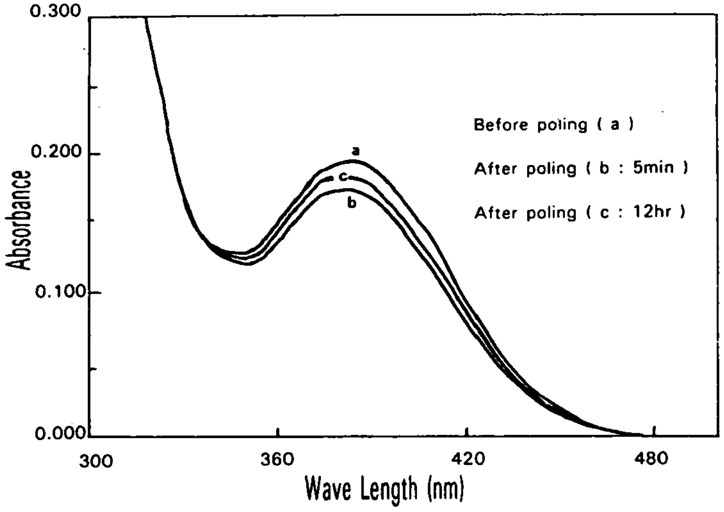

FIGURE 6 UV Spectra variation of carbazole-2 incorporated into NLO film with polarizing time.

An effect of polarization on carbazole-2 incorporated silica film was detected by in-situ polarization (Fig. 7). The changes of absorbance were observed in the electric field at various temperatures (from room temperature to 85 ℃). The absorbance was 0.144 at room temperature and it was reduced to 0.135 at 85℃ with slow relaxation rate. The intensity of absorbance was decreased with electric field due to the constantly aligned organic dye. And a sample showed a recovery of absorbance after electric field removal at same temperature. When the sample was heated up to 100℃ with polarizing, the absorbance was increased: Because a densification of carbazole-2 in the porous silica matrix was involved with the elavation of temperature and resulted in thermal stability of these matrix.[2] Thus, it is possible to generate organic/inorganic composite film with NLO property maintaining polarization since an increase of temperature on these silica films under electric field fix a constant alignment of organic dye with the slow relaxation.

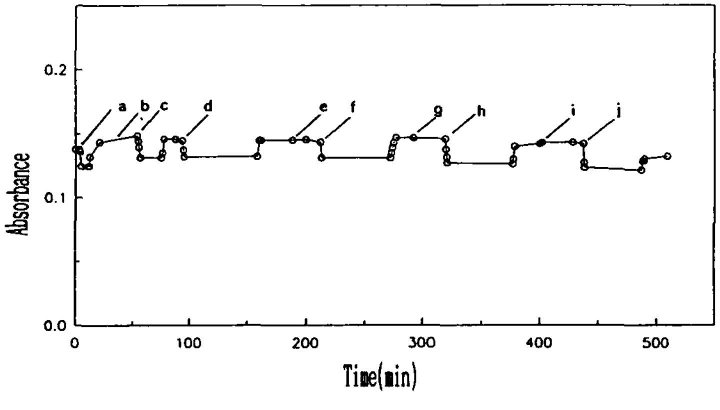

FIGURE 7 The change of UV absorbance in carbazole-2 incorporated silica film.
a : H.V. on (R.T.) b : Heater on (42℃) c : H.V. on (42℃)
d : H.V. on (42℃) e : Heater on (60℃) f : H.V. on (60℃)
g : Heater on (78℃) h : H.V. on (78℃) i : Heater on (85℃)
j : H.V. on (85℃)

SHG was measured rotating the incidence angle under the intensity of light being above 10^4 eV. In the case of the silica film with DR 1, the intensity of SHG was varied with the changes of incidence angle. NLO property of these films was maintained and observed in the experiment (Fig. 8).[11] But the silica film with carbazole-2 was impossible to measure due to the low value of SHG.

These results support that NLO property of organic compound is maintained even when the terminal functional groups chemically interacted with the silica matrix. To elucidate this behavior more in detail, further study is now underway.

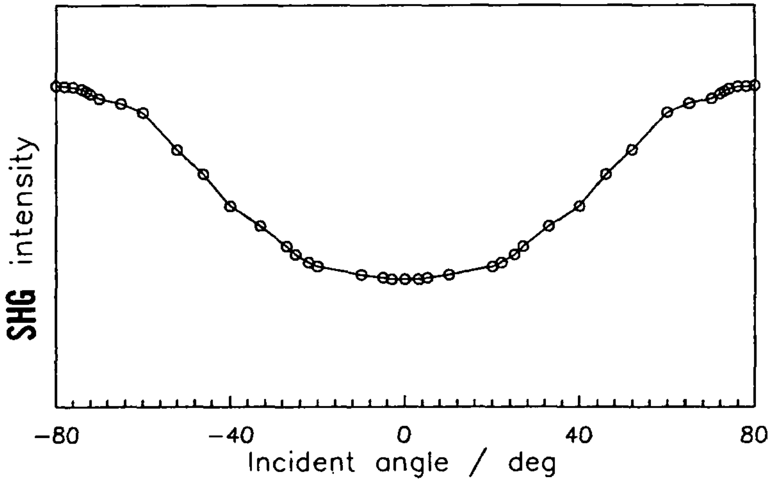

FIGURE 8 SHG intensity change for incident angle in DR 1 incorporated silica film.

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