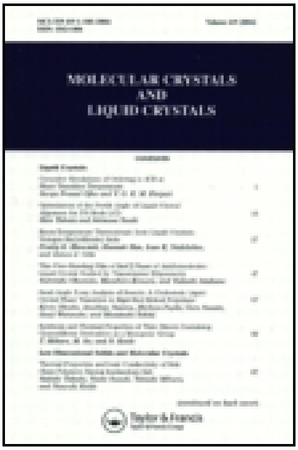

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UV STUDY ON THE THERMAL STABILITY OF DISPERSE RED 1 FILMS INCORPORATED WITH REACTIVE SILICA

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Abstract The thermal stability of thin DR1/PMMA, DR1/silica, and DRS/silica systems was studied by UV spectroscopy. DRS which can covalently bind with reactive silica was synthesized between 4-[ethyl(2-hydroxyethyl) amino]-4'-nitro azobenzene (disperse red 1, DRl) and 3-isocyanatopropyl triethoxy silane. The characterization of chemicals and incorporated films were carried out by UV/VIS spectroscopy, DTA, ^{1}H- and ^{13}C-NMR, and FT-IR. After poling of DR1 and DRS incorporated at various temperatures, the UV absorbance decreased due to the alignment of DR1 and DRS by electric field. The second harmonic generation response was obtained by using Nd:YAG laser. The thermal stability of DRS and DRS/silica system was enhanced, compared to that of DR1 and DR1/silica system, respectively.

INTRODUCTION

Photonics materials play a crucial role in the information and communication fields. Organic photonics materials offer ultrafast response time, low dielectric constants, good processability, and enhanced nonlinear optical (NLO) responses, compared to the traditional inorganic solids.[1] In a doped system, the thermal stability of ordered orientation induced by the electric field poling is generally poor, which limits their application. For this reason, DR1 was developed to enhance thermal stability because of it's large chromophore size which hinders rotational mobility. Such organic photonics materials can be used to dope polymer matrices without crystallization of chromophores. Furthermore, chromophore as a part of side chain attached to the polymer backbone has the advantage in that a high chromophore concentration can be incorporated without crystallization, phase separation and relaxation of poled order. However, there are a drawback in that organic materials have poor thermal stability.

Therefore, organic/inorganic system is suggested for NLO applications. Large optical nonlinearity and a fast response time can be expected due to the extensively delocalized-electron configuration of the organic compound. In addition, inorganic matrices are expected to give good thermal stability, processability, and transparency to the composite films. Sol-gel process provides an attractive route to the preparation of thermally stable organic/inorganic systems with high NLO property.[2]

Recently, NLO materials were synthesized by using phenoxyl molecules with multi-functional groups and alkoxysilane dye.[3] Also, a modified DR1 (DRS) was prepared and chemically incorporated into the silica matrices by using sol-gel techniques.[4]

In this paper, the thermal stability of chromophores and chromophore/matrices were studied by using UV/VIS spectroscopy. The orientation and relaxation behaviors of chromophores were studied at various temperatures.

EXPERIMENTAL

Chemicals

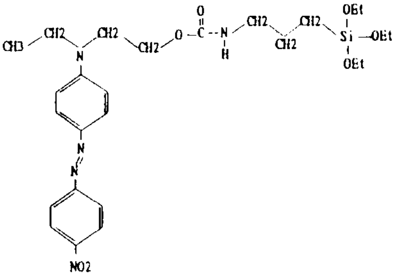

FIGURE 1 Chemical structure of modified DR1 (DRS)

Disperse red 1 (DR1) and modified DR1 (DRS) were used as organic chromophores (Figure 1). DRS was synthesized from 4-[ethyl(2-hydroxyethyl) amino]-4'-nitro azobenzene (DR1, Aldrich) and 3-isocyanatopropyl triethoxy silane (Petrarch). The details in synthesis were presented in a previous paper.[4] DRS structure was identified by ^{1}H-, ^{13}C-NMR (Varian, Gemini 200), and FT-IR (Mattson, Genesis). Differential thermal analysis (DTA, Shimazu 50A) was carried out under O_2 gas.

Preparation of Chromophores/Matrices Films

Matrices were PMMA, and silica which was prepared by the sol-gel process. Low molecular weight poly(methyl methacrylate) (PMMA, Aldrich, 5.0 g) was dissolved in N-dimethyl formamide (DMF, Aldrich, 7.0 ml), followed by the addition of DR1 (0.5 g). The precursor solution for silica consisted of tetraethyl orthosilicate (TEOS, Aldrich), ethyl alcohol, HCl, water and hexylene glycol. The precursor solution molar ratio of TEOS : EtOH : HG : HCl : H_2O : DMF was 1 : 10 : 0.1 : 0.05 : 2 : 0.1. DR1 and DRS dissolved in DMF was added to the precursor solution and the amount of chromophore in precursor solution was 10 wt% of TEOS. Conventional spin coating was employed to prepare thin films of precursor solution on a glass substrate, after aging 24 hours. The gelled films were densified at room temperature for 12 hours. Three films of DR1/PMMA, DR1/silica, DRS/silica systems were prepared in this investigation.

Corona Poling

In order to polarize the organic chromophores in the polymer and silica matrices, the electric field by corona discharge technique was used at room temperature, 80, 100, and 140℃ at 15 kV for 20 min. UV-VIS (Shimazu 160A) absorption spectra were obtained before and after poling at room temperature. Infrared spectra were also obtained to investigate the orientational change of DRS in the matrix. The SHG intensity was obtained with Nd:YAG laser (10mw/cm^2, pulse duration : ps).

RESULTS AND DISCUSSION

UV Spectra of Chromophores/Matrices Films

UV spectra of DRS/silica films before and after poling at 80℃ is shown in Figure 2. Absorbance decreased approximately 30 % due to the alignment of DR1 in PMMA matrix (Figure 2a). However, the absorbance difference between before and after poling of DRS doped silica films was 70 %, which might be related to the order parameter (Figure 2b). UV absorbance changes were also detected from before poling, and zero hour and 100 hours after poling.

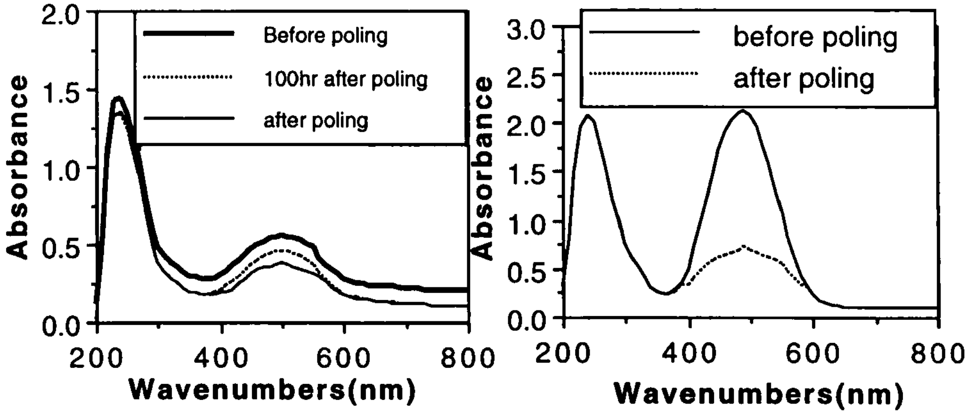

FIGURE 2 UV absorbance changes of chromophores/matrices films before and after poling, (a) DR1/PMMA (b) DRS/silica film.

Thermal Stability of Chromophores and Chromophores/Matrices Systems

As observed from the differential thermal analysis (DTA) spectra of the DR1 and DRS, thermal decomposition temperature of DRS was 320℃ , while that of DR-1 was 290℃. The thermal stability of DRS was better than that of DR1 because the modification of DR1 with silane compound.

The thermal stability of DR1/PMMA, DR1/silica and DRS/silica films was measured in air at 140℃. Figure 3 shows good thermal stability of the DRS/silica film. UV absorbance of DR1/PMMA film aged at 140℃ showed dramatic decrease which could be explained by thermal decomposition of DR1. Thermal stability of DR1/silica system was slightly better than DR-1/PMMA system as shown in Figure 3. However, UV absorbance of DRS/silica system was not changed even after 30 hours of aging at 140℃.

Effect of Poling Temperature on the Chromophores/Matrices Systems

Figure 4 shows the temperature effect of poling on DR1 incorporated PMMA film. The UV absorbance decreased by 30 % after poling which could be explained by the relaxation of chromophore molecules to a random orientation. Absorbance after poling which was carried out at room temperature showed almost 100 % recovery within 200 hours.

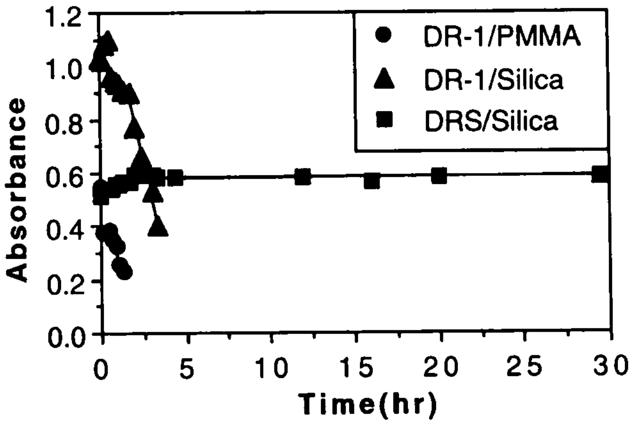

FIGURE 3 UV absorbance changes of chromophores/matrices films at 140℃.

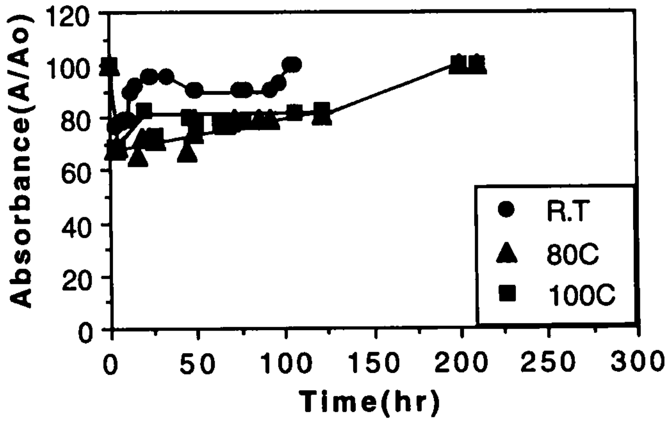

FIGURE 4 UV absorbance changes before and after poling, and relaxation behaviors of DR1/PMMA film. The denoted temperatures are the poling temperature.

Figure 5 shows the relaxation process of three systems at room temperature. Ao and A are UV absorbance (arbitrary intensity) before and after poling, respectively. The DRS/silica system showed small absorbance decrease due to large molecules of DRS, compared to DR1. The absorbance of DR1 increased to its original value quickly in PMMA, since the DR1/PMMA system is not crosslinked.

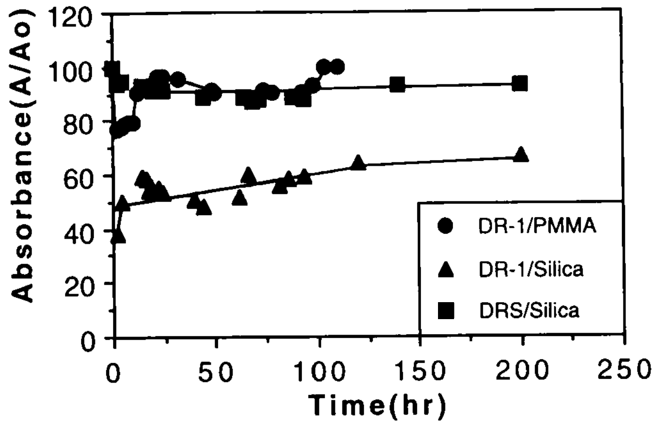

FIGURE 5 UV absorbance changes before and after poling and relaxation behaviors of three kinds of chromophores/matrices systems at room temperature.

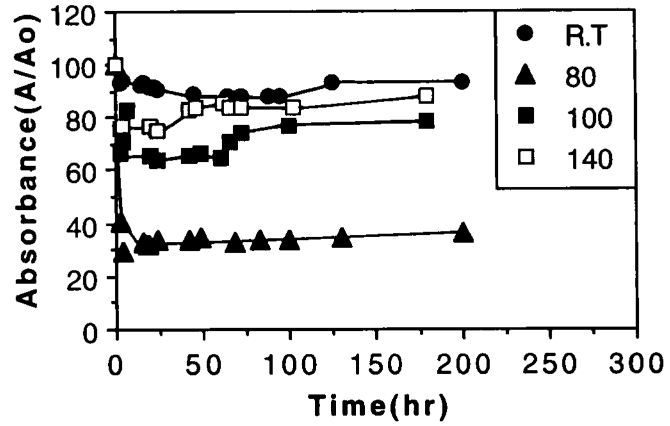

FIGURE 6 UV absorbance changes before and after poling, and relaxation behaviors of DRS/Silica film. The denoted temperatures are the poling temperature.

Temperature dependence on absorbance changes by poling is shown in Figure 6. It could be explained by order parameter which increased with temperature. Especially, the order parameter was large when the film was poled at 80℃. The poling voltage was turned off immediately after the chromophores/matrices systems were heated to various temperatures. Zhang and Prasad[6] studied the influence of heat treatment on the SHG intensity of organic molecules doped sol-gel system. They showed relatively fast decay of the SHG intensity after the poling and heating power were turned off simultaneously. This could be explained by the freedom of chromophore to relax to a random orientation.

In this study, UV absorbance was measured as a function of temperature, which did not change at all 80℃ test. This result could be explained by the temperature dependence on the orientation of organic molecules in the matrices. At room temperature, DRS was not free to move well because the size of DRS is lager than that of DR1. As the temperature increased, DRS could align into a highly ordered position by poling. Relatively high order parameter was observed at 80℃. However, the order parameter was smaller at 100 and 140℃, compared to that at 80℃, because of returning molecules to random orientation as soon as the voltage was turned off.

SHG Intensity of the Chromophores/Silica

The SHG intensity was obtained with Nd:YAG laser generated as a function of laser incident angle to the corona-poled sample to observe the NLO properties. SHG intensity of DRS changes with the incident angle as shown in the previous paper.[4] The minimum was observed at 0 °, and the maximum was observed at ±70 °. This behavior is similar to that of DR1 with slight deviation in the angle of maximum intensity.

CONCLUSION

The thermal stability of DRS was better than that of DR1, possibly due to the structure modification. Also, the DRS/silica system, which can covalently bond with the matrices, was the most thermally stable chromophore/matrices. From the results of UV studies, the temperature was the important factor for the orientation of NLO molecules in matrices. The absorbance difference between before and after poling of DRS/silica system was large at the poling temperature of 80℃. It could be said that the highly ordered orientation of DRS was obtained in silica matrix due to the large difference of UV absorbance.

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