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Young-Sun Cho [a], Kyung-Shin Min [a], Jae-Suk Lee [a], Gyoujin Cho [b], Kyeong Taek Jung [c], Yong Gun Shul [c], Tatsuo Wada [d] & Hiroyuki Sasabe [d]

[a] Dept. Mat. Sci. and Eng., Kwangju Ins. Sci. and Tech. (K-JIST), Kwangju, Korea

[b] Dept. Chem. Eng., Suncheon Nat. Univ., Suncheon, Korea

[c] Dept. Chem. Eng., Yonsei Univ., Seoul, Korea

[d] Lab. for Nano-Photonics. Mat., FRP, RIKEN, Wako, Japan

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NONLINEAR OPTICAL PROPERTIES OF MODIFIED DR1/SILICA FILMS WITH HIGHLY ORDERED STRUCTURES

YOUNG-SUN CHO, KYUNG-SHIN MIN, and JAE-SUK LEE
Dept. Mat. Sci. and Eng., Kwangju Ins. Sci. and Tech. (*K-JIST*), Kwangju, Korea.
GYOUJIN CHO
Dept. Chem. Eng., Suncheon Nat. Univ., Suncheon, Korea.
KYEONG TAEK JUNG, and YONG GUN SHUL
Dept. Chem. Eng., Yonsei Univ., Seoul, Korea.
TATSUO WADA, and HIROYUKI SASABE
Lab. for Nano-Photonics . Mat., FRP, RIKEN, Wako, Japan.

Abstract Crosslinkable organic NLO chromophore (DRS) has been prepared and chemically incorporated into silica matrices using a sol-gel process. By monitoring the decay of UV absorbance as a function of time and temperatures, a number of electrically poled DRS/silica matrice system has been investigated to elucidate the relaxation behaviors of the oriented organic chromophore by the poling. The value of the second order NLO coefficient d_{33} was 47 pm/V for the DRS/silica matrice films with 0.4 μm thickness. In addition, from the result of dramatic decreasing of UV absorbance after poling, it is speculated that the DRS may act as a liquid crystalline mesogenic groups and effectively oriented by the poling at the phase (nematic) transition temperature (80°C) and locked in by the crosslinking. The crosslinking reactions between silica matrices and DRS chromophores have been proved using ^{29}Si solid NMR measurement.

INTRODUCTION

Organic NLO materials were investigated as an alternative inorganic species in the field of NLO because of their low cost, fast and large nonlinear response over a broad frequencyrange, inherent synthetic flexibility, high optical damage thresholds, and intrinsic tailorability[1-3]. However, organic NLO chromophores also have a couple of problems, such

as lack of thermal stability, and the easy relaxation of oriented chromophores after poling[4]. One of the key issue in developing NLO materials is whether the materials have good thermal stability or not.

We try to elucidate the reason of both large absorbance change before and after poling at 80 ℃ using DSC and polarized optical microscope and the stability of oriented organic chromophores as proving crosslinking reaction between matrices and chromophores by ^{29}Si solid NMR spectroscopy.

EXPERIMENTAL

Modified disperse red 1 (DRS) was prepared as reported[5], and characterized by differential scanning calorimetry (DSC), FT-IR (Perkin Elmer) and FT-NMR (JEOL, JNM LA300WB). Precursor solution for the formation of silica matrices was prepared by previously reported method[11]. Thermal stability and relaxation behaviors of DRS/Silica films were measured by UV/VIS spectroscopy (Varian, Cary 1E) as a function of time and temperature. Second harmonic generation of DRS/Silica films were measured using Nd:YAG laser. Also, crosslinking reactions between silica matrices and chromophores were traced by ^{29}Si solid state NMR.

RESULTS AND DISCUSSION

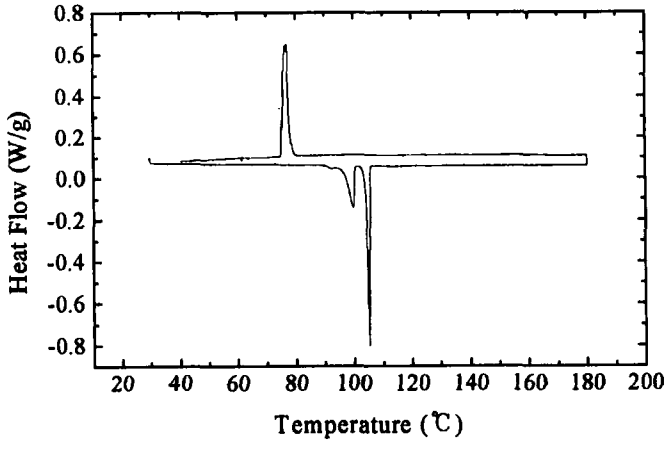

FIGURE 1. Differential scanning calorimeter analysis of DRS.

To investigate the relaxation behaviors of chromophores after the poling, the absorption behaviors of each sample were examined as a function of time. The absorption spectra were taken at regular intervals over 200 hours for the poled/cured samples kept at 25, 80, 100, and 140°C, respectively. Temporal retentions of DRS/silica matrices were excellent at all the temperature ranges. The absorbance differences of DRS/silica matrices between before and after poling at 80°C were about 70%.

We introduced differential scanning calorimetry (DSC) and polarized optical microscopy to see the phase transition behavior of the pendant mesogenic group (DRS here) in the crosslinked silica matrices. DSC scan of DRS were performed at 1, 5 10, 25°C/min. Figure 1 shows the DSC thermodiagram of DRS scan at 1 ℃/min. Two peaks were observed; the one is due to liquid crystal phase (nematic) transition and the other is due to the melting. The recrystallization temperature was exactly 80°C in cooling cycle while in heating cycle, the temperature was 100°C. The phase transition behaviors monitored by the optical microscope are consistent with the results obtained from DSC. From these results, we can speculate that the formation of nematic phase of DRS in the reactive silica matrices is a major factor in observed large absorbance changes before and after poling.

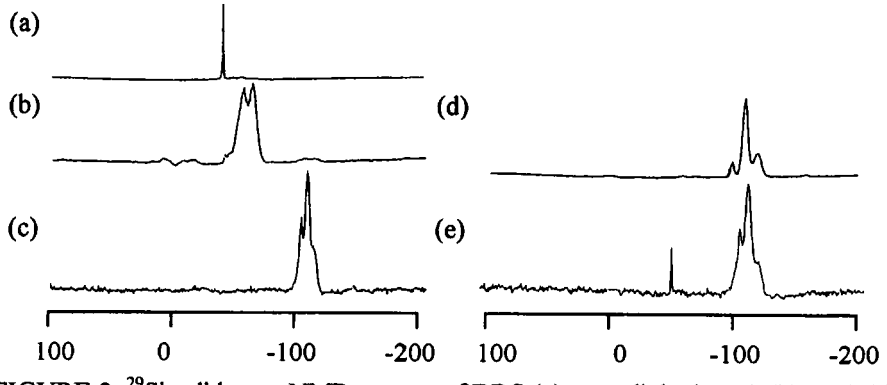

FIGURE 2. ^{29}Si solid state NMR spectra of DRS (a), crosslinked DRS (b), and silica monolith (c), chemically reacted DRS/silica (d), and physically mixed DRS/silica (e).

Crosslinking reactions between silica matrices and DRS were observed by ^{29}Si solid state NMR by CP/MAS method using poly(dimethyl siloxane) as an external reference. It is very sensitive to both the degree of TEOS condensation and the substitution degree of the other Si, $Si(OSi)_x(OH)_{4-x}$. ^{29}Si solid state NMR spectra of DRS, crosslinked DRS, silica monolith, chemically reacted DRS/silica, and physically mixed DRS/silica are shown in

Figure 2. In this Figure, DRS peak was observed at -46 ppm before crosslinking reaction, while crosslinked DRS peaks were observed at -60, and -66 ppm. These peaks are shifted about 20 ppm. This difference corresponds to the differential substitution degree of hydroxyl group; $Si(OSi)_2(OH)$ and $Si(OSi)_3$. Also, three peaks were observed for silica monolith at -91, -101, and -111 ppm. These peak shifts are assigned as the point of crosslinking, $Si(OSi)_2(OH)_2$, $Si(OSi)_2(OH)$, and $Si(OSi)_4$[6,7]. In chemically reacted DRS/silica, we observed peaks at -92, -101, and -111 ppm when 10wt% DRS was used. We could not find any peak from ^{13}C solid NMR spectra of silica monolith, because all of the ethoxy group of TEOS were hydrolyzed. Therefore, those peaks could be used to assign the amount of crosslinking of the alkoxysilyl groups between silica and DRS, $Si(OSi)_2(OH)_2$, $Si(OSi)_3(OH)_1$, and $Si(OSi)_4$, respectively.

The SH (second harmonics) intensity for the poled samples examined in this work was obtained with Nd:YAG laser to observe the NLO properties. From the results, DRS/silica matrice system has large SH intensity. The SH coefficient is determined by measuring the SH intensity as a function of the incident angle in transmission through the film. The nonlinear optical coefficient (d_{33}) of the poled and cured DRS/silica matrices was 47 pm/V even in very thin film (0.4 μm).

CONCLUSIONS

The formation of nematic phase of DRS in the reactive silica matrices is a major factor in observed large absorbance changes before and after poling. ^{29}Si solid state NMR was introduced to investigate crosslinking reaction between silica matrices and DRS. We observed that all alkoxysilyl groups of silica matrices and DRS were hydrolyzed and then the condensation reaction occurred even with has hydroxyl group.

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