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The crosslinked polyurethane PU-VP was prepared by the reaction of poly[(phenyl-isocyanate)-co-formaldehyde] and hydroxy-functionalized hemicyanine-type NLO chromophore. For the poled and cured polymer the $\chi^{(2)}$ value was 30.2 pm/V measured at a wavelength of 1.064 μm. Thermal stability studies performed on PU-PV sample by the second harmonic generation activity indicated a nearly no decay of $\chi^{(2)}$ value due to the lattice hardening of the polyurethane matrix with three bonding sites. The relaxation behaviors of aligned dipoles in PU-PV were also studied by varying poling and crosslinking conditions.

Keywords: crosslinked polyurethane; nonlinearity; relaxation dynamics

INTRODUCTION

In the development of second-order nonlinear optical (NLO) polymers, the ability to stabilize the electric field induced dipole alignment, particularly at elevated temperatures, has been the critical issue. Improvements over the dye-doped systems have been made by attaching chromophores as pendants to flexible polymer backbone or by incorporating them as components of the polymer backbone[1-3]. For device applications an additional lattice hardening is required. In order to achieve this, several investigators have utilized crosslinking reactions to stabilize the dipole orientation after electric or corna poling[4,5].

In the present investigation, hydroxy group containing monomer and poly[(phenylisocyanate)-co-formaldehyde](PPICF) with one crosslinking site (cyano group) at every phenylene moiety were reacted to produce crosslinked polyurethane. PPICF is an liquid polymer and thus expected to produce a high

optical quality film through effective and uniform crosslinking reaction. Physical properties and optical second-order NLO activities in terms of electrical poling and thermal stability will be presented. In particular, for crosslinked VP polyurethane (PU-VP), the relaxation dynamics is investigated through aligned dipole relaxation measurement by means of varying the poling and crosslinking conditions.

EXPERIMENT

Measurement

IR spectra of polymers were obtained from Boemen Michelson series FT-IR spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Dupont 9900 analyzer. UV-vis absorption spectra were measured on a Shimadzu UV-3101PC spectrophotometer. The second harmonic generation (SHG) experiments were performed with p-polarized beam at the fundamental frequency of a mode-locked Q-switched Nd:YAG laser operating at 500 Hz with 135 ps subpulses in each pulse train. The NLO acitvity of the polymer films was produced by using corona discharge induced electric poling.

Film Preparation

PU-VP1 (NCO/OH=1): To a solution of triol monomer VP-OH (0.24 g) in 0.25 g of anhydrous *N,N*-dimethylformamide (DMF) and 1 g of cyclopentanone was added 47.6 wt.% solution (320 $\mu\ell$, d=1.06) of PPICF in DMF. The solution was stirred for 10 min, then filtered by using a 0.45 μm microsyringe. A high quality polymer film sample was obtained by spin casting at 400 rpm. Since the crosslinking reaction occurred even at the room temperature, thermal crosslinking was performed under poling field right after the spin casting without removing the solvent.

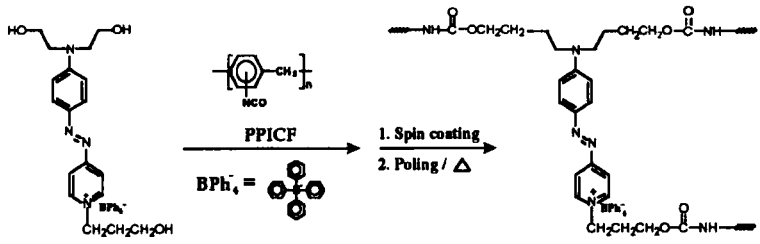
PU-VP2 (NCO/OH=2): To achieve higher mobility of the crosslinked polymer matrix and to obtain complete reaction of the monomers, NCO/OH=2 samples (PU-VP2) were prepared. PU-VP2 film was prepared by a spin casting at 400 rpm using 0.45 μm pore-size microsyringe filtered solution. Better quality films were obtained with PU-VP2 as compared to PU-VP1, and the

former used for the aligned dipole relaxation measurements.

RESULTS AND DISCUSSION

The synthetic approach to obtain monomer VP-OH was previously reported by Moon[6]. The synthetic route for crosslinked polyurethane system PU-VP is shown in Scheme 1. Highly viscous liquid PPICF was diluted to about 50 wt.% for microsyringe handling. The monomers were dissolved in solvent (DMF: cyclopentanone = 1:4 by weight) and the diluted PPICF was added and mixed thoroughly for 10 min. The resulting mixture was then filtered using 0.45 μm pore size syringe filter and directly spin-coated at 400 rpm. The solution did not exhibit the flow characteristics due to a fast gel formation. The quality of the spin-coated film improved with a cosolvent system, compared to when DMF was only used.

SCHEME 1



VP-OH PU-VP

The results of TGA and DSC from the crosslinked polyurethane PU-VP1 are given in Fig. 1. The glass transition was not observed and the thermal decomposition of this polymer began at about 156 ℃ under the ambient condition. This decomposition temperature is somewhat lower than that of other stilbene chromophore systems (~200 ℃). The deviation is due to tetraphenyl borate counter ion at the center of hemicyanine chromophore being more easily removed.

The effect of UV-exposure time on cured PU-VP1 system (100 ℃, 12 h, in vacuo) is given in Fig. 2. The absorption maximum and the absorption edge of cured sample were observed at 488 nm and around 600 nm, respectively. Photobleaching upon exposure to 365 nm and 55 mW/cm^2 light showed no

change in the absorption peak, but the reducing absorption intensity. These results indicate that the photobleaching of chromophores used in the present investigation did not occur through *cis* to *trans* transformation but the photodegradation occured mainly. The mechanism for photodegradation is not known at this time, however the oxidation of stilbene group is speculated.

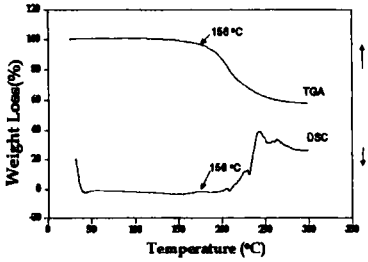


FIGURE 1 TGA and DSC thermograms of PU1-VP1

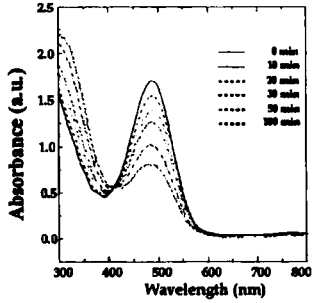


FIGURE 2 The change of UV-vis absorption spectra due to photobleaching of cured PU-VP1 sample

The NLO polymeric materials for the measurement of SHG are generally spin-coated on indium tin oxide (ITO). The ITO glass was initially used in the present investigation, however, the films became turbid during poling. In the case of ITO glass substrate, the surface charge of the film during poling was very small. This implies that the electric current passed through the film was large and resulted in deformation of the polymer film. When the substrate was changed to a normal Corning glass, turbidity disappeared and the transparent film was obtained after poling.

For the measurement of macroscopic second-order susceptibility $\chi^{(2)}$ upon completion of poling, the angular dependence of SHG was recorded for the Maker fringe method. The SHG intensity of PU-VP1 was compared with that of 1 mm thick, Y-cut quartz standard ($d_{11}=0.8\times10^{-10}$ esu). The value of $\chi^{(2)}$ for PU-VP1 was 7.2×10^{-8} esu (30.2 pm/V). Fig. 3 illustrates the thermal endurance of SHG activity for poled and cured PU-VP1, measured for every twenty minutes at every constant temperature interval during stepwise temperature increase from the room temperature to 150 ℃. The decay of thermal stability in PU-VP1 was minimized due to lattice the hardening of

polyurethane with three bonding sites. Also, the SHG intensity does not show any reduction until the temperature rises to 100 ℃.

Poling profiles of PU-VP2 (NCO/OH=2), uncured and cured samples are illustrated in Fig. 4. The latter sample was cured at 100 ℃ for 12 h in vacuum as such that a random crosslinking was achieved. The SHG signal was monitored from the sample under electric field in a complete temperature cycle between room temperature to 120 ℃ and back to the room temperature, at which time the electric field was removed. Temperature was changed in an increment of 15 ℃ and at each temperature the signal was recorded until saturation, which corresponded to approximately ten minutes.

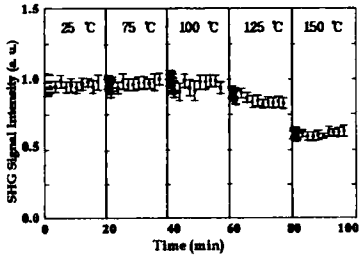


Figure 3 The thermal endurance of SHG activity for PU-VP1

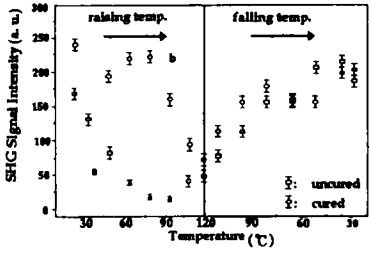


Figure 4 In-situ poling profiles obtained (a) from uncured and (b) cured PU-VP2 films

When the poling field is applied at room temperature, the chromophores in both samples effectively aligne and hence show similar poling profile shapes. During the temperature increasing region, the signal from uncured sample is seen to decay rapidly, while that form the cured sample, the initial signal strength is somewhat maintained up to 80 ℃, followed by a slower decay at higher temperatures. The reason for this difference may be explained by the degree of thermal fluctuation allowed in each samples. In the case of uncured sample, unreacted chromophores become easily disturbed by the increased thermal fluctuation with temperature and hence it results in a rapid signal decay with temperature increase. In a cured sample, on the other hand, the poling after a complete random crosslinking introduces the polymer matrix conformational change, causing aligned chromophores to be restrained by the matrix. As a consequence, the observed signal behavior with a temperature rise can be attri-

buted to a reduced thermal fluctuation as compared to the uncured sample.

The dynamics are similar in these two samples during decreasing temperature region. This is because the crosslinking takes place in the uncured sample (chromophores are being bonded to polymer backbone) during prior temperature rise phase and by the time the temperature decrease begins upon reaching 120 ℃, crosslinking is almost complete. Thus, during temperature decrease, thermal fluctuation in both samples are expected to be similar. The competing effect of electric field and temperature on the equilibrium of aligned dipole can be also depicted from Fig. 4. At lower temperatures, the aligned dipole portion is larger due to electric field having a greater effect than the temperature. Similarly for higher temperatures, the opposite becomes true and the aligned dipole portion decreases. This explains the symmetry of SHG signal profile between temperature increase and decrease regions observed for the cured sample. Such symmetry does not exist for the uncured sample because under the poling induced alignment in the direction of DC field, greater crosslinking exists in the temperature reduction region than the rise region.

Acknowledgments

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