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Nonlinear optical properties in novel crosslinked system with host–guest and side chain

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Abstract

Crosslinkable polymer with host–guest and side chain system was investigated to increase the content of NLO chromophores in second order nonlinear optics. Though very low poling temperature has been applied, the observed UV absorption difference before and after poling was large due to low glass transition temperature of the polymer and high content of chromophores introduced by side chain and guest molecules. Highly stable NLO properties have been achieved through crosslinked polymer matrices. The crosslink reaction between polymer matrix and chromophore was confirmed by FT-IR and ^{29}Si solid state NMR. The d_{33} values of modified DR1/polymer films are high, around 40 pm/V, and there is a no change during 2 months at ambient temperature though for some samples d_{33} values slightly decreased. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: NLO; Crosslinking system; ^{29}Si solid NMR

1. Introduction

It has been reported that crosslinkable polymers have many advantages over other systems, especially in terms of high thermal stability and less degree of relaxation of oriented chromophores in second order nonlinear optics (NLO) [1–10]. In order to prevent the randomization of the poled NLO chromophores that limit the lifetime of poled polymer devices [11,12], the NLO chromophores are usually incorporated into matrices by crosslink reaction. The resultant incorporated chromophores then display distinct advantages over physically incorporated guest–host polymer systems. Such an increase can be attained via the formation of interchain chemical bonds, resulting in the partial immobilization of organic chromophores in the resultant crosslinked polymer matrices. Here, the desired overall effectiveness (i.e. decrease in the mobility of organic chromophores in a polymer matrix) strongly depends on both the number and nature of available crosslinkable sites [12].

Tripathy et al. have reported improved NLO properties in a crosslinked epoxy system [12]. However, crosslinking decreases both the solubility in common solvents and the mobility of the polymer chain. Moreover, high content of NLO chromophores in crosslinkable systems leads to the additional burdens of crystallization, phase separation or even the formation of concentration gradients [13]. We have already reported [14–16] the second order nonlinearity in inorganic silica matrix. The phase separation and aggregation of the chromophores and matrices were observed on increasing the loading level of the chromophores in the system, though high nonlinearity and thermal stability were achieved. In addition, it was very difficult to control the thickness and quality of the film. Furthermore, it took long time for the optimum coating viscosity to make the films. The problems concerned with the inorganic silica system could be improved.

In this report, the stability of oriented organic chromophore (modified disperse red 1, DR1) in a polymer matrix with less brittleness and lowered light scattering is reported. The enhanced NLO properties were attained by increasing the mobility using polymers of low glass transition temperature and by a suitably adjusting the content of chromophores to prevent phase separation. FT-IR and ^{29}Si solid NMR studies were carried out to elucidate crosslink reaction

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between matrices and chromophores. SH intensity of poled samples was measured by Nd:YAG laser.

2. Experimental

2.1. Materials

2-[4-(4-Nitrophenylazo)-*N*-ethylphenylamino]ethanol (Disperse Red 1, DR1) from Aldrich was recrystallized in benzene prior to use. 3-(Triethoxysilyl)propyl isocyanate (TESPI) from Aldrich was used without further purification. Methyl methacrylate (MMA) and 3-(trimethoxysilyl)propyl methacrylate (TMSM) from Aldrich were purified by alumina column prior to use. The microscope glass slides (Fisher premium) as substrates were used after cleaning ultrasonically in a detergent solution, washing with deionized water, acetone, 1N HCl, acetone and deionized water and then drying at 50°C in a dust free oven and storing in a desiccator. Double-distilled, deionized water was used in all the experiments reported in this work.

2.2. Synthesis of modified DR1 (DRS)

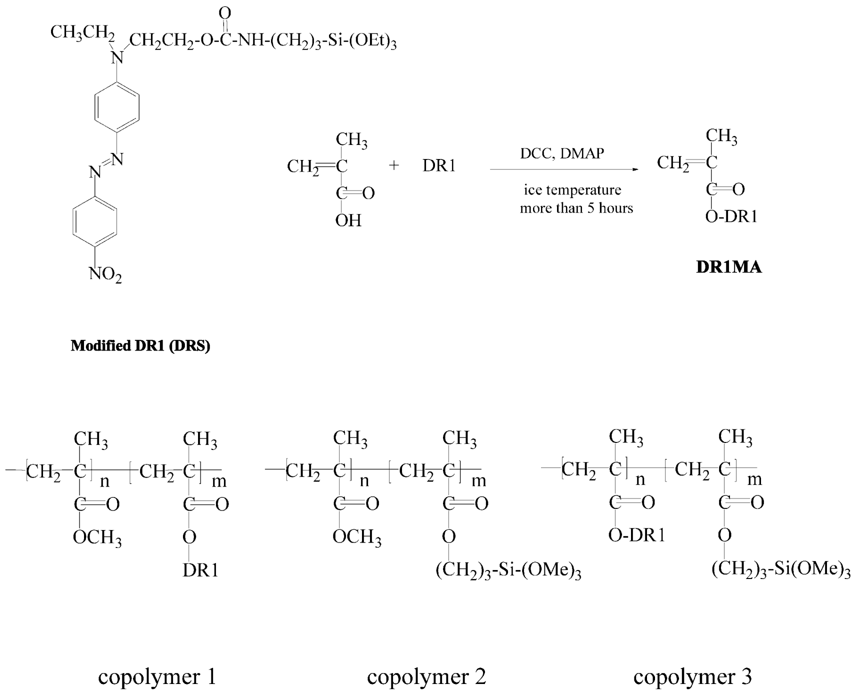
DR1 (3 g) was reacted with TESPI (3 g) in tetrahydrofuran (THF, 50 ml) by adding a couple of drops of dibutyltin dilaurate (Aldrich) as a catalyst for 5 h at room temperature and then the solvent was removed by rotary evaporator. Crude modified DR1 (DRS) was separated from the resultant unreacted materials by column chromatography using *n*-hexane and diethyl ether with 60% yield.

2.3. (4-Nitrophenyl)[4-[[2-(methacryloyloxy)ethyl]-ethylamino]phenyl]diazene (DR1MA)

Methacrylic acid (Junsei Chemical) was vacuum distilled at 10 Torr at room temperature. DR1 (0.8 g) and methacrylic acid (0.22 g) were dissolved in THF (25 ml) at 0°C. The coupling reaction was performed using 1,3-dicyclohexylcarbodiimide (Sigma, DCC, 0.53 g) and 4-(dimethylamino)pyridine (Sigma, DMAP, 0.31 g) as catalysts. The resultant mixture was stirred for 5 h at ice temperature and the solid salt was filtered out. The solvent was removed using a rotary evaporator. DR1MA was separated from the resultant crude materials by column chromatography using hexane and diethyl ether. DR1MA was recrystallized from *n*-hexane (Aldrich) and obtained with 90% yield.

2.4. Poly(MMA-co-DR1MA) (copolymer 1), poly(MMA-co-TMSM) (copolymer 2), poly(DR1MA-co-TMSM) (copolymer 3)

Copolymer of MMA (0.6 ml) with TMSM (0.98 ml) was synthesized by radical polymerization at 70°C in toluene using 2,2′-azobis(2-methyl-propionitrile) (AIBN, 0.01 g) as an initiator. The resultant mixture was dried using a rotary evaporator, washed three times with methanol and then freeze dried using benzene. Large amount of initiators were used in the case of copolymers containing DR1MA, because azo groups and nitro groups serve as radical scavengers. Scheme 1 shows the chemical structures of monomer and polymers.



Scheme 1.

Table 1
Characteristics of copolymers and d_{33} values of various kinds of polymers and DRS/polymer

Sample	Mixing ratio (wt%)	M_w[a]	T_d[b] (°C)	T_g[c] (°C)	Thickness (μm)	d_{33} (pm/V)	d_{33}^{*}[d] (pm/V)
Copolymer 1		104 000	270	117	1.25	12	0
DRS/copolymer 1	1/10				0.52	37	25
Copolymer 2		95 500	210	30			
DRS/copolymer 2	1/10				1.05	45	42
Copolymer 3		90 000	210	5	1.24	27	19
DRS/copolymer 3	1/10				0.83	43	42

[a] Molecular weight was measured by GPC.
[b] T_d was measured by TGA.
[c] T_g was measured by DSC.
[d] d_{33}^{*}: 2 months later.

2.5. Characterization

Glass transition temperature (T_g) and decomposition temperature (T_d) were measured with DSC (TA 2010) and TGA (TA-2050), respectively. Molecular weights (MW) of the polymers were estimated by using SEC with four columns (HR 0.5, HR 1, HR 3 and HR 4, Waters Styragel columns run in series with pore sizes of 50, 100, 10^3 and 10^4 Å, respectively.) with a refractive index detector at a flow rate of 1 ml/min using THF as the elution solvent, at 40°C and calibrated with PS standards (Scientific Polymer Products Inc.). The composition ratio of the each polymer was measured using ^{1}H NMR (JEOL JNM LA-300 WB).

For the polymer film, we deposited the coatings with the solutions obtained by mixing in ratio (wt%); polymer (1): DRS (zero or 10 wt% of polymer): H_2O (0.1): THF (10) with HCl as the catalyst [16]. Thickness of all the coated films ranged from 0.6 to 1.2 μm measured by Dectek II [16]. The poling was carried out using a corona discharge method with a wire. All coated polymer films were poled at room temperature, 80, 100 and 140°C during 30 min. During heating and cooling process, a 7 kV electric field was constantly applied. UV/Vis absorption spectra of the samples prepared at different poling temperatures were obtained before and after poling. The relaxation behaviors of the chromophores were observed by the UV/Vis spectroscopy after keeping the samples for longer than 20 days at room temperature.

Thermal stability of each polymer sample was examined by UV/Vis spectra after exposing the sample at 100°C. The SHG of the poled samples was measured with Nd:YAG laser radiation (1064 nm, 10 mW/cm^2, pulse duration: 7 ns, repetition time: 20 Hz). Refractive index of DRS doped films on the quartz substrate was measured using a M-line method and d_{33} value was calculated using SHG data and refractive index.

3. Results and discussion

3.1. Polymer characterization

Table 1 shows the characteristics of copolymers. T_ds measured by TGA are 270 and 210°C, respectively, and T_gs measured by DSC are 117, 30 and 5°C, respectively. Composition ratio of the polymers was obtained using ^{1}H NMR measurement by comparison between the OCH_2CH_3 peak of the alkoxy groups and CH_3 group of DR1. Composition ratio of DR1MA and TMSM in the polymers is lower than MMA due to the bulk side chain. The ratio of chromophore contents for copolymer 1 and 3 is 8:3.

3.2. ^{29}Si solid state NMR study

Crosslink reaction between organic chromophores and polymer matrices before and after doping in 2N HCl solution was traced by FT-IR. Fig. 1 shows that the strong absorption of the original film at 1140 cm^{-1} due to the Si–O–C stretching completely disappeared, and alternatively a new broad band appeared at 1047 cm^{-1}, which indicated the Si–O–Si crosslinking between polymer matrices and chromophores.

Crosslink reaction of the copolymer system was also traced using ^{29}Si solid state NMR. It is very sensitive to both the degree of condensation and the substitution degree of another Si which $Si(OSi)_x(OH)_{3-x}$ [13,17–27]. Fig. 2 shows the ^{29}Si solid state NMR spectra of DRS (a), crosslinked DRS (b), copolymer 2 (c), crosslinked copolymer 2 (d), chemically reacted DRS/copolymer 2 (e), physically mixed DRS/copolymer 2 (f) and physically

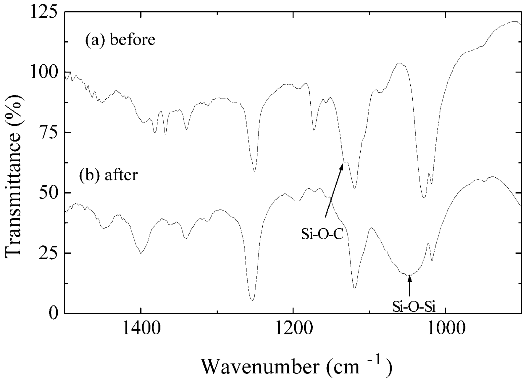


Fig. 1. FT-IR spectra before (a) and after (b) crosslink reaction of DRS with copolymer 1.

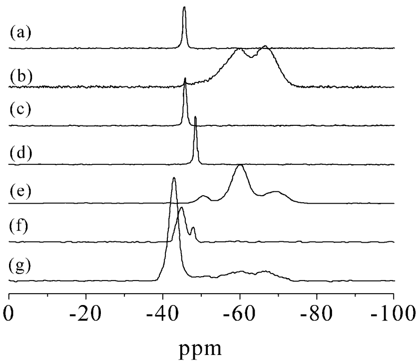


Fig. 2. ^{29}Si solid NMR spectra for DRS (a), crosslinked DRS (b), copolymer 2 (c), crosslinked copolymer 2 (d), chemically reacted DRS/copolymer 2 (e), physically mixed DRS/copolymer 2 (f) and physically mixed crosslinked DRS/crosslinked copolymer 2 (g) by CP/MAS using poly(dimethylsiloxane) as an external reference.

mixed crosslinked DRS/crosslinked copolymer 2 (g) by CP/MAS using poly(dimethylsiloxane) as an external reference. DRS shows a peak at −43 ppm; however, crosslinked DRS shows two peaks at −57 and −63 ppm, assigned to $-Si(OSi)_1(OH)_2$, $Si(OSi)_2(OH)_1$, respectively. The spectrum of copolymer 2 shows a peak at −42 ppm while the spectrum of crosslinked copolymer 2 shows a peak at −44 ppm. The peak shifted by 2 ppm after crosslink reaction. In Fig. 2(e), those peaks could be used to assign the amount of crosslink of the alkoxysilyl groups between polymer matrices and DRS, $Si(OSi)_1(OH)_2$, $Si(OSi)_2(OH)_1$, and $-Si(OSi)_3$. In physically mixed DRS/copolymer 2 with 10 wt% DRS, two peaks are observed at −48 and −46 ppm, which are assigned to DRS and crosslinked copolymer 2, respectively. For the physically mixed crosslinked DRS/crosslinked copolymer 2, three peaks are observed at −43, −60 and −66 ppm. Broad and weak DRS peaks appeared at −60 and −66 ppm regions (Fig. 2(g)). From those initial results, it is concluded that DRS was homogeneously dispersed and reacted with polymer matrices. All alkoxy silyl groups of polymer matrices and DRS got hydrolyzed before condensation reaction, though some unreacted hydroxyl groups still remained.

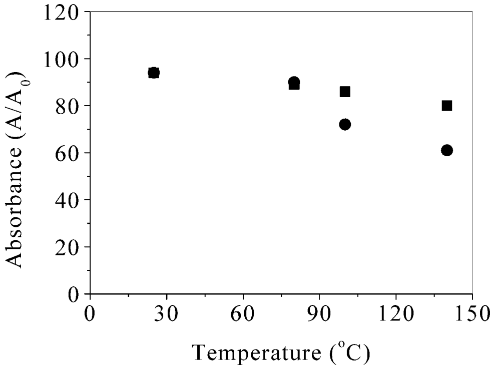


Fig. 3. UV absorbance changes before and after poling of copolymer 1 (■) and DRS/copolymer 1 (●) (the temperature indicates poling temperature).

3.3. NLO properties

We already reported NLO properties of DRS in silica matrix. DRS may act as a liquid crystalline mesogenic group and is effectively oriented in poling at the phase transition temperature, 80°C [16]. Fig. 3 shows the UV absorbance changes before and after the poling of copolymer 1 and DRS/copolymer 1. Maximum UV absorbance change of copolymer 1 is around 20% in all temperature ranges introduced in this work. The maximum absorption difference was observed at around 140°C, because the glass transition temperature of the copolymer 1 is around 117°C. Also, relaxation of the oriented chromophores occurred, and the recovery was around 90% after 250 h. However, the order parameter increased from 0.2 to 0.4 by introducing DRS into copolymer 1 (Fig. 3). This behavior is due to the different chromophore content in films. In DRS/copolymer 1 system, UV absorbance change is not so large at 80°C due to the large content of side chain chromophores. Temporal retentions of DRS/copolymer 1 were excellent compared to those of copolymer 1 at all the temperature ranges, even some absorption increased after several hours.

Fig. 4 shows the UV absorption changes before and after poling of DRS/copolymer 2, copolymer 3 and DRS/copolymer 3. The UV absorbance changes before and after poling in DRS/copolymer 2 are large at room temperature and 80°C due to low glass transition temperature of 30°C, and liquid crystalline behavior of DRS. Also, the small absorbance changes of the films at T_g of the PMMA matrices were observed. However, the absorption difference before and after poling is not so large above 100°C compared to that of room temperature. This behavior may be due to the fast crosslink reaction between alkoxy silyl groups of matrices and chromophores. This means that the crosslink reaction disturbs the formation of poled state during poling. In guest–host and crosslink systems, there is no randomization during 200 h after poling. This means that the relaxation of poled chromophore was disturbed by crosslink reaction. UV absorbance changes before and after poling of the copolymer 3 is not so large and is almost the same at all

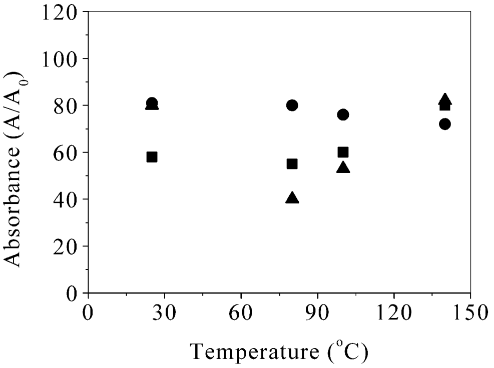


Fig. 4. UV absorbance changes before and after poling of DRS/copolymer 2 (■), copolymer 3 (●) and DRS/copolymer 3 (▲) (the temperature indicates poling temperature).

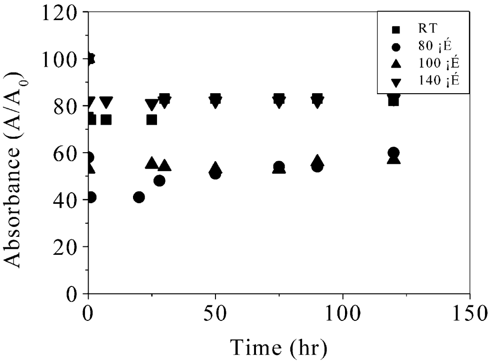


Fig. 5. UV absorbance changes before and after poling and relaxation behaviors of DRS/copolymer 3 (the temperature indicates poling temperature).

temperature ranges studied in this work, because the glass transition temperature of the polymer is low about 5°C.

To investigate the side chain, guest–host and crosslink system, crosslinkable chromophore was introduced to the copolymer 3 containing side chain DR1 and alkoxy silyl groups. In DRS/copolymer 3 (Fig. 5), large absorbance change was observed at 80 and 100°C. This behavior is due to the added DRS chromophore. Since the glass transition temperature of the polymer is 5°C, the expected effective poling temperature is around 5°C. The absorbance change of the copolymers with DRS are large at 80 and 100°C. However, the absorbance change of the copolymer with DRS at room temperature and 140°C are not so large as copolymer 3 without DRS. This may be due to the difficulty of DRS orientation at room temperature and the fast crosslink reaction between alkoxy silyl groups of matrices and chromophores at higher temperature, namely fast crosslink reaction disturbs the orientation of chromophores. The effect of side chain chromophore is not large, because the content of side chain chromophore is very small compared to other polymers. The major component of the poling process is not side chain chromophores but the guest molecules, DRS. Therefore, the added DRS plays a key role in the observation of the order parameter at 80 and 100°C. In the case of DRS/copolymer system, the order parameter increased with the addition of DRS. Since the stability of the orientational order of the molecule determines the potential of the system as a second order NLO material, these systems show a great potential as a host of matrices for the NLO chromophores.

The copolymer matrices were neither opaque nor brittle compared to the previously reported silica matrices [14–16]. In addition, since T_g of the copolymer is low, the chromophores are easily oriented at room temperature by electric field. The orientation of the chromophores in the crosslink system with host–guest and side chain system was increased by more than two times as high as that of chromophores in side chain system. Thermal stability of matrices was excellent even at 100°C. In addition, UV absorbance change was very small during the 20 days at 100°C. The stability of copolymers was excellent at 100°C except copolymer 1 and DRS/copolymer 1.

The SH intensity for the poled samples was obtained with Nd:YAG laser to observe the NLO properties. SH intensity of the polymers was measured and the NLO coefficient of the polymers was calculated. The SH intensity increased after doping the DRS chromophores. Table 1 also shows the sample thickness, d_{33} values of fresh sample, and d_{33}^* values two months later after poling for polymers and DRS/polymers. After two months, the d_{33}^* value is still same as the d_{33} value of DRS/copolymer 3. However, d_{33} values of copolymer 1 system and DRS/copolymer 1 system decreased, because those systems are only involved in side chain DR1. The results show that the SH values increased by adding chromophores (DRS) as guest and the stability of chromophores increased through crosslinked matrix system.

4. Conclusions

Crosslinkable polymeric matrices for incorporation of second order nonlinear optical materials were synthesized. The UV absorption difference before and after poling was large due to the addition of modified chromophores which was aligned well at 80°C. Highly stable UV absorbance after the incorporated chromophores has been achieved through crosslinked copolymer matrices. The reasons for both large absorption differences before and after poling and the enhanced stability of oriented chromophores are low glass transition temperature and crosslink reaction between matrices and chromophores, respectively. These phenomena have been proved by UV/Vis spectroscopy and ^{29}Si solid state NMR, respectively. SH intensities of the DRS/polymers are higher than the values of copolymers without DRS.

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